P(4) (complément à 2 u.v.) sera supérieure à celle reçue par O(3) ce qui conduira à une diminution de la longueur de liaison P(1)—O(1).

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Non-Bonded Interactions and the Crystal Chemistry of Tetrahedral Structures Related to the Wurtzite Type ($B4$)

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It has previously been suggested that bond angles in silicates, silica polymorphs and compounds with related structures composed of AX_4 tetrahedra sharing corners were determined by 'hard' $A\cdots A$ (non-bonded) contacts. In this paper the same argument is extended to a consideration of binary, ternary *etc.*, structures of (mainly) the sphalerite and wurtzite types. It is argued that, in the latter, cation···cation contact is common, and that the detailed geometry of the structures, particularly the relation between the c/a ratio and the atom parameter u, can be deduced from non-bonded radii, $R(A)$, and bond lengths, $l(A-X)$. This is demonstrated, semiquantitatively, with some success. The relative stabilities of the sphalerite, wurtzite, β-BeO and NaCl structure types are considered in the same terms, *viz* the ratios R/l for cations. Using this ratio as a measure of cation size, some incorrect predictions of the classical 'radius-ratio rule' are rectified, and the rule confirmed to be erroneous. In effect, we suggest that the effective size of an ion (atom) is measured by its ratio R/l (which is measurable) rather than by a hypothetical 'ionic radius' (which is not). Thus, the paper provides further evidence that cation···cation, rather than anion···anion, interactions are the effective determinants of structure type in oxides and nitrides.

Introduction

In a recent discussion of mainly ABO_4 oxides with structures related to those of the cristobalite forms of SiO_2 (O'Keeffe & Hyde, 1976) we called attention to the apparent role of $A\cdots B$ 'non-bonded' interactions in determining A—O—B bond angles. These angles were in fact predicted rather well from 'one-angle radii' for A and B (Glidewell, 1975), derived from the geometry of small molecules in which A and B share only *one* nearest-neighbour, directly bonded, O atom; and A—O and B—O bond lengths from the sums of 'ionic radii' (Shannon & Prewitt, 1969; Shannon, 1976). In these

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cases AO_4 and BO_4 tetrahedra were linked by sharing each corner with that of only one other similar tetrahedron; *i.e.* the O was two-coordinate.

Subsequently (O'Keeffe & Hyde, 1978), we examined in detail the Si—O—Si configuration in silicates. It was found that Si⋯Si non-bonded distances were usually close to 3·06 Å, and hence determine a one-angle radius or non-bonded radius for Si, $R(\mathrm{Si}) \simeq 1{\cdot}53$ Å. Small variations in Si⋯Si distances do occur, but shorter Si⋯Si distances are correlated with longer Si—O bond lengths and *vice versa*, so that it appears that compression of Si⋯Si is accompanied by tension (stretching) of the Si—O bonds. This effect can be considered as arising from non-bonded interactions with other cations* surrounding the oxygen. In these structures SiO_4 tetrahedra are also corner-connected, but the coordination number for O was often greater than two (although never more than two Si atoms).

In the present paper we examine the possible role of non-bonded interactions between cations surrounding an O or N atom on the stability of a crystal structure, particularly those structures related to the sphalerite and wurtzite modifications of ZnS (*Strukturbericht* symbols $B3$ and $B4$ respectively). In these, anions and cations each have four nearest neighbours in tetrahedral configuration, and tetrahedra are joined by sharing corners only. When tetrahedra share edges, four-membered $A\langle^{X}_{X}\rangle A$ rings are formed. These we largely exclude because, in molecular geometry and in crystals, one finds that the approximate constancy of non-bonded distances in $A—X—A$ configurations does not appear to extend to such cases – where the A atoms have *two* X neighbours in common. The study was prompted by the observation that in many oxides and nitrides with the structure types under discussion the shortest cation⋯cation distances are in fact close to the sum of the appropriate non-bonded radii, whereas there is a wide range of anion⋯anion distances, even in the structure of one compound. Thus we are led to analyse structures in terms of anion-centred polyhedra (tetrahedra) rather than from the more conventional viewpoint of cation-centred polyhedra. Furthermore, the question of the relative stabilities of the two polymorphs is a recurring one which has never been answered, although germane observations have not infrequently been made (*e.g.* Keffer & Portis, 1957; Lawaetz, 1972; Fleet, 1976).

In departing from the more traditional description of crystal structures we do not espouse any particular view of the nature of the interatomic forces in crystals. At this stage it is sufficient to present and correlate empirical observations which depend for their validity only upon the accuracy of reported crystal structures, but which nevertheless lead to some useful generalizations about structures and their stabilities.

* We use the term cation in the conventional sense of referring to the more electropositive elements in compounds with O, N *etc.*, without committing ourselves to an ionic description of interatomic forces in crystals.

Non-bonded radii

A table of non-bonded (one-angle) radii, R, has been given elsewhere [O'Keeffe & Hyde (1976), based largely on Glidewell (1975)]. Some of the values have been found to be in need of revision. We are still searching for the best way to do this; so that a definitive set cannot be provided at present. The problem is very much like that of summarizing bond lengths by ionic or covalent radii, especially the latter. In all cases, interatomic potentials are being replaced by single-value functions: a 'hard-sphere' approximation.

The structures best suited to determining non-bonded distances are those like cristobalite which are flexible, and which can adjust to a wide range of $A—X—B$ bond angles without deformation of the AX_4 and BX_4 tetrahedra. The number of such compounds is limited. In other cases, when X has a coordination number greater than two, a small range of $A\cdots B$ one-angle distances is observed.* For example, when X is surrounded by four atoms such that, with normal $A—X$ bond lengths, there is crowding along the non-bonded directions, then the $A\cdots B$ distances are short. This is the case, for example, in the OLi_2Si_2 tetrahedron in Li_2SiO_3 (discussed below). On the other hand, long $A\cdots B$ distances will occur if the $A—X$ bonds are long enough for there to be no direct $A\cdots B$ interactions ('contacts'). It may even be the situation when X has *more* than four nearest-neighbour cations, as in thortveitite, $Sc_2Si_2O_7$,

* Where appropriate, $A\cdots B$ should be taken as including $A\cdots A$ and $B\cdots B$; and likewise $A—X—B$ implies $A—X—A$ and $B—X—B$, and $A—X$ also implies $B—X$.

Table 1. *Non-bonded (one-angle) radii (R), bond lengths (l), and values of the ratio R/l for selected atoms*

A	$R(A)$ (Å)	$l(A-\mathrm{O})$ (Å)	$l(A-\mathrm{N})/R$	$R/l(A-\mathrm{O})$	$R/l(A-\mathrm{N})$
Li	1·5	1·97	2·05	0·76	0·73
Be	1·35	1·65	1·73	0·82	0·78
B	1·26	1·49	1·57	0·85	0·80
Na	1·68	2·37	2·45	0·71	0·69
Mg	1·66	1·95	2·03	0·85	0·82
Al	1·62	1·77	1·85	0·92	0·88
Si	1·53	1·64	1·72	0·93	0·87
P	1·46	1·55	1·63	0·94	0·90
S	1·45	1·50	1·58	0·97	0·92
V^{V}	1·59	1·74	1·82	0·91	0·87
Cr^{VI}	1·57	1·64	1·72	0·96	0·91
Mn^{II}	1·7	2·04	2·12	0·83	0·80
Fe^{III}	1·68	1·87	1·95	0·90	0·86
Zn	1·65	1·98	2·06	0·83	0·80
Ga	1·63	1·85	1·93	0·88	0·84
Ge	1·58	1·77	1·85	0·89	0·85
As	1·54	1·71	1·79	0·90	0·86

in which there are distorted OSc_4Si_2 octahedra with the two Si atoms at opposite vertices. Hence, the derivation of appropriate radii requires a careful evaluation of the anion coordination configuration, and an understanding of the way in which a compromise is found between the often conflicting requirements of bonded and non-bonded distances in crystal structures.

We have previously described how the non-bonded radii for Si and B were derived (O'Keeffe & Hyde, 1978). The value of R for P is one half of the mean value of 65 distances $d(\mathrm{P}\cdots\mathrm{P})$ in recently published structures, mainly those containing $(PO_3)_n^{n-}$ chains of corner-connected PO_4 tetrahedra. The value for Al likewise comes from data for $d(\mathrm{Al}\cdots\mathrm{Si})$ in ordered aluminosilicates, and for $AlAsO_4$. The non-bonded radii for Cr^{VI} and V^{V} come from data for dichromates (Löfgren, 1971, and references therein) and divanadates (Calvo & Faggiani, 1975, and references therein). Radii for Be, B and Ga are each based on a large number of interatomic distances in oxides. The value for As is taken as the difference between the distance $d(\mathrm{As}\cdots\mathrm{B}) = 2{\cdot}803$ Å in $BAsO_4$ which has the high-cristobalite structure, and R(B). Other radii were determined from data for cristobalite-like structures (O'Keeffe & Hyde, 1976). They are all summarized in Table 1.

Binary compounds with the wurtzite and/or sphalerite structures

(*a*) *Description of the structures*

About 40 binary compounds, see Table 2, have one or both of the sphalerite ($B3$) or wurtzite ($B4$) structures (Parthé, 1972).

The $B3$ structure is cubic [space group $F\bar{4}3m$; A in 4(*a*), 0,0,0 *etc.*; X in 4(*c*), $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ *etc.*], and the A and the X atoms each form f.c.c. arrays and hence are in cubic eutaxy (O'Keeffe, 1977). For comparison with other structures a (111) projection of this structure is shown in Fig. 1(*a*). Note that $B3$ is its own antitype, *i.e.* it is not altered if A and X are interchanged.

The $B4$ structure is hexagonal [space group $P6_3mc$; A in 2(*b*), $0,0,u_1$ *etc.*; X in 2(*b*), $0,0,u_2$ *etc.*]. Two parameters are sufficient to describe the structure completely: $\gamma = c/a$ and $u = u_2 - u_1$. Again the structure is its own antitype, both A and X being approximately in hexagonal eutaxy (arranged as in hexagonal close-packing) [see Fig. 1(*b*)].

The following observations are relevant to the subsequent discussion.

(i) The $B4$ structure is in several ways intermediate between the $B3$ and $B1$ (= **NaCl**)* types. Thus (Jeffrey, Parry & Mozzi, 1956), there are several compounds that have both $B4$ and $B1$ polymorphs, but not $B3$; and there are others that have both $B3$ and $B4$, but not $B1$. [The $B4$ structure is also intermediate between $B3$ and $B1$ on an 'ionicity' scale (Phillips, 1970).]

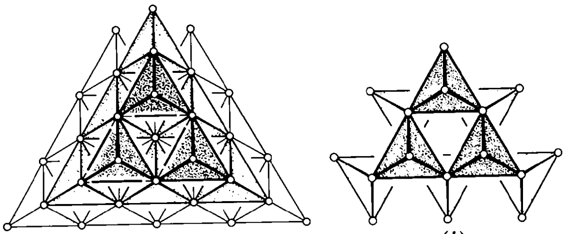
(ii) Compounds that have both the $B3$ and $B4$ structures have, for the $B4$ type, $\gamma \gtrsim \sqrt{(\frac{8}{3})}$ (= 1·6330), which is the value corresponding to perfect hexagonal eutaxy. On the other hand, compounds that have only a $B4$ (and not a $B3$) modification have $\gamma < \sqrt{(\frac{8}{3})}$ (Keffer & Portis, 1957; Lawaetz, 1972; Fleet, 1976).

(iii) Decreasing γ is associated with decreasing stability of the $B4$ structure with respect to $B1$. Thus, in

* Chemical formulae in bold type denote structure types, not compounds.

Table 2. *Unit-cell and atom parameters for binary compounds of the sphalerite* ($B3$) *and wurtzite* ($B4$) *structure types*

	$B3$	$B4$		
Compound	a (Å)	γ	a (Å)	u
CuH	–	1·602	2·89	–
BeO	–	1·6224	2·698	0·379
ZnO	–	1·6022	3·249	0·383
BN	3·615	1·647	2·55	–
AlN	–	1·600	3·104	0·385
GaN	–	1·625	3·180	–
InN	–	1·611	3·533	–
C	3·567	1·635	2·52	–
SiC	4·359	1·641	3·076	–
CuCl	5·416	1·642	3·91	–
BeS	4·862	–	–	–
MnS	5·606	1·618	3·976	–
ZnS	5·406	1·636	3·811	–
CdS	5·835	1·623	4·137	0·378
HgS	5·872	–	–	–
BP	4·538	1·656	3·562	–
AlP	5·467	–	–	–
GaP	5·447	–	–	–
InP	5·869	–	–	–
Si	5·431	1·653	3·80	–
CuBr	5·691	1·640	4·06	–
BeSe	5·139	–	–	–
MgSe	–	1·622	4·145	–
MnSe	5·83	1·63	4·12	–
ZnSe	5·669	1·634	4·003	–
CdSe	6·05	1·631	4·30	0·377
HgSe	6·085	–	–	–
BAs	4·777	–	–	–
AlAs	5·639	–	–	–
GaAs	5·654	–	–	–
InAs	6·058	1·638	4·274	–
Ge	5·657	–	–	–
CuI	6·055	1·645	4·31	–
AgI	6·486	1·635	4·592	0·375
BeTe	5·626	–	–	–
MgTe	–	1·63	4·53	–
ZnTe	6·103	1·645	4·310	–
CdTe	6·478	1·637	4·572	–
HgTe	6·460	–	–	–
AlSb	6·136	–	–	–
GaSb	6·095	–	–	–
InSb	6·479	–	–	–
Sn	6·489	–	–	–
BePo	5·838	–	–	–
ZnPo	6·309	–	–	–
CdPo	6·665	–	–	–



(*a*) (*b*)

Fig. 1. (*a*) The sphalerite ($B3$) structure depicted as AX_4 (or XA_4) tetrahedra, and projected on (111). The projection of the equivalent hexagonal unit cell is indicated. (*b*) The wurtzite ($B4$) structure projected on (0001).

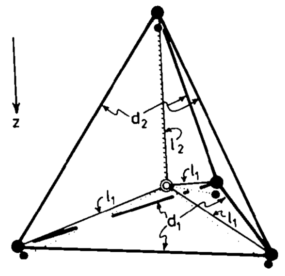


Fig. 3. The XA_4 (anion-centred) tetrahedron in wurtzite: X = open circle, A = filled circles. The smaller circles and dotted lines are, respectively, the atom positions and bonds in 'ideal' wurtzite, *i.e.* perfect hexagonal eutaxy with $\gamma = \sqrt{(\frac{8}{3})}$. The larger circles and light, full lines are the atom positions and bonds for $\gamma < \sqrt{(\frac{8}{3})}$. The heavy lines outline the tetrahedron in the latter case (X position unaltered), and are the $A\cdots A$ non-bonded distances. There are now two different bond lengths, l_1 and l_2 ($l_1 < l_2$), and two different non-bonded distances, d_1 and d_2 ($d_1 > d_2$).

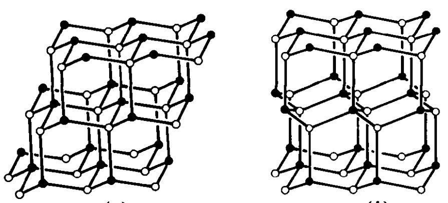
ZnO + MgO solid solutions, γ decreases from 1·602 for pure ZnO to 1·595 for (Zn,Mg)O containing 16 mol% MgO, which is the solubility limit – $B4$ and $B1$ in equilibrium – at 1573 K (Sapozhnikov, Kondrashev, Markoviskii & Omel'chenko, 1961).

(iv) In $B4$ compounds with $\gamma < \sqrt{(\frac{8}{3})}$ the $A-X$ bonds are of unequal length: those directed along **c** are always longer than the others (Mair & Barnea, 1975).

(*b*) *The axial ratio and the bond lengths in wurtzites*

Compounds AX that have the wurtzite structure but not a sphalerite modification [*cf.* (ii) above] are usually oxides or nitrides, with the $A\cdots A$ distances slightly *less* than $2R(A)$ [but $X\cdots X$ more than $2R(X)$]. By contrast, in sphalerites the $A\cdots A$ (and $X\cdots X$) distances are significantly greater than $2R$. An exception is SiC, which has $d(\text{Si}\cdots\text{Si}) = 3{\cdot}076$ Å, only slightly greater than $2R(\text{Si}) = 3{\cdot}06$ Å. But note that SiC can exist in many forms including $B3$ and $B4$. *We conclude that the existence of only a* $B4$ (*and not a* $B3$) *modification is related to cation···cation interactions.* In principle, anion···anion interactions could lead to the same result but, in practice, we know of no such case.

As far as $A\cdots A$ interactions are concerned, the difference between the ideal $B3$ and $B4$ structures (with regular tetrahedra) is illustrated in Fig. 2. In sphalerite each A atom has 12 equidistant A neighbours arranged



(*a*) (*b*)

Fig. 2. (*a*) The sphalerite structure in terms of $A-X$ bonds; eutactic planes (3^6 nets) are horizontal, and the [111] trigonal axis is vertical. Note the chair-form A_3X_3 rings parallel to the basal plane, and approximately parallel to [111]. (*b*) The wurtzite structure similarly depicted. Note the chair-form A_3X_3 rings parallel to the basal plane, and the *boat*-form A_3X_3 rings parallel to [0001] (vertical).

as in Fig. 2(*a*) (at the vertices of a cuboctahedron): all A_3X_3 rings are in the chair form. In wurtzite there are six equidistant neighbours in the same (0001) plane with this (A_3X_3 chair) arrangement, and six more [three in each adjacent (0001) layer] arranged as in Fig. 2(*b*). These are linked to those in the central (0001) layer *via* A_3X_3 rings which are in the boat form. The first six and the second six neighbours are equidistant from the central atom only if $\gamma = \sqrt{(\frac{8}{3})}$: they are then at the corners of a regular 'twinned cuboctahedron'. It seems reasonable to suppose that the $A\cdots A$ interactions will not be spherically symmetrical, but will be different for the two configurations (chair and boat). If the interaction is repulsive, screening by the valence electrons which are largely centred on the anions [see, for example, the calculated valence electron density in ZnO reported by Chelikowsky (1977)] would favour the boat configuration, which occurs in wurtzite, but not in sphalerite.* This same preference arises from the attractive interaction between A and X across the boat or chair. As mentioned in the *Introduction*, and discussed further below, it is invariably observed that the $A\cdots A$ distances in wurtzites are close to or less than $2R(A)$. In the light of the argument just given it is not surprising that, in the latter case, those distances corresponding to the boat conformation are less than those corresponding to the chair conformation, so that $\gamma < \sqrt{(\frac{8}{3})}$.

We now turn to a consideration of the atom spacings in a model of real wurtzites. Four distances characterize the XA_4 tetrahedron (see Fig. 3): the length of the $A-X$ bond parallel to **c**,

$$l_2 = au\gamma; \qquad (1)$$

the (equal) lengths of the other three bonds,

$$l_1 = a\sqrt{[\tfrac{1}{3} + (\tfrac{1}{2} - u)^2]}; \qquad (2)$$

* It is not possible to have a corner-connected array of centred tetrahedra, stoichiometry AX, with only boat-form A_3X_3 rings.

the three tetrahedron edges ($A\cdots A$) perpendicular to **c**, all of length

$$d_1 = a; \tag{3}$$

and the other three edges ($A\cdots A$), all of length

$$d_2 = a\sqrt{\left(\tfrac{1}{3} + \frac{\gamma^2}{4}\right)}. \tag{4}$$

The critical assumption, which we test repeatedly hereafter, is that when $d(A\cdots A)$ is shorter than $2R(A)$ the two associated $A-X$ bonds are under tension, *i.e.* $l(A-X)$ is lengthened. In the specific instance of the wurtzites it might be supposed, *as a first approximation*, that the compression of the $A\cdots A$ distance is proportional to the extension of the $A-X$ distance. Thus, if l_0 and d_0 are the unstressed bond length and non-bonded distance respectively, then

$$l_1 - l_0 = p(d_1 - d_0), \tag{5}$$

$$(l_1 + l_2)/2 - l_0 \simeq p(d_2 - d_0), \tag{6}$$

where p is a parameter of the order of -1. Subtracting equation (5) from equation (6) gives

$$(l_2 - l_1)/2 \simeq p(d_2 - d_1). \tag{7}$$

Equations (1) to (4) and (7) enable d_1, d_2, l_1, l_2 and a to be eliminated and then, in terms of γ and p only,

$$u \simeq \frac{(3\gamma^2)^{-1} + \frac{1}{4} - 4p^2\{\sqrt{[(3\gamma^2)^{-1} + \frac{1}{4}]} - \gamma^{-1}\}^2}{1 - 4p\{\sqrt{[(3\gamma^2)^{-1} + \frac{1}{4}]} - \gamma^{-1}\}}. \tag{8}$$

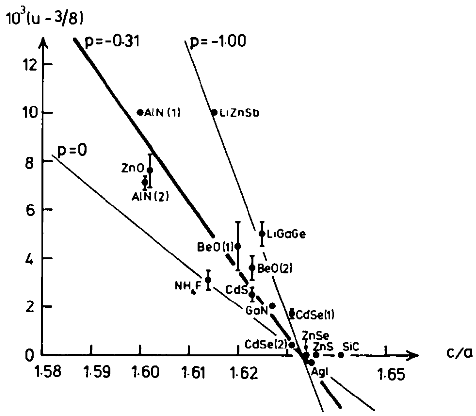


Fig. 4. The relation between the two parameters u and γ for wurtzites. Circles represent experimental values from the literature (with standard deviations, when available, indicated by bars). The lines are from equation (8), with different values of p. In the case $p = 0$, all $A-X$ bond lengths are equal [equation (9)]. The best fit to most of the data (for explanation of exceptions see text) is given by the heavy line, for which $p = -0{\cdot}31$. Data are those quoted by Mair & Barnea (1975) except for AlN(2) and GaN, which are from Schulz & Thiemann (1977). (Other data are available, but all have *assumed* values of $u = \frac{3}{8}$.)

If $p = 0$ (no $A\cdots A$, $X\cdots X$ interactions) one finds from (8) that

$$u \simeq (3\gamma^2)^{-1} + \tfrac{1}{4}. \tag{9}$$

This is the equation for all bond lengths equal, a situation not usually observed in crystals of the wurtzite type. Equation (9) implies that the 'ideal' value of $u = \frac{3}{8}$ will only occur if $c/a = \gamma = \sqrt{(\frac{8}{3})}$, the value for perfect hexagonal eutaxy. The parameter $u \neq \frac{3}{8}$, not only when there is $A\cdots A$ (or $X\cdots X$) contact and $\gamma < \sqrt{(\frac{8}{3})}$ but also when there is no contact, but $\gamma \neq \sqrt{(\frac{8}{3})}$. There are several known examples, *cf.* Table 2 and Fig. 4, where $\gamma > \sqrt{(\frac{8}{3})}$. In these cases, if u really is equal to $\frac{3}{8}$ (and, until fairly recently, this was often *assumed* in solving a wurtzite structure), then there must be two different bond lengths or, conversely, if all bond lengths are equal then $u < \frac{3}{8}$.

In fact, the available data for most wurtzites (Mair & Barnea, 1975, and references therein; Schulz & Thiemann, 1977) fit reasonably well to equation (8) with an average value of $p = -0{\cdot}31$ (Fig. 4). Exceptions are NH_4F which, not surprisingly since the N—F 'bonds' are long, falls on the line for equation (8) with $p = 0$, and two alloys, LiZnSb and LiGaGe, both of which fall close to the line for $p = -1{\cdot}00$ in equation (8). This too is not surprising since they are 'filled' wurtzites, with Li in the octahedral interstices: face-sharing between the octahedra and tetrahedra brings Li and A atoms close together, and so one would expect a strong $\mathrm{Li}\cdots A$ interaction.

It should be reiterated that only the most accurately refined structural parameters are sufficiently accurate and reliable to yield p values with any confidence. In this connection the work of Barnea and co-workers is relevant: their most recent paper (Whiteley, Moss & Barnea, 1977) shows that neglect of anharmonicity in thermal vibrations in the wurtzite-type structure of CdSe results in the u parameter being too high by 0·0014. The previously reported value of 0·3767 should be reduced to 0·3753, rather close to the 'ideal' $u = \frac{3}{8} = 0{\cdot}3750$; but $\gamma = 1{\cdot}631$ which is rather close to the 'ideal' value of $\sqrt{(\frac{8}{3})} = 1{\cdot}6330$. Put into proper perspective the difference is very striking: the significant parameter is $u_{\text{obs}} - u_{\text{'ideal'}} = u_{\text{obs}} - \frac{3}{8}$, and this is reduced from 0·0017 to 0·0003. Hence, seen in this context, the range $0 < p \leq -1$ appears to be a rather satisfactory result.

The stability of tetrahedral structures

The ideas developed in the previous section suggest criteria for the stability of tetrahedral AX structures.

(i) If the normal bond length $l(A-X)$ and non-bonded radius $R(A)$ are such that $R/l < \sqrt{(\frac{2}{3})} = 0{\cdot}8165$ {*i.e.* $\sin[(109° \, 28')/2]$}, then X can be coordinated (tetrahedrally) by four A atoms so that $d(A\cdots A) >$

$2R(A)$, and non-bonded repulsions are therefore unimportant. The crystal may adopt either the sphalerite or the wurtzite structures. This criterion is found to hold for *every* known compound with the sphalerite structure (including BN), using the observed values of l and the values of R in Table 1.

(ii) If $R/l > \sqrt{(\frac{2}{3})}$, then $d(A\cdots A) < 2R(A)$ and $A\cdots A$ 'contact' will occur. *Provided that the resulting strain is not too great* it can be accommodated by adopting the wurtzite structure and stretching the $A-X$ bonds (particularly those parallel to **c**) in the way already described.

Values of R/l for some oxides [using ionic radii from Shannon (1976) to calculate l] are: BeO 0·82, ZnO 0·83, MnO 0·83, MgO 0·85 (*cf.* Table 1). In accord with the above criteria, the first two have the $B4$ but not the $B3$ structure; the second two have neither, but the $B1$ type.

For nitrides there is a difficulty: ionic radii do not predict bond lengths well: the difference between $l(A—O)$ and $l(A—N)$ is not constant, *i.e.* is not independent of A. Calculated and observed values may differ by as much as 0·05 Å [*e.g.* for l(Si—N)]. However, if we ignore this for the moment and accept the implications of Shannon's table of radii, then for tetrahedral coordination $l(A—N)$ should be greater than $l(A—O)$ by 0·08 Å, and we can calculate R/l for nitrides also. Some values thus derived are: BN 0·80, GaN 0·84, FeN 0·86 and AlN 0·88. The observed structures are again in accord with expectation: the first, with $R/l < \sqrt{(\frac{2}{3})}$, has both a $B3$ and a $B4$ form with $\gamma = 1{\cdot}65$, *i.e.* $> \sqrt{(\frac{8}{3})}$; GaN and AlN have only a $B4$ modification (with $\gamma = 1{\cdot}627$ and $1{\cdot}601$ respectively); FeN has not been reported.

The highest permissible value for R/l (maximum tolerable bond stretching and non-bond compression) for wurtzite structures can be found only by experiment. We note that the highest known values (above which we expect the compound to adopt the $B1$ type) are, for oxides, 0·83 for ZnO [0·83$_3$ for (Zn,Mg)O] but, for nitrides, ~0·88 for AlN. Note also that in spite of this considerable difference in their R/l values they fall close together on Fig. 4, *i.e.* they have similar values of γ and u.

The conventional radius-ratio rule predicts that Zn would be less likely to be found in tetrahedral coordination than Mg but, in agreement with the facts, their values of R/l predict just the opposite. Thus, it emerges that R/l for a cation in (say) an oxide or a nitride is an important parameter in crystal chemistry: it correlates with structure type much better than the usually used cation/anion 'radius ratio' which, it may also be noted, says nothing about the relative stabilities of the $B3$ and $B4$ forms.

In what follows we discuss ternary oxides in terms of the values of R/l in Table 1. Note in particular that R/l is *smaller* for Na than for Li although the contrary is true for R and l separately. Hence, from the present viewpoint, but *not* from a consideration of radius ratios, it is not surprising that $NaAlO_2$ (average $R/l = 0{\cdot}82$) has an ordered wurtzite structure, but that $LiAlO_2$ (average $R/l = 0{\cdot}85$) does not. The only form of the latter with tetrahedrally coordinated cations has the filled low-cristobalite (ordered **β-BeO**) structure, which we will call B (*cf.* below). But it contains *edge*-shared pairs of tetrahedra or, more relevantly in the present context, $\overline{\mathrm{Li{-}O{-}Al{-}O}}$ four-membered rings – *i.e.* 'two-angle' contacts, see Fig. 5. It is clear that such four-membered rings allow closer $A\cdots B$ contact. [Doubling the number of $A—O—B$ bonds would be expected to increase the value of p in equation (8), *i.e.* increase the compression of $A\cdots B$ for a given stretching of $l(A\cdots O)$.] In that sense the B and related structures (*cf.* below) are intermediate between, on the one hand, the $B3$ and $B4$ types and, on the other, the $B1$ type: the former have only six-membered rings (and 'one-angle' contacts), the latter only four-membered rings (and 'two-angle' contacts), while B has both. Thus, large R/l values lead ultimately to the $B1$ structure, as found, for example, for MgO. $NaAlO_2$ also has a B modification, but the second modification of $LiAlO_2$ is a rhombohedral, ordered $B1$ type, with *octahedrally* coordinated cations. A similar example is provided by the pair $NaFeO_2$ and $LiFeO_2$: the former has both $B4$ and B polymorphs, both with fourfold coordination of Na (and Fe); but the latter has only structures based on the $B1$ type, with octahedral coordination of the cations. As with the corresponding aluminates, this difference is again entirely in accord with the trend in R/l values.

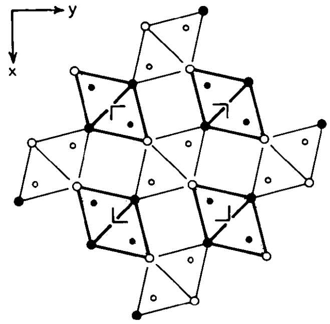


Fig. 5. The tetragonal β-BeO ('B') structure projected on (001).

Ternary compounds with structures related to the sphalerite and/or wurtzite types: description of the structures

(*a*) *Compounds* ABX_2 ($ABXY$)

The structures of the ternary compounds in this class can be discussed from several viewpoints. One description (O'Keeffe & Hyde, 1976) recognizes that, in the known structures, the topology of the BX_2 framework is that of cristobalite; so that these structures are usefully thought of as 'filled' cristobalites. This description is particularly appropriate when the anion arrangement is far from eutactic, *i.e.* when the $A-X$ and $B-X$ bond lengths are very different.

The customary notation for compounds with these structures is confusing: for example, α-$NaGeO_2$ and β-$NaFeO_2$ have the same structure while γ-$LiBO_2$ and γ-$LiAlO_2$ have different structures. In this paper we will therefore describe compounds with structures derived from the sphalerite and wurtzite types (by ordering the cations and/or the anions) by prefixes S and W respectively. The prefix B for **β-BeO** derivatives has already been introduced.

The family divides into two groups. In those compounds containing other than first-row anions (*i.e.* with S, P *etc.*) the anion array is fairly close to cubic eutaxy [filled, collapsed high-cristobalite structure (O'Keeffe & Hyde, 1976)]: the structure is sometimes referred to as the chalcopyrite $\mathbf{CuFeS_2}$ type ($E1_1$). In oxides and nitrides, such as S-$LiPN_2$ and S-$LiBO_2$, the structures are more open ($B-X-B$ bond angles $\geqslant 109° 28'$): there is a sizeable difference between the $A-X$ and $B-X$ bond lengths.

The W family, which is our main concern [and which is another collapsed form of filled cristobalite (O'Keeffe & Hyde, 1976)], is better expressed as $ABXY$, to emphasize the two non-equivalent anions. Hence, these structures are really quaternary, and compounds such as GaBeON and LiSiON are predicted to be isostructural. It is its own antistructure: all atoms are in positions $4(a)$ of the orthorhombic space group $Pna2_1$. An example, the structure of $LiGaO_2$, is shown in Fig. 6. In this standard setting, the orthorhombic c axis corresponds to the hexagonal c axis of the $B4$ parent structure (length c_h). The length of the pseudo-hexagonal a axis is calculated as $a_h \simeq [ab/\sqrt{(12)}]^{1/2}$, and hence an effective $\gamma_h \simeq c_h/a_h$ is deduced. It is listed in Table 3 for compounds known to have this structure. [Lattice constants are taken from the tables in O'Keeffe & Hyde (1976) and Parthé (1972).] We call attention to the observation that all ternary oxides and nitrides, but only one out of ten sulphides, have $\gamma_h < \sqrt{(\frac{8}{3})}$.*

(*b*) Compounds AB_2X_3 (AB_2XY_2)

Compounds derived from $B3$, such as S-$GeCu_2S_3$ and S-$GeCu_2Se_3$, are known (Parthé, 1972), but will not concern us here. However, the analogous compounds with structures derived from $B4$ form an important class. There are two types of anion (hence the formula AB_2XY_2), although we are not aware of any report of a quaternary compound in the chemical sense. The space group is $Cmc2_1$, with A and X in $4(a)$, B and Y in $8(b)$; and the structure is its own antitype. Compounds with this structure include W-$SiLi_2O_3$ (Hesse, 1977) (shown in Fig. 7), W-$GeLi_2O_3$ (Völlenkle & Wittmann, 1968), and W-$LiSi_2N_3$ (David, Laurent, Charlot & Lang, 1973). W-$SiNa_2O_3$ (McDonald & Cruickshank, 1967) and W-$GeNa_2O_3$ (Völlenkle, Wittmann & Nowotny, 1971) are isostructural, but Na and O(1) are almost five (4 + 1) coordinate: the Na atoms have moved towards the bases of their tetrahedra, exactly as described earlier, but by so much that they are almost in them. Since these bases are common to two tetrahedra, the Na atoms are almost at the centres of trigonal bipyramids.

Just as the high-cristobalite form of SiO_2 may be regarded as S-ABX_2 without the A atoms, so there are several compounds whose structures may be derived from W-AB_2XY_2 by omitting one kind of cation. Thus, representing the missing atom by □, one has W-$\square B_2O_3$ (Prewitt & Shannon, 1968) and W-$\square Si_2ON_2$ (Idrestedt & Brosset, 1964). Although of lower symmetry, the so-

* However, here and in the following two sections, it is clear that the differing $A-X$ and $B-X$ bond lengths result in the tetrahedra being distorted. Hence γ_h is by no means as accurate a measure of strain as is γ in the case of binary compounds.

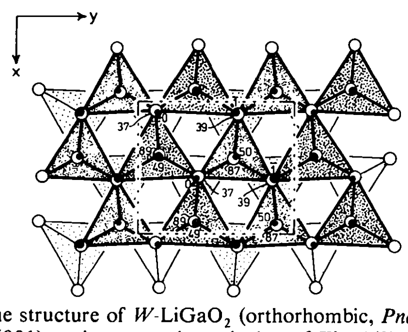


Fig. 6. The structure of W-$LiGaO_2$ (orthorhombic, $Pna2_1$) projected on (001); cation-centred tetrahedra, *cf.* Fig. 1(*b*). Small, filled circles are Ga atoms; medium, filled circles are Li atoms; large, open circles are O atoms; heights are in units of c/100; the unit cell is outlined. GaO_4 tetrahedra are lightly stippled; LiO_4 tetrahedra are heavily stippled.

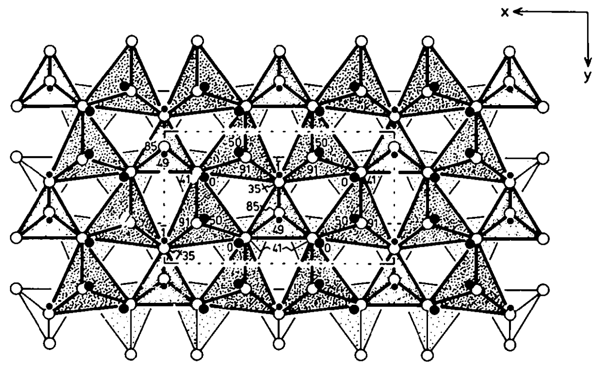


Fig. 7. The structure of W-Li_2SiO_3 (orthorhombic, $Cmc2_1$) projected on (001); *cf.* Figs. 1(*b*) and 6. Small, filled circles are Si atoms; medium, filled circles are Li atoms; large, open circles are O atoms. SiO_4 tetrahedra are lightly stippled; LiO_4 tetrahedra are heavily stippled.

called 'asbestos-like' form of SO_3 (Westrik & MacGillavry, 1954) is closely related and may be written as W-$S\square_2O_3$.

Data for these compounds are included in Table 3. The pseudohexagonal parameters are derived from those of the orthorhombic $Cmc2_1$ unit cell as follows: $c_h \simeq c$, $a_h \simeq [ab/\sqrt{(27)}]^{1/2}$.

(c) Compounds AB_3X_4 (ABC_2XYZ_2)

Again, $B3$-derived structures, such as famatinite, S-$SbCu_3S_4$, and luzonite, S-$AsCu_3S_4$, are known, but will not be considered here. There is also a $B4$-derived series: W-$AsCu_3S_4$ (enargite), W-Li_3PO_4, W-Li_3AsO_4 and W-Li_3VO_4, all of which are isostructural (Parthé, 1972). The space group is $Pmn2_1$; there are six non-equivalent atoms in the structure (ABC_2XYZ_2); and the structure is again its own antitype (which is not the case for the S analogue). An example, the structure of W-Li_3PO_4, is shown in Fig. 8, and data for these W types are included in Table 3.

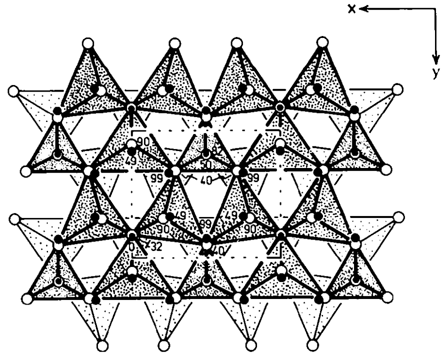


Fig. 8. The structure of W-Li_3PO_4 (orthorhombic, $Pmn2_1$) projected on (001); *cf.* Figs. 1(*b*), 6 and 7. Small, filled circles are P atoms; medium, filled circles are Li atoms; large, open circles are O atoms. PO_4 tetrahedra are lightly stippled; LiO_4 tetrahedra are heavily stippled.

Table 3. *Unit-cell parameters for ternary and quaternary compounds with superstructures of the wurtzite* ($B4$) *type*

Space group	Compound	a (Å)	b (Å)	c (Å)	γ_h
$Pna2_1$	$LiGaO_2$	5·402	6·372	5·007	1·588
	$NaAlO_2$	5·376	7·075	5·216	1·574
	$NaGaO_2$	5·519	7·201	5·301	1·565
	$NaFeO_2$	5·672	7·136	5·377	1·573
	$BeSiN_2$	4·977	5·747	4·674	1·626
	$MgSiN_2$	5·279	6·476	4·992	1·589
	$ZnGeN_2$	5·454	6·441	5·914	1·631
	$MnGeN_2$	4·977	5·747	4·674	1·627
	$MgGeN_2$	5·494	6·611	5·166	1·595
	$LiGaS_2$	6·513	7·864	6·217	1·617
	$LiInS_2$	6·883	8·066	6·543	1·634
$Cmc2_1$	Li_2SiO_3	9·392	5·397	4·660	1·492
	Li_2GeO_3	9·63	5·46	4·85	1·525
	Na_2SiO_3	10·484	6·070	4·813	1·375
	Na_2GeO_3	10·85	6·225	4·930	1·367
	Si_2LiN_3	9·186	5·302	4·776	1·560
	Cu_2SiS_3	10·98	6·416	6·046	1·642
$Pmn2_1$	Li_3PO_4	6·115	5·239	4·855	1·596
	Li_3AsO_4	6·27	5·38	4·95	1·59
	Li_3VO_4	6·33	5·45	4·96	1·57
	Cu_3PS_4	7·44	6·47	6·19	1·66
	Cu_3AsS_4	7·44	6·47	6·19	1·66
	Li_2MgSiO_4	–	–	–	–
	Li_2MgGeO_4	6·39	5·48	4·99	1·57
	Li_2ZnSiO_4	6·13	5·37	4·94	1·60
	Li_2ZnGeO_4	6·36	5·43	5·02	1·59
	Li_2CdSiO_4	6·47	5·35	5·10	1·61
	Li_2CdGeO_4	6·64	5·47	5·13	1·58
	Li_2MnSiO_4	–	–	–	–
	Li_2MnGeO_4	6·45	5·48	5·05	1·58
	Li_2FeSiO_4	6·26	5·32	5·01	1·62
	Li_2FeGeO_4	6·41	5·44	5·01	1·58
	Li_2CoSiO_4	6·17	5·36	4·93	1·60
	Li_2CoGeO_4	6·37	5·46	5·01	1·58
	Na_2MgGeO_4	7·45	5·60	5·35	1·57
	Na_2ZnSiO_4	7·02	5·44	5·24	1·58
	Na_2ZnGeO_4	7·17	5·56	5·32	1·57
	Cu_2ZnSiS_4	7·40	6·40	6·08	1·64
	Cu_2CdSiS_4	7·58	6·44	6·17	1·64
	Cu_2CdGeS_4	7·692	6·555	6·299	1·651
	Cu_2MnGeS_4	7·61	6·50	6·18	1·64
	Cu_2FeSiS_4	7·43	6·43	6·16	1·66

A detailed examination of bond lengths and non-bonded distances in the structures of some ternary 'wurtzites'

In the light of the earlier discussion of binary wurtzites, in this section we will examine the structures of three ternary compounds, one from each of the above groups (*a*), (*b*) and (*c*), *viz* $LiGaO_2$, Li_2SiO_3 and Li_3PO_4. Their structures have been rather well determined, and are shown in Figs. 6, 7 and 8 respectively.

(a) $LiGaO_2$ (*Marezio*, 1965)

In W-$LiGaO_2$ there are two different OLi_2Ga_2 tetrahedra: that about O(1) has a Li–O bond almost parallel to **c**, that about O(2) has a Ga–O bond in about the same direction. The following observations are completely in accord with those made for binary wurtzites; the relevant distances are summarized in Fig. 9.

(i) In each case the longest Ga–O and Li–O bond is that which is approximately parallel to **c**.

(ii) In each case the longest non-bonded distances $d(A\cdots B)$ are those approximately normal to **c**.

(iii) It therefore follows that in all $\overset{\;\;O}{A\cdots B}$ triangles the shorter non-bonded distances d are associated with the longer bond lengths l, and *vice versa*. It may also be noted that the differences are rather small, and that their unequivocal establishment depends on rather accurate structure determination.

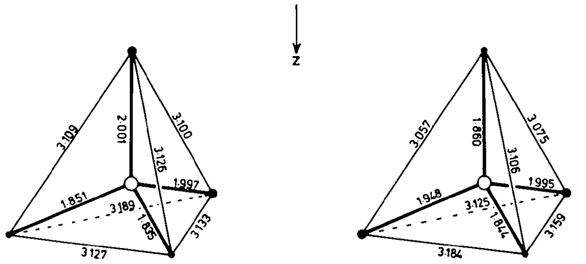


Fig. 9. Bond lengths (heavy lines) and non-bonded distances (lighter lines) (Å) in W-$LiGaO_2$. Small, filled circles are Ga atoms; medium, filled circles are Li atoms; large, open circles are O atoms. The (anion-centred) $O(1)Li_2Ga_2$ tetrahedron is on the left, and the $O(2)Li_2Ga_2$ tetrahedron on the right.

(*b*) Li_2SiO_3 (*Hesse*, 1977)

In W-Li_2SiO_3 there are also two kinds of anion-centred tetrahedra: $O(1)Li_3Si$ and $O(2)Li_2Si_2$. Because R/l is much less for Li than for Si there is a substantial difference between the average values of this parameter for the two cations: $0{\cdot}80_3$ and $0{\cdot}84_5$ respectively. This is reflected in the bond lengths and non-bonded distances, see Fig. 10.

In the tetrahedron about O(1) bond lengths are normal with, as one might expect, a slightly longer Li–O bond parallel to **c** and a longer distance $d(\mathrm{Li}\cdots\mathrm{Li})$ normal to **c**. In the tetrahedron about O(2) the greatly increased average value of R/l for the coordinating cations results in severe 'crowding', and very much longer bonds. As we would expect, the longer Si–O bond is approximately parallel to **c**; and is one of the longest known for tetrahedrally coordinated Si. Correspondingly, the Si⋯Si distance is one of the shortest that has been observed. The stress in the arrangement is reflected in the very low value of the axial ratio (calculated for the pseudohexagonal unit cell), $\gamma_h = 1{\cdot}492$. A comparison of the geometries in W-Li_2SiO_3 and the isostructural W-$LiSi_2N_3$ is informative [this has been given previously (O'Keeffe & Hyde, 1978)]. Here, however, there is a complicating factor: in contrast to the binary compounds and the ABX_2 compounds with $Pna2_1$ symmetry, Pauling's electrostatic valence rule is no longer exactly obeyed and some variation of bond length with bond strength is to be expected (Brown, 1977).

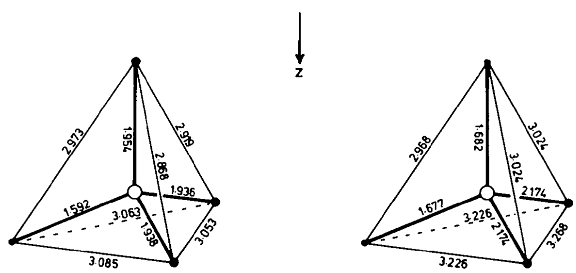


Fig. 10. Bond lengths and non-bonded distances (Å) in W-Li_2SiO_3. Small, filled circles are Si atoms; medium, filled circles are Li atoms; large, open circles are O atoms. The $O(1)Li_3Si$ tetrahedron is on the left, and the $O(2)Li_2Si_2$ tetrahedron on the right.

(*c*) Li_3PO_4 (*Keffer, Mighell, Mauer, Swanson & Block*, 1967)

In W-Li_3PO_4 there are three crystallographically distinct OLi_3P tetrahedra, and two distinct Li atoms in the unit cell. In comparing distances it is important to distinguish between Li(1) and Li(2). The length of the P–O bond parallel to **c** does not differ significantly from the lengths of the other P–O bonds: $l = 1{\cdot}54$ and $1{\cdot}55$ Å respectively (standard deviation $\simeq 0{\cdot}01$ Å). Of the Li(1)–O bonds, that parallel to **c** ($l = 2{\cdot}01$ Å) is definitely longer than the others ($l = 1{\cdot}91$, $1{\cdot}95$ and $1{\cdot}96$ Å). Of the Li(1)⋯Li(1) distances, that which is not normal to **c** ($d = 3{\cdot}02$ Å) is shorter than at least one of the other two, which are approximately normal to **c** [$d(\mathrm{Li}\cdots\mathrm{Li}) = 3{\cdot}03$ and $3{\cdot}08$ Å]. However, in this analysis we are clearly hampered by the limitation already mentioned; that, until recently at least, structures have only rather infrequently been determined with an accuracy sufficient for our purpose.

Further remarks on non-bonded interactions

It should be emphasized that, just as one replaces an interatomic interaction (bonding) potential by one number, a bond length, so the 'non-bonded radii' that we have used here replace 'non-bonded interaction' potentials. For the more electronegative elements such as Si, Ge, P, *etc.*, this appears to be a good approximation: variations in non-bonded distances of more than a few per cent are rare. On the other hand, for the more electropositive elements such as Li, Na, Be, *etc.*, it is our experience that variations in non-bonded distances are greater, so that a non-bonded 'radius' is less well defined. Doubtless this reflects a 'softer' interaction potential for these latter elements. Hill & Gibbs (1978) have recently analysed T–O–T configurations with T = Al, Si and P and suggest that $T\cdots T$ interactions may become progressively more important in the sequence Al, Si, P.

We have remarked that in wurtzites containing first-row anions there is stress arising from non-bonded interactions. The stress produces strain, manifested as stretched bonds, shortened non-bonded distances and changed X–A–X bond angles. As a rough, first approximation we assumed a linear relationship between the strains [*i.e.* equations (5) and (6)]. There is no *a priori* reason to expect this proportionality (measured by a constant value of the parameter p) to hold over a wide range, either of elements or of distances. The availability of realistic interatomic potentials would make it possible to predict whether formation of four-membered rings, with an increase in the number of (longer) bonds and (shorter) non-bonded distances (as in $B1$), would be favoured over 'one-angle' contacts (as in the six-membered rings of $B3$ and $B4$). It is our belief that this will be a more fruitful approach to the understanding of the relative stability of different structure types than current theories utilizing concepts such as radius ratio and/or ionicity.

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Structure Cristalline de $Pb_3Mn_7O_{15}$

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The structure of $Pb_3Mn_7O_{15}$ has been determined and refined to an R factor of 0·047 from single-crystal data. The unit-cell parameters are: $a = 17{\cdot}28$ (1), $b = 9{\cdot}98$ (1), $c = 13{\cdot}55$ (1) Å, $Z = 8$, the space group is $Cmc2_1$. The structure can be described as a succession of layers of octahedra perpendicular to the c axis containing randomly distributed Mn^{III} and Mn^{IV} atoms. The Pb atoms constitute hexagonal close packing with O. The electrostatic repulsion due to the lone pairs gives to half of them fourfold coordination analogous to that observed in the massicot variety of PbO and to the others sixfold coordination never before observed.

Introduction

Le système ternaire PbO—Mn_2O_3—MnO_2 n'avait fait l'objet d'aucune étude systématique avant celle entreprise récemment au laboratoire par Latourrette, Devalette, Guillen & Fouassier (1978).

Un seul composé de ce système avait été préparé antérieurement par Al'shin, Zorin, Drobyshev &