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Superconducting and normal-state gaps in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ studied by STM spectroscopy

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Abstract

Scanning tunneling microscope (STM) spectroscopy on the b–c plane of single crystals of an organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been performed in superconducting and normal states with varying temperature. The temperature dependence of the zero-bias conductance $dI/dV|_{V=0}$ is well explained by the d-wave gap model considering the T^2 dependence of the broadening parameter of the one-electron level $\Gamma(T)$, which is obtained from the fitting of the dI/dV–V curves to the d-wave gap model. The dI/dV–V curve shows a broad dip around the Fermi energy above $T_c = 10.4$ K. This pseudogap structure remains up to about 45 K. The magnitude of the pseudogap is much larger than that of the superconducting gap $\Delta_p \sim 3$ meV.

Keywords: A. Organic crystals; A. Superconductors; D. Tunneling

PACS: 74.70.Kn; 74.50.+r; 74.25.Jb

1. Introduction

Since the discovery of BEDT-TTF superconductors, much attention has been paid to the mechanism of superconductivity in those salts. Among them, the κ-(BEDT-TTF)$_2$X family, where X is an electron acceptor molecule such as Cu(NCS)$_2$ or Cu[N(CN)$_2$]Br has been intensively investigated by various methods because of the relatively high superconducting transition temperature $T_c \sim 10$ K. The salt of κ-(BEDT-TTF)$_2$X has the layered crystal structure and the quasi-two-dimensional electronic band structure. Furthermore, its superconducting phase appears in close proximity of an antiferromagnetic insulating phase [1,2], just like high-T_c cuprates. Various kinds of experiment have so far been performed to investigate the mechanism of the superconductivity in κ-(BEDT-TTF)$_2$X. For example, it is strongly suggested from the temperature dependence of the Knight shift $K_s(T)$ below T_c that the electron pair is in the spin-singlet state [3,4]. The analyses of the ^{13}C NMR spin-lattice relaxation rate $T_1^{-1}(T)$ [3–5], the electronic specific heat $C_{el}(T)$ [6] and some experimental results of the magnetic field penetration depth $\lambda(T)$ [7–9] suggest the d-wave gap, whereas other results of $\lambda(T)$ [10–12] support the isotropic s-wave symmetry.

To understand the mechanism of superconductivity, information about the behavior of the physical properties above T_c is also essential. Up to now, some remarkable behaviors in the normal state of κ-(BEDT-TTF)$_2$X have been reported. In ^{13}C NMR measurement, the spin-lattice relaxation rate $(T_1T)^{-1}$ shows a peak around 50 K [13,14], and the Knight shift $K_s(T)$ rapidly decreases below the same temperature [13]. Besides, the resistivity shows an inflection point [15,16], and the spin susceptibility $\chi(T)$ starts to decrease [14] at almost the same temperature. These behaviors suggest that the normal-state gap in the electronic excitation spectrum is present far above T_c. The presence of the pseudogap above T_c has been directly confirmed by measurements, such as angle-resolved photoemission spectroscopy [17,18] and scanning tunneling microscope (STM) spectroscopy [19,20] for a high-T_c cuprate $Bi_2Sr_2CaCu_2O_8$. The question is, therefore, raised as to whether the pseudogap is a common characteristic for the d-wave superconductors or not. The direct observation of the pseudogap gives a suggestive guideline to this question.

STM spectroscopy is one of the ideal methods for

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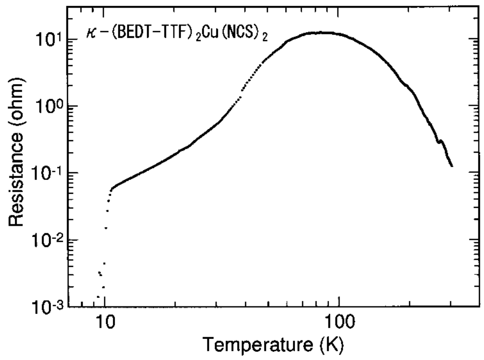

Fig. 1. Temperature dependence of the resistance for a κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ single crystal.

investigating the superconducting gap because of the direct observation of the electronic density of states with high-energy resolution ($\sim k_B T$). In our previous study of STM spectroscopy, we have found that the superconducting gap has the d-wave symmetry in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, and the direction of the line nodes is $\pi/4$ from the k_b- and k_c-axes [21,22]. In this study, we present the results of STM spectroscopy on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at various temperatures. We show that the temperature dependence of the zero-bias conductance $\mathrm{d}I/\mathrm{d}V|_{V=0}$ is consistent with the d-wave gap model considering the broadening parameter of the one-electron level $\Gamma(T)$, and a pseudogap exists in the electronic density of states in this material above T_c.

2. Experimental

Single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ used in the present study were grown by the electrocrystallization method [23]. The typical size of a single crystal was approximately $1 \times 1 \times 0.1\ \mathrm{mm}^3$. The superconducting transition temperature T_c was determined as 10.4 K from the midpoint of the resistive transition shown in Fig. 1. During the measurement, the sample was mounted in the STM unit filled with low-pressure helium as thermal exchange gas. A mechanically sharpened Pt–Ir alloy wire was used as the STM tip. The differential tunneling conductance $\mathrm{d}I/\mathrm{d}V(V)$ was directly obtained on the b–c plane by a standard lock-in technique with a 1 kHz AC modulation of about 100 μV added to the bias voltage.

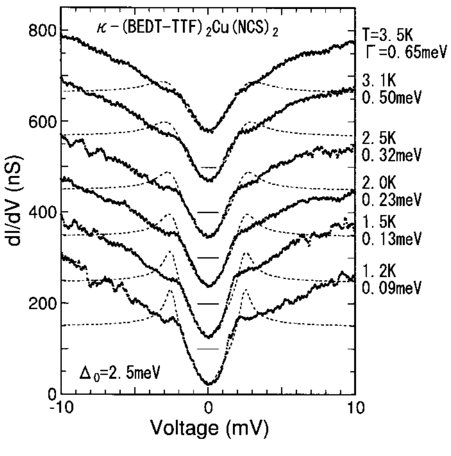

Fig. 2. $\mathrm{d}I/\mathrm{d}V$–V curves observed on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at $T = 1.2$, 1.5, 2.0, 2.5, 3.1 and 3.5 K. The dashed line represents the calculated curve using the d-wave gap model with the broadening parameter of the one-electron level Γ. Each curve is aligned at intervals of 100 nS for clarity.

3. Results and discussion

Fig. 2 shows the $\mathrm{d}I/\mathrm{d}V$–V curves observed on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at $T = 1.2$, 1.5, 2.0, 2.5, 3.1 and 3.5 K. In this figure, V_0 and I_0 denote the initial bias voltage and the initial tunneling current, respectively, and each $\mathrm{d}I/\mathrm{d}V$–V curve is aligned at intervals of 100 nS. The superconducting gap structure is clearly shown as a dip in the $\mathrm{d}I/\mathrm{d}V$ for each curve. The zero-bias differential conductance $\mathrm{d}I/\mathrm{d}V|_{V=0}$ rapidly increases with the increase of temperature. In Fig. 2, the dashed line represents the fitting curve using the d-wave gap model $\Delta = \Delta_0 \cos 2\theta$, where Δ_0 and θ are the maximum value of the gap and the azimuthal angle in k space, respectively, with the broadening parameter of the one-electron level Γ [24]. The gap structure is well fitted by the calculated curve with $\Delta_0 = 2.5$ meV for each $\mathrm{d}I/\mathrm{d}V$–V curve indicating that the superconducting gap has the d-wave symmetry, in agreement with our previous results [21,22].

In order to investigate the temperature dependence of Γ, we plot Γ, which is obtained from the fitting of the $\mathrm{d}I/\mathrm{d}V$–V curves shown in Fig. 2, as a function of T/T_c as exhibited in Fig. 3. The $\Gamma(T)$ monotonously increases with the increase of temperature. It is known that $\Gamma(T)$ coarsely follows the exponential law at low temperature for s-wave

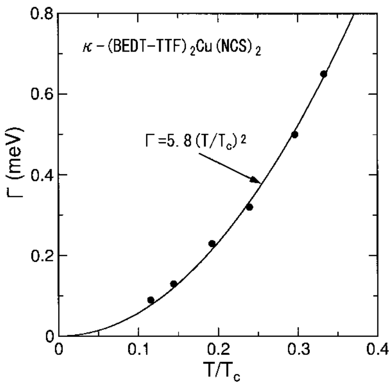

Fig. 3. Γ plotted as a function of T/T_c. The solid line represents the T^2 fitting.

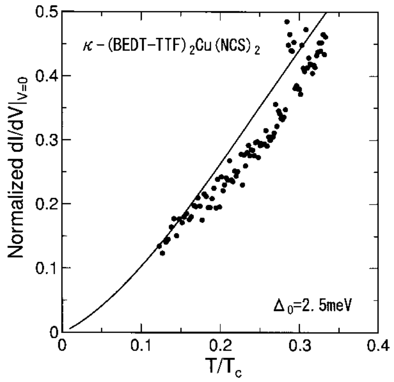

Fig. 4. Temperature dependence of $dI/dV|_{V=0}$. Each point is normalized to the conductance at the gap edge. The solid line represents the calculated curve by the d-wave gap model taking into account $\Gamma(T) = 5.8(T/T_c)^2$.

superconductors because of the finite gap on the whole Fermi surface [24,25]. For the present material, however, the exponential curve can be fitted only when Δ_0 is very small ($\Delta_0 \sim 0.3$ meV) compared with $\Delta_0 = 2.5$ meV obtained from the fitting of the dI/dV–V curves. In the present case, a T^2 fitting gives the better agreement with the data rather than the exponential fitting. In Fig. 3, the T^2-fitting curve $\Gamma(T) = 5.8(T/T_c)^2$ is represented by the solid line as the best fitting curve of the data. This power-law temperature dependence is presumably due to the presence of line nodes of the d-wave gap on the Fermi surface.

As shown in Fig. 2, the zero-bias conductance $dI/dV|_{V=0}$ varies with temperature. The temperature dependence of $dI/dV|_{V=0}$, which is obtained from the dI/dV–V curve on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at each temperature, is exhibited in Fig. 4. Each $dI/dV|_{V=0}(T)$ is

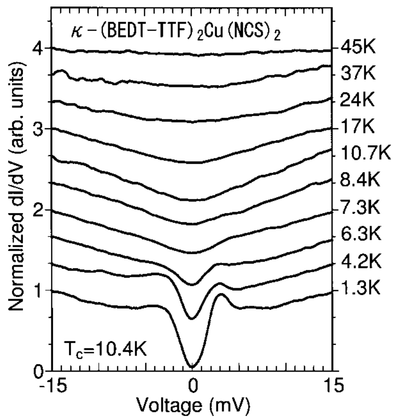

Fig. 5. dI/dV–V curves observed on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of temperature. Each curve is normalized to the conductance at $V = -15$ mV and offset vertically for clarity.

normalized to the conductance at the gap edge, which is almost the same as the calculated conductance outside the gap region as shown in Fig. 2. The $dI/dV|_{V=0}(T)$ rapidly increases with the increase of temperature showing the nearly T-linear dependence. The solid line represents the calculated curve using the above-mentioned d-wave gap model with $\Delta_0 = 2.5$ meV taking the T^2 dependence of $\Gamma(T)$ into account. The rapid variation of $dI/dV|_{V=0}(T)$ is well reproduced by the calculated curve. This is also consistent with that the gap has the d-wave symmetry.

We now focus on the temperature dependence of the dI/dV–V curve. Fig. 5 shows the dI/dV–V curves observed on the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at temperatures from 1.3 to 45 K. Each dI/dV–V curve is normalized to the conductance at $V = -15$ mV and offset vertically. At $T = 1.3$ K, the superconducting gap is clearly observed. With the increase of temperature, the zero-bias conductance $dI/dV|_{V=0}$ rapidly increases, and the gap structure is smeared. At about 8.4 K, the gap structure becomes obscure. There is no noticeable change of the dI/dV–V curve across $T_c = 10.4$ K. Just above T_c, a broad dip in dI/dV is still observed around $V = 0$. This broad dip remains up to about 45 K, and the flat dI/dV–V curve is observed above 45 K. This temperature dependence of the dI/dV–V curve is quite unusual compared with that for the conventional BCS superconductors. Henceforth, we refer to this normal-state gap structure as a pseudogap.

The pseudogap above T_c has also been reported for high-T_c cuprates by STM spectroscopy [19,20]. It is an interesting question as to whether the origin of the pseudogap is the same or not between κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and high-T_c cuprates. The remarkable difference in the dI/dV–V curve between the present material and high-T_c cuprates is the energy scale of the pseudogap with respect to that of the superconducting gap. For κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the magnitude of the pseudogap $E_g \gg 15$ meV, is much larger than that of the superconducting gap $\Delta_p \sim 3$ meV, where Δ_p is defined as half the energy difference between the gap edges. On the other hand, the magnitude of the gap structure does not change significantly across T_c for high-T_c cuprates. It is therefore suggested that the pseudogap does not directly evolve into the superconducting gap at least for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. It is worth mentioning that the temperature at which the pseudogap appears is close to the temperature (~50 K) at which the anomalous enhancement in the nuclear spin-lattice relaxation rate $(T_1T)^{-1}$ [13,14] and the rapid decrease in the Knight shift $K_s(T)$ [13] are observed by ^{13}C NMR. It seems that this fact raises a fundamental issue about the relationship between the origin of the pseudogap and the spin fluctuations in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

4. Conclusions

We have performed STM spectroscopy on the b–c plane of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ at various temperatures. The observed dI/dV–V curve is well fitted to the calculated curve using the d-wave gap model. From this fitting, it is found that the temperature dependence of the broadening parameter of the one-electron level Γ approximately follows the T^2 law. This is probably attributed to the presence of line nodes of the d-wave gap on the Fermi surface. The temperature dependence of the zero-bias conductance $dI/dV|_{V=0}$ is also explained by the d-wave gap model taking into account $\Gamma(T)$. We find that the pseudogap is observed above T_c in this salt, which evolves below about 45 K. This temperature corresponds to that at which the anomalous enhancement in the nuclear spin-lattice relaxation rate $(T_1T)^{-1}$ and the rapid decrease in the Knight shift $K_s(T)$ are observed by ^{13}C NMR. The energy scale of the pseudogap is much larger than the magnitude of the superconducting gap $\Delta_p \sim 3$ meV.

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