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Meissner Effect in an Organic Superconductor (BEDT-TTF)$_2$[Cu(NCS)$_2$]

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A quite large diamagnetic susceptibility corresponding to 83% of the perfect diamagnetism is observed for (BEDT-TTF)$_2$[Cu(NCS)$_2$] at 2 K. The critical temperature is determined to be 9.8 ± 0.3 K at 30 G. The magnetization shows a hysteresis loop with sharp maxima near 35 G, thereby indicating the type II superconducting nature. The lower critical field and the critical current density are estimated from the analysis of the hysteresis loop.

To our knowledge, nearly thirty organic superconductors have so far been synthesized. We have recently added a new ambient-pressure organic superconductor di[bis(ethylenedithiolo)tetra-thiafulvalene] bis(isothiocyanato)cuprate(I), (BEDT-TTF)$_2$-[Cu(NCS)$_2$],[1] which has a critical temperature $T_c \simeq 10$ K. This superconductor was discovered by magnetic measurements and confirmed by electrical ones.[2]

Superconducting nature should be established not only from the observation of zero resistivity but also from that of expulsion of magnetic flux under a finite field, namely Meissner effect. Some organic superconductors, however, have been claimed only by means of the measurements of resistivity, while the Meissner effect was observed for (TMTSF)$_2$PF$_6$,[3,4] (TMTSF)$_2$ClO$_4$,[5,6] β-(BEDT-TTF)$_2$I$_3$,[7] β-(BEDT-TTF)$_2$IBr$_2$[8,9] and β-(BEDT-TTF)$_2$AuI$_2$.[8,9]

In this letter, we report in details an investigation of d.c. susceptibility of (BEDT-TTF)$_2$[Cu(NCS)$_2$]. The results show a quite large diamagnetic susceptibility and provide clear evidence for the Meissner effect below 10 K. In addition, typical behavior of a type II superconductor is observed in the magnetic field dependence of magnetization measured in the superconducting state at 4.9 K.

The crystals of (BEDT-TTF)$_2$[Cu(NCS)$_2$] were prepared by galvanostatic electrochemical synthesis.[2] The d.c. magnetic susceptibility (defined as $\chi = M/H$) was measured with small crystals of (BEDT-TTF)$_2$[Cu(NCS)$_2$] oriented randomly by means of a Faraday susceptometer.[10]

The temperature dependence of the molar paramagnetic susceptibility under the constant applied field H_a of 30 kG (1 G = 10^{-4} T) is shown in Fig. 1. The diamagnetic contribution $\chi_d = -474 \times 10^{-6}$ emu mol^{-1} (1 emu mol^{-1} = 4π cm^3 mol^{-1}) was corrected using Pascal's law. The susceptibility above 10 K is nearly constant though a slight reduction is observed below about 90 K. Such behavior is characteristic of the Pauli paramagnetism and suggests the metallic nature of this complex whereas the semiconductive behavior is apparently observed in the

resistivity between 90 and 270 K.[2,11] The susceptibility below 10 K decreases very rapidly with decreasing temperature. The susceptibility changes to be diamagnetic at 2 K. This implies the superconducting nature of this complex, that is the Meissner effect.

In order to establish a further insight into the superconductivity of this complex, the susceptibility was measured under the applied field very much lower than 30 kG. After cooling the sample from 20 to 2 K at zero applied field, the temperature dependence of susceptibility was measured on increasing temperature at H_a = 30 G. As shown in Fig. 2, the volume diamagnetic susceptibility at 2.0 K corresponds to 83.3% of the perfect diamagnetism [$-(4\pi)^{-1}$ emu cm^{-3}]. This is obvious evidence for the occurrence of the transition to a bulk superconducting state. The critical temperature T_c thus determined is 9.8 ± 0.3 K at 30 G and would be somewhat higher than it at zero applied field. From the resistivity measurements, T_c was found to be 10.4 ± 0.1 K at zero applied field.[2,11]

When the temperature increases above about 6 K, the susceptibility increases somewhat slowly and reaches the Pauli paramagnetism above about 10 K. The susceptibility measured on cooling from about 20 K at H_a = 30 G exactly traces the curve of the heating process above about 6 K, with a sharp onset of diamagnetism at 9.8 ± 0.3 K. However, significant difference between the cooling and heating processes is recognized below 6 K as shown in Fig. 2. This phenomenon implies that H_a of 30 G exceeds the lower critical field H_{c1} in the temperature range between 6 and 10 K. That is to say, $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ is a type II superconductor with small H_{c1}.

The temperature dependence of magnetization as well as susceptibility measured with subsequent heating from 2 K is dependent upon the temperature at which the sample is quenched. The susceptibility for the sample quenched at 4.9 K is almost constant up to 6 K where the susceptibility

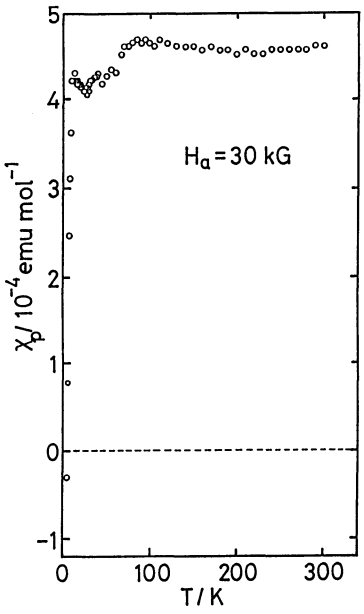

Fig. 1. Temperature dependence of the molar paramagnetic susceptibility at H_a = 30 kG.

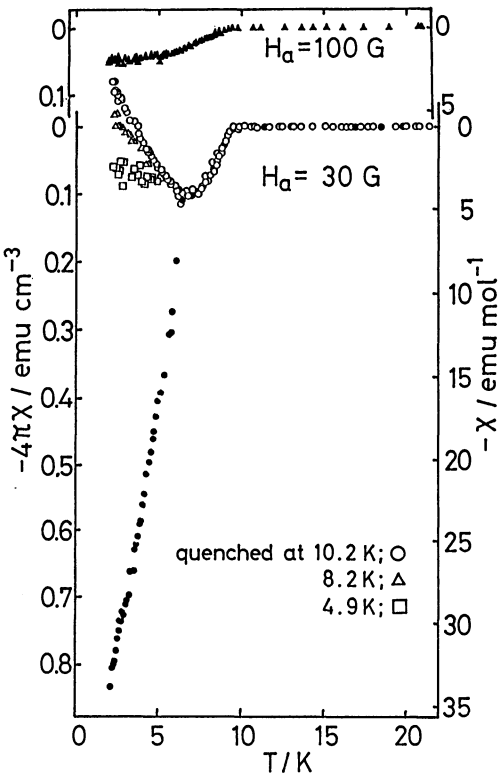

Fig. 2. Temperature dependence of the volume diamagnetic susceptibility at H_a = 30 and 100 G. Solid circles; cooling under zero applied field, the other symbols; cooling under the constant fields.

becomes independent of thermal history. In contrast, the susceptibilities for the samples quenched at temperatures higher than 6 K are rather positive at 2 K. This could be caused by the magnetic flux trapping effect. The diamagnetic susceptibility on cooling at H_a = 100 G is very much reduced even at 2 K. It is therefore suggested that H_{c1} would fall into the range between 30 and 100 G below 6 K. The critical temperature T_c = 9.3 ± 0.3 K at H_a = 100 G is somewhat lower than 9.8 ± 0.3 K at H_a = 30 G.

In order to estimate H_{c1} at a fixed temperature, magnetic field dependence of magnetization was measured at 4.9 K. The result is shown in Fig. 3. The measuring procedure was as follows; the sample was first cooled from about 15 K down to 4.9 K under H_a = 0 G, then H_a was changed step by step. The magnetization curve clearly shows a hysteresis loop. Such behavior is characteristic of a non-ideal (hard) type II superconductor. A maximum of magnetization is observed at H_a = 35 ± 5 G, which is related to H_{c1} of the bulk soft materials. For simplicity, we defined H_a at which the magnetization is maximum as H_{c1}. Thus H_{c1} at 4.9 K is 35 ± 5 G. As already mentioned above, H_{c1} = 30 ± 5 G at 6.0 ± 0.3 K. The temperature dependence of H_{c1} is plotted in Fig. 4. The upper critical field H_{c2} of the single crystal is very much higher than H_{c1}.[11]

The critical current density J_c at 4.9 K and 50 G is estimated to be 1060 A/cm^2 from the hysteresis.[12] J_c decreases exponentially with increase of applied field.

The magnetic susceptibility in the normal state also gives information concerning the superconducting nature of (BEDT-TTF)$_2$[Cu(NCS)$_2$]. Since the susceptibility in the normal state is almost independent of temperature, the density of states $D(E_F)$ per formula unit for a single spin direction may be calculated from χ_p with the following equation for the Pauli paramagnetism;

$$D(E_F) = \chi_p / (2 \mu_B^2 N_A)$$

where μ_B is the Bohr magneton and N_A is Avogadro's number, respectively and χ_p is not corrected for the Landau diamagnetism. From this equation, we estimate the

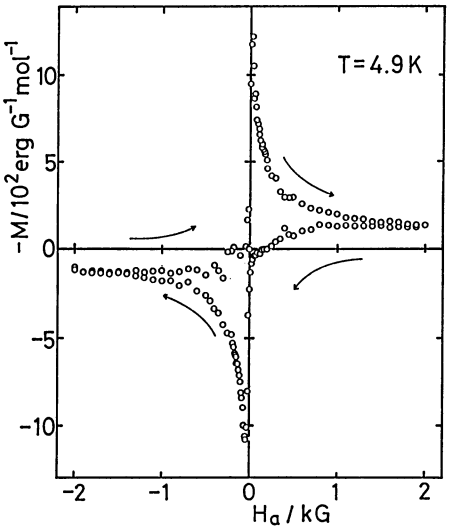

Fig. 3. Field dependence of molar magnetization at 4.9 K.

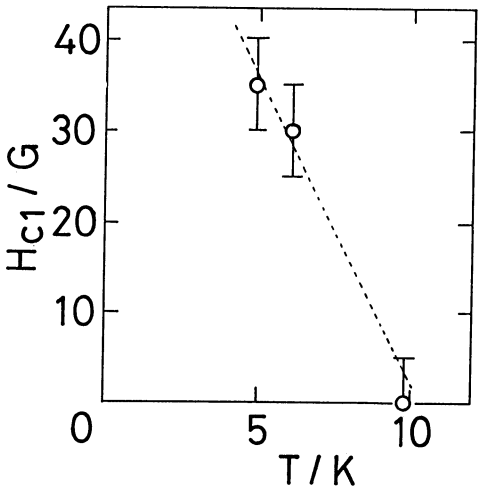

Fig. 4. Temperature dependence of the lower critical field H_{c1}.

density of states $D(E_F)$ = 7.1 eV^{-1} (1 eV = 1.602 x 10^{-19} J) above 90 K. The value is compared to 8.6, 6.5 and 6.6 eV^{-1} obtained for α- and β-$(BEDT\text{-}TTF)_2I_3$[13] and $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$,[14] respectively. The transfer integral t assumed to be isotropic in the two-dimensional sheet of BEDT-TTF species[1,2] may be related to the Pauli paramagnetism with the isotropic two-dimensional tight-binding approximation for the quarter-filled band by,

$$t = \mu_B^2 N_A / (4 \chi_p')$$

where χ_p' is the molar susceptibility for one mole of BEDT-TTF molecules; i.e., $\chi_p' = \chi_p / 2$, because the formula unit includes two BEDT-TTF molecules. From the above equation, we obtained the transfer integral t = 0.04 eV. This value is also compared to 0.03, 0.04 and 0.04 eV estimated for α- and β-$(BEDT\text{-}TTF)_2I_3$[13] and $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$,[14] respectively. The magnitude of t is a few times as small as that estimated from the tight-binding calculation,[15] the temperature dependence of the thermoelectric power,[16] and the Drude analysis of the reflectance spectra.[17] Such discrepancy would be interpreted in terms of the enhancement of Pauli paramagnetism due to on-site Coulomb repulsion.[18]

In conclusion, a new organic superconductor $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ is certified to the type II superconductor with the bulk nature by means of the magnetic measurements. In the normal state, the Pauli paramagnetic susceptibility is considerably enhanced by electron-electron interaction.

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