MAGNETIC EQUATION OF STATE AND SPECIFIC HEAT OF EuS NEAR THE CURIE POINT

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The specific heat of EuS near the critical point is a homogeneous function of field and temperature. In zero field $\alpha = 0$ and $\alpha' = -0.25$, and along the critical isotherm the field variation is logarithmic.

Of utmost relevance to the problem of continuous phase transitions is the critical comparison of theoretical predictions with experimental results of model systems. In this Letter we present the first experimental observations of the magnetic specific heat of a cubic Heisenberg ferromagnet, EuS, as a function of field along isotherms at and near the critical point, both above and below T_c. The exponents α and α' which describe the zero-field specific heat near T_c have been accurately obtained, and the variation of specific heat with field along the critical isotherm is reported. Furthermore, evidence is given that in the dependence of the magnetic specific heat C_M on field H and temperature T, the specific heat obeys the same special type of equation of state both above and below the critical point T_c. The equation of state followed by EuS is exactly analogous to that proposed by Widom[1] for a fluid near its critical point and leads to scaling laws relating the indices describing the variation with H and T of the principal thermodynamic properties near T_c. The first experimental confirmation of such an equation of state was observed by Kouvel and Rodbell[2] for measurements relating the magnetization to field and temperature of CrO_2 and Ni above T_c. The present work constitutes the first confirmation that thermal properties obey the same kind of equation of state.

The temperature dependence of the magnetic specific heat near T_c is described by the index α, such that

$$C_M = (A/\alpha)(\epsilon^{-\alpha} - 1) + B, \quad \text{for } T \to T_c^{+}, \tag{1a}$$

and

$$C_M = (A'/\alpha')(\epsilon^{-\alpha'} - 1) + B', \quad \text{for } T \to T_c^{-}, \tag{1b}$$

where

$$\epsilon = |T - T_c|/T_c. \tag{1c}$$

In the limit where $\alpha \to 0$, these expressions imply that $C = -a \ln\epsilon + b$, the familiar logarithmic divergence of the specific heat at the critical point.

The experimental results, shown in Fig. 1, extend over four decades from $5\times10^{-1}T_c$ to $5\times10^{-5}T_c$ and nearly a decade in C_M from 4 to 30 J/mole deg. A logarithmic form of divergence is clearly indicated down to $5\times10^{-4}T_c$ for $T > T_c$. For $T < T_c$ the specific heat is not divergent, indicating that α' in Eq. (1b) is negative.

In an attempt to assign significant values unambiguously to α, α', T_c, and T_c', a linear least-squares analysis was made of the data in terms of Eqs. (1a) and (1b). Let us consider the case $T > T_c$, the method of analysis being identical for $T < T_c'$. Fixed values were assigned to α and T_c. This linearizes Eq. (1a) to the form $Ax + B$, so that one is able to find the best values of A and B for this particular choice of α and T_c. The rms deviation of experimental points from this curve is a measure of the confidence which we can place in this particular choice of α and T_c. Holding α constant, we can calculate the rms deviations as a function of the parameter "T_c" and obtain a curve whose minimum is the best value of T_c for that particular choice of α. We now choose another value for α and repeat the procedure for a similar set of values of T_c. A family of these deviation curves for various

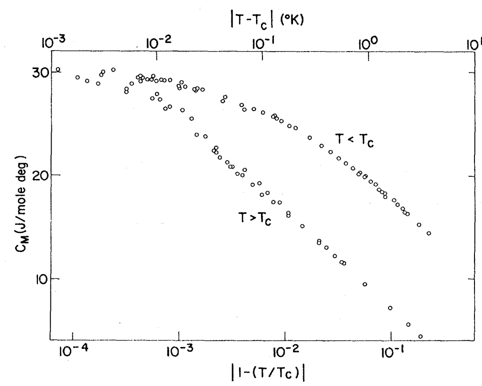

FIG. 1. Magnetic specific heat of EuS.

fixed values of α is represented in Fig. 2. The minimum of the family of curves represents the "best" value of α and T_c commensurate with the data. We are able not only to determine values for α and T_c in a sensitive manner, but also to place realistic confidence limits on our values for α by a simple technique.

The technique by which we determine confidence limits is the following: For the "best" value of α and T_c we have examined a plot of ΔC_M, the difference between the measured and calculated specific heat, as a function of temperature. This graph resembles a completely random array of deviations of ΔC_M about $\Delta C_M = 0$, within the limits of $\Delta C_M \sim \pm 0.02 C_M$. If T_c is now held constant and the same plot is redone for values of α about the "best" value, the random picture begins to show a systematic trend away from $\Delta C_M = 0$. We define the limits on α by the range over which α may be varied until the systematic trend becomes apparent. This turns out to be a range of ± 0.03.

By applying the identical procedure to the range $T < T_c'$, we obtain values for α' and T_c'. A summary of our results follows:

For $T \to T_c^+$,

$$\alpha = 0.00 \pm 0.03,\ A = 4.21,\ a = 9.47 \text{ J/mole deg},$$

$$T_c = 16.427°\text{K},\ B = -2.50,\ b = -2.50 \text{ J/mole deg}.$$

For $T \to T_c^-$,

$$\alpha' = -0.25 \pm 0.03,\ A' = 7.59 \text{ J/mole deg},$$

$$T_c' = 16.426°\text{K},\ B' = 4.33 \text{ J/mole deg}.$$

The most remarkable result of these calculations is clearly the existence of a negative α'. This negative α' character of the specific heat below T_c' persists to below 8°K. In fact, if we limit the least-squares analysis to a narrower temperature range near T_c, the same value of α' is obtained. In other words, the power law, Eq. (1b), accurately represents the variation in specific heat over the whole range.

We are now in a position to say that $\alpha = 0$ and $\alpha' < 0$ is an intrinsic property of the cubic Heisenberg system and has been observed experimentally for EuO,[3] $RbMnF_3$,[4] and Ni,[5] as well as EuS. By way of contrast, for MnF_2,[6] an anistropic Heisenberg antiferromagnet, both α and α' are very nearly zero.

Another feature of the results is the evidence for a width of ~5 mdeg K for the transition as indicated by the flat portion of the curves of Fig. 1 nearest T_c. The analysis for determining α and α' has excluded points in a so-called "grey" region which is described more fully in the following Letter.[7] In the present discussion we emphasize that the observation of $\alpha' < 0$ is distinct from these rounding effects.

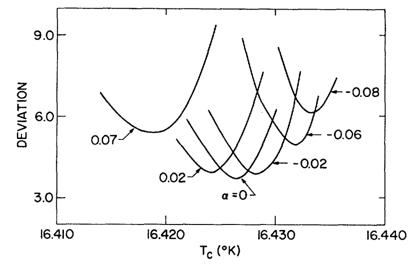

FIG. 2. Rms deviation of experimental points from calculated curve as a function of choice of α and T_c.

We have measured the specific heat of a 5-mm-diam sphere in fields of 220, 300, 360, 500, 600, 720, 915, 1350, and 1830 Oe. The magnetic field dependence of the specific heat along the critical isotherm has been derived from free-energy considerations by Helfand.[8] If ζ is defined as the index describing the behavior of $C_M(H)$ at T_c, then

$$C \propto H^{-\zeta} \text{ at } T = T_c. \tag{2}$$

The appropriate scaling law relating α, ζ, and γ is given by

$$\zeta = 2\alpha/(2+\gamma-\alpha), \tag{3}$$

where γ is the exponent which describes the susceptibility $\chi(T)$. Thus if α is equal to 0, then ζ is 0, which implies logarithmic variation of $C_M(H)$ at T_c. We have examined our results along isotherms near T_c as a function of $\log H$. The critical isotherm is a straight line, which implies that ζ is indeed 0. This constitutes the first experimental measurement of ζ, and also the first test of the scaling law, Eq. (3).

We will now show that $C(H,T)$ conforms to a simple qualitative scheme. Isotherms of $1/C$ vs H/C form a regular set of curves which, for small values of H/C, has the form

$$1/C = 1/C^0 + D(T)(H/C). \tag{4}$$

The remarkable result is that when the isotherms are normalized by intercept and initial slope, a universal curve is obtained:

$$\frac{1/C}{1/C^0} = 1 + \frac{H/C}{H^0/C^0}, \tag{5}$$

where

$$1/C^0(T) \equiv [1/C]_{H=0} \propto (T-T_c)^{\alpha}, \tag{6}$$

and

$$D(T) \equiv \left[\frac{\partial(1/C)}{\partial(H/C)}\right]_{H=0} = \frac{1}{H^0} \propto (T-T_c)^{\rho}. \tag{7}$$

We have done the above normalization for the isotherms of $1/C$ vs H/C above T_c up to a value of $T-T_c = 0.15°\mathrm{K}$, as well as for fields up to 1350 Oe, using the quantities defined in Eqs. (4) and (5). The results are shown in Fig. 3. It is clear that all the experimental points considered describe a single universal curve. For fields greater than 1350 Oe and $T-T_c$ greater than 0.15°, deviations from this universal curve begin to appear.

A similar analysis was done below T_c for $T_c - T < 0.01°\mathrm{K}$. For temperatures below this range, it becomes virtually impossible to define $D(T)$ because the lowest field curves merge into the zero-field curve on account of the rapid increase of the demagnetizing field in the ferromagnetic region. However, in this narrow temperature range the scaling procedure also yields a single universal curve, with the important exception of the zero-field specific heat.

Thus we have shown that EuS obeys a general relationship of the form

$$\frac{1/C}{1/C^0} = F\left(\frac{H/C}{H^0/C^0}\right), \tag{8}$$

where $F((H/C)(H^0/C^0)^{-1})$ reduces to the right-hand side of Eq. (5) for small values of H/C as indicated by the dashed line in Fig. 3. In particular, with the use of Eqs. (6) and (7), we observe that

$$C^0 \propto (T-T_c)^{-\alpha}, \tag{9}$$

and

$$H^0 \propto (T-T_c)^{-\rho}, \tag{10}$$

where

$$\alpha = 0 \text{ and } \rho \simeq -\tfrac{2}{3}.$$

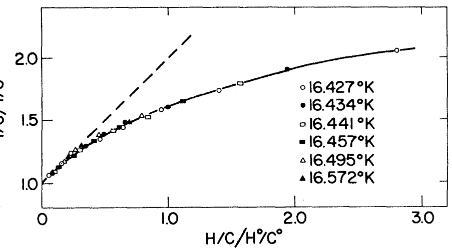

FIG. 3. Normalized isotherms for EuS.

In the limit as $T \to T_c$ [equivalent to $(H/C) \times (H^0/C^0)^{-1} \to \infty$], Eq. (8) must merge with Eq. (2) which defines $C \propto H^{-\zeta}$ at T_c. Thus, in this limit

$$C^0/C \propto (H^0/H)^{-\zeta}, \tag{11}$$

which may be rewritten as $C \propto [C^0/(H^0)^{-\zeta}]H^{-\zeta}$. For Eq. (2) to be valid it is required that $C^0/(H^0)^{-\zeta}$ be a constant.

Consequently, from Eqs. (9) and (10), $C^0/(H^0)^{-\zeta} \propto (T-T_c)^{-\alpha-\zeta\rho}$ and is constant. Therefore, $-\alpha-\zeta\rho$ must be zero, and we obtain

$$\zeta = -\alpha/\rho. \tag{12}$$

We now have a scaling law which relates ζ to α and ρ and again observe that when $\alpha \to 0$, $\zeta \to 0$. This behavior is borne out by the experimental result that $C_M(H) \propto \log H$ along the critical isotherm.

Equation (8) is exactly equivalent to one of the Widom equations of state, in which the free energy contains a homogeneous function of its variables. Thus the observation that EuS conforms to the same equation of state leading to the scaling law given in Eq. (12) verifies experimentally this theoretical approach to continuous phase transitions.

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SINGULAR BEHAVIOR OF A FERROMAGNET IN NONZERO FIELD

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The specific heat of EuS is found to remain logarithmic in nonzero field, and the behavior is discussed in terms of a complex critical temperature.

Our expectations were put succinctly by Domb[1]: "The key to a more precise approach to such relations between (critical) indices lies in the equation of state of a ferromagnet in a nonzero magnetic field using the result that all singularities disappear in the presence of such a field."

In the preceding Letter we have indeed derived the equation of state near the critical point from specific-heat measurements in nonzero field, and we have shown that specific-heat isotherms near the critical isotherm can be reduced to a single homogeneous function of field and specific heat by normalization to zero-field parameters. But contrary to expectation, we find that specific-heat isochamps – curves of temperature variation in constant field – are functionally insensitive to the application of fields as large as 10 % of the saturation Weiss field. Following a suggestion by Blume,[2] we have analyzed our results in terms of a complex temperature plane in which the singularity can exist under the influence of an applied field. The path described by the singularity in the complex plane may terminate ideally in zero field at a point on the real axis corresponding to the usual Curie temperature. In actual samples, however, the finiteness of the specific-heat maximum as seen from above T_C becomes a manifestation of a nonzero imaginary temperature component arising from inhomogeneous fields.

We believe this to be the first instance in which the critical point is treated as a complex quantity, and the analyses of other measurements from this point of view may be interesting.

The fundamental experimental result is shown in Fig. 1. Three specific-heat isochamps are plotted against reduced temperature, $(T-T_H)/T_H$, where T_H has been chosen for each field. At temperatures greater than $10^{-2}T_H$ the curves approach simple logarithmic behavior, but closer to T_H a finite value of specific heat is approached that depends inversely on the field strength. The solid curves are the computed specific heat along the real axis for a logarithmic pole of amplitude $a(H)$ located at $T_H+i\tau$. That is, the experimental isochamps can be represented by

$$c=a(H)\ln\{[(T_H-T)^2+\tau^2]/T_H^{\,2}\}^{1/2}+b(H), \qquad (1)$$

where, as $H\to 0$, $T_H\to T_C$, $\tau\simeq 0$, and

$$a(H), b(H)\to a, b,$$

the zero-field values reported in the preceding Letter.

We have compared Eq. (1) with nine isochamps

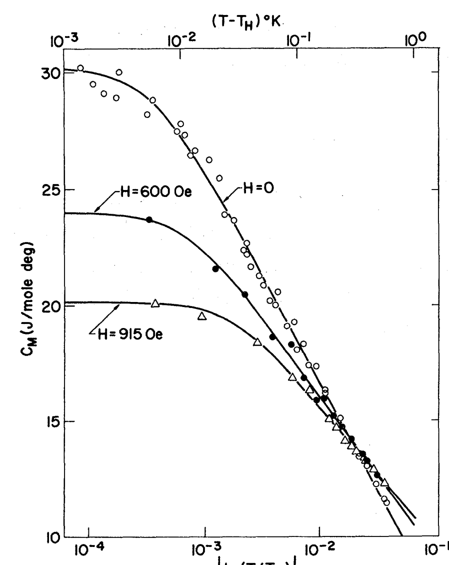

FIG. 1. Specific-heat isochamps for EuS. The solid curves are calculated using Eq. (1).