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The Geometrical Factor in the Crystal Chemistry of Metals: Near-Neighbour Diagrams

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In an attempt to gain some quantitative assessment of the influence of the geometrical principles of Laves for the structures of metals on the occurrence of phases, and on their structural dimensions, a model has been adopted that allows the atoms to be compressed until successively *A–A*, *A–B* and *B–B* contacts are formed. The 'near-neighbour diagrams' that are obtained are thus more suitable for metals than the space filling diagrams of Laves, which are based on an incompressible atom model. They permit an assessment of (1) the relative importance of coordination, and geometrical and bond factors with regard to the occurrence of phases as a function of radius ratio of the component atoms and (2) the influence of these factors on the unit-cell dimensions and atomic parameters of phases with a given structure. The quantitative aspect is introduced by comparing the actual structural dimensions of phases having a given structure, with interatomic separations permitted by the structural geometry.

Introduction

The geometrical principles of Laves (1956), that the structures of metals, in the absence of other dominant effects such as bond factors, should exhibit the highest degree of space filling, the highest symmetry and the greatest number of connexions between the atoms, have been a conversation piece for a decade. However, the difficulty in explicitly analysing the relative importance of these geometrical effects in structures is that they are amenable to discussion rather than quantitative measurement. Although Laves himself did introduce a space filling model for binary systems to compare the relative favourability of various structures at different radius ratios of the component atoms, it appears to be inappropriate for metals since it is based on a hard-sphere model of the atom, whereas one of the main properties of metals is the compressibility of the atoms. Furthermore, the space filling model as presented by Laves and extended by Parthé (1961) only compares *structures* and does not examine the *dimensional behaviour of phases with given structures*; also it has obvious difficulties of application to complex structures where many different atomic contacts may occur.

In order to examine in a more quantitative manner the geometrical influence on structure type, and the structural dimensions of phases with a given structure, we develop a model that permits the atoms to be compressed in order to realize successively all of the different *A–A*, *A–B etc.* contacts permitted by the geometry of the structure. The conditions for the formation of the various atomic contacts are satisfied by straight lines on the 'near-neighbour diagrams' (n.n.d.) which are obtained. The known lattice and atomic parameters of phases with a given structure permit their location on the near-neighbour diagram as points whose distribution can then be compared with the lines for various contacts in order to determine what bond or geometrical factors may influence (1) the occurrence of phases as a function of radius ratio, and (2) the structural dimensions of the phases. In this way some degree of quantitative assessment of the influence of structural features on the occurrence and unit-cell dimensions of phases can be obtained.

Near-neighbour diagrams

The model adopted for binary alloys allows compression of the atoms to establish A–A, A–B and B–B contacts, which are formally considered to occur when the interatomic distances d_A, d_{AB} and d_B equal $2r_A=D_A$, $r_A+r_B=\frac{1}{2}(D_A+D_B)$ and $2r_B=D_B$ respectively. Straight lines are obtained for conditions of A–A, A–B and B–B contacts on a diagram of a reduced strain parameter, $(D_A-d_A)/D_B$, *versus* the radius ratio $r_A/r_B=D_A/D_B$. It is immaterial whether, say $(D_A-dA)/D_B$ or $(D_B-d_B)/D_B$ is taken as the reduced strain parameter, since change from one to the other only rotates the diagram so that the line for B–B contacts lies at the zero value of the reduced strain parameter, instead of that for A–A contacts; the relative geometry of the diagram remains identical. In complex structures with several different A–A contacts one of these is arbitrarily selected for the d_A value, which sets the line for these contacts along $(D_A-d_A)/D_B=0$, and positions the scale of the strain parameter relative to the lines for the other atomic contacts. Data for phases with a given structure can be recorded on the diagram at the appropriate D_A/D_B values, since d_A can be calculated from the unit cell and atomic parameters, and the distribution of the points representing actual phases can be compared with the lines for the various contacts in order to assess which are important for the occurrence of phases with the structure. When a point representing a phase has a larger $(D_A-d_A)/D_B$ value than a particular contact line (*i.e.* lies above it on the n.n.d.), then these contacts are compressed in the structure of the phase. When the structure has variable axial ratios or variable atomic parameters, the lines for various contacts may change their position on the diagram as the structural parameters change. In many cases (see *e.g.* Fig. 5) the simultaneous change in the positions of the contact lines, and of the points for observed phases with change of axial ratio or atomic parameters, provides certain confirmation of the structural importance of a particular contact.

Analysis of data on near-neighbour diagrams

Experience with near-neighbour diagrams enables us to consider geometrical effects in structures explicitly, and to separate (i) a *coordination factor* which leads to the formation of phases with a given structure at a specific radius ratio and with specific cell dimensions such that the phases are located on the n.n.d. close to the crossing point of two or more lines for contacts giving high coordination, and (ii) a true *geometrical factor* which controls the structural dimensions so as to maintain a high coordination when the phases occur over a wide range of radius ratios of the component atoms. In this case phases are distributed not only about the crossing point of two lines giving high coordination but extend widely on either or both sides of it, lying between the lines. The maintenance of both sets of contacts (at the expense of compressing one set) results in a favourable free energy so that phases may adopt the structure, even though the radius ratio of their component atoms differs considerably from the value at which the contact lines cross and both sets of contacts occur without strain. Fig. 1 shows an example of this behaviour in the $MgZn_2$ Laves structure, where the phases occur over a wide range of radius ratios between the lines for $12-6$ A–B and 6 B–B contacts giving overall $16-12$ coordination when the compressed A–A contacts are included. A similar situation is found for the $MgCu_2$ structure which was discussed in greater detail by Pearson (1968). The coordination factor appears to control phases with the β-W structure whose n.n.d. is given in Fig. 2, since the great majority of phases with this structure are concentrated in a narrow region on the line for $12-4$ A–B contacts and between those for $8+2$ B–B contacts, giving $12-14$ coordination. This conclusion is not surprising since the β-W structure belongs to the class of Frank–Kasper (Frank & Kasper, 1958, 1959) tetrahedral packing structures and the components form C.N.12 icosahedra and the C.N.14 polyhedra; in such structures the coordination factor is expected to be the dominant influence. Fig. 3, on the other hand, shows an example where a strong coordination factor exerts no influence whatsoever on the radius ratio or structural dimensions of phases taking the α-$ThSi_2$ structure. Lines for A–A, A–B and B–B contacts intersect severally in the region of radius ratio values from about 1·8 to 2·1 so that phases located in this region would have a high $20-9$ coordination. However, all known phases with this structure are formed from components with radius ratios from about 1·15 to 1·4 and lie about the lines for A–B contacts, indicating dominance of a chemical bond factor.

The *chemical-bond factor* controls the structures of phases when certain valence and coordination conditions are satisfied, and on the n.n.d. we expect phases whose structure is dominated by a bond factor to lie along the contact line for the particular bonds. Thus on the n.n.d. for the sphalerite structure (Fig. 4), phases are distributed along the line for A–B contacts, consistent with the well-known bond factor. Similarly Fig. 3 demonstrates the importance of the A–B bond factor in the α-$ThSi_2$ structure. This Figure shows that in addition to being located about the lines for $8-4$ and $4-2$ A–B contacts, the phases are distributed with a slope parallel to that of the $2+1$ B–B contacts, suggesting a secondary importance of a B–B bond factor which represents the three-dimensional network of B atoms running throughout the structure. Nevertheless, it is the A–B contacts that control the magnitude of the cell dimensions rather than the B–B contacts, since the phases lie about the A–B, rather than the B–B contact lines. The importance of a bond factor is also evident in the CdI_2 structure since points for the various phases on the n.n.d. (Fig. 5) lie along the line for A–B contacts, and move with it as the axial ratio of the unit cell changes. Thus phases with $c/a \sim 1{\cdot}3$ lie close to the A–B line for $c/a = 1{\cdot}33$, whereas those with $c/a \sim 1{\cdot}75$ lie close to the line for A–B contacts for $c/a = 1{\cdot}75$. Significant bond factors between like components (A–A or B–B) must be distinguished from the triviality which causes the data for phases AB_x with $x > 3$ to lie parallel to the lines for B–B contacts, merely because 75% or more of the atoms in the structure are B atoms, and B–B contacts must to a large extent control the structural geometry.

We have constructed n.n.d. for many of the common structures of metallic phases using radii of Teatum, Gschneidner & Waber (1960) corrected to the appropriate coordination with Pauling's (1947) bond number relationship. Definite evidence has been found for a geometrical factor controlling phases with the following structures: superstructures formed from close-packed arrays of atoms ($AuCu_3$, $SnNi_3$, $TiNi_3$, *etc.*), NiAs (at low c/a values), $MgCu_2$, $MgZn_2$, AlB_2 (in part), $CuAl_2$, $MoSi_2$, $CrSi_2$ (probably), Si_3Mn_5 and

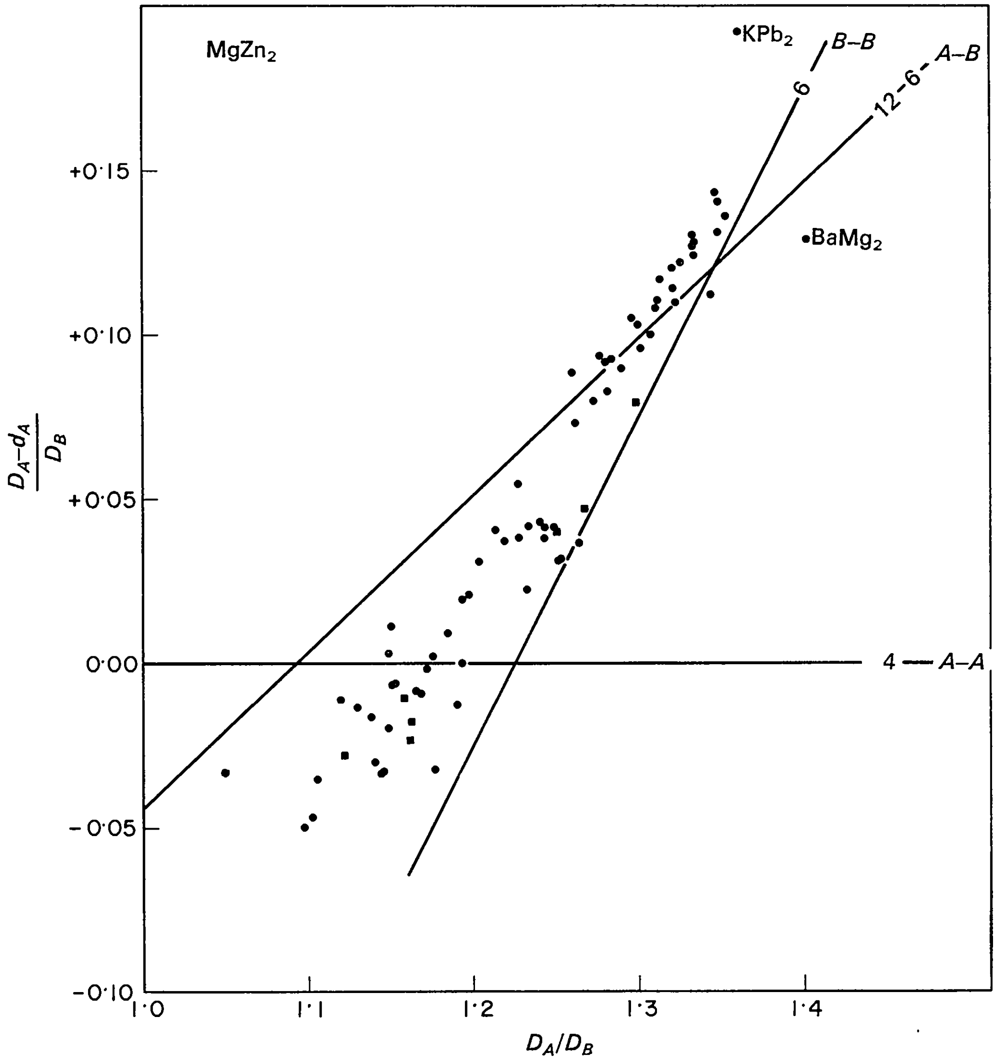

Fig. 1. Near-neighbour diagram for the $MgZn_2$ (AB_2) structure (hexagonal) constructed for the ideal axial ratio $c/a = 1{\cdot}63$ and ideal atomic parameters: $z_{Mg} = 1/16$, $x_{Zn} = 5/6$. See text. In these diagrams the coordination for the contact lines is indicated, and if these are drawn for different axial ratios these are also indicated. Points represent binary phases with the structure, and numbers by them give the axial ratio c/a in the structure of the phase. In Fig. 1, points shown as black squares are for some AMn_2 phases with Mn radius for valency six.

$AlCr_2C$, whereas the following structures are controlled by an *A–B* bond factor: CsCl, NaCl, ZnS, CrB, FeB, CdI_2, CaF_2, AlB_2 (in part), α-$ThSi_2$, $CaIn_2$ and $AsNa_3$. In some structures having variable axial ratios or atomic parameters, the factors controlling the structural dimensions are found to change at a certain value of the structural parameters. The AlB_2 structure provides a striking example of this behaviour, since at axial ratio values below about 0·9 the chains of *A* atoms running in the **c** direction of the crystal exert a strong influence on the structural dimensions, whereas at larger axial ratios this influence is negligible. Near neighbour diagrams of superstructures (such as $AuCu_3$, Fig. 6) formed from close packed solid solutions only show the influence of the geometrical factor resulting from the close packing; they provide no ex-

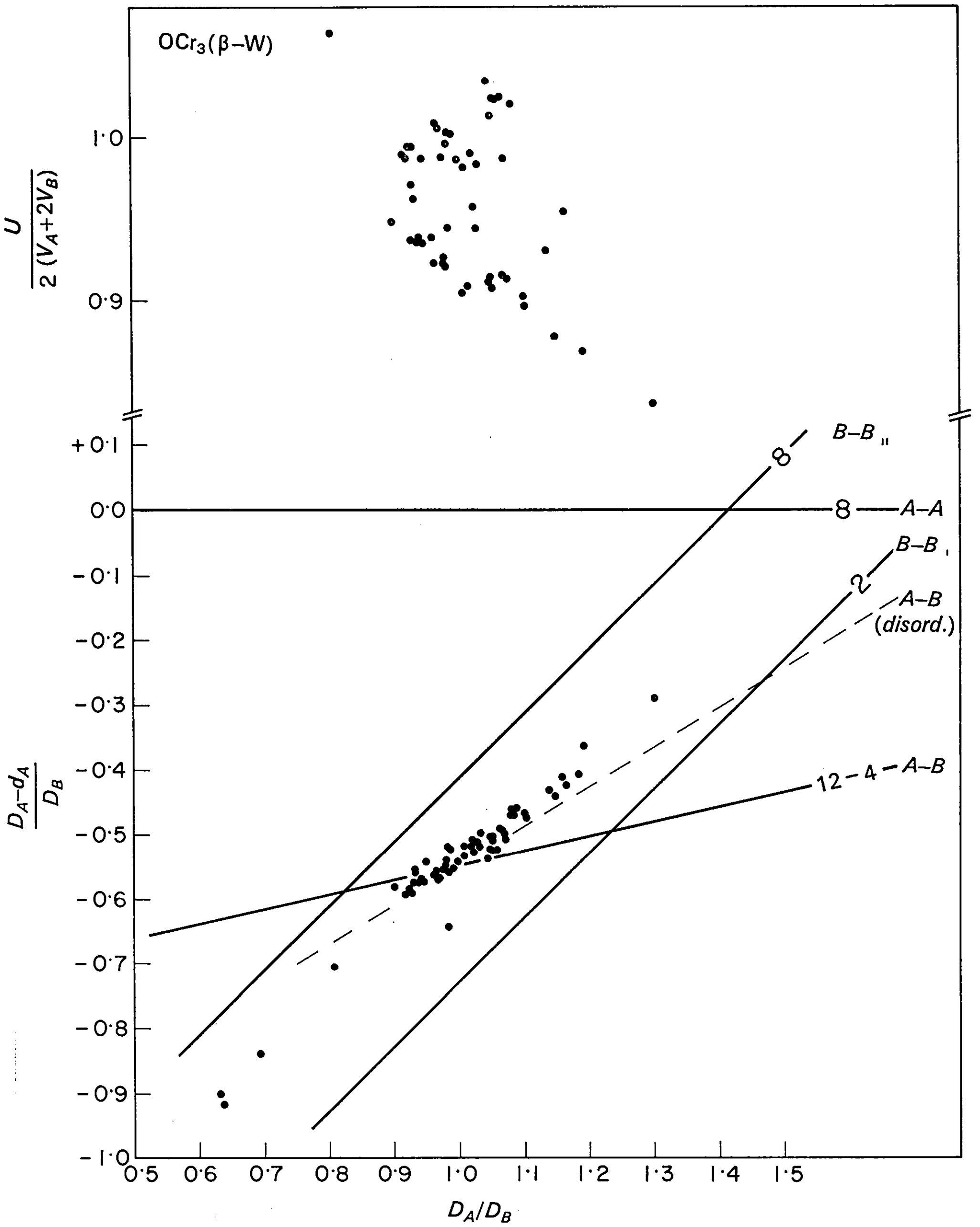

Fig. 2. Near-neighbour diagram for the β-W (OCr_3, AB_3) structure (cubic). See caption to Fig. 1. The upper portion of the diagram gives the ratio of the unit-cell volume to the sum of the atomic volumes of the elements for the number of atoms in the unit cell.

planation of the ordering which depends mainly on electronic effects (*cf.* Nicholas, 1953; Sato & Toth, 1961, 1962), and/or the elastic properties of the components.

Use of near-neighbour diagrams

Near neighbour diagrams can be used to examine the factors that control the occurrence and structural dimensions of phases with a given structure, provided that enough phases are known so as to obtain a reasonable analysis. Thus they are valuable for explicitly studying the influence of geometrical effects and, apart from the time involved in calculation, structural complexity does not impair their usefulness.

As an example we may examine the NaTl type structure which has variously been considered as ionic and/or involving strong diamond-like bonds between the atoms on one sublattice. The n.n.d. (Fig. 7, where

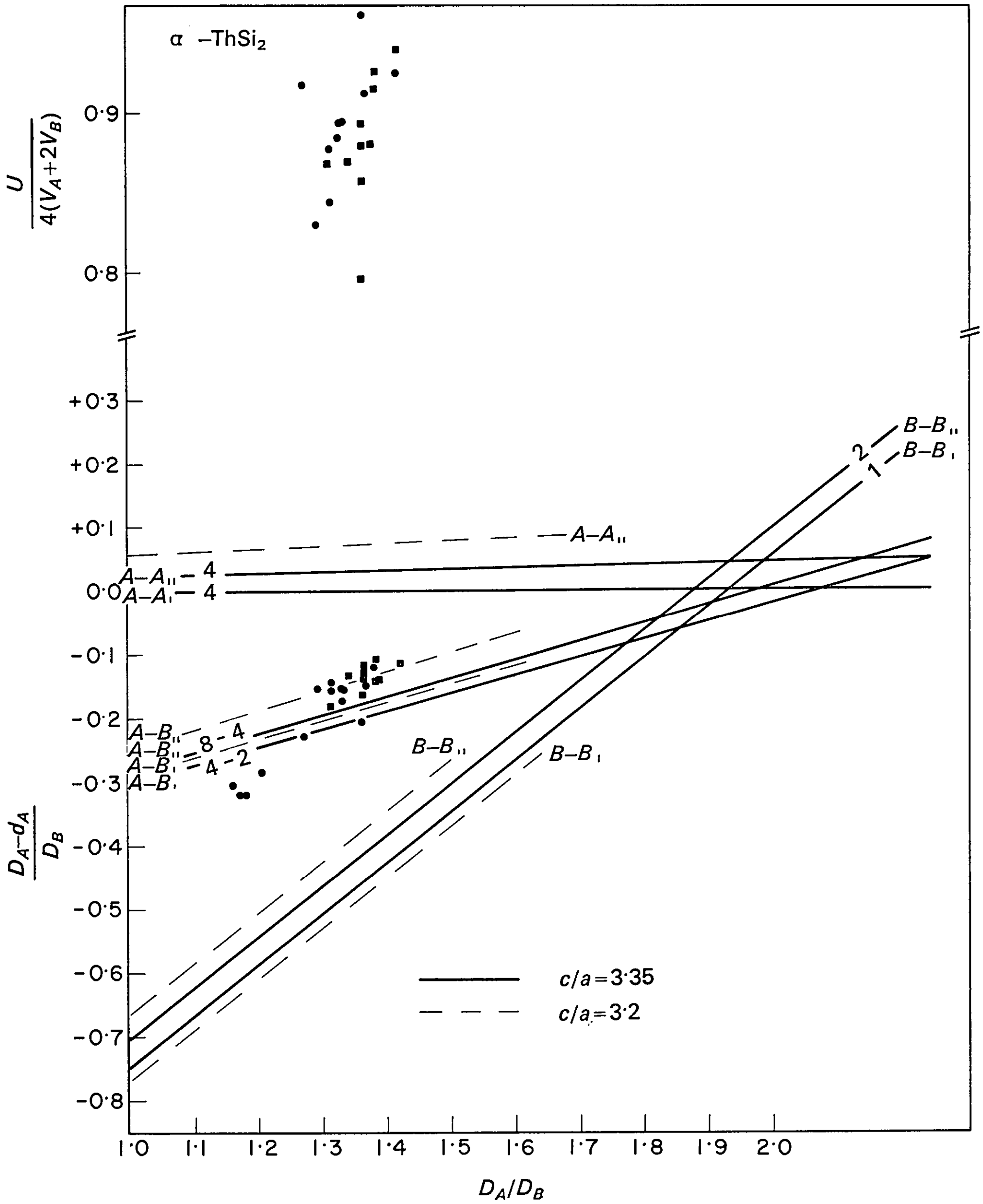

Fig. 3. Near-neighbour diagram for the α-ThSi$_2$ (AB_2) structure (tetragonal). See caption to Fig. 1. Constructed for axial ratios $c/a=3{\cdot}35$ and $c/a=3{\cdot}2$ and the ideal value of the Si parameter $z_{Si}=5/12$. Points ● normal structure, ■ defect structures. The upper portion of the diagram gives the ratio of the unit cell volume to the sum of the elemental atomic volumes for the ideal number of atoms in the unit cell.

the A component is chosen to make D_A/D_B larger than unity) shows that both A–A and A–B contacts are compressed until B–B contacts form, and this occurs no matter whether the Group III element is the smaller B component as in NaTl, or whether the Group I atom is, as in InLi. It can not therefore be argued that the A atoms are compressed so as to establish a strong diamond-like array of bonds between the B components from Group III, since the same situation arises when the B atom comes from Group I.

If the NaTl and CsCl structures are compared, it is seen that the occupation of sites in space is the same in each, resulting in 8 – 8 nearest neighbour coordination. In the CsCl structure this is achieved by 8 – 8 A–B contacts which control the structural dimensions, whereas in the NaTl structure it results from 4 A–A and 4 – 4 A–B contacts *which are compressed,* and 4 B–B contacts so that C.N. 8 is achieved at a lower overall atomic volume in the NaTl structure than the CsCl structure. If therefore the larger A component is compressible and the radius ratio does not depart too much from unity so that A–B and B–B contacts can be formed, the NaTl structure may be expected to have a lower free energy than the CsCl structure and occur in preference to it. We thus see the NaTl structure as neither ionic, nor dominated by strong diamond-like covalent bonds, but as a characteristically metallic phase adopting 8 – 8 coordination like the metallic phases with the CsCl structure. The favourable circumstances of highly compressible larger A atoms and radius ratio fairly close to unity are met in the known phases with the NaTl structure, but one or other of these conditions is not satisfied in, for example, LiTl, KIn or KTl which do not have the NaTl structure. [In InLi and CdLi where the Group II or III metal is the larger A component in the NaTl structure, the value of D_A/D_B is close to unity so that A–A, A–B and B–B contacts can all form readily (Fig. 7).]

Near-neighbour diagrams cannot generally be used to compare the relative suitability of one structure with

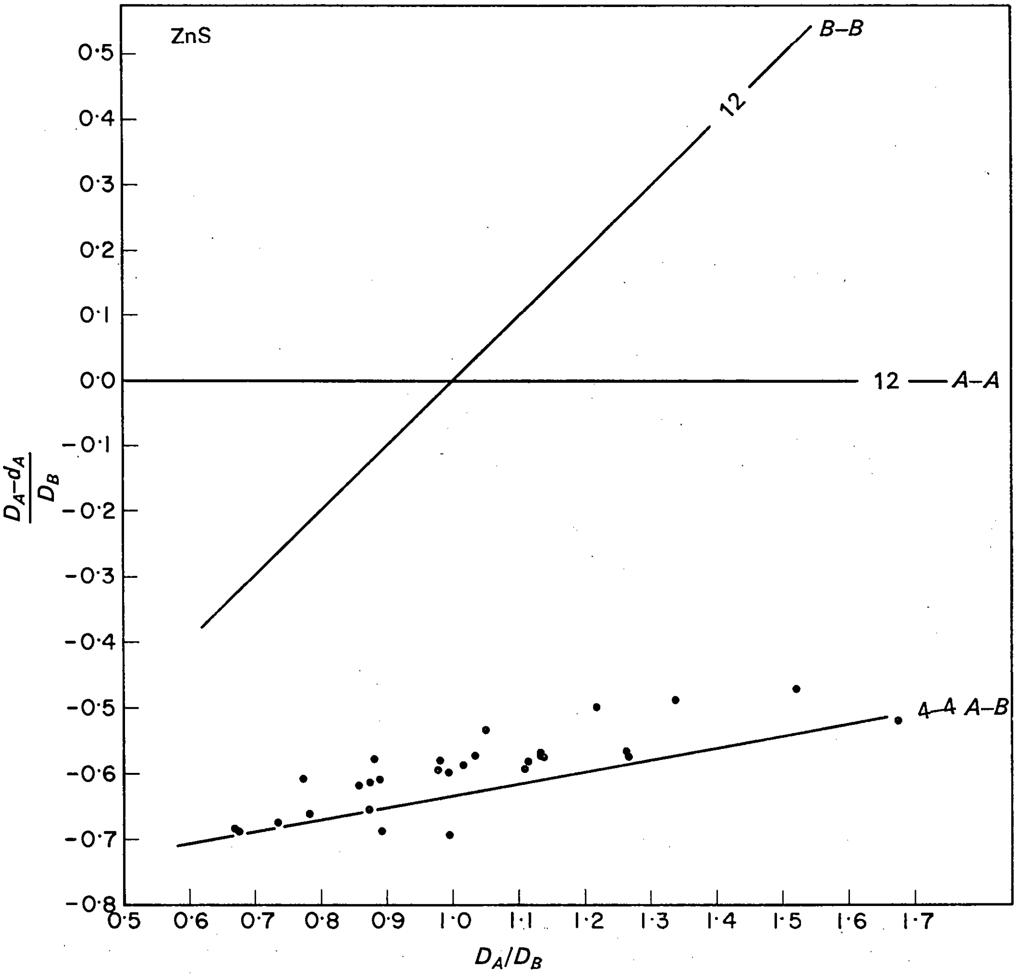

Fig. 4. Near-neighbour diagram for the sphalerite (ZnS, AB) structure (cubic). See caption to Fig. 1.

another from the point of view of space filling, because the selection of the contact which takes the zero value of the strain parameter is made arbitrarily. However, in structures such as the ZnS, NaCl, GeS and CsCl types which are dominated by the A–B bond factor, the relative space filling can be compared, at least at $D_A/D_B=1$, by establishing the zero value of $(D_A-d_A)/D_B$ for a d_A value equal to the edge of a cube representing the observed (average) volume per atom in the structure. Thus for the NaCl structure, for example, $d_A=\sqrt[3]{a^3/8}=a/2$. Then comparing the values of the strain parameter for A–B contacts at $D_A/D_B=1$, we find the space filling order (order with increasing compression of the A–B contacts) to be ZnS, NaCl, β-Sn (two component, 1:1 disordered) GeS (weighted average of four different A–B distances) and CsCl, which is exactly the order of structural change found in high-pressure experiments (*e.g.* ZnS → NaCl or β-Sn; NaCl → GeS), although we are not aware of any report of a high-pressure transition to the CsCl structure.

Conclusion

By studying the relationship between relative atomic size and the structural dimensions of phases with a given structure, rather than the relative degree of space filling of various structures (*cf.* Laves & Parthé), some degree of quantitative assessment of the influence of geometrical effects in structures appears possible, and structural control by chemical bond factors is readily

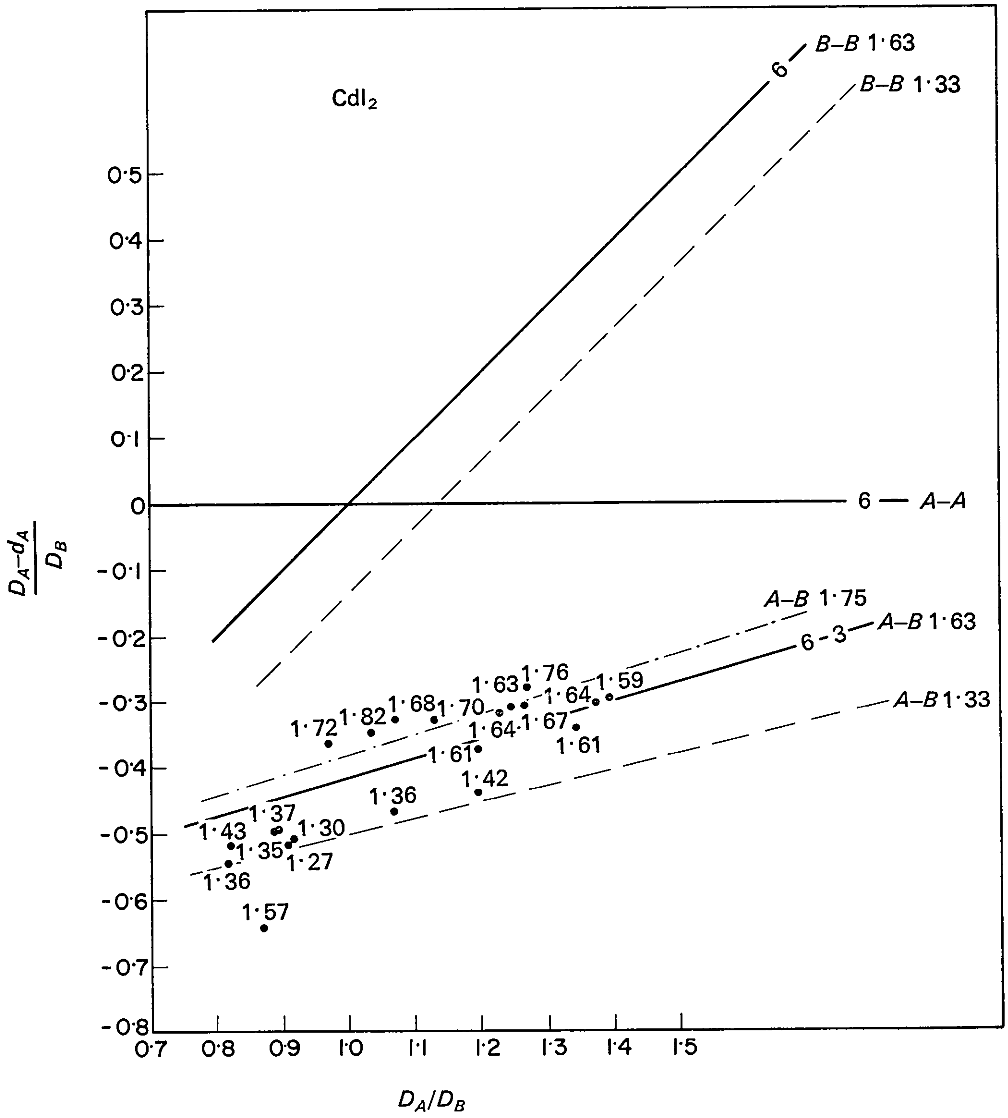

Fig. 5. Near-neighbour diagram for the CdI_2(AB_2) structure (hexagonal). See caption to Fig. 1.

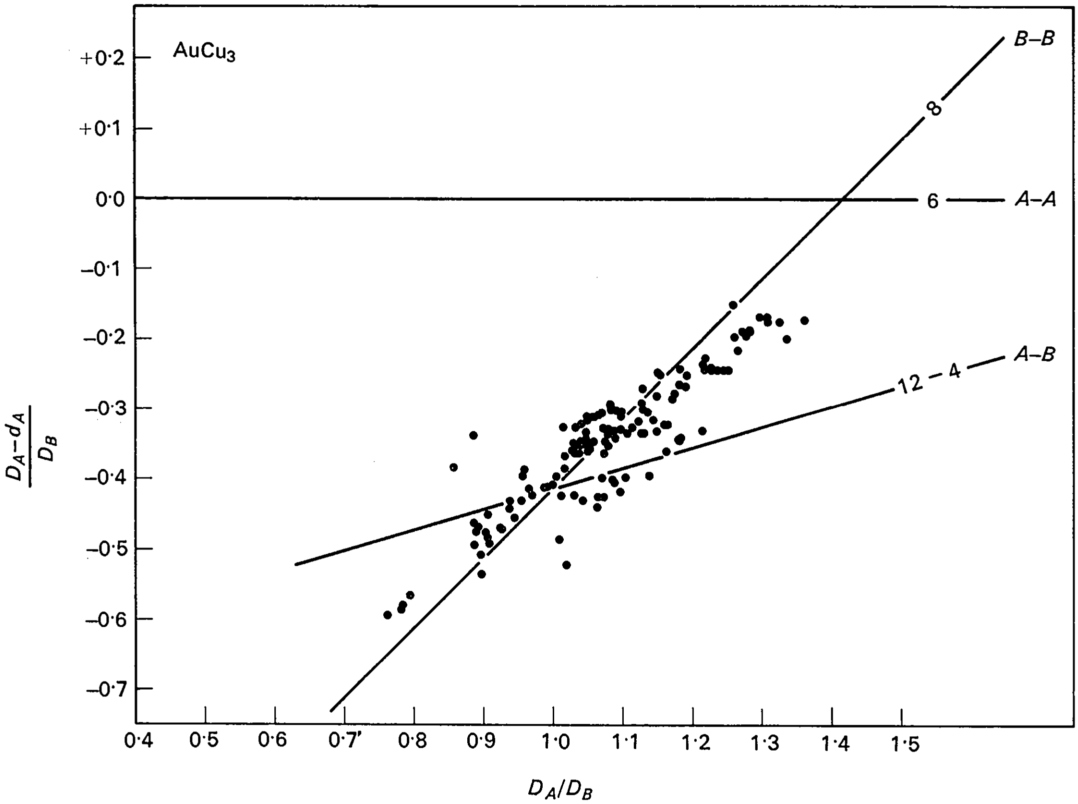

Fig. 6. Near-neighbour diagram for the $AuCu_3$ (AB_3) structure (hexagonal). See caption to Fig. 1.

recognized so that it can be separated from, or compared with geometrical influences.

I am indebted to Mr J. K. Byron and Mr A. C. Parshad for assistance with calculations.

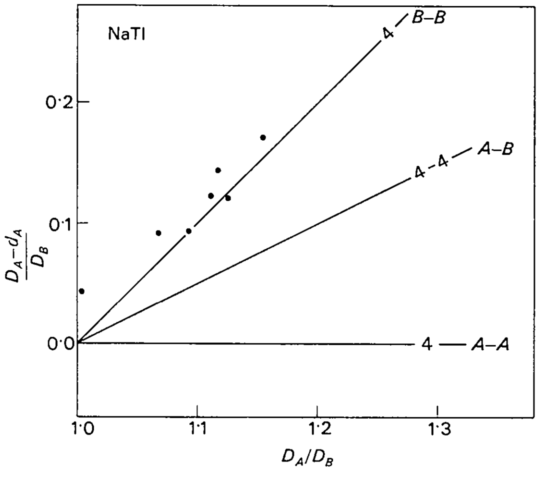

Fig. 7. Near-neighbour diagram for the NaTl (AB) structure (cubic). See caption to Fig. 1.

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