REVIEWS OF TOPICAL PROBLEMS

Diffuse martensitic transitions and the plasticity of crystals with a shape memory effect

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<u>Abstract.</u> The mechanism of diffusion-free (thermoelastic) martensitic transitions in solids is theoretically examined using a thermodynamic approach together with a self-consistent-field order parameter model. Based on the resulting equations, a theory of smeared martensitic transitions is constructed as a kinetic equilibrium theory of heterophase structures which takes into account heterogeneous martensite nucleation and the interaction of interphase boundaries with various types of structural defects in real materials. An extensive comparison is made between the theoretical predictions and the experimental data on thermoelastic martensitic transformations in alloys with shape memory. The universal nature of the theory of diffuse first-order phase transitions is illustrated by applying it to ferroelectric and ferroelastic transitions in some classical ferroelectric and high-temperature superconductors.

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1. Introduction

During the last few decades thermoelastic martensitic transformations in metal alloys have attracted much attention of researchers in view of the discovered potential of these materials in practical applications in many areas of science, technology, medicine, and industry. This potential is based on the characteristic property of alloys undergoing a thermoelastic martensitic transition to change their shape both reversibly and plastically and to restore the shape that existed before deformation. This phenomenon became known as the shape memory effect and found applications in space technology (the Sophor project [1]), in medicine [2, 3], and in the construction of technical devices [4, 5]. Alloys with shape memory belong to the class of what is known as 'smart' functional materials, since it is possible to control their behavior and, to a certain extent, program it.

From the physical viewpoint there are two reasons for the interest in thermoelastic martensitic transformations. First, a new remarkable mechanism of plastic deformation of crystals (in addition to the ordinary dislocation mechanism) operates in such materials. Second, martensitic-shear structural transformations constitute one more type of phase transformation in solids. Hence it would be interesting to establish to what extent martensitic-shear structural transformations obey the general thermodynamic phenomenology of phase transitions and to what extent their mechanism is close to, say, the well-known ferromagnetic and ferroelectric transitions. The present review is an attempt to answer these and other questions concerning thermoelastic martensitic transformations in crystals with the shape memory effect.

1.1 The results and history of investigations

For a long time, after the discovery of thermoelastic martensitic transformations [6-10] and the recognition of their specific features as those of diffusion-free structural transitions involving an athermal shear mechanism of atomic motion [11-17], such transformations have been studied by metal scientists and material scientists mainly from crystallographic and crystal-geometric viewpoints. This resulted in determining the crystal structures of martensitic crystals that form in austenitic matrices in such crystal alloys as CuAlNi, CuZnAl, AuCd, NiTi, etc. [4-10], which have become classical examples of alloys with shape memory. The results of these studies are summarized in various reviews (see, e.g., Refs [17-21]). By martensite, we imply here any lowtemperature phase that emerges because of a structural transition; by austenite, the original high-temperature phase with a higher symmetry lattice. In most alloys the hightemperature phase is a variant of a body-centered cubic (bcc) lattice and the low-temperature phase, of an orthorhombic lattice (9R, 18R, 2H).

In view of the sharp increase in the number of studies of deformation properties of alloys with the shape memory effect at the beginning of the 1970s [4, 23-34], much attention of physicists and mechanists has been attracted by diffusion-free martensitic transformations and related deformation effects.

The mechanists studied the new, martensitic channel of inelastic strain, modeled it mathematically, and incorporated the model into the system of macroscopic-plasticity equations [35, 36]. As for the physicists, they analyzed the formation mechanism for the nucleation centers of the martensitic phase in the austenitic matrix and the subsequent growth of martensitic lamellas (plates), since many experimenters (see, e.g., Refs [6-12]) found that the structural transformation of the lattice proceeds nonuniformly throughout the crystal and that interphase boundaries are formed, which is a characteristic feature of first-order phase transitions.

Two approaches have emerged. The thermodynamic approach is based on the classical energy balance between the free energy of the transition, the surface (interphase) energy, and the bulk (striction) energy, which makes it possible to estimate the critical size of the martensitic nucleation centers [37-41]. Further developments of the thermodynamic approach were based on analyses of premartensitic [42, 43] and martensitic [44-47] states using the Ginzburg–Landau theory of phase transitions. The results of this approach are discussed in Section 3.

The other approach to experimental and theoretical studies, which has been intensely developed over the last few decades, is the analysis of the formation and growth of nucleation centers of the martensitic phase on a microscopic level. The point is that the classical mechanism of nucleation of the new phase via heterophase fluctuations does not operate in thermoelastic martensitic transformations [48–50]. For instance, according to this mechanism, the volume density of martensitic nucleation centers should be of order $10^{20}-10^{23}$ centers per cubic centimeter, while the actual volume density is usually 10^6-10^{10} centers per cubic centimeter [50]. This indicates that the mechanism of nucleation is heterogeneous (which is confirmed by experiments). Optical and electron-microscope studies evidence

that the places where martensitic nucleation centers form are the crystal's surface [7-10], grain boundaries [51], separate dislocations [52], dislocation clusters [53], and other crystal defects [50].

Even at the 'optical' stage of studying thermoelastic martensitic transformations researchers noted [11, 12, 54] certain similarities between the shear mechanism of structural reorganization of the lattice under thermoelastic martensitic transformations and the mechanism of lattice reorientation related to the formation of elastic twins in the crystal. At that same time a dislocation mechanism was proposed [55, 56] for a lattice transformation) along the interphase boundary, similar to the motion of twinning dislocations along the twin boundaries [57, 58]. Later the dislocation mechanism was thoroughly studied by the transmission electron spectroscopy method [59–70] and theoretically developed and refined by various researchers (see, e.g., Refs [14, 15, 71–83].

This research established that atomic-sized steps exist at the interphase boundaries [59, 67-69] and that lattice dislocations (partial Shockley dislocations) [59, 65-70], the pole mechanism [84], and in some cases the cross-slip of dislocations [60, 61] directly participate in the formation of the martensitic phase. According to these observations, the microscopic mechanism of the growth of martensitic lamellas consists in the movement of transformation dislocations along the interphase boundary (Fig. 1a), which causes a local transformation of the lattice from the high-temperature phase to the low-temperature phase (sometimes this occurs inside lamellas with the density of partial transformation dislocations gradually increasing [66]). In the reverse martensitic transition the dislocations move in the opposite direction (Fig. 1b), causing a transition from martensite to austenite.

At present, thermoelastic martensitic transformations are studied on three scales: a microscopic (Fig. 1), a mesoscopic (Fig. 2), and a macroscopic (Fig. 3) one. Studies on the microscopic scale were pointed out above. On the meso-



Figure 1. Motion of steps along the interphase boundary in direct (a) and reverse (b) martensitic transformations.



Figure 2. Transition of austenite A (a) to martensite as a result of the formation of martensitic (M) and martensitic–twinned (MT) lamellas (b, c).



Figure 3. Deformation of the transformation in direct (1) and reverse (2) martensitic transitions in CuAlNi alloy [24] (a) and the strain–stress diagram for the pseudoelastic deformation of CuZn alloy [29] (b): 1, loading; 2, unloading; T = -77 °C.

scopic scale, a heterophase martensite-austenite structure is a system of martensitic plates with a width (thickness) of 0.1 to 100 μ m (Fig. 2b) of one or several orientations (variants of martensite) [6–10, 85]. Usually the plates are in a twinned state [10], which lowers the inner stresses and the deformations related to transformations of the lattice into a lower symmetry form (Fig. 2c). In the process of a martensitic transformation, the number and width of lamellas increase until the entire crystal is transformed into a martensitic state [28]. The same happens with austenite lamellas in the martensitic matrix in a reverse transition.

By the macroscopic scale, in such cases, one usually means the macroscopic manifestations of a thermoelastic martensitic transformation in a material, such as the plasticity of the transformation (Fig. 3a), the effects of superelastic deformation (Fig. 3b) and shape memory, and some effects related to the martensitic transition, such as internal friction [86–90], acoustic emission [91–94], and the resistometric [4], dilatometric [95], and calorimetric effects [4, 91]. Characteristic features of the macroscopic scale are (usually) smooth dependences and their hysteretic character, i.e. the fact that the curves for the direct and inverse transitions do not coincide (see Fig. 3).

1.2 The goal and plan of the review

Although numerous thorough investigations have been devoted to individual aspects and features of thermoelastic martensitic transformations, a well-substantiated physical theory of martensitic transitions, capable of quantitatively describing the laws that govern such transformations observed on mesoscopic and macroscopic scales, is not yet available (as was noted by Tanner and Wuttig [96]). The need to develop such a theory also follows from the experimental fact that, in real materials, thermoelastic martensitic transformations, their parameters (the transformation temperature and hysteresis), and macroscopic manifestations are extremely sensitive to the structure of the material, i.e. to the presence of impurities [18], disperse particles and precipitations [90], dislocations [97, 98], and radiation-induced and quenching defects [99, 100].

The character of the observed dependences is influenced by the sizes of the grains (in polycrystalline materials) [51, 101] and of the sizes of the samples under investigation [102]. It should also be added that thermoelastic martensitic transitions are sensitive not only to temperature and mechanical stress, but also to other external factors, such as hydrostatic pressure [103-105], magnetic field [104], and sound [106, 107]. Obviously, without having a proper theory available, one is forced to develop a separate theoretical model for each of the above factors. However, there is a more general reason why there is no quantitative theory of thermoelastic martensitic transformations at present, and that is the absence of a theory of first-order nonequilibrium phase transitions, or, specifically, the fact that the theory of the heterophase state (the theory of phase equilibrium), describing the evolution of this state in such transitions, is not adequately developed. Recently, this was pointed out in Martynov's review [108]. As shown in Sections 2.4 and 2.5, the effect of the above factors on phase equilibrium renders martensitic transformations highly sensitivity to them.

In addition to the above reasons, there was one more fact [46] that hindered the development of a quantitative theory of thermoelastic martensitic transformations: for a long time such transitions were considered in isolation from the general theory of phase transitions, being regarded as a particular phenomenon (similar to twinning), and the emphasis was on the leading role of elastic stresses and bulk forces in the origin and development of the structural transformation of a lattice. Hence it was assumed, for instance, that the entropy contribution to the thermodynamic (chemical) force, the cause of the structural transformation, plays no important role in martensitic transformations, in contrast to, say, second-order phase (orientational) transitions in ferromagnetic and ferroelectric substances [109–111].

The goal of the present review is to demonstrate that thermoelastic martensitic transformations and the related diffusion-free shear transformation of the lattice belong to the same class of phenomena as orientational transitions do. According to this general approach, the first part of the review (Sections 2 and 3) develops a phenomenological theory of first-order diffuse phase transitions [112, 113], analyzes its corollaries, and quantitatively compares the theory and experiment using thermoelastic martensitic transformations as an example [111-113]. This last fact is important since so far nobody has carried out such a comparison.

The theory of diffuse phase transitions focuses not on the process of nucleation of martensite, since this process is heterogeneous in real materials, but on the expansion and shrinkage of martensitic lamellas due to various factors, i.e. the process of phase equilibrium and its evolution. By a *diffuse* phase transition, we mean a first-order transition that requires a finite variation in a parameter (e.g. temperature, mechanical stress, hydrostatic pressure, etc.) for its completion. The curves in Fig. 3a provide an example of a diffuse martensitic transition. The theory does not claim to be complete and to encompass all aspects of the problem; it is of a demonstrative nature and reflects only the main laws governing thermoelastic martensitic transitions in real materials on mesoscopic and macroscopic scales.

Since the use of the Ginzburg–Landau theory of phase transitions in analyzing the mechanism of formation of inhomogeneous (heterophase) martensitic structures was not successful, in Section 3 a kinetic theory of the formation of such structures is developed. From a kinetic (or synergetic) viewpoint, the formation of such structures is the result of self-organization in elementary volumes of transformation.

In the second part of the review (Sections 4-6), the theory of diffuse phase transitions is used to analyze various deformation phenomena characteristic of thermoelastic martensitic transformations in alloys with shape memory, such as superelastic deformation and the shape memory effect (Section 4). Section 5 discusses the mechanisms of low- and high-frequency internal friction in alloys with shape memory, related to thermoelastic martensitic transitions.

Section 6 demonstrates the universal nature of the theory of diffuse phase transitions in real materials, using the example of ferroelastic transitions in classical ferroelectric and ferroelastic materials and high-temperature superconductors (YBa₂Cu₃O_{6+ δ}). The concluding Section 7 summarizes the review and discusses unresolved problems.

The review contains illustrative material consisting basically of theoretically revealed regularities (both previously published and obtained in the present analysis) and experimental data from the literature where needed for comparisons. The literature cited contains the main papers that provide a complete exposition of the history of the problem and of the current state of investigations.

2. Phenomenology of phase transitions

As noted in Section 1, there are reasons to believe that, phenomenologically, the structural transformation of a lattice in a thermoelastic martensitic transformation does not much differ from the well-known phase transitions in ferromagnetic and ferroelectric materials. What speaks in favor of this is the fact that, on mesoscopic and macroscopic scales, martensitic–shear and orientational transitions in crystals exhibit some common features, such as the existence of precursor effects (in particular, premartensitic transformations [114–117]) above the transition point, the formation of mesoscopic (domain, twinned, and martensitic) structures, and the transformation of these structures due to changes in the temperature or in the mechanical, electric, and/or magnetic fields applied to the crystal.

On a macroscopic scale, the general features of such transformations also include hysteresis phenomena (characteristic of all types of transitions) and the similarity in the hysteresis loops. This correspondence holds also on a microscopic scale. For instance, the growth or shrinkage of electric domains in ferroelectric materials is associated with the motion of steps along the domain boundaries [118–120].

The goal of the quantitative theory of structural phase transformations is to establish a relationship between the relative volume fraction φ of the new phase and various factors affecting the formation and evolution of this phase. Among such factors are temperature *T*, external fields {*I*} (mechanical σ_{ik} , hydrostatic *P*, electric *E*, and magnetic *H*), and different structural factors and lattice defects {*s*}, which, as experiments show, strongly affect the kinetics and parameters of the transition in a real material. These factors determine the phase state of the material:

$$\varphi = \varphi(T, \{I\}, \{s\}). \tag{2.1}$$

If the phase state is known, one can establish how various properties of the material (mechanical, acoustic, dilatometric, etc.) change in the transition process.

2.1 The self-consistent field equation

Within the scope of the thermodynamic approach, a change in the phase state of a system of interacting particles is determined by the change in the free energy of the system $\Delta F = \Delta U - T \Delta S$, where U is the internal energy, S is the entropy, and T is the temperature of the system. For a twophase system consisting of particles of concentrations (relative fractions) φ_1 and φ_2 , the expression for ΔF can be written in the fairly general form

$$\Delta F = U_1 \varphi_1 + U_2 \varphi_2 + U_{12}(\varphi_1, \varphi_2) - T \Delta S(\varphi_1, \varphi_2), \quad (2.2)$$

where U_1 and U_2 are the energies of the particles in states 1 and 2, respectively, and U_{12} is the interaction energy of the particles in these states. In the models of the self-consistent field described by equation (2.2) it is usually assumed [109, 121] that the interaction energy can be written in the form $U_{12}(\varphi_1, \varphi_2) = U_0\varphi_1\varphi_2$, where U_0 is a constant. This energy ensures spatial ordering of the particles, i.e. a second-order phase transition.

The inclusion of additional (nonlinear in the concentrations) terms in the energy U_{12} , e.g. in the form $U_{12}(\varphi_1, \varphi_2) = U_0 \varphi_1 \varphi_2 (1 - g \varphi_1 \varphi_2)$, leads to the formation of local deformations in the lattice, which triggers (if the parameter g is large) a first-order phase transition. Assuming that, in (2.2), the variation of the entropy of the crystal in a transition is primarily related to the energy of mixing of the states and allowing for the fact that $\varphi_1 = \varphi$ and $\varphi_1 + \varphi_2 = 1$ yield

$$\Delta F(\varphi, T) = \Delta U_{12}\varphi + U_0\varphi(1-\varphi) [1-g\varphi(1-\varphi)] + kT[\varphi \ln \varphi + (1-\varphi)\ln(1-\varphi)], \quad (2.3)$$

where $\Delta U_{12} = U_1 - U_2$, and k is the Boltzmann constant. Upon introducing the notation

$$\eta = \frac{\varphi_1 - \varphi_2}{\varphi_1 + \varphi_2} = 2\varphi - 1, \quad T_0 = \frac{U_0}{2k}, \quad f = \frac{4\Delta F}{U_0}, \quad (2.4a)$$

we can write the variation (2.3) of the free energy as a function of the order parameter η :

$$f(\eta, T) = f_0 + \frac{2\Delta U_{12}}{U_0} \eta - \left(1 - \frac{1}{2}g\right)\eta^2 - \frac{1}{4}g\eta^4 + \frac{T}{T_0}\left[(1+\eta)\ln(1+\eta) + (1-\eta)\ln(1-\eta)\right].$$
 (2.4b)

For small values of η the variation of the free energy has the standard form of a Landau expansion:

$$f(\eta, T) = f_0 + f_1 \eta + f_2 \eta^2 + f_4 \eta^4 + f_6 \eta^6 + \dots, \qquad (2.5a)$$

where f_0 is the value of f at $\eta = 0$, and

$$f_{1} = \frac{2\Delta U_{12}}{U_{0}}, \qquad f_{2} = \frac{T - T_{c}}{T_{0}},$$

$$f_{4} = \frac{T - T_{1}}{6T_{0}}, \qquad f_{6} = \frac{T}{15T_{0}},$$

$$T_{c} = \left(1 - \frac{1}{2}g\right)T_{0}, \qquad T_{1} = \frac{3}{2}gT_{0}.$$

(2.5b)

2.2 First- and second-order phase transitions

Figure 4a depicts the function $\Delta f(\eta) = f(\eta) - f_0$ at $\Delta U_{12} = g = 0$ for different temperatures. At temperatures below T_c the initial state of the system $\eta = 0$, $f = f_0$ proves to be unstable and the system undergoes a second-order phase transition. The new (equilibrium) state of the system is determined by the conditions

$$\frac{\partial \Delta f}{\partial \eta} = 0, \qquad \frac{\partial^2 \Delta f}{\partial \eta^2} \ge 0, \qquad (2.6)$$



Figure 4. Free energy as a function of the order parameter in phase transitions of (a) the second and (b) first orders at the following (reduced) temperatures T/T_c : 1, 1.1; 2, 1.0; 3 and 3', 0.9; 4, 0.6; 5, 0.577; 6, 0.55; and 7 and 7', 0.5.

from which follow the well-known relationships for the order parameter [109, 122]:

$$\eta = \tanh\left(\frac{T}{T_0}\eta\right), \quad T_c = T_0.$$
 (2.7a)

The first relationship in (2.7a) determines the temperature dependence of η (Fig. 5a),

$$\frac{T}{T_0} = 2\eta \ln^{-1} \frac{1+\eta}{1-\eta} , \qquad (2.7b)$$

and the second one determines the critical temperature of the phase transition, T_c . At temperatures above T_c , due to thermal disordering, the relative number of particles (atoms) in state 1 is equal to their number in state 2: $\varphi_1 = \varphi_2 = 0.5$, $\eta = 0$. At temperatures below T_c one of the states dominates: $\eta < 0$ or $\eta > 0$. The choice of the state is determined by the absolute value and sign of the thermodynamic force $(\partial \Delta f/\partial \eta)_{\eta=0} \propto \Delta U_{12}$.



Figure 5. Temperature dependence of the order parameter η and the relative volume of the martensitic phase, φ , for point (a – c) and diffuse (d) phase transitions at the following values of the parameter *g*: 0 (*I*), 0.5 (2), 1.0 (3), 2.0 (4), and 2.5 (5).

The inclusion of additional nonlinear higher order terms $(g \neq 0)$ in the interaction energy gives rise to a peak in the dependence $\Delta f(\eta)$ (curves 5 and 6 in Fig. 4b, g = 1), which is a barrier that hinders the transition of the system to an equilibrium state. According to (2.6), the temperature dependence of the order parameter and the transition temperature are given by the following formulas [112]:

$$\frac{T}{T_{\rm c}} = 2\eta (1 + c\eta^2) \ln^{-1} \frac{1 + \eta}{1 - \eta} ,$$

$$T_{\rm c} = \left(1 - \frac{1}{2}g\right) T_0 , \qquad c = \frac{g}{2 - g} .$$
(2.8)

Figure 5b depicts the temperature dependence of η according to (2.8) at different values of the parameter g. As g increases, the transition temperature lowers, and at g > 0.5 the curves acquire a transformation hysteresis loop *abcd* (Fig. 5c). The condition g > 0.5 indicates the change from a second-order to a first-order transition.

The thermodynamic equilibrium transition temperature T'_c is determined in this case by (2.8) and by the condition $\Delta f(\eta_c, T'_c) = 0$, where η_c is the jump in the order parameter at the temperature T'_c , which determines the jump in entropy, $\Delta S(\eta_c)$, and the heat of transition, $q = T'_c \Delta S(\eta_c)$. This temperature lies within the interval $T_c < T'_c < T''_c$, where T''_c is the critical overheating temperature in the reverse phase transition and corresponds to point *c* on the hysteresis curve (Fig. 5c).

At sufficiently large values of the parameter g the phase transition may be completely blocked (curve 5 in Fig. 5b) due to the elastic deformations accompanying the transition. This parameter, determining the nonlinearity of the interaction between atoms in states 1 and 2, was introduced somewhat formally into expressions (2.3) and (2.4) for the free energy. It can be shown that it determines the striction deformations accompanying the transition.

Indeed, in the presence of elastic deformations e_{ik} the expression for the variation in the free energy of the transition becomes [41, 42]

$$\Delta F(T,\eta,e_{ik}) = \Delta F(T,\eta,0) + \lambda \eta^2 e_{ii} + \frac{1}{2} \left(K - \frac{2}{3} G \right) e_{ii}^2 + G e_{ik}^2,$$
(2.9)

where λ is the striction constant relating the order parameter to the lattice deformations, *G* is the shear modulus, and *K* is the bulk modulus. Minimizing $\Delta F(T, \eta, e_{ik})$ with respect to deformations and using the equation of equilibrium of elastic stresses yield formulas for the equilibrium deformations [41]:

$$e_{ii} = -\frac{\lambda}{K + 4G/3} \eta^2, \quad e_{ik}^2 = e_{ii}^2.$$
 (2.10)

By substituting (2.10) into (2.9), we obtain

$$\Delta F(T,\eta) = \Delta F(T,\eta,0) - \frac{1}{2} \frac{\lambda^2}{K + 4G/3} \,\eta^4 \,. \tag{2.11}$$

A comparison of (2.4b) and (2.11) yields

$$g = \frac{8\lambda^2}{U_0(K + 4G/3)},$$
 (2.12)

i.e. the parameter g is related to the striction constant λ and, hence, according to (2.1), to elastic deformations.

2.3 Diffuse phase transitions

The classical second-order phase transition (in the case of ferromagnetic and ferroelectric materials) depicted in Fig. 5a occurs only in fairly pure, specially prepared crystals. The temperature dependence (characteristic of such a transition) of the order parameter near the transition temperature, of the form $\eta(T) \propto (T_c - T)^{1/2}$, determines the Curie–Weiss law for the temperature dependence of the dielectric constant $\varepsilon(T)$ and the magnetic permeability $\mu(T)$ at temperatures close to T_c [110, 111]:

$$\varepsilon(T) \propto \mu(T) \propto |T_{\rm c} - T|^{-m}, \quad m = 1.$$
 (2.13)

In real materials, which contain impurities and other defects (dislocations and grain boundaries), the Curie–Weiss law breaks down: the peak in the temperature dependence (2.13) becomes bell-shaped and smeared. The approximation of $\varepsilon(T)$ and $\mu(T)$ by (2.13) yields values of *m* lying in the interval from 1 to 2 [123–125]. The fact that the transition becomes diffuse means that the variation of the phase state of the system is not sudden but smooth and occurs within a certain temperature interval (the smearing of the transition) depending, as shown by experiments, on the defect concentration in the crystal [123, 125].

As for the thermoelastic martensitic transformation in alloys with shape memory, in view of their inhomogeneous structure their properties change (in most cases) smoothly near the transition temperature (Fig. 3a), which suggests that the phase transitions are diffuse in such materials. Thus, the smearing of the transition over temperature is independent of the type of transition (ferromagnetic, ferroelectric, or martensitic-shear), which means there is a common cause for such smearing.

In the case of ferroelectric transitions the smearing is usually assumed to be due to the influence of defects (dislocations [126]) and composition fluctuations [127] on the transition temperature T_c . According to this mechanism, because of the composition fluctuations and the presence of defects, the formation of critical nucleation centers of the new phase occurs at different local transition temperatures, i.e. above or below the nominal transition temperature. It is assumed that the local temperatures are distributed according to the Gauss law $f(T_c) \propto \exp[-(T_c - T_m)^2/2\sigma^2]$ (here T_m is the peak temperature in the $\epsilon(T)$ dependence, and σ is the standard deviation of the transition temperatures) [123–127]; this specifies an approximately quadratic temperature dependence of the dielectric constant in the case of a diffuse phase transition [$m \approx 2$ in (2.13)].

Another mechanism of formation of diffuse phase transitions in ferroelectric materials, thermodynamically more substantiated, was developed in Refs [128–133]. The main idea here is that the volume of the low-temperature (ferroelectric) phase increases in the process of the transition by portions, amounting to $10^{-18}-10^{-17}$ cm³ (Känzig regions [128, 132]), added to the new phase at the interphase boundaries. The formation of a Känzig region requires the temperature change by a finite value (supercooling, ΔT).

As the temperature is lowered, the low-temperature phase increases its volume, and at each temperature there is a phase equilibrium between the low-temperature and the hightemperature (paraelectric) phase, determined by the energy spent for the creation of a Känzig region. Experiments show that the volume occupied by this region depends on the amount of impurities and other defects in the material, i.e. a Känzig region is a structurally sensitive parameter that determines the smearing of the transition over temperature. Section 6 describes the results of a quantitative analysis of the temperature curves $\varepsilon(T)$ determined by this mechanism.

A generalization of the mechanism of diffuse ferroelectric transitions [128–133] to thermoelastic martensitic transformations is carried out in Refs [112, 113], and a quantitative comparison of this mechanism to the results of experiments involving alloys with shape memory and some ferroelectric materials is made in Refs [134, 135]. This comparison shows that the mechanism of diffuse phase transitions [112, 113, 129, 131] is fairly universal. Section 2.4 deals with the basic formulas related to such transitions.

2.4 Theory of diffuse phase transitions

In a point second-order phase transition, the phase transformation uniformly encompasses the entire volume of the crystal. As the temperature is lowered, the number of particles in the new state increases in accordance with the curve depicted in Fig. 5a. If changes in the state of the system are accompanied by inelastic deformations, they occur abruptly (Fig. 5c), but the transformation still encompasses the entire volume. In a reverse transition, a *thermodynamic* hysteresis manifests itself in the transformation.

According to the mechanism described in Refs [112, 131], the situation is quite different in the case of a diffuse phase transition. Due to the spatial instability of the transformation (see Section 3.2) and the formation of nucleation centers of the new phase with an order parameter $\eta \approx 1$ near defects, the lowering of the temperature leads to an increase in the volume of the embryos and to the formation of a *heterophase* domain structure in the crystal. Changes in the relative volume of the phases occur as a result of the motion of interphase boundaries via the formation of nucleation centers on these boundaries (Känzig regions in the case of ferroelectric materials) whose volumes are larger than the critical volume. The interaction between interphase boundaries and defects leads to two consequences — the smearing of the transition over temperature and the formation of force hysteresis in the transformation, due to the pinning of the boundaries by defects.

2.4.1 Basic relations. In view of the fact that in a diffuse transition the elementary volume of a nucleation center of the new phase ω exceeds the critical value, in equations (2.2) and (2.3) for the free energy variation we can drop the term U_{12} describing the interaction between the particles in states 1 and 2 at the interphase boundary, since this term is much smaller than the bulk energy variation ΔU_{12} associated with the formation of such a nucleation center. The result is the following expression:

$$\Delta F(\varphi, T) = \Delta U_{12}\varphi + kT[\varphi \ln \varphi + (1 - \varphi)\ln(1 - \varphi)].$$
(2.14)

Minimizing the energy (2.14) according to the first condition in (2.6), we find that the volume fraction of the new phase varies with ΔU_{12} and temperature as follows [112, 129–133]:

$$\varphi(T) = \left(1 + \exp\frac{\Delta U_{12}}{kT}\right)^{-1}.$$
(2.15)

Since the change in the relative fraction of the new phase occurs by volume portions ω , the change in the bulk energy is $\Delta U_{12} = \omega \Delta u$, where Δu is the change in the volume density of internal energy associated with the transition. Thus, phase equilibrium in a heterophase system is determined by the difference between the phases in internal energy, Δu . At $\Delta U_{12} = \Delta u = 0$ we have $\varphi_1 = \varphi_2 = \varphi = 0.5$ and $\eta = 0$. When $\Delta u > 0$, phase 2 prevails ($\varphi_2 > 0.5$), and when $\Delta u < 0$, it is phase 1 that prevails ($\varphi_1 > 0.5$).

Obviously, in the case of the heterophase state (2.15), the second condition in (2.6) (the phase-state stability condition) does not hold. Indeed, if the bulk energy of a nucleation center exceeds the center's surface energy, one embryo can, by increasing its volume, transform the entire volume V of the crystal into the new phase state. In a real crystal this does not happen only because the interphase boundary encounters, in its motion, an obstacle in the form of various defects present in the crystal. This stabilizes the heterophase state, since the volume of the new phase increases in small portions $\omega \ll V$, which depend on the defect concentration in the crystal (see below), and requires additional supercooling (superheating) of the crystal.

Near the temperature of a first-order phase transition the change in the density of the internal energy can be approximated by the expression

$$\Delta u = q \; \frac{T - T_{\rm c}}{T_{\rm c}} \;, \tag{2.16}$$

where $q = \Delta S_c T_c$ is the heat of transition, with ΔS_c the change in the entropy due to the transition. Substituting (2.16) into (2.15), we arrive at an expression for the temperature dependence of the volume fraction of the new phase:

$$\varphi(T) = \left[1 + \exp\left(B\frac{T - T_{\rm c}}{T}\right)\right]^{-1}, \quad B = \frac{\omega q}{kT_{\rm c}}.$$
 (2.17)

Here *B* is a parameter determining the smearing of the transition over temperature [112]:

$$\Delta T_{\rm M} = 4B^{-1}T_{\rm c} = \frac{4kT_{\rm c}}{\omega q} T_{\rm c} \,. \tag{2.18}$$

Figure 5d depicts the dependence (2.17) at B = 10.

A comparison of the curves depicted in Figs 5a and 5d shows that a diffuse phase transition differs substantially from a point phase transition. In a point transition the temperature derivative of the order parameter near the transition temperature has, according to (2.7), the form

$$\frac{\partial \eta}{\partial T} \propto \left(T_{\rm c} - T\right)^{-1/2},\tag{2.19}$$

i.e. the derivative tends to infinity as $T \rightarrow T_c$. In the case of a diffuse transition, the temperature derivative of the order parameter is, according to (2.17), given by the expression [112, 129]

$$\frac{\partial \eta}{\partial T} = 2 \frac{\partial \varphi}{\partial T} = -\frac{B}{2T_{\rm c}} \cosh^{-2} \left(\frac{1}{2} B \frac{T - T_{\rm c}}{T}\right) \left(\frac{T_{\rm c}}{T}\right)^2 \sim -\frac{B}{2T_{\rm c}} \cosh^{-2} \left(\frac{1}{2} B \frac{T - T_{\rm c}}{T_{\rm c}}\right).$$
(2.20)

At $T = T_c$ the derivative (2.20) is finite: $(\partial \varphi / \partial T)_{T=T_c} = B/4T_c$. The second relationship in (2.20) is written on the

assumption that the smearing of the transition over temperature is small: $\Delta T_{\rm M}/T_{\rm c} = 4/B \ll 1$.

Using (2.14) and the condition $\partial^2 \Delta F / \partial \phi \partial T = 0$, we can write the expression for the derivative $\partial \phi / \partial T$ as follows:

$$-\frac{\partial\varphi}{\partial T} = B \frac{T_{\rm c}}{T^2} \varphi(1-\varphi) \sim BT_{\rm c}^{-1} \varphi(1-\varphi) \,. \tag{2.21}$$

This relationship has a clear physical meaning: If $\varphi \leq 1$, we have $-\Delta \varphi / \Delta T \sim BT_c^{-1}\varphi \propto \omega \varphi$, i.e. a change in the temperature by ΔT brings about a change in the volume fraction of the low-temperature phase by $\Delta \varphi$, which is proportional to the elementary transformation volume ω and the volume fraction φ of the phase that has already formed. Since, as the transformation proceeds, the volume fraction of the high-temperature phase, $1 - \varphi$, decreases, the transformation rate also decreases as $\varphi \rightarrow 1$, i.e. $\Delta \varphi / \Delta T \propto \omega \varphi (1 - \varphi)$.

To see how the elementary transformation volume ω is related to the concentration *C* of defects in a crystal, which hinder the motion of interphase boundaries, we consider a diagram that illustrates the expansion and elongation of a martensitic lamella of current width *W* and length *L* in the crystal (Fig. 6). The dark circles indicate point obstacles of size h = 2r, where *r* is the radius of an obstacle. Because of the presence of obstacles, the lamella volume increases by layers *abcd* of thickness *h*, as the boundary surmounts an obstacle. This requires a finite change ΔT in the temperature of the crystal (supercooling or superheating).

Let the average distance between obstacles in the plane of a boundary be $ab = bc = cd = \lambda$. Then the elementary transformation volume is $\omega = h\lambda^2$, the volume concentration of obstacles is $n = (h\lambda^2)^{-1}$, and the relative obstacle concentration is $C = 4\pi r^3 n/3$. Hence the elementary transformation volume $\omega = 4\pi r^3/3C$ is greater, the larger the effective volume of the obstacles and the lower the obstacle concentration. Correspondingly, for the smearing of the transition over temperature, (2.18), we have

$$\Delta T_{\rm M} = \frac{3kT_{\rm c}^2}{\pi q r^3} C, \qquad (2.22)$$

i.e. the smearing is larger, the higher the obstacle concentration and the smaller the obstacle's radius. Obviously, in the



Figure 6. Expansion and elongation of a martensitic lamella in a crystal containing defects (dark circles) that hinder the motion of interphase boundaries.

absence of obstacles (C = 0) the elementary transformation volume ω tends to V, where V is the volume of the crystal, as $\Delta T_{\rm M} \rightarrow 0$. This means that instead of a diffuse transition we have a point transition.

2.4.2 Influence of defects and external fields. If there are external fields $\{I\}$ acting on the crystal, the change in internal energy caused by a phase transition is [113]

$$\Delta u(T,I) = q \, \frac{T - T_{\rm c}}{T_{\rm c}} - [i]\{I\}, \qquad (2.23)$$

where [i] is the jump in the parameter conjugate to the field, related to the phase transition. If a mechanical stress σ_{ik} or a hydrostatic pressure *P* or an electric field E_i (for ferroelastic materials) or a magnetic field H_i (for magnetoelastic materials) acts on the crystal, we have

$$\Delta u = q \, \frac{T - T_{\rm c}}{T_{\rm c}} - \xi_{ik} \sigma_{ik} - \delta_0 P - \overline{p}_i E_i - \overline{m}_i H_i \,. \tag{2.24}$$

Here ξ_{ik} and δ_0 are the shear deformation and dilatation of the lattice associated with its structural transformation, and \overline{p}_i and \overline{m}_i are the electric and magnetic moments induced by the lattice transformation.

At $\Delta u = 0$ equation (2.24) coincides with the equation for the balance of forces applied to the interphase (interdomain) boundary [136, 137]. According to (2.15), a departure from this balance in one or the opposite direction ($\Delta u > 0$ or $\Delta u < 0$) increases or decreases the fraction of the new phase in the crystal. The condition $\Delta u = 0$ at which $\varphi_1 = \varphi_2 = \varphi = 0.5$ determines the characteristic transition temperature. External fields applied to the crystal shift the characteristic temperature in accordance with the generalized Clausius–Clapeyron equation as follows:

$$T_{\rm c}(I) = T_{\rm c}(0) + \frac{T_{\rm c}(0)}{q} (\xi_{ik}\sigma_{ik} + \delta_0 P + \overline{p}_i E_i + \overline{m}_i H_i), \quad (2.25)$$

where $T_{\rm c}(0)$ is the characteristic temperature in the absence of fields.

The rate of variation in the volume of the new phase in the case where an external field is applied to the crystal is determined by the condition $\partial^2 \Delta F / \partial \varphi \, \partial I = 0$, from which an expression similar to (2.21) follows:

$$\frac{\partial \varphi}{\partial I} = B_{\rm I} \varphi (1 - \varphi) , \qquad B_{\rm I} = \frac{\omega[i]}{k T_{\rm c}} . \tag{2.26}$$

Here B_1 is the smearing of the phase transition initiated by the external field. In the case of a mechanical field, $B_{ik}^{(\sigma)} = \omega \xi_{ik} / kT_c$.

The influence of defects (impurities, dislocations, and precipitation particles) on the variation in the internal energy, Δu , and hence on the characteristic transition temperature can be related to a number of factors. For instance, if the transformation of the lattice into the low-temperature phase is accompanied by a change in the elastic constants and parameters of the lattice, this transformation will be accompanied by the following change in the intrinsic energy of defects $[u_d]$ [113]:

$$\Delta u(T, I, n_{\rm d}) = q \, \frac{T - T_{\rm c}}{T_{\rm c}} - [i] \{I\} + [u_{\rm d}] \, n_{\rm d} \,, \qquad (2.27)$$

where n_d is the number density of defects in the crystal.

If the defects generate long-range fields (elastic, electric, or magnetic), their effect on the characteristic transition temperature can be found by solving a boundary-value problem for the order parameter determining the size of the region around the defect (the correlation range) where the transformation occurs locally [138]. If this range does not exceed the average distance between defects, the characteristic temperature is, according to (2.27), a linear function of the number density of defects. Obviously, a short-range interaction between the interphase boundaries and the defect can pin the boundaries and lead to a *force* hysteresis in the transformation.

Thus, the above phenomenological theory of diffuse phase transitions (and martensitic transitions, in particular) allows for the results of the experimental investigations of thermoelastic martensitic transformations in alloys with shape memory (Section 1.1). On a microscopic scale this theory takes into account the presence, at the interphase boundaries, of transformation dislocations and steps interacting with defects in the crystal, while on a mesoscopic scale the theory allows for the presence of a heterophase state in the crystal. In accordance with numerous observations, the theory allows for the influence of defects and external fields on the parameters of the transitions. In the next section we compare the results of the theory with those of macroscopic experiments on alloys with shape memory.

2.5 Comparison with experimental data

Figure 3a depicts the temperature curves of the deflection of a crystal of CuAlNi alloy [24] for three-point bending in direct (curve *I*) and reverse (curve *2*) thermoelastic martensitic transformations. Since the deflection is $\Delta l \propto \varphi$, these curves demonstrate the temperature dependence of the volume fraction of martensite in the crystal, as it undergoes a martensitic transition, $\varphi(T) = \Delta l(T)/\Delta l_m$, where Δl_m is the maximum deflection after the completion of the transformation.

According to the model of diffuse phase transitions, the temperature curves are straight lines in the $\ln((1-\varphi)/\varphi)$, T plane. It follows from (2.17) that

$$\ln \frac{1-\varphi}{\varphi} = B \frac{T-T_{\rm c} \pm \Delta T_{\rm f}}{T_{\rm c}}, \qquad (2.28)$$

where $2\Delta T_{\rm f}$ is the transformation hysteresis in temperature. Curves *I* and *2* (Fig. 7) redrawn in accordance with (2.28) are indeed straight lines, which makes it possible to determine the phenomenological parameters of the transformation, i.e. $T_{\rm c} = 307.5$ K, $\Delta T_{\rm f} = 7.5$ K, B = 118, and $\Delta T_{\rm M} = 10.5$ K, as well as the elementary transformation volume $\omega = (kT_{\rm c}/q)B$, provided that the heat of transition *q* is known.

In deriving Eqn (2.17) we assumed that this expression should describe the formation of martensite on a macroscopic scale, i.e. on a scale comparable to the size of the crystal. Figure 8 depicts data demonstrating that (2.17) and (2.28) describe the martensitic transformation on a mesoscopic scale, i.e. on the scale of an individual martensitic lamella.

Curves 1 and 2 in Fig. 8a display the increases and decreases, respectively, in the width (thickness) W of a martensitic lamella in a crystal of CuZnAl alloy [100] as the lamella is cooled and heated. In this case $\varphi(T) = W(T)/W_m$, where $W_m = 77.5 \,\mu\text{m}$ is the equilibrium thickness of the lamella. Figure 8b shows that, in accordance with (2.28), the experimental points fit onto a straight line when the lamella is



Figure 7. Temperature dependence (in the coordinates of (2.28)) of the volume fraction φ of the martensitic phase in direct (1) and reverse (2) martensitic transitions in CuAlNi alloy [24].

cooled. In the reverse transition the points do not fit onto the straight line given by (2.28) because of the nonuniform (jerky) motion of the interphase boundary in the reverse transformation (the arrow in Fig. 8a), due to the pinning of the boundary by a strong obstacle. The jerky movement of the boundary is accompanied by acoustic emission [100]. The dashed curves in Fig. 8a describe the smooth motion of the boundaries in accordance with (2.17) at $T_c = 284$ K, $2\Delta T_f = 0.45$ K, $B = 3.9 \times 10^3$, and $\Delta T_M = 0.29$ K.

The influence of defects on the parameters of a thermoelastic martensitic transformation is demonstrated by Fig. 9. Curves 1 and 2 schematically illustrate the results of experiments on a CuZnAl alloy [100], similar to the results depicted in Fig. 8a. The difference between curves 1 and 2 is that in the case of curve 2 the expansion and shrinkage of a martensitic lamella take place not in an annealed crystal (curve 1) but in a quenched crystal, which contains quenching vacancy loops with a number density of $10^{15}-10^{16}$ cm⁻³ and a size of 10-15 nm. Figure 9 shows that the presence of obstacles — dislocation loops — in the crystal substantially changes the parameters of the transition: the characteristic transition temperature reduces by 10 K, while the smearing of



Figure 9. Expansion and shrinkage of a single martensitic lamella in an annealed (*1*) and a quenched (*2*) CuZnAl alloy [100].

the transition and its hysteresis increase by a factor of five to six.

The effect of vacancy loops on the smearing of the transition can be estimated in the following way. The overall number density of dislocations within the loops is $\rho = 2\pi R n_l$, where *R* is the loop radius, and n_l is the volumetric number density of loops. The loops intersecting an interphase boundary serve as an obstacle of height $h \sim 2R$ for this boundary. In this case the elementary transformation volume is $\omega = h/\rho$, and the smearing of the transition in temperature

$$\Delta T_{\rm M} = \frac{kT_{\rm c}^2}{qh} \rho = \pi \, \frac{kT_{\rm c}^2}{q} \, n_l \tag{2.29}$$

is greater, the higher the number density of loops.

The evolution of a heterophase system caused by changes in some factors, such as temperature, mechanical stresses, pressure, etc., may result from an increase in the number of martensitic lamellas with their size remaining constant, from a variation in the size of lamellas with their number remaining constant, or from variations in both the size and number of lamellas. In this situation a convenient quantitative indicator of the martensitic transformation process on a mesoscopic scale is the number of interphase boundaries at some moment during the transformation. At the crystal's surface (if only one form of martensite in present), the interphase boundaries constitute a system of parallel lines, with the total number of these lines in the crystal depending on the degree of transformation.

The pattern of experimental points depicted in Fig. 10 shows how the number of interphase boundaries in a crystal of CuZnAl alloy [139] changes with the volume fraction of martensite in the process of a thermoelastic martensitic



Figure 8. (a) Expansion (1) and shrinkage (2) of a single martensitic lamella in a CuZnAl alloy [100] caused by increases and decreases in the temperature. (b) The same data in the coordinates of (2.28).



Figure 10. Number of interphase boundaries as a function of the volume fraction of martensite in the CuZnAl crystal [139].

transformation. Clearly, as the volume fraction of martensite increases, the number of interphase boundaries increases, reaches a maximum when half the crystal transforms into the martensitic state, and then, as the martensitic state becomes predominant, diminishes, and approaches zero after the completion of the transformation.

The evolution of the number of interphase boundaries depicted in Fig. 10 can be understood if we allow for the fact that an interphase boundary is a place where the amount of martensite in the crystal changes. The total area of the interphase boundaries in the crystal depends on the volume fraction of particles in phase states 1 and 2, or $A = \alpha \varphi_1 \varphi_2$ (α is a proportionality coefficient), since there are no interphase boundaries without such particles (at $\varphi_1 = 0$ or $\varphi_2 = 0$).

The area of the boundaries reaches its maximum value A_{max} at $\varphi_1 = \varphi_2 = 0.5$. Bearing in mind that $\varphi_1 = \varphi$, $\varphi_2 = 1 - \varphi$, and $\alpha = 4A_{\text{max}}$, we can find the dependence of the area of the interphase boundaries on the volume fraction of martensite:

$$A = 4A_{\max}\varphi \left(1 - \varphi\right). \tag{2.30a}$$

A comparison of (2.30a) and (2.21) shows that in a heterophase system the variation rate of the volume of the new phase (determined, for example, by temperature variations) is proportional to the area of the interphase boundaries: $\partial \phi / \partial T \propto A(T)$.

The number of interphase boundaries in the crystal, $N = A/A_0$, is

$$N = 4N_{\max}\varphi \left(1 - \varphi\right). \tag{2.30b}$$

Here $N_{\text{max}} = A_{\text{max}}/A_0$, with A_0 the one-side area of a martensitic lamella. The curve in Fig. 10 represents the dependence (2.30b) in the $(N - N_0)/(N_{\text{max}} - N_0)$, φ plane, where $N_{\text{max}} = 1600$, and $N_0 = 380$ is the number of boundaries remaining after the completion of the transition. At $\varphi = 0.5$ the width of the martensitic lamellas reaches a minimum value of about 5 µm [139].

Thus, our comparison of the results of the theory of diffuse phase transitions with experimental data on thermo-

elastic martensitic transformations in alloys with shape memory reveals satisfactory agreement between theory and experiment.

3. A mesoscopic scale of martensitic transformations

The results of Fu, Miller, and Xu [139] depicted in Fig. 10 show that in the process of a structural transition a regular spatially periodic martensitic structure forms in the crystal. In the course of the transition the structure evolves in the relative number and size of domains (martensitic lamellas), with the result that finally the entire volume of the crystal is transformed into the martensitic state.

There have been several attempts to describe, more or less extensively, the formation of spatial martensitic structures on the basis of the Ginzburg–Landau theory of phase transitions [42-47, 140, 141]. For instance, Barsch and Krumhansl [43] examined the formation of premartensitic (tweed) structures. Falk [45, 46] studied the formation of martensitic structures. The results of these studies will be discussed in Section 3.1.

In view of the limitations of the results based on the Ginzburg–Landau theory, in Section 3.2 we will develop a *kinetic* theory describing the formation of martensitic structures in real crystals. Our consideration does not claim to answer all questions concerning the formation of such structures. Its goal is to formulate the existing problems and indicate possible approaches to solving them. The *nonclassic* mechanism of formation of martensitic structures was discussed by Olson and Cohen [48].

3.1 The premartensitic state

The literature contains several discussions of the reasons for the formation of a deformation relief with a tweed structure [114-116] or an 'orange-peel' structure [142] on the crystal surface at temperatures preceding the formation of a fullscale martensitic structure in the crystal. Tanner [143] and Wen, Khachaturyan, and Morris [144] assumed that the formation of this type of structure is the result of deformations related to fluctuations in the alloy composition and, hence, are not directly related to the subsequent martensitic transition.

Noda et al. [145] interpreted the premartensitic state as a state in which the nucleation centers of the new phase formed due to fluctuations are unable to combine, because the elasticstress relaxation time is longer than the nucleation-center formation time. As the temperature lowers, this time ratio changes to an opposite one and the nucleation centers begin to elastically interact, thus forming martensitic lamellas.

Indeed, the size of deformation domains (1-10 nm) characteristic of the premartensitic state [43, 142] and the larger number density of these domains suggest that their formation may be due to the classic mechanism of heterophase fluctuations. Another factor that speaks in favor of this is that such pretransitional tweed patterns are characteristic of other types of phase transitions, e.g. ferroelectric phase transitions [146].

According to Barsch and Krumhansl [43] and Kartha et al. [147], a tweed structure on the surface of a crystal is the result of the formation of nucleation centers of the martensitic phase at temperatures above T_c , when a full-scale (heterophase) martensitic structure begins to form in the crystal. Figure 11a depicts the function $\Delta f(\eta)$ (curve 1) with a



Figure 11. (a) Free energy as a function of the order parameter and (b) the phase portrait of equation (3.3).

characteristic maximum related to the striction blocking of nucleation (see curve 5 in Fig. 4b). The dashed curve in Fig. 11a represents the first two terms in the Landau expansion (2.5a):

$$\Delta f(\eta) = f_2 \eta^2 + f_4 \eta^4 \,. \tag{3.1}$$

We see that for $0 < \eta < 0.5$ this expansion does not differ markedly from the full function $\Delta f(\eta)$.

The Ginzburg–Landau equation for the evolution of the order parameter has the form

$$\gamma \,\frac{\partial \eta}{\partial t} = \delta \,\nabla^2 \eta - \frac{\delta \Delta f}{\delta \eta} \,. \tag{3.2}$$

Here γ and δ are parameters determined from microscopic considerations and *t* is time. There are different solutions of equation (3.2) [43, 46] in the case where the potentials $\Delta f(\eta)$ are of the type depicted in Fig. 4. Below we discuss the stationary $(\partial \eta / \partial t = 0)$ solutions of this equation in a one-dimensional case. Integrating (3.2) once, we obtain

$$\frac{\delta}{2} \left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 = \Delta f(\eta) + f_0 \,, \tag{3.3}$$

where f_0 is a constant of integration and x is the coordinate. The horizontal straight line 2 in Fig. 11a represents the constant of integration $f_0 < 0$. The phase portrait of equation (3.3) for $\Delta f(\eta)$ in the form (3.1) is depicted in Fig. 11b:

$$\left(\frac{\delta}{2}\right)^{1/2} \frac{\mathrm{d}\eta}{\mathrm{d}x} = \pm \left[\Delta f(\eta) - |f_0|\right]^{1/2}.$$
(3.4)

If the conditions

$$f_2 > 0$$
, $f_4 = -|f_4| < 0$, $\alpha = 4 \frac{|f_4|}{f_2^2} |f_0| < 1$ (3.5)

are met, the equation $\Delta f(\eta) - |f_0| = 0$ has two roots:

$$\eta_{1,2}^2 = \frac{f_2}{2|f_4|} \left[1 \mp (1 - \alpha^{1/2}) \right].$$
(3.6)

In the general case the equation has three roots, $\eta_3 > \eta_2 > \eta_1$; however, since usually $\eta_3 \gg \eta_1$, the effect of the third root on the solution of this equation can be ignored to a first approximation.

We integrate (3.4) with the following boundary conditions at the edges of the crystal 0, *L*:

$$\frac{\mathrm{d}\eta}{\mathrm{d}x}\Big|_{x=0} = \frac{\mathrm{d}\eta}{\mathrm{d}x}\Big|_{L} = 0, \quad |f_0| = \Delta f(\eta(0)) = \Delta f(\eta(L)). \quad (3.7)$$

This yields [43]

$$\eta(X) = \pm \frac{\eta_1}{\left[1 - k^2 \operatorname{sn}^2(X, k)\right]^{1/2}}, \qquad (3.8a)$$
$$X = \frac{x + x_0}{A_0}, \qquad k = \left(1 - \frac{\eta_1^2}{\eta_2^2}\right)^{1/2}.$$

Here sn (x, k) is the Jacobi elliptic function (sinus amplitudinis),

$$A_{0} = \left(\frac{\delta}{2}\right)^{1/2} \int_{\eta_{1}}^{\eta_{2}} \frac{\mathrm{d}\eta}{\left[\Delta f(\eta) - |f_{0}|\right]^{1/2}} \\ = \left(\frac{\delta}{2}\right)^{1/2} \left(|f_{4}|\eta_{2}\right)^{-1} F(\pi/2, k)$$
(3.8b)

is the spatial period of the structure $[F(\pi/2, k)]$ is the Legendre complete first-kind elliptic integral], and x_0 is a constant of integration. The plus and minus signs in (3.8a) correspond to the two variants of martensite which form a twinning pair.

The deformation of the crystal related to the formation of the structure (3.8) is

$$\varepsilon(x) = \xi \eta_+(x+x_0) + \xi \eta_-(x), \qquad (3.9a)$$

where ξ is the lattice distortion acquired in its structural transformation. The constant of integration x_0 can be found from the condition of equilibrium of stresses (elastic deformations) in the crystal,

$$\overline{\varepsilon(x)} = L^{-1} \int_0^L \varepsilon(x) \, \mathrm{d}x = 0 \,. \tag{3.9b}$$

The displacement relief on the crystal surface, related to the formation of a spatially periodic martensitic structure (3.8) in the crystal, has the form

$$u(x) = \int_0^x \varepsilon(x) \,\mathrm{d}x \,. \tag{3.10}$$



Figure 12. (a) Coordinate dependence of the order parameter and (b) the deformation and (c) surface reliefs of the crystal in the premartensitic state.

Figure 12 depicts the dependences on the coordinate *x* for the order parameter given by (3.8a) ($k^2 = 0.2$, $x_0 = A/2$), the deformation relief (3.9a) ($\varepsilon_m = \xi \eta_1$), and the surface relief (3.10) ($u_m = \varepsilon_m A$) at small values of the coefficient *k* in (3.8a) (at close values of the roots η_1 and η_2). Since $\operatorname{sn}(x,k)|_{k\to 0} \to \operatorname{sin}(\pi x/A)$, where $A = \pi A_0$ is the period of the tweed premartensitic structure, we have, for $k^2 \ll 1$, the following approximate expression for the order parameter (Fig. 12a):

$$\eta(x) \approx \eta_1 \left[1 + \frac{1}{2} k^2 \sin^2 \left(\pi \frac{x}{A} \right) \right]. \tag{3.11}$$

By combining the conditions (3.5) and the notation (2.5b) we can conclude that the premartensitic structures form within the temperature interval

$$T_{\rm c} < T < \frac{3g}{2-g} T_{\rm c} \,,$$
 (3.12)

provided that the parameter of nonlinearity for the interaction of atoms in states 1 and 2 obeys the condition 0.5 < g < 2. At $\eta_1 = 0.35$, $\eta_2 = 0.62$ (Fig. 11a), and $k^2 = 0.68$ an estimate of the period of the tweed structure, $\Lambda = \pi \Lambda_0$, based on (3.8b) yields, for $\delta = 10^{-16} - 10^{-15}$ cm² and $|f_4| = 0.15$, a value of 5 to 10 nm, which is close to experimental values.

3.2 Synergetics of martensitic structures

As shown in Section 3.1, a thermodynamic approach based on the Ginzburg–Landau theory leads to reasonable results when analyzing a martensitic state at temperatures above T_c . If the same approach is used at temperatures below T_c , the results are not so good and do not describe martensitic structures observed in real crystals and the evolution of such structures with the temperature decreasing. The only result obtained from this theory concerns the formation of martensitic domain walls [45, 46].

The reason for the ineffectiveness of the thermodynamic approach in analyzing martensitic structures lies in the fact that such structures are nonequilibrium heterophase entities — the product of the transition of the crystal lattice from one structural state into another. The transition proceeds nonuniformly over the volume of the crystal and is accompanied by the formation of a large number of interphase boundaries interacting with various defects in the lattice, which limit the mobility of the boundaries and smear the transition in temperature. The martensitic structures that form as a result of such a transition are kinetic entities, which are in a quasistatic equilibrium with the thermodynamic force acting on the interphase boundaries and lattice defects.

This raises the question as to how important the critical fluctuations of the order parameter are in the formation of martensitic structures. As shown in Section 3.1, such fluctuations can be related to the onset of a premartensitic state in the form of martensitic nucleation centers with an order parameter $\eta < 1$. In a defect-containing material there should be the clusterization of martensitic nucleation centers and the formation of elementary transformation volumes with an order parameter $\eta \sim 1$ near the defects. The further growth of these entities is determined by the motion of interphase boundaries in accordance with equations (2.14) and (2.15).

According to the kinetic (synergetic) approach, the formation of martensitic structures is a process of selforganization of elementary transformation volumes. Since the transformation occurs through the motion of transformation dislocations (see Fig. 1), we can write the following expression for the relative fraction of the martensitic phase: $\varphi = h\rho\lambda$, where ρ is the number density of the transformation dislocations (steps) crossing a unit surface area, *h* is the height of a step, and λ is the mean free path of a transformation dislocation from obstacle to obstacle. Thus, the elementary transformation volume per unit dislocation length is $ah\lambda$, where *a* is the lattice constant.

Transformation dislocations, just as ordinary lattice dislocations [148, 149], may be generated by sources in the bulk of the crystal or at the crystal's surface and are capable of multiplicating, annihilating, and diffusing. Without studying these processes on a microscopic scale we can write an evolution equation for the number density of transformation dislocations in the following phenomenological form:

$$\frac{\partial \rho_1}{\partial t} = n_0 wv + \frac{v}{\lambda_{\rm m}} \rho_1 - h_{\rm a} v \rho_1 \rho_2 + \lambda_D v \frac{\partial^2 \rho_1}{\partial x^2} . \qquad (3.13a)$$

Here v is the velocity of dislocations, n_0 is the volumetric number density of the sources (sinks) of transformation dislocations, λ_m and h_a are the characteristic multiplication and annihilation distances of martensitic and austenitic steps on the interphase boundaries, λ_D is a characteristic length of

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diffusion of transformation dislocations interacting with lattice defects, *t* is the time, *x* is the coordinate in the direction perpendicular to the habit plane of martensite, and ρ_1 and ρ_2 are the number densities of martensitic and austenitic transformation dislocations (steps) at interphase boundaries.

The thermodynamic probability (intensity) of generation of dislocations $(n_0 > 0)$ or of their disappearance in sinks $(n_0 < 0)$,

$$w(T) = \left(1 + \exp\frac{\Delta U_{12}}{kT}\right)^{-1}, \qquad (3.13b)$$

is determined by expression (2.15a), according to which the probability w(T) is exponentially small at high temperatures $(T > T_c)$ and tends to unity when $T < T_c$.

By substituting $\varphi_1 = \varphi = h\rho_1\lambda$ and $\varphi_2 = 1 - \varphi = h\rho_2\lambda$ into (3.13) and performing the necessary rearrangements, we arrive at a kinetic equation for the volume density of the martensitic phase:

$$\tau \frac{\partial \varphi}{\partial t} = k_0 w + k_m \varphi - k_a \varphi (1 - \varphi) + \lambda_d^2 \frac{\partial^2 \varphi}{\partial x^2}, \qquad (3.14)$$

where $k_0 = h\lambda^2 n_0$, $k_m = \lambda/\lambda_m$, $k_a = h_a/h$, and $\lambda_d = (\lambda\lambda_D)^{1/2}$ are coefficients that determine the intensity of the corresponding processes, and $\tau = \lambda/v$ is the characteristic time.

It is interesting to analyze the stationary $(\partial \varphi / \partial t = 0)$ solutions of equation (3.14). To this end it is more convenient to write this equation in the dimensionless form

$$2 \frac{d^2 \varphi}{dX^2} = -(\psi_0 + 2\psi_m \varphi + 3\varphi^2), \qquad (3.15a)$$

where we have introduced the following notation:

$$X = \frac{x}{\Lambda_0}, \qquad \Lambda_0 = \left(\frac{3\lambda_d^2}{2k_a}\right)^{1/2},$$

$$\psi_0(T) = \frac{3k_0}{k_a} w(T), \qquad \psi_m = \frac{3}{2} \left(\frac{k_m}{k_a} - 1\right). \tag{3.15b}$$

Integrating (3.15a) with allowance for the boundary condition for an extended crystal,

$$\left. \frac{\mathrm{d}\varphi}{\mathrm{d}X} \right|_{\varphi=1} = 0\,,\tag{3.16}$$

which implies the presence of a homogeneous martensitic structure after the completion of the transition, we arrive at the equation

$$\left(\frac{\mathrm{d}\varphi}{\mathrm{d}X}\right)^2 = \Phi(\varphi)$$
$$= (1-\varphi)\left[(1+\psi_0+\psi_\mathrm{m}) + (1+\psi_\mathrm{m})\varphi + \varphi^2\right]. (3.17)$$

The general solution of this equation is a first-kind elliptic integral

$$\mu^{-1} F(\theta, k) = \int_{\varphi}^{\varphi_n} \frac{\mathrm{d}\varphi}{\sqrt{\Phi(\varphi)}} = \frac{x}{\Lambda_0} \,. \tag{3.18}$$

The form of particular solutions of equation (3.17) depends on the values and ratio of the parameters ψ_0 and ψ_m (3.15b), which determine the coefficient μ and the

modulus k of the elliptic integral and the absolute values and signs of the roots φ_n of the cubic equation $\Phi(\varphi) = 0$:

$$\varphi_{1} = 1,$$

 $\varphi_{2,3} = \frac{1}{2} \left[-(1 + \psi_{\rm m}) \pm \sqrt{(1 - \psi_{\rm m})^2 - 4(1 + \psi_{0})} \right].$
(3.19)

In turn, according to the notation (3.15b), the parameters ψ_0 and ψ_m depend on the coefficients k_0 , k_m , and k_a and the temperature.

An analysis shows that for $(1 - \psi_m)^2 < 4(1 + \psi_0)$ (curve *I* in Fig. 13) the equation $\Phi(\varphi) = 0$ has a single root, $\varphi_1 = 1$. In this case the solution (3.18) describes a spatially periodic structure,

$$\frac{x}{A} = \frac{1}{4} \frac{F(\theta, k)}{F(\pi/2, k)}, \qquad A = 4\mu^{-1} F(\pi/2, k) A_0, \qquad (3.20a)$$

with the period Λ and the width of martensitic lamellas (Fig. 14a)

$$\Delta \Lambda_{\rm M} = \frac{\Lambda}{2} \frac{F(\theta_{\rm M}, k)}{F(\pi/2, k)}, \qquad (3.20b)$$

where

$$\cos \theta_{\rm M} = \cos \theta \Big|_{\varphi=0}, \qquad \cos \theta = \frac{\mu^2 - 1 + \varphi}{\mu^2 + 1 - \varphi},$$
$$k^2 = \frac{1}{2} + \frac{1}{4} \frac{3 + \psi_m}{\mu^2}, \qquad \mu^2 = (3 + 2\psi_{\rm m} + \psi_0)^{1/2}. \quad (3.20c)$$

In the parameter region A (see Fig. 13) the width of martensitic lamellas varies from 0 to $\Lambda/2$.



Figure 13. Regions *A*, *B*, and *C* of the parameters ψ_0 and ψ_m that determine the existence of the different types of martensitic structures.

Outside region A the equation $\Phi(\varphi) = 0$ has three real roots: $\psi_3 < \psi_2 < \psi_1$. The solution (3.18) determines in this case a martensitic structure:

$$\frac{x}{A} = \frac{1}{2} \frac{F(\theta, k)}{F(\pi/2, k)}, \qquad A = \frac{4A_0}{\sqrt{1 - \varphi_3}} F(\pi/2, k),$$
$$\sin \theta = \left(\frac{1 - \varphi}{1 - \varphi_2}\right)^{1/2}, \qquad k = \left(\frac{1 - \varphi_2}{1 - \varphi_3}\right)^{1/2}.$$
(3.21a)

Figure 14. Types of martensitic structure at reduced temperatures T/T_c equal to (a) 1.022, (b) 1.008, (c) 1.004, (d) 0.992, and (e) 0.96, and (f) the temperature dependence of the volume density of the martensitic phase.

If $\psi_m > -(1 + \psi_0)$ (straight line 2 in Fig. 13) the two roots φ_2 and φ_3 are negative. Straight line 2 is the boundary of the parameter region *B*, where the width of martensitic plates,

$$\Delta \Lambda_{\rm M} = \Lambda \, \frac{F(\theta_{\rm M}, k)}{F(\pi/2, k)} \,, \qquad \sin \theta_{\rm M} = \frac{1}{\sqrt{1 - \varphi_2}} \,, \qquad (3.21b)$$

varies from $\Lambda/2$ to Λ (Fig. 14b).

The point *c* at which the dashed horizontal line (see below) intersects the straight line 2 represents a heterophase structure that is half martensite and half austenite (Fig. 14c). Finally, if $\psi_m > -(3 + \psi_0)/2$ (straight line 3 in Fig. 13), there is a region *C* where the martensitic structure is almost homogeneous (Fig. 14d). For the parameter values corresponding to the intersection of the dashed line with the straight line 3 the martensitic structure becomes homogeneous (Fig. 14e).

The dashed straight line in Fig. 13 represents the path of variation of the parameters ψ_0 and ψ_m specified in (3.15b) at $k_0/k_a = -5/3$ and $k_m/k_a = 5/3$. The arrow indicates the direction of their variation as the temperature lowers. The points *a*, *b*, *c*, *d*, and *e* in Fig. 13 correspond to the martensitic structures in Figs 14a-e. The volume fraction $\varphi(T)$ of martensite in each structure is equal to the ratio of the hatched area to the total area of one structure period: $\varphi(T) \sim \Delta A_M(T)/2A(T)$. The curve in Fig. 14f demonstrates the temperature dependence $w(T) \equiv \varphi(T)$ according to the theory of diffuse martensitic transitions [see equations (2.15b) and (3.13b)], with the four dots representing the values of $\varphi(T)$ for the martensitic structures in Figs 14a-e. Clearly, these dots fit well in the curve.

Let us estimate the size of the martensitic lamellas, $\Delta \Lambda_{\rm M}$, and the average distance Λ between them. According to the notation (3.15b), the size is determined by the characteristic scale $\Lambda_0 \sim \lambda_{\rm d} = (\lambda \lambda_D)^{1/2}$, where $\lambda_D \sim (h\lambda)^{1/2}$ is the average diffusion length for martensitic steps of height *h*, with λ being their range between obstacles along the interphase boundary. At h = 1-10 nm and $\lambda = 10-100 \,\mu\text{m}$ we have $\lambda_D = 0.1-1 \,\mu\text{m}$ and $\Delta \Lambda_M \sim \Lambda \sim 1-10 \,\mu\text{m}$, i.e. values close to those observed in experiments.

Obviously, for a diffuse martensitic transition the characteristic temperature corresponds to that moment of transition when the heterophase structure is half martensite and half austenite. This is the case when the second root of the equation $\Phi(\varphi) = 0$ vanishes, i.e. straight line 2 in Fig. 13 intersects the dashed line. The intersection point corresponds to the equality $|\psi_0(T_c(s))| = 1 + \psi_m(s)$, where $T_c(s)$ is the characteristic transition temperature dependent on the structural factor s. Taking into account the notation (3.15b) and expression (3.13b) for the thermodynamic probability w(T) at $U_{12} = \omega q (T - T_{c0})/T_{c0}$, where T_{c0} is the transition temperature with the effect of the structural factor ignored, we arrive at the following expression for the characteristic temperature:

$$T_{\rm c}(s) = T_{\rm c0} \left[1 + B^{-1} \ln \left(\frac{3|k_0|}{\left(1 + \psi_{\rm m}(s) \right) k_{\rm a}} - 1 \right) \right]. \quad (3.22a)$$

As a structural factor, we examine the effect of the size of grain in polycrystalline samples on the characteristic transition temperature. A number of researchers found [150-152] that if the grains are small, the characteristic temperature increases logarithmically with the grain size. For sufficiently large grains, the dependence reaches a plateau.

The effect of grains on the characteristic transition temperature may be related to the fact that grain boundaries serve as barriers for transformation dislocations, limiting their free path, with the result that the parameter ψ_m (3.15b) becomes dependent on the grain size *d*:

$$\psi_{\rm m}(d) = \frac{3}{2} \left(\frac{\lambda}{\lambda_{\rm m}} + \frac{\lambda}{d} - \frac{1}{3} k_{\rm a} \right). \tag{3.22b}$$

The substitution of this expression into formula (3.22a) yields the dependence of the characteristic temperature on the grain size, similar to the dependence observed in experiments [150]:

$$T_{\rm c}(d) = T_{\rm c0} \left[1 + B^{-1} \ln \left(\frac{A}{1 + d_{\rm m}/d} - 1 \right) \right]$$
$$\sim T_{\rm c0} \left[1 + B^{-1} \ln \left(A \frac{d}{d_{\rm m}} \right) \right], \qquad (3.22c)$$
$$A = \frac{6|k_0|}{3\lambda/\lambda_{\rm m} - k_{\rm a}}, \qquad d_{\rm m} = \frac{3\lambda}{3\lambda/\lambda_{\rm m} - k_{\rm a}}.$$

From (3.22c) it follows that as the grain size *d* increases, the characteristic temperature T_c increases and, for $d \ge d_m$, becomes equal to the characteristic temperature for a single crystal, T_{c0} .

Thus, the unconventional *kinetic* approach to the problem of formation of martensitic structures makes it possible to understand their morphological features, to correctly estimate the physical scale of the phenomenon, and to explain such unusual (from the viewpoint of thermodynamics) facts as the effect of the grain size on the characteristic transition temperature. The kinetic approach is based on the results of active electronic-microscope investigations of the mechanism of formation of martensitic structures done in the last decades [59–70].



4. Deformation of crystals with a shape memory effect

As a crystal lattice undergoes a thermoelastic martensitic transition, its transformation to a less symmetric form is accompanied by shear deformations ξ_{ik} and dilatations $\xi_0 = \xi_{ii}$ of the lattice. If the transformation encompasses volumes of the crystal comparable to the crystal's size, the shape of the crystal changes. The deformation of the crystal is directly proportional to the relative transformation volume (2.1):

$$\varepsilon_{ik} = m_{il}\xi_{lk}\,\varphi\big(T,\{I\},\{s\}\big)\,,\tag{4.1}$$

where m_{il} are the coefficients determining the orientation of the habit plane and the direction of shearing with respect to the crystallographic axes, and $\{I\}$ and $\{s\}$ are, respectively, the sets of external fields applied to the crystal and the structural factors influencing the kinetics of the martensitic transition.

4.1 Superelastic deformation

Formula (4.1) determines the pseudoelastic, or superelastic, deformation of a crystal due to the martensitic transformation occurring in the crystal. In the absence of external stresses, the formation of martensite is not accompanied by changes in the shape and size of the crystal, since the action of the thermodynamic forces causing the transformation is isotropic and produces self-accommodated (twinned) layers of the martensitic phase [14, 76]. In the case of cubic lattices, the full accommodation of a layer generally requires four types of martensite, and altogether the crystal may contain 24 nonequivalent variants of martensite, with the orientational factor differing in absolute value and sign.

If, for example, a uniaxial stress σ is applied to the crystal, all variants that are unfavorably oriented in relation to the stress degenerate, which causes the size of the crystal to change. The contribution of each variant to the deformation ε depends on the absolute value and sign of the orientational factor m_k and the volume fraction of this variant in the crystal, $\varphi(m_k)$:

$$\varepsilon = \sum_{k=1}^{N} \varepsilon_k , \qquad \varepsilon_k = m_k \xi_k \, \varphi(m_k) , \qquad (4.2)$$

where N is the total number of variants of martensite.

Let us suppose, for instance, that there are two selfaccommodated variants with orientational factors m_1 and $-m_1$. Then, for a diffuse martensitic transition, with allowance for (2.15a), (2.24), and (4.2), we obtain

$$\varepsilon(T,\sigma) = m_1 \xi_1 \left\{ \left[1 + \exp B \left(\frac{T - T_c}{T_c} - \frac{m_1 \sigma}{\sigma_M} \pm \frac{\sigma_f}{\sigma_M} \right) \right]^{-1} - \left[1 + \exp B \left(\frac{T - T_c}{T_c} + \frac{m_1 \sigma}{\sigma_M} \pm \frac{\sigma_f}{\sigma_M} \right) \right]^{-1} \right\}.$$
 (4.3)

Here ξ_1 is the shear deformation of the lattice under structural transformation, $\sigma_M = q/\xi_1$, and σ_f is the stress due to the pinning of interphase boundaries by obstacles, which determines the *force* hysteresis of the transformation. Equation (4.3) implies that at zero stress the crystal is not deformed.

The dependence of the stress σ on the superelastic deformation (strain) ε can be found by inverting (4.3); however, in view of the cumbersome structure of the

expression and the strong dependence of the volume fraction of martensite on the orientational factor, it is sufficient, to illustrate the curve $\sigma(\varepsilon)$, to leave only the first term in (4.3). Then [134]

$$\frac{\sigma}{\sigma_{\rm m}} = \pm \frac{\sigma_{\rm f}}{\sigma_{\rm M}} + \frac{I - I_{\rm c}}{T_{\rm c}} + B^{-1} \ln \frac{\varepsilon/\varepsilon_{\rm m}}{1 - \varepsilon/\varepsilon_{\rm m}} , \qquad (4.4)$$
$$\sigma_{\rm m} = \frac{\sigma_{\rm M}}{m_{\rm l}} , \qquad \varepsilon_{\rm m} = m_{\rm l} \xi_{\rm l} .$$

Figure 15 depicts the shape of this dependence in the process of loading (curve *I*) and unloading (curve *I'*) the crystal $(T/T_c = 1.15, \sigma_f/\sigma_M = 10^{-2}, \text{ and } B = 40)$. The dashed curve represents the dependence (4.4) in the absence of force hysteresis of transformation. A drop in the deformation temperature to $T/T_c = 1.08$ leads to a decrease in the martensitic yield stress, while a rise in the friction stress to $\sigma_f/\sigma_M = 2 \times 10^{-2}$ leads to a widening of the hysteresis loop (curves 2 and 2'). At temperatures below the transition temperature (e.g. $T/T_c = 0.98$) superelastic deformation becomes irreversible (curves 3 and 3'). The deformation can be fully restored if the unloaded crystal is heated to a temperature above the transition point (see Section 4.2).



Figure 15. Superelastic deformation curves at T/T_c equal to 1.15 (1), 1.08 (2), and 0.98 (3).

The current slope of the superelastic deformation curve in Fig. 15 is determined by the deformation (martensitic) hardening coefficient $\theta = d\sigma/d\epsilon$. According to (4.4),

$$\theta = \frac{1}{4} \theta_{\rm m} \left[\frac{\varepsilon}{\varepsilon_{\rm m}} \left(1 - \frac{\varepsilon}{\varepsilon_{\rm m}} \right) \right]^{-1}, \qquad \theta_{\rm m} = \frac{\sigma_{\rm m}}{B\varepsilon_{\rm m}}, \qquad (4.5a)$$

where θ_m is the minimum value of this coefficient at $\varepsilon/\varepsilon_m = 0.5$. In Ref. [134] it is shown that the parabolic dependence of θ on superelastic deformation is corroborated by experiments. Allowing for the fact that $\varepsilon/\varepsilon_m = \varphi$, we can write the following expression for the martensitic hardening coefficient (more precisely, its inverse):

$$\frac{\theta_{\rm m}}{\theta} = 4\varphi(1-\varphi)\,. \tag{4.5b}$$

This formula clearly demonstrates the link between the coefficient θ and the kinetics of the martensitic transition.

In conclusion of this section two remarks are in order. The first one concerns the physical meaning of formula (4.4). The left-hand side of this formula contains the deforming stress σ .

The right-hand side contains three terms, which describe the resistance to deformation. The first term is the 'dry friction' stress, determined by the pinning of the interphase boundaries by lattice defects. The second one is the thermal stress $\sigma_T = \sigma_m(T/T_c - 1)$ due to the changes in the internal energy of the crystal in its structural transformation. Finally, the third term represents the contribution to the resistance to deformation from the changes in the crystal's entropy in such a transformation: $\sigma_S = (\sigma_m/B) \ln(\varphi/(1-\varphi))$. This stress σ_S ensures the 'rubber-like' nature of the superlastic deformation of the alloy, while the thermal stress σ_T at $T > T_c$ and $\sigma = 0$ makes the transformation reversible.

The second remark concerns the deformation of polycrystalline materials. It is obvious that a superelastic deformation in a polycrystalline material is equal to the sum of deformations of individual crystallites and depends on the texture of the material, i.e. on the distribution of grains over different orientations. Bearing in mind that each crystallite with a cubic lattice may contain up to 24 different variants of martensite, we can write, to a first approximation, the following expression for the deformation of a polycrystal under uniaxial loading:

$$\varepsilon(T,\sigma) \sim \xi_1 \int_{-m_{\text{max}}}^{m_{\text{max}}} \varphi(T,\sigma,m) f(m) \,\mathrm{d}m \,, \tag{4.6}$$

where f(m) is the distribution of grains over orientations.

4.2 The shape memory effect

Figure 15 shows (curves 3 and 3') that, as the crystal is unloaded, the irreversible deformation can be of order $\varepsilon_m = m_1\xi_1$. At values $\xi_1 = 0.05 - 0.15$, characteristic of metal alloys, and $m_1 = m_{max} = 0.5$, the 'frozen' superelastic deformation may be of order 5 - 10%. The most surprising property of such alloys is that their deformation can be entirely restored ('defrosted') simply by heating the alloy to a temperature above the transition temperature. The thermal reversibility of superelastic deformations is precisely the essence of the *shape memory effect* (SME) [4, 25, 30], which plays an important role in applications.

Figure 16a illustrates the observation of the shape memory effect in an alloy, i.e. the deformation of the alloy at temperatures below T_c to, say, the magnitude ε_m (indicated by the vertical arrow) with the subsequent heating of the the loaded alloy to a temperature above T_c . The curve in Fig. 16a demonstrates the temperature dependence of the recoverable deformation [134]

$$\varepsilon = \varepsilon_{\rm m} \left[1 + \exp B \left(\frac{T - T_{\rm c}}{T_{\rm c}} - \frac{\sigma_{\rm f}}{\sigma_{\rm M}} \right) \right]^{-1} \tag{4.7}$$

at $B = 10^2$ and $\sigma_f / \sigma_M = 5 \times 10^{-2}$. If the stress σ_f contains a fraction of internal elastic microstresses, which break down the thermal isotropy of the transformation, a new decrease in temperature can restore the previous deformation of the alloy that was deformed at a low temperature. This procedure can be repeated many times, as shown in Fig. 16b, which illustrates the multiple shape memory effect.

For a different sequence of deformations and temperature variations a reversible shape memory effect is possible. The sequence is as follows: the cooling of the loaded alloy to a temperature below T_c (curve 1 in Fig. 16c), followed by the unloading of the alloy (the vertical arrow), the deformation of the crystal by a stress opposite in sign to the state in which the initial deformation is fully balanced, and the heating of the



Figure 16. Types of shape memory effect: (a) single, (b) multiple, (c) reversible, and (d) martensitic-austenitic.

crystal to a temperature above T_c . This heating leads to a partial restoration of both the primary and secondary (opposite in sign) deformations, which is illustrated by curve 2 obtained through adding the primary and secondary shapememory deformations. As seen from Fig. 16c, because of the partial balance of these deformations, the total deformation $\Delta \varepsilon$ proves to be smaller than the primary and secondary deformations taken separately.

Likhachev, Kuz'min, and Kamentseva [30] and Malygin [134] describe other sequences of deformation and heating—the cooling of a crystal with shape memory which is loaded, for instance, in the austenitic state and whose shape is recovered by increasing the temperature. An example of a complex martensitic-austenitic shape memory effect is given by curves I and 2 in Fig. 16d. The flexibility, workability, and programmability, all of which are inherent in the shape memory effect.

4.3 Hysteresis of the stress – strain curves

The stress – strain curve is one of the main characteristics of crystals with shape memory. It reflects, on a macroscopic scale, the thermoelastic martensitic transformation that takes place in the crystal. If the loading is cyclic, then the curve acquires a characteristic loop shape because of transformation hysteresis. Below we analyze how the smearing of the phase transition affects the change in the character of the hysteresis loops.

In the case of a point phase transition, in view of (2.4b), (2.24) (q = 0), and the condition of phase equilibrium (2.6), have at the following stress-strain dependence:

$$\frac{\sigma}{\sigma_0} = -\left(1 - \frac{1}{2}g\right)\frac{\varepsilon}{\varepsilon_0} - \frac{1}{2}g\left(\frac{\varepsilon}{\varepsilon_0}\right)^3 + \frac{1}{2}\frac{T}{T_0}\ln\frac{1 + \varepsilon/\varepsilon_0}{1 - \varepsilon/\varepsilon_0}, \quad (4.8)$$

where $\sigma_0 = U_0 / \varepsilon_0$ and $\varepsilon_0 = \xi_1$.



Figure 17. Hysteresis in stress – strain curves in the case of (a) point and (b) diffuse transitions at reduced temperatures T/T_0 equal to 1.1 (1), 1.0 (2), 0.5 (3), and 0.1 (4) and at reduced temperatures T/T_c equal to 1.08 (1'), 1.05 (2'), 1.03 (3'), and 1.0 (4').

Figure 17a depicts the stress – strain curves corresponding to (4.8) for a crystal undergoing a second-order phase transition (g = 0) under cyclic loading. When g > 0.5, i.e. in a first-order phase transition, the picture remains basically the same. We see that at temperatures above the transition temperature ($T_c = T_0$) the dependence $\sigma(\varepsilon)$ (curves *I* and *2*) is nonlinear, but hysteresis is absent. Hysteresis appears at temperatures below the transition temperature (curves *3* and *4*) due to the existence of a range of unstable deformations (dashed curves), when the deformation hardening coefficient $d\sigma/d\varepsilon$ becomes negative.

The character of the hysteresis loop is quite different in a smeared martensitic transition. If we take into account (4.4) and the cyclic nature of loading, we have in this case

$$\frac{\sigma}{\sigma_{\rm m}} = \pm \frac{\sigma_{\rm f}}{\sigma_{\rm M}} + \frac{T - T_{\rm c}}{T_{\rm c}} + B^{-1} \ln \frac{1 + \varepsilon/\varepsilon_{\rm m}}{1 - \varepsilon/\varepsilon_{\rm m}} \,. \tag{4.9}$$

Figure 17b shows the function $\sigma(\varepsilon)$ for different temperatures according to this equation at $B = 10^2$ and $\sigma_f/\sigma_M = 2 \times 10^{-2}$. We see that as the temperature is decreased, the deforming stresses diminish, while in a point transition they increase.

Also, in a diffuse transition there is no distinct temperature at which hysteresis emerges. Finally, the stress-strain curves for a diffuse transition are stable for all deformations $(d\sigma/d\epsilon > 0)$, since an increase in the volume of the martensitic phase requires an ever-increasing stress because of the interaction between the interphase boundaries and obstacles.

4.4 Acoustoplastic effect

As shown by experiments done by Sapozhnikov et al. [106, 107], if in addition to applying a constant stress σ to a crystal undergoing a thermoelastic martensitic transition one applies an oscillating stress $\sigma_a \cos \omega t$ of acoustic or ultrasonic frequency, the result is a change in the deforming stress. This phenomenon has been observed and widely studied in

the case of ordinary dislocation plasticity and is known as the *acoustoplastic effect* (APE) [153–157]. Obviously, acoustic (or ultrasonic) waves acting on a crystal affect the kinetics of the phase transition and favor the increase or decrease of superelastic deformation.

In the conditions of uniaxial deformation at a constant rate $\dot{\varepsilon}_0$, the total deformation ε of the crystal is equal to the sum of an elastic deformation σ/E (*E* is the elastic modulus) and a superelastic, or pseudoelastic, deformation $\varepsilon_p(T, \sigma)$:

$$\varepsilon = \dot{\varepsilon}_0 t = \frac{\sigma}{E} + \varepsilon_p(\sigma, T) \,. \tag{4.10}$$

The superelastic deformation ε_p is determined by expression (4.3). If the crystal is loaded by acoustic stresses, the crystal deformation is given by the formula

$$\varepsilon = \frac{\sigma^{\sim}}{E} + \varepsilon_{\rm p}^{\sim}(T, \sigma, \sigma_{\rm a}), \qquad (4.11)$$

where (with allowance made for the superposition of constant and oscillating stresses)

$$\varepsilon_{\rm p}^{\sim}(T,\sigma,\sigma_{\rm a}) = \int_0^{2\pi} \varepsilon_{\rm p}(T,\sigma+\sigma_{\rm a}\cos\omega t) \,\mathrm{d}(\omega t) \,. \tag{4.12}$$

Figure 18a depicts the curves of the loading and unloading of a crystal in the absence (curves *I* and *2*) and presence (curves *3* and *4*) of acoustic waves with the amplitude $\sigma_a = 0.2\sigma_M$ action on the crystal. The curves were constructed according to equations (4.10) and (4.11) with $T/T_c = 1.3$, B = 40, $m_1 = 0.5$, $\sigma_f/\sigma_M = 0.1$, $\sigma_M/E\varepsilon_m = 0.1$, and $\varepsilon_m = m_1\xi_1$.

The figure shows that, if an oscillating stress is applied to the crystal, the average deforming stress changes. This change may be either a decrease or an increase in the stress. According to (4.10) and (4.11), the acoustoplastic effect is

$$\Delta \sigma(T, \sigma, \sigma_{\rm a}) = \sigma^{\sim} - \sigma = E \left[\varepsilon_{\rm p}(T, \sigma) - \varepsilon_{\rm p}^{\sim}(T, \sigma, \sigma_{\rm a}) \right]. \quad (4.13)$$



Figure 18. Curves of superelastic deformation in the absence (1 and 2) and presence (3 and 4) of (a) acoustic oscillations and (b) the acoustoplastic effect in the cases where the crystal is loaded (1) and unloaded (2).

It depends on the temperature, the current deforming stress, and the oscillation amplitude. Figure 18b depicts the dependence of the acoustoplastic effect on the deforming stress under the loading (curve *I*) and unloading (curve *2*) of the crystal, with $\Delta \sigma_m = E\epsilon_m$. In contrast to the ordinary dislocation acoustoplastic effect, in the case of a martensitic transformation the effect of an oscillating stress on the crystal may lead not only to a decrease but also to an increase in the deforming stress.

The inversion of the sign of the acoustoplastic effect under high stresses is due to the fact that at low stresses [158]

$$\Delta \sigma \sim \Delta \sigma_{\rm m} \varphi(T, \sigma) \left[1 - I_0 \left(B \, \frac{m_1 \sigma_{\rm a}}{\sigma_{\rm M}} \right) \right] < 0 \,, \tag{4.14a}$$

while at high stresses

$$\Delta \sigma \sim \Delta \sigma_{\rm m} \varphi^{-1}(T, \sigma) \left[I_0 \left(B \, \frac{m_1 \sigma_{\rm a}}{\sigma_{\rm M}} \right) - 1 \right] > 0 \,, \qquad (4.14b)$$

where $I_0(x)$ is the zero-order modified Bessel function. These two formulas show that the acoustoplastic effect increases with the amplitude of the oscillating stress σ_a .

4.5 Effect of hydrostatic pressure

Another example of external influences on martensitic transformations is the effect of hydrostatic pressure on the superelastic deformation related to this transformation. The effect of hydrostatic pressure on thermoelastic martensitic transformations is due to the fact that, according to (2.24), it affects the phase equilibrium in the crystal if the structural transformation is accompanied by a lattice dilatation ξ_0 .

If we take into account (2.24), the dependence of the volume fraction of the martensitic phase on pressure P can be written as

$$\varphi(T,P) = \left[1 + \exp B\left(\frac{T - T_{\rm c}}{T_{\rm c}} + \frac{P}{P_0}\right)\right]^{-1},\qquad(4.15)$$



Figure 19. Dependence of the volume fraction of the martensitic phase (a) on temperature at P = 0 (1) and $P = 0.08P_0$ (2) and (b) pressure at reduced temperatures T/T_c equal to 0.95 (1), 0.9 (2), and 0.8 (3); (c) dependence of the shape memory effect on temperature; and (d) dependence of superelastic deformation on stress at P = 0 (1) and $P = 0.08P_0$ (2).

where $P_0 = q/\xi_0$. If $\xi_0 < 0$, applying hydrostatic pressure to the crystal leads to a decrease in the amount of martensite.

Figure 19a depicts the temperature dependence of the volume fraction of martensite in the absence (curve 1) and presence (curve 2) of hydrostatic pressure at B = 40. Applying a pressure $P = 0.08P_0$ to the crystal at point *a* leads to a sudden drop (*ab*) in the amount (volume fraction) of martensite by $\Delta \varphi = 0.6$. Figure 19b demonstrates the dependence $\varphi(P)$ according to (4.15) for different temperatures. Such behavior was observed in the experiments of Ullakko, Sundquist, and Pietikainen [159]. In accordance with (4.15), the characteristic transition temperature either linearly increases [104] or linearly decreases [103], depending on the sign of ξ_0 .

Hydrostatic pressure also affects the deformation properties of crystals with shape memory [103, 105]. Figure 19c depicts the temperature curves for shape-memory deformation according to (4.15) in the absence (curve *I*) and presence (curve *2*) of hydrostatic pressure. Applying the pressure $P = 0.08P_0$ to the crystal at point *a* leads to a lag (*ab*) in deformation as a function of temperature in a repeated shape memory effect. Such steps in the curves representing the shape memory effect, which appeared as hydrostatic pressure was applied to the crystal, were observed by Belyaev et al. [103] and Egorov, Belyaev, and Lobachev [105].

Figure 19d demonstrates the effect of hydrostatic pressure of the superelastic deformation curve

$$\varepsilon(T, \sigma, P) = \frac{\sigma}{E} + \varepsilon_{\rm m} \left\{ \left[1 + \exp B \left(\frac{T - T_{\rm c}}{T_{\rm c}} - \frac{\sigma}{\sigma_{\rm m}} + \frac{P}{P_0} \right) \right]^{-1} - \left[1 + \exp B \left(\frac{T - T_{\rm c}}{T_{\rm c}} + \frac{\sigma}{\sigma_{\rm m}} + \frac{P}{P_0} \right) \right]^{-1} \right\}$$
(4.16)

in the absence (curve 1) and presence (curve 2) of pressure at $\sigma_{\rm m}/E\varepsilon_{\rm m} = 0.1$, B = 40, and $T/T_{\rm c} = 1.2$. Clearly, removing the pressure $P = 0.08P_0$ at point *a* produces a jump (*ab*) in the

value of superelastic deformation. Such jumps in the superelastic deformation curves for the TiNi alloy, which appeared after the hydrostatic pressure was removed and re-applied to the crystal, were observed by Egorov, Belyaev, and Lobachev [105].

5. Internal friction in crystals with shape memory

Numerous experiments have shown that in crystals with shape memory there is a special mechanism of energy scattering due to mechanical vibrations. This mechanism is related to the movement of interphase and twin boundaries. The most thoroughly studied mechanism is the low-frequency one $(1-10^3 \text{ Hz})$, or the so-called transient internal friction [89, 160–166]. According to recent reports by Sapozhnikov et al. [106, 107], some results concerning high-frequency (10^2 kHz) internal friction in such crystals have also been obtained.

5.1 Low-frequency internal friction

Low-frequency internal friction emerges in the process of variation (increase or decrease) of the temperature in the martensitic transition temperature range. Such friction is determined by the energy scattered by the variable stress σ_a in the course of one oscillation cycle, $\Delta W = \sigma_a \Delta \varepsilon$, where $\Delta \varepsilon = \xi_1 \Delta \varphi$ and $\Delta \varphi = (d\varphi/dT)\Delta T$ are, respectively, the superelastic deformation and increment of the volume fraction of martensite caused by a variation $\Delta T = \dot{T}/\omega_0$ in temperature during one oscillation period ω_0^{-1} , with \dot{T} the rate of temperature variation.

Bearing in mind that, in the absence of a transformation, the oscillation energy is $W = (2\sigma_a)^2/E$, we arrive at the following expression for the low-frequency internal friction [160, 162]:

$$Q^{-1}(T) = \frac{\Delta W}{W} = \frac{1}{2} \frac{\xi_1 E}{\sigma_a} \frac{T}{\omega_0} \frac{\mathrm{d}\varphi}{\mathrm{d}T}.$$
 (5.1a)

Next, in view of (2.21) and (2.17), we find that, according to the theory of diffuse martensitic transitions [135],

$$Q^{-1}(T) = 4Q_{\rm m}^{-1} \,\varphi(T) \big[1 - \varphi(T) \big] \,, \qquad Q_{\rm m}^{-1} = \frac{1}{8} \, \frac{\xi_1 E}{\sigma_{\rm a}} \, \frac{\dot{T}}{\omega_0 T_{\rm c}} \, B \,.$$
(5.1b)

Figure 20a depicts the temperature dependence of the lowfrequency internal friction in a crystal as it is heated (curve *I*) and cooled (curve *2*), according to (5.1b) ($B = 10^2$) with allowance for (2.17), interphase boundary pinning ($\sigma_f/\sigma_M = 2 \times 10^{-2}$), and low-frequency internal friction in single-phase states of martensite (Q_A^{-1}) and austenite (Q_A^{-1}):

$$Q^{-1}(T) = Q_{\rm M}^{-1}\varphi + Q_{\rm A}^{-1}(1-\varphi) + 4Q_{\rm m}^{-1}\varphi(1-\varphi).$$
 (5.2)

The dashed curve represents the temperature dependence of Q^{-1} in the absence of low-frequency internal friction $(Q_{\rm M}^{-1}/Q_{\rm m}^{-1} = 0.2 \text{ and } Q_{\rm A}^{-1}/Q_{\rm m}^{-1} = 0.1)$. Such hysteresis curves are characteristic of experiments on low-frequency internal friction in alloys with shape memory [161–163].

Figure 20b depicts the temperature dependence of the internal friction coefficient for Au-Cd alloy [161] minus the background component related to friction in the single-phase states of martensite and austenite. To establish whether the temperature dependence of the internal friction coefficient for this alloy corresponds to (5.1b), it is convenient to write the latter in the form

$$\ln \frac{1 \mp \sqrt{1 - R(T)}}{1 \pm \sqrt{1 - R(T)}} = B \frac{T - T_{\rm c}}{T_{\rm c}} , \qquad R(T) = \frac{Q^{-1}(T)}{Q_{\rm m}^{-1}} .$$
(5.3)

The results of processing the data for the Au-Cd alloy according to (5.3) are given in Fig. 20c. We see that in the coordinates (5.3) the temperature dependence of internal friction in this alloy is indeed a straight line. The slope of the straight line yields B = 51.

In agreement with equation (5.1b), the experimental data confirm the dependence of the low-frequency internal friction on the rate of temperature variation [162, 163], on the frequency and amplitude of the oscillations [164], and on the concentration *C* of disperse particles in the crystal [90]. The last factor is due to the dependence [see (2.17) and (2.22)] of the smearing degree of the martensitic transition on the concentration of obstacles: $\Delta T_{\rm M} \propto B^{-1} \propto C$ [113].

5.2 High-frequency internal friction

High-frequency (10² kHz) internal friction has been observed in crystals of CuAlNi alloy [165, 166] at constant temperature and stress σ . The damping of a high-frequency oscillation with the amplitude $\varepsilon_a = \sigma_a/E$ is related to hysteretic losses.





$$\delta_{\rm h} = \frac{\Delta W_{\rm h}}{W} \, .$$

Here

$$\Delta W_{\rm h} = \int_0^{2\sigma_{\rm a}} \sigma_{\sim} \, \mathrm{d}\varepsilon_{\rm p} = \sigma_{\sim} \varepsilon_{\rm p} \Big|_0^{2\sigma_{\rm a}} - \int_0^{2\sigma_{\rm a}} \varepsilon_{\rm p} \, \mathrm{d}\sigma_{\sim} \,, \tag{5.4}$$

 $W = (2\sigma_a)^2/E$, and the pseudoelastic deformation $\varepsilon_p(T, \sigma + \sigma_{\sim})$ is given by (4.3), σ_{\sim} being the oscillatory stress.

The substitution of the explicit expression for the pseudoelastic deformation into (5.4) and the calculation of the integral yield the dependence of the decrement on temperature, stress, and the amplitude of oscillatory stresses [158]:

$$\delta_{\rm h}(T,\sigma,\sigma_{\rm a}) = \frac{\delta_{\rm m}}{s_{\rm a}^2} \left\{ \left[\frac{2s_{\rm a}}{1+A_{-}\exp\left(-2s_{\rm a}\right)} - \frac{2s_{\rm a}}{1+A_{+}\exp\left(2s_{\rm a}\right)} \right] - \left[\ln \frac{\exp\left(2s_{\rm a}\right) + A_{-}}{1+A_{-}} + \ln \frac{\exp\left(-2s_{\rm a}\right) + A_{+}}{1+A_{+}} \right] \right\}, \quad (5.5a)$$

where

$$\delta_{\rm m} = \frac{\varepsilon_{\rm m}}{2} B \frac{E}{\sigma_{\rm m}} , \qquad s_{\rm a} = B \frac{\sigma_{\rm a}}{\sigma_{\rm m}} ,$$
$$A_{\mp}(T, \sigma, \sigma_{\rm a}) = \exp B \left(\frac{T - T_{\rm c}}{T_{\rm c}} \mp \frac{\sigma}{\sigma_{\rm m}} \pm \frac{\sigma_{\rm f}}{\sigma_{\rm M}} \right) . \tag{5.5b}$$

Figure 21 depicts the amplitude dependence of the internal friction (B = 40, $T/T_c = 1.1$, and $\sigma_f/\sigma_M = 10^{-2}$) in the process of loading the crystal, according to (5.5a) for various reduced stresses σ/σ_m . Clearly, the curves representing $\delta_h(\sigma_a)$ have, in accordance with the results of Hansch and Torok [165] and Koshimitzu and Benoit [166], sections of amplitude-independent and amplitude-dependent internal friction. For the CuAlNi alloy, $\sigma_m \approx 40$ MPa [28] and $E = 6.7 \times 10^4$ MPa; therefore, according to the data depicted in Fig. 21, the deformation $\varepsilon_a = \sigma_a/E \approx 6 \times 10^{-6}$ corresponds to the beginning of amplitude-dependent internal friction [165, 166].



Figure 21. Amplitude dependence of the hysteretic internal friction at reduced stresses $\sigma/\sigma_{\rm m}$ equal to 2×10^{-2} (*I*), 10^{-1} (*2*), 2×10^{-1} (*3*), and 3×10^{-1} (*4*).

The general expression (5.5a) suggests that as $\sigma_a \rightarrow 0$ the amplitude-independent internal friction is determined by the expression

$$\delta_{\rm h}(T,\sigma,0) = \delta_{\rm m} \left\{ \left[1 + \cosh B \left(\frac{T - T_{\rm c}}{T_{\rm c}} - \frac{\sigma}{\sigma_{\rm m}} \pm \frac{\sigma_{\rm f}}{\sigma_{\rm M}} \right) \right]^{-1} + \left[1 + \cosh B \left(\frac{T - T_{\rm c}}{T_{\rm c}} + \frac{\sigma}{\sigma_{\rm m}} \pm \frac{\sigma_{\rm f}}{\sigma_{\rm M}} \right) \right]^{-1} \right\}. (5.6)$$

We see that the dependence of the decrement on stress is represented by a curve with a maximum at $\sigma \approx [(T - T_c)/T_c]\sigma_m$ if $T > T_c$ and at $\sigma \approx [(T_c - T)/T_c]\sigma_m$ if $T < T_c$.

As for the temperature dependence of amplitude-independent internal friction, it has at $\sigma = \sigma_f = 0$, according to (5.6), a maximum near the transition temperature T_c . As the stress increases, the temperature dependence ceases to be singlevalued: two maxima of internal friction appear to the right and left of the transition temperature [158].

6. The universal nature of diffuse phase transitions

In Sections 4 and 5 we established that the theory of diffuse phase transitions provides a fairly good description, both qualitative and quantitative, for the experimental data on thermoelastic martensitic transformations in crystals with shape memory. In this section we will see this theory is of a fairly universal nature and phenomenologically is also capable of describing other types of transition (such as ferroelectric and ferroelastic) and of predicting the effect of these transitions on the properties of the respective crystals. This universality is caused by the emergence of interphase boundaries and hence the heterophase state of the crystal in the transition process.

6.1 Acoustic emission

Acoustic emission accompanying a martensitic transformation can serve as an indication for the emergence of interphase boundaries and a heterophase state in the crystal undergoing this transformation [167, 168]. Experiments show that acoustic emission is related to the emergence, expansion, and disappearance of individual martensitic lamellas. To establish a relationship between the dynamic of acoustic emission and the dynamics of the martensitic transformation, it is important to bear in mind that the total acoustic emission time t_A is a constant fraction of the total transition time, $t_A/t_M \sim 10^{-3}$, irrespective of the composition of the alloy and the rate of temperature variation [168].

Allowing for the fact that $t_A/t_M \sim \Delta V_A/V$ (where ΔV_A is the volume fraction of martensite whose formation is related to acoustic emission), we arrive at the following relationship between the number of acoustic pulses, $N_A \propto \Delta V_A \propto V \propto \varphi$, and the volume fraction of the martensitic phase, $\varphi(T)$:

$$\frac{N_{\rm A}}{N_{\Sigma}} = \varphi(T) \,, \tag{6.1}$$

where N_{Σ} is the total number of acoustic pulses during the transition.

In addition to the number of pulses, their rate of emission $\dot{N}_{\rm A}$ (the number of pulses per unit time) is also determined in acoustic measurements. Experiments show (see, e.g.,

Ref. [167]) that, in the transformation, the pulse emission rate $\dot{N}_{\rm A}$ first grows, reaches a maximum $\dot{N}_{\rm max}$, and then diminishes to zero. Since in a thermoelastic transformation

$$\dot{N}_{\rm A} = \frac{{\rm d}N_{\rm A}}{{\rm d}T} \ \dot{T} \propto \frac{{\rm d}\varphi}{{\rm d}T} \,,$$

we arrive at an equation describing the dynamics of acoustic emission in the transformation [135]:

$$\frac{\dot{N}_{\rm A}}{\dot{N}_{\rm max}} = 4 \, \frac{N_{\rm A}}{N_{\Sigma}} \left(1 - \frac{N_{\rm A}}{N_{\Sigma}} \right). \tag{6.2}$$

Thus, having the experimental curves $\dot{N}_A/\dot{N}_{max} = f_A(T)$ and $N_A/N_{\Sigma} = f_N(T)$ and using equation (6.2), we can establish how these curves agree with the dynamics of the transformation.

Figure 22 depicts the results of processing the data on acoustic emission in the process of direct and reverse martensitic transitions in CuAlNi alloy [167]. Clearly, in the direct transition, good agreement between theory and experiment is observed at the ascending phase of (6.2), while in the reverse transition such agreement is observed at the descending phase. In the direct transition this corresponds to the initial stage of martensite formation, while in the reverse transition this corresponds to the final stage of austenite formation. The discrepancy between theory and experiment at some stages of the transformation may be due to the irregularity and strong heterogeneity of the phase transformation in the CuAlNi alloy.

6.2 Polarization jumps

As phase transitions occur in ferroelectric and ferroelastic materials, polarization jumps (known as Barkhausen jumps) are observed [169–172]. The number of jumps, N_P , increases in proportion to the crystal polarization P [12]. Assuming that P varies in proportion to the volume of the crystal subjected to polarization, we find that

$$\frac{N_P}{N_{\Sigma}} = \varphi(\sigma) \,, \tag{6.3}$$

where N_{Σ} is the total number of jumps on the completion of the ferroelectric transition and $\varphi(\sigma)$ is the relative fraction of the crystal's volume polarized by the mechanical stress σ . Now, bearing in mind that $dN_P/d\sigma \propto d\varphi/d\sigma \propto \varphi(1-\varphi)$, we arrive at an expression similar to (6.2):

$$\frac{1}{N_{\Sigma}}\frac{\mathrm{d}N_{P}}{\mathrm{d}\sigma} = B_{P} \frac{N_{P}}{N_{\Sigma}} \left(1 - \frac{N_{P}}{N_{\Sigma}}\right),\tag{6.4}$$

where B_P is a constant determining the quantitative relationship between the jumps and the transformation kinetics.

Figure 23a depicts the results of processing, according to (6.4), the dependences $dN_P/d\sigma = f_P(\sigma)$ and $N_P/N_{\Sigma} = f_N(\sigma)$ for crystals of Rochelle salt [169]; here $(dN_P/d\sigma)_{max} = B_PN_{\Sigma}/4$. Clearly, agreement between theory and experiment is good.

In terms of crystal polarization, the effect of mechanical stress on a ferroelectric or ferroelastic crystal is equivalent to the effect of an electric field. This means that polarization jumps produced by an electric field of strength E acting on the crystal must obey an equation similar to (6.4). Figure 23b depicts the results of processing the data of Rudyak, Shuvalov, and Kamaev [171] on polarization jumps observed in triglycine sulfate crystals according to the equation

$$\frac{1}{N_{\Sigma}}\frac{dN_P}{dE} = B_E \frac{N_P}{N_{\Sigma}} \left(1 - \frac{N_P}{N_{\Sigma}}\right).$$
(6.5)

We see qualitative agreement between theory and experiment.

6.3 Dielectric constant

As noted in Section 2.3, ferroelectric transitions in real materials are diffuse. As an example, Fig. 24a depicts the temperature dependence of the dielectric constant of lead zirconate titanate $Pb(Zr_{0,53}Ti_{0,47})O_3$ to which 11% of lead magnesium niobate $Pb(Mg_{0,33}Nb_{0,67})O_3$ is added to increase the smearing of the transition [125]. In accordance with the theory of diffuse transitions, the crystal polarization is

$$P = \overline{p} \varphi(T, E)$$

where, according to (2.24),

$$\varphi(T,E) = \left\{ 1 + \exp\left[\frac{\omega}{kT} \left(q \, \frac{T - T_{\rm c}}{T_{\rm c}} - \overline{p}E\right)\right] \right\}^{-1}.$$
 (6.6)



Figure 22. Rate of acoustic pulse emission \dot{N}_A as a function of the number of pulses N_A in (a) direct and (b) reverse martensitic transitions in CuAlNi alloy [167]. The curves correspond to equation (6.2).



Figure 23. Intensity of polarization jumps (a) for Rochelle salt subjected to mechanical loading [169] and (b) for a triglycine sulfate crystal placed in an electric field [171] as a function of the number of jumps. The curves correspond to equations (6.4) and (6.5), respectively.

For the dielectric constant

$$\varepsilon(T, E) = 1 + 4\pi \frac{\mathrm{d}P}{\mathrm{d}E} = 1 + 4\pi \overline{p} \frac{\mathrm{d}\varphi}{\mathrm{d}E}, \qquad (6.7)$$

if $E \rightarrow 0$, we obtain the expression

$$\varepsilon(T) = 1 + 4\varepsilon_{\rm m}\,\varphi(T) \big[1 - \varphi(T) \big] \,. \tag{6.8}$$

Here $\varepsilon_{\rm m} = \pi \omega \overline{p}^2 / kT_{\rm c}$, with ω the size of the Känzig region [128–133]). By substitution of (6.6) into (6.8), we finally arrive at the expression

$$\varepsilon(T) = 1 + \varepsilon_{\rm m} \cosh^{-2} \frac{T - T_{\rm c}}{\Delta T_{\varepsilon}} , \qquad (6.9)$$

where $\Delta T_{\varepsilon} = 2T_{\rm c}/B$ is the smearing of the transition over temperature.

Equation (6.9) implies that near $T \sim T_c$ the inverse of the dielectric constant ε varies with temperature according to the parabolic law

$$\frac{\varepsilon_{\rm m}}{\varepsilon - 1} = \cosh^2 \frac{T - T_{\rm c}}{\Delta T_{\varepsilon}} \sim 1 + \left(\frac{T - T_{\rm c}}{\Delta T_{\varepsilon}}\right)^2,\tag{6.10}$$

in accordance with the experimental data gathered by Tsotsorin et al. [125] and Kirillov and Isupov [127].

Agreement between theory and experiment also exists far from the transition temperature. Figure 24b depicts the results of processing the curve $\varepsilon(T)$ of Fig. 24a according to equation (6.8), in the coordinates

$$\ln \frac{1 - \sqrt{1 - R(T)}}{1 + \sqrt{1 - R(T)}} = B \frac{T - T_{\rm c}}{T_{\rm c}}, \qquad R(T) = \frac{\varepsilon(T) - 1}{\varepsilon_{\rm m}}.$$
(6.11)

The temperature dependence of the dielectric constant ε in the coordinates of (6.11) is seen to be a straight line. The slope of this straight line yields B = 12.5 at $\Delta T_{\varepsilon} = 50$ K and $T_{c} = 314$ K.

Thus, as in the case of thermoelastic structural transformations, the theory of diffuse phase transitions describes the changes in the crystal properties caused by a ferroelectric transition. The transition is diffuse because of the presence of obstacles to the motion of domain boundaries. In particular, Chattopadhyaya et al. [173] found that in the well-known ferroelectric material PbTiO₃ a decrease in the grain size *d* from 81 to 21 nm completely smears the transition, i.e. the maximum in the curve $\varepsilon(T)$ disappears. Indeed, since $\varepsilon_m \propto \omega \propto d^2$ and $\Delta T_{\varepsilon} \propto \omega^{-1} \propto d^{-2}$, grain size reduction should facilitate this process.

6.4 Ferroelastic transitions in high-temperature superconductors

In addition to a high-temperature (920 K) structural transition related to the change in the type of lattice (from tetragonal to orthorhombic), yttrium cuprate can undergo a



Figure 24. (a) Temperature dependence of the dielectric constant of lead zirconate titanate [125] and (b) the result of processing this dependence in the coordinates (6.11).

number of low-temperature structural transformations. Presumably, these transformations are due to the high lability of oxygen atoms and to their ordering in some positions in the orthorhombic lattice, which occurs as the temperature is reduced. The presence of such structural transformations is evidenced by (i) the existence of peaks of internal friction near the temperatures 70-110, 210-250, and 370 K [174-177], (ii) acoustic emission accompanying these transitions [178, 179], and (iii) deformation phenomena like the shape memory effect [174] and an increase in the strain rate [180, 181].

As an example, Fig. 25a depicts the hysteresis in the shear modulus defect caused by a cyclic variation in the stress σ and related to the motion of martensitic twin boundaries in the high-temperature superconductor YBa₂Cu₃O_{6+ δ} at 295 K [174]. For the relaxed shear modulus *G* we have the formula $G^{-1} = G_0^{-1} + \theta^{-1}$, where G_0 is the unrelaxed shear modulus and $\theta = \theta(T, \sigma)$ is the relaxational addition to the shear modulus related to the movement of the boundaries. According to the theory of diffuse martensitic transitions, the relaxation term θ is given by formula (4.5b):

$$\theta^{-1} = 4\theta_{\rm m}^{-1}\varphi(1-\varphi)\,,$$

where $\varphi(T, \sigma)$ is the volume fraction of the martensitic phase, dependent on temperature and stress and described by the formula

$$\varphi(T,\sigma) = \left\{ 1 + \exp\left[\frac{\omega}{kT} \left(q \; \frac{T - T_{\rm c}}{T_{\rm c}} + \xi_1(\sigma \pm \sigma_{\rm f})\right)\right] \right\}^{-1}.$$
(6.12)

To compare the theoretical results with the experimental data, it is convenient to examine the force dependence of the relaxed shear modulus in the form of the relationship

$$R(\sigma) = \frac{G^{-1}(\sigma) - G_0^{-1}}{G_{\min}^{-1} - G_0^{-1}} = 4\varphi(\sigma) \left[1 - \varphi(\sigma)\right].$$
 (6.13)

Here $G_0 = 9.5$ GPa, $G_{\min} = 9.24$ GPa, $G_{\min}^{-1} = G_0^{-1} + \theta_m^{-1}$, and $\theta_m = 337.6$ MPa. According to (6.12) and (6.13), the



Figure 25. Hysteresis of the shear modulus defect in the high-temperature superconductor YBa₂Cu₃O_{6+ δ} caused by a cyclic variation of the stress with a frequency of 0.1 Hz (T = 295 K) [174] (a), and the result of process in the hysteresis curves in the coordinates of (6.14) (b). Curve *I* corresponds to loading and curve 2, to unloading.

function $G(\sigma)$ in the coordinates

$$\ln \frac{1 - \sqrt{1 - R(\sigma)}}{1 + \sqrt{1 - R(\sigma)}} = B \frac{T - T_c}{T_c} + B_\sigma(\sigma \pm \sigma_f), \qquad (6.14)$$

where $B_{\sigma} = \omega \xi_1 / kT$, is represented by a straight line. As Fig. 25b shows, this is indeed the case.

7. Conclusions

The results of the last few decades of electron-microscope studies of the formation mechanism for martensitic phase nucleation centers and of the growth (expansion) of martensitic lamellas in thermoelastic martensitic transformations in metallic alloys, along with the traditional equilibriumthermodynamic approach to investigating the mechanism of phase transformation, have focussed the researchers' attention on the kinetic aspect of this phenomenon.

An obvious drawback of the purely thermodynamic approach and of the classical Ginzburg–Landau theory of phase transitions is that these theories consider only the equilibrium initial and final states of the system, while in real materials, as experiments show, a much greater role is played by kinetically equilibrated intermediate heterophase states related to the kinetics of the transition and to such its manifestations as the heterogeneous formation mechanism for the nucleation centers of the new phase and the interaction of interphase boundaries with various structural defects in the solid.

The above-discussed theory of diffuse phase transitions takes into account this kinetic aspect of phase transitions in solids, making it possible to naturally consider the effects of structural factors on the parameters of the phase transition and to quantitatively compare the results of theory and experiment. Such comparisons given in this review, using martensitic-shear, ferroelectric, and ferroelastic transitions as examples, suggest that the theory is fairly universal, independent of the type of transformation, and provides a phenomenologically correct description of the heterophase state of the material undergoing a phase transition.

Obviously, the theory of diffuse phase transition requires further development to become an instrument for the analysis of experimental data, especially the analysis of the effects of various structural factors on the parameters and kinetics of the phase transformations and on the properties of the material undergoing the phase transition.

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