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Exceeding the Pauli paramagnetic limit in the critical field of $(TMTSF)_2PF_6$

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The resistive upper critical field along the b axis ($H_{c2}\|b$) in $(TMTSF)_2PF_6$ is investigated in detail in fields to 17.5 T and temperatures to $T/T_c \sim \frac{1}{60}$, at various pressures near the border between spin-density wave and metallic states. Remarkably, in an optimum pressure setting reported here, it is found that the onset of superconductivity persists up to 9 T ($>4H_p$), which strongly suggests triplet Cooper pairing. Strong upward curvature with nearly diverging behavior of the critical field seems to suggest a field-dependent dimensional crossover, although the H_{c2} enhancement is considerably more than that predicted by recent theories.

There have been extensive discussions of the symmetry of the superconducting ground state in the Bechgaard salts, which remains controversial. Possible p-wave pairing was suggested by Abrikosov,[1] and by Gor'kov and Jerome,[2] based on the fact that the superconducting critical temperature is extremely sensitive to the introduction of nonmagnetic defects[3,4] and substitutional impurities.[5,6] However, early specific heat,[7,8] and resistive upper critical-field studies[9–11] had indicated conventional BCS-like behavior. Others[12,13] argued in favor of nodes in the superconducting gap with p- or even d-wave pairing from the absence of a Hebel-Slichter peak and/or the T^3 dependence of the proton NMR relaxation rate,[14] while thermal conductivity studies[15] on $(TMTSF)_2ClO_4$ suggested a nodeless gap. Recently, light has been shed on the issue of order parameter symmetry[16–18] by measurements of the resistive upper critical field H_{c2}, with highly improved accuracy in angular alignment and with lower temperature. In these measurements,[19] mainly motivated by theoretical prediction by Lebed[20] and others,[21,22] Lee *et al.* found that, with a base temperature of $T/T_c \sim \frac{1}{15}$, the onset upper critical field persists to a field strength of 6 T which far exceeds the Clogston-Chandrasekhar[23] or Pauli pair-breaking limit given by $\mu_0 H_p = \Delta_0/\mu_B\sqrt{2} \approx 1.84 T_c \approx 2.2\,\mathrm{T}$ for $T_c = 1.2\,\mathrm{K}$. Since then, the issue has been expanded theoretically[24] and tested experimentally in different materials such as two-dimensional organic metals[25,26] and some high-T_c compounds.[27]

In this report, we present the highest upper critical field in the $(TMTSF)_2X$ system, $\mu_0 H_c \| b = 9\,\mathrm{T}$ with $T/T_c \sim \frac{1}{60}$. A high-quality single crystal was mounted inside a miniature BeCu clamp cell 12 mm long and 7.5 mm in diameter (small enough to do 4π steradian rotations in a 40 mm bore split coil superconducting magnet). The high precision of the angular positioning was obtained by combining an *ex situ* goniometer with rotational resolution 0.0025° in the crystal a-c plane with an *in situ* stepper motor-driven Kevlar string rotator providing ~0.05° resolution within the a-b plane. Electrical contacts were made on the sample a-b plane using silver paint and gold or annealed platinum wires for standard four probe interlayer transport measurements. Fairly low ac current densities of $10^{-4}\,\mathrm{A/cm^2}$ (0.1 to 1 μA) with low frequency ranging from 19 to 314 Hz were employed. From the known linear pressure dependence of the superconducting transition temperature of lead,[28] the pressure of each sample was obtained from the measured difference in T_c between two susceptibility coils stuffed with lead, one located inside and one outside the pressure cell.

The typical temperature dependence of the interlayer resistivity for several values of field along the b axis is shown in Fig. 1. Two slightly different pressures were used, one just above the metal-spin-density wave (SDW) critical pressure ($P_c \sim 5.8\,\mathrm{kbar}$) and the other just below P_c. The temperature dependence of the zero-field resistance was metallic ($\delta\rho/\delta T < 0$) in the former case and semimetallic ($\delta\rho/\delta T > 0$) in the latter, due to the SDW transition at 3.5 K. These data are shown in the lower and upper panels, respectively. In the upper panel (A), the field values above the 5 T trace are 5.25, 5.5, 5.75, 6.0, 6.5, 7.0, and 7.8 T. Data with applied field between 3 and 17.5 T are shown in the lower panel (B) with an interval of 0.5 from 3 to 8 T, followed by traces at 9, 10, 12, 13, 14, and 17.5 T. Despite the apparent absence of the SDW phase in the lower panel, the in-field temperature dependence is rather similar between the two sets of data. Remarkably, in Fig. 1(B), the onset of superconductivity can be seen even with $\mu_0 H = 9\,\mathrm{T}$ (detailed view in the inset), more than four times the Pauli limiting field, and immeasurably small resistivity persists to beyond 6 T at the base temperature of ~0.02 K. Considering that in the lower panel the data were taken with no control over the a-axis field component (i.e., with only 2π radian rotations rather than 4π steradians as in the case of the upper panel), and that there is only a small difference in pressure settings between two data sets, the lack of differences in the strength of the critical field could be due to a weak dependence of H_{c2} within the conducting plane for the magnetic field regime measured. The superconducting transition temperature at zero field was ~1.2 K, with a very sharp transition width of order 0.01 K, reflecting the high quality of the crystal. Introduction of a small magnetic field reduces the transition temperature as well as broadens the transition. As the applied magnetic field increases, due to negative temperature dependence in the normal state ($d\rho/dT < 0$), the trace forms a peak followed by the superconducting transition. The peak structure, once

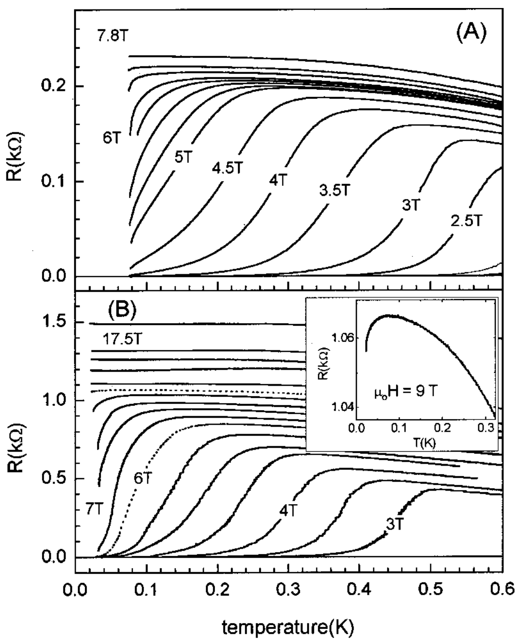

FIG. 1. Temperature dependence of interlayer resistance is shown for various fields. Data are taken for a sample under 5.7 kbar pressure (A), and another sample at 5.9 kbar (B). The traces at 6 and 9 T are shown in dotted lines in panel (B).

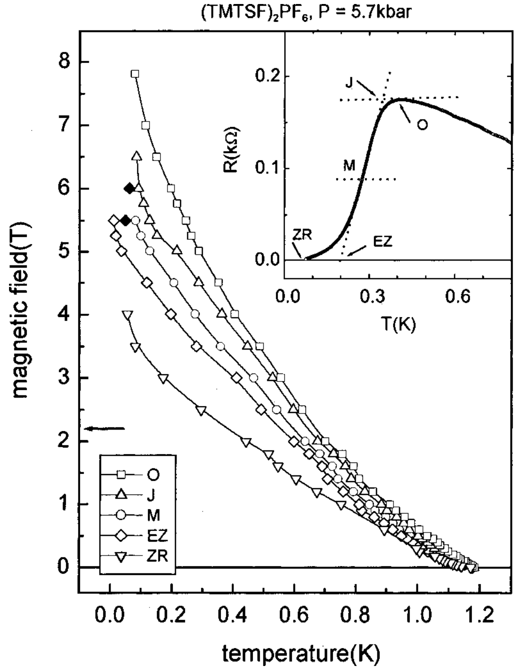

FIG. 2. Resistive upper critical field phase diagram is displayed with various criteria. Filled diamonds at 5.5 and 6 T are the other choices for EZ points reflecting a sharper slope near the base temperature.

sharply defined in intermediate fields ~1 T, broadens with increasing field and finally vanished when superconductivity is completely destroyed. Note here also the anomalous sharpening of the superconducting transition upon increasing the applied field and lowering the temperature. As seen in the Fig. 1(B), an ultimate reentrance of superconductivity was not found with field up to 17.5 T. However, complete 4π rotations could be crucial in the high-field regime to take full advantage of the crossover effects.

Based on the traces in Fig. 1, we have constructed temperature dependencies of the resistive upper critical fields as shown in Fig. 2. The Pauli field is indicated with an arrow on the vertical scale near 2 T. The inset shows five different criteria employed on the interlayer resistance trace at 4 T to define the critical temperature: an onset represented as O, a junction as J, a midpoint (50% drop) as M, an extrapolation to zero (ignoring the tail near zero) as EZ, and a point where the resistivity becomes zero (within experimental uncertainty) as ZR. Independent of the criteria employed, the similarities in the temperature dependence of the upper critical field are striking: first, there is a strong upward curvature and second, nearly diverging behavior at low temperature is ubiquitous as is the upper critical field far exceeding the Pauli limit. Due to limitations of the temperature range covered, only data points which can be defined within an error in the range of the symbol size are shown near the base temperature. The clear sharpening of the superconducting width at high fields (above 4.5 T) is mainly responsible for the near diverging behavior at low temperature. The validity of each resistive upper critical-field criterion could be confirmed as in Fig. 3, where we display the normalized critical fields $h_{c2}=H_{c2}/(-dH_{c2}/dT)T_c$ as a function of reduced temperature T/T_c. The essentially identical traces, even with different criteria, imply that the temperature dependence of the resistive upper critical fields could be defined consistently, strongly suggesting that neither flux flow resistivity nor irreversibility are dominant factors. The conventional WHH (Ref. 29) (Werthamer, Helfand, and Hohenberg) theoretical curve with no spin paramagnetic or spin-orbit effects is plotted as the dotted line. Finally, in Fig. 4, we have plotted an *H-T* phase diagram for three samples. As shown earlier, the temperature dependence is not sensitive to the criteria adopted. Here, the onset criterion is used for all three samples. The pressure regime measured is near the tricritical point in the *P-T* phase diagram, as depicted in the inset. Again, unique and remarkable temperature dependence of the upper critical field is found: positive curvature resulting from unusual enhancement of the upper critical fields as well as a critical field exceeding the Pauli paramagnetic limit by as much as four times.

Similar H_{c2} curves with strong positive curvature and nearly diverging behavior have been found in some of the high-T_c compounds. However, due to complications of the coexistence of the metallic in-plane resistivity with the semiconducting out-of-plane nature of the normal state, as well as the unclear role of substitutional impurities, direct comparison with some of the cuprates may not be valid here. In addition, there are few high-field data for the cuprates in the same field configuration as employed in this paper. In optimally doped cuprates, the temperature dependence changes with different definitions of H_{c2} (i.e., onset, midpoint, zero-point, etc.), whereas in our data all definitions collapse to a single curve. Furthermore, in Sr-deficient Bi-2201 single crystal,[30] it has been found that the temperature dependence of H_{c2} is in close agreement with conventional WHH theory, with criterion $H_{c2}=H(0.9\rho_{\mathrm{normal}})$. In any event, H_{c2} is always subject to the paramagnetic limit in the cuprates. Strong spin-orbit scattering model by Klemm, Luther, and Beasley[31] (KLB) could explain a kink or upturn behavior and

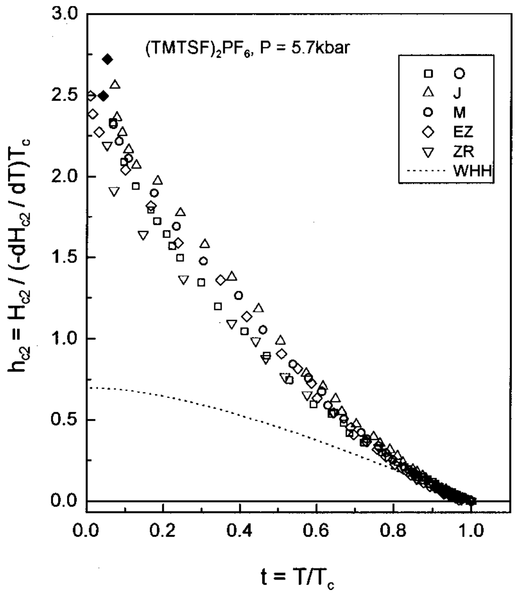

FIG. 3. Temperature dependence of the upper critical field from various criteria is shown on a normalized scale.

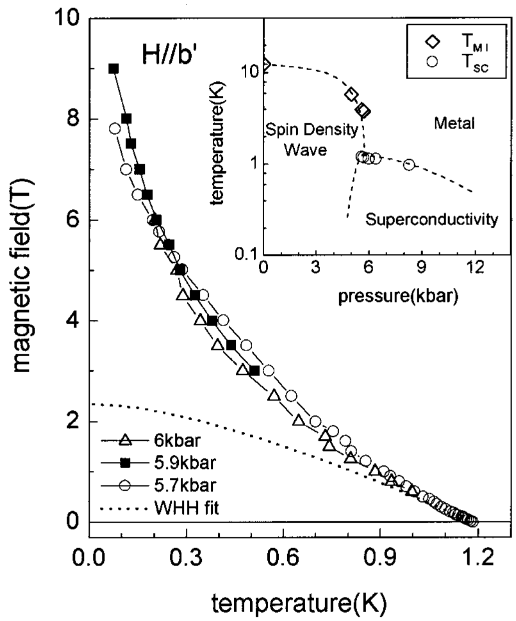

FIG. 4. Upper critical-field phase diagram for various pressures near the tricritical point are mapped. The inset shows the temperature-pressure phase diagram, where T_{MI} indicates metal-insulator (SDW) transition and T_{SC} stands for the superconducting transition.

high $H_{c2}(>H_p)$ as in the case of intercalated organic molecules $\mathrm{TaS_2}$ and $\mathrm{TaS_{1.6}Se_{0.4}}$.[32] Using a very conservative estimate for the orbital critical field for our material, $H_{c2}(0)=4\,\mathrm{T}$, and $T_c=1.2\,\mathrm{K}$, we estimate that we would need $1/\tau_{\mathrm{so}}\approx 10\,\mathrm{K}$ in order for the KLB model to explain our data. The result is consistent with Huang and Maki's (HM) estimate[33] in which they took $1/\tau_{\mathrm{so}}$ between 10 and 50 K to fit $H_{c2}(T)$ for $H\|a$ in $\mathrm{(TMTSF)_2ClO_4}$. However, it turns out that those required values are three to four orders of magnitude higher than the experimental values given by the Abrikosov formula,[34] $\tau_0/\tau_{\mathrm{so}}\sim(Ze^2/\hbar c)^4$, where $1/\tau_0(=0.1\,\mathrm{K})$ is the transport scattering rate and $Z(=34$, for Se) is the atomic number.

A more plausible explanation came from Lebed[20] and later Dupuis, Montambaux, and Sá de Melo[21] (DMS) who considered *magnetic field* induced dimensional crossover (3D to 2D). When a sufficient magnetic field ($\hbar\omega_c=eHv_Fc>t_c$) is applied parallel to the conducting plane, the electron wave function will localize within the plane. Semiclassically, the crossover would occur at the field strength ($H\|b$) where the amplitude of oscillatory motion along the c axis becomes comparable to the spacing s between planes, $s\approx 2t_c/eHv_F$, where v_F is Fermi velocity. As a result, orbital pair breaking significantly weakens and finally vanishes with further increase of magnetic field. The semiclassical estimate for the crossover field would be 4–8 T for a given t_c in the range 5–10 K. The fact that we observe upward curvature at fields below 1 T suggests that the crossover/decoupling effects are underestimated by the present models. Some indication of an effective renormalization of the c-axis transfer integral or the coherence length can be obtained by comparing the measured $H_{c2}\|b$ with the WHH curve: $H_{c2}(T=0)/H_{c2}^{\mathrm{WHH}}(T)\propto t_c(H=0)/t_c^{\mathrm{eff}}(H)$. From Fig. 3, this suggests that the effective transfer integral at 6 T would have to be about $\frac{1}{3}$ its zero-field value, $t_c^{\mathrm{eff}}(H\cong 6T)\approx t_c(H=0)/3$.

Even with field-induced dimensional crossover, which greatly increases the orbital critical field, an additional mechanism, such as the formation of either the inhomogeneous Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) state[35] or triplet superconductivity, is required to exceed the pair-breaking limit. Due to its finite momentum in the superconducting state, the LOFF phase is extremely sensitive to impurity scattering, and strongly influenced by the dimensionality of the system.[36] In a realistic system with non-negligible impurity scattering, the critical field for entering the LOFF phase is substantially reduced,[37] which makes observation of the state practically difficult, if not impossible, even for the one-dimensional case. Thus, for the ''singlet in combination with LOFF'' scenario to be correct, assuming perfect one-dimensionality as well as high purity in the system is essential. One can imagine that any curvature of the $E(\mathbf{k})$ dispersion near the Fermi level will significantly reduce the chance of realizing LOFF state with satisfactory pairing conditions. With the use of the nonlinearized dispersion law in a quasi-one-dimensional case, Lebed[17] estimated the LOFF field at zero temperature to be $H_p^{\mathrm{LOFF}}(0)\cong 0.6\sqrt{t_a/t_b}H_p$ where t_a and t_b are transfer energies along a and b. Thus even with a conservative estimate of the ratio in the range of $t_a/t_b=5-10$, the LOFF limiting field should be 3–4 T, which is a factor of 2 or 3 smaller than the observed upper critical field. Furthermore, the LOFF state should occur as a first-order-phase transition from a uniform to a nonuniform superconducting state. No evidence for such a transition has been observed.

In summary, the temperature dependence of the resistive upper critical field H_{c2} with $H\|b$ has been studied on $\mathrm{(TMTSF)_2PF_6}$ at various pressures near the tricritical point in the P-T phase diagram. Strong upward curvature with nearly diverging behavior at low temperature was found for all pressures employed. Superconductivity is found to persist to 9 T at $T/T_c\sim\frac{1}{60}$, at least four times the Pauli limiting field. The large value of the critical field, as well as the absence of a first-order-phase transition from a uniform superconducting state to a nonuniform LOFF state, argues against the possibility of a spin singlet and for a spin triplet superconducting state. No clear evidence for an ultimate reentrance of superconductivity as predicted by theory has been found, but better alignment in the higher field, lower-temperature regime is highly desirable.

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