Ab-initio investigation of spin states of sodium cobaltate Na\textsubscript{2/3}CoO\textsubscript{2}

Y V Lysogorskiy\textsuperscript{1,2}, O V Nedopekin\textsuperscript{2}, S A Krivenko\textsuperscript{2}, B Minisini\textsuperscript{1}, and D A Tayurskii\textsuperscript{2}

\textsuperscript{1} Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, 72000, 44 Av. Bartholdi, Le Mans, France
\textsuperscript{2} Institute of Physics, Kazan Federal University, 420008, Kremlyovskaya St. 18, Kazan, Russia

E-mail: yura.lysogorski@gmail.com

Abstract. Recent experiments in the lamellar system Na\textsubscript{x}CoO\textsubscript{2} detected a transition of Co planes into a puzzling metallic state at x \textgtrless 2/3, which co-exists with a robust arrangement of the 3d cobalt electrons: The triangular Co lattices are disproportionated in the spinless Co\textsuperscript{3+} sites (Co\textsubscript{1}), and Co\textsuperscript{4+} sites (Co\textsubscript{2}) with enhanced magnetism forming conducting sublattices. This textures concur with a tightening of the ferromagnetic (FM) interaction in planes, and emerge when the sodium ions become arranged in layers in between the CoO\textsubscript{2} slabs. In the present research we have investigated ab-initio the appearance of such state in Na\textsubscript{2/3}CoO\textsubscript{2}. Towards this end in view we studied an interplay between the electronic coupling to the superstructure of the Na\textsuperscript{+} ions and local correlations of the itinerant d electrons treated within the GGA+U approximation. Employing the exact crystallographic supercell, the electronic organization has been analyzed upon increasing the energy U of the Coulomb repulsion within the 3d shells at T = 0. The metallic ground state, being a spin density wave with the inplane FM and antiferromagnetic interplane correlations, has been obtained and established to posses two regimes. When U > 2 eV, a crossover develops from a uniform state of the d-lattice to the regular phase with the spin/charge disproportionation between the sites. In particular at the representative value U = 5 eV, the Co\textsubscript{1}\textsuperscript{3+} sites with suppressed magnetism appears, while the spin-active Co\textsuperscript{4+} holes are accumulated by the Co\textsubscript{2} sites. A related formation of an isolated, narrow conduction band at the Fermi level implies a considerable enhancement of the electron correlations in the crystal field imposed by the Na\textsuperscript{+} patterns.

1. Introduction

Intriguing behavior of the lamellar sodium cobaltates Na\textsubscript{x}CoO\textsubscript{2} is in focus of numerous resent researches. Large thermopower and relatively low resistivity make these material promising for thermoelectronics [1, 2]. The pronounced magnetic field effect on the thermopower implies considerable spin entropy and an importance of Co(3d) electronic correlations in the ground state. A discovery of superconductivity (T\textsubscript{c} \textapprox 5K) in Na\textsubscript{x}CoO\textsubscript{2} \cdot 1.3 H\textsubscript{2}O (x \textapprox 0.33) farther promotes the interest to the electron physics of the lamellar sodium cobaltates, providing an example of a layered non-cuprate oxide superconductor [3].

Structurally, Na\textsubscript{x}CoO\textsubscript{2} consists of quasi-two-dimensional CoO\textsubscript{2} slabs stacked along the crystallographic c-axis and separated by Na layers [Fig. 1(a)]. Forming the triangular lattice, the planar Co ions are surrounded by edge-sharing O\textsubscript{6} octahedra. To the first approximation, the octahedral crystal field splits the local 3d levels into the lower t\textsubscript{2g} orbital triplets and upper e\textsubscript{g}
Figure 1. (Color online) Structure of Na$_{2/3}$CoO$_2$ presented in accordance with NMR measurements of Alloul et al., see [10]. (a) Elementary cell with the respective sodium and cobalt ion positions. (b) Sketch of the cobalt plane: The violet (red) open circles specify the inert ions Co1a (Co1b) being Co$^{3+}$. The light (dark) blue circles stand for the magnetically-active Co2a (Co2b) ions Co$^{3.44+}$. The conducting kagome sublattice is indicated by the thin solid lines.

doublets with the gap about 2 eV between them [4]. This suggests the ground state configuration $t_{2g}^6 (S = 0)$ and $t_{2g}^5 (S = 1/2)$ for the Co$^{3+}$ and Co$^{4+}$ ion, respectively.

Sodium ions Na$^+$ donate $x$ electrons into the 3$d$ shells of the Co$^{4+}$O$_2^{2-}$ planes. Contr-intuitively, in the metallic cobaltates the correlations enhance upon increasing $x$ [i.e. upon decreasing the density $1 - x$ of the itinerant holes Co$^{4+}$($t_{2g}^5$)] in particular in the range $0.65 < x < 0.85$ about the band-insulator limit $x = 1$. The experimental indications of this are the following:

(i) Sommerfeld constant $\gamma$ is markedly increased from the low-$x$ value, about 11 mJ/mol K$^2$, to 30 – 50 mJ/mol K$^2$ [5], demonstrating the heavy-fermion behavior [6].

(ii) Localized spin states emerge, which are manifested by the Curie-Weiss behavior of magnetic susceptibility [7].

(iii) Simultaneously, intersite ferromagnetic (FM) spin correlations become strengthened at $x > 0.65$ [7], and the inplane FM order [more precisely A-AFM (antiferromagnetic) spin structure] is formed when $0.75 < x < 0.85$ [8, 9].

(iv) In addition, imprints of robust electronic arrangements, irrelevant for Fermi liquids, appear in the metal [10]: In the triangular lattice, the cobalt 3$d$-electrons become segregated between the Co1 and Co2 sites, being in different magnetic and valence states. In particular, at $x = 2/3$ the extended spin-active holes, repelled from the inert sites Co1$^{3+}$ are almost confined in the kagome sublattice Co2$^{3.44+}$ [10], see Fig. 1(b).

Experimentally, for $0.65 < x < 0.85$ the Na$^+$ ions become arranged in the positions Na1 and Na2 between the Co planes, when the temperature decreases below few hundred Kelvins [11], see Fig. 1(a). Then, a tunneling of the holes Co$^{4+}$ to the Co1 sites could be suppressed due to their electric repulsion from the adjacent cations Na1$^+$. A relevant description of this puzzling metal represents a problem, which we address in the present study. Previous theoretical approaches [4, 12–15] to the collective states of CoO$_2$ slabs disregarded the sodium ions superstructure, relying on a strong on-site/inter-site Coulomb
interaction between the 3d electrons. However, the repulsion energy of the itinerant holes from the Na$^+$ ions is considerable [16] and should be also included into the description of the electron physics. Within an approximation of a chaotic distribution of the Na$^+$ cations, sodium were established to markedly enhance the correlations in the metallic cobaltates [17, 18].

In the present work, we study the role of the realistic sodium arrangement in the formation of the unconventional metallic state of the CoO$_2$ planes. To this end, we consider the representative system Na$_2$CoO$_2$ and investigate an interplay between the two relevant interactions, (i) the on-site Coulomb repulsion with the energy $U$ between the 3d electrons and (ii) the electron coupling to the regular superstructure of the Na$^+$ ions. Starting with the experimental crystal supercell [10], we have described the electronic states at $T = 0$ in a dependence on $U$ within the GGA+U approximation. Our approach is detailed in Sec. 2, the electronic structure is deduced in Sec. 3, and results are discussed in Sec. 4.

2. Ab-initio approach

2.1. GGA+U method

We performed the first-principle calculations with the spin-polarized density functional theory (DFT). The generalized gradient approximation (GGA) was implemented with the functional form of the Perdew–Burke–Ernzerhof exchange correlation revised for solids (PBEsol), see Ref. [19]. The electron-ion interaction was represented with the projector augmented-wave method (PAW) [20] implemented in the Vienna Ab Initio Simulation Package (VASP 5.2.2) [21]. The plane-wave cutoff energy was 500 eV.

As the internal coordinates and so the crystal cell parameters were fully relaxed. The Brillouin zone (BZ) was sampled with a $5 \times 5 \times 5$ mesh, containing the gamma point; the corresponding density of the mesh was about one point per 0.004 Å$^3$. The energy convergence criteria $10^{-5}$ eV has been chosen. The strong electron correlations were treated with the simplified (rotationally invariant) LSDA+U approach, introduced by Dudarev et al. [22], and $U_{\text{eff}} = U - J$ was used as the Hubbard parameter $U$.

Two PAW potentials have been tested for sodium: one with seven valence electrons ($2p^63s^1$) and another with one valence electron ($3s^1$). In the first case, all the $p$-electrons were found to be localized at the sodium cations, signifying a sufficiency of the Na$^+$ potential with one valence electron for the calculations.

2.2. Supercell structure

In Ref. [10], using the NMR/NQR technique, the crystallographic positions of the sodium and cobalt ions in Na$_2$CoO$_2$ were identified and the unit cell with the symmetry group $R - 3c$ was established for this compound, see Fig. 1(a). In this cell the cobalt ions occupy four distinct positions [Fig. 1(b)]: The Co1a and Co1b sites have the minimal distance from the sodium ions Na$^+$, suggesting the larger crystal potential, ejecting the holes to the remaining Co2a and Co2b sites forming the kagome sublattice.

We performed a geometry optimization of such cell in the range from $U = 0$ eV to 6 eV, employing the GGA and GGA+U technique. The arrangement of the sodium ions remained robust even without symmetrization of charge densities and forces. Thus, the stability of the sodium pattern, reported in Ref. [10], was confirmed. Again, we have calculated the energies of the system as for FM and so for AFM interlayer spin configurations. The AFM order was found to have less energy ($\approx 7.5$ meV per one irreducible layer) and, thus, to be more favorable.

3. Results

First, we calculated electronic states for the hypothetic case $U = 0$, when the correlations are “switched off” in the cobalt 3d shells in Na$_2$CoO$_2$. Then, the GGA provides a uniform Fermi liquid state of the Co planes with the small FM spin-polarization $\approx 0.3 \mu_B$ of the band due to
weak correlations remaining in the system, see Fig. 2(a). The electronic spectrum, described in terms of the density of states (DOS), is presented in Fig. 3(a). The wide conduction band (with the width \( \approx 1.6 \text{ eV} \)) mostly originates from the \( t_{2g} \) levels, providing the relatively small DOS \( \rho_F \approx 1.1 \text{ eV}^{-1} \) at the Fermi energy \( E_F \). In turn the lower, valence band comes from the occupied \( O(2p) \) states, while the upper band corresponds to the \( e_g \) excitations, see Fig. 3(a). The coupling to the \( \text{Na}^+ \) does not crucially affects the \( \text{CoO}_2 \) planes when \( U = 0 \): The DOS resembles to that, obtained with the LSDA+U model, disregarding sodium effect [23].

When the correlations appear within the 3d shells \((U > 0)\) the obtained spin-density wave in the Co plane gradually transforms to a non-uniform regime: The marked disproportionation develops between the Co1 and Co2 sites when \( U > 3 \text{ eV} \), see Fig. 2(a). The effect is particularly strong when \( U \geq 5 \text{ eV} \): The enhanced moments \( \mu_{\text{Co2b}} \approx 0.6 \mu_B \) at the Co2b sites form the FM hexagon patterns, while the magnetism of the Co1 and Co2a sites becomes almost suppressed, see Fig. 2(b).

With the realistic value \( U = 5 \text{ eV} \) (taken in between the estimations 4.91 eV for the \( \text{Co}^{3+} \) ion and 5.37 eV for the \( \text{Co}^{4+} \) ion in the lithium cobaltate [24]), the effect of the sodium superstructure becomes crucial for the spectrum of the \( \text{CoO}_2 \) planes, see Fig. 3(b). In particular, at the Fermi level the isolated narrow \( d \)-band is formed, indicating a considerable enhancement of the correlations in the \( \text{CoO}_2 \) planes. This sharp feature has the bandwidth \( \approx 125 \text{ meV} \) and \( \rho_F \approx 5.42 \text{ eV}^{-1} \). Just the electron coupling to the sodium-cation system promotes the correlations, which otherwise remains weak: \( \rho_F \approx 0.5 \text{ eV} \) for \( U = 5 \text{ eV} \) [23].

As evident from Fig. 3(c), at the Co2b sites the DOS (taken in the average below \( E_F \)) becomes less than the respective DOS of the other cobalt sites, indicating that the spin separation [Fig. 2(b)] goes hand-in-hand with the charge redistribution in the Co lattice. The non-magnetic state of the Co1 and Co2a ions (having more populated 3d-shells) implies their closeness to the \( \text{Co}^{3+} \) \((t_{2g}^6, S = 0)\) configuration. Avoiding these sites, the magnetic holes \( \text{Co}^{4+} \) \((t_{2g}^5)\) tend to the Co2 sublattice, thereby forming the localized spin states in the metal [Fig. 2(b)]. We obtain the FM interaction between spins in plane and the AFM coupling between planes in accordance with the experimentally observed A-AFM correlations in \( \text{Na}_x\text{CoO}_2 \) \((0.65 < x < 0.85)\) [8, 9].
Figure 3. Energy dependence of the electronic density of states (DOS) within the GGA+U approximation. Plots (a) and (b): DOS for Na$_{\frac{2}{3}}$CoO$_2$ (bold line) calculated with $U = 0$ eV (a) and $U = 5$ eV (b). Corresponding cobalt (oxygen) contributions to the DOS are given by the solid (dash) lines. Plot (c): Electronic DOS at the cobalt sites obtained with $U = 5$ eV. The short (long) dash line represents DOS at the Co1a (Co1b) sites, and the thin solid (bold solid) line corresponds to the Co2a (Co2b) ions.

The narrow band obtained in the DOS at $E_F$ indicates, that the electronic disproportionation coexists with the robust metallicity ($\rho_F > 0$) of the Co planes up to $U \approx 6$ eV. Experimentally, the metallic state of the cobaltate was found, e.g., in Ref. [7].

The calculated Fermi surface (FS) has seven pockets. The central one, located about $\Gamma$ symmetric point of the BZ of the triangular lattice, always has a hole character (convex). The six pockets, found nearby the $K$ points, gradually change their nature from an electron-like at $U = 1$ eV to the hole-like at $U = 6$ eV. With $U = 1$ eV the volume $V_F$ of the FS encompasses 32% of the BZ volume ($V_{BZ}$), in close correspondence with the concentration of the holes ($1 - x = 1/3$) in the $d$-lattice of Na$_{x=2/3}$CoO$_2$. For $U = 6$ eV, we obtain $V_F = 0.31V_{BZ}$. Thus, the Luttinger’s theorem is satisfied with a good accuracy for such electronic liquid. The central pocket comprises 7% (12.5%) of $V_{BZ}$ for $U = 1$ eV ($U = 6$ eV).

We estimated the cobalt magnetic moment $\mu_{Co2} = 0.4\mu_B$ per Co2 site for $U = 5$ eV. Again, measurements of magnetic susceptibility of Na$_{2/3}$CoO$_2$ provided the larger value $\mu_{Co2}^{(exp)} \approx 1.2\mu_B$ in the temperature range from 50 K to 250 K [8]. A plausible way to resolve this discrepancy is to take into consideration excitations of Co ions towards higher spin states.

4. Discussion

The strong FM-correlations in the triangular Co planes are known to appear at $x \geq 2/3$ within the Hubbard-model approach for the cobaltates, which disregards the Na superlattice [12, 18, 25]. Then, a delicate treatment of the nearest and next-nearest neighbor correlations enabled to obtain imprints of the kagome-like charge/spin density wave (the M-point pike of the charge
susceptibility) in the metallic state [25]. This instability is related with a pronounced van Hoove singularity, existing in the DOS nearby the Fermi level in an effective kagome lattice [26]. However, such approach provided an electronic disproportionation, only when the 3d electron intersite repulsion ($V \approx 0.1 - 0.4$ eV) between the nearest-neighbor sites of the lattice was included into the model [18].

The present approach does not require an intersite electronic repulsion to produce the effect: The obtained metallic state, combining the strong spin/charge disproportionation and intersite FM spin correlations, results from a peculiar optimization of the double-exchange interaction [27, 28] in the crystal field imposed by the Na$^+$ arrangement. In more details, we shall discuss this physics elsewhere.

The deduced electronic structure of the metal (magnetic Co2b-hexagons) partially reproduces the realistic magnetic kagome Co2 lattice, cf. Fig. 2(b) with Fig. 1(b). However, the magnetism of the Co2a sites is suppressed [see Fig. 2(b)] indicating, that these ions are close to the Co$^{3+}$ state likewise the sites Co1a and Co1b. Virtual transitions of the Co$^{2+}$ ions to their high spin (HS) configuration $t_{2g}^2e_g$ ($S = 1$) could enhance their moments and proliferate the magnetism to the Co2a sites, reproducing the kagome lattice. We intend to clarify this issue in a future investigation. Resembling HS fluctuations were implemented, e.g., in the spin-polaron theories of the CoO$_2$ planes by Khaliullin and Chaloupka [13].

An existence of six small FS pockets, obtained nearby the $K$-points of the BZ in our study, were not revealed by ARPES experiments so far [29]. In principle, they could be hidden for ARPES, because this technique mostly detects surface electronic states, which could differ significantly from those in a bulk of a sample [30]. In turn, transport measurements, employing the Shubnikov–de Haas effect, corroborated the presence of the FS pockets in Na$_x$CoO$_2$ at $x = 0.71$ and $0.84$ [31]. Another evidences in favor of an existence of these features are provided by bulk measurements with the x-ray Compton scattering technique, performed in the unhydrated and hydrated sodium cobaltates [32]. On the theoretical ground, a more accurate treatment of the 3d correlations beyond the mean-field GGA+U approximation could verify a robustness of the FS pockets within the present approach.

5. Conclusion

In the present work we have calculated ab-initio electronic and magnetic properties of sodium cobaltate Na$_{2/3}$CoO$_2$ within GGA+U approximation. In contrast to previous studies [12, 23, 33], we have used the supercell of this compound, deduced from the experiments in Ref. [10]. We have established the sodium arrangement to remain stable, as it does not change after the full structure relaxation.

Electronic state of the FM metal Na$_{2/3}$CoO$_2$ has been described microscopically in a dependence on the energy $U$ of the Coulomb repulsion within the 3d shells. The metallic ground state, being a spin density wave with A-AFM correlations (FM-inplane and AFM-interplane), has been obtained. The state was found to posses the two regimes: A uniform phase of the $d$-lattice for $U < 2$ eV, and the regular phase with the spin/charge disproportionation between the sites for $U > 2$ eV. In particular at the representative value $U = 5$ eV, the Co$^{1+}$ sites with suppressed magnetism appears, while the spin-active Co$^{4+}$ holes are accumulated by the Co2 (more exactly Co2b) sites in accordance with the experimental behavior [34]. A related formation of an isolated, narrow conduction band at the Fermi level implies a considerable enhancement of the electron correlations in the crystal field imposed by the Na$^+$ patterns.

Such a peculiar metallic electronic structure appears due to the specific interplay between the electrostatic potential induced by the periodic Na$^+$ arrangement and the strong correlations in the 3d orbitals.
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