Pairing Symmetry Competition in Organic Superconductors

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A review is given on theoretical studies concerning the pairing symmetry in organic superconductors. In particular, we focus on (TMTSF)$_2$X and $\kappa$-(BEDT-TTF)$_2$X, in which the pairing symmetry has been extensively studied both experimentally and theoretically. Possibilities of various pairing symmetry candidates and their possible microscopic origin are discussed. Also some tests for determining the actual pairing symmetry are surveyed.

KEYWORDS: organic superconductivity, pairing symmetry, (TMTSF)$_2$X, $\kappa$-(BEDT-TTF)$_2$X, spin and charge fluctuations, Fermi surface

1. Introduction

Possible occurrence of unconventional superconductivity in organic conductors$^1$--$^3$ has been of great interest recently. Microscopically understanding the mechanism of pairing in those materials is an intriguing theoretical challenge. Among the various candidates of unconventional superconductors, in this paper we will focus on two groups of superconductors in which the pairing symmetry has been extensively studied both theoretically and experimentally, namely, (I) (TMTSF)$_2$X,$^4$ or the Bechgaard salts, where TMTSF is an abbreviation for tetramethyltetraselenafulvalene and X stands for an anion such as PF$_6$, AsF$_6$, ClO$_4$, etc., and (II) $\kappa$-(BEDT-TTF)$_2$X,$^5$, $^6$ where BEDT-TTF is an abbreviation for bisethylenedithio-tetrathiafulvalene and X= Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, Cu$_2$(CN)$_3$, I$_3$, etc. The key factors to be focused throughout the paper are the band structure and the shape of the Fermi surface, the band filling, and the wave number dependent pairing interactions mediated by spin and/or charge fluctuations and/or by phonons. Superconductivity near ordered state as in $\theta$-(BEDT-TTF)$_2$X and $\alpha$-(BEDT-TTF)$_2$X$^7$ has also been investigated extensively, but will not be discussed here.$^8$ Superconducting states induced under high magnetic fields, such as the Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state,$^9$, $^10$ are also beyond the scope of the present paper.$^11$

2. (TMTSF)$_2$X

2.1 Lattice Structure and the Phase Diagram

The lattice structure of (TMTSF)$_2$X is shown in Fig.1. The molecules are stacked along the $a$-axis (denoted as $a$ hereafter), which is the most conducting axis because the overlap of the molecular orbitals, oriented in the stacking direction, is large. The molecules are weakly dimerized along the stacks. The charge transfer with the anions existing in between the conducting stacks results in one hole per two molecules. There is a weak overlap of the orbitals in the $b$ direction, resulting in a weak two dimensionality.

A schematic phase diagram of (TMTSF)$_2$X is shown in Fig.1. At ambient pressure, (TMTSF)$_2$PF$_6$ undergoes a $2k_F$ spin density wave (SDW) transition at 12K. Upon increasing hydrostatic pressure, the SDW transition temperature decreases, and superconductivity with a transition temperature ($T_c$) of 0.9 K appears at 12 kbar.$^{12}$ A similar phase diagram is obtained for X=AsF$_6$.$^{13}$ It should be mentioned here that X-ray diffuse scattering experiments have revealed a coexistence of $2k_F$ charge density wave (CDW) in the SDW phase for X=PF$_6$.$^{14}$, $^{15}$ while the amplitude of the $2k_F$ CDW is very small for X=AsF$_6$.$^{15}$ It should also be noted that the easy axis of the SDW is in the $b'$ direction,$^{16}$, $^{17}$ which is the direction normal to the $a$-$c$ plane and somewhat tilted from $b$ due to the triclinic symmetry of the lattice.

(TMTSF)$_2$ClO$_4$ becomes superconducting at ambient pressure when the system is cooled down slowly enough for the anions to order at 24 K.$^{18}$ On the other hand, when the cooling rate is fast, the anions are frozen in random directions, and in this case, SDW takes place instead of superconductivity.$^{19}$ It has also been revealed that superconductivity is destroyed upon alloying (TMTSF)$_2$ClO$_4$ with a small amount of ReO$_4$, and with further alloying, an SDW phase appears.$^{20}$--$^{23}$
2.2 Electronic Structure

Reflecting the lattice structure and also the anisotropy of the orbitals, the band structure of (TMTSF)$_2$X is strongly one dimensional, i.e., the ratios of the hopping integrals in $a$, $b$, and $c$ directions are $t_b/t_a \sim 0.2$ and $t_c/t_b \sim 0.05$, where $t_a = 200 \sim 300$ meV. Since $t_c$ is extremely small, it is highly likely that the essential mechanism of the superconductivity lies within the two dimensional lattice ($a$-$b$ plane). A typical Fermi surface is shown in Fig.1, which is open in the $k_a$ direction due to the quasi-one-dimensionality. We stress here that the anisotropy of the hopping integrals within the $a$-$b$ plane largely owes to the fact that molecular orbitals are directed toward the $a$ direction, while the distance between the molecules in the $b$ direction is only about two times larger than that in the $a$ direction. The hopping integral $t_a$ alternates along the $a$ direction by about 10 ~20\% due to the dimerization of the molecules. If we neglect this dimerization, the system is described by a 3/4-filled single band model, whose band dispersion is given as

$$\varepsilon(k) = 2t_a \cos(k_a) + 2t_b \cos(k_b).$$

(1)

Here, only the hoppings between the nearest neighboring molecules in the $a$ and $b$ directions are considered. Lattice constants (neglecting the dimerization) are taken as the units of the length. Many of the theoretical approaches have been based on this 3/4-filled band model, but in some studies, the strong dimerization limit has been assumed, where each dimer of molecules is considered as a site, so that the band now becomes half filled.20,26 There is also a study based on a two band model that maintains the realistic dimerization structure.28

2.3 Experiments Concerning the Pairing Symmetry and Their Theoretical Interpretations

Early experiments for (TMTSF)$_2$X, such as the specific heat29,30 and the upper critical field measurements31–33 had been interpreted within the conventional $s$-wave pairing. However, Abrikosov34 pointed out the possibility of spin-triplet pairing based on the fact that $T_c$ is very sensitive to the existence of non-magnetic defects.20,21,35,36 More recently, Joo et al.22,23 have shown that the sensitivity of $T_c$ to non-magnetic impurities (ReO$_4$) in (TMTSF)$_2$ClO$_4$ is precisely what is expected from the $T_c$ reduction formula37,38 for unconventional pairing. Generally, in a superconducting state that satisfies the condition

$$\sum_k F(k, i\omega_n) = 0,$$

(2)

the presence of non-magnetic impurities is pair breaking, and thus strongly suppresses $T_c$.39 Here, $F$ is the anomalous Green’s function, and the condition (2) roughly corresponds to a vanishing summation of the superconducting gap function $\Delta(k)$ over the Fermi surface. The $T_c$ reduction in this case is given in the form.38

$$\ln \left( \frac{T_c}{T_{c0}} \right) = \psi \left( \frac{1}{2} \right) - \psi \left( \frac{1}{2} + \frac{\alpha}{2\pi T_c} \right),$$

(3)

where $\psi$ is the digamma function, $T_{c0}$ is the transition temperature without impurities, and $\alpha$ is the pair breaking parameter, which is determined by the scattering rate due to non-magnetic impurities. This is in fact the same as the formula derived by Abrikosov and Gor’kov for the case of $s$-wave pairing with magnetic impurities.37 Since a triplet superconductivity has an odd parity gap, $T_c$ should be sensitive to the introduction of non-magnetic impurities. Note, however, that the condition (2) can be satisfied for a superconducting state with an even parity gap that changes sign on the Fermi surface, so that the sensitivity to the presence of impurities alone of course does not necessarily imply triplet pairing. In this sense, the sensitivity of the $T_c$ to non-magnetic defects concerns the orbital part of the pair wave function.

Another experiment that indicated the possibility of unconventional pairing concerning the orbital part is the NMR experiment for X=ClO$_4$ performed by Takigawa et al.40 Namely, the proton spin-lattice relaxation rate $1/T_1$ at zero magnetic field exhibits no coherence peak, and follows a power law temperature dependence close to $T^3$. Such a behavior is generally characteristic to superconductivity with a gap having line nodes.39 In fact, Hasegawa and Fukuyama41 studied various types of singlet and triplet anisotropic pairings within the mean field approximation for a model with on-site and nearest neighbor attractive interactions, and calculated the spin-lattice relaxation rate. There it was shown that a singlet pairing without gap nodes on the Fermi surface exhibits a large coherence peak followed by an exponential decay of $1/T_1$, while for a triplet pairing with gap nodes at $k_a = 0$ and thereby no nodes on the Fermi surface, which will be called $p$-wave hereafter (Fig.2(c)), the coherence peak becomes smaller but still exists. Singlet and triplet pairings with line nodes of the gap intersecting the Fermi surface cannot be distinguished from the temperature dependence of $1/T_1$; they both exhibit essentially no (or very small) coherence peak and a power law decay roughly proportional to $T^3$, which is similar to the experimentally observed behavior.40 A more recent $1/T_1$ measurement has been performed on X=PF$_6$ by Lee et al.,42,43 who have found a similar behavior of $1/T_1$ when a small magnetic field $H$ is applied parallel to $b'$, but also an anomalous $1/T_1 \sim T$ at low temperatures for high magnetic fields. On the other hand, Belin and Behnia showed for X=ClO$_4$ that the thermal conductivity rapidly decreases with lowering the temperature below $T_c$, indicating the absence of low lying excitations, and thus a fully gapped superconducting state.44 A possible explanation for this discrepancy between the conclusions of the NMR and the thermal conductivity experiments will be discussed in section 2.7.

Before discussing the experimental results concerning the spin part of the pair wave function, let us briefly summarize some general aspects of spin triplet pairing.39 In the case of triplet pairing, both the diagonal and the non-diagonal elements of the superconducting order parameter matrix

$$\Delta(k) = \left( \begin{array}{ccc} \Delta_{\uparrow\uparrow}(k) & \Delta_{\uparrow\downarrow}(k) \\ \Delta_{\downarrow\uparrow}(k) & \Delta_{\downarrow\downarrow}(k) \end{array} \right),$$

(4)
remain finite in general, where $\Delta_{\sigma \sigma'}$ are given as $\Delta_{\uparrow \uparrow} = -d_x + id_y$, $\Delta_{\uparrow \downarrow} = \Delta_{\downarrow \uparrow} = d_z$, and $\Delta_{\downarrow \downarrow} = d_x + id_y$, using the vector $d = (d_x, d_y, d_z)$. The order parameter vector $d$ lies in the direction perpendicular to the total spin of the triplet pairs.

Spin-triplet superconductivity can be identified by the NMR Knight shift measurement, which probes the uniform spin susceptibility. The Knight shift decreases below $T_c$ for singlet pairing, while it stays constant for triplet pairing when the magnetic field $H$ is applied perpendicular to $d$. Another possible way of detecting triplet pairing is to measure the upper critical field $H_{c2}$. Cooper pairing under magnetic field is limited by both orbital and paramagnetic effects.\(^{45,46}\) For triplet pairing, however, the paramagnetic limit (the Pauli limit, or the Clogston-Chandrasekhar limit) is overcome when the magnetic field is applied perpendicular to $d$.

Now, as for the actual experimental results, Lee et al. found for $X$=PF$_6$ that the Knight shift does not decrease below $T_c$ for magnetic fields applied parallel to $a$\(^{42}\) (1.43T) or $b'$ (2.38T).\(^{43}\) These results indicate that the pairing indeed occurs in the spin-triplet channel, and that either $d \parallel c$, or $d$ rotates in accord with the direction of the magnetic field to satisfy $d \perp H$.

As for the upper critical field $H_{c2}$, Gor’kov and Jérôme pointed out in the early days that $H_{c2}$ extrapolated to $T = 0$ may largely exceed the Pauli limit, suggesting the possibility of spin-triplet pairing.\(^{47}\) More recently, the upper critical field has been studied with higher accuracy and with precise orientation of the magnetic fields. $H_{c2}^b$, the upper critical field for $H \parallel b'$ has been found to exceed the Pauli limit for $X$=PF$_6$\(^{48}\) and also for ClO$_4$.\(^{49}\) Even if a spin-triplet pairing occurs, the pairing can still be orbitally limited, but Lebed\(^{50}\) and later Dupuis et al.\(^{51}\) showed that a magnetic field induced dimensional crossover from three to two dimensions can strongly enhance the orbital limit of the critical field. Thus, as far as $H_{c2}^b$ is concerned, the experimental results seem to be consistent with the above interpretations of triplet pairing with $d \parallel c$, or a rotatable $d$.\(^{52}\) However, the interpretation on the temperature dependence of $H_{c2}^b$ has been controversial. For $X$=PF$_6$, there is an inversion between $H_{c2}^a$ and $H_{c2}^b$, where $H_{c2}^a > H_{c2}^b$ for small magnetic field, but $H_{c2}^a < H_{c2}^b$ for $H > 1.6$T. Moreover, $H_{c2}^a(T)$ as a function of $T$ changes from a convex to a concave curve above $H = 1.6$T. From these experiments, Lebed et al. proposed that $d_b = 0$ and $d_c \neq 0$ ($d = (d_a, d_b, d_c)$) assuming strong spin-orbit coupling, so that the pairing is Pauli-paramagnetically limited for $H \parallel a$ for $H < 1.5$ T, while the change of the curvature of $H_{c2}^a(T)$ for higher magnetic fields may be because $d$ rotates to become perpendicular to $H$, or may be due to an occurrence of the FFLO state.\(^{53}\) On the other hand, Duncan et al. argued that spin-orbit coupling should be weak since the heaviest element in (TMTSF)$_2$X is Se, so that $d$ should be able to rotate according to the direction of $H$ even for low magnetic fields.\(^{54}\) A clear understanding for the direction of $d$, provided that triplet pairing does indeed occur, requires further theoretical and experimental study.

### 2.4 Spin-fluctuation-mediated d-wave pairing

In this and the next two subsections, we discuss some mechanisms for anisotropic pairing in TMTSF salts. Since the superconducting phase lies close to the SDW phase, and a number of experiments suggest the possibility of anisotropic, unconventional pairing, it is natural to expect that the spin fluctuations mediate (or at least play an important role in) the Cooper pairing in TMTSF salts, as was pointed out by Emery.\(^{56}\) The spin-fluctuation-mediated pairing scenario has in fact been supported by several theoretical studies on the quasi-one-dimensional Hubbard model, in which the on-site repulsive interaction $U$ is considered along with the kinetic energy part considered in section 2.2. The Hamiltonian is given in standard notation as,

$$H = \sum_{<i,j>, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow},$$

where $c_{i\sigma}^\dagger$ creates an electron with spin $\sigma$ at site $i$ (i.e., the $i$-th molecule), $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$, and $t_{ij} = t_a$ and $t_{ij} = t_b$ for intrachain and interchain nearest neighbor hoppings, respectively. There, superconductivity has been studied using random phase approximation (RPA),\(^{57}\) fluctuation exchange approximation (FLEX),\(^{26}\) third order perturbation,\(^{27}\) or quantum Monte Carlo method.\(^{58}\) Here, based on RPA equations (which will be written down in a general form for later use) for the single band Hubbard model at quarter filling (quarter filling of holes, to be precise), we summarize the mechanism in which $2k_F$ spin fluctuations lead to $d$-wave like pairing. Within RPA, singlet and triplet pairing interactions are given in the form,\(^{59-61}\)

$$V^s(q) = U + V(q) + \frac{3}{2} U^2 \chi_s(q) - \frac{1}{2} (U + 2 V(q))^2 \chi_s(q)$$

$$V^t(q) = V(q) - \frac{1}{2} U^2 \chi_c(q) - \frac{1}{2} (U + 2 V(q))^2 \chi_c(q),$$

where $V(q)$ is the Fourier transform of the off-site interactions (electron interactions between nearest neighbors, etc.), which is 0 for the Hubbard model. Here, $\chi_s$ and $\chi_c$ are the spin and the charge susceptibilities, respectively, which are given as

$$\chi_s(q) = \frac{\chi_0(q)}{1 - U \chi_0(q)},$$

$$\chi_c(q) = \frac{\chi_0(q)}{1 + (U + 2 V(q)) \chi_0(q)}. \quad (6)$$

Here $\chi_0$ is the bare susceptibility given by

$$\chi_0(q) = \frac{1}{N} \sum_p \frac{f(\varepsilon(p + q)) - f(\varepsilon(p))}{\varepsilon(p) - \varepsilon(p + q)}$$

where $f(\varepsilon)$ is the Fermi distribution function. Within the weak coupling BCS theory, $T_c$ is obtained by solving the linearized gap equation,

$$\chi^\lambda \Delta^\lambda(k) = - \sum_{k'} V_{\lambda,t}(k - k') \tanh(\beta \varepsilon(k')/2) / 2 \varepsilon(k') \Delta^\lambda(k').$$

(7)
The eigenfunction $\Delta^{s,t}$ of this eigenvalue equation is the gap function. The transition temperature $T_c$ is determined as the temperature where the eigenvalue $\lambda$ reaches unity. In the summation over $k'$ in the right hand side of eq.(7), the main contribution comes from $k'$ on the Fermi surface because of the factor $\frac{\tanh(\beta \epsilon(k'))}{2\epsilon(k')}$. If we multiply both sides of eq.(7) by $\Delta^{s,t}(k)$ and take summation over the Fermi surface, we see that the quantity

$$V^{s,t}_{\text{eff}} = \frac{\sum_{k,k'} V^{s,t}(k-k')\Delta^{s,t}(k)\Delta^{s,t}(k')}{\sum_{k}(\Delta^{s,t}(k))^2}$$

has to be positive and large in order to have large $\lambda$, i.e., in order to have superconductivity with the gap $\Delta^{s,t}(k)$.

Due to the good nesting of the Fermi surface, the bare susceptibility $\chi_0(q)$ peaks at the nesting vector $q = Q_{2k_F}$, and since $U > 0$ and $V(q) = 0$, $\chi_s(q)$ becomes large at $q = Q_{2k_F}$, while $\chi_c(q)$ remains small at all $q$. Within this formulation, the SDW transition temperature is determined as the temperature where $U\chi_0(Q_{2k_F})$ reaches unity. Thus, in the vicinity of the SDW transition, the pairing interactions roughly satisfy the relation

$$V^{s,t}(Q_{2k_F}) = -3V^t(Q_{2k_F}) > 0.$$  \hspace{1cm} (9)

because the contribution from the spin fluctuations strongly dominates in eq.(5). Now, since the pairing interactions have large absolute values at $q = Q_{2k_F}$, the condition to have a positive $V_{\text{eff}}$ in eq.(8) can be approximately reduced to

$$V^{s,t}(Q_{2k_F})\Delta^{s,t}(k)\Delta^{s,t}(k+Q_{2k_F}) < 0, k, k + Q_{2k_F} \in \text{F.S.}$$ \hspace{1cm} (10)

From this condition and eq.(9), we can see that the gap function has to change sign between $k$ and $k + Q_{2k_F}$ for singlet pairing, while the sign has to be the same across the nesting vector for triplet pairing. Since the spin part of the pair wave function is antisymmetric (symmetric) with respect to the exchange of electrons for spin singlet (triplet) pairing, the orbital part of the wave function, namely the gap function, has to satisfy the condition $\Delta^s(-k) = \Delta^s(k)$ (even parity gap) and $\Delta^t(-k) = -\Delta^t(k)$ (odd parity), for singlet and triplet pairings, respectively. The gap functions satisfying these conditions are schematically shown in Fig.2(a),(b). We will call the singlet pairing “$d$-wave” in the sense that the gap changes sign as $+-+$ along the Fermi surface, while the triplet pairing will be called “$f$-wave” in the sense that the gap changes sign as $+-+$ as well. \hspace{1cm} (62)

Since the pairing interaction is three times larger for the singlet pairing, $d$-wave pairing takes place in this case. Note that a simpler form of an odd parity gap is the $p$-wave shown in Fig.2(c), which changes sign as $+-+$ along the Fermi surface. However, this gap does not satisfy the condition (10) because the triplet pairing interaction is negative for the Hubbard model at least within RPA.

Although we have adopted RPA equations in the above, similar conclusions have been drawn from other approaches as mentioned above. For example, an approach along the line of RPA, but more suitable for dealing with strong spin fluctuations, is the FLEX method.\hspace{1cm} (63)

In the FLEX, (i) Dyson’s equation is solved to obtain the renormalized Green’s function $G(k)$, where $k \equiv (k,\imath \epsilon_n)$ denotes the wave vectors and the Matsubara frequencies, (ii) the effective electron-electron interaction $V^{11}(q)$ is calculated by collecting RPA-type diagrams consisting of the renormalized Green’s function, namely, by summing up powers of the irreducible susceptibility $\chi_{\text{irr}}(q) \equiv -\frac{1}{N} \sum_{k} G(k+q) G(k)$ ($N$:number of k-point meshes), (iii) the self energy is obtained as $\Sigma(k) = \frac{1}{N} \sum_{q} G(k-q) V^{11}(q)$, which is substituted into Dyson’s equation in (i), and the self-consistent loops are repeated until convergence is attained.

To obtain $T_c$, the linearized Eliashberg equation for the singlet or the triplet gap function $\Delta^{s,t}(k)$,

$$\lambda \Delta^{s,t}(k) = -\frac{T}{N} \sum_{k'} V^{s,t}(k-k') G(k') G(-k') \Delta^{s,t}(k'),$$ \hspace{1cm} (11)

is solved, where the singlet or the triplet pairing interactions $V^{s,t}$ are given again in the RPA form but using the irreducible susceptibility obtained from the renormalized Green’s functions instead of the bare susceptibility. $T_c$ is the temperature where the eigenvalue $\lambda$ reaches unity.

Kino and Kontani applied FLEX to the half-filled Hubbard model, i.e., the model in the strong dimerization limit,\hspace{1cm} (26) where they obtained a finite $T_c$ for the $d$-wave pairing. Kuroki et al. applied FLEX to a two-band model with finite dimerization and with next nearest neighbor interchain hoppings, and also found that the $d$-wave pairing (Fig.2(d)) is the most dominant pairing, while triplet $f$-wave pairing (Fig.2(e)) is subdominant.\hspace{1cm} (28)

Another approach for the Hubbard model is the perturbational theory, where all the Feynman diagrams up to a certain order are taken into account in the calculation of the pairing interactions. Applying the third order perturbation theory to the half-filled model in the dimer limit, Nomura and Yamada obtained finite values of $T_c$.
for the $d$-wave pairing. It has been found there also that the $f$-wave pairing is subdominant.\textsuperscript{27}

As for numerical calculations for finite size systems, Kuroki and Aoki\textsuperscript{58} adopted the ground state quantum Monte Carlo (QMC) technique.\textsuperscript{64–66} This method enables us to accurately calculate correlation functions within statistical errors for finite size clusters. Since the superconducting order parameter is always zero for finite size systems, we instead calculate its fluctuation, namely, the pairing correlation function, given in the form $\langle \hat{c}_i \hat{c}^\dagger_j \rangle$, where $i, j$ denotes the sites, and $i$ and $i+\delta$ are the sites at which the Cooper pair is formed. When the tendency towards superconductivity is strong, the pairing correlation decays slowly at large distances between sites $i$ and $j$. Applying this method to the single band Hubbard model at quarter filling, it has been found that the $d$-wave pairing correlation function is enhanced at large distances by the presence of the on-site repulsion $U$.\textsuperscript{58} More recently, Kuroki et al. studied the pairing symmetry competition on the Hubbard model at quarter filling using the ground state QMC, where they found that $d$-wave and $f$-wave strongly dominate over $p$-wave.\textsuperscript{67}

Apart from the studies directly dealing with the Hubbard model, low energy theories using the interacting electron gas model like those for the purely one dimensional systems as will be mentioned in section 2.6 can be effective, but since the nodes of the $d$-wave gap run parallel to the $k_b$ axis, it is necessary to take into account the quasi-one-dimensionality (the warping of the Fermi surface) to study $d$-wave pairing in a realistic situation. Duprat and Bourbonnais indeed showed the occurrence of $d$-wave pairing near the SDW phase within a renormalization group study that takes into account the quasi one dimensionality.\textsuperscript{68}

2.5 Spin triplet $f$-wave pairing

Nevertheless, the spin-fluctuation-mediated $d$-wave pairing scenario contradicts with the experimental facts pointing towards spin-triplet pairing, especially for $X=\text{PF}_6$.\textsuperscript{12, 48} (Note that most of the $d$-wave theories appeared before the Knight shift measurements.) Kuroki et al.\textsuperscript{28} provided a possible solution for this puzzle by recalling that $2k_F$ CDW actually coexists with $2k_F$ SDW in the insulating phase for $X=\text{PF}_6$.\textsuperscript{14, 15} If $2k_F$ CDW coexists with SDW in the insulating phase, it is natural to assume that $2k_F$ spin and $2k_F$ charge fluctuations coexist in the metallic phase lying nearby. Assuming the presence of charge fluctuations along with spin fluctuations with possible magnetic anisotropy (i.e., presence of easy and hard axes), the pairing interactions are given in generic forms,

$$V^s(q) = \frac{1}{2} V^z_{sp}(q) + V^{z+}_{sp}(q) - \frac{1}{2} V_{ch}(q)$$

$$V^t_{\perp}(q) = -\frac{1}{2} V^z_{sp}(q) - \frac{1}{2} V_{ch}(q)$$

$$V^t_{\parallel}(q) = \frac{1}{2} V^z_{sp}(q) - V^{z+}_{sp}(q) - \frac{1}{2} V_{ch}(q) \quad (12)$$

where $V^z_{sp}$ and $V^{z+}_{sp}$ are the contributions from longitudinal and transverse spin fluctuations, respectively, while $V_{ch}$ is the contribution from the charge fluctuations. There are two triplet pairing interactions: $V^\perp$ for $d \perp z$ and $V^\parallel$ for $d \parallel z$. The contribution from the spin fluctuations is expected to be large in the easy axis direction of the SDW ordering. Then, taking the easy axis as the $z$-axis, we may assume $V^z_{sp}(Q_{2k_F}) \geq V^{z+}_{sp}(Q_{2k_F})$ because the longitudinal spin susceptibility should exhibit stronger divergence at $q = Q_{2k_F}$ than the transverse ones near the SDW transition. Thus, $-V^\perp(Q_{2k_F}) \geq -V^\parallel(Q_{2k_F})$ holds from eq.(12), where $-V^\parallel(Q_{2k_F})$ is always positive. Furthermore from eq.(12), we can see that

$$-V^\perp(Q_{2k_F}) \geq V^s(Q_{2k_F}) \quad (13)$$

holds when the condition,

$$V_{ch}(Q_{2k_F}) \geq V^{z+}_{sp}(Q_{2k_F}) \quad (14)$$

is satisfied. This kind of relation between the singlet and the triplet pairing interactions when spin and charge fluctuations coexist has been pointed out by Takimoto\textsuperscript{69} for another candidate for a triplet superconductor, $\text{Sr}_2\text{RuO}_4$.\textsuperscript{70}

Now, an important point for a quasi-one-dimensional system is that the number of gap nodes that intersect the Fermi surface is the same between $d$- and $f$-waves due to the disconnectivity of the Fermi surface, so that which one of these two dominates is determined solely by the magnitude of the pairing interactions. Thus, triplet $f$-wave pairing with $d$ perpendicular to the easy axis direction dominates over singlet $d$-wave when the contributions to the pairing interaction from the charge fluctuations is larger than that from the spin fluctuations in the hard axis direction.

The above argument can be summed up as a phenomenological phase diagram shown in Fig.3(a). In this phase diagram, there exists a region where $p$-wave pairing dominates because $V^\parallel(Q_{2k_F}) > 0$ holds when $V^{z+}_{sp} > 2V_{ch}$, namely, when the magnetic anisotropy is strong and the charge fluctuations are weak, so that a triplet gap that has different signs at both ends of the nesting vector can be favored. In this case, $d$ is parallel to the easy axis. This $p$-wave mechanism has in fact been proposed for $\text{Sr}_2\text{RuO}_4$.\textsuperscript{71, 72} $s$-wave pairing having the same gap sign over the entire Fermi surface is expected to dominate when the charge fluctuations are sufficiently strong because the singlet pairing interaction turns negative (which is unrealistic for $\text{TMTSF}_2\text{X}$).
An intuitive understanding for this phase diagram can be given as follows. In the $2k_F$ SDW configuration, electrons (or, actually, holes in a 3/4-filled system) with antiparallel spins sit at next nearest neighbors as shown in Fig.4(a), so if this configuration “melts” to become metallic, singlet pairing superconductivity with an even parity gap of $\Delta(k) = + \exp(i2k_a) + \exp(-i2k_a) \sim \cos(2k_a)$ is likely to occur. “2” in the argument of “exp” implies that the pairs are formed at second nearest neighbors, and the “+” signs in front of the “exp” corresponds to singlet wave functions having the same sign in the right and the left directions, as shown in Fig.4(a).

Since the gap cos($2k_a$) has even parity and has nodes at $k_a = \pm \pi/4$, this corresponds to the singlet d-wave. On the other hand, when $2k_F$ SDW and $2k_F$ CDW co-exist (namely when both SDW and CDW have a period of four lattice spacings), the electrons are aligned like in Fig.4(b), so that when this configuration melts, triplet superconductivity with an odd parity gap of $\Delta(k) = + \exp(i4k_a) - \exp(-i4k_a) \sim \sin(4k_a)$ is likely to take place. This corresponds to the f-wave gap. If we consider the magnetic anisotropy, a triplet pair formed at fourth nearest neighbors is expected to have a to-

Fig. 4. (a) $2k_F$ SDW configuration and (b) $2k_F$ SDW+$2k_F$ CDW configuration with likely pairings when the configuration “melts” to become metallic.

in the $b'$ direction, which may be an indication that the $2k_F$ spin fluctuations in the metallic state may not be so anisotropic within the $a$-$b'$ plane. The phase diagram for $z$ assuming isotropic spin fluctuations in the $a$-$b'$ plane is shown in Fig.3(b). Note that in this case, strong anisotropy in the spin fluctuations does not lead to p-wave pairing because the triplet pairing interactions always remain negative.

After this phenomenological proposal and also a similar phenomenological argument of f-wave pairing by Fuseya et al., studies based on microscopic models have followed. Tanaka and Kuroki considered a model which takes into account the off-site repulsive interactions $\sum_{<i,j>} V_{ij} n_in_j$ within the chains up to third nearest neighbors (Fig.5, but with $V_z = 0$), where the consideration of the second nearest neighbor repulsion $V'$ is the key. This has been based on a consideration that since the coexistence of $2k_F$ spin and $2k_F$ charge fluctuations is necessary for f-wave pairing, and since the coexistence $2k_F$ SDW and CDW is experimentally observed, a model that can account for this coexistence should be the right Hamiltonian to be adopted. The mechanism of the coexistence of $2k_F$ SDW and $2k_F$ CDW itself had already been proposed by Kobayashi et al. and also studied by Tomio and Suzumura, where the second nearest neighbor repulsion $V'$ plays an essential role. From Fig.4, it can be seen how $V'$ induces the $2k_F$ CDW in a quarter-filled system. When only the on-site $U$ and the nearest neighbor $V$ are present, the charges tend to take the $4k_F(= \pi)$ CDW configuration, which has a period of two sites, while when $V'$ is present, the pairs of electrons sitting at second neighbors repel each other to result in the $2k_F$ CDW(+SDW) configuration.

For the Hamiltonian that considers $U$, $V$, $V'$, and $V''$, the Fourier transform of the off-site repulsions, considered in the RPA eq.(6), is given as

$$V(q) = 2V \cos(q_z) + 2V' \cos(2q_z) + 2V'' \cos(3q_z)$$

(15)

From eqs.(5),(6), and (15), it can be seen that $\lambda^c(Q_{2k_F}) = \chi^c(Q_{2k_F})$ (where $Q_{2k_F} = (\pi/2, \pi)$), and consequently $-V'(Q_{2k_F}) = V^c(Q_{2k_F})$, apart from the first order terms such as $U + V(q)$, is satisfied when $V' = U/2$. Within the phenomenological argument, this corresponds to the condition for f-wave to be degenerate with d-wave in the absence of magnetic anisotropy.
the actual RPA calculation for $V' = U/2$, f-wave slightly dominates over d-wave due to the effect of the first order terms neglected in the phenomenological argument.\(^{75}\)

Fuseya and Suzumura\(^{81}\) approached the same problem using the renormalization group method for quasi-one-dimensional systems along the line of Duprat and Bourbonnais,\(^{88}\) where a similar conclusion has been reached. Since the pairing competition is subtle, they further proposed a possible singlet d-wave to triplet f-wave transition in the presence of magnetic field.

According to the above studies, f-wave dominates over d-wave when the second nearest neighbor repulsion $V'$ is equal to or larger than half the on-site repulsion $U$, which may be difficult to realize in actual materials. Nickel \textit{et al.} have proposed a possible solution for this difficulty, where they considered, in addition to the intrachain repulsions, the interchain repulsion and used the renormalization group technique for quasi-one-dimensional systems to reach a conclusion that f-wave dominates over d-wave in a more realistic parameter regime with a smaller second nearest neighbor repulsion.\(^{4,82}\) Independently, Kuroki and Tanaka also considered a model that considers the nearest neighbor interchain repulsion $V_{\perp}$ as shown in Fig.5.\(^{83}\) Within RPA, the term $2V_{\perp} \cos(q_y)$ is added in the right hand side of eq.(15), so that the condition for $\lambda_{el}(Q_{2k_F}) = \lambda_{el}(Q_{2k_F})$ now becomes $V' + V_{\perp} = U/2$. This is a much more realistic condition than $V' = U/2$ because the interchain distance is similar to the interchain second nearest neighbor distance, so that we can expect $V_{\perp}$ to be as large as $V'$. The actual calculation shows that f-wave dominates (has a larger eigenvalue $\lambda$) over d-wave for a parameter set, e.g., $U = 1.7$, $V = 0.8$, $V' = 0.45$, $V'' = 0.2$, $V_{\perp} = 0.4$, $t_b = 0.2$ in units of $t_0$(Fig.5), where the relative magnitude of the interactions can be considered as realistic.

### 2.6 Other Mechanisms for Triplet Pairing: Phonons, Ring Exchange

In this subsection, we discuss some other mechanisms for spin-triplet pairing proposed for (TMTSF)$_2$X. From the early days, possibility of spin-triplet superconductivity in (TMTSF)$_2$X has been discussed in terms of the low energy effective theory called the g-ology approach for the purely one dimensional interacting electron gas, i.e., the Tomonaga-Luttinger model.\(^{84}\) In the g-ology phase diagram, the spin-triplet superconducting phase and the SDW phase share boundary,\(^{85}\) so that it is tempting to relate this superconducting state with that of (TMTSF)$_2$X, as was discussed in some studies.\(^{86}\) More recently, this phase boundary between the SDW and the triplet superconductivity has been discussed as having SO(4) symmetry.\(^{87,88}\) Nevertheless, since exact numerical studies on the purely one-dimensional extended Hubbard model, where the on-site $U$ and the nearest neighbor $V$ is considered,\(^{89}\) show that superconductivity does not occur in a realistic parameter regime when the interactions are all repulsive, it is likely that some kind of attractive interaction, most probably originating from electron-phonon interaction, should be necessary in order to realize the triplet superconducting state in the g-ology phase diagram, as discussed in some studies.\(^{90,91}\)

Apart from the g-ology-type approach, there have been studies on the phonon mechanism of triplet pairing. Kohmoto and Sato proposed a p-wave pairing mechanism due to a combination of electron-phonon interaction, $2k_F$ spin fluctuations, and the disconnected Fermi surface.\(^{92}\) Assuming that the electron-phonon interaction is weakly screened, a long-ranged attractive interaction arises in real space, which means that the pairing interaction becomes large and negative around $q \sim 0$ in momentum space. If we denote this interaction as $-V_{el-ph}(q)$, and if the spin fluctuations also contribute to the pairing to some extent, the pairing interactions are given as

$$
V_{s}(q) = -V_{el-ph}(q) + \frac{1}{2}V_{sp}^{zz}(q) + V_{sp}^{+-}(q)
$$

$$
V_{t\perp}(q) = -V_{el-ph}(q) - \frac{1}{2}V_{sp}^{zz}(q)
$$

$$
V_{t\parallel}(q) = -V_{el-ph}(q) + \frac{1}{2}V_{sp}^{zz}(q) - V_{sp}^{+-}(q).
$$

In ref.\(^{92}\), the competition between s- and p-wave pairings was discussed, while the possibility of d- and f-wave was not considered because the warping of the Fermi surface was neglected. Let us first neglect the magnetic anisotropy, i.e., $V^{zz} = V^{+\prime \prime}$. Around $q \sim 0$, neglecting the spin fluctuation contribution, the pairing interaction is negative and has the same magnitude between singlet and triplet pairings. Thus, s- and p-wave pairings, whose gap does not change sign on each portion of the disconnected Fermi surface, are equally favored by this interaction around $q \sim 0$. At $q = Q_{2k_F}$ on the other hand, neglecting the electron-phonon interaction this time, the positive spin fluctuation contribution for the singlet pairing works destructively against s-wave because the gap does not change sign across $Q_{2k_F}$, while the negative contribution for the triplet channel also works against p-wave, whose gap changes sign. Since this destructive spin fluctuation contribution is smaller for triplet pairing, p-wave dominates over s-wave. Note that here again, the close competition between p-wave and s-wave arises from the disconnectivity of the Fermi surface owing to the (quasi) one dimensionality, i.e., the additional node in the p-wave gap as compared to the s-wave does not intersect the Fermi surface.

If we further take into account the magnetic anisotropy and assume $V^{zz} < V^{-\prime \prime}$ by taking the hard axis (c-axis) in the z direction, the negative spin fluctuation contribution in the triplet pairing interaction is smaller (and thus favorable for p-wave pairing) for $d \perp z$ than for $d \parallel z$. Therefore, if the direction of $d$ for p-wave pairing is governed by the magnetic anisotropy of the SDW, $d$ is likely to be perpendicular to the hard axis direction, namely, in the a-b plane for (TMTSF)$_2$PF$_6$.

Suginishi and Shimahara also proposed a phonon-mediated mechanism for p-wave pairing.\(^{93}\) By considering moderately screened phonons and also including the corrections due to charge fluctuations, they obtained an attractive pairing interaction that has a large magnitude around $q \sim 0$ and a small one around $q \sim Q_{2k_F}$. By further considering the Coulomb pseudo potential, which suppresses only the s-wave pairing, it has been found
there that p-wave pairing dominates in a certain parameter regime.

Recently, Ohta et al. proposed a non-electron-phonon mechanism for spin-triplet pairing.\textsuperscript{94} The mechanism is based on the fact that in a triangle lattice consisting of three sites with two electrons, a ferromagnetic interaction arises by considering a competitive exchange of the positions of the electrons.\textsuperscript{95} If ferromagnetic spin fluctuations arise due to this “ring exchange mechanism” on a certain lattice, triplet pairing superconductivity may take place. They considered the Hubbard model on a one-dimensional “railway-trestle” (or zigzag) lattice, where they used the density matrix renormalization group method to find that triplet pairing correlation functions decay more slowly than the singlet ones. Their numerical calculation has been restricted to purely one dimensional systems so far, but they further propose that this mechanism may be applicable to the quasi-one-dimensional material \((\text{TM}	ext{TSF})_{2}X\) since the signs of the intrachain and interchain hopping integrals (by considering also the next nearest neighbor interchain hopping)\textsuperscript{24, 25} satisfy the condition for the ferromagnetic interaction.\textsuperscript{95}

In all the mechanisms discussed in this subsection, at least one of the \(2k_F\) fluctuations, spin or charge, are not taken into account, although they should both be present at least for \(X=\text{PF}_6\). Then, whether both of these fluctuations play essential roles or not in the occurrence of superconductivity is the key toward clarifying whether \(f\)-wave discussed in section 2.5 or other triplet pairings dominate, provided that the pairing indeed occurs in the triplet channel.

2.7 Tests for the Pairing Symmetry Candidates

In this section, we discuss some experimental tests (already existing ones as well as proposals for future study) for the candidates for the pairing symmetry discussed above. For the pairing symmetries whose gap has line nodes on the Fermi surface such as \(d\)-wave and \(f\)-wave, the spin-lattice relation rate \(1/T_1\) exhibits essentially no (or very small) coherence peak and a power law decay \(\sim 1/T\) at low temperatures as well as a small peak below \(T_c\). For \(X=\text{ClO}_4\)\textsuperscript{40} and for \(X=\text{PF}_6\)\textsuperscript{43} at low magnetic fields. On the other hand, whether these pairings can account for the peculiar behavior of \(1/T_1\) observed for \(X=\text{PF}_6\) at high magnetic field, i.e., \(1/T_1 \sim T\) at low temperatures as well as a small peak below \(T_c\) for \(H \parallel a\),\textsuperscript{42, 43} remains open as an interesting future study.

At first glance, only \(p\)-wave and \(s\)-wave pairings seem to be consistent with the thermal conductivity measurement for \(X=\text{ClO}_4\) suggesting a fully gapped state.\textsuperscript{44} However, Shimahara has argued that a fully gapped state is possible even for \(d\)-wave pairing particularly in \((\text{TM}	ext{TSF})_2\text{ClO}_4\), because in this case, anion ordering takes place above the superconducting \(T_c\), so that a “gap” opens up on the Fermi surface at positions \((k_a = \pm \pi/4)\) where the nodes of the superconducting gap would otherwise intersect (see Fig.2(a)).\textsuperscript{97} Exactly the same argument holds for \(f\)-wave pairing since the positions of the gap nodes on the Fermi surface are the same between \(f\) and \(d\). A fully gapped state usually results in a coherence peak followed by an exponential decay in \(1/T_1\) as mentioned in section 2.3,\textsuperscript{41} which seems to be in contradiction with refs.\textsuperscript{40} and \textsuperscript{43} but since \(1/T_1\) can be affected by the presence of impurities,\textsuperscript{98} vortices,\textsuperscript{99} or correlation effects,\textsuperscript{100} the clarification of the relation between \(1/T_1\) and the thermal conductivity experiments is open for future study.

From the microscopic view discussed in the preceding sections, \(f\)-wave and \(p\)-wave are the main candidates for spin triplet pairing.\textsuperscript{42, 43, 48} As for the direction of \(d\), if we assume that the spin fluctuations in the \(c\) direction are weak while those in the \(a\)-\(b\) planes have similar magnitude, \(d\) of \(f\)-wave pairing should lie in the \(c\) direction as discussed in section 2.5, which is consistent with the Knight shift results.\textsuperscript{42, 48} If we assume on the other hand that the spin fluctuations are solely strong in the \(b\) direction compared to those in the \(a\)-\(c\) plane, then \(f\)-wave’s \(d\) is perpendicular to \(b\) and lies in the \(a\)-\(c\) plane as also discussed in section 2.5, which is more closer to the \(d\) direction proposed by Lebed et al.\textsuperscript{53} from the temperature dependence of \(H_{2a}^c\) and \(H_{2c}\).\textsuperscript{48} In the case of \(p\)-wave pairing, if the anisotropic spin fluctuations contribute to the pairing interaction in the form given in eqs.(16) \((\Delta_{\text{el-ph}}\neq \text{due to phonons})\), \(d\) is likely to lie in the \(a\)-\(b\) plane. Thus, it may be possible to distinguish \(f\) and \(p\) from the direction of \(d\), provided that the anisotropic spin fluctuations play a role in the Cooper pairing. Such a test, however, has to be done in the absence of, or under low, magnetic field since \(d\) may rotate regardless of the pairing symmetry if the magnetic field is sufficiently large to overcome the effect of the magnetic anisotropy.

Although there exist few experiments up to date, possibility of determining the pairing symmetry from tunneling spectroscopy measurements has been proposed theoretically by several groups. Sengupta et al. pointed out that the presence/absence of zero energy peak in the tunneling conductance can be used to distinguish various types of pairings in (TMIF)\(_2\)X.\textsuperscript{101} In fact, the zero energy peak in the tunneling spectroscopies of anisotropic superconductors (those with sign change in the gap) originates from the zero-energy Andreev bound state caused by the sign change of the pair potential felt by the quasiparticle in the reflection process at the surface,\textsuperscript{102, 103} and has turned out to be a powerful method for probing the pairing symmetry in anisotropic superconductors such as the high \(T_c\) cuprates.\textsuperscript{104} In the case of tunneling parallel to \(a\) in particular, the zero energy peak does not exist for \(d\)-wave. This is because the injected and the reflected quasiparticles feel the same gap due to \(\Delta_d(k_a, k_b) = \Delta_d(−k_a, k_b)\) (see Fig.2(b)). By contrast, the zero energy peak does exist for \(p\)-wave and \(f\)-wave, where \(\Delta_{f, p}(k_a, k_b) = −\Delta_{f, p}(− k_a, k_b)\) is satisfied (Fig.2(c)). Tamma et al. further pointed out that \(p\)-wave and \(f\)-wave can be distinguished from the overall shape of the surface density of states (overall structure of the tunneling spectrum) because \(p\)-wave is a fully gapped state, which results in a U-shaped surface density of states around the Fermi level, while \(f\)-wave results in a V-shaped one.\textsuperscript{105} Therefore, the combination of the absence/presence of the zero energy peak and the overall shape of the spectrum enables us to distinguish \(p\), \(d\), and
Further theoretical studies based on various shapes of the Fermi surface have been performed.\textsuperscript{106,107} Tamuna et al. showed that when the Fermi surface is warped in a certain manner, the zero energy peak can appear even in the case of $d$-wave. In this case, $d$ and $f$-wave can be distinguished by the way the zero energy peak splits in the presence of a magnetic field.\textsuperscript{106} Such studies show that the existence of the zero energy peak is sensitive to the shape of the Fermi surface (compare Fig.2(a) and (d), or (b) and (c)). Since the hopping integrals, and thus the Fermi surface, of (TMTSF)$_2$X depend on the pressure, the temperature, and the anions,\textsuperscript{24,25,108} it is necessary to strictly pin down the actual shape of the Fermi surface at the temperature and the pressure at which superconductivity takes place in order to distinguish the pairing symmetry from the presence/absence of the zero energy peak.

The tunneling tests above mainly concern the orbital part of the pairing. On the other hand, Bolech and Gamarchi proposed a tunneling experiment to distinguish directly the spin part of the pairing.\textsuperscript{109} They showed that the $I$-$V$ characteristics of a normal metal-triplet superconductor junction are unaffected by an application of magnetic field perpendicular to $d$, while the Zeeman effect affects the $I$-$V$ characteristics when $d \parallel H$ similarly to the case of normal metal-singlet superconductor junction. Therefore, the spin part of the pairing, whether it is singlet or triplet and also the direction of $d$ if triplet, can be determined by measuring the $I$-$V$ characteristics of the junction under a rotating magnetic field, provided that $d$ does not rotate according to the direction of the magnetic field. Vaccarella et al. also proposed a way of directly probing the spin part of the triplet pairing. Namely, they showed that the Josephson effect between two triplet superconductors is very sensitive to the direction of $d$ across the junction, and proposed that this sensitivity can be used as a test for triplet superconductivity.\textsuperscript{110}

As a final remark in this subsection, it is important to recognize that the pairing symmetry might be different for different anions. This possibility is suggested especially from the viewpoint discussed in section 2.5. For instance, the amplitude of $2k_F$ charge fluctuations, which has to be large for $f$-wave to dominate over $d$-wave, is found to be small for $X=$AsF$_6$, so that $f$-wave has less chance of dominating over $d$-wave than in the case of $X=$PF$_6$. Thus, the pairing symmetry of a TMTSF superconductor with a certain anion should be determined by a combination of multiple experiments on the salt with that very anion. Furthermore, we must keep in mind that the pairing symmetry might even change for the same salt under different environment, such as the pressure and the strength of the magnetic field, because several pairing symmetries may be closely competing. In particular, as mentioned in section 2.5, singlet to triplet transition may take place under high magnetic field since the singlet pairing is Pauli-paramagnetically limited.\textsuperscript{81,111,112}

Fig. 6. (a) The lattice structure of $\kappa$-(BEDT-TTF)$_2$X in the $b$-$c$ plane. $b_1$, $b_2$, \ldots represent the hopping integrals in the four band model. (b) The lattice structure of the dimer model. (c) Phase diagram of $\kappa$-(BEDT-TTF)$_2$X.\textsuperscript{5} (d) Band structure and the Fermi surface of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$. (Reprinted with permission from ref.119. Copyright 1988 by the American Physical Society.)

3. $\kappa$-(BEDT-TTF)$_2$X

3.1 Lattice Structure and the Phase Diagram

The lattice structure of $\kappa$-(BEDT-TTF)$_2$X is shown in Fig.6(a), which consists of dimers formed by a pair of face-to-face molecules. $b$- and $c$-axis are taken as in Fig.6, while the BEDT-TTF layers and the anion layers alternate along the $a$-axis. Relatively large overlap of the orbitals between the dimers exists (see section 3.2) while the overlap between the BEDT-TTF layers is very small, resulting in a strong two dimensionality.

In Fig.6(c), the generic phase diagram of $\kappa$-(BEDT-TTF)$_2$X is shown, which has been extensively studied by Kanoda et al.\textsuperscript{5} The superconducting and the antiferromagnetic insulating phases share a first order phase boundary. Recently, this boundary has been revealed to persist above the superconducting $T_c$ and the Néel temperature into the boundary of the paramagnetic insulating and the metallic phases, ending up at a certain critical point,\textsuperscript{113,114} where an anomalous criticality has been found recently.\textsuperscript{115} The horizontal axis in the phase diagram can be considered as hydrostatic or chemical pressure, where superconductivity with $T_c$ exceeding 10K occurs at ambient pressure for $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$\textsuperscript{116} and $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, while $\kappa$-(BEDTTTF)$_2$Cu[N(CN)$_2$]Cl is an antiferromagnetic insulator below 26K at ambient pressure\textsuperscript{117} and becomes superconducting with $T_c = 12.8$K under an applied pressure of 0.3kbar.\textsuperscript{118}
Fig. 7. (a) The $d_{x^2-y^2}$-wave gap in the original Brillouin zone and in the unfolded one (right). Note that although the gap changes sign at the Brillouin zone edge ($k_z = \pm \pi$), the nodes of the gap are not located there; the gap jumps from a positive to a negative value, as can be seen more clearly in the unfolded Brillouin zone. (b) The $d_{xy}$-wave gap. Here, we show the case when the two portions of the Fermi surface splits due to the lack of center-of-inversion symmetry. In this case, the $d_{xy}$ gap nodes do not intersect the Fermi surface, although the gap does become small near the Brillouin zone edge. On the other hand, if the two portions stick, the $d_{xy}$ nodes intersect the Fermi surface at the Brillouin zone edge. The solid (dashed) curves represent the portions of the Fermi surface where the gap has a positive (negative) sign. $Q$ represents the wave vector of the spin fluctuation mode that favors each pairing symmetry. The short arrows denote the positions of the gap nodes.

3.2 Electronic structure

The values of the intermolecular hopping integrals shown in Fig.6(a) have been estimated using the extended Hückel method,\textsuperscript{119,120} which is summarized in Table I. The hopping integral in the $b$-direction alternates as $t_{b1}, t_{b2}, t_{b3}, \ldots$, where $|t_{b1}| > |t_{b2}|$ because of the dimerization of the molecules. In Fig.6(d), the band structure of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$\textsuperscript{119} is shown. Four bands exist near the Fermi level because there are four BEDT-TTF molecules per unit cell. Due to the dimerization, a gap opens up between the bonding and the antibonding bands. There is one hole per dimer, so that the lower two bands, corresponding to adopting a single dimer as a unit cell, are gapped. The temperature dependence of the penetration depth also exists for $X=Cu[N(CN)$_2]$Br, where the existence of nodes in the superconducting gap, also, in a thermal conductivity measurement for $X=Cu(NCS)$_2, a $T$-linear term has been found at low temperatures, suggesting the existence of nodes in the gap.\textsuperscript{126}

On the other hand, there has been much controversy concerning the measurements of other quantities. The magnetic penetration depth has been measured using techniques such as muon spin relaxation,\textsuperscript{127,128} ac susceptibility,\textsuperscript{129,130} surface impedance,\textsuperscript{131,132} and dc magnetization.\textsuperscript{133,134} The penetration depth should exhibit an exponentially decaying behavior for a fully gapped state, while a power-law dependence is expected at low temperatures for gaps with nodes. Some studies have found for $X=Cu(NCS)$_2 that the temperature dependence of the penetration depth is consistent with a conventional full gap state,\textsuperscript{127,131,133} while others have found results consistent with a gap with nodes.\textsuperscript{128,129,132,135} Similar controversy on the penetration depth also exists for $X=Cu[N(CN)$_2]$Br, where the presence of gap nodes\textsuperscript{128,130,135} as well as the absence of them\textsuperscript{131,133,134} has been suggested.

The temperature dependence of the specific heat has also been another issue of controversy. Nakazawa and Kanoda found for $X=Cu[N(CN)$_2]$Br a $T^2$ dependence of the electronic specific heat,\textsuperscript{136} which was taken as an indication for the presence of nodes in the gap. However, more recent results for $X=Cu[N(CN)$_2]$Br\textsuperscript{137} and for $X=Cu(NCS)$_2\textsuperscript{138} have shown exponentially activated temperature dependence, indicating a fully gapped superconducting state.

The above experiments do not give direct information on the position of, if any, the nodes in the gap function. Several groups have in fact made attempts to directly determine the node positions. A millimeter-wave transmission experiment suggested a gap function which has nodes in the direction shown in Fig.7(a).\textsuperscript{139} If we unfold the Brillouin zone (right panel of Fig.7(a)), which corresponds to adopting a single dimer as a unit cell, (this is possible when $t_c = t'_c$), this gap function has

Table I. Hopping integrals estimated in ref.120. In units of $10^{-2}$eV.

| Anion                  | $b_1$  | $b_2$  | $p$  | $p'$ | $q$  | $q'$ |
|------------------------|--------|--------|------|------|------|------|
| $Cu[CN]_3$             | 22.36  | 11.54  | 8.01 | –    | –    | –    |
| $Cu(NCS)_2$            | 22.95  | 11.31  | 9.85 | 10.09| –    | –    |
| $Cu(NCN)_2$Br          | 24.37  | 9.16   | 10.14| –    | –    | –    |

\[ t_{b}/t_{c} \sim 0.7 \] for $X=Cu(NCN)$_2$Br. The system further reduces to a half-filled single band model when $t_c = t'_c$. 3.3 Experimental Results Concerning the Pairing Symmetry

Here, we summarize the experimental results concerning the pairing symmetry.\textsuperscript{9} In the NMR experiments for $\kappa$-(BEDT-TTF)$_2$Cu(NCN)$_2$Br, the $^{13}$C Knight shift has been found to decrease below $T_c$,\textsuperscript{123,124} which is consistent with singlet pairing. Also, the $^{13}$C spin-lattice relaxation rate $1/T_1$ for $\kappa$-(BEDT-TTF)$_2$Cu(NCN)$_2$Br exhibits no coherence peak, and a power law decay proportional to $T^3$ is seen below $T_c$,\textsuperscript{123,125} As in the case of (TMTSF)$_2$X, this is consistent with the presence of line nodes in the superconducting gap. Also, in a thermal conductivity measurement for $X=Cu(NCS)$_2, a $T$-linear term has been found at low temperatures, suggesting the existence of nodes in the gap.\textsuperscript{126}
nodes in the diagonal direction like the gap in the high $T_c$ cuprates.\cite{39,104} In this sense, we will refer to this pairing symmetry as $d_{x^2-y^2}$-like pairing hereafter. (Note that this terminology is the opposite to the one adopted in ref.140. Namely, we define the $x$ and $y$ axes by rotating $b$ and $c$ axes by 45 degrees.) However, different interpretations on this experiment have been proposed afterwards.\cite{141,142} On the other hand, Arai et al. showed for $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ using in-plane STM measurement that the gap is the largest in the $b$ and $c$ directions.\cite{143} This is more consistent with the gap function shown in Fig.7(b), which has nodes in between the $k_b$ and $k_c$ directions. Izawa et al. measured the thermal conductivity of $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ under a magnetic field rotating in the $b$-$c$ plane, where an oscillation again consistent with the gap in Fig.7(b) was observed.\cite{144} This conclusion is based on theoretical studies\cite{145} showing that the density of states of a superconducting state having gap nodes in some direction becomes large (small) when the magnetic field is applied in the antinodal (nodal) direction due to the Doppler shift of the quasiparticle energy spectrum.\cite{146} Since the gap in Fig.7(b) has nodes in the vertical and horizontal directions in the unfolded Brillouin zone, we will call this gap $d_{xy}$-like hereafter.

3.4 Phonon Mechanisms

If the symmetry is $s$-wave, the pairing is most likely due to electron-phonon interactions. Here we give a brief survey on the electron-phonon-interaction mechanism proposed for $\kappa$-(BEDT-TTF)$_2$X. Yamaji argued that intramolecular phonons (molecular vibrations) should play an important role in the occurrence of superconductivity in organic materials. The theory in which the coupling between the electrons and the molecular vibrations is taken into account was applied to $\beta$-(BEDT-TTF)$_2$I$_3$\cite{147} and to $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$,\cite{1} where $T_c$ for $s$-wave superconductivity was estimated.

Girlando et al.\cite{148} considered the coupling between the electrons and both the intramolecular and the intermolecular phonons (lattice vibrations), and estimated the $s$-wave $T_c$ for $\kappa$-(BEDT-TTF)$_2$I$_3$ and $\beta$-(BEDT-TTF)$_2$I$_3$ using the Allen-Dynes formula.\cite{149} They concluded that the contributions of both phonons are important in understanding the experimental values of the $T_c$.

On the other hand, Varelogiannis considered the phonons with small $q$ due to weak screening,\cite{150} similar to those discussed in section 2.6 for TMTSF salts. Adopting the single band dimer model, the BCS gap equation was solved by assuming the phonon-mediated attractive interaction in the form $\propto -1/(q^2 + q^2)$, where $q$ is a momentum cutoff parameter, and also taking into account the Coulomb pseudopotential. There, it has been found that a close competition between an anisotropic $s$-wave and $d_{x^2-y^2}$-wave pairings takes place.

3.5 Studies on the dimer model

If the superconducting gap in $\kappa$-(BEDT-TTF)$_2$X indeed has nodes, the most probable scenario is that electron correlation plays an important role in the pairing. In this and the next subsection, we discuss electronic mechanisms of superconductivity having gap with nodes.

Following the study by Kino and Fukuyama, who showed that the insulating state in $\kappa$-(BEDT-TTF)$_2$X can be understood as a Mott insulator of the half-filled dimer model in which the on-site repulsion $U$ (which corresponds to the effective repulsion within the dimer) is considered.\cite{5,122} Various theoretical studies concerning the superconductivity have been performed for the dimer model with on-site $U$ on the two band\cite{151} (for $t_e \neq t'_e$) or the single band (for $t_e = t'_e$) lattice\cite{58,152,153} with $t_b/t_e = 0.6 \sim 0.8$. In these studies, the $d_{x^2-y^2}$-wave has been found to be the most dominant pairing. Namely, in RPA or FLEX studies,\cite{151–155} the spin susceptibility is found to have a peak at the nesting vector $Q$ (near $(\pi, \pi)$ in the unfolded Brillouin zone, see Fig.7(a)) that bridges the open portions of the Fermi surface, although the nesting is not so good. Then, in order to have opposite signs of the gap across $Q$, and also to satisfy the even parity condition for spin-singlet pairing, the $d_{x^2-y^2}$ gap is favored. Within the FLEX studies, $T_c$ has been estimated to be $O(10K)$,\cite{152,153} consistent with the experiments. By using the third order perturbation theory, Jujo et al. showed that $d_{x^2-y^2}$-wave pairing dominates but with $T_c$ lower than those obtained in FLEX.\cite{156} They concluded that the vertex corrections that are not taken into account in FLEX have an effect of suppressing the $T_c$ especially for systems on frustrated lattices, at least up to third order. As for numerical approaches for finite size systems, Kuroki and Aoki applied the ground state QMC technique and showed that the $d_{x^2-y^2}$-wave pairing correlation function is enhanced at large distances accompanied by a development of the spin correlation near $q = (\pi, \pi)$.\cite{58} Quite recently, Liu et al. used the variational Monte Carlo technique, where $d_{x^2-y^2}$-wave superconducting order parameter is found to be enhanced in a certain range of $U/t$.\cite{157}

There have also been some strong coupling approaches along the line of Anderson’s resonating valence bond (RVB) theory for the high $T_c$ cuprates,\cite{158} in which large $U/t$ is assumed. In the large $U/t$ limit, the Hubbard model on a square lattice is transformed into the $t$-$J$ model which consists of the nearest neighbor antiferromagnetic superexchange term (the magnitude of the superexchange being $J = 4t^2/U$, where $t$ is the nearest neighbor hopping) and the hopping term in the space that prohibits double occupancy of electrons at a single site. At exactly half filling, the hopping term vanishes, so that the model reduces to the antiferromagnetic Heisenberg model, which describes the experimental situation for the cuprates to be an antiferromagnetic Mott insulator when carriers are not doped, i.e., for the half-filled band.\cite{159} However, in $\kappa$-(BEDT-TTF)$_2$X, a difference from the cuprates lies in that the band filling (of the dimer model) remains at half filling even when metallized or superconducting upon increasing the (chemical) pressure. In this context, Baskaran pointed out the possibility of “self-doping” of carriers at half filling, where an equal number ($N_0$) of doubly occupied sites and empty sites hop in the background of singly occupied sites, which is shown to be equivalent to the usual $t$-$J$ model with $2N_0$...
holes. On the other hand, Powell and McKenzie studied a model that contains the nearest neighbor (which will be denoted as $J_c$ here) and the next nearest neighbor ($J_b$) superexchange terms in addition to the Hubbard model. In this model, the double occupancy of a site is not prohibited, so that the hopping term does not vanish at half filling, thereby circumventing the difficulty in the usual $t$-$J$ model, which is always unstable at half filling. Assuming the parameter values $J_c/t_c = 1/3$ and $J_b/J_c = (t_b/t_c)^2 < 1$, a first order transition from $d_{x^2-y^2}$ wave superconductivity to a Mott insulating state was shown to occur upon increasing $U$ within the Hartree-Fock-Gor’kov approximation.

3.6 Studies for the Hubbard model on the original four band lattice

The $d_{x^2-y^2}$ pairing in the dimer model for $t_b/t_c < 1$ nevertheless contradicts at least with the experimental observation of $d_{xy}$-like gap for X=Cu(NCS)$_2$ in the thermal conductivity and STM experiments. Motivated by this discrepancy between the theories and the experiments, Kuroki et al. performed a FLEX study on the original four band lattice (Fig.6(a)), where they adopted the hopping integral values obtained from extended Hückel calculation for X=Cu(NCS)$_2$ given in Table I. It can be seen from these hopping integral values that the ratio between the intradimer hopping ($t_{b1}$) and the largest interdimer ones ($t_{b2}$) is about 2, which may not be considered as so large.

From the temperature dependence of the eigenvalues of the linearized Eliashberg equation for the two types of pairing shown in Fig.8(a), they concluded that $d_{xy}$-like pairing dominates over $d_{x^2-y^2}$. The origin of this result can be found in the spin structure. Namely, the spin susceptibility $\chi_s$ shown in Fig.8(b) peaks around $Q \sim (\pm 0.4\pi, \pm 0.6\pi)$, which is a consequence of a partial nesting between the open and the closed portions of the Fermi surface (Fig.7(b)). As a result, the gap function changes sign between the two portions of the Fermi surface, but does not change sign within each portion.

When the dimerization is strong, the four band model approaches the single band model, so that the nesting shown in Fig.7(a) dominates and $d_{xy}$-like pairing gives way to $d_{x^2-y^2}$ when $t_{b1}$ is large. In fact, further four band analysis has shown that whether $d_{xy}$ or $d_{x^2-y^2}$ dominates depends on (a) the strength of the dimerization, (b) whether $t_b/t_c=[-t_{b2}/(-t_p+t_q)]$ is close to unity (which is a measure for how close the system is to an isotropic triangular lattice in the strong dimerization limit), and (c) the magnitude of the Fermi surface splitting due to $t_c \neq t'_c$ (i.e., $t_p \neq t'_p$, $t_q \neq t'_q$). Namely, $d_{xy}$ is more favored when the dimerization is weaker, $t_b/t_c$ is closer to unity (closer to isotropic triangular lattice), and the Fermi surface splitting is larger. These factors strongly depend on the anions. For X=Cu[N(CN)$_2$]Br, the dimerization is stronger ($t_{b1}/t_{b2} \sim 2.7$ as compared to $\sim 2.0$ for Cu(NCS)$_2$), $t_b/t_c \sim 0.7$ is away from unity (compared to $\sim 0.8$ for Cu(NCS)$_2$, see Table I), and there is no Fermi surface splitting because $t_c = t'_c$. In this case, $d_{x^2-y^2}$-wave is expected to dominate over $d_{xy}$ at least within the FLEX approach.

Although the results of the four band approach seem to be consistent with the $d_{xy}$-wave pairing observed in the thermal conductivity and the STM experiments for $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$, there remains an issue concerning the $T_c$. Namely, $\kappa$-Ti exceeding 10K for X=Cu(NCS)$_2$ is almost the highest among charge-transfer-type organic superconductors. On the other hand, the eigenvalue $\lambda$ in Fig.8 remains small in the temperature range studied in the FLEX study. Although the low temperature regime was not studied in ref.140 due to the restriction of the calculation, it is questionable whether the eigenvalue actually reaches unity at around $T \sim 0.004t_{b1}$, which corresponds to the actual $T_c \sim 10K$.

The eigenvalue becomes larger in the presence of Fermi surface splitting (which was not considered in ref.140) because the nodes of the $d_{xy}$ gap do not intersect the Fermi surface, but the $T_c$ problem still exists even in that case. In fact, Kondo and Moriya have studied the four band model using FLEX, and showed that a realistic $T_c$ can be obtained only when the dimerization is extremely strong ($l_{b1}/l_{b2} > 5$). Such a strong dimerization indeed contradicts with the extended Hückel or the first principles calculations, and also leads to the $d_{x^2-y^2}$-wave pairing, which is not in agreement at least with the thermal conductivity and the STM experiments for X=Cu(NCS)$_2$.

This problem may be due to one (or more) of the following possibilities. (i) The FLEX approximation is not sufficient for quantitative estimation of $T_c$ particularly for the $\kappa$-type BEDT-TTF salts because the nesting of the Fermi surface is not good, so that a strong development of a single spin fluctuation mode, which is necessary to verify RPA-like approaches, is absent especially when the dimerization is not so strong. Note that the spin fluctuations tend to be weak when the dimerization is weak because the band becomes more closer to 3/4 filling, where the effect of the on-site repulsion $U$ is weaker than for half filling. (ii) In the limit of weak dimerization, the band is 3/4-filled and thus far away from half filling. In systems away from half filling, terms neglected in the FLEX approximation, such as the vertex corrections, may play an important role. (iii) The Hubbard model is oversimplified, and additional terms such as the off-site (inter-molecular) repulsions and/or...
electron-phonon interactions are necessary. Note that a phonon-mediated attractive interaction that gives large contribution around \( q \sim 0 \) as considered in section 3.4 is likely to enhance all types of pairings, so that a consideration of electron-phonon interaction together with the spin fluctuations might result in a superconductivity with appropriate \( T_c \), maintaining the dominant gap symmetry obtained by applying FLEX to the purely repulsive model.

Whether the above (i)–(iii) actually provides solution to this \( T_c \) puzzle remains open for future study,\(^{168} \) but some hints have been found in the recent theoretical studies on \( \beta'-(\text{BEDT-TTF})_2\text{ICl}_2 \).\(^{7,171,172} \) A superconductor which has been found under high pressure by Taniguchi et al.\(^{169} \) \( \beta'-(\text{BEDT-TTF})_2\text{ICl}_2 \) also has dimerization of molecules, and the \( T_c (\sim 14 \text{ K}) \) is the highest among the charge-transfer type molecular solids and somewhat close to the \( T_c \) of the \( \kappa \)-type salts, so that the comparison between the two types is intriguing. Using the hopping integral values obtained from the first principles calculation by Miyazaki and Kino,\(^{170} \) Kino et al. performed a FLEX study on the single band dimer model, and obtained a phase diagram in the pressure-temperature space, which is similar to the experimental phase diagram including the values of \( T_c \), although the superconducting phase is shifted to a somewhat higher pressure regime.\(^{171} \) The superconducting gap in this case has a \( d_{xy} \)-like structure, reflecting the good nesting of the Fermi surface. Later, Nakano and Kuroki\(^{172} \) performed a FLEX study on the two-band lattice with finite dimerization. This was motivated by the fact that the ratio between the intradimer hopping integral and the largest interdimer one was estimated to be about \( \sim 2 \),\(^{170} \) which is a situation similar to the case of \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \),\(^{120} \) so that adopting the dimer model might be questionable. Nevertheless, the gap structure, \( T_c \), and the phase diagram obtained in the two-band approach is found to be quite similar to the one obtained in the dimer model approach.\(^{172} \) This suggests that the possibility (ii) mentioned above is not, or at least not always, the case. The fact that the Fermi surface of \( \beta'-(\text{BEDT-TTF})_2\text{ICl}_2 \) is well nested may have some relevance to the point (i) mentioned above, as pointed out in ref.\(^{172} \).

### 3.7 Tests for the Pairing Symmetry Candidates

Here we survey some theoretical proposals for further experimental tests on the pairing symmetry.\(^{173} \) Powell and McKenzie\(^{174} \) showed that the \( T_c \) dependence on the level of structural disorder\(^{175,176} \) can be explained by assuming \( d \)-wave pairing and using the formula (3). Since the same applies to \( s \)-wave pairing in the presence of magnetic impurities, and there is indeed a possibility that disorder leads to a formation of local magnetic moments due to the proximity to antiferromagnetism, the two possibilities (\( d+ \)-non-magnetic defects or \( s+ \)-magnetic ones) cannot be distinguished within these experiments alone. They further proposed probing the presence/absence of magnetic impurities by, e.g., a \( \mu \)SR experiment.

Li showed that \( d_{xy}, d_{x^2-y^2}, \) and \( s \)-wave superconducting states all exhibit different spin structures, so that they can be distinguished by looking at the spin susceptibility below \( T_c \).\(^{177} \) Namely, for \( s \)-wave, a full gap opens on the Fermi surface so that the spin susceptibility is strongly suppressed. As for the pairings with gap nodes, since \( d_{xy} \) and \( d_{x^2-y^2} \)-wave pairings open up a gap at different portions of the Fermi surface, different types of nesting take place (as mentioned in section 3.6, two types of nesting are possible for the Fermi surface of the \( \kappa \) salts), resulting in a different spin structure.

Tanuma et al. proposed a magnetotunneling spectroscopy for determining the pairing symmetry.\(^{178} \) Namely, as mentioned in section 3.3, the density of states of a superconductor having nodes in the gap oscillates by rotating the direction of the magnetic field.\(^{145} \) This oscillation can be detected by looking at the surface density of states in the tunneling spectroscopy. The phase of the oscillation is different between \( d_{xy} \) and \( d_{x^2-y^2} \) pairings, so that the pairing symmetry can be determined as in the case of the thermal conductivity measurement.\(^{144} \)

As in the case of TMTSF salts, it is worth mentioning that the pairing symmetry need not be the same for different anions since here again, the competition among the pairing symmetries may be close. As mentioned in section 3.6, the competition between \( d_{xy} \) and \( d_{x^2-y^2} \) can be affected by various factors, such as the splitting of the Fermi surface and the strength of the dimerization, which depend on the anions. Speaking of anion dependence, it is also important to notice that \( d_{xy} \)-wave pairing in \( \kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2 \) may look like \( s \)-wave pairing from those experiments that detect only the amplitude of the gap because the nodes of the gap do not intersect the Fermi surface due to the splitting of the Fermi surface (see Fig.7(b)) just like \( d \)-wave and \( f \)-wave in the anion ordered \( (\text{TMTSF})_2\text{ClO}_4 \).

### 4. Concluding Remarks

In this paper, a review has been given on the theoretical studies concerning the pairing symmetry competition in \( (\text{TMTSF})_2\text{X} \) and \( \kappa-(\text{BEDT-TTF})_2\text{X} \). Some of the pairing symmetry candidates and their possible microscopic origins have been discussed. Existing experimental results concerning the pairing symmetry as well as some proposals for further tests have also been surveyed. Close competition among different pairing symmetries makes the problem of theoretically pinning down the symmetry difficult, and at the same time, very intriguing. One of the origin of this close competition is the peculiarity of the Fermi surface, i.e., disconnected Fermi surfaces in both \( (\text{TMTSF})_2\text{X} \) and \( \kappa-(\text{BEDT-TTF})_2\text{X} \) (although in different senses), and two types of nesting in \( \kappa-(\text{BEDT-TTF})_2\text{X} \). This also implies that several pairing symmetries can be closely competing in the actual materials, so that the symmetry might be different for different anions, or even for the same anion under different environment (magnetic field, pressure, etc.). Although a lot has been understood concerning the superconductivity in these materials, further theoretical and experimental studies are required for a more clear understanding of the nature of the superconducting state.
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