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**ANALYSIS OF ORIENTATION MATCHING  
AT A THIN INTERFACE BETWEEN TWO  
PHASES IN FERROELASTIC  $\text{Pb}_3(\text{PO}_4)_2$** **V.A. NEPOCHATENKO, I.A. NEPOCHATENKO**UDC 536.424.1  
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The dependence of the relative orientation of the ferroelastic phase with respect to the paraelastic one on the magnitude of spontaneous strain in  $\text{Pb}_3(\text{PO}_4)_2$  crystals has been analyzed. The first-order phase transition in those crystals has been demonstrated to occur at a temperature, at which the orientation relationship between two phases corresponds to the thin interface model.

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**1. Introduction**

The structural phase transitions in ferroelastics demonstrate main regularities which are common to those for the ferroelectric and martensitic phase transitions [1]. Nevertheless, in contrast to the latter two, the former are characterized by small spreads of the experimental heterophase structure parameters. A good optical quality and a small number of crystal lattice defects allow ferroelastics to be used as reference objects for studying the distortional structural phase transitions. The interest in studying the structure of phase interfaces is caused by their role in the formation of a domain structure, the phase orientation, the amplitude of temperature hysteresis, as well as in governing the conditions which give rise to the destruction of single crystals at phase transitions [2, 3]. The simplest type of the coherent phase interface is a thin phase interface.

The model of a thin phase interface at polymorphic phase transitions has been proposed in work [4]; the conditions of its formation between phases with different symmetries have been analyzed in works [5, 6]. The term “a thin phase interface” means a direct contact between two phases, when every point

of the phase interface is common for two crystal lattices. It was demonstrated that the formation of a thin phase interface is accompanied by a rotation of the crystallographic axes in one phase with respect to those in the other phase, and this rotation is related to either the matrix of coordinate system (CS) transformations  $D_{ij}$  or the Gibbs vector  $\mathbf{G}_{fi}$ . The mechanism of the orientation matching between two phases at a phase transition of the first kind remains obscured.

It is known [7, 8] that displacive phase transitions in the ferroelastic phase are characterized by the rotations of the crystallographic lattices of adjacent domains in different directions with respect to the domain wall, with these rotations being proportional to the spontaneous strain amplitude. Such parameters as the axis orientation and the rotation angle sign depend on the type and the orientation of the wall; as a result, close orientational (suborientational) states arise [9, 10]. It was shown in work [10] that the suborientational states in ferroelastic  $\text{Pb}_3(\text{PO}_4)_2$  belong to structural domains of different types; they are characterized by Gibbs vectors  $\mathbf{G}_i$  which are equal by magnitude but spaced by an angle of approximately  $170^\circ$  at the temperature  $t = 22^\circ\text{C}$ . Suborientational states are formed by those phase interfaces which are different by orientation. A conclusion was drawn [10] that such spontaneous rotations of the crystallographic lattices stem from cooperative displacements of a group of atoms with respect to other atoms in the ferroelastic phase. This means that the Gibbs vector  $\mathbf{G}_i$  is a macroparameter of the ferroelastic phase.

In this connection, we may assume that an unstressed thin phase interface is formed at a temperature when the corresponding vectors  $\mathbf{G}_i$  and  $\mathbf{G}_{f_i}$  become equal or the modulus of their difference  $|\Delta\mathbf{G}|$  becomes close to zero.

The vector  $\mathbf{G}_i$  can be determined, by using the equations for domain walls written down in the CS of two phases. In work [11], the method for writing the equations of domain walls in the ferroelastic phase CS was proposed. Since the dependence between the  $\text{Pb}_3(\text{PO}_4)_2$  lattice parameters is linear within the same phase [12] and the equations of domain walls in the paraphase CS are known [13], we can obtain the  $\mathbf{G}_i$  vectors for any temperature of the ferroelastic phase. It was shown [10] that this phase is characterized by a linear dependence of the Gibbs vector modulus  $|\mathbf{G}_i|$  on the crystallographic parameter  $c$ .

In this connection, it was of interest to study the dependence of the quantity  $|\Delta\mathbf{G}|$  on the parameter  $c$  for those phase interfaces which form suborientational states. As an example, we used ferroelastic  $\text{Pb}_3(\text{PO}_4)_2$ .

Lead orthophosphate  $\text{Pb}_3(\text{PO}_4)_2$  is a pure ferroelastic, in which the phase transition from the rhombohedral  $\beta$ -phase ( $R\bar{3}m$ ) into the monoclinic  $\alpha$ -phase ( $C2/c$ ) occurs at 180 °C [14]. In the ferroelastic phase (if small orientational differences of about 2° are neglected), there can exist three orientational states –  $C_1$ ,  $C_2$ , and  $C_3$  – and two types of domain walls –  $W'$  and  $W$  [7, 15]. The formation of a domain wall of the  $W$  type is accompanied by the variation of the crystal shape.

In the coordinate system where the  $X_1$  axis is parallel to the  $c$  one and the  $X_2$  axis to the  $b$  one, the spontaneous strain tensor looks like [16]

$$S_1 = \begin{pmatrix} -e_{11}^s & 0 & e_{13}^s \\ e_{11}^s & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (1)$$

where  $e_{11}^s = (b - c/\sqrt{3})/2b$  and  $e_{13}^s = (c + 3a \cos \beta)/(6a \sin \beta)$ . Below, the CSs in the  $\beta$ - and  $\alpha$ -phases will be designated as  $X_{0i}$  and  $X_{ji}$ , respectively, and the domain walls, which separate orientational states  $C_i$  and  $C_j$ , as  $W_{ij}$  or  $W'_{ij}$  in accordance with the wall type.

## 2. Determination of Gibbs Vectors in the ferroelastic Phase

The model of ferroelastic domain wall gives rise to the following result [9]. If orientational state  $C_1$  is separated from orientational states  $C_2$  and  $C_3$  by domain walls of

the  $W'$  type ( $W'_{12}$  and  $W'_{13}$ , respectively), the former is characterized by the following matrices of the CS rotation with respect to the  $\beta$ -phase:

$$A_{11} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix},$$

$$A_{12} = \begin{pmatrix} a_{11} & -a_{12} & a_{13} \\ -a_{21} & a_{22} & -a_{23} \\ a_{31} & -a_{32} & a_{33} \end{pmatrix}, \quad (2)$$

where  $a_{11} = 0.99984$ ,  $a_{12} = -0.01756$ ,  $a_{13} = -0.0019$ ,  $a_{21} = 0.01753$ ,  $a_{22} = 0.99976$ ,  $a_{23} = -0.0134$ ,  $a_{31} = 0.00213$ ,  $a_{32} = 0.01338$ , and  $a_{33} = 0.99991$ . If the orientation states concerned are separated by domain walls  $W_{12}$  and  $W_{13}$ , orientational states  $C_1$  is characterized by the rotation matrices  $B_{1j}$ , which are similar to matrices (2) taken in the inverse order, namely,

$$B_{11} = \begin{pmatrix} b_{11} & -b_{12} & b_{13} \\ -b_{21} & b_{22} & -b_{23} \\ b_{31} & -b_{32} & b_{33} \end{pmatrix},$$

$$B_{12} = \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix}, \quad (3)$$

where  $b_{11} = 0.99978$ ,  $b_{12} = -0.0186$ ,  $b_{13} = -0.0096$ ,  $b_{21} = 0.01854$ ,  $b_{22} = 0.99981$ ,  $b_{23} = -0.0056$ ,  $b_{31} = 0.00969$ ,  $b_{32} = 0.00548$ , and  $b_{33} = 0.99994$ . An insignificant difference between the components of the matrices  $B_{1j}$  and  $A_{1i}$  stems from the variation of the crystal shape caused by the formation of the domain wall.

Thus, if such small differences are neglected, there can exist two suborientational states in  $\text{Pb}_3(\text{PO}_4)_2$ . We use notations  $C_{11}$  and  $C_{12}$  for them, in accordance with the notation for  $A_{1j}$  matrices. It is convenient to describe the CS rotation by the Gibbs vector

$$\mathbf{G} = g_1\mathbf{e}_1 + g_2\mathbf{e}_2 + g_3\mathbf{e}_3, \quad (4)$$

where  $g_1 = c_1 \tan(\delta/2)$ ,  $g_2 = c_2 \tan(\delta/2)$ ,  $g_3 = c_3 \tan(\delta/2)$ ,  $\delta$  is the rotation angle, and  $c_i$  are the direction cosines of the positive rotation axis.

The components of the vector  $\mathbf{G}$ , which depend on the spontaneous strain value, are obtained using the equations for domain wall  $W'$  written down in two coordinate systems. The axis orientation is determined by the vector product of unit vectors that are normal

to the corresponding wall planes, while the angle by the scalar product of the same vectors.

The equation for domain walls  $W'_{12}$  and  $W'_{13}$  in the CS of the  $\beta$ -phase looks like [13]

$$X_{01} \pm \sqrt{3}X_{02} + K_1X_{03} = 0, \tag{5}$$

where  $K_1 = -2e_{13}^s/e_{11}^s$ . The equations for the same domain walls in the CS of the  $\alpha$ -phases were obtained in work [11]; they read

$$X_{31} + B_2X_{32} + K_2X_{33} = 0, \tag{6}$$

$$X_{41} - B_2X_{42} + K_2X_{43} = 0, \tag{7}$$

where

$$B_2 = \frac{\sqrt{3}e_{11}^s(1 - e_{11}^s - e_{13}^s{}^2)}{(1 + e_{11}^s)(e_{11}^s + 2e_{13}^s{}^2)}$$

and

$$K_2 = -\frac{2e_{13}^s(1 - e_{11}^s/2)}{e_{11}^s + 2e_{13}^s{}^2}.$$

According to the results of work [12], the quantities  $a$ ,  $b$ ,  $\beta$ ,  $n = a \sin \beta$ , and  $m = a \cos \beta$  for the  $\alpha$ -phase depend linearly on the parameter  $c$ :

$$a = k_1c + d_1, \quad b = k_2c + d_2, \quad \beta = k_3c + d_3,$$

$$m = k_4c + d_4, \quad n = k_5c + d_5, \tag{8}$$

where  $k_1 = 0.6326$ ,  $d_1 = 7.845$ ,  $k_2 = -1.506$ ,  $d_2 = 19.95$ ,  $k_3 = 0.0913$ ,  $d_3 = 0.927$ ,  $k_4 = -1.373$ ,  $d_4 = 9.969$ ,  $k_5 = 0.338$ , and  $d_5 = 10.298$ . This allows us to determine the components of a spontaneous strain, the parameters of Eqs. (5)–(7), and, hence, the components of Gibbs vectors for an arbitrary temperature of the  $\alpha$ -phase (or, equivalently, for the corresponding value of the parameter  $c$ ). Let us denote the Gibbs vectors, which correspond to the matrices  $A_{11}$  and  $A_{12}$ , as  $\mathbf{G}_1(g_{11}, g_{12}, g_{13})$  and  $\mathbf{G}_2(g_{21}, g_{22}, g_{23})$ , respectively. The components of those vectors are calculated from the following equations:

$$g_{11} = \frac{e_1 \operatorname{tg}(\delta/2)}{M}, \quad g_{12} = \frac{e_2 \operatorname{tg}(\delta/2)}{M}, \quad g_{13} = \frac{e_3 \operatorname{tg}(\delta/2)}{M},$$

$$e_1 = \sqrt{3}K_2 - B_2K_1, \quad e_2 = K_1 - K_2, \quad e_3 = B_2 - \sqrt{3}; \tag{9}$$

$$M = \sqrt{e_1^2 + e_2^2 + e_3^2},$$

$$\delta = \arccos\left(\frac{1 + \sqrt{3}B_2 + K_1K_2}{\sqrt{(4 + K_1^2)(1 + B_2^2 + K_2^2)}}\right); \tag{10}$$

$$g_{21} = -g_{11}, \quad g_{22} = g_{12}, \quad g_{23} = -g_{13}. \tag{11}$$

### 3. Determination and Coordination of the Gibbs Vectors at a First-Order Phase Transition

The model of a thin phase interface [4, 5] gives rise to the following equations for two phase interfaces in the CSs of the  $\beta$ - and  $\alpha$ -phases:

$$X_{01} + hX_{02} + dX_{03} = 0, \tag{12}$$

$$X_{01} - hX_{02} + dX_{03} = 0, \tag{13}$$

$$X_{11} + pX_{12} + kX_{13} = 0, \tag{14}$$

$$X_{21} - pX_{22} + kX_{23} = 0, \tag{15}$$

where  $h = 1.1759$ ,  $d = 0.1164$ ,  $p = 1.1679$ , and  $k = 0.11675$ . Equations (12), (14) and (13), (15) correspond in pairs to the following matrices of CS rotation  $D_{ij}$  and the Gibbs vectors  $\mathbf{G}_{f1}$  and  $\mathbf{G}_{f2}$  in the case where a thin phase interface is formed:

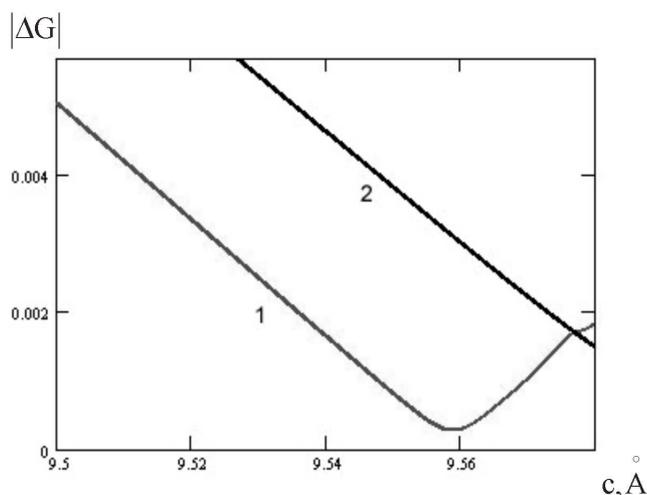
$$D_{11} = \begin{pmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{pmatrix},$$

$$D_{12} = \begin{pmatrix} d_{11} & -d_{12} & d_{13} \\ -d_{21} & d_{22} & -d_{23} \\ d_{31} & -d_{32} & d_{33} \end{pmatrix}, \tag{16}$$

$\mathbf{G}_{f1} = g_1\mathbf{e}_1 + g_2\mathbf{e}_2 + g_3\mathbf{e}_3$ , and  $\mathbf{G}_{f2} = -g_1\mathbf{e}_1 + g_2\mathbf{e}_2 - g_3\mathbf{e}_3$ , where  $d_{11} = 0.999994$ ,  $d_{12} = -3.35 \times 10^{-3}$ ,  $d_{13} = 1.46 \times 10^{-4}$ ,  $d_{21} = 3.35 \times 10^{-3}$ ,  $d_{22} = 0.999994$ ,  $d_{23} = 5.63 \times 10^{-3}$ ,  $d_{31} = -1.47 \times 10^{-4}$ ,  $d_{32} = -5.62 \times 10^{-4}$ ,  $d_{33} = 0.999998$ ,  $g_1 = 2.8 \times 10^{-4}$ ,  $g_2 = -7.3 \times 10^{-5}$ , and  $g_3 = -1.67 \times 10^{-3}$ .

The moduli of the Gibbs vector differences are determined as

$$|\Delta G_{11}| = |G_1 - G_{1f}|; \quad |\Delta G_{12}| = |G_1 - G_{2f}|. \tag{17}$$



Dependences of the vector magnitudes  $|\Delta\mathbf{G}_{11}|$  (1) and  $|\Delta\mathbf{G}_{12}|$  (2) on the value of crystallographic parameter  $c$

In the figure, the dependences of those moduli on the value of crystallographic parameter  $c$  are depicted. The modulus  $|\Delta\mathbf{G}_{11}|$  has a minimum in the phase transition region (at  $c = 9.56 \text{ \AA}$  [17]). Since the minimal value obtained is close to zero, there is an insignificant mismatch between orientational state  $C_{11}$  and the  $\beta$ -phase at the formation of a thin phase interface (see Eq. (12)). Analogously, it can be demonstrated that the thin phase interface, the orientation of which corresponds to Eq. (13), forms orientational state  $C_{12}$ .

Thus, on the basis of the analysis given above, a conclusion can be drawn that a perfect thin phase interface is formed provided that two conditions are satisfied. First, the parameters of crystal lattices of two phases must obey the condition (see work [5]) for a thin phase interface to be formed. Second, an orientational matching between the crystal lattices of two phases must take place, i.e. the corresponding Gibbs vectors  $\mathbf{G}_i$  and  $\mathbf{G}_{f_i}$  must be equal. Should the former condition be violated, the phase interface would be combined and would include an intermediate phase [18], which would give rise to the increase of the interface energy. Provided that the former condition is satisfied but the latter is violated, mechanical stresses would emerge in the phase interface region owing to orientational mismatches between two phases. For the mechanical stresses to be lower, the phase interface area has to diminish, which would result in the appearance of a fine-grained domain structure. At significant differences between the Gibbs vectors  $\mathbf{G}_i$  and  $\mathbf{G}_{f_i}$ , the formation of cracks and the destruction of the single crystal become possible. In the case of a phase transition in  $\text{Pb}_3(\text{PO}_4)_2$ , the interface

between two phases can be considered close to a perfect thin interface. Each phase interface forms a certain orientational state.

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#### АНАЛІЗ ОРІЄНТАЦІЙНОЇ ВІДПОВІДНОСТІ ДВОХ ФАЗ ПРИ ФОРМУВАННІ ТОНКИХ ФАЗОВИХ МЕЖ У СЕГНЕТОЕЛАСТИКУ $\text{Pb}_3(\text{PO}_4)_2$

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#### Резюме

Зроблено аналіз орієнтації сегнетоеластичної фази відносно парaelастичної в залежності від величини спонтанної деформації в  $\text{Pb}_3(\text{PO}_4)_2$ . Показано, що в цьому кристалі фазовий перехід першого роду утворюється при температурі, коли орієнтаційне співвідношення між двома фазами відповідає моделі тонкої фазової межі.