STM Spectroscopy on deuterated \( \kappa-(\text{BEDT-TTF-d}[n,n])_2\text{Cu}[\text{N(CN)}_2]\text{Br} \)

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Abstract. We performed the STM spectroscopy measurement on deuterated \( \kappa-(\text{BEDT-TTF-d}[n,n])_2\text{Cu}[\text{N(CN)}_2]\text{Br} \) to clarify the relation between the superconducting state and the strength of the electron correlation in organic superconductors BEDT-TTF family. We report the results for \( d[2,2]\)-salt and \( d[3,3]\)-salt with the stronger electron correlation than \( d[0,0]\)-salt. The superconducting gap observed as the differential conductance varied systematically depending on the direction of the lateral surface. From the analysis of angular dependent gap function, we found that the node direction of \( d\)-wave in \( d[2,2] \) and \( d[3,3] \) were along \( \alpha^* \) same as \( d[0,0] \). These directions were supported by the observation of the ZBCP near the node direction. It suggests that the dimerization, corresponding to the electron correlation, in both salts is still weak, although these salts are situated near a Mott boundary. While, the node direction rotates a little toward the \( c^* \) axis in \( d[3,3] \) with larger dimerization.

1. Introduction

A quasi-two dimensional electronic band, which accommodate the strongly correlated electrons, plays an important role in electronic properties of BEDT-TTF families. The superconducting phase appears adjacent to the antiferromagnetic phase in \( \kappa-(\text{BEDT-TTF})_2\text{X} \). Many attentions have been paid to a mechanism which brings about the superconductivity in the neighborhood of a Mott insulating phase. There are many investigations for the critical behavior of correlated electrons in both sides of the Mott boundary. Total behaviors are well summarized in the phase diagram with the effective electron correlation\(^1\), which is controlled by the external pressure. Salt of \( \kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N(CN)}_2]\text{Br} \) located near the Mott boundary shows 10 K class superconductivity. The effective correlation can be controlled finely near the Mott boundary by deuteration of BEDT-TTF molecules\(^2\). The salt of \( d[0,0] \) undergoes the superconducting transition, while the salt of \( d[4,4] \) is just on the boundary and shows the antiferromagnetic phase. As a result, the attractive interaction of electrons pair mediated by the spin fluctuation becomes a strong candidate for the mechanism of the superconductivity near the Mott boundary.

For the investigation of the superconducting state, the spectroscopy measurement using scanning tunneling microscope (STS) is useful to determine pair symmetry since the electronic density of state can be obtained directly with high energy resolution and less disturbance. In addition, the angle-resolved STS measurement can be done on one sample. The superconducting gap were investigated on both the conducting planes (\(a-c\) plane) and the lateral surfaces in \( d[0,0], d[2,2], \) and \( d[3,3] \) by the STS\(^3\). The superconducting gap has an anisotropic \( d\)-wave symmetry.
with the node direction along $a^* \pm c^*$ in $d[0,0][4]$ same as $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2[5]$ with slightly small electron correlation. The zero bias conductance peak (ZBCP) observed by the STS is also important feature for anisotropic superconductor[6]. The ZBCP observed at lateral surface in $d[0,0]$ reconfirmed the node direction noted above[4]. On the other hand, it is predicted by the spin fluctuation mechanism that the node direction of $d$-wave superconducting gap changes $\pi/4$ depending on the dimerization strength corresponding to the electron correlation[7]. Accordingly, if we adopt the spin fluctuation mechanism, then, the electron correlation is not large even in $d[0,0]$. Therefore, we need to carry out the further measurements in these salts closer to the Mott boundary and test the spin fluctuation mechanism.

In this paper, we report the results of the STS measurement on the lateral surfaces in $d[2,2]$ and $d[3,3]$ together with the observation of the ZBCP and discuss the node direction of $d$-wave superconducting gap.

2. Experimental

Single crystals were grown by the standard electro-chemical method[8]. Typical size of single crystals is about $1 \times 1 \times 0.3$ mm$^3$. In prior to the STS measurement, we took care of the slow cooling at around 80 K, because Meissner volume fraction decreases rapidly with increasing cooling rate for the present samples. The measurement was mainly done at 1.2 K well below $T_C$. The tunneling differential conductance was directly obtained by the lock-in detection, in which 500 Hz ac modulation with amplitude of 0.2 mV was superposed in the ramped bias voltage with period of 15 s.

3. Results and Discussion

3.1. $\kappa$-(BEDT-TTF-$d[2,2]$)$_2$Cu[N(CN)$_2$]Br

Figure 1 shows the tunneling differential conductance $dI/dV$ curves measured on the lateral surface perpendicular to the conducting plane ($a$-$c$ plane) in $d[2,2]$-salt. The curves obtained along tunneling directions at $\phi = 34^\circ$, $41^\circ$, and $57^\circ$, where $\phi$ is the angle from the $a$-axis in the $a$-$c$ plane, are shown together. We recognize the superconducting gap in each curve as a dip of $dI/dV$ around zero bias. The functional form of the superconducting gap systematically varies depending on the tunneling direction. The curves at $\phi = 34^\circ$ and $41^\circ$ are rounder in the low energy than the curve at $\phi = 57^\circ$. The value of $dI/dV$ at $\phi = 57^\circ$ rapidly varies around $V = 0$ mV depending on the bias voltage, and the gap width is smaller.

Figure 1. Tunneling differential conductance curves on the lateral surfaces of $\kappa$-(BEDT-TTF-$d[2,2]$)$_2$Cu[N(CN)$_2$]Br. The parameter $\phi$ denotes the angle from the $a$-axis in the $a$-$c$ plane. Each curve is normalized to the conductance at $V = 10$ mV and aligned at intervals of one division for clarity. The dotted line represents the calculated curve by the line nodes model.
We tried to fit each curve using the line nodes model, considering tunneling transition probability which depends on the wave vector $k$. The $d$-wave gap given as $\Delta(k) = \Delta_0 \cos \theta$ is assumed. The tunneling differential conductance $dI/dV$ was given as Eq. (4) in Ref. 5. In the present fitting, the material dependent parameter $\beta$ is fixed at $\beta = 20$. As shown in Fig. 1, the observed curves are well fitted by above model especially in low energy region, where the gap symmetry is correctly reflected. The $d$-wave gap has the fourfold symmetry in $k$-space. As a result, we discuss the azimuthal angle in the reduced range $0 \leq \phi \leq \pi/4$, as $\phi = 57^o$ corresponding to reduced $\phi' = 33^o$, although the $a^*$ axis is not completely equivalent to the $c^*$ axis. In Fig. 2, the fitting parameter $\theta$, the angle from antinode, is plotted against $\phi'$. The plotted points are aligned on the almost linear relation line represented by the broken line, although the data points are not many in the range of $\phi'$. We find that the node direction in $d[2,2]$ is along $a^* \pm c^*$, and the gap has the $d_{xy}$ waveform symmetry. The fluctuation exchange approximation\cite{7} suggests the competition between the $d_{xy}$-wave and the $d_{xy}$-wave symmetries depending on the dimerization strength. If we adopt such a mechanism, the electron correlation is still weak even in $d[2,2]$, in spite of the expected stronger dimerization than in the $d[0,0]$. We observed the ZBCP on the lateral surface of $d[2,2]$. The $dI/dV$ enhances anomalously at zero bias in contrast with the superconducting gap as shown in Fig. 3. It also strongly claims that the node direction is along $a^* \pm c^*$ since the ZBCP is observed only near $\phi' = \pi/4$.

![Figure 2](image2.png)  
**Figure 2.** The relation between the fitting parameter $\theta$ and the reduced angle $\phi'$.  

![Figure 3](image3.png)  
**Figure 3.** ZBCP on the lateral surface in $d[2,2]$-salt. The spectra of two different samples are shown together.

3.2. $\kappa-(BEDT-TTF-d[3,3])_2Cu[N(CN)_2]Br$

Figure 4 shows the tunneling conductance curves on the lateral surface in $d[3,3]$-salt. The curves obtained along the different tunneling directions at $\phi = 37^o$ and $55^o$ in the same crystal (sample C) are shown together. The functional form of the superconducting gap is of $V$ shaped around zero bias. The gap form at $\phi = 37^o$ is rounder and deeper than that of $\phi = 55^o$.

We also tried to fit using the line nodes model. The value of $\beta$ is again fixed at $\beta = 20$ for the best fitting. Both gaps fit well near low bias voltage. The assumed $d$-wave gap has the fourfold symmetry in $k$-space. But we discuss the azimuthal angle in the range $0 \leq \phi \leq \pi/2$, because we want to discuss the behavior of line nodes depending on the fine difference between the $a^*$ and $c^*$. In this case, we can’t distinguish $\theta$ from $\pi/2 - \theta$ in the fitting. In Fig. 5, the fitting parameter $\theta$, obtained from several different samples, is plotted against $\phi$. In the figure, solid symbols correspond to $\theta$ in the range $0 < \theta < \pi/4$, and open symbols correspond to $\pi/2 - \theta$. The plotted points are again aligned on the almost linear relation line. From the broken line, we
found that the node direction in d[3,3] is roughly along \( a^* \pm c^* \) like as d[2,2]. We also observed the ZBCP on the lateral surface of sample A near the node direction. Thus, the dimerization in d[3,3] is also still weak in the viewpoint of spin fluctuation mechanism, although the electron correlation is further stronger than d[2,2] and d[0,0].

On the other hand, we succeeded to measure the gap on different two tunneling directions of the same sample as shown in Fig. 4 for the first time. We also draw another shifted line as dotted line for this sample C in Fig. 5. It suggests that the node direction in d[3,3] rotates a little toward the \( c^* \) axis. This behavior may be the precursor of the change from the \( d_{x^2-y^2} \) to the \( d_{xy} \) with increasing electron correlation, i.e. dimerization.

![Figure 4. Tunneling differential conductance curve on the lateral surface of \( \kappa-(BEDT-TTF-d[3,3])_2Cu[N(CN)_2]Br \) observed along various tunneling directions. The curves are obtained at two lateral surfaces in the same crystal (sample C). The dotted lines represents the calculated one.](image)

![Figure 5. The relation between the fitting parameter \( \theta \) and angle \( \phi \). Solid and open symbols represent the corresponding results as described in the text.](image)

### 4. Conclusion

We investigate the superconducting gap by the STS measurement on the lateral surface of \( \kappa-(BEDT-TTF-d[n,n])_2Cu[N(CN)_2]Br \) (d[2,2] and d[3,3]). The superconducting gap varied systematically depending on the direction of the lateral surface in both salts. We also observed the ZBCP on the lateral surface in both salts. From the results, we found that the node direction in both salts is along about \( a^* \pm c^* \) and the gap has the \( d_{x^2-y^2} \)-wave symmetry. This suggests that the dimerization in both salts is still weak in the frame of the spin fluctuation mechanism. On the other hand, the results in d[3,3] suggest that the node direction rotates a little toward the \( c^* \) axis.

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