Tunneling spectroscopy on the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ using STM

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STM spectroscopy on the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been performed in the superconducting state with the use of single crystals. The anisotropy of the superconducting gap has been investigated both on the b-c plane, which is parallel to the two-dimensional conducting layers, and on the several surfaces perpendicular to the b-c plane. The tunneling spectra observed on the b-c plane are well explained by the anisotropic gap with the d-wave symmetry. The spectra on the lateral surfaces are also consistent with the d-wave gap with line nodes along the direction $\pi/4$ from the k_b and k_c axes considering the $\mathbf{k}$ dependence of the tunneling transition probability. These results strongly indicate that the superconducting pair wave function in this salt has the $d_{x^2-y^2}$-wave symmetry.

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I. INTRODUCTION

The κ-phase BEDT-TTF salts have the layered crystal structures consisting of conducting BEDT-TTF layers and insulating anion layers, and their electronic structures are quasi-two-dimensional. In the κ-phase family, it is known that the superconducting phase is situated in the vicinity of an antiferromagnetic insulating phase.[1,2] This suggests that the electron correlations may play an important role in the appearance of superconductivity. Thus there is a possibility that the mechanism of the superconductivity in those materials is different from that in conventional BCS superconductors. To elucidate the mechanism which brings an attractive interaction between electrons, the symmetry of the pair wave function is an important clue. Various kinds of experiments have so far been performed to investigate it. From the temperature dependence of the Knight shift $K_{\mathbf{s}}(T)$ below the superconducting transition temperature $T_{\mathbf{c}}$,[3,4] it is strongly suggested that the electron pair is in the spin-singlet state. This means that the s-wave and the d-wave symmetry are suitable candidates for the superconducting gap symmetry. The experimental results concerning the gap symmetry are, however, still controversial. For example, the ^{13}C NMR spin-lattice relaxation rate $T_1^{-1}(T)$ follows a T^3 low at low temperature.[3–5] One result on the electronic specific heat $C_{\mathbf{el}}(T)$ exhibits T^2 dependence below 1 K.[6] Some results of the magnetic-field penetration depth $\lambda(T)$ follow a power law.[7–11] These results are consistent with the d-wave symmetry. On the other hand, other results of $\lambda(T)$[12–14] and recent data on $C_{\mathbf{el}}(T)$[15] obey the exponential law, which support the isotropic s-wave symmetry.

The scanning tunneling microscope (STM) spectroscopy is one of the most powerful methods for investigating the gap symmetry. By STM spectroscopy measurement, one can directly measure the electronic density of states with high-energy resolution ($\sim k_{\mathbf{B}}T$). Previously, we have reported that the gap is highly anisotropic in the b-c plane,[16–18] consistent with the work of Bando *et al.*[19] The crystal structure of present material κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is monoclinic.[20] The conducting BEDT-TTF layers and insulating Cu(NCS)$_2$ layers, which are parallel to the b-c plane, are stacked along the a axis. In this paper, we present the detailed results of STM spectroscopy both on the b-c plane and on the lateral surfaces of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals in the superconducting state, and discuss the symmetry of the superconducting gap.

II. EXPERIMENT

Single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ were grown by the electrocrystallization method.[21] The typical size of a single crystal used in the present experiment was $1\times1\times0.1$ mm^3. The superconducting transition temperature $T_{\mathbf{c}}$ was determined as $T_{\mathbf{c}}=10.4$ K from the midpoint of the resistive transition. The crystal orientation was determined by x-ray diffraction. The surfaces measured were the as-grown surfaces of single crystals, except the lateral surface perpendicular to the $\phi=30°$ direction from the c axis in the b-c plane, which was prepared by cutting a single crystal with a razor blade in air at room temperature. We confirmed that each surface measured was flat with an optical microscope. A gold wire of 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 down to 1.5 K. A mechanically sharpened Pt-Ir alloy wire was used as the STM tip. The differential tunneling conductance $dI/dV(V)$ was obtained directly by a standard lock-in technique with a 1-kHz ac modulation of about 100 μV added to the bias voltage.

III. RESULTS AND DISCUSSION

A. STM spectroscopy on the b-c plane

1. Tunneling spectra at 1.5 K

Typical dI/dV-V curves on the b-c plane at 1.5 K are shown in Fig. 1. In this figure, four dI/dV-V curves succes-

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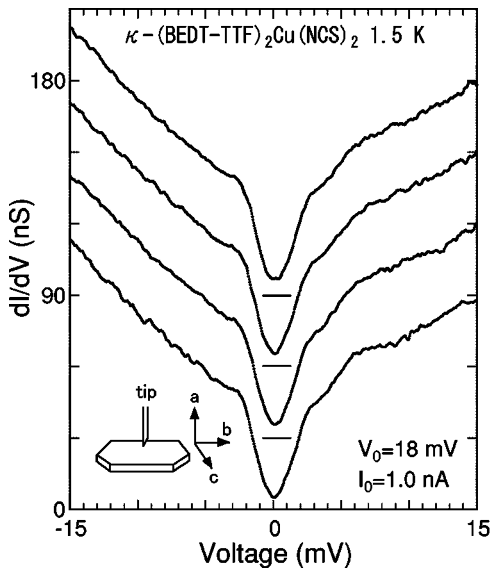

FIG. 1. Typical dI/dV-V curves successively obtained at a fixed position on the b-c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at 1.5 K. V_0 and I_0 denote the initial bias voltage and the initial tunneling current, respectively. Each curve is aligned at intervals of one division for clarity.

sively obtained at a fixed position are displayed at intervals of one division. The distance between the tip and the sample surface is indicated by the initial tunneling current $I_0 = 1.0$ nA at the initial bias voltage $V_0 = 18$ mV. As shown in Fig. 1, the tunneling spectra have good reproducibility. The superconducting gap structure is clearly seen as a dip in dI/dV for each curve. The zero-bias differential conductance $dI/dV(V=0)$ is reduced to about 10% of $dI/dV(|V| = \Delta_{\mathbf{p}}/e)$, where $\Delta_{\mathbf{p}}$ denotes the magnitude of the gap defined as half the energy difference between the gap edges. The differential conductance rapidly varies around $V=0$ depending on the bias voltage. This means that the gap is highly anisotropic in the b-c plane. We confirmed that the functional form of the dI/dV-V curve inside the gap edges is independent of the horizontal tip position within the limitation of the piezoelectric actuator movement ($\leqslant 1$ nm). The peaks at the gap edges are not obvious, and this feature of the dI/dV-V curve is repeatedly observed. A possible cause of the absence of distinct peaks at the gap edges is quasiparticle scattering at the sample surface due to the roughness.[22,23] However, we have no definite explanation on this point at present, and the further research is needed to elucidate the mechanism.

In the outside region of the gap ($|V| > \Delta_{\mathbf{p}}/e$), dI/dV exhibits the bias voltage dependence, which is so-called V-shaped background. This is likely to be caused by the energy dependence of the electron tunneling probability. If the tunneling probability has a certain energy dependence, dI/dV is no longer proportional to the electronic density of states of the sample. Since κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has the layered crystal structure along the a-axis direction, there is a possibility that the insulating Cu(NCS)$_2$ layer which is present at the sample surface[24] affects the character of the vacuum tunneling barrier. The similar bias voltage

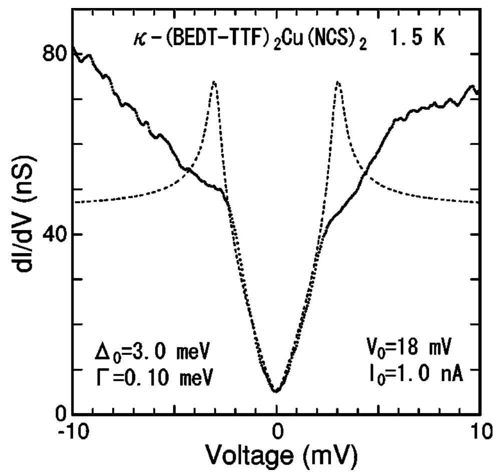

FIG. 2. Fitting of the dI/dV-V curve on the b-c plane shown in Fig. 1 to a simple d-wave gap model $\Delta = \Delta_0 \cos 2\theta$. The dashed line represents the calculated curve with $\Delta_0 = 3.0$ meV and $\Gamma = 0.10$ meV.

dependence of dI/dV has been reported for high-$T_{\mathbf{c}}$ cuprates,[25–27] and such materials also have insulating layers in their layered crystal structures. Another possibility of this V-shaped background is the strong electron correlation effects observed in tunneling measurements on metals near the Mott transition like amorphous $Ge_{1-x}Au_x$.[28] Since κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is near the Mott boundary,[2,29] strong electron-electron correlations are also expected in this salt. However, we should point out that linear background is rarely observed on the lateral surfaces as described later. This suggests that the strong electron correlation effects alone cannot explain the reason. Even in these situations, it is deduced that dI/dV correctly represents the electronic density of states of the sample in the low-energy region, because the energy dependence of the tunneling probability is expected to be sufficiently small around zero energy.

We try to fit the dI/dV-V curve on the b-c plane to a simple d-wave gap model given as $\Delta = \Delta_0 \cos 2\theta$. Here Δ_0 and θ are the maximum value of the gap and the azimuthal angle in $\mathbf{k}$ space, respectively. The dI/dV-V curve is described as

$$\frac{dI}{dV} \propto \int_0^{2\pi} \int_{-\infty}^{\infty} \mathrm{Re}\left[\frac{|E - i\Gamma|}{\sqrt{(E - i\Gamma)^2 - \Delta^2(\theta)}} \right] \times \left\{ -\frac{\partial f(E+eV)}{\partial V} \right\} dE \, d\theta, \tag{1}$$

where Γ is the broadening parameter of the one-electron level,[30] and $f(E)$ is the Fermi-Dirac distribution function. The calculated dI/dV-V curve using this model with $\Delta_0 = 3.0$ meV and $\Gamma = 0.10$ meV is shown by the dashed line in Fig. 2 together with one of the dI/dV-V curves shown in Fig. 1. The value of Γ is sufficiently small compared with that of Δ_0, so that it does not affect the essential functional form of the calculated gap structure. It is obvious that the calculated curve fits the present data satisfactorily in the low-energy region. Here it should be emphasized that the sym-

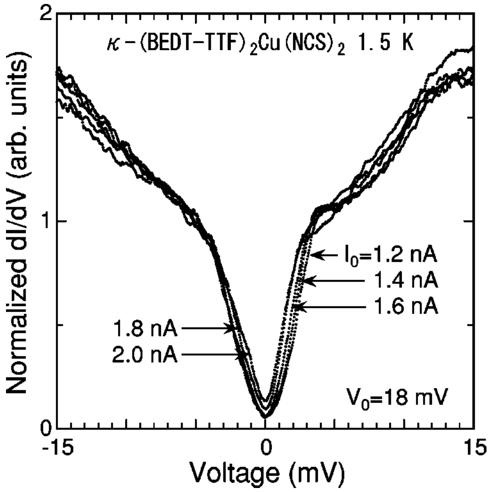

FIG. 3. Normalized dI/dV-V curves on the b-c plane with various tip-sample distances at 1.5 K. Curves for $I_0=1.2,1.4,1.6,1.8,$ and 2.0 nA at $V_0=18$ mV are shown together, normalized at $V=-4$ mV.

metry of the gap is most sensitively reflected on the behavior of dI/dV around $V=0$. Thus the gap structure observed on the b-c plane is consistent with the d-wave gap model. We confirmed that this result is also true of other dI/dV-V curves on the b-c plane for different samples. The corresponding value of $2\Delta_0/k_{\mathbf{B}}T_{\mathbf{c}}$ is 6.7, which is smaller than the previously reported value of $2\Delta_{\mathbf{p}}/k_{\mathbf{B}}T_{\mathbf{c}}\simeq 9.0$,[19] but substantially larger than the BCS value of 3.53.

2. Tip-sample distance dependence of the tunneling spectra

Figure 3 shows the dI/dV-V curves at a fixed position on the b-c plane with the various distances between the tip and the sample surface at 1.5 K. Each curve is normalized to the conductance at $V=-4$ mV. The tip-sample distance d is denoted by the initial tunneling current $I_0=1.2,1.4,1.6,1.8,$ and 2.0 nA at the initial bias voltage $V_0=18$ mV. The tunneling current I is most simply given as $I=I_{\mathbf{b}}(V)\exp(-d/d_0)$, where $I_{\mathbf{b}}(V)$ is the current factor depending on the bias voltage V, and d_0 (~ 0.1 nm) represents the characteristic extent of the electron wave function at the tip and the sample surface. As shown in Fig. 3, though the dI/dV-V curve exhibits the tendency of the slight reduction of $\Delta_{\mathbf{p}}$ with the increase of I_0, the functional form of the gap structure is essentially the same irrespective of the tip-sample distance as well as previously reported results of STM spectroscopy.[25,26] This was confirmed at different tip positions on the b-c plane and for different samples. This fact assures the vacuum tunneling barrier between the tip and the sample surface.

B. STM spectroscopy on the lateral surfaces

To investigate the in-plane gap anisotropy, we carried out STM spectroscopy measurement on the several lateral surfaces, which are perpendicular to the b-c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, varying the tunneling directions in the b-c plane. Typical dI/dV-V curves on the lateral surfaces observed along the tunneling directions of $\phi=0°$,

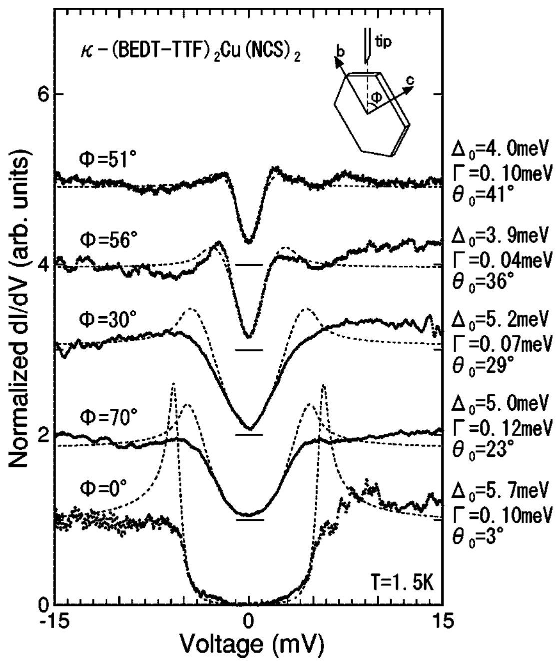

FIG. 4. dI/dV-V curves on the lateral surfaces of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals observed along various tunneling directions at 1.5 K. Curves along the tunneling directions of $\phi=0°$, 70° ($\phi'=20°$), 30°, 56° ($\phi'=34°$), and 51° ($\phi'=39°$) are shown together, where ϕ denotes the angle from the c axis in the b-c plane. Each curve is normalized to the conductance at $V=-15$ mV and aligned at intervals of one division for clarity. The dashed line represents the calculated curve by the d-wave gap model considering the **k**-dependent tunneling.

70°, 30°, 56°, and 51° at 1.5 K are shown together in Fig. 4, where ϕ denotes the angle from the c axis in the b-c plane. Each curve is normalized to the conductance at $V=-15$ mV and aligned at intervals of one division. The functional form of the dI/dV-V curve inside the gap edges systematically varies depending on the tunneling direction ϕ. For $\phi=0°$ and 70°, the curve is rather flat around $V=0$, and the magnitude of the gap $\Delta_{\mathbf{p}}$ is relatively larger. While, for $\phi=51°$, 56°, and 30°, the tunneling conductance rapidly varies around $V=0$ depending on the bias voltage, and $\Delta_{\mathbf{p}}$ is relatively smaller. In the outside region of the gap, the dI/dV-V curve is almost flat in contrast to that on the b-c plane (see Figs. 1 and 3). This is probably attributed to the electron tunneling only through the vacuum barrier. For each direction of ϕ, essentially the same dI/dV-V curves were reproducibly obtained irrespective of the tip position ($\leqslant 1$ nm). The tunneling direction dependence of the dI/dV-V curve indicates the following two: One is that the superconducting gap is highly anisotropic in the b-c plane. Another is that the dependence of the tunneling transition probability on the wave vector **k** is not negligible in STM measurement.

In the theoretical calculation of the dI/dV-V curve observed on the lateral surfaces, we assume the same d-wave gap model discussed in the previous section, given as $\Delta=\Delta_0\cos 2\theta$. On the basis of the two-dimensional (2D) WKB approximation,[31] we consider the **k** dependence of the tunneling transition probability for the electron with the azimuth θ of the wave vector $\mathbf{k}$ by introducing the factor $p(\theta-\theta_0)$ written as

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

with

$$\beta=\frac{E_F d}{\hbar}\sqrt{\frac{2m}{U-E_F}}. \tag{3}$$

Here θ_0 is a parameter representing the direction perpendicular to the tunneling barrier in $\mathbf{k}$ 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 the $\mathbf{k}$-dependent tunneling. Because of this factor p, electrons with large kinetic energy along the barrier normal mainly contribute to the tunneling current. Then, the dI/dV-V curve considering the $\mathbf{k}$-dependent tunneling is written as

$$\frac{dI}{dV}\propto\int_0^{2\pi}\int_{-\infty}^{\infty}p(\theta-\theta_0)\mathrm{Re}\left[\frac{|E-i\Gamma|}{\sqrt{(E-i\Gamma)^2-\Delta^2(\theta)}}\right]\times\left\{-\frac{\partial f(E+eV)}{\partial V}\right\}dE\,d\theta. \tag{4}$$

The calculated curve fitted to the dI/dV-V curve for each direction of ϕ using Eq. (4) with parameters Δ_0, Γ, and θ_0 is shown by the dashed line in Fig. 4. In the calculation, the value of β was fixed at $\beta=20$ for the best fitting. This value is relatively larger than the reported value of $\beta=8$ for $Bi_2Sr_2CaCu_2O_8$,[32] probably due to the smaller work function in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The systematic change of the functional form of the dI/dV-V curve around $V=0$ is reproduced well. The obtained value of $\Delta_0=3.9$–5.7 meV is almost consistent with that on the b-c plane, although the variation of the value of Δ_0 implies that the sample dependence of Δ_0 is substantially large. Consequently, the dI/dV-V curve observed on the lateral surfaces is also explained by the d-wave gap model considering the $\mathbf{k}$ dependence of the tunneling transition probability and the fourfold symmetry of the d-wave gap discussed further below.

We now focus on the fourfold symmetry of the d-wave gap. The d-wave gap has the fourfold symmetry in $\mathbf{k}$ space in respect to the magnitude of the gap $|\Delta|$. In addition, tunneling spectroscopic measurements are not sensitive to the sign of Δ except the measurement along the nodal direction. Considering these facts, we reduce the range of ϕ to $0°\leqslant\phi\leqslant45°$. Thus the directions of $\phi=51°$, $56°$, and $70°$ are equivalent to $\phi'=39°$, $34°$, and $20°$, respectively, where ϕ' denotes the reduced ϕ. In Fig. 5, 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 the $d_{x^2-y^2}$-wave symmetry. Thus it is concluded that the pair wave function in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has the $d_{x^2-y^2}$-wave symmetry.

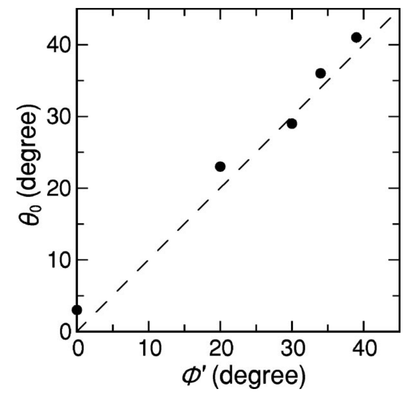

FIG. 5. Fitting parameter θ_0 against ϕ'. The linear relationship between θ_0 and ϕ' which intersects the origin indicates that the direction of line nodes of the gap is $\pi/4$ from the k_b and k_c axes.

Here we should mention the zero-bias conductance peak (ZBCP). The ZBCP is a narrow peak in dI/dV at $V=0$, which has been reported by some groups for high-T_c cuprates.[33–39] It is claimed that the ZBCP is attributed to the sign change of the gap parameter on the Fermi surface.[40–43] Thus it is observable by tunneling measurements just along the direction of the line nodes for the d-wave superconductors. In this study, however, the ZBCP could not be observed because of the difficulty to cut a crystal perpendicularly to the nodal direction. It should be also pointed out that there is a possibility that the ZBCP is not observed intrinsically for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ because a small energy gap exists on the Fermi surface[44] at the nodal direction. It is still now an open question as to whether or not the ZBCP for this salt is observed.

IV. CONCLUSIONS

We have investigated the superconducting gap structure in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by STM spectroscopy. We obtained the reproducible tunneling spectra both on the b-c plane and on the lateral surfaces varying the tunneling directions at 1.5 K. The dI/dV-V curve on the b-c plane exhibits rapid variation of the tunneling conductance with the bias voltage around $V=0$, and is well fitted by the d-wave gap model in the low energy region. The dI/dV-V curve on the lateral surfaces systematically varies in its functional form depending on the tunneling direction. This tunneling direction dependence of the dI/dV-V curve is also explained by the d-wave gap model considering the $\mathbf{k}$ dependence of the tunneling transition probability based on the WKB approximation. The nodal direction is determined to be $\pi/4$ from the k_b and k_c axes. Therefore we conclude that the symmetry of the pair wave function in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has the $d_{x^2-y^2}$-wave symmetry. The issue of the ZBCP is still now an open question for this salt.

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