

Ginzburg – Landau-type theory of antiphase boundaries in polytwinned structures

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The conventional Landau – Ginzburg theory of interphase boundaries is generalized to the case of not small values of order parameters, with application to polytwinned structures characteristic of cubic-tetragonal-type phase transitions. Explicit expressions for the structure and energy of antiphase boundaries via the functions entering the free energy functional are given. A peculiar dependence of equilibrium orientations of antiphase boundaries on the interaction type is predicted, and it qualitatively agrees with available experimental data.

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Ordering phase transitions between the cubic disordered and the tetragonal ordered phases are observed in many different solids. The known examples are the transitions between the disordered FCC phase (A1 phase) and the CuAu I-type ordered tetragonal phase (L1₀ phase) in a number of metallic alloys [1–3]; the ferroelectric transitions between the cubic paraelectric and the tetragonal ferroelectric phase in the BaTiO₃-type perovskites [4], etc. A characteristic feature of such transitions is the formation in the ordered phase of so-called “polytwinned” structures consisting of arrays of ordered bands separated by the antiphase boundaries (APBs) with (110)-type orientation, while the tetragonal axes of antiphase-ordered domains (APDs) in the adjacent bands have “twin-related” (100) and (010)-type orientations. As an example, in figure 1 we show a typical microstructure of the L1₀ phase in CoPt alloys observed by Leroux et al. [1]. The formation of polytwinned structures is explained by the elimination of the volume-dependent part of the elastic energy for such structures [4–7] discussed below.

Studies of microstructural features of polytwinned structures, such as the properties and distribution of APBs, attract interest from both fundamental and applied points of view, in particular, in connection with applications of such structures in various magnetic devices for which the structure and the distribution of APBs are very important [1–3]. Below we present a Ginzburg – Landau-type theory which enables one to explicitly calculate characteristics of APBs in polytwinned structures both phenomenologically and microscopically.

To be definite, we consider the A1→L1₀ transition in a binary alloy A_cB_{1–c}. Various distributions of atoms

over lattice sites i are described by the occupation numbers $\{n_i\}$ where $n_i = n_{Ai}$ is unity when the site i is occupied by atom A and zero otherwise. The mean occupation $\langle n_i \rangle = c_i = c(\mathbf{r}_i)$ (where \mathbf{r}_i is the FCC lattice vector) in the homogenous L1₀ phase can be written in terms of three long-ranged order parameters η_α , see e.g. [7]:

$$c_i = c + \eta_1 \exp(i\mathbf{k}_1\mathbf{r}_i) + \eta_2 \exp(i\mathbf{k}_2\mathbf{r}_i) + \eta_3 \exp(i\mathbf{k}_3\mathbf{r}_i), \quad (1)$$

where \mathbf{k}_α is the superstructure vector corresponding to η_α :

$$\mathbf{k}_1 = [100]2\pi/a, \quad \mathbf{k}_2 = [010]2\pi/a, \quad \mathbf{k}_3 = [001]2\pi/a, \quad (2)$$

and a is the FCC lattice constant. Within each L1₀-ordered domain with the tetragonal axis α only one nonzero parameter η_α is present being either positive or negative. Therefore, six types of ordered domains are possible with two types of APB. That separating two APDs with the same tetragonal axis will be for brevity called the “shift-APB”, and that separating the APDs with perpendicular tetragonal axes will be called the “flip-APB”.

Below we consider the “weakly inhomogeneous” states for which quantities c and η_α in equation (1) are not constants but slowly varying functions of coordinates $\mathbf{r} = \mathbf{r}_i$ with the characteristic length l (which in our problem is the APB width δ) much exceeding the interatomic distance $l_0 = a/\sqrt{2}$. Both theoretical and experimental studies of APBs show that the inequality $l \gg l_0$ is usually obeyed in alloy systems of practical interest, particularly in systems with an extended interaction range or at small values of order parameters, see e.g. [8]. The weakly inhomogeneous states can be de-

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Typical microstructure of the L1₀ phase in CoPt [1], with the (001) direction normal to the plane of figure and the (110) direction lying horizontally in the plane of figure. Bright areas in frame (a) or (b) correspond to the ordered domains oriented along the direction (100) or (010), respectively

scribed with the Ginzburg – Landau approach using the gradient expansion of the free energy density f .

Let us suppose for simplicity the concentration c to be close to the stoichiometric value $c_s = 0.5$. Then variations $\delta c = c(\mathbf{r}) - c$ of local concentrations $c(\mathbf{r})$ in the APB region are very small which is illustrated, for example, by the computer simulation results [9]. The smallness of δc follows from the symmetry of the free energy density for the homogeneous L1₀ ordering, $f_{0h}(c, \eta_\alpha)$, with respect to the substitution $(c - c_s) \rightarrow (c_s - c)$, which implies variations δc to be proportional to the small factor $(c - c_s)$. Therefore, in our gradient expansion we can neglect δc and keep only terms with the order parameter gradients $\nabla \eta_\alpha$ and the elastic strain $u_{\alpha\beta} = (\partial u_\alpha / \partial x_\beta + \partial u_\beta / \partial x_\alpha) / 2$. Then the Ginzburg – Landau functional F for our problem takes the form

$$F = \int d^3r \left[f_{0h} + \sum_{\alpha, \beta, \gamma, \delta=1}^3 \left(g_{\alpha\beta\gamma\delta} \frac{\partial \eta_\alpha}{\partial x_\beta} \frac{\partial \eta_\gamma}{\partial x_\delta} - q_{\alpha\beta\gamma\delta} \eta_\alpha \eta_\beta u_{\gamma\delta} + \frac{1}{2} c_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta} \right) \right]. \quad (3)$$

Terms with $q_{\alpha\beta\gamma\delta}$ in (3) will be called the “striction” terms, in an analogy with the terminology used in the ferroelectricity or magnetism theory [4]. The microscopic expression for coefficients $q_{\alpha\beta\gamma\delta}$ [9] shows that under usual approximations neglecting many-atom effective interactions (being usually small [10]) these coefficients do not depend on the order parameters η_α . Variation of elastic constants $c_{\alpha\beta\gamma\delta}$ with ordering is usually small, too, and for simplicity it will be neglected. However, coefficients $g_{\alpha\beta\gamma\delta}$ in (3) can, generally, significantly vary with η_α .

Taking into account the crystal symmetry, we can write the integrand in (3) as

$$f = f_{0h}(\eta_\alpha) + \sum_{\alpha, \beta, \gamma, \delta} g_{\alpha\beta\gamma\delta} \frac{\partial \eta_\alpha}{\partial x_\beta} \frac{\partial \eta_\gamma}{\partial x_\delta} - \sum_{\alpha} u_{\alpha\alpha} \left(q_{11} \eta_\alpha^2 + q_{12} \sum_{\beta \neq \alpha} \eta_\beta^2 \right) + \frac{1}{2} c_{11} \sum_{\alpha} u_{\alpha\alpha}^2 + c_{12} \sum_{\alpha \neq \beta} u_{\alpha\alpha} u_{\beta\beta} + c_{44} \sum_{\alpha < \beta} u_{\alpha\beta}^2. \quad (4)$$

Here elastic strains $u_{\alpha\beta}$ are counted from their values in the disordered cubic phase, and we use the usual Voigt-type notation [4] for coefficients q and c .

The equilibrium distribution of strains $u_{\alpha\beta}(\mathbf{r})$ is determined by the equation $\delta F / \delta u_\alpha = 0$:

$$c_{11} \frac{\partial^2 u_\alpha}{\partial x_\alpha^2} + c_{12} \sum_{\beta \neq \alpha} \frac{\partial^2 u_\beta}{\partial x_\alpha \partial x_\beta} + c_{44} \sum_{\beta \neq \alpha} \left(\frac{\partial^2 u_\alpha}{\partial x_\beta^2} + \frac{\partial^2 u_\beta}{\partial x_\alpha \partial x_\beta} \right) = q_{11} \frac{\partial \eta_\alpha^2}{\partial x_\alpha} + q_{12} \sum_{\beta \neq \alpha} \frac{\partial \eta_\beta^2}{\partial x_\alpha}, \quad (5)$$

while the distribution of order parameters $\eta_\alpha(\mathbf{r})$ is determined by the equation $\delta F / \delta \eta_\alpha = 0$ to be discussed below.

Let us first find the spontaneous strain $\bar{u}_{\alpha\beta}$ in the homogeneous (100)-ordered domain with the $|\eta_\alpha| = |\eta_1|$ value equal to the equilibrium order parameter $\eta_e = \eta_e(c, T)$. The nonzero strains \bar{u}_{11} and $\bar{u}_{22} = \bar{u}_{33}$

in this case can be found from the zero-stress condition $\sigma_{\alpha\beta} = \partial f / \partial u_{\alpha\beta} = 0$ which yields:

$$\begin{aligned} \bar{\varepsilon} &= \bar{u}_{11} - (\bar{u}_{22} + \bar{u}_{33})/2 = q_- \eta_e^2 / c_-; \\ \bar{u} &= \bar{u}_{11} + \bar{u}_{22} + \bar{u}_{33} = q_+ \eta_e^2 / c_+, \end{aligned} \quad (6)$$

where $q_- = q_{11} - q_{12}$, $c_- = c_{11} - c_{12}$, $q_+ = q_{11} + 2q_{12}$, and $c_+ = c_{11} + 2c_{12}$.

Analogous expressions for $\bar{u}_{\alpha\beta}$ can be obtained when several nonzero homogeneous η_α are present. After substitution of these $\bar{u}_{\alpha\beta}$ into Eq.(4) the function f can be written as the sum of the renormalized function f_h for the homogeneous ordering, the gradient term, and the elastic energy E_{el} , with the following expressions for f_h and E_{el} :

$$\begin{aligned} f_h(\eta_\alpha) &= f_{0h}(\eta_\alpha) - \frac{q_+^2}{6c_+} \sum_{\alpha,\beta} \eta_\alpha^2 \eta_\beta^2 - \\ &- \frac{q_-^2}{3c_-} \left(\sum_\alpha \eta_\alpha^4 - \sum_{\alpha<\beta} \eta_\alpha^2 \eta_\beta^2 \right), \end{aligned} \quad (7)$$

$$\begin{aligned} E_{el} &= \frac{1}{6} c_+ (u - \bar{u})^2 + \frac{1}{3} c_- (\varepsilon - \bar{\varepsilon})^2 + \\ &+ \frac{1}{4} c_- (\zeta - \bar{\zeta})^2 + c_{44} (u_{12}^2 + u_{23}^2 + u_{31}^2). \end{aligned} \quad (8)$$

Here $u = u_{11} + u_{22} + u_{33}$, $\varepsilon = u_{11} - (u_{22} + u_{33})/2$, and $\zeta = u_{22} - u_{33}$, while \bar{u} , $\bar{\varepsilon}$ and $\bar{\zeta}$ are expressed via η_α as follows:

$$\begin{aligned} \bar{u} &= q_+ (\eta_1^2 + \eta_2^2 + \eta_3^2) / c_+, \\ \bar{\varepsilon} &= q_- [\eta_1^2 - (\eta_2^2 + \eta_3^2) / 2] / c_-, \\ \bar{\zeta} &= q_- (\eta_2^2 - \eta_3^2) / c_-. \end{aligned} \quad (9)$$

Let us note that the "strictive" renormalization $f_h - f_{0h}$ in (7) is proportional to the ordering-induced elastic energy per atom, E_d , which usually is small. For example, for CoPt alloys [1] the tetragonal distortion $\bar{\varepsilon}$ is about 0.03; $\bar{u} \simeq 6 \cdot 10^{-4}$, and E_d is about 0.01 of the transition temperature T_c .

Let us apply Eq.(5) to the strains $u_{\alpha\beta}(\mathbf{r})$ near a plane flip-APB which is normal to vector $\mathbf{n} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ and separates the (100) and (010)-ordered domains. Then the functions u_α and η_α^2 in (5) depend only on the coordinate $\xi = \mathbf{r}\mathbf{n}$, and at $\xi \rightarrow -\infty$ the nonzero η_α^2 in Eq.(5) is $\eta_1^2 = \eta_e^2$, while at $\xi \rightarrow \infty$ the nonzero η_α^2 is $\eta_2^2 = \eta_e^2$. The strain ($u_{\alpha\beta} - \bar{u}_{\alpha\beta}$) should vanish at both $\xi \rightarrow \pm\infty$, otherwise the elastic energy E_{el} in Eq.(8) rises proportionally to the whole

volume of the ordered domain. Integrating Eq.(5) over ξ from $\xi = -\infty$ to ∞ we find that the above-mentioned conditions for elastic strains lead to the following equations for angles θ and φ :

$$\begin{aligned} c_{44} \bar{\varepsilon} [\cos^2 \theta + \sin^2 \theta (\sin^2 \varphi - \cos^2 \varphi)] &= 0; \\ c_{44} \bar{\varepsilon} [\cos^2 \theta + \sin^2 \theta (\cos^2 \varphi - \sin^2 \varphi)] &= 0, \end{aligned} \quad (10)$$

which implies: $\cos \theta = 0$; $\sin^2 \varphi = \cos^2 \varphi$. Therefore, an equilibrium flip-APB should have the (110)-type orientation, in accordance with experimental observations and theoretical considerations mentioned above [1–7]. The present Ginzburg – Landau-type approach is just a reformulation of previous theoretical treatments [5–7], but it is also convenient for studies of other properties of polytwinned structures.

Let us now consider the structure of a plane shift-APB in the (100)-ordered twin band with the APB plane normal to vector $\mathbf{m} = (\cos \alpha, \sin \alpha \cos \varphi, \sin \alpha \sin \varphi)$. The elastic equilibrium equations (5) now have a "local equilibrium" solution $u_{\alpha\beta} = \bar{u}_{\alpha\beta}(\eta_\gamma)$ for any orientation \mathbf{m} . Therefore, in finding the order parameters $\eta_\alpha(\mathbf{r})$ (which here depend on $\xi = \mathbf{r}\mathbf{m}$ only) we can retain in the right-hand side of Eqs.(3) and (4) only first two terms, with the substitution of f_{0h} by the renormalized function f_h from (7).

For consideration of symmetry, the only nonzero component η_α is $\eta_1 = \eta(\xi)$ which varies, say, from $\eta = -\eta_e$ at $\xi = -\infty$ to $\eta = \eta_e$ at $\xi = \infty$. Let us denote coefficients g_{1111} and $g_{1212} = g_{1313}$ at nonzero gradient terms as g_{11} and g_{12} , respectively. Then the functional (3) per unit area normal to the APB plane takes the form:

$$F = \int d\xi \left[f_h(\eta) + g(\eta) (d\eta/d\xi)^2 \right], \quad (11)$$

where

$$g(\eta) = g_{11}(\eta) \cos^2 \alpha + g_{12}(\eta) \sin^2 \alpha. \quad (12)$$

The equation $\delta F / \delta \eta = 0$ for the functional (11) can be written as

$$2g dy/d\xi + g' y^2 = f'_h, \quad (13)$$

where y is $d\eta/d\xi$, and prime means the derivative over η . Writing the derivative $dy/d\xi$ as $y dy/d\eta$ and integrating Eq.(13) over η from η_e to η we obtain:

$$y = d\eta/d\xi = [\Delta f_h(\eta) / g(\eta)]^{1/2}. \quad (14)$$

Here $\Delta f_h(\eta) = f_h(\eta) - f_h(\eta_e)$, and we took into account that at $\eta = \eta_e$, $y = y(\xi = \infty) = 0$. Eq.(14) and

(11) enable one to find both the coordinate dependence $\eta(\xi)$ and the APB surface energy σ :

$$\xi = \int_0^\eta d\eta' [g(\eta')/\Delta f_h(\eta')]^{1/2}, \quad (15)$$

$$\sigma = F\{\eta\} - F\{\eta_e\} = 4 \int_0^{\eta_e} d\eta [g(\eta)\Delta f_h(\eta)]^{1/2}. \quad (16)$$

The conventional Landau – Ginzburg theory corresponds to the case of small η when $f_h(\eta)$ is $(-a\eta^2 + b\eta^4)$, η_e^2 is $a/2b$, and g does not depend on η . Then Eqs.(15) and (16) yield the known expressions [11]: $\eta(\xi) = \eta_e \tanh(\xi/\delta)$, $\delta = (g/b\eta_e^2)^{1/2}$, and $\sigma = 8\eta_e^3(gb)^{1/2}/3$. The relations (11)–(16) generalize the conventional Landau – Ginzburg theory to the case of not small values of order parameters which is most interesting for applications.

Let us now discuss the orientation dependence of APB energies. For an isolated shift-APB this dependence is determined by the function $g(\eta)$ in Eq.(16), i.e. by the ratio of coefficients g_{12} and g_{11} in Eq.(12). The relation $g_{12} \simeq g_{11}$ corresponds to an approximately isotropic σ , and this case is characteristic of alloy systems with an extended-range interatomic interaction [9]. On the contrary, in the short-range-interaction systems where the nearest-neighbor interaction V_1 much exceeds the not-nearest-neighbor ones V_n , one has: $g_{12} \ll g_{11}$. It can be illustrated, for example, by the estimates of $g_{1\alpha}$ using the mean-field-approximation (MFA) which show that g_{12} is proportional to V_n . The APB energy $\sigma(\alpha)$ for such systems is strongly anisotropic, and its minimum value $\sigma_{\min} \sim (g_{12})^{1/2}$ corresponds to $\alpha = \pi/2$, i.e. to the APB plane parallel to the tetragonal axis, while the APB width δ in this case, according to Eq.(15), is also small: $\delta \sim (g_{12})^{1/2}$. These conclusions qualitatively agree with the results of more precise studies of APBs in the short-range-interaction systems [9], though at small δ under consideration the gradient expansion used above becomes quantitatively inapplicable.

Now let us take into account that evolution of shift-APBs in polytwinned structures actually occurs within a twin band which is formed at very first stages of phase transformation. Thus orientations of APBs tend to minimize their total excess free energy F_e not at the fixed APB area S but at the fixed cross-section of the twin band, S_b . Therefore, the APB energy here is more adequately characterized by the quantity $\sigma_b = F_e/S_b$ rather than by $\sigma = F_e/S$ given by Eq.(16). Taking also into account the relation $S_b = (\mathbf{m}\mathbf{n}_b)S$ where vector $\mathbf{n}_b = (1, 1, 0)2^{-1/2}$ describes the orientation of the twin band, we obtain:

$$\sigma_b = \sigma_b(\alpha, \varphi) = \sigma\sqrt{2}/(\cos \alpha + \sin \alpha \cos \varphi), \quad (17)$$

where $\sigma = \sigma(\alpha)$ is given by Eq.(16).

Minimization of expression (17) over φ yields: $\varphi = 0$, i.e. equilibrium APBs are oriented normally to the (100) plane, while minimization over α gives the equation:

$$\begin{aligned} \cot \alpha &= \\ &= \left(\int_0^{\eta_e} d\eta g_{12}(\Delta f_h/g)^{1/2} \right) / \left(\int_0^{\eta_e} d\eta g_{11}(\Delta f_h/g)^{1/2} \right). \end{aligned} \quad (18)$$

If the dependence of the ratio g_{12}/g_{11} on η is weak, in particular, when g_{12} and g_{11} do not depend on η (as in the case of small η or in the MFA calculations), Eq.(18) simplifies:

$$\cot \alpha = g_{12}/g_{11}. \quad (19)$$

Eqs.(18) and (19) show that in the isotropic case $g_{12} = g_{11}$ the equilibrium shift-APBs should be normal to twin boundaries, while at the usual relation $g_{12} < g_{11}$ the APB plane should be tilted to the tetragonality axis. It seems to agree with available experimental data. In particular, the figure shows a distinct tilting of shift-APBs to the tetragonality axes for both (100) and (010) twin bands, while in CuAu alloys (in which interatomic interactions seem to be short-ranged [9] and g_{12}/g_{11} is small) shift-APBs appear to be parallel to tetragonal axes [12]. Eqs.(18) and (19) can also be used to estimate the ratio g_{12}/g_{11} from experimental data on equilibrium tilting angles, which can provide both qualitative and quantitative information about interatomic interactions in an alloy.

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