

**Mechanism of occurrence of soft mode at proper ferroelastic phase transitions**

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It is shown that softening the acoustic mode, which brings about the occurrence of the 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. The equation for such crystals has been obtained, with whose help it appears possible to predict the pressure of the phase transition to a triclinic phase if the initial elastic moduli are known.

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Currently a number of molecular-dynamics simulations and lattice-dynamics calculations of the soft modes, causing ferroelastic phase transitions (FPT's) in crystals, have been made.<sup>1,2</sup> 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)Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>]. 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 the proper FPT, because the coupling mechanism of the edge and the angle deformations of a 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 this 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,<sup>3</sup> we come to a conclusion that the basic mechanism causing the proper FPT in some crystals is the “kinematic” anharmonicity. 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<sup>4,5</sup> 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<sup>6</sup> uses the terms of second and fourth orders in 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 and Blount<sup>7</sup> 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 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 the sum of static and dynamic parts:  $Q_i = Q_{istat} + Q_{idyn}$ . The static symmetry-breaking order parameters  $Q_{istat}$  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  $Q_{idyn}$  are caused by the acoustic lattice vibrations with the wave number  $\mathbf{q}$  and the frequency  $\omega(\mathbf{q})$  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  $\mathbf{q}_y$  and the frequency  $\omega_j(\mathbf{q}_y)$  become softer. For the monoclinic-triclinic transition in anorthites, the change in the point group is  $2/m \Rightarrow \bar{1}$ , 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 the  $Y$  axis and with the polarization  $[-c_{46}/c_{66}, 0, 1]$ .<sup>8</sup> 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 behavior of normal modes of a crystal. As each of these matrices can serve as a source of anharmonicity, let us first consider the anharmonicity con-

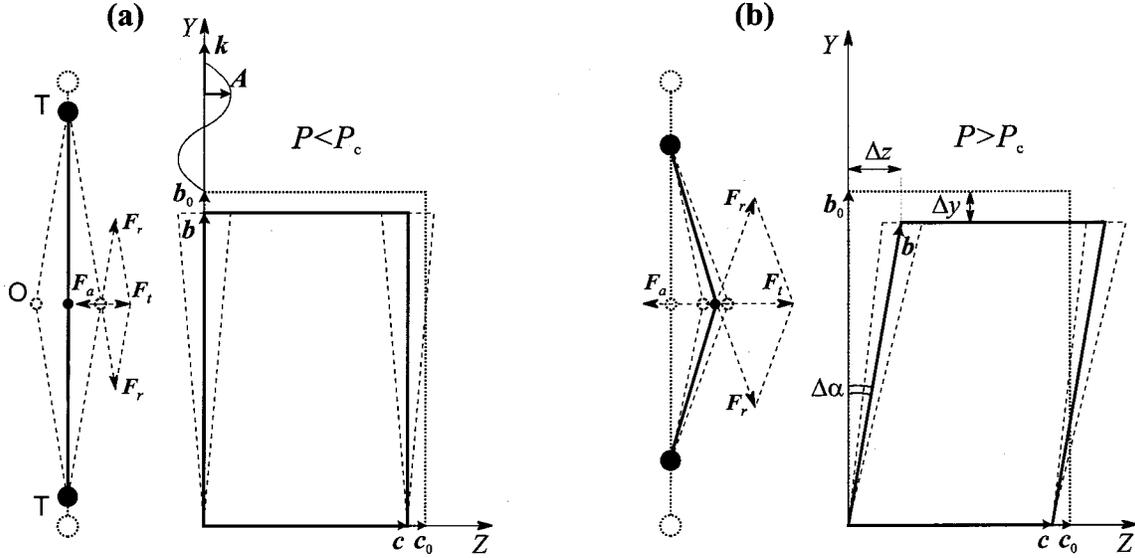


FIG. 1. Schematic illustration of phase transitions under the effect of the hydrostatic pressure  $P$  and the transverse optical wave (the soft optical mode) for the triatomic T-O-T molecule and the transverse acoustic wave (the soft acoustic mode) for a monoclinic unit-cell (a) before and (b) after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

nected 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.

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 the induced linear-quadratic coupling between the normal modes of different symmetry. Let us illustrate this “kinematic” mechanism of occurrence of the anharmonicity resulting in the softening of the optical vibrations at the improper phase transition in the triatomic molecule T-O-T. In 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 a 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  $F_t > F_a$ , 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<sup>3</sup> 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 an elementary 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 vector vibrations. 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 an elementary 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 the  $Y$  axis (see Fig. 1). Let us take the quadratic expansion of the free deformation energy of this cell in the natural curvilinear  $q$  coordinates  $(r_i, \varphi_k)$ :

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

where  $i, j = 1, 2, 3$ ;  $k, l = 4, 5, 6$ ;  $c_{ij}^0, c_{kl}^0$  are the initial elastic moduli for a high-symmetry phase;  $r_{0i}$  are the lattice parameters prior to deformation. Note that we consider the quadratic expansion of the free energy in Eq. (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 in-

cludes the compression strains of the edges  $b_0, c_0$ , and the shear strain  $\alpha$ . It is seen from Fig. 1(b) that  $\Delta\alpha = \Delta z/b_0$ , where  $b_0$  is a 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  $\Delta b$  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  $\Delta b$  involves both the linear components along the  $Y$  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 Eq. (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 the symmetry-breaking strain component  $e_{4dyn}$ , causing the change of the 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 a 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.<sup>9</sup> 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 the pressure increase, is to be introduced into Eq. (4) to obtain a more accurate quantitative estimation. As the edge  $b_0$  declines in the  $X$  and  $Z$  directions under the effect of the acoustic wave, the expansion  $\Delta b$  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  $c_{44}c_{66} - c_{46}^2 = (c_{44}^0 - p_{ext})(c_{66}^0 - p_{ext}) - c_{46}^0{}^2 = 0$  at the transition point. Hence

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

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 Ref. 1, we have  $p_c = 3.6$  GPa, and the experimental pressure from Ref. 10 for this transition is  $(3.2 \pm 0.4)$  GPa. When deriving Eq. (9) we used the perfect springs model, when only the kinematic anharmonicity can arise as result of the transition from the natural curvilinear atomic  $q$  coordinates (interatomic bonds and angles between them) to the Cartesian coordinates of the atomic displacements. Therefore the coincidence between Eq. (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  $\text{AlPO}_4$  ( $p_c \approx 15$  GPa),<sup>11</sup> quartz  $\text{SiO}_2$  ( $p_c \approx 22$  GPa),<sup>12</sup> 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) (Ref. 13) 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 Eq. (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 Eq. (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 Ref. 6 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.

Thus we show that the soft acoustic mode, causing the proper FPT in anorthite and some other crystals, is mainly due to the kinematic anharmonicity, when other kinds of anharmonicity are neglected.

To conclude, it is shown that the kinematic anharmonicity is expressed by the linear-quadratic coupling of the static

non-symmetry-breaking and the dynamic symmetry-breaking strain components. The fact that the above-mentioned anharmonicity in anorthite is the strongest is not so obvious, even because of neglecting it in the recent review<sup>9</sup> on the structural phase transitions. The authors<sup>9</sup> assume the terms  $e_i e_4^2$  to be neglected, due to the fact that the non-symmetry-breaking components  $e_i$  are nearly five times smaller than  $e_4$ . However, it follows from our equations that instead of the comparison of the terms  $e_i$  and  $e_4$  in the low-symmetry phase, the terms  $c_{44}^0 + 3B_4 e_4^2$  and  $\sum_i c_{2i}^0 e_i$  should be compared, where  $B_4$  is the coefficient of the term  $e_4^4$  of the free-energy expansion and  $i = 1, 2, 3, 5$ . This kinematic an-

harmonicity is common for the structural phase transitions, since it is caused by a nonlinear relation between the curvilinear space of  $q$  coordinates of interatomic separation and  $x$  space of the Cartesian atomic displacements. We have obtained the 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 the pressure of the phase transition to a triclinic phase if the initial elastic moduli are known.

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