

problem of all, a problem calling for intensive research on ecological lines.

In conclusion, I should like to stress once more the importance of combining different lines of attack on any problem. However valuable specialised studies may be—and that they possess great value no one will deny—they must be combined with a study of each problem as a whole, and that, in its essence, is the ecological method. Of all the sciences which deal with man, modern geography, as it is studied in the best schools, perhaps comes nearest to what I have called 'human' ecology. It is human ecology, but it scarcely attempts to cover the whole field of what I would

include in that subject. It has, however, largely adopted the ecological viewpoint. Similarly, the study of sociology on modern lines, so far as it goes, is pure ecology.

The study of human communities is not the only science which deals with man. Ecology has gone further than sociology in its efforts to synthesise. Human ecology is certainly concerned with social studies and should make full use of all the social sciences, but it should aim also at making equally good use of every other branch of humanistic study, in seeking as perfect an answer as possible to that all-embracing question of how and why man has come to be as he is and to behave as he does.

The Architecture of the Solid State.*

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

THE electrostatic basis of the interatomic forces explains in a very elegant way the structures of compounds which contain a number of ions of different kinds. The principle of electrostatic valency in such compounds has been formulated by Pauling.

Suppose a number of ions to come together to form a crystalline solid. The ions are of different sizes, each kind has a characteristic positive or negative charge, and their relative numbers are necessarily such that the whole structure is electrically neutral. How will they arrange themselves so that the electrostatic energy in the interspaces is as small as possible? The governing factors are those of size and charge.

The first feature is that of 'packing'. The ions will fit closely together in order to reduce the interspace with its electrostatic energy. The largest ions are the negative ones, which therefore have the main effect in determining the packing, and the positive ions fit into the spaces in between. To see what arrangement will make the electrostatic energy as small as possible, it is useful to make a picture of the structure in which the electrostatic field is represented by lines of force. These start from the positive ions and end on the negative ions, their numbers being determined by the charges. Our complicated three-dimensional condenser will tend to take up a form such that all lines of force have as short a path as possible.

The result may be illustrated by a structure such as that of beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, shown in Fig. 5. The large spheres are oxygen, and tucked between them one can see silicon (black), aluminium (shaded), and beryllium (white). The oxygens are the negative plates of the condenser, the other atoms the positive plates, and the packing is clear in the diagram. In order that all lines of force may have the shortest path, a certain relation must hold between the electric charges (Pauling's rule). Silicon has a valency 4, aluminium 3, beryllium 2. As shown in the lower part of the diagram, the lines of force Si^{4+} end on four oxygen ions, O^{2-} , thus balancing a charge $-e$ on each. Al^{3+} surrounded by six balances a charge $-e/2$ on each oxygen, and Be^{2+}

surrounded by four also balances a charge $-e/2$. The same structure is shown as a skeleton in Fig. 6, and it will be seen that the oxygen atoms (large circles) are of two kinds, and that each kind has its charge exactly neutralised. One kind of oxygen is linked to two silicon atoms ($4/4 + 4/4 = 2$) and the

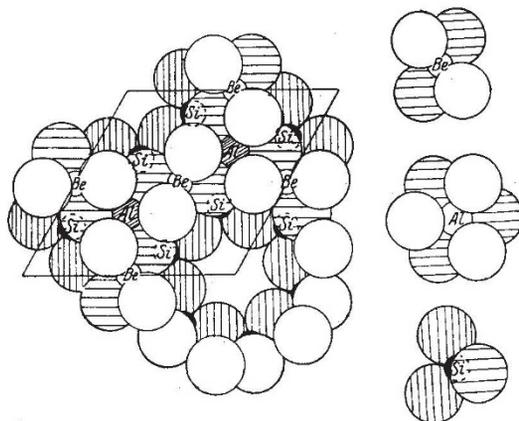


Fig. 5.—The arrangement of atoms in the structure of beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. The large oxygen atoms are densely packed, and the atoms of metal and silicon are in the spaces between them.

other to silicon, beryllium, and aluminium atoms ($4/4 + 3/6 + 2/4 = 2$). There is thus local neutralisation of charge in the crystal, and our picture of lines of force is one in which they merely join one atom to the next, and those starting from a positive ion are not forced to wander to distant atoms in the crystal before finding an equivalent negative charge on which to end.

It is surprising how the simple rule, with a few hints from X-ray analysis, enables one to build up very complex structures. One stacks the groups together, always obeying the electrostatic rule, and the whole crystal pattern falls into place. It is the electrostatic counterpart to the more rigid rule of valency in organic compounds, when each unit of valency is represented by a single indivisible bond. In the typical inorganic compound the valency can be divided into fractional parts, because it is due to an electrostatic charge, but it still remains true that when these fractional valency bonds between

* Continued from p. 212.

all the atoms are drawn the contributions of the bonds to every atom add up to its valency. As in the case of an organic compound, the formula of an inorganic compound cannot be expressed by a formula merely giving the relative numbers of atoms. The only complete formula is a model of the structure, showing the relationships of its constituent atoms; nothing less can express the valency laws involved.

Acid radicals, such as $(\text{ClO}_4)^-$, $(\text{SO}_4)^{2-}$, $(\text{PO}_4)^{3-}$, consist of four oxygen atoms surrounding the central atom. The group as a whole has a negative charge, and in a salt these groups are held to the positive ions by electrostatic forces. Now although an oxygen atom can be bound to one sulphur or chlorine atom in this way, forming part of an acid group, it cannot be bound to two without causing an intense localisation of positive charge, because the negative charge of the oxygen atom is more than balanced. Hence these acid groups generally only involve one central atom, such as sulphur or chlorine, rarely two or three. The position is different as regards silicon, for (as in beryl) an oxygen atom common to tetrahedral groups around two silicon atoms satisfies the rule as to equivalence of charge. There is thus no limit to the extent to which silicon-oxygen groups can link up, so that silicon builds a very characteristic class of compounds. The silicon-oxygen tetrahedra can form groups as in beryl, where each unit has the composition Si_6O_{18} . They can link by corners to form endless rows, like long negatively charged chains (Fig. 7). These

are attached sideways by positive ions, and form characteristic fibrous structures such as asbestos. They are linked side by side to form extended sheets, as in mica, with positive ions between. When we split a piece of mica we are pulling apart the plates of a condenser. Each acid radical, negatively charged, extends as a sheet, over the whole mica surface.

So far we have considered the crystal as a structure with static equilibrium between the forces of attraction and repulsion. This equilibrium is disturbed when the crystal is elastically strained, or the atoms set in motion by heat vibration.

A very interesting result of X-ray analysis is that we can measure the amplitude of vibration of the atoms at different temperatures, as was first predicted theoretically by Debye, and shown experimentally by Sir William Bragg. A series of such measurements by James is shown in Fig. 8. The X-ray results can be used to make a picture of sheets of atoms in the crystal planes, and the peaks in the diagram represent a cross-section of the crystal

density taken normally to certain crystal planes of sodium chloride. The large peak is chlorine, the smaller sodium. As the crystal is warmed, the sharp peaks become broadened, due to the vibration of the atoms, just as the image of an oscillograph is drawn out into a band when it vibrates. A very interesting feature, shown by James, Waller, and Hartree, is that even when the results are extrapolated to the absolute zero, the peaks are not so sharp as they should be according to Hartree's atomic models. The atoms appear to be vibrating even at absolute zero, and calculation shows that the vibration corresponds to the 'zero-point energy' of quantum theory. The extent of vibration is quite considerable at room temperature, and still greater nearer the melting-point. For

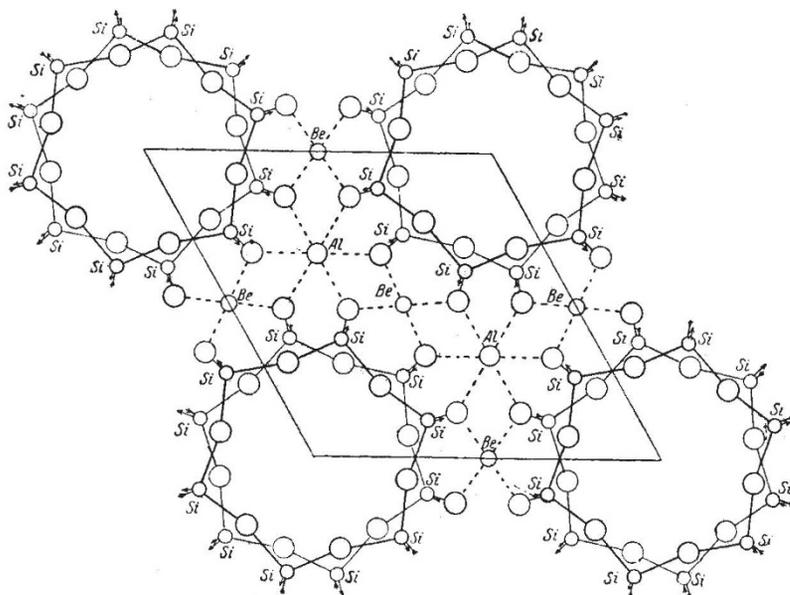


FIG. 6.—The structure of beryl arranged to show the way in which the two kinds of oxygen atoms (large circles) are linked to silicon and silicon, or to silicon, aluminium, and beryllium, in accordance with Pauling's rule.

example, sodium and chlorine atoms at room temperature have an average amplitude of 0.22×10^{-8} cm., and at 600°C . of 0.6×10^{-8} cm. as compared with their distance apart of 2.8×10^{-8} cm.

We may think of the crystal as a three-dimensional spring mattress, the atoms being linked together by springs. Heat causes shivers to sweep backwards and forwards through the solid, displacing the atoms from their normal positions. Two most important properties of the solid are those of thermal expansion and thermal conductivity, and it was first pointed out by Debye that these effects are both paradoxical unless a refinement in considering the repulsive forces between the ions is introduced. If the restoring forces when the atoms are displaced were simply proportional to the displacement, bodies would not expand when heated. In the spring mattress model, an atom vibrating between two neighbours pushes the one towards which it is displaced and pulls the one from which it is displaced; on the average, such pushes and pulls cancel. But when a departure from the linear

relation between displacement and force is taken into account, the pushes are increased and the pulls weakened. Each vibrating atom, then, helps to force the whole structure apart.

Thermal conductivity, in the case of those solids which are not electrical conductors, depends upon transference of atomic vibrations from hot to cold regions. The heat motion consists of waves, and if these waves traversed in the body quite independently of each other, any agitation at one end of the body would immediately rush to the other at the speed of elastic waves in the body. Hence thermal conductivity should be almost infinitely great. Actually the different wave-trains are not independent, but influence the motion of each other. They therefore scatter each other, and the advancing region of wave agitation has to fight its way towards the cold end of the body through a fog of waves which it itself creates.

The question of the outer form of a crystal, the relative growth of its crystal faces, falls in another category. The lattice theory can tell the relative surface potential energy of the various crystal faces, and the form of the crystal should be one which makes the total surface energy a minimum. However, one can scarcely expect successful prediction in this case, when we know how greatly crystals vary in form when grown under different conditions. Small traces of foreign bodies in the

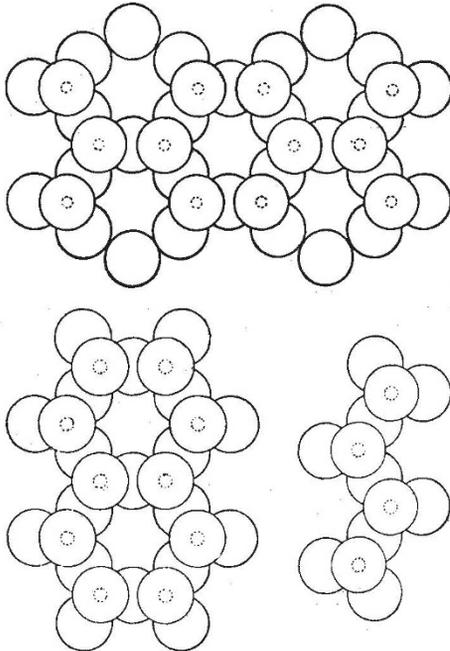


FIG. 7.—Chains and sheets of silicon-oxygen groups in the silicates. Silicon, shown as a small circle, always lies between four oxygen atoms and the tetrahedral groups are linked by sharing oxygen atoms.

solution or liquid entirely alter the crystal form. The energy of the surface is too small compared with that of the crystal as a whole, and reacts too sensitively to adsorbed layers.

In the explanation of the tensile strength, as ordinarily measured, the lattice theory breaks down entirely. Rocksalt should be rather stronger

than the strongest steel, whereas Joffe has shown that it breaks under a stress only 1/500th that calculated theoretically, and explains this by supposing a crack always starts at a weak place and the

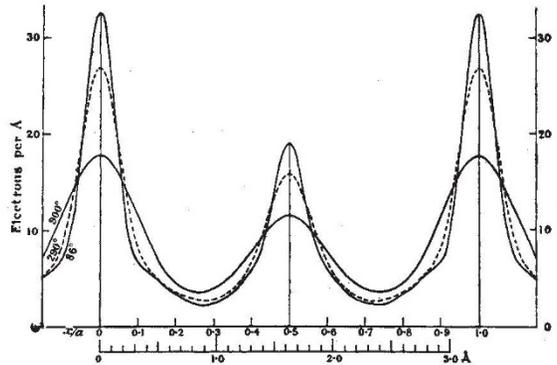


FIG. 8.—The vibration of the atoms when sodium chloride is heated. The octahedral crystal planes consist of alternate sheets of chlorine and sodium atoms, represented in the figure by the large and small peaks respectively. As the temperature is raised, the sheets become broader and more diffuse owing to thermal movement. (James and Firth.)

crystal tears rather than breaks. An initial break at any point in a crystal concentrates the strain upon the neighbouring regions, which break in their turn. In order to get a body which has a high tensile strength, it must be ensured that, when at any point a break does occur, the resulting increase of stress is distributed widely. Tensile strength is, in other words, not so much a question of strength of bonding in the direction of the stress, as of weakness of bonding at right angles to it. The strength of a sheet of mica, or a fibre of asbestos, is due to the very feeble forces with which the sheets or fibres are attached to each other laterally, so that if one fibre gives, the additional stress is shared by the rest of the bundle of fibres.

The tensile strength is one example of many in which the behaviour of the real crystal, built of a number of crystalline elements, differs from that of the ideal perfect crystal and requires a new type of treatment. X-ray analysis has always shown that actual crystals are composed of a number of small blocks, or 'mosaic' as Ewald terms it, of crystals which are nearly in the same orientation, but not quite. There must be a misfit at the boundaries between these blocks. For some crystalline properties, such as heat of formation or double refraction, the mosaic structure has no influence. For other properties it is all-important, and tensile strength appears to be such a property. Smekal has always insisted on the important difference between the 'ideal' and 'real' crystal, and believes many properties to be essentially dependent upon it.

Thus, when one considers the properties of the solids which are of technical importance, in contrast to those of the ideal crystal, little success in exact interpretation can be claimed. However, the knowledge of atomic arrangement has performed a service, the usefulness of which is not so obvious, but is yet very great; it has provided a new language, or series of conceptions, in which to express the vast amount of empirical knowledge about the behaviour of materials which has been accumulated.