PHYSICAL REVIEW B, VOLUME 65, 180502(R)

Angular-dependent upper critical field studies of $(TMTSF)_2PF_6$

I. J. Lee* and P. M. Chaikin
Department of Physics, Princeton University, Princeton, New Jersey 08544

M. J. Naughton
Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467
(Received 15 November 2001; published 18 April 2002)

It has been suggested that the strong upward curvature and large enhancement of the *b* axis critical fields in $(TMTSF)_2PF_6$ are the result of a magnetic field-induced dimensional crossover (FIDC) effect. In this paper we present a critical test of the FIDC for this material at a pressure of 5.7 kbar. Decoupled two-dimensional layers should exhibit a cusp in H_{c2} vs angle near H parallel to the layers. Rather we see no cusp in $H_{c2}(\theta)$ and the anisotropy decreases as temperature is reduced. Our data, in this pressure regime, are more consistent with a recently proposed insulator-superconductor slab model.

DOI: 10.1103/PhysRevB.65.180502 PACS number(s): 74.70.Kn, 74.60.Ec

The Bechgaard salts (quasi-one-dimensional systems) continue to serve as model systems for many theories of interacting electrons in reduced dimensions. Among them, $(TMTSF)_2PF_6$ is one of the most intriguing systems, since it exhibits many different physical properties, from insulating to unconventional superconducting,[1] depending on the applied magnetic field, the temperature, and the pressure. Recently, it has stirred interest as a possible triplet superconductor.[2–9] Magnetic fields destroy the superconducting state by two independent mechanisms. There is a spin effect from Zeeman splitting, which restricts the critical field of a spin singlet superconductor to the Pauli limit H_P (Ref. 10) ($\sqrt{2}\mu_B H_P = 1.76kT_c$). There is also an orbital effect associated with the induced currents generated to screen the external field, which is an effective pair breaker for both singlet and triplet superconductors. The main subject of this paper is the origin of the apparent lack of orbital pair breaking in $(TMTSF)_2X$, as evidenced by a large enhancement of the upper critical field, which persists up to four times the Pauli limit with strong upward curvature in the temperature dependence.[2,5] While pair breaking due to the Zeeman effect can be lifted either by triplet pairing or, to some extent, by the formation of Larkin-Ovchinnikov-Fulde-Ferrell (LOFF) state,[11–13] a field-induced dimensional crossover (FIDC) effect proposed by Lebed and others[14,15] allows Cooper pairs to overcome the orbital pairbreaking effect. A possible role of the LOFF state in $(TMTSF)_2PF_6$ is very slim as noted previously.[3,5] Moreover, unusually high critical fields and the absence of a resonant frequency shift in nuclear magnetic resonance (NMR) Knight shift experiments strongly suggest spin triplet pairing.[16] Therefore, to describe the unusual superconductivity in $(TMTSF)_2PF_6$, both triplet superconductivity and strong suppression of orbital superconducting frustration are essential.

The band structure of this highly anisotropic quasi-one-dimensional system can often be simplified to a tight-binding form, $E(\mathbf{k}) = -2t_a\cos(k_a a) - 2t_b\cos(k_b b) - 2t_c\cos(k_c c)$ with the transfer energy integrals given as $4t_a:4t_b:4t_c = 1:0.1:0.003$ eV.[1] The anisotropy in conductivity is $\sigma_a:\sigma_b:\sigma_c = 10^5:10^3:1$. The resulting Fermi surface consists of a pair of slightly warped sheets, opened along the k_b and k_c directions.

When a magnetic field is applied along the *b* axis, the electrons will undergo open orbit motion in the *a*-*c* plane, extended along *a* and oscillatory along the *c* direction. The oscillation amplitude along *c* is obtained as $2ct_c/\hbar\omega_c$ where $\hbar\omega_c = eHcv_F$ (c, t_c, v_F are the lattice constant and hopping integral along the *c* axis, and the Fermi velocity, respectively). Note that the amplitude of oscillatory electron motion is inversely proportional to the applied magnetic field. In an extremely strong magnetic field ($\hbar\omega_c \gg t_c$), the electron wave function shrinks to less than an interlayer spacing and the electrons reside within single *a*-*b* planes. This is an effective dimensional crossover from three-dimensional (3D) bands to discrete 2D layers. Under this condition, the energy loss from interlayer currents screening the applied field along *b* is greatly reduced and the orbital pair breaking becomes ineffective. Therefore, the superconducting critical temperature can even recover its zero-field value in an extremely strong magnetic field, if no other destructive limits to the superconductivity are present. This FIDC is thus predicted to occur, in a semiclassical picture, when $2t_c/\hbar\omega_c \approx 1$. Considering a realistic t_c ranging from 5 to 10 K for $(TMTSF)_2PF_6$, the required magnetic field for the FIDC effect (a decoupling field) can be obtained as $\mu_o H_d \sim 4-7$ T for $H \| b$, which appears to be consistent with our experimental observations in a sense that superconductivity was found to persist (up to 9 T) above this estimated decoupling field.[2,5]

The angular dependence of H_{c2} was considered theoretically by Lawrence and Doniach[17] for anisotropic 3D superconductor, and by Tinkham[18] for a thin film (2D) superconductor. A major difference between these two models is that $H_{c2}(\theta)$ has a smooth bell shaped dependence near the parallel field configuration in the 3D (anisotropic effective mass) model, while it has a cusp in the 2D model. Schneider and Schmidt[19] calculated the angular dependence of H_{c2} with various interaction strengths between thin superconducting slabs and obtained the same two results at extreme limits. The characteristic of decoupled 2D, cusp behavior has been confirmed experimentally in many highly anisotropic superconductors such as the high-T_c compound Bi-Sr-Ca-Cu-O (Ref. 20), the artificial multilayers Nb/CuMn (Ref.

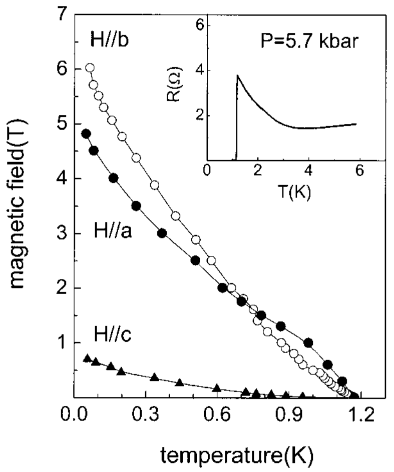

FIG. 1. Upper critical fields along three principal axes are shown with filled circles, open circles, and triangles for the applied field along the *a*, *b*, and *c* axes, respectively. The inset shows zero field resistance that has an upturn below 3 K due to an SDW phase.

21), and a quasi-two-dimensional organic superconductor κ-$(BEDT\text{-}TTF)_2Cu(SCN)_2$.[22] Here we present similar studies on a single crystal of $(TMTSF)_2PF_6$ at 5.7 kbar as a test for the proposed dimensional crossover scenario. We expect an anisotropic 3D effect for small critical fields near $T_c(H=0)$ and a 2D cusp as the layers decouple in high fields.

A black needlelike single crystal was mounted inside a miniature clamp-type BeCu pressure cell, 7.6 mm diameter and 12.7 mm long. A flipper rotator with the pressure cell attached was mounted on the bottom of the mixing chamber of a dilution refrigerator. A goniometer on which the refrigerator rests provides horizontal rotation with an angular resolution of 0.0025° and an internal string-driven stepper motor controlled vertical rotator allows us to position our sample with an angular resolution of 0.05° inside a split coil superconducting magnet. The dual axis rotation enabled us to orient our sample in any direction *in situ*, which plays an important role in our study. Electrical contacts were made on the *a-b* plane using silver paint and gold wires for standard four probe interlayer electrical transport measurements. Fairly low ac current densities of $\sim 10^{-4}$ A/cm^2 ($\leqslant 1\ \mu$A) with low frequencies ranging from 19 to 314 Hz were employed. The pressure of 5.7 kbar was determined at low temperature, using the measured difference in T_c of Pb from two ac susceptibility coils located inside and outside the pressure cell.

The temperature dependence of the resistance $R(T)$ at 5.7 kbar has a minimum around 3 K due to a spin-density wave (SDW) transition, followed by sharp drop at 1.2 K upon cooling, indicating the superconducting transition as shown in the inset of Fig. 1. The critical temperature at fixed magnetic field is defined by a 10% drop from the peak in $R(T)$ curves $[R(T_c)=0.9R_{\max}]$. Our obtained *H-T* phase diagram is shown in Fig. 1 for fields along the three principal axes. We note that the temperature dependence of H_{c2} is not sensitive to the criterion used to define $T_c(H)$.[5] From the equation obtained by Gor'kov and Jerome,[23] we estimate the ratio of transfer energy integrals as $t_a/t_b=4.3$, and $t_b/t_c=35.3$ where we used the measured slopes near T_c, $-\partial\mu_0H^a_{c2}/\partial T=5.91T/K$, $-\partial\mu_0H^b_{c2}/\partial T=2.65T/K$, and $-\partial\mu_0H^c_{c2}/\partial T=0.15T/K$. Considering Huang and Maki's estimate,[24] $t_a/t_b=4.7$ and $t_b/t_c=25.3$, on a sister compound $(TMTSF)_2ClO_4$, it is likely that our system (PF_6) has larger interlayer anisotropy, which is consistent with our observation that the PF_6 system at 5.7 kbar is closer to the SDW phase in the *P-T* phase diagram. By using the Ginzburg-Landau relation, $H^i_{c2}(0)=\phi_0/2\pi\xi_j(0)\xi_k(0)$ where ϕ_0 is the flux quantum and $\xi_i(0)$ is the coherence length along the ith direction at zero temperature, the anisotropic coherence lengths can be obtained as $\xi_a(0)=67$ nm, $\xi_b(0)=30$ nm, and $\xi_c(0)=1.7$ nm.

The temperature dependence of the upper critical field shown in Fig. 1 appears to be understandable qualitatively within the field-induced dimensional crossover or decoupling scenario. At low field, the slope of the upper critical field along a is higher than that along b, or $H_{c2}(H\|a)>H_{c2}(H\|b)$, as expected from the normal state anisotropy. When the in-plane magnetic field increases, the superconducting planes become less strongly coupled and thus less susceptible to orbital frustration. The most effective decoupling occurs with a magnetic field aligned along the *b* axis rather than the *a* axis, due to the large in-plane anisotropy, which likely leads to the crossover in the upper critical field curves shown in Fig. 1. The decoupling field with $H\|a$, $H_d(a)$, should scale roughly with the transfer energy ratio, $H_d(a)\sim H_d(b)\ t_a/t_b$. Thus the decoupling field along the *a* axis requires five to ten times the field strength that would be needed for the *b* axis. Upon further increase of magnetic field, $H_{c2}(b)$ surpasses the Pauli limit and appears to diverge near zero temperature. The system, still in reality under a weak orbital pair breaking effect given the applied field, would need much higher magnetic fields than those used to achieve the ultimate reentrance of superconductivity predicted by Lebed. We have previously shown that the critical field $H_{c2}(H\|b)$ exceeds the Pauli field ($\mu_0H_p\sim 2$ T) by more than a factor of four.[5]

One of the most unusual observations, however, is that a strong upward curvature in the temperature dependence was found with a magnetic field aligned along the *c* axis, perpendicular to the conducting layer and thus the worst field configuration for the dimensional crossover to occur. In addition, it is worth pointing out that H_{c2} along *b* starts to deviate from conventional behavior even at a very small magnetic field[5]—well below 1 T, which is too small to be accounted for by the decoupling effect. Note that $\mu_0H_d(H\|b)\sim 4-7$ T. These unexpected findings, in view of the suggested decoupling effect, led us to question the validity of the FIDC effect in $(TMTSF)_2PF_6$.

The angular dependence of the upper critical field in the *b-c* plane, from perpendicular to parallel to the conducting plane, is shown in Fig. 2. In the bottom panel, $H_{c2}(\theta)$ curves are shown at $T=0.75$ and 0.8 K in open and filled circles, respectively. The lines connecting experimental data are calculated from the 3D model by using measured critical field values along the *b* and *c* axes. No other fitting parameters were used in the calculation. The inset shows a magnified

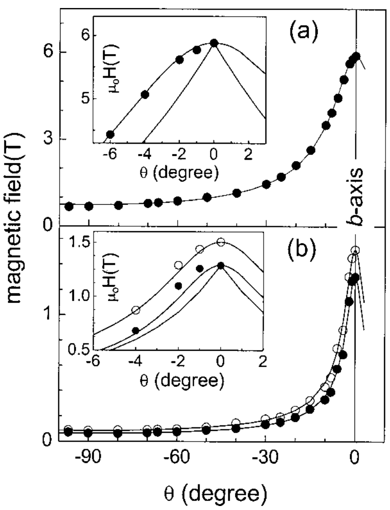

FIG. 2. Angular dependences of the upper critical fields from measurements (symbols) and calculations (lines). Data are taken at (a) $T=0.07$ K and (b) $T=0.75$ and 0.8 K (shown with open and closed circles, respectively). Lines through symbols in the main figures are obtained from calculations using the anisotropic effective mass model. The calculation from the decoupled thin film model (2D), which has a cusp at the *b* axis (zero degree), is shown in the insets of both (a) and (b) in comparison with the calculations from the anisotropic effective mass (3D) model.

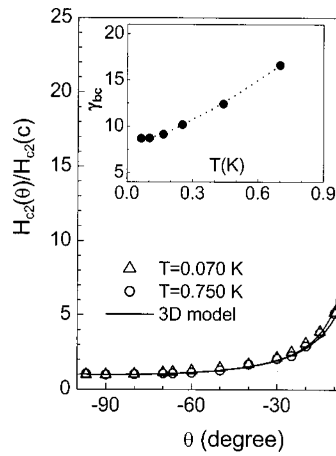

FIG. 3. Angular dependence of upper critical fields normalized by the *c*-axis value at $T=0.07$ and 0.75 K. Inset shows the temperature dependence of the critical field ratio, $H_{c2}(b)/H_{c2}(c)$, or the anisotropy ratio γ_{bc}.

view near the *b* axis along with calculated curves for the 3D and 2D models, the latter predicting a sharp cusp at the *b* axis. In the classical regime at high temperature and low magnetic field, as shown in Fig. 2(b), the 3D model fits the experimental data better than the 2D model. In the upper panel, the data displayed were taken at $T=0.07$ K where the nearly diverging behavior of $H_{c2}(T)$ was observed. This was previously accounted for by the FIDC effect as discussed above. Our major point lies in the inset of Fig. 2(a), where a clear deviation from the 2D model can be seen. $H_{c2}(\theta)$ is expected to have a cusp at the *b* axis if it originated from decoupled superconducting layers. Upper critical fields normalized by the *c* axis value, essentially the anisotropy ratio γ_{bc}, are shown in Fig. 3, where the symbols with open triangles and circles are taken at 0.07 and 0.75 K. The lines are calculated from the anisotropic effective mass 3D model. Again, in contrast to what we would have expected in a conventional superconductor where two sets of data should collapse when the anisotropy remained fixed, a deviation is observed starting near 10°. The interplane anisotropy ratio, $\gamma_{bc}=H_{c2}(b)/H_{c2}(c)$, *decreases* upon cooling (see the inset of Fig. 3). If the layers decoupled with increasing field, the anisotropy should increase upon cooling.

It appears that the proposed field-induced dimensional crossover is not responsible for the strong suppression of orbital pair breaking effect. An alternate model for strong enhancement of H_{c2} near an insulating phase was recently suggested.[25] It relies on both the enhancement of critical field in a thin film structure[26] and the coexistence of superconducting and SDW insulating phases[27] near the critical pressure (for a transition from SDW to superconducting phase) in $(TMTSF)_2PF_6$. If the system in domain structure is allowed to form a series of self-dividing interfaces in a magnetic field, ideally, a thin slab of superconductor (*S*) sandwiched by the SDW insulating phase (*I*), *I-S-I* structures, reduces orbital frustration and thus increases the critical field. Briefly, T_c is reduced by the kinetic energy of the screening current in the thin ($d \ll \lambda$) slabs and by the surface energy of the *S-I* interfaces, $\delta T=(T_c-T)\propto(d/\lambda)^2H^2+\gamma/d$, where d, λ, and γ are the slab thickness, the penetration depth, and the surface tension energy due to the SDW/superconductor interfaces, respectively. Minimizing δT with respect to d gives a power-law dependence of the upper critical field with respect to temperature, that is, $H_{c2}\propto(\lambda/\gamma)\delta T^{3/2}$. The slab surface should be oriented parallel to the applied magnetic field but perpendicular to the *a-b* crystallographic plane to take a full advantage of a large field penetration along the *a* axis, i.e., $\lambda_c\sim100\ \mu$m,[28] due to weak screening current along the *c* axis. Here, the penetration depth is indexed by the direction of the screening current.

In addition to a large enhancement of the upper critical field over the Ginzburg-Landau (GL) estimate and a power-law temperature dependence, one of the interesting consequences of the model is that, unlike the GL prediction, it predicts $H_{c2}(H\|a)\sim H_{c2}(H\|b)\gg H_{c2}(H\|c)$, which is fairly consistent with the observed angular dependence of the upper critical field as shown in Fig. 1. Note that the upper critical fields are determined by the largest penetration depth perpendicular to the applied field, that is, λ_c for both $H\|a$ and $H\|b$ and λ_b for $H\|c$. Moreover, we do not expect to a cusplike angular dependence of H_{c2} where both the critical fields ($H\|b$ and $H\|c$) are determined linearly with the appropriate penetration depth. To attain a critical field of up to 9 T as has been observed, we estimate the thickness of the slab to be 0.1 to 1 μm [from the known parameters $\lambda_c\sim100\ \mu$m,[28] and $\mu_0H_c\sim2$ to 4 mT (Ref. 29)]. Note that the slabs are still much larger than the interplane spacing (~1.3 nm) and the system is therefore still 3D. While the details of the mechanism at the SDW/superconductor interface need to be clarified, this simple idea appears to be consistent with the angular dependence of H_{c2}, the upward curvature of $H_{c2}(T)$, and strong enhancement of the upper critical field in all three principal axes.

In summary, the angular dependence of the upper critical field has been studied in detail as a test for the field-induced dimensional crossover suggested as a description for the unusual upper critical field behavior found in $(TMTSF)_2PF_6$. The proposed FIDC model would show a cusp in the angular dependence of H_{c2}, which we have not observed. The FIDC model can also not explain a strong enhancement and upward curvature in H_{c2} along the c axis. The dominant effect in these experiments appears to be the close proximity of the SDW phase. Our data are consistent with a new model where SDW and superconducting slabs align parallel to the applied field. The FIDC model may still be appropriate at higher pressure, far from the coexisting SDW-superconducting phase.

We would like to acknowledge A. G. Lebed for useful discussions. This work was supported by the National Science Foundation under Grant No. DMR-0076331 (M.J.N.), and DMR-9976576 and DMR-9809483 (P.M.C.).

*Author to whom correspondence should be addressed. E-mail address: ijlee@princeton.edu

[1] For a review, see T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, 2nd ed., Springer Series in Solid State Sciences Vol. 88 (Springer-Verlag, Berlin, 1998).

[2] I. J. Lee, M. J. Naughton, G. M. Danner, and P. M. Chaikin, Phys. Rev. Lett. **78**, 3555 (1997).

[3] A. G. Lebed, Phys. Rev. B **59**, R721 (1999).

[4] A. G. Lebed, K. Machida, and M. Ozaki, Phys. Rev. B **62**, R795 (2000).

[5] I. J. Lee, P. M. Chaikin, and M. J. Naughton, Phys. Rev. B **62**, R14 669 (2000).

[6] H. Shimahara, Phys. Rev. B **62**, 3524 (2000).

[7] C. D. Vaccarella and C. A. R. Sá de Melo, Phys. Rev. B **63**, 180505 (2001).

[8] K. Kuroki, R. Arita, and H. Aoki, Phys. Rev. B **63**, 094509 (2001).

[9] K. Kuroki and R. Arita, Phys. Rev. B **63**, 174507 (2001).

[10] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962); B. S. Chandrasekhar, Appl. Phys. Lett. **1**, 7 (1962).

[11] A. I. Larkin and Y. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **47**, 1136 (1964) [Sov. Phys. JETP **20**, 762 (1965)].

[12] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).

[13] A. I. Buzdin and V. Polonskii, Zh. Eksp. Teor. Fiz. **93**, 747 (1987) [Sov. Phys. JETP **66**, 422 (1987)].

[14] A. G. Lebed, Pis'ma Zh. Eksp. Teor. Fiz. **44**, 89 (1986) [JETP Lett. **44**, 114 (1986)].

[15] N. Dupuis, G. Montambaux, and C. A. R. Sa de Melo, Phys. Rev. Lett. **70**, 2613 (1993); N. Dupuis, Phys. Rev. B **51**, 9074 (1995).

[16] I. J. Lee *et al.*, Phys. Rev. Lett. **88**, 017004 (2002), for NMR Knight shift with $H \| b$, see cond-mat/0001332 (unpublished).

[17] W. E. Lawrence and S. Doniach, in *Proceedings of the 12th International Conference on Low-Temperature Physics*, edited by E. Kanda (Academic, Kyoto, 1971), p. 361.

[18] M. Tinkham, Phys. Rev. **129**, 2413 (1963).

[19] T. Schneider and A. Schmidt, Phys. Rev. B **47**, 5915 (1993).

[20] M. J. Naughton *et al.*, Phys. Rev. B **38**, 9280 (1988); R. Fastampa *et al.*, Phys. Rev. Lett. **67**, 1795 (1991); R. Marcon *et al.*, Phys. Rev. B **46**, 3612 (1992).

[21] C. Attanasio *et al.*, Phys. Rev. B **57**, 6056 (1998).

[22] F. Zuo *et al.*, Phys. Rev. B **61**, 750 (2000).

[23] L. P. Gorkov and D. Jerome, J. Phys. (France) Lett. **46**, L643 (1985).

[24] X. Huang and K. Maki, Phys. Rev. B **39**, 6459 (1989).

[25] I. J. Lee, M. J. Naughton, and P. M. Chaikin (unpublished); I. Chashechkina, I. J. Lee, S. E. Brown, D. S. Chow, W. G. Clark, M. J. Naughton, and P. M. Chaikin, Synth. Met. **119**, 13 (2001).

[26] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).

[27] L. J. Azevedo, J. E. Schirber, and E. M. Engler, Phys. Rev. B **27**, 5842 (1983). The formation of the mixed phase (domain structure) of the metallic and SDW insulating phases has been suggested by Azevedo *et al.* from the observation of the strong inhomogeneous broadening of NMR line shape near the critical pressure regime. The inset of Fig. 1 indicates a transition from the metallic, SDW to superconducting phase. Further NMR study indicates that SDW phase persists to deep in superconducting state, which is consistent with the concept of domain formation.

[28] H. Schwenk, K. Andres, F. Wudl, and E. Aharon-Shalom, Solid State Commun. **45**, 767 (1983); H. Schwenk, K. Andres, and F. Wudl, *ibid.* **49**, 723 (1984).

[29] P. Garoche, R. Brusetti, D. Jerome, and K. Bechgaard, J. Phys. (France) Lett. **43**, L147 (1982).