

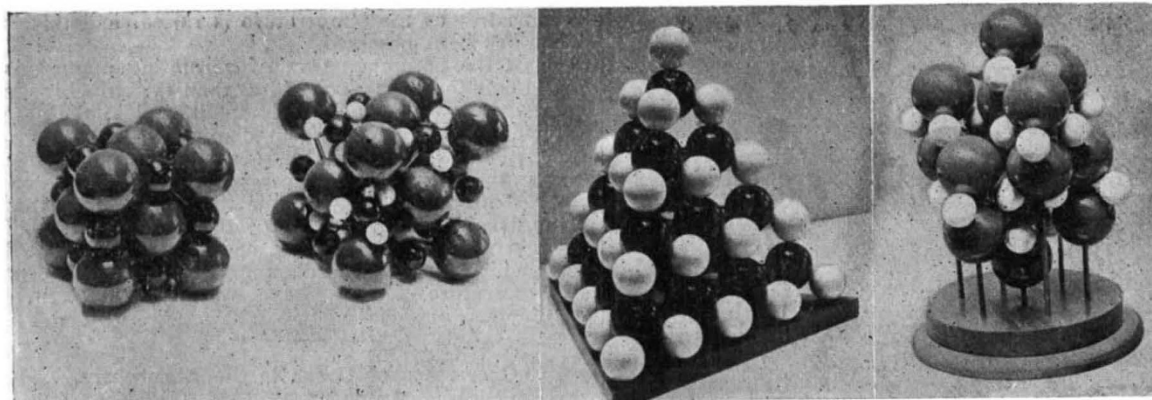
Crystal Structure.¹

By PROF. W. L. BRAGG.

THE arrangement of the atoms in many of the simpler crystalline forms has now been determined by X-ray analysis. In 1912 Laue published his classical research on the diffraction of X-rays by crystals, and the investigations thus initiated have immensely increased our knowledge of the nature of X-rays, of crystal structure, and of the structure of the atom. Several methods of analysing crystal structure have been used. Laue passed a composite beam of X-rays, consisting of radiations of all wave-lengths over a continuous range, through a thin plate of crystal, and he recorded the diffracted beams by allowing them to fall on a photographic plate. The results he obtained were too complex to admit of ready interpretation, and a simpler method was realised in the X-ray spectrometer devised by W. H.

In potassium chloride each potassium atom is symmetrically surrounded by six chlorine atoms, each chlorine atom by six potassium atoms. The atoms cannot be displaced from their positions without destroying the symmetry of the crystal structure; they are therefore fixed by symmetry alone. Such a crystal is analysed very simply. We have only to choose between various alternative arrangements, each quite determinate, in seeking an explanation of the observed diffraction effects.

When the symmetry does not fix the exact positions of the atoms, the analysis is more difficult. In such cases atoms may occupy any position along some axis or in some plane of the crystal structure, and yet be in accord with the symmetry provided the other atoms of the same kind are



Potassium chloride, KCl.

Calcium carbonate, calcite, CaCO_3 .

Zinc sulphide, zinblende, ZnS .

Aluminium oxide, ruby, Al_2O_3 .

FIG. 1

Bragg, in which monochromatic X-rays are reflected from individual crystal faces. In the course of a series of experiments in which the author took part, the structures of a number of crystals such as rock-salt, the diamond, fluor, zinblende, pyrites, and calcite were determined. New fields were opened up by the method of analysis initiated by Debye and Scherrer, in which a beam of monochromatic X-rays is passed through a mass of finely powdered crystalline material, and the resulting "haloes" recorded photographically. Hull has extended this work to a number of substances unobtainable as large single crystals such as must be used in the X-ray spectrometer. By these methods a wide range of crystal forms has been surveyed.

Some crystalline structures possess symmetry of a high order, examples being potassium chloride and zinblende, models of which are shown in Fig. 1. In such cases as these every atom occupies a symmetrical position in the crystal struc-

ture. In the structure of the ruby, Al_2O_3 (Fig. 1), the unit of which the structure is composed consists of a pair of aluminium atoms surrounded symmetrically by three oxygen atoms. The distance apart of the aluminium atoms along the axis joining their centres, and the distance of the oxygen atom from this axis, are both indeterminate in so far as the crystalline symmetry is concerned, and their exact values must be deduced by the X-ray analysis. It is these indeterminate parameters which make a crystalline structure complex.

The problem is simplified by regarding the atoms in a crystal as a set of spheres packed tightly together. This manner of regarding the structure was proposed in 1907 by Barlow and Pope, who assigned to the sphere representing an atom a volume proportional to its valency, and by packing these spheres together as closely as possible they obtained structures which accounted for crystal forms. We now know the structure of the crystals dealt with by Barlow and Pope,

¹ Discourse delivered at the Royal Institution on Friday, May 28.

and we know that it is in many cases not that predicted by the "valency volume" law. The law can be modified, however, so as to apply to the majority of crystals so far analysed. It may be shown that we can assign a definite diameter to the sphere representing the atom, a diameter characteristic of the element in question. Some atoms appear to occupy a small domain in a crystal structure, others a larger space. By finding the distances between the atomic centres in a number of crystals the diameters represented in Fig. 2 have been calculated. This figure summarises an empirical relation, which states that the distance between neighbouring atomic centres in a crystal structure is equal to the sum of two constants, characteristic of the atoms concerned. We can therefore picture the crystal structure as a set of spheres packed tightly together, just as Barlow and Pope did; but in this case the dimensions of the spheres are those in Fig. 2, not those given by the valency volume law.

arrangements, those of the inert gases, are those in which the outer shell has its full complement of electrons. Such forms are very stable; they are characterised by a weak external field. The chemical properties of the other elements represent their tendency to revert to a more stable electron system.

The crystal of potassium chloride, on this point of view, consists of alternate potassium and chlorine ions. The potassium atom is surrounded by nineteen electrons when electrically neutral. Eighteen of these electrons complete the three electron shells, represented, for instance, by the very stable arrangement of argon. The remaining electron has no place in the stable system, and there is therefore a tendency for the atom to part with it and become a positively charged potassium ion, the nucleus with nineteen elementary charges being surrounded by eighteen electrons. Chlorine similarly tends to gain an electron. The KCl structure may therefore be re-

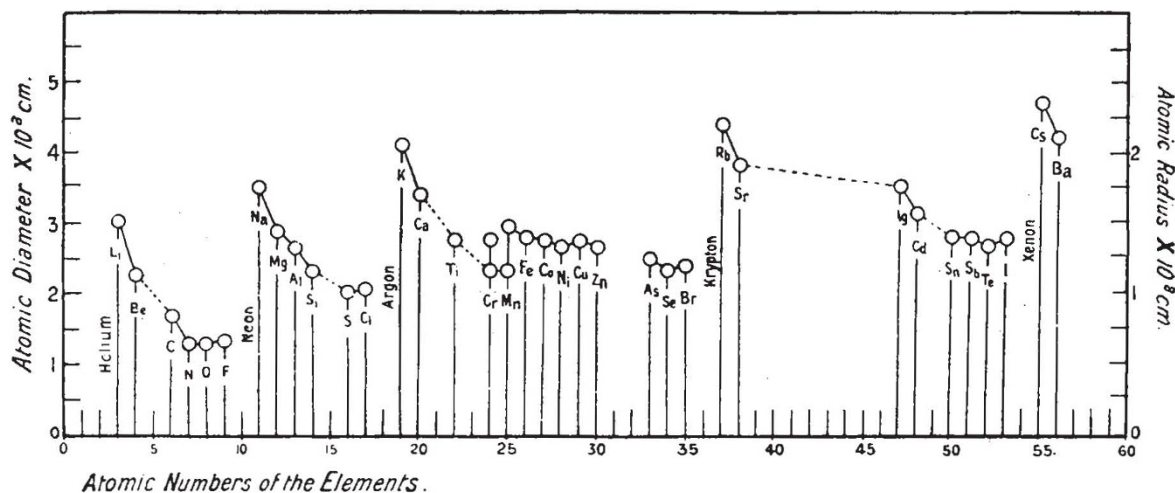


FIG. 2.

The atoms in a crystal are thus packed together as if they were inelastic spheres in contact. This is merely a way of visualising the structure, and must not be interpreted too literally. A ready explanation of the form of the graph in Fig. 2 is afforded by that conception of atomic structure which Stark, Born, Landé, Lewis, and others have helped to build up, and which has recently been so brilliantly summarised in a series of papers by Langmuir. Many independent lines of investigation have led to the conception of the atom as a positive nucleus surrounded by an electron system, in which the electrons are fixed at, or oscillate about, certain definite positions in the atomic structure. This is a view which forms a contrast to the Bohr atomic model, where the electron orbits enclose the atomic nucleus. In the "fixed electron" atom the electrons are arranged in a series of shells surrounding the nucleus, the numbers which complete the successive shells being 2, 8, 8, 18, 18, and 32. Certain

garded as an assemblage of argon shells, with resultant positive and negative charges, which are held together by their charges, and kept apart by some force of repulsion which we must suppose to exist between the outer electron systems. The result is the structure in Fig. 1 where every ion is surrounded symmetrically by the greatest possible number—six—of ions of the opposite sign.

In the case of two electro-negative elements which are chemically combined, both atoms have a smaller number of electrons than corresponds to stability of the outer shell. Stability is attained by their holding pairs of electrons in common. In this way Langmuir has succeeded in the most striking manner in explaining the complicated valency of such elements as nitrogen and phosphorus.

The structure of calcite (Fig. 1) is an example of both types of chemical combination. The calcium atom, represented by the large sphere, is

an ion with a double positive charge, the CO_3 group an ion with a double negative charge. These ions group themselves in the same way in the calcite and potassium chloride structures, as the models show, except that the form of the CO_3 group distorts the cube into a rhombohedron. The electro-negative atoms of carbon and oxygen hold electrons in common, and form a closely knitted group, and from their distance apart we can form an estimate of the dimensions of the outer electron shell; it is the lower limit to which the diameters tend at the end of each period in Fig. 2.

In this an explanation is found of the large diameters assigned to the electro-positive elements, and the small diameters assigned to the electro-negative elements, in Fig. 2. The electro-positive atoms never share electrons with their neighbours; they are therefore isolated in the crystal structure, and appear to occupy a large domain. The electro-negative elements, bound together by common electrons, have to be represented by small spheres.

Comparing two crystals such as sodium fluoride and magnesium oxide, which have identical structures, we see that both may be represented by alternate electron groups of the Neon type. In the case of magnesium oxide the ions carry a charge twice as great as the sodium and fluorine ions, and the consequence is that the MgO structure, though identical in form with the NaF structure, has its dimensions reduced. The side of the elementary cube has a length of 4.22×10^{-8} cm. in the case of MgO , a length of 4.78×10^{-8} cm. in the case of NaF .

In diamond every carbon atom is surrounded symmetrically by four other carbon atoms arranged at the corners of a tetrahedron. The carbon atom has four electrons in its outer shell, and, in order to complete the number eight required for stability, it shares a pair of electrons with each neighbouring atom. The whole crystal is thus one continuous molecule, and the great hardness and density receive a simple explanation.

A crystal of an electro-positive element cannot be bound together by common electrons. Here we must suppose that the crystal consists of ions and electrons, the ions representing the stable electron systems, and the electrons being present in sufficient numbers to make the whole assemblage electrically neutral. From the fact that all crystals of electro-positive elements are conductors of electricity we deduce that the electrons have no fixed place in the system; they move under the influence of an electromotive force.

It has been possible only to indicate the manner in which crystal structure helps to elucidate the structure of the atom, and many generalisations have been made to which there are exceptions. It is hoped that this discussion will show the interest of the study of crystals. In a crystal there are countless atomic groupings oriented with perfect regularity. Individually their effect is too small to observe, but by illuminating the crystal with X-rays, the wave-length of which is much less than the distance separating the atoms, we can make use of their concerted effect on the rays to enable us to see into the intimate structure of matter.

Researches on Growth of Plants.

By SIR JAGADIS CHUNDER BOSE, F.R.S.

II.

The General Principle Determining Tropic Movements.

THE movements in plants under the stimuli of the environment—the twining of tendrils, the effect of temperature variation, the action of light inducing movements sometimes towards and at other times away from the stimulus, the diametrically opposite responses of the shoot and the root to the same stimulus of gravity, the night and day positions of organs of plants—present such diversities that it must have appeared hopeless to endeavour to discover any fundamental reaction applicable in all cases. It has, therefore, been customary to assume different sensibilities especially evolved for the advantage of the plant. But teleological argument and the use of descriptive phrases, like positive and negative tropism, offer no real explanation of the phenomena. I propose to describe experimental results from which it will

¹ Continued from p. 617.

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be possible to discover an underlying law which determines the various tropic movements in plants.

Direct Effect of Stimulus.—In the motile pulvinus of *Mimosa* the excitation caused by stimulus causes a sudden diminution of turgor and contraction of the cells. With regard to this fall of turgor it is not definitely known whether excitation causes a sudden diminution in the osmotic strength of cell sap or increase in the permeability of the ectoplast. The state of excitation in a vegetable tissue may, however, be detected, as I have shown elsewhere, by the following indications: (1) diminution of turgor; (2) contraction and fall of leaf of *Mimosa*; (3) electromotive change of galvanometric negativity; (4) variation of electric resistance; and (5) retardation of the rate of growth.

Continuity of Physiological Reaction in Growing and Non-growing Organs.

In investigations on the effect of all modes of stimulation, mechanical, electrical, or radi-