

The structural behaviour of tetrahedral framework compounds—a review

Part II. Framework structures

D. TAYLOR

15 Leigh Road, Congleton, Cheshire CW12 2EG

ABSTRACT. Tetrahedral framework compounds, as defined in this paper, generally exist as tilted and distorted versions of ideal fully expanded structures at room temperature and atmospheric pressure. How pressure, temperature, and composition (P , T , and X) affect the tilting and distortion is critically reviewed. It is shown that although the effects of P , T , and X on the cell parameters are broadly analogous, the underlying structural changes are generally different. An important, and frequently neglected thermal effect is the apparent shortening of the framework bonds by the anisotropic thermal motion of the framework oxygens. Tilting models of framework compounds are critically examined and their failure to match the observed structural behaviour is attributed to changes in tetrahedral distortion. For quartz it appears that during compression the change in tetrahedral distortion is virtually all angular (O-Si-O angles), whereas during thermal expansion the change in distortion is in the Si-O distances. Such behaviour may typify the behaviour of many other framework compounds but the structural data needed to establish this are lacking. The review is illustrated by reference to the quartz and cristobalite analogues; to the sodalite, leucite, nepheline, scapolite, and feldspar families; and to the nitrides and oxynitrides of silicon and germanium. It is concluded that our understanding of the structural behaviour of framework compounds is still superficial and that much theoretical and experimental work remains to be done.

A PHASE having a tetrahedral framework structure is defined, for the purposes of this paper, as an inorganic compound consisting of largely covalently bonded tetrahedra linked by sharing all their vertices with a shared vertex common to two or three tetrahedra. Such structures may consist entirely of framework tetrahedra or may contain atoms within cavities or channels of the structure. The atoms of the framework will be referred to as framework 'cations' and 'anions' and the atoms contained within the framework will be referred to as cavity 'ions', without any implication in this terminology relating to the nature of the bonding in the framework or between the framework and the cavity ions.

Part I of this review (Taylor, 1983) noted how the description of a framework structure in terms of tetrahedral units or assemblies, such as 'rings' or 'chains' of tetrahedra, may infer that such assemblies or sub-units dominate or control the structural behaviour rather than simply being an aid to grasping the nature of the structure. This representation of a framework structure in terms of linked MA_4 tetrahedra (M and A represent the framework cations and anions respectively) has led to the concept of a tightly bonded tetrahedron flexibly linked to neighbouring tetrahedra by a 'soft' or 'flexible' $M-A-M$ bond angle (Megaw, 1971). This, in turn, has led to the general observation that, at room temperature, framework structures exist as tilted and distorted versions of ideal fully expanded structures. This approach to framework structures and their structural behaviour has not been critically examined.

The first part of this review also examined the three main variables which affect framework structures: pressure, temperature, and composition (hereafter referred to as P , T , and X respectively) and concluded that they should not be considered as analogous in their effects on framework structures. Their effects on phase transitions in framework structures (Taylor, 1983) lends support to this view.

This paper concludes the review and considers the structural behaviour of framework compounds, in particular the relevance of tilting models, with reference to the silica minerals, sodalites, leucites, nephelines, scapolites, feldspars, and the nitrides and oxynitrides of silicon and germanium.

Framework structures without cavity ions: each shared vertex common to two tetrahedra

The main compounds having tetrahedral frameworks without cavity ions are the three common polymorphic crystalline forms of silica: quartz,

TABLE I. Regression data for the axial expansions of quartz in the temperature range 0 to 773 K and for the axial compressions of quartz in the pressure range 0 to 12 GPa

Z	y	y ₀	10 ⁵ a	10 ⁸ b	10 ¹¹ c	10 ¹⁴ d	SE	R
T (°C)	a, Å	4.91182	1.354(26)	1.18(7)	-1.70(43)	4.4(7)	0.0005	0.9997
T (°C)	c, Å	5.40375	0.733(12)	0.86(4)	-1.01(20)	2.4(4)	0.0003	0.9997
			10 ³ a	10 ⁴ b	10 ⁵ c			
P (GPa)	a, Å	4.9121	-9.36(38)	4.5(8)	-1.28(48)		0.0053	0.9987
P (GPa)	c, Å	5.4030	-66.4(3)	4.6(7)	-1.56(43)		0.0052	0.9920

cristobalite, and tridymite, and their analogues. The most important features of the structural behaviour of these three silica polymorphs, on heating, are their displacive transformations. Ultimately, at high temperatures, each polymorph achieves a fully expanded state: β -quartz, β -cristobalite, and hexagonal high-tridymite.

Quartz family. For this family the β -quartz structure is the aristotype (nomenclature of Megaw, 1973) and the fully expanded structure. The hettotypes of the quartz family may be partially collapsed structures, such as α -quartz, and may contain cavity ions. Tilting models have been developed for the quartz family and geometrical relationships between the cell parameters, the size of the tetrahedron and the tilt angle, assuming regular tetrahedra, were reported independently by Taylor (1972), Megaw (1973), and Grimm and Dorner (1975). Grimm and Dorner (1975) also gave an equation for the calculation of the tilt angle of α -quartz in the presence of distorted tetrahedra, but their equation requires knowledge of the atomic co-ordinates.

The cell parameters and structure of quartz are known for a wide range of pressures and temperatures. Regression data* for the thermal expansion and isothermal compression of α -quartz are given in Table I and the thermal expansion curve of quartz is shown in fig. 1. The compression data used for the regression analysis were those of Olinger and Halleck (1976), Jorgensen (1978), d'Amour *et al.* (1979), and Levien *et al.* (1980). The expansion data used were those of Lindemann (1912), Buffington and Latimer (1926), Kôzu and Takané (1929), Jay (1933), Nix and McNair (1941), Rosenholtz and Smith (1941), Mayer (1960), Berger *et al.* (1966),

* Regression data throughout this paper are for modified polynomials of the form: $y = y_0(1 + aZ + bZ^2 + cZ^3 + dZ^4 \dots)$. The standard errors of the regression coefficients, a , b , etc., are given in parentheses after the coefficients and refer to the least significant digits. The standard error of the estimate, SE, and the multiple correlation coefficient, R, are also given in all tables of regression data.

Ackermann and Sorrell (1974), and White (1981, pers. comm.). Prior to the regression analyses the data were normalized to the cell parameters given for quartz at 18 °C in the International Tables for X-ray Crystallography (vol. iii, p. 122). The thermal expansion data for β -quartz showed no change in the a - or c -axes up to a temperature of at least 1373 K. The best values for the parameters of β -quartz are: $a = 4.9980(5)$, $c = 5.4579(7)$ Å, $V_m = 23.702$ cm³ (throughout this paper the molar volume will be represented by the symbol V_m).

The tilting models fail to account for the observed expansion and compression behaviour of α -quartz adequately. This can best be illustrated by calculating expansion and compression coefficients for the a - and c -axes using the equations for the tilting models. If the room-temperature cell parameters, $a = 4.913$ and $c = 5.404$ Å, and tilt angle, 16.2°, are substituted into the equation of Taylor (1972), values of 2.608 Å for the tetrahedron edge for the a -axis equation and 2.653 Å for the tetrahedron edge for the c -axis equation are obtained. New values of a and c can be obtained for simulated compression and thermal expansion by substituting these calculated values for the tetrahedron edge and new values of the tilt angle, increased by 1° to simulate compression and decreased by 1° to simulate expansion. For the simulated compression $a = 4.896$ and $c = 5.375$ Å and for the simulated thermal expansion $a = 4.927$ and $c = 5.430$ Å. These cell parameters give calculated mean coefficients of dimensional change of: -3.46×10^{-3} for a and -5.37×10^{-3} for c for compression, and $+2.85 \times 10^{-3}$ for a and $+4.81 \times 10^{-3}$ for c for expansion. These calculated results suggest that for both expansion and compression the relative change in c should be much greater than that in a . In fact, the reverse is the case. The cause of this serious discrepancy must be attributed to changes in tetrahedral distortion. Clearly a model based on the tilting of regular tetrahedra cannot account for such changes. Indeed, tetrahedral tilting can fail completely to account for the structural behaviour of some members of the quartz family (see below).

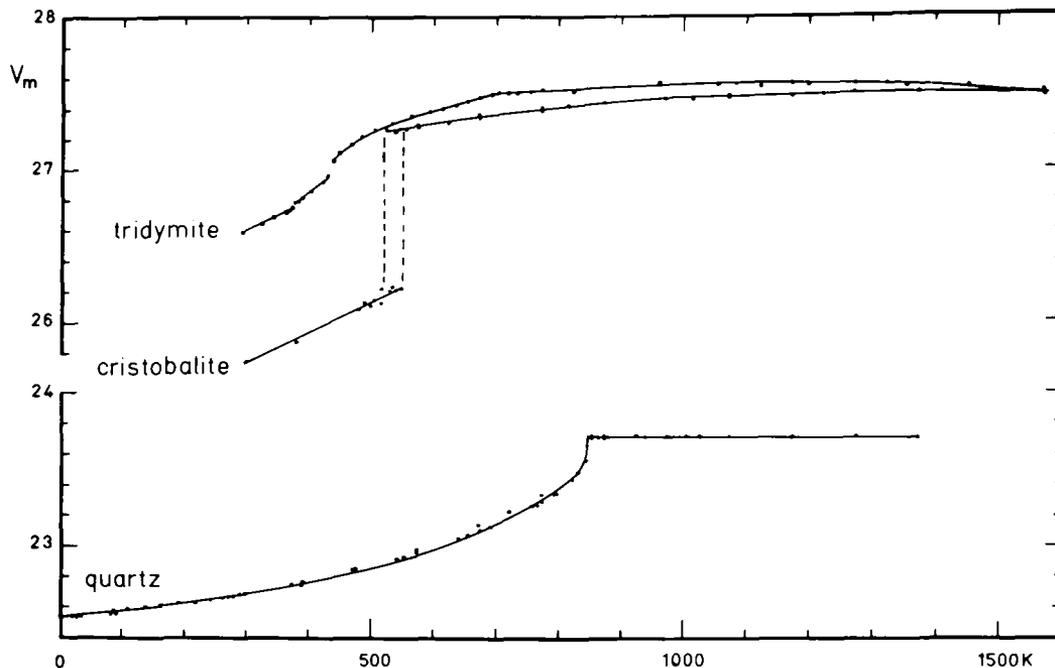


FIG. 1. Thermal expansion curves for cristobalite, quartz, and tridymite. The data on which the curves are based are listed in the text.

The hypothesis that compression is analogous to cooling has been examined for quartz by d'Amour *et al.* (1979). Although the resulting structural changes appear to be similar, in fact, there are sufficient differences in behaviour to demonstrate that compression and cooling are not analogous in their effect on the structure of α -quartz. For example, the ratio of the instantaneous coefficients of expansion and compression for a and c at room temperature and atmospheric pressure are significantly different. For compression $(da/adP)/(dc/cdP) = 1.34$ (Thurston, 1967) and 1.41 (calculated from the regression data of Table I); for cooling or thermal expansion $(da/adT)/(dc/cdT) = 1.84$ (White, 1964) and 1.82 (calculated from the regression data of Table I). Indeed, Levien *et al.* (1980) have already shown that the structural changes taking place during thermal expansion and isothermal compression are not simple inverses, because there is a discontinuity in the relationship between the molar volume and the Si-O-Si angle (fig. 2). The tilt angle, ϕ , is also a measure of the structural state of quartz and there is a smooth relationship between it and the Si-O-Si angle. There is likewise a discontinuity in the relationship between the molar volume and the tilt angle (fig. 2), but it is not as distinct as that for the relationship

between molar volume and the Si-O-Si angle. The reason for the discontinuity and the differences in structural behaviour, as was indicated earlier, is due to changes in tetrahedral distortion. There are two principal measures of tetrahedral distortion in α -quartz: the divergence of the two independent Si-O distances and the divergence of the O-Si-O angles from 109.47° . Tetrahedral distortion is also reflected in the c/a ratio, which shows a smooth relationship with the tilt angle (fig. 2), and which superficially implies that the tetrahedral distortion changes gradually as the tilt angle changes. However, the tetrahedra respond differently to temperature and pressure. As the pressure is increased the tilt angle increases, the mean Si-O distance decreases slightly, the difference between the two Si-O distances remains virtually constant and the variance of the O-Si-O angles increases markedly (fig. 2). As the temperature is increased the tilt angle decreases, the mean Si-O distance decreases (attributed to the anisotropic thermal motion of the framework oxygens), the difference between the two Si-O distances increases markedly and the variance of the O-Si-O angles remains low and virtually constant. Above the inversion there is only a single independent Si-O distance and so the smooth relationship between the c/a ratio and ϕ

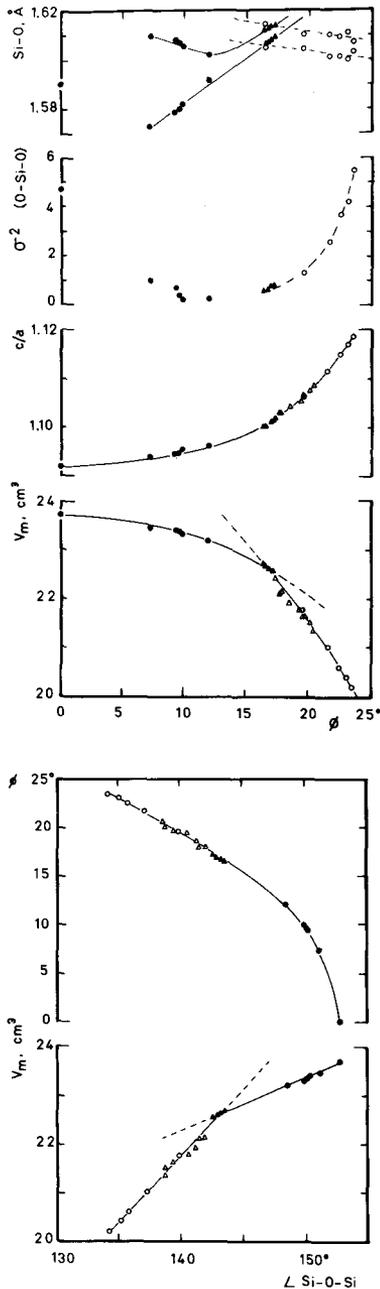


FIG. 2. The structural parameters of quartz as a function of (i) the Si-O-Si angle, and (ii) the tilt angle, ϕ . Open symbols are for structures determined at high pressures at room temperature and closed symbols are for structures determined at low and high temperatures at atmospheric pressure. Based on the data of: Δ Jorgensen (1978), \circ Levien *et al.* (1980), \bullet Young (1962), \blacktriangle Le Page *et al.* (1980).

is maintained by a dramatic increase in the variance of the O-Si-O angles.

Thus during the compression of α -quartz the tetrahedral distortion is virtually all angular, whereas during thermal expansion the distortion is in the Si-O distances, which are also apparently shortened by the anisotropic thermal motion of the framework oxygens.

AlAsO₄, berlinite (AlPO₄), BaSO₄, BPO₄, BeF₂, FePO₄, GaPO₄, GaAsO₄, and GeO₂ also occur as quartz hettotypes and do not contain cavity ions. Although thermal expansion data are available for most of them (Roy *et al.*, 1953; Rao *et al.*, 1973; Sarver, 1961; Kosten and Arnold, 1980), structural data are meagre and compression data are only available for the quartz form of GeO₂ (Jorgensen, 1978). Regression data for GeO₂ are given in Table II.

The quartz form of GeO₂ does not show the same structural behaviour as the mineral quartz. The DTA results of Sarver (1961) indicate that the α - β inversion occurs at $1000 \pm 20^\circ\text{C}$ just below the melting-point, $1116 \pm 5^\circ\text{C}$. From this, and the behaviour of the SiO₂-form, it is assumed that the α -GeO₂-form 'untwists' until the tetrahedral tilting is removed at the α - β inversion (although even this must be uncertain in the absence of structural data). On compression, however, the tilt angle does not change (Jorgensen, 1978) even though the Ge-O-Ge angle changes from 130.5° at atmospheric pressure to 126.7° at a pressure of 2.21 GPa. Thus unlike quartz there is no correlation between the tilt angle and the M -O- M angle. Jorgensen (1978) has shown that the change in the Ge-O-Ge angle without an associated change in the tilt angle is due to the distortion of the O-Ge-O angles. Clearly, the structural state of the quartz-form of GeO₂ cannot be characterized by the tilt angle. There is an even greater disparity than for SiO₂ between the ratios of the instantaneous coefficients for a and c of the quartz-form of GeO₂ at room temperature and atmospheric pressure: $(da/adP)/(dc/cdP) = 2.2$ for compression (from data of Table II, based on Jorgensen, 1978) and $(da/adT)/(dc/dT) = 7.0$ for thermal expansion (Sarver, 1961; Rao *et al.*, 1973). Structural data at elevated temperatures would give a more complete picture of the structural behaviour of this interesting compound.

The changes in the tilt angle of the quartz hettotypes as a function of temperature are only known for quartz and berlinite (Young, 1962; Ng and Calvo, 1976; Le Page *et al.*, 1980). For both minerals the rate of decrease of the tilt angle is gradual as the temperature is raised until quite close to the transformation temperature. The rate of decrease of the tilt angle then increases and

TABLE II. Regression data for the axial expansions of the quartz form of GeO_2 in the temperature range 298 to 1300 K and for the axial compressions of the quartz form of GeO_2 in the pressure range 0 to 2.2 GPa

Z	y	y_0	$10^5 a$	$10^8 b$	SE	R
T (°C)	a, Å	4.9839	1.09(3)	0.472(3)	0.0004	0.9999
T (°C)	c, Å	5.6474	0.258(3)	0.191(3)	0.0004	0.9990
			$10^3 a$	$10^4 b$		
P (GPa)	a, Å	4.9858	-10.5(3)	2.8(12)	0.0008	0.9999
P (GPa)	c, Å	5.6448	-47.8(3)	3.0(10)	0.0007	0.9996

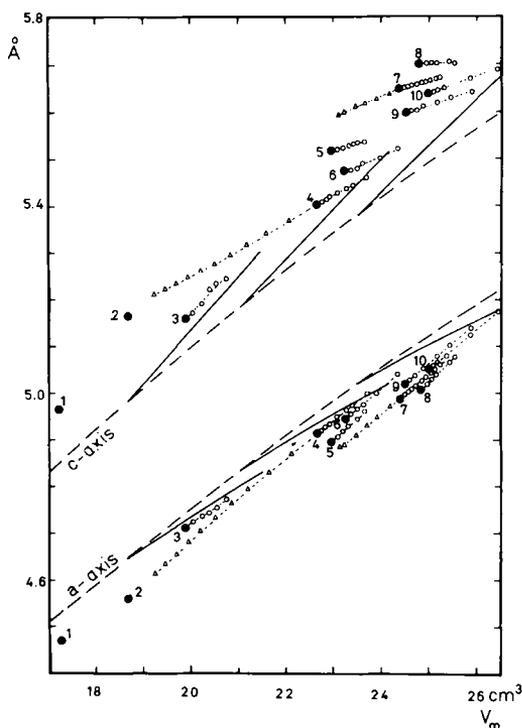


FIG. 3. Plot of the a - and c -parameters of α -quartz hettotypes as a function of their molar volumes. The heavy dashed lines show the relationships for the tilting model of Taylor (1972) for a tilt angle of 20° . The solid lines show the calculated trends for complete removal of the tilting for selected initial molar volumes. Symbols: \bullet room-temperature data, \circ thermal expansion data, \blacktriangle compression data. The quartz hettotypes shown are: (1) BPO_4 , (2) BAsO_4 , (3) BeF_2 , (4) SiO_2 , (5) GaPO_4 , (6) AlPO_4 , (7) GeO_2 , (8) GaAsO_4 , (9) AlAsO_4 , (10) FePO_4 .

ultimately there may be a discontinuous change from a tilt angle of about 8° to 0° (Taylor, 1972; Megaw, 1973). The mean rate of change for the tilt

angle is $0.010^\circ \text{ K}^{-1}$ for α -quartz in the temperature range 100 to 830 K and $0.011^\circ \text{ K}^{-1}$ for berlinite in the temperature range 298 to 773 K (in both cases the upper temperature quoted is just below the rapid change or discontinuity in the tilt angle).

The effects of framework composition on the structures and structural behaviour of the quartz hettotypes are shown in fig. 3. Unfortunately, the lack of structural data for many of the compounds has meant that molar volume has had to be used to characterize the structural state rather than the M - A - M angle. Fig. 3 shows the a - and c -parameters of the quartz hettotypes in relation to their molar volumes and with calculated relationships based on the tilting model of Taylor (1972). The figure shows that there is considerable scatter in the regression of the room-temperature cell parameters on the molar volume; the observed scatter from a straight line (not shown) fitted to the room-temperature data is much greater than the errors in the determination of the cell parameters. The solid lines, which show the calculated changes in the cell parameters as the tilt angle, initially 20° , is removed, do not correlate at all with the observed trends given by the data points. The c -parameter trends for GaAsO_4 and BeF_2 are different from those of the other quartz hettotypes, otherwise all the hettotypes show very similar trends in their cell parameters. However, this does not imply similar structural behaviour, for, as has been shown above, the quartz forms of SiO_2 and GeO_2 have different structural behaviour during compression (the tilt angle of SiO_2 changes whereas that of GeO_2 does not) and yet their cell parameter changes are similar.

The scatter in the regression of the room-temperature cell parameters on the molar volume indicates that there is not a simple structural relationship when the framework composition is changed. There is an equally large scatter for the regressions of M - A distance on molar volume and of M - A - M angle on molar volume. This degree of

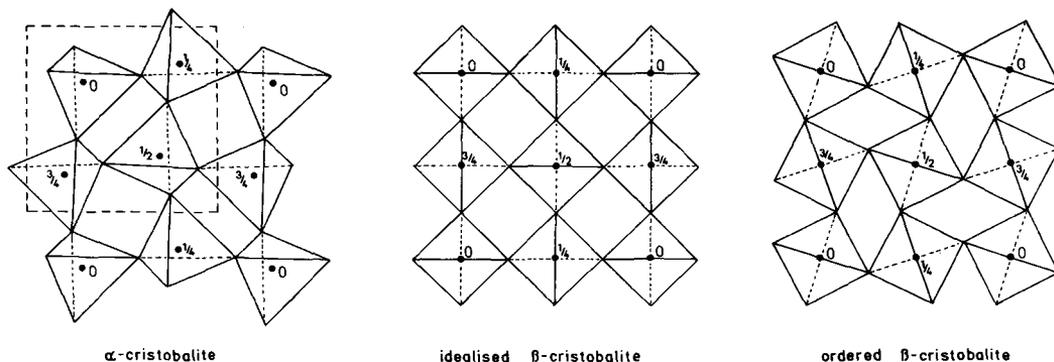


Fig. 4. Cristobalite structures showing the framework tetrahedra and the z -co-ordinates of the framework cations. The true unit cell of α -cristobalite is shown by a dashed line.

independent behaviour of each quartz hettotype relative to the general trends of fig. 3 is attributed to the influence of the $M-M$ non-bonded radii. The interaction between the framework cations is believed to be largely responsible for the equilibrium value of the $M-A-M$ angle at room temperature (Glidewell, 1977; O'Keeffe and Hyde, 1978).

Cristobalite family. For this family the structure of the aristotype is not known with certainty. From recent work it is clear that the idealized β -cristobalite structure (fig. 4) of Wyckoff (1925) is not the true structure of β -cristobalite. Wyckoff's structure has an unusually small Si-O distance of 1.54 Å and an unfavourably large Si-O-Si angle of 180°. In a re-examination of the structure Nieuwenkamp (1937) proposed that the oxygen atom was either revolving continuously, or statistically distributed, on a circle of radius 0.4 Å about the Si-Si join. Leadbetter *et al.* (1973) and Peacor (1973) made a further attempt to resolve the structure of β -cristobalite. They placed the eight silicon atoms in the special positions 8(a) of the space group $Fd\bar{3}m$ and distributed the sixteen oxygens statistically amongst the 96(h) equivalent positions with one-sixth of an atom at each position. Leadbetter *et al.* (1973) and Wright and Leadbetter (1975) have proposed that locally the oxygen atoms are ordered, resulting in a local structure (fig. 4) of orthorhombic symmetry corresponding to space group $Fdd2$ with $a_0 = b_0 = c_0$. A sixfold twinning of domains of a few unit cells gives the cubic average symmetry (Wright and Leadbetter, 1975). The Si-O distance and Si-O-Si angle obtained by Leadbetter *et al.* (1973) and Peacor (1973) are 1.612 Å and 146.7° at 300 °C and 1.611 Å and 148.9° at 310 °C respectively. These compare well with the corresponding values for α -cristobalite at room temperature, 1.605 Å and 146.8° (Dollase, 1965).

Taylor (1972) developed a tilting model for the

cristobalite structure, assuming regular tetrahedra and that the fully expanded structure was the idealized β -structure of Wyckoff (1925). Clearly this tilting model now needs revision. Fig. 4 shows the relationship between the structures of α -cristobalite and ordered β -cristobalite. It is clear from the latter structure that two tilt systems are involved. One, present in the original model, involves the co-operative tilting of the tetrahedra about one of the 4-fold axes lying in the $x-y$ plane (tilt system 1). The other tilt system involves a co-operative tilting of the tetrahedra about the 4-fold axis lying parallel to the z -axis (tilt system 2). The structural data of Peacor (1973) indicate that only the first tilt system is operative in α -cristobalite. This is not surprising since the space group, $P4_12_1$, and the equivalent positions of the oxygen atoms, 8(b), do not permit the second tilt system to operate. The thermal expansion data (fig. 1) and the structural data show a discontinuity at the tetragonal-cubic transformation in the cell parameters and the tilt angle. The removal of the remaining tilt of the first tilt system and the operation of the second tilt system is presumed to occur at the transformation. This, of course, assumes that the present structure of α -cristobalite is correct. Note that ordered β -cristobalite still has the possibility of co-operative removal of the second tilt system towards the idealized β -cristobalite structure. This possibility seems unlikely for cristobalite because of the unfavourable Si-O-Si angle formed, 180°, but it might be seen in an α - or β -cristobalite hettotype containing cavity ions.

$AlPO_4$, $BaAsO_4$, BPO_4 , $GaPO_4$, GeO_2 , and $MnPO_4$ occur as cristobalite hettotypes and do not contain cavity ions. Structural data are meagre, thermal expansion data are available for some (Kosten and Arnold, 1980), and compression data are absent. Regression data for the cristobalite

forms of SiO_2 and AlPO_4 are given in Table III based on the data of Büsser *et al.* (1935), Johnson and Andrews (1956), Berger *et al.* (1966), Wright and Leadbetter (1975), Ng and Calvo (1977), and Hummel (1980). The effects of framework composition on the structures and structural behaviour of the α -cristobalite hettotypes are shown in fig. 5 with calculated relationships based on the tilting model of Taylor (1972). The model calculations indicate that the a -parameter should always be greater than the c -parameter. The majority of the cristobalite hettotypes conform to this, BaAsO_4 and BPO_4 do not; in addition, GeO_2 has cubic symmetry. Although the symmetry of the α -form of GeO_2 is cubic its structure is tetragonal (Seifert *et al.*, 1971), space group $P4_12_1$, with tetrahedral tilting, $\varphi = 34^\circ$, similar to that in α -cristobalite (fig. 4). It achieves cubic symmetry by gross distortion of the GeO_4 tetrahedron: the O-Ge-O angles are 102, 102, 105, 105, 118, and 124° and the Ge-O distances are 1.75₇ and 1.75₄ Å. The tetrahedral distortion is, therefore, virtually all angular. The tetrahedral distortion in the α -quartz form of GeO_2 is likewise virtually all angular and an increase in this angular distortion is the predominant structural change observed during compression (see above).

The room-temperature cell parameters of the α -cristobalite forms of AlPO_4 , GaPO_4 , MnPO_4 , and SiO_2 show parallel trends to the dashed lines calculated for the tilting model (fig. 5), although there is some scatter. The trends for the thermal expansions of AlPO_4 , GaPO_4 , and SiO_2 are almost parallel to the solid lines, which represent the changes in cell parameters as the tilting is removed. Thus there is better agreement between observation and tilting model for certain of the α -cristobalite hettotypes than there is for any of the α -quartz hettotypes. However, even though the cell parameter trends are similar this does not mean that the underlying structural changes are similar for each cristobalite hettotype.

Structural data at elevated temperatures are only available for the α -cristobalite forms of SiO_2 (Peacor, 1973) and AlPO_4 (Ng and Calvo, 1977). The mean rate of change of the tilt angle of the first tilt system calculated from these structural data is $0.012^\circ \text{ K}^{-1}$ for α -cristobalite for the temperature range 301 to 503 K and $0.010^\circ \text{ K}^{-1}$ for the α -cristobalite form of AlPO_4 for the temperature range 293 to 458 K. These rates of change are very similar to those for the α -quartz forms of SiO_2 and AlPO_4 .

Tridymite. The position regarding the structure of tridymite is even more uncertain than that for cristobalite. The idealized, hexagonal high-tridymite structure of Gibbs (1927), by analogy with idealized β -cristobalite, is almost certainly incorrect, having an Si-O distance of 1.54 Å and an Si-O-Si angle of

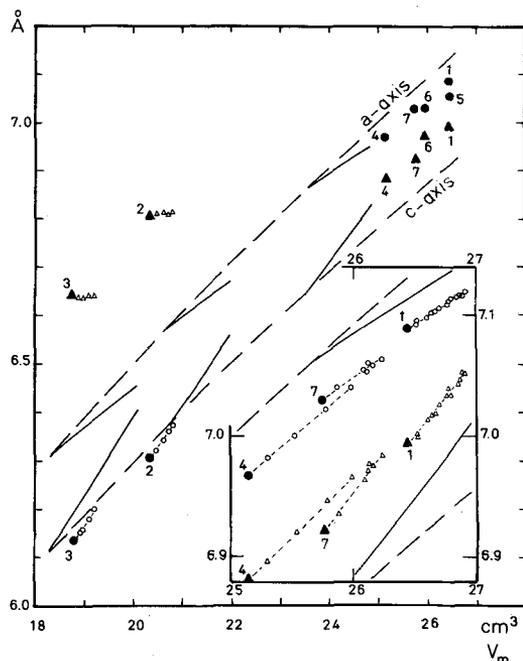


Fig. 5. Plot of the a - (in terms of the β -cristobalite unit cell) and c -parameters of α -cristobalite hettotypes as a function of their molar volumes. The heavy dashed lines show the relationships for the tilting model of Taylor (1972) for a tilt angle of 20° . The solid lines show the calculated trends for the complete removal of the tilting for selected initial molar volumes. Symbols: ●, ▲ room-temperature data for a - and c -parameters respectively; ○, △ thermal expansion data for a - and c -parameters respectively. The cristobalite hettotypes shown are: (1) AlPO_4 , (2) BaAsO_4 , (3) BPO_4 , (4) GaPO_4 , (5) GeO_2 , (6) MnPO_4 , (7) SiO_2 . The inset shows the structural behaviour of hettotypes 1, 4, and 7 on an enlarged scale.

180° . Kihara (1978) found that the oxygen atoms were located on a circle about the Si-Si join, and, following the precedent for cristobalite, placed the eight oxygens on the 12(j), 24(l), and 12(i) sets of equivalent positions in the space group $P6_3/mmc$ with one-sixth of an atom at each position. This arrangement gives a mean Si-O distance of 1.607 Å and a mean Si-O-Si angle of 149° . Kihara (1980) proposed that this statistical model could be resolved into six structures with ordered oxygens using the monoclinic space group Pm with $a_m = b_m$ and $\gamma = 120^\circ$ (fig. 6). A sixfold twinning of domains of the six ordered structures gives the hexagonal average symmetry.

Relative to idealized high-tridymite it can be seen that a tilt system and rotation are needed to obtain one of the six ordered high-tridymite structures (fig. 6). Both tilting and rotation involve the threefold

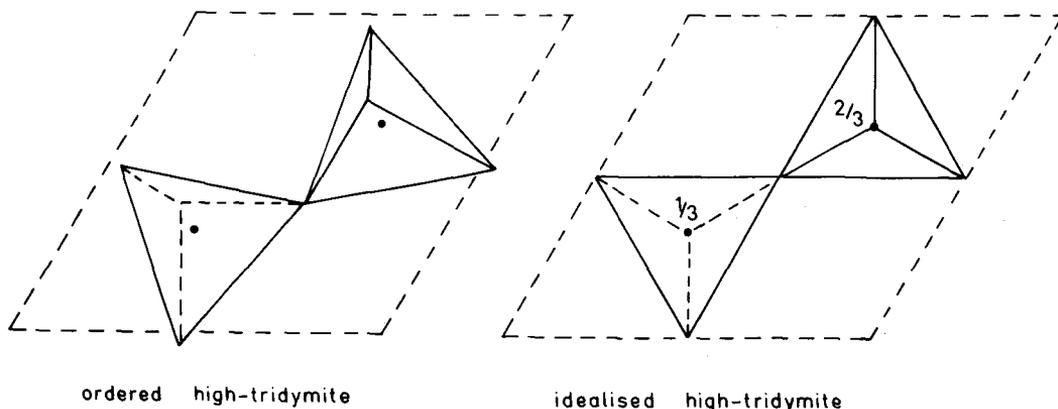


FIG. 6. Structures of ordered high-tridymite (Kihara, 1978, 1980) and idealized high-tridymite (Gibbs, 1927) projected on 0001. The tetrahedra and the framework cations are shown.

axes of the tetrahedra, which in the idealized structure lie parallel to the c -axis. In the ordered structure these threefold axes are tilted away from the c -axis and the tetrahedra are rotated through $\sim 20^\circ$ about these threefold axes. Kihara (1978) was of the opinion that idealized high-tridymite might be achieved at temperatures higher than that of his structural study. This is unlikely since it would mean the creation of energetically unfavourable Si-O-Si angles of 180° . The relationship between ordered high-tridymite and the room-temperature structures is much more complex. Recent structural studies at room temperature (Dollase and Baur, 1976; Kato and Nukui, 1976; Baur, 1977; Konnert and Appleman, 1978) have revealed complicated superstructures made up of different stacking sequences of at least two distorted forms of a single 'layer' of the idealized high-tridymite structure. These complicated structures exhibit strong hexagonal pseudosymmetry

and twinning leading to difficulties in structure determinations possibly accounting for the earlier reports of orthorhombic or hexagonal room-temperature tridymite. The present situation appears to be that terrestrial low-tridymites are triclinic (but strongly pseudo-orthorhombic) and that synthetic, meteoritic, and lunar low-tridymites are monoclinic.

There are few reliable data on the thermal expansion of tridymite. Although Austin (1954) has plotted the mean linear expansion coefficient as a function of temperature, the only data available for the individual axes are those of Kihara (1978) supplemented by those of Schneider *et al.* (1979). The expansion data are summarized in Table III and the thermal expansion curve is shown in fig. 1. The common feature of the thermal expansion behaviour of quartz, cristobalite, and tridymite is that the expansion coefficient falls to a very low level once the fully expanded state has been

TABLE III. Regression data for the axial expansions of the cristobalite forms of SiO_2 and AlPO_4 and the volume expansion of tridymite

Composition	Structure	y	y_0	$10^6 a$	$10^9 b$	SE	R
SiO_2 300–550 K	α -cristobalite	$a, \text{ \AA}$	4.9677	20.1(10)		0.0013	0.986
	α -cristobalite	$c, \text{ \AA}$	6.9167	23.7(69)	51(22)	0.0024	0.994
	β -cristobalite	$a, \text{ \AA}$	7.1089	11.6(5)	–5.91(35)	0.0015	0.988
AlPO_4 300–480 K	α -cristobalite	$a, \text{ \AA}$	7.0844	22.3(16)		0.0027	0.969
	α -cristobalite	$c, \text{ \AA}$	6.9880	25.8(73)	87(31)	0.0025	0.994
	β -cristobalite	$a, \text{ \AA}$	7.1875	7.67(87)	–4.22(71)	0.0015	0.974
SiO_2 (tridymite)	monoclinic	$V_m, \text{ cm}^3$	26.545	76.9(32)		0.0063	0.996
	orthorhombic II	$V_m, \text{ cm}^3$	26.426	127.4(71)		0.0094	0.994
	orthorhombic I	$V_m, \text{ cm}^3$	26.523	156(17)	–166(29)	0.016	0.995

achieved. This supports the hypothesis that the expansion of these minerals is largely due to the removal of the tilting in these structures, with the framework bonds having little, if any, expansion. For quartz and cristobalite the removal of the tilting in the α -structures appears to be discontinuous, or, at the very least, to involve two quite different rates of change of tilt angle; that is a much more rapid change near the inversion.

Framework structures with cavity ions: each shared vertex common to two tetrahedra

The structural state of framework structures without cavity ions at standard T and P is determined entirely by the framework atoms, and, according to Glidewell (1977) and O'Keeffe and Hyde (1978) by the M - M interactions in particular. If this latter hypothesis is correct then it implies that at a given temperature and pressure a framework without cavity ions will tend to adopt an equilibrium M - A - M angle determined by the composition and type of linkage of the framework. The presence of cavity ions in framework structures can prevent these equilibrium M - A - M angles from being achieved and can force the framework to adopt larger or smaller angles. For example, the room-temperature equilibrium Al-O-Si angle for aluminosilicate frameworks is about 145° (O'Keeffe and Hyde, 1978) but in the aluminosilicate-sodalites the Al-O-Si angle ranges from 125.6° for $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ to 155.4° for $\text{K}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ (Beagley *et al.*, 1982).

It is the effect on framework structures of solid-solution series involving the cavity ions which has led to the concept of composition being analogous to P and T in its structural effects. However, as we have already seen it is by no means easy to demonstrate whether the effects produced are structurally identical or only superficially so. In the sections which follow, attempts will be made to compare the structural behaviour of major families of framework compounds, which contain cavity ions, as a function of T and X .

Sodalites. The sodalite family is a mineral group which illustrate the difficulty of making a straightforward interpretation of structural behaviour without the benefit of high-temperature structural data. Basically, the sodalites consist of a framework cage which can adjust its size to accommodate a variety of cavity cations and anions by co-operative tilting of its tetrahedra and the associated adjustments in the M - A - M angle. Since the framework is largely covalent it can be argued that thermal expansion of such strong framework bonds should be negligible, and thus any significant thermal expansion of the structure can be attributed mainly

to the removal of the tilting. Following this line of argument it is to be expected that the expansion should fall to a very low rate when the tilting is completely removed, as is seen for the silica polymorphs (fig. 1). A study of natural noseans and haüynes (Taylor, 1968), which are members of the sodalite family, showed a transition in the thermal expansion curves from a relatively high, increasing, rate of expansion to a low constant rate, and this transition or discontinuity was attributed to the complete removal of the tilting (the achievement of the fully expanded state). Natural sodalite did not show such a discontinuity, but it was argued that for this mineral the tilting had not been removed in the temperature range examined. Originally, it was felt that the cell edge at the discontinuity, a_d , should be constant for a given Si/Al ratio, and hence a_d should be proportional to the Si/Al ratio. Instead, a_d is proportional to the size of the cavity cations for the noseans and haüynes. Furthermore, a_d is much smaller than the calculated cell edge for the fully expanded structure. Both of these effects were later (Taylor, 1972) attributed to the apparent shortening of the framework bonds by the anisotropic thermal motion of the framework oxygens and the size of the cell edge at room temperature. However, thermal expansion curves of synthetic $(\text{Na,K,Rb})_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ sodalites, and their bromine derivatives, failed to show discontinuities in their thermal expansion curves, even for those which were already close to the fully expanded state at room temperature (Henderson and Taylor, 1978). However, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$, did show a discontinuity in its thermal expansion curve. It was thus apparent that the discontinuity in the thermal expansion curves of the noseans, haüynes, and $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$ was not due to the achievement of the fully expanded state. Subsequently, modelling of the sodalite structure (Henderson and Taylor, 1978; Taylor and Henderson, 1978; Dempsey and Taylor, 1980) has suggested that the most likely cause of the discontinuity is when the co-ordinate of the cavity cation becomes 0.25, placing it midway between the cavity anions at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The indication from those studies is that discontinuities of this type are only likely to occur with large cavity anions, e.g. I and SO_4 . Subsequent studies of aluminate- and aluminogermanate-sodalites (Henderson and Taylor, 1979) failed to show the expected discontinuities in their thermal expansion curves. This may be due to differences in the structural behaviour of frameworks of different composition. There is clearly a great need for structural studies of this mineral group at elevated temperatures.

A feature shown by the sodalites, and frequently observed in other solid solutions with framework structures, is an inverse relationship between mean

expansion coefficients and the cavity cation size (Henderson and Taylor, 1978). There are several factors, which taken singly or in combination, could account for this observation.

(i) A correlation could exist between cavity cation size (for an isoelectronic series) and the bond strength between the cavity cation and the framework anion. As this bond strength increases it will impose a greater restraint on the removal of the tilting in the framework. Unfortunately, bond strength decreases as the cation size (bond length) increases and so has the opposite effect to that desired.

(ii) A correlation could exist between cavity cation size (for an isoelectronic series) and the expansion coefficient of the bond between the cavity cation and the framework anion. The expansion of this bond distance could influence the rate of removal of the tilting. (i) and (ii) may appear similar, but in (i) the cavity cation–framework anion bond is regarded as restraining the untwisting of the structure and in (ii) it is regarded as driving the untwisting of the structure.

(iii) A correlation between cavity cation size and cation mass for an isoelectronic series. The cations of higher mass will tend to have smaller amplitudes of thermal vibration at a given temperature and hence will have a lower thermally stimulated influence on the thermal motion of the structure and its consequential effects.

(iv) Where the structure can be described in terms of tilted tetrahedra the idealized relationship between a cell dimension and a framework dimension (for example, the tetrahedron edge) generally includes the cosine of the tilt angle, φ (Taylor, 1972). Depending on whether φ is large or small the same change in φ over a given range of temperature will have a large or small effect respectively on the cell dimension. Hence, the expansion coefficient for a more collapsed framework (higher φ and smaller cavity cation) will be higher than that for a less collapsed framework (lower φ and larger cavity cation). This is a purely geometrical effect.

(v) The effect of forcing the $M-A-M$ angle away from the equilibrium angle it would adopt in the absence of cavity ions. Structures with an $M-A-M$ angle smaller than the equilibrium angle may have a greater driving force for untwisting, and hence changing the $M-A-M$ angle towards the equilibrium angle, than structures with an $M-A-M$ angle greater than the equilibrium angle. Thus structures with a smaller angle might be expected to have a higher expansion coefficient and vice versa.

Leucites. Fig. 7 shows the relationship between the a - and c -parameters of aluminosilicate–leucite solid solutions, $(K,Rb,Cs)AlSi_2O_6$, and their molar volumes. The full lines were fitted to the composi-

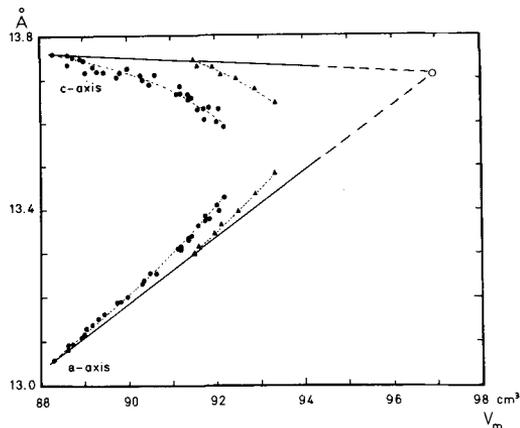


FIG. 7. The cell parameters of leucite solid solutions, $(K,Rb,Cs)AlSi_2O_6$, as a function of their molar volumes. The solid lines are for the compositional data of Martin and Lagache (1975). Symbols: ●, ▲ thermal expansion data for $KAlSi_2O_6$ and $RbAlSi_2O_6$ from Taylor and Henderson (1968), Sadanaga and Ozawa (1968), Hirao *et al.* (1976); ○ fully-expanded structure of synthetic pollucite from Henderson and Taylor (1968).

tional data of Martin and Lagache (1975). Data points, normalized at room temperature to the room-temperature cell parameters of Martin and Lagache (1975), are shown for the thermal expansions of $KAlSi_2O_6$ and $RbAlSi_2O_6$ (data of Sadanaga and Ozawa, 1968; Taylor and Henderson, 1968; Hirao *et al.*, 1976). The trend of the thermal expansion data points is very different from the trend of the composition lines. This difference in behaviour may arise because of the apparent shortening of the framework bonds due to the anisotropic thermal motion of the framework oxygens. The molar volume and the cell parameters are reduced but the a - and c -parameters will be closer to the cubic structure than the parameters for an equivalent molar volume at room temperature. This only partly explains the behaviour because the c -parameter has to decrease markedly to achieve the cubic structure; thus, unlike the a -parameter data points, most of the c -parameter data points cannot be translated horizontally to coincide with the c -parameter composition line. Note that the cell edge and molar volume for the fully expanded state of pollucite (Taylor and Henderson, 1968) coincide with the intersection of the composition lines.

Nephelines. Fig. 8 shows the relationship between the a - and c -parameters of nepheline solid solutions, $(Na,K)AlSi_3O_8$, and their molar volumes. The full lines were fitted to the compositional data of Smith and Tuttle (1957) and Ferry and Blencoe

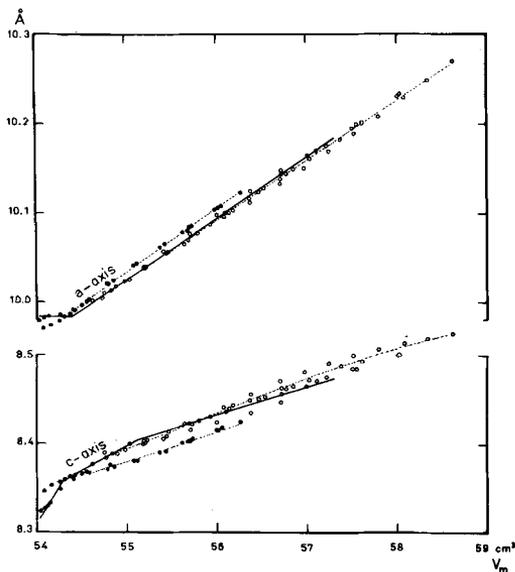


FIG. 8. The cell parameters of nepheline solid solutions, $(\text{Na,K})\text{AlSiO}_4$, as a function of their molar volumes. The solid lines are for the compositional data of Smith and Tuttle (1957) and Ferry and Blencoe (1978). Symbols: thermal expansion data for \bullet pure NaAlSiO_4 and \circ nepheline solid solutions based on the data of Sahama (1962), Foreman and Peacor (1970), and Henderson and Roux (1977).

(1978). Data points are shown for the thermal expansion data of Sahama (1962), Foreman and Peacor (1970), and Henderson and Roux (1977). For this solid solution series the trend of the thermal expansion data points is virtually identical to those of the compositional lines.

Henderson and Taylor (1982) have made a study of other members of the nepheline family: the $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solution series, which have kalsilite-like structures. The hexagonal members of the series show thermal expansion data with increasing degrees of departure from the compositional lines as Ba replaces Sr (Henderson and Taylor, 1982, fig. 12).

Scapolites. The scapolite solid solution series, ideally $\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl}-\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{CO}_3$, have tetragonal frameworks and show a linear variation of a with composition whilst c remains constant. Temperature has a similar effect (Levien and Papike, 1976); a increases linearly with temperature whilst c remains constant. However, Levien and Papike (1976) point out that the structural changes caused by composition are different from those caused by temperature (see fig. 8 of Levien and Papike, 1976). This emphasizes the danger of assuming that when changes in cell parameters,

whether caused by P , T , or X , are similar that the underlying structural changes are also similar. Some of the differences in the structural behaviour of the scapolites might be ascribed to the changes in the composition of the framework accompanying the replacement of Na^+ by Ca^{2+} as cavity cations.

Feldspars. The structural behaviour of the feldspar group has been examined by Brown *et al.* (1983) and so it is not appropriate to discuss this mineral group here. However, it is interesting to note that the dominant expansion direction in monoclinic feldspars lies at an angle of about 22° to the direction of the double crankshaft (Henderson, 1979). Thus the description of the monoclinic feldspars in terms of a 'flexible' crankshaft chain, which has been assumed to dominate the expansion (Saucier and Sapplevitch, 1962), is somewhat misleading. It appears that the compressed $M\text{-O}A2$ bond dominates the expansion behaviour.

Framework structures with some or all vertices shared between three tetrahedra: the nitrides and oxynitrides of silicon and germanium

The nitrides M_3N_4 ($M = \text{Si, Ge}$), and oxynitrides, M_2N_2O , of silicon and germanium do not show the type of co-operative tilting and structural collapse seen in the silica minerals, the leucites and the sodalites. In particular, they do not have displacive transformations. Contrary to the impression given by Srinivasa *et al.* (1977) and Srinivasa *et al.* (1979) there is little scope for significant tetrahedral tilting in the structures of $\text{Si}_2\text{N}_2\text{O}$ and $\text{Ge}_2\text{N}_2\text{O}$.* This is because the nitrogen atoms of the MN_3O tetrahedra are each in threefold co-ordination with the M cations, which effectively stiffens the $M\text{-N-M}$ linkage between the tetrahedra. The effect of this is seen if comparisons are made between α -quartz, which is relatively free to tilt its tetrahedra, and $\text{Si}_2\text{N}_2\text{O}$, which is not. When these structures are subjected to a pressure of ~ 2.4 GPa the effect on $\text{Si}_2\text{N}_2\text{O}$ is a change in the tilt angle of about $+1^\circ$ and a change in the Si-O-Si angle of -4.8° (Srinivasa *et al.*, 1977), whereas for α -quartz the changes are $+4.2^\circ$ and -5.3° respectively (Jorgensen, 1978). The constraint on the $M\text{-N-M}$ linkage, which prevents significant tilting, causes the structural strain to be accommodated by tetrahedral

* Note added during revision. The earlier interpretation of the high-pressure structural behaviour of $\text{Si}_2\text{N}_2\text{O}$ and $\text{Ge}_2\text{N}_2\text{O}$ by the authors cited has been revised by Cartz and Jorgensen (1981). Their present interpretation is closely similar to that given here—namely, that, as regards high-pressure behaviour, the quartz forms of SiO_2 and GeO_2 are 'flexible', the structures of $\text{Si}_2\text{N}_2\text{O}$ and $\text{Ge}_2\text{N}_2\text{O}$ are partially 'flexible', and the silicon nitride structures are 'inflexible'.

TABLE IV. Mean linear expansion coefficients, α (273–1273 K), and mean linear compressibility coefficients, K (0 to ~ 2.3 GPa), for silicon nitrides and $\text{Si}_2\text{N}_2\text{O}$ and $\text{Ge}_2\text{N}_2\text{O}$ (after Henderson and Taylor, 1975; Srinivasa *et al.*, 1977, 1979; Jorgensen *et al.*, 1976)

	$\alpha\text{-Si}_3\text{N}_4$		$\beta\text{-Si}_3\text{N}_4$		$\text{Si}_2\text{N}_2\text{O}$			$\text{Ge}_2\text{N}_2\text{O}$		
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
α ($\times 10^6 \text{ K}^{-1}$)	3.61	3.70	3.23	3.72	1.26	3.89	3.99	—	—	—
K ($\times 10^3 \text{ GPa}^{-1}$)	1.18	1.14	—	—	2.1	3.4	2.5	3.3	4.1	2.8

distortion. For example, α -quartz, which has a 'flexible' framework, has limited tetrahedral distortion at room temperature as shown by the range in Si–O and O–O distances and O–Si–O angles: 1.603 to 1.616 Å, 2.604 to 2.648 Å, and 108.6 to 110.7° respectively (Zachariassen and Plettinger, 1965). The range in Si–N and N–N distances and N–Si–N angles in the least distorted form of Si_3N_4 , $\beta\text{-Si}_3\text{N}_4$, are 1.704 to 1.767 Å, 2.774 to 2.878 Å, and 106.6 to 113.5°, respectively (Grün, 1979). The reduced 'flexibility' of these nitrides and oxynitrides indicates that their structural behaviour can be expected to be different from frameworks with tetrahedra which can tilt significantly.

Silicon nitride, Si_3N_4 , occurs in two modifications, α and β . The β -structure is less distorted than the structurally different α -structure (Henderson and Taylor, 1975); both have non-planar N_3Si groups. Neither structure has freely tilting tetrahedra and so the effects of P or T should only be seen in bond lengths, thermal motion, and tetrahedral distortion. Thermal expansion data show that the expansion behaviour of both forms are similar (Table IV), perhaps with the more strained α -form having the slightly higher volume expansion coefficients (Henderson and Taylor, 1975).

The structure of the oxynitrides can be pictured as built up of sheets of three-membered rings of MN_3O tetrahedra with only $M\text{-N}$ bonds in the plane of the sheet and with the sheets linked by sharing oxygen atoms (Idrestedt and Brosset, 1964, their figs. 4, 5, and 6). There is, therefore, a marked stereochemical anisotropy in the structure with $M\text{-N}$ bonds approximately parallel to the $y\text{-}z$ plane and $M\text{-O}$ bonds aligned approximately along the x -axis. This stereochemical anisotropy results in an anisotropy in the expansion behaviour. The mean linear expansion coefficients for the b - and c -axes of $\text{Si}_2\text{N}_2\text{O}$, attributable predominantly to Si–N bonds, are similar to one another, and also similar to the expansion coefficients of the a - and c -axes of the two silicon nitrides (Table IV). The mean linear expansion coefficient for the a -axis of $\text{Si}_2\text{N}_2\text{O}$, attributable pre-

dominantly to Si–O bonds, is much lower (Table IV). If tilting of tetrahedra was significant in $\text{Si}_2\text{N}_2\text{O}$ then the expansion of the a -axis would be expected to be similar to, if not greater than, the expansion of the other axes.

The compressibilities of $\alpha\text{-Si}_3\text{N}_4$ (Jorgensen *et al.*, 1976) and $\text{Si}_2\text{N}_2\text{O}$ (Srinivasa *et al.*, 1977) have been determined and $\alpha\text{-Si}_3\text{N}_4$ has a much lower volume compressibility coefficient, $3.6 \times 10^{-3} \text{ GPa}^{-1}$, than $\text{Si}_2\text{N}_2\text{O}$, $7.9 \times 10^{-3} \text{ GPa}^{-1}$. The greater volume compressibility of $\text{Si}_2\text{N}_2\text{O}$ arises because of the greater tetrahedral distortion permitted by the Si–O–Si linkage in an otherwise equally inflexible structure. Structural studies of $\text{Si}_2\text{N}_2\text{O}$ as a function of pressure (Srinivasa *et al.*, 1977) reveal that the only significant angular change is a reduction of the Si–O–Si angle by 4.8° for a pressure of 2.32 GPa. On its own, and neglecting any additional tetrahedral distortion, such a change would give a higher calculated compressibility along the a -axis, $5.3 \times 10^{-3} \text{ GPa}^{-1}$ (uncorrected). However, the angle change is accompanied by a slight increase in the Si–O distance, from 1.645 to 1.654 Å, which reduces the calculated compressibility to $3.0 \times 10^{-3} \text{ GPa}^{-1}$ (uncorrected); further tetrahedral distortion accounts for the observed compressibility of $2.1 \times 10^{-3} \text{ GPa}^{-1}$ (Table IV).

Pressure and temperature do not have analogous effects on the structural behaviour of $\text{Si}_2\text{N}_2\text{O}$ when the behaviour of the silicon nitrides is taken into account. Table IV shows that there is very little difference in the mean linear expansion coefficients for the individual axes of α - and $\beta\text{-Si}_3\text{N}_4$ and for the b - and c -axes of $\text{Si}_2\text{N}_2\text{O}$; average coefficient $3.7 \times 10^{-6} \text{ K}^{-1}$. This implies that temperature has the same effect on that part of the $\text{Si}_2\text{N}_2\text{O}$ structure dominated by Si–N bonds as it does on the structures of α - and $\beta\text{-Si}_3\text{N}_4$, which contain only Si–N bonds. Table IV shows that the mean linear compressibility coefficients for the individual axes of $\alpha\text{-Si}_3\text{N}_4$ are almost identical. In contrast, not only are the compressibility coefficients for the b - and c -axes of $\text{Si}_2\text{N}_2\text{O}$ markedly different but they

are also much greater than those for α - Si_3N_4 . The different behaviour with pressure is attributed to the greater scope for tetrahedral distortion in the $\text{Si}_2\text{N}_2\text{O}$ structure with its more deformable Si-O-Si linkage, and the effect this has on the bonds and angles within the tetrahedra.

$\text{Ge}_2\text{N}_2\text{O}$ is isostructural with $\text{Si}_2\text{N}_2\text{O}$ and shows the same structural changes with pressure but to a greater degree (Srinivasa *et al.*, 1979). Again there is little scope for tetrahedral tilting; the change in the tilt angle being less than $+3^\circ$, whilst the change in the Ge-O-Ge angle is -12.5° . It is worth noting that the Ge-O-Ge angle is reduced from 125.1° to the very small angle of 112.6° by 2.54 GPa pressure.

Discussion and conclusions

The present state of knowledge and the great deal of work still to be done mean that it is not appropriate to give more than a few general comments in the discussion of this paper.

The broad similarities in the behaviour of the cell parameters of compounds when subjected to increasing pressure, decreasing temperature, or decreasing size of cavity ion can clearly be used to estimate the behaviour of the cell parameters of a framework compound in the absence of experimental data. However, there are pitfalls in this approach which need to be fully realized before proceeding. Response to P and T will be different when a structure is close to, or at, the maximum size attainable by increasing the size of the cavity ions, and for structures of low symmetry one or more crystallographic directions may reach a structural limit before the others. Unfortunately, there is also a risk that the 'broad similarities in structural behaviour' will be mistaken for imperfect observations of 'identical structural behaviour' and that this may cause the experimentalist not to observe the subtle differences in behaviour which are crucial to a proper understanding of the structural chemistry of framework compounds. More seriously, this approach can lead to the belief that P , T , and X do have identical effects on structures. In several cases, for which structural data are available, it has been shown that the detailed structural changes attributed to effects of P , T , and X are significantly different. The effects of thermal motion are exclusively a temperature effect, and it is difficult to envisage departures from Vegard's law (e.g. fig. 3 of Part I of this paper) being anything other than a composition effect. Pressure tends to result in the distortion of the $A-M-A$ angles. There must also be considerable uncertainty when extrapolating behaviour for one structure to an analogous one of different framework composition; for example, note the differences in detailed structural

behaviour between the quartz forms of SiO_2 and GeO_2 , even though their cell parameter changes are broadly comparable.

Tetrahedral tilting appears only to be significant in those frameworks with the framework anion in twofold co-ordination. However, what is the status of tilting models? It has been shown for quartz frameworks that manipulation of the available tilting models completely fails to account for the observed structural behaviour, largely because they ignore the significant effects of tetrahedral distortion. This failure is not surprising because framework structures are not the mechanical devices implied by the tilting models, nor is the tilt angle likely to be a primary property of a given thermodynamic state of a framework compound. By the latter statement it is implied that P , T , and X will directly affect the $M-A$ and $M-M$ distances and the $A-M-A$ and $M-A-M$ angles and that these and the type of tetrahedral linkage determine the equilibrium configuration of the structure. The tilt angle, in such a situation, is only a geometrical device which defines the relative orientation of the tetrahedra. Nevertheless, the tilting model, although artificial, yields a useful parameter which is yet 'another aid to grasping the nature of the structure' (Bragg, 1930) and can be used to highlight divergences of behaviour. For structures in which there is a significant change of tilt angle over a range of temperature, the average change of tilt angle is relatively small, $\sim 0.01^\circ \text{ K}^{-1}$. This indicates how slowly the equilibrium configuration of bond distances and angles responds to changes in T .

An alternative approach to that of the tilting model is the Distance Least Squares (DLS) modelling technique. However, it is the author's experience that the use of this technique to model the expansion behaviour of framework compounds is beset by serious problems. The most serious are the great scope for accommodating inaccuracies in bond distances by the 'flexibility' of the $M-A-M$ angle and the need, therefore, for accurate values of the framework bond lengths at elevated temperatures (Dempsey and Taylor, 1980). Even at room temperature difficulty has been experienced in modelling the structure of BaAl_2O_4 using average Al-O, Ba-O, Al-Al, and O-O distances with the known cell parameters (Dempsey and Taylor, work in progress). Because of this it has not been possible to duplicate the observed changes (Henderson and Taylor, 1982) in the cell parameters of the hexagonal (Sr,Ba) Al_2O_4 solid solution series as a function of the molar volume. At the moment it appears that the DLS technique relies heavily on the availability of experimental data, generally the structure of an end member and the cell parameters

of a solid-solution series, before a reliable model can be established for a framework structure.

A survey of framework structures, such as in this paper, inevitably raises the doubt that the atomic structures of some framework compounds are not as simple as their reported structures indicate. It has taken many years to achieve more realistic structures for β -cristobalite and high-tridymite, and it may be many more years before their true structures are known. This uncertainty generally arises because X-ray data are an average over a large number of unit cells, and in many cases neighbouring cells may not be identical, particularly for solid solutions. Nevertheless, the averaged X-ray data have to fit the constraints of a space group which represents a 'perfect' structure of repeating identical unit cells. The situation is made more complex when superstructure reflections are present or when the X-ray data indicate a modulated structure. The changing fortunes of crystal structures may be illustrated by BaAl_2O_4 , which is regarded as a derivative of the high-tridymite structure. Despite the presence of superstructure reflections, the first structural studies were restricted to the sub-cell (Do Dinh and Bertaut, 1965; Uchikawa and Tsukiyama, 1966; Perrotta and Smith, 1968) and gave BaAl_2O_4 a framework linkage identical to that of high-tridymite but with a co-operative rotation of the tetrahedra about the threefold axes which lie parallel to the c -axis of the structure (fig. 12.14 of Megaw, 1973). Tilting of tetrahedra relative to the 0001 plane was not present, and indeed was not possible with the unit cell and space group adopted by these first studies as was pointed out by Henderson and Taylor (1982). The refinement of the superstructure of BaAl_2O_4 by Hörkner and Müller-Buschbaum (1979) showed tilting relative to 0001 for all tetrahedra except those on the triad axes of the structure. That the tetrahedra in BaAl_2O_4 are both rotated and tilted is supported by the significant changes in the a - and c -axes of hexagonal $(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ solid solutions as a function of T or X (Henderson and Taylor, 1982).

Many framework compounds are likewise regarded as derivatives of the silica polymorphs and yet they are often quoted as having the simple frameworks of the now-discredited frameworks of the polymorphs from which they are derived. The structure of kalsilite (Perrotta and Smith, 1965) is a case in point. Until 1979, when Hörkner and Müller-Buschbaum refined the superstructure of BaAl_2O_4 , kalsilite and BaAl_2O_4 were believed to have virtually identical structures if the compositional differences and the ordering of the Si and Al atoms in kalsilite were ignored. By analogy with BaAl_2O_4 , kalsilite should have a different structure

from its presently accepted one, and, in particular, the correct structure should allow both rotation and tilting of framework tetrahedra. This view is supported by the significant changes in the a - and c -axes of $(\text{Na},\text{K})\text{AlSiO}_4$ kalsilite solid solutions (Ferry and Blencoe, 1978). From similar reasoning, doubt can be cast on the accepted structure of nepheline (see fig. 8) which is notorious for structural refinement problems (Dollase, 1970; Foreman and Peacor, 1970). Uncertainty over the structure of a framework compound is a serious impediment to the understanding of its structural behaviour in terms of P , T , and X . Conversely, the structural behaviour of a framework compound, and particularly its associated solid solutions, may provide evidence that the structure of the framework compound is incorrect and may further suggest how the structure should be modified to give the observed structural behaviour.

The general impression given by this paper is that our understanding of the structural behaviour of framework compounds is only superficial and that a great deal of theoretical and experimental work, particularly involving the simultaneous effects of P and T , is needed to begin to deepen our understanding. It is hoped that this paper will be more than a partial catalogue of the structural behaviour of some framework compounds and that it will stimulate more research into a difficult subject which is of fundamental importance to our understanding of the structural chemistry of crystalline compounds.

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