Phase Nucleation of Elastic Defects in Crystals Undergoing a Phase Transition

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General properties of nucleation of elastic defects in crystals undergoing a phase transition are described in the framework of a Landau-type approach. For static defects the phase diagram topology of a nucleus is shown to be independent of the nature and geometry of the defects and may contain additional phases which are unstable in the bulk. For moving defects the nuclei have a specific configuration and arise only below a critical speed of the defects. [S0031-9007(98)06687-3]

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Elastic defects such as dislocations, cracks, inclusions, or twin boundaries often give rise, in the vicinity of a phase transition, to nuclei of a new phase close to the defects [1–8]. These nuclei have been observed in many categories of transitions and materials, i.e., in martensitic-type transformations in metals and alloys [1], in ceramics [2], in magnetic [3] and ferroelectric or ferroelastic transitions [4,5], in Mott transitions [6], in semicrystalline polymers [7], as well as in superconducting materials [8].

In contrast to the unstable Frenkel nuclei which are due to thermal fluctuations [9], nuclei associated with elastic defects are stabilized by the strain field induced by the defects. This fact was first recognized by Cahn [10], who proposed thermodynamic model of nucleation in the case of dislocations. Further theoretical approaches [11] described nucleation for specific elastic defects and geometries. There exists, however, a number of general static and dynamic properties, which are common to the nucleation processes and are independent from the nature and geometry of the defects. The aim of this Letter is to describe these properties in a unified way, in the framework of a Landau-type approach [12]. More precisely, we will demonstrate successively the following: (i) The phase diagram topology of the nuclei is independent from the nature and geometry of the defects. (ii) In the vicinity of a multiphase point the structure of the nucleus may correspond to a symmetry which cannot be obtained in the bulk. (iii) The nucleation does not occur above a critical speed of the defects. (iv) Nuclei at moving defects display a specific configuration.

Let us first consider a crystal undergoing a phase transition taking place at T_c, associated with a one-component order parameter η. The Landau-Ginsburg free energy of a crystal involving elastic defects can be expressed under the general form,

$$F(\eta, u_{ik}) = \int_V \left\{ \varphi(\eta) + A\eta^2 u_{ii} + f_{\text{ef}}(u_{ik}) + \frac{g}{2}(\nabla\eta)^2 \right\} dV , \quad (1)$$

where the sum runs over the volume V of the crystal. $\varphi(\eta) = \alpha\eta^2/2 + \beta\eta^4/4 + \gamma\eta^6/6$ is the standard free energy density describing the transition at T_c. $A\eta^2 u_{ii}$ is the striction coupling between the order parameter and the dilatation, u_{ik} is the strain tensor, and $f_{\text{el}}(u_{ik}) = C_{iklm}u_{ik}u_{lm}/2$ is the elastic energy. The Ginsburg invariant $\sim(\nabla\eta)^2$ accounts for the space dependence of the order parameter. The equations minimizing F are

$$g\Delta\eta - (\alpha + 2Au_{ii})\eta = \beta\eta^3 + \gamma\eta^5;$$
$$\partial\sigma_{ik}/\partial x_k = 0 , \quad (2)$$

where $\sigma_{ik} = C_{iklm}u_{lm} + A\eta^2\delta_{ik}$ is the stress tensor depending on the space variables x_k. The second Eq. (2) expresses the mechanical equilibrium of the system. Assuming a single isolated defect with a finite size, the system of Eq. (2) possesses two solutions: I $\eta = 0; u_{ij} = u_{ij}^{(0)}(\mathbf{r})$, where the strain field of the defect $u_{ij}^{(0)}(\mathbf{r})$ obeys the condition $u_{ij}^{(0)}(\infty) = 0$ and II $\eta = \eta(\mathbf{r}) \neq 0; u_{ij} = u_{ij}^{(0)}(\mathbf{r}) + O(\eta^2)$. One has the condition $\eta(\infty) = 0$, corresponding to the existence of a nucleus in the vicinity of the defect.

Solutions I and II describe stable states for different positive values of α. In order to determine the value α_* corresponding to the bifurcation from one solution to another, one has to linearize Eqs. (2) around the value $\eta = 0$ [13]. One gets the auxiliary Schrödinger-type equation;

$$g\Delta\psi_* = \{\alpha_* + 2Au_{ii}^{(0)}(\mathbf{r})\}\psi_* , \quad (3)$$

where ψ_* is the eigenfunction corresponding to the eigenvalue α_* of its basic state. For $\alpha \leq \alpha_*$, the solution II branches off solution I. The main term of this solution is determined by the eigenfunction ψ_* [13]. It takes the form

$$\eta = \xi\psi_*(\mathbf{r}) + O(\xi^2);$$
$$u_{ij}(\mathbf{r}) = u_{ij}^{(0)}(\mathbf{r}) + \frac{A\xi^2}{(2\pi)^3}\int G_{ik}(\mathbf{q})q_j q_k Q(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})\,d^3q , \quad (4)$$

where ξ is the amplitude. The second term in the expression for the strain (4) is a Fourier transform in q space

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representing the contribution of the strain induced by the nucleus. $G_{ik}(\mathbf{q})$ is the Fourier transform of the elastic Green function, and $Q(\mathbf{q}) = \int \psi_*^2(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})\, d^3r$. The asymptotic solution of Eqs. (4) for the order parameter is $\eta \sim \xi \exp(-r/r_n)$, where $r_n = (g/\alpha_*)^{1/2}$ is the size of the nucleus. Assuming a linear dependence $\alpha = a(T - T_c)$ $(a > 0)$, one finds $r_n = (g/a)^{1/2}(T_n - T_c)^{-1/2}$. Therefore, even at the point of nucleation $T = T_n$, the nucleus has a finite size.

The expression of $u_{ij}^{(0)}(\mathbf{r})$ in Eq. (4) depends on the particular type of defects which determines the specific form of ψ_* and the value of α_*. Since we aim to establish the general properties of nucleation on elastic defects independently from the type of defect, we will assume that ψ_* and α_* are known. Substituting (4) into Eq. (1), the free energy of the nucleus takes the form

$$F(\xi) = F_0 + r_n^3 \{\tfrac{1}{2}(\alpha - \alpha_*)\langle\psi_*^2\rangle\xi^2 + \tfrac{1}{4}\tilde{\beta}\langle\psi_*^4\rangle\xi^4 + \tfrac{1}{6}\gamma\langle\psi_*^6\rangle\xi^6\}. \quad (5)$$

F_0 is the free energy of the defect in the parent phase ($\eta = 0$). $\langle\psi_*^{2n}\rangle = r_n^{-3}\int \psi_*^{2n}(\mathbf{r})\, d^3r$ with $n = 1, 2, 3$; $\tilde{\beta} = \beta - 2A^2 \int G_{ik}(\mathbf{q}) q_i q_k Q^2(\mathbf{q}) d^3q/(2\pi)^3$. Equation (5) shows that $F(\xi)$ and ξ play, respectively, the role of the Landau free energy and of the order parameter associated with the transition between a state without nucleus ($\xi = 0$) and a state with a nucleus ($\xi \neq 0$). One can note that $F(\xi)$ has the same form as the Landau potential $\varphi(\eta)$ describing the transition in the bulk, and that this form is independent from the specific type of defects. The phase diagram constructed from the minimization of $F(\xi)$ is shown in Fig. 1(a) in the (α, β) plane. Figure 1(a) also represents the phase diagram corresponding to the transition in the bulk. One can verify that the two phase diagrams display the same topology. The only difference is that the phase diagram of the nucleus is shifted along α and β with respect to the bulk phase diagram, and the slopes of the first-order transition line between the respective parent phase ($\eta = 0$ and $\xi = 0$) and "daughter" phase ($n \neq 0$ and $\xi \neq 0$) are different.

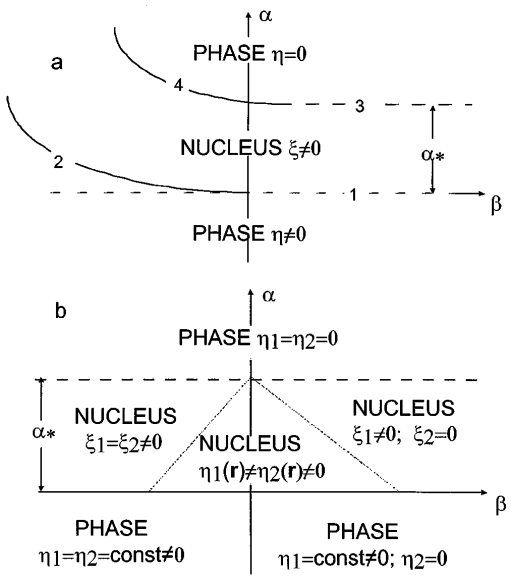

FIG. 1. (a) Phase diagram of nucleation on a static defect for a one-component order parameter. 1 and 2 denote a second-order and a first-order transition line within the bulk. 3 and 4 are the corresponding nucleation lines. (b) Phase diagram for a two-component order parameter.

Let us now consider the more complex situation of a system whose phase diagram contains a singular point at which different low-symmetry bulk phases may merge. This type of phase diagram is necessarily associated with a multicomponent order parameter [12]. To be concrete we will discuss the example of a two-component order-parameter case (η_1, η_2) involving two different low-symmetry bulk phases. The free energy has the form [12],

$$F(\eta_1, \eta_2, u_{ik}) = \int_V \left\{ \frac{g}{2}[(\nabla\eta_1)^2 + (\nabla\eta_2)^2] + \frac{\alpha}{2}(\eta_1^2 + \eta_2^2) + \frac{\beta}{4}(\eta_1^2 + \eta_2^2)^2 + \frac{\gamma}{2}\eta_1^2\eta_2^2 + A(\eta_1^2 + \eta_2^2)u_{ii} + f_{el}(u_{ik}) \right\} dV. \quad (6)$$

In addition to the parent phase $(\eta_1 = \eta_2 = 0)$, minimization of F with respect to η_1 and η_2 yields two low-symmetry bulk phases: phase 1 corresponding to the equilibrium relationship $\eta_1 \neq 0$; $\eta_2 = 0$ and to the stability conditions $\alpha < 0$, $\beta > 0$, $\gamma > 0$. Phase 2 is stabilized for $\eta_1 = \pm\eta_2 \neq 0$ and $\alpha < 0$, $\beta > 0$, $\gamma < 0$. The branching off solution is $\eta_1 = \xi_1\psi_*(\mathbf{r}) + O(\xi^3)$; $\eta_2 = \xi_2\psi_*(\mathbf{r}) + O(\xi^3)$, and $u_{ik}(\mathbf{r})$ is given by the second Eq. (4) with $\xi^2 = \xi_1^2 + \xi_2^2$. The nucleus free energy can be written analogously:

$$F(\xi_1, \xi_2) = F_0 + r_n^3 \{\tfrac{1}{2}(\alpha - \alpha_*)\langle\psi_*^2\rangle(\xi_1^2 + \xi_2^2) + \tfrac{1}{4}\tilde{\beta}\langle\psi_*^4\rangle(\xi_1^2 + \xi_2^2)^2 + \tfrac{1}{6}\gamma\langle\psi_*^4\rangle\xi_1^2\xi_2^2\} \quad (7)$$

which has again the same form as the bulk free energy and therefore corresponds to the same phase diagram topology. However, an *additional state can be stabilized in the phase diagram of the nucleus which is unstable in the bulk.* It corresponds to the equilibrium nucleus with $\eta_1(\mathbf{r}) \neq \eta_2(\mathbf{r}) \neq 0$, whose symmetry

coincides with the intersection of the symmetries of phases 1 and 2. More precisely, one can show that the stability of phase 2 in the nucleus ($\xi_1 = \pm\xi_2 \neq 0$) is lost for $\alpha = \alpha_* - \gamma\tilde{\beta}\langle\psi_*^4\rangle^2(\tilde{\beta} + \gamma)^{-2}S^{-1}$, where $S = \sum_{N\neq 0}\langle\psi_*^3\psi_N\rangle(\alpha_* - \alpha_N)^{-1}$. Here ψ_N and α_N, $N = 0, 1, 2, \ldots$ are the eigenfunctions and the corresponding eigenvalues of Eq. (3) ($\psi_* \equiv \psi_0$ and $\alpha_* \equiv \alpha_0$). Figure 1(b) shows the region of stability of this additional nucleus which is close to the three-phase point at which the bulk parent phase merges with the bulk phases 1 and 2. In other words, one may find in this region nuclei having structures with a symmetry which cannot be realized in the bulk.

It is well known that plastic deformation and fracture [14] imply the existence of moving defects. The equation of motion describing the time dependence of the order parameter and the displacement vector **u** are in the one-component case:

$$\kappa\frac{\partial\eta}{\partial t} = g\Delta\eta - (\alpha + 2Au_{ii})\eta - \beta\eta^3 - \gamma\eta^5;$$
$$\rho\frac{\partial^2 u_i}{\partial t^2} = \frac{\partial\sigma_{ik}}{\partial x_k}, \tag{8}$$

where κ is a kinetic coefficient and ρ is the density of the crystal. Assuming that the defect is moving with a constant velocity **v** (much smaller than the sound velocity), the solution of Eq. (8) for the parent phase is $\eta = 0$, $u_{ik} = u_{ik}^{(0)}(\mathbf{R})$ with $\mathbf{R} \equiv \mathbf{r} - \mathbf{v}t$. The auxiliary equation which determines its stability [13] is obtained by linearizing (8) as

$$g\Delta\Psi_*(\mathbf{R}) + \kappa(\mathbf{v}\cdot\nabla)\Psi_*(\mathbf{R}) - \{\alpha_*(v) + 2Au_{ii}^{(0)}(\mathbf{R})\}\Psi_*(\mathbf{R}) = 0. \tag{9}$$

It yields the solution corresponding to the nucleus at a moving defect: $\eta = \xi\Psi_*(\mathbf{R}) + O(\xi^3)$; $u_{ij} = u_{ij}^{(0)}(\mathbf{R}) + O(\xi^2)$. The eigenfunction of Eq. (9) and the correspondent eigenvalues have the form

$$\alpha_*(V) = \alpha_* - \frac{\kappa^2 v^2}{4g};$$
$$\Psi_*(\mathbf{R}) = \psi_*(\mathbf{R})\exp\{-\kappa(\mathbf{v}\cdot\mathbf{R})/2g\}, \tag{10}$$

where $\psi_*(\mathbf{R})$ is the eigenfunction and α_* is the eigenvalue found for the static defect. Equation (10) shows *that the nucleation process for a moving defect occurs only* for *values of* v *smaller than the critical value* $v_{\rm cr} = 2(g\alpha_*)^{1/2}/\kappa$. On the other hand, Eq. (10) *gives the nucleation temperature of the moving defect* $T_n(v) = T_n - \kappa^2 v^2/4ag$. The asymptotic form of the order parameter η can be expressed as $\eta \sim \xi\exp\{-\kappa(\mathbf{v}\cdot\mathbf{R})/2g - (\alpha_*/g)^{1/2}|\mathbf{R}|\}$ which reveals that the nucleus is compressed in front of the defect and stretched in the direction opposite to the defect. At last one can estimate the "trace" $l_n(v)$ of the nucleus for a moving defect by approximating $\eta \sim \xi\exp\{-x/l_n(v)\}$ (with $x < 0$). One finds $l_n(v) = r_n(1 - v/v_{\rm cr})^{-1}$, $l_n(v)$ diverging when $v \to v_{\rm cr}$. The trace follows the moving defect with the same velocity.

Let us illustrate the preceding general results by considering the concrete examples of a crack tip and of an edge dislocation. At the tip of a loaded brittle crack the magnitude of the induced stresses is very large and may be responsible for the brittle fracture [14]. In this case, the nucleation process takes place far from the transition in the bulk. In the vicinity of a crack tip the strain tensor trace has the form $u_{ii}^{(0)}(r,\theta) = 2K_{\rm I}(1-2\nu)(1+\nu)\cos(\theta/2)/\{(2\pi r)^{1/2}E\}$. where r and θ are the cylindrical coordinates in the $(x$-$y)$ plane, E is the Young's modulus, ν is the Poisson's ratio, and $K_{\rm I}$ is the stress intensity factor describing the crack loading [14]. If $A < 0$, the exact solution with the boundary condition $\psi(\infty) = 0$ is

$$\eta = \xi\exp\left\{-\frac{r}{\sqrt[3]{4}\,r_n} + \sqrt[3]{4}\left(\frac{r}{r_n}\right)^{1/2}\cos(\theta/2)\right\},$$
$$\alpha_* = \left\{\frac{2K_{\rm I}|A|(1-2\nu)(1+\nu)}{(2\pi)^{1/2}g^{1/4}E}\right\}^{4/3} \tag{11}$$

with $r_n = \{Eg\pi^{1/2}/|A|K_{\rm I}(1-2\nu)(1+\nu)\}^{2/3}/2$. The order-parameter distributions in the vicinity of the motionless and propagating crack tip are shown in Figs. 2(a) and 2(b). The edge dislocation gives rise to a strain field: $u_{ii}^{(0)} = b(1-2\nu)\sin\theta/\{2\pi(1-\nu)r\}$ [14], where b is the Burgers vector. In this case, the solution describing the nucleus can be found for positive as well as for negative values of A. One obtains the approximate solution

$$\eta \approx \xi\left\{1 - 0.62\left(\frac{r}{r_n}\right)^{1/2}\sin\theta\right\}\exp\left\{-0.34\left(\frac{r}{r_n}\right)\right\},$$
$$\alpha_* = \frac{0.11A^2b^2(1-2\nu)^2}{\pi^2(1-\nu)^2g} \tag{12}$$

with $r_n = \pi g(1-\nu)/|A|b(1-2\nu)$. Figures 2(c) and 2(d) show the order-parameter distribution in the vicinity of an edge dislocation. Taking $a \sim 10^5$ J m C^{-2} K^{-1}, $A/E \sim 10^{-1}$–10^{-2} m^4 C^{-2}, $E \sim 10^{11}$ Pa, $g \sim 10^{-8}$ J m^3 C^{-2}, and $\kappa \sim 10^{-4}$–10^{-5} J m s C^{-2}, which are typical values for ferroelectrics, and taking $K_{\rm I}$ of the order of a fracture toughness $K_{\rm I} \sim K_{\rm IC} \sim 0.1$ MPa m$^{1/2}$ [15], one finds for the nucleation at the crack tip $T_n - T_c \sim 10°$–$100°$; $r_n \sim 10^{-8}$ m and $v_{\rm cr} \sim 10^2$–10^3 m/s. For the nucleation at an edge dislocation, one finds in the same way $T_n - T_c \sim 1°$–$10°$; $r_n \sim 10^{-6}$–10^{-8} m and $v_{\rm cr} \sim 10^2$–10^4 m/s. These results are consistent with the experimental values reported in Refs. [1,3,5,8].

In summary, we have described theoretically a number of general properties of phase nucleation on elastic defects in crystals undergoing a phase transition. In this respect martensitic transformations constitute typical examples of transitions, where the onset of the low-symmetry phase is preceded above the transformation by the formation of

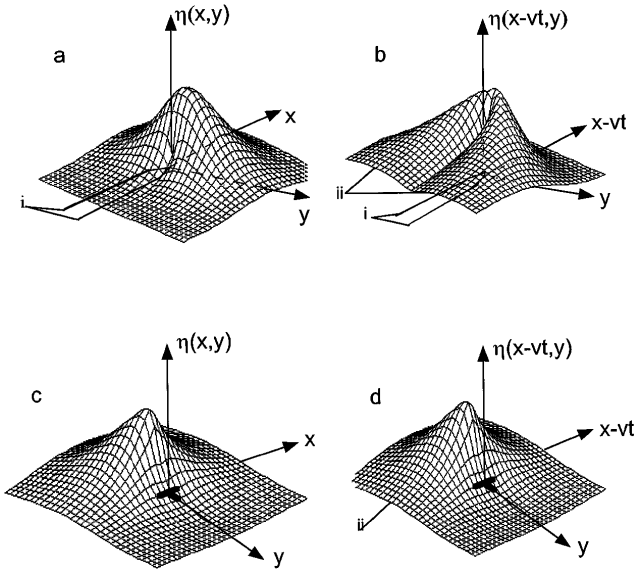

FIG. 2. Order-parameter distribution at the tip of the brittle crack. (a) Order-parameter distribution is localized in front of the tip of a motionless crack [Eq. (11)]. The crack contour is shown schematically (i). (b) Order-parameter distribution in the vicinity of the propagating crack tip. (ii) points out the trace. (c), (d) Order-parameter distribution in the vicinity of the edge dislocation. At motionless (c) and moving (d) edge dislocations as described by Eq. (12). In the vicinity of a moving defect the order-parameter distribution is compressed in front of the defect and stretched in its back, forming the trace (ii).

nuclei having the symmetry of the bulk [16]. However, in close packed martensites, the energies of different close packed polytypes (e.g., hcp, fcc, 9R) are nearly degenerate. In this case which is found in sodium [17], nuclei displaying different polytypic structures may give rise to a bulk martensite phase, where either the polytypes coexist in different proportions or only one of them is stabilized. In doped ZrO_2 ceramics, nucleation on the crack tip highly improves the strength of the material [2]. In Y_2O_3-ZrO_2-Al_2O_8, composite [18] nucleation is observed under indentation but not under thermal shock fracture. This can be the result of a high overcritical crack velocity which is higher than the critical velocity of nucleation ($v > v_{cr}$) under thermal shock fracture, while it is subcritical and smaller than the critical velocity of nucleation ($v < v_{cr}$) under indentation. In $Gd_3Fe_5O_{12}$ the nuclei appearing close to dislocation lines exhibit a sequence of magnetic phases. Some of the nuclei display a symmetry which does not appear in the bulk of the crystal [3].

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[1] S. K. Hann *et al.*, J. Mater. Sci. **32**, 1249 (1997).
[2] I. Birkby and R. Stevens, Key Eng. Mater. **122-124**, 527 (1997).
[3] V. K. Vlasko-Vlasov *et al.*, Sov. Phys. Solid State **23**, 1085 (1981).
[4] I. Drevensek *et al.*, Phys. Rev. B **49**, 3082 (1994).
[5] A. A. Bulbich *et al.*, Sov. Phys. JETP **71**, 619 (1990).
[6] J. C. Morris and D. L. Callahan, J. Mater. Res. **9**, 2907 (1994).
[7] J. Karger-Kocsis, Polym. Eng. Sci. **36**, 203 (1996).
[8] I. N. Khlyustikov and A. I. Buzdin, Sov. Phys. Usp. **31**, 409 (1988).
[9] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1980).
[10] J. M. Cahn, Acta Metalell. **5**, 169 (1957).
[11] A. A. Bulbich, J. Mater. Sci. **27**, 1070 (1992), and references therein.
[12] J. C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).
[13] M. M. Vajnberg and V. A. Trenogin, *Theory of Branching of Solutions of Nonlinear Equations* (Noordhoff International Publishing, Leyden, 1974).
[14] J. P. Hirth and J. Lothe, *The Theory of Dislocations* (McGraw-Hill, New York, 1967).
[15] R. C. Pohanka, *et al.*, J. Am. Ceram. Soc. **61**, 72 (1978).
[16] Z. Nishiyama, *Martensitic Transformations* (Academic Press, New York, 1978).
[17] W. Schwarz, O. Blaschko, and I. Gorgas, Phys. Rev. B **46**, 14 448 (1992).
[18] M. Ishitsuka *et al.*, J. Mater. Sci. Lett. **8**, 638 (1989).