low $|E_m|$ values, the results for $X'_C(E_m)$ become unreliable.

The calculated X_C values for 13 test structures applying four sin θ/λ thresholds, are collected in Table 6. This table clearly shows the tendency for centrosymmetric structures to have an X_C value near 1·0 and for non-centrosymmetric structures to have a value approaching 0. Upon decreasing the dependency on the 'input' structure, a better approximation for these ideal X_C values is obtained, especially for structures where at first sight a strong preference for 'heavy atom' centricity is clearly seen. Upon decreasing the sin θ/λ limit, the results sometimes become less reliable because of the small number of contributing reflections; on the other hand, this sometimes will improve the results (see Table 6, entry 5), as errors in thermal parameters become less important.

One example (Table 6, entry 12) does not give the expected X_C value. To explain this, we have calculated the distribution for the $|E|$ values of the rest structure, using the phases calculated after the refinement of the structure; it was found that this distribution resembles more the acentric than the centric curve. From this one example it is concluded that the results for X_C are not definite proof for the presence or absence of a center of symmetry.

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A Proposed Rigorous Definition of Coordination Number

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Abstract

It is proposed that a weighted coordination number, Z^*, be used as a measure of the number of neighbours of an atom in a crystal. Coordinating atoms contribute faces to the Voronoi polyhedron around a central atom and their contributions are weighted in proportion to the solid angle subtended by that face at the centre. The advantages of this definition over other proposals are pointed out.

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The concept of coordination number (CN) of an atom or ion in a crystal is very widely used and has proved very fruitful in crystal chemistry. The CN of atoms in crystals has become accepted as a basic parameter describing a structure, and many atomic properties such as atomic (or ionic) radius are considered to depend upon it directly. It is nevertheless true that it is hard to find an unambiguous definition of CN that is not in conflict with intuition in many instances. In this paper a rigorous yet logical and useful definition is proposed.

In a simple and symmetrical structure such as the $B1$ (NaCl) structure there is no difficulty; each ion has six equidistant neighbours of the other kind and one has no hesitation in ascribing a CN of six to each ion in the crystal. Difficulties arise in less symmetrical structures and when there is a high CN. Then one often finds near neighbours with slightly different interatomic distances and it becomes difficult to determine how many should be considered as coordinating a central ion.

Several authors have proposed schemes for unambiguously determining coordination number. These involve, for example, identifying a gap in the list of interatomic distances – a procedure that often leads to difficulties. A simple procedure that appears not to have been considered before, but which nearly always leads to an acceptable CN, is to add atoms to the coordination polyhedron in order of increasing interatomic distance, but to stop when adding the next atom would result in a non-convex polyhedron. Brunner (1977) suggests cutting off the coordinating atoms at the largest gap in the differences of the reciprocals of the interatomic distances. Brunner also suggests weighting the contribution of an atom with a weight that decreases with interatomic distance so that non-integral coordination numbers appear (*cf.* Bhandary & Girgis, 1977). It is clear, though, that a weighting scheme that is based on concepts of bond strength are unlikely to be satisfactory. Indeed, if bond strengths of the Pauling type are employed one simply finds their sum to be the formal valence of the atom (Brown & Shannon, 1973). To be useful, the concept of CN must be based on geometrical principles.

In the field of alloy structures, the most generally accepted definition of CN is that of Frank & Kasper (1958). These authors base their definition on a consideration of the Voronoi polyhedron surrounding each atom. This is the polyhedron enclosing the space (the *domain* of an atom) in which all points are closer to the centre of that atom than to any other. Any atom whose Voronoi polyhedron shares a face with the polyhedron of the central atom is counted as a neighbour; the number of neighbours so defined is the CN of the central atom.

However, this definition, although unambiguous, leads to difficulties, even in some very simple structures; we give just two examples. In the body-centred cubic structure, the Voronoi polyhedron is the Archimedean truncated octahedron $4 \cdot 6^2$ (Fig. 1*a*) sharing each of its 14 faces with another such polyhedron. The Frank–Kasper CN is accordingly 14, although there are only eight *nearest* neighbours of any atom. Intuitively a CN greater than that of closest packing (*viz* 12) does not seem entirely reasonable.

The difficulty becomes more acute in the diamond structure. Laves (1967) points out that here the Voronoi polyhedron is the figure derived by placing a triangular pyramid (with height equal to $1/\sqrt{24}$ times the base) on each of the triangular faces of an Archimedean truncated tetrahedron ($3 \cdot 6^2$). The Frank–Kasper CN is now 16. Frank (1967) suggested a way out of this particular difficulty by distinguishing between direct and indirect neighbours. A direct neighbour is one for which the line joining its centre to the centre of the atom in question passes through the shared face of the Voronoi polyhedra of the two atoms. All others are indirect neighbours. In this scheme each atom in the diamond structure has four direct and twelve indirect neighbours.

Even with the distinction between direct and indirect neighbours many difficulties remain (Laves, 1967); not the least of which is that a very small distortion of a crystal structure can result in a discontinuous change in CN. Thus if one starts with a simple cubic array and makes a small trigonal distortion (by compression along [111]) the Voronoi polyhedron (initially a cube) acquires eight new faces (Fig. 1*b*) so that from the Frank–Kasper point of view, the CN jumps discontinuously to fourteen. Alternatively, if one starts with a face-centred cubic array and subjects it to a small tetragonal distortion (compression along [001]) the Voronoi polyhedron, originally a rhombic dodecahedron, now acquires two new faces (Fig. 1*c*) and the CN jumps from twelve to fourteen. Thus, an infinitesimal distortion of the symmetrical array results in both simple cubic and face-centred cubic having the same CN as body-centred cubic.

It is worth noting in passing that in each case the polyhedra are topologically the same as the truncated octahedron that is the domain for the b.c.c. array. This reflects the fact that the b.c.c. array can be generated

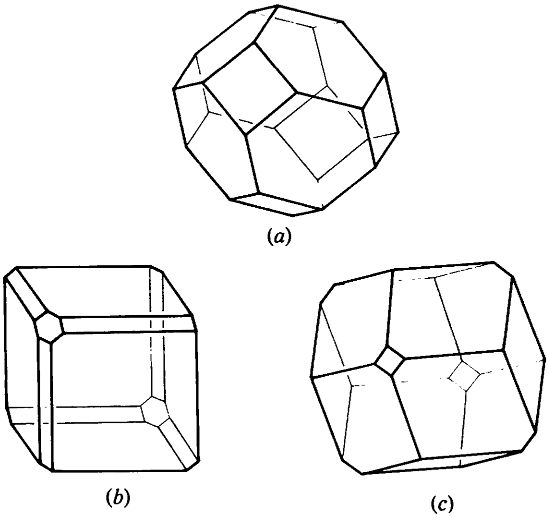

Fig. 1. (*a*) The Voronoi polyhedron for the body-centred cubic array. (*b*) The Voronoi polyhedron for the simple cubic array after a small trigonal distortion by compression along [111]. (*c*) The Voronoi polyhedron for the face-centred cubic array after a small tetragonal distortion by compression along [001].

from the simple cubic or f.c.c. arrays by distortions of the type described.

In these examples, the 'new' Frank–Kasper neighbours (which are direct neighbours) are associated with very small faces on the Voronoi polyhedron. It would seem appropriate to weight their contribution to the CN by some factor, such as one proportional to the area of the face. Actually a more appropriate weighting factor would be the solid angle subtended by the face at the centre of the polyhedron, as indirect neighbours can contribute faces of quite large surface area, but usually subtending a small solid angle at the central atom. Accordingly we adopt this weighting principle in what follows.

In metal crystals (in which atoms that are identical or similar chemically are counted as part of the coordination polyhedron), the Frank–Kasper definition of atomic domain is retained and again coordination number is related to the number of faces of the enclosing polyhedron. However, in counting CN it is supposed that each atom contributes an amount proportional to the solid angle subtended by the corresponding face at the centre of the polyhedron; the proportionality factor being such that the largest solid angle contributes unity to the coordination number. The CN so defined is denoted by Z^* in what follows.

Returning to the example of the body-centred cubic structure; the Voronoi polyhedron has eight hexagonal faces and six smaller square ones (Fig. 1*a*). Let r denote the ratio of the solid angle subtended by the square faces to that subtended by the hexagonal faces:

$$Z^* = 8 + 6r = \pi/\tan^{-1}(\sqrt{5}/7) = 10{\cdot}16. \qquad (1)$$

A similar calculation for the domain of diamond structure yields

$$Z^* = 4\pi/[2\pi - 3\cos^{-1}(7/18)] = 4{\cdot}54. \qquad (2)$$

For the simple cubic and the face-centred cubic arrays, one of course obtains the same CN's (6 and 12 respectively) by any method; the values of Z^* now obtained for the diamond and body-centred cubic arrays are in accord with these in the sense that Z^* increases in the sequence: diamond, simple cubic, body-centred cubic, face-centred cubic; as does the packing density.

In ionic crystals one may proceed in just the same way in many instances. Thus in the $B1$ (NaCl) structure, the Voronoi polyhedron around each ion is a cube sharing each face with a corresponding cube around the counter ion. Z^* is thus equal to the conventional coordination number, six. In other simple structures such as the $B2$ (CsCl) or $B3$ (ZnS) structures, one has the problem that next-nearest neighbours which are like ions contribute to defining the Voronoi polyhedron. There are two courses one may adopt at this stage. One may simply determine Z^* from faces corresponding to coordination by counter ions (getting eight and four respectively in these instances) ignoring the other faces. A second procedure, which seems to be more in line with the concept of coordination by counter-ions in ionic crystals, is to construct the domain of a central ion by including all that space nearer to the centre of that ion than to the centre of any other counter-ion in the crystal. Polyhedra bounding domains defined in this way will not be Voronoi polyhedra (as they are not space-filling without overlap). In the examples of the $B2$ and $B3$ structures they will be regular octahedra and regular tetrahedra, respectively, but Z^* will be eight and four as before. In general though, the two procedures will lead to slightly different results and which of the two will prove the more useful remains to be determined.

Determination of the appropriate polyhedra is readily performed by computer if the coordinates of the atoms are known (Mackay, 1972). For example, Mackay has calculated the Voronoi polyhedra around the atoms in a structure involving irregular coordination. This is the structure of $Ba_3(VO_4)_2$, one of a number of compounds isostructural with palmierite, $K_2Pb(SO_4)_2$ (Wyckoff, 1965). Ba(1) has six close oxygen neighbours and six more oxygen ions about 15% farther away; from Mackay's data we calculate $Z^* = 8{\cdot}91$. Ba(2) has a less regular coordination with one nearest neighbour, three somewhat farther away and six slightly farther still. Again Mackay's data yield $Z^* = 6{\cdot}68$ for this ion, reflecting the very different crystal chemical role of Ba(1) (replacing K) and Ba(2) (replacing Pb).

It would appear that accumulation of similar data for many structures could lead to useful correlations with ionic radii, prediction of the effects of pressure, *etc.*, much as now is done for more symmetrical structures.

A useful application of this rigorous definition of coordination may be in emphasizing the continuity between structure types (Hyde, Bursill, Andersson & O'Keeffe, 1972). The transition from the $B1$ to the $B2$ structure (and related transitions involving crystals of different stoichiometries) has been discussed from this point of view (Hyde & O'Keeffe, 1973). One of the two paths we discussed for this transformation involved the description of both structures by a rhombohedral cell with anion at 0,0,0 and cation at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. Variation of the parameter $u = \cos\alpha$ (where α is the rhombohedron angle) from 0 to $\frac{1}{2}$ corresponds to a transformation from the $B2$ to the $B1$ structure. This is the prototype of a number of transformations (Hyde, Bursill, Andersson & O'Keeffe, 1972) in which CN changes from six to eight.

In the $B1 \leftrightarrow B2$ (and related) transformation, Z^* may be simply calculated by determining the polyhedron surrounding the space in which all points are closer to the centre of the cation than to any anion. For a value of u between 0 and $\frac{1}{2}$ the polyhedron is an octahedron with six large and two smaller faces. Thus Z^* is between six and eight. The twelve vertices of the octahedron are readily described in terms of the equipoints of space group $R\bar{3}m$. Referred to hexagonal axes, half of them are in $18(h)$; $x = (3-2u)/(12-12u)$, $z = (3+14u)/(12+24u)$ and the other half in $18(h)$ with $x = (1-2u)/(4-4u)$, $z = \frac{3}{4}$. Z^* can be expressed as a function of u using elementary (but not trivial) trigonometry as

$$Z^* = 4\pi/\cos^{-1}[(6u^2-5u)/(3-2u)]. \qquad (3)$$

As u varies from $\frac{1}{2}$ to 0, Z^* changes smoothly from six to eight, and the polyhedron transforms from a cube to a regular octahedron. At $u = \frac{1}{4}$, $Z^* = 6{\cdot}52$; the polyhedron (Fig. 2) at this point bears a remarkable resemblance to Dürer's (1514) octahedron.

Another valuable use of the suggested procedure for determining Z^* will be in comparing the coordinations of ions with irregular coordination polyhedra in series of related structures, for example the rare-earth ions in their halides. Investigations of such series are in progress.

In the case of alloy structures, unreasonably high coordination numbers are eliminated. I suspect that for structures in which atoms are at nodes of a lattice (*i.e.* all equivalent) $Z^* \leq 12$. It is well known that in this instance the Voronoi polyhedra have no more than 14 faces (as in the examples of Fig. 1). For an array of equivalent points (a lattice complex) related by symmetry elements of a space group, the Voronoi polyhedra are congruent and often called stereohedra. Delaunay (Delone, 1961) has obtained the result that in n dimensions, the number of faces, F, of a stereohedron obeys†

$$F \leq 2(2^n - 1) + 2^n(h-1), \qquad (4)$$

where h is the ratio of the number of points of the lattice complex to the number of points of the associated Bravais lattice (for example, $h = 1$ for the b.c.c. array and $h = 2$ for the diamond array). For $n = 3$, $h = 2$, one has $F \leq 22$. I am not aware of an example in which the equality holds although Smith (1965) has given an example with $F = 20$ and of course for the stereohedra associated with the diamond array $F = 16$. In both these instances $Z^* < 5$. High CN's remain, however, where they might be expected, *i.e.* in coordination of 'large' atoms by 'small' ones (as in some metal borides).

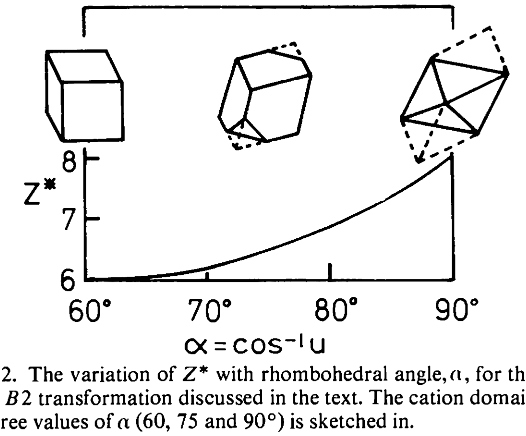

Fig. 2. The variation of Z^* with rhombohedral angle, α, for the $B1 \rightarrow B2$ transformation discussed in the text. The cation domain for three values of α (60, 75 and 90°) is sketched in.

Since this work was completed, a paper by Carter (1978) has appeared. Carter also considers the question of non-integral coordination numbers and the use of solid angles subtended by the faces of polyhedra around an atom. However, in his approach, the coordination number as defined is dependent on relative ion (atom) size in a given structure rather than on just the atomic arrangement. Thus in a compound AB with the $B2$ structure, the coordination numbers of A and B are not in general equal and may vary between 6 and 14 depending on how the A–B distance is divided into the sum of radii for A and B. Particularly for ionic crystals, there is no general agreement on how to partition bond lengths into sums of radii, rather, there is a growing realization that in principle this cannot be done unambiguously. Finally, Carter's weighting scheme [his equations (1) and (2)] does not in general assign a weight of unity to the nearest atom, which must surely be done if a more rigorous definition of coordination number consistent with current usage is to be developed.

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† *Note added in proof:* It has recently been conjectured (Brunner & Laves, 1978) that $F \leq 3^n - 1$.

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