Phase Diagram of Na$_x$CoO$_2$ Studied By Gutzwiller Density-Functional Theory

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The ground state of Na$_x$CoO$_2$ (0.0 < $x$ < 1.0) is studied by the local density approximation plus the Gutzwiller approach, where charge transfer and orbital fluctuations are all self-consistently treated 

\[ \vdots \]

In contrast to previous studies, which are parameter-dependent, we characterized the phase diagram as (1) Stoner magnetic metal for $x > 0.6$ due to $a_{1g}$ van Hove singularity near the band top, (2) correlated nonmagnetic metal without $e_g'$ pockets for 0.3 < $x$ < 0.6, and (3) $e_g'$ pockets appear for $x < 0.3$, and additional magnetic instability is revealed. Experimental quasiparticle properties are well explained, and the $a_{1g}$-$e_g'$ anticrossing is attributed to spin-orbital coupling.

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Transition-metal oxides have complex phase diagrams due to the interplay between the charge, spin, and orbital degrees of freedom. Among them Na$_x$CoO$_2$ is a typical system showing doping-dependent phase control [1]. It has been found experimentally as nonmagnetic (NM) metal for the Na-poor side, while Curie-Weiss metal for the Na-rich side [1,2], and A-type (layered) antiferromagnetic (AFM) state for $x \sim 0.75$ [3]. In addition, superconductivity is discovered for hydrated Na$_x$CoO$_2$•H$_2$O ($x \sim 0.35$) [4], and charge-spin-orbital ordered states are suggested for $x = 0.5$ due to Na ordering [5]. The rich properties of Na$_x$CoO$_2$ have attracted much of the research interest due to not only its potential applications, but also the challenging theoretical issues in this system generated by both the multiorbital nature and the strong e-e correlation.

Na$_x$CoO$_2$ is crystallized in planar triangle lattice, with each Co site being coordinated by edge-shared oxygen octahedron. The $e_g$ states are about 2 eV higher than $t_{2g}$, and the Fermi level is located within the Co $t_{2g}$ multiplet, which splits again into one $a_{1g}$ and two $e_g'$ orbitals under trigonal crystal field. For Na concentration $x$, the effective number of $t_{2g}$ electrons per Co is given as $5 + x$, and thus the low energy physics here is dominated by the multiple orbits ($a_{1g}$ + $e_g'$), where charge, spin, and orbital degrees of freedom are all active. The rigorous computational tools for such systems are still lacking, and the observed rich phenomena remains far from even qualitatively being understood. The main controversial issues are (1) for $x = 0.3$, are there any Fermi surface pockets for the $e_g'$ band? These pockets are predicted by local density approximation (LDA) calculations [6] but not observed by angle-resolved photoemission spectroscopy (ARPES) [7]. (2) Is the $x > 0.5$ side more “correlated” than the $x < 0.5$ side, as suggested by the Curie-Weiss behavior for the Na-rich side? It is expected from the simple band picture that $x = 1.0$ compound is a band insulator rather than a Mott insulator.

Both LDA and local density approximation plus the multiorbital mean-field Hubbard (LDA + $U$) methods fail for such a system due to the insufficient treatment of electron correlation. This is why many issues appear controversial following the LDA pictures. For instance, LDA predicts ferromagnetic metal as the ground state for the whole doping region, and LDA + $U$ even enhances the tendency to be ferromagnetic [8]; the band width obtained by LDA or LDA + $U$ is about 2 times larger than what is observed by ARPES [9]; the $e_g'$ pockets problem as mentioned above; etc. To treat the electron correlation more precisely, the Gutzwiller [10,11] and dynamic mean field theory (DMFT) [12] approaches have been adopted, where fluctuation effects are included. However, those studies [10,12] are mostly focused on the $x = 0.3$ compound using a tight-binding (TB) Hamiltonian extracted from LDA, and conflicting results are drawn due to different parameters [13].

In this Letter, we show that the above-mentioned theoretical challenging issues of this multiorbital correlated electron system can be well studied by using the recently developed LDA + Gutzwiller method [14], which keeps the parameter-free character of density-functional theory (DFT) and includes all possible charge transfer and orbital fluctuation effects self-consistently. As a result, a phase diagram for the whole doping region is constructed, which removes most of the above-mentioned controversial issues, and suggests that physics here dominates by the doping-dependent orbital, charge, and spin fluctuations.

To overcome the problem of LDA, the common procedure of LDA + $U$ and DMFT schemes [15] is to draw out from the LDA Hamiltonian the interaction terms for the localized orbitals, such as the 3$d$ or 4$f$ states, and then treat the interaction Hamiltonian explicitly in a proper way (beyond LDA). The total Hamiltonian reads

\[ H^{LDA+G} = H^{LDA} + H_{int} - H_{dc} \]

\[ H_{int} = U \sum_{\alpha \beta} n_{\alpha \sigma} n_{\beta \sigma} + \frac{U'}{2} \sum_{\sigma \alpha \beta} n_{\alpha \sigma} n_{\beta \sigma} - \frac{J}{2} \sum_{\sigma \alpha \beta} n_{\alpha \sigma} n_{\beta \sigma} \]

\[ \langle H_{dc} \rangle^{LDA} = UN(N - 1) - \frac{J}{2} \sum_{\sigma} [N_{\sigma}(N_{\sigma} - 1)], \]

(1)
where $|i\alpha\rangle^\sigma$ are a set of local orbitals with spin index $\sigma$ and occupation number $n_{i\alpha}$ for lattice site $i$; the $U$, $U'$, and $J$ give the intraorbital and interorbital repulsive interaction and Hund’s exchange coupling, respectively. The $H_{dc}$ is the double counting term from LDA, where interaction strength $\bar{U}$ and $\bar{J}$ are averaged over orbitals.

If the interaction term is treated by the Hartree-like scheme (LDA + $U$), the correction over LDA is a set of energy shift of the local orbitals, leaving the kinetic part unchanged. This is fine if the fluctuation effect is not strong, but will fail in the opposite case, such as the Na$_x$CoO$_2$ system studied here. In this sense, the DMFT method, in which frequency-dependent self-energy is properly computed, is much better than LDA + $U$. However, due to the heavy computational cost for multi-orbital systems, the current DMFT studies [12,13] are all applied to TB Hamiltonians extracted from LDA without full charge-density self-consistency. This is insufficient if the charge, spin, and orbital degrees of freedom are all active as discussed above for Na$_x$CoO$_2$.

In the LDA + Gutzwiller approach [14], the Gutzwiller wave function $|\Psi_G\rangle = \hat{P}|\Psi_0\rangle$ ($\hat{P}$ is a projection to many-body configuration) is used instead of the single Slater determinate wave function $|\Psi_0\rangle$. The orbital, charge, and spin fluctuations can be included by the multiconfiguration nature of the Gutzwiller wave function. As a result, a set of orbital-dependent kinetic energy renormalization factors $Z_\alpha$ is obtained for the correlated states in addition to the on-site energy shift [16]. Unlike the previous Gutzwiller or DMFT studies [10,12,13], here all charge transfer processes, crystal field, and orbital fluctuations are self-consistently treated within the framework of DFT, which allows for the accurate computation of ground state total energy.

We use the plane-wave pseudopotential method, and choose the Co 3d Wannier functions as the correlated local orbitals, which can be constructed from the projected Wannier function method [17]. The atomic-limit convention $U = U' + 2J$ is followed. How to determine the value of $U$ and $J$ is a common problem for LDA + $U$, DMFT, and present methods, and no unified way has yet been established. Nevertheless, reasonable estimations have been done for $U = 3.0$–5.0 eV and $J \sim 1.0$ eV for the Na$_x$CoO$_2$ system following the literature [10,12]. Instead of using single fixed $U$, various values have been studied, and our qualitative results are not changed, as shown below. In addition, since our main purpose is to establish a general picture for the physics of Na$_x$CoO$_2$, the structure differences among different doping $x$ are neglected, and the Na doping is treated by virtual crystal approximation (therefore the charge-ordered states with Na ordering at particular doping, which is interesting but not our purpose here, is out of the phase diagram).

Figure 1 shows the phase diagram computed for the whole doping range $0.0 < x < 1.0$. The solid lines and the dashed lines represent the stabilization energies of the ferromagnetic (FM) state and the layer-type AFM state relative to the NM state, respectively. The inplane AFM state is hard to stabilize due to the geometrical fluctuation of the triangle lattice. The LDA [shown in Fig. 1(a)] gives magnetic ground states for all doping $x$, which are inconsistent with experiments. In contrast, the phase diagram by LDA + Gutzwiller has three distinct regions, which can be understood as the consequence of competition among crystal-field splitting, interorbital charge, and spin fluctuation, as discussed in the following. As shown in Figs. 1(b) and 1(c), the features of phase diagram are qualitatively the same using $U = 3.0$ eV or $U = 5.0$ eV.

**Phase II:** Correlated nonmagnetic metal $(0.3 < x < 0.6)$.—First, the NM state is now correctly predicted for this region. It is known that LDA overestimates the tendency to be FM for several systems, such as ruthenates [18], and this artifact is even enhanced by LDA + $U$. The physical reason is that the correlation effect is not properly treated in LDA and LDA + $U$, but it is well included in the present formalism. In Fig. 2 we summarize the properties of the NM solutions for the whole doping range. For $x$ larger than 0.3, as shown in Fig. 2(a), the $e'_g$ bands are fully occupied and the interorbital fluctuation (defined as $F$ and $S$, see caption of

![Phase Diagram of Na$_x$CoO$_2$](image)
FIG. 2 (color online). Results for NM state as a function of doping $x$ with $U = 5.0$ eV and $J = 1.0$ eV. (a) Occupation numbers, (b) band renormalization $Z^b$ factors, interorbital charge fluctuation $F = \langle \hat{n}_{i\alpha_1} \hat{n}_{j\alpha_2} \rangle - \langle \hat{n}_{i\alpha_1} \rangle \langle \hat{n}_{j\alpha_2} \rangle$, interorbital spin fluctuation $S = \langle \hat{S}_{i\alpha_1} \hat{S}_{j\alpha_2} \rangle - \langle \hat{S}_{i\alpha_1} \rangle \langle \hat{S}_{j\alpha_2} \rangle$, and (c) level splitting $\Delta = e_{\alpha_1} - e_{\alpha_2}$. The inset of (a) gives the calculated $e'_g$ occupation for $x = 0.3$ as a function of $U$ and $\Delta$ by using the tight-binding Hamiltonian $H[Z]$ defined in Ref. [13]. It can be well compared to DMFT results [13].

Fig. 2 is weak, indicating an effective single band system. However, with $x$ approaching the phase boundary around $x_c = 0.3$, a crossover to multiband behavior has been detected from the strong interorbital spin and charge fluctuation as shown in Fig. 2(b). Such fluctuations in the low doping area are induced by the Hund’s rule coupling, which favors even distribution of electrons among different orbitals with the same spin. Because of the presence of the correlation effect, the quasiparticle band width (kinetic energy) is renormalized by a factor $Z^b$ which is about 0.5 (0.7) for the $a_{1g}$ ($e'_g$) state at $x = 0.3$ (as shown in Fig. 2). The same amplitude of renormalization is reported by ARPES [7].

Second, it has long been a controversial issue whether or not the $e'_g$ states cross the Fermi level. To answer this question, the correlation renormalized level shift is crucial (as shown in Fig. 2(c) the $a_{1g}$-$e'_g$ level splitting $\Delta$ is much renormalized compared to LDA results). Unfortunately, after including the correlation effect, two studies have been done, and conflicting results are drawn [10,12] for $x = 0.3$. It was recently pointed out by Marianetti et al. that the controversial is due to the different choice of crystal-field splitting $\Delta$ in their TB model [13]. Using the same TB Hamiltonian $H[Z]$ [13] for $x = 0.3$ and changing $\Delta$, we recover Marianetti’s results as shown in the inset of Fig. 2(a). This demonstrates that our Gutzwiller approach can be well compared with DMFT. To go further, in our studies not only the crystal field is treated parameter-free, but also the full charge self-consistency is achieved. To see the difference, we performed one-loop calculations (i.e., the charge density is fixed to the LDA value and only Gutzwiller wave functions are optimized), then the $e'_g$ pockets are not present for $x = 0.3$. In addition, we also found that even for $x = 0.2$ the $e'_g$ pockets are not present in this one-loop calculation. However, after including the charge-density self-consistency, the renormalization of level splitting is suppressed [see Fig. 2(c)]. As a result, we found that $x = 0.3$ is the critical point, i.e., $e'_g$ pockets are absent for $x > 0.3$ but present for $x < 0.3$. Our calculated quasiparticle bands (as shown in Fig. 3 and discussed below) can be well compared with ARPES. Since with the interactions we used ($U = 5.0$ eV and $J = 1.0$ eV) the static Hartree-Fock shift is zero [12], the renormalized energy level shift here is fully contributed by the fluctuation effect. From Fig. 2(c), we found that the $\Delta$ is peaked in the crossover region indicating that the interorbital fluctuation is the main reason for the renormalization effect on the energy levels.

Phase III: Weakly correlated Stoner metal for $x > 0.6$.—Clearly seen from the calculated density of states [Fig. 3(d)], a sharp van Hove singularity (VHS) is present near the $a_{1g}$ band top edge (due to the flat dispersion). For the Na-rich side, the Fermi level is shifted close to the VHS, the Stoner instability makes the system FM (in-plane). This conclusion is supported by the following facts for this region: (1) LDA works qualitatively well, (2) the magnetic solution only weakly depends on interaction strength $U$ and $J$ (see Fig. 1), (3) calculated spin and charge fluctuations are all weak [Fig. 2(b)]. It is therefore suggested that strong correlation is not the driving force for the magnetic state; instead the VHS is responsible. Furthermore, we correctly predict that the A-type AFM state is more stable than the FM state (see the difference between the solid lines and the dashed lines in Fig. 1). From Fig. 3(d) for $x = 0.8$, it is seen that spin moment mostly comes from the $a_{1g}$ states, which aligns towards the $z$ direction (interlayer) of the crystal. According to the Goodenough-Kanamori rule, the exchange coupling along the $z$ direction is dominated by AFM superexchange, which stabilizes the A-type AFM state. In fact, the estimated interlayer exchange coupling (from the total energy difference between FM and A-type AFM solutions) is about $J_c = 3.0$ meV, in good agreement with experimental results [3]. From itinerant FM theory, the size of the spin moment may change with rising temperature, but in the presence of strong VHS near the band edge, this possibility is prevented by the sharp density barrier. Indeed we found that the calculated moments of FM and A-type AFM solutions are the same. Therefore, the $a_{1g}$ moment will behave like a localized spin as observed experimentally. In other words, the Curie-Weiss behavior in this region does not necessarily suggest the enhanced correlation.
The calculated phase diagram of Na$_4$CoO$_2$ for (a) $x = 0.35$, (b) $x = 0.5$, (c) $x = 0.75$ in the NM state. (d) The projected density of states for $x = 0.8$ in the A-type AFM state. $U = 5.0$ eV and $J = 1.0$ eV are used, and the spin-orbital coupling is included.

**Phase I**: Magnetic correlated metal: The main difference between phase I and phase II is that the $e_g$ band starts to cross the Fermi level and the $e_g$ hole pockets are present. Therefore, phase I is effectively a multiband system. Meanwhile, the magnetic instability is recovered, and the system is stabilized in the FM ground state. Several points should be addressed here to understand this phase: (1) In contrast to phase III, the FM state is slightly more stable than the A-type AFM state, (2) both $e_g$ and $a_{1g}$ contribute to the spin moment; in other words, the stabilization of the FM state is due to the enhancement of interorbit (rather than intraorbit) spin fluctuation [Fig. 2(b)], which is induced by the Hund’s rule coupling, (3) strong correlation (rather than VHS) is responsible for the magnetic instability. It is interesting to note that the critical point $x \sim 0.3$ (boundary between phase I and phase II) is close to the doping level where superconductivity was observed. The experimental information for this region is quite limited and not conclusive due to the difficulty of sample preparation; our prediction should be evaluated by future experiments [19].

Finally, we show systematically in Figs. 3(a)–3(c) the calculated quasiparticle band dispersion for $x = 0.35, 0.5, 0.7$ after including the spin-orbital-coupling effect. The overall picture can be nicely compared to ARPES data [7]. In particular, (1) the band width renormalization around a factor of 2 is now obtained, (2) the $e_g$ Fermi surface pocket is absent, (3) the $a_{1g}$–$e_g$ anticrossing along the $\Gamma$–$K$ line is nothing but an effect of spin-orbital coupling, and the gap around 0.1 eV is comparable to experimental data [20].

In summary, using the recently developed LDA + Gutzwiller method, we are now able to calculate the ground state total energy of correlated multiorbital systems from *ab initio* after taking into account the orbital fluctuation. The calculated phase diagram of Na$_4$CoO$_2$ establishes a general understanding for the physics behind this. Most of the discrepancies between experiments and previous theories, such as the $e_g$ pocket, $a_{1g}$–$e_g$, anticrossing, and the Curie-Weiss behavior for $x > 0.5$, are self-consistently understood. Three distinct phase regions are identified, which is instructive to future experiments.

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[16] Gutzwiller approximation is used to solve the problem. See Ref. [14] for detailed formalism as well as benchmark results for several typical systems.
[19] Recently $x = 0.0$ end compound was studied experimentally [see, for example, C. de Vaulx et al., Phys. Rev. Lett. 98, 246402 (2007)], and correlated metallic state is suggested, consistent with our prediction. Unfortunately the samples are prepared from Li$_2$CoO$_2$, which has different crystal structure from Na$_4$CoO$_2$.