Logarithmic Corrections in the Magnetic Equation of State for $LiTbF_4$

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Using SQUID (superconducting quantum interference device) detection, the field and temperature dependence of the magnetization m has been measured close to the critical point of this uniaxial dipolar-coupled ferromagnet. It is shown for the first time that the Landau expansion of the field h holds if m is scaled by $[\ln(\partial m/\partial h)/\chi_0]^{1/3}$, while other equations (of Ising, mean field) yield less agreement and unrealistic parameters. The expansion coefficients of the present analysis can explain in detail formerly measured zero-field properties.

The critical-point singularities of uniaxial ferromagnets and ferroelectrics are expected to behave rather exceptionally in that they should not obey the conventional power-law forms, but the mean-field (MF) laws enhanced by logarithmic factors, which are due to dipolar anisotropic critical fluctuations[1,2]

$$X(r) \propto \tilde{X}(r)|\ln r|^{1/3}. \tag{1}$$

$\tilde{X}$ denotes the MF relation of the quantity X, e.g., order parameter, susceptibility, specific heat, or correlation length, while r measures the distance from the critical point. Equation (1) corresponds to exact solutions of the renormalization group available at the marginal dimension $d = d^*$ and, therefore, experimental checks for the logarithmic corrections on dipolar Ising systems, where $d^* = 3$, are of relevance for the modern theory of phase transitions.[2] In fact, a considerable number of data from an uniaxial ferro*magnets*, $GdCl_3$,[3] $LiTbF_4$,[4-6] $DyEtSO_4$,[7] and TbF_3,[8] proved to be consistent with Eq. (1), but in all cases pure power laws also provided equivalently good fits.

In the present work, we analyze our data for the magnetic equation of state of $LiTbF_4$, striving for a check of the full equation as derived in the original theory[1] for the order parameter in dipolar Ising systems

$$m = \tilde{m}|\ln r|^{1/3}. \tag{2}$$

Here $\tilde{m}$ follows from the Landau expansion of the field with $t = T/T_c - 1$,

$$h = \frac{t}{\Gamma}\tilde{m} + \frac{1}{\Gamma B^2}\tilde{m}^3, \tag{2a}$$

and r, except for a scale factor χ_0, is given by the inverse of the isothermal susceptibility $\chi = (\partial m/\partial h)_t$:

$$r = \chi_0/\chi(h,t). \tag{2b}$$

Γ and B represent the critical amplitudes of the susceptibility ($t > 0$) and magnetization ($t < 0$) at $h = 0$, respectively. In contrast to the previous investigations mentioned above, where special lines in the h-t plane were sampled by varying either the temperature at $h = 0$ or the field at $T = T_c$, our measurements encompass quasicontinuously the critical region of the h-t plane aiming at a more stringent test of the theory. Binder, Meissner, and Mais,[9] analyzing the equation of state for ferro*electric* triglycine sulfate (TGS) in a small region near the critical isochore ($t > 0$, $h \to 0$; setting $r = t$) stressed the value of this method by pointing out that the third-order term in Eq. (2a) should sense the relevance of the logarithmic correction much better than the linear one investigated hitherto.

The isothermal magnetizations shown in Fig. 1 normalized to saturation have been measured by means of a SQUID (superconducting quantum interference device) magnetometer on a single crystal (3 mm diam). Experimentally, the temperature of the sample was varied while the magnetic field was kept highly constant within a superconducting Pb shield. A Ge thermometer was in close thermal contact with the sample allowing a resolution of about 0.1 mK. The methods of calibration of the magnetization and the evaluation of the internal field H_{int} have been described elsewhere.[7] Some data near the phase boundary, which proved to contain larger systematic errors probably arising from imperfections, were omitted in Fig. 1. To compare the results with Eqs.

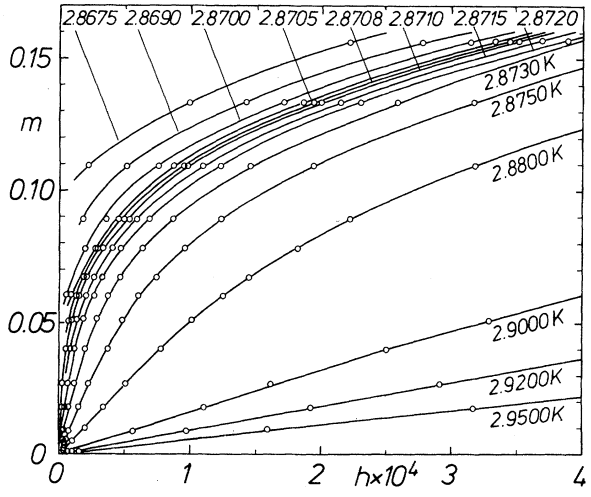

FIG. 1. Magnetization isotherms around the Curie temperature of $LiTbF_4$. Internal fields and magnetizations are normalized according to $h = g\mu_B H_{int}/2k_B T_c$ and $m = 2v_{spin}M/g\mu_B$. Full lines are explained in the text.

(2)–(4) we first determined the isothermal susceptibility $\chi(t,h)$, entering into the distance parameter r, by means of a generalized spline routine[10] (see full curves in Fig. 1). It is then straightforward to adjust the magnetization $m(t,h)$ to the equation of state, Eq. (3), by allowing both amplitudes of the Landau expansion and also T_c and χ_0 to vary freely. The experimental uncertainties were included in the weights, assigned to the 141 data points in the least-squares routine. Figure 2 compares the results of the fit with the experiment: Obviously, the agreement is excellent over several decades in both variables, which manifests itself in the small standard deviations of the free parameters too.

At first it is perhaps instructive to compare our data also with conventional equations of state, which can be expressed by

$$h = \frac{m^\delta}{\Gamma B^2} f\left(\frac{t}{(m/B)^{1/\beta}}\right) \tag{3}$$

containing the critical exponents β and δ and two nonuniversal critical amplitudes.[11] Brézin, Wallace, and Wilson[12] calculated the scaling function of the Ising model with short-range interactions up to second order in the $\epsilon = 4 - d$ expansion:

$$f_{Is}(x) = x + u/6 + f_1(x)\epsilon/6 + f_2(x)\epsilon^2/12, \tag{4}$$

where $u = 16\pi^2\epsilon/3$, $f_1 = \hat{x}\ln\hat{x} - 0.847u$, and

$$f_2 = [(\ln\hat{x})(\hat{x}+u)/6 + 25\hat{x}/27 - 0.847u]\ln\hat{x},$$

with $\hat{x} = x + u/2$. This function was found to agree closely with numerical results in three dimensions, i.e., for $\epsilon = 1$. Assuming for a moment that the dipolar Ising model can be described by f_{Is}, too, we would clearly have to allow ϵ to vary freely in the fit, because the exponents are also fixed in this approach by $1/\beta = 2 + 2\epsilon/3 + 16\epsilon^2/81$ and $\delta = 3 + \epsilon + 25\epsilon^2/54$.[12] The results are complied in Table I including the MF model, representing the other limit of extremely long-range interactions with $\beta = \frac{1}{2}$, $\delta = 3$:

$$f_{MF}(x) = 1 + x. \tag{5}$$

Obviously, the χ^2 test strongly confirms the equation of state, Eqs. (2), rejecting both the other models. This is based not only on their significantly larger χ^2, but also on the unrealistic parameters, e.g., the unphysical dimension $d = 4 - \epsilon = 3.75$ in $f_{Is}(x)$, and the large difference to the exact MF amplitudes, $B_{MF} = 1.7$ and $\Gamma_{MF} = 1$ in $f_{MF}(x)$.

In the following we examine some further questions related to the interpretation of the critical behavior of $LiTbF_4$ by logarithmic corrections. First we check the validity of a nonuniversal relation between B and Γ derived recently[13] from the original work[1]:

$$\frac{1}{\Gamma B^2} = \frac{16\pi}{9}\frac{(s^3\Lambda)^{1/2}}{v_0 T_c^2}. \tag{6}$$

Here v_0 is the volume per spin, Λ is Curie's constant, and s is the dispersion coefficient of the transverse magnetic excitations. For $LiTbF_4$, using 8.5(1) and 5.2(1.7) K Å^2,[13] one finds $\Gamma B^2 = 3.1(1.2)$ being consistent with 2.79(1) derived from our equation of state. It should be noted, that for nondipolar systems no similar relation exists so far, leaving two independent critical amplitudes ("two-scale-factor universality"[11]).

Further tests can be performed by calculating

TABLE I. Parameters obtained by fitting equation-of-state data for $LiTbF_4$ to various models. $\chi_0 = 2.25(5)$ and $\epsilon = 0.24(2)$.

Model	χ^2	T_c (K)	B	Γ
Dipolar, Eq. (2)	1.1	2.87075(3)	1.654(4)	1.032(2)
Ising, Eq. (4)	2.5	2.8714(1)	2.8(2)	1.7(1)
MF, Eq. (5)	4.8	2.8718(1)	2.6(1)	1.6(1)

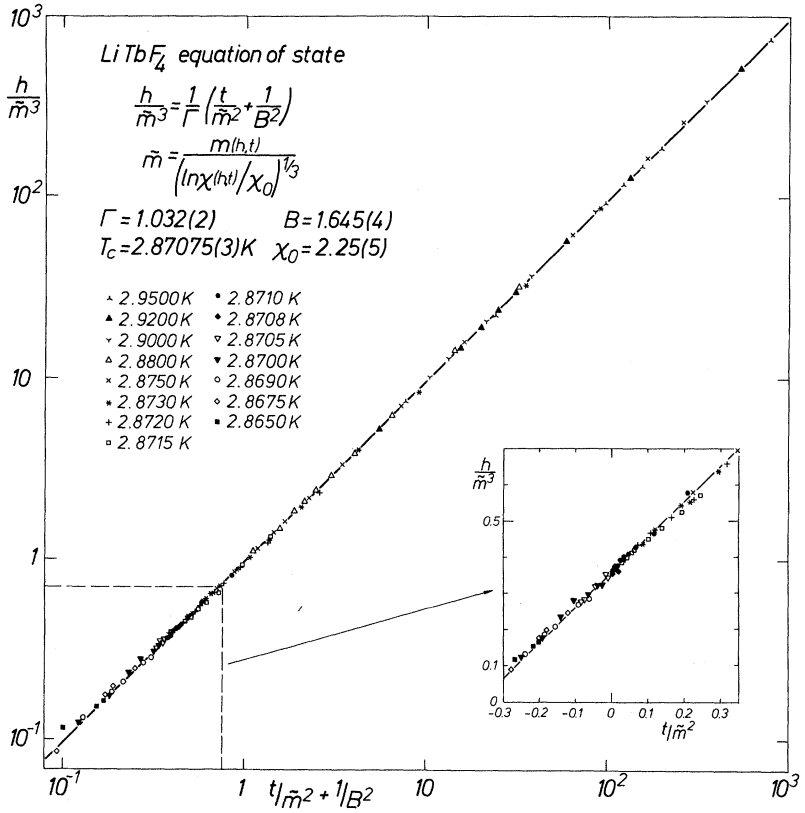

FIG. 2. Scaled representation of the experimental data of Fig. 1 and (full line) of the Landau expansion for the magnetization corrected for the logarithmic factor [Eqs. (2) and (3)].

from our numerical values for B and Γ the critical amplitudes of other singularities measured earlier on $LiTbF_4$ in zero field. The amplitude of the correlation length of the transverse fluctuation has been measured by Als-Nielsen, $\xi_0 = 1.44$ Å.[5] Using the static limit of the fluctuation-dissipation theorem, one finds $\xi_0 = (\Gamma s/T_c)^{1/2}$,[13] from which we eliminate the most uncertain quantity, s, with help of Eq. (6), arriving at

$$\xi_0 = (9v_0/16\pi B^2)^{1/3}(\Gamma T_c/\Lambda)^{1/6} = 1.42(1)\ \text{Å}.$$

Similarly good agreement exists between the amplitude of the specific-heat anomaly, $A = 0.439(1)$,[4] and $A = 0.437(1)$ following from our numbers and the universal relation $A = B^2/6\Gamma$.[13] We think, that this agreement can justify *a posteriori* the omission of higher-order logarithmic corrections[14] in both of these former analyses, where the distance parameter r [Eq. (2b)] was approximated by $|t|/t_0$.[15] In view of this agreement, the difference between $B = 1.77(6)$, from a light-scattering experiment,[6] and our value, $B = 1.65(1)$, appears to be significant. We refer this discrepancy to the fact that in Ref. 6 normalized magnetizations up to $m = M/M(T=0) = 0.64$ have been included in the fit, which presumably requires higher-order powers in the equation of state, Eq. (2), whereas the present analysis was confined to $m < 0.15$.

In conclusion, on the basis of this unusually rich experimental and theoretical material, we think that the magnetic and thermal properties of $LiTbF_4$ near its Curie point now belong to the best-explained critical phenomena.

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

[2]A. Aharony and B. I. Halperin, Phys. Rev. Lett. 35, 1308 (1975).

[3]J. Kötzler and W. Scheithe, Solid State Commun. 12,

643 (1973); J. Kötzler and G. Eiselt, Phys. Lett. 58A, 69 (1976).
[4]G. Ahlers, A. Kornblit, and H. J.Guggenheim, Phys. Rev. Lett. 34, 1227 (1975).
[5]J. Als-Nielsen, Phys. Rev. Lett. 37, 1161 (1976).
[6]J. A. Griffin, J. D. Litster, and A. Linz, Phys. Rev. Lett. 38, 251 (1977).
[7]R. Frowein and J. Kötzler, Z. Phys. B25, 279 (1976).
[8]J. Brinkmann, R. Courths, and H. J. Guggenheim, Phys. Rev. Lett. 40, 1286 (1978).
[9]K. Binder, G. Meissner, and H. Mais, Phys. Rev. B 13, 4890 (1976).
[10]Ch. Reinsch, Numer. Math. 10, 177 (1967).
[11]P. C. Hohenberg, A. Aharony, B. F. Halperin, and E. D. Siggia, Phys. Rev. B 13, 2986 (1976); A. Aharony and P. C. Hohenberg, Phys. Rev. B 13, 3081 (1976).
[12]E. Brézin, D. J. Wallace, and K. G. Wilson, Phys. Rev. Lett. 28, 548 (1972).
[13]J. Kötzler, Phys. Lett. 59A, 483 (1977).
[14]E. Brézin and J. Zinn-Justin, Phys. Rev. B 13, 251 (1976).
[15]Moreover, the approximation $r \approx |t|/t_0$, used in Ref. 4, disregards the asymmetry of r with respect to T_c following from Eqs. (2a) and (2b): $r(t>0) = 2r(t<0)$. One of us (J.K.) is grateful to Professor M. E. Fisher for raising this point.

Binding of D^- Ions in a Magnetic Field

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I present the first strong evidence for the observation of D^- centers in a semiconductor with a simple conduction band minimum at $k=0$. The identification is based primarily upon agreement between the predicted and observed curve of photodetachment threshold frequency vs magnetic field in CdS. New, relatively simple and physically motivated variation trail functions are employed which give eigenvalues of sufficient accuracy for critical comparison with experiment.

When a dilute assembly of shallow donors in an uncompensated semiconductor is subjected to room-temperature radiation some of the electrons initially excited into the conduction band by photoionization of donors may, at low temperatures, recombine with neutral donors to produce isolated D^- centers. Such centers consist of a hydrogenic donor with an extra electron attached; they have been found in Si and Ge,[1-5] semiconductors with multiple conduction-band minima. Surprisingly, no well-substantiated observations of D^- ions in any of the many semiconductors with "simple" conduction bands having a single isotropic $k=0$ minimum have been reported. D^- ions in such semiconductors would be analogs of H^- ions in the same way that simple hydrogenic donors are analogous to hydrogen atoms. The H^- ion has, in theory, a rich magnetic structure at fields much higher than can be reached in the laboratory.[6-9] This structure could, however, be elucidated at laboratory field strengths by experiments on D^- ions associated with "simple" conduction bands.

In this paper, I show by physical arguments how relatively simple variational trial functions for H^- states can be constructed which turn out to give accurate level energies in the field range of interest. My results are used to interpret previously published low-temperature magnetoabsorption data[10] on CdS, and a case is made for identifying one of the lines seen in that material as photodetachment of an electron from the ground state of the D^- ion.

The H^--ion zero magnetic field has exactly one bound state,[11] a singlet S level, which has been intensively studied theoretically.[12] The binding energy of this level is ~ -0.0555.[13] (By "binding energy" I shall always mean the minimum energy required to remove a single electron from the H^- or D^- ion without changing the two-electron spin configuration.)

For arbitrarily small nonzero magnetic field, there are, as shown in Ref. 8, an infinite number of bound states of H^-, at least one such state for each M_L for $M_L = 0, -1, -2, \ldots$, where M_L is the projection of the total electronic orbital angular momentum (in units of $\hbar$) of the H^- ion on the magnetic field direction. Although the trial functions employed in the discussion in Ref. 8 are not capable of giving accurate binding energies[14] they suggest that, consistent with the results presented here, the binding decreases monotonically

