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Electronic structure and states in two-dimensional triangular cobalt oxides: The role of electronic correlation

Liang-Jian Zou, J.-L. Wang, and Z. Zeng
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, China

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Electronic structures and states of Na_xCoO_2 ($x=0$, 0.35, 0.5, and 0.75) with the same lattice parameters as superconducting $Na_xCoO_2\cdot mH_2O$ have been studied by utilizing the full-potential linear muffin-tin orbital methods, from which some electronic interaction parameters are obtained. Most of the carriers in doped compounds have a_{1g} character. The effective on-site Coulomb interaction $\tilde{U}_{dd}=4$ eV for $x=0$; the pd hybridizations t_{pd}^{σ} and t_{pd}^{π} are -1.40 and 0.70 eV, respectively; the density of states at E_F for $x=0.35$ is about 1.0 states/eV in the local-density approximation (LDA)$+U$ scheme, much smaller than 6–7 states/eV in the LDA scheme. The role of the electronic correlation on the superconductivity in $Na_{0.35}CoO_2\cdot mH_2O$ is discussed.

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Triangular cobalt oxides Na_xCoO_2 with large thermopower coefficient synthesized recently[1,2] exhibit many characters similar to the resonating valence bond (RVB) phase:[3] well-defined local magnetic moment of Co^{4+} indicates low spin $S=1/2$,[4] highly anisotropic crystal structure implies quasi-two-dimensional (2D) character,[5] and the antiferromagnetically (AFM) coupling spins in the triangular symmetry Co layers may lead to strong frustration effect. Meanwhile, the good metallic conduction over wide doping regime and temperature range, and the thermoelectric coefficient, an order in magnitude larger than common metals,[2–4,6] are not expected in the RVB theory. Two distinct interpretations were proposed to account for the unusual large thermopower effect: Singh[7] explained the large thermoelectric effect in terms of the large density of states (DOS) near the Fermi surface (FS); whereas some others[8–10] proposed that the large thermopower at room temperature arises from the strong correlation of $3d$ electrons. The lack of a good understanding of the microscopic electronic states of Co and O in Na_xCoO_2 is the main obstacle for settling the debate.

Recently Takada *et al.*[11] reported a strange drop in resistivity and a significant diamagnetic susceptibility below the temperature $T_p=5$ K in $Na_{0.35}CoO_2\cdot mH_2O$, in which the water molecules were intercalated into the Na^+ and CoO_2 layers in $Na_{0.7}CoO_2$; he interpreted these unusual phenomena as the onset of superconductivity (SC) at T_p. More recently the diamagnetic signature was confirmed by further experiment,[12] and the unambiguous zero-resistance state was observed,[13] verifying the SC in hydrated 2D cobalt oxides. The question thus arises what the nature of the SC and its normal phases are. In many respects doped cobalt oxides resemble doped cuprates, such as quasi-2D layer structure, narrow-band metal upon doping, the strong frustration effect, etc. Baskaran[14] and Wang *et al.*[15] suggested that the Cooper pairing in the 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. The measurement on the thermopower[10] also suggested that the strong electron-electron correlation plays an important role in the metallic transport in Na_xCoO_2. However the present electronic structure results were based on weak correlated scenario.[7] Understanding the electronic states and structures of Co $3d$ and O $2p$ bands in the correlated electron scenario is crucial for gaining insight into the electronic properties in Na_xCoO_2 and the normal and SC phases of its hydrations. At present, our knowledge of the interaction parameters of $3d$ electrons in $Na_{0.35}CoO_2$ and $Na_{0.35}CoO_2\cdot mH_2O$, such as the hopping integrals $t_{\alpha\beta}$, and the Coulomb interaction U, etc., is rather poor; a good knowledge of these parameters in the correlated electron scenario is necessary for any further reliable quantitative model.

In this paper we present the electronic structures in Na_xCoO_2 ($x=0$, 0.35, 0.5, and 0.75) with the same structure parameters as $Na_{0.35}CoO_2\cdot mH_2$ (Ref. 11) by utilizing the first-principles full-potential linear muffin-tin orbital (FP-LMTO) method and the local-density approximation (LDA)$+U$ method. We find undoped CoO_2 is a quasi-2D charge transfer insulator; Na doped CoO_2 is quasi-2D correlated metal with the a_{1g} hole character dominant near E_F. The tight-binding parameters for $3d$ electron energy bands are obtained. The a_{1g} band becomes more narrow with the intercalation of water into Na and CoO_2 layers, in comparison with the metallic phase without water.

The CoO_6 octahedra in Na_xCoO_2 are connected via sharing their edges forming triangular CoO_2 layers; Na^+ ions are almost homogeneously distributed between CoO_2 layers; the intercalation of water molecules into the Co and Na^+ layers does not alter the triangular symmetry of the CoO_2 layers. Under the octahedral O_h crystalline electric field (CEF), the $3d$ orbits split into lower threefold degenerate t_{2g} and higher twofold degenerate E_g levels with the separation of $10Dq$. The low-spin configuration of Co (Ref. 4) showed that only t_{2g} orbitals are the most relevant to the low-energy process in the compounds. In the coordinate system where the z axis coincides with the Co-O bond of the CoO_6 octahedra, the wave functions of the t_{2g} orbitals are $|a_{1g}\rangle=(d_{x'y'}+d_{y'z'}+d_{z'x'})/\sqrt{3}$, $|e_{1g}\rangle=(d_{x'y'}-d_{y'z'})/\sqrt{2}$, and $|e_{2g}\rangle=(-2d_{x'z'}+d_{y'z'}+d_{x'y'})/\sqrt{6}$. In the D_{6h} point-group symmetry, it is more convenient to choose the threefold rotation axis as the z axis, thus the basis wave functions of the t_{2g} orbitals are rewritten as $|1\rangle=|a_{1g}\rangle=d_{3z^2-r^2}$, $|2\rangle$

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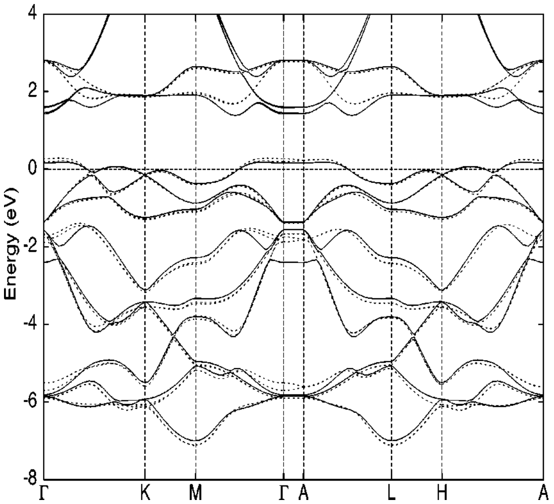

FIG. 1. Band structures of $Na_{0.35}CoO_2$ within the LDA scheme for different c/a ratios. Solid lines are for the ratio $c/a=6.95$, and dotted lines for the ratio $c/a=3.75$.

$=|e_{1g}\rangle=\sqrt{1/3}(\sqrt{2}d_{xy}+d_{yz})$, and $|3\rangle=|e_{2g}\rangle=\sqrt{1/3}(-\sqrt{2}d_{x^2-y^2}+d_{xz})$. The t_{2g} orbitals are further split by the trigonal CEF as $V_t(2d^{\dagger}_{i1\sigma}d_{i1\sigma}-d^{\dagger}_{i2\sigma}d_{i2\sigma}-d^{\dagger}_{i3\sigma}d_{i3\sigma})$ which lifts the a_{1g} orbit $3V_t$ higher than the twofold degenerate e_{1g} and e_{2g} orbits. We will show that in Na_xCoO_2, the e_{1g} and e_{2g} orbitals are almost filled, leaving a_{1g} orbit active. This indicates the orbital angular momentum of the $3d$ electrons vanishes, $\langle L\rangle=0$, therefore the magnetic moment and susceptibility completely contribute from the $3d$ spins. In the point-charge model of the ligand field theory, we find the order of these levels in single Co atom does not change in the hydration. In the following we demonstrate that the mixing between a_{1g} and two e_g orbits is weak; in contrast to vanadium oxide V_2O_3, this also rules out the influence of the orbital degree of freedom on the ground state.

The crystal structure of $Na_{0.35}CoO_2$ has already exhibited strong 2D character before oxidization; the ratio of the a- and c-axis lattice constants, $c/a\approx 3.75$, is much larger than that of ideal three-dimensional hexagonal close-packed structure, 1.63. The quasi-2D character in the electronic structures of CoO_2 layer is seen clearly from the flat a_{1g} band near FS in Fig. 1. The electronic structures are obtained by employing the FP-LMTO method[16] in the LDA scheme. To explore the influence of the expansion of the lattice parameter c upon water molecule intercalation into Na^+ and CoO_2 layers, we study the evolution of the band structures with increasing c/a ratio from 3.75, corresponding to $Na_{0.35}CoO_2$, 4.5, 5.75, and up to 6.95, corresponding to $Na_{0.35}CoO_2\cdot mH_2O$.

The trigonal CEF splitting $3V_t$ is about 0.2 eV from the separation of maximum of a_{1g} band to that of e_g bands. The e_{1g} and e_{2g} bands lie below E_F, and the a_{1g} band crosses the FS and contributes the major component near FS, this agreeing to our CEF analysis. An obvious shrink of the a_{1g} bandwidth is observed in Fig. 1 when the ratio c/a increases from 3.75 to 6.95, indicating that the localization character of the a_{1g} electrons becomes more significant after the intercalation of water molecules. The bandwidth of the a_{1g} electrons, $W_{11}=1.8$ eV, gives rise to the effective hopping integral between a_{1g} orbitals, $|t^{11}_{eff}|\approx 0.12$ eV, slightly larger than that in $NaCoO_2$.[7] The two e_g bandwidths are $W_{22}=W_{33}=1.6$ eV.

We further investigate how the DOS evolves with the doping concentration in Na_xCoO_2 for the ratio $c/a=6.95$ from $x=0$, 0.35, 0.5 to 0.75 within the usual LDA and the LDA$+U$ schemes. The DOS of "virtual" parent triangular phase CoO_2, with the same structure parameters to $Na_{0.35}CoO_2$, is presented for comparison. We find that in the LDA scheme all of the compounds are metallic, even for CoO_2. With the doping of Na, extra electrons from Na occupy the Co a_{1g} orbitals, different from cuprates in which the carriers are located in the oxygen atom in the Cu-O chain, therefore no Zhang-Rice singlet forms in doped 2D cobalt oxides. The E_g orbitals separate from the t_{2g} orbits about 1.7 eV, giving rise to $10Dq=1.7$ eV for $Na_{0.35}CoO_2$. Generally the e_{1g} and e_{2g} orbits are almost filled with the occupation numbers $n_{e1g}=n_{e2g}\approx 2.0$. The $3d$ DOS at E_F in Na_xCoO_2 is 6.2 states/eV for $x=0.35$, 3.0 states/eV for $x=0.5$ and 2.8 states/eV for $x=0.75$, respectively. The DOS of oxygen near E_F changes considerably with doping, from 3.8 states/eV at $x=0$ to 1.5 states/eV at $x=0.75$.

In the LDA scheme, the DOS in CoO_2 at E_F is as high as 8.1 states/eV, however, one would expect the "parent" compound CoO_2 with half-filled a_{1g} orbit to be an insulator due to electron correlation. It is known that the LDA scheme underestimates the electron correlation effect in many narrow-band systems. The LDA$+U$ scheme[17] is thus employed to study the electronic states of Co $3d$ electrons in CoO_2. In the LDA$+U$ scheme with $U=5.0$ eV, the charge transfer energy between Co $3d$ and O $2p$ orbits in CoO_2 is $\Delta=\epsilon_d-\epsilon_p=3.2$ eV; and we get the bare on-site Coulomb interaction of the Co $3d$ electrons, $U_{dd}=7.5$ eV; $\Delta\ll U_{dd}$ implies that the parent phase CoO_2 is a charge transfer insulator with energy gap $E_g=1.2$ eV. The spin-down band structure for the parent phase CoO_2 is shown in Fig. 2. The calculation is performed for the unit cell containing two Co atoms.

From this we find the bandwidth of the spin down a_{1g} is about 1.32 eV, giving rise to $t_{11}=-0.083$ eV, and the filled e_g bandwidth almost does not change. Obviously the a_{1g} band does not mix with the e_g bands, implying $t_{12}=t_{13}=0$. The $3d$ DOS decreases to zero at E_F in Fig. 3(a), in contrast with the metallic and the very large DOS behaviorw in the LDA results. The oxygen DOS is almost not affected by the correlation below E_F, as shown by the dotted lines in Fig. 3(a). In CoO_2, the spin-polarized calculation shows that the magnetic moment of cobalt ion is $1.09\mu_B$, and the moment of oxygen ion is $-0.06\mu_B$, leading to a net moment of $1.03\mu_B$. The planar coupling between Co spins is AFM, $J=2.9$ meV. The intra-atomic Hund's rule coupling J_H of Co in CoO_2 is similar to that in $LaCoO_3$,[18] smaller than 0.7 eV. These intra-atomic parameters in parent phase CoO_2 are also applicable for doped Na_xCoO_2.

Within the LDA$+U$ scheme, being quasi-2D metals, the band structures near E_F for different doped compounds Na_xCoO_2 do not change critically, however the DOS reduces considerably due to the shift of unoccupied band to high

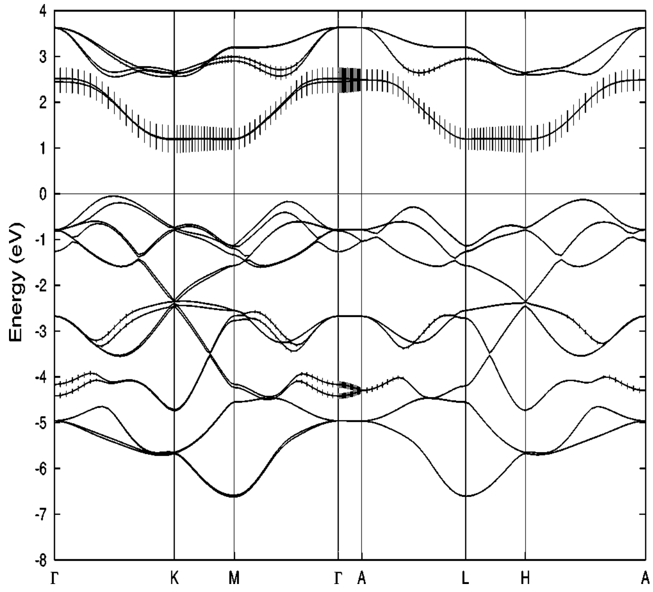

FIG. 2. Band structure of the "parent" phase CoO_2 for spin-down electrons within the LDA+U scheme; the bands with a_{1g} character are marked.

energy. The DOS's in the LDA+U scheme are shown in Figs. 3(b)–3(d). Three doped compounds have common characters: all compounds are metallic, and the a_{1g} bands have long tails above E_F, indicating that carriers have a hole character. 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. The unusual large thermoelectric power observed in Na_xCoO_2 cannot be explained based on such small DOS near E_F, as suggested in Ref. 8. With the doping, the extra electrons are filled into empty spin-down $a_{1g}^{\downarrow}$ band, and due to the Coulomb correlation, the filled $a_{1g}^{\uparrow}$ band shifts to deep position, leaving $a_{1g}^{\downarrow}$ band and small $3d$ DOS around E_F. In the ferromagnetic configuration the magnetic moment of cobalt ion is $0.57\mu_B$ for $x=0.35$, and the moment of oxygen is $0.03\mu_B$, giving rise to net moment $0.6\mu_B$; and we find that the favorable coupling between Co spins is ferromagnetic.

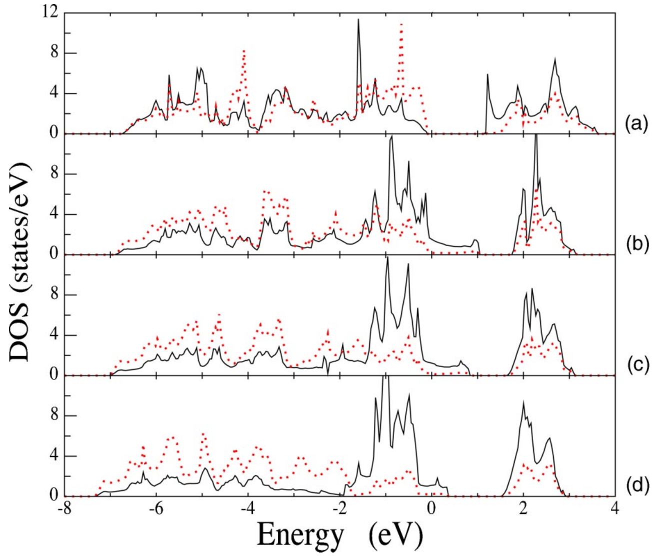

FIG. 3. Dependence of density of states in Na_xCoO_2 on doping concentration within the LDA+U scheme, subsequently, (a) $x=0$, (b) $x=0.35$, (c) $x=0.5$, and (d) $x=0.75$. Solid lines denote DOS of Co $3d$ orbitals, dotted lines DOS of O $2p$ orbitals.

In the LDA scheme, a large and a small FS are obtained in the half-doped compound, $Na_{0.5}CoO_2$, as well as seen in Fig. 1 in $Na_{0.35}CoO_2$, which is the same as 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 contrast, ithe LDA+U scheme, the on-site Coulomb interaction repulses the occupied e_g electrons to lower-energy position, diminishing the contribution of these electrons to the small FS; the small FS thus disappears.

The hopping integrals between Co $3d$ orbitals and the pd hybridizations between Co and O in the CoO_2 layers are the basic parameters for further modeling the physics in hydrated cobalt oxides. Direct calculation gives rise to the Co-O pd hybridization matrix elements: $t_{pd}^{\sigma}=-1.4$ eV, $t_{pd}^{\pi}=0.7$ eV. The direct hopping integrals between cobalts, $dd\sigma$, $dd\pi$, etc., are small, because the radius of cobalt ion is rather small. Also, the effective t_{2g} hopping integral due to the charge transfer via oxygen bridges can be obtained through perturbation approximation. The Wannier wave functions of the t_{2g} orbitals in the presence of oxygen anion, $|\xi_m^{\pi}\rangle$, are expressed as $|m\rangle'=(|m\rangle+t_{pd}^{\pi}/\Delta|\xi_m^{\pi}\rangle)/\sqrt{N_{\pi}}$, where $m=1,2,3$, and N_{π} is the normalized constant. In the second-order perturbation, the nonzero orbital-diagonal and off-diagonal t_{2g} orbital hopping integrals along x axis $t_{\alpha\beta}$ are $t_{11}=-2(t_{pd}^{\pi})^2/(3N_{\pi}\Delta)$, etc. This leads to $t_{11}=-0.086$ eV, $t_{22}=0.13$ eV, and $t_{33}=-0.043$ eV, respectively. t_{11} concides with that fitting from the LDA+U calculation. But the off-diagonal hopping integral $t_{13}=0.074$, suggesting that the electron-electron correlation separates the a_{1g} band from e_g bands and diminishes the off-diagonal electron hopping. Therefore the mixing between a_{1g} and e_g orbitals is negligible and the orbital degree of freedom does not play significant role in the ground-state properties of quasi-2D Co_2 and Na_xCoO_2.

As mentioned in the paragraph, the present experimental data and theoretical results do not settle the dispute on the electron correlation. The effective Coulomb interaction strength is an important parameter for understanding the electronic correlation in Na_xCoO_2 and its hydrations. In the parent phase CoO_2, in the presence of the $3d$ multipolar interaction,[19] the bare on-site Coulomb interaction U_{dd} is renormalized to $\tilde{U}_{dd}\approx 4.0$ eV by the multipolar parameters F_2 and F_4, suggesting a correlated insulator in comparison with the a_{1g} bandwidth $W=1.8$ eV. All of the electronic interaction parameters are listed in Table I. In the metallic phases Na_xCoO_2, due to the screening effect, the effective Coulomb strength is further reduced to $\tilde{U}_r=\tilde{U}_{dd}/(1+\tilde{U}_{dd}\Lambda)$,[20] about 2.0 eV in $Na_{0.35}CoO_2$, where Λ is the renormalized parameter depending on the conduction band. The ratio $\tilde{U}_r/W\sim 1$ indicates that $Na_{0.35}CoO_2$ is a correlated metal. The Wilson ratio deduced from experimental data also supports the electronic correlated scenario: the magnetic sus-

TABLE I. Electronic parameters (eV) in Na_xCoO_2 within the LDA+U scheme. Parameters $\tilde{U}_{dd}$, E_g, and J are for CoO_2.

$\tilde{U}_{dd}$	J	E_g	t_{pd}^{σ}	t_{pd}^{π}	$10Dq$	Δ	t_{11}
4	0.0029	1.2	-1.40	0.70	1.7	3.2	-0.083

ceptibility χ (Ref. 21) and the linear coefficient of the specific heat[22] give rise to the Wilson ratio $R = (\chi/\mu_{eff}^2)/(\gamma/k_B^2\pi^2) = 1.62$ for $x = 0.5$, significantly larger than the weak correlated Fermi liquid, $R = 1$, indicating the important role of the electronic correlation.

The role of water molecules in the mechanism of the SC in hydrated cobalt oxides is very interesting. The intercalation of water molecules into CoO_2 and Na^+ layers is simulated by stretching the distance between Na and CoO_2 layers along the c axis in the present study; it enhances the localization character of the a_{1g} electrons through narrowing the a_{1g} band. Obviously this only partially reproduces the realistic crystalline environment of the CoO_6 octahedra after the intercalation of water molecules. In the meanwhile the water molecules may interact with CoO_6 octahedra through hydrogen bond, as shown in a recent experiment;[23] the orientation of the water molecules may form ordered structure. These will affect the phonon vibration frequency and the interaction between electrons, which are under further study.

In summary, two-dimensional triangular compound CoO_2 is charge transfer insulator; Na_xCoO_2 with the same structure to its hydration is quasi-2D correlated metal with dominant a_{1g} hole character. The intercalation of water enhances the localization character of a_{1g} carriers.

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