

*Relation of the crystal-structure of some carbon compounds to those of graphite and diamond.*¹

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IT must be our aim to correlate the external appearance of a crystal, and its physical properties also, with the arrangement of the atoms inside and the forces that join the atoms together. We might hope to gain so much knowledge on these points that, given a certain set of atoms, it would become possible to anticipate the design of their arrangement and to describe all the characteristics of the crystalline substance as consequences. The analysis of crystals by means of X-rays has given us a little help along this road, and we begin to see certain principles in broad outline.

In the first place, we now divide the forces between atom and atom into three distinct classes.

In the second place, we find that the distance between the centre of an atom to the centre of a neighbour is a definite quantity persisting from crystal to crystal. It may, however, have more than one value depending on the nature of the bonding between the atoms.

To illustrate these statements we take a few examples. The diamond is an example of crystallization in which the only bonding is the most powerful of the three kinds mentioned above. According to modern ideas the strength of the forces which bind the atoms together in this particular way is connected with a sharing of electrons. The carbon atom lacks four electrons to complete the second 'electron shell', and it achieves its full complement by holding a pair of electrons in common with each of its four neighbours. Bonding of this kind takes place in general between atoms which require only a small number of electrons to complete a shell. Whether or no electron-sharing correctly describes the process is not of immediate consequence. The kind of bonding which the name describes certainly exists, and the explanation given by the modern theory so far fits the facts very well. The whole of the

¹ Fuller details with diagrams are given in a Presidential Address to the Physical Society: Sir W. H. Bragg, 'The structure of organic crystals.' Proc. Phys. Soc., 1921, vol. 34, pp. 33-50.

diamond, no matter what its size, is really one molecule. Combination of this kind occurs in other crystals such as carborundum or silicon; and, in addition, is often the basis of the formation of groups of atoms which enter into crystal formation as separate entities: for example, as in the case of the CO_3 of calcite, or the S_2 of pyrites, or the C_2 of calcium carbide.

The second type of force is brought into existence when an atom which requires one or two electrons to complete its shell derives them from atoms of electro-positive character in which the one or two electrons which form the commencement of a new shell are easily removed. Crystals of polar compounds are bound together in this way. The molecules are completely dissociated, each into positive and negative portions, and the rule of formation is that each ion is surrounded by ions of the other kind as neighbours. In rock-salt and isomorphous crystals each positive is surrounded by six neighbours and vice versa. In calcium fluoride the positive metal is surrounded by eight fluorine and each fluorine by four metal atoms. Another two to one arrangement is shown in ordinary ice, where each oxygen is surrounded by four hydrogens, and each hydrogen has two oxygens as neighbours. In the ruby, the aluminium has six oxygen neighbours and the oxygen has four aluminium neighbours. It is true that in the ruby the two aluminium atoms appear to be in contact, but it would seem to be against their will: they are driven together by the mutual repulsion of oxygen atoms. In the crystal of senarmontite the arrangement is different. The antimony atoms of senarmontite are arranged in a face-centred lattice and completely separated from each other. Of the eight small cubes into which the cubic lattice can be divided, six are occupied by oxygens. In the spinel crystals the divalent metal is surrounded by four oxygen neighbours and the trivalent by six. In all these polar cases the solid is completely dissociated.

We also find crystals in which two types of bonding exist at the same time. For example, in calcite the CO_3 is tied together by means of electron-sharing, but as a whole it is an ion, and having borrowed two electrons from the calcium draws round it six calcium neighbours, just as the chlorine in rock-salt gathers six neighbours of sodium. In bismuth and antimony, whose structure was examined independently by James and Tunstall and by Ogg, the bismuth atoms are not equally distant from all their neighbours. There is a puckered sheet of atoms parallel to the plane of cleavage in which the atoms are tied together, in all probability, by electron-sharing, and the distance between centre and

centre is nearly 2.9 \AA.U. But the distance from an atom in one layer to its nearest neighbour in the next layer is 3.3 and the binding forces are much weaker, as is shown by the position of the cleavage-plane. Perhaps this is a close parallel to the case of graphite in which layers of carbon atoms are joined, layer to layer, by comparatively weak forces, while in each layer the atoms are tied as tightly as in the diamond. The parallelism is strengthened by the fact that the expansion with heat along the axis is greater than in the perpendicular direction. The difference is very great in the case of graphite. Mr. Backhurst has found a total expansion of 3 per cent. for a rise of 900° C.

The third type of bonding is most clearly shown in crystals of organic substances. It has been found that in all probability the benzene single ring and naphthalene double rings persist in organic substances as definite structures having invariable size and form. This may be expected since the hexagonal ring is found to have survived the change from diamond to graphite and should, therefore, survive the further break-up of the graphite sheets into molecules founded of one or more rings. The dimensions of a ring can be given in Ångström units. The unit cell of an organic crystal can be determined by X-ray methods, and it becomes possible to fit together into the assigned space a molecular structure of which the rings are the basis. The structures are always very light in character and it is obvious that this must be so. The separate atom of carbon or even of hydrogen, assuming the usual values for size and weight, must have, so to speak, specific gravities very much greater than unity. If a structure such as that of naphthalene is to weigh little more than water, the atoms must be joined together in some very open design. But, while the atoms in the molecule are so tightly joined together that the molecule retains its shape, the forces that join one molecule to the next are weak. There is no electron-sharing, neither is there any electrical separation into ions. The forces may perhaps be classed as weak external fields due to uneven distribution of positive and negative electricities. They are exerted at rather large distances and are very local in character. One molecule attaches itself to the next at different points in a manner limited by the strictest geometrical considerations. It is due to all these facts taken together that there exists such a multiplicity of precise forms, although the ultimate constituents are atoms of carbon, oxygen, hydrogen, and very little besides. The weakness of the forces is shown by the softness of the materials and by the low temperatures at which they pass from solid to liquid and liquid to gas.