Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: D. U. Gubser , W. W. Fuller , T. O. Poehler , J. Stokes , D. O. Cowan , M. Lee & A. N. Bloch (1982): Resistive and Magnetic Susceptibility Transitions in Superconducting $(TMTSF)_2C10_4$, Molecular Crystals and Liquid Crystals, 79:1, 581-590

To link to this article: http://dx.doi.org/10.1080/00268948208071001

Mol. Cryst. Liq. Cryst., 1982, Vol. 79, pp. 225-234
0026-8941/82/7901-0225$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

RESISTIVE AND MAGNETIC SUSCEPTIBILITY TRANSITIONS IN SUPERCONDUCTING $(TMTSF)_2ClO_4$*

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Received for publication September 16, 1981

We report measurements of the ac magnetic susceptibility and dc resistive superconducting transitions in the organic superconductor $(TMTSF)_2ClO_4$. Inductive measurements show complete diamagnetic shielding below a broad transition and initial flux penetration at very low fields [$H_{c1}(0) < 1$ Oe]. The resistive transition is also broad, but occurs at a significantly higher temperature than the inductive transition, T_c = 1.0 K and 0.65 K respectively. Resistance measurements also show evidence of a phase transition in the vicinity of 24 K. Magnetic field induced transitions, measured both inductively and resistively, show marked anistropy both in magnitude and in breadth of the transition. Results suggest that $(TMTSF)_2ClO_4$ is a quasi 1D or 2D superconductor at high temperatures and high magnetic fields and an anisotropic bulk superconductor at low temperatures and fields. Associated thermoelectric power measurements suggest that spin density waves coexist with the superconducting state.

*Work supported by the National Science Foundation under Grants DMR78-23957 and DMR80-15318 and by the U. S. Navy.

Superconductivity at ambient pressures, as determined resistively, has recently been reported for the organic compound di-(tetramethylselinafulvalene)-perchlorate, $(TMTSF)_2ClO_4$. We report here resistance, thermoelectric power and magnetic susceptibility ($\chi = \chi' + i\chi''$) measurements for the organic crystal di-(tetramethylselinafulvalene)-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. We have confirmed the resistive superconducting transition and demonstrated the existence of complete diamagnetic shielding. Resistance measurements also suggest the existence of a phase transition in the vicinity of 24 K.

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 $\mu amp/cm^2$. Four probe resistance and thermoelectric power measurements were made on several $(TMTSF)_2ClO_4$ samples. Resistance and susceptibility measurements in the vicinity of the superconducting transition were carried out by procedures previously described.[2]

The resistivity for a typical $(TMTSF)_2ClO_4$ specimen is illustrated in Figure 1. The resistivity drops by more than three orders of magnitude between 300 K and 5 K. The characteristic shows none of the sharp jumps that have widely been observed in measurements of this family. While the resistivity falls with a uniform slope over most of the high temperature range, a drastic change is observed at 25 K.

The change in the resistive behavior of $(TMTSF)_2ClO_4$ is more apparent if the derivative $\partial\rho/\partial T$ is presented as a function of temperature. As shown in Figure 2, there is a critical divergence characteristic of a phase transition in $\partial\rho/\partial T$ at 24 K.

A recent experiment by Scott[3] shows a minimum in the spin-lattice relaxation time T_1 of $(TMTSF)_2PF_6$ in the same temperature range. This is explained as change in relaxation rate associated with the rotational motion of the methyl groups on the TMTSF molecules. This is a more plausible explanation than that offered for the sharp change in conductivity in $(TMTSF)_2NO_3$ at 45 K. That change was attributed to freeze out of NO_3 molecules, but it has been recently suggested that mechanism would be ineffective in $(TMTSF)_2ClO_4$ where the tetrahedral nature of the anion causes a gap to open at the fermi surface.

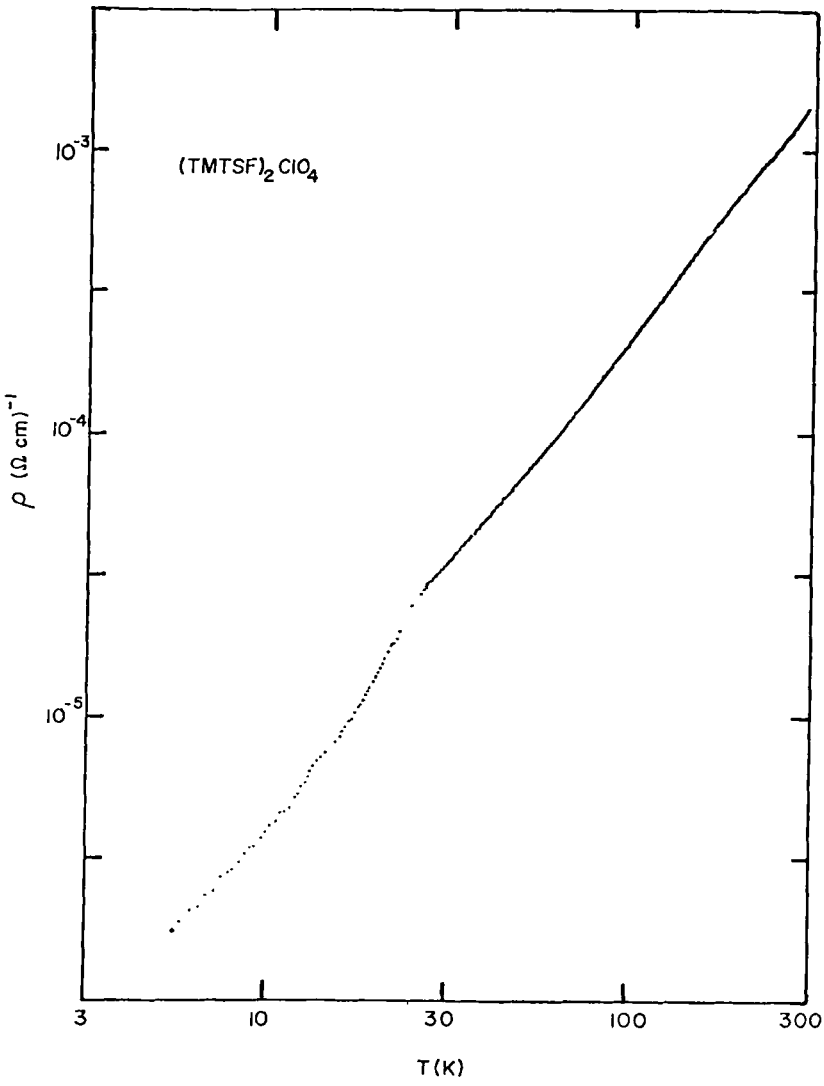

FIGURE 1 Resistivity versus temperature of $(TMTSF)_2ClO_4$.

The thermoelectric power as a function of temperature has a room temperature value and high temperature dependence similar to other $(TMTSF)_2$ X salts (Fig. 3). At temperatures below 6 K the thermopower drops drastically and even changes

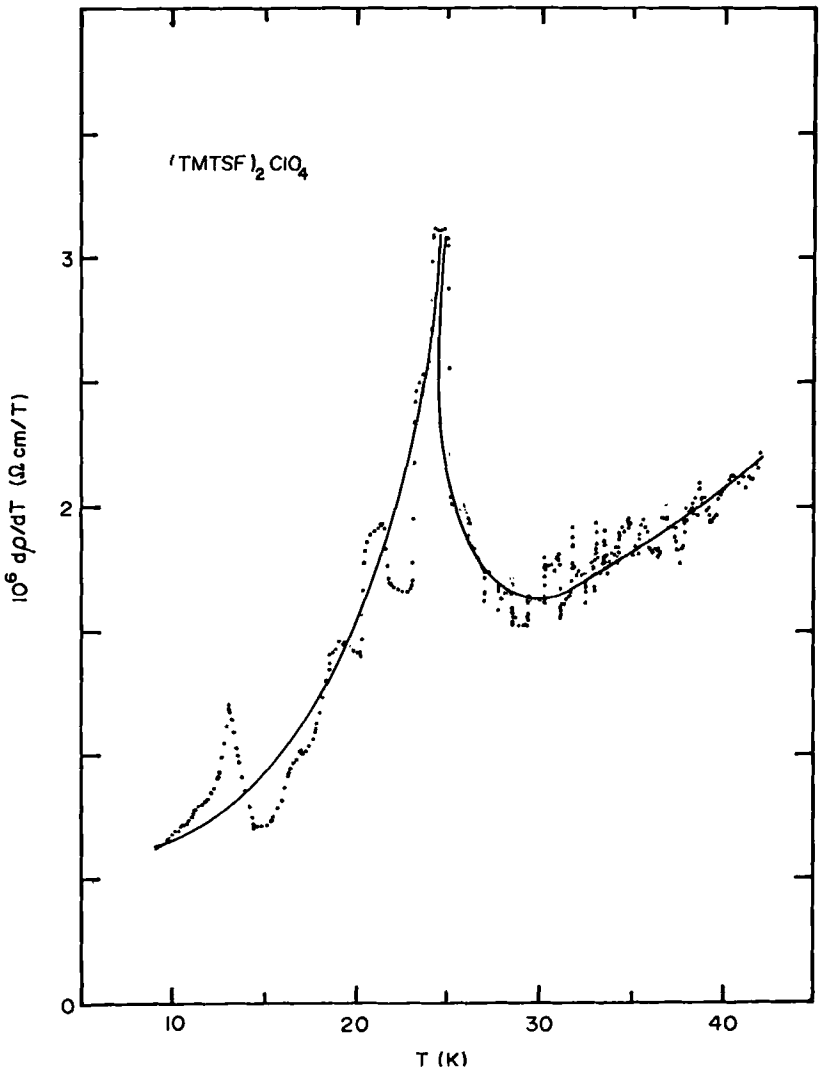

FIGURE 2 Temperature derivative of the resistivity of $(TMTSF)_2ClO_4$.

sign at about 5.5 K. This behavior is similar to that which occurs in $(TMTSF)_2PF_6$ at the magnetic phase transition. This supports the idea that the spin waves can co-exist with the superconductivity.

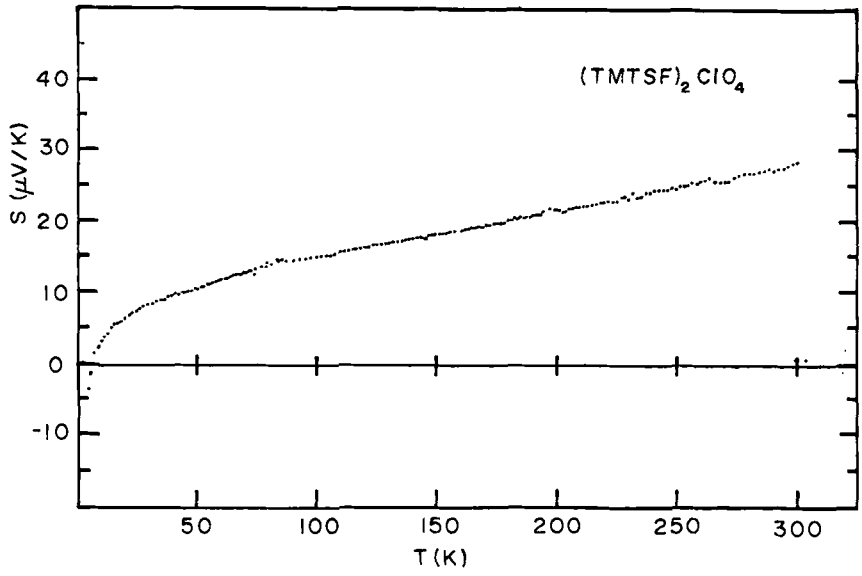

FIGURE 3 Thermoelectric power versus temperature of $(TMTSF)_2ClO_4$.

The results of the zero-applied-magnetic-field ($H_{dc} < 0.01$ Oe) transitions are shown in Fig. 4 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, $\Delta\chi''$ 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). Thus the resistive transition also appears reasonably reproducible from sample to sample.

There is a significant difference in the susceptibility and resistive transitions seen in Fig. 4. Since all samples reported here were from the same "batch" and since sample-to-sample reproducibility is quite good, we consider this difference real. 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 $(SN)_x$,[4] and is attributed to the quasi-one-dimensional (1D) nature of the material.

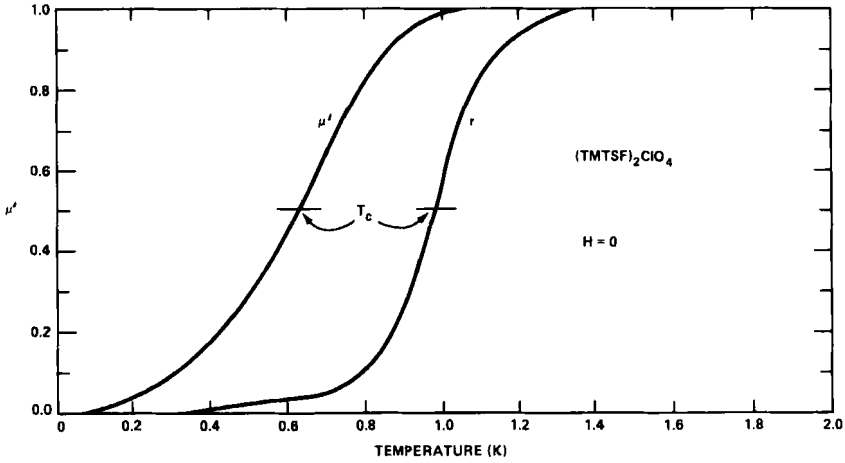

FIGURE 4 Relative susceptibility μ′ and the normalized resistivity r as a function of temperature in zero magnetic field. T_c is defined as the midpoint of the respective curves.

Figure 5(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 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 μ′ = 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 superconductivity 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 μ′ = 0.5 criterion, but clearly show a sus-

ceptibility change as the sample recovers more of its normal-state properties.

Figure 5(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 temperatures 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. 6(a) and 6(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) 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 $H_{c2}^{\parallel}(0) \approx 1.5$ kOe for resistive determination. ($H_c^{\perp}$ for resistance measurements was along the b crystallographic axis. $H_c^{\perp}$ was from susceptibility measurements randomly oriented with respect to the b and c axis.) Resistively, $H_{c2}^{\parallel}$ is the same order as the Pauli limiting field, $H_{c2}^{P} \approx 18.4\ T_c$ (kOe). This large $H_{c2}^{\perp}$ is again similar to $(SN)_x$.

Not only are the magnitudes of H_{c2} different for the two methods of determination, but also the anistropy $H_{c2}^{\parallel}/H_{c2}^{\perp}$ 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 and is strongly 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.

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 ~ 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 and "T_c" is often dependent on measuring techniques.

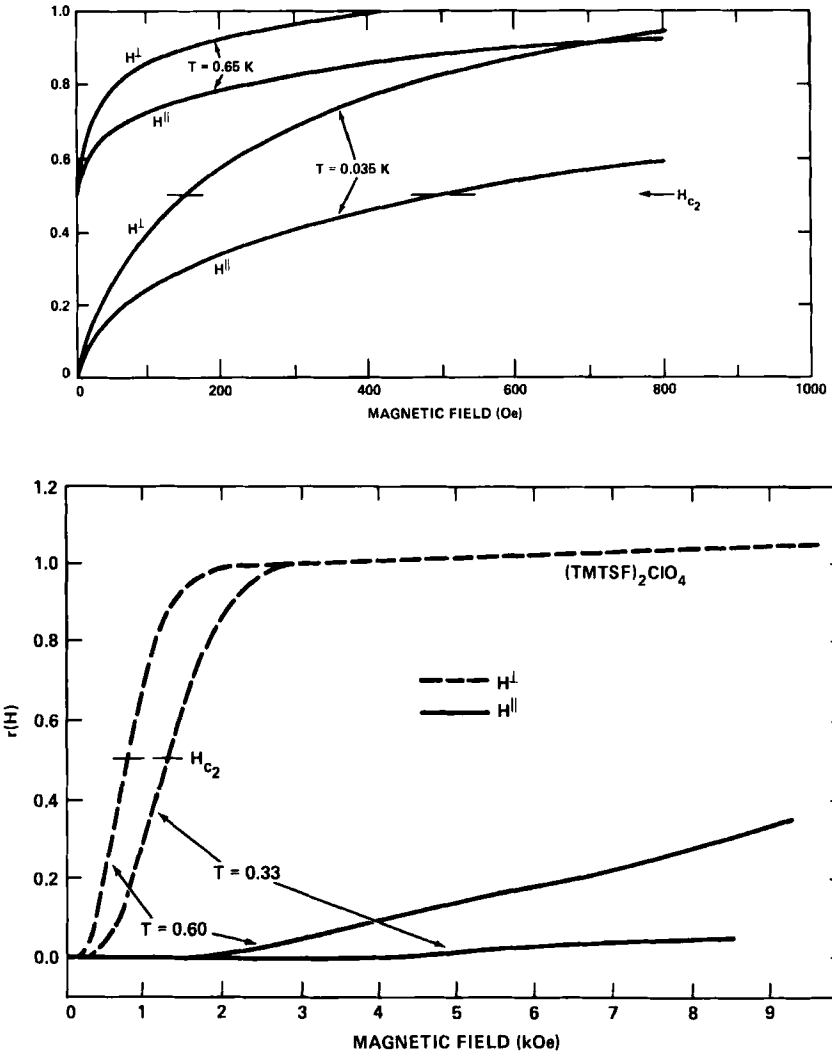

FIGURE 5 (a) Relative susceptibility as a function of applied magnetic field for fields oriented parallel, $H^{\parallel}$, and perpendicular, $H^{\perp}$, to the chain axis at two different temperatures. H_{c2} is defined as the field where $\mu' = 0.05$. (b) Normalized resistivity as a function of applied magnetic field for two field orientations at two different temperatures. H_{c2} is defined as the field where $r = 0.5$.

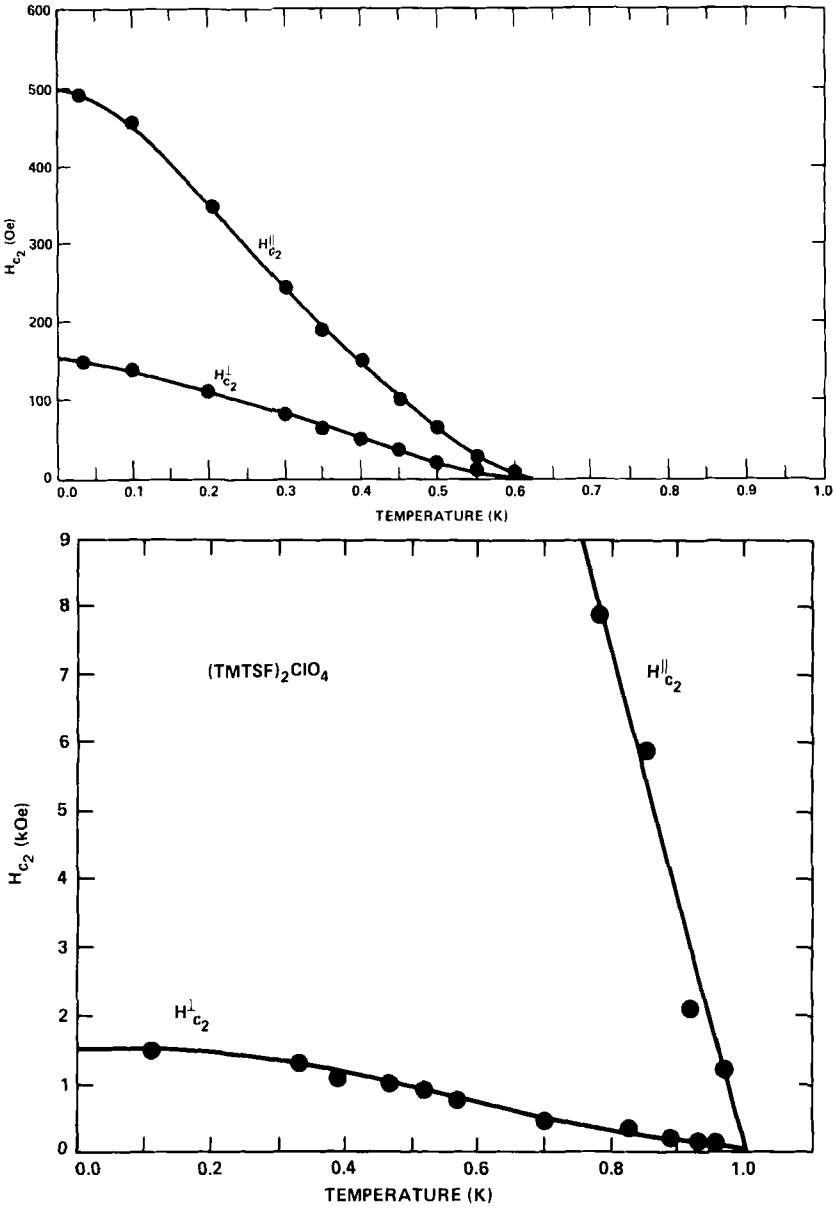

FIGURE 6 (a) Critical field of $(TMTSF)_2ClO_4$ as a function of temperature as obtained from μ′ data. Fields oriented both parallel and perpendicular to the chain axis are shown. (b) H_{c2} as a function of temperature as obtained from r data. Fields oriented both parallel and perpendicular to the chain are shown.

REFERENCES

1. K. Bechgaard, K. Carneiro, M. Olsen, F. B. Rasmussen, and C. S. Jacabsen, Phys. Rev. Lett. 46, 852 (1981).
2. D. U. Gubser, W. W. Fuller, T. O. Poehler, D. O. Cowan, M. Lee, R. S. Potember, L-Y. Chiang, and A. N. Bloch, Phys. Rev. B 24, 478 (1981).
3. J. C. Scott, H. J. Pedersen, K. Bechgaard, Phys. Rev. B 24, 475 (1981).
4. R. H. Dee, A. J. Berlinksy, J. F. Carolan, E. Klein, N. J. Stone, B. G. Tunrell, and G. B. Street, Solid State Commun. 22, 303 (1977).