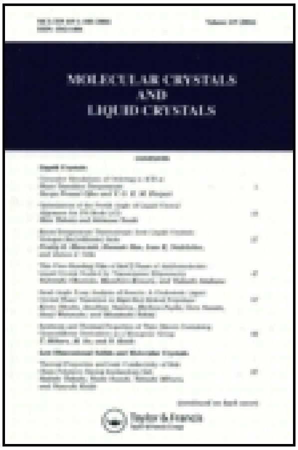

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Phase Diagrams of Organic Superconductors

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PHASE DIAGRAMS OF ORGANIC SUPERCONDUCTORS

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Abstract A contactless technique has been developed for tracking the metallic, spin density wave and superconducting ground states of organic superconductors as a function of pressure and temperature.

INTRODUCTION

Organic superconductors have rich phase diagrams over relatively small excursions in pressure, temperature and magnetic field. Pressure can suppress the spin density wave (SDW) state so that the material remains metallic to sufficiently low temperatures to enter the superconducting state.[1] Following these changes with conventional four-probe transport techniques with sufficient reproducibility to determine the phase diagrams is very difficult with these materials because the single crystal specimens are extremely small and fragile and therefore seldom survive temperature and pressure cycling. A further complication arises because, in the pressure-temperature regime of interest, all pressure media are solid with most techniques. The stress experienced by a single crystal sample is both non-uniform and somewhat uncertain in magnitude. We avoid these difficulties by using contactless techniques[2] in a solid He pressure medium.[3] We describe our techniques briefly and demonstrate their efficacy with a comprehensive study of $(TMTSF)_2PF_6$.

EXPERIMENTAL

The $(TMTSF)_2PF_6$ crystals used in this study were 0.3 x 0.6 x 1 mm platelets. The growth techniques will be described elsewhere.[4] A radio frequency coil was wound in a rectangular configuration to optimize the filling factor for each crystal. The crystal-coil configuration was such that the magnetic field could be rotated in the b-c plane of the crystal (the a axis is the high conductivity direction). With this arrangement, low-field electron spin resonance (ESR) can be detected by use of a Q meter circuit using field modulation techniques. The ESR peak-to-peak linewidths were ~1 Oe at low temperature in the metallic state. The ESR of the metallic state is shown in Fig. 1a.

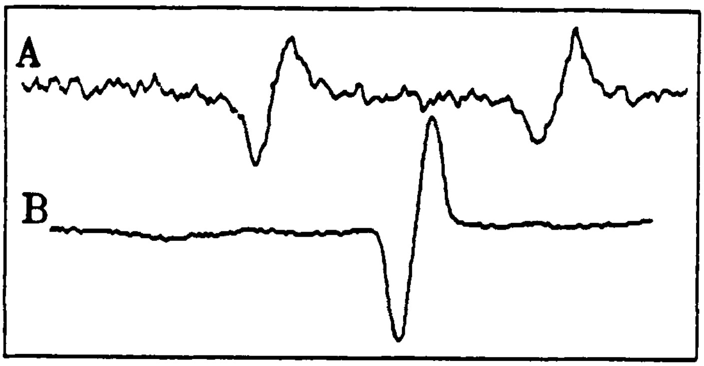

Figure 1: Electron spin resonance derivative signal (upper curve) vs. applied magnetic field at 29.007 MHz, 6.6 kbar and temperature 1.123 K. The resonances correspond to positive and negative magnetic fields of 10.4 Oe. The lower curve is taken at a temperature of 1.044 K with 1/40 of the gain and depicts the onset of superconductivity. The large feature centered around zero field is due to the lower critical field, H_{c1}. Smaller features at fields of ± 15 Oe are the upper critical field, H_{c2}.

This same coil arrangement can be used for nuclear magnetic resonance (NMR) or for rf penetration measurements to monitor the resistance of the sample. Thus detection of the superconducting state and observation of the upper and lower critical fields H_{c1} and H_{c2} is straightforward. The transition is about 10 mK wide in $(TMTSF)_2PF_6$ and is shown in Fig. 1b.

Pressures were generated in solid ^4He. In this technique, gaseous He pressure is imposed on the sample at a temperature just above where the He will freeze. At 10 kbar this is about 60K. The sample is cooled slowly ($\gtrsim$ 1 deg/minute) while adding He so that the fluid-solid line moves past the sample at constant pressure. This technique yields the maximum pressure for a given system, insures that there are no pressure gradients, and allows straightforward determination of the end pressure from the known phase diagram of ^4He. This careful isobaric freezing also precludes damage to the fragile samples so that many pressure-temperature cycles can be taken.

RESULTS

Our results for the pressure-temperature phase diagram of $(TMTSF)_2PF_6$ are shown in Fig. 2. In the high temperature, high pressure range, the ESR signal is narrow and the susceptibility is independent of temperature, indicative of a Pauli state. This signal disappears abruptly over a temperature range of about 0.1 K upon entering the SDW state. The SDW state occurs at 12 K at zero pressure in agreement with literature values.

The superconducting transition is observed only from 6.1 to 6.8 kbar due to our lower temperature limitation of 1.04 K. This transition is very sharp, typically 10-20 mK in width. We observe unexpected behavior near 6.1 kbar where at constant pressure by lowering the temperature the metallic, SDW and superconducting states are all observed in turn. Thus the phase boundary between

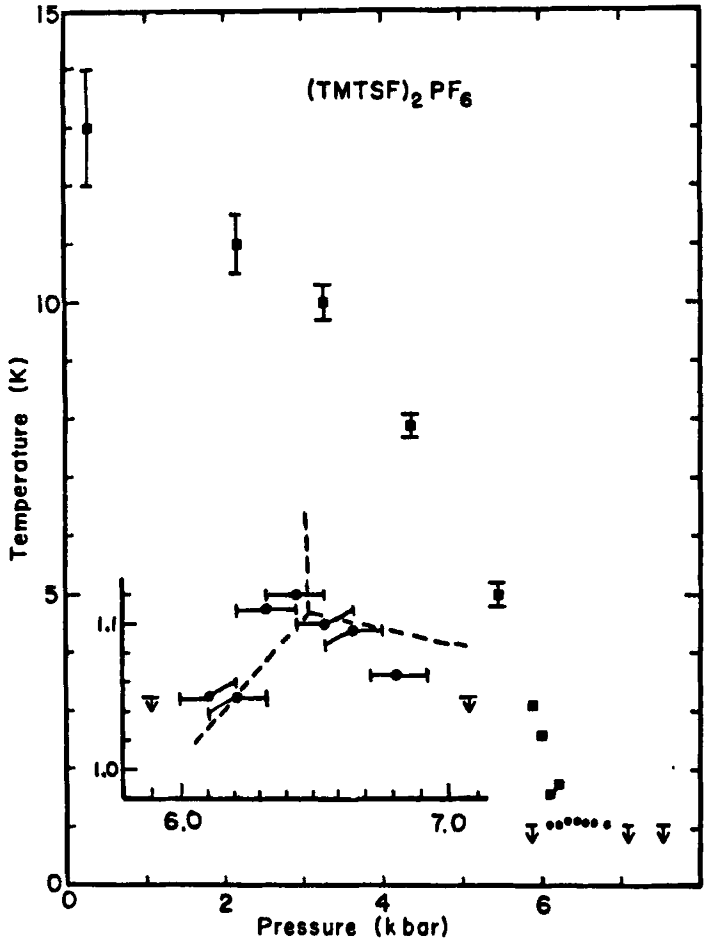

Figure 2: Temperature-pressure phase diagram showing metallic-SDW transitions (boxes) and superconducting transitions (circles). The inset shows details near the tricritical point. The data points with arrows represent pressures where no superconductivity was observed, down to the temperatures shown.

SDW and superconducting states is crossed by only a change of temperature. We observe this behavior over the pressure range from 6.0 to 6.2 kbar, the limitation being that the superconducting transition is depressed below our minimum temperature of 1.04 K.

We can eliminate the possibility of pressure gradients across the sample giving this unexpected behavior as a large pressure inhomogeniety would be required. Based on much experience with the technique, it is unreasonable to have such a gradient in the solid He pressure medium. Furthermore, the superconducting transition is extremely narrow -- an indication of uniform conditions on an unstrained sample. We also rule out the possibility that some portions of the sample are in the SDW state and others in the superconducting state from the observation that both the single resonance and the superconducting transition are sharply quenched upon entry into the SDW region. Finally, this behavior is consistent with earlier observation in this pressure range of an increase in resistivity with decreasing temperature, just before the sample becomes superconducting.

This type of competition between SDW, metallic and superconducting ground states has been treated theoretically by Yamaji.[5] He predicts a range of interchain transfer energy where a first order phase boundary exists between superconductivity and the SDW. His calculations give a width of 0.5 kbar for the "reentrant" region where the phase boundary between SDW and superconductivity exists. Clearly, lower temperature measurements are needed to test this prediction.

We have applied this contactless technique to a lesser extent to $(TMTSF)_2FSO_3$, $(TMTSF)_2ClO_4$ and to $(BEDT\text{-}TTF)_2BrO_4$ indicating that it has wide applicability. Very recently we have made preliminary investigations of the new ambient pressure superconductor

$(BEDT\text{-}TTF)_2I_3$ using this technique. We find a very strong depression of T_c with pressure (of the order of 0.9 K/kbar) and indications of magnetic ground states at modest pressure.

SUMMARY

We have shown that the metallic, spin density wave and superconducting states of organic conductors can be monitored by use of a contactless technique. Many pressure temperature cycles are possible resulting in an extremely accurate determination of the phase diagram. In $(TMTSF)_2PF_6$ we observe successive metallic, spin density wave and superconducting states at a given pressure by lowering temperature. This behavior is in agreement with recent theoretical modeling of Yamaji.

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