Electronic Structure of the Na_xCoO_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_xCoO_2 ($0.333 \le x \le 0.75$) has been frequently proposed to explain the discrepancy between local-density approximation calculations which find e'_g hole pockets present and Angle resolved photoemission spectra (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. We show that a combination of surface formation and contamination effects could resolve the ongoing controversy between ARPES experiments and theory.

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One long-standing controversial issue surrounding Na_xCoO_2 is the discrepancy between experimental measurements and theoretical predictions [1] concerning the small hole pockets along the Γ-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 local-density approximation (LDA) band structure calculations [2–5]. 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 the 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 calculations that incorporate correlation effects on a local level and might be expected to bring theory and experiment into closer agreement instead find that these serve only to *increase* the volume of the e'_g hole pockets when realistic estimates of the $a_{1g} - e'_g$ splitting are used [6–10]. If, however, the $a_{1g} - e'_g$ crystal field splitting had the opposite sign, accounting for local correlations would have led to shrinking the e'_g Fermi surface pockets [11].

Surface effects, as a broadly defined category, have also been proposed as a possible reason for the absence of the pockets in ARPES measurements. Several bulk-sensitive experiments have shown clear differences from ARPES measurements, including small pockets [12,13]. It is also clear from probing the Na $2p$ core-level intensity as a function of photoelectron emission angle that strong differences exist between the surface and bulk and that photoemission experiments contain a large amount of surface character [14]. This may be due to the existence of the surface itself or even possibly due to contaminants. In particular, common oxide defects such as oxygen vacancies allow for hydroxyl terminations to occur through interaction with water background in UHV or simply hydrogen contaminants adsorbing on the surface [15]. Indeed, many previous studies of oxide surfaces have found that it is nearly impossible to remove water and hydrogen contaminants in a UHV environment [16].

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 nontrivially 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 beneath 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) [17]. The projected augmented wave method [18] and the generalized gradient approximation [19] to the exchange correlation potential were used. Surface calculations were performed using a slab of six layers separated by 15 Å of vacuum. In order to compare the results with the bulk electronic structure, we have recalculated the latter using a six formula unit supercell, i.e., the same slabs but with no vacuum layer. For most calculations, we used a $\sqrt{3} \times \sqrt{3}$ 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 and density of states calculations, the Brillioun zone (BZ) integrations were performed on a $8 \times 8 \times 2$ mesh. For some calculations, an even larger $2\sqrt{3}x\sqrt{3}$ cell with six Co atoms per layer was required. Na can occupy the sites either atop Co (Na1), 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 $\sqrt{3} \times \sqrt{3}$ cell, so we present those results here. This agrees well with experimental results from Roger *et al.* [20], who observe from neutron diffraction experiments that, when $x = 1/3$, Na prefers the Na2 position, whereas at high doping, multivacancy clusters form with partial occupation of Na1 sites.

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 "overstoichiometric" compound that contains one Na atom on each surface and an "understoichiometric" 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 overstoichiometric surfaces by calculating the phase separation energy difference $\frac{E_{1/3-}+E_{1/3+}}{2} \geq E_{1/3}$, where $E_{1/3-}$, $E_{1/3+}$, and $E_{1/3}$ represent the energies associated with the understoichiometric, overstoichiometric, 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.

We have adjusted the electron count in calculations of both under- and overstoichiometric surfaces by shifting the Fermi energy appropriately to best mimic the most likely situation of a stoichiometric surface. As we discuss below, though the approximation is not perfect, none of our main conclusions are affected by it.

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. 1(a) and 1(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. 1(a), and the e'_g-derived small hole pockets are located inside the larger a_{1g} hexagonal pockets in Fig. 1(b). 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. 1(b) (right panel), we show the Fermi surface for the overstoichiometric surface compound. We present the overstoichiometric case because, although the effect of Na is exaggerated, it more closely mimics the stoichiometric case than neglecting it entirely. In the overstoichiometric 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. Despite the overly tangled structure of bands in the stoichiometric Brillouin zone, we were able to identify the 12 bands near E_F that give rise to the small e'_g elliptical pockets in the bulk system. Of these 12, two were depressed completely beneath E_F while two others were shrunken in comparison to those bands in the same region with predominantly bulk character. This indicates that our approximation of the stoichiometric case by the overstoichiometric case with a shifted Fermi energy is valid. Even the understoichiometric case shows a noticeable decrease in the size of the e'_g hole pockets. 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 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.

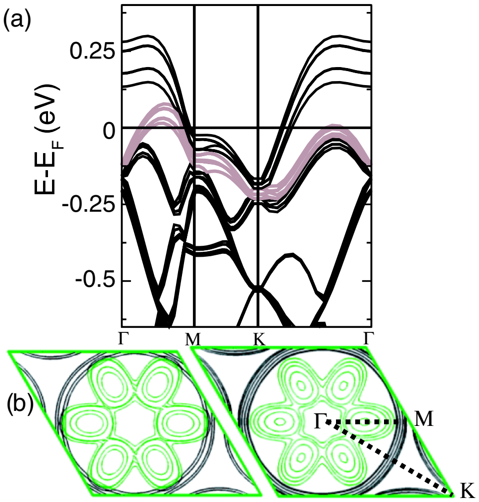

FIG. 1 (color online). (a) Band structure of bulk and (b)(left panel) Fermi surface of bulk and (right panel) overstoichiometric $Na_{1/3}CoO_2$. The light colored solid bands show e'_g character. The a_{1g} bands create the large, dark (black) cylindrical pockets. The elliptical hole pockets are shown in light (green) and arise from e'_g bands.

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. 1(b)]. 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 vs 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 [10].

The under- and overstoichiometric 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 (understoichiometric) or surplus (overstoichiometric) 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 out that the position of this band in intercalated graphites is crucial for superconductivity [21]. 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 [22]. 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_6 this drop was found to be 0.5 eV [23]). 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 overstoichiometric compound. Figure 2(a) shows the overstoichiometric band structure in which the Na band drops down below the unoccupied e_g' complex and overlaps with the unoccupied a_{1g} bands near the Γ 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 overstoichiometric 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 understoichiometric (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_2O molecules or H atoms is much more conceivable. Even assuming that a perfectly clean oxide sample was placed inside a UHV chamber, a H_2O 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 900 K, H still appears to be stuck to the surface of the oxide [24]. We have calculated that a single H atom will adsorb to the surface of the overstoichiometric compound with an energy of 2.84 eV. For the stoichiometric/understoichiometric compounds, this increases to 3.50/4.12 eV due to a reduction in Na-H repulsion.

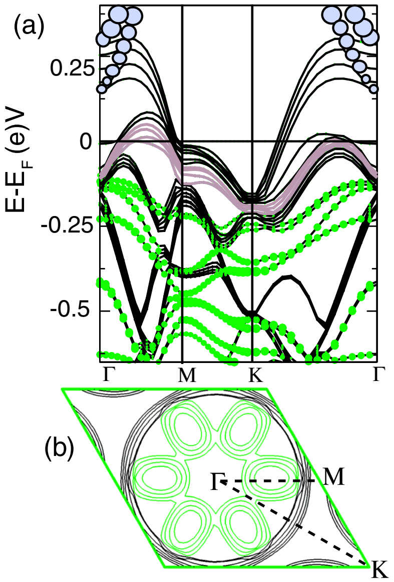

FIG. 2 (color online). Band structure for (a) H adsorbed on the overstoichiometric surface and Fermi surface of (b) H adsorbed on the understoichiometric surface for $Na_{1/3}CoO_2$. Large and small circles indicate Na intercalant character and e_g' character, respectively.

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. 2(a) to the bulk e_g' bands of Fig. 1(a), the presence of a H contaminant severely depresses the entire e_g' band complex. The suppression is strongest along Γ-M where the bands formerly crossed E_F without the contaminant, but the downshift in energy is obvious throughout the band structure. The approximately -110 meV shift is congruent with what is seen in ARPES measurements [2,3], though no conclusive reports of surface contamination have yet been published. Figure 2(a) illustrates the effect of H on the overstoichiometric surface, while Fig. 2(b) shows the Fermi surface that results from H adsorption on the understoichiometric surface. The suppression of the e_g' complex is weaker in the absence of Na on the surface but still quite sufficient to push the e_g' pockets below E_F.

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. 2(a) that the part of the e_g' band complex that gives rise to Fermi surface hole pockets (along Γ-M) decreases in energy more than the band complex as a whole, so a strong shift in the band center will clearly indicate suppression of these pockets. We find for the understoichiometric, stoichiometric, and overstoichiometric surface that the band shifts are -42, -120, and -137 meV vs 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 understoichiometric 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.

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 e_g pockets are already at the very top of the e_g' 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 e_g' 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 antibonding with e_g' and a_{1g} states is not uniform, there are also noticeable changes in the dispersion along Γ-M [see Figs. 2(a) and 2(b)].

Conclusions.—Formation of a surface results in the e_g' 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 e_g' 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 e_g' symmetry parts of the band complex that result in hole pocket formation, relative to the a_{1g} band complex. This results in e_g' hole pocket suppression. The decrease in size and absence of surface e_g' hole pockets are due to a combination of surface effects and surface contamination which agrees well with ARPES data.

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