Magnetic susceptibility and resistive transitions of superconducting $(TMTSF)_2ClO_4$: Critical magnetic fields

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We report measurements of the ac magnetic susceptibility and dc resistive transition in the zero-pressure organic superconductor di-tetramethylselenafulvalene perchlorate $[(TMTSF)_2ClO_4]$. Inductive measurements show complete diamagnetic shielding below a broad transition and initial flux penetration at very low fields $[H_{c1}(0) < 1 \text{ Oe}]$. The resistive transition is also broad, but occurs at a significantly higher temperature than the inductive transition, $T_c = 1.0$ and 0.65 K, respectively. Magnetic-field-induced transitions, measured both inductively and resistively, are broad and characteristically different. Critical magnetic fields measured inductively are moderately anisotropic $(H_{c2}^{\parallel}/H_{c2}^{\perp} \approx 3.2)$ and relatively small in magnitude $[H_{c2}^{\perp}(0) \approx 150 \text{ Oe}]$. Measured resistively, the critical magnetic fields are highly anisotropic $(H_{c2}^{\parallel}/H_{c2}^{\perp} \approx 20)$ and large in magnitude $[H_{c2}^{\perp}(0) \approx 1500 \text{ Oe}]$. Results suggest that $(TMTSF)_2ClO_4$ is a quasi-one-dimensional or quasi-two-dimensional superconductor at high temperatures and high magnetic fields and an anisotropic bulk superconductor at low temperatures and fields.

Superconductivity in organic crystals of the type di-tetramethylselenafulvalene X $[(TMTSF)_2X]$ has been observed under pressure for $X = PF_6$ (Ref. 1) and AsF_6 (Ref. 2) and most recently at zero pressure for $X = ClO_4$.[3] dc resistance,[1] ac magnetic susceptibility,[1] dc magnetization studies,[4] and pressure effects[5] on $(TMTSF)_2PF_6$ have confirmed the bulk superconducting character of this compound, i.e., zero resistance, complete diamagnetic shielding, and magnetic flux expulsion. In this paper, we report both ac magnetic susceptibility $(\chi = \chi' + i\chi'')$ measurements, which demonstrate the existence of complete diamagnetic shielding, and resistance measurements for the organic crystal di-tetramethylselenafulvalene perchlorate, $(TMTSF)_2ClO_4$. Similarly the critical magnetic fields, H_{c2}, as determined from both field-induced susceptibility and resistive transitions are reported as a function of temperature and sample orientation in the applied field.

Single crystals of $(TMTSF)_2ClO_4$ were grown by the electrochemical oxidation of gradient sublimed TMTSF in rigorously purified 1,1,2-trichlorethane containing tetra-N-butylammonium perchlorate as a supporting electrolyte. A platinum anode was used for the oxidation, and the current density was maintained at 5 $\mu A/cm^2$.

For susceptibility measurements, approximately 5–7 needlelike crystals were inserted longitudinally into a 1-mm-diam glass capillary tube for handling convenience. One end of this tube with samples was thermally anchored to a copper cold finger which was attached to the mixing chamber of a dilution refrigerator. The temperature of the sample was determined with a carbon resistor thermometer attached to the cold finger and calibrated against NBS superconducting fixed points. The sample was surrounded by a mutual-inductance coil system operating at 935 Hz with an rms amplitude of 0.1 Oe parallel to the high-conductivity axis of the crystal. Calibration of the coil system to determine complete diamagnetic shielding response was accomplished by measuring the superconducting transition of four small Nb wires of similar volume and shape to the $(TMTSF)_2ClO_4$ crystals. Magnetic fields were applied with a nitrogen-cooled solenoid capable of producing 800 Oe. For perpendicular magnetic field measurements, the sample and coil system were remounted on the mixing chamber oriented 90° from the original mounting.

Four-probe resistance measurements were made on two $(TMTSF)_2ClO_4$ crystals.[6] Needlelike samples were oriented and mounted on another cold finger in the dilution refrigerator which was surrounded by a 10-kOe superconducting NbTi magnet. Temperature was again determined with carbon resistor thermometers. The resistance ratio $R(300\ \mathrm{K})/R(4.0\ \mathrm{K})$ for the sample reported in this article was 20:1. Resistive measurements were made using a low-frequency (33 Hz) ac technique operating with a sample current of 10 μA rms. A dc measurement was done at one temperature to ascertain that there was no noticeable frequency effect.

The results of the zero-applied-magnetic-field ($H_{dc} < 0.01$ Oe) transitions are shown in Fig. 1 where the relative susceptibility $\mu'(T) \equiv \Delta\chi'(T)/\Delta\chi'_{max}$ and the normalized resistance $r(T) \equiv R(T)/R(2.0)$ are plotted as a function of temperature T. The inductive transition of $(TMTSF)_2ClO_4$ is quite broad, having an onset of about 1 K and a completion (perfect diamagnetic shielding) near 0.1 K. Both the real $\Delta\chi'$ and the imaginary $\Delta\chi''$ components of the complex signal change; however, $\Delta\chi''$ (not shown) is much smaller than $\Delta\chi'$. The transition temperature T_c, defined as the midpoint of this curve, is 0.65 K. Another sample, which had been broken into smaller segments and placed with random crystallographic orientations in the ac coil system, had a similar transition to that reported here with an identical T_c. Thus the susceptibility transition appears reproducible from sample to sample and independent of the direction of the ac excitation field. The resistive transition shown is also broad with an onset of about 1.2 K and a T_c (midpoint) of 1.0 K. The second resistive sample had a similar transition with a slightly higher T_c ($T_c \approx 1.1$ K).[6] Thus the resistive transition also appears reasonably reproducible from sample to sample.

There is a significant difference in the susceptibility and resistive transition seen in Fig. 1. Since all samples reported here were from the same "batch" and since sample-to-sample reproducibility is quite good, we consider this difference real even though not demonstrated on the same sample. The susceptibility transition onset occurs approximately at the resistive transition midpoint; i.e., only when the resistive transition nears completion do diamagnetic shielding currents develop. Similar behavior has been observed for polysulfur nitride $(SN)_x$,[7] and is attributed to the quasi-one-dimensional (1D) nature of the material.

Figure 2(a) shows the magnetic-field-induced susceptibility transitions at two temperatures for orientation perpendicular and parallel to the high-conductivity axis of the crystal. The lower two curves, measured at $T = 0.035$ K, show a very broad and incomplete transition toward the normal state up to fields of 800 Oe. The critical magnetic field H_{c2} is defined as $\mu' = 0.5$, consistent with the T_c definition. At the lowest temperature of 0.035 K, where the $H = 0$ transition appears complete, there is a very small region of field-independent susceptibility in the superconducting state ($H^{\parallel} \lesssim 4$ Oe and $H^{\perp} \lesssim 1$ Oe). The curves shown for $T = 0.65$ K are essentially at T_c of the sample, as defined by the $\mu' = 0.5$ criterion, but clearly show a susceptibility change as the sample recovers more of its normal-state properties.

Figure 2(b) shows the magnetic-field-induced resistive transitions at two temperatures, and two different field orientations. In the parallel case, fields up to 10 kOe had no noticeable effect on the $R = 0$ state at temperatures below 0.2 K. At higher temperatures there is an extremely wide, almost linear change in resistance back toward the normal state as the field is increased. In the perpendicular case, the field had a much more pronounced effect. At tem-

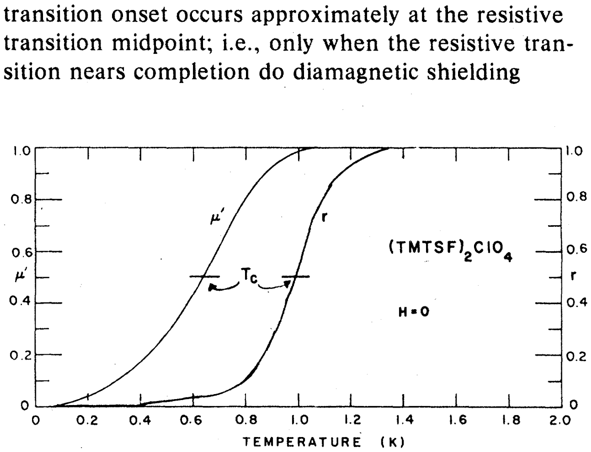

FIG. 1. Relative susceptibility μ' and the normalized resistivity r as a function of temperature in zero magnetic field. T_c is defined as the midpoint of the respective curves.

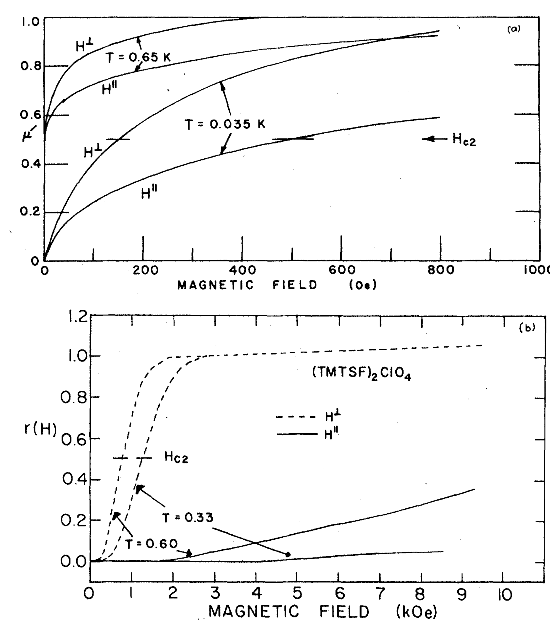

FIG. 2. (a) Relative susceptibility as a function of applied magnetic field for fields oriented parallel, $H^{\parallel}$, and perpendicular, $H^{\perp}$, to the chain axis at two different temperatures. H_{c2} is defined as the field where $\mu = 0.5$. (b) Normalized resistivity as a function of applied magnetic field for two field orientations at two different temperatures. H_{c2} is defined as the field where $r = 0.5$.

peratures near T_c (midpoint), the transition is relatively sharp, while at lower temperatures the transition begins to broaden.

The temperature dependences of $H_{c2}^{\perp}$ and $H_{c2}^{\parallel}$, determined both magnetically and resistively, are shown in Figs. 3(a) and 3(b). $H_{c2}^{\perp}(T)$ has a positive curvature near T_c for both methods of determination, which is characteristic of highly anisotropic superconductors such as (SN_x) (Ref. 7) or other quasi-1D or quasi-2D superconductors. Extrapolated $T=0$ critical magnetic fields are $H_{c2}^{\parallel}(0) \approx 500$ Oe and $H_{c2}^{\perp}(0) \approx 150$ Oe for susceptibility determination and $H_{c2}^{\parallel}(0) \approx 20-30$ kOe and $H_{c2}^{\perp}(0) \approx 1.5$ kOe for resistive determination. Resistively, $H_{c2}^{\parallel}$ is higher than the Pauli limiting field, $H_{c2}^{P} \approx 18.4 T_c$ (kOe). This large $H_{c2}^{\parallel}$ is again similar to $(SN)_x$.[7]

Not only are the magnitudes of H_{c2} different for the two methods of determination, but also the anisotropy $H_{c2}^{\parallel}/H_{c2}^{\perp}$ is markedly different. The anisotropy from susceptibility measurements is approximately 3.2 and is independent of temperature over the entire temperature range. From resistive measurements the anisotropy is approximately 20 near T_c. Higher-field data are needed to ascertain definitively whether or not this larger resistive anisotropy is temperature dependent. The small, temperature-independent anisotropy determined magnetically suggests that $(TMTSF)_2ClO_4$ is an anisotropic 3D superconductor at low magnetic fields and low temperatures. Large anisotropy and high magnetic fields determined resistively are more suggestive of a quasi-1D or -2D superconductor such as $(SN)_x$.[7]

In summary, the results of our measurements show (i) $(TMTSF)_2ClO_4$ exhibits complete diamagnetic response at temperatures below 0.1 K and magnetic fields less than 1 Oe; (ii) both inductive and resistive transitions are broad and give different values for T_c and H_{c2}; and (iii) anisotropy of the critical magnetic field is dependent on the measuring technique. These results suggest that superconductivity in $(TMTSF)_2ClO_4$ begins in a filamentary or layered manner which shows diminishing resistance but no bulklike magnetic properties for $T \sim 1.0$ K. As the temperature is lowered these superconducting regions couple together via the Josephson interaction to produce anisotropic 3D coupling and persistent diamagnetic shielding currents. Broad transitions are normal for such Josephson-coupled superconductors[8] and "T_c" is often dependent on measuring techniques.

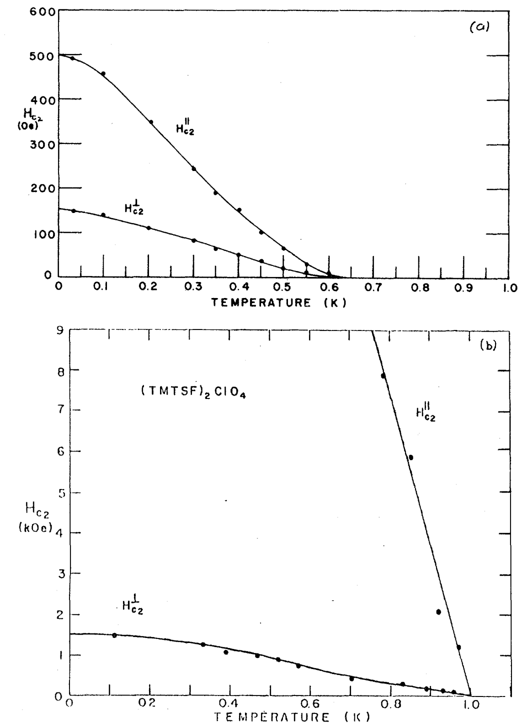

FIG. 3. (a) Critical field of $(TMTSF)_2ClO_4$ as a function of temperature as obtained from μ' data. Fields oriented both parallel and perpendicular to the chain axis are shown. (b) H_{c2} as a function of temperature as obtained from r data. Fields oriented both parallel and perpendicular to the chain are shown.

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[1]D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. Lett. 41, 95 (1980); M. Ribault, G. Benedek, D. Jerome, and K. Bechgaard, *ibid.* 41, 397 (1980).
[2]M. Ribault, J. P. Pouget, D. Jerome, and K. Bechgaard, J. Phys. Lett. (Paris) 41, L607 (1980).
[3]K. Bechgaard, K. Corneiro, M. Olsen, F. B. Rasmussen, and C. S. Jacabsen, Phys. Rev. Lett. 46, 852 (1981).
[4]K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek, and A. L. Stevens, Phys. Rev. Lett. 45, 1449 (1980).
[5]R. L. Greene and E. M. Engler, Phys. Rev. Lett. 45, 1587 (1980).
[6]D. U. Gubser, W. W. Fuller, T. O. Poehler, D. O. Cowan, M. Lee, R. S. Potember, L-Y. Chiang, and A. N. Bloch (unpublished).
[7]L. J. Azevedo, W. G. Clark, G. Deutscher, R. L. Greene, G. B. Street, and L. J. Suter, Solid State Commun. 19, 197 (1976).
[8]For a review see *Inhomogeneous Superconductors-1979,* edited by D. U. Gubser, T. L. Francavilla, J. R. Leibowitz, and S. A. Wolf, AIP Conf. Proc. No. 58 (AIP, New York, 1979).