

The structural behaviour of tetrahedral framework compounds—a review. Part I. Structural behaviour

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. Although P , T , and X are generally regarded as analogous variables in their effect on framework structures there is reason to believe that they have different structural effects. In particular, an important, and frequently neglected, thermal effect is the apparent shortening of the framework bonds by the anisotropic thermal motion of the framework oxygens. The effects of P , T , and X on displacive transformations in framework compounds are reviewed with particular reference to the disordered alkali feldspars and the leucites. It seems probable from the available evidence that displacive transformations do not take place at a critical size of the framework. Displacive transformations can take place with or without a volume discontinuity and hysteresis. Furthermore, the effects of P , T , and X on a solid-solution series with a displacive transformation can be different, one variable causing a volume discontinuity and another a smooth transition.

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.

Framework structures have been described in many ways. In some descriptions the tetrahedra are considered linked into larger finite units, for example six- or eight-membered rings, and structures built by linking these units in different ways (Smith and Rinaldi, 1962; Smith, 1968; Sato, 1979).

In contrast, the structures of many framework compounds have been described in terms of sub-units, for example analcime in terms of four- and six-membered rings of tetrahedra (Taylor, 1930), and coesite in terms of four-membered rings (Zoltai and Buerger, 1959). Other structures have been described in terms of 'infinite' planar or linear units, for example feldspar in terms of the 'crankshaft chain' (Taylor, 1933), and tridymite in terms of planes of tetrahedra (Konnert and Appleman, 1978). Relatively large structures, such as zeolites, have been described in terms of assemblies of polyhedral units (Moore and Smith, 1963; Chieh, 1979). However, when studying structural behaviour the implied presence of these sub-units can be misleading and one should always keep in mind the converse of Bragg's statement:

though the singling out of certain tetrahedra as belonging to a ring is quite artificial, it is an aid to grasping the nature of the structure (Bragg, 1930).

The concept of a framework being built from elemental units, the framework tetrahedra and cavity ion polyhedra, has led to the development of the idea that the behaviour of the whole structure may be defined in terms of the combined behaviour of its component polyhedra (Megaw, 1971), particularly by using the Distance Least Squares structure modelling technique (Hazen, 1977).

The picture 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). The 'flexibility' allows the tetrahedra to tilt, or twist, with respect to one another, generally in a cooperative fashion. The presence of such tilting implies the existence of a structure without tilting, here referred to as the fully expanded structure, by comparison with which the tilting of the tetrahedra in the tilted structures can be defined. This concept of a flexible tetrahedral framework is supported by

the general observation that, at room temperature, framework structures exist as tilted and distorted versions of ideal fully expanded structures. Pauling (1930) describes this tilting in the mineral sodalite thus:

the framework, while strong, is not rigid, for there are no strong forces tending to hold it tautly expanded. In sodalite the framework collapses, the tetrahedra rotating about the two-fold axes until the oxygen ions come into contact with the sodium ions, which themselves are in contact with the chlorine ions.

This concept of the sodalite structure was used to model its structure (Taylor and Henderson, 1978). The same concept has been used to describe the feldspars (Megaw, 1974).

Despite their widespread use and their value in depicting complicated crystal structures these approaches to the structures of framework compounds are too mechanical. A more realistic picture is a dynamic one, of bonded atoms with bonds and bond angles of differing 'strength' adopting an equilibrium configuration. The bonds and bond angles within the tetrahedra of the framework are much 'stronger' than the bond angle between the framework tetrahedra and the bonds with cavity ions, if present. The relative values of the force constants for $M-A$ bond stretching and $A-M-A$ and $M-A-M$ bond bending are of the relative magnitude 1.0, 0.1, and 0.01 respectively (Brand and Speakman, 1964). This picture also leads to the concept of tightly bonded tetrahedra flexibly linked to their neighbours and any cavity ions by 'soft' bonds, and hence, wrongly, back to the mechanistic concept of tilting tetrahedra. But, unlike the geometrical tilting models, the tetrahedra need not be regular. The equilibrium configuration can result in distorted tetrahedra; distorted with respect to $M-A$ distances or $A-M-A$ angles, or both.

The three main variables which affect framework structures are pressure, temperature, and composition (hereafter referred to as P , T , and X respectively). Recently, the broad similarities in the structural behaviour of framework structures when subjected to increasing pressure, decreasing temperature, or decreasing size of cavity ion have received particular attention (Hazen, 1977). Despite the fact that P , T , and X are independent variables the similar effects they have on structural behaviour have led to an implication that they are somewhat more than analogous. For example d'Amour *et al.* (1979) show a diagram (their fig. 4) with P and T on the same axis, and with the P and T scales adjusted to give an apparent continuity to the change of the dependent variable, the quartz tilt angle, between the two scales.

This paper will be concerned with an exploration of the structural behaviour of framework compounds with reference to P , T , and X and in relation to the concepts introduced above.

Pressure, temperature, and composition as analogous variables. One of the problems in making a critical analysis of the effects of P , T , and X on framework structures is the selection of a suitable reference state. The only common reference state for existing data is that at room temperature, 298 K, and atmospheric pressure, 0.101 MPa. This is necessarily so because almost all the crystallographic work at high pressures has been conducted at room temperature, and high-temperature crystallographic data have been collected at atmospheric pressure or under vacuum. Experiments involving elevated temperatures and pressures have generally been concerned with phase equilibrium diagrams and the effect of P and T on phase transformations. When P and T are fixed, the third variable which defines the state of the structure, its molar volume, is composition.

Unfortunately, neither molar volume nor cell parameters are ideal parameters for characterizing the state of a framework structure in terms of its structural behaviour, especially when Vegard's law is disobeyed and when tetrahedral tilting and distortion occur simultaneously. A better parameter, to which molar volume and cell parameters can be related, is one which directly reflects the structural state, such as a tilt angle or an $M-A-M$ angle.

It is possible to compare the effects of T and X , or of P and X over a wide range of molar volumes relative to the reference state. But currently, because of the data available, the effects of P and T can only be compared over a very limited range of molar volumes, those from room temperature to zero Kelvin. Unfortunately, molar volume changes very little in this temperature range, which means that the corresponding pressure range is experimentally small, and in consequence the precision required of structural parameters is generally beyond that possible for critical analysis. For example the molar volume of α -quartz changes from 22.68 cm³ at room temperature to 22.54 cm³ at zero Kelvin. Such a volume change is given by an increase in pressure from atmospheric to 210 MPa (the first data points in the pressure studies of Olinger and Halleck (1976), Jorgensen (1978), and Bridgman (1925) were: 3380, 500, and 196 MPa respectively). It is therefore very difficult to make a critical comparison of the structural effects of P and T .

Fortunately, silica glass and α -quartz show structural changes which are entirely a thermal phenomenon in the temperature range from room

temperature to zero Kelvin. Silica glass has a special kind of framework because of the long-range disorder manifested in the wide variation in the Si-O-Si angles (Mozzi and Warren, 1969). If one assumes that this long-range disorder makes silica glass unable to undertake *co-operative* tilting of its tetrahedra, then there can be little, if any, contribution to its thermal expansion curve from the 'untwisting' of a tilted structure. On heating from zero Kelvin the molar volume of silica glass decreases, reaching a minimum at ~ 200 K, above which the molar volume increases and achieves its initial volume again at ~ 450 K (fig. 1). White

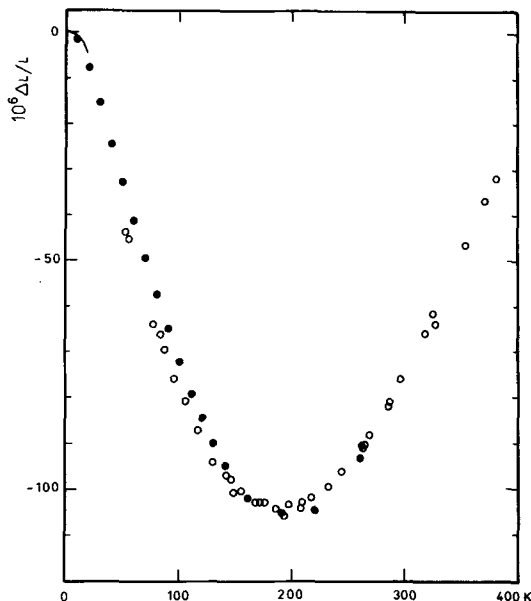


FIG. 1. Relative linear changes in silica glass as a function of temperature; based on the data of: ● Gibbons (1959), ○ Beattie *et al.* (1940-2), — White (1964).

(1964) attributes the very large negative expansion coefficients in silica glass to low-frequency transverse modes of the oxygen atom:

in the open structure of vitreous silica the oxygen atoms appear to be relatively free to vibrate in directions normal to that of the Si-O-Si linkage, with no near neighbours to exert a strong restoring force. This type of low frequency mode would be most easily excited at low temperatures and could lead to a contraction of the lattice.

This view is supported by ultrasonic data for silica glass at low temperatures (Anderson and Bömmel, 1955) and by the calculated heat capacities of Smyth *et al.* (1953). The structural behaviour of α -quartz in the same temperature range is compli-

cated by changes in the co-operative tilting of the tetrahedra. Nevertheless, the *c*-axis of α -quartz contracts on heating from zero Kelvin to about 12.5 K (White, 1964). This contraction can also be attributed to low-frequency transverse modes of the oxygen atom.

Effects attributable to thermal motion are not restricted to very low temperatures but are present throughout the temperature range. At room temperature and at elevated temperatures the transverse mode of the framework oxygen continues to have the largest amplitude of vibration of the oxygen modes. This results in an anisotropy of thermal motion sufficient to be observed by X-ray crystallography (Hahn and Buerger, 1955; Young and Post, 1962; Dollase, 1967). At high temperatures the anisotropy of thermal motion of the framework oxygens leads to a significant apparent shortening of the *M*-O distances of the framework. Framework structures with shortened framework *M*-O distances have been reported by Young (1962), Peacor (1968), Foreman and Peacor (1970), and Czank (thesis, ETH Zurich, 1971). Ways of correcting bond lengths shortened by thermal motion have been suggested by Cruickshank (1956), Busing and Levy (1964), and Megaw (1973).

There appears to be no corresponding phenomenon attributable to pressure or composition. Bridgman and Šimon (1953) report that silica glass behaves in a perfectly elastic manner up to pressures of about 10 GPa; above this pressure silica glass shows a permanent increase in density. Levien *et al.* (1980) found no abnormalities in the structural behaviour of α -quartz when subjected to increasing pressure.

Thus *P*, *T*, and *X* are not strictly analogous in their effects on framework structures. The changes in the thermal motion of atoms make a small, but significant, difference to changes in structure brought about by changes in temperature. In particular, the anisotropic thermal motions of the framework oxygens result in an apparent shortening of the framework *M*-O bonds which results in a real decrease of the cell parameters relative to the structure in the same structural state but free from thermal motion.

Effects of P, T, and X on phase transitions in framework structures. Hazen (1977) has suggested that some displacive structural transitions in framework structures take place at a critical size of the structure of the framework and cited the triclinic-monoclinic transformation in the alkali feldspars as an example. This implies that the cell parameters of alkali feldspars in a given state of Al-Si disorder, whether collected from experiments involving *P*, *T*, or *X*, would tend to lie on a common curve when plotted against their molar volumes.

The data for disordered alkali feldspars (fig. 2) are quite convincing despite the scatter in the c -axis data and the slightly lower molar volumes, 103 cm^3 , obtained by Grundy and Brown (1969) and

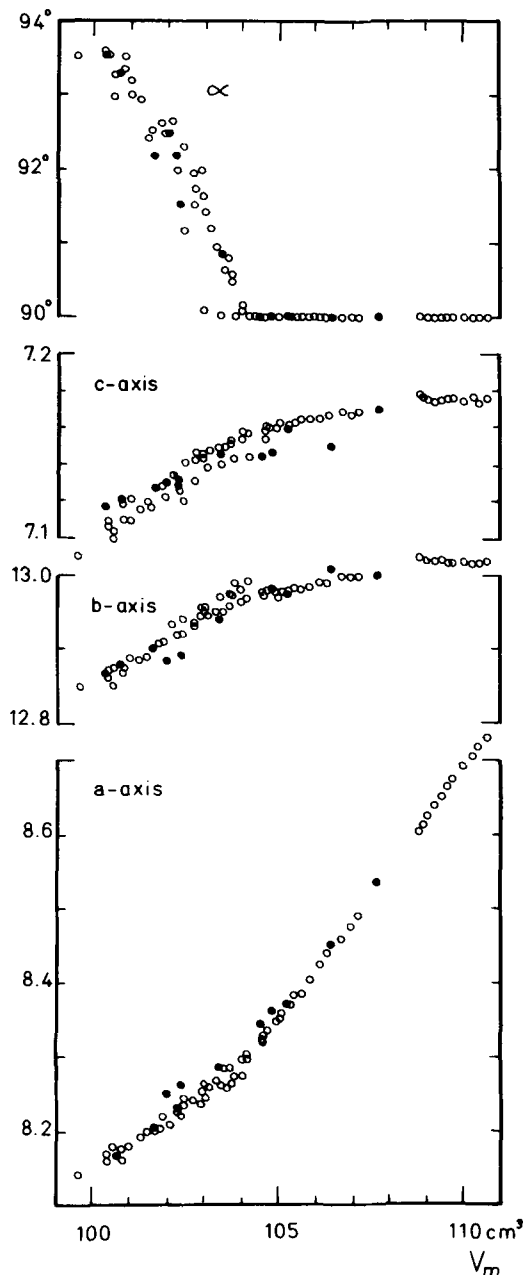


FIG. 2. The cell parameters of disordered alkali feldspars as a function of their molar volumes. Symbols: \circ thermal expansion data (Grundy and Brown, 1969; Henderson, 1979; Okamura and Ghose, 1975; Stewart and von Limbach, 1967), \bullet compression data (Hazen, 1976).

Okamura and Ghose (1975) at the transition of disordered albite. Note that the triclinic-monoclinic transformation is located from the data for the angle α . The data of fig. 2, apart from that for albite, indicate that for both P and T the transformation takes place at a critical molar volume of $104 \pm 0.2 \text{ cm}^3$ and monoclinic parameters of $a = 8.290$, $b = 12.960$, $c = 7.150 \text{ \AA}$ (all $\pm 0.010 \text{ \AA}$), and $\beta = 116.2^\circ$. Note that there is a break in the slopes of the relationships between the individual axes and the molar volume at the critical molar volume of 104 cm^3 .

The reasoning behind this suggestion by Hazen is easy to understand for framework structures which achieve an ideal fully expanded state during thermal expansion. The argument goes that given a solid-solution series for which the framework has a constant composition then the size of that framework when fully-expanded will be constant regardless of the cell parameters at room temperature. The cell parameters at room temperature for the type of solid-solution series being considered are generally proportional to the size of the cavity ions. Thus a member of the series with a small cavity ion will be in a more collapsed state at room temperature, and will generally achieve the fully expanded state at a higher temperature than one with a larger cavity ion. The effect of this temperature difference is that the one achieving the fully expanded state at the higher temperature will experience a greater apparent shortening of its framework bonds due to the greater anisotropic thermal motion of its framework anions, and hence will have the smaller cell parameters. This is presumably why disordered albite, with a transformation temperature of $c. 1000^\circ\text{C}$, has a smaller molar volume at the transformation than the remaining disordered alkali feldspars. Note that this neglects any contribution the cavity cation-framework anion bond may have on the rate of untwisting of the structure. It is undoubtedly difficult to make a critical study of this effect in the feldspars because of the problems associated with Al-Si ordering, the indexing of X-ray reflections and the generally lower precision of monoclinic and triclinic cell parameters compared with those for higher symmetries.

Unfortunately, there are relatively few detailed studies of other framework solid solutions with displacive transformations. The most detailed are those for the leucite family (see below) and for SrAl_2O_4 and the monoclinic $(\text{Sr,Ba})\text{Al}_2\text{O}_4$ solid solution series (Henderson and Taylor, 1982). These studies only involve the effects of T and X on the transformation. Although there has not been a systematic study of the effect of P and T on the cell parameters of a single framework compound at a displacive transformation, Klement (1968) has

deduced that the molar volume of quartz at the α - β transformation decreases as the pressure is increased. It, therefore, appears that there may not be a critical framework size associated with displacive transformations in framework structures.

High-temperature studies are available for leucites with $(\text{AlSi}_2\text{O}_6)^-$ and $(\text{FeSi}_2\text{O}_6)^-$ frameworks. The tetragonal-cubic displacive transformations of synthetic KAlSi_2O_6 and $\text{RbAlSi}_2\text{O}_6$ occur at cubic cell edges of 13.507 and 13.548 ± 0.005 Å respectively at elevated temperatures, and, at room temperature, the substitution of larger cavity cations is expected to make the tetragonal-cubic transformation take place at a cubic cell edge of 13.584 Å (Taylor and Henderson, 1968). Martin and Lagache (1975) have shown that the tetragonal-to-cubic transformations for the solid solutions $\text{Rb}_{1-x}\text{Cs}_x\text{AlSi}_2\text{O}_6$ and $\text{K}_{1-x}\text{Cs}_x\text{AlSi}_2\text{O}_6$ take place at cubic cell edges of 13.588 Å (13.58 Å for the data of Suito *et al.*, 1974) and 13.621 Å respectively at room temperature. The tetragonal-to-cubic transformations of KFeSi_2O_6 , $\text{K}_{0.5}\text{Rb}_{0.5}\text{FeSi}_2\text{O}_6$, $\text{RbFeSi}_2\text{O}_6$, $\text{Rb}_{0.8}\text{Cs}_{0.2}\text{FeSi}_2\text{O}_6$, and $\text{Rb}_{0.9}\text{Cs}_{0.1}\text{FeSi}_2\text{O}_6$ occur at cubic cell edges of 13.57, 13.62, 13.66, 13.68, and 13.70 Å respectively at elevated temperatures, and, at room temperature, the substitution of larger cavity cations is expected to make the transformation take place at a cubic cell edge of 13.72 Å (Hirao *et al.*, 1976).

These results indicate that the transformations of the leucites do not take place at a critical size of the framework. Instead, the cubic cell edge at the transformation is related to the cavity cation size (Taylor and Henderson, 1968). Based on all these data the transformation of pollucite under pressure to the tetragonal form is predicted to take place at a cubic cell edge of 13.61 Å. The reason for this dependence on the cavity cation size can be seen in the structural data for pollucite at room temperature (Newnham, 1967; Beger, 1969) and for cubic leucite at 635°C (Peacor, 1968). The structures, Table I, are seen to be in a very similar structural state (in terms of tilting of tetrahedra and the atomic coordinates) within the experimental errors. However, the cell edges are very different, as are the isotropic temperature factors. The result for the framework is considerably shorter O-O and Si,Al-O distances for the cubic leucite at 635°C, which Peacor (1968) attributed to the thermal motion of the framework oxygens. Therefore, cubic leucite has a greater shortening of its Si,Al-O bond length due to thermal motion than does pollucite, and so the framework of pollucite is significantly larger than that of cubic leucite. For this reason Taylor (1972) stated:

this suggests that the effect of an increase in temperature in increasing the cell volume should not be likened to the

increase in cell volume at a given temperature produced by the substitution of a larger interframework [cavity] cation, since temperature affects not only the degree of rotation [tilting] of the tetrahedra but also the amount of anisotropic thermal motion of the framework oxygens.

The data of Martin and Lagache (1975) for the two solid solutions $\text{Rb}_{1-x}\text{Cs}_x\text{AlSi}_2\text{O}_6$ and $\text{K}_{1-x}\text{Cs}_x\text{AlSi}_2\text{O}_6$ show that even the above statement does not fully explain the structural behaviour of the leucites. When their data are replotted in terms of cell volume versus mean cavity cation radius (fig. 3) the following is observed. Both solid-solution series show volume discontinuities at the tetragonal-cubic inversion at about the same mean cavity cation radius, 1.55 Å (identical to the values for the data of Suito *et al.*, 1974). This radius is smaller than that predicted by Taylor and Henderson (1968), and the reason is seen to be the marked departure of the cell volumes from the line joining the cell volumes of the end members. The departure is greater for the $\text{K}_{1-x}\text{Cs}_x\text{AlSi}_2\text{O}_6$ solid-solution series, which suggests that for dissimilar cavity cations the larger cation has the dominant effect on the size of the structure, and that the effect is more pronounced the greater the dissimilarity between the cation sizes. Thus for a given mean cavity cation radius the cell volume is always greater than the cell volume given by the line joining the end members. This effect appears to be purely a compositional phenomenon.

It is interesting to note that analcime, which has a similar aluminosilicate framework to leucite (with almost identical coordinates to those in Table I), shows a transition from a pseudocubic form to a distinctly non-cubic, monoclinic form at a pseudocubic cell edge of about 13.65 Å (Hazen and Finger,

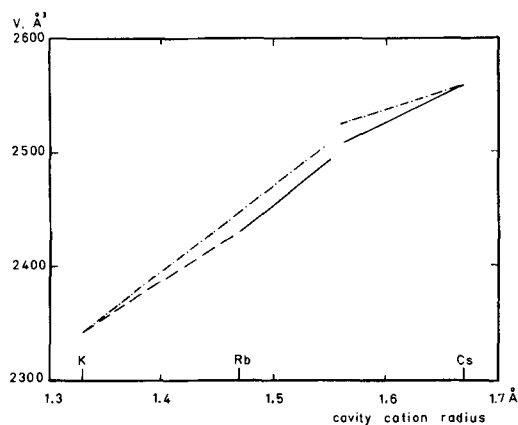


FIG. 3. The volumes of leucite solid solutions as a function of the mean cavity cation radius, based on the data of Martin and Lagache (1975). Symbols: --- (K,Rb)AlSi₂O₆, — (Rb,Cs)AlSi₂O₆, - · - · (K,Cs)AlSi₂O₆.

1979). However, it is not suggested that this result should be compared with those for the aluminosilicate-leucites because the cavity cations, which are responsible for the structural state of the framework at standard T and P , occupy structurally different sites in leucite and analcime. Data for the pressure-induced cubic-to-tetragonal transformation in pollucite and the cubic members of the $K_{1-x}Cs_xAlSi_2O_6$ and $Rb_{1-x}Cs_xAlSi_2O_6$ solid-solution series would add greatly to our knowledge of the leucite group of minerals and the structural behaviour of framework compounds.

It is doubtful whether any other family of framework compounds will provide the type of data given by the leucite family. However, a similar dependence of the molar volume at a displacive transformation on the cavity cation size has been reported for the $(Sr,Ba)Al_2O_4$ solid-solution series (Henderson and Taylor, 1982).

Before leaving the leucite family it is instructive to point out one further difference in their behaviour with respect to P , T , and X . There is no evidence of a volume discontinuity on heating or cooling stoichiometric leucites through the tetragonal-cubic transformation, although SiO_2 -rich non-stoichiometric leucites show inversion characteristics suggestive of such a discontinuity (Henderson, 1981). The coalescence of the (400, 040) and 004 X-ray reflections is quite gradual (Sadanaga and Ozawa, 1968; and also observed but not reported by Taylor and Henderson, 1968). In contrast a volume discontinuity (fig. 3) is apparent at room temperature for the solid-solution series $K_{1-x}Cs_xAlSi_2O_6$ and $Rb_{1-x}Cs_xAlSi_2O_6$ (Martin and Lagache, 1975). There are no data for the effect of pressure on pollucite, but the comparable mineral

analcime shows a volume discontinuity with increasing pressure (Hazen and Finger, 1979).

Other framework structures with displacive transformations have a volume discontinuity in their thermal expansion curves accompanied by additional effects. The transitions of the cristobalite forms of SiO_2 , $AlPO_4$, and $GaPO_4$ show marked hysteresis and also occur over a range of temperatures within which the α - and β -phases coexist (Leadbetter and Wright, 1976; Cohen and Klement, 1979; Kosten and Arnold, 1980; Krisement and Trömel, 1959). Similar effects have been reported for $SrAl_2O_4$ (Henderson and Taylor, 1982). The thermal hysteresis, the coexistence of the low- and high-temperature forms over a range of temperatures, and the apparent lack of a compositional difference between the two forms give the transformation additional characteristics similar to those of martensitic transformations in metals. The transformation takes place with a volume discontinuity and a marked anisotropy of shape change which together generate the elastic strain and strain energy associated with martensitic transformations. At high temperatures the transformation is athermal; that is, once the temperature for the start of the transformation is reached, the transformation only takes place when the temperature is changing. If the temperature is held constant part way through the transformation then an equilibrium proportion of the two forms is achieved, apparently instantaneously. Thus in addition to the conventional variables of P and T , strain energy is an extra variable for transformations of this type. This additional degree of freedom explains the apparent violation of the phase rule by the presence of coexisting isochemical low- and high-temperature

TABLE I. Structures of pollucite at room temperature and cubic leucite at 635 °C

	1	2	3
Cell edge, Å	13.682(2)	13.69	~13.52
Cavity cation B, Å ²	1.7(2)	2.15	15.4
Al ₁ Si			
<u>u</u>	0.6631(1)	0.6621(1)	0.6622(2)
B, Å ²	0.3(2)	0.68	2.7
Oxygen			
<u>x</u>	0.1036(12)	0.1037(4)	0.1033(10)
<u>y</u>	0.1333(14)	0.1340(5)	0.1322(10)
<u>z</u>	0.7216(13)	0.7203(3)	0.7200(7)
B, Å ²	1.8(4)	2.28	7.3
Mean T-O, Å	1.638	1.648	1.619
Mean O-O, Å	2.673		2.641
T-O-T°	145.1	144.5	145.4

1. Pollucite (Newnham, 1967), 2. pollucite (Beger, 1969), 3. leucite at 635 °C (Peacor, 1968).

forms. What is the effect of P and X on transformations of this type? Martensitic transformations in metals are sensitive to shear stress, because of its effect in relieving the strain generated during the transformation. This implies that caution should be exercised in interpreting the effects of pressure on transformations of this type, particularly if the pressure is obtained with an opposed anvil apparatus which can generate significant shear stresses.

The only effect of pressure reported in the literature, apart from its effect on the transformation temperature, is a decrease in the hystereses of the transformations of the cristobalite forms of SiO_2 , AlPO_4 , and GaPO_4 (Cohen and Klement, 1979). The effect of X is to increase the temperature range of coexistence (Henderson and Taylor, 1982). At room temperature, solid solutions showing this type of transformation generally possess a composition range over which the two phases coexist (Henderson and Taylor, 1982). Martin and Lagache (1975) reported a region of coexistence of tetragonal and cubic leucite solid solutions in the system KAlSi_2O_6 - $\text{CsAlSi}_2\text{O}_6$ and $\text{RbAlSi}_2\text{O}_6$ - $\text{CsAlSi}_2\text{O}_6$. This implies that some leucite transformations ought to have martensitic characteristics, and recent studies appear to confirm this for non-stoichiometric leucites at least (Henderson, 1981). The data for the $(\text{Sr},\text{Ba})\text{Al}_2\text{O}_4$ solid-solution series (Henderson and Taylor, 1982) suggest that these effects will be more obvious within the solid solution series rather than for end members. However, Hirao *et al.* (1976) did not report a region of coexistence in their thermal expansion studies of $\text{K}_{0.5}\text{Rb}_{0.5}\text{FeSi}_2\text{O}_6$ or the $\text{Rb}_{1-x}\text{Cs}_x\text{FeSi}_2\text{O}_6$ solid-solution series, but they may have overlooked the experimental evidence for such a region.

Conclusions. The main discussion and conclusions will be reserved for Part II of this review. However, it is relevant to highlight certain points here.

Cell parameters are poor indicators of structural state when making comparisons of the effects of P , T , and X . Ideally, structural parameters such as tilt angles and M - A - M angles and tetrahedral distortion parameters for A - M - A angles and M - A distances should be used to characterize structural behaviour. Unfortunately, this requires structural determinations to be made for appropriate ranges of P , T , and X .

There are structural effects which are unique to P or T or X . The apparent shortening of framework bonds as a result of the anisotropic thermal motions of the framework oxygens is entirely a thermal effect. Departures from Vegard's law, such as seen in fig. 3, are solely a result of solid solution amongst the cavity ions, and hence unique to X . There is, moreover, the evidence that a phase

transformation in a solid-solution series may or may not show a volume discontinuity depending on whether it results from a change in P , T , or X .

Displacive transformations exhibiting hysteresis in framework compounds have, with the exception of a few compounds (notably cristobalite), been seriously neglected. There is great scope for theoretical and experimental work in this field.

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