Fermi Surface of Na_xCoO_2

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Doping evolution of the Fermi surface topology of Na_xCoO_2 is studied systematically. Both local density approximation (LDA) and local spin density approximation (LSDA) predict a large Fermi surface as well as small hole pockets for doping levels $x \sim 0.5$. In contrast, the hole pockets are completely absent for all doping levels within LSDA + U. More importantly, we find no violation of Luttinger's rule in this system. The measured Fermi surface of $Na_{0.7}CoO_2$ can be explained by its half-metallic behavior and agrees with our LSDA + U calculations.

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Detailed knowledge of the Fermi surface topology is important for understanding various properties of metals. In the conventional BCS theory of superconductivity, electron-phonon couplings, and hence the superconducting transition temperature, depend sensitively on the electronic structure near the Fermi surface. In most unconventional superconductivity scenarios, the low energy excitations and pairing interactions of the system are presumably also determined by the electronic structure near the Fermi surface. Therefore, an accurate description of the Fermi surface is critical for both types of superconductivity. Recently, the discovery of superconductivity [1] in hydrated Na_xCoO_2 has generated renewed interest in this material and much effort has focused on the understanding of its normal state electronic properties [2–9]. One central issue is the shape (and the size) of the Fermi surface. Earlier local-density approximation (LDA) calculations [10] of the unhydrated system ($Na_{0.5}CoO_2$) suggested a rather interesting picture: A large circular Fermi surface surrounded by small pockets of holes near the K points in the Brillouin zone (BZ). This Fermi surface topology is the starting point for several proposed theories of nonphonon mediated superconductivity [11,12], and the existence of small hole pockets is essential for these theories. However, recent angle-resolved photoelectron spectroscopy (ARPES) experiments by at least two groups revealed a much simpler Fermi surface [13,14]. More surprisingly, the measured Fermi surface does not seem to satisfy the Luttinger electron counting rule if a half-filled paramagnetic two-dimensional band structure is assumed for the undoped system (CoO_2) [13,14].

In this Letter, the Fermi surface of Na_xCoO_2 ($x = 0.3$, 0.5, and 0.7) is calculated with three levels of approximations, namely, LDA, local spin density approximation (LSDA), and LSDA + U [15] with a moderate U of 4.0 eV. The system is modeled with a single layer CoO_2 doped with electrons and we assume that no charge disproportionation occurs in the metallic phase. Charge neutrality is assured by a balancing uniform positive background. We believe that this model captures the essential physics, and the presence of the Na potential will have minor effects on our results [3]. Charge disproportionation [6,16–20] and its implications on the observed insulating phase of $Na_{0.5}CoO_2$ at low temperature [16], as well as the subtle interplay between the Na ordering and the charge ordering in the CoO_2 layer, will be discussed in a separate publication. We find that the measured Fermi surface [13] of $Na_{0.7}CoO_2$ can well be explained by the half-metallic behavior of the system. Therefore, the Luttinger rule is obeyed in this system.

Figure 1 shows the LDA band structures of $(CoO_2)^{x-}$ ($x = 0.3$, 0.5, and 0.7) near the Fermi level. Only the Co d derived t_{2g} states are shown for clarity. Under the influence of the trigonal crystal field, the t_{2g} triplet splits into an a_{1g} state and an e_g doublet with a separation of about 1.5 eV at Γ. Interestingly, the bandwidth of the e_g doublet is also about 1.5 eV within LDA. As a result, the Fermi level crosses both the a_{1g} and one of the e_g bands at low doping level ($x \leq 0.6$), producing a large Fermi surface around the Γ point as well as small hole pockets near the K points in the BZ (see also Fig. 4). This is in good agreement with the result of Singh [10]. The small hole pockets disappear as the doping level x increases beyond 0.6, which seems to agree with the fact that no hole pockets are observed [13,14] in $Na_{0.6}CoO_2$ and $Na_{0.7}CoO_2$. However, due to a dip in the band energy of the a_{1g} state at Γ, a feature that can be understood within a second-nearest-neighbor tight-binding model, the Fermi surface splits into two concentric pieces (see Fig. 4 for details) at $x = 0.7$. This is not consistent with experiments where only one cylindrical Fermi surface was observed [13]. Moreover, the radius of the Fermi surface calculated within LDA is considerably smaller than the observed values [13], which raised the issue of possible violations of the Luttinger rule. However, there

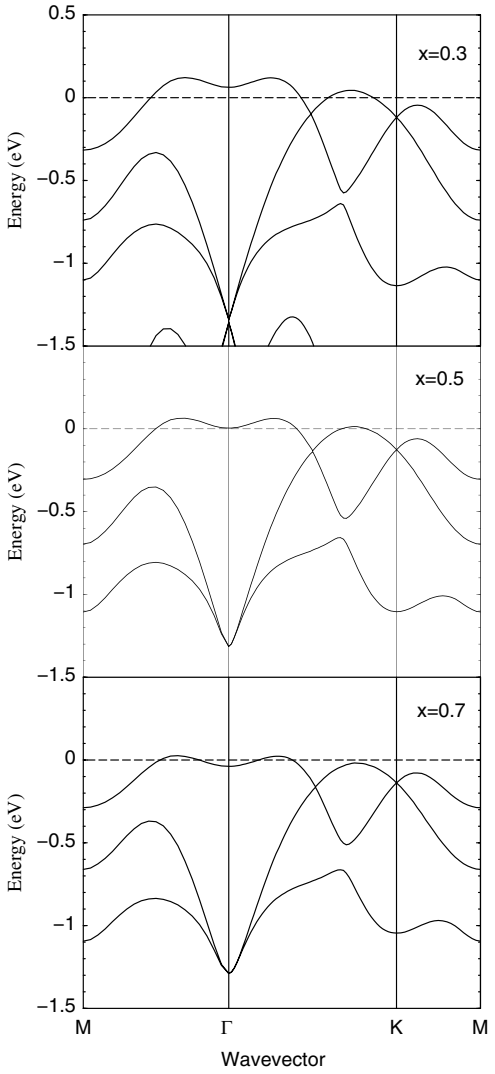

FIG. 1. LDA band structure of $(CoO_2)^{x-}$. Only the states derived from t_{2g} triplet are shown. The horizontal dashed line indicates the Fermi level.

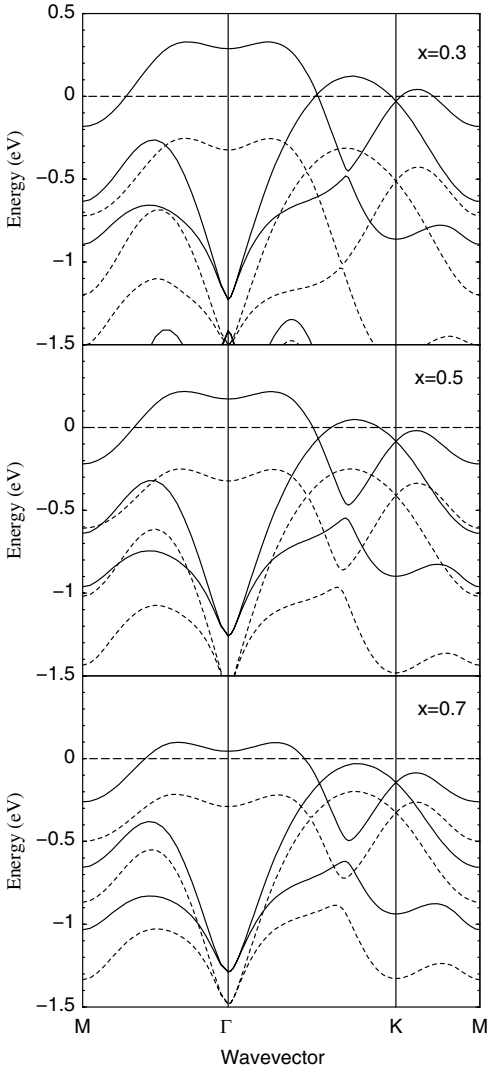

FIG. 2. LSDA band structure of $(CoO_2)^{x-}$ near the Fermi level. Solid and dotted curves are minority and majority spin bands, respectively. The horizontal dashed line indicates the Fermi level.

exists a simpler explanation, as will be discussed in the following.

Considering the relatively narrow bandwidth of the d states and the observed magnetism [21,22] in this system, one might expect that spin-polarized calculations within LSDA be more appropriate for describing its electronic structure. The calculated LSDA band structures of $(CoO_2)^{x-}$ near the Fermi level are shown in Fig. 2. The spin polarization energy pulls the majority spin a_{1g} state down by about 0.61, 0.49, and 0.34 eV at the Γ point for doping levels $x = 0.3$, 0.5, and 0.7, respectively. As a result, the t_{2g} derived majority spin states lie completely below the Fermi level and the system becomes a half metal. This is in agreement with a previous LSDA calculation [10]. At low doping level ($x = 0.3$), the Fermi level cuts all three sub-bands of the minority spin t_{2g} triplet, resulting in a rather complicated Fermi surface, as shown in Fig. 4. As the doping level x increases to 0.5, only two of the three sub-bands cross the Fermi level and hole pockets, considerably larger than those calculated within LDA, develop near the K points. At $x = 0.7$, only the a_{1g} state contribute to the Fermi surface and the small hole pockets disappear. Because of its half-metallic behavior, the phase space volume (holes) enclosed by the Fermi surface is twice as large as it would be if both spins contribute. Our calculation gives an average radius of $k_f \sim 0.72$ Å^{-1} for $x = 0.7$, which is in reasonable agreement with the measured value [13] (0.65 ± 0.1 Å^{-1} for $x = 0.7$). Therefore, we conclude that the half-metallic behavior of the system is consistent with the measured Fermi surface topology and that Luttinger's rule is satisfied.

Although there is still no consensus on the strength of the on-site Coulomb interaction U among the Co d electrons in the CoO_2 plane, it is generally agreed that Na_xCoO_2 is a moderately correlated system. (It is also possible that the correlation effects vary with the doping level due to the change in electron screening [20].) Therefore, the applicability of LDA or LSDA may be questionable. Here we employ the LSDA + U method introduced by Anisimov *et al.* [15] to study the electronic band structure and the Fermi surface of this system. The LSDA + U method can be regarded as a model Hartree-Fock approximation with the Coulomb interactions among the localized (e.g., Co d) electrons being replaced by statically screened parameters U and J. In addition to the splitting arising from trigonal crystal field effects, the on-site Coulomb interaction further pushes the partially occupied minority spin a_{1g} state up, resulting in a complete separation between the a_{1g} and the e_g states at low doping levels, as shown in Fig. 3. Consequently, the small hole pockets are absent for all doping levels within LSDA + U, as shown in Fig. 4. In fact, a very small on-site Coulomb U ($\sim$2 eV) is sufficient to suppress the hole pockets at low doping levels. Therefore, whether the hole pockets exist or not is a very subtle issue, especially at low doping levels. The absence of small hole pockets, if further confirmed, will strongly favor an intermediate correlation picture. We hope our results will stimulate more experimental work on this subject.

Finally, we compare the calculated Fermi surface within LDA, LSDA, LSDA + U with that measured by ARPES experiments [13], as shown in Fig. 5. Both LSDA and LSDA + U calculations give a Fermi surface which agrees well with the experiment, indicating that Luttinger's rule is satisfied. LDA, on the other hand, results in a qualitatively different Fermi surface topology from the measured one.

In summary, we have studied the electronic band structure and the Fermi surface topology of Na_xCoO_2 using three levels of approximations, namely, LDA, LSDA, and LSDA + U with a moderate Coulomb U of 4 eV. The calculated Fermi surface structure is nontrivial and depends sensitively on the doping level as well as on the theoretical approximations. Both LDA and LSDA predict

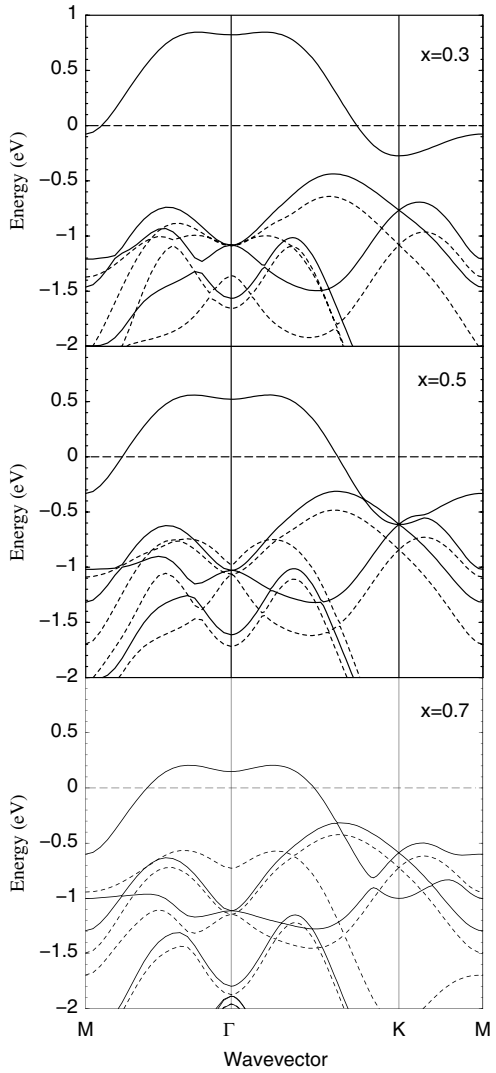

FIG. 3. LSDA + U band structure of $(CoO_2)^{x-}$ near the Fermi level. Solid and dotted curves are minority and majority spin bands, respectively. The horizontal dashed line indicates the Fermi level.

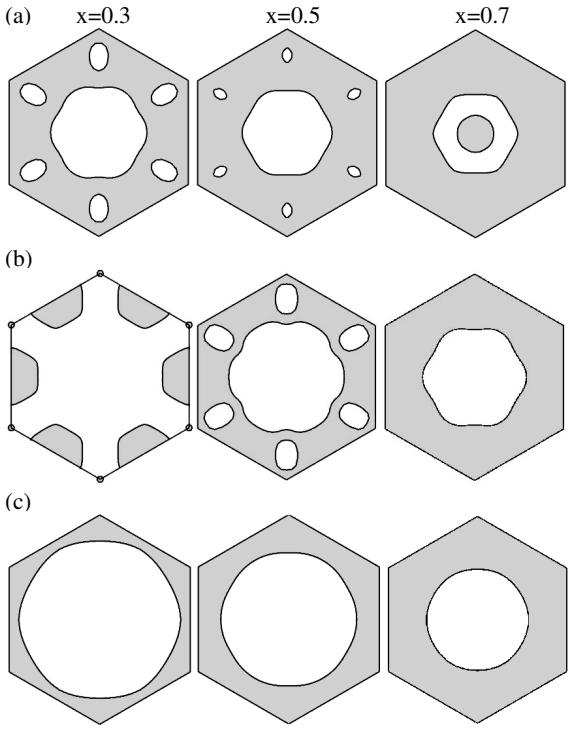

FIG. 4. Fermi surface topology of $(CoO_2)^{x-}$ calculated with (a) LDA, (b) LSDA, and (c) LSDA + U for doping levels $x =$ 0.3, 0.5, and 0.7, from left to right, respectively. Shaded areas are electron states and empty areas are holes.

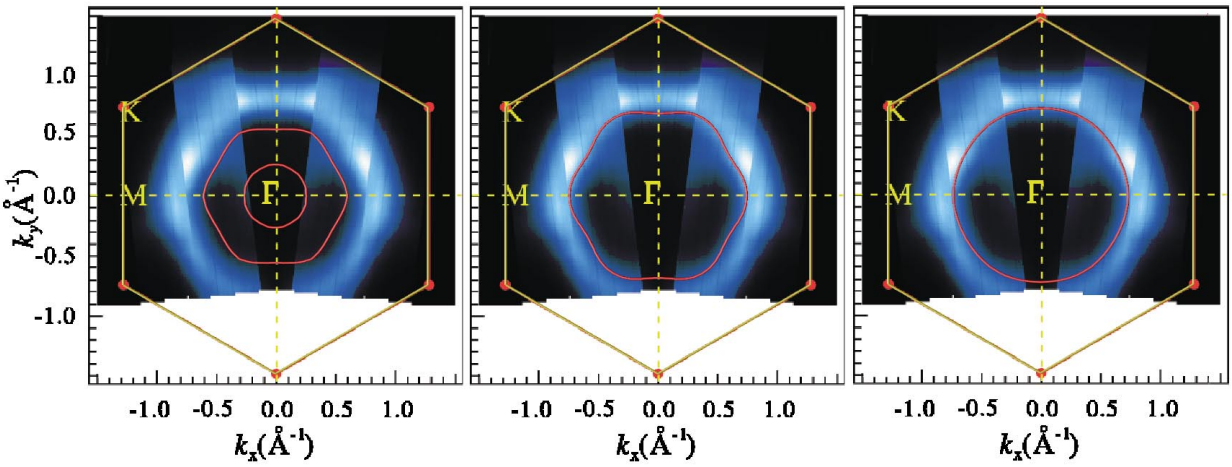

FIG. 5 (color online). Comparison between the measured and the calculated Fermi surface (red/gray curve) of $Na_{0.7}CoO_2$ using LDA (left), LSDA (middle), and LSDA + U (right). The ARPES experimental result is taken from the work of Hasan *et al.* [13].

a large Fermi surface around the Γ point and small hole pockets near the K points at doping levels $x \leq 0.5$. In contrast, no hole pockets are observed within LSDA + U for all doping levels. The measured Fermi surface at doping $x = 0.7$ agrees well with our LSDA and LSDA + U calculations, and we find no violation of Luttinger's rule in this system.

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[1] K. Takada, H. Sakural, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).
[2] K.-W. Lee, J. Kunes, and W. E. Pickett, Phys. Rev. B **70**, 045104 (2004)
[3] P. Zhang, W. Luo, V. H. Crespi, M. L. Cohen, and S. G. Louie, Phys. Rev. B **70**, 085108 (2004).
[4] C. A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. **92**, 196405 (2004).
[5] M. D. Johannes and D. J. Singh, Phys. Rev. B **70**, 014507 (2004).
[6] Z. Li, J. Yang, J. Hou, and Q. Zhu, cond-mat/0403727.
[7] M. D. Johannes, D. A. Papaconstantopoulos, D. J. Singh, and M. J. Mehl, cond-mat/0408698.
[8] W. B. Wu, D. J. Huang, J. Okamoto, A. Tanaka, H. J. Lin, F. C. Chou, A. Fujimori, and C. T. Chen, cond-mat/0408467.
[9] L. J. Zou, J. L. Wang, and Z. Zeng, Phys. Rev. B **69**, 132505 (2004).
[10] D. J. Singh, Phys. Rev. B **61**, 13397 (2000).
[11] K. Kuroki, Y. Tanaka, and R. Arita, Phys. Rev. Lett. **93**, 077001 (2004).
[12] M. D. Johannes, I. I. Mazin, D. J. Singh, and D. A. Papaconstantopoulos, Phys. Rev. Lett. **93**, 097005 (2004).
[13] M. Z. Hasan, Y.-D. Chuang, D. Qian, Y. W. Li, Y. Kong, A. Kuprin, A. V. Fedorov, R. Kimmerling, E. Rotenberg, K. Rossnagel, Z. Hussain, H. Koh, N. S. Rogado, M. L. Foo, and R. J. Cava, Phys. Rev. Lett. **92**, 246402 (2004).
[14] H.-B. Yang, S.-C. Wang, A. K. P. Sekharan, H. Matsui, S. Souma, T. Sato, T. Takahashi, T. Takeuchi, J. C. Campuzano, R. Jin, B. C. Sales, D. Mandrus, Z. Wang, and H. Ding, Phys. Rev. Lett. **92**, 246403 (2004).
[15] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[16] M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. **92**, 247001 (2004).
[17] I. R. Mukhamedshin, H. Alloul, G. Collin, and N. Blanchard, cond-mat/0402074.
[18] Q. Huang, B. Khaykovich, F. C. Chou, J. H. Cho, J. W. Lynn, and Y. S. Lee, cond-mat/0405677.
[19] N. L. Wang, D. Wu, G. Li, X. H. Chen, C. H. Wang, and X. G. Luo, cond-mat/0405218.
[20] K.-W. Lee, J. Kunes, P. Novak, and W. E. Pickett, cond-mat/0408411.
[21] T. Motohashi, R. Ueda, E. Naujalis, T. Tojo, I. Terasaki, T. Atake, M. Karppinen, and H. Yamauchi, Phys. Rev. B **67**, 064406 (2003).
[22] J. Sugiyama, H. Itahara, J. H. Brewer, E. J. Ansaldo, T. Motohashi, M. Karppinen, and H. Yamauchi, Phys. Rev. B **67**, 214420 (2003).