Electronic States in Two-Dimensional Triangular Cobalt Oxides: Role of Electronic Correlation

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We obtain the electronic states and structures of two-dimensional cobalt oxides, Na$_x$CoO$_2$ (x=0, 0.35, 0.5 and 0.75) by utilizing the full-potential linear muffin-tin orbitals (FP-LMTO) methods, from which some essential electronic interaction parameters are estimated: the bare on-site Coulomb interaction of cobalt $U_{dd}=7.5$ eV renormalizes to 5 eV for $x=0.35$, the $pd$ hybridizations $t_{pd}$ and $t_{pde}$ are -1.40 and 0.70 eV, respectively. The density of states at $E_F$ decreases from 6-7 states/eV in the local density approximation (LDA) to about 1.0 states/eV in the LDA+$U$ scheme. The role of the intercalation of water molecules and the microscopic mechanism of the superconductivity in Na$_{0.35}$CoO$_2$·mH$_2$O is discussed.

The triangular cobalt oxides Na$_x$CoO$_2$ synthesized in recent years [1,2] with large thermopower effect may be a hopeful candidate for the exotic resonating valence bond (RVB) phase [3]: well-defined local magnetic moment of Co$^{4+}$ indicates low spin $S=1/2$ [4], highly anisotropic crystalline structure implies quasi-2-dimensional (2D) character [5], and the triangular symmetry may lead to strong frustration effect of the antiferromagnetically coupled spins. However, the good metallic conduction in undoped spins. However, the good metallic conduction in Na$_x$CoO$_2$ seems against to the RVB phase, and its thermoelectric coefficient is an order of magnitude larger than common metals [2–4,6,7], not expected for RVB metal. Two distinct interpretations were proposed to account for the origin of the unusual large thermopower effect: Singh [8] suggested the large density of states (DOS) near the Fermi surface (FS) results in the large thermoelectric effect; meanwhile, a theory of strongly correlated interaction between 3d electrons [9–11] was proposed to explain the large thermopower at room temperature. The main obstruction to settle this debate is that the electronic states of cobalt and oxygen are not well understood.

Recently Takada et al. [12] reported a strange drop in resistivity and a significant diamagnetic signal in magnetic susceptibility below an temperature $T_p=5$ K in Na$_{0.35}$CoO$_2$·mH$_2$O, in which the water molecules were intercalated into the Na$^+$ and CoO$_2$ layers in Na$_{0.35}$CoO$_2$. These unusual phenomena are interpreted as the onset of superconductivity (SC) below $T_p$. The diamagnetic signature was confirmed by a more recent experiment [13], and furthermore an unambiguous zero-resistance state was found [14], verifying the the SC in hydrated 2D cobalt oxides. These anomalous properties are distinct evidences that a novel SC phase forms in Na$_{0.35}$CoO$_2$·mH$_2$O below $T_p$, the question thus arises what the nature of the novel SC and its normal phases is. Doped cobalt oxides resemble to doped high $T_C$ cuprates in many aspects, for example, quasi-2D layer structure, Mott insulator becomes metal upon doping, the frustration effect, etc. Baskaran [15] and Wang et al. [16] It was proposed that the Cooper pairing in SC phase originates from the instability of RVB metallic background in 2D triangular cobalt oxides, implying strongly correlated 3d electrons and the exclusion of double occupation in 3d orbitals. At present our the knowledge to some essential interaction parameters to model the physics in Na$_{0.35}$CoO$_2$ and Na$_{0.35}$CoO$_2$·mH$_2$O, such as the hopping integrals of the 3d electrons, $t$, and the Coulomb interaction between 3d electrons, $U$, etc, are very poor, understanding the electronic states and structures is an essential step to gain insight to the electronic properties and the role of the intercalated water molecules in the novel SC and normal phases, a good knowledge for Co 3d and O 2p band near Fermi surface is required for any further reliable quantitative model.

In this paper we present the electronic state and structure results in Na$_x$CoO$_2$ (x=0, 0.35, 0.5 and 0.75) utilizing the first principle full-potential linear Muffin-Tin orbitals (FP-LMTO) method and the local density approximation (LDA)+$U$ method. The essential interaction parameters for further modeling the nature of the new phase are estimated. We demonstrate that undoped CoO$_2$ is a quasi-2D intermediate correlated charge transfer insulator, Na-doped CoO$_2$ is quasi-2D metal with the $a_{1g}$ hole character dominant at $E_F$. With the intercalation of water, the $a_{1g}$ band becomes more narrow and system is near the broader of metal-SC transition. We suggest the Gossamer mechanism is responsible for the SC in Na$_{0.35}$CoO$_2$·mH$_2$O.

The CoO$_6$ octahedra in Na$_x$CoO$_2$ are connected via sharing their edges forming hexagonal CoO$_2$ layers, Na$^+$ ions are randomly and homogeneously distributed between CoO$_2$ layers, the intercalation of water molecules into the Co and Na$^+$ layers does not change the triangular symmetry of the CoO$_2$ layers in Na$_x$CoO$_2$·mH$_2$O.
Under the octahedral O₆ crystalline electric field, the 3d orbits split into lower threefold degenerate t₂g and higher twofold degenerate E_g levels with the separation of 10Dq. The low spin configuration of Co [4] showed that only t₂g orbitals are the most relevant to the low energy process in the compounds. In the coordinate system that the z-axis coincides with the Co-O bond of the CoO₆ octahedra, the three wavefunctions of the t₂g orbitals are: |a₁g⟩=(dₓ²−y² + dₓz)/√3, |e₁g⟩=(dₓ²−y²)/√2 and |e₂g⟩=(−2dₓz + dᵧ² + dₓy)/√6. For the D₆h point group symmetry in Na₆CoO₂, it is more convenient to choose the threefold rotation axis as the z-axis, thus the basis wavefunctions of the t₂g orbitals are:

The crystal structure of Na₆CoO₂ further splits t₂g orbitals as: Vᵢ(2dᵢ₁σdᵢ₁σ − dᵢ₂σdᵢ₂σ) which lifts the a₁g orbit 3Vᵢ higher than the twofold degenerate e₁g and e₂g orbitals; the trigonal crystal splitting 3Vᵢ is about 0.2 eV, estimated from the separation of a₁g band to e₂g bands in the following calculation. We will show that in Na₆CoO₂, the e₁g and e₂g orbitals are almost filled, leaving a₁g orbit active, this indicates the orbital angular momentum of the 3d electrons in cobalt ions vanishes, < L > =0, therefore the magnetic moment and susceptibility completely contribute from the spins of 3d electrons. In the following we will show that the mixture among the three t₂g bands is weak, in the contrast to vanadium oxide V₂O₃, this also excludes the influence of the orbital degree of freedom on the ground state.

The crystal structure of Na₀.₃₅CoO₂ has already exhibited strong 2D character before oxidation, the ratio of the lattice constant c/a ≈ 3.75, is much larger than that of ideal three-dimension hexagonal close packed structure. The quasi-two-dimension character in the electron structures of CoO₂ layer is seen clearly from the flat a₁g band near FS in Fig.1. The electronic structures are obtained by employing the FP-LMTO method [17] in the LDA. To explore the realistic situation with water molecules inserted between Na⁺ and CoO layers, we study the evolution of the band structures with increasing c/a ratio from 3.75, corresponding to Na₀.₃₅CoO₂, 4.5, 5.75 and up to 6.95, corresponding to Na₀.₃₅CoO₂·mH₂O. The e₁g and e₂g bands lie below E_F, the a₁g band crosses the FS and contributes the major component near FS, this agrees to our crystalline field analysis. Obvious shrink of the a₁g bandwidth is observed in Fig.1 when lattice ratio c/a varies from 3.75 to 6.95, indicating that the localization character of the a₁g electrons becomes more significant after the intercalation of water molecules. In Fig.1, the bandwidth of the a₁g electrons, W = 1.8 eV, giving rise to the effective hopping integral between cobalt ions, |t₁ff| ≈ 0.12 eV, which is larger than that in NaCoO₂ [8]. Due to being quasi-2D metal, the band structures near E_F do not change critically within the LDA+U scheme.

We further investigate how the density of states (DOS) evolves with the doping concentration of Na in NaₓCoO₂, from x=0, 0.35, 0.5 to 0.75 within the usual LDA scheme. The DOS of "virtual" parent phase CoO₂, which has the same structure to Na₀.₃₅CoO₂, is also presented for comparison. It is found that all of the compounds are metallic, even for CoO₂. With the doping of Na, the extra electrons from Na are introduced in the a₁g orbit of Co ions, different from cuprates that the carriers are located in the oxygen atom in the Cu-O chain outside the CuO₂ layers, therefore no Zhong-Rice singlet can form in doped 2D cobalt oxides. The E_g orbitals separate from the t₂g orbitals about 1.7 eV for Na₀.₃₅CoO₂, giving rise to the octahedral crystalline field splitting 10Dq = 1.7 eV. Generally the e₁g and e₂g orbitals are almost filled with the occupation numbers nₑ₁g=nₑ₂g ~ 2.0. The DOS of the 3d electrons at E_F in NaₓCoO₂ is 6.2 states/eV for x=0, 3.0 states/eV for x=0.5 and 2.8 states/eV for x=0.75, respectively. The DOS of oxygens near E_F changes considerably, from 3.8 states/eV at x=0 to 1.5 states/eV at x=0.75.

In the LDA scheme the DOS in CoO₂ at E_F is as high as 8.1 states/eV, however, one would expect the "parent" compound CoO₂ with half-filled a₁g orbit be an insulator. Obviously the LDA scheme underestimates the role of the Coulomb interaction in this system. The LDA+U scheme [18] is thus employed to correct the on-site Coulomb correlation of Co 3d electrons in CoO₂. Within the LDA+U scheme with U=5.0 eV, the charge transfer energy between Co 3d and O 2p orbits in CoO₂ is ∆ =ε₄d − ε₄p =3.2 eV; the bare on-site Coulomb interaction of the Co 3d electrons, Uₐ₃d =7.5 eV, which is smaller than about 10 eV of Cu in parent cuprates La₂CuO₄; ∆ =< Uₐ₃d implies that the "parent" phase CoO₂ is a charge transfer insu-
lator with energy gap $E_g=1.2$ eV. The 3d DOS decreases to zero at $E_F$, in contrast with the LDA result that the system is metallic with very large DOS. We notice that the oxygen DOS is almost not affected and is dominant over the 3d DOS below $E_F$, as seen the dot line in Fig.2a. In CoO$_2$, the magnetic moment of cobalt ion is $1.09 \mu_B$, the moment of oxygen ion is $-0.06 \mu_B$, leading to a net moment of $1.03 \mu_B$. The planar coupling between spins in CoO$_2$ is antiferromagnetic, $J=2.9$ meV, however long range order does not establish due to the spin fluctuation arising from the geometric frustration in triangular CoO$_2$ layers. The intraatomic Hund’s rule coupling $J_H$ of Co in CoO$_2$ is similar to that in LaCoO$_3$ [19], smaller than 0.7 eV. These intraatomic parameters are also applied for doped Na$_x$CoO$_2$.

Within the LDA+U scheme, the DOS for different doped compounds Na$_x$CoO$_2$ are shown in Fig.2 (b) to (c). The DOS near FS changes critically for doped compounds we studied ($x=0.35$, 0.5, 0.75), in comparison with the LDA results. Though all of the CoO$_2$ layers are metallic, the $a_{1g}$ bands near $E_F$ have long tails, and the DOS at $E_F$ is considerably reduced to 1.6, 1.3 and 1.2 states/eV for $x=0.35$, 0.5, and 0.75, respectively. With the doping, the extra electrons are filled in empty $a_{1g}^\downarrow$ band, due to the Coulomb interaction, the filled $a_{1g}^\uparrow$ band shifts to deep position, leaving $a_{1g}^\downarrow$ band around $E_F$ and smaller the 3d DOS. The magnetic moment of cobalt ion is $0.57 \mu_B$ for $x=0.35$, the moment of oxygen is $0.03 \mu_B$, giving rise to net moment $0.6 \mu_B$; and we find the favorable coupling between Co spins is ferromagnetic. The DOS at $E_F$ is not large enough to account for the unusual large thermoelectric power observed in Na$_x$CoO$_2$, after taking into account the electron correlation between 3d electrons. One possibility is the spin entropy of 3d electrons in Na$_x$CoO$_2$ [11]. In the LDA scheme, a large and a small FS are obtained in half-doped compound Na$_{0.5}$CoO$_2$, as the same to Ref.[8]. The large FS arises from the $a_{1g}$ orbit, while small FS pocket from the mixed $a_{1g}$ and $e_g$ component of cobalt ions. In the LDA +U scheme, the inclusion of the correction to the on-site Coulomb interaction repulses the occupied $e_g$ electrons to lower energy, diminishing the contribution of these electrons to the small FS, thus the small FS disappears.

We estimate the hopping integrals between 3d orbitals from the $pd$ hybridization between oxygen and cobalt in the CoO$_2$ plane. It is found the Co-O overlap integrals are: $t''_{pd} = -1.4$ eV, $t'_{pd} = 0.7$ eV. The direct hopping integrals between cobalts, $dd\sigma$, etc. are very small, since the Co ion radius is small. From which and considering the $pd$ hybridization effect and the nearly 90° angle of the Co-O-Co bridge, we find to the second-order approximation, the orbital-diagonal hopping integrals between Co 3d orbitals along x-axis are renormalized to: $t_{11} \approx -0.09$ eV, $t_{22} \approx 0.17$ eV, respectively; and the mixing hopping integral $t_{12}$ is very small, about 0.01 eV. The value of the hopping integral between $a_{1g}$ orbitals, $t_{11}$, is comparable with that from the $a_{1g}$ bandwidth. Intuitively the trigonal splitting $V_1$ is so small that three $t_{2g}$ bands, $a_{g1}$, $e_{g1}$ and $e_{g2}$ are almost degenerate, the orbital degree of freedom of $t_{2g}$ is expected to play important role in the low energy process. However, the obtained small hopping integrals between orbitals suggests the mixing between orbitals is negligible and the orbital degree of freedom does not affect the ground state and excited properties in quasi-2D cobalt oxides.

As to the electron correlation in 2D cobalt oxides, we note that the present experimental data and theoretical results support two distinct pictures, one is small Coulomb correlation scenario: Na$_x$CoO$_2$ behaves good metallic conduction, and low spin configuration allows double occupation in 3d orbits; On the other hand, Co ion exhibits well-defined magnetic moment, the magnetic susceptibility of Na$_x$CoO$_2$ exhibits Curie-Weiss law with finite Neel temperature $\Theta$ in high temperature regime, etc. supporting a strong correlation scenario. In the “parent” phase CoO$_2$, taking into account the correction from the renormalized parameters $F_2$ and $F_4$ of the 3d multipolar interaction [20], the bare on-site Coulomb interaction $U_{dd}$ is renormalized to $\tilde{U}_{dd} \approx 4.0$ eV, suggesting an intermediate correlated system.

| TABLE I. Electronic parameters in CoO$_2$ & Na$_{0.35}$CoO$_2$ (eV) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $U_{dd}$        | $J$             | $E_g$           | $t''_{pd}$      | $t'_{pd}$       | $10Dq$          | $\Delta$       | $3V_t$          | $W$             |
| 7.5             | 0.0029          | 1.2             | -1.40           | 0.70            | 1.7            | 3.2            | 0.2             | 1.80            |
in comparison with the \(a_{1g}\) bandwidth \(W = 1.8\) eV. In the metallic phases \(Na_xCoO_2\), due to the screening effect from the many-body interaction between 3d electrons, the effective Coulomb strength is further reduced to \(U_r = \hat{U}_{dd}/(1+\hat{U}_{dd}A)\) [21], about 2.3 eV in \(Na_{0.35}CoO_2\), where \(A\) is the renormalized parameter depending on the conduction band. The Wilson ratio deduced from experimental data also supports an intermediate correlated system: the magnetic susceptibility \(\chi\) [22] and the linear coefficient of the specific heat [23] gives rise to Wilson ratio \(R = (\gamma/\alpha_B^2 \pi^2)/(\chi/\mu^2_{gff}) = 0.62\) for \(x = 0.5\), lying between that of strongly correlated system, \(R = 2\), and that of weak correlated Fermi liquid, \(R = 1\). Therefore 2D cobalt oxides possess both weak-correlated itinerant and strong-correlated localized characters, the SC in \(Na_{0.35}CoO_2\cdot mH_2O\) seems not to arise from the instability of the strongly correlated RVB metal, the RVB scenario is not applicable.

In this study we try to unveil the role of water molecules to the novel SC in hydrated cobalt oxides. The intercalation of water molecules into \(CoO_2\) and Na layers is simulated by stretching the c-axis, since no configuration information about the water molecules in \(Na_{0.35}CoO_2\cdot mH_2O\) is available. This may not completely reproduce the realistic crystalline environment of the \(CoO_6\) octahedra. The role of intercalation of water lies in three aspects. First of all, it enhances the localization of the \(a_{1g}\) electrons, pushes the 2D \(CoO_2\) layers to the broader of metal-insulator transition, similar to the effect of doping on cuprates, favors the instability of metal-SC transition. Second, with the intercalation of water molecules, the hydrgens of water molecules approaching \(CoO_6\) octahedron tend to form hydrogen bond with the vertical oxygen of the \(CoO_6\) octahedra, the negative charge center in \(O^2-\) shifts to \(H^+\), thus we have such possibility that a fraction of holes may introduced in filled 2p band of oxygen, the spatial separation between the \(a_{1g}\) electrons and the 2p holes blocks the their combination. Third, though there exists strong electron-phonon (e-ph) coupling in 2D \(CoO_2\) layers in \(Bi_2Sr_2CoO_6\), one expects the e-ph coupling is not weak in Na-doped \(CoO_2\), the SC transition temperature would be high if considering the large DOS at \(E_F\) in the absence of Coulomb correlation; the elongation of c-axis in \(Na_xCoO_2\) weakens the vibration frequency of Co-O bond along c-axis, the vibration mode along c-axis is soften, this is not favorable of the e-ph coupling mediated pairing mechanism, but favors to other mechanism. The isotope effect experiment of the oxygens on \(CoO_2\) layer is expected to confirm this result.

In 2D triangular \(CoO_2\) layers the intermediate electronic correlation allowing double occupation excludes RVB SC, whileas, the antiferromagnetic spin fluctuation and the frustration effect are important, the antiferromagnetic long range order is suppressed. For the correlated electron system with intermediate Coulomb strength, like the present compound, Laughlin and Zhang [24] suggested in the new quasiparticle basis allowing double occupation in the electronic orbits, the electrons experience a powerful attracting force, providing a pairing mechanism, named Gossamer SC. In such a Gossamer SC, the superfluid carrier density is very thin, it is naturally expected the transition temperature \(T_C\) is low.

In summary, two-dimensional triangular \(CoO_2\) layer is intermediate correlated electron system, \(Na_{0.35}CoO_2\) is quasi-2D metal with dominant \(a_{1g}\) hole character. The intercalation of water enhances the localization character of \(a_{1g}\) carriers, the superconductivity arises from Gossamer pairing mediated by the spin fluctuations.

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