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Tricritical-Point Phase Diagram in $FeCl_2$

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Detailed measurements of the magnetization and sublattice magnetization of $FeCl_2$ in a magnetic field have been performed by use of polarized- and unpolarized-neutron-diffraction techniques. The phase diagram so determined is found to bear a close resemblance to that of ^{3}He-^{4}He mixtures near the tricritical point although there are a number of important differences which seem to require, at the minimum, an extension of present theories of tricritical phenomena.

In 1935 and 1937 Landau[1] gave a phenomenological theory for thermodynamic systems exhibiting a line of first-order transitions going over continuously into a line of second-order transitions. Three decades later, Graf, Lee, and Reppy[2] showed that just such a situation occurs in ^{3}He-^{4}He mixtures where, at the junction point, the superfluid λ line goes continuously into the phase-separation line. Shortly thereafter, Griffiths[3] considered in more detail the general ^{3}He-^{4}He phase diagram and he showed that the junction point actually occurs at the intersection of three lines of second-order transitions. He thence proposed the name *tricritical point* for this special point on the phase diagram. Griffiths further suggested that tricritical points might occur in a wide variety of physical systems and, in particular, in metamagnets such as $FeCl_2$.[4,5] In this case it is proposed that one has a simple isomorphism between thermodynamic variables with, for example, magnetization $M(H,T) \rightarrow X$, the ^{3}He concentration, and sublattice magnetization $M_s(H,T) \rightarrow |\psi|$, the superfluid order parameter. In this Letter we report a detailed neutron-diffraction study of $FeCl_2$ in a magnetic field. As we shall show, $FeCl_2$ does indeed exhibit tricritical behavior and, furthermore, the phase diagram around the tricritical point bears a close resemblance to that of ^{3}He-^{4}He mixtures. There are, however, a number of quantitative discrepancies with theory which necessitate both an extension of the existing theories together with further experiments.

We consider first the magnetic properties of $FeCl_2$, the experimental technique, and the salient results. We shall then discuss the current theoretical predictions in the context of the results. The crystal structure, magnetic properties, and critical behavior of $FeCl_2$ in zero magnetic field have been extensively discussed by Birgeneau, Yelon, Cohen, and Makovsky.[5] From the vantage point of critical phenomena, $FeCl_2$ may be viewed as being composed of hexagonal sheets of ferromagnetically coupled $S=1$ Ising spins with successive planes weakly coupled antiferromagnetically. At low temperatures as a function of increasing internal field H_{int} (we shall assume that all fields are applied along the crystalline c axis), $FeCl_2$ undergoes a first-order transition from an antiferromagnetic (A/f) to a paramagnetic (para) state. Above a critical temperature of ~21 K, however, the A/f-para transition appears to become continuous.[4] The Néel temperature in zero field is ~23.6 K. In a real experiment, it is, of course, the applied field, H_{app}, which is varied. H_{int} and H_{app} are related by

$$H_{int} = H_{app} - 4\pi N M(H_{int}, T), \tag{1}$$

where $M(H_{int}, T)$ is the magnetization and N is the demagnetizing factor. Unfortunately, in experiments reported to date[4] the samples have been highly nonellipsoidal in shape thence giving rise to a large distribution in internal fields. Hence, no detailed information could be obtained about the tricritical behavior.

The experiments reported here were performed on a triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor. The sample was an ellipsoidal platelet of dimensions $2.4\times1.1\times0.09$ cm^3 with the crystalline c axis perpendicular to the flat face. The crystal was masked with cadmium so that only the center 25% was illuminated with neutrons. The estimated spread in the demagnetizing field from geometrical effects was thus less than 10 G at the tricritical point. The crystal was mounted with its (010) axis vertical in a variable-temperature cryostat and the cryostat in turn was mounted on a conventional magnet with the field in the horizontal plane directed along the sample $(00l)$ direction. The sublattice magnetization could be determined in the usual fashion from the intensity at the (201) superlattice position while the magnetization was determined from the flipping ratio of polarized neutrons at the (300) nuclear reflection. This simultaneous access to both the ordering and nonordering densities represents a considerable advantage of the neutron-scattering technique.

The experiments consist mainly of a series of scans either in H_{app} at a fixed temperature or vice versa. At low temperatures as H_{app} is increased the superlattice intensity $I(201)$ decreases gradually up to a critical field $H_{app}(1)$ at which point there is a discontinuity in dI/dH_{app} signaling a first-order transition into the mixed A/f-para state. The intensity, $I(201)$, then decreases linearly with increasing H_{app} up to a critical field, $H_{app}(2)$, at which point $I(201)$ vanishes and the crystal enters a homogeneous paramagnetic state. The field difference, $H_{app}(2) - H_{app}(1)$, is just the demagnetizing-field difference $4\pi N \times[M(H_{int}(2), T) - M(H_{int}(1), T)]$ for the two states.

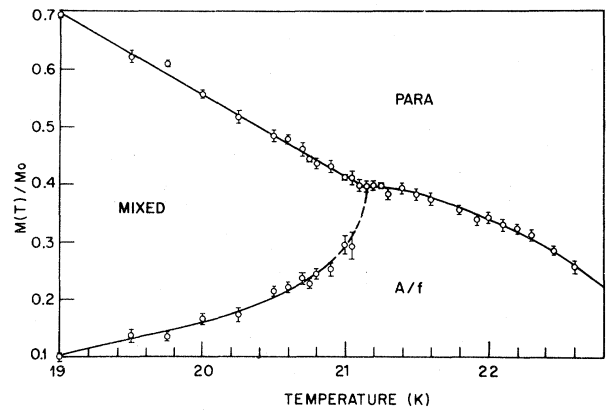

FIG. 1. Reduced magnetization versus temperature in $FeCl_2$ along the first-order phase-separation line and the second-order λ line. The solid (dashed) lines are guides to the eye.

As the temperature is increased the mixed-phase region decreases in size until beyond about 21.15 K the transition appears to be of second order. Measurements of the magnetization along the phase boundaries so determined may then be carried out with the use of polarized neutrons. We consider here only the results around the tricritical point, $H_{app} \sim 10\,200$ G, $T_t \simeq 21.15$ K. The normalized magnetization as a function of temperature along the phase boundaries is shown in Fig. 1. It is immediately evident that the $FeCl_2$ phase diagram does indeed bear a striking resemblance to the X-T phase diagram in ^{3}He-^{4}He mixtures. We shall discuss this correspondence in detail below. The thermodynamic variable conjugate to the magnetization $M(H_{int}, T)$ is the internal field H_{int}. Using Eq. (1) and the results shown in Fig. 1 one may immediately construct the H_{int}-T diagram. By definition, the upper and lower lines of the phase-separation curve must collapse onto a single line. The resultant H_{int}-T phase diagram is given in Fig. 2. The phase-separation line is seen to be continuous with the λ line through the tricritical point.

As an additional check, we also monitored the strength of the A/f critical fluctuations along the upper phase boundary, at the position (1.98, 0, 0.99), just off the (2, 0, 1) Bragg peak. The critical-scattering intensity is found to decrease gradually as one moves up the λ line. However at $T = 21.15 \pm 0.1$ K there is a distinct break in the slope with the critical scattering then decreasing rapidly in intensity with further decrease in temperature. This is a clear signature of the crossover from a second- to a first-order tran-

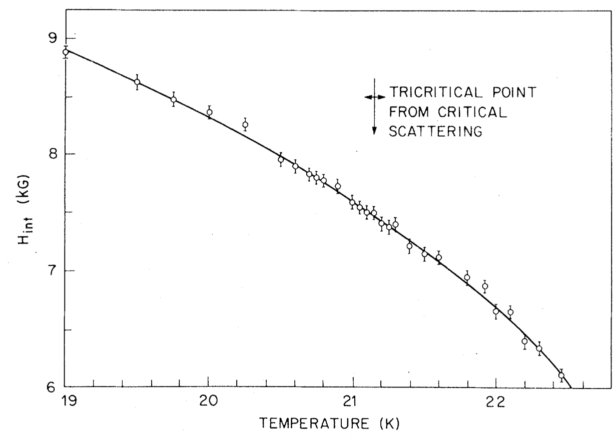

FIG. 2. Internal field versus temperature in $FeCl_2$ along the first-order phase-separation line and the second-order λ line. The solid line is a smooth curve drawn as a guide to the eye.

sition and it thus serves to locate independently the tricritical point at $T = 21.15$ K, $H_{app} = 10\,200$ G for our sample.

We have also carried out a wide variety of measurements of the staggered magnetization $M_s(H, T)$ along various paths in the H_{app}-T plane in order to test the concept of smoothness. These results are discussed in detail in a separate publication.[6] We consider here explicitly, however, the discontinuity in the sublattice magnetization, ΔM_s, across the first-order phase-transition line. This should exhibit characteristic tricritical behavior with respect to the tricritical temperature T_t. The results of these measurements are shown in log-log form in Fig. 3. Here we take $T_t = 21.15$ K, the value deduced both from Fig. 1 and from the critical-scattering measurements discussed above. Over the reduced-temperature range $4\times10^{-3} < 1 - T/21.15 < 2\times10^{-1}$ the square of the normalized sublattice magnetization is found to follow the simple power law

$$(\Delta M_s/M_0)^2 = 1.5(1 - T/21.15)^{0.38}. \qquad (2)$$

We now discuss the results given in Figs. 1–3 in the context of the current theories of tricritical phenomena. It has been demonstrated[7] by Riedel and Wegner and by Bausch that for lattice dimensionality $d > 3$ the tricritical point ought to be characterized by *classical* critical exponents. For $d = 3$ the classical power laws should be modified by logarithmic correction terms. In the M-T plane the Landau theory predicts that the three phase-boundary lines will approach the tricritical point linearly, that is, $\beta = 1$, with the second-

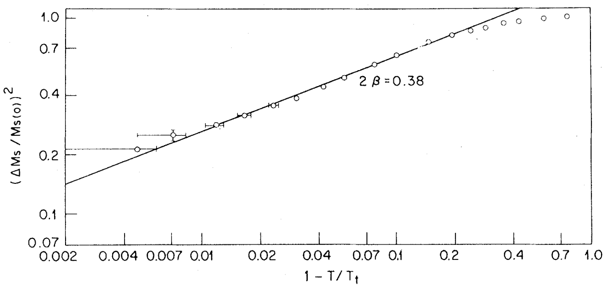

FIG. 3. Square of the normalized sublattice magnetization versus reduced temperature along the A/f side of the first-order line. Here $T_t = 21.15$ K. The solid line corresponds to the power law, Eq. (2).

order λ line joining onto the paramagnetic-phase-separation line with no discontinuity in slope. From Fig. 1 it is evident that this latter prediction is explicitly contradicted in $FeCl_2$; a similar result is found in ^3He-^4He mixtures.[8] The upper two lines in Fig. 1 do seem to approach the tricritical point linearly; however, the A/f first-order line deviates considerably from linearity up to at least 20.9 K, that is $1 - T/T_t \simeq 0.01$. Indeed over the reduced-temperature range $0.1 < 1 - T/T_t < 0.01$ an exponent $\beta_u^- \sim 0.36$ rather than 1 seems to be appropriate. Along the first-order line the Landau theory also predicts that the discontinuity in the sublattice magnetization should obey the power law $\Delta M_s^2 \propto 1 - T/T_t$, that is $2\beta_1 = 1$, compared to our result, Eq. (2), $2\beta_1 = 0.38$. These exponents are accurate, *over the temperature range covered*, to about 10%. There appears, therefore, to be a serious conflict between the classical theory and experiment along the A/f first-order line for both the magnetization and the sublattice magnetization, unlike the case of He^4-He^4 mixtures.[8] There is, of course, always the possibility that for some as yet unknown reason the asymptotic behavior is only attained very close to T_t along this particular path.[9] We should note, however, that along all other paths across the λ line the sublattice magnetization exhibits the predicted power-law behavior for $1 - T/T_c$ or $1 - H/H_c < 10^{-1}$, whereas here we have a significant discrepancy at $1 - T/T_t \sim 4\times10^{-3}$. Clearly, this requires further experimental and theoretical study. Unfortunately, any significant improvement of our neutron measurements of the phase-separation line near T_t is unlikely; the first-order transition manifests itself as a discontinuity in $dI(201)/dH_{app}$ and this point becomes very difficult to locate accurately beyond 21.0 K. However, it may be possible to complete the lower curve in Fig. 1 by using other techniques.

Finally, we consider the results in the H_{int}-T plane. Here the Landau theory predicts that the first-order line should go continuously into the λ line with a discontinuity only in the second derivative. It is evident that our results are in agreement with this prediction although the accuracy of the data precludes any statements about the second derivative. The shape of the H_{int}-T curve is consistent with a crossover exponent[7] of $\phi_t = \frac{1}{2}$, although again the data are not precise enough to determine this exponent accurately.

In conclusion, we emphasize that the qualitative behavior of $FeCl_2$ in a field gives support for our current picture of tricritical behavior. There are, however, a number of disturbing quantitative discrepancies. It is hoped that this work will stimulate both further, more precise experiments and a serious theoretical effort to calculate such detailed features as the explicit shape of the phase diagram around T_t and the magnitude of the logarithmic and higher-order correction terms to the asymptotic critical behavior.

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