The lattice spacings of solid solutions of different elements in aluminium

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Measurements have been made of the lattice spacings of solid solutions of lithium, magnesium, silicon, copper, zinc, germanium and silver in aluminium. The lattice of aluminium is expanded by the solution of magnesium or germanium, and contracted by the solution of lithium, silicon, copper or zinc. No change in lattice spacing can be detected when silver is dissolved in aluminium, although microscopic examination shows that a solid solution is formed, and this is confirmed by the absence of any diffraction lines other than those of the solid solution in aluminium.

If the lattice spacing/composition curve for dilute solutions is extrapolated to 100 % of solute, the resulting lattice spacing refers to a hypothetical face-centred cubic modification of the solute, and the corresponding closest distance of approach of the atoms is called the apparent atomic diameter (A.A.D.) of the solute when in solution in aluminium. Previous work enables the corresponding A.A.D. values to be deduced for the above solute elements when dissolved in univalent copper, silver or gold, and in divalent magnesium. The differences between the A.A.D. values of a given element when dissolved in various solvents are discussed, and it is suggested that they are controlled by the interplay of four factors: (1) the relative volume per valency electron in crystals of the solvent and solute, (2) the relative radii of the ions of solvent and solute, (3) Brillouin zone effects, and (4) the difference between solvent and solute in the electrochemical series. If this line of approach adopted be correct, it follows that it is only in exceptional circumstances that the so-called Vegard's law will apply to metallic solid solutions.

1. INTRODUCTION

The lattice spacings of solid solutions of different elements in copper and silver were investigated by Hume-Rothery, Lewin & Reynolds (1936), and later by Owen & Roberts (1939), who also examined solid solutions in gold (1945). In these alloys the solvent metal is univalent and the electron states of the first Brillouin zone are only half filled. The experimental results show that for any one solvent the lattice distortion produced by a given atomic percentage of the solutes in any one row of the periodic table (e.g. Ag, Cd, In, Sn, Sb) increases algebraically with the valency of the solute. The lattice spacings of solid solutions in magnesium were investigated by Hume-Rothery & Raynor (1940*a*), and by Raynor (1942). In these alloys the solvent metal is divalent, and with two valency electrons per atom, overlapping has occurred in some directions of the first Brillouin zone of the close-packed hexagonal structure. In the magnesium-rich alloys, the addition of relatively small amounts of solute of higher valency produces an overlap in another direction of the Brillouin zone, and the relations between lattice spacings and composition become more complicated. The present paper describes an investigation of the lattice spacings of solid solutions of lithium, magnesium, silicon, copper, zinc, germanium and silver in aluminium, this metal having been chosen as an example of a trivalent solvent with a face-centred cubic structure. The above solute elements are the only elements which dissolve in aluminium to an extent sufficiently great to permit an accurate lattice spacing/composition curve to be determined. The experimental methods and results are described in §§2 and 3 respectively, whilst in §4 the theoretical implications of the results are described, and the validity of Vegard's law is discussed.

2. EXPERIMENTAL DETAILS

(a) *Metals used*

The *aluminium* used in the present work was super-purity metal supplied by the British Aluminium Co. Ltd., the certificate of analysis showed the following impurities:

Silicon	0·0015 %
Iron	0·0010 %
Magnesium	0·0010 %
Copper	0·0020 %
Aluminium (by difference)	99·9945 %

The *lithium* used was from a batch of specially pure metal presented by Professor R. S. Hutton. This metal has not been analyzed in the elementary state, but a series of magnesium-lithium alloys prepared from it gave no indication of impurities. The *copper* was of 99·995 % purity and was kindly presented by the British Non-Ferrous Metals Research Association. The *magnesium* was provided by the Ministry of Supply, and was of Dominion origin, the purity being of the order 99·97 %. The *silicon* was introduced in the form of a high-purity master alloy of aluminium and silicon which was supplied by the British Aluminium Co. Ltd. The *silver* was pure assay silver, and the *germanium* was specially purified metal, these two metals being supplied by Messrs Johnson Matthey and Co. Ltd. The *zinc* was kindly presented by the Imperial Smelting Corporation, and was of a purity exceeding 99·99 %.

(b) *Preparation and heat treatment of ingots*

The ingots used in the present work were prepared by melting the super-purity aluminium in crucibles lined with alumina-fluorspar mixture, using a standard flux, the solute metal being introduced either in the elementary state, or in the form of a master alloy. After thorough stirring with an alumina rod, the alloy was cast into heavy copper moulds, to give cylindrical ingots $\frac{3}{8}$ in. in diameter. The ingots were placed in alumina collars in sealed evacuated hard glass tubes, and were annealed for periods of the order of 1 week at a temperature of approximately 500° C, after which they were quenched in iced water. A surface layer of about 1 mm. was removed on a lathe, and the remainder of the ingot was then used for the preparation of the filings.

(c) *Preparation and heat treatment of filings*

From 0·5 to 1·0 g. of filings were prepared from each ingot, using a dead-smooth file. The filings were cleaned with ether, using the methods described by Hume-Rothery & Reynolds (1936). The clean dry filings were then placed in thin alumina thermocouple sheaths in sealed evacuated glass tubes; in this way the filings were prevented from coming into contact with glass, and contamination by silicon was avoided.* The exact heat treatment given to the filings depended on the system concerned. For alloys lying within the range of the solid solution at low temperatures, the annealing treatment was followed by slow cooling. In many systems the limits of the solid solution under equilibrium conditions at low temperatures are so restricted that it was necessary to quench the filings after annealing at a temperature at which they were homogeneous. In some cases it was sufficient to cool the sealed glass tube in a blast of cold air, whilst in others more drastic quenching was necessary in order to retain the homogeneous solid solution. In all such cases the results were examined carefully to ensure that the measured lattice spacings referred to the true homogeneous state, and not to a partly decomposed specimen. After quenching, the filings were washed with alcohol and ether, and were dried in a vacuum. The dried filings were then passed through an 80-mesh sieve in order to remove broken glass, and any unduly large metallic particles.

(d) *Preparation of X-ray specimen and analysis of filings*

In the present work no results were obtained which suggested that the filings were of uneven composition, but the possibility of slight transverse segregation† in the ingots could not be avoided, and it was therefore desirable to carry out the chemical analyses on samples which were as nearly as possible identical with those of the X-ray specimen. For this reason the material which had passed the 80-mesh sieve was used both for the preparation of the X-ray specimen and for the chemical analysis. Experiment has shown that the use of a finer sieve has very little effect on measurements of lattice spacing, and it is felt that for the present purpose the increased accuracy in the analysis‡ outweighs any advantage which might be gained by the use of a finer sieve.

The X-ray specimens were made by mixing a small portion of the filings with a solution of Canada balsam in xylol until a pasty mass was obtained. The paste was then rolled into thin cylinders of diameter about 0·4 mm., and after these had been dried they were mounted in the X-ray camera.

The chemical analyses of the specimens were carried out by Messrs Johnson Matthey and Co. Ltd., and the authors must express their thanks to Mr A. R. Powell for his care and attention. In a few cases particles of glass were found mixed with the

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* Experiment has shown that aluminium filings pick up silicon when annealed in glass tubes.

† Experience with many polyphase aluminium alloys has shown that slight transverse segregation is often present in chill castings.

‡ It will be appreciated that if a very fine sieve is used, either the chemical analysis has to be carried out on a very small sample, or, alternatively, a much larger sample of metal has to be filed up, in which case the possibility of uneven composition is increased.

filings, and were weighed separately. All alloys were then analyzed for both constituents, and no indication of contamination was found. The work was straightforward except for the aluminium-germanium alloys for which very low results were at first obtained for the germanium. This source of error was eventually traced to the escape of germanium in the form of hydride, and the difficulty was avoided by dissolving the alloy in a mixture of nitric and sulphuric acids.

(*e*) *X-ray technique and lattice-spacing measurements*

The Debye-Scherrer photographs were taken in a 19 cm. diameter Unicam camera, using unfiltered copper radiation obtained from a Metro-Vickers demountable X-ray unit. With this radiation the pure aluminium gives (511), (422) and (420) reflexions at angles of 82, 69 and 58° respectively. The films were all of good quality, and could be measured accurately on a travelling microscope which had been tested against a standard scale calibrated at the National Physical Laboratory. The lattice spacings were calculated by standard methods, using the extrapolation function of Nelson & Riley (1945). During an exposure the temperature was measured by means of a thermometer placed on the camera, and for convenience all lattice spacings were calculated for a standard temperature of 25° C. For this purpose the coefficient of linear expansion was assumed to be $23{\cdot}1 \times 10^{-6}$, the value for pure aluminium.*

The values given for the lattice spacings are in kX units, and have not been corrected for refractive index. This policy has been adopted in order to make the data directly comparable with those of most other authors.

3. EXPERIMENTAL RESULTS

(*a*) *Pure aluminium*

In the course of the present work nine determinations of the lattice spacing of pure aluminium were made, involving the preparation of five completely different samples of filings. The measured lattice spacings, reduced to 25° C, lay within the extremes 4·0412(8) and 4·0414(2) kX, with a mean value of 4·0413(4) kX at 25° C. This value is in good agreement with the values† 4·0413(6) kX of Jette & Foote (1935), and 4·0413(1) kX of Wilson (1941), and is within 0·0002 kX of the work of several other investigators.

(*b*) *Solid solutions of lithium, silicon, copper and zinc in aluminium*

The lattice spacings obtained in the course of the present work are given in table 1, and the relations between lattice spacings and composition are shown in figures 1 and 2. All these elements‡ produce a lattice contraction, and the following points may be noted.

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* Experimental work has shown that the differences between the coefficients of expansion of the various alloys produces a negligible effect when the correction is for 10° C or less.

† In comparing the different papers care must be taken to see whether the correction for refractive index has been applied.

‡ The data for the aluminium-lithium alloys are included in figure 2 to avoid overlapping of points in figure 1.

TABLE 1

The table contains the measured lattice spacings of the aluminium-rich solid solutions which have been investigated. All values have been corrected to 25° C.

solute element	weight % solute	atomic % solute	lattice spacing at 25° C kX
Li	0·91	3·44	4·0396(7)
	1·29	4·83	4·0392(7)
	1·93	7·11	4·0381(9)
Mg	0·31	0·35	4·0422(1)
	0·57	0·63	4·0428(6)
	0·73	0·81	4·0435(7)
	1·13	1·26	4·0458(3)
	2·14	2·37	4·0495(7)
	2·69	2·97	4·0511(2)
	3·17	3·50	4·0543(6)
	3·72	4·11	4·0563(9)
	5·06	5·58	4·0630(6)
	6·14	6·76	4·0688(7)
	8·86	9·73	4·0820(9)
	9·62	10·56	4·0860(8)
Si	0·24	0·23	4·0408(1)
	0·36	0·35	4·0406(5)
	0·70	0·67	4·0402(1)
	0·77	0·74	4·0400(4)
	0·81	0·78	4·0399(0)
	0·95	0·91	4·0397(3)
	0·96	0·92	4·0396(4)
	0·97	0·93	4·0396(0)
Cu	0·11	0·06	4·0411(7)
	0·93	0·40	4·0394(0)
	1·82	0·80	4·0372(1)
	2·88	1·23	4·0353(9)
	3·12	1·37	4·0347(8)
	3·71	1·62	4·0335(5)
Zn	1·05	0·43(6)	4·0412(2)
	4·09	1·70	4·0403(8)
	6·45	2·76	4·0396(7)
	6·78	2·91	4·0393(5)
	12·24	5·44	4·0373(3)
	13·33	5·96	4·0369(6)
	14·88	6·72	4·0360(5)
Ge	1·0	0·37	4·0418(8)
	2·34	0·88	4·0426(0)
	2·99	1·13	4·0431(1)
	3·68	1·40	4·0434(7)
	4·85	1·86	4·0444(8)
	5·06	1·98	4·0446(5)
Ag	10·0	2·7	4·0413(3)
	20·0	6·0	4·0413(6)
Pure aluminium of 99·9945 % purity			4·0413(4)

In the system *aluminium-zinc* (figure 1) the lattice-spacing composition relation is not linear, but is a curve such that the lattice contraction per atomic per cent of solute increases with the concentration. The points lie well on a smooth curve with one exception, for which the divergence is 0·0002 kX. In the system *aluminium-copper* the lattice spacing/composition relation is linear. One point lies slightly below the best straight line, but the difference is within the limits of the experimental accuracy. In the system *aluminium-silicon*, a straight line can be drawn through all the points within the limits of experimental accuracy. In this system the solid solution is restricted, and experiments were made with two different rates of quenching, in order to ensure that partial decomposition had not occurred. The

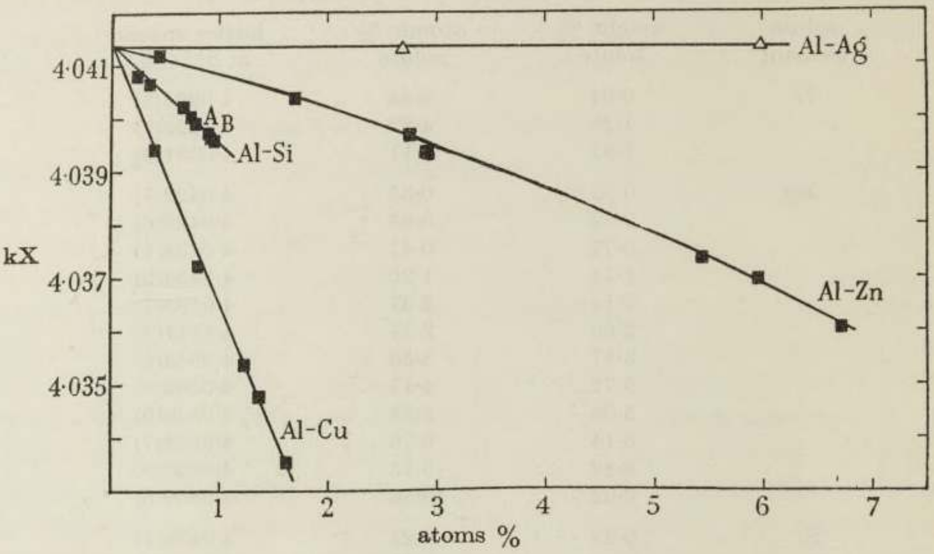

FIGURE 1

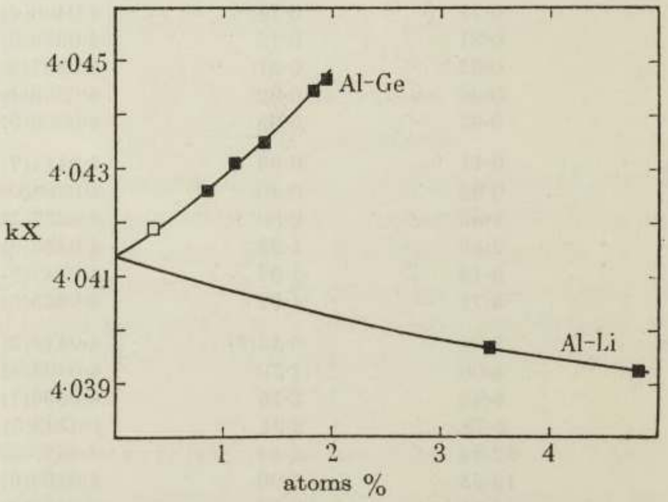

FIGURE 2

points marked *A* and *B* were obtained in this way, and their good agreement suggests that the solid solution had been retained. In the system *aluminium-lithium*, the previous work of Zintl & Woltersdorf (1935) suggested that the lattice of aluminium was expanded by the solution of lithium, whereas the data of Vosskuhler (1937) indicated a contraction. The present work confirms that a contraction of the lattice takes place, and as will be seen from figure 2, the lattice spacing/composition line is slightly curved.

(c) *Solid solutions of magnesium, germanium and silver in aluminium*

The lattice spacing of aluminium is expanded considerably by the solution of magnesium and germanium, and is unaltered by silver. The results obtained are given in table 1, and are shown in figures 1, 2 and 3.

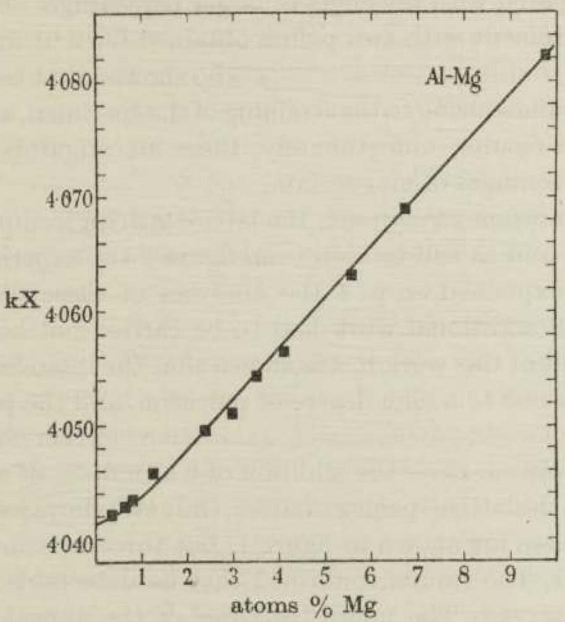

FIGURE 3

In the system *aluminium-magnesium*, the limits of the aluminium-rich solid solution are approximately 16 atomic % magnesium at 450° C, and 3 atomic % magnesium at 200° C. It was found that decomposition during quenching was effectively prevented by cooling in a blast of air. As will be seen from figure 3, ten of the twelve observed points lie on a curve which, after 2 atomic % magnesium, is practically a straight line, but which shows a definite curvature at the lower percentages. The two remaining points lie above and below this line by amounts of the order 0·001 A which is equivalent to 0·25 % on the composition axis. It is thought that most of this discrepancy is due to the analyses rather than to the lattice-spacing measurements, because the films were of good quality and could be measured well. A great deal of attention was given to the question of the curvature at low percentages of magnesium. The form of the lattice/spacing composition curve naturally suggests the presence of an impurity which is removed on alloying, but it would be necessary to assume a value of 4·0404 kX for the lattice spacing of the solvent metal in order to produce a lattice spacing/composition curve which was free from abnormal curvature at low percentages of magnesium. This would be in contradiction to the results of all previous investigators, and would also lead to improbable curvatures in the lattice spacing/composition curves for the other alloys investigated, unless it were assumed that the hypothetical impurity remained constant in these. No convincing explanation based on errors in analysis could be found to explain the abnormal curvature, and in general the synthetic and analyzed composition of the specimens were in good agreement. It seems, therefore, that additions of less than 1 atomic % of magnesium produce a slightly smaller expansion in the lattice as compared with the effect of larger percentages. The present results are in very good agreement with two points obtained for 6·61 and 9·01 atomic % magnesium by Brick, Phillips & Smith (1935), who showed that the use of quenched rods gave erroneous values owing to the straining of the specimen, although quenched filings gave accurate results; unfortunately, these investigators did not examine alloys with lower percentages of magnesium.

In the system *aluminium-germanium*, the lattice spacing/composition relation is very slightly curved, and as will be seen from figure 2 the experimental points are quite consistent. As explained on p. 4 the analyses of these filings gave rise to difficulties, and much additional work had to be carried out before the problem was solved. As a result of this work it was shown that the intended compositions of these alloys were attained to a high degree of precision, and the point marked with an open square which refers to an unanalyzed specimen has therefore been included.

In the system *aluminium-silver* the addition of 6 atomic % of silver produces no measurable change in the lattice spacing of silver. Only two alloys have been analyzed, and the points for these are shown in figure 1, but three measurements were also made for other alloys. The results confirmed that no detectable change in lattice spacing could be observed. The microstructures of the annealed and quenched alloys were therefore examined, and were found to indicate a homogeneous solid solution. The constancy of the lattice spacing appears therefore to be a genuine characteristic of the solid solution, and does not indicate a negligibly small solid solubility of silver in aluminium. This was confirmed by the absence of extra lines on the X-ray films.

4. Discussion

(*a*) *The apparent atomic diameters*

The results described in § 3 show clearly that the lattice spacing of aluminium is expanded by the solution of magnesium and germanium, and contracted by the solution of lithium. silicon, copper and zinc. In the alloys with silicon, copper and silver the lattice spacing/composition curves are straight lines, and if these are extrapolated to 100 atomic % of solute we obtain what may be called the apparent lattice spacings a of the solute in a hypothetical face-centred cubic structure, and the corresponding *apparent atomic diameters* are equal to $\frac{1}{2}(a\sqrt{2})$; we shall use the abbreviation A.A.D. for this quantity. In the alloys with lithium and zinc, the lattice spacing/composition curves are not exactly straight lines, but the curvature is so slight that tangents can easily be drawn to the curves at zero concentration of the solute, and the corresponding A.A.D. values can be obtained. In the alloys with magnesium, the abnormal curvatures referred to on p. 8 makes the above treatment less certain, and we have therefore estimated two A.A.D. values, one referring to the curve at zero concentration, and the other to the almost linear portion of the curve.

In this way the A.A.D. values for the above elements, when dissolved in aluminium, can be obtained, and existing data enable us to deduce the corresponding A.A.D. values for Al, Si, Zn, Ge and Ag when dissolved in copper, and for Mg, Al, Cu, Zn and Ge when dissolved in silver, and for Al, Cu, Zn and Ge when dissolved in gold. Since copper, silver and gold are univalent solvents the first Brillouin zone is only half filled, and the A.A.D. values deduced from the lattice spacings of dilute solutions are therefore free from any complications resulting from B.Z.* effects, and refer to a crystal structure (face-centred cubic) which is the same as that of aluminium. For solid solutions in magnesium the variation of the a-spacing with composition enables A.A.D. values to be obtained for lithium, aluminium and silver. These refer to a condition after a B.Z. overlap,† and since the crystal structure is normal close-packed hexagonal ($c/a = 1{\cdot}6235$), the co-ordination number is 12 as in the face-centred cubic structure. For abbreviation we use the symbol a to denote the distance between an atom and its six neighbours in the basal plane, and the symbol d for the distance between an atom and its six other close neighbours, three in the layer above and three in the layer below. In the ideal case where the axial ratio equals $\sqrt{(\frac{8}{3})}$, a and d are equal.

The above procedure enables us to compare A.A.D. values of the elements concerned when in dilute solid solution in univalent copper, silver and gold, divalent magnesium and trivalent aluminium. All these solvents crystallize with structures of co-ordination number 12, and so far as the crystal structures of the solvents are concerned, the conditions for comparison are favourable, and comparison may also be made directly with the atomic diameter (A.D.) values (i.e. the closest distances of approach) in the crystals in the elements aluminium, magnesium, copper, silver and gold.

Lithium crystallizes in the body-centred cubic structure of co-ordination number 8, whilst silicon and germanium crystallize in the diamond type of structure of co-ordination number 4, and it is clear that the different co-ordination numbers introduce a further complication in comparing the A.D. and A.A.D. values. According

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[*] For abbreviation the letters B.Z. are used for Brillouin zone.

[†] The variation of c-spacing in solid solution in magnesium cannot be used to calculate A.A.D. values because as little as 1 atomic % of a trivalent element causes a new B.Z. overlap in this direction (see Hume-Rothery & Raynor 1940; Raynor 1942).

to Goldschmidt contractions of 4 and 12 % result from changes of co-ordination number 12→8 and 12→4 respectively. Examination of the original Goldschmidt papers (1928) shows that many of the so-called Goldschmidt atomic diameters were obtained from X-ray crystal data for metallic phases which are now known to involve B.Z. overlaps, so that the whole position is much more complicated than was originally imagined (see p. 15). The above contractions of 4 and 12 % must therefore be regarded only as giving a rough indication of the magnitudes involved, and for this reason we have not tabulated values of the Goldschmidt atomic diameters, although we shall refer to these occasionally. The data obtained are summarized in table 2 which also gives the A.A.D. values of gallium, cadmium, indium and tin referred to later. Examination of table 2 will show that for the solid solutions in aluminium the following principles are apparent:

(*a*) The tetravalent elements silicon and germanium when in solid solution in aluminium give A.A.D. values greater than those for solid solutions of the same elements in univalent solvents, and greater than the A.D. values. The effect is so marked that the A.A.D. values would be greater than the A.D. values increased by 12 %, i.e. greater than the Goldschmidt atomic diameters.

(*b*) The univalent elements lithium, copper and silver when in solid solution in aluminium give A.A.D. values smaller than those for solid solutions in univalent elements, and smaller than the A.D. values; this effect is particularly marked for lithium.

Table 2

	solutes											
solvent	Li	Mg	Al	Si	Cu	Zn	Ga	Ge	Ag	Cd	In	Sn
copper	—	—	2·71	2·59	—	2·70	2·75	2·78	2·95	3·10	3·20	3·26
silver	—	2·94 to 2·95	2·97	—	2·63	2·75	2·83	2·90	—	3·03	3·10	3·18
gold	—	—	2·80	—	2·63	2·74	2·83	2·93	—	3·00	3·07	3·14
magnesium	$a=3·11$	—	2·81	—	—	—	2·83	—	2·64	3·00	3·08	3·13
	$d=3·00$	—	2·85	—	—	—	—	—	2·53	—	3·16	—
aluminium	2·82	3·15 or 3·04	—	2·73	2·51	2·85	—	2·96 or 2·98*	2·86	—	—	—
interatomic distances in element	3·03	3·19	2·86	2·35	2·55	$a=2·66$ $d=2·90$	—	2·44	2·88	—	—	—
co-ordination number in element	8	12	12	4	12	6	—	4	12	—	—	—

Table 2 shows A.A.D. values for solid solutions of

Al, Si, Zn, Ge, Ag, Ga, Cd, In and Sn in copper,
Mg, Al, Cu, Zn, Ge, Ga, Cd, In and Sn in silver,
Al, Cu, Zn, Ge, Ga, Cd, In and Sn in gold,
Li, Al, Ag, Ga, In and Sn in magnesium,
Li, Mg, Si, Cu, Zn, Ge and Ag in aluminium,

together with values for the interatomic distances in elemental crystals of Li, Mg, Al, Si, Cu, Zn, Ge and Ag.

* The two estimates for the A.A.D. value of Ge in Al arise from the curvature of the lattice spacing/composition curve in a manner similar to that already discussed for the solution of Mg in Al.

(*c*) The divalent elements magnesium and zinc when dissolved in aluminium give A.A.D. values which are slightly larger than those for solid solutions in univalent elements. The A.A.D. values from solutions in aluminium are smaller than the distances of approach in the crystals of zinc ($d = 2{\cdot}907$ kX) and magnesium ($d = 3{\cdot}20$ kX) in the direction of the main B.Z. overlaps. The A.A.D. value of zinc from solution in aluminium (2·85 kX) is larger than the *a* distance of approach in the crystal of zinc (2·66 kX); and this point is discussed later.

(*b*) *Vegard's law*

According to Vegard's law (1928) the lattice spacing/composition curve for a solvent and solute of the same crystal structure is a straight line joining the values for the two pure metals, and a similar relation with a correction for effects of co-ordination number exists for the A.D. values when the two metals have different structures. This law was originally (1921) advanced for salts in which oppositely charged ions are drawn together by Coulomb forces until their electron clouds overlap and produce intense repulsive forces which balance the attraction. It was later (1928) extended to metals, and although it is now recognized that many exceptionists exist, there is still a general tendency (cf. Huang 1947) to regard Vegard's law as a valid approximation. It appears to us that this view is incorrect, and that in a metal where the attractive forces are due to the electron gas, it is only in exceptional circumstances that we shall expect Vegard's law to hold. We may illustrate the principles involved by considering the solid solution of lithium in aluminium. Lithium itself crystallizes in the body-centred cubic structure with $a = 3{\cdot}50$ kX, and A.D. $= 3{\cdot}03$ kX. The Li^+ ion is very small compared with the closest distance of approach between two lithium atoms, so that the ions play a negligible part in determining the interatomic distances. The volume per valency electron, for which we may use the symbol V_e,* is 21·5 $(kX)^3$, so that the electron gas of the valency electrons is very dilute. The detailed calculations of Bardeen (1938) show that the electron density of the valency electrons is reasonably constant over a large fraction of the total volume, and that it is only near to the ions that the nodes, etc., of the wave function produce marked variations in the valency electron density. The metal has a high compressibility ($K = 8{\cdot}9 \times 10^{12}$ dynes/cm.^{2}) which is due mainly to the valency electrons, and only affected very slightly by the extremely small ionic overlap. We may therefore regard the crystal of metallic lithium as consisting of small Li^+ ions swimming in a very dilute valency electron gas, which is responsible both for the attraction holding the structure together, and for the repulsion which gives rise to the resistance to compression. As the attractive forces are due to the electron gas as a whole we cannot think of directed forces between adjacent atoms, but we may perhaps represent the relations involved by a model such as that of figure 4. In this figure the different atoms are represented by squares

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* For abbreviation we shall omit the units $(kX)^3$ in referring to the V_e values of different elements.

held together by very weak springs,* V_a representing the weak attraction of the dilute valency electron gas, and held apart by the very weak springs V_r representing the repulsion due to the valency electron gas. The much stronger springs I_r represent the repulsion of the electron clouds of the ions which is not yet effective because of the large interatomic distances. The interatomic distance 3·03 kX in lithium refers to a body-centred cubic structure, but the general condition of affairs would be the same in a hypothetical face-centred cubic structure, for which Goldschmidt's co-ordination factors would give an interatomic distance of 3·12 kX.

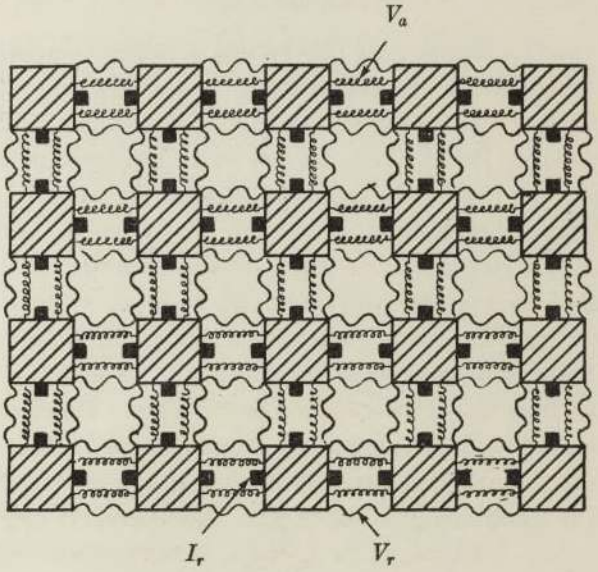

FIGURE 4

In the face-centred cubic structure of aluminium A.D. = 2·86 kX and the atoms are closer together than in lithium. There are now three valency electrons per atom, and V_e = 5·51, so that the valency electron gas is on the average about four times as concentrated in aluminium as in lithium. This concentrated electron gas is also less uniformly distributed than the dilute electron gas in lithium or sodium. As we proceed along the series Na → Mg → Al, the V_e values become progressively smaller, and the valency electron densities progressively greater, and at the same time the valency electrons tend to be more concentrated near to the ions. The melting-point of aluminium (659° C) is much higher than that of lithium (152° C), whilst its compressibility is much lower ($K = 1{\cdot}37 \times 10^{12}$ dynes/cm.^{2}). The attractive and repulsive forces are thus much stronger in aluminium, and are due mainly to the valency electrons, for the Al^{+++} ionic radii are smaller than the distances between the atoms in metallic aluminium, although the ionic overlap is greater than in an alkali metal. We may therefore represent the condition of affairs in aluminium by a diagram such as that of figure 5, where the valency attractive springs V_a and repulsive springs V_r

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* The springs will be non-linear and will not obey Hooke's law.

are much stronger than the corresponding springs in figure 4 for lithium, and the ionic repulsion springs are more nearly touching.

We can now readily understand why the A.A.D. of lithium (2·82 kX) when dissolved in aluminium is so much smaller than the A.D. value (3·03 kX). For the A.D. value of 3·03 kX refers to the equilibrium of the very weak forces represented by the weak springs of figure 4, but when one of these atoms is substituted for an aluminium atom, the much stronger forces of the aluminium lattice, represented by the stronger springs of figure 5, will cause an almost complete collapse of the weak springs. In this connexion there is a difference between the behaviour of a 1-dimensional row, and a 2- or 3-dimensional lattice. In a 1-dimensional row, a single atom could exert its own influence, but in 2- or 3-dimensional lattices a distortion round one atom affects the interatomic distances between other atoms. We can therefore understand why the A.A.D. (2·82 kX) of lithium when dissolved in aluminium is nearly the same as the A.D. of aluminium itself (2·86 kX), and since the ion of lithium is smaller than the ion of aluminium we can perhaps also understand why the A.A.D. of lithium in aluminium is slightly smaller than 2·86 kX.

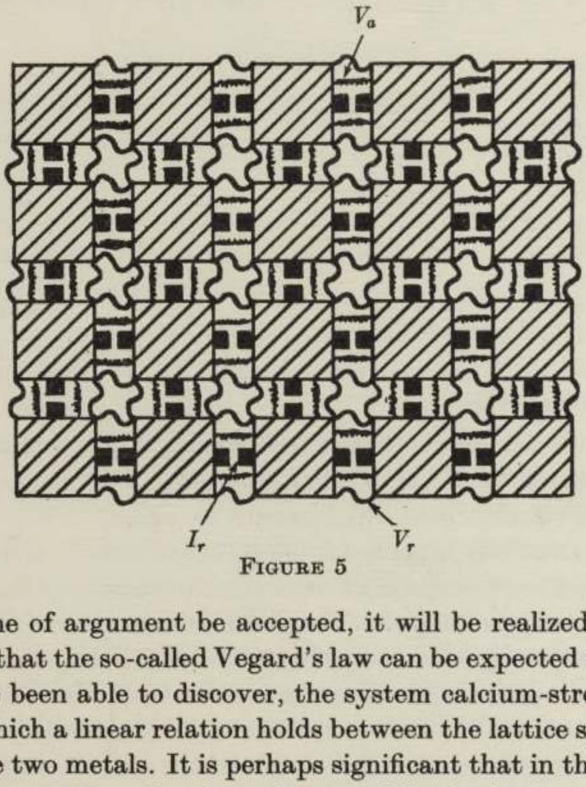

FIGURE 5

If the above line of argument be accepted, it will be realized that it is only in exceptional cases that the so-called Vegard's law can be expected to hold for metals. So far as we have been able to discover, the system calcium-strontium is the only alloy system in which a linear relation holds between the lattice spacing and atomic percentages of the two metals. It is perhaps significant that in this case the V_e value for strontium is larger than that for calcium, whilst its ionic radius is also larger. When strontium is dissolved in calcium we expect the valency electron effect to produce a smaller A.A.D. for the same reason as that described above for lithium in aluminium, but the larger ion of strontium may produce a counterbalancing expansion.

(c) *Factors controlling the apparent atomic diameters*

The exact A.A.D. values of one metal in different solvents will clearly depend on the exact details of the atomic fields and cannot be predicted, but we suggest that a general interpretation may be obtained by considering the following controlling factors.

(1) *The V_e effect*

In the above description we have seen why the A.A.D. of lithium when dissolved in aluminium is so much smaller than the A.D. for metallic lithium. In this case the V_e values for lithium and aluminium are 21·7 and 5·5 respectively. The V_e values for the remaining elements are given in table 3, and we suggest that as a first approximation these may be used to indicate the direction of effects analogous to those described for lithium and aluminium. That is to say, if the V_e value of the solute is greater than that of the solvent, we expect the A.A.D. to be made smaller, and, conversely, if the V_e of the solvent is larger than that of the solute we expect the A.A.D. to be made larger. This simple effect may then be obscured by the complicating factors described below.

TABLE 3

element	V_e for co-ordination no. 12	element	V_e for co-ordination no. 12
Li	21·7	Ga	c. 6–7
Cu	11·7	In	c. 8–9
Ag, Au	17·0	Si	3·2
Mg	11·6	Ge	3·6
Zn	6·7	Sn	5·6 grey tin
Cd	9·0		5·5 white tin
Al	5·51		

(2) *The effect of ionic radius*

We suggest that if the ionic radius of the solute is larger than that of the solvent, the effect is to increase the A.A.D. of the former, and, conversely, if the ionic radius of the solute is the smaller, its A.A.D. tends to be smaller. This effect is, however, only marked if a relatively large ion is being forced into a structure in which its electron cloud begins to overlap the electron cloud of the *ions* of the solvent, e.g. when silver is dissolved in copper. Figure 6 shows the univalent ionic radii of the elements concerned, and these may be taken (Hume-Rothery & Raynor 1940) as the least unsatisfactory values if the 'size' of an ion is to be represented by a single number; they must not, of course, be taken to indicate a sharp boundary surface to the ion. Thus in metallic copper, the electron clouds of the ions overlap appreciably, and are responsible for the low compressibility, although the univalent radius of the Cu^+ ion is only 0·96 kX as compared with a half distance of approach of 1·27 kX. It has also been emphasized (Hume-Rothery & Raynor 1938) that in the elements following an alkali metal (e.g. Na→Mg→Al→Si) the electron clouds of the ions shrink less rapidly than the interatomic distances, so that the crystal structures become less 'open' with increasing valency, whereas in the elements following copper, silver and gold (e.g. Cu → Zn → Ga → Ge) the ion shrinks the more rapidly and the structures become increasingly more open.

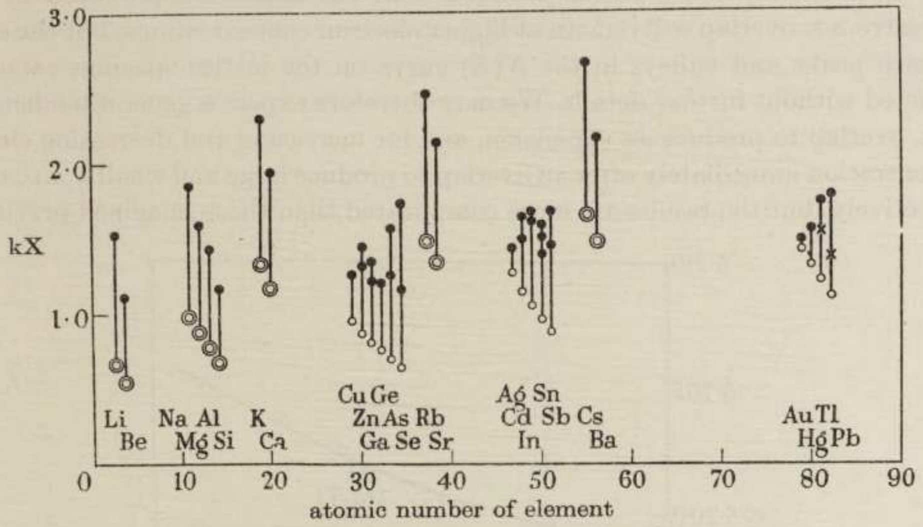

FIGURE 6. Atomic and ionic radii of the elements. (Reproduced from *Phil. Mag.* 1938, **26**, 136.) ● ½ (interatomic distance in the crystal of the element). ◎ Zachariasen univalent ionic radii. ○ Pauling univalent ionic radii. × Goldschmidt empirical ionic radii.

(3) *The effects of Brillouin zone overlaps*

It has been shown by Jones (1934) that the effect of a B.Z. overlap is to produce an expansion of the crystal in the direction concerned. Hume-Rothery & Raynor (1940) and Raynor (1942) have shown that when 3- and 4-valent elements are dissolved in magnesium, the lattice spacing/composition curves for the a-spacings are smooth, whilst those for the c-spacings show a kink in the direction of an expansion after a small percentage of solute (see figure 7). This was taken to imply that in pure magnesium a B.Z. overlap had already occurred in the a direction, but not in the c direction, although the latter overlap occurred after a very slight increase in the electron concentration. Hume-Rothery & Raynor suggested that the A.D. in aluminium (2·86 kX) was greater than its A.A.D. when dissolved in copper (2·71 kX) and silver or gold (2·79–2·80 kX), because no B.Z. overlap was concerned in the univalent solutes. From table 2 it is clear that the position is not really so simple: thus the A.A.D. value for indium dissolved in magnesium (3·08 kX) is almost the same as the values (3·07, 3·11 kX) for solutions in gold and silver,* whilst the A.A.D. value for gallium dissolved in magnesium (2·83 kX) is smaller than those (2·835, 2·838 kX) for solutions in silver and gold. It is, of course, clear that with a lattice spacing/composition curve such as that of figure 7, extrapolation of the curve immediately after the overlap will give a higher A.A.D. for the element of higher

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* The solid solution of indium in copper is affected by the overlapping of the ions as described below.

valency than the A.A.D. obtained by extrapolation of the curve immediately before the overlap, and similarly extrapolation of a curve after an overlap will give a lower A.A.D. value for the element of lower valency. If we consider a continually increasing electron concentration, it seems probable that the expansion produced by each successive B.Z. overlap will remain at higher electron concentrations, but the effects of sharp peaks and valleys in the $N(E)$ curve on the lattice spacings cannot be predicted without further details. We may therefore expect a general tendency for a B.Z. overlap to produce an expansion, and for increasing and decreasing electron concentration immediately after an overlap to produce large and small A.A.D. values respectively, but the results are more complicated than those imagined previously.

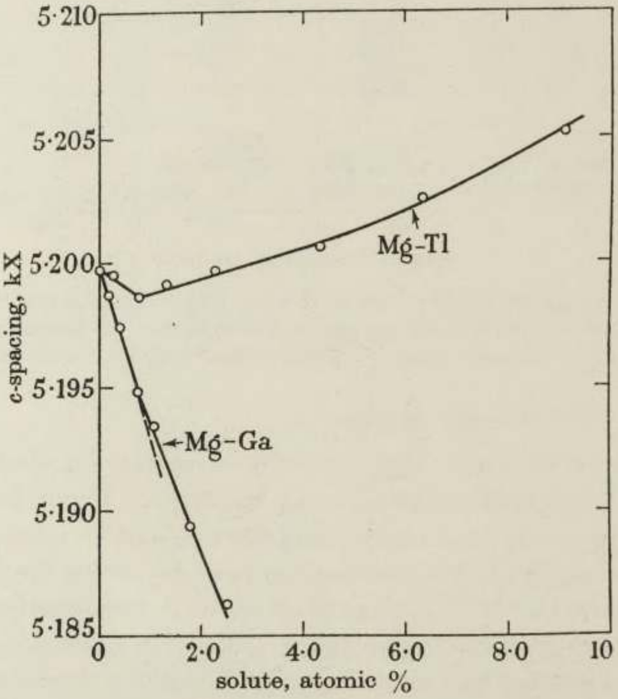

FIGURE 7

When we consider the lattice spacing/composition curves for 3- and 4-valent solutes in magnesium, extrapolation of the a-spacing curve, and of the c-spacing curve *after the kink*, will give us a and c values for a hypothetical structure with B.Z. overlaps in both a and c directions, and the corresponding A.A.D. values can be calculated for the a and d distances of approach. The c-spacing curve before the kink is too short for extrapolation. In contrast to this if we consider the corresponding curves for a *univalent* metal dissolved in magnesium, extrapolation will give us a and c values for a structure with no overlap in the c direction.

In the earlier papers of Hume-Rothery & Raynor it was assumed that the condition of affairs in aluminium was one following after the (200) B.Z. overlap of the face-centred cubic structure, since this was what was indicated by the simple B.Z.

theory of Mott & Jones (1937). It has lately been shown by Matyas* that the symmetry of the s and p states results in an $N(E)$ curve of the type shown in figure 8 in which, although the first zone is very nearly filled, the (200) overlap has not taken place. The unoccupied states in the first zone lie in thin slabs parallel to the (200) faces of the zone. This condition of affairs is quite different from that of the simple theory of electrons in the face-centred cubic structure, according to which the occupied states would have reached to, and spread out from, the centres of the (200) faces.

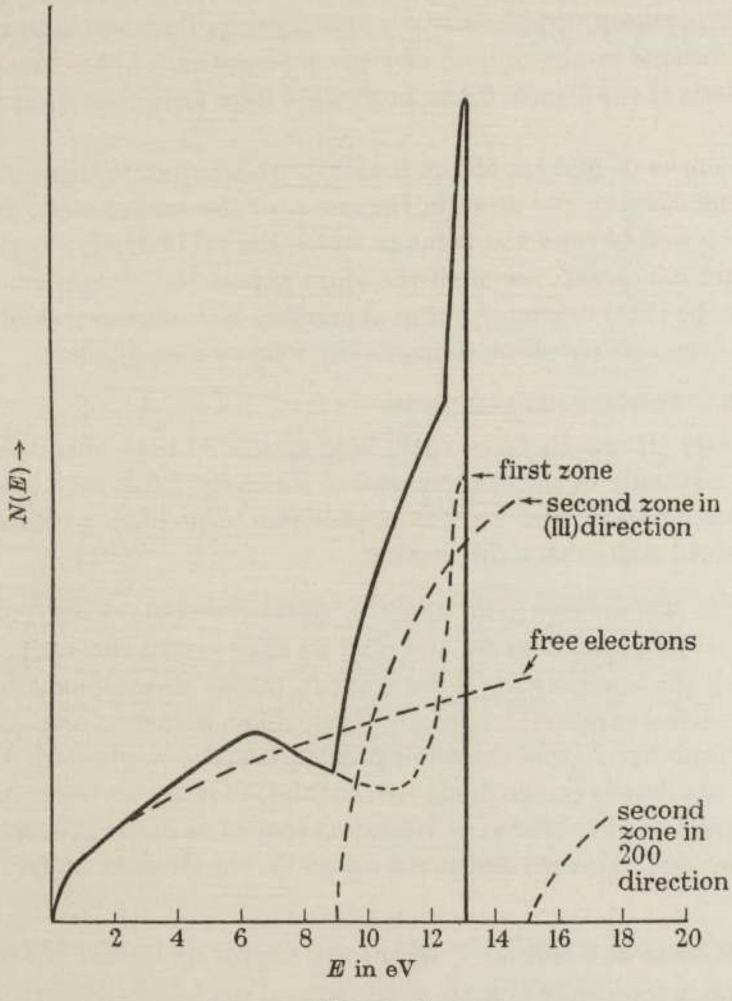

FIGURE 8

The new $N(E)$ curve is of very great interest, and offers one explanation of the scarcity of elements which form wide solid solutions in aluminium. For with elements of both higher and lower valencies, the formation of an appreciable solid solution would alter the electron concentration so that the latter corresponded to

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* We have to thank Dr Matyas for allowing us to use these results.

a lower position on the $N(E)$ curve, and hence to a structure which became relatively less stable compared with other possible structures whose $N(E)$ curves remained high. Actually the various equilibrium diagrams suggest that at low temperatures no element forms an appreciable solid solution in aluminium, whilst at high temperatures zinc is the only element whose solubility exceeds 20 atomic %. The complete absence of any solid solutions at low temperatures is not explained by the above $N(E)$ curve, since with a slight solid solution the electron concentration would still correspond to a relatively high position on the $N(E)$ curve. There is also no obvious reason why the trivalent elements gallium and indium do not form wide solid solutions in aluminium, and the explanation of this must presumably lie in the details of the atomic fields, as distinct from simple electron concentration effects.

The $N(E)$ curve of Matyas shows that in pure aluminium there will be slightly more than one electron per atom in the states of the second zone, and the Fermi surface will lie well beyond the point at which the (111) overlap begins. So far as B.Z. effects are concerned, we shall therefore expect the aluminium lattice to be expanded by the (111) overlap,* but in aluminium-rich alloys we shall not be in the region of electron concentration immediately following an overlap.

(4) *The effect of the electrochemical factor*

It has already (Hume-Rothery 1946) been suggested that when the solvent and solute differ markedly in the electrochemical series the effect is to introduce forces of a partly ionic nature, and we may expect this to produce a contraction of the lattice which will make the A.A.D. smaller.

(*d*) *Detailed examination of the apparent atomic diameters in different solvents*

If the preceding arguments are accepted we may expect the A.A.D. values to be determined by the interplay of (1) the V_e effect, (2) the effect of ionic radius, (3) the electrochemical factor and (4) B.Z. effects. These different factors may either reinforce or oppose one another, so that the whole problem is very complicated. No suggestion is made that the details can be predicted, but the following tentative interpretation of the figures in table 2 is offered as indicating that some of the principles have been correctly identified. For convenience we may divide the data under the following sub-headings.

Solid solutions in which the V_e effect tends to produce a small A.A.D. *value*

Of the systems concerned in table 4, the general tendency is clearly for the A.A.D. to be smaller than the A.D. An exception is presented by the solid solution of silver in copper, and this is the only case in which the formation of the solid solution involves the forcing of a larger ion into a structure which is already of the full type. This is therefore the system in which the effect of a larger ionic radius in producing an expansion is likely to be the greatest, and we can understand why the A.A.D. is 0·07 kX greater than the A.D.

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* Hume-Rothery & Raynor argued on the assumption of both (111) and (200) overlaps.

For the solid solution of lithium in magnesium the A.A.D. values are $a = 3{\cdot}11$, and $d = 3{\cdot}00$ kX, as compared with an A.D. value 3·03 kX. This last value refers to a co-ordination number of 8, and if we use the Goldschmidt correction factor for change of co-ordination no. 12 → 8, the value for a hypothetical face-centred cubic modification of lithium would be 3·13 kX. The A.A.D. values for lithium dissolved in magnesium are thus smaller than the A.D. value when corrected for co-ordination number. The magnesium-lithium data are from work by Hofmann (1936), and the experimental errors probably give too large* A.A.D. values, so that the actual difference between the A.A.D. and corrected A.D. values may be greater than that given.

TABLE 4

solute and V_e	solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Li 21·7	Al 5·5	contract	2·825	3·03
Li 21·7	Mg 11·6	contract	$a = 3{\cdot}11$ $d = 3{\cdot}00$	3·03
Cu 11·7	Al 5·5	expand	2·51	2·55
Ag 17·0	Al 5·5	expand	2·86	2·88
Ag 17·0	Mg 11·6	expand	$a = 2{\cdot}64$ $d = 2{\cdot}53$	2·88
Ag 17·0	Cu 11·7	large expansion: ionic overlap	2·95	2·88
Mg 11·6	Al 5·5	expand	3·04 or 3·15	$a = 3{\cdot}19$ $d = 3{\cdot}20$
Zn 6·7	Al 5·5	expand	2·85	$a = 2{\cdot}66$ $d = 2{\cdot}91$

For the solid solution of zinc in aluminium the V_e value of the solvent is only slightly less than that of the solute, so that we expect the V_e effect to be small. The effect of the ionic radius will also be small but tends to produce an expansion. The A.A.D. value of 2·85 kX lies between the two sets of interatomic distance in zinc, but the crystal structure of the latter is so abnormal that detailed comparison is hardly justified.†

Solid solutions of copper, zinc, cadmium, gallium, indium, germanium and tin in silver, copper and gold, and of copper in silver; in these systems the V_e effect tends to produce a large A.A.D.

The data for these systems are shown in table 5. For the solid solutions of zinc, gallium and germanium in copper, silver or gold, the V_e effect leads us to expect a large A.A.D., the expansion becoming greater with increasing valency. We can there-

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* The lithium used contained sodium and potassium, which may cause an expansion of the magnesium lattice. Further, any oxidation of the specimens would tend to give too large a lattice spacing, and no precautions against this source of error are described.

† In zinc the main B.Z. overlap is in the c direction, and there is a second and smaller overlap in the basal plane. The main overlap expands the crystal in the direction of the c-axis, and the elastic constants are such that this specimen tends to contract the distances in the basal plane, by an effect analogous to that of the Poisson ratio. The value $a = 2{\cdot}66$ kX is thus probably smaller than if no B.Z. overlaps had occurred.

fore understand why the A.A.D. values for a series such as (Cu → Zn → Ga → Ge) when dissolved in copper, silver or gold increases with the valency. Since the V_e of copper (11·7) is smaller than that of silver and gold (17·0), the V_e effect will tend to produce a greater expansion for solid solutions in the latter metals, and as will be seen from table 5 the A.A.D. values of zinc, gallium and germanium from solid solutions in silver and gold are uniformly greater than those from solid solutions in copper, so that the general interpretation is confirmed. The same explanation may be offered for the fact that when copper is dissolved in silver, the A.A.D. of copper (2·64 kX) is greater than the A.D. in copper itself (2·55 kX).

Table 5

solute and V_e	solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Cu 11·7	Ag 17·0	contract	2·64	2·55
Cu 11·7	Au 17·0	contract	2·63	2·55
Zn 6·7	Cu 11·7	contract	2·70	$a = 2·66$ $d = 2·97$
Zn 6·7	Ag 17·0	contract	2·75	$a = 2·66$ $d = 2·97$
Zn 6·7	Au 17·0	contract	2·74	$a = 2·66$ $d = 2·97$
Ga c. 6	Cu 11·7	contract	2·75	abnormal structures with distances from 2·44 to 2·79 kX
Ga c. 6	Ag 17·0	contract	2·835	
Ga c. 6	Au 17·0	contract	2·84	
Ga c. 6	Mg 11·7	very slight	2·83	
Ge 3·6	Cu 11·7	contract	2·78	2·44
Ge 3·6	Ag 11·7	contract	2·90	2·44
Ge 3·6	Au 11·7	contract	2·93	2·44
Cd 9·0	Cu 11·7	large expansion: ionic overlap	3·10	$a = 2·97$ $d = 3·29$
Cd 9·0	Ag 17·0	contract	3·04	$a = 2·97$ $d = 3·29$
Cd 9·0	Au 17·0	contract	3·00	$a = 2·97$ $d = 3·29$
In c. 8	Cu 11·7	expand: ionic overlap	3·21	3·24 3·37
In 8	Ag 17·0	contract	3·11	see p. 21
In 8	Au 17·0	contract	3·07	see p. 21
In 8	Mg 11·6	expand	$a = 3·08$ $d = 3·16$	
Sn 5·5	Cu 11·7	expand: ionic	3·27	2·80 grey
Sn 5·5	Ag 17·0	contract	3·18	3·02 3·18 white
Sn 5·5	Au 17·0	contract	3·14	—

Comparison with the interatomic distances in crystals of zinc, gallium and germanium is not so simple. The A.A.D. values of zinc when dissolved in copper, silver and gold are smaller than the distance of approach $d = 2·97$ kX in the crystal of zinc, and this can be understood because the latter involves the main B.Z. overlap. The value $a = 2{\cdot}66\,\text{kX}$ for the closest distance of approach in the basal plane is affected by the curious elastic properties of the zinc crystal, and can hardly be compared directly with any of the other values.*

In the complicated crystal structure of gallium, the distances of approach vary from 2·44 to 2·79 kX, and the V_e effect has produced the expected relatively large A.A.D. values. In germanium, the crystal structure is of the diamond type with A.D. 2·44 kX. The A.A.D. values for germanium when dissolved in copper, silver and gold vary from 2·78 to 2·93 kX, and are thus larger than the A.D. by more than the 12 %, which Goldschmidt postulated on the effect of a change in co-ordination number 12 → 4. The V_e principle is thus strikingly confirmed, particularly when it is remembered that the A.A.D. values from solutions in univalent solvents are not affected by B.Z. overlaps, whereas the A.D. value of 2·44 kX for germanium includes the effect of B.Z. overlapping.

For the solid solutions of silver, cadmium, indium and tin in copper, silver and gold, the effect of ionic radius is now different. The ions of cadmium, indium and tin are smaller than those of silver and gold, just as the ions of zinc, gallium and germanium are smaller than those of copper. The ions of cadmium, indium and tin are, however, larger than, or at least equal* to, the ions of copper, so that the formation of a solid solution in copper results in the insertion of a larger ion into an already full structure, and we suggest that it is for this reason that the A.A.D. values of cadmium, indium and tin, when dissolved in copper, are larger than when dissolved in silver or gold; the effect is the same as that for silver when dissolved in copper (see p. 18). If this interpretation is correct, the system silver-copper is of interest in that the large A.A.D. value of copper in silver is the result of the V_e effect, whilst the large A.A.D. value of silver in copper is due to the effect of ionic radius.

The relations between the A.A.D. values for cadmium in the univalent solvents, and the A.D. values in metallic cadmium are analogous to those described above for zinc. In the case of indium, the A.D. values ($d_1 = 3{\cdot}24$, $d_2 = 3{\cdot}37\,\text{kX}$) in the element are slightly greater than the A.A.D. values in the univalent solvents, and for solution in divalent magnesium. According to Raynor (1940*a*) this is due to the existence of incomplete ionization in the element. It was not, however, clear why the A.A.D. values of indium from solutions in univalent silver and gold (3·11 and 3·07 kX) were as large as the A.A.D. value ($a = 3{\cdot}08$, $d = 3{\cdot}16$) for solution in magnesium, for the latter refers to a position shortly after a B.Z. overlap, whereas the former does not. The data in table 5 show that the V_e effect is greater for the solutions in silver and gold, and so the large A.A.D. values are explained. The same explanation accounts for the fact that the A.A.D. value of gallium dissolved in silver or gold is as large as the A.A.D. values for the solution in magnesium. But when gallium is dissolved in copper (V_e 11·7) the solvent has almost exactly the same V_e as magnesium

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* See footnote on p. 19.

† The solid solubilities of indium and tin in copper indicate that the effect of the ionic overlap is considerable (see Hume-Rothery 1946).

(V_e 11·6), and consequently the V_e effects are the same, and the A.A.D. for the solution in magnesium (2·83 kX) is larger than that for the solution in copper (2·75 kX) because of the effect of the B.Z. overlap in magnesium.*

When tin is dissolved in copper, silver or gold the V_e effect indicates an expansion, and the larger A.A.D. in copper is the result of the ionic radius of tin being of the same order as that of copper, but smaller than those of silver and gold. The A.A.D. values for the solution in silver and gold are considerably greater than the A.D. (2·80 kX) in grey tin, and slightly greater than this value corrected for the Goldschmidt co-ordination effect.

TABLE 6

solute and V_e	solvent and V_e	effect of ionic radius	A.A.D.	A.D.
Mg 11·6	Ag 17·0	contract	2·94	$a = 3·20$ $d = 3·19$
Al 5·5	Cu 11·7	contract	2·71	2·86
Al 5·5	Ag 17·0	contract	2·79	2·81
Al 5·5	Au 17·0	contract	2·80	2·86
Al 5·5	Mg 11·6	contract	$a = 2·81$ $d = 2·85$	2·86
Si 3·2	Cu 11·7	contract	2·60	2·35
Si 3·2	Al 5·5	contract	2·73	2·35
Ge 3·6	Al 5·5	?	2·97	2·44

Solid solutions of magnesium, aluminium and silicon not previously discussed

The data for these systems are shown in table 6, and the following interpretation may be offered.

When magnesium ($V_e = 11·6$) is dissolved in silver ($V_e = 17·0$) the V_e effect indicates an expansion, which will be opposed by the relatively strong electrochemical factor, and by the effect of ionic radius. The resulting A.A.D. refers to a solid solution in which there is no B.Z. overlap, and we can understand why the resulting value is smaller than the interatomic distances $a = 3·20$ kX, $d = 3·19$ kX in pure magnesium.

When aluminium is dissolved in copper, silver or gold, the V_e effect indicates an expansion which is greater for the solutions in silver and gold. We suggest that it is for this reason that the A.A.D. values in silver and gold (2·79 and 2·80 kX) are greater than that for aluminium in copper (2·71 kX). The ionic radius effect indicates an opposing tendency which is greater for the solutions in silver and gold, but since this is a contraction it is a relatively small effect. All these figures refer to A.A.D. values for a univalent solvent in which B.Z. complications are absent, and as pointed out by Hume-Rothery & Raynor (1940), it is for this reason that they are smaller than the A.D. of aluminium itself (2·86 kX) in which a B.Z. overlap has occurred.

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* As explained above this condition of affairs does not apply to solutions of indium in copper and magnesium, because the solution in copper involves a greater increased ionic overlap.

When aluminium is dissolved in magnesium, the V_e effect indicates an expansion, and the ionic radius effect a slight contraction. The solution of aluminium in magnesium results in an increase in the electron concentration shortly after a B.Z. overlap, and we can understand why the A.A.D. values of $a = 2{\cdot}81$, $d = 2{\cdot}85$ are greater than the A.A.D. values in copper, silver and gold. Comparison with the A.D. in aluminium itself is clearly not simple, because both aluminium and magnesium involve B.Z. overlaps.

For the solid solutions of silicon in copper and aluminium the V_e effect indicates an expansion, which is opposed by the relatively small effect of ionic radius. The A.A.D. of silicon dissolved in copper is free from B.Z. overlap effects, and it may be for this reason that the value (2·60 kX) is smaller than the corresponding value (2·73 kX) for the solution in aluminium where the solvent has already been expanded by one B.Z. overlap. Both these values are much greater than the A.D. of silicon (2·35 kX) which refers to a crystal structure of co-ordination number 4. If this is increased to allow for the Goldschmidt change in co-ordination number, the resulting value is 2·66 kX. The A.A.D. value for the solution in aluminium is greater than this, so that a very considerable expansion has occurred. The A.A.D. value from the solution in copper is 0·06 kX less than the Goldschmidt value, and this may be because the value 2·35 kX for elementary silicon is itself expanded by a B.Z. overlap.*

When germanium is dissolved in aluminium the V_e effect produces an expansion, and the A.A.D. (2·97 kX) is greater than the A.D. (2·44 kX) and greater than the latter corrected by the Goldschmidt co-ordination factor. In this case, as with silicon, both aluminium and the A.D. of the solute involve B.Z. overlaps, and we can understand why the A.A.D. is large, and why it is larger than the corresponding values for solid solutions in copper, silver and gold which were dealt with above.

5. CONCLUSION

As emphasized before, no claim is made that the exact A.A.D. values can be predicted, but it does appear that the values from the different solid solutions given in table 2 can be understood satisfactorily by consideration of the four factors outlined in subsection (*c*) above. In particular, the influence of what we have called the V_e effect is very striking, and the systems in which it is not the controlling factor are clearly those in which overlapping ions, or Brillouin zone effects, are present.

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* Since silicon contains 4 valency electrons per atom there must be at least one B.Z. overlap.

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