

Chemical differences between K and Na in alkali cobaltates

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$K_x\text{CoO}_2$ shares many similarities with Na_xCoO_2 , as well as some important differences (no hydration-induced superconductivity has been reported). At $T_{c2}=20$ K, $\text{K}_{0.5}\text{CoO}_2$ becomes an insulator with a tiny optical gap, as happens in $\text{Na}_{0.5}\text{CoO}_2$ at 52 K. This similarity, with a known common structure, enables direct comparisons to be made. Using the K-zigzag structure recently reported and the local density approximation, we compare and contrast these cobaltates at $x=0.5$. Although the electronic structures are quite similar as expected, substantial differences are observed near the Fermi level. These differences are found to be attributable mostly to the chemical rather than the structural difference. Although Na is normally considered to be fully ionic, K has a somewhat more highly ionic character than does Na in these cobaltates.

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I. INTRODUCTION

Takada *et al.* found superconductivity in the layered quasi-two-dimensional Na_xCoO_2 when intercalating enough water ($\sim 1.3\text{H}_2\text{O}$) to form a separate water layer between CoO_2 and Na layers.¹ The nonsuperconducting dehydrated Na_xCoO_2 system shows a rich phase diagram, which significantly depends on x .² For $x < 0.5$, the system shows weakly correlated bandlike behavior, including Pauli paramagnetism, while the phase $x > 0.5$ displays a correlated behavior, such as large enhancement in linear specific heat coefficient, Curie-Weiss susceptibility,³ and magnetic ordering for $x \geq 0.75$.

The most peculiar aspect of this system is an insulating phase at $x=0.5$ (Ref. 2) with a tiny gap of ~ 15 meV.⁴ As the temperature is decreased, antiferromagnetic ordering of some Co spins appears at $T_{c1}=88$ K, and at $T_{c2}=52$ K there is a gap opening, which reflects the charge ordering of nonmagnetic $S=0$ Co1 ions and magnetic $S=\frac{1}{2}$ Co2 ions.^{5,6} Using neutron diffraction studies, Williams *et al.* inferred the charge difference of $0.12e$ between Co1 and Co2.⁷ This value is much smaller than the $1e$ value expected from a naive formal charge concept, but is roughly consistent with the theoretically calculated value of $0.2e$ using a correlated band theory local density approximation with Hubbard potential U (LDA+ U) method.^{8,9} As a result, even though there is a small charge difference between the Co ions, the charge disproportionation is accompanied by local moment formation and the spins are consistent with the formal valences Co^{3+} and Co^{4+} .^{8,9}

The discovery of an unexpected insulating state in $\text{Na}_{0.5}\text{CoO}_2$ and hydration-induced superconductivity has stimulated the study of isostructural and isovalent family $A_x\text{CoO}_2$ ($A=\text{K}, \text{Rb}, \text{Cs}$). In spite of a few attempts to produce superconductivity in hydrated K_xCoO_2 , the amount of intercalated water is 0.8 or less, forming only a monohydrate ($\text{K}+\text{H}_2\text{O}$) layer, and no superconductivity has been detected yet.^{10,11}

The K_xCoO_2 system has been known for three decades since Hagenmuller and co-workers reported^{12,13} structure, transport, and magnetic data on phases with $x=1.0$, 0.67, and 0.50. Recently, an insulating phase in $\text{K}_{0.5}\text{CoO}_2$ has been

studied in more detail by a few groups;^{14,15} Nakamura *et al.*¹⁶ in the mid-1990s had reported an almost temperature-independent resistivity well above a metallic value. In $\text{K}_{0.5}\text{CoO}_2$, using NMR and neutron diffraction studies, Watanabe *et al.* observed a similar temperature evolution as in $\text{Na}_{0.5}\text{CoO}_2$.¹⁵ At $T_{c1}=60$ K, a kink in the in-plane susceptibility χ_{ab} indicates an onset of antiferromagnetic ordering. The resistivity increases sharply at $T_{c2}=20$ K, signaling the charge ordering. At this temperature, there is an additional magnetic rearrangement, indicated by kinks in both χ_{ab} and χ_c . From μ^+ SR experiments, Sugiyama *et al.* have obtained similar transition temperatures, 60 and 16 K, in metallic $\text{K}_{0.49}\text{CoO}_2$.¹⁷ The former is a magnetic ordering temperature from a paramagnetic state. Based on a mean field treatment of a Hubbard model, they suggested that there may be a linear spin density wave (SDW) state between 16 and 60 K, while a commensurate helical SDW state exists below 16 K. Additionally, K or Na ion order (structurally), resulting in the formation of a $2 \times \sqrt{3}$ supercell at $T_{c0}=550$ and 470 K for K and Na ions, respectively.¹⁵ The tiny energy gap of a similar magnitude with $\text{Na}_{0.5}\text{CoO}_2$ has been observed by Qian *et al.* with angle-resolved photoelectron spectroscopy (ARPES) measurements.¹⁴

Several characteristics of Na_xCoO_2 , particularly the superconductivity upon hydration and effects of cation ordering, suggest that the behavior in this system is sensitive to details of the electronic structure. The fact that $\text{K}_{0.5}\text{CoO}_2$ is similar to $\text{Na}_{0.5}\text{CoO}_2$, yet shows clear differences in behavior, indicates that a comparison of the electronic structures of these systems is warranted. In this paper, we compare and contrast the two insulating systems $\text{K}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.5}\text{CoO}_2$. Here, correlation effects and detailed magnetic ordering are neglected, but the observed $\sqrt{3}a_H \times 2a_H$ supercell including Na/K-zigzag ordering is adopted (a_H is the hexagonal lattice constant).

II. CRYSTAL STRUCTURE AND CALCULATION METHOD

Although some aspects of the structure in the sodium cobaltates are still controversial (especially the alkali metal ordering), all existing information for $x=0.5$ is based on the

TABLE I. Crystal structure comparison between $K_x\text{CoO}_2$ and Na_xCoO_2 at $x=0.5$. The orthorhombic structures (space group: $Pmmn$, No. 59) determined from Na- or K-zigzag ordering are a $\sqrt{3}a_H \times 2a_H$ superstructure which is based on the hexagonal structure with a lattice constant a_H . In this structure, the oxygens have three site symmetries, two $4f$ and one $8g$. Here, z_O is an oxygen height from the Co layers. A main difference in these structures is that $\text{K}_{0.5}\text{CoO}_2$ has 12% larger c lattice constant. The data are from Ref. 7 for $\text{Na}_{0.5}\text{CoO}_2$ and from Ref. 15 for $\text{K}_{0.5}\text{CoO}_2$.

Parameters	a_H (Å)	c (Å)	z_O
$\text{Na}_{0.5}\text{CoO}_2$	2.814	11.06	0.971, 0.949, 0.983
$\text{K}_{0.5}\text{CoO}_2$	2.831	12.50	0.965, 0.946, 0.981

basic hexagonal structure. Recently, Watanabe *et al.* observed the orthorhombic $\sqrt{3}a_H \times 2a_H$ superstructure from a K-zigzag pattern for $\text{K}_{0.5}\text{CoO}_2$.¹⁵ For comparison, we have used this orthorhombic structure for both cobaltates.^{7,18} As shown in Table I, in this structure the oxygens have three different site symmetries and slightly different O heights (from the Co layers), leading to distorted CoO_6 octahedra. The averaged Co-O-Co bond angle is about 96.5° for $\text{K}_{0.5}\text{CoO}_2$ and 95.4° for $\text{Na}_{0.5}\text{CoO}_2$ (this angle would be 90° for undistorted octahedra). This distortion makes the three fold t_{2g} manifold split into singlet a_g and doublet e'_g bands.

The calculations reported here were carried out within LDA, using the full-potential local-orbital method (FPLO).¹⁹ The LDA parametrization of Perdew and Wang was used.²⁰ The basis sets were chosen as $(3s3p)4s4p3d$ for Co and K, $(2s2p)3s3p3d$ for Na, and $2s2p3d$ for O. (The orbitals in parentheses denote semicore orbitals.) The Brillouin zone was sampled with a $12 \times 12 \times 2$ k mesh, which shows accuracy in energy up to an order of tenth meV (based on convergence tests using a $20 \times 20 \times 2$ mesh).

III. RESULTS

A. Magnetic energy

In Na_xCoO_2 , the ferromagnetic state is generically favored energetically within LDA,^{3,21} although this picture is physically correct only for $0.7 < x < 0.9$. Our calculations show that this tendency is also true for K_xCoO_2 . The magnetization energy, defined by the energy difference between nonmagnetic and ferromagnetic states, in $\text{Na}_{0.5}\text{CoO}_2$ is 22 meV/Co, and the energy in $\text{K}_{0.5}\text{CoO}_2$ slightly increases to 26 meV/Co. The small energy difference can be attributed to the higher magnetic moment on Co in $\text{K}_{0.5}\text{CoO}_2$, resulting from a longer c parameter in $\text{K}_{0.5}\text{CoO}_2$. (This larger c lattice constant results in the increasing charge of each Co ion by $0.02e$ in $\text{K}_{0.5}\text{CoO}_2$; see below.) From a simple Stoner picture, the small magnetization energy is consistent with the small total magnetic moment of $0.5\mu_B/\text{Co}$.

B. Electronic structure

Now, we will focus on the nonmagnetic state to understand the microscopic chemical differences. As observed pre-

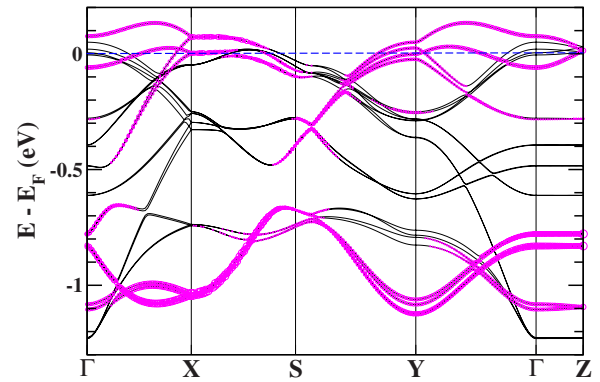


FIG. 1. (Color online) Enlarged band structures of nonmagnetic $\text{K}_{0.5}\text{CoO}_2$ at the t_{2g} manifold regime. The large t_{2g} - e_g crystal field splitting of 2.5 eV makes the e_g manifold (not shown here) unimportant for low energy excitations. The thickened (and colored) lines highlight bands having strong Co a_g character. The S point is a zone boundary along the $\langle 110 \rangle$ direction. The horizontal dashed line indicates the Fermi energy E_F (set to zero).

viously for all x in Na_xCoO_2 ,^{3,21} the crystal field splitting between the partially occupied t_{2g} manifold with a 1.3 eV width and the unoccupied e_g manifold with a 1 eV width is 2.5 eV. The large splitting makes the e_g manifold irrelevant for low energy considerations.

The band structure of the t_{2g} manifold, showing strong two dimensionality, is given in Fig. 1. (This two dimensionality is reflected in the Fermi surfaces displayed in Fig. 2.) The a_g character emphasized by the thickened (or colored) lines is represented by the “fatband” technique in Fig. 1. The

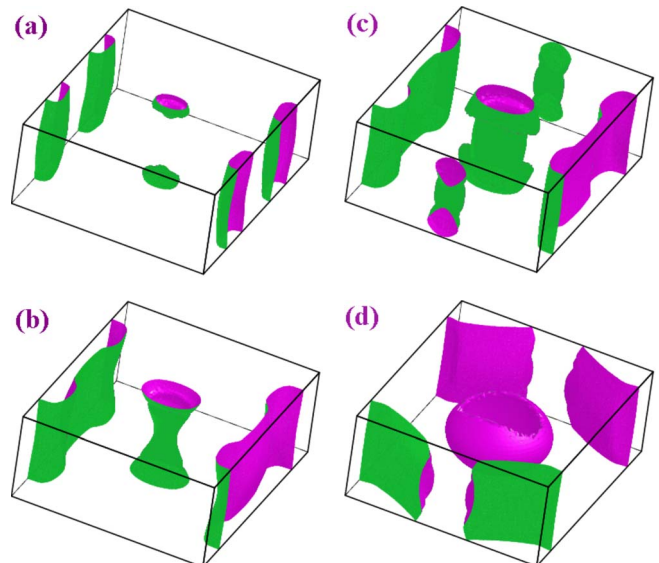


FIG. 2. (Color online) Fermi surfaces of nonmagnetic $\text{K}_{0.5}\text{CoO}_2$, showing a strong two dimensionality. The band structure leads to six Fermi surfaces (FSs), but the first and sixth FSs are not shown here. The first FS is similar to (a), except for a smaller cap at the Z points. The sixth FS has the same shape as (d), but it has no Γ centered egg. The pink (darker) colored surfaces contain holes, whereas the green (lighter) colored surfaces hold electrons.

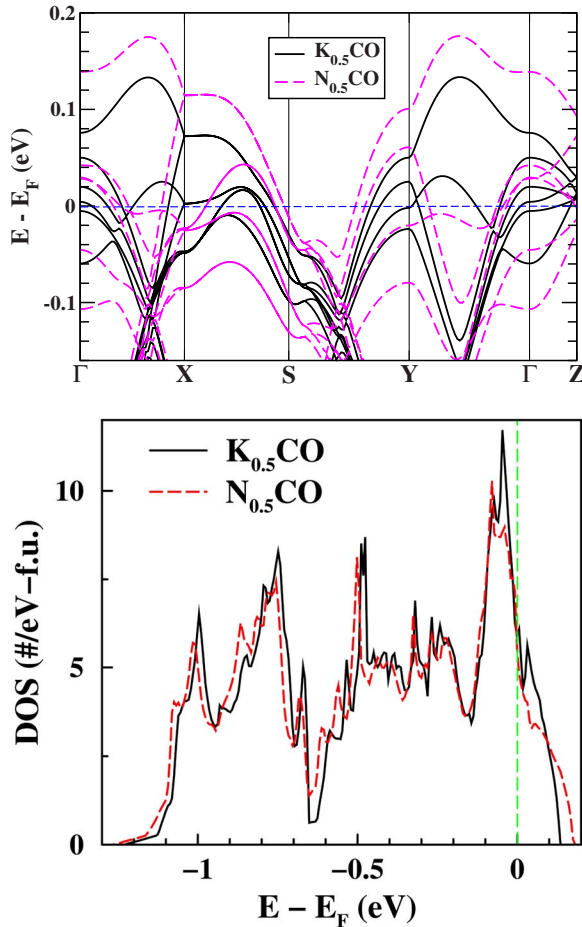


FIG. 3. (Color online) A comparison of electronic structure between nonmagnetic $K_{0.5}CoO_2$ and $Na_{0.5}CoO_2$. Top: Enlarged band structures near E_F . Differences between the band structures are more noticeable at E_F , particularly at the X and Y points and along the Γ - Z line. Bottom: Total densities of states per formula unit at the t_{2g} manifold. $K_{0.5}CoO_2$ has about 10% larger $N(0)$ than 5.4 states/eV per formula unit of $Na_{0.5}CoO_2$ (but invisible in this figure). The vertical dashed line denotes E_F .

a_g character appears at both the bottom and the top of the t_{2g} manifold, but the character is a little stronger in the bottom. This behavior is also observed in $Na_{0.5}CoO_2$.

As expected from the larger c lattice constant, $K_{0.5}CoO_2$ has a smaller bandwidth, seen in both the O p bands (not shown here) and Co t_{2g} bands. The change in the bandwidth appears clearly at the top valence band in the enlarged band structures near E_F depicted in the top panel of Fig. 3. The top valence band of $K_{0.5}CoO_2$ has about 60 meV lower energy at the Γ point and contains less holes, leading to an additional E_F -crossing valence band near the X point and along the Y - Γ line. This crossing produces additional Fermi surfaces of an unfolded scroll-like shape along the X - S line, as displayed in (b) and (c) of Fig. 2. These Fermi surfaces are almost flat near the X point, suggesting an enhancement of nesting effects. These nesting effects could lead to a SDW, suggested in $K_{0.49}CoO_2$ by Sugiyama *et al.* The absence of these Fermi surfaces in $Na_{0.5}CoO_2$ may explain why a SDW does not occur in the system.

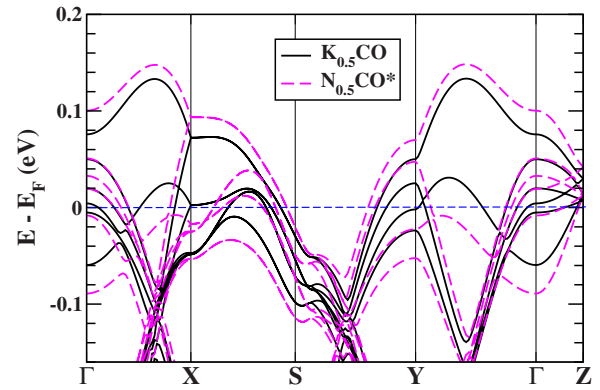


FIG. 4. (Color online) Comparison of band structure between nonmagnetic $K_{0.5}CoO_2$ and $Na_{0.5}CoO_2^*$ near E_F . $Na_{0.5}CoO_2^*$ is assumed to have the same crystal structure as $K_{0.5}CoO_2$ in order to investigate pure effects of K substitution.

An important distinction is the stronger two dimensionality in $K_{0.5}CoO_2$. At the X and Y points and along the Γ - Z line near E_F there are nearly flat bands and saddle points in $K_{0.5}CoO_2$. The bottom panel of Fig. 3 displays a comparison of the density of states (DOS) of the two cobaltates. Strikingly, the Fermi energy of $K_{0.5}CoO_2$ lies midway between two sharp peaks at -45 and 35 meV. In addition, a van Hove singularity appears just above E_F (at less than 10 meV). These more complicated structures near E_F lead to 10% higher DOS at E_F , suggesting an increased tendency toward magnetic instability.

C. Identifying differences

These differences between the two cobaltates can be clarified in two ways. First, we can determine the effects purely due to chemical difference (K vs Na) as opposed to the size difference leading to structural differences. For this, $Na_{0.5}CoO_2$ is assigned the same structure as in $K_{0.5}CoO_2$ and denoted as $Na_{0.5}CoO_2^*$. The resulting band structure enlarged near E_F is compared with that of $K_{0.5}CoO_2$ in Fig. 4. Even in the identical structure, substantial differences on an important energy scale are evident. The top valence band in $Na_{0.5}CoO_2^*$ is 20 meV higher in energy at the Γ point, although the t_{2g} bandwidth is about 5% smaller (not shown). Another difference is that the projected K and Na DOSs are almost identical (and small, of course) through most of the t_{2g} bands, except in an ~ 0.15 meV region at and below the Fermi level, where the Na projected DOS (PDOS) is 20%–35% larger (more than 50% larger at E_F). These distinctions indicate that the differences in electronic structure are mainly due to K substitution itself rather than indirectly through the change in structure.

Second, using the Mulliken charge decomposition, we obtained atom-decomposed charges, which are displayed in Table II. The K ion is very noticeably more ionic than the Na ion, consistent with the PDOS difference mentioned just above. The compensating charge is spread over the oxygen ions; the Co charges are essentially the same for $K_{0.5}CoO_2$ and $Na_{0.5}CoO_2^*$. This higher ionicity of K seems to be the

TABLE II. Atom-decomposed charges, which are obtained from the Mulliken charge decomposition in the FPLO method for each atom in $A_{0.5}\text{CoO}_2$ ($A=\text{Na}, \text{K}$). The absolute numbers do not have a clear meaning, but differences reflect real distinctions in bonding. $\text{Na}_{0.5}\text{CoO}_2^*$ denotes $\text{Na}_{0.5}\text{CoO}_2$ with the same crystal structure as $\text{K}_{0.5}\text{CoO}_2$.

Atom site label	A			Co			O			
	$2a$	$2b$	Average	$4f$	$4d$	Average	$4f$	$4f$	$8g$	Average
$\text{K}_{0.5}\text{CoO}_2$	+0.72	+0.68	+0.70	+1.58	+1.60	+1.59	-0.97	-0.97	-0.97	-0.97
$\text{Na}_{0.5}\text{CoO}_2$	+0.64	+0.63	+0.63	+1.60	+1.62	+1.61	-0.94	-0.97	-0.97	-0.96
$\text{Na}_{0.5}\text{CoO}_2^*$	+0.64	+0.61	+0.63	+1.59	+1.60	+1.59	-0.94	-0.95	-0.96	-0.95

most discernible difference between these cobaltates.

D. Comments on hydration

It is still unclear what water does in the system. The only unambiguous aspect is that hydration dramatically increases the c lattice constant, resulting in more two dimensionality of the electronic system.²² However, although the isostructural system $\text{Na}_{1/3}\text{TaS}_2 \cdot y\text{H}_2\text{O}$ shows a very similar change in the c lattice constant when hydrated,³ $T_c \approx 4$ K in this system is independent of y . This difference in behavior established that water has effects in the cobaltates that are not present in the transition metal disulfides and diselenides. In this respect, it is interesting that $(\text{Na}_{0.27}\text{K}_{0.12})\text{CoO}_2 \cdot 0.87\text{H}_2\text{O}$ shows superconductivity with $T_c \approx 3$ K and about 7 Å increment in the c lattice constant from $\text{K}_{0.55}\text{CoO}_2$, which is similar in amount to that of hydrated sodium cobaltate.²³

IV. SUMMARY

Using a crystal structure recently reported, we have investigated at the LDA level the differences in electronic structure between $\text{K}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.5}\text{CoO}_2$. A comparison shows a few substantial differences near E_F : smaller t_{2g} bandwidth by 60 meV in $\text{K}_{0.5}\text{CoO}_2$ and additional Fermi surfaces along the X - S line, which are almost flat near the X point. These differences are due more to chemical differences (higher

ionic character of K) rather than to the structural difference between the systems.

An angle-resolved photoemission comparison of the three systems $A_x\text{CoO}_2$, $A=\text{Na}, \text{K}$, and Rb , has appeared,²⁴ with the differences at equal doping levels being small, almost too small to quantify. Unfortunately, samples at precisely $x=0.5$ were not the focus of that study. Since the superstructure we have studied is confined to $x=0.5$, our results cannot be compared with this data. However, the structural disorder of the alkali sublattice at $x \neq 0.5$, which extends to the CoO_2 substructure, broadens the bands and hides small distinctions.²⁵ This observation suggests that carrying out spectroscopic studies of both systems in the insulating phase at $x=0.5$ should be an excellent way to identify and characterize more precisely the effects of the different alkali cations.

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