SOLIDS Structure

Role of Internal Pressure in a Ferroelastic Phase Transition

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Abstract—It is shown that the driving force of a ferroelastic phase transition is internal pressure. The pressure gives rise to symmetric deformation whose energy accumulates as pressure increases, and at the phase transition point the energy is partially transferred into antisymmetric deformations. © 2000 MAIK "Nauka/Interperiodica".

Ferroelastics are attracting a great deal of attention as high-temperature superconductors, They are also of interest because they have extensive applications in acoustooptic and acoustoelectric devices. Nonetheless, a great deal remains unclear in the nature and mechanisms of ferroelastic phase transitions (FPT). The phenomenological description of FPT employs the spontaneous deformation tensor and artifically chosen order parameters, one of which is considered to be critical [1]. If the order parameter and the spontaneous deformation transform under symmetry operations identically, then the ferroelastic is said to be proper. For a proper FPT one component of the spontaneous deformation tensor can be taken as the critical parameter [2]. The order parameters and the deformation tensor are essentially determined by the displacements of the atoms accompanying a change in external conditions, and it is strange that the force giving rise to these displacements and being the true reason for the transition has still not been studied. Consequently, such an approach cannot give the correct physical description of a FPT.

The physics of a proper FPT with lowering of symmetry down to triclinic, usually followed by amorphization, as shown for the example anortite and quartz [3, 4], is of special interest. For such FPT, characterized by two macroscopic parameters which break symmetry, there are no analytic solutions in the literature.

In this connection, in the present paper we develop a model of a proper FPT in which internal pressure, which is the driving force of the transition, is introduced. As an example illustrating this model we consider the monoclinic-triclinic proper FPT in Sr-anortite (Sr, Ca)Al₂Si₂O₈), induced by cationic exchange of Ca and Sr. This ferroelastic was chosen because the experimental values of the elastic moduli [5] and the composition dependences of the unit cell parameters [6] are available for it. The FPT is usually described by a linear deformation tensor, which has the Lagrangian form

$$e_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_{0j}} + \frac{\partial u_j}{\partial x_{0i}} \right).$$

Since the internal spontaneous deformation increases at a phase transition, the nonlinear terms may have to be taken into account in the deformation tensor. When the nonlinear terms are taken into account this tensor is said to be finite and has the form

$$E_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_{0j}} + \frac{\partial u_j}{\partial x_{0i}} + \sum_{k} \frac{\partial u_k}{\partial x_{0i}} \frac{\partial u_k}{\partial x_{0j}} \right),$$

where the vector $\mathbf{u} = \mathbf{x} - \mathbf{x}_0$ determines the displacement of the point whose coordinate is x_0 before the deformation and x after the deformation. The indices *i*, *j*, and *k* correspond to Cartesian coordinates, and each one runs through the values 1, 2, and 3. For convenience in comparing with experiment, we shall express the components of the deformation tensor in terms of the lattice parameters. The corresponding expressions for the components of the linear tensor are presented in explicit form in [7]. We obtain the relations for the components of the finite tensor, which can be expressed in terms of the components e_{ij} in the Voigt notations as follows:

$$E_{1} = e_{1} + e_{1}^{2}/2 + e_{6}^{2}/2,$$

$$E_{2} = e_{2} + e_{2}^{2}/2,$$

$$E_{3} = e_{3} + e_{3}^{2}/2 + e_{4}^{2}/2 + e_{5}^{2}/2,$$

$$E_{4} = e_{4} + e_{2}e_{4},$$

$$E_{5} = e_{5} + e_{2}e_{5} + e_{4}e_{6},$$

$$E_{6} = e_{6} + e_{2}e_{6}.$$

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Fig. 1. Illustration of the differences between the dependences of the components of the linear e_i (triangles) and finite E_i (circles) deformation tensors on the content of Ca. The curves were obtained using the unit cell parameters of Sr anortite [6]: (a) i = 3; (b) i = 5.

Substituting into the formulas obtained the experimental lattice parameters for Sr anortite [6] we found that there is a large difference between the corresponding components of the linear and finite deformation tensors (Fig. 1). Therefore, to decrease the error the finite deformation tensor must be used when calculating the FPT.

A systematic physical description of a FPT requires analysis of the displacements of the atoms and forces giving rise to these displacements. To a first approximation these forces can be expressed in terms of the isotropic internal pressure p_i . In order to close the system, the equations must also describe the internal pressure as a function of some thermodynamic parameters. To a first approximation it can be assumed that this pressure is a linear function of the cationic composition. Then the system of equations describing the FPT will have the form

$$\frac{\partial G(E_m, p_i)}{\partial E_m} = 0,$$

$$p_i = A_1 N,$$
(1)

where $G(E_m, p_i)$ is the Gibbs potential, E_m are the components of the deformation tensor, $m = 1, 2, ..., 6, A_1$ is a linear coefficient, and N is the molar fraction of the substituting cations.

The Gibbs potential of a crystal, to which the external pressure p_{ext} is applied, is expressed in the form

$$G = F + p_{\text{ext}}V$$

where F is the free energy and $V \approx E_1 + E_2 + E_3$ is the relative change in the unit-cell volume. It would be log-

ical to use the same expression for the Gibbs potential of the ferroelastic also, where the internal pressure p_i giving rise to spontaneous deformation is present:

$$G = F + p_i V. (2)$$

The internal pressure can be produced for various reasons: change in the cationic composition Ca-Sr, change in the degree of ordering Al-Si, disruptions of the crystal structure on grain boundaries and on dislocations, and temperature. Making use of the term $p_i V$ in Eq. (2), we introduced the action of a thermodynamic parameter on the linear terms in the expansion of the Gibbs energy in terms of the deformation tensor. The action of thermodynamic parameters on the quadratic and higher powers in the expansion of the Gibbs potential in the deformation tensor is taken into account in the free energy. Thus, we assume that the proposed Gibbs potential can completely describe a proper FPT. To calculate this transition it is necessary to choose an expansion for the free energy. Since the component E_4 of the finite tensor is maximal and destroys the symmetry of the monoclinic crystal we chose, following [2], it as the critical order parameter. The expansion of the part of the free energy in terms of the critical parameter E_4 , according to the Landau theory, has the form

$$F_4 = \frac{1}{2}(-4AE_4^2) + \frac{1}{4}B_4E_4^4 + \frac{1}{6}C_4E_4^6, \qquad (3)$$

where $A_4 = (p_{ic} - p_i)A_0$ the coefficient vanishes at the critical internal pressure $p_{ic}7$, while all other coefficients remain constants. The component E_6 of the finite deformation tensor also breaks symmetry, but since it is

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much smaller than E_4 near the phase transition, we shall assume it to be noncritical, i.e., we write the expansion of the part of the free energy in terms of the parameter E_6 in the form

$$F_6 = \frac{1}{2}A_6E_6^2 + \frac{1}{4}B_6E_6^4, \tag{4}$$

where the coefficients A_6 and B_6 are constants which do not depend on the cationic composition Ca–Sr. To simplify the main behavior of the FPT in the analytic form, in order to describe the interaction of the parameters with the same symmetry, E_4 and E_6 , we took only one bilinear term, dropping by the biquadratic terms,

$$F_{\rm int} = A_{4-6} E_4 E_6. \tag{5}$$

As the solution of Eqs. (1) show, the linear-quadratic interaction of symmetric components with antisymmetric components accompanying cationic exchange results only in a small additional contribution to the linear dependence of the coefficient A_4 in Eq. (3), and consequently, for simplicity, we drop it. The interaction of the symmetric component is expressed by the standard quadratic elastic deformation:

$$F_{\rm sim} = \frac{1}{2} \sum_{kl} A_{kl} E_k E_l, \qquad (6)$$

where the indices k, l = 1, 2, 3, 5. Now the total free energy is

$$F = F_4 + F_6 + F_{\rm int} + F_{\rm sim}.$$
 (7)

Solving the system of equations (1), we find the dependences of the components of the spontaneous-deformation tensor on the internal pressure with increasing Ca content. The four symmetric components are linear functions of the internal pressure:

$$E_{1} = k_{1}p_{i}, \quad E_{2} = k_{2}p_{i}, E_{3} = k_{3}p_{i}, \quad E_{5} = k_{5}p_{i},$$
(8)

(here the coefficients are expressed in terms of the elastic moduli). The antisymmetric components E_4 and E_6 are zero in the monoclinic phase with $p_i < p_{i0}$. In the triclinic phase, with $p_i \ge p_{i0}$, the analytic expressions for E_4 and E_6 near a phase transition have the form

$$E_4 = -\left[-\frac{K}{2} + \left(\frac{K^2}{4} - L\right)^{1/2}\right]^{1/2},$$
(9)

where $K = B_4/C_4$, $L = A_0(p_{i0} - p_i)/C_4$, and

$$E_{6} = \left[-Q + \left(Q^{2} + S^{3}\right)^{1/2}\right]^{1/3} + \left[-Q - \left(Q^{2} + S^{3}\right)^{1/2}\right]^{1/3},$$
(10)

where $S = A_6/3B_6$ and $Q = A_{4-6}E_4/2B_6$. Here the internal pressure at which a transition occurs,

$$p_{i0} = p_{ic} + \frac{A_{4-6}^2}{A_6 A_0}, \tag{11}$$

differs from the critical pressure as a result of the interaction of the components E_4 and E_6 . We attained agreement between theory and experiment by adjusting the coefficients in Eqs. (8)–(10) (Fig. 2).

Finally, the proposed model can explain the mechanism of a proper FPT, consisting in the fact that in the monoclinic phase, with increasing internal pressure, the elastic energy of the crystal accumulates as a result of the symmetric components E_i , while the elastic energy for the antisymmetric components remains zero. When the pressure p_{i0} is reached, part of the energy of the symmetric components is relaesed into the deformation of antisymmetric components. Thus it can be said that the internal pressure is the driving force that destabilizes the crystalline structure with respect to the antisymmetric components near the point of the phase transition p_{i0} . Similar arguments were presented in [8], where the mechanical stresses in a triatomic molecule accompanying distortion of the shape of the molecule under pressure from linear to bent were calculated. It is evident on this basis that the effect of the symmetric components of the deformation tensor cannot be ignored, as done previously, because they participate in the phase transition.

It is interesting to note that the internal and external pressures at which a FPT occurs differ by almost an order of magnitude. According to our model, from Eq. (11) $p_{i0} \approx 0.5$ GPa, and the external pressure for this transition is 3.2 GPa [9]. This difference is probably due to the fact that the external pressure changes the elastic moduli as a result of the anharmonicity of the interatomic potentials, while the internal pressure, in the presence of cationic exchange, acts directly on the chemical bonds and consequently changes the elastic constants more effectively.

The introduction of internal pressure elucidates a single mechanism whereby a change in the cationic composition Ca–Sr, Al–Si ordering and temperature affect a phase transition. The replacement of Sr atoms at lattice sites by smaller Ca atoms gives rise to compression of the lattice, which is equivalent to the action of an internal pressure, which varies linearly with the Ca concentration. The effect of Al–Si ordering on a phase transition can be studied similarly. Since the Al and Si atoms also differ in size and do not occupy their positions in the presence of disorder, an additional internal pressure of the disordered structure arises. As a result, the phase transition point depends linearly on the concentration of the disordered cations Al–Si. A temperature increase results in expansion of the lattice,

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Fig. 2. Comparison of model (solid lines) and experimental (triangles) dependences of the components of deformation tensors on the internal pressure. Here the internal pressure is measured from the Sr phase of the crystal, where $p_i = 0$.

which is equivalent to the action of a negative internal pressure, varying linearly with temperature. The thermal internal pressure for a α - β transition in quartz was studied in [10].

In conclusion, analytic expressions describing a proper FPT were obtained. The internal pressure was introduced in these expressions as the driving force of the transition. It was shown that the internal pressure destabilizes the crystal structure of the ferroelastic with respect to antisymmetric components of the deformation tensor near the phase transition point. It was also established that the transition energy is reached as a result of the symmetric components, and consequently their contribution cannot be neglected, as done previously. Moreover, the introduction of internal pressure made it possible to represent clearly a single micromechanism by which the cationic composition Ca–Sr, Al–Si, ordering and temperature affect the phase transition.

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