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A new triangular system: Na_xCoO_2

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Abstract

This is a review of the newly discovered triangular system, Na_xCoO_2. If water molecules are intercalated to this system, it shows superconductivity. Its electron density is more-than-half-filling in the Co t_{2g} band, so this material is considered to be an electron-doped system. The present situation of experiments on superconductivity as well as magnetism is reviewed. From a theoretical point of view, the results of a local density approximation (LDA) band calculation and the obtained Fermi surfaces are discussed. With regards to possible mechanisms of superconductivity, recent results in a multi-band model are summarized with an emphasis on the effects of trigonal crystal-field splitting and spin–orbit coupling. Finally, alternative mechanisms using a single-band model are also reviewed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Frustration is an interesting and important problem and it has been extensively discussed in spin systems. The resonating-valence-bond (RVB) state, which is a spin-liquid state with singlet bonds, was originally proposed for the Heisenberg model on a triangular lattice where the frustration is expected to destroy the long-range magnetic order, leading to a quantum spin liquid [1, 2]. On the other hand, the effects of frustration in itinerant electron systems have not been so well understood [3]. Just after the discovery of high-T_c superconductors, Anderson proposed that carrier doping to such a spin-liquid RVB state gives directly an unconventional superconductivity [4]. However, the high-T_c superconductors are realized in a square lattice without frustration. Thus Na_xCoO_2 has attracted much interest since it is a doped triangular lattice system, in which Co atoms form layered triangular lattices. Furthermore, superconductivity with $T_c \sim 5$ K was discovered by intercalating water molecules [5]. In this material, the CoO_6 octahedra are tilted, as shown in figure 1, with [111]-directions being aligned in the c-axis. In this way, the edge-shared CoO_6 octahedra form CoO_2 planes with a perfect triangular lattice of Co ions. This is in sharp contrast to high-T_c cuprates or ruthenates, Sr_2RuO_4, in which square lattices of Cu or Ru ions are realized.

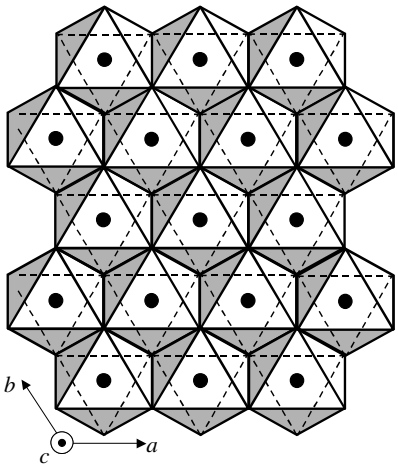

Figure 1. CoO_2 layer seen along the c-axis: the solid circles represent Co ions. The octahedra around each Co ion are tilted and form a perfect triangular lattice. O atoms are located on each corner of the octahedra. There is a trigonal compression along the c-axis.

Let us first consider the valence of Co ions in Na_xCoO_2. Although the material with $x = 0$ does not exist, the Co becomes Co^{4+} in this case. This corresponds to the $(3d)^5$ configuration. Due to the crystal-field splitting, there is one hole in the t_{2g}-orbitals leading to the case of half-filling. Thus the $x = 0$ compound, if realized, becomes a triangular spin-1/2 system. In the other limit of $x = 1$, which is also unavailable, the Co becomes Co^{3+}, corresponding to the filled t_{2g}-orbitals. Therefore, Na_xCoO_2 with $0 < x < 1$ is a system where some electrons are doped into the half-filling. This situation is confirmed in the local density approximation (LDA) band calculations [6].

Various experiments on this compound have clarified characteristic behaviours of strongly correlated electron systems [7–13]. Its magnetic property has been intensively studied since we recognize that its understanding is essential for elucidating the pairing mechanisms. The phase diagram as a function of x has been proposed [11, 14]. At $x = 0.5$, the material shows two phase transitions. One is at around $T = 90$ K, at which a magnetic order is formed, as found in μSR and neutron experiments [14]. Then at around $T = 55$ K, metal–insulator transition occurs, which is considered as a charge-ordering [15–18]. Furthermore, Na ordering at various values of x has been pointed out [19, 15]. In the low-x region ($x < 0.5$), the material shows Fermi-liquid-like behaviour. On the other hand, when $x > 0.6$ [14], the susceptibility shows a Curie–Weiss temperature dependence, and it is called as 'Curie–Weiss metal' [11]. The existence of some magnetic phase [20–25] in the range $x \sim 0.75$–0.82 also indicates the importance of the electron correlation. It has been confirmed that the magnetic structure is an A-type antiferromagnetism: ferromagnetic long-range order is formed in the CoO_2 planes and it alternates layer by layer [26–28]. This is rather surprising since the system will be described as a small number of holes doped in the fully occupied t_{2g} band. These magnetic states have not been well understood theoretically.

These circumstantial evidences indicate that the superconductivity in this system is an unconventional one induced by electron correlation.

2. Superconductivity

Superconductivity occurs when the water molecules, H_2O, are intercalated to this compound [5]. This intercalation enhances the two-dimensionality of the system. Since H_2O

is a neutral molecule, the Co valence should not change. However, recent chemical analysis shows that oxonium ions, H_3O^+, are simultaneously intercalated during the hydration [29, 30]. In this case, we have to take care of the change of the Co valence. The actual compound should be represented by $Na_x(H_3O)_zCoO_2{\cdot}yH_2O$, and the Co valence is $Co^{(4-x-z)+}$ [30]. Titration analysis shows that the Co valence in the composition which shows superconductivity is around 3.40–3.50, for example. This means that the electron number is in the right-half of the phase diagram or close to $x = 0.5$, i.e., 3/4-filling.

Another effect of the water intercalation will be to smooth the random Na potential by screening. This is actually observed in nuclear magnetic resonance (NMR) line distributions [31]. The other effect is the enhancement of the trigonal distortion of the CoO_6 octahedra, which we discuss later [32–35]. Actually the water intercalation increases the c-axis lattice constant drastically and, as a result, the thickness of the CoO_2 layer becomes slightly smaller.

Immediately after the discovery of superconductivity, the symmetry of the superconducting order parameter was studied by means of many experimental measurements. While some controversial results exist with respect to impurity effects [36], many experimental evidences for the unconventional superconductivity have been reported by NMR and nuclear quadrupole resonance (NQR) experiments, as well as specific heat measurements. For example, the absence of a coherence peak in NMR $1/T_1T$ [37–40], and the power-law behaviours in $1/T_1T$ [38–41] and specific heat measurements [42–44] support the anisotropic pairing. Recently, a magnetic phase has been discovered in the neighbourhood of the superconducting phase [30, 32, 33]. This observation clearly indicates the importance of electron correlation which generally leads to the non-s-wave superconductivity.

When the magnetic field is applied along the plane, the Knight shift decreases below T_c [45, 46]. This means singlet pairing or triplet pairing whose d-vector is fixed in the ab-plane occurs. With regard to the Knight shift in the magnetic field parallel to the c-axis, there has been some controversy between experiments. Quite recently, it was reported that the c-axis Knight shift decreases below T_c [47, 48], although another group claimed a constant Knight shift [49]. Complete understanding of the NMR results requires detailed theoretical studies on the direction of the d-vector by considering the effects of spin–orbit interaction and magnetic fields.

The symmetry of the Cooper pair is classified into s-, p-, d-wave, etc, in case of an isotropic system like ^{3}He. For metals, the Cooper pairing is classified into the finite species according to the symmetry of the crystal [50]. We denote 's-wave', 'd-wave', etc, in analogy with the isotropic case. While the s-, d-, and i-waves are spin-singlet pairings, the p- and f-waves are spin triplets. Note that there remains two-fold degeneracy in the p- and d-wave states, namely p_x- and p_y-waves, and d_{xy}- and $d_{x^2-y^2}$-waves, respectively. Time-reversal symmetry breaking is expected below T_c in the d-wave state, i.e., the $d_{x^2-y^2} + id_{xy}$ state, as discussed in the RVB mean-field theory [51–54] and confirmed by variational Monte Carlo simulation [55]. Since no time-reversal symmetry breaking was observed in the μSR experiment [56], this $d_{x^2-y^2} + id_{xy}$ state is not consistent with experiments so far. On the contrary, the time-reversal symmetry is not necessarily broken in the p-wave case because there is an internal degree of freedom representing the direction of $S = 1$ Cooper pairs. We discuss the possible pairings later.

3. Fermi surfaces and LDA bands

One of the interesting properties of the Na_xCoO_2 system is its orbital degeneracy. The conduction band of this material mainly consists of three Co t_{2g}-orbitals which hybridize with O 2p-orbitals, as shown by LDA calculations [6, 57–61]. First we deduced the tight-binding

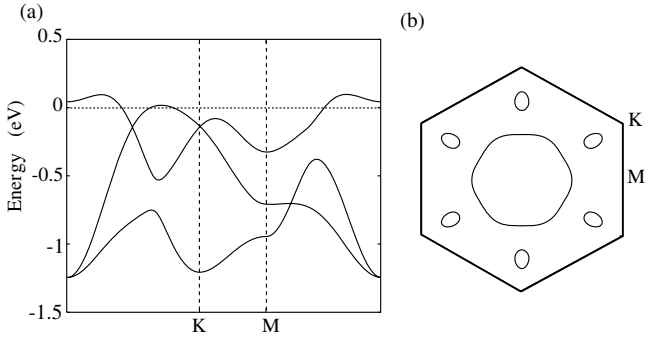

Figure 2. Tight-binding fitting of the LDA band calculation [62]. (a) Dispersion relations and (b) Fermi surface. The central hole pocket around the Γ point is composed of the a_{1g}-orbitals, and the six hole pockets near K points are from the e'_g-orbitals.

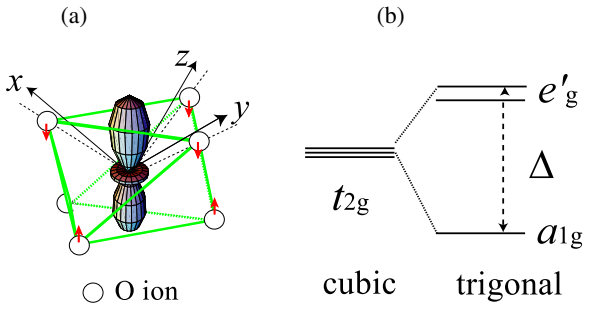

Figure 3. (a) Trigonal distortion of CoO_6 octahedron and a_{1g}-orbital. Arrows indicate the shift of O ions. (b) a_{1g}–e'_g level splitting of t_{2g} degeneracy due to the trigonal crystal field.

parameters which reproduce the LDA band dispersions [62]. The tight-binding fitting obtained is shown in figure 2(a). For this purpose, we find that up to the third-nearest-neighbour hoppings between Co orbitals are necessary. Then the LDA results are well reproduced, particularly near the Fermi level.

In figure 2(b), we show the corresponding Fermi surface. As shown in this figure, the Fermi surfaces consist of a large cylindrical one around the Γ point and six hole pockets near the K points. The central one mainly consists of the a_{1g}-orbital, while the six hole pockets near the K points are from the e'_g-orbitals. Here a non-degenerate a_{1g}-orbital and doubly degenerate e'_g-orbitals are defined from the three t_{2g}-orbitals as

$$|a_{1g}\rangle = \frac{1}{\sqrt{3}}(|xy\rangle + |xz\rangle + |yz\rangle), \tag{1}$$

$$|e'_g, 1\rangle = \frac{1}{\sqrt{2}}(|xz\rangle - |yz\rangle), \tag{2}$$

$$|e'_g, 2\rangle = \frac{1}{\sqrt{6}}(2|xy\rangle - |xz\rangle - |yz\rangle). \tag{3}$$

The wavefunction of the a_{1g}-orbital spreads along the c-axis (see figure 3(a)), and those of the e'_g-orbitals spread along the two-dimensional plane.

In $Na_xCoO_2{\cdot}yH_2O$, the CoO_6 octahedra are contracted along the c-axis, as shown in figure 3(a). The ligand oxygens with this distortion generate a trigonal crystal field on the

Co sites. This crystal field lifts the local Co t_{2g} degeneracy into lower a_{1g} and higher doublet e'_g levels with an energy splitting of Δ (figure 3(b)), whose importance will be discussed shortly.

Note that recent ARPES measurements for non-superconducting Na_xCoO_2 [63–67] observed the central a_{1g} Fermi surface, but did not find the e'_g Fermi surface. This can be due to a surface effect or some matrix elements [68]. Recently Yada and Kontani [71] discussed that the weak pseudogap behaviours [72] in the density of states and in the uniform susceptibility can be explained if the six hole pockets are absent. In the following, however, we discuss the mechanisms of superconductivity including possible effects from the six hole pockets [62, 73].

4. Theoretical studies in multi-band model and its superconductivity

4.1. Multi-band model

We analysed a multi-orbital Hubbard model constructed from the tight-binding fitting of figure 2 by using the fluctuation–exchange (FLEX) approximation [62]. This model consists of the three Co t_{2g}-orbitals and includes the intra-orbital, inter-orbital interactions, Hund's rule coupling, and pair hopping term in the standard way. The value of U has been estimated as 3–5.5 eV by photoemission spectroscopy [69] and as ∼3.7 eV by an *ab initio* calculation [70].

In the FLEX approximation, random-phase-approximation-type bubble diagrams and ladder diagrams are taken into account. By determining self-consistently the renormalized Green's function and fluctuation–exchange self-energy, the effects of mode–mode coupling between charge and spin fluctuations and quasiparticle lifetime due to damping are incorporated [62]. We also adopted a perturbative method, which gives similar results [73].

The results obtained are summarized as follows [62, 73].

(i) The e'_g-Fermi surface of the six hole pockets plays a substantial role for superconductivity. If we assume that the e'_g-Fermi surface does not exist, the pairing instability is suppressed and thus the realization of superconductivity with $T_c \sim 5$ K is difficult.
(ii) The spin-triplet p-wave and f-wave superconductivity, mainly realized on the e'_g-Fermi surface, are stable. Both are nearly degenerate.
(iii) A nearly ferromagnetic spin fluctuation along the plane in the e'_g-Fermi surface stabilizes the triplet pairing. This is enhanced by the inter-orbital Hund's rule coupling. The nearly ferromagnetic spin fluctuation was also pointed out in LDA calculations [6, 57], as well as by Kuroki *et al* [74, 75] and by Yada *et al* [76]. This spin fluctuation is consistent with the neutron scattering measurements which reported an A-type antiferromagnetism [26–28]. It has also been claimed by Co-NQR experiments in some groups [39, 40, 32, 33].
(iv) The e'_g-Fermi surface has a relatively large density of states due to the van Hove singularity near the Fermi level [6, 62]. This enhances the superconducting instability.
(v) The disconnectivity of the Fermi surface plays another important role. As discussed before the discovery of $Na_xCoO_2{\cdot}yH_2O$ [77, 78], this kind of disconnectivity favours superconductivity by avoiding the disadvantage from nodes on the Fermi surface.

Let us briefly discuss the superconducting properties of p- and f-wave states. As for the p-wave state, the p_x and p_y states are degenerate in the triangular geometry. In addition to this, there are three choices of the direction of the d-vector $(\hat{x}, \hat{y}, \hat{z})$, representing the S_z component of the $S = 1$ Cooper pairs. Below T_c, linear combinations of these six states should be realized, namely,

$$p_x\hat{x} \pm p_y\hat{y}, \qquad p_x\hat{y} \pm p_y\hat{x}, \qquad (p_x \pm ip_y)\hat{z}. \tag{4}$$

The superconducting gap is $\sqrt{\Delta_x(k)^2 + \Delta_y(k)^2}$, where $\Delta_x(k)$ and $\Delta_y(k)$ are the order parameters for p_x and p_y states, respectively. In this case, the superconducting gap does not

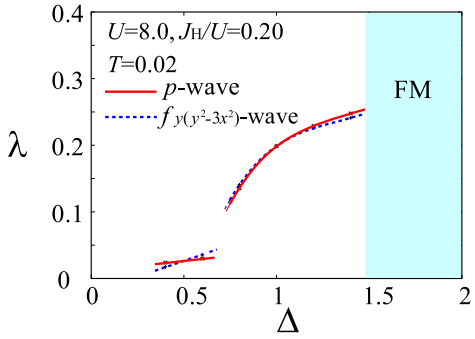

Figure 4. Eigenvalues of the Eliashberg equation, λ, for f-wave and p-wave pairings at $U = 8.0$, $J_H/U = 0.20$, and $T = 0.02$ as functions of the trigonal field splitting, Δ [34]. Although λ does not reach unity, its behaviour indicates the superconducting instability in the low temperatures. FM in the large-Δ region represents the instability to ferromagnetism.

vanish even on the a_{1g}-Fermi surface. However, we find a remarkable anisotropy of gap on the a_{1g}-Fermi surface which can explain the power-law behaviours of NMR $1/T_1T$ and so on, like in the case of Sr_2RuO_4 [79]. We note that this is an accidental result.

When the Hund's rule coupling is small, f-wave superconductivity with six-times alternation of the sign of $\Delta(k)$ is most stable. In this case, the e'_g-Fermi surface is nodeless, while the a_{1g}-Fermi surface has line nodes. The susceptibility along the plane decreases to half of its value in the normal state.

4.2. Crystal-field splitting

Quite recently, NQR measurements showed that there is a correlation between the magnetic fluctuation and NQR frequency ν_Q arising from the $\pm 5/2 \leftrightarrow \pm 7/2$ transition [32, 41]. A higher-ν_Q sample has a stronger magnetic fluctuation and a higher superconducting transition temperature T_c, suggesting a spin-fluctuation-mediated pairing. In addition, a non-superconducting order (probably magnetic) was found in a sample with the highest ν_Q [32]. Similar phase diagrams have also been proposed by other groups [80, 81]. This means that both magnetic fluctuation and T_c correlate with the distortion of the CoO_6 octahedra along the c-axis, because ν_Q is considered to scale with the CoO_6 distortion from the cubic symmetry. Such a relationship between T_c and the c-axis parameter was also pointed out by several groups [82, 83, 41].

This result can be explained if we consider the CoO_6 distortion and e'_g-Fermi surface [34]. As we noted above, when the CoO_6 distortion along the c-axis increases, the trigonal crystal field, Δ, increases. As a result, the a_{1g}–e'_g splitting becomes larger and the e'_g-level is pushed up. Then the hole pockets near the K points appear and become larger. We studied the superconducting instability by changing the crystal-field splitting, Δ, as a parameter. As shown in figure 4, we find that the nearly ferromagnetic spin fluctuation becomes stronger and the pairing instability in $Na_xCoO_2{\cdot}yH_2O$ is enhanced when Δ is increased [34]. When this spin fluctuation become much stronger, a magnetic instability occurs, which is consistent with NQR experiments [30, 32, 33]. Recently we have extended this calculation to explain the experimentally observed phase diagram which has two superconducting phases and a magnetic state [84].

4.3. Spin–orbit coupling

Another interesting subject in the multi-orbital superconductor is the role of spin–orbit coupling. This is particularly important in the spin-triplet superconductivity with an internal

degrees of freedom of the d-vector, which determines the magnetic properties such as Knight shift. If we neglect the spin–orbit coupling, the six-fold (three-fold) degeneracy remains in the p-wave (f-wave) state at $T = T_c$. We investigated the d-vector by including the spin–orbit coupling within the e'_g-orbitals [85]. The coupling constant 2λ has been estimated as 57 meV [86]. We find that the $p_x\hat{y} \pm p_y\hat{x}$ state is most stable among the three states in equation (4). This means that the d-vector is strongly fixed along the plane. On the other hand, the effect of the spin–orbit coupling is very small for the f-wave case, so that the d-vector can be rotated by a weak magnetic field.

The NMR Knight shift along the plane will decrease in the p-wave case, because the d-vector has both x and y components. On the other hand, the Knight shift will be almost temperature independent in the f-wave case in all directions of the applied magnetic field. As discussed in section 2, the Knight shift along the plane decreases below T_c [45, 46], which is consistent with the p-wave state. However, if the c-axis Knight shift decreases below T_c [47, 48], it will not be explained in the triplet superconductivity.

The search for the multiple phase transition under the magnetic field is another interesting problem. We have determined the phase diagram under a magnetic field applied parallel to the plane and found a phase transition accompanied by a rotation of the d-vector [87]. We find that the p-wave and p + f-wave coexistent state have a multiple phase, while the f-wave state does not.

5. Other possibilities

Although it can be due to surface effects, ARPES experiments [63–67] have not observed the evidence of the e'_g-Fermi surface which is the most important ingredient in the above theories. If the e'_g-Fermi surface is absent, we have to consider a single-band model. The t–J model calculation on the triangular lattice predicts the $d_{x^2-y^2} \pm id_{xy}$ state [51–55]. Then the absence of time-reversal symmetry breaking will be an issue to be resolved. The local distortion of the triangular lattice or the feedback effect will be a candidate of the resolution. More recently, another type of a_{1g}-Fermi surface with double cylinders around the Γ point has been proposed. In this case, extended s-wave superconductivity is realized [88, 84].

Some authors have pointed out the charge fluctuation near the possible charge ordering at the electron filling $n = 4/3$ [89–91]. In this case, f-wave superconductivity due to the charge fluctuation will be realized [92, 93], although more elaborate Monte Carlo calculation shows that the superconductivity appears only when there is a strong frustration or competition between a few kinds of charge ordering [94]. There have been several kinds of experiments which show the tendency of charge order at various electron fillings [16–18, 95–98].

The observed impurity effect seems to support s-wave pairing [36], but very short quasiparticle lifetime or significant anisotropy in the gap function has to be assumed for the absence of the coherence peak in $1/T_1T$. Actually, Yada and Kontani discussed the possible s-wave superconductivity by using breathing and shear phonons [99]. We consider that further vigorous investigations are highly desired for the identification of the pairing state in $Na_xCoO_2{\cdot}H_2O$.

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