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Magnetic tricritical behavior of ethylammonium tetrachlorocuprate

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In order to investigate the prediction by Tuthill that a tricritical point may exist in the phase diagram of spin-flop antiferromagnets with intermediate anisotropy, an experimental reexamination of the phase diagram of the quasi-two-dimensional system $(C_2H_5NH_3)_2CuCl_4$ was performed. Measurements were made of the differential magnetic susceptibility, dM/dH, vs dc field and temperature in the (10 K, 100 Oe) region of the proposed tricritical point. A low amplitude, low frequency, ac biphase SQUID susceptometer was used. The sample was a single crystal with field along the antiferromagnetic easy (orthorhombic a-axis) direction. The data show some evidence of the existence of at least one tricritical point, but the results are not definitive.

I. INTRODUCTION

Copper forms many oxides and halides in which the copper is divalent and magnetic. Many organically bonded compounds containing copper-halogen complexes order magnetically at low (10 K) temperatures and provide a menu of model systems for the study of magnetic critical phenomena. Herein is presented a reexamination of the magnetic phase diagram (applied field and temperature) of the orthorhombic crystal $(C_2H_5NH_3)_2CuCl_4$. This system was previously characterized by de Jongh, van Amstel, and Miedema as a quasi-two-dimensional spin-flop antiferromagnet.[1] The exchange within planes of CuII ions is ferromagnetic and stronger than the antiferromagnetic exchange between the adjacent basal planes. This easy axis anisotropy is thought[2] to be in the intermediate range required for the tricritical behavior recently predicted by Tuthill.[3]

When a uniform magnetic field is applied along the easy axis of an ordered two sublattice anisotropic Heisenberg antiferromagnet (AF), two general classes of phase behavior can occur.[3] If the anisotropy is strong, the system behaves as a metamagnet: An increase of the applied field drives the AF system directly into the saturated paramagnetic (p) phase. When sublattices of ferromagnetic coupling exist, the AF/p phase boundary may consist of first- and second-order segments connected by a tricritical point (TCP). If the anisotropy is weak, exchange dominates and spin-flop (SF) occurs: An increase of the applied field results in a first-order AF/SF transition, followed by a second-order SF/p transition. The AF/SF and SF/p boundaries degenerate into a bicritical point (BCP) where they join the low field line of AF/p transitions below the temperature T_N of spontaneous zero field antiferromagnetic ordering of the alternate planes of magnetic ions. The weak anisotropy AF/p transitions are all second order. An increase of field induces spin-flop before a TCP is reached.

Tuthill predicts, however, that an increase from weak anisotropy to more intermediate values moves the BCP to lower temperature, reducing the size of the SF region of the phase diagram, and eventually exposing the TCP.[3] Further increase of the anisotropy shrinks the SF region until the original strong anisotropy metamagnetic phase diagram results. If Tuthill's view of the roles of easy axis anisotropy and exchange prevails in a system of appropriately intermediate anisotropy, the AF/p boundary between the usual BCP and T_N should, consist of segments of first- and second-order AF/p transitions meeting in a TCP.

Although the anisotropy of $(C_2H_5NH_3)_2CuCl_4$ may be appropriately intermediate, it would appear that the effect, if present, would have been observed in previous studies.[1] It may be seen, however, that this may not be the case, when one observes that the BCP and T_N are separated by less than 0.1 K in this compound. Thus, these measurements were begun.

During these measurements, it was learned that Bogdanov, Zhuraviev, and Telepa had claimed an experimental observation of the TCP in this same compound.[4] Apparently those experiments were motivated by a theory by Bar'yakhtar, Vitebskii, and Yablonskii.[5] Neither report gave enough experimental detail or data to allow an evaluation of their claim. Herein, representative details of the experiment and of the temperature and field dependencies of the susceptibility are presented. A phase diagram in the region of the sought after TCP is developed from the susceptibility data.

II. EXPERIMENT

Crystals of $(C_2H_5NH_3)_2CuCl_4$ were grown by evaporation from an aqueous solution. platelets several millimeters in diameter and $\frac{1}{2}$ mm thick were obtained. Chartreuse hued and semitransparent in visible light, the plates were easily oriented in a polarizing microscope and then adhered to a ground flat on a sapphire rod with silicone grease. The sapphire rod terminated in a feedback temperature controlled copper block with temperature sensing and control by means of a Lakeshore carbon glass resistor and BTI conductance bridge controller. Sample, sapphire, and copper block were vertically positioned in a hard evacuated quartz tube, its lower end immersed in liquid helium. An astatic superconducting pair of pickup coils of a few turns each were

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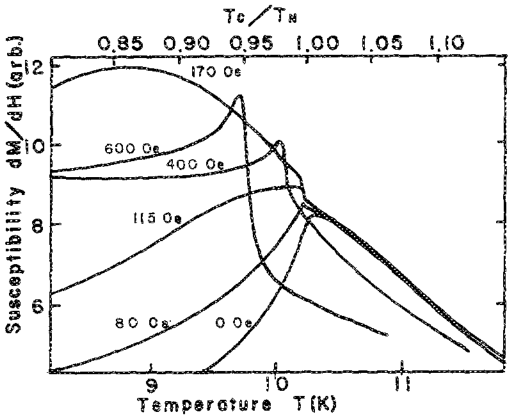

FIG. 1. Dependence of the differential susceptibility upon slowly cooling temperature at selected values of a dc applied magnetic field. Phase boundaries of Fig. 4 are marked by inflections.

wound on on the outside of the quartz tube. The sample was positioned for maximum signal in one coil of the pair. A superconducting ac solenoid of a few hundred turns and a larger dc solenoid were arranged coaxially about the outside of the astatic pickup and sample. The astatic pickup was connected to a BTI rf SQUID sensor. The output of the BTI SQUID control was input to a two-phase lock-in amplifier referenced to the 80-Hz signal from a BTI RBU impedance bridge, which provided the current to the ac solenoid. The two channel output of the lock-in was phased to provide dc voltages proportional to the rms values of the inductive(in phase) and dissipative(quadrature out of phase) parts of the susceptibility dM/dH of the sample. Both outputs were XY recorded with the X channel driven by voltage analogs of temperature or field. Fields ranged 0–1500 Oe and temperatures 5–35 K. Susceptibilities were left in arbitrary recorder units for purposes of critical point determination, and no demagnetizing factor corrections were made. The external fields were aligned with the (easy) a-axis of the platelets.

III. RESULTS

The field and temperature dependencies of the inductive (in-phase) part of dM/dH were similar to earlier work,[1] except that peaks in the field dependence at the SF/p boundary were stronger here. The dissipative (quadrature out of phase) component was completely different. Measurements did not reveal large quadrature peaks in the field dependence at the AF/SF boundary or a null response at the SF/p boundary; rather, a small (5% of in-phase) quadrature response was seen at both the AF/SF and SF/p boundaries. These differences may be associated with the much smaller ac magnetic field amplitudes used in SQUID detection, as compared to conventional Faraday law detection. The fact that comparable effects are observed at known first and second order boundaries should underscore the conclusion that the order of the transition cannot be clearly inferred from

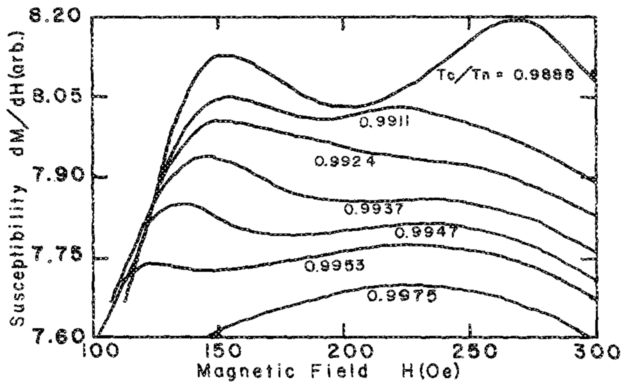

FIG. 2. Dependence of the differential susceptibility upon dc field at selected steady temperatures near the BCP expressed as fractions of T_N. The higher field peak representing the SF/p transition is seen to vanish. This appears to happen below the BCP. See the upper left arrow of Fig. 4.

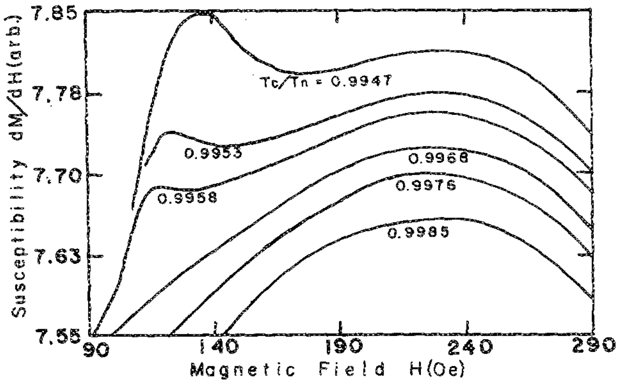

FIG. 3. Dependence of the differential susceptibility upon dc field at selected steady temperature above the BCP expressed as fractions of T_N. The peak representing the AF/p transition is seen to disappear, while a broad maximum remains. The broad maximum does not represent a phase change. The disappearance of the AF/p peak may mark a TCP. See lower arrow Fig. 4.

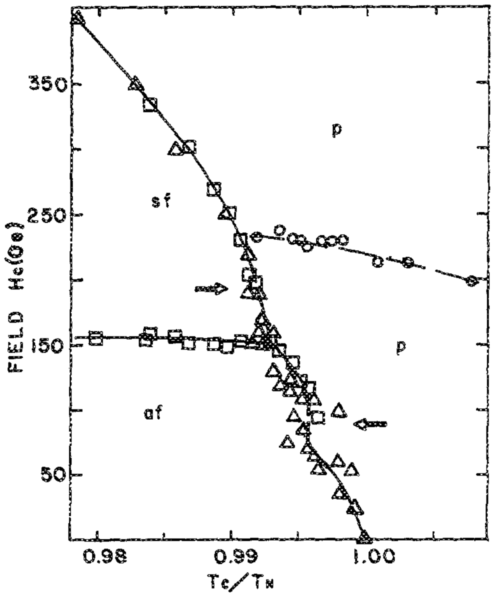

FIG. 4. Temperature-field phase diagram constructed from the loci of susceptibility extrema. The background maximum is marked by a line of circles which do not denote a phase change. Inflections in the temperature dependence depicted by Fig. 1 are denoted by triangles, and the maxima of Figs. 2 and 3 are denoted by squares. Arrows denote tricritical candidates where peaks in dM/dH vanish.

this data, though the locations of the transitions are well marked.

The temperature dependence (slow 1-mK/s free cooling) of dM/dH is shown in Fig. 1 at selected fields. At zero field is the 10.29-K easy axis p/AF ordering. The sharply peaked curve at 80 Oe shows the p/AF crossing at fields below the TCP candidate (denoted by the lower right arrow of Fig. 4). A square cornered curve at 115 Oe corresponds to a p/AF crossing above the point of interest. The 170-Oe curve attains the largest value attained by dM/dH. Its modest inflection near 10.2 K corresponds to a p/SF crossing. Well marked peaks in dM/dH at 400 and 600 Oe also correspond to p/SF crossings. These crossings appear as triangles on Fig. 4.

The dependence of dM/dH upon slowly (1 Oe/s) increasing field is shown in Figs. 2 and 3. The controlled temperatures are expressed as fractions of the zero field temperature T_N. The two peaks in the uppermost curve of Fig. 2 at $T/T_N = 0.9888$ correspond to AF/SF and SF/p crossings below the BCP. The next curve also makes both crossings below the BCP, which appears to be at $T/T_N = 0.992$. Thus, the higher peak is missing from the five lower curves of Fig. 2, and the lower peak on three of these curves corresponds to a crossing of the low field AF/p boundary. As the peaks disappear, a broad background maximum emerges which persists to temperatures well above T_N. The background maxima appear as open circles on Fig. 4, while the phase boundary peaks appear as squares.

Additional crossings of the AF/p boundary are shown on Fig. 3 and exhibit a striking feature. All cross the AF/p boundary between the BCP and T_N, but only the crossings at the three lower temperatures exhibit a crossing peak. This suggests that the peaks be identified with first order transitions with a TCP located at $T_C/T_N \simeq 0.996$. This leaves peaks at the SF/p boundary unexplained, as well as the fact that those peaks also disappear just below the BCP, suggesting a second TCP on the SF/p line of Fig. 4.

These results are summarized in the phase diagram of Fig. 4 with the two peak disappearances marked by arrows. The line through open circles is not a phase boundary.

IV. CONCLUSIONS

The boundaries of the $(C_2N_5NH_3)_2CuCl_4$ magnetic phase diagram have been remapped and evidence for a tricritical point at $T_C/T_N \simeq 0.996$ and $H_C \simeq 90$ Oe has been found in the form of a sudden appearance of field-dependent susceptibility peaks below that point. A definitive characterization of the various boundaries as first or second order appears to require calorimetric measurements.

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