Reentrant Meissner effect in the organic conductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl under pressure

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(Received 31 January 1994)

Metallic κ-(BEDT-TTF)$_2$Cu[N(CN$_2$]Cl turns semiconducting and insulating at low temperatures and ambient pressure and enters a ferrimagneticlike state below 20 K. Under hydrostatic pressure ($p \cong 300$ bar), previous investigations have shown that the metallic state can be stabilized and that reentrant superconducting behavior can be observed (by means of resistivity measurements) in a rather wide pressure range. By means of dc susceptibility measurements, we show that reentrant volume superconductivity actually exists only in a narrow critical pressure range. In contrast to previously found reentrant superconductors, this material does not contain rare-earth magnetic moments.

INTRODUCTION

The charge-transfer salts (BEDT-TTF)$_2$Cu[N(CN)$_2$]X with X = Cl, Br, and I are all isostructural and crystallize in the so-called κ phase.[1] The sensitivity of the electronic properties of the Cl compound to relatively small uniaxial or hydrostatic pressures has been known for some time: While the Br compound is metallic and is a bona-fide superconductor with $T_c = 12$ K showing a Meissner effect of some 40% of the ideal one,[2] the Cl compound only shows traces of superconductivity (SC) when it is cooled in Apiezon grease, these traces arising from a pressure effect due to the contracting grease.[3] A systematic study of the conductivity of the Cl compound as a function of hydrostatic pressure showed that at low pressure, the resistivity first rises slowly on cooling from room temperature, then much more rapidly below 45 K, ending practically in an insulating ground state.[4] This rise is suppressed and metallic behavior is restored at pressures above ~300 bar. At the same time, superconductivity occurs with $T_c = 13$ K, the highest transition temperature to date in an organic superconductor. SC was in fact observed to appear already in the semiconducting state (at $p \sim 100$ bar, Ref. 4), but only in small volume fractions as shown by Meissner-effect measurements.[5]

The next important observation was the evidence of ferro- and antiferromagnetism in the ambient pressure (and semiconducting) state of (BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl by Welp *et al.*[6] By means of magnetization measurements, signs of a Néel state were seen below 45 K, which coincides with the temperature below which the resistivity rises rapidly. Below $T_F = 22$ K, weak ferromagnetic behavior with hysteretic magnetization (including jumplike changes as a function of field and temperature), were observed, although not in all samples.

In this paper, we report on more detailed studies of these unusual magnetic phenomena as a function of pressure. We find that in a narrow pressure interval there is a competition between a magnetic and a SC ground state which leads to reentrance effects (i.e., transition from the SC back to the normal state at lower temperatures). Reentrant SC as a result of competing temperature-dependent interactions between a conduction-electron system and a system of localized magnetic moments has been observed before. Examples are the alloy LaAl$_2$:Ce (Ref. 7) and the compounds HoMo$_6$S$_8$ (Ref. 8) and ErRh$_4$B$_4$.[9] In the present case, however, it is one and the same system of π electrons that is responsible for both magnetism and SC and for the reentrant behavior. The first signs of reentrant SC behavior in this compound has been seen by Sushko *et al.*[10,11] by means of resistivity measurements under pressure.

EXPERIMENT

A special superconducting quantum interference device (SQUID) magnetometer, which is incorporated into a helium gas high-pressure system, was built for this purpose. It consists of a long slim copper-beryllium pressure bomb inside which the samples can be placed without the use of any grease. This bomb fits into a helium insert cryostat for variable temperature. The SQUID field- and detection-coil system is mounted on the outside of this insert cryostat, which is made out of lead-free brass and has an outside diameter of 1.4 cm. The earth field is reduced to less than 5 mOe by placing the whole cryostat (made mostly out of nonmagnetic plastic materials) into a μ-metal shield.

Great care was taken to build the magnetometer itself out of only weakly magnetic materials, in order not to confuse weak sample signals with signals from spurious magnetic impurities. This was done both by proper selection of materials and especially by rigorously etching all parts after machining. The remaining off balance of the two empty detection coils amounts to about 2×10^{-6} emu per Oe applied field.

Single crystals of (BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl were grown by anodic oxidation of (BEDT-TTF) in an electrolyte using Pt electrodes and low current densities ($\leq 1\ \mu A/cm^2$). For the crystals grown in Kyoto, the electrolyte was a mixture of (BEDT-TTF), $NaN(CN)_2$, CuCl, and 18-crown-6 ether, using PhCN with 5% ethanol as a solvent. For the crystals grown in Garching, its composition was (BEDT-TTF), CuCl, and $PPh_4N(CN)_2$ in 1,1,2 trichlorethane with 10% ethanol. We have found that the addition of CuBr enhances crystal growth. Besides a pure Cl crystal, grown at Kyoto University, we have therefore also investigated an alloy crystal of composition $Cl_{0.85}Br_{0.15}$ (as determined by microprobe analysis), grown in Garching. The masses of the typically platelike crystals were about 0.13 mg and their sizes $0.6\times 0.06\ cm^2$ with thickness 0.02 cm.

RESULTS

The crystals were mounted with the field both parallel and normal to the conducting planes formed by the BEDT-TTF-donor molecules (i.e., the *a-c* planes). In the pure Cl crystals and at low pressure, we observe a *spontaneous* magnetization below $T_F = 20$ K even *without* an applied field. This magnetization, an example of which is shown in Fig. 1, can be changed in sign and enlarged in magnitude (but only insignificantly) by an applied field. Its orientation is always in the *a-c* plane in the pure Cl crystal, while in the $Cl_{0.85}Br_{0.15}$ crystal, its predominant orientation is normal to the *a-c* plane. Fields as small as the residual field, which was determined to be -0.004 Oe, are sufficient to switch the sign of this remanence at temperatures around the ordering temperature. If it is the result of a canted antiferromagnetic spin structure, the antiferromagnetic spin alignment (in the pure Cl crystal) would therefore be along the normal to the *a-c* plane. Attempts to see directly the postulated Néel temperature around 45 K (Ref. 6) by the corresponding drop in susceptibility failed, presumably due to our insufficient available field strength ($H_{max} = 80$ Oe).

Upon increasing the pressure, the size of this ferrimagnetic signal diminishes and the ordering temperature decreases. At about 160 bar, the first traces of superconductivity appear. These can be seen either by cooling in small applied fields through the occurrence of a Meissner effect below T_c ($T_c < T_F$), or, more clearly, by cooling in zero field, applying the field and by monitoring the disappearance of the SC shielding signal at T_c.

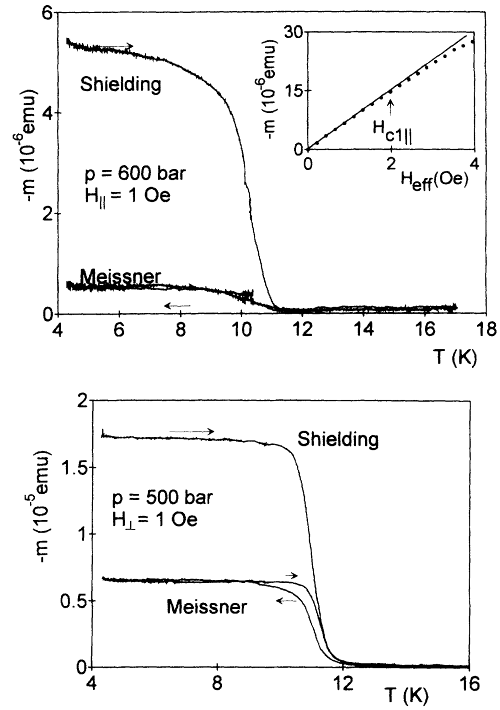

FIG. 2. (a) and (b) SC shielding and Meissner signals at $p = 600$ bar in a field of 1 Oe applied both in the *a-c* plane [(a), $H_\parallel$] and normal to it [(b) $H_\perp$]. Inset: Magnetic moment versus field at 4.2 K.

At pressures above 400 bar, there is no indication any more of ferrimagnetic order. Instead, the crystal is fully SC, showing a Meissner effect of 10% for fields applied in the *a-c* plane [Fig. 2(a)] and 30% in fields normal to it [Fig. 2(b)].

In a critical pressure range, which for the pure Cl crystal is between 290 and 310 bar and for the $Cl_{0.85}Br_{0.15}$ alloy crystal between about 70 and 160 bar, we see clear reentrance effects which must result from a coexistence of ferrimagnetic order and SC on a microscopic scale. The observations in fields parallel to the *a-c* plane are shown in Fig. 3. After cooling in the residual field of -4 mOe

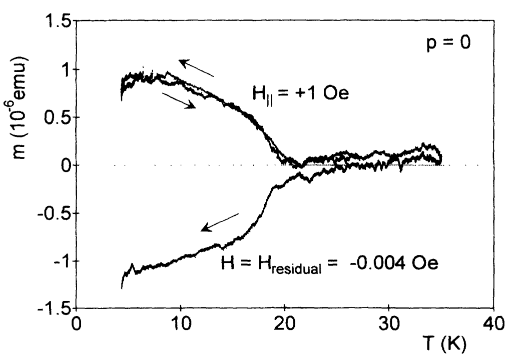

FIG. 1. Spontaneous magnetic moment observed at zero pressure in near zero and in a small applied field.

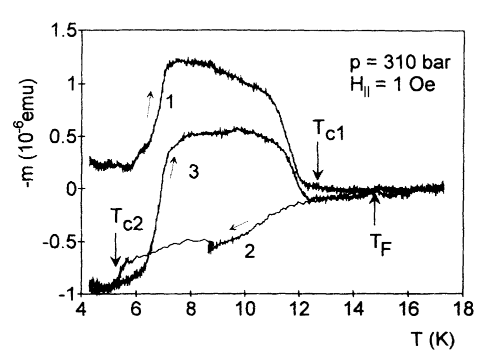

FIG. 3. Reentrant SC behavior at $p = 310$ bar in a field $H_\parallel = 1$ Oe applied in the *a-c* plane (see text).

to 4.2 K, a field of 1 Oe is applied and a small diamagnetic shielding signal is observed. This diamagnetic signal increases with increasing temperature to a maximum of 20% of the full SC shielding signal before dropping to zero at $T_{c1}=12.5$ K, the upper SC transition temperature (curve 1 in Fig. 3). On cooling back in 1 Oe, we still see signs of magnetic order (with a positive magnetization) below the downshifted ordering temperature of $T_F \cong 15$ K (curve 2 in Fig. 3). Below T_{c1}, a small diamagnetic Meissner signal superimposes and disappears again at $T_{c2}=5.2$ K, the lower SC transition temperature. At 4.2 K, we are left with a positive magnetization of the magnetically ordered state. Upon reheating, the Meissner signal now tends to follow more clearly the shielding signal (curve 3 in Fig. 3). This is therefore clear proof of the coexistence of magnetic order and SC.

Even more spectacular results are obtained in the critical pressure range when the field is aligned normal to the *a-c* plane. This is shown in Fig. 4. Again, the sample is first cooled in zero field to 4.2 K. Then a field of 1 Oe is applied and a small diamagnetic shielding signal is observed. Upon increasing the temperature, this signal first drops at 5.7 K, then increases in several discrete steps to a maximum of more than 50% of the full diamagnetic shielding signal (observed at higher pressures) before decreasing to zero at T_{c1} (curve 1 in Fig. 4). On cooling back, the Meissner signal shows almost complete reentrance with a lower transition temperature of $T_{c2}=5.5$ K (curve 2). Upon reheating, the Meissner signal, too, shows a steplike reentrant behavior similar to the shielding signal (curve 3). This again shows that the SC state competes with a presumably complex magnetic state which changes as a function of temperature.

Sushko *et al.*[10,11] found that the reentrant state below T_{c2} is not a good metallic, but a rather highly resistive state (with a resistivity higher than at room temperature). This contrasts with our observation that the reentrant state still contains traces of SC and indicates that we actually have an inhomogeneous reentrant state. At subcritical pressures ($p=240$ bar), Sushko *et al.*[11] find a jumplike increase in resistivity at the magnetic transition (i.e., around 20 K), and already traces of SC manifesting themselves in a drop of resistivity (but not to zero) between T_{c1} and T_{c2}. It seems that the homogeneity of the crystals is critical for observing the reentrant effect in a well-defined pressure range, and our Meissner-effect measurements clearly show that the bulk of the crystal shows the reentrant effect only in a small pressure range and that above that pressure range the bulk of the crystal no longer shows reentrance and stays SC down to low temperature.

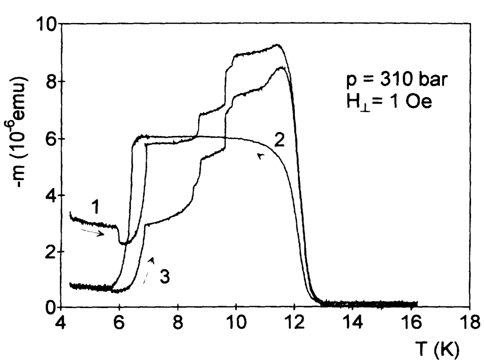

FIG. 4. Reentrant SC behavior at $p=310$ bar in a field of 1 Oe applied in the direction normal to the *a-c* plane (see text).

Sushko *et al.*[12] also investigated the magnetic-field dependence of the reentrant state and finds that high fields increase the resistivity of this state. These results show that even in overcritical fields, where SC is quenched, there still is a transition at T_{c2}, manifesting itself in a sudden increase in resistivity. This then reinforces our belief that the reentrant state must be some magnetically ordered state.

Most recently, the reentrant behavior has also been seen by ac susceptibility measurements.[13,14] Again, however, these measurements yield little more information than the resistivity measurements since they again do not probe the volume properties of the sample.

DISCUSSION

In compounds with a quasi-one-dimensional band structure, the ground state is expected to be either a superconducting state, a Peierls-distorted insulating state or a magnetically ordered spin-density-wave state (also insulating at $T\rightarrow 0$), depending on the relative sizes of overlap integrals (i.e., bandwidth), spin-exchange energies, and electron-phonon interaction energies.[15] In compounds with a quasi-two-dimensional band structure, such as the present compound, these instabilities should be much less pronounced, and it should also be possible to retain a metallic state as the ground state. The first surprise is therefore the proposed antiferromagnetic state below 45 K, and especially, the weak ferromagnetic (or presumably ferrimagnetic) state below 20 K. A possible cause of this is the considerable anisotropy of the two-dimensional band structure. Although the checkerboard-like arrangement of the donor dimers in the κ-phase structure looks fairly isotropic, it is in fact distorted in the orthorhombic structure, this orthorhombic distortion being mostly due to the anisotropy in the anion layers (i.e., their polymer-chain-like structure). This leads to overlaps between sulfur atoms, which are smaller in the direction of the longer *a* axis than in the direction of the shorter *c* axis. It leads to a correspondingly anisotropic Fermi surface, which together with the orthorhombic asymmetry of the Brillouin zone, is thought to cut this zone in the a^*—but not in the c^*—direction.[1] The two-dimensional Fermi surface thus separates into a closed and an open cylindrical sheet. This seems to be true for all κ-phase materials, and is corroborated in the case of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by SdH experiments yielding the predicted size of a closed orbit as well as a larger magnetic breakdown orbit.[16,17]

Now the two open sheets are only slightly warped and not far from planar, and therefore could show nesting properties. If the bandwidth is not too large (~ 0.65 eV, Ref. 1), spin-exchange interactions could stabilize a spin-density-wave structure with a wavelength given by the inverse nesting vector. While this would remove metallic conduction on the open sheets by the formation of an energy gap, metallic conduction could still occur over the closed sheet. This, however, is not what is observed. Both the observed magnetic order and the insulating state must then follow from other peculiarities of the BEDT-TTF-donor molecules and the κ-phase structure. A possible scenario might be as follows: the ethylene end members of the molecule are stable in two out-of-plane conformations. These end members in turn are linked through the hydrogen bridge bonds to the zig-zag chain structure of the anions, which in a way tries to follow the checkerboard-like packing of the donor dimers.[1] The conformational disorder has been linked before to the rather high electrical resistivity of the κ phases, especially the observed maximum in resistivity, which could be due to thermally activated conformational disorder.[18] In the Br compound (which is metallic and superconducting at ambient pressure), the disorder-order transition (on cooling) manifests itself by a sizeable increase in orthorhombic distortion (in the *a-c* plane).[2] The corresponding effect in the Cl compound is considerably smaller, indicating that, at zero pressure, some of the conformational disorder of the ethylene end groups remains frozen in, and, via the hydrogen bonds to the anions, in turn causes orientational disorder in the lattice of donor molecules.[19] This can seriously disturb the band structure and lead to localization of electron states. Within a localized region, the uncompensated spins of the donor dimers will still be antiferromagnetically coupled (as in the metal), but each such region will have one net spin, if the number of carriers in it is uneven. These "lone" spins are also exchange coupled and can now produce long-range antiferromagneticlike order. At low temperatures, the orientational disorder is most pronounced, leading to smaller localization regions and a larger number of lone spins and also to frustration effects which depend on the detailed geometry of those regions. This could eventually account for the observed ferrimagnetic behavior at low temperatures.

Application of hydrostatic pressure stiffens the lattice and makes the disordered states energetically less favorable. The ordered state is metallic and superconducting. We do not believe that the pairing mechanism is a magnetic one (via spin-exchange interactions) but think that it is mediated by the librational motion of the donor molecules which modulates the *S-S* overlaps and thus leads to a strong electron-phonon interaction. This modulation is strongest for a critical overlap, which we seem to obtain at 300 bar and which leads to the large observed SC transition temperature.

In the region of coexistence of superconductivity and magnetic order, the experiments indicate that it is the ferrimagnetic state which tends to destroy superconductivity: As the ferrimagnetic signal disappears, superconductivity starts to appear. This would agree with a conventional BCS superconducting state, which, in principle, is compatible with an antiferromagnetic state. We can only speculate at this time on the microscopic structure in the coexistence region. To explain the reentrance effect, in particular, it is tempting to speculate that it arises when the sizes of the disorder-induced localization regions match the superconducting coherence length. We would like to point out again that the superconducting reentrance is observed in a single conduction-electron system without the presence of bona-fide localized magnetic moments.

ACKNOWLEDGMENT

We would like to thank W. Biberacher, B. S. Chandrasekhar, D. Einzel, and K. Neumaier for reading the manuscript and for clarifying discussions.

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