Paramagnetic limiting of the upper critical field of the layered organic superconductor \( \kappa-(\text{BEDT-TTF})_2\text{Cu(SCN)}_2 \)

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We report detailed measurements of the interlayer magnetoresistance of the layered organic superconductor \( \kappa-(\text{BEDT-TTF})_2\text{Cu(SCN)}_2 \), for temperatures down to 0.5 K and fields up to 30 T. The upper critical field is determined from the resistive transition for a wide range of temperatures and field directions. For magnetic fields parallel to the layers, the upper critical field increases approximately linearly with decreasing temperature. The upper critical field at low temperatures is compared to the Pauli paramagnetic limit, at which singlet superconductivity should be destroyed by the Zeeman splitting of the electron spins. The measured value is comparable to a value for the paramagnetic limit calculated from thermodynamic quantities but exceeds the limit calculated from BCS theory. The angular dependence of the upper critical field shows a cusplike feature for fields close to the layers, consistent with decoupled layers.

I. INTRODUCTION

The layered organic molecular crystals \( \kappa-(\text{BEDT-TTF})_2X \) where BEDT-TTF is bis-(ethylenedithiatetrafulvalene) and \( X \) is an anion \( \{\text{e.g., } X=\text{I}_3, \text{Cu}[\text{N(CN)}_2]\text{Br, Cu(SCN)}_2\} \) are particularly interesting because they are strongly correlated electron systems with similarities to the high-\( T_c \) cuprate superconductors including unconventional metallic properties and competition between antiferromagnetism and superconductivity.\(^1\)\(^-\)\(^4\) Furthermore, they are available in high-purity single crystals and, in contrast to the cuprates, their lower superconducting transition temperature (\( T_c \sim 10 \) K) makes experimentally accessible in steady magnetic fields properties such as the upper critical field and Shubnikov-de Haas oscillations.\(^5\)\(^,\)\(^6\)

Recently it has been argued that a minimal theoretical model that can describe these materials is a Hubbard model on an anisotropic triangular lattice with one hole per site.\(^2\)\(^,\)\(^3\) Calculations at the level of the random-phase approximation\(^7\) and the fluctuation-exchange approximation\(^8\) suggest that at the boundary of the antiferromagnetic phase this model exhibits superconductivity mediated by spin fluctuations. As the anisotropy of the intersite hopping varies the model changes from the square lattice to the isotropic triangular lattice to decoupled chains.\(^2\) The wave vector associated with the antiferromagnetic spin fluctuations changes\(^9\) and the superconductivity has been predicted to change from \( d \)-wave singlet (as in the cuprates) to \( s \)-wave triplet in the odd-frequency channel.\(^7\)

Experimental results that are consistent with unconventional superconductivity include the temperature dependence of the NMR relaxation rate \( 1/T_1 \) (including the absence of a Hebel-Slichter peak),\(^10\)\(^,\)\(^11\) the temperature and magnetic field dependence of the electronic specific heat,\(^12\) the temperature dependence of the thermal conductivity,\(^13\) and the sensitivity of \( T_c \) to disorder.\(^14\)

The temperature dependence of the NMR Knight shift (which measures the electron spin susceptibility) in the superconducting state provides a means to distinguish triplet and singlet pairing. For triplet pairing the Knight shift does not change on entering the superconducting state, whereas for singlet pairing the Knight shift goes to zero as the temperature decreases to zero. The Knight shift of \( ^{13}\)C NMR on the \( X=\text{Cu}[\text{N(CN)}_2]\text{Br} \) is consistent with the latter. In contrast, the Knight shift of \( ^{17}\)O NMR on \( \text{Sr}_2\text{RuO}_4 \) is consistent with the former.\(^15\)

If the superconductivity is spin singlet then the upper critical field cannot exceed the paramagnetic limit \( H_p \), also known as the Pauli limit or Clogston-Shandrasekhar limit.\(^16\)\(^,\)\(^17\) Above \( H_p \) the Cooper pairs are destroyed by the Zeeman splitting produced by the magnetic-field coupling to the electronic spins. For weak-coupling BCS theory

\[
H_p = H_p^{\text{BCS}} = \frac{1.8k_BT_c}{\mu_B}.
\]

For \( T_c = 10 \) K, as in the material studied here, this gives \( H_p^{\text{BCS}} = 18 \) T. Strong coupling effects\(^18\) and \( d \)-wave pairing\(^19\) only change this value of \( H_p \) slightly. In most superconductors the paramagnetic limit is irrelevant because the supercon-
ductivity is destroyed at much lower fields due to the frustration of the orbital degrees of freedom associated with the formation of vortices. However, in layered superconductors with fields parallel to the layers the vortices can fit between the layers and paramagnetic limiting can become important.20

Previous determinations of the upper critical field of the κ-(BEDT-TTF)2X family21–26 have mostly focused on measurements of the slope of the $dH_{c2}/dT$ near $T_c$. The values obtained for $X = \text{Cu}[\text{N(CN)}_2]\text{Br}$ and $X = \text{Cu} \text{(SCN)}_2$ are in the range 10 to 20 T/K. Using the Werthamer, Helfand, and Hohenberg (WHH) formula27 for a three-dimensional superconductor, this very large slope would suggest a zero-field-limited zero temperature lies below or close to the Pauli paramagnetic temperature.

In pulsed magnet fields,28 a quasilinear temperature dependence was found with $H_{c2}$. The authors concluded that the upper critical field exceeded the Pauli limit. A study of the upper critical field of $X = \text{Cu} \text{(CN)}[\text{N(CN)}_2]$ (Ref. 29) determined from the resistive transition found an upper critical field of about 25 T for fields parallel to the layers. Studies on the lower $T_c$ organic compounds such as the κ-(BEDT-TTF)2I3 (Ref. 30) β-(BEDT-TTF)2I3, and β-(BEDT-TTF)2IBr2 (Ref. 31) have found that the $H_{c2}$ at zero temperature lies below or close to the Pauli paramagnetic limit predicted by BCS theory. Similar paramagnetic field-limited $H_{c2}$ have been reported in the cuprate YBa2Cu3O7−δ (Ref. 32) and the heavy fermion superconductors UPd2Al3 (Ref. 33).

If there is paramagnetic limiting there is theoretically the possibility that as the magnetic field is increased at low temperatures there is a first-order phase transition into the non-uniform superconducting state, originally proposed by Fulde, Ferrell, Larkin, and Ovchinnikov.25 As the dimensionality of the system decreases the magnetic-field range over which this phase is stable increases.25 Such a first-order phase transition was recently seen in ultrathin beryllium films.26 It is still controversial about whether this phase does exist in UPd2Al3.33 On the other hand, if the superconductivity is triplet there is also the possibility of reentrant superconductivity at high fields such that $T_c(H)$ actually increases with increasing field.25,38

In this paper we report the measurement of the interlayer resistivity of $X = \text{Cu} \text{(SCN)}_2$ down to 0.5 K and up to 30 T for a range of field directions. For magnetic fields parallel to the layers, the upper critical field increases approximately linearly with decreasing temperature to values that clearly exceed the BCS Pauli limiting field (1), but are consistent with the paramagnetic limit, estimated directly from the superconducting condensation energy. The upper critical field as a function of angle shows a sharp cusp for fields almost parallel to the layers, consistent with two-dimensional decoupled layers. We find no evidence of a first-order phase transition as a function of field at low temperatures.

II. THEORETICAL BACKGROUND

We now briefly summarize some theoretical results concerning the upper critical field, which we will use later in interpreting our results. A more complete discussion can be found in Ref. 39.

A. Angular dependence of the upper critical field

Anisotropic Ginzburg-Landau theory is valid when the coherence length perpendicular to the layers, $\xi_\perp$, is much larger than the interlayer spacing. It predicts that the dependence of the upper critical field on the angle $\theta$ between the field and the normal to the layers is20,39

$$\left[ \frac{H_{c2}(\theta \cos(\theta))}{H_{c2\perp}} \right]^2 + \left[ \frac{H_{c2}(\theta \sin(\theta))}{H_{c2\parallel}} \right]^2 = 1, \quad (2)$$

where $H_{c2\perp}$ and $H_{c2\parallel}$ are the upper critical field for fields perpendicular and parallel to the layers, respectively. The perpendicular upper critical field is determined by $\xi_\parallel$, the coherence length parallel to the layers,

$$H_{c2\parallel} = \frac{\Phi_0}{2\pi \xi_\parallel^2}, \quad (3)$$

where $\Phi_0$ is the flux quantum. The coherence lengths parallel and perpendicular to the layers are related by

$$\frac{\xi_\parallel}{\xi_\perp} = \frac{H_{c2\perp}}{H_{c2\parallel}}. \quad (4)$$

Klemm, Luther, and Beasley considered the upper critical field of layered superconductors when the layers were infinitely thin.20 For both Lawrence-Doniach theory and microscopic theory, they found that for fields parallel to the layers, if the interlayer coupling is sufficiently weak the upper critical field diverges at low temperatures unless spin-orbit effects or paramagnetic limiting is present. This is because the Josephson vortices associated with the field parallel to the layers have no normal core and can fit between the layers. Bulaevskii30 and Schneider and Schmidt40 considered a more general model where the layers have a finite thickness $d$, resulting in a finite upper critical field

$$\frac{H_{c2\perp}}{H_{c2\parallel}} = \frac{d}{\sqrt{12\xi_\parallel^2}. \quad (5)}$$

They also found that if the coupling between the layers is sufficiently weak, then the angular dependence of the upper critical field is given by

$$\left[ \frac{H_{c2}(\theta \cos(\theta))}{H_{c2\perp}} \right]^2 + \left[ \frac{H_{c2}(\theta \sin(\theta))}{H_{c2\parallel}} \right]^2 = 1 \quad (6)$$

This same angular dependence was found earlier for thin two-dimensional films by Tinkham using a simple fluxoid quantization argument.41 The main difference from the anisotropic three-dimensional result is that at $\theta = 90^\circ$, $H_{c2}(\theta)$ from Eq. (2) is smooth or bell-shaped with $dH_{c2}(\theta)/d\theta \neq 0$, whereas $H_{c2}(\theta)$ from Eq. (6) has a cusp at $\theta = 90^\circ$.

If the upper critical field is determined solely by coupling of the field to the spins, then it will be independent of the field direction. Bulaevskii30 considered the case where the paramagnetic limit is larger than the upper critical field for fields perpendicular to the layers but smaller than the upper critical field determined by orbital effects for fields parallel to the layers. The angular dependence is then given by
where $H_{c2}(\theta)$ is defined by Eq. \(\theta\). This also results in an $H_{c2}$ vs $\theta$ curve, which has a cusp at $\theta = 90^\circ$. Indeed the angular dependence is difficult to distinguish from Eq. \(1\).

**B. Estimating the paramagnetic limiting field**

The metallic phase has a finite Pauli spin susceptibility $\chi_e$ compared to the vanishing susceptibility (at zero temperature) of a spin singlet superconducting state. Hence, it will be energetically favorable to destroy the superconducting state when the magnetic energy density gained by the difference in susceptibilities exceeds the superconducting condensation energy density $U_e$. The critical field $H_P$ at which this occurs is given by

$$U_e = \frac{\mu_0}{2} \chi_e H_P^2,$$

where $\mu_0$ is the magnetic permeability of free space.

In BCS theory the condensation energy density is $U_e = \frac{1}{2} N(E_F) \Delta(0)^2$, where $N(E_F)$ is the metallic density of states and $\Delta(0) = 1.76 k_B T_c$ is the zero-temperature energy gap. Making use of these relations and $\chi_e = (\mu_0)^2 N(E_F)$, we obtain the expression (1) for $H_P$.

**Many-body effects.** In the $\kappa$-(BEDT-TTF)$_2X$ crystals there are significant many-body effects; the electron effective mass $m^* \kappa$ determined from magnetic oscillations can be two to five times larger than that predicted by band-structure calculations.\(^2\)\(^6\) The effect of this on the paramagnetic limit needs to be taken into account. Perez-Gonzalez\(^8\) finds that the paramagnetic limiting field is enhanced by a factor of $m^* \kappa / m_b$. However, he did not take into account the simultaneous effect on the Zeeman splitting; the $g$ factor changes to $g^\kappa$. When this is done one finds that within a Fermi liquid framework the Pauli limit is actually reduced from (1) by a factor of $g^\kappa / g$.\(^4\)\(^2\) This ratio can be estimated from thermodynamic measurements or from the spin-splitting of magnetic oscillations.\(^4\)\(^2\) The values obtained by these two methods for $X = \text{Cu(SCN)}_2$ are 0.8 and 1.4, respectively.\(^4\)\(^2\)

Alternatively, we can make a theory-independent estimate of $H_P$ by using Eq. \(8\) and the experimentally determined condensation energy density and spin susceptibility. This method of determining $H_P$ is very attractive because it does include all the many-body effects (without assuming a Fermi liquid picture) and does not assume the validity of any particular theory of superconductivity for the material in question. Haddon et al.\(^4\)\(^3\) found $\chi_e = 4.3 \times 10^{-4}$ emu per mole [corresponding to a density of states of 7 states per (eV molecule)] for the $X = \text{Cu(SCN)}_2$ salt. By a reanalysis of Graebner et al.\(^6\)\(^2\) specific heat data Wosnitza\(^6\) evaluated the condensation energy density in terms of the thermodynamic critical field $B_{th} = 90$ mT, where $U_e = 1/2 \mu_0 B_{th}^2$. Taking the unit-cell volume of 1695 Å$^3$ and two (BEDT-TTF)$_2X$ units in each unit cell gives $B_{th} = 30 \pm 5$ T. The uncertainty is estimated based on the uncertainty in the values for the condensation energy and the susceptibility.

**FIG. 1.** Determination of the upper critical field. The main figure shows the interlayer resistance as a function of magnetic field on a semilogarithmic scale, the upper critical field being defined as the field at which the resistance is $1 \Omega$. In the inset the upper critical field $H_{c2}^\kappa$ is determined by linear extrapolation. The temperature is 4.2 K and the field is parallel to the layers.

**III. EXPERIMENTAL DETAILS**

Single crystals of $\kappa$-(BEDT-TTF)$_2\text{Cu(SCN)}_2$ were synthesized by the electrol crystallization technique described elsewhere.\(^14\) The interlayer resistance was measured with use of the four-probe technique. Contact of the gold wires to the sample was made with a Dupont conducting paste or graphite paste. Typical contact resistances between the gold wire and the sample were about 10 $\Omega$. A current of 1 $\mu$A was used to ensure linear $I$–$V$ characteristics. The voltage was detected with a lock-in amplifier at low frequencies of about 312 Hz. To avoid pressure effects due to solidification of grease, the sample was mechanically held by thin gold wires. The data presented in this work were taken in a $^3$He system with field up to 30 T at the National High Magnetic Field Laboratory at Tallahassee. The sample can be rotated in the field and the orientation was determined by using a Hall probe at low fields.

**IV. RESULTS**

Shown in Fig. 1 is a typical field dependence of the interlayer resistance plotted in a semilog scale at a temperature of 4.2 K. The field is applied parallel to the planes. The resistive transition in parallel field is typical of the low-dimensional organic superconductors with a broad transition width in field and a large positive magnetoresistance in the normal state. The superconducting transition or the upper critical field $H_{c2}$ is defined at the 1 $\Omega$ level. To check the validity of this criteria, the critical field will be compared with that obtained by a more conventional definition. Shown in the inset are the same data in a linear scale. The two lines are extrapolations of the normal-state magnetoresistance and the superconducting transition with the upper critical field $H_{c2}^\kappa$ defined at the crossing point of the two lines.
Figure 2 is an overlay of resistive transitions in parallel field at different temperatures from \( T = 0.5 \) K to 10.2 K. With increasing temperature, the curves shift to the left toward lower critical fields. The transition curves are nearly parallel for all temperatures in the semilog scale. \( H_{c2} \) is almost the midtransition point as in a conventional superconductor, where parallel transitions are seen but in a linear scale.

The temperature dependences of the two fields \( H_{c2} \) and \( H_{c2}^* \) are shown in Fig. 3. Within the scatter of the points, the two upper critical fields have nearly the same linear temperature dependence with \( dH_{c2}/dT \approx 3 \text{ T K}^{-1} \). The offset in the superconducting transition temperature is due to the different definitions. The upper critical fields at zero temperature are about 30 T and 33 T for \( H_{c2} \) and \( H_{c2}^* \), respectively. The dashed line is the Pauli limit \( H_p = 18.4 \) T, calculated from Eq. (1) with \( T_c = 10 \) K. Clearly, \( H_p \) defined this way is well below the measured upper critical fields at low temperatures. On the other hand, \( H_{c2} \) is consistent with our estimate of \( H_p \) from thermodynamic quantities.

To look at the anisotropy of the upper critical field, systematic measurements have been taken as a function of angle \( \theta \), defined between the field direction and the normal of the plane. Plotted in Fig. 4 is an overlay of resistive transitions as a function of field at different angles. The six curves are representative of the angular dependence from field parallel to the layers \( (\theta = 90^\circ) \) to normal to the layers \( (\theta = 180^\circ) \). With increasing \( \theta \), the field dependence of the resistive transition is drastically changed. At \( \theta = 91.50^\circ \), \( H_{c2} \) is decreased by about 4 T. At \( \theta = 96.64^\circ \), a shoulderlike feature is developed in \( R(H) \) with a corresponding decrease in \( H_{c2} \) by about 12 T. The shoulderlike structure develops into a well defined peak at \( \theta = 178^\circ \) with the occurrence of the Shubnikov–de Haas (SdH) oscillation in the resistance at high fields. It should be noted that unlike for fields parallel to the layers, the resistive transition is relatively insensitive to the angles near \( \theta = 180^\circ \).

The inset in Fig. 4 shows an expanded view of the resistive transitions at angles close to \( \theta = 90^\circ \) direction. With a slight increment in \( \theta \), the transition is drastically broadened. The field component parallel to planes is almost constant for all angles shown in the inset and the maximum out-of-plane field component is about 0.5 T at \( \theta = 91.50^\circ \) and \( H = 30 \) T. \( H_{c2} \) defined at the 1 \( \Omega \) level as a function of angle is
If instead we consider the model of weakly coupled layers and use Eq. (3) for the ratio of the critical fields, we deduce that the thickness of the superconducting layer is $d = 40$ Å. Clearly, this is unrealistic because it should be smaller than the interlayer spacing. A more realistic value would be a few Å. This suggests that the parallel upper critical field being determined by paramagnetic limiting rather than orbital effects is more realistic.

Because of the extremely sensitive angular dependence of the resistive transition, a shoulderlike feature is developed in the resistive transition a few degrees away from the parallel to the plane direction. The upper critical field $H_{c2}^*$ can only be defined close to the planes. While the magnitude of $H_{c2}^*$ is larger than $H_{c2}$, as expected, it is difficult to distinguish the 2D and the 3D models with the available data. $H_{c2}^*$ decreases quasilinearly with angle within the errors.

The upper critical field determined from transport measurements has been under a lot of debate in the cuprate superconductors. For field perpendicular to the planes, $H_{c2}(T)$ defined at certain fractional normal-state resistance typically gives rise to a positive curvature at low temperatures. Various mechanisms have been proposed for the unconventional temperature dependence. However, it has been suggested that the $H_{c2}$ thus defined corresponds to the irreversibility or vortex melting line. For fields parallel to the layers, a vortex moving along the plane encounters negligible pinning as there is no normal core associated with Josephson vortices. Magnetization is practically always reversible in this orientation. The resistive onset field is clearly well separated from irreversibility field and reflects the true upper critical field.

In the case of Sr$_2$RuO$_4$ and the quasi-one-dimensional organic superconductor (TMTSF)$_2$X, where $X = $ ClO$_4$ and PF$_6$, the upper critical field in the plane has been found to exceed the Pauli limit, calculated from BCS theory. Combined with the strong dependence of the transition temperature on the impurity concentration and the temperature dependence of the Knight shift, triplet pairing or $p$-wave has been suggested in these systems. However, the quasilinear temperature dependence observed here for both $H_{c2}$ and $H_{c2}^*$ is remarkably different from that of Sr$_2$RuO$_4$ and Bechgaard salts. For both Sr$_2$RuO$_4$ and (TMTSF)$_2$ClO$_4$, the $H_{c2}$ is found to saturate for $T/T_c < 0.2–0.4$. While for (TMTSF)$_2$PF$_6$, $H_{c2}(T)$ along both $a$ and $b'$ axes where $X = $ ClO$_4$ displays a diverging temperature dependence near $T = 0$ K.

VI. CONCLUSIONS

In summary, for fields parallel to the layers we have observed an upper critical field determined from resistive transition, which is comparable to the paramagnetic limit estimated from thermodynamic quantities but is considerably larger than that calculated from BCS theory. There is no evidence of a first-order transition in the field dependence of the resistivity, which would occur if there was a transition to a Fulde-Ferrell phase. The observed anisotropy of the upper critical field is much less than would be predicted by a model without paramagnetic limiting. The upper critical field determined is quasilinear with temperature. The angular dependence of the resistive transition is consistent with the highly
anisotropic nature of the title compound with a cusplike angular dependence for field near the plane.

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