Highly anisotropic superconductivity in the organic conductor α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$

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Superconductivity in a layered organic compound, α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, has been characterized by measurements of the in-plane and out-of-plane resistivities and susceptibilities. The anisotropy of the normal state resistivity amounts to 10^5–10^6. The profiles of the in-plane and out-of-plane superconducting transitions are qualitatively different in both resistive and inductive measurements. The out-of-plane penetration depth is as long as 1.4 mm. All these results indicate that this material is a model system of Josephson-coupled two-dimensional layers with a high superconductive anisotropy,

A family of organic conductors, α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ [M=K,Rb,Tl,NH$_4$], are quasi-two-dimensional layered metals, where conducting layers composed of BEDT-TTF molecules are separated by thick insulating anion layers.[1] Reflecting this structure, the electronic state is known to be highly two dimensional. Within the conducting layer, the electronic band-structure calculation predicts two types of Fermi surfaces: a pair of open surfaces and a closed cylindrical one,[2] which was confirmed by observation of the quantum oscillations.[3] For M=K, Rb, and Tl, the systems undergo electronic phase transition around 10 K into another metallic state,[4] which is believed to originate from nesting of open parts of the Fermi surfaces. On the other hand, the NH$_4$ salt does not show this kind of phase transition but exhibits a superconducting transition around 1 K.[5] The superconductivity in this compound is expected to have a two-dimensional nature. Thus we consider that this 1 K organic superconductor serves as a model system for comprehensive understanding of phenomenological aspects of quasi-two-dimensional superconductivity in addition to the 10 K organic and 100 K oxide systems. In this work, anisotropy of the superconductivity in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ has been investigated through resistivity and ac-susceptibilty measurements in the in-plane and out-of-plane configurations at a zero magnetic field. A striking contrast between the in-plane and out-of-plane transitions revealed here indicates that this compound is one of the most highly anisotropic superconductors. The out-of-plane penetration depth is determined to be as long as 1.4 mm, which evidences extremely weak interlayer coupling.

Single crystals of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ were grown electrochemically. Samples with typical dimensions of $1\times0.5\times0.1$ mm^3 were used for the transport measurements while larger ones with dimensions of $(1–3)\times1\times0.5$ mm^3 were for the ac-susceptibility measurements. All the measurements were performed in a ^{3}He refrigerator surrounded by double μ-metal shields to shut out the earth field. The residual dc field was reduced to less than 1 mOe or lower. Sample temperature was monitored with a calibrated Cernox sensor in a temperature range of 0.4–300 K.

For resistive measurements, gold wires of 0.15 mm in diameter were attached to single crystals with carbon phase. The resistance of each contact was less than 10 Ω at 0.5 K. The in-plane (current $\parallel$ conducting layers) and out-of-plane (current $\perp$ conducting layers) resistivity measurements were made for four and sixteen crystals, respectively, with the standard four terminal method. Most samples show metallic temperature-variation of resistivity in both directions in a whole temperature range below 300 K, although several samples show a broad maximum at 50–150 K in the out-of-plane resistivity. The values of the in-plane and out-of-plane resistivities are 2–7 mΩ cm and 2–3 kΩ cm at room temperature and decrease to 10^{-2}–10^{-1} mΩ cm and 20–40 Ω cm at 3 K, respectively. The anisotropy ratio of the in-plane and out-of-plane values is 10^5–10^6, which exceeds by far the values of 10^2–10^3 for the 10 K organic superconductors, κ-(BEDT-TTF)$_2X$ [X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br],[6] and is comparable to or larger than those of the Bi-based cuprate superconductors.[7] The present compound is an extremely two-dimensional conductor.

The profile of the superconducting transition was qualitatively different in the in-plane and out-of-plane four terminal measurements; the in-plane resistivity starts to decrease around ~2.5 K and vanishes around 1.0 K while the out-of-plane resistivity exhibits a comparatively sharp transition around 1.0 K. To confirm the anisotropic behavior without ambiguity of sample dependence, we performed simultaneous measurements of the in-plane and out-of-plane resistivities for identical crystals, to which six leads were attached as is shown in the inset of Fig. 1. (In this six-terminal configuration for such highly anisotropic materials, one does not obtain the absolute value of the in-plane resistivity.) The contrast between the in-plane and out-of-plane behaviors is demonstrated in Fig. 1, which almost reproduces the result of the four terminal measurements. The in-plane gradual transition starting from 2.4 K completes around 1.0 K with a tail of positive curvature while a sharp decrease with negative curvature occurs at 1.0 K in the out-of-plane configuration. This suggests that, in the temperature range from 2.4 K down to 1.0 K, the superconducting coherence starts to grow gradually within the layers but does not between the layers. This characteristic will be discussed below along with the susceptibility data.

The ac complex susceptibility, $\chi=\chi'-i\chi''$, was measured with the standard mutual inductance technique down to 0.4 K. The apparatus was calibrated by two reference samples of conventional superconductors, Cd (T_c=0.52 K) and Al

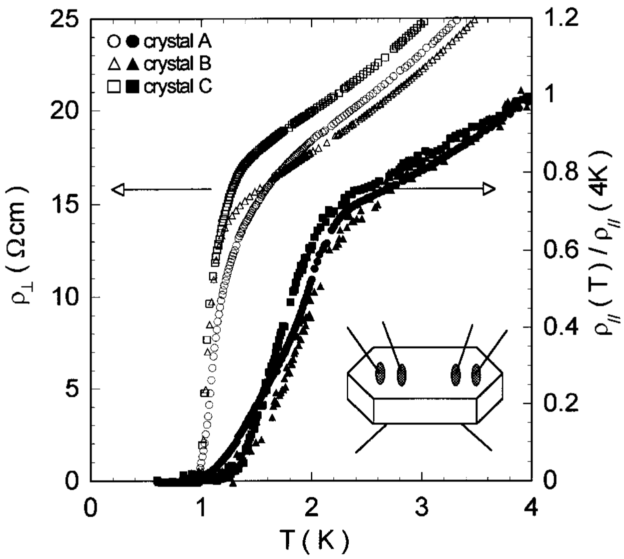

FIG. 1. In-plane ($\rho_\parallel$) and out-of-plane ($\rho_\perp$) resistivities measured with the six-terminal method for three crystals. $\rho_\perp$ is absolute values while $\rho_\parallel$ is normalized to the value at 4 K because the six terminal configuration depicted in the inset does not give the absolute value of $\rho_\parallel$. The same symbol stands for an identical crystal.

(T_c=1.18 K). The ac field was applied perpendicular (in-plane susceptibility) and parallel (out-of-plane susceptibility) to the conducting layers. Figure 2 shows in-plane ac susceptibility ($h_{ac}\perp$ conducting plane) under an ac field of 47 Hz and 0.16 Oe (in amplitude), which is confirmed to be in the low frequency and low amplitude limit from the frequency and amplitude dependence of the susceptibility. A sharp transition in χ' with an onset around 0.95 K appears and is followed by the saturation below 0.8 K. This indicates that the bulky coherence is established below ~0.95 K, which is consistent with the specific heat results.[8] The saturation value of $4\pi\chi'$ is 2.8 times larger than the complete diamagnetism due to a large demagnetizing effect in the present geometry of the field and the specific shape of the crystal used. Rough estimation of the demagnetization factor ensures that the saturation value is considered as the perfect diamagnetism. Above 1.0 K, $-4\pi\chi'$ is smaller than a level of 10^{-2}, which is a resolution of our inductive apparatus under the present condition of the low frequency, low amplitude, and crystal size.

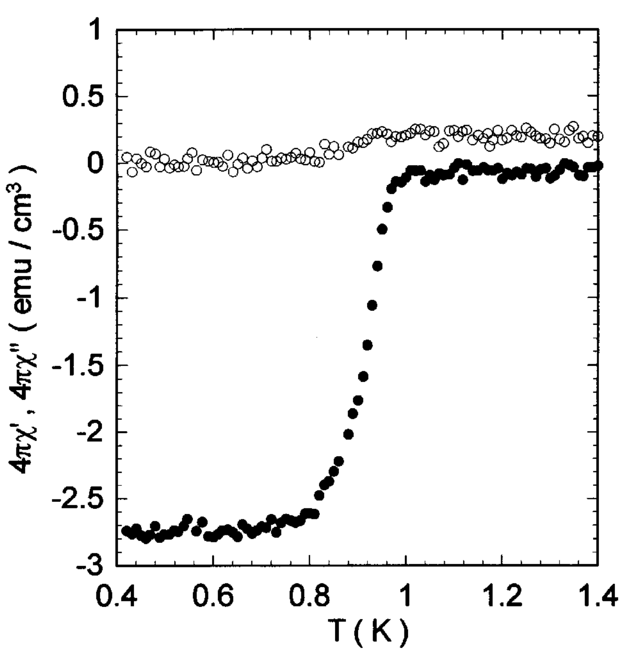

FIG. 2. ac susceptibility measured under an ac field of 47 Hz and 0.16 Oe (in amplitude) perpendicular to the layer.

In order to examine the diamagnetic response with higher sensitivity in the higher temperature range, where the in-plane resistance shows an appreciable and gradual decrease, a commercially available superconducting quantum interference device magnetometer was utilized for picking up very small ac response, although the lowest temperature available is limited to 1.8 K. A very small (less than 10^{-3}) but clear in-plane diamagnetic response was observed below ~2.5 K. We also measured frequency dependence of the susceptibility in a range from 1 to 10^3 Hz at 1.9 K and found no frequency dependence. Therefore, the diamagnetic signal is not due to the eddy current enhanced by the decrease in the normal-state resistance but to the superconductive diamagnetism. As for the out-of-plane geometry ($h_{ac}\parallel$ conducting layers), no diamagnetic signal was observed in this temperature range. This is consistent with the behavior of the out-of-plane resistivity and again indicates that the growth of the superconductive coherence is confined within the layer above 1 K. The behavior above 1 K can be considered to come from two-dimensional fluctuations of order parameter or inhomogeneity with slight admixture of higher T_c inclusion. The reproducibility of the transition profiles, the smooth in-plane resistive transition and good sample quality guaranteed by our observation of clear Shubnikov–de Haas oscillations in a sample used here seem to suggest that some intrinsic effect different from the inhomogeneity is involved in this quasisuperconducting behavior above 1 K. We note that some samples show in-plane current-voltage (I-V) characteristics reminiscent of the Kosteritz-Thouless transition; the Ohmic dependence is maintained down to 0.9 K, below which nonlinear dependence of $I \propto V^\alpha$ appears and α increases to 2.5 at 0.7 K.[9] This leads us to speculate that the in-plane gradual transition above 1 K is a manifestation of the thermally excited vortex-antivortex unbinding. However, somewhat sample-dependent results of the I-V characteristics, which may come from difficulty in reliable in-plane electrical measurements of such an extremely anisotropic material, requires further critical research for this speculation. In any case, the fact that the resistive and diamagnetic transitions appear only within the layer is an indication of the high two dimensionality.

The low-temperature out-of-plane susceptibility ($h_{ac}\parallel$ conducting layers) measured by the inductive method is shown in Fig. 3. In this geometry, the demagnetization effect is not significant. (This is also because the susceptibility value is much smaller than unity as seen below.) The applied ac fields is 0.16 Oe in amplitude and 1007 Hz in frequency. The onset of the transition is at 0.93 K, which coincides with that of the in-plane susceptibility. A strong contrast to the in-plane case is that $-4\pi\chi'$ increases gradually with decreasing temperature and reaches only 20% of the perfect

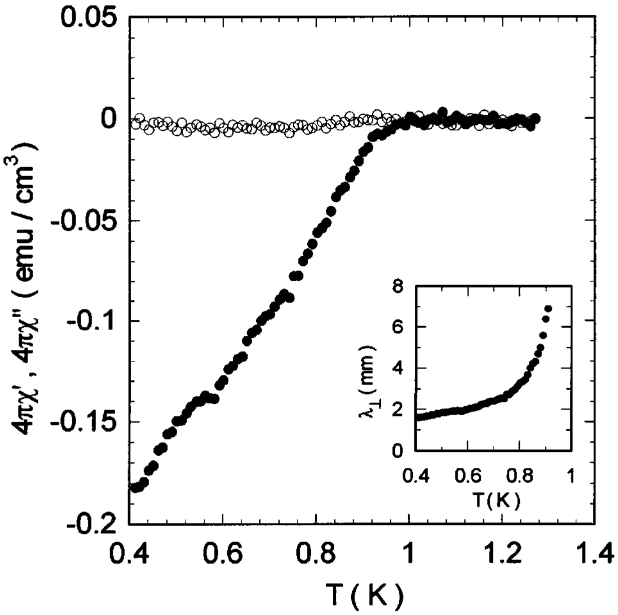

FIG. 3. ac susceptibility measured under an ac field of 1007 Hz and 0.16 Oe (in amplitude) parallel to the layer. Inset shows the out-of-plane penetration depth deduced from the susceptibility data.

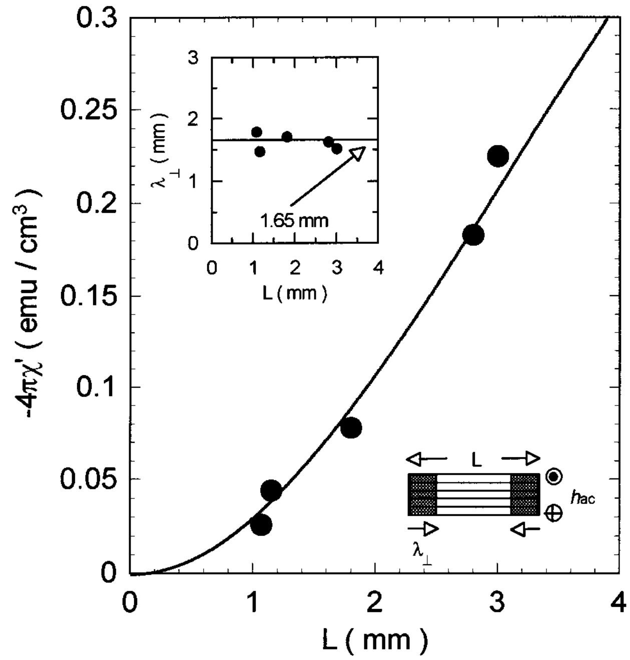

FIG. 4. The parallel-field susceptibility values at 0.4 K for five crystals are plotted as a function of sample size, L, which is the length parallel to the layer and perpendicular to the ac field. Inset shows the values of $\lambda_\perp$ deduced through Eq. (1) for each crystal. The values are well fitted by a value of $\lambda_\perp = 1.65$ mm, as shown by the solid curve and line.

diamagnetism at the lowest temperature available. This fact suggests that the penetration depth is comparable with the sample size. In this geometry of the ac field against the crystal, the field can penetrate both from the plane in the direction perpendicular to the layers and from the edges in the parallel direction. The former (in-plane) depth, which characterizes the shielding current flowing within the layer, is roughly given by the London penetration depth, which does not exceed an order of 1 μm. This is much smaller than the thickness of the crystal. Therefore, the latter (out-of-plane) penetration depth, $\lambda_\perp$, is responsible for the considerable reduction of $-4\pi\chi'$ from unity. This is a common situation to the weakly coupled layered organic superconductors.[10,11] The penetration depth is given implicitly by the following relation:

$$-4\pi\chi' = 1 - (2\lambda_\perp / L)\tanh(L/2\lambda_\perp), \tag{1}$$

where L is the sample length shown in the inset of Fig. 3. The value calculated by this formula is 1.65 mm at 0.4 K. Reproducibility of this result was examined by the measurements of five crystals with different dimension, L. All of the samples showed the similar temperature dependence of $-4\pi\chi'$ as in Fig. 3. The values of $-4\pi\chi'$ at 0.4 K for the five crystals are plotted as a function of crystal length, L, in Fig. 4. All of the results are fitted with excellent quality to a solid curve given by Eq. (1) with $\lambda_\perp = 1.65$ mm. The $\lambda_\perp$ deduced from Eq. (1) for each sample is shown in the inset of Fig. 4. These results guarantee reliability of the value of the penetration depth. To obtain the low-temperature limit of $\lambda_\perp$, measurements were extended down to 50 mK using the dilution refrigerator for two samples, giving a value of 1.4 mm in 0 K limit for both samples. Thus we conclude that the low-temperature $\lambda_\perp$ of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ is 1.4 mm. This value is one or two orders of magnitude larger than those of other layered organic superconductors of κ type: 200 μm for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (Refs. 10 and 11), 200 μm for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 10), 80 μm for κ-(BEDT-TTF)$_2$Ag(CN)$_2$H$_2$O (Ref. 10), and less than 20 μm for κ-(MDT-TTF)$_2$AuI$_2$ (Ref. 10). Since $\lambda_\perp$ probes the interlayer superconducting coupling, it turns out that the present compound is a quasi-two-dimensional superconductor with the largest anisotropy among the organic systems to date. In a model of Josephson-coupled multilayer,[12] the out-of-plane penetration depth at 0 K is given by $\lambda_\perp = [(4\pi^2\Delta)/(\hbar c^2 \rho_\perp)]^{-1/2}$ with Δ the gap parameter and $\rho_\perp$ the out-of-plane resistivity. Assuming the weak coupling BCS relationship, $\Delta = 1.76\ k_B T_c$, with $T_c = 0.93$ K in the present case, the value of $\rho_\perp = 20$–$40\ \Omega$ cm gives $\lambda_\perp = 0.5$–0.7 mm. This value is smaller but of the same order of magnitude as the experimental value. In the Josephson-coupled model, the two-dimensional character of the individual layer is introduced only through a condition that the layer thickness is far less than the in-plane penetration depth and other properties of the layer are assumed to be bulklike with the BCS weak coupling nature. The difference between the experimental and calculated values may come from two-dimensional order-parameter fluctuations inherent in the individual layer in the real layered system.

In summary, superconductivity of the layered organic superconductor, α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, was investigated by the in-plane and out-of-plane resistive and ac magnetic measurements, which have revealed that this system is one of the most highly anisotropic quasi-two-dimensional superconductors and is viewed as a weakly Josephson-coupled multilayer.

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