

Short Communications

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A definition of coordination and its relevance in the structure types AlB_2 and $NiAs$. By G. O. BRUNNER, *Institut für Kristallographie der Eidgenössischen Technischen Hochschule, Sonneggstrasse 5, 8006 Zürich, Switzerland*

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The largest gap in the list of reciprocal interatomic distances is used to limit the coordination polyhedra. For the structure types AlB_2 and $NiAs$, the polyhedra are evaluated according to *c/a*. In plots of *c/a* versus r_A/r_B , the various coordination types correspond to actually observed families of representatives. These results as well as others from more than 50 structure types support the view that coordination as limited by the largest gap is a realistic factor.

Despite its wide use, the term coordination has no satisfying definition allowing an unambiguous deduction of the coordination polyhedron from atomic parameters (Brunner & Laves, 1971). Frequently, coordination is limited by the feeling that some neighbours have distances comparable to the shortest distance while others lie further away. This intuitive decision regarding interatomic distances may be replaced by the unambiguous procedure to limit coordination by the *largest gap* in the list of interatomic distances $d_1, d_2 \dots d_n$. The difficulty, however, lies then in the adequate measurement of the gap width as is shown by the example of a planar square net: if the absolute difference $d_{n+1} - d_n$ is taken as the criterion, the largest gap appears between $d_4 = \sqrt{5}$ and $d_5 = \sqrt{8}$. Instead of the familiar 4 there are 20 points belonging to the coordination sphere. In an earlier paper the relative gap width d_{n+1}/d_n between subsequent distances was chosen to limit coordination in 54 topologically different structures (Brunner & Schwarzenbach, 1971). With the exception of about six structures, for each atomic position in each structure one gap was clearly larger than others and the resulting coordination looked reasonable. The example of the planar square net causes difficulties: there are two 'largest gaps' with a ratio of $\sqrt{2}$, d_2/d_1 and d_3/d_2 , and the CN is 4 or 8 respectively. Hence, a measure with a stronger compression of gaps at longer distances is needed. In this paper, the *difference in reciprocal distances*, $1/d_n - 1/d_{n+1}$ is chosen. In cases where the earlier measure was meaningful, the new measure renders essentially the same results. In some of the previously doubtful cases a satisfying result is now found, e.g. for the square net the CN 4 is found. In addition, an excellent survey of interatomic distances is rendered by the $1/d$ presentation (for convenience, the shortest distance of each atomic position in a structure is taken as unity for that position; values from $1/d_1 = 1$ to $1/d_n = 0.5$ are sufficient for the survey). Further, the reciprocal lengths have a physical background: the Coulomb energy vanishes with $1/d$, thus all neighbours with a particularly large contribution to the electrostatic energy are considered to belong to the coordination sphere of an atom. The procedure is based on the assumption of a more or less spherical charge distribution at the atoms (such a charge is equivalent to a point charge at the centre of the sphere). For structures with strongly polarized atoms or assembled ions such as OH^- , the 'effective

atomic position' is not defined and the procedure may need a refinement.

There is the question whether coordination polyhedra are simply a consequence of man-made definitions or whether chemical forces are responsible for the existence of particular polyhedra in crystal structures. Is there always one gap in the list of interatomic distances which is significantly larger than other gaps? The structure types of AlB_2 and $NiAs$ are outstanding examples for a check. Both structures

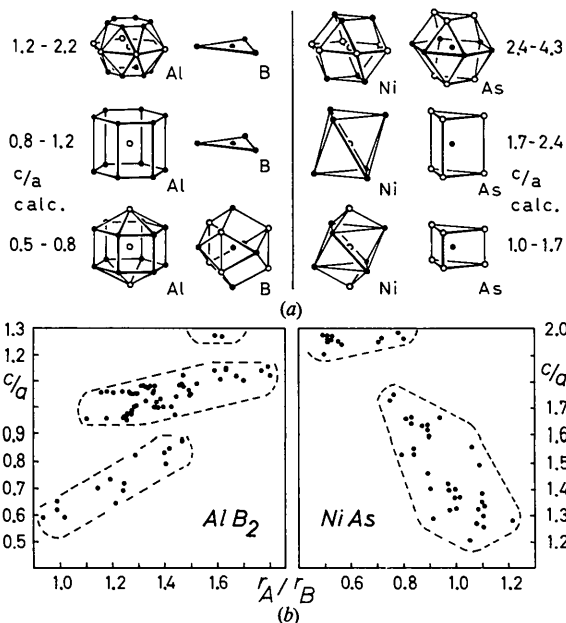


Fig. 1. (a) Coordination polyhedra in the AlB_2 and $NiAs$ structure types as defined by largest gaps in the $1/d$ lists. (b) Plots of axial ratio *c/a* versus radius ratio r_A/r_B of actually occurring representatives: A=Al, As, B=B, Ni. [AlB_2 data from Pearson (1972), $NiAs$ data from Schubert (1964).]

have many representatives, there is one parameter only and the parameter varies over a wide range. These properties are necessary for the check and are hardly offered by other structures. From a purely crystallographic point of view, the representatives belong to the same structure type and with the hard-sphere model in mind, a continuous trend in c/a values might be expected. However, various types of coordination may be predicted depending on c/a . At particular values of c/a , the coordination changes and is 'not defined' (the interatomic distances show two gaps of equal width). If coordination and our definition of it have a chemical background, these particular c/a values are unfavourable and should not be realized. Actually, in the plots of c/a versus r_A/r_B as shown in Fig. 1, there appear families of representatives with breaks at c/a values which are in acceptable agreement with the predicted change of the coordination polyhedra. Other interpretations of the plots do not disprove the explanation given here. Laves (1956) describes various types of homogeneous and heterogeneous connexions in the AIB_2 type, which have some analogy with the coordination polyhedra shown in Fig. 1. Laves's view implies a correlation between c/a and r_A/r_B which is not realized at values of $c/a > 0.9$. Pearson (1972) discusses a geometrical (which means coordination) and a bond factor in the AIB_2 type. Coordination is not clearly defined and implies a contact and a distance property. Schönberg (1954) and also Schubert (1964) refer to the correlation between c/a and r_A/r_B of the NiAs structure in terms of a hard-sphere model; a break near $c/a \approx 1.8$ is not considered. The representatives in the NiAs plot with $c/a \approx 2$ are compounds of the WC type. With their actual axial ratio $c/a \approx 1$, they might be regarded as AIB_2 representatives with one-half occupation of the B position or as h.c.p. representatives (M at 000, X at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$) with trigonal prismatic coordination which is defined for $c/a \approx 0.8$ to 1.2 in the h.c.p. structure. In all cases the WC compounds fit in a region of well defined coordination. In the AIB_2 and NiAs structures, the two components change coordination at slightly different values of c/a ; in Fig. 1, mean values are given.

Fig. 1 seems to support the view that the 'tendency to good coordination' is a chemical principle and that the $1/d$ largest-gap procedure puts it on a measurable basis. Of

course, predictions of unfavourable metrics may differ from reality to some extent owing to the complexity of the matter. The largest-gap limit does not deal with the radius ratio and with the contact of atoms and is an additional rather than a competitive view. Nevertheless, there are arguments to regard atoms as 'force centres' rather than as 'contacting spheres' (Brunner, 1971, 1975). If a structure type is defined as a particular linkage of particular coordination polyhedra, then the fields of representatives in Fig. 1 may be divided into three AIB_2 and possibly two NiAs structure types. A further type of NiAs is conventionally described as an $ABAC$ close-packed structure.

The number of atoms in the coordination polyhedron is generally called coordination number, CN. It is to be distinguished from a weighted coordination number, WCN. A suitable weighting procedure is as follows: the weight drops linearly with $1/d$; for neighbours with distance $1/d_1 = 1$, the weight is 1 and for neighbours following next after the largest gap it is 0. As an example, tungsten has CN=14 and WCN=11.9. For metallic structures, the average over all sites, AWCN, is an informative number and so far it seems that 12 is the uppermost AWCN. Encouraging results regarding the AWCN of some intermetallic compounds have been found by Bhandary & Girgis (1976).

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Values of ϵ for obtaining normalized structure factors.* By HITOSHI IWASAKI and TETSUZO ITO, *The Institute of Physical and Chemical Research, Wako-shi, Saitama, 351 Japan*

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The quantity ϵ , which is necessary to calculate the normalized structure factor $E(\mathbf{h})$ for a reflexion, is equal to the ratio of the number of symmetry-equivalent positions in a unit cell to the number of point-group equivalent (not Laue-group equivalent) reflexions. Values of ϵ are tabulated for all point groups.

The normalized structure factor $E(\mathbf{h})$ of a reflexion, commonly used in direct methods, is defined by

$$E(\mathbf{h}) = F(\mathbf{h}) / \left[\epsilon \sum_{n=1}^N f_n^2(\mathbf{h}) \right]^{1/2},$$

* *Editorial note.* This paper overlaps considerably with that of Stewart & Karle (1976). It is printed in full, as the approach is somewhat simpler and the table of results is more complete.

where the summation is taken over the atoms in a unit cell and f_n is the atomic form factor of the n th atom corrected for thermal vibration. The quantity ϵ is related to the mean square structure amplitudes as (*International Tables for X-ray Crystallography*, 1974)

$$\langle |F(\mathbf{h})|^2 \rangle = \epsilon \sum_{n=1}^N f_n^2(\mathbf{h}).$$