The Structure of Crystals

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Few discoveries have had a more far-reaching effect than that made by von Laue in 1912. Not only did it lead to a great increase in knowledge of the structure of atoms, but it also laid the foundation of a new branch of science—structural crystallography. The experiment which formed the basis of von Laue's discovery was a perfectly simple one. A narrow beam of X-rays defined by pinholes in lead sheets was allowed to pass through a thin slice of crystal placed a short distance in front of a photographic plate. (Fig. 1.)

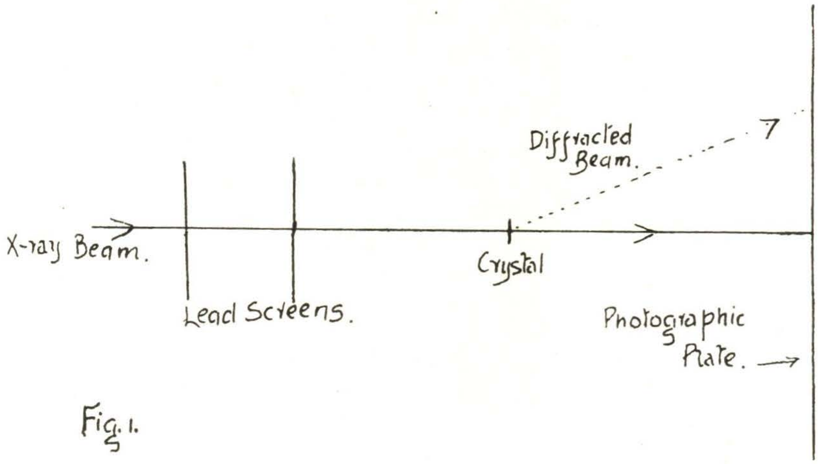

Fig. 1.

In addition to a central spot formed where the original beam struck the photographic plate, a whole array of symmetrically arranged smaller spots was found (see Fig. 2). The formation of these additional spots, produced by what are known as diffracted X-ray beams, established two facts of fundamental importance :

(1) The wave-like character of X-rays.

(2) The regular arrangement of atoms in a crystal.

It would be impossible, in a short space, to describe how this and similar experiments have been used to determine the arrangement of atoms in crystals. It will be sufficient to point out that X-rays have virtually provided science with a super microscope. Of course no such instrument as an X-ray microscope for viewing atoms directly exists ; nevertheless the results achieved by studying the diffraction of X-rays by crystals are equivalent to those that could be obtained if it were possible to take microphotographs of a 100,000,000 diameters magnification.

The atomic arrangements in many hundreds of crystals have now been worked out. These arrangements in themselves are perhaps not so interesting as their correlation with some of the more important physical properties of crystals such as strength, hardness and fusibility. Therefore in describing the atomic arrangements

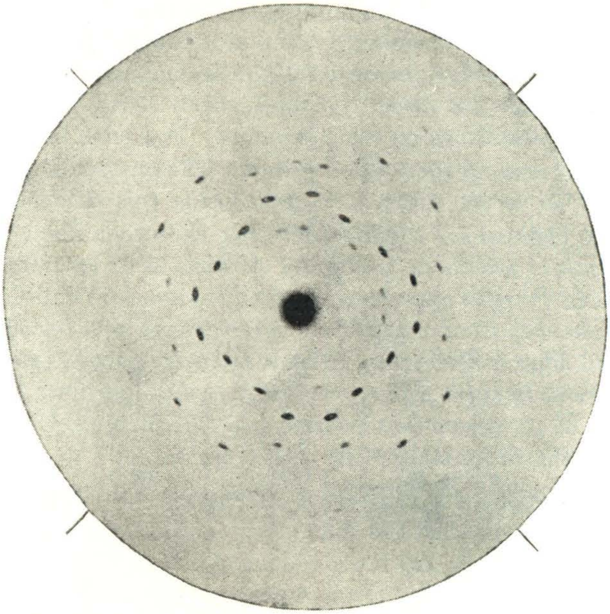

FIG. 2.
Laue photograph of zinc sulphide.

in a few familiar crystals, some attempt will be made to show how structure and physical properties are related. The term structure is used here to include both atomic arrangement and the nature of the linking of atom to atom which prevails in a given crystal.

SALT—SODIUM CHLORIDE.

Salt, one of the first crystals to be completely analysed by the X-ray method, proved to have a very simple structure. From Fig. 3 (*a*) it can be seen that the structure is a close packed arrangement of sodium and chlorine atoms.

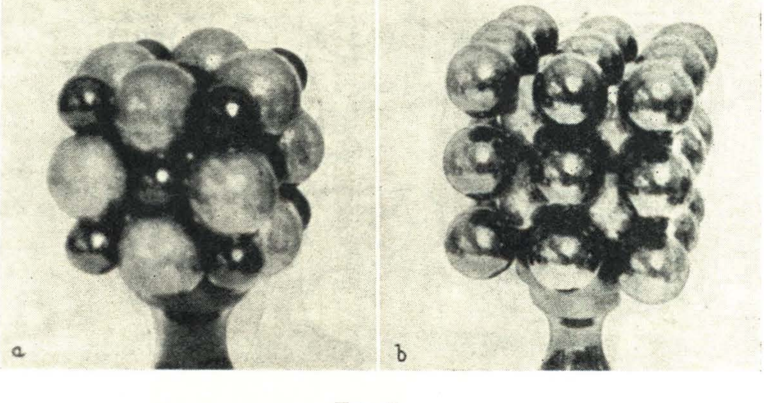

FIG. 3.
(*a*) Sodium chloride. Smaller spheres represent sodium ions.
(*b*) Cesium chloride. The darker spheres represent cesium ions.

Just as a wallpaper design is made up by the repetition of a small unit pattern, so a crystal is made up by the repetition of a unit three-dimensional pattern or cell, and it is this unit cell which is represented in the accompanying diagram. The atoms in salt are ionized, a fact not directly deduced from X-ray diffraction experiments, but nevertheless well established on other grounds. It is considered that the electrical charges on the atoms arise in the following way : The outermost electron of a neutral sodium atom is rather loosely held, and upon losing this electron the sodium atom becomes positively charged—a sodium ion. On the other hand a neutral chlorine atom has a tendency to attach an additional electron to its structure to give it a unit negative charge. In salt the oppositely charged sodium and chlorine ions formed by the transfer of an electron from one atom to the other are held together by the electrostatic attraction of opposite charges. These attractive forces manifest themselves equally in all directions in space around each ion, so that no chlorine ion is attached to any particular one of its six nearest sodium ion neighbours. One cannot therefore speak of a sodium chloride molecule in a salt crystal.

Salt is a good example of a very large class of crystals known as ionic crystals. Since salt is completely ionized in the solid state, it is not surprising that molten salt and solutions of salt in water are both good conductors of electric current. As a general rule ionic crystals are fairly hard and possess fairly high melting points ranging from roughly 500° to temperatures in the neighbourhood of 2000° C. Many other binary compounds of the type AX, such as MgO and CaO, are built on the sodium chloride pattern, but whether any particular compound will assume this arrangement depends largely on the relative sizes of the two ions. Where the oppositely charged ions are more nearly the same size than they are in salt, the different type of arrangement shown in Fig. 3 (*b*) results.

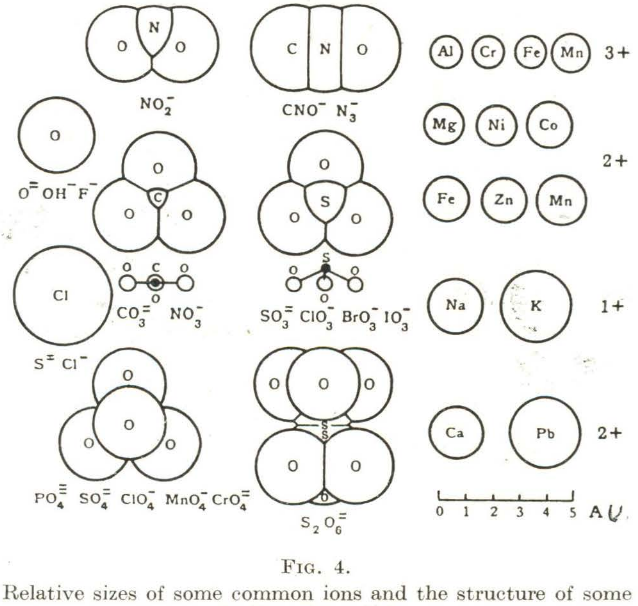

FIG. 4.

Relative sizes of some common ions and the structure of some simple acid radicles.

In ionic crystals atoms behave as impenetrable spheres whose diameters, thanks to X-ray measurements, are known to a high degree of accuracy. Fig. 4 gives some idea of the relative sizes of a few common ions, both simple and complex. It is worth noting that in general the larger the charge on a positive ion, the smaller its size; the converse holds for negative ions.

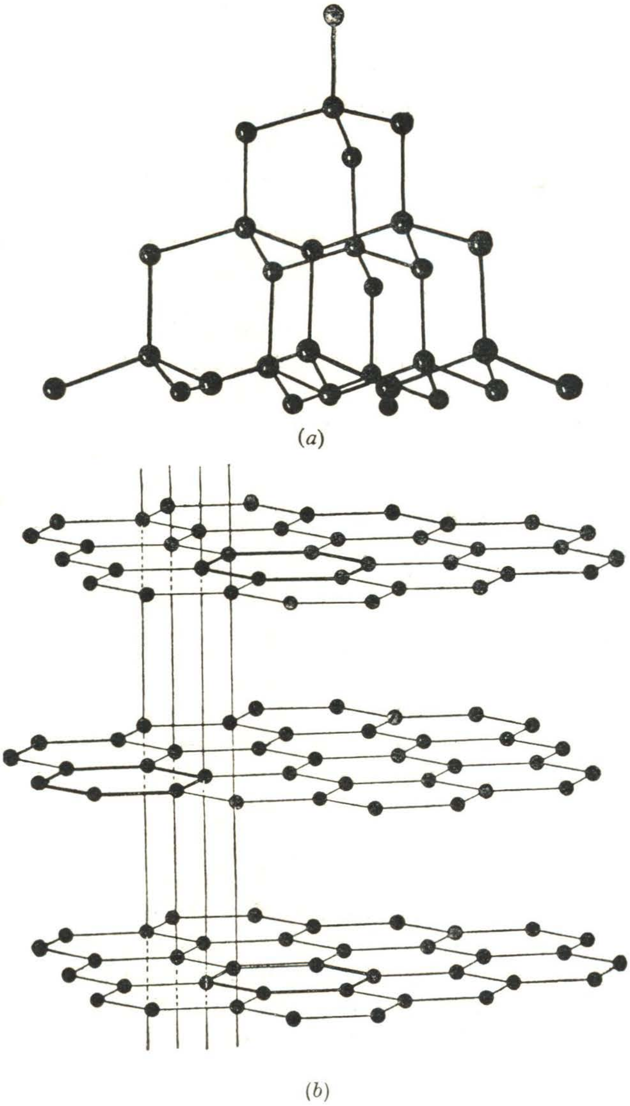

Fig. 5.
The structures of diamond and graphite.
(*a*) Diamond. (*b*) Graphite.

It is well known that metals like silver and gold, nickel and magnesium, etc., often occur together in nature. An important, but by no means the only factor, determining this association, is without doubt the very close resemblance in atomic dimensions of these pairs of metals. Nickel atoms can, for example, replace those of magnesium in certain magnesium compounds without in any way disturbing the general arrangement of atoms.

DIAMOND.

The simple structure of diamond [Fig. 5 (*a*)] is a good example of another very important type of crystal. The essential feature of diamond is that every carbon atom is bound by powerful forces to four others surrounding it equally in space (or, more accurately, tetrahedrally arranged). The links formed by sharing of electron pairs (covalent links) are definitely directed in space, and result in a certain amount of merging of the electronic structures of the atoms. Some idea of the extent of the merging may be gained by reference to structure of the carbonate ion ($CO_3^{=}$) shown in Fig. 4. Shared electron pair bonds link carbon to oxygen atoms in the $CO_3^{=}$ ion. It should be pointed out that in Fig. 5 (*a*) and (*b*) the centres only of carbon atoms are represented, since it would confuse the diagram to attempt to show the intermingling of the outer structures of the atoms. Instead of speaking of atomic diameters in diamond (and similar crystals), it is customary to refer to interatomic or internuclear distance. In diamond, for example, the internuclear distance, *C—C*, is 1·54 Å.U. (1 Å.U. $=10^{-8}$ cm.). Since the linking of atom to atom extends throughout the whole structure, a diamond may be regarded as a single molecule. In point of fact, structures of which diamond is typical are referred to as "giant molecules". The secret of diamond's hardness is to be found in this feature of its structure. In order to break a diamond the powerful covalent links between carbon atoms must be ruptured. Extreme hardness and infusibility characterise crystals of the giant molecule type. Although its atomic arrangement is as yet unknown, it can be safely predicted that boron, which is both difficult to fuse and extremely hard, also has a giant molecule structure. Carborundum, which comes fourth on the list of substances arranged in order of hardness, possesses a giant molecule structure very similar to diamond.

The extraordinary differences between the physical properties of diamond and graphite, the other allotropic form of carbon, are associated with important differences in atomic arrangement. It is not suggested that the differences in the two forms are due entirely to just a difference of atomic arrangement; the matter goes deeper than that. The change in atomic pattern is accompanied by important changes in the linking of atom to atom. As Fig. 5 (*b*) indicates, the carbon atoms in graphite are arranged in widely separated layers of hexagonal networks. Here again atomic centres only are represented. Within the layers covalent links are effective in linking carbon atoms, but between the layers only very weak forces come into play. It is difficult to explain precisely the nature of these inter-layer forces. Suffice it to say that this weak bonding of layer to layer accounts for the readiness with which graphite cleaves—in other words, for its flakiness and lubricating properties. The layers in graphite may be regarded as giant two-dimensional molecules. Other flaky substances like boric acid and mica have somewhat similar layer-like atomic arrangement. On the other hand fibrous materials like fix and asbestos owe their characteristic structure to giant chain or string-like molecules which extend throughout the crystal.

SULPHUR.

The structure of rhombic sulphur, one of the last of the elements to be analysed, affords a good example of a molecular crystal. Molecular weight measurements show that in the vapour condition and in solution sulphur molecules contain eight atoms. Sulphur molecules as such can be recognised in rhombic sulphur. There they take the form of eight membered rings, the atoms in which are joined together by strong covalent links. Without the aid of elaborate diagrams or models, it is not easy to show how the ring-shaped sulphur molecules are packed together in the crystal. But the important point is that when so packed together the molecules are held together by weak intermolecular or van der Waal's forces already referred to in connection with graphite. To melt a sulphur crystal it is necessary only to overcome the weak intermolecular attraction, as the molecules themselves are left intact. Consequently sulphur crystals are soft and easy to melt (M.P. 114°). Softness and low melting point are general characteristics of molecular crystals. As further examples of molecular crystals, one may mention iodine, camphor and naphthalene ; the simplest of these, iodine crystals, contain closely stacked diatomic, dumb-bell-shaped molecules. Sulphur molecules retain their ring shape in the pale yellow melt formed just after melting. As the temperature is raised the melt becomes darker and, contrary to the general rule, it becomes more viscous. It has been suggested that this unusual increase in viscosity with increase of temperature is due to the fact that the rings break open to form long thread-like molecules. With regard to the monoclinic variety of sulphur formed during the solidification of a sulphur melt, nothing is yet known about its precise crystal structure, but it is safe to predict that it will differ from the orthorhombic variety only in the nature of the stacking together of the molecules. Between the two varieties of sulphur crystals there is not the profound difference of structure noted in the case of graphite and diamond.