Commission on Crystallographic Teaching
International Union of Crystallography
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This issue's theme:
"Teaching Crystallographic Fundamentals"
http://www.iucr.org/iucr-top/comm/cteach/newsletters/

Table of Contents
(This Issue's Editor: Lachlan Cranswick)

(Editors' warning – unless you want to kill 113 pages worth of forest – DO NOT press the "print" button. For hardcopies – you may like to only print out the articles of personal interest.)

THE IUCr COMMISSION ON CRYSTALLOGRAPHIC TEACHING - TRIENNIUM 2005-2008

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Now Accepting Registrations via the school website

Siena 2006 : IUCr School on Basic Crystallography

(modeled on the British Crystallographic Association (BCA) Durham school)

Certosa di Pontignano, University of Siena, Italy
27th August – 2nd September 2006

http://www.iucr.org/iucr-top/comm/cteach/siena2006/

School organisers: Paola Spadon (Current chair of the Teaching Commission) and Marcello Mellini

Lecturers and tutors include: Alexander Blake, Gervais Chapuis, Jacqueline Cole, Giuseppe Cruciani, Robert Gould, Giovanni Ferraris, Anthony Linden, Peter Main and David Watkin.

The Venue

The Certosa di Pontignano has its origins as a medieval 14th century monastary. It is now run by the University of Siena. Attractively placed on the top of a hill, it is surrounded by vineyards; with a direct view to the town of Siena, and a famous Chianti winery.

The City

Siena is described as one of the finest examples of a Medieval city. It is in the Italian province of Tuscany and has direct bus connection to Florence (1 hour) and Rome (3 hours).

School Aims

This is an immersive school, focusing on the crystallographic fundamentals, modeled the school on the successful (BCA) Durham School. There will be a mixture of lectures and tutorials. All the tutorials are pen and paper exercises, consistent with the aims of properly teaching students the fundamentals of crystallography.

Lecture topics include:

Introduction; Introduction to diffraction; Direct Methods; Maths of refinement; LSQ Outline; Data Collection; Powder Diffraction; Neutron and Synchrotron Studies; Twinning; Derivation of results, analysis and interpretation; Database

Einstein's tongue for teaching crystallography to biologists

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Abstract

Teaching crystallography to students in Biology is a difficult task, particularly because many of them arrived there because '*there are no more Maths or Physics in Biology*'. In order to visualize really the phenomenon of diffraction without X-rays we have used a classical optical bench requiring a LASER (λ=0.6328 µm), a pinhole as a beam expander and two lenses.

Following a method originating from Bragg, and analysed in depth by Taylor & Lipson, we used as crystals 24x36 B&W photographs of a 80×60 repeats of the well-known 'Einstein's tongue' (cell parameters a = 0.45 mm, b = 0.4 mm.). This allowed to record a diffraction pattern on films mounted in the back focal plane of the second lens. The diffraction data extend to order 21 (more than 500 visible Bragg's spots), which corresponds to 20 µm resolution.

In order to illustrate the principle of the MIR method, we have made 'heavy atom derivatives' by adding small dots on Einstein's face (one site per derivative), and we have 'collected new data'. Our hope was to go really all the way through with experimental data to 'solve the structure'. For practical reasons, this structure solution step was illustrated with calculated data only. This nevertheless shows very well how a recognizable picture is obtained after 'MIR phasing' with only 50 reflections, and what is the effect of experimental noise.

All programming was performed with *Mathematica* (Wolfram Research), which allowed to develop very rapidly the necessary code and to make everything visible on our web site at http://ibmc6187.u-strasbg.fr:8080/webMathematica/bioCrystallographica/.

1. Introduction

One major issue when teaching crystallography to students in biology is their low average level in mathematics. Indeed, many of these students arrived there because '*there are no more Maths or Physics in Biology*'. In addition, even the knowledge of basic tools normally acquired much before going to university is often lacking. Many of them, for example, do not master anymore elementary algebraic calculations. For example, replacing an expression like $x^p x^q$ by x^{p+q} or recognizing that $|x+y| \neq |x| + |y|$ should not be considered as obvious. Needless to say, evoking a 'scalar product' or something like $e^{i\theta}$ usually pulls many faces. Such a situation may be tackled in three different ways. One approach corresponds to considering that a 'scalar product' and $e^{i\theta}$ are known since they should be known. Another approach is the exact opposite and corresponds to pretending that mathematics can be seen as superfluous since many students ignore them. Finally, a third approach corresponds to fighting with the real problems, that is using mathematics because this cannot be avoided, but by trying as much as possible to use intuitive arguments, graphics representation and interactive documents. This is obviously our approach and the goal of the present note is to present it. In particular, we will expose how we give strong weight to classical optics. The course span eight weeks with two-hour teaching classes per week and six 'travaux dirigés' (tutorials). In addition one class of 'travaux pratiques' (practicals) was devoted to using an optical bench for illustrating the diffraction phenomenon.

2. Students concerned by this course

The students concerned by our teaching were those at the level of 'License' or 'Maîtrise' of 'Université Louis Pasteur' in Strasbourg. Up to recently, these two years corresponded respectively to the third and fourth year at university. In fact, because of an ongoing reorganization of the French academic cursus in order to make it comparable with that of most European countries, the denomination of 'License' is now used collectively for the first three years at university (and not only for the third one), whereas the denomination of 'Maîtrise' (for the fourth year) has now disappeared since the fourth and fifth year are now grouped under the name of 'Master'. The students were broadly interested in biology swith, for a part of them, an emphasis on chemistry.

3. Refreshing their mathematical knowledge

If not original, it appears necessary to devote the first course to recalling the basic tools in mathematics. One considers essentially the elementary properties of complex numbers from the very beginning, essentially through their geometrical meaning. It often appears that several students appreciate to have these things recalled. One insists on the use of $e^{i\theta}$ and on the fact that this represents a considerable simplification in calculations. In order to demystify this cryptic formula involving '*complex*' numbers or, even worse, '*imaginary*' numbers, we make a simple heuristic 'proof' of it following either one of two possibilities.

The first possibility consists in writing that 'rotating a complex' z by $d\theta$ gives an elementary variation $dz = iz\,d\theta$ (which only involves elementary geometry). One then recall that this is formally equivalent to the differential equation $dN = \alpha N\,dt$ representing the growth of bacteria during their so-called 'exponential phase' if $\alpha > 0$, or the decrease of the number of radioactive atoms if $\alpha < 0$ (all biologists are aware of that !). It is then a game of arriving heuristically at $z = z_0\,e^{i\theta}$ in exactly the same way as one arrives at $N = N_0\,e^{\alpha t}$.

The second possibility consists in decomposing a rotation by θ into n steps θ/n and making $n \to \infty$. Starting with z_0, one elementary step yields $z_1 = z_0 + iz_0\,\theta/n = z_0(1 + i\,\theta/n)$, two elementary steps yield $z_2 = z_1 + iz_1\,\theta/n = z_1(1 + i\,\theta/n) = z_0(1 + i\,\theta/n)^2$, etc… from which one derives $z_n = z_0(1 + i\,\theta/n)^n$. Here also, one makes reference to real numbers by considering $(1 + x/n)^n$ for $n \to \infty$ and one recalls two elementary properties of the logarithms, *viz.* $\mathrm{Ln}\,(1 + x/n)^n = n\,\mathrm{Ln}\,(1 + x/n)$ and $\mathrm{Ln}\,(1 + x/n) \approx x/n$ for $x/n \to 0$ to show that $(1 + x/n)^n \to e^x$ when $n \to \infty$. Substituting $i\,\theta$ for x yields the result.

These two 'proofs' are not really complete since there always is a gap when passing from real to complex numbers, but our goal is not doing 'pure mathematics', but demystifying tools that are complicated only in appearance.

4. Making a detour to optics

X-rays have two obvious drawbacks: first, they are not visible and, second, they cannot easily and safely be manipulated. Therefore teaching diffraction with visible light is extremely valuable. In addition, this allows introducing the effects of diffraction in optical instruments, for example in the microscope, which is of real interest for biologists. Moreover, the expanded beam of a LASER falling onto a simple 24x36 B&W photograph gives rise to a very nice diffraction pattern in the back focal plane of a lens disposed behind the photograph. The system that we used is well known and is described on our web site.
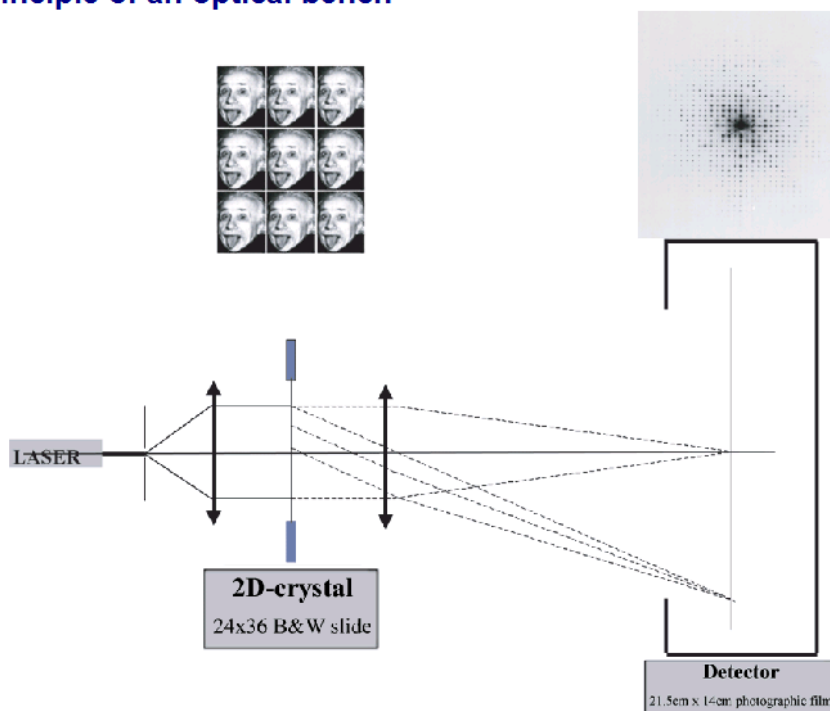
Principle of an optical bench

Fig 1: *Schematic of experimental apparatus to to convert Einstein's face into a 2D diffraction pattern via http://ibmc6187.u-strasbg.fr:8080/webMathematica/bioCrystallographica/teaching/teaching03.html*

It should be mentioned that this 'optical transform' method has a long history in crystallography and electron microscopy. A lot of details about the historical features can be found in Taylor & Lipson (1964), whose reading is of utmost interest! As recalled by Taylor & Lipson, Bragg (1939, 1942), when all computations were done by hand, was the first[1] to try obtaining a projection of an electron density map by an optical synthesis. Bragg, in fact, realized that, from Abbe's theory of image formation, such a projection could be obtained as the result of the interference of the beams diffracted by a screen with holes representing a weighted reciprocal lattice section. An important problem, however, had to be solved: each beam had to emerge from the corresponding hole with the correct phase. For that, Bragg covered each hole with a precisely cut piece of mica sheet in such a way that *'the light polarized in the slow direction lags precisely half a wavelength behind the light polarized in the fast direction'*. If all pieces of mica are oriented exactly in the same direction, then all holes introduce the same phase change to the diffracted rays, but rotating by 90° a piece of mica introduces a phase change by 180° relative to the others. Therefore, reconstructing an image of a centrosymmetric projection can be obtained by rotating correctly a set of the mica patches. Variations on this theme and improvements by others are referenced in Taylor & Lipson (1964) (see also Lipson & Cochran (1966)).

Our goal was not only to illustrate the formation of a diffraction pattern, but also how can be recovered by calculations the original image from the knowledge of the diffraction intensities, which is the essential problem in crystallography. For that, we wanted to be as close as possible of the method in use for solving a structure in real macromolecular crystallography.

As it is well known, there are two methods, first the venerable Multiple Isomorphous Replacement (MIR) method going back to Perutz, Kendrew, Harker and Blow & Crick (see Watenpaugh (1985) for a short summary and references) and, second, the Multiple Anomalous Dispersion (MAD) method, now widely used thanks to synchrotrons (Hendrickson, 1991). Although the two methods differ greatly in the way they are put into practice, they are conceptually extremely related. Indeed, in both cases the entire set of phases is recovered from very localized changes in the electron density. For the MIR method, the change

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[1] In fact Born & Wolff recall in their classic 'Principle of optics' (1959) that the same idea was independently proposed by Boersch (1938).

is of a chemical nature, *i.e.* it is obtained by introducing a heavy atom that binds at specific places, hopefully without introducing any other disturbances. For the MAD method, the change is of a purely physical nature, *i.e.* it is obtained by changing the response of some anomalous scatterers to X-rays merely by changing their wavelength. Therefore, at the basic crystallographic level of this course, it was quite justified to concentrate on the MIR method.

5. Making 'native crystals' : à tout Seigneur, tout honneur

Our original goal was to go all the way through the experimental steps of structure solution. Therefore, we wanted to measure the diffracted intensities of a 'native' 2D-crystal, as well as the diffracted intensities of two or more 'derivatives' of it. From these experimental measures, we planned to obtain really the necessary phases to compute the original image making the unit cell of our 2D-crystal. We evidently expected a lot of errors in phase determination and, for that reason, we chose as 'a molecule' the extremely well known *Einstein's tongue* that is most easily recognized (see our web site). Note that this points to the general problem of 'pattern recognition', which is quite relevant in crystallography, at least now, since we are no more faced, like Kendrew or Perutz, with the problem of building the first structure of myoglobin or of hemoglobin. Indeed, an experienced crystallographer recognizes most easily a β-sheet from an α-helix, even in a rather noisy electron density map. The same is true with the recognition of structural features in nucleic acids, particularly after the remarkable achievement of ribosome structure solution (for a review, Noller, 2005).

Our 2D-crystal was made of 80×60 repeats of Einstein's face. We first made a large 60cm×45cm image of the crystal by assembling carefully smaller photocopied pieces and we made a 24mm×36mm B&W photographic reduction of it.

6. Making 'heavy atom derivatives' from our 'native Einstein crystal'

In order to make a 'heavy atom derivative', we followed very closely its definition: 'a structure differing from the native one by addition of one or of a few heavy atom(s)'. We thus modified the original image of the august face by adding a gaussian 'beauty spot' representing faithfully an additional atom.
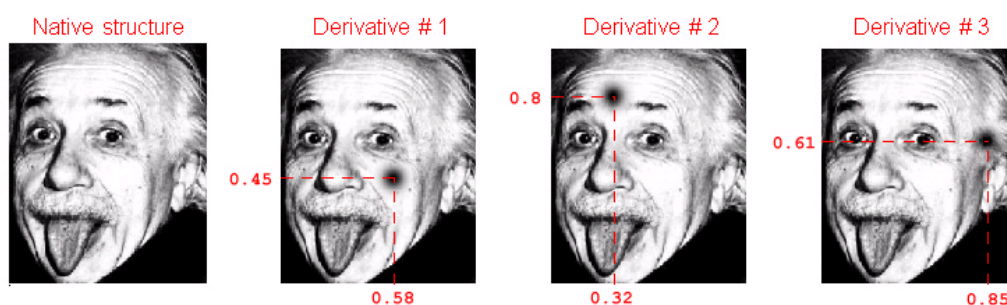
Fig 2: *Heavy atom derivatives of Einstein's face via http://ibmc6187.u-strasbg.fr:8080/webMathematica/bioCrystallographica/teaching/teaching08.jsp*

7. Building a detector, collecting and integrating data

We used photographic films as this was still the case in real crystallography 15-20 years ago. Since the diffraction pattern obtained from the 24mm×36mm slides is *ca.* 8 cm in diameter the films had to be maintained in a holder that was built in PVC. Also, the longest exposure time necessary to measure high resolution spots was as long as 20 minutes; it was thus necessary to darken completely the room and to

protect the film against all parasite light. For that, we simply made a box in heavy card board to enclose the holder. The film was protected against the intense direct beam by a piece of modeling clay. An example of a film is shown on our web site.

To integrate the data, the films were scanned and the resulting numerical images were processed with a program written in the *Mathematica* language. This will not be described further because of practical problems mentioned in the following.

8. The practical limitations of this educational project

As stated above, our initial goal was to go all the way through the steps of structure determination. There is no reason why this should not be possible. However, real life has many reasons to make difficult things that appear possible in principle. The first problem that was faced is that we did not have enough time with the students to go 'all the way through' these steps. It has to be recognized that the things remained essentially theoretical for the students (even though they had practicals with the optical bench). For example, it was totally unthinkable to ask them recording the diffraction patterns on films.

We should also recognize that we did not pay enough attention to the optical setup. In brief, after we had collected data on films, we realized that, quite unexpectedly, the diffraction patterns showed a violation of Friedel's law (see Fig 3). This was invisible by mere eye inspection of the projected diffraction pattern. This is only after reading of Taylor & Lipson (1964) that we understood that more care has to be brought on the alignment of the optical system.
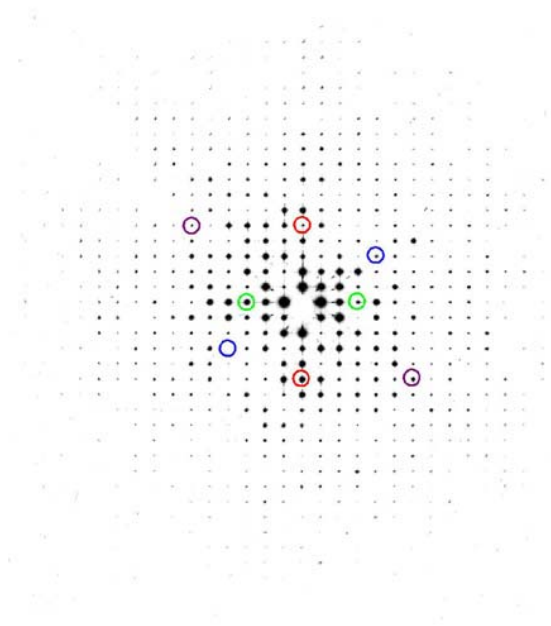
Fig 3: *Diffraction pattern obtained with an Einstein's face crystal and showing a violation of Friedel's law because of insufficient care in the optical setup; see Taylor & Lipson (1964). (image via http://ibmc6187.u-strasbg.fr:8080/webMathematica/bioCrystallographica/teaching/teaching07.jsp)*

Therefore, the phasing of the structure shown to the students was done with purely calculated data. Nonetheless, this allows us to illustrate very well how the phasing is obtained by minimizing a 'Lack Of Closure' function (Blundell & Johnson, 1976) and the deleterious effect of 'experimental' noise (see Fig 4). Even an experienced crystallographer, we think, may consider the resulting images with some interest.

Without noise   **With noise**   **Resolution in use**

hmax = 5 , Resolution = 80 μm

hmax = 9 , Resolution = 44 μm

hmax = 13 , Resolution = 31 μm

hmax = 17 , Resolution = 24 μm

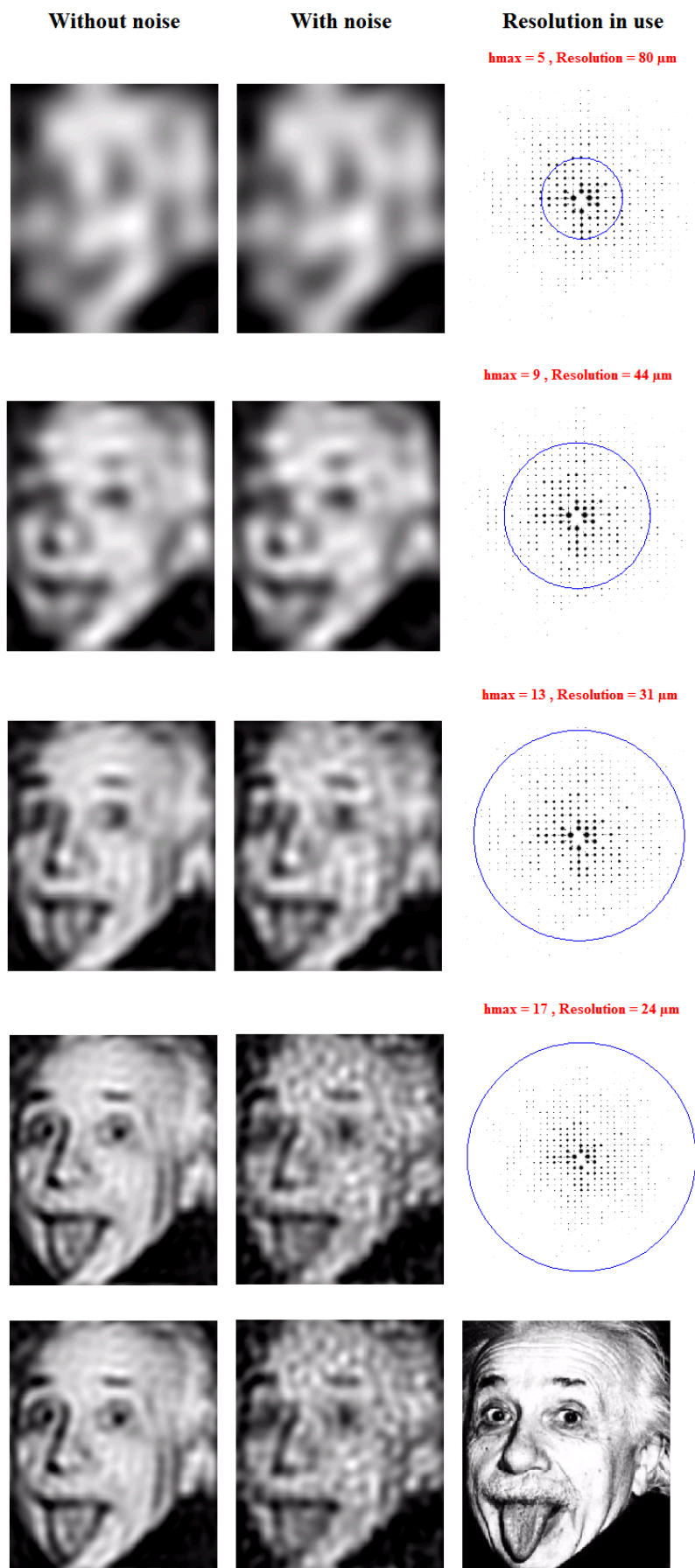**Fig 4:** *Phasing Einstein's face from the diffraction data using a noise level of "2" via http://ibmc6187.u-strasbg.fr:8080/webMathematica/bioCrystallographica/teaching/teaching16.jsp*

9. Practical aspects of programmation

All necessary calculations for the purpose of phasing and illustrating the experiment were performed with Mathematica from *Wolfram Research*. The Web site was made by use of *WebMathematica.* The code is available upon request. It is to be noted that our use of *Mathematica* in the field of crystallography extends much beyond educational purposes and that a full package has now been developed. A first account of it (Ambert, Vanwinsberghe & Dumas 2006) will soon appear in the CCP4 Newsletters.

This educational project was presented at the GTBIO ('Biological study group' from the 'Association française de cristallographie') meeting in Lyons, 22-25 June 2004 and at the 'teaching microsymposium' of the IUCr in Florence, 23-31 August 2005.

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Crystallography Education and Training in the United States

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Formalized Education and Training Policies

In 2001 and 2003, the United States National Committee for Crystallography (USNC/Cr) Education Subcommittee conducted two web-based surveys. The first survey aimed to determine the content and extent of coverage of crystallography in university curricula in the United States, while the second solicited the views of the broader crystallographic community on the status of crystallography education and training in the US, in both the physical and the life sciences. The results of these surveys suggested that (perhaps due to rapid technological advances in the field of modern crystallography) there is a declining number scientists who identify themselves as professional crystallographers, as well as a lack of sufficient education and training in crystallography for individuals who wish to understand and/or use crystallography in their hypothesis-driven research.

Recognizing the opportunity to communicate to the broader scientific community the research opportunities afforded by crystallography as well as the value of crystallographic information, the education committees of the American Crystallographic Association (ACA) and USNC/Cr organized a crystallography education summit, which took place June 1-2, 2005 at the conclusion of the ACA national meeting in Orlando FL. Financial support for this summit was provided by the USNC/Cr, the ACA, the California State University Program for Education and Research in Biotechnology (CSUPERB), and the National Science Foundation (NSF). A broad range of individuals, known for their experience and contributions in crystallography education and training participated in this summit: biologists, biochemists, chemists, geologists and physicists, all practicing crystallographers in their fields, representing both academia and industry. The outcome of the summit has been a consensus policy statement on crystallography education and training in the United States, which will be made available later this year through the National Academies Press website http://www.nationalacademies.org/publications/.

The ACA and the USNC/Cr intend that the document, which stands as the white paper on crystallography education and training, provides guidelines to professional societies and academic departments for crafting future crystallography curricula that adequately address the needs of the scientific community. The education committees of the ACA and the USNC/Cr will provide guidance and support to interested colleagues and policy makers who wish to put these recommendations into practice.

In creating the policy document, we have recognized that crystallography and molecular structure awareness should begin in K-12 education as core components for implementing the established national science standards for all students. Furthermore, there are many contexts in which crystallography can be incorporated in undergraduate education with minimal disruption to current courses. Crystallography should be included in curricula of all undergraduate programs in the physical and life sciences. We believe that formal courses and research opportunities in crystallography should be available to senior undergraduates, and that crystallography-rich courses should be available to all graduate students. In addition, professional development beyond the graduate degree, such as provided by crystallography certificate programs, short courses, summer schools and research opportunities, is a necessary aspect of crystallography training. This is particularly important in novel subjects such as modulated structures and time-resolved diffraction, where crystallography is increasingly being outsourced. Finally, the recommendations and resulting changes must benefit the broader scientific community and not just the community of professional crystallographers. Maintaining the vitality of crystallography is important to university departments advancing science. Education and training today will contribute to the production

of a successful workforce that will assist the nation to prosper in a world of global economic competition. We hope that the scientific community will embrace this document, and that it will remind scientists of the importance of crystallography in their research endeavors. In the following sections, we describe some current crystallography education and training activities in the United States.

Sponsored Workshops, Short Courses and Workshops

In recent years, crystallography education and training in the US has come to rely on professional development in the form of workshops, short courses and summer schools. The Continuing Education Committee (CEC) of the ACA regularly approves applications for summer schools, as well as daylong workshops on popular and specialty topics, or practical aspects of crystallography. The latter take place immediately preceding the ACA annual meetings. Course content for summer schools and workshops is reviewed by the CEC and subsequently disseminated through the ACA website. The ACA currently sponsors two summer schools: one in macromolecular crystallography hosted by Andy Howard and run at the Argonne National Laboratory (ANL) outside Chicago, IL; and the second in small molecule crystallography hosted by Bryan Craven and Charles Lake and run at the Indiana University of Pennsylvania. The USNC/Cr and ACA provide modest financial assistance to both summer schools to support participants from Latin America.

For the past 16 years, the Cold Spring Harbor Laboratory (CSHL) has hosted a "crystallography boot camp", formally known as "X-ray Methods in Structural Biology". This intense laboratory/computational course is organized by William Furey (V.A. Medical Center, Pittsburgh), Gary Gilliland (Centocor, Inc), Alexander McPherson (University of California Irvine) and James Pflugrath (Molecular Structure Corporation) and supported with funds from the National Cancer Institute. Using a combined theoretical and practical approach, with extensive hands-on experiments, the course teaches the fundamentals of macromolecular crystallography, from basic diffraction theory through coordinate deposition. Applicants are selected based upon the degree to which they would benefit from this training opportunity. Although scholarship support is now primarily available only to US citizens and permanent residents due to restrictions mandated by US federal funding agencies, the CSHL has made available some additional funds specifically earmarked for qualified foreign students.

The major synchrotrons in the United States also regularly hold summer schools and workshops. The Berkeley-Stanford Summer School on Synchrotron Radiation, organized by David Atwood and Anders Nilsson, is a weeklong residential program providing a comprehensive overview of the synchrotron radiation process, requisite technologies, and a broad range of scientific applications. Visits to both the Stanford Synchrotron Radiation Laboratory (SSRL) and the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL) are included. The summer school is limited to graduate students, with a preference for those pursuing doctoral research in a physical science where synchrotron radiation is expected to play a significant role in their work. This summer school is sponsored by UC Berkeley, LBNL, SSRL, and the Department of Business Technology, UC Berkeley Extension.

SSRL hosts an annual Structural Molecular Biology Summer School, which focuses on small angle X-ray scattering, X-ray absorption spectroscopy, macromolecular crystallography, and the application of these techniques to biological problems. This program, organized by Serena DeBeer George and Clyde Smith, is supported by a National Center for Research Resources (NCRR) grant from the National Institutes of Health. Additional funding, through corporate sponsorship, has come from Agouron Pharmaceuticals, Compaq Computer Corporation, Silicon Graphics, Area Detector Systems Corporation and the Collaborative Computing Project Number 4.

The Biology Department and National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) host "A Practical Course in Macromolecular X-ray Diffraction Measurement", known as "RapiData". Organized by Robert Sweet, Dennis Robertson, Howard Robinson, Lonny Berman, Dieter Schneider, Annie Héroux, Anand Saxena, and Alexei Soares, the course aims to provide participants with experience in rapid data collection and structure solution at the NSLS. RapiData is not a complete course

in crystallography; students are expected to have some fundamental knowledge of the field. This course is sponsored by a grant from the National Institute of Health NCRR and in part by support from the Department of Energy Office of Biological and Environmental Research. Additional financial support has come from the IUCr and USNC/Cr (to support Latin American scientists), Brookhaven Science Associates, Area Detector Systems Corp, Hoffmann - La Roche, Merck, Bruker AXS, Bristol-Myers Squibb, Molecular Structure Corp., and Hampton Research Corp.

The National Institute of Standards and Technology (NIST)/NSF Center for High Resolution Neutron Scattering (CHRNS) holds a week long course on neutron scattering each summer. These courses are aimed at potential new users of the neutron instruments at the NIST Center for Neutron Research (NCNR) and emphasize hands-on training at the instruments where participants carry out experiments and analyze data. In alternating years, the school focuses either on neutron spectroscopy or on small angle scattering and reflectometry. Some financial support is available for university students and postdocs to attend these summer schools. This support is provided jointly by the NCNR and the National Science Foundation through CHRNS. Some course materials from past summer schools are available for download from the CHRNS website.

In addition to the ACA macromolecular crystallography summer school, ANL also hosts the "National School on Neutron and X-ray Scattering". Organized by Raymond Osborn and Dean Haeffner, the purpose of this summer school is to educate graduate students on the utilization of major neutron and X-ray facilities. Lectures include basic tutorials on the principles of scattering theory and the characteristics of the sources, as well as seminars on the application of scattering methods to a variety of scientific subjects. Students conduct four short experiments at Argonne's Advanced Photon Source and Intense Pulsed Neutron Source to provide hands-on experience for using neutron and synchrotron sources. The school is supported by the US Department of Energy, Office of Science, and the Office of Basic Energy Sciences.

The International Centre for Diffraction Data runs two X-ray powder diffraction clinics each June. The ICDD X-ray Clinics are a continuation of the SUNY Clinics, which were held at the State University of New York at Albany for 25 years. The clinic is presented in two separate week-long sessions, each of which stands alone as a complete course. Session I, Fundamentals of X-ray Powder Diffraction, directed to both relative newcomers in the field and to more experienced users wishing to broaden their understanding of fundamental concepts and established procedures, emphasizes the acquisition of reliable experimental data and qualitative phase identification using manual search techniques. Session II, Advanced Methods in X-ray Powder Diffraction, is designed for the experienced user and focuses on computer-based methods of qualitative and quantitative phase analysis. New this year (September) will be a "Rietveld and Indexing Workshop" at ICDD.

In 1951, the University of Denver held perhaps the world's first one-day symposium on the application of X-rays to the study of materials and the importance of X-rays in research. Today, the Denver X-ray Conference (DXC) is the world's largest X-ray conference, also sponsored by the ICDD. Held each August in Denver, Colorado, the DXC still provides a unique mixture of sessions on training, education, and applications, as well as papers containing details about state-of-the-art techniques and future developments in X-ray fluorescence and X-ray diffraction techniques for the study of materials. Another important part of the meeting is the presence of leading manufacturers of X-ray equipment who exhibit their most recent equipment and have their technical people available to offer their suggestions on how one might use their equipment to solve problems.

Finally, for the professional development of faculty teaching primarily undergraduates, there is the Center for Workshops in the Chemical Sciences (CWCS), a National Science Foundation Division of Undergraduate Education Course, Curriculum, and Laboratory Improvement sponsored initiative. CWCS, headed by s Jerry Smith (Georgia State University), David Collard (Georgia Institute of Technology), Emelita Breyer (Georgia State University) and Lawrence Kaplan (Williams College), is a 12-institution consortium that provides workshops for faculty at eligible US institutions including 2- and 4-year

colleges and universities. Individuals, including post-docs and graduate students who plan to embark on a college teaching career, and conservators, forensic, biomedical and public health scientists with significant educational responsibilities, are also eligible. California State University Fullerton's Keck Center for Molecular Structure, directed by myself, hosts a variety of biennial workshops, including 'Modern Biomoleular Crystallography', and 'Crystallography for Chemists'. Additional financial support has come from Bruker-AXS, Oxford Diffraction Systems, Rigaku MSC, Hampton Research Corp., Molecular Dimensions, and Nextal Biotechnologies/Qiagen.

Graduate Programs

What we can conclude from the surveys taken in 2001 and 2003 is that the majority of formal courses in crystallography at the graduate level in the US are offered in chemistry departments (Figure 1), while the majority of crystallography-related abstracts submitted to national scientific meetings are usually in structural biology. Graduate students in biochemistry and molecular biology in the US infrequently take a formal course in crystallography at university, and they are often trained by other graduate students, post-docs, scientists at synchrotron beamlines, or through professional development courses. Furthermore, geologists have reported that because the emphasis in geological sciences has shifted heavily towards ecology and the environment, coverage of crystallography has been greatly reduced or eliminated from the curriculum.

With the migration of academic crystallography from a research specialty to a technique employed by a wide community of users, few university departments in the United States hire faculty capable of teaching crystallography, and representation of crystallography in university curricula has diminished markedly over the last decade. This has led to an increasing reliance on other, non-curricular resources (such as web pages) which allow crystallography to be self-taught. While web-based tutorials are often well-constructed and can provide an extremely valuable resource to the broader scientific community, such tutorials can not take the place of practical experience, nor do they transmit the fascination and excitement in the field that will interest a future generation of professional crystallographers. We hope that our policy document, endorsed by the USNC/Cr and ACA, will develop in scientists in these fields a renewed appreciation of the importance of crystallography in their research endeavors and help students recognize the broader applicability of their skills.
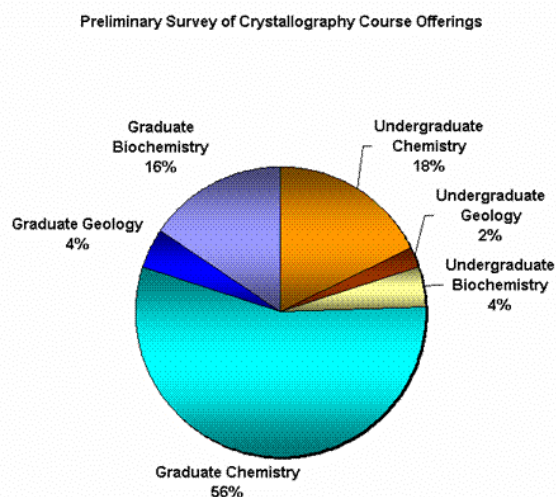
Fig. 1: *Distribution of Crystallography Course Offerings in United States Colleges and Universities. The majority of course offerings, both graduate and undergraduate, occur in chemistry programs, while the*

majority of abstracts submitted to national scientific meetings are in structural biology. Reproduced with permission[2].

Undergraduate Institutions

Because X-ray diffraction instrumentation is not considered a facilities requirement for university chemistry departments to receive undergraduate professional education certification by the American Chemical Society (ACS), crystallography has practically disappeared from the undergraduate chemistry curriculum in the United States. The subject where the majority of our undergraduate students will likely encounter crystallography, if they do at all, is physical chemistry. Yet, an informal survey of physical chemistry textbooks published in the last decade reveals that while ~50% mention crystallography, coverage of crystallography has been severely reduced or eliminated from physical chemistry texts published after 2000. Moreover, experimental techniques, when described, involve film-based precession cameras and not the modern era CCD area detectors. We are encouraged, however, that many of the latest first year, general chemistry textbooks devote 1-3 pages to X-ray diffraction, witih at least one giving attention to X-ray diffraction as a 'major technique' alongside infrared spectroscopy, UV/Vis spectroscopy, mass spectrometry and nuclear magnetic resonance.

In physics, although the undergraduate curriculum is rather homogeneous in the US, and general diffraction theory is covered, the physics community (unlike chemistry and engineering) has no formal certification or accrediting process for undergraduate programs. The National Association of State Boards of Geology (ASBOG) offers baccalaureate geology students the opportunity to pass certification exams, in which crystal systems and symmetry are considered as part of the knowledge base in mineralogy and petrology. However, the undergraduate geology curriculum is becoming a bit more heterogeneous as departments move away from traditional topics, and there is no formal certification or accrediting process for undergraduate programs. Although the American Society for Biochemistry and Molecular Biology (ASBMB) makes general recommendations about curricula that include physical biochemistry/molecular modeling/biomolecule structure/function, ASBMB also does not have a formal certification or accrediting process for undergraduate programs.

Predominantly undergraduate institutions (PUIs), despite their sometimes relatively small science programs, excel at attracting good students to science and encouraging them to enter graduate programs. Indeed, PUIs have a leading role in undergraduate education in the United States by providing the majority of baccalaureate graduates who go on to do a PhD in the sciences. Along with community colleges (CCs), they provide the primary pathway for recruiting the next generation of professional scientists in general, and crystallographers specifically, into professional careers. Although undergraduate research is recognized as an effective strategy for teaching and refining skills, faculty at PUIs, who generally carry heavier teaching loads than their counterparts at PhD-granting universities, are often challenged to conduct and maintain productive contemporary research programs by constraints on time and resources. It is to the benefit of the broader scientific community that PUI faculty members in the United States are supported in their efforts to integrate crystallographic topics into their teaching, and crystallographic methods into their research. Moreover, it is in the personal best interests of professional crystallographers and their institutions, funding agencies, and the nation to ensure that adequate support is in place to fully integrate crystallography into undergraduate teaching and research.

In 2005, an X-ray diffraction consortium of predominantly undergraduate institutions was launched - The Science Teaching and Research Brings Undergraduate Research Strengths Through Technology – Cyber Diffraction Consortium – STaRBURSTT-CDC (Figure 2). The consortium, headed by Allen Hunter at Youngstown State University, was established from five pre-existing regional core X-ray diffraction instrumentation facilities headed by Hunter at YSU, myself at Cal State Fullerton, Gregory Ferrence at Illinois State University Normal, Guy Crundwell at Central Connecticut State University, and Marcus

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[2] Kantardjieff, K.A. 2001, *CMolS: an X-ray collaboratory for research, education and training.* In Program Abstracts, American Crystallographic Association National Meeting, Los Angeles, CA.

Bond at Southeast Missouri State University. Instrumentation at the core nodal institutions includes an extensive array of the latest instruments, usually available for both remote and local operation at relatively low cost, and a wide range of areas of faculty expertise. STaRBURSTT-CDC aims to systematically and significantly changing the research and educational cultures at PUIs, with the value added benefits flowing from this change to our "customers" (the nation's major research universities and R&D and production organizations) through the currency of its students. Consortium members are PUIs, CCs, Historically Black Colleges and Universities (HBCUs), Hispanic Serving Institutions (His), and Tribal Colleges (TCs). STaRBURSTT also collaborates closely with a range of affiliate members, such as PhD granting universities, government labs, non-profit organizations, and companies.

Fig. 2: *The Science Teaching and Research Brings Undergraduate Strengths Through Technology – CyberDiffraction Consortium. Primary Nodes, indicated by the larger red stars in the map, provide substantial local and remote access to external users of their broad range of modern instrumentation. Secondary Nodes, indicated by the yellow stars in the map, provide local test sites and/or local and remote access for external users to their more limited range of modern instrumentation. Blue stars in the map denote community college members. (Figure design by Katherine Kantardjieff.)*

K-12 Education

Friedrich Fröbel, a crystallographer and the inventor of kindergarten, believed that the geometrically shaped surface planes of crystals demonstrated that fixed laws govern the natural world. Fröbel believed that these same laws guide the development of the child, the adult, and even whole societies, and therefore that the logic of creation could be illumined through the guided manipulation of forms. In grades K-12, United States National Science Education Content Standards expect science curricula to develop students' understanding and abilities aligned with the concepts and processes associated with a) systems, order and organization; b) evidence, models and explanation; c) form and function. Moreover, high school is a significant period in the education of students, because this is when they are exposed to science at a more significant level, and when they make their preliminary career choices. Well-qualified teachers must be able to present contemporary scientific topics in a way that attracts talented and enthusiastic young people to science, whether contributing to the development of scientifically literate citizens or science specialists in the future work force.

K-12 teachers should be given opportunities for continuing education in crystallography to give them knowledge and provide them with learning units, tools and modern examples to incorporate into their curricula, so that they are comfortable teaching the science. Completion of such professional development and innovative application of the knowledge gained should be rewarded through certification and in-

service credit. One such program for high school teachers exists at the University of California Irvine, where Ken Janda heads a team of chemists, geologists and engineers working together on a National Science Foundation Collaborative Research in Chemistry (CRC) Project to advance the state of knowledge of clathrate hydrates. The CRC Project also incorporates a community outreach program involving high school teachers, which includes a week-long summer workshop in crystallography held jointly between UCI and Cal State Fullerton.

Crystallography 'awareness' should begin in K-12 education. Students are easily enthused or put off by subjects in pre- and high school, often making life-altering decisions about future study and career goals. Natural curiosity and excitement about the scientific world must be encouraged and cultivated. Crystallography, which derives molecular structure and its implications in such fields as drug discovery and materials design, is a highly interdisciplinary and visually stimulating science (Figure 3), capable of providing cues for discussions of symmetry, chemical structure, biochemical processes and molecular disease.
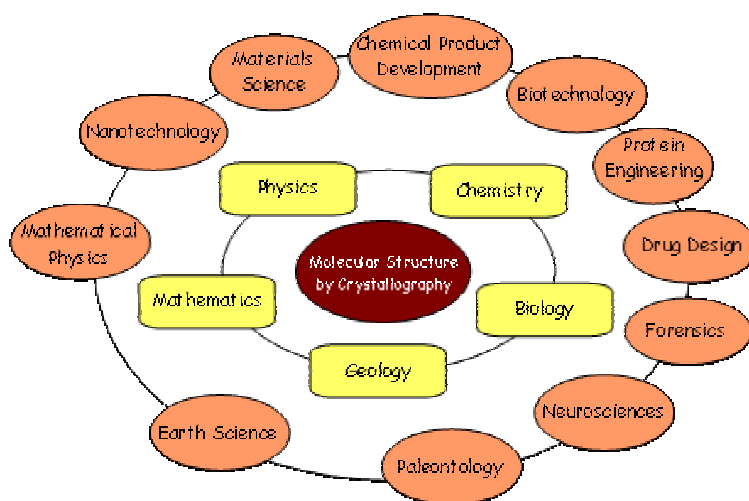

Fig. 3: *The 'Waves' of Crystallography. Crystallography is a highly interdisciplinary science, bordering on and integrating naturally with fields such as earth science, physics, chemistry, biology, biotechnology and mathematics. (Figure design by Andy Howard.)*

Concluding Remarks

Substantial advancements in crystallographic techniques made over the past 25 years allow individuals with quite diverse background and preparation interested in a specific structural problem to use crystallography as a tool in their problem-oriented, hypothesis-driven research. These same technical advances now enable users with little or no training (or deeper understanding) to often (but not always) produce quality results. The practitioner in crystallography today and perhaps even more in the future is the structural biologist, structural chemist or material scientist. He/she must be able to skillfully analyze a structure in its chemical or biological context, material preparation and synthetic methods. Furthermore, he/she must be in command of a solid repertoire of techniques aimed at determining more and more challenging structures.

Paul Ewald described our science in *Acta Crystallographica*[3]: "Crystallography borders, naturally, on pure physics, chemistry, biology, mineralogy, technology and also on mathematics, but is distinguished by being concerned with the methods and results of investigating the arrangement of atoms in matter, particularly when that arrangement has regular features." This statement is as true today as it was more than 55 years ago. Modern crystallography provides enabling technology, methodology and information, and the bounty of knowledge gained from analysis of its structures is a key underpinning of modern

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[3]*Acta Crystallographica*, 1948 1,2

science and technology. There is common ground in the fundamental physics of crystallography shared by scientists in the life sciences and by those in the physical sciences, but the objectives of each community in applying crystallography to their particular research problems are not necessarily the same. Life scientists are generally interested in overcoming the modern-day bottlenecks of crystallization and protein production, and in learning the basic requirements to use crystallographic techniques, namely data collection and executing various software applications that determine molecular structures in a nearly automated fashion. Physical scientists, particularly those from the fields of inorganic chemistry and materials science, are often concerned about fundamental symmetry, space groups and unit cells, which give rise to the material and reactive properties of the crystalline state. These topics naturally require greater depth of understanding of the underlying crystallographic principles.

The policy document summarizing the crystallography education and training policies endorsed by the ACA and the USNC/Cr makes recommendations for a comprehensive re-evaluation of crystallography education. It suggests ways to develop in the broader scientific community an appreciation for the value of crystallographic information, and it promotes ways in which the visual, aesthetic and quantitative nature of crystallography can provide an excellent path to introduce science and scientific methods to the general population. We hope that the policy document will facilitate further discussion and exchange of ideas in the national and international crystallographic communities, to share what we know, have developed and will develop, as well as to communicate "best practices" from around the world.

Acknowledgements

Crystallographic Teaching in Pakistan

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Pakistan came into being in 1947. The country at that time had only one university, the University of Punjab, Lahore. However, there were a few affiliated colleges enrolling the students for a Bachelors' degree and, in some of the disciplines, for a Masters' degree. The former required minimum two years of registration following the higher secondary school certification, while the latter required another two years of registration following the successful completion of the Bachelors' degree program. The admission to the University of Punjab was based on merit and there were a limited number of seats available in every discipline that the University offered. The entry criteria for most of the disciplines was successful completion of the Bachelors' degree, while a few disciplines also registered the students for a Bachelors' degree program which could be subsequently followed by the registration for a Masters' degree if the student both wished and qualified the required merit. The University of Punjab was founded in 1982. The University had a very rich tradition of scholarly learning in many disciplines of moral philosophy and natural philosophy, including Chemistry, Physics and life sciences. After the World War II, India was marred by widespread political disturbances following the independence movement. Even before the creation of Pakistan in 1947, most of the highly qualified foreign staff had already left the University for their homeland in U.K. The creation of Pakistan also deprived the University of a part of highly competent native staff who belonged to the *other side* of the border. The country also needed more universities since the students in Pakistan no longer had the access to the institutes of higher learning in other parts of united India. The Government of Pakistan instituted a few new universities early in 1950s including two universities in the Sindh province, University of Karachi, and University of Jam Shoro; one in the province called North West Frontier and/or Serhad (national language word), University of Peshawar; and once in the Baluchistan province, University of Baluchistan. All universities were having affiliated and constituent colleges. However, *majority* of the colleges offering B.Sc. in the disciplines of natural philosophy including Chemistry, Physics and other life sciences, and mathematics were affiliated with the University of Punjab. As mentioned earlier, The B.Sc. program was for two full academic years after 12 years of schooling and successful completion of higher secondary school certificate (equivalent to British A level).[4] The students were required to major in at least three subjects opted from amongst the natural sciences and pure sciences, including mathematics and statistics. The examinations used to be held twice a year. However, once enrolled for the degree, a student was first to appear in the examination after the completion of two full academic years. If unsuccessful in the first attempt, a student was allowed to avail another four chances for qualifying the examination. Initially, each successive chance required whole evaluation. Later, the part evaluation was also allowed, as not many students had the ability to get through the examination if taken otherwise.

Crystallography was included in the required course content of the subject of Chemistry and a part of it was also added in the subject of Physics. Therefore, a student opting to major in Chemistry, Physics and Mathematics had both theoretical perspectives and the analytical ability to learn the fundamentals of the subject, such as crystal systems, Weiss indices, Miller indices, Bragge's Law, X-ray diffraction, Powder method, single crystal method, general indexing and many other basic theories and laws.

In the 1960s, the syllabi were revised at all levels and modern atomic and molecular knowledge was added in the B.Sc. course requirement. Similarly, Masters' courses in the disciplines of Chemistry, Physics, life sciences and pure sciences, mathematics and statistics, were revised. The most significant addition to the B.Sc. course content was perhaps the modern concepts about symmetry. The total number

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[4] This system is being phased out now to establish the equivalence with the internationally reputable schools of higher learning. The proposed program requires four years of enrollment for the award of Bachelors' degree. Many of the private sector universities were already practicing it. Since last academic year, the public sector universities and the affiliated colleges are also required under the directive from the Higher Education Commission (HEC) to gradually phase into the standardized four-year Bachelors' degree program.

of contact hours for lectures on crystallography ranged from 20 to 30. Subsequently, however, the introduction of the semester system in some of the universities reduced the number of contact hours for lectures on crystallography. Moreover, another constraint, which appeared with time, was the unavailability of required number of specialists in solid state or crystallography to teach the subject across the board in all colleges and universities of the country. Finally, due to the wide option given between the questions in the exam paper, the students, while preparing for exam, either did not study crystallography in depth and detail or simply skipped that part of the course.

In the realm of higher education, another important part of the 1960s education policy was the overseas training of the university teachers. The government sponsored a large number of university teachers who got registered for a Ph.D. degree program, mostly in the institutes of higher learning in the industrially advanced countries. An overwhelming majority of the Ph.D. scholars opted for the universities in Western Europe, mainly U.K. and North America including both US and Canada. Unfortunately, the scheme was not devised in a manner ensuring coherence and need-based approach. Resultantly, a large number of scholars ended up doing Ph.D. in the offshoots of the disciplines, which did not require analytical rigor and ensured the completion of the degree with relative ease. In the discipline of Chemistry, the Ph.D. scholars mostly specialized in Organic, Bio and Inorganic Chemistry. Very few opted for crystallography, and even the Physical Chemistry. The very high cost and consequence of a scheme, which did not follow a need, based approach first started to be surface in the early 1970s. It was realized that the universities allover the country were not having the required expertise for covering the entire span of specialization topics included in the course requirement for a Masters' degree in Chemistry. Many universities did not include crystallography in the course requirement of any of the disciplines and/or the offshoots of the disciplines. There were one or two specialists of Physical Chemistry who included crystallography in the course requirement of M.Sc. degree in Chemistry. It was a part of optional specialization in Physical Chemistry in the 2nd year of the M.Sc. Program. Following topics were included in the required course content:

- Basic concepts;
- Crystal systems;
- Weiss and Miller indices;
- Single crystal and powder methods of X-ray diffraction;
- Indexing;
- Structure factor;
- Chemical applications of Group theory;
- Point groups;
- Character tables;
- General introduction to space groups.

In the 1970s, the overall educational standard at B.Sc. and M.Sc. level improved in Pakistan, as many overseas scholars returned home with M. Sc., M. Phil and Ph.D. degrees from European and North American universities. They started teaching in universities and colleges allover the country. More public sector universities were also opened, many in smaller cities. Revised syllabi and courses too were introduced. The medium of instruction and expression was English for both B.Sc. and M.Sc. degree programs. The examination system, however, was still biannual in most of the universities for evaluating both B.Sc. and M.Sc. degree candidates.

Crystallography was a compulsory part of the B.Sc. course. The colleges offering B.Sc. degree programs were affiliated to different universities and were therefore required to follow the course as per requirement of the university allowing affiliation. An official Text Book Board was established in Lahore, which was responsible to recommend textbooks not only for primary, secondary and higher secondary schooling, but also for learning at the B.Sc. level. Some very good B.Sc. level text books were written by Pakistani authors, mainly highly qualified university teachers, in various disciplines of sciences including Chemistry, Physics and other life sciences. However, foreign books written by American and European authors were also available in the market and widely in use allover the

institutions of higher learning. More significantly, each university was having its independent Board of Studies, which exercised the power to update/revise the syllabi.

In the late 1970s, some of the universities opted semester system of examination for M.Sc. degree programs and introduced some variation in the courses, which they offered under the new system of evaluation. The syllabi were designed keeping in view the availability of the teaching staff, rather than the required course contents. At the B.Sc. level on the other hand, the unavailability of the specialist teachers was already making it difficult for the students to thoroughly follow crystallography. As mentioned earlier, the required level of instructions needed 20 to 30 contact hours of lecturing by a specialist on the topic. The crystallography specialist at B.Sc. level was supposed to be a teacher having a sound knowledge of three subjects, Chemistry, Physics and Mathematics. For teaching at the M.Sc. level, a specialist necessarily required a Ph.D. either in Physical Chemistry or Chemical Physics. Unfortunately, most of the Ph.D. Chemistry teachers in the universities did not possess required analytical skills, as they did not have sound knowledge of Mathematics. The syllabi of Chemistry at M.Sc. level were therefore slightly unbalanced and did not favor the effective teaching of crystallography. The Board of Studies mainly consisted of the teaching staff of the concerned universities and the members favored and approved those topics or course contents, which they found *easy* to teach. Unfortunately, most of the teachers in Pakistan having a Ph.D. degree in Chemistry do not have the required level of expertise in Mathematics. Resultantly, crystallography was not made compulsory in the first year of M.Sc. Chemistry. In the second year, students were required to opt one of the following specializations:

- Physical Chemistry
- Organic Chemistry
- Inorganic Chemistry
- Applied Chemistry
- Polymer Chemistry
- Bio Chemistry

An optional research project was also part of the specialization. Those opting for research were required to do the experimental work and write the thesis duly supervised by the assigned research supervisor. Some of the universities were having separate departments of Biochemistry.

In the 1980s, the examination system was revised as a part of the effort to improve the educational standard. The students were required to take the separate exam for each of the required two years of M.Sc. duration. As mentioned in the foregoing, the opportunity to learn crystallography was offered in the 2nd year only to those students who opted to specialize in Physical Chemistry. The course content on the topic required was 25 to 30 contact hours of lecturing in the class. The major topics covered were crystal system, Basic laws, Weiss and Miller indices, Experimental detail of Powder and single crystal method along with illustrations to simple crystal systems (cubic etc). Structural factor, Fourier synthesis, symmetry, Point group, space group and general application of crystallography.

It is important to mention here that though the M.Sc. Physics course included *Solid State*, it did not cover the main crystallography since the contents mostly focused on Bragg's law and some mathematical equations. Even symmetry and Group theory were ignored. Probably, due to the ignorance of chemical properties of compounds, the teachers were unable to discuss single crystal and powder pattern of organic compounds and, it appears, that they only emphasized the cubic system. The upshot is that it was the teaching of *Physical Chemistry* in Pakistan, which offered most of the crystallographic knowledge.

X-ray diffractometer was never widely accessible in Pakistan. Only few of the universities purchased the instruments with Powder method facilities. Again, these instruments were used mostly for cubic systems, only to illustrate the Powder method. Moreover, the teaching aids were not technologically updated in many of public sector universities. Even in the early 1990s, the teachers were mostly provided black board and white chalk for lecturing in the classroom. Some of the teachers also failed to keep pace with the required level of competence and came to the class with lecture notes in the hand which they either

read from the sheet verbally or copied the contents on the board. Sometimes, the teaching quality was compromised to the extent that the students were given the copies of the lecture notes. Though the universities were having well equipped libraries containing *up-to-date* titles, majority of the students simply relied on the lecture notes handed by the teachers and/or inherited from the senior students.

One very positive development in the 1990s, however, was the beginning of the era of the usage of computer technology in the educational institutions of Pakistan. Indeed, since the second half of the 1990s, there has been a drastic change in the availability and accessibility of technologically *up-to-date* teaching aids in the universities, especially after the advent of Internet in the country, which was accompanied by a remarkable increase in the usage of personal computer (PC), both at the household and institutional level. Higher Education Commission (HEC) of Pakistan arranged a seven days workshop on *Computational Chemistry* and they invited teachers from all public sector universities of the country. It was decided to work on computational methods in future by accessing the updated software and sharing it between all universities. That was the major turning point in higher education in Pakistan. Many universities remarkably increased the usage of computer technology as a significant part of the teaching aids. Students were provided access to the updated software, which they could independently use, asked to use in the laboratories. The wide usage of computer technology provided significant boost to crystallographic illustrations, especially to the understanding of the fundamentals. In 1997, Internet arrived in Pakistan and soon the network spread to all major cities. The interested and active students and teachers started extensive use of Internet. Many software were freely available online. The real help came form CCP14, the Software distributed freely in the form of CDs. These CDs were a great source of learning both for the teachers and the students who now got clear concept of Space group, which was difficult to illustrate on a Board. Crystallographic calculations were demonstrated by PCs, as it was the best way to do that and the students even developed the ability to independently run the Software while working in the home. The Internet also provided access to a *depot* of online books and other related literature. Since the turn of the 21st century, syllabi have been re-arranged and, as mentioned above, the universities and colleges are required to phase into internationally compatible four-year Bachelors' degree program. Moreover, M. Phil. degree programs have also been introduced in many public sector universities. Although the crystallography course contents in the new four year B.Sc. Chemistry are similar to earlier two-year B.Sc. degree, teaching standard is much higher with the help of Internet and CCP14 Software. For M. Phil in Physical Chemistry, the Crystallographic syllabus includes the following topics:

- Basic concepts;
- Basic laws;
- Weiss and Millar indices;
- Powder and Single crystal methods;
- Indexing;
- Fourier synthesis;
- Structure factor;
- Introduction to various software;
- Group Theory;
- Point groups;
- Space groups;
- Software used in structure elucidation.

The above course contents require about 25 to 30 contact hours of class lectures during the first year of enrollment for the M. Phil. degree program, while the second year of the enrolled student is entirely devoted to individual research project carried out under the guidance of a supervisor appointed by the Board of Studies. It may be concluded that the Information Technology (IT) revolution has helped improve the quality of crystallography teaching, particularly in the new century. The HEC has provided free Internet access to students and teachers in all public sector universities. Learning and teaching has become both easier and challenging, as ready access to latest knowledge and analytical techniques,

incorporated in the updated Software, is making both students and teachers a lot more ambitious than ever before.

That said, there is also a downside of the IT revolution: the strengthening of already *victorious market* and commercialization of education. Following the neoliberalist ideology also in the realm of education, a number of private universities have cropped up in Pakistan. These universities are mainly offering IT and management diplomas / degrees. Given the market-oriented culture of the private universities, the cost of education is very high compared to their counterpart in the public sector. In a milieu where there is a general dearth of specialists and expertise, the private universities are offering very high pay packages to attract the quality teachers. Resultantly, many of the teachers in the public sector universities have joined the *rat race* and universities are facing serious vacuum as, along with joining the private sector, a large number of highly qualified faculty have also been sucked by the global market. Presently, a person of high caliber requires strong conviction for staying in the public sector universities, which, of course, are supposed to chaperon the process of progressive social transformation by helping enhance both technological development and sociological evolution. Unfortunately, none of the private sector universities are offering degrees in natural sciences, as the market does not presently favor these subjects. However, market failures have been rampant in the past and the contemporary times do not dole out any guarantee of the success of the market either. The upshot is that the market failure in the production of *intangibles* may have a lot more severe and far-reaching effects for an underdeveloped society like Pakistan, than it may be the case for tangible products.

Finally, the future of crystallography teaching is uncertain in Pakistan, as the public sector universities of the country are fast loosing to the local and global market the Ph.D. teachers, having degrees from internationally reputed schools. Furthermore, the market is not promoting the natural sciences and the *interventions* are not delivering the desired results either.

A Guided Tour in Fourier Space

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1. Introductory

The tour is intended for those that would like to get familiar with the concept of 'reciprocal space' and its relationship with the familiar 'direct space'. Since the main part of understanding is merely getting familiar, we will not pursue mathematical rigor. Especially those that have little or no experience with Fourier Space are invited for the round trip. For those that are well prepared and/or have a solid mathematical background it possibly can serve as an overview.

2. Fourier Transforms

The definition of the Fourier transformation (or Transform), we will use is:

$$F(S) = \int f(r) \exp(2\pi i r.S)\, dr.$$

It transfers a function $f(r)$ from the direct vector space, where r is the position vector and dr is a volume element at position r, into a function $F(S)$. $F(S)$ is a function in the reciprocal or Fourier space, where the positions are determined by a vector S. The integration extends over the whole space. Both functions, $f(r)$ and $F(S)$, may generally be complex functions, i.e. they can be written as the sum of a real part and an imaginary part or as a real modulus and argument or phase factor i.e. $f(r) = |f(r)|.\exp\{i.\varphi(r)\}$, where $|f(r)|$ is the modulus and φ is the argument (or phase). Beware of the fact that if $f(r)$ is a real function does by no means imply that the transform $F(S)$ is real.

The position vector r is measured in meters (or Å). Since an exponent is dimensionless, S is expressed in units m^{-1} (or $Å^{-1}$). The Fourier Transform will, as an operation, be denoted by the symbol FT^+:

$$FT^+[f(r)] = F(S).$$

The transformation which transfers the function $F(S)$ from reciprocal space back into the function $f(r)$ in direct space is called the Inverse Fourier Transform (FT^-) given by:

$$f(r) = \int F(S) \exp(-2\pi i r.S)\, dS.$$

No information is lost in the transformations, neither in FT^+ nor in FT^-. A presentation of the function $F(S)$ in reciprocal space is equally valuable as the presentation of the function $f(r)$ in direct space.

The here presented formulations of FT^+ and FT^- are generally used in structural science. All structural data published under the authority of the IUCr (International Tables and Acta Cryst.), are only consistent with the here given definition.

3. Why Fourier Transforms are so useful in structural science

As shown in Box 1, the scattering amplitude $A(S)$ of the radiation scattered by an object is, within certain assumptions, given by the transform $FT^+[f(r)]$:

$$A(S) = \int \rho(r) \exp(2\pi i r.S)\, dr.$$

S is called the scattering vector, $\rho(r)$ is the 'scattering power' at position r. The intensity I(S) is as usual given by $A(S) \times A^*(S)$.

The scattering power is, dependent on the type of radiation used, X-rays, neutrons or electrons, directly related to the structure of the sample.

So in structure analysis there is a close connection between the experiment and the theory of Fourier Transformations.

The intensity data are collected as a function of S. The main problem is how to find the function $\rho(r)$ in the direct space from the measured intensities in reciprocal space.

Box 1. Scattering of radiation by an object.
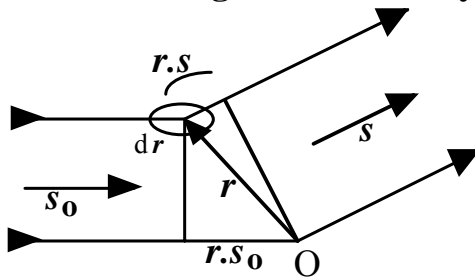
O is the origin; at 0 the phase is taken to be zero.
The parallel incident beam has direction s_o and the scattered beam direction s; $|s_o| = |s| = 1/\lambda$. dr is an infinitesimal volume element at position r; it is part of a scattering object. Its contribution to the scattered radiation is:

$$\rho(r)\exp 2\pi i\, r.(s - s_o)dr = \rho(r)\exp 2\pi i\, r.S\, dr,$$

where $\rho(r)$ is called the scattering power and $S = s\text{-}s_o$ the scattering vector.
The total scattering is the sum or rather the integral of all contributions.
This gives for the scattering amplitude:

$$A(S) = \int \rho(r)\exp 2\pi i\, r.S\, dr.$$

The related intensity I(S) is as usual the square of A(S), or rather the product of it with its complex conjugate:

$$I(S) = A(S) \times A^*(S).$$

The formula holds only when the scattered beam is not diffracted again (multiple scattering) and the scattering is elastic and kinematical.
For any direction of s_o with respect to the object, the maximum value $|S|$ can attain is reached if $s = -s_o$, then $|S|$ is $2/\lambda$. In the reciprocal space information can therefore only be obtained within a sphere with radius $2/\lambda$ centered at the origin. This sphere is called the Limiting Sphere.
The concepts of this Box apply to optics in general. The resolving power of an optical instrument for instance is limited because of the Limiting Sphere for that case.

4. Pair wise reciprocal functions

General rules about Fourier transformations of functions are:

What is 'skinny' in one space is 'wide' in the other and *vise versa.*

Sharp edges in one space result in wiggles in the other.

This will be illustrated by the following three examples in which we will for the time being stick to one dimension. The three dimensional cases follow by analogy.

1). *The 'Slit Function'*

It is zero everywhere except between -a/2 and + a/2 where it has de constant value 1/a. The FT$^+$ is :

$$F(X) = \frac{1}{a} \int_{-\frac{a}{2}}^{+\frac{a}{2}} \exp(2\pi i\, x.X)\, dx = \frac{\sin \pi aX}{\pi a X},$$

which is called a Sinc function.

The Slit function f(x) is displayed in figure 1 together with its FT$^+$, the Sinc function F(X).

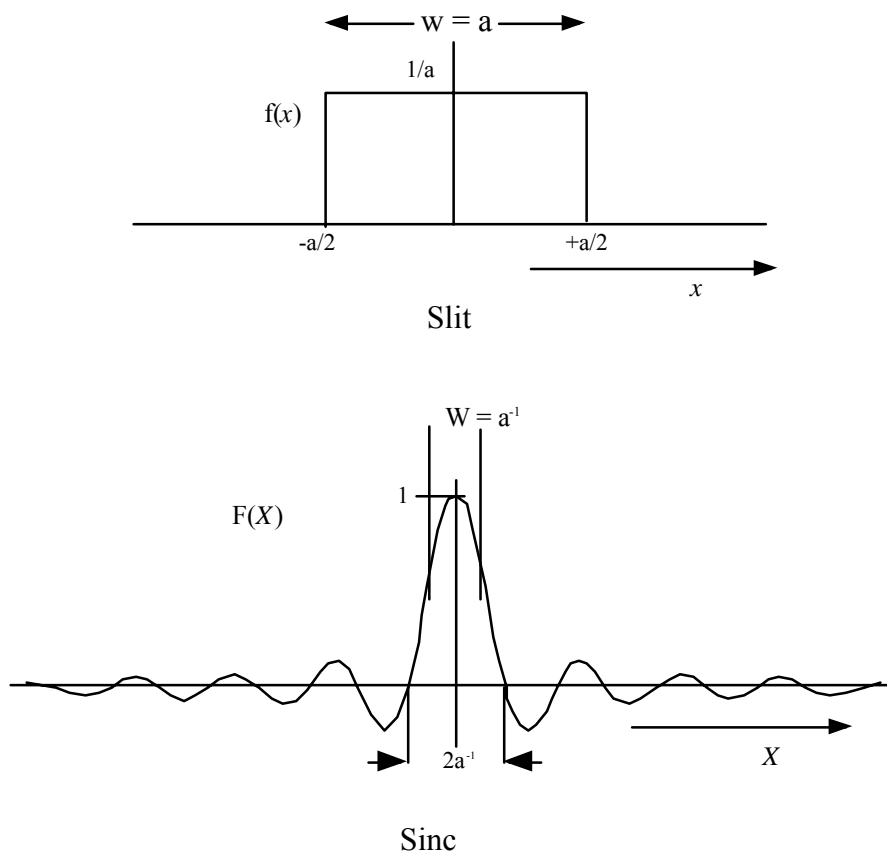The 'Slit function' and the 'Sinc function' form a *pair of reciprocal* functions.

Slit

Sinc

Figure 1
The Slit function and the Sinc function form a reciprocal pair .

The sharp edges at ±a/2 in the Slit generate the wiggles in the Sinc.

The width w of f(x) is a, the width W of F(X) can be taken to be 1/a (half of the base of the "triangular" central maximum); their product w.W = 1.

The narrower f(x), the wider F(X).

We have chosen the area of the Slit to be 1.

2). *The Gaussian function*

A one dimensional Gaussian is written as:

$$f(x) = \frac{1}{a\sqrt{\pi}} . \exp\left(-\frac{x^2}{a^2}\right),$$

then (with the aid of the standard integral $\int_{-\infty}^{+\infty} \exp(-x^2)dx = \sqrt{\pi}$) the FT$^+$ is found to be:

$$F(X) = \exp\left\{-\pi^2 a^2 X^2\right\}.$$

The transform of a Gaussian is another Gaussian.

The Gaussians f(x) and F(X) form a *reciprocal pair* of functions.

The width of a Gaussian is often defined as the width of a rectangle with the same area and the same height as the Gaussian itself. See figure 2.

The product of the widths of both functions is constant. They are 'reciprocal' in the sense that if one grows, the other one shrinks : w.W = 1.
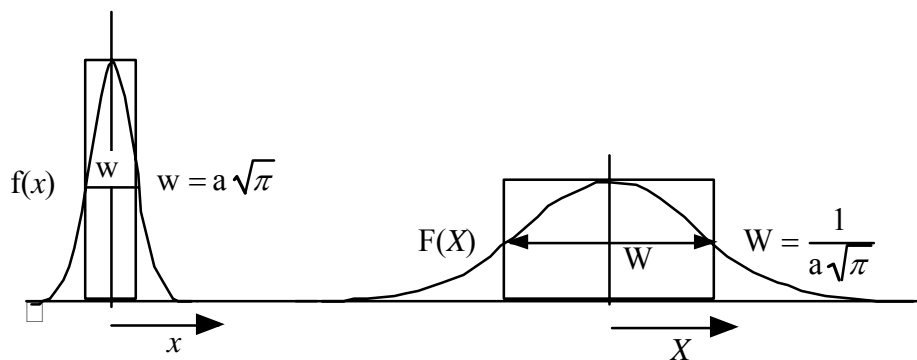

Figure 2.
A pair of reciprocal Gaussian functions.

Gaussians are exceptional in that they decay so smoothly that they produce no wiggles if Fourier transformed.

3). *The Dirac-δ-function*

If we take either the Slit function or the Gaussian and make it narrower and narrower its area will always be 1, even if we go to the limit a $\to$ 0. We then have a 'function' centered at $x = 0$, which has a width zero, its height goes to infinity but its area, that is the integral, still is 1. This is called the δ-function denoted by the symbol $\delta(x)$.

The δ-function is formally defined as:

$$\int_{-\infty}^{+\infty} \delta(x)dx = 1 \, ; \, \delta(x) = 0 \quad \text{if} \quad x \neq 0.$$

Its properties are discussed in Box 2.

The FT$^+$ of the δ-function follows directly from the definitions:

$$F(X) = \int_{-\infty}^{+\infty} \delta(x).\exp(2\pi i x.X)\, dx = 1.$$

Similarly:

$$f(x) = \int_{-\infty}^{+\infty} \delta(X).\exp(-2\pi i X.x)\, dX = 1.$$

The δ–function is as narrow as can be, and so its Fourier Transform is as wide as can be.

The δ–function and the function '1(x)', that has the value 1 everywhere, form a *reciprocal pair* of functions.

The three examples were, for simplicity reasons, given in one dimension. They can easily be extended into three dimensions.

The Slit function in three dimensions is called a "Box function": $f(\boldsymbol{r}) = f(x,y,z)$ has the value 1/a.b.c for $|x| < a/2$; $|y| < b/2$ and $|z| < c/2$; outside the 'box' $f(x, y, z) = 0$.
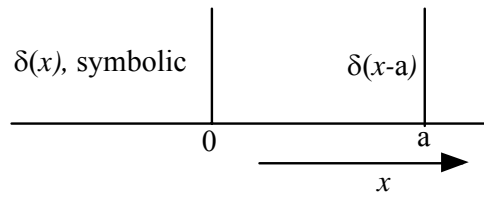
The FT$^+$ is:

$$F(\boldsymbol{S}) = F(X, Y, Z) = \frac{\sin \pi aX}{\pi aX} \cdot \frac{\sin \pi bY}{\pi bY} \cdot \frac{\sin \pi cZ}{\pi cZ}.$$

A three dimensional Gaussian is a product of three 1-D Gaussians in the x, y and z direction, respectively.

A three dimensional δ–function is $\delta(\boldsymbol{r})$: $\int \delta(\boldsymbol{r})d\boldsymbol{r} = 1;\ \int f(\boldsymbol{r})\delta(\boldsymbol{r})d\boldsymbol{r} = f(0)$;

its FT$^+$ is $F(\boldsymbol{S}) = 1$.

The same properties hold of course if an FT$^-$ is applied to a $F(S)$.

Box 2. The δ-function.

δ(x), symbolic   δ(x-a)

0   a

x

It mostly is defined by the property:

$$\int_{-\infty}^{+\infty}\delta(x)\,\mathrm{d}x = 1\,;\,\delta(x)=0 \quad \text{if}\quad x\neq 0.$$

δ(x) is not a function in the usual sense: its width is naught while its height is infinite; its Ōcontentō nevertheless is 1. In the theory of Fourier Transforms it is a very useful concept.
The δ-function can also be represented by:

$$\delta(x) = \int_{-\infty}^{+\infty}\exp(2\pi\mathrm{i}x.X)\,\mathrm{d}X$$

The most important property is illustrated by the equation:

$$\int_{-\infty}^{+\infty}\mathrm{f}(x)\,\delta(x)\,\mathrm{d}x = \mathrm{f}(0).$$

The contribution to the integral is everywhere zero except for $x = 0$, where δ(x) is non zero.
Consequently:

$$\int_{+\infty}^{-\infty}\mathrm{f}(x)\,\delta(x-\mathrm{a})\,\mathrm{d}x = \mathrm{f}(\mathrm{a}).$$

The definition in three dimensions is

$$\int_{-\infty}^{+\infty}\delta(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = 1;\delta(\boldsymbol{r})=0 \text{ if } \boldsymbol{r}\neq\boldsymbol{0}.$$

In diffraction theory the delta function often is called the "peak function" for obvious reasons.

5. Types of functions

In the three examples the functions as well as their transforms are real rather than being complex. The reason is that we chose f($\boldsymbol{r}$) to be both real and even (centro symmetric), that is f($\boldsymbol{r}$) = f(-$\boldsymbol{r}$).

In the case that f($\boldsymbol{r}$) is real, the Fourier integral can be split in a sum of a real and an imaginary part using the expression $\exp(\mathrm{i}.\phi) = \cos\phi + \mathrm{i}\sin\phi$.

$$\mathrm{F}(\boldsymbol{S}) = \int \mathrm{f}(\boldsymbol{r})\cos(2\pi\boldsymbol{r}.\boldsymbol{S})\,\mathrm{d}\boldsymbol{r} + \mathrm{i}.\int \mathrm{f}(\boldsymbol{r})\sin(2\pi\boldsymbol{r}.\boldsymbol{S})\,\mathrm{d}\boldsymbol{r}.$$

Changing the sign of $\boldsymbol{S}$ does not affect the real part but changes the sign of the imaginary part:

$$\mathrm{F}(-\boldsymbol{S}) = \int \mathrm{f}(\boldsymbol{r})\cos(2\pi\boldsymbol{r}.\boldsymbol{S})\,\mathrm{d}\boldsymbol{r} - \mathrm{i}.\int \mathrm{f}(\boldsymbol{r})\sin(2\pi\boldsymbol{r}.\boldsymbol{S})\,\mathrm{d}\boldsymbol{r} = F*(-\boldsymbol{S}).$$

Thus if f($\boldsymbol{r}$) is a real function $\mathrm{F}(-\boldsymbol{S}) = \mathrm{F}*(\boldsymbol{S})$; F($\boldsymbol{S}$) is not necessarily real. A real F($\boldsymbol{S}$) does occur however, if f($\boldsymbol{r}$) is real and additionally even. In that case the second integral vanishes because the sine function is odd.

If on the other hand f($\boldsymbol{r}$) is a real and odd function i.e. $\mathrm{f}(\boldsymbol{r}) = -\mathrm{f}(-\boldsymbol{r})$, the first integral will vanish, because the cos function is even, which makes F($\boldsymbol{S}$) pure imaginary.

6. Multiplication and Convolution are conjugate operations

The *Multiplication* of two functions f($\boldsymbol{r}$) and g($\boldsymbol{r}$) results in a function m($\boldsymbol{r}$) which has at the position $\boldsymbol{r}$ the value m($\boldsymbol{r}$) = f($\boldsymbol{r}$)× g($\boldsymbol{r}$).

The *Convolution* of two functions f and g is mathematically defined by :

$$c(\mathbf{r}) = f(\mathbf{r}) * g(\mathbf{r}) = \int_{-\infty}^{+\infty} f(\mathbf{r}') \cdot g(\mathbf{r} - \mathbf{r}') d\mathbf{r}'.$$

This formulation does not directly appeal to ones imagination. Convolution of a function f($\mathbf{r}$) with another function g($\mathbf{r}$) results generally in a smoothing or blurring of f($\mathbf{r}$), as the following example in one dimension illustrates in figure 3.
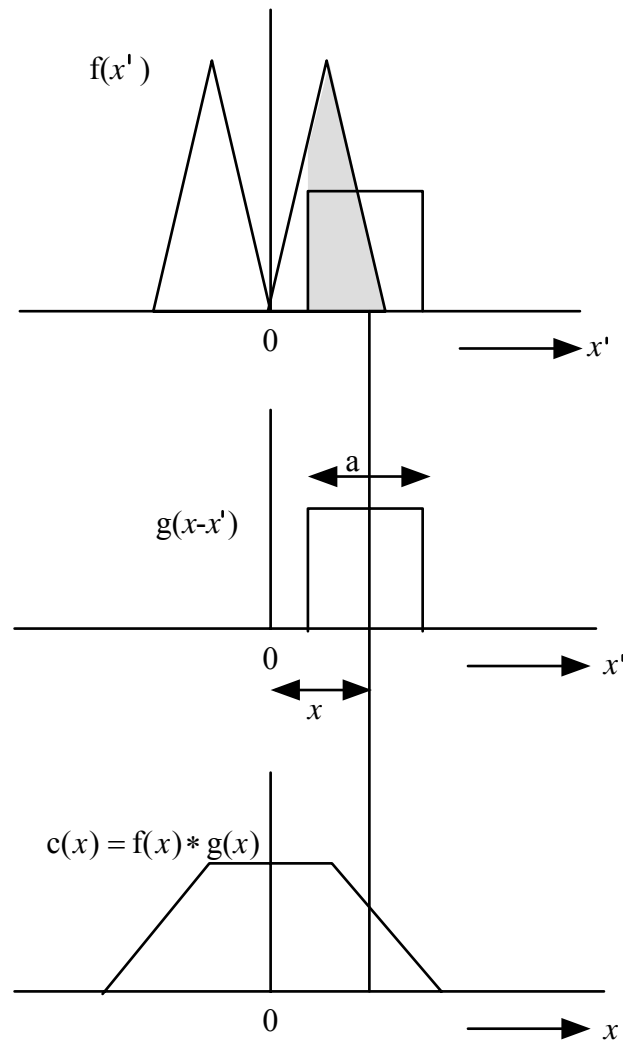

Figure 3
The convolution procedure.
f(x') is averaged over the area with width a.

Take for g(x') a one dimensional Slit function, that is g is everywhere zero except for x' between -a/2 and +a/2, where it has the value 1/a.

Now invert the function g with respect to 0 resulting in g($-x'$), then translate it over a distance x, that is changing the variable x' into $(x'-x)$. Than we have obtained
g(x-x').

In the present case we don't need to invert g, since the Slit function is even (symmetric).

Now, at the position x the function c will have the value

$$c(x) = \frac{1}{a} \int_{x-a/2}^{x+a/2} f(x')dx',$$

which is the average of f over a domain with 'width a' around the point where $x' = x$.

As figure 3 illustrates this is what we would call smoothing or blurring.

If, instead of the slit function, we take another symmetrical function which is substantially present only a limited domain, like for instance a Gaussian, the averaging will be slightly different but the procedure is essentially the same.

The blurring effect is also illustrated in an optical pin-hole camera, the so called 'Camera Obscura'. The image is convoluted with the area of the 'pin'-hole. The smaller the hole the sharper (and unfortunately weaker) the image; the larger the hole the more blurring.

And so in figure 3, the narrower the domain, i.e. the smaller a, the less blurring will occur. In the limit where $a \to 0$ the function g changes into the δ-function (see Box 2.) and the convolution will reproduce f(x) without any blurring.

In three dimensions:

$$f(\boldsymbol{r}) * \delta(\boldsymbol{r}) = f(\boldsymbol{r}).$$

Convolution of f($\boldsymbol{r}$) with a shifted δ-function $\delta(\boldsymbol{r} - \mathbf{a})$ results in the shifted function

f($\boldsymbol{r}$ - **a**):

$$f(\boldsymbol{r}) * \delta(\boldsymbol{r} - \mathbf{a}) = f(\boldsymbol{r} - \mathbf{a}).$$

The convolution operation itself has nothing to do with the Fourier transformation. It is just like the multiplication an operation where two functions are involved, both defined in the same space.

Rule: *Multiplication* of functions in the direct space implies in reciprocal space a *Convolution* of their transforms and *vise versa.*

The proof, which is straightforward, for the one dimensional case is:

$$FT^+[f(x) * g(x)] = \iint f(x').g(x - x').\exp(2\pi i x.X)dx'dx =$$
$$= \iint f(x').g(y).\exp\{2\pi i X.(x'+y)\}dx'dy =$$
$$= \int f(x').\exp 2\pi i\, x'.X\,dx'.\int g(y).\exp 2\pi i y.X\,dy = F(X) \times G(Y).$$

Multiplication and convolution form *a pair of reciprocal operations*:

$$FT^+[m(\boldsymbol{r})] = C(\boldsymbol{S}); FT^+[c(\boldsymbol{r})] = M(\boldsymbol{S}),$$

where C($\boldsymbol{S}$) is the convolution and M($\boldsymbol{S}$) the multiplication in reciprocal space.
Summarizing:

Direct space	f($\boldsymbol{r}$)	g($\boldsymbol{r}$)	$m(\boldsymbol{r}) = f(\boldsymbol{r}) \times g(\boldsymbol{r})$	$c(\boldsymbol{r}) = f(\boldsymbol{r}) * g(\boldsymbol{r})$
Rec. space	F($\boldsymbol{S}$)	G($\boldsymbol{S}$)	$C(\boldsymbol{S}) = F(\boldsymbol{S}) * G(\boldsymbol{S})$	$M(\boldsymbol{S}) = F(\boldsymbol{S}) \times G(\boldsymbol{S})$

7. The use of multiplication and convolution

1). *The resolving power*

As indicated in Box 1, complete knowledge of A(S) would offer a complete picture of ρ(r) in the direct space by application of an FT⁻. However, the function A(S) is only accessible to measurement within the Limiting Sphere (L.S.). We are deprived of any information about A(S) for |S|> 2/λ.

The question now is how this affects a reconstruction of ρ(r). In the most favorable situation we know A(S) exactly within the limiting sphere but nothing about it outside. That is, the observed scattering amplitude A'(S) is the ideal A(S) multiplied by a function T(S) which has the value 1 inside the L.S. and which is zero outside it:

$$A'(S) = A(S) \times T(S).$$

The FT⁻ of A'(S) thus is

$$\rho'(r) = \rho(r) * t(r),$$

where t(r) is the FT⁻ of T(S).

T(S) is a 'spherical Slit' function and t(r) thus has spherical symmetry, a radius of the order of λ /2 and some wiggles.

The picture we at best get from ρ(r) is one that is blurred by t(r). So using radiation with a wave length of 1Å in X-ray crystallography, will reveal the atomic positions, but for the finer details of for instance the electron distribution a shorter wavelength is necessary.

In a real scattering experiment additional instrumental limitations of the area in reciprocal space, where data can be collected, will be present. The effect on the resolution can then be found by constructing the corresponding truncation function T(S). Its FT⁻ will be the corresponding 'blurring function' t(r).

Though 'blurring' sounds messy, it is here a precise mathematical procedure.

2). *Forming a crystal in one dimension*

The convolution of a function with a $\delta-$function centered at position a is, as we saw, the function shifted over distance a:

$$f(x) * \delta(x - a) = f(x - a).$$

If f(x) describes the content of a unit cell, a one dimensional crystal is formed by the "crystal function":

$$f(x) * \sum_{n=-\infty}^{+\infty} \delta(x - na).$$

Though the sum extends from $-\infty$ to $+\infty$, the dimensions of a crystal are limited in direct space. This can be induced by limiting the summation over *n* from the numbers p to q. That is the same as multiplying with a shape function which has everywhere the value zero except for p.a $\leq x \leq$ q.a, where its value is 1. The size of the crystal is then a.(q $-$ p). The Fourier Transform of the finite crystal can now be found by the use of figure 4.

We first need to know the transform of the array of $\delta-$functions. The transform of a delta function at $x =$ n.a is:

$$FT^+\{\delta(x - na)\} = \exp(2\pi i na.X),$$

So the transform of an equidistant infinite array will be:

$$FT^+\left\{\sum_{n=-\infty}^{+\infty}\delta(x-n\mathrm{a})\right\}=\sum_{n=-\infty}^{+\infty}\exp(2\pi i n\mathrm{a}.X).$$

This is the sum of exponential functions $\exp(n.i.\phi)$ which can be represented by unit vectors in the complex plane making angle $n\phi$ with the real axis. Unless ϕ is a multiple of 2π, they will cancel each other. So $(\mathrm{a}.X)$ must be an integer i.e. X must have values h/a where h is an integer. The transform of an equidistant array of $\delta-$functions in one dimensional space with interspacing a is another equidistant array of $\delta-$functions in the reciprocal 1-D-space, the corresponding interspacing is 1/a.

We have found a new pair of mutually reciprocal functions: a row of $\delta-$functions and another row in the other space; the interspacings are the inverse of each other.

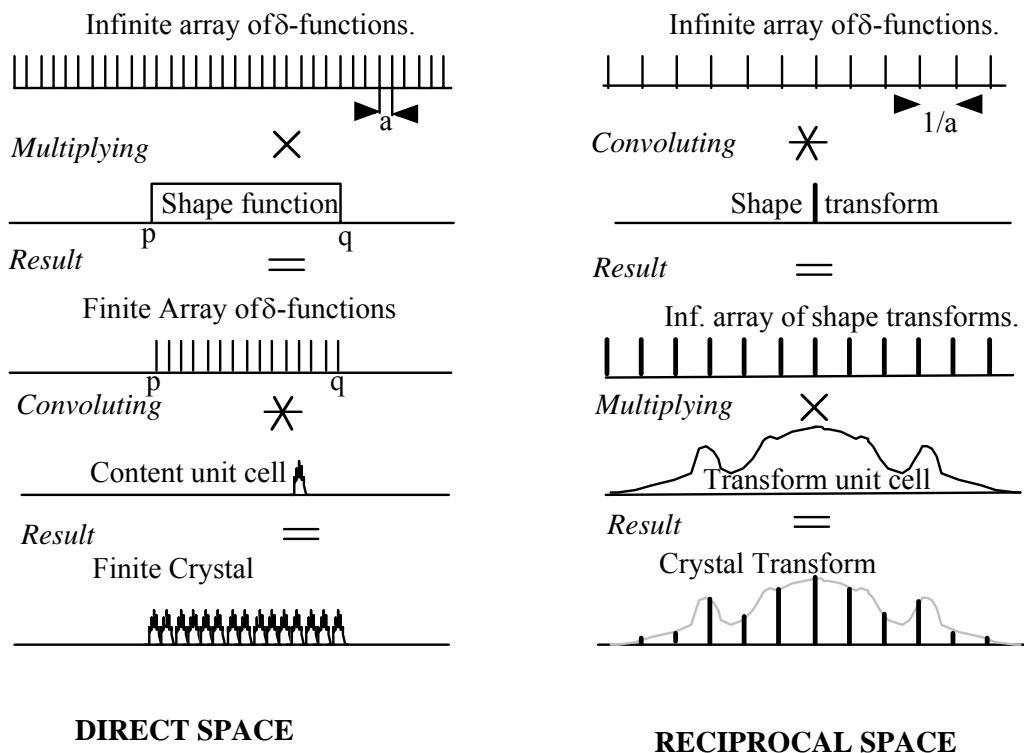**DIRECT SPACE**

RECIPROCAL SPACE

Figure 4
A crystal can be described by a sequential procedure of multiplication and convolution of the lattice, the shape and the content of the unit cell respectively. The transform of the crystal can be constructed with a sequence of the reciprocal operations applied to the respective reciprocals of the lattice, the shape and the unit cell.

In the next step this infinite array should be convoluted with the transform of the shape function, which is a 'Slit function'. Because the slit is wide in terms of the distance a, the result in reciprocal space is a row of very narrow Sinc functions (see example 1 in section **4**)

The last step is a multiplication with the transform of the unit cell, which is a broad function due to the details within it. So we end up with an array of shape transforms the height of which is determined by an envelope representing the transform of the cell content.

3). *The direct and reciprocal lattice in three dimensional space*

Extension of the array of $\delta-$functions from one dimensional $\delta-$functions into three dimensions is obtained by replacing x by the vector $\boldsymbol{r}$ and the distance a by the vector **a:**

$$\sum_{n_1=-\infty}^{+\infty}\delta(\boldsymbol{r}-n_1\mathbf{a}).$$

This is a row of equidistant three dimensional $\delta-$functions along the direction of a vector **a** with interspacing $|\mathbf{a}|$.

A two dimensional array, called a net, can be obtained by convoluting the given array with a similar array $\sum\limits_{n_2=-\infty}^{+\infty}\delta(r-n_2\mathbf{b})$ along a vector $\mathbf{b}$. Figure 5 illustrates the procedure.
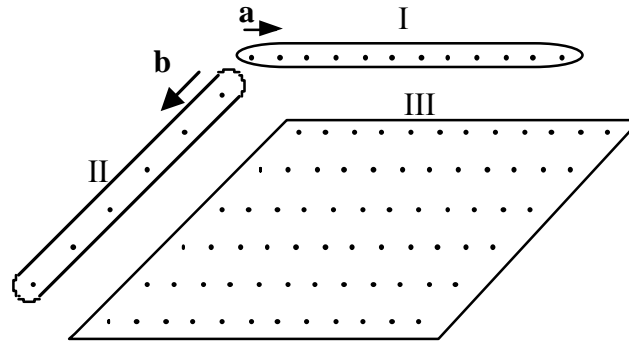

Figure 5
A planar lattice of δ functions III can be generated by a
convolution of an array I along vector $\mathbf{a}$, mutual distance $|\mathbf{a}|$
and a similar array II along vector $\mathbf{b}$ with
distance $|\mathbf{b}|$.

Extending the procedure with a third non-coplanar vector $\mathbf{c}$ results in a three dimensional space lattice of $\delta-$functions.

$$\sum_{n_1=-\infty}^{+\infty}\sum_{n_2=-\infty}^{+\infty}\sum_{n_3=-\infty}^{+\infty}\delta(r-n_1\mathbf{a}-n_2\mathbf{b}-n_3\mathbf{c}).$$

This expression represents the well known space lattice of a crystal, also introduced as the translation lattice. The unit cell is defined by the three vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, forming a parallelepiped.

We can easily construct the Fourier transform of the space lattice. Since it is a convolution of three linear arrays, in reciprocal space we should multiply the three transforms of the linear arrays.
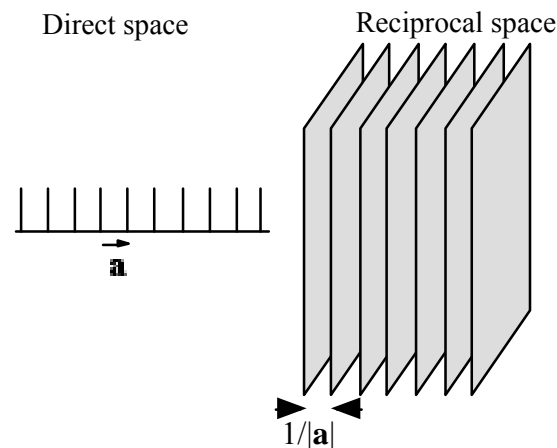

Direct space   Reciprocal space

$1/|\mathbf{a}|$

Figure 6
The Fourier transform of a row of $\delta-$functions is a set of
"$\delta-$planes".

Now, the transform of the array along the direction of vector $\mathbf{a}$ is:

$$\mathrm{FT}^{+}\left\{\sum_{n_1=-\infty}^{+\infty}\delta(r-n_1\mathbf{a})\right\}=\sum_{n_1=-\infty}^{+\infty}\exp(2\pi i n_1\mathbf{a}.S).$$

The latter expression is zero unless **a**.*S* is an integer. In the reciprocal space the projection of *S* on the direction of **a**, must be an integer times 1/|**a**|. In other words the end point of *S* is confined to a set of equidistant planes perpendicular to **a** with separation 1/|**a**|; in the rest of the space the FT$^+$ is zero. The transform is a set of planar δ−functions as illustrated in figure 6.

In order to generate the transform of the whole space lattice we must multiply this set of δ−planes with a similar set perpendicular to the vector **b** with spacing 1/|**b**|. The result is a sheaf of parallel "δ−lines" as illustrated in figure 7, where they are seen head on. The figure shows also the relationship between the vectors **a** and **b** of the direct lattice and **a*** and **b*** in reciprocal space: **a.a*** = **b.b*** = 1 and **a.b*** = **b.a*** = 0.

Finally the multiplication with a similar set of planes perpendicular to **c** produces a three dimensional lattice of δ − points in reciprocal space. This is the reciprocal lattice. Both the direct and the reciprocal lattice are introduced here as a three dimensional array of δ−functions. They form a pair of reciprocal functions, they are each others Fourier Transforms.

The relationship between the generating vectors **a**, **b** , **c** and their reciprocals **a***, **b*** and **c*** is:

$$\mathbf{a.a^*} = 1; \mathbf{b.b^*} = 1; \mathbf{c.c^*} = 1$$
$$\mathbf{a.b^*} = \mathbf{a.c^*} = \mathbf{b.a^*} = \mathbf{b.c^*} = \mathbf{c.a^*} = \mathbf{c.b^*} = 0$$

which generate the reciprocal lattice.

Box 3. Consequences of alternative formulations of the Fourier Transform.

In order to prevent confusion it should be noted that in other branches of science, notably Solid State Physics and Chemistry, slightly different formulations of the Fourier Transform are preferred. Though they are mathematically equivalent, mixing them up can lead to substantial confusion and errors.

In contrast with the definition we introduced in section 2, the FT$^+$ is sometimes given by

$$F(\mathbf{S'}) = \frac{1}{\sqrt{2\pi}} \int f(\mathbf{r}) \exp(-i\,\mathbf{r}.\mathbf{S'})\, d\mathbf{r}$$

or by

$$F(\mathbf{S'}) = \frac{1}{2\pi} \int f(\mathbf{r}) \exp(-i\,\mathbf{r}.\mathbf{S'})\, d\mathbf{r}.$$

Note that a minus sign in the exponent implies that a plus sign appears in the reverse transformation and that these signs are opposite to those in our definition. Note also the place of 2π. It implies that $\mathbf{S'} = 2\pi\mathbf{S}$; the reciprocal space is blown up by a factor 2π. As a consequence the relations between the direct and reciprocal lattice vectors change into **a.a*** = 2π. etc.

The second form for $F(\mathbf{S'})$ has the extra complication that the factor 2π must be omitted in the reverse transformation.

One of the advantages of the definition used in structural research is that one never has to worry where the factor 2π must be put. The expressions for FT$^+$ and FT$^-$ are symmetrical except for the plus and minus sign.

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4). *Forming the three dimensional crystal*

Since crystals, and thus their lattices, have limited size we should multiply the expression for the three dimensional space lattice in 3) with a shape function g(*x,y,z*). g(**r**) can be a box-function (possibly reduced to a thin plate), a sphere or whatever form the crystal might have. In order to construct a real crystal we should convolute the so properly truncated lattice with a three dimensional function f(*x,y,z*) describing the structure of the parallelepiped with edges **a**, **b** and **c** , the (primitive) unit cell.
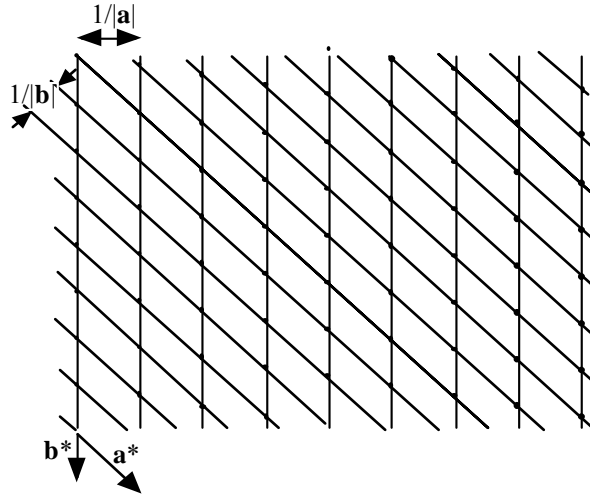
Figure 7
Two intersecting sets of parallel plane δ−functions
in the reciprocal space. The result of the multiplication is a sheaf of
parallel lines normal to the drawing paper.
It is the FT^+ of the lattice in figure 5.
The vectors **a*** and **b*** are the vectors generating a two-dimensional
lattice reciprocal to that of figure 5.

If f(Unit Cell) = f(**r**) describes the scattering power ρ(**r**), or any other feature of the unit cell, that feature for the whole crystal is given by the convolution of it with the truncated lattice:

$$\text{"Crystal Function"}(r) = f(\text{Unit Cell}) * \left\{ g(x,y,z) \times \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} \sum_{n_3=-\infty}^{+\infty} \delta(r - n_1 a - n_2 b - n_3 c) \right\}.$$

The Fourier transform of this 'Crystal Function' can now be found by successive convolution and multiplication of the transforms of the different parts in the expression, analogously to figure 4.

Thus:

In reciprocal space the transform F(**S**) of the Crystal Function is zero everywhere except close to points **H** = h.**a*** + k.**b*** + l.**c***, in which h, k and l are integers. All of these points are surrounded by a narrow nonzero area where the product of the transform of the shape function with the FT^+ of the content of the unit cell shows up.

5) *The scattering experiment.*

At the locations **S** = **H**, for instance scattered intensity I(**S**) will show up which is, according to Box 1, the scattering amplitude A(**S**) times its complex conjugate:

$$I(S) = A(S) \times A^*(S).$$

For X-ray diffraction the scattering power ρ(**r**) is the electron density in the sample, which is in general a real function[5]. Then, according to section 5, A(-**S**) = A*(**S**) and so I(**S**) = I(-**S**), i.e. the intensity in the reciprocal space is a centro-symmetric function. This rule is called *Friedel's Law*.

Since the scattering amplitude A(**S**) is the FT^+ of the electron density ρ(**r**) we have the relation:

---

[5] If anomalous scattering may be ignored.

$$FT^{-}\{A(S) \times A^*(S)\} = \rho(r) * \rho(-r).$$

The resulting function in the direct space is called the Patterson function. Although $\rho(r)$ is not directly obtained from it, the Patterson function forms a useful tool in structural analysis.

8. The operations 'Section' and 'Projection' form a reciprocal pair

A planar Section of a function f (x,y,z) along the x,y-plane is found by making $z=0$: f$(x,y,0)$. This function shows the x,y-dependence of f in the plane $z=0$.

Projecting of a function f(x,y,z) along the z direction is collecting for each combination (x,y) all of f along the z-direction. In mathematical terms it is taking the integral of the function f(x,y,z) along z:

$$f_p(x.y) = \int_{-\infty}^{+\infty} f(x.y,z) dz.$$

The function $f_p(x,y)$ is the projection of f(x,y,z) along the z- direction.

We will show now that the FT^{+} of the projection of f(x,y,z) along the z-direction is the planar section $F(X,Y,0)$ of $F(S)$.

The mathematics is simple but you may just skip it:

$$f(r) = f(x,y,z) = FT^{-}[F(S)] = FT^{-}[F(X,Y,Z)],$$

$$f_p(x,y) = \int f(x,y,z) dz =$$

$$= \int \left\{ \iiint F(X,Y,Z).\exp[-2\pi i(x.X + y.Y + z.Z)] dX dY dZ \right\} dz =$$

$$= \iiint \left\{ \int \exp(-2\pi i z.Z) dz \right\} F(X,Y,Z).\exp[-2\pi i(x.X + y.Y)] dX dY dZ =$$

$$= \iiint \delta(Z).F(X,Y,Z).\exp[-2\pi i(x.X + y.Y)] dX dY dZ =$$

$$= \iint F(X,Y,0).\exp[-2\pi i(x.X + y.Y)] dX dY.$$

The result is that $f_p(x,y)$ apparently is the FT^{-} of $F(X,Y,0)$. Of course reversing the procedure and exchanging direct and reciprocal space lead to similar true relations, which we will not explicitly prove.

The reasoning and the proof apply to Carthesian axes as well as to crystal axes where coordinates x, y and z refer to the axes $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ in the direct space and X, Y and Z to the reciprocal axes $\mathbf{a^*}$, $\mathbf{b^*}$ and $\mathbf{c^*}$ respectively.

So, if we have in some way obtained the values of $F(S)$ in the X,Y-plane, we can find, by Fourier transforming, the projection of f(x,y,z) along the z-direction, no more and no less.

In a similar way we can project a whole 3-D function onto a straight line. Integrate the function for instance over both x and y in the plane $z = z'$ and assign the result to the point $(0,0,z')$. The proof is a straightforward extension of the one given above. It shows that the function $F(0,0,Z)$ is the FT^{+} of the projection

$$f_p'(z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x,y,z) dx dy$$

of the f(x,y,z).

Thus if we know $F(S)$ along a straight line $S = Z.\mathbf{c}*$ through the origin, we know how the function $f_p'(z)$ looks like.

9. The use of sections and projections

If a crystal has an n-fold axis of symmetry, this axis is perpendicular to the other axes. The n-fold symmetry will then in reciprocal space show up in a section perpendicular to the direction of the axis. We take the z- and thus the Z-axis along the direction of the n-fold axis. Whether it is a simple axis or a screw-axis can be seen if F(S) is determined along the direction of the axis, which will reveal the projection of the structure onto the axis. For a 6_3-axis such a projection will have half the period of the crystal in that direction. In reciprocal space the interspacing along reciprocal lattice points is thus twice as large. The condition for possible reflections then is for $00l$ reflections $l=2n$ (even). If the periodicity is six times as large as expected from the crystal axes, the screw axis is a 6_1- or a 6_5-axis. See figure 8 for a 4_1 axis.

Possible $hk0$ reflections if $h+k=2n$ Possible $00l$ reflections if $l=4n$
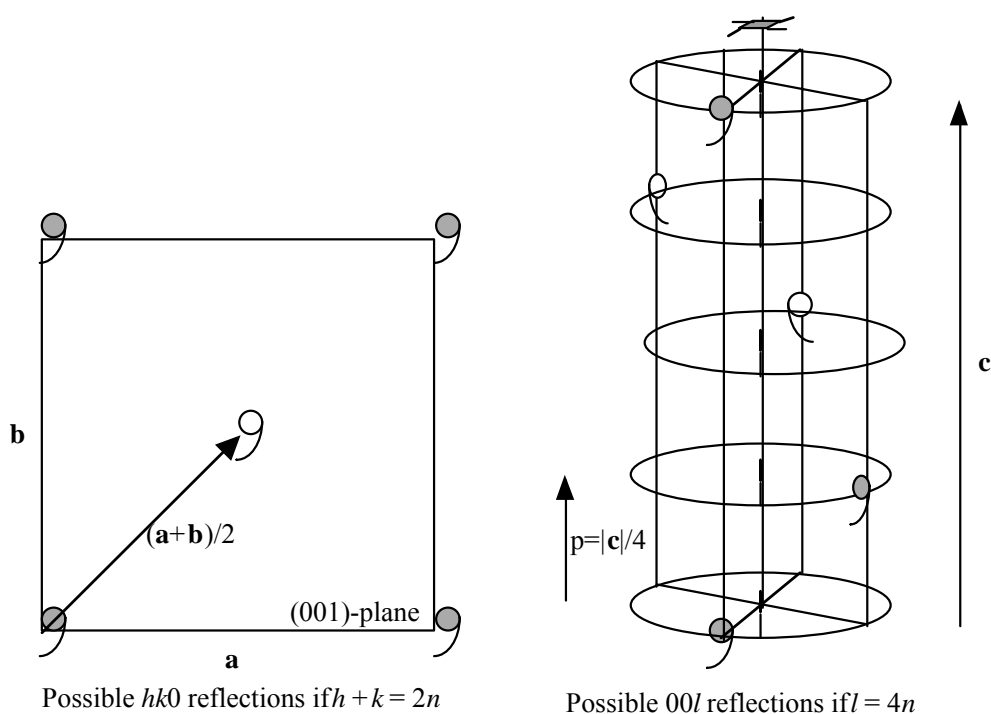
Figure 8.
Left: an illustration of an *n*-glide plane. The reflection plane is perpendicular to **c**.
In a projection of the structure onto (001) the two dimensional cell is twice as small as the crystalline one. In the corresponding section in reciprocal space the apparent cell is twice as large as the unit cell: $h\,k\,0$ - reflections are only possible for $h+k=2n$.
Right: the effect of the projection of the whole structure onto a 4_1-axis. The projection has the periodicity p = c/4 and therefore $00l$ reflections are only possible for $l=4n$.

The same reasoning applies to glide planes. Projection of the crystal structure onto a glide plane will reveal the projection of a fraction of the structure plus its 'glide reflected images'. In the projection they are identical but shifted due the glide over an integer fraction of the crystalline unit cell. In the reciprocal space the corresponding two dimensional section of the unit cell will be a few times larger than the true cell. The size depends on the kind of the glide plane considered: *a*, *b*, *n* or *d*. The apparent cell will reveal the sort of the glide plane by the 'Conditions for possible reflections' in the International Tables.

The same procedure will reveal the rules for possible reflections when applied to structures with centered lattices, (F, I, C, etc.) as they appear in the International Tables.

Acknowledgement

The British Crystallographic Association Intensive Courses in X-ray Structural Analysis

David Watkin

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By the mid-1980's X-ray structure analysis in the UK had fallen victim to a *Catch 22* scenario, and had then shot itself in both feet.

The massive advances in diffractometer technology and Direct Methods programs that had occurred in the previous 20 years, plus the tumbling cost of computers, meant that single crystal structure analysis was on the brink of becoming a routine analytical tool. Chemists realised that they now had access to a more-or-less reliable method for determining detailed molecular structure, and crystallographers emphasised this when preparing proposals for new equipment. Crystallography, one was told, was quick and easy. It had almost moved from being a science to being a technology, and as such was well funded in terms of diffractometers being installed. One of the down sides of this shift in emphasis from research to providing a service was the knock-on effect on teaching. Many UK universities, faced with the problem of fitting more new aspects of chemistry into an already packed time table, chose to reduce the time allocated to crystallography courses. Thus, ironically, at a time when X-ray crystallography was able to provide better information faster than ever possible before, undergraduates had less knowledge of how it worked.

During 1985 various members of the BCA talked over this problem. Amongst others, Michael Wolfson and Chris Gilmore were particularly keen to see something being done to restore the level of expertise amongst young UK crystallographers. In 1986 David Watkin was talked into taking a proposal to the BCA Council. There, it was decided that the BCA would give its blessing to the Chemical Crystallography Group running an Intensive Course. It was suggested that we formed a small committee to look into both the funding of the course (which the BCA could not underwrite), and its scientific content. The course was to be aimed at young (PhD and Post Doc) UK students, with any spare capacity on the course being offered to international participants. Olga Kennard was invited to be overall Director, though most of the detailed work devolved onto other people. A school was projected for January 1987.

I contacted all the UK companies that I felt might be benefiting from advances in X-ray crystallography, and Judith Howard took on the task of seeking matching funds from SERC. In addition to support from diffractometers manufacturers, (Enraf-Nonius Ltd, Nicholet Instruments Ltd and Siemens AG), we had support from software companies (Chemical Design, Ltd and IBM UK Academic Programs), and The Digital Equipment Company Ltd who loaned us a Microvax. At that time there was real diversity in the pharmaceutical industry, and eleven companies sponsored the project (Beecham Pharmaceuticals, Esso Chemicals, Fisons Pharmaceuticals, Glaxo, ICI Pharmaceuticals, ICI Plant Protection, Searle, Smith-Kline-French, Wellcome Foundation). Judith was able to convince both the Chemistry and the Physics Committees at the SERC to support us. In the event, we were able to offer bursaries to 42 participants. Several universities were contacted as possible venues for the school (Oxford being immediately eliminated because of the cost), and Aston was chosen because there was enthusiastic local support from Carl Schwalbe and Phil Lowe, there were good facilities and accommodation, and the price was right.

The programme was very ambitious, with 16 speakers lecturing 9.00-18.00 for six days, with only one free half-day mid way through. The participants were divided into 7 groups each with a new-generation crystallographer as group leader. The lectures took place in a traditional chemistry lecture theatre. Time was allocated in chunks - for example, Bill Clegg had from 2.15 to 4.45 on the first day to deal with cell determination and the orientation matrix. However, the speakers were supposed to break up the chunk by

setting problems for the participants from time to time. The evenings were given over to group problem-solving sessions, and interaction with the speakers.

In the post-mortem after the school, several problems were identified. The most serious were that many students had forgotten much of the basic mathematics they would need for the exercises, and that students working by themselves in the lecture theatre could not benefit from discussions with their peers. The responses on the student questionnaires convinced us that hands-on computing was not very effective use of time, and that there should be some adjustments to the time allocations. Very many students wanted explicit information on how to use certain programs. The program committee then (and now) was strongly opposed to this on the basis that a good understanding of fundamental principals should enable to students to use any program, and even be able to make informed decisions as to their merits. The school was felt to have been successful, and preparations were begin for a second school in 1989.

The second school was also well supported by the pharmaceutical industry, and backed by the SERC. The number of speakers was reduced slightly as a result of the student questionnaires, and the number of participants rose to 57. To improve group interactions, the course was re-organised. The lectures still took place in a standards lecture theatre, but the participants trailed out every 45 minutes to an adjacent room where they could work in groups round a table. The re-location proved to be time consuming, but the group working was an instant success. It gave the less experienced participants to learn from the more experienced ones, and brought them into better contact with their tutors.

For the third school in 1991, the number of participants had risen to 66 and the number of speakers to fallen to 13. Industrial sponsorship remained good. The main change was to abandon the use of the lecture room, and run the whole course in an open plan area where the students could remain in their groups round tables while the lecturers talked. This has remained a defining feature of the school ever since. In addition, formal evening sessions were replaced by 'scientific entertainments' that could take place in a bar, for example a bar quiz that included both general knowledge and crystallographic questions.

By 1993 the number of participants had risen to 73, and the number of tutors fallen to only 5. This reduction in the number of tutors came about largely through a detailed reassessment of the aims of the school and the changes in the skills of the participants. Each year, the participants had been set a simple, anonymous, multiple choice questionnaire to enable us to assess the student's background skills. It had become evident that most participants had been exposed to very little theoretical crystallography. The course now contained more basic material (matrix algebra, trigonometry etc), so that other interesting but marginal topics (exotic sources, powders, macromolecules) had to be excluded. The smaller number of speakers meant that they each had a much larger lecturing burden, but it did improve continuity and reduce the chance of small but important topics being covered by no-one.

This has remained the pattern until the current day. The lecturers have exchanged topics with each other from time to time to preserve vitality. Recent schools have attracted about 80 participants, who continue to work in groups of eight with a tutor. We are now beginning to see students from earlier courses returning either as tutors or lecturers. The lecture notes form a 20 chapter book, and in 2001 an edited version was published by OUP as Crystal Structure Analysis Principles and Practice, (Clegg, Blake, Gould and Main), ed Clegg. Perhaps the most sad reflection is that there was no sponsorship at all from pharmaceutical companies in 2005.

BCA Intensive Course in Crystallography: Multiple Choice Exercise

This is intended as a quick assessment of the general background knowledge of the group. Please do **NOT** sign the paper. Answer each question by circling the letters corresponding to your choice, and insert a number on the scale 1-5 indicating your degree of confidence in your reply (5 = very confident, 1 = very unsure).

1. The characteristic wavelength of a copper X-ray tube is:
    a) Directly proportional to the applied voltage.
    b) Inversely proportional to the tube current.
    c) Related by $E = hc/\lambda$ to the power consumption of the generator.
    d) Dependent on the gas used to fill the tube.
    e) None of the above.

2. Nearly perfect diamonds give diffraction patterns with I proportional to F instead of F^2. This is caused by:
    a) Primary extinction.
    b) Secondary extinction.
    c) Absorption.
    d) Anomalous dispersion.
    e) Negative quartets.
    f) None of the above.

3. Lowering the temperature of data collection should significantly reduce:
    a) Static disorder.
    b) Dynamic disorder.
    c) Anomalous scattering.
    d) Absorption.
    e) The density of the crystals.
    f) None of the above.

4. P2/c is by far the most common space group for molecular materials. An important reason for this is:
    a) It allows parallel chains of polar molecules.
    b) It is centrosymmetric, so crystallographers have tended to study materials in this space group.
    c) It provides efficient packing for many molecules.
    d) It can readily accommodate optically pure chiral molecules.
    e) None of the above.

5. Single enantiomers can crystallise in which of the following space groups:
    a) Pna2$_1$ b) Cc   c) P4$_1$2$_1$2   d) Fdd2   e) Pa3

6. The peaks in a Patterson synthesis represent:
    a) One end of interatomic vectors.
    b) Atomic positions.
    c) The midpoints of interatomic vectors.
    d) The reciprocal space equivalent of the diffraction pattern.
    e) None of the above.

7. Which of the following is not significant for the relationships used in direct methods.
    a) Matter is atomic in nature.
    b) Electron density is nowhere negative.
    c) Most space groups have alternative permitted positions for the origins.
    d) Data are normally present to a resolution better than 1 Å.
    e) None of the above.

8. In least squares refinement, the origin must be fixed in:
    a) All chiral space groups.
    b) All polar space groups.
    c) All centrosymmetric space groups.
    d) All C, I and F space groups.

e) All structures containing heavy atoms on special positions.

f) None of the above.

9. In a structure extracted from the Cambridge Data Base, a phenyl ring has all C-C bonds equal to 1.359Å. This is most likely because:

a) The structure has been very accurately determined.

b) The structure is very imprecise shown by the absence of e.s.d's.

c) A restrained refinement was carried out.

d) A constrained refinement was carried out.

e) Graphitic packing is possible in the structure

f) None of the above.

10. Bond lengths involving hydrogen are significantly underestimated in structures determined by X-ray diffraction. This may be attributed to:

a) The low scattering power of hydrogen.

b) The significant contribution of the hydrogen nucleus to the scattering of X-rays.

c) Hydrogen has more than one isotope.

d) The very low melting point of hydrogen.

e) The asymmetric distribution of the hydrogen electron density.

e) None of the above.

Approximate Timetable for Tenth BCA Intensive Course in X-Ray Structural Analysis, Trevelyan College, Durham, UK, 4 - 12 April 2005

	Monday 4	Tuesday 5	Wednesday 6	Thursday 7	Friday 8	Saturday 9	Sunday 10	Monday 11
0800-0900		Breakfast	Breakfast	Breakfast	Breakfast	Breakfast	Breakfast	Breakfast
0900-1000		Symmetry WC	Data acquisition JMC	Fourier/Patterson WC	Direct methods PM	Refinement PM	Refinement DJW	Derivation of Results SP
1000-1100		Symmetry WC	Data acquisition JMC	Fourier/Patterson WC	Direct methods PM	Refinement PM	Refinement DJW	Derivation of Results SP
1100-1130	**Today only:** Registration	Coffee	Coffee	Coffee	Coffee	Coffee	Coffee	Coffee
1130-1230	12:00 – 14:30	Symmetry WC	Data acquisition AJB	Fourier/Pattterson WC	Direct methods PM	Refinement PM	Refinement JSOE	Interpretation SP
1230-1400	**Today only:** Introduction 1	Lunch	Lunch	Lunch	Lunch	Lunch	Lunch	Lunch
1400-1500	starts at 14:45 DJW/PM	Symmetry WC	Data acquisition AJB	Fourier/Patterson WC	Free time	Refinement PM	Twinning SP	Interpretation/CIF SP/AJB
1500-1600	Introduction 2	Symmetry WC	Data acquisition AJB	Direct methods PM	Free time	Refinement DJW	Twinning SP	Databases AJB
1600-1630	Tea	Tea	Tea	Tea	Free time	Tea	Tea	Tea
1630-1730	Introduction 3	Crystallisation AJB	Data acquisition AJB	Direct methods PM	Free time	Refinement DJW	Derivation of Results S	Databases (CCDC)
1730-1830		Surgery WC (IT)	Neutrons JKC	Surgery	Free time	Powder IR-E	Surgery	Surgery
1830	Dinner	Dinner	Dinner	Dinner	Dinner	Dinner	Dinner	
2000	Matrices DJW	Bar Quiz	Ceilidh	Presentations	Free time	Expert Panel	Practical Issues - an optional bar session	Course Dinner

Teaching of the Fundamentals of Crystallography

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What *are* the Fundamentals of Crystallography? What *is* Crystallography? A general definition might be "*Geometry and patterns: the spatial arrangements of atoms in all types of matter; determination, description, classification, implications of atomic patterns.*" Even though the IUCr journals, the International Tables and most national societies of crystallography cover the full scope of this ambitious claim, the image and reputation of crystallography and of the profession of crystallographer has evolved from various traditions. In the English speaking world, people tend to classify a crystallographer as a chemist who determines crystal structures and is thus little better than a technician. Teaching crystallography is therefore not fundamental and should enable students only to master a somewhat complicated technique. In contrast, my thesis adviser Fritz Laves at ETH-Zurich in the early 1960s considered crystallography as the center of all natural science, in the core of mathematics, physics and chemistry. He was the former student and successor of the great Paul Niggli whose breadth of publications was gigantic although he considered himself as mineralogist. Laves used all sorts of tools for his research, including spectroscopic methods and electron-microprobe analysis. X-ray diffraction played an important role, but his students did not learn the art of structure determination. I made up for this deficiency very easily as a post-doc.

From 1954 to 1976, Laves read an important course of crystallography, about 56 hours (2 hours a week during two semesters) plus exercise sessions, that was compulsory for first-year chemistry and earth science students, and optional for physicists. The contents were :

– geometrical crystallography, indices, zones, stereographic projection and optical goniometers, twinning;

– symmetry, crystal classes, crystal systems, Bravais lattices, in-depth training with wooden models;

– diffraction, Laue and Bragg equations, reciprocal lattice, powder methods including indexing of cubic, tetragonal and hexagonal powder patterns (by hand), reflection conditions;

– birefringence and crystal optics;

– crystal chemistry, structure types, coordination polyhedra, closest sphere packings, binary A_mX_n compounds for many (m, n), intermetallic structures (Laves phases, of course), silicates.

Similar courses were given at that time at many German Universities as evidenced by the exceedingly popular textbook of W. Kleber, *Introduction to Crystallography* (1st edition 1955 in German, English translation by W.A. and A.M. Wooster 1970). Various excerpts of these fundamentals figure today in basic courses of chemistry, physics, materials sciences, earth sciences and biology, tailored to particular needs and dependent on the insights of the teachers, often using a nomenclature that differs from IUCr usage (compare *e.g.* standard text books of solid state physics).

The curriculum at ETH-Zurich in the 1960s for advanced students wishing to specialize in crystallography is of less interest today, except for a two-week full-day practical course of X-ray diffraction where the use of film cameras (Weissenberg, Retigraph, Precession) and of powder cameras (from Debye-Scherrer cameras to focussing monochromator methods) was taught. I encountered my first experimental observation of a multiply twinned feldspar in this course in 1958.

Starting in 1969, I gave a course with the same weight as the one of Laves at Zurich, 56 hours and accompanying exercises, at the University and the Swiss Federal Institute of Technology at Lausanne. It was compulsory for 2nd year physics and materials science students. The contents of this course evolved

over the years, and the number of hours fluctuated. But it still exists today as two separate courses for 2nd year physicists and materials scientists, given by Gervais Chapuis. During all these years, I endeavoured to include the following topics:

– geometrical crystallography, the mathematics of oblique coordinate systems and lattice bases leading directly to the reciprocal lattice base;

– symmetry, group-theoretical concepts for understanding International Tables A (space groups);

– diffraction, Fourier transform, phase problem and atomistic models for its solution, powder diagrams for materials identification and the study of phase transitions by observing the splitting of powder lines;

– anisotropy and tensorial properties of crystals, classical crystal optics;

– sometimes, I also included some crystal chemistry including simple inorganic structures important for solid state physics and materials science.

Materials scientists were then ready for a follow-up course on applications such as strain analysis from line broadening in powder diagrams, and grain orientation analysis. The physicists continued with a course on dislocation theory and plastic deformation (given by a specialist in this field). My basic course met with a mixed success with the students, their judgment showing a double-humped camelback-type curve: some gave it the highest grade, some found it abominable. The materials scientists found it somewhat too mathematical. The physicists with their very superior mathematical training experienced difficulties connecting the very abstract mathematics courses on group-theory with the corresponding crystallographic geometrical realizations and space visions. Many students gave quite flattering opinions on the course only in retrospect after their graduation.

As did Laves in Zurich, we also offered for over 30 years, and still offer, a two-week practical course in X-ray diffraction and structure determination that evolved from the use of all sorts of cameras and diffractometers to a structure determination course with today's modern methods. It is attended mainly by graduate students, sometimes post-docs, with very diverse backgrounds. More recently, a course on physical methods of structural biology is given by Marc Schiltz. For many years, Gervais Chapuis has read a 28 hour course without exercises on X-ray structure determination for 4th year chemists. This exists actually as an option that does not appear to be encouraged by the chemistry faculty.

I believe that crystallography should be included on the undergraduate and/or graduate level in many scientific disciplines. It belongs to a meaningful scientific education. I do not mind if the material is taught under a different name than crystallography as long as it is taught properly. I resent naive pictures of the 14 Bravais lattices, trivial deductions of Bragg's equation, and restricted presentations of the family of closest sphere packings. Notions on the following topics should be acquired by all students:

– The lattice symmetry of the ideal crystal is the key to understanding anisotropy, diffraction of radiations, electronic and vibrational band structure, and is the standard for the definition of crystal imperfections.

– Point groups, and not only the crystal classes, should be presented and memorized geometrically. This is fundamental for both spectroscopy and crystallography and should be taught in depth, rather than twice. A picture of the symmetry elements goes a long way to intuitively grasping the meaning of invariant subspaces and character tables.

– Some basic crystal chemistry is useful at least for materials scientists and solid state physicists (chemists do not seem to care any more for simple substances). A presentation of closest sphere packings presented as an OD-structure family (polytypes) easily includes diamond-Lonsdalite and semiconductor structures, ice, graphite, Laves phases.

– The Bragg equation should be familiar to every scientist. I would also include the powder method and the information it reveals.

It appears most important to me to show the general validity of the above notions. It is a pity that crystallographers and solid-state physicists use different languages and separate courses to express the same ideas.

What about X-ray structure determination, for chemists and biochemists? It may appear to the non-service crystallographer that I am, that very little needs to be taught in this field. Excellent programs for both the measurement process and for data interpretation handle most problems of symmetry. An understanding of the theory (*e.g.* origin definition, triplets, probabilities, ADPs, coordinates) is not necessary for successful structure determination. The molecule appears magically on the screen if only one knows how to handle the programs. Or is it not that easy, as hinted at by the number of problem papers received by Acta Cryst. C and E? It may of course happen that the solution does not readily appear. Intervention by a professional crystallographer becomes then necessary who's education is very much more demanding and not discussed here. A course on fundamentals needs only to cover the phase problem, the models for solving the phase problem and an assessment of the meaning and the quality of the results:

– The phase problem: Fraunhofer diffraction; representation of the electron distribution by waves, *i.e.* the Fourier transform explicitly or implicitly; image formation by interference of waves, *i.e.* the reciprocal Fourier transform.

– The missing phases require definition of a model, *i.e.* one looks for an electron distribution with certain properties. The standard methods are based on atomicity, *i.e.* the structure is a superposition of atomic electron distributions that are smeared by thermal motion and whose number and types are known. This idea may, but need not, be expanded to include electron density determination with aspherical atoms, as well as models of thermal motion. More importantly, the charge flipping (CF) method of Oszlanyi & Sütö (Acta Cryst. **A60**, 134-141, 2004; Acta Cryst. **A61**, 147-152, 2005) proposes a much simpler model where the electron density is supposed to be large in only about 20% of space and negligibly small in the other 80%. CF appears to solve just about any difficult structure with data at atomic resolution, with the added quirk that the use of symmetry is harmful. Thus, there is not even a need to teach symmetry at this stage! Starting from here, the teacher may address imaging of non-periodic objects with limited dimensions. I would rather do this than discussing recipes of structure determination.

– If recipes are to be discussed, I would start with the Patterson method. But rather than using a measured data set and the computer, I would devise an exercise where the students calculate from the known atom coordinates the vector space of a simple structure (I chose calcite, $CaCO_3$). I then would make the students manipulate by hand some triplet relations (examples may be found in M. M. Woolfson's textbook, 1970). Although this is old-fashioned, it is more informative than an impressive demonstration of structure solution with crystals brought by the course participants. The latter should be included only for its high propaganda value.

– The chapter on meaning and quality should include a discussion of acceptable bond lengths and angles. Aberrant thermal ellipsoids might be illustrated by *rms* displacements along interatomic bonds and the Hirshfeld test. The meaning of reliability factors and standard uncertainties cannot be avoided, although these are quite technical subjects.

I believe that useful information on the essence of X-ray structure determination can be taught in a post-graduate course of about 7 hours (*e.g.* 1 hour a week during half of a 14-week European semester), maybe as part of a course including other methods of analysis. A few exercise sessions could be offered via the Internet. I do not believe in flashy propaganda courses demonstrating to students the effortless marvels that can be wrought. Rather, I believe that a useful course tends to be a demanding course.

The sum of our teaching efforts in *Fundamentals of Crystallography* at Lausanne is published in French in a reasonably priced textbook: Dieter Schwarzenbach & Gervais Chapuis, *Cristallographie*, 2nd edition, Presses polytechniques et universitaires romandes, Lausanne (2006). Its 7 chapters are entitled: (1)

Geometrical crystallography, (2) Symmetry, (3) X-ray diffraction by crystals, (4) Determination of crystal structures, (5) Simple crystal structures, (6) Tensorial properties of crystals, (7) Exercises with solutions. The first edition of this textbook, without chapters 4 and 5, has also been translated into English by A. A. Pinkerton and published as a too expensive book by Wiley (1996).

In addition, we have created a series of interactive Java applets which can be directly accessed from the web at URL http://escher.epfl.ch/. They serve to familiarize students with the concepts of point and space group symmetry, reciprocal space, diffraction and Fourier transform. In addition, they offer access to a large database of crystal structures and intuitive tools for their representation.

Teaching Crystallography and Related Subjects at Novosibirsk State University, Russia

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As compared to some other countries, Russia still has many advantages in teaching crystallography and related subjects. The main advantage is that crystallography remains a compulsory course for chemistry students, mineralogy / geochemistry students, and, in some universities, also for physics students. Such universities and high schools as Lomonosov (Moscow) State University, S-Petersburg State University, Nizhnii Novgorod State University, Samara State Universities, Physical Technical Institute (Moscow), and many others have a long tradition in this field. Their experience is reflected in numerous text-books, original lecture courses and teaching materials, some of which can be found either at the corresponding internet sites (http://www.chem.msu.su/eng/, http://ns.crys.ras.ru, http://www.geol.msu.ru/english/, http://www.geol.msu.ru/english/deps/crystal.htm, http://www.inorg.chem.msu.ru/, http://www.chem.msu.su/eng/lab/cryschem/, http://www.chem.msu.su/eng/chairs2/welcome.html), or by contacting directly the responsible people (secr@ns.crys.ras.ru, nb_bolotina@hotmail.com, dekanat@phys.unn.ru, chuprun@phys.unn.ru, elbel@geol.msu.ru, slov@phys.chem.msu.ru, siicm@hotbox.ru, aslanov@struct.chem.msu.ru, http://www.che.nsk.su/education/). Some of the groups have also prepared short contributions to this Newletter, other will do this for the next issues. Apart of teaching the basics of crystallography, crystal chemistry, mineralogy, structural analysis, Russian universities provide also various courses in crystal physics, materials sciences, solid state chemistry, and related subjects. This is very important, to show that crystallography is a modern science, and not just a historically important, but no longer demanded subject. To give access of Russian students to the most recent achievements of crystallography, we have initiated preparing a series of teaching materials in the electronic format, to be accumulated at university servers, but also as a distributed electronic library. The information on this library will be available, when some "critical amount" of materials will be already accumulated.

Novosibirsk State University does not belong to very old universities in Russia. It has not celebrated its 50th year anniversary yet. It is a very dynamic university, that is aimed at training intelectual elite for Russian Science and therefore develops new approaches to teaching. It has its own experience in teaching crystallography and related subjects, which is somewhat different from what is common at other places.

An interesting point is that crystallography is being taught to all *chemistry* students, as in other universities, but not as a separate course – it is a part of a general course in solid state chemistry (Prof. E. Boldyreva, boldyrev@nsu.ru). All the basic notions of fundamental crystallography, crystal chemistry, crystal physics are being introduced in a comparison with the structure and properties of individual molecules, widely using group theory, basic physics, vector algebra, analytical geometry. This allows us to "compress" a very large material into 2 months time (2 hours of lectures and 3 hours of practicals per week). After the introduction into the basics of the structure description of ideal crystals, we consider more briefly incommensurate structures, quazicrystals, nanostructures, and then enter the second part of the course (2 months more) related to the structure of real solids – different types of point defects and dislocations are considered, surface structure and surface properties, the structure and properties of heterogeneous systems. Some details on the course are given in the paper: [Boldyreva E. V. An experience of teaching solid-state chemistry as a comprehensive course for chemistry students // J. Chem. Educ, 1993, 70(7), 551-556]. After this general course students getting special training in inorganic chemistry, catalysis, solid state chemistry attend also special courses in crystal chemistry (Prof. S. Solodovnikov, solod@che.nsk.su), structural analysis (Prof. E. Boldyreva, boldyrev@nsu.ru, Prof. S Tsybulya, tsybulya@catalysis.nsk.su), introduction into Cambridge Structural Database (Prof. E. Boldyreva, boldyrev@nsu.ru). Chemistry students show a large interest in crystallography and its various applications, and the competition for the corresponding specialities is high. Crystallography and crystal

chemistry are also taught as general courses at Geology department (Prof. Yu. Seryotkin, yuvs@uiggm.nsc.ru). Since 2006, crystallography, crystal chemistry, structural analysis and materials sciences will be taught also to physics students (Master level). This new specialization is supervised by Prof. S. Tsybulya, tsybulya@catalysis.nsk.su. Lecturers are invited from Chemistry and from Physics departments. As original courses, one can mention "Crystallography at extreme conditions" and "In situ studies of solid-state reactions (Prof. E. Boldyreva, boldyrev@nsu.ru). More information is available at www.phys.nsu.ru.

Fig. 1: a) *Practicals in structural analysis. Powder diffraction and* **b)** *single-crystal diffraction at non-ambient conditions – is an important original course*
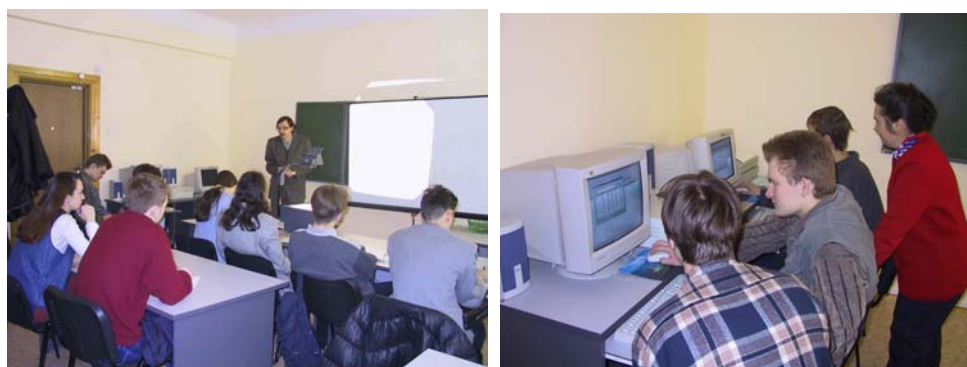
Fig. 2: a) *A lecture in structural analysis and* **b)** *practicals in crystallographic computing*

In addition to general and special lectures and practicals in the regular curriculum, Novosibirsk State University organizes comprehensive lectures for senior school-children at special Summer and winter schools. Another important field of activity is related to continued education for those who have graduated from the University some time ago and would like to up-date their knowledge. A multidisciplinary Research and Education Center (REC-008) plays an important role in this activity. As a bright recent event, a workshop "ICDD: powder diffraction file and grant-in-aid program" can be mentioned, that was organized in Novosibirsk from October 18th till October 20th jointly by Research and Education Center REC-008 at the Novosibirsk State University, Boreskov Institute of Catalysis, and Institute of Solid State Chemistry and Mechanochemistry Siberian Branch of the Russian Academy of Sciences. The Seminar was initiated and supported by the International Center of Diffraction Data (ICDD). The main purpose of the seminar was to give an overview of the ICDD activity, of the new version of the PDF-4 database, to discuss various applications of the powder diffraction techniques, and to involve researchers and students from Siberia into a cooperation with the ICDD via the "Grant-in-aid"-program. Russian and English were the working languages of the Seminar. 66 registered participants represented Novosibirsk, Krasnoyarsk, Ulan-Ude, Omsk, Tomsk, Barnaul, Tyumen', Kemerovo, Novokuznetsk, Irkutsk. The participation of 9 young researchers and students from outside Novosibirsk was financially supported by Civilian Research and Development Foundation (CRDF, USA). The Workshop has initiated a series of regular (one-two per month) seminars on powder diffraction, organized by REC-008 and attracting students from the Novosibirsk State University and researchers from various Institutes of the Novosibirsk Scientific Center.

Crystallographic Teaching at the Laboratory of Inorganic Crystal Chemistry at Moscow State University, Russia

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The laboratory of Inorganic Crystal Chemistry at Chemistry Department of Moscow State University exists over 50 years. It was organized as a service group by Prof. Yuri P.Simanov Since that time it covered the way from X-ray service group to the laboratory performing full scientific studies starting from syntheses of chemical compounds up to investigations of their structures and physical properties. Prof. Leonid M.Kovba in 1960's to 1980's did a lot to introduce X-ray powder diffraction as a common used method for the study of inorganic compounds. Since January 1996, the laboratory is headed by Prof. Evgeny V.Antipov.

Moscow State University is an educational institute, and the Laboratory participates in the teaching program as well. It starts with the beginning. At the first course Prof. Antipov presents several introductory lectures on X-ray diffraction and its application in chemistry. The second year one of groups, specialized in inorganic chemistry, has a special semester course of basis in X-ray powder diffraction, held by Prof. Antipov. Later, more detailed information, including theoretical basis of X-ray diffraction are presented in courses "X-ray analysis" and "Experiments in the X-ray analysis" for 3rd year students of the Department of Materials Sciences and 5th year students of Chemistry department by Assoc. Prof. Roman Shpanchenko and Dr. Andrei Mironov. Finally, the special course of "Diffraction methods (X-ray single crystal and electron microscopy) in structure analysis of inorganic compounds" for the Ph.D. students are delivered by laboratory researchers Andrei Mironov and Artem Abakumov.

In the 1990's, the time of active development of X-ray powder diffraction methods were unfortunately very rare for Russian science and, especially, industry. Nowadays, there is a great requirement in the specialists in this field. For that reason the laboratory performs the X-ray Diffraction Clinics. Late in June 2003-2005 three X-ray diffraction schools for the workers of metallurgy, cement and fertilizers industry were organized. They learned to make phase analysis from diffraction patterns with the help of PDF Data Base, index the diffraction patterns and calculate cell parameters, calculated diffraction patterns of solid solutions and use the results for quantitative analysis of raw materials and products (see pictures). Besides, several lectures devoted to the use of diffraction methods (including X-ray powder diffraction) were delivered at III-V "Actual problems of modern inorganic chemistry and material science", School for students and young scientists in 2003-2005.

Fig. 1: *1st XRD Clinic at Moscow State University (June 2003)*

Within the frame of ICDD activity seven Regional Workshops were organized devoted to the modern problem of X-ray powder diffraction, as well as the ICDD products and programs. The first seminar was organized in 1992 in Moscow. Since that time another 6 Workshops were held in different cities, covering different regions of Russia, Former Soviet Union Republics and even other countries (Sweden, France, Poland, Germany). The last one was held in Novosibirsk in Academy town, the largest scientific center in Siberia (see pictures). During these years several hundred participants took part in Workshops.

Several lectures on powder diffraction were delivered at national and international conferences: MSU HTSC, National Crystallographic Conferences in Chernogolovka (Moscow Region), conferences on "X-ray Diffraction and Crystal Chemistry of Minerals" in St.Petersburg, IX International Conference on Crystal Chemistry of Intermetallic Compounds in Lviv, Ukraine, (September 2005) and others.

Fig. 2 (a, b): *ICDD GiA Workshop in Novosibirsk (18.10-20.10 2005)*

M.Sc. Crystallography at Birkbeck College, University of London, UK

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J. D. Bernal (1901-1971) came as Professor of Physics to the old building (Breams Buildings) of Birkbeck College from Cambridge and as a newly elected FRS, in 1938 to succeed P. M. S. Blackett. His intention was to continue crystallographic research on the large molecules of living systems, but he was soon called to war duties and did not return to Birkbeck until 1945/6. Two old war-damaged houses in Bloomsbury were acquired for the new crystallographic laboratory and research resumed, although general teaching in Birkbeck had continued on a part-time basis right though the war. Bernal had, in Feb. 1945, produced a memo of his objectives which were: "to set up a research centre for the study of the structure and properties of large molecules of biological importance by all available physical and chemical methods". He collected his research group and set to work. C. H. Carlisle took proteins and viruses, J. W. Jeffery, inorganic materials and cement, W. Ehrenberg began to make X-ray tubes, A. D. Booth was commissioned to make a computer and R. Furth dealt with crystal physics. Other research workers began experimental work for Ph.D. theses.

It was clear that the formal teaching of crystallography for Ph.D. students, both at Birkbeck and elsewhere in London should be developed and about 1948 an M.Sc. by examination degree course was launched. It was inter-collegiate and included the participation of Kathleen Lonsdale (one of the first women to be FRS) at University College and G. I. Finch, FRS at Imperial College who, with H. Wilman, was developing electron diffraction crystallography. The course was to be two years part-time (but was later adapted to include people doing it in one year full-time) and was designed to cover the whole spectrum of crystallography, as for example, presented by W. L. Bragg in his book of 1939 "The Crystalline State" (Vol. 1). Indeed Bragg himself opened the laboratory at a ceremony in July 1948.

The course was under the supervision of the Advisory Board for Crystallography of the University of London which appointed external examiners. As well as students from the various colleges of the university there were students from industry - there were particular connections with the research laboratory of the General Electric Company at Wembley (H. P. Rooksby). The formation of the X-ray Analysis Group of the Institute of Physics, the appearance of the journal Acta Crystallographica and the International Union of Crystallography all helped to produce a coherent crystallographic community which persists today. Our first overseas students appeared and connections with, for example, Chile, India, Japan and Egypt, began and still continue. The external examiners, drawn from crystallography groups in other British universities contributed greatly to the recognition of uniform standards. Good connections with the Natural History Museum Department of Minerals helped research with key specimens and some of their staff came to the course.

There were, of course, many difficulties in the immediate post-war conditions. Luckily the main building of Birkbeck College had been begun before the war, and supplies of bricks had been stored for the duration, so that building could be resumed and the new building opened in 1954, although crystallography remained in slum conditions for another decade. Food rationing had continued until the early 1950s and equipment had to be made in-house so that a substantial workshop was a central feature. Workshop training was deemed essential for all and the workshop was vital in maintaining cars and bikes. Much could be acquired from war surplus equipment, both British and German, but this had to be adapted. A major problem was the dual use of equipment for research and for teaching. Teaching took place from 6-9 p.m. leaving the day clear for research so that many people worked long hours. Following Cambridge practice collective tea-times were essential social engineering for discussing politics as well as day-to-day difficulties and scientific work. All had to do almost everything for themselves and to learn all trades (like photography and X-ray safety - regular blood tests were required and control films were checked).

Lecture notes were prepared on a Gestetner machine. The experience of the Cambridge school, provided the texts which were used. Besides Bragg's book, those of W. A. Wooster, (Crystal Physics); F. C. Phillips (Introduction to Crystallography); R. C. Evans (Crystal Chemistry), were used at the start and many others followed. Students struggled with Linus Pauling's "The Nature of the Chemical Bond" (1939, 1940, 1960). In the early 1950s Bernal wrote a definitive account of crystallography for the Encyclopaedia Britannica but it was considered to be too long and was rejected but it summarised the M.Sc. course and was circulated to students. (He had earlier written the article "x-rays and crystal structure for the 1929 edition).

Computing always a limiting factor and Beevers-Lipson strips were used for Fourier synthesis for very many tedious years. For many years too the intensities of spots in X-ray diffraction photographs were measured by eye by comparison with standard strips. People were always scouring the front lines of development for computing facilities.

Crystal physics was included but turned out not to be popular. Although the course included how to cut a quartz oscillator plate for zero temperature coefficient nobody attempted the corresponding examination question. There was a lot of basic mineralogical crystallography and symmetry theory.

Bernal himself suffered a stroke in 1963 and became progressively incapacitated. At that time science was moving from "small science" to "big science" with the increasing availability of big machines, computing, neutron diffraction, electron microscopy, the synchrotron, etc. which he did not really see. As facilities appeared, the M.Sc. course adapted to include them.

The course continued to change with the headships of Harry Carlisle, the Tom Blundell and later David Moss. It continued to become more biomolecular and quite recently the materials section of the Dept. of Crystallography has moved to University College. This move reflects the continuing national run down in science education generally. Physics, chemistry, mathematics and geology at Birkbeck College have been forced to seek alliances with other college department to maintain the scale of operations necessary to take part in big science in a world arena.

As the focus of molecular biology shifts to systems, the M.Res. degree in Structural Biology has replaced classical crystallography and there are separate certificate courses in Principles of Protein Structure and in Protein Crystallography and in Techniques in Structural Molecular Biology.

There is an M.Sc. course and an M.Res. course in Bioinformatics. All these serve also to prepare Ph. D. students for increasingly specialised research work.

(Jeremy Cockroft has summarised the syllabus of the last M.Sc. course in crystallography and this is available on the internet http://img.cryst.bbk.ac.uk/www/cockcroft/msc-cryst/aims.htm . It is also reprinted below as an addendum)

Addendum 1: reprint of webpages containing the (now defunct) Birkbeck College M.Sc. Crystallography Course Syllabus in its final form (taken from Jeremy Cockcroft's website : http://img.cryst.bbk.ac.uk/www/cockcroft/msc-cryst/aims.htm)

Comment from Jeremy Cockroft (added by the newsletter editor): It needs to be made clear that some lecturers did not provide details of what they planned to teach following certain old-fashioned teaching traditions that are no longer acceptable practice: namely walking into the lecture room and giving a lecture on what they felt like on the day. Hence the web syllabus that I created has holes. How you wish to add this in I leave to you, but it is an important point since times have changed in this regard.

MSc Crystallography

Aims & Objectives

The overall aim of this MSc course is to give students a broad view of the subject of crystallography. The course is divided into two sections with the aim of providing a basic grounding in the subject followed by an illustration of how crystallography is applied to the various scientific disciplines. The aim of section one is to cover the concept of crystal structures and symmetry, the physics of scattering and diffraction theory, experimental diffraction from single crystals, instrumentation and powder diffraction. Section two explores the analysis of single-crystal data, techniques used in protein crystallography, electron microscopy, and provides in-depths studies of the application of crystallography in different situations. For students with a weaker mathematical background, a supplementary mathematics course is provided.

Section 1

- *Crystal Structures & Basic Symmetry*
  Objective is to explain the description of a crystal structure in terms of atom positions, unit cells, and crystal symmetry; and to relate the crystal symmetry to the symmetry observed in a diffraction experiment, for symmetries up to and including primitive orthorhombic.

- *Diffraction Techniques (with Camera & CAD4 practicals)*
  Objective is to give students a working knowledge of reciprocal space, X-ray photography with oscillation, Weissenberg, & precession cameras, single-crystal laboratory diffractometers, and Laue diffraction.

- *Scattering & Diffraction Theory*
  Objective is to give the students a grounding (both mathematical and intuitive) into the interaction of radiation with condensed matter and how this can be used in generalised crystallography. This grounding should supplement the lectures and practicals elsewhere in the course.

- *Instrumentation & Powder Diffraction (with D500 practical)*
  Objective is to give the students a background to the instrumentation used for powder diffraction, to illustrate the different uses of powder diffraction, and to give as much hands-on experience of data collection, data interpretation, and structure refinement as possible within the time allowed.

- *Advanced Symmetry*
  Objective is to explain the salient points of higher-symmetry space groups, namely those belonging to the tetragonal, trigonal, hexagonal, and cubic crystal systems.

- *Mathematics for Crystallographers*
  Objective is to revise the mathematical concepts required for an understanding of crystallography

for those students with a weak mathematical background. Specific aims include an understanding of vectors, their properties and manipulation; matrices and how to use them; simple trigonmetry and the trigonmetric functions; the use of complex numbers; and experimental counting statistics, systematic and statistical errors, and the significance and use of error values in the scientific literature.

Section 2

- *Chemical Crystallography*
  Objective is provide instruction on the methods and basis for determining low-molecular weight crystal structures using X-ray Crystallography; to enable interpretative assessment of the results of crystal structure analysis to be carried out; and to guide students through several actual analyses using the SHELX-program suite implemented on Pentium PC's.

- *Electron Microscopy (with EM practicals)*
  Objective is to introduce the students to the basic fundamentals of electron microscopy as a useful subsidiary technique for crystallographers; to explain and demonstrate the use of the electron microscope; to provide examples of its application in materials science and macromolecular structural biology.

- *Protein Crystallography*
  Objective is to teach the basics of modern protein crystallography using Web-based material; to discuss the different levels of structure exhibited by proteins; to demonstrate the instrumentation, steps, and methods used in protein crystallography with appropriate case studies; to introduce the concept of non-crystallographic symmetry to protein crystallography.

- *Applied Crystallography*
  Objective is to give the students a few in-depth examples of the applications of materials and solid-state chemical/physics crystallography in academic research, industrial research, and its general use in the outside world.

- *Non-Crystalline Systems*
  Objective is to provide students with some insight into the techniques used to examine either poorly-crystalline materials or totally non-crystalline materials and thus to provide a contrast with techniques such as powder diffraction.

- *Crystallography at EPSRC central facilities*
  Objective is to provide students with a background to the radiation sources provided by EPSRC central facilities, the type of diffraction experiments performed there, and an on-site experience.

MSc Crystallography

Crystal Structures & Basic Symmetry

Aims & Objectives

The overall aim of this MSc module is to explain the description of a crystal structure in terms of atom positions, unit cells, and crystal symmetry; and to relate the crystal symmetry to the symmetry observed in a diffraction experiment, for symmetries up to and including primitive orthorhombic.

The objectives of each lecture are given below:

- *Lecture 1*
  To introduce the concept of simple crystal structures in terms of atom (or cation/anion) positions, unit cells, and crystal symmetry;
  To demonstrate how the symmetry observed in a diffraction experiment is related to that of the crystal.

- *Lecture 2*
  To demonstrate that the packing of organic and organometallic molecules in a crystal follows similar principles to those observed for inorganic compounds.

- *Lecture 3*
  To develop the concept of proper and improper rotation axes;
  To show how they can be combined in a finite number of ways so as to form the 32 crystallographic point groups.

- *Lecture 4*
  To demonstrate how 2D space may be filled in a regular repeating manner;
  To develop the concepts involved in the plane systems: oblique, rectangular, square, & hexagonal;
  To demonstrate using optical diffraction the relationship between real and reciprocal space for the 17 plane groups.

- *Lecture 5*
  To describe the 7 crystal systems and the Bravais lattices;
  To introduce the concept of the triclinic lattice and its lattice planes;
  To give general equations relating *d*-spacing and the unit-cell parameters;
  To show how these equations simplify according to crystal system
  To introduce the triclinic space groups and their tables.

- *Lecture 6*
  To derive the 8 primitive monoclinic space groups;
  To demonstrate the existence of alternative unit cells with different space group symbols, but identical space group symmetry.

- *Lecture 7*
  To introduce the concept of systematic absences;
  To show how these may be used to distinguish the space groups of different crystals for the 8 primitive monoclinic space groups;

- *Lecture 8*
  To derive the 5 centred monoclinic space groups;
  To demonstrate the effect of a lattice centring in a diffraction experiment;
  To demonstrate the effect of combining a lattice centring with a primitive space group.

- *Lecture 9*
  To introduce the primitive non-centrosymmetric orthorhombic space groups;

To give the students practice at deriving space-group symmetry from single-crystal diffraction data.

- *Lecture 10*
  To discuss the centrosymmetric orthorhombic space groups;
  To teach the derivation of the symmetry operators from the space-group symbol;
  To give students more practice at deriving space-group symmetry from single-crystal diffraction data.

- *Lecture 11*
  To demonstrate how interatomic distances, bond angles, and torsion angles are calculated;
  To give the students practice in carrying out the above calculation in a fast and efficient manner.

MSc Crystallography

Diffraction Techniques

Aims & Objectives

The aims of this module are: (1) to provide instruction on the theory and practice of methods for recording crystal reciprocal lattices and measurement of the associated intensity values prior to structure analysis; (2) to introduce methods of measuring and interpreting reciprocal lattice geometry for the determination of unit cell dimensions, Laue symmetry and space group symmetry. The lecture course is supplemented by intensive practicals.

The objectives of each lecture are given below:

- *Lecture 1*
  To derive Bragg's equation, introduce the Ewald sphere analogue and concept of the reciprocal lattice. Problem solving and demonstration.

- *Lecture 2*
  To use basic techniques for the optical examination of crystal specimens using a polarising microscope. Crystal mounting techniques for camera work and diffractometry.

- *Lecture 3*
  The oscillation camera. Design, recording techniques and symmetry observable and calculation of crystal spacing. Indexing. Limitations of the method. Problem solving. Film measurements.

- *Lecture 4*
  The Weissenberg camera. Design, recording and interpretation of reciprocal lattice zero layers in terms of unit cell spacings and symmetry. Film measurement and indexing.

- *Lecture 5*
  Upper level Weissenberg photography by equi-inclination technique. Calculation of settings, symmetry observable and derived measurements. Problem solving and demonstration.

- *Lecture 6*
  Design of the 4-Circle Single Crystal Diffractomer. Crystal mounting, reflection scans, unit cell calculation and orientation matrix assignment. Equi-inclination geometry.

- *Lecture 7*
  The Nonius CAD4 single crystal diffractometer. Kappa geometry. Data collection strategies. Psi scans for empirical absorption correction. Data processing programmes. Practical involving crystal mounting, orientation, unit cell and Laue symmetry assignment and data collection and processing.

- *Lecture 8*
  Design of the precession camera. Comparison with oscillation camera. Recording zero-layer photographs of the reciprocal lattice. Unit cell calculations and observation of symmetry. Problem solving and measurements.

- *Lecture 9*
  Recording upper-level precession photographs. Comparison with Weissenberg camera. Observation of symmetry and determination of space group. Limitations of the method. Problems and calculations.

- *Lecture 10*
  Laue photography. The use of white radiation. Simple indexing procedures and inherent practical difficulties. Symmetry observable. Practicals, problems, calculations. Situations where Laue method is applicable.

- *Lecture 11*
  Data collection strategies. Symmetry considerations. Approximate number of intensities in a data set. Resolution. Data reduction procedures. Lorentz, polarization and absorption correction. Indices of data quality and expected values in practice.

MSc Crystallography

Powder Diffraction

Aims & Objectives

The overall aim of this MSc module is to give the students a background to the instrumentation used for powder diffraction, to illustrate the different uses of powder diffraction, and to give as much hands-on experience of data collection, data interpretation, and structure refinement as possible within the time allowed.

The objectives of each lecture are given below:

- *Lecture 1*
  To introduce the concept of diffraction from powdered crystalline materials;
  To discuss the generation of laboratory and synchrotron X-rays with additional emphasis on aspects relevant to powder diffraction;
  To discuss the history of powder neutron diffraction;
  To discuss the generation of reactor-based and pulsed source neutrons and to discuss the merits of both for powder neutron diffraction.

- *Lecture 2*
  To demonstrate the in-house powder diffractometers to the class;
  To emphasis the different geometries;
  To point out the different components (source, monochromator, sample stage, and detectors);
  To discuss the use of filters and monochromators and their application in powder diffraction;
  To describe the different types of X-ray and neutron detector with a brief explanation of how they work.

- *Lecture 3*
  To explain how good-quality powder samples are prepared;
  To get the students to prepare powder samples in the laboratory;
  To discuss powder diffractometer data acquisition and to relate this to experimental objectives (qualitative versus quantitative analysis, structure refinement versus structure solution);

To get each student to collect data on a different unknown binary misture using the PSD detector;
To discuss instrument calibration, errors, and standard samples.

- *Lecture 4*
  To explain the contents of the JCPDS database;
  To demonstrate the use of the database by the Hanawalt search method;
  To get the students to solve simple textbook problems using the teaching sub-set of the database.

- *Lecture 5*
  To teach the students how to visualise their data collected in lecture 3;
  To get the students to estimate peak positions and intensities;
  To give the students practice in phase identification from binary mixtures;
  To demonstrate some of the problems involved in qualitative analysis.

- *Lecture 6*
  To explain how the *d*-spacings of the peaks are related to the unit cell parameters;
  To show how these equations simply for higher-symmetry crystals;
  To demonstrate how powder diffraction patterns of cubic materials may be indexed manually;
  To give the students practice in manual indexing;
  To illustrate how the interplanar spacing of layered materials may be obtained by simple indexing of *00l* peaks;
  To briefly discuss the concepts used in various automatic computer indexing programs.

- *Lecture 7*
  To discuss the factors that determine peak intensity in powder diffraction;
  To show the effect of symmetry on the peak multiplicity;
  To discuss the factors effecting peak width;
  To discuss peak shapes for different instrumental conditions;
  To briefly mention instrument abberations and their effect on peak shape.

- *Lecture 8*
  To explain the concepts involved in the Rietveld method for the refinement of crystal strcutures from powder data;
  To give a slow step by step demonstration of the method using in-house software.

- *Lecture 9*
  To show how the Rietveld method can be taken a stage further to whole pattern fitting;
  To demonstrate with examples the steps involved in structure solution from powder data;
  To emphasise the difficulties and limitations of the method.

- *Lecture 10*
  To give the students hands-on experience of the Rietveld method using a variety of powder diffraction data sets from different instruments;
  To illustrate the importance of knowing the characteristics of the diffractometer used for the data acquisition.

- *Lecture 11*
  To give the students hands-on experience of powder diffraction at both a synchrotron radiation source (SRS) and a pulsed neutron source (RAL).

MSc Crystallography

Advanced Symmetry

Aims & Objectives

The overall aim of this MSc module is to explain the salient points of higher-symmetry space groups, namely those belonging to the tetragonal, trigonal, hexagonal, and cubic crystal systems.

The objectives of each lecture are given below:

- *Lecture 1*
  To explain the solution to symmetry problems set for the vacation;
  To revise the basic principles involved for orthorhombic space groups;
  To give students confidence in deriving space group information from single-crystal diffraction data.

- *Lecture 2*
  To illustrate the additional symmetry elements present in centred orthorhombic space groups;
  To discuss the concept of extended space-group symbols;
  To teach the students how to deduce space-group symmetry from diffraction data of a crystal possessing a centred lattice;
  To introduce the concept of *d*-glide planes with reference to space groups *Fdd2* and *Fddd*.

- *Lecture 3*
  To develop the concepts involved in tetragonal space groups belonging to the Laue class *4/m*;
  To briefly survey the higher-symmetry tetragonal space groups belonging to the Laue class *4/mmm*;
  To show how the two Laue classes may be distinguished in a diffraction experiment;
  To introduce the concept of enantiomorphic pairs of space groups.

- *Lecture 4*
  To develop the concepts involved in cubic symmetry;
  To discuss the differences between the two cubic Laue classes *m-3* and *m-3m*.

- *Lecture 5*
  To introduce the concept of trigonal symmetry and the diamond-shaped unit cell associated with it;
  To introduce the symmetry operators resulting from threefold symmetry;
  To introduce the concept of the reciprocal-space coordinates *hkil*;
  To develop the concepts involved with the Laue classes *-3m1* and *-31m* and to demonstrate the relationship between them;
  To show how the different Laue classes may be distinguished in a diffraction experiment;
  To introduce the concept of rhombohedral symmetry and the relationship between the R-centred hexagonal and primitive rhombohedral unit cells;
  To relate the rhombohedral and cubic unit cells.

- *Lecture 6*
  To extend the concepts of trigonal symmetry to hexagonal space groups;
  To show additional uses for *hkil* indices in hexagonal systems;
  To discuss the differences between the two hexagonal Laue classes *6/m* and *6/mmm*.

- *Lecture 7*
  To revise space-group symmetry from low to high symmetry;
  To illustrate sub-group and super-group relationships;

To very briefly discuss the concept of higher-symmetry systems;
To illustrate the latter with colour symmetry and magnetic spin.

MSc Crystallography

Chemical Crystallography

Aims & Objectives

The aims of this module are: (1) to provide instruction on the methods and basis for determining low molecular weight crystal structures using X-ray Crystallography; (2) to enable interpretative assessment of the results of crystal structure analysis to be carried out; and (3) to guide students through several actual analyses using the SHELX-program suite implemented on Pentium PC's. An introduction to Macromolecular Crystallography is provided at the end of the course in preparation for this module. Having undertaken the course students should be prepared to undertake extended project work using the methods covered in the course and are encouraged to do so at a later stage.

The objectives of each lecture are given below:

- *Lecture 1*
  To introduce the necessary concepts of diffraction theory in the context of single crystals. X-ray scattering from a single atom and from arrays of atoms, leading up to the formulation of the Structure Factor F(hkl) for centrosymmetric and non-centrosymmetric crystals.

- *Lecture 2*
  To introduce the concept and formulation of Fourier series as used in X-ray crystallography. Practical aspects of electron density calculations and interpretation in structural terms. The phase problem enunciated. To introduce the concept of the Patterson function, its calculation and properties, in particular when a structure contains an outstandingly heavy atom.

- *Lecture 3*
  To demonstrate the use of SHELX programs for calculating the Patterson function for a heavy atom containing crystal, and interpretation in terms of heavy atom positions. Hands-on use of the program package. Centrosymmetric case. Calculation of molecular geometry and chemical significance of bond lengths, bond angles and other geometrical features such as planarity.

- *Lecture 4*
  To continue with the analysis started in Lecture 3, to expand the structure using Fourier and difference Fourier methods. Use of graphics programs to interpret the results.

- *Lecture 5*
  To repeat the ground covered in previous lectures for a moderately complex non-centrosymmetrical structure.

- *Lecture 6*
  To provide the theoretical basis of Direct Methods of stucture determination. Concept of and rules for origin fixing. Practical examples for various centrosymmetric space groups.

- *Lecture 7*
  To intoduce the triple product sign relationship and expansion into the sigma2 formula. Symbolic addition and multi-solution methods for phase determination. The use of figures of merit for descrimination between phase sets.

- *Lecture 8*
  Practical applications of direct methods for structure solution. Use of SHELX-S and graphics programs. Non-centrosymmetrical structures.

- *Lecture 9*
  Expansion and completion of trial crystal structures from Patterson or direct methods. The use of Fourier methods and least-squares refinement. Isotropic and anisotropic models for atomic thermal vibrations. Pit-falls and precautions necessary in practice. Practicals and demonstrations.

- *Lecture 10*
  Methods for locating and/or calculating and refining H-atom positions. Determination of absolute configuration. More practicals.

- *Lecture 11*
  Introduction to macromolecular Crystallography. Isomorphous replacement and molecular replacement, basic concepts.

MSc Crystallography

Applied Crystallography

Aims & Objectives

The overall aim of this MSc module is to give the students a few in-depth examples of the applications of materials and solid-state chemical/physics crystallography in academic research, industrial research, and its general use in the outside world. The general aim is to be take examples mainly from materials and solid-state chemistry/physics so as to provide a complimentary view to the application of crystallography in structural molecular biology which is covered by the protein crystallography module.

The objectives of each lecture are given below:

- *Lecture 1*
  To illustrate the different types of crystal structures formed by inorganic oxides;
  To show how structures may be classified according to structural type;
  To introduce the concept of relating structure to physical properties;
  To discuss the application of diffraction methods to the structure determination of high-temperature superconductors;
  To demonstrate the similarity in structure of the various high-temperature superconductors.

- *Lecture 2*
  To discuss the importance of the SiO4 tetrahedron in the formation of different silicate mineral structures;
  To expand the concept of the relationship between structure and physical properties with reference to the rock-forming silicate minerals;
  To give the students a hands-on demonstration of the different optical properties of various minerals using two different sources of granite.

- *Lecture 3*
  To continue the concept of the relationship between structure and physical properties with reference to cements;
  To discuss the different complimentary methods used to investigate cements.

- *Lecture 4* (Invited Lecturer)
  To discuss the Cambridge Crystallographic Structural Database; what it contains; and how to use it;
  To discuss how databases may be used to deduce information about the molecular interactions between different chemical groups;
  To give the students hands-on experience of the use of the Cambridge CSD.

- *Lectures 5 and 6* (Invited Lecturer)
  To introduce the students to the concept of perfect crystals and crystal defects;
  To show how they may be studied by X-ray topography;
  To discuss the instrumentation required for X-ray topography;
  To outline the principles involved in X-ray topography;
  To illustrate X-ray topography using diamond and silicon crystals as examples;
  To demonstrate the difference between the kinematic and dynamic approach to diffraction theory;
  To introduce the students to the concepts involved in the dynamical theory.

- *Lecture 7* (Invited Lecturer)
  To discuss the structure and properties of zeolites;
  To outline their importance in industrial processes;
  To explain the limitations of diffraction in studying the behaviour of molecules within zeolites;
  To briefly explain the concepts involved in the computer simulation of crystal structures;
  To demonstrate how computer simulation and molecular graphics leads to a greater understanding of how zeolites function.

- *Lecture 8* (Invited Lecturer)
  To explain the concept of a patent;
  To discuss the importance of patents to the pharmaceutical industry;
  To outline the crystallographic contents of patents;
  To illustrate by example polymorphism in crystals;
  To explain why patents are contested and how pattern diffraction is used to both defend and attack patents in a court of law.

- *Lecture 9*
  To provide the students with a variety of practical examples of the use of electron microscopy for the study and characterization of materials;
  To briefly discuss the use of nano- and micro-technologies.

- *Lectures 10 and 11*
  To provide the students with a background to the scientific methods used in the study of archeological samples;
  To briefly discuss the merits and disadvantages of the scientific methods available;
  To show by illustration how forgeries are distinguished from the genuine objects;
  To demonstrate how optical and electron microscopy can be used to examine metal samples;
  To give the students hands-on experience in distinguishing between genuine and artificial metal corrosion;

In addition, one of the objectives of the visit to EPSRC central facilities (SRS and RAL) is to provide further examples of the application of the use of crystallography external to the home laboratory.

MSc Crystallography

Non-Crystalline Systems

Aims & Objectives

The overall aim of these additional lectures to the MSc course is to provide some insight into the techniques used to examine either poorly-crystalline materials or totally non-crystalline materials and thus to provide a contrast with techniques such as powder diffraction.

The objectives of each lecture are given below:

- *Lecture 1*
  To explain the concept of liquid and glass structures;
  To discuss the scattering instruments used to characterise these systems;
  To show by example how limited structural information can be obtained.

- *Lecture 2*
  To remind the students about thermal motion in solids and its effect on diffraction data;
  To explain why thermal diffuse scattering occurs;
  To explain how the measurement of thermal diffuse scattering leads to useful information in structural molecular biology.

- *Lecture 3*
  To introduce to non-biological polymers;
  To briefly discuss the structure of colloids;
  To describe small-angle diffractometers;
  To explain how small-angle scattering techniques can be used to characterise the structure of polymer and colloidal solutions;
  To show with examples the use of neutron scattering for contrast variation studies.

- *Lecture 4* (Daresbury)
  To briefly explain the concept of EXAFS as a tool for solid-state scientists;
  To see the setup of an EXAFS scattering station at the Daresbury synchrotron;
  To demonstrate the use of EXAFS as a complimentary scattering technique for the study of poorly crystalline materials.

Addendum 2: mid 1950's (rejected) submission on crystallography by J.D. Bernal et al to the Encyclopaedia Britannica. The article was rejected as too long but it embodied the syllabus and intention of the Birkbeck College M.Sc. course in crystallography.

Summarized comments between Alan Mackay and the newsletter editor about the article and history: Bernal's bit is on the X-ray analysis of crystals and the last paragraph (p.828D) bears perpetuation. The article was rejected as too long but it embodied the syllabus and intention of the M.Sc. course in crystallography.

JDB is J.D. Bernal. Other authors: WAW - W. A. Wooster; JDHD - J.D.H. Donnay; LJS - L.J. Spencer. ArFW - A.F. Wells. I believe that instead of Bernal's article the Encyclopaedia Britannica had a much shorter article by M. J. Burger.

The proof copy was copied (I think as Gestetner copies) and circulated to the M.Sc. class at the time to accompany JDB's lectures which were, of course, much less systematic. There is always the story of the student who came to Bernal after a lecture and said that is was so interesting that he could not take notes, could he borrow JDB's own notes. Bernal handed over three words on the back of an envelope.

As this EB submission was used by J.D. Bernal as part of the original Birkbeck M.Sc. notes, attempts to trace the article's copyright status were performed via queries to the estate of J. D. Bernal. It is included here as an addendum for its scientific history and scholarly value (with encouragement from J.D. Bernal's son, Mike Bernal) in this not-for-profit scientific publication.

—PATCHES for page 808—

For modern developments *see* CODES AND CIPHERS.

similar practices, *see* DIVINATION; HALLUCINATION; PSYCHICAL RESEARCH; SPIRITUALISM and allied articles.

CRYSTALLITE, a name given by Vogelsang to the microscopic bodies occurring in many glassy igneous rocks, such as obsidian, pitchstone and tachylyte. Though possessing no distinct reaction on polarized light and often no recognizable crystallographic form, they are to be regarded as incipient crystals. The larger bodies, often with good crystal form and evident double refraction, are termed microlites. According to their shape and structural arrangement crystallites are subdivided into globulites (small globules), margarites (coalescing globules arranged in rows), cumulites (cloudy aggregate of globules), and globospherites (groups of globulites with a radiate arrangement). Other crystallites assume thread-like forms (trichites) or appear as elongated cylinders or rods (longulites, belonites, baculites). When sufficiently large to be recognizable as mineral species (microlites) they can usually be referred to felspar, pyroxene, amphibole or iron oxides. Acicular microlites bearing divergent arborescent branches are termed scopulites. The pitchstones of Arran are well known for the variety and beauty of their crystallite and microlite constituents (amphibole). In the basaltic glasses of Hawaii similar growths are formed of pyroxene.

CRYSTALLIZATION, the art of obtaining a substance in the form of crystals. It is an important process in chemistry, since it permits the purification of a substance or the separation of the constituents of a mixture. Generally a substance is more soluble in a solvent at a high temperature than at a low, and consequently, if a boiling strong solution be allowed to cool, the substance will separate in virtue of the diminished solubility. The slower the cooling the larger and more perfect will be the crystals formed. If, as sometimes occurs, such a solution refuses to crystallize, the expedient of "inoculating" the solution with a minute crystal of the same substance, or with a similar substance, may be adopted; shaking the solution, or the addition of a drop of another solvent, may also occasion the desired result. "Fractional crystallization" consists in repeatedly partially crystallizing the salt content of a solution so as to separate the substances of different solubilities. Examples are especially presented in the study of the rare-earths. Other conditions under which crystals are formed are given in the article CRYSTALLOGRAPHY.

CRYSTALLOGRAPHY. Few fields of science changed more in the first half of the 20th century than did crystallography, and none so extended the range of its application. Before 1912, when Max von Laue's discovery provided the key to the inner structure of crystals, virtually nothing was known of the arrangements of atoms in solid matter. The methods of chemistry op-

CRYSTALLOGRAPHY

erated on them only after they had been melted, vapourized, or brought into solution. Even the science of crystallography itself, though of substantial antiquity, had not progressed further than measuring and registering the external faces of crystals. Its value was mainly that of identifying and classifying minerals. Knowledge of the properties of solids was a matter of practical testing without a clue as to the underlying reasons and therefore without the possibility of changing the properties except by repeated variations and trials. Sir Arthur Eddington could remark quite truly in 1927 that more was known about the interior of a star than about the interior of a table.

Later the situation was entirely transformed. As a result of new diffraction methods it became possible to determine the molecular structure of any kind of solid, whether apparently crystalline or not, and even to determine something of that of glasses and liquids. The results of these analyses, begun by Sir William Bragg and his son Sir Lawrence Bragg and carried on by armies of research workers in nearly every country in the world, soon had the effect of transforming many of the ideas of chemistry and mineralogy and notably influencing geology and biology. In industry the practical applications were quite as marked, particularly in metallurgy, where X-ray diffraction became as essential a tool as the microscope, and in the new industries of artificial fibres and plastics. Indeed as there is practically no industry where the properties of solids does not enter, the range of utility of the new crystallography, after it had shown its powers in practice, rapidly increased.

The knowledge of the precise ways atoms are arranged in crystals —their distance apart, the form of the regular geometrical patterns they make in space—gave many new qualitative and quantitative data to chemistry. The sizes of the different atoms and the lengths of the bonds joining them were revealed. Indeed the new crystallography furnished a microscope which, in competent hands, could discern molecules, atoms and even the distribution of electrons. These data were a valuable adjunct to the quantum theory in the reinterpretation of chemical formulas and in establishing new ones —notably that of penicillin. Inorganic chemistry—the chemistry of acids, bases and salts—was indeed largely rewritten in terms of ions or electrically charged atoms. The complexities of mineral chemistry, particularly of the silicates which constitute the bulk of the earth's crust, were unravelled as a result of crystallography. The science of geochemistry, which offers clues to the distribution of minerals in the earth, was largely built on a basis of crystal structures. Even greater was the contribution of crystallography to metallurgy. The composition of metals and alloys seemed to defy all the rules of chemistry. New rules were found for them in terms of relatively simple crystal structures. These same structures explained for the first time the plastic properties of metals that enable them to be rolled and drawn, as well as the inner mechanism of many age-old processes such as annealing and tempering.

In biology X-ray techniques revealed the fine structures of tissues which were beyond the range of the microscope or even of the electron microscope. These studies, because of their far grater complexity, were still in their introductory stages in the 1950s, but already much was known of the structure of hard parts—cell walls, hair, skin and tendons—and a start was being made with the attack on the great central problem of protein structure.

The first of the three sections which follow, that on the morphology of crystals, covers the field of classical crystallography but explains the external shape and faces of crystals in terms of an underlying structure. The second discusses the ways in which that structure can be found and the types of structure found in different kinds of matter; it is largely a treatise on crystal chemistry. The third, on crystal physics, deals with the explanation of the properties of crystals—mechanical, optical and electrical—and some of the practical applications of this knowledge.　(J. D. Be.)

MORPHOLOGY OF CRYSTALS

Crystalline matter is characterized by periodicity in its interatomic arrangement. A frieze is periodic, as it results from the repetition of the motif at equal intervals or periods. A wallpaper is an example of periodicity in the plane, the period being a square,

a rectangle or some other parallelogram. Crystalline matter is periodic in three independent directions, the period being a cube or some other parallelepiped. Crystallography even concerns itself with the study of matter periodic in less than three dimensions (e.g., fibres). The ideally perfect crystal is defined as a homogeneous portion of crystalline matter; real crystals, however, are seldom rigorously homogeneous. The word homogeneity must be taken here in the sense of periodic homogeneity, in contradistinction to statistical homogeneity; the latter is the homogeneity of a heap of sand, for instance. The following paragraphs will explain the concept of periodicity.

Consider any point O on a wallpaper. Let A be a similar point, closest to O. Build the row of parameter OA. Let B be a node outside the row OA, but as close to O as possible. Build the row of parameter OB. Through the nodes of each row, and parallel to the other one, pass a set of additional rows. All the nodes in the plane are seen to lie at the intersections of these two sets of parallel rows; they constitute a net, which is the geometric expression of the periodicity of the wallpaper (periodicity in two independent directions or diperiodicity). Any line passing through two nodes contains a row; it is a row line (also called a reticular line or a lattice line). Because there is no node inside the parallelogram built on OA and OB, the rows OA and OB are said to be conjugate and the parallelogram is a simple mesh. Other pairs of conjugate rows would give other simple meshes, usually different in shape but equal in size. This is easy to see, for, in order to cover a given portion of the plane, as many simple meshes (of any one shape) are needed as there are nodes in it. The area of the simple mesh is therefore a constant; it is called the reticular area of the net. A parallelogram built on nonconjugate rows is a multiple mesh: double, triple, . . . or n^{uple}, according as there are two, three, . . . or n nodes per mesh. Any multiple mesh may be used as a period, provided its multiplicity be stated, but the simple mesh is the smallest period of the net.

Let the concept of periodicity be extended into three-dimensional space. Starting again from any point O, build the row with the smallest parameter OC. Then, outside the row OC, take two nodes A and B as close to O as possible, but not in a straight line with O. Build the net on OA, OB. Through all the nodes of the row OC pass a set of additional nets parallel to OAB. Likewise through all the nodes of the rows OA and OB pass sets of nets parallel to OBC and OCA, respectively. All the nodes in space are seen to lie at the intersections of these three sets of parallel nets; they constitute a lattice, which is the expression of triperiodicity. Any plane passing through three nodes contains a net; it is a net plane (also called a reticular plane or a lattice plane). Because there is no node inside the parallelepiped built on OC, OA and OB, these rows are said to be conjugate and the parallelepiped is a simple cell. Other triplets of conjugate rows would give other simple cells, usually different in shape but equal in size, since, in order to fill a given portion of space, as many simple cells (of any one shape) are needed as there are nodes in it. The volume of the simple cell of a lattice is therefore a constant. A parallelepiped built on nonconjugate rows is a multiple cell: double, triple, . . . or n^{uple}, according as there are two, three, . . . or n nodes per cell. Any multiple cell may be used as a period, provided its multiplicity be stated, but the simple cell is the smallest period of the lattice.

The lattice is of fundamental importance in crystallography. It was used as a structural hypothesis long before X-ray diffraction experiments proved the distribution of matter in a crystal to be triperiodic. Since 1912, as a result of Max von Laue's celebrated experiment, it is known that a crystal is built up of regularly repeating particles (ions, atoms or molecules), the unit of structure being the motif or content of the cell (also called translation repeat or base).

History.—The word crystal is from the Gr. κρύσταλλος, meaning clear ice (Lat. crystallum), a name which was also applied to the clear transparent quartz (rock crystal) from the Alps, under the belief that it had been formed from water by intense cold. It was not until about the 17th century that the word was extended to other bodies, either those found in nature or obtained by the evaporation of a saline solution, which resembled rock crystal

in being bounded by plane surfaces, and often also in their clearness and transparency.

The first important step in the study of crystals was made by Nicolaus Steno, the famous Danish physician, afterward bishop of Titiopolis, who in his treatise *De solido intra solidum naturaliter contento* (Florence, 1669; English translation, 1671) gave the results of his observations on crystals of quartz. He found that although the faces of different crystals vary considerably in shape and relative size, yet the angles between similar pairs of faces are always the same. He further pointed out that the crystals must have grown in a liquid by the addition of layers of material upon the faces of a nucleus, this nucleus having the form of a regular six-sided prism terminated at each end by a six-sided pyramid. The thickness of the layers, though the same over each face, was not necessarily the same on different faces, but depended on the position of the faces

FIG. 1.—HEXAGONAL SCALENOHEDRON BUILT UP OF RHOMBOHEDRA

with respect to the surrounding liquid; hence the faces of the crystal, though variable in shape and size, remained parallel to those of the nucleus, and the angles between them constant. Robert Hooke in his *Micrographia* (London, 1665) had previously noticed the regularity of the minute quartz crystals found lining the cavities of flints and had suggested that they were built up of spheroids. About the same time the double refraction and the rhombohedral cleavage of crystals of calcite or Icelandspar were studied by Erasmus Bartholinus (*Experimenta crystalli Islandici disdiaclastici,* Copenhagen, 1669) and Christiaan Huygens (*Traité de la lumière,* Leyden, 1690); the latter supposed, as did Hooke, that the crystals were built up of spheroids. In 1695 Anthony van Leeuwenhoek observed under the microscope that different forms of crystals grow from the solutions of different salts. Andreas Libavius had indeed much earlier, in 1597, pointed out that the salts present in mineral waters could be ascertained by an examination of the shapes of the crystals left on evaporation of the water; and Domenico Guglielmini (*Riflessioni filosofiche dedotte dalle figure de dei sali,* Padua, 1706) asserted that the crystals of each salt had a shape of their own with the plane angles of the faces always the same.

FIG. 2.—OCTAHEDRON BUILT UP OF CUBES

The earliest treatise on crystallography is the *Prodromus Crystallographiae* of M. A. Cappeller, published at Lucerne in 1723. Crystals were mentioned in works on mineralogy and chemistry; for instance, C. Linnaeus in his *Systema Naturae* (1735) described about 40 common forms of crystals among minerals. It was not, however, until the end of the 18th century that any real advances were made, and the French crystallographers J. B. L. Romé de Lisle and the *abbé* René Just Haüy are rightly considered as the founders of the science. Romé de Lisle (*Essai de cristallographie,* Paris, 1772; *Cristallographie, ou description des formes propres à tous les corps du règne mineral,* Paris, 1783) made the important discovery that the various shapes of crystals of the same natural or artificial substance are all intimately related to each other; and further, by measuring the angles between the faces of crystals with the goniometer (*q.v.*), he established the fundamental principle that these angles are always the same for the

FIG. 3.—AXES OF CO-ORDINATES

same kind of substance and are characteristic of it. Replacing by single planes or groups of planes all the similar edges or solid angles of a figure called the primitive form, he derived other related forms. Six kinds of primitive forms were distinguished: the cube, the regular octahedron, the regular tetrahedron, a rhombohedron, an octahedron with a rhombic base, and a double six-sided pyramid. Only in the last three can there be any variation

in the angles: for example, the primitive octahedran of alum, nitre and sugar were determined by Romé de Lisle to have angles of 110°, 120° and 100° respectively. Haüy in his *Essai d'une théorie sur la structure des crystaux* (Paris, 1784; see also his treatises on mineralogy and crystallography, 1801 and 1822) supported and extended these views, but took for his primitive forms the figures obtained by splitting crystals in their directions of easy fracture or cleavage, which are always the same in the same kind of substance. Thus he found that all crystals of calcite (*q.v.*), whatever
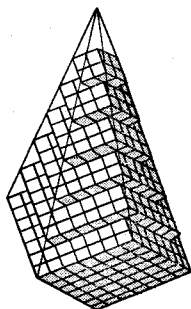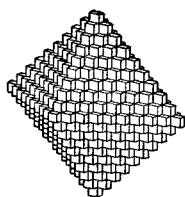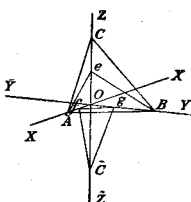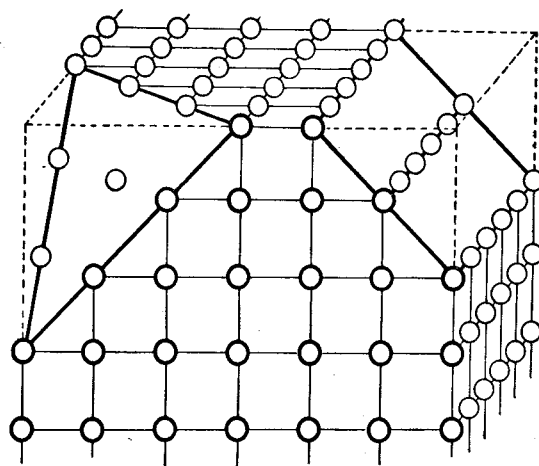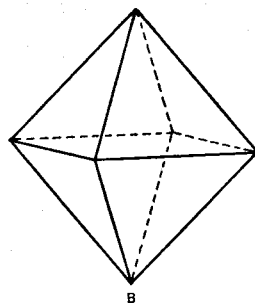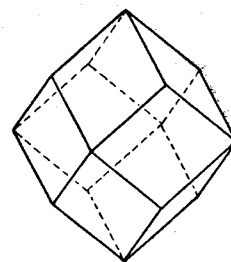
FIG. 4.—DEVELOPMENT OF CRYSTAL FACES AS A CONSEQUENCE OF INTERNAL CRYSTAL STRUCTURE

(A) faces develop parallel to nets; in primitive cubic lattice, the cube is most frequent, followed by rhomb-dodecahedron (C) and octahedron (B)

their external form, could be reduced by cleavage to a rhombohedron with interfacial angles of 75°. Further, by stacking together a number of small rhombohedra of uniform size he was able, as had been previously done by J. G. Gahn in 1773, to reconstruct the various forms of calcite crystals. Fig. 1 shows a scalenohedron built up of rhombohedra in this manner; and fig. 2 a regular octahedron built up of cubic elements, such as are given by the cleavage of galena and rock salt.

The external surfaces of such a structure, with their steplike arrangement, correspond to the plane faces of the crystal, and the bricks may be considered so small as not to be separately visible. By making the steps either one, two or three bricks in width and one, two or three bricks in height, the various secondary faces on the crystal are related to the primitive form or cleavage nucleus by a law of whole numbers, and the angles between them can be arrived at by mathematical calculation. By measuring with the goniometer the inclinations of the secondary faces to those of the primitive form, Hauy found that the secondary forms are always related to the primitive form on crystals of numerous substances in the manner indicated, and that the width and the height of a step are always in a simple ratio, rarely exceeding that of 1:6. This laid the foundation of the important "law of rational indices" of the faces of crystals.

The German crystallographer C. S. Weiss (*De indagando formarum, crystallinarum charactere geometrico principali dissertatio,* Leipzig, 1809; *Übersichtliche Darstellung der verschiedenen natürlichen Abtheilungen der Krystallisations-Systeme, Denkschrift der*

CRYSTALLOGRAPHY

Berliner Akad. der Wissensch., 1814–15) attacked the problem of crystalline form from a purely geometrical point of view, without reference to primitive forms or any theory of structure. The faces of crystals were considered by their intercepts on co-ordinate axes, which were drawn j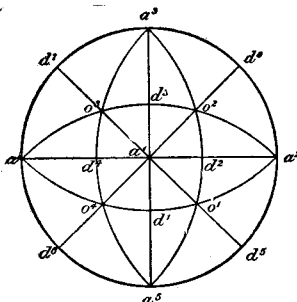oining the opposite corners of certain forms; and in this way the various primitive forms of Haüy were grouped into four classes, corresponding to the four systems described below under the names cubic, tetragonal, hexagonal and orthorhombic. The same result was arrived at independently by F. Mohs, who further, in 1822, asserted the existence of two additional systems with oblique axes. These two systems (monoclinic and triclinic) were, however, considered by Weiss to be only hemihedral or tetartohedral modifications of the orthorhombic system, and they were not definitely established until 1835 when the optical characters of the crystals were found to be distinct. A system of notation to express the relation of each face of a crystal to the co-ordinate axes of reference was devised by Weiss, and other notations were proposed by F. Mohs, A. Lévy (1825), C. F. Naumann (1826), and W. H. Miller (*Treatise on Crystallography,* Cambridge, 1839). For simplicity and utility in calculation the Millerian notation, which was first suggested by W. Whewell in 1825, surpasses all others and is now generally adopted, though those of Lévy and Naumann are still in use.

FIG. 5.—STEREOGRAPHIC PROJECTION OF A CUBIC CRYSTAL SHOWING CUBE *A*, OCTAHEDRON *O* AND RHOMB-DODECAHEDRON *D*

Although the peculiar optical properties of Iceland-spar had been much studied since 1669, it was not until much later that any connection was traced between the optical characters of crystals and their external form. In 1818 Sir David Brewster found that crystals could be divided optically into three classes, viz., isotropic, uniaxial and biaxial, and that these classes corresponded with Weiss's four systems (crystals belonging to the cubic system being isotropic, those of the tetragonal and hexagonal being uniaxial, and the orthorhombic being biaxial). Optically biaxial crystals were afterward shown by J. F. W. Herschel and F. E. Neumann in 1822 and 1835 to be of three kinds, corresponding with the orthorhombic, monoclinic and triclinic systems. It was, however, noticed by Brewster himself that there are many apparent exceptions, and the optical anomalies of crystals have been the subject of much study. The intimate relations existing between various other physical properties of crystals and their external form have subsequently been gradually traced.

As a consequence of Haüy's law of rational intercepts, or, as it is more often called, the law of rational indices, it was proved by J. F. C. Hessel in 1830 that 32 types of symmetry are possible in crystals. Hessel's work remained overlooked for 60 years, but the same important result was independently arrived at by A. Bravais in 1849 and by A. Gadolin in 1867. The 14 different ways of repeating a point by translations in space, the translation groups, were established by A. Bravais in 1849. The 230 ways of arranging asymmetric objects in space, repeating them by translations, rotations, reflections and all combinations of these operations, were discovered during the last decade of the 19th century by E. S. Fedorov, A. Schoenflies and W. Barlow independently. The historical development of the subject is treated in P. Groth, *Entwicklungsgeschichte der mineralogischen Wissenschaften* (Berlin, 1926).
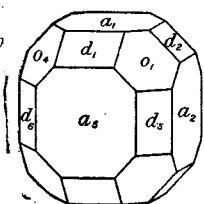
FIG. 6.—CLINOGRAPHIC DRAWING OF A CUBIC CRYSTAL

Some properties of matter do not depend on direction; they are scalar properties. Others do; they are vectorial properties.

At any point a vectorial property may be represented by a vec-

tor, the length of which varies with the direction. As one changes from any direction to a neighbouring one, this variation in the vector length may be gradual (the vectorial property is then continuous) or abrupt (the property is then called discontinuous). The rate of growth of a crystal, for instance, is a discontinuous vectorial property; it shows sharp minima in certain directions. Some crystals (called euhedral) are bounded by plane faces perpendicular to these directions. Another discontinuous vectorial property of a crystal is its cohesion. Some crystals break easily along planes that are perpendicular to the direction of minimum cohesion; such planes are called cleavage planes.

Faces, cleavage planes and other planes associated with discontinuous vectorial properties in a crystal may be called crystal planes. The fundamental fact, established by X-ray diffraction, that crystal planes are parallel to nets in the crystal lattice accounts for many of the observations of the early crystallographers. Since an edge of a crystal is the intersection of adjacent faces, it is parallel to a lattice row, which lies at the intersection of two nets.
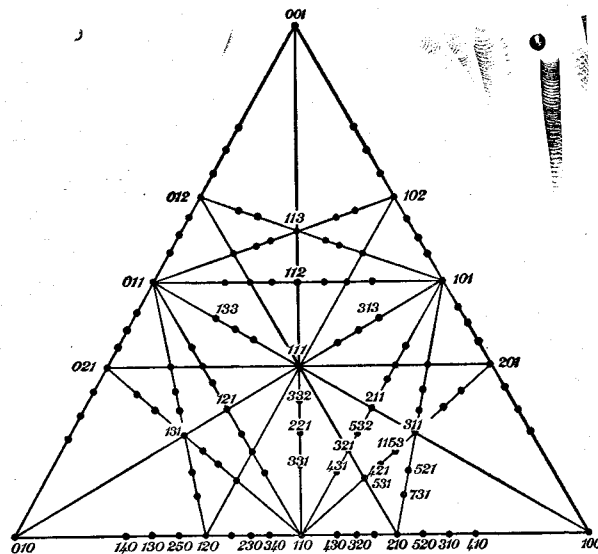
FIG. 7.—GNOMONIC PROJECTION OF A CUBIC CRYSTAL

The first laws of crystallography deal with the relative inclinations of faces to one another. Such angles are measured by means of goniometers (*q.v.*).

FUNDAMENTAL LAWS AND CONCEPTS

Law of Constancy of Angles.—At a given temperature the angle between two faces of a crystal is a constant because these faces are parallel to two definite nets in the lattice, so that another crystal of the same crystalline substance will show corresponding faces parallel to the same two nets in the lattice. This law holds true, of course, for other crystal planes besides faces. The angle between two edges is likewise constant because edges are parallel to lattice rows, and this is true for other crystal lines besides edges (for instance, the intersection lines of cleavage planes).

The angles of a crystal, being characteristic of the substance, serve as determinative criteria. Several methods of crystallochemical analysis have been proposed (E. S. Fedorov, A. Boldirev, T. V. Barker) for the identification of crystalline compounds on which angles can be measured.

Law of Rationality.—Through any point taken inside the crystal as the origin, pass lines parallel to three noncoplanar edges (or other crystal lines); that is to say, three edges formed by the intersection of three faces. Let these be the axes of co-ordinates OX, OY, OZ fig. 3). Take a fourth face (called unit face or parametral face) inclined on all three axes; let ABC be a plane parallel to it. Let ξ', η', ζ' be the angles (called direction angles) which the normal to the unit face makes with the axes of co-ordinates OX, OY, OZ, respectively. Take any fifth face on the crystal and let ξ, η, ζ, be the direction angles of its normal.

810B   # CRYSTALLOGRAPHY

It is a law of observation that the ratios of the quotients of corresponding direction cosines are rational; i.e., where h, k, l

$$\frac{\cos\xi}{\cos\xi'} : \frac{\cos\eta}{\cos\eta'} ; \frac{\cos\zeta}{\cos\zeta'} = h : k : l, \qquad (1)$$

are small integers, called the Miller indices of the face (hkl). The symbol of the unit face is obviously (111), as seen from the above equation.

It is known from geometry that the intercepts which a plane cuts on the axes of co-ordinates are inversely proportional to the direction cosines of its normal, so that it may be written

$$a : b : c = OA : OB : OC = \frac{1}{\cos\xi'} : \frac{1}{\cos\eta'} : \frac{1}{\cos\zeta'} \quad (2)$$

Substituting (2) in (1), results in

$$a \cos\xi : b \cos\eta : c \cos\zeta = h : k : l, \qquad (3)$$

which can also be written

$$\frac{a}{h} \cos\xi = \frac{b}{k} \cos\eta = \frac{c}{l} \cos\zeta. \qquad (4)$$

In this form, it is known as the fundamental formula. It is the basis of crystallographic calculations.

Let OH, OK, OL designate the intercepts cut on the co-ordinate axes by a plane parallel to the fifth face. In view of the proportionality between the intercepts of a plane and the direction cosines of its normal, (3) may be written

$$a/OH : b/OK : c/OL = h : k : l \qquad (5)$$

or

$$OH/a : OK/b : OL/c = 1/h : 1/k : 1/l \quad (6)$$

or again

$$OH : OK : OL = a/h : b/k : c/l \quad (7)$$

The latter form is expressed: the intercepts of any crystal face are proportional to small submultiples of the intercepts a, b, c, of any plane parallel to the unit face. Thus the intercepts of a face parallel to $A\,Be$ (fig. 3) are in the ratios $OA : OB : Oe = a/1 : b/1 : c/2$; such a face is designated (112). A face parallel to fgC has the symbol (231) since $Of : Og : OC = a/2 : b/3 : c/(-1)$.

In equation (7) reduce the fractions to the same denominator and multiply them by their common denominator, which does not alter their ratios, and obtain

$$OH : OK : OL = kla : lhb : hkc = ea : fb : gc, \qquad (8)$$

where e, f, g are small integers, known as the Weiss coefficients. This relation is expressed: any crystal face is parallel to a plane whose intercepts are equal to small multiples of the unit lengths a, b, c. This form of the law of rationality shows its meaning in terms of the lattice. Indeed, let a, b, c, be the three primitive translations of a lattice, then equation (8) means that any crystal face is parallel to a stratification of nets in the lattice. Moreover, the first net away from the origin in the stratification passes through three nodes H, K, L, not many parameters away from the origin, so that the triangle HKL is small. The smallest mesh of the net is either the parallelogram that is twice the triangle HKL, or a fraction thereof; consequently the smallest mesh of the net is small. Let it be designated by S and let d represent the interplanar distance in the strati-

FIG. 8 AND 9.—CLINO-GRAPHIC DRAWINGS AND PLAN DRAWINGS OF A ZIRCON CRYSTAL
Fig. 8, actual portrait; Fig. 9, idealized drawing

fication of nets parallel to HKL. Then $S.d = V$, where V, the volume of the smallest cell of the lattice, is a constant. A small mesh in the net corresponds, therefore, to a large interplanar distance. The reticular meaning of the law of rationality is thus that faces are parallel to stratifications of nets with large interplanar distances (fig. 4).

FIG. 10 AND 11.—MAL-FORMED OCTAHEDRA

Axial Elements.—The axial elements serve to characterize a crystalline substance. They are the axial ratios, $a : b : c$, and the interaxial angles, $\alpha = YOZ$, $\beta = ZOX$, $\gamma = XOY$. The latter are obtained from goniometric measurements, either directly or through calculations. The axial ratios are given by equation (2) provided the direction angles of the normal to the unit face have been measured or computed from other measured angles. Then the Miller indices (hkl) of any face are obtained from (4), provided the direction angles of its normal have been measured or computed from measurements.

Law of Bravais.—The law of Bravais is a more precise form of Haüy's law of rationality. The latter, translated into reticular language, states that the faces which occur on a crystal are parallel to nets with large interplanar distances. This is true, in general, regardless of the choice of the co-ordinate axes and unit face. The law of Bravais goes further; it states that the faces which occur are precisely those parallel to the nets with the largest interplanar distances, and the larger the interplanar distance the more important the face. By "importance" is meant the frequency with which a face occurs on various crystals of the same crystalline substance and, to a lesser extent, the size to which it usually grows. The choice of axial elements can be guided by the law of Bravais; they can be chosen so that the law holds true. This is not begging the question, however, as the law resides in the very fact that it is possible almost always uniquely to find such axial elements in all cases. The law of Bravais is only a first approximation to the truth; it suffers exceptions. Yet, in its imperfect form, it nearly always makes it possible to select a unit cell that is the same as that found by X-ray diffraction methods, namely, the cell that expresses the periodicity of the crystal structure.

Exceptions to the law of Bravais include the following: (1) The
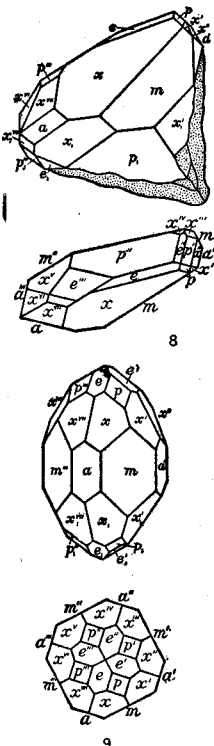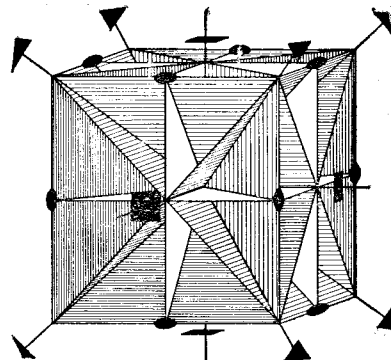
FIG. 12.—SYMMETRY ELEMENTS IN POINT GROUP $4/m\ \bar{3}\ 2/m$: THREE 4-AXES, EACH NORMAL TO A MIRROR; FOUR 3-AXES; SIX 2-AXES, EACH NORMAL TO A MIRROR

forms present on a crystal depend not only on factors within the crystal, but on external factors as well (conditions of crystallization). (2) The law holds for dominant forms only, even in the most favourable cases. (3) Frequently the best lattice that can be determined by the law of Bravais leads to an order of importance not wholly satisfactory even for the dominant forms; it may assign large interplanar distances to unknown or insignificant forms. (4) Complementary merohedral forms have the

same interplanar distance, yet do not always show equal morphological importance.

Zones.—Faces intersecting along parallel edges are said to be in a zone. Planes passed through the origin parallel to such faces
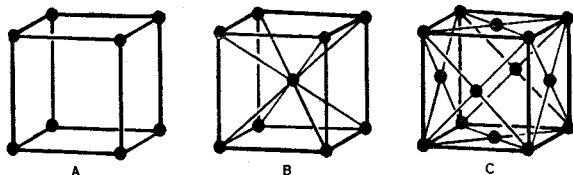

FIG. 13.—CELLS OF CUBIC LATTICES: (A) PRIMITIVE; (B) BODY-CENTRED; (C) FACE-CENTRED

will intersect along a straight line. The direction of this line is called the zone axis. The plane perpendicular to the zone axis contains the normals to the faces in the zone; it is called the zone plane. Example: in a crystal of zircon (fig. 8 and 9) the eight faces of the two tetragonal prisms a and m constitute a zone with the vertical 4-axis as zone axis.

Three faces, (hkl), $(h'k'l')$ and $(h''k''l'')$ will lie in a zone if the determinant $hkl/h'k'l'/h''k''l''$ is equal to zero. The expansion gives Weiss's zone law, $hu+kv+lw=0$, in which $u = k'l''-l'k'', v = l'h'' - h'l'', w = h'k'' - k'h''$. The symbol $[uvw]$ designates the zone axis; u, v, w being the trimetric co-ordinates of a point which, joined to the origin, gives the zone axis. The equation of the zone is symmetrical in hkl and uvw. It expresses the condition for a face to lie in a given zone, or for a zone to comprise a given face. Adding the indices of two faces, each to each, gives the indices of a face in zone with and between the given two faces. By this rule the indices of a face lying at the intersection of two zones can be determined. Example: (311) in fig. 7 lies at the intersection of the zones (210) (101) and (201) (110).

Crystal Projections and Crystal Drawing.—The shapes and relative sizes of the faces of a crystal being as a rule accidental, depending only on the distance of the faces from the centre of the crystal and not in their angular relations, it is often more convenient to consider only the directions of the normals to the faces. For this purpose projections are drawn, with the aid of which the zonal relations of a crystal are more readily studied and calculations are simplified.

The kind of projection most extensively used is the stereographic projection. The crystal is considered to be placed inside a sphere from the centre of which normals are drawn to all the faces of the crystal. The points at which these normals intersect the surface of the sphere are called the poles of the faces, and by these poles the positions of the faces are fixed. The poles of all faces in the same zone on the crystal will lie on a great circle of the sphere, which is therefore called a zone-circle. The calculation of the angles between the normals of faces and between zone-circles is then performed by the ordinary methods of spherical trigonometry. The stereographic projection, however, represents the poles and zone-circles on a plane and not on a spherical surface. This is achieved by drawing lines joining all the poles of the faces with the north or south pole of the sphere and finding their points of intersection with the plane of the equator inside the primitive circle, the projection being represented on this plane. In fig. 5 is shown the stereographic projection of a cubic crystal: a^1, a^2, etc., are the poles of the faces of the cube; o^1, o^2, etc., those of the octahedron: and d^1, d^2, etc., those of the rhombdodecahedron. The straight lines and circular arcs are the projections on the equatorial plane of the great circles in which the nine planes of symmetry intersect the sphere. A drawing of a crystal
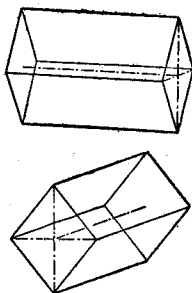
FIG. 14.—RHOMBIC PRISM AND PINACOID IN TWO DIFFERENT POSITIONS

showing a combination of the cube, octahedron and rhombdodecahedron is shown in fig. 6, in which the faces are lettered the same as the corresponding poles in the projection. From the zone-circles in the projection and the parallel edges in the drawing the zonal relations of the faces are readily seen: thus $[a^1o^1d^5]$, $a^1d^1o^5]$, $[a^5o^1d^2]$, etc., are zones. A stereographic projection of a rhombohedral crystal is given in fig. 64.

Another kind of projection in common use is the gnomonic projection (fig. 7). Here the plane of projection is tangent to the sphere, and normals to all the faces are drawn from the centre of the sphere to intersect the plane of projection. In this case all zones are represented by straight lines. Fig. 7 is the gnomonic projection of a cubic crystal, the plane of projection being tangent to the sphere at the pole of an octahedral face (111), which is therefore in the centre of the projection. (In this figure a left-handed system of co-ordinates is used.)

In drawing crystals the simple plans and elevations of descriptive geometry (e.g., the plans in the lower part of fig. 8 and 9)
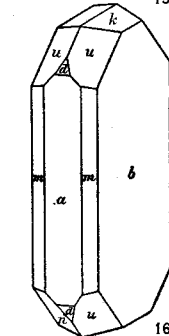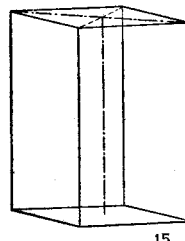
FIG. 15.—RHOMBIC PRISM AND PINACOID
FIG. 16.—HYPERSTHENE CRYSTAL

sometimes have the advantage of showing the symmetry of a crystal, but they give no idea of solidity. For instance, a cube would be represented merely by a square, and an octahedron by a square with lines joining the opposite corners. True perspective drawings are never used in the representation of crystals, since for showing the zonal relations it is important to preserve the parallelism of the edges. If, however, the eye, or point of vision, is regarded as being at an infinite distance from the object all the rays will be parallel, and edges which are parallel on the crystal will be represented by parallel lines in the drawing. The plane of the drawing which the parallel rays joining the corners of the crystal and the eye intersect may be either perpendicular or oblique to the rays; in the former case it is an orthographic drawing, and in the latter a clinographic drawing. Clinographic drawings have been used frequently for representing crystals. In representing, for example, a cubic crystal (fig. 6) a cube face a^3 is first placed parallel to the plane on which the crystal is to be projected and with one set of edges vertical; the crystal is then turned through a small angle about a vertical axis until a second cube face a^2 comes into view, and the eye is then raised so that a third cube face a^1 may be seen.

In order to obtain the corresponding orthographic drawing, the eye is not raised; instead, the cube is rotated through a small angle about a horizontal axis until the face a^1 becomes visible. The projecting lines are then perpendicular to the plane of projection, and the latter is no longer the face a^3.

EXTERNAL SYMMETRY

Symmetry Operations.—A direction AB is either homopolar or polar, according as the two senses in which it may be travelled (AB and BA) are, or are not, equivalent. Certain crystals possess directions different from all others in the crystal; such a direction is called a singular direction. A crystal direction may be polar for one property and homopolar for another.

A crystal in which all directions are singular and polar with respect to a certain property is said to be asymmetrical (or to lack symmetry) in that property. A crystal in which not all directions are singular and polar with respect to a given property is said to be symmetrical (or to have symmetry) in that property. In other words: in regard to the property considered, to any nonsingular direction in a symmetrical crystal there exists one, or more than one, equivalent direction. A singular direction AB, if polar, has no equivalent direction; if homopolar, AB is equivalent with its counterdirection BA.

810D CRYSTALLOGRAPHY

By the symmetry of a crystal, with no qualification as to which property is considered, is meant the symmetry common to all its properties (the equivalence of directions must hold true for any property). It is a law of observation that all crystals of the same substance (same chemical compound and, in case of polymorphism, same modification) show the same symmetry. This is the law of constancy of symmetry.

A natural crystal, because of accidental conditions of growth, is often malformed in that physically similar faces have neither the same size nor the same shape (fig. 10 and 11). In order to emphasize equivalent directions, the sheaf of face normals (passed through any one point in the crystal) is substituted for the crystal itself in the study of its symmetry.

A symmetrical crystal has been defined by the fact that it possesses equivalent directions or, if all its directions are singular, that they are homopolar. An operation which, applied to a symmetrical crystal, brings every direction into coincidence with an equivalent direction (the sense being taken into account for polar directions) is called a symmetry operation. The expression "bringing the crystal to self-coincidence" is often used; it is quite justifiable if, by crystal, is meant the sheaf of face normals, for a symmetry operation brings every line of the sheaf into coincidence with an equivalent line.

It is proved in geometry that there are only two different
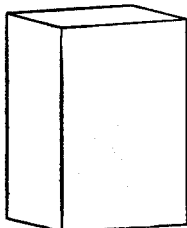
FIG. 17.—TETRAGONAL PRISM AND PINACOID
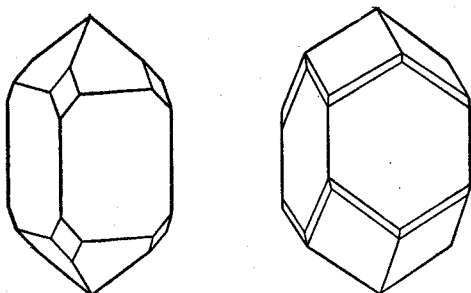
FIG. 18.—COMBINATIONS OF TETRAGONAL PRISMS AND DIPYRAMIDS

kinds of symmetry operations. The rotation around an axis is the operation of the first kind. The rotatory inversion is the operation of the second kind; it is a combination of a rotation around an axis with an inversion through a point situated on the axis. To invert a point P through a point C, join PC, extend an equal length, $CP' = PC$, and find point P'. (Some authors prefer to use the rotatory reflection as the operation of the second kind. It is a combination of a rotation with a reflection in a plane perpendicular to the rotation axis.)

Symmetry Elements.—If a symmetry operation is applied $2, 3, \ldots n$ times in succession, the result is a symmetry operation, for the crystal is thereby brought to self-coincidence. Borrowing the terminology from the mathematical theory of groups, this is conveniently expressed: the powers of a symmetry operation are symmetry operations. Likewise if $2, 3, \ldots n$ symmetry operations are applied in succession, the result is again self-coincidence. This is what is meant by: products of symmetry operations are symmetry operations. This multiplication is associative. There exists an identical operation which brings any figure back to its original position. If an operation transforms a figure F into F', the operation required to transform F' back into F is called its inverse operation. All the powers of a given symmetry operation constitute a symmetry element. There are two kinds of symmetry elements, corresponding to the two kinds of symmetry operations.

Let $\omega = 360° - n$ be the smallest angle through which a given

FIG. 19.—HEXAGONAL PRISM m AND PINACOID c

crystal can be rotated about a straight line to be brought to self-coincidence. All the powers of this rotation (that is to say the rotations through ω, 2ω, $\ldots$ etc.) form a symmetry element called a rotation axis of symmetry. (The straight line about which the rotation takes place is also termed rotation axis.)

Consider now a rotatory inversion. Again, let $\omega = 360° - n$ be the smallest angle through which the crystal is rotated in the course of a rotatory inversion that brings it to self-coincidence. All the powers of this rotatory inversion form a symmetry element called an inversion axis of symmetry. (The straight line about which the rotation takes place, combined with the point on that line through which the inversion is effected, is also termed inversion axis.)

In the international symmetry notation a rotation axis is represented by its period[1] n, and an inversion axis by its period surmounted by a bar $\bar{n}$ (pronounced "minus n," "inversion n" or "n bar"). For short, it is convenient to speak of an n-axis for a rotation axis and a $\bar{n}$-axis for an inversion axis. An inversion axis with an even period will be represented by $2n$.

It is proved, as a consequence of the law of rationality, that the only rotation axes possible in crystals are 1, 2, 3, 4, 6, and that the only inversion axes possible in crystals are 1, 2, 3, 4, 6.

FIG. 20.—TRIGONAL DIPYRAMID

By means of stereographic projections (projecting a general face and all its equivalent faces, created by the symmetry element), it is easy to show that a 1-axis is equivalent to a centre, that a 2-axis is equivalent to a mirror (m) perpendicular to the axis, that a 3-axis is equivalent to the combination of a 3-axis and a centre, that a 4-axis is irreducible, that a 6-axis could be replaced by a 3-axis and a mirror perpendicular to it ($6 = 3/m$). The independent symmetry elements are thus: the rotation axes, the centre, the mirror and the 4-axis. For convenience, the 6-axis is usually considered a distinct element.

Theorems on Symmetry.—
Definition—A singular axis is an axis parallel to a singular direction.

Theorem I: No mirror can be oblique to a singular axis, and the only kind of axis compatible with a singular axis is a 2-axis perpendicular to it.

Theorem II: Of the following three elements of symmetry, an evenfold rotation axis, a mirror perpendicular to it, and the centre at their intersection, no two can exist without the third.

FIG. 21.—RHOMBIC DIPYRAMIDS

Corollary: A rotation axis with an odd period cannot combine with both a mirror perpendicular to it and the centre. (Otherwise it would have an even period.)

Theorem III: A crystal that possesses an n-axis and one 2-axis perpendicular to it possesses in all n such 2-axes, intersecting at equal angles ($180°/n$), homopolar and of two different kinds if n is even, polar and of the same kind if n is odd.

Theorem IV: A crystal that possesses an n-axis and one mirror containing it possesses in all n such mirrors, intersecting in the n-axis at equal angles ($180°/n$), homopolar and of two different kinds if n is even, polar and of the same kind if n is odd.

Theorem V: A crystal that possesses a $2n$-axis and either one 2-axis perpendicular to it, or a mirror containing it, possesses in all n such 2-axes of the same kind and n such mirrors of the same kind. The mirrors bisect the angles between the 2-axes if n is even; they contain the 2-axes if n is odd. The mirrors and the 2-axes are homopolar or polar, according as n is even or odd.
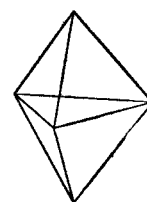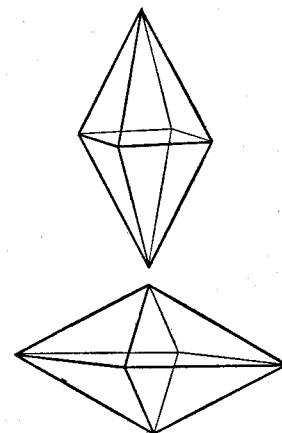
[1]Strictly speaking the period is $360°/n$.

Theorem VI: If a crystal possesses an n-axis, n 2-axes perpendicular to it and one mirror containing it, bisecting the angle between the 2-axes if n is even, containing a 2-axis if n is odd, then the crystal possesses n such mirrors in all and the n-axis is included in a $2n$-axis.

Theorem VII: A $2n$-axis is incompatible with either a mirror perpendicular to it, or the centre.

A 4-axis leads to the group $4/m$ in both cases. A 6-axis and the centre would lead to $6/m$. The inversion axis would become a rotation axis. Adding a mirror perpendicular to a 6-axis has no meaning, since 6 already includes such a mirror $(6 = 3/m)$.

FIG. 22 AND 23.—TETRAGONAL DIPYRAMIDS, OBTUSE AND ACUTE

Corollary: The only way in which a $2n$-axis can combine is with n lateral 2-axes perpendicular to it and n mirrors containing it.

Theorem VIII: In the absence of any singular axis, the only two combinations of rotation axes possible in crystals are: the axes of the octahedron (three 4-axes, four 3-axes, six 2-axes) and those of the tetrahedron (three 2-axes, four 3-axes).

(Proofs are omitted for lack of space.)

Possible Point Groups.—The problem is to combine, in all compatible manners, the following symmetry elements: axes (rotation axes: $1, 2, 4, 3, 6$; inversion axes: $\bar{4}, \bar{6}$), centre $(\bar{1})$ and mirror (m).

The method of derivation consists in establishing first all the axes and possible combinations of axes, then in combining them with the centre and mirrors. It is based on the dichotomous principle.

Either there is a singular axis, or there is no singular axis.

I. A Singular Axis.—It is either a rotation axis n, or an inversion axis $2n$.

A. The singular axis is a rotation axis n. It is either uncombined or combined.

    1. Rotation axis uncombined.   Groups: $1, 2, 4, 3, 6$.

    2. Rotation axis combined. Either there is no other axis, or there is at least another axis.

        a. No other axis. Two possibilities:

Centre present: The axes 1 and 3 become $\bar{1}$ and $\bar{3}$, respectively; each evenfold axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create another evenfold rotation axis (Th. II).

Groups $\bar{1}, 2/m, 4/m, \bar{3}, 6/m$.

No centre: Only mirrors that contain the singular n-axis are possible, for no mirror can be oblique to it (Th. I), while a mirror perpendicular to it would require the centre, if n is even (Th. II), or transform it into an inversion axis, if $n = 3$ ($3/m$ equivalent to $\bar{6}$). Each n-axis acquires n mirrors containing it, and no other (Th. IV).

Groups: $m, 2mm, 4mm, 3m, 6mm$.

FIG. 24.—HEXAGONAL DIPYRAMID

        b. At least another axis. It must be a 2-axis perpendicular to the singular axis (Th. I). Each n-axis acquires n lateral 2-axes, and no other (Th. III). Two possibilities:

No centre: In this case, there can be no mirror. For a mirror could only contain the singular n-axis. It would have to contain a lateral 2-axis, or to bisect the angle between two lateral 2-axes; otherwise it would, by reflection, create additional 2-axes. If n is even, a mirror containing a lateral 2-axis would be perpendicular to another 2-axis, thus demanding the centre (Th. II), while a mirror bisecting two successive lateral 2-axes would require them to be alike, whereas they are of different kinds (Th. III). If $n = 3$, a mirror containing a 2-axis would transform 3 into 6, while a mirror bisecting two successive 2-axes would be perpendicular to another 2-axis and create the centre (Th. II).

Groups: $2, 222, 422, 32, 622$.

Centre present: The 3-axis becomes $\bar{3}$; each evenfold axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional evenfold axis (Th. II).

Groups: $2/m, 2/m\ 2/m\ 2/m, 4/m\ 2/m\ 2/m, \bar{3}\ 2/m,$
$6/m\ 2/m\ 2/m$.

B. The singular axis is an inversion axis $2n$. It is either uncombined or combined.

    1. Inversion axis uncombined.   Groups: $\bar{4}$ and $\bar{6}$.

    2. Inversion axis combined.

The only way in which a $2n$-axis can combine is with n lateral 2-axes perpendicular to it, and n mirrors through it (Th. VII).

Groups: $\bar{4}2m$ and $\bar{6}2m$.

II. No Singular Axis.—The axes are either the tetrahedral axes or the octahedral axes (Th. VIII).

    1. Tetrahedral axes: $2\ 3$. It is imperative to consider two cases: either the 2-axes are not included in 4-axes, or they are.

        a. The 2-axes are not included in 4-axes. Two possibilities:

No centre: In this case, there can be no mirror. A mirror that does not contain any of the 2-axes would, by reflection, create additional 2-axes. A mirror that contains one 2-axis must bisect the angle between the other two, which are alike, hence it would transform the first 2-axis into a 4-axis (Th. VI). A mirror containing two 2-axes is perpendicular to the third, hence would demand the centre (Th. II).   Group: $2\ 3$.

Centre present: The 3-axes become $\bar{3}$-axes; each 2-axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional evenfold axis (Th. II).   Group: $2/m\ \bar{3}$.

        b. The 2-axes are included in 4-axes. Only one possibility:

The centre is excluded by the 4-axes (Th. VIII). Two 2-axes (included in 4-axes) are perpendicular to each 4-axis, hence they demand two mirrors alternating (Th. V). There are six mirrors in all, bisecting the 90° angles between the 4 axes. Any other mirror would, by reflection, create additional 4-axes. Group: $\bar{4}\ 3\ m$.

FIG. 25.—DITETRAGONAL DIPYRAMID

    2. Octahedral axes: $4\ 3\ 2$. The 2-axes cannot be included in 4 axes because each 2-axis is perpendicular to a plane containing one 4-axis, one 2-axis, two 3-axes, and a 4-axis cannot be perpendicular to such a combination. Two possibilities:

No centre: In this case, there can be no mirror. A mirror containing none of the 4-axes would, by reflection, create additional 4-axes. A mirror containing one 4-axis must bisect the angle between the other two, which are alike, and thus be perpendicular to a 2-axis, thereby requiring the centre (Th. II). A mirror containing two 4-axes is perpendicular to the third, hence would demand the centre (Th. II).   Group: $4\ 3\ 2$.

Centre present: The 3-axes become $\bar{3}$-axes; each evenfold rotation axis acquires a mirror perpendicular to it (Th. II). No other mirror is possible, for, with the centre, it would create an additional evenfold rotation axis (Th. II).   Group: $4/m\ \bar{3}\ 2/m$.

The results of the derivation are presented in tabular form.

TABLE I.—*Derivation of the 32 Point Groups*

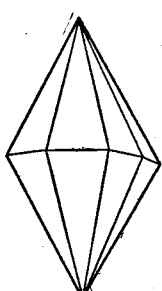| 1	2	4	$\bar{4}$	3	6	$\bar{6}$	$2\ 3$
$\bar{1}$	$\dfrac{2}{m}$		$\dfrac{4}{m}$	$\bar{3}$		$\dfrac{6}{m}$	$\dfrac{2}{m}\bar{3}$
m	$2\,m\,m$		$4\,m\,m$	$3\,m$		$6\,m\,m$	$\bar{4}\ 3\ m$
		$\bar{4}\ 2\ m$			$\bar{6}\ 2\,m$		
2	$2\ 2\ 2$		$4\ 2\ 2$	$3\ 2$		$6\ 2\ 2$	$4\ 3\ 2$
$\dfrac{2}{m}$	$\dfrac{2\ 2\ 2}{m\ m\ m}$		$\dfrac{4\ 2\ 2}{m\ m\ m}$	$\bar{3}\dfrac{2}{m}$		$\dfrac{6\ 2\ 2}{m\ m\ m}$	$\dfrac{4}{m}\bar{3}\dfrac{2}{m}$
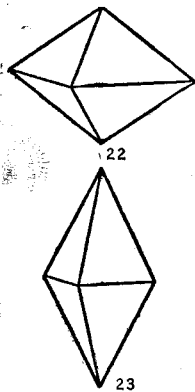
810F CRYSTALLOGRAPHY

Note that two groups have been found twice, namely 2 and $2/m$. The reason for this is that a 1-axis, combined with a 2-axis, is equivalent to a singular 2-axis alone. Notice that, on the first horizontal row, 4 and 6 are placed after 2 and 3, respectively. This arrangement emphasizes the fact that a 2-axis may exist as such or as part of a 4-axis; likewise a 3-axis may be alone or included in a 6-axis.

The symmetry elements of the group $4/m\ 3\ 2/m$ are shown in fig. 12.

CRYSTAL LATTICES, CRYSTAL SYSTEMS AND CRYSTAL FORMS

All the symmetry elements of a lattice (axes, mirrors, centre) can be made to pass through one node. They consti-

FIG. 26.—DIHEXAGONAL DIPYRAMID

tute the point-group symmetry of the lattice. There are seven such lattice symmetries. Some authors base the definition of the crystal systems on the symmetry of the lattice; they recognize seven systems. The rhombohedral lattice $(32/m)$ being isogonal with the hexagonal lattice $(6/m\ 2/m\ 2/m)$, the two can be grouped into a single hexagonal system, so that only six systems are necessary. More than one assemblage of points in space may have the same lattice symmetry; such assemblages are called lattice modes.

A cubic lattice, for example, may belong to either one of three modes: primitive, body-centred or face-centred (fig. 13). There are in all 14 lattices, differing in either symmetry or mode, or both. A crystal which possesses the same symmetry as its lattice is called holohedral (or holosymmetric). A crystal whose symmetry is less than that of its lattice is called merohedral; hemihedral, tetartohedral or ogdohedral, as the number of symmetry operations is $\frac{1}{2}$, $\frac{1}{4}$ or $\frac{1}{8}$ that in the corresponding holohedry.

All the physically similar faces on a crystal constitute a form. A form that completely encloses space is called a closed form; such a form can occur alone. Other forms, called open forms, cannot occur alone. Several forms occurring together on a crystal constitute a combination. In practice the symmetry of a crystal poly-hedron is determined from a study of its forms. Conversely one can predict which

FIG. 27 AND 28.—RHOMBOHEDRA IN TWO DIFFERENT POSITIONS

forms can occur in any point group, similar faces being disposed symmetrically about the various symmetry elements of the group. This is most conveniently done by means of the stereographic projection, as follows: The symmetry elements are plotted on the projection; then a face is plotted in general position (i.e., neither perpendicular to any mirror nor perpendicular to any axis of symmetry); then all the symmetry operations available in the group are applied to the original face and the similar faces are thereby obtained; this form, called the general form, has the largest number of faces a form may have in the group. Other faces, perpendicular to one or more than one symmetry element, are then plotted and the corresponding forms are found in the same manner; such forms are called special forms or limit forms. The number of faces of a special form is a submultiple of the number of faces of the general form, a fact which is easily understood, for a face that is perpendicular to a mirror is reflected into itself and therefore does not give rise to any additional face. Crystallographers also discriminate between invariable forms, which always have the same shape, and variable forms, which may show more than one shape, depending on the inclination of the faces to the co-ordinate axes.

The most satisfactory method of naming forms is based on geometrical principles, the name of a form being independent of the position of its faces with respect to the axes of co-ordinates. There are 47 different forms. A form composed of a single face is called a monohedron (or pedion). Two intersecting faces constitute a

dihedron (or sphenoid, gonioid or dome), whereas two parallel faces are a pinacoid. Similar faces in a zone constitute a prism; prisms are distinguished according to the shape of their cross section as trigonal, rhombic (fig. 14 and 15), tetragonal (fig. 17), hexagonal (fig. 19), ditrigonal, ditetragonal, dihexagonal. A pyramid consists of faces equally inclined on the vertical. A dipyramid is a double-ended form looking like two pyramids end to end, one being the reflection of the other in a mirror. Pyramids and dipyramids (fig. 20, 21, 22, 23, 24, 25 and 26) are distinguished according to their cross section, like the prisms. A rhombohedron (fig. 27 and 28) is a form with six faces which can be obtained by placing two trigonal pyramids end to end and rotating one with respect to the other about the 3-axis through 60°. A rhombo-

FIG. 29.—TETRAGONAL SCALENOHEDRON

hedron looks like a distorted cube; its faces are rhombs instead of squares. Two rhombic pyramids placed end to end, one of them being rotated with respect to the other about the 2-axis through one-half the period (i.e., through 90°), give a form known as a tetragonal scalenohedron (fig. 29); it has eight faces, in the shape of scalene triangles, meeting in four equal lateral edges in zigzag. The hexagonal scalenohedron (fig. 30) is obtained as the tetragonal one, except that it is necessary to start with two ditrigonal pyramids and rotate one through 60° with respect to the other; this form has six equal lateral edges. A disphenoid look like two sphenoids end to end; if one of them is rotated with respect to the other, about the 2-axis, through half the period (i.e., through 90°), the form is called tetragonal disphenoid (fig. 31), from the shape of its cross section; if one of the original sphenoids is turned with respect to the other, about the 2-axis, through an angle different from 90° so that the cross section becomes a rhomb, the form is called rhombic disphenoid (fig. 32). A trapezohedron is obtained by placing two pyramids end to end, and rotating one of them with respect to the other, about the axis, through an angle different from one-half the period. Trapezohedra are distinguished as trigonal (fig. 33), tetragonal and hexagonal, according to the kind of pyramid that is used as a starting point. A trigonal trapezohedron has six faces meeting in six lateral edges in zigzag, three long ones and three short ones.

The hexahedron (or cube), the octahedron and the tetrahedron (fig. 34 and 38) are three of the regular solids of geometry. The octahedron may be conceived as being obtained from the cube by truncating the eight corners (fig. 35 and 36). The cube would likewise be obtained by truncating the corners of the octahedron (fig. 37), or by truncating the edges of the tetrahedron (fig. 39). The rhomb-dodecahedron (fig. 40), which has 12 rhombic faces, is obtained from the cube or the octahedron by truncation of the edges (fig. 6 and 41). Replacing the faces of a hexahedron by low tetragonal pyramids gives a tetrahexahedron (fig. 42), in which the edges of a cube are still visible. Replacing the faces of a hexahedron by low dihedra gives a dihexahedron (or pentagon-dodecahedron or pyritohedron) (fig. 43), in which the edges of the cube are no longer visible. Replacing the faces of a dihexahedron by low dihedra

FIG. 30.—HEXAGONAL SCALENOHEDRON

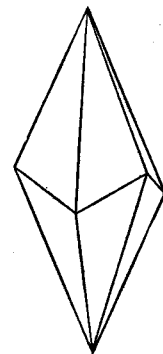gives a didodecahedron (or diploid) (fig. 44). Replacing the faces of an octahedron by low trigonal pyramids gives a form with 24 faces; according to the number of sides in each face, the form is called trigon-trioctahedron (or trisoctahedron) (fig. 45 and 46), tetragon-trioctahedron (or trapezohedron) (fig. 47 and 48), pentagon-trioctahedron (or gyroid) (fig. 49); the edges of the original octahedron are still visible in the trigon-trioctahedron. Likewise, it is possible to visualize the following forms obtained by modifications of the tetrahedron: trigon-tritetrahedron (or tristetrahedron) (fig. 50), tetragon-tritetrahedron (or deltohedron) (fig. 51), pentagon-tritetrahedron (or tetartoid) (fig. 52); the edges of the
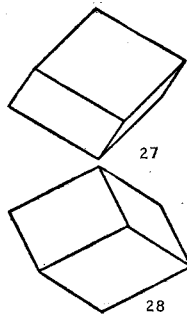
CRYSTALLOGRAPHY

original tetrahedron are visible only in the trigon-tritetrahedron. Replacing by low ditrigonal pyramids the faces of an octahedron or a tetrahedron gives rise to a hexaoctahedron (fig. 53 and 54) or to a hexatetrahedron (fig. 55).

Triclinic System.—The triclinic lattice has only one mode, primitive. The cell is a doubly oblique parallelepiped built on three conjugate rows. It may be advantageous in certain cases to use a multiple cell, but it is never imperative to do so. The conventional cell according to Charles E. Delaunay is built on the shortest three lattice translations that enable all three angles to be nonacute (they are not necessarily the shortest three noncoplanar translations); the cell edges should be named c, a, b, in order of increasing lengths. The axial cross should be right-handed.
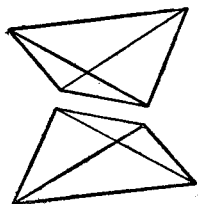
FIG. 31.—TETRAGONAL DISPHENOIDS

Point Group 1.—Holohedry. There is only a centre of symmetry. All forms are pinacoids. Paul Groth's *Chemische Krystallographie* lists 706 substances in this point group, 220 of which are inorganic and 486 organic.

Monoclinic System.—The 2-axis of the lattice is usually taken as the b-axis. The shortest two translations in the net perpendicular to the b-axis are taken as c and a, with c smaller than a. The angle β is taken obtuse; the other two interaxial angles are right angles (fig. 56). The cell may be primitive (P) or base-centred (C), which means that there is an additional node in the centre of the c face in every cell of the lattice. In order to comply with the convention $c < a$, it may be necessary to centre another face (A) or to centre the cell itself (I); in each case, the centring should be explicitly stated.

Point Group 2/m.—Holohedry. The general form $\{hkl\}$ is a rhombic prism. The only limit forms are the $\{h0l\}$ pinacoids and the $\{010\}$ pinacoid. Groth lists 2,786 examples, 287 inorganic and 2,499 organic. Example: augite (fig. 57).

Point Group 2.—Axial hemihedry. The general forms $\{hkl\}$ are dihedra. The $\{h0l\}$ forms are pinacoids; $\{010\}$ and $\{0\bar{1}0\}$ are monohedra. Groth lists 332 examples, 15 inorganic and 317 organic. Fig. 58 shows two crystals of tartaric acid.
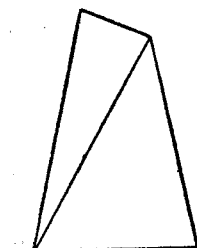
FIG. 32.—RHOMBIC DI-SPHENOID

Point Group m.—Antihemihedry. The general forms $\{hkl\}$ are dihedra. The $\{h0l\}$ forms are monohedra. There is one pinacoid, $\{010\}$. Groth lists 21 examples, 8 inorganic and 13 organic.

Orthorhombic System.—The cell is a rectangular parallelepiped. The three symmetry directions are chosen as axial directions; a symmetry direction, being either a symmetry axis or the perpendicular to a mirror or both, is always a row line in the lattice. The axes are called c, a, b in the order of increasing lattice translations. The three interaxial angles are equal to 90°. The lattice mode is either primitive (P), one-face-centred $(A, B$ or $C)$, body-centred (I) or all-face-centred (F).

FIG. 33.—TRIGONAL TRAPEZOHEDRON

Point Group 2/m 2/m 2/m.—Holohedry. The general form $\{hkl\}$ is a rhombic dipyramid (fig. 21). When one of the Miller indices is equal to zero the form is a rhombic prisms (figs. 14 and 15): $\{0kl\}$, $\{h0l\}$, $\{hk0\}$. There are three pinacoids: $\{100\}$, $\{010\}$, $\{001\}$. Groth lists 915 examples, 419 inorganic and 496 organic.

Point Group 2 2 2.—Holoaxial hemihedry. The general form $\{hkl\}$ is a rhombic disphenoid (fig. 32). The other forms are the same as in the point group $2/m\ 2/m\ 2/m$. Groth lists 429 examples, 15 inorganic and 414 organic.

Point Group 2 m m (or m 2 m or m m 2).—Antihemihedry.

The 2-axis which lies at the intersection of the two mirrors may be the a-axis ($2\ m\ m$), the b-axis ($m\ 2\ m$) or the c-axis ($m\ m\ 2$), as a consequence of the conventional rule $c < a < b$. In the setting $2\ m\ m$, $\{hkl\}$ and $\{h\bar{k}l\}$ are rhombic pyramids; $\{h0l\}$ and $\{h0\bar{l}\}$, $\{hk0\}$ and $\{h\bar{k}0\}$ are dihedra; $\{\bar{1}00\}$ and $\{100\}$ are monohedra. In the setting $m\ 2\ m$, $\{hkl\}$ and $\{hk\bar{l}\}$ are rhombic pyramids; $\{0kl\}$ and $\{0k\bar{l}\}$, $\{hk0\}$ and $\{\bar{h}k0\}$ are dihedra; $\{0\bar{1}0\}$ and $\{010\}$ are monohedra. In the setting $m\ m\ 2$, $\{hkl\}$ and $\{\bar{h}kl\}$ are rhombic pyramids; $\{0kl\}$ and $\{0\bar{k}l\}$, $\{h0l\}$ and $\{\bar{h}0l\}$ are dihedra; $\{00\bar{1}\}$ and $\{001\}$ are monohedra. All other forms are the same as in $2/m\ 2/m\ 2/m$. Groth lists 57 examples, 20 inorganic and 37 organic. Hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) is shown in fig. 60 in setting $m\ m\ 2$.
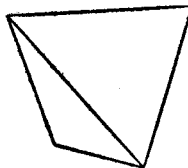
FIG. 34.—TETRAHEDRON

Tetragonal System.—The smallest cell is used. The 4-axis of the lattice is taken as c, the edges of the cell are a_1 and a_2 ($a_1 = a_2$). The three interaxial angles are equal to 90°. The lattice mode may be primitive (P) or body-centred (I).

Point Group 4/m 2/m 2/m.—Holohedry. The forms are as follows ($h < k$):

$\{hkl\}$ ditetragonal dipyramid (fig. 25);
$\{hk0\}$ ditetragonal prism;
$\{0kl\}$ tetragonal dipyramid (fig. 60 and 61);
$\{hhl\}$ tetragonal dipyramid (fig. 60 and 61);
$\{001\}$ pinacoid (fig. 17);
$\{010\}$ tetragonal prism (fig. 18);
$\{110\}$ tetragonal prism (fig. 17).

Groth lists 53 examples, 48 inorganic and 5 organic.

Point Group 4 2 2.—Holoaxial hemihedry. The general form $\{hkl\}$ is a tetragonal trapezohedron. The other forms are the same as in $4/m\ 2/m\ 2/m$. Groth lists 20 examples, 1 inorganic and 19 organic.

Point Group 4 m m.—Polar antihemihedry. The forms different from those in $4/m\ 2/m\ 2/m$ are: $\{hkl\}$, ditetragonal pyramid; $\{0kl\}$, tetragonal pyramid; $\{hhl\}$, tetragonal pyramid; $\{001\}$, monohedron. Groth gives three examples, all of them organic.

35

Point Group 4 2 m (or 4 m 2).—Homopolar antihemihedry. The only forms that are different from the holohedral forms are: $\{hkl\}$, tetragonal scalenohedron; $\{0kl\}$ (in setting $4\ m\ 2$) and $\{hhl\}$ (in setting $4\ 2\ m$), tetragonal disphenoids. Groth lists 19 examples, 18 inorganic and 1 organic. Chalcopyrite ($CuFeS_2$), shown in fig. 62, is a combination of two tetragonal disphenoids (P and P′), two tetragonal dipyramids (b and c) and the pinacoid (a).

36

FIG. 35.—CUBE TRUNCATED BY OCTAHEDRON
FIG. 36.—CUBO-OCTA-HEDRON

Point Group 4/m.—Parahemihedry. The general form $\{hkl\}$ is a tetragonal dipyramid, $\{hk0\}$ is a tetragonal prism. All other forms are the same as in $4/m\ 2/m\ 2/m$. Groth lists 18 examples, 10 inorganic and 8 organic. Example: fergusonite (fig. 63).

Point Group 4.—Polar tetartohedry. $\{hkl\}$ is a tetragonal pyramid; $\{hk0\}$, a tetragonal prism (as in $4/m$); $\{010\}$ and $\{110\}$, tetragonal prisms (as in $4/m\ 2/m\ 2/m$). The other forms are the same as in $4\ m\ m$. Groth gives four examples, three inorganic and one organic.

Point Group 4.—Homopolar tetartohedry. $\{hkl\}$ is a tetragonal disphenoid; $\{hk0\}$, a tetragonal prism (as in $4/m$); $\{0kl\}$ and $\{hhl\}$, tetragonal disphenoids. The other forms are the same as in $4/m\ 2/m\ 2/m$. Groth gives one inorganic example.

810H   CRYSTALLOGRAPHY

Hexagonal System.—The smallest cell of the primitive hexagonal lattice is a 120° rhombic prism. The 6-axis is placed vertically as the c-axis. The horizontal edges of the cell are a_1 and a_2 ($a_1 = a_2$), enclosing angle $\gamma = 120°$. The other angles are equal to 90°. A superabundant axis of co-ordinate, a_3, bisects the angle between a_1 and a_2. The Miller indices referred to such a set of axes are four in number; they are written, for instance, {hkil}, where the first three refer to the horizontal axes a_1, a_2, a_3 and the last one to the vertical axis c. From the construction of the horizontal axes it follows that the sum of the first three indices is zero, $h + k + i = 0$ or $i = -(h + k)$.

FIG. 37.—OCTAHEDRON TRUNCATED BY CUBE

The primitive (hexagonal) lattice mode is the only one possible in the seven point groups whose symmetry symbols begin with 6 or 6̄; it is also possible in the five trigonal point groups (those whose symmetry symbols begin with 3 or 3̄), where the rhombohedral lattice mode is another possibility.

The rhombohedral mode may be obtained by adding two nodes per cell, at points 1/3 2/3 2/3 and 2/3 1/3 1/3. The above Bravais axes of co-ordinates can still be used. Some authors prefer the Miller axes, a'_1, a'_2, a'_3, which are the three lower edges of a rhombohedral primitive cell. (They should never be used, however, if the lattice mode is not rhombohedral.) They are inclined to one another at equal oblique angles; they are equally inclined to the vertical axis; they are of equal length ($a'_1 = a'_2 = a'_3$). The interaxial angle is designated by α; it is the only axial element. The face symbols on fig. 64 are referred to Miller axes.

Point Group 6/m 2/m 2/m.—Holohedry. The list of forms follows ($h > k$):

{hkil}	dihexagonal dipyramid (fig. 26);
{hki0}	dihexagonal prism;
{hohl}	hexagonal dipyramid (fig. 24);
{h.h.2h.l}	hexagonal dipyramid;
{0001}	pinacoid;
{10ī0}	hexagonal prism;
{11̄20}	hexagonal prism.

Groth lists 14 examples, all inorganic.

38

Point Group 6 2 2.—Holoaxial hemihedry. The form {hkil} is a hexagonal trapezohedron. All other forms are the same as in 6/m 2/m 2/m. Groth gives six organic substances.

Point Group 6 m m.—Polar antihemihedry. The following forms differ from the holohedral: {hkil}, dihexagonal pyramid; {hohl} and {h.h.2h.l}, hexagonal pyramids; {0001}, monohedron. Groth gives six inorganic substances.

Point Group 6̄ 2 m (or 6̄ m 2).—Crystals of this homopolar antihemihedry may be referred to two settings, according as the 2-axes or the normals to the mirrors are parallel to the axes of co-ordinates (i.e., the horizontal edges of the smallest cell). The forms different from holohedral forms are as follows. In the

39

FIG. 38.—COMBINATION OF TWO TETRAHEDRA
FIG. 39.—TETRAHEDRON TRUNCATED BY CUBE

seting 6̄ 2 m : {hkil}, ditrigonal dipyramid; {hki0}, ditrigonal prism; {h.h.2h.l}, trigonal dipyramid; {11̄20}, trigonal prism. In the setting 6̄ m 2 : hkil , ditrigonal dipyramid; {hki0}, ditrigonal prism; {hohl}, trigonal dipyramid; {10ī0}, trigonal prism. Groth gives only one example, inorganic.

Point Group 6/m.—Only two forms of this hexagyre parahemihedry are different from the holohedral: {hkil} is a hexago-

nal dipyramid and {hki0} is a hexagonal prism. Groth gives seven substances, all inorganic.

Point Group 6.—Polar hexagyre antitetartohedry. The general form {hkil} is a hexagonal pyramid; {hki0} is a hexagonal prism (as in 6/m); {hohl} and {h.h.2h.l} are hexagonal pyramids and {0001} is a monohedron (as in 6 m m); other forms are the same as in the holohedry. Groth lists 11 examples, 6 of which are inorganic.

Point Group 6̄.—Homopolar antitetartohedry. The general form {hkil} is a trigonal dipyramid (fig. 20); {hki0} is a trigonal prism; {hohl} and {10ī0} are the same as in 6̄ m 2; {h.h.2h.l} and {11̄20} are the same as in 6̄ 2 m; {0001} is the same as in 6/m 2/m 2/m. Groth gives no example of this group.

Point Group 3̄ 2/m 1 (or 3̄ 1 2/m).—Trigyre parahemihedry of the hexagonal lattice. Holohedry of the rhombohedral lattice. The forms different from those in the hexagonal holohedry are: {hkil}, hexagonal scalenohedron (in both settings); {hohl}, rhombohedron (in setting 3̄ 2/m 1); {h.h.2h.l}, rhombohedron (in setting 3̄ 1 2/m). The first setting is always used in the rhombohedral holohedry, where the forms are the same as above. Some forms are complementary in the hexagonal trigyre parahemihedry; e.g., the positive and negative hexagonal scalenohedra, {hkil} and {khil}, but they are distinct forms in the rhombohedral holohedry. The same is true for positive and negative rhombohedra, {hohl} and {ohhl}. Groth lists 58 examples, 50 inorganic and 8 organic.

40

41

FIG. 40.—RHOMB-DODE-CAHEDRON
FIG. 41.—OCTAHEDRON TRUNCATED BY RHOMB-DODECAHEDRON

Point Group 3 2 1 (or 3 1 2).—Holoaxial tetartohedry of the hexagonal lattice. Holoaxial hemihedry of the rhombohedral lattice. The general form is a trigonal trapezohedron (in both settings). The other forms are the same as in 6/m 2/m 2/m, except as follows. In setting 3 2 1: {hki0}, {h.h.2h.l}, {11̄20} as in 6̄ 2 m; {hohl} as in 3̄ 2/m 1. In setting 3 1 2: {hki0}, {hohl}, {10ī0} as in 6̄ m 2; {h.h.2h.l} as in 3̄ 1 2/m. Groth lists 18 examples, 7 inorganic and 11 organic.

FIG. 42.—CUBE MODIFIED BY TETRAHEXAHEDRON

Point Group 3 m 1 (or 3 1 m).—Polar trigyre antitetartohedry of the hexagonal lattice. Antihemihedry of the rhombohedral lattice. The general form is a ditrigonal pyramid (in both settings); {hohl} in setting 3 m 1 and {h.h.2h.l} in setting 3 1 m are trigonal pyramids. The other forms are the same as in other groups, as follows. In setting 3 m 1 : {hki0} and {10ī0} as in 6 m 2; {h.h.2h.l} and {0001} as in 6 m m; {11̄20} as in 6/m 2/m 2/m. In setting 3 1 m; {hki0} and {11̄20} as in 6̄ 2 m; {hohl} and {0001} as in 6 m m; {10ī0} as in 6/m 2/m 2/m. Groth lists 14 examples, 13 inorganic and 1 organic. Example: tourmaline (fig. 65).

Point Group 3̄.—Paratetartohedry of the hexagonal lattice. Parahemihedry of the rhombohedral lattice. The general form is a rhombohedron. The other forms are the same as in 6/m 2/m 2/m, except as follows: {hki0}, as in 6/m; {hohl}, as in 3̄ 2/m 1; {h.h.2h.l}, as in 3̄ 1 2/m. Groth gives four examples, one inorganic and three organic. Example: dioptase (fig. 66).

Point Group 3.—Ogdohedry of the hexagonal lattice. Tetartohedry of the rhombohedral lattice. The general form is a trigonal pyramid. The other forms are the same as in other groups, as follows: {hki0}, as in 6; {hohl}, {0001}, {10ī0}, as in 3 m 1; {h.h.2h.l}, {0001}, {11̄20}, as in 3 1 m. Groth gives two examples, one inorganic and one organic.
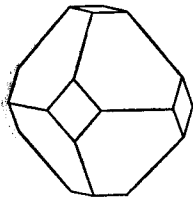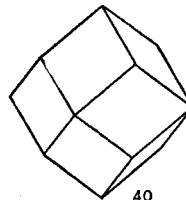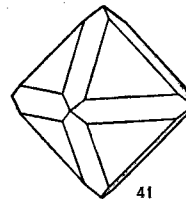
CRYSTALLOGRAPHY

Isometric (or Cubic) System.—The unit cell is a cube. The edges of the cube are fixed by symmetry; they are parallel to the 4-axes of the lattice. Three lattice modes are possible: primitive (P), body-centred (I) and face-centred (F). No axial elements can be given for an isometric crystal; all crystals in this system have the same interfacial angles.

Point Group $4/m\ 3\ 2/m$.—Holohedry. The forms are as follows

($h<k<l$): $\{hkl\}$, hexaoctahedron; $\{okl\}$, tetrahexahedron; $\{hhl\}$, tetragon-triocta-hedron; $\{hkk\}$, trigon-trioctahedron; $\{111\}$, octahedron; $\{011\}$, rhomb-dodecahedron; $\{001\}$, hexahedron (or cube). Groth lists 19 examples, all of them inorganic.
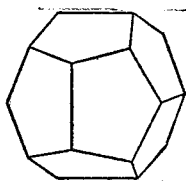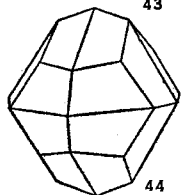
Point Group $4\ 3\ 2$.—Holoaxial hemihedry. The general form $\{hkl\}$ is a pentagon-trioctahedron; the other forms are the same as in $4/m\ 3\ 2/m$. Groth lists 12 examples, all of them inorganic.

Point Group $4\ 3\ m$.—Antihemihedry. The following forms differ from the corresponding forms in $4/m\ 3\ 2/m$: $\{hkl\}$, hexa-tetrahedron; $\{hhl\}$, trigon-tritetrahedron; $\{hkk\}$, tetragon-tri-tetrahedron; $\{111\}$, tetrahedron. Groth gives seven examples, six of which are inorganic.

Point Group $2/m\ 3$.—Parahemihedry. The general form $\{hkl\}$ is a didodecahedron and $\{okl\}$ is a dihexahedron. All other forms are the same as in $4/m\ 3\ 2/m$. Groth gives nine examples, eight of which are inorganic.

Point Group $2\ 3$.—Tetartohedry. The general form $\{hkl\}$ is a pentagon-tritetrahedron; $\{okl\}$ is the same as in $2/\ m\ 3$; $\{hhl\}$, $\{hkk\}$ and $\{111\}$ are the same as in $4\ 3\ m$; $\{011\}$ and $\{001\}$ are the same as in $4/m\ 3\ 2/m$. Groth lists eight examples, seven of which are inorganic.

INTERNAL SYMMETRY

In the crystal structure the cell is repeated by the translations of the lattice or translation group. Matter inside a cell, however, is arranged in a symmetrical manner, the symmetry operations include translation combined with either a rotation (screw rotation) or a reflection (glide reflection). Two new symmetry elements thus appear in the study of the internal symmetry of crystals, the screw axis (fig. 67) and the glide plane (fig. 68). By combining all the symmetry operations in all possible ways, the 230 space groups are found. By considering screw rotations only (and not glide reflections), only 65 of these groups are found (L. Sohncke, 1879).
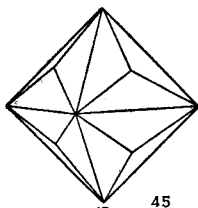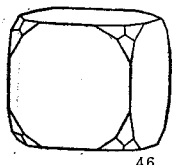
Generalization of the Law of Bravais.—The law of Bravais is based on the lattice only. It has been generalized (J. D. H. Donnay and D. Harker, 1937) by taking the space group into account; *i.e.*, by considering the effect which screw axes and glide planes have on interplanar distances. A series of nets parallel to the face (hkl) may become interleaved by additional planes, generated by space-group operations, so that the interplanar distance is divided by $n(n=2,3,4,6)$. This is written $d(nh.nk.nl)=(1/n).d(hkl)$, where multiple indices are used to designate the face so affected by the space-group symmetry. The predicted importance of such a face, therefore, decreases. The generalized law agrees with the observed facts better than the classical law of Bravais, although the agreement is not in all cases perfect. Some anomalies persist. In simple ionic crystals, such as sodium chloride, differently charged ions may have the same morphological effect; the space group of ionic sites then controls the form development.

The space group (or possible space groups), in most cases, can

be determined from morphological data, as was shown by Donnay and his coworkers. The study of the relative importance of the faces in a zone forms the basis for such a determination. G. Jungham (1874), H. Baumhauer (1903–05), P. Niggli (1919), H. Ungemach (1923–35) and M. A. Peacock (Harmonic-Arithmetic rule, 1936) have contributed to this question.

TWINNING

A twin is an assemblage of two (or more) crystals grown together in a single crystalline edifice and in such relative orientations

that one crystal is symmetrical of the other(s). Obviously the twin operation, which brings one crystal into coincidence with the other, cannot be a symmetry operation of the crystal. Common sense and good angular measurements must be used to distinguish a twin from a haphazard intergrowth of crystals.
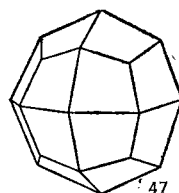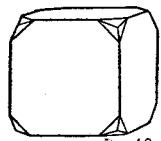
Gliding (Mechanical Twinning) in Calcite.—Baumhauer's experiment (fig. 69) shows that the twinned position is nothing more than a second position of equilibrium of crystalline matter; the latter may almost indifferently adopt either the parallel position or the twinned position (during growth or, after a single crystal has been grown, under mechanical stress). The conclusion is that the formation of a twin is not controlled by any law essentially different from those that govern the growth of a single crystal.

Haüy's Fundamental Observation (1801).—Haüy studied staurolite twins and observed that any face of one of the twinned individual I was parallel to a face (or a possible face) of the other individual II. This was true within the limits of error of his contact goniometer; viz., a few degrees. In reticular parlance, any face of I is a net in the lattice of II, or again, there is one lattice (the twin lattice) pervading the whole edifice, and the faces of I and II are nets of this lattice. The prolongation of this lattice from crystal I to crystal II may be exact or it may suffer a slight deviation at the contact between I and II (since the observation was made by means of a contact goniometer). The twin lattice must be either the crystal lattice or a multiple thereof. The prolongation of the twin lattice from I into II is the condition of stability of the twin.

If the twin lattice is a multiple of the crystal lattice, not all the nodes of the crystal lattice will be restored by twinning; only a certain number of them will be. Call these the S nodes. The lattice of the S nodes is the twin lattice. The number of S nodes cannot be too small a fraction of the total number of nodes in the crystal lattice; hence the twin lattice should be a small multiple of the crystal lattice. This prediction is substantiated by observation.

Types of Twinning.—From the above, it follows that there are four possible types of twinning:

1. Twinning by merohedry: The crystal lattice has (rigorously) elements of symmetry that the crystal does not have. (They are called the additional symmetry elements of the lattice.) This is the case in merohedral crystals.

2. Twinning by pseudomerohedry: The crystal lattice has elements of pseydosymmetry that the motif cannot have as elements of symmetry and does not ordinarily

have as elements of pseudosymmetry. By analogy with (1), such a crystal is called pseudomerohedral.

3. Twinning by reticular merohedry: A small multiple lattice of the crystal has (rigorously) elements of symmetry that the crystal lattice (and a fortiori the motif) cannot have as symmetry elements. These are additional symmetry elements of a multiple lattice; the simple lattice is merohedral with respect to the multiple
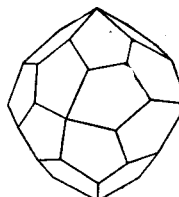
CRYSTALLOGRAPHY

810J

lattice as, in (1), the motif was merohedral with respect to the simple lattice; hence the name.

4. Twinning by reticular pseudomerohedry: A small multiple lattice of the crystal has elements of pseudosymmetry that neither the crystal lattice nor the motif can have as elements of symmetry or pseudosymmetry.

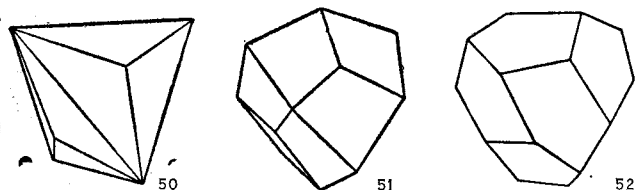The twin operation, which defines the twin law, is performed

FIG. 50.—TRIGON-TRITETRAHEDRON. FIG. 51.—TETRAGON-TRITETRAHEDRON
FIG. 52.—PENTAGON-TRITETRAHEDRON

about a twin element. The latter is one of the additional elements of symmetry (or pseudosymmetry) that the lattice has in addition to those of the crystal or that a small multiple lattice has in addition to those of the crystal lattice.

Twinning by Merohedry (A. Bravais).—In cases of hemihedry there are two possible orientations of the motif inside the cell; in cases of tetartohedry, there are four; in the cases of ogdohedry, eight. Hence the number of possible twinned individuals in each case.

The twin element may be any one of the additional symmetry elements of the lattice: either an axis, a plane or a centre. All these elements are reticular elements (row, net, node). The symmetry of the twin is the combination of the crystal symmetry plus the twin elements. (All the additional symmetry elements are simultaneously twin elements.)

The twined individuals are united by a surface (composition surface), usually irregular, which may be, but need not be, a plane. Indeed the condition of stability of the twin is rigorously satisfied at any point within the crystal, for the prolongation of the twin lattice from I to II is perfect everywhere.

As to the external appearance, two cases may occur: (1) Each twinned crystal shows merohedral crystal forms (i.e., forms that are not the same as in the holohedry). In this case the n twinned orientations show merohedral forms that, by their relative positions, simulate complementary forms. Often each twinned crystal retains its individuality and the twin looks like an interpenetration of two euhedral crystals. Hence the name penetration twins; e.g., pyrite iron-cross and staurolite. (2) The twinned crystals do not show merohedral forms but only forms that are the same in both the holohedry and the merohedry under consideration; e.g., pyrite, showing only the cube. The appearance is that of a single crystal, from the geometrical standpoint only. The physical

FIG. 53.—HEXAOCTAHED-RON
FIG. 54.—CUBE MODI-FIED BY HEXAOCTAHED-RON

appearance of the faces may show the merohedry (striations in pyrite). This imitation of a single crystal by a twin is called mimetism. Other types of twins show it. As to size, the twinned portions may be either a few large individuals or a great many tiny domains. In the latter case the twin simulates a holohedral crystal. For instance in low-temperature quartz a complex twin of many small crystals (some right-handed, the others left-handed), looks like a holohedral crystal devoid of rotatory power, called neutral quartz. This is a case of pseudoparamorphism.

Examples.—Tetrahedrite, chalcopyrite, hemimorphite and topaz.

Twinning by Pseudomerohedry (E. Mallard).—The pseudomerohedral crystal having a certain symmetry, either holohedral or merohedral, its lattice has in addition certain elements of pseudosymmetry (or quasi symmetry). The lattice thus has several orientations that are no longer identical, as in twinning by

merohedry, but are only approximately the same. These orientations are symmetrical with respect to the additional elements of pseudosymmetry. Such orientations, it is observed, can be associated in twins. The additional elements of pseudosymmetry are the twin elements. The prolongation of the lattice from one orientation to the next is no longer rigorous but only approximate. There is a slight change in the orientation of the lattice as it passes from I to II. This shows a certain tolerance in the principle of stability of the twin (prolongation of the lattice from I to II); this tolerance is of the order of a few degrees.

An element of pseudosymmetry is not and cannot be exactly defined in direction. Any plane that is almost parallel to a plane of pseudosymmetry is also a plane of pseudosymmetry. The same is true for the axes of pseudosymmetry; all the lines contained in a cone of small aperture are axes of pseudosymmetry if one of them is. How is it possible then to speak of twinning with respect to such ill-defined elements? Mallard gave the answer to this query.

FIG. 55.—HEXATETRA-HEDRON

Every symmetry axis of a lattice is a simple row of the lattice, and every symmetry plane of a lattice is a simple net of the lattice. Hence an axis of pseudosymmetry must always be close to a row, which is also an axis of pseudosymmetry. Likewise a plane of pseudosymmetry must always be close to a net, which is also a plane of pseudosymmetry. It has been observed, in the case of twinning by pseudomerohedry, that the twinned crystals are symmetrical of each other with respect to either the row that is an axis of pseudosymmetry, or the net that is a plane of pseudosymmetry. These reticular elements of pseudosymmetry are the twin elements. This observation has been called (by G. Friedel) the law of Mallard. The law of Mallard may also be stated as follows: When the lattice of a crystal has reticular elements of pseudosymmetry (net or row), these reticular elements can be twin elements (twin plane or twin axis).

The twin obliquity is the angle between the normal to the twin plane (reticular plane of pseudosymmetry) and the row that is almost normal to it or the angle between the twin axis (reticular axis of pseudosymmetry) and the normal to the net that is almost normal to it. This angle is usually small; it may exceptionally attain $5°$ or $6°$. In albite twinning the twin plane is (010); the obliquity, which varies with composition, is about $3°$ to $4°$. In twinning by merohedry the obliquity is 0.

When there is a twin plane, this plane is a plane of pseudosymmetry of the lattice, which means that the mirror image of the lattice in that plane almost coincides with the lattice itself. The coincidence is perfect for all the nodes located in the twin plane, since these nodes belong to both twinned orientations. The farther away from the twin plane, the greater the deviation between the original lattice and the reflected lattice will be. If the prolongation of a lattice from I to II is the condition for the stability of a twin, then the condition is here rigorously satisfied only in the twin plane itself. The growing crystal may change the orientation of its motif, and hence begin to twin off, from all the points situated in the twin plane, the latter will therefore be the composition surface, planar and reticular.

FIG. 56.—MONOCLINIC AXES OF CO-ORDINATES
FIG. 57.—AUGITE CRYS-TAL

When there is a twofold twin axis, the axis is a row and an axis of pseudosymmetry for the lattice. The lattice will nearly coincide with the lattice obtained after a $180°$ rotation about the axis. The coincidence of the original lattice and the rotated lattice is perfect only for the nodes situated on the axis itself. The composition surface must contain the axis. Consider the net quasinormal to the axis and the plane (not reticular) exactly normal
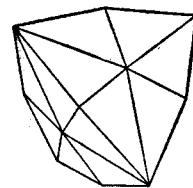
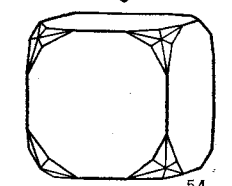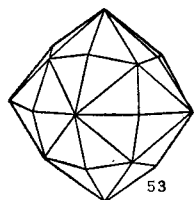to the axis. Let AB be their intersection. It is easy to see that the nodes in their original positions and the nodes after the 180° rotation will be the farther apart the farther one goes away from AB. The condition of stability of the twin is satisfied best therefore in a plane (not reticular) defined by the twin axis and the line AB. This plane will be the composition surface; it has been called the rhombic section.
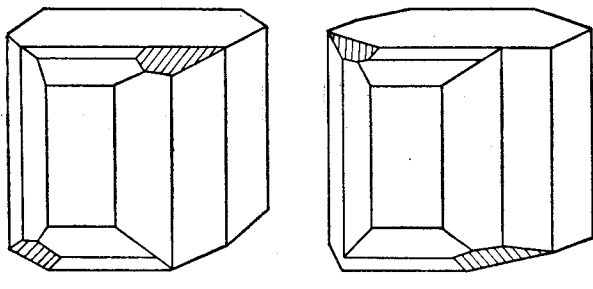
When there is a three-, four- or six-fold twin axis, the compo-

FIG. 58.—RIGHT-HANDED (A) AND LEFT-HANDED (B) FORMS OF CRYSTALS OF TARTARIC ACID

sition surface must contain the axis. Nothing more can be predicted.

All the predictions of the theory are verified by observation. The most striking example is the pericline law in plagioclases, in which the rhombic section was known to be nonreticular long before the fact was explained by this theory.

Repeated twinning: Some crystalline species show twinning repeated a great many times during growth. This means that at every moment the condition for the stability of the twin was satisfied. The laws of the composition surfaces are rigorous in such cases. Other species show only dual twinning (fig. 70 and 71); this means that at a certain moment the twinned orientation began to grow and kept on growing as a single crystal, departing more and more from the condition of stability of the twin. The composition surface in such case obeys the prediction of the theory only at the early stage of twinning; afterward the composition surface may become irregular for it is an accidental contact between two independent crystals which interfere with each other's growth.
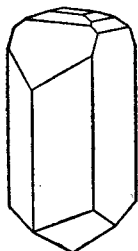
FIG. 59.—HEMIMORPHITE CRYSTAL

Examples.—Albite and other plagioclases are triclinic crystals. The cell is pseudomonoclinic: (o1o) is a plane of pseudosymmetry, [o1o] is an axis of pseudosymmetry. The angle (oo1):(o1o) = 86° 24′ in albite. Two twins are possible; both have been found: (1) albite twinning, in which the twin plane and composition plane is parallel to (o1o); (2) pericline twinning, in which the b-axis [o1o] is the twin axis and the composition surface is planar though not a net in the lattice. This plane cuts the vertical zone [{11o} {11o}] along a rhomb (defined by the row [o1o] and the normal to

FIG. 60 AND 61.—TETRAGONAL DIPYRAMIDS *Okl* AND *hhl* IN COMBINATION

it contained in the net (o1o); hence the two diagonals are perpendicular). This is the origin of the name rhombic section. The trace of the rhombic section on (o1o) varies with the chemical composition of the plagioclase, because to a different chemical composition there corresponds a different set of axial elements or, in other words, a differently shaped cell. The angle of the rhombic

section (as it is called) varies from +22° to −17° from albite ($NaAlSi_3O_8$) to anorthite ($CaAl_2Si_2O_8$). It is measured on (o1o) from the trace of (oo1) toward the trace of the rhombic section and is called (+) if clockwise, (−) if counterclockwise.

Note that, in albite twinning, II is symmetrical of I by reflection in the plane (o1o) or by a 180° rotation around a line perpendicular to (o1o). The two definitions of the twin are geometrically identical because of the presence of a centre of symmetry. Now the two orientations I and II′ of the pericline twinning are symmetrical of each other with respect to a 180° rotation around the b-axis [o1o], a row that is almost normal to (o1o). Hence the two orientations II and II′, obtained from I respectively by 180° rotations about the exact normal to (o1o) and about the pseudo-normal to (o1o), will not differ much from each other. The two twins, however, differ greatly by their composition surfaces, net (o1o) in albite twinning and rhombic section in pericline twinning, which are almost at right angles to each other.

Example.—Cerussite (and many species with a pseudohexagonal lattice). Holohedral orthorhombic, $a:b:c = 0.610:1:0.361$, the lattice is centred on (oo1). Draw the lattice on (oo1) and its hexagonal pseudosymmetry becomes apparent. The planes (11o) and (13o) are almost at right angles and hence are planes of pseudosymmetry of the lattice. Hence, there are two corre-

spondent twins: one that has (11o) as its twin plane and composition plane; the other (less frequent and of the nonrepeated type) has (13o) as its twin plane and composition plane. The angle (11o):(13o) = 92° 44′. The obliquity of the twin is 2° 44′ in both twins.

Twinning by Reticular Merohedry (G. Friedel).—*Examples.*—Spinel (fig. 72) and fluorite (fig. 73).

Twinning by Reticular Pseudomerohedry (G. Friedel).—*Examples.*—Pyroxene and orthoclase.

These are extensions of the preceding cases. The cell whose symmetry or pseudosymmetry conditions the existence of the twin is a multiple cell (instead of the smallest cell) of the crystal lattice.
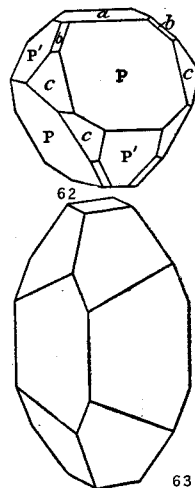
(J. D. H. D.)

FIG. 62.—CHALCOPYRITE CRYSTAL

FIG. 63.—FERGUSONITE CRYSTAL

GROWTH OF CRYSTALS

Character of Faces.—Only rarely do actual crystals present the symmetrical appearance shown in the figures given above, in which similar faces are all represented as of equal size. It frequently happens that the crystal is so placed with respect to the liquid in which it grows that there will be a more rapid deposition of material on one part than on another; for instance, if the crystal be attached to some other solid it cannot grow in that direction. Only when a crystal is freely suspended in the mother-liquid and material for growth is supplied at the same rate on all sides does an equably developed form result.

Two malformed or misshapen octahedra are represented in fig. 10 and 11; the former is elongated in the direction of one of the edges of the octahedron, and the latter is flattened parallel to one pair of faces. It will be noticed in these figures that the edges in which the faces intersect have the same directions as before, though here there are additional edges. The angles (70° 32′ or 109° 28′) between the faces also remain the same; and the faces have the same inclinations to the axes and planes of symmetry as in the equably developed form. Although from a geometrical point of view these figures are no longer symmetrical with respect to the axes and planes of symmetry, yet crystallographically they are just as symmetrical as the ideally developed form, and however much their irregularity of development, they still are regular (cubic) octahedra of crystallography. A remarkable case of irregular development is presented by the mineral cuprite, which is often found as well-developed cubes; but in the variety known as chalcotrichite it occurs as a matted aggregate of delicate hairs,
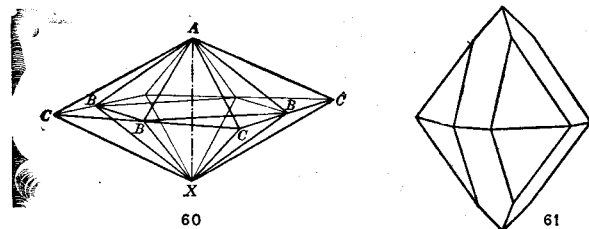
810L   CRYSTALLOGRAPHY

each of which is an individual crystal enormously elongated in the direction of an edge of the cube.

The symmetry of actual crystals is sometimes so obscured by irregularities of growth that it can be determined only by measurement of the angles. An extreme case, where several of the planes have not been developed at all, is illustrated in fig. 8, which shows the actual shape of a crystal of zircon from Ceylon; the ideally developed form (fig. 9) is placed with it for comparison, and the parallelism of the edges between corresponding faces will be noticed. This crystal is a combination of five forms; viz., two tetragonal prisms (a and m), two tetragonal dipyramids (e and p), and one ditetragonal dipyramid (x, with 16 faces).
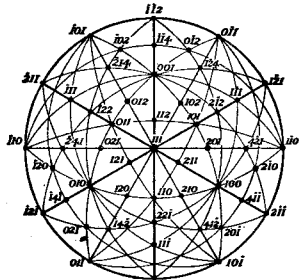
FIG. 64.—STEREOGRAPHIC PROJEC-TION OF A RHOMBOHEDRAL CRYSTAL WITH SYMMETRY $\bar{3}\ 2/m$

The actual form, or habit, of crystals may vary widely in different crystals of the same substance, these differences depending largely on the conditions under which the growth has taken place. The material may have crystallized from a fused mass or from a solution; and in the latter case the solvent may be of different kinds and contain other substances in solution, or the temperature may vary. Calcite (q.v.) affords a good example of a substance crystallizing in widely different habits, but all crystals are referable to the same type of symmetry and may be reduced to the same fundamental form.

When crystals are aggregated together, and so interfere with each other's growth, special structures and external shapes often result, which are sometimes characteristic of certain substances, especially among minerals.

Incipient crystals, the development of which has been arrested as a result of unfavourable conditions of growth, are known as crystallites (q.v.). They are met with in imperfectly crystallized substances and in glassy rocks (obsidian and pitchstone),

FIG. 65.—TOURMALINE CRYSTAL

or may be obtained artificially from a solution of sulphur in carbon disulphide rendered viscous by the addition of Canada balsam. To the various forms H. Vogelsang gave, in 1875, the names globulites, margarites, longulites, etc. At a more advanced stage of growth these bodies react on polarized light, thus possessing the internal structure of true crystals; they are then called microlites. These have the form of minute rods, needles or hairs, and are aggregated into feathery and spherulitic forms of skeletal crystals. They are common constituents of microcrystalline igneous rocks, and often occur as inclusions in larger crystals of other substances.

Inclusions of foreign matter, accidentally caught up during growth are frequently present in crystals. Inclusions of other minerals are specially frequent and conspicuous in crystals of quartz, and crystals of calcite may contain as much as 60% of included sand. Cavities, either with rounded boundaries or with the same shape (negative crystals) as the surrounding crystal, are often to be seen; they may be empty or enclose a liquid with a movable bubble of gas.

The faces of crystals are rarely perfectly plane and smooth, but are usually striated, studded with small angular elevations, pitted or cavernous, and sometimes curved or twisted. These irregularities, however, conform with the symmetry of the crystal, and much may be learned by their study. The parallel grooves or furrows, called striae, are the result of oscillatory combination between adjacent faces, narrow strips of first one face and then another being alternately developed. Sometimes
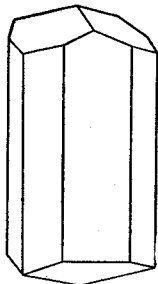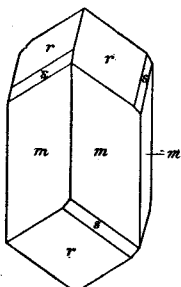

FIG. 66.—DIOPTASE CRYSTAL

the striae on crystal-faces are due to repeated lamellar twinning, as in the plagioclase feldspars. The directions of the striations are very characteristic features of many crystals; e.g., the faces of the hexagonal prism of quartz are always striated horizontally, while in beryl they are striated vertically. Cubes of pyrite (fig. 74) are striated parallel to one edge, the striae on adjacent faces being at right angles, and a result of oscillatory combination of the cube and the pentagon-dodecahedron; while cubes of sphalerite (fig. 75) are striated parallel to one diagonal of each face (i.e., parallel to the tetrahedron faces). Compare fig. 39). These striated cubes thus possess different degrees of symmetry and belong to different symmetry classes. Oscillatory combination of faces gives rise also to curved surfaces. Crystals with twisted surfaces (see DOLO-MITE) are, however, built up of smaller crystals arranged in nearly parallel position. Sometimes a face is entirely replaced by small faces of other forms, giving rise to a drusy surface; an example of this is shown by some octahedral crystals of fluorite (fig. 2) which are built up of minute cubes.

The faces of crystals are sometimes partly or completely replaced by smooth bright surfaces

FIG. 67.—EXAMPLE OF A SCREW AXIS IN A PLANT

inclined at only a few minutes of arc from the true position of the face; such surfaces are called vicinal faces, and their indices can be expressed only by very high numbers. In apparently perfectly developed crystals of alum the octahedral face, with the simple indices {111} is usually replaced by three faces of a very low trioctahedron, with indices such as { 251.251.250 }; the angles measured on such crystals will therefore deviate slightly from the true octahedral angle. Vicinal faces of this character are formed during the growth of crystals, and have been studied by H. A. Miers (Phil. Trans., series A, vol. 202 [1903]). Other faces with high indices, viz., prerosion faces and the minute faces forming the sides of etched figures (see below), as well as rounded edges and other surface irregularities, may result, however, from the corrosion of a crystal subsequent to its growth. The pitted and cavernous faces of artificially grown crystals of sodium chloride and of bismuth are, on the other hand, a result of rapid growth, more material being supplied at the edges and corners of the crystal than at the centres of the faces. (L. J. S.)

Mechanisms of Crystal Growth.—Crystals will only grow if the solution or vapour in contact with them is supersaturated or, in the case of a melt, undercooled. If the degree of supersaturation is very high the growing crystal lowers the concentration of atoms or molecules in its immediate neighbourhood. In this case projecting edges or corners are placed in a richer medium and grow faster, leading to the boxlike or feathery (dendritic) crystals familiar in frost patterns and snowflakes. If, on the other hand, the supersaturation is very slight, the growth of
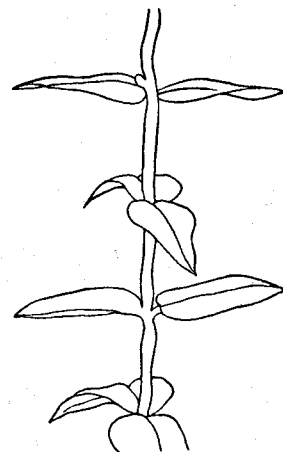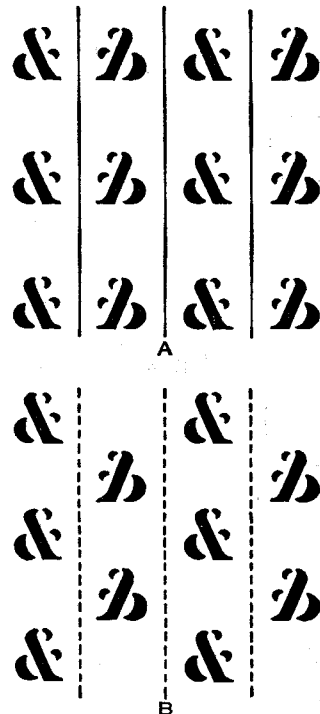

FIG. 68.—MIRRORS AND GLIDE PLANES IN TWO-DIMENSIONAL PATTERNS

the crystal may depend on the existence of surface irregularities or steps on the most slowly growing face. One source of such steps was found in the existence of internal spiral dislocations (F. C. Frank, 1949). These may be thought of as if made by slicing the crystal parallel to an axis and shearing one side of the slice over the other by one or more lattice intervals (Burger's vector)—*see* fig. 76. Where a spiral dislocation appears on a crystal face it gives rise to a step on which free molecules collect far more easily than on the flat face. Consequently the step moves forward, but because of the dislocation new steps are formed and spiral pyramids are set up, the existence of which has been frequently observed. Spirals may be right- or left-handed. Where both exist together on a face the steps belonging to each join to form a normal stepped pyramid. Both spiral and stepped pyramids can give rise to the vicinal faces which have been observed as slight distortions of normally plane crystal faces.   (AR. F. W.)
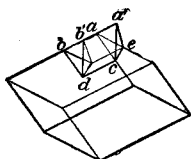
FIG. 69.—CLEAVAGE RHOMBOHEDRON OF CALCITE

Portion *abcde* goes over to *a'b'cde* under knife pressure at *b*

STRUCTURE OF CRYSTALS

Apart from some inspired guesses, knowledge of crystal structure began with the discovery, in 1912, by Max von Laue, W. Friedrich and P. Knipping, that X-rays can be diffracted by crystals (*see* X-RAYS, NATURE OF), a discovery used almost at once by Sir William Bragg and Sir Lawrence Bragg to find the structures of all the main types of simple crystal structure—rock salt, zinc blende, diamond, fluorspar, iron pyrites and calcite. Subsequently other methods, based on electron diffraction and later on neutron diffraction, were used for crystal analysis; but knowledge of crystal structure is mainly derived from X-ray studies.
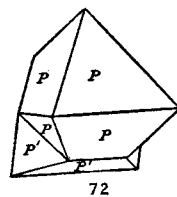
The first period of the history of crystal-structure analysis, already referred to, was the shortest though the most fundamentally important. It was interrupted by World War I, during which the only important advance was the use of the powder crystal method by A. W. Hull and P. Debye to determine the structure of metals. The second period began effectively in 1920 and lasted until 1928. The centre of activity lay still with the Braggs, with Sir William at the Royal institution in London and Sir Lawrence at Manchester university, the former specializing on organic and the latter on inorganic structures. It was the period of the development of all the chief methods of structure analysis, both physical and mathematical, and of the elucidation of more complex types of structure of the long-chain fatty acids and paraffins, of naphthalene and anthracene among the organic compounds, of quartz and the main types of silicates among the inorganic. This latter work, largely of the Manchester school, was to provide a key to the complexities of chemical mineralogy. It was to lead, in the hands of V. M. Goldschmidt, the founder of modern geochemistry, to the establishment of definite radii for most atoms and ions and to the concept of co-ordination as the guiding principle of crystal chemistry, the laws of which were more precisely formulated by Linus Pauling in 1928.

70

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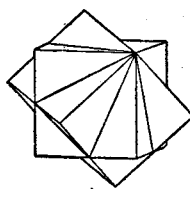
FIG. 70 AND 71.—GYPSUM. DUAL TWIN AND SINGLE CRYSTAL

In the third period, from 1929 to 1939, a rapid advance took place all along the line. Crystal structure analysis spread to other centres and other countries. Methods of analysis were greatly improved, particularly by the use of Fourier series, and really complex organic crystals began to be worked out. A turning point was the analysis of the dye phthalocyanin by J. Monteath Robertson, the first organic molecule whose structure was 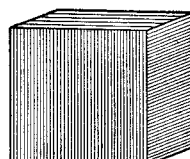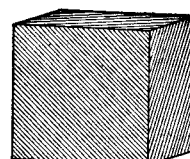determined without any dependence on chemical data. At the same time the correct formula of the biologically important group of sterols was determined largely with the help of X-ray methods. A start was even made on the structures of the far more complicated proteins through the work of W. T. Astbury on the fibrous proteins of wool and muscle, and that of J. D. Bernal on the globular proteins and crystallized viruses. During this period X-ray methods were used by A. Westgren, A. J. Bradley and W. Hume-Rothery to elucidate the structure of alloys and to discover the rules—very different from those prevailing in other branches of chemistry—that determine the composition of intermetallic compounds. World War II did not so much interrupt crystal structure analysis as turn it in different directions and concentrate it upon definite objectives. In the fourth period, which began in 1940, a rapid growth in the power and range of analytic methods was made possible by much greater resources in apparatus and even more in computational aids. Its first triumph was the analysis of penicillin in 1945 by D. M. Crowfoot and C. W. Bunn well in advance of chemical knowledge of the correct formula of the molecule. In the next few years the analysis of organic molecules of up to 40 or so atoms became almost a routine, if tedious, operation. Interest moved on, in one direction to the study of imperfect crystals and their relation to crystal growth and deformation, and in the other to the most complex structures of all—those of proteins—which the studies of Crowfoot and M. F. Perutz and the hypotheses of M. L. Huggins, Sir Lawrence Bragg and L. Pauling made the chief centre of interest in crystal structure analysis.

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FIG. 72.—SPINEL TWIN
FIG. 73.—FLUORITE TWIN

X-Ray Analysis of Crystal Structure.—It is impossible here to do more than outline the successive stages of crystal analysis. (The physical principles involved are described in the article on X-RAYS, NATURE OF.) Essentially, the experimental procedure is to allow a narrow beam of X-rays, usually limited by slits or pinholes, to fall on a crystal, and to study the X-ray beams—very much weaker than the incident beam—that are diffracted from it in different directions (*see* fig. 77).

In all but the original Laue method—of historical rather than practical interest—the incident X-rays are substantially monochromatic. The method now most commonly employed uses the K α radiation of copper, $\lambda = 1.54$ Å. (The Ångstrom unit, $Å = 10^{-8}$ cm., is that universally used for expressing cell dimensions; it is convenient because the sizes of atoms are of the order of a few units. All atomic radii are confined to the range of between 0.3 and 2.2 Å.) Planes in the crystal which repeat at a spacing d diffract such rays strongly only when θ, the glancing angle of the ray on the plane, satisfies the relation $\sin \theta = \dfrac{\lambda}{2d}$,

74

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FIG. 74.—STRIATED CUBE OF PYRITE
FIG. 75.—STRIATED CUBE OF BLENDE (SPHALERITE)

Bragg's law. To ensure that this occurs, two methods can be used, that of the rotating crystal and that of the powder. In rotating crystal methods the crystal is usually turned about some crystallographic axis in such a way that all the planes capable of reflecting come one after the other into the reflecting position (*see* fig. 77 A and B). In the powder method the number of crystals is made so great that some of them are certain to be in the reflecting position.

810N CRYSTALLOGRAPHY

The reflected beams are detected either by the image they make on a photographic film or by the ionization they produce in an ionization chamber—Bragg's original method—or in a Geiger or other counter. Numerous devices have been constructed, including moving film cameras by K. Weissenberg, W. F. de Jong,
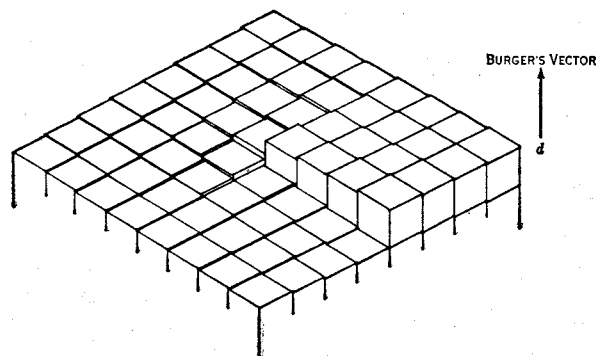

FIG. 76.—DIAGRAM OF SCREW DISLOCATION IN CUBIC CRYSTAL
The edge permanently left by such a dislocation can be the seat of addition of new elements to the crystal face

M. J. Buerger and J. Bouman (*see* fig. 77-C), and one- and two-circle spectrometers (to enable the diffracted rays to be conveniently registered and to ensure that there can be no confusion between reflections coming from different planes). The photographic methods are usually employed when a very large number of planes have to be registered, the ionization method when accurate values of a limited number of intensities are required.

The data which are the basis of all crystal analysis consist of two radically different types of information: that on the angles
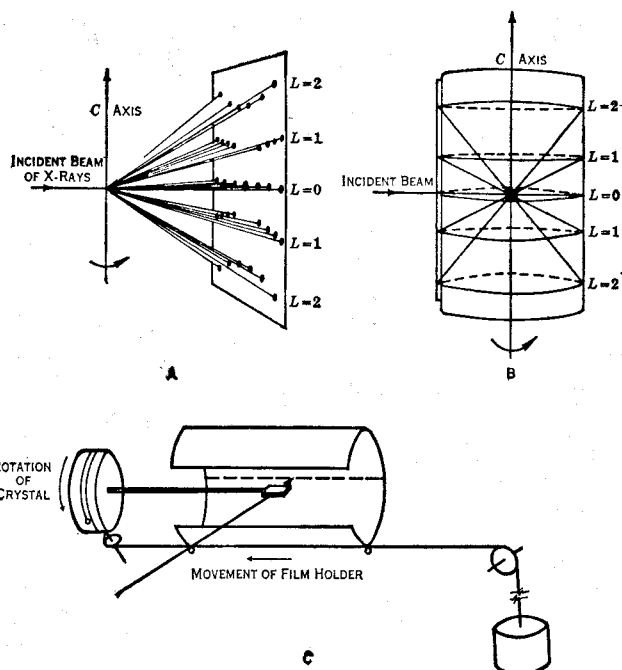

BY COURTESY OF (A) SIR LAWRENCE BRAGG AND G. BELL & SONS LTD. (LONDON), (B) JOHN WILEY AND SONS, INC., FROM BUERGER "X-RAY CRYSTALLOGRAPHY"

FIG. 77.—ROTATION PHOTOGRAPH. X-RAY ANALYSIS OF CRYSTAL STRUCTURE
(A) plane plate and (B) cylindrical film show rotating crystal methods; (C) is the Weissenberg photograph mechanism. A screen, not shown, limits reflected beams to one layer line

at which reflection takes place (*i.e.*, the different values of Θ corresponding to each crystallographic plane); and that on the intensity of each reflection as a proportion of the corresponding incident intensity. The former gives all the information on the metrics of the crystal, in particular the dimensions of the elementary cell by whose repetition the whole crystal may be deemed to be constructed. This geometrical part of crystal analysis is rapid and straightforward, but except for very simple

crystals it is insufficient to determine structure and can only be used for identification and comparative studies. All that can be known of the way atoms and electrons are arranged in the elementary cell must be derived from the study of the intensities of reflection. This second, optical, part of X-ray analysis can never be direct and is always difficult and often ambiguous in its implications. The reason is that unlike normal optical systems—for light, electrons and other image-forming radiations—the X-rays used are always divergent and different rays are never made to interfere, as are rays of light, in the formation of an optical image. In physical terms, all that can be done is to register their intensity and not their amplitude. This is a physical vectorial property, like a direction on a map, in which not only the length but the bearing or phase needs to be known. Thus although it is always possible to calculate precisely what the X-ray scattering from any disposition of matter may be, the converse process is in general impossible. From any measured scattering of X-rays the most that may be deduced directly is that the crystal may have any of a number, indeed an infinite number, of electronic
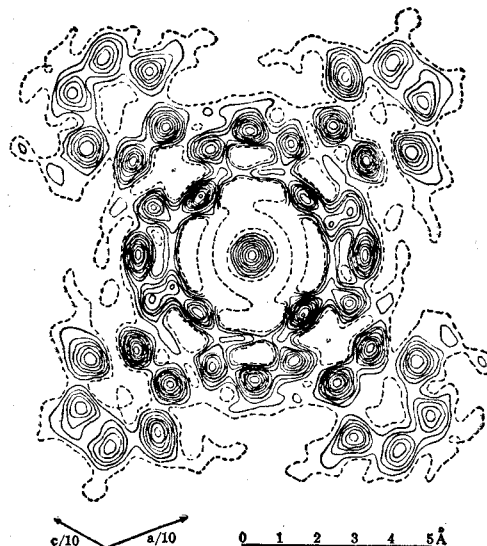
BY COURTESY OF PROF. J. M. ROBERTSON AND "JOURNAL OF THE CHEMICAL SOCIETY" (LONDON)

FIG. 78.—FOURIER PROJECTION OF MOLECULE OF NICKEL PHTHALOCYANINE
The positions of the atoms are near the centres of the main contoured peaks

distributions, each of which is capable of giving the same scattering pattern. Of the possible electronic distribution only a few will correspond to one having the right number of atoms of each kind that are known to exist in the crystal. The whole art of crystal structure analysis comprises the resolution of this fundamental ambiguity by invoking data about atomic and electronic distribution independently derived from other experiments.

The process of crystal analysis is essentially mathematical, an example of the application of Fourier inversion (used in many other fields of science and technology, for instance in determining the relation between a sound track and the notes or frequencies that go to build it up). The stages are briefly as follows.

1. Determination of the size of the unit or repeat cell. This is usually determined by a measurement of the positions of spots on a photograph or of the angular position of the ionization detector. It is expressed in terms of three axial lengths a, b, c and the angles between them α, β, γ, where these differ from a right angle. These measurements, if sufficiently accurate, provide a complete identification of the crystal.

2. Determination of the cell content. The absolute weight of material in the cell is given by multiplying its volume—$abc \times 10^{-24}$ c.c. (when a, b and c are at right angles and are measured in Ångstrom units)—by the measured density ρ. To express the cell content in molecular units it is necessary to divide by the weight of one atom of hydrogen—1.66×10^{-24} gm. The cell molecular weight is accordingly $\dfrac{abc \times \rho}{1.66}$. If the substance is one of known molecular weight M then the number of molecules in

CRYSTALLOGRAPHY

the cell $Z = \dfrac{abc \times \rho}{1.66 \times M}$. Z is a number determined by the symmetry, it is usually small—2, 4, 6 or 8. Where M is not known it can be found as $M = \dfrac{abc \times \rho}{1.66 \times Z}$ where Z has any of the values permitted by the symmetry. For example, in olivine $a = 10.2$ Å, $b = 4.73$ Å, $c = 5.96$ Å, $\rho = 3.2$. M for $Mg_2SiO_4 = 140.7$, cell volume $= 287$ Å³, cell weight $= 920 \times 10^{-24}$ gm. No. of molecules per cell $= \dfrac{920}{141 \times 1.66} = 3.94 \approx 4$. Each cell contains $Mg_8Si_4O_{16}$.

3. *Determination of the symmetry.* A crystal structure has all the elements of symmetry shown by its external appearance—rotation axes, planes, centres of symmetry (see *Morphology of Crystals* above)—but it will also have regular internal partial periodicities—screw axes, glide planes—the existence of which are shown by the absence of reflections of planes with certain indices. These can be determined usually with certainty by the use of tables, particularly the *International Tables for X-Ray Crystallography* (1952), which permit every crystal to be referred to one of the 230 possible geometrically different space groups. A certain indeterminacy persists as the presence or absence of a centre of symmetry cannot normally be found directly by X-ray methods, but these can be supplemented by crystal physical tests, particularly piezo- and pyro-electricity (see *Physical Properties of Crystals* below) and also by the use of A. J. C.

PATTERSON PROJECTION
A

CRYSTAL STRUCTURE
B
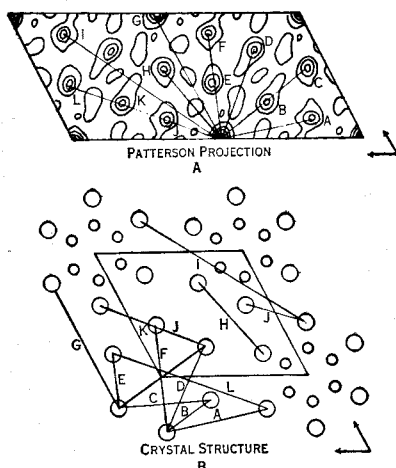
BY COURTESY OF VERLAG JULIUS SPRINGER

FIG. 79.—CORRESPONDENCE BETWEEN (A) PATTERSON PROJECTION AND (B) CRYSTAL STRUCTURE FOR HEXACHLOROBENZENE
Each peak in (A) corresponds to a vector or vectors in (B). Only Cl—Cl vectors show large peaks. The C—Cl peaks are the small peaks near the origin

Wilson's statistical methods based on the different distribution of reflection intensity in crystals with and without centres of symmetry. Once the space group is known, the problem of finding the positions of all the atoms of the cell is reduced to that of finding the positions of those in the asymmetric unit from which all the others can be deduced by means of the symmetry operations of the group.

4. This completes the information deducible from the positions of the X-ray reflections; the remainder is inferred from their intensities. These need in the first place to be measured and then corrected for geometrical and physical factors—angle polarization, absorption, temperature, etc. The object here is to arrive at a value $[F_{(hkl)}]^2$ for the scattering power of a plane of Miller indices h, k, l (see *Morphology of Crystals* above) which is independent of all instrumental and physical conditions. The value $[F]^2$ rather than F is obtained as only the intensity of the radiation is measurable and not its amplitude F which includes an undetermined phase angle factor.

The X-rays are scattered by electrons and as these are not concentrated in the centre of the atoms but spread over a finite volume the angular scattering of a single atom is not constant, becoming less at higher angles because of mutual interference.

Each kind of atom has therefore a characteristic scattering or f curve which, measured in terms of the scattering of one electron, rises to a value equal to the atomic number at low angles. If the position of the different atoms in the cell is known, expressed in

NONMETALS   METALS (A AND B TYPES)

METALS (TRANSITIONAL)
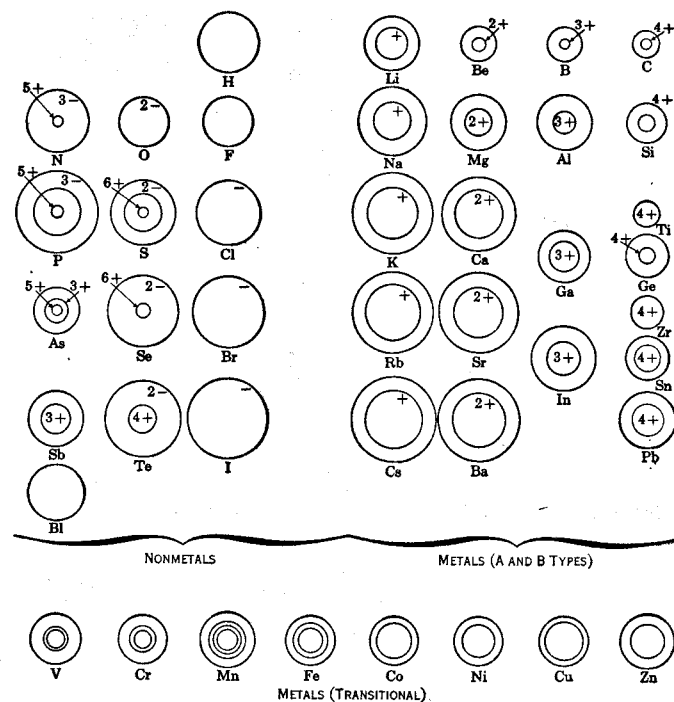
1 0 1 2 3 4 5 6 7 8 9 10Å

FIG. 80.—ATOMIC AND IONIC SIZES

parameters or proportions of the cell axes, then the $[F]^2$ value of any plane can be calculated—

$$[F_{(hkl)}]^2 = \{\sum_1^n f_r \cos 2\pi (hx_r + ky_r + lz_r)\}^2 +$$
$$\{\sum_1^n f_r \sin 2\pi (hx_r + ky_r + lz_r)\}^2 \qquad (1)$$

where the summation is carried out for all the n atoms in the cell and f_r is the value of the f curve for the rth atom at the angle corresponding to the reflection from the plane (h, k, l).

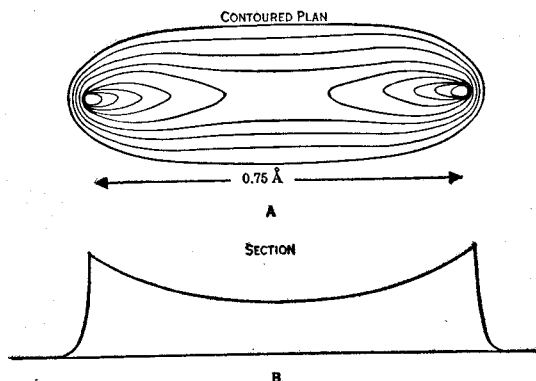To solve the inverse problem of finding the density of electrons

CONTOURED PLAN

0.75 Å

A

SECTION

B

FIG. 81.—ELECTRON DENSITY IN H_2 MOLECULE

at any point of parameters (x, y, z) in the cell there is the triple Fourier sum—

$$\rho(xyz) = \sum\sum_{-\infty}^{\infty}\sum \left[\frac{F_{(hkl)}}{V}\right] \cos [2\pi(hx + ky + lz) - \alpha(hkl)] \quad (2)$$

where $[F_{(hkl)}]$ is the measurable absolute value of the structure factor of the plane hkl and $\alpha(hkl)$ is the undetermined phase angle attributable to that plane, the summation being taken over all values of h, k and l, positive and negative. The determination of structure comes down to that of finding the values of $\alpha(hkl)$ for every plane.

CRYSTALLOGRAPHY

TABLE II.—Atomic and Ionic Radii

Legend:
State of ionization 3+ / Value of radius
Atomic number / Symbol
D = dispersion radius
M = metal radius
H = homopolar half-bond distance

Z	Sym	Radii
1	H	−1 1.54; H 0.46
2	He	D 1.60
3	Li	M 1.56; +1 0.78
4	Be	M 1.12; +2 0.34
5	B	H¹ 0.88; H² 0.76; H³ 0.68
6	C	H¹ 0.77; H² 0.66; H³ 0.60
7	N	H¹ 0.70; H² 0.66; H³ 0.55
8	O	−2 1.32; D ...; H² 0.50
9	F	−1 1.33; D 0.66; H² 0.64
10	Ne	D 1.91
11	Na	M 1.91; +1 0.98
12	Mg	M 1.60; +2 0.78
13	Al	M 1.43; +3 0.56
14	Si	H¹ 1.17; H² 1.04; 4+ 0.39
15	P	D 1.10; H² 1.00; 5+ 0.35
16	S	−2 1.74; D 1.04; H² 0.94; 6+ 0.30
17	Cl	−1 1.81; D 1.26; H² 0.99; 7+ 0.20
18	A	D 1.91
19	K	M 2.38; +1 1.33
20	Ca	M 1.96; +2 1.06
21	Sc	M 1.51; +3 0.83
22	Ti	M 1.46; +3 0.69; +6 0.64
23	V	M 1.35; +3 0.65; +4 0.61; +5 0.4
24	Cr	M 1.28; +3 0.64; +6 0.35
25	Mn	M 1.37; +2 0.91; +3 0.70; +4 0.52
26	Fe	M 1.26; +2 0.83; +3 0.67
27	Co	M 1.25; +2 0.82
28	Ni	M 1.24; +2 0.78
29	Cu	M 1.28; +1 0.96; +2
30	Zn	M 1.37; +2 0.83
31	Ga	M 1.39; +3 0.62; +4 0.44
32	Ge	M 1.39; H 1.22; +4 0.44
33	As	M 1.58; H 1.21; +3 0.69; +5 0.4
34	Se	−2 1.91; D 1.73; H² 1.16; 6+ 0.35
35	Br	−1 1.96; D 1.65; H² 1.14
36	Kr	D 2.01
37	Rb	M 2.51; +1 1.49
38	Sr	M 2.15; +2 1.27
39	Y	M 1.81; +3 1.06
40	Zr	M 1.60; +4 0.87
41	Nb	M 1.47; +4 0.69; +5 0.69
42	Mo	M 1.40; +4 0.68; +6 0.52
43	Tc	M 1.36
44	Ru	M 1.33; +4 0.65
45	Rh	M 1.34; +3 0.68
46	Pd	M 1.37
47	Ag	M 1.44; +1 1.13
48	Cd	M 1.52; +2 1.03
49	In	M 1.58; H 1.40; +4 0.74
50	Sn	M 1.58; H 1.40; +4 0.74
51	Sb	M 1.61; H 1.43
52	Te	−2 2.11; D 1.87; H² 1.43; 4+ 0.89
53	I	−1 2.20; D 1.77; H² 1.33
54	Xe	D 2.20
55	Cs	M 2.70; +1 1.65
56	Ba	M 2.24; +2 1.43
57	La	M 1.86; +3 1.22
72	Hf	M 1.58; +4 0.84
73	Ta	M 1.47; +5 0.68
74	W	M 1.41; +4 0.68
75	Re	M 1.37
76	Os	M 1.35; +4 0.67
77	Ir	M 1.35; +4 0.66
78	Pt	M 1.38
79	Au	M 1.44; +1 1.37; +3
80	Hg	M 1.55; +2 1.12
81	Tl	M 1.75; H 1.50; +1 1.32; +3 1.05
82	Pb	M 1.75; H 1.49; +2 1.32; +4 0.84
83	Bi	M 1.82; H 1.55
84	Po	M 1.7; H 1.4
85	Ab	
86	Rn	
87	Fr	
88	Ra	
89	Ac	M +3 1.28
90	Th	M 1.80; +4 1.10
91	Pa	M 1.63
92	U	M 1.54; +4 1.09; +5 0.87
93	Np	+4 1.07
94	Pu	+4 1.06
95	Am	+4 1.05
96	Cu	

Rare Earths:

Z	Sym	Radii
58	Ce	M 1.82; +3 1.18; +4 1.00
60	Nd	M 1.82; +3 1.16; +4 1.00
61	Il	M 1.82; +3 1.15
62	Sm	M 1.82; 3+ 1.14
63	Eu	M 1.81; +3 1.13
64	Gd	M 1.82; +3 1.12
65	Tb	M 1.81; +3 1.11; +4 0.89
66	Dy	+3 1.09
67	Ho	+3 1.07
68	Er	M 1.86; +3 1.04
69	Tm	M 1.86; +3 1.04
70	Yb	M 1.04; +3 1.00; +4 0.89
71	Lu	+3 1.00

When the α's have been determined or guessed at the results of the Founier analyses are usually set out in projection or sections such as those shown in fig. 78 in which the position of the atoms is shown in the centres of electron density indicated by the contours. The difficulty of determining may be circumvented, at the cost of introducing another indeterminancy, by deriving the Patterson function—

$$P_{(xyz)} = \sum\sum_{-\infty}^{\infty}\sum \frac{[F_{(hkl)}]^2}{V^2} \cos 2\pi (hx + ky + lz) \tag{3}$$

which only involves the observable absolute value of $[F]^2$, but P is not the electronic density at the point xyz but the average of densities for all pairs of points related to each other as the origin is to the point xyz. It is as though instead of a map a diagram was used which showed that every city had others on the average 25 mi. to the north and 35 mi. to the southeast. Where the P function shows a maximum there is a strong probability of the existence of pairs of atoms at a distance and direction apart corresponding to its position (see fig. 79).

Crystal analysis at this point may branch along three tracks: the finding of phase angles (5a below); approximating to structures by trial and error (5b); and the interpretation of Patterson charts (5c); all leading to a trial structure whose accuracy can be checked by means of the relation (i).

5a. This, the most rigorous and formal approach was much developed by many workers, notably D. Harker, J. S. Kasper, D. Sayre, W. Cochrane and W. H. Zachariasen. It depends on the fact that as crystals contain a finite number of atoms the phases of all the planes are not independent but those of the weaker can be found in terms of the stronger by the use of a series of inequalities. In the particular case where all the atoms have about the same scattering power, and this holds for most organic crystals as the scattering of hydrogen atoms can be neglected in the first instance, it is often possible to determine the phases of sufficient planes to derive a trial structure.
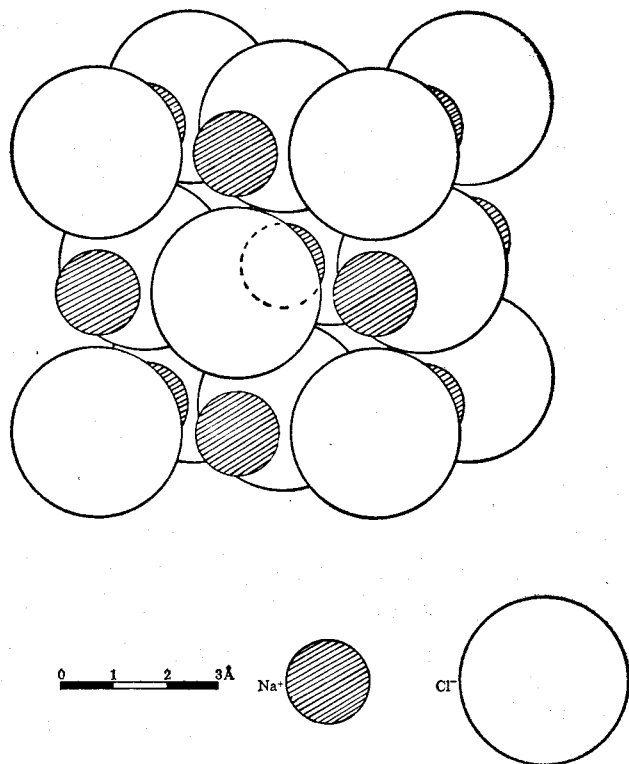

0 1 2 3Å   Na+   Cl⁻

FIG. 82.—SODIUM CHLORIDE (ROCK SALT) STRUCTURE.

Where one or two atoms have much greater scattering power, as in iodine derivatives or heavy metal salts, this process is even easier, for the phases are mainly determined by the contributions of the heavy atom and the structure can be analyzed in stages. In the special case where two almost identical (isomorphous)

structures can be found differing only by the presence of a heavy atom in one or its absence in another, the process is direct. The phases can be found by taking the sum or difference of intensities of the same plane in both crystals. It was in this way that the structure of phthalocyanine (fig. 78) was determined, using its
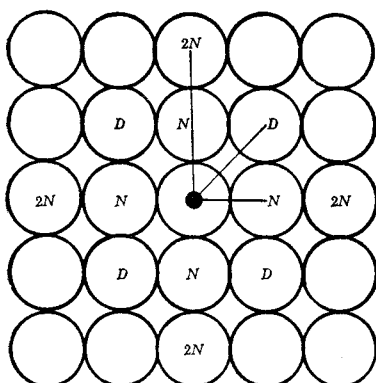

FIG. 83.—ATOMIC FORCES IN CRYSTAL STRUCTURE. *See* TEXT FOR EXPLANATION

nickel and hydrogen derivatives. The substitution method thus offers a powerful semichemical way of deriving crystal structures.

5b. The trial-and-error method was the first method used—and with great success—by the Braggs in their early crystal structures and even in elucidating many complex silicate structures. Strictly speaking, any crystal could be analyzed by calculating the F values for every possible arrangement of the atoms it contains and selecting the one which fitted the observed F values, although, except for the simplest crystals, this might take an infinite
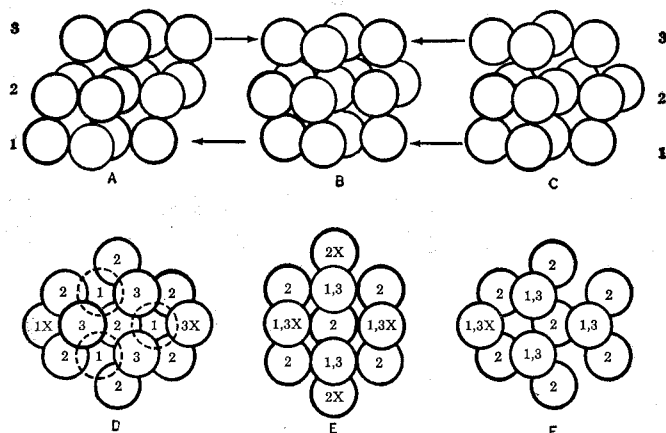

FIG. 84.—RELATIONS OF HIGH CO-ORDINATION STRUCTURES

Fourteen spheres in three layers (1.2.3.) are shown surrounding a central sphere (A) in cubic face-centred packing, axis vertical, (B) in cubic body-centred packing, axis vertical, (C) in hexagonal close packing. The corresponding plans are shown in (D) (E) and (F). It can be seen that (A) and (C) can be derived from (B) by shearing of alternate layers in opposite and similar directions respectively. In (A) and (C) there are 12 equidistant neighbouring spheres (spheres marked 1X and 3X are not neighbours). In (B) there are eight closest neighbours but six others marked 1 and 3X and 2X are at a distance only 1.15 times farther away and must be counted in a first co-ordination sphere of 14.

time to do. The whole art of the trial-and-error method consists of reducing the number of trials and keeping down the errors by intelligent guessing. The various devices for doing this are too numerous and special to discuss here. All that need be said is that every use is made of known interatomic arrangements, for it is clearly a waste of time to put forward structures which are physically impossible. Some atoms are first located on symmetry elements and then the rest of the structure is built around them. Use is made of strongly reflecting planes, in which nearly all the atoms must lie, and weak planes, where their contribution must largely cancel out. In such ways it has been possible to narrow down the position of the atoms to a few alternatives, one of which

The method of trial and error was made much easier and quicker by the use of electronic computing devices, particularly by that of R. Pepinski, which can project almost instantaneously on a screen the Fourier projection of a set of planes whose phases can be varied at will until a plausible structure is obtained.

5c. The Patterson interpretation method became almost universally used as the principal or auxiliary approach to finding possible atom positions. The interpretation of Patterson diagrams is also largely an art, but it was systematized, mainly through the work of Buerger, C. A. Beevers and others, by various devices of which the superposition method seemed the most promising. This is effectively a way of unscrambling the too copious information provided in a Patterson diagram by superposing it on itself, putting the origin in turn on every important maximum and counting
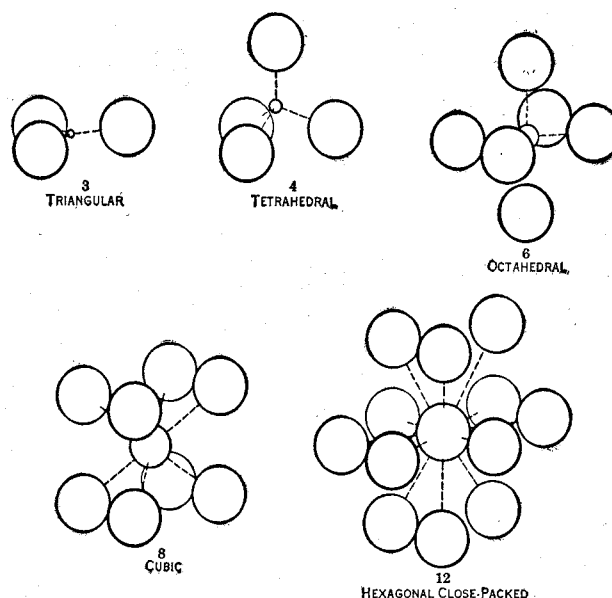
FIG. 85.—TYPICAL CO-ORDINATION ARRANGEMENTS

The radius of the smaller sphere is in the correct ratio for limiting co-ordination of 3, 4, 6, 8, respectively but the distances have been increased so that its position can be more clearly seen

the number of times where peaks occur in the same place. Patterson methods lead to particularly rapid solutions where atoms of different scattering power occur, for the height of a Patterson peak depends on the product of the scattering power of the atoms at each end of the corresponding vector. If one atom has double the f value of another the peaks corresponding to the vectors between such atoms will be four times as high and they can thus be located separately.

6. By whatever method or combination of methods a trial structure is arrived at, if it is correct within somewhat broad limits its accuracy can be improved by a process known as refinement. This consists of comparing observed and calculated structure factors and moving the atoms through small distances to improve the over-all agreement. This can be done by trial and error or by the more systematic, though laborious, methods of plotting the Fourier sections of (F calculated—F observed) and eliminating all its peaks by the methods of differential synthesis, or by such mathematical devices as the least-squares method and that of steepest descent. The final result is a structure in which the atom positions and electron densities are known to a known degree of accuracy limited only by the implications of the finite number of intensities used. In the best cases this is of the order of 0.006 Å for position and with a standard deviation 0.02e Å^{-3} in electron density. Naturally such accuracy is not obtainable except in relatively simple structures, but it is there that it is most needed.

This account of methods of structure determination should suffice to show that the knowledge of atomic position in crystals has long passed the speculative stage. Crystal structure determinations properly carried out can furnish more precise information

other method, chemical or physical, which must be far more indirect.

The Results of Crystal Structure Analysis.—The enormous variety of crystals whose structures have been determined, largely by X-ray methods, makes it impossible to attempt to describe them here, even summarily. What can be done is to set out some of the main principles which underlie different types of crystal structure and to illustrate these by a few simple examples.

The nature of a wall is determined by that of the bricks and mortar with which it is made and the way in which those bricks are bonded together. In the same way the nature of the crystal is determined by the properties of the atoms and of the forces that bind them together and by the geometrical pattern in which these

FIG. 86.—RELATION OF CRYSTAL TO GLASS
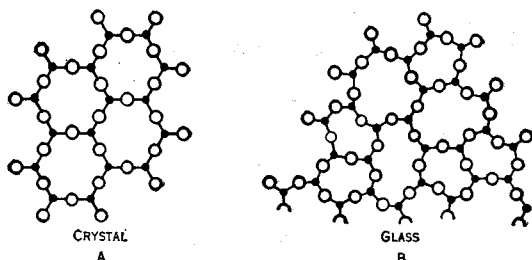A two-dimensional diagram showing a three co-ordinated arrangement with long range order—crystalline and without long range order—glassy with approximately the same binding energy

BY COURTESY OF CAMBRIDGE UNIVERSITY PRESS, FROM R. C. EVANS "CRYSTAL CHEMISTRY"

atoms are arranged. The differences in the appearance and physical properties of such diverse solids as diamond and butter, cork and lead, salt and sulphur depend largely on the differences of structure of the crystals of which they are made. As has been seen, the patterns of atoms in crystals can be discovered and measured by the methods of crystal analysis, while the nature of the atoms and the forces between them is the province of chemistry, enormously extended and deepened by physical discoveries about atoms and electrons and by the quantum theory which explains them. In this process of discovery crystal analysis played a great part and, indeed, it is only by crystal analysis that it was possible to observe and measure the arrangements of atoms as if they were being seen in a microscope. The observations of the crystal structures of all the major types of crystal together with their quantum chemical explanation constituted the virtually new subject of crystal chemistry, which, because it is not strictly limited to crystals but extends to liquids and glasses, is more properly the chemistry of the condensed states of matter.

To understand crystal chemistry it is necessary to have some, but not necessarily very deep, knowledge of chemistry, inorganic and organic, as well as some general notions of atomic structure and the quantum theory. Nevertheless, a general understanding of the architecture of crystals can be reached in a simple pictorial way by considering it in terms of actual models, in which the atoms are represented by balls and the forces between them by spokes of appropriate length holding them apart. Less easy to visualize in space, but having greater physical meaning is the picture of crystals as composed of balls of definite sizes arranged to touch one another. The old idea of the billiard ball atom, now so often derided, is adequate to represent to scale the structure of nearly all inorganic crystals and, slightly modified, organic crystals as well.

To the first approximation each different kind of atom met with in such structures has a definite size. As the space about the atom is occupied solely by electrons—the nucleus having negligible dimensions on this scale—the atomic size depends on the electronic state. The neutral, free atom, where the number of electrons is exactly equal to the number of positive charges in the nucleus (the atomic number Z), is extremely rare in crystal structures. Most atoms in inorganic crystals are found in a charged form as ions, in which a stable arrangement of electrons is achieved at the cost of loss of electric neutrality. Atoms which have lost electrons become positive ions, and those which have gained them become negative. For any particular element several

states of ionization are possible, ranging from positive to negative.

The effective sizes of a neutral atom or of an ion can best be measured by the methods of crystal analysis. There is, however, the difficulty, which occurred at the very beginning of crystal chemistry, that this size is indeterminate. Even in the simplest cases all that can be directly observed is the distance between two atoms; the point where one ends and the next begins is not immediately determinable. The case of the pure metals where all atoms are the same seemed at first an exception, for there the radius of an atom might be taken to be half the distance between nearest neighbours. The difference between a metal, in which much of the space is taken up by free electrons, and an ionic crystal such as rock salt, where all electrons are attached to ions, was not at first realized. In the ionic case all that was necessary was to determine the size of one ion; that of all the others followed. In 1927 V. M. Goldschmidt, adopting J. A. Wasastjerna's estimate (based on gas theory and ionic refractivity) that the radius of the oxygen ion o^- was 1.33 Å, was the first to put forward a complete table of ionic radii. (Pauling used the value 1.40 Å for the o^- radius with corresponding change for other radii, but the particular values are less important than the general concordance.) This was founded (Table II) on an extensive study of the crystal structures of simple compounds of most of the elements, and was so adjusted that the distance between two ions as measured appears as the approximate sum of their respective radii in the table. Goldschmidt's values for ionic radii were subsequently corrected and extended, but substantially they remain as he set them down.

The evidence that an atom or ion has a definite size, to which an almost constant radius can be attributed, points to the existence between all atoms of strong repulsive forces, which resist strongly any attempt to press them together more closely than the distance represented by the sum of their radii. This energy originates from the increase in energy of electrons in a compressed atom as they must move faster to remain in equilibrium nearer to the nucleus. The precise calculation of this repulsive force remained too complicated for mid-20th century quantum mechanical methods, but it can be estimated semiempirically. As it increases very rapidly
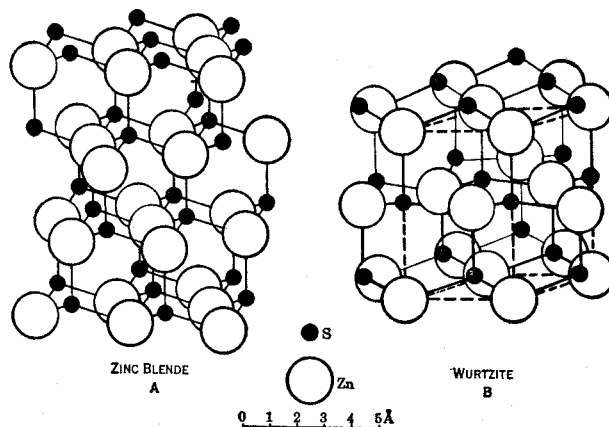
FIG. 87.—ZINC SULPHIDE STRUCTURES
The difference between them is only the cubic (A) and hexagonal close-packed (B) arrangements of the atoms. In both cases every zinc atom is tetrahedrally surrounded by four sulphur atoms and every sulphur atom is surrounded by four zinc atoms

with the degree of compression, it can be arbitrarily expressed in the form $\dfrac{A}{r^n}$, where n ranges from 8 to 14. The existence of repulsive forces is a scientific expression of the common-sense experience of the impenetrability of matter.

However, it is not possible to account for all interatomic distances on the basis of the putting together of incompressible spheres of definite size. In compounds of all nonmetallic atoms —and this includes the whole of organic chemistry—a closer union between atoms occurs. This is the homopolar (covalent) bond, so called because the atoms it links are more or less of the same nature. These atoms all have insufficient electrons to fill the next stable shell. Equilibrium is attained by sharing electrons,

CRYSTALLOGRAPHY

usually pairs of electrons. The simplest and shortest homopolar bond, and the only one whose quantum dynamics has been fully worked out, is that of molecular hydrogen, H–H, where the two electrons, one originally from each hydrogen atom, are shared indistinguishably, between them giving rise to a molecule very similar to the atom of helium which has two electrons in orbits of about the same energy around a single nucleus. A homopolar bond with two electrons in common is usually referred to as a single bond—bonds with odd numbers of electrons are very rare; with four in common a double bond; and with six a treble bond. The effect of homopolar bonds is to bring atoms very much closer together than when they are merely in contact and the more so the higher the order of the bond. Thus the distance between two
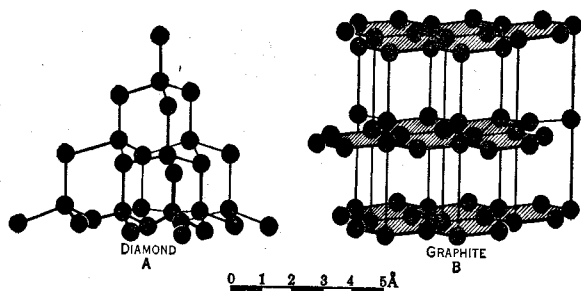
BY COURTESY OF CORNELL UNIVERSITY PRESS, FROM BRAGG "ATOMIC STRUCTURE OF MINERALS"

FIG. 88.—CARBON STRUCTURES

(A) diamond showing tetrahedral co-ordination of four single carbon bonds (aliphatic); (B) graphite showing planar hexagonal networks of conjugated double bond system (aromatic)

oxygen ions in contact in magnesium oxide MgO is 2.96 Å; in SiO_2 it is 2.58 Å ; while the distance between the single bonded oxygen atoms in hydrogen peroxide H–O–O–H is 1.48 Å, between the doubly bonded atoms of molecular oxygen[1] o=o it is 1.27 Å. Although the quantum theory of bonding was still rudimentary in the 1950s the lengths of many bonds had been measured from infra-red spectra, by electron diffraction and by X-rays and found to fit into a very simple, roughly additive scheme. For example, the single bond distance between hydrogen atoms is 0.75 Å; that between simply bonded oxygen atoms is 1.46 Å. Taking half of each of these and adding them results in 1.10 Å, near enough to the measured length 0.96 Å of the O–H bond. The contraction is due to the markedly polar nature of the OH bond and is about the largest that occurs. The result is that the length of any bond between two atoms A and B can be found by looking up the half-bond lengths for each in the table and adding them. The energy of homopolar bonds is relatively great and generally increases rapidly as the bond length decreases, but there is no simple relation between bond length and energy.

One characteristic of homopolar forces which distinguishes them from other interatomic forces, is that they are directed in space. For each kind of atom the bonds joining it to other atoms tend to set themselves at particular angles to each other. Where there are two bonds they may be pointed in opposite directions—linear (at 120°), triangular (at 107°), tetrahedral (at 90°); rectangular and intermediate values are possible. Where there are more than two they may point to all or some of the vertices of some geometrical figure—triangle, tetrahedron, octahedron or cube.

Ionic Forces.—In the greatest apparent contrast with the homopolar forces are the heteropolar or ionic forces. Though the internal electronic configurations of ions are stable as a result of their net positive or negative charges, they produce a powerful and long-range electrical field which has the effect of repelling ions of the same and attracting those of the opposite sign. As a result, when equal numbers of ions of both signs and the same charge are present they come together as closely as the repulsive forces permit—positive ions gathering around negative and negative around positive. The geometrically simplest case is where the arrangement is like a three-dimensional chessboard—white around black, black around white. This is the structure of common salt

(sodium chloride, NaCl), the first crystal to be analyzed (fig. 82). As the interaction of ions is purely electrostatic they follow Coulomb's law, and the forces of attraction and repulsion are proportional to $\frac{1}{r^2}$ the inverse square of the distance, and to the product of the charges. The energy associated with them falls off still more slowly as $\frac{1}{r}$. Unlike homopolar forces, ionic forces are not specific to particular kinds of ions, only like or unlike signs come into question. Nor are they directed, instead they extend through space equally in all directions.

Metallic Forces.—In metals the atoms have some electrons not included in stable shells. These electrons, referred to as free electrons because they are not attached to any particular atom, are responsible for the attraction between the residue of the atoms which are effectively positive ions. Metallic attraction is intermediate between homopolar and ionic. It may be considered as caused by electrons shared between every neighbouring pair of atoms or as caused by the electrostatic attraction between the negative free electron and positive residual ions. Neither explanation is complete, and the theory of metallic attraction was not yet adequate in the 1950s to account for it quantitatively. Nevertheless, a good empirical description can be given in terms of the packing of metallic atoms whose radii, first codified by Goldschmidt, are approximately constant and markedly larger than the radii of the corresponding ions (see Table II). The attraction between metal atoms is almost completely indiscriminate, every kind of metal atom attracting every other, and undirected in space. It therefore leads, as will be shown, to various types of close-packed arrangements.

Dispersion Forces.—Atoms with stable electronic shells and without net charge are extremely inert. They are, in fact, the rare gases of column O of the periodic table. Nevertheless, they do exert a small attraction on each other, as witness the fact that they can be condensed at very low temperatures to liquids and even to solids. This force, which was recognized by J. D. van der Waals in 1873 and explained in terms of quantum mechanics by
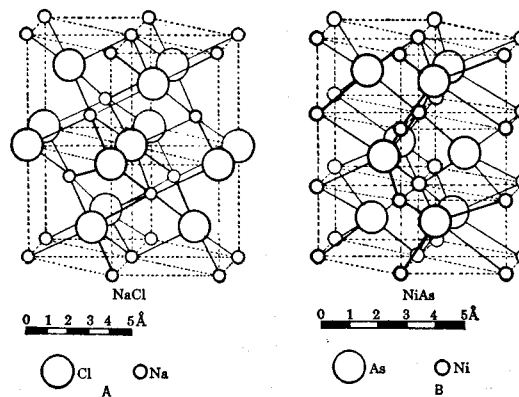
FIG. 89.—FORMS OF STRUCTURES WITH 6-FOLD CO-ORDINATION

(A) sodium chloride type: 6 Cl ions around each Na ion and 6 Na ions around each Cl ion octahedrally; (B) nickel arsenide type: 6 As atoms around each Ni atom octahedrally and 6 Ni atoms around each As atom in the form of a trigonal prism

F. London in 1930, is referred to here as a dispersion force. This is because it is dependent on the property of all atoms to be polarized in electric field giving a positive charge on one side and a negative on the other. It is this property in relation to the vibrating electromagnetic fields of light that gives rise to the optical dispersion or variation of refractive power of the atom. Two polarizable atoms in proximity mutually polarize each other, and the net result is an attractive strength which depends on the polarizability or dispersive force of each atom. The energy associated with it falls off inversely as the sixth power of the distance $\frac{1}{r^6}$. It is therefore only effective when the atoms are practically in contact. Dispersion forces are always present and are completely indiscriminate and undirected. Except between rare

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[1] The actual bond is somewhat more complex in this particular case.

816 CRYSTALLOGRAPHY

gas atoms and between stable nonpolar molecules held together internally by homopolar forces—for instance, such as in methane, CH_4—their effect is masked by the much stronger homopolar, ionic or metallic forces.

Dipole Forces.—In most molecules the homopolar forces do not lead to a complete neutralization of external field. One part of the molecule carries a permanent positive, the other a permanent negative charge. The result is an electrostatic molecular dipole. Such dipoles, like little magnets, cling together with the positive side of one molecule touching the negative side of the next. Such dipole forces are intermediate in their range of action between ionic and dispersion forces; their energy falls off as the third power of the distance $\frac{1}{r^3}$. A specially important case of dipole force is that produced by the presence of the positive charge of hydrogen atoms in certain molecules, notably in water. This is referred to as the hydrogen bond and will be discussed in detail later.

As can be seen even from this summary account of interatomic forces, they are not incompatible entities, but rather represent a set of ideal types selected out of a continuous range. Despite this they are, like the colours of the spectrum, sufficiently distinct to provide a good working basis for the classification of crystal structures.

One point which should emerge from this semiquantitative account is that except for ionic forces there is no need for practical purposes to pay any attention to the forces between atoms which are not nearest neighbours—that is, if considered as spheres—if they are not actually touching or nearly so. For example, for a set of atoms in square array (fig. 83), if the forces between nearest neighbours (N) be taken as unity, that between diagonal neighbours (D) is reduced for repulsive forces to about 3%, for dispersion forces to 8%, for dipole forces to 25%. For next neighbours ($2N$) the reduction is to 0.1%, 0.8% and 6% respectively. With metallic forces the law of fall-off of force with distance is known to hold, but empirically it is found to be more gradual than the dispersion and more rapid than the dipole. Ionic forces, strictly speaking, reach farther, but here, beyond the first neighbours of opposite sign with attractive forces, the attractive and repulsive forces practically balance out, so that effectively here also only the nearest neighbours need be taken into account.

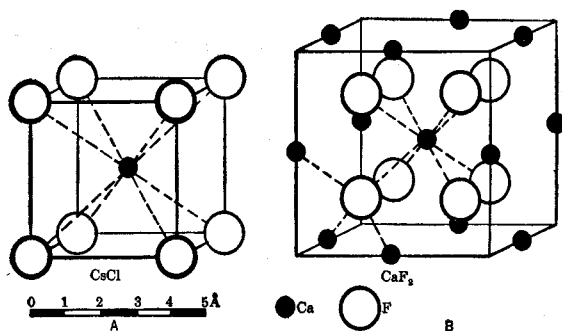

FIG. 90.—FORMS OF 8-FOLD CO-ORDINATION

(A) caesium chloride type: 8 Cl ions around each Cs ion and 8 Cs ions around each Cl ion; (B) fluorite type: 8 F ions around each Ca ion, 4 Ca ions around each F ion

Co-ordination.—A comprehensible and not too inadequate picture of crystal structures can be built up atom by atom, linked neighbour to neighbour, by one or another of the forces described, or by a combination or blend between them, using the model picture already mentioned. In this way crystal chemistry can be reduced to a description of the various geometrical ways of fitting together neighbouring atoms and ions according to the rules of linking, determined by their specific nature. In the first place it must depend on the different, purely geometrical ways of fitting spheres together in space. The number of atoms in close proximity to any particular atom is called the co-ordination number of that atom. Except for the cases of homopolar forces and hydrogen bonds, which have intrinsic directions in space, co-ordination is determined by the relative sizes of the atoms. Because atoms have a finite size, there must be an upper limit to the number of atoms of any particular size that can be packed around any one atom. If all the atoms are of the same size that limit lies between 12 and 14 (12 being the largest number that can be packed in equivalent and symmetrical positions as in cubic and hexagonal close pack-
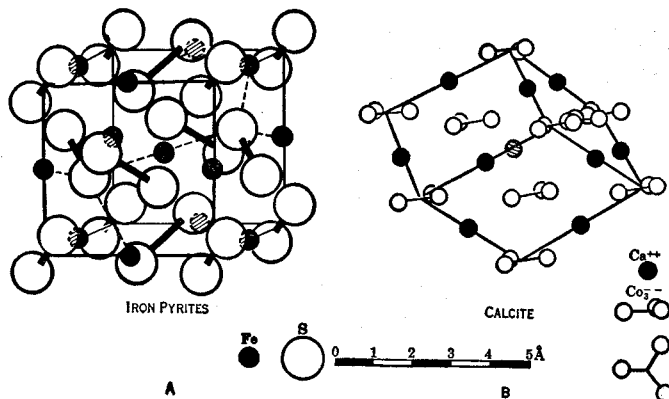

FIG. 91.—STRUCTURES BASED ON THE SODIUM CHLORIDE STRUCTURE

(A) Iron pyrites. In this case the Cl_ ion is replaced by the double sulphur molecule S-S. Each sulphur atom is linked in a tetrahedral arrangement with one sulphur and three iron atoms. (B) Calcite. Here the spherical Cl ion is replaced by the flat CO_3 —ion. This results in the flattening of the cubic into a rhombohedral cell. For the co-ordination of the ions *see* fig. 106

ing [*see* below] while if nearly equivalent positions can be taken into account the $8+6=14$ co-ordination of body-centred packing is permissible) (*see* fig. 84).

If the atoms (or ions) are of different sizes the greatest number of the larger sort that can pack around a smaller one must clearly be less than this, 8, 6, 4, 3 and 2 being lower co-ordination numbers which occur as the relative size of the smaller atom diminishes. The condition for the maximum co-ordination number is a purely geometrical one as Goldschmidt was the first to point out. It depends only on the ratio $r_A:r_x$ where these are respectively the radii of the small and the large atom or ion. The limits for $r_A:r_x$ are 0.732 for 8, 0.414 for 6, 0.225 for 4, and 0.155 for 3 co-ordination respectively (fig. 85). For intermediate values of the radius ratio, the co-ordination must always be that corresponding to the next lower limit. For example, for caesium chloride, $r_{Cs}=1.69$, $r_{Cl}=1.81$, $r_{Cs}:r_{Cl}=0.93>0.732$, the co-ordination number will be 8. For sodium bromide, $r_{Na}=0.95$, $r_{Br}=1.95$; $r_{Na}:r_{Br}=0.49>0.414$, the co-ordination number will be 6; while for beryllium oxide, $r_{Be}=0.31$, $r_O=1.35$, $r_{Be}:r_O=0.23>0.225$, it will be 4.

The co-ordination of the smaller atoms or ions about the larger cannot be determined so simply, for, in general, the number available does not approach that required to form a closed group. In simple cases, however, as in compounds of the type AX (sodium chloride, fig. 82), AX_2 (titanium dioxide, fig. 104), or AX_3 (aluminum trifluoride), it is necessarily equal to a half, or a third respectively of the co-ordination of the larger atom around the smaller. This is the case simply because every bond between A and X atoms must have an A and an X end; the more X atoms there are compared with A atoms the fewer AX bonds can end on any particular X atom.

The average degree of co-ordination is a measure of the proportion of the total space actually occupied by atoms or what may be called its steric density of the structure. The specific gravity is then the steric density multiplied by the average density of the atoms of which the crystal is composed. Thus the metals aluminum and silver, with approximately the same sized atoms ($r=1.4$ Å), have both a steric density of 0.73, but the measured specific gravities are 2.7 and 10.5 respectively because of the greater weight of the silver nucleus. The limit of high density is found for high co-ordination (12, 14), as in the close-packed metals whose structures resemble that of a pile of shot. The limit of low density is given by over-all co-ordinations of 4 or 3, as in the predominantly homopolar structures of diamond (steric density 0.34) or boron (steric density 0.37), the loose silicon-oxygen

CRYSTALLOGRAPHY

framework of quartz (steric density 0.44) and other forms of silica, or the hydrogen-bonded structure of ice (steric density 0.34). In these cases half or more of the structure is unoccupied by atoms and rather resembles a kind of three-dimensional network. As will be shown, the holes in such networks can be readily filled with other atoms, as in the common glasses and in crystal hydrates.

The general degree of co-ordination has an important bearing on the ease of crystallization of different structures. With high co-ordination the successive shells of neighbours, next neighbours, etc., are both more numerous and closer together than with low co-ordination. The distances in terms of the shortest distance and the numbers in brackets are, for instance, 1 (12), 1.41 (6), 1.73 (24) and 2.0 (12) for cubic close-packing, and 1 (4), 1.63 (12), 1.93 (12) and 2.31 (6) for the diamond structure. This implies physically that nearest neighbours count relatively more for low co-ordination structures and that variations in arrangement and even irregularities make less difference to the crystal stability. For that reason high co-ordination structures usually crystallize relatively well, and low co-ordination structures relatively poorly, tending to form amorphous solid aggregates or glasses in which the arrangement beyond the first neighbours is irregular (*see* fig. 86).

Fig. 92.—Two views of the Se₈ ring molecule

Simple Type-Structures.—The concept of co-ordination or the orderly arrangement of atoms around each other in crystal structures serves as a single unifying principle for classifying all crystal structures as modifications of a very few basic models. These models, on account of their simplicity and symmetry, were in fact the first to be studied in the classical early work of the Braggs and first set out in *The Structure of Crystals* in 1913. Indeed some of them had already been anticipated in the work of the earlier theoretical crystallographers, E. S. Fedorov and W. Barlow.

SIMPLE STRUCTURES

FACE-CENTRED (*e.g.*, COPPER) A — BODY-CENTRED (*e.g.*, IRON) B — HEXAGONAL CLOSE-PACKED (*e.g.*, MAGNESIUM) C

COMPLEX STRUCTURES
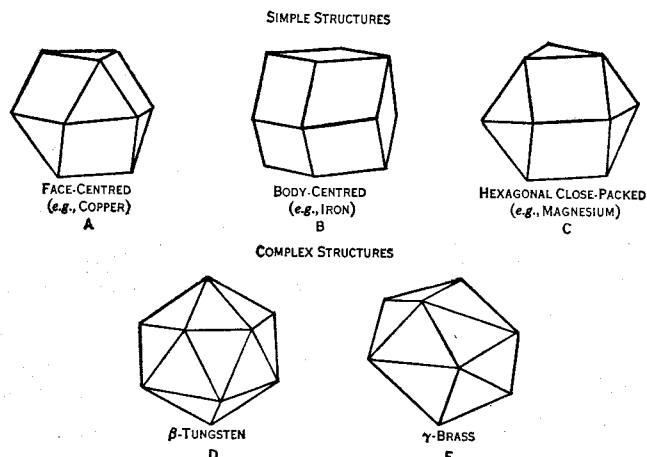
β-TUNGSTEN D — γ-BRASS E

FIG. 93.—ARRANGEMENTS OF NEIGHBOURING ATOMS IN THE STRUCTURES OF METALS AND ALLOYS

Though the geometrical disposition is different, the general high co-ordination of all the structures is evident

They can all be derived from the three most regular ways of packing spheres: the face-centred cubic close-packing (fig. 84A); the hexagonal close-packing (fig. 84C); and the body-centred cubic packing (fig. 84B). These are actually the structures of most metals and simple molecular crystals; those of many other compounds can be derived from them by omissions and substi-

tutions, or by the insertion of other atoms in their interstices.

From the face-centred cubic close-packed structure the addition of another atom half way along the cube edges leads to the simplest of ionic structures, that of rock salt, NaCl (fig. 82), where small sodium ions fit between every six close-packed chlorine ions (steric density 0.64). A relatively smaller ion inserted between four others results in the zinc blende structure, ZnS (fig. 87)—steric density 0.70—which is also the structure of diamond (fig. 88) with its tetrahedral co-ordination of carbon atoms.

The hexagonal close-packed structure differs only from the cubic by the way in which alternate layers of the close-packed planes are placed relative to each other (*see* fig. 84D, E), and consequently has the same steric density 0.73. Thus for every structure derived from cubic close-packing there is a corresponding hexagonal analogue with the same steric density. For rock salt there is the nickel arsenide (NiAs) structure (fig. 89B), for zinc blende the wurtzite (ZnS) structure (fig. 87B), which is also the arrangement of the oxygen atoms in ice.

From the body-centred structure (steric density 0.68) is obtained, by substituting alternative positive and negative ions for cube corners and centres, the caesium chloride (CsCl) structure (fig. 90A) or, substituting only half of the positive centres, the fluorite structure (CaF₂), steric density 0.57₂—*see* fig. 90B.

Other simple structures can be formed by substituting molecular groups or complex ions for the single atoms or ions of the simple
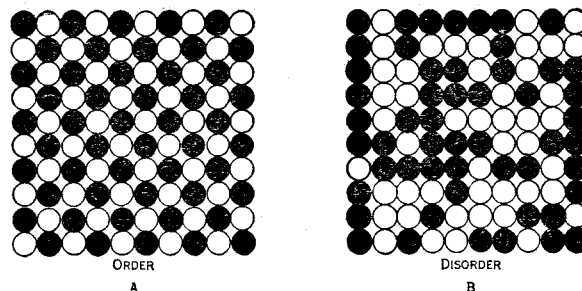
ORDER A — DISORDER B

FIG. 94.—ORDER, DISORDER ARRANGEMENT IN PLAIN SQUARE LATTICE WITH EQUAL NUMBERS OF ATOMS OF TWO KINDS

structures. Thus the structure of solid carbon dioxide (fig.   ) is essentially a face-centred packing of elliptical molecules OCO. The iron pyrites structure is one of rock salt in which the SS group replaces the simple chloride ion (fig. 91A). Similarly in the calcite structure, CaCO₃ (fig. 91B), its place was taken by the flat-

tened ion $\begin{smallmatrix} O & O \\ C \\ O \end{smallmatrix}$.

These few simple structures provide between them the models of the endless range of more complicated arrangements of atoms that are to be found in crystals. They are indeed more in number than the variety of chemical compounds, for each compound is capable of appearing in more than one—sometimes as many as five—different so-called polymorphous crystalline forms depending on the conditions of its formation and growth. In spite of this diversity the principles of construction of crystal structures are relatively few and depend essentially on a combination of special geometry with the particular physical character of the four main types of interatomic forces already discussed.

In all but the simplest structures two or more types of interatomic force can coexist, some of the atoms being bound together by one type of force, others by a different one. In ice, for example, the hydrogen atoms are bound to the oxygen atoms in the same H₂O molecule by homopolar forces, while the molecules as a whole are bound to each other by the far weaker forces of dipole attraction (hydrogen bond). In ammonium chloride, NH₄Cl, which has a CaCl structure, the hydrogen atoms are bound to the nitrogen by homopolar forces, but the resulting positively charged ammonium ion (NH₄)⁺ is bound to the negatively charged chlorine ion by heteropolar ionic attraction. But whereas in chemistry, which considers mainly separate molecules and their reactions, it is the strongest, usually homopolar, forces that are in question, in crystal structure it is the weakest that determine the existence and

CRYSTALLOGRAPHY

818

properties of the crystal. A chain is as strong as its weakest link. For this reason two crystals in which the interatomic forces and the total energy are the same may have widely different properties if the links between the atoms are differently arranged. Thus diamond (fig. 88A) and graphite (fig. 88B) both consist of carbon atoms joined together by homopolar bonds, but in the former case the bonds are all simple bonds and form a three-dimensional mesh-
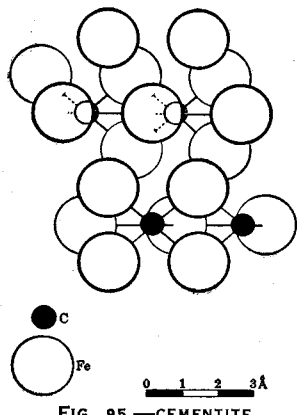
FIG. 95.—CEMENTITE

The iron atoms are arranged in a modified hexagonal close-packed structure with carbon atoms inserted at the centres of trigonal prisms

work resulting in an exceptionally hard compact crystal, in the latter they are joined by aromatic double bonds in two-dimensional sheets which readily slip over each other producing platy crystals of unctuous texture (black lead). Another example is furnished by the contrast in properties between aluminum trifluoride AlF_3, a hard solid melting at 1,040° C., and silicon tetrafluoride SiF_4, a liquid freezing at −55° C. The forces between Al and Si and F are approximately the same but, whereas in the former case they link Al ions together, in the latter all four are bound to one silicon atom forming easily separable molecules.

The degree and kind of spatial continuity of the stronger and weaker forces in a crystal determine the general physical type to which it belongs. Four general types can be distinguished with different degrees of spatial continuity. These can be conveniently referred to by their Greek affixes, which are translations of the German terms first introduced by Weissenberg. They are: (1) neso- types, crystals containing finite units; (2) ino- types, crystals with indefinitely extended fibrous units; (3) phyllo- types, with doubly extended or sheet-like units (4) tecto- types, crystals with trebly extended frameworklike units. They may be likened in common experience to a pile of shot, a bundle of sticks, a pack of cards and a sponge, re-

In the first or neso- type (Weissenberg's *insel*) the stronger forces produce finite closed systems, approximately equidimensional molecules or complex ions, which are in turn bound together by weaker forces. In the simplest case of all, the molecule or complex ion reduces to a single atom or ion. Crystals of the neso- type, which includes the vast majority of all crystals, are roughly isotropic mechanically, that is they show no grain, and if they cleave do so in three or more nonparallel directions. Such are, for instance, common salt, calcite, diamond, and crystals of complex molecules such as camphor, penicillin and strychnine. Closely related are the irregular structures of normal liquids.

In the second or ino- —chain lattice—type (Weissenberg's *ketten gitter*) the stronger forces form indefinitely extended long molecules, or molecule ions, joined together in bundles by weaker forces. Inotype crystals are easily cleavable in directions parallel to the fibres and extremely hard to break across them; they all show marked grain. Where the fibres are crossed, as in the mineral jade or in animal leather, they show great toughness.

The simplest example of ino- structure is that of metallic selenium which can be written . . . —Se—Se—Se . . . Chain lattices are found among all chemical groups: among inorganic compounds, in fibrous sulphur trioxide (SO_3) . . . O S O S O S O . . . .; in

polymetaphosphates ($-PO_3^-$) . . . O P O P O P O . . .; and in

metal silicates ($-SiO_3^-$) . . . Si O Si O Si . . ., such as the pyroxenes. The most characteristic of this group is the amphibole tremolite which contains the double chain ion $Si_4O_{11}^{6-}$—

spectively.
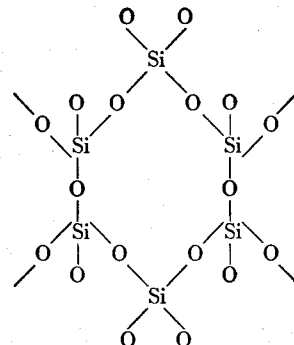
the fibrous character of which is made use of in some kinds of asbestos. With their side links blocked with organic groups, such silicon-oxygen chains have found great industrial use as fibrous or liquid silicones, which are stable at far higher temperatures than organic polymers. In organic chemistry ino- types are represented by the enormous class of fibrous linear polymers: hydrocarbons, such as the artificial polythene $[Ch_2]_n$, or rubber polyisoprene $[CH=CCH_3-C]_n$; carbohydrates or polyglucoses such as cellulose-cotton, linen, wood, rayon and starch; proteins or polyamino-acids such as silk, wool, horn and leather, as well as a host of plastics such as nylon and terylene. Most of such long polymers are crystalline or can be induced to crystallize.

There is a close chemical relation between the linear polymers and the fibrous crystals they form and the cyclic polymers produced by the same units joined in rings, but this brings out the enormous physical difference between them. For example, glassy volatile SO_3 has ring molecules—
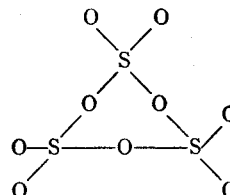
with exactly the same composition as the infusible fibres—
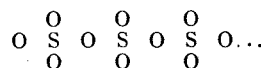
The element sulphur exhibits the whole range of change when it is heated. Flowers of sulphur contain crumpled ring molecules, S_8—

FIG. 96.—STEEL STRUCTURES

AUSTENITE (γ-IRON) A   MARTENSITE (TETRAGONAL) B   FERRITE (α-IRON) C
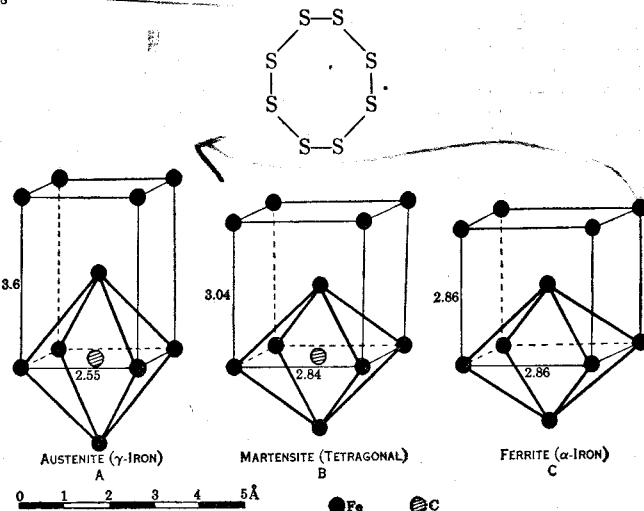
On heating, these break open and form the long chains of viscous melted sulphur, $S\infty$—,—which on

CRYSTALLOGRAPHY

SELENIUM
A

ARSENIC
B

WHITE TIN
C

0 1 2 3 4 5Å
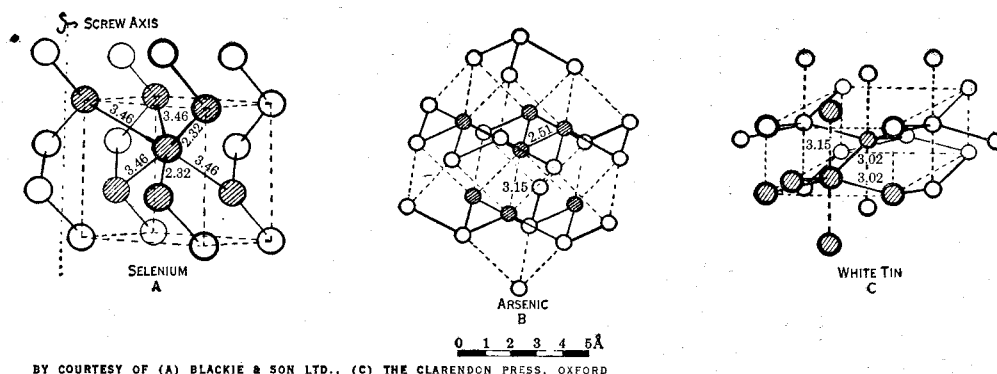
FIG. 97.—SEMIMETAL STRUCTURES TO ILLUSTRATE (8-N)RULE

further heating give the simple molecule S=S (S_2). Sudden cooling of the viscous sulphur gives rubberlike plastic sulphur with variously coiled chains which in time curl again into the stable S_8 ring molecules of crystalline sulphur. This transformation of compact into elongated molecular grouping, reversible or irreversible, occurs in all kinds of linear polymers, particularly in proteins where it is responsible for the phenomena of denaturation, as in the hardening of egg white by boiling, or in the clotting of blood. At higher temperatures or in solution linear fibre molecules give viscous liquids or solutions showing a preferred orientation of the fibres in relation to the lines of flow. An intermediate condition is one where there is a spontaneous parallel orientation of the fibres giving rise to the nematic or threadlike type of liquid crystals shown in such diverse substances as vanadium pentoxide, para-asoxy anisole and tobacco mosaic virus.

In the third or phyllo- type of structure the layer lattices (*schicht gitter*), stronger forces bind the atoms into sheets of finite thickness or indefinite extent. Such sheets are held together like the leaves of a book in parallel piles forming characteristic platy crystals. The simplest example is that of graphite (fig. 88B), already referred to, with its flat sheets of carbon atoms 1.4 Å apart, arranged in regular hexagons and separated by the much larger distance of 3.4 Å. Plane sheets are also to be found in the metals zinc and cadmium. Puckered sheets are found in metallic arsenic (fig. 97B), antimony and bismuth. Among sulphides and chlorides layer lattices are common, as in molybdenite, MoS_2 (fig. 99B), and cadmium chloride, $CdCl_2$ (fig. 99A). They are also found among the hydroxides such as slaked lime, $Ca(OH)_2$, and gibbsite (bauxite), $Al(OH)_3$, and in some hydrated salts, notably gypsum, $CaSO_4.2H_2O$, whose characteristic diamond-shaped crystals (macles) were the origin of the old-fashioned lattice window before glass came into use. More rigid sheets are found among the silicates as a result of the stability of the $-Si_2O_5^{2-}$ group—
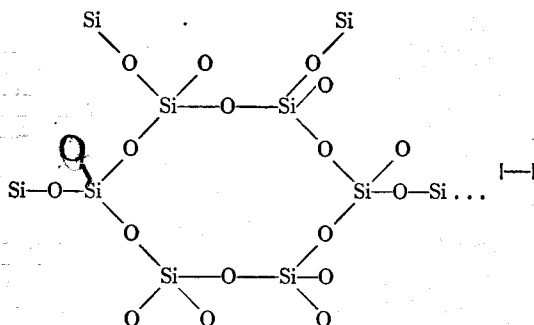
which is the basis, with different amounts of aluminum substituted for silicon, of the structures of micas and clays.

In organic crystals, plane two-dimensional networks of indefinite size, bound together by covalent forces, are confined to graphite derivatives, but layer lattices are here formed by the apposition of linear molecules held side by side through Van der Waals's forces into sheets of different thicknesses, these sheets being in turn held together by weaker Van der Waals's forces at the end of the

molecules. This is the characteristic structure of all fatty substances—paraffins, fatty acids, natural fats (triglycerides) and soaps, including, besides those based on single paraffin chains, the linear ring systems of the sterols. It is the existence of sheets in these cases that underlies the characteristic greasy and smearing properties of all these substances. The sheets persist to a certain extent in the liquid and in solution, giving rise to the smectic (greasy) liquid crystals, such as are found in the myelin sheath of nerves, and to the water-soluble miscelles of soap incorporating grease which is the basis of its washing properties.

The common characteristic of layer lattices is the single cleavage which runs across the weaker links separating the sheets. This is most evident in micas and gypsum. Another characteristic evident when the forces between layers are relatively weak is the capacity of the layers to slip over each other while remaining parallel like a pack of cards. This is the most common basis for the property of plasticity in certain solids, particularly in clays and fats. The other group of substances that shows plasticity—the metals—derives it from the same common structural pattern. Most workable metals and simple alloys have structures which can be considered as comprising parallel sheets like the horizontal layers which are formed in any pyramidal piling of shot. Such sheets of atoms can slide over each other without destroying the continuity of the metal structure and crystal physics.

Another characteristic of layer lattices is the readiness with which they can form what may be called sandwich structures in

CUPRITE (Cu_2O)

0 1 2 3Å

A

TENORITE (CuO)

0 1 2 3Å

●Cu ◯O

B
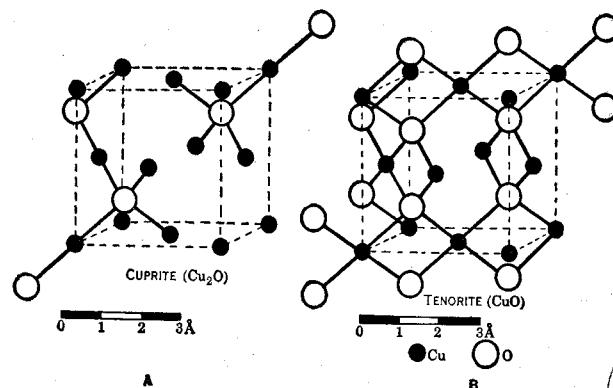
FIG. 98.—OXIDES OF COPPER

These illustrate the way in which the oxygen atoms are inserted in an expanded face-centred copper structure and the tendency of the copper atom to linear or square rather than tetrahedral co-ordination

which atoms and molecules can be attached to the outer surfaces of each layer and thus come to fill the space between the layers. The interstitial material causes the layer lattice to swell in one direction only. Thus graphite can absorb some metals, and micas and chlorites take up or exchange ions.

The most notable example, however, is given by the clays, particularly those very finely divided hydrated clays, montmorillonite (bentonite) and tillite—the swelling clays—which play such a predominating role in the soil. These can take up not only varying amounts of water and ions, but also incorporate a wide range of organic substances from fats to proteins. It is this property that gives these clays, in the form of fuller's earth, detergent powers like those of soaps and for essentially similar reasons. The capacity of layer lattices to form sandwich structures is of particular importance in chemistry. Such substances form the best catalysts (*see* CATALYSIS) because the extensive surface and the regular arrangements of atoms in them favour specific combinations and dislocations of small absorbed molecules. Thus clays

are the basis of catalytic cracking and the activated silica and alumina used in other catalytic processes have been found to have claylike structures.

The ion- and phyllo- types of relative internal binding are not absolutely distinct. Some fibrous molecules are not so much cylindrical as flat like ribbons, and some sheets are more closely bound in one direction than another. Thus platelike gypsum can also be found as fibrous alabaster or as coherent, set, plaster of paris. Indeed it would appear that the interlaced fibrous character is

CADMIUM CHLORIDE (CdCl₂)

MOLYBDENUM SULPHIDE (MoS₂)
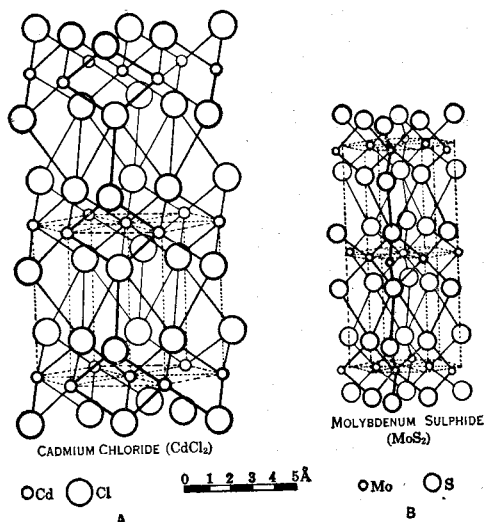
○Cd ◯Cl   0 1 2 3 4 5Å   ○Mo ◯S

A   B

FIG. 99.—LAYER LATTICES

The arrangements of the layers are based on hexagonal packing and only differ by the arrangement of 6 Cl ions around a Cd ion in octahedral co-ordination (A), while 6S atoms are arranged around a Mo atom in the form of a trigonal prism (B)

necessary to good cementing properties. Set portland cement or concrete seems also to owe its properties to intergrown ribbons of the hydrated silicate, tobermorite, $CaSiO_3.2H_2O$. The shrinkage of concrete on drying may be due to loss of water between the silicate layers.

The fourth or tecto- —three-dimensional framework—type structure is not geometrically distinct from the first or neso- type in that it exhibits no particularly favoured direction in space and possesses no marked grain or cleavage. It differs physically, however, by the looseness or lacelike quality—low co-ordination and steric densities (usually less than 0.5)—of the main structure, which may or may not contain other atoms or molecules not firmly bound to it. This type of structure is represented by quartz, the feldspars and the zeolites among minerals, and artificial varieties rapidly increasing in scientific and industrial importance at mid-20th century. This is because the property of capturing and holding atoms and molecules gives such substances selective powers, and because the presence of inserted groups can modify the properties of the enclosing substance in remarkable ways. Among metals tecto- types are found in the polyborides, such as $B_{13}Zn$, which contain frameworks of boron atoms in which the large zinc atoms are inserted. Of enormously greater importance are the so-called interstitial metal compounds of hydrogen, boron, carbon and nitrogen in the ferrous metals of which steel, with its great range of varieties, is the most eminent example. These, however, as most of the space is occupied by the metal atoms, are best treated with other metals and alloys.

Framework structures are found in all compounds where oxygen ions are shared between two other ions and where these links are distributed in three dimensions. To this type for instance belong the multiple derivatives of tungstic oxide, WO_3, a rectangular framework in which each oxygen is shared between two tungsten ions resulting in an openwork structure (steric density .054), in which there is room for other ions. This occurs among the perovskite ($CaTiO_3$) structures, of which one member, $BaTiO_3$, has notable ferroelectric properties. Most typical of framework structures are the various forms of silica and the so-called tecto-

silicates of the acid rocks—the superficial volcanic minerals analcite, leucite and the zeolites—where low pressure leads to loose structures; and the deep, plutonic minerals, feldspars, where high pressure leads to a collapsed silicate structure and compactness. The conditions in silicon aluminum oxygen frameworks are favourable for the formation of glasses. Here the excess negative charge of the silica-alumina framework is balanced by positive ions, such as sodium, potassium or calcium, in the interstices, so loosely held in some cases that they can be washed out with resultant shrinkage.

Corresponding irregular structures with homopolar binding are found in the cross-linked polymer resins, which are now made to capture ions and thus, for example, by removing in turn sodium and chlorine ions, are used to filter salt out of sea water, or, in the form of kryllium as a soil improver. Even more specific are the regular crystalline compounds in which a relatively firm framework lattice, maintained by hydrogen bonds, is constructed to enclose molecules of particular shape and size, the so-called clathrate compounds. The simplest of these, the cryohydrates, are built of extended frameworks of water molecules, forming a kind of expanded ice in the holes of which inert atoms such as argon, small molecules such as sulphur, or even ions of different signs, can find a place. The dipolar molecule urea, $^-O=C-(NH_2)_2^+$, and its derivatives can form a great variety of these with
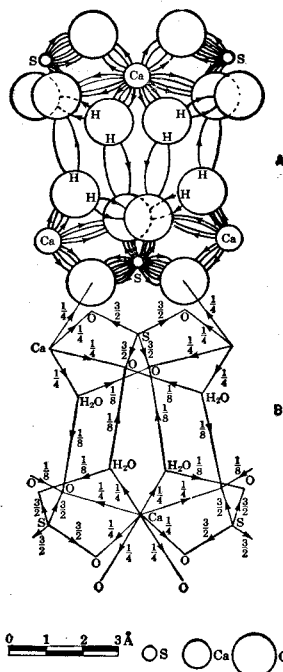
0 1 2 3Å   ○S ◯Ca ◯O

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FIG. 100.—IONIC CO-ORDINATION IN GYPSUM

The structure (see fig.) is shown in two parts, (A) showing diagrammatically the lines of force emanating from positive ions and terminating on neighbouring positive ions. The number of lines indicating roughly the strength of the bond. (B) The electrostatic valence diagram. On oxygen ions the total is -2, on water molecules 0

hollow compartments enclosing, for example, straight-chain and not branched-chain hydrocarbons. By using asymmetric molecules for the framework, such as d- or l- tri-o- thymotide, crystals have been made that can pick out and assimilate right-handed from left-handed molecules. The possibilities inherent in clathrate crystals were only just beginning to be realized in the mid-20th century. They promised to provide the most delicate and specific of chemical reagents equivalent in their action to picking molecules by hand.

CHEMICAL CRYSTALLOGRAPHY

The considerations so far used to distinguish the different crystal types have been geometrical and serve to account for the more apparent physical appearance and behaviour of the resulting materials. An entirely independent principle of classification is one based on the chemical nature of the atoms constituting the crystal and more particularly on the nature of the predominant type of interatomic force ultimately responsible for holding the crystal together. This classification, based on substance rather than form, divides crystals into four main categories: (1) metallic; (2) homopolar; (3) ionic; and (4) molecular. The first three roughly correspond to the field of inorganic chemistry, the fourth to that of organic chemistry. The distinctions between these classes are not sharp and many intermediate cases occur, but they can furnish the basis of a good working classification.

Such a classification, though essentially chemical, cannot be expected to follow traditional chemical lines. This is because in the first three categories, and especially for metals, the arrangement of atoms in the structure, and even the existence of any particular

CRYSTALLOGRAPHY

compound, is a consequence of crystallographic geometrical factors the nature of which was brought out only by X-ray analysis. A rational theory of alloys and intermetallic compounds was only made possible by this means, and the same is largely true of the silicate minerals. With organic substances the case is somewhat different. Except for very intricate molecules, such as those of penicillin or proteins, the inner arrangement of the atoms in the molecule has been, or could be, determined by the methods of classical organic chemistry, though even there far more detailed information could be obtained by X-ray methods. The arrangement of the molecules to form the crystal, however, lies beyond the scope of organic chemistry, and so therefore must the crystallographic classification of organic substances, which must depend more on the outer form and nature of charged groups than on the inner structure of the molecules.

Metals and Alloys.—Though metals have been used since the beginning of civilization and their properties well enough understood in practice, it was only after the application of X-ray crystallographic methods in conjunction with the quantum theory that any coherent and rational account could be given of them. Many of the puzzling features of metal chemistry have been elucidated, particularly the laws of determining the atomic proportions in intermetallic compounds, which are notably different from those in the rest of chemistry. In particular Dalton's law of constant proportions, which stipulates simple numerical relations between the number of atoms of different kinds in a compound, does not apply to metals. The ratios need not be simple and can be variable within wide limits. What defines a compound is not its formula but the existence of a single phase (in the thermodynamic sense) characterized by a definite crystal structure but without definite composition. Such a phase, particularly simple phases such as those of cubic close-packing (α solid solutions), may contain many kinds of different atoms without changing its identity.

The metal world is indeed both physically and chemically a world apart. It owes its common features to the defining characteristic of metals, the presence of free electrons, or more correctly phrased to that of unfilled bands of electrons. It is this that gives rise to their brilliant appearance and the electrical conductivity that distinguishes metals from all other substances. For these are insulators which, though they may be more or less deeply coloured, are essentially transparent. If all that glitters is not gold it is certainly a metal of some sort. The free electrons in metals and alloys furnish the cement which holds the atoms together. Metals indeed may be considered as compounds between positively charged ions and pervasive negatively charged electrons. It is the general nonspecific character of this metallic type of binding that greatly simplifies the chemistry of metals.

If two metallic atoms are brought close together the determinate energy levels of their outer electrons open out into bands giving rise to a net energy loss which serves to bind them together. This will be the case whether the atoms are the same or of different kinds. In ordinary language all metal atoms attract each other irrespective of their nature. The more atoms aggregate together, forming a crystal or a drop of liquid metal, the more smeared out do the electron energy bands become. The outer electrons in such an aggregate are common to the whole system and are no longer attached to individual atoms. The strength of the binding depends on the average electronic structure of the constituent atoms. The structure of the aggregate will also depend partly on this and partly on geometrical factors such as the sizes of the different atoms. This results in general in a much greater fundamental simplicity in metal and alloy structures than is found elsewhere. There are very few immiscible liquid metals; most metals all run together in the melt. Different atoms are mixed higgledy-piggledy and the properties of the liquid are an average of that of its constituents.

In metals the difference between the crystalline solid and the irregularly packed liquid is less than it is in other classes of substances. The increase in volume on melting is rarely more than 4%, as compared with 20% in the rare-gas liquids, indicating that the atoms in the liquid must be nearly close packed. The steric density of a metal or alloy is rarely less than 0.65 and most approach 0.73. Certainly in all the true metals the crystalline phase is a close-packed or nearly close-packed one; that is, it is of the cubic close-packed, hexagonal close-packed or body-centred type. These three types comprise them the structures of the great majority of metals and alloys, and a large number of more complex structures are simply slight variations of one or another of these, or represent intermediate arrangements (fig. 93). There is little difference in internal energy between these three structures, as witness the fact that a considerable number of elements, e.g., Fe, Ca, Co, Ce, Cr, La, Tl, are known to occur in two of them and the element Sr occurs in all three. Thus pure iron is body-centred up to 906° C. (α, magnetic, and β, nonmagnetic ferrite, phases) when it changes to the face-centred variety (γ, austenite, phase), but reverts to the body-centred (δ phase) at 1,403° C. The presence of slight impurities moreover can make either the α or the δ phase stable over a far wide range of temperatures. In the case of cobalt the face-centred and hexagonal close-packed forms are so much alike that without special precautions a specimen will contain portions having both structures.

The feature of approximate close-packing and indifference as to atomic neighbourhoods is common to all metals. To differentiate between them account must be taken of differences in electronic

TRIANGLE   TETRAHEDRON   OCTAHEDRON   DODECAHEDRON

A   B   C   D

TETRAHEDRA SHARING CORNER   OCTAHEDRA SHARING EDGE   OCTAHEDRA SHARING FACE
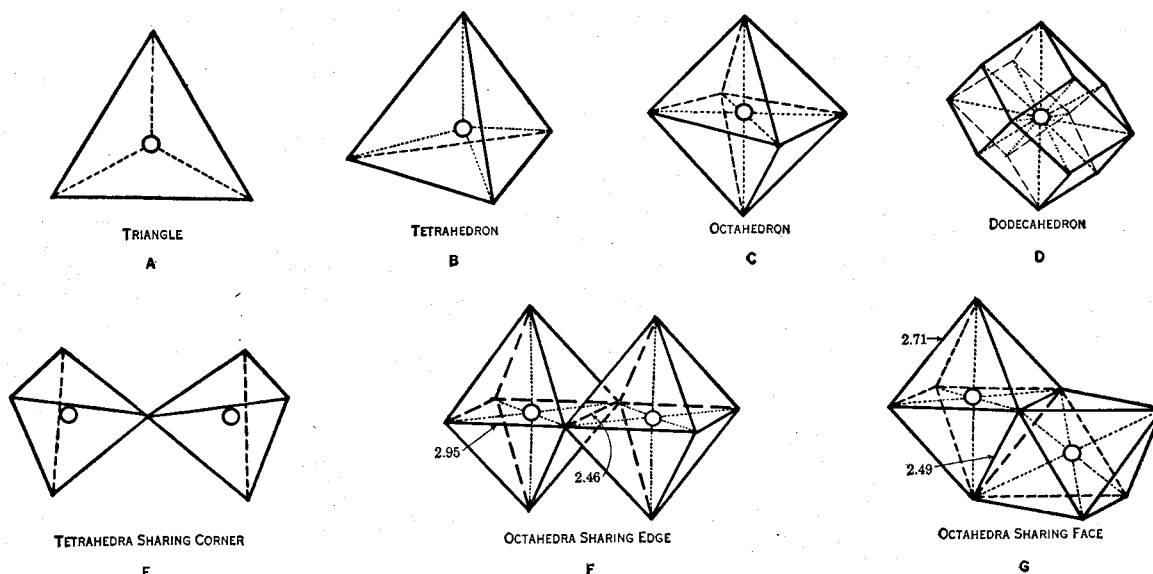
E   F   G

FIG. 101.—CO-ORDINATION POLYHEDRA A B C D SHOW TYPICAL POLYHEDRA, (E) (F) (G) SHOW HOW THEY CAN SHARE CORNERS, EDGES OR FACES; THE VALUES SHOWN FOR (F) AND (G) ARE DERIVED FROM TiO_2 AND Al_2O_3 RESPECTIVELY

CRYSTALLOGRAPHY

structure and in atomic size. The first affects the physical nature of the resulting metal or alloy; the second determines the geometry of possible arrangements.

Metals have been defined as substances with unfilled electronic bands. In this respect they may differ by the degree to which the levels are unfilled and by the number of bands available for filling. The classification of metals along these lines follows the periodic table (*see* Table II). Three major groups are distinguishable. The simplest metals, those of the alkalis and alkaline earths—the
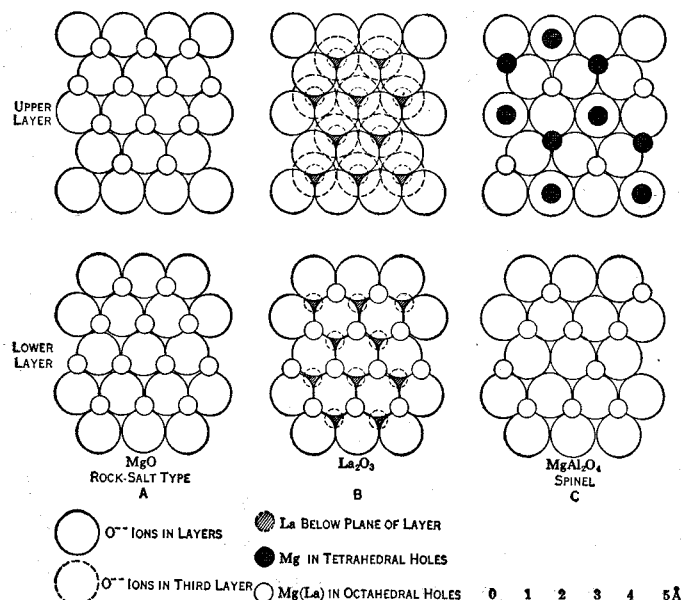
FIG. 102.—CLOSE-PACKED ANION STRUCTURES DERIVED FROM THE CUBIC—ROCK SALT—TYPE

The anion (oxygen ion) packing is the same cubic close-packing in all three cases. In (A) one complete set of octahedral holes is occupied by Mg^{2+} ions. In (B) one out of every three layers of La^{3+} ions is omitted—the second in this case. In (C) the octahedral holes in the first layer are occupied by Al^{3+} ions, one in four being left vacant. In the second layer there is an even distribution of metal ions with two Mg^{2+} ions in tetrahedral holes and one Al^{3+} in an octahedral hole

A-group metals—have one or two electrons in one unfilled band. These electrons are most loosely bound and the metals are the most electropositive.

The next group is represented by the corresponding B-group metals of the first to the sixth columns of the periodic table, such as Cu, Zn, Ga, Sn, Sb, Se. These, as the number of electrons increases, tend to fill up the vacant electron band and even, in the latter columns, tend to borrow electrons to complete them. These metals are correspondingly intermediate through a semimetal state to electron-sharing homopolar compounds. The metals of the first two columns, the coinage metals, Cu, Ag and Au, and Zn, Cd and Hg, behave very similarly to the A group and so in some respects do Sn and Pb.

Between these two groups is the large group of the transitional, or group T, metals, ranging from Ti to Ni, from Zr to Pd, and from Hf to Pt, with which may be included the metals of the rare earths. All these are characterized by having two unfilled electron bands with an easily alterable equilibrium between them. This leads to increased binding between the atoms, small interatomic distances, high melting points, hardness and poor electrical conductivity. The marked difference between the metals of the A and B groups on the one hand and the transitional group on the other provides the scientific basis for the great technical division between nonferrous and ferrous metals. Nearly all the metals used for alloy steels belong to the transitional group.

The laws of alloy formation are easier to understand if a metal phase is considered as a compound between atoms, disregarding their differences, and free electrons. The effective electron/atom ratio is generally more important than the ratio between the number of atoms of each element present—the ratio that dominates

other fields of chemistry. This is, for example, the explanation of the similarities between the compounds of the coinage metals (and some of the transitional metals) and A- and B-group metals. Thus in the so-called γ brass compounds $Mn_3^1 Zn_{10}^{20}$, $Fe_3^1 Zn_{10}^{20}$, $Cu_5^5 Zn_8^{16}$, $Cu_9^9 Al_4^{12}$, $Cu_{31}^{31} Sn_8^{32}$ ($Cu_{11} Sb_2$) (the superior numbers stand for the contribution of the metal atoms to the common electron pool), though very different in apparent formulae, all have the same complex structure with 52 atoms in the cell. However, as Hume-Rothery pointed out, the number of free electrons available, counting none for T metals, one for Cu, 2 for Zn, 3 for Al and 4 for Sn, is 84 per cell in each case, so that the general formula could be written $M_{13}e_{21}$, where M stands for the metal atoms indiscriminately and e for the free electrons. H. Jones explained the stability of this and other analogous compounds, such as the body-centred $M_2e_3 = M_{14}e_{21}$ or the hexagonal close-packed $M_4e_7 = M_{12}e_{21}$, in terms of the filling of a so-called Brillouin zone in electron levels, which confers low energy and high stability.

This treatment brings out the characteristic of metal structures of having a common pool of electrons which may be provided by some atoms and taken up by others. Thus in the Heusler alloys (copper-aluminum-manganese alloys), which are ferromagnetic though they contain no iron, the presence of copper and possibly of aluminum is sufficient to raise the electronic level of the manganese to that of iron. Another interesting case is furnished by the different forms of manganese. The first of these forms, α, has 58 atoms in a cubic cell in a structure which is a complex variant of close packing. This is also the structure of the alloy $Al_{12}Mg_{17}$. Similarly, the second, β, has 20 atoms in a cubic cell—also nearly close-packed—and is identical with that of the alloys Ag_3Al and Ca_5Si. This strongly suggests that in these forms manganese is not behaving as a simple element, but rather as an alloy of two kinds of atom, one with more and one with fewer electrons.

Easy substitution of different atoms is, however, only possible if these are of approximately the same size. This holds for most of the transitional elements which only range in atomic radius from 1.60 to 1.25 Å, all but five being less than 1.41 Å, and explains the mutual alloying possibilities of the ferrous metals. Where the size differs, notably with respect to the alkali metals (the radii of Li, Na and K are 1.56, 1.91 and 2.38 Å respectively) and to a lesser extent to Mg and Al, structures are largely determined by considerations of packing such as those of NaK, $MgZn_2$, Cu_2Mg and $CuAl_2$.

The technical importance of metals is largely dependent on their mechanical properties, particularly their plasticity—malleability and ductility. This in turn depends on the possibility of the existence of extended planes of atoms capable of slipping over each other, which can only occur in the simplest structures of the face-centred, body-centred and hexagonally close-packed types. Complicated intermetallic compounds, lacking such glide planes, are invariably brittle and of little use except when extremely hard. The greatest interest is therefore concentrated on such simple phases as those whose properties can be modified either by the substitution of some atoms or the addition of others. These two types of solid solution are the basis of most useful alloys, substitutional among the nonferrous metals (as in brasses, bronzes and duraluminum) interstitial in the ferrous (as in steels).

In most simple metal structures the atoms of one kind can be substituted for another without changing the basic crystal structure. These are solid solutions. This may be done to an unlimited extent, as in the case of silver and gold with their almost identical lattices ($a = 4.078$ and 4.070 Å respectively), or on a very limited scale as in duraluminum (limiting solubility of copper in aluminum 1% at room temperature). The resulting alloy is modified in one respect by a change in electronic level which may tighten or loosen the whole structure, and in another by the irregularity introduced, which, by interfering with easy glide, hardens the structure as well as raising its electrical resistance.

In certain cases prolonged annealing removes this irregularity and leads to an ordered substitution solution (*see* fig. 94) in which the different kinds of atoms alternate in regular sequences. The ordering removes the obstructions and leads to softening and increased electrical conductivity. The compounds Fe_3Al and Cu_3Au

are examples of such order, which is revealed by X-rays through the appearance of so-called superlattice lines. Permalloy, FeNi₃, is an example of a particularly useful ordered lattice. In most cases the range of solid solubility is greater at high temperatures. On cooling one constituent is precipitated, but if this process is slow enough it occurs in the very body of the lattice of the other in the form of fine plates only a few atoms across. The strains these set up in the lattice interfere markedly with glide, and this process provides the basis for many age-hardening techniques.

One characteristic of the transitional metals is their ability to incorporate in their lattices small quantities of the elements of the top row of the periodic table, H, B, C and N. When present in small enough quantities these elements fit into the interstices of the metal atoms slightly increasing the average distance between them and giving rise to interstitial solid solutions. It is probable that to do this the small atoms part with most of their electrons to the free pool of the metal and are reduced to ions of a fraction of an Ångstrom unit in diameter. An example of this is the interstitial solution of hydrogen in solid palladium in the form of protons which can move freely through the metal. In larger proportions interstitial atoms usually stabilize some arrangement other than the normal metal and form interstitial compounds such as the extremely hard WC, used for tools, or the carbide of cast iron, cementite, Fe₃C (fig. 95).

An intermediate state of great importance is found in the iron-carbon system. The solubility of carbon in face-centred γ-iron (austenite), stable above 900° C., is relatively high (1.7%), while that in α iron (ferrite) is very low.

On slowly cooling saturated γ-iron, the carbon comes out as cementite, but on rapid cooling the mixture turns into an unstable tetragonal compound, martensite, containing carbon, intermediate between austentite and ferrite and approaching the latter more closely as the carbon content falls (fig. 95 and 96). (For 1.5% C a=2.83 Å, c=3.04 Å; for 0.7% C a=2.85 Å, c=2.94 Å; for ferrite a=2.86 Å.) The plates of martensite are keyed to the ferrite so well that the effect of the strains caused by these slight differences is to brace and harden the structure. By reheating and suitable quenching, the size and distribution of the martensite crystals can be controlled, and this is the basis of the tempering of steel. Corresponding changes can be carried out using nitrogen in casehardening. For the last 3,000 years these processes have been successfully carried out without any inkling as to their nature.

Semimetals.—The boundary of the metallic structures is a particularly hard one to draw, as has been long recognized in the terms semimetallic and submetallic. Usually a set of substances can be found with properties intermediate between what is undoubtedly a metal, such as lead, and what is undoubtedly not, such as diamond. The same element (e.g., selenium) may function sometimes as a metal and sometimes as a nonmetal. The most valid criterion is the electrical one based on the presence of unfilled electron shells and showing itself in a metallic type of conductivity, absolutely large and decreasing with temperature. Many substances, such as iron pyrites, having a metallic appearance reveal their nature by the semiconductor type of conductivity, small and increasing with temperature.

Elementary metals and compounds between metals may lose their metallic character by changes in two different directions, one in that of ionic and the other of homopolar compounds. The first occurs when metals of electropositive character are combined with those of electronegative. In this case positive and negative ions tend to be formed, as for example in Mg₂Si and Mg₂Sn, which have an ionic fluorite (fig. 90B) type of structure. The formation of such ionic compounds is usually revealed by their exact composition and their stability.

On the other hand, the tendency to form homopolar compounds is practically confined to the compounds of the B-group metals among themselves and to the compounds of the transitional metals with fifth-and sixth-column elements. Wherever the possibility exists to complete the particularly stable eight-electron shell by electron sharing this will lead to structures whose space directed valencies show their homopolar tendency. This is the basis of the so-called (8-N) rule among the semimetals. It states that if N is

the group position in the periodic table, or the average group position of an element, or of the elements, in a homopolar compound each atom will tend to make (8-N) homopolar bonds shorter and stronger than any other it may make of a more metallic character. Thus the halogens (column 7; 8-N=1) can only form one and must therefore exist as diatomic molecules though the heaviest of them, astatine, may well be a metal. The sixth column (8-N=2) can form chains or rings: selenium and tellurium form structures with two short bonds, 2.32, 2.86 Å, and four long, 3.46, 3.74 Å (fig. 97A).

In the fifth column for As, Sb and Bi, (8-N=3), three short bonds (2.51, 2.87 and 3.10 Å) are formed and three long (3.15, 3.37, 3.47 Å) (fig. 102B). The fourth column (8-N=4) is transitional; C, Si and Sn (gray) are purely homopolar with only four tetrahedral valencies. In white (ordinary) tin (fig. 97C), however, the metallic character asserts itself by the collapse of the diamond structure along one of the cube axes leading to a structure with four short bonds (3.02 Å) and two long (3.15 Å). With lead, as in general with the multiple electron atoms at the lower part of the periodic table, the structure is purely metallic.

Apart from these transitional forms of the elements, there is one widespread structure intermediate between metallic and homopolar types, namely that of nickel arsenide, which is another six-co-ordinated structure (see fig. 89B) where each arsenic atom is surrounded by six nickel in an octahedron, while each nickel is surrounded by six arsenics in a trigonal prism, this being the hexagonal variant of the rock-salt structure.

Homopolar Crystals.—Structures in which the atoms are held together throughout by homopolar forces are rare, as they form a
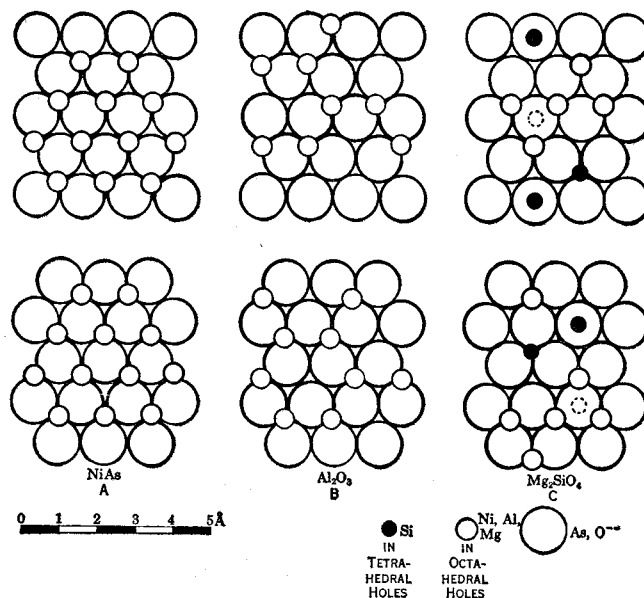
FIG. 103.—CLOSE-PACKED ANION STRUCTURES BASED ON THE HEXAGONAL —NICKEL ARSENIDE—TYPE

The anion—arsenic—arrangement is the same hexagonal or pseudohexagonal close packing in all cases. In (A), nickel arsenide, a complete set of octahedral holes is occupied in each layer but here, unlike fig. 89 (A), the nickel atoms on every layer are superposed. In (B), corundum-haematite, one in three of the octahedral holes in each set in each layer is left vacant. In (C), olivine, which has an orthorhombic pseudohexagonal structure, half the octahedral holes in each layer are filled with Mg²⁺ ions and in addition Si⁴⁺ occupy tetrahedral holes

relatively narrow transitional zone between the metals on the one hand and the ionic compounds on the other, and except for the diamond group all partake of one or the other nature. Although in quantity they do not compare with ionic compounds, as the minerals of the sulphide ores they are of great economic importance. Most of the structures, because of their simplicity, have already been described in this article. The type structure is that of the diamond or of zinc blende (fig. 87A), characterized by its fourfold co-ordination. It is found for all binary compounds with atoms

equidistant from the fourth column of the periodic table, *e.g.*—

I VII II VI III V IV IV
Cu Br Zn S Ga As Ge Gl

that is, with an electron atom ratio of 4:1 and wide substitution, and can occur as long as that ratio is preserved. Where this is ordered, distinct minerals such as chalcopyrite, $CuFeS_2$, and stannite, Cu_2FeSnS_4, are formed. A variant almost equivalent structure is that of wurtzite (ZnS; *see* fig. 87B) the hexagonal dimorph of blende. It has also a number of derivatives such as emargite Cu_3AsS_4, and wolfsbergite, $CuSbS_2$. The blende and wurtzite types can co-exist in the same crystal in a great variety of ways, as exemplified in the different forms of the most typical homopolar crystal, carborundum, CSi. Another variant found in the platinum and copper group is for the bonds to be arranged in a square rather than a tetrahedron. Cupric oxide (CuO), tenorite, has a deformed square co-ordination. In cuprous oxide (Cu_2O), cuprite, the structure is still further simplified by copper's having two oxygen neighbours only. Both may be considered as interstitial compounds of oxygen in metallic copper. Homopolar crystals are also to be found in the ino- (fibre) form, either simple as in the case of cinnabar, HgS (S–Hg–S–Hg–S. . .), double as in stibnite, Sb_2S_3, or consisting of linked tetrahedra in silicon sulphide SiS_2—

$$\ldots \overset{S}{\underset{S}{>}Si<}\overset{S}{\underset{S}{>}Si<}\overset{S}{\underset{S}{>}Si<}\ldots$$
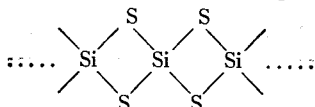
and also in the phyllo- (sheet) form both in the CdI_2 and MoS_2 structures (fig. 99).

In most homopolar structures apart from elements, bonds are formed between unlike atoms. In a small but important group however bonds are formed between atoms of the same kind as well. This is the case in the iron pyrites structure where sulphur atoms are attached in pairs—each being bound in addition to three iron atoms (fig. 91A)—and in its lower symmetry dimorph, marcasite.

The particular character of homopolar structures, intermediate as they are between ionic and metallic, shows itself in their electrical properties. Nearly all are semiconductors, and many show anomalously high photoconducting, fluorescent, phosphorescent thermoelectric and diamagnetic properties. All these properties derive from the existence of electron bands just under- or just over-filled with electrons and for that reason peculiarly susceptible to the effects of impurities and lattice defects. These properties were increasingly made use of in photocells, fluorescent lighting and television, and in transistor substitutes for electronic valves.

Ionic Structures, Salts and Stones.—The special fixed character of these substances has long been recognized. If, of the old *tria prima* of the alchemists, fluid mercury is the common nature of the metals, and fiery sulphur of the homopolar compounds, then fixed salt is the common nature of the ionic compounds—the salts and stones, the acids and alkalis of everyday life. Ionic compounds are characterized by the presence in them of charged rather than neutral atoms. The ions of which they are composed are held together by mutual electrical attraction and the crystals can accordingly be decomposed by the action of other ions or electrical dipoles. Where the attraction is relatively weak (with large and low-charged ions) they are all soft, easily fusible and soluble in water; where it is strong (with small and highly charged ions) they are hard, melt at high temperatures and dissolve only in fused soda. In chemical terms, the vast majority of ionic compounds are those of metals with elements of the sixth and seventh columns of the periodic table of which by far the most important is oxygen, either simple as oxide or as oxy- acid, and after that the halides—fluorine, chlorine, etc.

Because they contain no partially filled electron bands ionic compounds are generally transparent and coloured only if they contain coloured ions with unfilled inner electron shells, such as the blue ions of copper, or the brown and green of iron. They usually crystallize well and are familiar to us as crystals of salts or as gem stones and rock crystal. It is impossible to describe here the great variety of ionic crystal structures—several thousand are known—but something can be said of the general principle of their

construction and of a few of the most important structures.

The first guiding principle is that of the co-ordination of atoms—or, here, of ions—of determinate size. Here, in addition, as the elementary consequence of the existence of charges of two kinds, is the requirement that negative ions must be co-ordinated around
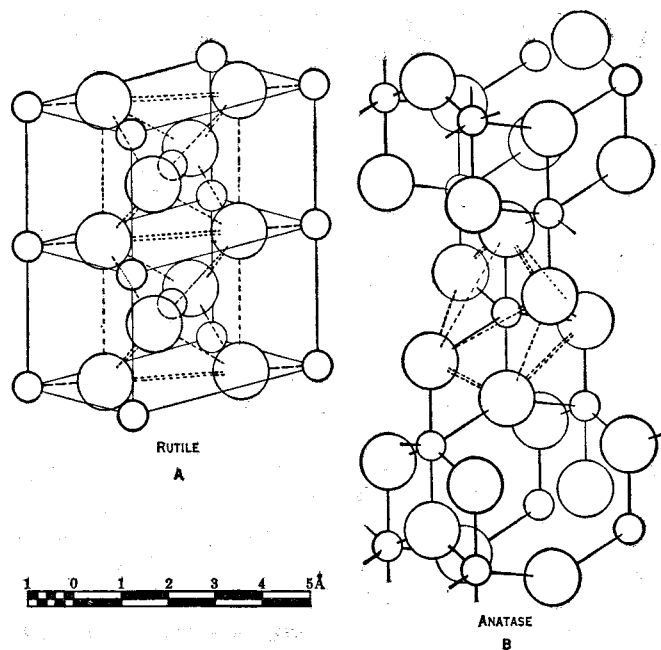

RUTILE

A

ANATASE

B

FIG. 104.—TITANIUM DIOXIDE STRUCTURES

Both structures are based on co-ordination octahedra of O– ions around Ti^{4+} ions. The difference lies in the way the octahedra share edges. In (A), rutile, two diametrically opposite edges are shared, shown by double line. Here the arrangement of O– ions is a slightly distorted body-centred packing. In (B), anatase, four edges of the octahedra are shared, leading to a less stable structure

positive, and vice versa. Because, with a few exceptions, positive ions are smaller than negative ones, it is easier to think of negative ions packed around positive ones up to the number limited by their mutual repulsion. The precise number—3, 4, 6, 8, 9 or 12—is given by the radius ratio rule discussed above.

The arrangements of the positive ions around the negative can only be determined directly in simple cases where there is one sort of ion of each sign. In general it depends on secondary considerations which were first set out explicitly as Pauling's rules in 1928. These are expressions of the condition of minimum electrostatic energy of an assembly of positive and negative charges which, expressed in Faraday's visual terms, consists in making the sum of the lines of force as short as possible. Pauling calls the electrostatic valency the charge of a positive ion divided by the number of negative ions immediately around it. This is proportional to the lines of force going to each. Thus an ion of aluminium (charge 3) surrounded by six oxygen ions will give an electrostatic valency of $\frac{3}{6}=\frac{1}{2}$, whereas one of potassium surrounded by 12 oxygen atoms will only give $\frac{1}{12}$. Pauling's rule simply states that the sum of electrostatic valencies around any negative ion must be nearly equal to the charge on that ion. This must, of course, be true on the average on account of the over-all equality of positive and negative charges, but for stability it must hold as near as possible for every ion, or in terms of lines of forces, all should begin and end on neighbouring ions (fig. 100). Ionic structures may be considered as consisting of polyhedra of negative ions, each surrounding a positive ion (fig. 101). These polyhedra can be linked together by the sharing of corners, edges or faces. In the latter two cases, owing to the repulsion of the positive charges, the negative ions will be squeezed closer together or the corresponding polyhedron edge shortened. Pauling's rules have not only been used to give a reasonable account of almost all ionic structures but in many cases to predict them in advance of crystal analysis. Their success bears witness to the essential simplicity of ionic structures.

CRYSTALLOGRAPHY

Ionic structures can be divided into two main groups. The first contains those in which the interionic forces between different ions are more or less of the same strength. These are the simple or mixed oxides and halides in which the electrostatic valency is never more than half the charge on the negative ion—one for oxides, a half for halides. In the second group, the presence of high positive charges and small ionic radii lead to very strong electrostatic valency greater than half the charge on the negative ions. This produces distinct complex ions, such as the oxy- ions—nitrate, carbonate, sulphate, phosphate, etc.—which are often stable as such in solution. Indeed, in these cases it may be more correct to think of the forces inside the ion as homopolar, though the crystal structure of the resulting salt is still ionic as the complex ion carries a charge all over its surface. These two groups are not absolutely distinct. The borates, silicates, tungstates, etc., where the electrostatic valency may be exactly or nearly, half the negative charge, might be attached to either group. As this condition is one which leads to extensive linking of the negative ions through common oxygen atoms, it is convenient to treat it separately as an intermediate group represented most extensively by the silicates.

The general principle of arrangement for salts without complex ions is that of approximate close-packing of the large negative ions with the small positive ions fitting into the interstices between them. This principle breaks down when positive ions are large, that is, when the co-ordination is greater than six times that of the largest hole of a close-packed structure, as, for instance, in the caesium chloride structure, or when the negative ions are highly polarizable, in which case layer lattices such as $CaCl_2$ are formed. Even there, however, the conditions of close packing may be observed, though whole layers of negative ions are held together only by dispersion forces.

Of the structures based on cubic close-packing the type is that of rock salt which is that of most simple halides, oxides and sulphides of the general formula AX (see fig. 102A). Here the metal atoms are placed in all the six co-ordinated holes of the structure. Where the positive ions are relatively smaller or have more polarizing power, the four co-ordinated holes are filled as in zinc blende, but there the structure is more homopolar than ionic. If one out of three metal layers is omitted the result is the so-called A sesquioxide structure A_2X_3 of the rare earths (fig. 102B). With mixed oxides some of the six co-ordinated and some of the four co-ordinated holes can be filled, the commonest of these structures is that of spinel, $MgAl_2O_4$, which is also that of the black iron oxide, magnetite, $FeFe_2O_4$ (fig. 102C). Corresponding structures are to be found in the hexagonal close-packing array where alternate layers of negative ions are found superposed. The six-co-ordinated rock salt analogue in the hexagonal series is nickel arsenide (fig. 103A), the four-co-ordinated zinc blende analogue is the wurtzitelike structure of beryllium oxide. Filling two out of three of the six co-ordinated holes gives the extremely compact structure of corundum, Al_2O_3, met as the gem stones, ruby and sapphire, and also that of red iron oxide, haematite (Fe_2O_3) (fig. 103B). The hexagonal analogue of spinel is olivine, Mg_2SiO_4, with the magnesium ions in the sixfold and the silicon in the fourfold position (fig. 103C). This crystal structure, or possibly an even more compact high-pressure form, forms the bulk of the earth and of most planetary bodies and is consequently the commonest crystal structure in the universe.

Only one important structure is based on a body-centred cubic arrangement of anions, that of TiO_2, rutile, or SnO_2, cassiterite, with one out of three of the possible six co-ordinated vacancies occupied (fig. 104A). Two important structures can be derived from a simple cubic packing of anions, those of CsCl and CaF_2 (see fig. 90). A variant, anatase (fig. 104B) differs only from rutile by a different arrangement of co-ordination octahedra.

The types of structures with complex ions must necessarily be far more numerous than those with simple ions, but they are not necessarily more difficult to understand if, as mentioned above,
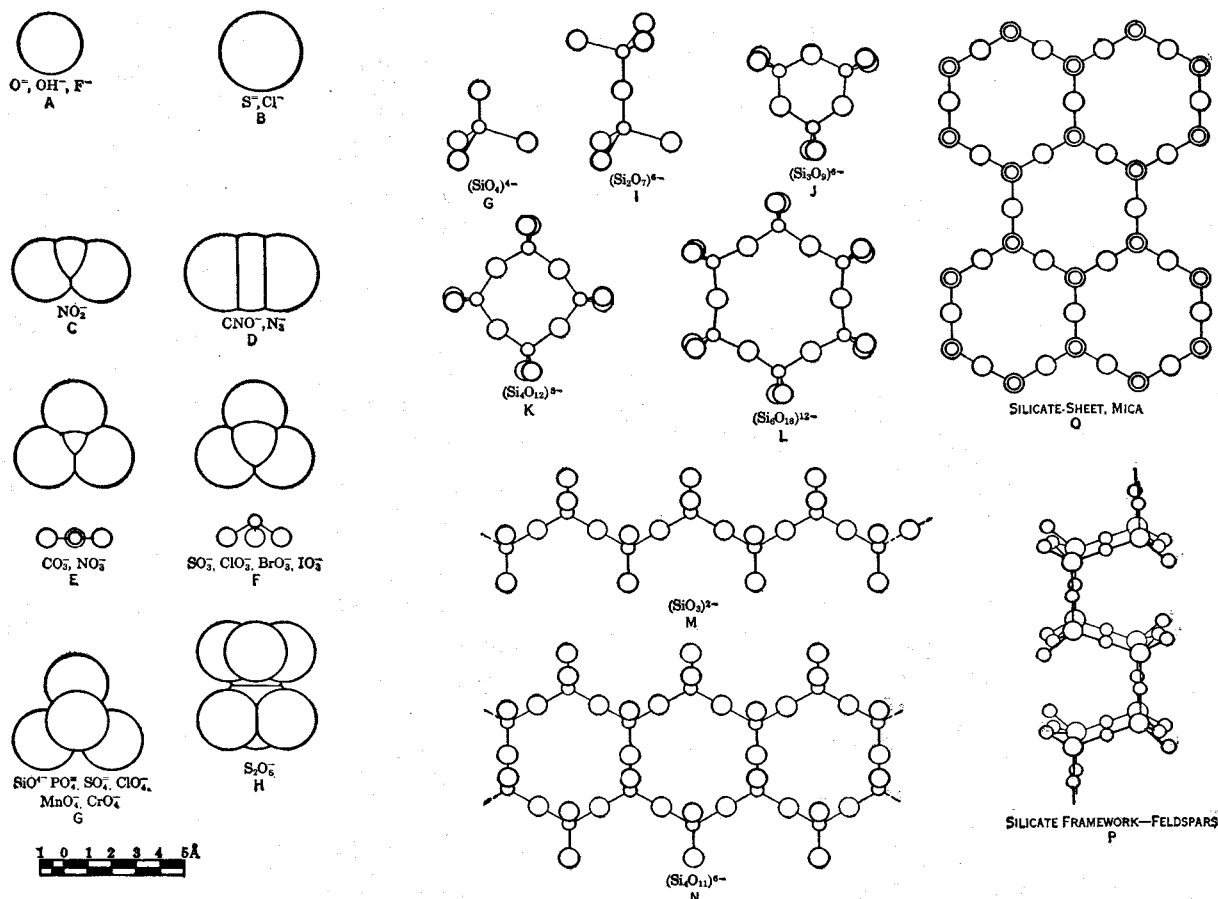
FIG. 105.—MONO- AND POLY-NUCLEAR COMPLEX IONS. THE SIMPLER IONS, (A) TO (H), ARE SHOWN WITH FULL IONIC RADII; THE MORE COMPLEX SILICATE IONS, (G) TO (P), DIAGRAMATICALLY

826   CRYSTALLOGRAPHY

the complex ions are treated as simple to a first approximation. The great majority of complex ions are oxy- ions, that is, consist of metallic or nonmetallic atoms completely covered by oxygen ions bound by very strong ionic or by homopolar forces. Complex ions can be mononuclear when several oxygen (anions) are bound


CO-ORDINATION OF CALCIUM ION

CALCITE A   CO-ORDINATION OF CARBONATE ION   ARAGONITE B
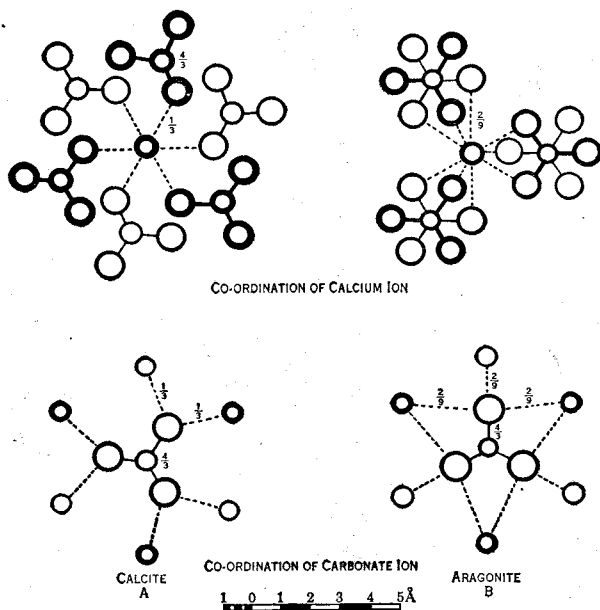
BY COURTESY OF CORNELL UNIVERSITY PRESS, FROM BRAGG "ATOMIC STRUCTURE OF MINERALS"

FIG. 106.—ARRANGEMENT OF IONS IN CALCIUM CARBONATES

(A) In calcite each calcium atom is surrounded by six oxygen atoms belonging to six carbonate ions on two different layers. (B) In aragonite each calcium atom is co-ordinated with nine oxygen atoms belonging to six carbonate ions on four different layers. Each carbonate group is co-ordinated with six calcium atoms in both cases but in calcite (A) each oxygen has two calcium neighbours while in aragonite (B) it has three. The fractions indicate the electrostatic valence

to a single cation as in $-SO_4$, sulphate, or polynuclear linear as in the $-S_2O_7^{--}$ $(=O_3 S O S O_3)$ pyrosulphate, or cyclic as in the trimetaphosphate ion, $-P_3O_9^{3-}$—
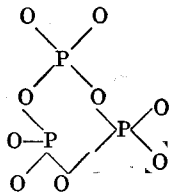
Other polynuclear ions can be formed by linking the nuclei directly, as with the dithionate ion $S_2O_6^{4-}$

$$\begin{array}{cc} O & O \\ OS\!-\!SO \\ O & O \end{array}$$

The commonest ion types are shown in fig. 105. The two major mononuclear types are the triangular ions BO_3^{---}, CO_3^{--} and NO_3^-, and the tetrahedra ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-} and ClO_4^-. The members of each group have the same size and number of electrons and differ only in charge. Thus, if combined with the same number of positive ions of the same size they give similar structures, as for example do calcite, $CaCO_3$, and sodium nitrate, $NaNO_3$. Calcite, the basis of shells, chalk, limestone and marble, is the most important of this group. The same chemical compound also crystallizes with a different crystal structure, as aragonite (fig. 106). The difference is merely that the calcium ion is co-ordinated with six oxygen atoms in the first case, and nine in the second. The aragonite form, in which the calcium atom has more room, is the form which is stable at higher temperatures. An example of a structure with tetrahedral ions is given in anhydrite, $CaSO_4$ (fig. 107A). The analagous structure with higher cation co-ordination is the highly insoluble barytes or heavy spar, $BaSO_4$, the basis of the X-ray barium meal. Occasionally. a par-

ticularly good fit is achieved in a highly symmetrical structure requiring an odd assortment of ions of different kinds. This is the case for the extremely stable apatite, $Ca_5(PO_4)_3F$, the structure of rock phosphate and tooth enamel. The fluorine ion needed to balance the charge can be replaced by hydroxy- (OH) giving rise to the slightly weaker structure of bones and teeth.

Highly complex polynuclear ions can be formed by linking together six co-ordinated groups through their oxygens. These can form virtual baskets stabilized by smaller ions at the centre (fig. 108). Such are the phosphotungstates $(PW_{12}O_{40})^{3-}$ in which vertical ionic radius is 5.2 Å.

The most complex ionic structures are those in which, though positive ions of different charge exist, it is impossible to distinguish finite complex ions. These form essentially three series in which the minimum co-ordination is three, four and six respectively, of which the borates, silicates and tungstates (fig. 109) are typical. Of these the silicates are far the most important and best studied. The principles of classification of the silicate structures have already been mentioned; they turn on the spatial extension of the silicon oxygen framework and correspondingly with the increasingly acid—silica-rich—character of the compound. When the silicate ions are isolated the result is the neso-silicates analogous to normal tetrahedral complex ion structures (fig. 105G), of which olivine (fig. 103C), Mg_2SiO_4, is typical. Next come the inosilicates with chains of the form

$$\begin{array}{ccc} O & & O \\ | & & | \\ O\!-\!Si\!-\!O\!-\!Si\!-\!O & \longrightarrow \\ | & & | \\ O & & O \end{array}$$
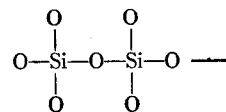
(fig. 105M) characteristic of the rock-forming fibrous pyroxenes (fig. 110) and amphiboles of which hornblende is the most common example and asbestos the most useful. When the chains are curled into rings (fig. 105L), as they are in beryl, the gem stone emerald $(Be_3Al_2Si_6O_{18})$, the fibrous character disappears but holes are left through which small atoms such as helium can pass. Next come the platy phyllosilicates (fig. 105O) of which mica, $KAl_2(OH)_2Si_3AlO_{10}$—see fig. 111—is the commonest mineral and clay, $Al_2(OH)_2Si_4O_{10}8H_2O$, the most common weathering product. Finally there are the tectosilicates (fig. 105P and 111) with their extended frameworks, the feldspars such as orthoclase, $KAlSi_3O_8$, and the zeolites—such as sodalite, $Na_3Al_3Si_3O_{12}.NaCl$, or its
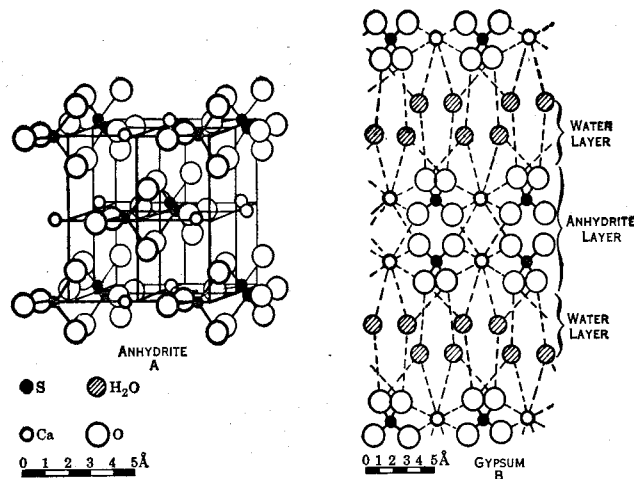
ANHYDRITE A

●S   ◐H_2O

○Ca   ○O

WATER LAYER

ANHYDRITE LAYER

WATER LAYER

GYPSUM B

BY COURTESY OF (A) CAMBRIDGE UNIVERSITY PRESS, FROM R. C. EVANS "CRYSTAL CHEMISTRY," (B) THE CLARENDON PRESS

FIG. 107.—CALCIUM SULPHATE

(A) anhydrite, $CaSO_4$, the arrangement is of a distorted NaCl type (B) gypsum, $CaSO_4.2H_2O$, the arrangement is essentially one of layers of anhydrite separated by layers of water. For electrostatic valence pattern see fig. 88

sulphur-containing variant, lapis lazuli—leading to silica itself as the end member.

Silica occurs in a great variety of forms, all having in common the tetrahedral $-SiO_4$ group joined through its corners to four others (fig. 113). This may be done irregularly as in silica glass,

CRYSTALLOGRAPHY

in the most expanded form of tridymite and cristobalite found in volcanoes and in crystalline opal, or in its most compressed form as quartz, commonly met in sand or flint. The quartz structure with its spiral twist has found many uses both in optics and in piezoelectric oscillators.

Role of Hydrogen and Water.—So far in discussing ionic compounds one most important ion has been omitted. That is the positive hydrogen ion, H^+, which is, in its free state, nothing more than a simple proton. In the presence of other atoms the simple proton never appears but is always masked by a negative charge collected around it within the outer region of the nearest atom. The negative hydrogen ion H^- possesses two electrons and behaves in its salts not unlike the negative fluorine ion. In its compounds with most nonmetallic atoms hydrogen behaves as if bound homopolarly and is externally inert as, for example, in the paraffins. Three atoms however, form important exceptions—nitrogen, oxygen and fluorine. Hydrogen combined with these—in the alkaline ammonia, NH_3, the neutral water, H_2O, and hydrofluoric acid, HF—is sufficiently near the surface of the atom to exert a powerful external electrostatic attraction as the electron cloud surrounding it only neutralizes about half of its positive charge. Further, hydrogen can leave the neutral molecule, giving the negative ions OH^- (hydroxyl) and F^- (fluorine), or can join it, giving the positive ion NH_4^+, ammonium, or OH_3^+, oxonium—the form of the "hydrogen ion" in water solutions.

The key to the behaviour of hydrogen is furnished by the forms of the old "element" water—as steam, water and ice. In steam the molecules are isolated. The two hydrogen atoms are not at its opposite poles, but form a dog-legged arrangement (fig. 114), with two positive charges located on the hydrogen atoms and two more diffuse negative charges at the opposite end of the molecule, forming an electric dipole analogous to a magnet. It is these dipoles that make water condense so readily despite the lightness of its molecule—it is no heavier than neon, which is a gas condensing at $-248.67°$ C.; even hydrogen sulphide, H_2S, which is nearly twice as heavy, is a gas condensable at $-61.8°$ C. In ice the molecules are arranged regularly but very loosely in a wurtzite structure (fig. 115), in which each is surrounded by four others at a distance of 2.76 Å arranged so that the two positive regions of one molecule link with negative regions in two neighbouring molecules, while the two negative regions are linked with positives from another two neighbours. These links, in which a hydrogen atom attached to one oxygen atom is linked with another oxygen, are called hydrogen (or hydroxyl) bonds. This is strictly a misnomer as the bond is really one of electrostatic polarization and not of electron interchange as in a true homopolar bond. Expressed in electrostatic valency as due to a hydrogen ion with its single charge and two neighbours, the strength of a hydrogen bond is exactly one-half. The shielding of the H ion, however, reduces this in most cases to values nearer one-eighth.

The concept of the hydrogen bond explains roughly most of the properties of compounds containing water or hydroxyl, such as clays, alcohols and carbohydrates, as well as those of acids and alkalis. When ice is melted the regular loose structure of steric density 0.37 is turned into an irregular one still bound together by hydrogen bonds but in which the molecules are more closely packed owing to the greater play of dispersion forces. This arrangement accounts for the expansion of water on freezing as well as for the existence of a temperature of maximum density of water. As water is heated, much of the energy goes into breaking hydrogen bonds, accounting for the large specific heat, but far more must be broken on boiling which gives steam its very high

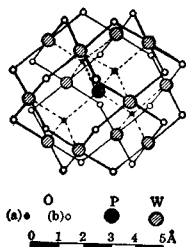
FIG. 108—PHOSPHOTUNGSTIC ION
The oxygen ions (a) are co-ordinated to both P and W atoms, those marked (b) to two W atoms only. Remaining O atoms co-ordinated to one W atom are omitted for clarity

latent heat.

The electric dipoles of the water molecules link together throughout its whole structure and can be orientated this way and that in groups by electric fields, which accounts for the high dielectric constant of water. It is also the explanation of its great solvent power, which is, in fact, limited to hydroxic compounds, alkalis, acids, sugars, etc., and ionic salts. It is notoriously feeble toward nonionic substances such as fats and paraffins. The water molecule dipoles attach themselves around positive and negative ions, lowering their effective charge density and producing hydrated ions (fig. 116) which, for highly charged ions, are extremely stable.

The water of crystallization, which is so common in ionic crystals, may exist in a number of geometrical arrangements, but in all cases the water molecules act as a kind of dielectric distance-piece between ions of opposite sign (fig.   ). Most water molecules, if bonded to a positive ion with an electrostatic bond of strength $\dfrac{1}{x}$ make bonds to two negative ions, each bond being of strength $\dfrac{1}{2x}$. Thus the presence of water lowers the average strength of electrostatic bonding. The water molecules may be arranged as isolated molecules, around ions as shells as in alum, $K(OH_2)_6Al(OH_2)_6(SO_4)_2$, in strings, in sheets as in gypsum, $CaSO_4 2H_2O$ (fig. 100 and 107B), or as a continuous framework as in the cryohydrates (fig. 115C).

The hydroxides, ranging from strong alkalis such as potassium hydroxide, $K(OH)$, to strong acids such as sulphuric acid, $O_2S(OH)_2$ ($=H_2SO_4$), and perchloric acid, $O_3Cl(OH)$ ($=HClO_4$), illustrate the effect of the attached atom on the bonding power and stability of the hydrogen atom. In the absence of a strongly polarizing ion, that is, for the alkali and most alkaline earth hydroxides, the hydroxyl ion is stable—has no tendency to lose hydrogen—and has a minimum power of forming hydrogen bonds even less than exists in water. In KOH, LiOH and Ca(OH)

A   B

BY COURTESY OF DR. HELEN D. MEGAW AND THE PHYSICAL SOCIETY
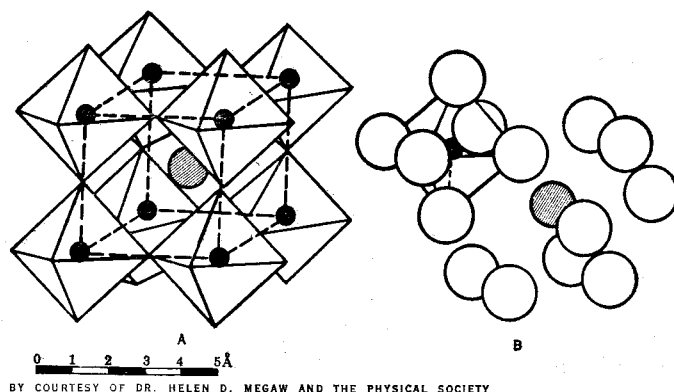
FIG. 109.—PEROVSKITE STRUCTURE, $CaTiO_3$
(A) shows the TiO_3 (ReO_3, WO_3) framework of oxygen octahedra sharing corners; (B)[3] the co-ordination 6-fold of the Ti^{4+} ion and the 12-fold co-ordination of the interstitial Ca^{2+} ion

with increasing polarizing power of the cation the OH-OH distances are respectively 3.26, 3.60 and 3.36 Å as compared with 2.76 Å in water. In the hydroxides of strongly polarizing ions, elements of the fifth, sixth and seventh groups of the periodic table, the high positive charge on the ion repels the hydrogen of the hydroxyl group. It may drive it off altogether if there is a hydrogen ion acceptor present, such as water, giving rise to a negative oxy- ion. In the acids themselves (see fig. 117C) it increases the effective charge of the hydrogen ion and leads to the formation of strong hydrogen bonds of lengths 2.5–2.6 Å, less than that in water. When these can link up throughout the structure, as in sulphuric acid, $O_2S(OH_2)$, with two donors and two acceptors of hydrogen, the result is a stable, viscous and high-boiling-point liquid, whose extreme affinity for water is due to the facility with which water molecules can link hydroxyl to oxygen ions.

In intermediate cases the so-called amphoteric hydroxides of such elements as aluminum, iron or silicon, neither free hydroxy- nor negative oxy- ions are formed, but the whole structure is linked together by hydroxyl bonds only slightly stronger than

INOSILICATE CHAINS

DIOPSIDE

O^{--} ◯
Si^{4+} ●
Ca^{2+} ◑
Mg^{2+} ◯
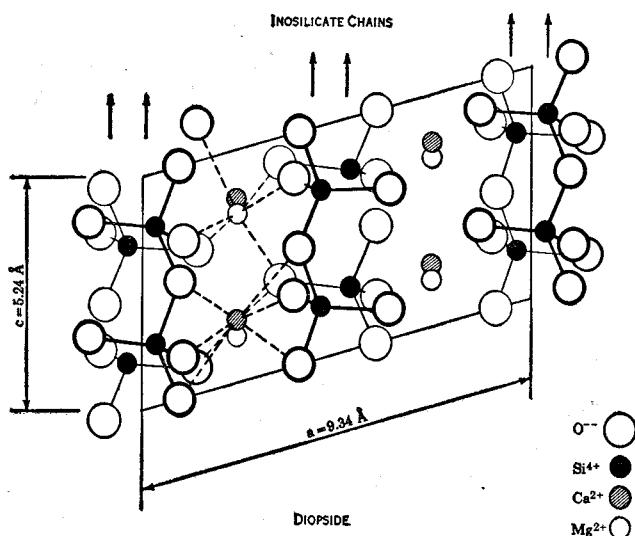
BY COURTESY OF CORNELL UNIVERSITY PRESS, FROM BRAGG "ATOMIC STRUCTURE OF MINERALS"

FIG. 110.—DIAGRAM OF A TYPICAL INOSILICATE, THE PYROXENE DIOPSIDE, CAMGSIO₃. SIX SiO_3^2 CHAINS ARE SHOWN HELD TOGETHER BY THE Ca^{2+} AND Mg^{2+} IONS

those of water, length 2.7–2.8 Å (see 117A, B), usually in the form of gels whose great absorptive power is due to the presence of attached hydroxyl groups.

Though the water molecule is by far the strongest dipolar neutral molecule, other dipole molecules can also play the same role in ionic crystals. Ammonia in particular can be strongly attached to certain ions, such as silver or cobalt, forming complex ions often stable in solution and having characteristic colours. These are the co-ordination compounds of A. Werner, the study of which by purely chemical methods gave rise to the idea of spatial co-ordination, afterward elucidated by X-ray analysis.

Molecular Crystal Structures.—Crystals containing finite molecules are legion: allowing for polymorphous forms, about 1,000,000 of them were already known by the 1950s. Of these, accurate and complete crystal-structure determinations had been made on about 200 and however much X-ray analysis might flourish it was unlikely to keep up with the chemical discovery and separation of new substances. Though enough was known to understand the general principles of architecture of molecular crystals, a systematic classification of the field, similar to that of ionic and metallic crystals, was not yet possible. It was, however, also of relatively smaller interest both scientifically and technically. Except for polymers, particularly fibres, the major interest in molecular crystals is not in their physical properties as crystals but in those of the molecules themselves as liberated by melting, vaporization or solution, or transformed by chemical reaction. The intramolecular structure is more important than the intermolecular.

The value of X-ray analysis is therefore markedly different for, molecular crystals as for other types. The major objective in this field has been to determine the inner molecular structure in more or less detail. Except in special cases the interest in the way the molecules pack together is secondary and incidental. Crystal analysis, mainly by X-rays, has been applied with success on three levels of detail apart from its routine use for identification and molecular weight determination. The first is the determination of molecules of unknown or disputed structures. The classical case is that of penicillin where X-ray analysis played an important part in determining the structure. This approach is likely to be more and more important in the biochemical and particularly in the antibiotic field. The second level is the determination of the stereochemical configuration of known molecules of particular interest. Examples are to be found in

the alkaloids with strychnine and in the steroids with calciferol (vitamin D_2). The third level, requiring the most precise analysis, is the accurate determination of bond lengths and angles and electron distribution in molecules of particular interest as a check and guide to the work of the quantum chemist, as for instance, in aromatic condensed ring systems such as naphthalene and anthracene.

Most of the results of crystal structure analysis are more appropriately treated under chemical topics and only that relevant to the building up of the crystals themselves is treated here. The characteristic of molecular crystals is that they should contain finite or at most one-dimensionally extended molecules held together internally by homopolar chemical valence forces. The molecules will in general be neutral, though it is convenient to classify crystals containing charged molecules, or molecule ions such as acetate or stearate ions, as molecular if the ions are not of the oxyacid type already described. The forces between the molecules will accordingly range from the ionic through the dipolar (hydrogen bond) type to the extremely weak dispersion forces due to mutually induced polarization.

The distinction between the ultimate, and therefore the weakest, forces holding the molecules together is shown by the parallelism of melting point, hardness and solubility. Where these forces have an ionic or hydrogen bond character the crystals have a relatively high melting point, are hard, and dissolve in water. Where they are dispersion forces the crystals have a relatively low melting point, are soft, and dissolve in paraffins or ether.

A MICA   B KAOLIN   C BENTONITE

CLEAVAGE

0 1 2 3 4 5Å

OAl ●$^{Al}_{Si}$ ◑K^+ ◯$^{O^{--}}_{OH}$
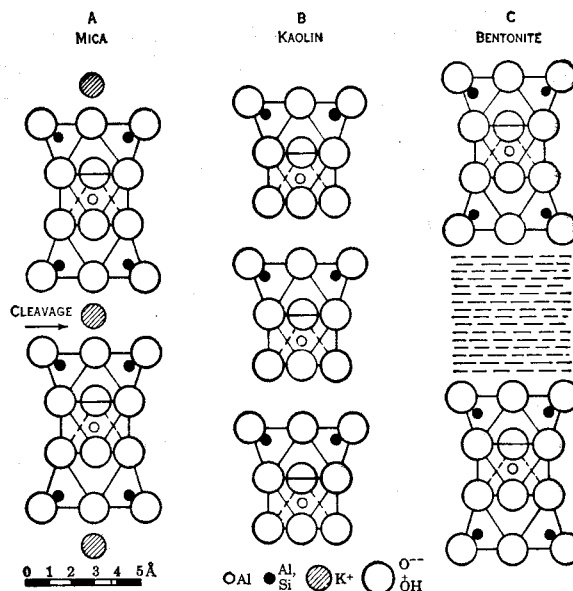
BY COURTESY OF CORNELL UNIVERSITY PRESS AND LINUS PAULING

FIG. 111.—DIAGRAM OF THREE TYPICAL PHYLLOSILICATES WITH THE PLATES EDGEWAYS, THE FLAT PROJECTION OF THE PLATES IS SHOWN IN FIG. 105 (O)

In (A) Muscovite mica, $KAl_2(AlSi_3O_{10})$ $(OH)_2$, he double silicate layers are held together by aluminium ions in octahedral co-ordination. The plates themselves are held much more weakly by potassium ions, hence the ready cleavage. In (B), china clay or kaolinite, $Al_2(Si_2O_5)(OH)_4$, there are only single silicate layers associated with the aluminate layers. The plates are uncharged and held together by hydroxyl bonds. In (C) montmorillonite or bentonite, $AlSi_2O_5(OH)$, the sheets are similar to those of mica but uncharged and even more weakly attached together; the space marked ☰ ☰ is filled with a variable amount of water or other absorbed substances

The nature of the forces is not the only factor determining crystal properties; another is the size of the molecule. The larger the molecule, as homologous series such as the paraffins (see PARAFFIN HYDROCARBONS, CHEMISTRY OF) show, the higher the melting point, the greater the hardness and the lower the solubility. But this does not affect the relative solubility in different solvents, which depends on the nature of the bonds the solvent has to break. The shape of the molecule for a given size also has an effect, but this is mainly on the melting point and ease of crystallization. Crooked and branched molecules, which are difficult to pack together, have low melting points and indeed may
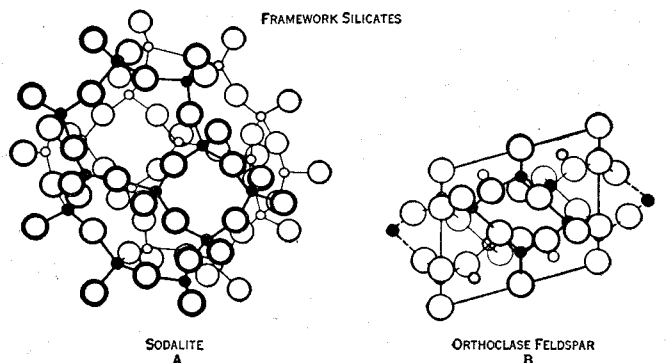
not readily crystallize at all, remaining oils at high temperatures and glasses at low.

Where different kinds of forces coexist, as in organic alcohols, acids, bases and salts, the nature of the crystal is affected by the geometrical character of the linkage of the stronger forces.

FRAMEWORK SILICATES

SODALITE
A

ORTHOCLASE FELDSPAR
B

0 1 2 3 4 5Å   0 1 2 3 4 5Å

BY COURTESY OF (A) THE CLARENDON PRESS, OXFORD, (B) CORNELL UNIVERSITY PRESS FROM BRAGG "ATOMIC STRUCTURE OF MINERALS"

FIG. 112.—DIAGRAM OF TYPICAL TECTOSILICATES

(A) represents the zeolite sodalite made of linked alumino silicate four-membered and six-membered rings. The large space in the centre may be filled by a variety of atoms or ions. (B) represents the feldspar orthoclase, $K(AlSi_3)O_8$. It consists of four-membered alumina silicate rings, linked in the manner shown in Fig. 105 (P), the potassium ions occupy the interstices. Both structures should be compared with those of the forms of silica in Fig. 113

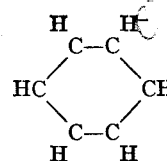If a molecule otherwise covered with CH_2 or CH_3 groups possesses one carboxy- group— C with O and OH, pairs of such groups tend to join together forming a double molecule as in acetic acid—

H_3C-C ... $C-CH_3$ (OHO)
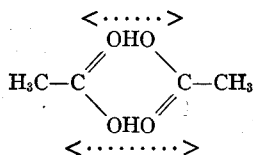
where the link between the molecules persists even in the vapour. The double molecules of such neso-compounds behave in some respects like those of single nonpolar molecules. This is why the fats (which are glycerol compounds of fatty acids), the fatty acids themselves, and the soaps which are their metal salts are physically similar and near enough in properties to the paraffins which lack carboxy- groups. If there is more than one active group in each molecule the result will be to form rings, chains, layers or extended networks by means of them in the ways already described above.

The primary classification of molecular crystals can be based on the shape of the molecules which may be divided into three rough groups— round, flat and long. A further group may be added for the extreme case of the very long molecules of polymers. Inside each group a distinction of a different kind may be made, according to the nature of the weakest binding force, into nonpolar and polar, usually hydrogen-bonded, structures.

Structures with Isosteric (Round)

Molecules.—As might be expected, crystals with molecules which are not far from spherical give, when they are not markedly polar, structures approximating to one or another of the forms of close packing. When the molecule is slightly elongated, as in carbon dioxide, OCO (fig. 118A), 5 Å long and 2.6 Å wide, the long axes are arranged to point in different directions. A somewhat less symmetrical arrangement is found in benzene—

HC (benzene ring structure)

(fig. 118B) which has a flattish molecule 5.8 Å wide and 3.4 Å thick. Parallel arrangements are not met with, as minimum space and energy conditions are provided by crossed arrangements.

The simplest of polar molecules of this type is that of water whose behaviour has already been described. Ice is the type for all crystals held together throughout by hydroxyl bonds, as in the poly-alcohols such as glycerine and in the enormous variety of sugars. Slightly stronger hydrogen bonding is provided by organic acids containing the carboxy- radical —C with O and OH. The simplest type of these is oxalic acid—

$C-C$ (oxalic acid structure)
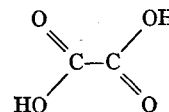
COOH.COOH. In the anhydrous state the molecules are held together in a diamond-type network by hydrogen bonds. If water is present a particularly simple sheet arrangement is formed with the acid linking through the water molecules (*see* fig. 119A) such as in maleic acid (fig. 119B). In other cases the hydrogen bonds are internal.

Stronger bonds still are formed when the H-bond links a posi-

QUARTZ
A

O ATOMS BELONGING TO DIFFERENT SPIRAL SYSTEMS

TRIDYMITE
B

CRISTOBALITE
C

0 1 2 3 4 5Å   ●Si ○O
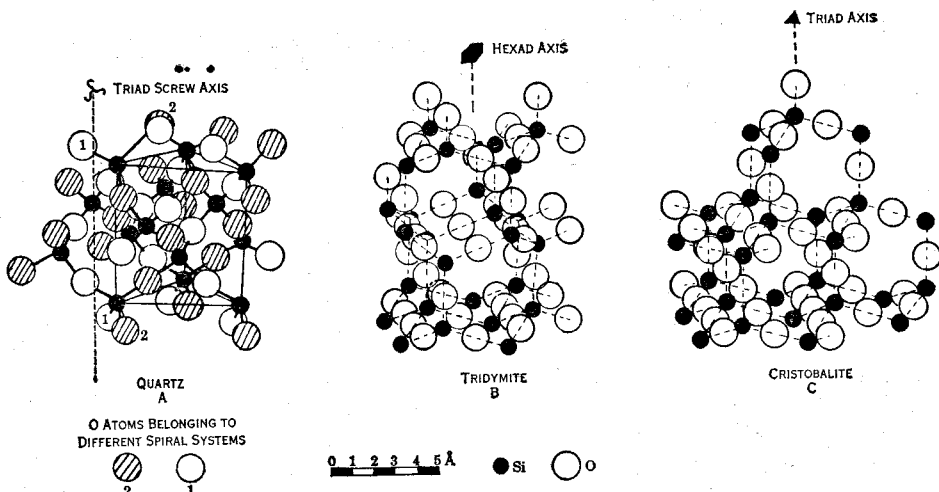
FIG. 113.—CRYSTALLINE FORMS OF SILICA

All types are built on the same general plan out of silicate tetrahedra sharing all four corners. The differences are in linkage patterns. In (A), quartz, the tetrahedra formed paired helices or distorted six-membered rings around trigonal screw axes. (In order to demonstrate this, oxygen atoms belonging to different helices have been distinguished in the drawing.) In (B), tridymite, the silicate tetrahedra are linked in fully open six-membered rings. (C) cristobalite only differ from (B) in the cubic rather than hexagonal arrangement of the ring systems. Both have a very much more open structure than quartz

828B

CRYSTALLOGRAPHY

tive amino- with a negative oxygen atom. The simplest case is

that of urea $O = C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$. By itself this forms a most compact

quasi-ionic structure (fig. 120A), but this is not the only possible arrangement in which positive can be linked with negative poles. One such structure is stabilized by interstitial hydrocarbons in the way already described (fig. 120B).

A still stronger binding is provided where actual positive and negative charges—zwitterions—exist on different parts of the same molecule. The simplest case is that of glycine, the first of the amino acids and a major constituent of silk. In the crystal the hydrogen of the carboxy group is transferred to the amino group—

$$\begin{array}{ccc} O & H_2 & \\ \diagdown & & \\ C-C & & \\ \diagup & \diagdown & \\ HO & NH_2 \end{array} \longrightarrow \begin{array}{ccc} O & H_2 & \\ \diagdown & & \\ C-C & & \\ \diagup & \diagdown & \\ O & NH_3 \\ - & + \end{array}$$

and these (fig. 121) link strongly with groups of the opposite sign in adjacent molecules. Larger round molecules show more complex varieties of close packing. Typical are the basketlike cross-linked molecules of adamantine, camphor, strychnine and hexamethylenetetramine. Even where the molecule is highly irregular, as in penicillin (fig. 122), the structure is approximately close-packed.

Crystals with Flat Molecules.—These are for the most part benzene derivatives or even condensed ring systems such as naphthalene and anthracene. The common characteristic which determines the aromatic nature of these molec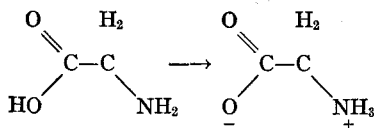ules is that the atoms all lie in one place. The simplest way of arranging such molecules is by stacking them together like piles of plates as in hexamethyl benzene (fig. 123). In most cases, however, the arrangement of lowest energy is of a herring-bone or folded-pile type, which provides (*see* fig. 124 and 125) a better fit at the edges of the molecule. In either case the crystal tends to grow faster in the direction of the piles of molecules, and fine needle-like crystals are characteristic of crystals with flat molecules.

A   **B**

WATER   0 1 2 3 4 5Å
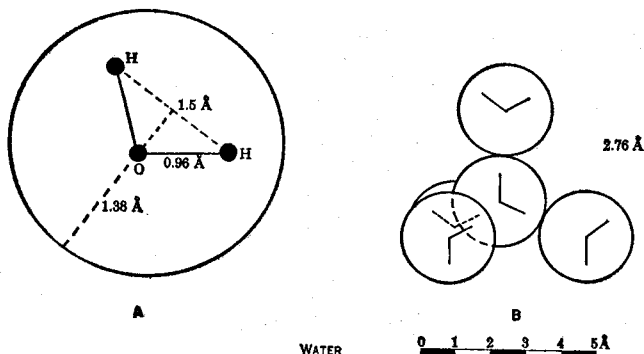
FROM J. D. BERNAL, BY COURTESY OF "JOURNAL OF CHEMICAL PHYSICS" (VOL. I, PP. 520, 528)

Fig. 114—WATER

(A) shows a sectional diagram of a water molecule; the hydrogen nuclei are seen to be well inside the normal oxygen ion sphere. (B) shows the arrangement of four such molecules in water or ice. Each molecule is surrounded by four others linked to it by hydroxyl bonds, two pointing toward and two away from each molecule

Among important aromatic crystal structures are those of several carcinogenic hydrocarbons, such as methylcholanthrene, the nucleolides, purines and pyrimidenes, the porphyrins (which are the basis of cell and blood pigments and of plant chlorophyll) and the related fast dye, phthalocyanine (fig. 79 and 125), that is of interest as the first complex organic molecule whose detailed structure was determined by crystal analytic methods above, without any chemical assumptions.

If the molecules are also elongated in one direction in their plane, as for instance in anthracene (fig. 126) or the steroid with

the common carbon skeleton , the fastest lateral growth

tends to be at right angles to this which leads to elongated platy or lath-shaped crystals. In general, Fedorov's rule is well
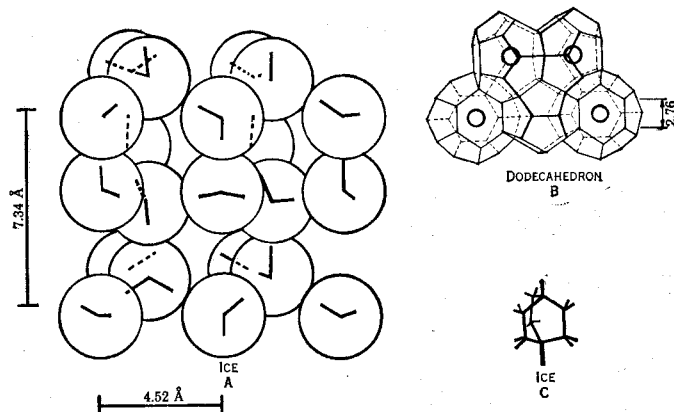
BY COURTESY OF (A) THE PHYSICAL SOCIETY AND SIR LAWRENCE BRAGG, F.R.S., (B) NATIONAL ACADEMY OF SCIENCES

FIG. 115.—FORMS OF CRYSTALLINE WATER

(A) The ice structure showing the positions of the oxygen atoms. Possible hydrogen positions are indicated by the diagrams. An infinite variety are possible, all satisfying the condition that two hydrogens and no more point to each oxygen atom in the structure. (B) The structure of chlorine hydrate, $6Cl_2 46H_2O$. Each point in the diagram represents a water molecule with four lines joining it tetrahedrally with other water molecules. The structure consists of tetrakaidecahedra, figures with 2 hexagonal and 12 pentagonal sides, and dodecahedra with 12 pentagonal sides. Only the first are occupied by chlorine, argon or other neutral molecules. A small diagram of ice on the same scale is shown at (C)

borne out by molecular crystals where the molecules are roughly parallel. Crystals are, as it were, inverted images of the molecules that build them up, long where these are short, short where they are long.

Molecular Compounds.—Because of the peculiar unsaturated nature of aromatic compounds (*see* CHEMISTRY: *Organic Chemistry, Classifications of Organic Compounds*), the dispersion forces they exert are both particularly strong and are directed in relation to the symmetry plane of the molecule. In some cases they are so strong as to attach different molecules together even in solution. In crystallizing, the different molecules usually pack in parallel and alternating. An example of these is the paraiodoaniline *s*-trinitrobenzene compound (fig. 127). Molecular compounds are analogous to the order-disorder compounds found in alloys. They are essentially of geometrical rather than chemical nature. The dimensions of two different molecules may be so adjusted to each other as to fill space better together than either does separately.

A striking example of this is provided by clathrate crystals which are particularly evident among aromatic compounds. This is especially the case where polar groups are present, for there, owing to the extended and rigid character of many aromatic molecules, framework structures with considerable vacant space can be formed. Quinol (*see* fig. 128) is one of the best known of this type. In its crystals two independent hydrogen-bonded frameworks are formed capable of accommodating other molecules ranging from the atoms of the rare gases to sulphur dioxide. Another aromatic clathrate compound is that of the asymmetrical type already discussed.

Crystals with Elongated Molecules.—Where one dimension of a molecule is more than about three times its other dimensions, as for instance in all long-chain hydrocarbon derivatives or, in general, fatty substances, the only stable form of packing is with the long axes parallel. The arrangement at right angles to this one approximates to two-dimensional hexagonal close-packing. The packed molecules form an extended sheet like corn in a field, but

CRYSTALLOGRAPHY

they need not be at right angles to the sheets. Indeed, only molecules with nonpolar ends, such as the paraffins, pack this way. Usually the oblique linking of two active groups—hydroxy-, carboxy-, amino- —determines a considerable slope which may be as much as 45°. In crystals the sheets tend to pile in layers to form thin platy crystals, usually of hexagonal or diamond shape. Where both end groups are nonpolar, the layers are held together by dispersion forces and readily slide over each other accounting for the soft and plastic nature of long-chain fatty compounds.

FIG. 116.—HYDRATED ION OF $Mg(OH_2)_6^{++}$.
The points indicate the position of the hydrogen atoms in the water molecules

for the soft and plastic nature of long-chain fatty compounds. Where one end group is polar, as in the fatty acids and soaps, the molecules tend to stick together in pairs, forming double layers between which the weaker dispersion forces operate.

The sheet structure is particularly stable, it persists in the liquid state in the so-called smectic (fatty) liquid crystals. Where the sheets are double they can accommodate polar liquid (like water), solids and salts between the polar faces of the molecules and nonpolar liquids and solids (oils and fats) between the nonpolar faces. This ability to act as an intermediate emulsifying layer between oils and water is the basis of the detergent properties of soaps.

Polymer Crystals.—The polymers are a most distinct and important group of molecules. Occurring in all natural fibres, they have been used by man for centuries, and by the mid-1950s the natural products were being supplemented at an increasing rate by new synthetic polymers. The simplest of these are the linear polymers which are multiple repeats of the same small-monomer molecule or residue joined together throughout by homopolar forces. More complicated are linear copolymers where two or more different monomers are linked together regularly or irregularly.

Regular linear polymers can, in general, pack together to form fibrous ino-type crystals. This parallel packing may occur, as it does in nature, in the process of polymerization, that is, new monomers are added one by one to several parallel chains, or it may be brought about by stretching, as in rubber or the drawing of nylon. As in the case of most polymers the chains are all of different lengths; layers, such as those of the pure paraffins, are not formed and the crystallization is limited to two dimensions.

The forces between the chains depend on the types of side groups. If these are nonpolar, such as the methyl and methylene groups of isoprene that form rubber, the chains are very loosely held and the polymer can melt. If the forces are of the hydrogen bond type, as in polysugars such as cellulose, the polymer cannot melt but chars on heating. Homopolar bonds can also be formed between chains. The number of these crosslinks determines the character of the polymer. When these are formed only between a small proportion of the residues the effect is simply to stiffen the structure and prevent viscous yield. This is the reason for the improvement of rubber by adding -S-S- cross links in vulcanization by means of sulphur. Analogous is the formation of wood from cellulose by the presence of the polyphenol binder lignin and of leather from skin by polyphenol tannins. If the number of cross links is great, hard and brittle products such as vulcanite are formed.

When cross links are not present smaller molecules can be inserted between the polymer molecules without destroying the regular arrangement of the chain. This is the phenomenon of swelling. Living muscle contains fibre molecules regularly packed but separated by four times their weight of water carrying salts and biochemically active small molecules in solution. At higher dilutions fibrous molecules can go into solution as single molecules or bundles (tactoids). If these are aggregated by cooling or chemical action, gels are formed such as the collagenous gels of gelatine which may contain only a small percentage of solid matter which
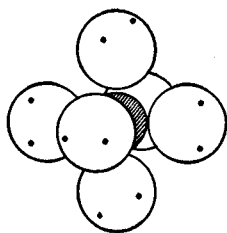
X-ray analysis proved to be of great value in the study of polymers. With fibrous polymers an X-ray photograph shows the degree of parallism of the molecules. Where they are approximately parallel the diagram usually shows: (1) in a direction at right angles to the fibre (equator) the distances apart of the molecules in the fibre and the effect on this of swelling agents; (2) by the spacing of the lines parallel to the equator (layer lines) the repeat period of the residues along the fibre; (3) in the direction of the fibre (meridian) any longer periodicities in the fibre itself. For example, in the keratin (horn) of a porcupine quill the major cross-spacing is 11 Å, the residue period is 5.2 Å and there is a long-range repeat of the pattern every 541 Å.

Many fibre molecules can exist in more than one form, either fully extended or more or less folded or coiled. Rubber is typical of a class of polymers in which the normal state is one of irregular coiling (fig. 131) giving an X-ray picture like that of a liquid which changes to a more or less fully extended molecule on stretching, giving a typical X-ray fibre diagram. The tendency to revert to an irregular shorter form is the explanation of the long-range elasticity of rubber. It is favoured by heat—the contraction of rubber being analogous to the expansion of a gas.

Carbohydrate polymers, because of their many hydrogen cross-bonds, have not the same possibility of changing their state. Cellulose, the basis of linen, cotton, wood and paper, has fully extended molecules and the fibres it forms have limited elasticity. In starch the sugar residues are rigidly coiled and indeed are natural clathrate compounds as is shown by the blue colour of iodine when it is absorbed in the holes of the structure.

Mg(OH)₂ A   Al(OH)₃ B   B(OH)₃ C

○ OH ION ◉ METAL ION
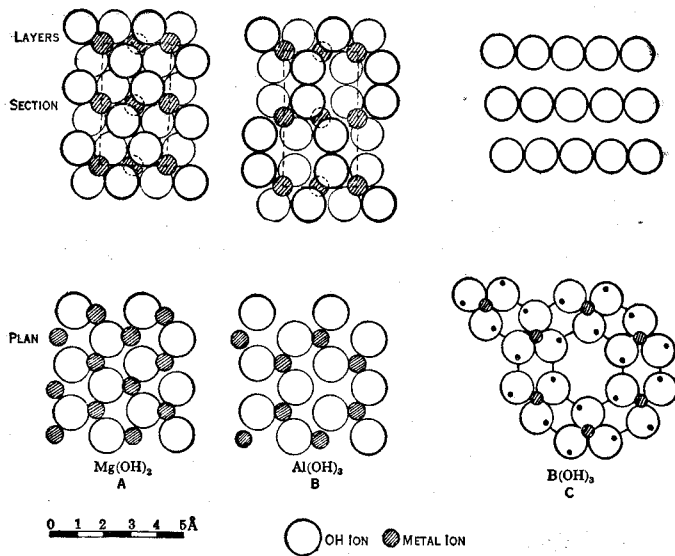
BY COURTESY OF THE CLARENDON PRESS, OXFORD

FIG. 117.—HYDROXIDE STRUCTURES

(A) $Mg(OH)_2$, brucite, and (B) $Al(OH)_3$, hydrargillite, are both composed of close-packed layers of hydroxyls. The difference is that in (B) one metal position in three is missing as shown in the plan and hydroxyl groups in adjacent layers are vertically above each other in (B) rather than stacked as in (A) as a result of more strongly directional hydroxyl bonding. This is shown in the section. (C) is the radically different structure of boric acid, $B(OH)_3$. Here the co-ordination around the metal atom is triangular and all the hydroxyl bonds lie in a plane. The layers are held together loosely by dispersion forces

Proteins.—The proteins, the polymers of amino acids, are the most various as well as the most important of polymers physically, chemically and biologically. A fibrous protein, the myosin of muscle, is responsible for all animal movement. Tougher fibrous proteins give supporting and defensive structure which man has made use of for his own purposes, collagen for skin and leather, fibroin in silk, keratin in hair, wool and horn. The nonfibrous, soluble and crystallizable proteins, the albumens and globulins, are the major constituents of cells of animals and plants alike. As chemical agents or enzymes they are responsible for the cycles of chemical interactions that maintain the metabolism which is the essence of life.

The fibrous proteins seem to belong to two great classes, the

binds the interspersed liquid in an extended three-dimensional

828D CRYSTALLOGRAPHY

rigid proteins of the collagen type whose structure was still not elucidated in the 1950s, and the contractile proteins of the myosin-keratin type whose molecules can, in general, exist in an extended form and in a folded or a coiled form. Silk fibroin is the only one that is found naturally with extended molecules similar to
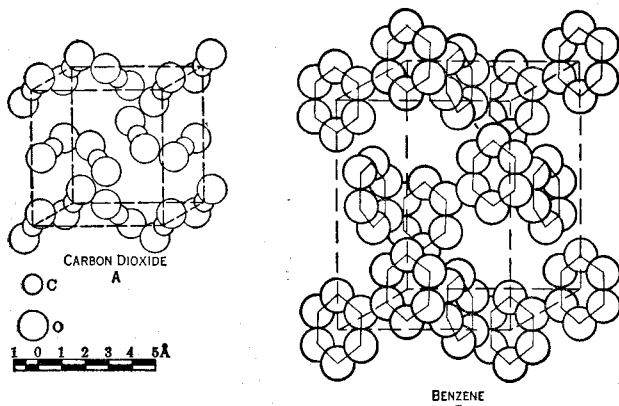

CARBON DIOXIDE
A

BENZENE
B

FIG. 118.—SIMPLE MOLECULAR CRYSTALS

The structures, which are both modifications of cubic close packing, occur from the action of nondirectional dispersion forces between nonpolar molecules. In (A), carbon dioxide, the molecules lie along a set of nonintersecting triad axes similar to that existing in iron pyrites, Fig. 91A. In (B), benzene, the planes of the molecules lie parallel to the longest axes but are alternately turned to make a herringbone pattern in the plane perpendicular to it

those found in synthetic dipeptides (fig. 132). The keratin molecules of hair and wool are normally coiled and held in position by -S-S- cross links. By weakening these through steaming or chemical solution the extended form can be produced by stretching, a process made use of in permanent waving (fig. 133). The myosin of muscle is always found in the coiled form but not in a fixed configuration, and the variation in its amount corresponds to the contraction and relaxation of muscle. The precise configuration of the fold or coil of the polypeptide chain is still much in dispute. An attractive solution, arrived at from stereochemical considerations, is that of Pauling. This is a tightly coiled spiral with 3.7 amino-acid residues per turn of length 5 Å or a 1.5 Å step between successive residues along the chain.

Once soluble proteins, and particularly enzymes, could be purified it was found possible to crystallize them and several of these crystals have been studied by X-ray methods. This has yielded much information about the general size and shape of protein molecules (fig. 134) but as yet little more than hints as to their internal constitution. This is not surprising, if it is borne in mind that the smallest protein molecule contains more than 1,000 atoms and that these must be arranged in a highly unsymmetrical way. The problem of protein structure, on account both of its intrinsic importance and of its difficulty, remains the goal of crystal analysis. It will probably require a combined attack of chemists, crystallographers and biologists to solve it.

What is known is that protein molecules of any relatively pure protein, such as insulin, haemoglobin, lysozyme or ribonuclease, are definite, almost identical, objects roughly ellipsoidal in shape, and of dimensions ranging from 20 to 60 Å. In the wet crystal, and presumably in solution, they are surrounded by a layer of water of about a third their weight, and more water, which may contain salts, is usually also found between the molecules in the crystal. Internally the general opinion is that the molecules contain several polypeptide chains arranged in parallel at a distance of about 10 Å. As the number of terminating chains found by chemical methods is usually less than that inferred crystallographically it is supposed that the same chemical chain may be bent backward and forward several times to form several crystallographic chains. Heat might be expected to break up this arrangement and join the chains haphazardly. This would account for the phenomenon of protein denaturation, the general hardening and insolubility produced by boiling solutions of soluble proteins, as for instance, in white of egg.

Crystalline Viruses.—The normal proteins are not the largest molecules that have been found to crystallize. Still larger are the nucleoproteins constituting a number of plant viruses such as those of tobacco mosaic, tomato bushy stunt and turnip yellow. A nucleoprotein is a relatively loose compound of protein and nucleic acid, itself a composite of phosphates, sugars and purine or pyrimidine derivatives.

The units or organisms that make up virus crystals are large enough—of the order of 100 to 400 Å—to be seen in the electron microscope, and the appearance of a virus crystal at a magnification of about 30,000 is a striking confirmation of pictures of crystal structure arrived at indirectly by X-ray diffraction or indeed of the logical guesses of Hooke, Huygens and Newton who spoke of crystals containing molecules arranged in "rank and file." The regularity of plant virus crystals goes, however, further than their merely regular packing. The X-rays, with their higher resolving power than the electron microscope, show that they have internal regularity and quasi identity down to atomic dimensions.

At this point, on the very limit of knowledge at mid-20th century, the subject of the structure of crystals may be left. New methods, such as that of neutron diffraction and new refinements, particularly in the use of computing machines, were rapidly driving those limits back. What had already been done, however, in the years since Laue's discovery of 1912 had already transformed almost out of recognition the knowledge of solids and liquids. In this respect it is as if science had acquired a microscope capable of magnifying 10,000,000-fold, capable of seeing atoms distinctly. As a result science was beginning to find explanations in terms of atoms and their combinations not only of the phenomena of physics and chemistry but of the behaviour of ordinary things. The beating out of metal under the hammer, the brittleness of glass and the cleavage of mica, the plasticity of clay, the lightness of ice, the greasiness of oil, the elasticity of rubber, the contraction of muscle, the waving of hair, and the hardening of a boiled egg are among the hundreds of phenomena that had already been com-
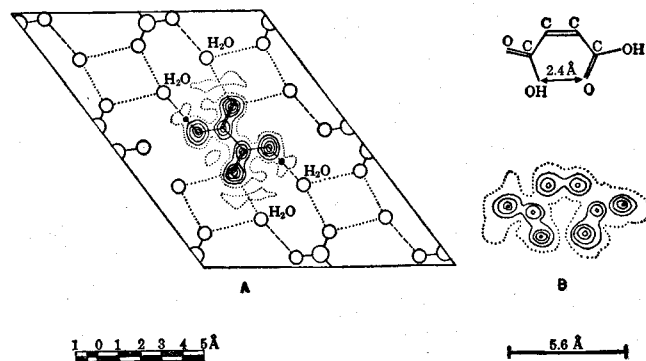
A

B

1 0 1 2 3 4 5Å   5.6 Å

FIG. 119.—ORGANIC ACIDS

(A) Oxalic acid dihydrate, Fourier projection of single molecule showing its position in the cell. The molecule is bound in a plane to others through water molecules. The probable position of the hydrogen atom responsible for the strongest hydrogen bond is shown. (B) Maleic acid, Fourier projection and bond diagram showing internal hydrogen bond reduced to a very small value 2.4 A by the strain of the rigid and plane molecule

pletely or partially explained. They were an earnest of the millions of others, old and new, that still had to be explained.

(J. D. Be.)

PHYSICAL PROPERTIES OF CRYSTALS

The great bulk of solid matter is crystalline, and therefore the properties of crystals are to a large extent also the properties of ordinary solid materials. The differences between the properties of single crystals and those of ordinary solid matter are due to the polycrystalline or partially crystalline character of ordinary solids. Thus the study of crystals is the study of solid matter in its simplest form. The properties considered here are those of thermal expansion, thermal and electrical conductivity, magnetic and dielectric induction, piezoelectricity and pyroelectricity, elasticity, optical properties, plasticity, cleavage and rectification. A special

section is devoted to a more detailed treatment of the optical properties.

Applications of Special Properties of Crystals.—The physical properties of crystals find many applications in other sciences and in industry. Some crystals, of which mica is the best example, possess the property of cleaving into thin layers. As it occurs in the rocks, a crystal of mica may be a foot across and an inch or so thick. On pressing a sharp point, or a sharp blade, into the side of such a crystal it cleaves in two. This cleavage may be repeated many times until layers as thin as $\frac{1}{1,000}$ in. are obtained. With some difficulty even thinner layers can be obtained. Such thin layers of mica are used in making condensers for radio apparatus, and for the windows of slow-combustion stoves. Certain crystals are valued for their resistance to fracture. Diamond is the hardest substance known and, because of its resistance to wear, it is used in rock-drills, precision lathe-turning and wire drawing as well as for a gem stone. Synthetic corundum, which when coloured red forms artificial ruby, is also used for watch bearings because of its hardness. Other crystals are very soft; e.g., talc owes its use as a cosmetic to this property and its white colour. Crystals of calcite

a = 5.67 Å
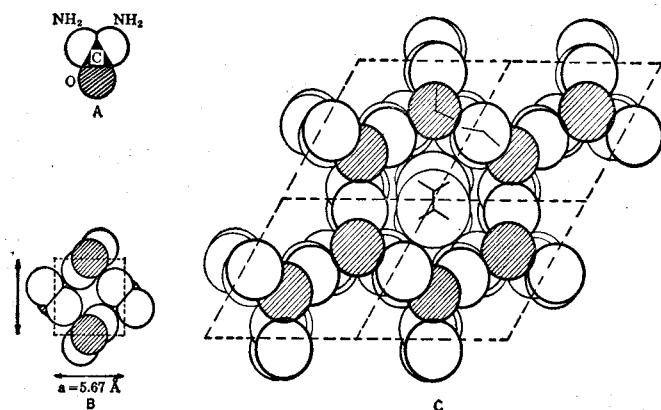
BY COURTESY OF (B, C) "ACTA CRYSTALLOGRAPHICA"

FIG. 120.—FORMS OF CRYSTALLINE UREA

The urea molecule O=CNH₂ is shown diagrammatically in (A). The spheres of NH₂ action of the positively polarized NH₂ groups and the negative O atom overlap that of the central carbon atom and are entirely responsible for the coherence of the molecules in the crystal. In (B) is shown the tetragonal form of the crystal of pure urea held together very compactly by the attractions between the positive and negative parts of the molecule. In (C) (on a slightly larger scale) is shown the hexagonal form of urea stabilized by the presence of a straight chain hydrocarbon—shown at the centre of the diagram. The molecules are held together as in the other case by electrostatic forces

are employed in producing polarized light. The science of petrology is largely based on the study of the appearance of thin sections of rocks in a microscope, fitted with two polarizing calcite prisms. In many instruments polarized light is produced by polaroid, a cellulose or other transparent base in which pleochroic crystals have been dispersed. These crystals have the property of absorbing polarized light vibrating in one direction and transmitting light vibrating in a perpendicular direction. Provided the crystals are spread on the base all parallel to one another they produce plane polarized light.

Another substance of great practical importance is quartz. All its physical properties are important, but its piezoelectricity is probably of the greatest practical application. Suitably shaped pieces of quartz can be made to vibrate under the influence of an alternating electric field and, conversely, when they vibrate they generate electric charges. This action and reaction between the applied electric field and the crystal makes it possible for the crystal to control the frequency of alternation of the electric field. So accurate is this control that when applied to clocks it results in timekeepers which do not gain or lose more than one second a year. In broadcasting and in all extensive telephone systems there is a need for accurate control of frequency and this usually depends on the properties of small bars of quartz. Single crystals of metals play an important part in industrial processes. Transformers and permanent magnets depend for their efficiency on the size and orientation of the iron crystals they contain.

Lastly, mention must be made of the properties of rectification shown by many semimetallic crystals. When used with appropriate contacts, crystals of copper oxide, selenium, silicon and germanium are capable of conducting electricity in one direction much better than in the opposite direction. This property is used in electrical engineering to produce direct current from alternating current and in radio reception to make audible the rapid variations of the alternating current in the receiving aerial.


5.06 Å
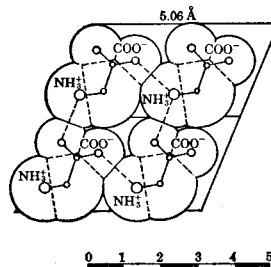
BY COURTESY OF JOURNAL OF THE AMERICAN CHEMICAL SOCIETY AND GUSTAV ALBRECHT

FIG. 121.—GLYCINE

Arrangement of molecules in b planes showing the effect of zwitter ion binding between the COO— radical on one amino acid molecule and the NH₃⁺ radical of two others. The layers thus formed are held together much less strongly by residual polar forces

Dependence of Physical Properties on the Perfection of the Crystal.—A number of the physical properties of crystals are practically the same even when the crystal is not quite perfect. Such properties are called structure insensitive and include, among others, thermal conductivity, diamagnetic susceptibility, piezo-electricity and elasticity. Other properties are dependent on the perfection of the crystal and these are known as structure sensitive. Perhaps the most important of these is plasticity which is connected with the processes of crystal growth. The variation of the physical properties with direction is subject to similar laws in the structure-sensitive as in the structure-insensitive group. It is much easier to measure the properties which are structure insensitive because they are reproducible from one specimen to another and the laws governing the variation with direction have been worked out in connection with structure insensitive properties.

Representation Surfaces.—It is convenient to represent the variation of a given physical property of a crystal with direction by means of a geometrical surface. These surfaces are known as representation surfaces and are directly related to the symmetry

FOURIER PROJECTION ON b PLANE
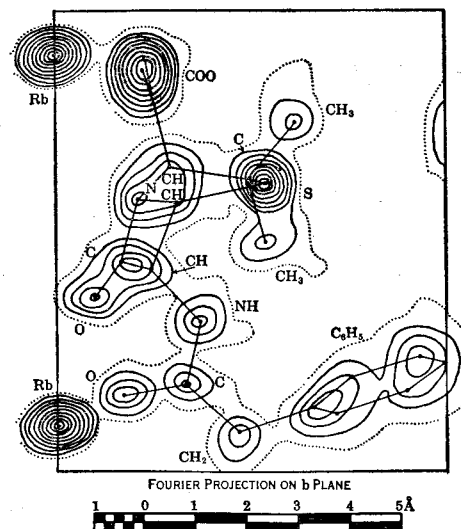
BY COURTESY OF PRINCETON UNIVERSITY PRESS, FROM "THE CHEMISTRY OF PENICILLIN"

FIG. 122.—RUBIDIUM BENZYL PENICILLIN

Simplified Fourier projection from which the chemical structure was deduced. Note the four-membered oxazolone ring, a most unexpected feature. The rubidium ions are co-ordinated to carboxy and hetonic oxygen groups

of the crystal. Properties representable by an ellipsoid include thermal and electrical conduction, thermal expansion, magnetic and electric susceptibility and certain optical properties; e.g., refractive index. The ellipsoid is triaxial in the orthorhombic, monoclinic and triclinic systems; it is an ellipsoid of revolution in the tetragonal, rhombohedral and hexagonal systems; and in the cubic system it degenerates into a sphere. The representation surfaces for piezoelectricity may have cigar-shaped lobes or consist of more or less ellipsoidal figures placed asymmetrically with

8₂8F   CRYSTALLOGRAPHY

respect to the origin. Surfaces representing elasticity are like crystals of the same symmetry with rounded corners and dimpled faces.

The number of coefficients required to define the property of a crystal depends on the nature of the representation surface. Thus a sphere has only one constant, namely, the radius; an ellipsoid of revolution has two constants corresponding to its major and minor axes; a triaxial ellipsoid has three constants corresponding to the lengths of its principal axes. The constants defining piezo-electric and elastic properties are more numerous than those de-
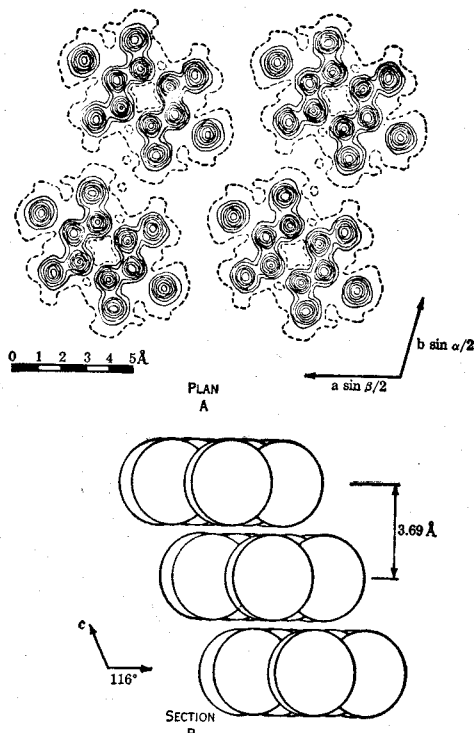
BY COURTESY OF (A) PROF. J. M. ROBERTSON AND "JOURNAL OF THE CHEMICAL SOCIETY"

FIG. 123.—HEXAMETHYLBENZENE

(A) Fourier projection nearly in plane of molecules. (B) Diagram of stacking of molecules in their own plane. The parallel arrangement contrasts with those of Fig. 124 and 125

fining an ellipsoid except when the symmetry of the crystal is very high.

Measurement of Structure-Insensitive Properties.—Most measurements of the physical properties of crystals are usually made difficult by the smallness of the specimens. A few natural and synthetic crystals can be grown in large blocks but the great bulk of crystals do not exceed a few millimetres in linear dimensions. For optical work this is already a large size and it is therefore not surprising that the optical properties of crystals are most extensively studied. By X-ray methods it is also possible to study the thermal expansion of small crystals. For thermal and electrical conduction, for magnetic and dielectric induction, for piezoelectricity, elasticity and other properties larger crystals than can usually be obtained are required and hence there is a great paucity of physical data about most crystalline substances. The apparatus used is usually the same as that employed for ordinary solids except that changes are made to take account of the variation of the physical property with direction and also, as far as possible, the small size of the crystal.

Thermal conductivity is measured in apparatus which is a variant of Forbes' bar; i.e., heat flows along a composite bar consisting of a plate of crystal sandwiched between two metallic plates. The temperature gradient in the crystal is measured and compared with that in the metal plates. The temperature gradients in the crystal and in the metal are inversely proportional to their thermal conductivities.

Electrical conductivity can be measured on single crystal wires by standard methods. It is necessary to grow "current" and "po-

tentials" leads which are all part of the same single crystal.

Magnetic induction is measured by suspending the crystal in a strong magnetic field (of the order of 1,000 oersted or more) and measuring the mechanical influence of the field on the crystal. There are two types of measurement: one carried out in a uniform
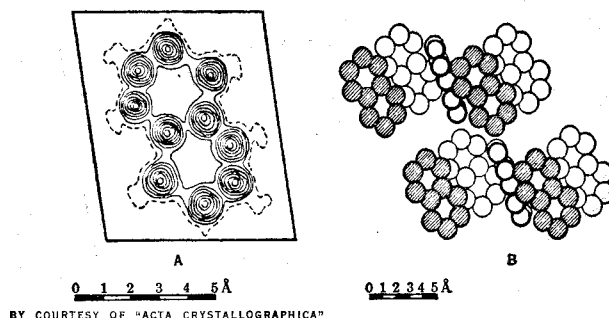

BY COURTESY OF "ACTA CRYSTALLOGRAPHICA"

FIG. 124.—NAPHTHALENE

(A) Three-dimensional Fourier section through plane of molecule. Note regularity of the distribution of intensity and the lowest contour line showing the positions of the hydrogen atoms. (B) Diagram of molecular packing showing herring bone arrangement. One set of molecules is seen almost edge on

magnetic field and the other in a nonuniform field. In the uniform field a crystal, suspended on a thin fibre of phosphor-bronze or fused silica, tends to set with the direction of its greatest paramagnetic susceptibility along the lines of force, or, if it is diamagnetic, with the direction of least diamagnetic susceptibility parallel to the field. If the crystal is twisted away from this position it tends to return under the influence of the field and the magnitude of this torque is measured. This provides information on the difference between the maximum and minimum susceptibilities perpendicular to the length of the fibre. By mounting the crystal in various ways on the fibre the differences between the three principal susceptibilities can be found. In a nonuniform field the crystal is subjected to a translational force. This force can be measured by the displacement of the crystal and is a measure of the susceptibility in the direction of the magnetic field. By mounting the
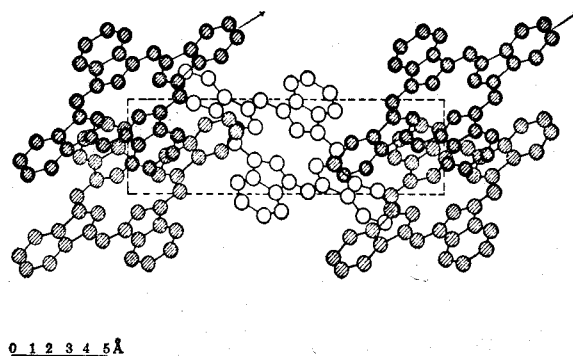
BY COURTESY OF PROF. J. M. ROBERTSON AND "JOURNAL OF THE CHEMICAL SOCIETY" (LONDON)

FIG. 125.—PHTHALOCYANINE

The diagram shows the molecular arrangement. (See Fig. 78.) The stippled atoms belong to molecules whose centres are in the plane of the paper. They are inclined about an axis in the plane of the paper with the lower rings upward and so overlap. The centre of the molecule with the open circle atoms lies half way down the cell. It is inclined about another axis and interleaves with the other molecules forming a very compact structure

crystal in two or three orientations relative to the direction of the field the principal susceptibilities may be found individually.

Ferromagnetism is the strongly developed magnetic property shown by crystals of lodestone, iron, nickel and various metallic oxides and alloys. The degree of magnetization shown by such materials is many million times greater than that shown by most other substances. This is explained by the mutual effect of neighbouring atoms on one another. Each atom behaves like a very weak bar magnet and under the influence of an external field these magnets tend to set parallel to one another. The external magnetic field is in part supplied by the surrounding atoms, and certain small regions called domains become spontaneously magne-

CRYSTALLOGRAPHY

tized due to the mutual effects of the atoms within any one domain. In contrast with ferromagnetic crystals, a class of antiferromagnetic crystals was found in which the mutual effect of neighbouring atoms is always to set the atomic magnets in oppositely directed groups. An example of such a crystal is a mixed oxide of zinc and iron, $ZnO.Fe_2O_3$. When this substance is placed in a magnetic field there is no possibility of causing all the atomic mag-

PROJECTION SHOWING RING ARRANGEMENT
A

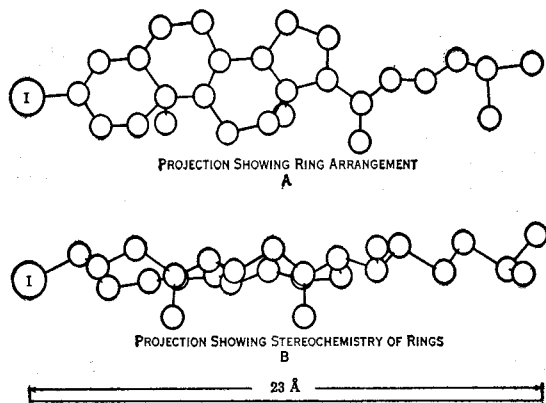PROJECTION SHOWING STEREOCHEMISTRY OF RINGS
B

|←————— 23 Å —————→|

FIG. 126.—CHOLESTERYL IODIDE

Scale diagram based on X-ray analysis showing the stereochemistry of the sterol ring system. The methyl groups projecting from the general plane of the molecule should be noted

nets to act co-operatively because they are locked firmly together, equal numbers being orientated in opposite directions.

Dielectric properties of crystals are usually measured in standard bridge or heterodyne circuits. The capacitors are made small because the capacity of a condenser containing a crystal of the dimensions usually obtainable is also small. A class of ferroelectric crystals was discovered in which the dielectric constant may reach values many thousand times greater than those found in normal dielectrics. These crystals are like ferromagnetic materials in that electric dipoles associated with neighbouring atoms tend to set parallel to one another. This leads to spontaneous polariza-
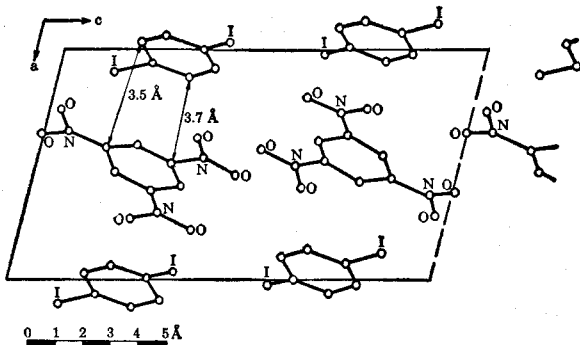
BY COURTESY OF H. M. POWELL, F.R.S., AND "JOURNAL OF THE CHEMICAL SOCIETY" (LONDON)

FIG. 127.—MOLECULAR COMPOUND OF PARAIODOANILENE AND S-TRINITROBENZENE

The molecules shown foreshortened are almost parallel; the distances between their planes are indicated

tion of domains and to a large polarization in an applied electric field. A well-known example of this class of crystal is Rochelle salt, $NaKC_4H_4O_6.2H_2O$. The dielectric constant varies greatly with the frequency of the applied field, and special attention must be given to the temperature, pressure and strength of the electric field in measuring the dielectric constant.

Piezoelectric properties may be studied either by measuring the electric charge developed on a crystal when it is bent or twisted or by studying the electrical characteristics of an oscillatory circuit in which the crystal is placed. In crystals of low symmetry it may be necessary to cut a large number of plates and bars and to study each one separately in order to obtain the magnitudes of the various piezoelectric constants.

Pyroelectricity is the property of certain crystals of developing electric charges on heating or cooling. It is well shown by tourmaline and the electric charges can be revealed by placing the crystal in an atmosphere of white smoke obtained by burning magnesium ribbon (fig.   ).

Elastic properties of crystals may be measured by two distinct methods. The first and older method depends on bending or twisting plates or bars and measuring the deformation as well as the applied forces. The second method depends on setting the crystal into vibration and finding the frequency of vibration and the wave length of the corresponding elastic wave. From these data the velocity of sound associated with this particular type of vibration can be calculated and, from that, one or more elastic constants. A variant of this method depends on the scattering of light or of X-rays from waves travelling in the crystal. A light beam is passed through a small polished cube of the crystal which is excited into rapid vibration by a piezoelectric oscillator underneath it. The alternating regions of compressed and extended material in the crystal act in the light as a diffraction grating. A complex diffraction pattern (fig.   ) is produced around the incident light beam and an analysis of this leads to values for the

CAGED MOLECULE

QUINOL MOLECULE   QUINOL MOLECULE

HYDROXYL   HYDROGEN BOND

A

|←—— 15 Å ——→|

B
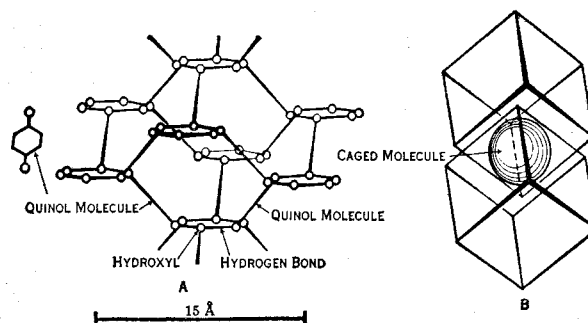
BY COURTESY OF (A) H. M. POWELL, F.R.S., AND "JOURNAL OF THE CHEMICAL SOCIETY" (LONDON); (B) D. E. PALIN AND "JOURNAL OF THE CHEMICAL SOCIETY" (LONDON)

FIG. 128.—CLATHRATE COMPLEX OF QUINOL MOLECULES

(A) Perspective drawing showing three-dimensional cage work of quinol molecules. The hexagons denote the hydrogen bonding between the molecules, each quinol molecule being shown schematically as a line. (B) Schematic representation of the enclosure of a molecule between two cage systems. Each point of the cage now replaces the hexagon of hydrogen bonds as seen in (A). The crystalline clathrate compound is the complete interpretation of two cage systems

elastic constants. If X-rays are used instead of visible light the elastic waves are not produced by any external agency, such as a piezoelectric oscillator, but arise from the vibrations of the atoms in the crystal. The higher the temperature, the greater the amplitude of these vibrations and the stronger the reflection of the X-rays they produce. From the direction of these diffusely reflected X-rays the wave length of these elastic waves is determined, and from the intensity of the X-rays the frequency of the elastic waves is found. Combining these data the velocity is again found and from that the elastic constants.

Optical properties of a crystal are completely defined by the three principal refractive indices (which may be reduced to two or only one according to the symmetry) and by the variation of these indices with wave length. The methods of measurement are adapted from those methods used in connection with isotropic materials such as glass. The essential requirement is, in general, that the vibration direction of the polarized light passing through the crystal shall have some known relation to the external shape of the crystal. To each direction of vibration there corresponds a characteristic refractive index. Prisms cut in various ways usually give rise to two refracted beams and the corresponding indices can be found from the minimum deviation. Total reflection of the light from the crystal when immersed in a liquid of high refractive index is also used to find accurate values of the indices. Various refractometers have been devised for this purpose and some can be used on the stage of a microscope for the study of very small specimens. A great wealth of optical phenomena is shown by doubly refracting crystals viewed between crossed nicols; i.e., in polarized light (fig.   ). For instance, a wedge-shaped piece of crystal shows a series of colours corresponding closely to those obtained with Newton's rings. The cause of this
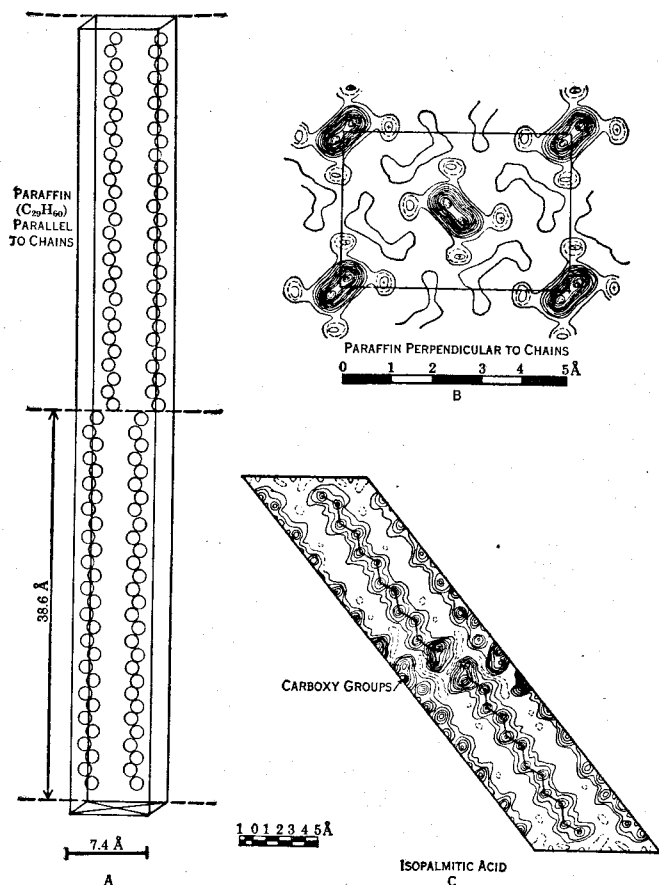
8₂8H   CRYSTALLOGRAPHY

association of a particular colour with a particular thickness of crystal is a result of double refraction, because of which certain colours additively interfere and others destructively interfere, leaving a coloured residuum. Between parallel nicols the complementary colours are observed. Some beautiful optical effects can be obtained in convergent light (fig.   ). When a crystalline plate cut perpendicular to an optic axis is viewed by means of a minifying telescope between crossed nicols, coloured circles or rings of more complicated form are observed. These are dependent principally on the variation of the double refraction with direction and can be used in finding important optical properties such as the differences between the principal refractive indices.

Rotatory polarization is a property possessed by certain crystals of rotating the plane of vibration of polarized light through an angle depending on the thickness traversed. Cubic crystals such as sodium chlorate, $NaClO_3$, show the effect in all directions, but in crystals such as quartz or cane sugar the effect is masked by the double refraction except along the optic axes.

Structure-Sensitive Properties.—Some individual crystals are perfect by all the tests which can be applied to them; all but these rare examples are imperfect. The exact way in which the

FIG. 129.—CRYSTAL STRUCTURES OF LONG CHAIN COMPOUNDS
(A) and (B) are of a straight chain paraffin, $C_{29}H_{60}$. In (A) a single cell is shown. The double layer contains molecules in a pseudohexagonal arrangement hexagonally close packed at the ends like the two layers of cells in a honeycomb. (B) shows an enlarged Fourier projection obtained by single crystal electronic diffraction, indicating clearly the positions of the staggered carbon atoms and the hydrogen atoms, very difficult to find by X-ray methods. (C) shows a Fourier projection of isopalmitic acid

atoms are arranged in the unit cell, the smallest repeating portion of the crystal, can be accurately determined but it is much more difficult to find the degree of imperfection in the stacking of these unit cells. An actual crystal may be likened to a large pile of regularly stacked bricks; each brick represents a unit cell and the whole pile represents the crystal. The imperfections of the crystal could be represented either by holes or by pieces of stone of irregular shape embedded in the pile. The interruptions of the regular rows of bricks by holes or stones correspond to some of

the defects which become incorporated in the crystal during growth. The growth of a crystal occurs in different ways according to its nature and the circumstances of its growth, but in many cases layer after layer is laid down in a regular way. If the growth rate exceeds a certain speed foreign atoms may be caught
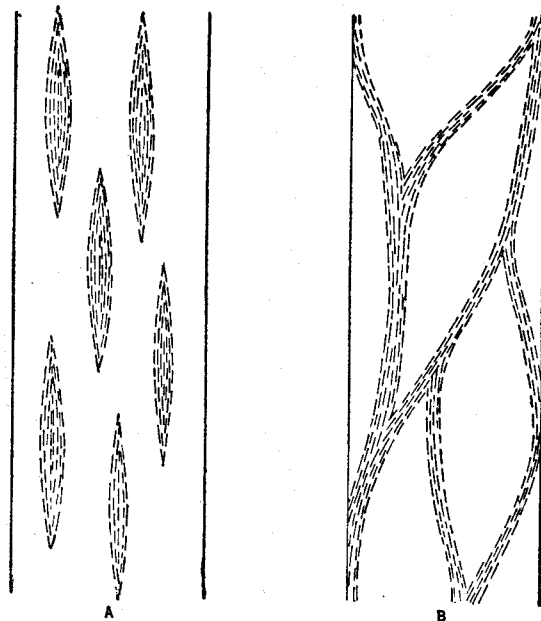

FIG. 130.—TACTOIDS AND GELS
(A) Diagram of the formation of tactoids in sols of tobacco mosaic virus preparations. The arrangements of the elongated virus particles in the spindle-shaped tactoids is indicated not to scale. In this condition the tactoids orient themselves parallel to the walls of the tube and free flow is possible. (B) On disturbing the preparation the tactoids jam together and form a gellike network whose internal constitution is similar to that of the tactoids but which is so connected as to block all movement

between successive layers, or atoms may be missed out of the places they should occupy. The nucleus from which the crystal starts to grow probably influences the whole of the succeeding growth and errors in stacking become perpetuated right through the crystal.

Plasticity.—A crystal is said to possess plasticity when under mechanical stress certain parts of the crystal can move over other parts, according to definite laws, in such a way as to relieve the stress. This is connected with the imperfections referred to above which concentrate the stress in localized regions around themselves. Although calcite, rock salt, quartz and many other well-known crystals show plasticity the phenomenon is most clearly revealed by single crystals of metals. If, for instance, a single crystal of zinc in the form of a wire is stretched, then the wire extends to twice, or more than twice, its original length before breaking. During the stretching the shape of its cross section changes from circular to elliptical. The gliding of one part of the crystal relative to the neighbouring parts occurs on glide planes and in one or more glide directions. The crystal behaves like a pack of playing cards in which there is a thick viscous fluid between successive cards. The phenomenon is coupled with work hardening; *i.e.*, those parts of the crystal which have been subjected to deformation show a greater resistance to further deformation than parts not already deformed. This phenomenon is also connected with the imperfections in the atomic stacking. Each imperfection concentrates a part of the stress applied to the whole crystal around itself and when the number of these imperfections is greatly increased by the plastic flow, the whole applied stress can be resisted by the localized effects of the imperfections.

It is easy to see how great is the importance of work hardening taken in conjunction with plasticity, for not only do metals yield at the place where the stress is greatest but also resist further deformation at that point until some other part has also experienced deformation.

Plasticity is sometimes associated with glide-twinning, a process
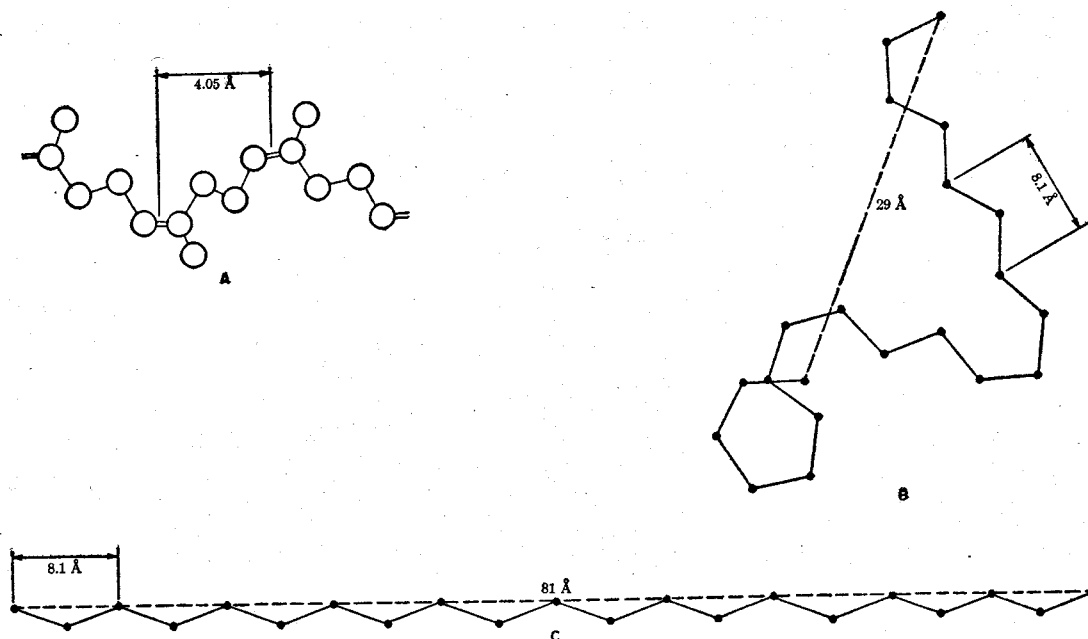
CRYSTALLOGRAPHY

FIG. 131.—RUBBER MOLECULES

(A) shows a possible arrangement of polyisoprene rubber in the normal crystalline form. (B) and (C) show diagrammatically how the chance coiling of the chain of isoprene units such as occurs in unstretched rubber leads to a marked shortening compared with that found in the fully extended chain formed by stretching

in which there is a sudden switching of the atoms to a second stable position related in a definite geometrical way to the first. This occurs toward the end of the range of plastic deformation and gives rise to a characteristic crackling noise similar to the cry of crumpled tin foil.

Cleavage is shown by many types of crystals when struck with a sharp knife held parallel to a certain plane in the crystal. Thus rock salt splits parallel to the face of the natural cube, calcite parallel to the face of a rhombohedron and mica parallel to the basal plane. The correlation between cleavage and the atomic structure is close; wherever the atoms are more firmly bound together in one direction (or directions) the cleavage tends to occur so that the plane of cleavage does not intersect any of the strongly bound lines of atoms. Thus layer structures tend to cleave parallel to the layers, chain structures parallel to the chains, and scaffold structures tend to have no cleavage at all except when the structure is very simple.

Rectification is the phenomenon shown by certain semiconducting crystals in which electric current flows more readily in one direction than in the opposite direction. This phenomenon could never occur in a homogeneous material and is in fact always associated with a boundary layer of different chemical or physical properties from the main crystal. The asymmetry of the electrical property is due to a difference of electronic character at points on a line passing through the boundary layer. (W. A. W.)

OPTICAL PROPERTIES

The complex optical characters of crystals are not only of considerable interest theoretically, but are of the greatest practical importance. In the absence of external crystalline form, as with a faceted gem stone, or with the minerals constituting a rock (thin, transparent sections of which are examined in the polarizing microscope), the mineral species may often be readily identified by the determination of some of the optical characters.

According to their action on transmitted plane-polarized light (*see* LIGHT: *Polarization And Electromagnetic Theory*) all crystals may be referred to one or another of the five groups enumerated below. These groups correspond with the six systems of crystallization (in the second group two systems being included together). The several symmetry classes of each system are optically the same, except in the rare cases of substances which are circularly polarizing.

1. Optically isotropic crystals—corresponding with the cubic system.

2. Optically uniaxial crystals—corresponding with the tetragonal and hexagonal systems.

3. Optically biaxial crystals in which the three principal optical directions coincide with the three crystallographic axes—corresponding with the orthorhombic system.

4. Optically biaxial crystals in which only one of the three principal optical directions coincides with a crystallographic axis—corresponding with the monoclinic system.

5. Optically biaxial crystals in which there is no fixed and definite relation between the optical and crystallographic directions—corresponding with the triclinic system.

Optically Isotropic Crystals.—These belong to the cubic system, and like all other optically isotropic (from ἴσος, like, and τρόπος, character) bodies have only one index of refraction for light of each colour. They have no action on polarized light (except in crystals which are circularly polarizing); and when examined in the polariscope or polarizing microscope they remain dark between crossed nicols or polaroids, and cannot be distinguished optically from amorphous substances, such as glass.
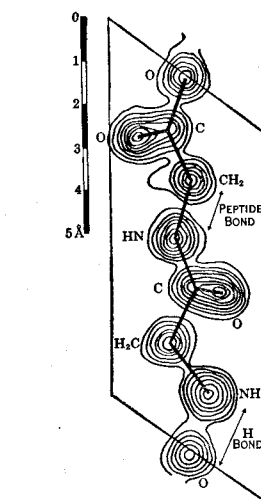
FIG. 132.—DIPEPTIDE MOLECULE

Fourier projection of the simplest dipeptide, glycylglycine. The molecules line up in chains as a result of hydrogen or zwitter ion bonding between the carboxy group at one end of the chain and the amino group at the other

Optically Uniaxial Crystals.—These belong to the tetragonal and hexagonal (including rhombohedral) systems, and between crystals of these systems there is no optical distinction. Such crystals are anisotropic or doubly refracting (*see* LIGHT: *Refraction and Double Refraction*); but for light travelling through them in a certain, single direction they are singly refracting. This direction, which is called the optic axis, is the same for light of all colours and at all temperatures; it coincides in direction with the principal crystallographic axis, which in tetragonal crystals is a fourfold (or 4) axis of symmetry, and in the hexagonal system a threefold or sixfold axis.

828J CRYSTALLOGRAPHY

For light of each colour there are two indices of refraction; namely, the ordinary index (ω) corresponding with the ordinary ray, which vibrates perpendicular to the optic axis; and the extraordinary index (ϵ) correspon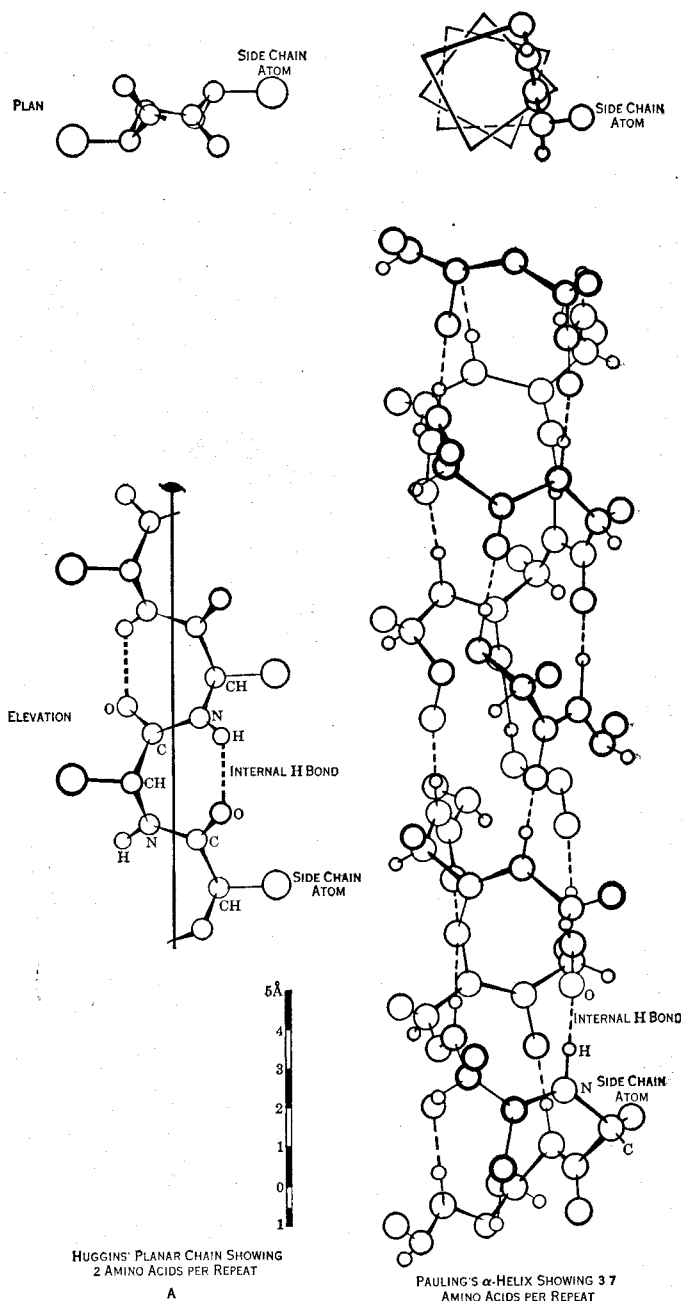ding with the extraordinary ray, which vibrates parallel to the optic axis. If the ordinary index of refraction be greater than the extraordinary index, the crystal is said to be optically negative, while if less the crystal is optically positive. The difference between the two indices is a measure of the strength of the double refraction or birefringence. Thus in calcite, for sodium (D) light, $\omega = 1.6585$ and ϵ 1.4863; hence this substance is optically negative with a relatively high double refraction of $\omega - \epsilon = 0.1722$. In quartz $\omega = 1.5442$, $\epsilon = 1.5533$ and $\epsilon - \omega = 0.0091$; this mineral is therefore optically positive with low double refraction. The indices of refraction vary, not only for light of different colours, but also slightly with the temperature.

The optical characters of uniaxial crystals are symmetrical not only with respect to the full number of planes and axes of symmetry of tetragonal and hexagonal crystals, but also with respect to all vertical planes, i.e., all planes containing the optic axis. A surface expressing the optical relations of such crystals is thus an ellipsoid of revolution about the optic axis. (In cubic crystals the corresponding surface is a sphere.) In the optical indicatrix (L. Fletcher, *The Optical Indicatrix and the Transmission of Light in Crystals*, London, 1892), the length of the principal axis, or axis of rotation, is proportional to the index of refraction (i.e., inversely proportional to the velocity) of the extraordinary rays, which vibrate along this axis and are transmitted in directions perpendicular thereto; the equatorial diameters are proportional to the index of refraction of the ordinary rays, which vibrate perpendicular to the optic axis. For positive uniaxial crystals the indicatrix is thus a prolate spheroid (lemon-shaped), for negative crystals an oblate spheroid (orange-shaped).

In Fresnel's ellipsoid the axis of rotation is proportional to the velocity of the extraordinary ray, and the equatorial diameters proportional to the velocity of the ordinary ray; it is therefore an oblate spheroid for positive crystals, and a prolate spheroid for negative crystals. The ray surface, or wave surface, which represents the distances traversed by the rays during a given interval of time in various directions from a point of origin within the crystal, consists in uniaxial crystals of two sheets; namely, a sphere, corresponding to the ordinary rays, and an ellipsoid of revolution, corresponding to the extraordinary rays. The difference in form of the ray surface for positive and negative crystals is shown in fig. 135 and 136.

When a uniaxial crystal is examined in a polariscope or polarizing microscope between crossed nicols (i.e., with the principal planes of the polarizer or analyzer at right angles, and so producing a dark field of view) its behaviour differs according to the direction in which the light travels through the crystal, to the position of the crystal with respect to the principal planes of the nicols, and further, whether convergent or parallel polarized light be employed. A tetragonal or hexagonal crystal viewed, in parallel light, through the basal plane, i.e., along the principal axis, will remain dark as it is rotated between crossed nicols, and will thus not differ in its behaviour from a cubic crystal or other isotropic body. If, however, the crystal be viewed in any other direction, for example, through a prism face, it will, except in certain positions, have an action on the polarized light. A plane-polarized ray entering the crystal will be resolved into two polarized rays with the directions of vibration parallel to the vibration-directions in the crystal. These two rays on leaving the crystal will be combined again in the analyzer, and a portion of the light transmitted through the instrument; the crystal will then show up brightly against the dark field. Further, owing to interference of these two rays in the analyzer, the light will be brilliantly coloured, especially if the crystal be thin, or if a thin section of a crystal be examined. The particular colour seen will depend on the strength of the double refraction, the orientation of the crystal or section, and upon its thickness. If, now, the crystal be rotated with the stage of the microscope, the nicols remaining fixed in position, the light transmitted through the instrument will vary in intensity,

and in certain positions will be cut out altogether. The latter happens when the vibration directions of the crystal are parallel to the vibration directions of the nicols (these being indicated by cross wires in the microscope). The crystal, now being dark, is said to be in position of extinction; and as it is turned through a complete rotation of $360°$ it will extinguish four times. If a prism face be viewed through, it will be seen that, when the crystal is in

PLAN

SIDE CHAIN ATOM

SIDE CHAIN ATOM

ELEVATION

CH
N
H
O
C
C
CH
INTERNAL H BOND
O
C
N
H
CH
SIDE CHAIN ATOM

5Å 4 3 2 1 0 1

INTERNAL H BOND
H
N SIDE CHAIN ATOM
C

HUGGINS' PLANAR CHAIN SHOWING 2 AMINO ACIDS PER REPEAT

A

PAULING'S α-HELIX SHOWING 3 7 AMINO ACIDS PER REPEAT

A

BY COURTESY OF (A) NATIONAL ACADEMY OF SCIENCES, (B) THE ROYAL SOCIETY (LONDON)

FIG. 133.—PROTEIN CHAIN MODELS DERIVED FROM ANALYSIS OF PEPTIDES
Both proposed models show internal hydrogen bonding as contrasted with the straight peptide chain of Fig. 132 which only shows external hydrogen bonding. Only one atom of each side group is shown

a position of extinction, the cross wires of the microscope are parallel to the edges of the prism: the crystal is then said to give straight extinction or parallel extinction.

In convergent light, between crossed nicols, a very different phenomenon is to be observed when a uniaxial crystal, or section of such a crystal, is placed with its optic axis coincident with the axis of the microscope. The rays of light, being convergent, do not travel in the direction of the optic axis and are therefore doubly refracted in the crystal; in the analyzer the vibrations will be reduced to the same plane and there will be interference of the

CRYSTALLOGRAPHY 828K

two sets of rays. The result is an interference figure (fig. 137), which consists of a number of brilliantly coloured concentric rings, each showing the colours of the spectrum of white light; inter-
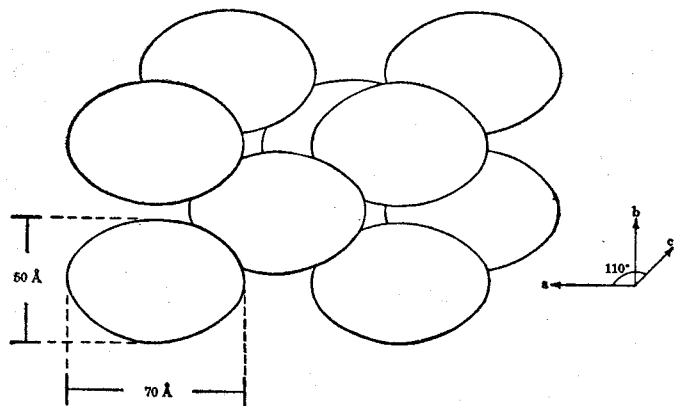
BY COURTESY OF "ACTA CRYSTALLOGRAPHIC"

FIG. 134.—DIAGRAM OF HORSE METHAEMOGLOBIN CRYSTAL STRUCTURE, SHOWING APPROXIMATE MOLECULAR SHAPE AND ARRANGEMENT

secting the rings is a black cross, the arms of which are parallel to the principal planes of the nicols. If monochromatic light be used instead of white light, the rings will be alternately light and dark. The number and distance apart of the rings depend on the strength of the double refraction and on the thickness of the crystal. By observing the effect produced on such a uniaxial interference figure when a quartz wedge, a gypsum plate or a mica plate is superposed on the crystal, it may be at once decided whether the crystal is optically positive or negative. Such a simple test may, for example, be applied for distinguishing certain faceted gem stones: thus zircon and phenakite are optically positive, while corundum (ruby and sapphire) and beryl (emerald) are optically negative.

Optically Biaxial Crystals.—In these crystals there are three principal indices of refraction, denoted by α, β and γ; of these γ is the greatest and α the least ($\gamma > \beta > \alpha$). T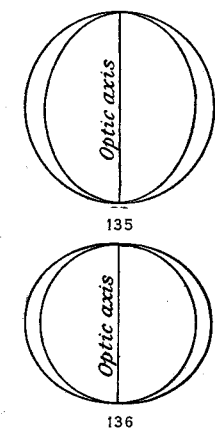he three principal vibration directions, corresponding to these indices, are at right angles to each other, and are the directions of the three rectangular axes of the optical indicatrix. The indicatrix (fig. 138) is an ellipsoid with the lengths of its axes proportional to the refractive indices; $OC = \gamma$, $OB = \beta$, $OA = \alpha$, where $OC > OB > OA$. The figure is symmetrical with respect to the principal planes OAB, OAC, OBC.

In Fresnel's ellipsoid the three rectangular axes are proportional to $1/\alpha$, $1/\beta$ and $1/\gamma$, and are usually denoted by $\mathfrak{a}$, $\mathfrak{b}$ and $\mathfrak{c}$ respectively, where $\mathfrak{a} > \mathfrak{b} > \mathfrak{c}$: these have often been called axes of optical elasticity, a term now generally discarded.

The ray surface (represented in fig. 139 by its sections in the three principal planes) is derived from the indicatrix in the following manner. A ray of light entering the crystal and travelling in the direction OA is resolved into polarized rays vibrating parallel to OB and OC, and therefore propagated with the velocities $1/\beta$ and $1/\gamma$ respectively: distances Ob and Oc (fig. 139) proportional to these velocities are marked off in the direction OA. Similarly, rays travelling along OC have the velocities $1/\alpha$ and $1/\beta$, and those along OB the velocities $1/\alpha$ and $1/\gamma$. In the two directions Op_1 and Op_2 (fig. 138), perpendicular to the two circular sections P_1P_1 and P_2P_2 of the indicatrix, the two rays will be transmitted with the same velocity $1/\beta$. These two directions are called the optic axes (primary optic axis), though they have not all the properties which are associated with the optic axis of a

135

136

FIG. 135.—RAY-SURFACE SECTION OF A POSITIVE UNIAXIAL CRYSTAL
FIG. 136.—RAY-SURFACE SECTION OF A NEGATIVE UNIAXIAL CRYSTAL

uniaxial crystal. They have very nearly the same direction as the lines Os_1 and Os_2 in fig. 139, which are distinguished as the secondary optic axes. In most crystals the primary and secondary optic axes are inclined to each other at not more than a few minutes, so that for practical purposes there is no distinction between them.

The angle between Op_1 and Op_2 is called the optic axial angle; and the plane OAC in which they lie is called the optic axial plane. The angles between the optic axes are bisected by the vibration directions OA and OC; the one which bisects the acute angle being called the acute bisectrix or first mean line, and the other the obtuse bisectrix or second mean line. When the acute bisectrix coincides with the greatest axis OC of the indicatrix, i.e., the vibration direction corresponding with the refractive index γ (as in fig. 138 and 139), the crystal is described as being optically positive; and when the acute bisectrix coincides with OA, the vibration direction for the index α the crystal is negative. The distinction between positive and negative biaxial crystals thus depends on the relative magnitude of the three principal indices of refraction; in positive crystals β is nearer to α than to γ while in negative crystals the reverse is the case. Thus in topaz, which is optically positive, the refractive indices for sodium light are $\alpha = 1.6120$, $\beta = 1.6150$, $\gamma = 1.6224$; and for orthoclase which is optically negative, $\alpha = 1.5190$, $\beta = 1.5237$, $\gamma = 1.5260$. The difference $\gamma - \alpha$ represents the strength of the double refraction.
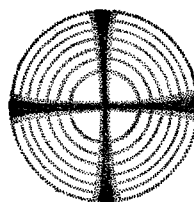

FIG. 137.—INTERFERENCE FIGURE OF A UNIAXIAL CRYSTAL

Since the refractive indices vary both with the colour of the light and with the temperature, there will be for each colour and temperature slight differences in the form of both the indicatrix and the ray surface; consequently there will be variations in the positions of the optic axes and in the size of the optic axial angle. This phenomenon is known as the dispersion of the optic axes. When the axial angle is greater for red light than for blue the character of the dispersion is expressed by $r > v$ and when less by $r < v$. In some crystals, e.g., brookite, the optic axes for red light and for blue light may be, at certain temperatures, in planes at right angles.
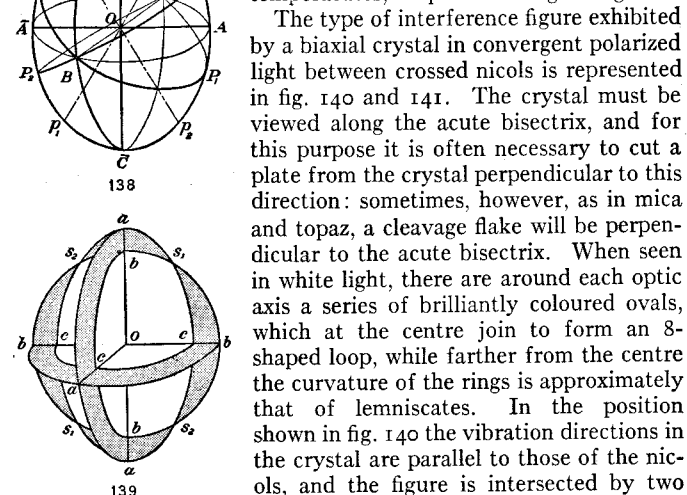
The type of interference figure exhibited by a biaxial crystal in convergent polarized light between crossed nicols is represented in fig. 140 and 141. The crystal must be viewed along the acute bisectrix, and for this purpose it is often necessary to cut a plate from the crystal perpendicular to this direction: sometimes, however, as in mica and topaz, a cleavage flake will be perpendicular to the acute bisectrix. When seen in white light, there are around each optic axis a series of brilliantly coloured ovals, which at the centre join to form an 8-shaped loop, while farther from the centre the curvature of the rings is approximately that of lemniscates. In the position shown in fig. 140 the vibration directions in the crystal are parallel to those of the nicols, and the figure is intersected by two black bands or brushes forming a cross. When, however, the crystal is rotated with the stage of the microscope the cross breaks up into the two branches of a hyperbola, and when the vibration directions of the crystal are inclined at 45° to those of the nicols the figure is that shown in fig. 141. The points of emergence of the optic axes are at the middle of the hyperbolic brushes when the crystal is in the diagonal position: the size of the optic axial angle can therefore be directly measured with considerable accuracy.

138

139

FIG. 138.—OPTICAL INDICATRIX OF A BIAXIAL CRYSTAL
FIG. 139.—RAY-SURFACE OF A BIAXIAL CRYSTAL

828L   CRYSTALLOGRAPHY

In orthorhombic crystals the three principal vibration-directions coincide with the three crystallographic axes, and have therefore fixed positions in the crystal, which are the same for light of all colours and at all temperatures. The optical orientation of an orthorhombic crystal is completely defined by stating to which crystallographic planes the optic axial plane and the acute bisectrix are respectively parallel and perpendicular. Examined in parallel light between crossed nicols, such a crystal extinguishes parallel to the crystallographic axes, which are often parallel to the edges of a face or section; there is thus usually straight extinction. The interference figure seen in convergent polarized light is symmetrical about two lines at right angles.

In monoclinic crystals only one vibration direction has a fixed position within the crystal, being parallel to the ortho-axis (*i.e.*, perpendicular to the plane of symmetry or the plane $\{010\}$). The other two vibration directions lie in the plane $\{010\}$, but they may vary in position for light of different colours and at different temperatures. In addition to dispersion of the optic axes there may thus, in crystals of this system, be also dispersion of the bisectrices. The latter may be of one or another of three kinds, according to which of the three vibration directions coincides with the orthoaxis of the crystal. When the acute bisectrix is fixed in position, the optic axial planes for different colours may be crossed, and the interference figure will then be symmetrical with respect to a point only (crossed dispersion). When the obtuse bisectrix is fixed, the axial planes may be inclined to one another, and the interference figure is symmetrical only about a line which is perpendicular to the axial planes (horizontal dispersion). Finally, when the vibration direction corresponding to the refractive index β, or the third mean line, has a fixed position, the optic axial plane lies in the plane $\{010\}$, but the acute bisectrix may vary in position in this plane; the interference figure will then be symmetrical only about a line joining the optic axes (inclined dispersion). Examples of substances exhibiting these three kinds of dispersion are borax, orthoclase and gypsum, respectively. In orthoclase and gypsum, however, the optic axial angle gradually diminishes as the crystals are heated, and after passing through a uniaxial position they open out in a plane at right angles to the one they previously occupied; the character of the dispersion thus becomes reversed in the two examples quoted. When examined in parallel light between crossed nicols monoclinic crystals will give straight extinction only in faces and sections which are perpendicular to the plane of symmetry (or the plane $\{010\}$); in all other faces and sections the extinction directions will be inclined to the edges of the crystal. The angles between these directions and edges are readily measured, and being dependent on the optical orientation of the crystal, they are often characteristic constants of the substance for example, *see* PLAGIOCLASE.

FIG. 142.—DICHROSCOPE

In triclinic crystals there is no relation between the optical and crystallographic directions, and the exact determination of the optical orientation is often a matter of considerable difficulty. The character of the dispersion of the bisectrices and optic axes is still more complex than in monoclinic crystals, and the interference figures are devoid of symmetry.

Absorption of Light in Crystals: Pleochroism.—In crystals other than those of the cubic system, rays of light with different vibration directions will, as a rule, be differently absorbed; and the polarized rays on emerging from the crystal may be of different intensities and (if the observation be made in white light and the crystal is coloured) differently coloured. Thus, in tourmaline the ordinary ray, which vibrates perpendicular to the principal axis, is almost completely absorbed, while the extraordinary ray

FIG. 140 AND 141.—INTERFERENCE FIGURES OF A BIAXIAL CRYSTAL

is allowed to pass through the crystal. A plate of tourmaline cut parallel to the principal axis may therefore be used for producing a beam of polarized light, and two such plates placed in crossed position form the polarizer or analyzer of tourmaline tongs, with the aid of which the interference figures of crystals may be simply shown. Uniaxial (tetragonal and hexagonal) crystals when showing perceptible differences in colour for the ordinary and extraordinary rays are said to be dichroic. In biaxial (orthorhombic, monoclinic and triclinic) crystals, rays vibrating along each of the three principal vibration-directions may be differently absorbed and, in coloured crystals, differently coloured; such crystals are therefore said to be trichroic or in general pleochroic (from $\pi\lambda\acute{\epsilon}\omega\nu$, more, and $\chi\rho\acute{\omega}s$, colour). The directions of maximum absorption in biaxial crystals have, however, no necessary relation with the axes of the indicatrix, unless these have fixed crystallographic directions, as in the orthorhombic system and the orthoaxis in the monoclinic. In epidote it has been shown that the two directions of maximum absorption which lie in the plane of symmetry are not even at right angles.

The pleochroism of some crystals is so strong that when they are viewed through in different directions they exhibit marked differences in colour. Thus a crystal of the mineral cordierite (called also dichroite because of its strong pleochroism) will be seen to be dark blue, pale blue or pale yellow according to which of three perpendicular directions is viewed. The face colours seen directly in this way result, however, from the mixture of two axial colours belonging to rays vibrating in two directions. In order to see the axial colours separately the crystal must be examined with a dichroscope, or in a polarizing microscope from which the analyzer has been removed. The dichroscope, or dichrooscope (fig. 142), consists of a cleavage rhombohedron of calcite (Iceland spar) p, on the ends of which glass prisms w are cemented: the lens l is focused on a small square aperture o in the tube of the instrument. The eye of the observer placed at e will see two images of the square aperture, and if a pleochroic crystal be placed in front of this aperture the two images will be differently coloured. On rotating this crystal with respect to the instrument the maximum difference in the colours will be obtained when the vibration directions in the crystal coincide with those in the calcite. Such a simple instrument is especially useful for the examination of faceted gem stones, even when they are mounted in their settings. A single glance suffices to distinguish between a ruby and a spinel ruby, since the former is dichroic and the latter isotropic and therefore not dichroic.

The characteristic absorption bands in the spectrum of white light which has been transmitted through certain crystals, particularly those of salts of the cerium metals, will, of course, be different according to the direction of vibration of the rays.

(L. J. S.; J. D. H. D.)

FIG. 143.—CONDUCTIVITY OF HEAT IN QUARTZ

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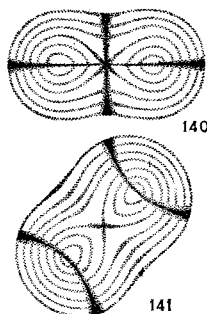Technique: A. D. Booth, *Fourier Technique in X-Ray Organic*

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CRYSTALLOID is a term of historic interest, introduced by Graham. Substances such as sugar or sodium chloride which are able to diffuse through a parchment membrane separating their aqueous solution from pure water are called crystalloid, whereas substances which are unable to diffuse through such a membrane are called colloids. Graham was led to this terminology by the observation that the former type of substances crystallized readily, whereas the latter type did not seem to form crystals. It became generally realized that this is not correct and that colloids may be both crystallizable and noncrystallizable; that they may represent either crystals or noncrystalline substances. It was furthermore generally agreed that the ability of a substance to diffuse through a membrane depends on the size of its units (*e.g.*, on the size of the molecules), on the electrostatic charge of the membrane and on the Donnan equilibrium. The continued use of the term "crystalloid" in Graham's sense (*i.e.*, as the antithesis to colloid) is therefore incorrect, notwithstanding its occasional use in modern chemical literature.   (WI. H.)

CRYSTAL PALACE, a well-known English resort in the neighbourhood of Sydenham just outside the southern boundary of the county of London. The building, chiefly of iron and glass, was designed by Sir Joseph Paxton (*q.v.*), and was originally erected in Hyde park for the 1851 exhibition. It was enlarged and re-erected on high ground in its new site in 1854 and for a quarter century was very popular as an amusement centre and show place. After that it declined somewhat, but after World War I it was chosen because of its spaciousness to house the Imperial War museum, comprising a large collection of war relics, souvenirs, photographs and other records. There were accommodations in the grounds for many sports and games. On Nov. 30, 1936, the building was almost wholly destroyed by fire.

CSARDAS or CZARDAS (chardash), a national dance of Hungary, distinguished especially by its violent alternations of tempo, so that it is now wild and furious, now slow and restrained.

CSENGERY, ANTAL (1822–1880), Hungarian publicist, and a historical writer of great influence on his time, was born at Nagyvarad on June 2, 1822. He took, at an early date, a very active part in the literary and political movements immediately preceding the Hungarian revolution of 1848. As a historical writer he excelled chiefly in brilliant and thoughtful essays on the leading political personalities of his time, such as Paul Nagy, Bertalan, Szemere and others. He died at Budapest on July 13, 1880.

CSIKY, GERGOLY (1842–1891), Hungarian dramatist, was born on Dec. 8, 1942, at Pankota, in the county of Arad. He studied Roman Catholic theology at Pest and Vienna, and was professor in the Priest's college at Temesvar from 1870 to 1878. In the latter year, however, he joined the Evangelical Church and took up literature. Beginning with novels and works on ecclesiastical history, which met with some recognition, he ultimately devoted himself to writing for the stage. Here his success

was immediate. His play *Az ellenállhatatlan (L'Irrésistible),*

Call for Contributions to the Next Teaching Commission Newsletter

Providing there is enough interest, the second issue of the Teaching Commission Newsletter is expected to appear around June of 2007 with the primary theme to be determined. If no-one is else is co-opted, the newsletter will be edited by Lachlan Cranswick.

Contributions would be also greatly appreciated on matters of general interest to the crystallographic teaching community.

Please send articles and suggestions directly to the editor.

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