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

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The superconducting phase of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ was investigated by the electron tunneling spectroscopy using low temperature STM. The tunneling differential conductance obtained at the *b-c* surface shows V-shaped gap structure consistent with the *d*-wave symmetry. The lateral surface of single crystals was also investigated. We found that the tunneling spectrum varies its shape depending on the tip direction. This indicates the gap anisotropy. Taking into account the ***k***-dependence of the tunneling transition probability, the in-plane anisotropy of the conductance is well explained by the *d*-wave symmetry with line nodes along the direction ϕ=45° from the *c*-axis. The *d*-wave pairing is strongly suggested in this material.

1. Introduction

A lot of interests have been attracted for the superconductivity in organic conductors such as BEDT-TTF salts. For this superconductivity, the quasi-two dimensional electronic band with strong correlation plays an important role similarly to high-T_c oxides. To elucidate the mechanism of the superconductivity, the temperature dependence of the magnetic field penetration depth was energetically investigated. The power law dependence suggesting gapless superconductivity was reported [1]. On the other hand, the temperature dependence consistent with the conventional BCS theory was reported [2]. These results are still now controversial.

The electron tunneling is suitable to search for the mechanism of the superconductivity, since it can obtain the electronic density of states directly. The Scanning Tunneling Microscopy (STM) is most useful in investigating the surface electronic state because of its non-contacting tunneling configuration. Bando *et al.* [3] 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 for the tunneling at the *b-c* surface [4], it was understood that the superconducting gap is highly anisotropic. In the present article, we report the in-plane anisotropy of tunneling spectra obtained by STM spectroscopic measurement at the lateral surface of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ in the superconducting phase 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 determined as T_c=10.4 K. As-grown surfaces both along and normal to the *b-c* plane were investigated by low temperature STM.

3. Results and Discussion

Figure 1 shows the typical tunneling differential conductance obtained at 1.5 K at the *b-c* surface. The energy gap structure is clearly shown. The linear background outside the gap often reported in high-T_c oxides is also observed. It is suggested that the top crystal surface is insulating $Cu(NCS)_2$ layer [5]. Electrons in BEDT-TTF layer must tunnel through the barrier which consists of insulating $Cu(NCS)_2$ layer and the vacuum gap. The linear background is partially explained by that the transition probability for the electron tunneling has the energy dependence in such a complicated tunneling configuration.

The conductance curve is V-shape at zero voltage. This curve is well fitted to the total density of states calculated from the *d*-wave with Δ_0=3 meV as the solid line in Fig. 1. In rare cases, we observed the U-shape conductance which is flat near zero voltage. We can not exclude at all the possibility that the tip contacts to the insulating surface. Such an instable tunneling configuration would bring a scatter in results at the *b-c* surface. We consider that the V-shape conductance is intrinsic.

We succeeded to obtain the tunneling conductance at the lateral surface. In this measurement, the tip approaches along the normal to as-grown lateral surfaces. Figure 2 shows the conductance at different tip direction which is described by the angle ϕ measured from the *c*-axis. The shape of spectra inside the gap edge varies depending on the tip

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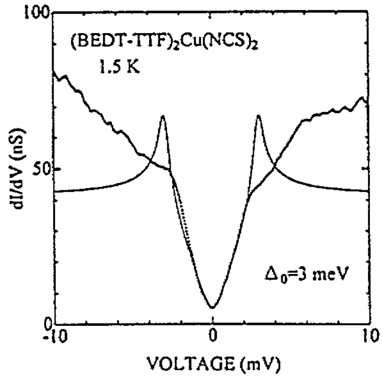

Figure 1. The tunneling conductance at the *b-c* surface. The solid line represents the calculated curve for the *d*-wave with Δ_0=3 meV.

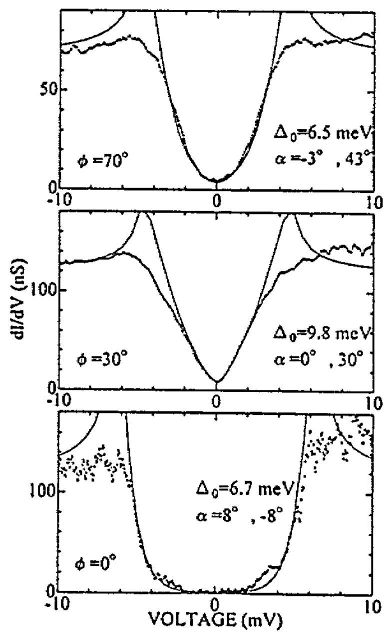

Figure 2. The tunneling conductance for different tip directions at the lateral surface. Curves for ϕ=0, 30 and 70° are shown. Solid lines are fittings described in the text.

direction as well as the gap width. The conductance at higher voltage is flat in contrast to that for the *b-c* surface. It suggests that electrons in BEDT-TTF layer tunnel through only the vacuum gap. Therefore the conductance at the lateral surface is expected to be directly proportional to the electronic density of states. The directional dependence indicates the gap anisotropy. This suggests that the ***k***-dependence of the transition probability for the electron tunneling is substantially larger in contrast to $Bi_2Sr_2CaCu_2O_8$ in our previous report [6].

In discussing the gap anisotropy, we assume a simple *d*-wave described as

$$\Delta(\phi) = \Delta_0 cos2(\phi+\alpha) \quad (1)$$

A constant α describes the angle, in which $\Delta(\boldsymbol{k})$ has its maximum, from the *c*-axis. The transition probability for the electron tunneling depends on the component of the kinetic energy perpendicular to the barrier and its dependence is described by the factor of $\exp(-\beta\sin^2\theta)$, where θ is the angle between the wave vector and the normal to the barrier and β is the constant depending on the potential height and the width of the barrier [7]. For the practical STM measurement, β is roughly estimated as β~20. Fittings for each direction, in which the gap anisotropy and the angular dependence of the transition probability are taken into account, are shown in Fig. 2 as solid lines. The fitting parameter α's are 8 or -8° for ϕ=0°, 0 or 30° for ϕ=30°, and -3 or 43° for ϕ=70°. Among these values, α~0° is most possible. In-plane anisotropy of the conductance is successfully explained by the above analysis with the *d*-wave symmetry. The nodal line of the gap is along the direction of about ϕ=45° from the *c*-axis.

The electronic band of BEDT-TTF salts is quasi-two dimensional and there is little dispersion along the a^*-axis. For the tunneling at the *b-c* surface, the obtained result is also consistent with the *d*-wave, because in-plane anisotropy is expected to be averaged out and that leads to the linear conductance near zero voltage. It is noteworthy that the both result for the *b-c* surface and directional dependence for the lateral surface are explained by the *d*-wave. It is suggested that the symmetry of the pair wave function for this superconductivity is the *d*-wave.

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