Charge ordering and Na-vacancy ordering in Na$_{0.75}$CoO$_2$ are investigated using first-principles electronic structure methods within the generalized gradient approximation (GGA) and GGA+$U$ approximations. We find that Na ordering is determined not only by a competition between different Na site energies and Na$^+$-Na$^+$ repulsion, but also by the Co$^{3+}$-Na$^+$ repulsion when charge localization occurs. We predict a ground-state structure for Na$_{0.75}$CoO$_2$ in good agreement with experimental transmission electron microscopy and neutron-diffraction data and find that Co$^{3+}$/Co$^{4+}$ charge ordering is strongly coupled to the Na-vacancy ordering.

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namic diffraction calculations were performed with CRYSTMATKER-SINGLCRYSTAL software for a specimen thickness of 10 nm with a 200 keV electron beam.

We investigated three Na-vacancy arrangements for Na$_{0.75}$CoO$_2$ compatible with the $4 \times \sqrt{3}a_{\text{hex}}$ supercell in the Na layer as identified by TEM, and one other cell compatible with the 1:2 occupancy of Na(1):Na(2) sites as reported by neutron diffraction. We report for each structure only the three-dimensional stacking with lowest energy and discuss the influence of stacking later. Figure 1(a) shows the ordering proposed by Zandbergen et al. The structure shown in Fig. 1(b) is the one we find to be the lowest in energy. It consists of patterns of zigzag lines of Na(2) and Na(1). Two zigzag lines of Na(2) alternate with a single zigzag line of Na(1), giving a 1:2 occupancy ratio of Na(1) and Na(2). The structure shown in Fig. 1(c) has the same 1:2 occupancy ratio for the Na(1) and Na(2) sites, though the supercell in the Na plane is $2 \sqrt{3} \times 1 a_{\text{hex}}$. This structure consists of straight rows of Na(1) and Na(2). Two straight lines of Na(2) alternate with a single straight line of Na(1). Fig. 1(d) shows ordering of Na(1) and Na(2) with the occupancy ratio of 1:5, a filled honeycomb (FHC) pattern of Na(2) is formed in this structure. We refer to these four structures as the diamond, zigzag, row, and FHC. Their energies in GGA and GGA+U are given in Table I and are referenced with respect to the energy of the zigzag structure. While in GGA we find the zigzag structure to be 0.2 meV lower than the row structure, and 0.6 meV lower than the FHC structure, these values are well within the numerical errors of our method, and the three arrangements can therefore be considered degenerate within the GGA. In the GGA+U the zigzag structure is well below the row and FHC structures. Notice that though we used $U$ value derived from the Li$_2$CoO$_2$ system, we have tested our conclusions with several different $U$ values and found that the results are very consistent.

We also probed the relation between Co charge ordering and Na-vacancy ordering. Spin and charge integration in a sphere around the Co ions can be used to determine the valence of each Co ion. As expected, we find that the charges on all Co are identical to the GGA and no distinct Co$^{4+}$ ions exist in the structures we calculated. In GGA+U, charge localization occurs and one quarter of the Co ions have magnetic moments of approximately 1 (in unit of electron spin) as expected for low-spin Co$^{4+}$. In all cases the +4 state forms on a Co ion which has its neighboring Na(1) sites unoccupied, consistent with the strong repulsion between face-

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**TABLE I.** Calculated energy and lattice parameters.

<table>
<thead>
<tr>
<th>Structure</th>
<th>GGA</th>
<th>GGA+U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>diamond</td>
<td>Zigzag</td>
</tr>
<tr>
<td>$\Delta E^p$ (FM) (meV/Co)</td>
<td>9.9</td>
<td>0</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>2.869</td>
<td>2.861</td>
</tr>
</tbody>
</table>

$^a$Experimental measured lattice parameters $a=2.84$ Å and $c=10.81$ Å (Ref. 15). Note that the calculated $a$ lattice parameter is extracted from the $4 \times \sqrt{3}a_{\text{hex}}$ supercell.
sharing Na(1)O₆ prisms and CoO₆ octahedra.

While GGA and GGA+U predict the same Na-vacancy ground state for Na₀.₇⁵CoO₂, there are distinct differences between the two methods. Within GGA, the strong self-interaction of d electrons leads to complete charge delocalization among the Co ions and the energy difference between the four different arrangements is solely a competition between the difference in Na(1) and Na(2) site energy, and the electrostatic repulsion between Na ions. The zigzag, row, as well as FHC structures are lower in energy than the diamond structure which has more Na(1) sites occupied. Though the FHC structure has the lowest Na(1):Na(2) ratio, the Columbic repulsion among the pile of Na(2) ions in the filled-honeycomb pattern raises the total energy. Hence the energy of these structures arises from a delicate balance between the site energies and the Na-Na repulsion. In addition, as can be observed in Figs. 1(b) and 1(c), the zigzag and row have a similar local in-plane environment of Na ions: Na(2) has on average four Na(2) nearest neighbors and Na(1) has on average two Na(1) nearest neighbors. Within GGA, where charges on Co are delocalized, the degeneracy of these two structures is therefore to be expected based on their similar nearest neighbor environments.

Removal of the self-interaction on the Co-3d states allows the electrons to localize and form distinct Co⁴⁺ and Co³⁺ in the GGA+U method. This has a significant effect on the relative energies of the different Na-vacancy orderings. In GGA+U, the energy differences between zigzag, row and FHC become larger and the energies of the row and FHC are now above that of diamond. This can be understood from the distinct Co environments that each Na-vacancy ordering creates. Figure 2 shows the spin density in a Co layer (each Co is indicated by a black dot), plotted together with the Na-vacancy layers above (left figure) and below (right figure). Co⁴⁺ (around which a higher net spin is seen) forms on Co sites that have no face-sharing Na(1) occupation and with as few as possible Na(2) nearest neighbors. In the FHC structure, these Co⁴⁺ sites have four nearest-neighbor Na(2) ions (two above and two below the Co layer). In the zigzag structure the Co⁴⁺ ion is surrounded by only three nearest-neighbor Na(2) ions (two in one layer and one in the other), hence it has substantially lower energy. By creating distinct Co³⁺ and Co⁴⁺ in GGA+U, the energy difference between zigzag and diamond becomes less than in GGA, since in diamond Co⁴⁺ has only two nearest neighbor Na(2) ions (one in each layer), and the charge localization in GGA+U has reduced the formal charge on the Co ions that face-share with Na(1) to +3, instead of +3.25 in the GGA. Hence, the penalty for Na(1) occupation is reduced in GGA+U. For each Na-vacancy ordering in the 4×√3 cell the Co⁴⁺/Co³⁺ charge ordering forms a 2×√3 cell as shown in Fig. 2(a) by the dotted line. In the row structure, the smaller Na-vacancy superstructure cell does not allow for such a Co⁴⁺/Co³⁺ cell and the inability for Co⁴⁺ and Co³⁺ to charge order into preferred sites raises its energy considerably in GGA+U, hereby illustrating the coupling between Na-vacancy ordering and charge ordering.

Based on the GGA and GGA+U results we believe that the structure of Na₀.₇⁵CoO₂ is one where Na and vacancies are ordered in a double-zigzag Na(2)–vacancy–single-zigzag Na(1)–vacancy pattern as shown in Fig. 1(b), rather than in the diamond pattern as previously proposed.¹⁶,¹⁷ Neither GGA nor GGA+U predicts the diamond pattern as having the lowest energy. The zigzag pattern has the lowest energy within GGA+U and is degenerate with the row and FHC pattern in GGA. For this system the GGA+U method, which gives distinct Co⁴⁺ and Co³⁺ ions, is more consistent with experimental data such as NMR, optical spectroscopy, and magnetic measurements.¹⁰¹¹ The occupancy ratio of Na(1) to Na(2) is 1:2 in the zigzag structure, in good agreement with the neutron-diffraction results.¹⁵ To further test our prediction, we also simulated the electron diffraction patterns for the zigzag ground state and find that it agrees well with the experimentally observed pattern from Zandbergen et al.¹⁶ Figures 1(a), 1(b), and 1(d) show the simulated electron diffraction patterns for all three structures with the 4×√3 hex supercell. Both the diamond and FHC structure have diffraction intensity at 1/2a₁₁₀ or 1/2a₂₁₀ (marked by circles in Fig. 1) while this intensity is absent in the experimental patterns in Fig. 1 of Ref. 16. We tested several stacking variants of the diamond and row structure and found that either 1/2a₁₁₀
or \(1/2a_{110}\) reflections are always present indicating that they are intrinsic to the in-plane Na-vacancy ordering. Zandbergen\(^{16}\) already pointed out this potential discrepancy between their TEM data and the structure they proposed but attributed the extra reflection to possible double diffraction. The zigzag ordering, however, does not show these reflections. While the simulated electron diffraction pattern of the zigzag ordering in its lowest-energy stacking sequence does exhibit extra reflections not observed experimentally [marked with arrows in Fig. 1(b)], simulations for different stacking sequences of the zigzag ordering demonstrate that these reflections change with the stacking sequence. Hence, we suggest that the absence of these spots in experiment could result from stacking disorder of the zigzag arrangement along the \(c\) axis. Such stacking variance along the \(c\) axis in \(\text{Na}_x\text{CoO}_2\) has been observed and discussed.\(^{16}\)

In conclusion, we find that significant factors compete to determine the Na-vacancy ordering with lowest energy. It was previously already pointed out that \(\text{Na}^+-\text{Na}^+\) repulsion competes with the \(\text{Na}(1)\)-\(\text{Na}(2)\) site energy difference, even in the absence of any \(\text{Co}^{3\text{+}}\)-\(\text{Co}^{4\text{+}}\) charge ordering.\(^{17}\) Charge localization into distinct \(\text{Co}^{3\text{+}}\) and \(\text{Co}^{4\text{+}}\), as obtained in GGA+\(U\), leads to several other factors that can control the Na-vacancy ordering: \(\text{Co}^{3\text{+}}\) requires sites with no Na(1) neighbors and as few as possible Na(2) neighbors. In addition, the reduction of charge on \(\text{Co}^{3\text{+}}\) by the formation of \(\text{Co}^{4\text{+}}\) leads to Na(1) sites with lower site energy than for the system with delocalized \(\text{Co}^{3\text{.25}\text{+}}\) charge. Hence, in contrast to the claim in Ref. 17 we find a significant coupling exists between \(\text{Co}^{3\text{+}}/\text{Co}^{4\text{+}}\) charge ordering and Na-vacancy ordering. On the cons of the GGA+\(U\) results, we also propose a ground-state structure for \(\text{Na}_{0.75}\text{CoO}_2\) which is consistent with available experimental information (if some stacking disorder is allowed). One final implication of the coupling between the \(\text{Na}^+\) and \(\text{Co}^{3+}\) is that samples with very different Na-vacancy ordering (either in-plane or perpendicular to the Na layers) may have somewhat different electronic behavior. In particular, when Na-vacancy ordering is not perfect, the system may be unable to create low energy sites on which holes can condense to form \(\text{Co}^{4\text{+}}\). This can be observed in a previous LDA+\(U\) study by Okabe \textit{et al.}\(^{27}\) who could not achieve complete charge disproportion to \(\text{Co}^{3\text{+}}\) and \(\text{Co}^{4\text{+}}\) because an improper Na-vacancy ordering was used. It would be of interest to reinvestigate the electronic properties of samples with different cooling rates (to control ordering) in this light.

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