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# *PHASE TRANSITIONS OF THE FIRST ORDER BUT NEARLY OF THE SECOND*

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In the elastically isotropic model of a solid body, allowance for compressibility and for interaction with acoustic phonons leads to a first order phase transition in those cases in which, without allowance for acoustic effects, the heat capacity becomes infinite. Near the transition, the thermodynamic derivatives remain finite but have an anomalous dependence on temperature.

## 1. INTRODUCTION

In many cases, phase transitions in solid bodies are transitions of first order but nearly of the second. The nearness cannot be accidental; it is due to the fact that near a second-order transition point, the lattice becomes unstable. It was Rice[1] who first called attention to this instability (see also[2]). He noted that in case the heat capacity at constant volume becomes infinite at some temperature dependent on the density, then in the vicinity of the transition temperature $\partial p/\partial V$ is proportional to the heat capacity and is positive. Consequently, the singular point lies in a region of absolute instability, and the transition must be of first order.

However, the assumption that the heat capacity at constant volume becomes infinite is incorrect. This is because allowance for motion of the centers of the cells leads to additional interaction by exchange of acoustic phonons[3,4]. This interaction has a singularity at small momentum and therefore influences the character of the transition. Thus Fisher[5] supposed that in a lattice that is being compressed, $C_V$ is finite and it is the heat capacity $C_p$ that becomes infinite, and the transition remains a second order transition. It is shown below, for the case of an elastically isotropic model, that this assumption is justified only in the unreal case of a vanishing compression modulus. With a nonvanishing compression modulus, a first-order transition occurs. The temperature dependence of the heat capacity, the spontaneous moment, the compressibility, and the susceptibility is found. Near the transition these quantities remain finite, but under small strain they change appreciably within a narrow temperature range.

## 2. THE HAMILTONIAN WITH ALLOWANCE FOR ACOUSTIC PHONONS

In each cell of the crystal, it is possible to choose a certain generalized coordinate $\eta_i$, whose mean value is a parameter of order $\eta$. For example, in ferroelectrics $\eta_i$ is proportional to the distance of the central atom from the center of the cell; in quartz, to the difference between the distances of neighboring oxygen atoms from the axis. Without allowance for acoustic oscillations, in the "clamped" case (zero deformation), the simplest form of Hamiltonian of the system has the form

$$H=\sum_i\left(-a\eta_i^2+\frac{1}{2}b\eta_i^4\right)+\sum_{ij}V_{ij}(\eta_i-\eta_j)^2. \tag{1}$$

When the parameters a and b are small, the Hamiltonian (1) corresponds to transitions of the displacement type; when they are large, to transitions of the order-disorder type. Thus if $a = b \gg T$, the important values of $\eta_i$ are those near $\pm 1$, and the Hamiltonian (1) differs little[3] from the Hamiltonian of the Ising model.

It is assumed below that the system described by the Hamiltonian (1) has, at a certain temperature $T_C^0$, a second-order transition point with an infinite heat capacity. Near $T_C^0$ the free energy depends only on the difference $T - T_C^0$:

$$F=-T\ln\int\prod_i d\eta_i\exp\left(-\frac{H}{T}\right)=-T_c{}^0 f\left(\frac{T-T_c{}^0}{T_c{}^0}\right). \tag{2}$$

For $T \to T_C^0$ the function f evidently has, just as in the Ising model, the form $A|T - T_C^0|^{2-\alpha}$, $\alpha \approx 1/8$. There is also possible a behavior of the form $-A(T - T_C^0)^2 \ln|T - T_C^0|$. If the parameters of the Hamiltonian (1) are such that there is a region of applicability of the self-consistent field approximation, then in this region the singular part of the free energy is proportional to $|T - T_C^0|^{3/2}$.

With allowance for interaction with long-wave acoustic phonons, which are described by a vector field $u_\alpha(\mathbf{r})$, the Hamiltonian of an elastically isotropic solid body can be written in the form

$$H=\sum_i\left\{\left(\frac{1}{2}K_0-\frac{1}{3}\mu\right)\left(\frac{\partial u_\alpha}{\partial r_\alpha}\right)^2+\mu\left(\frac{\partial u_\alpha}{\partial r_\beta}\right)^2\right.$$
$$\left.+\left(-a-q\frac{\partial u_\alpha}{\partial r_\alpha}\right)\eta_i^2+\frac{1}{2}b\eta_i^4+\sum_j V_{ij}(\eta_i-\eta_j)^2\right\}. \tag{3}$$

Here $K_0$ and $\mu$ are the nonsingular parts of the bulk and shear moduli.

## 3. THE GIBBS THERMODYNAMIC POTENTIAL

The Gibbs thermodynamic potential is determined by the formula

$$\Phi=-T\ln\int d\eta_i\,du_\alpha(\mathbf{r})\exp\left\{-\frac{1}{T}\left[H-\sigma_{\alpha\beta}\sum_i\frac{\partial u_\alpha(\mathbf{r})}{\partial r_\beta}\right]\right\}. \tag{4}$$

(Here and hereafter, the product sign with respect to i, $\alpha$, and $\beta$ is omitted.) We separate out the uniform-deformation tensor $u_{\alpha\beta}$:

$$\frac{\partial u_\alpha(\mathbf{r})}{\partial r_\beta}=u_{\alpha\beta}+\frac{1}{N}\sum_{\mathbf{k}\neq 0}ik_\beta u_\alpha(\mathbf{k})\exp(i\mathbf{kr}), \tag{5}$$

where N is the number of cells in unit volume. On substituting (3) and (5) into formula (4), we get

$$\Phi = -T \ln \int du_{\alpha\beta}\, d\eta_i\, du_\alpha(\mathbf{k}) \exp\Big\{-\frac{1}{NT}\sum_{\mathbf{k}\neq 0}\Big[\frac{1}{2}K_0 u_{\alpha\alpha}{}^2$$
$$+\mu(u_{\alpha\beta}-{}^1\!/_3\delta_{\alpha\beta}u_{\gamma\gamma})^2-\sigma_{\alpha\beta}u_{\beta\alpha}+({}^1\!/_2K_0+{}^2\!/_3\mu)\,|k_\alpha u_\alpha(\mathbf{k})|^2$$
$$+\mu(k^2|u_\alpha(\mathbf{k})|^2-|k_\alpha u_\alpha(\mathbf{k})|^2)-\sum_i(a+qu_{\alpha\alpha}+qik_\alpha u_\alpha(\mathbf{k})e^{i\mathbf{kr}_i})\eta_i{}^2$$
$$+\sum_i\frac{1}{2}b\eta_i{}^4+\sum_{ij}V_{ij}(\eta_i-\eta_j)^2\Big]\Big\}. \qquad (6)$$

We calculate the Gaussian integrals over $u_\alpha(\mathbf{k})$ and over the shear part of the tensor $u_{\alpha\beta}$. The result is

$$\Phi = \Phi_0 + \frac{1}{2\mu}(\sigma_{\alpha\beta}+p\delta_{\alpha\beta})^2 - T\ln\int du_{\alpha\alpha}\,d\eta_i \exp\Big\{-\frac{1}{T}\Big[\frac{1}{2}K_0u_{\alpha\alpha}{}^2$$
$$+pu_{\alpha\alpha}+\sum_{ij}V_{ij}(\eta_i-\eta_j)^2-\sum_i(a+qu_{\alpha\alpha})\eta_i{}^2+\frac{1}{2}b\sum_i\eta_i{}^4$$
$$-\frac{3q^2}{2N(3K_0+4\mu)}\sum_{\mathbf{k}\neq 0}\sum_{ij}\eta_i{}^2\eta_j{}^2\exp(i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j))\Big]\Big\}. \qquad (7)$$

Here $\Phi_0$ is a smooth function of temperature, and the pressure $p = -{}^1\!/_3\sigma_{\alpha\alpha}$. The dependence of $\Phi$ on the shearing stress is described by the second term of formula (7), which, in the model being considered, has no singularity, and which will hereafter be included in $\Phi_0$. The last term in formula (7) acquires the same form as the next-to-last if we add to it a term

$$-(1/2N)q^2(K_0+{}^4\!/_3\mu)^{-1}\Big(\sum_i\eta_i{}^2\Big)^2.$$

For this purpose, we make in the integral over $u_{\alpha\alpha}$ the substitution

$$u_{\alpha\alpha}=\frac{v}{K_0}\sqrt{\frac{3K_0+4\mu}{4\mu}}+\frac{q}{K_0}\Big(1-\sqrt{\frac{4\mu}{3K_0+4\mu}}\Big)\sum_i\eta_i{}^2-\frac{p}{K_0}, \qquad (8)$$

whereupon the expression (7) takes the form

$$\Phi=\Phi_0-\frac{p^2}{2K_0}-T\ln\int dv\,d\eta_i\exp\Big\{-\frac{1}{T}\Big[\frac{1}{2}\frac{3K_0+4\mu}{4\mu K_0}v^2$$
$$+\sum_i\Big(a+q\frac{v-p}{K_0}\Big)\eta_i{}^2+\frac{1}{2}\Big(b-\frac{3q^2}{3K_0+4\mu}\Big)\sum_i\eta_i{}^4$$
$$+\sum_{ij}V_{ij}(\eta_i-\eta_j)^2\Big]\Big\}. \qquad (9)$$

The integral over $\eta_i$ differs from the corresponding integral in formula (2) only by redefinition of the constants a and b. The integration over v can be carried out with statistical exactness by the method of steepest descents. As a result, we get the expression for $\Phi$ in parametric form

$$\Phi=\Phi_0-\frac{p^2}{2K_0}+\frac{1}{2}\frac{3K_0+4\mu}{4\mu K_0}v^2+F\Big(a+q\frac{v-p}{K_0},\ b-\frac{q^2}{K_0+{}^4\!/_3\mu}\Big), \qquad (10)$$

$$\partial\Phi/\partial v=0. \qquad (11)$$

When the shear modulus $\mu$ vanishes (as, for example, in the one-dimensional case), it follows from equation (11) that v = 0; then the thermodynamic potential $\Phi$ differs only by a change of parameters from the free energy F found without allowance for acoustic motion. When $\mu \neq 0$, the character of the transition changes.

The nonsingular part of F will lead to some change of the first three terms in formula (10) and will be disregarded below. In the singular part, what is of greatest importance is the dependence of $T_C^0$ on the parameter a, and therefore the singular part of F is determined by formula (2), in which $T_C^0$ varies smoothly with the parameter v. On introducing instead of v the new parameter

$$x=\frac{1}{T_c{}^0}\Big\{\frac{T-T_c{}^0}{T_c{}^0}-\frac{q}{K_0}\frac{\partial T_c{}^0}{\partial a}(p-v)\Big\},$$

we find the dependence of $\Phi$ on T in parametric form,

$$\Phi=\Phi_0-\frac{p^2}{2K_0}+T_c{}^0\Big[-f(x)+\frac{1}{2\lambda}\Big(\frac{T-T_c{}^0-cp}{T_c{}^0}-x\Big)^2\Big], \qquad (12)$$
$$\partial\Phi/\partial x=0,$$

where

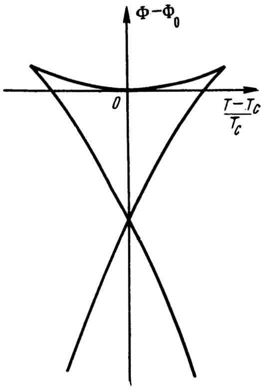
$$\lambda=\frac{4\mu K_0c^2}{T_c{}^0(3K_0+4\mu)},\qquad c=\frac{q}{K_0}\frac{\partial T_c{}^0}{\partial a}.$$

As will be shown below, the constant c is equal to the derivative of the transition temperature with respect to pressure.

The expression (12) can be rewritten in the form

$$\Psi=\Phi_0-\frac{p^2}{2K_0}+T_c{}^0\Big[-f(x)+\frac{\lambda}{2}(f'(x))^2\Big],$$
$$\frac{T-T_c{}^0-cp}{T_c{}^0}=x-\lambda f'(x). \qquad (13)$$

If the heat capacity of the system without allowance for acoustic phonons becomes infinite, then f″ increases at small x. In this case it follows from the second equation of (13) that T is a nonmonotonic function of x. Therefore x and consequently $\Phi$ are nonunique functions of T. The potential $\Phi$ as a function of T is shown in the figure. The singular point of $\Phi$, corresponding to x = 0, is in the region of absolute instability. The temperature of the first-order transition is found as the point of intersection of the two branches of the thermodynamic potential and is determined from the system of equations



$$T(x_-)=T(x_+),\quad \Phi(x_-)=\Phi(x_+). \qquad (14)$$

Since $x_+$ and $x_-$ are independent of p, the constant c in (13) is equal to the derivative of the first-order transition temperature with respect to pressure. If the singular part of the potential $\Phi$ is symmetric with respect to the transition point, then $x_- = -x_+$, and the temperature of the first-order transition is

$$T_C=T_C{}^0+cp. \qquad (15)$$

## 4. THERMODYNAMIC DERIVATIVES

On differentiating the thermodynamic potential with respect to temperature, pressure, and the external field h, we get for the thermodynamic quantities the expressions

$$S = S_0 + f'(x), \quad C_p = C_p{}^0 + \frac{f''(x)}{1 - \lambda f''(x)}$$

$$\Delta V = -\frac{p}{K_0} + cf'(x), \quad \frac{1}{K} = \frac{1}{K_0} + \left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{\lambda f''(x)}{1 - \lambda f''(x)}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{c}{T_C}\frac{f''(x)}{1 - \lambda f''(x)}, \quad \frac{1}{K_{\text{ad}}} = \frac{1}{K_0} + \left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{C_p{}^0}{C_p}\frac{\lambda f''(x)}{1 - \lambda f''(x)},$$

$$C_V = C_V{}^0 + \frac{f''(x)}{1 + \lambda(3K_0/4\mu)f''(x)}, \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{cK_0}{T_C}\frac{f''(x)}{1 + \lambda(3K_0/4\mu)f''(x)},$$

$$-\frac{\partial\Phi(T)}{\partial h} = T_C\frac{\partial f(x)}{\partial h}, \quad -\frac{\partial^2\Phi(T)}{\partial h^2} = T_C\left[\frac{\partial^2 f(x)}{\partial h^2} + \frac{\lambda(\partial f'(x)/\partial h)^2}{1 - \lambda f''(x)}\right] \tag{16}$$

In these formulas, the parameter x must be expressed in terms of T by means of the second equation (13).

In a state of thermodynamic equilibrium, the permissible values of x are determined by the inequalities $x \geq x_+$ and $x \leq x_-$ above and below, respectively, the point of the first-order phase transition. The metastable region is contained in the temperature interval $T(\tilde{x}_+)$, $T(\tilde{x}_-)$, where $\tilde{x}_-$ and $\tilde{x}_+$ are found, in accordance with (16), from the equation

$$1 - \lambda f''(x) = 0. \tag{17}$$

The maximum extent of the temperature hysteresis is

$$\delta T = T(\tilde{x}_-) - T(\tilde{x}_+). \tag{18}$$

It is clear from formulas (16) that all the thermodynamic quantities remain finite at the transition point. But the heat capacity $C_p$, the hydrostatic compressibility coefficient 1/K, and the coefficient of thermal expansion $(\partial V/\partial T)_p$ may be anomalously large in the vicinity of $T_C$, if the values of $f''(x_\pm)$ and of $f''(\tilde{x}_\pm)$ are close to each other.

## 5. THE CASE OF A LOGARITHMIC BEHAVIOR OF THE HEAT CAPACITY

We shall consider in more detail the case in which, without allowance for acoustic motion, the heat capacity increases logarithmically, while the spontaneous moment and the susceptibility vary with temperature according to a power law. Then

$$f''(x) = -A\ln|x|, \quad \frac{\partial f}{\partial h} = B|x|^\beta\theta(-x), \quad \frac{\partial^2 f}{\partial h^2} = B_\pm|x|^{-\gamma}.$$

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0. \end{cases} \tag{19}$$

The parameter x, in accordance with (13), is found from the equation

$$\frac{T - T_C}{T_C} = -A\lambda x \ln\frac{|x_\pm|}{x}, \tag{20}$$

where $x_\pm$ and also the values of $\tilde{x}_\pm$ and δT are given by

$$\begin{gathered} x_+ = -x_- = \exp(1 - 1/A\lambda), \\ \tilde{x}_+ = -\tilde{x}_- = \exp(-1/A\lambda), \\ \delta T = 2A\lambda\tilde{x}_+ T_C. \end{gathered} \tag{21}$$

In two limiting cases, we get from (20) an explicit form for the function x(T):

$$x(T) \approx \begin{cases} \dfrac{T - T_C}{T_C}, & \ln\dfrac{T_C}{|T - T_C|} \ll \dfrac{1}{A\lambda} \\ x_+ \exp\left(\dfrac{2|T - T_C|}{e\delta T}\right)\operatorname{sign}(T - T_C), & |T - T_C| \ll \delta T. \end{cases} \tag{22}$$

On substituting (19) into (16), we get

$$S = S_0 + Ax(1 - \ln|x|); \quad C_p = C_p{}^0 - \frac{A\ln|x|}{1 + A\lambda\ln|x|},$$

$$\Delta V = -\frac{p}{K_0} + cAx(1 - \ln|x|), \quad \frac{1}{K} = \frac{1}{K_0} - \left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{A\lambda\ln|x|}{1 + A\lambda\ln|x|},$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{c}\left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{A\lambda\ln|x|}{1 + A\lambda\ln|x|},$$

$$\frac{1}{K_{\text{ad}}} = \frac{1}{K_0} - \left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{C_p{}^0}{C_p}\frac{A\lambda\ln|x|}{1 + A\lambda\ln|x|}$$

$$C_V = C_V{}^0 - \frac{A\ln|x|}{1 - A\lambda(3K_0/4\mu)\ln|x|},$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{c}\left(1 + \frac{3K_0}{4\mu}\right)\frac{A\ln|x|}{1 - A\lambda(3K_0/4\mu)\ln|x|},$$

$$-\frac{\partial\Phi(T)}{\partial h} = \begin{cases} BT_C(-x)^\beta, & x < 0; \\ 0, & x > 0; \end{cases}$$

$$-\frac{\partial^2\Phi(T)}{\partial h^2} = \begin{cases} B_-T_C(-x)^{-\gamma} + T_C\lambda\beta^2B^2\dfrac{(-x)^{2\beta-2}}{1 + A\lambda\ln|x|}, & x < 0; \\ B_+T_Cx^{-\gamma}, & x > 0. \end{cases} \tag{23}$$

In the temperature range $|T - T_C| \gg \delta T$, x in formulas (23) can be replaced, with logarithmic accuracy, by $(T - T_C)/T_C$. Then if $A\lambda \ln|T_C/(T - T_C)| \ll 1$, the singular parts of the heat capacities $C_p$ and $C_V$ and of the coefficient of thermal expansion are proportional to $\ln|T_C/(T - T_C)|$. The susceptibility and the spontaneous moment in this temperature range behave the same as in a phase transition of the second kind.

When $\lambda A \ln|T_C(T - T_C)|$ approaches unity, the thermodynamic derivatives $C_p$ and $(\partial V/\partial T)_p$ increase faster, according to the law

$$\left(\ln\frac{T_C}{|T - T_C|}\right)\Big/\left[1 - A\lambda\ln\frac{T_C}{|T - T_C|}\right].$$

This law ceases to be obeyed in the temperature range $|T - T_C| \sim \delta T$. At the transition point $T = T_C$, the quantities $C_p$, $(\partial V/\partial T)_p$, 1/K, and $1/K_{ad}$ take the large but finite values

$$C_p = C_p{}^0 + \frac{1}{A\lambda^2}, \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{T_C}{Ac^3}\left(\frac{1}{K_0} + \frac{3}{4\mu}\right)^2,$$

$$\frac{1}{K} = \frac{1}{K_0} + \frac{1}{A\lambda}\left(\frac{1}{K_0} + \frac{3}{4\mu}\right), \quad \frac{1}{K_{\text{ad}}} = \frac{1}{K_0} + \frac{1}{A\lambda}\left(\frac{1}{K_0} + \frac{3}{4\mu}\right)\frac{C_p{}^0}{C_p(T_C)}. \tag{24}$$

The jumps in entropy and in volume at the first-order phase transition are

$$\delta S = \frac{e}{2\lambda^2A}\frac{\delta T}{T_C} = e[C_p(T_C) - C_p{}^0]\frac{\delta T}{T_C},$$

$$\delta V = \frac{ec}{2\lambda^2A}\frac{\delta T}{T_C} = e\left(\frac{\partial V}{\partial T}\right)_p\bigg|_{T=T_C}\delta T. \tag{25}$$

Here e is the base of natural logarithms.

A physical consequence of the general loss of stability of the system in the neighborhood of the first-order phase transition is the presence of a temperature interval, near $T_C$, in which Poisson's ratio $\sigma = (3K - 2\mu)/2(3K + \mu)$ becomes negative. At these temperatures, any unidirectional tension causes a hydrostatic expansion of the material. The isothermal Poisson's ratio is

$$\sigma = \frac{2(3K_0 - 2\mu) - 9K_0\lambda A\ln|x|}{4(3K_0 + \mu) + 9K_0\lambda A\ln|x|}. \tag{26}$$

A necessary condition for the existence of a negative σ is the inequality

$$\lambda A < (3K_0 + 4\mu)/9K_0. \tag{27}$$

It is seen from (26) that $\sigma(T_C) \neq -1$ for finite $\lambda A$. The temperature interval in which $\sigma \leq 0$ is determined by the inequality

$$|T - T_c| \leqslant \frac{3K_0 + 4\mu - 9\lambda A K_0}{18\lambda A K_0}\,\delta T \exp\frac{3K_0 + 4\mu}{9\lambda A K_0} \tag{28}$$

and may be much larger than the extent of temperature hysteresis $\delta T$.

The thermal coefficient of pressure at the transition point has no jump and is given by

$$\left(\frac{\partial T}{\partial p}\right)_V = \frac{\partial T_c}{\partial p}\left[1 + \frac{4\lambda A\mu}{(1 - \lambda A)(3K_0 + 4\mu)}\right]. \tag{29}$$

At small $\lambda A$ this differs little from the rate of change of $T_C$ with pressure along the curve of phase equilibrium. At the boundary of the metastable region, $(\partial T/\partial p)_V = \partial T_C/\partial p$.

## 6. GENERALIZATION OF THE MODEL; THE ISING MODEL

The model considered above, described by the Hamiltonians (1) and (3), is convenient because it enables us to obtain the quantitative results (16) with only a single assumption. It was assumed that the heat capacity corresponding to the Hamiltonian (1) becomes infinite. Such a model describes well transitions of the displacement type[6,7], in which the departures of the atoms from an equilibrium position are small and it is possible to limit consideration to anharmonic terms of the simplest form. In this case the interaction by exchange of acoustic phonons has the same form as the direct interaction. In transitions of the order-disorder type, the dependence of the energy of one cell on the coordinate $\eta_i$ is described by some function $U(\eta_i)$ with two minima. After elimination of the acoustic phonons, the form of this function changes somewhat. On the assumption that without allowance for acoustic phonons the heat capacity becomes infinite according to a law that does not depend on the specific form of the function $U(\eta_i)$, we obtain formulas (12) in this case also.

In the case of the Ising model, the Hamiltonian can be written in the form

$$\sum_{ij}\left\{\left(\frac{1}{2}K_0 - \frac{\mu}{3}\right)\left(\frac{\partial u_\alpha}{\partial r_\alpha}\right)^2 + \mu\left(\frac{\partial u_\alpha}{\partial r_\beta}\right)^2 + \left(1 + q\frac{\partial u_\alpha}{\partial r_\alpha}\right)V_{ij}\sigma_i\sigma_j\right\}.$$

After elimination of the acoustic phonons we obtain, analogously to formula (7),

$$\Phi = -T\ln\int du_{\alpha\alpha}\,\mathrm{Sp}\exp\left\{-\frac{1}{T}\left[\sum_{ij}(1 + qu_{\alpha\alpha})V_{ij}\sigma_i\sigma_j + \frac{1}{2}K_0u_{\alpha\alpha}{}^2 + \sum_{lm}W_{ijlm}V_{ij}\sigma_i\sigma_jV_{lm}\sigma_l\sigma_m + \frac{q^2}{2(K + {}^4/_3\mu)N}\left(\sum_{ij}V_{ij}\sigma_i\sigma_j\right)^2\right]\right\}. \tag{30}$$

The function $W_{ijlm}$ decreases rapidly with increase of the distance $i-1$ and is determined by the contribution from short-wave phonons. On repeating almost without change the derivation of (8) and (9), we obtain formulas (12) in this case also. We remark that the very fact of a first-order transition in the elastically isotropic model considered follows from the assumption that the heat capacity becomes infinite even in the presence of four-cell interaction. It seems to us reasonable that addition of a third term should not change the form of the singularity in the heat capacity. In this case the function $f(x)$ is universal, and formulas (23) are correct at small strain.

## 7. TRANSITION IN BINARY ALLOYS

The Ising lattice in a longitudinal magnetic field is a model of phase transitions in binary alloys, in which a change of symmetry is connected with a change of the order of the crystal[8,3]. In such a system, there occurs a phase transition of "antiferromagnetic" type; the case of equal numbers of atoms of different sorts corresponds to the absence of a magnetic field.

In this case the results obtained above are unchanged. If the concentration differs from the stoichiometric, then it is convenient to introduce, instead of the concentration difference n, the chemical potential, which is equivalent to an external magnetic field h in the Ising lattice. We shall assume, in conformity with the results of numerical calculations[9], that the magnetic field has no influence on the nature of the antiferromagnetic transition but only diminishes the transition temperature. It is therefore reasonable to assume that at constant h, the thermodynamic potential with allowance for acoustic phonons, in accordance with (12), has the form

$$\Omega(h; T; p) = \Omega_0 - \frac{p^2}{2K_0} - \frac{1}{2}\chi h^2 - T_c{}^0 f(x) + \frac{T_c{}^0}{2\lambda}\left(x - \frac{T - T_c{}^0 - cp}{T_c{}^0} - \Theta h^2\right)^2,$$
$$\partial\Omega / \partial x = 0. \tag{31}$$

The difference n in the number of atoms is found from the condition

$$n = -\partial\Omega / \partial h. \tag{32}$$

It follows from (31) and (32) that the thermodynamic function $\Phi = \Omega + hn$ at fixed n is

$$\Phi(n, p, T) = \Omega_0 - \frac{p^2}{2K_0} + \frac{n^2}{2\chi} - T_c{}^0 f(x) + \frac{T_c{}^0}{2\tilde\lambda}\left(x - \frac{T - T_c{}^0 - cp}{T_c{}^0} - \frac{\Theta n^2}{\chi^2}\right),$$
$$\frac{T - T_c{}^0 - cp}{T_c{}^0} + \frac{\Theta n^2}{\chi^2} = x - \tilde\lambda f'(x), \tag{33}$$

where

$$\tilde\lambda = \lambda - 4T_c{}^0\Theta^2 n^2 / \chi^3.$$

As is evident from (33), at a sufficiently large concentration difference n, corresponding to negative $\tilde\lambda$, x and $\Phi$ are single-valued functions of T, and the system undergoes a second-order phase transition at temperature $T_C = T_C^0 + cp - T_C^0\Theta n^2\chi^{-2}$.

The thermodynamic quantities $C_p$, $(\partial V/\partial T)_p$, K, and $K_{ad}$ are given by formulas (16), in the denominators of which it is necessary to make the substitution $\lambda \to \tilde\lambda$. In the expressions for $C_V$ and $(\partial p/\partial T)_V$, it is necessary to make the substitution $\lambda(3K_0/4\mu) \to \lambda(3K_0/4\mu) + 4T_C^0\Theta^2 n^2\chi^{-3}$. In a second-order phase transition, when $\tilde\lambda < 0$, the quantities $C_p$, $C_V$, $K^{-1}$, $K_{ad}^{-1}$, $(\partial V/\partial T)_p$, and $(\partial p/\partial T)_V$ remain finite at the transition point.

## 8. MAGNETIC TRANSITIONS

So far we have considered only the classical expression (2) for the free energy. The assumption of classicality is not essential to the result. We consider, for example, the Heisenberg model of a ferromagnet with allowance for acoustic phonons. The Hamiltonian of the system in this case is

$$H = (1 + qu_{\alpha\alpha})H_0 + \frac{K_0}{2}u_{\alpha\alpha}{}^2 + \frac{1}{N}\sum_{\mathbf{k}\neq 0}\Big[\,iqk_\alpha u_\alpha(\mathbf{k})\sum_{ij}V_{ij}\mathbf{S}_i\mathbf{S}_j e^{i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)}$$

$$+\left(\frac{K_0}{2}+\frac{2}{3}\mu\right)|k_\alpha u_\alpha(\mathbf{k})|^2\Big],$$

$$H_0=\sum_{ij} V_{ij}\mathbf{S}_i\mathbf{S}_j. \qquad (34)$$

Here $\mathbf{S}_i$ is the quantum operator of the spin at the site with coordinate $\mathbf{r}_i$.

In the expression for the free energy $F=-T \ln \operatorname{Sp} \exp(-H/T)$, the Gaussian integrals with respect to $u_\alpha(\mathbf{k})$ cannot now be calculated directly, since the operators with different $\mathbf{k}$ that enter in H do not commute with each other. Therefore we use the diagram analysis of perturbation theory[10]. We shall assume that the character of the transition will be the same as in the usual Heisenberg model with Hamiltonian $H_0$ in the case in which the diagrams for the effective interaction have no singularities at small momenta. Interaction by exchange of phonons is absent when the momentum exchanged is zero, but has a nonvanishing limit for $\mathbf{k} \to 0$. To remove this singularity, we add to the Hamiltonian a term $-\frac{1}{2}\nu H_0^2$, which describes a four-spin interaction with zero transferred momentum. We choose $\nu$ so that the complete interaction has no singularity at small $\mathbf{k}$. As a result, we write H in the form

$$H=\tilde{H}+\xi H^0+{}^1/_2\nu H_0^2+{}^1/_2 k_0 u_{\alpha\alpha}^2, \qquad (35)$$

where $\xi = qu_{\alpha\alpha}$ and $\nu = q^2/(K_0+\frac{4}{3}\mu)N$.

The Hamiltonian H leads to diagrams that have no singularities at small $\mathbf{k}$. The singular part of the free energy corresponding to it has the form (2). The second term in formula (35) does not change the form of the singularity but leads only to a change of the transition temperature. Consequently, if we consider $\nu$ and $\xi$ as independent parameters, we can write $F(\nu=0)$ in the form

$$F(\nu=0)=-T_C{}^0 f\left(\frac{T-T_C{}^0}{T_C{}^0}-g\xi\right)+\frac{K_0}{2}u_{\alpha\alpha}^2. \qquad (36)$$

At small strain the constant g is close to unity.

In order to determine F for $\nu \neq 0$, we use a formal method presented in[11]. With statistical accuracy, the mean square $\langle H_0^2\rangle$ is identical with the square of the mean $\langle H_0\rangle^2$. Therefore the function F satisfies the equation

$$2\frac{\partial F}{\partial \nu}=\left(\frac{\partial F}{\partial \xi}\right)^2$$

and the initial condition (36).

The solution of this equation can be described in the parametric form

$$F=-\frac{1}{2\nu g^2}\left(\frac{T-T_C{}^0}{T_C{}^0}-g\xi-x\right)^2-T_C{}^0 f(x), \qquad \frac{\partial F}{\partial x}=0. \qquad (37)$$

On substituting the values of $\nu$ and $\xi$ and expressing $u_{\alpha\alpha}$ in terms of the pressure p by use of the equation $p=-\partial F/\partial u_{\alpha\alpha}$, we get for the thermodynamic potential the Gibbs expression (12). Thus allowance for quantum effects makes no change in the results obtained above, and all the thermodynamic quantities in a ferromagnet are determined by formulas (16).

The same result is obtained also for a magnetic transition in metals, if the interaction with phonons is taken into account according to Fröhlich's model. The Coulomb interaction, however, complicates the situation in a metal, and therefore this problem requires special treatment.

## 9. CONCLUSION

The results obtained above pertain to the elastically isotropic case. Small deviations from isotropy will lead to small corrections but do not affect the results obtained. In the majority of cases, the anisotropy is not small. It may be supposed that the qualitative results and the order-of-magnitude estimates will be correct even in the general case.

It is to be expected that a first-order transition will occur when

$$\frac{1}{T_C}\frac{4\mu K_0}{3K_0+4\mu}\left(\frac{\partial T_C}{\partial p}\right)^2\Delta C_p>1, \qquad (38)$$

where $\Delta C_p$ is the anomalous part of the heat capacity of unit volume. In many cases it may be assumed that without allowance for acoustic phonons, the heat capacity will behave in the following manner: not very close to the transition, the heat capacity is described by Landau's phenomenological theory and has a jump; with approach to the transition temperature, correlation corrections proportional to $|T-T_C|^{-1/2}$ become important; in the immediate neighborhood of a transition point of the second kind, the heat capacity becomes infinite according to a law close to the logarithmic. Depending on the values of the quantities that occur on the left side of formula (38), a first-order phase transition has various characters. If the left side exceeds unity even in the phenomenological region, where $\Delta C_p$ is the jump in heat capacity, then the first-order phase transition can be described by the approximation of the self-consistent field[12]. If it is less than unity, but close to unity, then the first-order transition is described by formulas (16), where $f''(x)$ can be calculated in the first approximations of the self-consistent field.

At small strain, the first-order transition occurs in the asymptotic region, where $f''(x)$ has a form close to $-A \ln|x|$. In this case the thermodynamic quantities are described by formulas (23). For example, in quartz, $KH_2PO_4$, and $NH_4Cl$ the quantity $A\lambda$ that occurs in formula (23) $\sim\frac{1}{5}$. Then the temperature hysteresis $\delta T \sim 0.1^\circ K$, in agreement with experimental data. The change of the adiabatic moduli in these substances is of the order of the moduli themselves, in agreement with formulas (23). In quartz there is also observed[13] an anomalous behavior of Poisson's ratio, which becomes negative near the transition over a temperature range considerably exceeding the temperature hysteresis.

In triglycine sulfate and some magnetic materials, $A\lambda \leq 0.1$. Therefore the left side of formula (38) is less than unity over the whole experimentally attainable range of temperatures. In this range, the heat capacity behaves the same as for a second-order phase transition, but the anomalous additions to the elastic moduli are small, in agreement with experiment. In these substances the values of $\delta T$, $\delta S$, and $\delta V$, in accordance with formulas (21) and (25), are exponentially small and not observed experimentally.

For a quantitative test of formulas (23) it would be interesting to know the behavior of the heat capacity and the elastic moduli in substances with small anisotropy; for example, in $Y_3Fe_5O_{12}$.

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190