netization, and eventually Mössbauer-effect measurements down to below 10 mK.

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MAGNETIC EQUATION OF STATE OF $CrBr_3$ NEAR THE CRITICAL POINT*

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We present the results of analysis of our measurements of the magnetic properties of the insulating ferromagnet $CrBr_3$ near its critical temperature. From this analysis we obtain a mathematical representation of an equation of state valid over the entire critical region.

We have used the Faraday effect to measure the magnetization M of the insulating ferromagnet $CrBr_3$ as a function of field along 30 isotherms in the temperature range $T_C - 0.9°K < T < T_C + 6.7°K$, where the critical temperature is $T_C = 32.844°K$. In this Letter we present the results of an analysis of our measurements and report the first determination of a mathematical representation for the equation of state of a ferromagnet which is valid over the entire critical region. Our measurements[1] provided the first verification of the scaling hypothesis[2-4] for an insulating or localized-spin ferromagnet. Experiments to test the scaling hypothesis in metallic ferromagnets have been done by more conventional methods.[5-7]

We define the reduced magnetization $\sigma = M/M(0°K)$ and the scaled magnetization $m = \sigma|1-T/T_C|^{-\beta}$, where β gives the shape of the coexistence curve. Our data cover the range $0.01 \lesssim m \lesssim 6.5$ plus the critical isotherm where m is infinite. Scaling has been verified[5] in CrO_2 for $0.12 \lesssim m \lesssim 2.3$ but only for $T > T_C$. The experimental results of Kouvel and Comly[6] ($0.42 \lesssim m \lesssim 2.8$) and of Arrott and Noakes[7] ($0.23 \lesssim m \lesssim 4.6$) for nickel are consistent with scaling laws for both $T > T_C$ and $T < T_C$. A scaling law equation of state has been shown to hold for a number of fluids in the critical region.[8]

We first analyzed data near the critical isochore, the coexistence curve, and along the critical isotherm to determine the values $\gamma = 1.215 \pm 0.015$, $\beta = 0.368 \pm 0.005$, and $\delta = 4.28 \pm 0.1$. These exponents were used to compute the scaled magnetic field $h = H|t|^{-\beta\delta}$ and the scaled magnetization $m = \sigma|t|^{-\beta}$, where $t = (T-T_C)/T_C$.

The scaling laws predict that h is a function of m only, viz.,

$$h = h(m).$$

This is equivalent to the homogeneity argument of Widom[2] or the equation of state proposed by Griffiths.[4] Our measurements enable an experimental determination of the scaling function $h(m)$. The accuracy of our magnetization measurements is comparable to that of nuclear magnetic resonance and our data are sufficiently precise that we may use the experimental scaling function to establish the mathematical form of $h(m)$. This mathematical representation constitutes an equation of state valid over the entire critical

region. (We define the critical region to be that over which the scaling laws hold. This is the region $-0.03 \lesssim t \lesssim 0.20$ with $\sigma \lesssim 0.45$.)

To obtain a mathematical representation for the scaling function we have followed three approaches. First, we have assumed[2,4] that the free energy is an analytic function of σ, H, and t everywhere in the one-phase region. We have expanded the magnetic field in a power series about the critical isochore ($\sigma = 0$, $t > 0$) and also in a power series about the critical isotherm ($t = 0$, $\sigma \neq 0$). This approach was very successful and one or the other of two simple series represents $h(m)$ well within experimental error everywhere within the one-phase region.

Our second approach was to attempt to find a single equation of simple form that would serve approximately over the entire critical region. Here we were not so successful. We found an equation superior to any that had been suggested previously, but it was clearly incorrect near the critical isochore. Our third approach was to seek a parametric equation of state following a suggestion of Schofield. This approach was more successful in that we obtained simple functions that fit almost within the scatter of experimental points throughout the critical region.

We first discuss the power series representations for the equation of state. To be consistent with the scaling laws,[4] the power series near the critical isochore must have the form

$$H = a_1\sigma t^{\gamma} + a_3\sigma^3 t^{\gamma-2\beta} + a_5\sigma^5 t^{\gamma-4\beta} + \cdots, \quad (1a)$$

or the equivalent

$$h = a_1 m + a_3 m^3 + a_5 m^5 + \cdots. \quad (1b)$$

We found that this series with just three terms fits well within the experimental error for $0 \leq m \leq 1.8$ and $t > 0$. The coefficients are $a_1 = 0.89$ ($\pm 1\%$), $a_3 = 0.85$ ($\pm 6\%$), and $a_5 = 0.23$ ($\pm 20\%$) when the magnetic field is expressed in dimensionless units $\hat{H} = (g\mu_B/SkT_c)H$.

The power series about the critical isotherm has the form

$$H = b_0\sigma^{\delta} + b_1 t\sigma^{\delta-1/\beta} + b_2 t^2\sigma^{\delta-2/\beta} + \cdots, \quad (2a)$$

or its equivalent

$$h = b_0 m^{\delta} \pm b_1 m^{\delta-1/\beta} + b_2 m^{\delta-2/\beta} \pm \cdots. \quad (2b)$$

[The minus sign in (2b) is used for $t < 0$.] We found that three terms of this series fit our data well within experimental error from the coexistence curve ($t < 0$) to $m \geq 1.0$ (for $t > 0$). The coefficients are $b_0 = 0.63$ ($\pm 3\%$), $b_1 = 1.14$ ($\pm 5\%$), and $b_2 = 0.20$ ($\pm 25\%$). Widom[2] suggested that Eqs. (1) and (2) would be asymptotically valid for small and large values of m, respectively. The striking result we find is that with only three terms in each series, Eq. (1) represents our data for $0 \leq m \leq 1.8$ and Eq. (2) serves for $m \geq 1.0$. Therefore at any point in the critical region, one of the two equations is valid and there is considerable region of overlap (for $1.0 \leq m \leq 1.8$ and $t > 0$) where both series will suffice. In Fig. 1 we show the experimentally determined scaling function $h(m)$ and the fit provided by Eq. (1) (dashed line) and by Eq. (2) (solid line).

The two power series are the most accurate representation of the scaling function; however, a single function which is approximately correct over the entire critical region can be found rath-

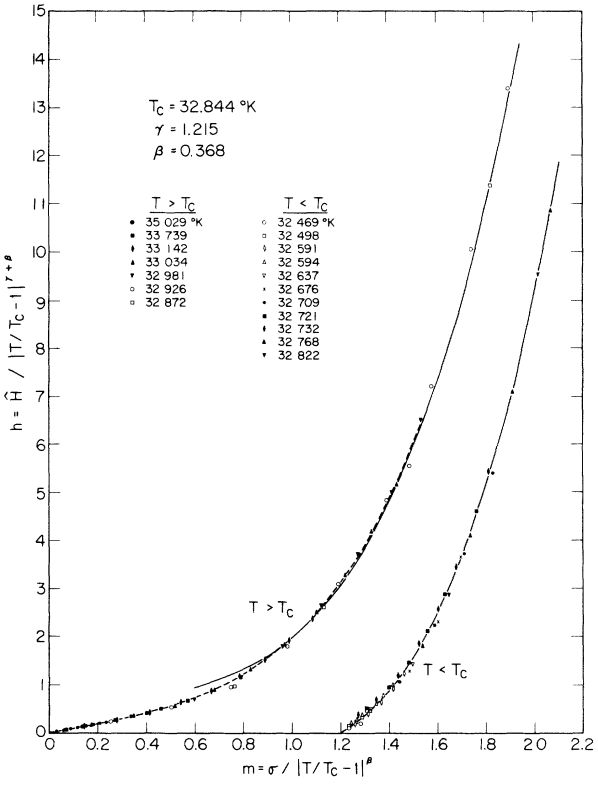

FIG. 1. A linear plot of scaled magnetic field $h(m)$ as a function of scaled magnetization m. The dashed line represents Eq. (1), and fits experimental points from $0 < m < 1.8$ when $T > T_c$. The solid lines are Eq. (2), and the dotted lines show Eq. (4) when it departs significantly from the experimental points. On this plot the origin is the critical isochore, the critical isotherm is at $h = m = \infty$, and the coexistence curve is represented by the point $h = 0$, $m \simeq 1.2$.

er easily. In the molecular field approximation the equation of state is

$$\hat{H} = A\sigma(t + B\sigma^{1/\beta}) \tag{3}$$

with $\beta = \frac{1}{2}$. Widom[2] has pointed out that (3) will yield the scaling laws if multiplied by a homogeneous function of degree $\gamma - 1$ of the variables t and $\sigma^{1/\beta}$. Choosing the simplest function we can think of, we obtain

$$\hat{H} = A\sigma(t + B\sigma^{1/\beta})(t + C\sigma^{1/\beta})^{\gamma-1}. \tag{4}$$

Although Eq. (4) is not analytic in σ along the critical isochore, it is a better approximation than other simple functions that have been tried.[7] If (4) is expanded about $\sigma = 0$, the second term is proportional to σ to the power $1 + 1/\beta = 3.7$. A careful examination of our experimental $h(m)$ shows the second term in an expansion of the correct equation of state varies as σ to the power 3.0 ± 0.3. Therefore we expect Eq. (4) must fail near the critical isochore. Our best fit was obtained with $A = 0.89$, $B = 0.61$, and $C = 2.12$; this is shown as the dotted line in Fig. 1. Agreement with the experimental results is good except for the range $0.2 \leq m \leq 1.2$; here the difference is about 10%, clearly outside the range of experimental error.

A single representation of the scaling function which is a very good approximation over the entire critical region can be obtained using the parametric form suggested by Schofield.[9] We make the following transformation of our measured thermodynamic quantities:

$$\hat{H} = ar^{\beta\delta}\theta(1-\theta^2), \quad t = r(1-2\theta^2), \quad \sigma = r^{\beta}g(\theta). \tag{5}$$

The singular behavior at the critical point is determined by the behavior as $r \to 0$ and we expect $g(\theta)$ to be a well-behaved function. With this particular transform the critical isochore is represented by $\theta = 0$, the critical isotherm by $\theta = 1/\sqrt{2}$, and the coexistence curve by $\theta = 1$. Eliminating r, one finds the scaled magnetic field to be

$$h(m) = a\theta(1-\theta^2)/|1-2\theta^2|^{\beta\delta}, \tag{6}$$

and the scaled magnetization is

$$m = g(\theta)/|1-2\theta^2|^{\beta}. \tag{7}$$

This transformation is similar to one suggested to us by Josephson[10] in which one represents h by a function similar to (6), but replaces (7) by

$$m = U/|1-2U^2|^{\beta}. \tag{8}$$

Using either transform one finds that $U(\theta)$ and $g(\theta)$ have similar mathematical forms.

The function obtained for $g(\theta)$ depends sensitively on the details of the transform chosen for $\hat{H}$ and t. Using the particular transform of Eq. (5) (with $a = 1.1$), we obtain the function $g(\theta)$ shown in Fig. 2. As can be seen from the figure, this can be very closely approximated by the equation $g(\theta) = k\theta$ with $k = 1.24 \pm 0.04$. One advantage of this parametric equation of state lies in the fact that it is readily integrated to obtain the free energy, and data for the entire critical region may be represented on one finite graph.

In conclusion, we remark that we have obtained several mathematical representations of the equation of state for $CrBr_3$ in the critical region. When only an approximate form is desired, Eq. (4) is suitable and preferable to other approximations that have been suggested.[7] A better approximation is obtained in the parametric form of Eq. (5), and this form is most amenable to

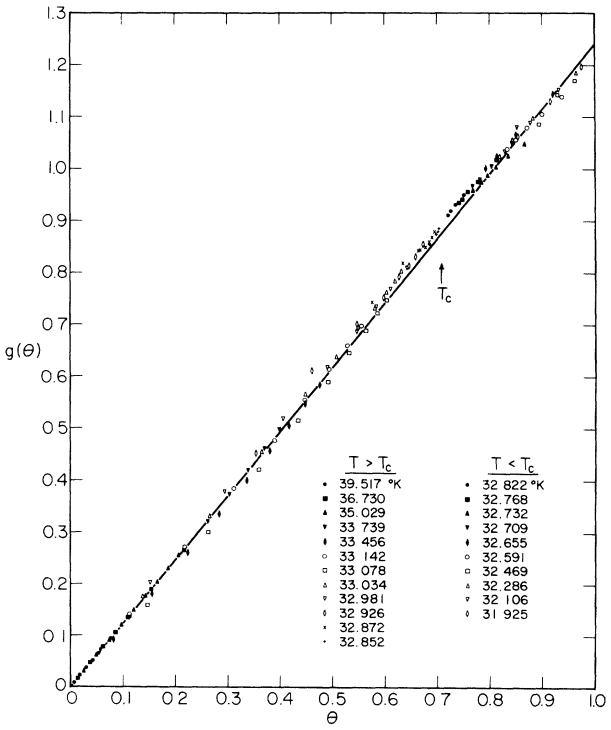

FIG. 2. A plot of the function $g(\theta)$ in the parametric equation of state, Eq. (5), obtained from an analysis of our $CrBr_3$ data with $a = 1.1$. The line has the equation $g(\theta) = 1.24\theta$.

mathematical analysis. The most accurate representation is provided by the two power series (1) and (2). These appear to be the best equations to check theoretical calculations when they become available and to compare various magnetic systems, pure fluids, and critical mixtures.

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PARAMETRIC REPRESENTATION OF THE EQUATION OF STATE NEAR A CRITICAL POINT*

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A parametric representation of the usual thermodynamic variables in the neighborhood of a critical point is proposed in terms of new variables r and θ. The representation is chosen so that the "scaling-law" behavior is entirely contained in the r dependence, the θ dependence being free of critical singularities. Preliminary calculations show that the θ dependence may be chosen to have a rather simple form both in a ferromagnet and in fluids.

It is now widely accepted (though not theoretically established) that Widom's hypothesis,[1] that the free energy of a ferromagnet or a fluid in the neighborhood of its critical point can be expressed as a homogeneous function of two of the thermodynamic variables, is essentially correct. In this Letter we propose a parametric representation of the thermodynamic behavior which automatically satisfies the so-called "scaling-law"[2] relations, which follow from the hypothesis of homogeneity.

Let T be the temperature measured from T_c as zero, let H be the magnetic field in the magnetic case and represent the chemical potential difference $(\mu-\mu_c)$ in the fluid, and let M be the magnetization (magnet) and density deviation $(n-n_c)$ (fluid). We consider the thermodynamic potential $\pi(H,T)$ defined by

$$\pi(H,T)=HM(H,T)-F(M,T)+F(0,0)-S_cT \text{ (magnet)} \quad (1)$$

$$=P(H,T)-P_c-n_cH-S_cT \text{ (fluid)}, \quad (2)$$

where F is the free energy, P the pressure, and S the entropy. Then M is given by $(\partial\pi/\partial H)_T$ and $(S-S_c)$ by $(\partial\pi/\partial T)_H$.

The transformation we suggest arises from the knowledge[3] that $\pi(H,T)$ is a well behaved function of H for a given T and the plausible assumption that it is also a well behaved function of T away from the coexistence curve, $H=0$, $T<0$. Thus we expect $\pi(H,T)$ to be well behaved along any contour leading from one side of the coexistence curve to the other. This suggests that if we transform to variables r, which gives a measure of the distance of a point (H,T) from the critical point, and θ, which measures the distance along a contour of constant r, then the singular behavior at the critical point should be determined by the behavior as $r\to 0$ and that the thermodynamic functions should be well behaved in θ.

The transformation proposed is

$$H=ar^{\beta\delta}\theta(1-\theta^2), \quad (3)$$

$$T=r(1-b^2\theta^2), \quad (4)$$

where a and b are disposable parameters with a