THIN PHASE INTERFACES AT POLYMORPHIC PHASE TRANSITIONS IN PHASES WITH SYMMETRY NOT LOWER THAN MONOCLINIC ONE

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On the basis of the model of a thin phase interface (TPI) between two monoclinic phases, an analysis of the TPI formation conditions has been carried out and their equations have been derived for phases of higher symmetry.

The problem of definition of phase interface (PI) orientation for some martensitic phase transitions has been resolved for the first time in Roitburd and Khachaturyan works [1—3]. The continuum theory proposed by them was based on an assumption put forward by Kurdyumov about the regular cooperative reconstruction of the crystal lattice at phase transitions and the coherent coexistence of phases [4,5]. But the definition of the PI orientation in the framework of this theory is a challenging problem, resolved only for several phase transitions [6].

Along with it, the model of TPI that coordinates two monoclinic phases [7] was proposed. The term "thin phase interface" corresponds to a direct contact of phases, without a coordination interlayer between crystal lattices. Its equation was obtained from a condition that provided the coordinate origin is chosen at the PI, the indices of an arbitrary node at the PI and the length of the position vector $\mathbf{R}$ are identical for two different crystal lattices. It means that the spontaneous deformation comes to an agreement at the TPI and the lattice periodicity is not violated within the phase limits.

For the TPI to develop, certain relations between the variations of lattice parameters have to be fulfilled at a phase transition of the first kind.

The TPI equations are used also to determine the structure of domain walls [8]. Therefore, the definition of conditions for the TPI formation and orientation between phases of higher symmetry is of special interest.

In the first part of the work, the case is considered where one phase is monoclinic and another one possesses a higher symmetry; in the second part, the case where both the phases have the symmetry higher than the monoclinic one.

1. TPIs Between Monoclinic Phases of Low-symmetry

According to [7,8], the equation of the TPI that coordinates two monoclinic lattices with parameters $a_1, b_1, c_1, \varphi_1 = \beta_1 - 90^\circ$ and $a_2, b_2, c_2, \varphi_2 = \beta_2 - 90^\circ$, respectively, when being written down in the coordinate system of the first lattice (the c-axis is parallel to the x-axis, the b-axis to the y-axis, and the z-axis forms the angle $\varphi = \beta - 90^\circ$ with the a-axis), looks like

$$X_1^2 A_{11} + Y_1^2 A_{22} + Z_1^2 A_{33} + 2X_1 Z_1 A_{13} = 0, \qquad (1)$$

where

$$A_{11} = 1 - (c_2/c_1)^2, \quad A_{22} = 1 - (b_2/b_1)^2,$$

$$A_{13} = -\frac{c_2}{c_1 \cos\varphi_1}\left(\frac{c_2}{c_1}\sin\varphi_1 - \frac{a_2}{a_1}\sin\varphi_2\right),$$

$$A_{33} = 1 - \frac{1}{\cos^2\varphi_1}\left(\left(\frac{a_2}{a_1}\right)^2 \cos^2\varphi_2 + \right.$$

$$\left. + \left(\frac{c_2}{c_1}\sin\varphi_1 - \frac{a_2}{a_1}\sin\varphi_2\right)^2\right),$$

and in the coordinate system of the second phase has the form

$$X_2^2 B_{11} + Y_2^2 B_{22} + Z_2^2 B_{33} + 2X_2 Z_2 B_{13} = 0, \qquad (2)$$

where

$$B_{11} = 1 - (c_1/c_2)^2, \quad B_{22} = 1 - (b_1/b_2)^2,$$

$$B_{13} = -\frac{c_1}{c_2 \cos\varphi_2}\left(\frac{c_1}{c_2}\sin\varphi_2 - \frac{a_1}{a_2}\sin\varphi_1\right),$$

$$B_{33} = 1 - \frac{1}{\cos^2\varphi_2}\left(\left(\frac{a_1}{a_2}\right)^2 \cos^2\varphi_1 + \right.$$

$$\left. + \left(\frac{c_1}{c_2}\sin\varphi_2 - \frac{a_1}{a_2}\sin\varphi_1\right)^2\right).$$

The equation of the second order (1), provided that

$$\det|A_{ij}| = 0, \tag{3}$$

corresponds to the equations of two intersecting planes (two TPIs). Since Eq. (3) corresponds to the equation

$$A_{22}(A_{11}A_{33} - A_{13}^2) = 0, \tag{4}$$

two cases are possible:

$$A_{22} = 0, \tag{5}$$

or

$$A_{11}A_{33} - A_{13}^2 = 0. \tag{6}$$

If Eq. (5) is valid, then $b_2 = b_1$ (the parameter b is constant at a phase transition) and, provided that $C_{13}^2 - C_{33} \geq 0$, Eq. (1) corresponds to the following equations:

$$X_1 + BZ_1 = 0, \tag{7}$$

$$X_1 + NZ_1 = 0, \tag{8}$$

where $B = C_{13} + \sqrt{C_{13}^2 - C_{33}}$, $N = C_{13} - \sqrt{C_{13}^2 - C_{33}}$, $C_{13} = A_{13}/A_{11}$, and $C_{33} = A_{33}/A_{11}$. If

$$C_{13}^2 - C_{33} = 0, \tag{9}$$

only one PI is developed. We shall call this state a "PI degeneration".

If condition (6) holds true at the phase transition and $A_{22}/A_{11} < 0$, Eq. (1) corresponds to the following TPI equations:

$$X_1 + DY_1 + CZ_1 = 0, \tag{10}$$

$$X_1 - DY_1 + CZ_1 = 0, \tag{11}$$

where $D = \sqrt{-A_{22}/A_{11}}$ and $C = A_{13}/A_{11}$. If both Eqs. (5) and (6) are valid, the PI degenerates.

The TPI equation can be obtained in a coordinate system of the second phase if one use Eq. (2) instead of (1).

Let us consider, as an example, the determination of the TPI orientation in a ferroelastic $Pb_3(PO_4)_2$ between the rhombohedral β-phase ($R\bar{3}m$) and the monoclinic α-phase ($C2/c$). The rhombohedral phase will be described as a pseudo-monoclinic one with corresponding parameters.

The following changes of the crystal lattice parameters take place in this crystal at a phase transition [9,10]: $b_1/b_2 = 1.003914$, $c_1/c_2 = 0.99716$, $a_1/a_2 = 0.9999$, and $\beta_1 = \beta_2 = 103.3°$. The variations of parameters correspond (to an accuracy of 10^{-9}) to Eq. (6), so, two PIs [Eqs. (10) and (11)], the equations of which in a coordinate system of the β-phase have the form

$$X \pm 1,1759Y + 0,1164Z = 0, \tag{12}$$

are possible. The trace of those PIs on the plane (001) produces an angle $\alpha = 49.62°$ with the Y-axis (the axis of the 2-nd order), which is in a good agreement with experimental data $\alpha = 50 \pm 0.5°$ [7].

In a similar way, it is possible to obtain the TPI equation for the case, where one of phases possesses higher symmetry, by substituting the parameters of a new phase into Eq. (1). For trigonal, rhombohedral, and hexagonal phases, one should pass to the parameters of a monoclinic cell (the pseudo-monoclinic symmetry). Consider the case where the first phase is of a cubic symmetry. In this case, Eq. (1) will look like:

$$X_1^2E_{11} + Y_1^2E_{22} + Z_1^2E_{33} + 2X_1Z_1E_{13} = 0, \tag{13}$$

where

$$E_{11} = 1 - (c_2/a)^2, \quad E_{22} = 1 - (b_2/a)^2,$$

$$E_{13} = \frac{c_2a_2\sin\varphi_2}{a^2}, \quad E_{33} = 1 - (a_2/a)^2.$$

Provided that

$$b_2 = a, \tag{14}$$

and

$$(c_2a_2)^2(\sin^2\varphi_2 - 1) - a^2(a^2 - a_2^2 - c_2^2) > 0 \tag{15}$$

at the phase transition, two different TPIs emerge:

$$X_1 + B_1Z_1 = 0, \tag{16}$$

$$X_1 + N_1Z_1 = 0, \tag{17}$$

where $B_1 = K_{13} + \sqrt{K_{13}^2 - K_{33}}$, $N_1 = K_{13} - \sqrt{K_{13}^2 - K_{33}}$, $K_{13} = E_{13}/E_{11}$, and $K_{33} = E_{33}/E_{11}$.

If the relations $E_{22}E_{11} < 0$ and

$$(c_2a_2)^2(\sin^2\varphi_2 - 1) - a^2(a^2 - a_2^2 - c_2^2) = 0, \tag{18}$$

hold true at the phase transition, two TPIs are possible again:

$$X_1 + D_1Y_1 + C_1Z_1 = 0, \tag{19}$$

$$X_1 - D_1Y_1 + C_1Z_1 = 0, \tag{20}$$

where $D_1 = \sqrt{-E_{22}/E_{11}}$ and $C_1 = E_{13}/E_{11}$. If both Eqs. (14) and (18) are valid, the PI degenerates.

2. TPIs Between the Phases of the Symmetry Higher than the Monoclinic one

If the phase of low symmetry is trigonal, rhombohedral, or hexagonal, then the conditions of the TPI formation and its equation do not differ essentially from the case considered above. Significant changes occur, if both the phases have orthogonal crystallographic axes. Consider the conditions for the formation of the TPIs, which coordinate two different orthorhombic lattices. From Eq. (1), the following equation of the second order is obtained:

$$X_1^2 D_{11} + Y_1^2 D_{22} + Z_1^2 D_{33} = 0, \tag{21}$$

where $D_{11} = 1 - (c_2/c_1)^2$, $D_{22} = 1 - (b_2/b_1)^2$, and $D_{33} = 1 - (a_2/a_1)^2$. Equation (21), provided that

$$\det |D_{ij}| = D_{11} D_{22} D_{33} = 0, \tag{22}$$

comprises the equations of two TPIs. Thus, one of the factors D_{ii} is equal to zero, and it means that one of the crystal lattice parameters does not vary at the phase transition.

Consider, for example, the case where

$$D_{11} = 0. \tag{23}$$

From Eq. (21), we obtain the relation

$$D_{22} Y_2^2 + D_{33} Z_2^2 = 0, \tag{24}$$

which, provided that

$$D_{22} D_{33} < 0, \tag{25}$$

is decomposed into the following equations of the two TPIs:

$$Y_2 + K Z_2 = 0, \tag{26}$$

$$Y_2 - K Z_2 = 0, \tag{27}$$

where $K = \sqrt{-D_{33}/D_{22}}$.

The TPI equations are obtained analogously in the cases where

$$D_{22} = 0, \tag{28}$$

or

$$D_{33} = 0. \tag{29}$$

If any two conditions from the set (23), (28), and (29) hold true, the PI degenerates and becomes a crystallographic plane. The TPI equations for the phases of higher symmetry can be obtained from Eqs. (21)—(27) by substituting the parameters of those phases into Eq. (21).

Consider, as an example, the case where the first phase is of the cubic symmetry and the second phase is of the tetragonal one. From Eq. (21), the following equation is obtained:

$$N_{11} X_3^2 + N_{22} Y_3^2 + N_{22} Z_3^2 = 0, \tag{30}$$

where $N_{11} = 1 - (c_t/a)^2$ and $N_{22} = 1 - (a_t/a)^2$. If

$$N_{11} = 0, \tag{31}$$

the TPIs are impossible. For

$$N_{22} = 0, \tag{32}$$

the PI degenerates and only one crystallographic TPI is developed:

$$X = 0. \tag{33}$$

If both the phases possess the cubic symmetry, the TPI does not arise.

Let us carry out the analysis of the PIs in a ferroelectric $BaTiO_3$ between the cubic ($Pm3m$) and tetragonal ($P4mm$) phases. According to [11], all the parameters of the crystal lattice of this crystal change at the phase transition of the first kind, and it means that, according to Eqs. (30)–(33), the appearance of the TPI is not possible. Therefore, a strained PI with monoclinic or triclinic distortions of the $BaTiO_3$ crystal lattice is formed.

Thus, if one of the phases possesses the monoclinic symmetry, the TPI formation is possible in the case where all the parameters of the crystal lattice vary at the phase transition of the first kind. If both the phases are of the symmetry higher than the monoclinic one (the crystallographic axes are orthogonal), the TPIs can emerge provided that one of the lattice parameters does not change at the phase transition, while two others differ in the sign of the parameter variation (one parameter grows and another one decreases). If one of the phases is tetragonal and the other is cubic, only a single PI, a normal to which is parallel to a tetragonal c-axis, is allowed. If both the phases possess the cubic symmetry, the TPIs are impossible, with only the strained PIs arising.

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ТОНКІ ФАЗОВІ МЕЖІ ПРИ ПОЛІМОРФНИХ ФАЗОВИХ ПЕРЕХОДАХ ДЛЯ ФАЗ ІЗ СИМЕТРІЄЮ, НЕ НИЖЧОЮ ЗА МОНОКЛІННУ

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Р е з ю м е

На основі моделі тонкої фазової межі (ТФМ) між двома моноклінними фазами проведено аналіз умов формування ТФМ і визначено їхнє рівняння для фаз із вищою симетрією.