CHEMISTRY LETTERS, pp. 1171-1174, 1988.

Bulk Superconductivity in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$

Tadashi SUGANO, Kenji TERUI, Shinji MINO, Kiyokazu NOZAWA, Hatsumi URAYAMA,
Hideki YAMOCHI, Gunzi SAITO, and Minoru KINOSHITA*
The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato-ku, Tokyo 106

The diamagnetic shielding is observed for an ambient-pressure organic superconductor $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ by means of a.c. susceptibility measurements. The diamagnetic susceptibility amounts to 100 ± 5% of the perfect diamagnetism below 7 K and exhibits a sharp transition at 10.3 ± 0.4 K. The thermodynamical critical field is estimated and discussed in terms of the BCS theory.

A very recent discovery of an ambient-pressure type-II organic superconductor $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ with transition temperature, T_c, higher than 10 K[1)] has opened new perspectives in the field of organic superconductivity. We have previously shown a large diamagnetic d.c. susceptibility corresponding to 83% of the perfect diamagnetism in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ at 2 K under the magnetic field of 3 mT.[2)] It is of still importance to measure a.c. susceptibility of the superconductor, since the diamagnetic shielding as well as the Meissner effect should be observed under a static field as low as possible to obtain information about the unmixed state free from the flux penetration due to a very small lower critical field H_{c1}.[2)]

In this letter, we describe an investigation of a.c. susceptibility of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ under the earth and low applied magnetic fields. The results show the diamagnetic shielding signal amounting to 100 ± 5% of the perfect diamagnetism below 7 K under the earth field. This demonstrates an almost complete bulk superconductivity in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$. The lower critical fields are obtained from the field dependence of a.c. susceptibility. From the lower and upper critical fields, thermodynamical critical fields are estimated and discussed in terms of the Bardeen-Cooper-Schrieffer (BCS) theory.

The crystals of $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ used here were the same as those used in the d.c. susceptibility measurements.[2)] The setup for the low-field a.c. magnetic susceptibility measurements basically consisted of a primary and a pair of pickup coils which are surrounded by a superconducting solenoid to generate static fields. The a.c. (typically ν = 570 Hz and H_{ac} = ± 0.04 mT) and static fields were applied to the crystals oriented randomly (demagnetization effects were not corrected). Flux changes in the pickup coils induced by insertion of the sample were detected by a Hartshorn bridge[3)] using a Tinsley Type 4229 variable mutual inductance and a PAR 128A lock-in amplifier. The sample in a quartz bucket was hung into a glass tube wrapped with a non-inductive copper heat-sink, on the upper side of which a heater was attached to. The sample could be heated up to 20 K without heating the coils and the solenoid. Magnetic susceptibilities were calibrated against a Ta (99.95%) sample for which we assumed the perfect diamagnetism ($\chi = -1$).

The a.c. diamagnetic susceptibility curve as a function of temperature under the earth magnetic field (ca. 0.03 mT) is shown in Fig. 1. The curve was obtained upon subsequent heating after cooling from above T_c down to well below T_c in zero applied field. Thermal cycling of the sample did not alter the transition temperature. The onset of the transition is detected magnetically at 10.3 ± 0.4 K; this agrees well with the result of the resistivity measurements.$^{1)}$ The transition was nearly completed within 1.5 ± 0.5 K and hence there would be no distinct distribution of T_c. The diamagnetic volume susceptibility corresponds to 100 ± 5% of the perfect diamagnetism at 5 K. Therefore, below 7 K, almost complete flux explusion occurs. This unambiguously demonstrates the bulk superconductivity in $(\mathrm{BEDT\text{-}TTF})_2[\mathrm{Cu(NCS)}_2]$.

Flux penetration takes place at very low static fields. The field dependence of the diamagnetic susceptibility at several temperatures is shown in Fig. 2. At 4.2 K, the penetration occurs above 1.5 ± 0.5 mT and the diamagnetic susceptibility reduces steeply. An inflection is observed in the plot near 4.5 ± 0.5 mT. This phenomenon can qualitatively be interpreted in terms of the anisotropy of critical field. For $(\mathrm{BEDT\text{-}TTF})_2[\mathrm{Cu(NCS)}_2]$, the upper critical field perpendicular to the conducting plane $H_{c2\perp}$ has been shown to be fifteen times as small as that parallel to the plane $H_{c2\parallel}$ at 4.2 K by the resistivity measurements.$^{4)}$ Therefore, the flux penetration is expected to take place at first for the crystals whose conducting plane is oriented nearly parallel to the applied field and then to exaggerate for the crystals whose conducting plane is nearly perpendicular to the field. The latter is responsible for the inflection observed near 4.5 mT. From these considerations, we assigned the field corresponding to the first decrease in the plot to the lower critical field parallel to the plane $H_{c1\parallel}$ and the field

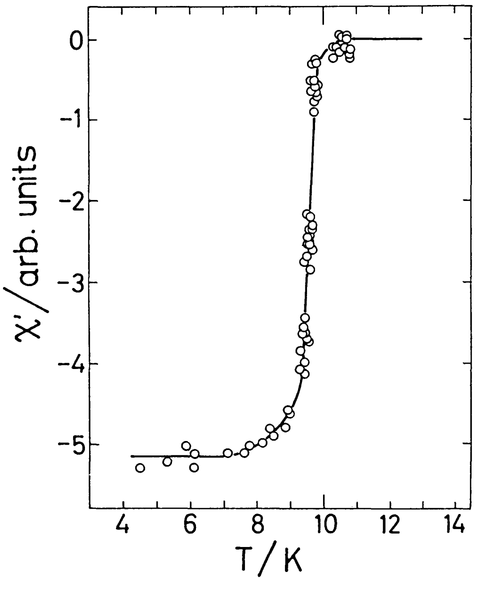

Fig. 1. Temperature dependence of the a.c. susceptibility of $(\mathrm{BEDT\text{-}TTF})_2[\mathrm{Cu(NCS)}_2]$ under the earth magnetic field (ca. 0.03 mT).

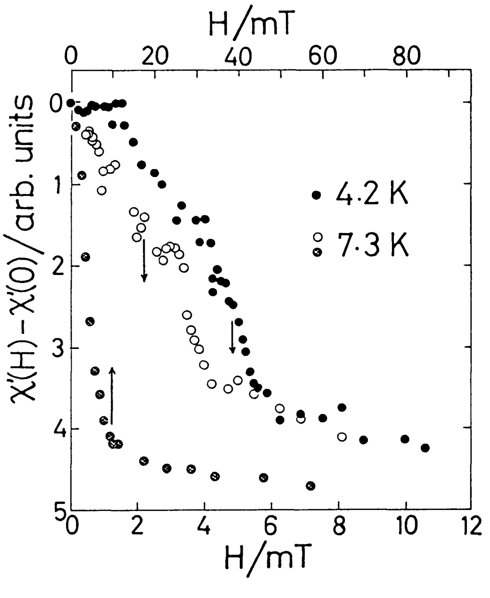

Fig. 2. Field dependence of the difference between the a.c. susceptibilities of $(\mathrm{BEDT\text{-}TTF})_2[\mathrm{Cu(NCS)}_2]$ at static fields H and 0.

Table 1. The lower and upper critical fields for $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$

T/K	$H_{c1\perp}$/mT	$H_{c1\parallel}$/mT	$H_{c2\perp}$/mT	$H_{c2\parallel}$/mT
4.2 ± 0.2	4.5 ± 0.5	1.5 ± 0.5	1.3×10^3	1.9×10^4
7.3 ± 0.4	3.0 ± 0.5	0.5 ± 0.2	3.0×10^2	8.8×10^3

corresponding to the inflection to $H_{c1\perp}$. $H_{c1\perp}$ is close to the lower critical field determined preliminarily from the d.c. magnetization measurements.[2)] As the temperature increases to 7.3 K, the flux penetration occurs at small field 0.5 ± 0.2 mT and the inflection shifts toward lower fields. The flux penetration tends to saturate but still continues near 60 mT; $H_{c2\perp}$ is expected to be 300 mT at 7.3 K.[4)]

The lower critical fields $H_{c1\parallel}$ and $H_{c1\perp}$ assigned above are summarized in Table 1 together with the upper critical fields $H_{c2\parallel}$ and $H_{c2\perp}$ evaluated from the results of the resistivity measurements[4)] by inter- and extra-polation of the observed values. Using the following equations,[5)]

$$\kappa = 2^{-1/2}\, H_{c2}/H_c \tag{1}$$

and

$$\kappa = 2^{-1/2}\, (H_c/H_{c1})(\ln\kappa + 0.497), \tag{2}$$

we calculated the Ginzburg-Landau parameter κ and the thermodynamical critical field H_c. The results are listed in Table 2. Since H_c is a thermodynamical quantity, it is independent of crystal orientation. Sizable difference between $H_{c\parallel}$ and $H_{c\perp}$, however, is recognized in our results. The difference is probably ascribed to inexactness of the lower critical fields because of the use of randomly oriented crystals instead of a single crystal. H_c at 0 K, $H_c(0)$, may be calculated by the equation:

$$H_c(T) = H_c(0)[1 - (T/T_c)^2]. \tag{3}$$

By using T_c =10.3 K, $H_c(0)$ = 42 ± 20 mT and $H_c(0)$ = 70 ± 40 mT are obtained from $H_{c\perp}$ and $H_{c\parallel}$, respectively.

Assuming a BCS-like gap $\Delta(0) = 1.76\, k_BT_c$, we can also evaluate $H_c(0)$ from the density of states at the Fermi level $N(E_F)$ by the equation,

$$H_c^2(0) = \mu_0\, \Delta^2(0)\, N(E_F), \tag{4}$$

where μ_0 is the permeability of free space. For $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$, $\Delta(0) = 2.50 \times 10^{-22}$ J and $N(E_F) = 5.25 \times 10^{46}$ J^{-1} m^{-3} which have been obtained from T_c and the Pauli paramagnetism in the normal state.[2)] From these, the thermodynamical critical field at 0 K, $H_c(0)$, based on the BCS theory becomes 64 mT, which is comparable with the values estimated from the results of the a.c. susceptibility

Table 2. The Ginzburg-Landau parameters and the thermodynamical critical fields estimated for $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$

T/K	$\kappa_\perp$	$H_{c\perp}$/mT	$\kappa_\parallel$	$H_{c\parallel}$/mT
4.2 ± 0.2	23 ± 3	40 ± 6	190 ± 40	71 ± 15
7.3 ± 0.4	12 ± 1	17.5±1.5	230 ± 50	27 ± 6

measurements. It is, therefore, concluded that the BCS theory is most probably applicable to the superconductivity in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$.

The penetration depths, $\lambda_{\parallel}$ and $\lambda_{\perp}$, may be obtained from the following equations:6)

$$\kappa_{\perp} = \lambda_{\parallel}/\xi_{\parallel} \tag{5}$$

and

$$\kappa_{\parallel} = (\lambda_{\parallel}\lambda_{\perp})^{1/2}(\xi_{\parallel}\xi_{\perp})^{-1/2}, \tag{6}$$

where $\xi_{\parallel}$ and $\xi_{\perp}$ are the coherence lengths parallel and perpendicular to the conducting plane. The coherence lengths at 0 K have been reported to be $\xi_{\parallel}(0)$ = 18.2 nm and $\xi_{\perp}(0)$ = 0.96 nm.4) With these values, we obtain $\lambda_{\parallel}$= 400 nm and $\lambda_{\perp}$ = 1500 nm at 4.2 K. Here, $\lambda_{\parallel}$ is the penetration depth for a field oriented perpendicular to the conducting plane but penetrating along the plane and $\lambda_{\perp}$ is that for a field oriented in the plane and penetrating also in the plane but in a direction perpendicular to the field. The values obtained amount only to 0.02-0.5% of the dimensions of the crystals employed here. The penetration depths are nearly identical with those obtained for β-$(BEDT\text{-}TTF)_2AuI_2$ with T_c = 4.1 K,6) whereas they are 2-3 orders of magnitude as small as those for $(TMTSF)_2ClO_4$.5) Such difference could result from the quasi-two-dimensionality in the two BEDT-TTF based superconductors7,8) in contrast with the quasi-one-dimensionality in the TMTSF based superconductor.9) Since the penetration depth is dependent on the effective mass, flux penetration occurs more extensively in a quasi-one-dimensional superconductor where the effective mass is large for two of orthogonal directions, whereas it is large for one direction in a quasi-two-dimensional superconductor.

In summary, we have shown that $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$ exhibits almost complete bulk superconductivity below 7 K. It is also shown that the lower critical field is anisotropic and very small for the field direction parallel to the conducting plane. The thermodynamical critical field and the penetration depth are evaluated in terms of the BCS and Ginzburg-Landau theories. The BCS theory is shown to be appropriate to interpret the superconductivity in $(BEDT\text{-}TTF)_2[Cu(NCS)_2]$.

This work was partly supported by a Grant-in-Aid for the Scientific Research from the Ministry of Education, Science and Culture.

References

1) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett., 1988, 55.
2) K. Nozawa, T. Sugano, H. Urayama, H. Yamochi, G. Saito, and M. Kinoshita, Chem. Lett., 1988, 617.
3) L. Hartshorn, J. Sci. Instrum., 2, 145 (1925).
4) K. Oshima, H. Urayama, H. Yamochi, and G. Saito, J. Phys. Soc. Jpn., 57, 703 (1988).
5) H. Schwenk, K. Andres, and F. Wudl, Solid State Commun., 49, 723 (1984).
6) H. Schwenk, S. S. P. Parkin, V. Y. Lee, and R. L. Greene, Phys. Rev. B, 34, 3156 (1986).
7) T. Sugano, H. Hayashi, H. Takenouchi, K. Nishikida, H. Urayama, H. Yamochi, G. Saito, and M. Kinoshita, Phys. Rev. B, in press.
8) C. S. Jacobsen, D. B. Tanner, J. M. Williams, U. Geiser, and H. H. Wang, Phys. Rev. B, 35, 9605 (1987).
9) C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, J. Phys. (Paris), 44, C3-859 (1983).

(Received April 20, 1988)