Logarithmic Corrections to the Landau Specific Heat near the Curie Temperature of the Dipolar Ising Ferromagnet $LiTbF_4$

Guenter Ahlers, Avinoam Kornblit, and H. J. Guggenheim
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 20 January 1975)

Quantitative experimental results for the logarithmic corrections to the Landau specific heat are reported for the dipolar Ising ferromagnet $LiTbF_4$ near its Curie temperature $T_c = 2.885$ K. The power of the leading logarithmic term is found to be 0.34 ± 0.03, and the corresponding amplitude ratio is 0.24 ± 0.01. These results are in agreement with the predicted values of $\frac{1}{3}$ and $\frac{1}{4}$, respectively.

It is known from modern theories of phase transitions[1] that systems with isotropic, short-range interactions have singularities near critical points which are given correctly by the classical Landau theory,[2] provided the dimensionality d is greater than 4. For $d=4$, Larkin and Khmel'nitskii[3] (LK) predicted Landau-like behavior, modified by terms which depend upon fractional powers of logarithms. These authors also showed that for the special case of uniaxial systems (spin dimensionality $n=1$) with dipolar interactions, logarithmic terms occur for $d=3$. In this case, the classical theory is correct for $d>3$. In recent years, this problem of borderline dimensionality has been studied more extensively,[1,4,5] and it was recognized that for each type of critical point there is a value d^* of the dimensionality such that Landau theory pertains for $d>d^*$. The logarithmic terms which occur for $d=d^*$ are a central result of the renormalization-group theory of critical phenomena; but they had not been observed previously by measurements on real systems. Indeed, there are only very few types of critical points for which d^* coincides with a dimensionality which is accessible in the laboratory. Even for these few cases it would be extremely difficult to obtain quantitative results for the logarithmic contributions to properties with strong leading singularities such as the magnetization or the susceptibility. However, the Landau specific heat depends upon the reduced temperature in a very simple way. In this case the logarithmic terms are in fact the leading singularity, and it is relatively easy to measure them with considerable accuracy. We report here on specific-heat measurements for the uniaxial ferromagnet $LiTbF_4$. For this material, it is known that dipolar forces make a sizable contribution to the interaction[6]; and indeed measurements of the magnetization and susceptibility have yielded classical leading exponents.[6] We find that the measured specific heat agrees in detail with the predictions regarding the logarithmic terms. Our data yield the values 0.34 ± 0.03 for the power of the logarithms, and 0.24 ± 0.01 for their amplitude ratio. For $n=1$, the corresponding predictions[1] are $\frac{1}{3}$ and $\frac{1}{4}$, respectively.

To a large extent our calorimeter has been described before.[7] We used a single crystal of $LiTbF_4$ and a previously established laboratory temperature scale.[8] Greater experimental detail will be given elsewhere.[9] Some of our results for C_p are shown on linear scales in Fig. 1 as a function of $t \equiv T/T_c - 1$. Figure 1(a) shows the data over a rather wide range, and illustrates the general shape of the specific-heat curve. The results yield a transition temperature $T_c = 2.8845 \pm 0.001$ K for our sample on the 1958 He^4 vapor pressure scale. Our T_c differs by 0.03 K from that reported by Holmes *et al.*,[10] but our C_p measurements generally agree quite well with theirs provided the temperature scales are shifted so that the values of T_c coincide. For Fig. 1(b), the temperature axis was expanded by a factor of 10, and the data cover roughly the range over which the asymptotically dominant critical behavior might be observed. For Fig. 1(c), the temperature axis was expanded by yet another factor of 10; and now it becomes apparent that very near T_c there is some "rounding" of the phase transition. A reduction of the local magnetic field to 0.05 Oe [see solid dots in Fig. 1(c)] had no effect upon C_p near T_c. Annealing of the sample near 700°C reduced the "width" of the transition by at most 30%.

Before comparing our results with the predictions of LK,[3] it is instructive to see whether the data can be understood in terms of the known behavior of C_p near other types of critical points. We therefore fitted[7] them by the power law $C_p = (A/\alpha)|t|^{-\alpha} + B$ for $t>0$, and to the same function with primed coefficients for $t<0$. The con-

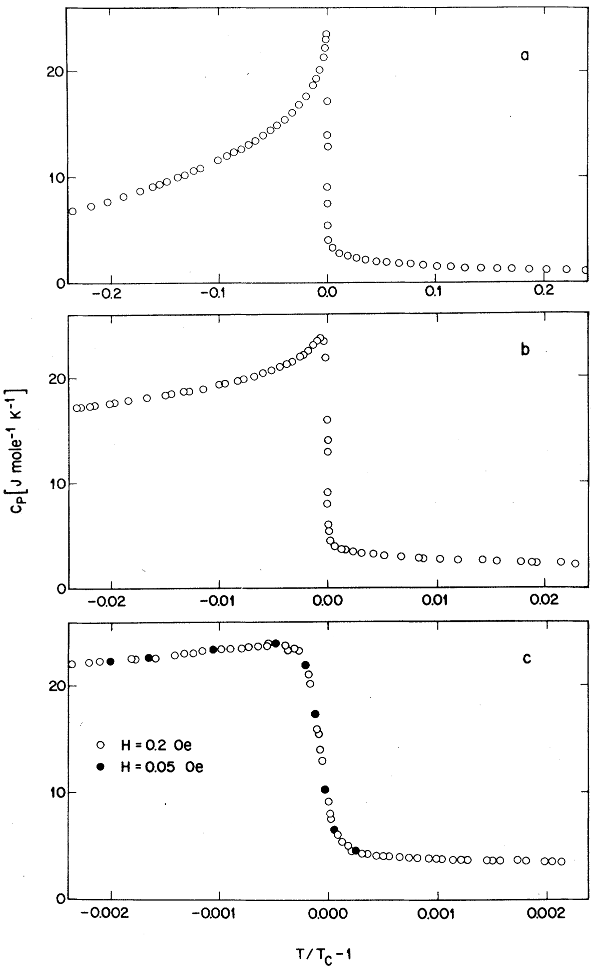

FIG. 1. The heat capacity of $LiTbF_4$ as a function of the reduced temperature on linear scales. Note the expansion of the temperature scale by factors of 10 when going from (a) to (b) to (c).

straint $\alpha = \alpha'$ was statistically allowed by the data. By using results with $10^{-3} \leqslant |t| \leqslant 10^{-2}$, and by least-squares adjusting $\alpha = \alpha'$, A/A', A, B, B', and T_c, we obtained $\alpha = \alpha' = -0.148 \pm 0.017$, $A/A' = 0.242 \pm 0.007$, $A/R = 0.1226 \pm 0.011$, $B/R = 0.755 \pm 0.043$, $B'/R = 4.057 \pm 0.159$, and $T_c = 2.884\,61 \pm 0.000\,16$ K ($R = 8.3144$ J mole^{-1} K^{-1}). Other reasonable ranges of t gave similar results.[9] The deviations of the data from the fitted function were random, and pure power-law behavior therefore cannot be ruled out on the basis of these data alone. However, with $\alpha = \alpha' < 0$ the result $B < B'$ indicates that C_p is *discontinuous* at T_c. For $\alpha < 0$, the discontinuity must be regarded as the leading singularity and corresponds to a leading exponent equal to zero. For critical points in systems with short-range forces previous experiments have been consistent with $B = B'$; and this equality is also predicted by theory.[11] Even if we ignore the discontinuity, it is impossible to reconcile the *values* of $\alpha = \alpha'$ and A/A' with the properties of short-range-force systems. The value $\alpha = -0.15$ implies Heisenberg-like behavior ($n = 3$, where n is the spin dimensionality),[7,12] whereas it is known that $LiTbF_4$ is a uniaxial system which in the absence of dipolar forces should be Ising-like ($n = 1$) with $\alpha \cong 0.1$.[12] Ignoring also this problem, we still find that A/A' is too small by a factor of 5 or 6 for $n = 3$,[7,12] and by a factor of 2 for $n = 1$.[12] We therefore conclude that the analysis in terms of a power law leads to results which are different from those on previously investigated materials, and which cannot be understood in terms of known critical behavior involving short-range forces.

We shall now proceed to compare the measurements with the prediction of LK.[3] For this purpose, we present some of our data as solid dots in Fig. 2 as a function of $\log_{10}|t|$. It is evident already from the figure that C_p increases less rapidly than $\ln|1/t|$, consistent with the LK prediction that $C_p \sim \ln^{1/3}|1/t|$. According to LK, C_p can be represented by

$$C_p^+ = (A/b^z)\{[1 + b\ln(a/t)]^z - 1\} + B \tag{1a}$$

for $T > T_c$, and by

$$C_p^- = (A'/4b'^{z'})\{4[1 + b'\ln(-a'/t)]^{z'} - 1\} + B' \tag{1b}$$

for $T < T_c$, with $a = a'$, $b = b'$, $z = z' = \frac{1}{3}$, $B = B'$, and $A/A' = \frac{1}{4}$. Equations (1) are expected to be correct in the limit as $|t|$ vanishes, and for $|t| < a$ they provide a reasonable interpolation between the behavior at small $|t|$ and the jump $3A/b^{1/3}$ which corresponds to the Landau theory. The term $B = B'$ in Eqs. (1) represents a regular contribution to C_p. It follows from Eqs. (1) and the predicted constraints upon the parameters that

$$\delta C_p = 3A/b^{1/3} - 3B, \tag{2}$$

where $\delta C_p \equiv C_p^- - 4C_p^+$. We note that δC_p is independent of t. This would be the case even for arbitrary z, and indeed for an arbitrary dependence upon t of the part of Eqs. (1) inside the square brackets. A constant δC_p therefore implies an amplitude ratio of $\frac{1}{4}$, to a large extent independent of other details of the singularity. Thus, we plotted $4C_p^+$ in Fig. 2 as open circles. The difference δC_p can now be read directly from

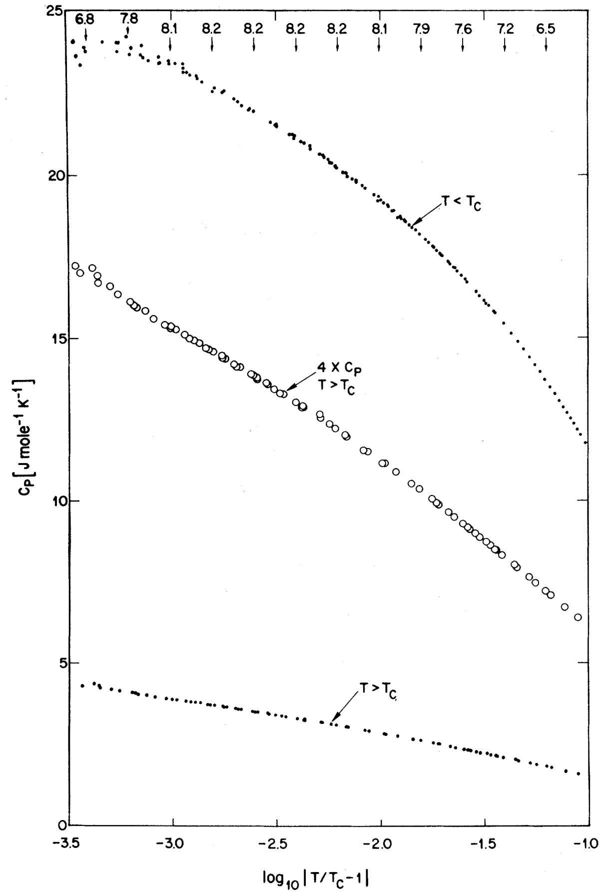

FIG. 2. The heat capacity of $LiTbF_4$ as a function of the logarithm of the reduced temperature. The numbers near the upper margin are the jumps $C_p^- - 4C_p^+$ which were read from the figure at the positions of the arrows. We used $T_c = 2.88445$ K.

the figure, and numerical values for it are given near the upper margin for several values of $\log_{10}|t|$. Over the decade $10^{-3} \leq |t| \leq 10^{-2}$, δC_p is indeed independent of t, consistent with the predicted amplitude ratio $A/A' = \frac{1}{4}$. For $|t| \lesssim 10^{-3}$, δC_p no longer is independent of t, an effect which we attribute to the "rounding" of C_p which was already evident in Fig. 1(c). Likewise, δC_p depends upon t for $|t| \gtrsim 10^{-2}$. This behavior is probably caused by higher-order contributions to C_p which are not contained in Eq. (1).

On the basis of the graphical analysis given above, we have chosen the range $10^{-3} \leq |t| \leq 10^{-2}$ for a more objective least-squares fit[7] of the data by Eqs. (1). We imposed all the predicted constraints, except that in addition to A, b, a, B, and T_c we also permitted A/A' and $z = z'$ to be

TABLE I. Parameters for Eq. (1) for two fixed values of B, determined over the range $10^{-3} \leq |t| \leq 10^{-2}$ with the constraints $A/A' = \frac{1}{4}$ and $z = z' = \frac{1}{3}$.

B/R	0.0	0.2
A/R [a]	0.4394 ± 0.0007	0.4394 ± 0.0007
$b = b'$	2.425 ± 0.020	0.5796 ± 0.0035
$a = a'$	0.2084 ± 0.0039	0.05605 ± 0.00069
$3A/b^{1/3}R$ [a]	0.981 ± 0.002	1.581 ± 0.002
T_c (K)	2.88445 ± 0.00004	2.88457 ± 0.00004

[a] Subject to additional possible systematic errors of ±1%.

least-squares adjusted. We obtained

$$A/A' = 0.244 \pm 0.009, \tag{3}$$

in excellent agreement with the LK prediction. However, Eqs. (1), without additional constraints, are not suitable for the determination of useful values of any of the other parameters. The reason for this can be seen by considering Eqs. (1) for very small t. In the limit as t vanishes, Eq. (1a) for instance yields $C_p^+ = A \ln^z(a/t) - A/b^z + B$, which in addition to B contains the additive constant A/b^z. Even for $|t| > 0$, this combination of parameters remains extremely highly correlated with B. We therefore chose to limit the regular term to the physically reasonable range $0 \leq B = B' \leq 0.2R$. The upper limit is based upon the assumption that the regular contribution near T_c should not be much larger than the total specific heat well above T_c, say at $t \cong 0.1$. Constraining B to the indicated range made it possible to obtain realistic values and uncertainties for the exponent of the logarithms, and we found

$$z = z' = 0.336 \pm 0.024, \tag{4}$$

in fine agreement with the predicted value of $\frac{1}{3}$.[13] Results similar to Eqs. (3) and (4), but with slightly different errors, were obtained also when data over somewhat larger or smaller ranges of $|t|$ were fitted.[9]

In an attempt to obtain estimates for the nonuniversal parameters A, b, and a, we next assumed that $A/A' = \frac{1}{4}$ and that $z = z' = \frac{1}{3}$, and carried out an analysis of the data with these additional constraints for the fixed values $B = 0.0$ and $B = 0.2R$. The results are given in Table I. Both b and a depend strongly upon the choice of B. A determination of these parameters therefore is not possible on the basis of our data alone, and must be postponed until independent information becomes available either about the constant B

or about the Landau jump $3A/b^z$.[14]

Although at this time the best documentation for the existence of sizable dipolar contributions to the interaction exists for $LiTbF_4$,[6] we consider it possible that there are many other dipolar Ising systems suitable for experimental study. Often, the microscopic interactions will be more complicated and perhaps unknown. For those cases we would like to suggest that our power-law parameters may serve as a useful indication of what can be expected from the customary analysis of specific-heat data when dipolar Ising behavior dominates over the experimental range of t.

We are grateful to E. Brézin, B. I. Halperin, and P. C. Hohenberg for helpful discussions regarding the interpretation of our measurements.

[1]See, for instance, K. G. Wilson and J. Kogut, Phys. Rep. 12C, 75 (1974).

[2]See, for instance, H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, Oxford, England, 1971).

[3]A. I. Larkin and D. E. Khmel'nitskii, Zh. Eksp. Teor. Fiz. 56, 2087 (1969) [Sov. Phys. JETP 29, 1123 (1969)].

[4]F. J. Wegner and E. K. Riedel, Phys. Rev. B 7, 248 (1973); M. J. Stephen, E. Abrahams, and J. P. Straley, to be published; E. Brézin, to be published.

[5]A. Aharony, Phys. Rev. B 8, 3363 (1973), and Phys. Lett. 44A, 313 (1973).

[6]J. Als-Nielsen, L. M. Holmes, and H. J. Guggenheim, Phys. Rev. Lett. 32, 610 (1974), and to be published.

[7]A. Kornblit and G. Ahlers, Phys. Rev. B 8, 5163 (1973).

[8]G. Ahlers, Rev. Sci. Instrum. 37, 477 (1966).

[9]G. Ahlers, A. Kornblit, and H. J. Guggenheim, to be published.

[10]L. M. Holmes, F. Hulliger, H. J. Guggenheim, and J. P. Maita, Phys. Lett. 50A, 163 (1974).

[11]See, for instance, G. Ahlers, Phys. Rev. A 8, 530 (1973); A. Kornblit and G. Ahlers, Phys. Rev. B 11, 2678 (1975), and Ref. 7; M. Barmatz, P. C. Hohenberg, and A. Kornblit, to be published; G. Ahlers and A. Kornblit, to be published.

[12]See, for instance, Fig. 28 of first paper by Ahlers in Ref. 11.

[13]Equation (1) gives the logarithmic terms correctly only to leading order, and provides a reasonable, but not rigorous, interpolation between the behavior near T_c and the behavior given by the Landau theory which pertains when $\ln|a/t|$ is small. A more complete expression, correct to $O[\ln|\ln t|/\ln t]$, was obtained by E. Brézin and J. Zinn-Justin (to be published). An analysis of our data in terms of this prediction yields parameters similar to those in Eqs. (3) and (4) (see Ref. 9).

[14]The Landau theory of phase transitions provides the relation $\Delta C_p = -B^2/2\Gamma T_c$ between the specific-heat jump $\Delta C_p = -3A/b^z$ and the amplitudes Γ of the susceptibility χ and B of the magnetization M. Measurements of χ and M can therefore be used to fix the value of $3A/b^z$. Reliable experimental results for Γ and B are not yet available, however. The determination of these amplitudes requires considerable care because the parameters a and b also occur in logarithmic corrections to χ and M (Ref. 3); and the choice of values for a and b will influence the results for Γ and B. Ideally, therefore, the data for χ, M, and C_p should be analyzed self-consistently.

Fluctuation Scattering of Magnetic Excitations in a Nearly Critical Singlet-Ground-State System: Double-hcp Pr†

Per Bak
Brookhaven National Laboratory, Upton, New York 11973
(Received 17 March 1975)

The temperature dependence of the magnetic-excitation spectrum in a singlet-doublet system is calculated by use of a generalized Vaks-Larkin-Pikin diagram technique. The first-order terms in the high-density expansion representing scattering on single-site fluctuations give an almost complete description of the line shapes in double-hcp praseodymium at any temperature.

Recently, the magnetic excitations propagating on lattice sites with hexagonal symmetry in paramagnetic, double-hcp (dhcp) praseodymium were studied by Houmann *et al.*[1] using inelastic neutron scattering. They found the temperature dependence of the excitation energies to be in excellent agreement with a random-phase approximation (RPA) in contrast to earlier measure-