

ELECTRICAL
AND MAGNETIC PROPERTIES

Studying Charge Ordering and Parameters of Exchange Interaction in Na_xCoO_2

V. I. Anisimov^a, A. O. Shorikov^a, A. V. Lukoyanov^{a, b}, J.-L. Wang^c, and Z. Zeng^c

^a Institute of Metal Physics, Ural Division, Russian Academy of Sciences, ul. S. Kovalevskoi 18, Yekaterinburg, 620041 Russia

^b Ural State Technical University (UPI), ul. Mira 19, Yekaterinburg, 620002 Russia

^c Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031 People's Republic of China

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Abstract—Results of first-principles calculations of the band structure of Na_xCoO_2 ($x = 0.33$ and 0.61) are presented. In $\text{Na}_{0.33}\text{CoO}_2$, charge ordering of Co^{3+} – Co^{4+} ions has been obtained. Ferromagnetic and antiferromagnetic orderings have been considered. Magnitudes of trigonal splitting of the t_{2g} band of Co and intersite hopping integrals have been determined in the basis of Wannier functions. Magnitudes of the parameter of exchange interaction have been calculated in terms of the Heisenberg model.

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During the last three years, the layered compounds on the basis of the cobalt dioxide CoO_2 attract attention of researchers owing to unusual effects observed in experiments on thermoelectric power, Hall effect, and magnetic resonance [1]. The possibility of obtaining a series of compounds of composition Na_xCoO_2 made it possible to significantly improve the understanding of effects of strong electron correlations underlying the unusual properties of these compounds [2]. The discovery of high-temperature superconductivity (HTSC) ($T_c = 5$ K) in the new class of layered compounds based on Na_xCoO_2 interstitial solid solutions intercalated with water raised a great interest in both theoreticians and experimentalists. The uniqueness of this discovery is in that, in fact, the superconductivity was for the first case found on a triangular lattice. The results of nuclear magnetic resonance (NMR) experiments showed the presence of two classes of cobalt ions differing in the magnitude of the magnetic moment in $\text{Na}_{1/2}\text{CoO}_2$. These classes were identified with Co^{3+} and Co^{4+} ions [4], which indicates the possibility of the existence of charge ordering in this system. The ratio of the numbers of ions belonging to different classes is 2 : 1.

The construction of an adequate microscopic model will permit a better understanding of the mechanism of origin of superconductivity in both these classes of compounds and in cuprates with which the solid solution under consideration has a certain similarity. In this work, we performed first-principles (ab initio) calculations of the structure of the interstitial solid solution Na_xCoO_2 with a sodium content $x = 0.33$ and 0.61 with allowance for water molecules intercalated between CoO_2 layers. We obtained the parameters of splitting of the Co $3d$ band by the crystalline field and the magni-

tudes of the parameters of exchange interaction within the Heisenberg model.

Sodium cobaltate NaCoO_2 , which is the parent compound for all interstitial solid solutions investigated here, crystallizes into a hexagonal structure (space group $P6_3/mmc$). The Co ions, in contrast to cubic cuprates, are located here in the sites of a *triangular* lattice, which is characterized by frustration and by the absence of both magnetic and orbital long-range order. Each Co ion is located at the center of an oxygen octahedron (Fig. 1). The octahedra themselves are connected by edges and form close-packed CoO_2 layers which alternate with randomly located Na ions and water molecules in the direction of the crystallographic axis c .

The crystalline field of an oxygen octahedron splits the fivefold degenerate (without allowance for spin) $3d$ level of Co into twofold degenerate empty e_g^σ (e_{g1}^σ and e_{g2}^σ orbitals) and partially filled threefold degenerate t_{2g} bands (Fig. 2), which are separated by a gap. In real compound there exist trigonal distortions, which lower the point symmetry group O_h to D_{3h} , so that the threefold degenerate t_{2g} band becomes split into twofold degenerate e_g^π bands (e_{g1}^π and e_{g2}^π orbitals) and a non-degenerate a_{1g} band.

Kohn and Sham [5] studied the electron structure of $\text{Na}_{0.61}\text{CoO}_2$ in the local-density approximation (LDA). The deviation from stoichiometry with respect to Na was taken into account in the virtual-crystal approximation. To this end, the number of valence electrons and the charge of the effective Na ion were assumed to be fractional. The Na atoms were located in three of six

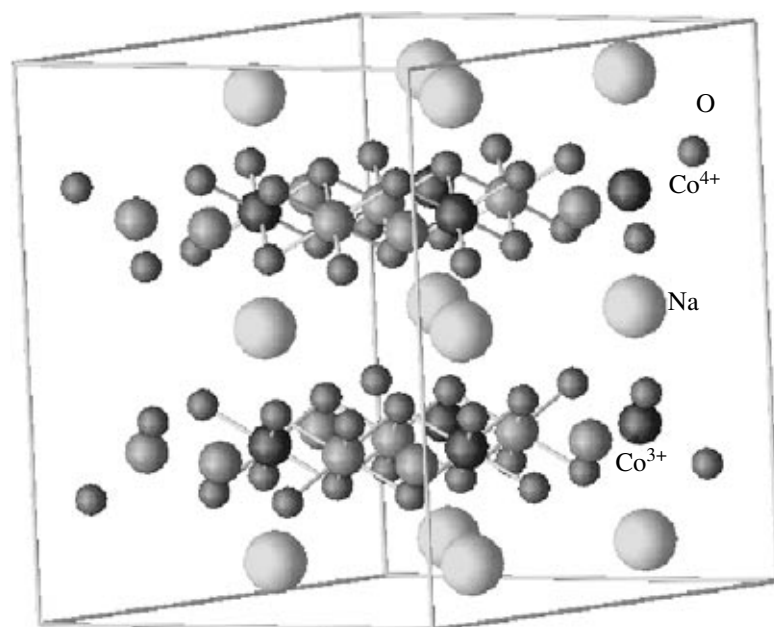


Fig. 1. Crystal structure of Na_xCoO₂. In the plane of the magnetic lattice of Co, solid and empty circles denote Co⁴⁺ and Co³⁺ ions, respectively.

equally spaced positions of the $6h$ type ($2x, x, 1/4$), where $2x = 0.522$ [6]. The calculations were performed using the TB-LMTO-ASA (TB—Tight Binding; LMTO—Linear Muffin-Tin Orbitals; ASA—Atomic-Sphere Approximation) code [7].

The results of the calculation are given in Fig. 3. The Fermi level lies in the almost completely filled t_{2g} band. However, the a_{1g} states are strongly mixed with the e_g^π states. The latter are virtually degenerate. The a_{1g} band is separated into a bonding and an antibonding components. Nevertheless, at the top of the valence band it is the a_{1g} states that are dominating. A similar electronic structure was obtained in [8]. For constructing a micro-

scopic model to explain experimental data, we should know the magnitudes and signs of splitting of the levels by crystalline field. The calculation of the elements of the Hamiltonian in the basis of Wannier functions [9, 10] shows that the splitting due to a trigonal crystal field (see Fig. 2) is $\Delta_{tr} \approx 0.02$ eV, whereas the e_g^σ bands are well separated from the packet of bands at the Fermi level and lie higher by 2.5 eV than the t_{2g} band. The integrals of intersite hopping between nearest neighbors in the plane and between planes are $t = 0.11$ eV and $t_\perp = 0.02$ eV, respectively.

For the investigation of the electronic structure of the superconducting solid solution Na_{0.33}CoO₂ · 1.2H₂O (the crystal structure was taken from [6]), we used a cell containing molecules of water for calculations. In [11], it was shown that the band structures of the Na_{0.33}CoO₂ and Na_{0.33}CoO₂ · 1.2H₂O compounds are quite similar. However, the intercalated compound has additional frustrations of oxygen octahedra, which leads to a broadening of the t_{2g} bands and a strengthening of the trigonal splitting. The calculation of the elements of the Hamiltonian in the basis of Wannier functions for Na_{0.33}CoO₂ · 1.2H₂O gives $\Delta_{tr} \approx 0.2$ eV; the integral of intersite hopping in the plane is $t = 0.14$ eV and that between planes is negligibly small, which is related to an increase in the distance between CoO₂ layers by a factor of about two upon intercalation. A calculation in which the water molecules were not introduced explicitly but were replaced by empty spheres (pseudoatoms without core electrons) with the retention of frustration gave analogous results.

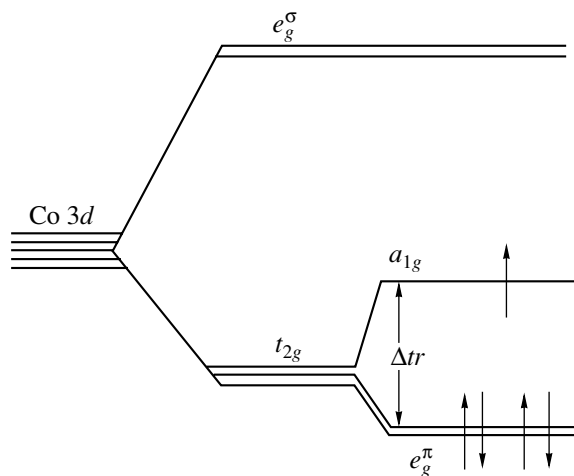


Fig. 2. Splitting of the 3d band of Co in the crystalline field of Na_xCoO₂.

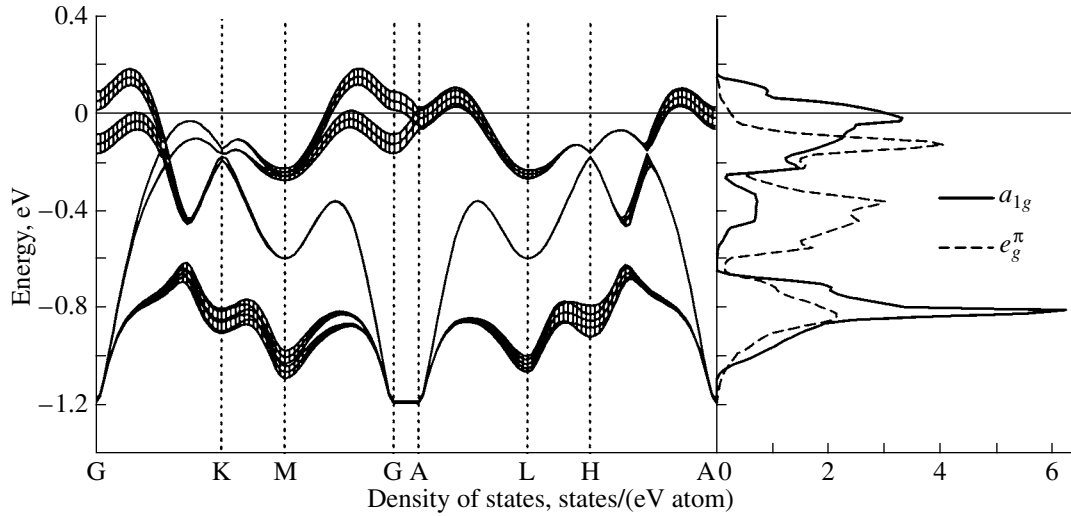


Fig. 3. Energy-band structure and partial a_{1g} and e_g^π densities of states of $\text{Na}_{0.61}\text{CoO}_2$ near the Fermi level (LDA calculation). The thickness of the line corresponds to the magnitude of the a_{1g} -orbital contribution. The Fermi level corresponds to the zero energy.

The calculation of the electronic structure of $\text{Na}_{0.33}\text{CoO}_2$ was performed for a supercell including six formula units of NaCoO_2 . The Na ions were arranged in an ordered way in positions $2b$ located above and under positions of the Co atoms. To retain stoichiometry, four of six Na ions were replaced by empty spheres. To take into account Coulomb correlations between d electrons of Co, we used the LDA + U method [12]. The parameters of the direct Coulomb interaction (U) and exchange Hund interaction (J_H) were taken to be 5.0 and 0.9 eV, respectively. Since the LDA + U method requires that a long-range magnetic order be specified, we first considered a simple ferromagnetic configuration. The calculation gave two classes of cobalt ions, Co_1 and Co_2 . The Co ions located above and under Na ions (Co_1) had a virtually zero spin moment ($0.03 \mu_B$). The magnetic moment of Co atoms that had no Na atoms above and below them (Co_2) were found to be $1.03 \mu_B$, which agrees well with the experimental

estimates $0.8\text{--}1.1 \mu_B$ [4, 13]. The ratio of the numbers of Co_1 to Co_2 ions is 1 : 2.

In this compound, there is observed a strong hybridization of the $2p$ states of oxygen with the d states of cobalt, whose magnitude can be formally estimated from the occupancy of e_g^σ states of Co. Analysis of the occupancy matrices given in the table shows that the total occupancy of the d shell is 7.51 electron at Co_1 sites and 7.25 electrons at Co_2 sites. The occupancy of the six t_{2g} orbitals of the Co_1 ion is on average 0.97 electron per orbital, which corresponds to the d^6 configuration. For the Co_2 ion, five t_{2g} orbitals contain 0.98 electron each, and one orbital (with spin down) of a_{1g} symmetry contains 0.14 electron; this arrangement corresponds to a configuration d^5 . The electron configurations d^6 and d^5 obtained can be associated with the ion states of cobalt Co^{3+} (class Co_1) and Co^{4+} (class Co_2). The difference of the total occupancies of

Occupancy of orbitals according to LDA + U calculations for the case of a ferromagnetic ordering (values are given for both spins and for two types of Co ions, Co^{3+} and Co^{4+})

Number of electrons	t_{2g} band			e_g^σ band		$n(t_{2g})$	$n(e_g^\sigma)$	$\Sigma n(d)$
	e_{g1}^π	e_{g2}^π	a_{1g}	e_{g1}^σ	e_{g2}^σ			
$n^\uparrow(\text{Co}^{3+})$	0.95	0.95	0.98	0.44	0.44	5.77	1.74	7.51
$n^\downarrow(\text{Co}^{3+})$	0.96	0.96	0.97	0.43	0.43			
$n^\uparrow(\text{Co}^{4+})$	0.98	0.98	0.97	0.60	0.60	5.03	2.22	7.25
$n^\downarrow(\text{Co}^{4+})$	0.98	0.98	0.14	0.51	0.51			

Note: In the last three columns, total occupancies of all t_{2g} , e_g^σ , and $3d$ orbitals are given, respectively (for the designations of orbitals, see the main text).

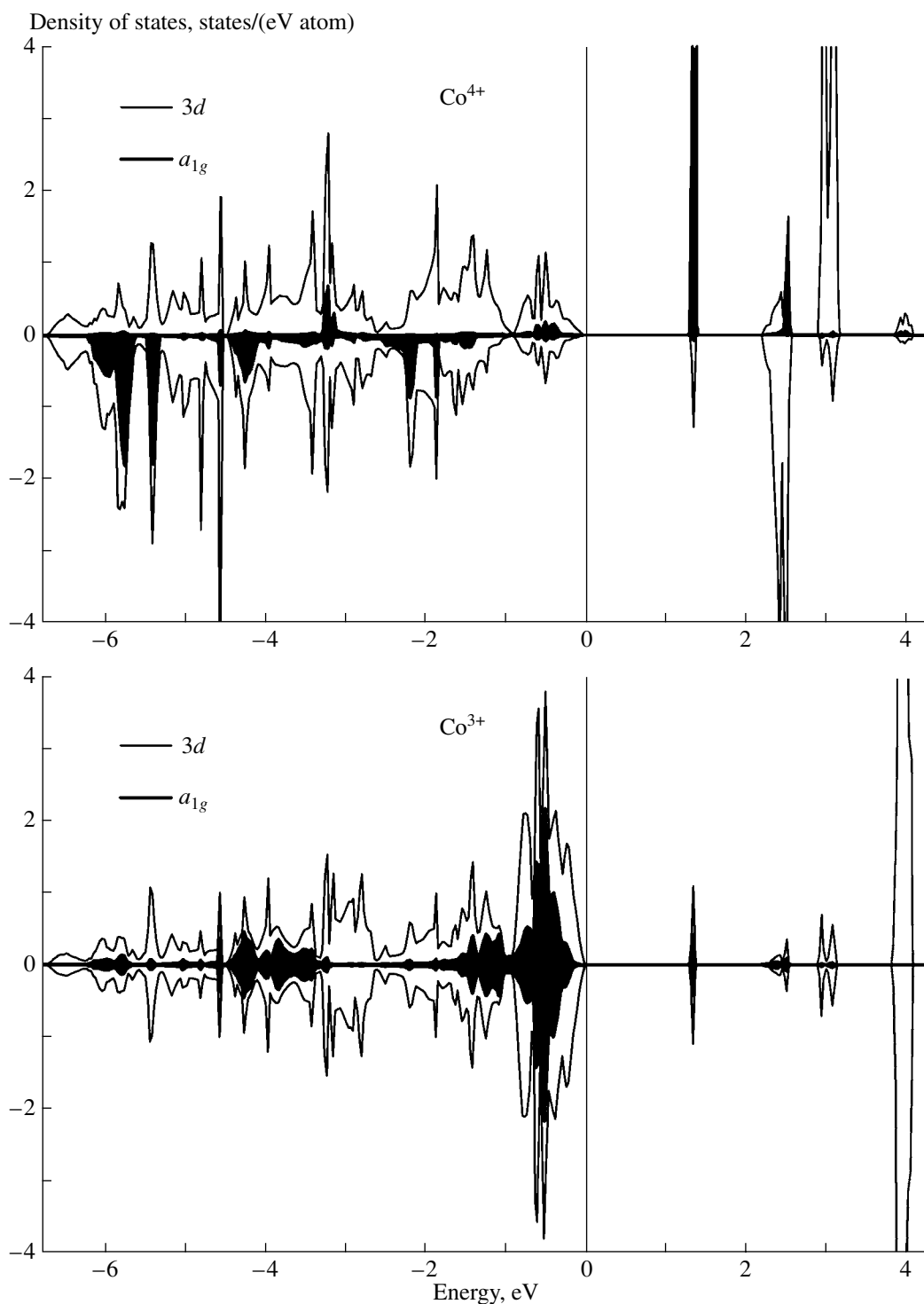


Fig. 4. Partial densities of states for Co^{4+} and Co^{3+} states for $\text{Na}_{0.33}\text{CoO}_2$ (LDA + U calculation). Dark regions correspond to the contribution of a_{1g} states to the total density of $3d$ states of Co ions. The Fermi level corresponds to the zero energy.

the d orbitals (7.51 and 7.25 electrons) from the integer values (6 and 5 electrons) is due to the admixture of e_g^σ states to the filled $2p$ states of oxygen. The total occupancy of the t_{2g} orbitals is 5.77 and 5.03 electrons for the

Co^{3+} and Co^{4+} ions, respectively. The difference in the total occupancies of the t_{2g} orbitals is 0.74 electron (for the a_{1g} orbitals, 0.83 electron). Although the unfilled e_g^σ states lie high in energy, their strong covalent bonding

with $2p$ states of oxygen leads to a sufficiently large contribution from these states to the total occupancy of the d level. The different strength of the covalent bonding for the magnetic and nonmagnetic ions of cobalt leads to a different total occupancy of the e_g^σ orbitals: 1.74 and 2.22 electrons for the Co^{3+} and Co^{4+} ions, respectively. The difference in the occupancy of the e_g^σ orbitals is equal to 0.48 electron and decreases the marked difference in the occupancy of the t_{2g} orbitals (0.74 electron), which results in 0.26 electron. Thus, in spite of the relatively small difference in the total occupancies of the d shell at the sites of Co^{3+} and Co^{4+} (0.26 electron), the results of this calculation can be considered as a confirmation of the existence of charge ordering. A similar result was obtained for the iron oxide Fe_3O_4 in [14].

The magnitudes of the exchange integrals for the Heisenberg model obtained by calculation are $J = 139$ K for cobalt ions Co^{4+} lying in the same plane and $J_\perp < 1$ K between Co^{4+} ions lying in different planes. However, the calculations gave a negative sign of exchange integrals, which indicates a more favorable antiferromagnetic ordering of Co^{4+} ions. Therefore, there was performed a calculation in which the local moments of neighboring ions both belonging to the same plane and located one under another along the c axis were ordered antiferromagnetically. In this case, there was also obtained a solution which the authors treat as confirming the existence of charge ordering, since the difference in the occupancies of the a_{1g} orbital of Co^{3+} and Co^{4+} ions is 0.84 electron. The magnetic moment at Co^{4+} ions was equal to $1.0 \mu_B$, and that at Co^{3+} ions was zero. The magnitudes of the parameter of exchange interaction are $J = 136$ K for Co^{4+} ions lying in the same plane and $J_\perp = 1$ K for Co^{4+} ions belonging to different planes, which agrees well with experimental estimates (~ 10 meV = 116 K) [4, 15]. The curves of the density of states of Co for a given calculation are displayed in Fig. 4. It is seen that in Co^{3+} the a_{1g} band is completely filled, whereas in Co^{4+} it is filled only partially and partially lies above the Fermi level by 1.2 eV. Thus, the hole in the t_{2g} band is localized at the orbital of symmetry a_{1g} , which, in the case of ordering of Na atoms, would lead to the appearance of orbital, spin, and charge ordering.

When describing the intercalated solid solution $\text{Na}_{0.33}\text{CoO}_2 \cdot 1.2\text{H}_2\text{O}$, we neglected the presence of water molecules to simplify the calculations. However, the lattice parameter c was increased in order to obtain the same distance between CoO_2 layers as in the real compound. The magnetic moment at the Co^{4+} ion was found to be about $1\mu_B$, the magnitude of the parameter of exchange interaction was found to be $J = 146$ K, and the exchange, be antiferromagnetic. The magnitudes of the integrals of exchange interaction between Co^{4+} ions

belonging to different planes were $J_\perp < 1$ K and also were antiferromagnetic in sign. The magnetic moment at the Co^{3+} ion is zero. The difference in the total occupancy of the d shells of ions Co^{3+} and Co^{4+} was 0.21 electron (7.48 and 7.27 electrons) and the occupancy of the a_{1g} orbital is 0.96 and 0.15 electron for the Co^{3+} and Co^{4+} ions, respectively. The difference in the occupancy of the a_{1g} orbitals is 0.81 electron, which is virtually coincident with the results obtained for the case of a small lattice parameter c .

We also performed a series of calculations to study the effect of the type of positions occupied by Na ions on the ordering pattern. The calculations were carried out in a tripled cell for the $\text{Na}_{0.33}\text{CoO}_2$ compound. The Na ions were placed in positions $2d$ one under another or in a random way in six possible positions. As a result, we observed the separation of Co ions into two classes: Co^{3+} and Co^{4+} , and the pattern itself strongly depended on the mutual arrangement of Na ions.

In later experiments on the determination of the crystal structure of Na_xCoO_2 , it was shown that Na atoms preferentially occupy those $6h$ positions ($2x, x, 1/4$) that are closer to the positions of the $2d$ type [6]. However, there are no experimental data on the appearance of ordering of Na atoms in some concrete type of positions even at low temperatures. In the interstitial solid solution under consideration, the Na ions are distributed randomly between the two types of crystallographic positions.

According to the calculations performed, the type of magnetic and charge ordering strongly depends on the position and concentration of Na ions in a given region of the crystal. Thus, a decrease in temperature can lead to a short-range order without long-range order (both magnetic and charge), which agrees well with experimental data.

CONCLUSIONS

In this work, we studied interstitial solid solutions Na_xCoO_2 ($x = 0.33$ and 0.61) using the LDA and LDA + U methods; calculated elements of the Hamiltonian in the basis of Wannier functions; obtained a solution with a magnetic and charge ordering in $\text{Na}_{1/3}\text{CoO}_2$; and determined exchange parameters for the Heisenberg model.

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