Journal of Applied Mechanics and Technical Physics, Vol. 40, No. 6, 1999

GENERALIZATIONS OF THE CLAUSIUS–CLAPEYRON EQUATION IN A COUPLED THERMOMECHANICAL MODEL

A. G. Knyazeva

UDC 536.46

Several modifications of the Clausius–Clapeyron equation for deformable media, including solid-phase transformations which depend on the change of additional parameters, are proposed. A model of the medium with tensor concentrations of the components for which the unique Clausius–Clapeyron equation is also valid is proposed. The tensor analog of the transition heat is introduced, and an expression for the total transition heat related to the energies of chemical bonds in the crystal lattice is obtained. At least for slow processes, the fundamental possibility of determining the self transition heat in the experiment is shown analytically.

The connectedness of thermophysical and mechanical processes and the phase transformation proper is generally not taken into account in constructing mathematical models of phase transitions [1–3]. However, in some situations, when the role of various energy effects or the dependence of the temperature of the phase transition on the parameters of the medium should be evaluated, the connectedness of various processes can be of primary importance. In the present study, the conditions of phase equilibrium and the possibility of determining the parameters that enter the model of [4] and characterize the medium and the first-order phase transition are analyzed. In the particular situations considered, the external load is absent, and the stress and strains are a consequence of the phase transformation.

1. GENERAL RELATIONS

We write the general relations used.

In terms of the model of [4], the basic equation of thermodynamics (Gibbs equation) for a local volume has the form

$$du = T\,ds + \rho^{-1}\sigma_{ij}\,d\varepsilon_{ij} + \sum_{k=1}^{n+2} g_k\,dN_k + \chi\rho^{-1}\,d\eta, \tag{1.1}$$

where u is the specific internal energy, s is the entropy, T is the temperature, ρ is the density of the medium, σ_{ij} and ε_{ij} are the components of the stress and strain tensors, g_k [J/kg] are the chemical potentials of the components (or their specific partial Gibbs energies) for $k = 1, 2, \ldots, n$, vacancies for $k = n + 1$, and dislocations for $k = n+2$, N_k are the corresponding mass concentrations, χ [J/m^3] is the energy potential of the macrodamages (or the structural potential), $\eta = v_p/v$, v_p [m^3/g] is the specific volume of the macrodamages (cracks and pores), and $v = \rho^{-1}$ is the specific volume of the medium. For small strains, the constant-density approximation $\rho \approx$ const is valid and it is convenient to determine the thermodynamic potentials for a unit volume. In the general case, the potentials for a unit mass should be introduced, because it is quite possible that the potentials cannot exist for a unit volume [5]. In variables T and ε_{ij}, Eq. (1.1) takes the form

---

Tomsk State University, Tomsk 634050. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 40, No. 6, pp. 103–111, November–December, 1999. Original article submitted November 25, 1996; revision submitted June 8, 1998.

$$df = -s\,dT + \rho^{-1}\sigma_{ij}\,d\varepsilon_{ij} + \sum_{k=1}^{n+2} g_k\,dN_k + \chi\rho^{-1}\,d\eta, \tag{1.2}$$

because $f = u - Ts$. Similarly, in variables T and σ_{ij} we have

$$dg = -s\,dT - \rho^{-1}\varepsilon_{ij}\,d\sigma_{ij} + \sum_{k=1}^{n+2} g_k\,dN_k + \chi\rho^{-1}\,d\eta, \tag{1.3}$$

where $g = u - Ts - \rho^{-1}\sigma_{ij}\varepsilon_{ij}$ is the Gibbs specific potential.

It is natural that if at least one potential is known, for example, f, the other potentials can be found via this known potential. In particular, for a thermoelastic isotropic body, the local function of free energy of a unit mass can be given in the form [6]

$$f = f_0 - \Big(3K\alpha_T(T - T_0)I_1 + \mu I_2 + \frac{\lambda}{2}\,I_1^2\Big)\rho^{-1}, \tag{1.4}$$

where f_0 is the fraction of the free energy that does not depend on strains, $f_0 = f_0(t, N_k, \eta)$, $I_1 = \varepsilon_{kk}$, $I_2 = \varepsilon_{ij}\varepsilon_{ij}$ (summation is performed over the repeated indices), $K = \lambda + (2/3)\mu$ is the isothermal modulus of overall compression, and λ and μ are the Lamé coefficients. If there are structural and concentration stresses and strains in the system, the function of free energy

$$f = f_0 - \Big(KwI_1 + \mu I_2 + \frac{\lambda}{2}\,I_1^2\Big)\rho^{-1}, \tag{1.5}$$

where

$$w = 3\Big[\alpha_T(T - T_0) + \sum_{k=1}^{n+2} \alpha_k(N_k - N_{k0}) + \alpha_s(\eta - \eta_0)\Big], \tag{1.6}$$

α_T is the coefficient of linear thermal expansion, α_k are the coefficients of concentration expansion relative to each component (similar concepts were introduced in [4] for vacancies and dislocations), and α_s is the coefficient of structural expansion, is the generalization of (1.4).

Using (1.2) and (1.4), we find

$$\sigma_{ij} = \rho\Big(\frac{\partial f}{\partial \varepsilon_{ij}}\Big)_{T,N_k} = 2\mu\varepsilon_{ij} + \delta_{ij}[\lambda\varepsilon_{kk} - Kw], \tag{1.7}$$

where δ_{ij} is the Kronecker symbol.

Using known relations between the Lamé coefficients and the elasticity modulus E, the Poisson ratio ν, and the modulus K, we rewrite relations (1.7) in the form

$$\varepsilon_{ij} = \frac{1}{E}\,[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij}] - \frac{1}{3}\,w\delta_{ij}.$$

In this case, the specific Gibbs potential has the form

$$g = f_0 + \frac{1}{2E\rho}\,[\nu\sigma_{kk}^2 - (1+\nu)\sigma_{ij}\sigma_{ij}] - \frac{w}{3\rho}\,\sigma_{kk} - \frac{E}{3(1-2\nu)}\,\frac{w^2}{2\rho}. \tag{1.8}$$

The equalities (1.4) and (1.8) allow one to write two equivalent relations for the entropy obtained as the partial derivatives of the potentials f and g with respect to the temperature. In the particular case where the mechanical properties do not depend explicitly on the temperature, we have the following simple relations:

$$s = -\Big(\frac{\partial f_0}{\partial T}\Big)_{\varepsilon_{ij}=0} + 3K\rho^{-1}\alpha_T I_1 = s(\varepsilon_{ij}, T, N_k, \eta),$$

$$s = -\Big(\frac{\partial f_0}{\partial T}\Big)_{\sigma_{ij}=0} + \rho^{-1}\alpha_T\sigma_{mm} + \frac{E\alpha_T}{1-2\nu}\,\rho^{-1}w = s(\sigma_{ij}, T, N_k, \eta).$$

Similarly, we find two equivalent definitions of the chemical potentials of the components. On a per-mole basis, we have

$$g_k = g_{k0} - 3K\rho^{-1}\alpha_k m_k I_1 = g_k(T, \varepsilon_{ij}), \quad g_k = g_{k0} - \rho^{-1}\alpha_k m_k \sigma_{mm} - \frac{\alpha_k m_k E}{1-2\nu}\,\frac{w}{\rho} = g_k(T, \sigma_{ij}).$$

In the simplest case, one can assume that $g_{k0} = g_{k,st} + RT\ln(N_k)$, where R is the universal gas constant, $g_{k,st}$ is the chemical potential of the component k for the standard state, and m_k is its molar mass. Clearly, we have $E/(1-2\nu) = 3K$.

The condition of phase equilibrium of phases Nos. 1 and 2 of the same substance follows immediately from the Gibbs equation, which is similar to (1.1) and is written for each phase separately $du_k = T_k\,ds_k + \rho_k^{-1}\sigma_{ij}^{(k)}\,d\varepsilon_{ij}^k + \chi_k\rho_k^{-1}\,d\eta_k + g_k\,dN_k$, where $k = 1$ and 2, and the condition of general thermodynamic equilibrium of an isolated system which does not do work [7] $ds = d(s_1+s_2) = 0$; for a deformable medium, these conditions lead to the equalities $g_1 = g_2$, $T_1 = T_2$, $\chi_1\rho_1^{-1} = \chi_2\rho_2^{-1}$, and

$$\sigma_{ij}^{(1)}\rho_1^{-1}\,d\varepsilon_{ij}^{(1)} = \sigma_{ij}^{(2)}\rho_2^{-1}\,d\varepsilon_{ij}^{(2)}, \tag{1.9}$$

where ρ_1 and ρ_2 are the partial densities of the phases and $\varepsilon_{ij}^{(1)}$ and $\varepsilon_{ij}^{(2)}$ are the components of the tensor of the strain that arises as a result of phase transitions. Here the necessary requirement is the additivity of the quantity $\chi\rho^{-1}$. For a system with an additional parameter η, we arrive at the conventional condition of phase equilibrium

$$g_1(T, p, \eta) = g_2(T, p, \eta), \tag{1.10}$$

where T and p are the temperature and the pressure equal in both phases only in the case of overall uniform compression. In the general case, it follows from the equality (1.9) that not all changes in the strain components are independent. Some independent components of the tensors of the strain that results from phase transitions are determined by the type of phase transition and the character and structure of the interface, which was thoroughly considered in [2]. If necessary, the specific interface can serve as an additional parameter; then $\chi\rho^{-1}$ is the surface energy.

Generally speaking, for a deformable system that does no do any work ($d\sigma_{ij} = dT = 0$) and for the condition $d\eta = 0$, the condition of thermodynamic equilibrium follows from the Gibbs equation (1.3) and has the form

$$g_1(T, \sigma_{ij}, \eta) = g_2(T, \sigma_{ij}, \eta). \tag{1.11}$$

If $d\chi = 0$ is valid for this system (the additional parameter η can vary), the condition of thermodynamic equilibrium is $dg_s = 0$ or $g_1(T, \sigma_{ij}, \chi) = g_2(T, \sigma_{ij}, \chi)$, where $g_s = u - Ts - \rho^{-1}\sigma_{ij}\varepsilon_{ij} - \rho^{-1}\chi\eta$ is the "structural" Gibbs potential.

2. VARIOUS FORMS OF THE CLAUSIUS–CLAPEYRON EQUATION FOR AN ISOTROPIC MEDIUM

2.1. The Simplest Generalization. Let the phase transition in a solid be connected only with the change in the temperature and concentration (mass fractions) of the phases. The other parameters of the medium, such as the concentration of vacancies, the density of the dislocation distribution, and the volume of cracks, remain unchanged. Here the phase transition from phase No. 1 to phase No. 2 is accompanied by the appearance of temperature and concentration stresses and strains, the magnitude of which is determined by the coefficients α_T, α_1, and α_2 in terms of the function (1.6). Since the point is that we are dealing with the phases N_1 and N_2 of the same substance, we have $m_1 = m_2 = m$.

By definition, during the phase transition of the first kind the first-order derivatives of the Gibbs energy of the phases $g = g_1N_1 + g_2N_2$ with respect to the temperature and pressure, i.e., the entropy and the volume, undergo a jump.

In the general case of transitions of the first kind, the relation between the temperature $T_{\mathrm{p\,h}}$ of the phase transition and the pressure p is established by the Clausius-Clapeyron equation

$$\frac{dT_{ph}}{dp} = \frac{\Delta v_{\rm ph}}{\Delta s_{\rm ph}} = \frac{\Delta v_{\rm ph} T_{\rm ph}}{Q_{\rm ph}}, \tag{2.1}$$

where $\Delta v_{\rm ph}$ and $\Delta s_{\rm ph}$ are the differences between the partial molar volumes and molar entropies of the phases and $Q_{\rm ph}$ is the latent heat of phase transition. Equation (2.1) is easily derived from the phase-equilibrium condition (1.10) for $\eta = 0$ at the temperature and pressure of the phase transition by means of the expansion in a Taylor series of the chemical potentials of the phases in terms of small deviations of T and p from their equilibrium values. In the case of a deformable medium, to construct an equation similar to (2.1), we use the equilibrium condition (1.11), according to which the scalar chemical potentials in an isotropic medium are meant to depend on the components of the stress tensors only through their invariants.

From (1.11) follow the expressions for the components of the tensor of the strain resulting from phase transitions:

$$\varepsilon_{ij}^{(k)} = \left(\partial g_k/\partial \sigma_{ij}\right)_T = -m\alpha_k \rho^{-1}\delta_{ij} \tag{2.2}$$

and the partial molar entropy of the kth phase

$$s_k = -\left(\partial g_k/\partial T\right)_{\sigma_{ij}} = s_{k0} + 9m\alpha_k\rho^{-1}\alpha_T K, \tag{2.3}$$

where $s_{k0} = -(\partial g_{k0}/\partial T)_{\sigma_{ij}} = 0$ $(k = 1, 2)$.

We assume that the temperature deviated from the equilibrium value dT. Since the phases remained in equilibrium, the change in temperature changed the components of the stress tensor by $d\sigma_{ij}$. For small deviations of the temperature and stresses from the equilibrium values, we have $g_k(T + dT, \sigma_{ij} + d\sigma_{ij}) \approx g_k(T, \sigma_{ij}) + (\partial g_k/\partial \sigma_{ij})_T d\sigma_{ij} + (\partial g_k/\partial T)_{\sigma_{ij}} dT$.

By virtue of the equality of the chemical potentials (1.11) and the expressions for the derivatives of the Gibbs energies of the phases (2.2) and (2.3), we find

$$(s_1 - s_2)\, dT = 3m\,\frac{\alpha_1 - \alpha_2}{\rho}\, dp, \qquad T = T_{\rm ph}, \qquad p = p_{\rm ph}, \tag{2.4}$$

where $p = -(1/3)\sigma_{mm}$.

The heat of phase transition from phase No. 2 to phase No. 1 is found from the equality $Q_{\rm ph}{=}T_{\rm ph}(s_1{-}s_2)$. With account of (2.3), we have

$$Q_{\rm ph} = Q_{\rm ph0} + \Delta Q_{\rm ph}, \tag{2.5}$$

where $Q_{\rm ph0} = T_{\rm ph}(s_{10} - s_{20})$ is the latent heat of phase transition without allowing for the connectedness of thermal and mechanical processes or the self heat of phase transition and $\Delta Q_{\rm ph}$ is its variation under the action of internal mechanical forces:

$$\Delta Q_{\rm ph} = (\alpha_1 - \alpha_2) 9m\alpha_T K\rho^{-1} T_{\rm ph}. \tag{2.6}$$

In experimental studies, one determines the quantity $Q_{\rm ph}$, which can consist of various components, including the work of internal forces, and can be different in different experimental conditions.

As a result, for an isotropic medium with small elastic strains the modified Clausius–Clapeyron equation (2.1) takes the form

$$dT_{\rm ph}/dp = 3(m/\rho)(\alpha_1 - \alpha_2)(T_{\rm ph}/Q_{\rm ph}). \tag{2.7}$$

It is noteworthy that if the chemical potential g_k is a scalar, as are all thermodynamic functions, it depends on the invariants of the stress tensors, and we shall always come to the unique Clausius–Clapeyron equation.

Equations (2.7) and (2.5) explain the appearance of the heat of phase transition $Q_{\rm ph} \neq 0$ in the cases where the self heat of phase transition is zero: $Q_{ph0} = 0$, which does not follow from the uncoupled models of mechanics.

In accordance with (2.1), from (2.7) we have that if the volume of the first phase is greater than that of the second phase, the pressure rise results in an increase in the temperature of the phase transition with

$Q_{\text{ph}} > 0$. For $\alpha_2 < \alpha_1$, the inverse effect occurs, i.e., with decrease in pressure, the transition temperature decreases. It follows from Eqs. (2.1) and (2.7) that, in the case of a phase transition of the first kind, the difference between the coefficients of concentration expansion of the phases is proportional to the difference between the molar volumes of the phases:

$$\alpha_2 - \alpha_1 = \rho \Delta v_{\text{ph}}/(3m). \tag{2.8}$$

However, if the phase transition in a solid occurs without changing the volume, i.e., $\Delta v_{\text{ph}} \approx 0$ (e.g., in several phase transitions of the martensite type), which is equivalent to the condition $\alpha_1 \approx \alpha_2$, one cannot obtain the dependence of the transition temperature on the stresses from Eq. (2.7); therefore, other models should be employed or the dependence of the properties on the temperature and concentration of the phases should be taken into account.

One can speak of the unvaried volume only conventionally, and the small changes in the volume (of the order of 1–2%) should be taken into account in the construction of the model. We assume that in both phases, the temperature varies by dT and that the stress increments in these phases are different. In this case, simple calculations with allowance for (1.11), (2.3), and (2.4) result in the equality

$$(s_1 - s_2)\,dT = 3m\rho^{-1}(\alpha_1\,dp_1 - \alpha_2\,dp_2), \tag{2.9}$$

where $p_1 = -(1/3)\sigma^{(1)}_{mm}$ and $p_2 = -(1/3)\sigma^{(2)}_{mm}$ are the pressure variations in the phases.

If such a phase transition occurs at constant temperature ($dT = 0$), from (2.9) we find

$$\alpha_1/\alpha_2 = \left(\partial p_2/\partial p_1\right)_T, \tag{2.10}$$

i.e., in these conditions the ratio between the pressure variations in the phases is inversely proportional to the ratio between the coefficients of concentration expansion. This equation is an analog of the Poynting equation [7].

We note that Eqs. (2.7), (2.8), and (2.10) can be used to determine experimentally the coefficients of concentration expansion of the phases if the phase transition occurs under different conditions.

2.2. Effect of Additional Parameters on the Phase Transition of the First Kind. Let now the transition of phase No. 2 to phase No. 1 be accompanied by damages of a certain type. In this case, the function (1.6), on which the thermodynamic potentials f and g and the chemical potentials of the phases depend, also includes the parameter α_s.

If the condition $d\eta = 0$ is not satisfied, with allowance for the equalities $N_1 + N_2 = \text{const}$ the condition of thermodynamic equilibrium for the two-phase system considered has the form $g_1(T, \sigma_{ij}, \eta) = g_2(T, \sigma_{ij}, \eta) + \chi\rho^{-1}(\partial\eta/\partial y)$, where $y = N_2/(N_{10} + N_{20})$. If η does not depend explicitly on y or the quantity χ is small, we again arrive at the equation of phase equilibrium in the form (1.11). Proceeding similarly as in Sec. 2.1, we present the chemical potentials of the phases as series in terms of small deviations from the initial state.

The partial derivative of the chemical potential of the kth phase with respect to the additional parameter is determined from the relation $\chi_k = (\partial g_k/\partial\eta)_{\sigma_{ij},T} = (\partial g_{k0}/\partial\eta)_{\sigma_{ij}=0} - 9m\rho^{-1}\alpha_k K\alpha_s$. In the simplest case of a damage-free medium in a undeformed state, we have $\partial g_{k0}/\partial\eta = 0$. Various variants of the Clausius–Clapeyron equation for a deformable medium follow from the relation

$$-(s_1 - s_2)\,dT - m\rho^{-1}(\alpha_1\,d\sigma^{(1)}_{ij} - \alpha_2\,d\sigma^{(2)}_{ij})\delta_{ij} - 9m\rho^{-1}K\alpha_s(\alpha_1\,d\eta_1 - \alpha_2\,d\eta_2) = 0. \tag{2.11}$$

It follows from (2.11) that if the phase transition occurs at the same pressure in the phases and at constant temperature $dT = 0$, then

$$(\alpha_1 - \alpha_2)\,dp = 3K\alpha_s(\alpha_1\,d\eta_1 - \alpha_2\,d\eta_2) \tag{2.12}$$

or

$$\alpha_1\left(\partial\eta_1/\partial p\right)_T - \alpha_2\left(\partial\eta_2/\partial p\right)_T = (\alpha_1 - \alpha_2)/(3K\alpha_s). \tag{2.13}$$

Equation (2.13) establishes a different dependence between the pressure variation in the phase transition at constant temperature and the change in the additional parameter η in different phases. In this case, if the pressure in the phases is also constant ($dp = 0$), from (2.12) follows one more analog of the Poynting equation

$$\alpha_1/\alpha_2 = \Big(\partial\eta_2/\partial\eta_1\Big)_{T,p} \equiv v_1/v_2, \tag{2.14}$$

where, as before, $v_k = 3m\alpha_k\rho^{-1}$ ($k = 1$ and 2) is the partial molar volume of the kth phase. According to (2.14), the variation in η in one of the phases relative to the other is inversely proportional to the relation of the partial molar volumes of these phases for a constant temperature and pressure.

Similarly to (2.13), from (2.14) we find

$$\alpha_1\Big(\partial p_1/\partial\eta\Big)_T - \alpha_2\Big(\partial p_2/\partial\eta\Big)_T = 3K\alpha_s(\alpha_1 - \alpha_2)$$

or a simple relation $(\partial p/\partial\eta)_T = 3K\alpha_s$ for $dp_1 = dp_2 = dp$; as a result, we have the principal possibility of determining experimentally the coefficient of structural expansion α_s relative to the angle of slope of the curve $p(\eta)$ in the origin of coordinates. Apparently, the change in the volume of damages (for example, per unit surface) and the density of the dislocation distribution are not the most complex parameters for measurement. The kinetic features of the phase transitions depend greatly on these quantities, in particular, in tin [8] and ammonium perchlorate [9].

If the phase transition occurs at constant pressure, the equation that relates the variation in η in different phases to the temperature has the form

$$\alpha_1\Big(\partial\eta_1/\partial T\Big)_p - \alpha_2\Big(\partial\eta_2/\partial T\Big)_p = -\rho(s_1 - s_2)/(9mK\alpha_s).$$

In the particular case $d\eta_1 = d\eta_2 = d\eta$, from the last equality we obtain

$$\Big(\frac{dT_{\rm ph}}{d\eta}\Big)_p = -\frac{9(\alpha_1 - \alpha_2)mK\alpha_s}{\rho(s_1 - s_2)} \equiv -\frac{9(\alpha_1 - \alpha_2)mK\alpha_s}{\rho Q_{\rm ph}}T_{\rm ph}.$$

In other words, the temperature of the phase transition can probably vary at constant pressure owing to the change in any additional parameter that describes this medium (for example, the low concentration of an impurity, the density of the dislocation distribution, the specific volume of damages, etc.); generally speaking, precisely this occurs in various experimental studies [8–10].

Assuming that the variation in pressure and the relative volume of damages (or any additional parameter η) occurs in the same manner in both phases, i.e., $dp_1 = dp_2 = dp$ and $d\eta_1 = d\eta_2 = d\eta$, from (2.11) we find

$$\frac{\partial T_{\rm ph}}{\partial p} = \frac{3m(\alpha_1 - \alpha_2)}{\rho Q_{\rm ph}}T_{\rm ph}\Big(1 - 3K\alpha_s\frac{\partial\eta}{\partial p}\Big), \tag{2.15}$$

where the magnitude of the second term in brackets is determined by the kinetics of the variation in the additional parameter with pressure and, possibly, by the transfer processes that correspond to η [8, 10, 11].

2.3. The Possibility of Determining the Heat of Phase Transition. We consider a slow phase transition that begins from the surface and propagates along a thick plate with a velocity much smaller than the sound velocity in a solid. The plate is assumed to be not fixed and free from external forces. The problem of mechanical equilibrium of a similar system is analyzed adequately in the literature. For a thick plate (the thickness is considerably greater than the dimensions of the phase-transition zone) we can set $\varepsilon_{mm} = Kw/(\lambda+2\mu) = (1/3)(1+\nu)w/(1-\nu)$ with good accuracy. Therefore, in the case considered, the change in the entropy during the phase transition is $s = -(\partial f_0/\partial T)_{\varepsilon_{ij}=0} + 3K\alpha_T\varepsilon_{mm} = s_0 + 3K^2\alpha_T w/(\lambda + 2\mu)$.

On a per-mole basis, with allowance for the condition $N_1 + N_2 = \text{const}$, we have

$$(\Delta s)_{\rm ph} = m\rho^{-1}\Big(\frac{\partial s}{\partial N_2}\Big)_T = \frac{(3K\alpha_T)^2}{\lambda + 2\mu}\,\frac{\alpha_2 - \alpha_1}{\alpha_T}\,\frac{m}{\rho}.$$

The last equality gives the expression for the transition heat in the form

$$Q_{\mathrm{ph}} = T_{\mathrm{ph}}(\Delta s)_{\mathrm{ph}} = -T_{\mathrm{ph}}\,\frac{(3K\alpha_T)^2}{\lambda+2\mu}\,\frac{\alpha_1-\alpha_2}{\alpha_T}\,\frac{m}{\rho}. \tag{2.16}$$

Comparing (2.16) and (2.5), with allowance for (2.6) we find the latent heat of phase transition $Q_{\mathrm{ph}0} = -6T_{\mathrm{ph}}\alpha_T K(\Delta v)_{\mathrm{ph}}(3\lambda+4\mu)/(\lambda+2\mu)$.

Using (2.16), for a slow phase transition, from (2.7) we find $dT_{\mathrm{ph}}/dp = -3\alpha_T(\lambda+2\mu)/(3K\alpha_T)^2 < 0$, i.e., the transition temperature decreases with increase in pressure; this is in agreement with the classical concepts of phase transitions (see, e.g., [7, 10]), where the concepts of stress tensors and the coefficients of concentration expansion of the phases are omitted.

Similarly, from (2.15) follows $dT_{\mathrm{ph}}/dp = -3\alpha_T((\lambda+2\mu)/(3K\alpha_T)^2)(1-3K\alpha_s\,\partial\eta/\partial p)$. The sign of the last equality depends on how η varies with pressure variation.

3. TENSOR CONCENTRATION AND CHEMICAL TENSOR POTENTIALS

For modeling phase transitions of the first kind, the variants based on the use of various models of deformable media are possible if these transitions are not accompanied by a change in volume or have some features of transitions of the second kind. In particular, the model of the medium used in [4, 8] admits a simple generalization to anisotropic media. In the present work, to describe phase transformations that are connected to the transition of one crystalline modification to another, we introduce the tensors of phase concentrations (or components) $N_{lm}^{(k)}$ and the corresponding tensors of the coefficients of concentration expansion $\alpha_{lm}^{(k)}$. The structure of these tensors and the number of their independent components are determined by the type of symmetry of the crystal lattices of real crystals and their modifications similarly to the thermal properties of crystals (e.g., $\hat{\alpha}_T$) in the models of anisotropic media. In contrast to known models, we consider that the anisotropy of the properties of substances is immediately (explicitly) related to the type of the tensors $\hat{N}_k$ and the character and energy of the chemical bonds in the crystal in different directions; however, the macrocharacteristics α_T, λ, μ, etc., remain scalars that depend on the concentration tensors through their invariants.

For the function w and all thermodynamic potentials to remain scalars, they should depend on either the invariants or invariant combinations of the new tensors. We assume that, in the general form, the function w has the form

$$w = 3\Big[\alpha_T(T-T_0) + \sum_{k=1}^{n}\alpha_{lm}^{(k)}(N_{lm}^{(k)} - N_{lm,0}^{(k)}) + \alpha_s(\eta-\eta_0)\Big].$$

Therefore, the corresponding tensors of the chemical potentials, which characterize the energy of chemical bonds in crystals or its change after the component k is added, depend on the quantities $\alpha_{lm}^{(k)}$. From the form of the free-energy function for an elastic body (1.5), we find

$$g_{lm}^{(k)} = \frac{\partial f_0}{\partial N_{lm}^{(k)}} - 3\alpha_{lm}^{(k)}K\varepsilon_{ii} - w\,\frac{\partial K}{\partial N_{lm}^{(k)}}\,\varepsilon_{ii} + \varepsilon_{nj}\varepsilon_{nj}\,\frac{\partial\mu}{\partial N_{lm}^{(k)}} + \frac{1}{2}\,\varepsilon_{ii}^2\,\frac{\partial\lambda}{\partial N_{lm}^{(k)}}.$$

For simplicity, we assume that the mechanical characteristics λ, μ, and K are certain mean quantities for the crystal and do not depend explicitly on the concentrations of the kth components. This approximation is suitable for describing the kinetics of the phase transition, but require clarification to model the mechanical behavior of crystals. Generally speaking, the quantities λ and μ are also determined by the energy of chemical bonds in the crystal; therefore, to construct a more complete model, concrete dependences between the parameters $\alpha_{lm}^{(k)}, \lambda, \mu$, etc., can be needed; this can become the object of a separate study. Here we confine ourselves to a simple approximation for the components of the tensors of chemical potentials $g_{lm}^{(k)} = g_{lm,0}^{(k)} - 3K\alpha_{lm}^{(k)}\rho^{-1}\varepsilon_{ii}$ $(k = 1, 2, \ldots, n)$. On a per-mole basis, we have $g_{lm}^{(k)} = g_{lm,0}^{(k)} - 3K\alpha_{lm}^{(k)}m_k\rho^{-1}\varepsilon_{ii} = g_{lm}^{(k)}(T, \varepsilon_{ij})$. With allowance for the link between the first invariants of the stress and strain tensors, we find

$$g_{lm}^{(k)} = g_{lm,0}^{(k)} - 3K\alpha_{lm}^{(k)}m_k\rho^{-1}[\sigma_{ii} + 3Kw] = g_{lm}^{(k)}(T, \sigma_{ij}). \tag{3.1}$$

As before, the condition of thermodynamic equilibrium between the phases is $dg = 0$. Similarly to the aforesaid (see Sec. 2), we find the following partial derivatives of the components of the tensors of chemical potentials of the phases relative to the temperature and the stress-tensor components:

$$s^{(k)}_{lm} = -\left(\frac{\partial g^{(k)}_{lm}}{\partial T}\right)_{\sigma_{ij}} = s^{(k)}_{lm} + 3m\rho^{-1}\alpha_T K \alpha^{(k)}_{lm}; \tag{3.2}$$

$$\varepsilon^{(k)}_{lm} = -\left(\frac{\partial g^{(k)}_{lm}}{\partial \sigma_{ij}}\right)_T = -m\rho^{-1}\alpha^{(k)}_{lm}\delta_{ij}. \tag{3.3}$$

By analogy with chemical scalar potentials, we have

$$g^{(k)}_{lm,0} = g^{(k)}_{lm,st} + RT\ln[N^{(k)}_{lm}], \qquad s^{(k)}_{lm,0} = -\left(\frac{\partial g^{(k)}_{lm,0}}{\partial T}\right)_{\sigma_{ij}=0}.$$

Therefore, in the model considered, the partial molar entropy of the kth phase (3.2) is a tensor quantity and is determined by the form of the concentration tensors and the coefficients of concentration expansion. In the general case, the strain that arises as a result of phase transitions is the tensor of the fourth order with components (3.3). It follows from the condition of thermodynamic phase equilibrium that

$$\frac{dT_{\text{ph}}}{dp} = 3m\rho^{-1}\Big(\Delta\alpha_{ii} + \sum_{\substack{l,m \\ l\neq m}} \Delta\alpha_{lm}\Big)\Big/\Big(\Delta s_{ii} + \sum_{\substack{l,m \\ l\neq m}} \Delta s_{lm}\Big). \tag{3.4}$$

It is logical to identify the tensor analog of the heat of phase transition $\hat{Q}_{\text{ph}} = (\hat{s}_1 - \hat{s}_2)T_{\text{ph}}$ with the energies of chemical bonds per mole. The type of the tensors $\hat{Q}_{\text{ph}}$ and $\hat{s}_k$ is determined by the symmetry of the crystal lattices of the phases. The heat of phase transition, which is determined in the experiment, is the quantity

$$Q_{\text{ph}} = \Big(\sum_{l,m}\Delta s_{lm}\Big)T_{\text{ph}} = \Big(\sum_{l,m}\Delta s_{lm,0} + 3mK\rho^{-1}\alpha_T\sum_{l,m}\Delta\alpha_{lm}\Big)T_{\text{ph}}.$$

Thus, Q_{ph} depends on the type of crystal lattice and the energies of atomic bonds in the lattice, to be more precise, on their difference in different phases of the crystal.

The change of the molar volume in this phase transition is $3m\rho^{-1}\Delta\alpha_{ii} = (\Delta v)_{\text{ph}}$. It is natural that if the molar volume during the phase transition does not vary, the expression (3.4) relates the change in the temperature of the phase transition as the pressure varies to the variation in the crystal shape (or the type of crystal lattice).

Therefore, if the phase transition occurs at constant temperature but at different pressures in the phases, then

$$\left(\frac{\partial p_1}{\partial p_2}\right)_T = \sum_{l,m}\alpha^{(2)}_{lm}\Big/\sum_{l,m}\alpha^{(1)}_{lm}.$$

We note once again that all the thermodynamic potentials in the proposed model of the medium are scalars, and all the parameters of the medium have the same physical meaning as in the simpler models. In studying the phase transitions of complex compounds, one needs, apparently, to introduce the concentration tensors and the coefficients of concentration expansion that characterize the types of sublattice formed by atoms of each sort.

This work was supported by the Competition Center for Fundamental Natural Sciences, St. Petersburg State University (Grant No. 95-0-4.3-39).

REFERENCES

1. A. L. Roitburd, "Modified Clausius–Clapeyron equation for the hysteresis of phase transformations in solids," *Fiz. Tverd. Tela*, **25**, No. 1, 33–40 (1983).
2. M. A. Grinfel'd, *Methods of Mechanics of Continuous Media in the Theory of Phase Transformations* [in Russian], Nauka, Moscow (1990).
3. V. A. Likhachev and V. G. Malinin, *Structural-Analytical Theory of Strength* [in Russian], Nauka, St. Petersburg (1993).
4. A. G. Knyazeva, "Connected equations of heat and mass transfer in a chemically reacting solid mixture with allowance for deformation and damage," *Prikl. Mekh. Tekh. Fiz.*, **37**, No. 3, 97–108 (1996).
5. L. I. Sedov, *Continuum Mechanics* [in Russian], Nauka, Moscow (1973).
6. L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, Pergamon Press, Oxford–New York (1970).
7. V. A. Kirillin, V. V. Sychev, and A. E. Sheindlin, *Technical Thermodynamics* [in Russian], Énergoatomizdat, Moscow (1983).
8. A. A. Matvienko, A. A. Sidel'nikov, and V. V. Boldyrev, "Dimensional effect in the polymorphic transformation of tin due to relaxation of mechanical stresses," *Fiz. Tverd. Tela*, **36**, No. 11, 3194–3201 (1994).
9. *Mechanism of Thermal Expansion of Ammonium Perchlorate* (Collected scientific papers) [in Russian], Joint Institute of Chemical Physics, Chernigolovka (1981).
10. R. A. Svelin, *Solid-State Thermodynamics* [in Russian], Metallurgiya, Moscow (1968).
11. A. G. Knyazeva, *Introduction to Locally Equilibrium Thermodynamics of Physicochemical Transformations in Deformable Media* [in Russian], Izd. Tomsk Univ., Tomsk (1996).