The recently renewed research interest in Na$_x$CoO$_2$ since the discovery of superconductivity [1] in the hydrated materials has revealed a range of interesting and intriguing properties of this system. One of the most interesting discoveries is the determination of its phase diagram as the doping level $x$ is varied [2]: Two metallic phases at low and high dopings are separated by an insulating state at $x = 0.5$. Along with this insulating state there is strong evidence of an ordered Na layer and commensurate charge orderings in the CoO$_2$ layer. This raises the possibility of a subtle interplay between the Na ordering and the charge ordering in the CoO$_2$ layer [2, 3]. At certain Na compositions, this interplay might have profound effects on the electronic or magnetic properties of the CoO$_2$ layer if a particularly stable Na ordering pattern exists and whether a commensurate charge ordering is allowed. Therefore, a unified theory of the Na ordering mechanism may be critical for a better understanding of the electronic structure in this system. The observed Na ordering pattern [2, 4] at $x = 0.5$ agrees well with our theoretical prediction [5], and this motivates us to extend our investigation on Na ordering at other compositions studied by recent electron diffraction experiments [6]. In this paper, we identify ground state Na ordering patterns at various compositions and show that the Na ordering is primarily driven by the intra-plane screened electrostatic interactions. The details of the electronic structure of the CoO$_2$ plane, on the other hand, have minimal effects.

The compound Na$_x$CoO$_2$ assumes a layered structure which consists of alternating triangular CoO$_2$ and Na planes. Although there have been reports [6, 7, 8] of several stacking patterns, we shall restrict our discussion to the so-called $\gamma$ phase, which is usually observed for low to intermediate Na compositions. There are two distinct Na sites within a given plane, denoted as Na(1) and Na(2) (Wyckoff indices 2b and 2d). The Na(1) site, being directly between two Co ions, is slightly higher in energy than the Na(2) site [2, 3]. Therefore, Na ions will normally prefer occupying the Na(2) sites.

We calculate the total energy of 82 ordered structures of Na$_x$CoO$_2$ using first principles techniques. The choice of structures for the ground state search was guided by the MAPS code [10]. Our calculations are based on density-functional theory (DFT) [11, 12] within the local density approximation (LDA) with the Ceperly-Alder exchange-correlation functional [13, 14]. Ab initio Troullier-Martins pseudopotentials [12] are used. Calculations are performed using the SIESTA code [16, 17], which expands the Kohn-Sham wavefunctions in a linear combination of atomic orbitals (LCAO). A double-zeta plus polarization (DZP) basis is used. The energy cutoff for the charge density grid is 1000 Ry. The irreducible Brillouin Zone is sampled using Monkhorst-Pack grids [18] with a density of k-points equivalent to $12 \times 12 \times 2$ for a primitive unit cell. Atomic positions are relaxed until forces are smaller than 0.005 eV/Å. We keep the lattice constants fixed at $a = 2.82\,\text{Å}$ and $c = 10.89\,\text{Å}$. Although the lattice constants of Na$_x$CoO$_2$ will vary slightly with Na concentration, our results are not sensitive to this small variation.

The energetics of Na ordering in Na$_x$CoO$_2$ can be studied using the well-established formalism for binary alloys [19]. The fundamental quantity that determines the stability of a given arrangement $\eta$ of Na ions and vacancies with Na composition $x$ is the formation energy $\Delta E^\eta$:

$$\Delta E^\eta_{\text{DFT}} = E^\eta - xE^{\text{NaCoO}_2} - (1-x)E^{\text{CoO}_2},$$

where $E^\eta$, $E^{\text{NaCoO}_2}$ and $E^{\text{CoO}_2}$ are the total energies per site of the structure $\eta$, and of the pure compounds NaCoO$_2$ and CoO$_2$, respectively, calculated within DFT. Fig. 1 shows the calculated formation energies of all 82 structures (open dots). We highlight the ground state structures (red dots) joined together by the hull-shaped curve (red line). Structures with formation energy above the convex hull are unstable against phase separation into the two ground states with nearby compositions. Red arrows indicate the structures proposed by Zandbergen et al. [4] (at $x = 0.11$, $x = 0.30$, $x = 0.33$, $x = 0.50$, $x = 0.53$, $x = 0.75$, $x = 0.90$, $x = 0.93$, $x = 0.98$, $x = 1.00$).
$x = 0.71$ and $x = 0.75$) based on electron diffraction experiments. The agreement between theory and experiment is remarkable in that all experimentally proposed structures are indeed ground states within DFT. Although the structure at $x = 0.30$ appears to be an exception (it is not a ground state within DFT), it is too close to the convex hull to be neglected as such, given the uncertainties in the calculation. Moreover, we find additional ground states at $x = 0.20$, $x = 0.25$, $x = 0.60$, $x = 0.80$ and $x = 0.83$. A structure at $x = 0.40$ is also too close to the convex hull to be ruled out. These structures have not been observed experimentally, perhaps because samples at these particular compositions were not analyzed. An ordered structure at $x = 0.64$ also appears experimentally. According to our results, at this composition the sample should be phase-separated between $x = 0.60$ and the $x = 0.71$ ground states. All ground state structures and the near ground states at $x = 0.30$ and $x = 0.40$ are depicted in Fig. 2. We also display the lowest energy structure at $x = 0.67$ (not a ground state), for discussion purposes.

Before discussing in detail the various ordered structures, let us first address the driving force for Na ordering in this system. The simplest explanation would be electrostatics since the Na atoms lose one electron each to the CoO$_2$ network, they arrange themselves so as to minimize electrostatic energy. We perform model calculations to test this hypothesis, in which the Ewald (ionic) energies of the different arrangements of Na$^{+1}$ ions are computed. In these calculations, we assume that the electronic charge is spread over the CoO$_2$ planes neighboring the Na-vacancy layer, which is consistent with our previous calculations. Also, the chemical difference between Na(1) and Na(2) sites is simulated by adding an energy $\epsilon_1$ per Na ion to the Ewald energies for a Na(1) site. Therefore, the total energy per unit cell for this electrostatic model is defined as:

$$E_{\text{model}}^\eta = E_{\text{Ewald}}^\eta + N_1^\eta \epsilon_1,$$

where $N_1^\eta$ is the number of Na atoms in Na(1) sites for the structure $\eta$.

Figure 3 shows, for each structure, $\Delta E^\eta_{\text{DFT}}$ (Eq. 1) versus the calculated formation energy using the above model ($\Delta E^\eta_{\text{model}}$). We clearly see that these two quantities are proportional: $\Delta E^\eta_{\text{DFT}} = \kappa \Delta E^\eta_{\text{model}}$. The best fit (rms deviation of 0.016 eV) is obtained for $\kappa = 0.514$ and an on-site energy difference between Na(1) and Na(2) sites $\kappa \epsilon_1 = 67$ meV. A value of $\kappa$ smaller than 1 is expected because of screening and partial ionization effects, which are absent from the model calculations and naturally included in the DFT calculations. Therefore, DFT formation energies can be described with good accuracy by a model of screened electrostatic interactions, showing unambiguously that the dominant driving force for Na ordering in Na$_x$CoO$_2$ is electrostatic.

We now discuss the geometries of the structures shown

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{DFT formation energies for 82 ordered structures of Na$\_x$CoO$_2$. The red dots represent the ground-state structures, joined together by the convex hull (red line). The arrows indicate the experimentally observed ground states.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Relevant ordered structures of Na$_x$CoO$_2$. The dashed lines represent the projected triangular lattice of Co atoms. Large red open circles and small red dots represent projected Na positions in different planes, at $z = 0$ and $z = 0.5c$, respectively. The Na(1) sites fall on top of the triangular lattice sites and Na(2) sites fall in the center of the triangles. Blue lines indicate the minimum unit cell in each case. A detailed discussion of each structure is presented in the text.}
\end{figure}
in Fig. 2. In the low concentration regime, we find a ground state at \( x = 0.11 \) (1/9) (Fig. 2b)), corresponding to an in-plane arrangement of Na “impurities” in a \( 3 \times 3 \) triangular lattice. Surprisingly, the lowest energy structure corresponds to placing both Na atoms (one in each plane) in the less favorable Na(1) sites. This structure prevails with respect to other arrangements because it minimizes the inter-plane electrostatic energy: The Na atoms can be as far as possible from each other. Interestingly, this arrangement corresponds to placing each Na atom in the middle of the projections of the three Na atoms of neighboring planes, and it is consistent with the experimental observation of a \( \sqrt{3} \times \sqrt{3} \) superstructure in the diffraction patterns of Ref. [4]. Indeed, we observe this pattern in all Na compositions except for Na ordering [4].

At \( x = 0.20 \), the ground state has a \( \sqrt{7} \times \sqrt{7} \) supercell, shown in Fig. 2c, with both Na ions in Na(2) sites. Periodic repetition of this cell leads to an arrangement of Na ions along rows perpendicular to the [110] direction (the horizontal direction in Fig. 2). The distance between Na ions in a row is \( \sqrt{3}a \). Such pattern of rows have been experimentally observed for different compositions and have been proposed to be the guiding principle for Na ordering [4]. Indeed, we observe this pattern in all other Na compositions except \( x = 1/9, 1/4, \) and 2/3 (not a ground state). The same pattern of rows is observed in the lowest energy structures calculated using the simple electrostatic model. Therefore, the rows arise naturally from the minimization of electrostatic energy, combined with the constraint that only discrete lattice sites can be occupied by Na ions.

Fig. 2d) shows the ground state for \( x = 0.25 \), a \( 2 \times 2 \) triangular lattice. In this case, both Na ions occupy the more preferable Na(2) sites. In Fig. 2e), the lowest energy structure for \( x = 0.30 \) is shown. It has precisely the same in-plane arrangement proposed by Zandbergen et al.[4]. Again, it corresponds to rows of Na ions perpendicular to [110] and all ions occupy Na(2) sites. As discussed above, it is not a ground state in our calculations (by merely 1 meV/site).

At \( x = 0.33 \) (1/3), the arrangement is again a triangular lattice (\( \sqrt{3} \times \sqrt{3} \)), as shown in Fig. 2f). This structure is exactly the same as proposed by Zandbergen et al. [4]. The \( x = 1/3 \) concentration is of particular interest due to the observed superconductivity in the hydrated system at \( x \sim 0.3 \). Although the role water plays is still unknown, the screening of the Na potential by water molecules might suppress the tendency of developing a commensurate charge ordering pattern in the CoO\(_2\) layer, which may then lead to a more homogeneous electronic system and favor a superconducting state over other competing phases at low temperature. Possible charge disproportionation and gap opening at this doping level in the unhydrated system has been studied previously [20]. However, so far such an insulating state has not been observed.

Fig. 2g) shows the lowest energy arrangement for \( x = 0.40 \) (not a ground state, by 0.6 meV/site). It also follows the rows pattern, and the ratio between Na(1) and Na(2) occupancies is 1.

In Fig. 2h), the ground state for \( x = 0.50 \) is shown, which is a \( \sqrt{3} \times 2 \) supercell. The arrangement also follows the pattern of rows and it has also been predicted theoretically [3] and observed experimentally [4]. This structure is particularly stable since all other in-plane arrangements with a similar unit cell at this composition are at least 25 meV/site (or 200 meV/cell) higher in energy. Note again that the ratio between Na(1) and Na(2) occupancies is 1. This ratio tends to be higher for structures with intermediate composition, since the on-site chemical energy difference between Na(1) and Na(2) sites becomes less important than arranging the Na ions as far as possible to minimize electrostatic energy. The existence of a particularly stable Na ordering pattern, together with the observed insulating state at this composition [4], strongly indicate an interplay between the Na ordering and the charge ordering in the CoO\(_2\) layer in this system. Our results suggest that, if such an interplay exists, it is more likely that an ordered Na potential drives the charge ordering or enhances this tendency. Studies of charge ordering in this system with the presence of a commensurate Na ordering will be reported in a separate paper.

At \( x = 0.60 \), the ground state structure is again a \( \sqrt{7} \times \sqrt{7} \) supercell, shown in Fig. 2i) with a pattern of rows and a Na(1)/Na(2) occupancy ratio of 1/2. The composition \( x = 0.67 \) (2/3), like \( x = 1/3 \), has been the subject of many discussions due to its apparent proximity to the lack of a stable and commensurate Na ordering. It is obvious that a honeycomb arrangement would be more compatible with the proposed charge ordering pattern [20, 21, 22]. Therefore, we propose that the nonexistence of a charge-ordered insulating state at this composition is due to the lack of a stable and commensurate Na ordering.

The ground state structure at \( x = 0.71 \) (5/7) is shown
in Fig. 2k). It is impressive that such a complex arrangement with a large supercell ($\sqrt{15} \times \sqrt{15}$) corresponds to a ground state structure, as seen experimentally [3]. For this structure we have a Na(1)/Na(2) occupancy ratio of 2/3 and once more the rows pattern is followed. In the high $x$ limit, this pattern becomes simpler to analyze: Low energy structures are composed of rows of Na(2) ions intercalated by rows of vacancies and Na(1) ions. For instance, for the $x = 0.71$ structure the repetition is $3 \times$ Na(2)-vac-$2 \times$ Na(1)-vac.

For $x = 0.75$ we find again the same ground state as proposed by experiments [4], a $\sqrt{3} \times 4$ supercell shown in Fig. 2l). In this case, the pattern of rows is $3 \times$ Na(2)-vac-$3 \times$ Na(1)-vac, i.e., there are equal numbers of Na(2) and Na(1) ions. This structure is lower in energy than that proposed by Shi et al. [22]. Measurements of local distortions of Na(2)O$_6$ polyhedra at $x = 0.75$ have been recently performed by neutron diffraction [24]. Apparently, Na(2) ions move to off-center positions, resulting in two long (2.56 Å) and four short (2.32 Å) Na-O bonds.

Our calculated Na-O bond lengths for this structure are 2.57 Å and 2.29 Å, in excellent agreement with experiment.

At $x = 0.80$ and $x = 0.83$ (5/6) (Figs. 2 (m) and (n), respectively) we find ground-state structures that belong to the same “family” as the $x = 0.75$ structure, i.e., they follow similar row patterns with $n \times$ Na(2)-vac-$3 \times$ Na(1)-vac rows in a $\sqrt{3} \times (n + 5)/2$ cell, with $n = 3$ for $x = 0.75$, $n = 5$ for $x = 0.80$ and $n = 7$ for $x = 0.83$. Therefore, it is very likely that beyond $x = 0.75$ one can construct infinitely many ground states (polytipoids) by simply intercalating odd numbers of Na(2) rows with the sequence of rows-vac-$3 \times$ Na(1)-vac-. In fact, if one takes into account entropic considerations, it is plausible that the thermodynamically stable configuration for $x > 0.75$ will consist of disordered arrangements of such rows. This result may be related to the order-disorder transition reported at $x = 0.75$ from neutron diffraction experiments [3, 24]. Finally, for $x = 1.0$ all Na(2) sites are occupied (Fig. 2o)).

In conclusion, we have carried out detailed DFT and model studies on the Na ordering mechanism in Na$_x$CoO$_2$. The ordering pattern is non-trivial and is sensitive to the Na concentration. The theoretically determined ordering patterns at various Na compositions agree well with those observed in recent electron diffraction experiments [4]. In addition, we identify several ground states that have not yet been observed. Our results indicate that the primary driving force for the Na ordering is the screened electrostatic interactions. Detailed electronic structure on the CoO$_2$ layer, on the other hand, plays no important role on the ordering of Na ions since the coupling between the CoO$_2$ plane and the Na plane is much weaker than the intra-plane Na-Na interactions. The converse effects, however, could be significant since the charge and magnetic orderings on the CoO$_2$ plane happen at extremely low energy scale [2] and may be vulnerable to external perturbations. Therefore, it is likely that the particularly stable Na ordering structure at $x = 0.5$ enhances the charge ordering tendency in the CoO$_2$ layer, resulting in a charge ordered insulating state at low temperature as observed experimentally [2]. Conversely, the nonexistence of such an insulating state at $x = 2/3$ may be due to the absence of an ordered honeycomb arrangement of Na ions at this composition.

We acknowledge useful discussions with A. van de Walle, H. W. Zandbergen, and Q. Huang. This work was partially supported by National Science Foundation Grant No. DMR04-39768 and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. RBC acknowledges financial support from the John Simon Guggenheim Memorial Foundation and Brazilian funding agencies CNPq, CAPES, FAPERJ, Instituto de Nanociências, FUJB-UF RJ and PRONEX-MCT. Computational resources were provided by NPACI and NERSC.

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