

## The Architecture of the Solid State.\*

By Prof. W. L. BRAGG, F.R.S.

A SOLID body is a mechanical system in equilibrium, an example of atomic engineering, with balance of stresses in the component parts. Analysis by X-ray methods, and more recently by those of electron diffraction, has given us a scale plan of its component parts. To what extent can we explain the way in which the atoms are arranged, and the properties of the body as a whole, by considering the forces which act between the atoms?

A broad generalisation divides solids into three classes—metallic, organic, and inorganic. Though it is easy to cite cases of solids which are intermediate in character, this division into classes is clearly marked, and corresponds to a very fundamental difference in the nature of the bonds which hold the atoms together. Metals are associations of electropositive atoms with each other, organic compounds are associations of electronegative atoms, and inorganic compounds associations of electropositive with electronegative atoms. The fundamental distinction between the laws which govern these associations has been implicitly recognised by assigning to each its own branch of chemistry, metallurgical, organic, and inorganic. The law of combination in inorganic compounds was first foreshadowed by Berzelius, those for organic compounds were founded by Kekulé, and confusion arose in the past from the attempt to bring both classes into a common scheme. The laws of atomic association in intermetallic compounds are again different, and are only now being understood through a study of alloy structures.

The success which has as yet been attained in

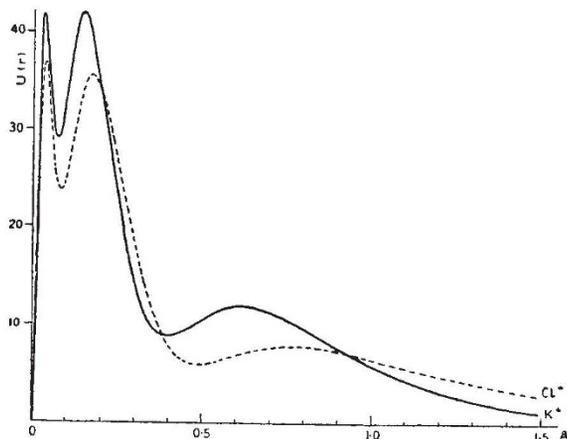


FIG. 1.—The radial distribution of electrons in the ions K and Cl<sup>-</sup>. The peaks in each curve of distribution represent the K, L, M electron groups, containing two, eight, and eight electrons respectively (Hartree).

explaining physical properties by atomic structure is different in these three classes. The structures of the metals are very simple, and were amongst the first to be discovered by X-ray analysis; many alloy structures have also been determined. The

difficulty of correlating structures and properties is not due to any lack of knowledge about atomic arrangement, but arises partly because the theory of the metallic state is very complex and as yet incomplete, and partly because the mechanical properties of the metals, which are so important to us, depend rather on the destruction of the perfect

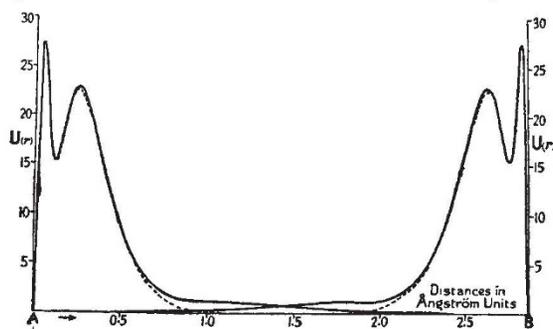


FIG. 2.—The ions Al<sup>3+</sup> are shown by the dotted curves, at a distance apart of 2.86 Å. as in the crystal of aluminium metal (James, Brindley and Wood). The distribution representing the remaining electrons is almost entirely confined to the space between the ions (metallic bond).

crystal than on its behaviour as an ideal crystal. Knowledge in this field is mainly descriptive. On the other hand, those organic substances the physical properties of which as solids are most interesting are very complex forms, such as cellulose or rubber. The difficulty here of giving even a descriptive account of the dependence of properties on structure is mainly that of discovering the atomic arrangement. This is one of the obvious fields in which to concentrate all the resources of X-ray technique in future. Such successes as those which Mark has had with cellulose and Astbury with the wool fibre show its interest and possibilities, but in all cases the structures can as yet be only guessed.

In comparison, the inorganic solids are not of such great technical importance, but I propose to discuss their properties because a more complete story can be told. Not only are the structures well known, but also the interatomic forces can to a large extent be treated quantitatively. The landmark in this field is, of course, Born's great work on the dynamics of the crystal lattice, and it is to the inorganic compounds that his ideas have been mainly applied.

The reason for the success in treating the inorganic crystal is that it can be regarded to a large extent as a problem in electrostatics. The typical crystal is built of component parts which are charged positively and negatively. These parts may be simple charged atoms or 'ions', or they may be charged groups of atoms. Further, the forces of repulsion which keep the ions apart and prevent their structures intermingling can be simply expressed, and their strength quantitatively estimated. So a theory of the physical properties of the solid can be built up, a few aspects of which I wish to discuss.

What is the justification for supposing that electrostatic forces bulk so largely in these com-

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pounds? It lies in the fact that when two ions approach each other, the force of repulsion which prevents further approach sets in when the structures have scarcely penetrated at all into each other.

The nucleus of an atom is surrounded by an atmosphere of electrons, a kind of space-charge which

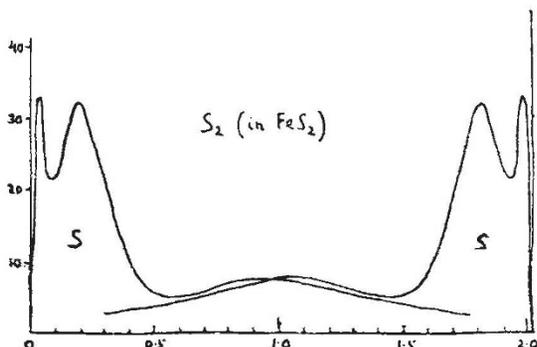


FIG. 3.—The group  $S_2$  in  $FeS_2$ , iron pyrites. The distance between the atoms (2.05 Å.) is so small that the  $M$  shells overlap (non-polar bond).

exactly (neutral atom) or nearly (ion) neutralises the positive charge on the nucleus. The former idea of a series of electron orbits has been replaced by a wave-mechanical distribution which cannot be visualised. It can be represented in a way which is a very good approximation for many purposes by supposing each electron to move in the field of the nucleus and the other electrons, representing it by the 'smeared out' continuous distribution which the solution of the wave equation gives, and then taking the electron atmosphere to be the sum of these distributions. These atmospheres have been worked out for many atoms, the most accurate results being those of Hartree. Instead of definite electron orbits, we get a continuous distribution with spherical symmetry which may be thought of as the density of the electron atmosphere, or probability of finding an electron in unit volume at different distances from the nucleus. A convenient way of showing the electron distribution is to plot  $U_r$  against the distance from the nucleus  $r$ , where  $(U_r)dr$  is the number of electrons between  $r$  and  $r + dr$ . Such a curve for chlorine, which has a charge of 17e on its nucleus, and is surrounded by eighteen electrons, is shown in Fig. 1. The distribution has peaks which correspond to the  $K, L, M$  electron groups of atomic theory.

A striking feature is the rapid rate at which the electron atmosphere thins out as the distance from the nucleus increases. For example, the electron density in various parts of the chlorine ion is as follows, the figures representing the number of electrons per cubic angstrom unit ( $10^{-24} \text{ cm.}^3$ ).

$K$ shell	3250
$L$ shell	111
$M$ shell	1.00
At $r = 1.84 \text{ Å.}$	0.04

The last distance of 1.8 Å. is called the 'ionic radius' of chlorine. This theoretically indefensible, but extremely useful, conception of ionic radii

expresses the fact that ions in crystals appear to take up a certain amount of space. For example, sodium has an ionic radius of 1 Å., chlorine of 1.8 Å., and the two ions are 2.8 Å. apart in sodium chloride. We may take it here as representing the point where the overlapping of one ion by another takes place. We can see, therefore, that the repulsive force sets in when an extremely tenuous part of each electron atmosphere is involved, in the case of chlorine only  $10^{-5}$  of that in the  $K$  shell.

The difference between the three types of inter-atomic bond is shown in a striking way if we take these atomic models, set them distances apart, such as are found in actual crystalline structures, and see to what extent the electron atmospheres overlap. Fig. 2 shows the state of affairs in an aluminium crystal. The aluminium ions  $Al^{3+}$ , shown as dotted lines, are separated by a wide gap. This interspace is occupied by the valency electrons, and metallic properties suggest that these electrons are not bound each to its own atom but are shared by all.

Fig. 3 shows the group  $S_2$  in iron pyrites,  $FeS_2$ . The bond between the sulphur atoms is of the non-polar type, such as characterises organic compounds, and the two atoms are so close that there is a merging of their  $M$  shells. The two structures combine to form a twin structure like a larger atom with two nuclei. Contrast with these the series of polar

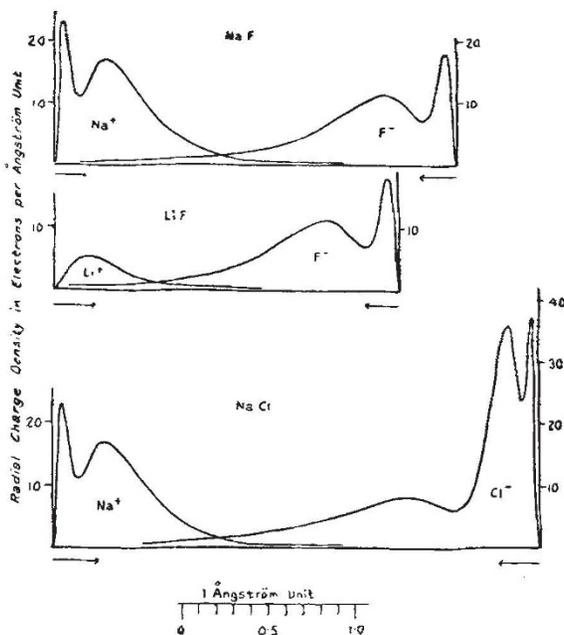


FIG. 4.—The electron distribution in compounds of the sodium chloride type (Brindley). The ionic structures overlap at points where the electron density is extremely small (polar bond).

crystals shown in Fig. 4 (taken from a paper by Brindley). The structures are of the sodium chloride type in which there is a simple alternation of positive and negative ions, and it is seen that the ions scarcely overlap at all. The diagram exaggerates the extent of overlapping, because the curve measures the distribution of electrons in complete spherical shells all round each nucleus, whereas the ions come in contact at one point only.

The first success of Born's theory lay in explaining the heat of formation of these compounds. Suppose the sodium and chlorine ions to remain in regular array, but to be widely separated, and then allow the whole structure to collapse uniformly, ending in the sodium chloride crystal. The energy of the electrostatic field between the ions is reduced in the process, just as when the plates of a condenser

come together. This energy can be calculated, and a correction due to the work done against the repulsive forces can be worked out. The latter is small because it only comes into play at the very end of the process. Born showed that the calculated loss of energy was in accord with the heat of formation of the crystal.

(To be continued.)

### Determination of Position in High Latitudes, with Particular Reference to Aircraft Observation.

By C. J. STEWART, O.B.E.

THE determination of position from land or air observations in high latitudes is rendered difficult, apart from conditions of temperature, by the unreliability of the magnetic compass and gyroscopic compass. On aircraft the latter is not yet a practicable instrument. Hence, astronomical methods must be utilised. In the consideration of any method of air navigation to the poles it must first be made clear that, even with assumed perfectly accurate instruments and accurate observations with them, astronomical observations from an aeroplane can give an exact position in two cases only: (1) by the observation of two stars; (2) by choosing the time of flight so as to render possible simultaneous observations of both sun and moon. The first case implies that the flight takes place at the season of perpetual night, and need not therefore be considered. The limitations of the second case are increased by the known inaccuracy of any form of sextant used in the air. Broadly, while sextant observations on the ground may be relied upon to give position within, say, one to three miles, aerial observations can only be relied upon to give position within about ten miles, and it is usually necessary to take the mean of a number of readings to secure this result. The use of automatically stabilised aircraft may render a somewhat more accurate location possible, but the utility of such aircraft under polar conditions can scarcely be regarded as established.

In view of such limitations, reliance has to be placed upon other means of navigation. Radio direction-finding is unlikely at the present stage of development to be of use, since its accuracy at a range of, say, four hundred miles would not, under favourable conditions, give position in line to within twelve miles. Radio signalling is, however, of value for providing exact time signals. The navigator is therefore compelled to rely upon the use of the most accurate instruments for—

- (1) indicating direction, and
- (2) indicating ground speed in magnitude and direction.

This, of course, is virtually the oldest method of navigating, namely, dead reckoning.<sup>1</sup> The instrument used for indicating direction must be some form of sun compass or a gyro azimuth. Of these alternatives, where the sun is available, the sun compass is likely to be the more accurate, since an instrument measuring the sun's position, in con-

junction with an accurate chronometer, would be simpler and less liable to variation than any form of gyro azimuth at present known. The feasibility of using gyroscopic devices will be referred to later, but since the sun compass formed an essential part of the equipment of both Amundsen and Byrd in their polar expeditions, a description of such an instrument is necessary.

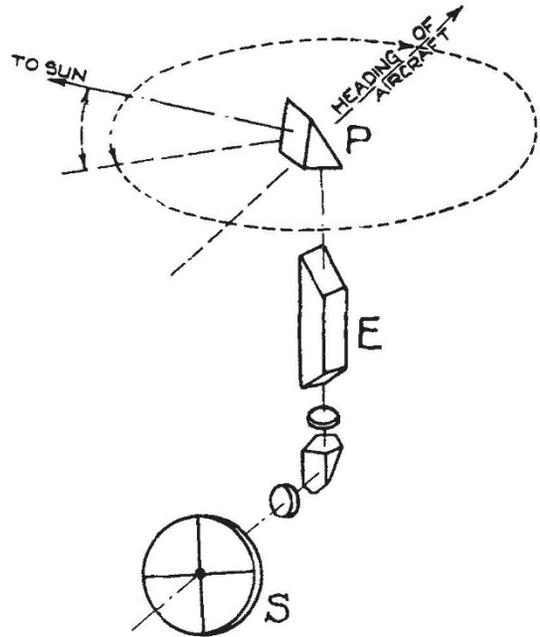


FIG. 1.—Optical arrangement of the Goerz sun compass.

Instruments for measuring ground speed and direction are quite well known<sup>2</sup> and, in their use under polar conditions of temperature, present no great difficulty.

Since the sun is above the horizon during the exploring season, and since it is always at a low altitude, the sun compass forms a very suitable instrument for determining directions. The Goerz sun compass was constructed specially for the Amundsen expedition in 1925 and, according to reports, gave very satisfactory results.<sup>3</sup>

This instrument comprises an optical arrangement which throws an image of the sun on a screen *S* (Fig. 1), when the aircraft is on the desired course. The reflecting prism *P* may be rotated