Cristobalites and Topologically-Related Structures

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Three related, regularly concerted patterns of rotations of BX_4 tetrahedra about their $\bar{4}$ axes, and within the $Fd3m$ unit cells of the $C9$ (BX_2) and 'filled' $C9$ (ABX_2) structure types, produce three series of structures. All [except 'unfilled' (III)] have known representatives. The limiting structures (rotation angle $\varphi = 45°$) have standard X arrays: (I) = c.c.p. (or b.c.c.), (II) = 'rutile-like', (III) = h.c.p. Pattern (I) is obtained in high cristobalite but, in real crystals, in three equivalent orientations. It is possible to construct coherent, unstrained 'composition planes' between these twin domains, some of which are elements of low cristobalite [sequence (II)] or sequence (III). A simple mechanism is proposed for the $\alpha \rightleftarrows \beta$ cristobalite transformation. It emphasizes that α is mimetically twinned β. In BX_2 the B–X–B bond angle (and hence φ) appears to be determined by non-bonded B–B repulsion.

Structures based on networks of corner-connected tetrahedra of anions coordinating a central cation are among the more important in crystal chemistry. The

(a)

(b)

Fig. 1. Two projections of the $C9$ structure, BX_2: (*a*) on (001), (*b*) on (110) of the cubic, $Fd3m$ unit cell. Small filled circles are B atoms, large open circles are X atoms. Heights are in multiples of $c/8$ or $a[1\bar{1}0]/8$.

almost endless variety of silicate structures is testimony to the many ways that tetrahedra can be thus linked.

This paper is concerned with one of the simplest of such networks, and the structures based on it. The starting point is the $C9$ structure originally proposed (Wyckoff, 1925), but now known to be incorrect, for high cristobalite. It belongs to space group $Fd3m$: BX_2, with B in 8(*a*) and X in 16(*c*). Two projections are shown in Fig. 1.

Although the anti-arrangement does occur as the NHg_2^+ framework in Millon's base, $Hg_2NOH.2H_2O$, the $C9$ type is not a likely structure for SiO_2. It would contain collinear Si–O–Si bonds whereas, although these are not unknown, bond angles of less than 180° are usual in silica polymorphs, *e.g.* 144° in quartz (Smith & Alexander, 1962; Young & Post, 1962), and are to be expected for partly covalent bonds. Indeed, the concern has been why this angle is so much larger than the tetrahedral angle of 109·47° (Glidewell, 1973). The same problems arise with the 'filled' $C9$ type, in which additional A cations occupy the 8(*b*) sites so that the composition is ABX_2. This was earlier, and also erroneously, reported to be the structure of $KAlO_2$ and $KFeO_2$ (Barth, 1935). In it the A cation is coordinated by 12 X ions at the vertices of a truncated tetrahedron. (The AX_2 arrangement is that in the cubic Friauf–Laves phase $MgCu_2$.)

We will examine some of the ways in which $C9$ and its 'filled' derivative may be deformed by decreasing the B–X–B bond angle without distorting the BX_4 tetrahedra or breaking any bonds: those topological operations which partly collapse the structure and decrease the bond angles uniformly.

In $C9$ the collinear B–X–B bonds lie along $\langle 111 \rangle$: decreasing the B–X–B angles uniformly corresponds to rotating the tetrahedra about axes equally inclined to
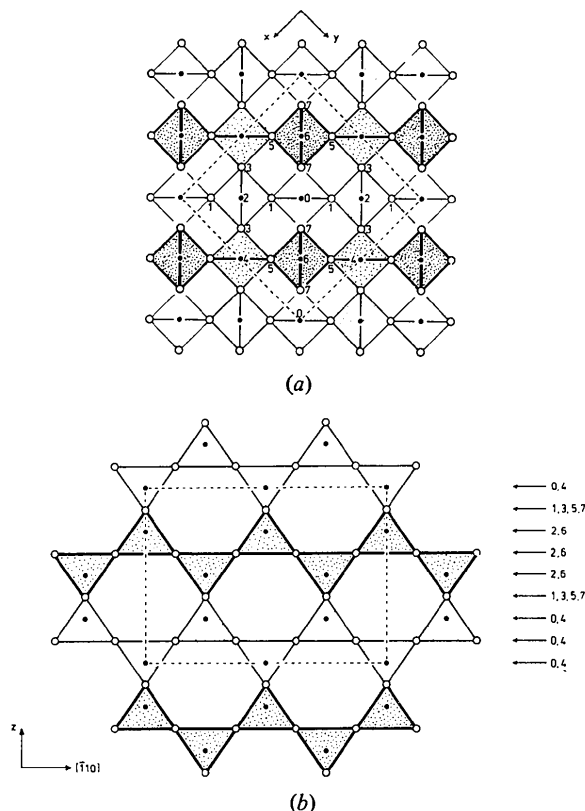
all four $\langle 111 \rangle$ axes, *i.e.* about $\langle 100 \rangle$: rotations of BX_4 tetrahedra about their $\bar{4}$ axes. Since the tetrahedra are corner-connected, rotation of one imposes restraints on possible rotations of its neighbors. Consider rotation about one axis only, say **c**: clockwise rotation of one tetrahedron permits only counter-clockwise rotation of the four connected tetrahedra. The pattern of (clockwise) rotations is that of Fig. 2(*b*), in which the rotation axes are indicated by arrows and only the positions of the tetrahedron centres are shown. As shown below, this pattern of rotations generates what is probably the correct structure of high cristobalite, and a number of related structures.

With two (non-collinear) rotation axes the situation is more complicated, and consideration is restricted to patterns with periodicities no greater than that of the *C*9 unit cell, every tetrahedron being rotated through the same angle. The first rotation axis is arbitrarily chosen as [001], passing through the tetrahedron center at $0,\frac{1}{2},\frac{1}{2}$ [origin at $\bar{4}3m$; *i.e.* at the centers of the (100) projections of the *C*9 structure in Fig. 2]. This tetrahedron has neighbors in the plane above it, centred at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ and $\frac{1}{4},\frac{3}{4},\frac{3}{4}$, and below it at $-\frac{1}{4},\frac{1}{4},\frac{3}{4}$ and $-\frac{1}{4},\frac{3}{4},\frac{1}{4}$. There are four possibilities for rotation axes in the planes parallel to (100) at these two levels [shown in Fig. 2(*b*),(*c*),(*d*),(*e*)]. In order of those at $x/a = -\frac{1}{4}$, then 0, and then $+\frac{1}{4}$ they are

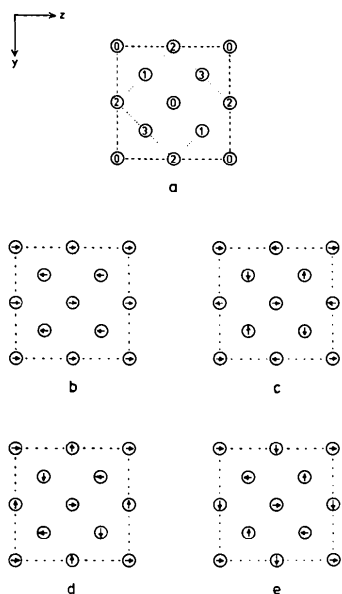| (I) | [00$\bar{1}$], [001], [00$\bar{1}$]; |
(II)	[0$\bar{1}$0], [001], [010];
(III)	[00$\bar{1}$], [001], [010];
(IV)	[0$\bar{1}$0], [001], [00$\bar{1}$].

Fig. 2. The possible patterns of rotation axes within the *Fd*3*m* cell of the *C*9 structure (projected along a). Only the centres of the tetrahedra, *i.e.* the B atoms, are shown. (*a*) Heights in multiples of *a*/4; rotation sequences (I) (*b*), (II) (*c*), (III) (*d*), (IV) (*e*).
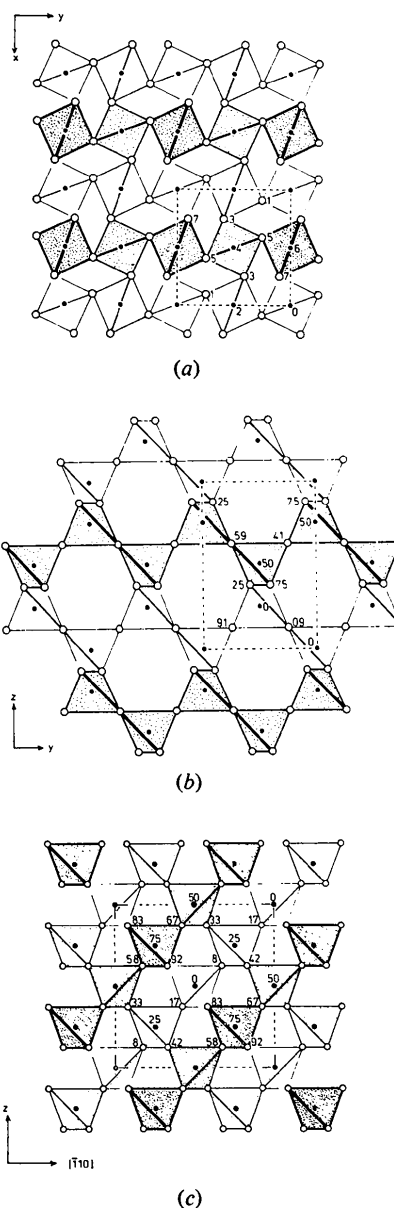

Fig. 3. Three projections of the β-cristobalite structure (after Leadbetter *et al.*, 1973), $\varphi \simeq 20°$: (*a*) on (001), (*b*) on (100), (*c*) on (110) of the *I*$\bar{4}$2*d* unit cell. Heights are in multiples of $0.01 \times c$, *a*, and *a*[110] respectively.

These are the only possibilities since there is only one sense of rotation axes at the next levels ($\pm\frac{1}{2}$) compatible with the previously determined directions of rotation at $\pm\frac{1}{4}$ (*i.e.* $\mp\frac{1}{4}$). Sequences (III) and (IV) are related as mirror images, and thus produce equivalent structures. Hence there are just three patterns of rotation axes: (I), (II) and (III) [Fig. 2(*b*), (*c*) and (*d*)]. A surprisingly large number of structure types can be simply related to each other by applying these rotation patterns to *C*9 and 'filled' *C*9.

Sequence (I): high cristobalite *etc.*

Since the work of Wyckoff (1925) there have been a number of investigations of the structure of high cristobalite. They are summarized in recent papers by Peacor (1973), by Leadbetter, Smith & Wright (1973), and by Wright & Leadbetter (1975), all of whom agree with much of the earlier work in finding that the space group of the *average* structure is $Fd3m$, with Si in 8(a), $\frac{1}{6}$O in 96(h) (*i.e.* 16 O atoms distributed over the 96 sites) with $x = +0.08$ (an average of the 300°C results of Peacor and the 310°C results of Leadbetter *et al.*).

The only plausible interpretation of this oxygen distribution, suggested by both sets of workers, is in terms of short-range order in domains of lower symmetry. In each domain a subset of one sixth of the 96(h) sites is occupied, and domains of each of the six possible subsets occur with equal probability. Within each domain almost regular tetrahedral groups of O occur around each Si atom. However, there must be strain at some domain boundaries at least (see below), and this is manifest in the large 'temperature factors' found in the structure analyses.

The subset of 16 positions of 96(h) in $Fd3m$ is a set of $F\overline{4}d2$ [not $Fdd2$, as stated by Leadbetter *et al.* (1973) and Wright & Leadbetter (1975)] or, choosing the more conventional body-centered unit cell of the same symmetry (tetragonal) and half the volume, the set 8(d) of $I\overline{4}2d$. In this smaller cell Si is in 4(a) and the O in 8(d) has $x = -0.09$. [In $I\overline{4}2d$ the parameter $x = (2x' - \frac{1}{4})$, where x' is the 96(h) parameter in $Fd3m$.] In Fig. 3 this structure is shown in three projections (analogous to those of the $C9$ type in Fig. 1). It is the structure of Leadbetter *et al.* (1973) and Wright & Leadbetter (1975).

A comparison of Figs. 1(a) and 3(a) shows that the true high cristobalite structure is derived from $C9$ by rotating SiO$_4$ tetrahedra about the axes shown in Fig. 2(b). The rotation angle φ and the O parameter x are simply related by

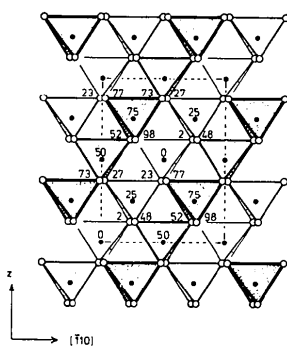$$\varphi = -\tan^{-1}(4x) . \tag{1}$$

Fig. 4. The almost completely collapsed $I\overline{4}2d$ BX$_2$ structure, $\varphi = 40°$, with regular tetrahedra, projected on (110). The anions are close to cubic close packing. Compare Fig. 3(c). (In ABX$_2$ the A cations superimpose on B, with heights differing by 50.)

If the tetrahedra remain regular c remains constant, but the axial ratio of the $I\overline{4}2d$ unit cell in each domain will differ from $\sqrt{2}$ (its value in the $C9$ structure):

$$c/a = \sqrt{2} \sec \varphi = \sqrt{(2 + 32x^2)} . \tag{2}$$

Thus, for $x = -0.09$, $\varphi = 19.80°$ and $c/a = 1.063\sqrt{2}$. The experimental value is $c/a = \sqrt{2}$, presumably because of the stress associated with the coexistence of the differently oriented domains and/or because the tetrahedra are distorted. The Si–O–Si bond angle is given by

$$\theta = \cos^{-1}[(1 - 4\cos^2\varphi)/3]$$
$$= \cos^{-1}(16x^2 - 3)/(48x^2 + 3) \tag{3}$$

so that $\theta = 147.89°$ for $x = -0.09$, $\varphi = 19.80°$. {Alternatively, for $c/a = \sqrt{2}$, $\theta = \cos^{-1}[(32x^2 - 3)/(32x^2 + 3)] = 147.24°$. (Leadbetter *et al.* deduced that $\theta = 146.7 \pm 0.3°$.)} Either value is in much better accord with the angle found in other forms of silica, *e.g.* 146.8° in low cristobalite (Dollase, 1965), than the 180° of the $C9$ structure.

Attempts to account for this particular value of the Si–O–Si bond angle are inevitable; as an alternative to specific valence forces one might consider the possibility that it is a consequence of repulsion between next-nearest-neighbor O ions. For regular tetrahedra the shortest O–O distance (a tetrahedron edge) is

$$\alpha = a\sqrt{(4x^2 + \tfrac{1}{4})} = c/\sqrt{8} . \tag{4}$$

When $|x| < (\sqrt{5} - 1)/8 = 0.155$ the next-nearest distance is

$$\beta = a\sqrt{(12x^2 - 2|x| + \tfrac{3}{4})} = c\sqrt{[\tfrac{3}{8} - |x|/(1 + 16x^2)]} \tag{5a}$$

and, when $|x| > (\sqrt{5} - 1)/8$, it is

$$\beta' = a\sqrt{(4x^2 - 4|x| + \tfrac{5}{4})}$$
$$= c\sqrt{[\tfrac{1}{8} + (1 - 4|x|)/(32x^2 + 2)]} . \tag{5b}$$

For the pseudo-cubic $Fd3m$ cell Peacor (1973) found $a' = 7.17$ Å which gives, for the $I\overline{4}2d$ cell, $c = 7.17$ Å or $a = 7.17/\sqrt{2} = 5.07$ Å. With equations (4) and (5) and $x = -0.09$ the c value yields $\alpha = 2.53$, $\beta = 3.90$ Å ($\beta' = 4.58$ Å), and the a value $\alpha = 2.69$, $\beta = 4.14$ Å ($\beta' = 4.87$ Å). Clearly the β values are far too large for repulsion between O atoms of adjacent tetrahedra to be the factor determining the Si–O–Si bond angle. [The α values are close to those generally found in silicates, *e.g.* 2.59 to 2.65 Å in low cristobalite at 230°C and, in high cristobalite, tetrahedron edge lengths $\alpha = 2.606$ ($\times 4$), 2.677 ($\times 2$) Å at 300°C (Peacor, 1973).]

If φ is increased to its maximum value and the tetrahedra remain regular (when $\beta' = \alpha$, $x = \pm\frac{1}{4}$, $\varphi = \mp 45°$ and $c/a = 2$) the anion array becomes that of cubic close packing (with the silicons in one quarter of the tetrahedral interstices) (Fig. 4). The structure of α-ZnCl$_2$ (Brehler, 1961) is very close to this: it has the same space group ($I\overline{4}2d$) and $x \simeq -0.25$, but $c/a = 1.917$ instead of 2.000, *i.e.* the tetrahedra are slightly compressed along **c**. (If the tetrahedra are regular then $c/a = 1.917$ corresponds to $x = -0.23$, $\varphi = 42.5°$.)

If the axial ratio is reduced to $\sqrt{2}$ by compressing still more along c, i.e. if it remains unchanged during the rotation of the tetrahedra, then (at $\varphi = 45°$) the anion array is body-centered cubic (although the symmetry is still tetragonal if the cation array is included). This provides an elegant transformation path from the anion array in $C9$ (the T complex; Fisher, Burzlaff, Hellner & Donnay, 1973) to the b.c.c. array (I_2), with no change in the shape of the unit cell. The resulting structure is close to those of the high-pressure polymorphs $GeS_2(II)$ and $SiS_2(II)$ (Prewitt & Young, 1965). These also have the same space group, x values are close to $\frac{1}{4}$, being 0·2387 and 0·2272 respectively (corresponding to $\varphi = 43·7$, 42·3°), and axial ratios fairly close to $\sqrt{2}$: $c/(\sqrt{2}a) = 1·18$, 1·14.

Starting with the 'filled' $C9$ structure the same operation again produces structures with space group $I\bar{4}2d$, the A atoms being in 4(b). The many chalcopyrite compounds exemplify the almost fully-collapsed structure, approaching cubic close packing of the anions. In chalcopyrite ($CuFeS_2$) itself $c/a = 1·971$ and $x = -0·243$ (Hall & Stewart, 1973), which corresponds to perfectly regular BX_4 tetrahedra: equations (1) and (2) give $x = -0·2427$ for $c/a = 1·971$ (and $\varphi = 44·2°$).

If A = B the structure is fully collapsed and is $B3$, i.e. the zinc blende (sphalerite) type. A disparity between the sizes of the A and B ions naturally results in lower φ values, as in $CdGeAs_2$ (Pfister, 1958) which, with $c/a = 1·889$ and $x = -0·215$ (i.e. $\varphi = 41°$), is slightly closer to the 'filled' $C9$ type, but still with regular BX_4 tetrahedra. The structure of γ-$LiBO_2$ (Marezio & Remeika, 1966) lies between all three extremes: 'filled' $C9$, c.c.p. anions and b.c.c. anions: $x = 0·157$, corresponding to $\varphi = 32·1°$ for regular tetrahedra and an

ideal ratio $c/a = 1·670$, compared with the observed 1·552. The structure of $CaGeN_2$ (Maunaye, Guyader, Laurent & Lang, 1971) and β-$KCoO_2$ (Delmas, Foussier & Hagenmuller, 1975) may also be derived from 'filled' $C9$ by rotating the tetrahedra (approximately 30°) but now the axial ratio is slightly less than $\sqrt{2}$, so that the tetrahedra are rather severely compressed along c, and much more like those in a b.c.c. array.

Data for $I\bar{4}2d$ structures are listed in Table 1 and plotted as c/a versus the anion parameter x in Fig. 5. [For compounds with the chalcopyrite structure the smaller cations B are placed in 4(a), and the larger cations A in 4(b) of $I\bar{4}2d$, in order to facilitate comparison with high cristobalite. Following Pauling & Brockway (1932) most authors interchange these two sets: the anion parameter is then $x'' = x - \frac{1}{2}$. Negative values of x are consistently used here.] Except for $CaGeN_2$ and β-$KCoO_2$, all structures fall in the range $\sqrt{(32x^2 + 2)} \geq c/a \geq \sqrt{2}$, i.e. from regular BX_4 tetrahedra to $a' = c'$ for the large, pseudo-cubic, $F\bar{4}d2$ unit cell ($Fd3m$ when $\varphi = 0°$). β-$KCoO_2$ and $CaGeN_2$ are exceptional: the A cations achieve their (quite common) bisdisphenoid coordination. The coordination polyhedron is actually AX_{4+4}, the two A–X distances being 2·71 and 3·17 Å in β-$KCoO_2$ (the more compressed) and 2·44 and 3·14 Å in $CaGeN_2$. (By reducing c/a a chain of three edge-shared tetrahedra along the c direction is compressed towards a bisdisphenoid.) The values of φ are 27 and 33° respectively. If we take an average $\bar{\varphi} = 30°$ then a fairly regular bisdisphenoid coordination of the A cation (eight equal A–X distances) requires a severely reduced axial ratio, $c/a = 0·92$, instead of the 'ideal' $c/a = 1·63$ (for $\bar{\varphi} = 30°$). The extreme alternatives are therefore regular tetrahedra and $c/a = 1·63$, or 'regular' bis-

Table 1. *Data for some structures related to the high cristobalite ($I\bar{4}2d$) type*

	a	c	c/a	$-x$	Reference
SiO_2	$7·17/\sqrt{2}$	7·17	1·414	0·09	Peacor (1973)
GeS_2	5·480	9·143	1·668	0·227	Prewitt & Young (1965)
SiS_2	5·420	8·718	1·608	0·239	Prewitt & Young (1965)
α-$ZnCl_2$	5·40	10·35	1·917	0·25†	Brehler (1961)
*$BeSO_4$	4·49	6·90	1·537	0·128	Grund (1955)
*BPO_4	4·332	6·640	1·533	0·138	Schulze (1934)
*$GaPO_4$	5·06	7·16	1·415	?	Mooney, Kissinger & Perloff (1954)
*$BAsO_4$	4·458	6·796	1·524	0·160	Schulze (1934)
*$InPS_4$	5·60	9·02	1·611	0·192	Carpentier et al. (1970)
β-$KCoO_2$	5·71	7·29	1·277	0·13	Delmas et al. (1975)
γ-$LiBO_2$	4·196	6·511	1·552	0·157	Marezio & Remeika (1966)
$CaGeN_2$	5·426	7·154	1·318	0·164	Maunaye et al. (1971)
$MgSiP_2$	5·721	10·095	1·765	?	Springthorpe & Harrison (1969)
$CdSiP_2$	5·680	10·431	1·836	0·213	Abrahams & Bernstein (1971)
$CdGeAs_2$	5·942	11·224	1·889	0·215	Pfister (1958)
$CdGeP_2$	5·740	10·775	1·877	0·217	Grigorovici, Mǎnǎlilǎ & Vaipolin (1968)
$ZnSiP_2$	5·398	10·434	1·933	0·231	Abrahams & Bernstein (1970)
$ZnSiAs_2$	5·60	10·88	1·943	0·234	Lind & Grant (1973)
$ZnGeP_2$	5·46	10·71	1·961	0·242	Lind & Grant (1973)
$CuFeS_2$	5·289	10·423	1·971	0·243	Hall & Stewart (1973)
$LiPN_2$	4·566	7·145	1·565	0·25†	Eckerlin, Langereis, Maak & Rabenau (1965)
‡ZnS	5·409	10·819/2	2·000/2	0·25	Skinner & Barton (1960)

* $B'B''X_4$, $I\bar{4}$ symmetry.
† Assumed.
‡ ABX_2 with A = B; parameters equivalent to completely collapsed high cristobalite. $F\bar{4}3m$ unit cell with halved c axis.
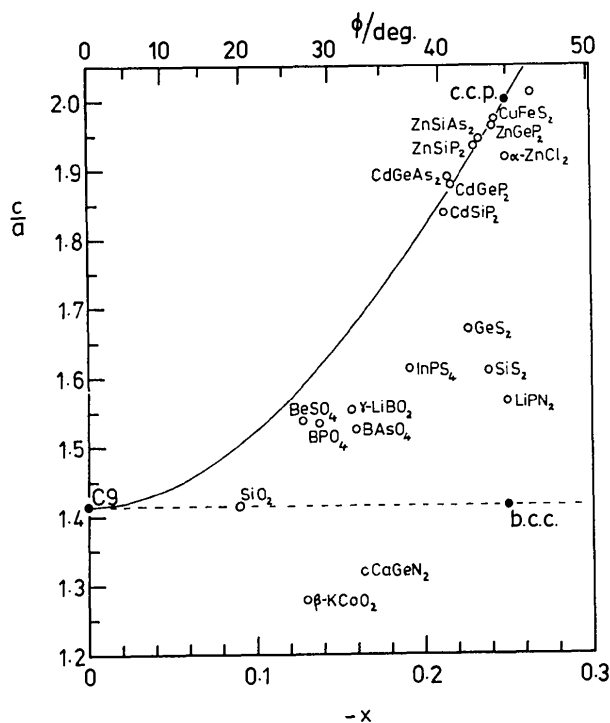
Fig. 5. Graph of c/a *versus* the anion parameter x for $I\bar{4}2d$ (β-cristobalite-related) structures. The full line is for regular BX_4 tetrahedra; the broken line for an unchanged unit-cell shape. The former ends with c.c.p. X atoms at the maximum rotation angle $\varphi = 45°$ ($x = -0.25$), and the latter with a b.c.c. array of X at $\varphi = 45°$.
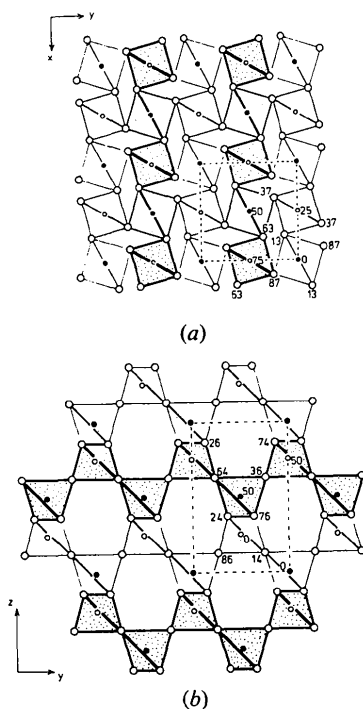

(a)

(b)

Fig. 6. The structure of BPO_4 in two projections analogous to Fig. 3(a) and (b). The small open circles are B; the small filled circles are P.

disphenoids and $c/a = 0.92$. A compromise is called for, and it is interesting that the mean of these values, $\langle c/a \rangle = 1.28$, is rather close to the observed ratios of 1.28 and 1.32 respectively for these two compounds.

A group of ternary compounds of lower symmetry has structures that are also simply related to those of this section. They contain an ordered array of two kinds of B ions: $B'B''X_4$ with space group $I\bar{4}$. $BAsO_4$ and BPO_4 (Schulze, 1934) and $BeSO_4$ (Grund, 1955) are examples (Fig. 6). The anion parameters x in $I\bar{4}$ and in $I\bar{4}2d$ are equivalent, and so equation (1) now gives a mean rotation angle $\bar{\varphi}$. $InPS_4$ (Carpentier, Diehl & Nitsche, 1970) is another member of this group of $I\bar{4}$ structures and, at first sight, appears to be one in which collapse has proceeded *beyond* the stage of c.c.p. anions. However, it is clear that the P atoms have been incorrectly placed in $2(d)$; they should be in $2(c)$. The correct x parameter for the anions is then 0.192 (instead of 0.308) and the rotation angle $\bar{\varphi} = 37.5°$ (instead of 50.9°). It is almost completely collapsed; a ternary analogue of α-$ZnCl_2$, as the authors point out. Its axial ratio $c/a = 1.611$ is fairly close to the ideal value of 1.783 for $x = 0.192$. Data for all these compounds are included in Fig. 5.

In principle, ordering of two types of A ions is also possible: $A'A''B'B''X_4$ with space group $I\bar{4}$ and A',A'',B',B'' in positions $2(b)$, $2(d)$, $2(a)$ and $2(c)$ respectively, and X in $8(g)$. However, compounds that might be expected to have this structure either adopt the common stannite type of Cu_2FeSnS_4, with space group $I\bar{4}2m$, or that of Ag_2HgI_4 with space group $I\bar{4}$ and A' in the Hg sites, A'' and B' in the Ag sites, and B'' in the site unoccupied in Ag_2HgI_4.

BeF_2 has also been reported as having the high cristobalite structure (Brandenberger, 1932; Kirkina, Novoselova & Simanov, 1956). The following argument suggests that the cubic $Fd3m$ cell is again for an average structure. According to Brandenberger $a' = 6.67$ Å: for $C9$ the B–X distance is $\sqrt{3}a'/8$ so that, for BeF_2, one would calculate the Be–F distance as 1.44 Å. However, for tetrahedrally coordinated Be one expects a Be–F bond length of 1.555 Å (Shannon & Prewitt, 1969; Deganello, 1973; Vicat, Tranqui, Aléonard & Richard, 1974). It is therefore likely that the BeF_4 tetrahedra are rotated in the manner described above. To achieve a bond length of 1.555 Å in an $Fd3m$ pseudo-cell with $a' = 6.67$ Å a rotation of $\varphi = 26°$ is required. This corresponds to a Be–F–Be angle $\theta = 138°$ and, for regular tetrahedra, a tetragonal distortion of $c/(\sqrt{2}a) = 1.113$ ($I\bar{4}2d$ unit-cell parameters). [According to Kirkina *et al.* (1956) $a' = 6.78$ Å which, by the same argument, gives $\varphi = 23°$, $x = -0.107$, $\theta = 142.5°$ and $c/\sqrt{2}a = 1.088$.] The value is sensitive to the bond length assumed, so that these should be considered only as estimates. But it is noteworthy that Brandenberger (1932) also found evidence of a small tetragonal distortion of the $C9$ structure for BeF_2. A quite different argument, introduced later, suggests that the bond angle $\theta(Be–F–Be) \geq 127°$. The minimum value, in

turn, implies that $\varphi = 33°$, $x = -0.163$ and $c/(\sqrt{2}a) = 1.194$. These conclusions are in fair agreement: that $\varphi \simeq 30°$, $x \simeq -0.1_4$, $\theta \simeq 13_2°$ and $c/(\sqrt{2}a) \simeq 1.1$.

It is also tempting to speculate that the tetragonal form of PNO (which should be an analogue of SiO_2) has a structure closely related to that of high cristobalite. The cell edges are approximately double the size expected for the $C9$ structure (Baltkaula, Millers, Lodzina, Ozolins & Vaivads, 1969), presumably because of anion ordering. The value $c/(\sqrt{2}a) = 1.551$ is close to the axial ratio c/a in BPO_4 for example.

Sequence (II): low cristobalite etc.

The structure of low cristobalite is well established, with recent refinements by Dollase (1965) and Peacor (1973) being in good accord. The space group is again tetragonal, $P4_12_12$ or its enantiomorph $P4_32_12$, and $a = 4.98$, $c = 6.95$ Å: Si is in $4(a)$ with $x = 0.300$, O in $8(b)$ with $x = 0.239$, $y = 0.105$, $z = 0.179$. Three projections of the structure are shown in Fig. 7. A comparison of Fig. 7(a) with Fig. 1(a) shows that it is derived from $C9$ by rotating the tetrahedra about the set of axes in Fig. 2(c). At room temperature the magnitude of the rotation is somewhat greater than that in high cristobalite: $\varphi = 23.5°$ compared with $19.8°$ in high cristobalite at 305 °C. The Si–O–Si bond angle is approximately the same as in high cristobalite: $\theta = 146.4°$ at room temperature rising to $\theta = 149.4°$ at 230 °C (Peacor, 1973), compared with $\theta \simeq 147°$ for the high form at 305 °C.

As for high cristobalite, the parameters of the low cristobalite structure are completely determined by the angle φ, through which the tetrahedra are rotated (if these are also assumed to remain regular). For BX_2 with space group $P4_12_12$ one has

$$c/a = 2\sqrt{2}/(1 + \sec \varphi), \tag{6}$$

B in $4(a)$, with $x = (1 + \cos \varphi + \sin \varphi)/(4 + 4 \cos \varphi)$, (7)

X in $8(b)$, with
$$\left. \begin{array}{l} x = (\cos \varphi)/(2 + 2 \cos \varphi) \\ y = (\sin \varphi)/(2 + 2 \cos \varphi) \\ z = (1 + \tan \varphi)/8 \ . \end{array} \right\} \tag{8}$$

Also in terms of φ the B–X–B bond angle is

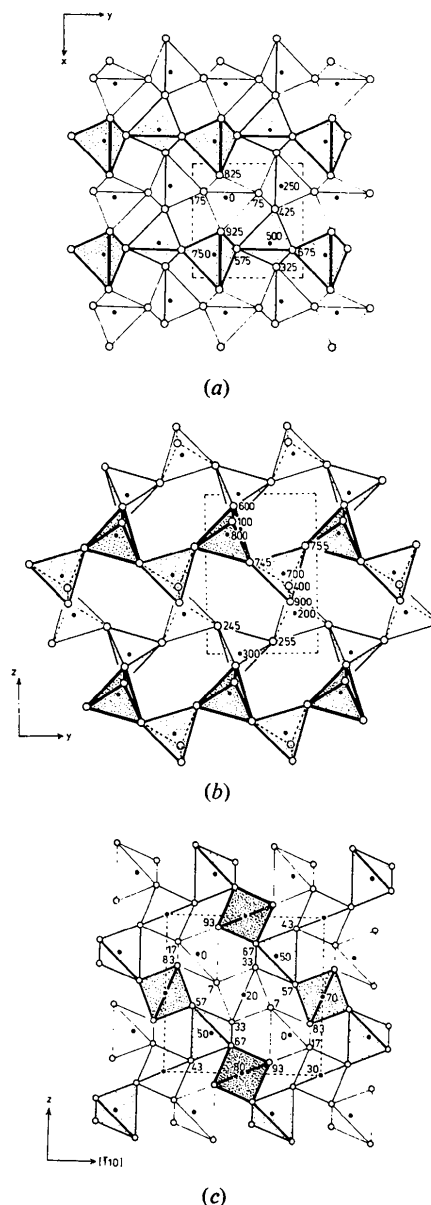$$\theta = \cos^{-1} [(1 - 2 \cos \varphi - 2 \cos^2 \varphi)/3] \ . \tag{9}$$

(a)

(b)

(c)

Fig. 7. The structure of α-cristobalite in three projections: (a) on (001), (b) on (100), (c) on (110) of the $P4_12_12$ unit cell. Heights are again in multiples of $0.01 \times$ the appropriate axis.

Table 2. Structures related to the low cristobalite ($P4_12_12$) type referred to a common unit cell

	a	c	c/a	x_A	x_B	x	y	z	Reference
Filled $C9$*	—	—	1.414	0.750	0.250	0.250	0.125	0.125	
SiO_2	4.978	6.948	1.396	—	0.300	0.240	0.103	0.178	Dollase (1965)
GeO_2	4.99	7.06	1.414	—	0.328	0.255	0.166	0.215	Seifert et al. (1971)
TiO_2, rutile†	4.594	5.916	1.288	—	(0.500)	0.195	0.195	0.250	
Ideal collapsed†			1.172	0.646	0.354	0.207	0.207	0.250	
β-BeO†	4.75	5.48	1.153	0.664	0.336	0.190	0.190	0.250	Smith et al. (1965)
γ-LiAlO$_2$	5.169	6.268	1.213	0.688	0.324	0.210	0.164	0.228	Marezio (1965a); Bertaut et al. (1965)
γ-NaFeO$_2$	5.56	7.30	1.313		n.d.				
γ-NaAlO$_2$	5.325	7.53	1.414		n.d.				Bertaut et al. (1965)
β-FNZn$_2$	5.86	6.53	1.114		n.d.				Marchand & Lang (1971)

* Correct space group $Fd3m$.
† Correct space group $P4_2mnm$.

After this work was completed an analysis of the low cristobalite structure by Fischer & Zemann (1975) appeared. It similarly describes the structure in terms of rotations of the tetrahedra of C9, and gives expressions for the atomic coordinates in terms of a rotation angle. Furthermore, and as we also deduced, it points out that second-nearest-neighbor O distances are too large to account for the observed value of θ (cf. high cristobalite, above).

If the rotation angle φ is increased until nearest and next-nearest-neighbor O distances are the same ($\alpha = \beta$) the resulting anion array is that in the structures of rutile and β-BeO (Fig. 8). The parameters are then $\varphi = 45°$, $\theta = \cos^{-1}(-\sqrt{2/3}) = 118 \cdot 13°$, $c/a = 4/(2 + \sqrt{2}) = 1 \cdot 172$, for the anions $x = y = (2 + 2\sqrt{2})^{-1} = 0 \cdot 207$ and $z = \frac{1}{4}$ and, for the cations, $x = (1 + \sqrt{2})/(4 + 2\sqrt{2}) = 0 \cdot 354$.

A similar 'complete collapse' of the 'filled' C9 structure puts the A cation into tetrahedral coordination, with $x(A) = 1 - x(B) = 0 \cdot 646$. This is close to the structure of γ-LiAlO₂ (Bertaut, Delapalme, Bassi, Durif-Varambon & Joubert 1965; Marezio, 1965a). γ-NaFeO₂
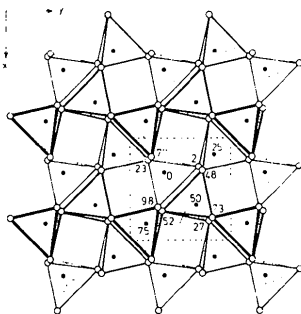

Fig. 8. The almost completely collapsed $P4_12_12$ BX₂ structure, $\varphi = 40°$, with regular tetrahedra. The X array is close to that in rutile and β-BeO (for which $\varphi = 45°$). Compare Fig. 7(a). (The A cations in the analogous ABX₂ structure have coordinates differing from those of B by $\Delta z = 0 \cdot 50c$.)
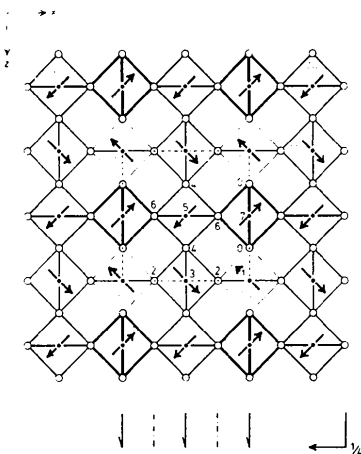

Fig. 9. Projection of the C9 structure together with rotation axes through tetrahedron centers, as in Fig. 2(c). Heights are in multiples of $b/8$ (but note that $\frac{3}{8}$ has been subtracted from the y coordinates of Fig. 2).

and γ-NaAlO₂ are presumed to have this structure also (Bertaut et al., 1965) and Zn₂NF probably has the anti-structure (Marchand & Lang, 1971). In these compounds, in contrast to those with the chalcopyrite structure (the high cristobalite analogues), the AX₄ and BX₄ tetrahedra have a common edge. Crystallographic data for them are collected in Table 2.

If A = B the collapsed structure has the higher-symmetry space group $P4_2/mnm$, and the c axis of the unit cell is halved. This is the structure of β-BeO (Smith, Cline & Austerman, 1965), for which data referred to the larger cell (with a doubled c axis) are also recorded in Table 2. Thus γ-LiAlO₂ etc. may be described as ordered derivatives of β-BeO. In Cu₃Se₂ (Morimoto & Koto, 1966) there are additional cations in tetrahedral coordination in the empty tunnels of the β-BeO type, and the c/a ratio is increased, from an ideal value of $0 \cdot 586$ ($0 \cdot 577$ in β-BeO) to $0 \cdot 668$.

The rutile structure has the same anion array, the same, smaller unit cell and higher symmetry (though a slightly-larger-than-ideal $c/a = 1 \cdot 288$ for the doubled cell) but, of course, the cations are octahedrally coordinated, their parameters being $x = \frac{1}{2}, z = \frac{1}{4}$, instead of $x = 0 \cdot 354, z = 0$. Silica transforms to the rutile-type structure at high pressure (Stišov & Belov, 1962; Chao, Fahey, Littler & Milton, 1962; Preisinger, 1962). This is considered below, and a mechanism proposed.

There are several ordered ternary compounds B'B''X₄ related to low cristobalite. The structures of two of them, AlPO₄ and the low-temperature form of GaPO₄, have been determined (Mooney, 1956). They have two different sizes of tetrahedra and their symmetry is orthorhombic, space group $C222_1$. The rotation angle φ is greater for GaPO₄ ($\theta = 135°$) than for AlPO₄ ($\theta = 145°$). As a consequence, the molar volume of the former is about 6% less than that of the latter, in spite of the fact that the Ga–O bond length is about 4% larger than the Al–O bond length. A 'filled' derivative of this structure is γ-Li₂BeSiO₄ which has the same symmetry (Howie & West, 1974).

A more complex compound with a related structure is Na₃AlBeSi₂O₈ (Kharitonov, Golyshev, Rastsvetaeva & Belov, 1974). It has only slightly lower symmetry, space group $P2_12_12$; the (AlBeSi₂)O₈ framework is very close to that of low cristobalite; and the Na ions fill three-quarters of the A sites. (Starting with 'filled' C9 the A ions are missing from $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $0,0,\frac{1}{2}$.)

Sequence (III): β-NaFeO₂ etc.

Fig. 9 shows the body-centered tetragonal subcell of C9 projected down the long axis, together with arrows (in the plane of the projection) indicating the rotation axes for the third sequence identified earlier [(III) and (IV), Fig. 2(d) and (e)].

When a rotation axis is reflected in a mirror (or glide) plane its orientation must be reflected and, as it represents the sense of the rotation, the direction of the arrow must also be reversed. With this in mind, it may

be verified that the space group is $Pna2_1$, and the projection in Fig. 9 is on (010) of the orthorhombic unit cell.

The rotation axes form two sets, one pointing along $\pm[101]$ and the other along $\pm[\bar{1}01]$. Initially, the angle between these two sets is 90°, but rotation of the tetrahedra by φ makes the cell edges a and c unequal, and the angle between the rotation axes $90° \pm \gamma$ where

$$\gamma = \tan^{-1}[(\sin \varphi \tan \varphi)/2] . \tag{10}$$

Hence, in this transformation a second operation is required by the first set of rotations: it corresponds to rotation of the tetrahedra by $\pm \gamma/2$ about axes orthogonal to the original set, $i.e.$ about [010]. This last rotation is rather small compared with the main one, $e.g.$ $\gamma/2 = 2.26°$ when $\varphi = 22.5°$ and $9.73°$ when $\varphi = 45°$. It is less than φ, very much less when φ is small.

For regular tetrahedra all the structural parameters are again completely specified in terms of φ:

$$\left. \begin{aligned} a/b &= \sqrt{(1 + \sec^2 \varphi)/2} \\ b/c &= \sqrt{(1 + \cos^2 \varphi)} \\ a/c &= (\cos \varphi + \sec \varphi)/2 , \end{aligned} \right\} \tag{11}$$

B in $4(a)$, with $\left. \begin{aligned} x &= (\tan \varphi)/(4 + 4 \sec^2 \varphi) \\ y &= \tfrac{1}{8} \\ z &= 0 , \end{aligned} \right\} \tag{12}$

A in $4(a)$, with $\left. \begin{aligned} x &= \tfrac{1}{2} - x(\text{B}) \\ y &= y(\text{B}) \\ z &= \tfrac{1}{2} - z(\text{B}) , \end{aligned} \right\} \tag{13}$

X(1) in $4(a)$, with $\left. \begin{aligned} x &= (\sin^2 \varphi)/(4 + 4 \cos^2 \varphi) \\ y &= (\tan \varphi)/8 \\ z &= (2 + \tan \varphi)/8 , \end{aligned} \right\} \tag{14}$

X(2) in $4(a)$, with $\left. \begin{aligned} x &= [1 + (\sin 2\varphi)/(1 + \cos^2 \varphi)]/4 \\ y &= (2 - \tan \varphi)/8 \\ z &= (8 - \tan \varphi)/8 . \end{aligned} \right\} \tag{15}$

Although there are two crystallographically distinct anions in the structure there is only one B–X–B angle

$$\theta = \cos^{-1}[(1 - 4 \cos^2 \varphi)/3] \tag{16}$$

[the same as for high cristobalite, equation (3)].

There appears to be no binary compound with this type of structure, but there are several ternaries ABX_2 derived from the 'filled' $C9$ type by the same transformation: crystallographic data, referred to a common origin and setting of the unit cell, are recorded in Table 3, together with the angle $\psi = \cos^{-1}(b^2/2ac)$. If the BX_4 tetrahedra were perfectly regular then ψ would be equal to the rotation angle φ (equation 11). It may be seen that ψ ranges from about 28 to almost 45°, approaching the latter value as the ratio of the radii of the two cations A and B (Shannon & Prewitt, 1969) becomes close to unity.

In Fig. 10 we show four different projections of a hypothetical ABX_2 compound with the $Pna2_1$ structure type and $\varphi = 22.5°$ (the middle of the accessible range). The type compound of this class is β-$NaFeO_2$, which has $\psi = 28.7°$. (It has $a/b = 0.775$ and $b/c = 1.361$, which

Table 3. Data for some ternary structures related to the 'Pna2₁ cristobalite' type

	a	b	c	φ^*	A $\times 10^3$			B			X(1) $\times 10^3$			X(2)			Reference
					x	y	z	x	y	z	x	y	z	x	y	z	
Filled $C9$				$0°$	500	125	500	0	125	500	0	0	250	250	250	0	
α-NaGaO₂	5·519	7·201	5·301	27·6	410	126	494	61	123	494	102	0	330	395	173	900	Vielhaber & Hoppe (1969)
β-NaFeO₂	5·672	7·316	5·377	28·8	400	135	500	75	128	500	100	0	385	380	125	900	Bertaut & Blum (1954)
MgSiN₂	5·279	6·476	4·992	37·3	417	100	500	70	130	500	125	0	356	417	150	905	David, Laurent & Lang (1970)
MnGeN₂	5·486	6·675	5·246	39·2	424	115	500	76	117	508	113	992	364	406	142	917	Winterberger, Guyader & Maunaye (1972)
MgGeN₂	5·494	6·611	5·168	39·7	417	125	508	83	125	494	125	0	371	417	125	893	David et al. (1970)
β-LiGaO₂	5·402	6·372	5·007	41·3	421	127	494	82	126	500	112	0	365	407	139	885	Marezio (1965b)
ZnGeN₂	5·454	6·441	5·194	42·9	417	120	500	83	125		115	0		405	140		Winterberger, Maunaye & Laurent (1973)
BeSiN₂	4·977	5·747	4·674	44·7													Eckerlin (1967)
Completely collapsed $C9$				45·0	417	125	500	83	125	375	125	0	375	417	125	875	

* $\psi = \cos^{-1}[b^2/(2ac)] \simeq \varphi$ (see text).

give ideal values of $\varphi = 32\cdot4$ and $22\cdot7°$. Clearly the tetrahedra are distorted.)

As for the previous sequences, the completely collapsed structure (Fig. 11) corresponds to $\varphi = 45°$, when the second-nearest-neighbor anion distances become equal to the tetrahedron edge length (in the ideal case of regular tetrahedra). The B–X–B bond angle θ is now equal to the tetrahedral angle, $\cos^{-1}(-\frac{1}{3}) = 109\cdot47°$, and the anion array is that of hexagonal close packing. If $A = B$ the ABX_2 structure is then the $B4$ type, e.g. of ZnO and BeO. Therefore an alternative description of the ABX_2 structures in this class, and especially of compounds such as $BeSiN_2$, is as superstructures of the $B4$ structure type (Parthé, 1964).

It might be noted that there is a series of ordered quaternary oxides $A_2B'B''O_4$ such as Na_2ZnSiO_4 that belong in this structural family (Joubert-Bettan, Lachenal, Bertaut & Parthé, 1969) although the ordering of B' and B'' reduces the symmetry to monoclinic (space group Pc).

Other ternaries related to the 'filled' $C9$ structure

$KAlO_2$ and $KFeO_2$, originally reported as 'filled' $C9$ with space group $Fd3m$, are now known to have lower symmetry. From X-ray powder diffraction patterns Pistorius & de Vries (1973) deduced that $KFeO_2$ was isotypic with $KGaO_2$, β-$NaGaO_2$ and $RbGaO_2$ (Vielhaber & Hoppe, 1969).

The latter authors report $KGaO_2$ as being orthorhombic, space group $Pbca$, with a unit cell approximately $1 \times 2 \times 2$ times the $Fd3m$ cell of $C9$. The structure, shown in Fig. 12, is rather complex. Its relation to the structure types described above is not immediately apparent. The GaO_2 framework consists of (001) layers of corner-connected tetrahedra $c/4$ wide. These are joined approximately as in low and high cristobalite in alternate layers, but there are additional distortions/rotations.

Further considerations

The texture of high cristobalite

Reflection twins that change the connectedness of the SiO_4 tetrahedra can be imagined; and partly coherent and/or strained coherent twin boundaries can also be constructed. But perfectly coherent boundaries which maintain the topology of the untwinned crystal are also possible: an example is given in Fig. 13. The boundaries X and Y are, not surprisingly, lamellae
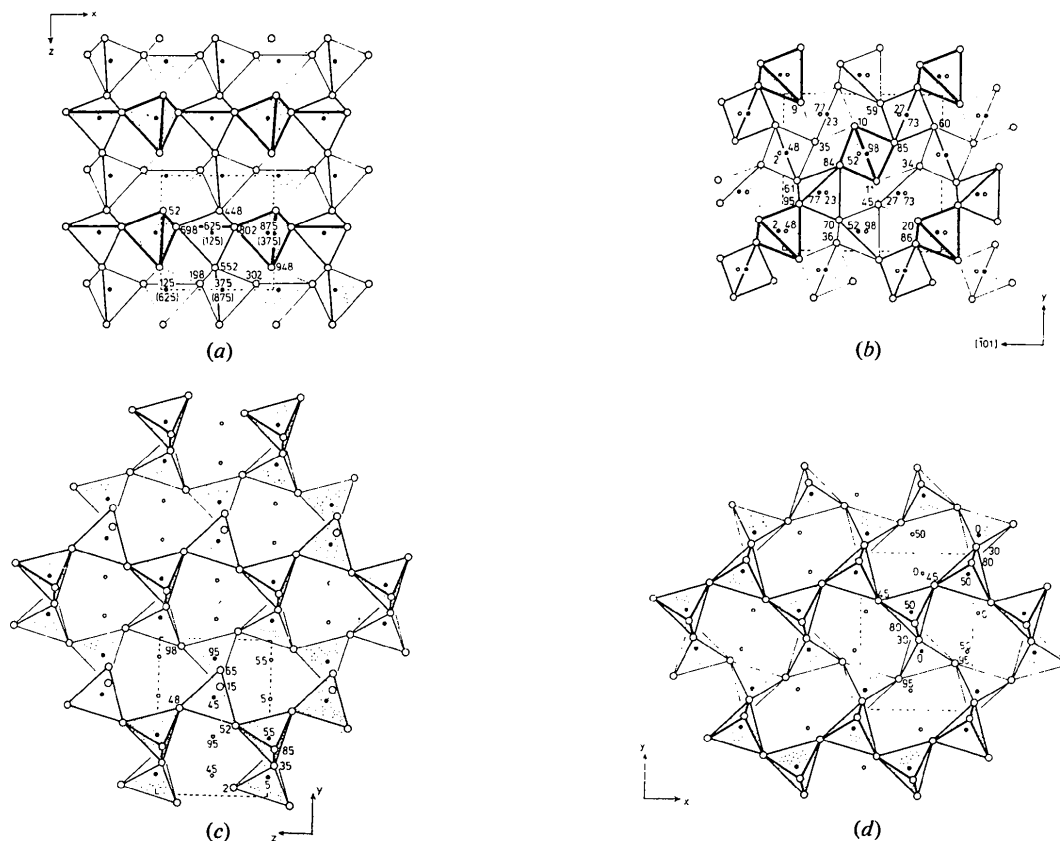

Fig. 10. Four projections of the partly collapsed $C9$ structure ($\varphi = 22\frac{1}{2}°$) with $Pna2_1$ symmetry: (a) on (010) [cf. Figs. 7(a) and 3(c)], (b) on (101) [cf. Figs. 7(c) and 3(a)], (c) on (100) and (d) on (001) [cf. both with Figs. 7(b) and 3(b)]. Small circles are B (filled) and A [empty; not shown in (a), where they superimpose on B, distance $b/2$].

of low cristobalite type. The boundary Z is of a new structure type: it contains next-nearest-neighbor O–O distances shorter than in the structures described above, but still slightly longer than nearest-neighbor distances (2·85 Å compared with the values of $\alpha = 2·53$ or 2·69 Å calculated above). Finally, it is also possible to replace the boundary Z with another of the same orientation (and between twins of the same orientation as in Fig. 13) but with the $Pna2_1$ structure type [sequence (III) above].

That such coherent twin boundaries may exist is made more plausible by the simple operation for interconverting high and low cristobalites, described next.

The relation between the high and low cristobalite structures, and a direct transformation mechanism between them

For a given value of φ or θ the volume per BX_2 unit is the same in the $I\bar{4}2d$ and $Pna2_1$ structures. For regular tetrahedra with unit edge length it is

$$V_1 = \sqrt{8}\cos^2\varphi_1 = (1 - 3\cos\theta_1)/\sqrt{2}. \qquad (17)$$

The corresponding volume for the $P4_12_12$ structure is

$$\begin{aligned}V_{11} &= \cos\varphi_{11}(1 + \cos\varphi_{11})^2/\sqrt{2} \\ &= (1 - 3\cos\theta_{11})[1 + (3 - 6\cos\theta_{11})^{1/2}]/(4\sqrt{2}). \qquad (18)\end{aligned}$$

The volume ratios are therefore

$$(V_{11}/V_1)_\varphi = (1 + \cos\varphi)^2/(4\cos\varphi) \quad \text{for equal } \varphi, \qquad (19)$$

and

$$(V_{11}/V_1)_\theta = [1 + (3 - 6\cos\theta)^{1/2}]/4 \quad \text{for equal } \theta. \qquad (20)$$

For a given bond angle $\theta \le 180°$, $(V_{11}/V_1)_\theta \le 1$; *i.e.* the low cristobalite structure is the denser, and therefore the stabler form at high pressure as well as at low tem-
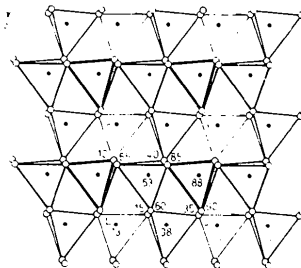

Fig. 11. The almost completely collapsed $Pna2_1$ structure, $\varphi = 40°$, with regular tetrahedra. The X array is almost hexagonally close packed. Compare Fig. 10(a).
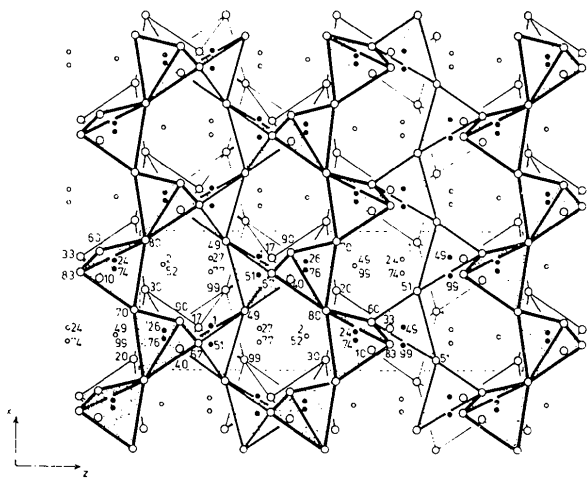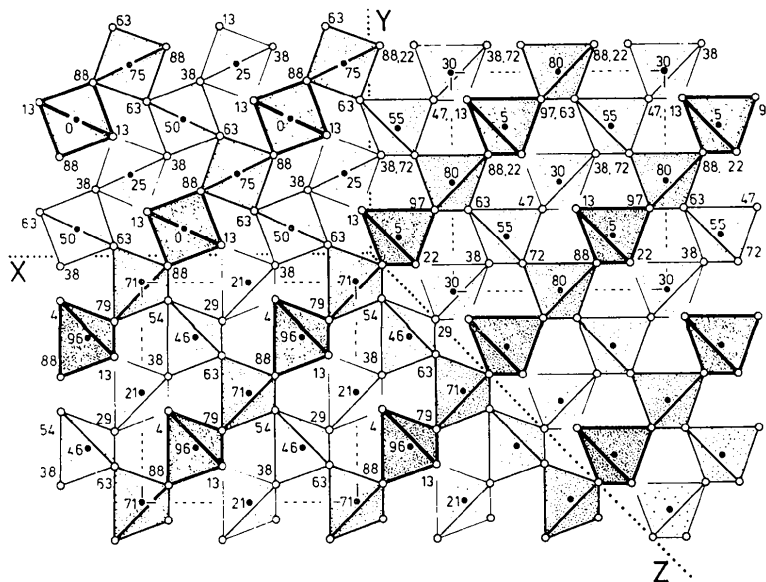

Fig. 12. The structure of $KGaO_2$ projected on (010).

Fig. 13. Domains of β-cristobalite in three different twin orientations, and with perfectly coherent boundaries X, Y, Z (shown dotted). Compare the structures along the composition planes X and Y with that of α-cristobalite in Fig. 7(c).

perature. However, for equal rotation angles the converse is true, $(V_{II}/V_{I})_{\varphi} \geq 1$.

A trivial consequence of the above analysis of sequences (I), (II), and (III) is that α- and β-cristobalites may readily be transformed into one another *via* the $C9$ structure type. But a more direct mechanism can also be envisaged. A comparison of Figs. 3(a), 3(c) and 7(c) [or Fig. 2(b) and (c)] shows that in both high and low cristobalite half the tetrahedra are rotated about parallel axes (actually one quarter about parallel axes and one quarter anti-parallel axes): the other half have their rotation axes at right angles, but it is not too difficult to see that these last may be brought into coincidence by another rotation; this time about a tetrahedral *edge*. Sequence (I) is [00$\bar{1}$], [001], [00$\bar{1}$]; sequence (II) is [0$\bar{1}$0], [001], [010]: the difference is [0$\bar{1}$1], 0, [011]. The two non-zero vectors are parallel to tetrahedron edges, *cf.* Fig. 1(a). These are marked by heavy arrows in Fig. 14, which shows the transformation from high cristobalite, on the right, to low cristobalite, on the left. Rotating the tetrahedra concerned about their edges has the effect of also rotating the central row of tetrahedra about their previous rotation axes (normal to the plane of the projection), but into the opposite sense: from clockwise to anticlockwise. Conversely the whole operation may be regarded as this latter rotation of only one quarter of the tetrahedra; the change in direction of the rotation axes of another half of the tetrahedra follows inevitably. In Fig. 14 the unit cells (doubled, pseudo-$Fd3m$ cells in each case) have been drawn the same size, in order to facilitate comparison of the two structures and to depict the transformation. In fact they are, of course, slightly different in size: that of α is $7\cdot0333 \times 7\cdot0333 \times 6\cdot9262$ Å, that of β is $7\cdot166 \times 7\cdot166 \times 7\cdot166$ Å. Thus there is also a change in shape and volume of this unit cell: $\Delta a_1 = \Delta a_2 = +1\cdot89$, $\Delta a_3 = +3\cdot47$, $\Delta V = +7\cdot4\%$, for $\alpha \rightarrow \beta$.

Put another way, it is obvious that low cristobalite is finely twinned high cristobalite, the composition

planes being parallel to $(001)_{\alpha}$ and the twin bands $c/4$ thick. [In Fig. 7(c) alternate (001) lamellae are oriented as in Fig. 3(a) and (c).]

Similarly Fig. 10(a) and (b) shows that the $Pna2_1$ structure is also finely twinned cristobalite: unit lamella of Fig. 3(a) alternating with *double* lamellae of Fig. 3(c). Consequently the $Pna2_1$ structure (and many other mimetic twins) can also be produced from high (or low) cristobalite by the operation relating the high and low forms, and depicted in Fig. 14.

The anion arrays in $C9$ and its completely collapsed variants

The various, related, rotation operation sequences described above provide elegant mechanisms for collapsing the $C9$ anion array into other prototype arrays: c.c.p., b.c.c., rutile type and h.c.p. The B–X–B bond angle θ is in each case determined by the rotation angle φ and the axial ratios. [The Bain relation between c.c.p. and b.c.c. is, of course, the difference between the two sequence (I) operations: maintaining regular tetrahedra or a metrically cubic cell.] They are relevant to a number of actual transformations/reactions in addition to those involving cristobalites.

The problem of why a given compound falls into one family (sequence) rather than another remains unsolved. (Since several compounds are polymorphic within this group the differences in free energy are probably rather small.) If we omit those compounds which have low values of φ [$\simeq C9$ structures, and therefore (I) $\simeq$ (II) $\simeq$ (III)] then we may note that sequence (I) covers, almost exclusively, compounds with anions *not* in the first row of the periodic table. The exceptions are SiO_2 with low φ, β-$KCoO_2$ and $CaGeN_2$ with strong preferences for bisdisphenoid coordination of the A cation, and γ-$LiBO_2$ and $LiPN_2$. On the other hand, sequences (II) and (III) occur almost exclusively for compounds with first-row anions, though there are a few exceptions for sequence (III) when $\varphi = 45°$ (hexag-
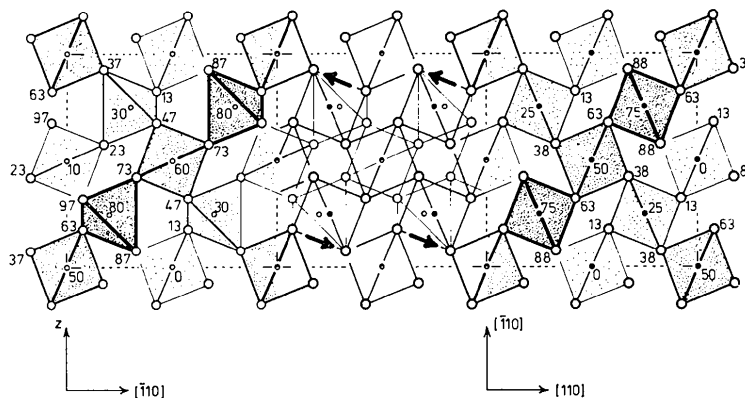

Fig. 14. A simple mechanism for the transformation $\beta \rightleftarrows \alpha$-cristobalite: α on the left [projected on (110) of $P4_12_12$], β on the right [projected on (001) of $I\bar{4}2d$]. In the centre both structures are drawn: α very lightly and β more heavily. The β form transforms to α if the tetrahedra centered at heights of $\pm\frac{1}{4}$ are rotated clockwise about their edges marked with heavy arrows. Simultaneously the central, horizontal row of tetrahedra rotates about axes normal to the plane of the drawing, and translates slightly. The small circles are Si in α (open) and β (filled); the large, open circles are O in α (light) and β (heavy).

onal ZnS type). It seems possible that, for ternary compounds, there may be some significant difference between the anion coordination of the A site, but we have not been able to decide on this.

The transformation cristobalite → rutile

The ideal 'completely collapsed' low cristobalite has an anion array identical with that in an 'ideal' rutile, in which the TiO_6 octahedra are perfectly regular. Clearly the transformation may be achieved by shifting the cations from 0·354, 0·354, 0 to 0·500, 0·500, −0·250, *i.e.* by 0·146, 0·146, −0·250 ≃ 1·7 Å through the face joining tetrahedron to octahedron (as shown by long thin arrows in the lower part of Fig. 15). A more elegant and more likely mechanism (shown in Fig. 15) is to shift the cation to 0·500, 0·500, 0; a displacement of 0·146, 0·146, 0 ≃ 1·0 Å into the tetrahedron edge. This will also cause small displacements of the O atoms (the affected tetrahedron edge must be lengthened – from l to $\sqrt{2}l$ – to provide the necessary space). This is achieved by changing the anion parameter from x to $x' = (\frac{1}{2} - x)$, which converts a pair of edge-shared tetrahedra to an octahedron. The anion shift vector is $(0·500 - 2x)$, $(0·500 - 2x)$, $0 \simeq 0·5$ Å, equivalent to the rotation of the square 'tunnels' from $+\omega$ to $-\omega$ (with respect to the a axes of the unit cell). Apart from satisfying space requirements this anion shift also improves the regularity of the anion coordination OTi_3, for better covalent bonding. This is still further improved by adjusting x' to 0·305 (from the 'ideal' value of 0·293), and by changing c/a from the ideal 1·17 to the actual (in rutile) 1·29. This improvement in the symmetry of the anion coordination is at the expense of some loss in the symmetry of the cation coordination: *regular* OTi_3 triangles and *regular* TiO_6 octahedra are not simultaneously possible in $P4_2/mnm$.

It would seem likely that during the transformation the cation and anion shifts would occur simultaneously, *e.g.* under pressure the Si in cristobalite move towards the tetrahedron edges as the O ions are compressed. In this connection the structure of TeO_2 (Leciejewicz, 1961) is interesting: it lies on this proposed transformation path. Although the low cristobalite anion array has not completely collapsed, the cation has moved through the tetrahedron edge and beyond it towards the position appropriate for rutile, and the anions have moved from x to $x' = 0·290$ (a mean of x and y in $P4_12_12$). The Te coordination is $2 + 2 + 2$, at 1·91, 2·09 and 2·89 Å. The last, long distance reflects the stereochemical activity of the lone pair of electrons on the Te, which possibly also renders the relation to the low cristobalite → rutile reaction path somewhat fortuitous.

The bond angle θ

Our particular concern has been to demonstrate how the $C9$ structure may deform by changing the B–X–B angle θ without distorting the tetrahedra. It varies

between 180 and 109°28′ or 118°8′ as φ changes from 0 to 45°. In the ternary compounds ABX_2 the available data suggest that θ and φ are related to the radius ratio for the two cations, r_A/r_B. This provides a geometrical constraint, relieved in some cases through distortion of the BX_4 tetrahedra; which also causes a change in the axial ratio(s). {Such a situation is reminiscent of that in high quartz where, for regular SiO_4 tetrahedra, θ is geometrically constrained to $\cos^{-1}[-(5 + 3\sqrt{3})/(6 + 3\sqrt{3})] = 155·6°$. In that case the only way in which θ may be modified to a more appropriate, lower value is by distorting the tetrahedra (*cf.* Megaw, 1973).}

In the case of the binaries, BX_2, a different explanation of the observed values of θ and φ must be sought. The main source of freedom is the flexibility of the $C9$ network: distortion of the tetrahedra is a relatively minor effect. The B–X–B angles are between the extremes. They vary from compound to compound; and it is natural to enquire into possible determining factors.

In terms of a point ion model, the angle θ will simply have that value which maximizes the Madelung constant, which is 180° (Fischer & Zemann, 1975). A decrease in Madelung energy attending a decrease in θ could be compensated by anion polarization, but then one would expect that θ would be less for SiO_2 than for GeO_2 whereas, in fact, the opposite is the case.

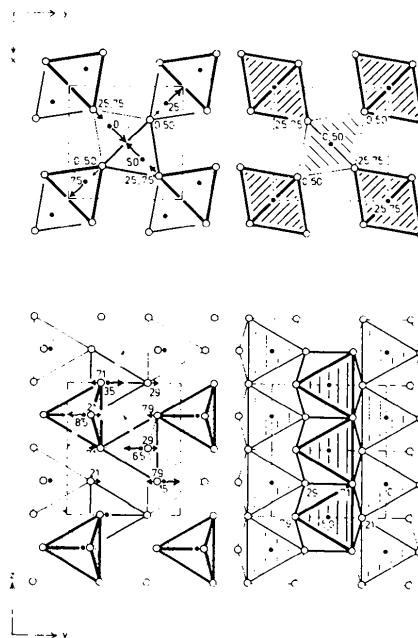On the other hand, starting with a covalent bond model – completely collapsed structures with $\theta =$

Fig. 15. A proposed mechanism for converting 'completely collapsed α-cristobalite' to stishovite (rutile-type SiO_2). On the left the cristobalite-related structure is shown (with axial directions) in two projections: the longer heavy arrows show the necessary cation shifts and the shorter arrows the minor anion shifts. The product structure is shown on the right, in identical orientations.

$109°28'$ – one could attempt to explain the measured, *larger* angles. We have already seen that repulsive forces between second-nearest-neighbor anions cannot be responsible for the increase. Another widespread (but not universally accepted) interpretation of the Si–O–Si angle in silicates invokes π-bonding between empty d orbitals on the cation and filled p orbitals on the anions (Cruickshank, 1961; Grimm & Dorner, 1975). However, this also leads to serious inconsistencies when the bond angles in different compounds are compared. In the low cristobalite form of GeO_2 $\theta = 128°$ (Seifert, Nowotny & Hauser, 1971) and in the quartz form $\theta = 130°$ (Smith & Isaacs, 1964), compared with $147°$ in SiO_2. In $AlPO_4$ the average atomic number of the cations is the same as in SiO_2, and $\theta = 145°$ is also about the same. In $GaPO_4$ $\theta = 135°$, intermediate between the values in SiO_2 and GeO_2, as is the average atomic number of the cations. If π-bonding were determining the bond angle one would expect a trend in just the opposite direction, *viz* θ increasing with atomic number. Furthermore, it is clearly unrealistic to invoke d-orbital participation in cristobalite analogues containing first-row cations (Be and B), which apparently fit into the general pattern, and are in no way anomalous.

A striking feature of the observations is the almost perfect constancy of $\theta(B-X-B)$ in different BX_2 structures with the same B and X. In the case of SiO_2 it is the same in high and in low cristobalite, in quartz ($144°$, Young & Post, 1962), and in silica glass ($147°$, Narten, 1972). Similar constancy is observed for Ge–O–Ge and other angles. Even more remarkably, this constancy persists in *molecules*, such as $(BH_3)_2O$, from a consideration of which Glidewell (1973) concluded that steric effects, rather than $p_\pi-d_\pi$ bonding, might be the determining factor. In a subsequent paper Glidewell (1975) took up the hypothesis of Bartell (1960), and derived a set of 'one-angle' radii for non-bonded interactions, on the assumption that $B'-X-B''$ angles could be limited by $B'-B''$ contacts (in the case that θ was greater than that expected for covalent bonding). These radii (intermediate between covalent and van der Waals radii) are remarkably successful in rationalizing *molecular* geometry (Bartell, 1960; Glidewell, 1975) and it is tempting to apply the same idea to nonmolecular crystals such as the cristobalites, in which the bond angle is not constrained by the topology.

We adopt Glidewell's (1975) radii, except that for Al which was determined only from the geometry of the $Al_2Cl_7^-$ ion, and which is clearly out of line with his other radii. The differences between 'one-angle' radii, R, of the first and the second-row elements in a column of the periodic table are fairly constant at about 0·30 Å; and we deduce $R(Al) = 1·63$ Å from Glidewell's $R(B) = 1·33$ Å and this fact. In addition, we adopt $R(As) = 1·58$ Å, equal to the radii of both neighbors in the same row (Ge and Se); and deduce $R(Ga) = 1·63$ Å from the observed value of θ in $GaPO_4$. The radii R are collected in Table 4.

Table 4. *'One-angle' radii (in Å) appropriate to* BB' *contact in* B–X–B *'configurations'*

From Glidewell (1975), except for values in parentheses for which see text.

Be	B	C	N	O	F
1·39	1·33	1·25	1·14	1·13	1·08
	Al	Si	P	S	Cl
	(1·63)	1·55	1·46	1·45	1·44
	Ga	Ge	As	Se	
	(1·63)	1·58	(1·58)	1·58	

We assume then that the $B'-X-B''$ angle is as close as possible to the tetrahedral angle, subject to the limitation of $B'-B''$ non-bonded repulsion [*i.e.* $\theta = 109°28'$ if $d(B'-B'') > R(B') + R(B'')$, and $\theta > 109°28'$ if the converse is true]. The value of θ may therefore be calculated with the 'one-angle' radii, R, of Table 4, and appropriate ionic radii, r, (Shannon & Prewitt, 1969) for the bonded distances $d(B'-X)$ and $d(B''-X)$.* In Table 5 'bond angles' calculated in this way are compared with those observed in the $C9$-derived structures discussed earlier. The agreement is impressive except, perhaps, for BeF_2 for which the structural parameters are still in considerable doubt and which might be expected to be the most nearly 'ionic' of the compounds discussed and thus most likely to have a value of θ greater than the minimum. It is hard to avoid the conclusion that the bond angles in all the other BX_2 crystals are determined by non-bonded cation–cation repulsions.

Table 5. *Observed (for references see text) bond angles in cristobalites compared with those calculated for nonbonded cation–cation contact*

	Observed	Calculated
Si—O–Si	147°	149°
Ge–O–Ge	128	129
B—O–P	133	138
Be–O–S	136	134
Al–O–P	145	143
B—O–As	128	134
Si–O–Al		143
Al–O–Al		139
Ga–O–P	135	
Be–F–Be	~140*	127

* Estimated from lattice constant.

SCF molecular-orbital calculations on the molecule H_4SiO_4 (Collins, Cruickshank & Breeze, 1972) indicate substantial occupation of the $3s$, $3p$ and $3d$ orbitals of Si, closely approximating bonding by a neutral silicon atom, and certainly quite different from an ionic picture of Si^{4+}. The substantial π-bonding by d electrons that this implies is, however, not inconsistent with our conclusion that the Si–O–Si angle is largely

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* A lack of precision in R and r results in an uncertainty of several degrees in the calculated value of θ: $\delta\theta \simeq \pm 4°$ for $\delta R \simeq \delta r \simeq \pm 0·01$ Å, and $\theta \simeq 140°$.

determined by Si–Si repulsion. Bartell (1960) has pointed out that it appears likely that bonds can be bent with only a modest expenditure of energy. Hence, bond lengths and energies are probably largely affected by π-bonding, but bond angles may still be determined by steric effects.

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