Coupling between electronic and structural degrees of freedom in the triangular lattice conductor Na$_x$CoO$_2$


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The ambient temperature crystal structures of compounds in the Na$_x$CoO$_2$ family, for 0.34 < $x$ ≤ 1.0, determined by powder neutron diffraction, are reported. The structures consist of triangular CoO$_2$ layers with Na ions distributed in intervening charge reservoir layers. The shapes of the CoO$_6$ octahedra that make up the Co$_2$ layers are found to be critically dependent on the electron count and on the distribution of the Na ions in the intervening layers, where two types of Na sites are available. Correlation of the shapes of cobalt-oxygen octahedra, the Na ion positions, and the electronic phase diagram in Na$_x$CoO$_2$ is made, providing an example of how structural and electronic degrees of freedom can be coupled in electrically conducting triangular lattice systems.

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INTRODUCTION

Square planes of metals and oxygen form the basis for scientifically and technologically important materials such as perovskite ferroelectrics, superconductors, and ferromagnets. Triangular arrangements of metals and oxygen are much less generally studied, except in the context of magnetism in electrically insulating materials, where the placement of antiferromagnetically coupled magnetic atoms in triangle-based lattices leads to frustration of the low-temperature magnetic state. The introduction of charge carriers into such triangular magnetic lattices in sufficient number to yield metallic conductivity has been a goal of research for some time. Na$_x$CoO$_2$, with a crystal structure consisting of alternating layers of Na ions and triangular CoO$_2$ layers, is the embodiment of such a system. (The CoO$_2$ layers consist of a sandwich of triangular O, Co, and O planes.) The charge on the CoO$_2$ layers is controlled by the degree of filling of the Na layer—in a manner fully analogous to the relationship between the charge reservoir layers and the CuO$_2$ planes in the high-$T_c$ superconductors. The properties of Na$_x$CoO$_2$ are not disappointing: a high thermoelectric power metallic conductor is found for Na$_{0.35}$CoO$_2$. Superconductivity is induced in Na$_{0.35}$CoO$_2$ when it is intercalated with water, and Na$_{0.5}$CoO$_2$ appears to be insulating at low temperatures due to ordering of Co ion charges. Compounds based on square-based transition-metal–oxygen lattices display a broad range of effects due to the coupling of electronic, magnetic, and structural degrees of freedom, but until now there has been no model system for investigating such effects in triangle-based electronic conductors. Here we report structural studies of the average crystal structure of Na$_x$CoO$_2$ over a wide range of Na content in the charge reservoir layer. Changes in the electron count due to changing Na content strongly affect the structure of the CoO$_2$ plane. The results suggest that conducting triangular lattice systems display their own class of structural and electronic coupling phenomena distinct from those previously studied in square-based systems.

Hexagonal Na$_x$CoO$_2$, which has two triangular CoO$_2$ layers per unit cell, has been reported to exist for 0.25 < $x$ < 0.8. It exhibits metallic behavior for a wide range of $x$, with the exception of $x$ = 1/2, where an insulating state is found at low temperatures. Magnetic ordering has been reported for compositions near Na$_{0.75}$CoO$_2$. Na contents lower than 0.7 in Na$_x$CoO$_2$ can only be obtained by room temperature deintercalation of sodium from Na$_{0.75}$CoO$_2$, and in one case crystals grown by the floating zone technique have been reported to have $x$ > 0.75. Crystal structures have been reported for some Na$_x$CoO$_2$ compositions, and Na$_{0.5}$CoO$_2$ has recently been studied by neutron diffraction due to its importance as the host for the superconducting phase. An electron diffraction study of the Na$_x$CoO$_2$ series has revealed a complex series of ordered Na distributions at different Na compositions.

This report describes the results of crystal structure determinations by powder neutron diffraction of a series of samples with $x$ between 0.34 and 1.0 in Na$_x$CoO$_2$, with an eye toward interpreting the electronic phase diagram. Because the Na charge is donated to the CoO$_2$ layers, this represents a change in the formal oxidation state of Co from Co$^{3+}$ to Co$^{4+}$. Although the basic two-layer hexagonal structure is maintained over the whole compositional range, we find substantial changes in the Na ion distribution as a function of composition, accompanied by significant changes in the geometry of the CoO$_2$ layer due to the changing electron count. The results indicate the presence of strong coupling between structural and electronic degrees of freedom in this system.

EXPERIMENT

Na$_{0.75}$CoO$_2$ was made by solid-state synthesis. Na$_2$CO$_3$ and Co$_3$O$_4$ in amounts corresponding to Na$_{0.77}$CoO$_2$ were...
mixed and heated to 800 °C under flowing O₂ for 16 h. Due to the volatility of Na oxides, the final Na composition is slightly lower than the starting composition. A sample of Na₃.₃₄CoO₂ was prepared by stirring 1 g of Na₀.₇₅CoO₂ with 1 × of NO₂PF₆ in dry acetonitrile under argon for 2 days ("1 ×") indicates that the amount of NO₂PF₆ used is exactly the amount that would theoretically be needed to remove all the sodium from Na₀.₇₅CoO₂). It is noted that this method produced NaNO₃ as a by-product. To prepare Na₀.₇₅CoO₂, Na₀.₇₅CoO₂ (1 g) was stirred in 120 ml of a 10% solution of I₂ in acetonitrile for 4 days. Na₀.₆₄CoO₂ was prepared by stirring Na₀.₇₅CoO₂ (1 g) in 40 ml of a 0.5% solution of I₂ in acetonitrile for 4 days. The products in all cases were washed with dry acetonitrile, dried in argon, and stored as an argon-filled glovebox.

For the synthesis of samples for x > 0.75, sodium metal (0.3 g) and tetrahydrofuran (40 ml) were placed in a 25 mm × 150 mm Pyrex screw-capped tube, and were heated by placing the lower 25 mm in an oil bath maintained at 95 °C. After 1 h, benzophenone (2.0 g) was added. After heating another hour, powdered Na₀.₇₅CoO₂ (1.5 g) was added, and the mixture was heated, with agitation by a magnetic stirring bar, for 48 h. The mixture was cooled to room temperature, and ethanol (20 ml) was added to destroy the benzophenone ketyl radical anion and any unreacted sodium metal. After 20 min, the mixture was centrifuged for 3 min at 2000 g in a stainless-steel centrifuge tube. The organic supernatant was decanted, the solid was resuspended in dichloromethane (20 ml), the mixture was centrifuged, and the organic supernatant was again decanted. Two more dichloromethane washes were performed in the same manner, and then the final black pellet was broken up and air-dried overnight to yield 1.5 g of sodium-enriched material. This process led in two different syntheses to materials of overall stoichiometry Na₀.₇₅CoO₂ and Na₀.₈₈CoO₂. As described below, this difference may be due to the presence of a two-phase region in the phase diagram at these compositions, or possibly due to uncertainties in the temperature of the reaction. The sodium contents of the samples were determined by multiple independent composition measurements by the ICP-AES method, and are considered to be reliable to ±0.02/formula unit. For all samples the Na content of the constituent phases was unambiguously determined through the structural refinements.

The neutron powder diffraction intensity data for the NaCoO₂ samples were collected using the BT-1 high-resolution powder diffractometer at the NIST Center for

### Table I. Structure parameters of Na₂CoO₂ at room temperature. Space group P6₃/mmc. Atomic positions: Co, 2a (0.0,0.0); Na(1), 2b (0.0,1/4) for structure types H1 and H2; Na(2), 2h (x,x,1/4) for structure type H1 or 2c (2/3,1/3,1/4) for structure types H2 and H3; O, 4f (1/3,2/3,z).

<table>
<thead>
<tr>
<th>x (chem.)</th>
<th>nd⁹</th>
<th>[0.49]b</th>
<th>0.64</th>
<th>0.75</th>
<th>nd</th>
<th>0.89</th>
</tr>
</thead>
<tbody>
<tr>
<td>x (refined)</td>
<td>0.34</td>
<td>0.56</td>
<td>0.63</td>
<td>0.71</td>
<td>0.77</td>
<td>0.76</td>
</tr>
<tr>
<td>Structure type</td>
<td>H1</td>
<td>O1</td>
<td>H1</td>
<td>H1 (31.1%)</td>
<td>H2 (68.9%)</td>
<td>H2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>2.8129(1)</td>
<td>[2.81508(3)]</td>
<td>2.82438(6)</td>
<td>2.8314(9)</td>
<td>2.84126(6)</td>
<td>2.84182(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.2152(6)</td>
<td>[11.1296(2)]</td>
<td>11.0046(3)</td>
<td>10.87564(4)</td>
<td>10.8143(4)</td>
<td>10.80703(3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>76.848(8)</td>
<td>[76.382(2)]</td>
<td>76.024(4)</td>
<td>75.8675(6)</td>
<td>75.606(4)</td>
<td>75.583(2)</td>
</tr>
<tr>
<td>Co B (Å²)</td>
<td>0.15(7)</td>
<td>[0.49(4)]</td>
<td>0.26(4)</td>
<td>0.36(3)</td>
<td>0.36(3)</td>
<td>0.33(7)</td>
</tr>
<tr>
<td>Na(1) B (Å²)</td>
<td>1.0</td>
<td>[2.9(2)]</td>
<td>1.7(2)</td>
<td>1.3(1)</td>
<td>1.3(1)</td>
<td>1.3(2)</td>
</tr>
<tr>
<td>n</td>
<td>0.12(1)</td>
<td>[0.264(9)]</td>
<td>0.220(9)</td>
<td>0.194(19)</td>
<td>0.226(10)</td>
<td>0.221(12)</td>
</tr>
<tr>
<td>Na(2) x</td>
<td>0.292(4)</td>
<td>0.289(2)</td>
<td>0.271(3)</td>
<td>1.0</td>
<td>[2.9(2)]</td>
<td>1.7(2)</td>
</tr>
<tr>
<td>O z</td>
<td>0.0855(2)</td>
<td>[0.08744(8)]</td>
<td>0.0887(1)</td>
<td>0.0904(2)</td>
<td>0.0909(1)</td>
<td>0.0907(2)</td>
</tr>
<tr>
<td>R_p (%)</td>
<td>4.25</td>
<td>[4.34]</td>
<td>4.82</td>
<td>6.24</td>
<td>2.77</td>
<td>5.10</td>
</tr>
<tr>
<td>R^(2) (%)</td>
<td>5.26</td>
<td>[5.83]</td>
<td>5.74</td>
<td>5.10</td>
<td>3.33</td>
<td>6.46</td>
</tr>
<tr>
<td>χ²</td>
<td>1.244</td>
<td>[2.855]</td>
<td>0.9538</td>
<td>0.9404</td>
<td>1.015</td>
<td>1.501</td>
</tr>
</tbody>
</table>

*This sample contains 23% NaNO₃; it was taken into account in the refinement.

*Orthorhombic structure. Refinement in hexagonal symmetry for comparison purposes only. Reference 18 reports orthorhombic refinement.
The Na positions [Na(1), in site \(2b\) \((0, 0, 1/4)\)] were found to be unambiguously defined for all compositions. Taking the \(x = 0.64\) sample as an example, we found that the Na(2) atom, in the site \(2c\) \((2/3, 1/3, 1/4)\), displayed a large temperature factor, \(\sim 3.0\ \AA^2\), when the diffraction data were fitted with one of the models previously reported for \(Na_{0.3}CoO_2\)\,14A refinement with Na(2) at the \(6h\) \((2x, x, 1/4)\) site [labeled as the Na(2)\('\) site], a model previously reported\,15 for \(x = 0.61\), allows for displacements of the Na(2) atoms from the centers of the ideal triangular prismatic coordination polyhedra at \((2/3, 1/3, 1/4)\). This model gave a substantially better agreement index and a more reasonable temperature factor for this Na. The possibility of a displaced position for Na(2) was therefore considered in the analysis for all compositions: if the \(x\) coordinate for the Na(2)' ions at the \(6h\) \((2x, x, 1/4)\) site converged to \(x = 1/3\), then the Na was considered to be in the Na(2) \(2c\) \((2/3, 1/3, 1/4)\) site. Satisfactory refinements were obtained for all compositions within these models.

The crystal structures of the three phases found in the Na\(_x\)CoO\(_2\) series (Table I) are shown schematically in Fig. 1. The compounds over the composition range from 0.34\(<x<0.74\) (with the exception of \(x = 0.5\)) are well described by a structure in which the Na(1) site is partially occupied and the Na(2) ions are displaced from the ideal centers of the NaO\(_6\) triangular prisms, i.e., in the Na(2)' sites. This structure type\,15 covers a large fraction of the phase diagram, and is designated as the H1 phase. Separated by a narrow two-phase region from the H1 phase, a different structure type is found for \(0.76<x<0.82\). This phase, designated as H2, has all the Na(2) ions directly in the center of the ideal Na(2) triangular prism, as well as Na ions in the Na(1) site. The sample of overall Na stoichiometry \(Na_{0.75}CoO_2\) is a mixture of the H1 and H2 phases and clearly shows the presence of the two-phase region (Fig. 2). It is of interest that the change in position from Na(2)' to Na(2) sites is abrupt, indicating that at a critical Na layer filling the system suddenly favors on-center Na(2) ion occupancy. The reason for this behavior is not yet understood.

Finally, a distinct phase [designated H3] is found at composition NaCoO\(_2\) after another two-phase region. In this compound, all the Na(1) sites are empty and all the Na(2) sites are filled: the Na are all in ideal trigonal prismatic sites that share only edges with the CoO\(_6\) octahedra. The crystal structure of H3 is distinctly different from that of the thermodynamically stable phase NaCoO\(_2\), which has all the Na in octahedral coordination with oxygen.\,12

FIG. 1. The three hexagonal structure types found for Na\(_x\)CoO\(_2\).

Layers of edge-shared CoO\(_6\) octahedra are seen in a triangular lattice with Na ions occupying ordered or disordered positions in the interleaving planes. Three different Na ion sites are found. In the H1 phase, \(0.3<x<0.75\), (with the exception of \(x = 0.5\)) Na atoms partially occupy the Na(1) \(2b\) and Na(2)' \(6h\) sites. In the H2 phase, \(0.76<x<0.82\), the Na(1) and Na(2) \(2c\) sites are occupied. In the H3 phase, \(x = 1\), only the \(2c\) site sites are occupied.

FIG. 2. Observed (crosses) and calculated (solid line) intensities for Na\(_{0.75}CoO_2\). Vertical lines indicate the Bragg peak positions for the phases H2 (bottom), H1 (middle), and 0.4 wt % CoO impurity (top). Differences between the observed and calculated intensities are shown in the bottom of the figure. The inset shows a portion of the pattern illustrating that the (106) and (107) reflections are good indications of the different lattice parameters for the phases H1 and H2 in this sample with overall composition Na\(_{0.75}CoO_2\).
centers of the regular antiprisms. We believe that this off-center position of the Na(2)' site is found due to repulsion of the Na(2)' ion by Na ions in occupied second-nearest-neighbor Na(1) sites. For the H1, H2, and H3 phases (lower part of Fig. 3), the Co—O bond lengths are all the same within the octahedra and the O—Co—O bond angles deviate from 90°, resulting in a significant flattening of the octahedra along an axis perpendicular to the CoO2 planes.

Figure 4 summarizes the compositional stability regions and general structural characteristics of the four phases found for Na$_x$CoO$_2$. (The O1 phase is the orthorhombic insulating phase at Na$_{0.5}$CoO$_2$. Schematic representations of the Na ion positions in the charge reservoir layer are at the top of the figure. The presence and extent of the two-phase regions (±0.02 Na per formula unit) have been determined from samples in which the overall Na content was determined by chemical analysis and two phases were observed in the neutron diffraction patterns. The fractional occupancies of the two types of sodium sites are a strong function of total Na content. The Na(1) site, where the Na ion is subject to repulsive interactions with the Co, is occupied for all compositions at a lower probability than the Na(2)' sites in the H1 phase. In the orthorhombic O1 phase ($x' = 0.5$), however, these two sites are occupied in equal proportions, an indication of the coupling of the Na positions to the charge distribution in the underlying Co lattice. As the Na content increases from $x = 0.5$ towards $x = 0.75$, the added Na fills the Na(2)' sites only. In the H2 phase, the Na(1) site occupancy decreases dramatically with increasing Na concentration, and the Na(2) sites becomes more and more preferentially occupied. A discontinuous change in the occupancies is apparent at $x = 0.8$: in the H3 phase all the possible Na(2) sites are occupied and the Na(1) sites are all empty.

The crystallographic $a$ axis, representative of the in-plane size of the CoO$_2$ octahedra, increases in a manner consistent with decreasing the formal oxidation state of Co with increasing Na content in Na$_x$CoO$_2$. The shrinkage of the c axis parameter with increasing Na content is a summation of two different effects. As the fractional occupancy of Na in the charge reservoir layer increases, the increasing positive charge results in an increasing Coulombic attraction between neighboring CoO$_2$ layers, and their separation decreases. This is shown in the upper panel of Fig. 5, which plots the thickness of a single NaO$_2$ layer (the CoO$_2$—CoO$_2$ layer separation) as a function of Na content. This CoO$_2$—CoO$_2$ layer separation changes continuously in the H1 phase, but there is a pronounced decrease in the H2 phase, in the composition region where all the Na(1) sites are being depopulated. This suggests that the Na(1) ion repulsion with the Co in CoO$_6$ octahedra directly above and below that share faces with it contributes significantly to pushing the layers apart. The overall trend to decreasing NaO$_2$ layer thickness is continued on passing from the H2 to the H3 phase.

The thickness of a single CoO$_2$ layer (Fig. 5) varies in a complex manner with composition, and indicates that substantial structural changes are taking place as a response to
This indicates that the CoO$_6$ octahedra do not change shape significantly though the electron count has remained constant.

We postulate that the CoO$_2$ layer thickness is the structural characteristic that most sensitively reflects the electronic state of Na$_x$CoO$_2$. For CoO$_6$ octahedra of ideal shape, the $t_{2g}$ states are energetically degenerate. For octahedra compressed by shortening the distance between opposing triangular faces, as is found in Na$_x$CoO$_2$, the degeneracy is partially lifted, yielding two lower energy two-electron $t_{2g}$ suborbitals and one higher energy two-electron $t_{2g}$ suborbital. The greater the compression of the octahedra, the more different in energy the upper and lower $t_{2g}$ suborbitals will be. The relative thickness of the Co$_2$ layer is a measure of that compression. Oxides based on Co$^{3+}$ are well known for displaying a delicate balance between different orbital occupancies, and different spin states, based on both structural distortion and temperature, which affect the balance between Hund’s rule coupling and crystal field effects. Also, in the current system, on hydration of Na$_{0.3}$CoO$_2$ to superconducting Na$_{0.3}$CoO$_2$·1.3H$_2$O, the layer thickness decreases significantly though the electron count has remained constant.

Our proposal for relationships between the structural and electronic properties of Na$_x$CoO$_2$ is summarized in Fig. 6. The main panel shows the electronic phase diagram as we currently understand it. The upper area shows a schematic representation of the Na distribution in the hexagonal layers, and the lower panel shows the ratio of the observed thickness of the CoO$_2$ layers in Na$_x$CoO$_2$ to that expected for layers of ideal octahedra. The “ideal” octahedral layer is derived by taking the lengths of the in-plane edges of the CoO$_6$ octahedra from the measured a lattice parameters and employing those values to calculate an ideal layer thickness, assuming 90° O—Co—O bond angles and equal Co—O bonds. We note that the CoO$_2$ layer is strongly compressed along the c axis to about of 85% of the expected thickness for ideal octahedra.

The smooth variation of CoO$_2$ layer thickness with $x$ in the H1 phase suggests that in this part of the phase diagram the effect of changing Na content on the electronic properties of Na$_x$CoO$_2$, which changes from superconductor host metal, through charge ordered insulator, to antiferromagnetic metal, must be a consequence of the continuously changing electron count in the CoO$_2$ plane, and not a consequence of discontinuous changes in the types of electronic states that are mixed in at the Fermi energy. Continuous changes in the relative proportions of different types of states at $E_F$ may be present, however, and mixing of the nominally empty $e_g$ states with the $t_{2g}$ and oxygen 2p states may be possible.

In contrast, the H2 phase occurs in a composition region ($0.75 < x < 0.80$) of dramatic structural and electronic changes in Na$_x$CoO$_2$. Most significant from a structural viewpoint are the changes from occupancy of the off-center Na(2)$'$ sites in the H1 phase to the ideally triangular prismatic Na(2) sites in the H2 phase, and the rapid depopulation of the Na(1) sites. A discontinuous change in the Co$_2$—Co$_2$ layer separation is observed. This is accompanied by a substantial change in the electronic state of the Co$_2$ layer, which rapidly increases in thickness in the H2 phase with increasing Na content. Whether these transitions

![Diagram of thickness of NaO$_2$ layers](Image)
There is an abrupt decrease in the CoO$_2$ layer thickness on passing into the $H3$ phase, where the Na(2) sites are fully occupied in a long range ordered hexagonal lattice. NaCoO$_2$ is expected in the simplest picture (3$d^9$Co$^{3+}$) to be a band insulator with fully occupied $t_{2g}$ orbitals. The decrease of the layer thickness on passing from the $H2$ to the $H3$ phase may reflect a change in the relative energies of filled $t_{2g}$ states compared to other states near $E_F$ at the $d^9$ electron count. The physical properties of the $H3$ NaCoO$_2$ phase are not currently known.

The insulating state at Na$_{0.5}$CoO$_2$ is found in a phase (the $O1$ phase) with a long-range ordered arrangement of zigzag Na chains, with Na atoms in both Na(1) and Na(2) sites, and an accompanying charge-ordered Co array. Metallic conductivity is observed in compounds with the $H1$ phase structure for $x$ values surrounding $x=0.5$. The displaced Na(2)$^+$ positions and the Na(1) occupancy in the average structure of the $H1$ phase, and the electron diffraction characterization, revealing rich variations of Na ordering schemes related to that found in Na$_{0.5}$CoO$_2$, suggest that the Na ion array forms zigzag fragments, either disordered or in short-range ordered arrays, in the whole $H1$ composition region. These zigzag fragments appear to vary in number and distribution as the Na plane filling changes. Even in preparations or at compositions where the Na ion distribution appears to be disordered, it is likely that such fragments appear on the short-range scale, much as disordered CuO$_2$ chain fragments are found in YBa$_2$Cu$_3$O$_7$. Due to the low proportion of Na(1) occupancy in the $H2$ and $H3$ phases, such zigzag Na fragments are not expected to occur.

In conclusion, the structural characterization of Na$_2$CoO$_2$ by neutron and electron diffraction has resulted in a picture of how the sodium ions are arranged in the charge reservoir layer, and how the CoO$_2$ layers respond structurally to changes in electron count and Na ion distribution. These changes are similar in character to those seen in the high $T_c$ superconductors, where structural and electronic degrees of freedom within a square conducting plane are often linked in a subtle manner (e.g., Ref. 22), suggesting that a similarly rich phenomenology remains to be fully elucidated in layered triangular conductors.

ACKNOWLEDGMENTS

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FIG. 6. Correspondence between structure and properties in Na$_x$CoO$_2$. Upper figure: schematic of the Na ion distributions in the four Na$_2$CoO$_2$ phases. Main panel: the electronic phase diagram. Lower panel: variation of the ratio of the observed CoO$_2$ layer thickness to the thickness of an ideal layer of octahedra.

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