

Role of Hybridization in Na_xCoO_2 and the Effect of Hydration

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Density functional theory is used to understand the electronic properties of $\text{Na}_{1/3}\text{CoO}_2$ and $\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$. Comparing the charge density of CoO_2 and the Na doped phases indicates that doping does not simply add electrons to the t_{2g} states. In fact, the electron added in the t_{2g} state is dressed by hole density in the e_g state and electron density in the oxygen states via rehybridization. In order to fully understand this phenomenon, a simple extension of the Hubbard Hamiltonian is proposed and solved using the dynamical mean-field theory. This model confirms that the rehybridization is driven by a competition between the on-site Coulomb interaction and the hybridization, and results in an effective screening of the low-energy excitations. Finally, we show that hydration causes the electronic structure to become more two dimensional.

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Na_xCoO_2 and its hydrated counterpart are receiving renewed interest due to the discovery of superconductivity [1], in addition to anomalous thermoelectric properties [2]. Understanding these properties requires a detailed understanding of the low energy Hamiltonian in this material. While there are many interesting parallels between the cuprates and Na_xCoO_2 , the details of the electronic structure are quite different. In Na_xCoO_2 , the Fermi level lies within the t_{2g} states, with $x = 1$ corresponding to a band insulator with filled t_{2g} states and $x = 0$ corresponding to one t_{2g} hole per cobalt (possibly a Mott insulator). One of the useful steps forward in understanding the cuprates was the work of Zhang and Rice, in which they derived an effective one band model [3]. Initial studies of the low energy physics of Na_xCoO_2 have assumed a one band model [4–7], given that the octahedra in this structure are distorted and the t_{2g} levels are split into a onefold a_{1g} level and a twofold e'_g level (not to be confused with the usual e_g levels) [8]. However, the potential influence of the e_g orbitals and the oxygen orbitals on the low energy physics has not yet been addressed.

Na_xCoO_2 crystallizes in a layered structure, in which the layers are two-dimensional triangular lattices of a given species. The layers alternate as Na-O-Co-O and this pattern is repeated. Both the Na and the Co reside in sites which are coordinated by distorted oxygen octahedra. Insertion of water causes the oxygen layers to be pried apart, resulting in an even more two-dimensional-like structure [1]. Co exists in the low spin state due to the appreciable crystal field splitting. When $x < 1$ Co is in a mixed valence state, $\text{Co}^{3+}/\text{Co}^{4+}$, yielding an average electronic configuration t_{2g}^{6-x} . However, the large overlap of the e_g and the oxygen states creates strong hybridization and therefore an appreciable occupation of the e_g states and hole density on the oxygen states. Previous density functional theory (DFT) calculations addressing

Na_xCoO_2 focused on the magnetic properties, in addition to rationalizing the transport properties in terms of the LDA density of states [9,10]. However, hydration was not explicitly considered.

All LDA calculations were performed using the Vienna *ab initio* simulation package (VASP) [11]. VASP solves the Kohn-Sham equations using projector augmented wave pseudopotentials [12,13] and a plane wave basis set. A cutoff energy of 600 eV was chosen and k -point meshes of $6 \times 6 \times 3$ were used for all cells. Experimental structural parameters were taken as a starting point for full structural relaxations [14,15]. Local density approximation (LDA) calculations were performed for $\text{Na}_{1/3}\text{CoO}_2$ and $\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$. The ordering of the Na atoms has been determined for both structures, and the ordering of the water molecules has been narrowed to a few possibilities [14,15]. We selected the higher symmetry configuration proposed by Jorgensen *et al.* [Fig. 8a in Ref. [15]]. Regardless of whether or not this particular ordering happens to be the ground state, the qualitative effect should be similar.

The LDA bands for $\text{Na}_{1/3}\text{CoO}_2$ and $\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$ are presented in Fig. 1. In both cases, a stable moment of $2/3$ Bohr magnetons per formula unit is found. The respective band structures demonstrate that the t_{2g} bands are similar, illustrating that hydration does not have any dramatic effect on the low energy physics. In both cases the dispersion in the z direction is small, which is a result of the two-dimensional nature of both the hydrated and nonhydrated compound. One notable difference is that the bands in the hydrated case display less splitting due to interlayer coupling at any given k point. Given the supercell that we have chosen, only nine t_{2g} bands would be distinguishable at a generic k point if the layers did *not* interact (i.e., the unit cell contains 3 Co basis atoms per plane). Interlayer coupling will induce band splitting, and this is more pronounced for $\text{Na}_{1/3}\text{CoO}_2$ than

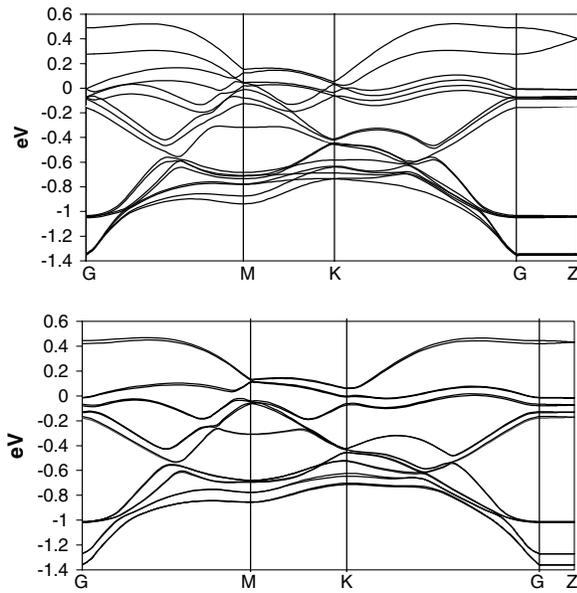


FIG. 1. LDA majority t_{2g} bands for $\text{Na}_{1/3}\text{CoO}_2$ (top panel) and $\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$ (bottom panel). The Fermi energy is at zero. $G = (0, 0, 0)$, $M = (1/2, 0, 0)$, $K = (2/3, 1/3, 0)$, and $Z = (0, 0, 1/2)$.

$\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$. This reflects the fact that the layers are more isolated in the hydrated case, and hence more two dimensional, which is commonly believed to be an important ingredient of superconductivity in the cuprates [16]. It might be argued that the differences in the band structures are small, but it may still be relevant considering that the superconducting transition temperature is roughly 4 K.

Upon doping CoO_2 with Na, the Na will largely donate its electron at the Fermi energy. Therefore the changes in the ground state upon doping should qualitatively resemble the nature of the low energy excitations of the system. Given that the LDA density of states (DOS) for Na_xCoO_2 shows the Fermi energy to lie within the t_{2g} states, which only have a relatively small mixing with oxygen, one might expect that the electron addition state upon doping is some linear combination of t_{2g} orbitals in addition to some small oxygen character. We shall demonstrate that this is not true, indicating that the LDA bands are behaving in an extremely nonrigid fashion. In order to accurately characterize the changes in the ground state upon doping CoO_2 , it is useful to plot the charge density which has been added to the system. This can be done by subtracting the charge density of CoO_2 from that of $\text{Na}_{1/3}\text{CoO}_2$ calculated with the same structural parameters.

The difference in charge density between CoO_2 and $\text{Na}_{1/3}\text{CoO}_2$ is shown in Fig. 2, which illustrates that the addition states are not simply t_{2g} orbitals. In fact, electron density is added to the t_{2g} states, hole density is added to the e_g states, and electron density is added to the oxygen states. This can be explained intuitively as a multistep process, and this hypothesis will be justified below. LDA

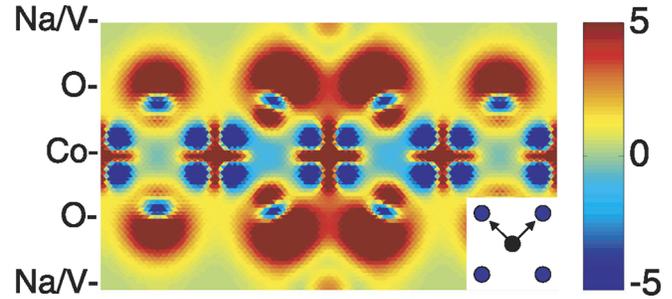


FIG. 2 (color online). The total charge density difference of $\text{Na}_{1/3}\text{CoO}_2-\text{CoO}_2$. A plane which cuts through the Co-oxygen octahedral plane was chosen. The horizontal rows of Na/vacancies, oxygen, and Co are labeled. Na atoms are located at the center of top and bottom rows. Units are in electrons/ \AA^3 . The inset shows the orientation of Co-O octahedron [black (center sphere) and blue (outer spheres), respectively].

predicts an appreciable occupation of the e_g orbitals for CoO_2 , roughly 1.7 electrons in a 1 \AA sphere around Co, due to the large hybridization between the directly overlapping oxygen and e_g states. When charge is added to the system, electron density in the t_{2g} orbitals will increase causing an increase of the Co on-site Coulomb repulsion. The on-site Coulomb repulsion can be minimized by unmixing the oxygen and e_g orbitals in order to decrease the occupation of the e_g orbitals. Therefore, this rehybridization mechanism is a *competition* between the e_g -oxygen hybridization and the Co on-site Coulomb interaction. Clearly, this logic can be inverted to explain the behavior of $\text{Na}_{1/3}\text{CoO}_2$ when Na is removed and holes are introduced into the system. In this case, holes are introduced into the t_{2g} states, in addition to electrons in the e_g states and holes in the oxygen states. The system increases the hybridization, and therefore the occupation of the e_g orbitals, because there is less t_{2g} density to interact with e_g density. One can think of the rehybridization as a quasiparticle in which the particle (electron or hole) in the t_{2g} states has been dressed by a rehybridization cloud. A more quantitative analysis of the effect can be given by integrating the change in charge density within a 1 \AA sphere centered on each atom. The oxygens gain 0.73 electrons per unit cell, while Co gains only 0.12 electrons per unit cell due to the rehybridization mechanism. It should be noted that the Na potential clearly does have a notable effect on the rehybridization. The oxygen orbitals nearest the Na are preferentially occupied in order to more effectively screen the Na potential.

Hints of this rehybridization effect were noticed computationally in a study of Li_xTiS_2 over 20 years ago [17]. The authors note that most of the net incoming charge ends up on the sulfur as Li is added to the material. Studies of Li_xCoO_2 characterized this phenomena much more clearly [18,19]. Wolverton and Zunger made an important realization in understanding this phenomenon by suggesting that it is driven by a need to minimize the change in the total Co d orbital occupancy and that it is

similar to what is observed for transition metal impurities in semiconductors [19]. This effect is likely to occur in many other transition metal oxides in which electrons or holes are being doped into the t_{2g} states, such as Na_xTiO_2 and Li_xVO_2 . A similar rehybridization effect may occur when doping electrons (holes) directly into the e_g manifold, and this has been explored in detail for the cuprates [20,21]. It was found that placing two holes on a single CuO_6 unit results in a rehybridization which reduces the Coulomb repulsion. X-ray absorption experiments for Li_xCoO_2 and Na_xCoO_2 show strong changes in the oxygen $1s$ signal

which is consistent with the rehybridization mechanism [22–25].

While LDA gives an indication of the nature of the addition state, it cannot even qualitatively predict the excitation energies of the system when the electronic correlations are strong. If the rehybridization mechanism is indeed the result of a competition between hybridization and the on-site Coulomb interaction, one should be able to capture this effect within a Hubbard-like model. The qualitative effects of the hybridization on the low energy excitations may then be explored within the modified Hubbard model. Consider the following model Hamiltonian:

$$H = \sum_{i,\sigma} [\varepsilon_p p_{i,\sigma}^\dagger p_{i,\sigma} + \varepsilon_e e_{i,\sigma}^\dagger e_{i,\sigma} + T_{p-e} (e_{i,\sigma}^\dagger p_{i,\sigma} + p_{i,\sigma}^\dagger e_{i,\sigma})] + \sum_{i,j,\sigma} w_{ij} t_{i,\sigma}^\dagger t_{j,\sigma} + U \sum_{i,\sigma} [e_{i,\sigma}^\dagger e_{i,\sigma} t_{i,\sigma}^\dagger t_{i,\sigma} + t_{i,\uparrow}^\dagger t_{i,\uparrow} t_{i,\downarrow}^\dagger t_{i,\downarrow} + e_{i,\uparrow}^\dagger e_{i,\uparrow} e_{i,\downarrow}^\dagger e_{i,\downarrow}] - \mu \sum_{i,\sigma} [p_{i,\sigma}^\dagger p_{i,\sigma} + e_{i,\sigma}^\dagger e_{i,\sigma} + t_{i,\sigma}^\dagger t_{i,\sigma}] \quad (1)$$

This model contains three orbitals (p , t , e) which can be analogously thought of as the oxygen p orbitals, the transition metal t_{2g} orbitals, and the transition metal e_g orbitals. The respective annihilation operators are denoted as p , e , and t . We allow for hybridization only between the p orbital and the e orbital as the oxygen orbitals hybridize much more strongly with the e_g orbitals than the t_{2g} for transition metals in an octahedral site. A Coulomb repulsion U is included for the e and t electrons, and for simplicity we allow only the t electrons to hop. The hopping parameters for the t electrons, w_{ij} , are

chosen to yield a semicircular density of states of width 1 eV centered about zero. Additionally, we choose $\varepsilon_p = -1.5$, $\varepsilon_e = 1$, $T_{p-e} = 2$, and $U = 3$ eV. This model contains all the necessary ingredients to qualitatively demonstrate the rehybridization mechanism.

The above model is not solvable in general, and we shall therefore employ the dynamical mean-field theory [26] (DMFT) as an approximation. Using a path integral representation of the partition function, the effective action for this model can be written in infinite dimensions as follows:

$$S_{\text{eff}} = \int_0^\beta \int_0^\beta d\tau d\tau' t^\dagger(\tau) G_t^o(\tau - \tau') t(\tau') + \int_0^\beta d\tau e^\dagger(\tau) G_e^o(\tau) e(\tau) + U \int_0^\beta d\tau \sum_{i,\sigma} [e_{i,\sigma}^\dagger(\tau) e_{i,\sigma}(\tau) t_{i,\sigma}^\dagger(\tau) t_{i,\sigma}(\tau) + t_{i,\uparrow}^\dagger(\tau) t_{i,\uparrow}(\tau) t_{i,\downarrow}^\dagger(\tau) t_{i,\downarrow}(\tau) + e_{i,\uparrow}^\dagger(\tau) e_{i,\uparrow}(\tau) e_{i,\downarrow}^\dagger(\tau) e_{i,\downarrow}(\tau)], \quad (2)$$

where

$$G_e^o(\tau) = \{\partial_\tau - \varepsilon_e + \mu - [T_{p-e}^2 / (\partial_\tau - \varepsilon_p + \mu)]\}^{-1}, \quad (3)$$

and G_t^o is the bath function for the t electrons which has to be determined self-consistently using Eq. (4), where D is the quarter bandwidth:

$$G_t^o(i\omega_n) = [i\omega_n + \mu - D^2 G_t(i\omega_n)]^{-1}. \quad (4)$$

The Grassman variables for the oxygen states have been integrated out. Because of the fact that we have assumed that the e electrons have no intersite hopping, G_e^o will remain unchanged. The above effective action corresponds to a two orbital Anderson impurity model, and we solve this by decoupling the quartic terms using a discreet Hubbard-Stratonavitch transformation [27], and evaluate the resulting summation using the Hirsch-Fye quantum Monte Carlo [26,28].

First, we demonstrate how the occupation of the t and e orbitals changes as the total density is varied (see Fig. 3).

When the t orbital is nearly empty, the e orbital has an occupation of roughly 0.45 electrons due to the strong hybridization with the oxygen. As the density increases and the t orbital is filled, the e orbital empties and the p orbital is filled. Thus we clearly observe the rehybridization mechanism in this simple model. It does not appear to be as strong as in LDA calculation of Na_xCoO_2 , where the gain in density in the t_{2g} orbitals is largely canceled by the loss in e_g occupation. However, this is not totally surprising given the simple nature of the model we have chosen. Most notably, we provided only one e orbital when there are two in the real material.

In order to explore the effect of the hybridization on the low energy excitations of the system, we have performed calculations at different values of T_{p-e} while maintaining a half filled t band. The parameters chosen for this model yield a Mott insulator, as indicated by the gap in the spectral function of the t electrons (see Fig. 4). The gap is shown to decrease as T_{p-e} is increased, demonstrating that the hybridization among the e and p orbitals results

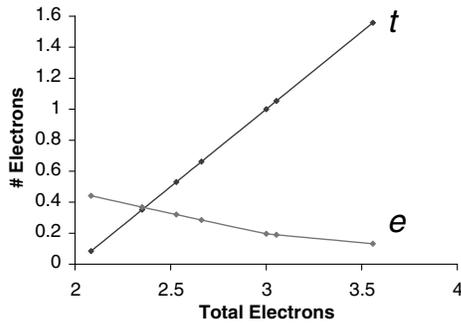


FIG. 3. Total occupation of the e and t orbitals as a function of the total density.

in an effective screening of the interactions among the t electrons. This can be most easily understood by considering the dispersionless limit of the t electrons [i.e., $w_{ij} = 0$ in Eq. (1)] in which the gap is $E_{\text{gap}} = E(N + 1) + E(N - 1) - 2E(N)$, where the energies correspond to a given lattice site. As we demonstrated above, the rehybridization mechanism will cause the e_g orbitals to empty for the $N + 1$ particle state and fill for the $N - 1$ particle state. Increasing T_{p-e} will cause the energy of all three terms to decrease. The $N - 1$ particle energy will decrease the most as it can hybridize the most due to the absence of the t electron, while the $N + 1$ particle energy will decrease the least as it can hybridize the least due to the doubly occupied t orbitals. The net effect is that the decrease in $E(N + 1) + E(N - 1)$ is greater than the decrease in $2E(N)$, and hence the gap is decreased. This is straightforward to verify by diagonalizing Eq. (1) for $w_{ij} = 0$.

To conclude, we have shown that the states added to CoO_2 are not simply electrons in the t_{2g} states, but rather an electron in the t_{2g} state dressed by hole density in the e_g state and electron density in the oxygen state. This rehybridization results from a competition between oxygen- e_g hybridization and the Co on-site Coulomb interactions. The LDA result is corroborated with a modified Hubbard model which we proposed and solved using

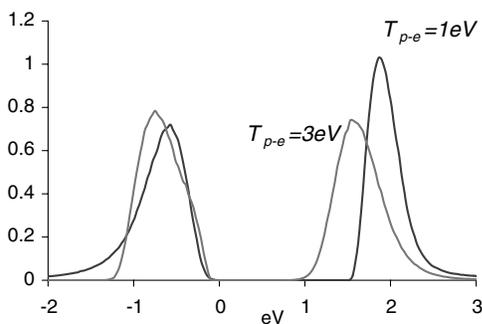


FIG. 4. Local spectral function for the t electrons $[(-1/\pi)\text{Im}G_t(\omega)]$. Spectral functions for the e and p electrons are not shown as they are higher or lower in energy.

DMFT. Our DMFT calculations indicate that the presence of e_g -oxygen hybridization effectively results in a screening of the low energy t_{2g} excitations. This indicates that the oxygen states and e_g states should be considered when deriving a low energy Hamiltonian for Na_xCoO_2 and its hydrated counterpart. We note that this behavior can be seen in several other similar materials, and that this is a rather general phenomenon. Comparing the LDA bands for $\text{Na}_{1/3}\text{CoO}_2$ and $\text{Na}_{1/3}\text{CoO}_2(\text{H}_2\text{O})_{4/3}$ shows a reduction in the band splitting due to a decrease of the interlayer coupling. This indicates that hydration does result in a more two-dimensional electronic structure, and this fact may be related to why hydration is required to create the superconducting state.

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