Volume Effect in the Landau Theory of Martensitic Phase Transitions in Cubic Crystals

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Abstract

An effect of the volume change upon proper ferroelastic (martensitic) phase transitions in cubic crystals is considered. Corresponding terms in the Ginzburg-Landau expansion of the Gibbs free energy are analyzed for the first- as well as second-order phase transitions from cubic to tetragonal lattice under the action of uniaxial and hydrostatic pressure. The pressure effect on the critical temperature as well as on the phase transition anomalies of isothermal compressibility and 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 non-linearity of thermal expansion leads to the special relation between the shear strain and volume change as a result of the elastic energy minimization. This phenomenon can provide the transformation from FCC lattice to BCC one, observed in the iron alloys.

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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., an 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 temperature. There is a particular sub-class of a so-called ”thermo-elastic” 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 product phase is coherent with respect to the parent one. This phenomenon gives the 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 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 *apriori* unknown external pressure from the lattice of the parent phase upon the regions under transformations. Thus, the heterogeneity of the system makes it difficult to analyze the thermodynamic of phase transition, and idealized single-crystal systems should be considered in order to study an equilibrium structure of the martensite phase as well as an 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 the Landau theory. In this approach the difference in free energy between the parent and product phase is considered as a function of some order parameter which is equal to zero in a high-temperature symmetrical phase and becomes non-vanishing below the critical temperature \( T_c \). The fundamental difference of the structure of a martensitic phase with respect to the parent lattice is well known to be spontaneous strain \[6\], 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 \[3\]. 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 referring to as a ”soft-mode” one. Though, the modes never become completely soften \[11\] and a finite (albeit – small) jump of the order parameter is usually observed, the martensitic phase transition still may be treated as a 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 the transition anomaly in the thermal expansion coefficient as well as in
the isothermal compressibility. For the case of the first-order transition some effect is found to occur in the low-temperature phase even at the temperature region outside fluctuation-induced singularities.

The effect of the uniaxial pressure, that preserves the symmetry of the low-temperature tetragonal phase is studied as well. It is an external field conjugated to the order-parameter which is known \cite{7} to suppress the continuous (second-order) phase transition for arbitrary small field value, however, the weakly-discontinuous transition is preserved under the field 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.

The non-linear analysis of the volume change shows, that the elastic energy minimization can provide the FCC structure of low-temperature phase for the BCC parent lattice through the special relationship between the shear strain and volume change. Hence, non-linear 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 the Landau theory is a content of the Section \[II\]. The Landau theory of a proper ferroelastic (martensitic) transformation is analyzed in Section \[III\]. The volume change due to such a phase transition is considered in Section \[IV\]. Non-linear thermal expansion and its possible contribution to the martensitic phase transition is studied in Section \[V\].

**II. THE LANDAU THEORY OF THE FIRST-ORDER PHASE TRANSITION**

**A. Continuous phase transition**

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

General expression for the (Ginzburg-Landau) expansion of the difference in Gibbs free energy between the phases has the following form

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

where $T_c$ is a critical temperature and the coefficients $\alpha$ and $C$ should be positive. The equilibrium value of $\eta$ is determined by the minimization of $\Delta G$ with respect to $\eta$:

$$\frac{\partial \Delta G}{\partial \eta} = 0 \quad \text{and} \quad \frac{\partial^2 \Delta G}{\partial^2 \eta} > 0.$$  \hspace{1cm}(2.2)

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

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

$$\Delta S = -\frac{\partial \Delta G}{\partial T} = \frac{\alpha^2}{2C} (T - T_c),$$

but the derivative manifests discontinuity

$$\Delta C_P = T \frac{\partial \Delta S}{\partial T} = -T \frac{\partial^2 \Delta G}{\partial T^2} = \frac{\alpha^2 T_c}{2C}.$$ \hspace{1cm}(2.5)

Vanishing of the coefficient of second degree in the Ginzburg-Landau expansion when the temperature approaches $T_c$ leads to the critical fluctuations of the order parameter. Mean square of the homogeneous order parameter fluctuations is given by well-known expression
\[ \langle \eta^2 \rangle \propto \frac{k_B T}{\alpha |T - T_c|^{-1}}. \]  

(2.6)

Inhomogeneous fluctuations appear to be crucial in many cases, however, for the purposes of present study they can be neglected due to long-range nature of elastic interactions in solids [18].

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 expansions takes the form

\[ \Delta G = \frac{\alpha}{2} (T - T_c) \eta^2 + \frac{C}{4} \eta^4 - E \eta \]  

(2.7)

and the minimization of \( \Delta G \) with respect to \( \eta \) leads to the cubic equation

\[ \frac{\partial \Delta G}{\partial \eta} = \alpha (T - T_c) \eta + C \eta^3 - E = 0 \]  

(2.8)

with discriminant

\[ Q = \left( \frac{\alpha (T - T_c)}{3C} \right)^3 + \left( \frac{E}{2C} \right)^2 \]  

(2.9)

It is seen that for any value of external field \( E \) the high-symmetry phase with \( \eta = 0 \) no longer provides the stable solution of the Eq.(2.2). Instead, we get \( \eta \neq 0 \) for any temperature. It is known [19], that the cubic equation has one solution in real numbers for \( Q > 0 \) and three ones for the case of \( Q < 0 \). It means that for temperatures below some critical one that now depends on \( E \)

\[ T_0(E) = T_c - \frac{3}{2\alpha} \left( 2CE^2 \right)^{\frac{1}{3}} \]  

(2.10)

the additional minimum of the Gibbs free energy appears that corresponds to new phase. However, the initial phase described by the high-temperature solution of (2.8) provides the minimum with lower value of the free energy and is, thus, stable. The free energy behavior

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as well as the order parameter dependencies on the temperature for different values of the external field are shown in the Fig.1 and Fig.2.

It is seen from the Fig.1 and might be proven rigorously that different minima of the \( \Delta G(\eta) \) curve have different energies for any temperature \( T < T_0 \). Thus, the high-temperature state remains stable throughout all the region of the phase co-existence. Only the condition of \( E = 0 \) leads to the degeneracy with respect to sign of \( \eta \) that implies the equal energies of different minima. It leads to a phase transition of the first order under the variation of 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 (2.7) in a different way, because the field variation may lead to the phase change but the temperature one may not.

The external field suppress the transition, however some decrease in

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

leads to enhanced fluctuations of the order parameter around \( T_c \) with smooth peak instead of divergence (2.6) shown in the Fig.(3). So, some transition anomalies are preserved in sufficiently small external fields \( E \).

C. Weakly-discontinuous phase transition in the Landau theory

The first-order phase transition arises in the Landau theory when the symmetry of the system allows to have non-vanishing third-degree invariant composed by the order-parameter component [7,20]. Corresponding term should be taken into account in the Ginzburg-Landau expansion:

\[
\Delta G = \frac{\alpha}{2}(T - T_c)\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4 - E\eta.
\]  

(2.11)

Choosing the case of \( B < 0 \), that gives positive \( \eta \) in the low-temperature phase, we can write the free energy expansion in the following form

\[
\Delta \tilde{G} = \frac{C^3}{B^4} \Delta G = \frac{\tau}{2} \zeta^2 - \frac{\zeta^3}{3} + \frac{\zeta^4}{4} - \sigma\zeta,
\]  

(2.12)
with

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

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

For the \( \sigma = 0 \) case minimization of the Gibbs free energy (2.12) with respect to \( \zeta \) implies the equation

\[ \frac{\partial \Delta \tilde{G}}{\partial \eta} = \tau \zeta - \zeta^2 + \zeta^3 = 0. \] (2.13)

For \( \tau > \tau_0 = \frac{1}{4} \) there is the only 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

\[ \eta = -\frac{B}{2C} \left(1 + \left(1 - \frac{4\alpha C}{B^2} (T - T'_c)\right)^{-\frac{1}{2}}\right) \] (2.14)

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 are possible. It means that the first-order phase transition takes place at the temperature \( T^* \). As well as in the second-order case, high-symmetry phase becomes unstable at \( \tau = 0 \).

At the temperature of the first-order transition \( T^* \) the order parameter jumps from the \( \eta = 0 \) to the

\[ \eta = -\frac{2}{3} \frac{B}{C^3}, \] (2.15)

overcoming the activation energy barrier

\[ \Delta G_b = \frac{1}{324} \frac{B^4}{C^3}. \] (2.16)

The entropy now has a finite change at transition temperature

\[ \Delta S = -\frac{2}{9} \frac{\alpha B^2}{C^2}. \] (2.17)
that correspond to latent heat of the phase transition
\[ \Delta Q = \frac{2}{9} \frac{\alpha B^2}{C^2 T_*}. \] (2.18)

In order the weakly-first-order transition to be properly identified and clearly separated from the background of critical fluctuations around \( T_c \) (2.9), the transition jump of the order parameter should be greater than its mean fluctuation. In other word, the energy scale of the problem should be larger than the thermal fluctuation energy \( k_B T \). It implies the condition for the value of the third-order coefficient in the Ginzburg-Landau expansion
\[ B \geq \left( C^3 k_B T_c \right)^{\frac{1}{4}}. \] (2.19)

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 (2.12), we get the third-order term excluded [21]:
\[ \Delta \tilde{G} = \tilde{\tau}^2 \zeta^2 + \tilde{\sigma} \zeta + \Delta \tilde{G}_0, \] (2.20)

where
\[ \tilde{\tau} = \tau - \frac{1}{3}; \quad \tilde{\sigma} = \sigma - \frac{\tau}{3} + \frac{2}{27} \]
and
\[ \Delta \tilde{G}_0 = \frac{\tau}{18} - \frac{\sigma}{3} - \frac{1}{108}. \] (2.21)

This is equivalent to the free energy expansion (2.7) for the second-order phase transition under the external field, the only difference consisting of the term \( \Delta \tilde{G}_0 \) that is independent on \( \tilde{\zeta} \). It appears because the free energy is counted with respect to the \( \zeta = 0 \) or \( \zeta = -\frac{1}{3} \) state, that implies \( \Delta \tilde{G}_0 = \Delta \tilde{G}(\zeta = 0) \neq 0 \).

The condition (2.2) leads to cubic equation (2.8) with the effective temperature \( \tilde{\tau} \) and field \( \tilde{\sigma} \) instead of the real ones. The sign of discriminant
\[ Q = \left( \frac{\tilde{\tau}}{3} \right)^3 + \left( \frac{\tilde{\sigma}}{2} \right)^2 \propto 4\sigma + 27\sigma^2 - 18\sigma\tau - \tau^2 + 4\tau^3 \quad (2.22) \]

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

Hence, (2.20) 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 non-zero values of 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 the Landau theory, however, the undistorted phase with \( \zeta = 0 \) can be treated as an analog of ideal high-symmetry "praphase" [22] 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 absence of external field appears to be equivalent to the second-order one under the action of ‘effective’ external field, the only feature of this situation is zero value of \( \eta \) for one of two minima of \( \Delta \tilde{G}(\tilde{\zeta}) \).

The phase diagram in \((\tau, \sigma)\) plane is shown at the Fig.4. Additional minimum of the free energy appears for \( \sigma_1 \leq \sigma \leq \sigma_2 \) with

\[ \sigma_{1,2} = -\frac{2}{27} \left( 1 \pm (1 - 3\tau)^{\frac{3}{2}} \right) + \frac{\tau}{3}, \quad (2.23) \]

that leads to the 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 transition described by (2.7), the different minima of the \( \Delta \tilde{G}(\tilde{\zeta}) \) 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 applied field on the transition temperature \( \tau_* \)

\[ \tau_*(\sigma) = 3\sigma + \frac{2}{9}. \quad (2.24) \]

For \( \sigma = 0 \) we get naturally \( \tau_*(0) = \frac{2}{9} \). The Eq.(2.24) corresponds to the straight line on \((\tau, \sigma)\) 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 the undistorted high-symmetry phase of the Landau theory without an external field which is unstable for $\tau < \frac{1}{3}$ and becomes a maximum of $\Delta \tilde{G}$, i.e. the energy barrier with a height of

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

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

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

As this line of the first-order transition in the phase diagram at $(\tau, \sigma)$ plane separates states without symmetry-breaking relationship [7], it terminates in critical point $(\tau_c = \frac{1}{3}, \sigma_c = \frac{1}{27})$. The discontinuity in 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 $\tau > \tau_c$, that means suppressing the weakly-first-order phase transition under the fields greater than the critical one. In a contrast with the second-order case where arbitrary small external field destroys the phase transition, here we find that the fields lower than $\sigma_c$ preserve the transition. The critical point is an analog of the continuous phase transition from state with $\tilde{\zeta} = 0$ corresponding to the breaking of symmetry with respect to change of the $\tilde{\zeta}$ sign.

**III. PROPER FERROELASTIC PHASE TRANSITION**

A phase transition characterized by the appearance of 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 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 vanishes 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 so-called
"soft-mode" class, because it is accompanied by a noticeable softening of the corresponding
acoustic mode of atomic vibrations \([18]\), visible as a central peak of the inelastic neutron
scattering.

A. Spontaneous strain in cubic lattice

In what follows the case of cubic symmetry of a high-temperature phase will be consid-
ered, that describes the martensitic transformations in the A15 compound \([23]\) as well as in
some metallic alloys. The spontaneous strain tensor has only diagonal components and the
order parameter is composed by their symmetrized linear combinations \([12]\)

\[
\eta_1 = \frac{1}{\sqrt{6}}(-\epsilon_{xx} - \epsilon_{yy} + 2\epsilon_{zz}) \quad (3.1)
\]
\[
\eta_2 = \frac{1}{\sqrt{2}}(\epsilon_{xx} - \epsilon_{yy}) \quad (3.2)
\]

The \(\eta_1\) corresponds to the extension along \(z\) axis without the volume change and \(\eta_2\) describes
the strain non-tetragonality in \(XY\) plane. The critical acoustic mode is a transverse phonons
distributing in \((110)\) directions.

The elastic free energy expansion can be written in the Ginzburg-Landau form \([24]\)

\[
\Delta G = A_2 (\eta_1^2 + \eta_2^2) + B_3 \eta_1 (\eta_1^2 - 3\eta_1\eta_2^2) + C_4 (\eta_1^2 + \eta_2^2)^2. \quad (3.3)
\]

with the following combination of the elastic constants as the coefficients \([13]\)

\[
\frac{A_2}{2} = \frac{\alpha}{2}(T - T_c) = \frac{1}{2}(C_{11} - C_{12}) \quad (3.4)
\]
\[ B = \frac{1}{6\sqrt{6}} (C_{111} - 3C_{112} + 2C_{123}) \]  
\[ C = \frac{1}{48} (C_{1111} + 6C_{1112} - 3C_{1122} - 8C_{1123}) . \]  

(3.5)  
(3.6)

Substituting \( \eta_1 = \eta \sin \theta \) and \( \eta_2 = \eta \cos \theta \),

we get the Ginzburg-Landau expansion in the form

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

(3.7)

The minimization with respect to \( \theta \)

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

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

\[ (\eta, 0), \ ( -\frac{1}{2} \eta, \frac{\sqrt{3}}{2} \eta ) \quad \text{and} \quad ( -\frac{1}{2} \eta, -\frac{\sqrt{3}}{2} \eta ) , \]  

(3.8)

corresponding to the low-symmetry tetragonal phases obtained by the extension of parent cubic lattice along three coordinate axis. The free energy dependence on \( \eta \) for these minima is the single-component Ginzburg-Landau expansion (2.11) 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 the Landau theory for the case of single-component order parameter.

The cubic symmetry allows the third-order term in the Ginzburg-Landau expansion to appear, hence, the Landau theory says that the phase transition should be of the first order. Indeed, for the case of Ni-Al and some other systems partial mode softening takes place and the finite strain appears at the transition, though the shear modulus decreases considerably near the phase transition temperature. Some other so-called ”pre-transformation” phenomena were found in a number of alloys [25–28]. This case respects to the weakly first-order transition mentioned in Section II C.
However, this third-degree term appears to be very small in In-Tl, V₃Si and some other alloys [29] where the critical mode becomes almost complete soften, i.e. shear modulus \((C_{11} - C_{12})\) vanishes as temperature goes to \(T_c\). Central peak of the inelastic neutron scattering as well as other critical phenomena appear and the order parameter undergoes very small change at the critical temperature \(T_c\) [30]. So, the transition is very weakly discontinuous, being sometimes of the second order within the 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 the second-order phase transformation considered in Section IIA.

**B. Effect of external stress on the transition**

An applied pressure gives rise the 'external' stress tensor \(\hat{\epsilon}\) corresponding to linear term \(-\hat{\epsilon} \hat{E}\) in the free energy expression [31]. The symmetry-breaking strain components are sensitive only to diagonal components of \(\hat{E}\), hence, relevant external stress is superposition of hydrostatic pressure \(P = \text{Tr}(\hat{E})/\sqrt{3}\) with ones applied (uniaxially) along \(z\) axis

\[
E_1 = (-E_{xx} - E_{yy} + 2E_{zz})/\sqrt{6}
\]

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 \(\eta_1\) and \(\eta_2\), respectively, whereas hydrostatic pressure will be shown below affect the ferroelastic phase transition through the volume change \(\eta_0\) related with the order parameter by the coupling term proportional to \(\eta_0(\eta_1^2 + \eta_2^2)\).

Applied non-hydrostatic pressure \(E_{1,2}\) breaks the symmetry of undistorted phase, moving out corresponding minimum of \(\Delta G(\eta_1, \eta_2)\) from the origin and lifts the degeneracy between three low-symmetry phases [3-8]. The pressure which is co-aligned with the spontaneous
strain corresponding to one of these solutions, e.g. \((\eta_1,0)\), preserves the tetragonal symmetry of distorted phase and the pressure value \(E_1\) is an external field conjugated to the value of symmetrized strain \(\eta_1\) as a single-component order parameter, considered in Section II C 2. Otherwise the stable low-temperature state of the system has rhombohedral lattice with three different lattice parameters that is characterized by the pressure-dependent \(\eta_1\) and \(\eta_2\). In what follows the effect of uniaxial pressure \(E_1\) conjugated to \(\eta_1\), which preserves the tetragonal symmetry of low-temperature phase is analyzed.

In the agreement with the analysis of Section II B the uniaxial pressure was found \([32]\) to suppress the ferroelastic phase transition from cubic to tetragonal lattice in the \(V_3\)\(Si\) compound, where third-order term is very small and the transition is of the second-order. For Ni-Al alloy, where the first-order phase transition takes place, the uniaxial pressure appears \([33]\) to shift the transition temperature linearly in complete agreement with the Eq. (2.24).

It should be noted that though this alloy exhibit martensitic transition where spontaneous homogeneous strain is accompanied by so-called shuffle \([11]\) related with \(q \neq 0\) critical mode, the central peak of the inelastic neutron scattering as well as noticeable softening of \(C_{11} - C_{12}\) elastic constant appear well above the transition temperature. Hence, this case can also be analysed in the frame of the Landau theory of ferroelastic phase transition.

**IV. VOLUME CHANGE IN THE ELASTIC ENERGY EXPANSION**

If the phase transition is sensitive to applied external hydrostatic pressure then there is a difference in the volume of elementary cell of the parent and product phases. The volume change, indeed, takes place in some cases and it was shown \([34]\) that 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 strain and volumetric one.
A. Linear energy of the thermal expansion

In the linear elasticity theory \[31\] the trace of strain tensor is a measure of the volume change, the corresponding symmetrized linear combination of the strain components having a form

\[
\eta_0 = \frac{\text{Tr}(\hat{\epsilon})}{\sqrt{3}} = \frac{1}{\sqrt{3}}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}).
\]  \hspace{1cm} (4.1)

Due to thermal strain as well as external pressure, the expansion of the elastic energy in series of \(\eta_0\) should start with the linear terms \[31\]:

\[
\Delta G_0(\eta_0) = -\kappa_0 A_0 (T - T_R) \eta_0 + \frac{A_0}{2} \eta_0^2 + P \eta_0,
\] \hspace{1cm} (4.2)

where \(T_R\) is some reference temperature for volume change, \(\kappa_0\) and \(A_0\) are the volume thermal expansion coefficient and bulk modulus, respectively and \(P\) is external pressure applied. The bulk modulus \(A_0 = \frac{1}{\sqrt{3}}(C_{11} + 2C_{12})\) is always positive.

The minimization of \(\Delta G_0(\eta_0)\) with respect to \(\eta_0\) implies equilibrium values of \(\eta_0(T)\) and \(\Delta G_0(T, P)\)

\[
\eta_0 = \kappa_0 (T - T_0) - \frac{P}{A_0}
\] \hspace{1cm} (4.3)

\[
\Delta G_0 = -\frac{A_0}{2} \alpha_0^2(T - T_0)^2 - \frac{P^2}{2A_0} + \kappa_0 P (T - T_0)
\] \hspace{1cm} (4.4)

It is easy to see that usual thermodynamical expressions for isothermal compressibility \(\beta_T\) and thermal expansion coefficient

\[
\beta_T = -\frac{\partial^2 \Delta G_0}{\partial P^2} = -\frac{\partial \eta_0}{\partial P} = \frac{1}{A_0}
\] \hspace{1cm} (4.5)

\[
\kappa_0 = \frac{\partial^2 \Delta G_0}{\partial P \partial T} = \frac{\partial \eta_0}{\partial T}
\] \hspace{1cm} (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 whole system equal to 1 for convenience).
B. Effect of the volume change on ferroelastic phase transition

The lowest-order term of coupling between the shear strains $\eta_{1,2}$ and volume change $\eta_0$ for the case of a cubic symmetry of the high-temperature phase is [13]

$$\Delta G_{int} = D \eta_0 (\eta_1^2 + \eta_2^2), \quad (4.7)$$

where $D = \frac{1}{2\sqrt{3}}(C_{111} - C_{123})$. Substituting this term into the expansion of elastic energy in a power series of the volume change, we get the expression (4.3) for the equilibrium value of $\eta_0$ in the following form

$$\eta_0 = \kappa_0 (T - T_0) - \frac{P}{A_0} - \frac{D}{A_0} (\eta_1^2 + \eta_2^2). \quad (4.8)$$

The coupling term does not induce any anisotropy in the $(\eta_1, \eta_2)$ 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 Z axis does not break the tetragonal symmetry of corresponding low-temperature phase. Thus, it is an external field conjugated to the $\eta_1$ order parameter and we can use the results of Section II C 2 to study its influence on the phase transition. The volume change $\eta_0$ as well as its derivatives – thermal expansion coefficient $\alpha$ and isothermal compressibility $\beta_T$ does not depend directly on $E_1$, but only follows the dependence of symmetrized shear strain $\eta_1$ through Eqs.(4.8).

The general expression for the free energy has the following form

$$\Delta G = \Delta G_0 + \Delta G_1 + \Delta G_{int} \quad (4.9)$$

where $\Delta G_1$ is the Ginzburg-Landau expansion (2.11) with respect to $\eta_1$ as the single-component order parameter with included effect of applied uniaxial pressure $E_1$ (3.9)

$$\Delta G_1 = \frac{\alpha_1}{2}(T - T_c)\eta_1^2 + \frac{B_1}{3}\eta_1^3 + \frac{C_1}{4}\eta_1^4 - E_1\eta_1. \quad (4.10)$$

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 renormed Ginzburg-Landau expansion of $\Delta G$ in the power series of $\eta_1$
\[ \Delta G(T, P, \eta_1) = \Delta G_0 + \frac{A'(T, P)}{2} \eta_1^2 + \]

\[ \frac{B'}{3} \eta_1^3 + \frac{C'}{4} \eta_1^4 - E_1 \eta_1, \]  

(4.11)

with the coefficients

\[ A'(T, P) = \alpha' (T - T'_c) = \]

\[ = \left( (\alpha_1 + 2\kappa_0 D)(T - T_c) - \frac{2PD}{A_0} \right), \]  

(4.12)

\[ B' = B_1 \quad \text{and} \quad C' = C_1 - \frac{2D^2}{A_0}. \]  

(4.13)

Here \( \Delta G_0(T, P) \) is the energy of a high-symmetry phase with \( \eta_1 = 0 \), given by the (4.4). The critical temperature

\[ T'_c = T_c + \frac{2DP}{A_0(\alpha_1 + 2\kappa_0 D)} \]  

(4.14)

is shifted by the applied hydrostatic pressure

\[ \frac{dT_c}{dP} = \frac{2D}{A_0(\alpha_1 + 2\kappa_0 D)}. \]  

(4.15)

in agreement with experimental studies, e.g. in In-Tl alloys [35]. New stiffness is given by the formula

\[ \alpha' = \alpha_1 + 2\kappa_0 D. \]  

(4.16)

In order the Eq.(4.11) be considered as an analog of Eq.(2.11), the \( \alpha' \) 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 phase transition could not be changed by applied hydrostatic pressure.
As the hydrostatic pressure change the transition temperature according to Eq.(1.13), the line (2.24) of the first-order phase transition becomes a surface in the 3D $(T, P, E_1)$ phase diagram given by a 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 variation of hydrostatic pressure under the fixed values of temperature $T$ and uniaxial pressure $E_1$ at the point

$$P_*(T, E_1) = \frac{\alpha'A_0}{2D} (T - T_c) - \frac{A_0B_1^2}{9DC''} + \frac{3A_0C''}{2DB_1} E_1. \tag{4.18}$$

The critical point of the end of transition line (2.24) 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 critical hydrostatic one that depends linearly on the temperature $P_c(T) = A_0 \left( \frac{\alpha'(T - T_c)}{2D} - \frac{B_1^2}{3C''} \right)$ and vanishes when $T$ goes to $T_{cp} = T_c + B_1^2/(3\alpha'C'')$. It means that some values of hydrostatic pressure suppress the transition, caused by the change of uniaxial pressure $E_1$. The closer temperature is to the $T_{cp}$ the smaller hydrostatic pressure needed for the transition to disappear.

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

The isothermal compressibility, thermal expansion coefficient and specific heat are expressed by Eqs.(1.5), (4.6) and (2.3), respectively, through the second derivatives of $\Delta G(T, P, \eta_1)$ with respect to temperature and hydrostatic pressure for an equilibrium value of $\eta_1$ given by the condition (2.2) in the form

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

For the first derivative we have the following formula
\[
\frac{\partial}{\partial T} (\Delta G - \Delta G_0) = \frac{\partial \Delta G}{\partial A'} \frac{\partial A'}{\partial T} + \frac{\partial \Delta G}{\partial \eta_1} \frac{\partial \eta_1}{\partial T}
\]

(4.20)

Second term in this expression vanishes as equilibrium \( \eta_1 \) is given by the Eq.(2.2) and taking into account Eq.(4.12) we get the formula

\[
\frac{\partial}{\partial T} (\Delta G - \Delta G_0) = \alpha' \frac{\eta_1^2}{2},
\]

(4.21)

that leads to the following expression for the transition anomaly of the specific heat

\[
\Delta C_P = -T \frac{\partial^2}{\partial T^2} (\Delta G - \Delta G_0) = -\alpha'^2 T \frac{\eta_1}{\partial A'} \eta_1 \frac{\partial \eta_1}{\partial A'}
\]

(4.22)

For isothermal compressibility and thermal expansion coefficient we get analogous expressions

\[
\Delta \beta_T = -\frac{\partial^2}{\partial P^2} (\Delta G - \Delta G_0) = -\frac{4D^2}{A_0^3} \frac{\eta_1}{\partial A'} \eta_1 \frac{\partial \eta_1}{\partial A'}
\]

(4.23)

\[
\Delta \kappa = \frac{\partial^2}{\partial P \partial T} (\Delta G - \Delta G_0) = -\frac{2D\alpha'}{A_0} \eta_1 \frac{\partial \eta_1}{\partial A'}.
\]

(4.24)

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

\[
\frac{dT_c}{dT} = \Delta \beta_T \Delta \alpha = \frac{T \Delta \alpha}{\Delta C_P}
\]

(4.25)

are satisfied.

Differentiating both sides of Eq.(4.19) we get

\[
\frac{\partial \eta_1}{\partial A'} = -\frac{\partial F}{\partial A'} \left( \frac{\partial F}{\partial \eta_1} \right)^{-1}
\]

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

\[
\eta_1 \frac{\partial \eta_1}{\partial A'} = -\frac{\eta_1^3}{E_1 + B_1 \eta_1^2 + 2C' \eta_1}.
\]

(4.26)

**D. Second-order case**

Let us consider the case of the martensitic phase transition of the second order for which \( B_1 = 0 \). In absence of the uniaxial pressure (4.26) does not depend on \( \eta_1 \) and, hence, neither on temperature nor on hydrostatic pressure:
\[ \eta_1 \frac{\partial \eta_1}{\partial A'} = -\frac{1}{2C'} . \]

Low-temperature phase appears at \( T'_c \) with continuous evolution of the order parameter that gives the volume difference between the parent and product phases

\[ \Delta \eta_0 = -\frac{\alpha' D}{A_0 C'} (T'_c - T) \]

(4.27)

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

\[ \Delta \beta_T = \frac{2}{C'} \left( \frac{D}{A_0} \right)^2 = \frac{2D^2}{A_0^2 C_1 - 2A_0 D^2} \]

(4.28)

\[ \Delta \kappa = \frac{\alpha' D}{C'} A_0 = \frac{(\alpha_1 + 2\kappa_0 D)D}{A_0 C_1 - 2D^2} \]

(4.29)

\[ \Delta C_P = \frac{T'_c (\alpha')^2}{2} \frac{(\alpha_1 + 2\kappa_0 D)^2}{C'} = \frac{T'_c A_0 (\alpha_1 + 2\kappa_0 D)^2}{2(A_0 C_1 - 2D^2)} \]

(4.30)

Thus, to find three independent parameters of the model - \( \alpha' \), \( C' \) and \( \frac{D}{A_0} \), we have four measurable values – \( \Delta C_P \), \( \Delta \beta_T \) and \( \Delta \alpha \) along with

\[ \frac{dT_c}{dT} = \frac{2}{\alpha'} \frac{D}{A_0} \]

(4.31)

which are related by Eq.(4.25).

As was mention above, for the case of second-order ferroelastic phase transition considerable critical fluctuations take place due to the softening of \( C_{11} - C_{12} \) shear modulus. The inhomogeneous fluctuations \( \eta_1(x) \) appear to be relevant only in very close vicinity of the critical temperature \[ 18 \]. From Eq.(2.4) that describes the homogeneous order parameter fluctuations taking into account Eq.(4.8) we get the following expressions for the critical fluctuations of volume

\[ \eta_0 \propto -\frac{D}{A_0} |T - T_c|^{-1} \]

(4.32)

and thermal expansion coefficient
\[
\kappa = \frac{\partial \Delta \eta_0}{\partial T} \propto \frac{D}{A_0} |T - T_c|^{-2}.
\] (4.33)

in the temperature interval around \(T_c\), where the fluctuations in \(\eta_1\) are important.

There are some experimental data available on the anomalies of thermal expansion in the single-crystal specimens near the martensitic phase transition \(^3\text{[36]}\), which are in agreement with the above results. In most of the alloys the thermal expansion coefficient increases near \(T'_c\), that implies the positiveness of \(D\). Outside the temperature region of thermal fluctuations the thermal expansion coefficient does not depend on the temperature. Besides, linear model of Eq.(4.2) leads to the independence of \(\alpha\) on the applied hydrostatic pressure.

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

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

For sufficiently small values \(E_1\) of external uniaxial pressure the difference in the isothermal compressibility, thermal expansion coefficient and specific heat outside close vicinity of the transition temperature appears to be described by Eqs.(4.28) - (4.30). The critical divergencies given by Eqs.(4.32) and (4.33) disappear and the smeared peaks around \(T'_c\) appear instead.

E. The first-order transition

1. Absence of external uniaxial pressure

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

\[
T'_* = T_c' + \frac{2}{9} \frac{B_1^2}{\alpha' C''} = T_c + \frac{2DP}{A_0 \alpha'} + \frac{2}{9} \frac{B_1^2}{\alpha' C''}
\] (4.35)

22
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 \( \eta_1 \) given by Eq. (2.14)

\[
\Delta \eta_0 = -\frac{DB_1^2}{4A_0C''} \left( 1 + \left( 1 - \frac{4\alpha' C'}{B_1^2} (T - T'_c) \right)^{-\frac{1}{2}} \right)^2.
\] (4.36)

This leads to finite volume change at the phase transition temperature

\[
\Delta \eta_0(T'_*') = -\frac{4}{9} \frac{B_1^2}{(C'')^2}
\] (4.37)

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

Eq. (4.26) takes the form

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

and along with Eq. (4.24) gives the temperature dependence of difference in thermal expansion coefficients between the low- and high-symmetry phases in the form

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

The change of thermal expansion coefficient at the transition point \( T'_* \) now has a form

\[
\Delta \kappa(T'_*) = \frac{4\alpha'}{C'} \frac{D}{A_0} = 4D \frac{\alpha_1 + 2\kappa_0 D}{A_0C_1 - 2D^2}.
\] (4.40)

The value of \( \Delta \kappa \) decreases to that given by Eq. (4.29) as \( T \) goes down from \( T'_* \) to \( T'_c \).

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

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

that gives us the phase transition discontinuity in the form
\[ \Delta \beta_T(T'_*) = \frac{8D^2}{C' A_0^2}. \] (4.42)

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

The specific heat has the following temperature dependence

\[ \Delta C_P = \frac{T \alpha'^2}{2 C'} \left( 1 + \left( 1 - \frac{4 \alpha' C'}{B_1^2} (T - T'_c) \right)^{-\frac{3}{2}} \right) \] (4.43)

with the jump at the transition temperature

\[ \Delta C_P(T'_*) = 2T'_* \frac{\alpha'^2}{C'} = 2T'_* \frac{A_0 (\alpha_1 + 2 \kappa_0 D)^2}{A_0 C_1 - 2D^2} \] (4.44)

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

\[ \frac{dT_c}{dP} = \frac{\Delta \eta_0(T'_*)}{\Delta S} = \frac{2D}{\alpha' A_0}. \] (4.45)

Both the thermal expansion coefficient and isothermal compressibility of undistorted phase with \( \eta = 0 \) do not depend on temperature, so, the 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 the effects can be seen for \( T'_* \) being sufficiently far from \( T_c \), outside the temperature region where thermal fluctuations are important, because the fluctuation-induced singularities of the thermal expansion coefficient as well as the other quantities become larger in critical region than the jumps in their equilibrium values. Thus, the third-order coefficient \( B_1 \) should satisfy condition (2.19).

Such a situation occurs in the case of Ni-Al and some other alloys where shear modulus at \( T'_* \) is soften only slightly – by 10 ÷ 20\%, and the experimentally measured temperature dependence of shear modulus can be interpreted as pointing even to negative \( T_c \) \[11\]. However, for In-Tl system where third-order term appears to be very small and the shear modulus almost vanishes at the transition temperature, the volume discontinuity is so small \[35\] that it is hidden by thermal fluctuations (4.32). The similar effect occurs with respect to other discontinuities at the transition temperature \( T'_* \), which is very close to \( T_c \).
2. The 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 general expression (2.25)

$$\Delta \eta_1 = -\frac{2B_1}{3C'} \left(1 + \frac{27C'^2 E_1}{B_3^2}\right)^{\frac{1}{2}}.$$ 

that leads to the following volume change at $T_*$

$$\Delta \eta_0(T_*) = -\frac{D}{A_0} \Delta(\eta_1^2) = -4 \frac{DB_3^2}{9A_0C'^2} \left(1 + \frac{27C'^2 E_1}{B_3^2}\right)^{\frac{1}{2}}$$ (4.46)

Both parent and product phases have $\eta_1 \neq 0$ and $\Delta G \neq 0$ 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.(1.19). Using the dimensionless variables (2.21) we can write Eq.(1.20) 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

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

that gives the expression

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

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

\[ \Delta C_P(T') = 2T'^{\prime} \frac{\alpha'^2}{C} \left(1 + \frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} \]  

(4.49)

\[ \Delta \beta_T(T') = \frac{8D^2}{C' A_0^2} \left(1 + \frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} \]  

(4.50)

\[ \Delta \alpha(T') = \frac{4\alpha' D}{C' A_0} \left(1 + \frac{27C'^2E_1}{B_1^3}\right)^{-\frac{1}{2}} \]  

(4.51)

In the limit of small values of external uniaxial pressure we get the Eqs. (4.44), (4.42) and (4.40), derived from their temperature dependence in the Section 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 FCC INTO BCC LATTICE VIA SPONTANEOUS STRAIN

A. FCC – BCC transformation through the Bain strain

There is the case of martensitic transformation of especial interest, namely FCC – BCC transformation in Fe and some ferrous alloys. Since, there is no group-subgroup relationship for the symmetry breaking, the Landau theory is, generally speaking, inapplicable to this case. However, there is an orientational relationship between lattices of the parent and product phase, and the transition could be described in terms of spontaneous strain of 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 cubic to tetragonal lattice. It is accompanied by the volume change, that is approximately 1.5% in the case of pure Fe, where transformation from austenite FCC \( \gamma \)-phase to ferrite BCC \( \alpha \)-one takes place at 910°C. If the lattice periods
for austenite and martensite (ferrite) are \( a_\gamma \) and \( a_\alpha \) respectively, then the strain tensor components have the form

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

The fundamental feature of this case as compared with the above considered phase transition from 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 non-zero value of the order parameter \( \eta_1 \) the symmetry of the lattice was tetragonal, whereas in the case of the FCC – BCC transformation the peculiar value of \( \eta_1 \) is needed to get the low-temperature BCC lattice. If we separate the shear strain from the volume change by taking the latter equal to zero, then we get single (and very large) value of 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 the Landau theory describes, where the value of the order parameter changes with temperature in low-symmetry phase according to the minimization of its Gibbs free energy (2.2).

However, coupling with the volume change \( \eta_0 \) makes it possible to have the \( \eta_1 \) variation in low-temperature phase without breaking of 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 the relationship between 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 value of \( \eta_1 \) preserves the BCC structure of the low-temperature phase, if \( \eta_0 \) is changed in such a way that this relationship is satisfied. It should be noted that (5.3) is meaningful only in restricted region of \( \eta_0 \) and \( \eta_1 \). For example, \( \eta_1 = 0 \) implies unreal result \( a_\alpha = 0 \) from (5.4). Thus, (5.3) is justified only in some vicinity of the transition that is characterized by small volume change \( \sqrt{3} \eta_0 \).

Having supposed FCC – BCC transformation to be ferroelastic one, we should get the minimum of elastic energy for the values of \( \eta_0 \) and \( \eta_1 \) obeying the condition (5.5). Let us study what are the coefficient in the expansion which provide such a minimum. Without careful analysis, it should be noted, however, that the linear approximation used above gives another kind of relationship (4.8) between the shear strain and volume change, thus, non-linear approximation for the thermal expansion energy should be used.

**B. Non-linear elasticity for the volume change**

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

\[
\frac{\delta V}{V} = (1 + \epsilon_{xx})(1 + \epsilon_{yy})(1 + \epsilon_{zz}) - 1. \tag{5.6}
\]

It could be expressed through the symmetrized combinations \( \eta_0, \eta_1 \) and \( \eta_2 \) as follows

\[
\frac{\delta V}{V} = \sqrt{3} \eta_0 + \eta_0^2 + \frac{\eta_0^3}{3\sqrt{3}} - \frac{\eta_1^2 + \eta_2^2}{2} - \frac{\eta_0 (\eta_1^2 + \eta_2^2)}{2 \sqrt{3}} + \eta_1 \left( \frac{\eta_1^2 - 3 \eta_2^2}{3 \sqrt{6}} \right). \tag{5.7}
\]

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 \( \eta_0 \) and \( \eta_1 \). Terms of the first and second order in the volume change \( \eta_0 \) within non-linear approximation have no longer simple relation with the thermal expansion and isothermal compressibility that was obtained
in Section IV A. Similarly, other terms in both $\Delta G_1$ and $\Delta G_{int}$ should be changed. General non-linear elastic energy expansion near the elastic instability with respect to $\eta_1$ now has the form

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

(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 $\eta_0$ implies

$$\frac{\partial \Delta G}{\partial \eta_0} = L_0 + A_0 \eta_0 + B_0 \eta_0^2 + D \eta_1^2 = 0$$

(5.9)

that leads to the following relationship between $\eta_0$ and $\eta_1$ in distorted phase with $\eta_1 \neq 0$:

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

(5.10)

For the high-symmetry phase we have

$$\eta_0 = -\frac{A_0}{2B_0} \left( 1 \mp \left( 1 - \frac{4B_0 L_0}{A_0^2} \right)^{\frac{1}{2}} \right)$$

(5.11)

As there is no co-existing high-symmetry equilibrium states with different values of $\eta_0$, the condition

$$A_0^2 - 4L_0B_0 = 0$$

(5.12)

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

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

(5.13)

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

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

$$\eta_0 = -\sqrt{-\frac{D}{B_0}} \eta_1 - \frac{A_0}{2B_0}$$

(5.14)
and Eq. (5.3) along with (5.12) lead to the following relations between the coefficients in the elastic energy expansion (5.8)

\[ L_0 = 3B_0 \] (5.15)

\[ A_0 = 2\sqrt{3}B_0 \] (5.16)

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

These relations could be, generally speaking, satisfied only in isolated points on 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 phase transition.

Substituting these expressions into the free energy (5.8) and excluding the volume change through Eq. (5.5) we get renormed expansion of the elastic energy with respect to symmetrized strain \( \eta_1 \)

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

which can be considered as a Ginzburg-Landau expansion for ferroelastic phase transition. The first term does not depend on \( \eta_1 \), 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 finite jump in \( \eta_1 \) and \( \eta_0 \) is given by an equation

\[ 9 A^3 - 3 A B^2 + C_1 B^2 = 0 \]

where \( A \) and \( B \) are the expressions in brackets of the first- and second-degree terms in Eq. (5.18). In order some transition line to exist on 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 cubic lattice of high-symmetry phase as an example. The minimization of elastic energy with respect to hydrostatic strain as a secondary order parameter is shown to renorm the second- and fourth-order coefficients of the Ginzburg-Landau expansion of elastic free energy in powers of symmetrized shear strain. The coupling between shear strain and volume change appears to shift the transition temperature under applied external hydrostatic pressure and lead to the finite volume effect of the weakly discontinuous ferroelastic phase transition.

The isothermal compressibility as well as thermal expansion coefficient is shown to diverge near the critical temperature of the second-order ferroelastic phase transition due to the homogeneous fluctuations of the order parameter. The difference between their values in parent and product phases outside the fluctuation region appears to be proportional to coupling coefficient. For the case of first-order transition 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 the change of divergencies for smeared peaks in the temperature dependencies of isothermal compressibility and thermal expansion coefficient around 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 critical point and the uniaxial pressure of magnitude lower than critical, shifts the transition temperature, but preserves the transition. The critical hydrostatic pressure that suppresses phase transition has linear temperature dependence. The order parameter discontinuity and the volume effect diverge at the critical line as well as the difference in 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 the 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 non-linear expression for the elastic energy of thermal expansion is shown to lead to proper relation between the shear strain and volume change for the minima of elastic energy.

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FIG. 1. The dependence of the Gibbs energy on the order parameter $\eta$ 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. Dashed line corresponds to the absence of external field, $\sigma = 0$. 

$\sigma_1 = 0.1$

$\sigma_2 = 0.05$

$\sigma_3 = 0.01$
< \eta^2 >,
arb. un.

\sigma_1 = 0.05
\sigma_2 = 0.025
\sigma_3 = 0.01

FIG. 3. Mean square of the homogeneous order parameter fluctuations around \( T_c \) (\( \tau = 0 \)) under different external fields.
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 \((\tau_c = 1/3, \sigma_c = 1/27)\).