Electronic Structure of Sodium Cobalt Oxide: Comparing Mono- and Bilayer-hydrate

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To shed new light on the mechanism of superconductivity in sodium cobalt oxide bilayer-hydrate (BLH), we perform a density functional calculation with full structure optimization for BLH and its related nonsuperconducting phase, monolayer hydrate (MLH). We find that these hydrates have similar band structures, but a notable difference can be seen in the \(a_{1g}\) band around the Fermi level. While its dispersion in the \(z\) direction is negligibly small for BLH, it is of the order of 0.1 eV for MLH. This result implies that the three dimensional feature of the \(a_{1g}\) band may be the origin for the absence of superconductivity in MLH.

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Layered sodium cobalt oxide bilayer-hydrate (BLH) is now attracting mounting attention due to the recent discovery of its superconductivity\textsuperscript{1}. One of the interesting characteristic feature of this superconducting phase is that it is derived through a soft-chemical process for the parent material Na\(_{40}\)CoO\(_{2}\). Namely, a part of the Na ions located between the CoO\(_2\) layers are extracted and H\(_2\)O molecules are inserted for this region. Here, the role of H\(_2\)O is of great interest from both a chemical and a physical point of view, since it can be a key to understand the pairing mechanism, and furthermore, it may provide some guiding principles to synthesize other novel superconductors in layered transition metal oxides.

It has been proposed from the beginning\textsuperscript{1} that the main effect of inserting H\(_2\)O molecules is expanding the interlayer distance \((d)\) of the CoO\(_2\) layers. Namely, while \(d=5.4\) Å for the parent material, that of superconducting BLH is expanded to \(d=9.8\) Å. Electronic structure calculations within the density functional theory\textsuperscript{2,3} have indeed shown that the electronic structure of BLH is highly two-dimensional, whereas the \(c\)-axis dispersion of the band structure as well as the bonding-antibonding band splittings due to the interlayer couplings are not negligible for unhydrated Na\(_{40}\)CoO\(_{2}\). In fact, the two-dimensional electronic structure is favorable for unconventional superconductivity where the pairing interaction has a characteristic structure in the momentum space\textsuperscript{4,5}.

On the other hand, to provide a deep insight into the role of the H\(_2\)O molecules, Takada \textit{et al.} synthesized monolayer-hydrate (MLH) by partial extraction of H\(_2\)O from BLH, and studied the magnetic properties\textsuperscript{6,7}. One may expect that MLH is also superconducting because \(d=6.9\) Å, which is larger than that of La\(_2\)CuO\(_4\) (=6.6 Å). However, they found that the superconductivity is completely suppressed, while the carrier density in the CoO\(_2\) layer is expected to be unchanged because the magnetic susceptibilities of MLH and BLH have similar values above 20K. Thus Takada \textit{et al.} concluded that the H\(_2\)O molecules in BLH may play an important role for the superconductivity besides the separation of the CO\(_2\) layers. In fact, in contrast to MLH where the H\(_2\)O molecules and the Na ions are placed on the same plane, in BLH, the H\(_2\)O molecules are placed between the CoO\(_2\) layers and the Na ions. Therefore, they proposed that the H\(_2\)O molecules in BLH may shield the (random) Coulomb potential of the Na ions.

While intensive first-principles calculations for BLH have been done up to present\textsuperscript{8–12}, those for MLH have yet to be carried out. The purpose of the present study is to investigate why BLH is superconducting but MLH is not by comparing the electronic structure of BLH and MLH, and to obtain some hints to understand the mechanism of superconductivity in BLH. We found that BLH and MLH have similar band structures, but a notable difference can be seen in the \(a_{1g}\) band around the Fermi level in that while its dispersion in the \(z\) direction is negligibly small for BLH, it is of the order of 0.1 eV for MLH.

Although various theoretical studies have been performed for the superconductivity in BLH, the mechanism is still controversial. Especially, clarifying which bands among the \(t_{2g}\) bands around the Fermi level dominate the superconductivity is of great interest. A variety of scenarios have been proposed. In fact, while there have been several works which claim that the \(a_{1g}\) bands are important\textsuperscript{13–19} or both \(a_{1g}\) and \(e'_{g}\) should be considered\textsuperscript{20,21}, the present author and his collaborators have proposed that the pocket-like Fermi surfaces of the \(e'_{g}\) bands are essential\textsuperscript{22}. Here, the advantage of first principles calculations is that it can give some hints on which band is important and should be taken into account for the model calculation. The present result that the main difference between BLH and MLH is the dispersion of the \(a_{1g}\) bands suggests that the \(a_{1g}\) band should not be ignored when we study superconductivity in BLH, and the three dimensional feature of the \(a_{1g}\) band may be the origin for the absence of superconductivity in MLH.

In the present study, we perform a first-principles band structure calculation within the framework of the generalized gradient approximation (GGA) based on the density functional theory. In the calculations, the
exchange-correlation functional introduced by Perdew, Burke, and Wang is adopted with the ultra-soft pseudopotential in a separable form. The wave functions are expanded by plane waves up to a cut-off energy of 30.25 Ry, and k point meshes of $8 \times 8 \times 2$ are used. The atomic configurations are optimized to minimize the total energy with the conjugate gradient scheme. We take a $\sqrt{3}a \times \sqrt{3}a \times c$ supercell, in which six cobalt atoms are included. During the optimization, the lattice constant $a$ and $c (= 2d)$ are fixed to the experimental values, i.e., $a = 2.8169$ (2.8345) Å and $c = 19.645$ (13.842) Å for BLH (MLH). While a variety of charge and spin orderings are observed in Na$_2$CoO$_2$ for $x \geq 0.5$, such orders have not been observed in BLH and MLH ($x \sim 0.3$). Therefore, we performed a density functional calculation for paramagnetic states without assuming any charge orderings for the initial state of the self-consistent calculation.

In this paper, we focus on the electronic structure for Na$_{1/3}$CoO$_2$(H$_2$O)$_{2/3}$ (BLH) and Na$_{2/3}$CoO$_2$(H$_2$O)$_{1/3}$ (MLH). On the other hand, recently, it was reported that the shift of the Fermi level does not change the qualitative tendency of the present result.

Before the actual calculation for Na$_{1/3}$CoO$_2$(H$_2$O)$_{2/3}$ and Na$_{1/3}$CoO$_2$(H$_2$O)$_{1/3}$, we first introduced a reference system where the Na ions and the H$_2$O molecules are represented by a corresponding electron doping into the CoO$_2$ layers. Namely, we calculated the electronic structure of the CoO$_2$ layers with an increased number of electrons and a uniform positive background charge to make the system charge-neutral. This reference system represents a situation where the H$_2$O molecules completely shield the potentials of the Na ions.

In Fig. 1(a) and (b), we show the band structure of the reference system where the lattice constants are set to those of BLH and MLH, respectively. Here, the eighteen bands comprising the $t_{2g}$ manifold are split into six $a_{1g}$ and twelve $e'_g$ bands. Note that only nine bands would be distinguishable if the two layers in the unit cell did not interact. We can see in Fig. 1 that while the band dispersion in (a) and (b) are almost identical to each other, for (b) a small band splitting can be seen in the $a_{1g}$ bands just above the Fermi level.

In Fig. 2, we plot $\rho(z) = \int |\phi_k(r)|^2 dxdy$, where $\phi_k$ is the Bloch wave function of the $k$-point indicated with arrows in Fig. 1 on the $a_{1g}$ and $e'_g$. Here, only the lower half of the unit cell is shown, and the Co planes reside around $z = 0$ and 0.5c. We can see that the main amplitude of $\rho(z)$ is localized within the Co layers. For BLH, the peaks on the Co planes are well separated for both $a_{1g}$ and $e'_g$. For MLH, on the other hand, the $a_{1g}$ state has finite amplitude there whereas the $e'_g$ state vanishes $z \sim 0.25c$.

These results suggest that the assumption that the effect of the Na ions and the H$_2$O molecules is irrelevant can be invalid for the $a_{1g}$ states in MLH. Especially, the effect of the random potential of Na can be serious for these states. In other words, it is suggested that (i) for unhydrated Na$_x$CoO$_2$$_{2/3}$, the c-axis dispersion in the band structure or the interlayer couplings are not negligible for both $e'_g$ and $a_{1g}$ orbitals because $d$ is not sufficiently large; (ii) for MLH, $d$ is large enough to suppress...
the interlayer transfers or couplings for $e'_g$ but not for $a_{1g}$ orbitals, because the wave functions of the latter extends to the $c$-axis; (iii) for BLH, $d$ is sufficiently large so that the whole $t_{2g}$ manifold is highly two-dimensional. It is expected that this qualitative tendency would not change even if we increased the amount of electron doping\textsuperscript{29}.

Next, let us discuss the actual calculation for BLH and MLH, i.e., Na$_{1/3}$CoO$_2$(H$_2$O)$_{2/3}$ and Na$_{1/3}$CoO$_2$(H$_2$O)$_{1/3}$. For the former, starting with the atomic configuration by Jorgensen et al. (Fig. 8a of Ref. 27), we performed a structure optimization. In Fig. 4(a), we show the side view of the optimized structure. As for the initial atomic configuration of the latter, we followed Takada et al.\textsuperscript{6} As is stressed in Ref.\textsuperscript{6}, it should be noted that the positions of the Na ions in MLH are different from those in BLH. Namely, while for BLH the Na atoms locate near the center of the trigonal prisms formed by the facing oxygen atoms of adjacent CoO$_2$ layers, they locate the midpoints of the prism edge for MLH (Fig. 4 in Ref\textsuperscript{b}). Since the atomic position of the H$_2$O molecules are not given in Ref\textsuperscript{6}, we started with several patterns of initial configurations, placing the oxygen atoms of the H$_2$O molecules on the same plane as the Na atoms. While we show the result for the most stable structure (Fig. 4(b)), the following argument does not depend on the detail of the atomic configuration of H$_2$O atoms\textsuperscript{30}.

In Fig. 5, we show the resulting band structure. The difference between Fig. 1 and Fig. 5 is whether the intercalated hydrate group is actually considered or not. By comparing Fig. 1 and Fig. 5, we can evaluate the effect of the potential of Na ions, the screening by the H$_2$O molecules, etc. We can see that the effect for the $e'_g$ bands in BLH and MLH is similar to each other. Especially, for MLH, the band splitting in the $e'_g$ bands just below the Fermi level is negligibly small, which contrasts with the case of unhydrated Na$_x$CoO$_2$, for which the band splitting is as large as 0.1 eV\textsuperscript{2,3}. This result implies that inserting single layer of H$_2$O molecules is sufficient to suppress the interlayer couplings for the $e'_g$ bands.

On the other hand, the $c$-axis dispersion and the band splitting of the $a_{1g}$ bands is of the order of 0.1 eV for MLH, while those for BLH are negligibly small. This suggests that inserting a single layer of H$_2$O molecules is not sufficient to separate the $a_{1g}$ states in each CoO$_2$ layer since they extend along the $c$-axis. Therefore, we expect for MLH that while the $e'_g$ bands are rather insensitive to the random potential of the Na ions, the $a_{1g}$ bands feel them seriously.

In Fig. 6, we plot $\rho$ for the $k$-points on the bonding $a_{1g}$ and $e'_g$ band which are indicated in Fig. 5. The $c$-axis dispersion is predominantly determined by the direct overlap between the tails of the adjacent main peaks.
rather than the amplitude on the H2O molecules (minor middle peak). We can see that the overlap is finite for the \(a_{1g}\) band of MLH but negligibly small for the other cases. (Note that for the \(e'_{g}\) band of MLH, \(\rho\) vanishes between the main peak and the small peak around the oxygen site in the H2O molecule.)

In conclusion, we found that BLH and MLH have quite similar band structures, but there is a notable difference in the dispersion of the \(a_{1g}\) band around the Fermi level. Namely, it is negligibly small in the \(x\) direction for the former, it is an order of 0.1 eV for the latter. This suggests that although a single layer of H2O molecules is sufficient to suppress the interlayer coupling for the \(e'_{g}\) bands, it is not sufficient for the \(a_{1g}\) bands.

If we assume that the three dimensional feature of the \(a_{1g}\) band can destroy superconductivity, we can understand why BLH is superconducting but MLH is not. In this sense, the present result suggests that the \(a_{1g}\) bands should not be ignored when we study superconductivity in Na\(_x\)CoO\(_2\)·\(y\)H\(_2\)O.

Recently, a systematic angle-resolved photoemission study has been performed for wide range of Na concentrations\(^{31}\). They concluded that the Fermi surface consists of the \(a_{1g}\) band for \(x=0.3\), which suggests that the \(a_{1g}\) band is important for the superconductivity. This is consistent with the present conclusion.

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### References

1. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature 422, 53 (2003).
2. M.D. Johannes and D.J. Singh, Phys. Rev. B 70, 014507 (2004).
3. C.A. Marianetti, G. Kotliar, and G. Ceder, Phys. Rev. Lett. 92, 196405 (2004).
4. R. Arita, K. Kuroki, and H. Aoki, Phys. Rev. B 60, 14585 (1999), J. Phys. Soc. Jpn. 69, 1181 (2000).
5. Monthoux and Lonzarich, Phys. Rev. B 59, 14598 (1999).
6. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R.A. Dilanian, and T. Sasaki, J. Solid. State. Chem. 177, 372 (2004).
7. H. Sakurai, F. Izumi, D.A. Dilanian, T. Sasaki, and E. Takayama-Muromachi, cond-mat/0310717.
8. K.-W. Lee, J. Kunes, and W.E. Pickett, Phys. Rev. B 70, 045104 (2004).
9. P. Zhang, W. Luo, V.H. Crespi, M.L. Cohen, and S.G. Louie, Phys. Rev. B 70, 085108 (2004).
10. L.J. Zou, J.L. Wang, and Z. Zeng, Phys. Rev. B 69, 132505 (2004).
11. M.D. Johannes, I.I. Mazin, D.J. Singh, and D.A. Papaconstantopoulos, Phys. Rev. Lett. 93, 097005 (2004).
12. P. Zhang, W. Luo, V.H. Crespi, M.L. Cohen, and S.G. Louie, cond-mat/0410596.
13. G. Baskaran, Phys. Rev. Lett. 91, 097003 (2003).
14. C. Honerkamp, Phys. Rev. B. 68, 104510 (2003).
15. A. Tanaka and X. Hu, Phys. Rev. Lett. 91, 257006 (2003).
16. B. Kumer and B.S. Shastry, Phys. Rev. B. 68, 104508 (2003).
17. D.J. Singh, Phys. Rev. B 68, 020503(R) (2003).
18. M. Ogata, J. Phys. Soc. Jpn. 72, 1839 (2003).
19. Q.H. Wang, D.H. Lee, and P.A. Lee, Phys. Rev. B 69, 092504 (2004).
20. W. Koshibae and S. Maekawa, Phys. Rev. Lett. 91, 257003 (2003).
21. M. Mochizuki, Y. Yanase and M. Ogata, cond-mat/0407094, Y. Yanase, M. Mochizuki, and M. Ogata,
cond-mat/0407563

22 K. Kuroki, Y. Tanaka, and R. Arita, Phys. Rev. Lett. 93, 077001 (2004), to appear in Phys. Rev. B.

23 J.P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1996).

24 D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).

25 K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B 47, 10142 (1993).

26 J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B 54, 5586 (1996).

27 J.D. Jorgensen, M. Avdeev, D.G. Hinks, J.C. Burley, and S. Short, Phys. Rev. B, 68, 214517 (2003).

28 K. Takada, K. Fukuda, M. Osada, I. Nakai, F. Izumi, R. A. Dilanian, K. Kato, M. Takata, H. Sakurai, E. Takayama-Muromachi, and T. Sasaki, J. Mater. Chem, 14, 1448 (2004).

29 This qualitative tendency should not depend on the choice of the exchange-correlation potential. Even if we stepped forward to more elaborated calculations such as LDA+U or LDA+DMFT, it would not be changed.

30 Here, for MLH (BLH), the distance between H in H₂O and O in CoO₂ plane is 1.72 (1.58-1.59) Å, that between O in H₂O and Na is 2.28 (2.24) Å, the bond length of Co-O is 1.91-1.93 (1.90-1.93) Å.

31 H.-B. Yang, Z.-H. Pan, A.K.P. Sekharan, T. Sato, S. Souma, T. Takahashi, R. Jin, B.C. Sales, D. Mandrus, A.V. Fedorov, Z. Wang, and H. Ding, cond-mat/0501403.