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STM spectroscopy of an organic superconductor

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Electron tunneling spectroscopy of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ using low temperature scanning tunneling microscope (STM) is reported. The tunneling differential conductance in the superconducting phase was obtained in the *b*–*c* plane of a single crystal, by varying the tip position on the sample surface. The differential conductance is reduced near zero bias voltage and enhanced at the gap edge, associated with the superconducting gap structure below $T_c \simeq 10$ K. The gap width differs slightly from sample to sample, while the overall functional shape of the conductance is sample-independent. The tunneling conductance is reduced to almost zero near zero bias voltage, while it is finite inside the gap edge. The curve obtained cannot be fit to the BCS density of states with *s*-wave pairing symmetry, even if the life-time broadening of one-electron levels is taken into account. Finite conductance inside the gap edge suggests anisotropy of the gap. However, the conductance curve obtained is not explained by a simple *d*-wave symmetry for $\Delta(\boldsymbol{k})$. The reduced conductance near zero bias voltage suggests a finite gap. An anisotropic model with a finite gap, in which $\Delta(\boldsymbol{k})$ varies depending on the direction in $\boldsymbol{k}$-space, is examined. The tunneling conductance in the low-energy region is almost fit by the model with $\Delta_{\min} = 2$ meV and $\Delta_{\max} = 6$ meV. The finite conductance is explained by introducing a small effect of life time broadening. We conclude that the gap is anisotropic and is finite (at least $\Delta_{\min} = 2$ meV) on the entire Fermi surface.

1. Introduction

BEDT-TTF, a charge transfer salt, where BEDT-TTF is bis(ethylenedithio)-tetrathiafulvalene, is one of the most famous organic conductors [1]. Since the synthesis of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [2], the superconducting transition temperature T_c of which is higher than 10 K, a lot of attention has been directed toward understanding why such a high T_c is realized in this and similar organic conductors. It has been asserted that a quasi-two dimensional electronic band with strong correlation plays an important role in this superconductivity. Many experiments to elucidate the symmetry of the superconducting pair wave function, which is related to the origin of the attractive interaction, have been carried out. The possibility of unconventional superconductivity is often suggested.

The temperature dependence of the magnetic field penetration depth has been extensively studied in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The T^2-dependence observed by a.c. magnetization measurements [3] and the

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T-linear dependence reported by μSR measurement [4] suggest gapless superconductivity. On the other hand, a thermally activated behavior fit to the conventional BCS curve was reported by surface impedance measurement [5]. These results are still controversial.

Electron tunneling spectroscopy is one of the most powerful tools in studying the mechanism of superconductivity, since it can obtain the electronic density of states directly. Maruyama *et al*. [6] measured the tunneling conductance for κ-(BEDT-TIF)$_2$Cu(NCS)$_2$/Al_2O_3/Au junctions. The tunneling current was unstable for their junctions, one must control the tunneling barrier microscopically. The scanning tunneling microscopy (STM) method is most useful in investigating surface electronic states, and has been reported by Bando *et al*. [7]. The tunneling conductance for the superconducting phase and its temperature dependence were obtained. However, they did not discuss the pairing symmetry. In our previous report [8], we found the superconducting gap to be highly anisotropic. In the present article, we report the tunneling conductance with low noise obtained at the *b–c* surface of the single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in the superconducting phase by low temperature STM and discuss the symmetry of the pair wave function.

2. Experimental

Single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, which are plate-like along the *b–c* plane, were synthesized electro-chemically. The superconducting transition temperature was measured as $T_c \simeq 10$ K from the midpoint of the resistive transition. The a.c. susceptibility was also measured. The Meissner volume fraction of about 60% at 1.4 K shows that the present sample experiences bulk superconductivity. The as-grown surface along the *b–c* plane, which is flat and shiny, was investigated by low temperature STM. A mechanically sharpened Pr–Ir wire, which is attached to a tube-type piezo actuator is used as the scanning tip, in which the electronic density of states is regarded as almost constant near the Fermi level. The cell which contains the STM unit is filled with helium gas at low pressure (for efficient thermal exchange) and immersed in liquid helium.

3. Results and discussion

Figure 1 shows a typical tunneling differential conductance obtained at 1.4 K for two different samples. The tip distance is controlled by an initial tunneling current I_0 at a constant bias voltage V. These curves are measured under the condition of $I_0 = 1$ nA at $V = 18$ mV. The energy gap structure associated with the superconducting state is clearly shown in both curves. The conductance inside the gap edge is very much reduced. Although the gap width slightly depends on sample, the functional form of the conductance curve is essentially the same. A dependence of the gap value on sample has been reported [7]. It is presumably because of differences in T_c or surface damage by the tip contacting to the sample surface. However, T_c (onset) of the bulk superconductivity which is determined as 10.2 K by a.c. susceptibility measurements scarcely differs among the present samples. The reproducible conductance curve at a fixed tip position above the sample, as described below, assures us that the tip did not collide with the sample. The sample dependence of the gap value has not been explained satisfactorily yet.

The so-called V-shape background often reported in high-T_c oxides [9] is also observed in the outside region of the gap edge in the present tunneling configuration where the tip approaches the *b–c* plane of the single crystal. BEDT-TTF salts have layered structures in which anion layers and cation layers are stacked alternately. It is well established that metallic electrons are confined within the cation (BEDT-TTF) layer and the anion layer is insulating [1]. It is assumed that the top crystal surface is an insulating Cu(NCS)$_2$ layer [10]. In an STM experiment at the *b–c* plane, therefore, electrons in the BEDT-TTF layer tunnel through the tunneling barrier which consists of a series of insulating Cu(NCS)$_2$ layers and the vacuum gap. In such a complicated tunneling configuration, the transition probability for the electron tunneling cannot be regarded as constant and has an energy dependence. The conductance at high energy is strongly enhanced while the energy dependence of the transition probability is small in the low energy region [11]. Additionally, the energy dependence of

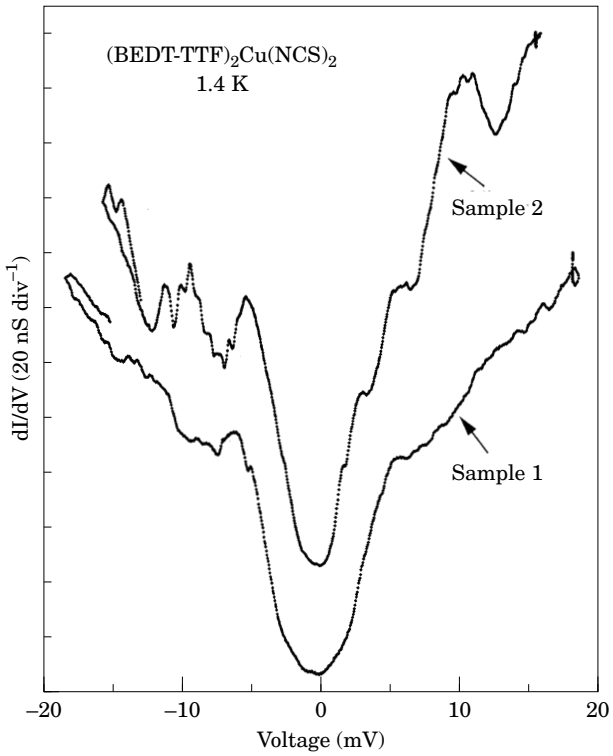

Fig. 1. The tunneling differential conductance for different samples obtained at 1.4 K. The initial tunneling current I_0, which characterizes the tip distance, is $I_0 = 1$ nA at the bias voltage $V = 18$ mV. The zero conductance line is shifted by two divisions for clarity.

the transition probability is modified by both the barrier height and width. The tunneling conductance is no longer proportional to the electronic density of states. The tip distance dependence of the conductance curve reported in $Bi_2Sr_2CaCu_2O_8$ [12] and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [8] is explained by such a mechanism. The enhancement of the conductance outside the gap edge observed in the present experiment could be explained as well. The conductance curve within the gap edge, on the other hand, represents the electronic density of states approximately.

For STM measurements at the lateral surface of a single crystal, where the BEDT-TTF layer is exposed, electrons confined within the BEDT-TTF layer tunnel through only the vacuum gap. The tunneling conductance, therefore, is expected to be directly proportional to the electronic density of states. We are trying to carry out STM spectroscopy at the lateral surface at present.

Figure 2 shows the tunneling conductance at various tip positions on the surface for sample 1. Positions A, B, C and D are located at corners of a square with a side of about 10 nm. The curve at a fixed tip-height position is reproduced whenever the tip has been moved and then returns to its original position. This assures us that the tip has not contacted the sample surface. The whole shape of the conductance curve is essentially the same, irrespective of the tip location, except both the mid-gap structure and the small peaks outside the gap edge due to foreign electrical noise. A small structure in the mid-gap region is sometimes observed, and its width and intensity seem to vary depending on the tip position. However, we failed to map the width of the structure since the structure is not fully reproducible at a fixed tip position. We cannot discuss the mid-gap structure in detail at present. In the preceding sections we discussed curve D, since it is most observable.

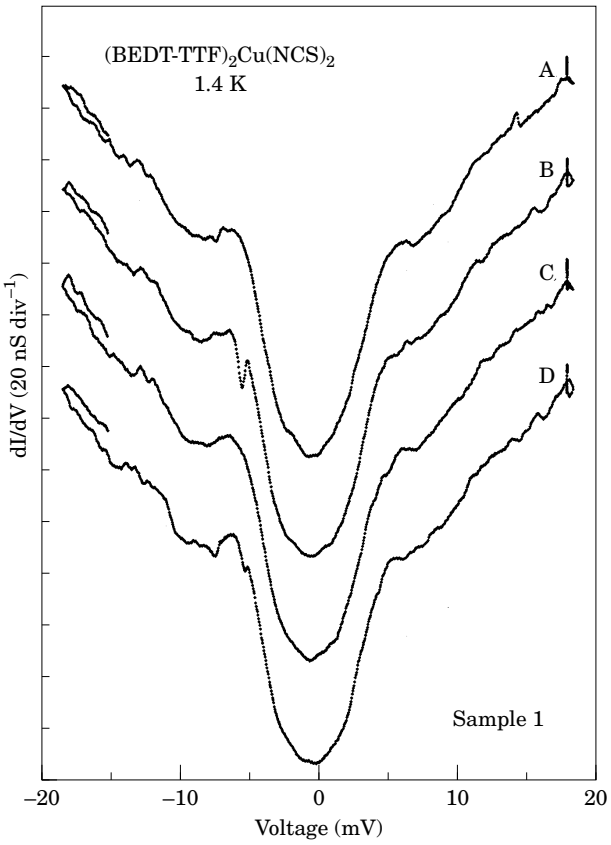

Fig. 2. The differential conductance at various positions on the surface for sample 1 under the condition of $I_0 = 1$ nA at $V = 18$ mV. Positions A, B, C and D are located at corners of a square with a side of about 10 nm. The zero conductance line is shifted by two divisions for clarity.

We compare the conductance curve at position D obtained in the present experiment (solid circle) with that of our previous measurement (open circle) [8] in Fig. 3. It is worth noting that the noise in the present tunneling conductance spectrum has been much reduced compared with that in the previous one. A small difference in the gap width (as described above) is observed. The conductance near zero bias voltage for the present result is slightly enhanced, presumably because of the broadening effect. However, the functional shape of these curves is essentially identical to those measured previously.

The obtained tunneling differential conductance clearly shows the energy gap structure. The differential conductance is reduced to almost zero and flat near zero bias voltage, similar to the BCS density of states with *s*-wave pairing symmetry. Finite conductance inside the gap edge is also observed. The solid line in Fig. 4 represents the broadened BCS density of states, the so-called Dynes equation, with gap parameter $\Delta = 5.5$ meV and the broadening parameter $\Gamma = 0.55$ meV. As shown in the figure, a finite conductance cannot be explained by the BCS density of states even if the broadening of the one-electron level is taken into account. It strongly suggests gap anisotropy. Next, we try to fit the data to the electronic density of states for anisotropic gap models.

At first, we discuss the *d*-wave symmetry with line nodes of the gap $\Delta(\boldsymbol{k})$. The *d*-wave is examined with

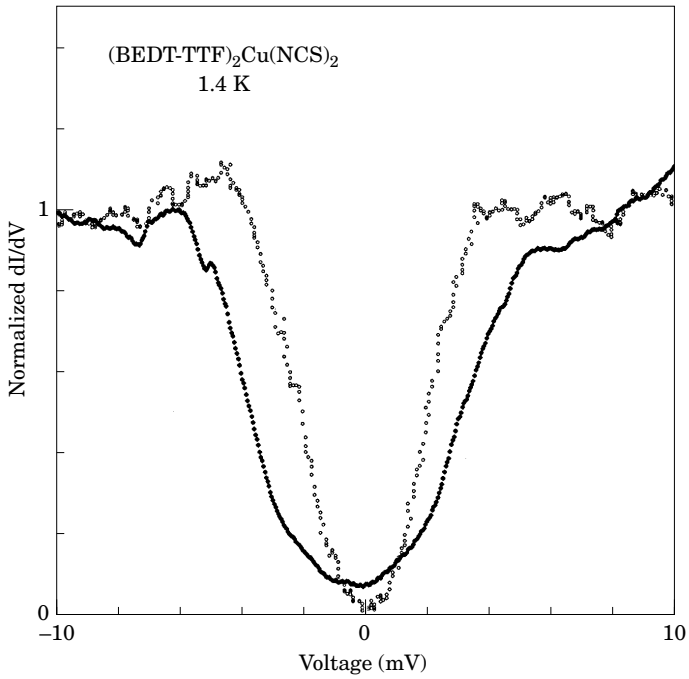

Fig. 3. The differential conductance for the present experiment (solid circle) and previous one (open circle) [8]. Each curve is normalized at $V = 10$ mV.

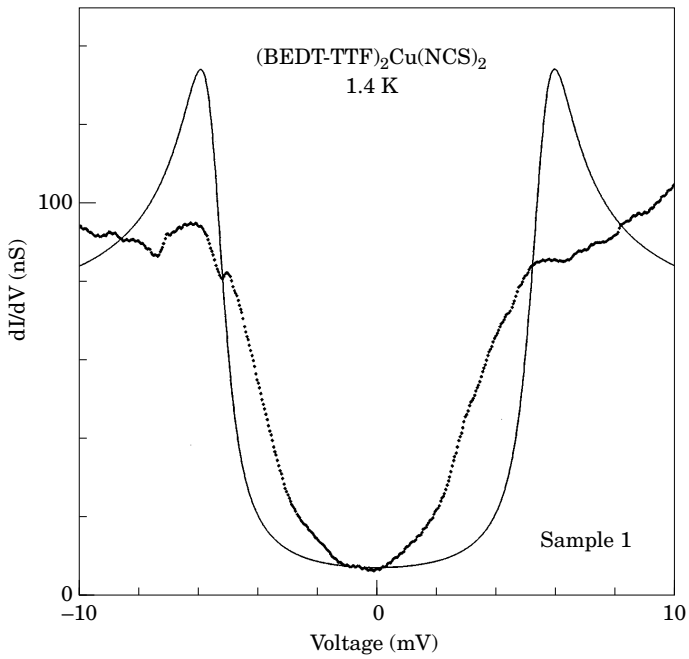

Fig. 4. Fitting of the observed conductance to the broadened BCS density of states. The solid line represents the calculated conductance for 1.4 K with $\Delta = 5.5$ meV and $\Gamma = 0.55$ meV.

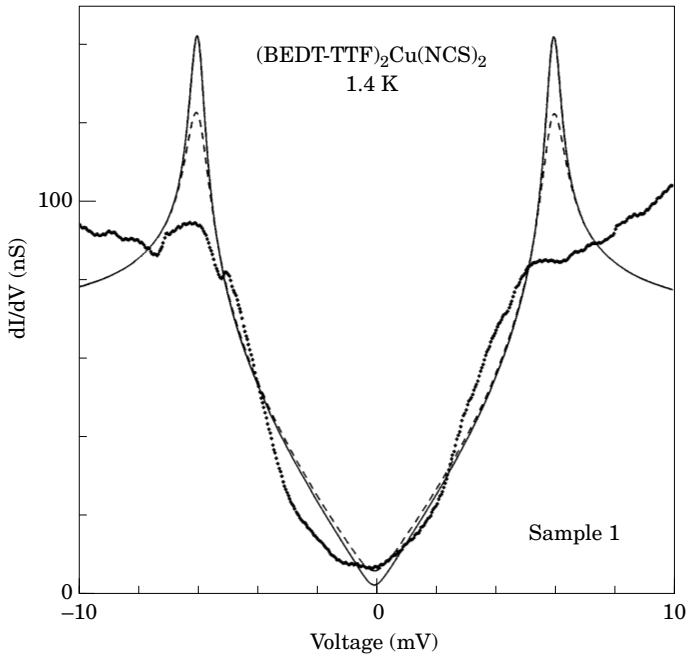

Fig. 5. Fitting of the observed conductance to the d-wave model. The solid line represents the calculated conductance for 1.4 K from the d-wave anisotropy of the gap with $\Delta_0 = 6$ meV. The broken line represents the broadened curve of the solid line with $\Gamma = 0.12$ meV.

the simplest form as

$$\Delta(\boldsymbol{k}) = \Delta_0 \cos 2\phi, \tag{1}$$

where Δ_0 is the amplitude of Δ and ϕ is the azimuth. For the sake of simplicity, we assume that the band dispersion is isotropic. Details of these calculations have been described in our previous article [13]. In BEDT-TTF salts, the metallic state which bears superconductivity is localized two-dimensionally at the BEDT-TTF layer. The Fermi surface of BEDT-TTF salts is indeed regarded as two dimensional. Naively, it is assumed that the tunneling electron which carries the current along the a^*-axis contains every wave number component in the k_b–k_c plane. Therefore, the tunneling can be compared with the total density of states, which is calculated by the integral over all directions in $\boldsymbol{k}$-space. The calculated differential conductance for 1.4 K with $\Delta_0 = 6$ meV is shown in Fig. 5 as the solid line. It is proportional to the energy in the low energy region. The broken line in Fig. 5 is the broadened curve of the solid line with the broadening parameter $\Gamma = 0.12$ meV. A small Γ value increases the conductance near zero bias voltage, while the energy dependence is still almost linear. It is obvious that the measured conductance is almost flat near zero bias voltage and cannot be explained by pure d-wave pairing alone, even if we take the broadening effect into account. It is clear that the gap is finite on the whole Fermi surface.

We examine another anisotropic model with finite gap, in which Δ varies, depending on the direction in $\boldsymbol{k}$-space. We introduce the gap density function of a rectangular form as [13]

$$D(\Delta) = \begin{cases} \frac{1}{\Delta_{\max} - \Delta_{\min}} & \text{for } \Delta_{\min} \leq \Delta \leq \Delta_{\max} \\ 0 & \text{for } 0 < \Delta < \Delta_{\min},\ \Delta > \Delta_{\max} \end{cases} \tag{2}$$

where $\Delta_{\min}$ and $\Delta_{\max}$ represent the minimum and maximum gap value, respectively. The solid line in Fig. 6 represents the calculated differential conductance at 1.4 K with $\Delta_{\min} = 2.2$ meV and $\Delta_{\max} = 6.5$ meV. The essential behavior is almost reproduced except for the observed finite conductance near zero bias voltage. In

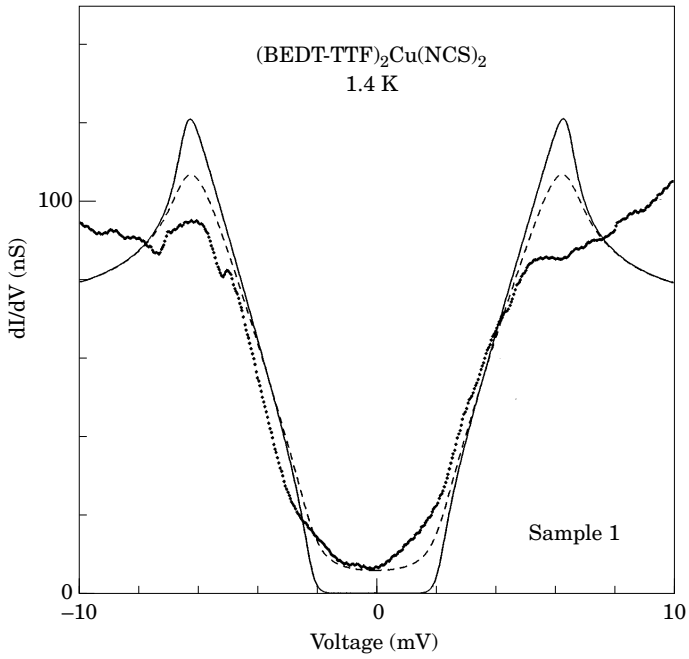

Fig. 6. Fitting of the observed conductance to the anisotropic model with finite gap. The solid line represents the calculated conductance for 1.4 K from the anisotropic gap model with $\Delta_{\min} = 2.2$ meV and $\Delta_{\max} = 6.5$ meV. The broken line represents the broadened curve of the solid line with $\Gamma = 0.33$ meV.

order to fit low energy region well, we introduce the broadening of the one-electron level. The broken line in Fig. 6 is the broadened curve of the solid line in the figure with the broadening parameter $\Gamma = 0.33$ meV. As shown in the figure, the obtained curve is almost reproduced by the model. The rectangular form of $D(\Delta)$ is too simple to describe the obtained conductance in enough detail. However, this form is not essential, but it is important that both finite $\Delta_{\min}$ and $\Delta_{\max}$ exist.

We tried to fit the model to the conductance obtained in another sample 2. Figure 7 shows the fitting. The solid line represents the calculation by this model with $\Delta_{\min} = 1.8$ meV and $\Delta_{\max} = 5.5$ meV. The broken line is the broadened curve of the solid line with $\Gamma = 0.28$ meV. The obtained conductance for sample 2 is also consistent with the model. Although the gap width slightly differs in samples, the qualitative behavior of the obtained conductance is reproduced by the anisotropic model with a finite gap. It is understood that the gap is finite on the whole Fermi surface while Δ varies from 2 to 6 meV depending on the direction in $\boldsymbol{k}$-space. Additionally, the observed finite conductance near zero bias voltage is presumably explained by the small broadening effect.

The obtained $2\Delta_{\min}/kT_c$ and $2\Delta_{\max}/kT_c$ are 5 and 15 for sample 1, and 4 and 13 for sample 2, respectively. The $2\Delta/kT_c$ value for $\Delta_{\max}$ is much larger and that for $\Delta_{\min}$ is still slightly larger than that of the weak-coupling limit. It suggests strong-coupling in this superconductivity.

Our present results show that the superconducting gap is highly anisotropic while it is finite. Naively, we speculate that the anisotropy is brought about by a d-wave component. It is assumed that the finite gap is brought about by the s-wave component and the d-wave component gives relatively large anisotropy. The $s + \mathrm{i}d$ symmetry proposed by Kotliar [14], in which the order parameter does not vanish, is also a possible pairing. However, we cannot distinguish $s + d$ from $s + \mathrm{i}d$ at present. Our tunneling results strongly suggest

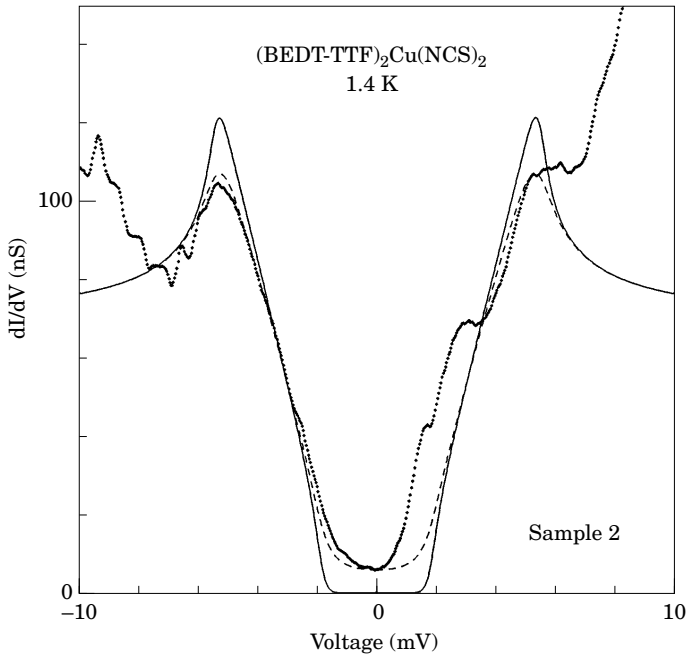

Fig. 7. Fitting of the obtained conductance at sample 2 to the anisotropic model with finite gap. The solid line represents the calculated conductance for 1.4 K from the anisotropic gap model with $\Delta_{\min} = 1.8$ meV and $\Delta_{\max} = 5.5$ meV. The broken line represents the broadened curve of the solid line with $\Gamma = 0.28$ meV.

a mixed pairing symmetry of *s*- and *d*-wave, although it is an open problem to determine the origin of the mixed symmetry.

4. Conclusions

Electron tunneling spectroscopy was done on the *b*–*c* plane of single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by low temperature STM. The energy gap structure associated with the superconducting state was observed. Although the whole functional shape of the conductance is identical, the gap width slightly differs from sample to sample. The observed conductance, which is reduced to almost zero near zero bias voltage and is finite inside the gap edge, is not well-fit by the BCS density of states, which suggests a gap anisotropy. However, it is not explained by the simple *d*-wave symmetry either. The conductance curve is fitted by another anisotropic model with finite gap in which $\Delta(\boldsymbol{k})$ varies from $\Delta_{\min}$ to $\Delta_{\max}$. The gap is found to be finite, at least $\Delta_{\min} = 2$ meV, on the entire Fermi surface. A mixed pairing symmetry *s*- and *d*-wave is suggested.

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