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Theory of Magnetic Fluctuations in Itinerant Ferromagnets*

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The statistical mechanics of a classical field theory describing mode-mode interactions is shown to lead to a theory of the Curie law and specific-heat anomaly observed in the weak itinerant ferromagnet Sc_3In.

A basic problem in the theory of itinerant ferromagnets is the explanation of the well-defined Curie-law behavior observed in a wide variety of metallic magnets. For strong ferromagnets, such as iron, it seems likely that the formation of local moments above the Curie temperature T_c is responsible, as discussed theoretically by Wang, Evenson, and Schrieffer.[1] For weak ferromagnets with a T_c of a few degrees Kelvin, however, the existence of small saturation moments at $T=0$ of a few percent of a Bohr magneton per formula unit conflicts with this picture, and an alternative description is needed.

In this Letter we give a model field-theory description of the thermodynamic (time-averaged) magnetization fluctuations in an itinerant ferromagnet, and use classical statistical mechanics to relate the observed properties (magnetization, susceptibility, and specific heat) in the transition region to those at $T=0$. Using this approach we are able to give a good account of the observed Curie-law behavior in the weak itinerant ferromagnet Sc_3In, and also to derive a theory of the specific heat in the region of T_c which fits qualitatively the observed specific heat in this material.

The main physical assumption made in the model, which is expressed as an energy functional

$$\mathcal{F}=\int d^3x\ \{\mu^2[\nabla m(x)]^2+\alpha m(x)^2+\tfrac{1}{2}\beta m(x)^4\} \qquad (1)$$

[where $m(x)$ is a scalar field representing the local order parameter[2]], is that the parameters μ, α, and β can be treated as approximately temperature independent from $T=0$ up to the region of the Curie temperature for a weak itinerant ferromagnet.

On forming the classical free energy[3,4]

$$F=-k_BT\ln\int\mathfrak{D}m\,e^{-\mathcal{F}/k_BT}, \qquad (2)$$

one then finds that the transition is driven by the mode-mode coupling term $\frac{1}{2}\beta m^4$ in Eq. (1). This mechanism for destroying the ordered state is quite different from the mechanism appearing in the Ginzburg-Landau approach to the theory of the superconducting transition.[5] In the latter case α varies as $T-T_c$ and, as the fluctuations are limited to wavelengths longer than the temperature-dependent inverse coherence length, it is the mode-softening effect which determines the transition.

Using the present assumption of temperature-independent parameters in Eq. (1), we may relate them to properties of the ground-state energy of the interacting electron gas

$$\begin{aligned}&\alpha=\tfrac{1}{2}\delta^2E_G/\delta m_{q=0}{}^2=\chi_{q=0}{}^{-1},\\&\mu^2=\tfrac{1}{2}(d\chi_q{}^{-1}/dq^2)_{q=0},\\&\beta=\tfrac{1}{6}\,\delta^4E_G/\delta m_{q=0}{}^4,\end{aligned} \qquad (3)$$

where χ_q is the generalized susceptibility at $T=0$. Here we are implicitly neglecting nonlocal effects (q dependence) in the m^4 term. Using Eq. (3), the parameters may then be related to the effective band-structure density of states and electron-electron interaction of the Stoner-Wohlfarth theory[6] by calculating $E_G(m)$ using the Hartree-Fock approximation. One then finds

$$\begin{aligned}&\alpha=N(0)^{-1}[1-U_{\mathrm{eff}}N(0)],\\&\beta\propto-N(0)^{-1}N''(0)/N(0)^3.\end{aligned} \qquad (4)$$

μ depends on details of the band structure and is of order $N(0)^{-1}p_F{}^{-2}N''/N^3$. For ferromagnetism one has $\alpha<0$ and $\beta>0$, corresponding to a peak in the one-electron density of states.

Our model is motivated by a microscopic calculation based on a functional integral approach (to be published elsewhere). In this calculation, a quasiclassical approximation essentially reproducing Eq. (4) at $T=0$ suggests that at finite temperatures the parameter α should vary as $1-(T/T_F)^2$. It is this slow temperature dependence which suggests that the transition to the paramagnetic state can be driven by the mode-mode coupling provided the number of effective modes is sufficiently large.

In order to calculate the properties of Eq. (2) in the transition region, we use a variational principle to construct an equivalent Gaussian energy

$$\varphi = V\textstyle\sum_q \Omega_q m_q m_{-q}, \tag{5}$$

where

$$m(x) = V^{-1/2}\sum_{q<q_{\max}} e^{i\vec{q}\cdot\vec{x}} m_q,$$

V being the volume. Using the convexity properties of exponentials, one then has

$$F < -k_B T \ln\int \mathfrak{D}m\, e^{-\varphi/k_B T} + \langle F-\varphi\rangle_\varphi. \tag{6}$$

On minimizing one finds a Hartree-like formula[7] for the fluctuation mode excitation energies,

$$\Omega_q = \mu^2 q^2 + \alpha + 3\beta\langle m^2\rangle \text{ for } T>T_c, \tag{7}$$

where

$$\langle m^2\rangle = V^{-1}\textstyle\sum_q k_B T/\Omega_q. \tag{8}$$

From Eq. (8) T_c is given by $2\pi^2(|\alpha|/3\beta)\mu^2/q_{\max}$. On comparing with the usual Stoner-Wohlfarth formula[6] for T_c, it may be seen that the fluctuation drive T_c occurs at a lower temperature than the Hartree-Fock T_c provided $q_{\max}$, which determines the effective number of fluctuation modes, is big enough.

The static susceptibility is given by

$$\chi(T) \propto \langle m_{q=0}{}^2\rangle/k_B T = (\alpha+3\beta\langle m^2\rangle)^{-1}. \tag{9}$$

Combining Eqs. (7) and (8) and defining $\Pi = (\alpha+3\beta\langle m^2\rangle)/\mu^2 q_{\max}$, one has a simple self-consistent equation

$$\Pi = -\frac{T_c}{T_0} + \frac{T}{T_0}\left[1-\sqrt{\Pi}\tan^{-1}\left(\frac{1}{\sqrt{\Pi}}\right)\right], \tag{10}$$

whose numerical solution (which varies as $T-T_c$ for T very close to T_c) shows that the apparent linearity in T given in Eq. (8), which leads to a Curie law through Eq. (9), is maintained over a large temperature range, provided that the parameter $T_c/T_0 = |\alpha|/\mu^2 q_{\max}{}^2$ is small compared to 1. From Eqs. (9) and (3) and the formula for T_c, one finds a relation between the Curie constant $\mathfrak{C}$ and the measured bulk susceptibility at $T=0$:

$$2\chi(T=0)T_c/\mathfrak{C} = R(T_c/T_0), \tag{11}$$

where R, calculated numerically from Eq. (10) and given in Table I, tends to 1 as $T_c/T_0 \to 0$. From the data of Gardner *et al.*,[8] R is about 0.62 for Sc_3In for the temperature range between T_c of 6°K and about 15°K, leading to a fit with Eq. (11) with $T_c/T_0 \cong 0.03$. However, at higher temperatures the experimental Curie constant decreases abruptly and can no longer be reconciled with Eq. (11). It seems possible that the effective mode cutoff $q_{\max}$ and the parameter β are strongly temperature dependent for temperatures above 15°K in Sc_3In.

For $ZrZn_2$ (for which $T_c \cong 25$°K) the data of Ogawa and Sakamoto[9] give a Curie constant which is about a factor of 3 to 5 smaller than that predicted from Eq. (11). It seems that the present assumption of the temperature independence of β and $q_{\max}$ break down in this case.

For $T<T_c$ the occupation m_0 of the $q=0$ mode becomes macroscopic; and minimizing Eq. (6) with respect to m_0, one finds, neglecting terms of order $\partial\langle m^2\rangle/\partial m_0$,

$$\begin{aligned} m_0{}^2 &= (|\alpha| - 3\beta\langle m^2\rangle)/\beta, \\ \Omega q &= \mu^2 q^2 + 2|\alpha| - 6\beta\langle m^2\rangle, \end{aligned} \tag{12}$$

with $\langle m^2\rangle$ defined as in Eq. (8). Thus, $m_0{}^2$ decreases approximately linearly with $T_c - T$ in contrast to the predictions of the Wohlfarth theory.[6] This linearity is borne out by the self-consistent solution of Eqs. (12) and (8). However, a small step in m_0 appears at T_c (for small T_c/T_0).

At temperatures far from T_c in a regime where $\epsilon = \frac{1}{8}\pi^2(T_c/T_0)[(T-T_c)/T]^{-1} \ll 1$, an investigation of the corrections to the Gaussian approximation arising from Eq. (1) shows that they modify the results of Eqs. (7) and (12) by correction factors of order ϵ for the specific heat, magnetization,

TABLE I. Renormalization factor for the Curie constant calculated from Eqs. (7) and (8).

T_c/T_0	0.01	0.05	0.1	0.3	0.5	1.0
R	0.75	0.55	0.46	0.30	0.23	0.16

and susceptibility for $T > T_c$. We also find that m^6 and higher terms in Eq. (1) give corrections of order T_c/T_0. As one approaches T_c, and ϵ becomes of order 1 (i.e., within about 3% of T_c for the Sc_3In case) critical-phenomena corrections become important,[10] and the above step behavior [which is probably an artifact of the approximation leading to Eq. (12)] is expected to be modified.

The contributions of the thermodynamic fluctuations to the entropy are obtained from the minimum of Eq. (6) as

$$S = -\frac{\partial F}{\partial T} = \sum_{q<q_{\max}} \left[1 + \ln\left(\frac{\pi k_B T}{\Omega_q}\right)\right], \tag{13}$$

leading to the specific heat

$$\begin{aligned} C &= n_{\text{eff}} - 3\beta\langle m^2\rangle\, d\langle m^2\rangle/dT\,, \quad T > T_c \\ &= n_{\text{eff}} + 6\beta\langle m^2\rangle\, d\langle m^2\rangle/dT\,, \quad T < T_c\,, \end{aligned} \tag{14}$$

where

$$n_{\text{eff}} = \sum_{q<q_{\max}} 1$$

is the number of fluctuation modes. The constant term n_{eff} in C is the Dulong-Petit classical term. The microscopic approach leads to the identical form of Eq. (14), except that this classical term is missing and replaced by the Sommerfeld term γT for the metallic electrons. The temperature-dependent term in Eq. (13) depends only on T_c/T_0 and is plotted in Fig. 1.

In order to compare with the experimental data of Knapp *et al.*,[11] a background nonmagnetic term of the form $\gamma T + \beta T^3$ has been selected by fitting the linear regions of the observed heat capacity above and below T_c to the quasilinear regions for C which result from Eq. (14). Given T_c/T_0 and estimating the experimental T_c as 6.8°K to give the best fit, the only remaining adjustable parameter is n_{eff}, which appears as a normalizing factor when Eq. (14) is expressed in terms of Π defined in Eq. (10). For the fit of Fig. 1 this comes out to be $0.06N_A$, where N_A is Avagadro's number, i.e., about 6% of the degrees of freedom participate in the transition.

The main physical consequence of the mode-mode–driven nature of the transition is the negative value of ΔC for $T > T_c$. This results from the stiffening of the modes as $\langle m^2\rangle$ increases with T.[12] The data suggest this effect is present as, if it is neglected, the background γ comes out about the same[11] as that for pure Sc, which seems unlikely in view of the fact that the existence of the magnetism suggests $\mathcal{S}_F$ must be near a peak in the one-electron density of states.

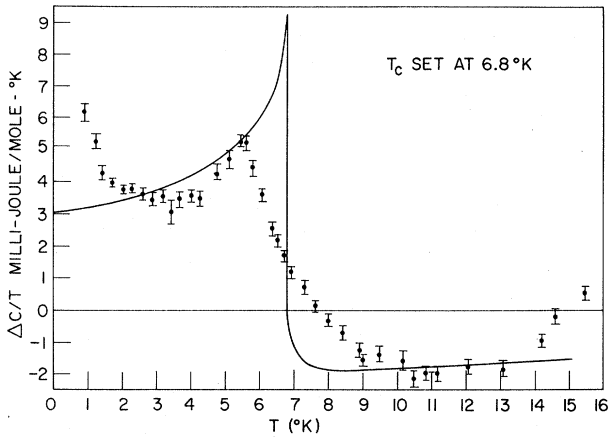

FIG. 1. Plot of the magnetic specific-heat anomaly predicted from Eq. (14) compared with data from Ref. 11 for Sc_3In. A background term $C_{\text{nonmag}} = 18.4T + 0.042T^3$ mJ/mol °K has been subtracted from the data. At higher temperatures the T^3 approximation to the lattice term is inadequate, which accounts for some of the deviation above 12°K. A distribution of T_c values due to minor sample inhomogeneity could explain the slope observed in the transition region.

At low temperatures the present classical statistical-mechanical approach disagrees with the observations as is to be expected.[3] The data may indicate a strong electron-paramagnon coupling effect[13] below 2°K.

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Electronic Specific Heat of Iron-Rhodium and Iron-Rhodium-Iridium Alloys

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The electronic specific heat was measured for the alloys $Fe_{49.5}Rh_{50.5-x}Ir_x$ ($x=1.5$, 3.0, 5.0, 6.5), $Fe_{49.1}Rh_{50.9}$, and $Fe_{52}Rh_{48}$. The coefficient of the linear term, γ_{AF}, in the specific heat of antiferromagnetic alloys was observed to contain a large magnetic contribution which is attributed to the small fraction of Fe atoms occupying Rh sites of nearly zero exchange field. The measured γ_{AF} values do not seem to confirm the simple electronic nature of the first-order antiferromagnetic-ferromagnetic transition assumed by the prevalent theory.

The abrupt increase in the magnetization of a nearly equiatomic Fe-Rh alloy with increasing temperature was first reported by Fallot and Hocart.[1] de Bergevin and Muldawer[2] showed by neutron diffraction that it is due to an antiferromagnetic-ferromagnetic (AF-F) phase transition. The crystal structure is the same (ordered CsCl type) on both sides of the transition temperature but the lattice volume of the F phase is about 1% larger than that of the AF phase.[3] Krén, Pál, and Szabó observed the coexistence of the F and AF phases in a relatively large temperature interval around the transition temperature.

The transition temperature depends on the composition, external pressure, and magnetic field.[5-11] This and other properties of the transition seemed to be consistent with the exchange-inversion model proposed by Kittel[12] and extended by Pál,[13] but when Kouvel[14] determined the total entropy change at the transition through the thermodynamical relationship

$$\frac{dT_t}{dH} = -\frac{\sigma_F - \sigma_{AF}}{S_F - S_{AF}} = -\frac{\Delta\sigma}{\Delta S}, \tag{1}$$

he found that, using the measured values of the change in the transition temperature due to magnetic field dT_t/dH and the change in magnetization $\Delta\sigma$, the total entropy change ΔS was 2–3 times larger than the change of the lattice entropy predicted by the model.

Tu *et al.*[15] suggested that the deviation might be accounted for by the entropy of the conduction-electron system,

$$S(T) = \int_0^T dT'\, C(T')/T' = \gamma T \tag{2}$$

(where γ is the coefficient of the linear term in the specific heat), if there is a considerable difference between γ_F and γ_{AF} due to the F and AF phases, respectively. By making use of the equilibrium condition for the two phases, it is easy to derive from the free energy $F = U - TS$ the following expression for the transition temperature:

$$T_t = \frac{U_{AF}^0 - U_F^0}{\gamma_F - \gamma_{AF}}. \tag{3}$$

Here U_{AF}^0 and U_F^0 are the ground-state internal