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Abstract

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CRYSTALLOGRAPHY

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ON THE THEORY OF GROWTH OF AN IDEAL CRYSTAL

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As was shown earlier ($^{1-3}$), in the condensed state, owing to the interaction between atoms, the boundary between phases is an extended region in which a gradual transition is effected from the structure of one phase to the structure of another. A necessary condition for this is the possibility of mutual transformation of the phases by continuous change of some parameter x or set of parameters characterizing the structure. The free energy of the system $f_0(x)$*, or more precisely its nonequilibrium analogue, as a function of the structural parameter, assumes minimal values for the equilibrium phases ($x = x_A,\ x = x_B$) and a maximal value for the intermediate structure (x^a). The relative height of the maximum
$\Delta f_0^a = \Delta f_0(x^a) = f_0(x^a) - f_0(x_A)$ determines the activation energy of the phase transition and characterizes the thermodynamic stability of the initial phase as a whole**. The excess of the free energy of a two-phase equilibrium system with a planar boundary over the sum of the energies of the equilibrium phases may be represented as

$$\Delta F_1 = \sum_k \Delta f_0(x_k) + \frac{\alpha}{2}(x_k - x_{k-1})^2 \quad \text{for} \quad \frac{\partial \Delta F_1}{\partial x_k} = 0. \tag{1}$$

Here the summation is carried out over all atomic planes k parallel to the boundary; α is an interaction parameter characterizing the degree of correlation between changes of structure at neighboring points. In a certain approximation (^{2}), the energy ΔF_1 may be regarded as a continuous periodic function of the position of the boundary, its mean value $\overline{\Delta F_2}$ corresponding to the surface energy of the boundary σ_1, while the amplitude of oscillations ΔF_1^a characterizes the activation energy of displacement of the boundary as a whole, i.e., the mobility of the boundary. The effective width of the boundary λ_1, expressed in interplanar distances d_1, is determined, on the one hand, by the dependence of the free energy on the structure $\Delta f_0(x)$, and, on the other, by the degree of correlation of the structure in neighboring regions. The boundary is the wider the greater α is and the smaller Δf_0^a is ($^{1-3}$). In this case, if the surface energy increases with the width of the boundary,

$$\sigma_1 \approx \lambda_1 \Delta f_0^a, \tag{2}$$

then the height of the barrier separating two neighboring metastable positions of the boundary, on the contrary, is the smaller the wider the boundary:

$$\Delta f_1^a = \Delta f_0^a L(\lambda_1). * ** \tag{3}$$

* Lowercase letters denote quantities referred to one atom.

** Curves of the dependence of the free energy of the equilibrium phases A and B on thermodynamic parameters, for example temperature, $F_A(T)$ and $F_B(T)$, are projections onto the plane (F, T) of the extremal curves $F(T, x_A)$ and $F(T, x_B)$ lying on the surface $F(T, x)$. The projection onto this same plane of the "watershed line" $F(T, x^a)$ would give the dependence of the activation energy on temperature.

*** The quantities σ_1 and Δf_1^a are referred to one atom at the boundary, i.e. $\sigma_1 = \overline{\Delta F_1}/N_1$, $\Delta f_1^a = \Delta F_1^a/N_1$, where N_1 is the number of atoms on the phase-boundary surface.

The function $L(\lambda_1)$ increases as λ_i decreases and is equal to 1 at $\lambda = 1$, which corresponds to the absence of correlation $(\alpha = 0)$. Thus, $\Delta f_1^a < \Delta f_0^a$.

The considerations presented above can be applied not only to the analysis of energy changes upon displacement of a two-dimensional phase boundary (a flat surface), but also to a one-dimensional boundary (a step on the surface of a crystal) and a zero-dimensional boundary (a kink on a step) (^{2}). In this connection, let us consider the growth of an ideal semi-infinite crystal with a simple rhombic lattice (d_1, d_2, d_3) (Fig. 1). In accordance with the usual theories of crystal growth (^{4}), let us assume that the transition of the dividing plane from one equilibrium position to the neighboring one by a lattice period d_1 along the x_1 axis occurs as a result of successive displacements of a monoatomic step along the x_2 axis. This process is accompanied by a periodic change in the energy of the system as a function of the position of the step and is characterized by the energy barrier Δf_2^a. The value Δf_2^a is determined by a relation analogous to (3), with the difference that, in deriving it, the expression (1) will contain, instead of $\Delta f_0(x)$, the dependence of the energy of the system on the position of the flat boundary, $\Delta f_1(x) = \Delta F_1(x)/N_1$, and the structural parameter will be the coordinate of the boundary, varying along the direction of step motion, $x_1 = x_1(x_2)$.

Fig. 1

Fig. 1

In turn, a shift of the step in the plane of the crystal face by one interplanar distance d_2 in the direction of the x_2 axis may be treated as the result of successive displacements, by the lattice period d_3 along the x_3 axis, of the boundary between the parts of an atomic row that have passed into the new phase (a kink on a step); this process is associated with overcoming the potential barrier Δf_3^a.*

Thus, expressions (1)–(3) may be generalized in the following form:

$$\Delta F_i = \Delta f_i N_i = \sum_k \Delta f_{i-1}(x_{i-1,k}) + \frac{\alpha_i}{2}\,(x_{i-1,k} - x_{i-1,k-1})^2; \qquad (1\,)$$

$$\sigma_i \simeq \lambda_i \Delta f_{i-1}^a; \qquad (2\,)$$

$$\Delta f_i^a = \Delta f_{i-1}^a L(\lambda_i), \qquad i = 1, 2, 3. \qquad (3\,)$$

Since $L(\lambda_i) < 1$, it follows that $\Delta f_i^a < \Delta f_{i-1}^a$, i.e., the energy barrier for displacement of a kink on a step ($i = 3$) is smaller than the activation energy for motion of a step ($i = 2$), which in turn is smaller than the activation energy for displacement of the entire dividing plane as a whole ($i = 1$). This is the essential difference between the present treatment and the classical one, for example the Kossel scheme, where the quantity Δf_i^a is constant for all stages of growth.

Under nonequilibrium conditions, in particular upon deviation from the temperature of thermodynamic equilibrium of the phases, displacement of the boundary toward the less stable phase is accompanied by a decrease in the free energy $\Delta f_0 = f_A - f_B$, which plays the role of the driving force of the growth process, and the height of the energy barriers for the processes leading to growth of the stable phase is lowered. At the critical value $\Delta f_{0\,\mathrm{cr}} = k\Delta f^a$ (k is a numerical coefficient of order 1), the energy gain in the phase transition can compensate the energy expenditure for overcoming the potential barrier, i.e., the activation energy at $\Delta f_0 \geq \Delta f_{0\,\mathrm{cr}}$ becomes equal to zero. Since $\Delta f_0^a > \Delta f_1^a > \Delta f_2^a > \Delta f_3^a$, then with increas–

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* Let us note the analogy with the dislocation theory of plastic deformation, which considers dislocation surfaces, linear dislocations, and kinks on dislocations (^{5}).

as the deviation from equilibrium increases, the system first loses stability with respect to the motion of a kink along a step (the activation energy of this process becomes equal to zero), then of steps over the surface and, finally, of the entire crystal face as a whole. Subsequently, a violation of the thermodynamic stability of the initial phase may occur, so that it changes from relatively stable to unstable.

In considering the growth of a crystal of finite size, it must be borne in mind that the driving force of growth depends not only on the thermodynamic parameters of the state of the system (temperature, pressure, etc.), but also on the size of the crystal l_i.

To a first approximation

$$\Delta f_i = \Delta f_{i-1} \left(1 - \frac{l_{ip}}{l_i}\right), \qquad i = 1, 2, 3. \tag{4}$$

Here Δf_i is the change in free energy upon enlargement by one atom of a three- ($i = 1$), two- ($i = 2$), or one-dimensional ($i = 3$) crystal having size l_1, l_2, or l_3, respectively. Evidently, $l_i \leqslant l_{i-1}$; l_{ip} is the equilibrium size corresponding to the maximum of the free energy as a function of l_i at constant l_{i-1}, l_{i-2}. If

$$\Delta F = -\Delta f_i(l_{i-1}, l_{i-2})\, l_i^{4-i} V_i + \sigma_i l_i^{3-i} S_i + \overline{\Delta F}(l_{i-1}, l_{i-2}),$$

where V_i and S_i are numerical coefficients depending on the shape of the crystal, and $\overline{\Delta F}(l_{i-1}, l_{i-2})$ is the change in free energy at $l_i = 0$, then from the condition $\partial \Delta F / \partial l_i = 0$ we obtain the equilibrium size

$$l_{ip} = \frac{3-i}{4-i} \frac{S_i}{V_i} \frac{\sigma_i}{\Delta f_{i-1}}$$

and the work of formation of an equilibrium nucleus (three-dimensional, two-dimensional on the face of a three-dimensional crystal, or one-dimensional on the side of a two-dimensional one)

$$\Delta F_{ip} = \Delta F_i(l_{ip}) = \frac{l_{ip}^{4-i} \Delta f_i V_i}{3-i}.$$

With an increase of l_i above the equilibrium value, the driving force of the process may, at some size $l_{i\text{cr}}$, reach the critical value $\Delta f_{i\text{cr}}^{a} = k_i \Delta f_i^{a}$, if $\Delta f_{i-1} > \Delta f_{i\text{cr}}$. In this case the process of crystal growth naturally splits into two stages: formation of a crystal of critical size, which may be fluctuation-induced, and spontaneous growth of a crystal of supercritical size, requiring no thermal activation. The quantity $\Delta F_{ip}{}^*$ may serve as an estimate of the work of formation of a crystal of critical size.

If $\Delta f_{i-1} < \Delta f_{i\text{cr}}$, then the process of nucleation of equilibrium crystals and their subsequent growth may be considered in the usual way.

Let us estimate the time required for the transformation of a volume, planar, or linear element of size l_{i-1}, if the nucleation rate of a center α_i and the mean linear rate $v_i = \overline{dl_i}/dt$ are given; for example, the rate of nucleation and growth of a two-dimensional crystal l_2, growing on the face of a three-dimensional crystal of size l_1. The probability of nucleation within the element under consideration during a time Δt of at least one center is

$$1 - \exp(-\alpha_i l_{i-1}^{4-i} \Delta t).$$

The waiting time for the nucleation of a center, Δt_3, is obtained by setting this probability close to 1, i.e.

$$\Delta t_3 \approx \frac{1}{\alpha_i l_{i-1}^{4-i}}.$$

The time required for growth of the center to the final size l_{i-1} is

$$\Delta t_p = l_{i-1}/v_i.$$

For sufficiently large v_1, $\Delta t_p \ll \Delta t_3$, and the transformation time of the element is determined by its size and by the rate of nucleation of centers. However, if l_{i-1} increases or v_i decreases, then, beginning from some moment, $\Delta t_3 \approx \Delta t_p$, and the total transformation time

$$\Delta t_{i-1} = \Delta t_3 + \Delta t_p \approx (\alpha_i v_i^{4-i})^{-1/(5-i)}$$

will not depend on the final size of the element. This result, which coincides with the conclusion of work (7), means that for sufficiently small l_{i-1}/v_i the entire "volume" l_{i-1}^{4-i} of the element under consideration the element can be divided into parts $(v_i/\alpha_i)^{1/(5-i)}$, each of which will transform from one center.

Thus, the linear growth rate of a three-, two-, or one-dimensional crystal is determined by the expression

$$v_i = \frac{d_i}{\Delta t_i} \simeq \begin{cases} d_i \alpha_{i+1} l_i^{3-i}, & \text{for } (v_{i+1}/\alpha_{i+1})^{1/(4-i)} > l_i^{3-i}, \\ d_i (\alpha_{i+1} v_{i+1}^{3-i})^{1/(4-i)}, & \text{for } (v_{i+1}/\alpha_{i+1})^{1/(4-i)} \ll l_{i-1}^{3-i}. \end{cases} \tag{5}$$

For the rate of motion of a kink along a step, both formulas give $v_3 = d_3 \alpha_4$, where α_4 is the frequency of transition of a kink from one metastable position to a neighboring one. If relation (5) is satisfied for two-dimensional and one-dimensional crystals, then $v_1 \simeq d_1 d_2^{2/3} d_3^{1/3} \sqrt[3]{\alpha_2 \alpha_3 \alpha_4}$, and in the case of fluctuation nucleation, when $\alpha_i \simeq (\nu / l_{i\mathrm{cr}}^{4-i}) \exp(-\Delta F_{i\mathrm{p}}/kT)$ (ν is a frequency factor),

$$v_1(l_1) \simeq d_1 d_2^{2/3} d_3^{1/3} \nu (l_{2\mathrm{cr}}^2 l_{3\mathrm{cr}})^{-1/3} \exp(-\Delta F_{2\mathrm{p}}(l_1)/3kT) \exp(-\overline{\Delta F}_{3\mathrm{p}}(l_1)/3kT) \times$$

$$\times \left[\exp(-\Delta f_3^a/kT)\, 2\,\mathrm{sh}(\Delta f_0/2kT)\right]^{1/3}.$$

Here it is assumed that $v_3 \simeq d_3 \nu \exp(-\Delta f_3^a/kT)\, 2\,\mathrm{sh}(\Delta f_0/2kT)$ (1); $\overline{\Delta F}_{3\mathrm{p}}$ is equal to $\Delta F_{3\mathrm{p}}(l_1, l_2)$, averaged over all possible l_2 ($l_{2\mathrm{p}} \ll l_2 \ll l_1$). An increase in the deviation from equilibrium may lead to the successive disappearance of the exponential factors, beginning with the one in square brackets; then, at $\Delta f_2 > \Delta f_{2\mathrm{cr}}$, σ_3 becomes zero and, consequently, $\Delta F_{3\mathrm{p}}$; and, finally, at

* In a more exact calculation it is necessary to take into account that the growth of a crystal may be accompanied by a change in its structure, so that $\Delta F_{i\mathrm{cr}}$ may be smaller than ΔF_{ip} (6).

$\Delta f_3 > \Delta f_{3\mathrm{cr}} - \Delta F_{2\mathrm{p}} = 0$. Thus, with increasing supercooling or superheating of the system relative to the phase-equilibrium temperature, as the crystal size grows, individual stages of the process cease to be limited by the rate of thermal fluctuations: first the motion of kinks along steps, then their nucleation and, consequently, the lateral growth of two-dimensional nuclei, and finally the nucleation of two-dimensional nuclei, which ensures the normal growth of crystal faces. In the latter case the linear growth rate of the crystal should not depend substantially on temperature, which apparently occurs in martensitic transformations in the solid phase (1).

According to the idealized scheme considered here, crystal growth proceeds in stages, the limiting links of the process being the initial moments of each successive stage: the formation of a two-dimensional nucleus of a new atomic plane, and the initial stage of attachment of an atomic row to the periphery of a two-dimensional crystal. In the growth of a real crystal such staging may be absent because of defects in the crystal structure. In particular, when screw dislocations exist, growth may occur bypassing two-dimensional nucleation ( ). Defects may play an analogous role in growth processes during transformations in the solid state ( ).

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