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STM Spectroscopy on Anisotropic Superconductors

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The superconducting phase of organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and (MDT-TTF)$_2$AuI$_2$ was investigated by the electron tunneling spectroscopy using low temperature STM. The tunneling differential conductance at the lateral surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ varies its shape depending on the tip direction. The in-plane anisotropy of the conductance is well explained by the *d*-wave symmetry with line nodes along the direction 45° from the *c*-axis. For (MDT-TTF)$_2$AuI$_2$, the tunneling conductance at $T = 1.4$ K shows the superconducting energy gap structure clearly. The finite conductance inside the gap edge suggests the gap anisotropy. The tunneling spectrum is explained by the *d*-wave pairing. The obtained gap $\Delta_0 = 2$ meV ($2\Delta_0/kT_c = 12$) is larger than that of the weak coupling limit. The pseudogap structure is observed near T_c.

KEY WORDS: STM; electron tunneling; organic superconductors; pairing symmetry.

1. INTRODUCTION

A lot of interests have been attracted for the superconductivity in organic conductors such as BEDT-TTF salts [1]. It is recognized that the quasi-two dimensional electronic band with strong correlation plays an important role similarly to high-T_c oxides. The evidence of the unconventional pairing in BEDT-TTF salts was often suggested by the power law temperature dependence of the magnetic field penetration depth [2,3], the NMR relaxation rate [4–6], and the electronic specific heat [7].

The electron tunneling spectroscopy is suitable for investigation of the superconducting state [8] because of its high energy resolution. Additionally, it is easy to analyze the tunneling data: the tunneling differential conductance gives the electronic density of states directly. The scanning tunneling microscope (STM) is most useful to probe the surface electronic state because of its noncontacting tunneling configuration. There is less disturbance to the sample surface. The movable tip enables to probe the local electronic state with atomic spatial resolution. Bando *et al.* [9] measured tunneling spectra for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by STM at first. They reported the gap parameter of $\Delta = 2.4$ meV, which is larger than that of the BCS prediction. In our previous report for the tunneling at the *b*–*c* surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [10], it was understood that the superconducting gap is highly anisotropic.

An organic superconductor (MDT-TTF)$_2$AuI$_2$, which has T_c of about 4 K [11], is based on an asymmetric donor MDT-TTF. The arrangement of MDT-TTF molecules, which are arranged at checked pattern, is the same as that of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The electronic band is two dimensional in the k_a–k_b plane. The Fermi surface of (MDT-TTF)$_2$AuI$_2$ was reported as essentially the same as κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [12]. For the symmetry of the pair wave function, the *s*-wave symmetry was suggested by the NMR measurement [13]. Kobayashi *et al.* measured the temperature dependence of ^{1}H relaxation

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rate $1/T_1$ by the field cycling method and observed an enhancement of the $1/T_1$ just blow T_c. They claimed that this enhancement corresponds to the Hebel–Slichter peak expected for the isotropic gap.

In order to determine the symmetry of the pair wave function in organic superconductors, we investigated the superconducting state by the electron tunneling using STM. In the present article, we report tunneling spectra at the lateral surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and at the a–b surface of (MDT-TTF)$_2$AuI$_2$. The symmetry of the pair wave function is discussed.

2. EXPERIMENTAL

Both single crystals of κ-(BEDT-TTF)$_2$ Cu (NCS)$_2$ and (MDT-TTF)$_2$AuI$_2$, which are plate like along the b–c and a–b plane, respectively, were synthesized electrochemically. The typical dimension of both crystals is about $1 \times 1 \times 0.1$ mm.[3] The superconducting transition temperature of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ was determined as $T_c = 10.4$ K from the midpoint of the resistive transition. For (MDT-TTF)$_2$AuI$_2$, the transition temperature was determined as T_c(onset) = 4.5 K from the temperature dependence of the magnetic susceptibility measured by SQUID magnetometer with applying the field of $H = 0.5$ G.

As-grown surfaces normal to the b–c plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ were investigated. For (MDT-TTF)$_2$AuI$_2$, as-grown surface of the a–b plane was investigated by low temperature STM. A mechanically sharpened Pt–Ir wire was used as the scanning tip.

3. RESULTS AND DISCUSSION

We succeeded in obtaining the tunneling conductance at the lateral surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. In this measurement, the tip approaches along the normal to as-grown lateral surfaces. Figure 1 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 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

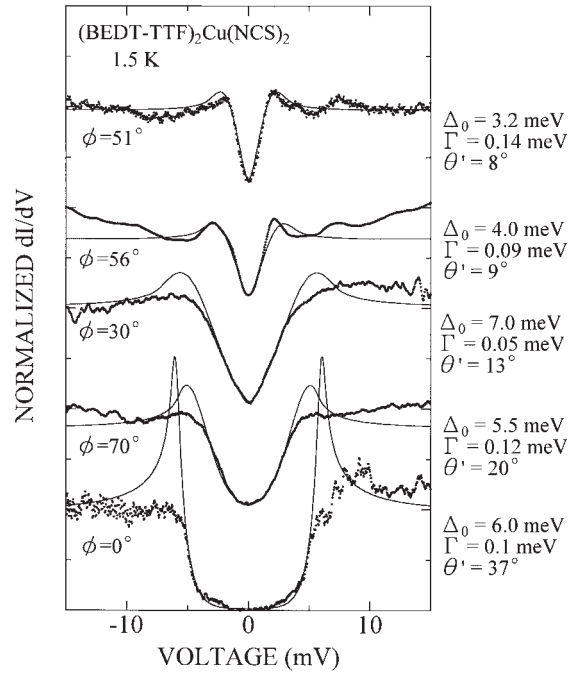

Fig. 1. The tunneling conductance for different tip direction at the lateral surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The zero-conductance of each curve is shifted by two divisions for clarity. Solid lines represent the calculation described in the text.

proportional to the electronic density of states [14]. The directional dependence indicates the gap anisotropy. This suggests that the $\boldsymbol{k}$-dependence of the transition probability for the electron tunneling is substantially large in the present configuration and that the angle-resolved measurement is possible in STM spectroscopy.

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

$$\Delta(\phi) = \Delta_0 \cos 2(\phi + \alpha) \qquad (1)$$

where α is a phase factor. 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 [15]. For the practical STM measurement, β is roughly estimated as $\beta \sim 20$. 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. 1 as solid lines. We need only a little broadening factor

Γ for better fittings. We use a fitting parameter θ' ($0 \leq \theta' \leq 45°$), which is an angle between the tunneling direction and a node of the gap. Figure 2 shows the fitting parameter θ' as a function of ϕ. Taking into account the fourfold symmetry of the gap anisotropy, one can reduce the range of ϕ as $0 \leq \phi \leq 45°$. As shown in the figure, all points are approximately alined in the straight line, which has a slope of -1, corresponds to the *d*-wave symmetry, and intersects vertical axis at $\theta' = 45°$. 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 $\phi = 45°$ from the k_b or k_c-axis. Therefore the $d_{x^2-y^2}$-wave symmetry is suggested.

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, we obtained the linear conductance near zero voltage [16], which is consistent with the *d*-wave symmetry. It is noteworthy that the both results for the *b*–*c* surface and directional dependence for the lateral surface are explained by the *d*-wave symmetry. It is suggested that the symmetry of the pair wave function for this superconductivity is the $d_{x^2-y^2}$-wave.

For single crystals of $(MDT\text{-}TTF)_2AuI_2$, the tunneling differential conductance was obtained at the *a*–*b* surface. Figure 3 shows the temperature dependence of the tunneling spectrum. At $T = 77$ K, the conductance is flat suggesting the metallic phase. The conductance at $T = 4.2$ K, which is close to T_c, already shows gap structure. The conductance near zero bias voltage is reduced by about 50% of the normal conductance. The conductance at zero bias voltage decreases with decreasing temperature. At $T = 1.4$ K, the tunneling spectrum clearly shows the energy gap

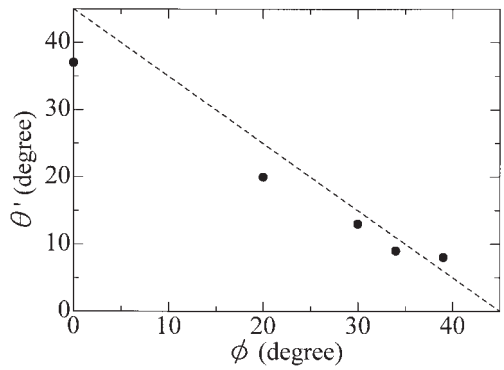

Fig. 2. The fitting parameter θ' as a function of ϕ. The broken line represents the $d_{x^2-y^2}$-wave symmetry.

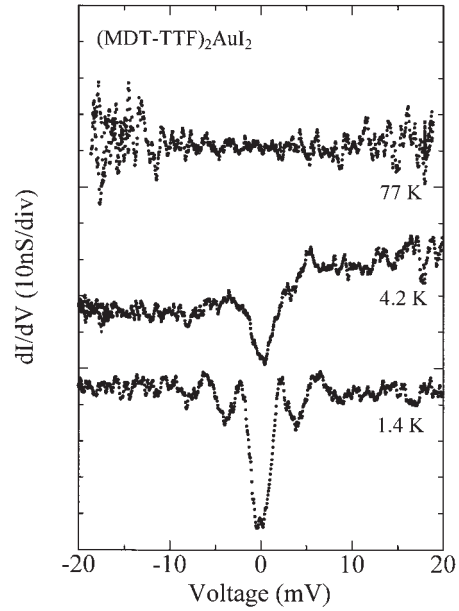

Fig. 3. The temperature dependence of the tunneling conductance at the *a*–*b* surface of $(MDT\text{-}TTF)_2AuI_2$. The zero-conductance line of each curve is shifted by two divisions for clarity.

structure associated with the superconducting state. The conductance at zero bias is reduced to about 10% of the normal conductance. The gap edge is observed clearly as the enhancement of the conductance at $V = 2$ mV. Another structure outside the gap edge was also found at $V = 6$ mV. However, we cannot explain well the origin of this structure. The inelastic tunneling or some kind of elementary excitation that mediates this superconductivity might bring about such a structure.

For tunneling spectrum at $T = 1.4$ K, we discuss about the functional form of the conductance inside the gap. At first, we examined the *s*-wave pairing. The broken line in Fig. 4 represents the calculation with $\Delta = 1.8$ meV and the broadening parameter $\Gamma = 0.27$ meV, which characterizes the lifetime broadening of the one-electron level. As shown in the figure, the finite conductance inside the gap cannot be explained by the isotropic gap. The gap anisotropy is strongly suggested.

Naively, the anisotropy is brought about by the *d*-wave pairing. We examine the *d*-wave symmetry as the simplest form described as Eq. (1). The solid line in Fig. 4 represents a calculation for the *d*-wave symmetry with $\Delta_0 = 2$ meV. As shown in the figure, the fitting is satisfactory. The observed anisotropy is explained by the *d*-wave pairing. The obtained gap $\Delta_0 = 2$ meV corresponds to $2\Delta_0/kT_c = 12$ with $T_c =$

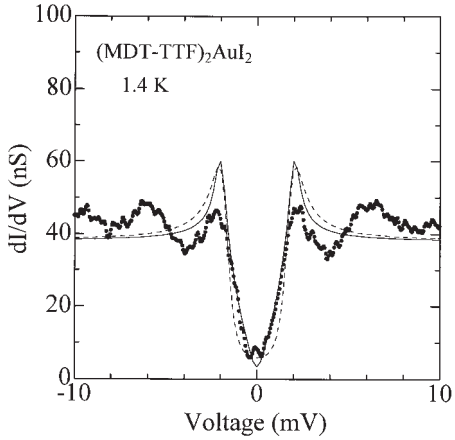

Fig. 4. The tunneling conductance for (MDT-TTF)$_2$AuI$_2$ at T = 1.4 K. The broken line represents the calculation for the *s*-wave symmetry with Δ = 1.8 meV and Γ = 0.27 meV. The solid line represents the calculation for the *d*-wave symmetry with Δ_0 = 2 meV.

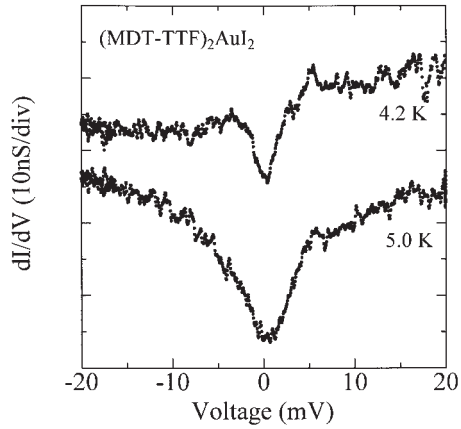

Fig. 5. The tunneling conductance for (MDT-TTF)$_2$AuI$_2$ at T = 4.2 and 5 K. The zero-conductance line for T = 4.2 K is shifted by two divisions for clarity.

4 K, which is much larger than mean field value of 3.5. However, this is almost consistent with that obtained at κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ of $2\Delta_0/kT_c$ = 7 ~ 12 [10].

For the symmetry of the pair wave function, the *d*-wave pairing is strongly suggested. However, we cannot completely exclude the symmetry which brings about the anisotropy with the finite gap such as the anisotropic *s, s* + *d,* or *s* + i*d* symmetry. But the observed large anisotropy is not explained by the finite gap. Even if the finite gap exists, the isotropic component would be very small. From our tunneling result, the *d*-wave is the most plausible candidate for the symmetry of the pair wave function. On the other hand, the *s*-wave pairing is suggested by the NMR relaxation rate [13]. It is not consistent with the present tunneling result. We cannot explain completely the difference in result between NMR and STS. One possibility is that the gap is finite but has anisotropy and that the isotropic component is relatively large. However, the STS measurement suggests that the isotropic component is very small or zero.

We found that the gap structure remains even above T_c. Figure 5 shows the differential conductance at T = 4.2 and 5 K. A relatively clear gap structure is observed at T = 4.2 K. The conductance at zero bias is reduced and the gap edge is observed as a sharp peak. Indeed, T = 4.2 K is lower than T_c(onset) = 4.5 K, the observed gap structure is clearer than expected. At T = 5 K, obviously above T_c, the broadened gap structure is observed. Therefore, we conclude that the gap exists even above T_c. This behavior is similar to pseudogap structure recently reported in high-T_c oxides. Renner *et al.* [17] reported the temperature dependence of STS spectra both on underdoped and overdoped $Bi_2Sr_2CaCu_2O_8$. They observed that the gap structure still exists even above T_c. At present, we cannot explain the origin and the relation between the pseudogap and the superconducting gap in (MDT-TTF)$_2$AuI$_2$.

In summary, organic superconductors κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and (MDT-TTF)$_2$AuI$_2$ were studied by the electron tunneling using a low temperature STM. We found that the tunneling spectrum varies depending on the tunneling direction at the lateral surface of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The directional dependence is explained by the *d*-wave symmetry with line nodes along the direction 45° from the *c*-axis. For (MDT-TTF)$_2$AuI$_2$, tunneling conductance at the *a*–*b* surface shows the energy gap structure clearly. The tunneling spectrum is explained by the *d*-wave pairing with Δ_0 = 2 meV, correspondingly $2\Delta_0/kT_c$ = 12. The pseudogap structure is also found above T_c.

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REFERENCES

1. T. Ishiguro and K. Yamaji, *Organic Superconductors,* 2nd ed. (Springer-Verlag, Berlin, 1998).

2. K. Kanoda, K. Akiba, K. Suzuki, T. Takahashi, and G. Saito, *Phys. Rev. Lett.* **65**, 1271 (1990).
3. L. P. Le, G. M. Luke, B. J. Sternlief, W. D. Wu, and Y. J. Uemura, *Phys. Rev. Lett.* **68**, 1923 (1992).
4. S. M. DeSoto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser, and J. M. Williams, *Phys. Rev. B* **52**, 10364 (1995).
5. H. Mayaffre, P. Wzietek, D. Jerome, C. Lenoir, and P. Batail, *Phys. Rev. Lett.* **75**, 4122 (1995).
6. K. Kanoda, K. Miyagawa, A. Kawamoto, and Y. Nakazawa, *Phys. Rev. B* **54**, 76 (1996).
7. Y. Nakazawa and K. Kanoda, *Phys. Rev. B* **55**, 8670 (1997).
8. I. Giaever, *Phys. Rev. Lett.* **5**, 147 (1960).
9. H. Bando, S. Kashiwaya, H. Tokumoto, H. Anzai, N. Kinoshita, and K. Kajimura, *J. Vac. Sci. Technol.* **A8**, 479 (1990).
10. K. Ichimura, T. Arai, K. Nomura, S. Takasaki, J. Yamada, S. Nakatsuji, and H. Anzai, *Synth. Metals* **85**, 1543 (1997).
11. G. C. Papavassiliou, G. A. Mousdis, J. S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C. W. Mayer, and J. Pfeiffer, *Synth. Metals* **27**, B379 (1988).
12. A. M. Kini, M. A. Beno, D. Son, H. H. Wang, K. D. Carlson, L. C. Porter, U. Welp, B. A. Vogt, J. M. Williams, D. Jung, M. Evain, M. H. Whangbo, D. L. Overmyer, and J. E. Schirber, *Solid State Commun.* **69**, 503 (1989).
13. Y. Kobayashi, T. Nakamura, T. Takahashi, K. Kanoda, B. Hilti, and J. S. Zambounis, *Synth. Metals* **70**, 871 (1995).
14. K. Ichimura, K. Nomura, F. Minami, and S. Takekawa, *Solid State Commun.* **82**, 171 (1992).
15. E. L. Wolf, *Principles of Electron Tunneling Spectroscopy,* (Oxford University Press, New York, 1989).
16. K. Ichimura, T. Arai, K. Nomura, S. Takasaki, J. Yamada, S. Nakatsuji, and H. Anzai, *Phys C,* **282–287**, 1895 (1997).
17. Ch. Renner, B. Revaz, J. Y. Genoud, K. Kadowaski, and Ø. Fischer, *Phys. Rev. Lett.* **80**, 149 (1998).