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Doctoral Thesis

STM Spectroscopy in Organic Superconductor
 κ -(BEDT-TTF-d[3,3])₂Cu[N(CN)₂]Br

有機超伝導体 κ -(BEDT-TTF-d[3,3])₂Cu[N(CN)₂]Br
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Chapter 1

Introduction

1.1 Study of the organic superconductor

A study of organic conductors started from an organic semiconductor of Perylene-Bromine synthesized by H. Akamatsu and H. Inokuchi in 1954[1]. This compound has a higher electric conductivity as well as a semimetal such as Ge and Te. In 1960, an acceptor molecule TCNQ (tetracyanoquinodimethane) composing an organic semiconductor was synthesized. In 1964, W. A. Little proposed the theoretical model for a room-temperature superconductivity[2] caused by the electron-electron attractive interaction through the electronic polarization. This model promoted successive studies in this field. An organic conductor TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), synthesized in 1970s[3], showed a metallic conductivity. It was expected from the steep increase of conductivity with decreasing the temperature down to 53 K that TTF-TCNQ undergoes the superconducting transition with the mechanism predicted by W. A. Little at that time. However, this compound shows the metal-insulator transition by forming the charge density

wave (CDW) at 53 K. In the recent study[4], it was found that this compound keeps a metallic state until 2.5 K under the pressure of 8.0 GPa. It was a problem that most of the organic conductors synthesized so far have the low-dimensional electronic band and shows the metal-insulator transition at low temperature caused by the Peierls transition with the nesting of the Fermi surface. To resolve this problem, a charge transfer salts (TMTSF)₂X were synthesized. The TMTSF salts, composed by the cation molecule TMTSF (tetramethyltetraselenafulvalene) and the counter anion X, are quasi-one dimensional conductors showing highly anisotropic electric conductivity. In (TMTSF)₂PF₆, the superconducting transition was found at $T_c = 0.9$ K under the pressure of 12 kbar for the first time in 1980[5], although the ground state at ambient pressure in this compound was the spin density wave (SDW), which is also caused by the nesting of the Fermi surface. In 1981, (TMTSF)₂ClO₄ were found to show the superconductivity at 1.2 K at ambient pressure[6]. However, most of (TMTSF)₂X with a stronger one-dimensionality undergo the SDW insulating transition at low temperature. For the second generation of the organic superconductor, the BEDT-TTF (bis (ethylenedithia) tetrathiafulvalene) salt was synthesized in 1982[7]. The BEDT-TTF salts have rather two-dimensional in contrast to the TMTSF salts. The superconductivity at higher $T_c = 8$ K was found in β -(ET)₂I₃ in 1984 [8]. After that, the BEDT-TTF salts with polymeric anions such as κ -(BEDT-TTF)₂X ($X = \text{Cu}(\text{NCS})_2$ and $\text{Cu}[\text{N}(\text{CN})_2\text{Br}$ etc.) showed the superconducting transition temperature exceeding 10 K. At present, various organic superconductors such as the magnetic field-induced superconductor λ -(BETS)₂FeCl₄[9] have been synthesized.

On the other hand, since the mechanism of the superconductivity in these organic superconductors has not been accurately understood so far, many researchers have actively studied to clarify the mechanism of the superconductivity in an organic superconductor until now.

1.2 Background of this study

In general, if the Cooper pair is formed in the superconducting state, the superconductivity is classified roughly as either spin singlet or spin triplet states[10]. In the narrowly-defined BCS theory, the origin of the pair in the superconducting state is electron-phonon attractive interaction by the phonon and the wave function of the pair is an isotropic in space. In this case, the orbital part of the pair wave function is described by an isotropic s -wave since the symmetry of electron-electron attractive force corresponds to that of the electron pair wave function. The pair wave function consists of the orbital part and the spin part, and these two parts have different parity for the exchange of the electron pair because the electron belongs to the Fermi particle. Therefore, if the orbital part has even parity, the spin part has odd parity. In the spin singlet case, the orbital part of the electron pair wave function has s -, d -... wave symmetry. On the other hand, in the spin triplet case, the orbital part of the electron pair wave function has p -, f -... wave symmetry.

The order parameter of the superconducting energy gap in the mean-field approximation is given as

$$\Delta(\mathbf{k}) = - \sum_{\mathbf{k}'} V(\mathbf{k} - \mathbf{k}') < c_{\mathbf{k}'\uparrow} c_{-\mathbf{k}'\downarrow} >, \quad (1.1)$$

where $V(\mathbf{k} - \mathbf{k}')$ and $c_{\mathbf{k}'\sigma}$ are the matrix element of the effective attractive interaction between electrons and the annihilation operator of an electron with the wavenumber $\mathbf{k}$ and spin σ . Namely, the symmetry of the order parameter $\Delta(\mathbf{k})$ depends on the attractive interaction $V(\mathbf{k} - \mathbf{k}')$.

The matrix element $V(\mathbf{k} - \mathbf{k}')$ is expanded by the Legendre polynomial function $P_l[11]$ and written as

$$V(\mathbf{k} - \mathbf{k}') = \sum_{l=0}^{\infty} \frac{2l+1}{2} V_l(|\mathbf{k}|, |\mathbf{k}'|) P_l(\cos \theta), \quad (1.2)$$

where θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. From this equation, the pairing states are described by the quantum number l , where $l = 0, 1, 2, \dots$ correspond to the s -, p -, d -, respectively. In the case of s -wave symmetry with $l = 0$, the attractive interaction becomes an isotropic one, while the attractive interaction of the d -wave symmetry with $l = 2$ becomes an anisotropic one. From these, there is a close relationship between the symmetry of the pair wave function and the origin of the attractive interaction. It is considered that the determination of the pair wave function is the key to clarify the mechanism of the superconductivity.

The symmetry of the orbital part of the pair wave function corresponds to that of the superconducting gap function in the $\mathbf{k}$ space. The gap structure can be investigated by the physical quantity reflected the quasi-particle excitation such as the electronic specific heat and the spin-lattice relaxation rate since the gap structure has a stronger relationship with the quasi-particle excitation. It is possible to investigate the superconducting gap symmetry by measuring the temperature dependence of the quasi-particle excitation at lower temperature. In the case of the usual BCS superconductivity, which has an isotropic energy gap, the temperature dependence of the physical property shows a thermal activation behavior. On the other hand, in the case of an anisotropic one such as the gapless superconductivity with nodes, the temper-

ature dependence of the physical property becomes a power-law one. However, these results obtained from the thermal excitation measurements do not reflect directly the superconducting gap symmetry in the $\mathbf{k}$ space. While, the angle-resolved scanning tunneling spectroscopy (STS) and the angle-resolved photoemission spectroscopy (ARPES) make it possible to directly investigate the gap symmetry with high energy resolution and less disturbance by measuring the electron density of states. Especially, the STS is possible for the investigation of a small area $\sim 0.1 \text{ mm} \times 0.1 \text{ mm}$ and quite useful for the organic conductor since it is very hard to prepare a large single crystal.

For the study of the organic superconductors, it has been unclear whether the mechanism of the superconductivity can be explained by the frame of the BCS theory. Various studies about the clarification of the mechanism of the organic superconductors have been done so far. Among them, the BEDT-TTF (ET) salts are one of the most studied organic superconductors. In the ET salts family, the system of $\kappa\text{-(ET)}_2X$ were widely investigated because this salts have a higher superconducting transition temperature than 10 K. These $\kappa\text{-ET}$ salts show some different electronic ground states such as the superconducting and the magnetic Mott insulating states depending on the effective pressure as shown the temperature-pressure phase diagram of $\kappa\text{-(ET)}_2X$ [12] in Fig.1.1. Total behaviors are well summarized in this phase diagram with the ratio of the electron correlation to the bandwidth U_{eff}/W , where U_{eff} is the effective on-site Coulomb energy on the ET dimer and W is the bandwidth, corresponding to the pressure. In this system, the strength of U_{eff} is dominated by the degree of the dimerization of the ET molecules[13, 14].

The effective on-site coulomb energy U_{eff} considering the ET dimer unit is described as

$$U_{eff} = \frac{U_{ET}}{2} \left[1 - \sqrt{1 + \left(\frac{4t_{dimer}}{U_{ET}} \right)^2} \right] + 2t_{dimer}, \quad (1.3)$$

where U_{ET} is the on-site coulomb energy of the ET molecule, and t_{dimer} is the intra-dimer transfer integral. Generally, $U_{eff} = 2t_{dimer}$ since U_{ET} is much larger than t_{dimer} in organic compounds. As a result, the effective strength of the electron correlation U_{eff} depends on the degree of the ET dimerization corresponding to the t_{dimer} . So, U_{eff} becomes stronger with increasing the dimerization and the decrease of the pressure provides the increase of U_{eff}/W .

From the phase diagram, the salts of κ -(ET)₂Cu(NCS)₂ and κ -(ET)₂Cu[N(CN)₂]Br located at the higher pressure region show the superconductivity at 10.4 K and 11.6 K, respectively. The superconducting transition temperature T_c increases gradually from the Cu(NCS)₂ to the Cu[N(CN)₂]Br salts with increasing the electron correlation towards the Mott boundary. On the other hand, κ -(ET)₂Cu[N(CN)₂]Cl situated at the lower pressure region than the Cu[N(CN)₂]Br salt shows the antiferromagnetic insulating transition below 30 K[15] at ambient pressure. This salt also shows the superconductivity around 13 K under the pressure above 30 MPa.

Furthermore, the U_{eff}/W can be also controlled finely by the deuteration of the ethylene groups of the ET molecule. The deuteration method increases the degree of the ET dimerization. The "n" in the d[n,n]-Cu[N(CN)₂]Br (d[n,n]-Br) salt means the number of ethylene groups of the ET molecule substituted by the deuterium as shown the upper right side of Fig.1.1. By using this

deuteration method, the d[0,0]-Br salt undergoes the superconducting transition, while the d[4,4]-Br salt is just on the boundary and shows the antiferromagnetic insulating phase at the ground state. From these, the superconducting phase appears adjacently to the antiferromagnetic insulating one at ground state as in the case of the cuprates high T_c superconductor. From the above, the attractive interaction of the electron pair mediated by the spin fluctuation becomes a strong candidate for the mechanism of superconductivity.

There were many approaches for clarifying the pairing mechanism of the superconductivity in κ -(ET) $_2$ X by the experimental and the theoretical investigation. We introduce the detailed electronic physical properties in κ -(ET) $_2$ X in the next chapter. In the experimental research, it was found that the symmetry in κ -(ET) $_2$ Cu(NCS) $_2$ was the d -wave superconductivity from the specific heat[16] and the angle-resolved STS measurements[17]. The nodal direction in the Cu(NCS) $_2$ salt is $\pi/4$ from the $\mathbf{k}$ axis with the $d_{x^2-y^2}$ from the angle-resolved STS measurement[17]. Another investigation about the superconducting gap symmetry in the Cu(NCS) $_2$ salt is also reported from the thermal conductivity measurement under the magnetic field[18]. It was suggested that the nodal direction is $\pi/4$ from the $\mathbf{k}$ axis corresponding to the $d_{x^2-y^2}$ as well as the result of the STS. From these, it was understood that the Cu(NCS) $_2$ salt is the d -wave superconductor with the $d_{x^2-y^2}$ -symmetry which has nodes at $\pi/4$ from the $\mathbf{k}$ axis.

In the theoretical research, the symmetry of the superconductivity has been discussed by the fluctuation exchange (FLEX) approximation theory using an original four band model[19]. Figure 1.2 shows the spin susceptibility χ in

the $\text{Cu}(\text{NCS})_2$ salt calculated from an original four band model at different strength of the dimerization ((a) a weak dimerization, (b) a strong dimerization). In the weak dimerization as shown in Fig.1.2(a), the value of the susceptibility χ has a maximum peak at $\mathbf{q} \sim (\pm 0.5\pi, \pm 0.6\pi)$ since the nesting of the Fermi surface occurs in part between α and β bands as shown $\mathbf{Q}$ vector in Fig.1.2(a). As a result, the $d_{x^2-y^2}$ -symmetry superconductivity, in which the nodal direction is along $\pi/4$ from $\mathbf{k}$ axis, appears. On the other hand, in the strong dimerization as shown in Fig.1.2(b), since the nesting occurs within the α band, the value of χ has a maximum peak at $\mathbf{q} \sim (0, \pm 0.25\pi)$. Therefore, the d_{xy} -symmetry, in which the nodal direction is along the $\mathbf{k}$ axis, gives a higher T_c than the $d_{x^2-y^2}$. In fact, it is predicted that the symmetry of the superconductivity changes from the $d_{x^2-y^2}$ to the d_{xy} with increasing the dimerization corresponding to the electron correlation. According to this spin fluctuation mechanism, it was suggested from the results in the $\text{Cu}(\text{NCS})_2$ salt obtained from the STS and the thermal conductivity measurements that the electron correlation is weak.

To investigate the relationship between the superconducting gap symmetry and the electron correlation as predicted by the spin fluctuation model in more detail, the gap symmetry was investigated for the d[0,0]-Br[20] and the d[2,2]-Br[21] salts, which are located at the stronger electron correlation region than that in the $\text{Cu}(\text{NCS})_2$ salt, by the angle-resolved STS measurement. It was found that the gap symmetry in the d[0,0]-Br and the d[2,2]-Br salts is the $d_{x^2-y^2}$ as well as that of the $\text{Cu}(\text{NCS})_2$ one. From these results, it is considered that the electron correlation is not strong enough in the frame of the spin

fluctuation mechanism, although the electron correlation becomes gradually large from the $\text{Cu}(\text{NCS})_2$ to the $d[2,2]\text{-Br}$ salts. Therefore, it is an interesting problem whether the symmetry of superconductivity in this system shows d_{xy} symmetry near the Mott boundary (more strong electron correlation) or not.

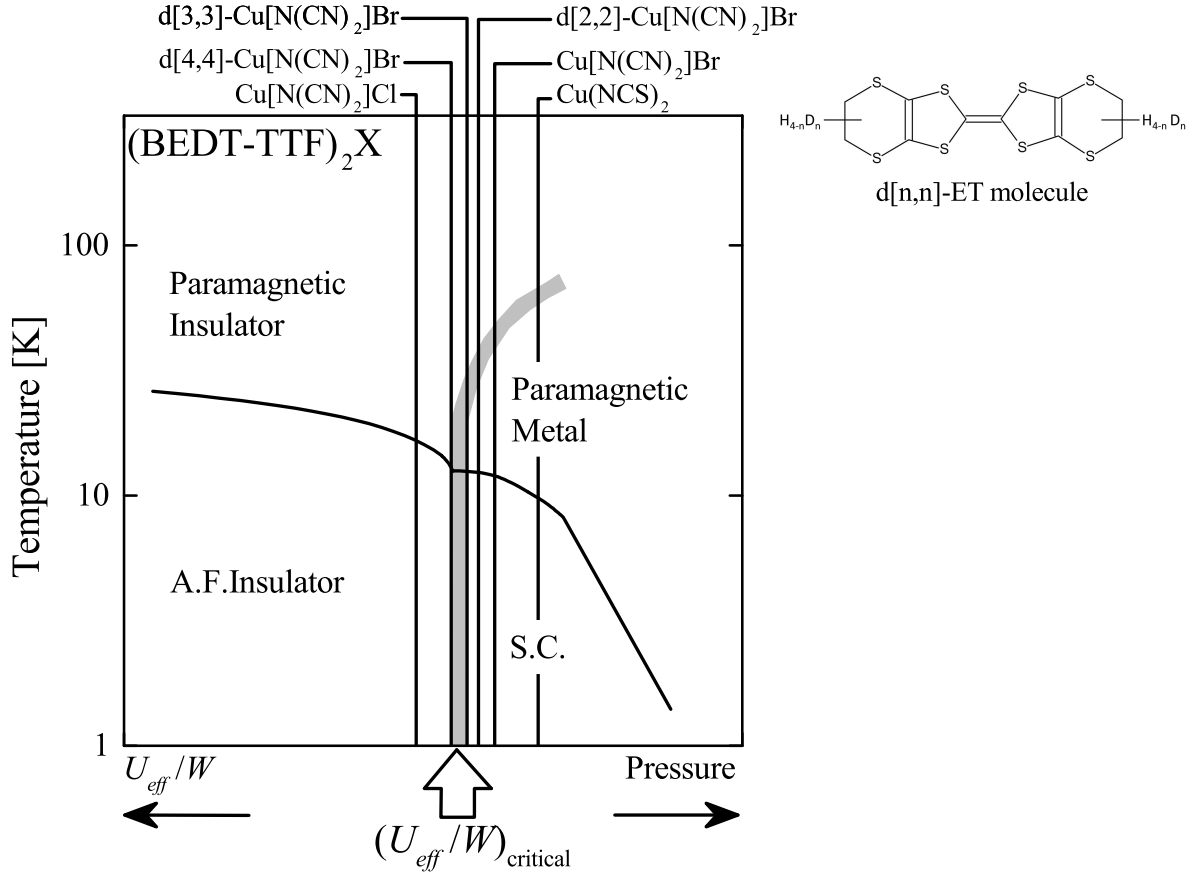


Figure 1.1: Temperature-pressure phase diagram in $\kappa\text{-(ET)}_2\text{X}$ [12].

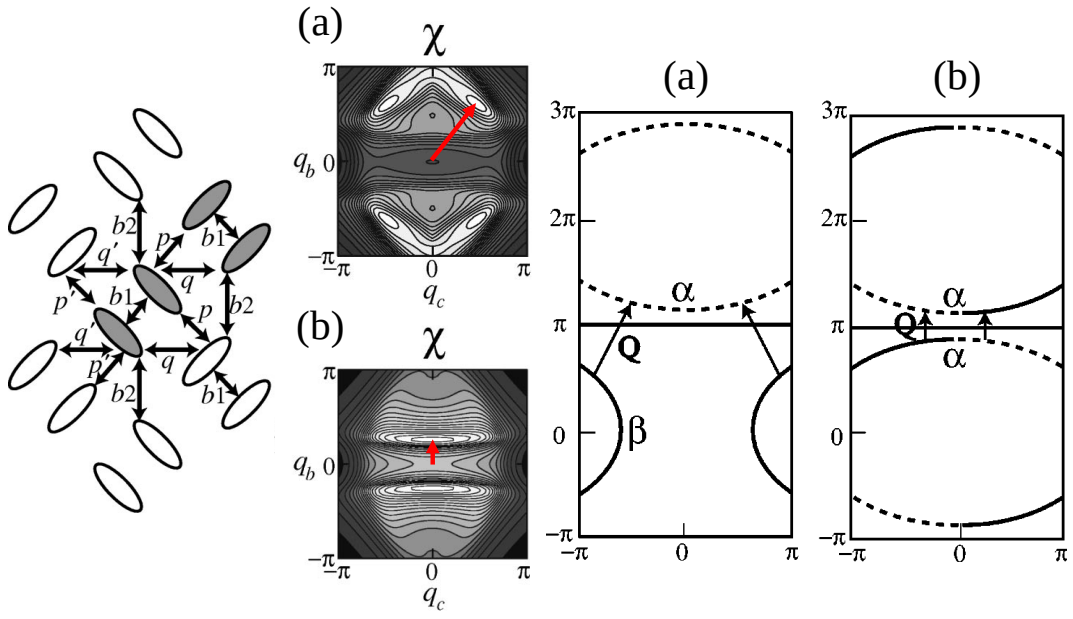


Figure 1.2: Spin susceptibility in κ -(ET) $_2$ Cu(NCS) $_2$ calculated from an original four band model: (a) Weak dimerization, (b) Strong dimerization[19].

1.3 Purpose of this study

In this study, we will clarify the mechanism of the superconductivity in an organic superconductor κ -(BEDT-TTF)₂X by investigating the superconducting gap symmetry near the Mott boundary using the angle-resolved STS. If the gap symmetry in the d[3,3]-Br salt located at a stronger electron correlation region than previously studied ET salts changes from the $d_{x^2-y^2}$ to the d_{xy} , it supplies a strong evidence that the mechanism of superconductivity in this organic superconductor is caused by the spin fluctuation mechanism.

Chapter 2

Physical properties of κ -(ET)₂X

2.1 κ -(ET)₂Cu(NCS)₂

The salt of κ -(ET)₂Cu(NCS)₂ has been widely investigated before the study of our title compounds κ -(ET)₂Cu[N(CN)₂]Br because the superconductivity with exceeding 10 K T_c was found for the first time in κ -(ET)₂X. In this section, we will briefly introduce the electronic physical properties of the Cu(NCS)₂ salt particularly for the pair symmetry before we describe the properties of the Cu[N(CN)₂]Br salt in detail in the next section. As discussed in section 1.2, this compound has lower dimerization than that of the Cu[N(CN)₂]Br salt and gives the basis for the present study.

The Cu(NCS)₂ salt is a quasi-two dimensional superconductor and has a similar crystal structure to the Cu[N(CN)₂]Br salt. While, the crystal system is a monoclinic one with $a = 1.6248$ nm, $b = 0.8440$ nm $c = 1.3124$ nm and $\beta = 110.3^\circ$ at room temperature. The Cu(NCS)₂ salt shows the superconducting transition at 10.4 K.

There were several investigations to clarify the symmetry of the supercon-

ductivity in this compound. K. Izawa *et al.* carried out the thermal conductivity measurement under the magnetic field rotated within the $b - c$ conducting plane[18]. Figure 2.1 shows the magnetic field angular dependence of the thermal conductivity in the $\text{Cu}(\text{NCS})_2$ salt. The fourfold symmetry of the thermal conductivity was observed depending on the magnetic field direction θ at low temperature. This field angular dependence of the thermal conductivity is caused that the density of states corresponding to the in-plane field direction is different by the influence of the change of the quasi-particle number due to the Doppler shift in the case of the gapless superconductivity with nodes. It has been considered that this fourfold symmetry phenomenon reflects the superconducting gap symmetry. Therefore, it has been suggested that the $\text{Cu}(\text{NCS})_2$ salt was d -wave superconductor with the fourfold symmetry and the nodal direction is along $\pi/4$ from wavenumber b^* and c^* -axis corresponding to the $d_{x^2-y^2}$.

T. Arai *et al.* performed the angle-resolved STS measurement and investigated the in-plane anisotropy of the superconducting gap directly in the organic superconductor for the first time[17]. Figure 2.2 shows the angular dependence of the tunneling differential conductance dI/dV in the $\text{Cu}(\text{NCS})_2$ salt[17]. The observed curve varies systematically from a U-shaped form to a V-shaped one depending on the tunneling direction. The obtained all gaps are also well fitted by the theoretical line nodes model assuming the d -wave. As a result, it has been found that the superconducting gap in this compound has the d -wave fourfold symmetry and the nodal direction is along $\pi/4$ from the wavenumber b^* and c^* -axis with the $d_{x^2-y^2}$ as well as the result of the

thermal conductivity measurement. From the results, it was understood that the electron correlation is weak in the frame of the spin fluctuation mechanism as described in section 1.2.

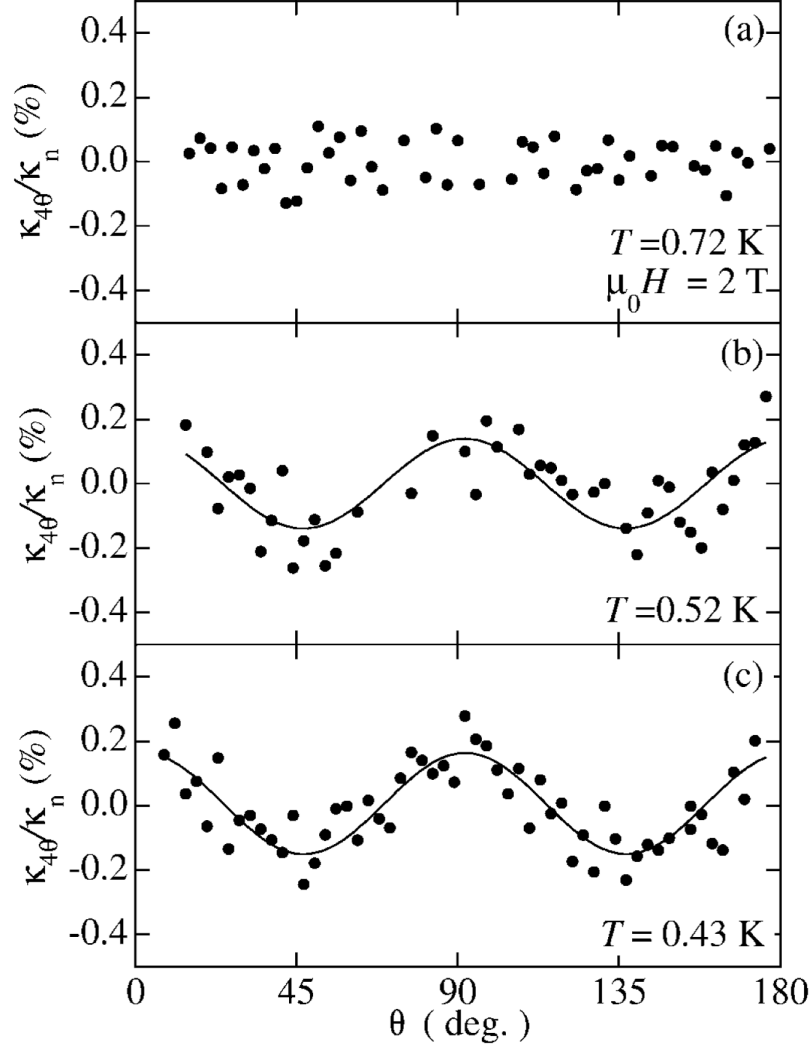


Figure 2.1: Magnetic field angular dependence of thermal conductivity in the $\text{Cu}(\text{NCS})_2$ salt[18].

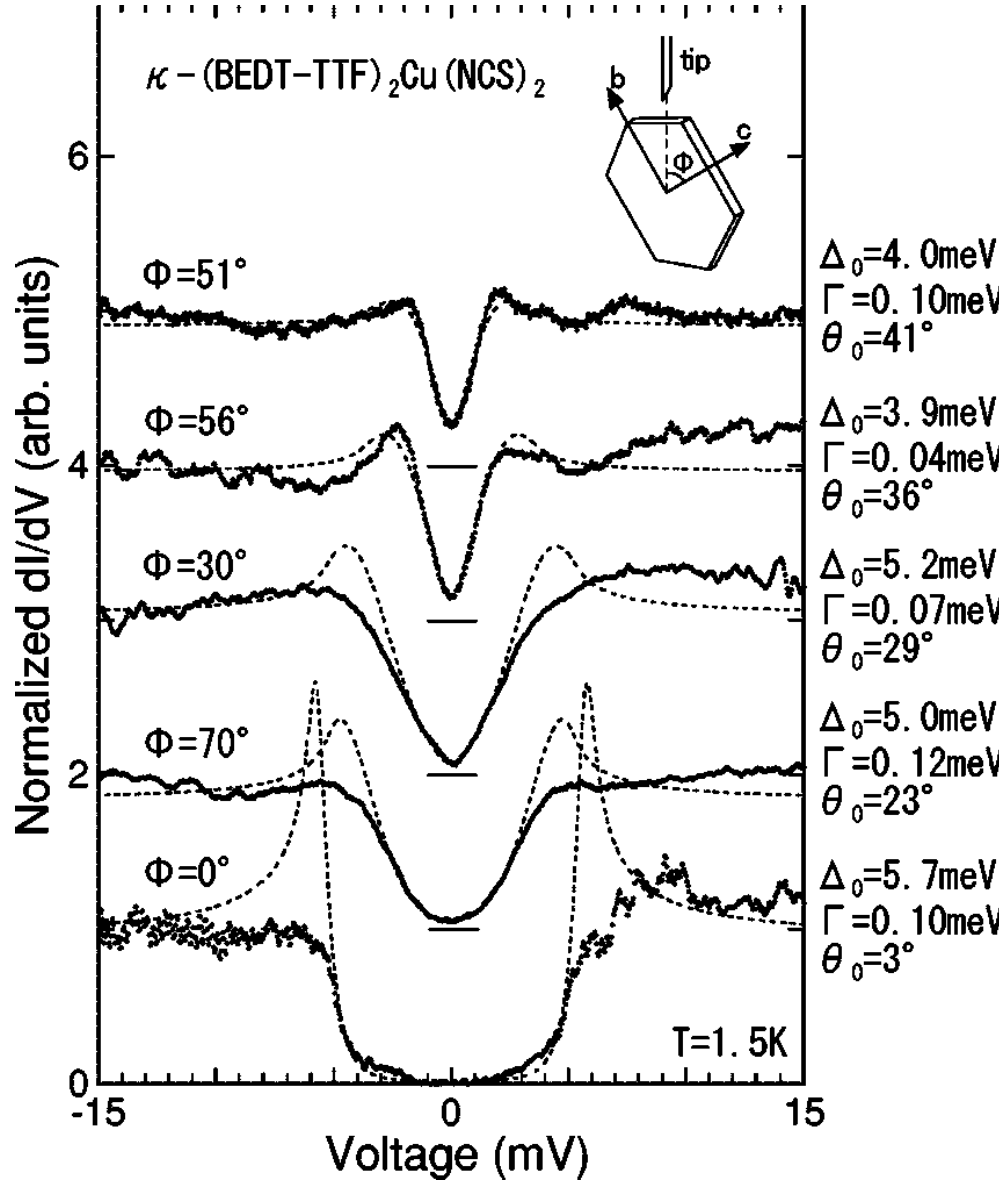


Figure 2.2: Angular dependence of tunneling differential conductance in the $\text{Cu}(\text{NCS})_2$ salt[17].

2.2 κ -(ET)₂Cu[N(CN)₂]Br

The crystal structure of κ -(ET)₂Cu[N(CN)₂]Br is shown in Figure 2.3. This salt is consisted of two cation ET molecules and one anion Cu[N(CN)₂]Br (Fig.2.3(c)[22]) molecule as shown in Fig.2.3(a) and has a layered structure. The crystal system belongs to an orthorhombic one with lattice constant $a = 1.2942$ nm, $b = 3.0016$ nm $c = 0.83539$ nm at room temperature, respectively. This ET family has a κ -type arrangement as shown in Fig.2.3(b)[23]. The κ -type arrangement is a distinguishing packing pattern in the ET salts and this arrangement is as follows: two ET molecules make a couple with their planes almost parallel, and those pairs are arranged almost perpendicular to one another in the $a - c$ plane. These cation ET molecules form a conducting layer and anion Cu[N(CN)₂]Br molecules form an insulating layer. The conducting and insulating layers alternatively stack along b -axis. From this, the intra-layer conductivity (parallel to the $a - c$ plane) is much larger than the interlayer one (along the b -axis).

Figure 2.4 shows the band structure and the Fermi surface calculated by the tight-binding method on the basis of the extended Hückel approximation in the Cu[N(CN)]₂Br salt [24, 15]. The highest occupied molecular orbital (HOMO) band in Fig.2.4(a) is half-filled because of the dimerization of the ET molecules. This salt has a quasi-two dimensional cylindrical Fermi surface along the b^* axis as shown in Fig.2.4(b). It is considered that there is no gap between X and M in the Fermi surface in contrast to that of the Cu(NCS)₂ salt because the anion molecules in the Cu[N(CN)]₂Br salt are arranged symmetrically in the $a - c$ plane as shown in Fig.2.3, while that of the Cu(NCS)₂

salt are arranged asymmetrically along the b -axis as described Ref.[23].

The $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt has stronger electron correlation than the that of the $\text{Cu}(\text{NCS})_2$ salt and is located near the Mott boundary as shown the phase diagram of $\kappa\text{-(ET)}_2X$ in Fig.1.1. Since the electron correlation can be finely controlled by the deuteration method, it is possible to investigate the electronic properties of $\kappa\text{-(ET)}_2X$ near the Mott boundary by composing the $\text{d}[n,n]\text{-Br}$ salts ($n \neq 0$). For example, the $\text{d}[4,4]\text{-Br}$ consisting of $\text{d}[4,4]\text{-ET}$ molecule salt has the most strong electron correlation in the $\text{d}[n,n]\text{-Br}$ salt and is located at just Mott boundary. It has been found that the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt shows the superconducting transition around 12 K from the electric resistivity measurement[25] and the magnetic susceptibility measurement. The superconducting transition temperature increases gradually from the $\text{Cu}(\text{NCS})_2$ salt to the $\text{d}[3,3]\text{-Br}$ salt with increasing the electron correlation as shown the phase diagram. The superconducting state begins to disappear in the $\text{d}[4,4]\text{-Br}$ salt and the antiferromagnetic insulating state appears in the $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ salt instead of the superconducting state. From the $^{13}\text{C}\text{-NMR}$ [26] in Fig.2.5, the enhancement of the spin-lattice relaxation rate $(T_1T)^{-1}$ from 200 K to 60 K corresponding to the development of the antiferromagnetic spin fluctuation was observed even in the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt with the superconducting ground state similarly to the case of the $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ salt with the antiferromagnetic insulating one. Its behaviors indicate that the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt is located near the Mott boundary with the stronger antiferromagnetic fluctuation. From these, it has been strongly suggested that the mechanism of the superconductivity is caused by the magnetic spin fluctuation.

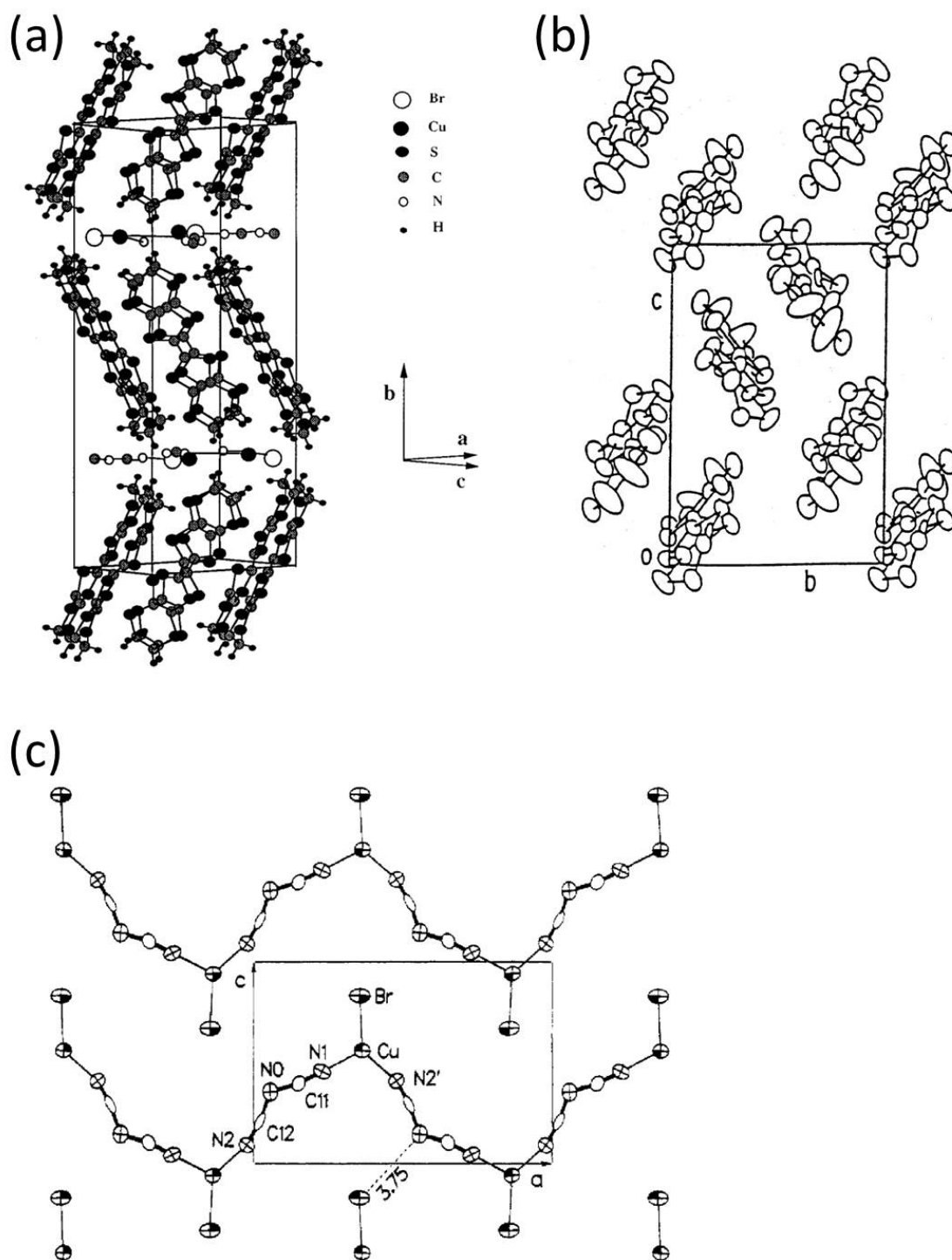


Figure 2.3: (a) The crystal structure in κ -(ET)₂Cu[N(CN)₂]Br[24], (b) κ -type crystal arrangement in κ -(ET)₂X[23], (c) The crystal structure in the anion molecule κ -(ET)₂Cu[N(CN)₂]Br[22].

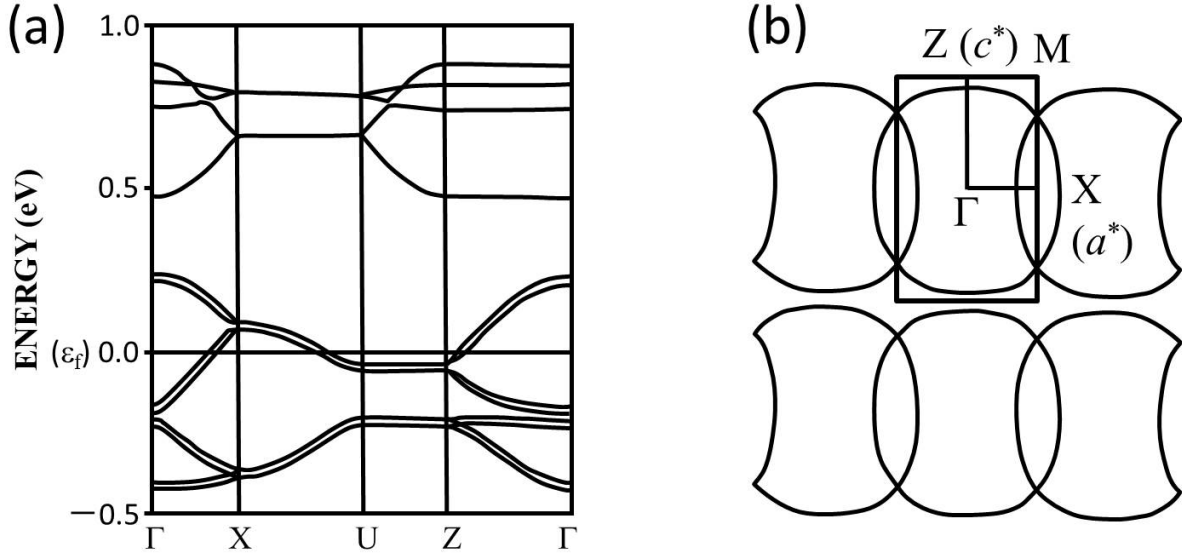


Figure 2.4: Electronic structure in κ -(ET)₂Cu[N(CN)₂]Br. (a) Band structure[24]. (b) Fermi surface[15].

There were some investigations to clarify the pairing mechanism of superconductivity in κ -(ET)₂X. The upper critical magnetic field H_{c2} of the Cu[N(CN)₂]Br salt parallel to the $a - c$ conducting plane was determined as 30.6 T[27] larger than that of the Pauli limit (21.5 T). For comparison, the value of H_{c2} in the Cu(NCS)₂ salt was estimated as 24.5 T and this value is also higher than that of the Pauli limit (20.4 T). Although this result suggested the spin-triplet electron pairing, it could not deny the spin-singlet one since the Pauli limit value was likely to be enhanced by the effect of the larger spin-orbit interaction. On the other hand, the Knight shift in the ¹³C-NMR[28, 29] decreases to zero with decreasing the temperature below T_c as shown in Fig.2.6. This decreasing of the spin susceptibility indicates that the electron pairing in κ -(ET)₂X is the spin-singlet. In the specific heat measurement[16, 30, 31], the electronic specific heat of the Cu(NCS)₂ and the Cu[N(CN)₂]Br salts shows

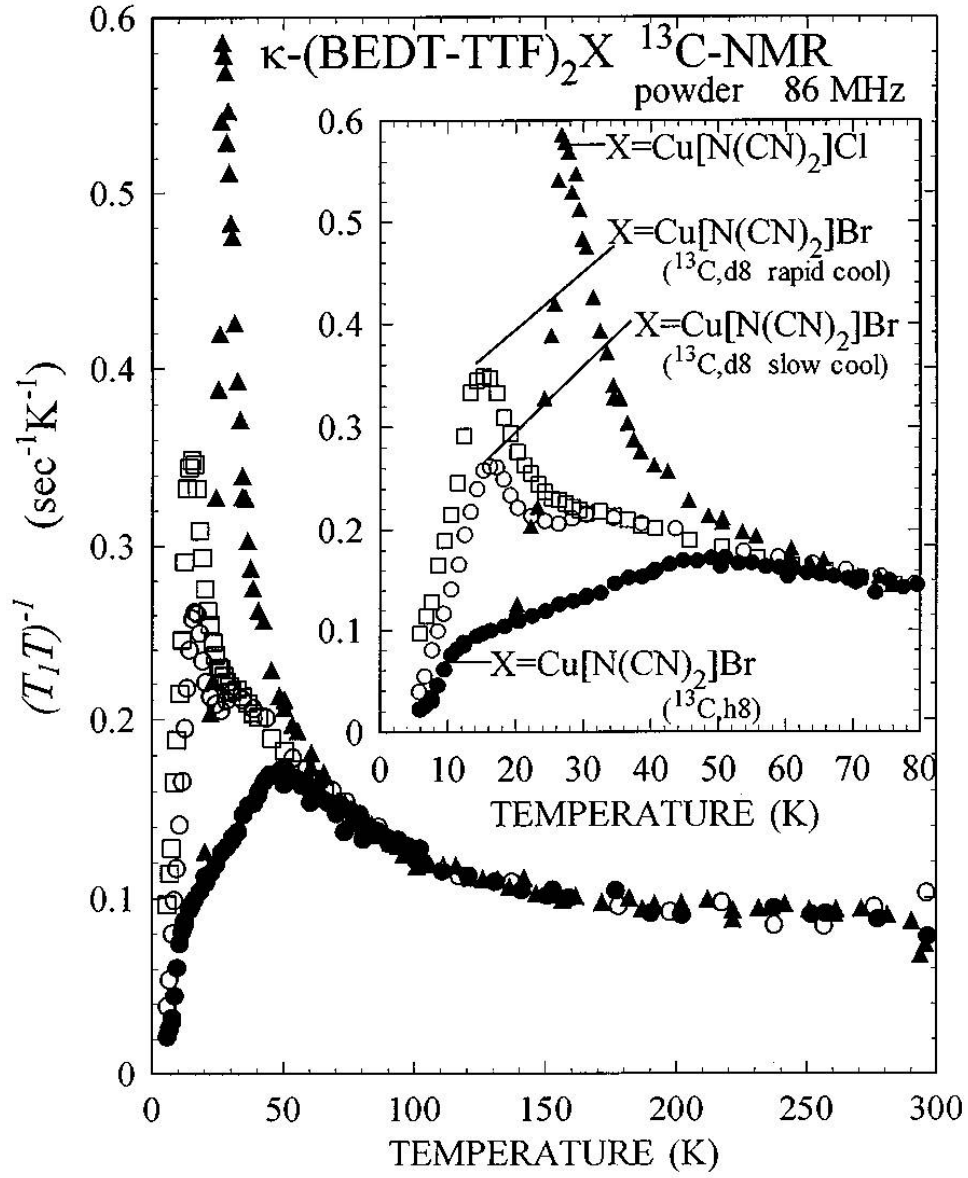


Figure 2.5: Temperature dependence of ^{13}C spin-lattice relaxation rate in $\kappa\text{-(ET)}_2\text{X}$ [26].

not the thermally activation dependence but the power law T^2 -dependence at lower temperature below T_c . These behaviors suggest the gapless superconductivity as the d -wave with nodes.

In the STS measurement, M. Takami *et al.* determined the superconducting gap symmetry in the d[0,0]-Br salt by the angle-resolved STS. Figure 2.7 shows the angular dependence of the differential tunneling conductance in the d[0,0]-Br salt[20, 32]. The value of ϕ is the azimuthal angle along from the a^* -axis in the $a - c$ plane and θ is the fitting parameter which is the angle from the antinodal direction. The solid line is the theoretical curve calculated by the line nodes model assuming the d -wave. The observed gap forms vary systematically from a U-shaped to a V-shaped with the change of ϕ and all gaps are well fitted by the line nodes model. As a result, it was found that the d[0,0]-Br salt has a d -wave fourfold symmetry. Figure 2.8 shows the relationship between the fitting parameter θ and the azimuthal angle ϕ . The plotted points are aligned on the almost linear relation line represented by the dotted line. The nodal direction is along $\pi/4$ from the a^* and the c^* axis corresponding to the $d_{x^2-y^2}$ symmetry as well as that in the Cu(NCS)₂ salt. From the result, it was considered that the electron correlation was still weak in the frame of spin fluctuation mechanism[19], although the electron correlation in the d[0,0]-Br salt is stronger than that in the Cu(NCS)₂ one.

For the anisotropic superconductor, the zero bias conductance peak (ZBCP) observed by STS measurement is also important feature[33]. The ZBCP is caused by the effect of the Andreev reflection around the nodal direction of the superconductivity near the Fermi energy. It is known that the ZBCP is

observed in the case of the gapless superconductivity such as the d -wave. In fact, the observation of the ZBCP has been reported in some cuprates such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [33], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [34], $\text{La}_{2-\delta}\text{Sr}_\delta\text{Cu}_4\text{O}_{7-\delta}$ [35]. The ZBCP was also observed in the $d[0,0]$ -Br salt on the lateral surface near the nodal direction as shown in Fig.2.9[20, 32]. The sharp peaks at zero bias was confirmed. While the ZBCP was not observed in the $(\text{NCS})_2$ salt because the gap of the Fermi surface near the nodal direction is opened. This result indicates the existence of the nodes in the $d[0,0]$ -Br salt.

R. Abe *et al.* carried out the angle-resolved STS measurement in the $d[2,2]$ -Br salt[21], which is located at the stronger electron correlation than the $d[0,0]$ -Br salt, to clarify whether the gap symmetry changes from the $d_{x^2-y^2}$ to the d_{xy} with increasing the electron correlation predicted as the spin fluctuation model[19]. Figure 2.10 shows the angular dependence of the tunneling spectra and the ZBCP in the $d[2,2]$ -Br salt by the angle-resolved STS. From the results, it was suggested that the gap symmetry in the $d[2,2]$ -Br salt is the $d_{x^2-y^2}$ as well as that of the $d[0,0]$ -Br salt although the data points are not many. Therefore, the electron correlation is not strong enough in the frame of the spin fluctuation mechanism even if the electron correlation in the $d[2,2]$ -Br salt is stronger than that in the $d[0,0]$ -Br one.

From the above, it is necessary to investigate the symmetry of the superconductivity in the $d[3,3]$ -Br salt with stronger dimerization than the previously studied κ -(ET) $_2$ X ($\text{Cu}(\text{NCS})_2$, $d[0,0]$ -Br, $d[2,2]$ -Br) for the clarification of the mechanism of superconductivity. In the $d[3,3]$ -Br salt, S. Higashi *et al.* already performed the STS measurement on the conducting plane[36, 37] as

shown in Fig.2.11. The observed gap has V-shaped functional form and is well fitted by the line nodes model with $\Delta = \Delta_0 \cos 2\theta$ represented by the solid line. As a result, it was found that the d[3,3]-Br salt is an anisotropic superconductor. However, the angular dependence of the superconducting gap in this compound was still offering the open problem because the STM measurement on the lateral surface was difficult by the effect of the small fraction of the superconducting region.

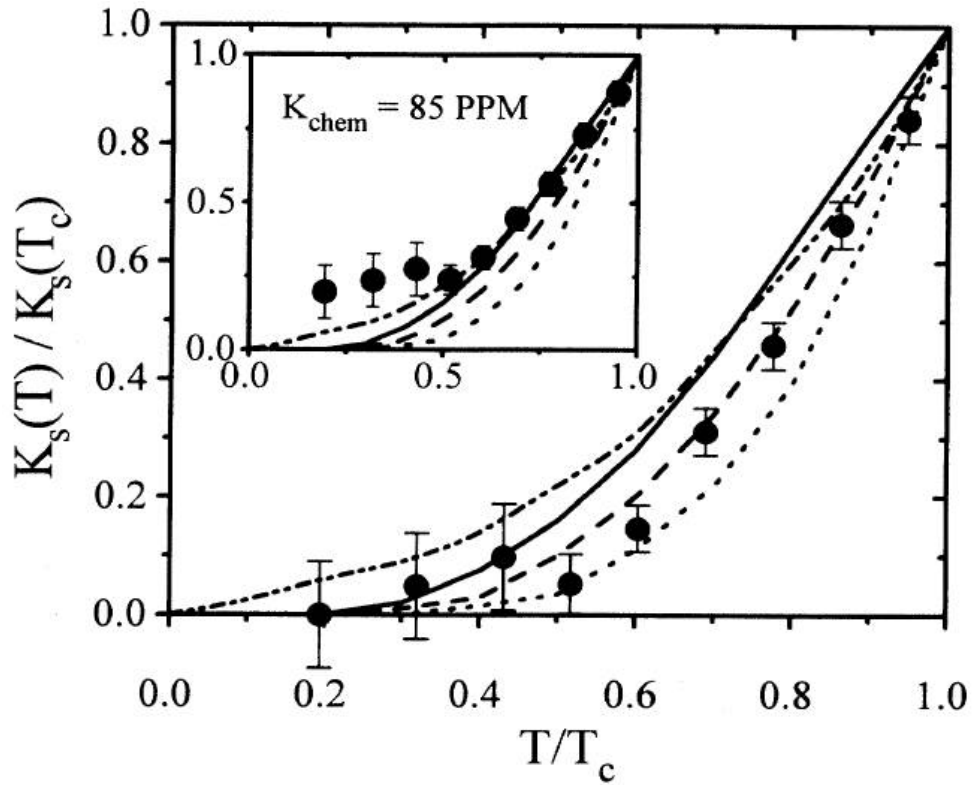


Figure 2.6: Temperature dependence of the ^{13}C Knight shift below T_c at $H \parallel a$ in κ -(ET) $_2$ Cu[N(CN) $_2$]Br[28].

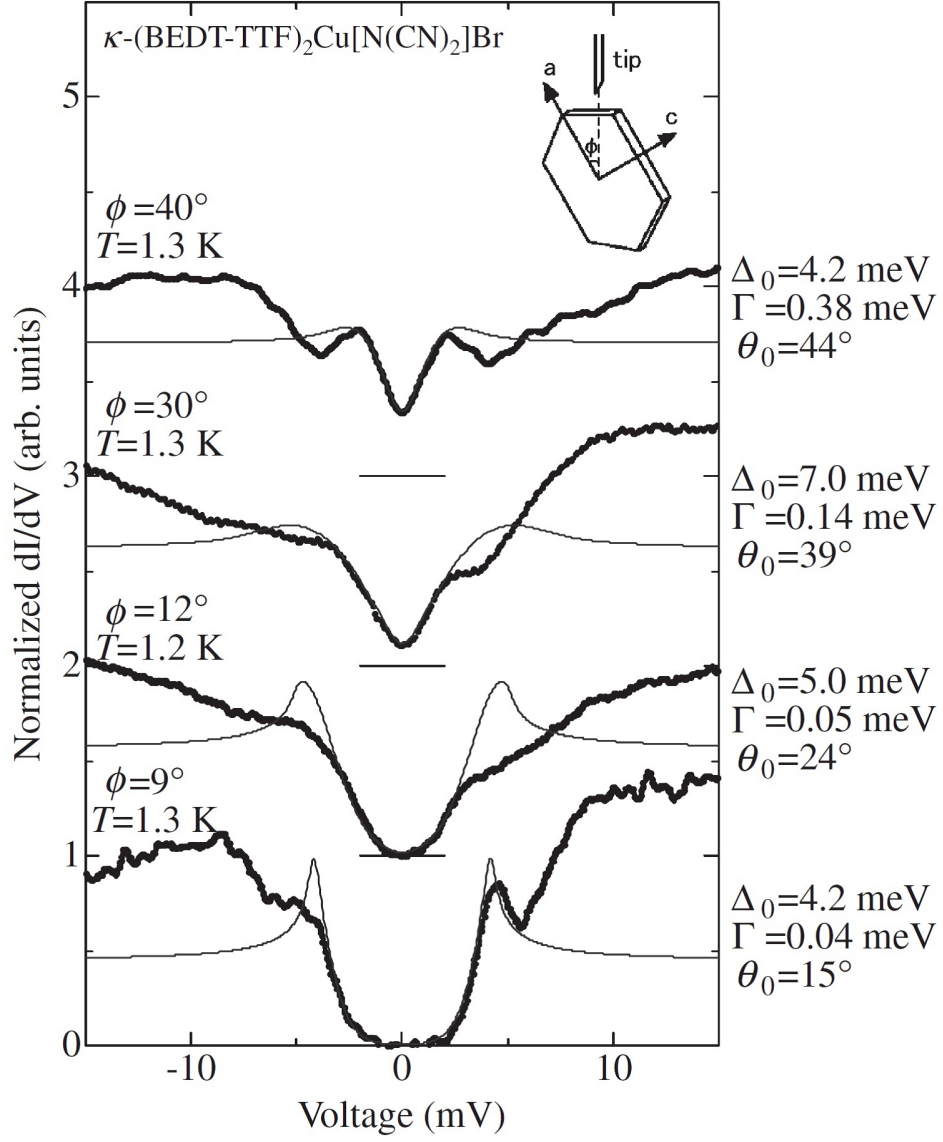


Figure 2.7: Angular dependence of differential tunneling conductance in κ -(ET)₂Cu[N(CN)₂]Br[20, 32].

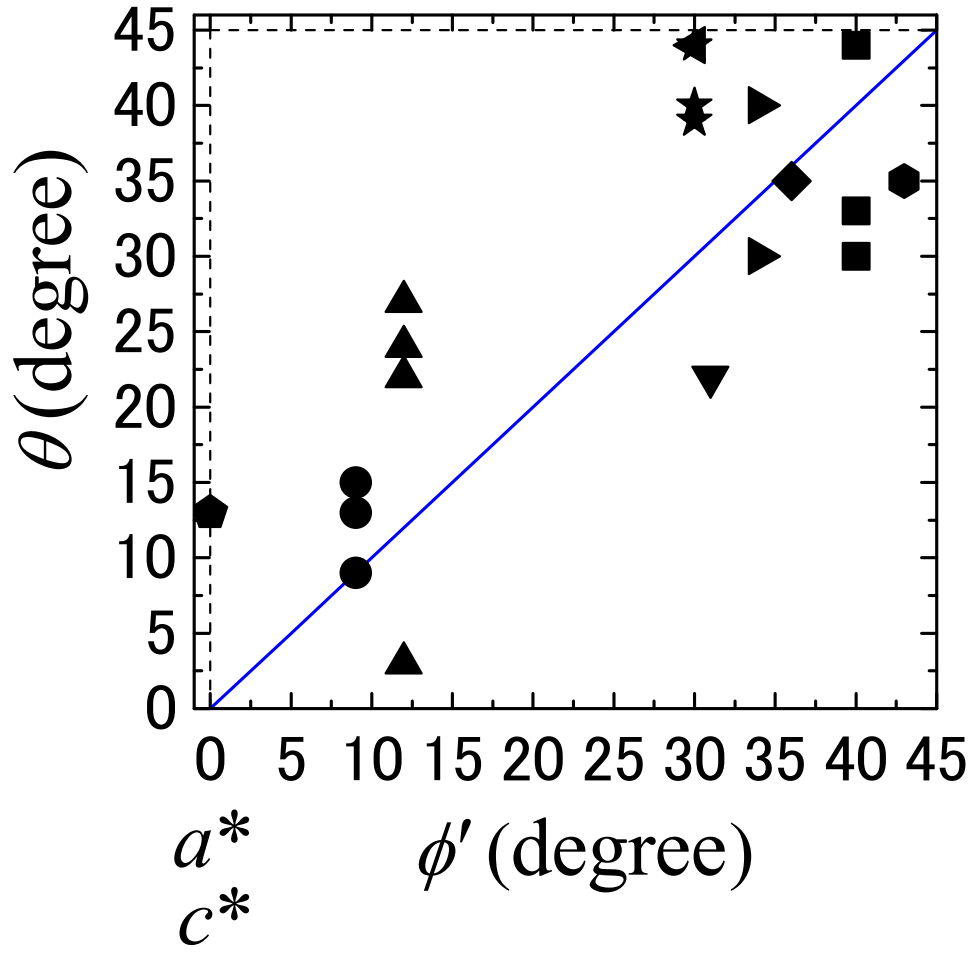


Figure 2.8: Relationship between the fitting parameter θ and the azimuthal angle ϕ in κ -(ET)₂Cu[N(CN)₂]Br[20, 32].

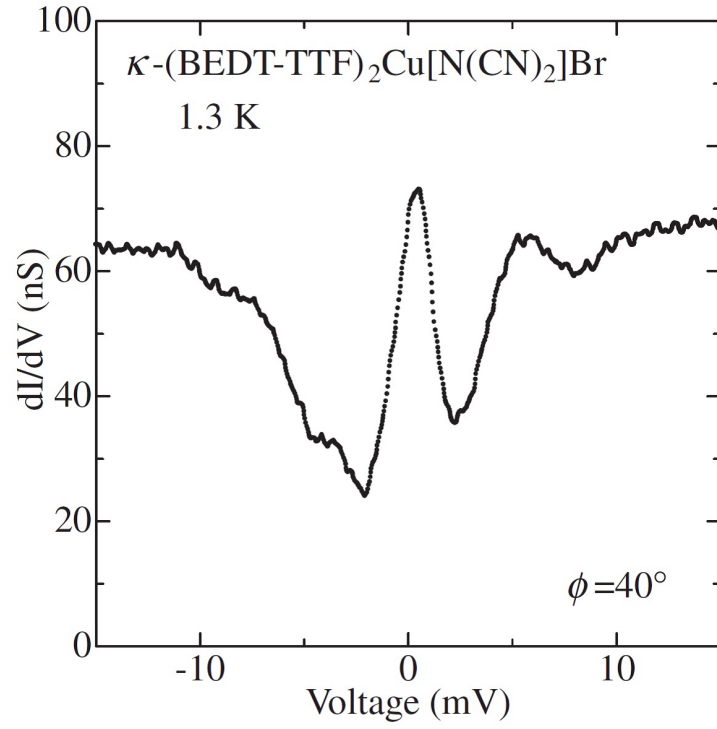


Figure 2.9: Zero bias conductance peak (ZBCP) in κ -(ET) $_2$ Cu[N(CN) $_2$]Br[20, 32].

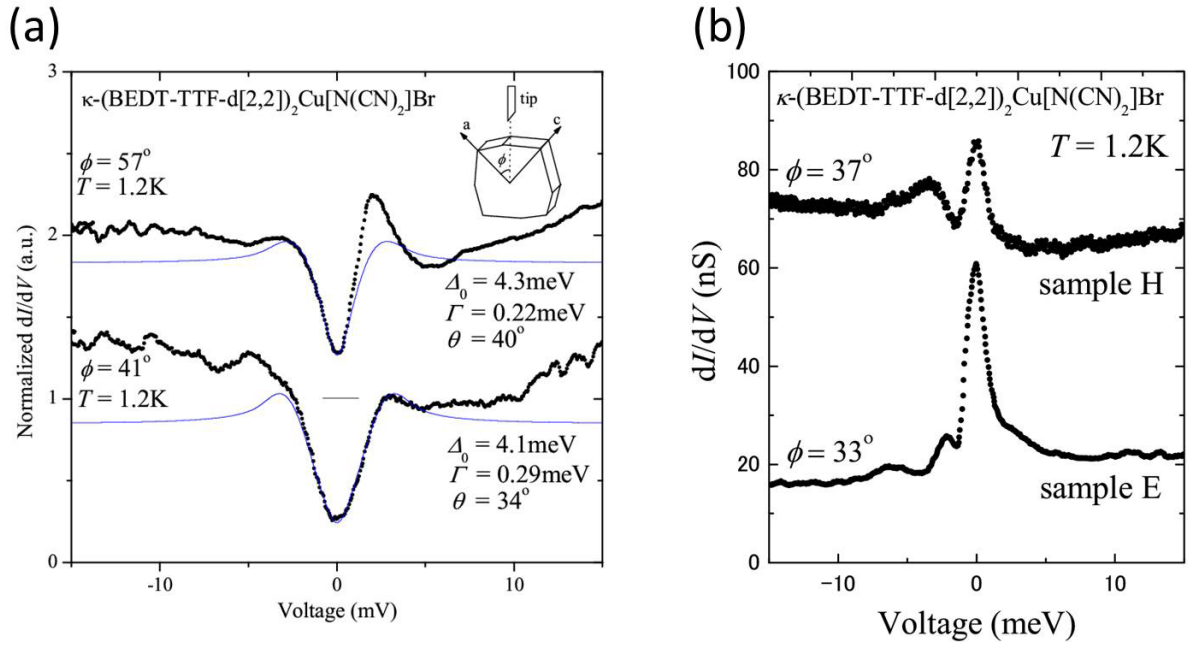


Figure 2.10: (a) Angular dependence of tunneling differential conductance in κ -(ET-d[2,2]) $_2$ Cu[N(CN) $_2$]Br, (b) Zero bias conductance peak (ZBCO) in κ -(ET-d[2,2]) $_2$ Cu[N(CN) $_2$]Br[21].

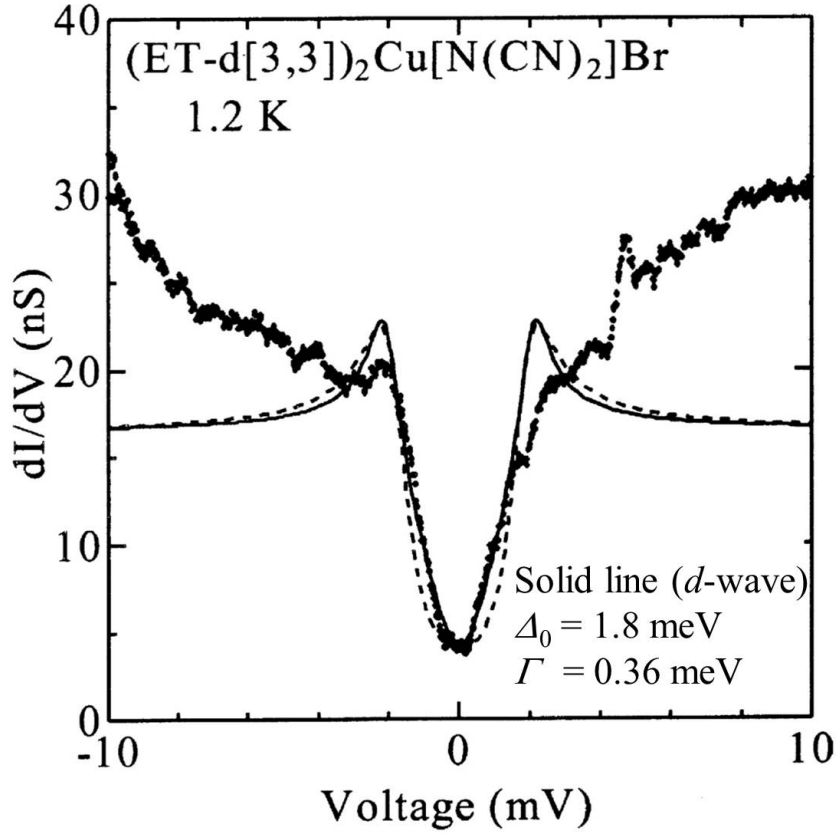


Figure 2.11: Tunneling differential conductance on the conducting plane in κ -(ET-d[3,3])₂Cu[N(CN)₂]Br[37]. The solid and broken lines are theoretical curves. The solid one corresponds to the line nodes model considering the *d*-wave superconductivity and the broken one corresponds to the Dynes model considering the *s*-wave.

Chapter 3

STM and STS

3.1 Basic principle of STM and STS

3.1.1 Scanning Tunneling Microscope: STM

The scanning tunneling microscope (STM) was developed by G. Binnig and H. Rohrer in 1981[38]. The STM is useful for investigating the surface and the interface since the STM has an atomic-level spatial resolution. This high spatial resolution is realized by the exponential dependence of the tunneling current on the distance between the tip and the sample surface. The tunneling current I under a bias voltage V is approximately given by

$$I = A \frac{V}{\lambda d} \exp\left(-\frac{2d}{\lambda}\right) \quad (3.1)$$

with

$$\lambda = \sqrt{\frac{\hbar^2}{2m\phi}}, \quad (3.2)$$

where d is a distance between the tip and the sample surface and λ is an attenuation length associated with an average work function ϕ . From Eq. 3.1,

the tunneling current I changes exponentially with d . The value of λ is about 0.1 nm (from $\phi = 1 \sim 5$ eV). Therefore, the amplitude of I becomes ~ 1 nA for the typical distance $d \sim 1$ nm.

The atomic level high resolution by the STM can be obtained by recording the change of the sample surface height with scanning the sample surface. There are two types of the STM mode as the way of imaging of the change of the surface height. One is the constant current mode. In this mode, the image can be obtained by recording the change of the piezoelectric actuator using the tunneling current feedback circuit to keep the distance between the tip and the sample. Another one is the constant height mode. In this case, the image can be obtained by recording the change of the tunneling current by scanning faster than the constant current mode with locking of the tip height. In fact, these two modes are controlled by the combination the feedback time constant and the scanning rate.

3.1.2 Scanning Tunneling Spectroscopy: STS

The scanning tunneling spectroscopy (STS) can investigate the local electron density of states using the STM technique. Assuming the structure in which the insulator is sandwiched between two metals (metal 1 and metal 2), the tunneling current I from a metal 1 to a metal 2 is expressed as

$$I_{1 \rightarrow 2} = \frac{2\pi e}{\hbar} \int_{-\infty}^{\infty} |T|^2 N_1(E) f_1(E) N_2(E) [1 - f_2(E)] dE, \quad (3.3)$$

where $f(E)$ is the Fermi distribution function, T is the tunneling matrix element and $N_{1(2)}(E)$ is the electron density of states of the metal 1 (2), respectively. On the other hand, the tunneling current I from the metal 2 to the metal 1 is expressed as

$$I_{2 \rightarrow 1} = \frac{2\pi e}{\hbar} \int_{-\infty}^{\infty} |T|^2 N_2(E) f_2(E) N_1(E) [1 - f_1(E)] dE. \quad (3.4)$$

Therefore, the net current between the junctions (metal 1 - insulator - metal 2) is given as

$$I = \frac{2\pi e}{\hbar} \int_{-\infty}^{\infty} |T|^2 N_1(E) N_2(E) [f_1(E) - f_2(E)] dE. \quad (3.5)$$

When the voltage is applied between the junctions if the tunneling-matrix element $|T|$ is assumed to be independent of the electron energy E , the current I is given as

$$I = \frac{2\pi e |T|^2}{\hbar} \int_{-\infty}^{\infty} N_1(E - eV) N_2(E) [f(E - eV) - f(E)] dE. \quad (3.6)$$

If the $N_1(E)$ is constant as in the case that the metal 1 is a normal metal like the STM tip, (3.6) becomes

$$I \propto N_1(0) \int_{-\infty}^{\infty} N_2(E) [f(E - eV) - f(E)] dE. \quad (3.7)$$

Thus, the differential tunneling conductance dI/dV is written as

$$\frac{dI}{dV} \propto \int_{-\infty}^{\infty} N_2(E) \frac{\partial f(E - eV)}{\partial V} dE. \quad (3.8)$$

As $T \rightarrow 0$, since the energy differential of the Fermi distribution function shows delta function like behavior, we obtain

$$\frac{\partial f(E - eV)}{\partial V} dE \simeq \delta(E - eV). \quad (3.9)$$

Therefore, the dI/dV at low temperature is written as[39]

$$\frac{dI}{dV} \propto N_2(eV). \quad (3.10)$$

If the metal 2 is the sample, the differential conductance dI/dV is proportional to the electron density of states of the sample. Namely, we can directly measure the local density of state of the sample by the STS measurement with high energy resolution whose range is smaller than $k_B T$ in the liquid helium temperature and less disturbance. In particular, the STS is useful to determine the pair symmetry of the superconductivity, since the electron density of states can be obtained directly.

3.2 Angle-resolved STS

By carrying out the angle-resolved STS measurement on the lateral surface perpendicular to the conducting plane in the layered superconductor as shown in Fig.3.1, we can directly investigate the in-plane anisotropy of the superconducting gap, since the tunneling probability of electrons from the lateral surface has strong $\mathbf{k}$ -dependence as described in Appendix A in detail. Therefore, this technique can finely determine the superconducting gap symmetry as shown in Fig.2.7, 2.2.

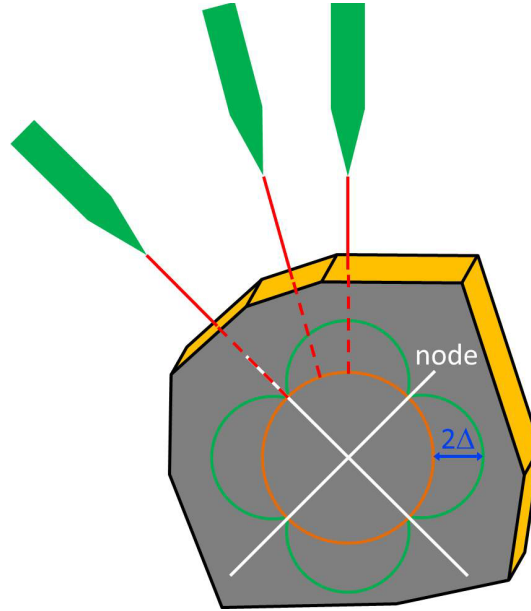


Figure 3.1: Pattern diagram of the angle-resolved STS.

Chapter 4

Experimental

4.1 Sample

4.1.1 Crystal growth

The single crystal of κ -(ET-d[3,3])₂Cu[N(CN)₂]Br was grown by the standard electro-chemical method[40] from mixing materials in the ratio shown in Table 4.1. Since the growing of the crystal with a clean surface was very im-

Material	Amount (100 [ml/cell])
d[3,3]-BEDT-TTF	40mg
P(C ₆ H ₅) ₄ [N(CN) ₂]	320mg
CuBr(I)	112mg
1, 1, 2 - trichloroethane	90mg
Ethanol	10mg

Table 4.1: Amount of crystal growth in κ -(ET-d[3,3])₂Cu[N(CN)₂]Br

portant for the accurate STS measurement, the dissolved oxygen was removed by argon gas bubbling in the solvent about two hours. In the process of applying current, we carried out the two types of the constant current method and the changing current one to bring up various shaped crystal. In the constant

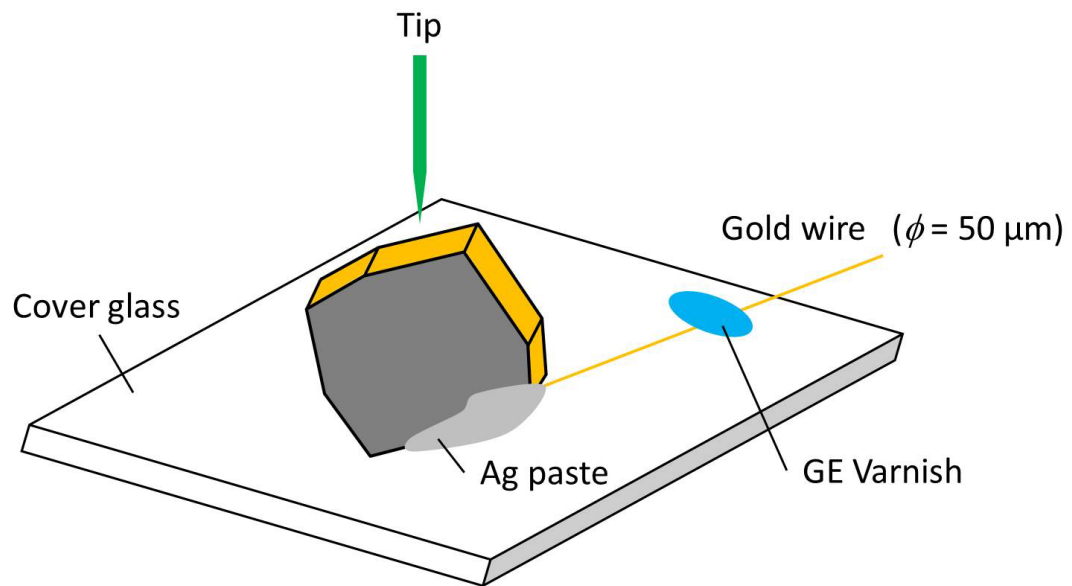
current method, the applied current was kept at $1\mu\text{A}$. On the other hand, in the changing one, the applied current was changed stepwise from 0.1 to $1.2\mu\text{A}$. The period of crystal growth was about a month. The obtained typical crystal size was about $1\text{ mm} \times 1\text{ mm} \times 0.3\text{ mm}$.

4.2 Experimental

4.2.1 Sample setting

Figure 4.1 shows the pattern diagram of the sample setting for the STS measurement on the lateral surface. The d[3,3]-Br salt was glued by a silver paste on the sample holder (glass plate). The current lead of a gold wire ($\phi = 50\mu\text{m}$) was attached to the sample with a silver paste as shown in Fig.4.1. In the case of thin sample surface in Fig.4.1(b), since it was difficult to mount the sample perpendicular to the glass plate, the sample was attached to the surface of the microscope glass as a support with silver paste as shown in Fig.4.1. The sample holder was mounted on the sample stage of the STM unit with Apiezon N grease.

(a) Normal sample



(b) Thin sample

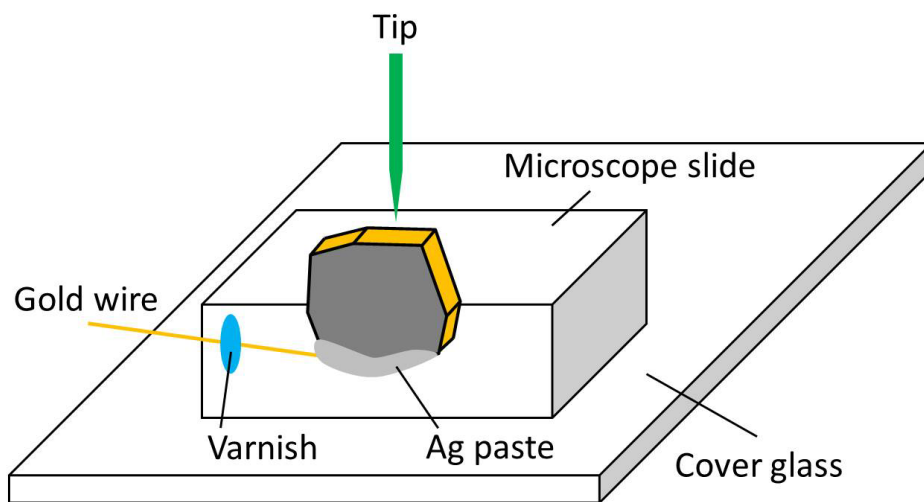


Figure 4.1: Pattern diagram of sample setting for the STS measurement on the lateral surface. (a) In the case of normal sample. (b) In the case of thin sample.

4.2.2 Sample cutting by FIB system and surface condition

For accurate determination of the in-plane anisotropy of the superconducting gap, it is very important to measure various direction surfaces by the angle-resolved STS. However, the d[3,3]-Br salt does not have enough various direction surfaces in the case of as-grown surface. It is rather difficult to investigate the in-plane superconducting gap anisotropy in detail. We tried to cut the single crystal perpendicular to the $a - c$ plane by the focused ion beam (FIB) system with gallium ion source to resolve this problem. In this method, the sample was cut along the plane with lower indices such as $(1,0,0)$ plane and $(0,0,1)$ one perpendicularly to the conducting plane for detecting the correct tunneling electron corresponding to the cut surface direction as shown in Fig.4.2.

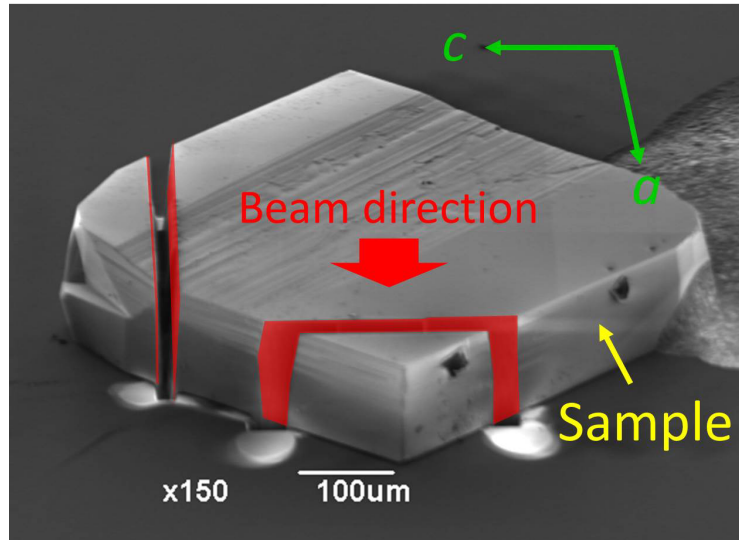


Figure 4.2: Cutting image of the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt by FIB method.

In order to check the surface condition by the FIB method, we performed the STM measurement on both the as-grown and the FIB cut surfaces at room

temperature. Figure 4.3, 4.4 shows the STM image and the line profile on the as-grown ((2,0,1) plane) and the FIB cut ((1,0,0) plane) surfaces in the d[0,0]-Br salt. In the STM image on the as-grown surface, we confirmed the ET molecular array with the correct lattice spacing denoted as the white arrows in the left side of Fig.4.3. The present ET molecular image on the lateral surface in the d[0,0]-Br salt is similar to that of the Cu(NCS)₂ one previously observed by other group[41]. In the as-grown surface over a wider area (600 nm x 600 nm) in the right side of Fig.4.3, the flat surface corresponding to the plane index (2,0,1) spreads to the entire sample surface. As a result, it enables us to carry out the angle-resolved STS. In the image of the FIB cut surface, we also recognized the ET molecular one with the correct lattice spacing in the left side of Fig.4.4. The flat surface with area about 70 nm x 70 nm corresponding to the (1,0,0) plane spreads as terraces as shown in white area of the right side in Fig.4.4. Therefore, it is considered that the tunneling electron from both the as-grown and the FIB cut surfaces primarily reflects the surface direction, although the other direction surface with a very small area is observed in the case of the FIB cut one as shown the line profile in Fig.4.4.

As-grown surface

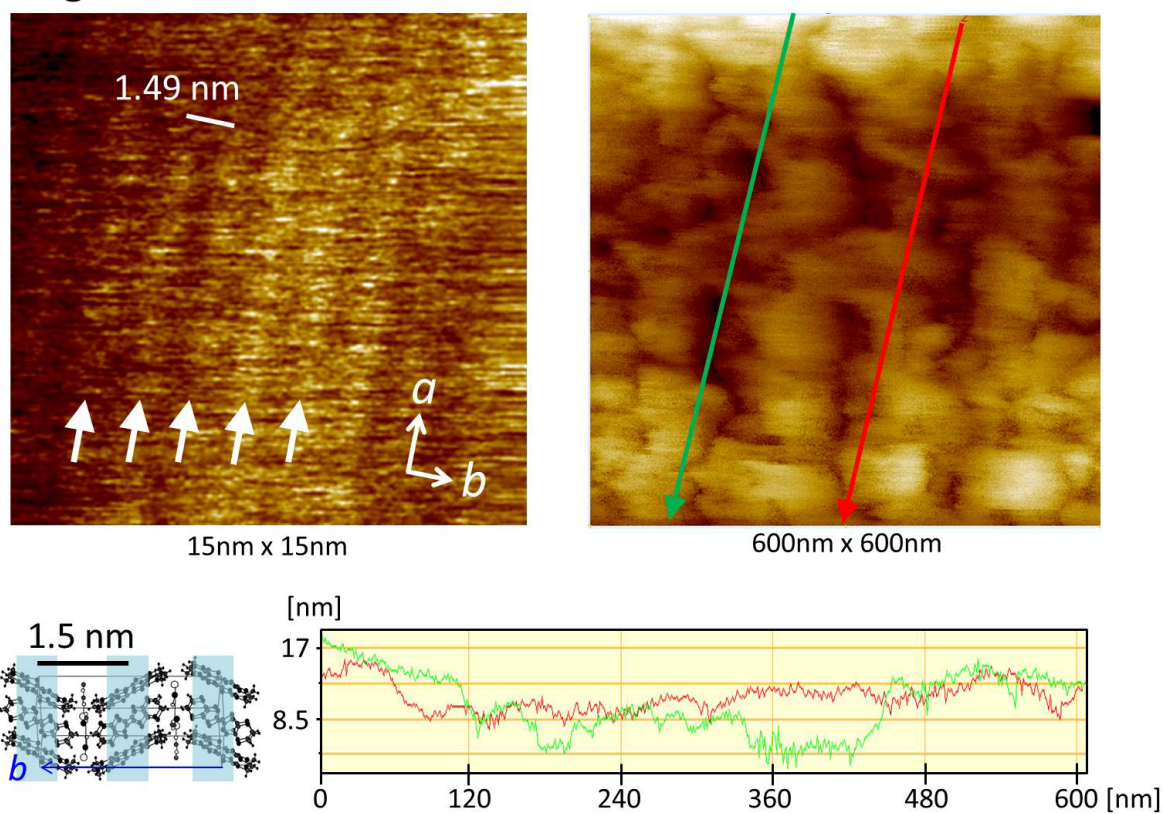


Figure 4.3: STM image on the as-grown surface in the d[0,0]-Br salt at room temperature.

Cut surface by FIB

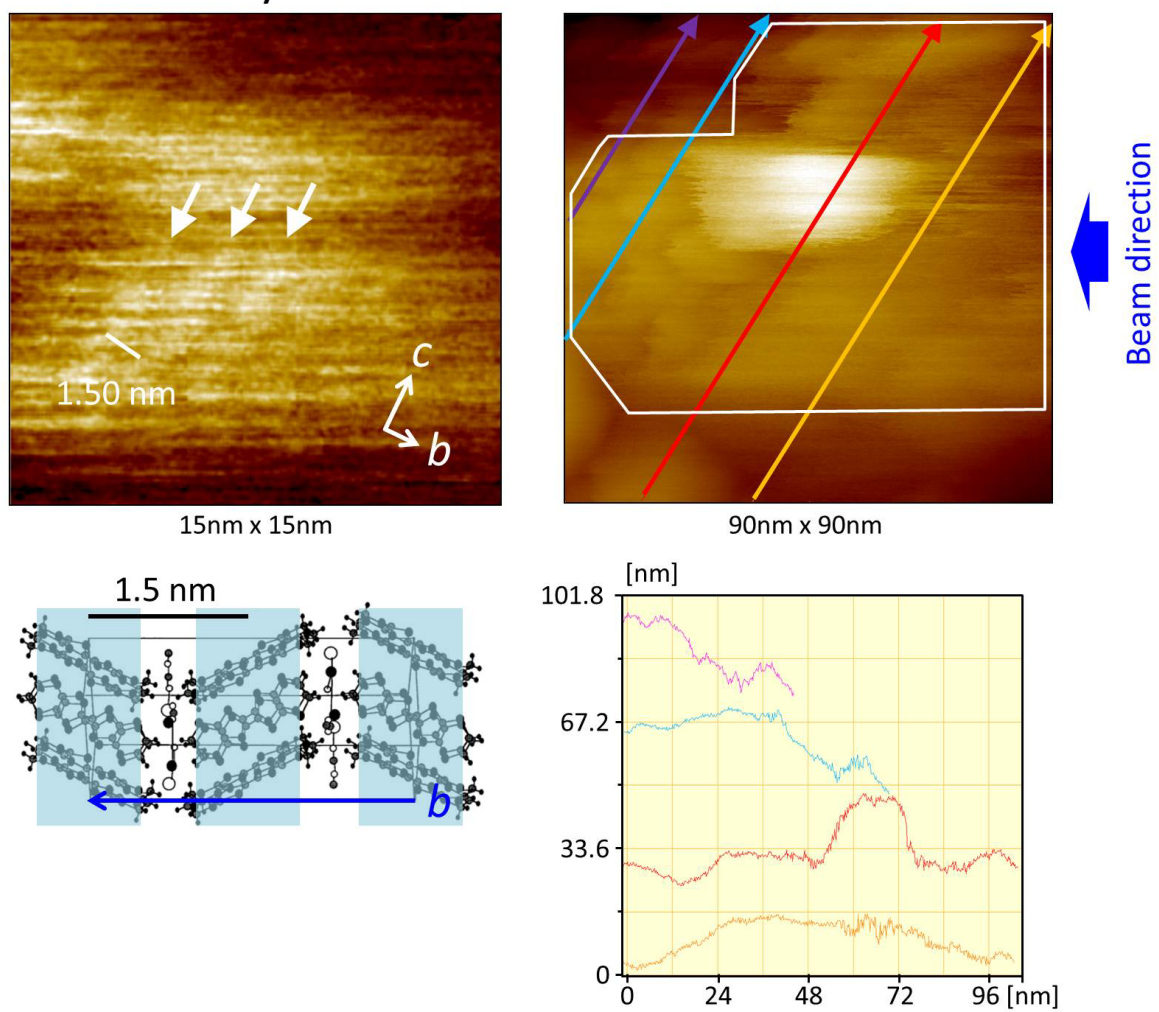


Figure 4.4: STM image on the FIB cut surface at (1,0,0) plane in the d[0,0]-Br salt at room temperature.

4.2.3 Experimental details of the STS measurement using STM

The STS measurement was carried out at 1.2 K using the low-temperature STM system. Figure 4.5 shows a Schematic diagram of the low-temperature STM system. The STM unit mainly consists of the platinum-iridium tip, the tube-type piezoelectric actuator and the sample stage. The mechanically sharpened platinum-iridium wire was used as the STM tip. The tube-type piezo electric actuator was used to change the tip-sample distance finely and the x-y position of the tip. For the low-temperature measurement, a helium gas was used as thermal exchange gas in the adiabatic cell of the STM unit which was directly cooled in liquid helium, and the liquid helium space was cooled down to 1.2 K well below T_c by the pumping with the mechanical vacuum pump. In the cooling process, we took care of the slow cooling ($-0.1 \sim -0.5$ K/min) around 80 K, because it was known that the volume fraction of the superconducting state decreases rapidly with increasing the cooling rate for the d[3,3]-Br salt[42]. The STS measurement was done under dynamic pumping to keep the 1.2 K. To avoid external vibration, the cryostat was mounted on the vibration isolator equipped with an air suspension system.

A schematic diagram of the STS measurement system was shown in Fig 4.6. The tunneling differential conductance dI/dV 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. The pre-amplifier (current - voltage converter) whose gain was 10^8 V/A was used to amplify the tunneling current signal. The differential conductance dI/dV and the voltage V data were measured by digital oscilloscope and recorded on

the PC.

The $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt is an octagonal plate-like crystal and a wide surface corresponds to the conducting $a - c$ plane. The inner angle of an octagonal from mainly has three-types whose angles are $\sim 105^\circ$, $\sim 115^\circ$ and $\sim 160^\circ$, respectively as shown in Fig.4.7. For X-ray diffraction analysis, it is found that the a - and the c -axis are almost along the angle bisector of $\sim 105^\circ$ and $\sim 115^\circ$ as shown in Fig.4.7. By using this crystal property, we could determine the plane indices of the as-grown and the FIB cut surface. When it was difficult to determine the plane indices of the measurement surface caused by small sample size or partially broken sample, the plane indices of the measured surface were directly determined by the single-crystal X-ray structure analysis apparatus.

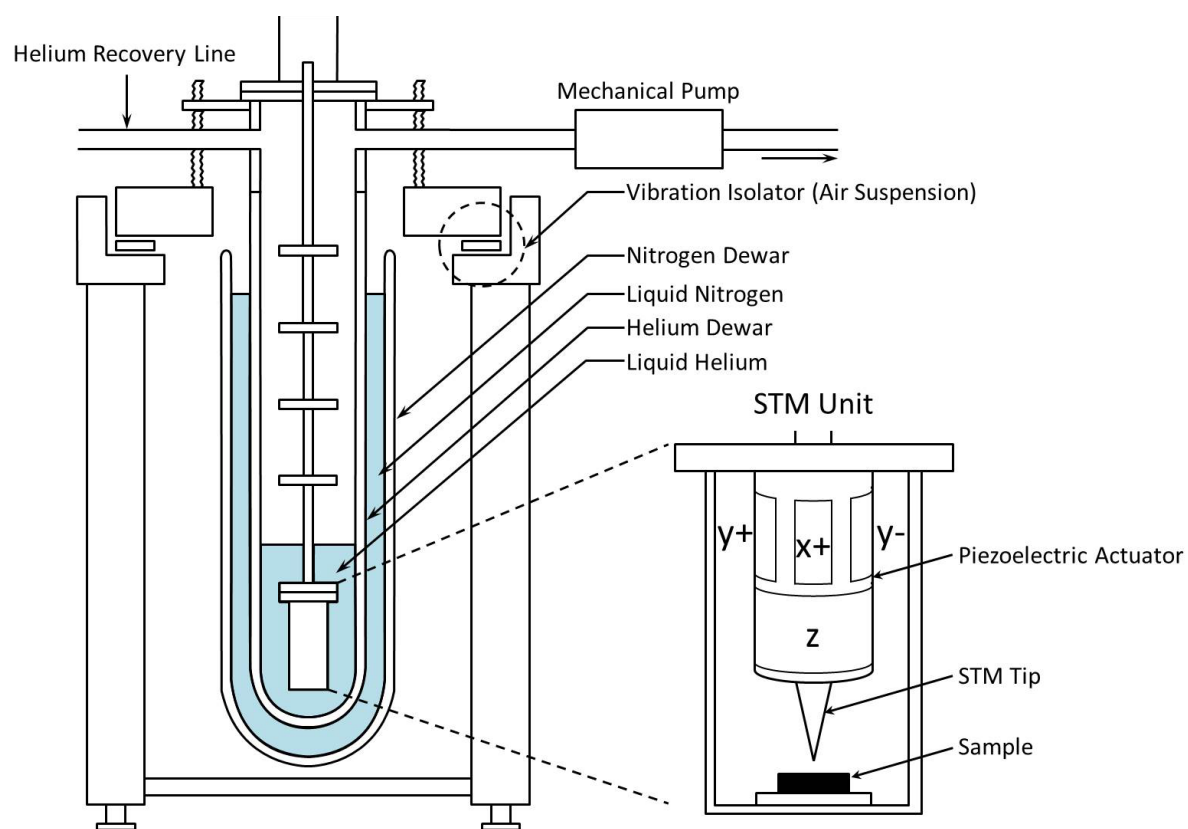


Figure 4.5: Pattern diagram of low-temperature STM system.

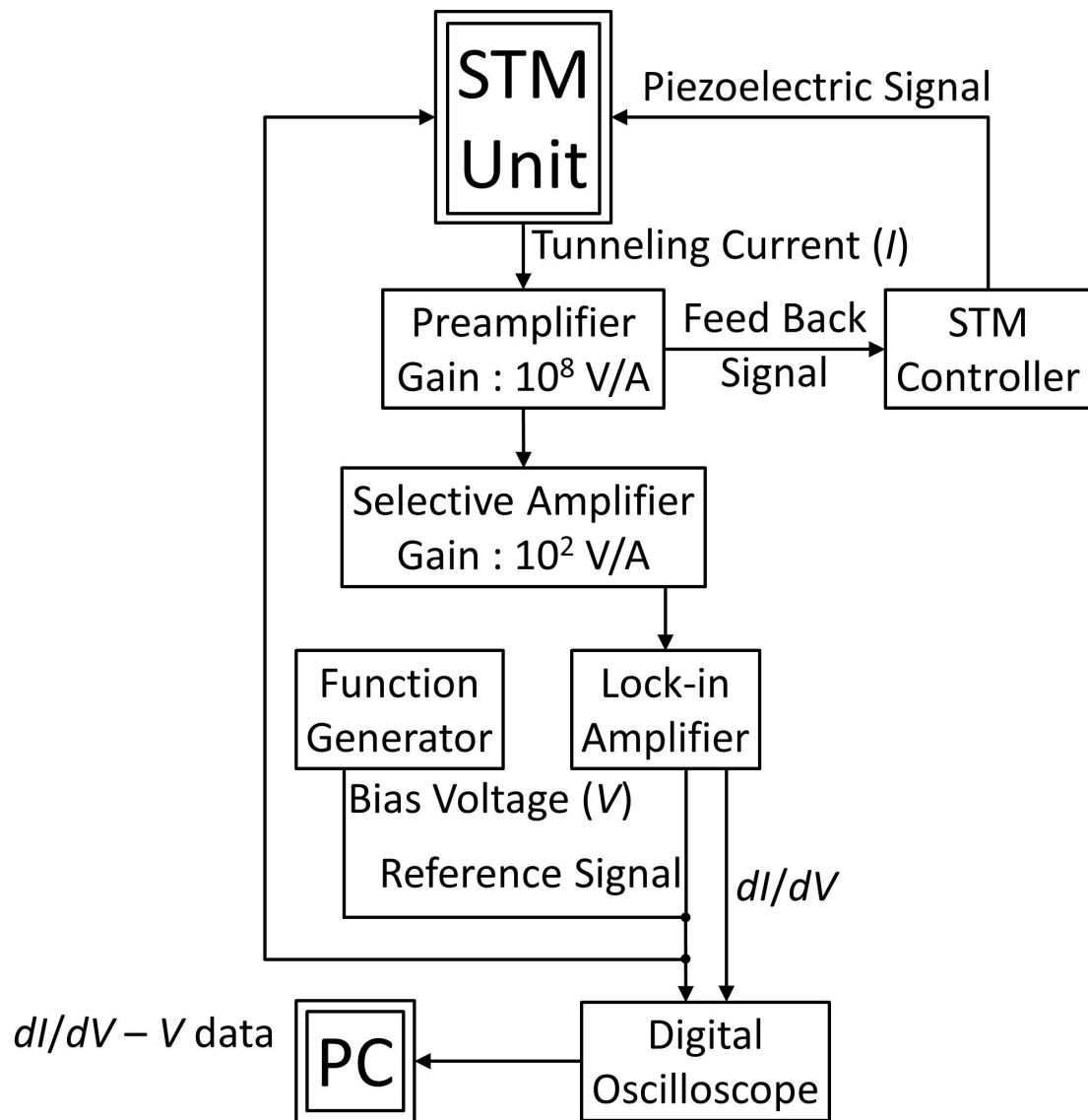


Figure 4.6: Schematic diagram of the STS measurement system.

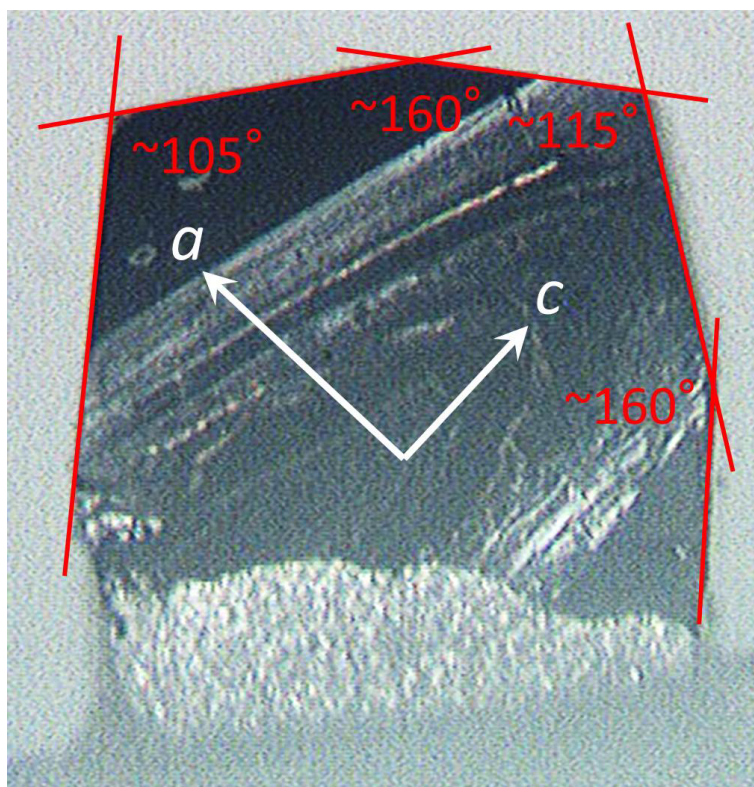


Figure 4.7: The crystal axis direction of the $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ salt.

Chapter 5

Results and Discussion

In this study, we performed the STM spectroscopy in the d[3,3]-Br salt on the conducting ($a-c$) plane and the lateral surfaces (the as-grown and the FIB cut ones). In the STS measurement, we sometimes observed some different tunneling conductance curves, because the superconducting and insulating areas were coexisting. So, it is important to select the essential and reliable data for the superconducting phase. We adopted the highly reproducible data obtained by repeating the tip approach on the same surface for the discussion of the STS results. It is considered that the obtained data is essential and reliable if the differential conductance has a high reproducibility by repeating the tip-approach because this repeating process corresponds to change the STS position at a wider range than the distance between the ET molecules array which is about 1.5 nm at the same direction surface.

5.1 STS on the conducting plane ($a - c$ plane)

The STS measurement on the conducting plane in the d[3,3]-Br salt have been previously carried out by S. Higashi *et al* as shown in Fig.2.11[36, 37]. We also measured the tunneling differential conductance on the conducting plane in the d[3,3]-Br salt for one sample as shown in Fig.5.1. The present result is consistent with the previous one (Fig.2.11) in low energy region. Both

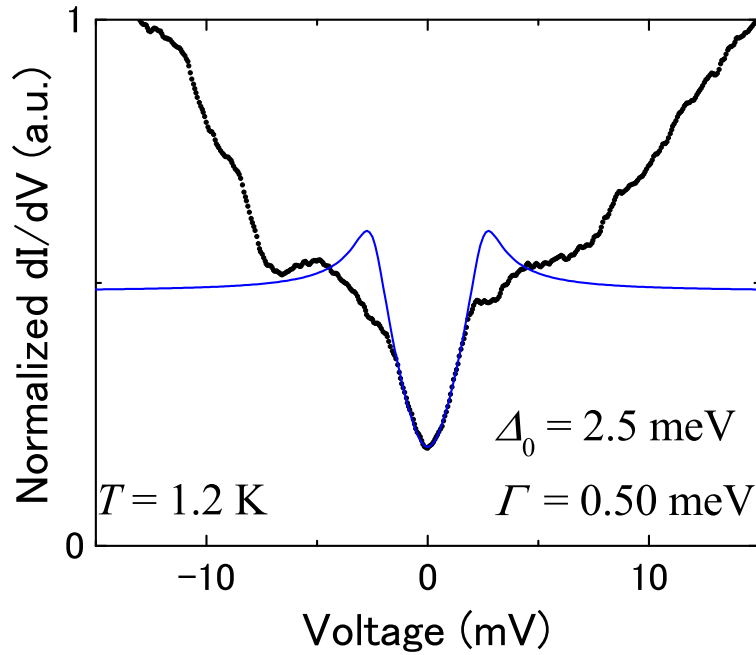


Figure 5.1: The tunneling differential conductance on the conducting plane in the d[3,3]-Br salt. The solid line represents the calculated curve by the line nodes model.

obtained differential conductance (Fig.2.11, 5.1) decreased rapidly around the Fermi energy (0 meV) and these gap structures suggested the superconducting gap. Although the differential conductance at high energy region sometimes increases anomalously caused by the influence of the pseudo gap[43] and the energy dependence of the tunneling probability[44], the functional form in the lower energy region which reflects the symmetry of the pair wave function

is identical[45]. The observed V-shaped functional form of the gap clearly indicates the anisotropic superconductivity different from the isotropic BCS-type one.

For fitting of the gap, we used the simple d -wave symmetry with the line nodes model described as $\Delta(\mathbf{k}) = \Delta_0 \cos 2\theta$, where Δ_0 and θ are the value of the maximum superconducting gap and the azimuthal angle in $\mathbf{k}$ -space, respectively. An equation of the conductance curve is described in Ref. [32]. The tunneling conductance curves are well fitted by the simple d -wave model around low energy region represented by the solid line in Fig.2.11 and 5.1, and the gap size Δ_0 is also consistent with the previous one. It was found from these results that the d[3,3]-Br salt is the anisotropic superconductor. We estimate the value of $2\Delta_0/k_B T_c$ in the d[3,3]-Br salt as 4.1 ± 0.7 . In addition, the value of $2\Delta_0/k_B T_c$ in κ -(ET) $_2X$ was also estimated as 5.6~11.0 (Cu(NCS) $_2$), 4.2 ± 0.2 (d[0,0]-Br) and 3.6 ± 0.8 (d[2,2]-Br) from the STS measurement on the conducting plane. The values in every κ -(ET) $_2X$ are comparable with that of the mean field approximation for the d -wave superconductivity ($2\Delta_0/k_B T_c \sim 4.28$) for the weak coupling[46]. On the other hand, it was not confirmed the systematic change of the gap size with increasing the strength of the electron correlation although T_c in κ -(ET) $_2X$ is gradually increasing. It cannot be denied the possibility of the strong coupling superconductivity in κ -(ET) $_2X$, since the estimation of $2\Delta_0/k_B T_c$ assuming the isotropic Fermi surface is probably incomplete without taking account into the in-plane anisotropy of the Fermi surface.

5.2 STS on the lateral surface

5.2.1 Results of STS

The angle-resolved STS measurement on the as-grown and the FIB cut lateral surfaces in the d[3,3]-Br salt was carried out along various tunneling directions at 1.2 K. The obtained tunneling differential conductance dI/dV data was selected on the condition that a dI/dV curve is obtained stably and higher reproducibly. Figure 5.2 ~ 5.7 show the typical tunneling differential conductance dI/dV in the d[3,3]-Br salt. Figure 5.2 and 5.3 correspond to the results on the as-grown surface, while Figure 5.4 ~ 5.7 correspond to those on the FIB cut one. The parameter ϕ represents to the azimuthal angle from the a^* -axis in the $a - c$ plane as shown in the upper right side of Fig.5.2. The plane indices corresponding to ϕ are estimated as (1,0,1) at $\phi = 56^\circ$, (2,0,1) at $\phi = 38^\circ$, (1,0,2) at $\phi = 72^\circ$, (3,0,1) at $\phi = 27^\circ$ and (1,0,0) at $\phi = 0^\circ$. Each curve is normalized to the conductance at $V = 10$ mV and aligned at intervals of one division for clarity. Although dI/dV (Fig.5.2, 5.5, 5.6) is increasing in high energy region ($|V| > 5$ mV) because of the energy dependence of the tunneling probability as well as the result on the conducting plane, the functional form in the lower energy region reflected correctly the symmetry of the pair wave function is identical in each spectrum[45].

In the results of the as-grown surfaces in Fig.5.2 and 5.3, a sharp dip associated with the superconducting gap was observed in the lower energy region. These spectra decrease sharply around the low energy region depending on the bias voltage. The gap form also varies depending on the tunneling direc-

tion as the gap width for the surface with $\phi = 38^\circ$ is smaller than that with $\phi = 56^\circ$. The observed V-shaped functional form of the gap indicates the anisotropic superconductivity. In the results of the FIB cut ones in Fig.5.4 $\sim$ 5.7, the various gap forms such as a U-shaped (Fig.5.6) and a V-shaped (Fig.5.4, 5.5, 5.7) were observed depending on each FIB cut surface direction. These gaps were also observed higher reproducibly for each surface direction. In particular, the spectrum in Fig.5.6 with the U-shaped functional form had been hardly observed at the as-grown surface. In addition, we observed not only the U-shaped gap but also the V-shaped one at the same FIB cut surface of the (1,0,0) plane with higher reproducibility as shown in Fig.5.6 and 5.7. Figure 5.8 shows the angular dependence of the tunneling spectra in the d[3,3]-Br salt. For the moment, we adopt the U-shaped gap at $\phi = 0^\circ$ in the angular dependence of the STS spectra in Fig.5.8 considering comprehensively the relationship between form of each gap and its azimuthal angle ϕ . We discuss the two type superconducting gaps in a later section. The observed gap forms systematically vary from the U-shaped to the V-shaped depending on the tunneling direction ϕ . Therefore, it is strongly suggested that the d[3,3]-Br salt is the anisotropic superconductor in the $a - c$ plane as well as the previously studied κ -(ET) $_2X$.

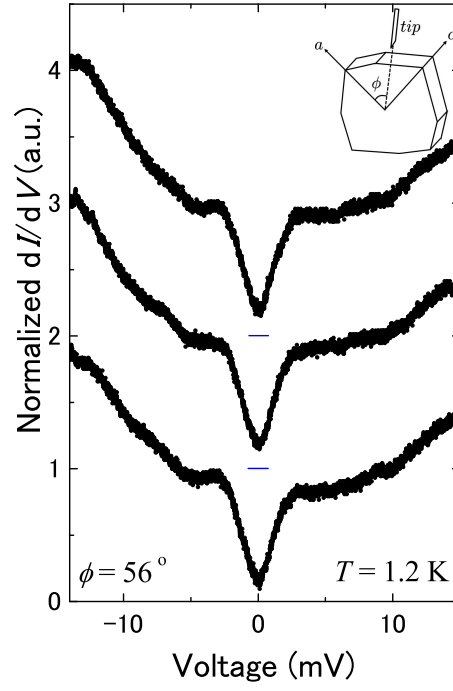


Figure 5.2: The tunneling differential conductance on the as-grown surface in the d[3,3]-Br salt at $\phi = 56^\circ$.

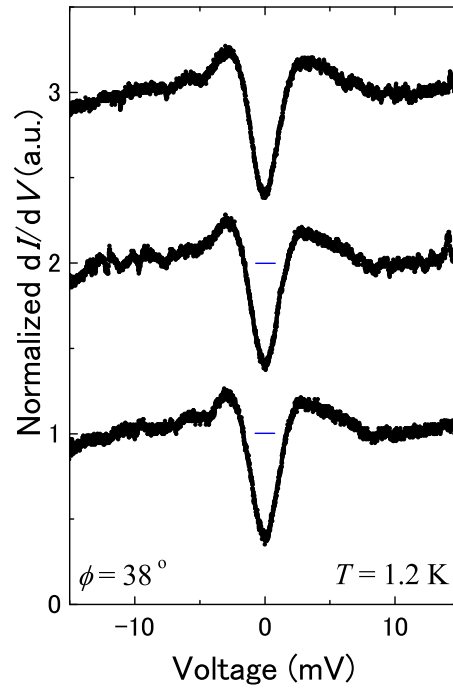


Figure 5.3: The tunneling differential conductance on the as-grown surface in the d[3,3]-Br salt at $\phi = 38^\circ$.

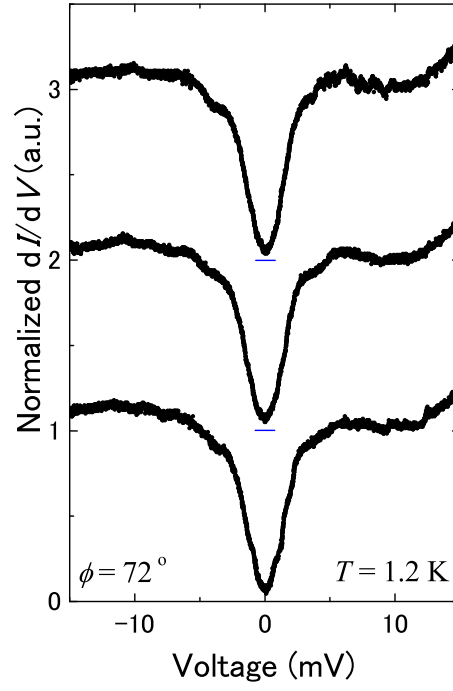


Figure 5.4: The tunneling differential conductance on the FIB cut surface in the d[3,3]-Br salt at $\phi = 72^\circ$.

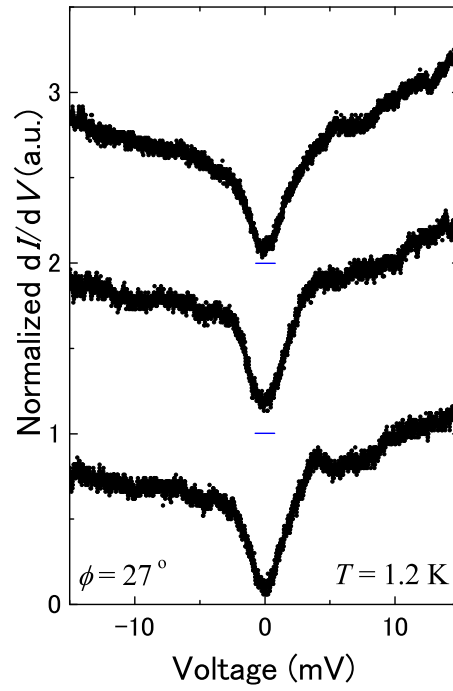


Figure 5.5: The tunneling differential conductance on the FIB cut surface in the d[3,3]-Br salt at $\phi = 27^\circ$.

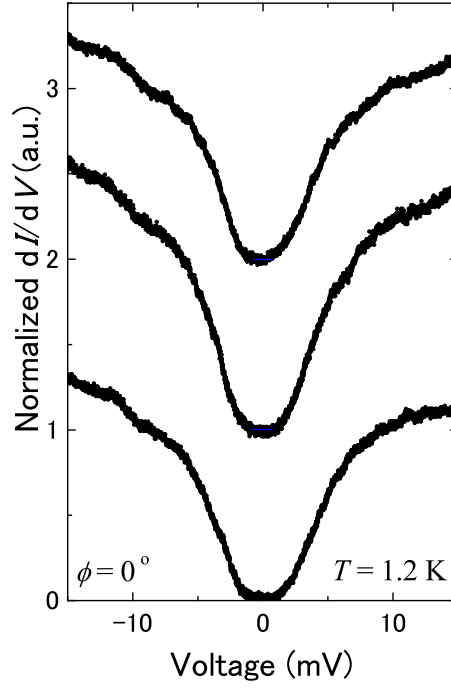


Figure 5.6: The tunneling differential conductance on the FIB cut surface in the d[3,3]-Br salt at $\phi = 0^\circ$ (U-shaped).

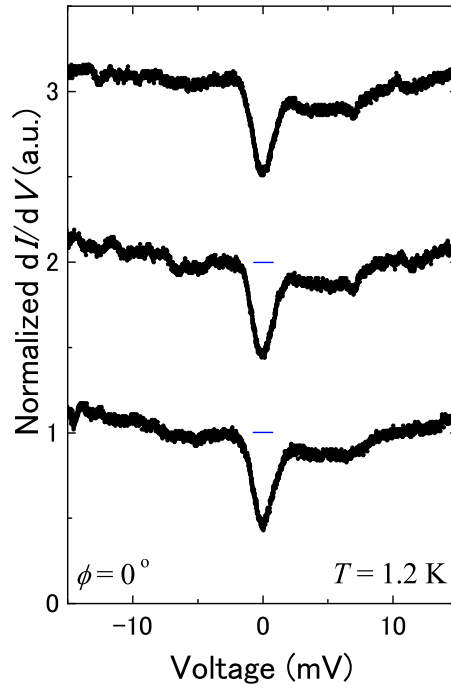


Figure 5.7: The tunneling differential conductance on the FIB cut surface in the d[3,3]-Br salt at $\phi = 0^\circ$ (V-shaped).

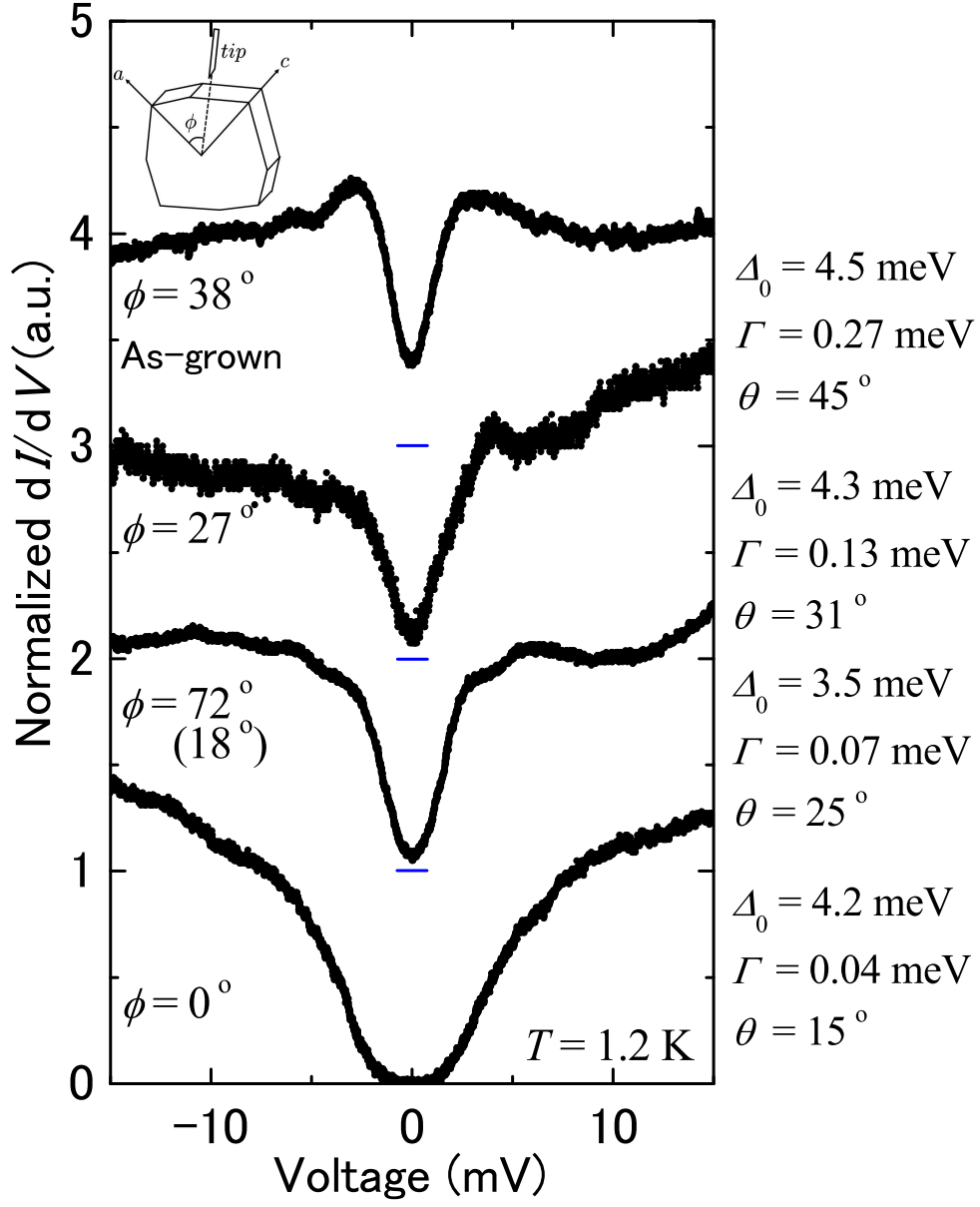


Figure 5.8: Angular dependence of the tunneling differential conductance in the d[3,3]-Br.

5.2.2 Fitting of the tunneling spectra on the lateral surface

From the angle-resolved STS measurement, it was suggested that the d[3,3]-Br salt has the anisotropic superconducting gap in the $a - c$ plane and the tunneling from the lateral surface has a strong $\mathbf{k}$ -dependence of the tunneling transition probability. Therefore, as described in Appendix A, we try to fit each curve on the lateral surface by the line nodes model considering the tunneling transition probability depending on the wave vector $\mathbf{k}$ which written as

$$dI/dV = G_{nn} \int \exp(-\beta \sin^2 \alpha) \int_{-\infty}^{\infty} N_s(E, \alpha) \left[-\frac{\partial f(E + eV)}{\partial(eV)} \right] dE d\alpha$$

with

$$N_s(E, \alpha) = N_0 \left(\text{Re} \left[\frac{E - i\Gamma}{\sqrt{(E - i\Gamma)^2 - (\Delta_0 \cos 2(\alpha + \theta))^2}} \right] \right),$$

where Γ , G_{nn} and θ are the electron lifetime broadening, the conductance of the sample at the normal state and the fitting parameter with the angle from the antinodal direction in the above model, respectively. The d -wave gap given as $\Delta = \Delta_0 \cos 2\theta$ is assumed. The material dependent parameter β is fixed at $\beta = 15$. Although this value is smaller than the previously studied κ -(ET)₂X (Cu(NCS)₂, d[0,0]-Br, d[2,2]-Br as $\beta = 20$), it gives better fitting. The reason of the small value β may be caused by the change of the work function $U_B - \mu_1$ of β by the influence of the increasing of the electron correlation in the case of the d[3,3]-Br salt located very near the Mott boundary than the previously studied ones.

Figure 5.9 ~ 5.14 show the result of fitting analysis by above model. The solid line corresponds to the theoretical curve. The observed all conductance curves on both the as-grown and the FIB cut surfaces are well fitted especially in the lower energy region, where the gap symmetry is correctly reflected. These results additionally prove that the FIB method is effective for the investigation of the gap anisotropy. In addition, the middle type gap, similar to the gap observed at $\phi \sim 36^\circ$ ((1,0,1) plane), was rarely observed in the case of the FIB cut surface ($\phi = 0^\circ$ or 90°). However, the observation number of the middle type gap was very small as compared with those of the other gaps including the two type ones. The reason of the observation of the middle type gap may be caused by the exposure of another lower plane index surface such as the (1,0,1) plane as small area connecting to the large flat area in the case of the FIB cut processing. Such structure was also observed as a narrow area by the STM measurement at room temperature as described in section 4.2.2. However, since most areas of the cut surface by the FIB processing are almost flat surface, it is considered that the two types of the superconducting gap observed with high reproducibility reflect the information from the correct plane. Therefore, we will proceed to a discussion without considering the middle type gap. Figure 5.15 shows the fitting of the tunneling spectra corresponding to the data in Fig.5.8. The systematic changes of gap from the antinodal U-shaped to the nodal V-shaped with the change of ϕ from 0 to $\pi/4$ are well reproduced by the theoretical curves, although the two type gaps corresponding to the antinodal type and the nodal one were observed at the same FIB (1,0,0) surface (Fig.5.13, 5.14). As a result, it is indicated that

the d[3,3]-Br salt is the *d*-wave superconductor with the fourfold symmetry as well as the previously studied κ -(ET)₂X.

The value of Δ_0 and $2\Delta_0/k_B T_c$ from the STS on the lateral surface are estimated as 4.0 ± 0.9 meV and 7.8 ± 1.8 , respectively. These values of the d[3,3]-Br salt are comparable to those of the previously studied κ -(ET)₂X ($\Delta_0 = 3.0 \sim 10.0$ meV, $2\Delta_0/k_B T_c = 6.7 \sim 24.6$ for the Cu(NCS)₂ salt, $\Delta_0 = 4.2 \pm 0.8$ meV, $2\Delta_0/k_B T_c = 8.1 \pm 1.5$ for the d[0,0]-Br salt, $\Delta_0 = 3.9 \pm 0.8$ meV, $2\Delta_0/k_B T_c = 7.6 \pm 1.5$ for the d[2,2]-Br salt). On the other hand, the value of $2\Delta_0/k_B T_c$ obtained from the STS on the lateral surface is larger than that on the conducting plane ($\Delta_0 = 2.1 \pm 0.4$ meV, $2\Delta_0/k_B T_c = 4.1 \pm 0.7$ for the d[3,3]-Br salt). This tendency is common in other all κ -(ET)₂X. This discrepancy between the gap sizes obtained from the lateral surface and the conducting plane is presumably caused by the incomplete estimation of the gap amplitude on the conducting plane. Since Δ_0 is estimated from the average conductance curve in the *d*-wave line nodes model assuming the isotropic 2D Fermi surface in the case of the STS on the conducting plane, the influence of the in-plane anisotropy for the shape of the Fermi surface and the tunneling transition probability is not rigorously taken into account. The density of states has probably less weight along the a^* and the c^* directions due to the non-cylindrical shape of the Fermi surface, and the group velocity component along the b^* direction with the a^* - and the c^* -axes corresponding to the tunneling probability may be small. As a result, the apparent gap size observed on the conducting plane is deduced to become a smaller value. While, we can directly obtain the superconducting gap in the case of the STS on the

lateral surface unaffected so much by the anisotropy of the Fermi surface. In fact, the values of the gap size Δ_0 estimated from the STS for the all directions in Fig.5.2~5.7 are comparable. Therefore, it is considered that the value obtained from the lateral surface measurement reflects the correct gap size.

The value of $2\Delta_0/k_B T_c$ estimated from the lateral surface measurement in every salts is about twice larger than that of the mean field approximation ($2\Delta_0/k_B T_c = 4.28$) for the weak coupling with the d -wave[46]. It is suggested that κ -(ET)₂X including the d[3,3]-Br salt are a strong coupling d -wave superconductor, although the systematic change of $2\Delta_0/k_B T_c$ is not confirmed within the experimental errors with increasing the electron correlation, which becomes stronger from the Cu(NCS)₂ to the d[3,3]-Br salts. The possibility of the strong coupling superconductivity has been discussed from the specific heat measurement in the d[0,0]-Br salt[30]. They estimated the Δ_0 and $2\Delta_0/k_B T_c$ as ~ 3.8 meV and ~ 7.4 using a strong coupling α -model. It was also suggested that the d[0,0]-Br salt is the strong coupling d -wave superconductor. These values are consistent with those from the STS measurement.

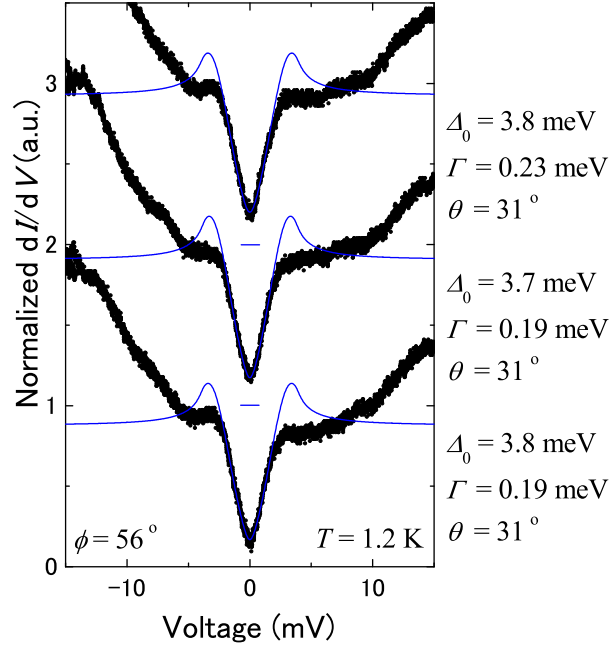


Figure 5.9: The tunneling differential conductance on the as-grown surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 56^\circ$.

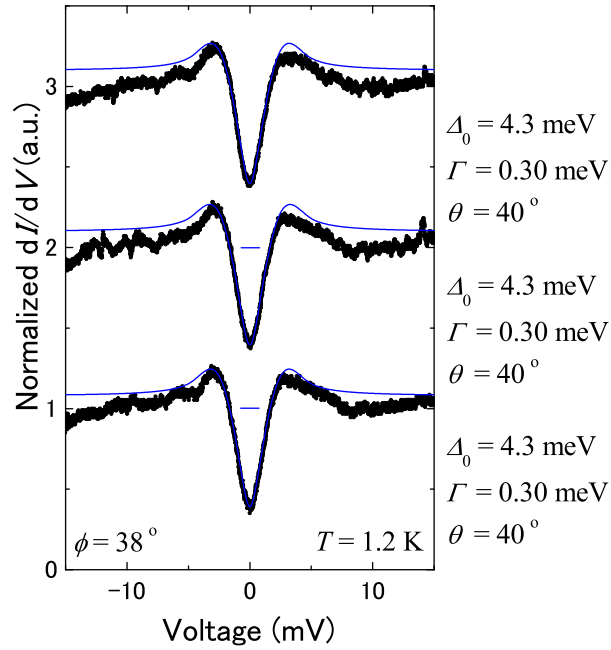


Figure 5.10: The tunneling differential conductance on the as-grown surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 38^\circ$.

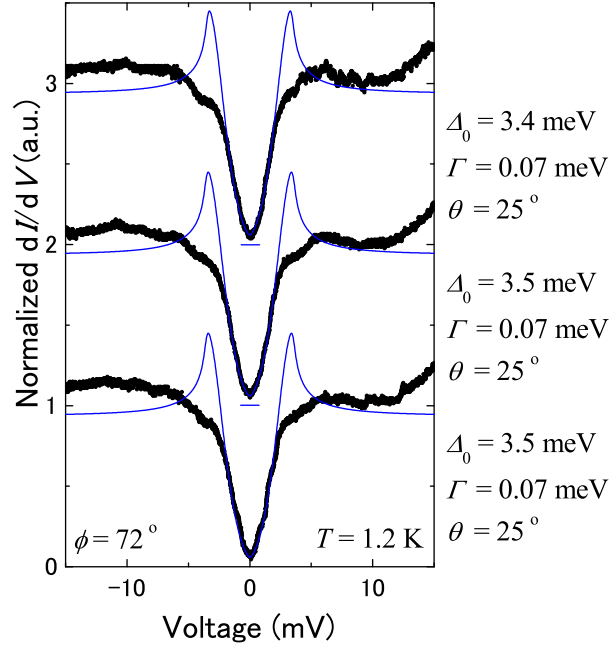


Figure 5.11: The tunneling differential conductance on the FIB cut surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 72^\circ$.

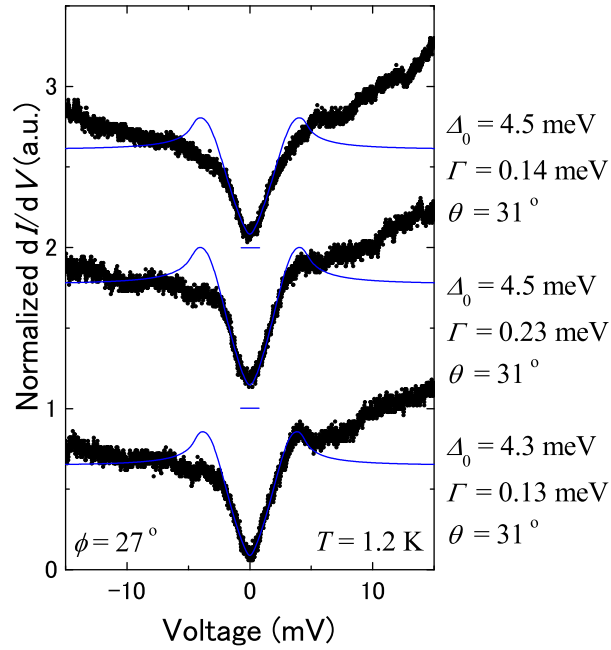


Figure 5.12: The tunneling differential conductance on the FIB cut surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 27^\circ$.

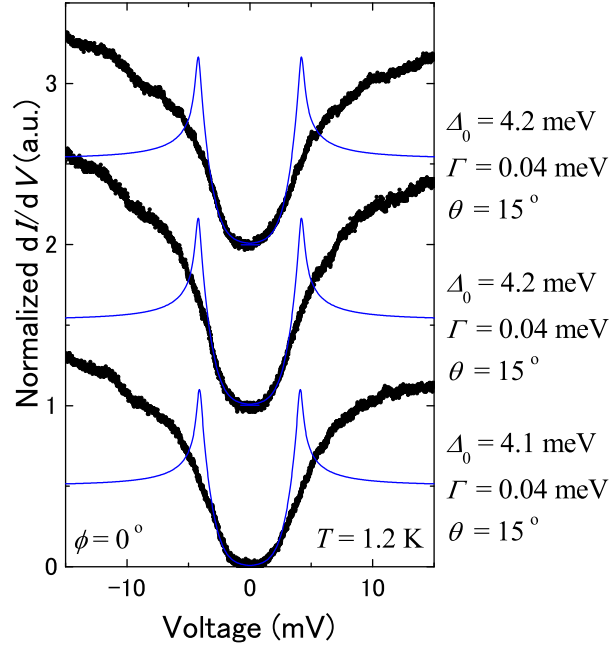


Figure 5.13: The tunneling differential conductance on the FIB cut surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 0^\circ$ (U-shaped).

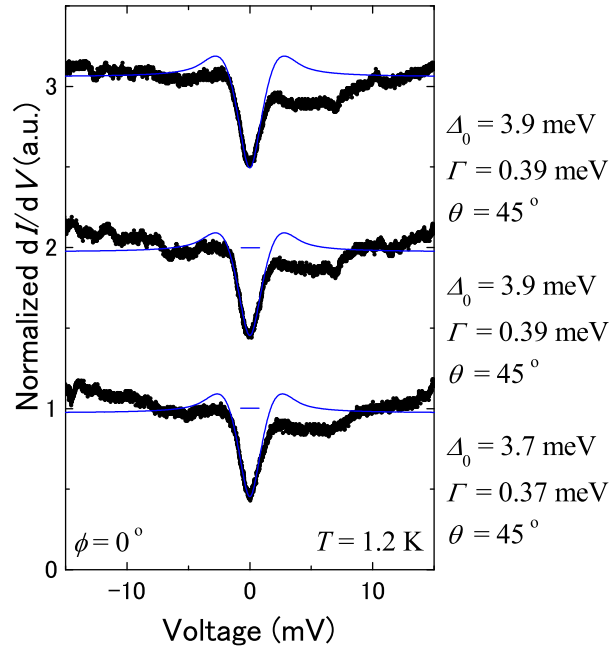


Figure 5.14: The tunneling differential conductance on the FIB cut surface fitted by the line nodes model considering the tunneling transition probability of the $\mathbf{k}$ dependence in the d[3,3]-Br salt at $\phi = 0^\circ$ (V-shaped).

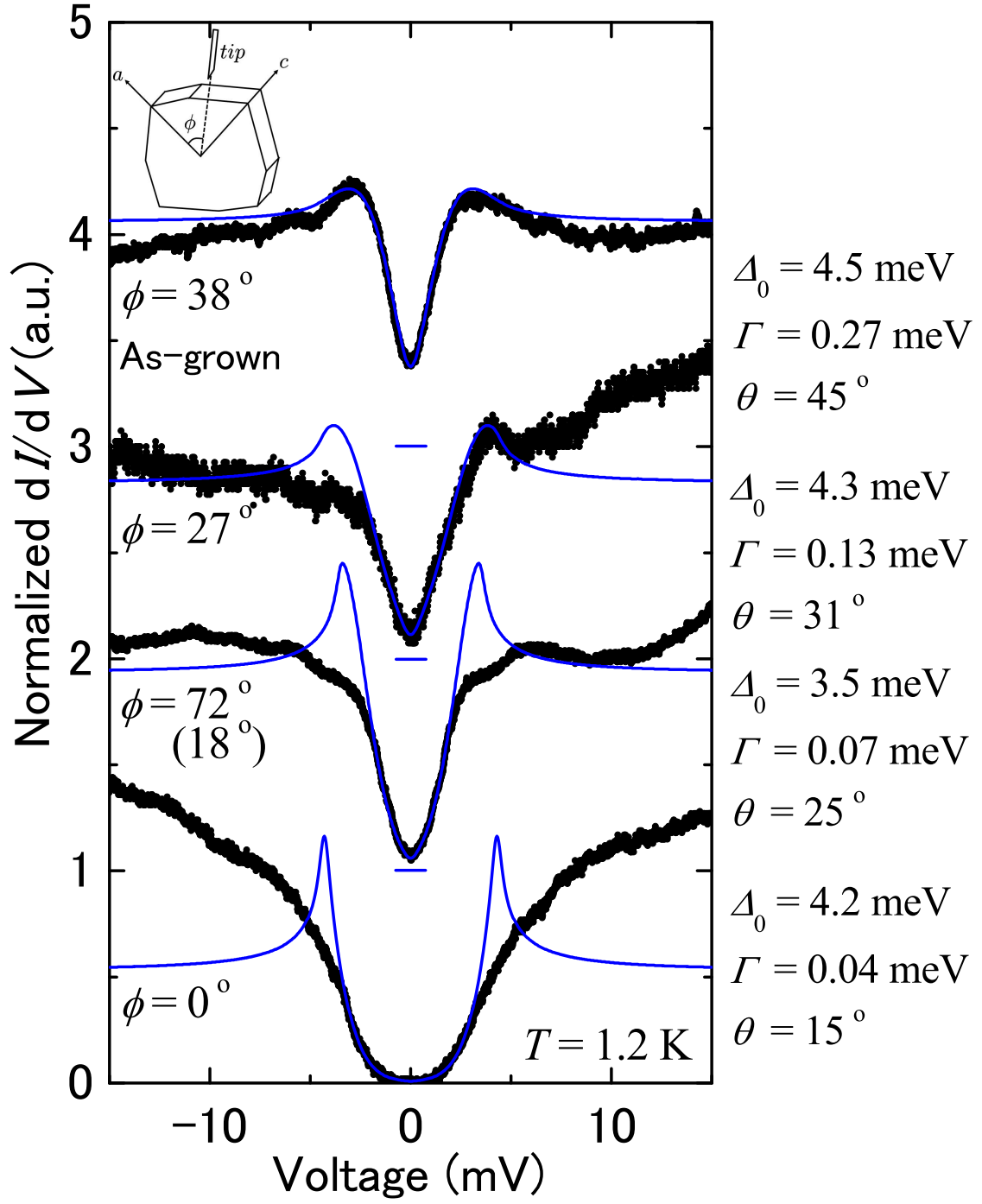


Figure 5.15: The angular dependence of the tunneling differential conductance in the d[3,3]-Br salt.

5.2.3 The nodal direction in the d[3,3]-Br salt

The relationship between the fitting parameter θ and the reduced azimuthal angle ϕ' is shown in Figure 5.16 to determine the nodal direction. We deal with the azimuthal angle ϕ in the reduced range $0 \leq \phi' \leq \pi/4$ assuming the four-fold symmetry $\Delta = \Delta_0 \cos 2\theta$ for simplicity because the a^* -axis is perpendicular to the c^* -axis. For example, the direction of $\phi = 72^\circ$ is reduced to $\phi' = 18^\circ$. The data points of both as-grown $((1,0,1), (2,0,1))$ and the FIB cut surfaces are shown together, where the data with $\phi' > 35^\circ$ and $\phi' < 35^\circ$ corresponds to the as-grown and the FIB surfaces, respectively. Here, we adopt the data of the U-shaped gap deduced from the entire tendency of the relationship between θ and ϕ' although two type gaps were observed at $\phi' = 0^\circ$. We discuss the V-shaped gap observed at $\phi' = 0^\circ$ in the next section. The plotted points are aligned on the almost linear relation line described as the solid line as shown in Fig.5.16. As a result, the nodal direction is determined along $\pi/4$ from the a^* - and the c^* -axes, and the symmetry of the superconductivity is the $d_{x^2-y^2}$ as illustrated at the right side of Fig.5.16. According to the theoretical study of the spin fluctuation mechanism[19], this symmetry is stabilized in the case of a relatively weak electron correlation. Therefore, the electron correlation is still not strong enough even for the d[3,3]-Br salt in the frame of this spin fluctuation model, although the electron correlation of the d[3,3]-Br salt is stronger than those of the previously studied κ -(ET) $_2X$.

In addition to the observation of the anisotropic gap, the ZBCP, indicating the feature of the anisotropic gapless superconductors with nodes, was also

observed in the STS measurement on the lateral surfaces near the nodal direction as well as the d[0,0]-Br and the d[2,2]-Br salts, when the STM tip was very close to the sample surface. As shown in Fig.5.17, the sharp peak at zero bias in dI/dV curve is recognized. The observation of the ZBCP reinforces that the d[3,3]-Br salt is the d -wave superconductor with line nodes and is also consistent with the $d_{x^2-y^2}$.

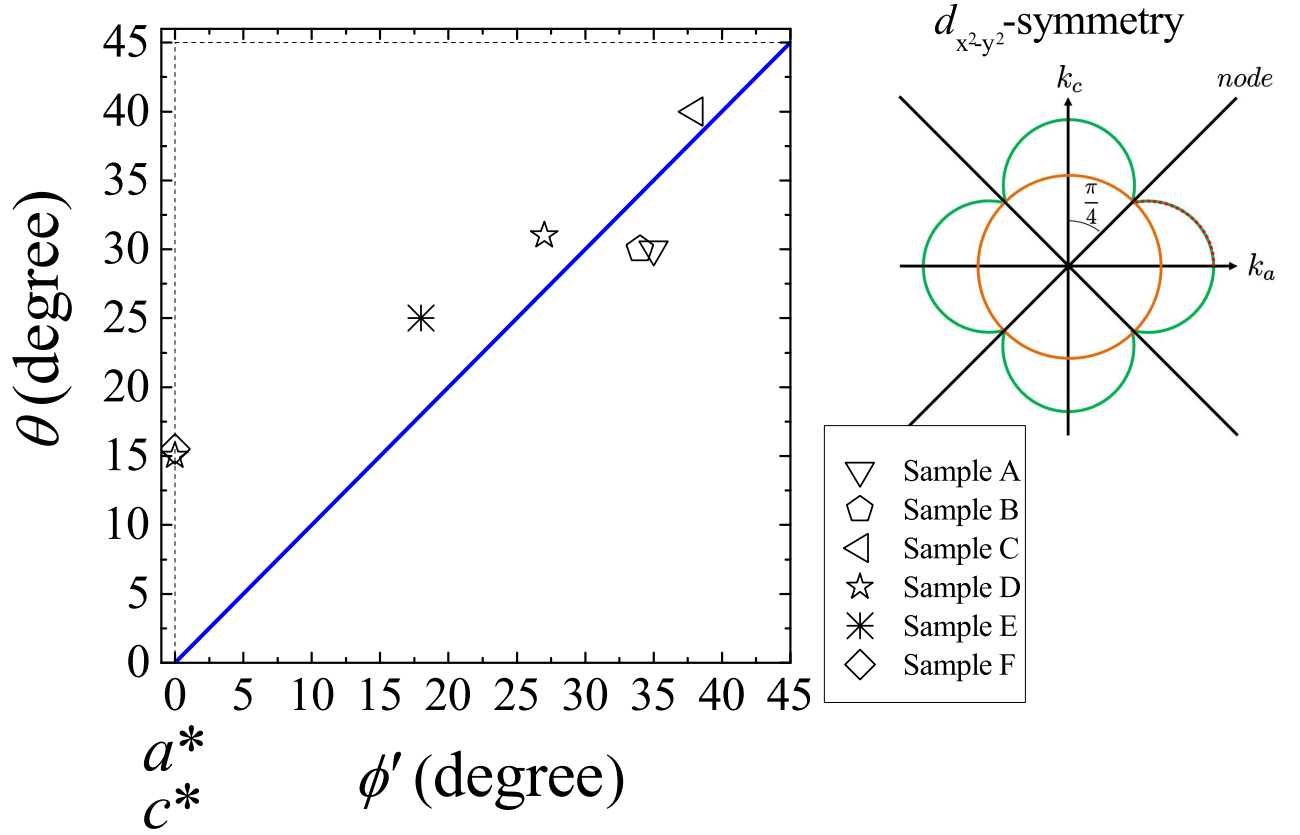


Figure 5.16: The relationship between the fitting parameter θ and the reduced azimuthal angle ϕ' . We adopt the data points of the U-shaped gap at $\phi' = 0^\circ$ as written in the text. The solid line represents the relation for the $d_{x^2-y^2}$. The schematic image of the $d_{x^2-y^2}$ is shown in the right side.

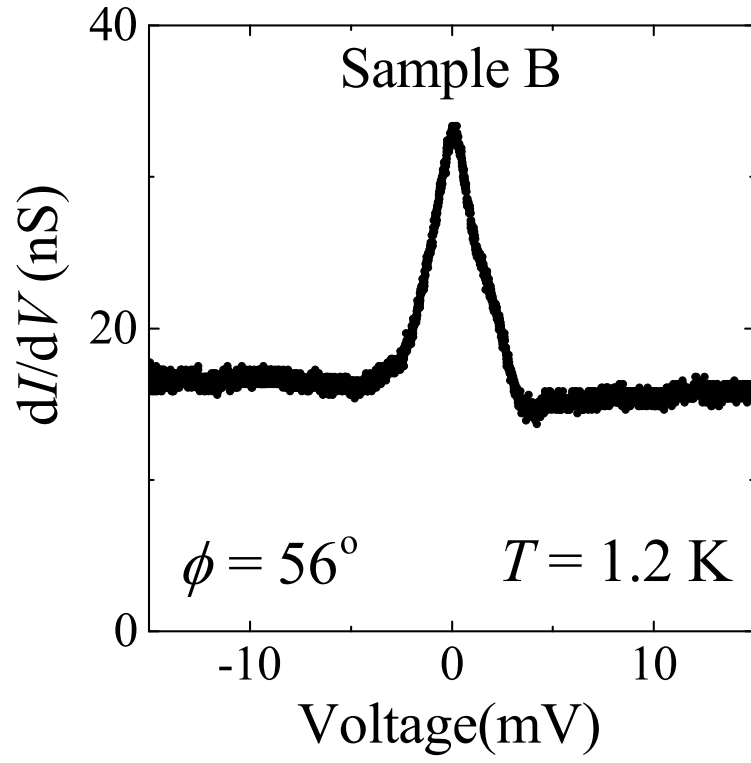


Figure 5.17: Tunneling spectra of the zero bias conductance peak (ZBCP). The ZBCP was observed near the nodal direction corresponding to the $d_{x^2-y^2}$.

5.3 The possibility of the coexistence the $d_{x^2-y^2}$ and the d_{xy}

Although we found that the symmetry of the superconductivity in the d[3,3]-Br salt is the $d_{x^2-y^2}$, we also observed the two types of the superconducting gap which are the antinodal and the nodal gaps at the same direction FIB cut surface ($\phi = 0^\circ$) as shown in Fig.5.13 and 5.14. The observed gaps at the same direction surface were primarily only two types and the other various gap forms could be hardly observed. As mentioned in section 5.2.3, we adopted the U-shaped gap observed at the FIB cut surface ($\phi = 0^\circ$) for the determination of the nodal direction in Fig.5.16. However, the V-shaped gap is firmly observed. We add the corresponding data points at $\phi' = 0^\circ$ to those in Fig.5.16 around $\theta \sim 45^\circ$ as shown in Fig.5.18. Furthermore, we sometimes observed the two type gaps on the as-grown surface though the reproducibility was not high. Such data points are also added as the bracketed symbol like ($\triangleright$) at $\phi = 36^\circ$, $\theta = 10^\circ$ in Fig.5.18. These data points do not correspond to the solid line representing the $d_{x^2-y^2}$. Instead, these additional points are aligned on another linear relation line described as the broken line in Fig.5.18 indicating the d_{xy} . Such two type gaps have been never observed in the d[0,0]-Br nor the Cu(NCS)₂ salts. It is known that the d[3,3]-Br salt has an antiferromagnetic insulating region in part at the superconducting state even if the sample is cooled slowly around 80 K. Such a mosaic pattern is sketched in Fig.5.19, although the detailed spatial structure is not yet known. The $d_{x^2-y^2}$ is stabilized in the bulk superconducting region, where the electron correlation is not strong enough. On the other hand, it is presumed

that the electron correlation becomes stronger locally around the insulating region. Therefore, the nodal gap at $\phi = 0^\circ$ corresponding to the d_{xy} could be observed near the insulating region as shown in Fig.5.19. The observation of two type gaps suggests the possibility of the coexistence of the $d_{x^2-y^2}$ and the d_{xy} . This behavior probably corresponds to the change from the $d_{x^2-y^2}$ to the d_{xy} with increasing the electron correlation predicted by the spin fluctuation model. It presumably indicates that the mechanism of the superconductivity in κ -(ET) $_2X$ is caused by the antiferromagnetic spin fluctuation.

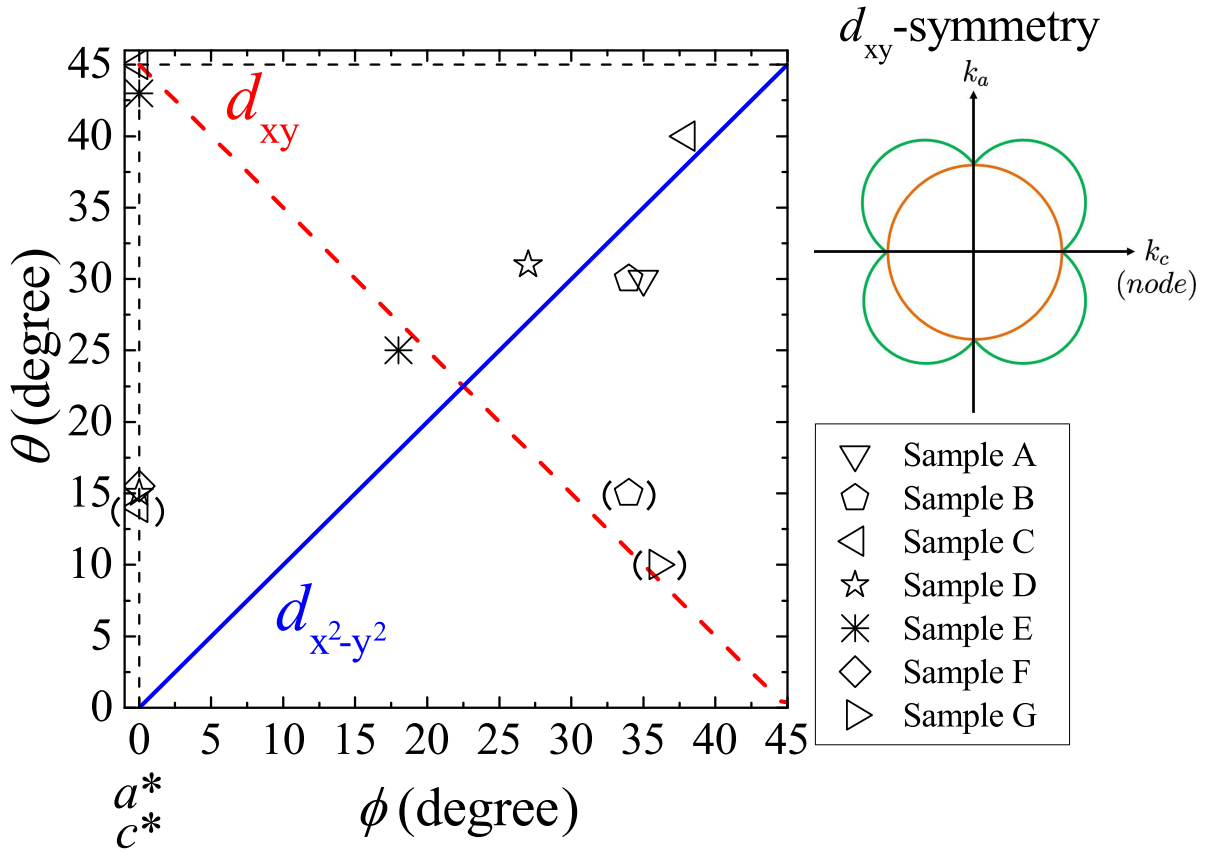


Figure 5.18: The relationship between the fitting parameter θ and the reduced azimuthal angle ϕ' containing the d_{xy} . The data points corresponding to another type gap are added. The broken line represents the relation for the d_{xy} . The schematic image for the d_{xy} is shown in the right side.

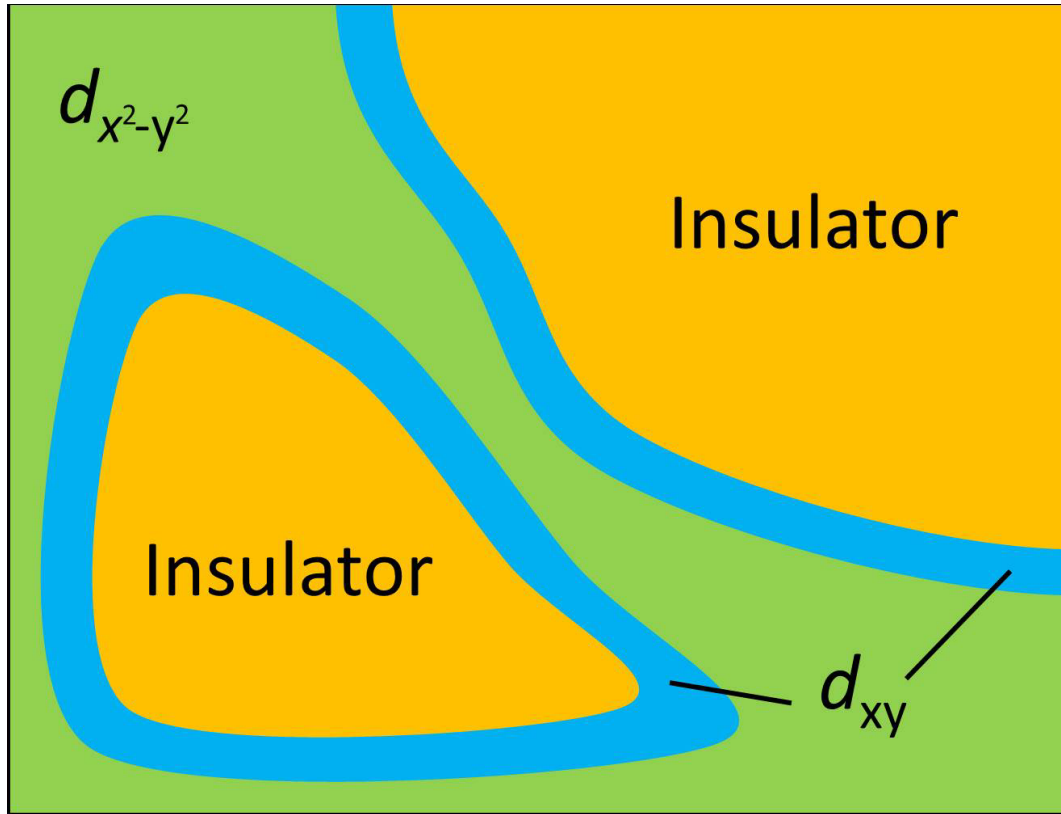


Figure 5.19: Schematic image of the coexistence of the $d_{x^2-y^2}$ and the d_{xy} . The $d_{x^2-y^2}$ is stabilized in the bulk superconducting phase, while the d_{xy} appears around the antiferromagnetic insulating region.

Chapter 6

Summary

We performed the angle-resolved STS measurement on the as-grown and the FIB cut lateral surfaces in κ -(ET-d[3,3])₂Cu[N(CN)₂]Br to clarify the mechanism of the superconductivity. We succeeded to observe the systematic in-plane anisotropy of the superconducting gap depending on the wave vector. As a result, we found that the superconducting gap in the d[3,3]-Br salt is a strong coupling *d*-wave superconductor. We also manifested that the FIB method is useful to investigate the in-plane superconducting gap anisotropy in organic compounds which have no cleavage. The gap symmetry is described by the $d_{x^2-y^2}$ in the bulk superconducting phase as well as the previously studied κ -(ET)₂X. This suggests that the electron correlation in the d[3,3]-Br salt is still not strong enough in the frame of the spin fluctuation model, although the electron correlation in the d[3,3]-Br salt situated very near the Mott boundary is stronger than that in the previously studied κ -(ET)₂X.

In addition, we also observed the two types of the superconducting gap at the same direction surfaces. It suggests the possibility of the coexistence of the $d_{x^2-y^2}$ and the d_{xy} regions. Its behavior probably corresponds to the change

from the $d_{x^2-y^2}$ to the d_{xy} with increasing the electron correlation predicted by the spin fluctuation model.

Chapter 7

Future works

Although we obtained the strong evidence that the superconductivity in κ -(ET)₂X is caused by the spin fluctuation, we could not clarify the detailed mosaic structure of $d_{x^2-y^2}$ and d_{xy} in space. Therefore, we need to investigate these mosaic pattern by STM at low temperature.

In addition, we may have to research the symmetry of the superconductivity in the d[4,4]-Br salt which is located at just Mott boundary.

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Appendix A

About the fitting of the lateral surface

- **The k -dependence of the tunneling transition probability**

As mentioned in the text, in the angle-resolved STS measurement, the tunneling electron from the lateral surface perpendicular to the conducting plane has a strong k -dependence of the tunneling transition probability. Therefore, for taking into account this k -dependence, we consider the angular dependence of the tunneling transition probability by the factor D which is a transmission coefficient of electron and written by the 2D WKB approximation as[47]

$$\begin{aligned} D &= \exp(-2\kappa t) \exp(-\kappa t \frac{\mu_1 \sin^2 \alpha}{U_B}) \\ &= D_0 \exp(-\beta \sin^2 \alpha) \end{aligned} \tag{A.1}$$

with

$$\kappa = \frac{\sqrt{2m(U_0 - E_\perp)}}{\hbar} \tag{A.2}$$

where α , t , U_B and $E_\perp$ are the incident angle of electrons from normal vector of tunnel barrier, the width of the tunnel barrier, the work function which

is the barrier height measured from Fermi energy μ_1 of metal of incident side, the kinetic energy component perpendicular to the tunnel barrier and $U_B = U_0 - \mu_1$, respectively as shown in Fig.A.1. From this, it is indicated that the tunneling probability is high around $\alpha = 0^\circ$. The parameter β given as

$$\beta = \frac{\kappa t \mu_1}{U_B}, \quad (\text{A.3})$$

depends on the material and the tunneling barrier. As shown in Fig.A.2, it is understood that electrons whose kinetic energy perpendicular to the tunneling barrier is much larger are more likely to tunnel depending on the wave vector with increasing β . As a result, we obtain dI/dV for the line nodes model considering the tunneling transition probability depending on the wave vector $\mathbf{k}$ as

$$dI/dV = G_{nn} \int \exp(-\beta \sin^2 \alpha) \int_{-\infty}^{\infty} N_s(E, \alpha) \left[-\frac{\partial f(E + eV)}{\partial(eV)} \right] dE d\alpha \quad (\text{A.4})$$

with

$$N_s(E, \alpha) = N_0 \left(\text{Re} \left[\frac{E - i\Gamma}{\sqrt{(E - i\Gamma)^2 - (\Delta_0 \cos 2(\alpha + \theta))^2}} \right] \right), \quad (\text{A.5})$$

where Γ , G_{nn} and θ are the one-electron lifetime broadening, the conductance of the sample at normal state and the fitting parameter which is the angle from the antinodal direction in the model, respectively. The d -wave gap given as $\Delta = \Delta_0 \cos 2\theta$ is assumed. We show the theoretical lines calculated by Eq.A.4 with changing the fitting parameter θ described in Fig.A.3, where the beta is fixed at 15, the gap size is 5.0 meV and the broadening parameter Γ is

0.01 meV. The calculated curves change from the U-shaped to the V-shaped with increasing the fitting parameter θ .

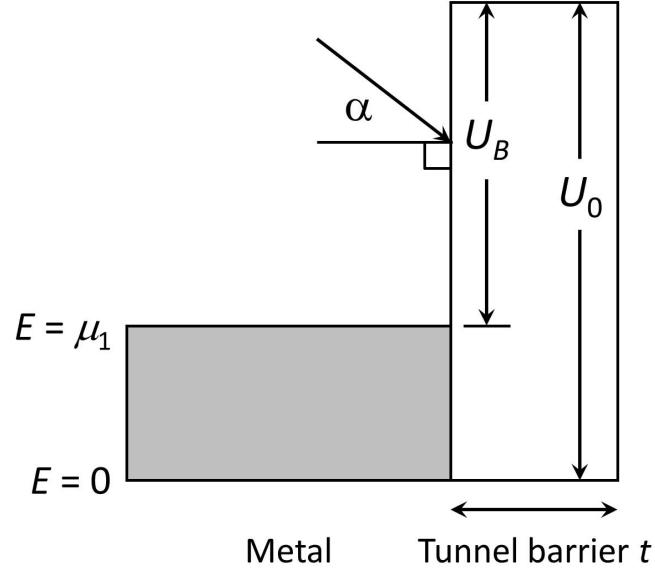


Figure A.1: Schematic image of tunneling barrier.

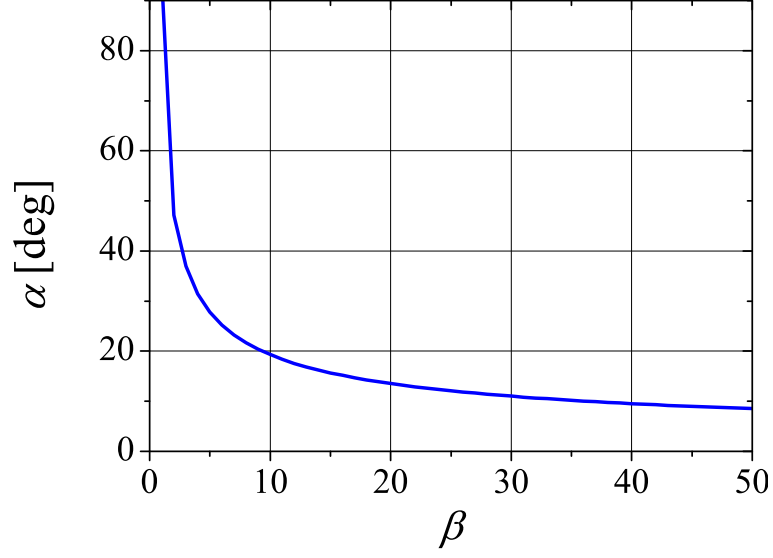


Figure A.2: The relationship between α and β when $D = 1/e$.

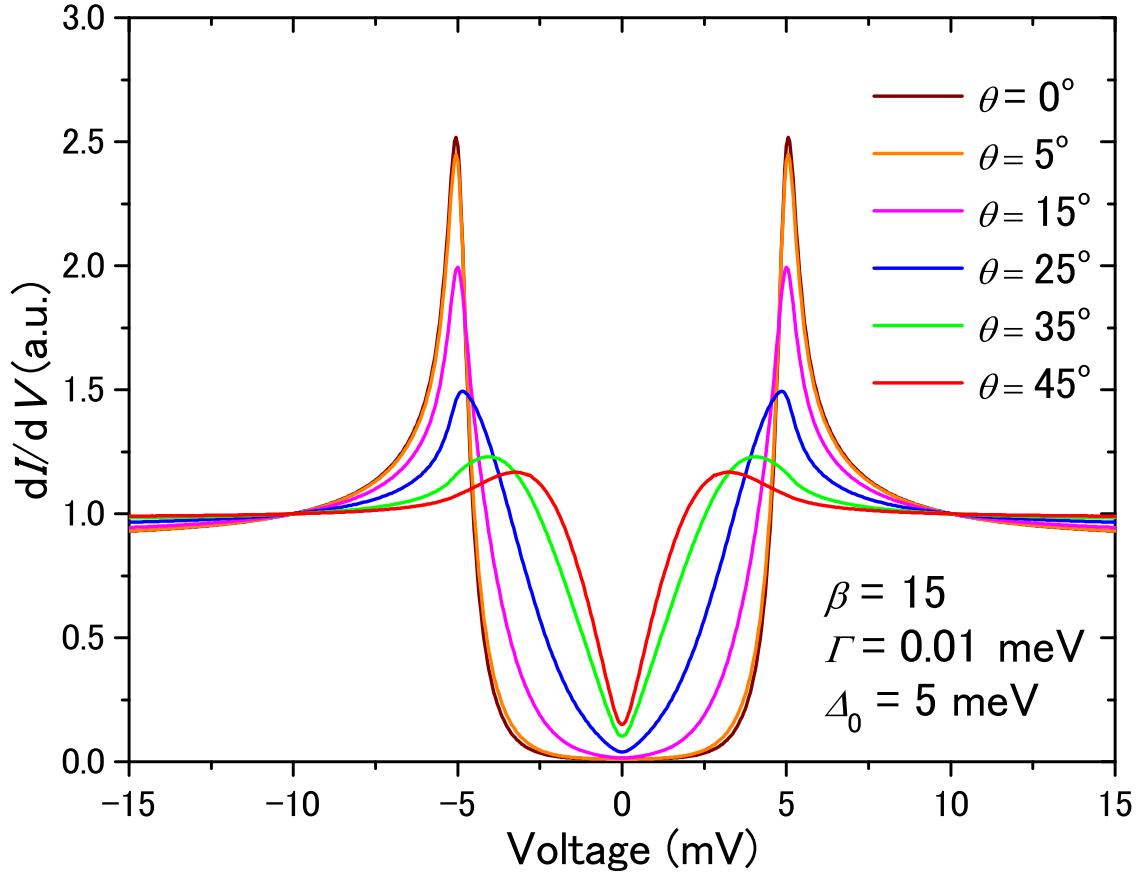


Figure A.3: The theoretical curve calculated by the line nodes model considering the $\mathbf{k}$ dependence of the tunneling transition probability with fitting parameter θ .