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# Phase diagrams near the Lifshiftz point. II. Systems with cylindrical, hexagonal, and rhombohedral symmetry having an easy plane of magnetization

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Paramagnetic (I)-ferromagnetic (II)-helical (III) phase diagrams near a Lifshitz point are studied for systems with cylindrical, hexagonal, and rhombohedral symmetry having an easy plane of magnetization. We show that the II $\rightleftarrows$ III phase-transition line in these systems is not tangent to the order-disorder transition line at the Lifshitz point. We also show that the II $\rightleftarrows$ III phase transition is second order (but with some peculiar features) in the case of cylindrical symmetry and first order in the case of hexagonal or rhombohedral symmetry. These results differ from those obtained in the uniaxial case and also manifest a dependence on the symmetry of the system. The results for hexagonal systems are compared with experimental data for Gd-Dy, Gd-Sc, and Gd-Y alloys.

## I. INTRODUCTION

In our previous paper,[1] hereafter referred to as I, we studied the phase diagram near a Lifshitz point[2] for a system having a single easy axis of magnetization. In particular, we have shown that the lines of the I $\neq$ II, I $\neq$ III, and II $\neq$ III phase transitions (the notations I, II, III have been used to designate the paramagnetic, ferromagnetic, and sinusoidal phases, respectively) are tangent to each other at the Lifshitz point (see Fig. 1 in I) and that the II $\neq$ III phase transition is first order. Since there exists a variety of systems having an easy plane, rather than easy axis, of magnetization, it is of interest to develop the thermodynamics of the Lifshitz point for such systems and to compare the results with those obtained in the uniaxial case.

An easy plane is generally normal to a rotational axis of order $n>2$, which can be taken as the $z$ axis. The magnetization involved represents a two-component order parameter $\vec{M}=M_x\hat{x}+M_y\hat{y}$. One of the ordered phases (phase II) is ferromagnetic, with spontaneous magnetization parallel to a certain direction in the $xy$ plane, the other (phase III) is helical, with $\vec{M}$ rotating in the $xy$ plane as one moves along the $z$ direction. Since in the helical state $\vec{M}$ is a (periodic) function of $z$, it is essential to take into account $\vec{M}'$ and $\vec{M}''$ (the prime is used in our work to denote the differentiation of $\vec{M}$ and its components with respect to $z$) in the expansion of the free energy $F(\vec{M})$, when dealing with the vicinity of the Lifshitz point (see Refs. 1 and 2).

We demonstrate in this paper that the thermodynamical properties in this vicinity depend on the symmetry of the paramagnetic phase (phase I), namely, on the order of the rotational $z$ axis. In Sec. II we consider the case of cylindrical symmetry, which is characteristic of a system isotropic in the $xy$ plane. In Sec. III the case of hexagonal and rhombohedral symmetry is considered. We show that in the case of cylindrical symmetry the II $\neq$ III phase transition is second order (though with some peculiar features), while in the case of hexagonal or rhombohedral symmetry it is first order. As regards the shape of the phase transition lines, we show that in all the above cases the I $\neq$ II and I $\neq$ III phase transition lines have a common tangent at the Lifshitz point, as in the uniaxial case, whereas the II $\neq$ III phase transition line is not tangent to these two lines, as distinct from the uniaxial case. In Sec. IV we compare the results of Sec. III with experimental data for hexagonal binary systems Gd-Dy, Gd-Sc, and Gd-Y.

## II. CYLINDRICAL SYMMETRY

In dealing with cylindrical symmetry it is convenient to use the complex components

$$M_\xi=M_x+iM_y,\quad M_\eta=M_\xi^*, \tag{2.1}$$

which in their turn are related to the cylindrical components $M,\theta$ by the formulas

$$M_\xi=Me^{i\theta},\quad M_\eta=Me^{-i\theta}. \tag{2.2}$$

The free energy $F(\vec{M})$ must be invariant under rotation about the $z$ axis by an arbitrary angle $\phi$ ($M_\xi\rightarrow M_\xi e^{i\phi}$). Therefore, retaining in the expansion of $F(\vec{M})$ the terms pertinent to the Lifshitz-point problem, we have

$$F(\vec{M})=\int\left(\tfrac{1}{2}A_0M_\xi M_\eta+\tfrac{1}{4}BM_\xi^2M_\eta^2+\tfrac{1}{2}\alpha M_\xi'M_\eta'+\tfrac{1}{4}\beta M_\xi''M_\eta''\right)d^3r. \tag{2.3}$$

Here $B>0,\beta>0$, and the lines

$$A_0(P,T)=0 \tag{2.4}$$

and

$$\alpha(P,T)=0 \tag{2.5}$$

intersect at the Lifshitz point $(P_L, T_L)$. As in I, we ignore the dependence of $B, \beta$ on $P, T$ in the vicinity of $(P_L, T_L)$. The order-disorder transition line $T_\lambda(P)$ is given by the same equations as in the uniaxial case (see I, Sec. II): The part of this line lying in the region of $\alpha>0$ coincides with the line $T_0(P)$ defined by Eq. (2.4), and the part lying in the region of $\alpha<0$ is described by the equation

$$A_{k_0}=A_0-\alpha^2/2\beta=0\,. \tag{2.6}$$

The two parts of $T_\lambda(P)$ have a common tangent at $(P_L, T_L)$.

The equilibrium magnetization in the magnetically ordered state is determined by the minimization of the expression (2.3) at $T<T_\lambda(P)$. This leads to the variational equation

$$\tfrac{1}{2}\beta M_\xi''''-\alpha M_\xi''+A_0M_\xi+BM^2M_\xi=0 \tag{2.7}$$

(and a complex-conjugate equation for $M_\eta$). This equation has the exponential solutions

$$M_\xi(z)=M_k e^{i(kz+\phi)}, \tag{2.8}$$

with

$$M_k=(-A_k/B)^{1/2}, \tag{2.9}$$

where $A_k$ are defined by the equation

$$A_k=A_0+\alpha k^2+\tfrac{1}{2}\beta k^4 \tag{2.10}$$

[see I, Eq. (2.7)]. Note that these solutions are meaningful only for $A_k<0$. The values of $F(\vec{M})$ corresponding to these solutions are

$$F_k=-A_k^2/4B \tag{2.11}$$

(we have put the volume $V=1$ for short). In the state of thermodynamic equilibrium the value of $F(\vec{M})$ is equal to the smallest of $F_k$, i.e.,

$$F_{eq}=F_{min}=-A_{min}^2/4B; \tag{2.12}$$

$A_{min}$ is given by

$$A_{min}=\begin{cases}A_0 \text{ for } \alpha>0\\ A_{k_0} \text{ for } \alpha<0\,,\end{cases} \tag{2.13}$$

where

$$k_0=(-\alpha/\beta)^{1/2}. \tag{2.14}$$

It follows that in the region where $\alpha>0$ and $A_0<0$ the stable state of the system is ferromagnetic (phase II), and in the region where $\alpha<0$ and $A_{k_0}<0$ the stable state is helical (phase III). In phase II the equilibrium (spontaneous) magnetization is given by Eqs. (2.8), (2.9) with $k=0$

$$M_{\xi,eq}=M_{\xi II}=M_0e^{i\phi}\,. \tag{2.15}$$

It has an arbitrary direction in the $xy$ plane [arbitrary $\phi$ in (2.15)] and the magnitude

$$M_{II}=M_0=(-A_0/B)^{1/2}\approx(CB)^{-1/2}[T_0(P)-T]^{1/2} \tag{2.16}$$

[compare with Eq. (3.1) in I], where $C$ is the Curie-Weiss constant for the paramagnetic susceptibility. In phase III the equilibrium magnetization is given by

$$M_{\xi,eq}=M_{\xi III}=M_{k_0}e^{[\pm i(k_0z+\phi)]}, \tag{2.17}$$

with the magnitude

$$M_{III}=M_{k_0}=(-A_{k_0}/B)^{1/2}=(-A_0+\alpha^2/2\beta)^{1/2}B^{-1/2}\,. \tag{2.18}$$

The fact that $\phi$ in (2.17) is arbitrary reflects the invariance of $F(\vec{M})$ under arbitrary rotations of $\vec{M}$ in the $xy$ plane and arbitrary displacements along the $z$ axis.

The result expressed by Eqs. (2.17), (2.18) was obtained by comparing the values of $F(\vec{M})$ corresponding to the solutions (2.8) of Eq. (2.7). Generally speaking, Eq. (2.7) may also have other solutions, which cannot be expressed in a simple analytical form. Let us show that the allowance for the possibility of such solutions does not affect the result (2.17), (2.18). According to the argument in I, Sec. III, the asymptotic form of $M_{\xi III}(z)$ at $T\to T_\lambda(P)-0$ must be

$$[M_{\xi III}(z)]_{asym}=M_{k_0}e^{i(k_0z+\phi)}+M_{-k_0}e^{-i(k_0z+\psi)}, \tag{2.19}$$

where $M_{k_0}, M_{-k_0}$ must be determined by the minimization of the expression $F(M_{k_0}, M_{-k_0})$ obtained by substituting (2.19) for $M_\xi$ in (2.3). We have

$$F(M_{k_0},M_{-k_0})=\tfrac{1}{2}A_{k_0}(M_{k_0}^2+M_{-k_0}^2)+\tfrac{1}{4}B(M_{k_0}^4+M_{-k_0}^4+4M_{k_0}^2M_{-k_0}^2)\,. \tag{2.20}$$

The minimum of $F(M_{k_0}, M_{-k_0})$ corresponds to

$$M_{k_0}=(-A_{k_0}/B)^{1/2},\quad M_{-k_0}=0 \tag{2.21a}$$

or

$$M_{-k_0}=(-A_{k_0}/B)^{1/2},\quad M_{k_0}=0\,. \tag{2.21b}$$

Thus the asymptotic form of $M_{\xi III}(z)$ coincides with the *exact* solution (2.17), (2.18) of Eq. (2.7). Hence the latter does indeed minimize $F(\vec{M})$.

As follows from the above, the II $\rightleftarrows$ III phase transition line $T_H(P)$ is described by Eq. (2.5). This result differs substantially from that obtained in the uniaxial case (see I, Sec. III). The line $T_H(P)$ in the present case meets the line $T_\lambda(P)$ at an angle (see Fig. 1) rather than being tangent to it at $(P_L, T_L)$.

The wave number $k_0=(-\alpha/\beta)^{1/2}$ increases continuously from zero as the point $(P, T)$ on the phase diagram moves from the line $T_H(P)$ into phase

III. In the neighborhood of an arbitrary point $(P', T')$ on the line $T_H(P)$

$$k_0 \propto (P - P')^{1/2} \tag{2.22}$$

at $T = T'$, and

$$k_0 \propto (T - T')^{1/2} \tag{2.23}$$

at $P = P'$. As seen from Eqs. (2.15)–(2.18), not only $k_0$ but also the order parameter itself changes continuously in the II $\rightleftarrows$ III phase transition at any *fixed* point in space:

$$\lim_{T \to T_H(P)} M_{\xi III}(z; P, T) = M_{\xi II}(P, T_H(P)) \tag{2.24}$$

(on the assumption that the arbitrary phase $\phi$ is the same in $M_{\xi II}$ and $M_{\xi III}$). One might infer at first sight that this is a typical continuous phase transition. However, as pointed out by Shtrikman,[3] this continuity is not *uniform* throughout the system. Indeed, for a point $(P, T)$ in phase III arbitrarily close to a point $(P', T')$ on the line $T_H(P)$—so that $k_0$ is made arbitrarily small—one can find $z$ so large that $k_0 z \sim 1$, and the difference $M_{\xi III}(z; P, T) - M_{\xi II}(P', T')$ for such $z$ is *finite*. The fact that the system is actually finite ($|z| \leq L$) does not remove this difficulty, because the values of allowed $k$ are actually "quantized," and the smallest nonzero $k_0$ is of the order of $L^{-1}$, so that again for $z \sim L$ one has $k_0 z \sim 1$. In this respect the II $\rightleftarrows$ III phase transitions differ from typical continuous transitions, such as, e.g., the I $\rightleftarrows$ II and I $\rightleftarrows$ III phase transitions. [In the latter, as follows from Eqs. (2.15)–(2.18), $\vec{M}_{II}$ and $\vec{M}_{III}(z)$ tend to $\vec{M}_I = 0$ uniformly throughout the system when $T \to T_\lambda(P) - 0$.] In our opinion, it would be appropriate to term the II $\rightleftarrows$ III phase transitions "quasicontinuous."

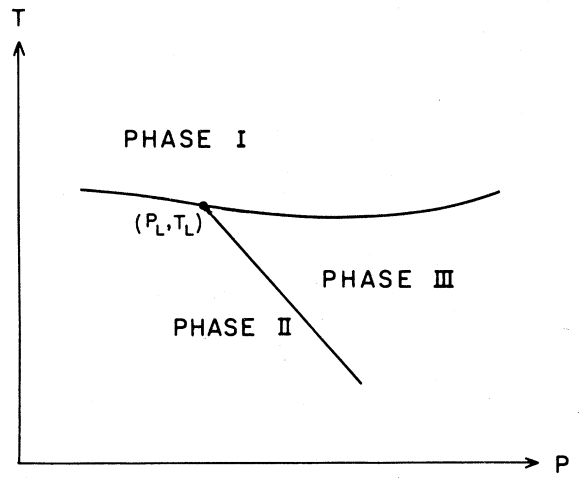


FIG. 1. Form of the phase diagram near a Lifshitz point $(P_L, T_L)$ in the case of an easy plane of magnetization in systems with cylindrical, hexagonal, or rhombohedral symmetry.

Let us now find the changes of thermodynamic quantities taking place in the II $\rightleftarrows$ III phase transitions. According to (2.12), (2.13), we can write for $F_{eq}$ in phases II and III, respectively,

$$F_{II} = -A_0^2/4B, \tag{2.25}$$

$$F_{III} = -A_{k_0}^2/4B = -(A_0 - \alpha^2/2\beta)^2/4B. \tag{2.26}$$

The corresponding entropies are

$$S_{II} = -\frac{\partial F_{II}}{\partial T} = \frac{A_0}{2B}\frac{\partial A_0}{\partial T}, \tag{2.27}$$

$$S_{III} = -\frac{\partial F_{III}}{\partial T} = \frac{A_0 - \alpha^2/2\beta}{2B}\left(\frac{\partial A_0}{\partial T} - \frac{\alpha}{\beta}\frac{\partial \alpha}{\partial T}\right). \tag{2.28}$$

It follows that the entropy changes continuously as the line $T_H(P)$ is crossed ($\alpha = 0$ on this line).

Neglecting the second derivatives $\partial^2 A_0/\partial T^2$, $\partial^2 \alpha/\partial T^2$, we obtain for the specific heat (at constant $P$)

$$c_{II} = \tfrac{1}{2} TB^{-1}\left(\frac{\partial A_0}{\partial T}\right)^2, \tag{2.29}$$

$$c_{III} = \frac{T}{2B}\left(\frac{\partial A_0}{\partial T} - \frac{\alpha}{\beta}\frac{\partial \alpha}{\partial T}\right)^2 - \frac{T}{2B\beta}\left(\frac{\partial \alpha}{\partial T}\right)^2\left(A_0 - \frac{\alpha^2}{2\beta}\right). \tag{2.30}$$

It follows that the specific heat experiences a jump on the line $T_H(P)$:

$$\Delta c = (c_{III} - c_{II})_{\alpha=0} = -T(2B\beta)^{-1}\left(\frac{\partial \alpha}{\partial T}\right)^2 A_0. \tag{2.31}$$

For points $(P, T)$ on this line that are sufficiently close to $(P_L, T_L)$,

$$\Delta c \propto A_0 \propto T - T_L \propto P - P_L. \tag{2.32}$$

Observe that the change in the specific heat is *positive* for the II $\to$ III phase transition, where the symmetry *decreases*. This coincides with Landau's result[4] for continuous phase transitions. In a similar manner one can show that $\partial F/\partial P$ (which represents the volume of the system if $P$ denotes pressure) is continuous on the line $T_H(P)$, whereas $\partial^2 F/\partial P^2$ and $\partial^2 F/\partial P \partial T$ (which represent, respectively, the isothermal compressibility and the coefficient of thermal expansion if $P$ is pressure) are discontinous. In this respect the II $\rightleftarrows$ III phase transitions are typical *second-order* transitions according to Ehrenfest's classification.

Further, let us find the second variation of $F(\vec{M})$ for the ferromagnetic state,

$$\delta^{(2)} F_{(f)} \equiv \delta^{(2)} F(\vec{M}_{II}, \delta\vec{M}). \tag{2.33}$$

Expanding $\delta M_\xi = \delta M_x + i\delta M_y$ in Fourier series

$$\delta M_\xi = \sum_k (\delta M_{xk} + i\,\delta M_{yk}) e^{ikz}, \tag{2.34}$$

where

$$\delta M_{x,-k} = \delta M_{xk}^*, \quad \delta M_{y,-k} = \delta M_{yk}^*, \tag{2.35}$$

and for convenience putting $\phi = 0$ in (2.15), we obtain with the aid of (2.3), (2.10), (2.15), and (2.16)

$$\delta^{(2)} F_{(f)} = \frac{1}{2} \sum_k (A_k - 3A_0) \left| \delta M_{xk} \right|^2 + \frac{1}{2} \sum_k (A_k - A_0) \left| \delta M_{yk} \right|^2 . \tag{2.36}$$

Let us now consider $\delta^{(2)} F_{(f)}$ at some point $(P, T)$ where $\alpha < 0$. Putting in (2.36) $\delta M_{xk} = 0$ for all $k$ and $\delta M_{yk} = 0$ for $k \neq k_0$, we have

$$\delta^{(2)} F_{(f)} = \tfrac{1}{2}(A_{k_0} - A_0) \left| \delta M_{yk_0} \right|^2 < 0 . \tag{2.37}$$

This means that the ferromagnetic state described by Eqs. (2.15), (2.16) does not correspond even to a local minimum of $F(\vec{M})$ at those $(P, T)$ where $\alpha < 0$ i.e., this state is not metastable in the region where phase III is stable. As for the helical state, it is altogether meaningless to speak of its metastability in the region where $\alpha > 0$, since its wave number $k_0$ is not defined in this region. The observed property of absence of metastability is also characteristic of second-order phase transitions.

One can use the expression (2.36) for the evaluation of the thermodynamic fluctuations of Fourier components of $M(z)$ in the phase II. According to standard formulas of statistical mechanics,[4] we obtain for the mean-square fluctuations of $M_{xk}, M_{yk}$:

$$\langle \left| \delta M_{xk} \right|^2 \rangle = \frac{k_B T}{A_k - 3A_0} = \frac{k_B T}{-2A_0 + \alpha k^2 + \frac{1}{2}\beta k^4}, \tag{2.38}$$

$$\langle \left| \delta M_{yk} \right|^2 \rangle = \frac{k_B T}{A_k - A_0} = \frac{k_B T}{\alpha k^2 + \frac{1}{2}\beta k^4}, \tag{2.39}$$

where $k_B$ is the Boltzmann constant. We see that formally the fluctuation $\langle \left| \delta M_{y0} \right|^2 \rangle = \infty$, as should be expected, since the variation $\delta\vec{M} = \delta M_{y0}\hat{y}$ is equivalent to infinitesimal rotation of $\vec{M}_{II} = M_0\hat{x}$ in the $xy$ plane and $F(\vec{M})$ is invariant under such rotation. This singularity exists throughout phase II and is *not* a "critical phenomenon," in the sense that it is unrelated to the existence of phase transitions in the system. On the other hand, the divergence of $\langle \left| \delta M_{x0} \right|^2 \rangle = -k_B T/2A_0$ at $T \to T_0(P)$ is the well-known critical singularity[5,6] associated with the existence of a continuous I $\rightleftarrows$ II phase transition at $T = T_0(P)$. As can be observed from Eqs. (2.38), (2.39), there is no specific singularity associated with the II $\rightleftarrows$ III phase transition: $A_0$ tends to a finite negative value as $T \to T_H(P)$, and all the fluctuations but $\langle \left| \delta M_{y0} \right|^2 \rangle$ remain finite on the line $T_H(P)$. In this respect the II $\rightleftarrows$ III phase transitions are "noncritical" second-order transitions. The "noncritical" character of these transitions is probably associated with their "quasicontinuity" mentioned above.

In concluding this section let us find the magnetic susceptibility in phase III with respect to a homogeneous magnetic field parallel to the $xy$ plane. For definiteness we shall take the field to be parallel to the $x$ axis. In order to find the reciprocal susceptibility $\chi_{III}^{-1}$, one has to evaluate the second variation $\delta^{(2)} F(\vec{M}, \delta\vec{M})$ for $\vec{M} = \vec{M}_{III}$ and $\delta\vec{M} = \delta M\hat{x}$, where $\delta M$ is independent of coordinates. A simple calculation with the help of Eqs. (2.3), (2.17), (2.18) yields in this case.

$$\delta^{(2)} F = \tfrac{1}{2}(A_0 - 2A_{k_0})\,\delta M^2 , \tag{2.40}$$

whence

$$\chi_{III}^{-1} = A_0 - 2A_{k_0} . \tag{2.41}$$

This result is exactly the same as in the uniaxial case [see I, Eq. (4.3)]. In particular, on the line $T_\lambda(P)$ (at $P > P_L$)

$$\chi_{III}^{-1} = \chi_I^{-1} = A_0 = C[T_\lambda(P) - T_0(P)] = 2C\gamma^{-1}(P - P_L)^{-2} , \tag{2.42}$$

with $\gamma$ defined in I, Eq. (2.16).

In phase II the longitudinal magnetic susceptibility is given by

$$\chi_{II}^{-1} = -2A_0 . \tag{2.43}$$

Hence on the line $T_H(P)$, where $A_{k_0} = A_0$,

$$\chi_{II}^{-1} = 2\chi_{III}^{-1} = -A_0 \propto T - T_L \propto P - P_L . \tag{2.44}$$

## III. HEXAGONAL AND RHOMBOHEDRAL SYMMETRY

The form of the expansion of $F(\vec{M})$ for a rhombohedral crystal is virtually the same as for a hexagonal one. Indeed, this form is determined by the symmetry of the paramagnetic phase, which contains time inversion. The latter changes the sign of $\vec{M}$ and thereby doubles the number of equivalent positions of $\vec{M}$ in the $xy$ plane from three to six. In this respect the combination of a threefold axis with time inversion is equivalent to the presence of a sixfold axis. We shall therefore speak only of hexagonal symmetry.

The free energy must be invariant under the rotation by $\frac{1}{3}\pi$ about the $z$ axis, which transforms $M_\xi$ into $M_\xi e^{i\pi/3}$. The only fourth-order term invariant under this transformation is $M_\xi^2 M_\eta^2$. Hence to the fourth order in $\vec{M}$ the expansion of $F(\vec{M})$ for a hexagonal crystal has the same form (2.3) as the free energy of a two-dimensionally isotropic system considered in Sec. II. The anisotropy (depend-

ence on $\theta$) appears only in the sixth order in $\vec{M}$: besides the isotropic invariant $M_\xi^3 M_\eta^3 = M^6$ there are two additional hexagonal invariants:

$$M_\xi^6 + M_\eta^6 = 2M^6 \cos 6\theta \tag{3.1a}$$

and

$$i(M_\eta^6 - M_\xi^6) = 2M^6 \sin 6\theta\,. \tag{3.1b}$$

In order to find the effect of hexagonal anisotropy upon the phase diagram near $(P_L, T_L)$, one must therefore expand $F(\vec{M})$ to the sixth order in $\vec{M}$. For simplicity we shall consider only those hexagonal point groups that contain the transformation $M_\xi \to M_\eta$. The latter can be represented by the rotation by the angle $\pi$ about the $x$ axis or by the reflection in the $yz$ plane. In this case the invariant (3.1b) does not exist, and the expansion of $F(\vec{M})$ to the sixth order in $\vec{M}$ has the form

$$F(\vec{M}) = F^{(0)}(\vec{M}) + \frac{1}{6}\int [C_1 M_\xi^3 M_\eta^3 + \tfrac{1}{2}C_2(M_\xi^6 + M_\eta^6)]d^3r\,, \tag{3.2}$$

where $F^{(0)}(\vec{M})$ is given by the expression (2.3). (In order to distinguish in this section the quantities referring to the case of cylindrical symmetry from analogous quantities referring to the case of hexagonal symmetry, we shall add the superscript $^{(0)}$ to the notations of the former.)

Equations (2.4) and (2.6) describing the two parts of the order-disorder transition line $T_\lambda(P)$ obviously remain valid in the present case. In phase II, where $\vec{M}' = 0$, the expansion (3.2) takes the form

$$F(\vec{M}) = F(M,\theta) = \tfrac{1}{2}A_0 M^2 + \tfrac{1}{4}BM^4 + \tfrac{1}{6}(C_1 + C_2\cos 6\theta)M^6\,. \tag{3.3}$$

The minimization of $F(M,\theta)$ with respect to $\theta$ at fixed $M$ yields the following values of $\theta$:

$$\theta = \tfrac{1}{3}n\pi\,, n = 0, 1, \ldots \text{ if } C_2 < 0 \tag{3.4a}$$

$$\theta = \tfrac{1}{6}\pi + \tfrac{1}{3}n\pi\,, n = 0, 1, \ldots \text{ if } C_2 > 0\,. \tag{3.4b}$$

Equation (3.4a) describes six possible directions of $\vec{M}_{II}$ that are crystallographically equivalent to the $x$ direction. Correspondingly, Eq. (3.4b) describes six directions equivalent to the $y$ direction. Substituting any one of the values of $\theta$ from (3.4) into (3.3), one obtains

$$F = F(M) = \tfrac{1}{2}A_0 M^2 + \tfrac{1}{4}BM^4 + \tfrac{1}{6}(C_1 - |C_2|)M^6\,. \tag{3.5}$$

($C_1 - |C_2|$ must be positive to ensure the thermodynamic stability of the system against infinite increase of $M$.) The minimization of the expression (3.5) yields

$$M_{II} = \left(\frac{-B + [B^2 - 4A_0(C_1 - |C_2|)]^{1/2}}{2(C_1 - |C_2|)}\right)^{1/2}. \tag{3.6}$$

Sufficiently close to the line $T_0(P)$, so that

$$A_0 C_1/B^2 \ll 1\,,\quad A_0|C_2|/B^2 \ll 1\,, \tag{3.7}$$

one obtains from (3.6)

$$M_{II} = M_{II}^{(0)} + \Delta M\,,\quad |\Delta M| \ll M_{II}^{(0)}\,, \tag{3.8}$$

where $M_{II}^{(0)}$ is given by Eq. (2.16). As should be expected, the sixth-order terms in $F(\vec{M})$ may be considered as a small perturbation at $T$ sufficiently close to $T_0(P)$.

Substituting the expression (3.6) for $M$ in (3.5), one finds

$$F_{II} = \frac{B^3 - 6BA_0(C_1 - |C_2|) - [B^2 - 4A_0(C_1 - |C_2|)]^{3/2}}{24(C_1 - |C_2|)^2}\,. \tag{3.9}$$

Under the conditions (3.7) one can write

$$F_{II} = F_{II}^{(0)} - \frac{A_0^3(C_1 - |C_2|)}{6B^3} + O(A_0^4) \tag{3.10}$$

where $F_{II}^{(0)}$ is given by Eq. (2.25). Observe that the main correction to $F_{II}^{(0)}$ in (3.10) is obtained by the substitution of $M_{II}^{(0)}$ for $M$ in the sixth-order term in (3.5), or more generally, by the substitution of $\vec{M}_{II}^{(0)}$ for $\vec{M}$ in the sixth-order term in the expansion (3.2) of $F(\vec{M})$.

Let us now consider phase III. The variational equation for the determination of the components $M_{\xi III}, M_{\eta III} = M_{\xi III}^*$ of $\vec{M}_{III}$ is

$$\tfrac{1}{2}\beta M_\xi'''' - \alpha M_\xi'' + A_0 M_\xi + BM^2 M_\xi = -C_1 M^4 M_\xi - C_2 M_\eta^5\,. \tag{3.11}$$

Sufficiently close to the I $\rightleftarrows$ III phase transition line

$$M_{\xi III} = M_{\xi III}^{(0)} + \Delta M_\xi\,,\quad |\Delta M_\xi| \ll M_{III}^{(0)} \tag{3.12}$$

where $M_{\xi III}^{(0)}$ and $M_{III}^{(0)}$ are given by Eqs. (2.17) and (2.18). Substituting (3.12) into (3.2), one obtains

$$F_{III} = F_{III}^{(0)} + \delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M}) + \cdots - A_{k_0}^3 C_1/6B^3\,, \tag{3.13}$$

where $F_{III}^{(0)}$ is given by Eq. (2.26), and $\delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M})$ is the second variation of $F^{(0)}(\vec{M})$ corresponding to the variation $\Delta\vec{M}$ of $\vec{M}$ for $\vec{M} = \vec{M}_{III}$. [$\delta^{(1)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M}) = 0$, since $\vec{M} = \vec{M}_{III}^{(0)}$ corresponds to the minimum of $F^{(0)}(\vec{M})$.] The last term in (3.13) represents the contribution to $F_{III}$ arising from the sixth-order term in (3.2), which is evaluated with neglect of $\Delta\vec{M}$ in comparison with $\vec{M}_{III}^{(0)}$. By analogy with (3.10), one may expect that

$$|\delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M})| \ll -A_{k_0}^3 C_1/B^3\,, \tag{3.14}$$

so that

$$F_{III} \approx F_{III}^{(0)} - A_{k_0}^3 C_1/6B^3 . \tag{3.15}$$

Let us prove the relation (3.14). According to Eqs. (2.3), (2.17) and (2.18),

$$\delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M}) = \int \{\tfrac{1}{2}A_0 \Delta M_\xi \Delta M_\eta + \tfrac{1}{4}B[(M_{\eta III}^{(0)})^2(\Delta M_\xi)^2 + (M_{\xi III}^{(0)})^2(\Delta M_\eta)^2 + 4(M_{III}^{(0)})^2 \Delta M_\xi \Delta M_\eta] + \tfrac{1}{2}\alpha \Delta M_\xi' \Delta M_\eta' + \tfrac{1}{4}\beta \Delta M_\xi'' \Delta M_\eta''\} d^3r . \tag{3.16}$$

On the other hand, substituting $M_{\xi III}$ from (3.12) for $M_\xi$ in Eq. (3.11), we get the following equation for $\Delta\vec{M}$:

$$\tfrac{1}{2}\beta \Delta M_\xi'''' - \alpha \Delta M_\xi'' + [A_0 + 2B(M_{III}^{(0)})^2]\Delta M_\xi + B(M_{\xi III}^{(0)})^2 \Delta M_\eta = -C_1(M_{III}^{(0)})^4 M_{\xi III}^{(0)} - C_2(M_{\eta III}^{(0)})^5 . \tag{3.17}$$

In deriving Eq. (3.17) from Eq. (3.11) we have neglected the terms of the second and higher orders in $\Delta\vec{M}$ appearing on the left-hand side of the equation, as well as the terms of the first and higher orders in $\Delta\vec{M}$ on the right-hand side of the equation. Let us now multiply Eq. (3.17) by $\frac{1}{4}\Delta M_\eta$ and add to the result its complex conjugate. Integrating the resulting equation over the volume of the crystal and comparing with Eq. (3.16), we find

$$\delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M}) = -\tfrac{1}{4}C_1(M_{III}^{(0)})^4 \int (M_{\xi III}^{(0)} \Delta M_\eta + \text{c.c.}) d^3r - \tfrac{1}{4}C_2 \int [(M_{\eta III}^{(0)})^5 \Delta M_\eta + \text{c.c.}] d^3r . \tag{3.18}$$

Since $|\Delta\vec{M}| \ll M_{III}^{(0)}$, it follows from (3.18) that

$$|\delta^{(2)}F^{(0)}(\vec{M}_{III}^{(0)}, \Delta\vec{M})| \ll \tfrac{1}{2}(C_1 + |C_2|)(M_{III}^{(0)})^6 < C_1(M_{III}^{(0)})^6 ,$$

which, in view of (2.18), proves the relation (3.14).

Comparing (3.10) with (3.15), we see that the II $\rightleftarrows$ III phase transition line $T_H(P)$, on which necessarily

$$F_{II} = F_{III} , \tag{3.19}$$

does not coincide with the line $T_H^{(0)}(P)$ given by Eq. (2.5). In the vicinity of $(P_L, T_L)$ where the conditions (3.7) are fulfilled, the equation of the line $T_H(P)$ is obtained by substituting (3.10) and (3.15) into Eq. (3.19), whence

$$A_0^2 + \frac{2A_{k_0}^3(C_1 - |C_2|)}{3B} = A_{k_0}^2 + \frac{2A_{k_0}^3 C_1}{3B} . \tag{3.20}$$

Assuming that the line $T_H(P)$ is only slightly displaced with respect to the line $T_H^{(0)}(P)$, so that

$$\alpha^2/\beta \ll A_0 \approx A_{k_0} \tag{3.21}$$

on the line $T_H(P)$, we get from (3.20)

$$\alpha = A_0(2\beta|C_2|/3B^2)^{1/2} . \tag{3.22}$$

In view of (3.7), the result (3.22) is consistent with the assumption (3.21). From (3.22) one readily obtains

$$\left(\frac{dT_H}{dP}\right)_{P=P_L} = \frac{(dT_H^{(0)}/dP)_{P=P_L} - v(dT_0/dP)_{P=P_L}}{1 - v} , \tag{3.23}$$

where

$$v = \left(\frac{2\beta|C_2|}{3B^2}\right)^{1/2} \left[\frac{\partial A_0}{\partial T}\left(\frac{\partial \alpha}{\partial T}\right)^{-1}\right]_{P, T=P_L, T_L} . \tag{3.24}$$

Equations (3.23), (3.24) show that on neglecting the anisotropy (i.e., on putting $C_2 = 0$) the line $T_H(P)$, coincides with the line $T_H^{(0)}(P)$, as should be expected. The presence of hexagonal anisotropy *displaces* the II $\rightleftarrows$ III phase transition line into the region of $\alpha < 0$. Accordingly, phase II partially extends into this region. Equation (3.23) also shows that the line $T_H(P)$ meets the line $T_\lambda(P)$ at an angle (see Fig. 1), as in the case of cylindrical symmetry, rather than being tangent to it at $(P_L, T_L)$, as in the uniaxial case [see I, Eq. (3.11) and Fig. 1].

The line $T_H(P)$ is determined from the condition of II-III phase equilibrium; hence the II $\rightleftarrows$ III phase transitions must be *first order*. Indeed, using the expressions (3.10) for $F_{II}$ and (3.15) for $F_{III}$, we find that the jump in the entropy on the line $T_H(P)$ is

$$\Delta S = (S_{III} - S_{II})_{T_H(P)} = \left[\frac{1}{3B}\frac{\partial A_0}{\partial T} - (6\beta|C_2|)^{-1/2}\frac{\partial \alpha}{\partial T}\right]\frac{A_0^2|C_2|}{B^2} , \tag{3.25}$$

where the terms of the third and higher orders in $A_0$ and $\alpha$ have been neglected. It follows from (3.25) that at a point $(P, T)$ on the line $T_H(P)$

$$\Delta Q = T\Delta S \propto (T - T_L)^2 \propto (P - P_L)^2 , \tag{3.26}$$

where $\Delta Q$ is the latent heat of the II $\rightleftarrows$ III phase transition. We see that the decrease of the symmetry of the paramagnetic phase from cylindrical to hexagonal effects in the change of the order of the II $\rightleftarrows$ III phase transition from second to first.

The helical wave number $k_0$ changes abruptly on the line $T_H(P)$ from zero in phase II to the value

$$k_0=(-\alpha/\beta)^{1/2}=(-A_0)^{1/2}(2|C_2|/3\beta B^2)^{1/4}\propto(T-T_L)^{1/2} \tag{3.27}$$

in phase III when the line $T_H(P)$ is crossed. At the same time $k_0$ increases continuously along this line [as well as along the line $T_\lambda(P)$] from the zero value at $(P_L, T_L)$.

As in the uniaxial case (see I, Appendix B), we can find the metastability region for the ferromagnetic state. Putting for definiteness $C_2>0$ and choosing the $x$ axis along the vector $\vec{M}_{II}$, we find the corresponding second variation of $F(\vec{M})$:

$$\begin{aligned}\delta^{(2)}F_{(f)}&\equiv\delta^{(2)}F(\vec{M}_{II},\delta\vec{M})\\&=\frac{1}{2}\sum_k[A_k+3BM_{II}^2+5(C_1-|C_2|)M_{II}^4]|\delta M_{xk}|^2+\frac{1}{2}\sum_k(A_k+BM_{II}^2+5|C_2|M_{II}^4)|\delta M_{yk}|^2\\&=\frac{1}{2}\sum_k[A_k-3A_0+O(A_0^2)]|\delta M_{xk}|^2+\frac{1}{2}\sum_k[A_k-A_0+6A_0^2|C_2|/B^2+O(A_0^3)]|\delta M_{yk}|^2.\end{aligned} \tag{3.28}$$

The quadratic form (3.28) is positive definite in the region of $\alpha<0$, $A_0<0$, if

$$A_{k_0}-A_0+6A_0^2|C_2|/B^2>0. \tag{3.29}$$

Hence the ferromagnetic state is metastable in the region between the line $T_H(P)$ and the line $T_f(P)$ determined by the equation

$$A_0-A_{k_0}=6A_0^2|C_2|/B^2, \tag{3.30}$$

or

$$\alpha=A_0(12\beta|C_2|/B^2)^{1/2}. \tag{3.31}$$

By analogy with (3.23), one gets

$$\left(\frac{dT_f}{dP}\right)_{P=P_L}=\frac{(dT_H^{(0)}/dP)_{P=P_L}-3\sqrt{2}v(dT_0/dP)_{P=P_L}}{1-3\sqrt{2}v}. \tag{3.32}$$

The problem of finding the metastability region for the helical state is very complicated: the corresponding second variation $\delta^{(2)}F_{(h)}\equiv\delta^{(2)}F(\vec{M}_{III},\delta\vec{M})$ is nondiagonal in the variables $\delta M_{xk}$, $\delta M_{yk}$ [see, e.g., Eq. (B7) in I], and furthermore, a cutoff similar to that made in I is unjustified here because in the region between the lines $T_H(P)$ and $T_H^{(0)}(P)$, $A_k<0$ for $k\gg k_0$. We shall therefore not treat this problem here.

Finally, the formulas (2.41)–(2.43) for $\chi^{-1}$ obtain also in the present case, because the contributions to $\chi_{II}^{-1}$ and $\chi_{III}^{-1}$ due to the sixth-order terms in the expansion of $F(\vec{M})$ are negligible if the conditions (3.7) are fulfilled. Then, in view of (3.21), one again arrives at Eq. (2.44) on the line $T_H(P)$.

## IV. COMPARISON WITH EXPERIMENT

It is interesting to compare the results of Sec. III with experimental data for the Gd-Dy,[7–9] Gd-Sc,[10,11] and Gd-Y,[11,12] binary alloy systems. All of these alloys possess the hcp structure, and their $x-T$ diagrams ($x$ is the concentration of one of the components) exhibit a triple point where the paramagnetic, ferromagnetic, and helical phases meet. We use the term "triple point" rather than "Lifshitz point" in this connection, because the latter is associated with a particular theoretical model which may or may not be applicable to the phenomena in question. In particular, the theory developed in our work seems to be inapplicable to the Gd-Sc binary system, in view of the neutron diffraction data concerning this system.[11] According to these data, the spin alignment in the ferromagnetic phase near the triple point in this system is parallel to hexagonal $c$ axis. This means, in terms of our work, that the helical to ferromagnetic phase transitions in the Gd-Sc alloys are accompanied by the transition from an easy plane to an easy axis of magnetization, whereas the theory in this paper is developed for the cases where the vector of magnetization lies in the easy plane in both of the ordered phases. On the other hand, the neutron diffraction data for the Gd-Y binary system[11] show that the spins are aligned at an angle of 70° with the $c$ axis in the ferromangetic phase near the triple point. This fact is suggestive of the possible relevance of our theory to the experimental situation in the Gd-Y system, if one regards the small deviation of the spin direction from the hexagonal $ab$ plane as a secondary effect. No precise data on the magnetic structure of the Gd-Dy binary alloys are, to our knowledge, as yet available. However, the fact that the spin arrangement in pure ferromagnetic Dy is parallel to the hexagonal $ab$ plane[13] suggests that this arrangement exists also in the vicinity of the triple point of the Gd-Dy system.

For comparison of the experimental phase diagrams obtained for the Gd-Dy (see Fig. 3 in Ref. 8, or Fig. 1 in Ref. 9) and Gd-Y (see Fig. 7 in Ref. 12) systems with Fig. 1 of our work, the concentration of Dy in the Gd-Dy alloys and of Y in the Gd-Y alloys must be identified with the parameter $P$ figuring in our work. This comparison

shows that there is a certain qualitative agreement between our theory and the experiments: For instance, the extrapolations of the experimental ferromagnetic to paramagnetic phase transition curves beyond the triple points lie below the paramagnetic to helical phase transition curves and above the helical to ferromagnetic phase transition curves, in agreement with the results of this paper. [Incidentally the phase diagram for the Gd-Sc alloys (see Fig. 4 in Ref. 10) exhibits the same property.] Also, all the ferromagnetic-helical phase transitions in question were found to be first order. However, the density of experimental points on the phase transition curves in the immediate vicinity of the triple points in question is insufficient for testing our results concerning the geometry of this vicinity (intersection or tangency of different transition lines). To facilitate a dependable delineation of experimental phase transition curves in this region, precise measurements of phase transition temperatures for a larger variety of concentrations in the ranges of interest (between 30 at.% and 70 at.% of Dy in the Gd-Dy system, and between 60 at.% and 70 at.% of Y in the Gd-Y system) are desirable. It is also of interest to test the relations (2.44) and (3.26) experimentally.

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