Anisotropy of the Upper Critical Field in $(TMTSF)_2PF_6$

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The temperature dependence of the upper critical magnetic field $H_{c2}(T)$ in the quasi-one-dimensional molecular superconductor $(TMTSF)_2PF_6$ was determined via resistivity, for the intrachain (**a**), interchain (**b**), and interplane (**c***) directions. For H along **a** and **b**, $H_{c2}(T)$ exhibits pronounced positive curvature, with no sign of saturation to 0.1 K. A novel anisotropy inversion is observed, wherein H_{c2}^b grows larger than H_{c2}^a and exceeds the paramagnetic limit by more than 200%. The anomalous shape of $H_{c2}(T)$ is consistent with recent predictions of unconventional behavior in anisotropic superconductors, including the possibility of triplet pairing and reentrant superconductivity in very high field. [S0031-9007(97)02889-5]

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Studies of organic or molecular conductors based on the tetramethyltetraselenafulvalene (TMTSF) molecule have enriched our knowledge of low-dimensional electron systems and have been the source of much new physics since the discovery by Jerome *et al.* [1] of superconductivity in 1979. The linear chain aspect of the crystal structure exposes the system to all the exoticity of low-dimensional, and especially one-dimensional, electron physics. The field-induced spin density wave [2], which contains within it new aspects of the integer quantum Hall effect, and a variety of angular magnetoresistance oscillations [3–5] are but a few examples of new phenomena seen in the Bechgaard salts $(TMTSF)_2X$. Following the discovery of organic superconductivity, a period of intense activity ensued, focused on determining the critical parameters and searching for more superconductors based on TMTSF and is derivatives, such as TMTTF (sulfur replacing the selenium) and BEDT-TTF. These efforts paid off in that there are now more than 50 molecular superconductors, only of handful of which contain TMTSF [6].

There have, however, been lingering questions concerning the symmetry of the superconducting order parameter in the TMTSF system. For example, the possibility of triplet pairing was suggested [7] to explain the strong suppression of T_c with nonmagnetic impurities [8,9]. Also a number of papers have suggested that unusual features in the H-T phase diagram in type II superconductors might arise at high fields, due either to field-induced [10] dimensional crossover [11,12], or low Landau level energetics [13]. The quasi-one-dimensional TMTSF system appears to be an appropriate one in which to test some of these models. In spite of the large body of published work on this initial family of organic superconductors, little has been reported on H_{c2} well below T_c. In fact, most reports concentrated on the anisotropic behavior near T_c [14–17]. In recent work [18], we reported a nonsaturating $H_{c2}(T)$ for field close to the intraplane, interchain **b**′ direction in the ambient pressure superconductor $(TMTSF)_2ClO_4$, and found general agreement between the $H_{c2}(T)$ line and a model expression taken from the dimensional crossover theory. However, the resistive transition in this "ClO_4" compound was incomplete for fields above ~1 T, such that no strong statements could be made regarding the low temperature limit of H_{c2}.

In this Letter, we present evidence for unusual behavior in the superconducting phase diagram for a sister compound, $(TMTSF)_2PF_6$ at 6.0 kbar, a pressure sufficient to suppress a spin density wave and leave a metallic/superconducting state [19]. From resistance measurements as a function of temperature in various magnetic fields, we extract $T_c(H)$ to 6 T and 0.1 K for field precisely along three principal directions **a**, **b**′, and **c***. The **a** direction is along the TMTSF molecular chain, **b**′ is normal to **a** in the **a**-**b** plane, and **c*** is normal to the **a**-**b** (and **a**-**b**′) plane. For simplicity, we will refer to **b**′ as **b**, and **c*** as **c**, for the remainder of this Letter. The resulting phase diagram near $T_{c0} = 1.13$ K is consistent with previous results on the $(TMTSF)_2X$ materials [14–17], with $H_{c2}^a > H_{c2}^b > H_{c2}^c$. However, three new features are observed at low temperature. The phase diagram displays pronounced upward curvature without saturation for $H \parallel$ **a** and $H \parallel$ **b**, H_{c2}^b becomes larger than H_{c2}^a, and H_{c2} in both these basal plane directions exceeds the theoretical limit imposed by the paramagnetic effect of the applied magnetic field on the susceptibility of the electron spins [20]. When considered in conjunction with previous observations of a strong suppression of T_c by nonmagnetic impurities [8,9], and the close proximity of the superconducting state to a spin-density wave (SDW) state, the possibility of unconventional (equal spin p-wave) pairing is raised anew.

The measurements were made in a dilution refrigerator in a split-coil superconducting magnet, the refrigerator resting on a goniometer which provides *ex situ* angular rotation ($\pm 360°$) about the vertical with $0.000\,25°$

resolution. A sample rotator for *in situ* rotation ($\pm 180°$) about a horizontal axis with $\sim 0.05°$ precision is provided by a stepper motor-driven kevlar string. The sample in its miniature BeCu pressure bomb and the copper inner rotator reside *in vacuo,* thermally linked to the mixing chamber by a copper rod and $\sim$2000 wire copper braid. The finer angular resolution of the external rotator was used to eliminate any interlayer component ($H \parallel \mathbf{c}$), with inner rotations used to orient the in-plane directions **a** and **b**. This way, the small critical field [$H_{c2}(0) \sim 0.1$ T] along **c** would not affect the in-plane measurements. For the data here, the alignment along **b** is accurate to within $\pm 0.015°$ with respect to **c**, and to within 0.1° with respect to **a**. For the **a**-axis measurement, again the accuracy is $\pm 0.015°$ against **c**, and $\sim 1°$ against **b**. A measurement current of 0.1 $\mu A_{\mathrm{rms}}(\sim 10^{-5}$ A/cm^2) at 77 Hz was employed to monitor the interlayer resistivity ρ_{zz}. The response was Ohmic with no apparent self-heating effects at this current level.

The temperature dependence of the resistivity for several values of magnetic field applied along the intermediate **b** direction is shown in Fig. 1. The normal state behavior is metallic in zero applied field, but rapidly changes with increasing H, such that $\partial\rho/\partial T < 0$ for $H > 1$ T. This T-dependence possibly results from an interlayer decoupling effect of the in-plane field. Due to the combination of this negative normal state slope, an intrinsically broad transition into the superconducting state (in spite of the cleanliness of the materials), and an incomplete transition at the highest fields, several criteria will be used to extract the critical temperature at each magnetic field. These are shown in Fig. 1, where we define fve temperature criteria: an onset T_0, a "junction" T_J, a midpoint T_M, a zero resistance extrapolation T_X (ignoring the tail near $R = 0$), and a zero resistance point T_Z. In this manner, we can assess the extent to which the resulting curves $T_i(H)$ represent $H_{c2}(T)$.

Measurements were made in a similar fashion for $H \parallel \mathbf{c}$ and $H \parallel \mathbf{a}$, and Fig. 2 shows a cumulative phase diagram for all three directions, using the junction criterion. Similar diagrams result from the use of the other criteria. A lack of saturation in H_{c2} as T approaches zero can be seen for $H \parallel \mathbf{a}$ and $H \parallel \mathbf{b}$. The nonsaturating critical fields in Fig. 2 result in H_{c2} exceeding the paramagnetic, or Clogston-Chandrasekhar [20], limit by at least a factor of 2. This limit is given by $H_p(T = 0) = 1.84 T_c(H = 0)$ for isotropic s-wave pairing in the absence of spin-orbit scattering, or $1.58 T_{c0}$ for the case of anisotropic singlet pairing [21]. In the present case, these correspond to 2.1 and 1.8 T. At low temperature, $H_{c2}^b > 3H_p$ for the T_O and T_J criteria, and at least $2H_P$ for T_M and T_X. One striking result of the positive curvature in the critical field parallel to the **b** axis can be seen in Fig. 2: H_{c2}^b becomes larger than H_{c2}^a above a characteristic field H^*. The fact that this anisotropy inversion was not seen previously may be due to the strong sensitivity of H_{c2} to sample alignment in the magnetic field. For example, a 0.1° tilt of H away from the **b** axis, toward **c**, is sufficient to bring H_{c2} back below H_{c2}^a at low temperature. Another reason may be that the early work was done on the ClO_4 salt (at $P = 0$), or on the PF_6 or AsF_6 salts at higher pressure (and thus lower T_c) than in the present case. The present pressure is very close to a critical value for suppression of an insulating SDW phase, and yields a maximized T_c.

Figure 3 serves to demonstrate that the positive curvature and anisotropy inversion occur for any resistive criterion, showing H_{c2} along the **a** and **b** axes for four criteria

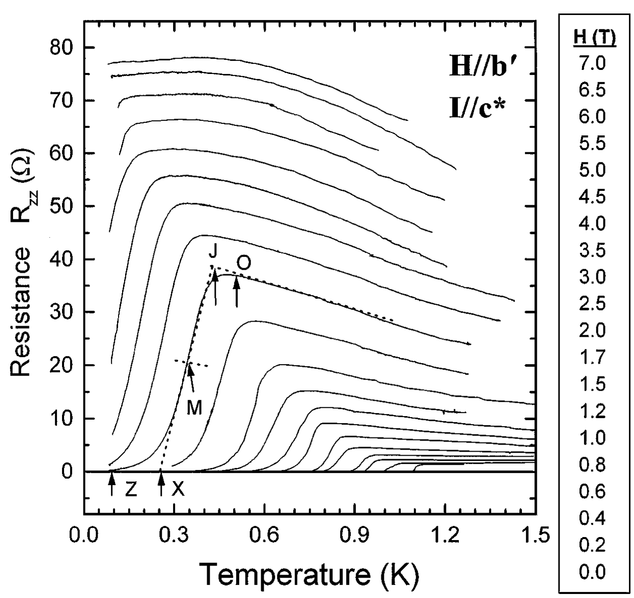

FIG. 1. Interlayer resistance vs temperature for various fields $H \parallel \mathbf{b}$ in $(TMTSF)_2PF_6$ at $P = 6.0$ kbar. Five criteria for $T_c(H)$ are depicted, O (onset), J (junction), M (midpoint), X ($R \rightarrow 0$), and Z ($R = 0$).

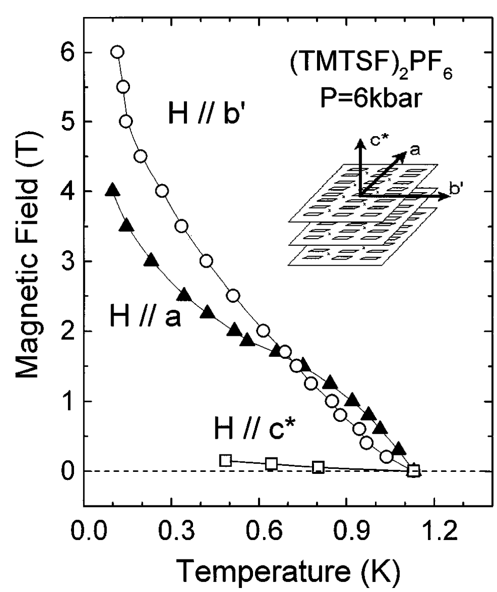

FIG. 2. H-T phase diagram in $(TMTSF)_2PF_6$ using the junction criterion for field aligned along the **a**, **b**$'$, and **c*** directions.

mentioned above. We have fewer data points for $R = 0$, but note that the inversion still occurs, at $\sim$0.35 K. Aside from a shift of the crossover temperature due to the breadth of the transition, the data sets look similar. The magnetic field value at the crossover is essentially independent of criterion, with $H^* \sim 1.6$ T. Notice for H_{c2}^a, we also observe strong upward curvature without saturation, for fields above H^*. The fact that superconductivity for the field along the intermediate **b** direction is more resilient to the field than that along **a** suggests that the one-dimensional nature of the system is becoming important.

There have been theoretical investigations of low-dimensional superconductors which may be relevant to the present work. Efetov and Larkin [22] pointed out that superconductivity could survive in large magnetic fields in quasi-1D by having electrons on different chains form pairs, with total spin equal to one. It was also noted [7] that the relatively high observed critical fields in the TMTSF materials could be construed as favoring triplet pairing, in that both the dirty and clean limits seem to be applicable. Lebed' proposed an unusual reentrance of superconductivity in quasi-1D materials in a strong magnetic field, based on a dimensional effect on the orbital motion of Cooper pairs [11]. If a sufficiently strong field were applied in such a way as to constrain electron excursions between neighboring 1D chains, then orbital frustration-induced pair breaking is suppressed. In this model, the magnetic field is applied perpendicular to the 1D chains, but within the quasi-2D planes. This corresponds to the **b** axis in our system. Lebed's work was extended by Dupuis, Montambaux, and Sá de Melo (DMS) [12], who derived a more general gap equation, and showed that a series of first order phase transitions should occur at high magnetic field, within the superconducting state. In the Lebed'-DMS theory, reentrance occurs for both singlet

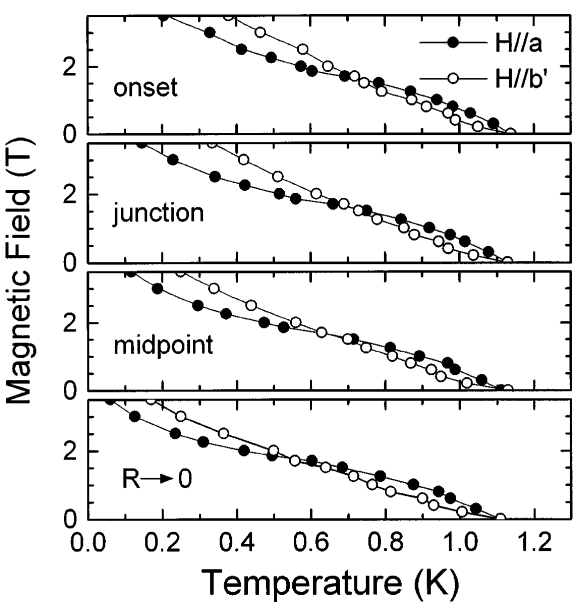

FIG. 3. The anisotropy inversion along **a** and **b**$'$ axes via four resistance criteria.

and triplet pairing, but is much more evident for the latter case. Because Zeeman splitting is unable to suppress this putative reentrance at high field, a singlet superconducting ground state is expected to be nonuniform, a type of LOFF state, after Larkin-Ovchinnikov [23] and Fulde-Farrell [24]. Both Lebed' and DMS stressed the necessity of accurate alignment in field.

On the other hand, Huang and Maki [25] have analyzed H_{c2} data [14] on $(TMTSF)_2ClO_4$ in both the clean and dirty limits, and found that the clean limit without Pauli paramagnetism describes $H_{c2}(T)$ along the **b** axis. For $H \parallel \mathbf{a}$, a fit to the data of Ref. [14] required the dirty limit with both Pauli and spin-orbit scattering terms, with spin-orbit scattering rate $\tau_{SO}^{-1} \sim 10$–50 K. Another group [26] suggested that an anisotropic *d*-wave analysis could explain H_{c2}, using weak coupling theory for $H \parallel \mathbf{b}$ and strong coupling for $H \parallel \mathbf{a}$, with Pauli but without spin-orbit terms. However, the data in Ref. [14] with which the authors of Refs. [25] and [26] compared their theories do not show any of the unusual effects presented here. The effect of spin-orbit scattering in our system can be estimated [27] using $\tau_0/\tau_{SO} \sim (Ze^2/\hbar c)^4$, where τ_0^{-1} is the transport scattering rate obtained from the normal state resistivity, and Z is the atomic number. For TMTSF, the heaviest element is Se, $Z = 34$, and $\tau_0^{-1} \sim 0.1$ K [7], such that $\tau_{SO}^{-1} \sim 4 \times 10^{-3}$ K. The value required by Huang and Maki [25] in their H_{c2} fits is 4 orders of magnitude larger than this experimental estimate. Thus, it is unlikely that our data can be explained by strong spin orbit scattering.

There are perhaps other theories which can explain portions of our data, such as those being developed with the cuprates in mind. In one paper [28], the pair-breaking ability of magnetic impurities is shown to weaken at low temperatures in a layered superconductor, leading to positive curvature in $H_{c2}(T)$. Magnetic scattering should be negligible in our system, however, especially the out-of-plane kind discussed in Ref. [28], since the PF_6 anion is nonmagnetic. Another theory [29] suggests that strong positive curvature in H_{c2} being detected in some cuprate superconductors for field normal to the layers is associated with a quantum critical point at $T = 0$. An equation describing this phenomenon was derived as $H_{c2}(T) \sim 1 - t^{\alpha}$, with $t = T/T_c$ and $\alpha = 2/5$, and shown to reproduce a small portion of experimental data close to $T = 0$ for underdoped cuprates. Surprisingly, it turns out that this equation fits our data quite well for $H \parallel \mathbf{b}$, over the entire temperature range $0.1 < t < 1$. In spite of this agreement, we are unable to justify the use of the equation in our system, for H parallel, rather than perpendicular, to the layers.

One theory which remains consistent with the experimental facts presented here is that due to Lebed' and DMS [11,12]. This theory predicts a *magnetic field-induced* dimensional crossover for the field in the *y* direction in an open orbit, quasi-1D superconductor (*x*-axis chains forming *x*-*y* planes). Interlayer motion δz is then confined to

$\pm z_0 t_z / \hbar \omega_c$, where z_0 is the third direction layer spacing, t_z is the bandwidth along z, and ω_c is the semiclassical Brillouin-zone crossing frequency, $\omega_c = e z_0 v_F H / \hbar$. The dimensional crossover occurs when ω_c is comparable to t_z. Using a Fermi velocity $v_F = 2 \times 10^5$ m/s, interlayer spacing $z_0 = 1.3$ nm, and bandwidth t_z between 5 K [12] and 10 K [5], ω_c reaches t_z in a crossover field of 2 to 4 T, the same magnitude as our H^* in Fig. 2. At high field, $\omega_c \gg t_z$, such that $\delta z \ll z_0$, and interlayer motion is inhibited. As a result, the orbital pair-breaking term is weakened, with superconductivity persisting. The new state is of laminar type, with Josephson-coupled vortices of a type rather different from that proposed for isotropic 2D superconductors [10]. This theory explains the lack of saturation for H_{c2}^b and the resulting anisotropy crossover for H_{c2}^b versus H_{c2}^a as a natural consequence of the dimensional crossover, which occurs only for $H \parallel \mathbf{b}$. The fact that the in-plane (**a** and **b**) H_{c2} exceeds the paramagnetic limit by such a large amount suggests either the possibility of equal spin pairing (i.e., *p*-wave) which, in the Lebed'-DMS theory, provides for a much stronger effect compared to *s*-wave pairing, or the formation of a singlet but inhomogeneous (LOFF) state.

In summation, we have shown that the upper critical field in $(TMTSF)_2PF_6$ displays strong positive curvature, without saturation, for magnetic field aligned along the **a** and **b** directions. Furthermore, despite the fact that $(-dH_{c2}/dT)_{Tc}$ for $H \parallel \mathbf{b}$ is smaller than along **a**, H_{c2}^b exceeds H_{c2}^a at low temperature, after an unusual anisotropy inversion at 1.6 T. The critical field in both directions exceeds the Pauli limit by at least a factor of 2. All these facts can be explained by the theory of Lebed' and DMS, which predicts a reentrant superconducting state at a very high field in quasi-1D systems for precisely the orientation employed here ($H \parallel \mathbf{b}$). The possibility of triplet pairing remains, since impurity and spin-orbit scattering are expected to be very weak in these clean materials, yet T_c is rapidly suppressed by a small amount of nonmagnetic defects. Further measurements in higher fields are now required to look for the predicted reentrant superconducting phase, as well as a possible first order [30] transition into the LOFF state.

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[1] D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris) Lett. **41**, L92 (1980).
[2] J. F. Kwak *et al.*, Phys. Rev. Lett. **46**, 1296 (1981).
[3] A. G. Lebed', JETP Lett. **43**, 174 (1986); A. G. Lebed' and P. Bak, Phys. Rev. Lett. **63**, 1315 (1989); T. Osada, S. Kagoshima, and N. Miura, Phys. Rev. B **46**, 1812 (1992).
[4] T. Osada *et al.*, Phys. Rev. Lett. **66**, 1525 (1991); M. J. Naughton *et al.*, Phys. Rev. Lett. **67**, 3712 (1991); W. Kang *et al.*, Phys. Rev. Lett. **69**, 2827 (1992).
[5] G. Danner, W. Kang, and P. M. Chaikin, Phys. Rev. Lett. **72**, 3714 (1994).
[6] See Proceedings of the International Conference on Synthetic Metals (ICSM'96), [Synth. Met. (to be published)].
[7] A. A. Abrikosov, J. Low Temp. Phys. **53**, 359 (1983); L. P. Gor'kov and D. Jerome, J. Phys. (Paris) Lett. **46**, L-643 (1985).
[8] M. Y. Choi, P. M. Chaikin, and R. L. Greene, Phys. Rev. B **34**, 7727 (1984); M. Y. Choi *et al.*, *ibid.* **25**, 6208 (1982).
[9] S. Tomic *et al.*, J. Phys. (Paris), Colloq. **44**, C3-1075 (1983); C. Coulon *et al.*, J. Phys. (Paris) **43**, 1721 (1983).
[10] This is distinct from a *temperature-induced* crossover seen in layered superconductors. See C. T. Rieck, K. Scharnberg, and R. A. Klemm, Physica (Amsterdam) **170C**, 195 (1990); D. E. Prober, R. E. Schwall, and M. R. Beasley, Phys. Rev. B **21**, 2717 (1980); R. V. Coleman *et al.*, Phys. Rev. B **27**, 125 (1983).
[11] A. G. Lebed', JETP Lett. **44**, 114 (1986); L. I. Burlachkov, L. P. Gor'kov, and A. G. Lebed', Europhys. Lett. **4**, 941 (1987).
[12] N. Dupuis, G. Montambaux, and C. A. R. Sá de Melo, Phys. Rev. Lett. **70**, 2613 (1993).
[13] M. Rasolt and Z. Tesanovic, Rev. Mod. Phys. **64**, 709 (1992).
[14] K. Murata *et al.*, Jpn. J. Appl. Phys. **26**, 1367 (1987); Mol. Cryst. Liq. Cryst. **79**, 23 (1982).
[15] D. Gubser *et al.*, Mol. Cryst. Liq. Cryst. **79**, 225 (1982).
[16] R. L. Greene *et al.*, Mol. Cryst. Liq. Cryst. **79**, 183 (1982); P. M. Chaikin, M. Y. Choi, and R. L. Greene, Physica (Utrecht) **31–34**, 1268 (1983).
[17] R. Brusetti, M. Ribault, D. Jerome, and K. Bechgaard, J. Phys. (Paris) **43**, 52 (1982).
[18] I. J. Lee, A. P. Hope, M. J. Leone, and M. J. Naughton, Synth. Met. **70**, 747 (1995); Appl. Supercond. **2**, 753 (1994).
[19] A preliminary report of these findings, by M. J. Naughton *et al.*, can be found in Ref. [6].
[20] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962); B. S. Chandrasekhar, Appl. Phys. Lett. **1**, 7 (1962).
[21] Y. Hasegawa and H. Fukuyama, J. Phys. Soc. Jpn. **56**, 877 (1987).
[22] K. B. Efetov and A. I. Larkin, Sov. Phys. JETP **41**, 76 (1975).
[23] A. I. Larkin and Y. N. Ovchinnikov, Sov. Phys. JETP **20**, 762 (1965).
[24] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).
[25] X. Huang and K. Maki, Phys. Rev. B **39**, 6459 (1989).
[26] M. Prohammer and J. P. Carbotte, Physica (Amsterdam) **165B–166B**, 883 (1990).
[27] A. A. Abrikosov and L. P. Gor'kov, Sov. Phys. JETP **15**, 752 (1962).
[28] Y. N. Ovchinnikov and C. Varma, Phys. Rev. Lett. **77**, 2296 (1996).
[29] G. Kotliar and C. Varma, Phys. Rev. Lett. **77**, 2296 (1996).
[30] L. W. Gruenberg and L. Gunther, Phys. Rev. Lett. **16**, 996 (1966); K. Maki and T. Tsuneto, Prog. Theor. Phys. **31**, 945 (1964).