

The theory of the formation of a heterophase structure in phase transformations in solids

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A thermodynamic theory of heterophase structures is proposed, describing the relation of the volumes, shape, internal structure, and mutual disposition of the crystals that are formed in a phase transformation in the solid state. An important feature of solid heterophase systems is the presence of internal-stress fields arising as a consequence of the contact between the phases. The tendency to reduce the elastic energy of the internal stresses leads to the breakdown of the crystals composing the heterophase system into elastic domains and to the formation of ensembles of crystals arranged in an ordered manner. As a result of the competition between the elastic energy of the internal stresses and the interphase surface energy in a solid, metastable many-phase states arise, characterized by a regular spatial distribution of plate-like structural elements.

CONTENTS

Introduction	326
1. Geometry of the Distortion of the Crystal Lattice, and Internal Stresses in a Heterophase System	328
2. Equilibrium of a Heterophase System	330
3. Single-Domain Crystal of the New Phase	332
4. Many-Domain Plate. Elastic Domains	335
5. Elastic Interaction of Crystals and Formation of Ensembles of Platelike Crystals	339
6. Conclusion	341
Bibliography	343

INTRODUCTION

As a rule, phase transformations in solids proceed in the following way: separate regions or crystals of the new phase first appear in the initial phase, then grow, interact and form a complicated heterophase system. The shape, volume and crystallographic orientation of the individual crystals and their internal structure and mutual alignment, i.e., the real structure of the heterophase system arising in the phase transformation, determine to a considerable extent many physical properties of crystalline solids. The study of the real structure is therefore of considerable interest for solid-state physics, metallography and physico-chemical mechanics. An enormous amount of factual material has been accumulated in this field.

Despite individual successes in the physical interpretation of the data obtained, until recently the overall picture has appeared extremely patchy and confused. In recent years there has been definite progress in our understanding of the general laws governing the formation of a real structure. It is evidently possible, at the present time, to talk of a sufficiently general theory of heterophase structures that not only explains satisfactorily the principal features of real substances but also makes it possible to give a quantitative treatment of the observed phenomena. In this article, this theory is expounded systematically for the first time. The main attention is given to the fundamentals of the theory and to the new physical results stemming from the theory. Therefore, the article does not contain concrete quantitative calculations, and experimental material is invoked only as illustrations; the mathematical apparatus used is extremely simplified, and preference is given to qualitative physical estimates.

Morphologically, the structural states formed in phase transformations are extremely diverse, but there

are certain sufficiently general structural features, among which are included the following:

1. There is a definite orientational relationship between the lattices of the initial and final phases.
2. The typical structural shape of the new phase is a plate with a small ratio of thickness to the other linear dimensions.
3. The habit faces of the crystals of the new phase being formed have a definite crystallographic orientation.
4. The transformation of any part of the old phase into the new leads to a macroscopic change in the shape of this part, which is manifested in the form of a characteristic relief on a plane surface of the sample. The parameters of the macroscopic deformation are specific for each type of transformation.
5. The crystals of the new phase have a regular internal structure. In a number of cases the structure of the new phase is not mono- but polycrystalline, e.g., the new phase can be produced in the form of a polysynthetic twin.
6. There is a definite tendency to an ordered mutual alignment of the crystals.

As an illustration we shall consider the structure that is formed in the alloy Fe-33% Ni as a result of a martensitic transformation. Figure 1a shows the microstructure, exposed by pickling. The light regions are the initial high-temperature fcc phase, and the dark regions are plates of the stable bcc phase. The plane of the plates is oriented relative to the crystallographic axes of the matrix ($\sim\{3, 10, 15\}$). It can be seen that the plates are arranged in a definite order, forming characteristic truss-like groups. Trusses of higher orders are distributed in the gaps between the "links" in the large-scale trusses.



FIG. 1. Macro- and microstructure of the alloy Fe-33% Ni after a martensitic transformation (X500 (a) and X10,000 (b)).

A study of the relief which arises on the plane surface of the initial phase at the point at which the plate of the new phase emerges reveals the pattern represented in Fig. 2. An analysis of the relief makes it possible to determine the parameters of the macrodeformation accompanying the formation of the plate. Usually, the macrodeformation is a combination of a simple displacement along the plane of the plate and an expansion or contraction normal to this plane. This is a so-called invariant-plane deformation—the planes parallel to the habit faces of the crystal are displaced as a whole relative to each other, without being distorted or rotated (Fig. 3). The macrodeformation parameters—the displacement and expansion—are specific for each transformation (in the example under consideration, the displacement $\gamma \approx 0.2$ and the expansion $\delta \approx 0.05$).

A study of the internal structure of the plates of the bcc phase shows that they are not monocrystals but polysynthetic regions composed of alternating plane-parallel layers, situated in a twinned relationship (see the electron-microscope photograph in Fig. 1b). The relationship between the thicknesses of these layers, and also their orientation relative to the lattice of the surrounding initial phase, are well defined for each alloy. The orientational relationship between the crystal lattices of the fcc and bcc phases, which can be determined using x-rays (one obtains a quantity averaged over the many bcc plates formed within the boundaries of the one fcc crystal), is an almost constant characteristic (to within 1°) for a specific transformation.

We must call attention to one other characteristic feature of the structure considered—the presence in it of the initial phase. The relative quantity of the new phase is a function of the thermodynamic conditions of the transformation—the temperature, pressure, etc. The greater the deviation from the point of thermodynamic phase equilibrium, the greater is the relative quantity of the new phase, the new phase being formed only when the deviations from the point of phase equilibrium are greater than a certain minimum size. In particular, at a constant pressure the transformation begins at a temperature T_m different from the phase-equilibrium temperature T_0 . On further deviation from equilibrium the extent of the transformation increases and, finally, at a certain temperature T_f , the initial phase disappears (Fig. 4). A study of the kinetics of the transformation shows that the limiting extent of an isothermal transformation is attained extremely rapidly, and then remains unchanged for arbitrarily long time intervals. This points to the fact that we are dealing here not with

FIG. 2. Relief on the surface, caused by the emergence of a crystal of the new phase.

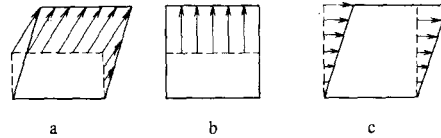
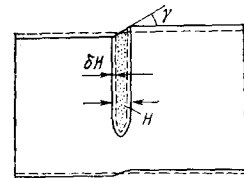
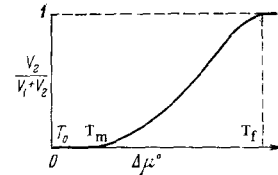


FIG. 3. An invariant-plane deformation. (a) General case; (b) uniaxial expansion; (c) simple shear.

FIG. 4. Dependence of the extent of transformations on the magnitude of the deviation from the point of thermodynamic phase equilibrium.



a kinetic effect but with a manifestation of a thermodynamic feature of the transformation: in the temperature interval $T_m - T_f$ a distinctive two-phase equilibrium is established in the system. The nature of this phenomenon is difficult to understand from the standpoint of ordinary thermodynamic concepts: in the process of a martensitic transformation the composition of the phases does not change, and in a first-order phase transformation in such a quasi-one-component system only one phase can be stable.

The features of the formation of the structure that have been demonstrated in the example considered are most clearly manifested in the martensitic transformations^[1,2], but to varying extents they are characteristic of all phase transformations in the solid state. In the course of the subsequent account we shall show that the structural pattern presented is typical for transformations in crystals and can be reconstructed as a result of a theoretical analysis of the equilibrium states of a heterophase system. The possibility of applying a thermodynamic analysis to the real structure of heterophase crystalline solids is not obvious and requires some explanation. Indeed, if a solid has attained stable equilibrium as the result of a phase transformation, then, in accordance with the Gibbs phase rule, a limited number of phases exist in it. In particular, a one-component single crystal should be transformed into a single crystal, a two-component one into a two-phase bicrystal, and so on. On the other hand, the observed real structure of a solid is not infrequently nonequilibrium and is determined as a whole by the kinetics of the transformation. Thus, in crystallization, a polycrystal is formed as a result of the impact of crystals growing from independent nucleation centers, and the fundamental parameter of the structure—the average size of the crystals (grains)—is determined by the rate of nucleation and growth. Between the two extreme cases indicated there are a number of intermediate cases, in which the resulting structure depends both on kinetic and on thermodynamic factors. For example, it is often assumed that the growing crystal of the new phase has an equilibrium shape corresponding to the minimum of the free energy for fixed volume of the crystal. This

assumption corresponds to reality if the shape relaxation time is substantially shorter than the time in which the volume of the crystal changes (e.g., if the shape changes as a result of surface diffusion while the increase in the volume of the crystal requires a supply of atoms from the bulk of the initial phase). In this article we also consider another situation, arising as a consequence of the fact that the new-phase crystal being formed interacts with the surrounding initial phase and changes its state. As a result the development of neighboring crystals turns out to be interrelated, and the formation of the structure in a certain region proceeds in a self-consistent manner. The size of this region is determined by the impact and interaction with other "colonies" developing from independent centers, and, consequently, depends on the kinetic the internal-stress fields which arise in all transformations and are a specific feature of solid-state heterophase systems. Below we consider those transformations in which the internal-stress fields play a dominant role amongst other long-range fields, i.e., electric or magnetic fields are absent or their energy is negligibly small compared with the elastic energy of the internal stresses. By varying the thermodynamic potential with respect to the phase composition of the heterophase system, the volume and shape of the phases, and also with respect to their mutual disposition, with certain additional conditions pertaining to the system being studied we can find the equilibrium structure corresponding to the minimum of the thermodynamic potential. Alongside the above-mentioned kinetic condition limiting the size of the transformed region, the supplementary condition for metastable equilibrium is that plastic relaxation of the internal stresses be absent.

1. GEOMETRY OF THE DISTORTION OF THE CRYSTAL LATTICE, AND INTERNAL STRESSES IN A HETERO-PHASE SYSTEM

The stress fields arising in phase transformations in the solid state are determined by two factors: the characteristic parameters of the transformation. In particular, it can be individual grain of a polycrystal. At the same time, within the boundaries of the region of self-consistent development of the transformation, the structure is determined by the tendency of the system toward minima of the free energy and corresponds to metastable equilibrium. Of course, a real structure can differ from a metastable one by virtue of the kinetic factors determining the development of the transformation. But even in those cases in which an equilibrium state is not attained, we may expect (and this is confirmed by analysis of the experimental material) that the tendencies that are characteristic for equilibrium structures will appear in the study of real structures, which can be kinetically fixed at some or other stage of the approach to equilibrium.

To find the equilibrium structures, it is necessary to calculate the thermodynamic potential of the heterophase system, which is made up of the volume "chemical" energy of the phases, the surface energy of the interphase boundaries, the energy of long-range fields and the work by external forces. Included in the long-range fields are electric or magnetic fields (if electric or magnetic phases are formed in the system), and also deformation accompanying the phase transition, and the nature of the contact between the phases in the heterophase system. For each phase transformation we can

assign a characteristic deformation, i.e., the average deformation acquired by the new phase relative to the initial phase in the absence of external forces:

$$\hat{\epsilon}^0(\eta_1, c_1; \eta_2, c_2) = \hat{\epsilon}_I^0(\eta_2 - \eta_1, c_2 - c_1) + \hat{\epsilon}_{II}^0(\eta_1, c_1). \quad (1.1)$$

Here $\eta_{1,2}$ and $c_{1,2}$ are the order parameters ($\eta^1, \eta^2, \dots, \eta^K$) (atomic, magnetic or electric) and concentrations (c^1, c^2, \dots, c^m —one for each component) in the initial phase 1 and in the phase 2 being formed, and $\hat{\epsilon}_I^0$ is the characteristic deformation associated with the change of order or concentration in the phase transition. In the case of magnetic transitions this is the magnetostriction, in atomic ordering it is the cell deformation induced by the rearrangement of the atoms over the sublattices of the superstructure, in diffusion transformations it is the average change in lattice constant as a result of the deviation of the concentration of the diffusing component from the initial concentration, and so on. In the first approximation, the deformation $\hat{\epsilon}_I^0$ is proportional to the change of the corresponding parameters. For example, in transformations accompanied only by a change in the composition of the phases, $\hat{\epsilon}_I^0 = \hat{w}(c_2 - c_1)$, where \hat{w} is the concentration expansion tensor (analogous to the temperature expansion coefficient). The presence of the second term in the expression (1.1) is due to the fact that a phase transition is not always determined entirely by a change in the composition or degree of order. Moreover, there is a large class of transformations—the martensitic transformations, in which the concentrations and order remain unchanged and the only parameter of the transition is the deformation. In martensitic transitions the state of a phase is uniquely specified by the characteristic deformation, and in particular cases the transformation reduces directly to a certain microscopic uniform deformation of the lattice^[3].

The characteristic deformation $\hat{\epsilon}^0$ defines a linear transformation (\hat{U}^0), which, when applied to the sites of the initial lattice (r_1), gives the sites of the final lattice (r_2)^[1]

$$r_2 = \hat{U}^0 r_1, \quad \hat{U}^0 = \hat{1} + \hat{\epsilon}^0; \quad (1.2)$$

$\hat{1}$ is the unit matrix

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

For example, the deformation

$$\hat{\epsilon}^0 = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \eta \end{pmatrix}, \quad \delta = \frac{c}{a_0} - 1, \quad \eta = \frac{a}{a_0} - 1, \quad (1.3)$$

describes the transition of a cubic lattice with parameter a_0 into a tetragonal one with parameters a and c ; for $\delta = (a/a_0) - 1$, $\eta = (\sqrt{2}a/a_0) - 1$, this deformation leads to the transformation of a face-centered cubic (fcc) lattice into a body-centered cubic (bcc) lattice (Fig. 5)^[4].

The observed orientational relationships of the phases are directly connected with the characteristic deformation. We shall elucidate this connection with the example of the fcc-bcc transition. The deformation (1.2) leads to a transformation of the crystallographic planes and directions of the initial fcc phase into the corresponding (i.e., related by the lattice-correspondence matrix \hat{U}^0) crystallographic elements of the final bcc phase. The different experimentally established orientational relationships between the fcc and bcc phases in two-phase systems indicate the close orientations of some of the

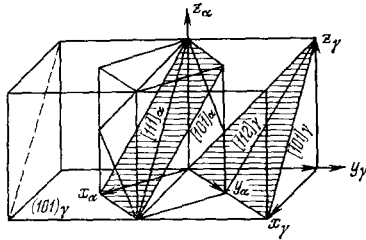


FIG. 5. Tetragonal deformation in the transition of an fcc lattice (γ) into a bcc lattice (α).

corresponding elements. In particular, in transformations in alloys based on iron, it is usually observed that the corresponding close-packed planes $(11\bar{1})_{\text{fcc}}$ and $(101)_{\text{bcc}}$ (cf. Fig. 5) are almost parallel; in this case, $[101]_{\text{fcc}} \parallel [11\bar{1}]_{\text{bcc}}$ (the Kurdjumov-Zaks orientational relation) or $[\bar{1}12]_{\text{fcc}} \parallel [10\bar{1}]_{\text{bcc}}$ (the Nishiyama relation)^[1,2]. We note that the observed mutual orientations of the phases is not such that the cubic axes are parallel, which would correspond to unchanged positions of the principal axes of the deformation (1.3), i.e., the observed lattice distortion contains a certain rotation in addition to the pure deformation (1.2). This rotation, like the internal stresses, is the result of interaction of the phases.

The presence of the characteristic deformation in a transformation is not a sufficient condition for the appearance of internal stresses. It is also necessary that the new phase undergoing deformation in the transformation remain in contact with the old phase. What is the nature of this contact? A natural generalization of the concept of a characteristic lattice deformation leading to a unique correspondence between the sites of the initial and final structures within the transformed region is the idea that a unique correspondence of this type remains valid for all points of the heterophase system, including points lying on a phase-contact surface. This conjecture corresponds to the condition that the connectivity of the lattice is conserved at all points, including the interphase surface: any closed contour drawn through the sites of the initial lattice will remain closed after the transformation. This is equivalent to the requirement that there be no formation or motion of dislocations in the transformation. Correspondingly, any violation of the microscopic connectivity can be regarded as the result of a plastic deformation or plastic yielding. This assumption of the absence of violation of the microscopic connectivity of the crystal lattice is equivalent to the concept, widely used in metallography, of phase coherence, according to which the neighborhood of each atom is the same on the interphase boundary as in the initial phase (i.e., the arrangement of the atoms is such that it can be obtained by a continuous small distortion of the initial phase). If several phases coherent with the initial one are formed in the transformation, they will clearly also be coherent with each other.

The coherence of phases on the boundary implies that each vector connecting two points on the interphase surface before the transformation goes over into the same vector after the transformation, irrespective of which of the contiguous phases it is regarded as belonging to, i.e.,

$$(\hat{1} + \hat{u}_1) \mathbf{r}_b = (\hat{1} + \hat{u}_2) \mathbf{r}_b, \quad \text{OR} \quad (\hat{u}_2 - \hat{u}_1) \mathbf{r}_b = 0, \quad (1.4)$$

where \hat{u}_1 and \hat{u}_2 are the full distortions of the adjoining phases relative to the initial one-phase state, and \mathbf{r}_b is a vector on the interphase boundary²⁾. If we consider a

plane boundary element with normal \mathbf{n} , then $\mathbf{r}_b \mathbf{n} = 0$ for every vector \mathbf{r}_b , and the requirement (1.4) that the contact remains the same is fulfilled under the condition

$$\hat{u}_2 - \hat{u}_1 = \mathbf{s} \circ \mathbf{n} \quad (1.5)$$

with an arbitrary vector \mathbf{s} . The dyadic tensor $\mathbf{s} \circ \mathbf{n}$ describes an invariant-plane distortion: all planes with normal \mathbf{n} are undistorted, since the displacements in each of the planes are equal: $\mathbf{u} = (\mathbf{s} \circ \mathbf{n}) \mathbf{r} = \mathbf{s}(\mathbf{n} \mathbf{r}) = \mathbf{s} \mathbf{x}$, where \mathbf{x} is the distance of the plane considered from the coordinate origin (cf. Fig. 3). When the condition (1.5) is fulfilled the relative deformation of the contiguous phases reduces to a simple shear and a normal displacement of the stack of planes parallel to the boundary, these planes being geometrically identical in the two phases.

Below we shall assume all deformations to be small (the changes in the lattice parameters are small compared with these parameters). In this case the principle of superposition of distortions is valid, each distortion in its turn being made up of a deformation and a rotation, and the condition (1.5) of conservation of the connectivity reduces to definite restrictions on the possible discontinuity in the deformations and on the disorientation of the phases at the interphase boundary:

$$\Delta \hat{\epsilon} \equiv \hat{\epsilon}_2 - \hat{\epsilon}_1 = (\hat{\epsilon}_2^s + \hat{\epsilon}_2^a) - (\hat{\epsilon}_1^s + \hat{\epsilon}_1^a) = \frac{1}{2} (\mathbf{s} \circ \mathbf{n} + \mathbf{n} \circ \mathbf{s}), \quad (1.6)$$

$$\Delta \hat{\omega} \equiv \hat{\omega}_2 - \hat{\omega}_1 = (\hat{\omega}_2^s + \hat{\omega}_2^a) - (\hat{\omega}_1^s + \hat{\omega}_1^a) = \frac{1}{2} (\mathbf{s} \circ \mathbf{n} - \mathbf{n} \circ \mathbf{s}), \quad (1.6')$$

where $\hat{\epsilon}_{1,2}^s$ and $\hat{\omega}_{1,2}^s$ are the symmetric and antisymmetric parts of the characteristic distortions of the phases 1 and 2, and $\hat{\epsilon}_{1,2}^a$ are the elastic deformations which the phases acquire as a result of conservation of continuity (Fig. 6). In the case when $\hat{\epsilon}_2^s - \hat{\epsilon}_1^s = (\mathbf{s} \circ \mathbf{n} + \mathbf{n} \circ \mathbf{s})/2$, elastic deformations are absent, i.e., the phases are in contact along a common undistorted plane. Conversely, the deviation of the discontinuity in the characteristic deformations from deformations with an invariant plane determines the extent of the mutual elastic distortion of the phases and serves as a source of internal stresses in heterophase systems³⁾.

The internal stresses in a heterophase crystalline system can be studied within the framework of the classical theory of the elasticity of a continuous medium, if the following assumptions are fulfilled.

First, the deformations and stresses do not change significantly over distances of the order of interatomic distances ($|\nabla \hat{\epsilon}| a \ll 1$). Then we can neglect the discrete atomic-molecular structure of the phases and treat the crystal as a continuous medium, the free (elastic) energy of which at each point depends on the value of the

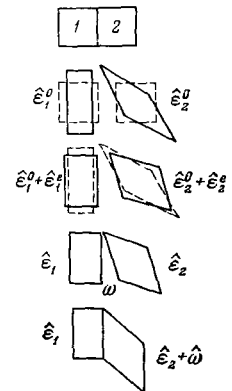


FIG. 6. Discontinuity of the deformations at a boundary between coherent phases.

deformation at the same point. This assumption is not fulfilled on an interphase boundary, where the deformations experience a discontinuity. Therefore, the results obtained by neglecting the gradients of the deformations in the local free-energy density are valid for points that are at a sufficient distance from the boundary, compared with its effective thickness.

Secondly, application of the classical theory of elasticity implies the existence of a linear relationship between the elastic deformation and the stress (a quadratic dependence of the elastic-energy density on the deformations). A necessary condition for this is that the characteristic deformations be small and that the interphase surfaces be "smooth" (with no angular points, edges, etc.). Despite the limitations indicated, the theory of elasticity is an effective instrument for analyzing the real crystal structure, as is confirmed by its successful use in the theory of crystal-structure defects.

The study of the stressed state of a heterophase system within the framework of elasticity theory presupposes the calculation of the displacement field, deformation and stress from a given distribution of characteristic deformations or, if the phases are homogeneous, from the discontinuity of the characteristic deformations at the interphase boundaries. The solution of this problem has been obtained in explicit form only for certain particular cases of elastic anisotropy, and for the simplest geometry of the heterophase system (the most general of the solutions obtained pertains to the ellipsoidal inclusion of one phase in an unbounded matrix of another, with equal elastic moduli of the phases^[7-10]). However, if we confine ourselves to treating phases whose moduli are the same, the problem is substantially simplified, inasmuch as the equilibrium solutions, as will be shown in the next Section, correspond to one-dimensional distributions of the characteristic deformations.

c In the one-dimensional case, when the characteristic-deformation field is constant in a plane normal to the direction of \mathbf{n} , and $\hat{\epsilon}^0(\mathbf{r}) = \hat{\epsilon}^0(x)$ where $x = \mathbf{r}\mathbf{n}$, the total deformation, by virtue of the compatibility condition (1.6), has the form

$$\hat{\epsilon}^0(x) = \frac{1}{2} [s(x) \cdot \mathbf{n} + \mathbf{n} \cdot s(x)] + \bar{\epsilon}^0, \quad (1.7)$$

where $\bar{\epsilon}^0$ is a certain constant. From the equation of equilibrium, $\hat{\sigma}\mathbf{n} = 0$, and the fact that the total force

acting on the system equals zero, $\int_{-L}^L \sigma dx = 0$ (here $\hat{\sigma}$ is

the stress: $\hat{\sigma} = \hat{\mathbf{G}} \cdot \hat{\epsilon}^0 = \hat{\mathbf{G}} \cdot (\hat{\epsilon}(x) - \hat{\epsilon}^0(x))$ where $\hat{\mathbf{G}}$ is the elastic modulus, and $2L$ is the length of the system), it follows that

$$s(x) = (\hat{\mathbf{G}}\mathbf{n})^{-1} (\hat{\mathbf{G}}\mathbf{n}) \cdot (\hat{\epsilon}^0(x) - \bar{\epsilon}^0), \quad (1.8)$$

$$\hat{\sigma}(x) = \hat{\mathbf{G}}^* \cdot (\hat{\epsilon}^0(x) - \bar{\epsilon}^0), \quad \hat{\mathbf{G}}^* \equiv (\hat{\mathbf{G}}\mathbf{n}) (\hat{\mathbf{G}}\mathbf{n})^{-1} (\hat{\mathbf{G}}\mathbf{n}) - \hat{\mathbf{G}}, \quad (1.9)$$

$$\bar{\epsilon}^0 = \frac{1}{2L} \int_{-L}^L \hat{\epsilon}^0(x) dx. \quad (1.10)$$

The elastic-energy density in the layer with coordinate x equals⁴

$$e(\hat{\epsilon}^0(x), \mathbf{n}) = \frac{1}{2} (\bar{\epsilon}^0 - \hat{\epsilon}^0(x)) \cdot \hat{\mathbf{G}}^* \cdot (\bar{\epsilon}^0 - \hat{\epsilon}^0(x)). \quad (1.11)$$

It follows directly from the expressions (1.7)–(1.10) that the discontinuity in the stresses at the boundary between phases with characteristic deformations $\hat{\epsilon}_1^0$ and $\hat{\epsilon}_2^0$ equals

$$\hat{\sigma}_1 - \hat{\sigma}_2 = \hat{\mathbf{G}}^* \cdot (\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0), \quad (1.12)$$

and the characteristic field in the vicinity of the interphase boundary has the form

$$\hat{\sigma}_1 = -\hat{\sigma}_2 = \frac{1}{2} \hat{\mathbf{G}}^* \cdot (\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0). \quad (1.13)$$

As will be shown below, the above relations, describing a field of one-dimensional distributions of characteristic deformations^[11, 12], are sufficient for the effective solution of variational problems concerning optimal heterophase structures. These formulas can be generalized to the case of different elastic moduli^[11]. In this case, however, it is far from always the case that one-dimensional distributions are an acceptable approximation for the description of equilibrium structures^[13]. Therefore, we shall confine ourselves to treating systems consisting of phases for which the difference in the moduli can be neglected. Apparently, this assumption is fulfilled for many phase transformations for which there is no change in the type of interatomic bonding. Moreover, this restriction is lifted if the heterophase system attains a state in which there are no internal stresses.

2. EQUILIBRIUM OF A HETEROPHASE SYSTEM

We shall formulate the equation of equilibrium of a heterophase system with respect to displacement of the interphase boundaries. For this we shall introduce the concept of the configurational force acting on an element of the interphase surface^[11].

We shall consider a portion of a boundary separating phases 1 and 2, the mutual transformation of which is accompanied by a discontinuity ($\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0$) in the characteristic deformations (Fig. 7). The change in the thermodynamic potential, associated with a local increase of the volume of phase 2 at the expense of phase 1 at the point \mathbf{r}_S (with normal \mathbf{n}), equals

$$\delta\Phi_{1 \rightarrow 2} = [f_2^0 - f_1^0 + e(\mathbf{r}_S) - (\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) \cdot \hat{\sigma}_1(\mathbf{r}_S)] \delta V, \quad (2.1)$$

where f_1^0 and f_2^0 are the specific free energies of the unstressed phases 1 and 2, $e(\mathbf{r}_S)\delta V$ is the energy of formation in phase 1 of the crystal A of phase 2, equal in volume and shape to the variation of the region 2 on displacement of the interphase boundary at the point \mathbf{r}_S , and $(\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) \cdot \hat{\sigma}_1(\mathbf{r}_S)\delta V$ is the work of the stress field in phase 1 at the surface separating the phases as the crystal A is formed. The change in the thermodynamic potential in the inverse process—increase of the volume of phase 1 at the expense of phase 2 at the point \mathbf{r}_S —is

$$\delta\Phi_{2 \rightarrow 1} = [f_1^0 - f_2^0 + e'(\mathbf{r}_S) - (\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0) \cdot \hat{\sigma}_2(\mathbf{r}_S)] \delta V, \quad (2.1')$$

where $e'\delta V$ is the elastic energy of the crystal B of phase 1 (the characteristic deformation is $(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0)$ in phase 2), and $\hat{\sigma}_2(\mathbf{r}_S)$ is the stress at the surface, due to the phase 2.

The above changes in the thermodynamic potential can be regarded as the work of a force \mathbf{F} acting on the boundary:

$$\mathbf{F} = [f_2^0 - f_1^0 + (\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) \cdot \frac{\hat{\sigma}_1 + \hat{\sigma}_2}{2}] \mathbf{n}, \quad (2.2)$$

where $\delta\Phi_{1 \rightarrow 2} = -\delta\Phi_{2 \rightarrow 1} = \mathbf{F}\mathbf{n}\delta n\delta S$ ($\delta n\delta S \equiv \delta V$, δn is the displacement of the boundary along the normal, and δS is the area of the variation). For the existence of a force \mathbf{F} defined in this way, it is necessary and sufficient that $e = e' = (\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) \cdot (\hat{\sigma}_2 - \hat{\sigma}_1)/2$, which is equivalent to the requirement that the crystals A and B have the shape of a plate with a small ratio of the thickness δn to the other linear dimensions $\delta L \sim (\delta S)^{1/2}$. In fact, by making use of

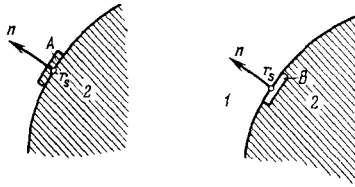


FIG. 7. Illustration to define the configurational force.

the expression (1.12) for the stress discontinuity at the interphase boundary, it is not difficult to show that the energy e is equal to the elastic-energy density inside a plane-parallel plate (cf. (1.11)) having normal \mathbf{n} and characteristic deformation $(\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0)$. Consequently, as will be shown Sec. 3, to within small terms proportional to $(\delta n / \delta L)^2$, e is equal to the elastic energy of a crystal with dimensions δn , δL , δL . In other words, if the variations of the boundary configurations are sufficiently smooth, we can introduce the concept of a configurational (i.e., dependent on the position of the boundary) force (2.2).

The stress $\hat{\sigma} \equiv (\hat{\sigma}_1 + \hat{\sigma}_2)/2$ is the stress, continuous at the boundary, that will exist at the point \mathbf{r}_S if the portion of the interphase surface adjacent to this point is removed, i.e., if we subtract the discontinuous field (1.13) of the planar boundary with normal $\mathbf{n}(\mathbf{r}_S)$ from the stress field at the surface. It is appropriate to divide the stress $\hat{\sigma}(\mathbf{r}_S)$ into an external stress $\hat{\sigma}^C(\mathbf{r}_S)$ associated with the action of forces applied to the solid and also with all fixed sources of internal stresses, and an internal stress $\hat{\sigma}^S(\mathbf{r}_S)$ due to the discontinuity in the characteristic deformations at the interphase boundaries $\{S\}$. The configurational force can then be regarded as the resultant of two forces: a thermodynamic driving force $\Delta\mu^0 = f_1^0 - f_2^0 - (\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0) \cdot \hat{\sigma}^C(\mathbf{r})$ directed toward the less stable phase, and the response of the characteristic field of the interphase surface, this field being a functional of the configuration of this surface^[8]:

$$\hat{\sigma}^S(\mathbf{r}) = \sum_i \int_{S_i} \hat{\mathbf{G}} \nabla \hat{\mathbf{U}}(\mathbf{r} - \mathbf{r}') (\mathbf{n}(\mathbf{r}') \cdot \hat{\mathbf{G}} \cdot \Delta \hat{\epsilon}_i^0(\mathbf{r}')) dS; \quad (2.3)$$

here $\Delta \hat{\epsilon}_i^0(\mathbf{r}')$ is the discontinuity in the characteristic deformations at the point \mathbf{r}' of the i -th phase boundary⁵⁾, $\hat{\mathbf{U}}(\mathbf{r} - \mathbf{r}')$ is a tensor Green function, or elastic-field source function (cf. [14], and also p. 27 in the English edition of [15]), i.e., the displacement field at the point \mathbf{r} induced by the action of a unit force at the point \mathbf{r}' ; $\mathbf{n} \hat{\mathbf{G}} \cdot \Delta \hat{\epsilon}_i^0 dS$ is the force acting on an element of the interphase surface. The integration over one boundary and summation over the different boundaries are the result of the principle of superposition of elastic displacements; the multiplication by the elastic modulus and the spatial differentiation ($\hat{\mathbf{G}} \nabla$) are associated with the transformation from the displacement to the stress. In equilibrium the interphase surface occupies a position in which, at all its points, the configurational force equals zero, i.e.,

$$\Delta\mu^0(\mathbf{r}_S) - (\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) \cdot \hat{\sigma}^S(\mathbf{r}_S) = 0. \quad (2.4)$$

The condition (2.4), together with (2.3), is the integral equation for determining the configuration of the interphase boundary in a given field $\Delta\mu^0(\mathbf{r})$.

In deriving Eq. (2.4) we neglected the surface energy of the interphase boundary and the action of the surface-tension forces $\sim \Gamma/R$ (where Γ is the surface energy and R is the radius of curvature of the interphase surface). This means that the equilibrium equations derived are applicable to sufficiently large-scale structural com-

ponents, such that forces that are elastic in origin are substantially greater than the surface-tension forces ($\hat{\sigma} \cdot \Delta \hat{\epsilon}^0 \gg \Gamma/R$). In order to emphasize this fact, we shall call such structures macroscopic, in contrast to "microscopic" structures for which the elastic and surface-tension forces are comparable in magnitude.

The equilibrium of a heterophase system as a whole corresponds to the minimum of the thermodynamic potential or, in the absence of external fields, to the minimum of the free energy

$$\mathcal{F} = \sum_k \int_{V_k} f_k(\mathbf{r}) dV = \sum_k \int_{V_k} \left[f_k^0 + \frac{1}{2} (\hat{\epsilon} - \hat{\epsilon}_k^0) \cdot \hat{\mathbf{G}} \cdot (\hat{\epsilon} - \hat{\epsilon}_k^0) \right] dV, \quad (2.5)$$

where $f_k(\mathbf{r})$ is the free-energy density at the point \mathbf{r} of the k -th phase, and f_k^0 is the same in the absence of stresses; the second term is the elastic energy at the point \mathbf{r} and is determined by the difference between the total and characteristic deformations at this point. In phase transitions in crystals, two fundamentally different cases are possible:

a) Martensitic transformations: the state of the phase is completely determined by the deformation $\hat{\epsilon}$. In this case, for specified external conditions, $\hat{\epsilon}_k^0$ and f_k^0 are the given phase parameters. The condition for equilibrium of the system reduces to the condition that F be a minimum with respect to variation of the total deformations, i.e., reduces to the mechanical equilibrium describable by the equations of elasticity, of which (2.3)–(2.4) are a consequence. Therefore, the equilibrium of a heterophase system is equivalent to the equilibrium of the interphase boundaries and is determined by Eq. (2.4). Mechanical twinning—the reorientation of a crystal lattice under the action of a load—can be regarded as a particular case of a martensitic transformation. For the initial crystal and the twin, $f_2^0 = f_1^0$, but the specific thermodynamic potentials differ by the work done, $-\hat{\sigma}^C \cdot \hat{\epsilon}^0$, where $\hat{\epsilon}^0$ is the twinning displacement^[16, 17].

b) Nonmartensitic transformations: together with the deformation, the order parameters (η) and concentrations (c) are the internal parameters defining the state of a phase. In this case, f_k^0 and $\hat{\epsilon}_k^0$ in (2.5) are variable quantities, depending on η and c . To the condition for equilibrium of the interphase boundaries we must add the condition that F be a minimum with respect to variations of η and c . For example, for a phase transition associated with a change of order, this additional condition, at each point of the k -th phase, has the form

$$\frac{\partial f_k(\mathbf{r})}{\partial \eta} = \frac{\partial f_k^0}{\partial \eta} - \hat{\sigma} \cdot \frac{\partial \hat{\epsilon}_k^0}{\partial \eta} = 0, \quad (2.6)$$

where, clearly, $\partial \hat{\epsilon}_k^0 / \partial \eta = \partial \hat{\epsilon}_{\mathbf{I}k}^0 / \partial \eta$ (cf. (1.1)), and $\hat{\sigma} = \hat{\sigma}^C + \hat{\sigma}^S + \hat{\sigma}^\eta$ is the stress which is produced at the point considered by the action of the external forces and interphase boundaries and by the nonuniform distribution of the order parameter:

$$\hat{\sigma}^\eta = \sum_k \int_{V_k} \hat{\mathbf{G}} \nabla \hat{\mathbf{U}}(\mathbf{r} - \mathbf{r}') \hat{\mathbf{G}} \nabla \epsilon_k(\eta(\mathbf{r}')) dV \quad (2.7)$$

((2.7) is the analog of (2.3) for internal-stress sources distributed over the volume; cf. pg. 160 in the (second) Russian edition of [15]). If the internal parameters are the concentrations, the condition (2.6) corresponds to constancy of the chemical potentials of the components. The coupled equations (2.4) and (2.6) determine the equilibrium of a heterophase system. In general in a phase transformation there occurs both a change of order and concentration, and a rearrangement of the

crystal lattice, unconnected with the former changes and characterized by a characteristic deformation $\hat{\epsilon}_{II}^0$. In this case, the relaxation of the atomic order or redistribution of the concentrations, being effected by diffusional transfer of atoms, may proceed much more slowly than the displacement of the interphase boundaries separating the phases with different $\hat{\epsilon}_I^0$. Therefore, the formation of metastable martensitic phases is possible in phase transitions which, in equilibrium conditions, proceed with a change in the concentrations or degree of order (e.g., diffusionless transformations in many-component systems^[1]).

3. SINGLE-DOMAIN CRYSTAL OF THE NEW PHASE

The simplest heterophase system is an isolated crystal of the new phase, situated inside the initial phase. What are the shape and orientation of an equilibrium crystal of the new phase with constant characteristic deformation $\hat{\epsilon}^0$ in an unbounded elastic matrix? Equation (2.4) for equilibrium of the interphase surface has, in this case, the form

$$\Delta\mu^0 - \hat{\epsilon}^0 \hat{\sigma}^S(r_s) = 0, \quad (3.1)$$

$$\sigma^S(r_s) = \int \hat{G} \cdot \nabla \hat{U}(r_s - r_s') (n \hat{G} \cdot \hat{\epsilon}^0) dS(r_s');$$

the crossed integral denotes that the stress is regularized as a result of the exclusion of the vicinity of the point considered in the interphase surface. It is clear from dimensionality arguments that for a constant driving force, i.e., in a uniform field $\hat{\sigma}^C$, an equilibrium state does not exist for a macroscopic crystal: it is impossible to form a parameter having the dimensions of length from the physical quantities (G , $\hat{\epsilon}^0$, $\Delta\mu^0$) appearing in the equation of the elastic equilibrium^[6]. In an inhomogeneous external field, the shape and size of an equilibrium crystal are determined by this externally introduced inhomogeneity. For example, the shape and size of a twin in mechanical twinning are determined by the character of the distribution of stresses arising under the action of the external load^[18]. In phase transformations, the inhomogeneity of the system usually reduces to local obstacles limiting the possible maximum sizes of a crystal of the new phase. For example, in a polycrystal of such a type the obstacle is the grain boundary, and the maximum size of a crystal of the new phase is equal to the diameter of a grain of the initial phase. In the presence of local inhomogeneities, not possessing long-range fields, in a doubly-connected heterophase "crystal-matrix" system a characteristic equilibrium state is attained, corresponding to a crystal in the form of a thin plate oriented in a definite way (Fig. 8)^[11]. In fact, the solution of the equilibrium equation (3.1) with a constant driving force should be a configuration ensuring the constancy of the internal stresses $\hat{\sigma}^S$ at the interphase boundary. This requirement is fulfilled if the crystal of the new phase has the shape of an unbounded plane-parallel plate: at each point of the unbounded interphase plane its self-interaction equals zero, and $\hat{\sigma}^S$ is the constant stress from the second face of the plate. According to (1.13), for a plate with normal n , $\hat{\sigma}^S = -\hat{G}^*(n) \cdot \hat{\epsilon}^0/2$ and the equilibrium condition (3.1) takes the form

$$\Delta\mu^0 - e(n) = 0, \quad (3.2)$$

where, in accordance with (1.11), $e(n)$ is the elastic-energy density inside the plate. The elastic field of a plate-layer is similar to the electrostatic field of a planar capacitor: outside the plate the fields of the planar faces cancel each other, and inside they add and

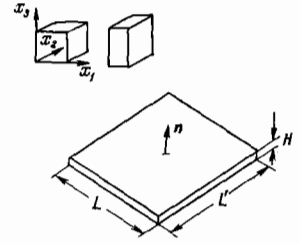


FIG. 8. A single-domain plate.

give a uniform field $\hat{\epsilon}^0 = 1/2(s \circ n + n \circ s) - \hat{\epsilon}^0$ (1.8).

Accommodation of the phases proceeds entirely as a result of elastic distortion of the layer-phase, in which the parallel faces of the plane become identical with the boundary plane of the matrix-phase. For the equilibrium (3.2) to be stable, it is necessary that the phases border on the plane n_0 corresponding to the minimum of $e(n)$ (otherwise, a change of n can lead to decrease of $e(n)$ and to violation of the equality (3.2)). The adjunction of the phases occurs along crystallographically similar planes and is associated with minimum distortion of the new phase. Distortion is absent if in the transformation any plane remains unchanged and, consequently, the characteristic deformation is an invariant-plane deformation. Any planar deformation in which one of the principal values is greater and another less than zero is such a deformation:

$$\hat{\epsilon}^0 = \begin{pmatrix} \epsilon' & 0 & 0 \\ 0 & -\epsilon'' & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2}(s_0 \circ n_0 + n_0 \circ s_0), \quad (3.3)$$

where $n_0^{i,2} = \sqrt{\epsilon'/s_1} \pm \sqrt{\epsilon''/s_1}$, $s_0^{i,2} = s_0 n_0^{i,2}$, $s_0 = \epsilon' + \epsilon''$, and i and j are unit vectors along the coordinate axes; the two values of n_0 correspond to the two conjugate invariant planes. In the formation of a plate of the new phase along the invariant plane n_0 , $\hat{\epsilon}^0 = 0$ and $e(n_0) = 0$. The characteristic deformation has the form (3.3) in the cases of twinning and fcc-hcp (hexagonal close-packed structure) transformations. The invariant plane in the first case is the twinning plane, and in the second case is the basal plane of the hcp phase or the $\{111\}$ plane of the fcc phase. The equality

$$\Delta\mu^0 - e_0 = 0 \quad (e_0 \equiv e(n_0)) \quad (3.4)$$

for an unbounded layer-plate corresponds to neutral equilibrium. When $\Delta\mu^0 > e_0$ a plate of the new phase tends to expand. However, if it terminates inside the matrix crystal, there is an inhomogeneous elastic field at its edge, the energy of which increases with increasing thickness (H) of the plate and stabilizes the plate. The energy of the edge field in the first approximation is proportional to the perimeter of the plate, the coefficient of proportionality having the meaning of the linear energy of the plate edge. Inasmuch as the inhomogeneous field of the plate is concentrated mainly in a region of radius $\sim H$ at the edge of the plate, the linear energy of the edge equals $e_L H^2$, where

$$e_L \approx \frac{1}{2} \frac{\partial e(n)}{\partial n_i \partial n_j} m_i m_j \sim G(e^0)^2$$

(m is the normal to the perimeter of the plate in the plane of the plate; cf. Fig. 8)^[19]. In the case when $\hat{\epsilon}^0$ is an invariant-plane deformation (3.3), the edge field is equivalent to the field of an effective dislocation passing round the plate along the perimeter and having the Burgers vector $B = s_0 H$, and $e_L \sim G s_0^2$. This approximation corresponds in the theory of dislocations to the so-called linear-tension approximation usually used in the analysis of dislocation configurations^[20]. In a more ex-

act treatment one takes into account the nonlocal character of the linear energy, which is manifested, in particular, in the fact that $e_L \sim \ln(H/L)$, where L is the length of the plate. The exact calculation of the edge energy of the plate requires knowledge of the configuration of the edge of the plate. For an equilibrium crystal this configuration is the solution of Eq. (3.1), and depends on the form of the inhomogeneous fields compensating the edge of the crystal. A similar problem has been solved (in the thin-crystal approximation) in the determination of the configuration of the point of a twin^[21] or of the orifice of a fraction (cf. ^[22] and also p. 179 in the (second) Russian edition of ^[15]). However, if we do not consider the shape of the edges of the individual crystals, which is determined by the concrete form of the obstacles and, in a real structure, is to a considerable extent random in character, we can confine ourselves to the qualitative estimate of the edge energy given above. The neglect in this case of the dependence of the linear energy on the crystallographic direction of the edge of the plate is also unimportant: the contour of real crystals is apparently determined to a greater extent by the elastic and contact interaction with obstacles (including other crystals) than by the anisotropy of the linear energy of the characteristic edge field.

Thus, when the inhomogeneity of the initial field reduces to the presence of obstacles acting over short distances and limiting the maximum size of a crystal of the new phase, the equilibrium shape of the crystal can be a plane-parallel plate⁹⁾. The smaller the thickness of the crystal and, correspondingly, the effective range of the edge field, the greater will be the part of the crystal surface on which the condition (3.2) is fulfilled: for $H/L \ll 1$, the plate is an asymptotically exact solution of the equilibrium equation (3.1). For $H/L \ll 1$, the change of thermodynamic potential accompanying the formation of the equilibrium crystal equals

$$\Phi = (-\Delta\mu^0 + e_0) \alpha_V L^2 H + e_L \alpha_L L H^2 + 2\Gamma(n_0) \alpha_S L^2 + \Gamma' \alpha_L H L, \quad (3.5)$$

where $\alpha_S L^2$ is the area, $\alpha_V L$ the perimeter and $\alpha_V L^2 H$ the volume of the plate, α_S , α_L and α_V are numerical coefficients of order unity, depending on the configuration of the plate, and Γ and Γ' are the specific surface energies of the planar faces and edge of the plate. For macroscopic crystals ($H \gg \Gamma'/e_L$), the surface energy of the edge can be neglected in comparison with the elastic energy of the edge field, which is represented by the second term. Sufficiently far from the edges, the field inside the plate is homogeneous and coincides with the field of an unbounded layer n_0 : the total deformation (1.8) is $\hat{\epsilon}_1 = (\mathbf{s} \circ \mathbf{n}_0 + \mathbf{n}_0 \circ \mathbf{s})/2$, and $\mathbf{s} = (\mathbf{n}_0 \hat{\mathbf{C}} \mathbf{n}_0)^{-1} (\mathbf{n}_0 \hat{\mathbf{C}} \circ \hat{\epsilon}^0)$. The new phase experiences, as a whole, a rotation $\hat{\omega} = (\mathbf{s} \circ \mathbf{n}_0 - \mathbf{n}_0 \circ \mathbf{s})/2$. The regions of initial phase separated by the plate that has been formed undergo a rigid displacement relative to each other, by an amount $\mathbf{s}H$. The emergence of the plate at the free surface leads to the formation of the characteristic relief (cf. Fig. 2) which, if we neglect effects due to image forces, repeats the invariant-plane deformation $\hat{\epsilon}_1$.

If the greatest dimension $L = L_0$ of the crystal is given as a structural parameter of the initial phase, then, minimizing Φ with respect to H , we obtain

$$H_0 = \frac{\Delta\mu^0 - e_0}{e_L} \frac{\alpha_V}{2\alpha_L} L_0, \quad (3.6)$$

i.e., the thickness of the equilibrium crystal depends on the deviation from the point of phase equilibrium. In

certain cases such a reversible change in the sizes of crystals of the new phase on variation of the temperature or external stress has been observed experimentally, e.g., in elastic twinning^[16,18] and in the thermoelastic equilibrium of martensitic crystals^[1,26]. The relation (3.6) expresses the equilibrium of points at the center of a planar face of the plate under the action of stress from the other face and of the edge field ($\sigma \sim e_L H / \epsilon^0 L$) stabilizing the planar shape of the crystal.

For fixed L_0 , formation of a crystal of the new phase is thermodynamically favored if $\Phi(L_0, H_0) < 0$, i.e., for

$$\Delta\mu^0 > e_0 + \sqrt{\frac{8\alpha_S \alpha_L}{\alpha_V^2} e_L \Gamma \frac{1}{L_0}}. \quad (3.7)$$

The relation (3.7) determines the boundary of stability of the initial phase in real crystalline systems: the deviation $\Delta\mu^0$ from the equilibrium point of the undistorted phases that is required to start the transformation is greater, the smaller the grain size or the smaller the distance between the defects in the initial phase that are insurmountable for the new crystals. This dependence on, e.g., the grain size has been observed for the temperature of the onset of a martensitic transformation in polycrystals.

On the other hand, since crystals that have been formed earlier can serve as obstacles to the growth of the crystals, in a two-phase system L_0 is determined by the relative quantity of the new phase ($L_0 = f(V_2/V_1)$) and decreases as the transformation develops. The relation (3.7) can then be used to determine the limiting extent of the transformation, $V_2/V_1 = f^{-1}(L_0(\Delta\mu^0))$, for a constant driving force $\Delta\mu^0$ in, e.g., isothermal conditions. With increase of the deviation $\Delta\mu^0$ from true phase equilibrium, the amount of the new phase increases as a consequence of the increase in the equilibrium thickness of the existing crystals and the formation of new crystals, and an elastic two-phase equilibrium is established in the system. In transformations in many-component systems the elastic equilibrium is superimposed on the ordinary thermodynamic phase equilibrium, distorting the latter; in one-component systems this is manifested in the smearing-out of the transition temperature over a range of temperatures.

It should be emphasized that the relation (3.7) is applicable to the study of the elastic equilibrium due to the stabilization of the sizes of each crystal of the new phase by its own stress field. Therefore, it is valid only for small amounts of the new phase, when the elastic interaction of the crystals can be neglected⁹⁾. The role of the elastic interaction of the crystals is considered in Sec. 5.

For $L_0 \rightarrow \infty$ the inequality (3.7) goes over into the relation (3.4) determining the magnitude of the thermodynamic hysteresis in the phase transformation. The expression (3.4) can be interpreted as the equality of the thermodynamic potentials of the initial undistorted phase ($\mu_0 = f_0^0$) and the uniformly stressed phase being formed ($\mu_1 = f_1 - \hat{\epsilon}^0 \cdot \hat{\sigma}^C = f_1^0 + e_0 - \hat{\epsilon}^0 \cdot \hat{\sigma}^C$)¹⁰⁾. A transformation in a solid, with conservation of the microscopic continuity of the crystal, is possible if the undistorted initial phase becomes less stable than an elastically deformed new phase arising in conditions of minimum expenditure of energy on the creation of internal-stress fields. The relation

$$f_0^0(T_{0 \rightarrow 1}) = f_1^0 - \hat{\epsilon}^0 \cdot \hat{\sigma}^C + e_0(\hat{\epsilon}^0) \quad (3.8)$$

can be regarded as the definition of the limiting tem-

perature $T_{0 \rightarrow 1}$ of the transformation of phase 0 into phase 1, phase 0 being in equilibrium with a layer of phase 1. The temperature $T_{1 \rightarrow 0}$ of the inverse transformation of unbounded phase 1 into phase 0 is determined by the relation

$$f_0^0(T_{1 \rightarrow 0}) - (-\hat{\epsilon}^0) \cdot \hat{\sigma}^C + e(-\hat{\epsilon}^0) = f_1^0(T_{1 \rightarrow 0}) \quad (3.9)$$

(if we neglect the difference of the elastic moduli of the phases, the elastic energy e_0 is the same in the direct and inverse transformations). We note that external and internal stresses affect the phase equilibrium in fundamentally different ways. Since the work done by the external forces is linear in the characteristic deformation, external stresses displace the position of equilibrium⁽¹¹⁾, whereas the internal stresses, the energy of which is quadratic in the characteristic deformation, lead to a splitting of the phase equilibrium point into two points, between which lies a region in which a two-phase state is less favored thermodynamically than the one-phase state (Fig. 9a). This splitting of the phase equilibrium point into two (the points of the direct and inverse transformations) determines the hysteresis of the transformation in a system of coherent phases. In, e.g., a one-component system, where $f_1^0 - f_0^0 \approx q\Delta T/T^0$ (q is the heat of the transformation and T^0 is the temperature of equilibrium of the undistorted phases), this hysteresis is clearly equal to $\Delta T = T_{1 \rightarrow 0} - T_{0 \rightarrow 1} \approx 2e_0/q$.

If several virtual phases exist in the system, then, for given external conditions (temperature, external stress), that phase for which the thermodynamic potential

$$\mu_i = f_i^0 - \hat{\epsilon}_i^0 \cdot \hat{\sigma}^C + e_0(\hat{\epsilon}_i^0) \quad (3.10)$$

is lowest will be formed preferentially from the initial phase. Because of this, in a solid there can arise different intermediate phases, which, while not being stable in the isolated state (i.e., the potential $\mu_i^0 = f_i^0 - \hat{\epsilon}_i^0 \cdot \hat{\sigma}^C$ is not a minimum for them), couple better with the initial phase, and, consequently, are characterized by a lower elastic energy $e_0(\hat{\epsilon}_i^0)$ than is the stable phase. The formation of intermediate phases is often observed in the early stages of the break-up of solid solutions.

In those cases when the transformation occurs with a lowering of the crystal symmetry, phases are formed that are physically identical (but with different characteristic deformations) and connected with each other by twinning relationships. In particular, the transformation of a cubic phase into a tetragonal one is possible in three ways, differing in the choice of the tetragonal axis from the original cubic axes. The corresponding characteristic deformations differ by a reorientation of the principal axes through 90° (Fig. 10):

$$\hat{\epsilon}_1^0 = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \eta \end{pmatrix}, \quad \hat{\epsilon}_2^0 = \begin{pmatrix} \eta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \eta \end{pmatrix}, \quad \hat{\epsilon}_3^0 = \begin{pmatrix} \eta & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \delta \end{pmatrix}. \quad (3.11)$$

The higher the symmetry of the initial phase and the lower the final symmetry, the greater is the number of equivalent variants of the transformation (e.g., in the transformation of a cubic into a rhombic phase, there are twice as many of them as in the transformation into a tetragonal phase). In the presence of an external field, the structurally equivalent variants of the transformation become physically distinguishable. The result of this lifting of the degeneracy is a splitting of the phase-equilibrium point into several points, corresponding to transitions with different characteristic deformations

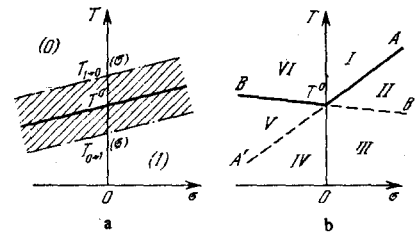


FIG. 9. ($T - \hat{\sigma}^C$)-diagram of the phase equilibrium. (a) Forbidden region for the coexistence of two phases; (b) regions of different relative stability of the phases (I— $\mu_0 < \mu_1 < \mu_3$; II— $\mu_1 < \mu_0 < \mu_3$; III— $\mu_1 < \mu_3 < \mu_0$; IV— $\mu_3 < \mu_1 < \mu_0$; V— $\mu_3 < \mu_0 < \mu_1$; VI— $\mu_0 < \mu_3 < \mu_1$).

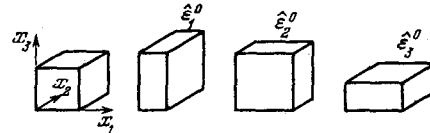


FIG. 10. Possible variants of the cubic-tetragonal transition.

and, consequently, with different thermodynamic potentials of the phases being formed:

$$\mu_i^0 = f_i^0 - \hat{\epsilon}_i^0 \cdot \hat{\sigma}^C. \quad (3.12)$$

As an example, Fig. 9b shows the $T - \hat{\sigma}^C$ diagram of the equilibrium of cubic and tetragonal phases under the action of a uniaxial stress σ along $[001]$. The line of equilibrium of the cubic phase (phase 0) with the tetragonal phases 1 (AA' : $dT/d\sigma = T^0\eta/q$) and 3 (BB' : $dT/d\sigma = T^0\delta/q$) divides the $T - \sigma$ plane into six regions of different relative stability of the phases 0, 1 and 3 (the phase 2 is energetically equivalent to phase 1) (cf. (3.11) and Fig. 10). The cubic-tetragonal transition becomes thermodynamically favored below the line AT^0B . If η and δ have opposite signs (as in Fig. 10), then the equilibrium temperature is raised under the action of a uniaxial stress, irrespective of the sign of σ . In the regions II and V the cubic phase is intermediate in stability between the two variants of the tetragonal phase. Therefore, if phase 3 is taken as the initial phase, its transition into phase 0 becomes possible on heating from the region III to the region II. But, on the other hand, in region II the transition $0 \rightarrow 1$ is favored. Since phase 1 remains stable in region III, as a result of the temperature cycle III \rightarrow II \rightarrow III the transition $3 \rightarrow 0 \rightarrow 1$ occurs, i.e., the initial state is not regenerated and a twinning orientation of the initial phase, stable under the stress, is formed: mechanical twinning of the tetragonal phase in the regions II and V proceeds via the formation of an intermediate cubic phase. It is obvious that the above effects can be observed if they are not suppressed by the elastic interaction of the phases (see Fig. 9a).

For nonmartensitic transformations, in the minimization of the thermodynamic potential $\Delta\mu^0$ and $\hat{\epsilon}^0$ are themselves variable parameters, and the solution of the variational problem (2.6)–(2.7) should give (besides the characteristics of the structure) the equilibrium values of the parameters of the phases in the metastable state, which, in principle, differ from the parameters of the stable phases. But for plate-like crystals with $H/L \ll 1$ in elastic equilibrium, these parameters, like the elastic deformation of the new phase, turn out to be uniform over the phase and sufficiently constant so that the distorted phase can be taken as an intermediate phase having special crystal structures, composition or degree of order. Evidently, it is necessary to keep this fact in mind when analyzing experimental data on processes of

precipitation and formation of zones, on the initial stages of ordering, and so on.

4. MANY-DOMAIN PLATE. ELASTIC DOMAINS

In the case when the transformation of the initial phase can lead to different resultant characteristic deformations (in particular, if two or more new phases arise), the formation of polysynthetic regions that are a conglomerate of domains with different characteristic deformations $\hat{\epsilon}_i^0$ may turn out to be energetically favored^[29,30]. If the dimensions of the domains are small compared with those of the polysynthetic region, we can talk of an average, or macroscopic, characteristic deformation $\hat{\epsilon}^0 = \sum_i \alpha_i \hat{\epsilon}_i^0$, where α_i is the volume fraction of domains of the i -th sort ($\sum_i \alpha_i = 1$). For a uniform macrodeformation $\hat{\epsilon}^0$, i.e., when the domain composition over the region is constant, as in the formation of a single-domain crystal, the optimal shape of the polysynthetic region inside the initial phase is that of a thin plate. But in the case of the formation of a many-domain plate, there appears the additional possibility, as compared with the single-domain case, of lowering the energy of the elastic interaction between the phase being formed and the initial phase at the expense of a change in the domain composition. In particular, by variation of the domain composition (α_i) and the orientation of the plate (\mathbf{n}), we can reduce to a minimum the energy associated with the incompatibility of the macrodeformation at the plane surfaces of the plate

$$e(\hat{\epsilon}^0(\alpha_i), \mathbf{n}) = \frac{1}{2} \hat{\epsilon}^0(\alpha_i) \cdot \hat{G}^*(\mathbf{n}) \cdot \hat{\epsilon}^0(\alpha_i). \quad (4.1)$$

If there exists a solution of the compatibility equation

$$\mathbf{n} \times \hat{\epsilon}^0(\alpha_i) \times \mathbf{n} = 0, \quad (4.2)$$

then for the α_i and \mathbf{n}_0 satisfying this equation the plane surfaces do not create a macroscopic elastic field (i.e., the fields from the boundaries between the different domains and the matrix mutually cancel), and (4.1) vanishes.

At the same time, the breakdown of the new phase into domains is accompanied by extra expenditure of energy on the production of internal stresses as a consequence of contact between domains with different characteristic deformations, on the creation of the interdomain boundaries and on the microdistortions at the points at which the domains emerge on to the interphase boundaries. The first two terms form the self energy of the polysynthetic "phase" and the last makes a contribution to the energy of interaction of this phase with the initial matrix. We shall estimate these additional energy terms in the case of formation of a many-domain plate from two sorts of domain ($\hat{\epsilon}_1^0, \hat{\epsilon}_2^0, \alpha_1 = 1 - \alpha, \alpha_2 \equiv \alpha$).

In a uniform field the equilibrium equation (2.4) is satisfied by a system of plane-parallel domains, the elastic-energy density of which equals, according to (1.11),

$$e_m = \sum_{i=1}^2 \alpha_i \frac{1}{2} (\hat{\epsilon}^0 - \hat{\epsilon}_i^0) \cdot \hat{G}^*(\mathbf{m}) \cdot (\hat{\epsilon}^0 - \hat{\epsilon}_i^0) = \alpha (1 - \alpha) e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{m}). \quad (4.3)$$

The interdomain interaction energy (4.3) is additive with the macrofield energy (4.1), since the energy of the interaction between the field generated by the deviation of the characteristic deformation from the average and the uniform field ($-\sum_i \alpha_i (\hat{\epsilon}^0 - \hat{\epsilon}_i^0) \cdot \hat{\sigma}$) equals zero, by definition of $\hat{\epsilon}^0$. Together with the elastic energy of the

interdomain interaction, the surface energy of the domain boundaries, which for a packet of domains is equal to $2\gamma(\mathbf{m})/D$, where $\gamma(\mathbf{m})$ is the specific surface energy of the domain boundary with normal \mathbf{m} and D is the average period of the domain structure, appears in the self energy of the many-domain "phase." It is assumed that the surface energy of the domain boundaries is less than the elastic energy. Otherwise, if $D < 2\gamma/e_m$, plane-parallel domains are unfavorable and the formation of a many-domain structure in the form of spheroidal domains of one of the phases being formed, in a matrix of a second phase, will be preferred. Such a structure has been observed in the formation of thin layers of a surface martensite.

The emergence of domains on to the interphase surface of the plate leads to the appearance of microdistortions, which are due to the deviation of the true characteristic deformation from the average and are absent on the boundary of a single-domain crystal. The field of a plane boundary of the polysynthetic phase is produced by alternating portions of the boundaries of the initial phase with the phases 1 and 2. Interference of the fields from these portions gives an average macrofield $\hat{\sigma} = \hat{G}^*(\mathbf{n}) \times \hat{\epsilon}^0/2$, at distances greater than D' from the boundary (where D' is the period of the domain structure at the boundary), and an oscillating field of microdistortions in the layer adjacent to the boundary. The microdistortions, like the field from the domain walls, is incoherent with the macrofield of the plate and makes an additive contribution to the total energy of the system. The energy of the microdistortions is a minimum for a constant period of the oscillations, and makes an additional contribution to the interphase-surface energy of the boundary of the plate with the initial phase, which can be estimated by means of (1.11) and (1.13):

$$\Delta\Gamma \sim \frac{1}{D'} \sum_{i=1}^2 e(\hat{\epsilon}^0 - \hat{\epsilon}_i^0, \mathbf{n}) (\alpha_i D')^2 \approx \xi \alpha^2 (1 - \alpha)^2 e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{n}) D \equiv e_s D, \quad (4.4)$$

where $\xi \sim \sin(\mathbf{n}, \mathbf{m}) \ln \alpha$ is a factor of order 1.

Thus, the equilibrium structure of the many-domain region is a plate consisting of a regular alternation of plane-parallel domains (Fig. 11). The change in the thermodynamic potential when it is formed is equal to

$$\Phi = \{ -(1 - \alpha) \Delta\mu_1^0 - \alpha \Delta\mu_2^0 + \alpha (1 - \alpha) e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{m}) + 2\gamma/D + e(\hat{\epsilon}^0, \mathbf{n}) \} \alpha_v H L^2 + (\Gamma + \Delta\Gamma) \alpha_s L^2 + e_L (\hat{\epsilon}^0) H^2 \alpha_L L. \quad (4.5)$$

Minimizing Φ with respect to \mathbf{n} , H , α , D and \mathbf{m} for a given maximum dimension $L = L_0$, we can determine the equilibrium domain composition α_0 , the structure, the habit and the energy of the many-domain plate.

The variation with respect to D leads immediately to the relation

$$D_0 = \sqrt{\frac{2\gamma H}{e_s}}, \quad (4.6)$$

i.e., the thickness of the domains is determined by the competition between the surface energy of the interdomain boundaries and the energy of the microdistortions. These two energy terms together constitute an effective increment in the surface energy of the habit faces of the plate:

$$\Delta\Gamma_0 = \sqrt{8e_s \gamma H}. \quad (4.7)$$

The thermodynamic potential Φ can then be represented in the form

$$\Phi = (\mu_{12} - \mu_0) \alpha_v H L^2 + (\Gamma + \Delta\Gamma_0) \alpha_s L^2 + e_L \alpha_L H^2 L, \quad (4.8)$$

where $\mu_{12} = (1 - \alpha)(f_1^0 - \hat{\epsilon}_1^0 \cdot \hat{\sigma}^C) + \alpha(f_2^0 - \hat{\epsilon}_2^0 \cdot \hat{\sigma}^C)$

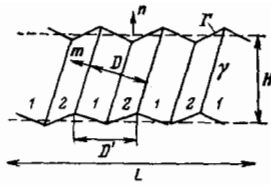


FIG. 11. Structure of plane-parallel domains.

+ $\alpha(1 - \alpha)e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{m}) + e(\hat{\epsilon}^0, \mathbf{n})$ is the specific thermodynamic potential of the polysynthetic phase (1; 2) composed of domains of phases 1 and 2 and forming a layer with normal \mathbf{n} inside the initial phase. For a crystal of sufficiently large volume, we can assume that the composition and orientation of the interphase boundaries is determined by the first term in (4.8), while the second and third terms determine the linear dimensions of the structure—the equilibrium thickness H_0 and, consequently, by (4.6), D_0 . (Note added in proof: The condition $\partial\Phi/\partial\alpha = 0$ for $\alpha = 0$ determines the boundary separating the regions of stability of the single- and many-domain plates in the H, L plane; for small dimensions of the plate, a single-domain state is the more stable.) It is not difficult to see that the condition for the volume energy of the polysynthetic phase to be a minimum with respect to variation of the domain composition ($\partial\mu_{12}/\partial\alpha = 0$) is equivalent to equating the configurational force at the interdomain boundaries to zero:

$$\mu_1 = f_1^0 - \hat{e}_1^0 \cdot \hat{\sigma} = f_2^0 - \hat{e}_2^0 \cdot \hat{\sigma} = \mu_2, \quad (4.9)$$

where $\hat{\sigma} = (\hat{\sigma}_1 + \hat{\sigma}_2)/2 = \bar{\sigma} + \hat{\sigma}_m + \hat{\sigma}^C$ is the stress at the interdomain boundary due to the interaction with the initial phase ($\bar{\sigma}$), the action of the interdomain boundaries (other than the one being considered) ($\hat{\sigma}_m$), and the external stress ($\hat{\sigma}^C$); $\hat{\sigma}_1$ and $\hat{\sigma}_2$ are the stresses in phases 1 and 2. Stable equilibrium of phases 1 and 2 at the interdomain boundary corresponds to that orientation \mathbf{m}_0 of the boundary which ensures that μ_{12} is a minimum, i.e.,

$$\frac{\partial\mu_{12}}{\partial\mathbf{m}} = \frac{\partial e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{m})}{\partial\mathbf{m}} = 0 \text{ for } \mathbf{m} = \mathbf{m}_0. \quad (4.10)$$

The fact that the configurational force at a plane face of the many-domain plate equals zero or that the thermodynamic potentials of the initial and polysynthetic phases are equal

$$\mu_{12} = \mu_0 \quad (4.11)$$

corresponds to equilibrium of these phases that is stable for \mathbf{n}_0 such that

$$\frac{\partial\mu_{12}}{\partial\mathbf{n}} = \frac{\partial e(\hat{\epsilon}^0, \mathbf{n})}{\partial\mathbf{n}} = 0. \quad (4.12)$$

The system of equations (4.9)–(4.12) defines the point of equilibrium between phases 1 and 2 and between the initial phase and the polysynthetic phase (1; 2). It is pointless to consider the equilibrium of each of the homogeneous phases 1 and 2 with the initial phase, since the effective width of the interphase boundary between the many-domain region and the initial phase is commensurable with the thickness D of the domains. The many-domain composite structure on the plane boundary with the initial phase can be regarded as one polysynthetic phase, since it is stable, or at least metastable, with respect to separate development and formation of a "comb" of the more stable component. (This is easily shown by means of an estimate similar to (4.4).) A measure of the absolute stability is provided by the difference in the energies of the many-domain phase and the final product of separation—a packet of parallel

plates of the stable phase, considered in the next section. Local equilibrium at the surface of the many-domain plate is attained as a result of fine adjustment of the microscopic (over scales $\sim D$) configuration of this surface, which on average is parallel to the plane \mathbf{n}_0 . The thermodynamic variables describing a system of the three phases (0, 1 and 2) are $T, \hat{\sigma}^C, \alpha, \mathbf{m}$, and \mathbf{n} . Solution of the system of four equations (4.9)–(4.12) gives $\alpha_0, \mathbf{m}_0, \mathbf{n}_0$ and the temperature $T_{0 \rightarrow (1; 2)}$ at which the transformation of the initial phase into the many-domain phase becomes thermodynamically possible, as functions of the external stress. As we move along the line $T_{0 \rightarrow (1; 2)}(\hat{\sigma}^C)$, the domain composition of the equilibrium polysynthetic phase and the orientation \mathbf{n} of the plate change; the orientation of the domain boundaries, according to (4.10), does not change. A monovariant equilibrium of the three phases with two external parameters is possible because of the presence of the additional (as compared with a system of noninteracting phases) internal parameter α —the ratio of the volumes of the phases forming the polysynthetic phase.

Apart from the simplest many-domain structure considered, which is formed of domains of two types, polysynthetic crystals composed of domains of three or more forms can exist. The introduction of an additional type of domain leads to an increase, by one, of the number of thermodynamic parameters of the polysynthetic phase—the additional parameter is the relative fraction of the new domains. The number of variants of the equilibrium of the many-domain structure is not changed if the number of equations of the type (4.9) and (4.11) expressing the fact that the configurational forces at the interphase boundaries are equal to zero is also increased by one, i.e., if each new domain leads to the appearance of only one new interdomain boundary (the type of the boundary is determined by its orientation and by the contiguous phases). For this, it is necessary that a domain of phase 3 be a plane-parallel layer inside a domain of phase 1 or 2. Since the new 3–1 (or 3–2) boundary need not necessarily be parallel to the 1–2 boundary (the orientation of \mathbf{m}_{13} is determined by the condition $\partial e(\hat{\epsilon}_3^0 - \hat{\epsilon}_1^0, \mathbf{m})/\partial\mathbf{m} = 0$), in the general case (for $D \cot(\mathbf{m}_{12}, \mathbf{m}_{13}) \ll H$) the new boundary intersects the old and the introduction of a third type of domain into the structure should be accompanied by a transition to a second-order domain structure in which the role of the domains is played by the polysynthetic plates of domains of two types that were considered above. A polysynthetic phase of three types of domain should have one of the two structures shown in Fig. 12. In the first case (Fig. 12a), as compared with a two-domain structure an additional degree of freedom appears—the volume fraction of the domains 3 and the extra boundary between phase 3 and the polysynthetic phase (1; 2); in the second case (Fig. 12b), two additional degrees of freedom appear—the volume fraction of the domains 3 in the "phase"

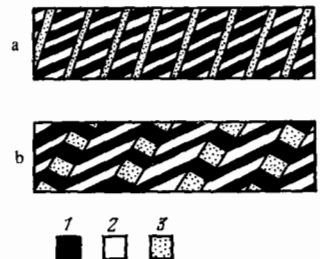


FIG. 12. Second-order domain structures.

(1; 3) and the fraction of domains (1; 3) in the whole many-domain structure ((1; 3)(1; 2)). Correspondingly, two new types of boundary appear, between domains 1 and 3 and between the polysynthetic domains (1; 2) and (1; 3). The orientations of the additional boundaries are determined by equations of the type (4.10), (4.12), the number of which coincides with the number of characteristics \mathbf{m}_{13} , $\mathbf{m}_{12,13}$, etc., being sought. A polysynthetic phase formed from four phases should have either a structure of the second-order type ((1; 2)(3; 4)) considered above, or a structure of the third-order type $\{((1; 1)(1; 3))(1; 4)\}$, etc. The domain hierarchy becomes more complicated as the number of phases increases, but this does not exclude the possibility in principle that any number of stable or virtual phases are in equilibrium; a polysynthetic phase formed from domains of $2n - 1$ homogeneous phases has an n -th-order structure, and one formed from $2n$ phases has either an n -th or an $(n + 1)$ -th-order structure. The physical stimulus tending to make the structure more complicated lies in the decrease in the elastic energy of the macrofields and microdistortions at the interphase boundaries. Since the dimensions of the structure are limited, the formation of domains inevitably leads to an increase in the number of domain boundaries per unit volume; this determines the optimal order of the domain hierarchy. In particular, for many-domain structures formed from two phases the formation of structures of higher order should be unfavorable, while for many-phase composite structures the formation of structures of a higher order than is required by the "phase rule" formulated above is also unfavorable. That many-domain structure which has the minimum energy will be realized. Thus, the transformation of a crystal into a polysynthetic phase may turn out to be thermodynamically more favorable than the single-domain formation of stable (in the isolated form) phases. This is of fundamental importance not only for the study of phase transformations but also for the interpretation of real phase-equilibrium diagrams of a solid.

Different phases, both stable and metastable, may emerge in the role of domains. In one-component systems or, in particular, in diffusionless transformations in many-component systems, domains of virtual phases can arise if the potential of the system containing these phases is lower than the potential of the system containing single- or many-domain formations of stable phase^[31]. Here it is not necessary that all the phases appearing be more stable than the initial phase (in (4.5), $\Delta\mu_2^0$ can be less than zero, if $\Delta\mu_1^0 > 0$). As an example of the formation of a structure with participation of a virtual phase, we can point to the formation of the "duplex structure" formed in the "massive" transformations in alloys of copper^[32]. In a diffusionless transformation of the high-temperature bcc phase, what is formed is not the stable (according to the equilibrium diagram) hcp phase but a double layer structure consisting of alternating layers of hcp and fcc phases. In this case, the virtual fcc phase is stable in another region of the equilibrium diagram, but, clearly, in heterophase structures phases can be present which are not realized at all in the isolated state.

In those cases when one phase is formed in the transformation, domains with different characteristic deformations arise, because of the point or translational symmetry of the crystalline phases^[29]. For example, in the case (3.11) of the transformation of a cubic phase into a tetragonal one, with formation of a new phase of domains

of two types, e.g., $\hat{\epsilon}_1^0$ and $\hat{\epsilon}_2^0$, the discontinuity in the deformation between neighboring domains is the invariant-plane deformation (3.3):

$$\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0 = \begin{pmatrix} \delta - \eta & 0 & 0 \\ 0 & \eta - \delta & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2} (s \circ \mathbf{m} + \mathbf{m} \circ s), \quad (4.13)$$

$$\mathbf{m}_{1,2} = \sqrt{1/2} \mathbf{i} \pm \sqrt{1/2} \mathbf{j}, \quad \mathbf{s}_{1,2} = s \mathbf{m}_{2,1}, \quad s = 2(\delta - \eta).$$

If the domains are contiguous over the plane \mathbf{m} , i.e., $(110)_{\text{cub}}$ or $(\bar{1}\bar{1}0)_{\text{cub}}$, no stresses arise in their contact. The planes of the interdomain boundaries in this case are coherent twinning planes, the discontinuity $\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0$ in the deformations is equal to the twinning displacement, and the many-domain phase is a polysynthetic twin (Fig. 13).

Under the condition that the principal values of the tetragonal deformation (3.11) have opposite signs and the magnitude of the principal value along the tetragonal axis is the greater of the two, i.e., $\eta(\eta + \delta) < 0$, the average characteristic deformation for a given domain composition α_0 satisfies Eq. (4.2), i.e., is an invariant-plane deformation, e.g.,

$$\hat{\epsilon}_{12}^0 = (1 - \alpha_0) \hat{\epsilon}_1^0 + \alpha_0 \hat{\epsilon}_2^0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \eta + \delta & 0 \\ 0 & 0 & \eta \end{pmatrix} = \frac{1}{2} (s \circ \mathbf{n} + \mathbf{n} \circ s) \quad \text{for } \alpha_0 = \frac{\delta}{\delta - \eta}, \quad (4.14)$$

where $\mathbf{n}_{1,2} = \sqrt{(\eta + \delta)/(-\delta)} \mathbf{j} + \sqrt{\eta/(-\delta)} \mathbf{k}$, $\mathbf{s}_{1,2} = s \mathbf{n}_{2,1}$, and $s = -\delta$. Combined in pairs, the domains $\hat{\epsilon}_i^0$ (3.11) (the index i shows the direction of the tetragonal axis) give six variants of the invariant-plane deformation, each of which corresponds to two polysynthetic crystals, with normals \mathbf{n}_1 and \mathbf{n}_2 . The scheme shown in Fig. 14 indicates the macrodeformations $\hat{\epsilon}_{ik}^0$ ($i \neq k$, $i, k = 1, 2, 3$) of the polysynthetic crystals, where the indices i and k indicate the domains from which the crystal is composed, the first being the index of the domain of the greater relative proportion. (We note that the first index coincides with the position of the deformation ϵ'' (ϵ_2) and the second with the position of the zero.)

The formation of a many-domain plate with normal \mathbf{n} (4.14) does not lead to the appearance of a macrofield inside the plate, except for an edge field equivalent to the field of an enclinging dislocation with Burgers vector $s\mathbf{H}$. For $\Delta\mu_1^0 = \Delta\mu_2^0 = \Delta\mu^0$, i.e., for $\hat{\sigma}^C = 0$ or $\hat{\epsilon}_1^0 \cdot \hat{\sigma}^C = \hat{\epsilon}_2^0 \cdot \hat{\sigma}^C$, such a plate is the equilibrium shape and its formation is accompanied by a change of thermodynamic potential equal to

$$\Phi = -\Delta\mu^0 \alpha_V L^2 H + (\Gamma + \Delta\Gamma_0) \alpha_S L^2 + e_L(s) H^2 \alpha_L L. \quad (4.15)$$

The linear dimensions H_0 and D_0 are determined by the relations (3.6), (4.6).

A similar type of breakdown into domains, leading in the absence of external fields to the formation of an undistorted new phase in the form of a polysynthetic twin, is highly characteristic for many martensitic^[33,34] and nonmartensitic^[35,36] transformations: ordering^[37], including antiferromagnetic ordering^[38], formation of interstitial phases^[39], Jahn-Teller transitions^[40], etc. The absence of uniform macroscopic elastic fields in the phase being formed enables us to reduce the problem of determining the equilibrium domain composition and the orientation of the interdomain boundaries and habit faces of a many-domain plate to the purely geometrical problem of finding the invariant planes. The solution of this geometrical problem does not depend on the elastic properties of the phases and can be obtained even if we

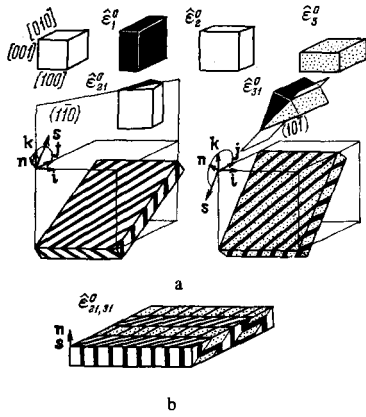


FIG. 13. Many-domain plates composed of domains with tetragonal deformation. (a) First-order domain structure formed by domains 1 and 2, and 1 and 3; (b) second-order domain structure formed by domains 1, 2 and 3.

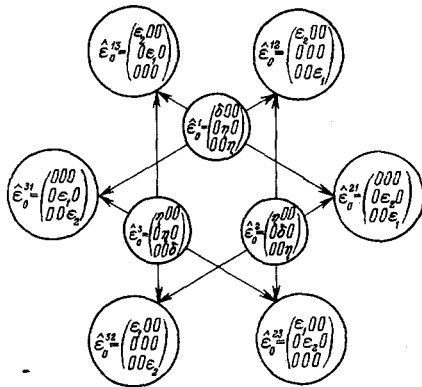


FIG. 14. Possible forms of polysynthetic crystals in a cubic-tetragonal transformation. The microdeformations of the domains are written in the small circles, and the macrodeformations of the crystals in the large circles. The lengths of the arrows are inversely proportional to the fraction of domain of the given form.

do not invoke the assumption that the characteristic deformations are small. Thus, if the tetragonal deformation (3.11) describes the fcc-bcc transformation (1.3), we can find the equilibrium structure. From these standpoints the crystallographic aspects of martensitic transformations based on iron^[3, 45] have been studied in detail.

The number of possible many-domain structures is substantially increased because of the fact that the characteristic deformations in the domains can differ by a translational displacement, i.e., domains can arise for which

$$\hat{\epsilon}^0 = \hat{\epsilon}_i^0 + \hat{g}, \quad (4.16)$$

where $\hat{\epsilon}_i^0$ ($i = 1, 2, 3$) are the minimum characteristic deformations (3.11), and $\hat{g} = \mathbf{gmp}$ is the translational displacement (\mathbf{g} , \mathbf{p} and \mathbf{m} are the magnitude, direction and plane of the displacement). In certain cases confirmation of the presence of such translational domains has been obtained^[42]. If the domains differ only by a displacement they degenerate into glide planes, and the phase being formed has a monocrystalline structure^[2].

The tendency of the thermodynamic potential (4.15) to be lowered on account of the decrease in the energy of the edge field ($e_L \sim Gs^2$) can lead to the formation of a second-order structure from the domains (3.11). For

example, a combination of a polysynthetic "phase" (1; 2) with a polysynthetic "phase" (1; 3) having the average deformation

$$\hat{\epsilon}_{12}^0 = (1-\alpha)\hat{\epsilon}_1^0 + \alpha\hat{\epsilon}_3^0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \eta & 0 \\ 0 & 0 & \eta + \delta \end{pmatrix}, \quad \alpha = \frac{\delta}{\delta - \eta}, \quad (4.17)$$

gives crystals with a second-order domain structure, in which the characteristic macrodeformation equals

$$\hat{\epsilon}_{12,13}^0 = (1-\alpha)\hat{\epsilon}_{13}^0 + \alpha\hat{\epsilon}_{12}^0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2\eta + \delta \end{pmatrix} \quad (4.18)$$

$$= \frac{1}{2}(s \cdot \mathbf{n} + \mathbf{n} \cdot s) \text{ for } \alpha = -\frac{\eta}{\delta},$$

where $\mathbf{n} = \mathbf{k}$, $\mathbf{s} = \mathbf{sk}$, and $s = 2\eta + \delta$.

The second-order domains are contiguous over the bisector planes between the axes j and k (Fig. 13b). An example of such a structure, arising in ordering, is shown in Fig. 15a. The magnitude of the macrodisplacement vector \mathbf{s} directed along the normal to the plate is equal to the volume effect $\Delta v/v$ in the transformation, and the energy of the edge field is correspondingly lower than for two-domain plates and equals zero if the transformation is not accompanied by a volume change^[3]. The formation of a many-domain plate whose characteristic deformation is a uniaxial expansion or contraction along the normal to the plate (equal to the volume effect of the transformation) corresponds to the maximum possible decrease of the edge energy as a result of breakdown into domains. Therefore, for transformations with a significant volume effect, subdivision into domains with formation of higher-order structures is relatively ineffective.

In the above investigation of equilibrium many-domain structures it was not taken into account that the characteristic deformations and free energies can be variable quantities even under constant external conditions (T , $\hat{\sigma}^C$, and also L_0). Therefore, in analyzing nonmartensitic transformations it is necessary to supplement the above treatment by allowance for the dependence of these

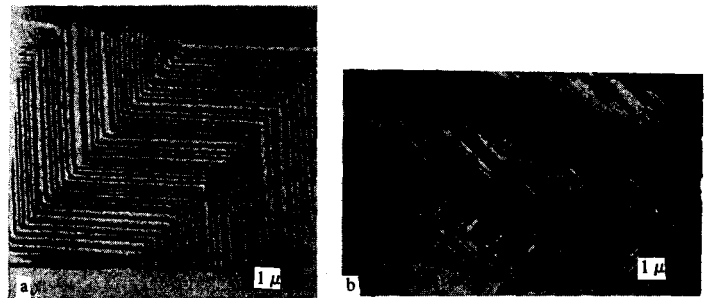


FIG. 15. Higher-order domain structures arising in ordering in the alloy Cu-Al^[37] (a), in a martensitic transformation in Cu-Al (b), and in the transformation of the tetragonal structure into a monoclinic structure in NbTe₂^[43] (the microdistortions at the boundaries of the domains are visible) (c).

phase characteristics on the order and composition parameters. In particular, in ordering with the formation of two phases (which, in particular, may differ only in their orientation), the supplementary conditions (2.6)–(2.7) must be fulfilled, and these, together with Eqs. (4.9)–(4.12), determine the equilibrium degrees of order in the phase 1 and phase 2 forming the polysynthetic phase that is in equilibrium with the given initial phase. We note that, in this case, the orientation \mathbf{m} of the domain boundaries can turn out to depend on the position on the equilibrium line $T_0(\bar{c}^C)$.

In transformations in many-component systems, regions of stable phases may serve as domains. The case, often encountered in practice in metallography, of a domain structure arising in the breakdown of a cubic solid solution into two isomorphous solutions was treated in [44]. It was assumed that the characteristic deformations are associated only with change in the composition, with $\hat{\epsilon}_i^0 = w\hat{1}(c_0 - c_i)$, $i = 1, 2, 3$, i.e., a linear relation between the concentration changes and the lattice parameters (the Vegard rule) is fulfilled. It was also assumed that the average concentration in the region that has broken down is equal to the initial concentration ($\bar{c} = c_0$) (accordingly, $\bar{\epsilon}^0 = 0$), and that, as in the case treated above of formation of a three-domain phase with zero volume effect, the stimulus for the many-domain region to have a plate-like shape disappears. The crystallographic orientations of the faces of the many-domain region that has broken down coincide with those of the interdomain boundaries and are determined by the minimum of the expression $\hat{1} \cdot \hat{G}^*(\mathbf{n}) \cdot \hat{1}$ and do not depend on the composition of the phases.

As an interesting case of breakdown into virtual phases, we can point to the stratification of the solution that is formed in a solid when the concentration dependence of the characteristic deformation of the solution is not described by the Vegard rule. If the concentration of the solution separating out is close to that at which the volume effect is extremal, stratification of the solution into domains with concentrations greater and less than the initial concentration can lead to a decrease of the total volume effect and, consequently, to a decrease of the elastic interaction with the initial phase. Under the condition that this lowering of the elastic energy exceeds the increase in the self energy of the inhomogeneous phase, this stratification into concentration domains will be thermodynamically favorable. Another case of possible realization of virtual phases in a many-component system is the formation of ordered phases in a region in which the disordered phase is stable in the isolated state (i.e., above the Curie temperature). Since ordering leads to lowering of the symmetry, when the ordered instead of the disordered phase is formed there arises the additional possibility of reducing the elastic energy by breakdown of the ordered phase into domains.

It is obvious that a combination of the possible ways in which domains can be formed in one-component systems with the ways that can be realized by redistribution of components should lead to a large variety of domain structures in heterophase many-component systems^[44].

5. ELASTIC INTERACTION OF CRYSTALS AND FORMATION OF ENSEMBLES OF PLATE-LIKE CRYSTALS

There exists another way of decreasing the stress fields in the matrix of the initial phase besides making the internal structure of the regions of new phase being

formed more complicated, namely, by combining these regions into groups or colonies. The long-range field of a crystal can be reduced on account of interference with the fields of other crystals, and this possibility is realized in the formation of ensembles of regularly distributed crystals of the new phase inside the initial phase. In order to determine which systems of crystals are energetically optimal, it is necessary to calculate the energy of the stresses for crystals of arbitrary shape, arbitrarily distributed in space, and then minimize the free energy of the system with respect to the shape and internal structure of each crystal and with respect to the mutual arrangement of the crystals. The problem formulated is extremely complicated, but it is possible to obtain an approximate solution of it that is sufficiently effective to describe real cases, if we neglect the influence of the interaction of the crystals on the equilibrium shape and structure of each crystal, i.e., if we disregard the perturbation induced in the structure of the given crystal by the elastic fields of the other crystals. This perturbation is small if the crystals are thin, i.e., if $H/L \ll 1$. Then, energetically favorable systems can be "built" from the many-domain plates described in the preceding section, which are the optimal "bricks" for constructing a heterophase structure.

The procedure for determining the structure of the optimal groups formally reduces to the problem, considered in Sec. 4, of the equilibrium structure of a many-domain plate, if we regard the whole group as a "super-crystal" inside the initial phase, the role of the domains in the initial phase being played by plates of the new phase and regions of the initial phase. If the crystals are arranged in an ordered manner, so that the average characteristic deformation of a group, $\bar{\epsilon}^0 = \sum_i \beta_i \hat{\epsilon}_i^0$

(β_i and $\hat{\epsilon}_i^0$ are the volume fractions and characteristic macrodeformations of the crystals belonging to the group), is uniform, the fields of the crystals cancel to the maximum extent if the group has a planar shape with the normal determined by a relation analogous to (4.2). In the absence of incompatibility of the characteristic deformations on the interphase surfaces, the structure of the optimal groups is determined entirely by the geometrical requirement

$$N \times \sum_i \beta_i \hat{\epsilon}_i^0 \times N = 0, \text{ or } \sum_i \beta_i \hat{\epsilon}_i^0 = \frac{1}{2}(SN + NS), \quad (5.1)$$

from which there follows the relationship of the volumes of the crystals belonging to the group, their relative thickness and length, and also, for a given maximum size of the group, the absolute dimensions of its structural components.

As an illustration, we shall consider the possible optimal groups of crystals in the transformation of a cubic phase into a tetragonal one (3.11)^[46]. Crystals with the deformation $\hat{\epsilon}_{ik}^0$ (cf. the scheme in Fig. 14) can form groups satisfying Eq. (5.1) with crystals whose characteristic deformation $\hat{\epsilon}_{mn}^0$ is not linked to $\hat{\epsilon}_{ik}^0$ in the scheme, i.e., one of the types of domain should be different in the crystals combining into the group, and the common type of domain should not be simultaneously preponderant in both crystals. For example, polysynthetic crystals with the macrodeformation $\hat{\epsilon}_{ik}^0 = \hat{\epsilon}_{23}^0$ in combination with crystals with macrodeformation $\hat{\epsilon}_{mn}^0 = \hat{\epsilon}_{31}^0, \hat{\epsilon}_{12}^0, \hat{\epsilon}_{13}^0$ form truss-like groups (Fig. 16a). The field produced by the vertex of the dihedral angle at which neighboring crystals come together is equivalent to the field of a dislocation with Burgers vector $\mathbf{B} = s\mathbf{H} + s'\mathbf{H}'$, lying along this vertex. If $\mathbf{B}^2 < (s\mathbf{H})^2 + (s'\mathbf{H}')^2$,

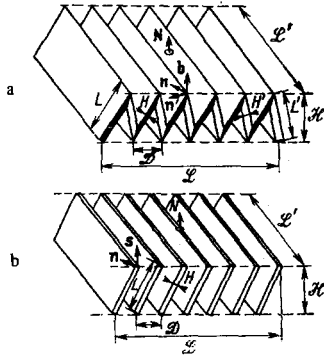


FIG. 16. Energetically favorable groups of polysynthetic crystals in a tetragonal deformation.

the energy of the resultant field of the combination of the two crystals is less than the sum of the energies of the edge fields of each crystal, and a combination of this type is energetically favorable. A pairwise combination of the same types of crystal with formation of either an acute or an obtuse dihedral angle between the habit planes will be favored, depending on the relative orientation of \mathbf{s} and \mathbf{s}' .

Besides the above-mentioned short-range order effect in the arrangement of the crystals, a long-range order effect occurs in the groups considered. Interference of the fields of the pair combinations forming the surface of the group leads to the cancellation of these fields at a distance of order Q from this surface: $\mathbf{B} \parallel \mathbf{N}$, and the field of the group is equivalent to the field of two parallel vertical walls of edge dislocations. A long-range order effect is clearly also realized in the formation of a packet of parallel identical plates, arranged in such a way that their edges perpendicular to \mathbf{s} lie in one plane, with normal $\mathbf{N} = \mathbf{s}/s$ (Fig. 16b)¹⁵.

For the cubic-tetragonal transformation, the four cases considered encompass all the possible groups, formed from crystals of one or two orientations, that obey Eq. (5.1). Groups of such types are a characteristic element of the structures arising in different phase transformations in the solid state. The "truss-like" groups are a typical morphological feature of martensitic transformations in a number of alloys based on iron and nonferrous metals. Systems of parallel crystals are especially characteristic for the so-called massive transformations^[47], and also for the structure of an isothermal martensitic transformation^[48]. Analogous groups are observed in ordering, ferroelectric transitions, etc.

The stability of a group, and also the probability of its formation, are determined by the difference between the stress energy per crystal in the group and the energy of the field of the isolated crystal. The elastic energy of each of the groups considered is made up of the energy of the short-range stresses, concentrated in a layer $\sim Q$ at the surface of the group, and the energy of the long-range field of the group. In estimating the relative energetic favorability of one group or another, it is necessary to take into account that the dimensions of the group, i.e., primarily, the greater of Q and Q' , are limited by the grain sizes in the polycrystal, the distance between the crystals that have been formed earlier, defects, etc. This circumstance imposes certain limitations on the optimal compactness of the groups. For example, the change in the free energy on formation of a group from crystals of one form (see Fig. 16b) equals (to within numerical and logarithmic factors)

$$\Phi \approx -\Delta\mu^0 L H \mathcal{L}' p + G (sH)^2 \mathcal{L}' p + \Gamma L \mathcal{L}' p + G (sH)^2 p^2 \left(\frac{L}{\mathcal{L}}\right)^2 (\mathcal{L} + \mathcal{L}'), \quad (5.2)$$

where Γ is the surface energy of the plane faces of the crystals, and $p = Q/Q'$ is the number of crystals in the group. It follows from (5.2) that, for given dimensions (L, L') of the crystals and length L of the group, there are a definite number of crystals

$$p_0 = \frac{1}{2} \left(\frac{\Delta\mu^0}{\sqrt{\Gamma G s^2}} \sqrt{L} - 1 \right) \left(\frac{\mathcal{L}}{L} \right)^2 \frac{\mathcal{L}'}{\mathcal{L} + \mathcal{L}'} \quad (5.3)$$

and crystal thickness $H_0 = \sqrt{(\Gamma/Gs^2)L}$ corresponding to the minimum of Φ . If p is constant, the energy has a minimum corresponding to certain values L_0 and H_0 ; an increase in the quantity of the new phase on account of the growth of each crystal leads to an increase in the free energy of the system. The thickening of each crystal leads to an increase in the space factor of the "supercrystal," and elongation leads to an increase of its thickness; both these effects are associated with an increase of the energy of the long-range peripheral field of the "supercrystal," which, in competition with the volume decrease of free energy that accompanies the formation of the stable phases, leads to the establishment of thermoelastic equilibrium of the "supercrystal": the equilibrium of the structure of the group as a whole and of each crystal belonging to the group depends on the deviation from the phase-equilibrium point. The limiting size for an individual crystal is determined by the elastic interaction of the crystals in the group. This state may be metastable compared with an equilibrium continuous crystal with dimensions equal to the maximum length of the group. However, the relative stability of these states can vary as a function of the quantity $\Delta\mu^0$, and the transition from one state to the other is associated with a considerable energy barrier. Thermoelastic equilibrium of systems of parallel crystals has been repeatedly observed experimentally^[49] (Fig. 17). An analogous thermoelastic equilibrium should also occur for other groups.

The above treatment can be generalized to the case when the incompatibility at the interphase boundaries is not equal to zero. In particular, putting $\hat{\epsilon}_1^0 = 0$, $\hat{\epsilon}_2 = \hat{\epsilon}^0$, $\mathbf{m} \rightarrow \mathbf{n}$ and $\mathbf{n} \rightarrow \mathbf{N}$ in (4.5), we obtain the expression

$$\Phi = [-\alpha \Delta\mu^0 + \alpha(1-\alpha)e(\hat{\epsilon}^0, \mathbf{n}) + \alpha^2 e(\hat{\epsilon}^0, \mathbf{N})] \mathcal{H} \mathcal{L} \mathcal{L}' + [\alpha \Gamma_1 + (8\alpha^2(1-\alpha)^2 e_s \Gamma \mathcal{H})^{1/2}] \mathcal{L} \mathcal{L}' + \alpha^2 e_L(\hat{\epsilon}^0) \mathcal{H}^2 (\mathcal{L} + \mathcal{L}'), \quad (5.4)$$

which describes the potential of a planar packet of parallel crystals of the new phase (see Fig. 15b). Since $e(\hat{\epsilon}^0, \mathbf{n}) = \min e(\hat{\epsilon}^0) \equiv e_0$, two cases are possible:

a) $\Delta e = e(\hat{\epsilon}^0, \mathbf{N}) - e(\hat{\epsilon}^0, \mathbf{n}) > 0$. In this case, even for arbitrarily large \mathcal{H} and \mathcal{L} , if $\mathcal{H}/\mathcal{L} \ll 1$ and the packet is surrounded by the matrix, the minimum of the thermodynamic potential corresponds to $\alpha = (\Delta\mu^0 - e_0)/\Delta e$. For

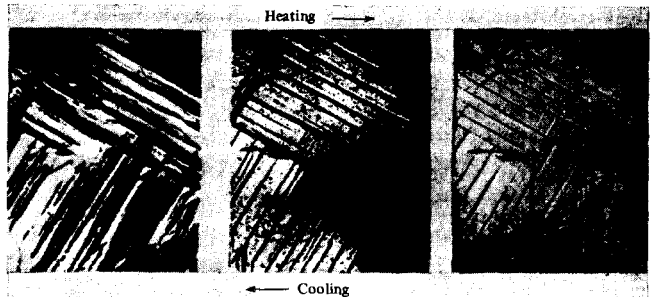


FIG. 17. Reversible change of the sizes of the crystals in heating and cooling in the alloy Cu-Al-Mn^[49].

$e_0 < \Delta\mu^0 < e_0 + \Delta e$, the stable state is a two-phase state in which the amount of the new phase (α) increases in proportion to the deviation from the point of equilibrium of the coherent phases ($\Delta\mu^0 = e_0$). With decreasing \mathcal{H} and \mathcal{L} , the two-phase region, like the hysteresis of the transformation, is displaced toward larger deviations from equilibrium.

b) $\Delta e = 0$. This case is possible if, by virtue of the symmetry of the crystal and of the tensor $\hat{\epsilon}^0$, there are several planes n ensuring a minimum of $e(\hat{\epsilon}^0, n)$. Then, if the conditions of the formation of the structure permit variation of the plane \mathbf{N} , the packet of crystals occupies a position corresponding to the minimum interaction energy between the packet and the surrounding matrix. Then $e(\hat{\epsilon}^0, \mathbf{N}) = e_0$, and the minimum energy of the edge field of the packet as a whole (the last term in (5.5)) is attained as a result of variation of the amount α of the new phase. In fact, minimizing Φ with respect to α , we obtain

$$\alpha_0 \approx \frac{1}{2} \frac{[(\Delta\mu^0 - e_0)/e_L] - \sqrt{\mathcal{H}_0/\mathcal{L}}}{\sqrt{\mathcal{H}_0/\mathcal{L}} - (\mathcal{H}/\mathcal{L})}, \quad (5.3)$$

where $\mathcal{H}_0 \equiv 8e_S\Gamma/e_L^2$. For a given magnitude of \mathcal{H} , i.e., a given length of the crystals making up the packet, if $(\mathcal{H}_0/\mathcal{L})^{1/2} < (\Delta\mu^0 - e_0)/e_L < 2\mathcal{H}/\mathcal{L} - (\mathcal{H}_0/\mathcal{L})^{1/2}$, α_0 increases from zero to 1 with increase of $\Delta\mu^0$. For $\mathcal{H} \gg \mathcal{H}_0$, the presence of the initial phase in the many-domain region is favored ($\alpha_0 < 1$) when $(\Delta\mu^0 - e_0)/e_L < 2\mathcal{H}/\mathcal{L}$, i.e., under the condition that the width \mathcal{H} of the region is greater than the equilibrium thickness of a single-domain crystal of length \mathcal{L} for the same deviation $\Delta\mu^0$ from phase equilibrium. Corresponding to the change of α_0 , there is a change of the period \mathcal{L} , or of the equilibrium number and thickness of the crystals. For $(\Delta\mu^0 - e_0)/e_L > 2\mathcal{H}/\mathcal{L}$, the crystals coalesce into one crystal. More complicated ensembles of crystals or polysynthetic plates of crystals can be treated in an analogous way.

It should be emphasized that the equilibrium ensembles and the internal domain structure of an individual crystal are obtained as solutions of the same variational problem on the optimal structure arising as a result of a transformation in a bounded region of the initial phase, enclosed in an elastic matrix. Here, structures that are formed in regions having the shape of a parallelepiped with a small ratio of the thickness to the other linear dimensions correspond to the minimum free energy. The internal structure of this region depends on its dimensions and orientation. If the thickness of this region is less than a certain limiting thickness ($H_{\text{lim}} \sim \gamma/e_0$), the breakdown of the region into domains in the transformation is energetically unfavorable. Conversely, with increase of the relative thickness of the region (for $H/L > \sim e_0/e_L$), the presence of the initial phase in the equilibrium structure becomes favorable, i.e., an ensemble, or colony, of crystals corresponds to a metastable state. It is obvious that the crystals in an ensemble retain their individuality—in particular, the characteristic equilibrium shape for an individual crystal, if their interaction energy is small compared with their self energy. (Note added in proof: If the distance between the crystals is much greater than their sizes, they may be arranged at the sites of a regular space lattice. The "direct" elastic interaction between the crystals leads to the establishment of a two-phase equilibrium, and prevents their coalescence.) In the opposite case, which is realized when the distance between the crystals is sufficiently short, the crystals coalesce, being trans-

formed into domains of polysynthetic regions. If the ensembles are formed by polysynthetic plates, second-order domain structures are formed when these coalesce. For example, on coalescence, the second-order domain structure described by the expression (4.18) is formed from the group $(\hat{\epsilon}_{23}^0; \hat{\epsilon}_{13}^0)$.

The groups of crystals can serve, in their turn, as elements of higher-order structures. This should lead to the formation of a textured structure and, as a consequence, to anisotropy of the properties of the disperse systems that are formed in transformations in monocrystals or coarse-grained polycrystals. Experimental structural confirmation of such anisotropy has recently been obtained^[50].

6. CONCLUSION

Thus, as a result of the self-consistent development of the transformation, a hierarchy of structures of increasing scale (domains—polysynthetic regions—ensembles of regions) is formed in a certain region of the initial phase. The extent of the structural hierarchy and the scale of the structure are determined by the relationship of the elastic and surface effects, and also by the maximum linear dimensions of the system; specifying these, together with the thermodynamic characteristics of the phases and interphase surfaces, determines the equilibrium parameters of the structure in all stages of the structural hierarchy. The maximum linear parameters of the system are determined by the real structure of the initial phase or by the kinetic parameters of the transformation; on the relationship between the rates of nucleation and growth of the crystals depends the size of the region of self-consistent development of the transformation, which is limited by impact with crystals developing from independent neighboring centers. In principle, for each specific case it is possible to indicate the optimal combination of processes of differentiation of the structure (breakdown into domains) and integration of the structure (combination of crystals into groups) that ensures the minimum free energy of the heterophase system.

The appearance of many-phase metastable states characterized by a regular spatial arrangement of the phases is one of the noteworthy features of the formation of a heterophase structure in phase transformations in solids. Once again, the thermodynamic nature of the dispersity of the heterophase systems considered, which is associated with the tendency to reduce the elastic energy of the internal stresses, should be noted. The individual structural elements of the heterophase system can be interpreted as elastic domains, in complete analogy with magnetic or electric domains.

The presence of elastic domains is a factor that determines many of the physical properties of crystalline solids. This applies not only to properties which are traditionally regarded as structurally sensitive and which are due to processes of scattering of electrons, phonons, etc. at structural boundaries or due to the interaction of the latter with dislocations or with the boundaries of magnetic and electric phases (e.g., mechanical hardening, magnetic hardness, the hardness of type-II superconductors, etc.). In a finely dispersed system of elastically interacting phases, because of the relatively large specific volume of the interphase boundaries, and also because of the considerable elastic deformation of the phases, essentially all the physical

properties should differ appreciably from the additive sum of the properties of the isolated phases. This fact, like the possibility, considered in Sec. 4, of formation of domains of phases that do not exist in the isolated state, makes it possible to look forward to the creation of heterophase materials with qualitatively new and unexpected properties.

The theoretical analysis of the structure of heterophase systems is a necessary stage in the study of the physical properties of real crystalline materials. The ideas described enable us to treat a wide class of problems associated with structural transformations from unified standpoints, and to construct a quantitative theory of real structures. In the framework of this theory, for each specific transformation and for a given small number of initial parameters, the spatial distribution and deformation of the phases can be found, and the phase-equilibrium diagram in a real heterophase system, which is substantially different from the equilibrium diagram of the isolated phases, can also be calculated. From this point of view, it is necessary to carry out a systematic analysis of the existing experimental data.

Transformations accompanied by formation of electrically or magnetically ordered phases can evidently serve as a possible sphere of application of the theory. In certain cases (e.g., for large magnetostriction and small magnetization), the elastic energy of the internal stresses that arise from the incompatibility of the strictional deformations at the interphase boundaries may be comparable with the energy of the magnetic (or electric) fields, and may have an important influence on the character of the magnetic (electric) domain structure. In particular, the elastic energy can lead to the formation of an equilibrium domain structure in antiferromagnets or antiferroelectrics.

In considering the prospects for development of the theory, and its possible applications, we cannot fail to note a certain limitation of the theory. Lying at the basis of the effects considered are stress-relaxation processes resulting from redistribution of the characteristic deformations under the condition that the continuity of the crystal lattice is conserved¹⁰⁾. We have not taken into account the possibility of relaxation as a result of a change in the connectivity of the crystal due to the formation of fractures or to change in the number of dislocations and displacement of dislocations. In real cases, phase transformations, as a rule, are accompanied by creation (or destruction) and migration of defects, and the shaping of the structure is the result of the self-consistent development of two mutually connected subsystems of the heterophase system: the "phase" and "defect" subsystems. A systematic solution of this self-consistent problem, incorporating an analysis of the evolution of the dislocation structure, is hardly possible at the present time. Fortunately for the theory, the universal mechanism of plastic relaxation is quite frequently found to be unable to compete with specific relaxation mechanisms in the phase subsystem. First, for sufficiently dispersed systems, the energy of the incoherent fields of the microdistortions arising in the formation of new dislocations is greater than the energy of the microdistortions accompanying the formation of elastic domains (cf., e.g., the footnote¹²⁾, and also^[51]). Secondly, the dislocation mechanism of relaxation, being a secondary process relative to the development of the transformation, is less favorable kinetically than breakdown into domains. Moreover, the role of plastic relaxa-

tion can be important in the formation of the large-scale elements of the structural hierarchy, and also in the removal of stresses remaining in the domain structure. Evidently, in the future the theory should be supplemented by a study of the relation between plastic deformation and processes of dispersal of the structure. On the other hand, it is clear that the formation of elastic domains under certain conditions can serve as an effective mechanism of relaxation of stresses in a stable heterophase system, i.e., a system consisting of phases that are incapable of mutual transformation.

In conclusion, it is appropriate to characterize, if only in a few words, the place of the theory described in the total complex of the physical disciplines devoted to the study of real crystals. In its methodology, the theory of heterophase structures presented is a component part of the physical theory of internal stresses^[5,6]. In this connection, the central idea of the work on elastic domains can be regarded as being the development of a magnetostatic analogy for dislocation theory. On the other hand, the theory is based on the results of the study of structural transformations—primarily, those transformations in which the effects of internal stresses are manifested most prominently, namely, martensitic transitions and twinning. The study of these phenomena has long-standing fruitful traditions in our country, where considerable progress has been achieved in understanding the physical nature of martensitic transformations (the work of G. V. Kurdjumov and his school, S. S. Shteinberg, V. D. Sadovskiy, et al.) and twinning (the experimental investigations of I. V. Obreimov, R. I. Garber, V. I. Startsev, M. V. Klassen-Neklyudova, et al., and the theoretical work of I. M. Lifshitz, V. L. Indenbom, and A. M. Kosevich and co-workers).

It is a pleasure to end the article with deep thanks to G. V. Kurdjumov for his constant interest and support in the work, and to V. L. Indenbom for numerous useful discussions on fundamental points.

¹⁾In the case of martensitic transformations the matrix \hat{U}^0 connects not only the sites of the lattices but also the positions of the atoms themselves in the initial and final phases.

²⁾In the article we use an abbreviated notation for tensors and tensor operations: a is a vector, \hat{a} is a tensor of rank 2, $\hat{\hat{a}}$ is a tensor of rank 4, and $a \cdot b \leftrightarrow a_i b_i$; tensors standing side-by-side are contracted with respect to one inner index, and, if there is a dot between them, with respect to two (e.g., $\hat{\hat{a}} \cdot \hat{\hat{b}} \leftrightarrow a_{ijk} b_{kij}$, $a \cdot b \leftrightarrow a_{ijk} b_{kij}$; $\hat{a} \times b \leftrightarrow \epsilon_{ijk} a_k b_j$ (ϵ_{ijk} is the antisymmetric unit tensor).

³⁾The condition (1.6) is equivalent to the requirement that the full deformations on the phase boundaries are compatible ($n \times (\hat{\epsilon}_2 - \hat{\epsilon}_1 \times n = 0$), which is a particular case of the compatibility of the full deformations at all points of the crystal ($\nabla \times \hat{\epsilon} \times \nabla = 0$)^[5,6]. Accordingly, the surface incompatibility of the characteristic deformations, $\hat{\eta} \equiv n \times (\hat{\epsilon}_2 - \hat{\epsilon}_1) \times n$, is a source of internal stresses in a heterophase system.

⁴⁾The effective elastic modulus $\hat{G}(n) = (G_{iklm}^* \equiv G_{ijkl} n_j n_k)^{-1} \times n_\alpha G_{\alpha\beta\delta\gamma} \delta_{\alpha\beta} Q_{\delta\gamma} = \delta_{\alpha\beta}$ vanishes on contraction over any index with the vector n . Therefore, in $e = \hat{\epsilon} \cdot \hat{\sigma} / 2 = (\hat{\epsilon} - \hat{\epsilon}^0) \cdot \hat{\sigma} / 2 = (s \cdot n + \hat{\epsilon}^0) \cdot \hat{\sigma} / 2$, $(s \cdot n) \cdot \hat{\sigma} = 0$.

⁵⁾By a phase in this case we mean a singly-connected region of the solid, within which the internal parameters characterizing the phase vary in a continuous manner, and experience a discontinuity at the boundary.

⁶⁾For a microscopic crystal such a parameter exists: for a crystal size $R \sim \Gamma / \Delta \mu^0$, the configurational force is balanced by the surface-tension forces. This equilibrium is unstable and corresponds to the intermediate state through which a two-phase system passes in the process of nucleation of the new phase.

⁷⁾The thin-crystal approximation is effective if we are considering an interphase surface that is almost parallel to some plane (with normal n). It is assumed that this surface is composed of plane terraces, normal

to \mathbf{n} and separated by vertical steps. The length of each terrace is much greater than the height of a step. Furthermore, by analogy with the laminar growth of a crystal from the uncondensed phase [23], it is assumed that tangential displacement of the steps along the surface occurs more easily than normal displacement of the terraces. Then the condition for equilibrium of the interphase surface reduces to the condition for equilibrium of the steps. It is usually assumed that all the steps have monatomic height. In this case they can be interpreted as certain dislocations of the phase transformation [24]. If $\hat{\epsilon}^0 = \frac{1}{2}(s \cdot \mathbf{n} + \mathbf{n} \cdot s)$, the mechanical part of the configurational force $\hat{\epsilon}^0 \cdot \hat{\sigma} = s \hat{\sigma} \mathbf{n}$ acting on a step coincides with the component, normal to \mathbf{n} and to the step, of the force acting on a dislocation with Burgers vector s , in accordance with the usual Peach-Koehler definition [20, 25], and the steps of the dislocation are the only source of stress on the interphase surface. If we neglect variation in the heights of the steps, (3.1) goes over into the equation for the equilibrium of a thin crystal, and the problem of the equilibrium of twins ($s \perp \mathbf{n}$) [21] and fractures ($s \parallel \mathbf{n}$) [22] reduces to the problem of the equilibrium of a planar pile-up of dislocations (cf. [20] and p. 174 in the (second) Russian edition of [15]). In certain cases the steps can be identified with real defects of the crystal lattice. For example, in twinning in fcc crystals or in the fcc-hcp transformation, the twinning dislocations or transformation dislocations are Shockley partial dislocations. In the general case, however, the theoretical justification of the step structure of an interphase surface requires a microscopic analysis of the boundary.

⁸⁾We are led to an analogous conclusion about the plate-like equilibrium shape of a region of the new phase by studying the question of the optimal shape and orientation of a crystal when its volume is fixed. The corresponding problem was solved for the two-dimensional case [26], and then for the three-dimensional case [27]. The solution of the variational problem of the minimum elastic energy of a doubly-connected region with the supplementary condition indicated is an infinitesimally thin plate oriented along the plane of optimum union of the phases; the corresponding elastic energy is $e(\mathbf{n}_0)V$, where V is the volume of the new phase [27]. Allowance for the surface energy makes it possible to determine the dimensions of the plate, of which one is microscopic, $H \sim F/F$, and the other is determined by the total volume of the plate: $L \sim V/H^2$.

⁹⁾If the initial phase is characterized by a certain distribution $N(L_0)$ of defectless regions over a length L_0 , then in the initial stages of the transformation

$$\frac{V_2}{V_1} \approx \alpha_V H_0 L_0^3 \int_0^{L_0(\Delta\mu^0)} N(L_0) dL_0 / L_0^3 \int_0^0 N(L_0) dL_0.$$

¹⁰⁾In the thermodynamic potentials $\mu = f - \hat{\epsilon} \cdot \hat{\sigma}$ we have omitted the terms $\hat{\epsilon}^C \cdot \hat{\sigma}^C/2$, which are the same in all phases for phases with equal moduli.

¹¹⁾In accordance with the generalized Clapeyron-Clausius equation, $\delta f^0 = q \delta T/T^0 = -\hat{\epsilon}^0 \cdot \delta \hat{\sigma}^C$.

¹²⁾This degenerate case of translational domains is equivalent to a uniform plastic deformation, leading to violation of the coherence at the interphase boundary and to relaxation of the stresses. The study of the conditions under which a combination of a uniform slip or twinning with the characteristic deformation of the transformation gives a macrodeformation with an invariant plane is the subject of the phenomenological theory of martensitic transformations [33, 41]. We note that, despite the universality of slip as a mechanism of relaxation of stresses, it may turn out to be less energetically favorable than breakdown into domains, because of the large energy of the microdistortions. For example, comparing $\Delta\Gamma_0 \sim (G(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0)^2 \alpha^2 \gamma H)^{1/2}$ for twinning domains (i.e., when $e(\hat{\epsilon}_1^0 - \hat{\epsilon}_2^0, \mathbf{m}) = 0$) with the minimum energy of the microdistortions in slip ($\Delta\Gamma_0 \sim Gbg$) and taking into account that the macrodeformation is the same in both cases and corresponds to the minimum of the energy (4.1), i.e., $\hat{\epsilon}^0 = \hat{\epsilon}_1^0 + \alpha(\hat{\epsilon}_2^0 - \hat{\epsilon}_1^0) = \hat{\epsilon}_1^0 + \hat{g}$, we obtain the criterion for the transition from domain-twins to slip: $H > \sim Gb^2/\gamma$. This fact may provide one of the reasons for the observed two-zone structure of polysynthetic crystals: the central zone is formed by alternation of twins, and signs of slip are observed in the regions adjacent to the faces. The physical nature of this effect is analogous to the branching of ferromagnetic domains at a surface.

¹³⁾In this case, there is no macroscopic field and the optimal shape of the region of new phase is not necessarily a plate: the most favored shape is determined by the anisotropy of the effective interphase surface energy.

¹⁴⁾The domain structures described are quite frequently observed in natural minerals that have been formed as a result of phase transformations in the earth's crust (cf., e.g., [45]).

¹⁵⁾For the best cancellation of the stress fields, it is clearly necessary that $L' \gg L$, where L' is the length of the crystals along the joined edges (see Fig. 16a), i.e., that the crystals have the shape of "racks" along L' .

¹⁶⁾No fundamental difficulties are encountered when relaxation as a result of redistribution of vacancies is included in the treatment; if the number of vacancies in the system is conserved (the condition of unchanged continuity), they can be treated as an additional component of the solid solution.

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