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Scanning Tunneling Spectroscopy on Organic Superconductors

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The superconducting phase of organic superconductors (BEDT-TTF)$_2$X was studied by electron tunneling using scanning tunneling microscope (STM). Tunneling both at the conducting plane and lateral surfaces was performed on single crystals of (BEDT-TTF)$_2$Cu(NCS)$_2$. The tunneling conductance curve obtained at the conducting plane is explained by d-wave gap symmetry. Tunneling spectra at lateral surfaces vary depending on the tunneling direction, suggesting the in-plane anisotropy of the gap. The directional dependence is also consistent with d-wave symmetry with line nodes $\pi/4$ from the k_b- and k_c-axes. This indicates that the superconducting pair wave function has $d_{x^2-y^2}$-wave symmetry. Protonated and partially deuterated (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br samples were also studied. Tunneling spectra are consistent with d-wave symmetry in all salts. Gap parameters are obtained as functions of the effective correlation. The large gap value suggests the strong coupling superconductivity. The zero-bias conductance peak, which is evidence for nodes of the superconducting gap, was found.
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KEYWORDS: organic superconductor, tunneling spectroscopy, pairing symmetry

1. Introduction

Organic superconductors (BEDT-TTF)$_2$X[1] have a layered structure consisting of conducting BEDT-TTF layers and insulating anion layers. The quasi-two-dimensional electronic band with strongly correlated electrons plays an important role in (BEDT-TTF)$_2$X, similar to that in high-T_c oxides. It is recognized that the superconducting phase adjoins the antiferromagnetic phase[2] in contrast to high-T_c cuprates in which these phases are separated by the anomalous metallic phase.[3] Much attention has been given to determining which mechanism brings about the superconductivity in the neighborhood of the Mott insulating phase. There is a possibility that the mechanism of the superconductivity in those materials is different from that in conventional Bardeen–Cooper–Schrieffer (BCS) superconductors. The d-wave pairing has been discussed theoretically.[4–6] Various kinds of experiments have thus far been performed to investigate the pairing symmetry. From the temperature dependence of the Knight shift $K_s(T)$ below the superconducting transition temperature T_c,[7,8] it is strongly suggested that the electron pair is in the spin-singlet state. This means that s-wave and d-wave symmetries are suitable candidates for the superconducting gap symmetry. The ^{13}C NMR spin–lattice relaxation rate $T_1^{-1}(T)$ follows a T^3 law at low temperature.[7–9] One result on the electronic specific heat $C_{el}(T)$ exhibits a T^2 dependence below 1 K.[10] Some results of the magnetic field penetration depth $\lambda(T)$ follow a power law.[11–15] These results are consistent with d-wave symmetry. On the other hand, other results on $\lambda(T)$[16–18] and $C_{el}(T)$ by Elsinger *et al.*[19] obey an exponential law, which support isotropic s-wave symmetry.

In investigating the superconducting state, electron tunneling is useful since the electronic density of states can be obtained directly with high energy resolution.[20] Tunneling spectroscopy using scanning tunneling microscope (STM), i.e., scanning tunneling spectroscopy (STS), especially has an advantage because of non contacting tip configuration. For (BEDT-TTF)$_2$Cu(NCS)$_2$, we have reported that the superconducting gap is highly anisotropic.[21–23] This result is consistent with the first work on STS by Bando *et al.*[24]

The phase diagram[2] of (BEDT-TTF)$_2$X with respect to the effective correlation strength has been proposed. In the superconducting phase, T_c increases with the effective correlation. We are concerned with two materials: (BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c \simeq 10$ K) and (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br ($T_c \simeq 11.5$ K). (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, which has a higher effective correlation than (BEDT-TTF)$_2$Cu(NCS)$_2$ and is located near the boundary between the superconducting and antiferromagnetic phases. The deuteration of end protons of the donor molecule is a useful method of modifying the band width and correlation strength. Protonated d[0,0] salt undergoes superconductivity, whereas fully deuterated d[4,4] salt is just on the phase boundary. Kawamoto *et al.*[25] revealed that the effective correlation can be controlled finely near the Mott boundary by partial deuteration of BEDT-TTF molecules.

In §3.1, we present STS results both on the conducting plane and lateral surfaces of (BEDT-TTF)$_2$Cu(NCS)$_2$ and discuss the anisotropy of the superconducting gap. We also report the gap parameter in partially deuterated (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br as a function of the effective correlation strength in §3.2.

The bound state on the gap node is an important feature which characterizes anisotropic superconductors, since it reflects the phase of the order parameter. Such a bound state is observed as the zero-bias conductance peak (ZBCP) in tunneling spectra.[26] The ZBCP is popular in high-T_c cuprates[27–29] of which pairing symmetry is of d-wave. Although d-wave pairing has been suggested in (BEDT-TTF)$_2$X, the ZBCP has not been observed yet. We present the first observation of the ZBCP in organic superconductors in §3.3.

2. Experimental

Single crystals of (BEDT-TTF)$_2$X were grown by electro crystallization.[30] The typical size of a single crystal used in the present experiment was $1 \times 1 \times 0.1\,\mathrm{mm}^3$. A gold wire 50 µm in diameter was attached to the crystal with gold paste as a current lead. The sample was mounted in the STM unit filled with low-pressure helium exchange gas, and cooled to 1.2 K. A mechanically sharpened Pt–Ir alloy wire, which is

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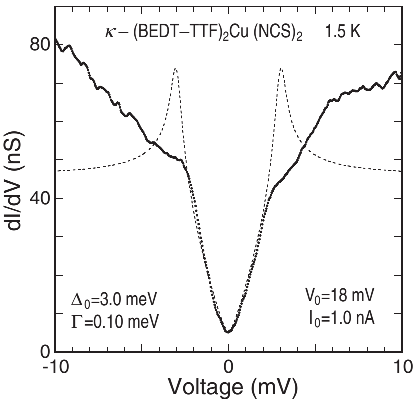

Fig. 1. Typical tunneling conductance curve obtained at *b–c* surface of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 1.5 K. The broken line represents the calculated curve produced by the *d*-wave gap model with $\Delta = 3.0\,\mathrm{meV}$ and $\Gamma = 0.10\,\mathrm{meV}$.

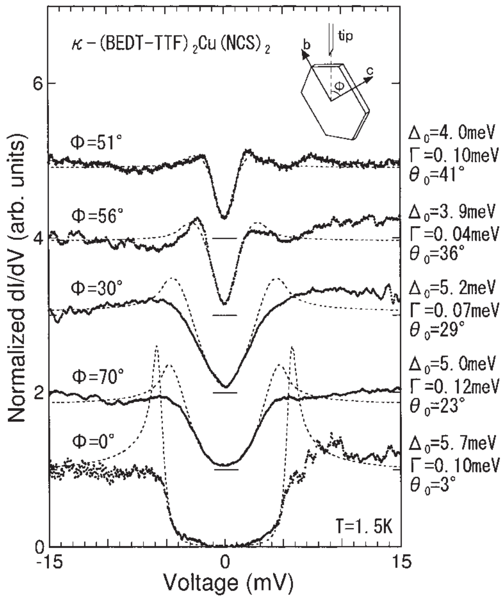

Fig. 2. Tunneling conductance curves on lateral surfaces of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ single crystals observed along various tunneling directions at 1.5 K. Curves along tunneling directions of $\phi = 0$, 70 ($\phi' = 20°$), 30, 56 ($\phi' = 34°$) and 51° ($\phi' = 39°$) are shown together, where ϕ denotes the angle from the *c*-axis in the *b–c* plane. Each curve is normalized to the conductance at $V = -15\,\mathrm{mV}$ and aligned at intervals of one division for clarity. The broken line represents the calculated curve produced by the *d*-wave gap model considering ***k***-dependent tunneling.

attached to the tube scanner, was used as the STM tip. The differential tunneling conductance dI/dV was directly measured by lock-in detection, in which 1 kHz AC modulation with an amplitude of 0.1 mV was superposed in the ramped bias voltage.

3. Results and Discussion

3.1 Tunneling spectra on $(BEDT\text{-}TTF)_2Cu(NCS)_2$

At first, we measured the tunneling differential conductance at the *b–c* surface, which is the conducting plane, of $(BEDT\text{-}TTF)_2Cu(NCS)_2$. In this configuration, the tunneling current flows perpendicular to the conducting plane. Figure 1 shows a typical tunneling conductance curve. The superconducting gap structure is clearly observed in tunneling spectra. The conductance at zero-bias voltage is well reduced. The gap edge is observed as shoulders around $|V| = 2.5\,\mathrm{mV}$. Inside the gap edge, the conductance depends linearly on the energy in contrast to the case of *s*-wave symmetry, suggesting gap anisotropy. We examine the simple *d*-wave gap model given as $\Delta(\boldsymbol{k}) = \Delta\cos 2\theta$. The broken line in Fig. 1 represents the fitting by the model with $\Delta = 3.0\,\mathrm{meV}$ and $\Gamma = 0.10\,\mathrm{meV}$, where Γ is the quasi-particle lifetime broadening parameter.[20] Γ is sufficiently small as compared with Δ. It assures the validity of an argument about pairing symmetry in our tunneling spectra. As shown in the figure, the conductance curve in the low-energy region, in which the symmetry of the gap is reflected, is well fitted by the model. The gap structure observed in the *b–c* plane is consistent with *d*-wave symmetry.

In order to investigate the in-plane gap anisotropy, we carried out STS on lateral surfaces, which are perpendicular to the *b–c* plane of $(BEDT\text{-}TTF)_2Cu(NCS)_2$. Conductance curves at lateral surfaces obtained along tunneling directions of $\phi = 0$, 70, 30, 56, and 51° are shown together in Fig. 2, where ϕ denotes the angle from the *c*-axis in the *b–c* plane. The functional form of the conductance curve inside the gap edges systematically varies depending on the tunneling direction. For $\phi = 0$ and 70°, the curve is flat around $V = 0$ and the gap width is larger. On the other hand, for $\phi = 51$, 56, and 30°, the conductance rapidly varies around $V = 0$ depending on the bias voltage, and the gap width is smaller. The directional dependence of the conductance curve indicates that the superconducting gap is anisotropic in the *b–c* plane.

We try to fit using the model, in which the ***k***-dependence of the tunneling transition probability is taken into account. In the calculation, the *d*-wave gap given as $\Delta(\boldsymbol{k}) = \Delta\cos 2\theta$ is assumed. According to the two-dimensional WKB approximation,[31] the transition probability $p(\theta - \theta_0)$ for the electron with the azimuth θ of the wave vector $\boldsymbol{k}$ is given as

$$p(\theta - \theta_0) = \exp[-\beta \sin^2(\theta - \theta_0)] \tag{1}$$

with

$$\beta = \frac{E_F d}{\hbar}\sqrt{\frac{2m}{U - E_F}}. \tag{2}$$

Here, θ_0 is a parameter representing the direction perpendicular to the tunneling barrier in ***k***-space, U and d are the potential height and width of the tunneling barrier, respectively, and E_F is the Fermi energy. The dimensionless parameter β characterizes ***k***-dependent tunneling. Because of this factor p, electrons with a large kinetic energy along the barrier normal mainly contribute to the tunneling current. The conductance curve is calculated on accounting the weight function $p(\theta - \theta_0)$.[32] Broken lines in Fig. 2 represent calculated curves for each direction ϕ with parameters Δ, Γ and θ_0. In the calculation, β was fixed at $\beta = 20$ for the best fitting. This value is larger than the reported value of $\beta = 8$ for $Bi_2Sr_2CaCu_2O_8$[33] probably due to the smaller work function in $(BEDT\text{-}TTF)_2Cu(NCS)_2$. The systematic change of the functional form of the conductance curve around $V = 0$ is reproduced well. Consequently, the conductance curve observed on the lateral surfaces is also explained by the *d*-wave gap model considering the ***k***-dependence of the

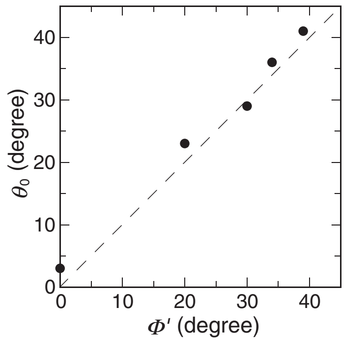

Fig. 3. Fitting parameter θ_0 against ϕ'.

tunneling transition probability and the 4-fold symmetry of the *d*-wave gap discussed below.

The *d*-wave gap has the 4-fold symmetry in $\boldsymbol{k}$-space with respect to the magnitude of the gap $|\Delta|$. We reduce the range of ϕ to $0^\circ \leq \phi \leq 45^\circ$. Thus, the directions $\phi = 51$, 56, and 70° are equivalent to $\phi' = 39$, 34, and 20°, respectively, where ϕ' denotes the reduced ϕ. In Fig. 3, the fitting parameter θ_0 is plotted against ϕ'. The plotted points coarsely show the linear relationship between θ_0 and ϕ', which intersects the origin. This means that the direction of line nodes of the gap is $\pi/4$ from the k_b- and k_c-axes, i.e., the gap has $d_{x^2-y^2}$-wave symmetry. Tunneling spectroscopic measurements are not sensitive to the sign of Δ except the measurement along the nodal direction, in which the ZBCP should be observed. We could not observe the ZBCP. The observed 4-fold symmetry might suggest the anisotropic *s*-wave. However, there are two possible reasons why we did not observe the ZBCP. One reason is that we could not probe just the nodal direction. Another reason is the geometry of the Fermi surface. On the Fermi surface of (BEDT-TTF)$_2$Cu(NCS)$_2$, there are gaps around $\pi/4$ from the k_b- and k_c-axes.[34] Our conclusion is that $d_{x^2-y^2}$-wave symmetry occurs in (BEDT-TTF)$_2$Cu(NCS)$_2$.

3.2 *Gap parameter of partially deuterated (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br*

The superconducting phase of protonated and partially deuterated (BEDT-TTF-d[n,n])$_2$Cu[N(CN)$_2$]Br was also studied. Tunneling spectra were obtained in d[0,0],[35] d[2,2][36] and d[3,3] salts. The superconducting gap is clearly observed in all salts. The conductance curve is fitted by the *d*-wave calculation similarly to the tunneling at the conducting plane of (BEDT-TTF)$_2$Cu(NCS)$_2$ as mentioned in §3.1. Gap parameters are obtained by the fitting in three salts as listed in Table I. The scatter in Δ is due to the sample dependence. These Δ values are almost consistent with that for (BEDT-TTF)$_2$Cu(NCS)$_2$.[23] The ratio U/W, where U is the on-site Coulomb interaction and W is the band width, becomes large due to the deuteration of end protons in BEDT-TTF. In comparing between d[0,0] and d[2,2], the reduced gap $2\Delta/kT_c$ increases with U/W. However, the reduced gap for d[3,3] salt is smaller than that for both d[0,0] and d[2,2] salts. We find that $2\Delta/kT_c$ does not increase monotonically close to the Mott boundary. The dependence is rather complicated. We plan to study the slowly cooled d[4,4] salt, which is located just on the boundary between superconducting and antiferromagnetic insulating phases.

Table I. Gap parameter Δ and corresponding $2\Delta/kT_c$ for (BEDT-TTF-d[n,n])$_2$Cu[N(CN)$_2$]Br.

	Δ (meV)	$2\Delta/kT_c$
d[0,0]	2.1–3.9	4.3–7.9
d[2,2]	3.0–4.8	5.8–9.3
d[3,3]	1.4–3.3	2.7–6.4

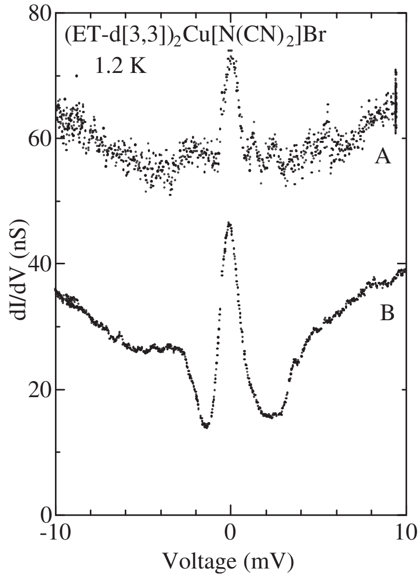

Fig. 4. Tunneling spectra with zero-bias anomaly. Curves for two different samples are shown together. The zero-conductance line of each curve is shifted by 20 nS for clarity.

It is noteworthy that the $2\Delta/kT_c$ for (BEDT-TTF-d[n,n])$_2$Cu[N(CN)$_2$]Br and (BEDT-TTF)$_2$Cu(NCS)$_2$[23] is larger than the predicted 4.35, which is based on the mean field theory for *d*-wave superconductors.[37] This suggests the strong coupling superconductivity in (BEDT-TTF)$_2$X.

3.3 *Zero-bias conductance peak*

It should be noted that an anomalous enhancement of conductance around $V = 0$ is observed occasionally in (BEDT-TTF-d[3,3])$_2$Cu[N(CN)$_2$]Br. Figure 4 shows the tunneling spectra with such an anomaly. Curves for two different samples are shown together. The tunneling conductance at $V = 0$ increases divergently in contrast to the case of the superconducting gap. We think that this sharp peak corresponds to the ZBCP unique to *d*-wave superconductors. The ZBCP has already been found in high-T_c cuprates $Bi_2Sr_2CaCu_2O_8$,[27] $La_{2-x}Sr_xCuO_4$[28] and $YBa_2Cu_3O_7$.[29] The present result is the first observation of the ZBCP in (BEDT-TTF)$_2$X. The ZBCP is caused by the zero-energy state, which is the bound state formed around gap nodes where the sign of the order parameter changes.[26] The essential point on the origin of the bound state is that electron- and hole-like quasi-particles, which are due to electrons injected into the superconductor, feel opposite signs of pair potentials. It should be noted that the ZBCP is a phase-sensitive phenomenon. Therefore, the ZBCP is thought to be direct evidence for nodes of the superconducting gap. The ZBCP in our tunneling spectra strongly supports d-wave pairing symmetry in (BEDT-TTF)$_2$X. We found no ZBCP in the study, described in §3.1, on lateral surfaces of (BEDT-TTF)$_2$Cu(NCS)$_2$. The observation of the ZBCP in (BEDT-TTF-d[3,3])$_2$Cu[N(CN)$_2$]Br suggests the possibility of a difference in gap symmetry between both salts; $d_{x^2-y^2}$-wave symmetry for (BEDT-TTF)$_2$Cu(NCS)$_2$ and d_{xy}-wave symmetry for (BEDT-TTF-d[3,3])$_2$Cu-[N(CN)$_2$]Br. A detailed discussion will be described elsewhere.[38)]

4. Conclusions

The superconducting gap structure in organic superconductors (BEDT-TTF)$_2$X was investigated by STS. Tunneling spectra were obtained on both the conducting plane and lateral surfaces of single crystals of (BEDT-TTF)$_2$Cu(NCS)$_2$. The tunneling conductance curve is explained by d-wave gap symmetry. In-plane gap anisotropy was clearly observed in tunneling spectra on lateral surfaces by varying tunneling direction. The directional dependence is also explained by d-wave symmetry considering the $\boldsymbol{k}$-dependence of the tunneling transition probability based on the WKB approximation. The nodal direction is determined as $\pi/4$ from the k_b- and k_c-axes. This indicates that the superconducting pair wave function in (BEDT-TTF)$_2$-Cu(NCS)$_2$ has $d_{x^2-y^2}$-wave symmetry. Protonated and partially deuterated (BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were also studied. The large $2\Delta/kT_c$ suggests the strong coupling superconductivity. We observed the existence of the ZBCP, indicating nodes of the superconducting gap. The d-wave symmetry is confirmed as the pair wave function in (BEDT-TTF)$_2$X.

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