

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  $\epsilon$  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  $\epsilon$ , 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  $\epsilon$  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  $\epsilon$  is related to the mean square structure amplitudes as (*International Tables for X-ray Crystallography*, 1974)

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

Table 1. Values of  $\epsilon$  for all point groups

$M$  is the rank of the point group. For a non-primitive cell, all figures must be multiplied by the multiplicity of the compound lattice,  $L$  (see text).

## (i) Triclinic, monoclinic, orthorhombic

Point group	$M$	$hkl$	$OkI$	$h0l$	$hk0$	$h00$	$Ok0$	$00l$
1	1	1	1	1	1	1	1	1
$\bar{1}$	2	1	1	1	1	1	1	1
$2^*$	2	1	1	1	1	1	2	1
$m^*$	2	1	1	2	1	2	1	2
$2/m^*$	4	1	1	2	1	2	2	2
222	4	1	1	1	1	2	2	2
$mm2^\dagger$	4	1	2	2	1	2	2	4
$mmm$	8	1	2	2	2	4	4	4

\*  $b$  axis unique.

†  $c$  axis unique.

## (ii) Tetragonal

Point group	$M$	$hkl$	$h0l, OkI$	$hhl, h\bar{h}l$	$hk0$	$hh0, h\bar{h}0$	$h00, Ok0$	$00l$
4	4	1	1	1	1	1	1	4
$\bar{4}$	4	1	1	1	1	1	1	2
$4/m$	8	1	1	1	2	2	2	4
422	8	1	1	1	1	2	2	4
$4mm$	8	1	2	2	1	2	2	8
$\bar{4}2m$	8	1	1	2	1	2	2	4
$4m2$	8	1	2	1	1	2	2	4
$4/mmm$	16	1	2	2	2	4	4	8

## (iii) Trigonal and hexagonal

## (a) Hexagonal cell

Point group	$M$	$hkl$	$hk0$	$hhl, h, 2\bar{h}, l$ $2h, \bar{h}, l$	$hh0, h, 2\bar{h}, 0$ $2h, \bar{h}, 0$	$h0l, OkI$ $h\bar{h}l$	$h00, Ok0$ $h\bar{h}0$	$00l$
3	3	1	1	1	1	1	1	3
$\bar{3}$	6	1	1	1	1	1	1	3
312	6	1	1	1	1	1	2	3
321	6	1	1	1	2	1	1	3
$31m$	6	1	1	2	2	1	1	6
$3m1$	6	1	1	1	1	2	2	6
$\bar{3}1m$	12	1	1	2	2	1	2	6
$\bar{3}m1$	12	1	1	1	2	2	2	6
6	6	1	1	1	1	1	1	6
$\bar{6}$	6	1	2	1	2	1	2	3
$6/m$	12	1	2	1	2	1	2	6
622	12	1	1	1	2	1	2	6
$6mm$	12	1	1	2	2	2	2	12
$\bar{6}m2$	12	1	2	1	2	2	4	6
$\bar{6}2m$	12	1	2	2	4	1	2	6
$6/mmm$	24	1	2	2	4	2	4	12

## (b) Primitive rhombohedral cell

Point group	$M$	$hkl$ $OkI, h0l, hk0$ $h\bar{h}l, hk\bar{h}, h\bar{h}l$	$hhl, hkh, hll$ $hh0, h0h, 0ll$ $\bar{h}hh, h\bar{h}h, hh\bar{h}$ $h00, Ok0, 00l$	$h\bar{h}0, h0\bar{h}, 0ll$	$hhh$
3	3	1	1	1	3
$\bar{3}$	6	1	1	1	3
32	6	1	1	2	3
$3m$	6	1	2	1	6
$\bar{3}m$	12	1	2	2	6

## (iv) Cubic

Point group	$M$	$hkl$	$hhl, h\bar{h}l$ $hkh, hk\bar{h}$ $hll, h\bar{h}l$	$hhh$ $\bar{h}hh, h\bar{h}h, hh\bar{h}$	$OkI$ $h0l$ $hk0$	$hh0, h\bar{h}0$ $h0h, h0\bar{h}$ $0ll, 0\bar{h}l$	$h00, Ok0, 00l$
23	12	1	1	3	1	1	2
$m\bar{3}$	24	1	1	3	2	2	4
432	24	1	1	3	1	2	4
$\bar{4}3m$	24	1	2	6	1	2	4
$m\bar{3}m$	48	1	2	6	2	4	8

An expression for  $\varepsilon$  was derived by Karle & Hauptman (1956) in rather a complicated form, and the physical meaning of the  $\varepsilon$  value was discussed by Wilson (1950). This paper shows that  $\varepsilon$  is equal to the ratio of the number of symmetry-equivalent positions in a unit cell to the number of point-group equivalent reflexions without Friedel's law.

Let the  $s$ th equivalent position  $\mathbf{r}_s$  of a given position  $\mathbf{r}$  be generated by operating a  $3 \times 3$  rotation matrix  $\mathbf{R}_s$  to  $\mathbf{r}$  and then by adding a translation vector  $\mathbf{t}_s$ :

$$\mathbf{r}_s = \mathbf{R}_s \mathbf{r} + \mathbf{t}_s.$$

We consider a structure composed of many similar isotropic atoms randomly distributed in an asymmetric unit. The structure factor can be written in the form:

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} \sum_{s=1}^M f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_{js}) \\ = \sum_{j=1}^{N/M} f_j \left[ \sum_{s=1}^M \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j) \exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s) \right], \quad (1)$$

where the subscript  $j$  runs through the atoms in an asymmetric unit,  $\mathbf{h}_s \equiv \mathbf{h} \mathbf{R}_s$  is the  $s$ th equivalent index for  $\mathbf{h}$  (Waser, 1955) and  $M$  is the number of equivalent positions in a unit cell.

First let us assume that the cell is primitive and each component of  $\mathbf{t}_s$  is 0(mod 1) for all  $s$ . The equation (1) then reduces to the form:

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} f_j \left[ \sum_{s=1}^M \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j) \right]. \quad (2)$$

For a general index  $\mathbf{h}$  there are  $M$  different indices  $\mathbf{h}_1, \dots, \mathbf{h}_M$ , corresponding to  $M$  independent  $\mathbf{R}$  matrices, and the number of equivalent reflexions,  $m$ , is equal to  $M$ . For a certain kind of special index  $m$  may be less than  $M$ , and  $M/m$  terms in the square bracket of equation (2) have a common index  $\mathbf{h}_s$ . In general we obtain

$$F(\mathbf{h}) = \sum_{j=1}^{N/M} f_j (M/m) \sum_{s=1}^m \exp(2\pi i \mathbf{h}_s \cdot \mathbf{r}_j),$$

and this expression immediately leads to the mean square structure factors as

$$\langle |F(\mathbf{h})|^2 \rangle \sim \sum_{j=1}^{N/M} (M^2/m) f_j^2 = (M/m) \sum_{n=1}^N f_n^2. \quad (3)$$

The above result is valid also for a case in which some  $\mathbf{t}_s$ 's are different from lattice vectors. Even in such a case, exponential factors  $\exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s)$  in equation (1) present no new problems for most kinds of indices, and the relation (3) can

be obtained from (1) in a similar way as from (2). The special kinds of indices to be considered are those which are associated with the space-group absences. As far as non-vanishing reflexions are concerned, however, relation (3) is valid because for these reflexions we always have, by selecting a proper origin of the unit cell,

$$\exp(2\pi i \mathbf{h} \cdot \mathbf{t}_s) = 1. \quad (4)$$

This can be seen, for example, by considering a screw axis  $p_q$  along the  $b$  axis. The index  $\mathbf{h}$  we are concerned with is  $0k0$  with  $k = pn$ . Since the relevant  $\mathbf{t}_s$  has the form  $(t_1, nq/p, t_3)$ , relation (4) is obviously satisfied. A similar situation can also be found for glide planes. A strict proof of relation (4) for a non-vanishing reflexion will be given elsewhere (Iwasaki, 1977).

If the cell is non-primitive, the same index  $\mathbf{h}_s$  always appears  $L$  times in the square bracket of (1). Here  $L$  is the multiplicity of the compound lattice: 2 for a body or base-centred cell, 3 for a hexagonal-rhombohedral and 4 for a face-centred. A similar calculation leads again to the same result as (3) for a non-vanishing reflexion, provided that  $N$  is the number of atoms in the compound unit cell and  $M$  is the number of equivalent positions in the *same* unit cell.

Therefore, we always have

$$\varepsilon(\mathbf{h}) = M/m(\mathbf{h}), \quad (5)$$

i.e. the quantity  $\varepsilon$  for a given index  $\mathbf{h}$  is equal to the ratio of the number of space-group equivalent positions in the unit cell to the number of point-group equivalent reflexions for that reflexion. It must be noted that  $m$  is not the number of Laue-group equivalent reflexions which is known as the multiplicity of a plane in powder diffractometry: reflexions  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  are not equivalent for non-centrosymmetric structures.

The  $\varepsilon$  values based on the table of equivalent reflexions (Iwasaki, 1971) are listed in Table 1.

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**Dispersion corrections for X-ray atomic scattering factors.** By M. J. COOPER, *Materials Physics Division, AERE Harwell, Oxfordshire, OX11 0RA, England*

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Recently tabulated values of dispersion corrections for X-ray atomic scattering factors are misleading since they imply an unrealistically high reliability and do not take into account their variation with  $\sin \theta/\lambda$ , which can in general be quite significant.

In a recent paper Cromer (1976) has given the results of new calculations for the values of the dispersion corrections  $\Delta f'$  and  $\Delta f''$  for Co  $K\alpha_1$  radiation which were made in response to numerous requests. Previous values for the dispersion

corrections for Co  $K\alpha$  radiation were in fact published (Cooper, 1963) as a function of both atomic number and  $\sin \theta/\lambda$ . Comparison of these two sets of values shows quite large differences for some elements, but although the new