PHYSICAL REVIEW B **78**, 012501 (2008)

# Origin of $a_{1g}$ and $e_g'$ orderings in $Na_xCoO_2$

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(Received 23 April 2008; published 8 July 2008)

It has often been suggested that correlation effects suppress the small $e_g'$ Fermi-surface pockets of $Na_xCoO_2$ that are predicted by LDA, but absent in ARPES measurements. It appears that within the dynamical mean-field theory (DMFT) the ARPES results can be reproduced only if the on-site energy of the $e_g'$ complex is lower than that of the $a_{1g}$ complex at the one-electron level, *prior* to the addition of local correlation effects. Current estimates regarding the order of the two orbital complexes range from −200 to 315 meV in terms of the energy difference. In this work, we perform density-functional theory calculations of this one-electron splitting $\Delta = \epsilon_{a_{1g}} - \epsilon_{e_g'}$ for the full two-layer compound, accounting for the effects of Na ordering, interplanar interactions and octahedral distortion. We find that $\epsilon_{a_{1g}} - \epsilon_{e_g'}$ is negative for all Na fillings and that this is primarily due to the strongly positive Coulomb field created by $Na^+$ ions in the intercalant plane that disproportionately affects the extended $a_{1g}$ orbital. We discuss also the effects of octahedral compression and multiorbital filling on the value of $\Delta$ as a function of Na content. Our results indicate that if the $e_g'$ pockets are indeed suppressed, that can only be due to nonlocal correlation effects beyond the standard DMFT.

DOI: 10.1103/PhysRevB.78.012501 PACS number(s): 74.25.Jb, 74.72.−h, 74.70.−b

Since shortly after the discovery of superconductivity in hydrated $1.4H_2O \cdot Na_{0.35}CoO_2$,[1] there has been controversy surrounding the discrepancy between the calculated and observed Fermi surfaces (FS) of the parent compound, $Na_xCoO_2 (x=1/3)$ density functional theory (DFT) calculations show a large central FS, surrounded by six small elliptical hole pockets,[2] while angular-resolved photoemission (ARPES) measurements find the large pocket but do not see the smaller ones.[3–6] The presence or absence of these small pockets drastically changes the response properties of the system, and a number of proposed superconductivity models depend on them.[7–10] There are two basic ways to resolve the controversy: either the experiment is not representative of the bulk electronic states, or correlation effects beyond the DFT calculations qualitatively change the Fermiology. The latter seems rather plausible, given the narrow width of the Co $t_{2g}$ bands and the fact that DFT fails to reproduce the nonmagnetic ground state for $x \lesssim 0.7$. The effects of adding correlation have been recently addressed through DMFT calculations which account for both on-site Coulomb repulsion (Hubbard $U$) and local fluctuation effects (albeit not for long-wavelength ferromagnetic calculations, compatible with the observed at $x \gtrsim 0.5$ magnetic interactions in this system). Despite initial controversy,[11–13] it has been firmly established that DMFT calculations only agree with ARPES if the centroids of the $a_{1g}$ and $e_g'$ Co $d$-bands are such that $\epsilon_{a_{1g}}$ is higher than $\epsilon_{e_g'}$, which would yield a positive splitting, $\Delta = \epsilon_{a_{1g}} - \epsilon_{e_g'} > 0$. If, on the other hand $\epsilon_{a_{1g}} - \epsilon_{e_g'} < 0$, then the small hole pockets are preserved and even slightly enlarged. This result does not depend on the value of $U$ or the particular Hamiltonian used in the calculation.[14] The sign of $\Delta$ is therefore of great importance, but difficult or impossible to access experimentally. A tight-binding fit to full potential density-functional theory calculations[7] employing all 5 Co $d$ orbitals and 3 O $p$ orbitals in a double layer system found a strongly negative $\Delta \sim -200$ meV for $x=0.3$. Other tight-binding models fit to a one-layer system and employing a smaller basis set of Co $t_{2g}$ orbitals[11,15] found $\Delta \sim -144$ meV, and an alternate procedure for extracting $\Delta$ from the band structure yielded a value of $\sim 100$ meV.[12] On the other hand, quantum chemical calculations of embedded clusters for hydrated $Na_{1/3}CoO_2$ [16,17] invariably find a positive $\Delta = 315$ meV. There has so far been little understanding of what might cause such strong discrepancy between the values obtained through the two different methodologies.

In this work, we present DFT calculations of $\Delta$ that include both layers of the double-layer unit cell and real Na ions (no virtual crystal or other approximation) and we extract our values directly from the DFT calculation without employing a tight-binding fit. It is crucial to understand that $\Delta$ is controlled entirely by the electrostatic field at the Co site and Co-O overlap integrals, which are both accurately described by DFT. Note that, within DFT, the Fermi surface itself hardly depends on the sign of $\Delta$, as long as $|\Delta|$ is moderate, but the effect of the local correlation effects (as evaluated by DMFT) is drastically different. At every Na doping level and for every reasonable value of octahedral compression, we find that $\Delta$ is negative. We find that the main cause of the ordering between $a_{1g}$ and $e_g'$ orbitals is the positive Na potential in the interstitial plane that drives the out-of-plane $a_{1g}$ orbitals downward in energy.[18] The possibility of this effect was noted in Ref 19, but because an artificially orbital-independent Na potential was employed, the large effect on $\Delta$ was missed. Interestingly, we find that octahedral distortion as an isolated factor *increases* $\Delta$, a reversal of crystal-field predictions for $CoO_6$ octahedra. This highlights the strong role of Na to re-establish a negative $\Delta$ and emphasizes that Co-O hybridization depends on interactions beyond the $CoO_6$ octahedra.

## I. CALCULATIONAL METHODS

All calculations have been performed using a plane-wave density-functional theory code, the VIENNA AB-INITIO SIMU-

LATION PACKAGE (VASP).[20] The projected augmented wave method (PAW)[21] was used along with the generalized gradient approximation[22] to the exchange-correlation potential. A $1\times1$, $2\times2$, and $\sqrt{3}\times\sqrt{3}$ cells were used to simulate the bulk with varying concentrations of Na. Ground state geometries were fully optimized using a Monkhorst Pack $k$-point mesh of $6\times6\times2$ for the $1\times1$ cell and $4\times4\times2$ for the $2\times2/\sqrt{3}\times\sqrt{3}$ cell. For the total-energy calculation and density of states (DOS), the Brillouin zone integrations were performed on a $8\times8\times4$ mesh.

To calculate $\Delta$, we first consider the Co plane in a cubic coordinate system where three Co atoms are located equidistant along the $x$, $y$, and $z$ axes, i.e., they form a plane perpendicular to the 111 cubic axis which is also the $z$ axis in the hexagonal system. In this cubic system, it is easy to explicitly write out the $a_{1g}$ and $e_g'$ orbitals:

$$a_{1g} = \frac{XY + YZ + XZ}{2}$$

$$e_g' = XY - \frac{XZ - YZ}{2}$$

$$e_g' = \frac{\sqrt{3}(YZ - XZ)}{2} \tag{1}$$

Standard band-structure codes project the density of states onto the three symmetry representations appropriate for a hexagonal symmetry, that is, $N_{z^2}$ projects onto the $3z^2-1$ orbital, and $N_{x^2-y^2,xy}$ and $N_{xz,yz}$ each give the total projection onto the two orbitals belonging to each respective representation. Since the projected density of states contains the square of the projected orbital, we square each term in Eq. (1), rotate to the hexagonal system and keep only the terms conforming to the correct symmetry. This serves to eliminate (to first order) the unoccupied $e_g$ states that share the same irreducible representation as the $e_g'$ states and mix with them to some degree[17,23] in the hexagonal symmetry. The resulting recipe is:

$$N_{a_{1g}}(\epsilon) = N_{z^2}(\epsilon) \tag{2}$$

$$N_{e_g'}(\epsilon) = N_{x^2-y^2,xy}(\epsilon) + 2N_{xz,yz}(\epsilon) \tag{3}$$

The onsite parameters from this procedure are not identical to those in the effective $3\times3$ Hamiltonian, so far used in DMFT calculations because the latter contain not only the Co-based $a_{1g}$ and $e_g'$ states, but also the hybridized O states. These can be obtained only by downfolding the calculated Bloch functions onto Wannier functions, as has been done before.[11,12,15,24] Still, our method can be used to estimate the changes in $\Delta$ brought about by different factors, such as octahedral distortion, Na filling, or Na ordering. In several cases where we have compared our values of $\Delta$ to those calculated from the Wannier functions of a three band model, we have found that the latter are always *more* negative than the values extracted directly from DFT. It is worth noting that these Wannier functions are very long range, having a sizeable weight not only on O and on nearest-neighbor Co's but even at the third neighbor Co sites. This may have an effect on the onsite energy ordering, although we believe it will be quantitative, not qualitative. An additional effect of this extent is a strong reduction of the Hubbard $U$ as compared to typical values for local $d$ orbitals in transition-metal oxides.

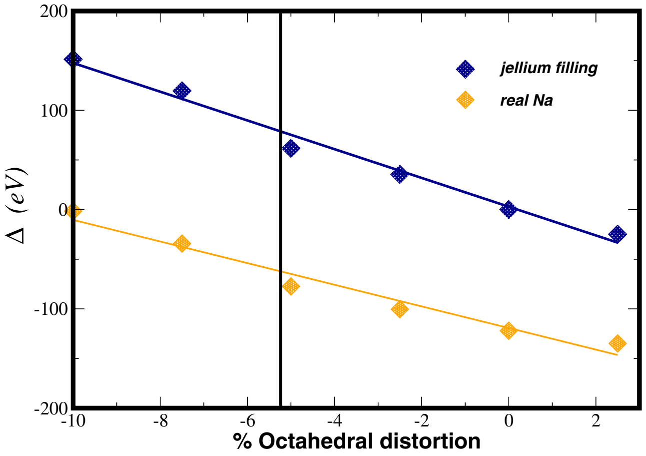

FIG. 1. (Color online) $\Delta \equiv \epsilon_{a_{1g}} - \epsilon_{e_g'}$ as a function of octahedral distortion in the jellium filled and real Na filled compounds. The vertical bar at ~5.2% marks the position of the octahedral compression obtained through relaxing the oxygen height in our calculations.

### A. Results and discussion

We first address the effect of the octahedral compression (trigonal distortion) that lowers the symmetry at the Co site and splits the $t_{2g}$ triplet into the $a_{1g}$ and $e_g'$ complexes. Some previous works have assumed that the distortion destabilizes the $a_{1g}$ state,[25–28] while others assume oppositely that the $e_g'$ state is higher in energy.[24,29] We have examined this question from two points of view. First, we have constructed a tight-binding model of a $CoO_6$ octahedron (including the three Co $t_{2g}$ orbitals and three $p$ orbitals on each of the six O atoms) and diagonalized the resulting matrix for both compressive and expansive distortions. Using the canonical scaling of the $t_{dp\sigma}$ and $t_{dp\pi}$ parameters, namely $t_{dp\sigma}=\sqrt{3}t_{dp\pi}$, we find that the compressive distortion, as seen in $Na_xCoO_2$ for all $x$, destabilizes the $e_g'$ state. However, if the ratio of the two parameters were to be increased by approximately a factor of two, as has been seen in some cases,[30] the order of energies is reversed and the $a_{1g}$ state is destabilized. Second, we have performed a full DFT calculation of $\Delta$ as a function of the trigonal distortion. We use a fictitious compound, $e^-CoO_2$, in which one electron per formula unit has been added to the $CoO_2$ compound to achieve the band-insulating state, analogous to $NaCoO_2$. The extra charge is compensated by a uniform positive background. We use this technique, termed "jellium filling," to eliminate the effects of the Na potential and of unequal band fillings, which we discuss in later sections. As can be seen in Fig. 1, octahedral compression always produces a positive $\Delta$, i.e., the $a_{1g}$ state is raised above the $e_g'$. This demonstrates that the scaling of $t_{dp\sigma}$ and $t_{dp\pi}$ is outside the canonical range and points to the

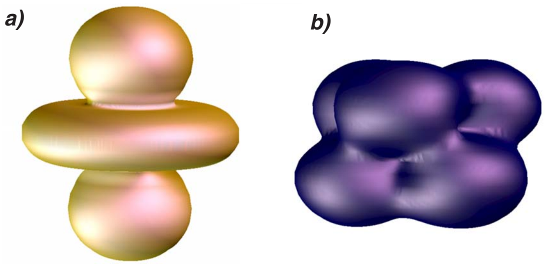

FIG. 2. (Color online) Charge density plots for (a) the $a_{1g}$ and (b) the $e'_g$ complexes of $NaCoO_2$. The plots employ squared wave functions, produced using full DFT calculations, taken at the Γ point where the $a_{1g}$ and $e'_g$ states are pure. The sum over both squared $e'_g$ orbitals is shown in (b).

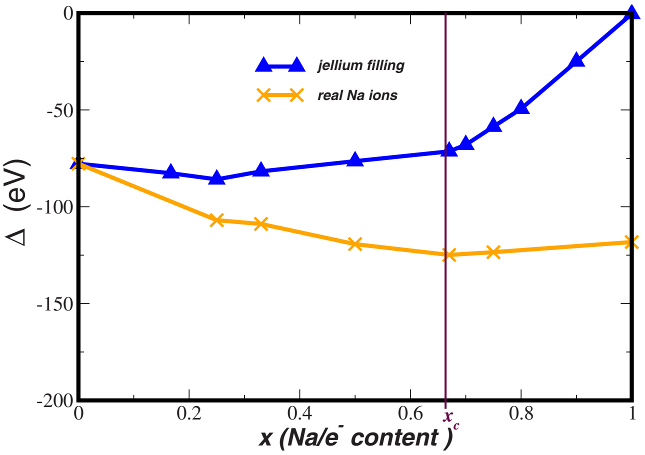

FIG. 3. (Color online) $\Delta \equiv \epsilon_{a_{1g}} - \epsilon_{e'_g}$ as a function of electron filling for jellium filled and real Na filled compounds. The critical doping $x_c$ where the $e'_g$ complex becomes completely filled is marked by a vertical bar.

importance of neighbors beyond the surrounding O atoms.

By far, the strongest factor determining the value of Δ is the presence of ionized Na atoms in the intercalant plane (their strong influence was noted for other reasons in Ref. 31). The positive Coulomb field, which the Na ions produce strongly, shifts the $a_{1g}$ orbital downward compared to the $e'_g$ orbital. As seen in Fig. 2, the $a_{1g}$ orbital has a greater extent along the $z$ direction ($c$ axis of the crystal) and therefore penetrates further into the Na plane. The resultant lowering of the $a_{1g}$ states is sufficient to shift the sign of Δ from positive to negative. Replacing the jellium filling discussed above with real Na ions, we find a negative shift of approximately 150 meV in Δ for all trigonal distortions, as seen in Fig. 2. Because quantum chemical calculations consider the *hydrated* structure in which the Na ions are far above the Co-oxide plane, the influence of the Coulomb field on the two Co-derived orbitals is so strongly diminished such that the sign of Δ is reversed. Not surprisingly, when Na ions are located directly atop a Co ion ($2b$ site), the effect is stronger than when they are located equidistant between three Co ions ($2c$ site).

The final factor contributing to the size of Δ is the nonuniform filling of the two band complexes. For all $x$, the $a_{1g}$ bands are less filled than the $e'_g$ bands. At a critical filling of $x_c \sim 0.67$, the $e'_g$ complex becomes entirely filled, leaving holes only in the $a_{1g}$ bands. The increased on-site Coulomb repulsion due to greater filling drives the $e'_g$ states upward in energy compared to $a_{1g}$ bands. In the absence of real Na ions (hence, no positive interstitial Coulomb field) and without octahedral distortion, the calculated Δ for $CoO_2$ is −77 meV, reflecting this multiband effect. We have calculated Δ for $Na_xCoO_2$ and for $xe^-CoO_2$ (jellium filling) as a function of $x$, with all oxygen positions fixed to perfect octahedra. For the jellium filled compounds, Δ initially remains approximately constant and then increases dramatically at $x_c \sim 0.67$ where the $e'_g$ bands become entirely filled, as seen in Fig. 3. The $Na_xCoO_2$ curve, on the other hand, decreases initially and then flattens out once the $e'_g$ complex is full. In the former case, electrons are added to both $e'_g$ and $a_{1g}$ states at low $x$, pushing both complexes upward nearly equally. Once the $e'_g$ holes are filled, all further electrons enter the $a_{1g}$ complex, pushing the $a_{1g}$ onsite energy up relative to $e'_g$ and causing Δ to increase. The situation is more complex when real Na ions are added. At low $x$, both $e'_g$ and $a_{1g}$, electrons are added to both complexes and on-site repulsion raises both energies together, but the increasingly positive Coulomb field created by adding Na ions pushes the $a_{1g}$ states downward. Δ therefore increases with $x$ as long as holes remain in both symmetry complexes. After $x_c$, where additional electrons enter only the $a_{1g}$ complex, the positive Coulomb field acts oppositely to the increased on-site repulsion. Apparently the magnitude of these two effects is approximately equal, as evidenced by the nearly constant Δ at $x > x_c$.

The effect of octahedral distortion on Δ competes with the effect of the positive $Na^+$ potential, and both are a function of the Na filling, $x$, which separately affects the $a_{1g}$ and $e'_g$ ordering. Having studied each of these factors individually, we proceed to calculate Δ as a function of $x$, accounting for all factors simultaneously. Both $a$ and $c$ lattice parameters and the ionic positions are relaxed at each Na filling in supercell calculation that include real Na ions. Our results are tabulated in Table I. Lechermann *et al.* have derived Δ for $x=0.5$ with Na in the Na2 position, by integrating the partial density of states and also by constructing first-principles Wannier functions, arriving at an estimate of −100 meV, in excellent agreement with our Table I. Their estimate for Delta at $x=1$ is also consistent with ours.[12] It is clear that Δ is a nonmonotonic function of $x$, owing to competition between the various effects associated with Na filling, but that it remains negative for all Na content $0 < x < 1$.

TABLE I. $\Delta \equiv \epsilon_{a_{1g}} - \epsilon_{e'_g}$ values for full DFT calculations. Values for Na placed at Na1 ($2b$ trigonal site) and at Na2 ($2c$ octahedral site) positions are given for comparison.

| $x$ | Na1 position | Na2 position |
|---|---|---|
| 0 | −80 meV | - |
| 1/3 | −100 meV | −95 meV |
| 2/3 | −114 meV | −101 meV |
| 1 | −77 meV | −6 meV |

## II. CONCLUSIONS

The crystal-field splitting $\Delta\ \epsilon_{a_{1g}}-\epsilon_{e_g'}$ is the parameter that controls the presence or absence of the controversial $e_g'$ pockets at the Fermi level in $Na_xCoO_2$. We have shown that, within the DFT framework, $\Delta$ is always negative and strongly so for low $x$, mainly due to the electrostatic crystal field of Na. We have demonstrated that the O ligand field (octahedral distortion) leads to the opposite sign of $\Delta$. This result indicates that local correlation and/or fluctuation effects are not responsible for suppressing the $e_g'$ Fermi sheets. Either long-range fluctuations, outside the scope of DMFT, or strong deviations from the bulk structure/stoichiometry such as surfaces, defects, or vacancies, must therefore account for the nonobservation of these pockets in ARPES.

## ACKNOWLEDGMENTS

We thank A. Liebsch for many helpful discussions and F. Lechermann for a critical reading of our manuscript and for sharing unpublished results. Research at NRL is funded by the Office of Naval Research. D.P. acknowledges support from the National Research Council Associateship Program.

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