

Stoichiometric oxygen content in Na_xCoO_2 L. Viciu,¹ Q. Huang,² and R. J. Cava¹¹*Department of Chemistry, Princeton University, Princeton, New Jersey 08540, USA*²*NIST Center for Neutron Research, NIST, Gaithersburg, Maryland 20899, USA*

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The crystal structure and oxygen stoichiometry in two-layer $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$ at room temperature are analyzed by powder neutron diffraction. Two sets of diffraction data for each sample, taken at different incident neutron wavelengths, $\lambda = 1.1968 \text{ \AA}$ and $\lambda = 1.5403 \text{ \AA}$, are analyzed simultaneously by the Rietveld method, allowing for the independent refinement of all structural parameters. The fractional oxygen site occupancies are found to be 1.01(1) for $\text{Na}_{0.74}\text{CoO}_2$ and 0.99(2) for $\text{Na}_{0.38}\text{CoO}_2$, respectively. These results indicate that the oxygen content of these phases is stoichiometric to a precision of 1 to 2%, and therefore the formal cobalt oxidation state is determined solely by the sodium content. The analysis also reveals that both types of sodium ions in the structure are in off-center distorted trigonal prismatic geometry.

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I. INTRODUCTION

The structural variety and diversity of properties in the Na_xCoO_2 layered sodium cobalt oxides have made them the subject of continuing research for both chemists and physicists. Their magnetic and electronic properties are nominally tuned by changing the number of charge carriers in the CoO_2 layers through sodium intercalation or deintercalation.¹⁻³ The recent discovery of superconductivity in $\text{Na}_{0.3}\text{CoO}_2$ intercalated with water has further suggested that unconventional superconductivity and novel quantum states arising from strong electron correlations may occur in this family.⁴ The origin of superconductivity in this material is not yet fully understood.

The electronically active structural components of Na_xCoO_2 are sheets of edge sharing CoO_6 octahedra. The Co layers have a triangular lattice, and close packed triangular layers of oxygen are found both above and below the Co plane. Each oxygen in the close packed oxygen layer is bonded to three Co in the neighboring Co layer and 1-3 Na in the interleaving Na plane, depending on the Na stoichiometry. The Na_xCoO_2 electronic phase diagram shows that a paramagnetic metal is found for $0.5 < x < 0.75$, an insulator is found for $x = 0.5$, and a normal metal is found for $x < 0.5$.⁵ Critical to any interpretation of the properties of the system is knowledge of the formal charge in the CoO_2 layers. This has generally been taken to be determined by measurement of the Na concentration and the requirement of charge neutrality to yield formal Co oxidation states given by $\text{Na}_x\text{Co}^{+(4-x)}\text{O}_2$. In the range of interesting properties, $0.3 < x < 1.0$, the oxidation state of Co is then between +3.7 and +3.0. Early in the studies of the superconducting oxyhydrate, however, and also in studies of the simpler nonhydrated Na_xCoO_2 phases, the use of the Na content as a measure of the Co oxidation state was called into question. These questions have been raised primarily based on the interpretation of chemical titration data, which, in the ideal case, measures the oxidizing power of solid particles suspended in a liquid containing an indicating reagent. Precision application of this method requires excellent technique, rigorously single-phase powder samples with fine particle size, and un-

ambiguous knowledge of the chemistry of the reactions. Such methods have yielded lower Co oxidation states in these materials than are expected from the nominal compositions. Thus, titration-based analyzes have suggested that for the superconducting phase, $\text{Na}_x\text{CoO}_2 \times 1.3\text{H}_2\text{O}$, the oxidation state of cobalt is between +3.3 and +3.5, which is substantially lower than what is expected from the sodium content.^{6,7} Time dependent neutron diffraction analysis of the superconducting sample indicated that the Co oxidation state changes in time, and the maximum T_c occurs when Co is in $\sim +3.5$ oxidation state.⁸ These discrepancies have been attributed to the presence of H_3O^+ or H^+ , whose presence has not been detected directly, or to oxygen vacancies. Titration analyzes have been performed on unhydrated Na_xCoO_2 , with the conclusion that no further oxidation of Co is possible beyond Co +3.5.⁹ In the simple ternary compound, then, this means that oxygen would have to be removed from the close-packed layer under oxidizing conditions, i.e., that for $x < 0.5$ the formula of the compound is $\text{Na}_x\text{Co}^{+3.5}\text{O}_{1.75+x/2}$ and the Co oxidation state is constant at +3.5. In one instance, thermogravimetric analysis of a high x , $\text{Na}_{0.75}\text{CoO}_2$ sample, was interpreted to indicate an oxygen deficiency of ~ 0.08 , or a Co oxidation state of +3.09 when one of +3.25 is expected from the Na content.¹⁰

Here we present the results of careful neutron diffraction measurements on Na_xCoO_2 in both the high x and low x regions, designed specifically to be sensitive to the presence or absence of oxygen vacancies. The quality of the data and the model fits are excellent. No oxygen vacancies are found. Combined with the results of recent high resolution neutron diffraction measurements on $\text{Na}_{0.5}\text{CoO}_2$,¹¹ it can be concluded that the Na content is a good measure of the formal oxidation state in Na_xCoO_2 and, therefore, a measure of the charge in the CoO_2 layer in the range of interesting compositions.

II. EXPERIMENTAL

$\text{Na}_{0.74}\text{CoO}_2$ was prepared by solid-state reaction. Stoichiometric quantities of Co_3O_4 (Alfa, 99.99%) and Na_2CO_3 (Alfa, 99.9985%) were ground together and annealed at

TABLE I. Structure parameters of $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$.

Compound	Atom	Site	x	y	z	$U_{\text{iso}} \times 100$	Occ
^a $\text{Na}_{0.74}\text{CoO}_2$	Co	$2a$	0	0	0.5	0.54(5)	1
	Na(1)	$6h$	0.051(8)	0.025(4)	0.25	1.5(1)	0.071(2)
	Na(2)	$6h$	0.559(2)	0.2796(8)	0.25	1.5(1)	0.177(2)
	O	$4f$	$1/3$	$2/3$	0.09047(7)	0.76(1)	1.01(1)
^b $\text{Na}_{0.38}\text{CoO}_2$	Co	$2a$	0	0	0.5	0.72(5)	1
	Na(1)	$6h$	0.104(6)	0.052(3)	0.25	1.5(2)	0.038(2)
	Na(2)	$6h$	0.571(3)	0.285(1)	0.25	1.5(2)	0.090(2)
	O	$4f$	$1/3$	$2/3$	0.08585(5)	0.69(2)	0.99(2)

^a $\chi^2=1.51$; for $\lambda=1.5403 \text{ \AA}$: $wRp=7.59\%$; $Rp=6.34\%$; $Re=5.02\%$; for $\lambda=1.1968 \text{ \AA}$: $wRp=6.46\%$; $Rp=5.28\%$, $Re=4.28\%$

^b $\chi^2=1.38$; for $\lambda=1.5403 \text{ \AA}$: $wRp=5.95\%$; $Rp=4.99\%$; $Re=4.31\%$; for $\lambda=1.1968 \text{ \AA}$: $wRp=5.52\%$; $Rp=4.51\%$; $Re=4\%$;

800 °C for 16 h under flowing O_2 . 5% excess of Na_2CO_3 was added to balance the Na lost due to volatilization. $\text{Na}_{0.38}\text{CoO}_2$ was prepared by stirring 1 g of $\text{Na}_{0.74}\text{CoO}_2$ with 40X Br_2 dissolved in acetonitrile. After five days of stirring at room temperature, the product was washed with acetonitrile and stored under dry conditions to prevent water intercalation.

Two sets of neutron powder diffraction intensity data for each Na_xCoO_2 sample were collected using the BT-1 high-resolution powder diffractometer at the NIST Center for Neutron Research. For one data set, a Cu (311) monochromator was used to produce a neutron beam of wavelength 1.5403(1) Å. A Ge(733) monochromator, producing neutrons with wavelength 1.1968(1) Å was used to collect data in a higher 2θ range to reduce correlations between temperature factors and occupancy parameters. Collimators with horizontal divergences of 15', 20', and 7' of arc were used before and after the monochromator, and after the sample, respectively. The data were collected in two separate banks in steps of 0.05° in the 2θ range 3°–168°. Rietveld refinements of the structures were performed on the two sets of data simultaneously with the GSAS suite of programs.¹² The peak shape was described with a pseudo-Voigt function. The background was fitted with 12 terms in a linear interpolation function. The neutron scattering amplitudes used in the refinements were 0.363, 0.253, and 0.581 ($\times 10^{-12}$ cm) for Na, Co, and O, respectively.

III. RESULTS

Structural models for both $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$ have been previously reported.^{5,13} The structures both have crystal symmetry $P6_3/mmm$, differing primarily in the fractional sodium site occupancies. There are two sodium sites, both in trigonal prismatic coordination with oxygen. One prism [Na(2)] shares edges with the neighboring CoO_6 octahedra, while the other prism [Na(1)] shares faces with the neighboring CoO_6 octahedra. The Na(2) atom is found to be displaced from the center of the trigonal prism in a $(2x, x, \frac{1}{4})$ site. Previously proposed models have Na(1) on the $(0, 0, \frac{1}{4})$ site,⁵ centered in the trigonal prism, but large thermal param-

eters for this atom suggested that it might also be displaced from its position.

The structures found here are basically the same as those reported previously but are defined to better precision. The refined hexagonal lattice parameters are found to be $a=2.8375(1) \text{ \AA}$ and $c=10.8781(1) \text{ \AA}$ for $\text{Na}_{0.74}\text{CoO}_2$ and $a=2.8120(1) \text{ \AA}$ and $c=11.2289(1) \text{ \AA}$ for $\text{Na}_{0.38}\text{CoO}_2$, respectively (note: the refined cell parameter standard deviations do not include the uncertainty in the neutron wavelength). The displacements of the Na(2) atoms from the centers of the trigonal prisms are similar to what has been previously found.^{5,14} However the quality of the present data allowed consideration of whether the Na(1) position is similarly displaced. The displacements of the Na(1) atoms from the ideal positions in the center of the prism to $(2x, x, \frac{1}{4})$ positions was found to be significant in both compounds and yielded conventional magnitude thermal parameters. The displacement is more significant for $\text{Na}_{0.38}\text{CoO}_2$ with fractional displacements of 17 standard deviations from the ideal site. For $\text{Na}_{0.74}\text{CoO}_2$, the Na(1) displacements are smaller but are also significant, at 8 standard deviations. The sodium compositions for the two compounds can also be defined to high precision in the refinements, yielding $x=0.744(2)$ and 0.384(2), consistent with expectations based on the known chemistry of these materials. Finally, the quantity and quality of the data allow for simultaneous free refinement of the occupancies and thermal parameters for the oxygen atoms in the close packed layers. The fractional oxygen site occupancies are found to be 1.01(1) and 0.99(2) for $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$, respectively. Thus, within the experiment precision, the oxygen sites are found to be filled.

The models presented in Table I for the two compositions give excellent fits to the diffraction data for both wavelengths. This can be seen directly in the observed, calculated, and difference plots for the refinements, presented in Figs. 1 and 2. It can also be seen in the statistical agreement indices presented in Table I, which are $\chi^2=1.51$ and $\chi^2=1.38$ for all diffraction data for $x=0.74$ and $x=0.38$, respectively. Selected bond distances and angles are shown in Table II: the values are in close agreement with the earlier reported data.⁵

The present work finds both sodium sites, Na(1) and Na(2), to have a distorted trigonal prismatic configuration.

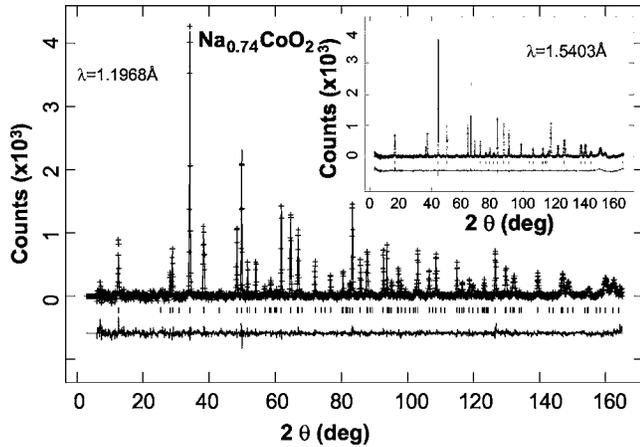


FIG. 1. Observed (crosses) and calculated (solid line) neutron diffraction intensities for $\text{Na}_{0.74}\text{CoO}_2$. Vertical bars show the Bragg peak positions. The data for $\lambda = 1.5403 \text{ \AA}$ are shown in the inset.

Figure 3 presents, as an example, the crystal structure of $\text{Na}_{0.74}\text{CoO}_2$. The off-center positions result in two types of Na-O bond lengths within the prisms. The displacements of Na(1) and Na(2) in $\text{Na}_{0.38}\text{CoO}_2$ results in virtually identical bonding environments (left side of Fig. 3). The figure also shows the coordination environments in $\text{Na}_{0.74}\text{CoO}_2$, where the Na(2) site is quite similar in geometry to what is found in $x=0.38$, but the Na(1) coordination is much less distorted. The fact that the Na(1) site is less displaced in the compound with a higher sodium filling in the plane suggests that ion repulsion within the layer forces it to become on center: the implication is that the naturally occurring positions within the prism, without the influence of in-plane Na-Na repulsion, are off center. The fractional occupancies of the oxygen sites indicate that there is no oxygen deficiency at an uncertainty of 1 to 2%. This result demonstrates that the sodium content is an accurate measure of the formal oxidation state of Co in Na_xCoO_2 . That is +3.26 and +3.62 for $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$, respectively. As a result, the level of electron doping is well defined by the sodium content. The possibility of oxygen loss during the Na deintercalation process is ex-

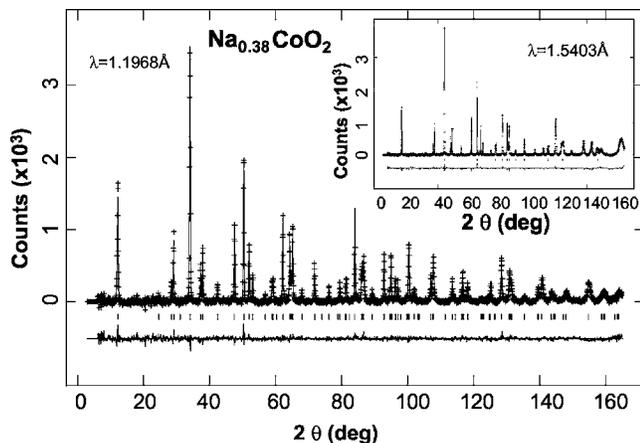


FIG. 2. Observed (crosses) and calculated (solid line) neutron diffraction intensities for $\text{Na}_{0.38}\text{CoO}_2$. Vertical bars show the Bragg peak positions. The data for $\lambda = 1.5403 \text{ \AA}$ are shown in the inset.

TABLE II. Selected bond distances and angles for $\text{Na}_{0.74}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$.

Bond distance (Å)/angle (deg)	$\text{Na}_{0.74}\text{CoO}_2$	$\text{Na}_{0.38}\text{CoO}_2$
Co-O $\times 6$	1.9111(4)	1.8882(3)
Na(1)-O $\times 4$	2.347(6)	2.389(2)
$\times 2$	2.47(1)	2.616(5)
Na(2)-O $\times 4$	2.309(1)	2.384(4)
$\times 2$	2.575(3)	2.63(1)
O-Co-O	84.13(3)	83.74(2)

cluded by the present results on $\text{Na}_{0.38}\text{CoO}_2$. The only prospect for oxygen deficiency in the superconducting phase would, therefore, have to be oxygen vacancies forming during the hydration process. This, in fact, has been previously reported.⁸

IV. CONCLUSIONS

High precision powder diffraction analysis of the structures of $\text{Na}_{0.75}\text{CoO}_2$ and $\text{Na}_{0.38}\text{CoO}_2$ indicates that there is no oxygen nonstoichiometry either in the thermodynamically obtained composition $\text{Na}_{0.75}\text{CoO}_2$ or in the deintercalated product $\text{Na}_{0.38}\text{CoO}_2$. A previous high resolution diffraction study of $\text{Na}_{0.5}\text{CoO}_2$ also found no oxygen deficiency. It can therefore be concluded that in the range of compositions that displaying the interesting electronic and magnetic properties in the Na_xCoO_2 system the formal charge on Co is given only by the sodium content. Conclusions about the presence or absence of H^+ , H_3O^+ , or oxygen vacancies in the superconducting superhydrate cannot be drawn from the current work. However, if oxygen vacancies are indeed present in the superconducting material the fact that they are not present in the $\text{Na}_{0.38}\text{CoO}_2$ host material implies they would

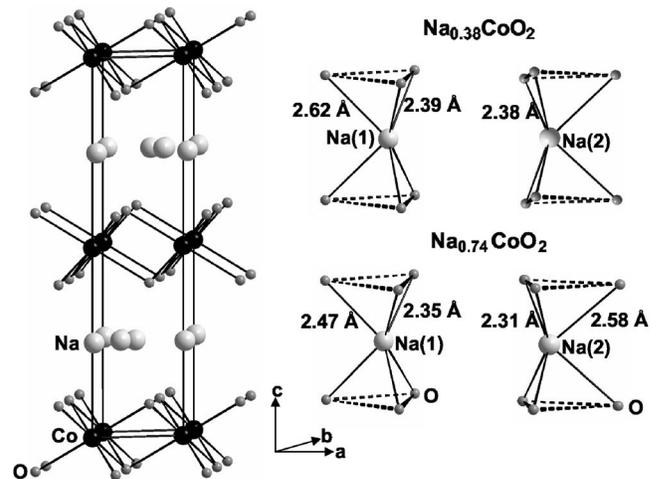


FIG. 3. The crystal structure of $\text{Na}_{0.74}\text{CoO}_2$. Edge-shared CoO_6 octahedra are separated by layers of sodium ions. The two sodium sites in this structure are distorted triangular pyramids, represented on the right.

have to be formed during the hydration process.⁸ The refinements of the two structures also revealed that the two sodium sites have distorted trigonal prismatic configurations. The finding that off-center positions of the Na are preferred in this system for both types of Na sites, those that share edges with the CoO₆ octahedra and those that share faces, suggests that these are energetically preferred positions for Na within

the layer. Why this is the case is an interesting crystal-chemical question that remains to be answered.

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