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Pressure-temperature phase diagram, inverse isotope effect, and superconductivity in excess of 13 K in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene

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The pressure-temperature phase diagram of the highest-T_c organic superconductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is determined, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene. Semiconducting, insulating, metallic, and superconducting regimes are seen at pressures below 1 kbar. Superconductivity at 12.5 K and 0.3 kbar *increases* by 0.5–1.5 K upon deuteration of BEDT-TTF, in striking contrast to the normal isotope effect determined previously for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br.

INTRODUCTION

Organic superconductivity is a relatively new phenomenon. Its discovery at 0.9 K under pressures of over 10 kbar a decade ago[1] was followed by a steady stream of new materials with ever higher superconducting transition temperatures.[2] The (BEDT-TTF)$_n X_m$ family of organic charge-transfer salt [where BEDT-TTF, or ET, is bis(ethylenedithio)tetrathiafulvalene] has produced the largest number of organic superconductors, with several members now having superconducting transition temperatures, T_c, over 10 K. These members are κ-(ET)$_2$Cu(NCS)$_2$ with $T_c = 10.4$ K,[3] κ-(ET)$_2$Cu[N(CN)$_2$]Br with $T_c = 11.6$ K,[4,5] which currently represents the highest ambient-pressure T_c for an organic superconductor, and the isostructural analogue κ-(ET)$_2$Cu[N(CN)$_2$]Cl with $T_c = 12.8$ K at 0.3 kbar,[6,7] which represents the highest achieved T_c for an organic superconductor.

The electrical transport in these κ-phase organic charge-transfer salts, each of which possesses a similar crystallographic packing motif for the ET donor molecules, is unusual. At temperatures above 100 K at ambient pressure, the electrical resistivity exhibits semiconductive behavior. Below 100 K at ambient pressure, κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br become metallic conductors and finally superconductors. However, κ-(ET)$_2$Cu[N(CN)$_2$]Cl at ambient pressure remains semiconductive below 100 K and finally undergoes a transition near 40 K to an insulating ground state.[6] The superconducting state is realized only with the application of a mild hydrostatic pressure[6] or some simple mechanical stress such as frozen stopcock grease.[7] In this paper we present a study of the pressure-temperature phase diagram of κ-(ET)$_2$Cu[N(CN)$_2$]Cl, which reveals a hierarchy of transitions ranging from insulating-to-semiconducting through metallic-to-superconducting behavior.

Also in this paper, we report on the isotope effect for κ-(ET)$_2$CuN(CN)$_2$Cl with substitution of deuterium for the normal hydrogen atoms in the ET molecule. Although the isotope effect is an important probe of the influence of phonons on superconductivity, such effects for organic superconductors have not been extensively studied, and the results are inconsistent. The organic superconductor (TMTSF)$_2$ClO$_4$ ($T_c = 1$ K) with deuterium substitution possesses a "normal" isotope effect,[8] i.e., a decrease in T_c with increase in mass, in accordance with elementary BCS theory. However, with deuterium substitution, β-(ET)$_2$I$_3$ ($T_c = 1.15$ K) exhibits an "inverse" isotope effect,[9] whereas its pressurized phase β^*-(ET)$_2$I$_3$ ($T_c \sim 8$ K at 0.5 kbar) exhibits a normal effect.[10] Moreover, with deuterium substitution, κ-(ET)$_2$Cu(NCS)$_2$ shows an inverse effect[11] and κ-(ET)$_2$Cu[N(CN)$_2$]Br shows a normal effect.[7] It is therefore of interest to investigate the isotope effect for κ-(ET)$_2$Cu[N(CN)$_2$]Cl. In fact, we observe an *inverse* isotope effect for this salt with deuterium substitution, in contrast to the normal effect exhibited by its isostructural Br analogue, and this effect amounts to a substantial increase in T_c, which establishes the deuterated salt κ-(d_8-ET)$_2$Cu[N(CN)$_2$]Cl as a new record holder for the highest achieved T_c for an organic superconductor.

EXPERIMENT

Synthesis of the κ-(ET)$_2$Cu[N(CN)$_2$]Cl samples was described previously[6] and the deuterated material, κ-(d_8-ET)$_2$Cu[N(CN)$_2$Cl, was prepared similarly with the use of deuterated ET. Superconducting transition temperatures were detected by the use of a rf impedance technique[12] in which the single-crystal samples were slipped into custom wound rf coils (typically 0.025-mm-diam wire). The onset of the signature detected with this technique corresponds to the onset of diamagnetism detected with a superconducting quantum interference device (SQUID) magnetometer. This correspondence has been demonstrated on a large variety of organic, high-T_c ceramic oxide, and conventional superconductors. The temperature determination was made by use of a carbon-glass resistance thermometer anchored to the outside of the pressure vessel immediately adjacent to the sample. The thermometer calibration was checked regularly against the vapor pressure of ^{4}He and against known superconducting transitions. An internal calibration with a piece of Nb affixed to the rf coil was also used in these studies.

Four terminal resistance measurements were also used to detect the superconducting transitions and to monitor the other electronic transitions discussed below. Temperature was varied by lowering the pressure system toward a ^{4}He bath and data were taken both increasing and decreasing temperature. Pressures were generated in He gas and were, therefore, completely hydrostatic for the low-pressure (<1 kbar) aspects of the work. At higher pressures, the He freezes, so that hydrostatic conditions were achieved by careful isobaric freezing of the He about the sample assembly.[13]

RESULTS AND DISCUSSION

κ-(ET)$_2$Cu[N(CN)$_2$]Cl crystals were found to be semiconducting down to ~40 K where "insulating" behavior began. No indication of superconductivity was observed on unconfined or unstressed samples. A very slight hydrostatic pressure was found to sharply depress this "semiconductor-insulator" transition at a rate of ~150 K/kbar. By 0.2 kbar, the observed "semiconducting" behavior was replaced near 70 K by metallic behavior (i.e., the resistance decreases with temperature). Figure 1 shows a plot of resistance versus temperature at 0.4 kbar. The peak in resistance is defined as the boundary between semiconducting and metallic behavior. The "semiconductor-to-metal" transition was found to increase strongly at low pressures and then at a more gradual rate with further increases in pressure. Measurements on several crystals, with both normal and deuterated ET, showed very similar behavior except that the values for the temperature were shifted a few degrees. These differences arise because the choice of the change in slope for the "semiconductor-insulator" transition and the peak in the resistance for the "semiconductor-metal" transition are qualitative and likely sample dependent. In all normal samples, however, an abrupt transition to the superconducting state occurred at 12.8 (±0.3) K, as determined by the rf technique or resistive measurements. The 5–95% resistance transition width was found to be 0.2 K, which is a remarkably sharp transition for an organic superconductor.

Figure 2 represents the pressure-temperature phase diagram that we have determined from our measurements. This diagram exhibits some similarities to the first organic superconductors reported[2] for the (TMTSF)$_2X$ family, with $X=\mathrm{PF}_6^-$ and AsF_6^-. These materials are antiferromagnetic [spin-density wave (SDW)] insulators at ambient pressures and low temperatures. Pressures of 6–10 kbar suppress the transition to this antiferromagnetic state so that metallic behavior and superconductivity at 1–2 K occur. We find similar behavior, except that the room-temperature behavior is semiconducting or occasionally weakly metallic down to ~250 K, after which it becomes semiconductive, and both the "insulating" and "semiconducting" regions of the phase diagram must be depressed with pressure before the metallic and superconducting regimes are accessed. Further studies are necessary to identify in detail the nature of the "insulating" phases. We wish to emphasize, however, that the suppression of an insulating state to achieve a metallic state with an applied pressure of only 0.3 kbar represents the lowest known pressure for such a suppression in an organic superconductor.

Replacement of the eight hydrogen atoms with deuterium in the ethylene groups of the ET molecule has a dramatic effect on T_c, as shown in Fig. 3. This figure also shows a large effect of pressure on T_c. The values of T_c are higher for the deuterated than the normal salt at every pressure. One sample shows an enhancement at each pressure of 1.5 K with deuteration. A second sample (shown as the points between the curves in Fig. 3) is less enhanced. To ensure that the difference was real, the resistance of a deuterated and a nondeuterated sample was measured in a series resistance configuration with the crystals in close physical proximity. Thus, the *difference*

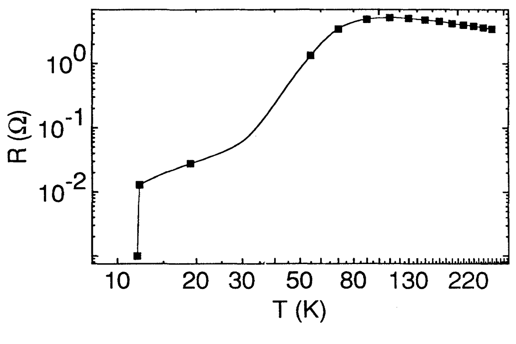

FIG. 1. Resistance vs temperature at 0.4 kbar for the deuterated salt κ-(d_8-BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The curve for the normal salt is very similar, and the solid line indicates the totality of several different measurements.

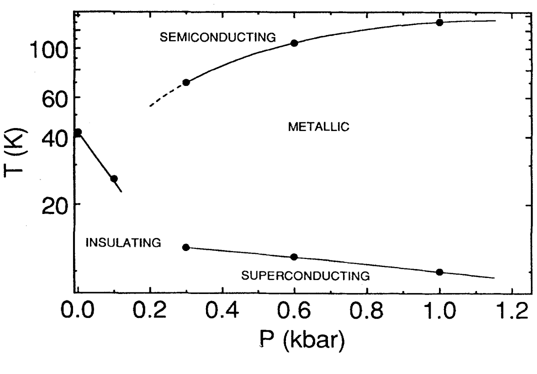

FIG. 2. Pressure-temperature phase diagram κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The region between 0.1 and 0.3 kbar is not well established because of experimental difficulties at these low pressures.

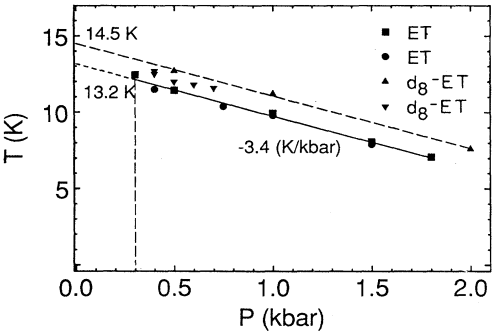

FIG. 3. Superconducting transition temperature vs hydrostatic pressure for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and the isostructural deuterated salt κ-(d_8-BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.

in T_c was measured very accurately to be 0.5 K at each pressure. This result is completely consistent with the data shown in Fig. 3.

Because of experimental difficulties at the low pressures, we are unable to make a direct evaluation of the isotopic shift at the pressure thresholds of superconductivity which were 0.3 kbar for h_8-ET and 0.4 kbar for d_8-ET. Furthermore, our data indicate problems with sample-dependent T_c's which are common to all organic superconductors. However, the data indicate a definite *inverse* isotope effect with an upward shift of *at least* 0.5 K and as large as 1.5 K. This places the threshold T_c of κ-(d_8-ET)$_2$CuN(CN)$_2$Cl in excess of 13 K near 0.3 kbar. Like its undeuterated analogue, κ-(d_8-eT)$_2$CuN(CN)$_2$Cl has a very large negative-pressure coefficient for T_c: $dT_c/dP = -3.2$ K/kbar. This is larger than the previous record value for dT_c/dP of -3.0 K/kbar that we observed[14] in κ-(ET)$_2$Cu(NCS)$_2$ and the value[15] of -2.4 K/kbar in κ(ET)$_2$Cu[N(CN)$_2$]Br. If we were able to retain the superconducting phase in the best deuterated material at ambient pressure, Fig. 3 projects a T_c well over 14 K.

The occurrence of an inverse isotope effect for κ-(ET)$_2$Cu[N(CN)$_2$]Cl is not unexpected in view of the precedent for inverse effects established by the β-(ET)$_2$I$_3$ and κ-(ET)$_2$Cu(NCS)$_2$ organic salts. However, the *difference* in isotope effects for κ-(ET)$_2$Cu[N(CN)$_2$]Cl and κ-(ET)$_2$Cu[N(CN)$_2$]Br (normal effect) is surprising because these two salts are strictly isostructural. Perhaps the difference reflects a subtle variation in the strengths of the Coulomb interactions that govern the competition between the insulating and metallic (superconducting) ground states. As shown by Swihart,[16] differences in the Coulomb interactions of elemental superconductors are the source of deviations from the simple BCS prediction for the isotope effect, $T_c \propto M^{-1/2}$, where M is an elemental mass. An inverse isotope effect does not rule out superconducting electron pairing by phonon mediation. Recent theories for the organic superconductors have shown that an appreciable inverse isotope effect can be accounted for within the framework of the BCS model through coupling with intramolecular vibrations of the organic donor molecules.[17,18]

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