Mechanism of the Formation of a Soft Mode in Ferroelastic Phase Transition

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It is shown that the softening of the acoustic mode and the ensuing ferroelastic phase transition are due to the linear-quadratic interaction between the symmetric and antisymmetric deformations, which is presently neglected in the literature. An expression is obtained which can be used to predict the phase transition pressure if the initial elastic moduli are known. © 2001 MAIK "Nauka/Interperiodica".

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In recent years, lattice dynamics and molecular dynamics methods were used to numerically calculate the soft modes causing ferroelastic phase transitions in crystals [1, 2]. Calculations of this type do not use analytical expressions describing the mechanism for the appearance of soft modes. It is assumed that symmetrybreaking deformation arises spontaneously without applying any force and appears due to critical softening of elastic moduli. In the Landau theory of ferroelastic phase transitions, the free energy is expanded in powers of order parameters breaking crystal symmetry. The deformations not breaking symmetry are not treated as order parameters, because it is assumed that they are not involved in the transition. Next, it is postulated that the coefficient of the quadratic term of expansion, i.e., the elastic modulus, must vanish when the external variable thermodynamic parameter reaches its critical value. Within this approach, the reason for the formation of a soft mode remains unclear.

Of particular interest is physics of high-pressure ferroelastic phase transitions. Under pressure, the symmetry lowers to triclinic, after which amorphization occurs, as was demonstrated by an example of anorthite and quartz in [3, 4]. In this work, we consider the proper monoclinic-triclinic ferroelastic phase transition in Sr-anorthite (Sr,Ca)Al₂Si₂O₈). A ferroelastic phase transition is considered proper when the order parameter and the spontaneous deformation behave identically under symmetry operations. In a proper ferroelastic phase transition, one of the components of the spontaneous deformation tensor can be taken as a critical parameter [1]. We studied a proper ferroelastic phase transition because in this case cell deformation can be treated as a whole, i.e., without specifying displacements of particular atoms, as in the case of an improper transition, and, hence, the mechanism of interaction between deformations of cell edges and angles becomes more pictorial. We aimed at revealing the most general reason for crystal destabilization. We demonstrated that the soft acoustic mode responsible for the instability of the ferroelastic lattice is due to the linear–quadratic interaction between symmetric and antisymmetric deformations, which is presently neglected in the literature [5], although this interaction is the strongest among the anharmonic interactions.

In our previous work [6], we found that the energy of ferroelastic phase transition is due to symmetric components, and, therefore, their contributions cannot be neglected, as was done previously. The effect of symmetric components of the deformation tensor on the phase transition is accounted for by the term $p_{ext}V$ in the Gibbs potential of a crystal subjected to external pressure $G = F + p_{ext}V$, where F is the free energy, $V \approx e_1 + e_2 + e_3$ is the relative change in the volume of the unit cell, and e_i are components of the deformation tensor. The importance of making allowance for the effect of symmetric deformations was also pointed out in [7], where mechanical stress was calculated for a triatomic T–O–T molecule distorted under pressure from linear to bent. In that work, the authors examined how the transverse destabilizing force appears under the action of external forces applied to the molecule on two sides along the T...T line.

Recall that in the general case the symmetric and antisymmetric order parameters can be represented as the sum of the static and a small dynamic components related to lattice vibrations: $Q_j = Q_{j\text{stat}} + Q_{j\text{dyn}}$. The antisymmetric order parameters $Q_{j\text{stat}}$ describe the system in thermodynamic equilibrium and are zero in the symmetric phase. The antisymmetric order parameters $Q_{j\text{dyn}}$ describe lattice vibrations with certain frequencies ω_j and wave vectors \mathbf{k}_j and occur in both symmetric and low-symmetry phases. On approaching the point of phase transition, some vibrations with eigenfrequencies $\omega_j(\mathbf{k}_j)$ are softened. In the case of the monoclinic–triclinic transition, the B_g representation, to which the acoustic branch belongs, is the eigenvalue of the dynamic matrix that accounts for the direction and polarization of the acoustic phonon wave vector. The stability condition for the dynamic matrix can be represented as $(c_{44}c_{66} - c_{46}^2) > 0$. This matrix corresponds to the propagation of three acoustic waves, with the lowest frequency soft mode being the transverse acoustic wave propagating along *Y* with the polarization $[-c_{46}/c_{66}, 0, 1]$ [5].

Figure 1 shows the origin of the transverse antisymmetric force by an example of the phase transition in a triatomic T–O–T molecule. Solid lines show the static positions of atoms in thermodynamic equilibrium, and dashed lines show the transverse vibrations of the O atom. The forces F_r appear under the action of the contracted interatomic bonds, and their sum gives the tangential force F_t that provokes the bending phase transition in Fig. 1b if $F_t > F_a$, where F_a is the restoring force caused by the stiffness of the T–O–T angle.

In our analysis of the monoclinic-triclinic transition, we will use analogous reasoning. We assume that, on applying hydrostatic pressure to the unit cell, antisymmetric destabilizing forces also appear under the action of contracted interatomic bonds. By analogy with the triatomic molecule, Fig. 1 illustrates the action of static pressure and dynamic shear stress caused by a transverse acoustic wave on the monoclinic cell.

Let us consider a monoclinic cell with the normal to symmetry plane aligned with the Y axis. For this cell, the quadratic expansion of the free energy of deformation in the natural curvilinear q coordinates (r_i, φ_i) is

$$F = \sum_{ij} c_{ij}^{0} (\Delta r_{i}/r_{0i}) (\Delta r_{j}/r_{0j})/2 + \sum_{kl} c_{kl}^{0} \Delta \phi_{k} \Delta \phi_{l}/2,$$
(1)

where *i*, *j* = 1, 2, 3; *k*, *l* = 4, 5, 6; c_{ij}^{0} and c_{kl}^{0} are the initial elastic moduli in the symmetric phase; and r_{0i} are the initial cell parameters; small nondiagonal terms of the angle–bond type are omitted. For the sake of simplicity, we will first consider the two-dimensional deformation of one of the faces b_0c_0 , which includes the deformation of edges b_0 and c_0 and angle α . In Fig. 1b it is seen that $\Delta \alpha = \Delta z/b_0$, where b_0 is a parameter corresponding to the *Y* axis in the initial cell. The corresponding quadratic expansion of free energy is written as

$$F = c_{22}^{0} (\Delta b/b_{0})^{2}/2 + c_{23}^{0} (\Delta b/b_{0}) (\Delta c/c_{0}) + c_{33}^{0} (\Delta c/c_{0})^{2}/2 + c_{44}^{0} (\Delta z/b_{0})^{2}/2.$$
(2)

Let us express this energy in Cartesian coordinates. Since the edge b_0 departs in the Z direction under the



Fig. 1. Schematic illustration of phase transitions under the action of hydrostatic pressure P and transverse acoustic wave for the triatomic T–O–T molecule and the monoclinic crystal lattice (a) before and (b) after phase transition.

action of the acoustic wave, the power-series expansion of Δb has the form

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

It is seen that Δb contains not only linear components along the Y axis, but also quadratic components along the perpendicular direction. This means that linear deformations in the natural curvilinear space, in which the deformations of chemical bonds and angles in the crystal lattice are considered, cause nonlinear deformations in Cartesian coordinates, in which atomic displacements are considered. In terms of the deformation tensor components, Eq. (3) takes the form $\Delta b/b_0 = e_2 +$

 $e_4^2/2$, because in the monoclinic cell $\Delta \varphi_4 = \Delta \alpha = -e_4$. As

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a result, for the Gibbs energy $G = F + p_{ext}V$, one obtains the expression

$$G \cong c_{22}^{0} e_{2}^{2}/2 + c_{23}^{0} e_{2} e_{3} + c_{33}^{0} e_{3}^{2}/2 + (c_{22}^{0} e_{2} + c_{23}^{0} e_{3} + c_{44}^{0}) e_{4}^{2}/2 + p_{\text{ext}}(e_{2} + e_{3}),$$
(4)

from which it follows that, upon applying hydrostatic pressure to the unit cell, the symmetric static deformations of the $e_{2\text{stat}}$ and $e_{3\text{stat}}$ bonds come into linear–quadratic interaction with the dynamic deformations of the transverse acoustic wave $e_{4\text{dyn}}$, leading to a change in the force constants of transverse vibrations. Hence, for the direction of symmetry-breaking deformations distorting the cell so that the angle $\varphi_4 \neq 90^\circ$, the effective force constant is

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

Under equilibrium conditions, $\partial G/\partial e_2 = c_{22}^0 e_2 + c_{23}^0 e_3 + p_{\text{ext}} = 0$; hence, for the symmetric phase one finds

$$c_{44} = c_{44}^0 - p_{\text{ext}}.$$
 (6)

It is seen that the elastic modulus c_{44} softens upon the pressure buildup and vanishes (i.e., acoustic instability appears) at the critical pressure

$$p_c = c_{44}^0.$$
 (7)

As was mentioned above, the amplitude vector of the soft acoustic mode has components not only along Z, but also along X. Therefore, for a more accurate quantitative estimation, one must introduce in Eq. (4) the second antisymmetric parameter e_6 , which also softens under pressure. Now, because the edge b_0 departs in the X and Z directions under the action of the acoustic wave, the power-series expansion of Δb has the form

$$\Delta b/b_0 \cong \Delta y/b_0 + (\Delta x)^2/2b_0^2 + (\Delta z)^2/2b_0^2$$

$$= e_2 + e_4^2/2 + e_6^2/2.$$
(8)

Due to the interaction between parameters e_4 and e_6 , the

combination of moduli $c_{44}c_{66} - c_{46}^2$ approaches zero faster than the individual modulus c_{44} ; therefore, after substituting expansion (8) into the Gibbs potential, one obtains that $c_{44}c_{66} - c_{46}^2 = (c_{44}^0 - p)(c_{66}^0 - p) - (c_{46}^0)^2 = 0$ in the transition point. Hence,

$$p_{c} = (c_{44}^{0} + c_{66}^{0})/2 - [(c_{44}^{0} + c_{66}^{0})^{2}/4 - c_{44}^{0}c_{66}^{0} + c_{46}^{02}]^{1/2}.(9)$$

Using the data for the initial moduli of Sr anorthite [1] $c_{44}^0 = 11.6$ GPa, $c_{66}^0 = 24.7$ GPa, and $c_{46}^0 = -12.7$ GPa, one finds $p_c = 3.86$ GPa, whereas the experimental pres-

sure for this transition is 3.2 ± 0.4 GPa [8]. The above moduli were obtained within the pair potential model with parameters fitted so that the calculated and experimental cell parameters were the same. These calculated moduli should be considered as approximate because of the lack of experimental data for the elastic moduli of Sr anorthite. Therefore, it is unreasonable to expect full coincidence between the theory and experiment.

As a result, we have demonstrated that the soft acoustic mode responsible for the proper ferroelastic phase transition is caused by the linear-quadratic interaction between the static symmetric and the dynamic antisymmetric deformations, which is currently neglected in the literature, although it is the strongest among the anharmonic interactions. The authors of [5] justify the neglect of the terms $e_i e_4^2$ by the fact that symmetric components e_i are smaller than e_4 by about a factor of five. However, it follows from our expressions that the terms c_{44}^0 and $\sum_i c_{2i}^0 e_i$ with i = 1, 2, 3, and 5 must be compared rather than e_i and e_4 . This interaction is common to structural phase transitions because it results from the nonlinear relation between the curvilinear natural coordinate space, in which the deformations of chemical bonds and angles in the crystal lattice are considered, and the Cartesian space of atomic displacements upon applying hydrostatic pressure to the ferroelastic. In addition, we have obtained an expression which can be used to predict phase transition pressure provided that the initial elastic moduli are known.

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