

Role of internal pressure in a ferroelastic phase transition

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Abstract: It is shown that softening the acoustic mode, which brings about the occurrence of a proper ferroelastic phase transition in some crystals, is substantially due to the "kinematic" anharmonicity. The latter arises at the transition from the natural curvilinear coordinates of interatomic separation to the Cartesian atomic displacements. It is shown that the internal pressure may be represented as driving force for a proper ferroelastic phase transition induced by cation exchange. It has been found that the internal stress tensor, generated by the cation exchange, is of a more complicated nature than the tensor of the external stress. This difference comes from a specific coupling of the substituting cations with local, microscopic displacements of the neighbouring atoms inside the unit cell. It becomes evident why in a number of experiments a significant difference in the action of internal and external pressures on the crystal structure is observed and, also, why the internal pressure causes the greater anisotropy than the external one. We have obtained an equation for the crystals, in which the softening of the acoustic modes is caused only by the kinematic anharmonicity, with whose help we can predict either the external pressure of the ferroelastic phase transition to a triclinic phase if the initial elastic moduli are known or the internal pressure induced by cation exchange for the isotropic case.

Key-words: internal (chemical) pressure, Sr-anorthite, cation exchange, kinematic anharmonicity, soft acoustic modes, phase transitions.

1. Introduction

Ferroelastics are widely applied in acoustooptic and acoustoelectric devices. In addition, the basic features of ferroelastics, such as mechanical twinning, are observed in high temperature superconductors. Nevertheless, there is still some vagueness in the nature of ferroelastic phase transitions (FPTs). Currently a number of molecular-dynamics simulations and lattice-dynamics calculations of the soft modes, causing FPTs in crystals, have been made (see, for example, Dove & Redfern, 1997, or Watson & Parker, 1995). The analytical equations describing the mechanism of occurrence of the soft mode are absent in these simulations. It is believed that the symmetry-breaking strain arises spontaneously without any force being applied, occurring as a result of criticality in the elastic moduli. When studying the FPT according to the Landau theory, the free-energy expansion in terms of the critical parameter, breaking the crystal symmetry, is done. Thereafter it is postulated that the coefficient of the quadratic term of such an expansion falls to zero at the critical value of the external variable parameter. Thus, within this phenomenological approach, the mechanism causing the occurrence of the soft mode remains unclear. To understand this mechanism it is necessary to use a microscopic model, which is developed in the present work. As an example, which illustrates this model, we consider the proper monoclinic-triclinic FPT in Sr-anorthite (Sr,Ca)Al₂Si₂O₈. The physics of proper FPTs at high

pressures is of particular interest, when the crystal symmetry is reduced to the triclinic structure with subsequent amorphization. The occurrence of the latter has been demonstrated with anorthite and quartz (*e.g.* Redfern, 1996, and Ovsyuk & Goryainov, 1999, respectively). We have selected this compound, because there is a complete set of experimental data for it, namely, the experimental values of elastic constants, the experimental value of pressure for this transition, and the type of symmetry at transition. We consider a proper FPT, because the coupling mechanism of the edge and the angle deformations of the unit cell appears more evident. This is due to the fact that we can consider deformation of the entire unit cell, omitting displacements of individual atoms, as this takes place with improper phase transition with participation of microparameters. In the present work we try to clarify the most general reason for elastic instability of a crystal in the symmetric phase at the proper FPT. On the basis of the analysis made, using the "ball-and-perfect springs" model according to Mirgorodsky & Smirnov (1994), we come to the conclusion, that the basic mechanism causing a proper FPT in some crystals is the "kinematic" anharmonicity (Ovsyuk & Goryainov, 2002). It is shown that even in the expression for the free energy, when only the terms containing linear elastic moduli are taken into account, it is possible to obtain anharmonic terms by conserving the quadratic terms in the expression of the strains as functions of the space derivatives of the displacements. The above anharmonic terms are expressed by linear-quadratic

coupling between the non-symmetry-breaking strain components and the symmetry-breaking strain components. So far the softening of the acoustic mode at the proper FPT at the expense of this coupling has not been described. For example, Pouget (1991, 1993) uses the terms of third and fourth orders when expanding the free energy in the non-symmetry-breaking strain components. In contrast to the present work, the above-mentioned components do not cause changes in the crystal symmetry but give rise to the formation of modulated-strain structures. Cowley (1976) uses the terms of second and fourth orders in the expansion of the free energy, but does not consider the linear-quadratic coupling between the static strains and acoustic waves which form a part of the cubic anharmonicity. Anderson & Blount (1965) have considered the cubic term in the free-energy expansion in terms of the symmetry-breaking strain components, which are equal to zero in the symmetric phase for a nondegenerate order parameter. And in our work, the cubic term, i.e. the linear-quadratic coupling between the parameters of different symmetry, results in softening of the acoustic mode even in the symmetric phase. Thus, this term, as opposed to the above-mentioned work, is not equal to zero in the symmetric phase.

It should be recalled that, generally, non-symmetry-breaking and symmetry-breaking order parameters are represented as sum of static and dynamic parts: $Q_i = Q_{i\text{stat}} + Q_{i\text{dyn}}$. The static symmetry-breaking order parameters $Q_{i\text{stat}}$ describe a system in the thermodynamic equilibrium and they are equal to zero in the high-symmetry phase. In the considered case, the dynamic symmetry-breaking order parameters $Q_{i\text{dyn}}$ are caused by the acoustic lattice vibrations with the wave number q and the frequency $\omega(q)$ and they are present both in the high-symmetry and the low-symmetry phases. As the phase transition point is approached, the acoustic vibrations with the wave number q_y and the frequency $\omega(q_y)$ become softer. For the monoclinic-triclinic transition in anorthites, the change in the point group is $2/m \rightleftharpoons \bar{1}$, for which the active representation is B_g . The stability condition with respect to this

transition is given by the eigenvalue B_g of the symmetry-adapted dynamic matrix and is of the form: $(C_{44}C_{66} - C_{46}^2) > 0$. The dynamic matrix yields the soft acoustic mode with the propagation direction along Y axis and with the polarization $[-C_{46}/C_{66}, 0, 1]$ (Salje, 1993). The origin of anharmonicity and destabilization of a crystal is disguised in the dynamic matrix, as it is the product of the elastic-constant matrix and the kinematic coefficients matrix, which are responsible for the behaviour of normal modes of a crystal. As each of these matrices can serve as a source of anharmonicity, let us first consider the anharmonicity connected only with elastic-constant matrix. This "proper" anharmonicity generally leads to an increase in elastic constants with pressure and, consequently, to a decrease in the amplitude of the symmetry-breaking transverse acoustic vibrations. Hence, the proper anharmonicity brings about an increase in the structure stability, and this cannot be related to the appearance of instability.

2. Role of kinematic anharmonicity for the structural phase transitions

Let us now consider the anharmonicity connected only with the kinematic coefficients matrix. We assume and further this will be shown that the kinematic coefficients matrix, expressing the transition from the natural curvilinear q coordinates of interatomic separation to the Cartesian atomic displacements can result in an induced linear-quadratic coupling between the normal modes of different symmetry. The introduction of the curvilinear internal valence coordinates describing of molecular vibrations with the help of the displacements of bond distances and valence angles, reduces the number of dynamic potential parameters by inclusion of the kinematic anharmonic effects directly in the description of molecular vibrations. Let us illustrate this "kinematic" mechanism of occurrence of anharmonicity resulting in the softening of the optical vibrations at the improper phase transition in the triatomic molecule T-O-T. In

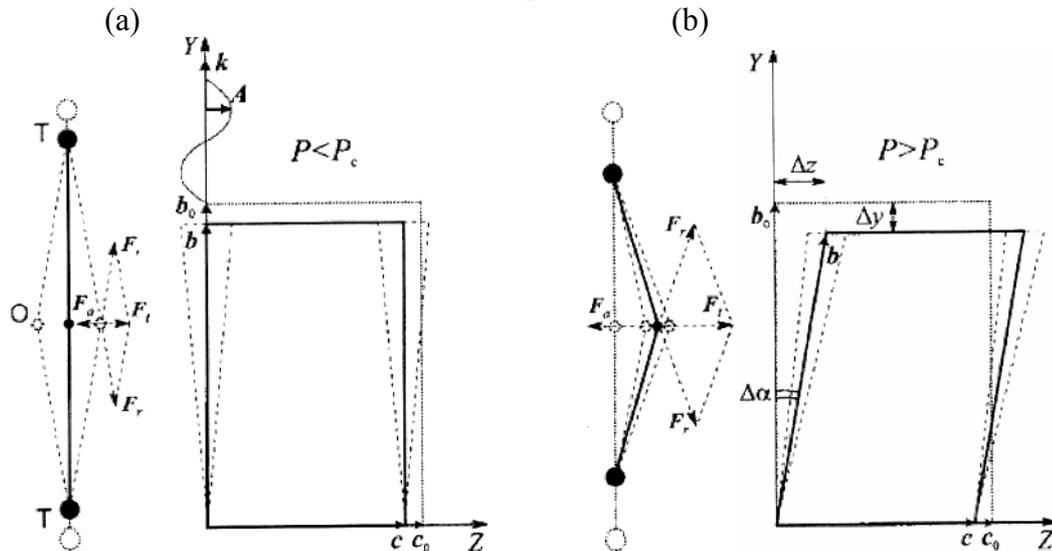


Fig. 1 . A schematic illustration of phase transitions under the effect of the hydrostatic pressure P and the transverse optical wave (the soft optical mode) for the triatomic T-O-T molecule and the transverse acoustic wave (the soft acoustic mode) for a monoclinic unit cell (a) before and (b) after phase transition.

Fig.1, the solid lines correspond to the static states of atoms in the thermodynamic equilibrium; the dashed lines correspond to the transverse optical vibrations of the O atom. If the molecule is contracted, the forces F_r (bond tensions) will arise. The sum of these forces gives the transverse force F_t which causes the linear-bend phase transition [see Fig. 1(b)], when $F_r > F_a$, where F_a is a restoring force, which is determined by the stiffness of the T-O-T angle. When verifying the model, the authors Mirgorodsky & Smirnov (1994) found out that in some crystals the kinematic anharmonicity completely describes soft optical modes at the improper phase transition. When analyzing the monoclinic-triclinic FPT we use similar reasonings for the soft acoustic modes, which have a number of essential differences from the optical modes. First, the frequency of the optical vibrations poorly depends on a wave vector, and the frequency of acoustic modes linearly depends on a wave vector and approaches zero at $\mathbf{k} = 0$, therefore dynamic matrices for these vibrations should differ. In addition, the volume of a unit cell does not vary for the optical modes at vibrations and under pressure, while it varies for the longitudinal acoustic modes, which can result in supplementary anharmonicity. Examination of the coupling between the acoustic modes is more complicated, since they occur from changes in the deformation tensor, while the optical modes, occurring from changes in the relative coordinates of atoms, are the vibrations having vector character. So, by analogy with the triatomic molecule, let us trace the occurrence of the transverse unstable forces which cause the monoclinic-triclinic FPT. We expect that when the hydrostatic pressure is applied to a unit cell, the symmetry-breaking destabilizing forces also occur due to the effect of stressed interatomic bonds. Let us consider a monoclinic unit-cell with a plane of symmetry with the normal oriented along Y axis (see Fig. 1). Let us take the quadratic expansion of the free deformation energy of this cell in the natural curvilinear internal valence q coordinates $(\Delta r_i, \Delta \varphi_k)$:

$$F = \sum_{ij} C_{ij}^0 (\Delta r_i / r_{0i}) (\Delta r_j / r_{0j}) / 2 + \sum_{kl} C_{kl}^0 \Delta \varphi_k \Delta \varphi_l / 2 + \sum_{ik} C_{ik}^0 (\Delta r_i / r_{0i}) \Delta \varphi_k \quad (1)$$

where $i, j = 1, 2, 3$; $k, l = 4, 5, 6$; C_{ij}^0, C_{kl}^0 are the initial elastic moduli for the high-symmetry phase; Δr_i and $\Delta \varphi_k$ are the displacements of bond distances and valence angles from equilibrium values; r_{0i} are the lattice parameters prior to deformation. Note that we consider the quadratic expansion of the free energy in equation (1), assuming the contribution of the next cubic term of expansion to be insignificant, *i.e.* we use the "perfect springs" model and hence the anharmonicity connected with a change of the elastic constants of interatomic bonds is not taken into account. For simplicity, we consider the two-dimensional distortion of the side $b_0 c_0$ of the unit cell. This distortion includes the compression strains of the edges b_0, c_0 , and the shear strain α . It is seen from Fig. 1(b) that for small deformations $\Delta \alpha = \Delta z / b_0$, where b_0 is the lattice parameter along the Y axis prior to deformation. Now the quadratic expansion of free energy is written down as

$$F = C_{22}^0 (\Delta b / b_0)^2 / 2 + C_{23}^0 (\Delta b / b_0) (\Delta C / C_0) / 2 + C_{33}^0 (\Delta C / C_0)^2 / 2 + C_{44}^0 (\Delta z / b_0)^2 / 2. \quad (2)$$

Now let us present this energy in terms of the Cartesian atomic displacements. As far as the edge b_0 deviates in the Z direction under the effect of the acoustic wave, the expansion of the Δb may be written as

$$\Delta b = [(b_0 + \Delta y)^2 + (\Delta z)^2]^{1/2} - b_0 \cong \Delta y + (\Delta z)^2 / 2b_0. \quad (3)$$

It is seen that Δb involves both the linear components along Y axis and the quadratic components along the perpendicular Z axis. That is just a result of the action of the kinematic matrix and nonlinear transformation from the natural q coordinates to the Cartesian coordinates. Physically, this means that the linear strains in the curvilinear q space of interatomic separation would provide nonlinear strains in the rectangular x space, in which atomic displacements are considered. As a result, we obtain that the expansion in equation (3) may be written down as $\Delta b / b_0 = e_2 + e_4^2 / 2$, as in the monoclinic cell $\Delta \varphi_4 = \Delta \alpha = -e_4$. As a result we obtain the following expression for the Gibbs energy

$$G = F + p_{ext} V \cong C_{22}^0 e_2^2 / 2 + C_{23}^0 e_2 e_3 + C_{33}^0 e_3^2 / 2 + (C_{22}^0 e_2 + C_{23}^0 e_3 + C_{44}^0) e_4^2 / 2 + P_{ext} (e_2 + e_3). \quad (4)$$

From this equation it follows that the static non-symmetry-breaking strain components e_{2stat} and e_{3stat} enter the linear-quadratic coupling with symmetry-breaking strain component e_{4dyn} , causing the change of force constants of transverse vibrations. Hence the elastic modulus for the deformation, which breaks the crystal symmetry so that $\varphi_4 \neq 90^\circ$, may be written down as

$$C_{44} = \partial^2 G / \partial e_4^2 = b_0^2 \partial^2 F / \partial z^2 = C_{44}^0 + C_{22}^0 e_2 + C_{23}^0 e_3. \quad (5)$$

In equilibrium, for high-symmetric phase it follows that $\partial G / \partial e_2 = C_{22}^0 e_2 + C_{23}^0 e_3 + P_{ext} = 0$. Hence

$$C_{44} = C_{44}^0 - P_{ext}. \quad (6)$$

It is seen that the elastic modulus C_{44} is softened with an increase in pressure and becomes zero, *i.e.*, the acoustic instability arises at the critical pressure:

$$P_c = C_{44}^0. \quad (7)$$

Thus in our model the coupling between the acoustic modes of different symmetry which equals " $-P_{ext}$ " linearly grows in absolute magnitude with pressure and cannot be neglected as it was done in the recent review by Carpenter & Salje (1998). As mentioned above, the amplitude vector components are present both along the Z and X axes in the soft acoustic mode. Therefore the second symmetry-breaking parameter e_6 , which is also softened with increasing pressure, is to be introduced into equation (4) to obtain a more accurate quantitative estimation. As the edge b_0 declines in X and Z directions under the effect of the acoustic wave, the expansion Δb will have the following form:

$$\Delta b / b_0 \cong \Delta y / b_0 + (\Delta x)^2 / 2b_0^2 + (\Delta z)^2 / 2b_0^2 = e_2 + e_4^2 / 2 + e_6^2 / 2. \quad (8)$$

As the tensor components e_4 and e_6 interact, a combination of the moduli $C_{44}C_{66} - C_{46}^2$ tends to zero faster than a separate modulus C_{44} . In this case, after substitution of expansion (8) into the Gibbs potential, we obtain: $C_{44}C_{66} - C_{46}^2 = (C_{44}^0 - P_{ext})(C_{66}^0 - P_{ext}) - C_{46}^2 = 0$ at the transition point. Hence

$$P_c = (C_{44}^0 + C_{66}^0)/2 - [(C_{44}^0 + C_{66}^0)^2/4 - C_{44}^0 C_{66}^0 + C_{46}^2]^{1/2}. \quad (9)$$

Using the data $C_{44}^0 = 11.5$ GPa, $C_{66}^0 = 24.6$ GPa, $C_{46}^0 = -12.9$ GPa, for the initial moduli of Sr-anorthite from Dove & Redfern (1997), we have $P_c = 3.6$ GPa, and the experimental pressure from McGuinn & Redfern (1994b) for this transition is (3.2 ± 0.4) GPa. When deriving equation (9) we used the perfect springs model, where the kinematic anharmonicity can arise as the result of the transition from natural curvilinear atomic q coordinates (interatomic bonds and angles between them) to Cartesian coordinates of the atomic displacements. Therefore the coincidence between equation (9) and experiment has appeared to be unexpected, since this means that predominantly kinematic anharmonicity brings about a decrease of the sound velocity with pressure, when all other anharmonicities are neglected, *i.e.*, thus leading to instability of the anorthite crystal lattice. It turned out that berlinite AlPO_4 [$P_c \approx 15$ GPa according to Gillet *et al.*, (1995)], quartz SiO_2 [$P_c \approx 22$ GPa according to Gregoryanz *et al.*, (2000)], and natrolite $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}] \cdot 16\text{H}_2\text{O}$ [$P_c \approx 3$ GPa according to Goryainov & Smirnov, (2001)] behave like anorthite at transition from different symmetry phases to the triclinic one. The experimental pressures of the transitions, shown in the brackets, approximately coincide with the pressures obtained from equation (9). The above-indicated crystals as well as anorthite have the elastic stability condition $(C_{44}C_{66} - C_{46}^2) > 0$ with respect to the transition to the triclinic phase. We cannot check up equation (9) for other crystals because of the absence of a complete set of experimental data, namely, the experimental values of elastic constants, the experimental value of pressure for the phase transition and the type of symmetry at transition. However, we believe that it is possible to obtain similar equations for the FPT in other crystals if we use combinations of the elastic moduli, expressing the elastic stability conditions given in Cowley (1976) to be appropriate for the transitions in these crystals as well as the mechanism of the softening of the shift moduli considered in the present work. This mechanism is based on the fact that each shift modulus linearly falls with pressure, which is in line with the kinematic anharmonicity.

3. Difference of the action of the external and the internal pressures on the crystal structure

Now we consider the proper monoclinic-triclinic FPT in Sr-anorthite induced by Ca and Sr cation exchange rather than by the external pressure, as it was described above. In other words, the same approach is used for the case of the internal (chemical) pressure. Owing to the fact that the Ca^{2+} radius is smaller than the Sr^{2+} ionic radius, the effective radius of the A-site decreases with increasing Ca content, thus enhances

the internal strain in the crystal. We believe that this "chemical" tension of the interatomic bonds is most convenient to use as thermodynamic parameter of the Gibbs potential instead of a usual cation content, because a correct physical description of the FPT requires a consideration of both the atomic displacements and the forces which cause them. We will try to show the validity of the introduction of internal (chemical) pressure into the Gibbs potential as the driving force for the proper FPT, because the internal pressure is interpreted by many scientists as an imaginary, unreal and unobservable value.

Based on papers (Ulyanov *et al.*, 2001; Radaelli *et al.*, 1997; Marezio *et al.*, 2000a; Moron *et al.*, 1996; Marezio *et al.*, 2000b; Itoh *et al.*, 2001; Licci *et al.*, 1998; Huang *et al.*, 1998), which deal with the internal pressure in crystals, it follows that the internal pressure is a real value which is capable of going into action differing from the external pressure. For example, according Ulyanov *et al.* (2001) conclude that the "chemical" pressure is a more complicated parameter than the mechanical one. Various types of the "chemical" pressure can lead to the $Pbnm-R \bar{3}c$ phase transition in manganites with different signs of cell volume change. According to Radaelli *et al.* (1997), the authors find an unexpected minimum of Mn-O bond lengths in manganites as a function of cation radius and connect it with the reversal of sign of the internal pressure. This reversal of sign of the internal pressure could, in fact, be a common effect in perovskites, which deserves to be explored in other materials as well. They advocate that application of the external pressure on these compounds produces quite different structural effects than the "internal" pressure. In Marezio *et al.* (2000a), the authors believe the application of the mechanical pressure to copper-oxide superconductors to induce an increase in Curie temperature T_c . If the mechanical pressure is replaced by a chemical one, the effect becomes negative and a decrease of T_c is observed. In addition, it was observed that the chemical pressure anisotropy is greater than the mechanical one. To sum up, we can say that, first, the experiments show that the internal pressure brings about a greater anisotropy. And, second, at the present time, the cause of the fact that the internal and the external pressures in anisotropic materials are not similar parameters, is poorly understood.

Let us discuss how to describe the difference of the action of the external P_{ext} and the internal P_{int} pressures on the crystal structure and why the internal pressure is a more complicated parameter, bringing about a greater anisotropy. Let us dwell on the crystal compressed by the hydrostatic pressure P_{ext} . A complete description of the geometrical structure of a lattice is given by 6 independent parameters determining a primitive cell (three lengths of the translation vectors and three corners between them) and by $3n$ coordinates of the atoms in the cell (n is the number of atoms in a primitive cell). The basis of the internal deformations is determined by a set of atomic Cartesian displacements x , identical in all primitive cells, *i.e.* by the shifts of the absolutely rigid reciprocal Bravais sublattices. It is clear that from $3n$ internal deformations only $(3n - 3)$ are linear-independent deformations, and 3 correspond to translations of the crystal as a whole. The external deformations are determined by a 6-dimensional basis,

which is given by the deformation tensor \mathbf{E}_{ij} of second rank, with diagonal elements describing relative changes of the linear sizes of a crystal along the Cartesian axes, and non-diagonal elements describing the shear deformations (Born & Huang, 1954). The absolute Cartesian coordinates of the atomic displacement \mathbf{X} are clearly related to the deformation tensor of a primitive cell \mathbf{E} and to the change of the atomic coordinate \mathbf{x} inside the primitive cell relative to the chosen centre of masses with the coordinates \mathbf{R} by the following correlation: $\mathbf{X} = \mathbf{x} + \mathbf{E}\mathbf{R}$. The change of the density of the Gibbs free energy as function of \mathbf{x} and \mathbf{E} is written down in quadratic approximation as

$$G(\mathbf{x}, \mathbf{E}) = -\mathbf{f}_x \mathbf{x} - \mathbf{f}_E \mathbf{E} + \mathbf{x} \mathbf{F}_{xx} \mathbf{x} / 2 + \mathbf{x} \mathbf{F}_{xE} \mathbf{E} + \mathbf{E} \mathbf{F}_{EE} \mathbf{E} / 2, \quad (10)$$

where we use the tensor notation for derivatives $\mathbf{f}_x = -\partial G / \partial \mathbf{x}$, $\mathbf{f}_E = -\partial G / \partial \mathbf{E}$, $\mathbf{F}_{xx} = \partial^2 G / \partial \mathbf{x} \partial \mathbf{x}$, $\mathbf{F}_{xE} = \partial^2 G / \partial \mathbf{x} \partial \mathbf{E}$, $\mathbf{F}_{EE} = \partial^2 G / \partial \mathbf{E} \partial \mathbf{E}$, initially taken at $\mathbf{x} = 0$, $\mathbf{E} = 0$.

In equilibrium a crystal should satisfy the following conditions: 1) the internal resulting forces on any atom be equal to $\mathbf{f}_x = 0$; 2) the external forces, acting on a unit cell are $\mathbf{f}_E = (\sigma_{ext})_{ij} = -P_{ext} \delta_{ij}$, because the hydrostatic pressure corresponds to the diagonal stress tensor, which has equal components $\sigma_{ii} = -P_{ext}$ for isotropic crystals; 3) in equilibrium, the Gibbs potential has a minimum relative to the internal atomic displacements \mathbf{x} and the deformations \mathbf{E} : $\mathbf{F}_{xx} \mathbf{x} + \mathbf{F}_{xE} \mathbf{E} = 0$, $\mathbf{F}_{xE} \mathbf{x} + \mathbf{F}_{EE} \mathbf{E} + P_{ext} \delta_{ij} = 0$. Taking into account these equilibrium conditions, the Gibbs potential can be reduced to the form: $G(\mathbf{E}) = P_{ext} V + \mathbf{E} \mathbf{C} \mathbf{E} / 2$, where $F = \mathbf{E} \mathbf{C} \mathbf{E} / 2$ is a free energy in quadratic approximation, $V \approx E_{11} + E_{22} + E_{33}$ is a relative change of the volume of a unit cell and the matrix of elastic constants \mathbf{C} is determined as

$$\mathbf{C} = \mathbf{F}_{EE} - \mathbf{F}_{xE} \mathbf{F}_{xx}^{-1} \mathbf{F}_{xE} \quad (11)$$

It is seen that these elastic moduli are of a complex origin (see also Mirgorodsky *et al.* (1995) and Cousins (2001)) because the first term on the right-hand side of equation (11) is a contribution of the external deformations, and the second term is a contribution of the internal deformations. It is evident from this equation that just the second term, which is connected with the optical-acoustic coupling \mathbf{F}_{xE} , determines the ferroelastic instability.

Now, we can consider the origin of the internal pressure in the process of the cation exchange. In this case, the introduction of the new ions generally produces an overall cell deformation \mathbf{E} as well as a change in local atoms coordinates \mathbf{x} . Two tensors correspond to these two kinds of the deformations: σ_{dir} (direct) - the mechanical stress tensor, directly affecting the lattice parameters due to the change in radii of nodal atoms in the lattice in the process of the cation exchange, and σ_{ind} (indirect) - the mechanical stress tensor, indirectly affecting the lattice parameters due to the change in radii of non-nodal atoms inside a unit cell. Thus, the complete tensor of the internal stress is equal to $\sigma_{int} = \sigma_{dir} + \sigma_{ind}$. In this case, the forces, responsible for the direct coupling with lattice parameters, are $\mathbf{f}_E = (\sigma_{dir})_{ij} = -P_{dir} \delta_{ij}$ and, also, the internal resulting forces on atoms, responsible for the indirect coupling with lattice parameters, are $\mathbf{f}_x = -\partial G / \partial \mathbf{x}$. We emphasize that $\mathbf{f}_x \neq 0$ only when these forces act on the atoms at sites lacking inversion symmetry (Cousins, 2001). In

equilibrium, the Gibbs potential has a minimum relative to the internal atomic displacements \mathbf{x} and the deformations \mathbf{E} : $\mathbf{F}_{xx} \mathbf{x} + \mathbf{F}_{xE} \mathbf{E} - \mathbf{f}_x = 0$, $\mathbf{F}_{xE} \mathbf{x} + \mathbf{F}_{EE} \mathbf{E} - \sigma_{dir} = 0$. The solution to this system of equations is the following:

$$\begin{aligned} \mathbf{x} &= \mathbf{F}_{xx}^{-1} (1 + \mathbf{F}_{xE} \mathbf{C}^{-1} \mathbf{F}_{xE} \mathbf{F}_{xx}^{-1}) \mathbf{f}_x + \mathbf{F}_{xx}^{-1} \mathbf{F}_{xE} \mathbf{C}^{-1} \sigma_{dir}, \\ \mathbf{E} &= -\mathbf{C}^{-1} \mathbf{F}_{xE} \mathbf{F}_{xx}^{-1} \mathbf{f}_x - \mathbf{C}^{-1} \sigma_{dir} = -\mathbf{C}^{-1} (\sigma_{ind} + \sigma_{dir}) = -\mathbf{C}^{-1} \sigma_{int} \end{aligned} \quad (12)$$

where $\sigma_{ind} = -\mathbf{F}_{xE} \mathbf{F}_{xx}^{-1} \mathbf{f}_x$ and \mathbf{C} is determined by equation (11).

It is clear that the tensor σ_{int} , generated by the cation exchange, is of a more complicated nature than the tensor of the external stress, because not only the term which is similar to the external pressure, but also the anisotropic term σ_{ind} is present. This difference comes from a specific coupling of the substituting cations with local, microscopic displacements of the neighbouring atoms inside the unit cell. Thus, the macroscopic strain is partly a secondary effect of the cation exchange, whereas it is a primary effect of an external stress. In the first approximation, this internal stress can be expressed in terms of the isotropic internal pressure $(\sigma_{int})_{ij} = -P_{int} \delta_{ij}$. It is seen from equation (12) that the term σ_{ind} is anisotropic, therefore its approximation by the internal pressure is rough and it is appropriate only for the isotropic crystals. Also, this approximation is possible due to the presence of spherically symmetrical cations in the cation exchange making all relevant forces spherically symmetrical or isotropic (assuming a disordered cation arrangement). Spontaneous strain, caused by internal isotropic pressure, can be anisotropic because of the anisotropy of elastic constants. Now it is possible to give the following definition of the internal pressure: **“internal pressure due to the concentration N of new ions is equal to such an external pressure which at the presence of additional forces on atoms \mathbf{f}_x would result in the same macroscopic deformation as does the concentration N ”**.

We believe that the internal pressure can be experimentally measured. In Gibson & Chernuschenko (1999) and Wen *et al.* (1996), the authors declare that Cr^{3+} containing crystals have been extensively used to measure temperature and pressure, since Cr^{3+} ions exhibit the strong luminescent lines of R_1 and R_2 . The origin of the R fluorescence lines is a radiative decay of excited d^3 electrons of substitutional Cr^{3+} ions. The ions are in octahedral coordination with the oxygen ions in the corundum structure. When the octahedral arrangement is strained, the crystal field at Cr^{3+} ions alters, and consequently the frequency of R lines changes. This is the basis for high-pressure measurements in diamond-anvil cells and for the measurement of stresses in ce-ramics and composites (Ma & Clarke, 1993). We expect that if we manage to introduce Cr-ions into the solid solutions of $(\text{Sr}, \text{Ca})\text{Al}_2\text{Si}_2\text{O}_8$ with different content of substituting cations, then we will be able to measure the value of the internal pressure due to the cation exchange by the shifts of the luminescent lines R_1 and R_2 in the spectra of each sample.

4. Comparison of model and experimental dependences

Hereinafter we are going to study the Gibbs potential for Sr-anorthite, using for simplicity the internal pressure

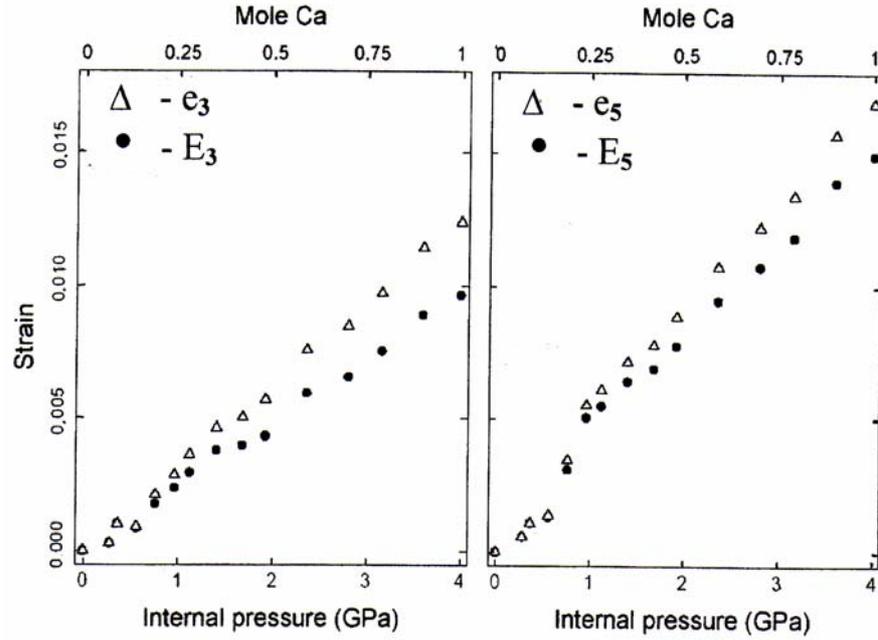


Fig. 2. Differences between the dependences of the components of the linear e_i (triangles) and finite E_i (circles) strain tensors on the internal pressure and the molar content of Ca. The curves were obtained using the unit cell parameters of Sr-anorthite in McGuinn & Redfern (1994a).

approximation: $G(\mathbf{E}) = P_{\text{int}}V + \mathbf{E} \mathbf{C} \mathbf{E} / 2$. The linear Lagrangian strain tensor of the form $e_{ij} = (1/2)(\partial u_i / \partial x_{0j} + \partial u_j / \partial x_{0i})$ is commonly used to describe the FPT. As in the process of the phase transition, spontaneous deformation increases, it may appear that non-linear terms should be taken into account in the strain tensor. This tensor is called finite and defined as $E_{ij} = (1/2)[(\partial u_i / \partial x_{0j} + \partial u_j / \partial x_{0i}) + \sum_k (\partial u_k / \partial x_{0i})(\partial u_k / \partial x_{0j})]$, where the vector $\mathbf{u} = \mathbf{x} - \mathbf{x}_0$ determines displacements of a point, located at \mathbf{x}_0 prior to deformation and at \mathbf{x} after the deformation. The indices i, j, k correspond to Cartesian coordinates, each of them running from 1 to 3. For the sake of convenience of comparison with experiment, we shall express the components of the strain tensor in terms of the crystal lattice parameters. The corresponding expressions for the components of the linear strain tensor in the explicit form are obtained in Schlenker *et al.*, (1978). We have obtained the relations for the components of the finite strain tensor, which can be expressed in terms of the components e_{ij} in the Voigt notations with the unique b axis in the following form: $E_1 = e_1 + e_1^2/2 + e_6^2/2$; $E_2 = e_2 + e_2^2/2$; $E_3 = e_3 + e_3^2/2 + e_4^2/2 + e_5^2/2$; $E_4 = e_4 + e_2e_4$; $E_5 = e_5 + e_1e_5 + e_4e_6$; $E_6 = e_6 + e_2e_6$;

Substituting the experimental crystal lattice parameters for Sr-anorthite (McGuinn & Redfern, 1994a) into the above formulas, we found that the corresponding components of the linear and the finite strain tensors are greatly distinguished (Fig. 2). Hence, to minimize the error in calculations of the FPT, the finite strain tensor has to be applied.

For the completeness of the system of equations, it is also necessary to describe the dependence of the internal pressure on some thermodynamic parameters. In the first approximation, this pressure can be considered as linear function of the cation content. Then the system of equations for the FPT will take the form

$$\frac{\partial G(E_m, P_{\text{int}})}{\partial E_m} = 0,$$

$$P_{\text{int}} = \alpha N,$$

13)

where $G(E_m, P_{\text{int}})$ is the Gibbs potential, $m = 1, 2, \dots, 6$, α is a linear coefficient, N is the molar fraction of the substituting cations.

Now let us choose the terms of the free energy expansion so that they gave the best fit to the experimental data (McGuinn & Redfern, 1994a). Since the component E_4 of the finite tensor is maximum and breaks the symmetry of a monoclinic crystal, we take the expansion of a part of the free energy in the parameter E_4 up to the term E_4^6 : $F_4 = A_4 E_4^2/2 + B_4 E_4^4/4 + C_4 E_4^6/6$, where all the coefficients are constants. Let us emphasize that we do not state the vanishing of the coefficient A_4 at the critical value of a thermodynamic parameter as it was done in the Landau phenomenological theory. The component E_6 of the finite-strain tensor also breaks the symmetry, but it is much smaller than E_4 in the phase transition area, so we take the expansion of a part of the free energy in the parameter E_6 up to the term E_6^4 : $F_6 = A_6 E_6^2/2 + B_6 E_6^4/4$, where the coefficients A_6 and B_6 are constants, independent of Ca/Sr ratio. It turned out that it was necessary to introduce supplementary terms E_4^4 , E_6^4 and E_4^6 into the elastic energy to better approximate the experimental data from McGuinn & Redfern (1994a). It should be underlined that these terms are correction ones, not affecting the occurrence of a soft mode. In order that the main regularities of the FPT in the analytical form be simplified, we have taken only one bilinear term, dropping the biquadratic and linear cubic terms when describing the coupling of the parameters E_4 and E_6 with the same symmetry: $F_{\text{asym}} = A_{4-6} E_4 E_6$. The coupling of the non-symmetry-breaking strain components is expressed by an ordinary quadratic elastic strain: $F_{\text{sym}} = \sum_{ij} A_{ij} E_i E_j / 2$, with the indices $i, j = 1, 2, 3, 5$.

We have shown above that the soft acoustic mode, causing the proper monoclinic-triclinic FPT in anorthite, is mainly due to the "kinematic" anharmonicity, which is expressed by the linear-quadratic coupling of the static non-symmetry-breaking and the dynamic symmetry-breaking

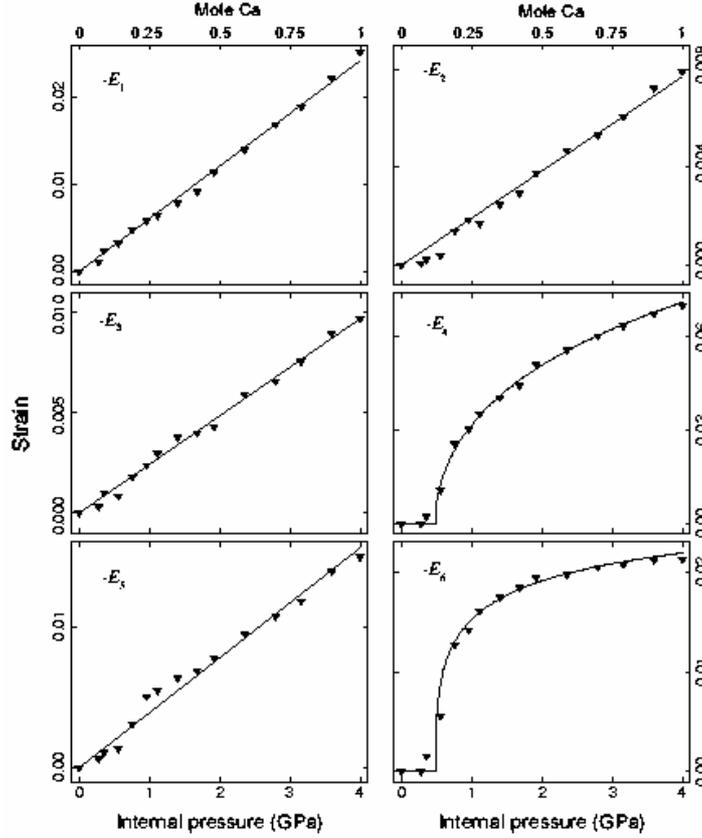


Fig. 3. Comparison of dependences of model (solid lines) and experimental (triangles) components of the strain tensors from McGuinn & Redfern (1994a) on the internal pressure and the molar content of Ca. Here the internal pressure is measured from Sr-phase of the crystal, where $P_{\text{int}} = 0$.

strain components. Here we use the same approach, but in this case the static non-symmetry-breaking strain components are caused by the internal pressure instead of the external one. Therefore, to take into account the coupling of the non-symmetry-breaking as well as the symmetry-breaking strain components, we made use of the linear-quadratic terms only: $F_{\text{inter}} = (\sum_j D_{4j} E_j) E_4^2 / 2 + (\sum_j D_{6j} E_j) E_6^2 / 2$, with the indices $j = 1, 2, 3, 5$. For the soft acoustic mode with the propagation direction along the crystallographic Y -axis, $F_{\text{inter}} = \sum_j C_{2j} E_j (E_4^2 + E_6^2) / 2$. Now the total free energy is written down as $F = F_4 + F_6 + F_{\text{sym}} + F_{\text{asym}} + F_{\text{inter}}$.

When solving the system of equations (13), the dependences of the spontaneous strain tensor components on the value of the internal pressure are determined when the Ca content increases. Four non-symmetry-breaking strain components are linearly dependent on the internal pressure:

$$E_j = k_j P_{\text{int}}, \quad (14)$$

with the indices $j = 1, 2, 3, 5$. Here the coefficients k_j are the linear compressibility of a crystal along the Cartesian axes, which can be determined by the elements of the compliance matrix $\mathbf{S} = \mathbf{C}^{-1}$ as follows: $k_j = \sum_m S_{jm}$. Substituting E_j in the above-mentioned terms of the linear-quadratic coupling yields the coefficients of the quadratic terms $E_4^2/2$ and $E_6^2/2$ in the free-energy expansions equal to $A_4 + \sum_j D_{4j} S_j P_{\text{int}}$

and $A_6 + \sum_j D_{6j} S_j P_{\text{int}}$. It is clear that these coefficients fall to zero at partial critical pressures $P_{c1} = -A_4 / \sum_j D_{4j} S_j$ and $P_{c2} = -A_6 / \sum_j D_{6j} S_j$. The symmetry-breaking strain components E_4 and E_6 are zero at the monoclinic phase at $P_{\text{int}} < P_c$, where P_c is the experimental pressure of the phase transition. At the triclinic phase, at $P_{\text{int}} \geq P_c$, to a first approximation, the analytical expressions for E_4 and E_6 in the phase transition are the following:

$$\begin{aligned} E_4 &\cong -\{-B_4/2C_4 + [(B_4/2C_4)^2/4 - L]^{1/2}\}^{1/2}, \\ E_6 &\cong [-Q + (Q^2 + S^3)^{1/2}]^{1/3} + [-Q - (Q^2 + S^3)^{1/2}]^{1/3}, \end{aligned} \quad (15)$$

where $S = (A_6 - P_{\text{int}}) / 3B_6$, $Q = A_{4-6} E_4 / 2B_6$, $L = [(A_4 - P_{\text{int}})(A_6 - P_{\text{int}}) - A_{4-6}^2] / C_4(A_6 - P_{\text{int}})$.

A real non-zero solution is possible at $L \leq 0$. The phase transition pressure at $L = 0$ is

$$P_c = (A_4 + A_6) / 2 - [(A_4 + A_6)^2 / 4 - A_4 A_6 + A_{4-6}^2]^{1/2}. \quad (16)$$

Here, the critical phase transition pressure is different from the partial critical pressures P_{c1} and P_{c2} due to the coupling of the components E_4 and E_6 . Now the elastic constants C_{44} , C_{46} and C_{66} can be obtained in the usual way: $C_{44} = \partial^2 G / \partial E_4^2 = A_4 - P_{\text{int}}$, $C_{46} = \partial^2 G / \partial E_4 \partial E_6 = A_{4-6}$ and $C_{66} = \partial^2 G / \partial E_6^2 = A_6 - P_{\text{int}}$. It is seen that P_c is the solution to the equation $C_{44} C_{66} - C_{46}^2 = 0$. As is shown in Carpenter &

Salje (1998), the monoclinic-triclinic phase transition in feldspars is driven by the instability associated with the same combination of elastic constants, which confirms the validity of our model.

For the experimental data E_j ($j = 1, 2, 3, 5$) presented in Fig. 3, we substituted the content of Ca cations along the abscissa for the internal pressure in the following manner. In our model, we describe the behaviour of the crystal structure with the help of the average internal pressure for the three directions along the Cartesian axes $P_{\text{int}} = 1/3(P_{\text{int}1} + P_{\text{int}2} + P_{\text{int}3})$. We equated the theory to the experiment in the extreme right points along the abscissa with the help of the following formula: $P_{\text{int}} = \sum_j C_{ij} E_j$, where $j = 1, 2, 3, 5$, and $i = 1, 2, 3$. The values of the non-symmetry-breaking strain components E_j were taken from Fig.3 for Ca-anorthite, *i.e.*, for $N = 1$, and the values of the elastic moduli for these points were borrowed from Ryzhova (1964). It has been estimated that the internal pressure obtained for $x = 1$ in $\text{Ca}_x\text{Sr}_{1-x}\text{Al}_2\text{Si}_2\text{O}_8$ solid solution is equivalent to the mechanical pressure of about 4 GPa. Hence, from the formula $P_{\text{int}} = \alpha N$, it follows that $\alpha \cong 4$ GPa. In this case, it is not difficult to calculate P_{int} for any N .

It should be noted that equation (9) is in good agreement with the experimental external pressure at which a FPT occurs, while the internal pressure obtained from a similar equation (16), differs by almost one order of magnitude. According to our model from equation (16), $P_c \cong 0.43$ GPa, and the external pressure for this transition is 3.2 GPa (McGuinn & Redfern, 1994b). This difference can be conditioned by several reasons. The first reason is that it can be caused by the fact that the term σ_{ind} is anisotropic, therefore its approximation by the internal pressure is rough and it is appropriate only for the isotropic crystals. Second, as we have mentioned above, that the external pressure changes the elastic moduli as a result of anharmonicity of the interatomic potentials, while the internal pressure contains the term $F_{xE} \mathbf{F}_{xx}^{-1} \mathbf{f}_x$ which acts directly on the chemical bonds and, consequently, changes the elastic constants more effectively. Third, the internal forces \mathbf{f}_x can change the phase transition pressure owing to interaction of the optical and the acoustic modes F_{xE} .

5. Conclusion

To conclude, it should be noted that we have obtained an equation, with the help of which it appears possible to predict the internal pressure of the proper monoclinic-triclinic ferroelastic phase transition if the initial effective elastic moduli are known. It is shown that the internal pressure may be represented as a driving force for the proper ferroelastic phase transitions induced by cation exchange. It has been found that the internal stress tensor, generated by cation exchange, is of a more complicated nature than the tensor of external stress. This difference comes from a specific coupling of the substituting cations with local, microscopic displacements of the neighbouring atoms inside the unit cell. Thus, it becomes evident why in a number of experiments a significant difference in the action of the internal and the external pressures on the crystal structure is observed and, also, why the internal pressure causes a greater

anisotropy than the external one.

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