First-order magnetic phase transitions and fluctuations

S. A. Brazovskiĭ, I. E. Dzyaloshinskiĭ, and B. G. Kukharenko

L. D. Landau Theoretical Physics Institute, USSR Academy of Sciences
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In a number of magnetic transitions the fluctuations are so strong that the second-order transition, that is possible in principle according to the Landau theory, becomes first-order. The antiferromagnetic transitions in the cubic lattices UO_2, MnO, TbAS, NdTe, etc. are considered. Calculations performed by means of the ϵ-expansion show that a second-order transition is impossible in all the cases listed, and this corresponds to the experimental situation for MnO and UO_2. The possible types of first-order transition are considered.

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1. INTRODUCTION

Back in the first paper on the renormalization-group method,[1] Wilson and Fisher remarked that, for certain relationships between the parameters in the simplest models, a second-order phase transition becomes impossible as a result of the growth of the fluctuations and is transformed into a first order transition. Subsequently this question was considered by a number of authors (cf., e.g.,[2]). Finally, in a previous paper,[3] the authors considered an example of a transition in which the fluctuations are so strong that the second-order transition that is possible in principle is transformed into a first-order transition for any values of the parameters of the problem. In effect, the transitions in compounds of the type TbSb etc., were considered.

At the present time we know of two firmly established examples (MnO[4,5] and UO_2[6]) of first-order magnetic phase transitions which, from the point of view of the Landau theory, are classical second-order transitions. Up to now the entropy discontinuity in UO_2 has had no explanation. The discontinuity in MnO has been explained either by magnetostriction, giving a dependence of the exchange integrals on the order parameter, or by biquadratic exchange.[5,7] We shall show that the character of the transition in these and other cases can be explained naturally by the fluctuations.

We shall start from the Landau theory. However, the expression for the free energy in the Landau form is valid only in the molecular-field approximation and does not have a direct relation to the problem near the transition point, where the situation must be described by the method of the renormalization group (RG) (cf., e.g.,[8,9]). In the general case, therefore, we cannot solve the problem of the character of the transition, inasmuch as we know nothing about the general structure of the RG and assume from the outset that the transition under consideration is second-order ("scaling"). The situation changes in Wilson's ε-expansion method (again, cf.[8,9]), when the structure of the RG is entirely determined by a free energy in the Landau form, and the RG coincides, in essence, with the group of Gell-Mann and Low.[10] The Landau free energy (with small changes that will be discussed below) now determines the equation of state and the character of the magnetic structure that arises in the first-order transition.

When the present work was completed we received a preprint by Bak *et al.* in which results, overlapping in particular places with our conclusions, of investigations carried out by a somewhat different method and submitted to various journals* for publication were briefly described. To avoid duplication, we shall confine ourselves to the case precisely opposite to that considered by Bak *et al.*[11] (see below). Namely, we shall assume that the anisotropy energy is so small that the character of the transition is determined entirely by the exchange fluctuations (the case of large anisotropy was considered by us earlier[3] for the transition in TbSb, etc.).

2. THE TRANSITION IN UO_2

The magnetic structure that arises UO_2 is well known.[6] The Landau theory for this type of transition was constructed by Man'ko and one of the authors.[12] To describe the transition it is natural to follow the Landau method and use the language of irreducible group representations (for the details see the book by Landau and Lifshitz[13]).

UO_2 crystals have face-centered cubic close-packing (the group $O_h^5 - Fm3m$). The magnetic structure found experimentally corresponds to the star $(\frac{1}{2}00)$, $(0\frac{1}{2}0)$, $(00\frac{1}{2})$. The corresponding spin density is specified by three "vectors" $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$:

$$\mathbf{s}_1=\mathbf{s}_{10}\cos 2\pi x, \quad \mathbf{s}_2=\mathbf{s}_{20}\cos 2\pi y, \quad \mathbf{s}_3=\mathbf{s}_{30}\cos 2\pi z, \tag{1}$$

where the $\mathbf{s}_{i0}$ are arbitrary constant vectors. The relations (1) determine the coordinate dependence of the spin density $\mathbf{s}(\mathbf{r})$, which is a certain linear combination of the "vectors" $\mathbf{s}_i$.

The nine-dimensional representation specified by the vectors $\mathbf{s}_i$ is reducible. It decomposes into two irreducible representations—a three-dimensional one consisting of s_{1x}, s_{2y}, and s_{3z}, and a six-dimensional one incorporating the remaining components of the $\mathbf{s}_i$. The Landau energy is written in the form[12]

$$\begin{aligned} F=&\tfrac{1}{2}\tau(s_1^2+s_2^2+s_3^2)+\tfrac{1}{2}a(s_{1x}^2+s_{2y}^2+s_{3z}^2)\\ &+\tfrac{1}{8}\Gamma_1(s_1^4+s_2^4+s_3^4)+\tfrac{1}{4}\Gamma_2(s_1^2s_2^2+s_1^2s_3^2\\ &+s_2^2s_3^2)+\tfrac{1}{2}\Gamma_3((\mathbf{s}_1\mathbf{s}_2)^2+(\mathbf{s}_1\mathbf{s}_3)^2+(\mathbf{s}_2\mathbf{s}_3)^2), \end{aligned} \tag{2}$$

where $\tau \sim (T-T_c)/T_c$. The constant a describes the anisotropy energy; the constants τ, Γ_1, Γ_2 and Γ_3, as can be seen from the structure of the expression (2),

are determined by the exchange interactions. We have omitted unimportant fourth-order nonexchange terms. If the quantity a is large and positive, a transition occurs to a state in which $\mathbf{s}_1$ has projections s_{1y} and s_{1z}, $\mathbf{s}_2$ has projections s_{2x} and s_{2z}, and so on. This case was considered by Bak *et al.*[11] and we shall not dwell on it. If a is large and negative, a state arises in which only s_{1x}, s_{2y} and s_{3z} are nonzero. We can verify that in this case second-order transitions become possible.

We shall confine ourselves to the case when a is small—more precisely, $a \ll \tau_0$, where τ_0 is the value of τ at which a first-order transition would occur if the exchange interaction alone were taken into account (and we shall see now that, even with neglect of the anisotropy, second-order transitions are impossible). The anisotropy energy can now be taken into account as a perturbation. It will determine the orientation, with respect to the crystal axes, of the purely exchange structure that arises in the first-order transition (see below).

As already mentioned above, we shall treat the transition using the Wilson ε-expansion. All the necessary calculations are simple and obvious generalizations of the calculations carried out in the papers of Larkin and Khmel'nitskiĭ[14] and Abrahams *et al.*[15] (cf. also[9]). There is no need to repeat them, and we shall immediately write out the results.

For small ε the Landau expression for the free energy F is essentially unchanged. Formula (2) now determines the equation of state, i.e., it is that part of the total energy[1)] which depends explicitly on the average values of the order parameter $\mathbf{s}_i$. The only difference is that the quantities Γ_1, Γ_2 and Γ_3, which are constants in the Landau theory, now become functions of the temperature τ and of the $\mathbf{s}_i$ themselves; viz., $\Gamma \equiv \Gamma(\xi)$, where

$$\xi = \frac{1}{\varepsilon}\left\{\left(\frac{\Lambda}{\max(\tau, s_0^2)}\right)^{\varepsilon} - 1\right\} \tag{3}$$

where $s_0^2 = s_1^2 + s_2^2 + s_3^2$ and Λ is the cutoff parameter. When $\varepsilon \to 0$ the quantity ξ becomes

$$\xi = \ln \frac{\Lambda}{\max(\tau, s_0^2)}. \tag{3'}$$

Strictly speaking, it is necessary also to replace the reduced temperature τ in (2) by $\tau C(\xi)$, where C is a known function of ξ. However, this circumstance does not affect the conclusions that are reached below with logarithmic accuracy. We note also that, in studying the question of first-order transitions, when, in practice, τ and s_0^2 in (3) are not too small, we can always use the limiting formula (3′) for ξ as the leading approximation.

The functions $\Gamma_i(\xi)$ are the so-called exact vertex parts. For these it is easy to write, for small ε, the renormalization-group equations of Gell-Mann and Low. In the first approximation the equations of Gell-Mann and Low coincide with the so-called parquet equations (cf., e.g.,[9,14,15]). These equations are first-order differential equations; their concrete form is again determined by the expression (2). In our case they have the form

$$\begin{aligned}
-\frac{d\Gamma_1}{d\xi} &= 11\Gamma_1^2 + 6\Gamma_2^2 + 8\Gamma_2\Gamma_3 + 8\Gamma_3^2,\\
-\frac{d\Gamma_2}{d\xi} &= 10\Gamma_1\Gamma_2 + 4\Gamma_1\Gamma_3 + 7\Gamma_2^2 + 4\Gamma_2\Gamma_3 + 4\Gamma_3^2,\\
-\frac{d\Gamma_3}{d\xi} &= 4\Gamma_3(\Gamma_1 + 2\Gamma_2 + 3\Gamma_3).
\end{aligned} \tag{4}$$

The system (4) must be solved with the initial conditions $\Gamma_i(0) = \Gamma_{i0}$, where the Γ_{i0} are the "bare" values of the vertices Γ_i far from the transition point, where $\xi = 0$.

We shall first investigate the second-order phase transitions that are possible in our problem. Second-order phase-transition points are, as is well known (cf., e.g.,[8,9]), fixed points of the RG equations. In our case, when the right-hand sides of the RG equations (4) are homogeneous functions of the variables and the right-hand side of the equation for Γ_1 vanishes only when Γ_1, Γ_2 and Γ_3 are identically equal to zero, the fixed points are the so-called projective points

$$\Gamma_i = \frac{\text{const}}{\xi}$$

According to (3), a second-order phase transition corresponds to $\xi \to \infty$, i.e., to the vanishing of the Γ_i.[2)]

The system (4) has three fixed points:

$$\begin{aligned}
&O\text{:}\quad \Gamma_1 = \Gamma_2 = 1/17\xi, \quad \Gamma_3 = 0,\\
&A_1\text{:}\quad \Gamma_1 = 6\Gamma_2 = 6/67\xi, \quad \Gamma_3 = 0,\\
&A_2\text{:}\quad \Gamma_1 = 1/11\xi, \quad \Gamma_2 = \Gamma_3 = 0.
\end{aligned} \tag{5}$$

To investigate the trajectories of the system it is convenient to introduce in place of Γ_2 the new variable

$$\Gamma_4 = -\Gamma_1 + \Gamma_2 + 2\Gamma_3.$$

Equations (4) are then rewritten in the form (the prime denotes the derivative with respect to ξ)

$$\begin{aligned}
-\Gamma_4' &= \Gamma_4(12\Gamma_1 + \Gamma_4 + 8\Gamma_3),\\
-\Gamma_3' &= 4\Gamma_3(3\Gamma_1 + 2\Gamma_4 - \Gamma_3),\\
-\Gamma_1' &= 11\Gamma_1^2 + 4(\Gamma_1 + \Gamma_4 - 2\Gamma_3)^2 + 2(\Gamma_1 + \Gamma_4)^2.
\end{aligned} \tag{6}$$

As can be seen from the last equation of the system (6), the vertex Γ_1 is a monotonically decreasing function of ξ. It is therefore natural to introduce new variables $u = \Gamma_4/\Gamma_1$, $v = \Gamma_3/\Gamma_1$ and regard them as functions of the positive (see below) monotonic time Γ_1. Figure 1 shows the pattern of the "trajectories" of the system (6) in the uv plane. In this plane the fixed points (5) have the coordinates

$$O(00), \quad A_1(-5/6, 0), \quad A_2(-1, 0).$$

The flow in the direction of increasing ξ for positive Γ_1 is indicated by arrows on the trajectories (see below).

The trajectories in Fig. 1 determine the behavior of the system with decreasing temperature (increasing ξ). Leaving its starting point $u_0 = \Gamma_{40}/\Gamma_{10}$, $v_0 = \Gamma_{30}/\Gamma_{10}$, the system will move along the corresponding trajectory. Meanwhile the average values of the spins in (2) will be equal to zero for so long as τ and the fourth-order form remain positive-definite (the latter requirement imposes certain restrictions on the bare constants Γ_{i0}; cf. below). The flow can be interrupted in two cases. First,

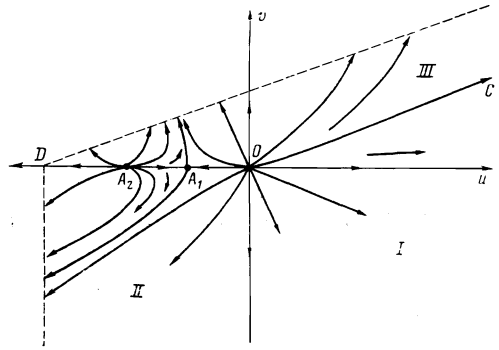

FIG. 1.

the trajectory can terminate at one of the fixed points, and this corresponds to a phase transition at $\tau=0$ ($\xi=\infty$). Secondly, the trajectory can intersect the boundary of the region of positive-definiteness, and then (cf. below) a transition occurs immediately to a state with a finite value of $\mathbf{s}$.

In our case second-order transitions are impossible, inasmuch as all the fixed points are either saddle points or unstable foci. To determine the regions of positive-definiteness it is necessary to investigate the absolute minima of the fourth-order form in (2). It has three absolute minima: at three points of the type

$$s_1\neq 0,\quad s_2=s_3=0, \tag{I}$$

where the energy (2) has the form

$$F_I=\tfrac{1}{2}\tau s_0^2+\tfrac{1}{8}\Gamma_1 s_0^4; \tag{7}$$

at a point where

$$\mathbf{s}_1=\pm\mathbf{s}_2=\pm\mathbf{s}_3, \tag{II}$$

near which

$$F_{II}=\tfrac{1}{2}\tau s_0^2+\tfrac{1}{24}(\Gamma_1+2\Gamma_2+4\Gamma_3)s_0^4; \tag{8}$$

and, finally, at a point

$$\mathbf{s}_1\perp\mathbf{s}_2\perp\mathbf{s}_3,\quad s_1=s_2=s_3, \tag{III}$$

$$F_{III}=\tfrac{1}{2}\tau s_0^2+\tfrac{1}{24}(\Gamma_1+2\Gamma_2)s_0^4. \tag{9}$$

Thus, the boundaries of the region of stability are defined by three equations:

$$\Gamma_1\geqslant 0\quad (I);\quad \Gamma_1+2\Gamma_2+4\Gamma_3\geqslant 0\quad (II);\quad \Gamma_1+2\Gamma_2\geqslant 0\quad (III).$$

The bare constants Γ_{i0} should, of course, also satisfy these conditions. In Fig. 1, flow toward the boundary $\Gamma_1\geqslant 0$ is flow to infinity. The equations of the regions (II) and (III) have the form (the dashed lines in Fig. 1)

$$3+2u\geqslant 0\quad (II);\quad 3+2u-2v\geqslant 0\quad (III).$$

Near, e.g., the stability boundary $\Gamma_1=0$, the vertex part Γ_1 obviously has the form

$$\Gamma_1=\gamma(\xi_0-\xi),\quad \gamma>0,$$

where $\xi_0=\ln(\Lambda/\tau_0)$ and the constants ξ_0 and τ_0 are determined from solutions of the system of equations (6) and depend, of course, on the initial values Γ_{i0} on the trajectory. For the other two boundaries, the corresponding combination of vertex parts vanishes in accordance with a law of the same form.

In accordance with the definition of ξ given in (3′), for $\tau>\tau_0$ the energy F_I has the form

$$F_I=\frac{1}{2}\tau s_0^2+\frac{1}{8}\gamma s_0^4\ln\frac{\max(\tau,s_0^2)}{\tau_0};$$

it is obvious that this function has a minimum at $s_0^2=0$ only. For $\tau<\tau_0$ the form of the energy depends essentially on the relative size of s_0^2 and τ_0. For $s_0^2<\tau_0$,

$$F_I=\frac{1}{2}\tau s_0^2-\frac{1}{8}\gamma s_0^4\ln\frac{\tau_0}{\max(\tau,s_0^2)},$$

and for $s_0^2>\tau_0$,

$$F_I=\frac{1}{2}\tau s_0^2+\frac{1}{8}\gamma s_0^4\ln\frac{s_0^2}{\tau_0}.$$

Such a function has (with logarithmic accuracy) a minimum at

$$s_0^2=2\tau_0/\gamma.$$

Thus, a first-order transition does indeed occur in this case.

Summarizing finally the results, we can give the following description of the situation. From the region of initial charge values Γ_{i0} that lies to the right inside the region bounded by the lower half ordinate axis and the trajectory OC that is asymptotically parallel to the dashed straight line $3+2u-2v=0$, a transition occurs to the state I, in which only one of the vectors $\mathbf{s}_i$ is nonzero. The orientation of $\mathbf{s}$ with respect to the crystal axes is determined, as indicated above, by the sign of a. For $a>0$, two of the three possible components of $\mathbf{s}_i$, e.g., s_{1y} and s_{1z} in the case of $\mathbf{s}_1$, are nonzero. A transition of this type actually occurs in UO_2. We remark again that it was considered by Bak *et al.*[11] in the other limiting case of large a.

For $a<0$ a transition with one component of $\mathbf{s}_i$ (s_{1x} in the case of $\mathbf{s}_1$) is realized. Apparently, such a transition has not yet been observed. We note that in the limit of large $|a|$ this transition is a second-order transition. In effect, this means that there is a tricritical point at a certain value $\Gamma_0\sim a$.

In the region of initial values lying in the half-strip $v<0$ bounded by the ordinate axis and the straight line $u=-\frac{3}{2}$, all trajectories intersect the dashed straight line $u=-\frac{3}{2}$, at which a transition to the state II with $\mathbf{s}_1=\pm\mathbf{s}_2=\pm\mathbf{s}_3$ occurs. Apparently, such a state has not yet been observed. The second-order anisotropy does not determine the orientation of the vector $\mathbf{s}_i$ in this case. As always in cubic crystals, allowance for the fourth-order anisotropy leads to orientation either along a cubic axis or along a principal diagonal of the cube.

We note that, according to the aforementioned results of Man'ko and one of the authors,[12] the state II is ferromagnetic with $m\sim s_0^3$.

Finally, from the region bounded by the line OD, the dashed straight line and the trajectory OC, a transition to the state III with $\mathbf{s}_1\perp\mathbf{s}_2\perp\mathbf{s}_3$ occurs when the trajectories intersect the straight line $3+2u-2v=0$. Either the state $s_{1x}=s_{2y}=s_{3z}$, or one of the states $s_{1y}=s_{2z}=s_{3x}$ and $s_{1z}=s_{2x}=s_{3y}$, arises, depending on the sign of a. Evidently, states of the type III have also not yet been observed.

3. A SIMPLE EXAMPLE

It is instructive to consider also the simple example studied earlier by one of the authors in a paper on helicoidal structures.[16] This is the transition specified by the star $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $(\bar{\frac{1}{4}}\bar{\frac{1}{4}}\bar{\frac{1}{4}})$ in a body-centered cubic crystal (the group $O_h^9 - \mathrm{Im}3m$). The spin density is now described by two vectors:

$$\mathbf{s}_1=\mathbf{s}_{10}\cos\pi x\cos\pi y\cos\pi z, \quad \mathbf{s}_2=\mathbf{s}_{20}\sin\pi x\sin\pi y\sin\pi z. \tag{10}$$

This six-dimensional representation is irreducible and therefore the expression for the Landau energy, with allowance for quadratic anisotropy only, has the form

$$F=\tfrac{1}{2}\tau(s_1^2+s_2^2)+\tfrac{1}{3}\Gamma_1(s_1^4+s_2^4)+\tfrac{1}{4}\Gamma_2 s_1^2 s_2^2+\tfrac{1}{2}\Gamma_3(\mathbf{s}_1\mathbf{s}_2)^2. \tag{11}$$

The theory of the phase transitions in the framework of the ε-expansion is, in essence, a repetition of the discussions of the preceding section. The RG equations for the vertices Γ now have the form

$$\begin{aligned}-\Gamma_1'&=11\Gamma_1^2+3\Gamma_2^2+4\Gamma_2\Gamma_3+4\Gamma_3^2,\\ -\Gamma_2'&=10\Gamma_1\Gamma_2+4\Gamma_1\Gamma_3+4\Gamma_2^2+4\Gamma_3^2,\\ -\Gamma_3'&=2\Gamma_3(2\Gamma_1+4\Gamma_2+5\Gamma_3).\end{aligned} \tag{12}$$

They have five fixed points:

$$\begin{aligned}&O: \ \Gamma_1=\Gamma_2=\tfrac{1}{11}\xi, \ \Gamma_3=0,\\ &A_1: \ \Gamma_1=3\Gamma_2=\tfrac{3}{33}\xi, \ \Gamma_3=0,\\ &A_2: \ \Gamma_1=\tfrac{1}{11}\xi, \ \Gamma_2=\Gamma_3=0,\\ &B_1: \ \Gamma_1=\Gamma_2=2\Gamma_3=\tfrac{1}{17}\xi,\\ &B_2: \ \Gamma_1=\Gamma_2=\Gamma_3=\tfrac{1}{22}\xi.\end{aligned}$$

The investigation is conveniently carried out by introducing the variable

$$\Gamma_4=-\Gamma_1+\Gamma_2.$$

Then,

$$\begin{aligned}-\Gamma_4'&=\Gamma_4(12\Gamma_1+\Gamma_4-4\Gamma_3),\\ -\Gamma_3'&=2\Gamma_3(6\Gamma_1+4\Gamma_4+5\Gamma_3),\\ -\Gamma_1'&=11\Gamma_1^2+2(\Gamma_4+\Gamma_1)^2+(\Gamma_1+\Gamma_4+2\Gamma_3)^2.\end{aligned} \tag{13}$$

For the investigation it is useful to keep in mind that, instead of the variable Γ_4, we can introduce the quantity $\Gamma_5 = -\Gamma_1+\Gamma_2+2\Gamma_3$, the equation for which, as in the preceding section, will have the form

$$\Gamma_5'\sim\Gamma_5.$$

We again draw the trajectories in the plane of

$$u=\Gamma_4/\Gamma_1, \quad v=\Gamma_3/\Gamma_1,$$

denoting the direction of increasing ξ (or of decrease of the positive vertex Γ_1) by arrows. In this plane the special points have the coordinates (cf. Fig. 2): $O(00)$, $A_1(-\frac{2}{3}0)$, $A_2(-10)$, $B_1(0\frac{1}{2})$ and $B_2(01)$. It can be seen from Fig. 2 that, again, all the fixed points are unstable and, therefore, second-order phase transitions are again impossible.

Violations of the positive-definiteness, and with them the first-order transitions, again occur for three possible configurations of the $\mathbf{s}_i$:

$$s_1\neq 0, \ s_2=0 \quad \text{or} \quad s_1=0, \ s_2\neq 0; \tag{I}$$

$$s_1=\pm s_2; \tag{II}$$

$$\mathbf{s}_1\perp\mathbf{s}_2, \ s_1=s_2. \tag{III}$$

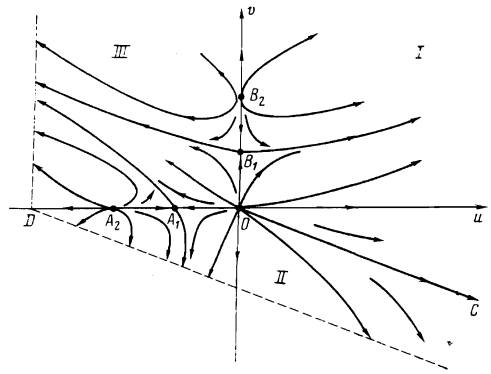

FIG. 2.

The equations of the stability boundaries now have the form

$$\Gamma_1\geqslant 0 \ \ (\mathrm{I}); \quad \Gamma_1+\Gamma_2+2\Gamma_3\geqslant 0 \ \ (\mathrm{II}); \quad \Gamma_1+\Gamma_3\geqslant 0. \ \ (\mathrm{III}).$$

In the uv plane the boundary (I) again corresponds to an infinitely remote point, while the boundaries (II) and (III) correspond, respectively, to the dashed lines $u+2v+2\geqslant 0$ (II) and $u+2\geqslant 0$ (III).

From the region of initial values lying in that part of the plane which is bounded by the positive semi-axis v and the straight line OC, the integral curves go away to infinity, and this corresponds to a first-order transition to the state I. We note that the straight line OC is the separatrix $\Gamma_5=0$ (see above), having the form $u+2v=0$ in the variables u and v.

In the region bounded by the section OD of the abscissa axis, the separatrix OC and the straight line $u+2v+2=0$ parallel to the separatrix, the trajectories intersect this dashed straight line, i.e., a first-order transition to the state II occurs. Finally, in the half-strip $(v>0)$ between OD and the straight lines $u=0$ and $u+2=0$, the trajectories intersect the dashed line $u=-2$, at which a transition to the state III occurs.

4. THE TRANSITION IN MnO, TbSb AND OTHER SUBSTANCES

Finally, we shall consider the fairly well-studied transitions in MnO, NiO, MnSe,[4] α-MnS,[17], EuTe,[18] ErP, ErSb, TbAs, TbSb, TbP,[19] CeS, TbSe, NdSe and NdTe.[20] Like UO_2, all these substances have a face-centered cubic lattice (the group $O_h^5 - Fm3m$). The antiferromagnetic transition in them corresponds to the star $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $(\bar{\frac{1}{4}}\frac{1}{4}\frac{1}{4})$, $(\frac{1}{4}\bar{\frac{1}{4}}\frac{1}{4})$, $(\frac{1}{4}\frac{1}{4}\bar{\frac{1}{4}})$ and is described, correspondingly, by four vectors $\mathbf{s}_i$:

$$\begin{aligned}&\mathbf{s}_1=\mathbf{s}_{10}\cos\pi(x+y+z), \quad \mathbf{s}_2=\mathbf{s}_{20}\cos\pi(-x+y+z),\\ &\mathbf{s}_3=\mathbf{s}_{30}\cos\pi(x-y+z), \quad \mathbf{s}_4=\mathbf{s}_{40}\cos\pi(x+y-z).\end{aligned} \tag{14}$$

This 12-component representation decomposes into two irreducible representations: the four-dimensional representation formed by the projections of the vectors $\mathbf{s}_1$, $\mathbf{s}_2$, $\mathbf{s}_3$ and $\mathbf{s}_4$ on, respectively, the axes [111], $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$ (we denote these by s_{11}, s_{22}, s_{33} and s_{44}), and the eight-dimensional representation consisting of the remaining components of the vectors $\mathbf{s}_i$. The four-dimensional representation corresponds to the magnetic structure in TbAs, TbSb, TbP, CeS, TbSe, NdSe and

NdTe, and the eight-dimensional representation to the magnetic structure in MnO, NiO, MnSe, α-MnS, ErP, ErSb and EuTe.

With allowance for the second-order anisotropy the Landau free energy has the form

$$F=\tfrac{1}{2}\tau(s_1^2+s_2^2+s_3^2+s_4^2)+\tfrac{1}{2}a(s_{11}^2+s_{22}^2+s_{33}^2+s_{44}^2)$$
$$+\tfrac{1}{8}\Gamma_1(s_1^4+s_2^4+s_3^4+s_4^4)+\tfrac{1}{4}\Gamma_2(s_1^2s_2^2+s_1^2s_3^2+s_1^2s_4^2+s_2^2s_3^2+s_2^2s_4^2+s_3^2s_4^2)$$
$$+\tfrac{1}{2}\Gamma_3((s_1s_2)^2+(s_1s_3)^2+(s_1s_4)^2+(s_2s_3)^2+(s_2s_4)^2+(s_3s_4)^2)$$
$$+\Gamma_4((s_1s_2)(s_3s_4)+(s_1s_3)(s_2s_4)+(s_1s_4)(s_2s_3)). \qquad (15)$$

When $a\to-\infty$ only the components s_{11}, s_{22}, s_{33} and s_{44} will be nonzero. This case, corresponding to TbAs, etc., was considered by us earlier.[3] The correspondence between the notation used there and the notation in the present article is given by the formulas

$$s_1=3^{-1/2}\eta_1[111],\ s_2=3^{-1/2}\eta_2[\bar{1}11],\ s_3=3^{-1/2}\eta_3[1\bar{1}1],\ s_4=3^{-1/2}\eta_4[11\bar{1}];$$
$$\gamma_1=3\Gamma_1,\quad \gamma_2=\Gamma_2+{}^2/_3\Gamma_3,\quad \gamma_3=-{}^1/_3\Gamma_4,\quad \tau\to\tau+a.$$

The case $a\to+\infty$, when only the eight-dimensional representation is nonzero (the transition in MnO, etc.), was considered in the aforementioned work of Bak *et al.*[11] We therefore confine ourselves to the case of small a, when the character of the transition is determined by all 12 components of the vectors $\mathbf{s}_i$.

The RG equations now have the form

$$-\Gamma_1'=11\Gamma_1^2+9\Gamma_2^2+12\Gamma_2\Gamma_3+12\Gamma_3^2,$$
$$-\Gamma_2'=10\Gamma_1\Gamma_2+4\Gamma_1\Gamma_3+10\Gamma_2^2+8\Gamma_2\Gamma_3+4\Gamma_3^2+8\Gamma_4^2,$$
$$-\Gamma_3'=4\Gamma_1\Gamma_3+8\Gamma_2\Gamma_3+14\Gamma_3^2+18\Gamma_4^2, \qquad (16)$$
$$-\Gamma_4'=4\Gamma_4(3\Gamma_2+8\Gamma_3).$$

In view of the large number of unknown functions, the study of these equations is cumbersome and loses clarity. We therefore confine ourselves merely to describing the final results, after first noting a fact that is extremely useful in the investigation. Namely, it follows from (16) that, for the two quantities $\Gamma_{5,6}=-\Gamma_1+\Gamma_2+2\Gamma_3\mp2\Gamma_4$, we have the equations

$$-\Gamma_{5,6}'=\Gamma_{5,6}(11\Gamma_1+\Gamma_2+10\Gamma_3\mp22\Gamma_4).$$

These relations substantially simplify the determination and investigation of the fixed points of the system (16).

As before, investigation of the system (16) shows that all its fixed points are unstable. Thus, taking even only one exchange interaction into account makes second-order transitions impossible. This confirms the conclusion reached earlier by us[3] and by Bak *et al.*[11] for large anisotropy. Finally, we shall list the possible types of first-order transitions.

I. Transitions of the type $s_1\neq0$, $s_2=s_3=s_4=0$. It is this type of transition that has been observed in all the aforementioned experiments. For $a<0$ only the component s_{11} (s_{22}, s_{33}, s_{44}, respectively) is nonzero, and for $a>0$ the vector $\mathbf{s}_1$ is perpendicular to the [111] axis. Thus, the case of small anisotropies explains the well-known transitions in MnO, etc., and in TbAs, etc.

In addition there are a number of possibilities not yet observed experimentally:

II. Structures of the type $s_1=0$, $\mathbf{s}_2\perp\mathbf{s}_3\perp\mathbf{s}_4$, $s_2=s_3=s_4$;

III. $\mathbf{s}_1=\pm\mathbf{s}_2=\pm\mathbf{s}_3=\pm\mathbf{s}_4$;

IV. $\mathbf{s}_1=\pm\mathbf{s}_2\perp\mathbf{s}_3=\pm\mathbf{s}_4$, $s_1=s_2=s_3=s_4$;

V. $\mathbf{s}_1+\mathbf{s}_2+\mathbf{s}_3+\mathbf{s}_4=0$, $s_1=s_2=s_3=s_4$.

In the latter case the vectors $\mathbf{s}_i$ can be visualized as directed along the four diagonals of the cube.

It is interesting to note that, as the extremal points of the fourth-order form in (15), the solutions I–V correspond to definite symmetry elements of the cubic group O, which is the symmetry group of the Landau energy (15). Thus, the solutions I and II have C_3 symmetry, the solutions III and IV have C_4 symmetry, and the solution V has the full symmetry of the group O.

Analogously, the solution I in both the preceding sections has C_4 symmetry, the solution II has C_3 symmetry, and the solution III has the full O symmetry.

5. CONCLUSION

It is natural to ask what relation the results obtained above can have to transitions in real three-dimensional space rather than in a fictitious space of dimensions $d\approx4$. The answer is that, no matter how the structure of the RG changes as the dimensionality is varied continuously from $d=4$ to $d=3$, "with fifty per cent probability" its fixed points, unstable for $d=4$, will remain unstable at $d=3$, and no new stable points will arise on the way. Therefore, it is certain that for the real $d=3$ there are systems (and UO_2, MnO, etc. are, "with fifty per cent probability," such systems) in which the fluctuations transform a second-order transition into a first-order transition.

The second conclusion of the theory for $d=4$ is the fact that the structure that arises as a result of a first-order transition is determined from the condition for the minimum of the Landau energy for a specified $s_0^2=\Sigma s_i^2$. It is reasonable to assume that, in essence, this situation also obtains in the three-dimensional case, when the s_0^2 that arises in the transition can, in principle, be large. The point is that the energy associated with the onset of magnetic order is, as a rule, small compared with the total energy of formation of the crystal. Therefore, we can assume that the free energy of the magnetic phase has the form of a certain function

$$F(I_1, I_2, \ldots),$$

where the I_i are the independent invariants which can be formed from the $\mathbf{s}_i$ for a given s_0^2, and the magnetic structures that arise are again determined from the minimum of F.

In practice, the number of invariants I_i can appreciably exceed the number of invariants appearing in the Landau expressions (2), (11) and (15). Although in the simple case of Sec. 3 there are no new invariants at all, inasmuch as

$$I_1=s_1^2s_2^2,\quad I_2=(\mathbf{s}_1\mathbf{s}_2)^2$$

exhaust all the possible invariants (for given $s_1^2+s_2^2$), in the case of UO_2 there are, e.g., the following independent fourth- and sixth-order invariants:

$$I_1=s_1^2s_2^2+s_1^2s_3^2+s_2^2s_3^2,\quad I_2=(\mathbf{s}_1\mathbf{s}_2)^2+(\mathbf{s}_1\mathbf{s}_3)^2+(\mathbf{s}_2\mathbf{s}_3)^2,\quad I_3=s_1^2s_2^2s_3^2,$$
$$I_4=(\mathbf{s}_1\mathbf{s}_2)(\mathbf{s}_1\mathbf{s}_3)(\mathbf{s}_2\mathbf{s}_3),\quad I_5=(\mathbf{s}_1\mathbf{s}_2)^2s_3^2+(\mathbf{s}_1\mathbf{s}_3)^2s_2^2+(\mathbf{s}_2\mathbf{s}_3)^2s_1^2.$$

In the case of MnO, etc., even the number of exchange invariants of sixth-order alone is extremely large.

*)See Phys. Rev. B13, 5065, 5078, 5086 (1976) (Transl. note).
[1)]The total free energy differs from (2) by a quantity $F_0(\tau)$, which gives the specific heat.
[2)]This situation must not be confused with that obtaining in the RG introduced by Wilson (cf., e.g.,[8]). There, the RG equations are written for other charges g. In our approximation, $g \sim \xi\Gamma$, and, in agreement with Wilson, g tends to constant values, proportional to ε, at the transition point.

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Size quantization and the surface states in semiconductors

V. A. Volkov and T. N. Pinsker

Institute of Radio Engineering and Electronics, USSR Academy of Sciences

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The boundary conditions that must be satisfied by the envelopes of the electron wave function on the three-dimensional-semiconductor surface, near which the potential sharply varies over atomic distances, are derived. These conditions are used to determine energy spectrum of a semiconducting film under some simplest cases. The dispersion equation thus obtained describes both size quantization levels and Tamm levels. A condition for existence of Tamm states is formulated and the behavior of the states with variation of film thickness is studied. A new length R is introduced which characterizes the surface properties and which may be large in narrow-band semiconductors. It is shown that the quasiclassical quantization law for the transverse quasimomentum component is not applicable to lower levels in thin films ($d \lesssim 2R$). The approach employed in the present investigation can be used to find the conditions of applicability of the zero boundary conditions for the envelopes, as well as to go beyond the scope of the effective-mass approximation and take the nonquadratic behavior of the real dispersion law into account.

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1. INTRODUCTION

It is known[1-4] that the limitation of the transverse motion of an electron in a film leads to quantization of the transverse component k_z of the quasimomentum and to a substantial change of the energy spectrum of the electrons as compared with the spectrum in bulky crystals. The rules for the quantization of k_z were first obtained within the framework of a quasi-classical approximation[1] and take in the isotropic case the form

$$k_z = \pi n/d, \tag{1}$$

where d is the film thickness and n is an integer.

To determine the lower levels of the size-effect quantization (SQ), an important factor in semimetallic and semiconducting films, it is necessary to solve the complete Schrödinger equation. It is convenient for this purpose to represent the wave function of the electron inside the film in the form[5]