Magnetic Determination of H_{c2} under Accurate Alignment in $(TMTSF)_2ClO_4$

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(Received 1 July 2003; published 10 February 2004)

Cantilever magnetometry has been used to measure the upper critical magnetic field H_{c2} of the quasi–one-dimensional molecular organic superconductor $(TMTSF)_2ClO_4$. From simultaneous resistivity and torque magnetization experiments conducted under precise field alignment, H_{c2} at low temperature is shown to reach 5 T, nearly twice the Pauli paramagnetic limit imposed on spin singlet superconductors. These results constitute the first thermodynamic evidence for a large H_{c2} in this system and provide support for spin triplet pairing in this unconventional superconductor.

DOI: 10.1103/PhysRevLett.92.067001 PACS numbers: 74.70.Kn, 74.20.Rp, 74.25.Dw

The molecular organic conductors $(TMTSF)_2X$ are novel electronic materials in the sense that their metallic, insulating, and superconducting phases all have unconventional aspects to them. Because of highly anisotropic structure, strong one- and two-dimensional electronic character is observed, such as spin density wave transitions, and the quantized Hall effect, respectively, in addition to anisotropic, three-dimensional superconductivity. This latter phase has generated a great deal of interest and its share of controversy since its discovery as the first organic superconductor nearly a quarter century ago [1]. After a rather thorough series of experiments in the early 1980s, the majority opinion concerning the nature of superconductivity in $(TMTSF)_2X$ was that they were conventional, albeit anisotropic, BCS superconductors. Nonetheless, after noting rather effective suppression of superconductivity by nonmagnetic defects [2], Abrikosov suggested in 1983 that there was reason to suspect that quasiparticles paired in a spin triplet state, as opposed to conventional spin singlet [3]. One possible consequence of triplet pairing is the absence of a paramagnetic pair-breaking effect, the "Pauli limit" maximum magnetic field in which singlet superconductivity can survive, due to the Zeeman energy difference of oppositely directed spins becoming comparable to the condensation energy [4]. However, resistively derived critical magnetic field values from early experiments showed little evidence for exceeding the Pauli limit in $(TMTSF)_2X$ [5].

Lebed [6] and then others [7] later suggested that orbital pair breaking, which generally acts independently of the spin effect, could be circumvented in quasi–one-dimensional (Q1D) superconductors such as $(TMTSF)_2X$ by a magnetic field-induced dimensional crossover (FIDC) mechanism for an in-plane aligned field. In theory, this circumvention could even lead to reentrant superconductivity in very large magnetic fields. Generally speaking, such reentrance would be hard to realize, since spin pair breaking would kill the superconducting state before FIDC became effective. That is, unless the Q1D system was also a spin triplet superconductor, in which case, FIDC could in principle be tested. If such a test were to find the dimensional crossover mechanism to be effective, then one would be presented with a situation where *no amount of magnetic field could destroy the superconducting state*. Motivated by this idea, a second generation of H_{c2} experiments was initiated, first in $(TMTSF)_2ClO_4$ [8] and then in a sister compound $(TMTSF)_2PF_6$ [9]. In both systems, it was shown that H_{c2} along the in-plane, interchain direction (precisely that predicted by theory to be the most effective for FIDC) significantly exceeded the conventional Pauli limit. Again, these results were derived solely from electrical resistivity measurements. In light of the characteristically broad superconducting transition widths (in temperature and magnetic field) observed in $(TMTSF)_2X$ materials via resistivity, the exact extent to which H_{c2} exceeds the Pauli limit depends on the resistive criterion one chooses to define $T_c(H)$ or $H_{c2}(T)$. Using an "onset" criterion, H_{c2} was found to exceed H_P by nearly a factor of 4 in $(TMTSF)_2PF_6$ [10], clearly an unconventional situation. On the other hand, if a zero resistance extrapolation were to be used, this value could be rather lower, potentially making a case for triplet pairing based on H_{c2} less apparent.

Recently, independent support for triplet superconductivity in $(TMTSF)_2X$ was provided by NMR Knight shift (K_s) and tunneling experiments. K_s, being a measure of the spin susceptibility, should fall toward zero below T_c for a superconductor with Cooper pairs of zero net spin ($\uparrow\downarrow$), but was instead found for $X = PF_6$ not to change upon entering the superconducting state, as would be expected for a triplet state with equal spins ($\uparrow\uparrow$ or $\downarrow\downarrow$) [11]. Bicrystal junction measurements on $X = ClO_4$ revealed the existence of a large zero bias conductance peak indicative of an Andreev midgap state, interpreted as representing p-wave symmetry [12]. On the other hand, another possible mechanism for achieving large critical fields in these materials, distinct from the FIDC model, was recently introduced by Lee *et al.*, involving the formation of slabs of superconductor sandwiched between insulating regions [13]. Furthermore, a recent prediction by Shimahara has a low-field singlet state evolving into a triplet state at high fields [14], mediated by antiferromagnetic fluctuations. Thus, core issues relating to spin (pairing symmetry, and whether these materials are spin singlet Pauli limited or spin triplet unlimited) and orbital (FIDC versus slabs) angular momenta, each potentially contributing to a large critical field, require resolution. A thermodynamic determination of H_{c2} would cement the existence of this as-yet only resistively determined large critical field. We provide such a determination in this work. From simultaneous torque magnetization and electrical resistivity measurements under accurately aligned magnetic field, we have mapped $H_{c2}(T)$ down to 25 mK, or $T_c/60$. From both measurements, we obtain a zero temperature extrapolation of $H_{c2}(0) \cong 5\,\mathrm{T}$, approximately twice the Pauli limiting field and 3 times a theoretical limit [15] which accounts for orbital as well as spin effects.

A $0.9 \times 0.4 \times 0.4\ \mathrm{mm}^3$ $(TMTSF)_2ClO_4$ crystal, wired for interlayer resistivity ρ_{zz} measurements, was mounted onto a micromachined cantilever magnetometer [16], with gold wires connecting to integrated gold electrodes facilitating simultaneous and independent resistivity and magnetization measurements. The sample was then mounted onto a stage rotatable about a horizontal axis (θ rotation) inside a dilution refrigerator, itself attached to a goniometer to provide rotation about the vertical (ϕ rotation) mated to a 13.5 T split-coil magnet. Both rotators provided angular resolution of 0.0025°. The resulting H-T-θ-ϕ configuration allowed us to accurately align the sample in any orientation.

The magnetic signal was calibrated using integrated planar coils on the cantilever through which a current produces a calibrating torque. The resulting cantilever deflection is detected capacitively with a 1 Hz bandwidth. The sample was slowly cooled ($\sim$1 K/h), its high quality quantified by a residual resistivity ratio $RRR = \rho_{zz}(300\ \mathrm{K})/\rho_{zz}(T_0) = 1400(450)$, where $T_0 \sim 0\ \mathrm{K}$ (4.2 K). All the magnetic data were obtained on the second thermal cooldown of the sample. The $\rho(T)$ curve, RRR value, and resistive $H_{c2}(T)$ phase diagram of this second run were identical to those of the first, except for the latter below $\sim$0.3 K, where a dramatic difference was observed, as discussed below.

We show in Fig. 1 the simultaneously measured torque and resistivity signals at our lowest temperature, 25 mK, for magnetic field precisely aligned along the sample b' direction. This is the direction within the highly conducting a-b layers that is perpendicular to the most conducting chain a axis. That is, in this triclinic crystal, b' is the projection of the real space lattice direction b onto the plane normal to a. The field is oriented in this direction because theoretically, this is the most favorable direction for FIDC, and empirically, this is indeed where anomalously large critical fields have been observed in transport measurements [8–10]. The inherent ambiguity in defining H_{c2} from transport is evident in Fig. 1: resistivity becomes measurable above about 2.5 T, signaling the beginning of the transition out of the superconducting state, with the transition appearing to be complete near 5 T (see dashed line extending from the high field, normal state, as well as vertical arrow). Where one places H_{c2} on such a curve is nonobvious, without the benefit of other physical evidence (note that this problem is quite a bit more severe in the high T_c cuprates). This evidence is provided by the torque signal.

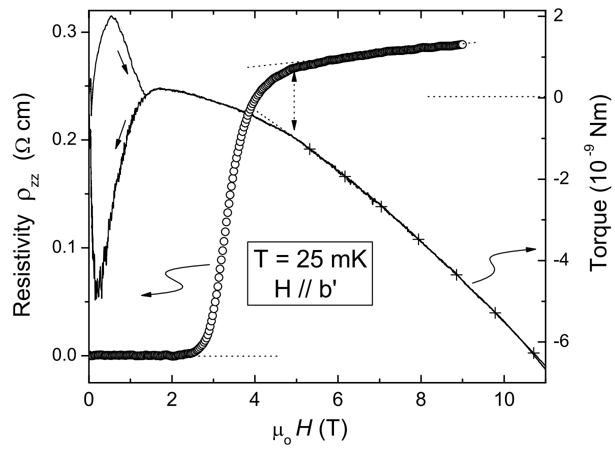

FIG. 1. Resistivity (left scale) and torque magnetization (right) in $(TMTSF)_2ClO_4$ at 25 mK, $H \parallel b'$. The dotted line and + symbols on the torque curve represent a temperature-independent normal state contribution. The onsets of diamagnetism and decreasing resistivity, upon decreasing field, are indicated by the arrow near $H_{c2} \sim 5$ T. Arrows in the low field vortex state indicate field sweep directions.

First, in referring the torque data in Fig. 1, a hysteretic (irreversible) regime is evident below $\sim$1.3 T. This is but one aspect of a complex superconducting vortex phase uncovered in this material in the process of measuring H_{c2}. Beyond this field, the torque and magnetization are reversible in field sweep direction (i.e., a vortex liquid state), evolving to a well-behaved, T-independent, quadratic torque signal at high field in the normal metal phase. Such a signal in the normal state is consistent with expectations for a clean metal, since both Pauli paramagnetic and Landau diamagnetic susceptibilities are generally T and B independent. A fit (using data above 7 T) to this normal state signal is plotted atop the raw torque signal as (+) symbols and also as a dotted line in the vicinity of 5 T. It is near this field that the measured signal begins to deviate from the normal state background, and we interpret this deviation as a magnetic signature of the upper critical field H_{c2}. Note that even in the conventional description of a type II superconductor-to-normal metal transition in a magnetic field, H_{c2} is a subtle magnetic feature. As the point where the magnetic field, in the form of overlapping superconducting vortices of growing number (in H) and size [$\lambda \to \infty$ as $T \to T_c(H)$] fully penetrates the sample, thus degrading the diamagnetic susceptibility associated with Meissner currents, H_{c2} is generally marked by only a gradual change in magnetic moment versus field. Nonetheless, a slope change and departure from the normal state behavior can clearly be seen in the present data, starting at the field indicated by the double arrow. Note that this field position coincides with the onset of the resistive transition into the superconducting state, as indicated in the figure. This validates the use of the transport onset criterion employed in prior reports of $H_{c2}(T)$ in $(TMTSF)_2X$ superconductors for $H \parallel b'$.

A brief discussion about the origin of the magnetic torque, which of course results from a magnetization vector tilted with respect to the applied field, is required. The symmetry axis for the normal state moment is b^* [17], the normal to the *a-c* planes, and this direction is $\sim 5.5°$ away from the field direction, $H \parallel b'$. This explains the nonzero background torque signal, which we have verified vanishes as H approaches b^*. For the superconducting state, the symmetry axis is b', where, in the absence of shape anisotropy or vortex pinning, there should be no torque signal. The fact that there is a finite signal at b', including in the reversible vortex liquid regime ($\sim$ 1.3 to 5 T in Fig. 1), tells us that both of these terms are present. We have verified from tilted field studies that the low-field torque signal indeed varies as $\sin(\theta - \theta_{b'})$, in addition to the small yet finite (and auspicious) shape anisotropy contribution.

Torque and resistivity data such as those in Fig. 1 were taken at several temperatures up to 2 K. We show in Fig. 2 representative magnetic moment data derived from the torque, after subtracting the background term discussed above, yielding $\Delta m = \Delta\tau/\mu_0 H$, where $\Delta\tau$ is the raw torque less background. The data shown include both up and down sweeps, showing the reversible nature of the magnetization. On this scale, the onset in decreasing field [above the noise baseline of $\sim 10^{-12}$ Am^2 (10^{-9} emu)] of the diamagnetic signal associated with the formation of the superconducting state becomes evident, as indicated in the figure. At the lowest temperature at which we have torque data, 25 mK, the onset H_{c2} is 4.92 ± 0.05 T. The resistivity signal collected during that field sweep yielded an onset H_{c2} of 5.02 ± 0.15 T, the larger uncertainty due to the rounded transition characteristic of such measurements (see Fig. 1).

The resulting phase diagram appears in Fig. 3, where we plot onset datum points from magnetization and resistivity field sweeps and from resistivity temperature sweeps. There are several features of note in this phase diagram. First, the two resistive determinations are well matched by the magnetic $H_{c2}(T)$ over the entire temperature regime. Second, the zero temperature critical field reaches 5 T, close to twice the Pauli limit for singlet superconductivity, defined as $\mu_0 H_P = \Delta_0/\sqrt{2}\mu_B = 1.84T_c = 2.6$ T for our sample (Δ_0 is the $T = 0$ superconducting energy gap, and μ_B the Bohr magneton). In fact, the measured $H_{c2}(0)$ is nearly 3 times a calculated critical field $H_P^{\mathrm{LOFF}} = 1.7$ T that accounts for both spin and orbital pair breaking in singlet Q1D superconductors [15] including the possibility of an inhomogeneous LOFF state [18]. Third, after a regime of Landau-Ginzburg negative curvature ($0.4\ \mathrm{K} \leq T \leq 1$ K), $H_{c2}(T)$ displays positive curvature down to the lowest temperature. Finally, the inset to Fig. 3 shows a portion of these $H_{c2}(T)$ data replotted along with resistive data from the initial, "virgin" cool of the same sample. These latter data appear nearly identical to those reported earlier for $(TMTSF)_2ClO_4$ [8–10] for this field orientation, with a distinct upturn in $H_{c2}(T)$ below $\sim$0.25 K, and indeed are similar to that reported for $(TMTSF)_2PF_6$ [9,10], also for $H \parallel b'$. The overall behavior is very much consistent with that anticipated by the Lebed FIDC effect [6,7,15]: positive curvature developing in $H_{c2}(T)$ as H

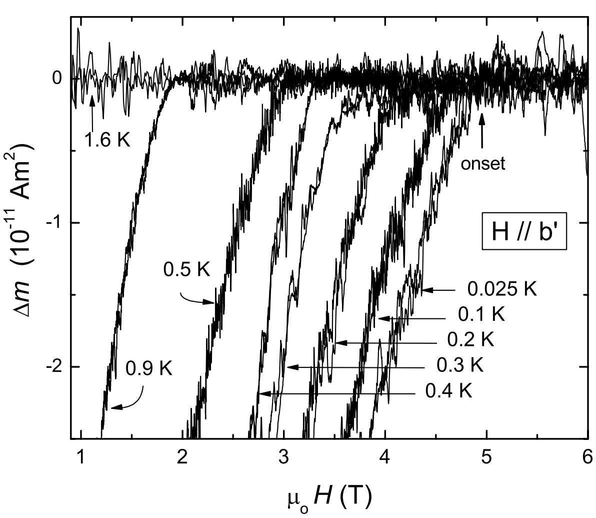

FIG. 2. Contribution to the magnetization due to superconductivity for $H \parallel b'$ in $(TMTSF)_2ClO_4$ at several temperatures. $H_{c2}(T)$ is obtained at the onset of finite moment $\Delta m(H)$, as indicated for $T = 25$ mK.

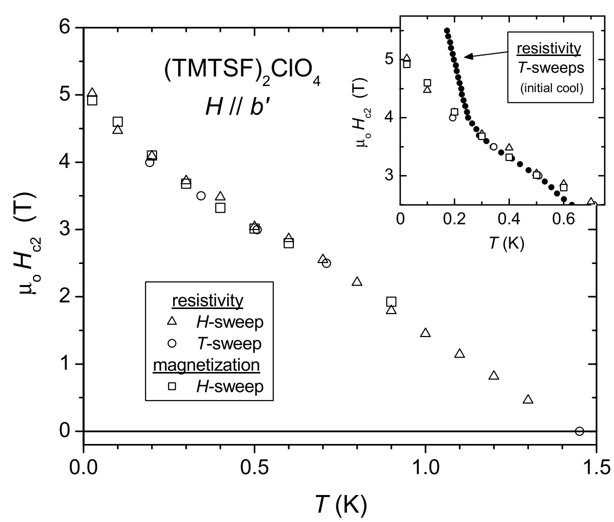

FIG. 3. Upper critical field H_{c2} along the b' axis in $(TMTSF)_2ClO_4$, from both resistivity and magnetization. The inset also shows resistive H_{c2} data from the same sample's initial cooldown.

increases (followed ultimately by reentrant superconductivity at very high fields — as yet not confirmed experimentally).

We do not have magnetization data to report for this initial cool, but we speculate on the origin of the intriguing difference in $H_{c2}(T)$ below 0.25 K between the first and second cooldowns. As mentioned above, the $\rho(T)$ curves in zero field were indistinguishable between the two runs. However, the normal state magnetoresistance in the first run was significantly larger than in the second ($\sim$20 times so at 25 mK). We suggest that sample microcracks, known to arise in these materials upon cooling, have created interlayer charge channels (i.e., more during the second cooldown) in parallel with the sample's intrinsic interlayer conductance. A simple model mimics the fact that the zero-field $R(T)$ curves for the two successive cooldowns are identical, while those for magnetoresistance $R(H)$ are quite different. Basically, these microcrack channels short out the intrinsic H^2 magnetoresistance at low temperature, when $R_i \gg R_e$, since $R_{zz}(H) = R_e R_i/(R_e + R_i) \sim R_e$ at high field, where R_i is the pristine, intrinsic sample resistance having quadratic magnetoresistance, and R_e is the "extrinsic" field-independent contribution due to microcracks. The presence of such extrinsic interlayer conduction paths will act to hinder the ability of a strong magnetic field to decouple the layers, thereby suppressing the FIDC mechanism's ability to facilitate an increase in H_{c2} at high fields and low temperatures. In a pristine/low microcrack density sample, on the other hand, interlayer transport in magnetic fields is dominated by the intrinsic resistivity since, with fewer microcracks, $R_e \gg R_i$, so that $R_{zz}(H) \sim R_i$. This can explain why the dramatic upturn in $H_{c2}(T)$ seen in the inset for the virgin cool is not as prevalent in the subsequent cool data. The model also may be used to explain inconsistencies in reported transverse magnetoresistance magnitudes in $(TMTSF)_2X$ conductors: each cooldown of each sample has a different microcrack profile.

It is well established that $(TMTSF)_2X$ crystals are easily mechanically "kinked" about a (210) dislocation plane [19], causing large jumps in the in-plane resistance, with basically no impact on T_c or ρ_{zz}. It may be that microcracks result from stress-induced kinks of this sort. This relationship was also alluded to by Ishiguro *et al.* [20]. Thus, microcracks should not be considered as impurities in the usual sense, but rather as mesoscopic mechanical deformations that affect the connectivity of the sample, and thus its conductivity. As the dislocation plane is parallel to the interlayer c direction, the above model can explain the minimal influence of microcracks on $R_{zz}(T)$, since $R_e \gg R_i$ in zero-field, such that $R_{zz}(T) \sim R_i(T)$ (i.e., intrinsic). A future thorough test of this model will require quantifying microcracks and correlating them with $H_{c2}(0)$, with their diminishment possibly facilitating the full impact of FIDC: reentrant superconductivity.

The persistently large critical field observed in this material, now verified from a thermodynamic probe, is not easy to explain in the context of singlet superconductivity. This fact alone leads us to suggest that the superconductivity is spin triplet in nature. In conjunction with the complementary experiments mentioned above [2,11,12], this case is now considerably strengthened.

We acknowledge A. G. Lebed and P. M. Chaikin for beneficial discussions, H. I. Ha and J. Moser for assistance, and the support of NSF Grants No. DMR-0076331 and No. DMR-0308973.

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