

Effect of small perturbations on the behavior of thermodynamic quantities near a second-order phase transition point

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The review is devoted to an analysis of the influence of typical factors present in a real experiment (impurities, phonons, domain structure, etc.) on the behavior of thermodynamic quantities near a second-order phase transition point. Chapter II discusses equilibrium thermodynamic perturbations. Perturbations that differ in nature are considered from a unified point of view in which the idea of isomorphism is used. In the first stage, in each concrete case, thermodynamic variables called "isomorphic" are introduced, in which the ordinary second-order phase transition takes place. It is frequently difficult or impossible, however, to carry out an experiment in which the "isomorphic" variables remain constant. The second stage therefore consists of a transition from "isomorphic" variables to "experimental" variables, which can be conveniently maintained constant in the experiment. In terms of the "experimental" variables, the picture of the phase transition can differ strongly from the usual picture of a second-order phase transition. Thus, in the case of impurities, if the measurements are carried out at constant concentration, a third-order phase transition takes place, and if the ordering parameter interacts with longitudinal or transverse phonons (at constant pressure), the phase transition is of first order. Chapter III discusses the influence of nonequilibrium perturbations (mainly immobile impurities and inhomogeneities) on the thermodynamics of the phase transitions. In this case there may exist several (at least two) points that are nonanalytic in the temperature and have weak singularities of the thermodynamic quantities. A temperature interval of the "smearing" of the transition is indicated for each type of perturbation. The theory is compared with experiment.

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I. INTRODUCTION

The phase-transition picture in ideal systems has recently been under very intensive study. By ideal system we mean here an incompressible ferromagnet with spins rigidly fixed at the sites that make up a regular lattice. Such a ferromagnet can be described by the well-known models of Heisenberg or Ising. The lattice-gas model, which describes the liquid-vapor transition near the critical point, turns out to be the equivalent of the Ising model for a ferromagnet placed in an external magnetic field, and can also serve as an example of a phase transition in an ideal system.

The exact solution of the two-dimensional Ising model, first obtained by Onsager^[1], and also computer calculations, have shown that at the phase-transition point the free energy of such systems is a nonanalytic function of the temperature and of the magnetic field. Computer calculations have now yielded a fairly accurate quantitative description of the behavior of all the thermodynamic quantities near the Curie point in the two-dimensional and three-dimensional models of Ising and Heisenberg.

In real experiments, however, the picture of the phase transition is strongly distorted (in comparison with the corresponding picture in ideal systems) by a

large number of extraneous factors, which are very difficult or impossible to get rid of. Thus, in solids there are always lattice vibrations (phonons), which are not taken into account in calculations performed within the framework of ideal models.

The present review is devoted to an analysis of the influence of typical factors present in a real experiment on the behavior of thermodynamic quantities near a second-order phase transition point.

The following classification of the possible perturbations is proposed:

1) Perturbations in which the measurement is performed slowly enough to enable the system to arrive at the state of thermodynamic equilibrium with respect to all the variables of the system (this case is considered in Chap. II).

2) Perturbations in which the measurement process is so carried out that there is not enough time for equilibrium to be established with respect to the variable characterizing the perturbation (Chap. III).

If we consider the influence of impurities on the thermodynamics of a phase transition, then both the first and the second cases can be realized, depending on the rate at which the experiment is performed.

TABLE I. Definitions of the critical exponents ($h = \mu_B H/kT_C$ is the dimensionless magnetic field, where μ_B is the Bohr magneton)

Specific heat C	Susceptibility χ	Magnetization m	Correlation radius r_c	Correlation function $C(r)$
$\tau^{-\alpha}$	$ \tau ^{-\gamma}$	$(-\tau)^\beta$	$ \tau ^{-\mu}$	$R^{-\nu}$
$ h ^{-\epsilon}$	$ h ^{-\lambda}$	$ h ^{1/\delta}$		

The difficulty of solving the problems formulated above lies in the absence of a small parameter even in the case when the perturbation (of the order of $\bar{\epsilon}$) is small in comparison with kT_C , where $k = 1$ is Boltzmann's constant and T_C is the phase-transition temperature. In fact, if we are close to the singular point T_C , then the parameter of the expansion of the partition function or of the free energy in a Taylor series is not $\bar{\epsilon}$, but $\bar{\epsilon}/\tau^{\bar{c}}$, where \bar{c} is a constant.

In the temperature range $\tau \lesssim \bar{\epsilon}^{1/\bar{c}}$ about the critical point, small perturbations can lead to large changes of the thermodynamic quantities. The "smearing" interval $\bar{\tau} \sim \bar{\epsilon}^{1/\bar{c}}$ is an important characteristic of the influence of the perturbation on the picture of the phase transition.

We shall make extensive use of the scaling-theory method formulated by Widom, Patashinskiĭ, Pokrovskii, and Kadanoff^[2-5]. Scaling theory approximates the singularities of thermodynamic quantities by power-law functions. The definitions of the critical exponents are given in Table I. It is assumed that the only length parameter is the correlation radius of the ordering parameter, which tends to infinity when the temperature approaches the phase-transition point. This assumption enables us to express all the exponents listed in Table I in terms of two independent parameters x and y (Table II).

In cases when it is impossible to obtain exact solutions, we shall use the method of self-consistent fields in the most general form, as given by Landau^[6].

The present review deals with classical systems (magnets, ferroelectrics, and the liquid-gas and liquid-liquid critical points); the numerous results obtained for quantum systems (liquid helium and superconductors) are not considered here.

To facilitate the reading, long mathematical derivations are relegated to appendices; the conclusions are presented at the end of each section. Those who wish to become rapidly acquainted with the problems touched upon here can confine themselves to reading the introduction, the deductions, and the conclusion.

II. THERMODYNAMIC EQUILIBRIUM PERTURBATIONS

In this chapter we consider systems that are in thermodynamic equilibrium with respect to all the thermodynamic variables. The solution of problems considered in the present chapter breaks up into two stages. In the first stage, the thermodynamic potential of the perturbed system reduces to the potential of an ideal system. This reduction is obtained by a successful choice of the thermodynamic variables. If the choice of variables makes it possible to reduce the thermodynamic potential of a perturbed system to the corresponding potential of an ideal system, then we shall talk of isomorphism of the phase transition of the perturbed

TABLE II. Expressions for the critical exponents in terms of two independent parameters x and y .

α	β	γ	δ	ϵ	λ	μ	ν
$2 - \frac{d}{y}$	$\frac{d-x}{y}$	$\frac{2x-d}{y}$	$\frac{x}{d-x}$	$\alpha \frac{y}{x}$	$\gamma \frac{y}{x}$	$\frac{1}{y}$	$2(d-x)$

and unperturbed systems, and call the variables isomorphic^[7,8]. Variables that determine the conditions of thermodynamic equilibrium can also be isomorphic. Thus, in the case of mixtures, the isomorphic variables are the temperature and the chemical potential, since the constancy of these variables over the sample determines the thermodynamic-equilibrium conditions. In the presence of a domain structure, when the external field is directed along the easy magnetization axis in a uniaxial crystal, the isomorphic variables are the temperature and the internal magnetic field, which are constant along the sample. It is frequently difficult or impossible, however, to perform an experiment and maintain the isomorphic variables constant. For example, in solutions it is very difficult to measure thermodynamic quantities at a constant chemical potential; the measurements are carried out at constant concentration. The second stage will therefore consist of changing over from isomorphic variables to "experimental" variables, in which it is convenient to perform the experiment. The isomorphic variables are distinguished by the fact that they determine the thermodynamic equilibrium conditions, while the "experimental" variables are accidental. Therefore, whereas the thermodynamic potential expressed in isomorphic variables has the same form for different types of perturbations, in the "experimental" variables we have different types of singularities for different perturbations.

As will be shown below, a solution at constant concentration has a phase transition of third order in the temperature, whereas the interaction of phonons with the ordering parameter at constant pressure leads to a first-order phase transition.

1. Mixtures in thermodynamic equilibrium. We divide the calculation of the thermodynamic quantities in a system with impurities into three stages. In the first stage we calculate the thermodynamic potential of a system with the chemical potential as a variable, within the framework of the so-called decorated model. An important result of this stage is the proof of the phase-transition isomorphism of a system with impurities and an ideal system. In the second stage we find the dependence of the chemical potential on the concentration and on the temperature, and in the last stage we calculate the specific heat of the system at constant concentration. In the conclusion of this section we discuss certain assumptions that enable us to obtain an expression for the thermodynamic potential without using any models.

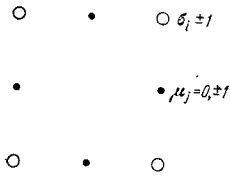


FIG. 1. The decorated Syozi model.

Using the thermodynamic inequality $(\partial \bar{g} / \partial c)_T > 0$, it is easy to prove that the specific heat at constant chemical potential $C_{\bar{g}}$ exceeds the specific heat at constant concentration C_c ($C_{\bar{g}} > C_c$). (This inequality is analogous to the relation $C_p > C_v$ in Sec. 16 of the book^[9].) By representing the specific heat near the critical point in the form $C_{\bar{g}} \sim \tau^{-\alpha} \bar{g}$ and $C_c \sim \tau^{-\alpha} c$, we obtain $\alpha \bar{g} \geq \alpha c$. As will be shown below, $\alpha \bar{g} = \alpha$ and $\alpha c = -\alpha / (1 - \alpha)$ (α is the specific-heat exponent of the pure substance), and the inequality cited above holds true.

a) We consider first the "decorated" model of a ferromagnet with impurities^[9-11], shown in Fig. 1. The light circles show the atoms of the main substance with spin σ_i (i is the number of the site), which takes on two values, ± 1 . The dots show the sites in which magnetic impurities can be located. The state of this site is characterized by the variable μ_j , which takes on three values: the state $\mu_j = 0$ corresponds to the absence of the impurity, and $\mu_j = \pm 1$ denotes that there is an impurity atom with appropriate spin at the given site.

The energy of such a system is expressed in the form

$$E = -(I_1/2) \sum (\sigma_i + \sigma_{i'}) \mu_j - (I_2/2) \sum \sigma_i \sigma_{i'} - (\Delta I/2) \sum \sigma_i \sigma_{i'} \mu_j^2. \quad (1.1)$$

The first term describes the interaction of impurity atoms with atoms of the main substance (i, i' are the numbers of the nearest-neighbor sites of the main substance). The second term describes the interaction of the atoms of the main substance, and the third term characterizes the change in the direct interaction of the atoms of the main substance if an impurity falls between them.

This model is a generalization of the models considered in^[9-11]. In the particular case $I_2 = \Delta I = 0$ we obtain the Syozi model^[9], and at $I_1 = 0$ we obtain the case considered by Lushnikov^[10] and Shapoval^[11].

The partition function \bar{Z} with the temperature, magnetic field, and chemical potential g as variables is given by ($g = \bar{g}/T$)

$$\bar{Z}(T, H, g) = \sum_{\{\sigma, \mu\}} \exp \left[\theta_1 \sum_{i,j} (\sigma_i + \sigma_{i'}) \mu_j + \theta_2 \sum_{i,j} \sigma_i \sigma_{i'} + \theta_3 \sum_{i,j} \sigma_i \sigma_{i'} \mu_j^2 + g \sum_j \mu_j^2 + h \left(\sum_i \sigma_i + \sum_j \mu_j \right) \right], \quad (1.2)$$

where $\theta_1 = J_1/2T$ and $\theta = \Delta J/2T$. Summing expression (1.2) over μ_j at small impurity concentrations ($c \ll 1$), we obtain near an arbitrary point g_0 on the critical curve (see Appendix 1)

$$\Omega/T = -A_1 e^g - A_2 \tau(g) + \Phi_0[\tau(g)] + O(e^{2g}, \tau^2(g), e^g \tau(g)), \quad (1.3)$$

where $\Phi_0[\tau(g)] = -A\tau(g)^{2-\alpha}$ is the thermodynamic potential of the unperturbed system, $A > 0$ and A_1 are constants on the order of unity,

$$\tau(g) = \tau - (1/T_0) (dT_c^*/dg) \Delta g, \quad \tau = (T - T_c^*(g))/T_0,$$

$\Delta g = g - g_0$, and $O(e^{2g}, \tau^2(g), e^g \tau(g))$ is an aggregate of quantities of order $e^{2g}, \tau^2(g)$, and $e^g \tau(g)$.

Thus, Ω can be represented in the form of the sum of a part that is regular in $\tau(g)$ (first term) and a singular part (second term). An important property of this model is the isomorphism of the singular parts of the thermodynamic potential of the mixture (in terms of the variable g) and of the thermodynamic potential of the ideal system.

b) The connection between the concentration and the chemical potential is given by the equation

$$c = -\frac{1}{T} \left(\frac{\partial \Omega}{\partial g} \right)_T = A_1 e^g - \frac{A_2}{T_0} \frac{dT_c}{dg} - A(2-\alpha) \text{sign } \tau(g) |\tau(g)|^{1-\alpha} \frac{1}{T_0} \frac{dT_c}{dg}. \quad (1.4)$$

Using the formula $(1/T_0) dT_c/dg = A_4 e^g$, which follows from (A1.7), we obtain in the zeroth approximation

$$c = A_5 e^{g_0}, \quad A_5 = A_1 - A_2 A_4, \quad (1.5)$$

from which we obtain the dependence of the chemical potential on the concentration in the principal approximation

$$g = \ln c, \quad (1.6)$$

which coincides with the analogous formula for weak solutions far from the critical point. Using the last formula, we obtain

$$(1/T_0) dT_c^*/dg = (c/T_0) dT_c^*/dc. \quad (1.7)$$

From (1.4), (1.5), and (1.7) we obtain in the next approximation the equation

$$\Delta g = A(2-\alpha) \text{sign } \tau(g) |\tau(g)|^{1-\alpha} (1/T_0) dT_c^*/dc. \quad (1.8)$$

At very small τ and Δg we have $\tau(g)^{1-\alpha} \gg \Delta g$, so that in first approximation $\tau(g) = 0$, whence

$$\Delta g^{(1)} = \tau [(c/T_0) dT_c^*/dc]^{-1}. \quad (1.9)$$

In the second approximation we have the equation

$$\tau \left(\frac{c}{T_0} \frac{dT_c}{dc} \right)^{-1} = A(2-\alpha) (\text{sign } \tau(g)) \frac{1}{T_0} \frac{dT_c}{dc} \left| \frac{c}{T_0} \frac{dT_c}{dc} \Delta g^{(2)} \right|^{1-\alpha}. \quad (1.10)$$

This equation has a solution if the sign of τ coincides with the sign of $\tau(g)$, whence

$$\text{sign } \tau(g) = -\text{sign} [(1/T_0) dT_c^*/dc] \text{sign } \Delta g^{(2)} = \text{sign } \tau$$

and

$$\text{sign } \Delta g^{(2)} = -\text{sign } \tau \cdot \text{sign} [(1/T_0) dT_c^*/dc].$$

From (1.10) we obtain an expression for $\Delta g^{(2)}$:

$$\Delta g^{(2)} = -\Delta g^{(1)} \text{sign } \tau \text{sign} [(1/T_0) dT_c^*/dc] \bar{\tau}^{\alpha/(1-\alpha)}, \quad (1.11)$$

where

$$\bar{\tau} = \tau/\tau_0, \quad \tau_0 = [(2-\alpha) A c (1/T_0)^2 (dT_c^*/dc)^2]^{1/\alpha}.$$

The condition for the applicability of perturbation theory, $\Delta g^{(2)}/\Delta g^{(1)} \ll 1$, takes the form

$$\tau \ll \bar{\tau}. \quad (1.12)$$

We consider now Eq. (1.8) in the region $|\tau| \gg \bar{\tau}$ that is the inverse of (1.12). As will be shown below, in this region the specific heat behaves as in the pure substance, so that in first approximation we can let the concentration tend to zero, whence

$$\Delta g^{(1)} = A(2-\alpha) \text{sign } \tau(g) |\tau|^{1-\alpha} (1/T_0) dT_c^*/dc. \quad (1.13)$$

In the second approximation we have

$$\Delta g^{(2)} = -\Delta g^{(1)} (1-\alpha) |\bar{\tau}|^{-\alpha}. \quad (1.14)$$

c) We now calculate the specific heat of a constant concentration. The entropy is calculated from the formula

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_g = - \frac{1}{T} \left(\frac{\partial \Omega}{\partial \tau} \right)_g - c g$$

$$= A(2-\alpha) (\text{sign } \tau) |\tau(g)|^{1-\alpha} - c g_0 - c \Delta g \quad (1.15)$$

$$= \left[\left(\frac{1}{T_0} \frac{dT_c}{dc} \right)^{-1} - c \right] \Delta g = \Delta g \left(\frac{1}{T_0} \frac{dT_c}{dc} \right)^{-1}.$$

In the derivation of the final formula we used Eq. (1.8), neglected the term cg_0 , which leads to the regular part of the specific heat, and assumed that $(c/T_0)dT_c/dc \ll 1$ in dilute solutions.

Substituting (1.9) and (1.11) in (1.15), we obtain an expression for the specific heat in the region $\tau \ll \bar{\tau}$

$$C_s/B = 1 - (1-\alpha)^{-1} \bar{\tau}^{\alpha/(1-\alpha)}, \quad (1.16)$$

and in the region $\tau \gg \bar{\tau}$

$$C_s/B = (1-\alpha) |\bar{\tau}|^{-\alpha} [1 - (1-2\alpha) \bar{\tau}^{-\alpha}],$$

$$\bar{\tau} = [(1-\alpha)^{-1} C_0 c (1/T_0)^2 (dT_c/dc)^2]^{1/\alpha}, \quad (1.17)$$

where

$$B = 1 \left[c \left(\frac{1}{T_0} \frac{dT_c}{dc} \right)^2 \right]^{-1}, \quad C_0 = A(1-\alpha)(2-\alpha)$$

(in the pure substance $C_S = C_0 |\tau|^{-\alpha}$).

The quantity $\bar{\tau}$, which characterizes the temperature interval over which the phase transition is "smeared" by the impurities, was calculated by Anisimov, Voronel', and Gorodetskii^[8].

We can assume that in the entire region

$$C_s/B = f(\bar{\tau}), \quad f(\bar{\tau}) = (1 + \bar{\tau}^\alpha)^{-1}, \quad (1.18)$$

where $f(\bar{\tau})$ is a function of one variable and is universal for all mixtures. At small α , the interpolation formula for $f(\bar{\tau})$ correctly conveys both asymptotic expressions (1.16) and (1.17).

So far we have calculated the singular part of the specific heat C_S . For a numerical comparison of the theory with experiment, it is necessary to know also the regular part of the specific heat. Without performing the calculations, we shall show that the regular part can be described by different constants \bar{C}_0 and C_1 (which do not depend on the temperature and concentration) in regions $\tau \gg \bar{\tau}$ and $\tau \ll \bar{\tau}$, respectively. To explain the reason why the constants are different in the two regions, let us consider the previously discarded term $\tau(g)$ in the entropy. In the region $\tau \gg \bar{\tau}$ we have $\tau(g) = \tau$, and this term yields a constant contribution to the specific heat. In the region $\tau \ll \bar{\tau}$, however, this term does not lead to a constant, but results in a small correction (in terms of the parameter $c(1/T_0)^2(dT_c/dc)^2$) to the second term of (1.16).

Starting from the foregoing, we can qualitatively describe the regular part of the specific heat by a very simple interpolation formula of the type

$$C_r = (\bar{C}_0 - C_1) [\bar{\tau}/(1 + \bar{\tau})] + C_1.$$

The constant \bar{C}_0 should agree approximately with the corresponding constant that describes the regular part of the pure substance. C_1 is the parameter that must be determined from experiment. Using (1.18), we write down the complete expression for the specific heat

$$C = C_s + C_r = B f(\bar{\tau}) + (\bar{C}_0 - C_1) [\bar{\tau}/(1 + \bar{\tau})] + C_1. \quad (1.19)$$

Thus, in the region $|\tau| \gg \bar{\tau}$ the behavior of the specific heat is close to the behavior in an ideal system. The role of impurities reduces to small increments. In the region $|\tau| \ll \bar{\tau}$, the impurities exert an appreciable influence on the specific heat. At a con-

stant impurity concentration and when the temperature tends to the critical value, the specific heat tends to a finite limit. Using the general expression for the partition function of a system in a magnetic field (A1.2), we can obtain the behavior of the magnetic moment, the susceptibility, etc. as functions of all the variables. We present the final results obtained by Essam and Garelick^[12]. At $H = 0$ and at a fixed concentration we have

$$m \sim \tau^{\beta/(1-\alpha)}, \quad \chi \sim \tau^{-\nu/(1-\alpha)}, \quad (1.20)$$

and a fixed temperature $T = T_c(c_0)$, when the concentration c tends to c_0 , we have

$$m \sim \Delta c^{\beta/(1-\alpha)}, \quad \chi \sim \Delta c^{-\nu/(1-\alpha)}, \quad \Delta c = c - c_0. \quad (1.21)$$

d) We now consider the assumptions that have led to expression (1.3) for the thermodynamic potential, without using the model presented above.

Fisher has proposed^[7] that if the calculations are carried out at a fixed value of the conjugate "generalized force," the singularities of the thermodynamic quantities remain the same as in an ideal system when a perturbation described by a "generalized coordinate" is turned on. In the example considered above, the "generalized coordinate" is the impurity concentration, and the "generalized force" is the chemical potential. This assumption is equivalent to the isomorphism hypothesis. From Fisher's hypothesis we obtain directly the singular part of the thermodynamic potential in terms of the variables T and g :

$$\Omega_s \sim |\tau(g)|^{2-\alpha}.$$

Adding to this expression the regular part expanded in a Taylor series in $\tau(g)$, we obtain expression (1.3). Repeating the derivations given above, we arrive at expressions (1.18), (1.19), and (1.20).

In^[8,13] we considered the thermodynamic quantities near the liquid-vapor and liquid-liquid critical points of two-component mixtures. In such systems it is necessary to take into account the fact that not only the critical temperature, but also the critical volume are functions of the chemical potential. At constant volume equal to the critical value and at constant concentration, the specific heat is given by (1.18) and (1.19). The results of calculations of other quantities, which will not be presented here, are detailed in^[8,13]. We note only that $(\partial c/\partial \bar{g})_{p,T}$ is described by the same formulas as the susceptibility, namely (1.20) and (1.21), respectively. In most mixtures, we have $\bar{\tau} < 10^{-6} - 10^{-8}$, and therefore experiments performed with present-day accuracy should not reveal a "smearing" of the specific heat by the equilibrium impurities. In liquid helium, in view of the low value of T_0 which enters in the expression for $\bar{\tau}$, the "smearing" region is large enough to be observed.

Gasparini and Moldover^[14] investigated the behavior of the specific heat $C_{p,c}$ (p is the pressure) in an He⁴-He³ mixture. In the presence of impurities, the specific heat becomes finite. At the same time, the experimentally determined^[14] $\alpha/(1-\alpha)$ turned out to be equal to approximately 0.2 ($\alpha \approx 0$ in a pure substance), so that no quantitative agreement between theory and experiment was observed there.

In^[15] they investigated the influence of a water impurity on the behavior of C_p (at constant concentration of all components) of a mixture of methanol and cyclo-

hexane near the stratification point. Their experimental value of $\bar{\tau}$ agrees satisfactorily with the theoretically calculated one.

It is convenient to reduce the measured values of the specific heat at constant concentration, in accordance with formula (1.18), in terms of the coordinates C/B and $\tau/\bar{\tau}$, inasmuch as if the isomorphism hypothesis holds the connection between these coordinates is given by a universal relation for all substances at all concentrations. Voronel', Shmakov, and Gorbunova^[16] have investigated the behavior of the specific heat of an ethane-heptane mixture at 3 and 1% heptane. This mixture has the anomalously large value $dT_c/dt \approx 600$ deg/mole, so that the region of "smearing" of the specific heat is easily observed. The measurement results were reduced in terms of the coordinates C/B and $\tau/\bar{\tau}$. According to (1.19), the two curves corresponding to 3 and 1% heptane should coincide. Experiments, however, revealed a difference on the order of 20% between the two curves.

Thus, study of the influence of impurities on the behavior of the specific heat reveals qualitative agreement between theory and experiment. At the same time, there is a noticeable quantitative discrepancy. Figure 2 shows plots of the specific heat of an ethane-heptane mixture, taken from^[16].

Conclusions. 1) Certain exactly-solvable models of system with thermodynamic-equilibrium impurities show that the singularity of the thermodynamic potential Ω as a function of the chemical potential is the same as in an ideal system.

2) The specific heat of a system with impurities can be described by formula (1.19). At a finite concentration and when the temperature tends to the critical value, the specific heat tends to a finite limit (whereas in an ideal system the specific heat tends to infinity).

3) The magnetic moment and the susceptibility (or $\partial c/\partial \bar{g}$)_{P,T}, as a function of the temperature (or the concentration), is described near T_c by formulas (1.20) and (1.21).

4) There is qualitative agreement between theory and experiment.

5) The temperature interval of the "smearing" of the specific heat by the impurities is given by the expression $\bar{\tau} = [(1 - \alpha)^{-1} C_0 c (1/T_0)^2 (dT_c/dc)^2]^{1/\alpha}$.

6) To verify the isomorphism hypothesis, the results of the measurements of the specific heat are best re-

duced in coordinates $\tau/\bar{\tau}$, since the specific heat is expressed, according to (1.19), in terms of a function that is universal for all substances and depends on $\bar{\tau} = \tau/\bar{\tau}$.

2. Influence of acoustic phonons. Rice^[17] was the first to call attention to an instability, connected with the lattice compressibility, near the phase-transition point. He proposed that the singular part of the free energy can be written in isomorphic form

$$F = F_r(V) - A(T - T_c(V))^{2-\alpha}. \quad (2.1)$$

From the condition that the heat capacity is constant, we have $A > 0$; the transition point T_c depends on the volume of the systems. From (2.1) we obtain the principal term in the expression for $(\partial p/\partial V)_T$ near the transition point:

$$(\partial p/\partial V)_T = A(2 - \alpha)(1 - \alpha)(T - T_c(V))^{-\alpha}(dT/dV)^2 > 0,$$

which contradicts the condition of thermodynamic stability.

However, Rice's assumption, which leads to formula (2.1), is incorrect since in addition to the homogeneous compressibility it is necessary to take into account the inhomogeneous oscillations of the lattice (phonons). The volume of the system does not determine the conditions of thermodynamic instability and cannot be an isomorphic variable.

a) The most consistent classical theory of the influence of acoustic phonons on the behavior of thermodynamic quantities near a second-order phase transition point was developed by Larkin and Pikin^[18]. In accordance with the general procedure, we expressed in the first stage the thermodynamic potential of the perturbed system in terms of the corresponding potential of the ideal system. In the second stage, we change over from the isomorphic to the "experimental" variables, namely the temperature and pressure. When both the transverse and longitudinal branches of the phonon spectrum are taken into account, we obtain a first-order transition. If the transverse branch is disregarded, a second-order transition is obtained.

Following^[18], we separate in each crystal cell a generalized coordinate η_i . For example, in ferroelectrics, the parameter η_i is proportional to the distance between the central atom and the center of the unit cell. Disregarding the phonons and assuming zero deformation, the energy of the system is

$$E_0 = \sum_i (-\bar{a}\eta_i^2 + (1/2)b\eta_i^4) + \sum_{i,j} V_{ij}(\eta_i - \eta_j)^2; \quad (2.2)$$

here \bar{a} , b , and V_{ij} are constants, and at $\bar{a} = b \gg T$ the essential values of η_i are close to ± 1 and the energy (2.2) goes over to the Hamiltonian of the Ising model.

It is proposed below that the system described by the Hamiltonian (2.2) has a second-order transition point T_0 with infinite specific heat.

Near T_0 , the singular part of the thermodynamic potential is given by

$$\Phi_0(\bar{a}, b) = NT_0\Phi_0(\tau_0), \quad \Phi_0(\tau) = -A|\tau|^{2-\alpha}, \quad \tau_0 = (T - T_0)/T_0, \quad (2.3)$$

where $A > 0$ is a constant on the order of unity.

We write down the energy of an elastic and isotropic solid, with allowance for the interaction η_i with the long-wave phonons described by the vector field $U_\alpha(\mathbf{r})$:

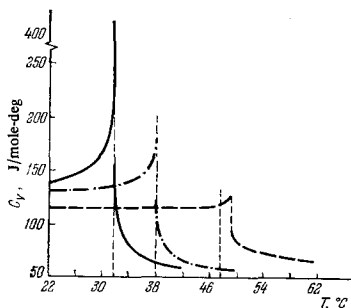


FIG. 2. Specific heat of a mixture in thermodynamic equilibrium^[16]. Solid line—specific heat of pure ethane; dash-dot curve—specific heat of a mixture of ethane and heptane at a heptane concentration 0.94%, dashed line—at 3.16%.

$$E = \sum_i \left[\frac{K_0}{2} \left(\frac{\partial U_\alpha}{\partial r_\alpha} \right)^2 + \mu \left(\frac{\partial U_\alpha}{\partial r_\beta} - \frac{1}{3} \delta_{\alpha\beta} \frac{\partial U_\alpha}{\partial r_\alpha} \right)^2 + \left(-\bar{a} - q \frac{\partial U_\alpha}{\partial r_\alpha} \right) \eta_i^2 + \frac{b}{2} \eta_i^4 + \sum_j V_{ij} (\eta_i - \eta_j)^2 \right], \quad (2.4)$$

where K_0 and μ are the nonsingular parts of the hydrostatic-compression and shear moduli; the coupling constant q will henceforth be expressed in terms of an experimentally measured quantity, namely the derivative of the transition temperature with respect to pressure.

b) The thermodynamic potential is defined by the formula

$$\Phi = -T \ln \int \exp \left[-(1/T) (E - \sigma_{\alpha\beta} \sum_i \partial U_\alpha / \partial r_\beta) \right] d\eta_i dU_\alpha(\tau); \quad (2.5)$$

here $\sigma_{\alpha\beta}$ is the stress tensor, and the sign of the product with respect to i, α , and β has been left out.

For the strain tensor we have the expression

$$U_{\alpha\beta} = (\partial U_\alpha / \partial r_\beta + \partial U_\beta / \partial r_\alpha) / 2 = \bar{U}_{\alpha\beta} + (1/2N) \sum_{\mathbf{k} \neq 0} i (k_\beta U_\alpha + k_\alpha U_\beta) \exp(i\mathbf{k}\mathbf{r}), \quad (2.6)$$

where $\bar{U}_{\alpha\beta}$ is the homogeneous part of the tensor and N is the number of particles in the system. After calculations described in Appendix 2, we obtain an expression for Φ :

$$\Phi = \Phi_r + \Phi_0[\tau(v)] + (T_0/2\bar{\lambda}) (\tau_0 - cp - \tau(v))^2, \quad \partial\Phi/\partial\tau(v) = 0, \quad (2.7)$$

where Φ_r is the regular part of the thermodynamic potential and does not depend on v ,

$$\tau(v) = \tau_0 - (q/T_0 K_0) (dT_c/d\bar{a}) (v - p), \quad \bar{\lambda} = 4\mu K_0 c^2 T_0 / (3K_0 + 4\mu).$$

It will be shown below that the constant \bar{c} is equal to the derivative of the temperature with respect to pressure ($\bar{c} = (1/T_0) dT_c/dp$).

We have reduced the thermodynamic potential to isomorphic form. Expanding the second equation of (2.7) and using expression (2.3) for Φ_0 , we obtain the connection between v and the experimental variables p and T :

$$(q/T_0 K_0) (dT_c/d\bar{a}) (v - p) - \bar{c}p = -\bar{\lambda}A(2 - \alpha) |\tau(v)|^{1-\alpha} \text{sign } \tau(v).$$

At $p = 0$, this equation differs from the corresponding equation (1.8) by the sign in front of the expression in the right-hand side, which leads to a qualitatively different solution of the last equation.

c) If we introduce $\tau(v) = \bar{x}$, then expressions (2.7) can be rewritten in the form

$$\Phi/T_0 = (\Phi_r/T_0) + \Phi_0(\bar{x}) + (\bar{\lambda}/2) \Phi_0''(\bar{x}), \quad \tau_0 - \bar{c}p = \bar{x} + \bar{\lambda}\Phi_0'(\bar{x}). \quad (2.8)$$

If the specific heat of the system without allowance for the phonons tends to infinity, i.e., $-\Phi_0''(\bar{x})$ increases without limit at small \bar{x} , then it follows from the second equation of (2.8) that T is a nonmonotonic function of \bar{x} . Thus \bar{x} and Φ are nonunique functions of T . Plots of \bar{x} and Φ against $\tau = (T - T_0 - \bar{c}p)/T_0$ are shown in Figs. 3 and 4. The singular point Φ , which corresponds to $\bar{x} = 0$, lies in the region of absolute instability. The functions \bar{x} and Φ are multiple-valued in the regions $-\bar{x}_{\min} < \bar{x} < \bar{x}_{\min}$, where $\bar{x}_{\min} \sim \bar{\lambda}^{1/\alpha}$ is determined from the equation

$$\bar{\lambda}\Phi_0'(\bar{x}_{\min}) = -1. \quad (2.9)$$

The maximum value of the temperature hysteresis is equal to $-\tau_0 < \tau < \tau_0$, where

$$\tau_0 = |\bar{x}_{\min} + \bar{\lambda}\Phi_0'(\bar{x}_{\min})| \sim \bar{\lambda}^{1/\alpha}. \quad (2.10)$$

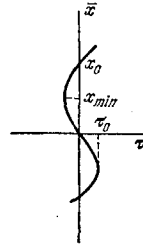


FIG. 3

FIG. 3. Plots of \bar{x} against τ .

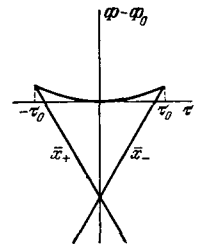


FIG. 4

FIG. 4. Temperature dependence of the thermodynamic potential.

The temperature of the first-order transition is obtained as the point of intersection of the two branches of the thermodynamic potential shown in Fig. 4 by the solid lines, and is determined from the system of equations

$$T(\bar{x}_-) = T(\bar{x}_+), \quad \Phi(\bar{x}_-) = \Phi(\bar{x}_+).$$

Since \bar{x}_+ and \bar{x}_- do not depend on p , the constant \bar{c} in (2.7) is equal to the derivative of the transition temperature with respect to the pressure, i.e.,

$$T_c = T_0 + cp.$$

If we put $\mu = \bar{\lambda} = 0$, then, as can be seen from (2.9) and (2.10) there is no hysteresis region and a second-order phase transition takes place, just as in the unperturbed system.

d) The specific heat in quartz, KH_2PO_4 , and NH_4Cl is close to logarithmic, $\bar{\lambda}\bar{\lambda} \approx 1/5$, and the temperature hysteresis is $\delta T \sim 0.1^\circ\text{K}$, in agreement with the experimental data. The changes of the adiabatic moduli in these substances are of the order of the moduli themselves. In triglycine sulfate and in certain magnetic materials, we have $\bar{\lambda}\bar{\lambda} \ll 1$, so that, at the present measurement accuracy, the specific heat behaves just as in a second-order phase transition, and the anomalous increments to the elastic moduli are small.

In this section we consider the case of an isotropic model, and a small anisotropy leads to small corrections to the obtained formulas. It can be assumed that in the case of large anisotropy the fundamental results will not be qualitatively altered.

The influence of the compressibility of the lattice on the behavior of the thermodynamic quantities near the Curie point was also considered in [19-21]. However, the shear forces were not taken into account in [19], so that the singularities of the thermodynamic quantities did not change at a fixed pressure, as would follow from (2.8) if $\mu = \bar{\lambda} = 0$. At constant volume it is possible to obtain, by the same method as in Sec. 1, the singular part of the thermodynamic quantities

$$C_V \sim |\tau|^{\alpha/(1-\alpha)}, \quad m \sim (-\tau)^{\beta/(1-\alpha)}, \quad \chi \sim |\tau|^{-\gamma/(1-\alpha)},$$

where α, β , and γ are the corresponding exponents of the ideal system.

In [20], only the homogeneous part of the shear forces was taken into account. (The inhomogeneous part, unlike the above-described treatment of [18], was not taken into account.) The homogeneous part of the shear forces reduces to boundary conditions and in the case of infinite samples does not change the answer obtained in [19]. Figure 5 shows a plot of the specific heat as a function of the temperature for NH_4Br , where an

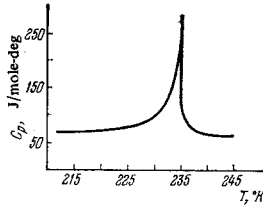


FIG. 5. Specific heat in the case of a first-order transition close to a second order transition (in NH_4Br , as measured by G. A. Mil'ner).

orientational first-order transition close to a second-order transition is realized.

Conclusions. 1) Allowance for the interaction of the phonons (longitudinal and transverse) with the ordering parameters responsible for the second-order phase transition leads to the onset of a first-order transition.

2) The region of "smearing" of the phase transition by phonons is determined by formula (2.10): $\bar{\tau} \sim \bar{\lambda}^{1/\alpha}$, where $\bar{\lambda} = 4\mu K_0(\partial T_C/\partial p)^2/3K_0 + 4\mu T_0$.

3. Effect of domain structure. Obviously, the domain structure (DS) can greatly alter the behavior of the magnetic susceptibility of a sample. In fact, in a single-domain sample, the increase of the magnetic moment following application of an external magnetic field H is due only to the ordering of the spins in the external field. On the other hand, in the presence of a DS, the principal contribution to the magnetization is due to the motion of the domain walls or to rotation of the magnetic-moment vector (without a change in the absolute magnitude of this vector).

The influence of the DS on the behavior of thermodynamic quantities near the Curie point was investigated in^[22].

a) We consider an ideal uniaxial ferromagnetic (or ferroelectric) single crystal of ellipsoidal shape, with the easiest magnetization axis coinciding with one of the axes of the ellipsoid. We direct the external field along this axis.

The energy can be expressed in the form of a sum of the exchange, anisotropy, and dipole-dipole energies. The anisotropy energy differs from zero in our case only inside the domain walls, so that this energy can be neglected accurate to terms of order $\bar{\delta}/t$ (where $\bar{\delta}$ is the thickness of the domain wall and t is the domain dimension). With the same accuracy, we neglect the energy of the emergence of the domains to the surface. The dipole-dipole energy can be represented by a sum of two parts: the first part is accounted for by the demagnetizing factor, and the second is added to the exchange energy (we denote this sum by E_0).

Taking the foregoing into account, we can express the energy \mathcal{E} in the form

$$\mathcal{E} = E_0 - \mu_B H \sum_i \sigma_i + (\bar{\alpha}/2N) \mu_B^2 (\sum_i \sigma_i)^2, \quad (3.1)$$

where σ_i is the z component of the spin at the site i , $\bar{\alpha} = 4\pi n$, and N is the number of atoms in the system.

For the partition function we obtain the expression

$$Z = \sum_{\{\sigma_i\}} \exp \left[- (E_0/T) + (H\mu_B/T) \sum_i \sigma_i - (\bar{\alpha}/2NT) (\mu_B \sum_i \sigma_i)^2 \right]. \quad (3.2)$$

Calculations detailed in Appendix 3 give the following expression for the thermodynamic potential per particle:

$$\Phi(T, H) = \Phi_0(T, \bar{H}_S) - [(H - \bar{H}_S)^2/2\bar{\alpha}]. \quad (3.3)$$

Thus, we have obtained the thermodynamic potential in a form that is isomorphic to the ideal system. As will be shown below, the isomorphic variable \bar{H}_S has the physical meaning of the internal magnetic field, and this field does not change on going from one domain to another.

The connection between the isomorphic variable \bar{H}_S and the "experimental" variable H is given by the equation

$$m_0(T, \bar{H}_S) = (H - \bar{H}_S)/\bar{\alpha}, \quad (3.4)$$

where m_0 is the magnetic moment of the ideal system.

b) From (3.3) we have

$$m(T, H) = -\partial\Phi(T, H)/\partial H = (H - \bar{H}_S)/\bar{\alpha} = m_0(T, \bar{H}_S). \quad (3.5)$$

The last equation in (3.5) follows from (3.4). We rewrite Eq. (3.5) in the form

$$H = \bar{H}_S + \bar{\alpha} m(T, H) = \bar{H}_S + 4\pi n m. \quad (3.6)$$

Comparing this expression, which represents the connection between the internal field \bar{H}_S , the magnetic moment m inside the ellipsoid, and the external field H , we arrive at the conclusion that \bar{H}_S does indeed have the physical meaning of the internal field.

In a uniaxial crystal, the domains are parallel to the easy-magnetization axis. Since the external field is also directed along this axis, and the internal field is parallel to the domain wall, the internal field is constant along the sample, by virtue of the continuity of the tangential component on going through the domain wall.

From (3.5) we obtain an expression for the magnetic susceptibility

$$\chi = \partial m/\partial H = (1/\bar{\alpha})(1 - \partial \bar{H}_S/\partial H). \quad (3.7)$$

Obviously, Eq. (3.4) has no solution at $H < \bar{\alpha} |m_0(T, \bar{H}_S = 0)|$, since m_0 and \bar{H}_S should be of the same sign. In the region $H \geq \bar{\alpha} |m_0(T, 0)|$, differentiating (3.4) with respect to \bar{H}_S , we obtain

$$\partial \bar{H}_S/\partial H = 1/(1 + \bar{\alpha}\chi_0) = 1/(1 + 4\pi n\chi_0),$$

where $\chi_0 = \partial m_0/\partial \bar{H}_S$. Substituting this expression in (3.7), we obtain the susceptibility in the region $H \geq \bar{\alpha} |m_0(T, 0)|$:

$$\chi_1 = \chi_0(T, \bar{H}_S)/(1 + 4\pi n\chi_0(T, \bar{H}_S)). \quad (3.8)$$

If $H = 0$ and $T > T_C$, then it follows from (3.4) that $\bar{H}_S = 0$, and from (3.8) we obtain an expression for χ_1 :

$$\chi_1 = \chi_0(T, 0)/(1 + 4\pi n\chi_0(T, 0)). \quad (3.9)$$

Representing $\chi_0(T, 0)$ in the form $\chi_0(T, 0) = \chi_0 |\tau|^{-\gamma}$ (χ_0 is a constant), we obtain from (3.9) the characteristic interval of the "smearing" of the susceptibility by the domain structure $\bar{\tau}$:

$$\bar{\tau} \sim (4\pi n\chi_0)^{1/\gamma}. \quad (3.10)$$

In the region $H < \bar{\alpha} |m_0(T, 0)|$, Eq. (3.4) has no solutions. If we recognize that Φ_0 is a function even in \bar{H}_S and has at $\bar{H}_S = 0$ a singularity connected with the discontinuity of m_0 at this point, then we can easily see that the principal contribution to the partition function is made by the point $\bar{H}_S = 0$. From (3.6) we have in this region

$$m = H/\bar{\alpha} = H/4\pi n, \quad \chi_2 = 1/\bar{\alpha} = 1/4\pi n. \quad (3.11)$$

Let us calculate the discontinuity of the susceptibility on the line $H = \bar{\alpha} |m_0(T, 0)|$. On this line, the solution of (3.4) is $\bar{H}_S = 0$, and near this line expression (3.8) goes over to (3.9). The jump of the susceptibility is equal to

$$\Delta\chi = \chi_2 - \chi_1 = 1/4\pi n (1 + 4\pi n \chi_0(T, 0)).$$

At $T \rightarrow T_C$ we have $\Delta\chi \rightarrow 0$ and the susceptibility is continuous but has a kink.

Let us calculate the specific heat of the system

$$C = -T \frac{\partial^2 \Phi}{\partial T^2} = -T \frac{\partial^2 \Phi_0(T, \bar{H}_s)}{\partial T^2} - T \frac{\partial^2 \Phi_0(T, \bar{H}_s)}{\partial T \partial \bar{H}_s} \frac{\partial \bar{H}_s}{\partial T} \\ = C_0(T, \bar{H}_s) - T \frac{\partial^2 \Phi_0(T, H_s)}{\partial T \partial \bar{H}_s} \frac{\partial \bar{H}_s}{\partial T},$$

where C_0 is the specific heat of the ideal system. In the region $H \geq \bar{\alpha} |m_0(T, 0)|$ we obtain $\partial \bar{H}_S / \partial T$ by differentiating (3.4) with respect to T :

$$\partial \bar{H}_s / \partial T = -\bar{\alpha} (\partial m_0 / \partial T) (1 + \bar{\alpha} \chi_0(T, \bar{H}_s))^{-1}.$$

Recognizing that $\partial^2 \Phi_0 / \partial T \partial \bar{H}_S = -\partial m_0 / \partial T$, we obtain

$$C_1 = C_0(T, \bar{H}_s) - T (\partial m_0(T, \bar{H}_s) / \partial T)^2 [4\pi n / (1 + 4\pi n \chi_0(T, H_s))].$$

In the region

$$H < \bar{\alpha} |m_0(T, 0)|, \quad \bar{H}_s = 0 \text{ and } C_2 = C_0(T, 0).$$

The discontinuity of the specific heat on the line $H = \bar{\alpha} |m_0(T, 0)|$ is equal to

$$\Delta C = C_2 - C_1 = T (\partial m_0(T, 0) / \partial T)^2 4\pi n / (1 + 4\pi n \chi_0(T, 0)).$$

At $T \rightarrow T_C$ we have

$$\Delta C \sim |\tau|^{-\alpha} \quad (\tau = (T - T_C) / T_C).$$

c) To elucidate the physical meaning of the results, we present calculations in the self-consistent-field approximation. The density of the thermodynamic potential (without allowance for terms of order $\bar{\delta}/t$) is equal to

$$\Phi = (1 - d_1) (-\alpha_1 \tau m_1^2 + \beta_1 m_1^4 - H m_1) + d_1 (-\alpha_1 \tau m_2^2 + \beta_1 m_2^4 + H m_2) \\ + 2\pi n [(1 - d_1) m_1 - d_1 m_2]^2,$$

where d_1 is the fraction of the domains directed opposite to the field, the subscripts 1 and 2 pertain respectively to domains directed parallel and antiparallel to the field, and α_1 and β_1 are constants.

Minimizing Φ with respect to m_1 , m_2 , and d_1 , we obtain two regions of the solutions:

1) At $H < 4\pi n m_0$ - multidomain case: $m_1 = m_2 = m_0 = (\alpha_1 \tau / 2\beta_1)^{1/2}$, $d_1 = [1 - (H / 4\pi n m_0)] / 2$;

2) At $H \geq 4\pi n m_0$ - single-domain case ($m_1 = -m_2$). The results for χ and C coincide with those obtained earlier.

In^[22] we also considered the behavior of $\bar{\delta}$ and t as functions of the temperature and of the magnetic field.

d) A number of experiments^[23-25] have shown that at $T < T_C$ the susceptibility remains constant. This behavior of susceptibility can be attributed to the presence of a domain structure.

Miyatani^[23] measured the temperature dependence of the magnetization of a spherical single crystal of CdCr_2Se_4 ($1/4\pi n = 3/4\pi = 0.24$) in different fields from 6 to 90 Oe. In all the fields, there was a clearly pronounced horizontal section in accordance with formula (3.11), i.e., a temperature region in which the magnetization is independent of the temperature. The ratio

of the magnetization to the field on the horizontal sections is constant for all fields at 0.23 - 0.25, i.e., $m/H = \partial m / \partial H = \chi = 0.23 - 0.35$, which is in good agreement with the theoretical value calculated from formula (3.11).

Analogous conclusions were obtained in^[24] for nickel. Boyarskiĭ and Starikov^[25] investigated the temperature dependence of the magnetic susceptibility of gadolinium near T_C . At $T < T_C$, the susceptibility turned out to be independent of the temperature and amounted to 1/11 to 1/4 for different samples. The samples were nearly cylindrical in form, with a length/diameter ratio 1.3 to 2.5. The demagnetizing factors for samples of this shape^[26] range from 0.09 to 0.2. Consequently, the expression $1/4\pi n$ overestimates the susceptibility. This is apparently due to the impurities that interfere with free motion of the domain walls and decrease the susceptibility. A plot of the susceptibility of a gadolinium sample against the temperature in weak magnetic fields, taken from^[25], is shown in Fig. 6. We see that below the Curie point the magnetic susceptibility is constant in accordance with (3.11). At $T > T_C$ the susceptibility is described by expression (3.9).

e) The arguments presented above pertain to a sample situated in an infinite free space. The electrical properties of ferroelectrics are, as a rule, investigated in parallel-plate capacitors. In this case, the "demagnetizing" field is concentrated in the gap between the sample and the electrodes of the capacitor. The energy of this field is small to the extent that the gap volume is small. Elementary calculations, which will not be presented here, yield for the demagnetizing factor n a value

$$n = g_1/g, \quad (3.12)$$

where g_1 is the gap thickness and g is the distance between the capacitor electrodes.

Substituting (3.12) in the formulas presented above we obtain the behavior of all the thermodynamic quantities. The susceptibility measured in this manner is of the order of 100-1000.

Conclusions. 1) The saturating field H_{sat} at which a multidomain structure becomes single-domain is $H_{\text{sat}} = 4\pi n m_0$.

2) The magnetic susceptibility of a sample is equal to $1/4\pi n$ in the multidomain region and is constant both as a function of the field and as a function of the temperature.

3) In the region of uniform magnetization at $H = 0$ the magnetic susceptibility is described by formula (3.9).

4) The "smearing" interval $\bar{\tau}$ in the region of uniform magnetization is given by (3.10).

On the $H_{\text{sat}}(T)$ line, χ experiences a discontinuity that equals zero at the Curie point and increases with decreasing temperature.

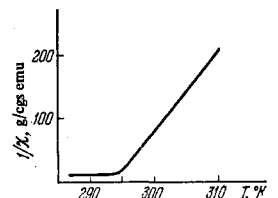


FIG. 6. Temperature dependence of the susceptibility of a Gd sample in the presence of a domain structure^[25].

6) The susceptibility is finite everywhere, including at the nonanalytic points.

7) At zero magnetic field, neglecting the wall thickness in comparison with the domain dimension, the specific heat is the same as in an ideal system. In a nonzero field, the specific heat is discontinuous on the $H_{\text{sat}}(T)$ line.

8) Ferroelectrics placed between capacitor electrodes have a demagnetizing factor equal to $n = g_1/g$, where g_1 is the thickness of the gap between the sample and the electrodes and g is the distance between the capacitor electrodes.

4. Effect of gravitational field. Let us examine the influence of the gravitational field on the behavior of the thermodynamic functions near the critical liquid-vapor point. The gravitational field leads to a dependence of the density on the height, so that the density ρ can be equal to ρ_c (the critical value) only at a certain definite height (inside the meniscus), and not through the entire volume of the vessel. Therefore the part of the free energy proportional to the volume should be an analytic function of the temperature and of the density. The nonanalytic part of the free energy, which is connected with the meniscus, is proportional to the surface area and will henceforth not be considered. Inclusion of the external field $U(\mathbf{r})$ leads to a change in the chemical potential \bar{g} ($\bar{g} = \bar{g}_0(\mathbf{P}, T) + U(\mathbf{r})$, where \bar{g}_0 is the chemical potential of the unperturbed system (see^[6], Sec. 25)). Therefore, if \bar{g} is chosen as the variable, then the thermodynamic potential of the perturbed system should be expressed in the isomorphic form $\Omega = \Omega_0(T, \bar{g})$. The transition from the isomorphic variable \bar{g} to the "experimental" variables \mathbf{P} and T is accomplished with the aid of the equation $\bar{g} = \bar{g}_0(\mathbf{P}, T) + U(\mathbf{r}) = \text{const}$. Subsequently, however, instead of using these equations, we shall employ a more lucid method.

The equation of states of the unperturbed system is^[5]

$$p = \tau^{2-\alpha-\beta} f(\rho/\tau^\beta) + f_r(\tau), \quad (4.1)$$

where $\rho = (\mathcal{P} - \mathcal{P}_c)/\mathcal{P}_c$, $p = P/P_c$, \mathcal{P} and P are the density and the pressure, respectively, \mathcal{P}_c and P_c are the critical values of the density and of the pressure, and f and f_r are unknown functions (f_r is analytic).

Equation (4.1) can be used in the case of a sufficiently homogeneous system, when $r_c \ll h_0$ (r_c is the correlation radius and h_0 is the characteristic inhomogeneity length). As will be seen below, this inequality is satisfied for all the experimentally attainable values of τ .

Directing the z axis upward (against the force of gravity), we have the differential relation

$$-dP = \mathcal{P} \tilde{g} dH = \mathcal{P}_c \tilde{g} dH + (\mathcal{P} - \mathcal{P}_c) \tilde{g} dH; \quad (4.2)$$

Here \tilde{g} is the acceleration due to gravity and H is the height reckoned from the center of the vessel along the z axis. (In the preceding sections, the letters H and h denoted the magnetic field; we do not deal with the magnetic field in this section, so that our notation should lead to no confusion). Changing over to dimensionless variables and bearing in mind the inequality $\rho \ll 1$, we rewrite (4.2) in the form

$$-dp = dh, \quad (4.3)$$

where $h = \mathcal{P}_c \tilde{g} H / P_c$.

Combining (4.3) and (4.1), we obtain

$$-h = \tau^{2-\alpha-\beta} [f(\rho/\tau^\beta) - f(\rho_0(\tau)/\tau^\beta)]; \quad (4.4)$$

Here $\rho_0(\tau)$ is the dimensionless density at the midpoint of the vessel. The function f has the following asymptotic values^[5]:

$$f(x) \approx \begin{cases} P_1 x & \text{for } x \ll 1, \\ P_2 x^\delta & \text{for } x \gg 1, \end{cases} \quad (4.5)$$

where P_1 and P_2 are constants.

a) We consider first the case $\tau > 0$ and $\rho \ll \tau^\beta$ over the entire height of the vessel. Using (4.4) and the scaling-theory relation $\alpha + 2\beta + \gamma = 2$, we obtain an equation for the density as a function of the height

$$-h = P_1 \tau^\nu [\rho - \rho_0(\tau)], \quad (4.6)$$

whence

$$\rho = \rho_0(\tau) - (h/P_1) \tau^{-\nu}. \quad (4.7)$$

Averaging the density ρ over the height \bar{h} of the vessel in accordance with the formula $\bar{\rho} = (1/\bar{h}) \int_{-\bar{h}/2}^{\bar{h}/2} \rho(h) dh$,

where \bar{h} is the height of the vessel, we obtain $\rho_0(\tau) = \bar{\rho}$. The conditions for the applicability of (4.6) are given by the two inequalities

$$\bar{\rho} \ll \tau^\beta, \quad \bar{h} \ll P_1 \tau^{\beta+\nu} = h_{01}. \quad (4.8)$$

We can ultimately rewrite (4.6) in the form

$$\rho = \bar{\rho} [1 - (h/h_{01}) (\tau^\beta/\bar{\rho})]. \quad (4.9)$$

b) We consider now the case $\rho \gg \tau^\beta$ over the entire height of the vessel. Using the lower expression of (4.5), we obtain from (4.4) an equation for ρ :

$$-h = P_2 (\rho^\delta - \rho_0^\delta), \quad (4.10)$$

with a solution

$$|\rho| = | |\rho_0|^\delta - (h/P_2) |^{1/\delta}. \quad (4.11)$$

In the case $\rho_0 \gg (h/P_2)^{1/\delta}$ we get from (4.11)

$$\rho = \rho_0 [1 - (h/P_2 \delta \rho_0^\delta)] = \bar{\rho} [1 - (h/P_2 \delta \bar{\rho}^\delta)] \quad (4.12)$$

with the applicability condition

$$\bar{\rho} \gg \tau^\beta, \quad \bar{h} \ll P_2 \bar{\rho}^\delta = h_{02}. \quad (4.13)$$

In the case $\rho_0 \ll (h/P_2)^{1/\delta}$ we get from (4.11)

$$\rho = \text{sign } h |h/P_2|^{1/\delta}, \quad (4.14)$$

if $\bar{h} \gg h_{02}$.

We now calculate the specific heat. It would be incorrect to average C_ρ over the height, for when the temperature varies the substance can flow from one part of the vessel to the other and the density at each height is not constant. The average specific heat at constant volume is proportional to the derivative of the entropy $S(\rho(h, \tau), \tau)$ with respect to temperature:

$$C_V = \left(\frac{\partial S}{\partial \tau} \right)_h = \bar{C}_\rho + \left(\frac{\partial S}{\partial \rho} \right)_\tau \left(\frac{\partial \rho}{\partial \tau} \right)_h = \bar{C}_\rho - \frac{P_c}{\mathcal{P}_c T_c} \left(\frac{\partial p}{\partial \tau} \right)_\rho \left(\frac{\partial \rho}{\partial \tau} \right)_h. \quad (4.15)$$

The average of any quantity over the height of the vessel will be designated by a superior bar.

In the case specified by the inequalities (4.8), C_ρ can be expressed as a function of the temperature and of the density in the form

$$C_\rho = C_0 \tau^{-\alpha} [1 - (C_2 \rho^2/\tau^{2\beta})]; \quad (4.16)$$

here C_0 and C_2 are constants. Substituting into this formula $\rho(h)$ from (4.9) and averaging the specific heat over the height of the vessel, we obtain

$$\bar{C}_p = C_0 \tau^{-\alpha} [1 - C_2 (\bar{\rho}^2 / \tau^{2\beta} + \bar{h}^2 / 12 h_{01}^2)]. \quad (4.17)$$

The expression that enters in (4.15) for $(\partial p / \partial \tau)_\rho$ can be obtained from (4.1), (4.5), and (4.9):

$$(\partial p / \partial \tau)_\rho = s_0 + s_1 \tau^{\nu-1} \rho = s_0 + s_1 \tau^{\nu-1} \bar{\rho} [1 - (h/h_{01}) (\tau^\beta / \bar{\rho})]. \quad (4.18)$$

s_i are constants. Furthermore,

$$s_0 (\partial \bar{\rho} / \partial \tau)_h = s_0 (\partial \bar{\rho} / \partial \tau)_h = 0, \quad (4.19)$$

since the experiment is carried out under the condition $\bar{\rho} = \text{const}$.

Using (4.18), (4.19), and (4.9), we obtain

$$(\partial p / \partial \tau)_\rho (\partial \bar{\rho} / \partial \tau)_h = - (s_1 \gamma / 12) (\bar{h}^2 / h_{01}^2) \tau^{-\alpha}. \quad (4.20)$$

Substituting (4.17) and (4.20) in (4.15), we ultimately obtain an expression for the specific heat

$$C_V = C_0 \tau^{-\alpha} [1 - (C_2 \bar{\rho}^2 / \tau^{2\beta}) - (C_3 \bar{h}^2 / h_{01}^2)], \quad (4.21)$$

where

$$C_3 = (C_3 / 12) - (P_c s_1 \gamma / 12 \beta_c T_c C_0).$$

We note once more that this expression is valid in the region specified by the inequalities (4.8), so that the last two terms of (4.21) are much smaller than unity. The rapid growth of the specific heat stops at those values of $\bar{\tau}$ at which the corrections $C_2 \bar{\rho}^2 / \tau^{2\beta}$ and $C_3 \bar{h}^2 / h_{01}^2$ begin to approach unity. The "smearing" $\bar{\tau}$ of the specific heat by the gravitational field can be estimated from the formula

$$\bar{\tau} \sim \max \{ (C_2 \bar{\rho}^2)^{1/2\beta}, (\bar{h} C_3^{1/2} / P_1)^{1/(\nu+\beta)} \} \quad (4.22)$$

and from (4.22) we can estimate the maximum attainable value of the specific heat:

$$C_{V \max} \sim \min \{ C_0 C_2^{-\alpha/2\beta} \bar{\rho}^{-\alpha/\beta}, C_0 (\bar{h} C_3^{1/2} / P_1)^{-\alpha/(\beta+\nu)} \}. \quad (4.23)$$

In the presence of a gravitational effect, the critical temperature of an ideal system can be determined from measurements of the specific heat only accurate to the quantity $\bar{\tau}$.

In the case specified by the inequalities (4.13), the specific heat behaves like

$$C_V \sim \bar{\rho}^{-\alpha/\beta}$$

and in view of the analytic behavior in the gravitational field, it tends to the maximum values given by (4.23).

If we put $\bar{\rho} = 0$ in the final formulas and use the classical values of the critical exponents, we obtain the expressions derived in [27, 28].

Assuming typical values of the critical parameters ($P_c = 50$ atm, $\mathcal{P}_c = 0.5$ g/cm³), we get

$$h \approx 10^{-5} H, \quad H_{01} \approx 10^5 \tau^{\beta+\nu}, \quad \tau_c \sim 10^{-8} \tau^{-(2-\alpha)/\beta},$$

where H , H_{01} , and r_c are measured in centimeters. It is easy to see that the inequality $H_{01} \gg r_c$ holds for all $\tau \gtrsim 10^{-6}$, i.e., we can use formula (4.1), which is valid for a homogeneous substance. It can be assumed that the meniscus is produced at temperatures such that the correlation radius becomes comparable with the inhomogeneity parameter H_{01} . This occurs in the interval $\tau \sim 10^{-6}$. Therefore, the critical temperature of an ideal system can be determined with relative accuracy 10^{-6} by observing the vanishing (or appearance) of the meniscus. At $\tau \gtrsim 10^{-4}$ we have $H_{01} \sim 10^{-1}$ cm, i.e., to make the influence of the gravitational effect relatively small it is necessary to choose a vessel (calorimeter) height less than 1 mm. In other words, it follows from

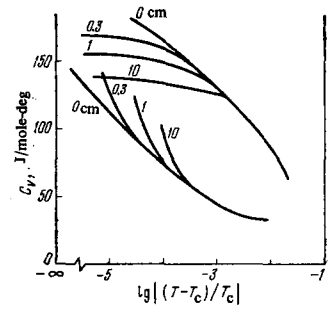


FIG. 7. Influence of gravitational effect on specific heat of xenon at cylindrical-vessel heights 10, 1 and 0.3 cm [30]. T_c is the critical temperature.

(4.22) that at a vessel height 1 mm - 1 cm the specific-heat "smearing" interval is $10^{-4} - 10^{-3}$. Thus, the critical temperature of an ideal system can be determined much more accurately from the vanishing (appearance) of the meniscus than from data on the specific heat. (This circumstance was pointed out to the author by S. P. Malyschenko.)

The gravitational effect can be used in the study of the equation of state of an ideal system. It is possible to investigate the dependence of the density on the temperature at different heights of the vessel, since the pressure difference is proportional to the height difference, as seen from (4.3). Alekhin and Krupskii [29] investigated the equation of state of cyclopentane near the critical point in this manner.

Let us mention some numerical calculations of the influence of the gravitational effect on the thermodynamics of the critical point. Schmidt [30] carried out the calculations using in place of the equation of state (4.1) the empirical formula proposed in [31]:

$$\Delta \bar{g}(\rho, \tau) = \bar{g}(\mathcal{P}, \tau) - \bar{g}(\mathcal{P}_c, \tau) = \text{sign } \rho |\rho|^\beta h(x),$$

where

$$h(x) = E_1 [(x + x_0)/x_0] \{1 + E_2 [(x + x_0)/x_0]^{2\beta}\}^{(\nu-1)/2\beta},$$

$x = \tau |\rho|^{1/\beta}$, and \bar{g} is the chemical potential of the system; the numerical values of the constants E_1 and E_2 are given in [30, 31]. Figure 7 shows calculations of the heat capacity of xenon with allowance for the gravitational force. We see that the larger the vessel height, the larger are the deviations from the behavior of the heat capacity of an ideal system. At a vessel height on the order of 1 cm, the deviations begin at temperatures $\tau \sim 10^{-3} - 10^{-4}$, which agrees with calculations in accord with (4.22).

Let us also point out certain effects which are not considered in detail in the present review. In [28] we investigated the motion of the meniscus inside a vessel with changing temperature and average density. In [32] it was found that the maximum of the specific heat and the "jump" resulting from the transition through the coexistence curve occur at different temperature, owing to the presence of the gravitational field.

Conclusions. 1) Allowance for the gravitational force leads to analytic behavior of the thermodynamic quantities.

2) In the case when $\bar{\rho} \ll \tau^\beta$ and $\bar{h} \ll P_1 \tau^{\beta+\nu} = h_{01}$, the distribution of the density over the height of the vessel is given by $\rho = \bar{\rho} [1 - (h/h_{01}) (\tau^\beta / \bar{\rho})]$.

3) In the case $\bar{\rho} \gg \tau^\beta$ and $\bar{h} \ll P_2$ we have $\bar{\rho}^\delta = h_{02}$, $\rho = \bar{\rho} [1 - (h/P_2 \delta \bar{\rho}^\delta)]$, and in the case $\bar{\rho} \gg \tau^\beta$ and $\bar{h} \gg h_{02}$ we have $\rho = \text{sign } h |h/P_2|^{1/\delta}$.

3) In the case $\bar{\rho} \ll \tau^\beta$ and $\bar{h} \ll h_{01}$, the average heat

capacity at constant total volume of the vessel is given by

$$C_V = C_0 \tau^{-\alpha} [1 - (C_2 \bar{\rho}^2 / \tau^{2\beta}) - (C_3 \bar{h}^2 / h_{01}^2)],$$

and its maximum value can be estimated from the expression

$$C_{V_{\max}} \sim \min [C_0 C_2^{-\alpha/2\beta} \bar{\rho}^{-\alpha/\beta}, C_0 (\bar{h} C_3^{1/2} / P_1)^{-\alpha/(\beta+\gamma)}].$$

5) The interval in which the heat capacity is "smeared out" by the gravitational field near the critical point is given by (4.22).

5. Effect of small perturbations on the shift of the critical point. Isomorphism of phase transitions. In this section, using scaling-theory methods, we derive general formulas for the shift of the critical point under the influence of small perturbations^[33,34], obtained independently by Abe and by the author. It turns out that in all cases when the perturbation leads to a complication of the unit cell, regardless of the dimensionality of the space, the shift of the critical point T_C is linear in the small perturbation. We consider also an example when the shift of T_C is not analytic in the small perturbation. In this case the perturbed system is not isomorphic to the local system.

a) We choose for concreteness an Ising model in which the energy E of the system consists of two parts:

$$E = E_0 + E_1, \quad (5.1)$$

where $E_0 = -I \sum \sigma_i \sigma_j$, I is the exchange energy of the ideal lattice, $\sigma_i = \pm 1$ is the spin variable, i is the number of the lattice site at which the given spin is located, $E_1 = -\bar{\epsilon} \sum \sigma_i \sigma_{i_2} \dots \sigma_{i_n} = -\epsilon \sum_j E_j$ is the perturbation

superimposed on the system, $\bar{\epsilon}$ is a small parameter ($\bar{\epsilon} \ll I$), and $E_j = \sigma_{i_1} \dots \sigma_{i_n}$; the index j includes the aggregate of coordinates i_1, \dots, i_n . The characteristic distances between the spins that enter in E_j are the interatomic distances.

The partition function corresponding to the energy (5.1) is given by

$$Z = \sum_{\{\sigma\}} \exp(-E_0/T) \exp[(\bar{\epsilon}/T) \sum E_j]. \quad (5.2)$$

The summation in (5.2) is carried out over all the spin configurations. It is easy to verify the identity

$$\exp(\bar{\epsilon}/T) E_j = \text{ch}(\bar{\epsilon}/T) (1 + X E_j), \quad X = \text{th}(\bar{\epsilon}/T), \quad (5.3)$$

which we shall use to rewrite (5.2) in the form

$$Z = \text{ch}^{N\bar{h}}(\bar{\epsilon}/T) \sum_{\{\sigma\}} e^{-E_0/T} \prod_j (1 + X E_j) = \text{ch}^{N\bar{h}}(\bar{\epsilon}/T) Z_0 \sum_{p=0}^{\infty} X^p \sum_j \langle E_j E_{j_2} \dots E_{j_p} \rangle; \quad (5.4)$$

here \bar{h} is a constant that depends on the rules for the summation in E_1 ,

$$Z_0 = \sum_{\{\sigma\}} \exp(-E_0/T), \quad \langle E_{j_1} \dots E_{j_p} \rangle = \sum_{\{\sigma\}} E_{j_1} \dots E_{j_p} \exp(-E_0/T) / Z_0$$

is the correlator of p energies (5.1), each of which is a product of n spins. Formula (5.4) contains the correlators of the unperturbed system.

Using the method of Patashinskiĭ and Pokrovskii^[3], we introduce the irreducible correlators Q in accordance with the formulas

$$\begin{aligned} Q(j) &= \langle E_j \rangle, \quad Q(j_1, j_2) = \langle E_{j_1} E_{j_2} \rangle - Q(j_1) Q(j_2), \\ Q(j_1, j_2, j_3) &= \langle E_{j_1} E_{j_2} E_{j_3} \rangle - Q(j_1) Q(j_2, j_3) \\ &\quad - Q(j_2) Q(j_1, j_3) - Q(j_3) Q(j_1, j_2) - Q(j_1) Q(j_2) Q(j_3). \end{aligned} \quad (5.5)$$

The correlators Q vanish if any distances between the spins contained in Q exceed the correlation radius $\sim r_{C0}$ of the unperturbed system.

Substituting (5.5) in (5.4) and using the theorem from the book^[35] (Sec. 15), which makes it possible to express the free energy only in terms of irreducible correlators, we obtain

$$\Phi = \Phi_r + \Phi_0 - T \sum_{p=1}^{\infty} X^p \sum_j Q(j_1 \dots j_p), \quad (5.6)$$

where Φ_r is the regular part of the free energy and Φ_0 is the free energy of the unperturbed system.

Formula (5.6) can also be obtained by direct expansion of the expression $\Phi = -T \ln \text{Tr} \exp[T^{-1}(E_0 + E_1)]$ in a Taylor series in E_1 .

Estimating the correlators that enter in (5.6) by the scaling-theory method, we obtain the dimensional estimate (see Appendix 4)

$$\Gamma_p = \sum_j Q(j_1, \dots, j_p) \sim N r_{0c}^{d(p-1)} / r_{0c}^{pa} \sim N \tau_0^{d/y_0} \tau_0^{-p(d-a)/y_0}, \quad (5.7)$$

where d is the dimensionality of space and a is the exponent in the Kadanoff transformation of the quantity E_1 .

Substituting (5.7) in (5.6), we rewrite the expression for the singular part of the free energy Φ_s in the form

$$\Phi_s = N \tau_0^{d/y_0} \sum_{p=1}^{\infty} b_p (X/\tau_0^{(d-a)/y_0})^p = N \tau_0^{d/y_0} f(\xi), \quad (5.8)$$

where b_p are constants, $\xi = X/\tau_0^{(d-a)/y_0}$, and $f(\xi)$ is unknown function. The series (5.8) should converge at $\xi \ll 1$ ($\tau_0 \rightarrow \infty$, $T \rightarrow \infty$), since the thermodynamic potential has no singular points at $T \rightarrow \infty$.

The function $f(\xi)$ has a singularity at the phase-transition point, i.e., there exists a point ξ_0 at which the function $f(\xi)$ is not analytic. We do not have at our disposal parameters from which to make up small (or large) numbers, and therefore $\xi_0 \sim 1$.

From (5.8) follows an equation for the transition temperature T_C of the considered system

$$\xi_0 = X/\tau_{0c}^{(d-a)/y_0}, \quad \tau_{0c} = (T_c - T_0)/T_0. \quad (5.9)$$

From (5.9) we have the sought formula for the dependence of T_C on X :

$$T_c = T_0 [1 + (X/\xi_0) y_0/(d-a)], \quad (5.10)$$

i.e., the shift of the transition temperature following application of the perturbation is proportional to $\bar{\epsilon} y_0/(d-a)$.

Let us consider a number of examples. As the zeroth approximation we take the Ising model with nearest-neighbor interaction. For E_1 we introduce the interaction along the diagonal. Then E_1 is transformed like the energy, $a = d - y_0$, and from (5.10) we get $\tau_{0c} \sim \bar{\epsilon}$. This result agrees with the exact formulas obtained by Vaks, Larkin, and Ovchinnikov^[36]. We emphasize that this result does not depend on the dimensionality of space.

By way of a more complicated example we consider a system consisting of two interacting planes arranged one over the other. The energy of such a system is given by

$$E = E_0 - \bar{\epsilon} \sum_{i,j} \sigma_{k1i} \sigma_{k12j}$$

here E_0 is the energy of the interaction inside the Ising planes, $\bar{\epsilon}$ is the interaction constant of spins located in different planes, and the subscript $i = 1, 2$ numbers the planes.

In this case the partition function breaks up in the zeroth approximation into the product of partition functions pertaining to the first and second planes, and the spins belonging to different planes are averaged independently in formula (5.6). Therefore E_j is transformed like the square of the magnetic moment, i.e., E_1

$\rightarrow \bar{\epsilon}^{2(x_0-d)} E_1$, whence $a = 2(d - x_0)$. Substituting this value of a in (5.10), we obtain the sought formula

$$T_c = T_0 [1 + (X/\xi_0)^{4/7}], \quad (5.11)$$

i.e., the temperature of the transition shifts in proportion to $\bar{\epsilon}^{4/7}$.

It is shown in^[34] that the result (5.11) remains in force (accurate to the value ξ_0) if there are L interacting planes, provided that $L \ll r_{0c}$.

A similar situation also holds in the two-dimensional Ising model in the case when the interaction I_1 along the diagonals is much larger than the interaction I_0 of the nearest neighbors. In the zeroth approximation in I_0 we have two noninteracting lattices. Reasoning analogous to that used in the case of two weakly interacting Ising planes leads to formula (5.11) for the shift of the critical temperature. (The role of $\bar{\epsilon}$ is assumed by the quantity I_0 .)

In^[34] they obtained the $\bar{\epsilon}$ -dependence of the coefficients of the powers of τ in the specific heat, in the magnetic moment, and in the susceptibility.

Assume that in the region $\tau \ll X^{y_0/(d-a)}$ these quantities are described by the formulas

$$C \sim \bar{\epsilon}^{\alpha_1 \tau^{-\alpha}}, \quad m \sim \bar{\epsilon}^{\beta_1 \tau^\beta}, \quad \chi \sim \bar{\epsilon}^{\gamma_1 \tau^{-\gamma}}.$$

We can then express α_1 , β_1 , and γ_1 in terms of the Kadanoff transformation exponents of the temperature and magnetic field in the perturbed (y, x) and unperturbed (y_0, x_0) systems:

$$\alpha_1 = \frac{(y-y_0)d}{y(d-a)}, \quad \beta_1 = \frac{dy-yx_0-dy_0+y_0x}{y(d-a)}, \quad \gamma_1 = \frac{dy-2x_0y-dy_0+2xy_0}{y(d-a)}.$$

b) We shall prove that if the shift of the critical point is not analytic in the perturbation, then the phase transition in the perturbed system is not isomorphic to the transition in the ideal system^[37]. Let us assume the opposite, that isomorphism exists. Then the singular part F_S of the free energy can be written in the form

$$F_s = C(T, \bar{\epsilon}) \tau^{2-\alpha_0}, \quad (5.12)$$

where $C(T, \bar{\epsilon})$ is an analytic function of T and $\bar{\epsilon}$, while α_0 is the critical exponent in the unperturbed system.

Let the shift of the critical temperature be equal to

$$(T_c - T_0)/T_0 = \tilde{A} \bar{\epsilon}^\kappa, \quad (5.13)$$

where $\tilde{A} \sim 1$ is a constant and κ , by assumption, is a noninteger number. Substituting (5.13) in (5.12), we obtain the following expression for F_S :

$$F_s = C(T, \bar{\epsilon}) (\tau_0 - \tilde{A} \bar{\epsilon}^\kappa)^{2-\alpha_0}. \quad (5.14)$$

However, the expression (5.14) with noninteger κ cannot be represented in the form of a series (5.8) in integer powers of $\bar{\epsilon}$ at small $\bar{\epsilon}$. We arrive at a contradic-

tion, thus proving that it is impossible to represent the singular part of the free energy in the form (5.12).

Thus, an Ising model consisting of several weakly-interacting planes cannot have a free energy in the form $F_S = C(T, \bar{\epsilon}) \tau^2 \ln \tau$, where $C(T, \bar{\epsilon})$ is an analytic function in T and $\bar{\epsilon}$. These questions are treated in greater detail in^[33,37]. In particular, it is indicated in^[37] that the isomorphic form (1.3) of the thermodynamic potential of a system with impurities may be violated when account is taken of the direct interaction between the impurities in the Syozi model.

Conclusions. 1) The shift of the critical point following application of a small perturbation can be calculated from formula (5.10).

A nonlinear shift of the transition point is possible. In the model of two weakly interacting Ising planes, the shift of the transition point is proportional to $\bar{\epsilon}^{4/7}$.

2) If the shift of the critical point is not analytic in the perturbation, then the phase transition in the perturbed system will not be isomorphic to the transition in the ideal system.

III. NONEQUILIBRIUM IMPURITIES AND INHOMOGENEITIES

In the preceding chapter we considered systems that are in thermodynamic equilibrium in terms of all the thermodynamic variables. In this chapter we consider the case when the experiment is carried out so rapidly that the impurities and inhomogeneities of the sample cannot "follow" the changes of the temperature, and no thermodynamic equilibrium is established. We shall call this case the model of frozen-in impurities (MFI). The influence of such impurities on the phase transition reduces to the appearance of regions with different impurity concentrations in different regions, i.e., to the appearance of inhomogeneities. Since no exact and complete solutions have been obtained to date in the MFI, we consider the influence of the sample inhomogeneities on a second-order phase transition by the self-consistent-field method, assuming a characteristic inhomogeneity length l large in comparison with the direct-interaction radius r_0 .^[38] It turns out that under certain conditions such systems can have at least two nonanalytic points. The point with the higher temperature is connected with the onset of regions of unlimited dimension with a stable ordering parameter η . The value of η averaged over the entire sample, however, is equal to zero. The second point is connected with the onset of a nonzero ordering parameter in the entire sample.

Using the LeChatelier principle (see^[6], Sec. 22) it is easy to show that, other conditions being equal, the heat capacity is maximal under conditions of equilibrium in terms of all the variables. Therefore the heat capacity in the MFI is smaller than the heat capacity C_c in the model of equilibrium impurities, if the impurity concentrations are the same. As seen in Sec. 1, the value of C_c is finite everywhere, including the phase-transition point, and therefore the heat capacity in the MFI should also be a finite quantity at all temperatures.

6. Thermodynamic potential of inhomogeneous media.

We write down the Landau expansion of the free energy Φ in terms of the ordering parameter η and its derivatives, thereby describing the inhomogeneity by the de-

pendence of the expansion coefficients on the coordinates.

$$\Phi[\eta] = \int [\hat{\alpha}(r, T)(T - T_c(r))\eta^2 + \hat{\beta}(r, T)\eta^4 + \hat{\gamma}(r, T)(\nabla\eta)^2] dV; \quad (6.1)$$

here T is the temperature and V is the volume of the sample over which the integration is carried out. It is assumed in this expansion that the volume element, which is small in comparison with the inhomogeneity dimension, remains isotropic and consequently there are no linear or cubic terms in η , and the only scalar that depends on the derivatives of η is $(\nabla\eta)^2$.

We assume that the expansion-coefficient increments connected with the inhomogeneities are much smaller than the coefficients themselves. In this approximation we can regard $\hat{\alpha}$, $\hat{\beta}$, and $\hat{\gamma}$ as constants, and take the inhomogeneity of the medium into account only in $T_C(r) = T_0 + T_1(r)$, where T_0 is the average value of the function $T_C(r)$ and $T_1 \ll T_0$. It is not assumed that T_1 is small in comparison with $T - T_0$.

It is meaningful to take into account the influence of the inhomogeneity in the self-consistent field approximation only in the case when the "temperature smearing" connected with the temperature inhomogeneities is much larger than the "smearing" connected with the fluctuations of the ordering parameter. In the self-consistent-field theory it is shown that the temperature region in which the fluctuations are significant is of the order of r_0^{-6} [39-41] and we shall therefore require satisfaction of the inequality $T_1/T_0 \gg r_0^{-6}$ ($r_0 \gg 1$). We take the interatomic distance as the unit length. The region of applicability of the considered theory is ultimately given by the inequalities $1 \gg T_1/T_0 \gg r_0^{-6}$ and $l \gg r_0$.

The ordering parameter η is obtained from the condition that the functional (6.1) be a minimum, and the corresponding equation is

$$\hat{\gamma}\Delta\eta = \hat{\alpha}(T - T_c(r))\eta + 2\beta\eta^3. \quad (6.2)$$

In superconductivity theory this equation is called the Ginzburg-Landau equation [42]. In the considered theory, η varies over macroscopic distances, and η and η' can be regarded as continuous.

We shall prove that $T_C(r)$ is an analytic function (as will be assumed from now on), then the ordering parameter either vanishes identically or never vanishes. For simplicity we consider the case of a one-dimensional distribution of the inhomogeneities (the proof can be generalized in trivial fashion to the three-dimensional case).

Let η vanish at the point x_0 . If $\eta'(x_0) = 0$ at the same point, then we can show by differentiating (6.2) that a derivative of η with respect to x of any order also vanishes at the point x_0 , i.e., that $\eta \equiv 0$. If $\eta'(x_0) \neq 0$, then we can construct a function $\tilde{\eta}(x)$, which is continuous and has a continuous first derivative, such that $\Phi[\tilde{\eta}] < \Phi[\eta]$ and $\tilde{\eta}$ never vanishes. We introduce $\tilde{\eta}_1 = |\eta|$. It is seen from (6.1) that $\Phi[\eta] = \Phi[\tilde{\eta}_1]$. In a small vicinity of x_0 ($x_0 - \tilde{\epsilon}, x_0 + \tilde{\epsilon}$), we write down $\eta(x) = \eta'(x_0)(x - x_0)$. We define $\tilde{\eta}$ in such a way that $\tilde{\eta} = \tilde{\eta}_1$ everywhere except in the vicinity of x_0 , and we put in that vicinity

$$\tilde{\eta} = (\eta'(x_0)/2)\tilde{\epsilon} + (\eta'(x_0)/2\tilde{\epsilon})(x - x_0)^2.$$

It is easy to verify that $\tilde{\eta}$ and $\tilde{\eta}'$ are continuous and the equality $\Phi[\eta] = \Phi[\tilde{\eta}]$ is satisfied in the integration over the entire space, with the exception of the vicinity of

x_0 . The values of the functionals (6.1) in the integration over the vicinity of x_0 are respectively

$$\Phi[\eta] = 2\hat{\gamma}\eta'^2(x_0)\tilde{\epsilon}, \quad \Phi[\tilde{\eta}] = (2/3)\hat{\gamma}\eta'^2(x_0)\tilde{\epsilon},$$

i.e., $\Phi[\tilde{\eta}] < \Phi[\eta]$, Q.E.D.

7. Long-wave inhomogeneities. In this section we consider the case when the characteristic length of the inhomogeneities is much larger than the correlation radius in the region $\tau \sim T_1$ ($l \gg r_C(T_1) \sim (\hat{\gamma}/\hat{\alpha}T_1)^{1/2}$).

a) **Ordered phase.** In the spatial region $\tilde{\tau} > 0$ ($\tilde{\tau} = T_C(r) - T$) we have the estimate $\hat{\gamma}\Delta\eta \sim \hat{\gamma}\eta/l^2$. In the temperature region $\tilde{\tau} \sim T_1$ we obtain $\hat{\gamma}\Delta\eta/\hat{\alpha}\tilde{\tau}\eta \sim \hat{\gamma}^2/l^2\hat{\alpha}T_1 \sim r_C^2(T_1)/l^2 = \delta$. In the zeroth approximation

$$\eta_{(0)}^2 = \hat{\alpha}\tilde{\tau}/2\hat{\beta}. \quad (7.1)$$

In the first approximation in δ we obtain

$$\eta_{(1)} = [\hat{\gamma}/4(2\hat{\alpha}\hat{\beta})^{1/2}] (1/\tilde{\tau}^{5/2}) [\tilde{\tau}\Delta T_1 - (1/2)(\nabla T_1)^2]. \quad (7.2)$$

If $\tilde{\tau} \gtrsim T_1$, we get

$$\eta_{(1)}/\eta_{(0)} \ll \hat{\gamma}/\hat{\alpha}T_1 l^2 = \delta \ll 1,$$

i.e., formulas (7.1) and (7.2) hold. These expressions however, do not hold near the points \bar{r}_0 at which $\tilde{\tau}(\bar{r}_0) = 0$. If r_0 is not an extremum point of $\tilde{\tau}$ ($\nabla\tilde{\tau}(\bar{r}_0) \neq 0$), then the limits of applicability of (7.1) and (7.2) are given by the inequality

$$\hat{\gamma}T_1^2/\hat{\alpha}\tilde{\tau}^3 l^2 = \delta T_1^2/\tilde{\tau}^3 \ll 1.$$

Writing down $\tilde{\tau}$ in the vicinity of \bar{r}_0 in the form

$$\tilde{\tau} = \nabla T_1(\bar{r}_0)(r - \bar{r}_0),$$

we obtain an upper bound on the spatial region of applicability of these formulas;

$$|r - \bar{r}_0|^{2/3} \gg \delta. \quad (7.3)$$

b) **Disordered phase.** We consider now the space region $\tilde{\tau} < 0$. If we neglect the correlation of the ordering parameter of the regions with $\tilde{\tau} < 0$ and $\tilde{\tau} > 0$, then, taking into account the fact that the integrand in (6.1) is not negative, we obtain $\eta = 0$. It is therefore natural to assume that the ordering parameter is small, to neglect the last term in (6.2), and to solve the simplified equation in the quasiclassical approximation. As a result we obtain in the case of a one-dimensional distribution of the inhomogeneities

$$\eta = (\hat{D}/l|\tilde{\tau}|^{1/4}) \exp \left\{ \pm \int_{x_0}^x [(\hat{\alpha}/\hat{\gamma})|\tilde{\tau}|]^{1/2} dx \right\}, \quad (7.4)$$

where \hat{D} is a constant. The sign in (7.4) should be chosen such that the solution attenuates in the interior of the region $\tilde{\tau} < 0$. Inasmuch as

$$\int_{x_0}^x [(\hat{\alpha}/\hat{\gamma})|\tilde{\tau}|]^{1/2} dx \sim (\hat{\alpha}T_1/\hat{\gamma}l)^{1/2}(x - x_0)^{3/2} \sim (x - x_0)^{3/2}/r_C(T_1)l^{1/2},$$

while the characteristic length of penetration of the ordering parameter into the disordered phase is of the order of $r_C^2/3l^{1/3}$ and is much smaller than the inhomogeneity dimension l , the quasiclassical case is applicable. The spatial limit of applicability of formula (7.4), just as for (7.1) and (7.2), is given by the inequality (7.3).

8. Mean values of the ordering parameter and of the heat capacity. Let us calculate the mean values of the ordering parameter and the heat capacity $\bar{\eta}$ and \bar{c} , neglecting the exponentially small contribution of the regions with $\tilde{\tau} < 0$, using the formulas

$$\bar{\eta} = \int (\hat{\alpha}/2\hat{\beta})^{1/2} \bar{\tau}^{1/2} dV, \quad \bar{C} = -T\hat{\alpha} \int (d\eta^2/dT) dV = (T\hat{\alpha}^2/2\hat{\beta}) \int dV. \quad (8.1)$$

The integration in (8.1) is carried out only over the regions where $\bar{\tau} > 0$.

We introduce the function $\rho(T_1)dT_1$, which describes the distribution of the probabilities of T_1 in the temperature interval dT_1 on a segment of length $\sim l$ (for the sake of simplicity, we neglect the dispersion of the inhomogeneity length), with a normalization condition

$$\int_{-\infty}^{\infty} \rho(T_1) dT_1 = 1.$$

If we use this function, then we can rewrite (8.1) in the form

$$\bar{\eta} = (\hat{\alpha}/2\hat{\beta})^{1/2} \int_{T-T_0}^{\infty} (T_0 + T_1 - T)^{1/2} \rho(T_1) dT_1, \quad (8.2)$$

$$\bar{C} = (T\hat{\alpha}^2/2\hat{\beta}) \int_{T-T_0}^{\infty} \rho(T_1) dT_1.$$

We consider the case when T_1 has an upper bound $T_{1\max}$. In the region of temperatures close to $T_0 + T_{1\max}$, $\rho(T_1)$ can be represented in the form

$$\rho(T_1) \approx [\rho^{(n)}(T_{1\max})/n!] (T_1 - T_{1\max})^n.$$

This case takes place when the inhomogeneities are produced by the "frozen-in" impurities. If the impurities are nonmagnetic, then $T_C(r)$ is bounded from above by the critical temperature of the pure substance. In the temperature interval $\tau_{\max}^2/T_1^2 \gg \hat{\delta}$ ($\tau_{\max} = T - T_C(x_{\max})$), the correlation radius $r_C^2 \sim \hat{\gamma}/\hat{\alpha}$ ($T_0 + T_{1\max} - T$) is much smaller than the average length of the region with positive τ in the vicinity of the point x_{\max} where the maximum value of T_C is reached; we have

$$\bar{\eta} = (\hat{\alpha}/2\hat{\beta})^{1/2} [\rho^{(n)}(T_{1\max})/n!] \int_{T-T_0}^{T_{1\max}} (T_0 + T_1 - T)^{1/2} (T_1 - T_{1\max})^n dT_1$$

$$= [2^{n+1}/(2n+3)!!] (\hat{\alpha}/2\hat{\beta})^{1/2} |\rho^{(n)}(T_{1\max})| \tau_{\max}^{n+3/2},$$

$$\bar{C} = (\hat{\alpha}^2 T/2\hat{\beta}) [|\rho^{(n)}(T_{1\max})|/(n+1)!] \tau_{\max}^{n+1}.$$

In the second limiting case $\tau_{\max}^2/T_1^2 < \hat{\delta}$, the principal contributions to $\bar{\eta}$ and \bar{C} are made by the regions with $\bar{\tau} > 0$ and length l on the order of the correlation radius, which is much larger than the average length of such regions (fluctuations in the distribution of T_1 over the specimen have low probability). In regions that are small in comparison with the correlation radius, the value of η is exponentially small, just as in the disordered phase. From the condition $\bar{l} \sim r_C(\tau_{\max}) \sim (\hat{\gamma}/\hat{\alpha}\tau_{\max})^{1/2}$, the probability of having a region with $\tau > 0$ and of volume \bar{l}^3 , consisting of $(\bar{l}/l)^3 \sim (r_C/\bar{l})^3$ regions of average dimensions, is estimated from the formula

$$[\rho^{(n)}(T_{1\max}) \int_{T-T_0}^{T_{1\max}} (T - T_{1\max})^n dT_1]^{(r_C/l)^3} \sim \tau_{\max}^{A_1}, \quad (8.3)$$

$$A_1 \sim [(\hat{\gamma}/\hat{\alpha}\tau_{\max})^{1/2}/l]^3 = (\hat{\delta}T_1/\tau_{\max})^{3/2}.$$

Hence

$$\bar{\eta} \sim \tau_{\max}^{A_1+1/2}, \quad \bar{C} \sim \tau_{\max}^{A_1+1}.$$

The point \bar{T} , which is nonanalytic in the temperature, coincides with the maximum value of T_C , i.e.,

$$\bar{T} = T_0 + T_{1\max}$$

at which the heat capacity and all its derivatives are continuous. An account of the fluctuations, which will be given below, leads to a second nonanalytic point.

Calculations of the ordering parameter and of the specific heat in the case when $\rho(T_1)$ has the form of a Gaussian distribution are given in.^[35]

9. Short-wave inhomogeneities. In Secs. 7 and 8 we considered the case $\hat{\delta} < 1$ ($r_C(T_1) \ll l$). We now consider the opposite limiting case $\hat{\delta} \gg 1$ ($r_C(T_1) \gg l$). We represent η in the form

$$\eta(r) = \eta_0 + \eta_1(r), \quad \eta_0 = \overline{\eta(r)}. \quad (9.1)$$

The quantity η_1 is always smaller than η_0 , for otherwise $\eta(r)$ can vanish, in contradiction to the results of Sec. 6. In the zeroth approximation, the inhomogeneities average out over large regions with dimension $\sim r_C$, and it can be assumed that $\eta \approx \eta_0$. In this approximation, in a rough analysis, $\eta(r)$ can be replaced by its mean value, and this leads to the same expressions for η and C as in the case of a homogeneous sample. In first-order approximation we take into account $\eta_1(r)$ ($\eta_1 \ll \eta_0$). Averaging expression (6.2), rewritten in the form

$$\hat{\gamma}\Delta\eta_1 = \hat{\alpha}(T - T_0 - T_1(r))\eta_0 + \hat{\alpha}(T - T_0)\eta_1 - \hat{\alpha}T_1\eta_1 + 2\hat{\beta}(\eta_0^2 + 3\eta_0\eta_1 + 3\eta_0\eta_1^2 + \eta_1^2) \quad (9.2)$$

over the entire volume of the sample, we obtain

$$\hat{\alpha}(T - T_0)\eta_0 - \hat{\alpha}\overline{T_1(r)\eta_1(r)} + 2\hat{\beta}\eta_0^2 + 6\hat{\beta}\eta_0\overline{\eta_1^2} = 0. \quad (9.3)$$

Subtracting (9.3) from (9.2), we have

$$\hat{\gamma}\Delta\eta_1 = -\hat{\alpha}T_1(r)\eta_0 + \hat{\alpha}(T - T_0)\eta_1 - \alpha(T_1(r)\eta_1(r) - \overline{T_1(r)\eta_1(r)}) + 6\hat{\beta}\eta_0^2\eta_1 + 3\hat{\beta}\eta_0(\eta_1^2 - \overline{\eta_1^2}) + 6\hat{\beta}\eta_1^2. \quad (9.4)$$

Using the condition $\eta_1 \ll \eta_0$, we obtain from (9.3) and (9.4) in the zeroth approximation

$$\hat{\alpha}(T - T_0)\eta_0 - \hat{\alpha}\overline{T_1(r)\eta_1(r)} + 2\hat{\beta}\eta_0^2 = 0, \quad (9.5a)$$

$$\hat{\gamma}\Delta\eta_1 = -\hat{\alpha}T_1(r)\eta_0 + \hat{\alpha}(T - T_0)\eta_1 + 6\hat{\beta}\eta_0^2\eta_1. \quad (9.5b)$$

The solution of (9.5) leads to the following results (see Appendix 5)

$$T_c = T_0 + (\hat{\alpha}/2\pi^2\hat{\gamma}) \int_0^{\infty} G(k) dk, \quad \eta_0^2 = \eta_{00}^2 + \eta_{01}^2,$$

$$\eta_{00}^2 = (\hat{\alpha}/2\hat{\beta})(T_c - T_0), \quad \eta_{01}^2 = -(\hat{\alpha}^{1/2}G(0)/8\pi\hat{\gamma}^{3/2}\hat{\beta})(3T_c - T_0 - 2T)^{1/2},$$

$$G(|r_1 - r_2|) = \overline{T(r_1)T_1(r_2)}, \quad G(0) = \lim_{r_1 \rightarrow r_2} G(|r_1 - r_2|).$$

We present asymptotic expressions for η_0^2 :

$$\eta_0^2 = \begin{cases} \frac{\hat{\alpha}}{2\hat{\beta}}(T_c - T) \left[1 - \frac{2^{1/2}\hat{\alpha}^{3/2}}{4\pi\hat{\gamma}^{3/2}} G(0) \frac{1}{(T_0 - T)^{1/2}} \right], & \text{when } T_c - T \gg \Delta T, \\ \frac{\hat{\alpha}}{2\hat{\beta}} \left[1 - \frac{\hat{\alpha}^{3/2}G(0)}{4\pi\hat{\gamma}^{3/2}\Delta T^{1/2}} (T_c - T) \right], & \text{when } T_c - T \ll \Delta T, \Delta T = T_c - T_0. \end{cases} \quad (9.6)$$

We now calculate the heat capacity below the transition point, using the formula

$$\bar{C} = -T\hat{\alpha}d\bar{\eta}^2/dT, \quad \bar{\eta}^2 = \eta_0^2 + \overline{\eta_1^2}. \quad (9.7)$$

The quantity $\overline{\eta_1^2}$ is calculated from (A5.2);

$$\overline{\eta_1^2} = \int \frac{dk}{(2\pi)^3} \eta_1^2(k) = \frac{\hat{\alpha}^2\eta_0^2}{\hat{\gamma}^2} \int \frac{dk}{(2\pi)^3} \frac{T_1^2(k)}{(\hat{\lambda}^2 + k^2)^2}$$

$$= \frac{\hat{\alpha}^2\eta_0^2}{2\pi^2\hat{\gamma}^2} \int k^2 dk \frac{G(k)}{(\hat{\lambda}^2 + k^2)^2} = \frac{\hat{\alpha}^2\eta_0^2 G(0)}{8\pi\hat{\gamma}^2 \hat{\lambda}}.$$

Using this formula and (9.6), we obtain an expression for the heat capacity from (9.7):

$$\bar{C} = \begin{cases} \frac{\hat{\alpha}^2 T_c}{2\hat{\beta}} \left[1 - \frac{3 \cdot 2^{1/2}}{32\pi} \left(\frac{\hat{\alpha}}{\hat{\gamma}} \right)^{3/2} \frac{G(0)}{(T_0 - T)^{1/2}} \right], & \text{when } T_c - T \gg \Delta T, \\ \frac{\hat{\alpha}^2 T_c}{2\hat{\beta}} \left[1 - \frac{1}{8\pi} \left(\frac{\hat{\alpha}}{\hat{\gamma}} \right)^{3/2} \frac{G(0)}{(\Delta T)^{1/2}} \right], & \text{when } T_c - T \ll \Delta T. \end{cases}$$

Thus, the expressions for the ordering parameter and

for the heat capacity coincide, apart from small corrections, with the corresponding expressions in an ideal sample in the entire range of temperatures.

10. Account of the ordering-parameter fluctuations.

The fluctuation length can have two scales, l and r_c . We estimate first the role of fluctuations with a characteristic length r_c in the case $\hat{\delta} \ll 1$. According to^[39-41], these fluctuations (in first-order approximation in the parameter $r_0^{-3} \tau^{-1/2} T_0^{1/2}$), accurate to an inessential numerical factor, give the following correction to the specific heat:

$$C_1 \sim (\hat{\alpha}^2 T_0^{3/2} / \hat{\beta} r_0^3) \int (T - T_0 - T_1)^{-1/2} \rho(T_1) dT_1.$$

In the case of a Gaussian function $\rho(T_1)$, this contribution is significant at $T - T_0 \gg \hat{l}$ and $T > T_0$ (the fundamental term is small), and is given by

$$C_1 \sim (\hat{\alpha}^2 T_0^{3/2} / \hat{\beta} r_0^3) [\hat{l} / (T - T_0)^{1/2}].$$

The case $\hat{\delta} \gg 1$ in the zeroth approximation can be regarded as homogeneous, so that the corrections that must be introduced in the theory as a result of the fluctuations of the ordering parameter and the region of applicability of the theory are of the same order of magnitude as in homogeneous samples.

We now estimate, in the case $\hat{\delta} \ll 1$ ($l \gg r_t$) the probability that the ordering parameter will reverse sign in one spatial region with $\tilde{\tau} > 0$. We use the formula $w \sim \exp(-R_{\min}/T)$ (see^[6], Sec. 144), where R_{\min} is the minimal work necessary to realize the given fluctuation. It is easily seen that the work will be minimal if the change in the sign and in the value of η occur in a spatial region $T > T_c(r)$ of thickness r_c , in a region where η is minimal in absolute magnitude. In the remaining region, where the fluctuation took place, η reverses sign, but its absolute value does not change. The order of R_{\min} can be estimated from the formula

$$R_{\min} \sim \hat{\gamma} \int (\nabla \eta)^2 dV \sim \hat{\gamma} (\eta_{\min}/r_c)^2 V_1, \quad (10.1)$$

where V_1 is the volume of the region in which η changes in absolute magnitude, and η_{\min} is the lower bound of η in this region.

If the temperature is close to $T_{1\max}$ ($T_1 < T_{1\max}$), then according to (7.4) the order of η_{\min} is exponentially small, and therefore $R_{\min} \ll T$ and the probability of reversal of the sign in one of the regions with $\tilde{\tau} > 0$ is of the order of unity. The coupling between the different spatial regions with $\tilde{\tau} > 0$ is exponentially small and the fluctuations upset the formation of the order parameter (which differs from zero in the entire volume of the sample in the absence of fluctuations) at the point $\tilde{T} = T_0 + T_{1\max}$. When the temperature is lowered from the point \tilde{T} , the share of the regions with $\tilde{\tau} > 0$ increases. These regions begin to approach one another, and R_{\min} increases. The ordering of the regions begins at an average distance of the order of the correlation radius between regions. At a certain point $\tilde{T}_1 < \tilde{T}$, a nonzero ordering parameter averaged over the sample sets in.

The process of ordering regions can be described very roughly by the energy

$$E = -R_{\min}(T) \sum \sigma_i \sigma_j,$$

where R_{\min} is determined by (10.1) and $\sigma_i = \pm 1$, depending on the sign of the ordering parameter in the

region. Estimates obtained in^[38] by the self-consistent-field method show that at the point \tilde{T}_1 at which $R_{\min}(T)$ becomes of the order of T_0 the heat capacity experiences a small "jump." The main reason why the "jump" is small is that the heat capacity of the entire sample is proportional to the number of regions Nl^{-3} in which $\tilde{\tau} > 0$, i.e., is smaller by a factor l^{-3} than the heat capacity of the ideal sample.

11. Application of the Ising model to the problem of "frozen-in" impurities. Comparison with experiment.

In the preceding sections of this chapter we considered the influence of "frozen-in" impurities and inhomogeneities on the thermodynamics of the phase transition by the self-consistent-field method. In this section we describe very briefly the results of calculations by methods more accurate than the self-consistent field method.

a) In^[43], the author analyzed the influence of nonmagnetic impurities on the thermodynamics of the phase transition within the framework of the two-dimensional Ising model. The estimates have shown that the heat capacity ceases to be an analytic function at a temperature equal to the Curie temperature T_0 of the pure substance. Near this point, at $T > T_0$ and $c \ll 1$ (c is the concentration of the nonmagnetic impurities), the heat capacity is given by

$$C = C_r + C_s, \quad (11.1)$$

where

$$C_r \sim \ln \{c + (\sqrt{2} + 1) [(T - T_0)/T_0]\},$$

$$C_s = \sum_{r=c-1}^{\infty} x^r (\sqrt{2} + 1)^r \exp(-2r^{2/3} |\ln c|^{1/3}),$$

$x = \tanh(I/T)$ and I is the exchange integral of the unperturbed lattice. From the expression for C_s we see that the point of transition of the pure substance, determined from the equation $x_c = \tanh(I/T_0) = \sqrt{2} - 1$, is a point that is nonanalytic in the temperature. The heat capacity and all its derivatives with respect to the temperature are finite at this point. The point T_0 is an essential singularity. The behavior of the singular part of the heat capacity, described by formula (11.1), coincides qualitatively with the expression (8.3) obtained by the self-consistent-field method, for as $T \rightarrow \tilde{T}$ we also have an essential singularity with a similar behavior of the heat capacity and of all its derivatives.

The nonanalyticities in the "frozen-in" impurity model are quite weak. If we are interested only in the analytic (smooth) part of the heat capacity, then we can use formula (8.2) and the expression for the heat capacity of an ideal system, $C_{\pm} = A_{\pm} |\tau|^{-\alpha}$. Such calculations were carried out in^[44,45]. These calculations have shown that the heat capacity of inhomogeneous samples is finite. The maximum of the heat capacity decreases with increasing contamination of the sample. The maximum point and the inflection point occur at different temperatures, and this separation can be interpreted as the experimentally observed "jump".

b) Griffiths^[46] has proved the following theorem. In the Ising model of "frozen-in" impurities, the magnetic moment ceases to be an analytic function of the magnetic field and of the temperature at $H = 0$ and at the temperature \tilde{T} , with \tilde{T} higher than the temperature \tilde{T}_1 at which a nonzero ordering parameter is produced in the entire sample. According to Griffiths' estimates, if the impurities are nonmagnetic, then \tilde{T} coincides with the transition temperature of the pure substance. This

theorem agrees with the results presented above. The physical meaning of the temperatures \tilde{T} and \tilde{T}_1 is the same in this theorem as in Secs. 8 and 10.

c) In solids, the impurity relaxation time is on the order of days, whereas the experimental times are of the order of several hours, so that the impurities can be regarded as "frozen in." The heat capacities of contaminated magnet samples were measured in a number of investigations. Voronel' et al.^[47] measured the heat capacity of Gd samples of different purities. It can be concluded from their results that the maximum of the heat capacity is smaller in more contaminated samples, and the heat-capacity curve is more smeared out, in agreement with formula (8.3) and with the calculations of^[43-45]. Similar results were obtained in measurements of the heat capacity of Fe_3O_4 samples^[44]. Two characteristic points are singled out on the experimental curves: the maximum point and the kink point, which the experimenters called a "jump." With increasing contamination of the sample, the temperature interval between the maximum point and the "jump" point increases.

Starting from the foregoing, we emphasize once more the difference between the effects of equilibrium and "frozen-in" impurities: 1) if the impurities are in equilibrium, then the derivative of the heat capacity with respect to the temperature becomes infinite at the maximum point, and this point is the phase-transition temperature. In the model of "frozen-in" impurities, there can be no singularities at all at the maximum point. 2) In this model, the heat-capacity curves have a kink point, which the experimenters call a "jump." There is no such point in the model of equilibrium impurities.

Figure 8 shows the dependence of the heat capacity of air (a mixture of nitrogen and oxygen) on the temperature, taken from the paper of Voronel', Shmakov, and Gorbunova^[16]. The speed at which this curve was measured was insufficient to establish equilibrium with respect to the impurity concentration. The authors believe that during the course of the measurements the impurities can be regarded as "frozen-in." The figure shows that the point of the maximum and the kink point occur at different temperatures.

Conclusions. 1) The thermodynamic functions of a system with non-equilibrium "frozen-in" impurities have at least two nonanalytic temperature points at zero external field. The point with higher temperature is connected with the onset of infinite-dimension regions with a stable ordering parameter η . The average value of η over the entire volume is equal to zero. The second point is connected with the onset of a nonzero ordering parameter in the entire sample.

2) In systems with "frozen-in" impurities and inhomogeneities, the heat-capacity curve develops a "kink," interpreted by the experimenters as a "jump,"

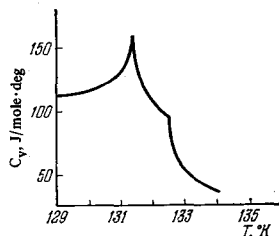


FIG. 8. Heat capacity of a mixture in the case of "frozen-in" impurities-dependence of the heat capacity of air on the temperature^[16]. Two characteristic points, the maximum point and the kink point, are seen.

and the temperature interval between the maximum and the kink increases with contamination of the sample.

3) In the case of long-wave inhomogeneities (length of the inhomogeneities much larger than the characteristic correlation radius), a significant change takes place in the behavior of the thermodynamic quantities near the phase-transition point, in comparison with the behavior in an ideal crystal.

4) Short-wave inhomogeneities (apart from small corrections) do not lead to a change in the behavior of thermodynamic quantities in comparison with the corresponding behavior in the ideal crystal.

5) There is qualitative agreement between theory and experiment.

IV. CONCLUSION

Starting from the foregoing, let us briefly review the results, which can be useful in the organization and reduction of experiments.

1) Let us first analyze which perturbations are the most significant for different substances. At a liquid-liquid critical point (phase transition of the stratification type) or at a liquid-vapor critical point, the main factors distorting the transition are the gravitational effect and the impurities. The influence of the gravitational effect can be eliminated by choosing as the object of investigation a liquid-liquid system with components of nearly equal atomic weight. In such systems, on the one hand, the compressibility is low and the density is constant over the height of the vessel with sufficient accuracy. On the other hand, owing to the small difference between the atomic weights of the components, there is no large drop in the concentrations of the components over height. Thus, a liquid-liquid system thoroughly rid of impurities should simulate more readily the behavior of ideal systems.

Depending on the speed of measurements of the thermodynamic quantities near the liquid-vapor critical point, the impurities can be either "frozen-in" or in equilibrium. Voronel', Shmakov, and Gorbunova^[16], measuring the heat capacity of a solution of CO_2 in ethane, reached the conclusion that when the temperature is measured at a rate of $\sim 10^{-2}$ deg/hr, the impurities behave as "frozen-in", and at rates of 10^{-3} deg/hr they have time to reach equilibrium.

In solids, the ideal phase-transition picture can be distorted by "frozen-in" impurities, inhomogeneities, the interaction between the ordering parameter and the phonons, and the domain structure. The interaction with phonons is quite strong in ferroelectrics, while in magnets this interaction is quite weak and can be neglected. The domain structure influences the behavior of the magnetic moments and the susceptibility, but does not affect the behavior of the heat capacity at $H = 0$. To exclude the influence of the domain structure, the susceptibility measurements can be carried out in fields stronger than the saturation field but much weaker than the exchange fields at the given temperature, and the measurement results can be then extrapolated to zero magnetic field.

The main cause of the distortion of the behavior of the thermodynamic quantities at the transition point in solids is the nonideal character of the crystals.

2) In real experiments, analysis of the results is

TABLE III. Interval of "smearing" of the phase transition by different disturbances.

Effect	Equilibrium impurities (Sec. 1)	Phonons (Sec. 2)	Domains (Sec. 3)	Gravitational field
"Smearing interval"	$\left[C_0 c \left(\frac{1}{T_0} \frac{\partial T_c}{\partial c} \right)^2 \right]^{1/\alpha}$	$\left[\frac{4\mu K_0 \left(\frac{\partial T_c}{\partial p} \right)^2}{(3K_0 + 4\mu)T} \right]^{1/\alpha}$	$(4\pi n \chi_0)^{1/\nu}$, $\tau > 0$	$\max \left\{ \rho^{-1/\beta}, \bar{h}^{-1/(\beta+\gamma)} \right\}$

made complicated by the fact that the phase-transition picture is distorted by several factors simultaneously. Thus, possible simultaneous disturbances in solids might be the domain structure, phonons, and inhomogeneities of the sample. It is quite difficult to analyze the experimental data under such conditions. From among the theoretical investigations of this type we mention the work by Korotkikh and Nabutovskii^[4a], who considered the simultaneous influence of equilibrium impurities and phonons. As shown in Sec. 2, allowance for the interaction of the ordering parameter with the longitudinal and transverse parts of the phonon spectrum leads to the appearance of a first-order phase transition if the heat capacity in the incompressible crystal tends to infinity. On the other hand, impurities (see Sec. 1) cause the heat capacity to become finite. Therefore, if the impurity concentration is high enough (the heat capacity is small at the critical point), then the phonons cause no first-order phase transition. To obtain quantitative criteria, let us compare the temperature intervals τ_{imp} and τ_{ph} over which the phase transition becomes smeared by the impurities and by the phonons, respectively (Table III). We find that in the case when $[\mu K_0 / (K_0 + \mu) T_0] (\partial T_c / \partial p)^2 > C_0 c (dT_c / T_0 dc)^2$, the influence of the impurities can be neglected, and a first-order phase transition is obtained. In the opposite limiting case, the influence of the phonons can be neglected.

If the phase-transition picture is distorted by several factors, then comparison of the "smearing" temperature intervals listed in Table III can identify the principal cause. For example, if equilibrium impurities and the gravitational effect compete, then in the case $C_0 c [(1/T_0) dT_c/dc]^2 \ll h^{-\alpha(\beta+\gamma)}$ (if $\rho = 0$) the principal influence is exerted by the gravitational effect. In the other case, the principal influence is exerted by the impurities.

When estimating the experimental errors, it is necessary to take into account not only the errors of the instrument, but also the effects of the perturbations listed above. The question can be posed in the following manner. Let the apparatus ensure a temperature accuracy $\tau \sim 10^{-5}$. What equilibrium-impurity concentration is permissible in the study of the behavior of the pure substance if this accuracy is to be maintained? Using the value of τ_n from Table III, we get $c \lesssim 10^{-1} / C_0 [(1/T_0) dT/dc]^2$.

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APPENDIXES

1. We sum expression (1.2) with respect to μ_j . It is easy to verify the identity

$$\sum_{(i)} \exp [\theta_i (\sigma_i + \sigma_{i'}) \mu_j + \theta \sigma_i \mu_i^2 + g \mu_i^3 + h \mu_j] \\ = 1 + 2 \exp (g + \theta \sigma_i \sigma_{i'}) \text{ch} [\theta_i (\sigma_i + \sigma_{i'}) + h] = A \exp (K \sigma_i \sigma_{i'} + L (\sigma_i + \sigma_{i'}));$$

$$\bar{A}^4 = (1 + 2e^{g-\theta} \text{ch } h)^2 [1 + 2e^{g+\theta} \text{ch} (2\theta_1 - h)] [1 + 2e^{g-\theta} \text{ch} (2\theta_1 + h)], \\ e^{4K} = [1 + 2e^{g-\theta} \text{ch} (2\theta_1 - h)] [1 + 2e^{g+\theta} \text{ch} (2\theta_1 + h)] / (1 + 2e^{g-\theta} \text{ch } h)^2, \quad (\text{A1.1}) \\ e^{4L} = [1 + 2 \exp (g + \theta) \text{ch} (2\theta_1 + h)] / [1 + 2 \exp (g + \theta) \text{ch} (2\theta_1 - h)].$$

Substituting (A1.1) in (1.2), we obtain

$$\bar{Z}(T, H, g) = A^{NdZ} (K + \theta_2, h + 2L), \quad (\text{A1.2})$$

where d is the dimensionality of space, N is the number of sites of the fundamental system, and $Z(\theta, h)$ is the partition function of the ideal system. We have thus expressed the partition function \bar{Z} of a model of a ferromagnetic with impurities in terms of the partition function of an ideal ferromagnet.

We consider the case $H = 0$. From (A1.1) we have

$$\bar{A}^2 = (1 + 2e^{g-\theta}) (1 + 2e^{g+\theta} \text{ch } 2\theta_1), \quad e^{2K} = (1 + 2e^{g+\theta} \text{ch } 2\theta_1) / (1 + 2e^{g-\theta}), \quad L = 0. \quad (\text{A1.3})$$

The thermodynamic potential $\Omega = -\ln \bar{Z}$ is given by

$$\Omega = -T \ln \bar{A} + \Omega_0 - T \bar{A}_1 (K + \theta_2 - \theta_0) - \bar{A}_2 T |K + \theta_2 - \theta_0|^2 - \alpha, \quad (\text{A1.4})$$

where \bar{A}_1 , \bar{A}_2 , and Ω_0 are constants, $\theta_0 = (I_2/T_0)$, T_0 is the transition temperature of the pure substance; the second and third terms in (A1.4) are obtained from expansion of the regular part of Ω in the parameter $K + \theta_2 - \theta_0$, while the last term in (A1.4) is the singular part of the free energy of an ideal system.

We consider the case of small impurity concentrations c ($c \ll 1$). As will be shown below, in this case $g \rightarrow -\infty$ and $e^g \rightarrow 0$. Confining ourselves to terms linear in e^g , we obtain from (A1.3)

$$K = e^{g-\theta} (x-1), \quad x = e^{2\theta} \text{ch} (2\theta_1). \quad (\text{A1.5})$$

Let us find the dependence of the transition temperature T_c on the chemical potential g from the equation

$$K + \theta_2 = (I_2/T_c) + e^{g-\theta_0} (x_c - 1) = \theta_0; \quad (\text{A1.6})$$

The subscript c signifies that the critical value of the temperature is substituted in the corresponding quantities. Using the smallness of e^g , we easily solve Eq. (A1.6):

$$T_c = T_0 \{1 + [e^{g-\theta_0} (x_c - 1)/\theta_0]\}; \quad (\text{A1.7})$$

the temperature T_0 is substituted in the quantities marked by the subscript $c0$.

We choose an arbitrary point g_0 on the critical curve. Near this point we have

$$\theta_2 + K - \theta_0 = -\theta_0 \tau + (\partial K / \partial g)_T \Delta g = -\theta_0 [\tau - (\Delta g / T_0) (dT_c / dg)] = -\theta_0 \tau (g). \quad (\text{A1.8})$$

In the derivation of (A1.8) we used expressions (A1.5) and (A1.7), and also

$$\tau = (T - T_c(g_0)) / T_0, \quad \tau(g) = \tau - (1/T_0) (dT_c / dg) \Delta g, \quad \Delta g = g - g_0.$$

Substituting (A1.3) and (A1.8) in (A1.4), we have expression (1.3) for Ω , accurate to terms linear in e^g .

2. Substituting (2.6) in (2.4), we obtain

$$E - U_{\alpha\beta} \sigma_{\alpha\beta} = N \{ \mu (\bar{U}_{\alpha\beta} - (1/3) \delta_{\alpha\beta} \bar{U}_{\gamma\gamma})^2 + (K_0/2) \bar{U}_{\alpha\alpha}^2 - \sigma_{\alpha\beta} \bar{U}_{\alpha\beta} \} \\ + (1/N) \sum_{k \neq 0} \{ (\mu/2) (k^2 |U_{\alpha}(k)|^2 - |k_{\alpha} U_{\alpha}(k)|^2) + [(K_0/2) + (2/3) \mu] |k_{\alpha} U_{\alpha}(k)|^2 \} \\ - \sum_i [\bar{a} + q \bar{U}_{\alpha\alpha} + (iq/N) \sum_{k \neq 0} k_{\alpha} U_{\alpha}(k) e^{ikr}] \eta_i^{\dagger} + (b/2) \sum_i \eta_i^{\dagger} + \sum_{ij} V_{ij} (\eta_i - \eta_j)^2. \quad (\text{A2.1})$$

Substituting this expression in (2.5) and integrating over the shear part of $\bar{U}_{\alpha\beta}$ and $U_{\alpha}(k)$, we obtain

$$\Phi = \Phi_r - N/2\mu (\sigma_{\alpha\beta} + p \delta_{\alpha\beta})^2 - T \ln \int \exp \left\{ -1/T \left[N ((K_0/2) \bar{U}_{\alpha\alpha}^2 + p \bar{U}_{\alpha\alpha}) \right. \right. \\ \left. \left. + \sum_{ij} V_{ij} (\eta_i - \eta_j)^2 - \sum_i (\bar{a} + q \bar{U}_{\alpha\alpha}) \eta_i^{\dagger} \right] \right\}$$

$$+ \frac{b}{2} \sum_i \eta_i^2 - \frac{q^2}{4N[(K_0/2) + (2\mu/3)]} \sum_{h \neq 0} e^{ik(r_i - r_j)} \eta_i^2 \eta_j^2 \} \} d\bar{U}_{\alpha\alpha} d\eta_i; \quad (\text{A2.2})$$

here $\Phi_{\mathbf{r}}$ is an analytic function of the temperature, and $p = -\sigma_{\alpha\alpha}/3$ is the pressure. The second term in (A2.2) likewise has no singularities and will henceforth be included in $\Phi_{\mathbf{r}}$. The last term in (A2.2) has the same form as the next to last term, to which we add the expression

$$-q^2/4N[(K_0/2) + (2\mu/3)] \left(\sum_i \eta_i^2 \right)^3.$$

To this end we make in the integral with respect to $\bar{U}_{\alpha\alpha}$ the substitution

$$\bar{U}_{\alpha\alpha} = \frac{v}{K_0} \left(\frac{3K_0 + 4\mu}{4\mu} \right)^{1/2} + \frac{q}{NK_0} \left[1 - \left(\frac{4\mu}{3K_0 + 4\mu} \right)^{1/2} \right] \sum_i \eta_i^2 - \frac{p}{K_0}. \quad (\text{A2.3})$$

after which the expression (A2.3) takes the form

$$\Phi = \Phi_0 - \frac{Np^2}{2K_0} - T \ln \int \exp \left\{ -\frac{1}{T} \left[\frac{N}{2} \frac{3K_0 + 4\mu}{4\mu K_0} v^2 - \sum_i \left(\bar{a} + q \frac{v-p}{K_0} \right) \eta_i^2 + \frac{1}{2} \left(b - \frac{3q^2}{3K_0 + 4\mu} \right) \sum_{i,j} \eta_i^2 + \sum_{i,j} v_{ij} (\eta_i - \eta_j)^2 \right] \right\} dv d\eta_i. \quad (\text{A2.4})$$

The integral with respect to η_i differs from the corresponding integral of the unperturbed problem by a redefinition of the constants \bar{a} and b . Integrating with respect to v by the saddle-point method, we obtain an expression for Φ from (A2.4):

$$\Phi = \Phi_0 - N \left(\frac{p^2}{2K_0} - \frac{3K_0 + 4\mu}{8\mu K_0} v^2 \right) + \Phi_0 \left(\bar{a} + q \frac{v-p}{K_0}, b - \frac{q^2}{K_0 + \frac{4}{3}\mu} \right), \frac{\partial \Phi}{\partial v} = 0. \quad (\text{A2.5})$$

The singular point of the thermodynamic potential Φ_0 is determined by formula (2.3), with T_0 dependent on v via the variable $\bar{a} + [q(v-p)/K_0]$. Introducing in place of v the new parameter

$$\tau(v) = \tau_0 - (q/T_0 K_0) (\partial T_c / \partial \bar{a})(v-p),$$

we rewrite Eq. (A2.5) in the form (2.7). The quantity $Np^2/2K_0$ is included in $\Phi_{\mathbf{r}}$.

3. To calculate Z , we use the technique employed by Berlin and Kac^[49]

$$\begin{aligned} Z &= \int_{-\infty}^{\infty} \sum_{(M)} \delta \left(\mu_B \sum \sigma_i - M \right) \exp \left(-\frac{E_0}{T} + \frac{HM}{T} - \frac{\bar{\alpha}}{2NT} M^2 \right) dM \\ &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \sum_{(M)} \exp \left(-\frac{E_0}{T} + \frac{HM}{T} - \frac{\bar{\alpha} M^2}{2NT} \right) dM \int_{-\infty}^{\infty} \frac{1}{T} \exp \left[\frac{\bar{H}}{T} \left(\mu_B \sum \sigma_i - M \right) \right] d\bar{H} \\ &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \exp \left[\frac{1}{T} \left(HM - \frac{\bar{\alpha} M^2}{2N} \right) \right] dM \\ &\quad \times \int_{-\infty}^{\infty} \frac{1}{T} \exp \left(-\frac{\bar{H}M}{T} \right) \sum_{\sigma} \exp \left[\frac{1}{T} \left(-E_0 + \bar{H} \mu_B \sum \sigma_i \right) \right] d\bar{H}. \end{aligned}$$

Integrating over all the values of the total magnetic moment M , we obtain

$$Z = (1/2\pi i T) (2NT/\pi \bar{\alpha})^{1/2} \int_{-\infty}^{\infty} \exp \{ (N/T) [-\Phi_0 + (1/2\bar{\alpha})(H - \bar{H})^2] \} d\bar{H},$$

where $\Phi_0(T, \bar{H})$ is the thermodynamic potential of an ideal system (per particle without allowance for the demagnetizing factor). The integration with respect to \bar{H} is carried out by the saddle-point method. The equation for the saddle point \bar{H}_S is (3.4).

4. The correlators that enter in (5.6) are estimated by scaling theory^[4]. The Kadanoff transformations from microscopic quantities to cell quantities (with cell dimension \bar{L}) are

$$R \rightarrow R/\bar{L}, \quad \tau_0 \rightarrow \tau_0 \bar{L}^{\nu_0}, \quad E_1 \rightarrow \bar{E}_1 \bar{L}^{-\alpha},$$

where R is the distance between the spins, $\tau_0 = (T - T_0)/T_0$, and T_0 is the critical point of the unperturbed system, while ν_0 and α are the critical exponents

in the unperturbed system; the constant α depends on the number of spins and on the summation rules in E_1 .

For estimates it can be assumed that all the distances between the spins in the correlator are of the same order $R \sim r_{0c}$. Then

$$Q_p(R, \tau_0) = Q(j_1 \dots j_p) \sim \langle E_{j_1} \dots E_{j_p} \rangle = \bar{L}^{-p\alpha} \langle \bar{E}_{j_1} \dots \bar{E}_{j_p} \rangle = \bar{L}^{-p\alpha} Q_p(R/\bar{L}, \tau_0 \bar{L}^{\nu_0}).$$

The general solution satisfying this equation is

$$Q_p(R, \tau_0) = \tau_0^{p\nu_0/\alpha} Q_p(R \tau_0^{1/\nu_0}).$$

In the limiting case $R \tau_0^{1/\nu_0} \ll 1$ (or $R \ll r_{0c}$) we have

$$Q_p(R, \tau_0) \sim R^{-p\alpha}. \quad (\text{A4.1})$$

Using formula (A4.1), we obtain the dimensional estimate (5.7) for Γ_p .

5. Changing from the coordinate representation to the Fourier representation in accordance with the formulas

$$\eta_i(r) = \int \eta_i(k) e^{ikr} \frac{dk}{(2\pi)^3}, \quad \eta_i(k) = \int \eta_i(r) e^{-ikr} dr, \quad (\text{A5.1})$$

we obtain a solution of (9.5b)

$$\eta_i(k) = \hat{\alpha} T_1(k) \eta_0 \gamma (\hat{\lambda}^2 + k^2), \quad (\text{A5.2})$$

where

$$\hat{\lambda}^2 = [\hat{\alpha}(T - T_0) + \beta \bar{g} \eta_0^2] / \bar{g}.$$

As will be shown below, in the temperature range $T - T_0 \sim T_1$ we have $\eta^2 \sim T_0 - T$, and in the immediate vicinity of the Curie point of an inhomogeneous system we can neglect the quantity η_0^2 in the expression for λ^2 in comparison with $T - T_0$; we therefore have in the entire temperature range

$$\hat{\lambda}^2 \sim \hat{\alpha}(T - T_0) / \bar{g} \ll r_c^{-2}(T_1). \quad (\text{A5.3})$$

If we introduce the temperature correlation function in accordance with the formula

$$G(|r_1 - r_2|) = \overline{T_1(r_1) T_1(r_2)}, \quad G(k) = T_1(k) T_1(-k) = T_1^2(k) \quad (\text{A5.4})$$

(in deriving the last equation of (A5.4), we used the relation $T_1(k) = T_1(-k)$, which follows from the condition that $T_1(\mathbf{r})$ be real), we can rewrite the expression for $\overline{T_1(\mathbf{r}) \eta_1(\mathbf{r})}$ contained in (9.5a) in the following form:

$$\begin{aligned} \overline{T_1(r) \eta_1(r)} &= [\hat{\alpha} \eta_0 / (2\pi)^3 \bar{g}] \int dr \int dk [T_1(r) T_1(k) e^{ikr} / (\hat{\lambda}^2 + k^2)] \\ &= [\hat{\alpha} \eta_0 / (2\pi)^3 \bar{g}] \int [G(k) / (\hat{\lambda}^2 + k^2)] dk. \end{aligned} \quad (\text{A5.5})$$

Using (A5.5), we rewrite (9.5a):

$$\hat{\alpha}(T - T_0) \eta_0 - [\hat{\alpha}^2 \eta_0 / (2\pi)^3 \bar{g}] \int [G(k) / (\hat{\lambda}^2 + k^2)] dk + 2\beta \bar{g} \eta_0^2 = 0. \quad (\text{A5.6})$$

It will be convenient for future use to transform the integral in the second term of this equation in the following manner:

$$\int dk G(k) / (\hat{\lambda}^2 + k^2) = 4\pi \left\{ \int_0^{\infty} G(k) dk - \hat{\lambda}^2 \int_0^{\infty} [G(k) / (\hat{\lambda}^2 + k^2)] dk \right\}.$$

In the second term on the right-hand side, the characteristic region of integration with respect to k , according to (A5.3), is of the order of $k \sim \hat{\lambda} \ll r_c^{-1}(T_1) \ll l^{-1}$, whereas the characteristic region of the variation of $G(k)$ is of the order of l^{-1} ; therefore

$$\begin{aligned} \int [G(k) / (\hat{\lambda}^2 + k^2)] dk &= 4\pi \left[\int_0^{\infty} G(k) dk - \hat{\lambda}^2 G(0) \int_0^{\infty} (\hat{\lambda}^2 + k^2)^{-1} dk \right] \\ &= 4\pi \left[\int_0^{\infty} G(k) dk - (\pi/2) \hat{\lambda} G(0) \right]. \end{aligned}$$

Taking the last relation into account, Eq. (A5.6) in the ordered phase takes the form

$$\hat{\alpha}(T-T_0) - (\hat{\alpha}^2/2\pi^2\hat{\gamma}) \left[\int_0^\infty G(k) dk - (\pi/2) \hat{\lambda}G(0) \right] + 2\beta\eta_0^2 = 0. \quad (\text{A5.7})$$

Putting $\eta_0 = 0$ in the last equation, we obtain the critical point T_C :

$$\Delta T = (\hat{\alpha}^2/2\pi^2\hat{\gamma}) \int_0^\infty G(k) dk - (G(0)/4 \cdot 2^{1/2}\pi^2) (\hat{\alpha}^2/\hat{\gamma}^2) \left(\int_0^\infty G(k) dk \right)^{1/2}, \quad (\text{A5.8})$$

where $\Delta T = T_C - T_0$.

Using the estimate

$$\int_0^\infty G(k) dk \sim G(0) l^{-1}, \quad G(0) = \int G(r) dr \sim T_1^3 l^3$$

we can easily show that the second term in (A5.8) is much smaller than the first relative to the parameter $\hat{\delta}^{-1}$.

Let us examine Eq. (A5.7). In this equation, $\hat{\lambda}G(0) \ll \int G(k) dk$. We seek the solution in the form $\eta_0^2 = \eta_{00}^2 + \eta_{01}^2$, where $\eta_{01} \ll \eta_{00}$. In the zeroth approximation, Eq. (A5.7) takes the form

$$\hat{\alpha}(T-T_{c0}) + 2\beta\eta_{00}^2 = 0,$$

whence

$$\eta_{00}^2 = (\hat{\alpha}/2\beta)(T_{c0}-T), \quad T_{c0} = T_0 + (\hat{\alpha}/2\pi^2\hat{\gamma}) \int_0^\infty G(k) dk.$$

In the first approximation

$$\eta_{01}^2 = -(\hat{\alpha}^2/8\pi\hat{\gamma}) G(0) \hat{\lambda}(\eta_{00}^2) = -(\hat{\alpha}^5/8\pi\hat{\gamma}^3/2\beta) G(0) (3T_{c0}-T_0-2T)^{1/2}.$$

We now estimate the term $\hat{\alpha}(T_1(\mathbf{r})\eta_{11}(\mathbf{r}) - T_1(\mathbf{r})\eta_{11}(\mathbf{r}))$ in Eq. (9.4), which was previously discarded. The Fourier component (at $\mathbf{k} \neq 0$) of this term takes the form

$$(\hat{\alpha}\eta_0/\hat{\gamma}) \int \{T_1(-\mathbf{k})T_1(\mathbf{K}+\mathbf{k})/(\hat{\lambda}^2 + (\mathbf{K}+\mathbf{k})^2)\} d\mathbf{k}/(2\pi)^3,$$

and the correction η_{11} due to this term, calculated from (9.4) by perturbation theory, is equal to

$$\eta_{11}(\mathbf{K}) = [\hat{\alpha}^2\eta_0/\hat{\gamma}(\hat{\lambda}^2 + \mathbf{K}^2)] \int \{T_1(\mathbf{k})T_1(\mathbf{K}-\mathbf{k})/(\hat{\lambda}^2 + (\mathbf{K}-\mathbf{k})^2)\} d\mathbf{k}/(2\pi)^3.$$

The characteristic region of integration with respect to \mathbf{k} is $\sim l^{-1}$. Using expression (A5.2) for η_1 and the estimate $T_1(\mathbf{K}) \sim T_1 l^3$, we obtain

$$\eta_{11}(\mathbf{K})/\eta_1(\mathbf{K}) \sim [\hat{\alpha}/\hat{\gamma}T_1(\mathbf{K})] \int \{T_1(\mathbf{k})T_1(\mathbf{K}-\mathbf{k})/(\hat{\lambda}^2 + (\mathbf{K}-\mathbf{k})^2)\} d\mathbf{k} < (\hat{\alpha}/\hat{\gamma})/T_1 l^2 \sim l^2/r_c^2(T_1) \ll 1.$$

Thus, the discarded terms do indeed lead to small corrections.

LIST OF SYMBOLS

I - exchange integral
 $\sigma_i = \pm 1$ - spin variable
 i - number of site

Indices:

0 - as a subscript to a letter, denotes that this letter pertains to the unperturbed system,
 s, r - as subscripts, denote respectively the singular and regular parts of the corresponding quantities,
 c - designates the value of the corresponding quantity at the critical point.

Thermodynamic Quantities:

T - temperature
 $\tau = (T - T_C)/T_C$ - dimensionless temperature
 P - pressure
 V - volume
 \mathcal{P} - density
 $\rho = (\mathcal{P} - \mathcal{P}_C)/\mathcal{P}_C$ - dimensionless density
 N - number of particles in the system and number of sites in the lattice
 c - impurity concentration
 H - external magnetic field
 h - dimensionless magnetic field
 Z - partition function at a constant number of particles
 \bar{Z} - partition function at a fixed chemical potential
 E - energy
 S - entropy
 $\Phi = E - TS + PV$ - thermodynamic potential
 $\Omega = -PV$ - thermodynamic potential
 \bar{g} - chemical potential ($g = \bar{g}/T$)
 η - ordering parameter
 C - heat capacity
 m - magnetic moment
 χ - susceptibility
 r_C - correlation radius

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