

INTERNATIONAL TABLES
FOR
X-RAY CRYSTALLOGRAPHY
VOLUME I
SYMMETRY GROUPS

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INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY

VOL. I. SYMMETRY GROUPS
VOL. II. MATHEMATICAL TABLES
VOL. III. PHYSICAL AND CHEMICAL TABLES

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INTERNATIONAL TABLES
FOR
X-RAY CRYSTALLOGRAPHY

Volume I
SYMMETRY GROUPS

Edited by
NORMAN F. M. HENRY and KATHLEEN LONSDALE

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OF THE
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ERRATA (Volume I)

- p. 1. End of 4th paragraph: Axel, not Alex.
- p. 2. Column 1, line 22: 76, not 16.
- p. 14. Fig. 2.4.1 is not quite geometrically exact; in particular the direction 000-110 should be normal to the (110) planes.
- p. 24. Tertiary position, hexagonal system: Mirror lines parallel, not Mirror lines at 90°.
- p. 34. Notes to Table 3.5.1. Add:
9. For the space groups Nos. 149, 151, 153, 157, 159, 162, 163, all belonging to the Laue group $\bar{3}m$, and based on a hexagonal lattice, the entry under $h0\bar{h}l$, $h0\bar{h}\bar{l}$ should be 12, and that under $hh2\bar{h}l$, $hh2\bar{h}\bar{l}$ should be 6, 6.
- p. 136. $P2c/\dots$ at top of page should be $P2/c\dots$
- p. 208. No. 118 should be $P4n2$, not $P4n2$.
- p. 252. Top of page, right hand side. 3 should be $\bar{3}$.
- p. 294. Some copies only have the bar over the 6 in $P\bar{6}m2$ missing (large type, top left corner of page).
- p. 308. No. 200. $P2/m3$ should be $P2/m\bar{3}$.
- p. 319. No. 210. 32 e has the extra condition $hk0 : h+k=4n$.
- p. 356. Line 21. $(|F_{\text{obs}}| - |F_{\text{calc}}|)$ should be $||F_{\text{obs}}| - |F_{\text{calc}}||$.
- p. 360. Formula at top of page should read:

$$A = 16 \cos 2\pi \frac{h+k+l}{4}$$

$$\times \left\{ \cos 2\pi \left(hx + \frac{l}{4} \right) \cos 2\pi \left(ky + \frac{h}{4} \right) \cos 2\pi \left(lz + \frac{k}{4} \right) \right.$$

$$+ \cos 2\pi \left(hz + \frac{l}{4} \right) \cos 2\pi \left(kx + \frac{h}{4} \right) \cos 2\pi \left(ly + \frac{k}{4} \right)$$

$$+ \cos 2\pi \left(hy + \frac{l}{4} \right) \cos 2\pi \left(kz + \frac{h}{4} \right) \cos 2\pi \left(lx + \frac{k}{4} \right)$$

$$+ \cos 2\pi \left(h+k+\frac{l}{4} \right)$$

$$\times \left[\cos 2\pi \left(hx + \frac{k}{4} \right) \cos 2\pi \left(ly + \frac{h}{4} \right) \cos 2\pi \left(kz + \frac{l}{4} \right) \right.$$

$$+ \cos 2\pi \left(hy + \frac{k}{4} \right) \cos 2\pi \left(lz + \frac{h}{4} \right) \cos 2\pi \left(kx + \frac{l}{4} \right)$$

$$+ \cos 2\pi \left(hz + \frac{k}{4} \right) \cos 2\pi \left(lx + \frac{h}{4} \right) \cos 2\pi \left(ky + \frac{l}{4} \right) \Bigg\}$$

The trigonometrical formula two-thirds down this page should read:

$$\sin A + \sin B + \sin C + \sin(A+B-C)$$

$$= 4 \sin \frac{A+B}{2} \cos \frac{C-A}{2} \cos \frac{C-B}{2}$$

The formula has been applied in its correct form.

p. 435. End of 5th line from bottom: $|(Fhk\bar{l})|$ should be $|F(hk\bar{l})|$.

p. 451. No. 133 should read:

$$B = -8 \sin^2 \dots (\dots + \dots)$$

$$\begin{cases} h+k+l=2n+1 & A=0 \\ & B = -8 \sin 2\pi lz \\ & \quad [\sin 2\pi hx \sin 2\pi ky + \\ & \quad \sin 2\pi kx \sin 2\pi hy] \\ l=2n & A=B=0 \text{ if } h=0 \text{ or } \\ & k=0 \text{ or } l=0 \end{cases}$$

$$\begin{cases} h+k+l=2n+1 & A=0 \\ & B = 8 \sin 2\pi lz \\ & \quad [\cos 2\pi hx \cos 2\pi ky - \\ & \quad \cos 2\pi kx \cos 2\pi hy] \\ l=2n+1 & A=B=0 \text{ if } h=\pm k \end{cases}$$

- p. 454. $P4/mnm$ should be $P4_2/mnm$.
- p. 461. D_{4h}^{02} (top right-hand corner) should be D_{4h}^{20} .
- p. 478. Co-ordinates for $P6_22$. $y, x, \frac{1}{2}+z$ should be $y, x, \frac{1}{2}-z$.
- p. 479. Under $l=6n+1$, equation for B should read:

$$B = 2\{\cos 2\pi lz [\sin 2\pi(hx+ky) + \sin 2\pi(hx+iy)]$$

$$+ \cos 2\pi(lz+\frac{1}{2}) [\sin 2\pi(kx+iy) + \sin 2\pi(ix+ky)]$$

$$+ \cos 2\pi(lz-\frac{1}{2}) [\sin 2\pi(ix+hy) + \sin 2\pi(kx+hy)]\}$$
- p. 505. Interchange (9) and (13)
 (12) and (16)
 (11) and (15)
 (10) and (14)
 at the ends of appropriate rows.
- p. 520. (6) The formula should read:

$$A = 32\{\cos 2\pi lz \cos \pi(h+k)(x+y) \cos \pi(h-k)(x-y)$$

$$+ \sin 2\pi lz \sin \pi(h-k)(x+y) \cos \pi(h+k)(x-y)$$

$$+ \cos 2\pi lx \cos \pi(h+k)(y+z) \cos \pi(h-k)(y-z)$$

$$+ \sin 2\pi lx \sin \pi(h-k)(y+z) \cos \pi(h+k)(y-z)$$

$$+ \cos 2\pi ly \cos \pi(h+k)(z+x) \cos \pi(h-k)(z-x)$$

$$+ \sin 2\pi ly \sin \pi(h-k)(z+x) \cos \pi(h+k)(z-x)\}$$

$$F(hkl) = F(\bar{h}\bar{k}\bar{l}) = F(\bar{h}kl) = -F(h\bar{k}l) = F(hk\bar{l})$$

(7) should read:
 Change $h \rightarrow k \rightarrow l \rightarrow h$ in formulae (6).

(8) should read:
 Change $h \rightarrow l \rightarrow k \rightarrow h$ in formulae (6).

$$F(hkl) = F(\bar{h}\bar{k}\bar{l}) = -F(\bar{h}kl) = F(h\bar{k}l) = F(hk\bar{l})$$

p. 528. Line 9 should read:
 form (though not of value) of $|F(hk\bar{l})|$ but also of the value of the phase angle α , for all reflections.

p. 529. Last line: $x, 0, \frac{1}{2}$ should be $\bar{x}, 0, \frac{1}{2}$.

p. 534. Table 5.1.1. The diagrams for the 2nd and 6th case of the monoclinic system should be interchanged in some copies. The 2nd should have the PQRPTR lettering, the sixth SQUOTO. The text is correct.

p. 536. Line 17 from bottom: hexagonol should be hexagonal.

p. 551. In space group 125:

$$C4/nmb$$
 should be $C4/amb$

$$\frac{4}{n} \frac{2}{m} \frac{2}{b}$$
 should be $\frac{4}{a} \frac{2}{m} \frac{2}{b}$
 and similarly $4/n$ should be $4/a$ in space groups 126, 129, 130, 133, 134, 137, 138 and $4_1/a$ should be $4_1/d$ in space groups 141, 142.

Information concerning any further errata will be gratefully received by the Editors.

Volume I. ADDITIONAL ERRATA

- p. 20. 4th line from bottom: R_{obs} should be R_{obv} .
- p. 52. 8th line from bottom: *Zeit. f. Kryst.* should be *Z. Kristallogr.* (elsewhere *Zeit. f. Krist.* and *Zeits. Krist.* would be better written as *Z. Kristallogr.*).
- p. 275. Symmetry diagram. Add two sets of horizontal screw axes at $z = \frac{1}{4}, \frac{3}{4}$ respectively, passing respectively through
 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ and
 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}, \frac{3}{4})$
- p. 346. 3rd line from bottom: 4.4.2. should be 4.4.3.
- p. 423. In space group $I4_1/a$, the second set of structure factor formulae should refer to $h+k+l=2n$ and not, as given, to $h+k+l=n$.
- p. 428. In space group No. 94, $|F(hkl)|$ should be $|F(hkl)|$.
- p. 542. 4th reference: *Ibid.* should read *Z. Kristallogr.*

GENERAL PREFACE

THE Editorial Commission of the International Union of Crystallography was originally charged with the task of preparing a new edition of the *International Tables for the Determination of Crystal Structures* published in 1935. Although much of the matter in the 1935 *Tables* has been preserved, the changes and the amount of new material are so considerable that the present work must be considered as being a separate publication: consequently it has received a new name which expresses the wider field embraced. Only the English language has been used, but a dictionary of crystallographic terms in English, French, German, Russian and Spanish is included in each of the three volumes.

The aim of the present compilation is to facilitate the work of three categories of scientists: those who are actually engaged in the determination of crystal structures, those who are using X-ray methods in the study of crystals in general, and students of crystallography. This aim has been borne in mind in deciding the contents. The Commission has tried to produce a definitive presentation of all the data which are firmly established as essential to the work of the X-ray crystallographer. In addition, some space has been given to topics which give promise of becoming essential during the next ten years, and provision has been made for the supplementary issue of tables of data for such topics if necessary.

That Commission members owe a debt to the

pioneers of the 1935 *Tables* goes without saying, and in particular they owe much to the former editor, Dr. Carl Hermann. The Commission wishes also to express its gratitude to Dr. Wessenberger, of the firm of Borntraeger, Berlin, for permission to use and to reproduce parts of the 1935 *Tables*.

The work of the Editorial Commission has been greatly facilitated by the willingness of crystallographers in all parts of the world who have helped with the compilation of tables and lists of references, by careful checking of the data, and by giving advice on the selection of material. Although limitation of space prevented the publication of all the material which was received, the work of all has helped towards the shaping of the present publication. Specific reference to individual helpers is made in the prefaces to each volume. Since it would be too much to hope that all errors have been eliminated, the Commission would be grateful for notification of any mistakes which may be discovered, and indeed for any expressions of opinion or further suggestions regarding the present *Tables*. These should be sent to Professor Kathleen Lonsdale, Department of Chemistry, University College, Gower Street, London W.C.1, England.

Finally, the Commission would like to express thanks to The Kynoch Press, Birmingham, England, for the great care taken in the difficult work of printing.

PREFACE TO VOLUME I

THIS Volume includes such information concerning the crystallographic symmetry groups in two and three dimensions as is currently used in X-ray crystallographic work. No attempt has been made by the editors to aim at theoretical completeness, their intention being rather to tabulate and display only essential material. Under the heading of Notes on Special Topics there is, however, discussion of several subjects (some of which may be included in Volumes II and III also) which are either in the process of development or which have not been much used since the publication of the 1935 *Tables*. If there is a sufficient demand for any of these, or for other subjects which may subsequently be developed, the Editorial Commission would be prepared to publish data tables as supplementary issues. This applies also to the field of semi-crystalline symmetry, where the methods of representation are still in the experimental stage.

A considerable amount of the material given here was included in the *International Tables for Crystal Structure Determination*, 1935, Volume I, which was edited by Dr. Carl Hermann, the contributing authors being W. T. Astbury, E. Brandenberger, C. Hermann, K. Lonsdale, C. Mauguin, P. Niggli and R. W. G. Wyckoff. The present editors wish to affirm their great debt to these original authors. To one of the two honorary chief editors of the 1935 *Tables*, Professor M. von Laue, they are indebted for the Historical Introduction which he has so kindly written for these new *Tables*. Sir Lawrence Bragg has also contributed to this introduction an account of the early work done by himself and by his father, Sir William Bragg, to whose inspiration the original *Tables* owed so much.

Use has been made of a considerable amount of published work and, where possible, references have been given to papers which should be consulted for further explanatory details. A number of crystallographers have helped greatly with the preparation of material and its arrangement for printing, with proof-reading or with general advice. Among these are, of course, our fellow-members of the Editorial Commission and especially Dr. R. C. Evans, the Secretary of the International Union of Crystallography, in his capacity as an *ex-officio* member of the Commission. It is impossible to name all those who have assisted in various ways, but we should like to record our thanks to the following, and to many others who have also helped in the preparation of this Volume.

Members of the *ad hoc* 1946 Committee

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The editors wish to thank Mr. Walkey of the Cambridge University Press, and Mr. Rickson of the Department of Mineralogy and Petrology, Cambridge, for preparation of the new diagrams. They also wish to thank the Managers of the Royal Institution for permission to use Lonsdale's *Simplified Structure Factor Tables*, which have been reproduced in modified form. All the material taken over from the 1935 *Tables* has also been rearranged, tabulated and displayed in new ways which, it is hoped, will make for greater convenience in use. The data on geometrical structure factors have been separated from the other data on the 230 space groups for convenience in printing layout.

Certain kinds of space-group symbols and class names no longer in use have been dropped. Enquiry has also shown that sufficient use was not actually made of data on sub-groups and lattice complexes to justify the space that would have been required to display them properly in the present *Tables*. If the need for them should ever develop, complete tables of these data could be published separately.

Data relating to two-dimensional lattices, point groups and space groups are included because of their importance in the development and teaching of systematic group theory, in the representation of projection symmetry and in work on certain types of layer structure.

A suggestion made to the Editorial and Nomenclature Commissions by Prof. M. J. Buerger, that the *z*-axis should be taken as the unique axis in the monoclinic system, was circulated to a number of crystallographers and crystallographic societies in as many countries as possible. So many favourable replies were received that it was agreed that the present *Tables* must include duplicate

descriptions of the monoclinic point groups and space groups. The description using the z -axis as the unique axis is taken as the "1st setting," that using the y -axis as the unique axis is called the "2nd setting."

At the Stockholm General Assembly of the International Union of Crystallography in 1951 it was agreed that the 2nd setting should be accepted as standard for morphological and structural crystallographic studies, but that the 1st setting could be used where there was a special reason for this alternative.

Various changes in nomenclature and layout have been made, to conform to modern usage and for the sake of consistency. The space groups have each been given a number, for reference purposes only. The use of the C and F settings in the tetragonal system has been dropped, P and I only being used. In the trigonal and hexagonal systems the use of the H setting has been dropped for systematic descriptions and the primitive hexagonal lattice is called P and not C .

This has necessitated the redrawing of a considerable number of tetragonal, trigonal and hexagonal diagrams. In addition, the outline of the hexagonal (triple) unit cell has been given in the diagrams of the 7 space groups with the R -lattice. The other non-cubic diagrams have been reproduced unchanged, except for the correction of errors. These diagrams have stood the test of time well, but it was felt that the cubic diagrams, if included, would have to be revised. Enquiry showed, however, that comparatively little use was being made of the cubic diagrams, and in the interests

of economy and compactness it was decided that they should be omitted from the present publication. Again, it would be easy to publish these as a supplementary issue in the future if the demand were sufficient and if a more satisfactory method of representation could be devised.

The arrangement of material has been systematic as far as is consistent with the object of the *Tables*. The lattice is basic to the crystal structure, and the reciprocal lattice to the understanding of diffraction effects. These are considered in Section 2. The external form of the crystal indicates the point-group symmetry, and a systematic study of all the kinds of point-group symmetry that can be applied to a lattice is therefore next given in Section 3. The addition of translations to the rotations and rotatory inversions of point-group symmetry gives the space groups, which are fundamental in crystallographic group theory. The main part of Section 4 of this volume consists of data for the 230 three-dimensional space groups, and of tables used in the interpretation of diffraction effects from crystals belonging to any of these. Volume I, however, does not include such tables as atomic scattering factors for the different elements, or values of mathematical functions which occur in the intensity formulae.

The staff of The Kynoch Press have been most patient and tireless in rearranging these *Tables* in order to produce a result which shall be both pleasing to the eye and convenient in use. We believe that they have been most successful in achieving both objects, and we are exceedingly grateful to them.

SYMBOLS USED IN THIS VOLUME

a, b, c	Lengths of unit-cell edges.
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Unit-cell vectors.
α, β, γ	Interaxial angles $y \wedge z, z \wedge x, x \wedge y$.
$x^-, y^-, z^-, (u^-)$	Directions of crystallographic axes of co-ordinates.
x, y, z	Co-ordinates of any point (equivalent position) in the unit cell, expressed in terms of a, b, c , except on rhombohedral axes.
x, y, z	Co-ordinates of equivalent position in the primitive rhombohedral unit cell, expressed in terms of rhombohedral axes.
x_r, y_r, z_r	Co-ordinates of an atom r , expressed in terms of a, b, c .
$X, Y, Z \}$ $U, V, W \}$	Co-ordinates of any one of a series of systematically spaced points (expressed as fractions of a, b, c), filling the unit cell at regular intervals (Fourier and Patterson analyses respectively).
u, v, w	Co-ordinates of any lattice point, expressed in terms of a, b, c as units.
$[u \ v \ w]$	Indices of a direction in the direct (real-space) lattice (zone axis).
$\langle u \ v \ w \rangle$	Indices of a "form" of zone axes (related by symmetry).
$(h \ k \ l)$	Indices of a crystal face, or of a single plane, or of a set of parallel planes.
$h \ k \ l$	Indices of the reflection from a set of parallel planes; co-ordinates of a reciprocal lattice point.
$\{h \ k \ l\}$	Indices of a form of planes, or of the reflections from a form of sets of parallel planes.
$\{h \ k \ l\}$	Ditto for the hexagonal co-ordinate axes x^-, y^-, u^-, z^- .
a^*, b^*, c^*	Lengths of reciprocal-lattice unit-cell edges.
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	Unit-cell vectors in reciprocal space.
$\alpha^*, \beta^*, \gamma^*$	Interaxial angles in reciprocal space.
d_{hkl}	Interplanar spacing of planes (hkl).
V or V_c ; V^*	Unit-cell volume in direct and in reciprocal space.
$p, c; p$	Primitive and centred two-dimensional lattices; one-dimensional lattice.
$P, R, A, B, \}$ $C, F, I, H \}$	Lattice symbols in three dimensions.
1, 2, 3, 4, 6	Rotation-axis symbols (X) (or rotation-point symbols in two dimensions).
$\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}$	Inversion-axis symbols (\bar{X}).
$2_1, 3_1, 3_2, 4_1, 4_2, 4_3, \}$ $6_1, 6_2, 6_3, 6_4, 6_5 \}$	Screw-axis symbols.
m	Mirror-reflection plane in three dimensions, mirror-reflection line in two dimensions, or mirror-reflection point in one dimension.
g	Glide-reflection line in two dimensions.
a, b, c, n, d	Glide-reflection planes in three dimensions.
$f(hkl)$	Atomic scattering factor for the particular value of $(\sin \theta)/\lambda$ corresponding to the Bragg reflection hkl .
$F(hkl)$	Structure factor for the unit cell, corresponding to the Bragg reflection hkl .
$ F(hkl) $	Modulus of the structure factor for hkl (sometimes shortened to $ F $).
$\alpha(hkl)$	Phase of the structure factor for hkl (sometimes shortened to α).
A, B	$ F \cos \alpha, F \sin \alpha$ respectively.
$\rho(XYZ)$	Electron density at the point X, Y, Z .
$P(UVW)$	Patterson function at the point U, V, W .
n, m	Any integers.

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1. HISTORICAL INTRODUCTION

by M. VON LAUE

THE science which the *International Tables* are intended to serve is concerned primarily with the atomic theory of crystals, and secondarily with optical theory as applied to the short wavelengths of X-radiation. Moreover, now that we know of electron and neutron diffraction by crystals, it must include quantum mechanical wave theory, which is also, as it happens, of importance in the branch of optics already mentioned. This introduction has to deal, therefore, with the history of these three branches of physics. Let us begin with the most important and the oldest branch, the theory of crystals.

We may take as a beginning the small pamphlet written in the year 1611 by the great astronomer Johannes Kepler, which bears the title *Strena seu de nive sexangula*, or in translation "A New Year's present; on hexagonal snow." It is dedicated to one of his patrons at the court of the Emperor Rudolph II, whose friendship Kepler enjoyed during his stay in Prague. Kepler's astronomical works show that throughout his life he believed that the material world was the creation of a Spirit delighting in harmony and mathematical order. Had he not tried in his youth to deduce the radii of the planetary orbits from the dimensions of certain regular polyhedra, and did not his principal work (1619) bear the title *Harmonice Mundi*? It need not surprise us, therefore, that it was the appearance of these regular and beautifully shaped snowflakes rather than the appearance of the crystals of the mineral world that inspired Kepler with the idea that this regularity might be due to the regular geometrical arrangement of minute and equal brick-like units. Thus he was led to think of close-packed spheres, and, although he did not coin the expression "space-lattice" and although his development of these ideas is not always correct, we can find among his illustrations the first pictures of space-lattices.

Nevertheless Kepler felt uneasy about these speculations. He realised, quite correctly, that his way would lead to an atomic theory; yet the idea of the atom, as handed down from the ancient Greeks, lacked an empirical foundation and therefore has often been the subject of excessively fanciful speculation even until well into the nineteenth century. Hence it was not without reason that the natural scientist in Kepler mistrusted this idea and

would not take it seriously. He toyed with the double meaning of the word "nix," which in Latin means snow but in German dialect "nichts" —nothing. And so from beginning to end he repeatedly explained the whole idea away as a mere "nothing."

In these circumstances the little pamphlet, even though it was printed, naturally made no deep impression on his contemporaries, and was gradually forgotten. Crystallography took another direction, that of the description of the external form of crystals, after Niels Stensen had in 1669 pointed out the existence of characteristic angles between crystal faces. By devious ways this led eventually to the Millerian indexing of faces (1839), to the laws of symmetry and to the classification of crystals in 32 classes, which was accomplished in 1830 by Johann Friedrich Christian Hessel and in 1867, independently and rather more simply, by Alex Gadolin.

This consistently phenomenological approach was not abandoned, even though the crystal-optical discoveries made early in the nineteenth century by such men as Baptiste Biot, David Brewster, Augustin Fresnel and Frederick William Herschel had led to the development of the important idea that the same laws of symmetry which were valid for the positions of crystal faces also controlled the physical events inside the crystal. This was first made clear by Franz Neumann in 1833.

Apart from these trends of thought, however, ideas about the internal structure of crystals continued to appear. Thus Christiaan Huygens' fundamental work on the wave theory of optics, *Traité de la lumière*, which was published in 1690, contains among other things a wave-theoretical explanation of birefringence, and ascribes to calcite a structure made up of ellipsoidal particles; the threefold periodicity of this arrangement characterises it as a space-lattice, although Huygens, like Kepler, did not define it as such. It was the cleavage along three planes which led him to this idea. Like Kepler's pamphlet, however, this part of the otherwise famous work was soon forgotten. Independently of Huygens, crystal cleavage in general led Torbern Bergman in 1773 and René Just Haüy in 1782 to suppose that all crystals consist of a kind of masonry of equal, parallelepipedal building bricks. That these "molécules soustractives"

were often supposed to consist of "molécules intégrantes" of other shapes need not concern us here. A structure of this kind involves a space lattice, and Haüy could therefore easily go on from this idea to deduce the laws governing the geometry of crystal faces, already empirically known. But it would be premature to describe this as an atomic theory of crystals. No wonder! For the scientific theory of atoms had yet to be created, in its own good time, by the great chemists of the eighteenth century. The theorem that a lattice may be divided into unit cells, as we should say today, in an infinite number of different ways would have made no physical sense whatever to Haüy (although he would have admitted, of course, its geometrical correctness), since the shape of the "molécules soustractives" was fixed unambiguously by Nature.

Thus the true beginning of the atomic theory of crystals must be dated from a paper published in the year 1824 by Ludwig August Seeber, physicist in Freiburg, in Gilbert's *Annalen der Physik*, vol. 16, page 229. Seeber, who certainly knew of Haüy's works but probably did not know the part we have quoted from Huygens', was trying to find an explanation of the thermal expansion and the elasticity of solids, of which he quite rightly believed crystals to be the normal type. He found the bricklike structure unsuitable for his purpose, since, he argued, the only view compatible with this picture would be that the single bricks themselves possess these physical properties, which does not solve the problem but only pushes it one step farther back. Seeber, whose outlook was essentially modern, introduced instead the idea of a structure consisting of chemical atoms or molecules (at the time these two concepts were not strictly differentiated), whose mutual distances are determined by the balance of attractive and repulsive forces, thus forming a system of stable equilibrium. External disturbances cause certain changes of position—this is his explanation of elasticity—and possibly also elastic vibrations about the equilibrium positions. Seeber, of course, did not visualise thermal vibration: he explained thermal expansion in terms of the temperature dependence of the attractive and repulsive forces. In order to retain the sound parts of Haüy's postulate, Seeber placed each of his molecules, assumed by him to be spherical, at the midpoint of the cell which would have formed one of Haüy's "molécules soustractives"; he thus arrived at a "parallelepipedal arrangement of the indivisible parts of matter," as he describes it at the end of his paper. In our language such an arrangement implies a

primitive translation lattice, and it is not far from this concept to the idea that each unit cell of the space lattice is occupied by several atoms.

This was the earliest application of the scientific atomic theory to a purely physical problem. The kinetic theory of gases, which is usually regarded as the beginning of atomic theory in physics, did not appear until thirty-two years later. Seeber was therefore far ahead of his time, and it was no wonder that his contemporary physicists failed to respond to his ideas, which were forgotten until Sohncke revived them in 1879. But at least one mathematical problem had been raised—the number of geometrically possible space lattices that correspond to the 32 crystal classes and to their symmetry operations. Moritz Ludwig Frankenheim and Auguste Bravais took up this problem, and in 1850 Bravais described the 14 pure translation lattices which have been named after him. Incidentally, his papers also contain the concept of the reciprocal lattice, which was later rediscovered and used in connection with the study of interference effects from crystals. This purely group-theoretical investigation was extended by Leonhard Sohncke in 1879 through the introduction of further symmetry operations, thus arriving at 65 different "space groups." The complete solution of the problem, taking into account *all* possible symmetry operations on a lattice, was given simultaneously in the year 1890 by Evgraph Stepanovitch Fedorov and by Artur Schoenflies. They derived the 230 space groups which are used in modern structural research.

Investigations pursued by English scientists of the following decade were less systematic and far more hypothetical, but their ideas possessed the advantage that they could be visualised more easily. Inspired by the success of stereochemistry, they devised three-dimensional models of atomic structures based on lattices. Lord Kelvin published a paper on this subject in 1894. Reasoning along these lines was most fully expressed in a series of long papers by W. Barlow in the last decade of the nineteenth century. Barlow took up the idea of close packing, and distinguished for the first time correctly between the cubic and hexagonal forms of packing. He also considered the question of packing of spheres of two or three different sizes and described, for example, the sodium chloride structure, although neither in this nor in any other case did he in these early papers name a substance which might be expected to have one of the proposed structures. This was undoubtedly one of the reasons why the whole of his structure

theory at first attracted little attention. Moreover, the very reality of atoms was doubted again and again right up to the end of the nineteenth century. Even in the absence of such doubts, and even when collaboration with Pope had given the chemical application of Barlow's theory, there was still no way of bringing the hypothetical structures into relation with experiment. In order to establish structure theory on a firm basis, yet another set of ideas, those of physical optics, had to be brought in.

The diffraction of visible light by gratings, which mostly consisted of lines scratched on glass or metal, had already been described by Grimaldi in the seventeenth century, and again by Joseph Fraunhofer at the beginning of the nineteenth. The relevant theory can be found in the comprehensive treatise by Friedrich Magnus Schwerd: *Die Beugungserscheinungen, aus den Fundamentalgesetzen der Undulationstheorie analytisch entwickelt* (1835). The grating was and still is the most important instrument in spectroscopy. Later physicists engaged in work on optics have often returned to Schwerd's theory. In particular, Lord Rayleigh frequently emphasised that the essential characteristic of a grating is the periodic repetition of its elements and not the nature of those elements. Round about 1910 M. von Laue, in writing an article on wave theory for the *Encyklopädie der mathematischen Wissenschaften*, set himself the task of elaborating, as clearly as possible, this idea of Rayleigh's, and arrived at an equation for the position of the diffraction maxima which could be extended without difficulty to the case of double periodicity as it exists in cross-gratings; in the latter case two such equations had to be formulated.

In the meantime the science of optics had been extended far beyond the limits of the visible spectrum. The farthest extension on the short-wave side had come about in 1895 through Röntgen's discovery of X-rays; soon afterwards (1896) Emil Wiechert and George Gabriel Stokes concluded from the way in which X-rays are produced that they must be short waves consisting of electromagnetic pulses. This was confirmed by the observation of their polarisation, made by C. G. Barkla in 1906. Wilhelm Wien in 1907 estimated their wavelength to be 7×10^{-9} cm. on the basis of their observed photoelectric effect, while A. Sommerfeld in 1912 calculated a value of 4×10^{-9} cm. from their diffraction by a slit. On the other hand, they showed such strong quantum effects that some very eminent physicists held firmly to the corpuscular theory of X-rays.

Both these questions and that of the fine structure of crystals were decided by the researches of W. Friedrich and P. Knipping, which were published in the summer of 1912 in the *Sitzungsberichte der Bayerischen Akademie*. Von Laue's diffraction theory, which had provided the inspiration for these experiments and which had indeed been confirmed by their results, simply consisted of the diffraction conditions for a cross-grating, with the addition of a third condition to take account of the three-dimensional periodicity of a space lattice. Admittedly von Laue had expected, in accordance with the Stokes-Wiechert pulse theory, that many more interference spots would appear on the photographs than were actually observed, and he could only explain their absence by ascribing to the atoms of the crystal a strongly selective scattering power for X-rays: this idea, though it later proved to be mistaken, was not altogether unreasonable in view of the characteristic X-ray emission of the elements which had been found by Barkla. Towards the end of 1913, at the second Solvay Congress, von Laue used the rediscovered reciprocal-lattice theory to extend to the general case of any crystal the geometrical construction for the interference maxima from cubic crystals that had been given by P. P. Ewald. He thus provided the foundation for a simple "geometrical" theory of X-ray diffraction.

Meanwhile the experiments of Friedrich and Knipping, and von Laue's interpretation of them, had become known in England, and had inspired much discussion and further investigation, particularly by W. H. and W. L. Bragg. The story of what happened is here continued by Sir Lawrence Bragg:

"In the summer of 1912 my father showed me von Laue's paper, which had aroused his intense interest because of his work on the exciting of cathode rays by X-rays, which pointed to the projectile-like properties of X-rays, and he discussed with me possible alternative explanations for the effects which von Laue had found. I undertook some experiments at Leeds that summer to see whether we could explain von Laue's spots by the shooting of particles down avenues in the crystal lattice rather than by the diffraction of waves, experiments which were of course abortive.

"On returning to Cambridge in the autumn of 1912 I studied von Laue's photographs very intensively, and was very naturally forced to the conclusion that they must be due to diffraction. I also concluded at the same time that one must modify the explanation of them which von Laue had given.

Von Laue had remarked that one did not get all the spots one would expect from a simple cubic lattice, but only a selection of the whole range. He ascribed this to the existence in the X-radiation of five characteristic wavelengths chosen so that they approximately satisfied the diffraction conditions for the spots which actually appeared in the photographs. I, on the other hand, concluded that von Laue's spots were due to the diffraction of 'white' X-radiation, representing a continuous band of wavelengths over a certain range. I was led to this first by noting the changing shape of the Laue spots when the distance from the photographic plate to the crystal was altered. This in turn led me to consider the diffraction effect as a reflection of X-ray pulses by the lattice planes of the crystal. I pointed out that this was equivalent to the selection from the continuous spectrum of a wavelength determined by the lattice spacing of the crystal. I tested this by reflecting the X-rays from a mica plate set at a series of angles, getting in every case a spot in the reflected position and so showing, as I believed, that all wavelengths were represented over a certain range in the X-rays. The problem then remained to explain why only certain spots appeared in the Laue photographs, and I ascribed this to the fact that the essential underlying lattice of the crystal was face-centred and not simple cubic. I communicated these results to the Cambridge Philosophical Society in November 1912. The 'Bragg equation' appeared in this paper (p. 46) in the form $\lambda = 2d \cos \theta$, but in later papers θ was defined as the glancing angle and not the angle of incidence.

'Professor Pope at Cambridge was very interested in these results, because the close-packed lattices which he and Barlow had devised for atoms which they believed to be of equal size were face-centred cubic. He procured crystals of potassium chloride and sodium chloride for me, and I took their Laue photographs. I showed that these could be explained by an arrangement of alternate scattering centres in two interleaved face-centred lattices, the NaCl structure in fact, and that these centres must be equal in scattering power in KCl but different in scattering power in NaCl.

'This work was done at Cambridge before I collaborated with my father. We worked along divergent lines at first, which came together later. My father was very interested in my explanation of the diffraction effect as a reflection, and he set up at Leeds the first X-ray spectrometer. He was primarily interested in the nature of X-rays. He checked that the reflected rays were really X-rays,

a point on which he wished to satisfy himself because of his speculations about the corpuscular nature of X-rays. He found as I did that there appeared to be a continuous spectrum, but his spectrum also showed some peaks superimposed upon this continuous range, and by improving the apparatus he soon narrowed these down so much that it was clear that they were monochromatic components characteristic of the target. Incidentally I think it is not often realised how much work he did on characteristic X-rays before Moseley made his brilliant generalisations. My father constructed tubes with about a dozen different anticathodes and identified Barkla's *K* and *L* radiation, showing that the *K* contained two peaks and the *L* three peaks. He related the wavelengths to the atomic weights of the metals in each anticathode (the idea of atomic number had not yet come to the fore) by a simple law. In fact he gave the first hint of Moseley's relations, and it was his work which inspired Moseley to his broader generalisations.

'My father then examined with his spectrometer crystals of KCl and NaCl such as I had used for my Laue photographs, and found the reflections of the characteristic peaks from the (100), (111) and (110) faces. It was clear at once that the spectrometer was a far more powerful way of investigating crystal structure than the Laue photographs, which I had used. It was only at this stage that we joined forces. In particular, I had been trying to analyse the diamond structure by Laue methods without success, but my father mounted it on the spectrometer and the structure became immediately obvious. We wrote a paper on the diamond structure together, but the results which gave the clue to it were obtained by him. I was able, however, to work along with him with the spectrometer in the summer of 1913, and so to work out the structures of zincblende, fluorspar, pyrites and some of the carbonates, which showed how powerful the spectrometer could be. My father was at first principally interested in X-ray spectra and X-ray absorption edges, but crystal structures also fascinated him, and from that point on we both mainly devoted ourselves to crystal structure analysis.'

These experiments, together with those of Friedrich and Knipping, not only confirmed von Laue's diffraction theory but gave a direct proof of the existence of the space-lattice, and provided a simple expression (the Bragg law) for the relationship between the wavelength of the X-rays used and the lattice spacings of the crystal. The ionisation

curves obtained by means of the Bragg spectrometer showed clearly that the "mirror-image reflection" postulated by Bragg is selective and is conditioned by multiple interference. The Bragg equation was first published in its usual form in a paper by W. H. and W. L. Bragg in the *Proceedings of the Royal Society*, vol. 88, page 428 (1913). Soon afterwards von Laue [*Physikalische Zeitschrift*, 14, 421 (1913)] was able to show that this equation was only another way of expressing the results of the geometrical space-lattice theory.

Ionisation spectrometer measurements also revealed another reason for the absence of many of the interference spots at first expected by von Laue. The pulse theory of X-rays predicted much too wide an extension of their spectrum in the short-wave direction. In fact, as W. Duane and F. L. Hunt established in 1915, this spectrum ends abruptly at the short-wavelength limit given by the now well-known quantum rule.

Still further credit is due, however, to W. H. and W. L. Bragg. X-ray diffraction patterns had made it possible to compare the wavelengths of X-rays with the three lattice constants, whose axial ratios were already known. Absolute measurements, however, remained impossible without a knowledge of the absolute value of the lattice constant of at least one substance. It was necessary for this purpose to know the number of atoms in the unit cell, and this was impossible without a knowledge of the structure. The Braggs' measurements, however, had shown that sodium chloride really did possess one of the hypothetical structures postulated by Barlow. Thus it was possible to obtain the absolute value of the lattice constant of this salt; this in turn provided an absolute measure of the wavelengths of X-rays, and hence the absolute lattice constants of all other crystals investigated. Rarely has the value of hypothesis in research been so strikingly demonstrated.

This brings us to the end of the historical introduction as far as X-rays are concerned, since all

that has followed is merged into present-day practice. Yet the space lattice has had another most important part to play in physics.

In 1924 L. de Broglie put forward in his *Thèses* the basic idea of wave mechanics. In the summer of 1925 Walter Elsasser, in a letter to the editor of *Naturwissenschaften*, pointed out that the de Broglie waves of electrons must cause space-lattice interference effects, and that experiments by Davisson and Kunzman on the reflection of electrons from a platinum sheet had actually shown maxima of the expected kind. When in 1926 E. Schrödinger published his communications on *Quantisierung als Eigenwertproblem*, C. J. Davisson and L. H. Germer began systematically to look for these effects. In March 1927 they were able to publish a note in *Nature* to say that their efforts, made on a single crystal of nickel, had been crowned with success. In May of the same year G. P. Thomson and A. Reid announced that an electron beam of several thousand volts had, on passing through a celluloid film, produced Debye-Scherrer rings, and G. P. Thomson found the same effect even more clearly with metal foils. Thus Elsasser's prediction was confirmed and the plainest of all proofs had been given of the connection of a wave with the movement of a corpuscle.

Admittedly the geometrical theory of space-lattice interference does not apply so well to electrons as it does to X-rays, especially not to low-energy electrons. But it has enjoyed further triumphs in the diffraction of neutrons, observed first by D. P. Mitchell and P. M. Powers, then since 1946 by W. H. Zinn, E. Fermi, C. Shull and other American physicists using the cyclotron or the uranium pile as a source. Here a new possibility has to be taken into account: the atomic structure factor, which is characteristic for the scattering of single atoms, may be negative as well as positive. This branch of research is, however, still in its infancy. It appears to be capable of great development.