Ferromagnetic Heat Capacity in an External Magnetic Field near the Critical Point*

ROBERT B. GRIFFITHS
Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
(Received 28 April 1969)

Some thermodynamic principles useful for understanding the heat capacity of a ferromagnet in an external field near its critical (Curie) point are discussed, with special emphasis on the influence of demagnetizing effects. Two simple examples show the variety of behavior which may be expected, depending on the magnitude of the external field. The utility of considering low-field and high-field limits is pointed out, with particular reference to Ni and EuS.

I. INTRODUCTION

HEAT-CAPACITY measurements play an important role in the investigation of phase transitions in magnetic materials.[1] While these measurements are commonly carried out in zero external field, heat capacities in a finite field can provide additional information. However, the analysis of finite-field data is quite complicated if demagnetizing effects are significant.[2] In this paper, we shall discuss some thermodynamic principles which are useful in understanding the heat capacity of a ferromagnet in a constant external magnetic field near its critical or Curie temperature, a situation in which (due to the large susceptibility) demagnetizing effects are generally quite significant.

General thermodynamic principles and the influence of demagnetizing fields are discussed in Sec. II. Section III contains results of calculations on two hypothetical model systems and a discussion of why similar features would be expected in real ferromagnets. The singular (nonsmooth) behavior of the heat capacity in a finite field is treated in Sec. IV. The utility of considering low- and high-field regions is shown in Sec. V, and estimates are given of where these regions lie for Ni and EuS.

II. GENERAL THERMODYNAMICS CONSIDERATIONS

A. Heat Capacity and Magnetization

Let $\mathbf{M}$ be the total magnetization of a sample (we use Gaussian units) with component M parallel to a uniform external applied field $\mathbf{H}_e$ (the field that is present if the sample is removed while external currents producing the field remain constant) of magnitude H_e. The thermodynamic relation[3]

$$TdS=dU_e-H_e dM \tag{2.1}$$

(with a suitable definition of magnetic energy U_e) leads to the Maxwell relation[4]

$$(\partial M/\partial T)_{H_e}=(\partial S/\partial H_e)_T. \tag{2.2}$$

If (2.2) is combined with the definition

$$C_e=T(\partial S/\partial T)_{H_e} \tag{2.3}$$

of heat capacity in an external field, we obtain the important result

$$(\partial C_e/H_e)_T=T(\partial^2 M/\partial T^2)_{H_e}, \tag{2.4}$$

which upon integration allows us to relate the heat capacity at two different fields:

$$C_e(H_{e2},T)=C_e(H_{e1},T)+T\int_{H_{e1}}^{H_{e2}}\left(\frac{\partial^2 M}{\partial T^2}\right)_{H_e}dH_e. \tag{2.5}$$

Equations (2.4) and (2.5) show the intimate connection between measurements of heat capacity and magnetization. Thus if C_e for $H_e=0$, which we denote by C_0, is known, together with $M(T,H_e)$, C_e for any nonzero H_e can be calculated, *in principle*, from (2.5). Even if C_0 is not known, its singular behavior, if any, near the critical point, in principle, can be calculated from $M(T,H_e)$. Thus if H_{e1} is a reasonably large field, one expects that $C_e(H_{e1},T)$ will be a smooth function of temperature for T near T_c. By setting $H_{e2}=0$, we see that any singular (nonsmooth) behavior of C_0 is entirely determined by the integral in (2.5), i.e., by $M(T,H_e)$.

This does not mean that the availability of magnetization data makes all heat-capacity measurements superfluous. Numerical evaluation of $(\partial^2 M/\partial T^2)_{H_e}$ from experimental data is necessarily of limited precision. However, the intercomparison of heat-capacity and magnetization data when both are available should be a valuable check on experimental procedures. We also expect that certain thermodynamic quantities are more accurately determined by heat capacity than by magnetization measurements.

* Research supported in part by the National Science Foundation and the Alfred P. Sloan Foundation.

[1] C. Domb and A. R. Miedema, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964), Vol. IV, p. 296. See also Ref. 19.

[2] P. M. Levy and D. P. Landau, J. Appl. Phys. **39**, 1128 (1968).

[3] A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1957), pp. 23 ff.

[4] Procedures for deriving elementary thermodynamic relations are found in the standard textbooks, e.g., H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), Chaps. 7 and 14.

B. Spheroidal Samples

The relations (2.1)–(2.5) are very general and hold for a sample of arbitrary (possibly irregular) shape. But it is well known that when $H_e \neq 0$, M and S depend on the shape (as well as the mass) of the sample, making it difficult to compare data for different samples. A major simplification occurs with a uniformly magnetized sphere or spheroid when M and H_e are parallel to each other and to the symmetry axis of the spheroid.[5] Elementary magnetostatic arguments[6] then imply that S and M for a sample of given mass are unique functions of T and an internal field

$$H = H_e - DM/V, \tag{2.6}$$

where V is the sample volume, and D is the demagnetizing factor, which is $\frac{4}{3}\pi$ for a sphere, 0 for a long, thin needle, etc. We shall assume below that changes in D and V due to thermal and magnetostrictive effects have a negligible effect in (2.6) near the critical point.

In a sense, (2.6) amounts to choosing the long, thin needle ($D=0$) as a "standard" shape. While this choice is to a large degree arbitrary, it is very convenient in discussing ferromagnetism. For certain magnetic materials[7] it is found that below the critical temperature,

$$M = VH_e/D \quad \text{for} \quad |M| \leq M_s(T), \tag{2.7}$$

where M_s is the spontaneous magnetization and depends on the temperature. A plot of M versus H made with the help of (2.6) (see Fig. 1) then shows a discontinuity at $H=0$. This is the behavior commonly assumed in theoretical analysis[8] of phenomena near critical points, and thus the "field" appearing in such analyses, and in the Ising and Heisenberg models,[9] is to be associated with H rather than H_e in real materials.

One obtains (2.7) upon setting $H=0$ in (2.6). But for $|M| < M_s$, domains or other more complicated nonuniformities[6] should be present in the sample's magnetization. Thus one may doubt the validity of (2.6), as its derivation requires uniform magnetization. However, we expect that in sufficiently large samples the nonuniformity, while large on a microscopic scale, will still be sufficiently fine so that (2.6) holds approximately and is strictly satisfied in the "bulk" limit, where extensive quantities are proportional to sample size. (There is some evidence for this at $H_e=0$.[10]) Obtaining the bulk limit and finding samples with sufficiently small hysteresis so that equilibrium thermodynamics applies may in practice be rather difficult.

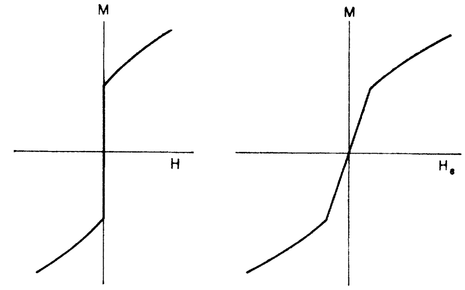

FIG. 1. Comparison (schematic) between M as a function of internal field H and external field H_e.

III. TWO EXAMPLES

Two purely hypothetical examples will help to elucidate the expected behavior of C_e near the critical point. Details of these examples, which we label I and II, will be found in the Appendix. They correspond to a "homogeneous" or "scaling" equation of state[11,12] with classical critical point indices $\alpha=\alpha'=0$, $\beta=\frac{1}{2}$, $\gamma=\gamma'=1$, $\delta=3$, but with a logarithmic singularity in C_0 at T_c, the critical or Curie temperature. For $T<T_c$, example I has a finite initial susceptibility (compare Fig. 1)

$$\chi = \lim_{H\to 0} (\partial M/\partial H)_T. \tag{3.1}$$

Note that this susceptibility refers to $D=0$ (a needle-shaped sample), whereas in II,

$$M - M_s \propto H^{1/2} \tag{3.2}$$

as $H \to 0$. [Note that (3.2) is the prediction of ele-

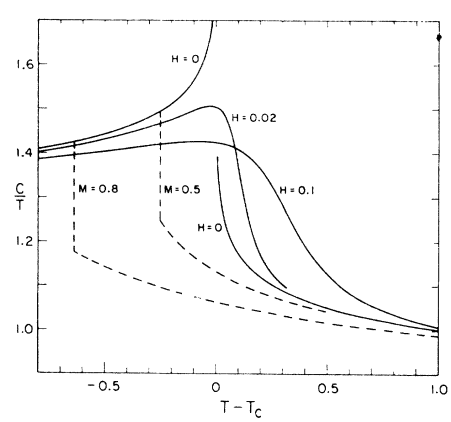

FIG. 2. Heat capacities C_0, C_H, and C_M for example I. Curves of C_M are shown as dashed lines. Horizontal and vertical scales are to some degree arbitrary.

[5] The more general ellipsoidal shape appears to be mainly of interest as an exercise in mathematics. (Our considerations do apply to the infinite cylinder with M and H_e perpendicular to the axis.) The case where M and H_e are not parallel is of greater interest and the thermodynamic analysis offers no difficulty in principle.

[6] See, e.g., W. F. Brown, Jr., *Magnetostatic Principles in Ferromagnetism* (North-Holland Publishing Co., Amsterdam, 1962).

[7] Ref. 1, p. 310 and Ref. 19, p. 765.

[8] See, e.g., M. E. Fisher, Rept. Progr. Phys. **30**, 615 (1967).

[9] These models omit the long-range magnetic dipole-dipole interactions responsible for demagnetizing effects.

[10] R. B. Griffiths, Phys. Rev. **176**, 655 (1968).

[11] B. Widom, J. Chem. Phys. **43**, 3898 (1965).

[12] R. B. Griffiths, Phys. Rev. **158**, 176 (1967).

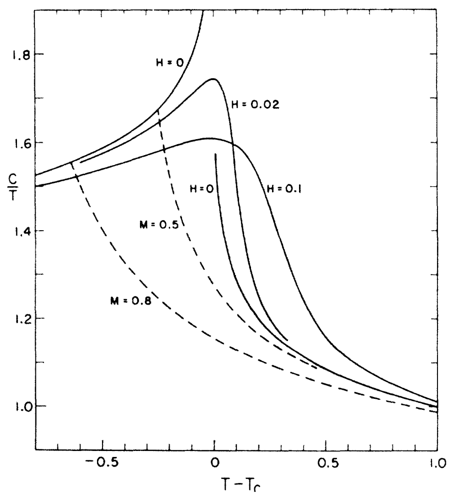

FIG. 3. Heat capacities C_0, C_H, and C_M for example II. Curves of C_M are shown as dashed lines. Horizontal and vertical scales are to some degree arbitrary.

mentary spin-wave theory for a completely isotropic ferromagnet.[13]]

Curves of heat capacity at constant magnetization and internal field,

$$C_M = T(\partial S/\partial T)_M, \quad C_H = T(\partial S/\partial T)_H, \qquad (3.3)$$

respectively, are plotted in Figs. 2 and 3 for examples I and II. Note that C_H and C_e coincide for $H=0$. Both C_M and C_H "scale" in the sense that curves for different M (or H) can be superimposed by a suitable stretching of the horizontal and adjustment of the vertical scale; this is a consequence of assuming a "homogeneous" equation of state. By contrast C_e, shown in Figs. 4 and 5 for the two examples with $D/V=1$, does not scale, and the curves for small and large H_e are qualitatively different (further comments in Sec. V).

From Figs. 2 and 3, we see that C_H and C_M are qualitatively quite different. The former is less than C_0 for all temperatures below T_c, but has a maximum near T_c and crosses C_0 a short distance above T_c. On the other hand, C_M is equal to C_0 for temperatures below the temperature where $M = M_s(T)$, and then decreases rapidly (for I, discontinuously) and lies below C_0 at all higher temperatures.

Elementary thermodynamic considerations indicate that similar behavior should occur in real ferromagnets if curves of $M(T)$ at fixed H are qualitatively similar to those shown in Fig. 6 for example II. At low temperatures, $M(T)$ resembles $M_s(T)$ with negative curvature, but at high temperatures the curvature is positive. Since[4]

$$(\partial C_H/\partial H)_T = T(\partial^2 M/\partial T^2)_H, \qquad (3.4)$$

we expect that C_H will decrease with $|H|$ at low temperatures and increase with $|H|$ at high temperatures, with a changeover near T_c when $|H|$ is small. On the other hand, for $M \geq 0$,[4]

$$(\partial C_M/\partial M)_T = -T(\partial^2 H/\partial T^2)_M \qquad (3.5)$$

will be negative provided H is a convex function of the temperature at fixed $M>0$. This is found to be the case empirically[14] for several magnetic materials near their critical points, and thus one would expect C_M to decrease as $|M|$ increases.

IV. SINGULAR BEHAVIOR OF C_e AT $T = T_1$

The question of whether the heat capacity in a field should exhibit any singular (i.e., nonsmooth) behavior as a function of temperature was raised by Van der Hoeven, Teaney, and Moruzzi in connection with their experimental measurements on EuS.[15] In the case of C_H, one expects a completely smooth (in the case of an Ising ferromagnet, analytic[16]) curve for $H \neq 0$. On the other hand, C_e may be expected to show some singular behavior[17] at the temperature T_1 determined by

$$M_s(T_1) = VH_e/D. \qquad (4.1)$$

If $M_s(T)$ is a monotone decreasing function (as we shall assume), then for fixed H_e (2.7) is satisfied and the right-hand side of (2.4) vanishes for $T<T_1$. Consequently, C_e and C_0 are identical in this temperature range. At temperatures just above T_1, C_e falls below C_0 (which we assume is a smooth function of tempera-

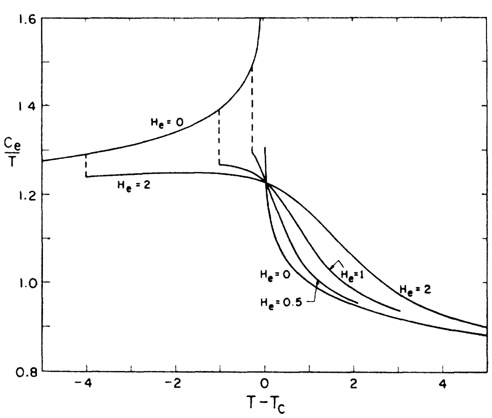

FIG. 4. Heat capacity C_e (constant external field) for example I with various choices of H_e. Note the discontinuity indicated by a dashed line.

[13] F. Keffer, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1966), Vol. 18/2, pp. 27 ff.

[14] M. Vicentini-Missoni, J. M. H. Levelt Sengers, M. S. Green, and R. I. Joseph, Bull. Am. Phys. Soc. **14**, 593 (1969).

[15] B. J. C. Van der Hoeven, Jr., D. T. Teaney, and V. L. Moruzzi, Phys. Rev. Letters **20**, 719 (1968); **20**, 722 (1968). Note that these authors use the symbol C_M for heat capacity in a constant external field, that is, C_e in our notation.

[16] J. L. Lebowitz and O. Penrose, Commun. Math Phys. **11**, 99 (1968).

[17] A slightly abbreviated version of material presented here will be found in R. B. Griffiths, J. Appl. Phys. **40**, 1542 (1969).

ture at $T=T_1$), and its behavior can be analyzed as follows:

Assume the free energy F has the form

$$F=F_0(T)-HM_s(T)-H^{1+1/\phi}\Lambda(T)+\cdots \tag{4.2}$$

for small values of $H>0$ and temperatures near to but less than T_c. In writing (4.2) we make the relatively mild assumption (as compared to scaling,[12] which is much stronger) that the magnetization curves for $T<T_c$ bear a "family resemblance" to one another in the limit of small H. The constant ϕ is not less than one. The following analysis is not appreciably altered if ϕ is a slowly varying function of temperature. Magnetization and entropy are given by

$$M=-(\partial F/\partial H)_T=M_s(T)+(1+\phi^{-1})H^{1/\phi}\Lambda(T)+\cdots, \tag{4.3}$$

$$S=-(\partial F/\partial T)_H=S_0(T)+HM_s'(T)+H^{1+1/\phi}\Lambda'(T)+\cdots. \tag{4.4}$$

For fixed H_e, consider the region where H and

$$\Delta T=T-T_1 \tag{4.5}$$

are small and positive. To lowest order, we may approximate (4.3) by

$$M=M_s(T_1)+\Delta TM_s'(T_1)+(1+\phi^{-1})H^{1/\phi}\Lambda(T_1). \tag{4.6}$$

When inserted in (2.6) and combined with (4.1), this yields

$$H+\tilde{D}(1+\phi^{-1})H^{1/\phi}\Lambda(T_1)=-\tilde{D}\Delta TM_s'(T_1), \tag{4.7}$$

where $\tilde{D}$ stands for D/V. Next solve (4.7) for H and insert the result in (4.4). Two cases should be distinguished.

(a) $\phi=1$. This means that χ, Eq. (3.1), is finite (as in example I of Sec. III). To lowest order in T,

$$\Delta S=S-S_0(T)\simeq-\tilde{D}[M_s'(T_1)]^2\Delta T/[1+2\tilde{D}\Lambda(T_1)], \tag{4.8}$$

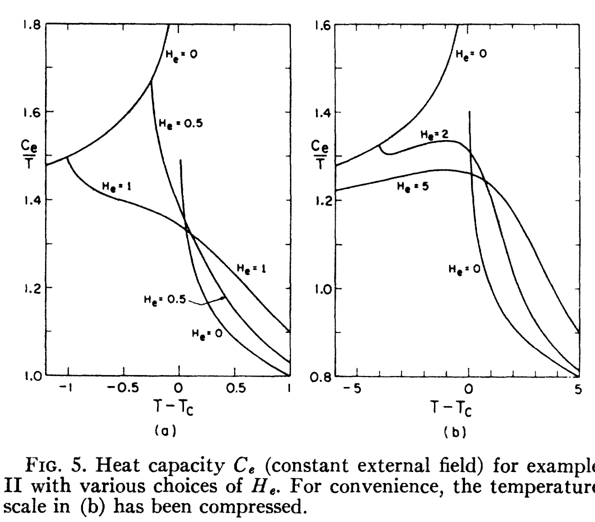

FIG. 5. Heat capacity C_e (constant external field) for example II with various choices of H_e. For convenience, the temperature scale in (b) has been compressed.

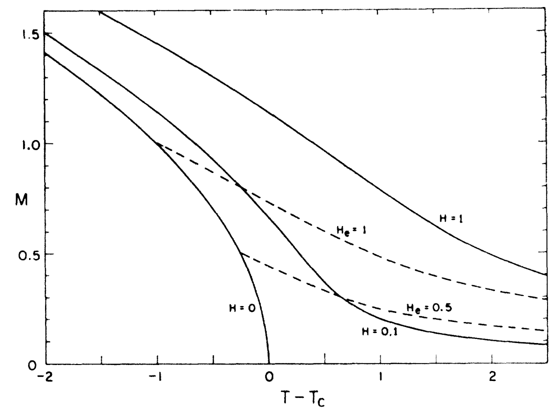

FIG. 6. Magnetization versus temperature for constant H (solid curves) and H_e (dashed curves) for example I. The curve $H=0$ is the spontaneous magnetization. Example II yields qualitatively similar results except that curves of constant H_e have zero slope where they intersect the curve $H=0$.

and thus

$$\Delta C=C_e-C_0=Td(\Delta S)/dT\simeq-\tilde{D}T_1[M_s'(T_1)]^2/(1+\tilde{D}\chi) \tag{4.9}$$

is finite as $\Delta T\rightarrow 0$, indicating a jump discontinuity at $T=T_1$. This behavior is exhibited in example I (Fig. 4) and in a case considered by Wojtowicz and Rayl.[18] It should characterize any ferromagnet which has finite initial susceptibility. Note that the magnitude of the discontinuity depends on the sample shape.

(b) $\phi>1$. For this case χ is infinite, and to *lowest* order (4.7) yields

$$H\simeq[-\Delta TM_s'(T_1)]^\phi(1+\phi^{-1})^{-\phi} \tag{4.10}$$

and

$$\Delta C\simeq-(\Delta T)^{\phi-1}|M_s'(T_1)|^{1+\phi}T_1(1+\phi^{-1})^{-\phi}, \tag{4.11}$$

which goes to zero with ΔT. In example II, $\phi=2$ [see (3.2)] and ΔC is initially linear in ΔT. Figure 5 shows that the region of linear behavior can be quite small. It is interesting that (4.11) is formally shape-independent, though higher-order terms will depend on $\tilde{D}$.

Note that in both cases (a) and (b) the singular behavior at $T=T_1$ has no necessary connection with that at $T=T_c$ when $H_e=0$. In particular, for our two examples C_0 has a logarithmic divergence, while C_e has a quite different behavior at $T=T_1$.

V. LOW- AND HIGH-FIELD LIMITS

At temperatures very near the critical temperature and in a sufficiently small magnetic field, the susceptibility of a ferromagnet becomes quite large and we can expect to find $M/V\gg H$. Under these conditions it should be a good approximation to set $H=0$ in (2.6), which means that $C_e\simeq C_M$, with M given by (2.7). Figures 4 and 5 show that C_e for our examples does

[18] P. J. Wojtowicz and M. Rayl, Phys. Rev. Letters **20**, 1489 (1968).

resemble C_M when H_e is small. As H_e increases, however, C_e develops a maximum near T_c and the singular behavior near T_1, while still present, is less pronounced. In sufficiently high fields, we expect $M/V \ll H$, so $M=0$ should be a good approximation in (2.6) and $C_e \simeq C_H$. [Compare Figs. 3 and 5(b).]

Let us define the "characteristic" internal field H_h by the requirement that at $T=T_c$ it induces a magnetization

$$M=VH_h/D. \tag{5.1}$$

The corresponding external field [see (2.6)] is $2H_h$. Then it is reasonable to suppose that the low- and high-field limits, for which C_e resembles C_M or C_H, correspond to $H_e \ll H_h$ or $H_e \gg H_h$. In examples I and II, Figs. 4 and 5, H_h is 1.22 and 1.41, respectively.

For real materials it is convenient, following Heller,[19] to relate M and H on the critical isotherm by

$$H/H_I=E(M/M_0)^\delta, \tag{5.2}$$

where M_0 is the saturation magnetization at zero temperature for a sample containing n moles, and

$$H_I=nRT_c/M_0, \tag{5.3}$$

with R the gas constant. The index δ generally falls between four and five, while E is a dimensionless constant on the order of 1. Upon combining (5.1), (5.2), and (5.3) we obtain

$$H_h/H_I=(1/E)^{1/(\delta-1)}(DM_0^2/nVRT_c)^{\delta/(\delta-1)}. \tag{5.4}$$

In the case of a Ni sphere, the data in Ref. 19 yield $H_h \simeq 250$ G. Thus for an external field on the order of 100 G, C_e should resemble C_M. However, in this situation $(T_c-T_1)/T_c$ is on the order of 10^{-4}, and since heat-capacity data generally show "rounding" effects this close to the critical temperature, it is doubtful whether one can observe the characteristic features of C_M in Ni. In fairly moderate fields, $H_e \gtrsim 1000$ G, C_e should resemble C_H.

The situation is quite different for EuS. Though magnetization data near the critical point have not (so far as we know) been published, M_0 is known,[20] and if we assume $\delta \simeq 4.5$, $E \simeq 1$, (5.4) yields $H_h \simeq 2500$ G for a sphere. Thus we expect that the measurements of Van der Hoeven *et al.*, with H_e from 0 to 1350 G, should be classified as low field. Indeed, C_e for $H_e=915$ G, shown in Fig. 3 of Ref. 15, exhibits the features one would expect qualitatively on the basis of the foregoing discussion, with one exception. The data of Heller and Benedek[21] indicate that $T_1 \simeq 16.35$°K for this situation, but C_e is less than C_0 down to $T \simeq 16.25$°K. This indicates that (2.7) breaks down at some $M<M_s$, a result which is confirmed by direct magnetization measurements.[22] Such "rounding" could be due to material inhomogeneity of some kind in the sample, in which case it is not implausible that C_e for an ideal sample would resemble Fig. 5(a).

ACKNOWLEDGMENT

We wish to thank Dr. Van der Hoeven for sending us unpublished heat-capacity data for EuS.

APPENDIX: DETAILS OF EXAMPLES I AND II

We use the procedure and (with minor modifications) the notation of Ref. 12 for constructing "homogeneous functions." Let the equation of state have the form[23]

$$H=M^3h(\tau M^{-2}), \tag{A1}$$

where

$$\tau=T-T_c. \tag{A2}$$

For examples I and II, we choose

$$h(x)=(x+1)(x+2)(x+3)^{-1}, \tag{A3a}$$

$$h(x)=(x+1)^2(x+2)^{-1}, \tag{A3b}$$

respectively, for $x \geq -x_0=-1$. Using Ref. 12, C_M has the form

$$T^{-1}C_M=C_0(T)+c(\tau M^{-2})-h''(0)\ln|M|, \tag{A4}$$

where $c(x)$ [$=-a_0''(x)$ in Ref. 12] satisfies the equation

$$2xc'(x)=h''(x)-h''(0), \tag{A5}$$

with solutions

$$c(x)=\frac{1}{27}\left(\frac{6(x+3)+9}{(x+3)^2}-2\ln(x+3)\right), \tag{A6a}$$

$$c(x)=\frac{1}{8}\left(\frac{2(x+2)+2}{(x+2)^2}-\ln(x+2)\right) \tag{A6b}$$

corresponding to (A3a) and (A3b). In Figs. 2–5, we have set the smooth function $C_0(T)$ in (A4) equal to 1.

Curves of C_e at constant H_e can be computed using

$$T^{-1}C_e=T^{-1}C_M+\frac{[(\partial H/\partial T)_M]^2}{(\partial H/\partial M)_T+\tilde{D}} \tag{A7}$$

provided that at some temperature the right-hand side is evaluated for an appropriate M determined by eliminating H between (A1) and (2.6). To derive (A7), use the relation

$$dS=(\partial S/\partial T)_M dT+(\partial S/\partial M)_T dM, \tag{A8}$$

to obtain

$$\left(\frac{\partial S}{\partial T}\right)_{H_e}=\left(\frac{\partial S}{\partial T}\right)_M+\left(\frac{\partial S}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_{H_e}. \tag{A9}$$

[19] P. Heller, Rept. Progr. Phys. **30**, 731 (1967).
[20] S. H. Charap and E. L. Boyd, Phys. Rev. **133**, A811 (1964).
[21] P. Heller and G. Benedek, Phys. Rev. Letters **14**, 71 (1965).
[22] B. J. C. Van der Hoeven, Jr. (private communication).
[23] We shall not be concerned with any normalization for H and M which, for present purposes, may be treated as dimensionless. Similarly, replacing $t=(T-T_c)/T_c$ of Ref. 12 by τ represents an inconsequential (for our purposes) change of scale.

However,

$$\left(\frac{\partial M}{\partial T}\right)_{H_e}=-\frac{(\partial H_e/\partial T)_M}{(\partial H_e/\partial M)_T}=-\frac{(\partial H/\partial T)_M}{(\partial H/\partial M)_T+\tilde{D}},\tag{A10}$$

where the second equality utilizes (2.6). Finally, the Maxwell relation[4]

$$(\partial S/\partial M)_T=-(\partial H/\partial T)_M\tag{A11}$$

completes the derivation.

In computing C_e it is convenient, given H_e, to first choose M, then evaluate $x=\tau M^{-2}$ by combining (2.6) and (A1), and express the right-hand side of (A7) in terms of x and M. If $\tilde{D}=D/V$ is set equal to zero in (A7), C_e is identical to C_H.

It is clear from (A4) that $T^{-1}C_M$ satisfies a "scaling" relation. The same is true of $T^{-1}C_H$. It can, in fact, easily be shown that

$$T^{-1}C_H=C_0(T)+f(\tau|H|^{-2/3})-\lambda\ln|H|\tag{A12}$$

for an appropriate function $f(x)$ and constant λ.

PHYSICAL REVIEW VOLUME 188, NUMBER 2 10 DECEMBER 1969

Numerical Study of the t Matrix in the Kondo Problem*

R. K. M. Chow† and H. U. Everts‡
Department of Physics, University of Toronto, Toronto, Canada
(Received 7 July 1969)

A numerical study of the Kondo problem is presented. The calculations are based on the Suhl-Abrikosov-Nagaoka integral equation for the scattering amplitude $t(\omega,T)$ of the s-d exchange Hamiltonian. Use is made of the exact analytic solution first given in detail by Zittartz and Müller-Hartmann. It is shown that, because of the resonance in $\mathrm{Im}t(\omega,T)$ which occurs at the Fermi energy ($\omega=0$) at low temperatures, the tunneling density of states of a dilute paramagnetic alloy is very slightly reduced at zero bias voltage. There is, however, a possibility of detecting this change by studying the derivative of the conductance. The details of the Zittartz-Müller-Hartmann expression are found to be unimportant for the low-temperature behavior of the transport coefficients with the exception of the thermoelectric power. A reinvestigation of the thermoelectric power shows that some care is necessary in the evaluation of the integrals $K_n=\int_{-\infty}^{\infty}d\omega\,\omega^n n_0(\omega)\tau(\omega,T)\partial f/\partial\omega$, because of the strong ω dependence of the electronic lifetime $\tau(\omega,T)\propto[\mathrm{Im}t(\omega,T)]^{-1}$ at low temperatures. While the transport coefficients reflect the behavior of the scattering amplitude in a small energy interval about the Fermi energy, the specific-heat anomaly is found to be related to the temperature derivative of $t(\omega,T)$ at large values of the energy variable ω comparable to the bandwidth. We also point out that the quasiparticle approximation is not valid for electrons interacting with impurity spins due to the rapid variation of $t(\omega,T)$ near the Fermi energy.

I. INTRODUCTION

In this paper, we study numerically the low-temperature anomalies of dilute magnetic alloys. The s-d exchange model (or Kondo Hamiltonian) is widely accepted as a reasonable description of the interaction between conduction electrons and the localized magnetic moments of the impurity ions. This model Hamiltonian consists of a simple contact interaction between the impurity spin $\mathbf{S}_j^{\mathrm{imp}}$ and the electron spin density at the position of the impurity:

$$H_{sd}=H_{\mathrm{kin}}-\frac{J}{N}\sum_j \mathbf{S}_j^{\mathrm{imp}}\cdot\mathbf{s}^{\mathrm{el}}(\mathbf{R}_j).\tag{1.1}$$

Here H_{kin} is the kinetic energy of the noninteracting electron system, N is the number of atomic cells, and J is the coupling constant. We shall consider only the case of antiferromagnetic coupling ($J>0$).

In the course of explaining the resistance minimum of dilute magnetic alloys on the basis of the s-d exchange Hamiltonian, Kondo[1] discovered that in perturbation theory the one-electron scattering amplitude has a logarithmic singularity at small temperatures and energies. Various nonperturbational methods[2–7] have since been developed to explain quantitatively the anomalous behavior of the physical properties of dilute magnetic alloys. Of particular interest to us are the methods of

* Research sponsored by research grants from the National Research Council of Canada.
† Present address: Department of Physics, Simon Fraser University, Burnaby, B. C., Canada.
‡ Present address: Institut Max von Laue–Paul Langevin, Aussenstelle Garching, 8046 Garching, Germany.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).
[2] H. Suhl, Phys. Rev. **138**, A515 (1965); **141**, 483 (1966); Physics **2**, 39 (1965).
[3] A. A. Abrikosov, Physics **2**, 5 (1965).
[4] Y. Nagaoka, Phys. Rev. **138**, A1112 (1965); Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966).
[5] J. Appelbaum and J. Kondo, Phys. Rev. Letters **19**, 906 (1967); Phys. Rev. **170**, 542 (1968).
[6] K. Yosida, Phys. Rev. **147**, 223 (1966); Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966).
[7] A. Okiji, Progr. Theoret. Phys. (Kyoto) **36**, 712 (1966).