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Pressure-induced structural phase transitions on $\text{Na}_{0.5}\text{CoO}_2$: a first principles study

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Abstract

First principles calculations have been carried out to study the pressure effects on the structural, electronic and magnetic properties of $\text{Na}_{0.5}\text{CoO}_2$. An unexpected Na ion structural transformation has been predicted from our calculations. The main factor for such a transformation has been attributed to the increasing Coulomb repulsion between the Na1 and Co ions with the increase of pressure. The experimentally observed insulator–metal transition has been found to be induced by this structural transformation. Furthermore, due to the strong coupling between Na ordering and Co magnetic ordering, a magnetic phase transition follows after the structural transformation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The layered transition metal oxide Na_xCoO_2 has attracted great interest in recent years due to its unusually large thermopower [1], unexpected superconductivity when hydrated at $x \sim 0.3$ [2] and rich phase diagram as the doping level x is varied [3]. As a layered structure, Na_xCoO_2 is composed of alternate Na layers and CoO_2 layers, as shown in figure 1(a). Experiments have reported several structures with different stacking sequences of CoO_2 layers [4]. Among all these structures, P2- Na_xCoO_2 has attracted the most attention. Various Na ordering patterns have been observed in electron diffraction experiments with the variation of Na content x [5]. Notably, a $\sqrt{3}a \times 2a \times c$ orthorhombic superlattice has been found at $x = 0.5$ above room temperature [5, 6]. At $x = 0.5$, the system undergoes a metal–insulator transition at 53 K [7, 8] and a magnetic phase transition at 88 K [9].

In addition to the dependence of structural, electronic and magnetic properties on Na composition and temperature, pressure can also play an important role in these properties of the compound. In the similar system of Li_xCoO_2 , a pressure-induced structural phase transition has been predicted in $\text{Li}_{0.5}\text{CoO}_2$ [10]. Experimental measurements under high pressure have reported that the ground state of $\text{Na}_{0.5}\text{CoO}_2$

undergoes an insulator–metal transition when pressure $P > 11$ GPa [11]. On the other hand, when $P < 11$ GPa, the metal–insulator (MT) transition temperature increases with the increase in pressure [11]. This complex behavior has been considered to be closely related to the Na ordering in this compound. However, there is no theoretical investigation of the pressure-induced insulator–metal transition in this compound. Furthermore, deep insight into the pressure effects on the structural, electronic and magnetic properties is needed.

In this work, we have investigated the pressure effects on $\text{Na}_{0.5}\text{CoO}_2$ from first principles calculations. We find that Na ions undergo a structural phase transition at a critical pressure of 16.34 GPa, which is comparable to the experimental value of 11 GPa. Upon the Na ordering rearrangement, a magnetic transition occurs. Without such transformations, the insulator–metal transition pressure has been predicted to be about 53 GPa, which is very much overestimated. Our calculations show that the structural transformation has been induced by the increasingly strong Coulomb repulsion between Na1 ions and Co ions under high pressure.

2. Methods

The total energy calculations have been performed using VASP (the Vienna *ab initio* simulation package) [12, 13]. The

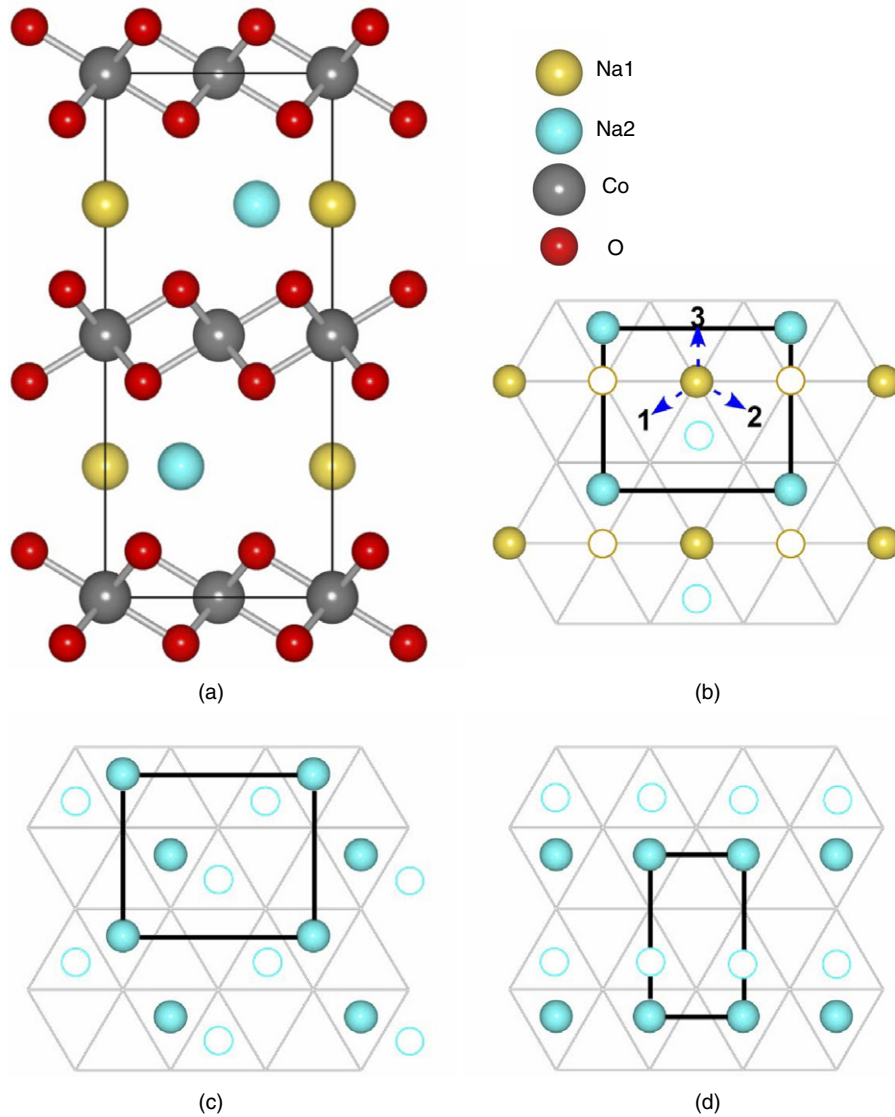


Figure 1. (a) Schematic crystal structure of P2- $\text{Na}_{0.5}\text{CoO}_2$. The Na ordering pattern for (b) zigzag1, (c) zigzag2 and (d) row structures. The arrows 1, 2 and 3 in (b) denote the possible movements of the Na1 ions to the nearest Na2 sites. The triangular lattice in (b), (c) and (d) denotes the Co sites at $z = 0$. Solid lines denote the unit cell of the ordering patterns. Solid and hollow circles represent Na ions above and below the Co layer, respectively. Na1 sites sit on top of the Co ions and Na2 sites are at the center of the Co triangular lattice.

projector augmented wave (PAW) [14, 15] method is used to describe the electron–ion interaction. For the exchange and correlation functional, the Perdew–Wang functional form [16] of the generalized gradient approximation (GGA) is adopted. $\text{Na}(2p^63s^1)$, $\text{Co}(3d^74s^2)$ and $\text{O}(2s^22p^6)$ are treated as valence states. The plane-wave cutoff energy is set to be 500 eV. The orthorhombic crystal structure has been adopted as the initial structure. The structural optimizations are performed until the forces on the atoms converge to less than $5 \text{ meV } \text{\AA}^{-1}$. The pressure on the cell is minimized within the constraint of constant volume. The Brillouin zone integration was done with the origin at Γ point on a $5 \times 5 \times 3$ mesh for large systems with 56 atoms and a $7 \times 7 \times 3$ mesh for small systems with 28 atoms. To test the convergence with respect to the plane-wave cutoff and the k -point sampling, we repeated the calculations, increasing the k -mesh to $7 \times 7 \times 5$ for large systems and $9 \times 9 \times 5$ for small systems with cutoff

energy of 800 eV. The change of the total energy is less than 3 meV/atom, which indicates that the chosen cutoff energy and k -points are sufficient for our calculated systems. Spin-polarized calculations have also been performed.

3. Results

Thompson and Downs have suggested that many structures achieve their closest packing with pressure [17], and therefore $\text{O3-Na}_x\text{CoO}_2$ will be expected to be the most favorable structure due to its most closely packed structural feature. However, the transformation from $\text{P2-Na}_x\text{CoO}_2$ to $\text{O3-Na}_x\text{CoO}_2$ requires breaking of the strong Co–O bond, and the high energy barrier prevents such transformation under pressure at room temperature [18]. Actually, experimental measurements have reported that the P2-type stacking structure is maintained up to 47 GPa [19]. Therefore, the pressure

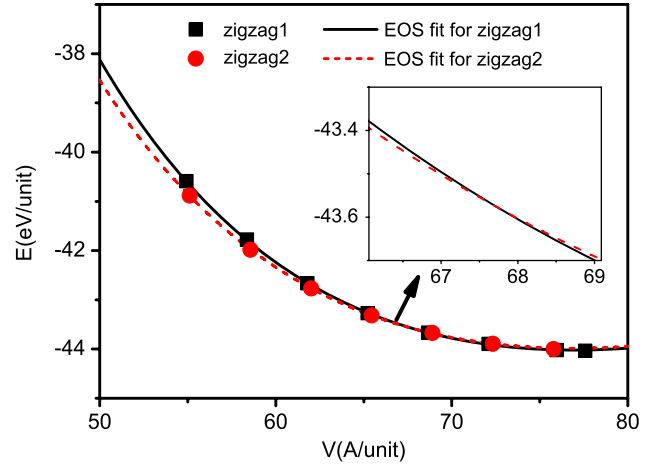
Table 1. The calculated and experimental values of structural parameters, bulk modulus B_0 and its derivative B' of the zigzag1 and zigzag2 structures.

Structure	Method	a (Å)	b (Å)	c (Å)	V_0 (Å ³)	B_0 (GPa)	B'
Zigzag1	Calc.	5.662	4.904	11.100	308.21	105.225	3.248
	Expt.	5.630 ^a	4.876 ^a	11.063 ^a	303.70 ^a	112 ± 2.3 ^b	2.3 ± 0.1 ^b
Zigzag2	Calc.	5.657	4.911	11.067	307.471	100.638	3.107

^a From [8].^b From [11].

only induces Na ordering transformation without change in the stacking structure. In P2-Na_xCoO₂, there are two types of Na sites within a Na plane, namely Na1 and Na2. The Na1 ions sit on top of the Co ions and the Na2 ions are at the center of the Co triangular lattice. To investigate whether there is any structural change under pressure, we have considered three different structures, as shown in figures 1(b)–(d). All these structures have an orthorhombic unit cell. In figures 1(b) and (c), Na ions arrange themselves in zigzag chains; we call them zigzag1 and zigzag2 structures. Both of them have the same $\sqrt{3}a \times 2a$ orthorhombic unit cell. In the zigzag1 structure, the Na ions occupy Na1 and Na2 sites equally. While in the zigzag2 structure, Na ions occupy Na2 sites only. However, the zigzag2 structure can be constructed from the zigzag1 structure by moving Na1 ions to the nearest Na2 sites in the direction of 1 or 2, as indicated by the arrows in figure 1(b). Another possible movement of Na1 ions is along the direction of 3, as shown in figure 1(b). This movement results in the configuration of figure 1(d) with alternate rows of Na ions and vacancies. However, the row structure has a $\sqrt{3}a \times a$ orthorhombic unit cell, which is different from the experimental observation that the $\sqrt{3}a \times 2a$ orthorhombic symmetry is maintained up to 47 GPa [19]. Furthermore, our first principles calculations show that the energy of the row structure is always higher than the zigzag2 structure under pressure. Thus we only focus on the zigzag1 and zigzag2 structures.

The bulk modulus B_0 , its first derivative B' and the equilibrium volume V_0 have been estimated by fitting the calculated relationship between the total energy and volume by the Murnaghan equation of state [20], as listed in table 1. For the zigzag1 structure, our calculated bulk modulus B_0 agrees with the experimental result [19], although its derivative B' is larger than the experimental result. The calculated structural parameters and the equilibrium volume V_0 of the zigzag1 structure also agree well with the experimental results [6, 19]. The maximum deviation is only 0.574% along the b -axis. The slight overestimation is usually found within the GGA approximation [21]. From table 1 we can also see that B_0 , B' and V_0 of the zigzag1 and zigzag2 structures are quite close. This can be explained by the similarity of the two structures. Figure 2 shows the curves of the total energy versus the volume for the two zigzag structures. The existence of a crossing point of the two curves suggests that there will be a transformation from the zigzag1 structure to the zigzag2 structure. In order to determine the transition pressure at $T = 0$ K, the enthalpy $H = E_0 + pV$ is calculated. The stable structure has the lowest enthalpy. The transition pressure P_c is

**Figure 2.** The curves of the total energy versus volume for the zigzag1 and zigzag2 structures. Solid squares and circles denote the data for the zigzag1 and zigzag2 structures, respectively. The inset shows an enlarged picture near the crossing point. Solid and dashed lines represent the fitted equation of states (EOS) for the zigzag1 and zigzag2 structures, respectively.

determined to be 16.34 GPa. For $P > P_c$, the zigzag2 structure becomes more stable than the zigzag1 structure. There is a very small volume collapse of about 0.6 Å³/unit in the structural transformation. This small value suggests that the volume discontinuity could be easily neglected in experiments. This might be the reason why such structural transformation has not been reported experimentally [19]. However, the two structures are quite different in their electronic and magnetic properties.

Due to the strong coupling between structural and electronic degrees [22], the magnetic ordering of Co ions has been found to be directly linked with the Na ordering [23]. For the zigzag1 structure, due to the special Na ordering, the ground state is antiferromagnetic with alternate stripes of nonmagnetic Co1 and magnetic Co2 ions [9], and we call it AFM1. Co1 has one of the nearest neighbor sites occupied by a Na ion, while Co2 has no Na ions in the nearest neighbor sites [6]. While for the zigzag2 structure, each Co ion is surrounded by three nearest Na2 ions above and below. With the same Na environment, charge disproportionation does not occur among the Co ions. Therefore it is reasonable to construct ferromagnetic ordering within the Co plane. With respect to the interlayer interaction, we have considered the ferromagnetic and antiferromagnetic interlayer magnetic orderings of Co planes in the zigzag2 structure. Our results indicate that antiferromagnetic ordering between Co planes is more stable than ferromagnetic ordering. We call the

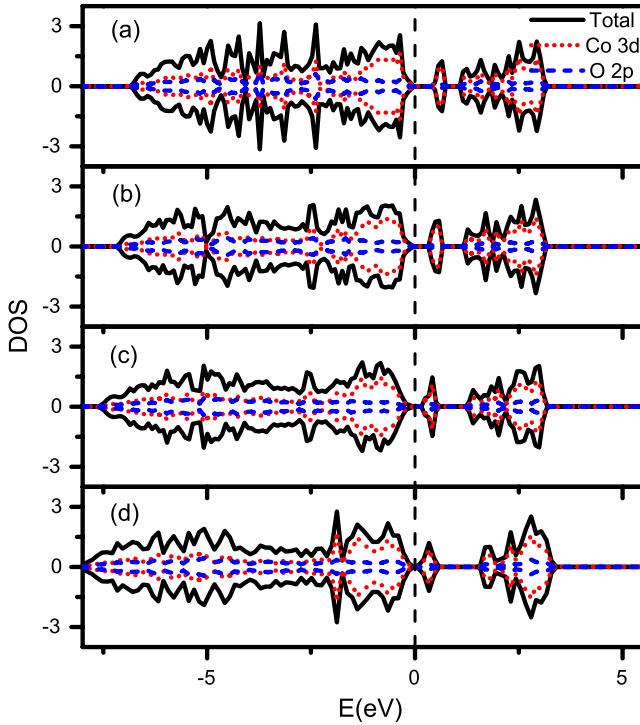


Figure 3. The density of states (DOS) of the zigzag1 structure. The total DOS and partial DOSs of the Co 3d and O 2p orbital are shown with the volume of (a) 75.925, (b) 68.630, (c) 61.766, (d) 54.904 \AA^3 /unit using the DFT + U (4 eV) method.

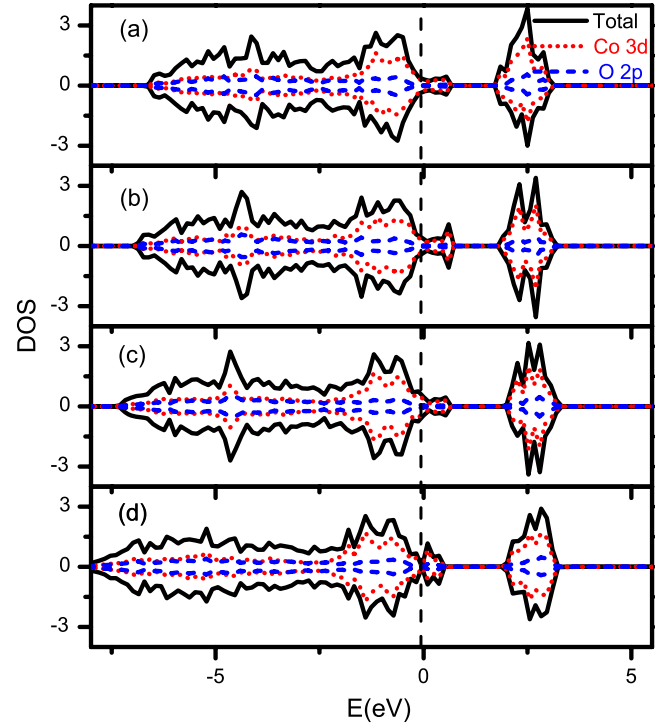


Figure 4. The density of states of the zigzag2 structure. Total DOS and partial DOSs of the Co 3d and O 2p orbital are shown with the volume of (a) 75.755, (b) 68.63, (c) 61.7675, (d) 54.905 \AA^3 /unit using the DFT + U (4 eV) method.

Co magnetic ordering AFM2, with ferromagnetic ordering within the Co plane and antiferromagnetic ordering between Co planes. Thus the pressure-induced Na ion transformation intrigues the Co magnetic transition from AFM1 to AFM2.

Considering the correlation effect in this compound [24, 25], density function theory (DFT) + Hubbard U calculations have also been performed. We adopt the DFT + U version proposed by Dudarev *et al* [26]. The parameter U is applied to the Co 3d orbital only and is set to be 4 eV [25, 27]. The screened exchange parameter J is kept fixed to 1 eV. Figure 3 shows the density of states (DOS) of the zigzag1 structure with various volumes using the DFT + U method. At ambient pressure, our calculations predict an insulating ground state, which is in agreement with the experiment [6]. However, for the zigzag2 structure, our calculations show that it displays a metallic ground state in the whole pressure range, as shown in figure 4. This means that after the Na ion transformation at 16.34 GPa, the sample will undergo an insulator–metal transition. The predicted transition pressure is comparable to the experimental value of 11 GPa. So we can conclude that the experimentally observed insulator–metal transition is induced by the Na ordering transition.

Previous experimental and theoretical investigations have suggested that at zero pressure the Na ordering pattern is a consequence of the competition between the Na–Na Coulomb interaction and the energy difference between Na1 and Na2 sites [5, 28]. Experimental measurements have reported that the c -axis is easily compressed [29, 19] and the decrease of distance along c -axis is mainly due to the O–O distance

between CoO_2 layers [29]. The inplane lattice constants change very little under pressure [19]. As the pressure increases, the decreasing O–O distance results in a stronger screening effect on the Na ions by the surrounding negative O ions. Thus the Na–Na interaction decreases with the increase of pressure. On the other hand, the energy difference between the Na1 and Na2 ions increases rapidly from 0.1875 to 0.302 eV/Na as the pressure increases from 0 to 38.90 GPa. This is attributed to two factors: (i) the extra energy for the Na1 site occupancy results from the direct repulsion between Na1 ions and Co ions above and below; (ii) the strong decrease of the lattice constant c with the increase in pressure. The decreased distance between Na–Co ions leads to the increase of the Coulomb repulsion between them. As a consequence, the Na1 sites become more and more unfavorable and thus the relative stability of the Na2 sites is largely enhanced. This effect induces the Na1 ions to move towards the favorite Na2 sites nearby. Thus the increase of Na–Co repulsion under increasing pressure is the main driving force for the structural phase transition from the zigzag1 structure to the zigzag2 structure.

Our calculations also show that pressure has induced changes in the electronic properties. From figure 3 we can see that, at ambient pressure, the ground state of the zigzag1 structure exhibits an insulating behavior, which is in good agreement with the experiments [6–8]. The insulating behavior is believed to be Mott type. For the Mott insulator, the energy gap depends on the bandwidth W and the on-site Coulomb interaction U . With a large enough ratio of U/W , the metal–

insulator transition occurs. With the increase in pressure, the bandwidth W is enlarged accordingly. Consequently, the value of U/W decreases with increasing pressure, which induces the decrease in the bandgap and finally transforms the compound to the metallic state. Our calculations have predicted such insulator–metal transition at about 53 GPa within the zigzag1 configuration. The enlargement of the bandwidth with the increase in pressure also occurs in the zigzag2 structure. Figures 3 and 4 give the partial DOSs of the Co 3d and O 2p orbital for both structures within various volumes. Both figures show a common feature that in the low energy range the energy band has both the O 2p and the Co 3d characteristic, indicating the strong hybridization between them. With the increase in pressure, the hybridization feature is enhanced. The stronger hybridization induces not only the enlargement of the energy band, but also the enhancement of the covalent bonds between Co ions and O ions.

4. Summary

In summary, using the first principles method we have predicted a pressure-induced structural transformation from the zigzag1 structure to the zigzag2 structure due to the increase in Na–Co repulsion under increasing pressure. A magnetic phase transition has been induced due to the strong coupling between the structural and electronic properties [22]. The experimentally observed insulating–metal transition has been found to be induced by the structural transformation.

Acknowledgments

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