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Competition between superconductivity and spin-density waves in an organic conductor, bis-tetramethyltetraselenafulvalenium hexafluorophosphate

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The pressure-temperature phase diagram of the organic superconductor bis-tetramethyltetraselenafulvalenium hexafluorophosphate [$(TMTSF)_2PF_6$] has been carefully measured by electron-spin resonance in a single crystal at low magnetic fields. We present the first microscopic evidence for the transition from the spin-density-wave state to superconductivity as the temperature is lowered at constant pressure. Comparison is made with recent theoretical calculations on the competition between spin-density-wave and superconducting ground states.

INTRODUCTION

Since the discovery of superconductivity in organic metals[1] a great deal of research has been concentrated on the details of the pressure-stabilized metallic state. Pressure suppresses the spin-density-wave (SDW) transition and a knowledge of its effect is essential in studies of the physics of the competition between the SDW and superconductivity. Previous attempts at defining phase diagrams have been hampered by imprecise pressure measurement in solid media and the fact that electrical contracts on crystals usually do not survive several temperature or pressure cycles.

Based on earlier work[2] we use a contactless technique to monitor the metallic, SDW, and superconducting states. We exploit the fact that the electron-spin resonance (ESR) in the metallic state in the $(TMTSF)_2X$ Bechgaard salts, where TMTSF means tetramethyltetraselenafulvalene, is relatively narrow.[2,3] We measure the low-field ESR resonance with a radio frequency coil wound directly on a single-crystal sample mounted inside a pressure vessel. He gas pressure[4] techniques enable us to apply pressure at temperatures as low as 50 K thus reducing strains and pressure inhomogeneities due to solidification of the pressure medium. This technique allows indefinite cycling of pressure and temperature without harming the sample. We find a narrow pressure range where, with only a decrease in temperature, the metallic, SDW, and superconducting phases are successively observed. This observation is the first microscopic demonstration that the superconducting phase extends below (in temperature) the SDW phase along an isobar.

EXPERIMENTAL DETAILS

The samples used in this study were platelets of dimensions 0.3 mm×0.6 mm×1 mm. That the samples were single crystals was confirmed by x-ray analysis. After measuring the dimensions of the sample, a radio frequency coil made of 50-μm copper wire was wound in a rectangular configuration to optimize the filling factor. The rf coil and sample were then mounted inside the Be-Cu pressure vessel. The sample was oriented so that the magnetic field could be rotated in the b-c plane of the crystal (a axis is the highly conducting direction at 300 K). Pressures are accurate to 0.1 kbar. Temperatures below 4 K were measured by the vapor pressure of liquid He in which the bomb was immersed and temperatures above 4 K were measured by a calibrated resistance thermometer. The ESR signal was detected by the use of a Q-meter circuit.[5] The resonance frequency of 28 MHz corresponds to a resonance field of 10 Oe. Field modulation was employed and the first derivative of the resonance was measured. The ESR peak-to-peak linewidths were 1 Oe in the low-temperature, high-pressure metallic regime, in agreement with earlier low-field measurements.[2]

The usefulness of this technique comes from the observation that the ESR signal and the measured absorption in the rf coil are strongly dependent upon the magnetic state of the sample. In the high-temperature, high-pressure regime, the ESR signal is narrow and the susceptibility is independent of temperature, indicative of a Pauli state and SDW state is

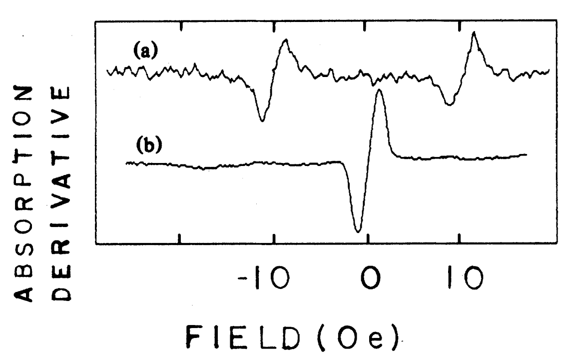

FIG. 1. Electron-spin resonance derivative signal (upper curve) vs applied magnetic field at 29.007 MHz, 6.6 kbar, and temperature 1.123 K. The resonances correspond to positive and negative magnetic fields of 10.4 Oe. The lower curve is taken at a temperature of 1.044 K with 1/40 of the gain and depicts 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 is the upper critical field, H_{c2}.

very sharp as one decreases the temperature at constant pressure, typically having a width in temperature of 0.1 K. The ESR signature in the metallic state is shown in Fig. 1(a).

Passage into the superconducting state at higher pressure and the Meissner currents induced in the sample led to a change in the inductance of the rf coil. We can also observe both the lower and upper critical fields, H_{c1} and H_{c2}, respectively [see Fig. 1(b)]. This transition width is extremely narrow, typically 10 mK wide. In addition, while at a pressure and temperature where superconductivity is observed at zero field, increasing the field above the upper critical field enables one to recover the normal state and the ESR should be observable. If, on the other hand, no ESR signal were observed, then the occurrence of spin-density waves could be inferred.

RESULTS

The pressure-temperature phase diagram depicting the metallic, SDW, and superconducting (SC) regimes is shown in Fig. 2. The inset shows the detailed behavior near the superconducting transition. The SDW transition at zero pressure occurs at 12 K in agreement with other measurements.[6] The superconducting transition is observed from 6.1 to 6.8 kbar and due to temperature limitations (our lowest temperature was 1.04 K) is not observed above these pressures. The superconducting transition is very sharp; typically 10–20 mK in width.

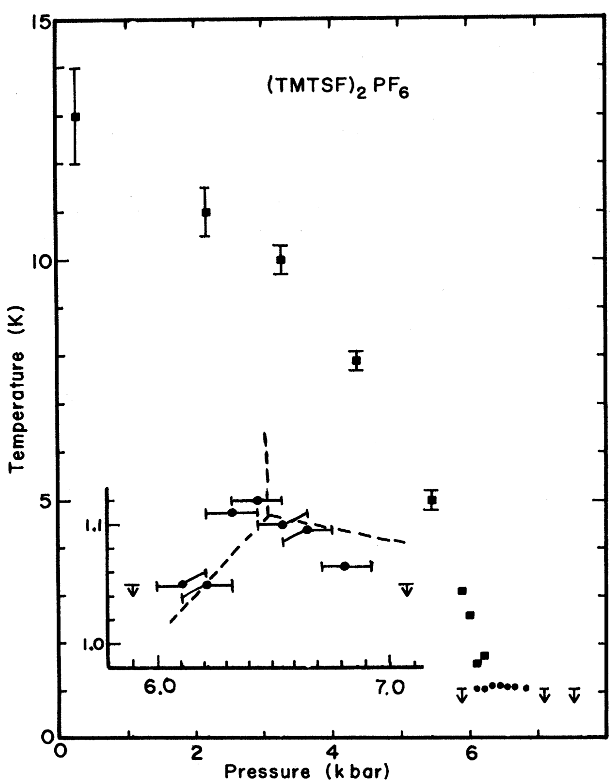

FIG. 2. Temperature-pressure phase diagram showing metallic-SDW transitions (boxes) and superconducting transitions (circles). The inset shows details near the tricritical point. Also shown are theoretical calculations by KY as discussed in the text. The data points with arrows represent pressures where no superconductivity was observed, down to the temperatures shown.

Unusual behavior occurs in a pressure range around 6.1 kbar where, upon lowering the temperature at constant pressure, we observe the metallic SDW, and finally the superconducting state. Here the phase boundary between the SDW and superconducting states is crossed by only a change of temperature. This behavior is observed over the pressure range from 6.0 to 6.2 kbar and may extend to lower pressure (our lowest temperature was 1.04 K).

One might argue that uninteresting mechanisms such as pressure or sample inhomogeneities, are responsible for this behavior. It is difficult to imagine that large pressure gradients exist across the sample due to the He gas presssurization method employed and the fact that the He solidifies at temperatures below 50 K and therefore differential thermal contractions between the pressure medium and sample are minimal. Furthermore, one would need on the order of kbar pressure inhomogeneities across the sample volume to account for our observations. Finally, the superconducting transition is very narrow indicative of an unstrained sample.

We can also rule out the possibility that some portions of the sample are in the SDW state and other parts are in the superconducting state from the observation that T_c is suppressed in this pressure regime and that a single resonance is observed (see Fig. 1).

We are confident that we have an unambiguous microscopic demonstration of a phase boundary between the SDW and superconductivity that is accessible by only a change of temperature. This behavior is consistent with the observation that the resistivity in this pressure range increases slightly before passing into the superconducting state at lower temperature.

INTERPRETATION

Recent theoretical calculations[7,8] by Yamaji address the problem of the competition between the SDW, metallic, and superconducting states in the Bechgaard salts. Yamaji uses a quasi-one-dimensional Hubbard model with both interchain and intrachain coupling. He concludes that there is a narrow range of interchain transfer energy t' where a first-order phase boundary exists between superconductivity and the SDW. The superconducting state extends into the SDW regime and in this sense the superconductivity could be termed reentrant. The role of pressure is to change t'. According to these calculations, the tricritical point occurs at a value of $t_c' = 287.5$ K in his units. The interchain transfer, t' is considered to be pressure dependent.

The reasoning for the extension of the superconducting phase below the SDW phase is as follows. On the boundary between the metallic and SDW phases the free energy of the metallic and SDW are equal, by definition. At a critical pressure, P_c (corresponding to $t_c' = 287.5$ K), above which the SDW is suppressed to zero temperature, superconductivity occurs when the free energy of the superconducting state is less than the free energy of the metallic state. Yamaji argues that it is reasonable to expect the free energy of the superconducting state to be less than the SDW state for some pressure range such that $P < P_c$. The range over which this "reentrant" regime extends into the SDW regime is determined by

$$\Delta t' = N(0)\Delta^2(0)/[\partial N(0)\epsilon_0^2(t')/\partial t']_{t'=tc'}$$

where $N(0)$ is the density of states, $\Delta(0)$ is the zero-temperature gap parameter, and ϵ_0 is given by $\epsilon_0(t') = t_1 t'^2/2t_2^2$ with $t_1 = t\cos ak_F$ and $t_2 = t\sin ak_F$. Here t is the intrachain transfer and t' is the interchain transfer. Yamaji found $\Delta t' = 0.3k_B$ for the reentrant regime. In order to cast these units into a corresponding pressure range, we use the known dependence of the interchain transfer on pressure from the depression of T_c as $dt'/dP = 0.3k_B$/kbar and obtain a width of 0.5 kbar for the reentrant regime.

The data in the vicinity of the peak in T_c strongly support theory although our measurements do not extend low enough in temperature to provide the definitive test. The calculated SDW-SC boundary shown in Fig. 2 is quite consistent with the data. Certainly our direct observation of the successive transitions from metallic (observation of ESR) to SDW (disappearance of ESR) to superconductivity demonstrates that the SDW and superconducting phases exist along an isobar. A systematic survey to lower temperature is needed for a critical test of theory. Earlier work by Brusetti, Ribault, Jerome, and Bechgaard[9] observed similar effects in the $(TMTSF)_2AsF_6$ salt by the use of resistivity measurements. They found that the superconducting state in the AsF_6 derivative could be reached from the semiconducting state by only a temperature change for a certain narrow pressure range.

CONCLUSIONS

We have demonstrated that the metallic, spin-density-wave, and superconducting states can be easily monitored by the use of a contactless technique. An extremely accurate and reproducible phase diagram can be mapped out in the temperature-pressure plane. Furthermore, this technique has the advantage that many pressure and temperature cycles are possible without damaging the sample. We observe multiple transitions from metallic to SDW to superconducting states as a function of temperature over a narrow pressure regime. These measurements show that it is possible to pass directly from an ordered magnetic state (i.e., SDW) to superconductivity by a change of temperature. Calculations of Yamaji agree with our measurements.

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