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The Crystal Chemistry of the Laves Phases

By R. L. Berry

Department of Metallurgy, University of Birmingham, Edgbaston, Birmingham 15, *England*

and G. V. Raynor*

Institute for the Study of Metals, University of Chicago, Chicago 37, *Illinois, U.S.A.*

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The C_{14}(MgZn$_2$), C_{15}(MgCu$_2$) and C_{36}(MgNi$_2$) crystal structures frequently occur at the composition AB_2 in alloy systems for which the ratio of the atomic radii of the components is approximately 1·2. In certain ternary magnesium alloys interesting structural changes from one type to another occur as other metals are substituted for zinc and copper in MgZn$_2$ and MgCu$_2$ respectively. In an attempt to understand these changes, and the factors determining which of the closely related structures is assumed in a given case, an examination has been made of the interatomic distances in phases for which data are available. A parameter S which measures the deviation of particular interatomic distances (d_{AA} or d_{BB}) from the corresponding distances in the pure components (d_A or d_B) is plotted against $W = d_A/d_B$. For series of phases with common A or B components, the relationship between W and S is approximately linear. If W lies close to the ideal value for the formation of a Laves phase, S is small, and hexagonal C_{14} structures occur. As W deviates from the ideal value, S increases numerically, and cubic C_{15} structures occur. This suggests that, for a given series of phases with common A or B components, the C_{14} structure is not in general stable above or below a critical W value. When the B component is a transitional metal, more complex graphs are obtained; there is evidence in these cases for relatively strong A–B interactions. Assuming that increasing S favours the C_{15} structure, and taking into account the effect of changing Fermi energy, an interpretation of the structural changes observed in ternary magnesium alloys is possible. The considerations outlined in this paper should help in the prediction of Laves phases in alloy systems as yet not investigated.

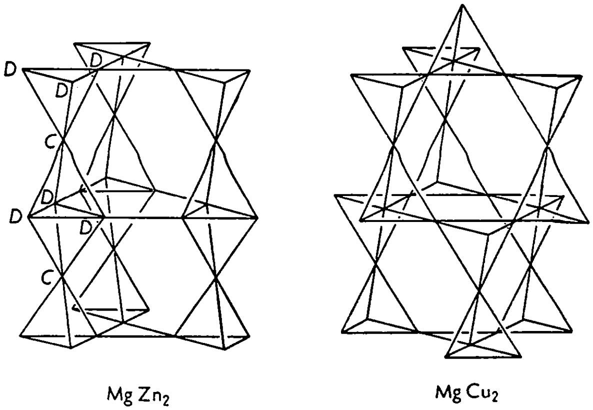
1. Introduction

Many intermetallic compounds of composition AB_2 crystallize in one of three closely related structures. These are:

(i) The C_{14} structure, typified by the phase MgZn$_2$: hexagonal.
(ii) The C_{15} structure, typified by the phase MgCu$_2$: cubic.
(iii) The C_{36} structure, typified by the phase MgNi$_2$: hexagonal.

These compounds, the 'Laves phases', involve the association of large A atoms and small B atoms. Since the ratio of the atomic diameters of the components d_A/d_B is approximately 1·2, the phases are regarded as controlled essentially by atomic size relationships. This interpretation is supported by the observation that the A and B components may be taken from any group of the Periodic Table, while the same element may form either the A or the B component in different compounds. Lists of known Laves phases have been published (Smithells, 1949; Raynor, 1949).

The structures may be described in terms of hexagonal lattices, in which the atomic arrangement leads to the assumption of axial ratios in the proportions 2:3:4 for MgZn$_2$, MgCu$_2$ and MgNi$_2$ respectively. In each case B atoms occupy the corners of tetrahedra, joined alternately point-to-point and base-to-base in MgZn$_2$, but point-to-point throughout in MgCu$_2$ (Fig. 1). The MgNi$_2$ structure contains both types of junction. A atoms are accommodated in holes in the arrangement of tetrahedra, and are disposed relatively to each other as shown in Fig. 2. Again the MgNi$_2$



Mg Zn$_2$ Mg Cu$_2$

Fig. 1. Arrangement of small atoms in the MgZn$_2$ and MgCu$_2$ structures.

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* Present address: Department of Metallurgy, University of Birmingham, Edgbaston, Birmingham 15, England.

structure contains a mixture of both types of A-atom arrangement.

There has been little discussion of the factors which affect the choice of one structure rather than another. It is impossible, in general, to assign characteristic electron : atom ratios to phases crystallizing in the $MgZn_2$, $MgCu_2$ and $MgNi_2$ types of structure, but there is evidence that valency considerations are important in certain complex alloys containing magnesium and metals of the appropriate atomic diameter for Laves-phase formation. Thus the isomorphous phases MgNiZn, $Mg_3Zn_2Cu_2Ni_2$ and $MgCu_2$ have equal electron:atom ratios (assuming nickel to be zero valent); MgCuAl and $MgZn_2$ (electron:atom ratio 2·0) are also isomorphous (Doering, 1935). Relationships between structure and valency in ternary magnesium alloys have been studied by Laves & Witte (1936), whose results, which are summarized in Fig. 3, indicate that: (i) On increasing the electron:atom ratio of $MgCu_2$ by substituting for copper a metal of higher valency, the cubic structure is succeeded by the $MgNi_2$ structure at approximately 1·8 electrons per atom, and by the $MgZn_2$ structure as the electron:atom ratio approaches 2·0. (ii) The reverse sequence of changes occurs on reducing the electron:atom ratio of $MgZn_2$ by substituting for zinc a metal of lower valency. The intervention of the $MgNi_2$ structure between the other two types might suggest that the effective valency of nickel in these ternary phases is not zero, but between 1·0 and 2·0; it is, however, more likely that the $MgNi_2$ structure is a structural intermediate in which periodic 'faulting' facilitates the change from the $MgZn_2$ arrangement to that of $MgCu_2$ (Raynor, 1949).

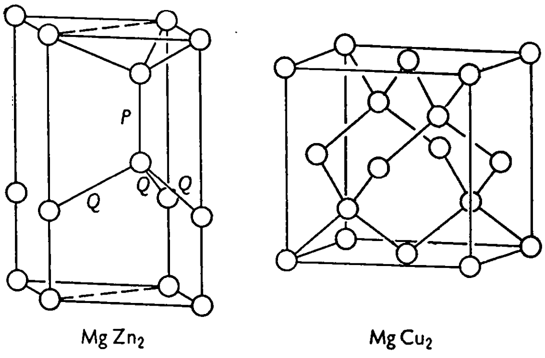

Fig. 2. Arrangement of large atoms in the $MgZn_2$ and $MgCu_2$ structures.

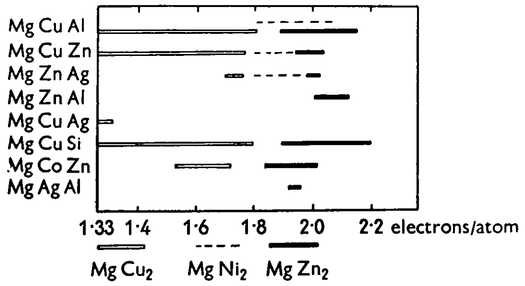

Fig. 3. Structural changes in ternary magnesium alloys: effect of replacing copper in $MgCu_2$ and zinc in $MgZn_2$ by other metals.

Previous work has emphasized that the C_{14}, C_{15} and C_{36} structures represent particularly stable packings of atoms for which the size ratio d_A/d_B is close to 1·2. Much of the discussion relates to 'ideal' structures, and little attention has been paid to interatomic distances in individual compounds. An examination of the geometry of the phases has, however, been made by Schulze (1939), who interprets the structure assumed in terms of the electronic structures of the components. Taking as an example the $MgCu_2$ structure, nearest neighbour B–B distances are all equal; nearest neighbour A–A distances are also equal, and the ratio $(A–A)/(B–B)$ is $\sqrt{1{\cdot}5}$. The A–B distances are all equal, but greater than $\frac{1}{2}\{(A–A)+(B–B)\}$. The structure is thus considered in terms of two interpenetrating atomic configurations or 'sub-structures' (for the A and the B metal respectively), and on this basis, A–A and B–B distances relative to those in the pure components are discussed separately. According to Schulze, B–B distances in the compounds are less than the corresponding interatomic distances in the element. The absence of such regularity in A–A distances suggests that the sub-structure of B atoms is the more important, and that the characteristics of the B component dominate the structure. Assuming that the effective valency of a metal is dictated by the structure of which it forms a component, Schulze classifies the elements in groups which should occur only as A or as B components in Laves phases, together with a third group which may occur as either component. This treatment systematizes many data; somewhat arbitrary assumptions are necessary, however, with regard to the effective valencies of the metals.

Boky & Wainstein (1943) criticize the postulate that effective valency is controlled by lattice type, and point out that many metals which occupy only A or B sites are precluded from occupying any other because of their atomic sizes. Thus the small beryllium atom can only occupy B sites. Boky & Wainstein suggest that the ideal relationship between the interatomic distances in the compounds must be established, and that where the ratio of the atomic diameters of the components differs from 1·225, polarization occurs on compound formation, causing changes in effective atomic size which enable the geometrical requirements to be satisfied.

It is, however, not clear why a specific structure type should be preferred in any given case, nor why the structures of Laves phases in ternary magnesium alloys should show dependence upon the electron : atom ratio in spite of the fact that no wider generalization in terms of electronic factors is possible.

2. Interatomic distances in the Laves phases

(i) *The* $MgCu_2$ *type*

This structure is cubic, with 24 atoms per unit cell of side a. The interatomic distances are:

$$d_{AA} = a\sqrt{3}/4;\ d_{BB} = a\sqrt{2}/4;\ d_{AB} = a\sqrt{11}/8\,.$$

(ii) *The* $MgZn_2$ *type*

This structure is more complex than that of $MgCu_2$, and may be discussed by reference to Figs. 1 and 2. Unless the axial ratio c/a is exactly $\sqrt{(8/3)}$, the A atoms are not all equidistant; the distance P is $c(\frac{1}{2}-2z)$ and the distance Q is $[a^2/3+(2cz)^2]^{\frac{1}{2}}$, where z is a parameter defining the distances of the A atoms above or below the basal plane of the unit cell, or the plane at height $c/2$, and is equal to 1/16. Two types of B atom may be distinguished, with co-ordinates as follows:

(*a*) Atoms marked C at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$.
(*b*) The atoms marked D at $\pm(x, 2x, \frac{1}{4})$, $\pm(-2x, -x, \frac{1}{4})$ and $\pm(x, -x, \frac{1}{4})$, where $x = -1/6$.

The important interatomic distances involved are:

(*a*) $D\text{–}D = -3xa = (1+3x)a$.
(*b*) $C\text{–}D_i$ (where $i = 1, 2, \ldots, 6$) $= (3x^2a^2+c^2/16)^{\frac{1}{2}}$.

(*a*) and (*b*) are equal only when $c/a = \sqrt{(8/3)}$. The three important $A\text{–}B$ distances are:

(*a*) $M\text{–}C = (a^2/3+c^2z^2)^{\frac{1}{2}}$.
(*b*) $M\text{–}D = [a^2(1/3+x+3x^2)+c^2(\frac{1}{4}-z)^2]^{\frac{1}{2}}$.
(*c*) $M\text{–}D = [3a^2(1/3+x)^2+c^2(z+\frac{1}{4})^2]^{\frac{1}{2}}$.

(iii) *The* $MgNi_2$ *type*

Owing to the relative complexity of this structure, only approximate distances, derived from the ideal structure, are given:

(*a*) $A\text{–}A$ distance $=3c/16$.
(*b*) $B\text{–}B$ distance $= a/2$.
(*c*) $A\text{–}B$ distance $= a[1/3+(1/32.c/a)^2]^{\frac{1}{2}}$.

For $MgCu_2$, there are $A\text{–}A$ and $B\text{–}B$ contacts, but no $A\text{–}B$ contacts, if the ratio of the atomic diameters of the components is equal to $\sqrt{1{\cdot}5}$; this value is ideal for the cubic structure, and any departure from it for the pure components leads to differences between the interatomic distances in the crystals of the elements and the corresponding interatomic distances in the compound. Similar implications apply to the $MgZn_2$ structure.

The formation of Laves phases clearly depends on the satisfaction of stringent geometrical conditions; interatomic distances in the compounds may thus be greater or less than the corresponding distances in the components. On compound formation, the atoms on each of the interpenetrating sub-structures are forced further apart or closer together than the equilibrium distance in the pure components, and in this respect the two structures may be considered as in a state of internal strain. It is of interest to examine the deviations in interatomic distance which occur in compounds for which adequate data are available.

3. Deviations of interatomic distances in AB_2 phases from those in the components A and B

If the interatomic distances between like atoms in the compound are d_{AA} and d_{BB}, then the percentage

Table 1. $MgCu_2$ *structure* (C_{15})

Phase	S value (%)			
AB_2	AA	BB	AB	W
$NaAu_2$	−9·16	−4·34	−2·06	1·29
$MgCu_2$	−4·39	−2·55	+1·64	1·251
$CaAl_2$	−11·58	−0·699	−2·06	1·37
$TiBe_2$	−4·12	+2·72	+4·007	1·31
$AgBe_2$	−5·38	+0·255	+2·35	1·295
$LaMg_2$	+1·48	−3·45	+4·48	1·17
$LaAl_2$	−4·84	+0·875	+2·92	1·30
$LaNi_2$	−1·56	+3·02	−3·28	1·50
$CaMg_2$	+3·85	−3·60	+5·87	1·14
$CaAl_2$	−3·85	−0·349	+2·92	1·27
$CeNi_2$	−14·32	+2·01	−2·65	1·46
$CeCo_2$	−14·62	+1·606	−3·04	1·455
KBi_2	−10·82	+8·04	+1·86	1·33 (1·49)
$PrNi_2$	−14·18	+2·208	−2·52	1·46
$GdMn_2$	−5·63	+22·3	+10·75	1·58
$GdFe_2$	−0·93	+6·05	+2·09	1·43
ZrW_2	+4·43	−1·825	+7·05	1·155
$ZrCo_2$	−5·54	−2·01	+1·03	1·265
$ZrFe_2$	−3·49	+0·403	+3·61	1·277
$TaCo_2$	+2·03	−4·12	+4·46	1·14
$NbCo_2$	+2·63	−4·02	+4·90	1·14
$PbAu_2$	−1·86	−2·78	+2·92	1·212
$BiAu_2$	+1·06	−2·43	+9·83	1·08 (1·175)

Table 2. $MgZn_2$ *structure* (C_{14})

Phase AB_2	*S* value (%) AA	BB	AB	W
KNa_2	−0·78	+1·187	+5·69	1·246
$MgZn_2$	+0·37	−2·03	+4·72	1·200
$CaLi_2$	−2·595	+3·166	+5·399	1·296
$CaCd_2$	−8·015	+0·572	+1·506	1·322
$SrMg_2$	−8·636	+0·752	+0·694	1·347
$BaMg_2$	−7·968	+4·042	+3·292	1·361
$TiMn_2$	+1·339	+7·635	+9·658	1·301
$TiFe_2$	+0·175	−3·793	+3·730	1·176
ZrV_2	+2·432	+0·685	+6·947	1·205
$ZrCr_2$	−0·885	+2·888	+6·292	1·270
$ZrMn_2$	−2·716	+12·32	+9·139	1·414
$ZrRe_2$	+1·643	−4·022	+4·398	1·157
$ZrRu_2$	−0·632	−2·156	+3·890	1·198
$ZrOs_2$	+0·789	−2·996	+4·249	1·186
$NbMn_2$	+4·522	+8·752	+12·26	1·274
$NbFe_2$	+4·732	−2·745	+7·055	1·152
$TaMn_2$	+4·310	+8·484	+11·86	1·275
$TaFe_2$	+3·014	−3·148	+5·551	1·152
WFe_2	+5·886	−4·762	+6·407	1·104
VBe_2	+2·284	−1·531	+6·189	1·182
$CrBe_2$	+4·131	−4·636	+5·473	1·122
$MoBe_2$	+0·368	−0·270	+5·667	1·225
WBe_2	−0·768	−0·135	+5·044	1·231
$MnBe_2$	+15·67	−4·77	+11·16	1·103
$ReBe_2$	−2·78	−2·21	+2·945	1·231
$FeBe_2$	+3·955	−5·67	+5·06	1·115
$CaMg_2$	−3·64	−2·915	+2·415	1·231
$CaAg_2$	−10·86	−0·815	−1·53	1·362

deviations from the interatomic distances, d_A and d_B, in the pure components are:

$$S_{AA} = 100(d_{AA}-d_A)/d_A;\quad S_{BB} = 100(d_{BB}-d_B)/d_B.$$

For the distance d_{AB},

$$S_{AB} = \frac{100[d_{AB}-\frac{1}{2}(d_A+d_B)]}{\frac{1}{2}(d_A+d_B)}.$$

Although the interatomic distance in the pure metal is not necessarily a good measure of the size of an atom, it has been used in this work as the least objectionable assessment. On this basis, calculations have been made for many Laves phases. *S* values for *A–A*, *B–B* and *A–B* distances in the C_{15} structures are summarized in Table 1. C_{14} structures, of axial ratio different from 1·633, give two S_{AA}, two S_{BB} and three S_{AB} values. For the purposes of comparison the maximum values, which differ only slightly from the minimum values, have been collected in Table 2.

The results were examined by plotting S_{AA}, S_{BB} and S_{AB} against $W = d_A/d_B$ for phases with either a common *A* component, or a common *B* component. Of the fourteen series examined three typical graphs are reproduced; these refer to compounds with cerium (Fig. 4) or zirconium (Fig. 5) as the *A* component, and with cobalt as the *B* component (Fig. 6). In general, the graphs take the form of Fig. 7(*a*) or (*b*). In the simpler form, S_{AA} is slightly negative, or is positive for $W < W_{\text{ideal}}$, and negative for $W > W_{\text{ideal}}$. S_{BB} is slightly negative or is positive for $W > W_{\text{ideal}}$, and negative for $W < W_{\text{ideal}}$. The relationship between the *S* values and *W* is frequently approximately linear, and, if corresponding points near to, but on opposite sides of, W_{ideal} are joined by straight lines, the two intersect accurately at W_{ideal}. The complex form of diagram (Fig. 7(*b*)) shows a number of intersecting curves of the simple type, which are displaced

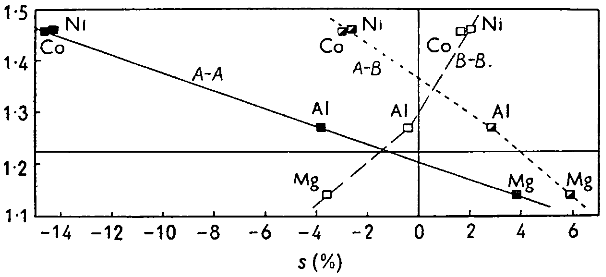

Fig. 4. *W* plotted against *S* for AB_2 Laves phases, *A* = cerium.

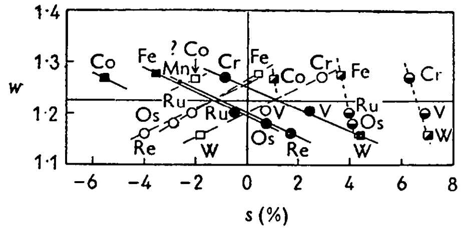

Fig. 5. *W* plotted against *S* for AB_2 Laves phases, *A* = zirconium.

relatively to each other along the S axis; this form is discussed in § 5.

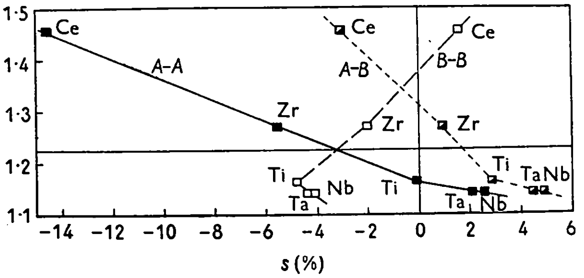

Fig. 6. W plotted against S for AB_2 Laves phases, B = cobalt.

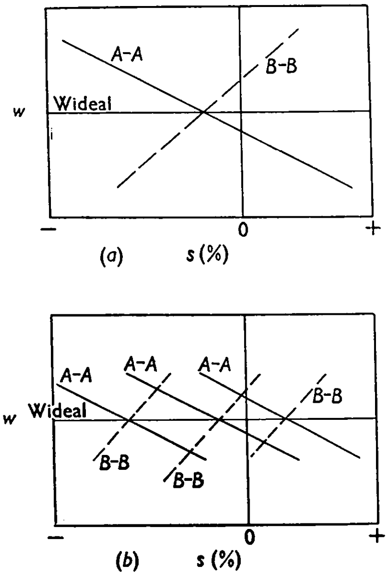

Fig. 7. (a) General form of simple W–S plot. (b) Complex form of W–S plot.

Graphs of the type of Fig. 7(a) may be discussed in terms of the $MgCu_2$ structure. For $W_{\text{ideal}} = 1{\cdot}225$, A atoms should be in contact at the same interatomic distances as in the pure components; the same applies to the B atoms. The fact that the curves of S_{AA} and S_{BB} intersect at W_{ideal}, but at a small negative value of S, shows that this is not quite accurate. Even at W_{ideal}, there appears to be a small contraction of both interatomic distances; the reason for this may lie in atomic interactions, or in the use of closest distances of approach in the crystals of the elements as a standard of comparison. Qualitatively, however, the above interpretation of the $MgCu_2$ structure appears justified. Where the W value for a given phase differs from W_{ideal}, the graphs show that readjustment of the effective atomic size occurs in both the A and B configurations. Thus, a large B atom, corresponding with a low value of W, results in B atoms being closer together, and A atoms further apart, than in the crystal of the pure components. The reverse is true for high W values. The two configurations may thus be considered as under the action of 'internal stresses' causing abnormal interatomic distances, in opposite senses, for the A and B components in the structure. Since the compressibility, β, is, to a first approximation, a measure of the resistance of a substance to change of interatomic distance under hydrostatic stresses, a qualitative correlation between the change of interatomic distance on compound formation and the β values for the elements concerned might be expected; quantitative interpretation is not possible since it cannot be assumed that β is an equally good measure of resistance to changes of interatomic distance in both compression and expansion. The data in Fig. 4 are consistent with a rough correlation between the S values and β. Thus, the compressibilities of cerium and magnesium are similar, and the expansion of the A–A distance relative to d_A is nearly equal to the contraction of the B–B distance relative to d_B. Aluminium, however, has a lower β value than cerium, and is more difficult to distort under the action of a given stress; accordingly, S_{BB} is only approximately one-tenth of S_{AA}. For the less compressible B atoms cobalt and nickel, the deviation for B–B distances is again only a fraction of that of A–A distances. On compound formation, therefore, the sub-structures on which the A and B atoms lie are mutually affected, and cannot be considered to be independent.

As noted above, it would be expected that, for the C_{15} and C_{14} structures, S_{AA} and S_{BB} would be zero at $W = 1{\cdot}225$. Assuming approximate linearity between S and W, the value of S at $W = 1{\cdot}225$ for several of the series of compounds examined may be derived by interpolation. In all cases the S_{AA} and S_{BB} curves intersect accurately at W_{ideal}; the S values for the A and B configurations are equal but not zero, and generally correspond with a slight contraction of the interatomic distances relative to the pure components.

One factor which prevents the S values from becoming zero at the ideal W value may be connected with the change of electron : atom ratio, and hence of Fermi energy, on compound formation. The energy of a metallic crystal may for many purposes be regarded as the sum of E_0, the energy of the lowest state of the valency electrons, and E_F, the mean energy of the valency electrons. The minimum in the curve of (E_0+E_F) against d occurs at the equilibrium interatomic distance. Assuming temporarily that the curves of E_0 against d for components A and B are not markedly altered when these components form the A and B configurations of a Laves phase, a decrease in Fermi energy from that in the pure component will lead to a shift of the minimum of (E_0+E_F) to smaller interatomic distances, while an increase will lead to larger interatomic distances. This effect will be superimposed upon purely geometrical considerations.

The effects of change of electron : atom ratio on the S_{AA} and S_{BB} values are unlikely to be equal;

further, the simple electronic factor will be modified by factors which affect the curve of E_0 against d for the component concerned, such as changes in the coordination number of a given component on compound formation, or the existence of a marked electrochemical interaction between the components. It is thus unprofitable to discuss in detail the actual magnitudes of the non-zero S values existing for d_{AA} and d_{BB} at the ideal W values. The fact that these are small, however, justifies the interpretation of the Laves phases developed above.

Consideration of graphs of S_{AA}, S_{BB} and S_{AB} against W for all the series studied show that the C_{14} and C_{15} structures tend to form within discrete ranges of W. Thus, in Fig. 8* (series of compounds with A = Ca) the C_{15} structure occurs only for $W > 1{\cdot}37$; at lower W values, the C_{14} structure occurs. In Fig. 9 (series of compounds with B = Mg) the C_{14} structure is found at $W > 1{\cdot}175$, and the C_{15} structure occurs at lower W values. Similar discrete ranges of W are observed in all the series listed in Tables 1 and 2, except that compounds containing manganese appear misplaced if d_{Mn} is taken as 2·24 Å (shortest distance of approach of atoms in α-Mn). The complex structure of manganese, however, makes it difficult to define an interatomic distance characteristic of the element for use in the accurate assessment of W, S_{AA} or S_{BB} and no further discussion of these phases is justified.†

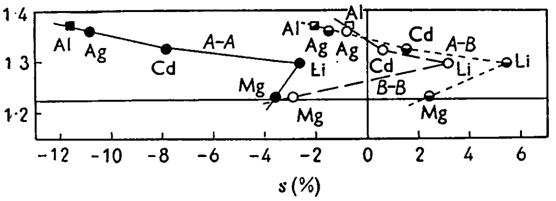

Fig. 8. W plotted against S for AB_2 Laves phases, A = calcium.

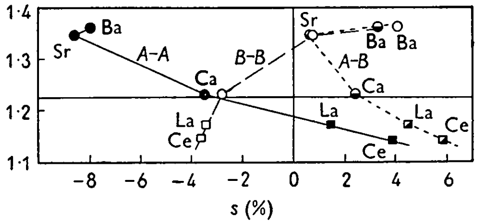

Fig. 9. W plotted against S for AB_2 Laves phases, B = magnesium.

The data suggest that, in a given series of compounds, the W value affects the type of structure assumed. In general the C_{14} structure tends to occur in W ranges close to W_{ideal}, and (see Fig. 7(*a*)) is generally favoured by the smaller deviations of S_{AA} from that corresponding to the intersection at W_{ideal}. It is significant that in series of phases such as that summarized in Fig. 4 where only C_{15} structures occur, the region near W_{ideal} contains no phases yet reported. The C_{15} structure appears at both higher and lower W values than those characteristic of the C_{14} structure; it is thus the magnitude, rather than the sign, of W which is important in deciding the structures assumed.

In the series of phases with zirconium as the A component (see § 5) both types of structure occur at similar W values near the border-lines of the range containing the C_{14} structures; in each sub-series the C_{15} type tends, however, to be characterized by the largest deviations of S_{AA} from those at W_{ideal}, in agreement with the general principle.

The ranges of W for which the C_{14} structure occurs differ for the various series examined, probably because it has been necessary to consider second components from several groups of the Periodic Table in association with a common A or B component. For components where the ions in the crystal of the element are in contact, the interatomic distance is a reasonable measure of the atomic size, but for other components where the ionic diameter is small compared with the interatomic distance, the latter is not necessarily a good approximation to the atomic size. This introduces some uncertainty into the comparison of the critical W values for change in structure in different series of compounds. The general tendency for C_{15} structures to occur at the larger differences of S_{AA} from that at W_{ideal} is, however, established. (Attempts to compensate for the effects of including 'full' and 'open' metals in the same series were made by comparing only phases, with a common A or B component, in which the second component was taken from a single group of the Periodic Table. Characteristic W ranges were again observed, but insufficient data were available for critical definition of the boundaries of these ranges.)

For a C_{14} structure, with $W = 1{\cdot}225$ and S small (e.g. $MoBe_2$), the free energy of the phase will be near the minimum for the structure. On increasing W, the S values deviate from that at W_{ideal}, and the free energy may be expected to rise as the lattice becomes distorted from its ideal form. At some stage, the increment in free energy must become greater for the C_{14} structure than for the alternative C_{15} structure, and change from one to the other occurs. It is difficult to ascertain the major factor in causing this change. From the graphs examined, S_{AA}, S_{BB} and S_{AB} for the C_{14} structures occurring at W values close to the critical limit for this type of phase are commensurate with the corresponding values for C_{15} structures with W values just outside the limit. Thus in Fig. 8 the points for $CaLi_2$, $CaCd_2$, $CaAg_2$ and $CaAl_2$ lie on smooth curves with no obvious discontinuity where the structure change occurs.

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* In Figs. 8 and 9, C_{14} structures are distinguished by circles.

† An arbitrary value of $d_{\text{Mn}} = 2{\cdot}51$ Å would avoid any conflict between the manganese-containing phases and the remainder.

In general, for B components of the 'full' type (ionic and atomic diameters comparable), the C_{15} structure tends to be assumed, except where the A component is an 'open' metal (ionic diameter small relative to atomic diameter). This suggests that the cubic structure is better able to accommodate ion-ion interactions in the BB and AB directions, and would be expected to form when the ions would approach too closely in the C_{14} structure. The observed interatomic distances do not, however, support this suggestion. No systematic difference in the degree of closeness of approach of ions in the two structures can be traced, if Pauling's univalent ionic radii are taken to measure the extension in space of metallic ions (Hume-Rothery & Raynor, 1938*a*, *b*).

4. The compounds of magnesium

As shown above, at increasing deviations of W from W_{ideal}, the C_{14} structure tends to give way to the C_{15} structure; the critical value depends upon the series of phases considered. Similar considerations may be used to discuss the structural changes in ternary magnesium alloys referred to in § 1; some consideration of the nature of the $MgNi_2$ structure is, however, necessary. Too few C_{36} binary phases of composition AB_2 are reported to permit a detailed analysis of the type described above. The existence of this structure in ternary alloys, or binary alloys of composition other than AB_2 may be considered as follows. If the S values for a given C_{14} compound AB_2 lie close to the critical limits, they may be moved towards the critical limits by the substitution of a third metal for one of the components, or alternatively by substitution of A for B, or the reverse, leading to a compound of non-stoichiometric composition. The critical values may then be exceeded locally, giving rise to regions of structure similar to that of $MgCu_2$ in the crystal. This would produce a crystal structure analogous in many respects to that of $MgNi_2$, which may be regarded as a structural intermediate between the main types. Further substitution would be expected to complete the structural change, as observed in the ternary magnesium alloys considered.

In discussing the changes brought about by the solution of a third metal in $MgZn_2$ or $MgCu_2$, two factors must be considered: (i) Alteration in the effective W and S values on the introduction of a third metal. (ii) Alteration in Fermi energy due to change in electron:atom ratio.

The structure of $MgZn_2$ corresponds with a W value of 1·200; the individual S values for the various interatomic distances are (referring to Figs. 1 and 2):

$$P+0{\cdot}376,\quad Q+0{\cdot}031,\quad CD-1{\cdot}805,\quad DD-2{\cdot}031\,.$$

For $MgCu_2$ ($W = 1{\cdot}25$) the corresponding S values are:

$$A\text{–}A\ -4{\cdot}39,\quad B\text{–}B\ -2{\cdot}55\,.$$

In these magnesium compounds, therefore, S values for the B–B distances are much less affected by change in W than S values for the A–A distances. As noted above, $MgCu_2$ structures tend to occur at both high and low W values. Since a rise in W from 1·200 to 1·25 (substitution for zinc of the smaller copper atom) gives sufficient of a negative S_{AA} value to stabilize the cubic structure, it may be expected that a decrease in W (substitution for zinc of a larger atom) will tend to give rise to a sufficiently increased positive S_{AA} value again to give a tendency towards the formation of the cubic structure.

The W value for the $MgCu_2$ phase is 1·25. Solute atoms larger than the copper atom will tend to lower this value and give smaller S values, favouring the $MgZn_2$ structure, while solutes of smaller atomic size than copper would not be expected to have this effect.

The effect of electronic changes may be discussed in terms of the dilation produced by an increase in the Fermi energy of a structure, and the contraction produced by a decrease. In $MgZn_2$ itself only the P distance is markedly expanded. The remaining three Mg–Mg distances are almost zero; all six Zn–Zn distances are contracted. A decrease in electron:atom ratio will thus decrease the S value in the P direction, but will numerically increase the negative S values for all other directions in the A and B sub-structures. According to the hypothesis that the $MgCu_2$ structure occurs at large values of S, the electron:atom ratio decrease will favour the formation of the cubic structure. An increase in the electron:atom ratio, on the other hand, will first reduce the S_{BB} values towards zero; the 'internal strain' in the lattice is thus reduced so that conditions will remain favourable for the $MgZn_2$ structure. Only on relatively large increases in electron:atom ratio, which may be unattainable in practice, would any tendency towards the $MgCu_2$ structure be expected.

The structural changes summarized in Fig. 3 may now be discussed:

(i) *Replacement of zinc in* $MgZn_2$ *by copper, silver or aluminium*

On adding copper to $MgZn_2$, both factors favour the formation of the $MgCu_2$ structure, and the change of structural type occurs at approximately 1·93 electrons per atom. For replacement by silver, the electronic factor remains similar, but the size effect is greater ($d_{\text{Zn}} = 2{\cdot}66$ Å; $d_{\text{Cu}} = 2{\cdot}55$ Å; $d_{\text{Ag}} = 2{\cdot}88$ Å). The structural change accordingly occurs at a smaller concentration of third metal, and at a higher electron:atom ratio (approximately 1·98). In the case of replacement of zinc in $MgZn_2$ by aluminium, which is of similar atomic size to silver, the size effect favouring the formation of the $MgCu_2$ structure is opposed by an increasing electron:atom ratio which favours the retention of the $MgZn_2$ structure. The structure remains hexagonal and the $MgCu_2$ structure does not occur (see Fig. 4). These systems are consistent with the general hypothesis.

(ii) *Replacement of copper in* $MgCu_2$ *by zinc, aluminium or silver*

In these cases, the substitution of the third metal for copper reduces the effective W value, favouring the formation of the $MgZn_2$ structure. Increase in electron:atom ratio reinforces this tendency, so that, on substituting zinc or aluminium for copper, the cubic structure becomes unstable at approximately 1·8 electrons per atom. The electron:atom ratio at which the $MgZn_2$ structure is formed is lower for the substitution of aluminium than for that of zinc, in agreement with the larger size of the atom of aluminium. For the substitution of silver, although the size effect would tend to favour the $MgZn_2$ structure, the constant electron:atom ratio does not reinforce this tendency, and no hexagonal form occurs. This suggests that the electronic factor is the more important.

(iii) *Replacement of copper in* $MgCu_2$ *by silicon, and of zinc in* $MgZn_2$ *by cobalt*

In the magnesium–copper–silicon system, the increase in the electron:atom ratio tends to stabilize the $MgZn_2$ structure; owing to the small size of the silicon atom, the effective W value is increased, and the tendency towards the hexagonal structure is opposed. In spite of this the $MgZn_2$ structure is formed, again suggesting that the electronic factor outweighs the size effect. For magnesium–zinc–cobalt alloys, both factors favour the formation of the $MgCu_2$ structure (assuming cobalt to be effectively zero-valent) and the existence of the cubic structure may be understood. The range of electron:atom ratios over which the $MgZn_2$ structure is stable, however, is wider than expected from the corresponding homogeneity range in the magnesium–zinc–copper and magnesium–zinc–silver systems. This suggests that the presence of a transitional metal introduces complicating factors, some of which are examined below.

5. Evidence for the existence of interatomic forces

Discussion of the graphs of the type illustrated in Fig. 7(*a*) indicates that the A and B sub-structures are mutually inter-dependent, insofar as expansion or contraction in one cause corresponding changes in the other. The form of graph shown in Figs. 5 and 7(*b*), however, requires more complex interpretation. Referring to Fig. 5 (compounds of zirconium), the W and S values for the A and B configurations lie on pairs of intersecting lines; each individual pair resembles the simple form of Fig. 7(*a*), but its position along the S axis varies according to the group of the Periodic Table from which the B partner is taken. Although cubic C_{15} structures occur at similar W values to hexagonal C_{14} structures, the former occur at the largest S values for a given series, in agreement with the general hypothesis. Further, for compounds of zirconium with transitional elements of the first long period, the cubic structure tends to occur as the 3*d* shell of the B partner is filled up.

Three characteristic plots, similar except for displacement along the S axis, are defined by points representing phases with B partners taken from the same group of the Periodic Table:

(i) W, Cr; (ii) Mn,* Re; (iii) Fe, Os, Ru .

The points for ZrV_2 and $ZrCo_2$ probably lie on similar plots which cannot be defined owing to lack of data. An additional factor thus seems to be involved for compounds containing transitional metals. The additional factor depends upon the nature of the B partner, and may expand or contract the whole lattice, so that the W–S graphs are displaced along the S axis; it therefore probably takes the form of an interaction between the A and B atoms. This conclusion is supported by the fact that the S values for the A–B distances shown on Fig. 5 are again separated into groups, and are approximately equal within each group. Similar arguments apply to several other series of phases with other common A and B components.

For zirconium alloys, where the data are most complete, it appears, by comparison with the simpler form of diagram (e.g. Fig. 4), that repulsive forces exist, leading to positive S values at W_{ideal}, for B metals of groups V and VI, decreasing in that order. For B partners belonging to the manganese, iron and cobalt groups, attractive forces, increasing in the order given, appear to exist. If the metals of groups V and VI exert their classical valencies, interatomic repulsion might be understood in terms of the interaction between highly charged ions; it is, however, improbable that chromium should be considered as exerting its group valency. Attractive forces are also difficult to understand. In many cases of alloy formation with transitional metals it is probable that electrons may be absorbed into vacant levels in the partially filled 3*d* band of the transitional atom. This process leads to the development of heteropolarity, and hence to attractive forces. In the present case, since the number of vacant levels in the *d*-shell increases in the order Co $<$ Fe $<$ Mn, it might be expected that the attractive forces would also increase in the order $ZrCo_2$, $ZrFe_2$, $ZrMn_2$. This is the reverse of the observed order; the filling of *d*-shell vacancies in the transitional metal atoms is thus unlikely to be responsible for the contractions observed. It is, however, possible that the small, highly charged zirconium ion is able to polarize the transitional metal atoms, resulting in attractive forces which would be expected to increase in the order $ZrMn_2$, $ZrFe_2$, $ZrCo_2$.

From the W–S graphs, the existence of strong

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* Assuming $d_{Mn} = 2{\cdot}51$ Å.

interatomic forces between zirconium and the metals from vanadium to cobalt appears probable, though the nature of the interaction is not clear. Similar behaviour is shown by the Laves phases formed by titanium, niobium and tantalum with the same B metals, where data are available, so that, in these cases, it is certainly not justifiable to consider the A and B sub-structures as independent.

6. Conclusions

In an ideal C_{15} or C_{14} structure ($d_A/d_B = 1{\cdot}225$) the A atoms touch, and the B atoms touch, while there are no AB contacts. The A and B sub-structures in Laves phases may thus be considered, to a rough approximation, to be independent. In practice, however, Laves phases occur for values of $W = d_A/d_B$ which vary over a relatively wide range. Examination of the interatomic distances in those phases for which sufficient data are available shows that the substructures upon which the large A and small B atoms lie cannot be considered as independent. A parameter S which measures the contraction or expansion of the interatomic distances as compared with the corresponding distances in the pure components, may be derived from A–A, B–B and A–B distances in the compounds and plotted against the corresponding W values. Two general cases may be distinguished for compounds with a common A or B component.

First, curves of W against S are approximately linear, and so disposed that at $W > W_{\text{ideal}}$, A–A distances are contracted while B–B distances are expanded, relative to those in the pure components. For $W < W_{\text{ideal}}$, the reverse is the case. Thus the introduction of a B atom which is too small relative to a given A atom causes contraction of the A substructure by an amount which increases as W increases, while the introduction of too large a B atom causes an expansion of the A sub-structure, by an amount again dependent on the value of W. The deviations of the A–A and B–B distances in a given compound from d_A and d_B may be correlated in certain cases with the compressibilities of the components, suggesting that the two lattices interact in such a way as to cause the stresses in the two to be equal and opposite. If this were the only factor concerned, however, S_{AA} and S_{BB} should be zero at W_{ideal} ($=1{\cdot}225$). Curves of S_{AA} and S_{BB} against W do in fact intersect accurately at W_{ideal}, but at an S value which is slightly offset from zero, usually in the direction of negative S. Thus, while the model of the two substructures interacting in a mechanical sense appears substantially correct, there is an additional factor which affects the A–A and B–B distances approximately equally and in the same direction. This factor may be a weak interaction between the A and B atoms, or a change in the Fermi energy on alloying. C_{14} ($MgZn_2$ type) structures tend to occur at W values close to W_{ideal}, and hence in general at small deviations of the interatomic distances from those characteristic of the components. As W increases or decreases, C_{15} ($MgCu_2$ type) structures tend to occur, suggesting that the C_{14} structure becomes unstable at a critical W value, which, however, varies for series of phases with different common A or B elements.

In the second case, graphs of W against S for phases with a given A component take the form of a series of intersecting curves; each intersecting pair corresponds with points for B metals of the same group or subgroup of the Periodic Table, and the S values at the intersections vary according to the group from which B (in general a transitional metal) is taken. These phenomena are consistent with the existence of considerable interaction between A and B atoms.

The occurrence of C_{14} structures at W values close to $1{\cdot}225$ and of cubic C_{15} phases as W increases or decreases together with consideration of the effect of Fermi energy changes on interatomic distances, enables an interpretation of the structural changes which occur in ternary magnesium alloys when other metals, of similar atomic size, are substituted for zinc in $MgZn_2$ or copper in $MgCu_2$. In general, any change in the effective S value of $MgZn_2$ favours the assumption of the $MgCu_2$ structure; an electron:atom ratio decrease reinforces this tendency. For $MgCu_2$, reduction of the effective S value and increase in the electron:atom ratio favour the $MgZn_2$ structure. The effects expected according to this treatment are in general agreement with observation, but suggest that the electronic factor is predominant.

More phases with the C_{14} and C_{15} structures probably exist than are already known. The considerations outlined in this paper should help to predict their occurrence in systems as yet unexamined, and to assess whether the structure is likely to be cubic or hexagonal.

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