

# Role of surface energy in the phase transition from the paramagnetic state to the ferromagnetic

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The thermodynamic characteristics of a ferromagnetic plate of finite thickness are calculated. The boundaries are described by a surface energy proportional to the square of the magnetization. A measure of the boundary energy is the coefficient of proportionality  $q$  which may have an arbitrary value and, in particular, may be either positive or negative. The effect of the parameter  $q$  (its sign and magnitude) on the nature of the transition and on the values of the thermodynamic quantities is described. The transition to a half-space is traced, and the role of fluctuations is analyzed.

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## 1. INTRODUCTION

The effect of finite specimen dimensions on a phase transition of the second kind has repeatedly attracted the attention of investigators. It is impossible to give a complete enumeration of the papers devoted to this question (but see the reviews, Refs. 1-3). Even if one excludes the experimental investigations in this area, one can note several different approaches to the theoretical study of the role of the surface: numerical calculations of the magnetism of thin films that consist of a few atomic layers (in these papers, principal attention is paid to calculation of the critical dimension at which a cooperative phenomenon is first possible in the system); investigation by modern methods that are being applied to the solution of many-body problems; model Hamiltonians (Heisenberg, Ising, XY models) that allow for the existence of one or several boundaries<sup>10</sup>; and finally, use is made of the method of the self-consistent field and of a phenomenological approach that goes back to the Ginzburg-Landau method in the theory of superconductivity.<sup>5</sup>

We shall start from the phenomenological description of a phase transition that assumes a change of sign in one of the coefficients in the expansion of the free-energy density in powers of the order parameter. The difference of the surface forces from the bulk forces leads to nonuniformity of the magnetization in the boundary layer and thereby influences the phase transition. Theoretical and experimental investigations on uniform and nonuniform resonance in ferromagnetic films<sup>6</sup> have shown that the behavior of the magnetic moment at the boundary of the specimen depends substantially on the structure of the surface (for example, the surface anisotropy may exceed the volume anisotropy by many times). The problem arises of explaining the role of surface energy in the properties of ferromagnetic specimens at temperatures close to  $T_c$ . The approach adopted in the present paper is similar to the work of Ginzburg and Pitaevskii<sup>7</sup> (see also the paper of Ginzburg and Sobyannin<sup>8</sup>), which applied to superfluid helium equations analogous to the Ginzburg-Landau equations. We shall describe the special behavior of the magnetic system at the boundary by introducing a surface energy, which for simplicity we shall take proportional to the square of the magnetization: the coefficient of proportionality serves as an additional phenomenological parameter of

the theory (see Refs. 9 and 10 and below).

In a phenomenological approach to the investigation of a phase transition in a plate, one must bear in mind that in the immediate vicinity of  $T_c$ , because of the unbounded increase of the radius of correlation, two-dimensionalization occurs: the order parameter ceases to depend on the coordinate along the normal to the boundary. Our treatment must of course not infringe upon this temperature range. Furthermore, as always, the phenomenological approach is correct only outside the fluctuation region.<sup>11,12</sup> An attempt to evade this limitation by modification of the temperature dependence of the coefficients of the expansion,<sup>8</sup> as we shall see, does not eliminate the difficulties (see the Conclusion).

It has been shown<sup>9</sup> that magnetic surface energy leads to a shift of the Curie temperature in a plate of finite thickness. Since the sign of the magnetic surface energy  $\mathcal{F}_s$  has not been determined, the shift of Curie temperature  $\Delta T_c = T_c(d) - T_c$  ( $d$  is the half-thickness of the plate) may be either toward lower ( $\mathcal{F}_s > 0$ ) or toward higher ( $\mathcal{F}_s < 0$ ) temperatures. A distinctive feature of the second case ( $\mathcal{F}_s < 0$ ), as was mentioned in Ref. 9, is the following:  $\Delta T_c$  does not approach zero as  $d \rightarrow \infty$ . In the case of a bulk specimen, between the high-temperature paramagnetic phase and the low-temperature ferromagnetic ( $T < T_c$ ) there is a special phase (in the interval  $T_c < T < T_s$ ) characterized by the existence of surface magnetism: for  $T_c \leq T < T_s$ , the magnetic moment  $\mathcal{M} \neq 0$ , but it attenuates with distance from the surface. For  $T \rightarrow T_c$  ( $T > T_c$ ), the decay distance  $\delta$  becomes infinite ( $\delta \rightarrow \infty$  for  $T \rightarrow T_c$ ,  $T > T_c$ ). For finite plate thickness, of course, there is only one transition, at  $T = T_{cd}$ , where  $T_{cd} \neq T_c$  ( $T_{cd}$  is the temperature at which a magnetic moment  $\mathcal{M}(z) \neq 0$  appears in a plate of thickness  $2d$ ; see Ref. 10).

In Refs. 9 and 10, the treatment stayed within the framework of the Landau theory.<sup>13</sup> The only things determined were the shift of the Curie temperature, the dependence of the mean magnetic moment of the plate on temperature in the immediate vicinity of the phase-transition point  $T_{cd}$ , and the value of the magnetic-moment density at the boundary as  $T \rightarrow T_{cd}$ . The present communication investigates in detail the effect of the surface energy on all the thermodynamic characteristics: in particular, a calculation is made of the level of fluctuation

tuations of the magnetic moment in a plate of finite thickness. Principal attention is paid to the case of negative surface energy.<sup>2)</sup>

We shall start from an expansion of the free-energy density in even integral powers of the magnetic moment and of its gradient ( $H$  is the magnetic field):

$$f = A\mathcal{M}^2 + B\mathcal{M}^4 + C(d\mathcal{M}/dz)^2 - H\mathcal{M}. \quad (1)$$

One can derive many conclusions in terms of the coefficients  $A$ ,  $B$ , and  $C$ . But to obtain specific temperature dependences, one must specify precisely the temperature dependences of  $A$ ,  $B$ , and  $C$ . Following Ginzburg and Sobyenin<sup>8</sup> (see also the review by Luban<sup>15</sup>), we shall suppose that

$$\begin{aligned} A(\tau) &= \beta(T/\mu\mathcal{M}_0)\tau|\tau|^{l-1}, \quad \mathcal{M}_0^2 B(\tau) = \beta'(T/\mu\mathcal{M}_0)|\tau|^p, \\ C &= (T/\mu\mathcal{M}_0)a^2, \quad \tau = (T - T_c)/T_c, \quad \beta, \beta' > 0. \end{aligned} \quad (2)$$

For estimates, one can take  $a$  of the order of the interatomic distance,  $\mathcal{M}_0$  the ferromagnetic moment of unit volume far from  $T_c$ ,  $\mu$  the Bohr magneton, and  $\beta, \beta' \approx 1$ . In general, the critical index of the coefficient  $C$  is nonvanishing but small,<sup>15</sup> and we shall neglect the variation of  $C$  with  $\tau$ . We shall take account of later terms of the expansion of  $f$  in powers of  $\mathcal{M}$  only when the approximation being used would be insufficient.

The expansion (1) with the temperature dependence (2) of the coefficients is, according to Ref. 15, not correct over the whole range of values of  $\mathcal{M}$  and of  $\tau$ . In the construction of a theory in which the order parameter is calculated from a differential equation (cf. the  $\psi$  theory of He II<sup>9</sup>), this fact introduces substantial, possibly even insurmountable, complication. As will be seen from what follows (see also Ref. 14), with positive surface energy the results of solution of the problem do not get into contradiction with the expressions (2). When  $\mathcal{F}_s < 0$ , we shall use the usual Landau expansion, supposing that the expansions (1) and (2) lead to contradictions.<sup>3)</sup> Therefore for  $\mathcal{F}_s < 0$  we shall use the usual Landau expansion, supposing that  $A \propto \tau$  and that  $B$  and  $C$  are constants.  $A \propto \tau$  and that  $B$  and  $C$  are constants.

In the interior of an infinite specimen, when the role of the gradient is insignificant and  $H = 0$ ,

$$\mathcal{M} = \mathcal{M}_\infty = \begin{cases} 0, & \tau > 0, \\ (A/2B)^{1/2} \approx \beta\mathcal{M}_0|\tau|^{(l-p)/2}, & \beta = (\beta/2\beta')^{1/2}, \tau < 0, \end{cases} \quad (3)$$

and

$$f_\infty = -A^2/4B = -(\beta^2/4\beta')\mathcal{M}_0^2|\tau|^{2l-p}, \quad \tau < 0. \quad (4)$$

From (3) and (4) one can draw comparatively general conclusions about the values of the parameters  $l$  and  $p$ . Since the magnetic moment  $\mathcal{M}_\infty$  vanishes at  $T = T_c$ , therefore of necessity

$$l > p. \quad (5)$$

In the notation usually adopted (see, for example, Ref. 16),  $f \propto |\tau|^{2-\alpha}$ , where  $\alpha > 0$ ; that is,  $2l - p = 2 - \alpha$ , and the specific heat  $C_\alpha \propto |\tau|^{-\alpha}$ . In all existing theories, as compared with the experimental facts, the index  $\alpha$  is either very small or zero (in the latter case,  $f$  may contain a logarithmically divergent factor, which is not picked up by the expressions (1) and (2)). In the greater part of the paper we shall assume that  $\alpha = 0$ , i.e.  $2l - p = 2$  and

$$l = 1 + p/2, \quad p < 2 \quad (6)$$

[see (5)], while

$$\mathcal{M}_\infty = \tilde{\beta}\mathcal{M}_0|\tau|^{h-p/4}, \quad p < 2. \quad (7)$$

In Landau's theory,  $p = 0$ . If we suppose (see Ref. 17) that  $\mathcal{M}_\infty \propto |\tau|^{1/3}$ , then  $p = 2/3$ . According to (1), the singularity of the magnetic susceptibility  $\chi_\infty$  of an infinite specimen is determined by the coefficient  $A$ ,

$$\chi_\infty = \begin{cases} 1/2A, & \tau > 0, \\ -1/4A, & \tau < 0, \end{cases} \quad (8)$$

i.e.,  $\chi_\infty \propto |\tau|^{-(1+p/4)}$ , and the behavior in strong fields by the coefficient  $B$ :

$$\mathcal{M}_\infty^H \approx (H/4B)^{1/2} \approx h^{1/2}|\tau|^{-p/2}, \quad h = H/\mathcal{M}_0. \quad (9)$$

The "parasitic" divergence when  $p \neq 0$  can be removed by adding to (1) a term  $D\mathcal{M}^6$  with  $D > 0$  ( $\mathcal{M}_0^6 D = \beta''T_c/\mu\mathcal{M}_0$ ,  $\beta'' \approx 1$ ), which, without changing the behavior of  $\mathcal{M}_\infty$  as  $T \rightarrow T_c$ , leads to a finite value of  $\mathcal{M}_\infty^H$  as  $T \rightarrow T_c$ :

$$\mathcal{M}_\infty^H \approx (H/6D)^{1/5}, \quad h \gg |\tau|^{5(1+p/2)/4} \text{ and } h \gg |\tau|^{5p/2}. \quad (9')$$

If  $p < 2/3$ , the more stringent condition is the second; if  $p > 2/3$ , the first.

For analysis of the role of the surface energy, we shall use the expression

$$\mathcal{F}(T, d) = \int_{-d}^d \left\{ A\mathcal{M}^2 + B\mathcal{M}^4 + C\left(\frac{d\mathcal{M}}{dz}\right)^2 - H\mathcal{M} \right\} dz + 2\mathcal{F}_s, \quad (10)$$

in which the integral is the volume part of the free energy, the second term the surface part (the coefficient 2 appears because of the two identical boundaries of the plate). Not being interested in the effects of anisotropy,<sup>10</sup> we shall suppose that the vectors  $\mathcal{M}$  and  $H$  are parallel to each other and to the plane of the plate, which occupies the layer  $|z| < d$ . Having the symmetrical case in mind, we shall seek  $\mathcal{M}(z)$  for  $0 \leq z \leq d$ , adding the boundary condition at  $z = 0$

$$d\mathcal{M}/dz|_{z=0} = 0. \quad (11)$$

We describe the surface part of the free energy, like the volume part, phenomenologically:

$$\mathcal{F}_s = qC\mathcal{M}^2(d), \quad [q] = 1/\text{cm}. \quad (12)$$

The coefficient  $C$  is introduced in  $\mathcal{F}_s$  for the sake of convenience. Strictly speaking,  $\mathcal{F}_s$  is not the total surface energy. When  $\mathcal{F}_s = 0$  the surface energy is nonzero. In fact, the natural boundary condition of the variational problem (10) without allowance for  $\mathcal{F}_s$  requires vanishing either of  $\mathcal{M}(d)$  or of  $d\mathcal{M}/dz|_{z=d}$ . In the second case the term  $C(d\mathcal{M}/dz)^2$  in  $f$  is simply unimportant ( $\mathcal{M} = \text{const}(z)$ ), and the surface energy is zero; but in the first case ( $\mathcal{M}(d) = 0$ ) the term  $C(d\mathcal{M}/dz)^2$  must be taken into account:  $\mathcal{M}$  depends on the coordinate  $z$  near the boundary, and consequently the surface energy is nonzero. As we shall see, the condition  $\mathcal{M}(d) = 0$  corresponds to  $q \rightarrow +\infty$ . We have retained in (12) only the first term of the expansion of  $\mathcal{F}_s$  in powers of  $\mathcal{M}^2$ , since there is no basis for expecting the parameter  $q$  to vanish within the temperature interval of interest to us.

The minimum of the free energy (10) is attained by the solution of the equation

$$2C\mathcal{M}^2/dz^2 = 2A\mathcal{M} + 4B\mathcal{M}^3 - H, \quad (13)$$

that satisfies the boundary condition

$$d\mathcal{M}/dz|_{z=0} + q\mathcal{M}|_{z=0} = 0. \quad (14)$$

Equation (13) of course permits solution in the form of a quadrature, and therefore the whole analysis reduced to an investigation of integrals of a definite form and to solution of a transcendental equation, which contains a function of the parameters that cannot be expressed as a combination of elementary functions (the integral in question reduces to an elliptic integral; see below). An exception is the "plate of infinite thickness"—a half-space: in this case the solution can be expressed as a combination of exponential functions.

## 2. HALF-SPACE

In this case it is convenient to place the origin at the boundary, i.e., to suppose that the magnetic material occupies the region  $z \geq 0$ . Condition (11) is moved to infinity, and condition (14) to zero:

$$d\mathcal{M}/dz|_{z=0} = q\mathcal{M}|_{z=0}. \quad (15)$$

We begin with the case  $H=0$  and  $T < T_c$ . Both for  $q > 0$  and for  $q < 0$ , the  $\mathcal{M} = \mathcal{M}(z)$  relation looks formally the same:

$$\mathcal{M}(z) = \mathcal{M}_\infty \frac{(\mathcal{M}_s + \mathcal{M}_\infty) + (\mathcal{M}_s - \mathcal{M}_\infty) \exp(-z/\delta_s)}{(\mathcal{M}_s + \mathcal{M}_\infty) - (\mathcal{M}_s - \mathcal{M}_\infty) \exp(-z/\delta_s)}; \quad (16)$$

here

$$\delta_s = (C/2A)^{1/2} = (a/\sqrt{2}) |\tau|^{1/2 - p/4}, \quad (17)$$

$\mathcal{M}_s \equiv \mathcal{M}|_{z=0}$  is determined by the condition (15),

$$\mathcal{M}_s = (q^2 C/4B + \mathcal{M}_\infty^2)^{1/2} - (q/2)(C/B)^{1/2}, \quad T < T_c, \quad (18)$$

and  $\mathcal{M}_\infty$  is given by the expression (3); when  $q > 0$ ,  $\mathcal{M}_s < \mathcal{M}_\infty$ , and vanishing of  $\mathcal{M}_\infty$  (for  $T \rightarrow T_c$ ) is accompanied by vanishing of  $\mathcal{M}_s$ ; thereby  $\mathcal{M} \equiv 0$  for  $T \geq T_c$ . Here  $\mathcal{M}_s$  vanishes faster than  $\mathcal{M}_\infty$ . According to (18)

$$\mathcal{M}_s|_{T \rightarrow T_c} \approx (\mathcal{M}_\infty^2/q)(B/C)^{1/2} \sim \mathcal{M}_0 |\tau|/q, \quad q > 0. \quad (19)$$

It should be noted that the index  $p$  has dropped out of this formula. If  $q = \infty$ , then  $\mathcal{M}_s = 0$  for all  $T$ ; when  $q = 0$ , according to (18),  $\mathcal{M}_s = \mathcal{M}_\infty$  (that is,  $\mathcal{M}(z) \equiv \mathcal{M}_\infty$ ).

When  $q < 0$  and  $T \leq T_c$ , the surface moment does not vanish:

$$\mathcal{M}_s = |q|(C/B)^{1/2}. \quad (20)$$

In the phenomenological approach,  $q$  is an arbitrary constant; but formula (20) shows that there must exist (in a microtheory) a bound to the value of  $|q|$  (when  $q < 0$ ). For example, the transition  $|q| \rightarrow \infty$  is inadmissible,<sup>4)</sup> since it leads to  $\mathcal{M}_s \rightarrow \infty$ .

Temperatures higher than the transition temperature  $T_c$  ( $T > T_c$ , i.e.,  $A > 0$ ) require separate treatment (we are considering the case  $q < 0$ ). When  $\mathcal{M}_\infty = 0$ ,

$$\mathcal{M}(z) = \tilde{\mathcal{M}} \operatorname{sh}^{-1}(\kappa + z/\delta_s); \quad (21)$$

$$\kappa = \frac{1}{2} \ln \frac{(\tilde{\mathcal{M}}^2 + \mathcal{M}_s^2)^{1/2} + \tilde{\mathcal{M}}}{(\tilde{\mathcal{M}}^2 + \mathcal{M}_s^2)^{1/2} - \tilde{\mathcal{M}}}, \quad \tilde{\mathcal{M}} = \sqrt{A/B} = \sqrt{2}\mathcal{M}_\infty.$$

As always,  $\mathcal{M}_s$  is determined by the boundary condition (15):

$$B\mathcal{M}_s^2 = Cq^2 - A. \quad (22)$$

When  $z \rightarrow \infty$ , the magnetic moment vanishes exponential-

ly:

$$\mathcal{M}_s(z) \approx 2\tilde{\mathcal{M}} \exp(-z/\delta_s - \kappa), \quad \delta_s = (C/A)^{1/2} = 2^{1/2}\delta_\infty. \quad (23)$$

The index  $s$  emphasizes that this has to do with surface magnetism. The difference between  $\delta_s$  and  $\delta_\infty$  has the same cause as does the difference in the susceptibility  $\chi$  to the left and to the right of  $T_c$  [see (8)]. The existence bound  $T_s$  for the surface magnetism is determined by the condition for vanishing of  $\mathcal{M}_s$ :

$$\tau_s = (aq)^2/\beta. \quad (24)$$

The measure of nonuniformity of the magnetic-moment density is different far from the boundary and in the boundary layer: far from the boundary, it is  $\delta_s$  or  $\delta_\infty$ , which is proportional to  $|\tau|^{-1/2}$  and becomes infinite for  $T \rightarrow T_c$ . In the surface layer,

$$\mathcal{M}(z) \approx \mathcal{M}_s(1 + qz). \quad (25)$$

The fact that  $\delta_s$  and  $\delta_\infty$  become infinite at  $T = T_c$  shows that at this temperature the relation  $\mathcal{M} = \mathcal{M}(z)$  is a power law:

$$\mathcal{M}(z) = \mathcal{M}_s/(1 + |q|z), \quad q < 0, \quad T = T_c. \quad (26)$$

This expression can be obtained by a limiting process from formulas (21) and (16).

Thus the transition from the paramagnetic state through surface magnetism occurs as follows:  $\mathcal{M}(z) \equiv 0$  for  $T > T_s$ . At  $T = T_s$ ,  $\mathcal{M}_s$  appears; for  $T_c < T \leq T_s$ , the moment  $\mathcal{M}(z)$  is determined by formula (21); for  $T \rightarrow T_c$  ( $T > T_c$ ),  $\mathcal{M}_\infty \equiv 0$  and  $\delta_s \rightarrow \infty$ . At  $T = T_c$ , a nonvanishing  $\mathcal{M}_\infty$  appears; for  $T \leq T_v$ , the moment  $\mathcal{M} = \mathcal{M}(z)$  is given by the formulas (16) and (17); for  $T \rightarrow T_c$  ( $T < T_c$ ),  $\delta_\infty \rightarrow \infty$ . The phase transition at  $T = T_s$  is called a surface transition, that at  $T = T_c$  an extraordinary one (see, for example, Ref. 18).

The transition to a state with a surface magnetic moment is accompanied by a discontinuity  $\Delta C_s$  of the specific heat, which is easily determined from the expression for the surface density of free energy  $f_s$ , valid near  $T_s$  ( $T \leq T_s$ ),

$$f_s = -(q^2 C - A(T))^2 (C/AB^2)^{1/2}. \quad (27)$$

From this and from (24),

$$\Delta C_s = 2ST_s \mathcal{M}_0 \beta^2 / \beta' T_c |q| \mu, \quad (28)$$

where  $S$  is the area of the surface of the magnetic material.

We shall now consider the effect of a magnetic field  $H$  applied, as we have said, parallel to the surface. The equation for  $\mathcal{M}(z)$  can be formally integrated, but it is more convenient to write the solution as an integral and to extract the consequences from it. In both cases ( $q \leq 0$ )

$$\frac{z}{C} = \int_{\mathcal{M}_s}^{\mathcal{M}} \frac{d\mathcal{M}'}{(\mathcal{M}_\infty - \mathcal{M}') [B(\mathcal{M}' + \mathcal{M}_\infty)^2 + H/2\mathcal{M}_\infty]^{1/2}}. \quad (29)$$

The value of  $\mathcal{M}_\infty$  is determined by minimization of the homogeneous part of the free-energy density  $f$  [see (1),

$$2A\mathcal{M}_\infty + 4B\mathcal{M}_\infty^3 = H, \quad (30)$$

and that of  $\mathcal{M}_s$  by the boundary condition (15),

$$C^{1/2} q \mathcal{M}_s = (\mathcal{M}_\infty - \mathcal{M}_s) [B(\mathcal{M}_s + \mathcal{M}_\infty)^2 + H/2\mathcal{M}_\infty]^{1/2}. \quad (31)$$

According to (29) and (30) we have in the interior of the specimen, apart from a preexponential factor,

$$\begin{aligned} \mathcal{M}_\infty - \mathcal{M}(z) &\propto \exp(-z/\delta_H), \\ \delta_H &= [C/(4\mathcal{M}_\infty^2(H) + H/2\mathcal{M}_\infty(H))]^{1/2}. \end{aligned} \quad (32)$$

The magnetic field decreases the depth of penetration—a natural result, signifying a tendency of the field to magnetize the specimen uniformly. In small magnetic fields ( $H \rightarrow 0$ ).

$$\delta_H \approx \begin{cases} (C/A)^{1/2}, & T > T_c, \\ (C/2|A|)^{1/2}, & T < T_c. \end{cases} \quad (33)$$

In large magnetic fields,  $\delta_H = (2^{1/3}C/3HB^{1/3})^{1/2}$  [see the remark after formula (9)].

Equation (31) enables us to determine the value of  $\mathcal{M}_s \neq \mathcal{M}_\infty$ . Treating  $a|q|$  as a small parameter, we have

$$\mathcal{M}_\infty - \mathcal{M}_s \approx q\delta_H \mathcal{M}_\infty, \quad |q|\delta_H \ll 1. \quad (34)$$

In the contrary limiting case, when  $q\delta_H^2 \gg 1$ ,

$$\frac{\mathcal{M}_s}{\mathcal{M}_\infty} \approx \frac{1}{q\delta_H^2}, \quad \delta_H^2 = \left( \frac{C}{B\mathcal{M}_\infty^2 + H/2\mathcal{M}_\infty} \right)^{1/2}. \quad (35)$$

When  $q < 0$ , just as in the absence of a field, formally  $\mathcal{M}_s \rightarrow \infty$  if  $|q| \rightarrow \infty$  [but see the remark after formula (20)]. The asymptotic behavior of  $\delta_H^2$  differs insignificantly from the behavior of  $\delta_H$  [compare (35) with (32) and (33)].

### 3. PLATE OF FINITE THICKNESS ( $q > 0$ )

As we have already said, a detailed discussion of the behavior of the thermodynamic characteristics in this case has been given in a paper of one of the authors.<sup>14</sup> Here we shall restrict ourselves to a summary of the results on the limiting transition from a plate of finite thickness to a half-space at temperatures in the immediate neighborhood of  $T_c$  ( $|\tau| \rightarrow 0$ ,  $d \rightarrow \infty$ ). According to Refs. 9 and 14, for  $d \neq \infty$  the transition from the paramagnetic phase to the ferromagnetic is a phase transition of the Landau type, even if we suppose that  $p \neq 0$  whereas  $l \neq 1$  [see (1) and (2)]. For  $d = \infty$ , the nature of the singularities depends on the values of  $p$  and  $l$ . This shows that at large thicknesses  $d$  there is a narrow range of temperature (the narrower, the larger  $d$ ) within which the temperature variation of the thermodynamic characteristics of a thick plate differs substantially from the temperature variations of the characteristics for a half-space.<sup>5)</sup> The nonanalytic variation of the coefficients  $A$  and  $B$  with  $\tau$  manifests itself in a nonanalytic variation of the coefficients of the expansion of the thermodynamic characteristics in  $(T - T_{cd})/T_{cd}$  with the plate thickness  $d$ . From Table I one can see the correlation between the behavior of the characteristics of a half-space with respect to  $T$  and of the characteristics of a plate with respect to  $d$ . The last line of the table gives the temperature variation of the correlation radius  $r_c$  of

TABLE I.

Quantities	Half-space	Plate
$\mathcal{M}_0, \bar{\mathcal{M}}$	$\tau^{(1-p)/2}$	$d^{p/(p+2)} (\tau_{cd} - \tau)^{1/2}$
$\mathcal{M}_s$	$ \tau $	$d^{-2/(2+p)} (\tau_{cd} - \tau)^{1/2}$
$\chi$	$ \tau ^{-(1+p)/2}$	$d^{2p/(2+p)}  \tau_{cd} - \tau ^{-1}$
$\Delta C$	$ \tau ^{-2}$	$d^{2p/l}$
$r_c$	$ \tau ^{(1+p)/2}$	$d^{p/(2+p)}  \tau_{cd} - \tau ^{-1/2}$

the fluctuations. It must be emphasized that the results reproduced in the table relate to an arbitrary value of the positive coefficient  $q \neq 0$ . The results relating to the  $\psi$  theory of He II in a fine capillary<sup>8</sup> are thereby generalized (in our notation, they correspond to  $q = +\infty$ ). Ref. 8 furthermore gives (see §3.3) certain results relating to a nonvanishing value of the order parameter. In a comparison with our results, it is necessary to bear in mind that the parameter  $1/\lambda$  of Ref. 8 is equivalent to our  $q$ ; in Ref. 8, an expansion is carried out in powers of  $\lambda$ .

### 4. PLATE OF FINITE THICKNESS ( $q < 0$ )

In order to determine the spontaneous magnetic moment, the specific heat, and other characteristics, it is of course necessary to solve equation (13) with the boundary conditions (14) and (11), to substitute the solution in (10), and to perform the appropriate differentiations. Since the solution is completely determined by the value of the magnetic-moment density at the origin [when  $z = 0$ ,  $\mathcal{M}(z = 0) = \mathcal{M}(0)$ ], one must begin with a solution of the dispersion equation, which we write for  $H = 0$  in the following form (see Introduction):

$$\Delta = \sqrt{|\gamma|} \int_0^\zeta (x^2 - 1)^{-1/2} [\gamma + \eta(x^2 + 1)]^{-1/2} dx, \quad \zeta = (\zeta^2 - 1) [\gamma + \eta(\zeta^2 + 1)], \quad (36)$$

where

$$\begin{aligned} \Delta &= d(|A|/C)^{1/2}, \quad \gamma = A/q^2C, \quad \eta = B\mathcal{M}^2(0)/q^2C, \\ \zeta &= \mathcal{M}(d)/\mathcal{M}(0). \end{aligned} \quad (37)$$

We note that here it proved more convenient to introduce dimensionless parameters different from those used in Ref. 14. The parameters  $\Delta$  and  $\gamma$  describe the "conditions of the problem"; they describe the plate dimension and the temperature, while  $\eta$  and  $\zeta$  describe the quantities being sought. Formally the range of variation of  $\gamma$  is from  $-\infty$  to  $+\infty$ . When  $\gamma < 0$ , equation (36) requires satisfaction of the condition

$$\eta \leq |\gamma|/2,$$

which means that for  $q < 0$  the magnetic-moment density in a plate of finite thickness is larger than  $\mathcal{M}_\infty$  [ $\mathcal{M}(z) \geq \mathcal{M}(0) \geq \mathcal{M}_\infty$ ].

The region of existence of magnetism ( $\eta \geq 0$ ) is bounded by the curve

$$\Delta = \ln \frac{1 + \gamma^{1/2}}{(\gamma - 1)^{1/2}}, \quad \gamma > 1, \quad (38)$$

shown in Fig. 1. Equation (38) determines the variation of the Curie temperature  $T_{cd} = T_c(1 + \tau_{cd})$  with plate thickness:

$$A(\tau_{cd}) = C\Delta^2/d^2, \quad \Delta \text{ th } \Delta = |q|d. \quad (39)$$

We shall give an expression, in terms of the parameters introduced above, for the mean value, over the plate thickness, of the magnetic moment:

$$\bar{\mathcal{M}} = d^{-1} \int_0^d \mathcal{M}(z) dz. \quad (40)$$

The integral (40) has been evaluated,<sup>19</sup> and we have  $\bar{\mathcal{M}} = \Delta^{-1} (|A|/B)^{1/2} \ln \{ [(\zeta^2 - 1)\eta / (\gamma + 2\eta)]^{1/2} + [1 + \eta(\zeta^2 - 1) / (\gamma + 2\eta)]^{1/2} \}$ . (41)

The other characteristics in general cannot be expressed in terms of  $\Delta$ ,  $\gamma$ ,  $\eta$ , and  $\zeta$  by means of elementary functions.

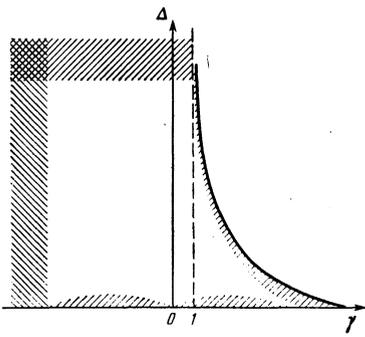


FIG. 1. Phase plane in the variables  $\Delta = d(|A|/C)^{1/2}$  and  $\gamma = A/q^2 C$  when  $q < 0$ .

Since  $\tau_{cd} > 0$ , the magnetic moment is nonzero even at  $T = T_c$ .

Consideration of a plate of finite thickness when  $q < 0$  shows especially clearly the inapplicability of the expansions (1) and (2) to this case: the presence of a nonanalytic variation of  $A$  and  $B$  with  $\tau$  leads to singularities of  $\mathcal{F}(T, d)$  at  $T = T_c$ , while, at the same time, for  $d \neq \infty$  there must be only a single transition point  $T = T_{cd}$ . One might attempt to use an expansion in fractional powers of the magnetic moment (see Ref. 15). This possibility has not been analyzed in detail. But it seems to us that with allowance for a quadratic variation of  $f$  with  $(d\mathcal{M}/dz)^2$  (this is the basis of the  $\psi$  theory<sup>8</sup>), only an expansion in even powers of the moment leads to vanishing of  $\mathcal{M}(d)$  and  $\mathcal{M}(0)$  at  $T \rightarrow T_{cd}$ ; that is, to a phase transition of the second kind.<sup>6)</sup> In fact, the equations for determination of the values of  $\mathcal{M} \equiv \mathcal{M}(0)$  and  $\mathcal{M}(d) = \zeta \mathcal{M}$ , for an arbitrary relation  $f = f(\mathcal{M})$ , have the form<sup>7)</sup>

$$\frac{d}{C^{1/2}} = \int_1^\zeta dx \left[ \frac{f(\mathcal{M}x) - f(\mathcal{M})}{\mathcal{M}^2} \right]^{-1/2}, \quad |q|C^{1/2}\zeta = \left[ \frac{f(\zeta\mathcal{M}) - f(\mathcal{M})}{\mathcal{M}^2} \right]^{1/2}, \quad (42)$$

from which the assertion made above follows: for a phase transition of the second kind, it is necessary that

$$\lim_{\mathcal{M} \rightarrow 0} \frac{f(\mathcal{M}x) - f(\mathcal{M})}{\mathcal{M}^2} \neq 0, \infty.$$

In general, of course, equations (36) permit only numerical solutions. Figure 1 represents the phase plane of a plate in the variables  $\Delta$  and  $\gamma$ . A magnetically ordered state exists to the left of the curve (38). In Fig. 1, those regions are shaded in which it is possible to obtain comparatively simple analytic expressions for the characteristics of plates. Here we shall consider only two cases. We begin with  $T = T_c$  ( $A = 0$ ). We shall determine the dependence of the spontaneous magnetic moment on  $|q|d$ . It is convenient to put equation (36) into the following form:

$$|q|d = \frac{(\zeta^4 - 1)^{1/2}}{\zeta} \int_0^\zeta (x^4 - 1)^{1/2} dx, \quad \mathcal{M}(0) = |q|\zeta \left( \frac{C}{B(\zeta^2 - 1)} \right)^{1/2}. \quad (43)$$

Hence

$$\mathcal{M}(0) \approx (C|q|/2Bd)^{1/2}, \quad \zeta - 1 \approx |q|d/2, \quad |q|d \ll 1; \quad (44)$$

$$\mathcal{M}(0) \approx (1.3/d)(C/B)^{1/2}, \quad \zeta \approx |q|d/1.3, \quad |q|d \gg 1. \quad (45)$$

From (41), (44), and (45) we find

$$\mathcal{M} \approx \begin{cases} (C|q|/2Bd)^{1/2}, & |q|d \ll 1 \\ (C/B)^{1/2} d^{-1} \ln(|q|d), & |q|d \gg 1, \end{cases} \quad (46)$$

TABLE II.

Function	Parameter	
	$ q d \ll 1$	$ q d \gg 1$
$K$	$1 - 1/3 q d$	$1/ q d$
$N$	$1 - 1/6 q d$	$2\sqrt{2}\exp(- q d)$
$L$	$1/2[1 - 1/6 q d]$	$\sqrt{2} q d$
$R$	$1 + 1/3 q d$	$\sqrt{2}$
$P$	$1/4[1 - 1/20(qd)^2]$	$1/ q d$

We note the increase of the mean magnetic moment on decrease of the plate thickness, caused by the action of a delta-function surface energy conducive to ferromagnetic ordering (here  $\mathcal{M}d$  of course tends to zero as  $d \rightarrow 0$ ).

We shall now discuss the region bordering on the phase-transition curve,  $|T_{cd} - T| \rightarrow 0$ . As in the case  $q > 0$ , the transition is found to be a transition of the Landau type; that is

$$\begin{aligned} \Delta C &= (dT_{cd} S \beta^2 \mathcal{M}_0 / T_c \beta' \mu) K(qd), \\ \mathcal{M}(0) &= \mathcal{M}_0 (\beta / 2\beta')^{1/2} N(qd) (T_{cd} - T)^{1/2}, \\ \bar{\mathcal{M}} &= \mathcal{M}_0 (\beta / 2\beta')^{1/2} L(qd) (T_{cd} - T)^{1/2}, \\ \mathcal{M}_* &= \mathcal{M}_0 (\beta / 2\beta')^{1/2} R(qd) (T_{cd} - T)^{1/2}, \\ \chi^+(T - T_{cd}) &= 2\chi^-(T_{cd} - T) = (2\mathcal{M}_0 \mu / \beta) P(qd); \end{aligned} \quad (47)$$

$\chi^+$  and  $\chi^-$  are the magnetic susceptibilities to the right and to the left of the transition point. The quantities  $K$ ,  $N$ ,  $L$ ,  $R$ ,  $P$ —functions of  $\Delta$ —have the form

$$\begin{aligned} K &= 2^{1/2} (1 + \psi(2\Delta))^2 [1 + 1/3\psi(2\Delta) + 1/3\psi(4\Delta)], \\ N &= L/\psi(\Delta) = R/\text{ch } \Delta \\ &= (2/\sqrt{3}) [1 + \psi(2\Delta)]^{1/2} [1 + 1/3\psi(2\Delta) + 1/3\psi(4\Delta)]^{-1/2}, \\ P &= \psi^2(\Delta) / (2 + 2\psi(\Delta)), \quad \psi(x) = \text{sh } x/x. \end{aligned} \quad (48)$$

In order to obtain the explicit dependence of the quantities  $K$ ,  $N$ ,  $L$ ,  $R$ , and  $P$  on  $qd$ , it is necessary to substitute the value of  $\Delta$  from (39). The limiting values of all the quantities (for  $qd \gg 1$  and for  $qd \ll 1$ ) are given in Table II.

We note that the transition  $d \rightarrow \infty$  corresponds to a transition to a state with a surface magnetic moment:  $\Delta C$  ceases to depend on  $d$  [compare with formula (28)]; the mean magnetic moment and magnetic susceptibility tend to zero, the surface moment to a constant.

## 5. FLUCTUATIONS OF THE MAGNETIC MOMENT

To elucidate the role of surface energy in fluctuations of the magnetic moment, we shall consider them above the Curie point (at  $T > T_c$ ); we shall start from an expansion of the fluctuation field  $\mathcal{M}(\mathbf{r})$  in the complete system of functions determined by the equation

$$\Delta\varphi + k^2\varphi = 0, \quad \Delta = \partial^2/\partial z^2 + \partial^2/\partial x^2 + \partial^2/\partial y^2 \quad (49)$$

and the boundary conditions

$$d\varphi/dz|_{z=\pm d} \pm q\varphi|_{z=\pm d} = 0. \quad (49')$$

The statement (49) and (49') of the problem permits solutions symmetric and antisymmetric in  $z$ . The complete set of functions (for  $q > 0$ ) is

$$\begin{aligned} \psi_n^+ &= \cos k_n z e^{i\mathbf{x}\cdot\boldsymbol{\rho}}, \quad k^2 = \kappa^2 + (k_n^a)^2, \quad n = 1, 2, \dots, \\ \psi_n^- &= \sin k_n z e^{i\mathbf{x}\cdot\boldsymbol{\rho}}, \quad k^2 = \kappa^2 + (k_n^a)^2, \quad n = 1, 2, \dots, \end{aligned} \quad (50)$$

where  $\boldsymbol{\rho}$  and  $\boldsymbol{\kappa}$  are two-dimensional vectors:  $\boldsymbol{\rho} = (x, y)$ ,

$= (\kappa_x, \kappa_y)$ ;  $k_n^s$  and  $k_n^a$  are determined, respectively, by the dispersion equations

$$k_n^s d \operatorname{tg} k_n^s d = qd, \quad k_n^a d \operatorname{ctg} k_n^a d = -qd, \quad n=1, 2, \dots \quad (51)$$

On expanding  $\mathcal{M}(\mathbf{r})$  as a series in the functions (50) and substituting in the expression for the fluctuational part of the free energy, we get

$$\Delta \mathcal{F} / Sd \mathcal{M}_0^2 = \Delta \mathcal{F}_s / Sd \mathcal{M}_0^2 + \Delta \mathcal{F}_a / Sd \mathcal{M}_0^2, \quad (52)$$

where

$$\frac{\Delta \mathcal{F}_s}{Sd \mathcal{M}_0^2} = C \sum_{n=1}^{\infty} |\eta_n^s|^2 \left[ (k_n^s)^2 + \frac{A}{C} + \kappa^2 \right] \left( 1 + \frac{qd}{(k_n^s d)^2 + q^2 d^2} \right), \quad (53)$$

$$\frac{\Delta \mathcal{F}_a}{Sd \mathcal{M}_0^2} = C \sum_{n=1}^{\infty} |\eta_n^a|^2 \left[ (k_n^a)^2 + \frac{A}{C} + \kappa^2 \right] \left( 1 + \frac{qd}{(k_n^a d)^2 + q^2 d^2} \right). \quad (53')$$

Here  $\eta_n^s$  and  $\eta_n^a$  are dimensionless coefficients in the expansion of  $\mathcal{M}(\mathbf{r})$  in the functions (50). According to the general theory of thermodynamic fluctuations,<sup>13</sup>

$$\langle (\eta_n^a)^2 \rangle = \frac{T}{2 \mathcal{M}_0^2 Sd C [(k_n^a)^2 + A/C + \kappa^2]} \left( 1 + \frac{qd}{(k_n^a d)^2 + q^2 d^2} \right)^{-1}. \quad (54)$$

The transition temperature  $T_{cd}$  is determined by the equation  $(k_1^s)^2 + A/C = 0$  (see Ref. 9). The analogous factors in  $\Delta \mathcal{F}_s$  and  $\Delta \mathcal{F}_a$  vanish at temperatures much lower than  $T_{cd}$ . For example, it is evident from Fig. 2 that  $(k_1^a)^2 > (k_1^s)^2$ . Hence it is clear that the only "dangerous" fluctuation is the symmetric one with  $n=1$  and  $\kappa \rightarrow 0$ . The surface energy lowers the fluctuation level insignificantly as compared with an infinite magnet; the fraction  $qd / [(k_n^s d)^2 + q^2 d^2]$  approaches unity for  $qd \rightarrow 0$  and approaches zero for  $qd \rightarrow \infty$ .

Before analyzing the magnetic-moment fluctuations for  $q < 0$ , we shall find the eigenfunctions of the problem (49)-(49') in this case.

**Symmetric solution.** We have

$$\begin{aligned} \chi_1^s &= \operatorname{ch} k_1^s z e^{i \kappa x}, & k^2 &= \kappa^2 - (k_1^s)^2, \\ \chi_n^a &= \cos k_n^a z e^{i \kappa x}, & k^2 &= \kappa^2 + (k_n^a)^2, \quad n=2, 3, \dots \end{aligned} \quad (55)$$

The value of  $k_1^s$  is determined by the equation

$$\operatorname{th} k_1^s d / k_1^s d = 1 / |q| d, \quad (56)$$

which, as is evident from Fig. 3, always has a solution, and the values of  $k_n^s$  by the equation

$$k_n^s d \operatorname{tg} k_n^s d = -|q| d, \quad n=2, 3, \dots \quad (57)$$

It is seen from Figs. 3 and 4 that the root  $k_1^s$  is "detached" from the "ordinary" roots.

**Antisymmetric solution.** The set of functions is dif-

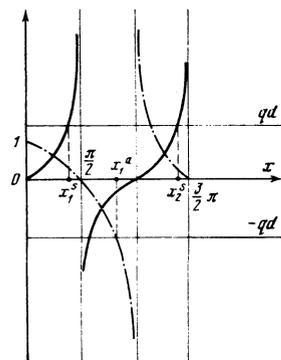


FIG. 2. Graphical solution of equations (51). Solid curve,  $x \tan x$ ; dash-dot curve,  $x \cot x$ .

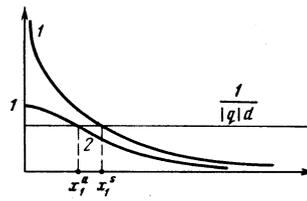


FIG. 3. Graphical solution of equations (56) and (59'). Curve 1,  $(\coth x)/x$ ; Curve 2,  $(\tanh x)/x$ ;  $x_1^s = k_1^s d$ ,  $x_1^a = k_1^a d$ .

ferent for  $|q|d < 1$  and for  $|q|d > 1$ :

$$\begin{aligned} \chi_n^a &= \sin k_n^a z e^{i \kappa x}, & k^2 &= \kappa^2 + (k_n^a)^2, & n=1, 2, \dots, & |q|d < 1; \\ \chi_1^a &= \operatorname{sh} k_1^a z e^{i \kappa x}, & k^2 &= \kappa^2 - (k_1^a)^2, & |q|d > 1; \\ \chi_n^a &= \sin k_n^a z e^{i \kappa x}, & k^2 &= \kappa^2 + (k_n^a)^2, & |q|d > 1, & n=2, 3, \dots \end{aligned} \quad (58)$$

The values of  $k_n^a$  are determined by the equation

$$k_n^a d \operatorname{ctg} k_n^a d = |q| d, \quad (59)$$

which for the hyperbolic solution becomes

$$\operatorname{th} k_1^a d / k_1^a d = 1 / |q| d, \quad |q|d > 1 \quad (59')$$

and has a solution only when  $|q|d > 1$ ; then  $k_1^a < k_1^s$  (see Fig. 3). On expanding  $\mathcal{M}(\mathbf{r})$  as a series in the functions (55) and (58) and substituting in the expression for the fluctuational part of the free energy, we get the following expressions for  $\Delta \mathcal{F}_s$  and  $\Delta \mathcal{F}_a$ :

$$\begin{aligned} \frac{\Delta \mathcal{F}_s}{Sd \mathcal{M}_0^2} &= C |\eta_1^s|^2 \left[ \frac{A}{C} + \kappa^2 - (k_1^s)^2 \right] \left( 1 + \frac{|q|d}{(k_1^s d)^2 - q^2 d^2} \right) \\ &+ C \sum_{n=2}^{\infty} |\eta_n^s|^2 \left[ \frac{A}{C} + \kappa^2 + (k_n^s)^2 \right] \left( 1 - \frac{|q|d}{(k_n^s d)^2 + q^2 d^2} \right), \\ \frac{\Delta \mathcal{F}_a}{Sd \mathcal{M}_0^2} \Big|_{|q|d > 1} &= C |\eta_1^a|^2 \left[ \frac{A}{C} + \kappa^2 - (k_1^a)^2 \right] \left( \frac{|q|d}{q^2 d^2 - (k_1^a d)^2} - 1 \right) \\ &+ C \sum_{n=2}^{\infty} |\eta_n^a|^2 \left[ \frac{A}{C} + \kappa^2 - (k_n^a)^2 \right] \left( 1 - \frac{|q|d}{q^2 d^2 + (k_n^a d)^2} \right); \end{aligned} \quad (60)$$

$$\frac{\Delta \mathcal{F}_a}{Sd \mathcal{M}_0^2} \Big|_{|q|d < 1} = C \sum_{n=1}^{\infty} |\eta_n^a|^2 \left[ \frac{A}{C} + \kappa^2 + (k_n^a)^2 \right] \left( 1 - \frac{|q|d}{q^2 d^2 + (k_n^a d)^2} \right).$$

The transition temperature  $T_{cd}$  is determined by the condition  $A(T_{cd})/C - (k_1^s)^2 = 0$ . At temperatures  $T > T_{cd}$ , all the coefficients of  $(\eta_n^s)^2$  ( $n=2, 3, \dots$ ) are greater than zero. It is evident that, as for  $q > 0$ , the only "dangerous" fluctuation is the symmetric fluctuation with  $n=1$  and  $\kappa \rightarrow 0$ . The factor

$$Q = 1 + |q|d / [(k_1^s d)^2 - q^2 d^2],$$

which determines the level of the "dangerous" fluctuation, increases with  $q$ , from  $Q \approx 2$  when  $|q|d \ll 1$  to  $Q \approx \exp(2|q|d)/4|q|d$  when  $|q|d \gg 1$ . Negative surface

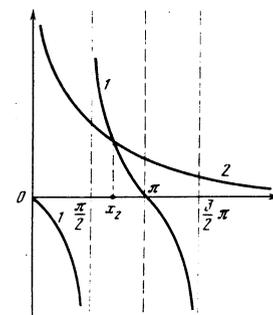


FIG. 4. Graphical solution of equation (57). Curve 1,  $\tan x$ ; Curve 2,  $|q|d/x$ ;  $x_2 = k_2^s d$ .

energy suppresses the "dangerous" fluctuation and consequently narrows the fluctuation region.

The correlation function  $\langle m(\mathbf{r})m(\mathbf{r}') \rangle$ , because of the presence of the boundary, depends on  $\rho = |\rho - \rho'|$  and separately on  $z$  and on  $z'$ . Therefore one can speak of a correlation radius only in the plane of the plate. Since the fluctuational part of the free energy separates into a symmetric and an antisymmetric part [see (52), (53) and (60)], it is clear that  $\langle m_s(\mathbf{r})m_a(\mathbf{r}') \rangle = 0$ , if  $m_s(\mathbf{r})$  and  $m_a(\mathbf{r}')$  denote the symmetric and antisymmetric parts of the magnetic-moment fluctuation. The fluctuations of  $m_a(\mathbf{r})$  behave regularly. Therefore the quantity of greatest interest is

$$G_s = \langle m_s(\mathbf{r})m_s(\mathbf{r}') \rangle. \quad (61)$$

By expanding the moments in Fourier series and integrating over  $\mathbf{x}$ , we can show that the function  $G_s(\rho)$  is defined by a series in  $K_0(\kappa_n^* \rho)$ , where  $k_0(x)$  is the zero-order Bessel function of imaginary argument,<sup>21</sup> and where

$$\kappa_n^* = ((k_n^*)^2 + A(T)/C)^{1/2} \quad (62)$$

in the case of "trigonometric" fluctuations and

$$\kappa_n^* = (A(T)/C - (k_n^*)^2)^{1/2} \quad (63)$$

in the case of "hyperbolic." Thus each fluctuation has its own correlation radius

$$r_c^{(n)} = \kappa_n^{-1}, \quad (64)$$

the only correlation radius that becomes infinite at  $T \rightarrow T_{cd}$  is, of course, the one corresponding to the "dangerous" fluctuation.

The dependence on  $z$  and  $z'$  is not on their difference—a natural consequence of boundaries. Therefore we cannot introduce a correlation radius in the direction normal to the plate surface.

## 6. CONCLUSION

The phenomenological nature of this treatment requires an estimate of its range of applicability. Since, even with allowance for the nonanalytic dependence of the coefficients  $A$  and  $B$  on  $\tau$ , there are "dangerous" fluctuations characteristic of the Landau theory, the whole treatment is of course invalid in the immediate vicinity of the transition point. In the three-dimensional case, the existence of a temperature range in which the Landau theory is valid is determined by the Levanyuk-Ginzburg criterion (see Ref. 13, §146). In our case, because of the inhomogeneity of the order parameter produced by the surface energy, direct application of the Levanyuk-Ginzburg criterion is difficult. It would be necessary to calculate the corrections to the various characteristics (specific heat, magnetic moment, susceptibility) required by the fluctuations<sup>8)</sup> and to select the temperature interval in which they were small. The occurrence of "dangerous" fluctuations mentioned above causes us to believe that the range of applicability of the Landau theory to ferromagnetic plates is somewhat broader than to bulk ferromagnets.

True, there is still one fact that limits our treatment: because of the increase of the correlation radius as  $T \rightarrow T_c$ , the behavior of a plate of thickness  $d$  becomes

similar to that of a two-dimensional magnet. This occurs when  $r_c^* \geq d$ ; or if we suppose that  $r_c^* \approx \tilde{a}/|\tau|^{1/2}$ , when  $|\tau| \lesssim (\tilde{a}/d)^{1/2}$  (the factor  $\tilde{a}$  is of the order of interatomic distances;  $r_c^*$  is the correlation radius in a bulk specimen). A rigorous criterion for the applicability of the formulas obtained here is difficult to formulate primarily because it depends on the exact value of the parameters of the magnet. It is possible that the formulas will be valid for some magnetic materials and not for others. We note that for a ferromagnet a combination of parameters which, according to the Levanyuk-Ginzburg criterion [see formula (146.16) of Ref. 13], should be much smaller than unity, becomes, on substitution of values, of order of magnitude unity.

In conclusion, we take this opportunity to thank I. M. Lifshitz for useful and stimulating discussions, and also A. A. Sobyenin, whose comments were taken into consideration in the final version of this paper.

<sup>1)</sup>In the study of the temperature dependence of the magnetization in a semiinfinite specimen whose interatomic interactions are described by a Heisenberg Hamiltonian, there must occur under certain conditions, at a temperature exceeding  $T_c$ , a phase transition analogous to the Kaplan-Stanley transition.<sup>4</sup>

<sup>2)</sup>The properties of ferromagnets with  $\mathcal{F}_s > 0$  are investigated in detail in Ref. 14.

<sup>3)</sup>We shall consider some of these below.

<sup>4)</sup>We emphasize: this result can not be remedied within the framework of a phenomenological theory. If  $\mathcal{M}_s > \mathcal{M}_c$ , then  $\mathcal{M}_s \rightarrow \infty$  when  $|q| \rightarrow \infty$ . This is evident if we write equation (18) without specification of the function  $f = f(\mathcal{M})$ :

$$|q| C = \{ [f(\mathcal{M}_s) - f(\mathcal{M}_c)] / \mathcal{M}_s \}^{1/2}, \quad \mathcal{M}_s > \mathcal{M}_c.$$

If  $\mathcal{M}_s$  and  $\mathcal{M}(z)$  for  $z$  close to the boundary are large, then it is of course not possible to use an expansion of  $f$  in powers of the magnetic moment. This also imposes a bound on  $q$ .

<sup>5)</sup>Such a region exists even when  $p = 0$  and  $l = 1$ , since the slopes of the curves at  $T \rightarrow T_{cd}$  and at  $T \rightarrow T_c$  differ by a finite quantity. This fact was mentioned in Ref. 9.

<sup>6)</sup>We have not investigated the possibility of a radical change of character of the transition as a result of surface energy.

<sup>7)</sup>The deduction of concrete expressions of the type (42), valid for an arbitrary relation  $f = f(\mathcal{M})$ , offers in principle a possibility of using, in the calculation of the properties of plates and a half-space, empirically found expansions of  $f(\mathcal{M})$  (see, for example, Ref. 20).

<sup>8)</sup>By analogy with the calculation of the fluctuational correction to the specific heat<sup>22</sup> (see also the problem in §147 of Ref. 13).

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## Orientalional phase transitions in the vicinity of the Curie point in terbium-gadolinium alloys

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By measurements of the magnetization and of the magnetocaloric effect in monocrystals of the rare-earth alloys  $Tb_xGd_{1-x}$  ( $x < 0.94$ ) along various crystallographic directions, it is shown that in the region of the Curie temperature, in a magnetic field directed along an axis of difficult magnetization, a magnetic phase transition of the spin-reorientation type occurs in an anisotropic ferromagnet. The experimental results are discussed on the basis of Landau's thermodynamic theory of phase transitions. By means of the Ginzburg-Levanyuk criterion, the theory is shown to be applicable over a quite broad temperature interval near the Curie point.

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In the study of magnetic phase transitions at the Curie point (of the order-disorder type), use is often made of Landau's theory of phase transitions of second order.<sup>1</sup> On the basis of it, there exists for an isotropic magnetic material a well developed thermodynamic-coefficient procedure<sup>2</sup> that enables one to determine the spontaneous magnetization  $\sigma_s(T)$  and also the Curie point  $\Theta$ .

But in a strongly anisotropic ferromagnet in the presence of a magnetic field, there is a possibility, in the temperature range  $T < \Theta$  below the Curie point, of reorientation phenomena, which may produce changes in the phase-transition picture near  $\Theta$  and, accordingly, may lead to a change of the physical properties of the magnet. Here the order parameter in the theory of a phase transition is, in contrast to the isotropic case, multicomponent. The effect of the anisotropy of the ferromagnet manifests itself in the fact that the vanishing of the thermodynamic coefficients of the second-order terms in the expansion of the thermodynamic potential will occur at different temperatures for different components. This, in particular, may lead to anisotropy of the paramagnetic Curie point.<sup>3,4</sup>

The present paper is devoted to study of the influence

of phenomena of the reorientation type on phase transitions in the Curie-point region of a uniaxial magnetic material. The experimental investigations were made on  $Tb_xGd_{1-x}$  alloys with various contents of gadolinium ( $x < 0.94$ ). These compounds are solid solutions and provide a typical example of a strongly anisotropic uniaxial ferromagnetic crystal. They have a hexagonal structure, with the axis of hard magnetization along the hexagonal axis  $c$ .

The technology of growing monocrystalline terbium-gadolinium alloys and the monitoring of their quality have been described earlier.<sup>5</sup>

The literature<sup>6</sup> contains information about the investigation of the magnetic properties of gadolinium in a magnetic field directed along the axes of easy and of hard magnetization. Gadolinium, however, has a magnetic anisotropy two orders of magnitude smaller than the anisotropy of heavy rare-earth metals. Therefore  $Tb_xGd_{1-x}$  alloys are of considerable interest, since no investigation has hitherto been made of high-anisotropy ferromagnets, near the Curie point, in a magnetic field directed along the axis of hard magnetization.