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STM Spectroscopy on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

T. Arai [a,*], K. Ichimura [a], K. Nomura [a], S. Takasaki [b], J. Yamada [b], S. Nakatsuji [b], H. Anzai [b]

[a] *Division of Physics, Hokkaido University, Sapporo 060-0810, Japan*

[b] *Department of Material Science, Himeji Institute of Technology, Kamigori, Hyogo 678-1297, Japan*

Abstract

The dI/dV-V curves in the superconducting phase of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals have been measured by STM spectroscopy. The tunneling spectra on the lateral surfaces systematically vary depending on the tunneling direction in the b-c plane. This is explained by the $d_{x^2-y^2}$-wave gap model considering the $\boldsymbol{k}$ dependence of the tunneling transition probability. The pseudogap-like behavior is observed at temperatures between T_c and 45 K. It is strongly suggested that the pair wave function has the $d_{x^2-y^2}$-wave symmetry in this salt.

Key words: scanning tunneling microscopy, superconducting phase transitions, organic superconductors

1. Introduction

The symmetry of the pair wave function is an important clue to clarify the mechanism of the superconductivity. However, there is a divergence of the experimental results for κ-(BEDT-TTF)$_2$X. The ^{13}C NMR spin-lattice relaxation rate $T_1^{-1}(T)$ [1], the electronic specific heat $C_{el}(T)$ [2] and some experimental results of the magnetic field penetration depth $\lambda(T)$ [3] suggest an unconventional pairing with a highly anisotropic superconducting gap, whereas some measurements of $\lambda(T)$ support the s-wave symmetry [4].

Scanning tunneling microscope (STM) spectroscopy is a powerful method for direct observations of the electronic density of states with high energy resolution. The highly anisotropic gap in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been reported by the STM spectroscopy [5–7]. In this paper, we present the results of STM spectroscopy on the lateral surfaces of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals along various tunneling directions in the b-c plane, and discuss the symmetry of the pair wave function. Furthermore, it is shown that the pseudogap-like behavior is observable above T_c in this salt.

2. Experimental

κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystals were grown by the electrocrystallization method. The superconducting transition temperature T_c was determined as T_c=10.4 K from the midpoint of the resistive transition.

* Corresponding author. E-mail: arai@phys.sci.hokudai.ac.jp

3. Results and Discussion

The dI/dV-V curves observed at 1.5 K along various tunneling directions in the b-c plane are shown together in Fig. 1, where the tunneling direction is denoted by the angle ϕ from the c-axis. These curves clearly show the superconducting gap structure. The functional form of the curve inside the gap edge varies systematically depending on ϕ. For ϕ=0°, the curve is rather flat around V=0, and the magnitude of the gap Δ_p, defined as half the energy difference between the gap edges, is relatively larger. While, the curves along ϕ=51° and 56° show the linear voltage dependence of dI/dV around V=0, and Δ_p is relatively smaller. The dI/dV-V curves outside the gap edge are flat in contrast to those on the b-c plane [7]. This is probably attributed to the tunneling of electrons in the BEDT-TTF layer only through the vacuum barrier. For each tunneling direction, essentially the same curves were observed reproducibly irrespective of the tip position and the tip distance from the surface within the limitation of the piezoelectric actuator. The tunneling direction dependence of the dI/dV-V curve indicates the highly anisotropic gap in the b-c plane. Besides, this also signifies that the dependence of the tunneling transition probability on the wave vector $\boldsymbol{k}$ is not negligible in STM measurement.

In the theoretical calculation of the electronic density of states, we assume a simple d-wave gap model, given as $\Delta=\Delta_0 \cos 2\theta$, where Δ_0 and θ are the maximum value of the gap and the angle from the maximum gap direction in $\boldsymbol{k}$ space, respectively. According to the WKB approximation [8], the $\boldsymbol{k}$-dependent tunneling is described

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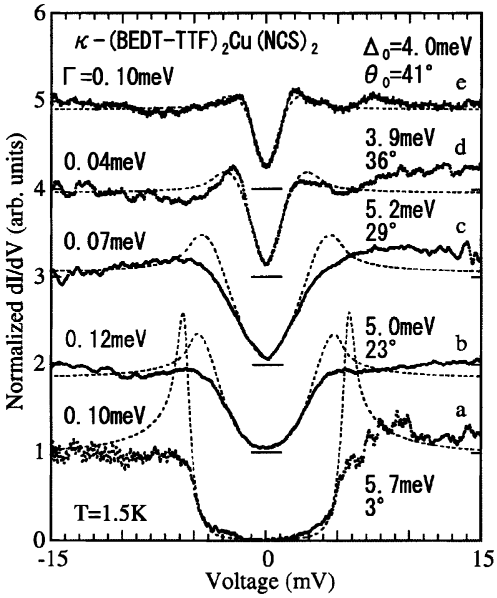

Fig. 1. The dI/dV-V curves on the lateral surfaces of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ along the directions of ϕ=0° (a), 70° (b), 30° (c), 56° (d) and 51° (e) from the c-axis in the b-c plane. Each curve is normalized at the bias voltage V=−15 mV and aligned at intervals of one division. The broken curve represents the calculated conductance curve by the d-wave gap model considering the $\boldsymbol{k}$ dependence of the tunneling transition probability.

by the factor $p(\theta-\theta_0) = \exp[-\beta\sin^2(\theta-\theta_0)]$, where $\beta = E_F d\sqrt{2m/(U-E_F)}/\hbar$. 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. The value of β, which characterizes the $\boldsymbol{k}$ dependence of the tunneling transition probability, was roughly estimated as $\beta\sim20$. This value is relatively larger than the reported value of β=8 for $Bi_2Sr_2CaCu_2O_8$ [9] probably due to the smaller work function. The calculated dI/dV-V curve for each direction using this model is shown by the broken curve in Fig. 1, where Γ is the broadening parameter of the one-electron level. The systematic change of the functional form of the dI/dV-V curve is reproduced well around V=0. The obtained value of Δ_0=3.9−5.7 meV is almost consistent with that on the b-c plane, although the variation of the value implies that the sample dependence of Δ_0 is substantially large.

The d-wave gap has the four-fold symmetry in $\boldsymbol{k}$ space in respect to the magnitude of the gap. Considering this, one can reduce the range of ϕ to $0°\leq\phi\leq45°$. Thus, the directions of ϕ=51°, 56° and 70° are equivalent to ϕ'=39°, 34° and 20°, respectively, where ϕ' denotes the reduced ϕ. The value of θ_0 is almost the same as ϕ' for each dI/dV-V curve. This means that the nodal direction 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 suggested that the order parameter in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has the $d_{x^2-y^2}$-wave symmetry.

Figure 2 shows the temperature dependence of the

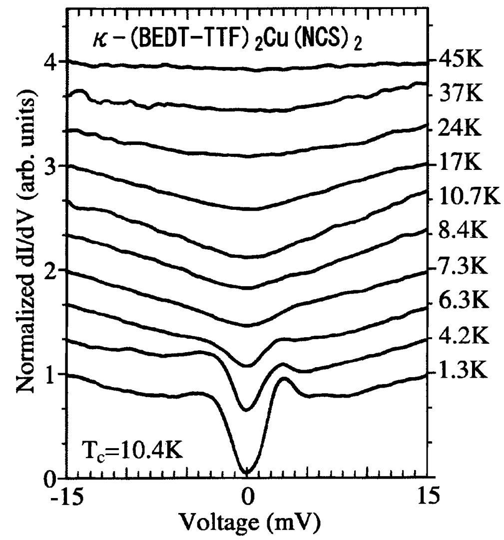

Fig. 2. Temperature dependence of the dI/dV-V curve on the b-c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Each curve is normalized to the conductance at V=−15 mV and offset vertically for clarity.

dI/dV-V curve on the b-c plane. The superconducting gap is clearly observed at 1.3 K. With the increase of temperature, the zero-bias conductance $dI/dV|_{V=0}$ rapidly increases, and the gap structure is smeared. Just above the T_c=10.4 K, a broad dip in the electronic density of states is observed around the Fermi energy. This broad dip still remains up to about 45 K. This unusual temperature dependence is reminiscent of that for high-T_c cuprates. The temperature at which the broad dip disappears is close to the temperature at which the anomalous enhancement in $(T_1T)^{-1}$ is observed by ^{13}C NMR. We consider the broad dip in the electronic density states as the pseudogap.

Acknowledgments

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