Weak Ferromagnetism in κ-(ET)$_2$Cu[N(CN)$_2$]Cl, where ET is Bis(ethylenedithio)tetrathiafulvalene

U. Welp, S. Fleshler,[a] W. K. Kwok, G. W. Crabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman[b]

Science and Technology Center for Superconductivity, Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439

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Magnetization measurements at ambient pressure on κ-(ET)$_2$Cu[N(CN)$_2$]Cl, an organic salt that is superconducting under pressure (T_c = 12.8 K at 0.3 kbar), reveal an antiferromagnetic transition near 45 K and, *for the first time in this class of materials*, a transition near 22 K to a state displaying weak ferromagnetic hysteresis with a saturation moment of $(8\times10^{-4})\mu_B$/formula. This low-temperature state is characterized by a sequence of first-order magnetization jumps.

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The study of organic charge-transfer salts has attracted considerable interest because of the occurrence of superconductivity in these materials, the rapid increases in T_c, and the unusual physics relating to their low dimensionality. Superconducting salts of the organic electron-donor molecule TMTSF (tetramethyltetraselenafulvalene), of which (TMTSF)$_2$PF$_6$ is the first organic superconductor to be discovered [1], are quasi one-dimensional (1D) systems. Superconducting salts of the organic-donor molecule ET [bis(ethylenedithio)tetrathiafulvalene] and several other organic donor molecules of similar structure are largely quasi two-dimensional (2D) systems. The 1D salts are especially notable for the competition between magnetic insulating and superconducting ground states mediated by applied pressures [2]. The 2D salts, although possessing phases that are superconducting only under applied pressures, are notable for yielding organic superconductors with the highest T_c and the largest number of ambient-pressure superconductors [3,4]. Because of the 2D character of these salts, electronic instabilities are generally considered to be not as important as they are in 1D systems.

κ-(ET)$_2$Cu[N(CN)$_2$]Cl is remarkable because it possesses the highest T_c (12.8 K onset) among these low-dimensional systems. It is superconducting only under an applied pressure (0.3 kbar), yet this pressure is the smallest of any required in organic salts to suppress an insulating ground state [5]. Here, we report on dc magnetization studies of κ-(ET)$_2$Cu[N(CN)$_2$]Cl that establish the existence of an antiferromagnetic transition near 45 K and, *for the first time in this class of materials*, a weakly *ferromagnetic* state below 22 K with a saturation moment of $(8\times10^{-4})\mu_B$/formula. Within this state a sequence of first-order magnetization jumps reminiscent of spin-flip transitions is observed. We thus demonstrate for this quasi 2D organic system a direct competition between magnetic insulating and superconducting ground states, a phenomenon preeminently associated with the quasi 1D systems.

The magnetization data were obtained with a SQUID magnetometer on single crystals grown by methods previously described [6,7]. The single crystals were bricklike specimens of ~2-mg mass. In order to avoid the application of mechanical stress, we lightly wrapped the crystal in tissue paper and enclosed it in a Mylar pouch glued to a quartz holder in appropriate orientations with respect to the applied magnetic field H. The 2D layers of the organic donor molecules lie in the crystallographic a-c plane, which coincides with the large face of the crystal, and these layers are alternately separated by anion layers along the b axis.

Figure 1 shows the temperature dependence of the total magnetization $M = M_{\rm core} + M_{\rm spin}$ for a single crystal of κ-(ET)$_2$Cu[N(CN)$_2$]Cl in a field of 1 T applied parallel ($M_\parallel$) and perpendicular ($M_\perp$) to the a-c plane. $M_{\rm core}$ is the temperature-independent isotropic core contribution of all the atoms and $M_{\rm spin}$ is the temperature-dependent paramagnetic spin contribution. $M_{\rm core}$ can be estimated from tabulated values [8] yielding for a field of 1 T the value $M_{\rm core} = -9.1\times10^{-3}$ emu/cm^3. At temperatures above 45 K the spin contribution is temperature indepen-

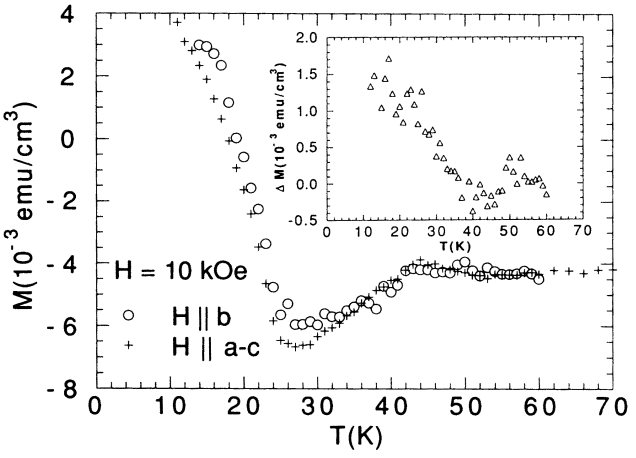

FIG. 1. Temperature dependence of magnetization at H = 1 T applied $\|a$-c and $\|b$. Inset: The onset of anisotropy, $\Delta M = M_\perp - M_\parallel$. M is the total magnetization uncorrected for the diamagnetic core contribution of -9.1×10^{-3} emu/cm^3.

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dent at a value of 4.9×10^{-3} emu/cm^3. At a temperature near 45 K we observe the onset of a shallow decrease in M with decreasing temperature and the onset of an increasing anisotropy, $\Delta M = M_\perp - M_\parallel$. These are characteristic signatures of an antiferromagnetic transition [9]. This transition correlates with the reported resistive transition from semiconducting to insulating behavior [5,6,10] and with the reported anomalies in the electron-spin-resonance (ESR) spectra [11] near 40 K. Similar behavior in the magnetization has been observed in $(TMTSF)_2AsF_6$ [12] and α-$(ET)_2KHg(SCN)_4$ [13], which exhibit metal-to-SDW (spin-density-wave) transitions. The same anisotropy $M_\perp > M_\parallel$ in α-$(ET)_2KHg(SCN)_4$, although much larger than in the material studied here, has been interpreted as indicating an antiferromagnetic axis lying in the a-c plane. A spin-Peierls transition, which is suggested to occur in the semiconducting salts of TMTTF (tetramethyltetrathiafulvalene) [2], can be ruled out because x-ray diffraction studies at temperatures as low as 15 K gave no evidence of superlattice reflections [11]. At temperatures above 45 K the magnetization, in agreement with ESR results [11], is temperature independent, showing no Curie-Weiss contribution that would indicate local magnetic moments.

The most prominent feature in Fig. 1 is the steep increase of the magnetization below 25 K. Figure 2 shows the magnetization $M_\parallel$ in this low-temperature region and a complete hysteresis loop for the magnetization at 10 K. One observes a perfectly symmetrical ferromagnetic hysteresis loop and a remarkable series of sharp jumps in the magnetization. The application of 100 Oe is sufficient to convert the sample to a state of positive magnetic saturation. The jumps are most easily discerned at 5 K, where they occur at equispaced intervals of 8.5 Oe and are labeled by the numbers 1 through 4. The saturation magnetization of 9×10^{-3} emu/cm^3 for the hysteresis loop at 10 K corresponds to a moment of $(8\times10^{-4})\mu_B$/formula. For 10 K in the main panel, two magnetization curves are shown for fields rotated within the a-c plane by 45° with respect to each other. We observe a striking isotropy of the hysteresis and magnetization jumps within the a-c plane, indicating that κ-$(ET)_2Cu[N(CN)_2]Cl$ is magnetically uniaxial even though the lattice structure is orthorhombic.

The magnetization jumps were observed also in the temperature dependence of the magnetization in fixed magnetic fields applied along a-c. Figure 3(a) shows the magnetization for several low fields up to 100 Oe measured on warming after zero-field cooling of the crystal to 5 K in each case. The "zero" field actually refers to the combination of the Earth's field plus a small negative remnant field (< 0.5 Oe) of the superconducting magnet. Therefore, with our experimental apparatus, the cooled specimen was always prepared in a state of negative magnetic saturation. Figure 3(a) shows the same sharp

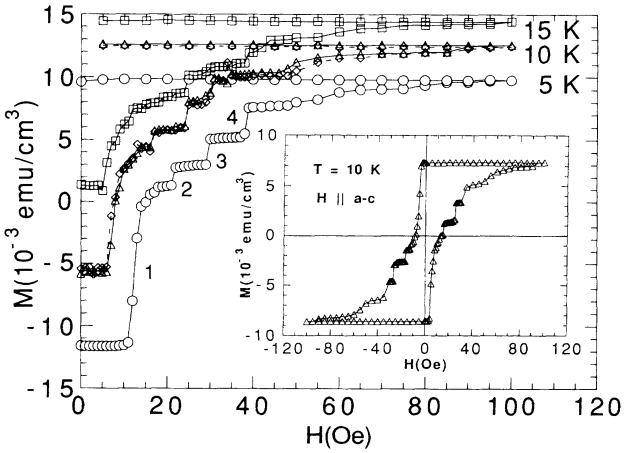

FIG. 2. Field dependence of magnetization for $H \| a$-c. For clarity the results for 10 and 15 K have been shifted up by 4×10^{-3} emu/cm^3 and 8×10^{-3} emu/cm^3, respectively. The data for 10 K contain two superimposed measurements for H rotated in the a-c plane by 45°. Inset: Full hysteresis loop at 10 K.

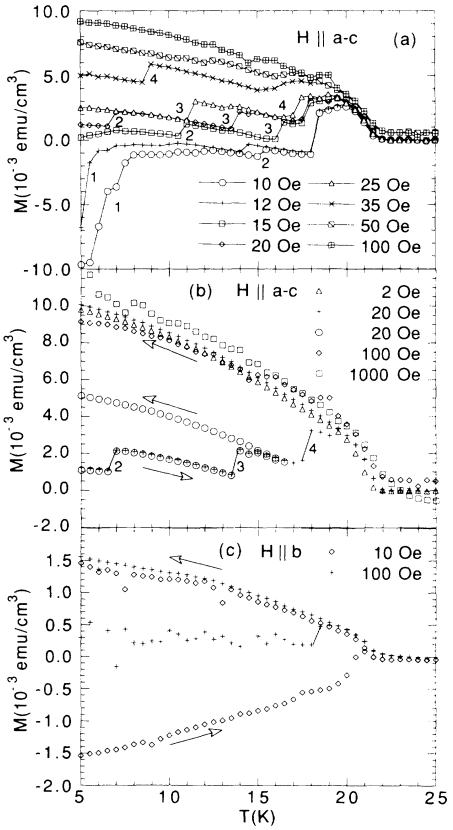

FIG. 3. Temperature dependence of magnetization in various fields. (a) $H \| a$-c; M on warming. The numbering of the jumps corresponds to Fig. 2. (b) $H \| a$-c; field-cooled M from 25 K for applied fields of 2, 100, and 1000 Oe. Data for 20 Oe are shown for warming up to 16.5 K (○) and 25 K (+) following zero-field cooling, and subsequent cooling. (c) $H \| b$; M on warming and cooling.

jumps as those of Fig. 2, and these are indexed by the same numbering scheme.

Each of these jumps is hysteretic, as demonstrated by the plots in Fig. 3(b). On warming after zero-field cooling, the magnetization for 20 Oe shows jumps indexed as 2, 3, and 4, and on reaching a temperature of 22 K, the magnetization attains a state of nearly zero moment. On cooling from 25 K in the same field, the magnetization curve traces out the temperature dependence of the state of positive magnetic saturation. On the other hand, warming the crystal to 16.5 K, below transition 4, yields on cooling an incompletely saturated magnetization curve. Figure 3(b) additionally shows the field-cooled magnetization for fields of 2 Oe, 100 Oe, and 1 kOe, which demonstrate that the saturation moment is little affected by the applied field. The onset of the magnetic transitions is about 22 K for low applied fields, and it increases to higher temperatures with increasing field at a rate of 0.2 K/kOe. The temperature dependence of M for fields of 10 and 100 Oe applied perpendicular to a-c is shown in Fig. 3(c). In comparison to the measurements for $H \| a$-c, there is a uniform decrease in magnetization by a factor of 5 and a suppression of the jumps. This is consistent with spins lying in the a-c plane.

The magnetization behavior described here for one crystal specimen has been observed, although not as cleanly, in five other crystal samples derived from different synthetic batches. Four of the crystals studied in fields of 0.1–3 T showed the magnetic transition near 45 K. All five crystals exhibited either positive or negative signals at low fields for zero-field or field cooling, respectively, with onset near 22 K, and four showed traces of superconductivity. Two of the four crystals studied in detail at low fields showed the sharp magnetization jumps below 20 K. We conclude from these results that the magnetic transitions we observed cleanly in one crystal specimen are reproducible and an intrinsic property of ambient-pressure κ-$(ET)_2Cu[N(CN)_2]Cl$ and that the more typical state of the ambient-pressure crystal is an artificial mixture of magnetic and superconducting phases, possibly induced by mechanical stresses. When the crystal of Figs. 1–4 was cooled while immersed in Apiezon N-grease, the saturation moment was reduced by a factor of 7 and traces of superconductivity appeared at temperatures below 12–13 K.

κ-$(ET)_2Cu[N(CN)_2]Cl$ belongs to the class of organic compounds with formal composition and valence $(ET)_2{}^+X^-$. The anions X^- form inert, generally nonmagnetic layers (Cu is in the Cu^{1+} state) serving as a charge reservoir, whereas the charge transport and magnetism are located in the $(ET)_2{}^+$ layers. Considerations of electron count as well as electronic band-structure calculations [5] indicate that κ-$(ET)_2Cu[N(CN)_2]Cl$ should be metallic with a half-filled conduction band. The restricted dimensionality and the low charge carrier density (10^{21} cm^{-3}) imply strong on-site Coulomb repulsions and the possibility of a transition to a Hubbard-Mott insulator, in which the charge degrees of freedom freeze out. This mechanism is believed to occur in 1D TMTTF salts [2] as well as in the 2D $(ET)_2X$ salts with $X^- = ICl_2{}^-$, $IClBr^-$, $AuBr_2{}^-$ [14]. The latter exhibit both semiconducting resistivity and temperature-independent spin susceptibility like κ-$(ET)_2Cu[N(CN)_2]Cl$. These considerations suggest that κ-$(ET)_2Cu[N(CN)_2]Cl$ is a Hubbard-Mott insulator and that near 45 K essentially localized spins order antiferromagnetically.

The steep increase of the magnetization near 22 K (Fig. 1) signals another magnetic transition within the antiferromagnetic phase. Similar temperature dependences of M have been observed for $(TMTSF)_2AsF_6$ [12] and $(TMTTF)_2SbF_6$ [15] in magnetic fields applied parallel to the antiferromagnetic axis and in excess of a critical spin-flop field which is several kOe in these materials. However, the appearance of a ferromagnetic hysteresis, the field independence of the saturation moment (i.e., $\chi \approx 0$), and the increase in M for $H \| b$ at low fields seems to exclude the occurrence of a spin flop for the present salt. Hysteretic jumps in the magnetization have been observed [16] for $(TMTSF)_2ClO_4$ in high fields (> 5 T). They have been attributed to the field dependence of the Landau-level quantization, a mechanism which is not important in the field range presented here.

One observes a striking similarity of the jumps in $M(T)$ and the reentrant phase boundary to the results on some cerium monopnictides [17]. In these materials, antiferromagnetic phases characterized by a sequence of different antiferromagnetic propagation vectors and stacking patterns are separated by first-order transitions. The very small values of the uniform moment in κ-$(ET)_2Cu[N(CN)_2]Cl$, however, seem to contradict such a mechanism involving the flip of local spins. Instead, they indicate transitions in a weakly ferromagnetic structure which arises from a slight canting of the magnetic moments in different sublattices. κ-$(ET)_2Cu[N(CN)_2]Cl$ has an orthorhombic structure with the space group $Pnma$, for which weak ferromagnetism is possible as long as the antiferromagnetic vector and the ferromagnetic moment lie in the a-c plane [18], in agreement with our results. If the weak ferromagnetic moment arises from a two sublattice magnetic structure with an ordered moment of $1\mu_B$, the measured saturation moment corresponds to a canting angle of 0.046°. An angle of 0.17° has been recently determined [19] for weakly ferromagnetic La_2CuO_4. In the absence of magnetic neutron scattering data or detailed magnetic resonance data, we cannot unambiguously delineate the magnetic structure and the nature of the first-order magnetic transitions. Magnetization jumps have been observed in the study of classical ferromagnets, where they are related to avalanche effects or domain wall motion. However, the complete symmetry and in-plane isotropy of the hysteresis loops here indicates that the jumps are intrinsic first-order transitions between different magnetic structures

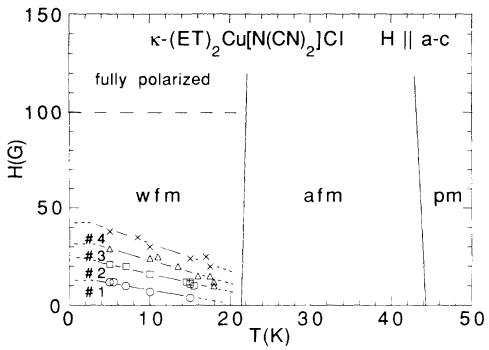

FIG 4. Schematic phase diagram of κ-$(ET)_2Cu[N(CN)_2]Cl$ at ambient pressure for $H \| a$-c: pm, paramagnetic; afm, antiferromagnetic; wfm, weakly ferromagnetic. The phase lines of the magnetization jumps are shown for low H and T.

involving the motion of many interacting spins.

Our results are summarized in the schematic phase diagram shown in Fig. 4, which shows for $H \| a$-c the transition from a paramagnetic to an antiferromagnetic state and the reentrant phase boundary of a weakly ferromagnetic state. This state is fully polarized in fields in excess of 100 Oe, whereas in lower fields a complex magnetic structure that exhibits a series of first-order transitions is realized. This structure reflects on the subtle balance between localization of charge carriers due to Coulomb correlations and restricted dimensionality and the metallic (superconducting) states which can be induced with minute lattice deformations.

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[a]Also at Department of Physics, Purdue University, Lafayette, IN 47907.

[b]Also at Department of Chemistry, Alma College, Alma, MI 48801.

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