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Phase diagrams near the Lifshitz point. I. Uniaxial magnetization

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A paramagnetic (I)-ferromagnetic (II)-sinusoidal (III) phase diagram near a Lifshitz point is studied for the case of uniaxial magnetization. The shape of the phase diagram in the vicinity of this point is determined. It is found that the II ⇄ III phase transition line is tangent to the order-disorder (I ⇄ II and I ⇄ III) transition line at the Lifshitz point. The II ⇄ III phase transition is shown to be first order, with latent heat and metastability regions. The behavior of magnetic susceptibility is determined. Binary alloy systems are suggested in which the considered type of phase diagram may be expected.

I. INTRODUCTION

Hornreich *et al.*[1] recently considered a new multicritical point, which they have termed the Lifshitz point. To introduce this point, they considered the expansion of the free-energy functional $F(\vec{M})$ in terms of the order parameter $\vec{M}(\vec{r})$ and its spatial derivatives, concentrating their attention on the term $\sum_{ijkl} \alpha_{ijkl} \nabla_i M_k \nabla_j M_l$ in this expansion. In the case of second-order phase transitions from a paramagnetic to a ferromagnetic phase, this term must be positive definite. However, the matrix of coefficients α_{ijkl} in general depends on temperature T and some parameter P. (As pointed out in Ref. 1, the parameter P need not necessarily be identified with pressure; it may be, for instance, material composition.) Hence it is, in principle, possible that, moving along the line of paramagnetic to ferromagnetic phase transitions on the P-T diagram, one may reach a point (P_L, T_L) where one of the eigenvalues of the matrix α_{ijkl} vanishes. In the region where this eigenvalue is negative, second-order phase transitions from the paramagnetic state lead not to a ferromagnetic but to a modulated (sinusoidal or helicoidal) state characterized by a certain wave vector $\vec{k}_0$. The point (P_L, T_L) called in Ref. 1 the Lifshitz point is thus a triple point between the paramagnetic, ferromagnetic, and modulated phases. As emphasized by Hornreich *et al.*,[1] a characteristic feature of this point is that $\vec{k}_0$ increases *continuously* from $\vec{k}_0 = 0$ at (P_L, T_L).

In Ref. 1 the critical exponents and the scaling relations for a Lifshitz point were obtained, using renormalization-group techniques. There are, however, many other aspects of the theory of Lifshitz points that have not yet been studied, e.g., the geometrical and analytical details of the P-T diagram in the vicinity of a Lifshitz point,[2] the thermodynamics of the phase transitions between the ordered phases, the detailed description of the modulated phase, the dependence of the thermodynamical properties on the number of components of the order parameter and on the symmetry of the system, etc. These and related topics are the subject of the present series of papers. In this paper we consider the case of uniaxial (one-component) magnetization. In the following paper (paper II) the case of two-component magnetization will be studied for systems with cylindrical, hexagonal, and rhombohedral symmetry having an easy plane.

The main results of our work concern the shape of the phase diagram in the vicinity of the Lifshitz point. In the present paper we show that the two parts of the order-disorder transition line, namely, the paramagnetic-ferromagnetic (I ⇄ II) and paramagnetic-modulated (I ⇄ III) phase transition lines, have a common tangent at (P_L, T_L) (see Sec. II), and the ferromagnetic-modulated (II ⇄ III) phase transition line is also tangent to both of them (see Sec. III). The latter result is characteristic of the uniaxial case: in the cases discussed in paper II, the II ⇄ III phase transition line is not tangent to the order-disorder transition line. Another important result concerns the order of the II ⇄ III phase transition. In the uniaxial case it is found to be first order (see Sec. III). As will be shown in paper II, in the case of an easy plane of magnetization, this transition may be either first or second order, depending on the symmetry of the system. In Sec. IV of the present paper we discuss the behavior of magnetic susceptibility. The susceptibility is shown to be continuous on the I ⇄ III phase transition line and to have a finite discontinuity on the II ⇄ III phase transition line. In Sec. V binary alloy systems are suggested in which the considered type of phase diagram may be expected.

The results of our work are obtained on the basis of the minimization of the expansion of $F(\vec{M})$, as in the Landau theory of second-order phase transitions.[3] As is known, this is equivalent to a mean-field approach; hence all the general remarks concerning mean-field results[4] apply also to the results of the present paper. Therefore we expect that the quantitative results of our work are valid up to the critical region around the Lifshitz point, while the qualitative results are applicable also inside this region.

II. ORDER-DISORDER TRANSITION LINE

As mentioned in Sec. I, we consider the case where there is a single axis of spontaneous magnetization. For definiteness one may think of the c axis (z axis) in tetragonal, rhombohedral, or hexagonal crystals, or of any of the three axes a, b, c in orthorombic crystals. In this case the order parameter $\vec{M}$ has a single component $M = M_z$ (in terms of group representations, $\vec{M}$ transforms according to a one-dimensional representation of the paramagnetic point group). The expansion of $F(\vec{M})$ has the form

$$F = \int \left(\tfrac{1}{2} A_0 M^2 + \tfrac{1}{4} B M^4 + \frac{1}{2} \sum_{i=x,y,z} \alpha_i (\nabla_i M)^2 + \cdots \right) d^3r \,. \tag{2.1}$$

The line

$$A_0(P, T) = 0 \tag{2.2}$$

is the line of second-order phase transitions between para- and ferromagnetic states, if on this line $B > 0$ and $\alpha_i > 0$. In the paramagnetic phase $A_0 > 0$, and in the ferromagnetic phase $A_0 < 0$. Suppose now that α_z vanishes on a certain line

$$\alpha_z(P, T) = 0 \,, \tag{2.3}$$

changing sign as this line is crossed. If this line intersects with the line $T_0(P)$ defined by Eq. (2.2), we obtain the Lifshitz point (P_L, T_L). To ensure the thermodynamic stability in the region of $\alpha_z < 0$ against infinitely rapid variation of M in the z direction, the expansion (2.1) must contain a positive term $\beta(\nabla_z^2 M)^2$. On the other hand, the terms $\alpha_x(\nabla_x M)^2$ and $\alpha_y(\nabla_y M)^2$—which are assumed to remain positive in the neighborhood of (P_L, T_L) we are going to consider—render the system stable against the appearance of spatial inhomogeneities in the x and y directions. We may therefore treat M as depending only on z, and accordingly rewrite the expansion of $F(M)$ in the form

$$F(M) = \int [\tfrac{1}{2} A_0 M^2 + \tfrac{1}{4} B M^4 + \tfrac{1}{2} \alpha (M')^2 + \tfrac{1}{4} \beta (M'')^2 + \cdots] d^3r \,, \tag{2.4}$$

where we have put $\alpha \equiv \alpha_z$, $M' \equiv \nabla_z M$. In what follows we shall assume B and β to be independent of P, T. The expansion of $F(M)$ can be presented in an alternative form by expanding $M(z)$ in Fourier series,

$$M(z) = \sum_k M_k e^{ikz} \,, \tag{2.5}$$

namely,

$$F = \frac{1}{2} \sum_k A_k |M_k|^2 + \frac{B}{4} \sum_{k+k'+k''+k'''=0} M_k M_{k'} M_{k''} M_{k'''} \tag{2.6}$$

(we have taken into account that $M_{-k} = M_k^*$ and have put the volume $V = 1$), where

$$A_k = A_0 + \alpha k^2 + \tfrac{1}{2} \beta k^4 \,. \tag{2.7}$$

A second-order phase transition from the paramagnetic (disordered) to a magnetically ordered state occurs[3,5] when $A_{\min}$, the minimum of A_k as a function of k, changes its sign from positive to negative with the change of P, T. The line $T_\lambda(P)$ of such transition is defined by the equation

$$A_{\min}(P, T) = 0 \,. \tag{2.8}$$

In the region of $\alpha > 0$, $A_{\min} = A_0$ and $T_\lambda(P)$ coincides with $T_0(P)$. In the region of $\alpha < 0$, $A_{\min} = A_{k_0}$, where

$$k_0 = (-\alpha/\beta)^{1/2} \,, \tag{2.9}$$

and $T_\lambda(P)$ is defined by the equation

$$A_{k_0} = A_0 - \alpha^2/2\beta = 0 \,. \tag{2.10}$$

We see that in this region $T_\lambda(P) > T_0(P)$ (it is implied that $\partial A_0/\partial T > 0$).

Let us show that the two parts of the line $T_\lambda(P)$ have a common tangent at (P_L, T_L) (see Fig. 1). Assuming for definiteness that $\partial\alpha/\partial P < 0$, so that $\alpha > 0$ and $T_\lambda(P) = T_0(P)$ in the region $P < P_L$, we have

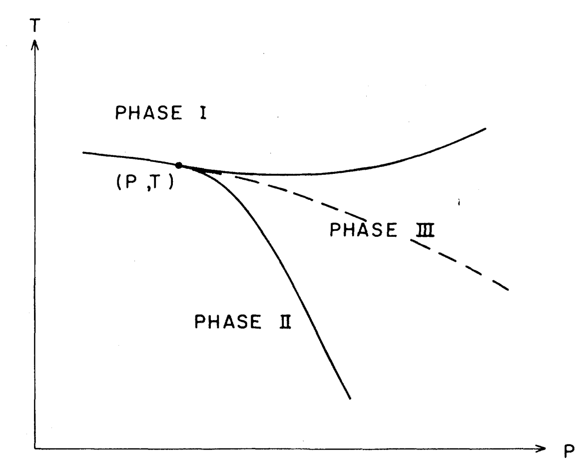

FIG. 1. Phase diagram near the Lifshitz point (P_L, T_L). The dashed line is $T_0(P)$, the extrapolation of the I–II phase transition line into phase III.

$$\left(\frac{dT_\lambda}{dP}\right)_{P=P_L-0}=\left(\frac{dT_0}{dP}\right)_{P=P_L}=-\left(\frac{\partial A_0/\partial P}{\partial A_0/\partial T}\right)_{P,\,T=P_L,\,T_L}, \tag{2.11}$$

$$\left(\frac{dT_\lambda}{dP}\right)_{P=P_L+0}=\lim_{P,L\to P_L,T_L}\left(-\frac{\partial A_{k_0}/\partial P}{\partial A_{k_0}/\partial T}\right)_{\alpha<0}$$
$$=-\left(\frac{\partial A_0/\partial P-\alpha\beta^{-1}\partial\alpha/\partial P}{\partial A_0/\partial T-\alpha\beta^{-1}\partial\alpha/\partial T}\right)_{P,\,T=P_L,\,T_L}$$
$$=\left(\frac{dT_\lambda}{dP}\right)_{P=P_L-0}. \tag{2.12}$$

In the vicinity of (P_L, T_L)

$$A_0(P,T)\approx\left(\frac{\partial A_0}{\partial T}\right)_{P,\,T=P_L,\,T_L}[T-T_0(P)]$$
$$=C^{-1}[T-T_0(P)], \tag{2.13}$$

where C is the Curie-Weiss constant for the susceptibility in the paramagnetic phase near (P_L, T_L); similarly

$$\alpha(P,T)\approx\left(\frac{\partial\alpha}{\partial P}\right)_{P,\,T=P_L,\,T_L}(P-P_L)$$
$$+\left(\frac{\partial\alpha}{\partial T}\right)_{P,\,T=P_L,\,T_L}(T-T_L). \tag{2.14}$$

Substituting (2.13) and (2.14) into (2.10), and taking into account (2.11) and (2.12), one obtains for $P>P_L$

$$T_\lambda(P)-T_0(P)\approx C\alpha^2/2\beta\approx\tfrac{1}{2}\gamma(P-P_L)^2, \tag{2.15}$$

where

$$\gamma\equiv\left[\left(\frac{\partial\alpha}{\partial T}\right)_{P,\,T=P_L,\,T_L}\left(\frac{dT_0}{dP}\right)_{P=P_L}+\left(\frac{\partial\alpha}{\partial P}\right)_{P,\,T=P_L,\,T_L}\right]^2\beta^{-1}C. \tag{2.16}$$

III. FERROMAGNETIC-SINUSOIDAL PHASE TRANSITION LINE

Let us investigate the magnetically ordered phases. The magnetization at thermodynamic equilibrium $M_{eq}(z)$ corresponds to the minimum of $F(M)$. In the region where $\alpha>0$, M_{eq} is obviously constant throughout the crystal and equal to

$$M_{eq}=M_0=(-A_0/B)^{1/2}\approx(CB)^{-1/2}[T_0(P)-T]^{1/2}, \tag{3.1}$$

which corresponds to the ferromagnetic phase. For $\alpha<0$ the minimization of $F(M)$ is mathematically more complicated. However, one can show (see Appendix A) that in the region

$$0<T_\lambda(P)-T\ll10^2\gamma(P-P_L)^2,\quad P>P_L \tag{3.2}$$

M_{eq} is quite accurately described by the equation

$$M_{eq}(z)=2M_{k_0}\cos(k_0z+\phi) \tag{3.3}$$

with arbitrary ϕ and

$$M_{k_0}=(-A_{k_0}/3B)^{1/2}. \tag{3.4}$$

In the vicinity of the Lifshitz point

$$\frac{\partial A_{k_0}}{\partial T}=\frac{\partial A_0}{\partial T}-\frac{\alpha}{\beta}\frac{\partial\alpha}{\partial T}\approx\frac{\partial A_0}{\partial T}=C^{-1}, \tag{3.5}$$

and therefore

$$M_{k_0}\approx(3BC)^{-1/2}[T_\lambda(P)-T]^{1/2}. \tag{3.6}$$

Equation (3.3) describes a static longitudinal wave of magnetization with the wave vector $\vec{k}_0=k_0\hat{z}$, which is characteristic of a sinusoidal phase. The presence of an arbitrary constant ϕ in (3.3) reflects the independence of F on the choice of the origin.

Thus, the magnetically ordered phase consists of two subphases, ferromagnetic and sinusoidal, which we shall denote as phases II and III, respectively (phase I is paramagnetic). It might seem at first sight that these two phases are separated by the line (2.3). However, it is not so. The substitution of the expressions (3.1) and (3.3) [with M_{k_0} from (3.4)] for $M(z)$ in (2.4) yields the following values of F in phases II and III, respectively:

$$F_{II}=-A_0^2/4B, \tag{3.7}$$

$$F_{III}=-A_{k_0}^2/6B=-(A_0-\alpha^2/2\beta)^2/6B \tag{3.8}$$

The comparison of F_{II} and F_{III} (in the region where $A_0<0$ and $\alpha<0$) shows that if

$$-A_0>(\sqrt{6}-2)^{-1}\alpha^2/\beta\approx2.2\alpha^2/\beta, \tag{3.9}$$

then $F_{II}<F_{III}$; conversely, if

$$-A_0<(\sqrt{6}-2)^{-1}\alpha^2/\beta, \tag{3.10}$$

then $F_{III}<F_{II}$. The inequalities (3.9) and (3.10) are satisfied when $T<T_H(P)$ and $T>T_H(P)$, respectively, where

$$T_H(P)\approx T_0(P)-2.2\left(\frac{\partial A_0}{\partial T}\right)^{-1}_{T=T_0(P)}\frac{\alpha^2}{\beta}$$
$$\approx T_0(P)-2.2C\alpha^2/\beta$$
$$\approx T_0(P)-2.2\gamma(P-P_L)^2. \tag{3.11}$$

[The last line in (3.11) has been obtained with the aid of Eq. (2.15).] This result means that phase II extends into the region where $\alpha<0$ and is separated from phase III by the line $T_H(P)$. This line starts at the point (P_L, T_L) and has a common tangent with the line $T=T_\lambda(P)$ at this point (see Fig. 1).

The result (3.11) is characteristic of the uniaxial case. As will be shown in the next paper, different results obtain for systems with cylindrical, hexagonal, and rhombohedral symmetry having an easy plane of magnetization. In these systems the line $T_H(P)$ is *not* tangent to the line $T_\lambda(P)$. Furthermore, in the case of cylindrical symmetry the line $T_H(P)$ coincides with the line (2.3), and the *whole* region of $\alpha<0$ is occupied by phase III.

The comparison of (2.15) and (3.11) yields (for $P>P_L$)

$$\frac{T_0(P)-T_H(P)}{T_\lambda(P)-T_0(P)}\approx 4.4\,. \tag{3.12}$$

This relation can, in principle, be tested experimentally [the function $T_0(P)$ at $P>P_L$ can, for this purpose, be obtained by the parabolic extrapolation of the curve $T_\lambda(P)=T_0(P)$ found experimentally at $P<P_L$].

The line $T_H(P)$ lies within the region satisfying condition (3.2). Hence the "single-harmonic approximation" given by Eqs. (3.3) and (3.4) is applicable *throughout* phase III. In particular, the derivation of Eq. (3.11) for $T_H(P)$ with the aid of Eqs. (3.3) and (3.4) is consistent.[6]

The fact that the line $T_H(P)$ is a line of phase equilibrium indicates that the transition between phases II and III is first order. Indeed, as follows from (3.7) and (3.8),

$$S_{\rm III}-S_{\rm II}=\frac{\partial F_{\rm II}}{\partial T}-\frac{\partial F_{\rm III}}{\partial T}=\frac{A_{k_0}}{3B}\frac{\partial A_{k_0}}{\partial T}-\frac{A_0}{2B}\frac{\partial A_0}{\partial T}\,, \tag{3.13}$$

or according to (3.5) and (2.10),

$$\begin{aligned} S_{\rm III}-S_{\rm II}&\approx (BC)^{-1}(\tfrac{1}{2}|A_0|-\tfrac{1}{3}|A_{k_0}|)\\ &=(6BC)^{-1}(|A_0|-\alpha^2/\beta)\,. \end{aligned} \tag{3.14}$$

Hence there is a jump in the entropy on the line $T_H(P)$:

$$\begin{aligned}\Delta S=(S_{\rm III}-S_{\rm II})_{T=T_H(P)}&=\alpha^2(2\sqrt{6}\,\beta BC)^{-1}\\ &\approx 0.20\alpha^2(\beta BC)^{-1}\approx 0.20(BC)^{-1}\gamma(P-P_L)^2\,,\end{aligned} \tag{3.15}$$

characteristic of a first-order phase transition. With the aid of (2.15) and (3.11) the latent heat $\Delta Q=T_H(P)\Delta S\approx T_L\Delta S$ of this transition can be presented in the form

$$\Delta Q\approx 0.15\Delta c[T_\lambda(P)-T_H(P)]\,, \tag{3.16}$$

where $\Delta c\approx T_L B^{-1}C^{-2}$ is, according to Landau's theory,[3] the jump in the specific heat at constant P occurring in the I⇄II phase transition (near the Lifshitz point). As should be expected, ΔQ tends to zero as one approaches the Lifshitz point.

The wave number k_0 experiences a finite jump in the II⇄III phase transition, from zero in phase II to the value of $(-\alpha/\beta)^{1/2}$ at $T=T_H(P)$. However, k_0 increases continuously from zero as one moves from (P_L,T_L) along the lines $T_H(P)$ or $T_\lambda(P)$ (or between these lines) in the direction of larger P. Neglecting terms of the order of $(P-P_L)^2$, one can write for points (P,T) in phase III $[T_H(P)<T<T_\lambda(P)]$ that are sufficiently close to the Lifshitz point

$$T-T_L\approx\left(\frac{dT_0}{dP}\right)_{P=P_L}(P-P_L)\,, \tag{3.17}$$

whence

$$k_0(P,T)\approx k_0(P)=\left[-\left(\frac{\partial\alpha}{\partial P}\right)_{P,T=P_L,T_L}-\left(\frac{\partial\alpha}{\partial T}\right)_{P,T=P_L,T_L}\left(\frac{dT_0}{dP}\right)_{P=P_L}\right]^{1/2}\beta^{-1/2}(P-P_L)^{1/2}=(\gamma/BC)^{1/4}(P-P_L)^{1/2}\,. \tag{3.18}$$

Thus[7] $k_0\propto(P-P_L)^{1/2}$.

Since the II⇄III phase transition is first order, there must be a region at $T>T_H(P)$ in which the ferromagnetic state is metastable, and a region at $T<T_H(P)$ in which the sinusoidal state is metastable. Appendix B contains the determination of the upper boundary $T_f(P)$ of the first region and also an estimation of the lower boundary $T_s(P)$ of the second one [see Eqs. (B6) and (B17)]. A characteristic feature of these boundaries is that they, like the I⇄III and II⇄III phase transition lines, are tangent to the line $T_0(P)$ at (P_L,T_L), with the differences $T_f(P)-T_0(P)$ and $T_0(P)-T_s(P)$ being proportional to $(P-P_L)^2$.

IV. MAGNETIC SUSCEPTIBILITY

The expressions (B2) and (B7) for $\delta^{(2)}F$ obtained in Appendix B make it possible to determine the susceptibility with respect to a homogeneous magnetic field parallel to the z axis. The reciprocal susceptibility is given by the formula

$$\chi^{-1}=2\left(\frac{\delta^{(2)}F(M,\delta M)}{\delta M_0^2}\right)_{M=M_{\rm eq}}\,, \tag{4.1}$$

where one has to put the Fourier components δM_k with $k\neq0$ equal to zero. In phase II one obtains, with the aid of (B2), the familiar Curie-Weiss expression for the ferromagnetic phase:

$$\chi_{\rm II}^{-1}=-2A_0=2C^{-1}[T_0(P)-T]\,. \tag{4.2}$$

In phase III, according to (B7) and (4.1),

$$\chi_{\rm III}^{-1}=A_0-2A_{k_0}=C^{-1}[2T_\lambda(P)-T_0(P)-T]\,, \tag{4.3}$$

i.e., also a linear dependence on T. Finally, in the paramagnetic phase

$$\chi_{\rm I}^{-1}=A_0=C^{-1}[T-T_0(P)]\,. \tag{4.4}$$

Note that at $P > P_L$, χ^{-1} does not vanish at any T. Indeed, the line $T = T_0(P)$, on which $\chi_{I}^{-1} = \chi_{II}^{-1} = 0$, lies within phase III, where $\chi = \chi_{III}$; correspondingly, the line

$$T = 2T_\lambda(P) - T_0(P)\,, \tag{4.5}$$

on which $\chi_{III}^{-1} = 0$, lies in phase I. As follows from (4.3) and (4.4), χ is continuous on the phase transition line $T_\lambda(P)$ at $P > P_L$:

$$\chi_I[T_\lambda(P)] = \chi_{III}[T_\lambda(P)] = C[T_\lambda(P) - T_0(P)]^{-1} = 2C\gamma^{-1}(P - P_L)^{-2}\,. \tag{4.6}$$

At the same time χ diverges with a critical index 2 as one approaches the Lifshitz point along $T_\lambda(P)$. On the line $T_H(P)$

$$\chi_{II}[T_H(P)] = \tfrac{1}{2}C[T_0(P) - T_H(P)]^{-1} \approx 0.23C\gamma^{-1}(P - P_L)^{-2}\,, \tag{4.7}$$

$$\chi_{III}[T_H(P)] = C[2T_\lambda(P) - T_0(P) - T_H(P)]^{-1} \approx 0.31C\gamma^{-1}(P - P_L)^{-2}\,, \tag{4.8}$$

i.e., there is a discontinuity in χ,

$$(\Delta\chi)_{T=T_H(P)} \approx 0.08C\gamma^{-1}(P - P_L)^{-2}\,, \tag{4.9}$$

along with the divergence like $(P - P_L)^{-2}$ when $P \to P_L + 0$. The dependence of χ^{-1} on T along a line $P = \text{const} > P_L$ is plotted in Fig. 2.

V. CONCLUSION

Let us now summarize the results obtained in this paper. We have found that the paramagnetic (I)-ferromagnetic (II)-modulated (III) phase diagram near the Lifshitz point (P_L, T_L) in the case of uniaxial (one-component) magnetization has the following features:

The I $\rightleftharpoons$ II, I $\rightleftharpoons$ III, and II $\rightleftharpoons$ III phase transition lines are *tangent to each other* at the Lifshitz point. The extrapolation $T_0(P)$ of the I $\rightleftharpoons$ II phase transition line into the region of $P > P_L$ lies *within* phase III, i.e., below the I $\rightleftharpoons$ III phase transition line $T_\lambda(P)$ and above the II $\rightleftharpoons$ III phase transition line $T_H(P)$. The three lines satisfy near the Lifshitz point the relation

$$T_0(P) - T_H(P) = 4.4[T_\lambda(P) - T_0(P)] \propto (P - P_L)^2\,.$$

Phase II extends partially into the region where $\alpha < 0$.

The magnetic ordering throughout phase III is satisfactorily described by a single sinusoidal harmonic [see Eq. (3.3)]: the third and higher harmonics can be neglected. The II $\rightleftharpoons$ III phase transition is first order, with a jump in the modulation wave vector from zero in phase II to the value $k_0 = (-\alpha/\beta)^{1/2} \propto (P - P_L)^{1/2}$ in phase III. The latent heat ΔQ absorbed in this transition at given P is related by Eq. (3.16) to the corresponding temperatures $T_\lambda(P)$ and $T_H(P)$ and to the jump Δc in specific heat occurring in the I $\rightleftharpoons$ II phase transition; ΔQ tends to zero like $(P - P_L)^2$ when $P \to P_L + 0$. The metastability regions for the ferromagnetic and sinusoidal states have been estimated. The boundaries of these regions, $T_f(P)$ and $T_s(P)$, are tangent to the phase transition lines at the Lifshitz point and satisfy the relations

$$T_f(P) - T_H(P) \propto (P - P_L)^2\,,$$

$$T_H(P) - T_s(P) \propto (P - P_L)^2\,.$$

The susceptibility χ with respect to a uniform magnetic field is continuous on the I $\rightleftharpoons$ III phase transition line and experiences a finite jump when the II $\rightleftharpoons$ III phase transition line is crossed. The values of χ at $T = T_\lambda(P)$ and $T = T_H(P) \pm 0$ diverge like $(P - P_L)^{-2}$ when $P \to P_L + 0$.

Phase diagrams of the type discussed in this paper may be expected in Gd-Tm and Gd-Er binary alloys. Pure Gd is ferromagnetic at $T < 289$ °K and $53 < T < 80$ °K, respectively. Identifying the concentration of Tm (Er) in a Gd-Tm (Gd-Er) alloy with the above parameter P, one may expect that the P-T phase diagram of each of these binary systems exhibits a triple point at which the paramagnetic, ferromagnetic, and sinusoidal phases meet. It is therefore desirable to investigate experimentally the P-T diagrams of these systems in order to detect such triple points. Further, it is necessary to perform neutron diffraction measurements in the vicinity of these points, in order to find out whether the wave vector k_0 of the sinusoidal phase goes *continuously* to zero as these

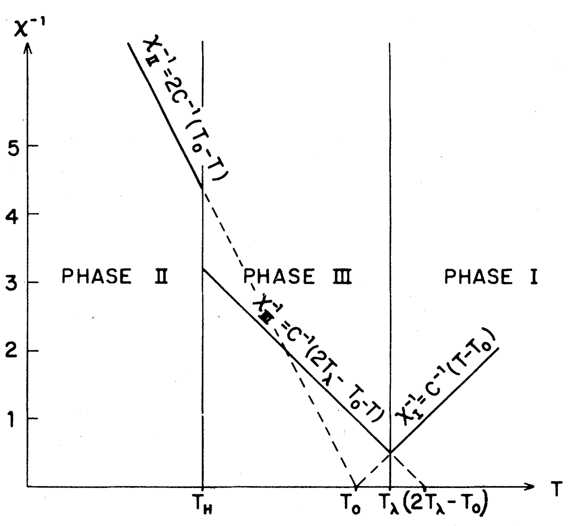

FIG. 2. Reciprocal susceptibility χ^{-1} vs temperature T along a line $P = \text{const} > P_L$; χ^{-1} is given in units $C^{-1}\gamma(P - P_L)^2$.

points are approached; otherwise the triple points in question are not Lifshitz points.

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APPENDIX A: MAGNETIC ORDERING IN PHASE III

In order to determine $M_{eq}(z)$ in the region where $\alpha < 0$, one has to solve the differential equation

$$\tfrac{1}{2}\beta M'''' - \alpha M'' + A_0 M + BM^3 = 0 \tag{A1}$$

obtained from the variation of $F(M)$ [Eq. (2.4)] with respect to M, and to select that solution of Eq. (A1) which yields the smallest value of $F(M)$. This problem cannot be solved exactly. However, one can find the asymptotic form of $M_{eq}(z)$ at $T \to T_\lambda(P) - 0$. For this purpose, it is convenient to consider the expression (2.6) for $F(M)$ rather than Eq. (A1). When $T_\lambda(P) - T \ll T_\lambda(P) - T_0(P)$, the coefficients A_k in (2.6) are negative only for the values of k lying in small intervals $|k \pm k_0| < \epsilon$, where $\epsilon \ll k_0$ (see Fig. 3). The large positive A_k in (2.6) (large in comparison with $|A_{k_0}|$) are expected to "suppress" the corresponding M_k, i.e., to make these M_k vanish in order to decrease $F(M)$. Therefore, in order to find the asymptotic form of $M_{eq}(z)$, one can make a suitable cutoff in the k space. Namely, one can seek $M_{eq}(z)$ in the class $\{M_\kappa\}$ of functions of the type

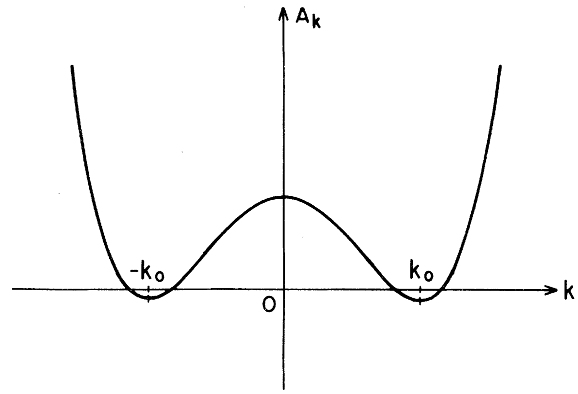

FIG. 3. A_k vs k for $\alpha < 0$ and $T_\lambda(P) - T \ll T_\lambda(P) - T_0(P)$.

$$M_\kappa(z) = \sum_{-\kappa \le q \le \kappa} M_{k_0+q} e^{i(k_0+q)z} + \text{c.c.}, \tag{A2}$$

with $\kappa \ll k_0$; equivalently one can write

$$M_\kappa(z) = \mu_\kappa(z) e^{ik_0 z} + \mu_\kappa^*(z) e^{-ik_0 z}, \tag{A3}$$

where

$$\mu_\kappa(z) \equiv \sum_{-\kappa \le q \le \kappa} M_{k_0+q} e^{iqz}. \tag{A4}$$

It goes without saying that the final asymptotic expression for $M_{eq}(z)$ *should not* depend on the arbitrary cutoff parameter κ.

In view of (A2), (A4), and (2.6), the expansion of $F(M_\kappa(z))$ consists of the following terms:

$$\frac{1}{2}\sum_k A_k |M_k|^2 = \sum_{-\kappa \le q \le \kappa} A_{k_0+q}|M_{k_0+q}|^2 \approx A_{k_0} \sum_{-\kappa \le q \le \kappa} |M_{k_0+q}|^2 + \frac{1}{2}\left(\frac{\partial^2 A_k}{\partial k^2}\right)_{k=k_0} \left(\sum_{-\kappa \le q \le \kappa} q^2 |M_{k_0+q}|^2\right)$$

$$= \int (A_{k_0}|\mu_\kappa|^2 + 2|\alpha|\,|\mu_\kappa'|^2) d^3r, \tag{A5}$$

$$\frac{1}{4}B \sum_{k+k'+k''+k'''=0} M_k M_{k'} M_{k''} M_{k'''} = \frac{3}{2}B \sum_{\substack{-\kappa \le q, q', q'', q''' \le \kappa \\ q+q'=q''+q'''}} M_{k_0+q} M_{k_0+q'} M_{-k_0-q''} M_{-k_0-q'''} = \frac{3}{2}B \int |\mu_\kappa|^4 d^3r; \tag{A6}$$

hence

$$F(M_\kappa) = \int (A_{k_0}|\mu_\kappa|^2 + \tfrac{3}{2}B|\mu_\kappa|^4 + 2|\alpha|\,|\mu_\kappa'|^2) d^3r. \tag{A7}$$

The minimum of the expression (A7) corresponds to

$$|\mu_\kappa| = (-A_{k_0}/3B)^{1/2}. \tag{A8}$$

As should be expected, this result does not contain κ. Thus, for $T_\lambda(P) - T \ll T_\lambda(P) - T_0(P)$,

$$M_{eq}(z) = 2M_{k_0} \cos(k_0 z + \phi), \tag{A9}$$

with arbitrary ϕ and

$$M_{k_0} = (-A_{k_0}/3B)^{1/2}. \tag{A10}$$

As one moves away from the line $T_\lambda(P)$ (remaining in the region where $\alpha < 0$) so that $T_\lambda(P) - T$ increases, one has to take into account higher odd harmonics of k_0 which are contained in the exact solution of Eq. (A1) corresponding to $M_{eq}(z)$: first the third harmonic, then the fifth, etc. Let us determine the region on the P-T plane in which the higher harmonics can still be neglected as compared to the first harmonic (A9). For this purpose it is sufficient to consider only the third harmonic. Designating the amplitude and the phase of the third harmonic as M_{3k_0} and ψ, respectively, we can present $M_{eq}(z)$ in the form

$$2M_{k_0}\cos(k_0 z+\phi)+(M_{3k_0}e^{i(3k_0 z+\phi)}+\text{c.c.})\,. \quad \text{(A11)}$$

Substituting (A11) for M in Eq. (A1) and assuming that $M_{3k_0} \ll M_{k_0}$ we find

$$M_{3k_0} \approx \frac{BM_{k_0}^3}{A_{3k_0}+6BM_{k_0}^2}=\frac{|A_{k_0}|M_{k_0}}{3A_{3k_0}+6|A_{k_0}|}\,. \quad \text{(A12)}$$

The result (A12) is consistent with the assumption $M_{3k_0} \ll M_{k_0}$ if

$$|A_{k_0}| \ll 3A_{3k_0}+6|A_{k_0}|\,. \quad \text{(A13)}$$

According to (2.7) and (2.9), condition (A13) is equivalent to

$$|A_{k_0}| \ll 3|A_{k_0}|+96\alpha^2/\beta\,, \quad \text{(A14)}$$

which can be written more simply as

$$|A_{k_0}| \ll 10^2\alpha^2/\beta\,. \quad \text{(A15)}$$

In the vicinity of the Lifshitz point, according to (2.13) and (2.15), condition (A15) is equivalent to the condition

$$T_\lambda(P)-T \ll 10^2\gamma(P-P_L)^2\,. \quad \text{(A16)}$$

Thus, in the region satisfying condition (A16) the third harmonic in $M_{eq}(z)$ is negligible compared with the first harmonic given by (A9).

Calculating in this region the amplitude M_{5k_0} of the fifth harmonic, one obtains

$$M_{5k_0} \approx \frac{3BM_{k_0}^2 M_{3k_0}}{A_{5k_0}+6BM_{k_0}^2}=\frac{|A_{k_0}|M_{3k_0}}{A_{5k_0}+2|A_{k_0}|}\,.$$

It follows that

$$\frac{M_{5k_0}}{M_{3k_0}}=\frac{|A_{k_0}|}{A_{5k_0}+2|A_{k_0}|}=\frac{|A_{k_0}|}{|A_{k_0}|+288\alpha^2/\beta} \ll 1\,.$$

Hence the neglect of the fifth and higher harmonics is all the more justified.

APPENDIX B: DETERMINATION OF METASTABILITY REGIONS

In order to find the region in which the ferromagnetic state is metastable, let us calculate, with the aid of (2.4), the second variation of the free energy, $\delta^{(2)}F(M,\delta M)$, for M given by Eq. (3.1) and

$$\delta M(z)=\sum_k \delta M_k e^{ikz}\,, \quad \delta M_{-k}=\delta M_k^*\,. \quad \text{(B1)}$$

Dropping from $F(M+\delta M)-F(M)$ the terms of the third and higher orders in δM, we obtain

$$\delta^{(2)}F=\delta^{(2)}F_f=\frac{1}{2}\sum_k (A_k-3A_0)|\delta M_k|^2\,. \quad \text{(B2)}$$

The Hermitian form (B2) is positive definite when

$$A_{\min}-3A_0>0\,. \quad \text{(B3)}$$

Applied to the region of $\alpha<0$ and $A_{k_0}<0$, the inequality (B3) can be written as

$$-3A_0>-A_{k_0}>0\,, \quad \text{(B4)}$$

or

$$-A_0>\alpha^2/4\beta\,. \quad \text{(B5)}$$

The condition (B5) is satisfied when $T<T_f(P)$, where

$$T_f(P)\approx T_0(P)-C\alpha^2/4\beta \approx T_0(P)-0.25\gamma(P-P_L)^2\,. \quad \text{(B6)}$$

Thus the ferromagnetic state is metastable in the region $T_H(P)<T<T_f(P)$.

The calculation of $\delta^{(2)}F(M,\delta M)$, for M given by (3.3), (3.4) yields

$$\delta^{(2)}F=\delta^{(2)}F_s=\sum_k \left[(\tfrac{1}{2}A_k-A_{k_0})|\delta M_k|^2-\tfrac{1}{2}A_{k_0}(e^{2i\phi}\delta M_k\delta M_{-k-2k_0}+\text{c.c.})\right]. \quad \text{(B7)}$$

The quadratic form (B7), as distinct from (B2), is nondiagonal; therefore we cannot determine exactly the region of metastability of the sinusoidal state. We can, however, make a rough estimate of this region by cutting off the Fourier components δM_k with $|k|>2k_0$. Then $\delta^{(2)}F_s$ decomposes into a sum of independent Hermitian forms $\delta^{(2)}F_k$, each of them containing two of the variables δM_k:

$$\delta^{(2)}F_s=\sum_{0\le k\le k_0}\delta^{(2)}F_k\,, \quad \text{(B8)}$$

where

$$\delta^{(2)}F_k=(A_k-2A_{k_0})|\delta M_k|^2+(A_{2k_0-k}-2A_{k_0})|\delta M_{2k_0-k}|^2-A_{k_0}(e^{2i\phi}\delta M_{-k}\delta M_{k-2k_0}+\text{c.c.}) \quad \text{for } 0<k<k_0\,; \quad \text{(B9)}$$

$$\delta^{(2)}F_{k_0}=-A_{k_0}|\delta M_{k_0}|^2-\tfrac{1}{2}A_{k_0}(e^{2i\phi}\delta M_{-k_0}^2+\text{c.c.})\,; \quad \text{(B10)}$$

$$\delta^{(2)}F_0=\tfrac{1}{2}(A_0-2A_{k_0})|\delta M_0|^2+(A_{2k_0}-2A_{k_0})|\delta M_{2k_0}|^2-A_{k_0}(e^{2i\phi}\delta M_0\delta M_{-2k_0}+\text{c.c.})\,. \quad \text{(B11)}$$

Applying the Silvester criterion to the Hermitian forms (B9), we find that in the region where $\alpha < 0$ and $A_{k_0} < 0$ all of them are positive definite. The expression (B10) is positive unless $\delta M_{k_0} = \pm |\delta M_{k_0}| i e^{i\phi}$ [with ϕ from (3.3)]; in the latter case $\delta^{(2)} F_{k_0} = 0$, which reflects the physically insignificant invariance of F under an arbitrary change of ϕ in (3.3). Finally, the Hermitian form (B11) is positive definite when

$$A_0 - 2A_{k_0} > 0 \tag{B12}$$

and

$$(A_0 - 2A_{k_0})(A_{2k_0} - 2A_{k_0}) - 2A_{k_0}^2 > 0 \,. \tag{B13}$$

The inequality (B12) is obviously satisfied at least in the region where $\alpha < 0$ and $A_{k_0} < 0$. The inequality (B13) can be written, according to (2.7) and (2.9), in the form

$$A_{k_0}^2 + 5(\alpha^2/\beta)A_{k_0} - \tfrac{9}{4}(\alpha^2/\beta)^2 < 0 \,, \tag{B14}$$

which results in

$$-A_{k_0} < \frac{5 + (34)^{1/2}}{2}\frac{\alpha^2}{\beta} \approx 5.4\frac{\alpha^2}{\beta} \tag{B15}$$

and

$$-A_0 < 4.9\alpha^2/\beta \,. \tag{B16}$$

From (B16) one obtains the line

$$T_s(P) = T_0(P) - 4.9\gamma(P - P_L)^2 \tag{B17}$$

as the lower boundary for the metastability region of the sinusoidal state. As previously mentioned, this result is only a rough estimate. However, we expect that for the actual line $T_s(P)$ the difference $T_0(P) - T_s(P)$ is proportional to $(P - P_L)^2$, as for the rest of the characteristic lines in this phase diagram, and the quantity $\gamma^{-1}[T_0(P) - T_s(P)](P - P_L)^{-2}$ is of the same order of magnitude as in Eq. (B17). Incidentally, the term in the sum (B8) that ceases to be positive definite below the line (B17) is $\delta^{(2)}F_0$, which involves the infinite-wavelength component δM_0 of $\delta M(z)$. This may be interpreted as an indication of the fact that the instability of the sinusoidal phase in this region is associated with the emergence of the ferromagnetic component of magnetization.

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[6]It can be shown that the relative error in the value of F_{III} on the line $T_H(P)$ caused by the neglect of the third harmonic equals $A_{k_0}/(3A_{3k_0} + 6|A_{k_0}|) \approx 2 \times 10^{-2}$.

[7]The fact that k_0 is small in the vicinity of (P_L, T_L) justifies the neglect of the term $(M')^2M^2$ in the expansion (2.4) as being small compared with the term M^4. Indeed, $(M')^2M^2 \sim k_0^2M^4 \propto (P - P_L)M^4$.