Effects of local oxygen distortions on electronic structures of Na\textsubscript{x}CoO\textsubscript{2}

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By using pseudopotential method with local spin density functional approximation, the electronic band structures of Na\textsubscript{x}CoO\textsubscript{2} are calculated for \(x = 0.25, 0.5, 0.75\), and \(x = 1\) in the presence of the structure relaxations. As increasing Na content, the hybridization between cobalt and oxygen orbitals is decreased, and a phase transition is predicted from a wide-band ferromagnetic to a narrow band paramagnetic metals. The itinerant ferromagnetism is strongly suppressed by the local distortions of the oxygens around the cobalts. Moreover, straining the CoO\textsubscript{2} layers corresponding to the hydrated superconductor Na\textsubscript{0.35}CoO\textsubscript{2}\cdot1.3H\textsubscript{2}O strongly enhances both the hybridization and ferromagnetism.

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Since the discovery of high critical temperature superconductivity in layered copper oxide compounds, the search for layered superconductors without copper atoms has been regarded as an important route to understand the unknown mechanism behind the highest superconducting transition temperatures. Recently, Takada and coworkers\textsuperscript{1} have discovered a novel superconductor Na\textsubscript{0.35}CoO\textsubscript{2}\cdot1.3H\textsubscript{2}O with \(T_c = 5\text{K}\), which is synthesized when a sodium cobalt oxide Na\textsubscript{0.75}CoO\textsubscript{2} is hydrated to reduce its sodium content and intercalated with water molecules to further separate the CoO\textsubscript{2} layers. Based on the analogy of its layered transition metal oxide structure, it has been speculated that the displayed superconductivity may be closely related to that of the high \(T_c\) cuprates\textsuperscript{1, 2}. Along this line, several theoretical analysis\textsuperscript{3, 4, 5} have been carried out in terms of resonant valence bond states on a strongly correlated two-dimensional t-J model on triangular lattices.

However, unlike the parent compounds of high \(T_c\) cuprates as an antiferromagnetic Mott insulator, the parent compounds Na\textsubscript{x}CoO\textsubscript{2} (\(x < 1\)) have been known for their anomalous large thermoelectric power and low electronic resistivity\textsuperscript{6}. Na\textsubscript{0.75}CoO\textsubscript{2} consists of a two-dimensional triangular lattice of cobalt ions formed by a network of edge-sharing CoO\textsubscript{6} octahedra, separated by layers of sodium ions. Band structure calculations using a general potential linearized augmented plane wave method\textsuperscript{7} for Na\textsubscript{0.5}CoO\textsubscript{2} indicates that it is a ferromagnetic half metal with little hybridization between the oxygen and cobalt orbitals, while no distinct magnetic ordering has been observed experimentally\textsuperscript{8, 9}. But for the samples of Na\textsubscript{0.75}CoO\textsubscript{2}, a magnetic phase transition associated with the antiferromagnetic interactions has been confirmed below \(T = 22\text{K}\), being accompanied by a specific heat jump, a small magnetization, and a kink in the temperature dependence of the resistivity\textsuperscript{10, 11}.

Moreover, it has been reported that the crystal structure of the superconducting Na\textsubscript{0.35}CoO\textsubscript{2}\cdot1.3H\textsubscript{2}O compound only differs from the parent compound Na\textsubscript{0.75}CoO\textsubscript{2} by the intercalation of water molecules to enlarge the CoO\textsubscript{2} layers and to reduce the sodium charges\textsuperscript{12, 13}. It is thus of great interest to scrutinize the electronic band structures of the parent compound Na\textsubscript{x}CoO\textsubscript{2} for different sodium contents and to study the electronic structure with a large CoO\textsubscript{2} layers as the same as that of the hydrated compound.

In this paper, by using pseudopotential method with local spin density functional approximation\textsuperscript{12, 13, 14}, we present the first principles electronic structure calculations on Na\textsubscript{x}CoO\textsubscript{2} for different Na content. The electronic structure is found to be highly two dimensional, giving rise to a good metal for \(x = 0.25, 0.5, 0.75\) and a semiconductor for \(x = 1\). In particular, at \(x = 0.25\) it is an itinerant ferromagnetic metal with large hybridization between cobalt and oxygen orbitals. As increasing the Na content, both the ferromagnetism and hybridization are decreasing. When \(x = 0.5\), only tiny ferromagnetism is left, and the hybridization vanishes. A phase transition is thus yielded from the wide band ferromagnetic metal to a narrow band paramagnetic metal by changing the Na content. The ferromagnetism is totally absent and a narrow conduction band appears below the Fermi energy when \(x = 0.75\). We find that such a strong suppression of the ferromagnetism is mainly originated from the local distortions of the oxygen ions around the cobalt atoms. However, the present treatments for the narrow band paramagnetic state may underestimate the tendency of the material towards local moment formation and possible magnetic ordering. In addition, straining the separation of the CoO\textsubscript{2} layers hypothetically corresponding to the hydrated superconductor Na\textsubscript{0.35}CoO\textsubscript{2}\cdot1.3H\textsubscript{2}O, we find that both the hybridization and ferromagnetism are enhanced, and the corresponding superconductivity might be associated with a triplet (p-wave) pairing state in the presence of strongly ferromagnetic fluctuations\textsuperscript{15, 16}, analogous to those in UGe\textsubscript{2}, URhGe, and ZrZn\textsubscript{2} (Ref.\textsuperscript{17, 18, 19}).

The crystal structure used in the present numerical calculations is based on the neutron diffraction data reported by Balsys and Davis\textsuperscript{20}. Neutron data for Na\textsubscript{0.75}CoO\textsubscript{2} shows that it belongs to the hexagonal P\textsubscript{6}\textsubscript{3}/mmc space group with lattice parameters \(a = \)}
2.840Å and c = 10.811Å. There are two CoO₂ sheets per unit cell. The triangles formed by the oxygen ions in the oxygen layers have two directions. We use A and B to represent these two oxygen layers. The oxygen packing in the structure is AABB. The experimental results indicate that the oxygen atoms are at the sites (1/3, 2/3, ±0.088). The Na ions are intercalated with a trigonal prismatic site between the octahedral sheets of cobalt oxide. There are two available sites for the sodium ions: (2/3, 1/3, 1/4) and (0, 0, 1/4). The sodium ions occupy these two sites unequally due to the influence of the Co atoms above and below in the second layer. The probability of finding sodium ions at the site (2/3, 1/3, 1/4) being approximately twice that on the other site (0, 0, 1/4) 20.

In order to take into account the different stoichiometry \(x = 0.25, 0.5, 0.75\), an enlarged unit cell \((2 \times 2 \times 1)\) of the crystal structure is introduced. The electronic Kohn-Sham orbitals for the momentum \(k\)-points in the Brillouin zone are expanded in plane waves with a cut-off of 24 Ryd. The PWSCF code 21 is used in the calculations with the ultrasoft pseudopotential 22 and Perdew-Wang exchange correlation potential 14. Using this method, we can properly treat the atomic relaxations and consider their relations with the electronic structures. We further assume the sodium ion setting on the site (2/3, 1/3, 1/4). In fact, in our framework the position of sodium ions have little effect on the electronic structures, because the role played by sodium ions mainly donates charges to the CoO₂ layers. More importantly, we have performed the structural relaxation to determine the optimized atomic positions. In particular, it is found that there are additional local distortions of the oxygen ions. While the earlier first principle calculations 7, 16 did not consider such local distortions.

During the calculations, we have noticed that the local distortions of the oxygen ions strongly depend on the sodium content. As increasing the Na content, the oxygen distortions are large, and the itinerant ferromagnetism of Na₅CoO₂ is reduced significantly. To describe these local distortions, we define that \(z_i\) denotes the heights of the oxygen ions of each layer in their z-direction to the Co layer in the unit of lattice spacing \(c\). All the oxygen layers (A and B) have the same magnitudes of the local distortions. The relaxed positions of the oxygen ions have been evaluated with respect to the sodium content and given in Table 1. We would like to point out that the case with sodium ions on the site (0, 0, 0) has similar relaxations for the oxygen ions.

Table I. The oxygen positions and spin magnetizations per cobalt atom for the unrelaxed \((m_u)\) and relaxed structures \((m_r)\) with respect to the sodium content \((x)\).

| \(x\) | \(z_i (c) \) (i=1,2,3,4) | \(m_u(\mu_B)\) | \(m_r(\mu_B)\) |
|---|---|---|---|
| \(x=0.25\) | \(z_1=0.0750\), \(z_2=0.0784\) | 0.715 | 0.340 |
| \(x=0.5\) | \(z_1=0.0826\), \(z_2=0.0773\) | 0.534 | 0.018 |
| \(x=0.75\) | \(z_1=0.0861\), \(z_2=0.0824\) | 0.263 | 0 |
| \(x=1\) | \(z_1=0.0921\) | 0 | 0 |

The electronic band structures are displayed in Fig.1 and Fig.2 for \(x = 0.25\) and \(x = 0.75\), respectively. The Fermi energy \(E_F\) has been set at zero and denoted by the dotted lines. The left column corresponds to the spin-up electrons and the right column to the spin-down electrons.

FIG. 1: The electronic band structure for Na₃.₅₃CoO₂. The Fermi energy \(E_F\) has been set at zero and denoted by the dotted lines. The left column corresponds to the spin-up electrons and the right column to the spin-down electrons.

and Fig.2 for \(x = 0.25\) and \(x = 0.75\), respectively. The energy scale is relative to the Fermi energy, and the density of states is in atomic unit (Ryd⁻¹). In Fig.1, the left column corresponds to the spin minority electronic structure, and the right column to the spin majority one. Both the spin minority and majority electronic structures are the same for Na₀.₇₅CoO₂. The spin density of states (DOS) is calculated and delineated in Fig.3 for the Na content \(x = 0.25, 0.5, 0.75,\) and 1. It is seen that a ferromagnetic metal with the wide hybridized bands is obtained for \(x = 0.25\). For \(x = 0.5\), there is a very weak ferromagnetism and little hybridization between the cobalt and oxygen orbitals. Moreover, a paramagnetic metal with a narrow band below the Fermi energy is found for \(x = 0.75\). By adding electron charges to the CoO₂ layers, the Fermi energy approaches to the top edge of the conduction band, and the difference between the spin minority and spin majority is decreasing quickly. For the case of \(x = 1\), NaCoO₂ becomes a semiconductor, consistent with the earlier experimental result. However, in the earlier density functional calculations without the local distortions of oxygen ions 7, 16, a ferromagnetic half metal state is obtained for all the sodium contents in \(x = 0.3, 0.5,\) and 0.7. In fact, we have also reproduced these results within the present calculation scheme.

Moreover, the local spin density functional calculations can also self-consistently determine the spin magnetization of the ferromagnetically ordering state for low Na content \((x \leq 0.5)\). In Table 1, the corresponding spin magnetizations per Co atom are given for both unrelaxed and relaxed structures. For \(x = 0.5\), our result with the unrelaxed oxygen position is 0.534\(\mu_B\) per cobalt atom.
strongly coupling narrow band paramagnetic metal. Par-
weakly coupling wide band ferromagnetic metal from the
vicinity of the critical sodium content separating the
states (LDOS) at Fermi energy defined by
distribution, we also calculate the local density of
instability.
be adequate to considering the possible antiferromagnetic
present spin density functional approximation may not
larger than the conduction electron bandwidth, and the

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fore, it is expected that the material Na
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are clearly quasi-two dimensional systems.
the cobalt and oxygen orbitals, and that the compounds
bonding are associated with the hybridization between
results clearly exhibit that a mixed metallic and covalent

However, in the relaxed structure of material, it is the
local oxygen distortions that reduce the spin magnetization
to 0.018µB per cobalt ion. This result is consistent
with the experimental observation and the nominal valence of +3.5 of each cobalt ion in Na0.5CoO2. There-
fore, it is expected that the material Na0.5CoO2 is in
the vicinity of the critical sodium content separating the
weakly coupling wide band ferromagnetic metal from the
strongly coupling narrow band paramagnetic metal. Par-
particularly, the Coulomb interaction in Na0.75CoO2 may be
larger than the conduction electron bandwidth, and the
present spin density functional approximation may not
be adequate to considering the possible antiferromagnetic
instability.

In order to exhibit the anisotropy of the charge
distribution, we also calculate the local density of
states (LDOS) at Fermi energy defined by n(EF, r) =
sum |ψr|^2δ(EF - Ei), which can provide some insights
into the electron bonding around the individual atoms.
The LDOS at the Fermi energy contour maps for the
(001) surface are given in Fig.4. For both Na0.75CoO2
and Na0.25CoO2, Co ions have a spherically symmetric
density distribution around each site on the Co layer
(Fig.4b and 4e), while their local density distributions
change from a down-triangular symmetry below Co layer
(Fig. 4a and 4d) to an up-triangular symmetry above
Co layer (Fig.4c and 4f). The down- and up-triangles in
the lower sodium content have more sharper edges than
the higher sodium content, and the oxygen ions with a
spherically symmetric distribution have higher density in
low sodium content as well. There is a little charge den-
sity around Na ions, reflecting that the role of Na atoms
is mainly to donate charges to the CoO2 layer. These
results clearly exhibit that a mixed metallic and covalent
bonding are associated with the hybridization between
the cobalt and oxygen orbitals, and that the compounds
are clearly quasi-two dimensional systems.

Finally, to understand the hydration effects of the
compounds Na_xCoO_2 (x < 1) on the electronic band
structures and the corresponding superconducting mecha-
nism, we strain the separation of the CoO2 layers for
Na0.25CoO2 and Na0.75CoO2 without taking into account
the water molecules. The corresponding DOS with c =
3.47Å are displayed in Fig.5. It is clearly seen that the
hybridization between the cobalt and oxygen orbitals are
considerably increased and the ferromagnetism prevails
even in the high sodium content. Na0.25CoO2, for ex-
ample, the corresponding spin magnetization is increased
to 0.785µB, nearly two times of the corresponding value
with normal separation of CoO2 layers. Thus, an effec-
tive one-band model Hamiltonian may exist to describe
the obtained electronic structure of this material. Actu-
ally, the singularity in the DOS seen in Fig.5 can induce
strong quantum ferromagnetic fluctuations, from which
an effective attraction among itinerant electrons is gener-
ated as the same as the conventional low-temperature su-
perconductors driven by the electron-phonon interaction
23, 24, 25, 26. The possible mechanism of superconduc-
tivity in sodium cobalt oxides may thus originate from

FIG. 2: The electronic band structure for Na0.75CoO2. There
are no differences between the spin-up and spin-down elec-
trons. The Fermi energy EF has been set at zero and denoted
by the dotted lines.

FIG. 3: The density of states of Na_xCoO_2 for the different
sodium content with relaxed structure. The density of states
is in atomic unit (Ryd)^{-1}. The up-spin DOS is shown above
the horizontal line and the down-spin below.

FIG. 4: The spatial distributions of the local density of states
at the Fermi energy for the (0,0,z) surface in unit of c. For
Na0.75CoO2, (a) z = −0.0370, (b) z = 0.0, (c) z = 0.0462.
For Na0.25CoO2, (d) z = −0.0370, (e) z = 0.0, (f) z = 0.0462.
In conclusion, pseudopotential method with local spin density functional approximation is used to calculate the electronic band structures of Na$_{x}$CoO$_2$ ($x = 0.25$, 0.5, 0.75, and 1) with the structure relaxations. By increasing the Na content, both the hybridization between cobalt and oxygen orbitals and the itinerant ferromagnetism are decreased, and a phase transition is predicted from a wide-band ferromagnetic to narrow band paramagnetic metals. It is the local distortions of the oxygen ions that reduces the itinerant ferromagnetism as increasing the sodium content. We also found that straining the CoO$_2$ layers enhances both the hybridization and ferromagnetism. Whether the superconductivity of Na$_{0.35}$CoO$_2$·1.3H$_2$O is related to a triplet (p-wave) electron pairing is required further investigation.

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