Restoration of Metallic Behavior in Organic Conductors by Small Electric Fields

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The electrical conductivity of two linear-chain organic compounds in their semiconducting states is found to increase drastically with the application of electric fields of ~10 mV/cm and with the increase of frequency to ~10 GHz. Also, the electron-spin-resonance line is found to switch abruptly from unresolvable to fully resolved (narrow and metal-like) at fields of 0.1 V/cm. One speculative explanation of these observations is the presence of spin-density waves.

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Many organic charge-transfer salts exhibit anisotropic metallic conductivities and undergo transitions to semiconducting states below characteristic temperatures T_{MS}. Recently Bechgaard and co-workers[1] have synthesized and studied some new salts, including $(TMTSF)_2PF_6$ (tetramethyltetraselenafulvalenium hexafluorophosphate), whose dc conductivity increases beyond 10^5 $(\Omega\ \mathrm{cm})^{-1}$ upon cooling to ~20 K and then decreases rapidly below $T_{MS} \sim 15$ K. Subsequently Jerome *et al.*[2] have observed that hydrostatic pressure depresses T_{MS} to 0 K near 9 kbar and that superconductivity appears at higher pressure ($T_c \sim 0.9$ K at 12 kbar). Pedersen, Scott, and Bechgaard,[3] have examined the electron-spin resonance (ESR) of $(TMTSF)_2PF_6$ and found that the resonance line narrows monotonically as the conductivity increases, then rapidly broadens and loses intensity near T_{MS}.

We have found that the conductivity and spin paramagnetism of $(TMTSF)_2PF_6$ (and the isostructural AsF_6 compound) are drastically affected by small applied electric fields at atmospheric pressure and temperatures well below their nearly identical T_{MS} values.

Samples of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ were grown electrochemically from chlorobenzene with use of tetrabutylammonium salts as supporting electrolytes. TMTSF was prepared by a modified procedure not requiring carbon diselenide.[4] Typical samples were ~ $1 \times 0.05 \times 0.02$ cm^3. Scanning electron microscopy revealed that a number of crystals in a batch were hollow with large voids extending deeply into the needles. These needles exhibited at least two types of morphology; flat (parallelepiped cross section) and polygonal (octagonal cross section). The $(TMTSF)_2PF_6$ and the AsF_6 salts were strictly isomorphous with the monoclinic structure described by Jerome *et al.*[2]

Our dc resistance measurements on single crystals of $(TMTSF)_2PF_6$ at low currents (100 μA), as shown by the solid curves in Fig. 1, confirm the findings of Bechgaard *et al.* A conventional, four-probe, gold-paint contact arrangement was used with strain minimized by using long, 0.0013-cm-diam gold wires supported only at one end. The sample was slowly cooled in 0.1 mm of He exchange gas, with a thermocouple

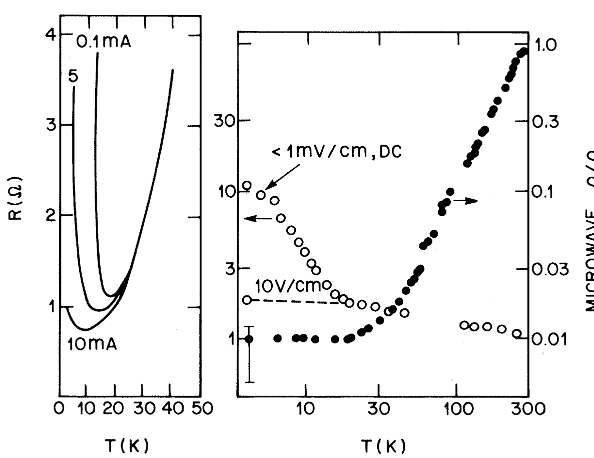

FIG. 1. Graphs of the electrical resistance of $(TMTSF)_2PF_6$ as a function of temperature. On the left is the dc behavior of a single crystal at three different applied currents as labeled. On the right is the microwave resistivity relative to that at $T = 273$ K of a similar crystal (solid circles, right axis) and the dc resistivity ratio of a compressed pellet (open circles, left axis) at currents equivalent, at 4.2 K, to the electric fields labeled.

heat sunk to the lead support.

At currents of 5 and 10 mA the sample of Fig. 1 behaved in a metallic fashion to temperatures below T_{MS}. In these runs, the primary sources of heating were the current contacts which had resistances of ~ 100 Ω and thus dissipated powers ≤ 10 mW. Independent of the magnitude of this heating, a real conductivity enhancement appears to be present because the sample resistance in the 10-mA case at 10 K nominal temperature was less than any value observed at higher temperature. The same crystal was also examined while immersed in superfluid He and a nonlinear increase in conductivity was observed for $E \gtrsim 10$ mV/cm at 1.2 K.

The dc resistances of polycrystalline $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$ samples were also measured via a two-lead compressed-pellet technique. The results for the PF_6 salt are shown as the open circles in Fig. 1. The absence of metallic behavior above 20 K arises from substantial resistance between crystallites in the pellet and the unavoidable averaging over low transverse and surface conductivities. However, the changeover to a semiconducting state at low temperatures and the suppression of this state with increasing electric field are apparent. Nonlinear behavior occurred for $E \geq 40$ mV/cm at 1.2 K in these measurements, in qualitative agreement with the single-crystal results considering the polycrystalline nature of these samples. Essentially identical nonlinear behavior was observed for the AsF_6 salt.

Microwave conductivity measurements via cavity perturbation techniques were made at 9.35 GHz on several single-crystal samples of $(TMTSF)_2PF_6$. As shown by the solid circles in Fig. 1 the high-frequency results closely resemble the four-probe dc data for $T \gtrsim 20$ K. At lower temperatures, however, no marked transition to a semiconducting state was observed. Reducing the incident power P from $P \approx 10^{-6}$ to 10^{-8} W at 6.5 K did produce a decrease in conductivity ($\sigma \sim P^{1/3}$) but with no indication of a sharp transition. The sample was suspended in He exchange gas at the electric-field maximum of a cylindrical TE_{011} cavity. The electric-field strength in the skin-effect region of the conducting samples was ~ 1 mV/cm at $P \approx 10^{-6}$ W.

While microwave conductivity barely shows any evidence of the metal-semiconductor transition the ESR response of these materials is remarkably nonlinear. In accord with Pedersen, Scott, and Bechgaard[3] a resonance with g tensor char-

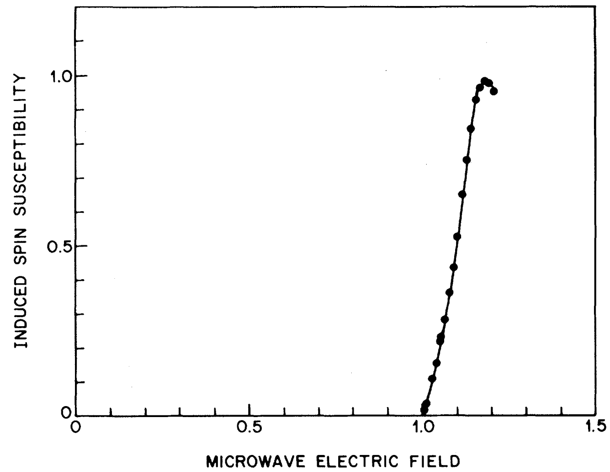

FIG. 2. Peak intensity of the ESR signal induced by the applied microwave electric field at $T = 4.2$ K (normalized, linear units).

acteristic of degenerate TMTSF spins is observed to narrow markedly down to 20 K and then to broaden and become unobservable below ~ 15 K at low P. However, as shown in Fig. 2, when the microwave electric field is directed along the high conductivity needle axis and raised to a critical level E_0 (~ 0.1 V/cm in the sample) a narrow ESR signal rises rapidly to intensity levels comparable to that observed to 20 K. In very thin samples the signal increases continuously but much more rapidly than the gradual electric-field–induced increases in conductivity observed in the dc measurements.

In somewhat thicker samples the "stimulated" ESR at 4.2 K rises discontinuously with P and switches from the lowest trace to the center trace illustrated in Fig. 3. In such a case there is a marked difference in signal shape from 20 to 4.2 K. At 20 K the signal is unexpectedly symmetric, as in the upper curve of Fig. 3, whereas the stimulated signal has the asymmetry characteristic of spins in a conducting medium whose thickness is appreciably greater than the microwave skin depth.

The nonlinear dc conductivity results are reminiscent of those[5,6] in $NbSe_3$, where the nonlinearities have been attributed to depinning[7] of an incommensurate charge-density wave[8] (CDW). In our results, as in $NbSe_3$, electric fields of ~ 10 mV/cm provide a much smaller energy on a microscopic length scale than $k_B T_{MS}$ so that destruction of a condensed state, such as a CDW, is impossible. However, in the TMTSF salts the static susceptibility and ESR results rule out a

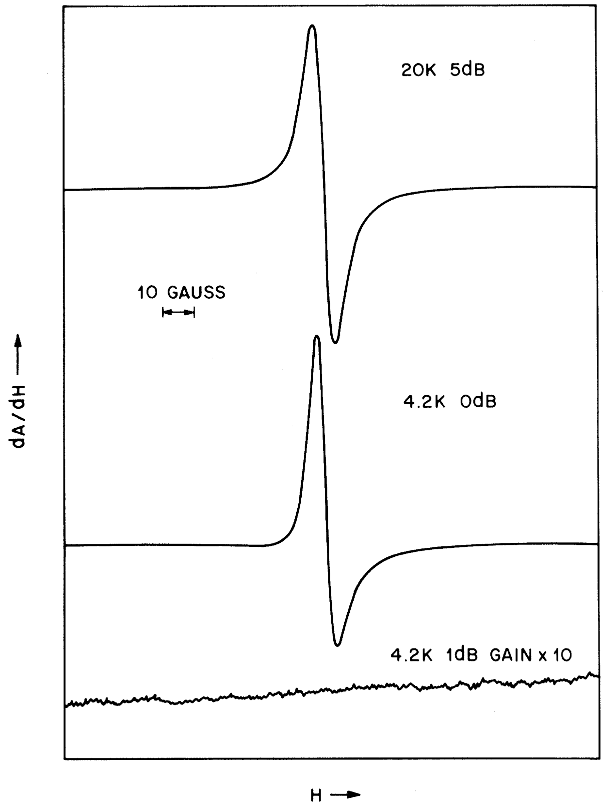

FIG. 3. Derivative of the ESR absorption amplitude with respect to magnetic field as a function of magnetic field in the normal, metallic state (upper curve, $T=20$ K, attenuation of microwave power = 5 dB), in the microwave-induced high conductivity state (middle curve, $T=4.2$ K, attenuation = 0 dB) and in the insulating state (lower curve, $T=4.2$ K, attenuation = 1 dB, gain 10×).

CDW with a spin-singlet ground state since the susceptibility should tend to zero below T_{MS} and should not be restored by depinning the CDW.

It is tempting to speculate that a transition to a spin-density-wave (SDW) state[9] may occur in the TMTSF salts. An SDW can be formed from a single band in a charged structure and therefore can carry current when it slides.[10] Furthermore, the SDW pinning energies are generally weaker than those of a CDW because the SDW is pinned to ordinary impurities only by spin-orbit coupling and so its strongest interaction with the lattice may arise from the $4k_F$ CDW harmonic that is expected to coexist with the $2k_F$ SDW.

In contrast to a CDW, an antiferromagnet shows very little decrease in its static magnetic susceptibility below its ordering temperature if the spin anisotropy field H_A is small. The anisotropy field is reduced from that in a usual antiferromagnet by the magnitude of the oscillating moment, which is of order $T_{MS}/\epsilon_F \simeq 10^{-3}$. The antiferromagnetic resonance is expected to be at $g\mu(H_0^2+2H_AH_E)^{1/2}$ where H_0 is the applied field and H_E is the exchange field. The smallness of H_A may also explain why the resonance when restored at low temperature is not shifted from the paramagnetic value. We may interpret the ESR line of the TMTSF salts below T_{MS} as due to electrons thermally excited across the SDW gap. To explain the restoration of the ESR signal, we need to postulate that the antiferromagnetic resonance at low fields is too broad to be observable and that the random fields responsible for the broadening depend on the phase of the SDW relative to the lattice. When the SDW oscillates in the rf field, motional narrowing occurs when the amplitude of the oscillation is comparable to the lattice spacing. Estimates based on the conductivity indicate, that at the ESR frequency, this occurs at $E \simeq 1$ V/cm. An important point is that the characteristic field is larger than that for the dc conductivity. While these ideas are in accord with the data, clearly much more work is required to confirm our speculation. Important questions are whether the SDW is commensurate, and if so whether the commensurability energy is sufficiently weak.

In conclusion, we have discovered a facile restoration of the metallic state at temperatures below the T_{MS} of $(TMTSF)_2PF_6$ and $(TMTSF)_2AsF_6$. This observation, coupled with results of static magnetic susceptibility measurement,[11] suggests that an SDW distortion may be responsible for the disappearance of the metallic state in these salts and that this state should be considered in the explanation of the effect of pressure on T_{MS} and the appearance of superconductivity.

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Inhomogeneous Superconducting Transitions in Granular Al

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Granular Al films have been measured in a microwave cavity at 9.4 GHz together with their dc resistance, $R(T)$. The change in resonant frequency is proportional to the number of superconducting electron pairs which is finite *above* the temperature T_c^{ρ}, where $R(T) \simeq 0$. Microwave loss has been identified which appears to be specific to granular materials and vanishes only well below T_c^{ρ}. This is shown to be due to normal conduction between grains, which upon cooling becomes progressively more Josephson-like.

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The interest in granular superconductors has increased considerably over the past years.[1] More recently, Al samples at the high-resistivity end, containing 30- to 50-Å Al grains and more than 30% Al_2O_3, have come under focus. For example, the 100-Å films needed to observe the Kosterlitz-Thouless transition were granular in nature.[2] Earlier studies of the resistive transition used thicker films.[3] These, and the more recent specific heat measurements[4] on similar films, were aimed at understanding how long-range superconductivity in these materials arises. A model with an inhomogeneous distribution of grain coupling, referred to as percolative, accounts for the smeared and shifted specific-heat peak.[5] On the other hand, renormalization-group theory for weak and uncorrelated distributions yields a homogeneous transition.[6] If this is not the case, the experimentally observable transition can be spatially inhomogeneous. The criteria where one or the other situation prevails are not well established.[6]

In the present work we have employed microwave measurements to examine the superconducting transition in a variety of granular Al films. The films were sufficiently thin that the electric fields penetrated the whole sample. Thus the technique is still useful even if a superconducting path is established and dc measurements cease to give information. Our measurements show that there is a temperature range in which *all* the Al metal is superconducting but there does not exist a uniform phase relation between the grains.

The experiments were conducted using a Varian Model-4500 electron-spin-resonance spectrometer. The samples were mounted along the axis of cylindrical TE_{01} microwave cavity operating near 9.4 GHz. To minimize losses the films were positioned with their surfaces parallel to the microwave magnetic vectors. The microwave data were taken by locking the klystron frequency to the cavity. Then the shift in frequency, $\Delta\nu$, due to the superconductivity of the sample was measured by recording the output of an attached Hewlett-Packard spectrum analyzer, as a function of the applied external magnetic field of the spectrometer. Simultaneously, the change in Q of the cavity, due to the microwave loss, was monitored by the change of power reflected from the cavity. For the range of temperatures reported here the available magnetic field of 6500 Oe was sufficient to induce the normal state. Therefore the changes due to the superconducting state would be obtained. The microwave power was kept low enough so that the data were power independent.

The dc conductivity was probed by pressing

