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STM Spectroscopy of $(BEDT\text{-}TTF)_2Cu(NCS)_2$

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Abstract

The superconducting phase of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ was investigated by the electron tunneling spectroscopy using low temperature STM. The tunneling differential conductance was obtained at the *b-c* plane of single crystal varying the tip position. The tunneling conductance is reduced to almost zero and flat near zero bias voltage while it is finite inside the gap edge suggesting the gap anisotropy. The obtained curve is not fitted to the BCS density of states nor the simple *d*-wave. The anisotropic model with finite gap in which $\Delta(k)$ varies depending on the direction in *k*-space is examined. It is suggested that the superconducting gap is finite and highly anisotropic.

Keywords: atomic force microscopy, scanning tunneling microscopy, organic superconductors

1. Introduction

A lot of effort has been made to elucidate the mechanism of the superconductivity in organic conductors such as BEDT-TTF salt. It has been recognized that the quasi-two dimensional electronic band with strong correlation plays an important role for this superconductivity similarly to high-T_c oxides. The possibility of the unconventional superconductivity is often suggested. The temperature dependence of the magnetic field penetration depth was energetically investigated. The power law dependence suggesting gapless superconductivity was reported [1, 2]. On the other hand, the thermally activated behavior fitted to the conventional BCS curve was reported by surface impedance measurement [3]. These results are still now controversial.

The electron tunneling spectroscopy is one of the most powerful tools in searching for the mechanism of the superconductivity, since it can obtain the electronic density of states directly. Among tunneling methods, the Scanning Tunneling Microscopy (STM) is most useful in investigating the surface electronic state because of its non-contacting configuration to the sample surface. Bando *et al.* [4] measured tunneling spectra for κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ by STM. However, they did not discuss about the pairing symmetry. In our previous report [5], it is understood that the superconducting gap is highly anisotropic. In the present article, we report the tunneling conductance with low noise obtained at the *b-c* surface of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ in superconducting phase by STM and discuss about the symmetry of the pair wave function.

2. Experimental

Single crystals of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, which are plate like along the *b-c* plane, were synthesized electro-chemically. The superconducting transition temperature were measured as $T_c \approx 10$ K from the midpoint of resistive transition. The Meissner volume fraction of about 60 % at 1.4 K shows that the sample undergoes the bulk superconductivity. As-grown surface along the *b-c* plane, which is flat and shiny, was investigated by low temperature STM. Mechanically sharpened Pr-Ir wire attached to the tube type piezo actuator was used as the scanning tip.

3. Results and Discussion

Figure 1 shows the typical tunneling differential conductance obtained at 1.4 K for two different samples. The energy gap structure associated with the superconducting state is clearly shown in both curves. Although the gap width slightly depends on sample, the functional form of the conductance curve is essentially the same. Additionally, it is confirmed that the functional shape of present spectra is almost consistent with our previous one [5] while the gap width differs slightly. It is open problem that the gap value differs from sample to sample.

So-called V-shape background often reported in high-T_c oxides is also observed. It is assumed that the top crystal surface is insulating $Cu(NCS)_2$ layer [6]. In STM experiment at the *b-c* plane, therefore, electrons in BEDT-TTF layer tunnel through the tunneling barrier which consists of in series of insulating $Cu(NCS)_2$ layer and the vacuum gap. In such a complicated tunneling configuration, the transition probability for the electron tunneling has the energy dependence [7]. The tunneling conductance is no longer proportional to the electronic density of states. The tip distance dependence of the conductance curve reported in $Bi_2Sr_2CaCu_2O_8$ [8] and κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ [5] is explained by such a mechanism. The enhancement of the conductance outside the gap edge 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 measurement at the lateral surface of single crystal, where the BEDT-TTF layer is exposed, electrons confined within BEDT-TTF layer tunnel through only the vacuum gap. Therefore, the tunneling conductance 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.

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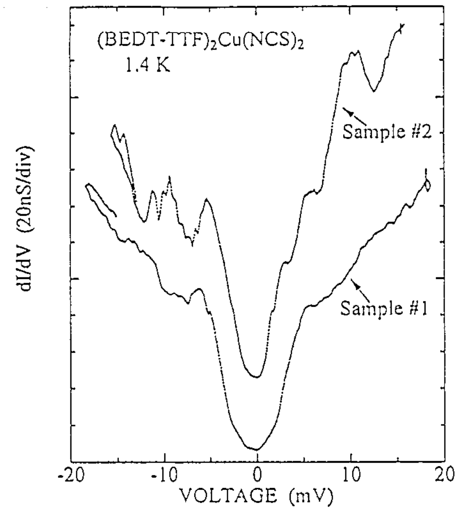

Figure 1. The tunneling differential conductance for different samples. The zero conductance line of each curve is shifted by two divisions for clarity.

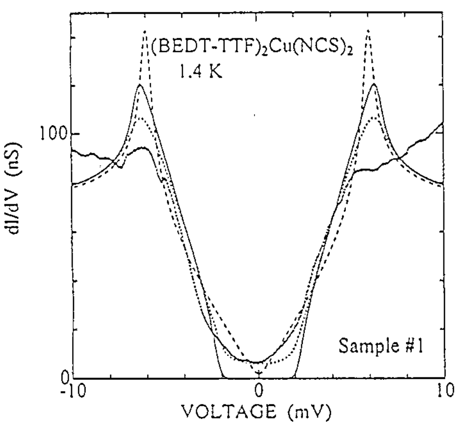

Figure 2. Fittings of the conductance to anisotropic gap models.

Whole shape of the conductance curve is essentially the same irrespective of the tip position except of mid-gap structure. Small structure in 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 the fixed position. We cannot discuss about the mid-gap structure in detail at present.

The differential conductance is reduced to almost zero and flat near zero bias voltage, similarly to the BCS density of states with s-wave pairing symmetry. However, a finite conductance inside the gap edge can not be explained by the BCS density of states even if the broadening of the one-electron level is taken into account. It strongly suggests the gap anisotropy.

Figure 2 shows fittings of the conductance obtained for sample #1 to anisotropic gap models. At first, we examine the d-wave symmetry with line nodes of the gap. The Fermi surface of BEDT-TTF salts is regarded as two dimensional. Naively, it is considered 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, it is allowed to be compared with the total density of states which is calculated by the integral over all directions in k-space. The broken line in the figure represents the calculated differential conductance for 1.4 K with Δ_0=6 meV, where Δ_0 is the gap amplitude. It is obvious that the measured conductance is almost flat near zero bias voltage and cannot be explained by the pure d-wave pairing alone. It is clear that the gap is finite on the Fermi surface.

We examine another anisotropic model with finite gap, in which Δ varies depending on the direction in k-space. We introduce the gap density function of a rectangular form as [8]

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

where Δ_{min} and Δ_{max} represent the minimum and maximum gap value, respectively. The solid line in Fig. 2 represents the calculated differential conductance at 1.4 K with Δ_{min}=2.2 meV and Δ_{max}=6.5 meV. In order to fit low energy region well, we introduce the broadening of the one-electron level. The dotted line in Fig. 2 is the broadened curve of the solid line in the figure with the broadening parameter Γ=0.33 meV. As shown in the figure, the obtained curve is almost reproduced by the model. Additionally, we confirm that the conductance curve for another sample #2 is as well reproduced by the above model with Δ_{min}=1.8 meV and Δ_{max}=5.5 meV. Although the gap width slightly differs in samples, the qualitative behavior of the obtained conductance is explained by the anisotropic model with a finite gap. It is understood that the gap is finite on the Fermi surface while Δ varies from 2 to 6 meV depending on the direction in k-space. 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 Δ_{max} is much lager and that for Δ_{min} is still slightly larger than that of the weak-coupling limit. It suggests the strong-coupling in this superconductivity.

Our present result shows that the superconducting gap is highly anisotropic while it is finite. Naively, the anisotropy is brought about by the d-wave. It is considered that the finite gap is brought about by the s-wave component and the d-wave component gives relatively large anisotropy. Our tunneling result suggests the mixed pair symmetry of s and d-wave, although it is an open problem to make the origin of the mixed symmetry clear.

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