Superconductivity in Na$_x$CoO$_2 \cdot y$H$_2$O by charge fluctuation

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A new mechanism for superconductivity in the newly discovered Co-based oxide is proposed by using charge fluctuation. A single-band extended Hubbard model on the triangular lattice is studied within the random phase approximation. $f$-wave triplet superconductivity is stabilized in the vicinity of charge-density-wave instability, which is in sharp contrast with the square-lattice case. The physical origin of the realization of the $f$-wave triplet state as well as the relevance to experiments are discussed.

KEYWORDS: Co-based oxides, charge fluctuation, triplet superconductivity

Recently discovered superconductivity in Na$_x$CoO$_2 \cdot y$H$_2$O$^{1-2}$ has attracted great interest since it is realized in a frustrating system. Compared with high-$T_c$ cuprates and Ru-based superconductivity, Sr$_2$RuO$_4$, Co oxides have various unique and interesting properties. Firstly this is the first Co-based oxide superconductivity. Secondly Co atoms form two-dimensional triangular lattice, which is in sharp contrast with the high-$T_c$ cuprates or Sr$_2$RuO$_4$. Thirdly there are three bands close to the Fermi surface. Recent intensive experiments have shown that the superconductivity is unconventional$^{3-6}$ and the material has strong correlation.$^{7,8}$

Superconductivity in the systems with frustration is a very interesting subject. Originally the resonating valence bond (RVB) idea by Anderson was proposed in the frustrating triangular Heisenberg spin system.$^9$ This concept was developed to the idea of RVB superconductivity which is expected to be realized in the doped Heisenberg system like high-$T_c$ superconductivity.$^{10}$ Since the high-$T_c$ cuprates are based on the square lattice without frustration, superconducting materials in frustrating systems have been long desired. The new superconductor, Na$_x$CoO$_2 \cdot y$H$_2$O, is in this sense an ideal material which has a perfect triangular lattice of Co atoms. Basically frustration destroys the long-range order like antiferromagnetism and induces large fluctuations. There is a potential possibility that there appears high-$T_c$ superconductivity using these large fluctuations.

One candidate in the Co oxides is spin fluctuation, which has been discussed using $t$-$J$ models on the triangular lattice.$^{11-15}$ Another candidate is charge fluctuation which is realized in the extended Hubbard model. They contain new physics induced by frustration. In the present paper, we focus on the latter possibility in Na$_x$CoO$_2 \cdot y$H$_2$O system.

Let us first discuss the effects of multi-orbitals.$^{16,17}$ In the case of Sr$_2$RuO$_4$, the three orbitals ($d_{xy}$, $d_{yz}$ and $d_{zx}$) do not mix so much. On the contrary, in the present material, Na$_x$CoO$_2$, the three orbitals mix relatively strongly and three bands are formed near the Fermi energy. However it has been pointed out that the main band centered around the Γ point ($k = (0, 0)$) is made out of the symmetric combination of the orbitals, i.e., $a_{2g}$-orbital, or $1/2(d_{xy} + d_{yz} + d_{zx})$.$^{16}$ Thus, in the present paper, we use a single band effective Hamiltonian as a first approximation.

The $t$-$J$ model on the triangular lattice has been extensively studied by various groups.$^{11-15}$ However every mean-field-type theory has concluded that the most probable RVB superconductivity has $d_{x^2-y^2}+id_{xy}$-wave symmetry. This state has been confirmed by high-temperature expansion studies.$^{18}$ However, recent µSR experiment$^{19}$ has shown that no evidence for the broken time-reversal-symmetry is found, which contradicts with the prediction in the $t$-$J$ model. Alternatively it has been proposed that charge ordering is realized near the electron density $n = 1 + 1/3$ and $n = 1 + 2/3$ (more-than-half-filling).$^{20}$ It is apparent that the 1/3- or 2/3-filling is a special filling for the triangular lattice. Motrunich and Lee$^{21}$ have discussed a strongly correlated electron system just next to the charge ordering.

Having these in mind, we discuss superconductivity due to charge fluctuation in the vicinity of charge density wave (CDW). We use a single-band extended Hubbard model on the triangular lattice which is given by

$$H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_{i\uparrow} n_{j\downarrow} , \quad (1)$$

where $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ denote electron creation and annihilation operators respectively and $\langle ij \rangle$ represents the summation over the nearest neighbor pairs. $\varepsilon_k$ is the dispersion relation of the triangular lattice, namely

$$\varepsilon_k = -2t(\cos k_y + 2 \cos \frac{\sqrt{3}}{2} k_x \cos \frac{\sqrt{3}}{2} k_y) - \mu .$$

In this extended Hubbard model, we expect a CDW state when $V$ is very large and $U > V$. For the intermediate $V$, superconductivity is predicted in the vicinity of the CDW instability.$^{22-24}$ Since previous theories only discussed the square or cubic lattice, it is necessary to study the case of triangular lattice. Surprisingly we find that the triplet $f$-wave state is stabilized, instead of $d_{xy}$-wave obtained in the square lattice.

The LDA calculation$^{16}$ showed that there is a large hole-like Fermi surface around the Γ point so that the effective hopping integral is $t < 0$. For the Co oxides, the electron density $n$ is more than unity ($n$ is around
In the following, we use a convention with $t > 0$ and $n < 1$, which is equivalent to the case with $t < 0$ and $n > 1$ by electron-hole transformation, $c_k \rightarrow e^{i k}$. The “hole-doped case” in the present paper corresponds to the Co oxides. We also study the “electron-doped case” for comparison.

To study the effective interaction between electrons arising from charge and spin fluctuations, we use random phase approximation (RPA). In RPA, the effective pairing potentials for the singlet and triplet channels are

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

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

where $V(q) = 2 V(\cos q_y + 2 \cos \frac{\sqrt{2}}{4} q_x \cos \frac{\sqrt{2}}{4} q_y)$ and $\omega_l$ is the Matsubara frequency. $\chi_s$ and $\chi_c$ are spin and charge susceptibilities, respectively. These quantities are calculated within RPA as follows,

$$\chi_s(q, \omega_l) = \chi_0(q, \omega_l) / \left[ 1 - U \chi_0(q, \omega_l) \right],$$

$$\chi_c(q, \omega_l) = \chi_0(q, \omega_l) / \left[ 1 + \left\{ U + 2 V(q) \right\} \chi_0(q, \omega_l) \right].$$

Here $\chi_0$ is the bare susceptibility given by

$$\chi_0(q, \omega_l) = \frac{1}{N} \sum_p \frac{f(\epsilon_p + q) - f(\epsilon_p)}{\omega_l - (\epsilon_p + q - \epsilon_p)}.$$

Note that the terms proportional to $\chi_c$ in eqs. (2) and (3) represent effective pairing potentials due to charge fluctuation. This charge fluctuation contributes equally to $V^s$ and $V^t$ since it comes from charge degrees of freedom.

Figure 1 shows the momentum dependences of the spin and charge susceptibilities at $T = 0.01$. In the following we use $t$ as a unit of energy and $k_B = 1$. We calculate both hole-doped ($n < 1$) and electron-doped ($n > 1$) cases, since there is no particle-hole symmetry in the triangular lattice. Let us discuss the hole-doped case with $n = 0.8$ (Fig. 1(a)), which corresponds to the Co oxides. When $V = 0$ (i.e., $(U, V) = (3.64, 0)$), the spin fluctuation is much larger than the charge fluctuation, whereas there is no particle-hole symmetry in the system because the system is close to the spin density wave (SDW) instability. $\chi_s$ has a peak at $Q = \left( 0, \frac{\pi}{2} \right) \equiv \text{(K-point)}$ due to the nesting condition of the system. On the other hand, when $V \neq 0$, i.e., $(U, V) = (3.21, 1.2)$, $\chi_c$ has a peak at $q = Q$ where $V(q)$ has its maximum value. This shows that $V$ induces the charge density wave (CDW) instability for large-$V$.

For the electron-doped case ($n = 1.2$), in contrast, the peak in $\chi_s$ for $V = 0$ moves away from $Q$ as shown in Fig. 1(b). Near the CDW instability, i.e., $(U, V) = (2.0, 1.06)$, on the other hand, $\chi_c$ becomes large at $q = Q$. Apparently the peaks of $\chi_s$ and $\chi_c$ are located at different positions from each other in contrast to the hole-doped case where both spin and charge fluctuations become large near $q = Q$.

Next, we calculate the pairing potentials, $V^s$ and $V^t$, as shown in Fig. 2. For $V = 0$, the momentum dependence of $V^s$ is similar to that of $\chi_c$ in both hole- and electron-doped cases because contributions from $\chi_s$ are negligible. $V^t$ has the same property as $V^s$ although the sign is opposite and the magnitude is smaller than $V^s$. Near the CDW instability ($V \neq 0$), on the contrary, both $V^s$ and $V^t$ show a negative (i.e., attractive) peak at $q = Q$. Note that constant shift in $V^s$ or $V^t$ does not affect anisotropic superconductivity. In the region away from $Q$, $V^s$ remains positive due to the contribution from the spin fluctuation, whereas $V^t$ is negative for almost all region because both spin and charge fluctuations lead to the attractive interaction as shown in eq. (3).

To obtain the onset of the superconducting state, we solve the linearized Eliashberg’s equation within the weak-coupling theory:

$$\lambda \Delta(k) = -\sum_{k'} V^{s(t)}(k - k', 0) \frac{\tanh(\beta \xi_{k'}/2)}{2 \xi_{k'}} \Delta(k'),$$

with $\xi_k = \varepsilon_k - \mu$. The transition temperature $T_c$ determined by the condition, $\lambda = 1$. In the weak-coupling theory, $\omega$ dependence of the order parameter $\Delta(k)$ is neglected. Although this approximation is quantitatively insufficient, it is expected to be valid for investigating the pairing symmetry of $\Delta(k)$ and for grasping the basic idea of the superconductivity mediated by charge fluctuation.

The point symmetry group of the triangular lattice is $D_6$, which has six irreducible representations as shown in Table I. According to these representations, we classify $\Delta(k)$ or eigenfunctions of Eliashberg’s equation $\Delta(k)$.
where \( p_x d \) is respectively. This means that the realized superconductivity is two-dimensional representation \( (E_t, 3(b), respectively. The temperature is fixed at \( T = 0 \) for term \( E_d \), which corresponds to the divergence of \( \Delta \). These two states form \( d_{x^2-y^2} + id_{xy} \) state below the CDW \( T_c \) predicted in the \( t-J \) model. Interestingly we did not find \( p \)-wave state for the triplet channel in contrast to the SrRuO\(_4\) case where \( p_x + ip_y \) state is realized.

In the proximity to the CDW boundary, the superconductivity with \( B_2(f) \) symmetry becomes dominant. The momentum dependence of the order parameter is shown in Fig. 4. The \( f \)-wave solution has three peaks with the same sign which are connected by the wave vectors \( (0, \frac{\pi}{\sqrt{3}}), (\frac{\pi}{\sqrt{3}} \pi, -\frac{\pi}{\sqrt{3}}) \) and \( (\frac{\pi}{\sqrt{3}} \pi, \frac{\pi}{\sqrt{3}} \pi) \) in the triangular lattice Brillouin zone. The order parameter with this property is favorable because of the momentum dependence of \( V^d \) which gives large attractive interactions at these wave vectors. In fact, for the triplet pairing, both spin and charge fluctuations give attractive interactions and work cooperatively since their magnitude are large at the same wave vector, \( \mathbf{q} = \mathbf{Q} \), as shown in Fig. 1(a). Furthermore, in the real-space picture, we can understand the stability of the \( f \)-wave triplet state as follows. The effect of \( V \) repels electrons from the nearest-neighbor sites. Then it is natural that the amplitude of the order parameter in real space becomes large at the six next-nearest-neighbor sites. After Fourier transformation, this real-space order parameter results in the \( f \)-wave symmetry in \( k \)-space.

Next we consider the electron doped case, \( (n = 1.2) \) (Fig. 3(b)). In this case, the obtained phase diagram differs from the hole-doped case. This difference mainly

![Figure 2](image-url)

**Fig. 2.** Effective interactions for singlet \((V^s)\) and triplet \((V^t)\) pairing for (a) hole-doped and (b) electron-doped cases, respectively at \( T = 0.01 \).

![Figure 3](image-url)

**Fig. 3.** Phase diagram on the \((U, V)\) plane at \( T = 0.01 \) for (a) hole-doped and (b) electron-doped cases. The dashed lines correspond to the CDW and SDW instabilities. On the solid and the dotted lines, the eigenvalues which belong to \( E_2(d) \) and \( B_2(f) \) symmetry reach unity, respectively. In (a), the \( d \)-wave pairing is dominant near SDW and the \( f \)-wave pairing is dominant near CDW. In (b), the eigenvalue of the \( f \)-wave solution reaches unity only in the region where that of the \( d \)-wave solution is larger than unity.

### Table I. Irreducible representations (IR) of \( D_{0h} \)

| IR (symmetry) | Basis functions |
|---------------|-----------------|
| \( A_1(s) \)  | 1               |
| \( A_2(i) \)  | \( \sin \frac{1}{2} \sqrt{3} k_x \sin \frac{1}{2} k_y \) + \( \sin \frac{2}{2} k_x \sin \frac{2}{2} k_y \) |
| \( B_1(f) \)  | \( \sin \frac{1}{2} (\cos \frac{1}{2} k_x - \cos \frac{1}{2} k_y) \) |
| \( B_2(f) \)  | \( \sin \frac{1}{2} (\cos \frac{1}{2} k_x - \cos \frac{1}{2} k_y) \) |
| \( E_1(p) \)  | \( \sin \frac{1}{2} k_x \cos \frac{1}{2} k_y \) |
| \( E_2(d) \)  | \( \sin \frac{1}{2} k_x \sin \frac{1}{2} k_y \) |

The obtained phase diagrams on the \((U, V)\) plane for \( n = 0.8 \) and \( n = 1.2 \) cases are shown in Figs. 3(a) and 3(b), respectively. The temperature is fixed at \( T = 0.01 \). The dotted lines which correspond to the divergence of \( \chi_s \) or \( \chi_0 \) determine the boundary of SDW or CDW state, respectively.

Let us discuss the hole doped case \( (n = 0.8) \) first. In Fig. 3(a), the eigenvalue with the \( E_2(d) \) symmetry becomes larger than unity in the right-hand side of the solid line. In this case, the effect of \( V \) suppresses the \( d \)-wave pairing, which is understood as follows. For \( n = 0.8 \) and without \( V \), the effective interaction for the singlet pairing is large at \( q = Q \) as shown in Fig. 2(a), inducing the \( d \)-wave superconductivity near the SDW. In the presence of \( V \), however, the charge fluctuation gives an opposite contribution at \( q = Q \) and thus suppresses the pairing potential \( V^s \), which results in the suppression of \( d \)-wave pairing.
comes from the momentum dependence of $\chi$, which has peaks away from $Q$ in contrast to the hole-doped case. As a consequence, for the singlet pairing, both spin and charge fluctuations mediate $d$-wave superconductivity as shown in Fig. 3(b). As for the triplet case, the effect of $V$ is necessary for the stability of the $f$-wave pairing. The peaks in $V^f$ in Fig. 2(b) for $V = 0$ case do not give $f$-wave state because the peak positions are away from $Q$. Near the CDW instability, $V^f$ becomes large but $V^s$ is also enhanced. As a result, $d$- and $f$-wave states compete with each other.

In summary we have shown that $f$-wave triplet superconductivity is realized in the vicinity of CDW instability in the triangular lattice. Superconductivity induced by charge fluctuation is a very new and interesting phenomenon. In the square or cubic lattice, $d_{xy}$-wave singlet superconductivity was discussed so far. However the situation is drastically different in the triangular lattice as shown here.

The reason why the $f$-wave state is stable is summarized as follows. 1) Charge fluctuation is equally helps singlet and triplet pairing, since it is the charge degrees of freedom. Symmetry of superconductivity is determined by the geometry of the Fermi surface. 2) Due to the effect of the nearest-neighbor repulsion $V$, the Cooper pairs tend to be formed on the next-nearest-neighbor sites avoiding the nearest-neighbor sites. 3) Since there are six next-nearest-neighbor sites in the triangular lattice, the sign of the Cooper pairing can take $(+ - + - + -)$ which fits very well to the lattice structure.

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