The electronic structure of the Na$_x$CoO$_2$ surface

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The idea that surface effects may play an important role in suppressing $e'_g$ Fermi surface pockets on Na$_x$CoO$_2$ ($0.333 \leq x \leq 0.75$) has been frequently proposed to explain the discrepancy between LDA calculations (performed on the bulk compound) which find $e'_g$ hole pockets present and ARPES experiments, which do not observe the hole pockets. Since ARPES is a surface sensitive technique it is important to investigate the effects that surface formation will have on the electronic structure of Na$_{1/3}$CoO$_2$ in order to more accurately compare theory and experiment. We have calculated the band structure and Fermi surface of cleaved Na$_{1/3}$CoO$_2$ and determined that the surface non-trivially affects the fermiology in comparison to the bulk. Additionally, we examine the likelihood of possible hydroxyl contamination and surface termination. Our results show that a combination of surface formation and contamination effects could resolve the ongoing controversy between ARPES experiments and theory.

One longstanding controversial issue surrounding Na$_x$CoO$_2$ is the discrepancy between between experimental measurements and theoretical predictions concerning the small hole pockets along the $\Gamma$–$K$ direction. Angle resolved photoemission spectra (ARPES) experiments have clearly shown the existence of a large $a_{1g}$ cylindrical hole on the Fermi surface which is consistent with LDA band structure calculations. However, the small hole pockets which are also present in band structure calculations due to the partially filled $e'_g$ band are absent. Whether this should be interpreted as a failure of LDA to account for some crucial correlation effects or as a failure of ARPES to detect the bulk structure is a subject of much discussion.

Dynamical mean field theory (DMFT) calculations that incorporate correlation effects on a local level and that might be expected to bring theory and experiment into closer agreement, instead find that these only serve to increase the volume of the $e'_g$ hole pockets. Nevertheless, since long range correlations such as ferromagnetic spin fluctuations are not treated by this method, one cannot rule out alterations to the Fermi surface caused by such correlations.

Surface effects, as a broadly defined category, have also been proposed as a possible reason for the absence of the pockets in ARPES measurements. By probing the Na 2$p$ core-level intensity as a function of photoelectron emission angle, it was clearly shown that strong differences between the surface and bulk exist and that photoemission experiments contain a large, if not dominant, amount of surface character. In particular, oxygen vacancies are common on oxide surfaces allowing hydroxyl terminations to occur through a combination of oxygen vacancies and a water background in UHV or simply hydrogen contaminants adsorbing on the surface. Indeed, many previous studies of oxide surfaces have found that it is nearly impossible to remove water and hydrogen contaminants in a UHV environment.

It is therefore desirable to understand, from a theoretical point of view, the differences between the electronic structure of a cleaved surface layer and that of the bulk material and to investigate the role of common defects such as unintended adsorbates on the fermiology of NaCoO$_2$. In this Letter, we use density functional theory (DFT) to examine the band structure and Fermi surfaces of a cleaved Na$_{1/3}$CoO$_2$ surface. We show that these differ non-trivially on a surface as compared to the bulk and are sensitive to many uncontrollable factors, such as Na ordering, surface contaminants, and defects. Intriguingly, we find that the surface is extremely susceptible to electron donor adsorbates and that these strongly depress the $e'_g$ hole pockets well below the Fermi energy, very similar to what has been observed in ARPES.

Calculational Methods All calculations have been performed using a plane wave DFT code, the Vienna Ab-initio Simulation Package (VASP). The projected augmented wave method (PAW) and the generalized gradient approximation to the exchange correlation potential were used. The surface and bulk Na$_x$CoO$_2$ structures were modeled using a six stoichiometric layer slab (a 15Å vacuum is added between successive slabs for surface calculations), so that both BZs are the same. For most calculations, we used a $\sqrt{3} \times \sqrt{3} \times 1$ hexagonal cell with three Co atoms per layer. The two top and bottom layers were relaxed while the middle two were held in their bulk relaxed positions. Ground state geometries were fully optimized using a Monkhorst Pack k-point mesh of $6 \times 4 \times 2$. For total energy density of states (DOS) calculations, the Brillouin zone (BZ) integrations were performed on an $8 \times 8 \times 2$ mesh. For some calculations, an even larger $2\sqrt{3} \times \sqrt{3} \times 1$ cell with six Co atoms per layer was required. Na can occupy either the sites atop Co (Na1) or at the center of an equilateral triangle formed by Co atoms at the vertices (Na2), or a combination of the two. We have found that the energetics associated with Na2 ordering are most favorable in the $\sqrt{3} \times \sqrt{3} \times 1$ cell, so we present those results here. This agrees well with experimental results from Roger et. al who observe from neutron diffraction experiments that when $x=1/3$, Na prefers the Na2 position, whereas at high doping, mult-
stoichiometric surfaces by calculating the phase separation.

We have investigated the stability of the under- or over-stoichiometric systems, respectively. We find this inequality to be true and therefore it is highly likely that the stoichiometric surface will not phase separate into areas that are either under- (Na depletion) or over- (Na excess) stoichiometric.

We have adjusted the electron count in calculations of both under- and over-stoichiometric surfaces by shifting the Fermi energy appropriately to best mimic the most likely situation of a stoichiometric surface. As we discuss, this approximation is not perfectly representative because the Na atoms in some cases have a non-negligible effect on the surface Fermiology. It does, however, allow us to "bracket" expected electronic structure modifications between over- and under-stoichiometric results.

**Surface Calculations** The bulk band structure and Fermi surfaces for Na$_{1/3}$CoO$_2$ in a six-layer $\sqrt{3} \times \sqrt{3}$ unit cell is shown in Figs. 1a and b. There are six sets of a$_{1g}$ and e$_{g}'$ Fermi surfaces (degeneracies prevent them from being individually distinguishable), corresponding to the six different layers. Because of BZ backfolding the two types of Fermi level crossings occur along the same high symmetry line, Γ-M, in Fig. 1a and the e$_{g}'$-derived small hole pockets are located inside the larger a$_{1g}$ hexagonal pockets in Fig. 1b. For the bulk compound, locating the Na atoms at the Na1 vs. the Na2 position has an imperceptible effect on the Fermi surface or band structure. In Fig. 1b, (right panel) we show the Fermi surface for the over-stoichiometric surface compound. We present the over-stoichiometric case because although the effect of Na is exaggerated it more closely mimics the stoichiometric case than neglecting it entirely. Moreover, the under-stoichiometric case also shows a noticeable decrease in the size of the e$_{g}'$ hole pockets, though smaller than the over-stoichiometric case. The stoichiometric case, if it were possible to calculate it in this unit cell, would lie somewhere between the two. In the over-stoichiometric case one of the e$_{g}'$ pockets is clearly shrunken and another has been suppressed entirely. These can be clearly identified, using atom-based projection, as the surface-originated pockets. The corresponding surface a$_{1g}$ bands, identified in the same way, expand proportionately. Thus, any technique that probes the surface electronic structure cannot be expected to detect Fermi surfaces in agreement with bulk calculations and, additionally, surface sensitive results should not be extrapolated to represent the bulk electronic structure. While the e$_{g}'$ hole pockets are not fully eliminated by the existence of the surface, they are rather dramatically shrunken. The origin of this effect is in the noticeably shortened Na-O distance (it decreases by 0.32 Å at the surface). The Na$^+$ Coulomb field lowers the energy of the O electron bands and, by increasing the energy separation between O and Co states, decreases Co-O bonding. Although we do not show it here, a projection of the O character of the Co-derived t$_{2g}$ bands shows that Co-O hybridization is stronger in the e$_{g}'$ symmetry parts of the band complex relative to the a$_{1g}$ parts and particularly strong at and near the part of the dispersion that gives rise to the small e$_{g}'$ Fermi surfaces.

**FIG. 1:** (a) Band structure of bulk and (b)(left panel) Fermi surface of bulk and (right panel) over-stoichiometric Na$_{1/3}$CoO$_2$. The light colored solid bands show e$_{g}'$ character. The a$_{1g}$ bands create the large, dark (black) cylindrical pockets. The elliptical hole pockets are shown in light (green) and arise from e$_{g}'$ bands.

In order for the stoichiometry of the bulk compound to be maintained and for the surface Co atoms to have the same valency as those in the bulk, the number of Na atoms on each of the two surfaces should be half the number between bulk layers. For the $x=1/3$ compound, this requires one Na for every six Co and cannot be achieved with only 3 Co atoms per layer. We have therefore investigated an "over-stoichiometric" compound that contains one Na atom on each surface and an "under-stoichiometric" compound that has no Na on either surface. The stoichiometric compound was also investigated by further lowering the symmetry (doubling the cell size). Although we discuss the energetics of this calculation, the extensive backfolding of the BZ makes it impossible to visually interpret the Fermi surfaces. We have investigated the stability of the under- or over-stoichiometric surfaces by calculating the phase separation energy difference $E_{1/3} + E_{1/3} \geq E_{1/3}$, $E_{1/3}$ and $E_{1/3}$ represent the energies associated with the under-stoichiometric, over-stoichiometric, and stoichiometric systems, respectively. We find this inequality to be true and therefore it is highly likely that the stoichiometric surface will not phase separate into areas that are either under- (Na depletion) or over- (Na excess) stoichiometric.
Thus, an energy lowering of the O states disproportionately affects these areas.

In contrast to the bulk, the surface Fermi pockets (both small and large) are slightly sensitive to the Na position. The Fermi surfaces corresponding to Na in the Na1 position show slightly larger $e_g'$ hole pockets than when Na is in the Na2 position (shown in Fig. 1b). The position of Na varies the size of the hole pockets due to electrostatic interaction between Na$^+$ and the Co $a_{1g}$ orbitals. The $a_{1g}$ orbitals are shifted downward compared to the $e_g'$ orbitals by positive Na$^+$ ions. This effect is stronger when Na is in the Na1 position versus the Na2 position because the $a_{1g}$ orbital is elongated along the z-direction. The smaller shift of $a_{1g}$ downward when Na is in the Na2 position results in a smaller hole pocket [16].

The under- and over-stoichiometric compounds are, as noted previously, adjusted so that their electron count is equal to the stoichiometric one. Although the Fermi surfaces are mainly insensitive to this approximation, there is one notable difference that occurs due to the lack (under-stoichiometric) or surplus (over-stoichiometric) of Na on the surface itself. Na, being a free-electron metal, features a parabolic, nearly free-electron band as a free atom or when it serves as an intercalant in a compound. It was recently pointed that the position of this band in intercalated graphites is crucial for superconductivity [17]; in some compounds it is so low in energy that it crosses the Fermi level. It was observed that the position of this intercalant band is quite sensitive to the interplanar distance [18]. The interplanar distance determines how squeezed the Na electrons are between the host layers. Naturally, if the electrons are unbound on one side (surface), the intercalant band drops substantially (for CaC$_2$ this drop was found to be 0.5 eV [19]). In the bulk, the Na band is high enough to be neglected when considering the Co-O bands, even at high Na concentrations (it sinks upon adding Na, for electrostatic reasons). On the surface, however, it is 4.21 eV lower than in the bulk for the over-stoichiometric compound. Fig. 2 shows the over-stoichiometric bandstructure in which the Na band drops down below the unoccupied $e_g'$ complex and overlaps with the unoccupied $a_{1g}$ bands near the $\Gamma$ point at approximately 250 meV above $E_F$.

For the stoichiometric compound (not shown), the bottom of the surface Na band is 670 meV higher than for the over-stoichiometric compound. Although the surface Na band does not cross $E_F$ for the low Na content ($x=1/3$) considered here, it does dip substantially beneath it for $x=2/3$, and therefore changes the fermiology significantly. This may have relevance for the abrupt discontinuity in hole count compared to Luttinger’s theorem noticed in systematic ARPES experiments.

The adsorption energy of a Na atom on the under-stoichiometric/stoichiometric surface is 3.92 eV/2.55 eV. These results indicate that it is highly favorable for Na to remain on the surface rather than desorb and that the cleaved surface of Na$_{1/3}$CoO$_2$ is highly susceptible to contamination by electron donor adsorbates. Although it seems unlikely that excess Na could be found to attach to the surface under UHV conditions, the presence of H$_2$O molecules or H atoms is much more conceivable. Even assuming that a perfectly clean oxide sample was placed inside a UHV chamber, a H$_2$O background and H contaminants are almost impossible to get rid of despite annealing at high temperatures and high vacuum pressures. In fact, it has been observed for some oxide surfaces that even after annealing to temps around 900K, H still appears to be stuck to the surface of the oxide [20]. We have calculated that a single H atom will adsorb to the surface of the over-stoichiometric compound with an energy of 2.84 eV. For the stoichiometric/under-stoichiometric compounds this increases to 3.50 eV /4.12 eV due to a reduction in Na-H repulsion.

Surprisingly, the effect of adsorption of an H atom on the band structure and fermiology of Na$_{1/3}$CoO$_2$ is considerably more dramatic than simple electron donation would suggest. As can be seen by comparing the highlighted $e_g'$ surface bands of Fig. 2a to the bulk $e'_g$ bands of Fig. 1, the presence of a H contaminant severely depresses the entire $e_g'$ band complex. The suppression is strongest along $\Gamma$-M where the bands formerly crossed $E_F$ for the stoichiometric compound (not shown), the bottom of the surface Na band is 670 meV higher than for the over-stoichiometric compound. W e have calculated that a single H atom will adsorb to the surface of the over-stoichiometric compound with an energy of 2.84 eV. For the stoichiometric/under-stoichiometric compounds this increases to 3.50 eV /4.12 eV due to a reduction in Na-H repulsion.

Although the Fermi surfaces in the stoichiometric unit cell are too complex to provide useful information, the position of the $e_g'$ surface complex can nonetheless be gauged by examining the position of the $e'_g$ band center in comparison to the bulk. Note in Fig. 2a, that the position of the $e'_g$ band complex that gives rise to Fermi surface hole pockets (along $\Gamma$-M) decreases in energy more than the band complex as a whole, so a strong shift in band center will clearly indicate suppression of these pockets. We find for the under-stoichiometric, stoichiometric and over-stoichiometric surface the band shifts are -42, -120 and -137 meV versus the bulk (two CoO$_2$ layers beneath the surface). We have also checked that the bulk numbers are unaffected by H adsorption on the surface (or by the existence of the surface itself) by comparing third-layer band centers to full bulk calculation band centers. Since the under-stoichiometric case exhibits the smallest band center shift and already has no surface $e_g'$ hole pockets, these numbers demonstrate that the hole pockets are surely absent in the stoichiometric case.
FIG. 2: Band structure for (a) H adsorbed on overstoichiometric surface and Fermi surface of (b) H adsorbed on understoichiometric surface for Na$_{1/3}$CoO$_2$. Large and small circles indicate Na intercalant character and eg’ character, respectively.

The dramatic effects of H on the surface owe to two underlying physical effects. The first is a simple filling of the Co-derived band complex due to electron donation from the adsorbed H. This is, in reality, a very small effect, but since the eg’ pockets are already at the very top of the eg’ band complex and are the first part of the spectrum to fill upon electron addition, at higher Na content, even small amounts of H adsorbed on the surface could destroy the small Fermi surface pockets. The second and dominant effect involves the positive Coulomb field created by ionized H just above the negative O ions which serves to exaggerate the main surface effect: O bands are strongly lowered, which decreases eg’ antibonding and destroys the pockets. This effect is operative even if the adsorbate is H$^+$ rather than atomic H, as may be the case for dissociated water molecules in the vacuum. Because O anti-bonding with eg’ and a$_{1g}$ states is not uniform, there are also noticeable changes in the dispersion along Γ-M (See Figs. 2a and b).

Conclusions Formation of a surface results in the eg’ hole pockets shrinking and possibly disappearing. This effect is highly dependent on Na ordering and content on the surface. Surface hydroxyl termination, which can occur through hydrogen contamination in UHV, results in complete suppression of the eg’ hole pockets. Our energetics indicate that once hydrogen is adsorbed it will be very difficult to remove. This is in good agreement with hydrogen adsorption studies on other oxide surfaces. The Coulomb field of Na$^+$ or H$^+$ lowers the energy of the O electron bands which subsequently decreases Co-O bonding. Co-O hybridization increases along the eg’ symmetry parts of the band complex that result in hole pocket formation, relative to the a$_{1g}$ band complex. This results in eg’ hole pocket suppression. The decrease in size and absence of surface eg’ hole pockets is due to a combination of surface effects and surface contamination which agrees well with ARPES data.

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[1] D. J. Singh, Phys. Rev. B 61, 13397 (2000).
[2] H. -B. Yang et al., Phys. Rev. Lett. 95, 146401 (2005).
[3] D. Qian et al., Phys. Rev. Lett. 97, 186405 (2006).
[4] H. -B. Yang et al., Phys. Rev. Lett. 92, 246403 (2004).
[5] M. Z. Hasan et al., Phys. Rev. Lett. 92, 246402 (2004).
[6] H. Ishida, M. D. Johannes, and A. Liebsch, Phys. Rev. Lett. 94, 196401 (2005).
[7] F. Lechermann, S. Biermann, and A. Georges, Prog. Theor. Phys. Suppl. 160, 233 (2005).
[8] C. A. Marianetti, K. Haule, and O. Parcollet, Phys. Rev. Lett. 99, 246404 (2007).
[9] T. Arakane et al., J. Phys. Soc. Japan 76, 054704 (2007).
[10] S. Wendt et al., Phys. Rev. Lett. 96 (2006).
[11] G. E. Brown et al., Phys. Rev. 99, 77 (1999).
[12] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
[13] P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
[14] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[15] M. Roger et al., Nature 445, 631 (2007).
[16] D. Pillay, M. D. Johannes, I. I. Mazin, and O.K. Andersen, Phys. Rev. B 78, 02501 (2008).
[17] G. Csanyi et al., Nature Physics 1, 42 (2005).
[18] L. Boeri, G. B. Bachelet, M. Giantomassi, and O. K. Andersen, Physical Review B 76 (2007).
[19] M. Calandra and F. Mauri, Phys. Rev. B 76, 161406(R) (2007).
[20] S. Suzuki, K. Fukui, H. Onishi, and Y. Iwasawa, Phys. Rev. Lett. 84, 2156 (2000).