

Comparison of the electronic structures of hydrated and unhydrated Na_xCoO_2 : The effect of H_2O

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We report electronic structure calculations within density functional theory for the hydrated superconductor $\text{Na}_{1/3}\text{CoO}_2 \cdot 1.33\text{H}_2\text{O}$ and compare the results with the parent compound $\text{Na}_{0.3}\text{CoO}_2$. We find that the intercalation of water into the parent compound has little effect on the Fermi surface outside of the predictable effects of expansion, in particular increased two dimensionality. This implies an intimate connection between the electronic properties of the hydrated and unhydrated phases.

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Two important discoveries during the past year, the likely unconventional superconductivity of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x \sim 1/3, y \sim 4/3$) and the unusual magnetotransport properties of Na_xCoO_2 ($x \sim 2/3$), have focused attention on these materials and the connection between them.¹ In fact, layered cobalt oxide materials have been the subject of considerable fundamental and practical interest in the last year for several reasons. Li_xCoO_2 is an important cathode material for lithium batteries. In that context, the interplay between the transition metal-oxygen chemistry, the Co mixed valence, and magnetism are important ingredients in the performance of the material.² Layered cobaltates, A_xCoO_2 also form for $A=\text{Na}$ and K , but in more limited concentration ranges.³ Single crystals of Na_xCoO_2 , with nominal $x=0.5$ were investigated by Terasaki and coworkers.⁴ Remarkably, they found that even though the material is a good metal, it also has a large thermopower of approximately $100 \mu\text{V}/\text{K}$ at room temperature. Thus an oxide showed promise of matching the thermoelectric performance of conventional heavily doped semiconductors for thermoelectric power conversion. Interest in modifications of this material to minimize its thermal conductivity for thermoelectric applications led to the discovery that similar anomalously high thermopowers were present in other materials with hole doped CoO_2 layers, especially so-called misfit compounds in which the intercalating Na is replaced by more stable rocksaltlike oxide blocks.⁵⁻⁸ This demonstrates that the exceptional thermopower of metallic Na_xCoO_2 is not essentially related to the details of the intercalating layer.

Theoretical studies, stimulated by these discoveries, emphasized both the bandlike nature of the material,^{9,10} consistent with its good metallic properties, the proximity to magnetism, and possible renormalizations related to a magnetic quantum critical point,¹¹ the proximity to charge ordering (which is seen at some doping levels),¹² and possible strongly correlated electron physics.¹³ Intriguingly, both band structure and strong correlated models (i.e., the Heikes model) are able to explain the high thermopowers.^{14,15} Recently, it was demonstrated by magnetotransport measurements that the thermopower at $x \sim 0.68$ is strongly reduced in magnetic field with a universal scaling law¹⁶ showing that spin entropy underlies the high thermopower and thus again emphasizing the role of magnetic fluctuations in the system

as well as possible strong correlated electron physics.^{16,17} Indeed, some of the misfit compounds are in fact magnetic, with ferromagnetic ground states.¹⁸

Takada and co-workers¹⁹ recently showed that Na_xCoO_2 can be readily hydrated to form $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$. This material has the same CoO_2 layers, but with a considerably expanded c axis, which accommodates the intercalating water and Na. In this material, $x \sim 0.3$, is lower than the range readily formed in Na_xCoO_2 . Remarkably, Takada and co-workers and Schaak *et al.*²⁰ found that $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ is a superconductor with $T_c \sim 5$ K. The nearness to magnetism and possible strong correlations immediately lead to suggestions of unconventional superconductivity in this material, beginning with the discovery paper of Takada *et al.*, as well as discussions of the role of water in producing the superconductivity. Scenarios that have been advanced include no role at all, screening Na disorder, preventing competing charge ordered states, modifying the doping level via unusual chemistry, enhanced two-dimensionality, and others.²¹⁻²⁷

Since superconductivity is fundamentally an instability of the metallic Fermi surface, a first step is to understand the relationship of the electronic structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ with its unhydrated parent Na_xCoO_2 . Here we present nonspin-polarized²⁸ density functional based band-structure calculations using the linearized augmented planewave (LAPW) method^{29,30} for $\text{Na}_{1/3}\text{CoO}_2 \cdot 4/3\text{H}_2\text{O}$ with both Na ions and water molecules explicitly included (no virtual crystal approximation is made). Despite the probable presence of strong correlations in both hydrated and unhydrated compounds, we expect that, as is the case with the high T_c cuprates, a local-density approximation (LDA) bandstructure will give valuable and accurate information about the Fermi surface. Angle-resolved photoelectron spectroscopy measurements on the parent compound of the superconducting cobaltate^{31,32} studied here already match well with previously calculated (unhydrated) band-structure results.⁹ We show that, from an electronic structure point of view, the hydrated and unhydrated compounds are identical, aside from structural effects due to the expansion of the c -axis.

There are a variety of ideas about the exact structure of the hydrated compound. All reports^{20,21,33-35} indicate that it belongs to the hexagonal symmetry $\text{P6}_3/\text{mmc}$ (#194), but

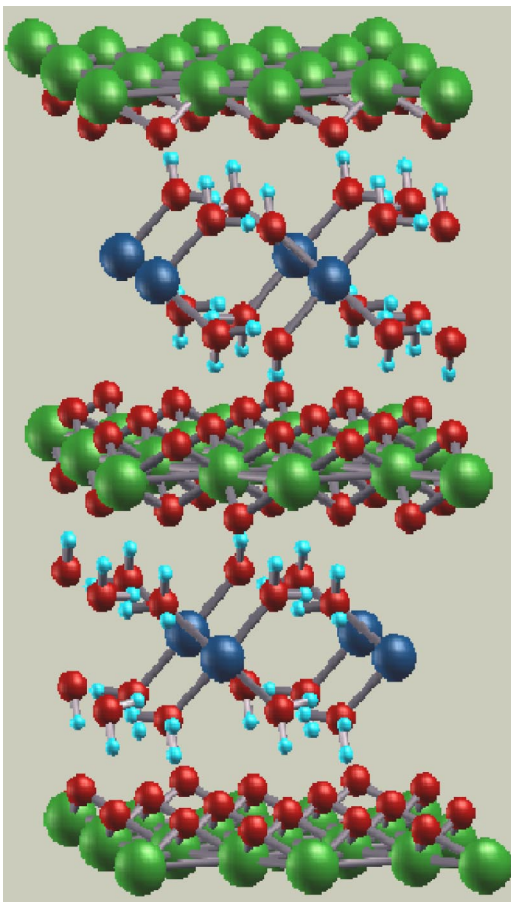


FIG. 1. (Color online) The tripled, hydrated structure corresponding to the superconductor. The three planes of distorted octahedra are Co-O, the intercalated Na ions are drawn with bonds to the water molecules to emphasize the fourfold coordination. H ions point generally toward the Co-O planes.

refinements of the water molecule positions, Na ion positions, and apical oxygen heights vary. Lynn *et al.*³⁵ find that the Na ions are displaced compared to the unhydrated parent compound and are surrounded by H₂O molecules with basically the same structure as D₂O ice. However, other neutron diffraction studies show that,³⁶ even below the freezing point of water, there may be no static position for the water molecule as a whole, emphasizing disorder.

The structure we used for our calculation was based on the neutron and x-ray diffraction results of Ref. 33 shown in Fig. 1, employing the observed symmetry sites, lattice constants, and composition. Jorgensen *et al.*³³ obtained their model by systematically removing ions/molecules from the partially occupied Na (*6h*) and H₂O (*24l*) sites according to coordination and bonding rules until the observed proportions were obtained. They held bond angles to 109° and O-H bond distances to 0.99 Å, i.e., the water was assumed to maintain its molecular characteristics. To employ this structural configuration, we tripled the formula unit of the parent compound Na_{2x}Co₂O₄ (already doubled to account for both Co-O planes), expanded the *c*-lattice to its reported value³³ of 37.1235 a.u. and added four H₂O molecules for each Na ion, resulting in a formula unit with integer values of all

constituent atoms: Na₂Co₆O₁₂8H₂O. This eliminated the need for the virtual crystal approximation while maintaining the proper proportion of each ion, allowing us to take into account the possible effects of Na ordering, which we find *a posteriori* to be unimportant for the CoO₂ derived electronic structure, based on comparison with previous virtual crystal results. Since the Na and H₂O sites are only partially occupied in the P6₃/mmc symmetry, we required a different space group for computation. Our structure has the considerably lowered P2₁/m symmetry (#11), but remains pseudo-hexagonal with lattice vectors of length $\sqrt{3}a$ such that the planar area of the unit cell is tripled. In other words, we include the local structure and coordination, but not long range disorder in the Na H₂O layers, yielding a lower average symmetry. However, electronic structure around the Fermi level is hexagonal to a high precision, indicating that scattering from disorder in the Na H₂O layers is weak. This may be important for superconductivity considering the pair breaking effect of scattering in unconventional superconductors. Since no data is available for the exact orientation of the water molecules, they were oriented with H ions pointing away from the Na ion and toward the Co-O plane, as suggested by various experimental observations.^{33,35,36} One hydrogen ion was brought as near as possible to an oxygen in the Co-O plane to model possible O-H bonding. The position of the other hydrogen was then established by respecting the bond angles and lengths as described above. We found that the electronic structure aspects that we discuss in subsequent sections were insensitive to our particular choices for the water molecules. The apical O height in the presence of water was then resolved to its optimal height of 1.86 a.u. above the Co plane. The present local density approximation calculations were done using the LAPW method as implemented in the WIEN code with well converged basis sets employing an Rkmax of 4.16, sphere radii of 1.86 (Co), 1.6 (O), 2.0 (Na), and 1.0 and 0.88 for the O and H, respectively, of water. The water molecules were treated using LAPW basis functions, whereas all other ions were treated with an APW+LO basis set. Additional local orbitals were added for Co and Na *p*-states and O *s*-states.

The most important bands in the conventional hexagonal Brillouin zone (BZ) of the unhydrated parent compound are four E'_g and two A_{1g} Co-derived bands near the Fermi energy. Our expanded hexagonal unit cell results in a BZ one third the volume of the original and rotated by an angle of 30°. The rotation and compression of the original BZ necessitates a double downfolding process as illustrated in Fig. 2, and needs to be remembered when comparing our band structure and prior results.^{9,12}

To clarify the similarities and differences between the hydrated and unhydrated structures, we performed a second calculation in a similar unit cell, neglecting the water molecules. We found that artificially expanding the *c*-axis with a vacuum produced unphysical and highly dispersive bands. The *c*-axis in our comparison calculation was fixed at its lower unhydrated value of 20.4280 a.u. for this reason. Taking into account the somewhat complex zone folding of bands, our unhydrated band structure agrees very well with previously published results calculated for a smaller unit cell.⁹

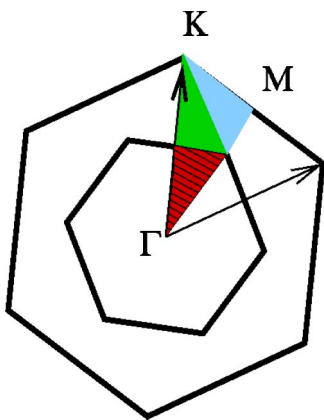


FIG. 2. (Color online) The bands along the Γ - M in the small zone are formed by folding the upper shaded triangle down onto the adjacent one and then folding again into the irreducible Brillouin zone. The symmetry points marked are those of the *larger* (unhydrated compound) zone, those of the smaller zone are easily identifiable by analogy.

Figure 3 shows both band structures on the same energy scale, each centered around its respective Fermi energy. The difference in c -axis parameter is reflected in the Γ - A distance which is nearly twice as big in the parent compound. An inspection of the bands crossing and just above the Fermi energy reveals a somewhat greater splitting in the unhydrated compound than in the superconducting compound, but a nearly identical overall band dispersion. Bands containing water character are determined to be at least 0.2 Ry below the Fermi energy by looking at the projected atomic character of each eigenvalue. The observable increase in splitting can be attributed to interplanar coupling which is substantially suppressed when the c -axis expands to accommodate water. Thus, the sole effect of the water on the electronic structure is to collapse the two (nearly) concentric Fermi surfaces of the unhydrated compound until they are practically a single degenerate surface in the hydrated compound. While this collapse may be important, it is a purely structural effect achieved by the forced separation of Co-O planes and is unrelated to the specific chemical composition of water. This shows that the water itself, at least in this or similar structural configurations, is completely irrelevant to the electronic structure of $\text{Na}_{0.33}\text{CoO}_2\cdot 1.33\text{H}_2\text{O}$ and that the Fermi surface is insensitive to its presence. This result does not depend on the specific position or orientation of the water as we have obtained identical results for the partially filled Co bands by calculating the band structure with water positions based on the alternate icelike model of Ref. 35. The similarity of the hydrated and unhydrated band structures and the absence of any water character near the Fermi level indicate that the effect of water can be successfully modeled with, for example, a tight-binding approach, through expansion of the c -lattice parameter. Hubbard and t - J type models or dynamical mean-field theory calculations that can further include correlation effects, such as magnetic fluctuations which have important ramifications for superconductivity, can proceed similarly by assuming increased two dimensionality as the primary effect of water intercalation.

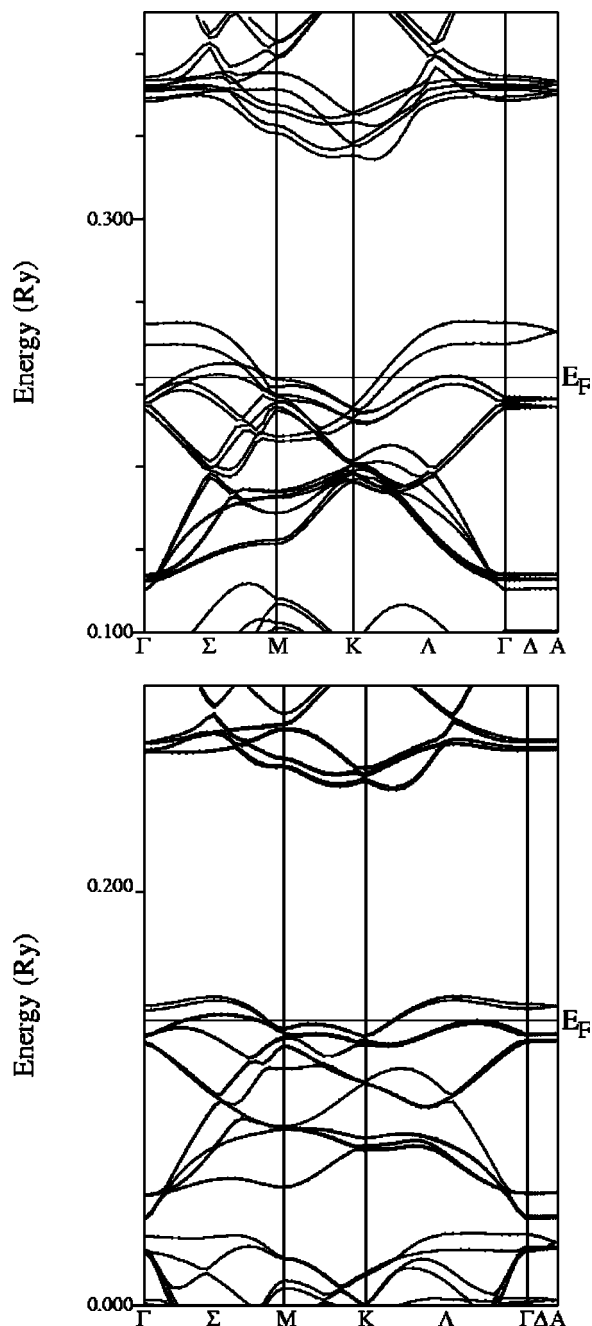


FIG. 3. A comparison of the hydrated compound (right panel) with its expanded c lattice parameter and an unhydrated compound with identical dimensions with the exception of the c -axis which remains at the unhydrated value. The differences in dispersion between the two structures are completely attributable to interplanar interaction which is reduced by hydration.

The measured susceptibility of $\text{Na}_{0.3}\text{CoO}_2$ is anisotropic and temperature independent, consistent with a picture of delocalized spins.^{37,38} Both the anisotropy and magnitude of χ increase as water is added and a very weak Curie-Weiss behavior develops, possibly due to impurities or defects.³⁸ The linear specific heat coefficient γ is also measured to be higher in the fully hydrated compound than in the parent compound.^{39,40} Not surprisingly, resistivity measurements on the hydrated compound reveal a high degree of anisotropy³⁴

($\sim 10^3$), but no single crystal data at similar Na content is available for comparison to the unhydrated compound, though presumably the anisotropy would increase due to greater planar separation.

The differences observed between parent and superconducting compounds are consistent with our calculated electronic structures for the two materials. Two Fermi surface types, one large a_{1g} -type hole pocket and six smaller e_g -type elliptical hole pockets, were previously calculated for the unhydrated compound⁹ and both are preserved after hydration. The a_{1g} Fermi sheets are Γ -centered and have been observed by photoemission experiments,^{31,32} but so far the e_g surfaces near the K -points of the Brillouin zone are not seen. The absence of these pockets may be due to surface effects such as the formation of a surface magnetic moment which exchange splits the bands or to surface expansion/contraction of the Co-O plane which could shift the e_g energies relative to the a_{1g} . The smaller surfaces carry only $\sim 30\%$ of the total holes, but these are extremely heavy and comprise nearly 70% of the density of states. Thermodynamic properties such as specific heat, susceptibility, and spin fluctuations therefore derive primarily from these smaller pockets, while transport takes place mainly through the lighter, faster holes of the large surface. The small amount of z -dispersion present in both Fermi sheets in the unhydrated system is removed entirely by the intercalation of water, which additionally raises the density of states at the Fermi level [$N(E_F)$]. A higher $N(E_F)$ can account for the increase in both γ and Pauli susceptibility. One interesting possibility is that the small pock-

ets may lead to spin fluctuations because of their heavier mass and nesting, and that these would scatter the carriers that are responsible for the transport on the large sheet.

We have shown, by explicitly including water in an LAPW calculation, that the effect of the water in $\text{Na}_{1/3}\text{CoO}_2 \cdot 1.33\text{H}_2\text{O}$ is overwhelmingly structural and imperceptibly electronic. The band structures of the hydrated and unhydrated compounds differ only through suppression of interplanar coupling. The resulting decrease in band splitting may have relevance to superconductivity, but the same effect can be achieved with any spacer that sufficiently separates the Co-O planes. Based on the expected Hubbard U for Co orbitals and our bandwidth, correlation effects may well be important. Our LDA band structure can provide a starting point for calculations that include many-body effects, particularly effects due to magnetic fluctuations likely to be present in the system. The question of water's particular role in the superconductivity is still very open, but we have shown that it has no effect on the electronic structure near the Fermi surface, other than to make it more two dimensional.

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