Superconducting Meissner effect under hydrostatic pressure in the ambient-pressure semiconductor κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene

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The known pressure-induced superconductivity in single crystals of κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene has been investigated by static measurements of the diamagnetic shielding and Meissner magnetizations. It is of special interest, since according to previous resistivity measurements, the transition occurs directly from a semiconducting to a superconducting state. The first traces of diamagnetism are observed at a pressure of 80 bars. Both its magnitude and its transition temperature first increase monotonically with pressure, then increase abruptly (between 150 and 200 bars) to develop into a shielding signal of 75% of its ideal value, with a Meissner effect of 25%. At still higher pressures the magnitude of both Meissner and shielding signals becomes pressure independent, while T_c, after reaching a maximum near 13 K, decreases in a fashion similar to related organic superconductors.

I. INTRODUCTION

Organic superconductivity very often manifests itself in the vicinity of the metal-insulator transition. The inherent instability of the metallic state in these materials is principally caused by the low dimensionality of their electron structure and often displays itself in the development of charge- or spin-density-wave states. It is still not known whether these collective phenomena play a role in the formation of the superconducting (SC) state.

A most attractive example for studying the interplay between insulating and superconducting ordering is the compound κ-(BEDT-TTF)$_2$Cu (N(CN)$_2$)Cl. This compound is an ambient pressure semiconductor and begins to be superconducting under rather small pressures of 300 (Ref. 1) or even 90 bars.[2] Most interesting is the fact that the SC transition in the pressure range from 90 to 150 bars starts, according to resistivity measurements,[2] immediately from the high-ohmic semiconducting state. It should be noted, however, that the resistively observed transition could result from filamentary or surface superconductivity. In order to further test this, we have carried out static measurements of both the diamagnetic shielding and the Meissner susceptibilities of this material in the same pressure range.

II. EXPERIMENT

The samples were prepared by essentially the same method as reported before.[2] Single crystals of κ-(BEDT-TTF)$_2$ Cu(N(CN)$_2$)Cl were grown by electrochemical oxidation of BEDT-TTF in 1,1,2-Trichloroethane (TCE) under a constant current of 0.44 mA, using a mixture of 18-crown-6 ether, CuCl, and NaN(CN)$_2$ as an electrolyte. The measurements were carried out using a S.H.E. DC SQUID system model 440 for monitoring magnetization changes, and a UNIPRESS helium-gas pressure apparatus, with which pressures can be generated and changed at any temperature down to the solidification pressure of helium.

Since we want to study superconductivity in very low applied fields, the earth magnetic field is shielded by a double μ-metal shield around the whole cryostat, resulting in a residual field of about 0.05 mOe. The pressure cell was directly immersed in liquid helium, with heaters attached to it to warm it above 4.2 K during pressure changes. A cross section of the pressure cell is shown in Fig. 1. Its cylindrical inside volume of 0.7 cm diameter and 3.5 cm length contained a thin-walled lead-free brass

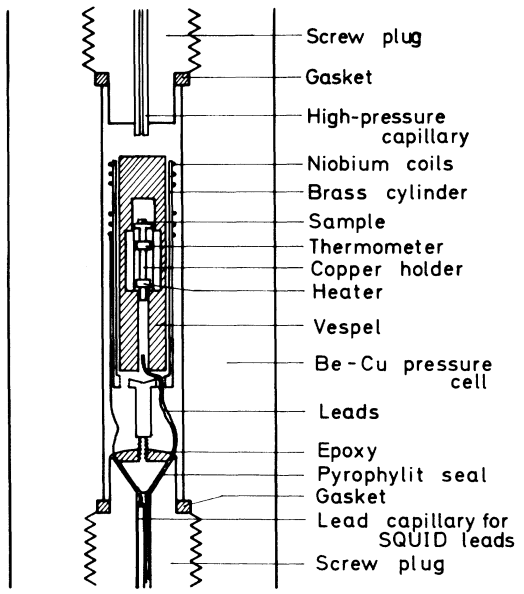

FIG. 1. Measuring arrangement inside the helium-gas pressure cell.

cylinder on to which two counterwound Nb coils (three turns each) of a SQUID detection system were located. These Nb leads, together with sample heater and thermometer leads, were led out of the presssure cell through a conical high-pressure seal using pyrophylite and epoxy as sealing agents. The samples were located on a copper holder inside a plastic cylinder made out of Vespel, which, in turn, was placed loosely inside the brass cylinder. This permitted the samples to be heated to temperatures around 20 K, while leaving the temperature of the brass cylinder and the Nb coils below 9.2 K (the T_c of Nb). In order to perform our investigation of the very delicate pressure effect under strain-free conditions, crystals of κ-BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl were attached to the copper holder using only cotton located inside the Vespel cell, without any grease. A small amount of grease was used to fix in place on the same surface the small reference samples of Pb, Nb, and Nb_3Sn. The superconducting transitions of these samples were used to calibrate our *in situ* thermometer at *every pressure.* Both thermometry and heating were done with RuO_x-chip resistors of dimensions $1.5\times2\times0.5$ mm, which were soldered to the copper holder with indium (Fig. 1). A carbon resistor of similar size was also used as a thermometer in a few experiments. When heating and cooling at high pressures, the solid helium inside the presssure cell was transformed into (overcritical) liquid and back to the solid. This sometimes resulted in forces between the Vespel and the brass cylinders, leading at times to breaks in the electrical leads. Although care was taken to run the heater leads in parallel in order to avoid the generation of stray magnetic fields, a small such effect is left over and is the cause of the slight downward curvature of the curves of Fig. 2 between the SC transitions.

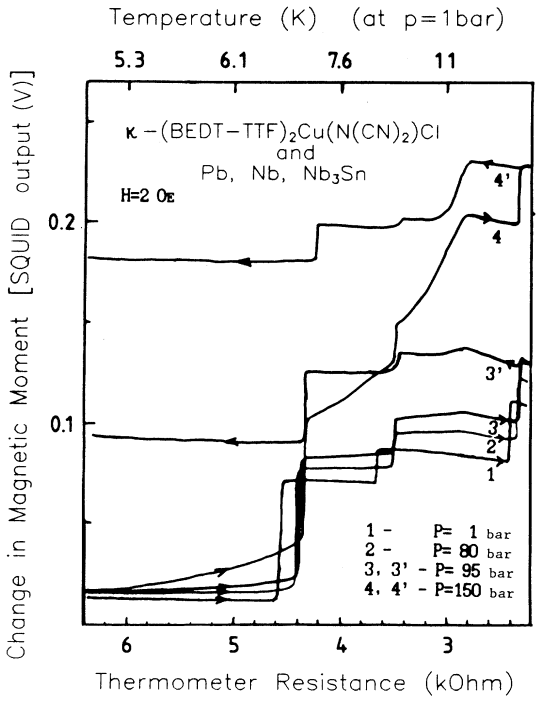

FIG. 2. Plot of change in the magnetic moment of a single crystal of κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl and calibration samples of Pb, Nb, and Nb_3Sn vs carbon thermometer resistance at different pressures. Both warming (shielding) and cooling (Meissner) curves are presented. The appropriate values of temperature at ambient pressure are shown at the top of the frame. Values for curve 3' (Meissner signal at $P=95$ bars) are scaled up two times for visuality.

III. RESULTS AND DISCUSSION

The diamagnetic moment of a single crystal of κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Cl in a constant magnetic field of 2 Oe applied along the crystallographic b^* axis (i.e., normal to the conducting ac plane), measured together with small calibration samples of Pb, Nb, and Nb_3Sn, is shown in Fig. 2. Data are presented for four pressures: 1, 80, 95, and 150 bars. At every pressure the sample was first cooled down to 4.2 K in zero field, then the field was applied and the diamagnetic shielding signal was recorded upon warming the sample. Up to a pressure of 73 bars, no diamagnetic signal was observed. At 80 bars, however, we clearly see a small diamagnetic shielding signal which vanishes above 11.7 K. On subsequent cooling in the same field, a definite small Meissner effect was also observed below 11.7 K. With increasing pressure, both the shielding and Meissner signals increase, and so does the transition temperature, above which they vanish. The transitions are initially quite wide (~5 K), getting narrower as the pressure increases. At 150 bars, the shielding signal corresponds to $\sim13\%$ of the ideal diamagnetic value, and the Meissner effect (determined as the ratio of Meissner to shielding signal in the same magnetic field of 2 G) is about 30%. The evolution with pressure of both shielding and Meissner signals in a field of 1 G (for two samples) is shown in Fig. 3. Above 150 bars, there is an abrupt increase in the diamagnetic signals to a

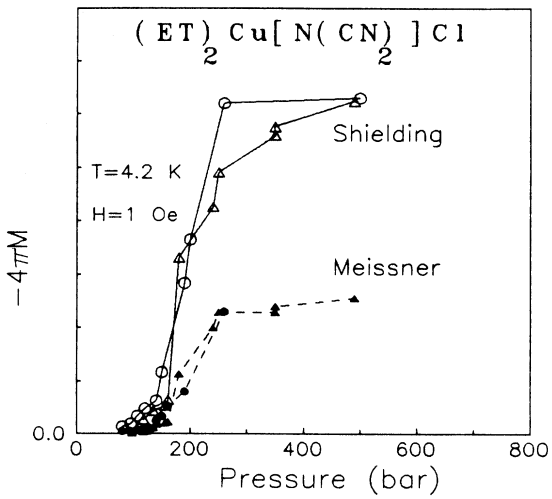

FIG. 3. Pressure dependence of the diamagnetic shielding and the Meissner expulsion in the field of $H=2$ Oe normal to the conducting ac plane of the crystal. Data for two samples are shown.

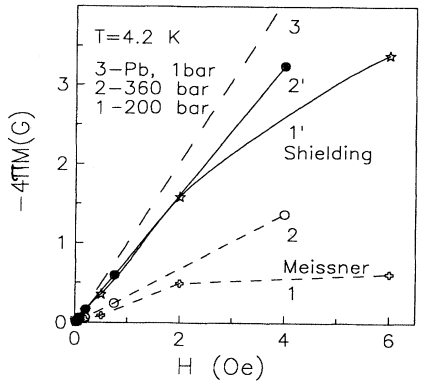

FIG. 4. Diamagnetic magnetization vs field applied normal to the conducting ac plane for two crystals (curves 1, 1′ and 2, 2′, respectively) at $T=4.2$ K and under pressures of 200 and 360 bars.

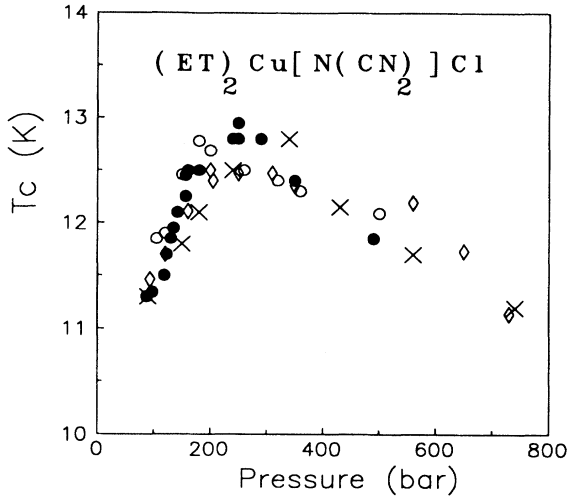

FIG. 5. T_c as a function of pressure derived from the onset temperature of the Meissner effect for three crystals (circles and rhombus) and from the superconducting resistive transitions (crosses, from Ref. 2).

value which remains constant at pressures above 250–300 bars and which amounts to 75% of ideal diamagnetic shielding. The Meissner effect in this finally developed SC state is about 25%.

The limiting value of ~ 75% of bulk SC's found at 4.2 K is similar to those found in the other "high-T_c" organic SC's with T_c exceeding 10 K, namely, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Refs. 3 and 4) and κ-(BEDT-TTF)$_2$Cu(N(CN)$_2$)Br.[5] This reduced value cannot possibly be explained by a field penetration effect, since the London penetration depth for fields normal to the conducting plane is still much smaller than the sample size.[6,7] We, therefore, must conclude that the sample is not entirely and homogeneously superconducting.

The magnetic field dependence of the magnetization also shows features common to all "high-T_c" organic superconductors. Our data obtained for two samples at two different pressures are presented in Fig. 4. At 4.2 K and in small applied fields, the magnetization initially follows the linear (type-I) behavior, and starts deviating from this behavior in higher fields. Taking account of the demagnetization effect, the lowest observed value of the lower critical field H_{c1} is about ~10 Oe at 4.2 K.

Figure 5 shows the onset temperature of diamagnetism (obtained from the onset of the Meissner effect) as a function of pressure for three crystals. These T_c vs P data coincide quite well with those from resistivity measurements[2] (also plotted for comparison in Fig. 5). Most notable is the fact that in the pressure range where the SC develops (see Fig. 3), T_c is increasing rapidly. After reaching the maximum SC fraction of 75%, T_c also shows a maximum of about 12.8 K and then starts decreasing with further increase of pressure in the usual manner.

Comparing our data with those of Ref. 2, we have thus shown that for pressures above 200 bars, where the crystals are in a metallic state,[2] they show bulk superconductivity with a Meissner effect of about 25%. At lower pressure, where they are in a semiconducting state, they show superconductivity only in a small volume fraction of the crystal. It would be natural to assume that this same volume fraction is in a metallic state and that the transition from a semiconductor to a metal does not occur homogeneously in the sample. This, however, does not yet explain why this fraction increases its T_c so rapidly with increasing pressure. This interesting fact seems to point to a direct relation between those interactions which cause the carriers to localize (in the semiconducting state) and the pairing interactions in the superconducting state.

In principle, the observed small initial superconducting fractions could also result from small carrier densities, which rapidly increase with pressure and which cause the London field penetration depth to initially be larger than the sample size. In this case, however, we would expect the initial shielding and Meissner signals to be of the same size (since no flux trapping should be possible), which is not what we observe.

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