CRYSTAL STRUCTURES
OF MINERALS

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PREFACE

The senior author (W.L.B.) paid a visit to Cornell University as Baker Non-resident Professor in the Spring of 1934. The customary plan for the guests of the Baker Chemical Laboratory to present in book form the course of lectures which they are invited to give could not be adhered to because the substance of the lectures had been contained in the recently written first volume of *The Crystalline State*. The arrangement of the atoms in most of the important mineral structures had at that time been determined by X-ray analysis and the opportunity was taken to write instead the *Atomic Structure of Minerals* in which it was possible to give an account of nearly all the main types. This book was published in February 1937 by the Cornell University Press in America and the Oxford University Press in Great Britain.

Some ten years ago we made plans to revise the book and bring it up to date. The project has taken much longer than we anticipated when we embarked upon it. When the first book was written thirty years ago it was possible to include almost every mineral structure which had been determined up to that date. Although we have dealt with many new structures in the present volume, the body of work on minerals is now so vast that it is no longer possible to achieve such a complete account in a reasonable compass. We have, therefore, described the investigations of the more common and important minerals and those with particularly interesting structures, and at the end of each chapter we have listed a key reference or references to all the other structures of minerals we have been able to trace up to the end of 1963. We hope that in this way the book will be of use both as a general survey for students and as a reference book for more advanced workers. The former book contained a brief account of the methods of X-ray analysis. These methods are now so adequately described in other books that we have judged it unnecessary to include it in the present volume.

We have been very fortunate in being able to arrange that the chapter on the feldspars (14) should be written by Dr W. H. Taylor. Dr Taylor has made an outstanding contribution in this field; he and his pupils have, to a large extent, unravelled the complex tangle of the many varieties of feldspar structure.

We are grateful for assistance with the drawings of text figures from Mr R. T. W. Atkins, Mrs M. Levesconte, and Mr V. M. Garton, and in reference checking from Mrs M. E. Caughey. Our particular thanks are due to Miss Eva Fejer both for the initial work in preparing up-to-date lists of references to crystal structure determinations which have

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made possible the relative completeness of coverage of the book, for checking references and unit cell data during the reading of the proofs, and finally in the preparation of the index. Lastly we would like to express our gratitude to Mr A. W. Ready and Mr H. Hadaway of G. Bell and Sons Limited for their unfailing advice, assistance and patience.

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W. L. B.
G. F. C.

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September 1964

CHAPTER 14. It was my aim, in writing this chapter in January 1962, not only to present a general account of the main features of the feldspar structure as they had been known for some time, but also to describe and discuss the important recent developments arising from our increasingly accurate knowledge of the finer details which differentiate one feldspar structure from another. This was made possible only by the willing cooperation of many present and former collaborators in these studies, who very kindly allowed me to use work which was at that time unpublished. In this connection it is a pleasure to acknowledge my great indebtedness to Dr S. W. Bailey, Dr S. G. Fleet, Dr P. Gay, Dr J. B. Jones, Dr C. J. E. Kempster, Dr E. W. Radoslovich, Dr P. H. Ribbe and—above all—to Dr H. D. Megaw. I must also thank these and other colleagues for reading the text; they made many helpful suggestions for its improvement.

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W. H. T.

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Notification of errors, misprints, and omissions will be welcomed by G. F. Claringbull, British Museum (Natural History), Cromwell Road, London, S.W.7.

ACKNOWLEDGEMENTS

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INTRODUCTORY NOTES

Text. The basic crystallographic data for a mineral in Chapters 3–15 are usually given in a standard form as in the following example.

Azurite, $Cu(OH)_2(CO_3)_2$ Monoclinic

$$C_{2h}^5 = P2_1/c$$
$$Z = 2$$

a 5·00 Å

b 5·85 Å β 92°20′

c 10·35 Å

The space-group symbol is given in Schoenflies and in standard symbols. In using the latter for the orthorhombic and monoclinic systems the space-group symbol has been related to the orientation of the unit cell chosen. Space-group symbols for alternative orientations are given in the Appendix (p. 383). The symbol Z stands for the number of times the formula unit is contained in the unit cell.

Of the crystallographic axes a, b, c the b axis in the monoclinic system is always taken at right-angles to the other two. In the orthorhombic system the axial directions given in the original description of the structure are normally followed, although for some well-known minerals the classical morphological axial directions have been retained.

Unit cell dimensions have sometimes been altered from those given in the older descriptions of structures to the best available for the mineral and have with a few exceptions been rounded off arbitrarily to two places of decimals.

Diagrams. In the projections of structures showing heights of atoms these are measured above the face of the unit cell along the axis of projection in hundredths of the projected unit cell edge; thus an atom in the lower face of the unit cell is at 0 and one in the top face at 100. This has been done to facilitate the making of rough models. The heights so given are only heights above the plane of the diagram in those cases where the face of the unit cell is perpendicular to the axis of projection.

End of chapter reference lists. The general criterion for inclusion of a reference to a structure in these lists has been that the description gives parameters for at least some of the atoms. The formula unit for each mineral is enclosed in a square bracket and prefixed by the Z value. For conciseness these lists usually give only the most recent key references but care has been taken to see that they lead to relevant earlier work.

ERRATA

CONTENTS

CHAPTER 1

GEOMETRY OF CRYSTAL PATTERNS

INTRODUCTION

It is no longer necessary as it was in the *Atomic Structure of Minerals*[1] to emphasize the importance of the symmetry of the atomic arrangement in contrast to the external symmetry of a crystal because not only do most mineralogical textbooks give due consideration to it but many of them use a structural classification for the minerals they describe. The following outline of space geometry is, nevertheless, included in the present work for the convenience of those readers who are not familiar with the concepts to enable them to appreciate the descriptions of crystal structures which follow.

The fundamental concepts are: the space-lattice, the point-group and the space-group.

THE SPACE-LATTICE

A crystal is essentially a pattern. The atoms are arranged according to a plan, such that the same configuration is repeated at regular intervals in all three dimensions.

Consider a two-dimensional pattern such as a wall-paper. Fix attention upon some particular feature such as the tip of a flower in a spray that is repeated again and again. These points will be seen to be arranged on a regular network (Fig. 1). If another bit of the pattern is chosen, although the network will be shifted in position it will have just the same orientation and dimensions as before, as shown by the dotted lines.

Further, if these points be joined by lines as in the figure, it will be seen that each of the parallelograms or cells so outlined contains a complete sample of the pattern. Such a cell is termed a unit cell and the whole pattern is formed by stacking unit cells together.

Although the network of points upon which a given pattern is based is always of the same form, the way of outlining the cells is arbitrary. Any way of drawing the cells so that a corresponding point is at each corner and no other points are included will serve. The cells so formed are alike in that each contains a unit of pattern and in that the area of the unit cell is always the same. Fig. 2 shows two alternatives for the same pattern. The pattern is represented in part only, to make the diagram simpler, but it is obvious that every part will be included once in each cell.

When the pattern is three-dimensional, as in a crystalline structure, the array of points at which the pattern repeats is called a space-lattice.

[1] By W. L. Bragg, Cornell University Press (1937)

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FIG. 1. A two-dimensional pattern
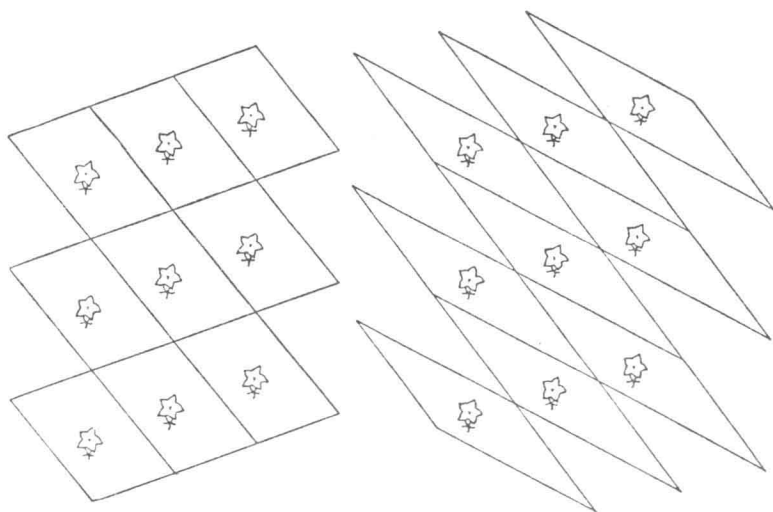
FIG. 2. Alternative ways of outlining cells, each containing a unit of pattern

Fig. 3 shows such an array of points. By joining the points, space can be divided into a series of parallel-sided unit cells each of which contains a complete unit of pattern. The whole structure is formed by stacking unit cells side by side. The form of the space-lattice is unique but the way of outlining unit cells is arbitrary, and alternative ways are shown in Fig. 3. The volume of each type of unit cell is the same.
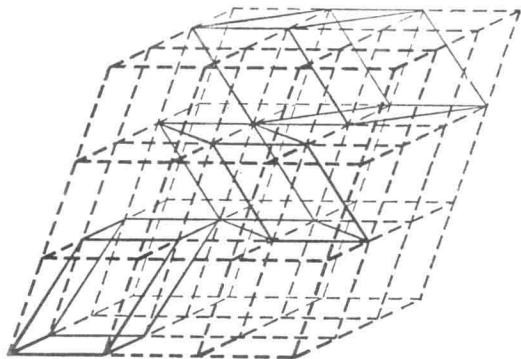
FIG. 3. A space-lattice. Alternative ways of outlining the unit cell are shown.
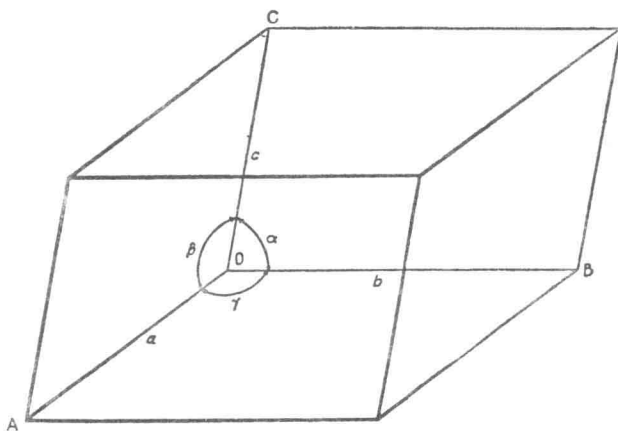
FIG. 4. The unit cell

Although the way of outlining the unit cell is arbitrary, in practice the choice of unit cell for a given crystalline pattern is generally decided by considerations of convenience and conformity with symmetry. It is defined by the lengths of its edges a, b, c, and the angles α, β, γ included between them (Fig. 4). These edges of the unit cell are termed unit translations in the pattern. Starting from any point in the structure and going a distance equal to and parallel to any cell edge, or by any combination of such movements, we arrive at a point where the

whole surrounding structure has the same form and orientation as at the point from which we started.

The unit translations correspond to the classical crystallographer's axes of reference which are used to define the indices of the various crystal faces. An important difference must be noted, however. In naming the crystal faces, one is only concerned with their relative orientation. It is therefore only necessary to define the ratio between the crystal axes; the b axis is given the value unity by convention, and the a and c axes are expressed as ratios to b. In X-ray analysis we are able to measure the actual lengths of the unit translations. In the orthorhombic crystal aragonite, for example, the morphological crystallographic axial ratios are given as

$$a : b : c = 0.623 : 1 : 0.721$$

whereas by means of X-rays it is ascertained that

$$a = 4.94 \text{ Å}, \quad b = 7.94 \text{ Å}, \quad c = 5.72 \text{ Å}.$$

THE LAW OF RATIONAL INDICES

If any two points of the lattice are joined by a straight line and this line is produced, it will continue to pass through a series of equally spaced points. This must be so, since in going from the first point to the second we have arrived at a place where the surrounding structure is identical with that around the point where we started, and there must therefore be a third point at an equal distance beyond. Similarly, if we join a point to any two other points of the lattice which are not in the same straight line, the plane including all three passes through a regular network of points. There are endless ways of drawing these row-lines and net-planes in the lattice. The more simple ways have a high density of points as compared with those that are less obvious. Such rows and sheets are seen in Fig. 3, as edges or sides of the alternative unit cells.

If we take the first point as origin, the coordinates of any other point of the lattice when referred to the edges of the unit cell as axes will be ua, vb, wc where u, v, w are integers. The row direction defined by joining this point to the origin is a zone axis $[uvw]$.

The planes are defined as follows. Let the broken lines in Fig. 5 represent a series of equally spaced net planes. One such plane passes through O, the next is the plane $a_1b_1c_1$, the next $a_2b_2c_2$ etc. Since both O and A must lie on planes, the axis OA must be divided into h equal parts by the planes, where h is any integer. Similarly OB is divided into k parts and OC into l parts. In the figure, h, k, l are 3, 4, 2, respectively. The set of planes is defined by the indices (hkl) in round brackets to distinguish them from the zone indices $[uvw]$.

This is the origin of the *Law of Rational Indices* of crystallography. Guided by the external form, the crystallographer chooses three non-

parallel faces of the crystal whose intersections give the directions of the crystal axes OA, OB, OC. A fourth face is chosen as standard plane, and called the face (111). Its intercepts on the axes are taken to be proportional to a, b, c. It is then found that *Faces of the crystal are parallel to planes making intercepts a/h, b/k, c/l on the axes where h, k, l are small integers.* This is a consequence of the fact that the external crystal faces are parallel to the more densely crowded net planes of the space-lattice.
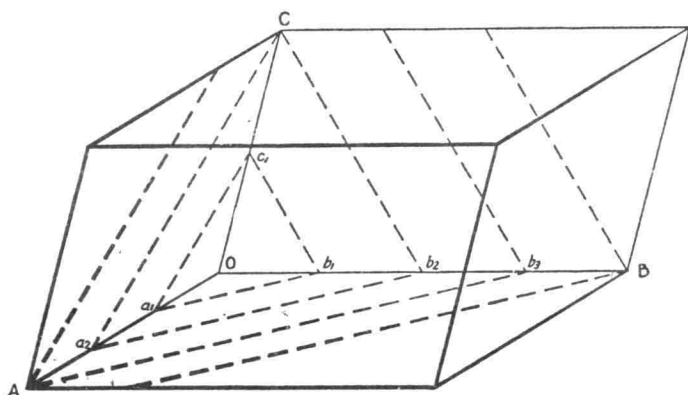

Fig. 5. The law of rational indices

Now it has been seen that there is only one true space-lattice for each crystal pattern, whereas the choice of crystallographic axes and standard planes is arbitrary. The only guide to their choice is that they should make the indices of the commonly occurring faces as simple as possible. This criterion is surprisingly good; when a crystal is measured by X-ray methods it is generally found that the true primitive translations are proportional to the axial ratios assigned to it as the result of measurements with the goniometer. It is sometimes found, however, that an axis must be halved or doubled in order that it may conform to the true unit cell.

THE FOURTEEN SPACE-LATTICES

The general form of the space-lattice has three unequal axes a, b, c, enclosing angles α, β, γ, which are not right angles. The majority of crystals are based on lattices, however, which have some degree of symmetry. For instance, when there are three equal axes at right angles the symmetry is of the cubic type.

If we explore the various possibilities, it is found that there are only fourteen different lattices (Fig. 6). This was first demonstrated by Auguste Bravais in 1848. The cells which are outlined in Fig. 6 are not in every case simple; 1, 2, 4, 8, 9, 10, 12 are simple, but the remainder involve additional lattice-points. To take the cubic lattices as examples,

12 is simple, 13 has an additional point at the cube centre, and 14 has points at the centres of cube faces. If we start with a lattice in which OA, OB, OC are all equal and make equal angles with each other, we find that the structure has cubic symmetry not only when the angles between
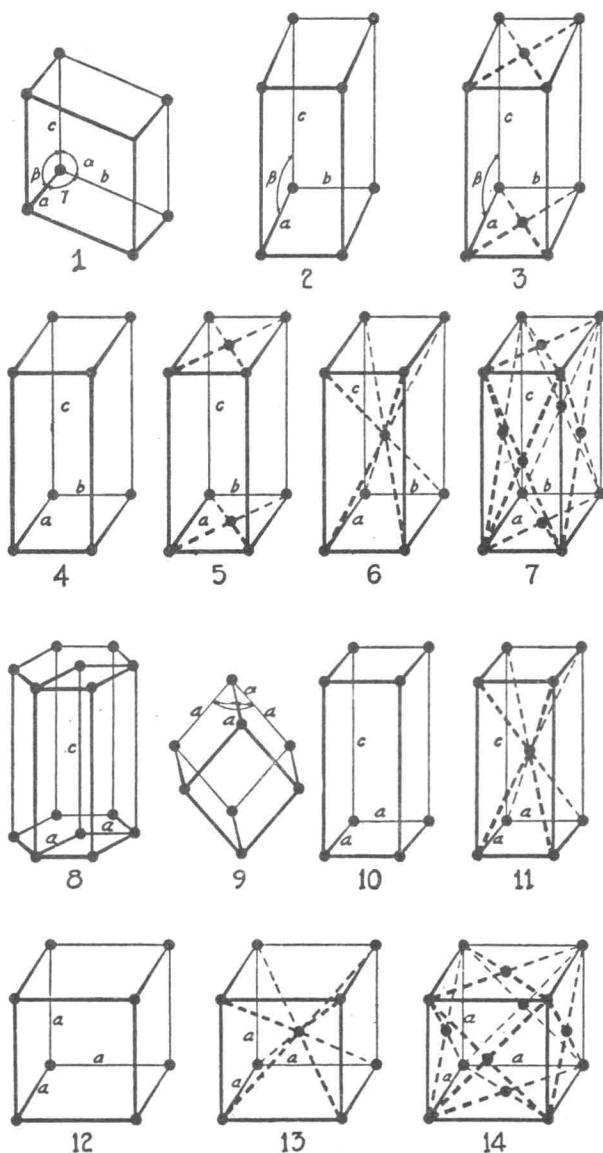

FIG. 6. The fourteen space-lattices. 1, Triclinic. 2, 3, Monoclinic, 4, 5, 6, 7, Orthorhombic. 8, Hexagonal. 9, Rhombohedral. 10, 11, Tetragonal. 12, 13, 14, Cubic.

the axes are right angles, but also when they are 60°, or 109° 28'. Fig. 7 illustrates the point, the simple unit cell being outlined solidly in each case and additional lattice-points shown so as to indicate the cubic form. Fig. 7(b) is the face-centred cubic lattice 14, and Fig. 7(c) the body-centred cubic lattice 13; trial shows that these three are
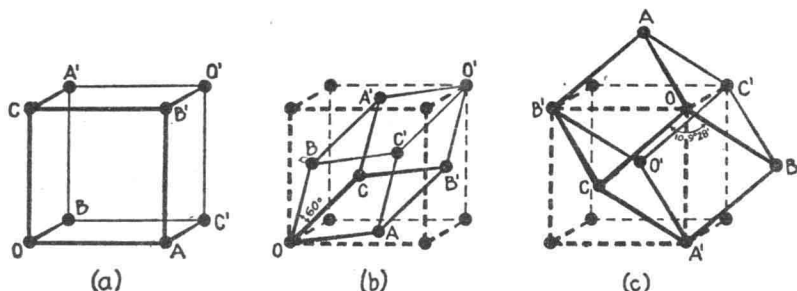

FIG. 7. The three cubic space-lattices. Forms (b) and (c) may be regarded as derived from (a) by extension or compression respectively along the diagonal OO'.

the only possible lattices with cubic symmetry. An exploration of other possibilities leads to two tetragonal, one rhombohedral, one hexagonal, four orthorhombic, two monoclinic, and one triclinic lattice.

THE POINT-GROUP

A point-group is a group of symmetry elements which characterizes one of the thirty-two crystal classes. In the cubic system, for example, there are five such classes. The highest form of cubic symmetry is represented by such crystals as fluorite, spinel, halite and galena, which have the following symmetry elements:

(a)	Fourfold axes	[100]
(b)	Threefold axes	[111]
(c)	Twofold axes	[110]
(d)	Reflection planes	{100}
(e)	Reflection planes	{110}
(f)	A centre of symmetry.	

In the remaining classes, some of these symmetry elements are absent. In the holoaxial class, for which no example is at present known, (a) (b) and (c) are retained but (d) (e) and (f) are absent. Blende and tetrahedrite have (b) (c) and (e), whereas (a) is replaced by fourfold inversion axes. Pyrite has (b) (d) and (f), (a) being replaced by two-fold axes. Ullmannite has (b) and twofold axes [100] alone.

All the space-lattices of Fig. 6 have the highest symmetry of the respective systems to which they belong. The symmetry of the 32 crystal classes is derived from the symmetry of the pattern-units of the groups of atoms associated with each point of the space-lattice. The

arrangement of symmetry elements over the space-lattice as a whole is known as the space-group.

THE SPACE-GROUP

The nature of a space-group may be best understood by taking actual examples of structures. Fig. 8 represents the structure of copper, which is very simple since the atoms are arranged on a cubic face-centred lattice. The pattern, continued indefinitely in space, has a net-work of symmetry elements. Rotation of the pattern through 90° around an axis [100] passing through any copper atom, for instance, brings the structure into self-coincidence. In fact all the types of symmetry listed in the last paragraph are repeated at every copper atom
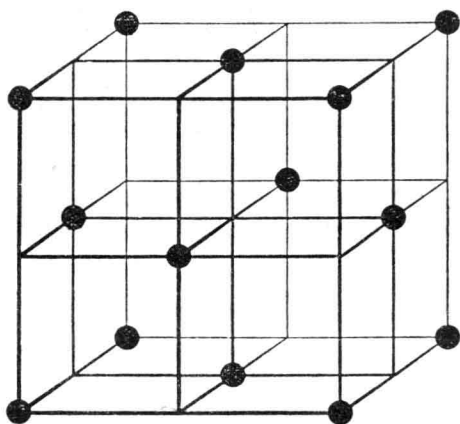

FIG. 8. The arrangement of the atoms in a copper crystal (cubic face-centred lattice).

as well as at other points in the structure. The symmetry elements form a network in space on which the whole structure is based. Starting with the lattice, if we place a single copper atom at one point it will be multiplied into the complete pattern by the symmetry elements. The whole array of symmetry elements is called a space-group.

We may compare these elements to the mirrors of a kaleidoscope. This instrument has three strips of mirror joined so as to form a tube of equilateral triangular cross-section. A collection of beads and other objects at one end is viewed by an eyepiece at the other. Repeated reflection by the mirrors produces a symmetrical pattern.

The symmetry of the crystal as a whole, i.e. its point-group, results from the symmetry of its space-group. It is easily seen, however, that several different space-groups may produce a crystal with a given point-group. Fig. 9, for instance, represents the structure of diamond. Copper and diamond belong to the same (holohedral) cubic class. The structure of diamond, however, has no fourfold axes of rotation.

There are fourfold screw axes, two of which are indicated in the figure, which turn atom (1) into (2), (2) into (3), (3) into (4), etc. Similarly there are no reflection planes, but glide planes (dotted line), parallel to (001). An atom (1) is reflected across the plane and simultaneously translated to coincide with (2), when (2) becomes (3) and so forth.

It is the possibility of screw axes and glide planes, in addition to rotation axes and reflection planes, which gives rise to the large number of space-groups. A point-group can only possess rotation axes and reflection planes, because by definition all its symmetry elements are
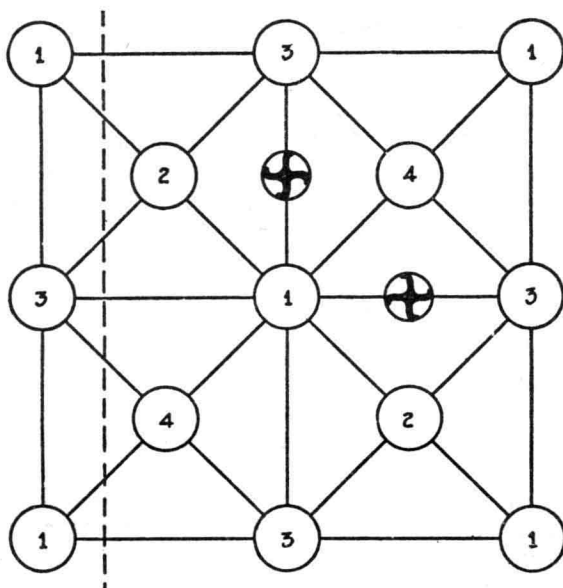

Fig. 9. Glide planes and screw axes of the diamond structure. Atoms marked (1) are on the lower face of the cubic unit cell and repeat again in the upper face. If the cube edge be denoted by a, atoms marked (2), (3), (4) are at heights $a/4$, $a/2$, $3a/4$ respectively.

associated with a single central point and translation is impossible. In the space-group, however, the result of a repeated symmetry operation may be, not to bring the structure into coincidence with its original position (as it must for a point-group), but to bring it into coincidence with a new position related to the original one by a primitive translation. Hence a turn around an axis may be accompanied by a translation parallel to that axis (screw axis), or reflection across a plane by a translation parallel to the plane (glide plane). The translation must be such that after the completed turn, or repeated reflection, the translations add up to a movement from one point of the lattice to another.

If the structure has a screw axis, the point-group has a corresponding rotation axis. The macroscopic properties of the crystal cannot dis-