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2007 J. Phys.: Condens. Matter 19 086203

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# Effect of electronic correlation on the Na ordering of $\text{Na}_x\text{CoO}_2$

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Received 2 November 2006, in final form 16 January 2007

Published 6 February 2007

Online at [stacks.iop.org/JPhysCM/19/086203](http://stacks.iop.org/JPhysCM/19/086203)

## Abstract

We have studied the ground-state structures of  $\text{Na}_x\text{CoO}_2$  using the correlation band theory (DFT +  $U$ ). We find that the correlation effect plays an important role in the Na ordering at low concentration. For  $x = 1/9$ , only the DFT +  $U$  scheme predicts the correct Na ordering structure when the on-site Coulomb repulsion  $U$  is larger than 2 eV. Meanwhile, at high concentration, the DFT scheme gives the ground state as observed by experiment. At  $x = 1/2$ , the correlation effect is shown to change the coupling between the Na ordering and Co magnetic ordering.

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

## 1. Introduction

Because of the unusual thermoelectric power [1] of  $\text{Na}_x\text{CoO}_2$  and the superconductivity [2] in the hydrated oxides,  $\text{Na}_x\text{CoO}_2$  hydrate and its unhydrated analogue have been the subject of extensive study in recent years. The structure of  $\text{Na}_x\text{CoO}_2$  has been reported [3–9] to consist of triangular layers of Co ions between close-packed layers of O separated by layers of Na ions. There are two types of Na sites within a given plane, namely Na1 and Na2, both of which are trigonal prismatic sites. However, the Na1 site shares faces with the adjacent  $\text{CoO}_6$  octahedral, while the Na2 site shares edges with the  $\text{CoO}_6$  octahedral.

The phase diagram of  $\text{Na}_x\text{CoO}_2$  [10] shows that  $\text{Na}_x\text{CoO}_2$  exhibits metallic behaviour for a wide range of doping levels  $x$ . But for  $x = 1/2$  it is an insulating state.  $^{23}\text{Na}$  nuclear magnetic resonance (NMR) provides evidence for the occurrence of the charge-ordered state of Co accompanied by the Na ordering for  $x \sim 0.7$  [11]. Despite the influence of the doping level  $x$  on the  $\text{Co}^{3+}/\text{Co}^{4+}$  ratio, Na ordering over the available sites is important for the electronic and magnetic properties. There have been experimental and theoretical investigations of the Na ordering. Using electron diffraction, Zandbergen *et al* [12] have shown the existence of an Na ordered superstructure over a wide range of  $x$  in  $\text{Na}_x\text{CoO}_2$ . Zhang *et al* studied the Na

ordering at various concentrations  $x$  [13] by performing calculations based on the DFT scheme. But there is a discrepancy between the experimental and theoretical results at the low doping level  $x = 1/9$ . The lowest-energy structure of  $\text{Na}_{1/9}\text{CoO}_2$  within the DFT scheme corresponds to placing Na ions in the Na1 sites [13], while the experiment shows that the Na2 sites are occupied [12].

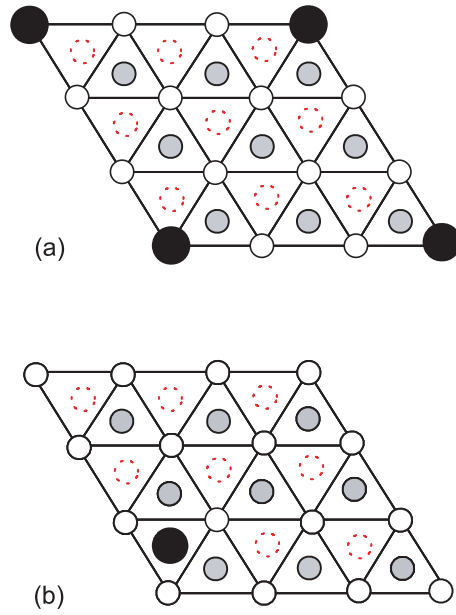
$\text{Na}_x\text{CoO}_2$ , as a transition metal oxide, is a strongly correlated system with rather localized d electrons. As an improvement of the DFT scheme, the DFT +  $U$  scheme [14] has been proposed by taking into account the correlation effect in the first-principles calculations. Using the DFT +  $U$  scheme, Pickett and co-authors [15, 16] have investigated the effect of the Coulomb correlation in the  $x = 1/3$  and  $2/3$  regimes of  $\text{Na}_x\text{CoO}_2$ . They discovered that there is a critical  $U_c = 3$  eV above which charge disproportionation occurs and antiferromagnetic coupling in a  $\text{Co}^{3+}\text{--Co}^{4+}$  ordered state is favoured, and below which ferromagnetism is favoured. Zhang [17] *et al* presented a systematic DFT +  $U$  study of the electronic structure properties of the single layer  $\text{CoO}_2$  and discovered that it depends sensitively on the doping level  $x$ . Lee *et al* [18] gave the critical value of  $U \sim 3.5$  eV for charge ordering and metal–insulator transition of  $\text{Na}_{1/2}\text{CoO}_2$  by using the DFT +  $U$  scheme.

In order to solve the discrepancy of the Na ordering between the experimental results and the DFT calculations, we have investigated the correlation effect in the Na ordering using the DFT +  $U$  scheme. We find that correlation is critical to the Na ordering of ground-state structures at low concentration. Above the critical value 2 eV, the structure with Na2 sites occupied becomes the ground-state structure for  $\text{Na}_{1/9}\text{CoO}_2$ , which agrees with the experiment. The structure with Na<sub>2</sub> sites occupied becomes more stable as  $U$  increases. For  $x = 1/2$ , both the DFT and DFT +  $U$  schemes predict the same ground-state structure, i.e. the orthorhombic superstructure of the Na plane with antiferromagnetic ordering Co layers above and below. The correlation effect is shown to change the coupling between the Na ordering and Co magnetic ordering.

## 2. Methods

We have performed the calculations using VASP (the Vienna *ab initio* Simulation Package) [19, 20]. The approach is based on an iterative solution of the Kohn–Sham equation of the density-function theory in a plane-wave set. The projector augmented wave (PAW) [21, 22] method was used to describe the electron–ion interaction. In our calculations, the Perdew–Wang functional form [23] of the generalized gradient approximation (GGA) was adopted. We set the plane-wave cutoff energy to be 500 eV. With the consideration that  $\text{Na}_x\text{CoO}_2$  is a paramagnetic metal at  $x < 1/2$ , a charge ordered insulator at  $x = 1/2$  [10] and a nonmagnetic insulator at  $x = 1$ , we performed the unpolarized calculations of  $\text{Na}_{1/9}\text{CoO}_2$  and  $\text{NaCoO}_2$  and spin-polarized calculations of  $\text{Na}_{1/2}\text{CoO}_2$ . The lattice constants are fixed at  $a = 2.82$  and  $c = 10.89$  Å. The optimizations of the atom coordinates are made at the  $\Gamma$  point for  $x = 1/9$  and  $1/2$  due to the large super cell that we used, while for  $x = 1$  a mesh of  $4 \times 4 \times 2k$  space was adopted. The tolerance of energy for the optimization is  $10^{-4}$  eV. We use a simple DFT +  $U$  version proposed by Dudarev *et al* [24]. The Hubbard on-site Coulomb interaction was applied to the Co 3d orbital only and the screened exchange parameter  $J$  is kept fixed to 1 eV during all the DFT +  $U$  calculations.

In the DFT +  $U$  scheme, there are mainly two distinct recipes for the double counting (DC) term, namely the AMF (around mean field) function and the FLL (fully localized limit) function. For well-localized electrons, the FLL function correctly describes the important physics and the AMF function is exact in the material with uniform orbital occupancy. Petukhov *et al* [30] proposed a DC recipe to treat the intermediate case by using a linear



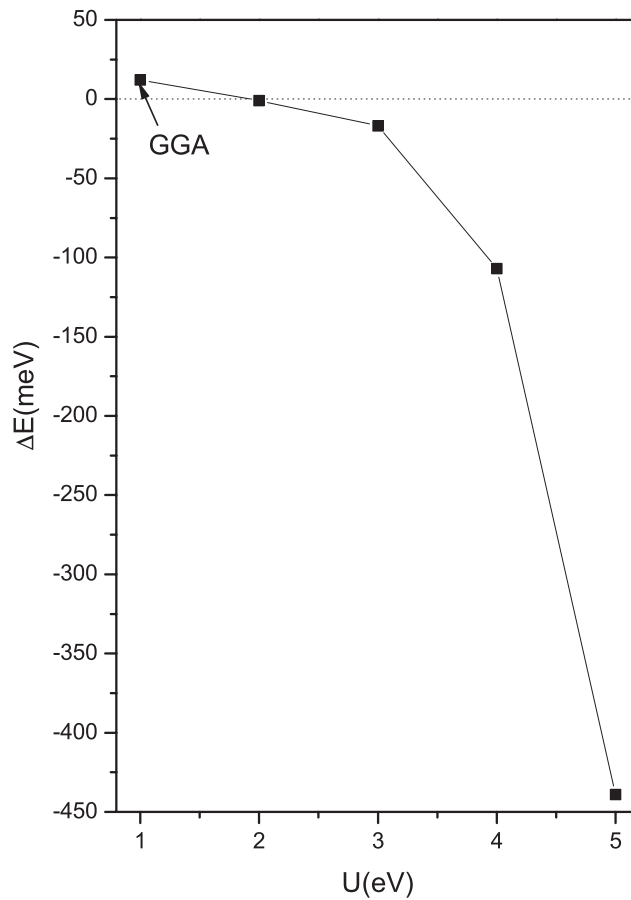
**Figure 1.** Superstructures with different Na ordering of  $\text{Na}_{1/9}\text{CoO}_2$ . (a) and (b) are structures with Na ions occupying Na1 sites and Na2 sites, respectively. The small white circles represent Co ions at the layer  $z = 0$ . The large black solid circles represent Na ions at the layer  $z = 1/4$ . The small grey circles and the dashed hollow circles denote the O ions at the layer above and below Co layer, respectively.

interpolation between the two extremes AMF and FLL. For  $\text{Na}_x\text{CoO}_2$  with rather localized d electrons, we use the FLL function, which has been adopted in VASP.

### 3. Results

#### 3.1. Correlation effect on the structures of $\text{Na}_x\text{CoO}_2$

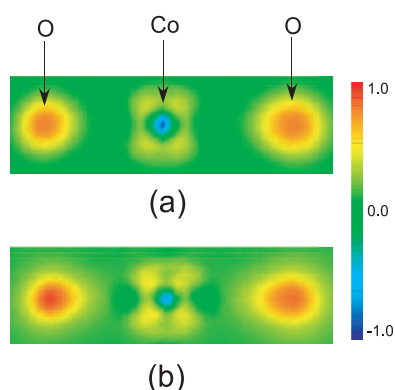
The Na ions are contained in O prisms defined by the O triangular lattice. There are two types of sites: Na1 sites are directly above a Co ion and Na2 sites are directly above the O atoms in the O layer on the opposite side of the Co sheet. The neutron diffraction data shows that the structure of  $\text{Na}_{1/9}\text{CoO}_2$  is a  $3 \times 3 \times 1$  superstructure, with two intervening layers in the unit cell, and all the Na ions occupy Na2 sites, leaving Na1 sites empty [12]. We have investigated the two structures with Na1 sites and Na2 sites occupied respectively using both the DFT and DFT +  $U$  schemes. The two structures are shown in figures 1(a) and (b), which will be denoted as  $\alpha$ -phase and  $\beta$ -phase in our work. Figure 2 describes the energy difference between the  $\alpha$ -phase and the  $\beta$ -phase as a function of the on-site Coulomb repulsion  $U$ . Within the DFT scheme, the  $\alpha$ -phase is the ground state, which agrees with the DFT result of Zhang [13]. When  $U$  reaches the critical value 2 eV, the  $\beta$ -phase becomes the ground state, which is in agreement with the experiment. As  $U$  increases, the energy difference becomes larger, which means that the relative stability of the  $\beta$ -phase is enhanced with the increase of  $U$ . Our investigation shows that this is mainly due to the charge transfer from Co ions to O ions with the correlation effect taken into account. This leads to an enhanced electrovalent bond and more localized electrons. The effective positive electrical charges of Co ions increase with the increase in  $U$ , which



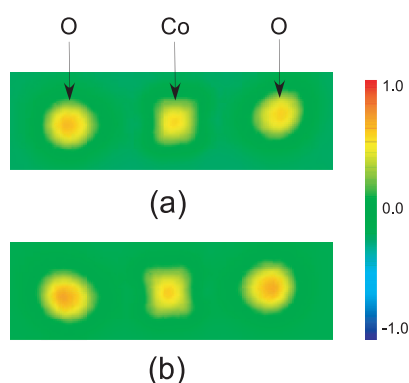
**Figure 2.** The energy difference per unit cell between  $\alpha$ -phase and  $\beta$ -phase as a function of  $U$ .

results in stronger repulsion between the Co ions and Na ions and more preference to the Na2 sites.

According to experimental and theoretical investigations [12, 13], the driving force for Na ordering mainly comes from two aspects: the Na–Na intralayer electrostatics and the Na–Co Coulomb repulsion [13]. In addition, at some composition, the Na ordering is influenced by the interaction of the Na position with the distribution of  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  ions [12]. Our calculations show that the correlation effect has little effect on the position variation of the ions of the two phases, thus it is not the change of the structure configuration that is responsible for the ground-state transition. One possible reason for the occurrence of the ground-state transition is the charge transfer caused by the on-site Coulomb repulsion  $U$ . As  $U$  increases, the charges are transferred from Co ions onto O ions. Lee *et al* [18] has calculated the amount of the charge transferred from Co ions to O ions, which is about  $0.04\text{--}0.05e/eV$ . Because of the charge transfer, the electrovalent bond is enhanced and the electrons are more localized. Figures 3 and 4 give the charge density difference of the  $\text{CoO}_2$  layer. The central part represents Co ions and the two sides represents O ions. From figures 3(a) and (b), we can see that, with the correlation effect taken into account, the intensity of the charge density difference around the O ions becomes stronger. This is due to the charge transfer from Co ions to O ions. More charges

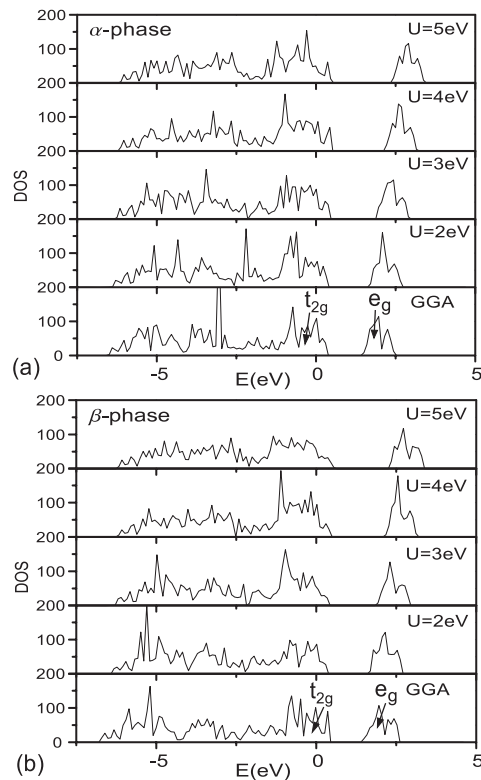


**Figure 3.** The charge density difference of  $\text{CoO}_2$  for  $x = 1$ : (a) for DFT scheme; (b) for DFT +  $U$  scheme with  $U = 5$  eV.



**Figure 4.** The charge density difference of  $\text{CoO}_2$  for  $x = 1/9$ —the charge density difference of the Co ion for this figure is not the one with Na ions above it: (a) for DFT scheme; (b) for DFT +  $U$  scheme with  $U = 5$  eV.

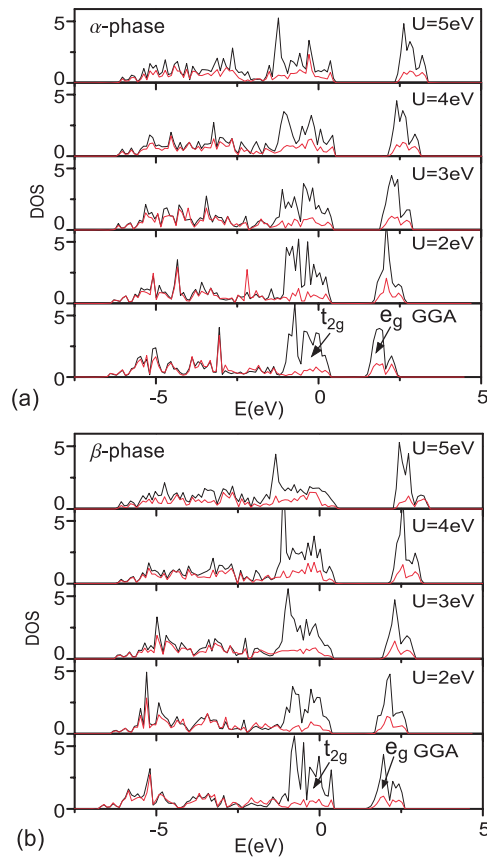
are localized to O ions with the increase of  $U$ . The same effect occurs on Co ions. Another difference between (a) and (b) is that the charge density of Co ions becomes dispersed, which is an indication of charge transfer. The intensity difference is mainly due to the localization of the electrons, and the shape difference is mainly due to charge transfer from Co ions to O ions. Within the DFT +  $U$  scheme, a small amount of charges are transferred from Co ions to O ions. Our calculations show that the larger the Coulomb repulsion  $U$  applied to the system, the higher the total energy is, and the charges transferred from Co ions to O ions is about  $0.01e/eV$ . The same effect can be seen from figure 4 for  $x = 1/9$ , but it is not so strong compared with that of figure 3 for  $x = 1$ . This suggests that the concentration  $x$  has an important effect on the charge transfer and electron localization. Our atom-sphere calculation shows that the Na ion donates  $0.81e$  to the  $\text{CoO}_2$  layers. The change in the charge distribution can affect both the interaction within the  $\text{CoO}_2$  layers and the interplay between the  $\text{CoO}_2$  layers and Na ions. With more effective positive electrical charges, the repulsion between the Co ions and Na ions becomes stronger, which results in more preference to Na2 sites. On the other hand, the attraction between Na ions and O ions is stronger due to the more negative charges of O ions. With the increase of  $U$ , more charges are transferred, which results in more preference to the Na2 sites.



**Figure 5.** The total densities of states of the two phases as a function of  $U$ : (a) and (b) are for the  $\alpha$ -phase and the  $\beta$ -phase, respectively.  $t_{2g}$  orbitals and  $e_g$  orbitals of Co ions are indicated with arrows.

In addition to the charge transfer, the correlation effect has an important effect on the electronic properties. The Co d orbitals are split into a lower-lying triplet  $t_{2g}$  and an upper-lying doublet  $e_g$  in the crystal field of the octahedral O environment. The total densities of states of the two structures are shown in figure 5, from which we can see that for both structures both the DFT and the DFT +  $U$  schemes predict a metallic ground state with the Fermi surface lying in the  $t_{2g}$  level. For both structures, the correlation effect pushes the unoccupied  $e_g$  levels upwards, resulting in further splitting between the occupied  $t_{2g}$  levels and the unoccupied  $e_g$  levels with the increase of  $U$ . There is large hybridization between the the Co 3d and O p states. The energy of the system increases quickly when the on-site Coulomb repulsion is applied to the system. In order to reduce the unfavourable high energy induced by the on-site Coulomb interaction, rehybridization occurs. A small amount of negative charges are transferred from Co 3d orbitals to O p orbitals. This process results in more effective positive charges of Co ions and more negative charges of O ions, and hence the preference of the Na2 sites.

This small value of the critical  $U$  may be explained by the rehybridization of the oxygen and  $e_g$  orbitals [25]. The large overlap of the Co 3d and O 2p states creates strong hybridization. When an on-site Coulomb repulsion is applied to the system, the total energy increases quickly. Then a small amount of charges are transferred from Co ions to O ions, which leads to the decrease in the occupancy of the Co 3d orbitals and the increase in the occupancy of the O 2p orbitals. These changes in occupancies then cause the unmixing of the oxygen and the Co 3d



**Figure 6.** The atom-projected density of states of the two phases: (a) and (b) are for the  $\alpha$ -phase and the  $\beta$ -phase, respectively. The dark and light colour lines (black and red lines online) represent the DOSs of Co 3d and O 2p, respectively.  $t_{2g}$  orbitals and  $e_g$  orbitals of Co ions are demonstrated with arrows.

orbitals, which leads to the decrease in the on-site Coulomb repulsion [25]. This accounts for the smallness of the critical value  $U$  for the phase transition.

Figure 6 shows the atom-projected density of states of the two structures, from which we can see that, within the DFT scheme, the Fermi energy lies at about 0.39 eV below the upper edge of the  $t_{2g}$  band for the  $\alpha$ -phase, while it is 0.45 eV for the  $\beta$ -phase. The DOSs of the two structures exhibit a similarity in the vicinity of the Fermi energy. These differences suggest that the Na potentials of different sites can influence not only the occupancy of each orbital of both Co ions and O ions, but also the distortion of the  $\text{CoO}_2$  layers, to which the hybridization of the  $e_g$  orbitals of Co ions and the p orbitals of O ions is sensitive. With the correlation effect taken into account, the bandwidth of the DOSs for both structures below the Fermi energy shrinks and the shape of the lines exhibits clear changes.

The system has both ionic and covalent bondings: the Co 4s electrons are fully ionized and the d electrons are covalently bonded with O p electrons due to the large overlap between the two wave functions. Figure 6 shows that the low-energy states have both the O p character and the Co d character, but in the high-energy level the DOS shows mainly the Co d character. With the increase of  $U$ , the O p character becomes more explicit with higher DOS, which implies

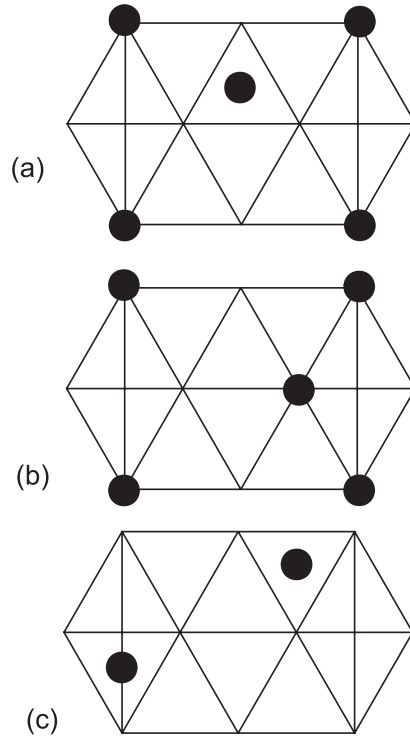


more occupancy. The higher occupancy of the O p orbital implies a lower occupancy of the Co d orbitals, considering that the total charge of the system is conserved. With the increase of  $U$ , the increasing occupancy of the O p orbitals and decreasing occupancy of the Co d orbitals demonstrate the negative charge transfer from Co ions to O ions, which results in the increasing stability of the  $\beta$ -phase. A more quantitative analysis has been given by integrating the charge changes of each atom. In our calculations, the atom-sphere radii are 1.70 Å for Na ions, 4.10 Å for Co ions and 1.10 Å for O ions respectively, with which the conservation of the total charges can be assured. The local charge of each atom is obtained by the integration of the charge density within the radius of the sphere centred at the positions of the respective ions. So the change in charge of each ion can be obtained. Our results show that, with the increase of  $U$ , charges are transferred from Co ions to O ions. From GGA (equivalent to  $U = 1$  eV in our calculation) to  $U = 5$  eV, the total charge changes for one Co ion are  $0.012e$ ,  $0.009e$ ,  $0.008e$  and  $0.01e$ , respectively, by a 1 eV increase of  $U$ . The average is about  $0.01e/eV$ . The change in the charge of Na ions can be negligible due to the strong ionization; the transferred charge is mainly of Co ions and O ions. As the ratio of the number of Co ions to the number of O ions is 1:2, the average gain of the O ions is  $0.005e/eV$ . Although the increase in the occupancy of the O ions is small at the critical value  $U = 2$  eV with relatively small amount of charges ( $0.005e$ ) transferred from the Co ions, the increase in the occupancy at an enlarged  $U$  of 5 eV can be seen much more clearly in partial DOS with a larger amount of charge transfer ( $0.02e/eV$ ).

In our calculations, we also find that the Na ordering can influence the shape and thickness of the CoO<sub>2</sub> layers. For the  $\alpha$ -phase, Co ions with Na ions above and below will deviate by about 0.16 Å from the ideal positions in the  $c$  direction, which is much larger than that of the other Co ions, the average of which is 0.02 Å. This is mainly due to the Coulomb repulsion from Na ions. The distance of the O ions nearest to Na ions from the Co plane is  $0.087c$ , while that of the other O ions is  $0.084c$ . The deviation of Na ions from the ideal positions is very small. For the  $\beta$ -phase, the Co ions nearest to the Na ions deviate by about 0.09 Å in the  $c$  direction, while the average of the other Co ions is 0.03 Å. The average distance of the O ions nearest to the Na ions from the Co plane is  $0.0855c$ , while that of the other O ions is  $0.083c$ . The deviation of Na ions is still very small for this phase. The sensitivity of the geometry of the CoO<sub>2</sub> layers to the distribution of Na ions indicates the strong coupling between the Na ions and the CoO<sub>2</sub> layers. This result agrees well with the experiment reported by Huang *et al* [26].

We have also investigated the effect of the correlation on the structure at  $x = 1/2$ . The structures with a different ordering of Na ions and a different magnetic ordering of Co ions have been calculated. As a charge-ordered insulator, the structure of Na<sub>1/2</sub>CoO<sub>2</sub> consists of both the ordering of Na ions and the magnetic ordering of Co ions. A  $\sqrt{3} \times 2$  orthorhombic superlattice of Na planes has been found from the experiments [12, 27]. Figure 7(a) displays the orthorhombic superstructure of the Na layer, denoted Na12. The Na1 and Na2 orderings have also been constructed, as shown in figures 7(b) and (c). The Na1 ordering represents the superstructure with Na ions occupying Na1 sites only and the Na2 ordering with Na ions occupying Na2 sites only. For the magnetic ordering of Co ions, we consider three cases: one is the ferromagnetic ordering (FM) and the others are the two antiferromagnetic orderings of Co ions (AFM1 and AMF2). The AFM1 antiferromagnetic structure consists of alternating rows of ordered and non-ordered Co ions observed by the recent neutron scattering measurement [28]. The AFM2 is an antiferromagnetic ordering of Co ions consisting of two FM Co layers with opposite magnetic moments of each layer.

We have calculated the energies of the structures of Na<sub>1/2</sub>CoO<sub>2</sub> with different combinations of Na ordering and Co magnetic ordering. The energies of different structures are listed in table 1. From table 1, it can be seen that both the DFT scheme and the DFT+ $U$  scheme give the ground state (Na12, AFM1), which is in agreement with the experiment. The correlation effect



**Figure 7.** Three different superstructures of the Na ordering at  $x = 0.5$ : (a) the  $\sqrt{3} \times 2$  superstructure of the Na planes observed by experiment; (b) the superstructure with Na ions occupying Na1 sites only; (c) the superstructure with Na ions occupying Na2 sites only. Solid circles represent the projected Na positions at  $z = 0.25$ .

**Table 1.** The energies of different  $\text{Na}_{1/2}\text{CoO}_2$  structures. Na12, Na1 and Na2 represent the Na ordering structures as shown in figures 3(a)–(c). AFM1, AFM2 and FM represent different magnetic orderings of Co ions. (Na12, FM) represent the structure with the Na12 ordering of Na ions and the ferromagnetic ordering of Co ions. The energy of the structure (Na12, FM) is set as the energy origin; the relative energies for different structures are given.

	GGA			$U = 4 \text{ eV}$			$U = 8 \text{ eV}$		
	AFM1	AFM2	FM	AFM1	AFM2	FM	AFM1	AFM2	FM
Na12	-0.231	-0.002	0.00	-0.13	-0.05	0.00	-0.93	-0.01	0.00
Na1	0.22	0.269	-0.028	0.053	0.50	0.399	-0.89	0.67	0.66
Na2	0.223	0.009	0.0119	0.057	0.16	0.397	-0.92	-0.05	-0.04

has a significant influence on the electronic properties of this material. The DFT scheme cannot predict the insulating state of  $\text{Na}_{1/2}\text{CoO}_2$  reported by the experiment; it exhibits a metallic behaviour with a large density of states at the Fermi surface and the energy gap appears only when a large enough  $U$  is applied to the system, which is in agreement with previous study [29].

In addition, we have also studied the case of high concentration  $x$ . We have calculated the correlation effect on the Na ordering of  $\text{Na}_x\text{CoO}_2$  at  $x = 1$ . The case is different from that at  $x = 1/9$  and  $1/2$ . The DFT scheme has already given that the structure with Na2 sites occupied was 0.21 eV per unit cell lower in energy than the structure with Na1 sites occupied. When  $U$

is 4 eV, the energy difference between the two structures is 0.255 eV, and it is 0.253 when  $U$  is 8 eV. Although the stability is increased with the correlation effect taken into account, the energy difference between the two structures seems to be insensitive to the correlation effect.

### 3.2. Correlation effect on the magnetic properties of $\text{Na}_{1/2}\text{CoO}_2$

In this section, we will study the magnetic ordering of  $\text{Na}_{1/2}\text{CoO}_2$  in relation to the ordering of Na ions. For the Na1 ordering, the magnetic ordering FM of Co ions has the lowest energy within the DFT scheme, while it is the AFM1 ordering that is the most stable magnetic ordering when  $U$  is 4 and 8 eV. For the Na2 ordering, the DFT scheme predicts that the AFM2 ordering is the most favourable magnetic ordering, while the DFT +  $U$  scheme predicts that the AFM1 ordering is the most stable. The case is different for the Na12 ordering, with which both the DFT and DFT +  $U$  schemes predict the same magnetic ordering AFM1. This suggests that the correlation effect has an important influence on the magnetic ordering. When  $U$  reaches a large enough value, the AFM1 is more favourable than the other magnetic orderings. As  $U$  increases, the energy difference between the AFM1 ordering and other magnetic orderings becomes larger, which is an indication of the increasing stability of the AFM1 ordering with the increase of  $U$ .

On the other hand, for the AFM1 ordering, both the DFT and the DFT +  $U$  schemes give the same Na ordering, i.e. Na12. For FM, the DFT scheme predicts that the Na1 ordering is most favourable. When  $U$  is 4 eV the most stable ordering is Na12, and when  $U$  is 8 eV it becomes Na2. For the AFM2 ordering, the DFT scheme predicts that the Na12 ordering is most favourable, which remains stable when  $U$  is 4 eV. But when  $U$  is 8 eV, Na2 ordering becomes the most stable. This means that the Na12 ordering observed by experiment is not always the most stable when the magnetic orderings of the underlying Co layer are changed. Both the coupling between the Na ordering and the magnetic Co ordering and the correlation effect contribute to the ground-state structure. Thus changing the magnetic Co ordering can lead to the change of Na ordering.

Considering that the deviation of each ion with Na12 ordering is very small no matter what the magnetic ordering of Co ions is, the interaction between the adjacent Co layers can be obtained through the energy difference of (Na12, AFM2) and (Na12, FM). Within the DFT scheme, it is  $-0.002$  eV, while within the DFT +  $U$  scheme the values are  $-0.05$  and  $-0.01$  eV with  $U$  being 4 and 8 eV, respectively. The small values indicate that the interaction between the adjacent Co layers is very small, which is in agreement with the result of that of Li *et al* [29] and it is insensitive to the correlation effect.

## 4. Conclusion

Using the DFT +  $U$  schemes, we have investigated the correlation effect on the Na ordering of  $\text{Na}_x\text{CoO}_2$ . We show that the correlation effect plays an important role in the Na ordering at low concentration. At  $x = 1/9$ , when  $U$  is larger than 2 eV, the DFT +  $U$  method predicts that the structure with Na ions occupying the Na2 sites is the ground state, which agrees with the experimental result. As  $U$  increases, the energy difference between the two structures becomes larger, which indicates an increasing stability of the structure with Na2 sites occupied. The charge transferred from Co ions to O ions increases with the increase of  $U$ , which has a crucial effect on the ground-state structure. At  $x = 1$ , the Na2 structure is already the stable structure without considering the correlation effect. For  $x = 1/2$ , both the DFT and DFT +  $U$  schemes predict the same ground-state structure (Na12, AFM1), which is in agreement with the experiment. The correlation effect has a great influence on the electronic structure and it is shown to change the coupling between the Na ions and the Co magnetic ordering.

## Acknowledgments

This research was supported by the National Science Foundation of China under grant nos 10674076 and 10474049, the National Basic Research Program of China and the Key Grant Project of the Chinese Ministry of Education (No. 306020).

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