Magnetic-Field Penetration Depth of an Organic Superconductor: Evidence for Anisotropic Superconductivity of Gapless Nature

Kazushi Kanoda, Keishi Akiba, Kumi Suzuki, and Toshihiro Takahashi
Department of Physics, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171, Japan

Gunzi Saito
Department of Chemistry, Kyoto University, Sakyo-ku, Kyoto 606, Japan
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The temperature dependence of the magnetic-field penetration depth λ of the organic superconductor κ-[*bis*(ethylenedithio)-tetrathiafulvalene]$_2$Cu(NCS)$_2$ has been determined by means of complex susceptibility measurements for single crystals. λ was found to follow a power law, $\lambda(T)/\lambda(0)-1 \propto (T/T_c)^2$, at low temperatures instead of the exponential behavior expected from BCS theory. This result is considered as the first evidence for anisotropic superconductivity with nodes of the gap parameter on the Fermi surface in this material.

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Since the discovery of superconductivity in tetramethyl-tetraselenafulvalene (TMTSF) compounds, the question of whether the mechanism of the superconductivity in organic materials is of the conventional Bardeen-Cooper-Schrieffer (BCS) type or not has attracted wide interest.[1] The first organic superconductor, $(TMTSF)_2PF_6$, has a spin-density-wave (SDW) ground state at ambient pressure, and the superconducting state appears under pressure; the SDW state, which indicates a strong on-site Coulomb interaction, is situated just beside the superconducting state in the pressure-temperature phase diagram.[1] One may ask how the strong Coulomb repulsion can be overcome by the attractive force responsible for the superconductive pairing. This is one of the reasons why we expect that something novel occurs in the organic superconductors. Actually, the ^{1}H nuclear spin-lattice relaxation rate in the superconducting state of $(TMTSF)_2ClO_4$ was reported to not follow the BCS temperature dependence but to agree with the behavior expected for an anisotropic superconductor with lines of zeros of the superconducting order parameter on the Fermi surface.[2,3]

The *bis*(ethylenedithio)tetrathiafulvalene (BEDT-TTF) family is the second generation of the organic superconductors. The Cu(NCS)$_2$ salt, κ-(BEDT-TTF)$_2$-Cu(NCS)$_2$, has the highest transition temperature ($T_c \sim 10.4$ K) among the organic systems to date.[4] This compound has a layered structure consisting of alternating sheets of BEDT-TTF molecules and $Cu(NCS)_2^-$ ions, which are characterized by quasi-two-dimensionality of the electronic state. Several experiments aiming at clarification of the type of superconductivity have been made. The specific heat was measured by Katsumoto *et al.*,[5] who found that it follows a T^3 law at low temperatures. However, a possible large contribution of phonons did not allow them to discuss the electronic part. The ^{1}H nuclear spin-lattice relaxation rate T_1^{-1} was found[6] to have an anomalous temperature dependence, which was far from any behavior already predicted. This suggests the existence of some other relaxation mechanism never considered,[6] but the problem remains open.

The magnetic-field penetration depth λ probes the type of superconductivity. In the present work, we have made precise measurements of complex susceptibility χ for single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and derived the penetration depth in two orientations of external field. This is the first report on the temperature dependence of λ in organic superconductors and gives direct evidence for anisotropic superconductivity of a gapless nature. A preliminary report appears in Ref. 7.

Single-crystal samples were prepared by the standard electrochemical method.[4] The crystal shape was a thin plate with a typical dimension of $1.5\times1.5\times0.05$ mm^3; the flat surface is the crystallographic b-c plane, that is, parallel to the two-dimensional molecular sheets. The measurements of complex susceptibility χ ($=\chi'-i\chi''$) were performed at temperatures as low as 1.5 K with a Hartshorn-type mutual inductance bridge, the resolution of which is $\sim$5 nH. The ac field of 195 Hz was applied either perpendicular or parallel to the crystal plane.[8] When the ac field was parallel to the plane, the demagnetizing effect could be neglected, so that the absolute value of the susceptibility was determined. For calibration, we used the complete diamagnetism of Sn films (7–500 μm thick).

The χ measured in perpendicular fields is shown in Fig. 1, where the demagnetizing effect is not corrected for so that the scale of the vertical axis is arbitrary. A sharp transition in χ' is observed at 9.2 K. With increasing field, χ' around T_c becomes gradually reduced but the low-temperature values lie on the "universal curve" of the zero-field limit. The imaginary part χ'' forms a sharp peak around the transition region. The peak diminishes with decreasing field. At the lowest field, 11.6 mOe, no peak was observed (the data are not shown in

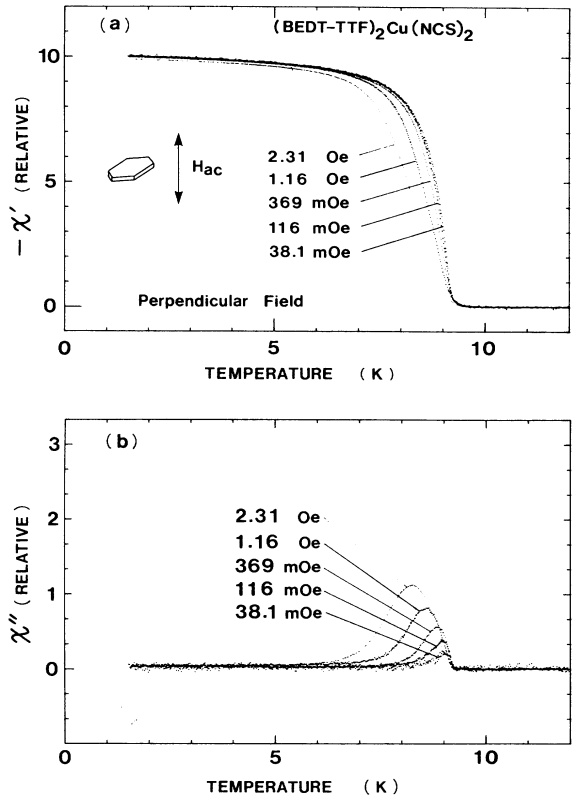

FIG. 1. (a) Real part and (b) imaginary part of complex susceptibility at different ac fields perpendicular to the crystal surface (the b-c plane).

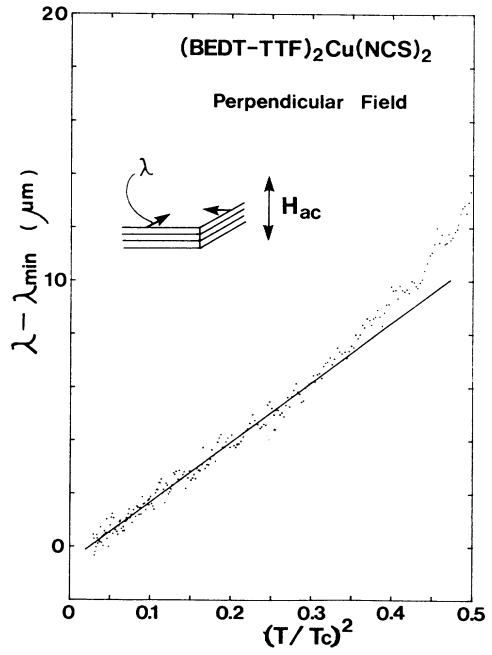

FIG. 2. Deviation of the perpendicular penetration depth from the minimum value, $\lambda-\lambda_{\min}$, plotted as a function of $(T/T_c)^2$. Inset: Directions of the applied ac field and the penetration with respect to the crystal surface (the b-c plane).

the figure). This field dependence unambiguously reveals that the χ'' component appears due to the hysteresis loss caused by vortex motion, and it assures that there are no vortices inside the sample when χ'' vanishes (for example, below 8 K at 116 mOe). Keeping the field low enough to avoid the entrance of vortices is very important when one wants to deduce the penetration depth from the susceptibility. The ac measurements of susceptibility are advantageous in the sense that χ'' can be used as a monitor of vortex entrance; dc measurements could not check it.

In the perpendicular direction of the field, one cannot obtain the absolute value of λ from the susceptibility data. However, it is possible to determine the deviation of λ from the minimum value at low temperatures by use of the following procedure: Suppose that the sample is a thin disk with a diameter of $2R$ and a thickness of $2d$ ($R\gg d$). When the field applied perpendicular to the disk penetrates by λ from the edge, as shown in the inset of Fig. 2, the observed susceptibility χ' is written as $\chi'=\bar{\chi}'/(1-N)=[2(R-\lambda)/\pi d]\bar{\chi}'$, where N is the demagnetizing factor, given as $1-\pi d/2(R-\lambda)$, and $\bar{\chi}'$ denotes the "intrinsic susceptibility" after correcting for the demagnetization, that is, $-4\pi\bar{\chi}'=(R-\lambda)^2/R^2$. Thus we get $R-\lambda(T)\propto[-\chi'(T)]^{1/3}$. Considering $R\gg\lambda$, we finally obtain

$$\lambda(T)-\lambda_{\min}=R\{1-[\chi'(T)/\chi'(T_{\min})]^{1/3}\},$$

with $\lambda_{\min}=\lambda(T_{\min})$. This expression is free from the simplifications made above. The results thus obtained from χ' at 116 mOe and $R=700$ μm for the samples used in this measurement are plotted as a function of $(T/T_c)^2$ in Fig. 2. The temperature dependence of λ is well approximated by the T^2 law at low temperatures of $(T/T_c)^2<0.35$, i.e., $T/T_c<0.6$. Experimentally, the exponent α of the power law T^α lies in the range of 1.7–2.2. The power-law behavior is in remarkable contrast with the behavior expected in a BCS superconductor, where λ varies exponentially at low temperatures.

Next, the results in the ac field parallel to the crystal plane are given. Figure 3 shows χ' of a crystal with dimensions of $3.3\times1.5\times0.072$ mm^3 for two different ac-field directions, shown in the inset of the figure; the field remains parallel to the crystal plane in both cases. The results are independent of the amplitude of the ac field, at least up to 1.16 Oe. χ' shows a clear transition at 9.2 K, the same temperature as in the perpendicular field. The imaginary part χ'' is zero throughout the entire temperature range at fields below 1.16 Oe; a peak in χ'' only appears in the vicinity of T_c at 2.3 Oe. Therefore, the deviation from perfect diamagnetism ($-4\pi\chi'<1$) in the low-field region is caused by field penetration, and not by vortex entrance.

It should be noted that the field in this direction

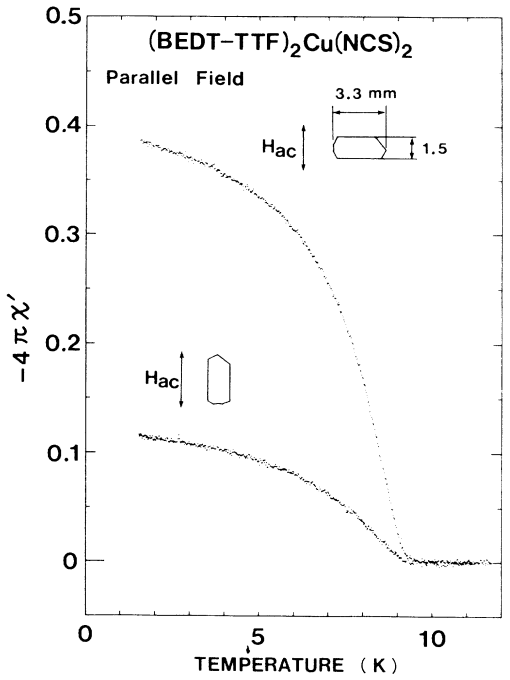

FIG. 3. Real part of complex susceptibility at an ac field of 1.16 Oe parallel to the crystal surface (the b-c plane). Insets: Directions of the ac fields with respect to the crystal; the fields are parallel to the crystal surface in both cases.

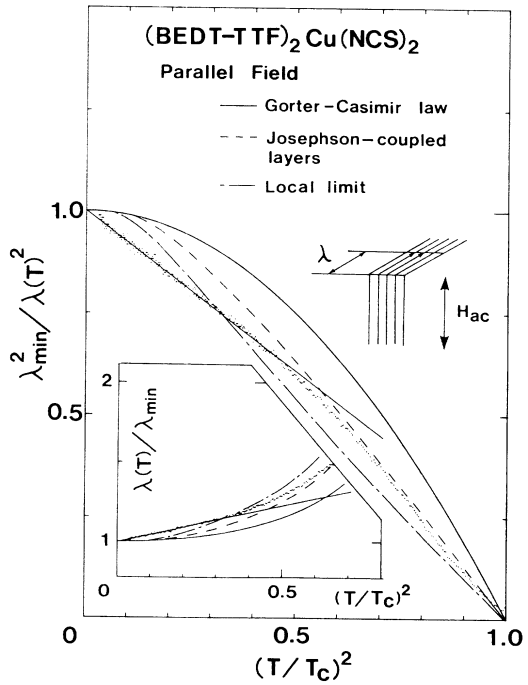

FIG. 4. $[\lambda_{min}/\lambda(T)]^2$ plotted as a function of $(T/T_c)^2$. Lower inset: Plot of $\lambda(T)/\lambda_{min}$ as a function of $(T/T_c)^2$. Upper inset: Directions of the ac field and penetration with respect to the crystal surface (the b-c plane).

penetrates not only from the plane in the direction perpendicular to the plane but also from the edges in the parallel direction. In layered materials, the latter is often dominant. The observed difference between χ' in the two orientations gives evidence that the parallel penetration (shown in the inset of Fig. 4) determines χ' in the present system: If the perpendicular penetration were responsible, the two measurements would have given the same result since the in-plane transport properties are almost isotropic.[4] An estimate of the perpendicular penetration depth is given by a calculation of the London penetration depth from the reported effective mass and carrier density,[4] which yields ~ 500 nm; this is very small compared with the sample thickness. Now, λ can be calculated by the equation[9] $-4\pi\chi' = 1 - (2\lambda/D)\tanh(D/2\lambda)$, where D is the sample width in the direction of field penetration. The agreement between the values of parallel penetration depth determined in the two orientations is satisfactory.

At the lowest temperature (1.5 K) λ is ~ 1.2 mm, which should be considered as the upper limit since a possible crack in the sample might have reduced the effective sample size. Nevertheless, this value is extraordinarily large compared with the values of the usual superconductors. In low-dimensional superconductors composed of weakly coupled planes or chains, the magnetic field would penetrate deep in a certain direction reflecting the weak coupling. For example, $\lambda(0)$ values for TaS_2(pyridine)$_{1/2}$ and for $(TMTSF)_2ClO_4$ have been reported to be 130 μm (Ref. 10) and 170 μm (Ref. 11), respectively. Therefore the present value is not so surprising. It has also been suggested by a model calculation for the Josephson-coupled layers that the parallel penetration depth of layered superconductors can be of macroscopic size.[12]

The temperature dependence of λ is shown in Fig. 4, where the quantity $[\lambda(0)/\lambda(T)]^2$, which has the meaning of the fraction of superfluid electrons in the London theory, is plotted as a function of $(T/T_c)^2$, together with the empirical Gorter-Casimir law, $[\lambda(0)/\lambda(T)]^2 = 1 - (T/T_c)^4$, the theoretical curve in the local limit, and the model calculation[13] of the Josephson-coupled layers based on the BCS framework. As seen in Fig. 4, our results exhibit T^2 dependence, $[\lambda(0)/\lambda(T)]^2 = 1 - 0.8 \times (T/T_c)^2$, at low temperatures. This is equivalent to $\lambda(T)/\lambda(0) = 1 + 0.4(T/T_c)^2$, shown in the inset of the figure. Now, the temperature dependence of λ is again a power-law, instead of an exponential BCS, behavior. The results were fairly reproducible for four measurements on different crystals.

Generally, the low-temperature variation of the penetration depth is determined by quasiparticle excitation. In the local limit, which is relevant to our compound, the BCS theory predicts

$$[\lambda(0)/\lambda(T)]^2 = 1 - (2\pi\Delta/kT)^{1/2} e^{-\Delta/kT}$$

at $T \ll \Delta/k$. The exponential dependence in the BCS theory is a consequence of a finite gap Δ for the quasi-

particle excitations. On the other hand, the power-law dependence means nonvanishing density of states above the Fermi energy and is expected for anisotropic superconductivity with nodes of the gap parameter. Such unconventional superconductivity was identified in the heavy-electron systems, UBe_{13} (Ref. 14), UPt_3, and $CeCu_2Si_2$ (Ref. 13). The present results give evidence that the superconductivity in the organic conductor κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ is also "unconventional" in this sense. Unfortunately, the type of nodes (points or lines) of the gap parameter cannot be specified from the exponent of the observed power law, because the exponent is known to be sensitive to the effects of strong coupling,[15] impurities,[16] and so on. Moreover, there is no calculation of the penetration depth in the unconventional state of a two-dimensional system.

Anisotropic superconductivity in quasi-two-dimensional organic systems was theoretically investigated by Hasegawa and Fukuyama.[17] They considered possible types of superconductivity in the presence of various kinds of attractive force with different symmetries, together with on-site Coulomb repulsion. According to their analysis, the observed gapless nature may suggest the existence of a nonlocal attractive force, which is advantageous for forming pairing states, avoiding the large on-site Coulomb repulsion, as discussed in the TMTSF compounds.[2,3] Extension of the present measurements to other BEDT-TTF salts should provide a crucial key to understanding the pairing mechanism in organic superconductors.

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