

Solid Solutions and Inter-Metallic Compounds.

By Dr. WALTER ROSENHAIN, F.R.S.

METALLURGICAL research during the past twenty years has been largely devoted to the study of alloys, and as one result we now possess a series of more or less complicated equilibrium diagrams representing the constitution of most of the binary and of some of the ternary systems. While, on one hand, increasing accuracy of methods has rendered these diagrams far more complex than was at first supposed, a careful examination of those which are most thoroughly established suggests that, widely as they vary among themselves, there are certain regularities which point to some common fundamental principle which, if once grasped, would exhibit these varied diagrams as parts of an intelligible whole. Fortunately, at the time when this great mass of disconnected knowledge lies awaiting synthetic treatment, the results of X-ray analysis applied to the study of the inner structure of crystals have become available. As the result of an endeavour to apply these results to the explanation of the behaviour of alloys systems, the writer has arrived at a theory which, on a simple basis, promises to afford an easy explanation of many, if not of all, of the properties of alloys, and to afford a much deeper insight into the nature of solid solutions and of inter-metallic compounds, and through them to throw new light on the nature of inter-atomic relationships.

The theory in question has been fully stated in two recent papers, and need only be briefly summarised here.¹ A metallic solid solution is an aggregate of crystals which, when in equilibrium, are homogeneous in composition, so that both the solvent metal and the solute metal are present in the same proportions in all the crystals. The present theory of the constitution of such crystals is based on three fundamental principles, the first of which has now received considerable experimental verification, while the other two appear to follow almost unavoidably. The first is that a solid-solution crystal is built up of the two kinds of atoms, those of the solvent and of the solute, upon a single space-lattice which is, substantially, that of the solvent, so that the atoms of the solute may be regarded as being simply substituted for an equal number of atoms of the solvent on the "parent" lattice. Measurements of the lattice-constants of certain groups of solid-solution alloys and comparison of the results with the measured densities of the alloys have strongly confirmed this view. The evidence already obtained indicates that this is the inner structure of practically all inter-metallic solid solutions, but some room for doubt may still exist in regard to certain metalloids, such as carbon or phosphorus.

Next, in a crystal built up in this manner of two kinds of atoms upon a single, simple space-lattice, the inference can scarcely be avoided that a certain degree of distortion of the lattice must result. The nature of this distortion must depend upon the character of

the two kinds of atoms concerned; there may be either expansion or contraction of the parent lattice, and this may be either mainly local or mainly general. The degree and nature of this distortion will depend upon the extent to which the solute atom differs from the solvent, and also upon the general character of the solvent lattice, but these are details which need not be considered here. We may pass on to the third fundamental conception—that the extent to which any given space-lattice can be distorted, and particularly expanded, is strictly limited—that there is, in fact, for each pair of atoms a limiting distance beyond which the bond between them—whatever its nature—ceases to act. This rule of a limiting maximum lattice constant or parameter leads to a series of interesting inferences. Thus, a uniform undistorted lattice of a pure substance will be uniformly expanded by heat until the limiting parameter is attained; at this point the atoms throughout the lattice will lose their power of cohesion and the crystal melts. In a solid solution crystal, the lattice may be locally expanded by the presence of solute atoms; under thermal expansion those expanded regions of the lattice will reach the limiting parameter at a temperature where the less expanded portions of the lattice are still well below the limiting value; the result will be commencement of fusion in those regions of the crystals richest in solute and the formation of a liquid richer in solute than the remaining solid. This consideration explains why, in solid solutions, we generally find a melting range instead of a single melting point. Where the solute atoms cause expansion of the lattice the melting temperatures will be depressed by successive additions of solute. On the other hand, where the presence of the solute atoms causes a contraction of the solvent lattice, there will be a rise of melting point and the first liquid to be formed on fusion is richer in solute than the residual solid. These latter inferences have been strikingly verified in such cases as those of solid solutions formed by the addition of palladium to silver or of nickel to copper.

A considerable number of further inferences can be drawn from the three fundamental principles of the present theory of the inner structure of solid solutions—for example, the striking inverse relationship which is found to hold between the solubility of one metal in another and its hardening effect upon it, and the relationship between the hardness, high melting point, and high elastic modulus of a metal on one side and its power of forming solid solutions on the other. The theory has even made it possible to suggest an explanation of the properties of metals and alloys in regard to electrical conductivity. Whatever the true mechanism of electric conduction, there can be no doubt that it is associated with the movement of electrons through the metal; it is now suggested that where the atoms lie on perfectly straight lines on the space-lattice the movement of electrons is entirely unhindered and the metal in that state should exhibit super-conductivity. This can only be fully realised very near the absolute zero, since at higher tempera-

¹ "Solid Solutions," Second Annual Lecture of the Inst. of Metals Division, American Inst. Mining Engineers, New York, Feb. 1923; and "The Inner Structure of Alloys," Thirteenth May Lecture to the Inst. of Metals, London, May, 1923. Journ. Inst. Metals, 1923, ii.

tures the thermal agitation of the atoms disturbs their perfect alignment even in a pure metal. Since it is sufficient for one line or at most a few lines of atoms to be perfectly straight at any given instance—since such a single line would conduct infinitely well—super-conductivity must set in at a temperature slightly above and not only at actual absolute zero. In a solid solution crystal, however, the atoms can never attain perfect alignment, owing to the lattice-distortion, and consequently the electrical conductivity of a solid solution will always be relatively very low, and even at absolute zero, real super-conductivity cannot occur. Further, since the solid-solution lattice is considerably distorted to begin with, the disturbing effect of thermal agitation will be relatively much less than in a pure metal; in certain circumstances, indeed, thermal expansion may partially relieve the distortion—in those cases, in fact, where solid solubility increases with rising temperature. Consequently, in solid solution alloys the temperature coefficient of electrical conductivity will be much lower than in pure metals, while in some special cases it may even become negative. The theory, as comparison of these inferences with well-known facts at once indicates, offers at all events a good qualitative explanation, and at a later stage even quantitative prediction of electrical properties should be possible. The difficulty here, and indeed throughout the theory, in arriving at numerical results lies in the fact that while the average distorting—*i.e.* expanding or contracting effect of dissolved atoms on a lattice—can be measured with considerable ease and accuracy by the aid of X-ray spectrometry, the maximum local distortion cannot as yet be determined directly. When this difficulty has been overcome, considerable further progress should become possible.

We may now briefly consider inter-metallic compounds. These are known to metallurgists from the occurrence of certain kinds of singular points on equilibrium diagrams and from characteristic features of micro-structure and of physical properties, but there are a number of alloys in which the existence of definite compounds has hitherto been regarded as doubtful. Again, the results of X-ray analysis, combined with the indications of the above theory, prove helpful. Very typical of inter-metallic compounds is the body CuAl_2 found in copper-aluminium alloys. It is a hard, brittle body, tending to crystallise in well-formed long needles. Its atomic structure has been determined by Dr. Owen and Mr. Preston at the National Physical Laboratory. The lattice-structure is shown in the accompanying diagram (Fig. 1). The most striking feature is that certain pairs of aluminium atoms approach one another within a range, centre to centre, of only 2.42 Ångström units. In an aluminium crystal the lattice-constant is 4.85 Å and the closest approach is 2.86 Å, and it would be quite impossible, by the application of external pressure, for example, to force the atoms so closely together as they are placed in the compound. The inference, which is justified by comparison with the known lattice structures of other chemical compounds, is that the very much closer approach of atoms in this manner is a characteristic, if not *the* characteristic, feature of chemical combination as distinct from the

“cohesion bonding” which occurs in the building up of a crystal. It would seem, in the present case, that the copper atom which is combined with the two aluminium atoms has taken away or absorbed something from the aluminium atoms which now allows them to come much closer together. This may well be the absorption of certain exterior electrons by the copper atom; whatever the detailed mechanism may be, it is probably the essence of chemical combination, and furnishes us at once with a definite criterion for distinguishing between solid solutions and compounds. At first sight one might perhaps expect that intermediate classes of structure should be found, in which the inter-atomic distances might be only slightly less than in the typical solid solutions. If our current views of the structure of the atom in “shells” or layers of electrons is correct, however, this should not be the case; we should find either substances in which there is nothing more than “cohesion bonding” without closer approach of the atoms, or bodies in which the atoms are drawn closer by a definite step.

There is a further distinction which can be inferred from the present theory. In a body of the solid

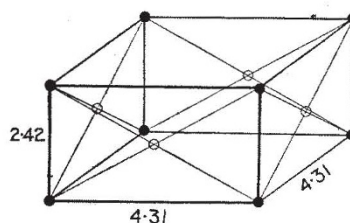


FIG. 1.—Lattice structure of CuAl_2 .
● Cu. ○ Al.

solution type, atoms of one kind are readily replaceable by atoms of the other; in a compound, on the other hand, it would be difficult to conceive of any atom being replaced by an atom of the other constituent. In the CuAl_2 structure, for example, it is scarcely possible that any of the aluminium atoms could be replaced by a copper atom. This very definite inference is verified by reference to the equilibrium diagrams of alloy systems in which typical well-defined compounds are to be found—these bodies never exhibit any appreciable amount of dissolving power for their constituents. If we may extend this view to those cases which, metallurgically, are still regarded as doubtful, it will at once serve to classify them into compounds and solid solutions respectively. A well-known group of alloys of this kind is the copper-zinc alloys (brasses), which exhibit a series of solid solutions generally called the alpha, beta, and gamma phases. These are micrographically distinct, and vary widely in many of their properties, and it has been thought that each was based upon a definite chemical compound possessing a wide range of dissolving power for copper and zinc.

In one of the papers mentioned above (May lecture) the writer suggested that these bodies need not be, and probably were not, based on definite compounds, but that they would probably be found to be based upon what might be termed allotrope lattices of copper. In the case of iron and nickel, for example, it is known

that the presence of a sufficient proportion of nickel will maintain the iron in the face-centred cubic lattice of the gamma phase at a temperature at which, in the absence of nickel, the iron would have reverted to the body-centred cube of the alpha phase. Presumably the iron remains in the gamma condition because in that condition it can retain a larger proportion of nickel atoms on the lattice, and because this arrangement involves less potential energy than any alternative. In the same way it was thought that the usual face-centred cubic lattice of copper might, when in the presence of more zinc atoms than can be carried on that lattice without undue distortion, be transformed into another lattice—still essentially a lattice of copper—but capable of carrying a larger number of zinc atoms, and that at a still higher concentration of zinc a further modification of the lattice might occur. Each successive modification would, in such a case, be expected to show an increasing approximation to the hexagonal lattice of zinc itself. Actual determinations of the lattices of the beta and gamma phases of the copper-zinc system, made by Owen and Preston in consequence of this suggestion, have completely verified it. The two phases show no compound lattice, but a modified copper lattice.

Another point of some interest in the distinction between solid solutions and compounds may be briefly considered. A good deal of consideration has been given by Tammann² to the chemical properties of solid solutions, Tammann's work being based on the idea of a substitution structure, but without reference to lattice distortion. If this principle is applied, however, an interesting conclusion may be drawn, to which attention was first directed by Mr. Preston, in regard to what may be termed "symmetrical" solid solutions. In any alloy system forming a continuous series of solid solutions between two metals, alloys must occur in which the two kinds of atoms are present in some simple ratio such as one to one, two to one, three to one, etc. According to the particular nature of the lattice system in each case, some of these simple ratios will allow the atoms to arrange themselves in a perfectly symmetrical manner. Such perfectly symmetrical atomic arrangement, however, is not likely to be attained or approached except in specially favourable circumstances. Very gradual cooling from fusion and a considerable rate of diffusion are essentials, but there is the further condition that the symmetrical arrangement in question should be a simple one. Thus in any lattice, an arrangement in which alternate

² Tammann, *Zeitschr. f. Anorg. u. Allgem. Chemie*, July 1919.

layers or planes of atoms consist each exclusively of one kind of atom would seem to be such a simple arrangement. In the face-centred cubic lattice a one-to-one ratio allows of such an arrangement, all the atoms at the cube corners and those at the centres of two opposite faces being occupied by one kind of atom and the remaining four face-centres by the second kind of atom. In such a lattice, another simple symmetrical arrangement, but one less easily formed by the process of diffusion required by the present theory, is that in which all the face-centres are occupied by one kind of atom and all the cube corners by the other, this implying an atomic ratio of three to one.

The special interest which attaches to such perfectly symmetrical arrangements is that, if fully attained, there will be in such a lattice a perfectly uniform atomic spacing. The consequence must be, if the present theory is correct, a single melting-point and relatively low hardness and electrical resistivity. In some alloy systems, this state of affairs is so closely approached that it becomes plainly visible on the equilibrium diagram as experimentally determined, and the presence of a compound at the simple atomic ratio in question has sometimes been inferred—wrongly, according to the present view. In other systems, where diffusion is slow and uniform geometrical arrangement, therefore, is practically unattainable, the ideal condition is never reached experimentally, but the "solidus" curve shows an inflexion towards the "liquidus" in the neighbourhood of the "symmetrical" composition—in several examples near the one-to-one ratio of atomic concentration. In some alloy systems two such inflexions, corresponding approximately to two such ratios, have been observed. Although these inflexions have become increasingly definite in the best-determined diagrams, so that they could not be ascribed to experimental error, no explanation has as yet been offered. The fact that these details are only to be seen clearly in recent diagrams, prepared by methods of extremely slow cooling of the alloys, tallies well with the requirements of our theory.

Inferences from the substitution and lattice-distortion theory could be pursued at much greater length; so far, no failure of such an inference, when tested by means either of older well-established fact or by special experiments, has yet been found. There is thus some hope that a small but real step has been taken towards the better understanding of the nature of alloys, and particularly of solid solutions and intermetallic compounds.

Weather Influences in the British Isles.

By C. E. P. BROOKS.

THE sun is the only source of terrestrial weather in the sense that the difference between the amount of solar radiation received in different latitudes is the driving force of the atmospheric circulation. The complexity of the earth's surface combined with its rotation about an axis introduces corresponding complexities into this circulation, but H. H. Clayton considers that "if there were no variation in solar radiation

the atmospheric motions would establish a stable system with exchanges of air between equator and pole and between ocean and land, in which the only variations would be daily and annual changes set in operation by the relative motions of earth and sun; the existing changes we call weather have their origin chiefly, if not entirely, in the variation of solar radiation." It has been found that some parts of the