Crystal structure and elementary properties of Na$_x$CoO$_2$ (x=0.32, 0.51, 0.6, 0.75, and 0.92) in the three-layer NaCoO$_2$ family


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The crystal structures of Na$_x$CoO$_2$ phases based on three-layer NaCoO$_2$, with $x=0.32, 0.51, 0.6, 0.75$, and 0.92, determined by powder neutron diffraction, are reported. The structures have triangular CoO$_2$ layers interleaved by sodium ions, and evolve with variation in Na content in a more complex way than has been observed in the two-layer Na$_x$CoO$_2$ system. The phases with highest and lowest Na content studied ($x=0.92$ and 0.32) are trigonal, with three CoO$_2$ layers per cell and octahedral Na ion coordination. The intermediate compositions have monoclinic structures. The $x=0.75$ compound has one CoO$_2$ layer per cell, with Na in octahedral coordination and an incommensurate superlattice. The $x=0.6$ and 0.51 phases are also single layer, but the Na is found in trigonal prismatic coordination. The magnetic behavior of the phases is similar to that observed in the two-layer system. Both the susceptibility and the electronic contribution to the specific heat are largest for $x=0.6$.

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I. INTRODUCTION

Na$_x$CoO$_2$ has been widely studied as the solid-state cathode in Na batteries. The discovery in 2003 of superconductivity ($T_c$=4.5 K) in two-layer Na$_{0.75}$CoO$_2$ intercalated with water made the study of the Na$_x$CoO$_2$ system an active area of research. The degree of filling of the Na layer controls the charge in the CoO$_2$ planes, giving rise to different properties as a function of $x$. The two-layer form of Na$_x$CoO$_2$ has been of significant recent interest, as it displays a variety of interesting properties. In addition to the superconductivity in the hydrated phase, a large thermopower (100 µV/K at 300 K) has been found for $x\sim0.7$, and attributed to the spin entropy carried by strongly correlated electrons hopping on a triangular lattice. A transition to an insulating state takes place in Na$_{0.5}$CoO$_2$ at low temperatures, which has been attributed to charge ordering.

Four different phases have been previously reported in the thermodynamic Na$_x$CoO$_2$ chemical system. In all the phases, sheets of edge-sharing CoO$_6$ octahedra are interleaved by sodium ions. The stacking sequence of the oxygen layers gives the number of sheets within a unit cell. Either two or three CoO$_2$ sheets per unit cell are found. Three of the four phases are reported to be three-layer structures, delineated as (1) the $\alpha$ phase for $0.9\leq x\leq1$, (2) the $\alpha'$ phase for $x=0.75$, and (3) the $\beta$ phase for $0.55\leq x\leq0.6$. Only one thermodynamic phase has a two-layer structure; it is known as the $\gamma$ phase, for $x\sim0.7$. The coordination of sodium ions in these structures is either octahedral or trigonal prismatic. These four thermodynamically stable phases in the Na$_x$CoO$_2$ system can be obtained by classic solid-state reactions. Topochemical methods can be used to tune the sodium composition within these structures. Thus, two-layer Na$_{0.5}$CoO$_2$ and Na$_{0.3}$CoO$_2$ have been obtained by chemical deintercalation of the higher-$x$ counterparts. In addition, chemical intercalation can be used to increase the sodium content of the $\gamma$ phase from $x=0.7$ up to $x=1$. The crystal structure of two-layer Na$_x$CoO$_2$ with $0.3\leq x\leq1$ has been extensively studied by Rietveld refinement using neutron diffraction data. In the three-layer structure, however, crystallographic studies are reported only for $x=1$ (single crystals), and for $x=0.67$ (polycrystalline powder). At $x=1$ the reported structure is trigonal [R3m with $a=2.889(2)$ and $c=15.609(3)\text{ Å}$] while at $x=0.67$ the crystal structure is single-layer monoclinic [C2/m, with $a=4.9023(4)$, $b=2.8280(2)$, $c=5.7198(6)\text{ Å}$ and $\beta=105.964^\circ$]. Early on, the powder patterns for $x=0.5$ and 0.6 were indexed with a monoclinic cell but the structure was not determined.

Here we report a structural study, by neutron powder diffraction analysis, of the Na$_x$CoO$_2$ phases derived from three-layer NaCoO$_2$, for $x=0.92, 0.75, 0.60, 0.51$, and 0.32. It is found that the crystal structure changes from one sodium composition to another in an unexpected way. For example, Na$_{0.92}$CoO$_2$ is trigonal, with Na in octahedral coordination. Deintercalation of this compound using Br$_2$ results in the formation of Na$_{0.3}$CoO$_2$, which has the same crystal structure. Deintercalation of trigonal Na$_{0.92}$CoO$_2$ with I$_2$ forms Na$_{0.5}$CoO$_2$, which has a monoclinically distorted single-layer structure. Na$_{0.6}$CoO$_2$ has also a single-layer unit cell and is found to be isostructural with the previously reported Na$_{0.67}$CoO$_2$. Na$_{0.75}$CoO$_2$ has a complex crystal structure. An average structure for this phase is reported based on the main reflections in the neutron diffraction data, indexed with a monoclinic cell. Susceptibility and heat capacity measure-
TABLE I. The types of structures found for the Na₅CoO₂ compounds (0.3 < x < 1). The structure types are (distinguished by Na coordination type and the number of layers per unit cell) P2, prismatic, two layer; O3, octahedral, three layer; P1, prismatic, one layer; O1, octahedral, one layer.

<table>
<thead>
<tr>
<th>Refined composition</th>
<th>Space group</th>
<th>Sodium coordination</th>
<th>Structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₀.₃₄CoO₂</td>
<td>P6₃/mmc</td>
<td>Trigonal prism</td>
<td>P2</td>
</tr>
<tr>
<td>Na₀.₃₄CoO₂</td>
<td>R₃m</td>
<td>Octahedral</td>
<td>O3</td>
</tr>
<tr>
<td>Na₀.₆₃CoO₂</td>
<td>C2/m</td>
<td>Trigonal prism</td>
<td>P1</td>
</tr>
<tr>
<td>Na₀.₅₁CoO₂</td>
<td>C2/m</td>
<td>Trigonal prism</td>
<td>P1</td>
</tr>
<tr>
<td>Na₀.₇₅CoO₂</td>
<td>C2/m</td>
<td>Trigonal prism</td>
<td>P1</td>
</tr>
<tr>
<td>Na₀.₉₂CoO₂</td>
<td>R₃m</td>
<td>Octahedral</td>
<td>O3</td>
</tr>
</tbody>
</table>

aData from Ref. 7.
bData from Ref. 14.
cThis work.
dData from Ref. 9.

ments are also reported for these phases. Although different crystal structures are found for the three-layer as opposed to the two-layer structures (Table I), the basic electronic properties of these materials are similar, supporting the general understanding that the electronic systems, dominated by the in-plane character of the CoO₂ layers, are highly two dimensional in character.

II. EXPERIMENT

Samples of Na₅CoO₂ with x=0.92, 0.75, and 0.60 were obtained as previously described.8 Stoichiometric amounts of Na₂O₂ (Alfa, 93% min) and Co₃O₄ (Alfa, 99.7%) were mixed together in an argon-filled glove box. The powders were then quickly removed from the glove box and placed in a tube furnace to prevent the hydration of sodium peroxide by air exposure. The temperature was slowly (5 °C/min) increased to 550 °C, held constant for 16 h, and then slowly (5 °C/min) cooled to room temperature under flowing oxygen. No sign of contamination with two-layer structure materials was observed for three-layer derived materials synthesized under the employed conditions. Each targeted compound was reproducibly obtained by choosing the appropriate Na:Co stoichiometry.

Na₀.₃₃CoO₂ and Na₀.₃₃CoO₂ were synthesized by chemical deintercalation of Na₀.₉₂CoO₂. Na₀.₃CoO₂ was prepared by mixing NaCoO₂ with excess I₂ (10 ×) dissolved in acetonitrile. After 5 days of stirring, the product was washed with acetonitrile, dried, and stored under argon. Single crystals of Na₀.₅CoO₂ were obtained by chemical deintercalation of NaCoO₂ single crystals stirred with H₂O at room temperature for 5 days. Na₀.₃CoO₂ was obtained by mixing Na₀.₉₂CoO₂ with a molar excess of 40 × bromine dissolved in acetonitrile. The reaction time was 5 days, after which the product was washed with acetonitrile and stored under argon. Minimum exposure to atmospheric conditions is required to prevent water intercalation.

All samples were analyzed by powder x-ray diffraction using Cu Kα radiation and a diffracted beam monochromator. Neutron diffraction data were collected on each sample at the NIST Center for Neutron Research on the high-resolution powder neutron diffractometer with monochromatic neutrons of wavelength 1.5403 Å produced by a Cu(311) monochromator. Collimators with horizontal divergences of 15°, 20°, and 7° of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the 2θ range of 3°–16° with a step size of 0.05°. The structural parameters were refined using the program GSAS.11 The neutron scattering amplitudes used in the refinements were 0.363, 0.253, and 0.581 (×10⁻¹² cm) for Na, Co, and O, respectively. All sodium contents for the phases were determined by the structure refinements, and were in good agreement with those expected from nominal compositions.

TABLE II. The cell parameters for three-layer derived Na₅CoO₂ (x=0.92, 0.6, 0.51, and 0.32).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Cell constants (Å)</th>
<th>Volume (Å³)</th>
<th>Volume/f.u. (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₀.₉₂CoO₂</td>
<td>R₃m</td>
<td>a=2.88878(5)</td>
<td>112.740(5)</td>
<td>37.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=15.5998(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₀.₇₅CoO₂</td>
<td>C2/m</td>
<td>a=4.9020(5)</td>
<td>75.57(1)</td>
<td>37.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=2.8723(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₀.₆₅CoO₂</td>
<td>C2/m</td>
<td>a=4.9043(2)</td>
<td>76.089(6)</td>
<td>38.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=2.8275(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₀.₅₁CoO₂</td>
<td>C2/m</td>
<td>a=4.8809(1)</td>
<td>76.439(4)</td>
<td>38.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b=2.81535(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₀.₃₂CoO₂</td>
<td>R₃m</td>
<td>a=2.81202(7)</td>
<td>114.58(1)</td>
<td>38.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c=16.732(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CRYSTAL STRUCTURE AND ELEMENTARY PROPERTIES

Electron microscopy analysis was performed with Philips CM300UT electron microscopes having a field emission gun and operated at 300 kV. Electron-transparent areas of specimens were obtained by crushing them slightly under ethanol to form a suspension and then dripping a droplet of this suspension on a carbon-coated holey film on a Cu or Au grid.

The magnetic susceptibilities were measured with a Quantum Design MPMS superconducting quantum interference device system. Zero-field cooled magnetic data were taken between 2 and 300 K in an applied field of 5 kOe. The main reflections of the neutron diffraction pattern fit the cell parameters presented in Table II. In the following, the nomenclature introduced earlier to describe layered structures of this type\textsuperscript{13} is employed to most easily distinguish the phases: $O$ and $P$ designations refer to octahedral or prismatic coordination, respectively, of Na in the phase, and the numerical designation 1, 2, or 3 refers to the number of CoO$_2$ layers in a unit cell repeat. In this system of nomenclature, the two-layer phases commonly studied are $P2$ compounds, whereas the parent compound for the current studies, NaCoO$_2$, has the $O3$ type.

### III. RESULTS

The purity of the Na$_x$CoO$_2$ compounds was confirmed by x-ray diffraction analysis, while structural investigations were performed by neutron diffraction analysis. Only Na$_{0.92}$CoO$_2$ and Na$_{0.32}$CoO$_2$ had powder diffraction patterns that could be indexed with a hexagonal cell. Their neutron powder patterns were indexed within the trigonal space group $R\bar{3}m$ (no. 166), with the cell parameters given in Table II. None of the intermediate sodium compositions maintained the hexagonal structure. The neutron diffraction patterns of Na$_{0.5}$CoO$_2$ and Na$_{0.6}$CoO$_2$ were indexed based on centered monoclinic cells in the space group $C2/m$ (no. 12). The cell constants are presented in Table II. The monoclinic cells arise through shifts of the CoO$_2$ planes of approximately 1 Å relative to each other to accommodate changes in the local Na–O coordination. The shifts are in one direction, parallel to the crystallographic $a$ axis. The x-ray diffraction pattern of Na$_{0.75}$CoO$_2$ could be well indexed based on a monoclinic cell (space group $C2/m$), but the neutron diffraction pattern showed the presence of relatively strong incommensurate superstructure reflections also seen in electron diffraction (described below). The main reflections of the neutron diffraction pattern fit the cell parameters presented in Table II. In the following, the nomenclature introduced earlier to describe layered structures of this type\textsuperscript{13} is employed to most easily distinguish the phases: $O$ and $P$ designations refer to octahedral or prismatic coordination, respectively, of Na in the phase, and the numerical designation 1, 2, or 3 refers to the number of CoO$_2$ layers in a unit cell repeat. In this system of nomenclature, the two-layer phases commonly studied are $P2$ compounds, whereas the parent compound for the current studies, NaCoO$_2$, has the $O3$ type.

#### A. Structural characterization

1. $x=0.92$ and 0.32 ($O3$ structure type)

The Na$_{0.92}$CoO$_2$ and Na$_{0.32}$CoO$_2$ phases have been found to be isostructural. Their structural analysis by the Rietveld method was carried out in the space group $R\bar{3}m$. The sodium ions are on the ($0, 0, 1/2$) site, and are coordinated octahedrally to the oxygens from the CoO$_2$ layers. The refined structural

### TABLE IV. Crystallographic data for $O3$-type Na$_{0.33}$CoO$_2$ in the space group $R\bar{3}m$ (no. 166). $\chi^2=1.19$; $wR_p=5.26$%; $R_p=4.33$%. (Uiso=isothermal temperature factor; Occ=occupancy.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso*100</th>
<th>Occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$3a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.78(6)</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>$3b$</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>1.2(2)</td>
<td>0.32(1)</td>
</tr>
<tr>
<td>O</td>
<td>$6c$</td>
<td>0</td>
<td>0</td>
<td>0.2762(1)</td>
<td>1.074(4)</td>
<td>1</td>
</tr>
</tbody>
</table>

### TABLE V. Crystallographic data for $P1$-type Na$_{0.5}$CoO$_2$ in the space group $C2/m$ (no. 12). $\chi^2=1.48$; $wR_p=4.51$%; $R_p=3.74$%. (Uiso=isothermal temperature factor; Occ=occupancy.)

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso*100</th>
<th>Occ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>$2a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.86(5)</td>
</tr>
<tr>
<td>Na</td>
<td>$4i$</td>
<td>0.806(2)</td>
<td>0</td>
<td>0.491(2)</td>
<td>2.11(2)</td>
</tr>
<tr>
<td>O</td>
<td>$4i$</td>
<td>0.387(1)</td>
<td>0</td>
<td>0.1740(4)</td>
<td>0.92(3)</td>
</tr>
</tbody>
</table>
parameters for both phases are presented in Tables III and IV. Sodium contents of 0.921(7) and 0.32(1) were determined by refinement for these two phases. As an example, the structural model for Na$_{0.92}$CoO$_2$ is shown in Fig. 1.

2. $x=0.6$ and 0.51 (P1 structure type)

Na$_{0.6}$CoO$_2$ and Na$_{0.51}$CoO$_2$ have similar crystal structures and are found to be isostructural with Na$_{0.67}$CoO$_2$. This is a single-layer structure (space group $C2/m$) where the sodium ions are in trigonal prismatic coordination. The structural parameters for Na$_{0.6}$CoO$_2$ and Na$_{0.51}$CoO$_2$ are presented in Tables V and VI, respectively. Whereas in Na$_{0.51}$CoO$_2$ the sodium ions are found on the 4$i$ site $(x,0,z)$, in Na$_{0.6}$CoO$_2$ the sodium ions are displaced from the 4$i$ site to a more general position $8j$ $(x,y,z)$. No such displacement of the sodium ions was detected for Na$_{0.51}$CoO$_2$ within the standard deviations of the positional parameters. In these structures, each sodium layer of Na$_{0.51}$CoO$_2$ has only $\sim$25% of a honeycomb-geometry sodium lattice occupied, while in Na$_{0.6}$CoO$_2$ the sodium ions form a distorted honeycomb lattice only 30% filled. No information about any possible ordering of the Na ions within the partially occupied sites was obtained in the present study. The peaks observed at 2$\theta$ = 24.7° and 26.6° in the Na$_{0.51}$CoO$_2$ neutron powder pattern (see Fig. 2) can be well indexed by doubling the $b$ axis. This suggests that sodium ordering occurs in chains in this structure, much as it does in two-layer Na$_{0.5}$CoO$_2$. No such peaks are observed in the neutron diffraction pattern for three-layer derived Na$_{0.6}$CoO$_2$. A very good agreement of the sodium content with the nominal compositions is found for both phases by Rietveld refinement: $x=0.596(3)$ and 0.512(4). As an example, the observed and calculated and the difference plots of the refinement for the $x=0.51$ phase are presented in Fig. 2. The idealized crystal structure is shown in Fig. 1.

3. $x=0.75$ (O1 structure type)

A different crystal structure from the ones described above is found for Na$_{0.75}$CoO$_2$. The Rietveld refinement was performed in the $C2/m$ space group based on a single-layer structure. The crystal structure of the $x=0.92$ phase was used as a starting model with the atom coordinates in the three-layer structure transformed into the single-layer monoclinic cell. This model gave a very good fit to both the powder x-ray diffraction data ($\chi^2=1.26$, $wR_p=7.86\%$, $R_p=6.22\%$) and the main reflections in the neutron diffraction pattern. The refined structural parameters based on the neutron diffraction data are presented in Table VII. Figure 3 shows the observed and calculated and difference plots for the refinements based on this model for both x-ray data and neutron data (inset in Fig. 3). The structural model is presented in Fig. 1.

Electron diffraction studies were performed to characterize the superstructure observed in the neutron diffraction pattern of Na$_{0.75}$CoO$_2$. Figure 4 shows a [010] electron diffraction pattern of Na$_{0.75}$CoO$_2$ taken in nanodiffraction mode.
with a spot size of about 10 nm. A quite dominant superstructure can be distinguished. The superstructure reflections can be indexed best using four dimensions, resulting in four Miller indices \(hklm\), in which \(m\) indicates the order of the satellite measured from the nearby main reflection. The \(hklm\) indexing of two super-reflections is shown in Fig. 4. The super-reflections in the electron diffraction patterns are much more visible than in the neutron powder diffraction pattern; they are not seen in the x-ray powder pattern. This is due to the strong dynamic scattering in electron diffraction, which results in an enhancement of the weak reflections compared to the strong ones. The observed superstructure for \(x=0.75\) is relatively strong, since quite a number of first-order super-reflections can be seen in the neutron diffraction pattern (see Fig. 3). The indexing of the super-reflections in the neutron diffraction pattern is based on the 0.030\(a^*\)–0.247\(c^*\) modulation vector determined from electron diffraction data. Determination of the incommensurately modulated structure of Na\(_{0.75}\)CoO\(_2\) from the powder diffraction data is beyond the scope of the present study.

**B. Magnetic characterization**

The variation of molar susceptibility with \(x\) is presented in Fig. 5. At temperatures higher than 50 K, the temperature dependence of the susceptibility \((\chi \text{ vs } T)\) for \(x \geq 0.6\) follows the Curie-Weiss law \(\chi = \chi_0 + (C/T - \theta)\), with the Curie constant \((C)\), Weiss constant \((\theta)\), and temperature independent term \((\chi_0)\) presented in Table VIII. The negative Weiss constants indicate antiferromagnetically interacting spins. Given

![FIG. 3. Observed (crosses) and calculated (solid line) x-ray diffraction intensities for O1-type Na\(_{0.75}\)CoO\(_2\). Vertical bars show the Bragg peak positions. The inset shows the super-reflection peaks (marked with arrows) in the neutron diffraction pattern indexed in a four-dimensional cell.](image)

![FIG. 4. [010] diffraction pattern of O1-type Na\(_{0.75}\)CoO\(_2\). Strong super-reflections are present. The diffraction pattern was taken with the beam partly on a relatively thick area and partly over the adjacent hole, which configuration resulted in a tail of the reflections to the upper left corner. The indexing of some of the reflections is given. The vector \(q\) describing the satellites is 0.330\(a^*\)–0.247\(c^*\).](image)

![FIG. 5. Temperature dependence of the magnetic susceptibility for three-layer derived Na\(_x\)CoO\(_2\) with \(x=0.92, 0.75, 0.6, 0.51\), and 0.3.](image)
TABLE VIII. Summary of magnetic data for three-layer derived Na$_x$CoO$_2$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>C (cm$^3$ K/mol)</th>
<th>$\mu_{\text{eff}}$ (units of $\mu_B$)</th>
<th>$\theta$ (K)</th>
<th>$\chi_0$ (emu/moleCo Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>0.0130(5)</td>
<td>0.32</td>
<td>$-55(\pm3)$</td>
<td>0.00008(1)</td>
</tr>
<tr>
<td>0.75</td>
<td>0.0984(9)</td>
<td>0.88</td>
<td>$-48(\pm1)$</td>
<td>0.00011(1)</td>
</tr>
<tr>
<td>0.6</td>
<td>0.084(3)</td>
<td>0.82</td>
<td>$-97(\pm3)$</td>
<td>0.00037(8)</td>
</tr>
</tbody>
</table>

a simple localized picture where only Co$^{4+}$ ions carry the
spin moment $S=1/2$, the effective moments for the 0.92,
0.75, and 0.6 compositions are expected to be 0.49$\mu_B$,
0.87$\mu_B$, and 1.09$\mu_B$ per formula unit, respectively. The ob-
served moments are 0.32$\mu_B$, 0.88$\mu_B$, and 0.82$\mu_B$ per formula
unit, respectively. Although the differences between the cal-
culated values assuming a simple model and the observed
ones are not large, developing experiments in the two-layer
phase indicate that a more complex electronic and magnetic
system is at play (see, e.g., Ref. 16). It can be inferred, how-
ever, that low-spin configurations for Co$^{3+}$ and Co$^{4+}$ ions are
found in these phases. Small deviations from the Curie law
are noted for $x=0.92$ and 0.6 below 30 K, and a magnetic transition at $\sim30$ K is seen for $x=0.75$, at a similar tempera-
ture to that observed for the two-layer $x=0.75$ phase.\textsuperscript{16} For
$x=0.5$, $\chi$ vs $T$ has a different shape and no Curie-Weiss
behavior is found. Two cusps are observed in the $\chi$ vs $T$ data:
one at $\sim88$ K and another one at $\sim52$ K. These two tran-
sitions are observed at nearly the same temperatures where
transitions are observed for two-layer Na$_{0.5}$CoO$_2$.\textsuperscript{5} In the
two-layer structure the two anomalies signal the onset of an
insulating state that has been attributed to a charge ordered
phase. For $x=0.3$ in the three-layer structure, $\chi$ is indepen-
dent of temperature above 75 K. A Curie contribution is seen
at lower temperatures. The origin of this behavior is not
known.

C. Resistivity measurements

Resistivity measurements were performed on $x=0.5$
single crystals (Fig. 6). A transition to an insulating state is
observed. The primary resistive transition is observed at
50 K, but the derivative of the resistivity data (inset, Fig. 6)
shows that the transition observed in the susceptibility near
88 K also impacts the resistivity. The behavior of the resis-
tivity in the three-layer derived phase is very similar to that
of two-layer Na$_{0.5}$CoO$_2$, though in the latter case the resistive
transition often shows an initial increase near 50 K with the
main transition at lower temperatures.

D. Heat capacity

The heat capacity data as a function of $x$ for the three-
layer derived Na$_x$CoO$_2$ phases are presented in Fig. 7. The
specific heat for all compositions decreases as the tempera-
ture approaches 2 K. For $x=0.75$, a small transition is seen
around 25 K, associated with the magnetic ordering ob-
served in the $\chi$ vs $T$ data. The electronic contribution to the
specific heat ($\gamma$) was extracted from the Debye formula at
temperatures lower than 10 K. The inset of the figure shows
$\gamma$ for each composition. As expected, the lowest $\gamma$ is found
for $x=0.5$ where a transition from metallic to insulator takes
place. Below and above this composition, the larger carrier
concentrations are expected to result in larger values for $\gamma$.

IV. DISCUSSION

In contrast to the relatively straightforward structural be-
havior of the frequently studied two-layer Na$_x$CoO$_2$ system,
significant structural changes take place when the sodium
composition is varied in three-layer derived Na$_x$CoO$_2$. In the
two-layer system, $P2_1$-type phases exist over a large compo-
sition range, dominating the phase diagram from $x=0.3$ to 1.
In that two-layer system, $x=0.5$ is a special composition
structurally, and there are small two-phase regions between
different $P2_1$-type structures in the high-sodium-content re-
region. The Na is in trigonal prismatic coordination across the
whole two-layer series, resulting in the fact that neighboring
CoO$_2$ layers are stacked in the same position relative to each other in all compounds. The same is not the case for the three-layer derived family. Our studies show that octahedral coordination for Na is apparently destabilized near half filling (i.e., $x \approx 0.5$) of the Na planes. The energetic reason for this is not known. The appearance of $P1$ phases in the middle of the three-layer derived phase diagram due to this octahedral site destabilization is the major factor in complicating the structural phase diagram. Thus, unlike the two-layer system, the regions of solid solution in the three-layer Na$_x$CoO$_2$ are relatively narrow and compositions intermediate to those described here are classic two-phase mixtures.

The changes in Na coordination across the series cause the CoO$_2$ layers to shift relative to each other to create the appropriate shape coordination polyhedra for Na and the right position of the adjacent O layers. The Na coordination polyhedra observed are presented in Fig. 8. Both the bond lengths and shapes of the octahedra and trigonal prisms are consistent with expectations for Na–O polyhedra and very similar to what is seen in the two-layer series. As in the two-layer series, the NaO$_2$ plane layer expands as Na is removed: when the sodium site occupancy within the layers decreases, the repulsion between the CoO$_2$ sheets is enhanced, and also the Coulombic forces holding the layers together decrease. Figure 9 shows that in spite of the changes in coordination of the Na across the series, the thickness of the NaO$_2$ layers changes continuously with Na content.

A characterization of the relation of the CoO$_2$ planes relative to one another across the series is presented in Fig. 10. In the top panel, the distances between the CoO$_2$ planes (from Co plane to Co plane) are shown for all studied compounds. There is a uniform change to smaller separation with increasing Na concentration, due primarily to the changing concentration of Na in the NaO$_2$ plane, as described above.

The structures change symmetry across the series and the Na coordination changes from octahedral to trigonal prismatic and back again. A uniform description of the family can be made, however, by defining a pseudomonoclinic cell for all cases, with $a=2a_{\text{hex}}$ and $b=a_{\text{hex}}\sqrt{3}$ for the in-plane cell parameters, and $c$ the distance from one Co to its equivalent Co one layer away. The pseudomonoclinic $\beta$ angle gives the angle between the $c$ and $a$ pseudomonoclinic axes, and is a good measure of the relative positions of neighboring layers. As an example, Fig. 11 shows the pseudomonoclinic cell derived from the hexagonal cell for $x=0.92$ and 0.75.

To characterize how the planes shift relative to one another across the series, the pseudomonoclinic angle and the actual distance of the plane shift on going from one compound to the next are shown in the bottom two panels of Fig. 10. The middle panel suggests that the $x=0.75$ compound has an unexpectedly large shift of the layers relative to the
behavior of the rest of the series, where the angles change continuously with Na concentration. This unusual character for the \( x=0.75 \) phase is also suggested by the bottom panel: though the coordination of the Na remains octahedral when decreasing the Na content from \( x=0.92 \) to 0.75, the layer has shifted by 0.6 Å. Interestingly, this shift is of the same magnitude, though in the opposite sense, as occurs when the layers shift between \( x=0.75 \) and 0.6 to accommodate a change in the Na coordination from octahedral to prismatic. A somewhat smaller shift is observed on going from the trigonal prismatic to octahedral coordination between \( x=0.51 \) and 0.32. It is interesting that in all cases the magnitudes of the shifts are relatively small, 0.6 Å in the largest case.

As sodium content is varied in \( \text{Na}_x\text{CoO}_2 \), the formal oxidation state of Co must change. For ideal \( \text{NaCoO}_2 \), \( \text{Na}_{0.5}\text{CoO}_2 \) and \( \text{CoO}_2 \), for example, the Co formal oxidation states will be +3, +3.5, and +4, respectively. Thus, as in the copper oxide superconductors where the charge in the CuO2 planes can be deduced from the oxygen content or electronegative nontransition metal ratios (e.g., in \( \text{La}_{2-x}\text{Ba}_x\text{CuO}_4 \)), the sodium content can be used as a measure of the charge state of the electronic system in the \( \text{CoO}_2 \) planes in \( \text{Na}_x\text{CoO}_2 \). There are two caveats: the strict use of Na content for this purpose in two-layer \( \text{Na}_x\text{CoO}_2 \) has been called into question for compositions where \( x \) is less than 0.5 by titration measurements,\(^\text{17}\) and, second, as in other highly oxidized transition metal compounds, the formal charge value says nothing about how the excess positive charge, on going from Co\(^{3+}\) to Co\(^{3.5+}\), is distributed among the Co or its coordinating oxygens. Plotting of structural parameters relevant to the electronic system as a function of Na content is straightforward, however, and can be used to infer general characteristics of the electronic system.

The structural characterization of the \( \text{CoO}_2 \) plane as a function of Na content in three-layer derived \( \text{Na}_x\text{CoO}_2 \) is presented in Fig. 12. As the sodium composition decreases, the in-plane Co-Co distance decreases, as seen in the top panel. In the simplest picture, this is a result of increasing the formal oxidation state of cobalt from mainly Co\(^{3+}\) in \( \text{Na}_{0.92}\text{CoO}_2 \) to Co\(^{3.68+}\) in \( \text{Na}_{0.32}\text{CoO}_2 \); the in-plane size of the \( \text{CoO}_6 \) octahedra is expected to shrink as the Co\(^{4+}\) to Co\(^{3+}\) ratio increases. It is of interest that the size change, though monotonic, is not linear across the series, but changes most in the mid-composition regions. Structural study of the two-layer \( \text{Na}_x\text{CoO}_2 \) system has led to the suggestion that the thickness of the \( \text{CoO}_2 \) layers may be a good reflection of redistribution of charge among different electronic orbitals with variation of electron count in that system.\(^\text{7}\) The thickness of the \( \text{CoO}_2 \) layer as a function of sodium content in the three-layer derived system is shown in the middle panel of Fig. 12. As expected, for \( x=0.92 \) where the cobalt ions are mainly Co\(^{3+}\), the \( \text{CoO}_2 \) layer thickness is largest, because the octahedra are largest, while for \( x=0.32 \), where the formal oxidation state is Co\(^{3.68+}\), the \( \text{CoO}_2 \) layer thickness is smallest. The figure shows (middle panel), however, that the variation in layer thickness, in this series is not monotonic, suggesting that there is a significant redistribution of charge among different electronic orbitals across the three-layer derived series as a function of Na content. Significantly, the Co-O bond length varies continuously across the series, reflecting a systematic, continuous change in the formal Co oxidation state. The data presented in this figure suggest that in three-layer derived \( \text{Na}_x\text{CoO}_2 \), the electronic system...
changes, and the crystal structure responds, over the whole composition region, from $x=0.32$ to 0.92.

Finally, Figs. 13 and 14 and present a general comparison of the electronic characteristics of the CoO$_2$ planes as a function of Na concentration in the two-layer and three-layer derived systems. Figure 13 shows that the variations in Co-O bond length across the two series are very similar, and follow the expected trend toward larger size with decreased Co oxidation state. There do appear to be subtle differences observed, but more detailed study would be required to clarify them. This type of continuous bond length change with $x$ would not be expected if oxygen vacancies occurred in significant numbers for $x/0.5$, halting the possible oxidation state of Co at an upper limit of +3.5.

Figure 14 shows the thickness of the CoO$_2$ plane relative to that expected if the CoO$_6$ octahedra have an ideal shape, as a function of composition. This quantity is determined from the length of the edges of the in-plane face of the CoO$_6$ octahedra and the ideal geometric relationship between the edge length and the diagonal height of an octahedron. The CoO$_2$ layer is highly compressed from what is expected for ideal octahedra ($1/2$ of the ideal value) in both phase families, suggesting that the structural distortion should be large enough to strongly influence the relative energies of different Co 3$d$ suborbitals. This thickness varies across the series, reflecting a redistribution of charge within the CoO$_2$ layers as a function of composition and comparison of the two-layer and three-layer derived phases suggests that there are subtle differences in the electronic systems. In particular, the figure suggests that the three-layer derived Na$_{0.75}$CoO$_2$ phase has a different kind of electronic structure than is seen in the two-layer variant at the same composition. Also shown in Fig. 14 are the single-phase and multiple regions in the two families of compounds. This indicates how strongly the type of stacking influences the crystal chemistry of these systems. In addition, the figure illustrates a comparison of the Co positions in the two-layer and three-layer derived structure types. In the former, the Co planes are eclipsed while in the latter the Co planes are staggered.

V. CONCLUSIONS

The crystal structures of the Na$_x$CoO$_2$ phases derived from three-layer NaCoO$_2$ are more complex than the much studied two-layer structures. This is due in large part to the fact that unlike the two-layer system, in the three-layer derived system the Na coordination changes in the structural series. In the two-layer family, the sodium forms many ordered phases, both commensurate and incommensurate with the underlying CoO$_2$ lattice. In the present system, due to the different types of sites encountered (i.e., octahedral rather than prismatic) the Na ordering may be expected to be different. No information on that ordering is provided in the average structure determinations presented here, and would be of interest in future studies. The structural complexity of the system is reflected in the crystal structure of the $x=0.75$ composition, where unlike the case of the analogous two-layer variant, the high intensities of the incommensurate superlattice reflections suggest that the underlying CoO$_2$ lattice experiences some kind of structural modulation. The de-
termination of this structure will be of interest, as well as modeling to determine whether the structural modulation is electronically driven.

Magnetic susceptibility data in the current family are consistent with Co$^{3+}$ and Co$^{4+}$ ions being in low-spin configuration, and the magnetic behavior is similar to that observed in the two-layer system, though some differences are seen, particularly the presence of a Curie-Weiss susceptibility in the $x=0.3$ sample. The three-layer derived $x=0.5$ phase, in its initial characterization reported here, appears to be analogous to the two-layer variant, suggesting that the electronic instability that gives rise to the insulating behavior is strongly two dimensional in character, due to the fact that the stacking of the CoO$_2$ layers differs in the two systems. Finally, the composition dependence of the electronic contribution to the specific heat in the three-layer system appears to be substantially different from what has been reported in the two-layer system, in the present case showing the largest $\gamma$ value at $x=0.6$. This may be due to the special character of the $x=0.75$ composition in the three-layer system, which may suppress $\gamma$. These similarities and differences suggest that further work on the three-layer derived phases and comparison to the two-layer phases will be of interest.

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12Certain commercial products or equipment are identified in this paper to describe the subject adequately. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the equipment identified is necessarily the best available for the purpose.