

## Origin of electron disproportionation in metallic sodium cobaltates

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Recently, an unusual metallic state with a substantially nonuniform distribution of the charge and magnetic density in  $\text{CoO}_2$  planes was found experimentally in the  $\text{Na}_x\text{CoO}_2$  compound with  $x > 0.6$ . We have investigated the origin of such an electron disproportionation in the lamellar sodium cobaltates by calculating the ion states as a function of the strength of the electron correlations in the  $d(\text{Co})$  shells within the GGA+ $U$  approximation for a system with a realistic crystal structure. It was found that the nonuniformity of spin and charge densities are induced by an ordering of the sodium cations and enhanced correlations. Two important magnetic states of cobalt lattice competing with each other at realistic values of the correlation parameter were found—low-spin hexagons lattice (LS) and higher-spin kagome lattice (HS-KSL). In the heterogeneous metallic HS-KSL phase, magnetic Co ions form a kagome structure. In LS phase, the kagome pattern is decomposed into hexagons and the Co ions possess the minimal values of their spin. Coexistence of these states could explain the emergence of the disproportionation with the peculiar kagome structure experimentally revealed in previous studies of the cobaltates.

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### I. INTRODUCTION

The mechanisms of correlations between  $d$  electrons, hopping in the lattices of transition metal (TM) ions, are crucial for complex many-particle phenomena in the TM compounds: the insulator-to-metal transition (IMT), high-temperature superconductivity, colossal magnetoresistance, and charge/magnetic ordering [1]. Metallic systems with strong correlations are conventionally obtained from either Mott or charge-transfer insulators, adding a small amount of doped charge carriers in their lattices, as in the case of cuprates and manganites. However, in some cases, strongly correlated metallic states arise in doped band insulators, as in ruthenates and iron pnictides/chalcogenides, representing puzzles for the researchers [2].

A spectacular example of such systems with unconventional correlations is the lamellar cobaltates  $\text{Na}_x\text{CoO}_2$ , composed of  $\text{CoO}_2$  layers with  $\text{Na}^+$  ions between them. The layers, containing triangular cobalt lattices, are formed by the edge-sharing  $\text{CoO}_6$  octahedra slightly compressed along the crystalline  $c$  axis [3–8].  $\text{Na}_1\text{CoO}_2$  is the band insulator with the spinless  $\text{Co}^{3+}$  ions [9]. When the sodium content is decreased in the compound, a metallic state with a rather good electric conductivity is evidenced within the entire range of  $x$  except  $x = 1/2$ .

In the range between  $x = 1/2$  and 1, simplified intuitive considerations suggest that, when the hole becomes localized at the  $3d$  shells of the cobalt ions, the corresponding  $d^5$  magnetic states with  $S = 1/2$  should appear instead of the spinless  $d^6$  state ( $\text{Co}^{3+}$ ). Then, in the lattice, the proportion  $1 - x : x$  between the  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  states should exist for any given value of  $x$ . However, experiments unambiguously indicate that such a picture of the  $\text{Co}^{3+}/\text{Co}^{4+}$  segregation is invalid in the cobaltates. On the contrary, a very peculiar charge/magnetic state called the “charge disproportionation” appears [10,11]. In particular, in the doped  $\text{CoO}_2$  layers, a

small amount ( $\leq 25\%$ ) of  $\text{Co}^{1+}$  ions remains in the localized nonmagnetic state  $\text{Co}^{3+}$ , whereas the holes are delocalized over the remaining part of the cobalt lattice, the  $\text{Co}^{2+}$  sites. In the range  $0.65 < x \lesssim 0.80$ , at least four stable phases  $x = 2/3$ , 0.71, 0.72, and 0.77 exist in the system, which are distinguished by the sodium atom arrangements [10]. Experiments exhibit a well defined correlation between the disproportionation of the  $d$  electrons and the ordering of the ions in the sodium layers [11]. Both phenomena emerge concurrently, disappearing at temperatures higher than  $T^* \approx 400$  K. The magnetic susceptibility of the system with the disproportionation is temperature dependent, resembling the Curie-Weiss law relevant for localized magnetic moments. Above 100 K, the dependencies  $\chi(T)$  look very much alike for all phases, whereas at smaller temperatures they are different [10]. Namely, upon decreasing  $T$  down to 50 mK, the phases with  $x < 0.75$  remain paramagnetic with inplane/interplane ferromagnetic (FM)/antiferromagnetic (AFM) correlations between  $d$  moments, while the  $x = 0.77$  phase exhibits a transition to the A-AFM order at  $T_N = 22$  K.

The  $x = 2/3$  crystal phase was investigated in greater detail than the other ones. Its three-dimensional structure has been reliably established employing both the NMR/NQR and x-ray diffraction techniques [12,13]. An elementary cell of this phase comprises 264 atoms. In particular, the cell has six sodium layers, alternating with six  $\text{CoO}_2$  layers. In the sodium planes, the ions occupy the two positions: Na1 sites located just above and below the  $\text{Co}^{1+}$  ions, and Na2 sites being more distant from the nearest  $\text{Co}^{2+}$  ions. A sodium layer pattern contains the lone Na1 ions interlaced with six clustered Na2 ions forming triangles, see Fig. 1(a). In the cobalt plane, the holes are pushed out from the  $\text{Co}^{1a}$  and  $\text{Co}^{1b}$  sites; this makes these ions nonmagnetic. These itinerant holes are delocalized over the  $\text{Co}^{2+}$  sites making them magnetic.  $\text{Co}^{2+}$  sites bearing magnetic moments form a regular kagome sublattice (KSL), see Fig. 1(b) [12]. To be more precise, the KSL contains the less magnetic and more magnetic  $\text{Co}^{2a}$  and  $\text{Co}^{2b}$  ions, respectively. The  $^{59}\text{Co}$  NMR measurements detected a strongly pronounced in-plane anisotropy of the  $d(\text{Co}^{2+})$  shells of the  $\text{Co}^{2+}$  sites

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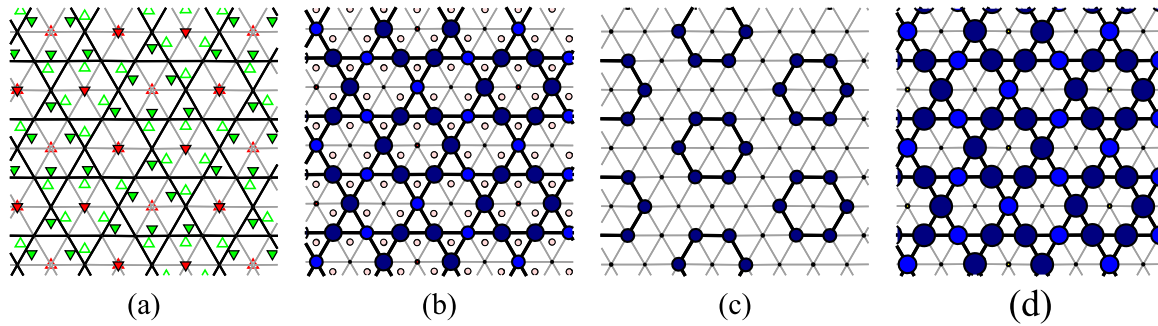


FIG. 1. Structure of the lamellar cobaltate  $\text{Na}_{2/3}\text{CoO}_2$ . The crystal axis  $c$  is directed orthogonally to the figure. The solid lines connect the nearest sites of the triangular Co sublattice in the  $\text{CoO}_2$  layers. Co2 sites form kagome sublattice highlighted by the thick solid lines. (a) Ordering of the  $\text{Na}^+$  ions above (filled symbols) and below (open symbols) the  $\text{CoO}_2$  layer. Na1 (Na2) atoms are presented by red (green) triangles (in the sodium layers the Na2 ions form the triangular clusters, containing six adjacent atoms, where the apex positions are conventionally denoted as Na2a sites, and the remaining Na2 positions are denoted as Na2b sites). (b) Experimentally established disproportionated state of the  $d$  electrons [12,13]. The nonmagnetic Co1a and Co1b ions are denoted by the black and red dots, whereas the magnetic Co2a and Co2b ions are given by the light-blue and dark-blue circles, respectively. Pink circles represent the oxygen atoms in the layer just above the Co layer. (c) and (d) *Ab initio* calculated electronic states with  $U = 5$  eV: (c) hexagonal LS phase and (d) HS-KSL phase. Circle size is proportional to the magnetic moment at cobalt ion.

[13]. This implies that the KSL is formed concurrently by a redistribution of the holes from the axially symmetric  $a_{1g}$  orbitals to other  $d$  states of the Co2 sites [12,13]. The origin of such intricate states of the  $\text{CoO}_2$  layers remains unclear.

In previous studies of the cobaltates, several theoretical approaches to the problem of their unusual correlated state were developed. As a first approximation, the interaction of the Co ions with the ligands splits their  $3d$  states into the lower  $t_{2g}$  triplets separated from the upper  $e_g$  doublets by the large gap with the energy  $\Delta \approx 2$  eV [14]. The “minimal” approach treats the ground-state configurations of the ions,  $t_{2g}^6$  with  $S = 0$  and  $t_{2g}^5$  with  $S = 1/2$ , as being the low-spin (LS) states of the sites  $\text{Co}^{3+}$  and holes  $\text{Co}^{4+}$ , respectively. In this case, the relevant interaction between the itinerant holes comes from their mutual repulsion within the ion  $t_{2g}$  shells with the corresponding Hubbard energy  $U$  [15–30]. For a temperature greater than a few hundred degrees Kelvins, when the sodium layers are disordered, the correlation effects in the cobaltates are well described by the Hubbard model for the holes in the triangular  $d$  lattice [21,23,30]. At the very high temperature  $T \approx 500$  K, the model reveals some tendency towards a spatially nonuniform state of the holes at  $x \approx 0.7$ , with a weak redistribution of their density over the sites possessing a symmetry of the KSL [23]. Unfortunately, the theory of Ref. [23] does not take into account the patterning of  $\text{Na}^+$  cations, which arise concurrently with the charge redistribution in the Co lattice upon decreasing  $T$  [12,13]. The nonuniform Coulomb potential introduced by the sodium layers could substantially affect the hole states in the cobaltates [19,22,31]. The disproportionation *per se*, when the holes are almost completely pushed out from the Co1 sites, was not achieved in this model. Besides, the employed  $a_{1g}$  states of the holes [23] do not produce the anisotropy of the  $d$  shells, which was observed experimentally. Again, the Hubbard model does not explain why the KSL disproportionation, inherent to the sodium cobaltates, is not observed in other systems with the triangular  $d$  lattices, e.g., the metallic lithium cobaltates  $\text{Li}_x\text{CoO}_2$ .

The approach used in Refs. [32–36] suggests that the hole could hop from its site to the nearest  $d$  sites, when the counterdirectional electron hops back to the  $e_g$  orbital. At the original site, this results in the excitation of the  $\text{Co}^{3+}$  ion to its higher-spin (HS) state  $t_{2g}^5 e_g$  with  $S = 1$ .<sup>1</sup> Such processes are allowed in the layers, because the angles of the Co-O-Co bonds are about  $90^\circ$ . Moreover, these processes are plausible because the Hund coupling between the electrons within the  $d$  shells substantially reduces the energy  $\approx \Delta - 2 J_H \approx 300$  meV [32,36] for the corresponding transitions of the  $\text{Co}^{3+}$  ions across the crystal gap.<sup>2</sup> Then the holes become “dressed” by clouds of the HS-spin excitations to the  $e_g$  orbital. When such polarons propagate throughout the  $d$  lattice, they mix the HS and LS states of  $\text{Co}^{3+}$  ions [36]. However, the polaron scenario contradicts the picture of the disproportionation, where a significant part  $\approx 25\%$  of the Co1<sup>3+</sup> sites are not affected by the hole hopping, remaining in the nonmagnetic state according to the NMR experiments. Also, this approach does not take into account the effect of ordering of the sodium ions in the cobaltates.

Thus the electron disproportionation with the peculiar KSL structure was not obtained by the previous theories, and the physics of the cobaltate metallic state remained controversial. Following the LS scheme, Koshibae and Maekawa put forward a model, where the charge disproportionation in the layer

<sup>1</sup>The  $S = 1$  and  $S = 2$  states of the  $\text{Co}^{3+}$  ion are conventionally called the intermediate and high-spin states, respectively. In the present study, the non-LS states of the  $d$  ions are called the higher-spin states. However, the  $S = 2$  states of the  $\text{Co}^{3+}$  ions do not participate in the hopping of the holes in the idealized  $\text{CoO}_2$  layers with the  $90^\circ$  angles of the bonds, see Ref. [36].

<sup>2</sup>For the nearest  $d$  sites in the  $\text{CoO}_2$  slabs with the  $90^\circ$  bonds Co-O-Co, the magnitude  $t'$  of the parameters of the electron hopping between the  $t_{2g}$  and  $e_g$  states is close to the value of the hopping integral  $t$  between the  $t_{2g}$  states of the neighbors:  $t' \gtrsim t \approx 0.2$  eV, see Ref. [35].

resulted from the orbital states of  $t_{2g}$  holes, having assumed that a splitting of their  $t_{2g}$  triplets by the crystal distortions is negligible [15]. In this theory, an energy dispersion of the noninteracting holes was found to possess four degenerated branches each corresponding to one of the four separate kagome sublattices. Each KSL is formed by its own sequence of the hole hoppings between the respective orbitals of the  $t_{2g}$  triplets. It was suggested in Ref. [15] that the kagome state of the holes is hidden in the LS excitations of the layers in the vicinity of the Fermi level, and the commensurate order of the  $\text{Na}^+$  ions could stabilize it. In subsequent calculations, it was established that when the coupling with such order is taken into account, the LS states with hole disproportionation indeed appear, possessing charge/spin patterns of various types (the zigzag, striped, honeycomb, and hexagonal) which depend on the presumed Na arrangement [24–29]. However, the ordering of  $\text{Na}^+$  ions drastically changes the electronic low-energy states [24], and the KSL structure expected for the phase  $x = 2/3$  was not obtained in the LS states of the lattice even with the realistic sodium structure [29].

The aim of the present study is to investigate conditions for the origin of a metallic state with the KSL structure of the  $d$  electron charge and spin disproportionation in cobaltates, employing the *ab initio* calculations for the system with ordered Na ions. Our approach to the problem takes into account the interaction between the itinerant holes and the *HS excitations* of the lattice.

Then in Sec. II, employing the GGA+ $U$  approximation, we calculate the collective electronic states and magnetic/charge structure of the cobalt layers for the  $x = 2/3$  crystal phase with the realistic ordering of the sodium ions. We analyze the nonuniform LS and HS states of the Co lattice in a dependence on the parameter  $U$ - $J$  of the electronic correlations within the  $d$  shells and compare the energy of the states. In Sec. III, we discuss the electron organization of the obtained metallic states with the charge/magnetic disproportionation.

## II. AB INITIO STUDY

### A. Method

In our study, we calculate the electronic states of the sodium cobaltate from first principles, using the spin-polarized density functional theory [37] (DFT) with the generalized gradient approximation (GGA). The GGA employs the functional form of the Perdew-Burke-Ernzerhof exchange correlation revised for solids (PBEsol) [38]. The Coulomb interaction between the electrons and ionic cores is taken into account using the projector augmented-wave method (PAW) [39], which was implemented in the Vienna *ab initio* simulation package [40] (VASP 5.2.12) (a part of the MEDEA software package<sup>3</sup>). The plane-wave cutoff energy is 500 eV. The Brillouin zone is sampled by the  $5 \times 5 \times 5$  mesh, containing 125 points including the  $\Gamma$  point (0,0,0) in the reciprocal space. Correspondingly, the linear density of the mesh is one point per  $\approx 0.150 \text{ \AA}^{-1}$ . Again, the convergence criteria  $10^{-6}$  eV is chosen for the electronic energy.

We calculate the states of correlated electrons within the rotationally invariant GGA+ $U$  approach, formulated in Ref. [41]. Then, the related integrals of the Coulomb and exchange interaction between the electrons within the  $d$  shells are approximated by their spherically-averaged values  $U$  and  $J$ , correspondingly. In terms of the density functional, the theory contains the one explicit parameter  $U_{\text{eff}} = U - J$ , controlling the strength of the exchange correlations of the electrons within the shells, see Eq. (5) in Ref. [41]. The subscript “eff” is hereafter skipped for brevity. Previously, such GGA+ $U$  approach was successfully applied to the insulating phase of cobaltate  $\text{Na}_{1/2}\text{CoO}_2$  with a sodium stripelike ordering, describing the formation of the nonuniform charge and magnetic stripelike pattern by the correlated  $d$  electrons in the  $\text{CoO}_2$  planes in agreement with the experimental observations [25,27,28]. In the present study, the electronic states of the nonuniform metallic system  $\text{Na}_{2/3}\text{CoO}_2$  were calculated as a function of  $U$  in the range from 0 to 6 eV. For the cobaltates, the relevant value of  $U$  is about 5 eV, see Ref. [42].

In our calculations, we employ a lattice with the complete crystallographic cell of the  $\text{Na}_{2/3}\text{CoO}_2$  compound, containing 264 atoms, which was previously deduced from the NMR/NQR experiments and verified by XRD Rietveld measurements in Ref. [10]. To optimize the total energy of the model, we “relax” the lattice using the conjugated gradient method: the sites are slightly shifted towards their equilibrium positions in such a way that a maximal force affecting the sites becomes less than  $0.01 \text{ eV \AA}^{-1}$ .

To obtain the different charge/magnetic collective states of the given model, in the calculations we examined the respective trial (initial) magnetic moments of the eight nonequivalent cobalt positions in the crystal. Both the LS and HS configurations of the Co ions were taken into account in our study. In particular, to get the hexagonal LS state of the lattice Fig. 1(c)] the initial assumptions of  $0 \mu_B$  magnetic moment for the Co1 sites and  $0.5 \mu_B$  for the Co2 positions were found to be useful, whereas for the HS-KSL state [Fig. 1(d)] those were  $0 \mu_B$  and  $1.5 \mu_B$ , respectively.

### B. Electronic states

Now we consider the electronic states, calculated at  $T = 0$  K within the GGA+ $U$  approximation for the system, for the realistic crystal structure of the  $\text{Na}_{2/3}\text{CoO}_2$  compound with ordered sodium ions. In such an approach, the nonuniform charge/magnetic states of the electrons appear when their correlations are enhanced within the  $d$  shells. When the correlations are weak, the interaction of the charged  $t_{2g}$  holes with the nonuniform crystal potential introduced by the sodium order is not efficient: at  $U = 0$ , the model has a metallic state, being almost *uniform* in the cobalt planes, which has a slight FM instability of the itinerant character [43]. The hole conduction  $t_{2g}$  band has a large width  $W \approx 1.5$  eV and is separated from the upper  $e_g$  band by a gap  $\approx 1$  eV. The energy dependence of the corresponding electronic density of states (DOS) is presented in Fig. 2(a). The calculated state resembles that which was obtained in the cobaltates with the uniform sodium ion distribution within the LSDA approximation [14].

<sup>3</sup>MEDEA version 2.16. MEDEA is a registered trademark of Materials Design, Inc., Angel Fire, New Mexico, USA.

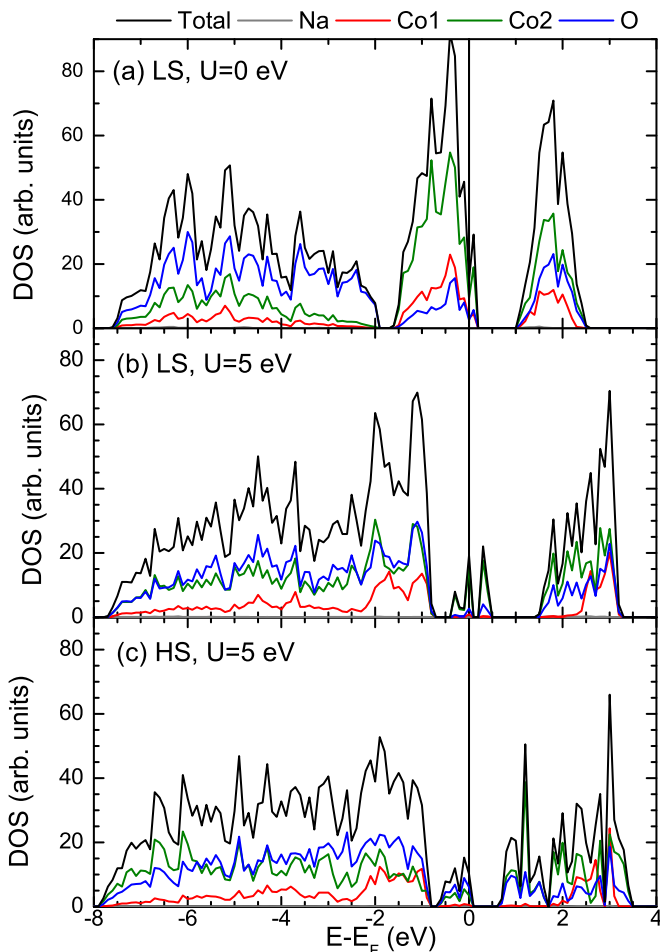


FIG. 2. Density of electronic states of the  $\text{Na}_{2/3}\text{CoO}_2$  crystal vs energy: (a) LS state at  $U = 0$  eV, (b) hexagonal LS and (c) HS-KSL states at  $U = 5$  eV. The solid vertical line indicates the Fermi level.

When the correlations in the  $d$  shells become stronger, qualitatively new metallic states, being heterogeneous in the Co sublattice, emerge in our model. The magnetic moments of the  $d$  shells serve as indicators of the redistribution of the  $d$ -electron spin and charge density between the Co ions in their triangular lattice [12,24,25,27,29].

In our previous study we have discussed the LS “phase” of the electrons, [29] see Fig. 1(c). This nonuniform LS state emerges upon increasing  $U$ : when  $U \gtrsim 2$  eV, the moments of Co2b sites increase progressively together with a marked decrease of the Co1 and Co2a site moments, see Fig. 3(a). When  $U$  exceeds 4 eV, the LS state becomes strongly heterogeneous.

In the present investigation we have found another state, called HS-KSL phase: the moments of the  $d$  sites are enhanced [see Fig. 3(a) and Table I] and the KSL in triangular cobalt lattice is formed, see Fig. 1(d). Initially, the energy of the HS-KSL state is larger by  $\approx 150$  meV than the energy of the LS phase, see Fig. 3(b). Then, the difference between the energies of these states decreases upon increasing  $U$ , and the HS-KSL phase becomes the ground state of the system when  $U \gtrsim 5.4$  eV. The energies of these two collective states are

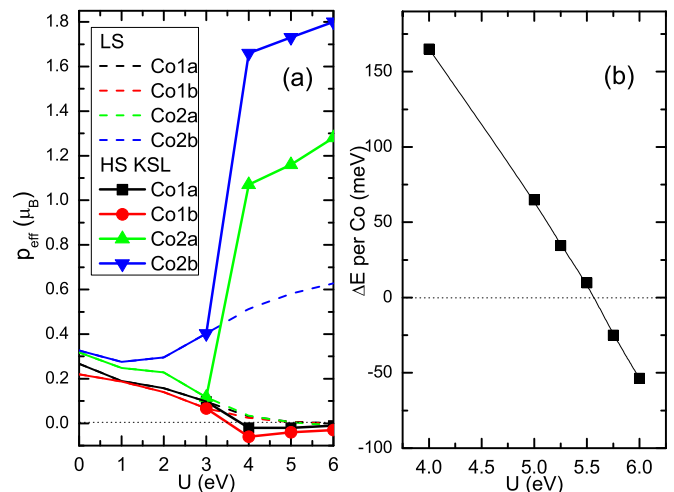


FIG. 3. Magnetic moments and energy of the system, calculated in dependence on the parameter of the electronic interaction within the  $d(\text{Co})$  shells. (a) Moments  $\mu$  of the Co sites. (b) Difference between the energy of HS-KSL and LS states estimated per Co ion.

close, and they compete with each other in the system with a realistic  $U \approx 5$  eV.

In both phases the Co1 sites become almost nonmagnetic at realistic  $U$ , see Figs. 1(c), 1(d), and 3(a). This implies the states of these ions to be close to the spinless state  $t_{2g}^6$  ( $\text{Co}^{3+}$ ): magnetic holes  $\text{Co}^{4+}$  avoid the Co1 positions due to sodium ions being close to these cobalt sites, [12] see Fig. 1(a). However, in the LS phase, holes also avoid the Co2a sites, remaining nonmagnetic as well, see Fig. 3(a). Instead, the holes tend to the Co2b sites, forming the magnetic hexagons in the triangular lattice [Fig. 1(c)]. The magnetic moments of these sites are small, so that their spins  $S < 1/2$ , see Table I. It means that Co2b ions are mostly in their LS states. The organization of the collective LS state resembles the droplet formation phase of the multiorbital Hubbard model on the triangular lattice [44]. In our approach, the hexagonal hole “droplets” are likely “trapped” by the sodium potential, arranging them in the form of a triangular superlattice with doubled period.

On the contrary, in the HS-KSL phase, Co2a sites are also magnetic along with the Co2b sites, thereby the hexagons become connected resulting in the kagome pattern, see Fig. 1(d). Such state of the model is consistent with the magnetic and charge structure, established in the cobalt sublattice of the  $\text{Na}_{2/3}\text{CoO}_2$  compound using the NMR/NQR technique [12,13] cf. Fig. 1(b) with 1(d). In our calculations, the

TABLE I. Calculated magnetic moments of the nonequivalent Co sites (in units of  $\mu_B$ ).<sup>a</sup> Average values are given in the last column.

Model state	Co1a	Co1b	Co2a	Co2b	$\langle \mu \rangle$ per Co
LS, $U = 0$ eV	0.174	0.254	0.299	0.344	0.297
LS, $U = 5$ eV	0.016	0.018	0.020	0.621	0.320
HS-KSL, $U = 5$ eV	0.015	0.046	1.233	1.879	1.254

<sup>a</sup>The moments were estimated by integrating the electronic spin density over a sphere with a radius 1.16 Å centered at the respective Co sites.

average magnetic moment on the Co2 sublattice  $m = 1.66 \mu_B$  corresponds to the enlarged average spin  $S = 0.83$ , indicating the existence of HS states in the KSL.

Both the LS and HS-KSL phase have the A-AFM structure with inplane/interplane FM/AFM ordering of the  $d$  moments. The GGA+ $U$  approximation is known to overestimate the FM interaction within the CoO<sub>2</sub> layers. For instance, it results in the band ferromagnetism for the cobaltates with  $x < 0.5$ , which experimentally has the in-plane AFM correlations [45]. Nevertheless, both calculated states correctly represent the character of the correlations between the  $d$  moments in the disproportionation domain  $0.65 \lesssim x \lesssim 0.8$  of the phase diagram of Na <sub>$x$</sub> CoO<sub>2</sub>. Again, both the LS and HS-KSL states are found to be metallic. In particular, the narrow band with width  $\approx 0.5$  eV is formed at the Fermi level instead of the initial wide conduction band, cf. Figs. 2(b) and 2(c) with 2(a). This implies that the heterogeneity of the many-particle states and enhanced electronic correlations appears concurrently.

The decrease of the energy gap between the HS-KSL and hexagonal phase and the formation of HS states of the sites of KSL go hand in hand upon increasing  $U$ , cf. Figs. 3(a) and 3(b). This suggests that the energy of the HS-KSL phase reduces towards that of the LS phase due to a gain in the energy of the electron Hund interaction within the  $d$ (Co2) shells. A likely origin of such dependence on  $U$  could be the following: the intersite hopping of electrons with arbitrary spin states results in local magnetic fluctuations in the metal [46]. Then, within the  $d$  shells, these spin fluctuations oppose the spin arrangement due to the FM Hund coupling between the electrons, which tends to maximize the on-site total spins. However, upon increasing  $U$ , both the on-site and intersite correlations between the itinerant particles become enhanced [47]. The correlations thereby help the Hund mechanism to overcome and increase the  $d$  moments in the KSL by attenuating the arbitrary spin fluctuations in the metal to some extent.

We have not found an ‘‘LS kagome’’ phase possessing both the small spins  $S < 1/2$  of the Co2 ions and the KSL disproportionation of the lattice. This implies that the LS  $t_{2g}$  states of the Co2a sites, which play the role of bridges for the hole hopping between the hexagons to form the KSL-state, are not efficient by itself. However, the obtained HS-KSL state provides the possibility for the holes to bridge the hexagons and to form the KSL, involving the HS  $e_g$  states of the sites.

### III. DISCUSSION

The NMR measurements detected the marked violation of the axial symmetry of the  $d$  shells of the magnetic Co2 sites, which appears in the cobalt planes simultaneously with the electron disproportionation [13]. Within the LS approach, the Co<sup>4+</sup> ( $t_{2g}^5$ ) holes hop between the  $t_{2g}$  on-site states in the lattice of the inert Co<sup>3+</sup> ( $t_{2g}^6$ ) ions. The chemical compression of the CoO<sub>2</sub> layers along the  $c$ -axis direction yields the trigonal deformation of the CoO<sub>6</sub> octahedra, and the on-site  $t_{2g}$ -triplet states split into the ground  $e'_g$  and excited  $a_{1g}$  orbital states with the axially symmetric  $a_{1g}$  wave functions extended along the  $c$  direction [48]. Then, to obtain the asymmetry of the local  $d$  shells, one has to take into account the transitions of the holes into their anisotropic  $e'_g$  orbital states along with the  $a_{1g}$

orbitals. However, the *ab initio* calculations for the cobaltates indicate that the energies  $\approx 300$  meV of these LS  $e'_g$  excitations of the holes [48] match the typical energy  $\approx 250$ – $300$  meV of excitations of the Co<sup>3+</sup> ions from their spinless to HS  $e_g$  states in the transition metal oxides [35,49]. This suggests that the theory of charge disproportionation in the cobaltates should take into account both the LS states of the holes and HS states of their neighboring  $d$  ions. Thus the anisotropy of the  $d$  shells, accompanying the appearance of the kagome state in the experiments, just implies that the coupling between the holes and the HS states of the  $d$  lattice are relevant for this phenomena. We shall now discuss the formation of the KSL disproportionation within our approach.

As shown in Sec. II B, when the LS states become heterogeneous, the itinerant holes are almost bound within the Co2b hexagons, see Fig. 1(c). The holes localized in these hexagons reduce the energy of mutual on-site Coulomb repulsion between them, correlating their spins ferromagnetically. This manifests itself as a small increase of the magnetic moments of Co2b sites upon increasing  $U$ , see Fig. 3(a). However, the localization of itinerant holes increases a kinetic energy of the system.<sup>4</sup>

The hybridization between the states of the holes in  $t_{2g}$  orbitals and HS  $e_g$  states of the lattice [32] promotes the tunneling of the holes from the Co2b hexagons to the  $d$  shells of their nearest neighbors: this decreases the kinetic energy. To this end, among the nearest Co<sup>3+</sup> ions the holes prefer to involve the  $e_g$  states of Co2a sites rather than those of Co1 sites, see Fig. 1(d). For both the Co2a and Co2b ions, the energy of their on-site excitations from the lower  $t_{2g}$  states to the upper HS  $e_g$  states is reduced due to the strong violation of the trigonal symmetry  $C_{3v}$  of the crystal environment in these atomic positions. This symmetry breaking results in the splitting of the  $e_g$  doublets of the Co2 sites.

On the contrary, for the Co1 ions, the symmetry  $C_{3v}$  is not violated, and does not affect the energy gap for the on-site  $e_g$  excitations. Again, the Coulomb repulsion from the Na<sup>+</sup> ions, being particularly close to the Co1 positions, suppresses the hopping of the holes, occupying the Co2 sites, to the Co1 sites, cf. Fig. 1(a) with 1(d). As a result, the hybridization between the states of the holes and Co1 sites turns out to be small. This explains the nonmagnetic states of the Co1 sites, resembling the LS spinless state  $t_{2g}^6$  of the Co<sup>3+</sup> ions, in the  $d$  lattice. Therefore the itinerant holes, interacting with the HS  $e_g$  states of the cobalt ions, form the metallic HS-KSL state extended over the triangular lattice, which *competes* with the almost localized hexagonal LS state.

<sup>4</sup>At present, a mechanism of formation of the hexagonal LS state of  $t_{2g}$  holes, obtained in our *ab initio* study of the cobaltates, is not evident and could be investigated further within a simplified model. The hexagonal arrangement of the holes is likely related with their ‘‘kinematic interaction,’’ predicted in Ref. [15]. Then, such organization of the hole states reflects a peculiarity of the  $t_{2g}$  orbital space of the compressed layers CoO<sub>2</sub>, where the trigonal deformations of the octahedra split the on-site  $t_{2g}$  triplets of the Co planes. Again, these states appear in the nonuniform crystal field introduced by the sodium ion order. In particular, the electric field of Na<sup>1+</sup> cations pushes the holes out of the Co1b sites, the centers of the hexagons.

Now we consider a plausible mechanism that results in a considerable splitting of the  $e_g(\text{Co2})$  doublets and weakly affects the doublets of the Co1 sites. An interaction relevant to such an effect could be the coupling between the  $e_g$  electrons of Co sites and the deformation of the octahedra of the oxygen anions, ligands of the corresponding  $d$  ions.

In particular, in our model, the optimization of atom positions reveals a peculiar distortion of the  $\text{CoO}_2$  layers, which is specific for the Co1 and Co2 sites. Namely, we have found that the  $\text{Co2-O}_6$  octahedra could possess substantial deformation modes with  $E_g$  symmetry,  $Q_\epsilon(x^2 - y^2)$  and  $Q_\theta(2z^2 - x^2 - y^2)$  [50], whereas these deformations are not developed in the case of  $\text{Co1-O}_6$  octahedra. Broadly speaking, such deformations exist in the every electronic states, calculated as with  $U = 0$  and so with its larger values. However, in the HS-KSL phase, the  $E_g$  modes are by an order of magnitude stronger than those evaluated in the other states of the system. To be specific, the magnitude reaches the substantial value  $\approx 0.2 \text{ \AA}$  at  $U = 5 \text{ eV}$ , i.e., about 10% of the Co-O bond length  $\approx 1.9 \text{ \AA}$ . Such strong  $Q_{\epsilon,\theta}$  deformations of the Jahn-Teller (JT) form are typical for the systems with active  $e_g$  electrons, e.g., for the manganites [51].

Cooperative JT distortions polarize the  $e_g$  wave functions  $x^2 - y^2$  and  $2z^2 - x^2 - y^2$ , extended along the Co-O bonds, thereby splitting these doublets. In turn, the  $t_{2g}$  states,  $xy$ ,  $yz$ , and  $zx$ , weakly interact with the JT lattice modes, because the lobes of these orbitals are directed aside from the anionic sites [32]. As a result, the crystal gap between the  $e_g$  and  $t_{2g}$  states decreases together with the energy of the HS states of Co2 ions containing the  $e_g$  electrons. The interaction between the  $e_g$  electrons and the crystal deformation thereby promote the reduction of the energy of the HS-KSL state with respect to the LS state. In the collective LS states, this interaction is relatively weak, because they mostly have the  $t_{2g}$ -orbital type.

Surprisingly, the Co2 positions, forming the kagome lattice, are disposed along sides of the triangles of Na2 atoms, cf. Fig. 1(d) with 1(a). Thus the deformation modes  $Q_{\epsilon,\theta}$ , promoted by the interaction with the HS  $e_g$  states distributed over the KSL by the hole motion, could be triggered by the chemical tension, accumulated in the  $\text{Co2-O}_6$  octahedra at the border of the sodium clusters. This suggests an explanation of the pronounced electron-lattice effect observed in the HS-KSL state. Compressing the  $\text{CoO}_2$  layers from the opposite sides, the triangular Na blocks tend to skew the octahedra in question situated between their edges. On the contrary, the  $\text{Co1-O}_6$  octahedra are mainly squeezed along the direction of the  $c$  axis, because the Co1 sites are placed about the centers of the Na2 triangles and about the lone ions Na1, see Fig. 1(a). Then, the related octahedra distortion does not substantially violate the trigonal symmetry of the crystal environment at the Co1 positions, and, thus, does not considerably affect the  $e_g$  states of these sites.

When the sodium ions are distributed randomly above and below the cobaltate layers, the GGA+ $U$  approximation results in uniform HS states of the  $\text{CoO}_2$  layers, which are separated from the corresponding uniform LS ground state by a large energy gap. This implies that the uniform HS state could unlikely appear in the metallic cobaltates [52].

In our approach, the interaction with the ordered sodium layers “reconstructs” the electron wave functions and the energy spectrum of the system around the Fermi level at realistic  $U$ . As a result, *both* the LS and HS states become heterogeneous and competing states, being almost degenerate in their energy. This is evident in Fig. 3(b): when  $U \approx 5 \text{ eV}$ , the energy of the HS-KSL state is larger by only 60 meV than the energy of the LS state, and already at the same values  $U \gtrsim 5.5 \text{ eV}$  the HS state has less energy as compared with the LS one. The competing LS and HS states could be intermixed by collective fluctuations, which should become intensive in the critical region [53].

One of the mechanisms, introducing such low-frequency fluctuations, could be the electron-phonon coupling, which provides a creation and annihilation of virtual phonons in the lattice [54]. In the cobaltates, a typical frequency of the phonons with  $E_{1g}$  symmetry, interacting with the  $e_g$  orbitals, is just  $\approx 60 \text{ meV}$  [55]. Another mechanism mixing the LS and HS states could be the intersite electron hopping within the  $90^\circ$  Co-O-Co bonds [32]. This results in spin-orbital correlations between the  $d$  sites [33,34,36], which are underestimated in the GGA+ $U$  approximation.

Again, the HS states have larger entropy than the LS states. Then, upon increasing the temperature, the emergence of HS states, introduced in the Co2 sublattice by the hole hopping, could be additionally supported by the thermal activation. On the contrary, in the  $\text{Co1}^{3+}$  positions, the HS thermal excitations within the  $d$  shells could be substantially suppressed by the crystal energy gap, estimated to be about 300 meV for the  $\text{Co}^{3+}$  ions [35,49].

Another origin of the appearance of HS states could be the thermal expansion of lattice upon increasing  $T$ , which reduces the energy of the  $e_g$  excitations. In particular, the expansion enlarges the distance between the  $d$  ions and ligands, thereby reducing the hybridization between their wave functions. Consequently, the splitting of the  $d$  levels of Co sites decreases. For instance, it was established that such mechanism is indeed able to stabilize the uniform HS state [49], which was experimentally observed in the perovskite  $\text{LaCoO}_3$  at  $T < 130 \text{ K}$  [56].

To evaluate the influence of thermal expansion on the energy difference between the HS-KSL and LS phases, we have correspondingly enlarged their crystal cells, calculated at  $T = 0 \text{ K}$  in our model. Namely, the initial cells with the respective volumes  $V_{0,\text{LS}} = 2618 \text{ \AA}^3$  and  $V_{0,\text{HS-KSL}} = 2717 \text{ \AA}^3$  were evenly expanded to reach the cell volume  $V_T = 2730 \text{ \AA}^3$ , established experimentally in  $\text{Na}_{2/3}\text{CoO}_2$  at  $T = 300 \text{ K}$ . After this, the energies of HS-KSL and LS electronic phases were calculated for expanded lattices at  $U = 5 \text{ eV}$ . We have thereby obtained that such an expansion indeed markedly reduces the initial energy gap to the value of 37 meV per Co site at room temperature. A comprehensive analysis of such a temperature effect demands experimental data on the crystal parameters as a function of  $T$ .

A careful description of the temperature dependence of the metallic state of the cobaltates demands an explicit account of the effects of quantum and thermal fluctuations. Such research is beyond the scope of the present GGA+ $U$  approach and we leave it for future studies.

In the picture of the competing hexagonal LS and HS-KSL states, the Co1 sites remain inert in the triangular  $d$  lattice, cf. Fig. 1(c) with 1(d). The holes are related with the Co2 KSL, where the more and less magnetic Co2b and Co2a sites are formed, respectively. Such structure conforms to the pattern of disproportionation of the  $d$ -ion states deduced from the NMR/NQR measurements in  $\text{Na}_{2/3}\text{CoO}_2$  [12], see Fig. 1(b). The suggested heterogeneous HS state substantially differs from the polaronic HS state proposed in Ref. [36], which runs over the whole sites of the triangular lattice doped by the itinerant holes.

#### IV. CONCLUSION

In the present work, we have investigated the origin of the disproportionation state of the metallic lamellar cobaltate  $\text{Na}_x\text{CoO}_2$ , i.e., a substantially heterogeneous distribution of the charge and magnetic density of the electrons among the  $d$  ions in the triangular cobalt lattice. To this end, we have calculated the electronic states and their energy spectrum from first principles for a system possessing a realistic crystal structure. The states have been analyzed in dependence on the strength of the electron correlations between the electrons at the  $d$  sites. The model takes into account the correlations caused by the electron Coulomb repulsion and their Hund spin coupling within the  $d$  shells, treating this on-site interaction with the GGA+ $U$  approximation. To be specific, we have calculated the magnetic and charge structure of the Co lattice of the representative crystal phase with  $x = 2/3$  of the cobaltate. In our approach, the heterogeneity of the  $d$  states is triggered by the clustering of the  $\text{Na}^+$  cations at the Na1/Na2 position of the sodium layers.

The heterogeneity was obtained to increase upon increasing the parameter of the on-site correlations. First, an electronic LS state with a small  $d$  moment develops, and then the HS-KSL state with increased moments emerges. When the heterogeneity becomes strong, these states remain metallic.

We have established that the HS-KSL state of the  $d$  lattice combines the inherent features of the experimental state of the cobaltate [12,13]. It is the disproportionation state that contains the nonmagnetic and magnetic  $d$  sites with the ratio 1 : 3 between their portions. In this state, the kagome structure appears, which contains the itinerant holes. The KSL is formed by the more magnetic Co2b sites assembled in the hexagons, connected by the less magnetic Co2a sites, see Fig. 1(d). On the contrary, in the LS state, the kagome structure splits into separate hexagons, see Fig. 1(c). We have found that the energies of the HS-KSL and LS states become close to each other at realistic values of the correlation parameter. Their competition could therefore provide the KSL structure of the disproportionation, revealed in the compound  $\text{Na}_{2/3}\text{CoO}_2$  in Refs. [12,13] with the NMR/NQR technique. We have pointed out that the enhanced moments obtained in the HS-KSL state imply the participation of the HS states of Co  $d$  orbitals in the formation of the KSL structure.

The present study thereby suggests the key to understand the physics of the intricate metallic states of the cobaltate in the range  $0.65 < x < 0.8$ , where the enhanced many-particle correlations and the disproportionation of the  $d$  electrons emerge concurrently. In the given approach the relevant correlations are related both with the on-site Coulomb repulsion and the Hund coupling between the  $d$  electrons.

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