External field in the Landau theory of a weakly discontinuous phase transition: Pressure effect in the martensitic transitions

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The effect of hydrostatic as well as uniaxial pressure upon proper ferroelastic (martensitic) phase transitions in cubic crystals is considered. The volumetric strain is considered to be the secondary order parameter conjugated to the symmetrized shear strain that governs the reduction of point symmetry to a tetragonal one. Corresponding terms in the Ginzburg-Landau expansion of the Gibbs free energy are analyzed for transitions of the first as well as of the second order. The pressure effect on the transition temperature as well as on the anomalies of isothermal compressibility and the linear thermal-expansion coefficient are studied and recent experimental data on thermal expansion anomalies in V_3Si, In-Tl, and Ni-Al are discussed. The nonlinearity of thermal expansion is found to imply a special relation between the shear strain and volume change that can lead to the transformation from a fcc lattice to a bcc one, as observed in the iron alloys.

I. INTRODUCTION

There is a growing attention in recent years to the physics of martensitic phase transformations in metal alloys,[1,2] though these phenomena were known by materials scientists for many years as diffusionless transformations characterized by specific transformation kinetics[3] not described by the classical nucleation theory.[4] Two different kinds of martensitic transformations are known, i.e., athermal and isothermal ones. In the athermal case the transformation begins at some start temperature M_s, but the parent phase still exists until the temperature goes down to M_f, a martensite finish point. In the isothermal case the transformation proceeds in time at a constant temperature and, generally speaking, could be completed in some finite time, which might be very long and depends in turn on the temperature. There is a particular subclass of so-called "thermoelastic" martensite within this class of transformation, which is characterized by the reversibility of a structure change—the alloy regains its high-temperature structure upon heating from a martensitic low-temperature state through the transition point. This means that the lattice of the product phase is coherent with respect to the parent one. This phenomenon gives ground for the "shape-memory effect"[5] and is, thus, of a great practical importance.

Due to a spontaneous strain release during the transformation, some elastic distortions appear in the matrix of the parent phase surrounding the martensite nuclei. The minimization of elastic long-range energy determines the shape of new phase precipitates and provides an equilibrium state that has a complicated heterogeneous structure which involves multiple twin bands for deeper relaxation of the elastic strain.[6] Thus, a real development of transformation takes place in complicated conditions of *a priori* unknown external pressure from the lattice of the parent phase upon the regions under transformation. Thus, the heterogeneity of the system makes it difficult to analyze the thermodynamic of the phase transition, and idealized single-crystal systems should be considered in order to study the equilibrium structure of the martensite phase as well as the equilibrium development of the transformation.

The reversibility of the transformation means that a phase transition between equilibrium phases takes place and the structure coherence as well as the symmetry breaking at a critical temperature implies that the transition can be analyzed within the frame of Landau theory. In this approach the difference in free energy between the parent and product phases is considered as a function of some order parameter which is equal to zero in a high-temperature symmetrical phase and becomes nonvanishing below the critical temperature.[7] The fundamental difference of the structure of a martensitic phase with respect to the parent lattice is well known to be spontaneous strain,[6] and so this phase transition belongs to the class of proper ferroelastics.[8] It means that the structure change takes place through the elastic instability of the crystalline lattice of a parent high-temperature phase with respect to a spontaneous homogeneous strain of a special kind.[9] In other words, some combination of the elastic modulii vanishes at the critical temperature.

It gives rise to the drastic lowering of the frequency of a corresponding mode of the acoustic vibration, leading to a central peak of the inelastic neutron scattering,[10] and this is the reason why this sort of phase transition is often referred to as a "soft-mode" one. Though the modes never become completely softened[11] and a finite (albeit small) jump of the order parameter is usually observed, the martensitic phase transition still may be treated as weakly discontinuous and considered in the frame of the Landau theory of a continuous phase transition. A corresponding Ginzburg-Landau expansion of the free energy in series of the symmetrized strain components has been developed[12–14] and the heterogeneous fluctuations,[15] nucleation of the martensite phase around the defects,[16] and

some other phenomena[17] were studied in such a formalism.

In the present paper the role of hydrostatic strain in the martensitic phase transitions is considered for the case of a cubic lattice of a high-temperature phase. A cubic point symmetry leads to a coupling between the shear strain and volume change in the elastic energy expansion near the critical temperature, and the volume change can be considered as an additional order parameter not related with the symmetry breaking. The coupling is shown to lead to a transition anomaly in the thermal expansion coefficient as well as in the isothermal compressibility. For the case of a first-order transition some effect is found to occur in the low-temperature phase even at the temperature region outside fluctuation-induced singularities.

The hydrostatic strain or volume change can be coupled with the order parameter in various physical systems undergoing phase transitions. For example, the macroscopical parameter for ordering transition from fcc lattice to a structure with $Pa3$ symmetry in crystalline fullerenes C_{60} has the same quadratic coupling with the volume change.[18] The results of the present study are, hence, valid in this case and the shift of the transition temperature by applied hydrostatic pressure as well as the transition anomalies of the thermal-expansion coefficient and isothermal compressibility have the same form.

The effect of the uniaxial pressure, which preserves the symmetry of the low-temperature tetragonal phase, is studied. It is an external field conjugated to the order parameter which is known[7] to suppress the continuous (second-order) phase transition for an arbitrary small field value; however, the weakly discontinuous transition is preserved under a field that is lower than the critical one. The dependence of the transition temperature on the external uniaxial as well as hydrostatic pressure is derived and the critical pressure is found.

A nonlinear analysis of the volume change shows that the elastic energy minimization can provide the fcc structure of the low-temperature phase for the bcc parent lattice through the special relationship between the shear strain and volume change. Hence, nonlinear elastic effects might be responsible for the challenging fcc-bcc martensitic transformation in pure iron and some ferrous alloys.

The paper is organized as follows. A brief description of a weakly first-order transition within Landau theory is the content of the Sec. II. The Landau theory of a proper ferroelastic (martensitic) transformation is analyzed in Sec. III. The volume change due to such a phase transition is considered in Sec. IV. Nonlinear thermal expansion and its possible contribution to the martensitic phase transition are studied in Sec. V.

II. LANDAU THEORY OF THE FIRST-ORDER PHASE TRANSITION

A. Continuous phase transition

Let us recall briefly the main ideas of the Landau theory of continuous phase transitions.[7] As Landau supposed, if the symmetry group of the low-symmetry phase G_1 is a subgroup of the symmetry group G_0 of the high-symmetry one, then there is some variable η, called an "order parameter," which is invariant under all the transformations from G_1 whereas some transformations from G_0 change it. The thermodynamic potential—the Gibbs free energy—could be expanded as a power series in η near the critical temperature. As the thermodynamic potential should not change under the symmetry transformations which do not change the structure, the η in the high-temperature phase should vanish.

The general expression for the (Ginzburg-Landau) expansion of the difference in the Gibbs free energy between the phases has the form[7]

$$\Delta\mathcal{G} = \frac{\alpha}{2}(T - T_c)\eta^2 + \frac{C}{4}\eta^4 , \tag{2.1}$$

where T_c is the critical temperature and the coefficients α and C should be positive. The equilibrium value of η is determined by the minimization of $\Delta\mathcal{G}$ with respect to η:

$$\frac{\partial\Delta\mathcal{G}}{\partial\eta} = 0 \quad \text{and} \quad \frac{\partial^2\Delta\mathcal{G}}{\partial^2\eta} > 0. \tag{2.2}$$

The solutions are the high-symmetry phase with $\eta = 0$, stable for $T > T_c$, and low-temperature phase with $\eta^2 = \alpha(T_c - T)/C$, which is stable for $T < T_c$. The dependence of η on T is continuous in the critical point T_c; hence this model describes the second-order phase transition. The Gibbs free energy

$$\Delta\mathcal{G} = -\frac{\alpha^2}{4C}(T - T_c)^2 , \tag{2.3}$$

as well as the entropy, changes continuously through the transition temperature T_c but the specific heat manifests discontinuity.[7]

The vanishing of the coefficient of second degree in the Ginzburg-Landau expansion (2.1) when the temperature approaches T_c leads to critical fluctuations of the order parameter. The mean square of the homogeneous order parameter fluctuations is given by the well-known expression[7]

$$\langle\eta^2\rangle \propto \frac{k_B T}{\alpha\,|T - T_c|^{-1}}. \tag{2.4}$$

Inhomogeneous fluctuations appear to be crucial in many cases; however, for the purposes of present study they can be neglected due to the long-range nature of the elastic interactions in solids.[19]

B. External field effect

Let us consider the effect of the external field E conjugated to the physical variable of the order parameter. In what follows it is an external pressure conjugated to the symmetrized spontaneous strain. The Ginzburg-Landau expansion takes the form

$$\Delta\mathcal{G} = \frac{\alpha}{2}(T - T_c)\eta^2 + \frac{C}{4}\eta^4 - E\eta \ , \qquad (2.5)$$

and the minimization of $\Delta\mathcal{G}$ with respect to η leads to the cubic equation

$$\frac{\partial\Delta\mathcal{G}}{\partial\eta} = \alpha(T - T_c)\eta + C\eta^3 - E = 0 \ , \qquad (2.6)$$

with discriminant

$$Q = \left(\frac{\alpha(T - T_c)}{3C}\right)^3 + \left(\frac{E}{2C}\right)^2 . \qquad (2.7)$$

It is seen that for any value of the external field E the high-symmetry phase with $\eta = 0$ no longer provides the stable solution of Eq. (2.2). Instead, we get $\eta \neq 0$ for any temperature. It is known[20] that the cubic equation has one solution in real numbers for $Q > 0$ and three for the case of $Q < 0$. It means that for temperatures below some critical one that now depends on E,

$$T_0(E) = T_c - \frac{3}{2\alpha}(2CE^2)^{\frac{1}{3}}, \qquad (2.8)$$

the additional minimum of the Gibbs free energy appears, which corresponds to a new phase. However, the initial phase described by the high-temperature solution of (2.6) provides the minimum with a lower value of the free energy and is, thus, stable. The free energy behavior as well as the order parameter dependences on the temperature for different values of the external field are shown in Figs. 1 and 2.

It is seen from Fig. 1 and it might be proved rigorously that different minima of the $\Delta\mathcal{G}(\eta)$ curve have different energies for any temperature $T < T_0$. Thus, the high-temperature state remains stable throughout all the region of the phase coexistence. Only the condition $E = 0$ leads to a degeneracy with respect to the sign of η that implies equal energies of different minima. It leads to a phase transition of the first order under the variation of the external field at constant temperature $T < T_c$. In other words, the variation of temperature and external field act on the systems described by the expression (2.5)

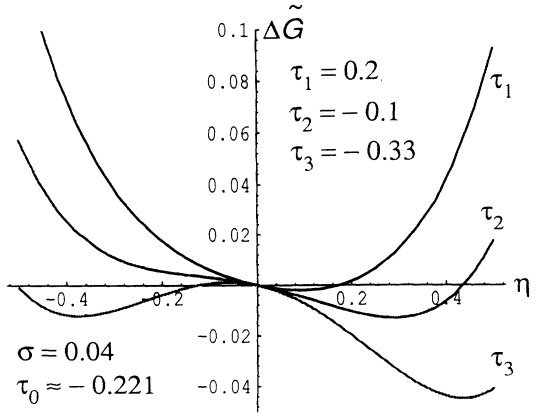

FIG. 1. The dependence of the Gibbs energy on the order parameter η under the applied field for different temperatures $\tau_1 > \tau_2 > \tau_0 > \tau_3$ in the case of the second-order phase transition.

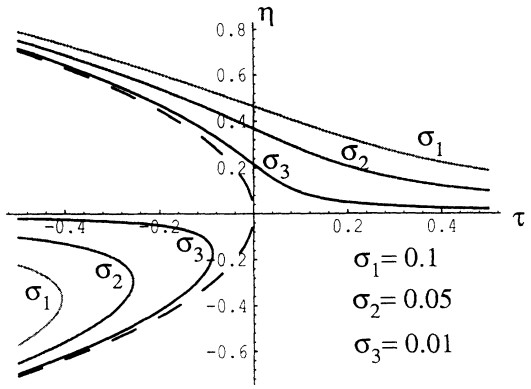

FIG. 2. The order parameter dependence on the temperature in various fields for the case of the second-order phase transition. The dashed line corresponds to the absence of an external field, $\sigma = 0$.

in a different way, because the field variation may lead to a phase change but the temperature one may not.

The external field suppress the transition; however, some decrease in

$$\frac{\partial^2\Delta\mathcal{G}}{\partial\eta^2}(T, E) = \alpha(T - T_c) + 3C\eta^2(T, E)$$

leads to enhanced fluctuations of the order parameter around T_c with a smooth peak instead of a divergence [Eq. (2.4)] shown in Fig. 3. So some transition anomalies are preserved in sufficiently small external fields E.

C. Weakly discontinuous phase transition in the Landau theory

A first-order phase transition arises in the Landau theory when the symmetry of the system allows nonvanishing third-degree invariant composed of the order-parameter component.[7,21] The corresponding term should be taken into account in the Ginzburg-Landau expansion:

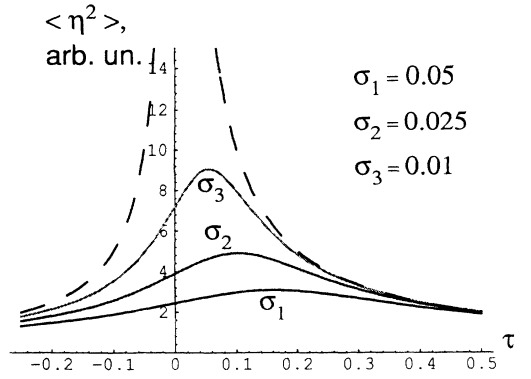

FIG. 3. Mean square of the homogeneous order parameter fluctuations around T_c ($\tau = 0$) under different external fields.

$$\Delta\mathcal{G} = \frac{\alpha}{2}(T - T_c)\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 - E\eta. \qquad (2.9)$$

Choosing the case of $B < 0$, which gives a positive η in the low-temperature phase, we can write the free energy expansion in the form

$$\Delta\tilde{\mathcal{G}} = \frac{C^3}{B^4}\Delta\mathcal{G} = \frac{\tau}{2}\zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4} - \sigma\zeta\ , \qquad (2.10)$$

with

$$\eta = -\frac{B}{C}\zeta\ ,\quad \tau = \frac{\alpha C}{B^2}\ (T - T_c)\ ,\ \text{and}\ \ \sigma = -\frac{C^2}{B^3}\ E\ .$$

1. First-order transition in the absence of an external field

For the $\sigma = 0$ case minimization of the Gibbs free energy (2.10) with respect to ζ implies the equation

$$\frac{\partial\Delta\tilde{\mathcal{G}}}{\partial\eta} = \tau\zeta - \zeta^2 + \zeta^3 = 0\ . \qquad (2.11)$$

For $\tau > \tau_0 = \frac{1}{4}$ there is only a minimum at $\zeta = 0$ corresponding to a high-temperature undistorted phase. The second minimum at $\zeta = \frac{1}{2}\left(1 + \sqrt{1 - 4\tau}\right)$ or

$$\eta = -\frac{B}{2C}\left[1 + \left(1 - \frac{4\alpha C}{B^2}\left(T - T_c'\right)\right)^{\frac{1}{2}}\right] \qquad (2.12)$$

appears at T_0 and corresponds to a low-temperature distorted phase which initially has higher free energy. The phase energies become equal at $\tau_* = \frac{2}{9}$, though the supercooling of the high-temperature state as well as superheating of the low-temperature one is possible. It means that the first-order phase transition takes place at the temperature T_*. As in the second-order case, the high-symmetry phase becomes unstable at $\tau = 0$.

At the temperature of the first-order transition T_* the order parameter jumps from $\eta = 0$ to $\eta = -\frac{2}{3}\frac{B}{C}$, overcoming the activation energy barrier $\Delta\mathcal{G}_b = \frac{1}{324}\frac{B^4}{C^3}$. The entropy now has a finite change at the transition temperature corresponding to a nonzero value of the latent heat of the transition.

In order for the weakly first-order transition to be properly identified and clearly separated from the background of critical fluctuations around T_c [Eq. (2.4)], the transition jump of the order parameter should be greater than its mean fluctuation. In other words, the energy scale of the problem should be larger than the thermal fluctuation energy k_BT. It implies the condition for the value of the third-order coefficient in the Ginzburg-Landau expansion

$$B \ \geq\ \left(C^3 k_B T_c\right)^{\frac{1}{4}}. \qquad (2.13)$$

If this condition is not satisfied, the phase transition is "too weak" to be first order and will be seen in the experiments as a continuous one.

2. Effect of the external field on the weakly discontinuous phase transition

Substituting $\zeta = \tilde{\zeta} + \frac{1}{3}$ into the Ginzburg-Landau expansion (2.10), we get with the third-order term excluded[22]

$$\Delta\tilde{\mathcal{G}} = \frac{\tilde{\tau}}{2}\tilde{\zeta}^2 + \frac{\tilde{\zeta}^4}{4} - \tilde{\sigma}\tilde{\zeta} + \Delta\tilde{\mathcal{G}}_0\ , \qquad (2.14)$$

where

$$\tilde{\tau} = \tau - \frac{1}{3}\ ,\quad \tilde{\sigma} = \sigma - \frac{\tau}{3} + \frac{2}{27}\ ,$$
$$\Delta\tilde{\mathcal{G}}_0 = \frac{\tau}{18} - \frac{\sigma}{3} - \frac{1}{108}. \qquad (2.15)$$

This is equivalent to the free energy expansion (2.5) for the second-order phase transition under the external field, the only difference consisting of the term $\Delta\tilde{\mathcal{G}}_0$ that is independent of $\tilde{\zeta}$. It appears because the free energy is counted with respect to the $(\zeta = 0)$ or $(\tilde{\zeta} = -\frac{1}{3})$ state, which implies $\Delta\tilde{\mathcal{G}}_0 = \Delta\tilde{\mathcal{G}}(\tilde{\zeta} = 0) \neq 0$.

The condition (2.2) leads to cubic equation (2.6) with the effective temperature $\tilde{\tau}$ and field $\tilde{\sigma}$ instead of the real ones. The sign of the discriminant

$$Q = \left(\frac{\tilde{\tau}}{3}\right)^3 + \left(\frac{\tilde{\sigma}}{2}\right)^2 \propto 4\sigma + 27\sigma^2 - 18\sigma\tau - \tau^2 + 4\tau^3 \qquad (2.16)$$

of this equation indicates whether it has one root or three roots in real numbers. The latter case corresponds to the appearance of different minima on $\Delta\tilde{\mathcal{G}}(\tilde{\zeta})$, the second minima of the free energy appearing when $Q(\tau, \sigma) < 0$.

Hence, (2.14) can be considered as the Ginzburg-Landau expansion for the phase transition between the states, related with different minima of the Gibbs free energy. The minima have nonzero values of the order parameter, because the symmetry is broken already by the applied field for any temperature. As there is no symmetry breaking, it is not a true phase transition, described by Landau theory; however, the undistorted phase with $\zeta = 0$ can be treated as an analog of ideal high-symmetry "praphase"[23] that would allow the symmetry reduction to both of the phases which provide minima of the free energy. It is interesting to note that the first-order phase transition in the absence of an external field appears to be equivalent to the second-order one under the action of an "effective" external field; the only feature of this situation is the zero value of η for one of two minima of $\Delta\tilde{\mathcal{G}}(\tilde{\zeta})$.

The phase diagram in (τ, σ) plane is shown in Fig. 4. An additional minimum of the free energy appears for $\sigma_1 \leq \sigma \leq \sigma_2$ with

$$\sigma_{1,2} = -\frac{2}{27}\left[1 \pm (1 - 3\tau)^{\frac{3}{2}}\right] + \frac{\tau}{3}, \qquad (2.17)$$

which leads to hysteresis with respect to the external field $\Delta\sigma = \frac{4}{27}(1 - 3\tau)^{\frac{3}{2}}$.

According to an analogy with the second-order phase

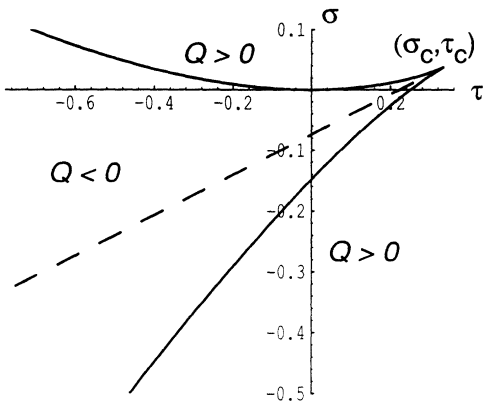

FIG. 4. The region of the phase coexistence. The dashed line corresponds to points of the first-order phase transition. It terminates in the critical point ($\tau_c = 1/3, \sigma_c = 1/27$).

transition described by (2.5), the different minima of the $\Delta\tilde{\mathcal{G}}(\tilde{\zeta})$ have equal energy only at $\tilde{\sigma} = 0$. This is the condition of the first-order phase transition between corresponding phases and it determines the effect of the applied field on the transition temperature τ_*:

$$\tau_*(\sigma) = 3\,\sigma + \frac{2}{9}\ . \tag{2.18}$$

For $\sigma = 0$ we get naturally $\tau_*(0) = \frac{2}{9}$. Equation (2.18) corresponds to the straight line on the (τ, σ) plane (Fig. 4). For $\tau > \frac{1}{3}$ on this line the equilibrium phase has $\zeta = \frac{1}{3}$. This state is an analog of undistorted high-symmetry phase of Landau theory without an external field which is unstable for $\tau < \frac{1}{3}$ and becomes a maximum of $\Delta\tilde{\mathcal{G}}$, i.e., the energy barrier with a height of

$$\mathcal{E}_b = \frac{9}{4}\sigma^2 - \frac{\sigma}{6} + \frac{1}{324},$$

for the first-order transition between two different minima with $\tilde{\zeta}_{1,2} = \pm\sqrt{-\tilde{\tau}}$, separated by the order parameter discontinuity

$$\Delta\tilde{\zeta} = \Delta\zeta = \frac{2}{3}\sqrt{1 - 27\sigma}\ . \tag{2.19}$$

As this line of the first-order transition in the phase diagram at (τ, σ) plane separates states without a symmetry-breaking relationship,[7] it terminates in a critical point ($\tau_c = \frac{1}{3}, \sigma_c = \frac{1}{27}$). The discontinuity in the order parameter as well as the potential barrier separating different minima of the free energy vanishes when approaching this critical point. There is no transition for $\sigma > \sigma_c$ or $\tau > \tau_c$, which means suppressing the weakly first-order phase transition under the fields greater than the critical one. In contrast with the second-order case where an arbitrary small external field destroys the phase transition, here we find that fields lower than σ_c preserve the transition. The critical point is an analog of the continuous phase transition from the state with $\tilde{\zeta} = 0$ corresponding to the breaking of symmetry with respect to the change of the $\tilde{\zeta}$ sign.

III. PROPER FERROELASTIC PHASE TRANSITION

A phase transition characterized by the appearance of a spontaneous strain at the transition temperature is called ferroelastic.[8] When this spontaneous strain describes the symmetry breaking at the transition, and is, thus, an order parameter, the proper ferroelastic transition takes place. For the case of improper ferroelastics the spontaneous strain is a complimentary order parameter, coupled with the primary one.

The free energy difference between the parent and product phases for the case of a proper ferroelastic transition is due to the elastic strain and corresponds to the Ginzburg-Landau expansion of the elastic energy in series of the strain components.[12] The second-order term in the Ginzburg-Landau expansion is a linear combination of the second-order elastic constants that vanish at the critical temperature. It is the eigenvalue of the lattice stiffness matrix corresponding to the relevant irreducible representation of the symmetry group of the high-temperature phase.[7] The strain tensor components transforming with respect to this representation form the order parameter and the phase transition belongs to the so-called "soft-mode" class, because it is accompanied by a noticeable softening of the corresponding acoustic mode of atomic vibrations,[19] visible as a central peak of the inelastic neutron scattering.

A. Spontaneous strain in a cubic lattice

In what follows the case of cubic symmetry of a high-temperature phase will be considered, which describes the martensitic transformations in the $A15$ compound[24] as well as in some metallic alloys. The spontaneous strain tensor has only diagonal components and the order parameter is composed of their symmetrized linear combinations,[12]

$$\eta_1 = \frac{1}{\sqrt{6}}(-\epsilon_{xx} - \epsilon_{yy} + 2\epsilon_{zz})\ , \tag{3.1}$$

$$\eta_2 = \frac{1}{\sqrt{2}}(\epsilon_{xx} - \epsilon_{yy})\ . \tag{3.2}$$

The η_1 corresponds to the extension along the z axis without a volume change and η_2 describes the strain nontetragonality in the XY plane. The critical acoustic mode is transverse phonons distributing in $\langle 110\rangle$ directions.

The elastic free energy expansion can be written in the Ginzburg-Landau form[25]

$$\Delta\mathcal{G} = \frac{A}{2}(\eta_1^2 + \eta_2^2) + \frac{B}{3}\eta_1(\eta_1^2 - 3\eta_1\eta_2^2) + \frac{C}{4}(\eta_1^2 + \eta_2^2)^2\ , \tag{3.3}$$

with the following combination of the elastic constants as the coefficients:[13]

$$\frac{A}{2} = \frac{\alpha}{2}(T - T_c) = \frac{1}{2}(C_{11} - C_{12}) , \quad (3.4)$$

$$B = \frac{1}{6\sqrt{6}}(C_{111} - 3C_{112} + 2C_{123}) , \quad (3.5)$$

$$C = \frac{1}{48}(C_{1111} + 6C_{1112} - 3C_{1122} - 8C_{1123}) . \quad (3.6)$$

Substituting

$$\eta_1 = \eta \sin\theta \quad \text{and} \quad \eta_2 = \eta \cos\theta ,$$

we get the Ginzburg-Landau expansion in the form

$$\Delta\mathcal{G} = \frac{\alpha}{2}(T - T_c)\eta^2 - \frac{B}{3}\eta^3 \sin(3\theta) + \frac{C}{4}\eta^4 . \quad (3.7)$$

The minimization with respect to θ,

$$\frac{\partial \Delta\mathcal{G}}{\partial\theta} = -B\eta^3 \cos(3\theta) = 0 \quad \text{and} \quad \frac{\partial^2 \Delta\mathcal{G}}{\partial^2\theta} > 0,$$

implies $\sin(3\theta) = \pm 1$ depending on the sign of B. In the case of $B < 0$ we get three solutions

$$(\eta, 0) , \quad \left(-\frac{1}{2}\eta, \frac{\sqrt{3}}{2}\eta\right) , \quad \text{and} \quad \left(-\frac{1}{2}\eta, -\frac{\sqrt{3}}{2}\eta\right) , \quad (3.8)$$

corresponding to the low-symmetry tetragonal phases obtained by the extension of the parent cubic lattice along three coordinate axes. The free energy dependence on η for these minima is the single-component Ginzburg-Landau expansion (2.9) for the weakly discontinuous phase transition. As the solutions are related through the symmetry transformation from the cubic point symmetry group and, thus, are completely equivalent, we can consider further only one of them, e.g., $(\eta, 0)$, without loss of generality. Hence, we can use Landau theory for the case of a single-component order parameter.

Cubic symmetry allows the third-order term in the Ginzburg-Landau expansion to appear; hence, Landau theory says that the phase transition should be of first order. Indeed, for the case of Ni-Al and some other systems partial mode softening takes place and a finite strain appears at the transition, though the shear modulus decreases considerably near the phase transition temperature. Some other so-called "pretransformation" phenomena were found in a number of alloys.[26–29] This case corresponds to the weakly first-order transition mentioned in Sec. II C.

However, this third-degree term appears to be very small in In-Tl, V_3Si, and some other alloys[30] where the critical mode becomes almost completely softened; i.e., the shear modulus $(C_{11} - C_{12})$ vanishes as temperature goes to T_c. The central peak of the inelastic neutron scattering as well as other critical phenomena appears and the order parameter undergoes a very small change at the critical temperature T_c.[31] So the transition is very weakly discontinuous, being sometimes of second order within experimental accuracy. The considerable enhancement in the acoustic wave magnitude occurs in the vicinity of the critical temperature T_c. Hence, this case corresponds to the second-order phase transformation considered in Sec. II A.

B. Effect of external stress on the transition

An applied pressure gives rise the "external" stress tensor $\hat{E}$ corresponding to the linear term $-\hat{\epsilon}\hat{E}$ in the free energy expression.[32] The symmetry-breaking strain components are sensitive only to diagonal components of $\hat{E}$; hence, relevant external stress is a superposition of the hydrostatic pressure $P = \mathrm{Tr}(\hat{E})/\sqrt{3}$ with ones applied (uniaxially) along the z axis,

$$E_1 = (-E_{xx} - E_{yy} + 2E_{zz})/\sqrt{6} , \quad (3.9)$$

and within XY plane,

$$E_2 = \frac{1}{\sqrt{2}}(E_{xx} - E_{yy}).$$

Hence, E_1 and E_2 are external fields, conjugated to the primary order parameter components η_1 and η_2, respectively, whereas the hydrostatic pressure will be shown below to affect the ferroelastic phase transition through the volume change η_0 related to the order parameter by the coupling term proportional to $\eta_0(\eta_1^2 + \eta_2^2)$.

The applied nonhydrostatic pressure $E_{1,2}$ breaks the symmetry of the undistorted phase, moving out the corresponding minimum of $\Delta\mathcal{G}(\eta_1, \eta_2)$ from the origin and lifts the degeneracy between three low-symmetry phases [Eq. (3.8)]. The pressure which is coaligned with the spontaneous strain corresponding to one of these solutions, e.g., $(\eta_1, 0)$, preserves the tetragonal symmetry of the distorted phase and the pressure value E_1 is an external field conjugated to the value of the symmetrized strain η_1 as a single-component order parameter, considered in Sec. II C 2. Otherwise the stable low-temperature state of the system has a rhombohedral lattice with three different lattice parameters, which is characterized by the pressure-dependent η_1 and η_2. In what follows the effect of the uniaxial pressure E_1 conjugated to η_1, which preserves the tetragonal symmetry of low-temperature phase, is analyzed.

In agreement with the analysis of Sec. II B the uniaxial pressure was found[33] to suppress the ferroelastic phase transition from a cubic to tetragonal lattice in the V_3Si compound, where the third-order term is very small and the transition is of second order. For the Ni-Al alloy, where the first-order phase transition takes place, the uniaxial pressure appears[34] to shift the transition temperature linearly in complete agreement with Eq. (2.18). It should be noted that though this alloy exhibits a martensitic transition where spontaneous homogeneous strain is accompanied by a so-called shuffle[11] related to the $q \neq 0$ critical mode, the central peak of the inelastic neutron scattering as well as a noticeable softening of the $C_{11} - C_{12}$ elastic constant appears well above the transition temperature. Hence, this case can also be analyzed in the frame of the Landau theory of ferroelastic phase transitions.

IV. VOLUME CHANGE IN THE ELASTIC ENERGY EXPANSION

If the phase transition is sensitive to an applied external hydrostatic pressure, then there is a difference in the volume of the elementary cell of the parent and product phases. The volume change, indeed, takes place in some cases and it was shown[35] that a virtual volumetric strain could reduce the potential barrier for the system to overcome in the phase transition development. In order to analyze the volume change one needs to include corresponding terms into the Ginzburg-Landau expansion of the Gibbs free energy. Then the equilibrium state of the system should provide the minimum of the free energy with respect to both shear and volumetric strains.

A. Linear energy of the thermal expansion

In the linear elasticity theory[32] the trace of a strain tensor is a measure of the volume change, the corresponding symmetrized linear combination of the strain components having the form

$$\eta_0 = \frac{\mathrm{Tr}(\hat{\epsilon})}{\sqrt{3}} = \frac{1}{\sqrt{3}}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}). \tag{4.1}$$

Due to thermal strain as well as external pressure, the expansion of the elastic energy in a series of η_0 should start with the linear terms[32]

$$\Delta\mathcal{G}_0(\eta_0) = -\kappa_0 A_0 (T - T_R)\eta_0 + \frac{A_0}{2}\eta_0^2 + P\eta_0, \tag{4.2}$$

where T_R is some reference temperature for the volume change, κ_0 and A_0 are the volume thermal expansion coefficient and bulk modulus, respectively, and P is the applied external pressure. The bulk modulus $A_0 = \frac{1}{\sqrt{3}}(C_{11} + 2C_{12})$ is always positive.

The minimization of $\Delta\mathcal{G}_0(\eta_0)$ with respect to η_0 implies equilibrium values of $\eta_0(T)$ and $\Delta\mathcal{G}_0(T, P)$:

$$\eta_0 = \kappa_0(T - T_R) - \frac{P}{A_0}\ , \tag{4.3}$$

$$\Delta\mathcal{G}_0 = -\frac{A_0}{2}\kappa_0^2(T - T_R)^2 - \frac{P^2}{2A_0} + \kappa_0 P(T - T_R)\ . \tag{4.4}$$

It is easy to see that usual thermodynamical expressions for the isothermal compressibility β_T and thermal expansion coefficient,

$$\beta_T = -\frac{\partial^2 \Delta\mathcal{G}_0}{\partial P^2} = -\frac{\partial \eta_0}{\partial P} = \frac{1}{A_0}\ , \tag{4.5}$$

$$\kappa_0 = \frac{\partial^2 \Delta\mathcal{G}_0}{\partial P \partial T} = \frac{\partial \eta_0}{\partial T}\ , \tag{4.6}$$

are satisfied for such an expression of the Gibbs free energy if one bears in mind that P is opposite of the pressure *inside* the system, which is a thermodynamical variable (we also put the volume of the whole system equal to 1 for convenience).

B. Effect of the volume change on the ferroelastic phase transition

The lowest-order term of coupling between the shear strains $\eta_{1,2}$ and volume change η_0 for the case of a cubic symmetry of the high-temperature phase is[13]

$$\Delta\mathcal{G}_{\mathrm{int}} = D\eta_0(\eta_1^2 + \eta_2^2), \tag{4.7}$$

where $D = \frac{1}{2\sqrt{3}}(C_{111} - C_{123})$. Substituting this term into the expansion of the elastic energy in a power series of the volume change, we get the expression (4.3) for the equilibrium value of η_0 in the form

$$\eta_0 = \kappa_0(T - T_R) - \frac{P}{A_0} - \frac{D}{A_0}(\eta_1^2 + \eta_2^2)\ . \tag{4.8}$$

The coupling term does not induce any anisotropy in the (η_1, η_2) plane; hence, three equivalent minima of the Gibbs free energy at low temperature have a form (3.8). We consider one particular solution of the form $(\eta_1, 0)$. The uniaxial pressure E_1 applied along the Z axis does not break the tetragonal symmetry of the corresponding low-temperature phase. Thus, it is an external field conjugated to the η_1 order parameter and we can use the results of Sec. II C 2 to study its influence on the phase transition. The volume change η_0 as well as its derivatives—the thermal expansion coefficient κ and isothermal compressibility β_T—does not depend directly on E_1, but only follows the dependence of the symmetrized shear strain η_1 through Eq. (4.8).

The general expression for the free energy has the form

$$\Delta\mathcal{G} = \Delta\mathcal{G}_0 + \Delta\mathcal{G}_1 + \Delta\mathcal{G}_{\mathrm{int}}\ , \tag{4.9}$$

where $\Delta\mathcal{G}_1$ is the Ginzburg-Landau expansion (2.9) with respect to η_1 as the single-component order parameter with the included effect of applied uniaxial pressure E_1 [Eq. (3.9)]:

$$\Delta\mathcal{G}_1 = \frac{\alpha_1}{2}(T - T_c)\eta_1^2 + \frac{B_1}{3}\eta_1^3 + \frac{C_1}{4}\eta_1^4 - E_1\eta_1\ . \tag{4.10}$$

Substituting (4.8) with $\eta_2 = 0$ into Eq. (4.9) and taking T_c as a reference temperature T_R for the volume change, we get the following renormalized Ginzburg-Landau expansion of $\Delta\mathcal{G}$ in the power series of η_1:

$$\Delta\mathcal{G}(T, P, \eta_1) = \Delta\mathcal{G}_0 + \frac{A'(T,P)}{2}\eta_1^2 + \frac{B'}{3}\eta_1^3 + \frac{C'}{4}\eta_1^4 - E_1\eta_1, \tag{4.11}$$

with the coefficients

$$A'(T,P) = \alpha'(T - T_c') = \left((\alpha_1 + 2\kappa_0 D)(T - T_c) - \frac{2PD}{A_0}\right), \tag{4.12}$$

$$B' = B_1 \quad \text{and} \quad C' = C_1 - \frac{2D^2}{A_0} \ . \tag{4.13}$$

Here $\Delta\mathcal{G}_0\,(T,P)$ is the energy of a high-symmetry phase with $\eta_1 = 0$, given by (4.4). The critical temperature

$$T_c' = T_c + \frac{2DP}{A_0(\alpha_1 + 2\kappa_0 D)} \tag{4.14}$$

is shifted by the applied hydrostatic pressure

$$\frac{dT_c}{dP} = \frac{2D}{A_0(\alpha_1 + 2\kappa_0 D)} \ , \tag{4.15}$$

in agreement with experimental studies, e.g., in In-Tl alloys.[36] The new stiffness is given by the formula

$$\alpha' = \alpha_1 + 2\kappa_0 D \ . \tag{4.16}$$

In order for Eq. (4.11) to be considered as an analog of Eq. (2.9), α' and C' should be positive.

The inequality $C' < C_1$ corresponds to the smoothening of the potential relief when additional degrees of freedom appear, which allows the system to relax easily. It should be noted that the inclusion of the terms corresponding to the possible volume change into the Ginzburg-Landau expansion (4.10) does not affect the third-order term B_1; hence, the order of the phase transition could not be changed by the applied hydrostatic pressure.

As the hydrostatic pressure changes the transition temperature according to Eq. (4.15), the line (2.18) of the first-order phase transition becomes a surface in the three-dimensional (3D) (T, P, E_1) phase diagram given by the formula

$$T_*'(P, E_1) = T_c + \frac{2B_1^2}{9\alpha' C'} + \frac{2D}{\alpha' A_0} P - \frac{3C'}{\alpha' B_1} E_1 \ . \tag{4.17}$$

The transition can be induced by a variation of the hydrostatic pressure under fixed values of temperature T and uniaxial pressure E_1 at the point

$$P_*(T, E_1) = \frac{\alpha' A_0}{2D}\,(T - T_c) - \frac{A_0 B_1^2}{9DC'} + \frac{3A_0 C'}{2DB_1} E_1 \ . \tag{4.18}$$

The critical point of the end of the transition line (2.18) is now a line in the (T, P, E_1) phase diagram given by the uniaxial pressure $E_c = -B_1^3/(27C'^2)$ and the critical hydrostatic one that depends linearly on the temperature,

$$P_c(T) = \frac{A_0}{2D}\left(\alpha'(T - T_c) - \frac{B_1^2}{3C'}\right) \ ,$$

and vanishes when T goes to $T_{cp} = T_c + B_1^2/(3\alpha' C')$. It means that some values of the hydrostatic pressure suppress the transition, caused by the change of the uniaxial pressure E_1. The closer the temperature is to T_{cp}, the smaller the hydrostatic pressure needed for the transition to disappear.

C. Transition anomalies of isothermal compressibility, thermal expansion coefficient, and specific heat

The isothermal compressibility and thermal expansion coefficient are expressed by Eqs. (4.5) and (4.6), respectively, along with the specific heat through the second derivatives of $\Delta\mathcal{G}(T, P, \eta_1)$ with respect to the temperature and hydrostatic pressure for an equilibrium value of η_1 given by the condition (2.2) in the form

$$\mathcal{F}(A', \eta_1) = A'\,\eta_1 + B_1\,\eta_1^2 + C'\,\eta_1^3 - E_1 = 0 \ . \tag{4.19}$$

For the first derivative we have the formula

$$\frac{\partial}{\partial T}\,(\Delta\mathcal{G} - \Delta\mathcal{G}_0) = \frac{\partial \Delta\mathcal{G}}{\partial A'}\,\frac{\partial A'}{\partial T} + \frac{\partial \Delta\mathcal{G}}{\partial \eta_1}\,\frac{\partial \eta_1}{\partial T} \ . \tag{4.20}$$

The second term in this expression vanishes for the equilibrium η_1 given by Eq. (2.2) and taking into account Eq. (4.12) we get the formula

$$\frac{\partial}{\partial T}\,(\Delta\mathcal{G} - \Delta\mathcal{G}_0) = \alpha'\,\frac{\eta_1^2}{2} \ , \tag{4.21}$$

which leads to the following expression for the transition anomaly of the specific heat:

$$\Delta C_P = -T\frac{\partial^2}{\partial T^2}\,(\Delta\mathcal{G} - \Delta\mathcal{G}_0) = -\alpha'^2\,T\,\eta_1\,\frac{\partial \eta_1}{\partial A'} . \tag{4.22}$$

For the isothermal compressibility and thermal expansion coefficient we get analogous expressions:

$$\Delta\beta_T = -\frac{\partial^2}{\partial P^2}\,(\Delta\mathcal{G} - \Delta\mathcal{G}_0) = -\frac{4D^2}{A_0^2}\,\eta_1\,\frac{\partial \eta_1}{\partial A'} \ , \tag{4.23}$$

$$\Delta\kappa = \frac{\partial^2}{\partial P \partial T}\,(\Delta\mathcal{G} - \Delta\mathcal{G}_0) = -\frac{2D\alpha'}{A_0}\,\eta_1\,\frac{\partial \eta_1}{\partial A'} \ . \tag{4.24}$$

It is easy to see that the Keesom-Ehrenfest relationships[7]

$$\frac{dT_c}{dP} = \frac{\Delta\beta_T}{\Delta\kappa} = \frac{T\Delta\kappa}{\Delta C_P} \tag{4.25}$$

are satisfied.

Differentiating both sides of Eq. (4.19) we get

$$\frac{\partial \eta_1}{\partial A'} = -\frac{\partial \mathcal{F}}{\partial A'}\left(\frac{\partial \mathcal{F}}{\partial \eta_1}\right)^{-1} \ ,$$

and resolving (4.19) with respect to A', we can finally obtain the expression

$$\eta_1\,\frac{\partial \eta_1}{\partial A'} = -\frac{\eta_1^3}{E_1 + B_1\,\eta_1^2 + 2C'\,\eta_1^3} \ . \tag{4.26}$$

D. Second-order case

Let us consider the case of the martensitic phase transition of second order for which $B_1 = 0$. In absence of uniaxial pressure (4.26) does not depend on η_1 and,

hence, neither on temperature nor on hydrostatic pressure:

$$\eta_1 \frac{\partial \eta_1}{\partial A'} = -\frac{1}{2C'} .$$

A low-temperature phase appears at T_c' with continuous evolution of the order parameter, which gives the volume difference between the parent and product phases,

$$\Delta\eta_0 = -\frac{\alpha' D}{A_0 C'} (T_c' - T) , \tag{4.27}$$

and the discontinuities of the isothermal compressibility, thermal expansion coefficient, and specific heat at the phase transition take the forms

$$\Delta\beta_T = \frac{2}{C'} \left(\frac{D}{A_0}\right)^2 = \frac{2D^2}{A_0^2 C_1 - 2A_0 D^2} , \tag{4.28}$$

$$\Delta\kappa = \frac{\alpha'}{C'} \frac{D}{A_0} = \frac{(\alpha_1 + 2\kappa_0 D)D}{A_0 C_1 - 2D^2} , \tag{4.29}$$

$$\Delta C_P = \frac{T_c'}{2} \frac{(\alpha')^2}{C'} = T_c' \frac{A_0(\alpha_1 + 2\kappa_0 D)^2}{2(A_0 C_1 - 2D^2)} . \tag{4.30}$$

Thus, to find three independent parameters of the model, α', C', and $\frac{D}{A_0}$, we have four measurable values ΔC_P, $\Delta\beta_T$, $\Delta\kappa$, and

$$\frac{dT_c}{dP} = \frac{2}{\alpha'} \frac{D}{A_0}, \tag{4.31}$$

which are related by Eq. (4.25).

As was mentioned above, for the case of the second-order ferroelastic phase transition considerable critical fluctuations take place due to the softening of the $C_{11} - C_{12}$ shear modulus. The inhomogeneous fluctuations $\eta_1(\mathbf{x})$ appear to be relevant only in very close vicinity of the critical temperature.[19] From Eq. (2.4), which describes the homogeneous order parameter fluctuations taking into account Eq. (4.8), we get the following expressions for the critical fluctuations of the volume:

$$\eta_0 \propto -\frac{D}{A_0} |T - T_c|^{-1} \tag{4.32}$$

and the thermal expansion coefficient

$$\kappa = \frac{\partial \Delta\eta_0}{\partial T} \propto \frac{D}{A_0} |T - T_c|^{-2} \tag{4.33}$$

in the temperature interval around T_c, where the fluctuations in η_1 are important.

There are some experimental data available on the anomalies of the thermal expansion in the single-crystal specimens near the martensitic phase transition[37] which are in an agreement with the above results. In most of the alloys the thermal expansion coefficient increases near T_c', which implies the positiveness of D. Outside the temperature region of thermal fluctuations the thermal expansion coefficient does not depend on the temperature. Besides, the linear model of Eq. (4.2) leads to the independence of κ on the applied hydrostatic pressure.

The second-order phase transition disappears under the applied external field E_1; hence, C_P, β_T, and κ manifest continuous behavior near the temperature T_c under an arbitrary small external field. However, from Eq. (4.26) we get in such a case

$$\eta_1 \frac{\partial \eta_1}{\partial A'} = -\frac{\eta_1^3}{2C'} \left(\frac{E_1}{2C'} + \eta_1^3\right)^{-1} . \tag{4.34}$$

For sufficiently small values E_1 of the external uniaxial pressure the difference in the isothermal compressibility, thermal expansion coefficient, and specific heat outside the close vicinity of the transition temperature appears to be described by Eqs. (4.28)–(4.30). The critical divergences given by Eqs. (4.32) and (4.33) disappear and smeared peaks around T_c' appear instead.

E. First-order transition

1. *Absence of external uniaxial pressure*

If the third-order coefficient in the Ginzburg-Landau expansion (4.10) has a nonzero value, then Eq. (4.11) in the absence of external uniaxial pressure describes the first-order phase transition at the temperature

$$T_*' = T_c' + \frac{2}{9} \frac{B_1^2}{\alpha' C'} = T_c + \frac{2DP}{A_0 \alpha'} + \frac{2}{9} \frac{B_1^2}{\alpha' C'} . \tag{4.35}$$

The shift of the transition temperature by the applied hydrostatic pressure has the same form (4.14) as for the second-order transition. The volume difference between the phases appears to depend on the temperature through the temperature dependence of η_1 given by Eq. (2.12):

$$\Delta\eta_0 = -\frac{DB_1^2}{4A_0 C'^2} \left[1 + \left(1 - \frac{4\alpha' C'}{B_1^2} (T - T_c')\right)^{\frac{1}{2}}\right]^2 . \tag{4.36}$$

This leads to a finite volume change at the phase transition temperature,

$$\Delta\eta_0(T_*') = -\frac{4}{9} \frac{DB_1^2}{(C')^2 A_0}, \tag{4.37}$$

which can be observed in diffraction as well as dilatometric studies.

Equation (4.26) takes the form

$$\eta_1 \frac{\partial \eta_1}{\partial A'} = -\frac{\eta_1}{B_1 + 2C'\eta_1} = -\frac{1}{2C'} \left[1 + \left(1 - \frac{4\alpha' C'}{B_1^2} (T - T_c')\right)^{-\frac{1}{2}}\right] , \tag{4.38}$$

and along with Eq. (4.24) gives the temperature depen-

dence of the difference in the thermal expansion coefficients between the low- and high-symmetry phases in the form

$$\Delta\kappa = \frac{\alpha'}{C'}\frac{D}{A_0}\left[1+\left(1-\frac{4\alpha' C'}{B_1^2}(T-T_c')\right)^{-\frac{1}{2}}\right] . \quad (4.39)$$

The change of the thermal expansion coefficient at the transition point T_*' now has the form

$$\Delta\kappa(T_*') = \frac{4\alpha'}{C'}\frac{D}{A_0} = 4D\,\frac{\alpha_1+2\kappa_0 D}{A_0C_1-2D^2} . \quad (4.40)$$

The value of $\Delta\kappa$ decreases to that given by Eq. (4.29) as T decreases from T_*' to T_c'.

For the difference in isothermal compressibility between the low-temperature phase and high-temperature one we can find similarly

$$\Delta\beta_T = \frac{2D^2}{C'A_0^2}\left[1+\left(1-\frac{4\alpha' C'}{B_1^2}(T-T_c')\right)^{-\frac{1}{2}}\right] , \quad (4.41)$$

which gives us the phase transition discontinuity in the form

$$\Delta\beta_T(T_*') = \frac{8D^2}{C'A_0^2} . \quad (4.42)$$

It should always be positive according to general thermodynamical arguments.[7]

The specific heat has the temperature dependence

$$\Delta C_P = \frac{T}{2}\frac{\alpha'^2}{C'}\left[1+\left(1-\frac{4\alpha' C'}{B_1^2}(T-T_c')\right)^{-\frac{1}{2}}\right] , \quad (4.43)$$

with the jump at the transition temperature

$$\Delta C_P(T_*') = 2T_*'\frac{\alpha'^2}{C'} = 2T_*'\frac{A_0(\alpha_1+2\kappa_0 D)^2}{A_0C_1-2D^2} . \quad (4.44)$$

The phase transition discontinuities of volume and entropy are related through the Clapeyron-Clausius relationship with the slope [Eq. (4.15)] of the equilibrium line at the phase diagram,

$$\frac{dT_c}{dP} = \frac{\Delta\eta_0(T_*')}{\Delta\mathcal{S}} = \frac{2D}{\alpha' A_0} . \quad (4.45)$$

Both the thermal expansion coefficient and isothermal compressibility of the undistorted phase with $\eta = 0$ do not depend on temperature, and so, expressions (4.39) and (4.41) describe the temperature dependence of these quantities in the low-symmetry phase that can be observed experimentally below the transition temperature T_*'. It should be noted, however, that effects can be seen for T_*', being sufficiently far from T_c, outside the temperature region where the thermal fluctuations (2.4) are important, because the fluctuation-induced singularities of the thermal expansion coefficient as well as the other quantities become larger in the critical region than the jumps in their equilibrium values. Thus, the third-order coefficient B_1 should satisfy condition (2.13).

Such a situation occurs in the case of Ni-Al and some other alloys where the shear modulus at T_*' is softened only slightly, by 10–20%, and the experimentally measured temperature dependence of the shear modulus can be interpreted as pointing even to negative T_c.[11] However, for the In-Tl system where the third-order term appears to be very small and the shear modulus almost vanishes at the transition temperature, the volume discontinuity is so small[36] that it is hidden by thermal fluctuations [Eq. (4.32)]. A similar effect occurs with respect to other discontinuities at the transition temperature T_*', which is very close to T_c.

2. *Effect of external uniaxial pressure on the anomalies around the first-order phase transition*

For the case of the first-order phase transition the dependence of the discontinuity in the order parameter on the uniaxial pressure E_1 follows from the general expression (2.19),

$$\Delta\eta_1 = -\frac{2B_1}{3C'}\left(1+\frac{27C'^2E_1}{B_1^3}\right)^{\frac{1}{2}} ,$$

which leads to the following volume change at T_*:

$$\Delta\eta_0(T_*') = -\frac{D}{A_0}\Delta(\eta_1^2) = -\frac{4}{9}\frac{DB_1^2}{A_0C'^2}\left(1+\frac{27C'^2E_1}{B_1^3}\right)^{\frac{1}{2}} . \quad (4.46)$$

Both parent and product phases have $\eta_1 \neq 0$ and $\Delta\mathcal{G} \neq 0$ under applied external uniaxial pressure; thus, the differences in the isothermal compressibility, thermal expansion coefficient, and specific heat are proportional to

$$\Delta\left(\eta_1\frac{\partial\eta_1}{\partial A'}\right) = \eta_{1,1}\frac{\partial\eta_{1,1}}{\partial A'} - \eta_{1,2}\frac{\partial\eta_{1,2}}{\partial A'} ,$$

where $\eta_{1,1}(T,P)$ and $\eta_{1,2}(T,P)$ correspond to two different minima of the free energy given by the different solutions of Eq. (4.19). Using the dimensionless variables (2.15) we can write Eq. (4.26) in the form

$$\eta_1\frac{\partial\eta_1}{\partial A'} = -\frac{1}{C'}\frac{(\tilde\zeta+\frac{1}{3})^3}{\sigma-(\tilde\zeta+\frac{1}{3})^2+2(\tilde\zeta+\frac{1}{3})^3} .$$

At the transition point we have $\tilde\sigma = 0$ and

$$\tilde\zeta = \pm\sqrt{-\tilde\tau} = \pm\frac{1}{3}\sqrt{1-27\sigma} ,$$

which gives the expression

$$\eta_1\frac{\partial\eta_1}{\partial A'} = \frac{(\tilde\zeta+\frac{1}{3})^2}{2C'\tilde\zeta^2} . \quad (4.47)$$

Taking into account that $\tilde\zeta^2$ has the same value $-\tilde\tau$ at the transition point for both phases, we can finally obtain

$$\Delta\left(\eta_1 \frac{\partial \eta_1}{\partial A'}\right) = -\frac{2}{C'}(1-27\sigma)^{-\frac{1}{2}} . \quad (4.48)$$

From Eqs. (4.22)–(4.24) we get the expressions for the phase transition discontinuities of the specific heat, isothermal compressibility, and thermal expansion coefficient as follows:

$$\Delta C_P(T'_*) = 2T'_* \frac{\alpha'^2}{C'}\left(1+\frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} , \quad (4.49)$$

$$\Delta\beta_T(T'_*) = \frac{8D^2}{C'A_0^2}\left(1+\frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} , \quad (4.50)$$

$$\Delta\alpha(T'_*) = \frac{4\alpha'}{C'}\frac{D}{A_0}\left(1+\frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} . \quad (4.51)$$

In the limit of small values of external uniaxial pressure we get Eqs. (4.44), (4.42), and (4.40), derived from their temperature dependence in Sec. IV E 1. When E_1 goes to the value of the critical point E_c, these discontinuities diverge as $\propto |E_c - E_1|^{-\frac{1}{2}}$.

V. TRANSFORMATION FROM A fcc INTO bcc LATTICE VIA SPONTANEOUS STRAIN

A. fcc-bcc transformation through the Bain strain

There is the case of a martensitic transformation of special interest, namely, the fcc-bcc transformation in Fe and some ferrous alloys. Since there is no group-subgroup relationship for the symmetry breaking, Landau theory is, generally speaking, inapplicable to this case. However, there is an orientational relationship between lattices of the parent and product phases, and the transition could be described in terms of a spontaneous strain of the so-called Bain type.[6]

The Bain strain is the single-axis shear of the same kind as an order parameter of the ferroelastic phase transition from a cubic to tetragonal lattice. It is accompanied by a volume change, which is approximately 1.5% in the case of pure Fe, where the transformation from an austenite fcc γ phase to a ferrite bcc α one takes place at 910 °C. If the lattice periods for austenite and martensite (ferrite) are a_γ and a_α, respectively, then the strain tensor components have the form

$$\epsilon_{xx} = \epsilon_{yy} = \sqrt{2}\frac{a_\alpha}{a_\gamma} - 1 \quad \text{and} \quad \epsilon_{zz} = \frac{a_\alpha}{a_\gamma} - 1 . \quad (5.1)$$

The fundamental feature of this case as compared with the above considered phase transition from a cubic lattice to the tetragonal one is the fixed value of the spontaneous strain needed to get the symmetry properties of the low-temperature phase. In the above considered case for any nonzero value of the order parameter η_1 the symmetry of the lattice was tetragonal, whereas in the case of the fcc-bcc transformation a peculiar value of η_1 is needed to get the low-temperature bcc lattice. If we separate the shear strain from the volume change by taking the latter to be equal to zero, then we get a single (and very large) value of the symmetrized shear strain (3.1),

$$\eta_1 = -\frac{\sqrt{6}(\sqrt{2}-1)}{2\sqrt{2}+1} \approx -0.256 . \quad (5.2)$$

Hence, this phase transition is completely different from the continuous ones, which Landau theory describes, where the value of the order parameter changes with the temperature in the low-symmetry phase according to the minimization of its Gibbs free energy (2.2).

However, the coupling with the volume change η_0 makes it possible to have an η_1 variation in the low-temperature phase without breaking its symmetry. Indeed, the strain tensor (5.1) implies the following expressions for the symmetrized combinations used above as the order parameter components:

$$\eta_0 = \frac{(2\sqrt{2}+1)}{\sqrt{3}}\frac{a_\alpha}{a_\gamma} - \sqrt{3} , \quad (5.3)$$

$$\eta_1 = -\sqrt{\frac{2}{3}}(\sqrt{2}-1)\frac{a_\alpha}{a_\gamma} , \quad \eta_2 = 0 , \quad (5.4)$$

and we get a relationship between the shear strain and volume change in the form

$$\eta_0 = -\frac{2\sqrt{2}+1}{2-\sqrt{2}}\eta_1 - \sqrt{3}. \quad (5.5)$$

Hence, the variation in the value of η_1 preserves the bcc structure of the low-temperature phase if η_0 is changed in such a way that this relationship is satisfied. It should be noted that (5.5) is meaningful only in a restricted region of η_0 and η_1. For example, $\eta_1 = 0$ implies an unreal result $a_\alpha = 0$ from (5.4). Thus, (5.5) is justified only in some vicinity of the transition that is characterized by a small volume change $\sqrt{3}\eta_0$.

Having supposed the fcc-bcc transformation to be a ferroelastic one, we should get the minimum of the elastic energy for the values of η_0 and η_1 obeying the condition (5.5). Let us study what the coefficients are in the expansion which provide such a minimum. Without a careful analysis, it should be noted, however, that the linear approximation used above gives another kind of relationship [Eq. (4.8)] between the shear strain and volume change; thus, a nonlinear approximation for the thermal expansion energy should be used.

B. Nonlinear elasticity for the volume change

Non-linearity arises naturally when taking into account a large value of the strain tensor component. The $\mathrm{Tr}(\hat{\epsilon})$ for the Bain strain in pure iron is approximately 3 times larger than the real value of the volume change for this transformation given by direct multiplication of the lattice periods of the low-temperature phase,

$$\frac{\delta V}{V} = (1+\epsilon_{xx})(1+\epsilon_{yy})(1+\epsilon_{zz}) - 1. \quad (5.6)$$

It could be expressed through the symmetrized combinations η_0, η_1, and η_2 as follows:

$$\frac{\delta V}{V} = \sqrt{3}\,\eta_0 + \eta_0^2 + \frac{\eta_0^3}{3\sqrt{3}} - \frac{\eta_1^2+\eta_2^2}{2} - \frac{\eta_0(\eta_1^2+\eta_2^2)}{2\sqrt{3}} + \frac{\eta_1(\eta_1^2-3\eta_2^2)}{3\sqrt{6}} . \quad (5.7)$$

For the fcc-bcc transition we have $\eta_2 = 0$ and proper account for the volume change should, thus, involve the terms of higher order in η_0 and η_1. Terms of first and second order in the volume change η_0 within a nonlinear approximation no longer have a simple relation with the thermal expansion coefficient and isothermal compressibility that was obtained in Sec. IV A. Similarly, other terms in both $\Delta\mathcal{G}_1$ and $\Delta\mathcal{G}_{\rm int}$ should be changed. The general nonlinear elastic energy expansion near the elastic instability with respect to η_1 now has the form

$$\Delta\mathcal{G} = L_0\eta_0 + \frac{A_0}{2}\eta_0^2 + \frac{B_0}{3}\eta_0^3 + D\eta_0\eta_1^2 + \frac{A_1}{2}\eta_1^2 + \frac{B_1}{3}\eta_1^3 + \frac{C_1}{4}\eta_1^4 , \quad (5.8)$$

where the coefficients B_0 and C_1 in highest-order terms should be positive and we again consider the particular expression with $\eta_2 = 0$.

The minimization with respect to η_0 implies

$$\frac{\partial\Delta\mathcal{G}}{\partial\eta_0} = L_0 + A_0\eta_0 + B_0{\eta_0}^2 + D{\eta_1}^2 = 0 , \quad (5.9)$$

which leads to the following relationship between η_0 and η_1 in the distorted phase with $\eta_1 \neq 0$:

$$\left(\eta_0 + \frac{A_0}{2B_0}\right)^2 + \frac{L_0}{B_0} - \frac{A_0^2}{4B_0^2} = -\frac{D}{B_0}\eta_1^2 . \quad (5.10)$$

For the high-symmetry phase we have

$$\eta_0 = -\frac{A_0}{2B_0}\left[1 \mp \left(1 - \frac{4B_0L_0}{A_0^2}\right)^{\frac{1}{2}}\right] . \quad (5.11)$$

As there are no coexisting high-symmetry equilibrium states with different values of η_0, the condition

$$A_0^2 - 4L_0B_0 = 0 \quad (5.12)$$

should be satisfied. Substituting this expression into Eq. (5.10), we get

$$\eta_1^2 = -\frac{B_0}{D}\left(\eta_0 + \frac{A_0}{2B_0}\right)^2 . \quad (5.13)$$

In order for the right-hand side of this expression to be positive the condition $D < 0$ must be satisfied, because of the positiveness of B_0.

Finally, we can get the following expression for the minimum of the free energy (5.8):

$$\eta_0 = -\sqrt{-\frac{D}{B_0}}\,\eta_1 - \frac{A_0}{2B_0} , \quad (5.14)$$

and Eq. (5.5) along with (5.12) leads to the following relations between the coefficients in the elastic energy expansion (5.8):

$$L_0 = 3B_0 , \quad (5.15)$$

$$A_0 = 2\sqrt{3}\,B_0 , \quad (5.16)$$

$$D = -\frac{9+4\sqrt{2}}{3-2\sqrt{2}}B_0 . \quad (5.17)$$

These relations could be, generally speaking, satisfied only in isolated points on the phase diagram and the phenomenological approach used in the present study is unable to find their origin. It could be done only in some microscopic theory beyond the scope of the paper. However, as far as these relations are satisfied, we can try to find their consequences for the elastic properties of the system under the phase transition.

Substituting these expressions into the free energy (5.8) and excluding the volume change through Eq. (5.5) we get a renormalized expansion of the elastic energy with respect to the symmetrized strain η_1,

$$\Delta\mathcal{G} = -\sqrt{3}\,B_0 + \left(A_1 + \sqrt{3}\,B_0\frac{18+8\sqrt{2}}{3-2\sqrt{2}}\right)\frac{\eta_1^2}{2} + \left(B_1 + B_0\frac{815+580\sqrt{2}}{116-41\sqrt{2}}\right)\frac{\eta_1^3}{3} + \frac{C_1}{4}\eta_1^4 , \quad (5.18)$$

which can be considered as a Ginzburg-Landau expansion for the ferroelastic phase transition. The first term does not depend on η_1, the critical temperature T_c is defined by the condition

$$A_1 + \sqrt{3}\,B_0\frac{18+8\sqrt{2}}{3-2\sqrt{2}} = 0 ,$$

and the temperature T_* of the first-order transition with a finite jump in η_1 and η_0 is given by the equation

$$9A^3 - 3AB^2 + C_1B^2 = 0 ,$$

where A and B are the expressions in brackets of the second- and third-degree terms in Eq. (5.18). In order for some transition line to exist on the phase diagram, the B_0 coefficient should be temperature and pressure dependent.

VI. CONCLUSIONS

We have analyzed the volume change effect on ferroelastic (martensitic) phase transitions and considered the case of a cubic lattice of a high-symmetry phase as an example. The minimization of the elastic energy with respect to the hydrostatic strain as a secondary order parameter is shown to renormalize the second- and fourth-order coefficients of the Ginzburg-Landau expansion of the elastic free energy in powers of the symmetrized shear strain. The coupling between the shear strain and vol-

ume change appears to shift the transition temperature under applied external hydrostatic pressure and lead to a finite volume effect of the weakly discontinuous ferroelastic phase transition.

The isothermal compressibility as well as the thermal expansion coefficient is shown to diverge near the critical temperature of the second-order ferroelastic phase transition due to homogeneous fluctuations of the order parameter. The difference between their values in the parent and product phases outside the fluctuation region appears to be proportional to the coupling coefficient. For the case of a first-order transition the isothermal compressibility and thermal expansion coefficient depend on the temperature in the low-symmetry phase according to the square root law.

The uniaxial pressure conjugated to the symmetrized shear strain is shown to suppress the second-order transition, leading to a change of the divergences for smeared peaks in the temperature dependences of the isothermal compressibility and thermal expansion coefficient around the critical temperature. We have found the first-order transition surface at the phase diagram in coordinates of the temperature and hydrostatic as well as uniaxial pressure. This terminates at the line of the critical point and the uniaxial pressure of a magnitude lower than critical shifts the transition temperature, but preserves the transition. The critical hydrostatic pressure that suppresses the phase transition has a linear temperature dependence. The order parameter discontinuity and the volume effect diverge at the critical line as well as the difference in the isothermal compressibility and thermal expansion coefficient between the parent and product phases.

The coupling between the volume change and shear strain is shown to lead to a fcc-bcc martensitic transformation for some special relations between the coefficients in the free energy expansion. Though some fixed value of the Bain strain is needed to get the low-temperature bcc lattice, the volume change as a secondary order parameter makes it possible to have some temperature variation of the shear strain preserving the bcc lattice and changing its period only. The nonlinear expression for the elastic energy of the thermal expansion is shown to lead to a proper relation between the shear strain and volume change for the minima of the elastic energy.

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