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Driving force for the proper ferroelastic phase transitions induced by cation exchange

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Abstract. – It is shown that the internal pressure may be represented as the driving force for the proper ferroelastic phase transitions 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 a greater anisotropy than the external one. An equation has been obtained, with the help of which it appears possible to predict the internal pressure of the proper monoclinic-triclinic ferroelastic phase transition induced by cation exchange if the initial effective elastic moduli are known.

Ferroelastics are practised widely in acousto-optic and acoustoelectric devices. In addition, the basic features of ferroelastics, such as mechanical twinning, is observed in the hightemperature superconductors. Nevertheless, there is still some vagueness in the nature of the ferroelastic phase transitions (FPTs). In the previous work [1], using the "ball-and-perfect springs" model, we have determined the mechanism of occurrence of a soft mode at a proper FPT in Sr-anorthite ((Sr, Ca)Al₂Si₂O₈) and some other crystals under the external pressure. In the present paper, we consider the proper monoclinic-triclinic FPT in Sr-anorthite induced by Ca and Sr cation exchange rather than by the external pressure. 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 enhancing 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 introduction of the 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 [2–9], which dealt with the internal pressure in crystals, it follows that the internal pressure is a real value which is capable of going into action differently from the

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external pressure. For example, in ref. [2] the authors conclude that the "chemical" pressure is a more complicated parameter than the mechanical one. Various types of "chemical" pressure can lead to the Pbnm-R3c phase transition in manganites with different signs of cell volume change. In ref. [3], 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 ref. [4], the authors believe the application of the mechanical pressure to copper-oxide superconductors to induce an increase in the Curie temperature $T_{\rm c}$. If the mechanical pressure is replaced by a chemical one, the effect becomes negative and a decrease of $T_{\rm c}$ 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 —being a more complicated parameter as compared to the external one— 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 $P_{\rm int}$ 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 a 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 atoms in a 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 \boldsymbol{x} , identical in all primitive cells, *i.e.* by the shifts of the absolutely rigid Brave sublattices. It is clear that from 3n internal deformations only (3n-3)are linear-independent deformations, and 3 correspond to translations of a crystal as a whole. The external deformations are determined by the 6-dimensional basis, which is given by the deformation tensor of the second rank E_{ij} , with diagonal elements describing relative changes of the linear sizes of a crystal along the Cartesian axes, and non-diagonal elements describing the shift deformations [10]. The absolute Cartesian coordinates of the atomic displacement X are clearly related to the deformation tensor of a primitive cell E and to the change of the atomic coordinate x inside the primitive cell relative to the chosen centre of masses with the coordinates **R** by the following correlation: X = x + ER. The change of density of the Gibbs free energy as a function of x and E is written down in quadratic approximation as

$$G(\boldsymbol{x}, \boldsymbol{E}) = -\boldsymbol{f}_x \boldsymbol{x} - \boldsymbol{f}_E \boldsymbol{E} + \boldsymbol{x} \boldsymbol{F}_{xx} \boldsymbol{x}/2 + \boldsymbol{x} \boldsymbol{F}_{xE} \boldsymbol{E} + \boldsymbol{E} \boldsymbol{F}_{EE} \boldsymbol{E}/2, \qquad (1)$$

where we use the tensor notation for the derivatives $f_x = -\partial G/\partial x$, $f_E = -\partial G/\partial E$, $F_{xx} = \partial^2 G/\partial x \partial x$, $F_{xE} = \partial^2 G/\partial x \partial E$, $F_{EE} = \partial^2 G/\partial E \partial E$, initially taken at x = 0, 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 $\mathbf{f}_E = (\sigma_{\text{ext}})_{ij} = -P_{\text{ext}}\delta_{ij}$, because the hydrostatic pressure corresponds to the diagonal stress tensor, which has equal components $\sigma_{11} = \sigma_{22} = \sigma_{33} = P_{\text{ext}}$ 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} : $\mathbf{F}_{xx}\mathbf{x} + \mathbf{F}_{xE}\mathbf{E} = 0$, $\mathbf{F}_{xE}\mathbf{x} + \mathbf{F}_{EE}\mathbf{E} + P_{\text{ext}}\delta_{ij} = 0$. Taking into account these equilibrium conditions, the Gibbs potential can be reduced to the form: $G(\mathbf{E}) = P_{\text{ext}}V + \mathbf{ECE}/2$, where $F = \mathbf{ECE}/2$ 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 C is determined as

$$\boldsymbol{C} = \boldsymbol{F}_{EE} - \boldsymbol{F}_{xE} \boldsymbol{F}_{xx}^{-1} \boldsymbol{F}_{xE}.$$
(2)

It is seen that these elastic moduli are of a complex origin (see also refs. [11] and [12]), because the first term on the right-hand side of eq. (2) 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 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 \boldsymbol{E} as well as a change in local atoms coordinates \boldsymbol{x} . Two tensors correspond to these two kinds of the deformations: $\boldsymbol{\sigma}_{\text{dir}}$ (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 $\boldsymbol{\sigma}_{\text{int}} = \boldsymbol{\sigma}_{\text{dir}} + \boldsymbol{\sigma}_{\text{ind}}$. In this case, the forces, responsible for the direct coupling with lattice parameters, are $\boldsymbol{f}_E = (\boldsymbol{\sigma}_{\text{dir}})_{ij} = -P_{\text{dir}}\delta_{ij}$ and, also, the internal resulting forces on atoms, responsible for the indirect coupling with lattice parameters, are $\boldsymbol{f}_x = -\partial G/\partial \boldsymbol{x}$. We emphasize that $\boldsymbol{f}_x \neq 0$ only when these forces act on the atoms at sites lacking inversion symmetry [12]. In equilibrium, the Gibbs potential has a minimum relative to the internal atomic displacements \boldsymbol{x} and the deformations $\boldsymbol{E}: \boldsymbol{F}_{xx}\boldsymbol{x} + \boldsymbol{F}_{xE}\boldsymbol{E} - \boldsymbol{f}_x = 0$, $\boldsymbol{F}_{xE}\boldsymbol{x} + \boldsymbol{F}_{EE}\boldsymbol{E} - \boldsymbol{\sigma}_{\text{dir}} = 0$. The solution to this system of equations is the following:

$$\boldsymbol{x} = \boldsymbol{F}_{xx}^{-1} (1 + \boldsymbol{F}_{xE} \boldsymbol{C}^{-1} \boldsymbol{F}_{xE} \boldsymbol{F}_{xx}^{-1}) \boldsymbol{f}_{x} - \boldsymbol{F}_{xx}^{-1} \boldsymbol{F}_{xE} \boldsymbol{C}^{-1} \boldsymbol{\sigma}_{\text{dir}}, \boldsymbol{E} = -\boldsymbol{C}^{-1} \boldsymbol{F}_{xE} \boldsymbol{F}_{xx}^{-1} \boldsymbol{f}_{x} + \boldsymbol{C}^{-1} \boldsymbol{\sigma}_{\text{dir}} = \boldsymbol{C}^{-1} (\boldsymbol{\sigma}_{\text{ind}} + \boldsymbol{\sigma}_{\text{dir}}) = \boldsymbol{C}^{-1} \boldsymbol{\sigma}_{\text{int}},$$
(3)

where $\boldsymbol{\sigma}_{\text{ind}} = -\boldsymbol{F}_{xE}\boldsymbol{F}_{xx}^{-1}\boldsymbol{f}_x$ and \boldsymbol{C} is determined by eq. (2).

It is clear that the tensor $\sigma_{\rm int}$, generated by the cation exchange, is of a more complicated nature than the tensor of the external stress, because not only a 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 cations 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 $(\boldsymbol{\sigma}_{int})_{ij} \approx -P_{int}\delta_{ij}$. It is seen from eq. (3) that the term $\boldsymbol{\sigma}_{ind}$ 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 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 refs. [13] and [14], 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 line is a radiative decay of excited d^3 electrons of substitutional Cr^{3+} ions. The ions are in the octahedral coordination with the oxygen ions in the corundum structure. When the octahedral arrangement is strained, the crystal field at Cr 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 ceramics and composites [15]. We expect that if we manage to introduce Cr-ions into the solid solutions 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.

Hereinafter we are going to study the Gibbs potential for Sr-anorthite, using, for simplicity, the internal pressure approximation: $G(\mathbf{E}) = P_{\text{int}}V + \mathbf{ECE}/2$. In the previous paper [1], using the "ball-and-perfect springs" model, we have determined the mechanism of occurrence of the soft mode in Sr-anorthite and some other crystals at proper FPT, applying the external pressure. The same approach is used for the case of the internal pressure. This approach differs from the conventional one in that the cause of mechanical instability of a crystal is associated with first-order terms, due to microscopic tensions of bonds in the lattice rather than with the presence of terms, exceeding second order. In this case, only "kinematic" anharmonicity, described for the optical modes in ref. [16] and for the acoustic modes in ref. [1], can occur.

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 the non-linear terms should be taken into account in the strain tensor. This tensor is called finite and is defined as $E_{ij} = (1/2)[(\partial u_i/\partial x_{0j} + \partial u_j/\partial x_{0i}) + \sum_k (\partial u_k/\partial x_{0j})(\partial u_k/\partial x_{0j})]$, where the vector $\mathbf{u} = \mathbf{x} - \mathbf{x}_0$ determines displacements of a point, located at x_0 prior to deformation and at x after the deformation. The indices i, j,k correspond to the Cartesian coordinates, each of them running 1, 2, 3. We have found out that the components of the finite-strain tensor and the commonly used linear strain tensor are greatly distinguished for anorthite. Hence, to minimize the calculation error 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 a linear function of the cation content. Then the system of equations for the FPT will take the form

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

 $P_{\text{int}} = \alpha N,$
(4)

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

Now let us choose the terms of the free-energy expansion so that they give the best fit to the experimental data [17]. 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 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 the Ca-Sr cation composition. It turned out that it was necessary to introduce supplementary terms E_4^4 , E_4^6 and E_6^4 into the elastic energy to better approximate the experimental data from ref. [17]. 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: $F_{asym} = A_{4-6}E_4E_6$. The coupling of the non-symmetry-breaking strain components is expressed by an ordinary quadratic elastic strain: $F_{sym} = \sum_{ij} A_{ij} E_i E_j/2$, with indices i, j = 1, 2, 3, 5.

In ref. [1] we have shown that the soft acoustic mode, causing the proper monoclinictriclinic 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 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 nonsymmetry-breaking as well as the symmetry-breaking strain components, we made use only of the linear-quadratic terms: $F_{\text{inter}} = (\sum_j D_{4j}E_j)E_4^2/2 + (\sum_j D_{6j}E_j)E_6^2/2$, with 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 $F = F_4 + F_6 + F_{\text{sym}} + F_{\text{inter}}$.

When solving the system of equations (4), 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:

$$E_j = k_j P_{\text{int}},\tag{5}$$

with 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: $k_j = \sum_m \mathbf{S}_{jm}$. 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 $A_4 + \sum_j D_{4j} \mathbf{S}_j P_{\text{int}}$ and $A_6 + \sum_j D_{6j} \mathbf{S}_j P_{\text{int}}$. It is clear that these coefficients fall to zero at partial critical pressures $P_{c1} = -A_4 / \sum_j D_{4j} \mathbf{S}_j$ and $P_{c2} = -A_6 / \sum_j D_{6j} \mathbf{S}_j$. 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 $P_{\text{int}} \ge P_c$, to a first approximation, the analytical expressions for E_4 and E_6 in the phase transition are the following:

$$E_4 \cong -\left\{-B_4/2C_4 + \left[(B_4/C_4)^2/4 - L\right]^{1/2}\right\}^{1/2},$$

$$E_6 \cong \left[-Q + \left(Q^2 + S^3\right)^{1/2}\right]^{1/3} + \left[-Q - \left(Q^2 + S^3\right)^{1/2}\right]^{1/3},$$
(6)

where $S = (A_6 - P_{int})/3B_6$, $Q = A_{4-6}E_4/2B_6$, $L = [(A_4 - P_{int})(A_6 - P_{int}) - A_{4-6}^2]/C_4(A_6 - P_{int})$. A real non-zero solution is possible at $L \le 0$. The phase transition pressure at L = 0 is

$$P_{\rm c} = (A_4 + A_6)/2 - \left[(A_4 + A_6)^2/4 - A_4 A_6 + A_{4-6}^2 \right]^{1/2}.$$
 (7)

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: $C_{44} = \partial^2 G/\partial E_4^2 = A_4 - P_{int}$, $C_{46} = \partial^2 G/\partial E_4 E_6 =$ A_{4-6} and $C_{66} = \partial^2 G/\partial E_6^2 = A_6 - P_{int}$. It is seen that P_c is the solution to the equation $C_{44}C_{66} - C_{46}^2 = 0$. As is shown in ref. [18], 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.



Fig. 1 – Comparison of model (solid lines) and experimental (triangles) dependences of the strain components tensors from ref. [17] on the internal pressure and the molar content of Ca. Here the internal pressure is measured from Sr-phase of the crystal, where $P_{\text{int}} = 0$.

For the experimental data E_j (j = 1, 2, 3, 5) presented in fig. 1, 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. 1 for Ca-anorthite, *i.e.*, for N = 1, and the values of the elastic moduli for these points were borrowed from ref. [19]. It has been estimated that the internal pressure obtained for x = 1in $\text{Ca}_x \text{Sr}_{1-x} \text{Al}_2 \text{Si}_2 \text{O}_8$ 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 is interesting to note that the values of the internal and the external pressures, at which the FPT occurs, differ by almost one order of magnitude. According to our model from eq. (7), $P_c \approx 0.43$ GPa, and the external pressure for this transition is 3.2 GPa [20]. This difference can be conditioned by several reasons. The first reason is that it can be caused by the fact that the external pressure changes the elastic moduli as a result of anharmonicity of the interatomic potentials, while the internal pressure contains the term $F_{xE}F_{xx}^{-1}f_x$ which acts directly on the chemical bonds and, consequently, changes the elastic constants more effectively. Second, as we have mentioned above, the term σ_{ind} is anisotropic, therefore its approximation by the internal pressure is rough and it is appropriate only for the isotropic crystals. Third, the internal forces f_x can change the phase transition pressure owing to interaction of the optical and the acoustic modes F_{xE} .

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 the 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. 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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