

sten as 6, which with equation (1) would lead to bond lengths an average of 0.027 Å larger than those observed. If the assumption is made that the two kinds of bond orbital of the tungsten atom have different amounts of *d* character, we may assign the values $n=0.333$ to the silicon-silicon bonds (as given by equation (1) and the single-bond radius of silicon), $n=0.467$ to the silicon-tungsten bonds, and $n=0.333$ to the tungsten-tungsten bonds. The values of R_1 and δ for the bond orbitals of tungsten involved in the bonds to silicon atoms are 1.262 Å and 47.7%, and for the bonds to tungsten atoms 1.464 Å and 24.1%, respectively. The average value of δ , 42.5%, corresponds to $R_1=1.306$ Å for the tungsten atom, which is 0.012 Å less than for the element.

A similar discussion of transition-metal bond lengths has been reported for FeSi and other silicides with the B31 structure (Pauling & Soldate, 1948), and Co₂Al₉ (Pauling, 1951).

In the above discussion the effect of difference in electronegativity of unlike atoms on bond length (usually a decrease) has been ignored. There is the possibility also of a small change in bond length between unlike atoms, such as of a metal and a metalloid, that reflects the difference in the nature of the overlapping orbitals, in addition to the effects of partial ionic character and of electron transfer. I believe that a thorough

analysis of this problem, with consideration of the present great amount of experimental information about bond lengths in metals and intermetallic compounds, would now permit the formulation of a table of metallic radii reliable to 0.001 Å and a set of structural principles that would allow bond lengths and lattice constants to be predicted to within about 0.1%.

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Laves Structures, MgCu₂, MgZn₂, MgNi₂

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It is in some measure demonstrated that the formation of A-B and B-B contacts provides the energy for the compression of the A atoms and permits AB₂ phases with radius ratios so much larger (up to 1.67) than the ideal (1.225) to adopt the MgCu₂ type structure. At radius ratios somewhat lower than the ideal, the B atoms are insufficiently compressed for A-B and A-A contacts to form. This is probably a consequence of there being twice as many B atoms as A atoms, and it results in fewer known Laves phases with radius ratios below the ideal value than above it.

There have been many reviews and discussions of the crystal chemistry of the Laves phases (among the more recent see Berry & Raynor, 1953; Laves, 1956; Elliott & Rostoker, 1958; Bardos, Gupta & Beck, 1961; Dwight, 1961; Nevitt, 1963) but none of these explicitly discuss what we find to be their most remarkable features:

(i) Phases adopt structures which result mainly from the geometrical facility of packing together two components in the proportion AB₂ if the ratio of their radii, r_A/r_B , is 1.225, when the actual size ratios of the components may differ greatly (values from 1.05 to 1.67) from the ideal value.

(ii) Structural compression in the Laves phases may amount to more than 35% in unit-cell volume compared with the sums of the elemental volumes. Such large compressions might be expected in structures of phases with strong A-B interactions, but scarcely in those of the ideal Laves structures which, on the hard sphere atomic model, have only A-A and B-B contacts.

Space filling models based on the concept of incompressible atoms (Laves, 1956; Parthé, 1961) are of no assistance in understanding these features, but the problem can be discussed in terms of a model which allows compression of the A (or B) atoms to establish

(i) A–B and (ii) B–B (or A–A) contacts, that are assumed to occur only when $R_A + R_B \geq d_{AB}$, $2R_B \geq d_B$ and $2R_A \geq d_A$. Here d_A , d_B and d_{AB} are respectively the observed A–A, B–B and A–B distances and R_A, R_B (D_A, D_B) are the radii (diameters) of the two components for 12 coordination (we take the values of Teatum, Gschneidner & Waber, 1960). With this model we can compare as a function of the ratio of the atomic diameters, D_A/D_B , the observed reduced contractions of the A atoms, say $(D_A - d_A)/D_B$, with the calculated values required to establish A–A, B–B and A–B contacts (Fig. 1). We shall consider only the cubic Laves phases because the MgCu₂ structure has no free parameters other than the unit-cell edge (d_A/d_B is always 1.225), whereas the hexagonal structures, MgZn₂ and MgNi₂, have both variable axial ratios and atomic parameters (generally not accurately known) giving more than one near-neighbour A–A, B–B and A–B distance, except at the ideal values. Since the interatomic distances in the MgCu₂ structure are $d_A = \sqrt{3}/4a$, $d_B = \sqrt{2}/4a$ and $d_{AB} = \sqrt{11}/8a$, it follows that the lines in Fig. 1 are given by the expressions:

$$\text{A–A contact } (d_A = D_A): \frac{D_A - d_A}{D_B} = 0$$

$$\text{B–B contact } (d_B = D_B): \frac{D_A - d_A}{D_B} = D_A/D_B - 1.225$$

$$\begin{aligned} \text{A–B contact } [d_{AB} = \frac{1}{2}(D_A + D_B)]: \frac{D_A - d_A}{D_B} \\ = 0.4778(D_A/D_B) - 0.5222. \end{aligned}$$

Similar expressions could be derived for the reduced compression of the B atoms, say $(D_B - d_B)/D_B$, for A–A and A–B contacts, with $(D_B - d_B)/D_B = 0$ for B–B contact, but a plot of $(D_B - d_B)/D_B$ versus D_A/D_B only rotates the whole of the diagram of Fig. 1, so that the line for B–B contact lies along $(D_B - d_B)/D_B = 0$; the relative geometry of the diagram remains the same and no new information is gained.

From consideration of Fig. 1 we can now in some measure account for the two features noted above, and also observe several other points of interest. First, note that at a D_A/D_B value of 1.347, the lines for B–B and A–B contact intersect, and at this point (*i.e.* with $d_A/d_B = 1.225$), A–A, B–B and A–B contacts all occur, although there is some strain due to compression of the A atoms. This suggests that although the ideal condition for the formation of the Laves phases is always considered to be $D_A/D_B = 1.225$ giving A–A and B–B contacts without strain (but no A–B contacts), in practice *larger radius ratios are considerably favoured because of the formation also of A–B contacts*. The distribution in Fig. 1 of the main body of the Laves phases with D_A/D_B values between 1.45 and 1.225 which lie between the lines for B–B and A–B con-

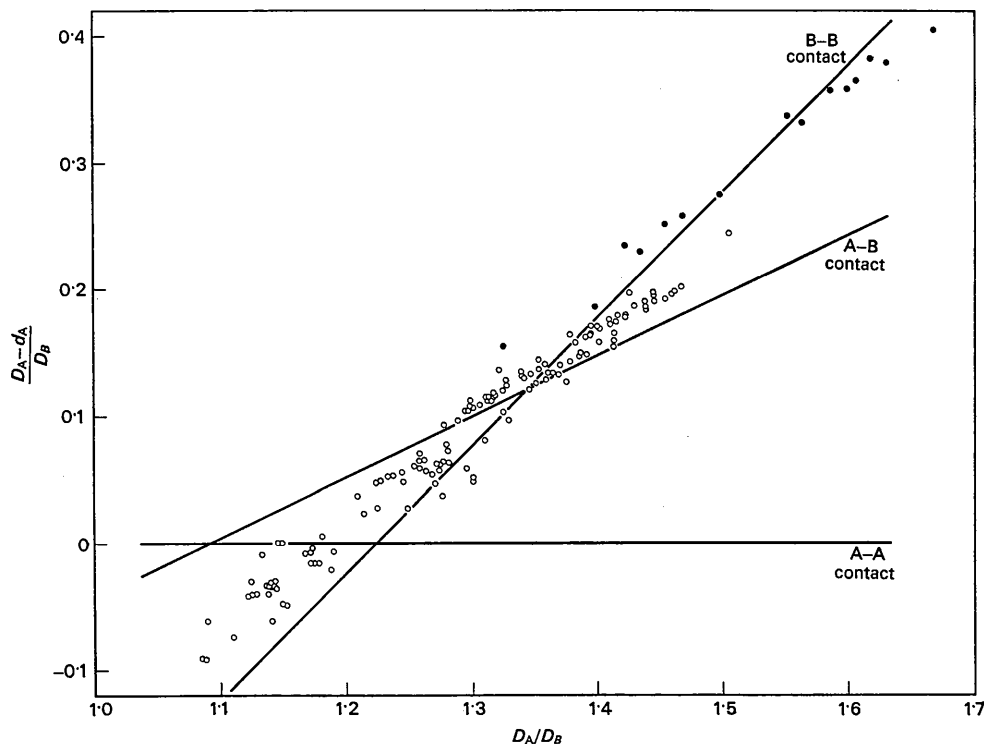


Fig. 1. $(D_A - d_A)/D_B$ versus D_A/D_B data for binary phases with the MgCu₂ type structure (Nevitt, 1963; Pearson, 1967) excluding Mn compounds. Filled circles represent phases with electronegativity difference $|x_A - x_B| \geq 1.0$. Lines represent values for the occurrence of A–A, B–B and A–B contacts given by $d_A = D_A$, $d_B = D_B$ and $d_{AB} = \frac{1}{2}(D_A + D_B)$ respectively (see text).

tact, agrees with this supposition and gives some reason for the observed compression of the atomic volumes in Laves phases, since this is a structural feature associated with A-B contacts in metals.

SmRu₂ with $D_A/D_B=1.346$ is an ideal example of a Laves phase with B-B and A-B contacts and compressed A-A contacts as the following data show:

$D_A = 3.604 \text{ \AA}$	$d_{A_{\text{obs}}} = 3.252 \text{ \AA}$	A-A contact with compression
$D_B = 2.678$	$d_{B_{\text{obs}}} = 2.680$	B-B contact
$D_{AB} = 3.142$	$d_{AB_{\text{obs}}} = 3.141$	A-B contact

At radius ratios above 1.347 compression of the A atoms leads to the formation of A-B contacts before B-B contacts, whereas below this value, B-B contacts occur first.

Phases with large electronegativity differences ($|x_A - x_B| \geq 1.0$) (Fig. 1) extend to the highest radius ratios and in all cases the compression of A is essentially such as to establish both A-B and B-B contacts, and at radius ratios less than 1.5 to compress the B-B contacts also. Thus the effect of a large electrochemical factor in the Laves phases is not, as might have been expected, only to establish A-B contacts, but it leads to considerably greater compression of the A atoms, even when the radius ratio departs greatly from the ideal value.

At D_A/D_B values less than the ideal 1.225 we would expect compression of the B atoms, but Fig. 1 indicates that with decreasing radius ratio this becomes insufficient to establish either A-A or A-B contacts. (Note that at $D_A/D_B=1.093$, both A-A and A-B contacts can occur simultaneously.) This failure to establish other than B-B contacts at radius ratios below about 1.15 probably accounts for the asymmetry in the distribution of Laves phases about the ideal radius ratio, there being far fewer at low radius ratios (cf. Fig. 1). Secondly, an expansion of the space occupied by the A atom at low radius ratios means that the contraction of the atomic volume in these phases is generally less than that of phases occurring at radius ratios greater than the ideal value.

In sum then, we have demonstrated the occurrence of A-B and B-B contacts and A-A compression in the AB₂ phases with the MgCu₂ structure at radius ratios larger than the ideal, and shown that the B atoms do not compress sufficiently to allow other contacts at small radius ratios. We account for these effects in terms of the overall crystal energy, suggesting that the formation of A-B (and B-B) contacts in phases

with large radius ratios provides the energy required to compress the A atoms, but because there are twice as many B atoms as A atoms, the energy is insufficient to permit compression of the B atoms and the establishment of A-B and A-A contacts at small radius ratios. Certainly comparison of the A components at radius ratios above 1.225 with B components below this value does not reveal any obvious chemical reason for this difference in behaviour.

Throughout this discussion, metallic radii for C.N. 12 have been used, since it is uncertain what other value to take for a particular compound. This is not serious and, for example, increasing the radii of the A atoms by 2% for C.N. 16 only shifts the observed $(D_A - d_A)/D_B$ data in Fig. 1 a small amount parallel to the line for B-B contacts.

Finally, Fig. 1 can be used to estimate the valency of Mn in the five known rare-earth compounds with the MgCu₂ structure. Using a radius for Mn^{VI}, the data for these compounds lie right outside the range of the other Laves phases in Fig. 1, but if a Mn^{II} radius is assumed, then the data match those of the other phases quite well, and it can be concluded that this is the appropriate valence state of Mn in these phases.

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To Professor Ewald crystal chemists owe a particular debt for his foresight in having started (with C. Hermann) *Strukturbericht* in whose volumes, together with those of their successor, *Structure Reports*, a continuous record of all structural determinations can be found!

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