The authors are grateful to N. Ishizawa who provided access to the JEOL diffractometer. Thanks are due to Daniel Louër for a copy of *DICVOL*91. Assistance with the draft preparation from N. Sudo is appreciated.

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Phase Transition in Sr$_8$[Al$_{12}$O$_{24}$](MoO$_4$)$_2$ Aluminate Sodalite (SAM)

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Abstract

The cubic–tetragonal phase transition at 571 K of the aluminate sodalite Sr$_8$[Al$_{12}$O$_{24}$](MoO$_4$)$_2$ (SAM) has been studied by following the position of the (pseudo-)cubic {400} reflections as a function of temperature. The high resolution of the synchrotron powder diffraction experiment allowed the temperature dependencies to be followed with good precision. The tetragonal **a** lattice parameter appears to be a linear extrapolation of the cubic one, with only a small upward shift at the transition, whereas the **c** parameter decreases strongly below 571 K. These observations can be explained by a model which assumes the superposition of a ferroelastic strain component, and a volume strain component. The volume strain can be rationalized as being the result of a 'shearing' of the sodalite framework. Causes and consequences of the 'shearing' in relation to the sodalite framework are discussed. The weakly first-order transition is nearly tricritical; power-law exponents seem to be influenced by defects. The thermal expansion of the cubic lattice parameter, as well as of the tetragonal **a** axis, is nearly linear. The linear thermal-expansion coefficient α is 8.6 (4) × 10^{-6} K^{-1}. The tetragonal **c** axis also expands linearly between room temperature and about $T_c - 100$ K with practically the same coefficient, but behaves non-linearly nearer to the transition temperature.

Introduction

Aluminate sodalites of the general formula M_8[Al$_{12}$O$_{24}$](XO$_4$)$_2$, where X = S, Cr, Mo, W, ... and M represents Ca or Sr, have been studied in our group for some time (Depmeier, 1988). For all pure end members of the family, one or more structural phase transitions have been identified by various methods (Depmeier, 1988). It was found that most of the phase transitions are of ferroic character. For the title compound, Sr$_8$[Al$_{12}$O$_{24}$](MoO$_4$)$_2$ (SAM for short), in particular, a temperature-dependent neutron powder diffraction study revealed the

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potentially ferroelastic character of its weakly first-order phase transition at 571 K (Depmeier & Bührer, 1991). Because of the limited resolution of that experiment, and owing to the small number of full data sets which could be collected at different temperatures in the available time, only preliminary statements on the temperature-dependent behaviour of SAM could be made. It was stated that future experiments, with better resolution in both reciprocal space and temperature, should concentrate on the region close to the phase transition in order to obtain more reliable results. Such an improved experiment has now been performed using synchrotron radiation and a newly developed furnace (Arnold, 1991).

One purpose of the present paper is to report the magnitude and temperature dependence of some quantities, such as lattice parameters, spontaneous strain and excess volume, and to relate them to each other. Furthermore, we want to discuss a hitherto not appropriately dealt with microscopic distortion mechanism of the sodalite framework, shearing, which is the cause of the observed volume reduction of the unit cell.

The present experiment still has its limitations. Only one aspect of the nature of the phase transition could be investigated, i.e. we studied the evolution of the metrical relationships, rather than attempting to determine the structural aspects of the phase transition. The present results already enable us to draw some conclusions which are important not only for the understanding of SAM, but of the sodalite family as a whole (cf. Depmeier & Bührer, 1991; D&B hereafter, and references·given therein).

Experimental details

As-synthesized samples of SAM corresponding to those of the earlier neutron powder experiment (D&B) were used. The ground powders were mixed with a binder and packed into the sample holder. The diffraction experiment was performed on the Aachen/Frankfurt (Darmstadt)/Tübingen powder diffractometer (Arnold et al., 1989) with synchrotron radiation of $\lambda = 1.2122$ Å from an $Si(511)$ monochromator at beamline B2 of HASYLAB at DESY, Hamburg, Germany. The furnace was described by Arnold (1991). The transition temperature was assumed to be 571 K (Depmeier, 1988). This temperature was used to calibrate linearly the nominal temperatures as measured by thermocouples in the two halves of the furnace. The temperature stability was about 0.2 K, and the maximum deviation between nominal and calibrated temperature was about 50 K. Because of uncertainties in the calibration procedure and owing to the probable presence of a temperature gradient across the sample, the

Table 1. *Measured tetragonal and cubic (italic) lattice parameters (Å) a_t, c_t, a_c of $Sr_8[Al_{12}O_{24}](MoO_4)_2$ aluminate sodalite (SAM) as a function of temperature, and derived quantities*

Derived quantities are the volume V, the excess volume $\Delta = V_0 - V$ and the excess lattice parameter $\delta = a_0 - V^{1/3}$. V_0 and a_0 are extrapolations from the cubic values by linear regression. Errors are estimated to be 0.001 Å in the lattice parameters and 0.3 Å³ in the volume.

T (K)	a_t, a_c	c_t	V	Δ	δ
300.0	9.456	9.403	840.8	4.2	0.016
385.4	9.462	9.412	842.7	4.3	0.016
428.0	9.465	9.418	843.7	4.3	0.016
470.7	9.470	9.425	845.2	3.8	0.014
513.3	9.474	9.435	846.9	3.1	0.011
521.9	9.475	9.437	847.2	3.0	0.011
526.2	9.476	9.439	847.6	2.7	0.010
530.4	9.476	9.440	847.7	2.7	0.010
534.7	9.477	9.442	848.0	2.5	0.009
539.0	9.477	9.443	848.1	2.5	0.009
547.5	9.478·	9.446	848.6	2.2	0.009
556.1	9.478	9.450	848.9	2.1	0.007
564.6	9.480	9.456	849.8	1.4	0.005
568.0	9.480	9.459	850.1	1.2	0.004
572.3	*9.477*		*851.2*		
573.1	*9.478*		*851.4*		
641.4	*9.484*		*853.1*		
726.8	*9.492*		*855.2*		
812.1	*9.498*		*856.8*		

temperatures reported here are estimated to be correct to within ± 5 K.

Results

The 2θ positions of the reflections from (pseudocubic) tetragonal {400} and (004), or cubic {400} planes, respectively, were determined and the corresponding lattice parameters calculated (Table 1). It is not easy to give a reasonable estimate of the errors in the (pseudo-)cubic lattice parameters, the largest source of error probably being the uncertainty in the temperature measurement (see above). We estimate the error to be of the order of ± 0.001 Å. From error propagation the calculated uncertainties in the values for the unit-cell volume, the spontaneous strain and the coefficient of the linear thermal expansion are then ± 0.3 Å³, $\pm 7 \times 10^{-5}$ and 4×10^{-7} K^{-1}, respectively. Just below the transition an apparent increase of the width of the tetragonal {400} reflection indicated an overlap with co-existing cubic {400} reflections. It is not clear, whether this effect is caused by a small hysteresis associated with the weakly first-order character of the phase transition, or from a temperature gradient across the sample. Since a deconvolution was believed to result in ambiguities, it was decided to exclude the temperature range between T_c and about $T_c - 2$ K from further consideration.

Fig. 1 shows the determined lattice parameters a_c (crosses), a_t (squares) and c_t (circles), where subscripts c or t indicate the cubic or tetragonal phase,

respectively. A thin solid line represents a linear regression fit to the values of a_c as a function of temperature. Extrapolation of this line into the field of the tetragonal phase is marked a_0. The dot-dashed line in the tetragonal phase represents the cube root of the unit-cell volume $V^{1/3}$. Of course, this value coincides with a_c in the cubic phase, and should practically coincide with a_0 in the tetragonal phase, if the phase transition was to be classified as proper and pure ferroelastic (Salje, 1990), with a traceless tensor of the spontaneous strain. Obviously, as this is not the case, it has to be considered as possibly improper and/or impure therefore. This is supported by the knowledge (D&B) that the phase transition involves a symmetry change from $Im\bar{3}m$ to $I4_1/acd$, and a doubling of all three cubic basic vectors. The transition is therefore improper ferroelastic.

The expression for the symmetry-adapted spontaneous strain is (Salje, 1990):

$$e_t = 1/3^{1/2}(2e_3 - e_1 - e_2) = 2/3^{1/2}(e_3 - e_1). \quad (1)$$

From Fig. 1 it is clear that a_t coincides practically with a_0, hence $e_1 \simeq 0$, and

$$e_t \simeq 2/3^{1/2}e_3. \quad (2)$$

The observed enlargement of the unit cell across the phase transition testifies to its improper character. The coupling between the spontaneous strain and the primary order parameter is therefore linear-quadratic,

$$e_t \propto Q^2, \quad (3)$$

where the primary order parameter Q is given in a simplified form, thus neglecting its actual six-component character.

The (pseudo-)cubic unit-cell volumes V, V_c and V_0 are shown as a function of temperature in Fig. 2. V_0 is the extrapolation of V_c into the tetragonal phase. Because of the first-order character of the phase transition, $\Delta V/V = (V_0 - V)/V$ is allowed to change

discontinuously at T_c. Again because of the zone boundary transition,

$$\Delta V/V \propto Q^2 \quad (4)$$

to lowest order. Hence, we find

$$e_t \propto Q^2 \propto \Delta V/V. \quad (5)$$

Plots of e_t^2 or $(\Delta V/V)^2$ against $(T_c - T)$, for T not too far from T_c, result in fairly linear relationships (Fig. 3). If as usual we set $Q \propto (T_c - T)^\beta$, the almost linear relationships show that $\beta \simeq 0.25$, and the phase transition is therefore nearly tricritical.
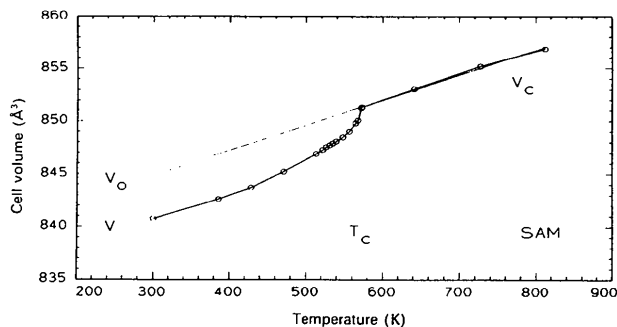

Fig. 2. Unit-cell volumes V_c and V in the cubic and tetragonal phases, respectively, as a function of temperature. The thick curve joining the experimental data (open circles) is a guide to the eye. The linear regression line (thin line) to the cubic values extrapolates into the tetragonal phase, V_0.
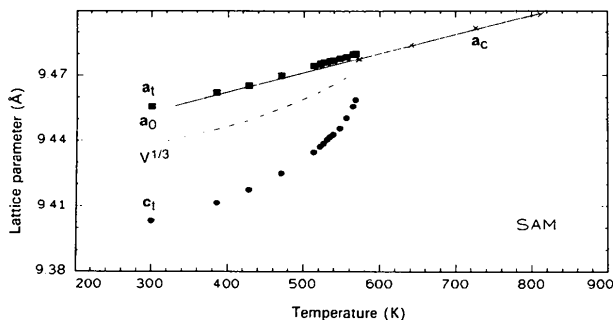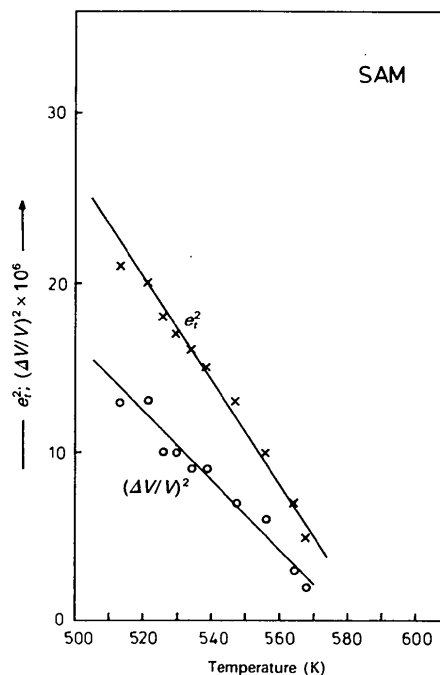

Fig. 3. e_t^2 and $(\Delta V/V)^2$ as a function of temperature. The linear behaviour demonstrates the nearly tricritical behaviour of the primary order parameter. Solid lines are guides to the eye.

Fig. 1. As-measured cubic a_c (crosses), tetragonal a_t (squares) and tetragonal c_t (circles) lattice parameters as a function of temperature. The linear regression line to the experimental values of a_c extrapolates into the tetragonal phase (thin line, a_0). The cube root of the pseudocubic cell volume is also shown.

Power laws can also be fitted to e_t and $\Delta V/V$ in Figs. 1 and 2, respectively. The resulting exponents (~ 0.3) deviate quite strongly from the expected value (0.5) derived from the relationships (3)–(5).

Discussion

SAM has space groups $Im\bar{3}m$ and $I4_1/acd$ in its high- and low-temperature phases, respectively. The cubic lattice parameter **a** is about 9.5 Å and the tetragonal unit cell is a 2**a**, 2**b**, 2**c** multiple of the cubic cell. The lattice parameters quoted in this work refer to a (pseudo-)cubic cell without any multiplicity taken into account.

An apparent discrepancy (about 0.02 Å) between the absolute values of the lattice parameters reported in D&B and found in this study is almost certainly due to the uncertainty in the neutron wavelength used (Bührer, 1991). The temperature dependencies agree well, however.

One of the most conspicuous results of this study on SAM is the almost one-dimensional contraction of its unit cell across the phase transition, as revealed by Fig. 1. This is unexpected and surprising in view of the three-dimensional sodalite framework and its latent cubic symmetry. A model which explains this behaviour relies on the partition of the total spontaneous strain e_t into two different mechanisms, viz. (i) a symmetry-breaking ferroelastic spontaneous strain e_s and (ii) an additional, non-symmetry-breaking volume strain e_v. We set

$$e_s = (2e_{3'} - e_{1'} - e_{2'}) \qquad (6)$$

and

$$e_v = (e_{3''} + e_{1''} + e_{2''}), \qquad (7)$$

where primed and double-primed symbols refer to mechanism (i) or (ii), respectively. If

$$e_{1'} \simeq e_{1''} \quad \text{and} \quad e_{2'} \simeq e_{2''} \qquad (8)$$

one obtains

$$e_s + e_v \simeq 2e_{3'} + e_{3''}, \qquad (9)$$

which may be compared with the expression for e_t in (2). Thus, because of the accidental near equality (8), the two effects happen to compensate each other in the tetragonal **a** directions, whereas they add up in the **c** direction. Actually both $e_{3'}$ and $e_{3''}$ express a shrinking of **c**. From (9) it can be seen that both add up to a higher degree of shrinking than would be caused by either effect alone. The net result of (6)–(9) is the experimentally observed nearly one-dimensional volume change.

Structural work (D&B) indicates that the volume component e_v in the mechanism described is almost isotropic, *i.e.* $e_{3''} \simeq e_{1''} = e_{2''}$. This information can be employed to convert the observed excess volume

(Fig. 2) into 'correction terms' for the observed lattice parameters. One can then calculate a 'spontaneous strain', in the absence of an excess volume, and fit it to $(T_c - T)$. This procedure allows the temperature dependencies of the lattice parameters to be modelled very well, as shown by the solid curves in Fig. 4.

We now discuss in some detail the question of how the volume reduction may be brought about. Possible clues are provided by the structure determination of SAM (D&B). The main structural changes which happen at the cubic–tetragonal phase transition of SAM are:

(i) A freezing of the MoO_4 tetrahedra, which are dynamically disordered over six equivalent, so-called 'tetragonal', orientations in the cubic phase. In the low-temperature phase the MoO_4 tetrahedra are ordered, the 'tetragonal' orientation, however, is preserved.

(ii) A concomitant modulation of the Sr cation positions.

(iii) A particular distortion pattern of the sodalite framework ('shearing').

All three mechanisms are in agreement with the symmetry reduction from $Im\bar{3}m$ (a_1, a_2, a_3 unit cell) to $I4_1/acd$ ($2a_1$, $2a_2$, $2a_3$ unit cell), and correspond to either the N_1^- or N_2^- irreducible representation of $Im\bar{3}m$ (D&B; Stokes & Hatch, 1988), but only (iii) gives rise to a substantial volume reduction of the sodalite framework and, thus, of the unit cell of SAM.

Shearing is not the sole distortion mechanism of a sodalite framework that is capable of reducing the unit-cell volume. This is illustrated in Fig. 5, where lattice parameters are indicated by tick marks. Fig. 5(a) represents an elemental fragment of an ideal, undistorted, fully expanded sodalite framework. The framework is in its topological, *i.e.* highest possible symmetry, space group $Im\bar{3}m$. In Figs. 5(b)–5(d) three distinct distortion mechanisms are shown which reduce the (pseudo-)cubic lattice parameters,
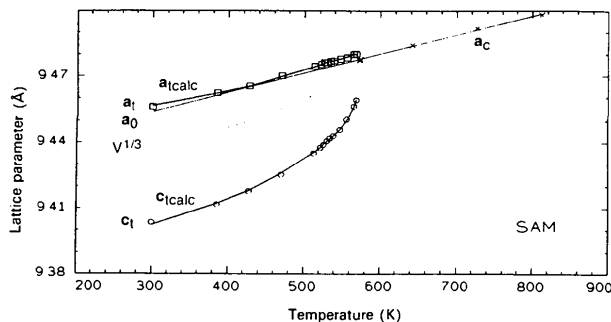

Fig. 4. Experimental a_t and c_t values (open symbols), and the modelling functions a_{tcalc} and c_{tcalc} (thick solid curves), as a function of temperature. a_c, a_0 and $V^{1/3}$ as in Fig. 1.

and thereby the volume of the unit cell, but carry different symmetry properties.

(I) In Fig. 5(b) the so-called 'tetragonal tetrahedron' distortion is shown. When acting alone this mechanism preserves the symmetry. For aluminosilicate sodalites the extent of this distortion has been found to depend sensitively on the average framework composition, but to be independent, to a first approximation, of the non-framework species (Depmeier, 1984a). The tetragonal tetrahedron distortion is very important for aluminate sodalites, but it is not supposed to, and indeed does not, change significantly at the cubic–tetragonal phase transition of SAM (D&B).

(II) The well known tilt mechanism of Fig. 5(c) also reduces the volume ('partial collapse'). The tilt mechanism can be considered as the response of a given sodalite framework to the incorporation of spherical cage ions of different sizes. It destroys the centre of symmetry, but preserves the cubic system. The highest possible symmetry reduces from $Im3m$ to $I\bar{4}3m$. Since the space groups of both phases of SAM are centrosymmetric, the tilt is not regarded as playing a significant role in its phase transition. This is supported experimentally by the structure refinement (D&B).

(III) Fig. 5(d) now illustrates the so-called 'conformational shearing' (Depmeier, 1983b, 1984b, 1988). This mechanism is characteristic for ordered aluminate sodalites, and is closely related to the presence of tetrahedral cage anions, their 'tetragonal' orientation, and their mutual arrangement (Fig. 6).

The first two mechanisms have been described elsewhere (Depmeier, 1984a), the third will be discussed here, in order to help understand our actual problem: Without going into too much detail we mention beforehand that the sodalite framework can be described as being composed entirely of so-called 4-rings (rings of four corner-connected TO_4 tetrahedra). The conformational shearing concerns the 4-rings. It can be regarded as a shear-like distortion of the rings, brought about by cooperative rotation of the rigid tetrahedra about axes which are perpendicular to the plane of the undistorted 4-ring and which pass through the corresponding T atoms. The degree of rotation can be measured by the angle τ. A τ value of $0°$ would correspond to the situation in Fig. 5(a). Appropriate signs for the rotation can also

Ideal
(a)

Angular distortion
(b)
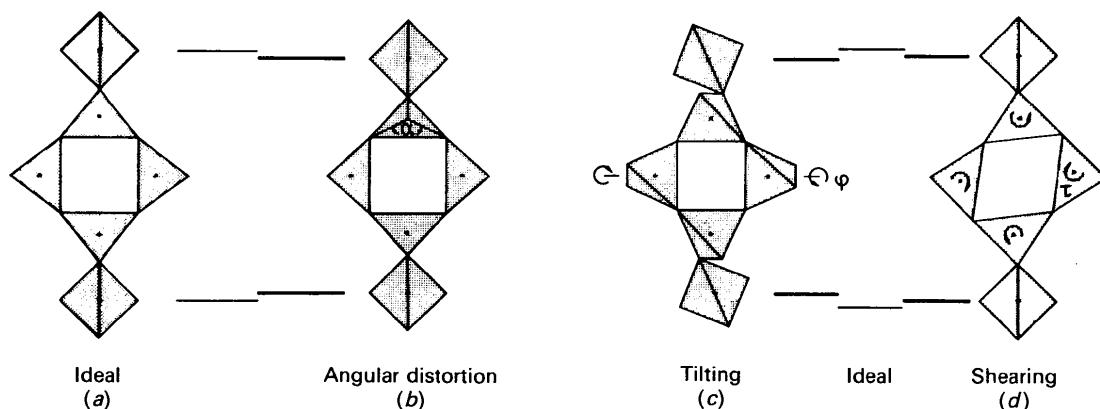
Tilting
(c)

Ideal
(d)

Shearing
(d)

Fig. 5. Distortion mechanisms of a sodalite framework. Only a part of the framework is shown. Tick marks in the respective margins indicate the lattice parameter. (a) An ideal framework showing the maximally attainable lattice parameter. (b) Tetragonal tetrahedron distortion. (c) The tilt mechanism. (d) The shearing mechanism.
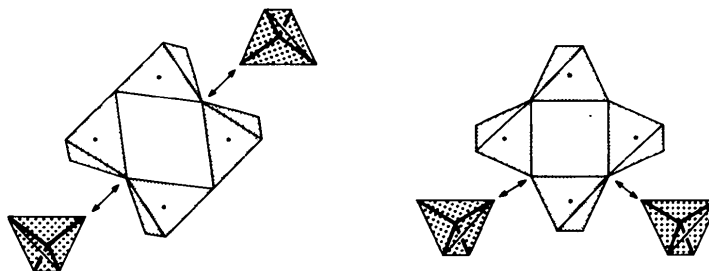

Fig. 6. 'Shearing' (Fig. 5d) is the result of repulsive interactions between oxygens of tetrahedral anions and of a 4-ring of the framework. The tetrahedral cage anions must not only be in a special orientation ('tetragonal orientation'), but neighbouring anions must also have a particular mutual arrangement, as shown on the left side. The situation on the right-hand side does not result in shearing.

be defined. In projection, such as in Fig. 5, 4-rings affected by shearing become rhombs, rather than squares.

Shearing is not an innate property of the bare sodalite framework, but results from repulsive interactions between oxygens of the cage anions and of the sodalite framework, such that the non-bonded O···O interatomic distances remain above about 2.7 Å (cf. Hyde, Sellar & Stenberg, 1986). A quite intuitive picture of such interactions can be found elsewhere (Depmeier, 1988). Special geometric conditions must be met for shearing to occur (Fig. 6). In fact, sodalite frameworks can be imagined which exhibit no shearing, despite the presence of ordered cage anions in 'tetragonal orientation' (see, e.g., Fig. 1 of Depmeier, 1988).

Unlike the tilt mechanism, conformational shearing is a local effect, as the cooperation is restricted to isolated 4-rings. Therefore, neighbouring 4-rings having the same orientation with respect to $\langle 100 \rangle$, may have shearings of different magnitudes and signs. Shearing systems can be conceived as occurring with respect to one, two or three of the $\langle 100 \rangle$ directions. Usually, shearing will break the cubic symmetry. On the other hand, the centrosymmetry is not necessarily broken, as shown by SAM. Furthermore, complex superstructures can be formed, which are, indeed, typical of aluminate sodalites. The particular shearing patterns in the (001) and {100} planes of the room-temperature phase of SAM display its tetragonal symmetry (Fig. 7). Besides, unlike the tetrahedron distortion and tilt mechanisms, shearing results in changes in the fractional coordinates of the T (i.e. Al) atoms, because translational movements of the relatively rigid TO_4 tetrahedra are inherently involved.

A given shearing system reduces the translations along those $\langle 100 \rangle$ directions which are normal to its axis. For the special case of Fig. 5(d) one can easily

obtain the expression

$$\mathbf{a}' = d(1 + \cos\tau) + 2t\cos\nu\cos\tau, \qquad (10)$$

where $\mathbf{a}'$ is a pseudocubic lattice parameter in the plane normal to the axis of the shearing system, d is the length of the TO_4 tetrahedron edge, t is the height of a tetragonal face and ν is the angle between t and the height of the tetrahedron. For regular tetrahedra ν is $35.26°$. Values for τ different from $0°$ result in a lattice parameter $\mathbf{a}'$, which is smaller than the unaffected one.

Quite obviously, (10) is only valid for the specific case shown in Fig. 5(d). Other patterns of shearing systems require different expressions. Furthermore, for real systems, such as that of SAM (Fig. 7), small secondary contributions from mechanisms (I) and (II), as well as irregular distortions of the TO_4 tetrahedra, must also be taken into account. This may even be the case in the absence of actively acting mechanisms (I) or (II) as primary distortion mechanisms.

It is easy to show that the excess volume $\Delta = V_0 - V$, and also the excess lattice parameter $\delta = \mathbf{a}_0 - V^{1/3}$, are proportional to τ^2. The shearing can also be expressed by the shift ξ of the oxygens along the diagonal of a 4-ring, away from the cubic positions (Fig. 6). Geometrically $\xi \propto 1 + \sin\tau - \cos\tau$, hence, $\xi \propto \tau$ for small, i.e. meaningful, values of τ. It can be expected that ξ is proportional to the combined Coulombic forces directed in opposite directions along the diagonal of a 4-ring of the framework. The forces result from the repulsive O···O interactions between two anion tetrahedra and the embraced 4-ring (see left-hand side of Fig. 6). On the other hand, the distortion measured by ξ should be inversely proportional to the resistance of the framework to this action, i.e. its elastic stiffness. If the geometrical relationships are different, such as shown on the right-hand side of Fig. 6, shearing does
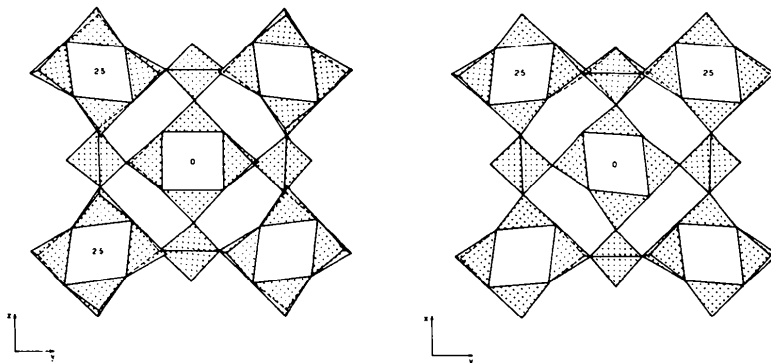

Fig. 7. The projection of the framework of the room-temperature phase of SAM along [00$\bar{1}$] and [100] (left) demonstrating the different shearing patterns.

not occur. The magnitudes of ξ, τ, δ and Δ may be supposed to vary significantly from one sodalite to another, as these quantities depend on geometrical conditions, controlled by atomic sizes, effective charges, and elastic properties of the framework.

Despite several attempts it has not been possible to find a structural parameter which describes the shearing mechanism in such a simple and intelligible manner as, e.g., the tilt angle describes the partial collapse. In an attempt to overcome this problem, at least in part, the use of a so-called distortion parameter D was proposed, which measures the average angular distortion of the 4-rings of a given sodalite framework, if necessary for different directions (Depmeier, 1983a,b). For the determination of this parameter the structure must be known in detail. In the particular case of SAM the structure determination (D&B) demonstrated that the magnitudes of the D values in different directions are about the same, despite the fact that the cubic symmetry is broken and the patterns of deformation are different (Fig. 7). Hence the statement given above, namely that for SAM the volume reduction caused by shearing is practically isotropic. Shearing results from the peculiar oxygen–oxygen interactions described above. It is therefore unlikely to occur in sodalites containing spherical cage anions. The question, whether non-spherical anions of a shape different from that of a tetrahedron can also produce a kind of shearing, remains to be studied.

The cubic–tetragonal phase transition of SAM

For the sake of argument we neglect for a moment the fact that the phase transition is slightly first order. This seems to be justified, because it is known that the character of the transition can be pushed towards being 'less discontinuous' by changing the composition (Setter & Depmeier, 1984).

The following scenario describes how the phase transition might be imagined to happen: Although it has not yet been conclusively established, there is every reason to believe that the cage anion tetrahedra in the cubic phase are dynamically disordered. The tetrahedra jump between six so-called 'tetragonal' orientations (Depmeier, 1984b), the residence time in each such state being considerably longer than the jump time. The probability of finding a tetrahedron in a given orientation i ($i = 1, ..., 6$) is $p_i = \frac{1}{6}$. In each 'tetragonal' orientation state the cubic symmetry around a given MoO_4 tetrahedron is locally and instantaneously broken. The framework may feel the broken symmetry as well, and under certain conditions local shearings may occur. On the time scale of the X-rays the cubic phase is realized by averaging over regions of lower local symmetry, fluctuating in space and time. The size of these regions may change

as a function of temperature. It is beyond the scope of this paper to discuss this interesting point any further.

During the phase transition the anion tetrahedra start to prefer certain out of the, under cubic symmetry equivalent, 'tetragonal' orientations, such that the p_i become unequal on the X-ray time scale, and the symmetry is broken. The unit cell relaxes in response to these microscopic distortions and a macroscopic spontaneous strain is built up.

As neighbouring anions take their respective 'correct' orientation, the fluctuating local shearings also become progressively stable and result in the described macroscopic volume strain.

A scalar parameter which describes locally the ordering of a given MoO_4 tetrahedron, is

$$\kappa = p_i - \tfrac{1}{5} \sum_{j \neq i} p_j \ (i, j = 1, ..., 6). \qquad (11)$$

κ is zero in the cubic phase and non-zero in the tetragonal phase. It approaches unity when the cage anion becomes fixed in its appropriate tetragonal orientation. This is not the global order parameter OP of the phase transition, which, of course, must conform with the N_1^- or N_2^- irreducible representation of $Im\bar{3}m$, identified to drive the transition (D&B). For the discussion of OP its multicomponent character has to be taken into account, such that the OP is a linear combination of its components η_i with $i = 1, ..., 6$. It can be found, for instance in the tables of Stokes & Hatch (1988), that the direction of the six-component vectorial OP, which leads to the stable solution $I4_1/acd$ for the N_1^- or N_2^- irreducible representation of $Im\bar{3}m$, is given by the symbol $P9$, with components $(a, a, a, -a, 0, 0)$.

The tables of Stokes & Hatch (1988) indicate that Landau theory allows the phase transition, driven by either possible irreducible representations N_1^- or N_2^- of $Im\bar{3}m$, to be continuous. However, the experimental facts, for example the discontinuity of the lattice parameters, the small hysteresis, the coexistence of the two phases, and the latent heat (Depmeier, 1988), demonstrate that the transition is weakly first order. We do not wish to explore the causes for the discontinuous character here, but just mention negative coefficients of the quartic terms of the free energy expansion, possibly driven negative by coupling with elastic spontaneous strain (see, e.g., Salje, 1990), as possible candidates for an explanation. This is supported by the observation that changing the composition is able to drive the character of the transition towards being less discontinuous, judged by the diminishing heat of transition (Setter & Depmeier, 1984). Hence, it is at least conceivable that under certain conditions a compositionally altered SAM crystal will undergo a continuous phase transition.

It should be noted that for the present case renormalization group theory predicts an instability against critical fluctuations, and does not therefore allow continuity (cf. Stokes & Hatch, 1988). However, the N_1^- and N_2^- irreducible representations are associated with six-component order parameters, and doubt has recently been cast upon renormalization group theory in cases of multi-component order parameters (Meimarakis & Tolédano, 1985). Therefore, the experimentally observed discontinuities should not necessarily be considered as a manifestation of the predictive power of renormalization group theory.

It was stated earlier that the numerical values for the exponents of the power laws fitted to e_t and $\Delta V/V$ (~0.3) deviate quite significantly from the expected value, 0.5, derived from the relationships (3)–(5). We propose to regard these 'non-classical' values as not definite and, therefore, subject to revision by future studies. The main reasons for choosing this caveat are (i) the weakly first-order character of the phase transition, (ii) the necessity to exclude the region just below T_c, and thus the critical region, if there is any in SAM, (iii) the quite high uncertainty in the temperature, and (iv) the use of as-synthesized samples. These samples have not been characterized with respect to the defect density, nor to the nature of the defects. In this connection it is interesting to note that the structure determination of SAM was successful with single-crystal data, but the refinement was not. The refinement was therefore carried out on powder data (D&B). Tolédano (1984) discussed the frequently found deviations of power-law exponents from predicted values, particularly in the case of ferroelastic phase transitions, and emphasized the importance of defects for such observations. He highlighted the fact that coupling of defects with the OP should be outstandingly important for incommensurately modulated phases. We recall that certain phases of aluminate sodalites, including SAM, can conveniently be described as modulated – others are in fact incommensurately modulated (Depmeier, 1992) – and propose that this point should be considered in more detail.

It is also interesting that Giddy, Dove & Heine (1989) suggest the possibility of explaining 'non-critical, non-standard' values of β exponents by strongly temperature-dependent fourth-order-term coefficients in the conventionally used Landau free-energy expansion, and raise the question as to whether the polynomial approach is actually appropriate. Salje (1986) points to the importance of non-linear relationships between microscopic and macroscopic strains in certain structures also giving rise to non-standard exponents. It has been stated earlier that the volume component of the strain in SAM depends in a complicated way on the peculiari-

ties of the structure, and the mutual interactions of the substructures. The ferroelastic component may also be expected to depend in a complex way on these interactions, and nonlinear relationships, as mentioned by Salje (1986), may well be present in aluminate sodalites.

For future work aimed at the determination of critical exponents of the phase transition, it may be preferable to concentrate on measuring the temperature dependence of the intensities of superstructure reflections, rather than measuring the splitting of main reflections as in the present study. Superstructure reflections should reflect the order parameter associated with the transition more directly. Thus, the problem of overlap, as encountered in the present study, could be avoided, or reduced, and access to the critical region becomes easier.

In order to compare SAM with other materials, it is convenient to use a scalar spontaneous strain, e_{sc}, such that $e_{sc} = (\Sigma e_i^2)^{1/2}$. With the e_i as defined above, and using the room-temperature values of a_t, c_t and a_0, we obtain 5.3×10^{-3}, a rather small value, which, however, is in good agreement with other improper ferroelastics (cf. Tolédano, 1974).

Thermal expansion

Fig. 1 indicates that below about $T_c - 100$ K the thermal expansion of both a_t and c_t becomes similar to that of a_c in the cubic phase. In the intermediate temperature range, a_t and c_t behave quasi-linearly and highly non-linearly, respectively. The cubic a_c curve extrapolates quite smoothly into that of a_t. Supposing a linear relationship between a_c or a_t, and T, and using the data points at 812 and 300 K, we can calculate the linear thermal-expansion coefficient $\alpha = 8.6\,(4) \times 10^{-6}\,K^{-1}$.

This value is smaller than that reported in the earlier neutron work (D&B): $12 \times 10^{-6}\,K^{-1}$. The reason for this discrepancy is that the value in D&B was calculated from the cube root of the pseudocubic cell volume, rather than from the a_t values as in the present work. If the neutron results are treated in the same manner, an excellent agreement is obtained.

Fig. 1 demonstrates that at temperatures well below T_c the thermal expansion of c_t is similar to that of a_t. Thus, it seems reasonable to assume that for α a value of about $8.5 \times 10^{-6}\,K^{-1}$ can be regarded as characteristic of a fully expanded aluminate sodalite, provided that the effects of the phase transition can be neglected.

Henderson & Taylor (1978) studied the thermal expansion for a whole series of synthetic alumino-silicate sodalites. Those sodalites which could be considered to be fully expanded, or to approach this state, showed coefficients α which are comparable with that of SAM. Sodalites with smaller lattice

constants, indicating partial collapse *via* the tilt mechanism, exhibited greater values. For higher degrees of partial collapse the behaviour became quite complex. Obviously, the contribution of the tilt mechanism to the thermal expansion is significant. For the fully expanded SAM no tilt mechanism is active. Furthermore, the (static) shearing mechanism is absent in the cubic phase, and can be supposed to be saturated in the region where a_t and c_t change linearly. The value of about $8.5 \times 10^{-6} \, K^{-1}$ for the linear thermal-expansion coefficient α should therefore be regarded as essentially reflecting the contribution from the normal bond-length expansion.

Concluding remarks

The present work was undertaken in order to shed some light on the phase transition behaviour of aluminate sodalites in general, and of the fully expanded SAM in particular. Special emphasis was given to the discussion of a special type of symmetry-breaking framework distortion, termed 'shearing', which is responsible for a volume reduction of the unit cell. The peculiarities of the phase transition of SAM at 571 K, *i.e.* the quasi-one-dimensional volume contraction of the unit cell, were explained by the proposed superposition of two strain components – associated with the shearing and a ferro-elastic distortion of the unit cell, respectively – such that both components add up for the tetragonal (pseudocubic) **c** lattice parameter, but cancel out for **a**. Power-law behaviour is observed for the coefficient of the spontaneous strain and for the excess volume, with exponents which indicate the nearly tricritical character of the transition. Deviations from the classical values are probably related to defects.

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Ionic Distribution in the Solid-State Laser Material Na$^+$/Nd^{3+} β''-Alumina

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Abstract

The crystal structure and ionic distribution in the conduction planes in neodymium-doped Na$^+$ β''-alumina [refined composition: $Na_{0.58\,(2)}Nd_{0.36\,(1)}Mg_{0.67}Al_{10.33}O_{17}$, $M_r = 632.2$] has been investigated at room temperature by single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). The layered structure of this solid laser-like material comprises spinel-type blocks of Al^{3+}, Mg^{2+} and O^{2-} ions which interleave two-dimensional conduction planes containing the Nd^{3+} and Na^+ ions. The spinel