Makita, 1978). However, it was not clear whether the potential for H(7) was the single-minimum or double-minimum type. In the case of $(ND_4)_3D(SO_4)_2$ the electron density distribution around D(7) has apparently separated into two peaks. This suggests that D(7) is in the symmetric double-minimum potential well. Hence, on deuteration the H-bond situation seems to change as follows: (1) from the symmetric effectively centred H bond, O···(H,H)···O, to the symmetric disordered H bond, O···(D)···(D)···O; or (2) from the symmetric disordered H bond to that with a higher potential barrier. The above suggests that the bond O(2)—D(7)···O(2′) is involved in the appearance of ferroelectricity.

The O—D and N—D bond lengths obtained are shorter than those from neutron diffraction experiments; this seems to be due to the bonding electrons; further analysis is required on this point.

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Dimensional Analysis of Laves Phases: Phases with the $MgCu_2$ Structure

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Abstract

Equations are derived for the unit-cell dimensions of phases with the $MgCu_2$, MN_2, structure in terms of the coordination number 12 diameters of the component atoms. These are interpreted in terms of the interatomic contacts (4 M—M, 12–6 M—N and 6 N—N) that control the cell dimensions. Phases with this structure are by no means a homogeneous group and at least seven groups exhibiting different dimensional behaviour are identified; in this respect the grouping of atoms in the Periodic Table is at least as important as the diameter ratio of the component atoms. Relationships between the dimensional equations and the 'near-neighbour diagrams' of Pearson [*Acta Cryst.* (1968), B**24**, 7–9, 1415–1422] are examined.

1. Introduction

(*a*) *Laves phases*

So much has been written about Laves phases ($MgCu_2$, MN_2, structure and polytypes) that it seems inconceivable that there is anything significant still to be said. We have come to recognize them as the epitome of the 'good metallic phase' in whose structural architecture geometrical principles play a strong role. The occurrence of phases with the $MgCu_2$ (cubic) and $MgZn_2$ (hexagonal) structures has been discussed by many authors from the point of view of (1) the cell dimensions [mostly as $D_M - (\sqrt{3}/4)a$ and $D_N - (\sqrt{2}/4)a$ *versus* D_M/D_N for the $MgCu_2$ structure], (2) atomic valency and (3) the Periodic arrangement of the

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component atoms (*cf.*, for example, Laves & Witte, 1936; Schulze, 1939; Berry & Raynor, 1953; Laves, 1956; Elliott & Rostoker, 1958; Dwight, 1961; Nevitt, 1963; and Pearson, 1968). Their elegant geometry, as an arrangement of interpenetrating icosahedra and Friauf polyhedra that have triangulated surfaces, or as an A, B, C, ... *etc.* stacking of fourfold slabs consisting of three equilateral-triangular layers and a Kagomé network layer, has been discussed particularly by Frank & Kasper (1958, 1959). The latter description shows why polytypic variations of the basic structural arrangement can occur. Their role as members of the group of tetrahedrally close-packed phases has been emphasized by Shoemaker & Shoemaker (1967).

A diameter ratio, $D_M/D_N = \sqrt{3}/\sqrt{2} = 1{\cdot}225$, where a spherical M atom has twice the volume of a spherical N atom, has come to be regarded as 'ideal', but phases with observed diameter ratios up to $D_M/D_N = 1{\cdot}67$ must be very far removed from this simple geometrical picture. Pearson (1968, 1972) has accounted for this (and also for the asymmetry of distribution of phases about the 'ideal' diameter ratio of 1·225, since the lowest D_M/D_N values found for $MgCu_2$ phases are about 1·10) on the basis of competing energies of the atomic contacts which involves both the multiplicities of the contacts and the composition ratio, as an attempt is made to satisfy 16–12 coordination.

This paper will show that phases with the $MgCu_2$ structure are by no means a homogeneous group – a number of main groups of phases can be distinguished according to the combination of component atoms, in which the cell edge is controlled by different combinations of the interatomic contacts. Previous intimations of this lack of homogeneity have been observed in many of the references cited above, but none have been effectively analysed to determine the reasons therefor. Figs. 4 and 5 in Dwight (1961) probably come closest to the findings of this paper.

(*b*) *Method of analysis*

In a method of analysing the unit-cell dimensions of binary metallic phases, M_xN_y, with a given crystal structure (Pearson 1979, 1980*a*), the cell dimensions are examined as a function of D_M and D_N, the diameters of the component atoms for coordination number (CN) 12, regardless of the actual coordination(s) of the atoms in the structure. Thereafter, the linear equations obtained are interpreted in terms of the atomic arrays in the structure that control the cell dimensions and, from this, new quantitative information regarding the structure is frequently apparent. The method presumes the validity of Pauling's (1947) equation $R(1) - R(n) = 0{\cdot}3 \log n$ (n is the valency divided by the coordination number) and thus it avoids altogether the coordination problem, which is but a nuisance, and it has the advantage of revealing when atomic valency in the phases considered differs from that in the elemental structure from which the CN 12 diameter was derived (provided that the appropriate atomic contacts control the cell dimensions). This we call a 'valency effect'.

The method has been applied successfully to phases with many structures, but we are now attempting to apply it to tetrahedrally close-packed structures which, if regular, are built up of interpenetrating CN 12, 14, 15 and 16 polyhedra with triangulated surfaces, in which several different sets of interatomic contacts involved in the polyhedra (*i.e.* from the central atom to the surrounding atoms) may together act to control the cell dimensions.

In the analyses that follow, lattice parameters of the phases have been taken from Pearson (1967), or later volumes of ***Structure Reports***. The CN 12 diameters are those of Teatum, Gschneidner & Waber (1960). Omitted from the analyses are phases whose atoms have uncertain valencies and therefore uncertain diameters (Ce, Eu, Yb, and the actinides) and a few phases (*e.g.* $LaNi_2$) whose reported cell dimensions are inexplicable. In all, seven different groups of phases exhibiting characteristic dimensional behaviour have been recognized:

	M	N	Number of phases
(i)	rare earth	Fe, Co, Ni	27
(ii)	rare earth	Rh, Ir, Pt, Ru and Os	29
(iii)	rare earth	Mn	4
(iv)	rare earth	Al and Mg	18
(v)	non rare earth	Rh, Ir, Pd and Pt	11
(vi)	non rare earth	Cr and remaining metals	36
(vii)	alkali metals	Ag, Au, Bi	5.

When the number of phases in the sample is small there is always a danger that the analysis will be distorted to accommodate phases whose cell dimensions are incorrect due to non-stoichiometry or other reasons, but the characteristics of the major groups of phases appear to be well established.

2. Discussion

(*a*) *Relation between dimensional equations and the near-neighbour diagram for* $MgCu_2$ *phases*

When this method of dimensional analysis was first applied to phases with the $MgCu_2$ structure, many different types of behaviour became apparent which required so many equations and parameters to describe them, that the analysis appeared unprofitable. However, as the analysis proceeded, it was found that the near-neighbour diagram for phases with the $MgCu_2$ structure (Pearson, 1968) was useful in establishing that coherent groups of phases had been chosen.

Table 1. *Analysis of the cell dimensions of*

	System	Initial equations from n.n.d. or plots of *a versus* D_M and D_N	Final equations from further analysis of data
(ii)	Rare-earth phases of Ru, Os, Rh, Ir, Pt	Ru, Os: $a = 0{\cdot}923D_M + 1{\cdot}585D_N$ Rh, Ir, Pt: $a = 0{\cdot}923D_M + 1{\cdot}560D_N$ (see Fig. 2)	$a = 0{\cdot}923D_M + 1{\cdot}585D_N - 0{\cdot}021S$ S represents a valency effect involving the N atoms and has relative values of: 0 for Os Group, 3 for Ir Group and 4 for Pt Group. The difference of the a dependence on D_N in the two initial equations (which is not linear with D_N) is seen to result from a valency effect involving the N atoms. The equation reproduces a_{obs} values to within $\lvert 0{\cdot}009 \rvert$ Å.
(iii)	Rare-earth phases of Mn	$a \propto 2{\cdot}6$ to $3{\cdot}0D_M$ (Fig. 1).	$a = 3{\cdot}00D_M - 1{\cdot}177D_N^*$ obtained from the n.n.d. (Fig. 1) with slight adjustment, and assuming $D_{Mn^{VI}} = 2{\cdot}624$ Å. The equation reproduces a_{obs} to within $\lvert 0{\cdot}010 \rvert$ Å.
(iv)	Rare-earth phases of Al and Mg	Al: $a = 1{\cdot}386D_M + 1{\cdot}025D_N^*$ Mg: $a = 1{\cdot}386D_M + 1{\cdot}128D_N\ (A)^*$ The equations reproduce a_{obs} to within $\lvert 0{\cdot}011_8 \rvert$ Å for Al and $\lvert 0{\cdot}010_4 \rvert$ Å for Mg alloys. They were obtained from the n.n.d. (Fig. 3).	Alternately: Mg: $a = 1{\cdot}109D_M + 1{\cdot}448D_N\ (B)^*$ reproduces a_{obs} to within $\lvert 0{\cdot}006 \rvert$ Å. There are insufficient data to decide which equation is the most appropriate. If a is assumed to be a linear function of D_N for the Al and Mg alloys, then $a = 1{\cdot}4D_M + 1{\cdot}98D_N - 2{\cdot}784$ reproduces a_{obs} equally well.
(v)	Non-rare-earth phases of Rh, Ir, Pd, Pt	Seven equations of the form $a = 0{\cdot}462D_M + fD_N,^*$ where f has values from 2·078 to 2·167 depending on M valency 2, 3 or 4 and the N component, were obtained from the n.n.d. (Fig. 4). Coefficients f were linear with D_N, but the slopes for M^{II} and M^{III} phases were not the same.	M valency 2: $a = 0{\cdot}46D_M + 0{\cdot}85D_N + 0{\cdot}046S + 3{\cdot}419$ M valency 3 or 4: $a = 0{\cdot}46D_M + 1{\cdot}55D_N + 0{\cdot}046S + 1{\cdot}523$, where S, the valency effect involving M, has relative values 0 for Group II, 2·4 for Group III and 3·4 for Group IV M atoms. The equations reproduce a_{obs} to a mean precision of $\lvert 0{\cdot}004_3 \rvert$ Å. The final equations agree with the slopes of *a versus* D_M and D_N (Fig. 4) and recognize the valency effect involving the M components as illustrated for Ir alloys in Fig. 4.
(vi)	Non-rare-earth phases of Cr and other N components: Al, Au, Be, Co, Cr, Cu, Fe, Mo, Ni, V, W, Zn	Figs. 5–7 show evidence of valency effects involving both M and N components, and that $a \propto {\sim}0{\cdot}9\ D_M$ and ${\sim}1{\cdot}58\ D_N$. The basis of Fig. 7 is the equations: Cr, *etc.*: $a = 0{\cdot}927D_M + 1{\cdot}583D_N + 0{\cdot}042S$ Fe, Al: $a = 0{\cdot}886D_M + 1{\cdot}583D_N + 0{\cdot}042S$ Co, Ni: $a = 0{\cdot}870D_M + 1{\cdot}583D_N + 0{\cdot}042S$. S, the valency effect involving M, has relative values 1 for Groups I and II, 3 for Group III, 5 for Group IV and 6 for Group V M atoms. Fig. 7 indicates that the different coefficients of D_M are absorbing the valency effect of the N atoms; hence the final equation which recognizes it.	For all phases: $a = 0{\cdot}923D_M + 1{\cdot}58D_N + 0{\cdot}047S - 0{\cdot}040V$. S and V are, respectively, the valency effects for the M and N components, with relative values: S: Groups I and II 0 V: Co and Ni 2 III 1 Fe and Al 1 IV 3 Cr, *etc.* −1·5. V 4 This equation reproduces a_{obs} to a mean value of $\lvert 0{\cdot}017 \rvert$ Å. This poor precision indicates an oversimplification in choosing a single equation with a minimum of added parameters in order to describe the whole groups of alloys.
(vii)	Alkali-metal phases		$a = 0{\cdot}360D_M + 2{\cdot}636D_N - 1{\cdot}175$ The equation reproduces a_{obs} to a mean precision of $\lvert 0{\cdot}005 \rvert$ Å.

* These are only apparent coefficients of D_N; the true coefficient is

Phases with the $MgCu_2$ structure are scattered widely on the near-neighbour diagram, but mainly between the lines for 12–6 M–N and 6 N–N contacts; however, phases forming a coherent group are found to lie along a single line, or along parallel lines, according to the N component. The self-coherence of the first six groups of phases listed above is shown in Figs. 1 to 5. This led us to examine the relationship between the near-neighbour diagram and the dimensional equations obtained from plots of *a versus* D_M and D_N.

six groups of phases with the $MgCu_2$ *structure*

Interatomic distances in phases			
Smaller than radius sums	Greater than radius sums	Control of the cell dimension	Comments
M–M, M–N, N–N except N–N for Ru and Os phases which are slightly greater.		The cell dimension is controlled by all three sets of contacts acting together. On the n.n.d. (Fig. 2) phases lie on a line parallel to that representing the root-mean-square of the lines for the three contacts, weighted for multiplicity. With eq. (1) this line gives $a = 0{\cdot}926D_M + 1{\cdot}61D_N$ in the region of the D_M/D_N values concerned, in agreement with the observed equations.	
M–M	M–N, N–N	The cell dimension is controlled by the M–M (rare-earth) contacts. The negative dependence of a on D_N results from this and has nothing intrinsically to do with D'_{Mn}.	The negative slope of $(D_M - d_M)/D_N$ against D_M/D_N on the n.n.d. indicates a dependence of a on D_M which is greater than 2·309 (§2). It has nothing to do with the diameter assumed for Mn. The analysis indicates a Mn diameter corresponding to Mn^{VI} rather than, *e.g.*, Mn^{II} (2·91 Å). In the latter case M–N and N–N contacts would also be made, but this is contrary to the observed dependence of a on D_M and D_N, thus correcting Pearson (1968)!
N–N Al: M–M	M–N Mg: M–M	Uncertain.	That the M–M distances are greater than D_M in Mg alloys favours $1{\cdot}109D_M$ (B) rather than (A). The $GdMg_2$ phase is omitted from the analysis as its cell edge appears to be inaccurate.
M–M, M–N, N–N except M–N for $ScIr_2$, $ZrIr_2$ N–N for $SrRh_2$.		The only way of accounting for the small dependence of a on D_M is by an average of all M–N and N–N contacts, or of the M–N and N–N contacts in the icosahedron about N, weighted for multiplicity and composition, which give, respectively, $a = 0{\cdot}513D_M + 2{\cdot}05D_N - \Delta$ and $a = 0{\cdot}434D_M + 2{\cdot}17D_N - \Delta$. The influence of the close M–M contacts in the Friauf polyhedron appears to be picked up in the valency effect involving the M atoms.	As this group of alloys covers a wide range of D_M/D_N values from 1·17 to 1·60, it is not surprising that a different dependence of a on D_N is found for alloys of divalent M components which all lie at $D_M/D_N >$ 1·40. Excluded from the results are phases with Ba as the M component; Pearson (1980*b*) showed these must have cell edges too large to agree with those of other phases. Phases with Pd as N are also excluded as their reported cell edges are larger than those of the Pt phases!
N–N, generally, but not always. M–M either smaller or greater depending on D_M/D_N.	M–N, except Sc and Y phases of Fe, Co, Ni..	$a \propto 0{\cdot}9D_M + 1{\cdot}58D_N$ indicates control of the cell edge by the average of all three contacts, weighted for multiplicity and composition which gives $a = 0{\cdot}923D_M + 1{\cdot}583D_N - \Delta$ (§2).	The n.n.d. (Fig. 5) shows these phases to form a homogeneous group, but they extend over a very broad range of D_M/D_N values, and there is doubt of the extent to which they meet the analytical condition that 'the coordination is the same for all alloys'. Nevertheless, plots of *a versus* D_M and D_N (Figs. 6 and 7) appear normal, compared to those for other alloys. It is impossible to tell whether the apparent valency effects represent real differences in number of electrons per bond, adjusted to CN 12 for the alloys, compared to the elemental structures from which the CN 12 diameters were determined, or whether they reflect changes in the effectiveness of the 16–12 coordination – if indeed they are not both the same. Excluded from the analyses are $CaAl_2$, YNi_2 and $PbAu_2$, whose cell edge, a, appears to be disparate.
		The small dependence of the cell edge on D_M is to be expected in view of the large compressibility of the alkali metals. The coefficient of D_N is approaching the value of 2·829 expected for control of the cell edge by N–N contacts alone.	$NaAg_2$ is excluded from the analysis as its cell edge does not appear to be compatible with that of $NaAu_2$.

undetermined relative to an added constant term in the equations.

The *slope* and the D_M/D_N *intercept* at $(D_M - d_M)/D_N = 0$ of any particular line on the near-neighbour diagram establish the a dependence on D_M and D_N for the contact or combination of contacts represented by the line, since

$$\left(D_M - \frac{\sqrt{3}}{4}a\right)/D_N = [D_M/D_N - (\mathit{intercept})]\,(\mathit{slope}), \quad (1)$$

whence it is seen that the coefficient of D_M depends only on the *slope* of the line, but the coefficient of D_N depends on the product of the *slope* and the *intercept*. Thus phases of the same N atom lying on a line parallel to, but displaced from the line for 12–6 $M–N$ contacts, would have the a dependence on D_M predicted for control of the cell edge by the $M–N$ contacts, but a different a dependence on D_N because the zero intercept would be different. Also, these coefficients of D_N must differ from the true value of the dimensional equation if the constant term thereof is non-zero.

Also, it can be seen that phases of the same N atom whose cell dimension is dependent on D_N alone would have to lie along or parallel to a line for $N–N$ contacts, and that such lines must always have a slope of unity in order that the a dependence on D_M is zero [*cf.* equation (1)]. Similarly the $M–M$ contact line must not only have a slope of zero but lie along $(D_M - d_M)/D_M = 0$ if the a dependence on D_N is to be zero. If a line has zero slope but is displaced from $(D_M - d_M)/D_N = 0$, then there is also a small dependence of a on D_N, depending on the size of the displacement, as its value must be added to the right-hand side of equation (1). Since equation (1) gives $a = 2{\cdot}309 D_M$ for the $M–M$ contact line at $(D_M - d_M)/D_N = 0$, it follows that a larger dependence of a on D_M than this requires a line of negative slope on the near-neighbour diagram. Herein we have an explanation of the strange behaviour of rare-earth–manganese phases $M\mathrm{Mn}_2$ with the $MgCu_2$ structure which, unlike any other phases, always lie on a line of negative slope on the near-neighbour diagram, regardless of what diameter is assumed for Mn – the behaviour merely indicates an a dependence on D_M of greater than $2{\cdot}309 D_M$ (see Table 1)!

(*b*) *Interpretation of dimensional equations in terms of atomic arrays that control the cell dimension*

The $MgCu_2$ structure can be regarded as composed of interpenetrating icosahedra and Friauf polyhedra. The icosahedra are built of 6 M and 6 N atoms and centred by N atoms, whereas the Friauf polyhedra are composed of 4 M and 12 N atoms and centred by M atoms. Thus we may variously expect the 4 $M–M$, 12–6 $M–N$ and 6 $N–N$ contacts to act in conjunction in controlling the cell dimensions of phases with the structure. According to a lemma (Pearson, 1981), when the different sets of contacts occur in the same coordination polyhedron, they combine by some averaging process in controlling a, but when two sets of contacts combining together to control a are involved in quite independent polyhedra – as, for example, the octahedra of N atoms and the cubo-octahedron of M atoms are in the rocksalt structure, MN – their effects combine by simple addition.

The problem is therefore to find some suitable means of averaging that permits interpretation of the dimensional equations (which have the form $a = fD_M + f'D_N + k$) in terms of the combination of contacts that control a in the particular circumstances that are observed. If all three sets of contacts act together in controlling a, it can be presumed that the observed a value provides the best energy balance between those contacts that are compressed [*e.g.* $D_M > (\sqrt{3}/4)\,a$ for 4 $M–M$] and those that may not be fully made [*e.g.* $D_N < (\sqrt{2}/4)a$ for 6 $N–N$] to give the minimum free energy in satisfying the overall 16–12 coordination to the best extent possible. Thus contacts that are compressed will seek to expand a, and those that are not effectively made will seek to contract a. Therefore, contact multiplicity and the relative numbers of M and N atoms in the formula are also expected to be involved in the energy balance (Pearson, 1968). One method that appears to give results consistent with other data is to average the difference between the appropriate diameters and the calculated distances, these being weighted according to their multiplicities:

$$\frac{1}{19}\left[4\left(D_M - \frac{\sqrt{3}}{4}a\right) + \frac{12+6}{2}\left(D_M/2 + D_N/2 - \frac{\sqrt{11}}{8}a\right) + 6\left(D_N - \frac{\sqrt{2}}{4}a\right)\right] = \Delta,$$

whence $a = 1{\cdot}121 D_M + 1{\cdot}385 D_N + \Delta'$, where Δ, Δ' are numbers. Alternately, the $M–N$ distances can be expressed as $\frac{1}{3}(D_M + 2D_N)$ instead of as $\frac{1}{2}(D_M + D_N)$ in order to take account of composition, whence $a = 0{\cdot}923 D_M + 1{\cdot}583 D_N - \Delta'$. Similarly, averages can be obtained for the contacts in the Friauf polyhedron about M, the icosahedron about N, for combinations of $M–M$ and $N–N$ contacts only, *etc.* For single contacts alone the calculated dependences of a on D_M and/or D_N are:

$$M\text{–}M\colon D_M = \frac{\sqrt{3}}{4}a, \text{ whence } a = 2{\cdot}309\, D_M,$$

$$N\text{–}N\colon D_N = \frac{\sqrt{2}}{4}a, \text{ whence } a = 2{\cdot}829\, D_N,$$

$$M\text{–}N\colon \tfrac{1}{2}(D_M + D_N) = \frac{\sqrt{11}}{8}a, \text{ whence } a = 1{\cdot}206 D_M + 1{\cdot}206 D_N,$$

$$\text{or } \tfrac{1}{3}(D_M + 2D_N) = \frac{\sqrt{11}}{8}a, \text{ whence } a = 0{\cdot}804 D_M + 1{\cdot}608\, D_N.$$

Somewhat similar results can be obtained from the near-neighbour diagram by averaging the $(D_M - d_M)/D_N$ values at given D_M/D_N ratios for the three sets of contacts, weighted according to their multiplicity, thus deriving a new line on the near-neighbour diagram, whose D_M/D_N intercept at $(D_M - d_M)/D_N = 0$ and slope give equation (1), whence $a = 1{\cdot}062D_M + 1{\cdot}459D_N$ for all three contacts acting together. The near-neighbour diagram, of course, gives the same results as above for the M–M, M–N and N–N contacts alone, but the conditions are not quite the same as in the first example, and the averages that one obtains for the various combinations generally differ slightly ($<0{\cdot}1$) in coefficients of D_M and D_N from those calculated by the first method.

3. Analysis of the cell dimensions of the seven groups of phases with the MgCu$_2$ structure

We now present an analysis of the seven different groups of phases with the MgCu$_2$ structure, according to the methods discussed above. Although the analysis of the first group – rare-earth phases of Fe, Co, and Ni – is given in full to illustrate the method used, the results for the remaining groups have to be summarized in tabular form (Table 1 and Figs. 1–7), in order to conserve space. The full manuscript covering material in Table 1 has been deposited.*

(i) *Rare-earth phases of* Fe, Co *and* Ni

The rare-earth phases of N components Fe, Co and Ni appear as a group on the near-neighbour diagram (Fig. 1) where they lie parallel to the line for the 12–6 M–N contacts. The 27 phases in this group have their

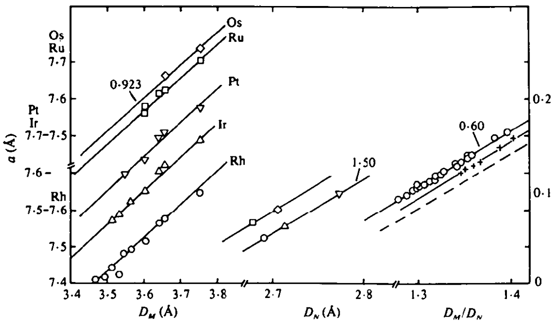

Fig. 2. Rare-earth (M) alloys of Os, Ru, Pt, Ir and Rh N components. Left: a *versus* D_M. Centre: a at $D_M = 3{\cdot}6$ Å *versus* D_N. Right: Near-neighbour diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N. The broken line represents a weighted average for the 4 M–M, 12–6 M–N and 6 N–N contacts (see text). Symbols indicate N components as follows: ◇ Os, □ Ru, ▽ Pt, △ Ir and ○ Rh. The scale of a *versus* D_N is that marked Rh.

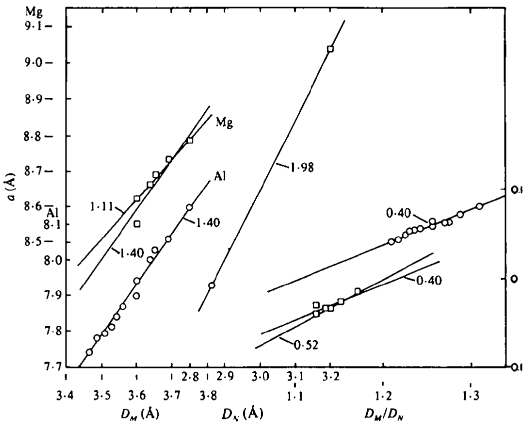

Fig. 3. Rare-earth (M) alloys of Al and Mg N components. Left: a *versus* D_M. Centre: a at $D_M = 3{\cdot}6$ Å *versus* D_N. The scale of a is that for Al. Right: Near-neighbour diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N. ○ indicates Al and □ Mg alloys.

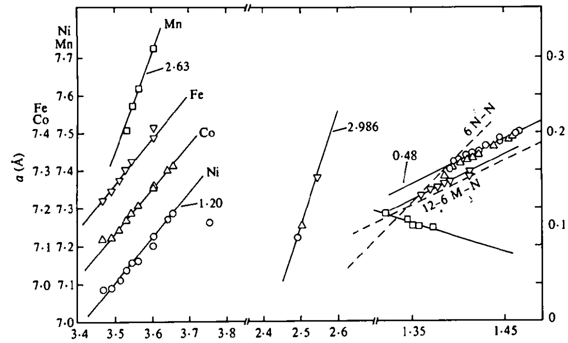

Fig. 1. Rare-earth (M) alloys of Mn, Fe, Co, and Ni N components. Left: a *versus* D_M. Centre: a at $D_M = 3{\cdot}6$ Å *versus* D_N. Right: Near-neighbour diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N. The broken line indicates when the 12–6 M–N distances exactly equal $\frac{1}{2}(D_M + D_N)$. Symbols indicate N components as follows: □ Mn, ▽ Fe, △ Co and ○ Ni. Numbers indicate slopes of lines on this and subsequent figures.

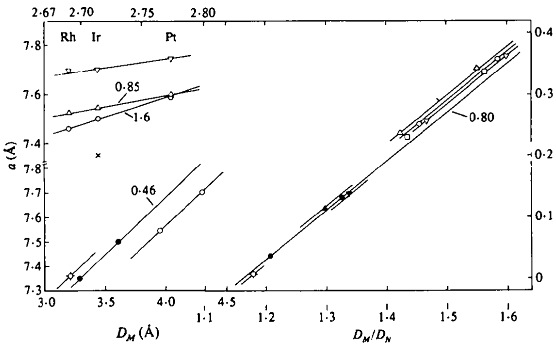

Fig. 4. Non-rare-earth (M) alloys of Rh, Ir, Pd and Pt N components. Upper left: a *versus* D_M for × Sc, ○ Y, △ Ca and ▽ Sr alloys of Rh, Ir, and Pt. Right: Near-neighbour diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N. N components are represented by the following symbols: ▽ Rh, ○ Ir, □ Pd and △ Pt. Open symbols are alloys of divalent M components, filled symbols trivalent M components and -○- is ZrIr$_2$. Lower left: a *versus* D_M for Ir alloys, indicating the valency effect for the M components.

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* That portion of the full manuscript covering material in Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35973 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

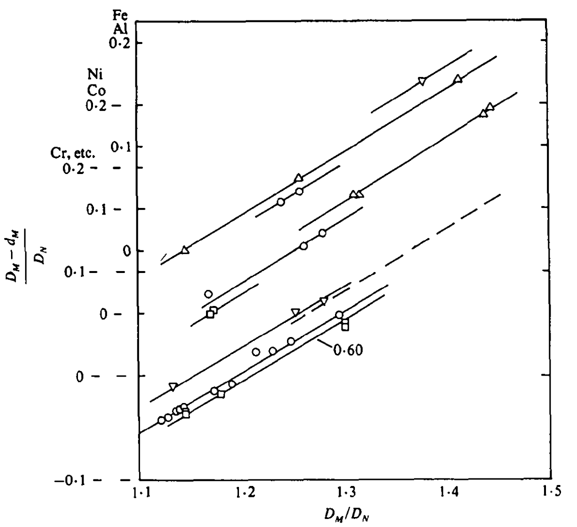

Fig. 5. Non-rare-earth (M) alloys of Cr and other N components. Near-neighbour diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N. Note the scales for Ni and Co, and for Fe and Al alloys are displaced upwards. The broken line represents a weighted average for the 4 M–M, 12–6 M–N and 6 N–N contacts (see text). Symbols indicate the valency of the M components as follows: ▽ one and two, △ three, ○ four and □ five.

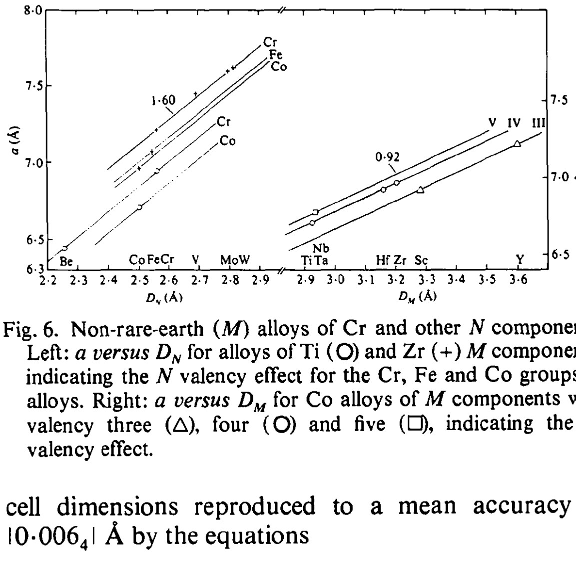

Fig. 6. Non-rare-earth (M) alloys of Cr and other N components. Left: a *versus* D_N for alloys of Ti (○) and Zr (+) M components, indicating the N valency effect for the Cr, Fe and Co groups of alloys. Right: a *versus* D_M for Co alloys of M components with valency three (△), four (○) and five (□), indicating the M valency effect.

cell dimensions reproduced to a mean accuracy of $|0{\cdot}006_4|$ Å by the equations

$$\text{Fe: } a = 1{\cdot}20D_M + 1{\cdot}202D_N, \qquad (2)$$

$$\text{Co: } a = 1{\cdot}20D_M + 1{\cdot}170D_N, \qquad (3)$$

$$\text{Ni: } a = 1{\cdot}20D_M + 1{\cdot}160D_N, \qquad (4)$$

which are derived from the data on the near-neighbour diagram. The coefficients of D_N are seen to vary linearly with D_N. Using this, and with slight adjustment to obtain the best result, a single equation is obtained for phases of Fe, Co and Ni: $a = 1{\cdot}20D_M + 0{\cdot}70D_N^2 - 0{\cdot}582D_N$. In the range of interest this equation is seen to be

$$a = 1{\cdot}20D_M + 2{\cdot}986D_N - 4{\cdot}544, \qquad (5)$$

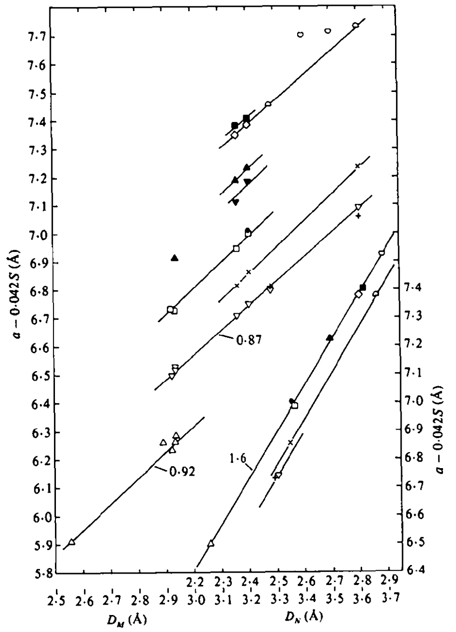

Fig. 7. Non-rare-earth (M) alloys of Cr and other N components identified by the symbols: ⌓ Al, ▿ Au, △ Be, ▽ Co, □ Cr, ● Cu, × Fe, + Ni, ◇ Mo, ■ W, ▲ V and ▼ Zn. Left: a, corrected for the M atom valency effect ($a - 0{\cdot}042S$; see text) *versus* D_M. Right: a at $D_M = 3{\cdot}2$ Å *versus* D_N, which again reveals the valency effect for the three groups of N components.

which reproduces a for the 27 phases to a mean accuracy of $|0{\cdot}006_9|$ Å. Fig. 1 also shows that a varies with $1{\cdot}20D_M$ for the three sets of alloys and that a at a constant D_M value of 3·6 Å appears to vary with $2{\cdot}986D_N$, confirming equation (5).

If the M–N distances control the cell edge and the atomic diameters are not weighted according to composition, then $(\sqrt{11}/8)a = \frac{1}{2}(D_M + D_N)$, whence $a = 1{\cdot}206D_M + 1{\cdot}206D_N$, which reproduces equation (2) exactly. Thus the near-neighbour diagram observations and equations (2) to (4) all indicate that the 12–6 M–N contacts alone control the cell dimension for this group of phases, and this agrees with the observation that the M–N contacts are closer than $\frac{1}{2}(D_M + D_N)$, whereas the N–N distances are all greater than D_N. The M–M distances are, however, less than D_M.

The apparent dependence of a on $2{\cdot}986D_N$ [equation (5) and Fig. 1] is therefore incorrect. It arises from a valency effect involving the N atoms which has been absorbed as an additional dependence on D_N. Confirmation of this assessment comes from the rare-earth phases of Ru, Os, Rh, Ir, and Pt (Table 1) where, similarly, slightly different a dependences on D_N are found. In this case, however, the D_N dependences are *not* a linear function of D_N; instead they correlate with the Group of the N atoms in the Periodic Table. Taking the valency effect into account gives the final equation for the cell dimensions of all phases of Ni, Co and Fe:

$$a = 1{\cdot}20D_M + 1{\cdot}202D_N - 0{\cdot}026S, \qquad (6)$$

where $S = 0$ for Fe, 3 for Co and 4 for Ni. The valency effect means that the numbers of valency electrons used in bonding by the Fe, Co and Ni atoms differ from those in the elemental structures from which their CN 12 diameters were determined and that these differences differ from each other. The S values of 0, 3 and 4 in equation (6) are only relative numbers and do not have particular significance *per se.* Zero for Fe merely indicates that a has the largest values for the Fe alloys, corresponding to the lowest number of valence electrons used by Fe in the 6 N–M and 6 N–N bonds.

Relative to the CN 12 diameter of Ni for a valency of six, the Co CN 12 diameter in the alloys is 0·0217 Å larger, corresponding to 5·53 valency electrons and that of Fe is 0·087 Å larger, corresponding to 4·30 valency electrons. The differences $[\frac{1}{2}(D_M + D_N) - (\sqrt{11}/8)a]$ for the M–N contacts are independent of D_M/D_N and increase for the N components in the order Fe, Co, Ni, whereas $[D_N - (\sqrt{2}/4)a]$ for the N–N contacts decreases with increasing D_M/D_N, but is *the same* function of D_M/D_N for the three N components. Hence the valency effect involving the N atoms has its origins in the M–N, rather than the N–N, contacts, which is also consistent with the M–N contacts controlling the cell dimensions. It is interesting to compare these observations with those on the valency effect in rare-earth alloys of Ru, Os, Rh, Ir and Pt, described in Table 1.

Relative to the CN 12 diameter of Pt and a valency of 6, the Ir and Rh CN 12 diameters in the alloys are 0·0126 Å larger corresponding to 5·72 valency electrons, and those of Ru and Os are 0·0505 Å larger, corresponding to 4·94 valency electrons. There is a difference between these alloys and those of Fe, Co, and Ni, corresponding to all contacts acting together to control a in this case. Here the differences $[D_N - (\sqrt{2}/4)a]$, although decreasing with increasing D_M/D_N, are *not the same* for all the N components. The Pt alloys have the largest values, followed by Ir and Rh alloys that have similar values, and the Ru and Os alloys have the smallest differences. The differences $[\frac{1}{2}(D_M + D_N) - (\sqrt{11}/8)a]$ vary only very slightly with D_M/D_N, and as in the case of the Fe, Co and Ni alloys, the Pt, and Rh and Ir, and the Ru and Os alloys have different values. Therefore here the valency effect has its origins in both the M–N and N–N contacts.

Although the size of the valency effect varies in the Fe, *etc.* and Ru, *etc.* sets of alloys, it is interesting that the ratio of the changes in diameter from Ni to Co and from Pt to Rh and Ir: 0·0217/0·0126 = 1·722 is the same as that from Ni to Fe and from Pt to Ru and Os: 0·0870/0·0505 = 1·722.

4. Conclusions

(1) Atomic size depends on both valency and coordination number. Valency is a fundamental atomic property which must be known for complete analysis of physical properties relative to structure. Coordination, on the other hand, is not a fundamental atomic property – it is only a *situation.* Any situation that becomes difficult should be avoided (*e.g.* if atoms in a structure have more than one CN, or if the distances to their neighbours are very disparate, or change drastically with changing D_M/D_N as sometimes in the $MgCu_2$ structure); it is unprofitable to attempt to tackle the situation by devising schemes of fractional coordination numbers, *etc.* Fortunately, the coordination situation can be avoided if Pauling's $R(1) - R(n) = 0{\cdot}3 \log n$ equation is valid, as physical properties (*e.g.* cell dimensions) of a series of phases with a given structure can be examined as a function of the diameters of the component atoms for some standard CN (here 12), since change from the standard CN to any other CN that exists in the structure only adds or subtracts a constant term in the equations obtained.

Such analyses have worked very well in metallic structures where a single linear or planar array of interatomic contacts has been found to control the cell dimensions. The problem is more complex in tetrahedrally close-packed structures such as the $MgCu_2$ structure, where different interatomic contacts may together act to control the cell dimensions – where the first interatomic contacts to be made are 6 N–N below a value of $D_M/D_N = 1{\cdot}225$ and 4 M–M above – and where the 12–6 M–N contacts cannot be made, except at the expense of compressing either or both of the other contacts depending on the D_M/D_N value for the alloy.

Thus it is expected that the contacts or combinations of contacts that control the cell dimension of phases with the $MgCu_2$ structure would depend on the diameter ratio of the phases. Such expectations as a function of D_M/D_N are indicated by the full lines in Fig. 8, and the broken lines indicate that these expectations

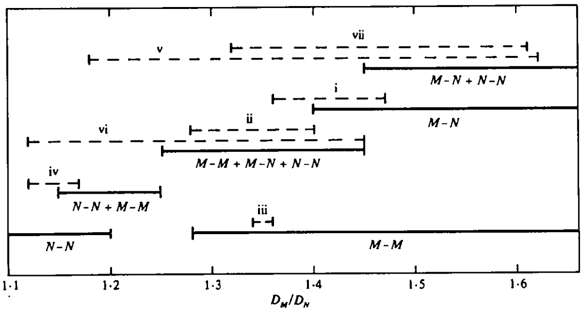

Fig. 8. Diagram indicating in terms of D_M/D_N the contacts, or groups of contacts acting together, that are expected to control a (full lines). The broken lines situated above the full lines represent groups of alloys observed to have that behaviour. (i) Rare-earth alloys of Fe, *etc.*, (ii) rare-earth alloys of Ru, *etc.*, (iii) rare-earth alloys of Mn, (iv) rare-earth alloys of Mg, (v) non-rare-earth alloys of Rh, *etc.*, (vi) non-rare-earth alloys of Cr, *etc.* and (vii) alkali-metal alloys.

are in the main borne out by the results of the analyses. However, the significant feature of Fig. 8 is that certain groups of phases far transcend these expectations, the same combinations of contacts controlling a over a wide range of diameter ratios. The non-rare-earth phases of Rh, *etc.* (Table 1 and Fig. 4) are a striking example. Thus it is apparent that the groupings of the atoms in the Periodic Table can have a stronger influence on the interactions that control the length of the cell edge, than the relative diameters of the atoms alone.

The empirical relationships between interatomic distances and diameter ratios that have been described in many papers are here replaced by equations giving the cell dimensions in terms of the CN 12 diameters of the atoms. The equations are interpreted in terms of the atomic contacts that control the cell dimensions. Groups of phases, according to the location of the atoms in the Periodic Table, are identified that exhibit specific behaviour.

(2) The lemma proposed in Pearson (1981) appears to be upheld in the present analysis, since in the $MgCu_2$ structure the three sets of interatomic contacts occur in the same two coordination polyhedra. In this circumstance the lemma requires that if different contacts act together in controlling a, they do so in some form of averaging, not by addition of individual dependences. Although the appropriate method of averaging is subject to difficulty, the two methods used with weighting for contact multiplicity appear to provide sensible interpretation of the dimensional equations obtained. Such interpretations are subject to independent check, since they must be consistent with the observed $[D_M - (\sqrt{3}/4)a]$, $[D_N - (\sqrt{2}/4)a]$ and $[\frac{1}{2}(D_M + D_N) - (\sqrt{11}/8)a]$ values for the group of phases concerned.

(3) Valency is a fundamental atomic property that must be known for a complete analysis of physical properties of phases with a given structure. The method of analysis gives information about the valency of a component involved in the contacts that control the cell edge, if this (*i.e.* the average number of electrons per bond adjusted to CN 12) differs from that in the elemental structure from which the CN 12 diameter was determined. Such evidence is relative from elements of one Group, or valency, to another. When the valencies are standard – *e.g.* two or six electrons used in bonding by sulphur (Pearson, 1980*d*) – or when the differences between the radius sum and the observed distances are constant, as in phases with the $AlCr_2C$ structure (Pearson, 1980*e*), the valency effects can be interpreted quantitatively.

Much evidence of valency effects is found in dimensional analyses of phases with the $MgCu_2$ structure, but it can only be interpreted on a relative basis, since basic valencies are uncertain. Neither can it be calculated on an absolute basis as the differences between the radius sums and the observed interatomic distances are not constant with change of D_M/D_N on going from one phase to another, so the apparent number of valency electrons changes from phase to phase. Furthermore, the basis of the apparent valency effects in phases with the $MgCu_2$ structure is uncertain, since it is not known, for example, if the influence of 4 M–M contacts that are closer than D_M, yet do not appear to control a, is also picked up in an apparent valency effect involving the M atoms. A suggestion of similar behaviour was observed during analysis of phases with the β-wolfram structure (Pearson, 1981). It also involved the major ligands (2 N–N in $\langle 100 \rangle$ directions) which were very compressed, yet did not appear to control a. In the $MgCu_2$ structure at large D_M/D_N values, the major ligands, 4 M–M, are very compressed. Far too many valency electrons would be required to attain these close distances through chemical bonding, and it appears that they result from geometrical constraints arising elsewhere in the structure, so that few, if any, bonding electrons are involved.

(4) Despite the 16–12 coordination in these phases and the great differences in $[D_M - (\sqrt{3}/4)a]$, $[D_N - (\sqrt{2}/4)a]$ and $[\frac{1}{2}(D_M + D_N) - (\sqrt{11}/8)a]$ values with changing D_M/D_N ratio of the phases, standard CN 12 diameters can be used to reproduce the observed cell dimensions in a satisfactory manner, taking into account the precision obtained and the number of additional parameters required for the equations. Pearson (1980*c*) has devised a method of assessing the validity of calculations of cell dimensions from atomic diameters with added parameters, that takes account of the competing factors: (i) percentage precision attained and (ii) number of parameters involved. In the present work nine equations have been used to calculate the cell dimensions of 125 phases, using a total of 36 parameters, additional to the CN 12 diameters of the atoms. According to Pearson (1980*c*), these data give a slope of $-0{\cdot}20$ ($-0{\cdot}15$ if the Cr, *etc.* phases are excluded) which is lower (*i.e.* better) than the value of $-0{\cdot}30$, assessed as representing a satisfactory calculation.

(5) As observed for the structures of many other alloys (Pearson, 1980*b*), rare-earth phases (M) with the $MgCu_2$ structure have a different dependence of a on D_M and D_N, compared to corresponding non-rare-earth phases with the same N components.

(6) Finally, this paper seeks to give quantitative expression, in terms of CN 12 diameters, to qualitative observations that have been reported in many previous papers dealing with phases having the $MgCu_2$ structure. It must, however, be admitted that assessment and interpretation of the data presented is by no means complete at the present time.

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Dimensional Analysis of Laves Phases: Observations on the Axial Ratios of Certain Phases with the $MgZn_2$ Structure

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Abstract

The a and c cell dimensions of phases with the hexagonal $MgZn_2$ (MN_2) structure vary linearly with D_M and D_N, the diameters of the component atoms for coordination number 12, in series of phases that have the same N or M component respectively. The coefficients of these a and c dependences on D_M and D_N for series of phases formed between the rare earths (M) and Ru, Os, Tc or Re (N) are such as to provide an analytical result, not normally available, that change of axial ratio (c/a) in series of phases with the same N component results from a special adjustment of the c axis of the cell alone. Such behaviour is interpreted in terms of the atomic arrangement in the structure, and this also leads to the prediction that a similar effect should be found in phases with the hexagonal wurtzite structure. This is confirmed insofar as the available data permit. Additional observations are made on the cell dimensions of phases formed by Y, Ca, Sr and Ba (M) with Mg (N), that have the $MgZn_2$ structure.

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1. Introduction

Dimensional analyses have been carried out for phases with both the cubic ($MgCu_2$) and hexagonal ($MgZn_2$) Laves phases, MN_2. The results reported for the cubic phases (Pearson, 1981) are quite complex and the situation is further compounded for phases with the $MgZn_2$ structure because of the variable axial ratio and two variable atomic parameters, x and z, accurate values of which are practically unknown. For this reason the only feature of the analyses to be reported here is some interesting observations concerning the axial ratios of certain of the phases.

2. Analysis

We proceed as discussed in §§1, 2 and 4 of the paper dealing with phases having the $MgCu_2$ structure (Pearson, 1981) and separate phases with the $MgZn_2$ structure into five distinct groups according to their