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THE ANALYSIS OF CRYSTAL STRUCTURE BY X-RAYS[1]

IN this address I propose to consider the new methods of analyzing the structure of materials by means of X-rays, considering especially the stages by which they move towards their objective. It is convenient to recognize three such stages, of which the first comprises the simplest and most direct measurements and the last the most indirect and complex.

The fundamental measurement of the method is the angle at which rays of a given wave-length are reflected by a set of planes within the crystal. The planes of a "set" are all exactly like one another: an imaginary observer within the crystal could not tell by any change in his surroundings that he had been moved from one plane to another. Sometimes there is no reflection of the first order from a set so defined, because the planes may be interleaved by other planes so spaced and of such strength as to annul the true reflection; but this can always be allowed for. When the wave-length of the X-rays is known, the angular measurement can be used to find the spacing of the set of planes, and in this way a linear dimension of the crystal is measured. The spacing is the distance between any plane and its nearest like neighbor on either side. If the spacings of three different sets of planes are found, the volume of the unit cell is found. The crystal unit cell is bounded by six faces, each set of planes furnishing a pair. The pair consists of two neighboring planes of the set. The cell may have a great variety of forms, but has always the same volume. The specific gravity of the substance being known, it is possible to find the number of atoms of various kinds which the cell contains; the proportion of the various kinds is necessarily the same as in the molecule of the substance. The cell is in practice found always to contain a small integral number of molecules, one, two, three or four, rarely more. This assemblage of molecules is fully representative of the crystal; by the mere repetition of the cell, without the addition of any new features, the crystal with all its properties is produced.

There are, therefore, three types of assemblage. The simplest is that of the single atom, as in helium in the gaseous state, in which the behavior of every atom is on the whole the same as the behavior of any other. The next is that of the molecule, the smallest portion of a liquid or gas which has all the properties

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[1] Address of the president of Section A—Mathematical and Physical Science of the British Association for the Advancement of Science, Toronto, August 11, 1924.

of the whole, and lastly, the crystal unit, the smallest portion of a crystal (really the simplest form of a solid substance) which has all the properties of the crystal. There are atoms of silicon and of oxygen; there is a molecule of silicon dioxide, and a crystal unit of quartz containing three molecules of silicon dioxide. The separate atoms of silicon and oxygen are not silicon dioxide, of course; in the same way the molecule of silicon dioxide is not quartz; the crystal unit consisting of three molecules arranged in a particular way *is* quartz.

The final aim of the X-ray analysis of crystals is to determine the arrangement of the atoms and the molecules in the crystal unit, and to account for the properties of the crystal in terms of that arrangement.

The first step is the determination of the dimensions of the crystal unit cell: any one of the possible ways in which the cell can be drawn will do. When this has been completed it is a simple calculation in geometry to find the distance between any atom and any other atom in the crystal of like kind and condition, or, in other words, the distance an observer would have to travel from any point within the crystal to any other point from which the outlook would be exactly the same and would be similarly oriented. This is the only measurement which the X-rays make directly; any other measurement of distance is made indirectly, by aid of some additional physical or chemical reasoning. It is not possible by direct X-ray measurement to determine the distance between any two points—atom centers, for example—within the same cell.

Let us take an example. The crystal unit of naphthalene has the dimensions defined in the usual way by the statement:

$$a = 8.34\text{Å} \quad b = 6.05\text{Å} \quad c = 8.69\text{Å} \quad \beta = 122^\circ\ 49' \quad \alpha = \gamma = 90^\circ.$$

It contains two molecules: an integral number, as always. These facts are given directly by the X-ray measurements. But there is no direct determination of the distance between any carbon atom and any other carbon atom contained within the same cell; the measurements given are those of the distances between any atom and the nearest neighbors, in three principal directions, which are exactly like itself, these distances being the lengths of the edge of the cell. There is not even a measurement of the distance between the two molecules in the same cell, because they are not similarly oriented. In fact, there is no clear meaning in the term "distance" in this case, just as we can not state the distance between an object and its image in a mirror, unless the object is a point of no dimensions. If the molecule of naphthalene has a center of symmetry, as is indeed indicated during the development of the results of the X-ray analysis, it is possible to state the distance between the centers of symmetry of the two molecules in the same cell, but this does not define the distance between any atom in one of the two molecules and any atom in the other. All such distances, if they are to be defined and measured, can only be found by the aid of fresh considerations.

Or again, let us take the case of rock-salt. The crystal unit cell of rock-salt contains one molecule; one form of the cell has for its eight corners the six middle points of the faces of a certain cube (edge = 5.62 A.U.) and two of the opposite ends of any diagonal of the cube. The so-called face-centered cube is four times as large as the cell and contains four molecules. The dimensions of the cell are determined directly by the X-rays, which measure the distance between each of the three pairs of parallel faces that contain it. The cell may be placed so that each corner of it is associated in the same way with a molecule of sodium, let us say: and, of course, the knowledge of the dimensions of the cell is equivalent to a knowledge of the distance between any two sodium atoms in the crystal, which atoms are all alike in every respect. But we have no direct measurement by the X-ray methods of the distance between a sodium and a chlorine atom. We infer that the chlorine atom lies at the center of the sodium cell, or *vice versa,* from considerations of symmetry. Crystallographic observations of the exterior form of the cell assign to the crystal the fullest symmetry that a crystal can possess. If the cell that has been described is to contain the elements of such full symmetry, the chlorine atom must lie at the center of it. It can not lie anywhere else, for every cell would contain a chlorine atom similarly placed. There would then be unique directions in the crystal; that is to say, polarities. Moreover, both the sodium and the chlorine atoms must themselves contain every symmetry of the highest class: the full tale of planes of symmetry, axes of rotation, and so on. They both have centers, and we can state the distance between a chlorine atom and a sodium atom because we can state it as between center and center, and put it equal to half the distance between two sodium atoms on either side of the chlorine. The structure of sodium chloride is then determined completely.

It may possibly be a difficulty that the cell so described does not at first appear to have all the symmetries of the rock-salt cube, but it is to be remembered that we are to expect the full display of symmetries only when the cell has been repeated indefinitely in all directions. We may take a simple case, as in Fig. 1.

Suppose sodium and chlorine atoms were to be arranged in a line as in the figure, just as they are in any of the three principal directions in the crystal. A plane of symmetry perpendicular to the line of atoms indefinitely prolonged may be drawn through the center of any atom. The unit cell is one molecule: one chlorine and one sodium. The unit by itself has not this symmetry, but the repetition of the same molecule in either direction on either side provides the symmetry. Moreover, each sodium and each chlorine must itself have a plane of symmetry, and the planes are equally spaced. We can state the distance between a sodium and a chlorine atom as half the distance between two sodiums.

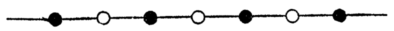

FIG. 1

Let us take one more instance, the diamond. The crystal unit cell contains two atoms of carbon: as in the case of rock-salt, it may be so chosen that, of its eight corners, six are the middle point of the faces of a certain cube and two are the ends of any diagonal of the cube. The sides of this cell are determined by the X-rays, and are all equal to 2.52 A.U. This is the distance between any carbon atom and the nearest carbon atom which is exactly like itself. The distance between the two carbon atoms in the same cell is not measured directly, but can be inferred after it has been defined. This we are able to do because the carbon atom is tetrahedral; a tetrahedron has a center, and we can state the distance between the centers of two tetrahedra, no matter how the tetrahedra are oriented. We know that the carbon atom, as built into the crystal, is tetrahedral, because the X-ray observations show that the four trigonal axes meet in it. The two atoms in the cell are oriented differently; one may be said to be the image of the other, if translation shifts are ignored, in each of the faces of the cube. Considerations of symmetry or X-ray observations show that the center of an atom of the one orientation lies at the center of a tetrahedron formed by four atoms of the other orientation. The edge of this tetrahedron is the edge of the unit cell, and its length is 2.52 A.U. It may then be calculated that the distance between the one atom and the others, its nearest neighbors, is 1.54 A.U. We may call this distance the diameter of the carbon atom, but we must remember our original definition of the meaning of the term. Thus the 2.52 A.U. is the result of a direct unaided X-ray measurement, but the 1.54 A.U. is not, and has no meaning except after special definition.

Only such distances between atoms as can be calculated from the dimensions of the unit cell can be measured directly and without qualification. The determination of these distances may be looked on as the result of the *first stage* of the analysis by X-rays.

We now come to a *second stage.* It is possible to make other statements of the relative positions of atoms and molecules which, though less complete and informative than those of distances, and their orientations, are necessary to the solution of the crystal structure problem. These also are deduced by means of the X-ray methods.

It often occurs that the atoms or molecules in one cell can be divided into two portions which are the reflections of one another across some plane, or can be brought to be the reflection of each other by a shift parallel to the plane. In that case the orientation of the plane and the amount of the shift can be stated definitely, the former by inspection of the crystal or by X-ray observations, the latter by X-ray observations alone. So also it may happen that the atoms or molecules in the same cell may be divided into portions which can be made to coincide with each other by a rotation round some axis with or without a shift parallel to that axis. The direction of the axis can be found by inspection of the crystal or by X-ray observations; the amount of the shift can be found by X-ray observations alone.

In these cases the distances that are found by the X-ray method are all that can be stated without special definition. It is not possible to state the distance between an object and its image in a mirror, if the object has any extension in space; but it is possible to state the magnitude of a shift.

Measurements of this sort constitute a characteristic feature of the X-ray analysis, for which reason I would like to discuss them briefly.

We know that it is possible to separate crystals into thirty-two classes, according to the kind of external symmetry which they display. As we have hitherto been unable to look into the interior of the crystal, we have been obliged to be content with this imperfect classification by outer appearance. It has been shown, however, that there is a classification by inner arrangement which is perfect and includes the other. It is beyond the limits of ordinary vision: out of the range of the lens and the goniometer. The interior arrangements of the crystal, of which the outer form is one consequence, are so varied as to furnish 230 different modes. With very few exceptions the X-rays now allow us to carry the classification to this higher degree. If the modes are grouped according to the external features of the crystals that follow them, we come to the well-known thirty-two classes, there being several modes in every class. I may be permitted to illustrate this important point by examples, although it is familiar to those who have studied crystallography. Let us consider

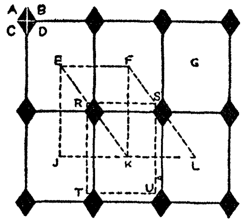

Fig. 2.

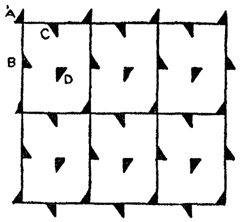

Fig. 4.

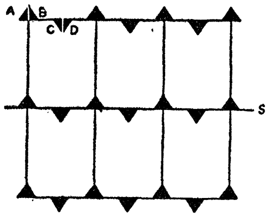

Fig. 3

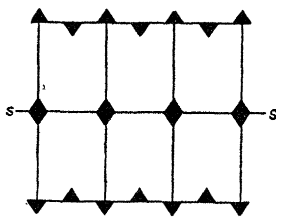

Fig. 3A.

first a two-dimensional example, which is much easier to describe than the three dimensional actuality, and contains all the essential ideas.

Consider an arrangement of figures in a plane which displays symmetry across two planes at right angles to one another. Such arrangement may be exhibited diagrammatically, as in Fig. 2. The unit cell may be drawn in various ways, EFKJ, EFLK, RSUT, and so on. The cell contains, however it is drawn, either a whole diamond or enough parts to make up a whole diamond. Each diamond can be divided into four parts: B and D are the reflections of A and C across a plane; C and D are the reflection of A and B across a plane at right angles to the first plane. Unless the diamond, the content of one cell, could be divided in this way there could not be the double symmetry. But, granted this division into four portions, it is not necessary that the four should be arranged as in the figure in order that the double symmetry may be obtained. There are two alternatives (Figs. 3 and 4).

In Fig. 3 the lower half of each diamond—that is to say, the portions C and D—are shifted, whether to right or to left is immaterial, by an amount equal to one half of one side of the cell EFKJ. The symmetry about a vertical line in the plane of the paper is obviously retained. It is not so obvious that there is still any symmetry about the horizontal line until we realize that we mean only "observable symmetry": that which is to be seen in the outer form of the indefinitely extended figure, corresponding to the crystal. Clearly, the whole figure will present the same appearance from below as from above. In fact, we can see that as a whole the lower part of the figure is symmetrical with the upper part by imagining the upper and the lower to be further shifted relatively as in Fig. 3A: the two parts sliding on one another along the line SS. The two parts are then the image of each other across SS in the full sense of the word.

From Fig. 2A we may also realize that the amount of the original shift must be equal to one half of EF: no other shift will give the symmetry which Fig. 3A shows. In Figs. 5 and 5A a different shift has been given, and the failure is clear.

In Fig. 4 not only are C and D shifted parallel to the horizontal line, but also B and D are shifted parallel to the vertical; this time the amount of shift is one half of the side EJ.

The three modes of Figs. 2, 3 and 4 all lead to the same external symmetry. There is one more which is based, as we should say, on a different lattice and is symmetrical, like the others, about two lines at right angles to each other. It is shown in Fig. 6. There are no variations of Fig. 6, as of Fig. 2, to be obtained by the introduction of shifts. If in Fig. 6 we shift C and D relatively to A and B, as we did in Fig. 3A, we find that they can now be described as the direct reflection of A′B′ into CD and of A′C into B′D, and the mode of Fig. 6A is the same as that of Fig. 6.

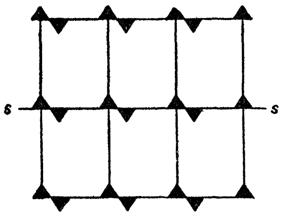

Fig. 5.

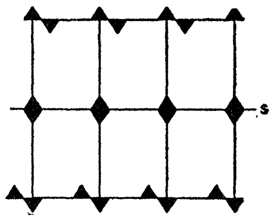

Fig. 5A.

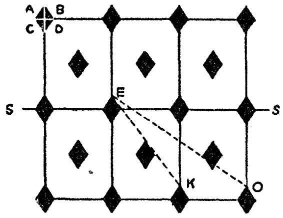

Fig. 6.

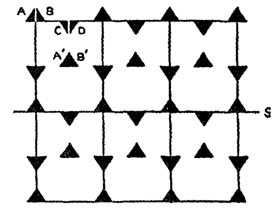

Fig. 6A.

There are therefore four *modes* in one *class:* four varieties of internal arrangement which all lead to the same external appearance of symmetry.

Our example is two-dimensional, and the crystal has three dimensions. But there are no new ideas to be added: it is only the numbers of symmetries, modes and classes that are increased. If, for example, we continue the study of the modes of arrangement that lead to an external symmetry of reflection across two planes at right angles to each other, we find that there are four lattices instead of two, and twenty-two modes instead of four. The class containing crystals that possesses this particular form of symmetry is generally called the "hemimorphic class in the orthorhombic system." Its symbol is C_{2v}: the symbols of the four lattices are Γ_0 Γ_0' Γ_0'' Γ_0'''. In every case the content of the unit cell is divisible into four parts, corresponding to the ABCD of Figs. 2 to 6.

The ten modes in the Γ_0 lattice are shown in Fig. 7, which will serve to show the numerical increase due to the introduction of the third dimension. Under each separate figure is given, beside the crystallographic symbol, another symbol which describes the shifts: D^x means a direct reflection across a plane parallel to *yz*; E^x_y a reflection across a plane parallel to *yz*, together with a shift parallel to the axis of *y* equal to half the *y* edge of the cell, and M^x a reflection across a plane parallel to *yz*, together with a shift parallel to the diagonal of the *yz* face and equal to half that diagonal.

Let us now see how the X-ray analysis distinguishes the mode. Let us imagine that Fig. 2 represented a number of pits in a plane reflecting surface. The surface could be used as a grating having many spacings instead of one. If, for example, we so placed it that the horizontal lines of the figure were parallel to the slit of the spectroscope the spacing would be equal to EJ: if the vertical, the spacing would be equal to EF. Again, if the grating were so placed that EK, for example, were vertical, the spacing would be the perpendicular distance between EK and FL. If the surface is pitted as in Fig. 3, the spacing when the horizontal line is parallel to the slit is the same as before; but when the vertical is parallel to the slit the effective spacing is only half what it was in Fig. 2. This follows from the fact that if we divided the surface into a number of vertical narrow strips the diffracting effect of each such strip, for this position, depends on the total amount of reflecting surface contained in the strip, but not on its distribution along the slip. It does not matter that C and D are upsidedown as compared to A and B. The strata consisting of C and D portions have interleaved the strata of A and B portions. This halving of a spacing of Fig. 3 as compared with Fig. 2 occurs only when the grating is placed so that the slit is parallel to the vertical line of Fig. 3, and not when any other line is vertical, except by some odd chance connected with the shape of the pits. In this way it is possible to distinguish between Fig. 2 and Fig. 3. The mode shown in Fig. 4 is distinguished by the halvings of both the horizontal and vertical spacings, and of no others. In the case of Fig. 6, as compared with Fig. 1, the spacing is halved when the slit is parallel to the horizontal or the vertical line of the figure, and also whenever the grating is so placed that the parallel to the slit passing through one of the corners of a cell does not pass through the center of that or any other cell, as, for example, if EO but not EK is parallel to the slit. It is therefore easy to distinguish each of the four modes.

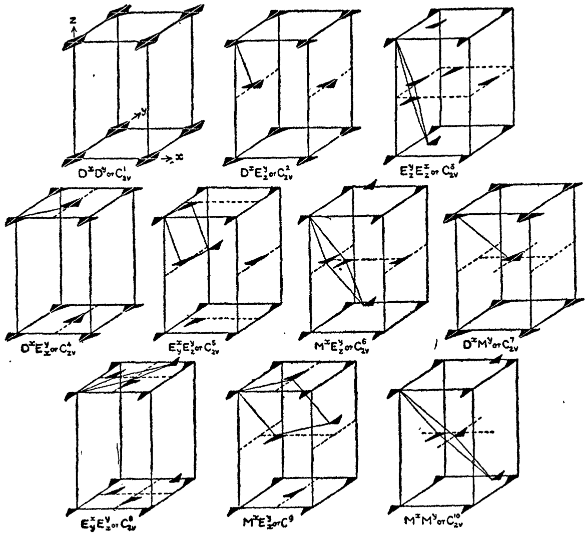

Fig 7.

Similar methods are applicable to the three-dimensional crystal. If, for example, we consider the case of C^2_{2v} or $D^xE^y_z$ we can show that, whereas in general the spacings of planes are such as are proper to a cell of the dimensions and form drawn in the figure, all planes of the form $lx/a + mz/c =$ an integer, show halved spacings, unless l is odd and m is even: which is sufficient identification of the mode of arrangement. The symbols a and c denote edges of the cell.

If we follow this line of reasoning through all the thirty-two classes, we end, of course, with the discovery of 230 modes which are known to exist: and with the identification marks of each, with certain qualifications. These last are of two kinds. One of them is general in nature and is a consequence of the fact that the X-rays can measure only the distance between two like points in neighboring cells, say A and B. But they do not indicate any difference that may exist between AB and BA. If such a difference exists it may be expected to show in the external characteristics of the cell, giving it polarity. A good example is to be found in zinc blende. Layers of zinc and of sulphur atoms alternate with one another as in Fig. 9, all of them being perpendicular to a trigonal axis of the crystal. The distance between a zinc atom in the layer A to a zinc atom in the layer B is found without question by the X-ray method. Now we know from observation of the crystal that there is a difference between AB and BA: the crystal is polar. A crystal plate cut so that its faces are perpendicular to the axis shows different properties on its two sides: if heated, one face becomes positively and one negatively electrified. Whichever face we use in the X-ray spectrometer we

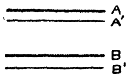

Fig 8

obtain the same value for the spacing, and we find ourselves unable to detect any difference between the two aspects by means of the spectrometer observations.

We may see this point in another way. Suppose that Fig. 9 represents a section of a crystal consisting of two kinds of atoms, indicated respectively by full and empty circles. The arrangement clearly has no symmetry about a vertical line in the plane of the paper. But if X-rays were incident from above, as shown, there would be equal reflections from the planes 11′ and 22′. If the incident rays were heterogeneous and a photographic plate were placed to receive the Laue reflections in the usual way, there would be a symmetry distribution of spots on either side of A, although there is no symmetry in the crystal to correspond.

It is only when we have taken other considerations into account and have determined the structure that we can establish the polarity of the crystal. We may take, for example, the fact that zinc blende is cubic, and therefore has four trigonal axes, a fact which we may discover from X-rays as well as from the external form. Also, the unit cell contains only one molecule of zinc sulphide, and may be drawn of the same form as in diamond: that is to say, its eight corners can consist of the six centers of cube faces and the two ends of a diagonal. If we put zinc atoms at the corners of the unit cell, the sulphur atom must lie either at the center of the unit cell or at the center of the regular tetrahedron formed by four of the corners of the cell: only by the adoption of one of these alternatives do we get the four trigonal axes. The former gives the rock-salt structure and is distinguished by the fact that the (100) and (110) spectra decrease regularly in intensity from lower to higher orders, whereas in the (111) spectrum the even orders are relatively greater than the odd. In the latter alternative the even orders of (100) are relatively greater than the odd, (110) spectra are normal and the second order of the (111) is abnormally small. It is easy to distinguish between the two cases. The latter is adopted by zinc blende. Each atom has the symmetry of Class 31, to which the crystal belongs, there being only one atom of each in the unit cell.

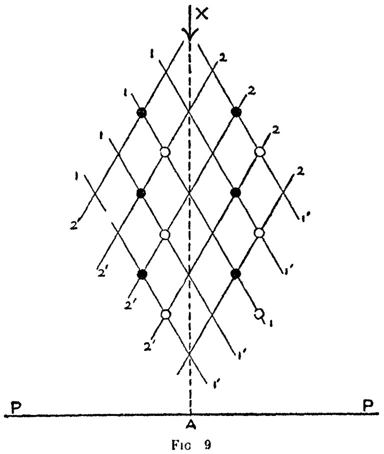

Fig 9

In this case we are successful from X-ray measurements alone in determining the mode of arrangement of the crystal, although the crystal is polar and the X-rays can not detect polarity directly. We have been able to determine the structure completely, and the polarity then appears.

When the determination of structure can not be carried far enough, the X-rays may fail to decide between the presence and absence of polarity. For example, resorcinol is an orthorhombic hemihedral crystal: this is known by its external form. The X-rays show that, this being so, its internal arrangement must be that of M^xM^y or C^{10}_{2v} in Fig. 7. If we had no help from the study of external form, or from any other source, we should not be able to decide between C^{10}_{2v} and the more symmetrical mode known as Q^{12}_h : the symmetry of the latter is obtained by adding a center of symmetry to the elements of symmetry possessed by C^{10}_{2v} : that is to say, by removing the polarity of the crystal. As a matter of fact, the external form of resorcinol clearly shows polarity: or, if we could be sure that the molecule had no symmetry, we could infer that the crystal was unsymmetrical about the *xy* plane, there being only four molecules in the cell and all these being wanted to give the symmetry observed by X-rays. Thus there are cases where the X-rays can not decide between two modes, one of which can be derived from the other by the addition of a center of symmetry. As, however, the existence of a center of symmetry can generally be decided by other means—for example, by such means as I have described above in the case of zinc blende or of resorcinol—this incapacity of the X-ray method is of no great consequence.

The addition of a center of symmetry moves a structure from one class to another—Class 1 to Class 2, Class 31 to Class 32. Consequently, the X-ray methods are by themselves sometimes in doubt between two modes in different classes when they are rarely in doubt as to the mode within a class. It will readily be understood that the doubt as to class may be of far less importance than the doubt as to mode; though hitherto the former kind of difference has been given all the attention because it has been the only kind that could be observed. A very slight relative movement of the atoms would be sufficient to reduce the symmetry of the crystal from one class to another: but the change from one mode to another within the same class would mean a complete rearrangement of the molecules.

There are two cases in which the X-rays can not distinguish between two modes in the same class. These are Q^8 and Q^9 in the enantiomorphous class of the orthorhombic system, and T^3 and T^5 in the tetartohedral class of the cubic system. The ambiguity disappears, however, if there are only two molecules in the unit cell, when the former alternative is alone permissible in each case: it would disappear also in any case in which the structure could be determined completely by any other means.

It has been known for many years, thanks to the work of Fedorow, Schonflies and Barlow, that the 230 modes of arrangement represent all the possible forms of internal crystal structure. In each mode of arrangement there is a relative disposition of planes, axes and center of symmetry, which is characteristic of the mode, and the mode may be described in terms of these symmetries. This was the language used in the original work on the subject, and the term space group was used, instead of the term mode of arrangement, in reference to the particular group of symmetry planes, axes and center in space. When the subject is approached from the point of view of the X-ray worker, the language of the mode of arrangement has its special conveniences. A list of the 230 modes and of the X-ray tests for each mode has recently been published in the Transactions of the Royal Society by Astbury and Yardley. Lists of the same 230 space groups have already been published in different terms by writers on crystallography: recently a list by Wyckoff has been published by the Carnegie Institution of Washington, in which each space group is expressed in terms of the coordinates of the arrangement of points required to give each space group its special characteristics.

It may be of interest to look at these matters from a somewhat different point of view, which takes in the question of the permanence of the chemist's molecule when built into the solid structure.

In every crystal the unit can be divided into a certain number of parts, each of which has no symmetry of its own, but may be made to coincide with any other part by some combination of reflections, rotations and shifts. The number is always either one, two, three, four, six, eight, twelve, twenty-four or forty-eight. The division into 230 modes of arrangement refers to the arrangements of these parts. In the case of a crystal of the rock-salt type both the positive and negative portions of the cell can be so divided. Very often the part in question is the chemical molecule. For example, the cell of the monoclinic prismatic class can be divided into four such parts. The X-ray measurements show that the unit cell of benzoic acid which belongs to this class contains four molecules. Also they detect the existence of the four parts, and determine the mode of their arrangement. It is natural to make the assumption that each part is a molecule. This, it may be noted, involves the existence of right- and left-handed molecules, as built into the crystal.

Sometimes the division into parts involves the division of the molecule. The molecule then consists of two or three or more parts, and therefore possesses a corresponding symmetry. For example, the naphthalene molecule in the naphthalene crystal contains two parts, and has a center of symmetry. The molecule of FeS_2 in the crystal of iron pyrites consists of six parts, and has a center of symmetry and a trigonal axis. Each of the two atoms in the rock-salt cell, sodium and chlorine, has—that is to say, its relations to its neighbors have—forty-eight parts, and therefore the full symmetry of the crystal.

Much more rarely a part consists of more than one chemical molecule. So far a few instances have been met with. The "part" in the crystal cell of sulphur certainly contains two, perhaps more, atoms. Miss Yardley finds that the "part" in the fumaric acid crystal contains three, perhaps six, of the molecules as ordinarily defined $(COOH.CH:)_2$. In the cell of α-naphthylamin at least three molecules go to a part. The part has no symmetry, so that the molecules that compose it differ from each other in some way. These are really examples of polymerization in the crystal.

Is the grouping of the atoms in the molecule as displayed in chemical reactions maintained without change? When the first results of the new methods were published, with their determinations of diamond and rock-salt structure, there was some unnecessary alarm as to the apparent disappearance of the molecule. If there had been anything to suggest a complete disruption of all the alliances in the molecule, which had been so long and so successfully studied by the chemists, the alarm would have been justified. Atomic bonds would have been annoyingly variable and dependent on conditions, and we should have been put back to the starting point in the investigation of the solid. This condition of things appears, fortunately, to have no existence. The conclusions of chemistry are carried into the solid, with only such modifications as might reasonably be expected. Our new science is in full and close alliance with chemical science already established: it is in fact a constant and delightful experience to find some direct confirmation or illustration of an inference already drawn from other sources. So far as experience has to tell us, the chemical molecule generally takes its place as such in the crystal structure with little change.

To sum up, we are now able to replace the rough division into thirty-two by the finer division into 230. This is advancing a whole stage towards the final solution of the structure problem. We carry the analysis right up to the limits which can be foreseen by the mathematical investigation of the geometry of space. We require only a sufficient number of X-ray measurements: if these can be obtained, the crystal then—with certain additional information as to polarity—can be assigned to its particular mode or space group, with one or two exceptions as already noted. It may be that the structure of the crystal is so simple that having got so far the full solution is already in sight. In the vast majority of cases this is not so; we have only come to the end of the second stage of the work.

The first stage was complete when we had found the dimensions of the crystal unit cell: the second is completed when we know which of the 230 possible arrangements of molecules, or, in other words, space groups, the crystal structure follows.

If the structure of the crystal is not yet obvious—and in the great majority of cases this is far from being the case—we enter on a third stage, in which the mode of procedure is less stereotyped and more difficult, perhaps all the more interesting. We have now to find, if we can, the arrangement of the atoms within the cell, to which task the knowledge already gained is an indispensable though, it may be, a quite insufficient contribution.

As I have said already, the X-rays do not tell us directly the relative positions of the atoms within the unit cell. They have, however, much to tell us as to the relative intensities of the different orders of reflection by each plane, and these must depend on the atomic arrangements. It is to be admitted, however, that we are as yet unskilled in the interpretation of this evidence. We do not completely understand how varying conditions affect intensities of reflection, though we have learned a great deal through the work of W. L. Bragg, Darwin, Compton and others. And, of course, when the cell contains many molecules, their positions being as yet unknown and their separate contributions to the intensities in any case doubtful, the observations of intensity are very difficult to make use of, though they can be accurately measured. We can only avail ourselves of such bold indications as that a very strong reflection implies the location of many atom centers on or near the plane in question, particularly if there are higher orders: or we may find ourselves able to show that an especially strong second or third or other order implies the adoption of some particular alternative arrangement. A very interesting example of a general influence of form upon intensity is to be found in the reflections from the fatty acid layers which have been investigated by Muller and Shearer. The first, third and other odd orders are much more intense than the second, fourth and other even orders. A simple explanation is found in the fact that these long chains face opposite ways alternately, and that the number of scattering centers is distributed fairly evenly along their length. At the ends, however, the uniformity of distribution is interrupted; at one end, probably the carboxyl end, there is an excess per unit length; at the other, the methyl end, a deficiency. Thus we may say that the effect on an odd order of the spectrum due to a single layer, the thickness of a layer being twice the length of a molecule, contains a factor:

$$A \sin(\omega t - \alpha) - B \sin(\omega t - \alpha - \overline{2n + 1\pi}) = (A + B) \sin(\omega t - \alpha).$$

The factor for an even order is:

$$(A - B) \sin(\omega t - \alpha).$$

If at both ends there had been an excess of scattering centers, we should have found the even orders stronger than the odd: the effect we find, for example, in the (111) planes of rock-salt. In the case of the simpler inorganic crystals like rock-salt, diamond and so on, intensity observations are conclusive as to the structure: in the case of iron pyrites or calcite they are very nearly so. But in the case of quartz, where the cell contains nine atoms, still more in the case of an organic compound, they do not carry us very far. We hope that greater experience will give us in the future the power of using them to better advantage.

In what other direction then shall we look for additional means of approaching more nearly to the final solution of the problem of structure?

The answer to this question will take account of all the store of physical and chemical knowledge which we already possess. Having solved, wholly or in great part, the structure of some of the simpler crystals, and being able to proceed in all cases, even of the most complicated crystals, to the determination of the number of molecules in the cell, and of their mode of arrangement, we must try to correlate what we have found with the properties of the crystal. By that means we shall become gradually more certain of the general connection between the structure and its physical and chemical properties; we shall become able to settle further structural details in various cases, and so, by alternate and mutually supporting advances, we may hope to reach our goal.

Let us consider what is being done in this direction. First of all there is the question of the distribution of the atoms in space. Given so many atoms, to be packed into a cell of known dimensions, what information have we as to the space that each must occupy? The answer to the question can not be simple, because we may not expect that the atoms are always to be treated as spheres, still less as spheres of constant radius. It is as generally difficult to state the distance between one atom and another as to state the distance between a table and a chair. Nevertheless, the atom-radius is a useful conception, especially when its dependence on the nature of combination is taken into account. The question has been considered by W. L. Bragg, Wyckoff, Davey and others, and it appears that an atom does make a definite contribution to the distance between its center—when it can be assumed to have a center—and the center of a neighbor, so long as the nature of the bond remains the same. This is a valuable contribution to the study of structure. It is proved by the examination of simple structures like those of the alkaline halides, and we may assume its reliability in our attempt on more complicated problems. And, of course, it is interesting from the point of view of atomic structure itself and atomic linkages.

The radius seems to depend on the tightness of the bond as in bismuth or in graphite, where there are two kinds of bonding, and the plane of cleavage cuts across all the longer distances from center to center. In calcium fluoride the centers of calcium atoms are closer together than they are in the metal itself in spite of the interposition of the fluorine atoms; and in calcium oxide they are still closer. The change in the type of the bonding has altered the value of the radius.

There is also the very interesting but still more unsettled question of the mutual orientation of the bonds between an atom and its neighbors. It is, of course, the carbon atom which is the occasion of this problem in its most pressing form. In the diamond the exactly tetrahedral arrangements of bonds is associated with great rigidity, which implies great stiffness of orientation. The analysis of the structure of graphite has lately been carried by Bernal to a stage very near completion, but the only point in any doubt is unfortunately the very one as to which certainty would be welcome. Has the great weakening of one bond interfered with the relative orientation of the other three? Debye thought that the structure was trigonal, and that the atoms were arranged in layers which were like the layers of diamond, except that they were flattened out without a sideways extension of the network. This would involve a closer approach of carbon atom centers from 1·54 A. U. to 1·45 A. U.; against which no obvious objection can be offered, but it would be interesting to know how it happened. Hull believed the structure to be hexagonal, and that the layers remained as in the diamond. Bernal, having found some good graphite crystals to which the single crystal methods could be applied, finds that Hull is correct as to the hexagonal structure, but inclines to the belief that the layer is flattened. In the latter case, we must suppose that the carbon atom has three very strong bonds almost coplanar with the carbon and one weak bond at right angles to this plane.

The question arises in another form in the investigations of the long carbon chains by Piper and others, and especially by Muller and Shearer. If the chains are formed by the linking of carbon atoms together in such a way that the junctions of one atom to its two carbon neighbors are inclined to one another at the tetrahedral angle of 109°28′, as in diamond, then there are three possible forms of chain. In one of them, each two carbon atoms imply an increase of 2.00 A. U. in the length of the chain, and, in a second, an increase of 2.44 A. U. In these two cases the carbon atoms of a chain can lie in a plane. With one exception, all the cases examined show one or other of these two rates of increase. The third form of chain is a spiral, for which the growth of each single atom added is 1.12. In one case this rate of increase is found to hold: it is that in which the chain contains a benzene ring. This agreement between calculation and experiment shows with some force that the relative orientation of the bonds is maintained. Even when two or four hydrogens are stripped from the chain at various points, so as to leave a double or triple bond between consecutive carbon atoms, to adopt the ordinary chemical language and theory, no measurable change is found in the length of the chain. This does not mean that there is no change in the distance between neighbors: such a change would be small and might escape detection. But it does mean that there is no great change in the general straightness of the chain, such as might be expected from any large change in the mutual orientation of the bonds between the carbon atom and its neighbors.

In calcite the three oxygens which surround a carbon atom must lie in one plane. It is supposed, however, that in this case the bonds are electrostatic: the carbon atom has lost its four valency electrons, and with them its powers of tetrahedral orientation.

Now if we can discover the extent to which an orientation is maintained under different conditions we are provided with one more guiding principle in our attempt to discover the structure of the crystal which contains carbon atoms. And, of course, the organic compounds center round the carbon atom and its tetrahedral structure.

The question of orientation in respect to other atoms is more obscure, but it is clearly one of importance. There must be some reason why ice has such an open structure, and here the oxygen atom is largely concerned. In the ruby the oxygen atom has no plane of symmetry in relation to its neighbors. In organic substances the great emptiness of the structure implies that atoms are attached to one another at points which have definite positions on the surfaces of the atoms and are limited in number. And, generally speaking, the consideration of organic crystal structure is against any idea that atoms and molecules are to be treated as spheres surrounded by uniform fields of electric force, except in certain cases where by loss or gain of electrons an atom has been reduced to the outer form of one of the rare gases. They must have highly irregular fields, having forms which more or less resist any change. The weak bonds which hold molecule to molecule in the organic substance are not due to electron sharing as in diamond, or to ionization as in rock-salt, but to an intermingling of stray fields belonging to definite positions on the surfaces of the molecules.

Our attempt to discover the effect of orientation is part of a general attempt to discover the field of force of the atom, which is naturally a very difficult matter. But if we can learn only a few rules, even empirical rules, we are so much the further on our way.

Yet another obvious and most important source from which help may be obtained is to be found in chemistry itself. Although the chemist has had no means until now of measuring distances and angles, he has been able to build up a wonderful edifice of position chemistry. An atom A of a molecule is certainly linked, it may be to B, and not to C; or again, of a number of atoms of the same nature and contained in the same molecule, so many must be alike, and so many may be different.

The chemist has, for example, come to the conclusion that the naphthalene molecule is a double benzene ring, and the anthracene a triple benzene ring. The X-ray observations show that one of the sides of the unit cell of the latter crystal is longer by 2·5 A. U. than the corresponding side of the other, all other dimensions of the two cells being very nearly the same. The width of the hexagonal ring in the diamond is 2·5 A. U., so that on the one hand the chemical evidence suggests that the length of the molecule is parallel to that edge of the two cells which shows differing values, and on the other the X-ray conclusions give material support to the chemical view. Let us take another example from basic beryllium acetate $Be_4O(C_2H_3O_2)_6$. The substance is remarkable for the ease with which it sublimes into a vapor consisting of whole molecules, from which we may infer that the molecule does not suffer much change in the process. The relative positions and mutual alliances of the atoms are nearly the same when the molecule is free as when it is built into the solid. From the X-ray evidence we learn that the molecule has four intersecting trigonal axes. We must place the unique oxygen at the center of a regular tetrahedron, and the four beryllium atoms at its corners. Each of the six acetate groups must be associated with one of the tetrahedron edges, and in such a way that the four trigonal axes are maintained. This necessitates, as crystallographic theory shows, the existence of a dyad axis through the middle points of each pair of opposite edges of the tetrahedron. The $C_2H_3O_2$ groups must be added so as not to interfere with the existence of these axes. If they are placed correctly for the trigonal axes, each of them has a dyad axis of the kind mentioned. All this agrees with the chemical evidence as partly stated in the formula, which implies:

(1) That there is one oxygen differently situated to the rest.

(2) That the four beryllium atoms are all alike.

(3) That the acetate groups are all alike.

Further, chemists would say that the carbon atoms are not alike; in that case, they must both lie on the dyad axis, since if they did not they would necessarily be symmetrically placed with respect to that axis and would be equivalent. On the other hand, the oxygen atoms in the acetate group can not lie on the axis if, as is probable, they are equivalent to one another. They must be placed symmetrically with respect to the dyad axis. As to the hydrogens, we must assume either that they do not count, which is not at all unlikely, or that they are not all alike. It is impossible to place eighteen hydrogen atoms so that the group has four intersecting trigonal axes and that every hydrogen is like every other. The molecule has no plane of symmetry, the fault lying with the oxygens. It could not be due to the hydrogens because there are marked differences in the intensities of reflection of pairs of planes, which differences would not exist if there were planes of symmetry, and would be small if due to dissymmetry in the positions of hydrogens only. It is by reasoning along such lines as these that X-ray evidence and chemical evidence can help each other. Many other instances might be given; indeed, no complex crystal can be studied with success without calling in the assistance of chemical arguments.

A fourth example of the connection between arrangement and properties is to be found in the recent work by W. L. Bragg on the indices of refraction of crystals. It has been found possible to calculate the indices of refraction of calcite, given the dielectric capacities of calcium, carbon and oxygen atoms separately. The difference between the two principal refraction indices is almost entirely due to a difference between the dielectric capacities of a set of three oxygen atoms, at equal distances from one another, when placed:

(1) So that the plane in which they lie contains the direction of the field.

(2) So that this plane is perpendicular to the field.

If we are able to calculate the refractive indices on these data, then it must be possible to find conditions governing the arrangement of the atoms, when we know the composition of the crystal and its refractive indices. For instance, the near equality of the refractive indices of potassium sulphate implies that the dielectric capacity of the SO_4 group is much the same in all directions, and this is in agreement with the hypothesis that the oxygen atoms are grouped in some sort of tetrahedral fashion about the sulphur atom.

There are still other connections between structure and properties which we begin to understand, and can use in proportion to our understanding. The cleavage plane, and the occurrence of certain faces in preference to others are connected with the nature of the bonds and the size of the spacings. We are not surprised to find that in bismuth or graphite or naphthalene the cleavage plane cuts across the ties which we should expect to be the weakest of those that bind the molecules together; or again, that natural faces follow the planes that are richest in atoms or molecules and may be assumed to contain relatively large numbers of linkages. In naphthalene the cleavage plane passes between the ends of the molecules, where the β hydrogens are, and where there is a deficiency in the number of scattering centers, as the X-rays indicate by the strengths of several orders of the (001) reflection. The other faces found on the crystal cut across the ties at the positions of the α hydrogens.

There are many other connections between the structure and other properties of a substance, such as dielectric capacity, rigidity and compressibility, conductivity both thermal and electric, magnetic constants. In fact, the only properties of solid bodies which are not directly and obviously related to crystal structure are those, few in number, that depend on atomic characteristics alone, such as weight; and the absorption coefficients for α, β, γ and X rays, all the rays which involve high quantum energies. With few exceptions every aspect of the behavior of a solid substance depends on the mode of arrangement of its atoms and molecules. We have, therefore, an immense field of research before us, into which the X-ray methods have provided an unexpected and welcome entrance.

They tell us directly, as I have said, the number of molecules in the crystal unit cell, and the mode of their arrangement with such determination of lengths and angles as are required to define the mode of arrangement in full. They leave us then to ally our new knowledge to all that we possess already as to the physical and chemical properties of substances. By this comparison we hope in the end to determine the position of every atom, and explain its influence through its nature and position upon the properties of the substance. It is the chemistry of the solid that comes into view, richer in its variety even than the chemistry we have studied for the past century, and possessing an importance which is obvious to us all. Every side of scientific activity takes part in this advance, for all sciences are concerned with the behavior of matter.

W. H. Bragg

REMINISCENCES OF LORD KELVIN

On the hundredth anniversary of the birth of Lord Kelvin, celebrated by the scientific world, it may be permitted for the writer to record personal experiences of his kindness and impressions of his interesting personality.

When in England among the scientists in the late eighties of the last century, it was most gratifying to receive from Lord Rayleigh a letter of introduction to Sir William Thomson. When Lord Rayleigh came to America to attend a meeting of the British Association in Canada, he visited the laboratories of Wellesley College and was graciously disposed to put in the way of the first woman undertaking a department of physics in a college access to the best in her subject in England.

Though it was summer and vacation in the University of Glasgow, there was received from Lady Thomson a cordial letter, stating that she and Sir William were to come up from their country place in Ayrshire to assist in doing the honors in the university for the British Medical Association, then in session. She enclosed a card of invitation to the reception to be given to the medical men and asked me to come at nine o'clock to go with them.

At the appointed hour I was welcomed by our host, a man of quiet, almost quaint appearance and manner, but shining from his kind eyes a winning friendliness. Lady Thomson, in garnet velvet, tall and handsome, quite resplendent with pearls and diamonds, stood beside him. The reception was in the stately Gothic senate chamber, lately given to the university by the Marquis of Bute. All the faculty in academic dress and the ladies were gathered on the daïs.

After being presented to Principal Caird and others, from a point of vantage amid the brilliant group, one saw all Glasgow, much of Edinburgh and the British doctors file past.

It was evident that Lady Thomson was the acknowledged social leader, and that Sir William was the one whom all the guests were most eager to meet.

The next day several memorable hours were spent