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Superconducting Transition of a Grease-Coated Crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

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Superconducting transition of the grease-coated crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl has been confirmed. There are at least three types of these crystals with different resistivity behaviors, of which the crystal exhibiting a resistivity anomaly around 50 K, undergoes a superconducting transition at 12.5 K, when it is coated with Apiezon L grease.

Since the discovery of the "κ-type organic superconductor" of BEDT-TTF in 1987, κ-type salts have attracted considerable interest because of their high possibilities for giving superconducting states.[1-5] The organic superconductor with the highest T_c record at present is κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (12.8 K at 0.3 kbar), which transforms to an insulating ground state at ambient pressure.[4] The ambient-pressure organic superconductor with the highest T_c is κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (T_c=11.6 K).[3] They were discovered by the group of Argonne National Laboratory.

Recently we have examined the electrical and structural properties of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X (X=Cl, Br) and have confirmed the "grease-induced superconductivity" of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The black crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X were grown electrochemically according to the procedure analogous to that reported.[6]

Examination of the resistivities of crystals of κ-(BEDT-TTF)$_2$-

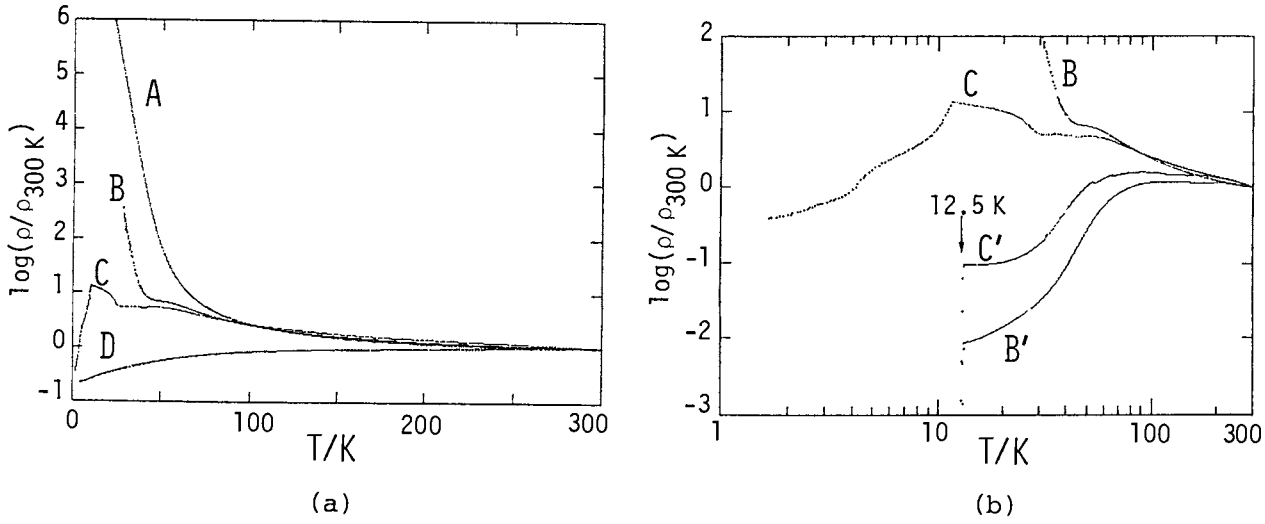

Fig. 1. Resistivities of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.
(a) Resistivities of four samples (A-D) without grease coating.
(b) Comparison of the resistivities with (B′, C′) and without (B, C) grease coating.

Cu[N(CN)$_2$]Cl has revealed that there are at least more than three types of crystals with different temperature dependences of the resistivity (Fig. 1).[7] Sample A (see Fig. 1) exhibited a gradual resistivity increase down to 100 K (ρ(100 K)/ρ(300 K)$\simeq$2, ρ(300 K)$\simeq$0.2 Ω cm) and transformed to an insulator around 60 K. This resistivity behavior is similar to that reported.[6] Wang et al. have pointed out that coating a crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl with Apiezon N grease provides sufficient stress to induce superconductivity.[6] According to them, the effect of the grease is to cause changes in the resistivity (suppression of the insulating state), the ESR spin susceptibility and the onset of a strong diamagnetic signal at 12.5 K, indicating the onset of superconductivity.[6] Although the effect of the grease coating was negligible in the sample A, we have indeed obtained quite sharp resistivity drops in the samples B and C, when they were coated with Apiezon L grease. Before coating, samples B and C exhibited resistivity anomalies around 50 K. At low temperature, sample B became an insulator but sample C showed another resistivity anomaly around 10 K and changed to metallic behavior. Despite the difference in the low-temperature electrical properties of samples B and C, the resistivity behavior of both samples became almost the same after the grease coating. The 50 K anomaly disappeared and the resistivities decreased rapidly below 50 K. Then they showed extremely sharp resistivity drops at 12.5 K, where

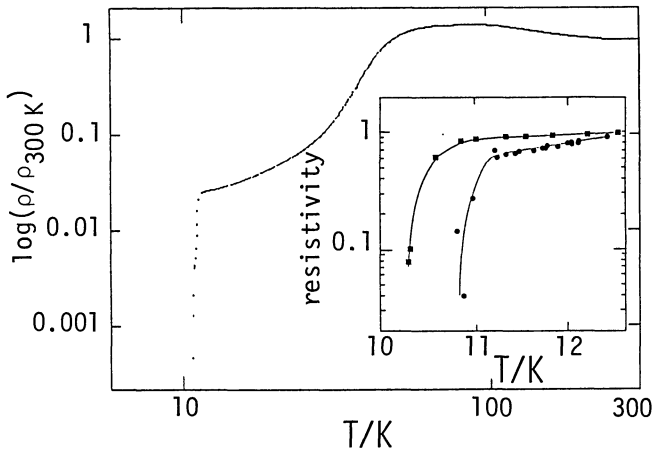

Fig. 2. Resistivities of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br ($\rho_{300\,K} \simeq 0.07$ Ω cm). Inset shows the superconducting transitions of the crystal with (square) and without (circle) grease coating.

the resistivities dropped more than three orders of magnitude within the range of 0.1 K. The initial resistivity behavior was recovered after the removal of the grease. Thus, the "grease-induced superconductivity" of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl has been confirmed by us.

In order to examine the grease coating effect on the superconducting transition temperature of another κ-type superconductor, we have examined the superconducting transitions of the crystals of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with and without grease coating. As shown in Fig. 2, T_c was depressed by about 0.5 K with grease coating. The P-T_c diagram reported by Schirber et al. ($dT_c/dP = -2.4$ K kbar^{-1})[8] indicates that the grease coating described here corresponds to applying a pressure of about 0.2 kbar.

There is another type of the crystal (sample D) that exhibits metallic behavior down to 4.2 K (Fig. 1), whose resistivity behavior was not affected by the grease coating. X-Ray diffraction patterns of samples A, C, and D were examined after the resistivity measurements. The lattice constants were identical to those of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.[6] Further work will be required in order to clarify the origin of "the extraordinary grease effect".

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7) At Argonne National Laboratory we discovered that when preparing the chloride derivative by electrocrystallization another phase (needle crystals) also grows as the chloride concentration decreases. This phase is (BEDT-TTF)Cu[$N(CN)_2$]$_2$, i.e., it contains no chloride and is a semiconductor containing tetrahedrally coordinated Cu atoms (H. H. Wang et al., manuscript in preparation).

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