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Metal-insulator transitions and superconductivity in ditetramethyltetraselenafulvalenium fluorosulfonate [$(TMTSF)_2FSO_3$]

R. C. Lacoe, S. A. Wolf,* and P. M. Chaikin
Department of Physics, University of California, Los Angeles, California 90024

F. Wudl and E. Aharon-Shalom
Bell Laboratories, Murray Hill, New Jersey 07974
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We have investigated the phase diagram of the orgainic charge-transfer salt ditetramethyltetraselenafulvalenium fluorosulfenate [$(TMTSF)_2FSO_3$] which contains an asymmetric dipolar anion. At low pressures there is a metal-insulator transition related to anion ordering. Between 5 and 6 kbar, there is a dipolar glass phase with increased resistivity. However, thermopower and superconducting measurements indicate that the Fermi surface remains ungapped. Above 5 kbar there is a superconducting transition with $T_c > 2$ K. This is the highest T_c for this family of compounds and suggests that the anions can enhance T_c.

The organic charge-transfer salts based on the cation molecule ditetramethyltetraselenafulvalenium (TMTSF) have provided physicists with a rich set of phase diagrams and a wealth of interesting phase transitions. At ambient temperatures and pressures many of these materials are highly anisotropic or quasi-one-dimensional metallic conductors.[1–5] Upon cooling, several of the salts undergo low-temperature, 4–20-K, spin-density-wave (SDW) transitions to an insulating phase.[3] Upon application of moderate pressure, < 15 kbar, the SDW transition can be suppressed and superconductivity often results. As a function of pressure, a maximum T_c of ~ 1.4 K has been observed for all superconductors in this family. In the ReO_4 salt,[6,7] metal-insulator transitions have been observed (at considerably higher temperatures ~ 200 K) coupled with a three-dimensional ordering of the asymmetric anion. It is particularly interesting that under pressure the ReO_4 salt also remains metallic to low temperatures and undergoes a superconducting transition with a T_c or ~ 1.4 K. It therefore appeared as if the maximum superconducting transition temperature (1.4 K) of this entire family was determined solely by the cation TMTSF chain.

The FSO_3 salt was synthesized to study the effect of a small asymmetric anion which additionally contained a permanent electric dipole moment.[8] The crystal structure reveals a unit-cell volume that is virtually identical with that of the ClO_4 salt but with a slightly reduced a dimension. At low pressure there is a sharp metal-insulator transition at 87 K.[8] Although there is not yet structural data below this transition, we presume that it is closely related with the anion ordering transition observed in the ReO_4 salt. Between 5 and 6 kbar the resistive transition is suppressed and considerably smeared similar to the effect of moderate pressure on the ReO_4 salt.[6] However, the additional measurement of the thermopower in the present case strongly suggests that a gap does not open at the Fermi surface and that the main effect is on the mobility of the conduction electrons. The large resistance increase may be due to the scattering of the electrons from the disordered charges and moments in a frozen dipole glass formed by the FSO_3 anions. The observed superconducting transition is also greatly smeared, but the onset temperature and the critical field are the highest reported for the TMTSF family. Above 6 kbar the dipole transitions are suppressed and the stable metallic phase shows a T_c (> 2 K) which remains larger than the other members of this family. Additional electron-electron coupling may be the result of an interaction mediated by coupling to the dipoles.

The experiments were performed in a BeCu pressure clamp of similar design to that described in Ref. 9. The samples were mounted for simultaneous measurement of the thermopower and four-probe resistance using the technique described in Ref. 10. Samples were mounted on 1-mil gold wires with silver paint contacts. The pressure medium was heptane. The pressure was measured by the T_c of Sn and, occasionally, by the phase diagram of $(TMTSF)_2PF_6$. We find $P_c = 6.5$ kbar for $(TMTSF)_2PF_6$.

In Fig. 1 we show the pressure-temperature phase diagram as determined from the logarithmic derivative of the resistance. In the region below 5 kbar there is very little hysteresis in resistive measurements. In the region from 5–6 kbar the resistance increases with decreasing temperature over a very broad range, and rewarming and recooling curves are quite different. Above 6 kbar the resistance remains metallic down to the superconducting transition. Above 5 kbar there is a superconducting transition at $T_c > 2$ K.

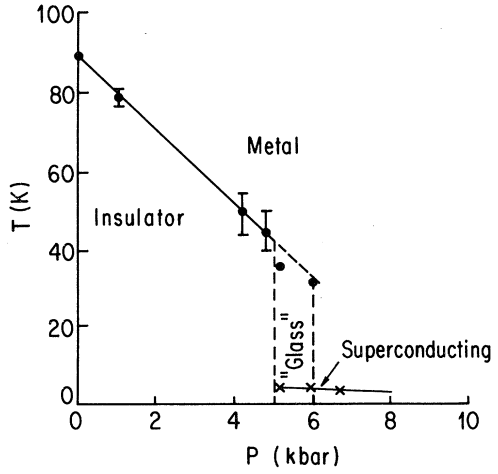

FIG. 1. Phase diagram for $(TMTSF)_2FSO_3$.

In Fig. 2 we shown the temperature dependence of the normalized resistance of a sample of $(TMTSF)_2FSO_3$ for a pressure of 5 kbar. From 250 to ~80 K the resistance is a monotonically decreasing function of temperature indicative of the metallic nature of the sample. There is an ill-defined minimum at ~80 K below which the resistance gradually rises to a maximum at ~17 K. At this temperature the resistance is more than an order of magnitude greater than at the minimum at 80 K. Below the maximum at ~17 K the resistance again begins to decrease slowly until the onset of the superconducting transition.

The thermoelectric power taken simultaneously with the resistance discussed above is shown in Fig. 2. At atmospheric pressure the thermopower of this sample was 22 μV/K at room temperature. Surprisingly, the thermopower increased to 28 μV/K as pressure was increased in steps to 10 kbar. As temperature is lowered the thermopower remains small and monotonically decreases, indicating the metallic conduction process. These data are very similar in sign, magnitude, and temperature dependence to the thermopower measured for most of the other salts in the TMTSF family when they are in the metallic state.[11] Of particular importance for the present work is the absence of any structure which can readily be associated with the increasing resistance in the region between ~17 and 80 K. From the thermopower one would conclude that the material is metallic down to the superconducting transition. Below the superconducting transition the thermopower falls toward zero.

The superconducting transition that is observed for samples under a pressure of 5–6 kbar is typically wide and incomplete in the temperature range that we have explored—down to 1.2 K. Data for the 6-kbar sample are shown in Fig. 3. The resistance is still increasing as temperature is decreased from 10 to below 4 K. The onset of the superconducting transition is *above* 3 K. For this sample the ratio between the minimum and maximum resistance (80–3.7 K) was greater than 200. Also shown in Fig. 3 is the superconducting transition measured at 6.5 kbar where both the metal-insulator and the glass transition have been suppressed. The superconducting transition is sharper and T_c is ~2.1 K. The resistance measured at 1.4 K is less than 0.3% of the resistance at 4 K.

The gradual increase in the resistance that we observe under pressure between ~80 and 17 K is unusual. At ambient pressure the sharp, high-temperature metal-insulator transition that is observed is assumed to result from an antiferroelectric-like transition of the dipolar anions. Above the transition there is one conduction electron per unit cell

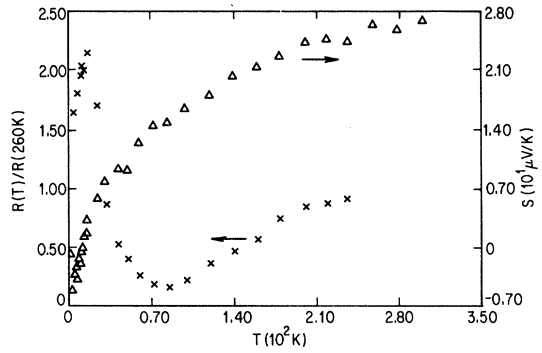

FIG. 2. Temperature dependence of the resistance (×) and the thermopower (Δ) of a single crystal of $(TMTSF)_2FSO_3$ at 5 kbar.

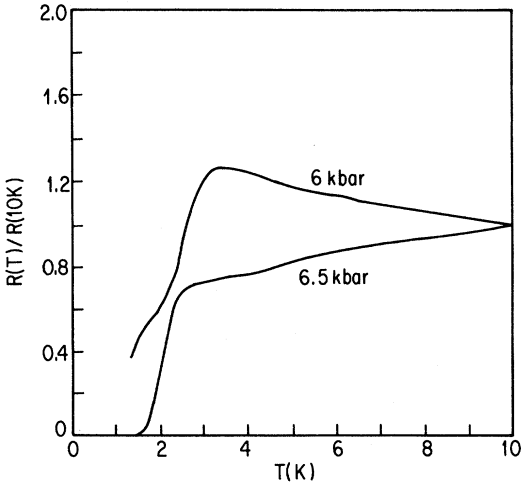

FIG. 3. Resistance vs temperature for samples at 6 and 6.5 kbar. (The 10-K resistivity of the 6-kbar sample is ~100 times that of the 6.5-kbar sample.)

on the TMTSF chain and the antiferroelectric ordering would correspond to a doubling of the lattice periodicity, and hence the opening of a gap at the Fermi surface. The same phenomenon is observed in the ReO_4 salt. In that case the anions have no dipole moment and the potential which causes the gap is assumed to result from a slight transverse motion of the anions as they order.[7]

The resistance curves, such as in Fig. 2, suggest that the anion ordering has been "smeared out" either by the presence of large scale inhomogeneities or by the suppression of the ordering transition and the appearance of a freezing transition which leads to a metastable glasslike phase. A freezing transition has been suggested for the ReO_4 salt.[7] The ratios between maximum and minimum resistances that we have observed range as high as a factor of 200 (again similar to observations on the ReO_4 salt). Such large changes in resistance would normally be associated with the opening of a (disordered) gap.

The thermopower measurement, however, is inconsistent with the opening of a gap at the Fermi energy. The thermopower remains small and varies very smoothly through the range where the resistance is rapidly changing. In many previous studies of systems which undergo either total or partial gapping of the Fermi surface the thermopower invariably signals this transition even in the presence of a great deal of disorder. The transitions seen in disordered $NbSe_3$ (Ref. 12) and $Eu_{1.2}Mo_6S_8$ (Ref. 13) are very broad and involve a fraction of the Fermi surface but show up easily in both thermopower and resistivity. The conclusion must be that the observed resistance increase is predominantly a mobility effect rather than a carrier density change. The change in mean free path would, of course, show up in the thermopower,[11,14] but would have a much smaller effect than reducing the density of states by a factor of 200.

The appearance of superconductivity at low temperature also suggests that the Fermi surface remains intact through the resistive anomaly. Metal-insulator transitions complete with superconductivity for density of states at the Fermi surface.[13,15] The main effect is the exponential dependence of the superconducting transition on the density of states.

For a 6-kbar sample superconductivity is completely destroyed for a field along a for ~ 50 kG at 1.6 K, roughly corresponding to the Pauli limit[16] for an onset temperature of 3.5 K, as observed. In a perpendicular field superconductivity was destroyed at ~ 10 kG. For a 6.5-kbar sample the critical-field anisotropy (between b^* and c^* direction) was ~ 10 with a critical field perpendicular to c^* of ~ 3.5 kG at ~ 1.4 K (Fig. 4).

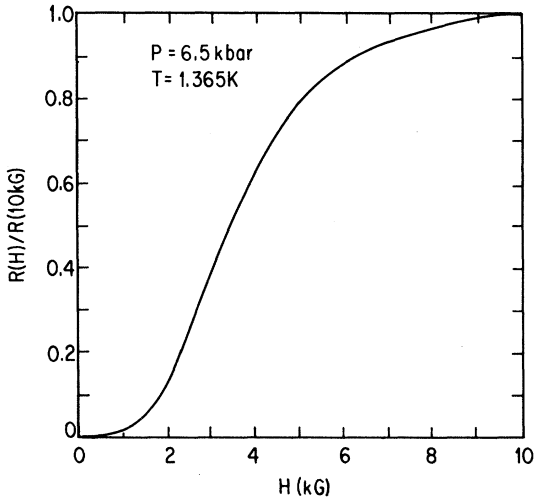

FIG. 4. Resistance vs magnetic field (perpendicular to c^*) for the sample at 6.5 kbar.

T_c for the 6.5-kbar sample and especially the onset temperature for the 5–6-kbar samples are appreciably higher here than for other members of the TMTSF family. Since the main difference beetween the present material and the other $(TMTSF)_2X$ salts is the existence of a permanent dipole moment on the anion,[17] it is tempting to attribute the increased T_c to an increased electron phonon interaction via the dipoles. This is particularly attractive since the freezing transtion occurs at such low temperatures that the degrees of freedom involved must be reasonably soft—low-frequency modes which are important for superconductivity.

In conclusion, we have shown that pressure suppresses the metal-insulator transition in $(TMTSF)_2FSO_3$ and that in the range 5–6 kbar a glasslike transition occurs, probably due to the freezing of the anion dipole moments. The large resistance increase which follows this freezing is the result of a decreased mobility rather than the opening of an energy gap on part of the Fermi surface. The superconducting transitions which we observe correspond to the highest T_c's and H_c's yet observed in this family. We suggest that the high T_c is related to electronic interaction with the anion dipoles.

ACKNOWLEDGMENTS

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*Permanent address: Naval Research Laboratories, Washington, D.C. 20375.

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