The Relation between Molecular and Crystal Symmetry as shown by X-Ray Crystal Analysis

IX. *The Relation between Molecular and Crystal Symmetry as shown by X-Ray Crystal Analysis.* *By* G. SHEARER, M.A., B.Sc.

ABSTRACT.

The methods of X-ray analysis enable the number of molecules associated with the unit cell to be determined. With the help of this information an attempt is made to connect the symmetry properties of the crystal with this number and with the symmetry properties of the molecules from which the crystal is formed.

The symmetry number for each of the 32 crystal classes is given, and is shown to mean the minimum number of asymmetric molecules necessary in the unit cell to satisfy the symmetry conditions. The relative orientations and positions of these molecules in the cell are discussed.

It is suggested that this symmetry number is the actual number of molecules in the cell when the molecule is asymmetric; further that, if the molecule possesses symmetry, this symmetry appears also in the crystal, and the number of molecules in the unit cell is obtained by dividing the symmetry number of the crystal by the symmetry number of the molecule.

Evidence is produced in support of these hypotheses and examples are given of their application to inorganic and organic crystals.

IT has long been known that the various crystals can be divided into 32 classes distinguished from one another by the symmetry which they possess. Much geometrical work has been done on these crystal forms* but, so far, little progress has been made towards a physical interpretation of these geometrical properties. Recent work by the methods of X-ray analysis has thrown much light on the nature of the elementary lattice and the structure of molecules and has provided a basis for an advance in this direction.

The elementary lattice is the smallest which, repeated through space, will build up the crystal. As each lattice is identical with all others, it must show in itself all the symmetry properties of the crystal. These symmetry properties belong to three classes, (1) those associated with planes of symmetry, (2) those associated with axes of symmetry, (3) those associated as an axis of compound symmetry or a centre of symmetry.

Bravais† in 1850 showed that there are 14 space lattices which in themselves show the full symmetry of the various crystal classes. All of these lattices do not, from an X-ray point of view, appear to be independent. Thus, Bravais differentiates between the simple cube, the centred cube and the face-centred cube. These may all be regarded as one or more interpenetrating simple cubes. The same applies to the centred lattices in the orthorhombic and tetragonal classes. If these are eliminated, there are left nine different lattices, one each associated with the triclinic, hexagonal, tetragonal and cubic classes, two each with the monoclinic, orthorhombic, and trigonal systems. The hexagonal lattice is identical with one of the

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* For a full account of the mathematical theory of the space lattice and its symmetry properties, *see* H. Hilton's " Mathematical Crystallography," Oxford (1903).

† Bravais, Paris Ecole Polytechn. Journal, 19, 1-128 (1850).

Mr. G. Shearer on

two trigonal lattices. There have thus been eliminated from consideration all lattices which show more than one molecule associated with the unit cell. The view here adopted of an elementary lattice is that of a parallelopiped which, with perfectly symmetrical molecules placed at its vertices, shows the full symmetry of the class of crystal with which it is associated. It will be shown that by a combination of a definite number of similar interpenetrating lattices the symmetry of any class can be obtained even if the molecule possesses no symmetry of its own.

First of all, it is necessary to define what is meant by a plane or axis of symmetry in the elementary lattice. Take the parallelopiped which is the elementary lattice of the crystal class (Fig. 1) and consider molecules placed at its vertices. As the lattice has to repeat through space all these molecules must be orientated in exactly the same way relative to the lattice. Consider, for example, the vertex A of the lattice. At A eight lattices meet and the molecule at A belongs equally to all of them. The molecule* A of this cell corresponds to the molecules $B, C, D, E,$
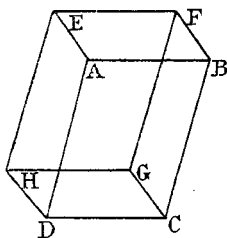

Fig. 1.

F, G, H of the other cells which meet at A. It follows that all the molecules at the vertices must be orientated relative to the lattice in exactly the same way.

Suppose the crystal has a plane of symmetry parallel to the face A, B, C, D. There must exist a set of molecules—" B " molecules—which are the mirror images of the molecules at the vertices—the " A " molecules. As these cannot coincide with the " A " molecules unless the molecule mirror images into itself there must be a separate lattice precisely similar in shape to the first but displaced in some way relative to the first lattice. It is clear that, to pass from an " A " molecule to a " B " molecule, we must take the mirror image of the "A " molecule in some plane parallel to the plane of symmetry and then give it a translation to some point in the cell. A reflection in the same plane and an equal translation applied to any other " A " molecule must give rise to another " B " molecule. Fig. 2 shows these two interpenetrating lattices, the arrow-heads denoting the orientation of the molecules.

Exactly the same process applied to the " B " molecules must give rise to " A " molecules. This reciprocal relation puts certain restrictions on the relative positions of the " A " and " B " molecules in the cell. These will be considered later.

* The term "Molecule" is used in this Paper to denote "Crystal Molecule." It does not follow that the arrangement of atoms in it is identical with the arrangement in the molecule in solution as dealt with in chemistry. There appears, however, to be a strong resemblance between the two in many cases. It has, of course, the same component atoms and molecular weight.

In the same way, the existence of a digonal axis gives rise to a second set of molecules whose orientations relative to the " *A* " molecules are obtained by rotating these about the axis through 180°. Once more, to pass from the one set to the other, in addition to the rotation there must be a translation and this translation must be such that the operation which, applied to the first set, gives the second, will, applied to the second set, give the first. Similar relations hold for axes other than digonal.

Having now defined what we mean by the elementary cell and planes and axes of symmetry, we may now proceed to determine the number of interpenetrating simple lattices, or, in other words, the number of molecules in the elementary cell which are necessary to satisfy the symmetry properties of the 32 crystal classes. First of all, let it be assumed that the molecule from which the crystal is constructed possesses no symmetry of its own. It is clear that the existence of a digonal axis must give rise to a second molecule in the cell whose orientation
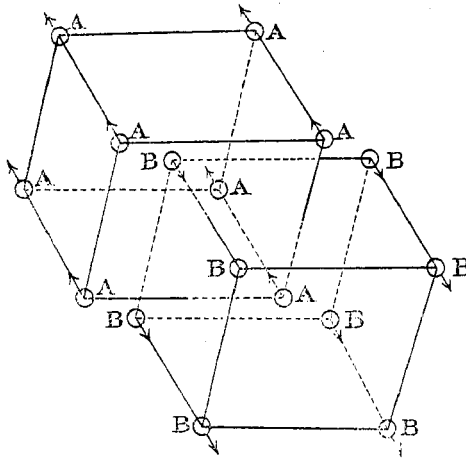

Fig. 2.

relative to the first is obtained by a rotation of 180° about the axis. A trigonal axis will give rise to two other molecules in the cell whose orientations are obtained by rotations of the first through angles of 120° and 240° about the axis. In the same way a plane of symmetry will give rise to a second which is the mirror image of the first in the plane of symmetry. A combination of a plane of symmetry and a digonal axis at right angles to it will give an elementary cell with four differently orientated molecules—" *A*," " *B*," " *C* " and " *D* " molecules. The orientation of the " *B* " molecules is obtained by reflection in the plane of symmetry, that of the " *C* " molecules by rotation of the " *A*'s " about the axis, while that of the " *D* " molecules may be obtained either by a rotation of the " *B* " molecules or by a reflection of the " *C* " molecules.

In this way it is possible to construct a table of the 32 classes and tabulate the minimum number of asymmetric molecules which must necessarily appear in the elementary cell in order to satisfy the symmetry properties of the crystal. This

number is most readily obtained by taking the stereographic projection of the crystal and finding the number of points on the diagram corresponding to the general face. This number may conveniently be called the " Symmetry Number " of the crystal class.

<div align="center">TABLE.</div>

Crystal class.				Symmetry number or number of asymmetric mole- cules per cell.
No.	Schönfliess symbol.	System.	Class.	
1	C_1	Triclinic ...	Triclinic Asymmetric	1
2	S_2		,, Pinakoidal	2
3	S	Monoclinic	Monoclinic Domal	2
4	C_2		,, Sphenoidal	2
5	C_2^h		,, Prismatic	4
6	V	Orthorhombic	Rhombic Bisphenoidal	4
7	C_2		,, Pyramidal	4
8	V^h		,, Bipyramidal	8
9	C_4	Tetragonal ...	Tetragonal Pyramidal	4
10	S_4		,, Bisphenoidal	4
11	D_4		,, Trapezohedral	8
12	C_4^h		,, Bipyramidal	8
13	C_4^v		Ditetragonal Pyramidal	8
14	S_4^u		Tetragonal Scalenohedral	8
15	D_4^h		Ditetragonal Bipyramidal	16
16	C_3	Trigonal ...	Trigonal Pyramidal	3
17	C_3^i		,, Rhombohedral	6
18	D_3		,, Trapezohedral	6
19	C_3^h		,, Bipyramidal	6
20	C_3^v		Ditrigonal Pyramidal	6
21	D_3^d		,, Scalenohedral	12
22	D_3^h		,, Bipyramidal	12
23	C_6	Hexagonal ...	Hexagonal Pyramidal	6
24	D_6		,, Trapezohedral	12
25	C_6^h		,, Bipyramidal	12
26	C_6^v		Dihexagonal Pyramidal	12
27	D_6^h		,, Bipyramidal	24
28	T	Cubic ...	Tetragonal Pentagonal Dodecahedral	12
29	O		Pentagonal Icositetrahedral ...	24
30	T^h		Dyakis Dodecahedral	24
31	T^d		Hexakis Tetrahedral	24
32	O^h		Hexakis Octahedral	48

It has already been mentioned that it is possible to lay down certain restrictions as to the relative positions of the variously orientated molecules in the lattice. Take, for example, a crystal with a plane of symmetry perpendicular to the " b " axis of the crystal. Place " A " type molecules of the verticles of a parallelopipedon of sides a, b, c, with angles $90°$, β, $90°$—one of the monoclinic lattices. Suppose that the molecule at the origin may be represented by the set of points

$$x_1, \ y_1, \ z_1$$
$$z_2, \ y_2, \ z_2$$
$$. \quad . \quad . \quad .$$
$$z_n, \ y_n, \ z_n$$

All the molecules of type " A " in the crystal may then be represented by the set

$$x_1+la, \ y_1+mb, \ z_1+nc$$
$$x_2+la, \ y_2+mb, \ z_2+nc$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$x_n+la, \ y_n+mb, \ z_n+nc$$

where l, m, n are any positive or negative integers.

A reflection of these molecules in the plane $y=0$ combined with a translation $aa, \beta b, \gamma c$ parallel to the three axes gives the set of " B " molecules,

$$x_1+la+aa, \ -y_1-mb+\beta b, \ z_1+nc+\gamma c$$
$$x_2+la+aa, \ -y_2-mb+\beta b, \ z_2+nc+\gamma c$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$x_n+la+aa, \ -y_n-mb+\beta b, \ z_n+nc+\gamma c$$

The same operation applied to this set must bring it into coincidence with the " A " set. If we carry out this operation we obtain the set,

$$x_1+la+2aa, \ y_1+mb, \ z_1+nc+2\gamma c$$
$$x_2+la+2aa, \ y_2+mb, \ z_2+nc+2\gamma c$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$x_n+la+2aa, \ y_n+mb, \ z_n+nc+2\gamma c$$

For these to represent the " A " set, we must have

$$2aa=0 \text{ or } a \text{ or } 2a, \text{ \&c., and } 2\gamma c=0 \text{ or } c \text{ or } 2c, \text{ \&c.}$$

Hence $\qquad a=0 \text{ or } \tfrac{1}{2}, \text{ and } \gamma=0 \text{ or } \tfrac{1}{2}$

Hence the " B " molecules must lie on lines parallel to the " b " axis either coinciding with the edges of the lattice or passing through the middle points of the sides or faces.

Consider now a digonal axis of symmetry parallel to the " b " axis. A rotation of the " A " molecules through 180° combined with a translation $a'a, \beta'b, \gamma'c$ parallel to the axes gives the set of " C " molecules

$$-x_1-la+a'a, \ y_1+mb+\beta'b, \ -z_1-nc+\gamma'c$$
$$-x_2-la+a'a, \ y_2+mb+\beta'b, \ -z_2-nc+\gamma'c$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$-x_n-la+a'a, \ y_n+mb+\beta'b, \ -z_n-nc+\gamma'c$$

The same operation applied to this set must bring it into coincidence with the " A " set. This gives the set

$$x_1+la, \ y_1+mb+2\beta'b, \ z_1+nc$$
$$x_2+la, \ y_2+mb+2\beta'b, \ z_2+nc$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .$$
$$x_n+la, \ y_n+mb+2\beta'b, \ z_n+nc$$

Hence, we must have $\qquad \beta'=0 \text{ or } \tfrac{1}{2}$

Hence, the " *C* " molecules must lie either in the *a—c* planes or in planes half-way between successive *a—c* planes.

Similar relations may be worked out for the other symmetries which the crystal may possess.   For example, the existence of a trigonal, tetragonal or hexagonal axis involves the existence of three, four or six molecules, derived from each other by successive rotations of 120°, 90°, or 60° about the axis.   The projections of corresponding points of these on a plane perpendicular to the axis form an equilateral triangle, square or regular hexagon according to the nature of the axis.   Their distribution in a direction parallel to the axis is such that either they all lie in the basal planes or are equally distributed between successive basal planes.   In the latter case the successive molecules form a regular spiral which may be right or left-handed.   The simultaneous existence of a plane of symmetry passing through the axis or perpendicular to it gives rise to a second spiral which is in the opposite sense to the first.   The position of this spiral relative to the first one obeys the conditions already worked out as we may consider the whole of the first spiral as a more complicated molecule.

In this connection it is interesting to note that the rotation of the plane of polarisation of light by a crystal is intimately associated with the existence of this spiral arrangement and the dextro or lævo nature of the rotation depends on the type of spiral.   If any spiral has this property it is clear that the existence of a plane of symmetry introduces a spiral which will give an equal and opposite rotation and the crystal will appear inactive.   This is, of course, shown by the fact that the only crystals which show this rotation are those whose only symmetry is associated with axes of symmetry.   A digonal axis is, of course, inactive as it is impossible to distinguish between a rotation of 180° in a right or left-handed direction.   Any biaxial crystal which rotates the plane of polarisation must do so owing to the existence of some spiral arrangement within the molecule itself.

In this way we can go a very considerable distance towards the solution of the crystal structure of any crystal using only the ordinary crystallographic data and, in the case of a symmetrical molecule, the number of molecules in the unit cell. Certain quantities remain to be determined.   These are such quantities as β, a', γ' in the above discussion and the sides of the equilateral triangle, square or hexagon in the case of uniaxal crystals.

So far it has been assumed that no symmetry exists in the molecule.   As long as an asymmetric molecule is in question the number of molecules in the unit cell must be that given in the table or an integral multiple of it.   If it were less, the crystal could not possibly have its full symmetry.

If, however, the molecule possesses a certain amount of symmetry of its own, a number less than that given in the table may suffice.   Thus a molecule with a plane of symmetry may form a crystal of, say, class 5 with only two molecules per cell,- the second being derived from the first by a rotation about the digonal axis. This can only happen, however, if the plane of symmetry of the molecule is set in the crystal parallel to the plane of symmetry of the crystal, in this case a plane perpendicular to the " *b* " axis.

The converse of this propostion is of importance.   If it is found that the number of molecules in the unit cell is less than the symmetry number for the crystal, it follows that the molecule must possess some symmetry and that this symmetry is reproduced in the crystal.   As the number of molecules in the elementary cell

must be an integer, it follows that the symmetry which the molecule shares with the crystal must be represented by an integer which is obtained by dividing the number given in the table corresponding to this class of crystal by the number of molecules in the unit cell. Thus, if n is the number characteristic of the class and m the number per unit cell, then n/m is an integer and the crystal shares n/m fold symmetry with the molecule. This number may be called the Symmetry Number of the molecule.

So far it has not been claimed that the number of molecules given in the above table is the actual number present when the molecule is asymmetric, but only that the number in the cell must be either this number or an integral multiple of it. It naturally suggests itself that this number is the actual number. This means that the number of molecules in the elementary cell is the minimum necessary to satisfy the symmetry conditions. It seems natural to suppose that a crystal will be constructed with the minimum material. If this is true, it implies that each unit cell contains one and one only of each differently orientated molecule.

A very considerable amount of experimental evidence exists in support of this hypothesis. In testing it, attention must be confined to asymmetric molecules. W. H. Bragg* has recently investigated a number of aromatic organic compounds, and many of these have molecules which can possess little or no symmetry. A large percentage of these form monoclinic prismatic crystals and show four molecules in the elementary cell. This is what is to be expected if the assumption made above is true. So far no example has been found where the number is greater than the symmetry number of the crystal. Certain cases have been found where the number is less than the symmetry number. This must mean that the molecules themselves possess some symmetry which they share with the crystal. In all the cases where this occurs there is good reason to suppose that the molecule does possess symmetry. For example, both naphthalene and anthracene form monoclinic crystals with two instead of four molecules in the unit cell. This shows that these molecules both possess a twofold symmetry. The use of such information will be discussed later. Both a- and β-naphthol belong to the same class, but have four molecules in the elementary cell. It is only to be expected that the addition of an OH group to one side of the naphthalene double ring will destroy any symmetry which the naphthalene ring possessed. In the same way the addition of the COOH, &c., groups in such substances as benzoic, salicylic and phthalic acids apparently destroys the symmetry of the benzene molecule, as these compounds all form monoclinic prismatic crystals with four molecules per cell. Tartaric acid is a monoclinic sphenoidal crystal and, as is to be expected, has two molecules in the unit cell.

As no case has occurred which contradicts the hypothesis, and as there is a considerable mass of evidence in its favour, it seems reasonable to conclude that it is generally true that the number of molecules in the elementary cell is always the minimum number necessary to impart to the crystal the necessary symmetry properties.

The question of molecules which do possess symmetry must now be considered. Here again a natural hypothesis suggests itself, viz., that all the symmetry of the molecule is reproduced in the crystal. It seems reasonable to assume that nature in forming a crystal will make use of all the symmetry already existing in the molecule.

* Bragg. Proc. Phys. Soc., Vol. 34, p. 33 (1921).

Indeed, this is really the same assumption as has already been made in the discussion of asymmetric molecules. It simply amounts to the statement that the minimum amount of material is used in the building up of a crystal. If this hypothesis is true it follows that the crystal must always show at least as much symmetry as the molecule from which it is formed. Indeed, there is evidence in favour of the fact that in general the symmetry of the crystal is higher than that of the molecule.

In the present state of our knowledge of molecular structure it is more difficult to test this assumption. There is no doubt that much of the symmetry is certainly made use of, but it is impossible to say at present exactly what symmetry any particular molecule possesses. There seems, however, to be considerable evidence that all the symmetry of the molecule is used in the formation of the crystal. The fact that most of the elements form crystals of a high order of symmetry with relatively few molecules in the unit cell shows that a considerable amount, if not all, of the symmetry of the atoms is reproduced in the crystal. The same applies to many simple inorganic salts. For example, $CaCO_3$ and Al_2O_3 are both likely·to possess a trigonal axis, the oxygen atoms being arranged trigonally round the rest of the molecule. A calculation of the symmetry of the molecule from the number of molecules in the unit cell and the nature of the crystal shows that the molecules must possess a trigonal axis. Quartz forms a crystal of class 18 with three molecules in the elementary cell. This implies that the SiO_2 molecule itself possesses a digonal axis and that the molecules are so arranged in the crystal that this digonal axis of the crystal coincides with one of the digonal axes of this type of crystal. So far no case has been investigated which does not seem to agree with the assumption that all the symmetry of the molecule is reproduced in the crystal.

If this hypothesis is true, it should be of great service in determining the structure of molecules. If, in addition to being able to say that a molecule possesses such and such symmetry we can also say that it possesses no other symmetry, we are in a strong position to decide on the nature of the molecule and also on the question of what symmetry in a molecule really means. In dealing with an atom it is clear that the outer electrons must be the important factors in deciding the crystal structure and the information to be derived from such arguments as those given above should throw considerable light on the distribution of these outer electrons. It is immaterial whether the electrons are considered as stationary or as moving in orbits. In the latter case the distribution of the orbits or of the normals to the orbits must show the symmetry properties.

Our knowledge of the distribution of the outer electrons is still too vague to permit of a complete interpretation of the results which the information derived from crystallographic measurements gives, but certain·steps may be made in this direction. For example, many of the elements crystallise in the highest form of cubic symmetry and possess two or four atoms in the unit cell. This means that the atoms in question possess either a 24-fold or a 12-fold symmetry. An examination of the table suggests that the symmetry of the atoms is that of one of the lower forms of cubic symmetry. This leads to the conclusion that there is some form of cubic arrangement of the electrons or of the electron orbits. Similar conclusions as to the existence of some such cubic arrangement have been reached as a result of the consideration of the chemical properties of various atoms. Carbon in the form of the diamond is a crystal of class 31 with eight atoms in the unit cell. This fact ascribes to the carbon atom a symmetry number 3—that is to say, a trigonal axis.

Bohr has arrived at the conclusion that the four outer electrons in the carbon atom move in four 2_1 orbits whose normals are arranged tetrahedrally. Such an arrangement provides a ready explanation of the existence of a trigonal axis in the atom, but would also suggest the existence of other trigonal axes of symmetry. It may, of course, be necessary also to consider the two inner electrons, or the arrangement may not be perfectly tetrahedral. The structure of graphite is still somewhat uncertain. Debye and Scherrer* found that their observations agreed with the assumption of a rhombohedral lattice with eight atoms in the unit cell. On the other hand, Hull† suggests four interpenetrating hexagonal lattices. A consideration of the numbers given in the table for the various classes of trigonal crystals shows that if the above assumptions are true it is impossible to have eight atoms in the unit cell. The same objection does not apply to Hull's suggested structure. Hull's structure supports the idea that the carbon atom in graphite possesses a trigonal axis just as it does in the case of diamond.

A few typical examples of the application of these principles may now be con-
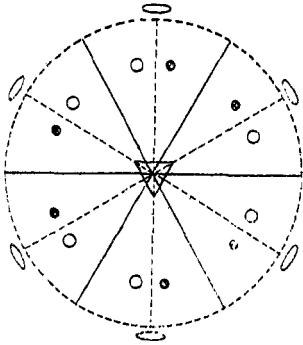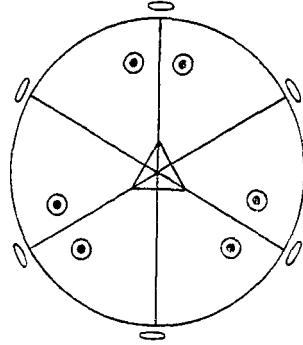

FIG. 3.   FIG. 4.

sidered in more detail. Take first the case of ruby—Al_2O_3. This forms a crystal of class 21, possessing a trigonal axis, three digonal axes inclined at angles of 120 deg. to each other and perpendicular to the trigonal axis, and three planes of symmetry passing through the trigonal axis and bisecting the angles between successive digonal axes. The stereographic projection of the crystal class is shown in Fig. 3.

How much of this symmetry can the Al_2O_3 molecule possess? If the two aluminium atoms are placed along the trigonal axis and the oxygens are placed at the corners of an equilateral triangle in the equatorial plane of the two aluminiums, a highly symmetrical molecule is formed. If the component atoms are considered as spheres, the symmetry of the molecule is that shown in Fig. 4. It has a trigonal axis, three digonal axes, three planes of symmetry each passing through the trigonal axis and one of the digonal axes and an equatorial plane of symmetry. Although this molecule possesses, like the crystal, both planes and axes of symmetry, the distribution of these is not that of the crystal. In fact, Fig. 4 corresponds

* Debye and Sherrer, Phys. Zeit., **13**, 297 (1917).
† Hull, Phys. Rev., **10**, 692 (1917).

to a crystal of class 22. The ruby crystal has planes of symmetry bisecting the angles between the digonal axes. In order to form such a crystal from the above molecule it would be necessary to introduce a second molecule into the lattice, whose orientation is such that it is the mirror image of the first in a plane of symmetry bisecting the angle between two of the digonal axes of the molecule. If this were done the symmetry of the resulting molecule would be that shown in Fig. 5. The
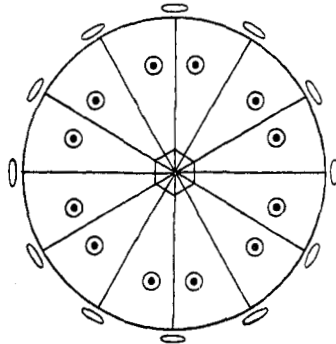

FIG. 5.

crystal would then belong to the dihexagonal bipyramidal class. As observations show that the crystal is ditrigonal scalenohedral and not dihexagonal bipyramidal, it follows that the molecule cannot have all the symmetry attributed to it above. It is clear that the maximum symmetry which the molecule can possess is (1) a trigonal axis, (2) either three digonal axes or three planes of symmetry. It cannos possess both the planes and the axes. It is difficult to decide whether it is the planet
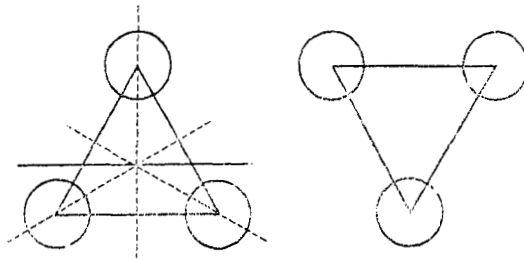

FIG. 6.

or the axes which actually exist in the molecule. It is obvious, however, that it is not possible to consider the various atoms as spheres. The deciding factor in the determination of the symmetry must be the distribution of the outer electrons in the component atoms.

As the moleule cannot possess the full symmetry of the crystal there must be at least two molecules in the unit cell. The second of these is derived from the first

by a reflection in a plane of symmetry or a rotation about a digonal axis according as the molecule possesses in itself the axes or the planes of symmetry. The result will be two sets of Al_2O_3 molecules whose oxygen atoms are arranged as shown in Fig. 6. This is in entire agreement with the results obtained by Bragg* from measurements by X-ray methods.

Quartz (SiO_2) provides another interesting example. It forms a crystal of the trigonal trapezohedral class and has three molecules in the unit cell. If the molecule were asymmetric six molecules would be necessary. Hence the crystal must share with the molecule a two-fold symmetry. Since the crystal possesses no planes of symmetry this common element of symmetry must be a digonal axis. Hence the SiO_2 molecule must be capable of reproducing itself when rotated through 180 deg. about some axis. It must therefore be of some such form as is shown in Fig. 7. Here again, if the atoms are regarded as spheres, the molecule would possess in addition two planes of symmetry. As the crystal does not show these planes it is clear that the outer electrons in the oxygen atoms are so distributed that the molecule will not reflect into itself across a plane bisecting the angle between the two Si—O directions or across a plane passing through the centres of the three atoms. This fact throws further light on the symmetry of the ruby molecule. In that
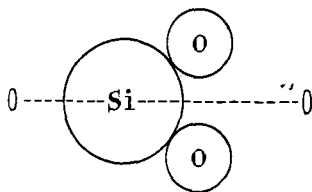

FIG. 7.

case it was not found possible to decide whether the molecule possesses the planes or the digonal axes of symmetry. The fact that the oxygens in the quartz molecule can rotate into each other but not reflect into each other makes it extremely probable that the same is true in the case of ruby, and that therefore the Al_2O_3 molecule possesses three axes but no planes of symmetry.

By placing three SiO_2 molecules in the unit cell, obtained from each other by successive rotations of 120 deg. about the trigonal axis and equally spaced along this axis, and such that the projections of corresponding points of these three molecules on a plane perpendicular to the trigonal axis form an equilateral triangle, all the necessary symmetry is given to the crystal. It is, of course, obvious that the trigonal axis of the crystal must be perpendicular to the digonal axis of the molecule. W. H. Bragg's measurements by X-ray methods result in a model which supports these arguments.

An examination of the crystal models of many simple inorganic compounds fails to reveal the presence of a definite molecule in the crystal. Thus in NaCl each sodium atom is surrounded by six chlorine atoms, and each chlorine atom by six equidistant sodium atoms. The same applies to KCl. In Ice each hydrogen is surrounded by two oxygens, and each oxygen by four hydrogens giving the necessary

* See W. H. and W. L. Bragg, X-Rays and Crystal Structure, 2nd edition.

proportion of hydrogen to oxygen. In fact Bragg* has used this fact to construct a crystal model of ice, and has shown that the result agrees with the X-ray measurements made by Dennison. In more complex compounds the molecule certainly appears in the crystal, and it seems reasonable to assume that even in the above cases the molecule really exists and that, in the case of NaCl for example, each chlorine atom has its own particular sodium. It will be shown that if the molecule does actually exist, the sodium to which any particular chlorine belongs is not one of the six surrounding it at equal distances, but one of the sodiums arranged diagonally relative to the chlorine.

If it is assumed that the molecule does actually exist, even in polar compounds, some interesting results as to the symmetry of various molecules follow.

NaCl and KCl form cubic crystals of classes 32 and 29 respectively. Both have four molecules in the unit cube. The symmetries which the molecules share with the crystals are therefore twelve-fold and six-fold respectively.

Consider the case of KCl. This six-fold symmetry must consist of (1) a trigonal
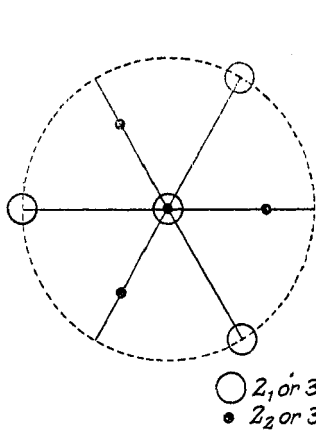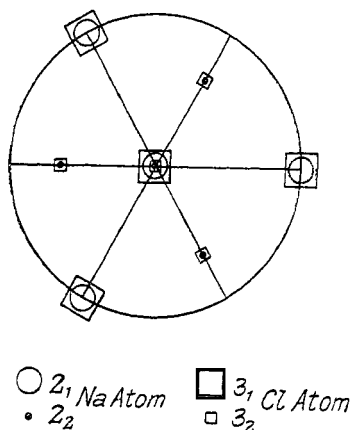

FIG. 8.   FIG. 9.

axis, and (2) a digonal axis perpendicular to the trigonal axis. Such a symmetry involves the presence of two other digonal axes perpendicular to the trigonal axis, and inclined to each other and to the first digonal axis at angles of 120 deg.

The question arises—how can the KCl molecule possess this symmetry ? If the K and Cl atoms are placed on the trigonal axis then there must be three digonal axes perpendicular to the K—Cl line. A rotation of the molecule through 180 deg. about one of these axes brings the K atom to the position of the Cl atom. It follows that the K and Cl atoms must be interchangeable as far as symmetry considerations go. This is not so unreasonable as it appears at first sight when it is remembered that what we have to deal with is a combination of a positively charged K atom with a negatively charged Cl atom. The outermost electron of K atom has passed over into and been absorbed by the Cl atom. Each atom has then the electron

* W. H. Bragg, Proc. Phys. Soc., Vol. 34, p. 98 (1922).

arrangement of the inert gas Argon. They differ only in the existence of positive and negative charges on the two atoms. It is quite conceivable that this difference of charges has no bearing on the question of crystal symmetry, and we may therefore regard the K atom as being able to rotate into the Cl atom without making any difference in the molecule from a crystal point of view.

Similar arguments apply to the case of NaCl. The Na atom becomes a positively charged Neon atom, while the Cl atom becomes a negatively charged Argon atom. It appears that for crystallographic purposes a positively charged Na atom is identical with a negatively charged Cl atom. Such arguments point to the fact that in crystallographic questions the governing factor is not the nature of the nucleus, but the electron arrangement around the nucleus and more especially the arrangement of the outer electrons.

Consider the electron arrangement in these atoms. The following table is that given by Bohr* for the numbers of electrons in the various types of orbit :—

<div align="center">TABLE.</div>

Element.	Number of electron orbits of various types.							
	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2
Ne ...	2	4	4	—	—	—	—	—
Na ...	2	4	4	1	—	—	—	—
Cl ...	2	4	4	4	3	—	—	—
A ...	2	4	4	4	4	—	—	—
K ...	2	4	4	4	4	—	1	—

Both Neon and Argon possess two sets of outer electrons, four in each set. In Neon, the four 2_1 orbits are such that the normals to their planes are arranged tetrahedrally in space. The four 2_2 orbits are circular. Bohr does not state how these are arranged. The most symmetrical arrangement appears to be obtained by arranging three of the normals in a plane normal to one of 2_1 normals at angles of 120 deg. to each other, and the fourth normal in a direction perpendicular to this plane. The direction cosines of these planes may be represented by

$$\left.\begin{matrix}111\\ 1\bar{1}1\\ \bar{1}1\bar{1}\\ 1\bar{1}\bar{1}\end{matrix}\right\} \text{ for the } 2_1 \text{ orbits and } \left.\begin{matrix}\bar{1}1\bar{1}\\ 01\bar{1}\\ 1\bar{1}0\\ \bar{1}01\end{matrix}\right\} \text{ for the } 2_2 \text{ orbits.}$$

The stereographic projection of these orbits is shown in Fig. 8.

The atom possesses one trigonal axis and three planes of symmetry, but no digonal axes of symmetry. If we consider two of these atoms placed end to end in opposite directions we obtain a molecule which possesses one trigonal axis, three digonal axes and four planes of symmetry as shown in the stereographic projection, Fig. 9.

This is the symmetry of the NaCl molecule. Fig. 10 shows the suggested distribution of electron orbit normals. If we rotate the lower atom of the molecule through some angle about the trigonal axis so as to destroy the planes of symmetry,

* Bohr, Zeitschr. fur Physik, 9, 1 (1922).

we obtain a molecule which possesses a trigonal axis and three digonal axes—the necessary symmetry of the KCl molecule. The stereographic projection of such a molecule is shown in the figure given below.

We thus see that by considering the distribution of tne electrons round the nuclei we can construct molecular models which have the desired symmetry. It is, of course, not claimed that these figures represent the actual arrangement of the electrons ; many other arrangements could no doubt be constructed. The important thing is that it can be demonstrated that it is the electron distribution around the nuclei which matters and not the nuclei themselves.

Ice forms another interesting example. X-ray data indicate that the crystal is hexagonal with four molecules in the unit cell. An examination of Table I. shows
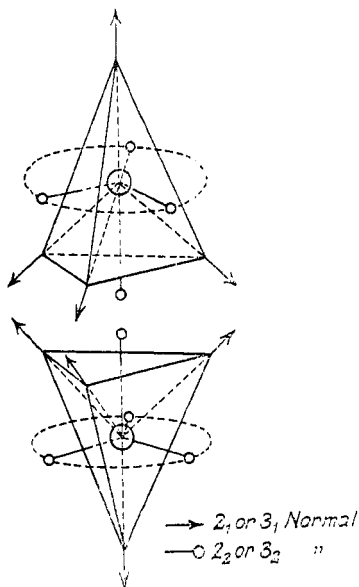

FIG. 10.

that the molecule must possess at least a trigonal axis. This the molecule cannot do unless the three atoms of the molecule are arranged along the trigonal axis. X-ray data show that such is not the case. The hydrogen atom consists of a nucleus with one outer electron ; the oxygen atom has six outer electrons. If the two electrons from the hydrogens join with the six oxygen electrons to form the electron arrangement of neon, what has to be considered is a doubly charged neon atom surrounded by two hydrogen nuclei. It is possible that these nuclei play no part in the determination of the symmetry of the molecule from a crystallographic point of view, and that all that has to be considered is a doubly charged neon atom. In the discussion of the NaCl crystal it has been shown that this atom has probably a six-fold symmetry. As there are four ice molecules in the unit cell it follows that

the crystal should possess 24-fold symmetry. This is in agreement with the assumption. of a hexagonal form for the crystal.

It is also of interest that in the case of ice the distance between the centres. of the oxygen and hydrogen atoms is 2·76 A.U., a distance considerably greater than. the commonly accepted value. This fact may be explained if it is assumed that the. hydrogens are playing no part except in determining the residual electric field round. the molecule and that what has been measured is the distance between the centres. of two negatively charged neon atoms.

In the same way the symmetry of ZnS should be similar to that of KCl. The. crystal is cubic (hexakis tetrahedral) and possesses four molecules in the unit cell. The symmetry of the molecule must therefore be six-fold, that is to say, the same. as that of the KCl molecule.

There are, of course, many inorganic polar compounds which cannot be con- sidered as an aggregate of inert gas atoms. Such molecules as ·CaCO$_3$, NaNO$_3$,.

$\bigcirc$ 3$_1$ K Atom $\square$ 3$_1$ Cl Atom
• 3$_2$ ▫ 3$_2$
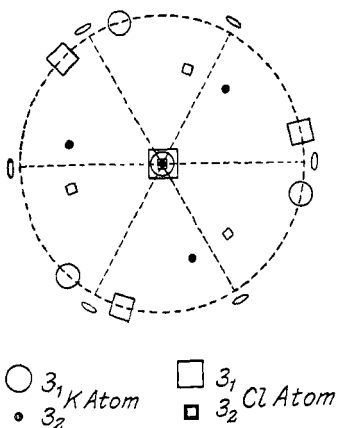
FIG. 11.

NaClO$_3$, &c., cannot be so regarded. The ClO$_3$ ion has 18 outer electrons which. is the number possessed by Argon. The distribution of these electrons is, however, very different from that of the Argon atom, and we cannot consider the two as equivalent in any respect. As is to be expected, crystallographic measurements show that the molecule possesses a trigonal axis but no planes or digonal axes. In general, where two or more different atoms occur in one of the ions, this ion will not become identical in electron arrangement, with an inert gas atom. Hydrogen is anomalous in so far as it possesses only one electron, and when it has lost this electron only the positively charged nucleus remains, and it may be permissible in some cases to ignore the effect of this nucleus in dealing with the symmetry of the molecule from a crystallographic point of view. Ice appears to be an example of this.

The application of these principles to organic crystals is somewhat more limited as the molecules of such compounds themselves possess little or no symmetry. A very large number of the crystals so far investigated are monoclinic prismatic and

possess four molecules in the elementary cell. This would indicate a complete absence of symmetry in the molecules. There are, however, some notable exceptions. For example, both naphthalene and anthracene belong to this class, but have only two molecules in the unit cell. This must mean that these molecules share a two-fold symmetry with the crystal. Benzene forms a rhombic bipyramidal crystal and has two molecules per cell. This gives to the benzene molecule a four-fold symmetry, possibly a plane of symmetry and an axis of symmetry perpendicular to the plane. In view of the fact that the structure of the benzene ring has been the subject of much debate, this new information may be of considerable importance. There have been many suggestions as to the arrangements of the fourth valency bonds, but most of these would appear to give to the molecule a trigonal axis. This is not supported by crystallographic work. Whatever the arrangement of the bonds, the molecule, in its crystalline state at least, must show a plane of symmetry with a digonal axis perpendicular to it or some equivalent symmetry.

Neither the Kekulé nor the Claus formula conforms with this condition. On the other hand, the Ladenburg formula does, and so also does the formula suggested by Dewar. Ingold* has recently shown that this Dewar formula has much chemical evidence to support it. The arrangement of bonds is that shown in Fig. 12. If

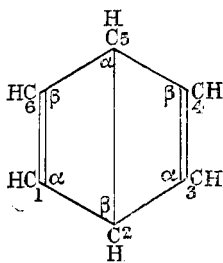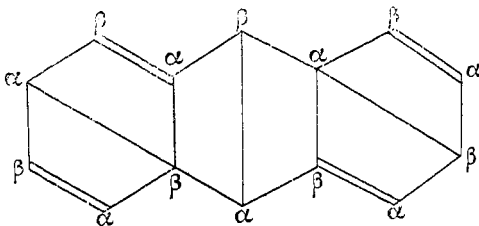FIG. 12.   FIG. 13.

the puckered hexagon suggested by Bragg† is assumed and the bonds are arranged in this way, it is found that the molecule has the required symmetry. Fig. 12 shows the symmetry of the molecule. The points marked α are supposed to lie above the plane mean plane of the ring and those marked β below the mean plane.

If this is extended to the case of anthracene the molecule has a centre of symmetry, and this is represented in Fig. 13. Naphthalene presents greater difficulties. The X-ray measurements show that the molecule has a twofold symmetry—probably a centre of symmetry. Such formulæ as those of Fig. 14 satisfy this condition. All the formulæ usually given for naphthalene appear to possess too great symmetry. Bragg's measurements of the naphthalene crystal show that there are two molecules in the unit cell and indicate further that the second is derived from the first by a rotation of 180° about the " b " axis. The presence of these two molecules, together with the existence of a centre of symmetry in the molecule, gives to the crystal the full symmetry of the monoclinic prismatic class.

* Ingold, Journal Chem. Soc., June (1922).
† Bragg, Proc. Phys. Soc., Vols. 33, 34 (1921).

An examination of the measurements made by crystallographers on benzene substitution products would appear to indicate that when two of the hydrogens are replaced by the same groups the 1-3 product is a crystal of higher symmetry than the 1-2 or the 1-4 product. This probably implies that the 1-3 compound possesses in itself some symmetry, while the 1-2 and 1-4 compounds are in general asymmetric. If the 1, 2, 3, 4 positions are as shown in Fig. 12, it is clear that the 1-3 compound possesses a plane of symmetry, while the others are asymmetric. The objection to this point of view is that it is to be expected that there would exist more than one 1-3 compound and that these various compounds would show differences in crystalline and probably in chemical properties. No such differences have been observed. Until X-ray data are available as to the structure of some of these substances it is of little use pushing the question further.

Another interesting problem in crystallography is the determination of the conditions governing the choice by any molecule of some particular crystal form. If the molecule is asymmetric it is theoretically possible for it to crystallise in any of the 32 classes. On the other hand, it seems extremely improbable that 48 molecules will arrange themselves in such a way as to form a crystal of class 32. In fact, it appears that eight is about the maximum number of molecules probable in the elementary cell. It is to be expected that asymmetric molecules will crystallise
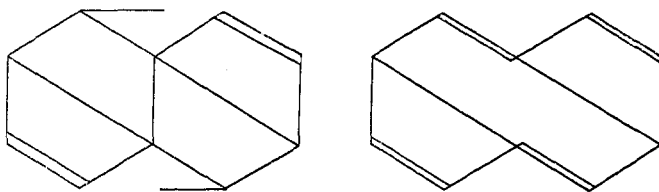

FIG. 14.

in classes of low symmetry, and this is amply supported by the measurements made by crystallographers. For example, a statistical investigation of about 1,000 of the aromatic organic crystals described by Groth shows that approximately 60 per cent. form crystals which would require four asymmetric molecules, about 20 per cent. would require eight, and about 20 per cent. four. Some of these molecules may have some symmetry of their own, and the 20 per cent. containing eight is probably an over estimate. It seems that there is a decided tendency for four asymmetric molecules to come together, grouping themselves about an axis and plane of symmetry.

If the molecule possesses symmetry and our second hypothesis is true, that the symmetry of the molecule is reproduced in the crystal, then it is clear that the selection will fall on more highly symmetrical classes. The symmetry of the molecule imposes a lower limit to the symmetry of the crystal. It appears to be generally true that there is more than one molecule in the elementary cell. This means that the crystal is of higher symmetry than the component molecule. The only cases where we should expect only one molecule in the cell are in classes 1 and 32, the latter with a molecule or atom which in itself possesses perfect symmetry if such exists.

While these conditions impose certain restrictions on the choice of a crystal form by any particular molecule they still leave a considerable margin of choice. The remaining conditions must depend on the molecule and it seems fairly certain that an important factor is the distribution of the residual forces 'round the molecule. That such forces exist is shown by the fact that the crystals actually form. These forces are presumably of an electrical nature and it is on the distribution of these charges over the molecule that the final choice of a crystal form must depend. It is possible to imagine distributions of positive and negative charges over the molecular surface such that when two molecules came within each other's sphere of action they would naturally orientate themselves about a digonal or other axis of symmetry.

In the case of simple polar compounds, the two atoms of the molecule are oppositely charged and there will be a strong tendency for the negatively charged atom of any molecule to become surrounded by the positively charged atoms of other atoms and *vice-versa*. This is what happens in the case of NaCl and similar molecules.

Some of the considerations stated above have recently been used in attempts to solve the structure of somewhat complicated crystals and have proved of considerable value in the interpretation of the data derived from X-ray observations.

SUMMARY.

1. The nature of the elementary lattice and the meaning of axes and planes of symmetry in the lattice are discussed.

2. A table is given showing the number of asymmetric molecules necessary per unit lattice to produce the symmetry of the various crystal classes. The existence of fewer molecules in the unit cell is shown to imply the existence of symmetry in the molecule.

3. The relative positions of the variously orientated molecules in the lattice are considered, and it is shown that only certain positions are possible.

4. It is suggested that the number of molecules in the elementary cell is always the minimum necessary to satisfy the symmetry conditions ; also that any symmetry of the molecule is reproduced in the crystal.

5. Applications of these principles to particular cases of inorganic and organic crystals are given.

6. The factors underlying the selection by a molecule of some particular crystal class are briefly discussed.

In conclusion, the author has much pleasure in acknowledging his indebtedness to Prof. Sir W. H. Bragg, F.R.S., for much help during the development of these ideas.

This Paper originated in connection with work being carried out at University College, London, under the Department of Scientific and Industrial Research.

DISCUSSION.

The PRESIDENT, before calling on Sir William Bragg, congratulated him in the name of the Society on the honour recently conferred upon him by the Paris Academy of Sciences.

Sir WILLIAM BRAGG, after acknowledging the congratulations tendered to him, said that the Paper before the meeting was an important one, throwing a new light on the possibilities of investigating crystal structure. The Author's intricate but lucid argument affords a great simplification of the problem. Three unitary structures have to be considered : (1) The chemical

molecule, as it exists in solution ; (2) the elementary crystal lattice or cell, consisting of groups of (3) crystal molecules, in which the atoms and electrons are not necessarily arranged in the same manner as in chemical molecules. The Author's method enables one to determine the symmetry of these groups at once from the geometry of the crystal, with a very little help from X-rays. A considerable vista of research is thus opened up, which may serve to settle such questions as that of the static versus the dynamic model of the atom.

Dr. J. W. EVANS thought that the methods employed by Mr. Shearer gave promise of proving of great assistance in working out the structure of crystals. There were, however, some considerations that must not be neglected :

(1) It is by no means certain that molecules always maintain their identity in the crystalline state.

(2) Even where they exist in the crystal, they may not retain the same form and symmetry as in a free state.

(3) Although in an ideal crystal all the cells are identical, and have identical orientation, this is by no means always actually true. We know that cells of different composition may be employed indiscriminately if they are approximately the same in form and volume, as in the case of the plagioclase felspars.

In the same way, if the outer forms of cells of the same substance approximate to a higher symmetry than the cell itself, these cells may, even when differently orientated, be employed in building up a crystal structure. The same may be true with cells that are enantiomorphically related. In these cases the whole structure may have a higher symmetry than the individual cells as the result of either (a) a symmetrical arrangement of the cells in the nature of molecular or ultramicroscopic twinning—twinning is usually an attempt to attain higher symmetry—thus forming lattice cells of greater size ; or (b) indiscriminate occurrence of cells differing in orientation or in enantiomorphic character. In the former case it might be very difficult to recognise by means of X-ray analysis the primary cells. In the latter case it would, I should think, be impossible.

The explanation of the crystalline structure of potassium chloride is not convincing. The symmetry of the molecules shown in Fig. 11 is that of the quartz or trigonal trapezohedral class which is represented by the symbol IIIUh (J. W. Evans, Min. Mag., Vol. 15, pp. 398-400, 1910), with three digonal axes at right angles to a trigonal axis, and making angles of 120° with each other ; whereas that of the crystal structure is stated to belong to the cuprite or pentagonal eikositetrahedral, CUh, class, in which there are four trigonal axes corresponding to the diagonals of the cube and three digonal axes at right angles to one another and parallel to the edges of the cube. The cell contains four molecules, and the trigonal axes of these are supposed by the author to be parallel to the diagonals of the cube, but it is not explained how the 4×3 digonal axes at right angles to the diagonals are transformed into three digonal axes at right angles to one another.

From the examination of the material prepared at the Imperial College and a comparison of the work of other observers, Miss Knaggs, of the Imperial and Birkbeck Colleges, has shown that the symmetry of the crystal structures of the simpler carbon compounds frequently bears close relation to that of the molecule. Substances of the type CX_4, where X is an element, are usually cubic. Those of the types CX_3Y are trigonal or hexagonal, unless X is hydrogen, when the symmetry is lower. Those of the form $C(CX_3)_4$ are as a rule cubic, and those with $C(CX_2Y)_4$ are tetragonal. In all cases the symmetry is apt to be that of a higher or different class than would have been expected, though one belonging to the same system. In the case of the $C(CX_2Y)_4$ compounds the symmetry of the molecule would be that of chalcopyrite or tetragonal scalenohedral, IVBk, class, whereas that of the crystal usually belongs to the IVBc, or in one case IVBu class. It can be shown that symmetry of this character would be obtained by appropriate molecular twinning. Some of the compounds considered are dimorphic, crystals with less symmetry forming at lower temperatures.

The Speaker threw out the suggestion that crystal structure might possibly be due to the repulsion of the electrons of different atoms combined with an attraction of the atoms as a whole. If it be supposed that, contrary to the usual view, there are six outer electrons in chlorine having their mean position arranged like the points of an octahedron, and that in potassium there are eight electrons arranged like the points of a cube, it will be evident that a position of stability would be obtained when the points of each chlorine octahedron were opposite the centres of the faces of the surrounding potassium cubes, and the points of each potassium cube were opposite the centres of faces of chlorine octahedra, and that the potassiums and chlorines would then be arranged alternately in a cubic lattice just as we know to be the case.

Mr. SHEARER, in reply, thanked Sir William Bragg for his remarks on the Paper He agreed with Dr. Evans as to the possibility of a difference between the molecule in a crystal and the molecule in solution. The two were not necessarily identical, although there was evidence that in many cases there was a strong resemblance.

Dr. Evans appeared to doubt the possibility of the determination of the true unit cell. What was done by X-rays was to measure the distance between two successive *identical* planes; in this way, the method of X-rays was much more powerful than any other method at present at the disposal of the crystallographer.

Dr Evans was apparently under a misapprehension as regards the author's suggestions as to the KCl molecule. Although the KCl molecule was given the symmetry of the quartz class, there were present in the unit cell four such molecules. By giving these the proper orientations in the cell it was possible to give the crystal the symmetry of the pentagonal icositetrahedral class. The trigonal axis of the molecule lay along—not perpendicular to—the diagonal of the cube. The three digonal axes were parallel to three diagonals of the faces of the cube. Thus, if 111 were proportional to the direction cosines of the cube diagonal, or trigonal axis, the direction cosines of the three digonal axes of the molecule were proportional to $1\bar{1}0$, $\bar{1}01$ and $01\bar{1}$. These were parallel to three of the diagonals of the faces of the cube, and made angles of 120° with each other and were perpendicular to the trigonal axis. The directions of these axes coincided therefore with those of the cubic class to which KCl belonged. The rest of the symmetry of the crystal arose from the presence of four of these molecules in the unit cell.

The results obtained by Miss Knaggs were interesting, and appeared to support the suggestions put forward in the Paper. The crystal in general possessed more symmetry than the molecule owing to the presence of more than one molecule in the unit cell. Until the number of molecules in the cell had been determined it was unsatisfactory to discuss the symmetry of the molecule.

As far as external evidence went there seemed nothing in support of the suggestions of Dr. Evans as to the electron arrangements in the K and Cl atoms. Our knowledge of atomic and molecular forces was at present extremely limited.