Crystal structure of the sodium cobaltate deuterate superconductor $Na_xCoO_2 \cdot 4xD_2O$ ($x \approx \frac{1}{3}$)

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Neutron and x-ray powder diffraction have been used to investigate the crystal structures of a sample of the newly-discovered superconducting sodium cobaltate deuterate compound with composition $Na_{0.31(3)}CoO_2 \cdot 1.25(2)D_2O$ and its anhydrous parent compound $Na_{0.61(1)}CoO_2$. The anhydrous parent compound $Na_{0.61(1)}CoO_2$ has two partially occupied Na sites sandwiched, in the same plane, between CoO_2 layers. When Na is removed to make the superconducting composition, the Na site that experiences the strongest Na–Co repulsion is emptied while the occupancy of the other Na site is reduced to about one third. The deuterate superconducting compound is formed by coordinating four D_2O molecules (two above and two below) to each remaining Na ion in a way that gives Na–O distances nearly equal to those in the parent compound. One deuteron of the D_2O molecule is hydrogen bonded to an oxygen atom in the CoO_2 plane and the oxygen atom and the second deuteron of each D_2O molecule lie approximately in a plane between the Na layer and the CoO_2 layers. This coordination of Na by four D_2O molecules leads in a straightforward way to ordering of the Na ions and D_2O molecules consistent with the observation of additional shorter-range scattering features in the diffraction data. The sample studied here, which has $T_c = 4.5$ K, has a refined composition of $Na_{0.31(3)}CoO_2 \cdot 1.25(2)D_2O$, in agreement with the expected 1:4 ratio of Na to D_2O. These results show that the optimal superconducting composition should be viewed as a specific hydrated compound, not a solid solution of Na and D_2O (H_2O) in $Na_xCoO_2 \cdot D_2O$. The hydrated superconducting compound may be stable over a limited range of Na and D_2O concentration, but studies of T_c and other physical properties vs Na or D_2O composition should be viewed with caution until it is verified that the compound remains in the same phase over the composition range of the study.

INTRODUCTION

The recent discovery of superconductivity at 4.5 K in hydrated sodium cobaltate with a reported composition of $Na_{0.3}CoO_2 \cdot 1.4H_2O$ (Ref. 1) has generated renewed interest in the compositional chemistry and crystal structure of these materials. In recent years, the related anhydrous compound, Na_xCoO_2, has been studied because of its interesting transport properties. Wang *et al.*[2] have argued that spin entropy arising from the two-dimensional triangular Co lattice is the explanation for an enhanced thermopower.[3] More recently, the same authors have reported an anomalous Hall effect for Na_xCoO_2.[4] They observe that Na_xCoO_2 exhibits "strange metal physics as observed in the cuprates." Na_xCoO_2 is made superconducting by removing part of the Na, which changes the oxidation state of Co, and intercalating water to dramatically increase the separation between the CoO_2 layers. Bulk superconductivity with $T_c > 2$ K has been reported to exist over a very narrow range of Na compositions, approximately $1/4 \leq x \leq 1/3$, in the hydrated compound $Na_xCoO_2 \cdot 1.3H_2O$ with the maximum T_c (4.5 K) at $x \approx 0.3$.[5] This domelike behavior of T_c is reminiscent of the layered cuprates, suggesting that this new layered compound may be the first noncopper example of the same physics. The importance of the two-dimensional nature of the structure is emphasized by the fact that a lower hydrate, $Na_{0.3}CoO_2 \cdot 0.6H_2O$, with the same Co formal oxidation state but substantially less separation between the CoO_2 layers is not superconducting.[6]

Prior to the recent interest in transport properties and superconductivity, compounds of this family were studied because of their fast-ion conducting properties.[7] The Na ions are in two partially occupied crystallographic sites, both of which lie in a plane between layers of edge-sharing CoO_6 octahedra. The ability to change the Na (or other cation) content and to intercalate water has been investigated for isostructural compounds such as $Na_{2/3}(Co_xNi_{1/3-x}Mn_{2/3})O_2$,[8] and $Li_{0.12}K_{0.35}MnO_{2.14} \cdot 0.45H_2O$.[9] However, the structural details of the water intercalation and, in particular, the crystal structure of $Na_xCoO_2 \cdot yH_2O$, have never been reported. Clearly, an understanding of the crystal structure is fundamental to interpreting the physical behavior.

In this paper, we report the crystal structures of the starting anhydrous compound, $Na_{0.61}CoO_2$ and the deuterated superconducting composition, $Na_{0.31}CoO_2 \cdot 1.25D_2O$. We show that, when the Na concentration is reduced, Na is selectively removed from one of the two inequivalent Na sites. Then, after D_2O is incorporated, the D_2O molecules occupy sites between the CoO_2 layers and the Na ions in such a way that the coordination of Na to the oxygen ions of the D_2O molecules is similar to its previous coordination to oxygen ions in the CoO_2 layers in $Na_{0.61}CoO_2$, except that the D_2O to Na ratio is four, resulting in two D_2O molecules above the Na ion and two below. One deuteron of each D_2O molecule is hydrogen bonded to an oxygen atom in the CoO_2 layer. The constraint of minimizing Na–D and D–D repulsions leads in a straightforward way to two-dimensional ordering of Na ions and D_2O molecules. In the supercell structure, the second deuteron of each D_2O molecule is hydrogen bonded to the oxygen atom of a neighboring D_2O molecule to form hydrogen bonded zigzag D–O···D–O···D–O··· chains. The

diffraction data are consistent with this ordering in the plane and also show that ordering along the c axis, with a shorter length scale, is present. A possible explanation is that both Na ions and D_2O molecules are ordered in the plane, but D_2O ordering has a much shorter coherence length than Na ordering along the c axis. The refined composition of the sample studied here, $Na_{0.31(3)}CoO_2 \cdot 1.25(2)D_2O$ manifests the ideal 1:4 ratio of Na to D_2O. The findings reported here shed important new light on studies of T_c vs composition[5] which show a domelike behavior of T_c and a recent theory[10] that predicts that the highest T_c is achieved at a composition between two ordered structures, where Co charge ordering is disrupted. This work shows that the maximum T_c is achieved in an ordered structure, but with a composition slightly off the ideal ordering composition of $Na_{1/3}$.

SYNTHESIS

A powder sample of the anhydrous compound with composition $Na_{0.61(1)}CoO_2$ was made by repeated heating and grinding of a mixture of Na_2CO_3 and Co_3O_4 in air at $850\,°C$. An initial powder stoichiometry of $Na_{0.7}CoO_2$ resulted in a sample of composition $Na_{0.61(1)}CoO_2$ due to a slight loss of Na during the heating cycles. (All compositions stated in the paper are those determined by Rietveld refinement using neutron powder diffraction data.) The chemical oxidative deintercalation of Na from this material is generally done using Br_2 (Ref. 11) or I_2 (Ref. 12) in acetonitrile. For the neutron diffraction experiments, a fully deuterated sample was desired in order to avoid the large neutron incoherent scattering from hydrogen, which adds background to the diffraction data. In order to eliminate any possible hydrogen incorporation during the oxidative deintercalation, either from the acetonitrile or residual H_2O in the acetonitrile, we used Br_2 in D_2O as the oxidizing medium. About 10 wt. % of $Na_{0.61}CoO_2$ powder in D_2O with a 100% to 200% excess of Br_2 was shaken overnight in an air-tight pyrex tube. The resulting powder was then separated by either filtration or centrifuging from the Br_2 solution with as little exposure to the atmosphere as possible. After washing with D_2O to remove excess Br_2 and NaBr the resulting material was kept in a container with 100% relative humidity of D_2O.

This "as-oxidized" deuterated material contained free D_2O, as evidenced by the appearance of peaks from ice in a neutron powder diffraction pattern taken at low temperature. In order to remove only the free D_2O and none of the lattice D_2O, knowledge of the vapor pressure of D_2O in equilibrium with the higher deuterate phase is required. Approximately 2 g of the material was placed in a vacuum system and pumped to remove air. The D_2O pressure over the hydrate was measured using a capacitance manometer as the D_2O was volumetrically removed by cooling a calibrated glass bulb attached to the vacuum system to liquid nitrogen temperature. To allow the sample to come to equilibrium at each partial pressure of D_2O, this cryopumping was done in small steps—typically a few minutes of pumping followed by equilibration times of up to several hours. All measurements were done at $23.0\pm0.2\,°C$. Figure 1 shows the D_2O pressure as a function of removed D_2O. The long plateau at
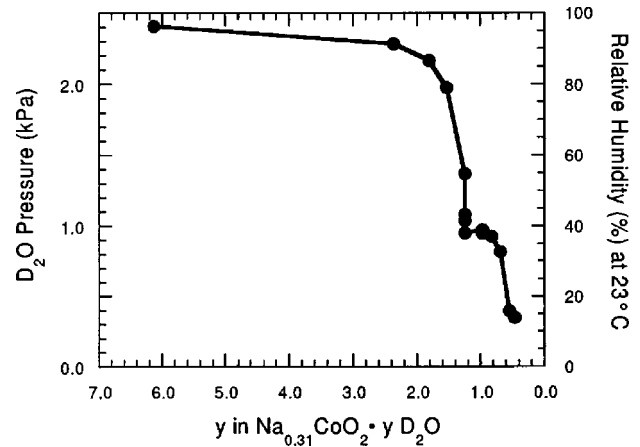

FIG. 1. Pressure of D_2O as a function of the amount of D_2O removed by cryopumping a sample of $Na_{0.31(3)}CoO_2 \cdot yD_2O$ at room temperature ($\sim 23\,°C$), where the starting sample contained both lattice D_2O and excess liquid D_2O. Using the sample mass and the results from neutron powder diffraction for the amount of D_2O in a sample equilibrated at 1.2 kPa, the amount of removed D_2O has been expressed in terms of D_2O molecules per formula unit. The plateau at $P\approx 1$ kPa is the coexistence region for both stable deuterates ($y\approx 4/3,2/3$).

2.3–2.4 kPa pressure indicates that the sample is a mixture of free D_2O and the higher deuterate phase (plus, perhaps, some D_2O adsorbed on the walls of the vacuum system). In this particular experiment, ~ 1.6 cc of free D_2O was removed before reaching the point where little additional free D_2O remained and the D_2O pressure dropped sharply with further pumping. The plateau at about 1 kPa indicates the transition to a two-phase deuterate mixture; i.e., a mixture of the higher deuterate phase and the lower deuterate phase reported to have the composition $Na_{0.3}CoO_2 \cdot 0.6D_2O$.[6] A single phase of the higher deuterate with a minimum amount of free D_2O can be made by equilibrating at a D_2O pressure just above 1 kPa. The sample used for the diffraction measurements was equilibrated at 1.2 kPa D_2O pressure overnight.

For neutron diffraction, the sample was loaded into an indium-sealed vanadium can in a helium-filled glove bag with only about a ~ 45 s exposure to the dry helium atmosphere during loading. Once the sample is sealed in the can with helium, there is not enough free volume to allow a significant change in the D_2O content of the sample. The diffraction pattern showed only the higher deuterate phase; none of the lower deuterate phase[6] (which is easily identified by its shorter c axis) was present, indicating no loss of D_2O during sample loading. Additionally, no D_2O ice peaks were seen at low temperature, indicating that no free D_2O existed in this sample. To minimize handling of the sample, AC susceptibility measurements were not done until after the neutron diffraction measurements (described below). The AC susceptibility data are shown in Fig. 2. A superconducting transition with an onset at 4.5 K is seen. This equals the highest onset temperature seen in this material, confirming that the sample is at an optimal superconducting composition. The width of the transition is similar to that seen for
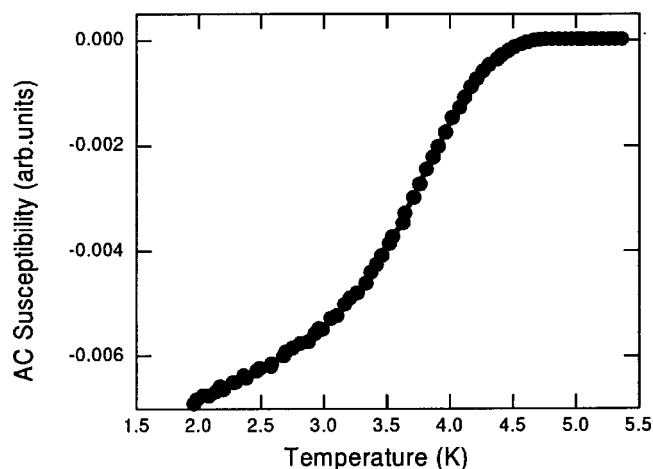
FIG. 2. AC susceptibility vs temperature for the sample of $Na_{0.31}CoO_2 \cdot 1.25D_2O$ used for neutron and x-ray diffraction measurements.

optimally doped samples in other studies,[5] confirming the quality of the sample. This post-diffraction measurement of T_c confirms that the sample remained at the superconducting composition during the neutron diffraction measurements.

NEUTRON AND SYNCHROTRON X-RAY POWDER DIFFRACTION

Neutron powder diffraction data were collected on the Special Environment Powder Diffractometer[13] at the Intense Pulsed Neutron Source for powder samples of $Na_{0.61}CoO_2$ and superconducting $Na_{0.31}CoO_2 \cdot 1.25D_2O$. Data were collected at various temperatures between room temperature (~ 295 K) and 12 K with the samples sealed in vanadium cans along with helium exchange gas and cooled using a Displex closed-cycle helium refrigerator.

For the superconducting sample, following the neutron diffraction experiment, high-resolution synchrotron x-ray diffraction data were collected at room temperature at beam line 5-BMC (DND-CAT) at the Advanced Photon Source (Argonne National Laboratory). The sample was sealed in a 1mm dia. glass capillary to prevent D_2O loss. The high-resolution x-ray data were used to look for any subtle distortions of the fundamental hexagonal unit cell and to further investigate additional diffraction peaks from shorter-range ordering (to be discussed later).

RIETVELD STRUCTURE REFINEMENTS

The neutron powder diffraction data for both samples were analyzed by the Rietveld method using the previously reported[1] $P6_3/mmc$ hexagonal space group. Rietveld refinement profiles are shown in Fig. 3. This structural model correctly indexes all of the sharp diffraction peaks for both compositions. For the higher deuterate superconducting composition, additional scattering resulting from ordering on shorter length scales was also seen. The most prominent additional scattering is a broad, modulated feature extending from about 2.8–2.5 Å. Somewhat sharper features of the
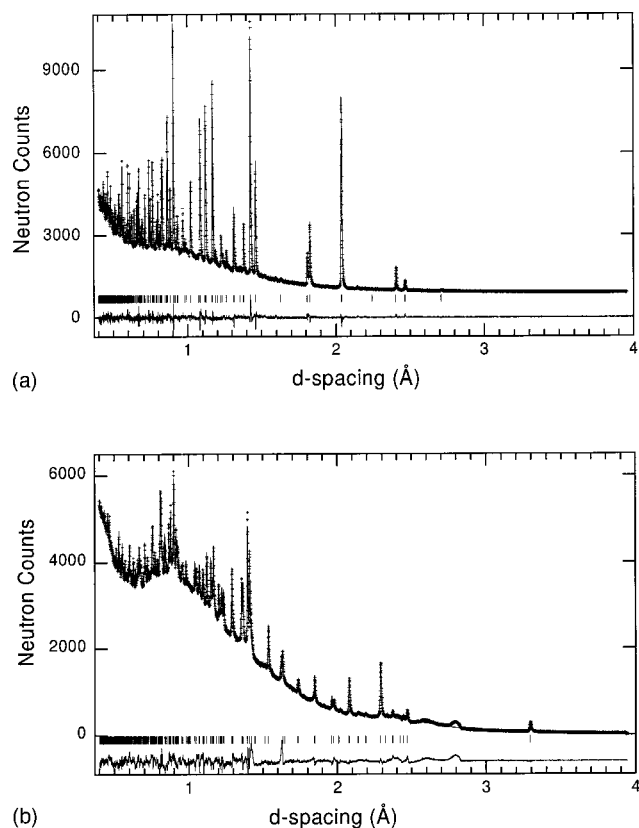

FIG. 3. Rietveld refinement profiles for (a) $Na_{0.61}CoO_2$ at 12 K and (b) $Na_{0.31}CoO_2 \cdot 1.25D_2O$ at 12 K. All data are refined in the same hexagonal space group $P6_3/mmc$. Crosses are the raw time-of-flight neutron powder diffraction data. The solid line is the calculated diffraction pattern. Tick marks indicate the positions of allowed reflections. A difference curve (observed minus calculated) is plotted at the bottom. Additional features in the pattern for $Na_{0.31}CoO_2 \cdot 1.25D_2O$, e.g., the broad scattering at 2.5–2.8 Å and the sharper features seen in the difference plot at about 1.4 Å and 1.6 Å, are from supercell ordering on shorter length scales (discussed in the text).

additional scattering can most clearly be seen in the difference plot of Fig. 3(b). These broadened supercell peaks were also seen in the high-resolution x-ray diffraction data, where the difference in peak widths, compared to peaks of the fundamental hexagonal cell, was much more obvious. The interpretation of this supercell scattering will be discussed later.

The refined structural parameters and selected bond lengths at 295 K and 12 K for $Na_{0.61}CoO_2$ are given in Table I. The structure is shown in Fig. 4. The CoO_2 layers are formed from edge-sharing CoO_6 octahedra, where the Co–O bond length is 1.908 Å (at room temperature). The oxygen atoms lie in two planes, above and below the plane of Co atoms. Na ions lie in two partially occupied sites in a plane halfway between the CoO_2 layers. The two Na sites differ in their coordination to the oxygen atoms in the CoO_2 layers, as shown in Fig. 5. The Na1 site is coordinated to six oxygen atoms that are bonded to six different Co atoms (three above and three below). The Na2 site is also coordinated to six oxygen atoms (three above and three below), but the sets of three oxygen atoms (above and below Na) are bonded to the

TABLE I. Refined structural parameters for $Na_{0.61}CoO_2$ based on Rietveld refinement using neutron powder diffraction data for various temperatures. The structure is refined in hexagonal space group $P6_3/mmc$ with Co at $2a(0,0,0)$, O at $4f(1/3,2/3,z)$, Na1 at $6h(2x,x,1/4)$, and Na2 at $2b(0,0,1/4)$. The Na1 ion position is refined at the displaced $6h$ site, rather than its average, high-symmetry site $2d(1/3,2/3,3/4)$, in order to better model the static and dynamic displacements seen for this ion. Site occupancies are expressed in terms of the chemical formula unit to simplify understanding the refined composition.

Temperature	12 K	295 K
a, Å	2.83176(3)	2.83287(2)
c, Å	10.8431(2)	10.8969(1)
z(O)	0.09057(7)	0.09024(5)
n(Na1)	0.438(6)	0.396(6)
$2x$(Na1)	0.577(2)	0.574(2)
n(Na2)	0.171(5)	0.170(5)
$U_{11}=U_{22}=2U_{12}$(Co), Å^2	0.0020(3)	0.0030(3)
U_{33}(Co), Å^2	0.0065(7)	0.0072(6)
$U_{11}=U_{22}=2U_{12}$(O), Å^2	0.0043(2)	0.0061(1)
U_{33}(O), Å^2	0.0084(2)	0.0105(2)
U(Na1), Å^2	0.005(1)	0.008(1)
U(Na2), Å^2	0.004(1)	0.015(2)
Co–O ($x6$), Å	1.9072(4)	1.9084(3)
Na1–O, Å $x4$	2.313(1)	2.321(1)
$x2$	2.535(3)	2.550(3)
Na2–O ($x6$), Å	2.3794(5)	2.3887(4)

same Co atoms. The average Na–O bond lengths are identical (by symmetry) for the two Na sites (2.379 Å at 12 K). It has previously been proposed[14] that slightly weaker bonding of the Na2 site results from Na–Co Coulomb repulsion, which is greater for this site when both first- and second-nearest neighbor Na–Co repulsions are considered. This leads to a smaller occupancy for the Na2 site compared to the Na1 site. The Na ions show displacements from their ideal sites at both room temperature and low temperature. This probably results from repulsion of randomly located neighboring Na ions, locally violating the hexagonal symmetry. In Rietveld refinement, such displacements can be modeled with anisotropic temperature factors or by assigning the Na ions to displaced, partially occupied sites. The latter model has been used for the Na1 site in the refinements reported in Table I. For the Na2 site, the displacement was not large enough to statistically justify a displaced-site model. Because this detail of the structural model does not give any additional insight into the compound, all figures show only the average, high-symmetry, Na sites and average Na–O bond lengths (i.e., bond lengths to the ideal, high-symmetry site). The tables, however, list the Na1–O bond lengths resulting from the use of a displaced-site model for Na1.

Rietveld refinement of the $Na_{0.31}CoO_2 \cdot 1.25D_2O$ structure was approached by first using the same model as for the anhydrous compound, with different lattice parameters, and not including any D_2O in the model. These refinements im-
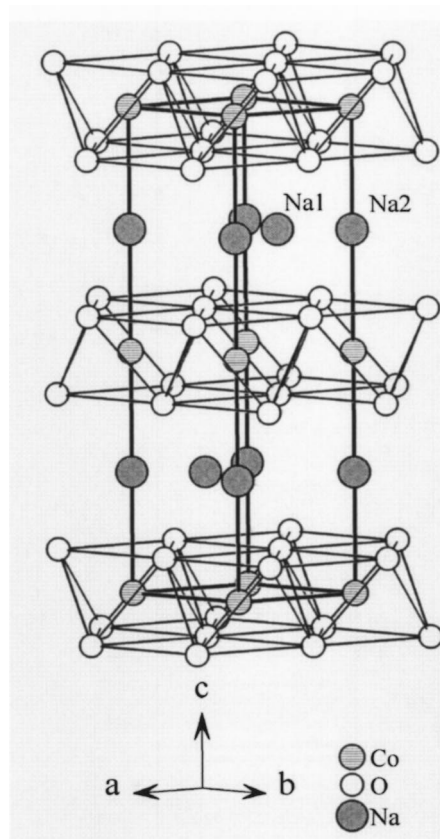

FIG. 4. Crystal structure of $Na_{0.61}CoO_2$ (hexagonal space group $P6_3/mmc$). Co atoms are octahedrally coordinated to six oxygen atoms. The CoO_6 octahedra share edges to form layers. Na ions are in two partially occupied sites, Na1 and Na2, that cannot be simultaneously occupied in the same region of the cell because of impossibly close Na1–Na2 distances. Average Na sites are shown, ignoring small static displacements for Na1 used in the refinement model (see Table I).

mediately showed that when Na is removed, it comes selectively from the more weakly bonded Na2 site, leaving that site empty within the accuracy of the refinement. In the final refinements, the occupancy of the Na2 site tended to go slightly negative ($\sim$ one esd) so it was set to zero. To achieve the $x\approx0.3$ composition, part of the Na is also removed from the Na1 site (which was initially only partially occupied). In the deuterate compound, the displacement of the Na1 ion off its ideal site is even larger than for the anhydrous compound. Thus, in the refinement model, Na1 has been assigned to a partially occupied $[6h(2x,x,1/4)]$ displaced site.

To locate the D_2O molecules, Fourier difference maps were plotted. These maps showed scattering density suggesting that the oxygen atoms of the D_2O molecules were located in layers between the CoO_2 layers and Na layers. Additionally, the maps showed two possible deuterium sites: one approximately in the same plane as the oxygen atoms and one closer to the CoO_2 layers. Fourier maps from room-temperature and low-temperature data were not dramatically different. Rietveld refinements were then attempted by adding D_2O molecules in general positions $[24l(x,y,z)]$ with
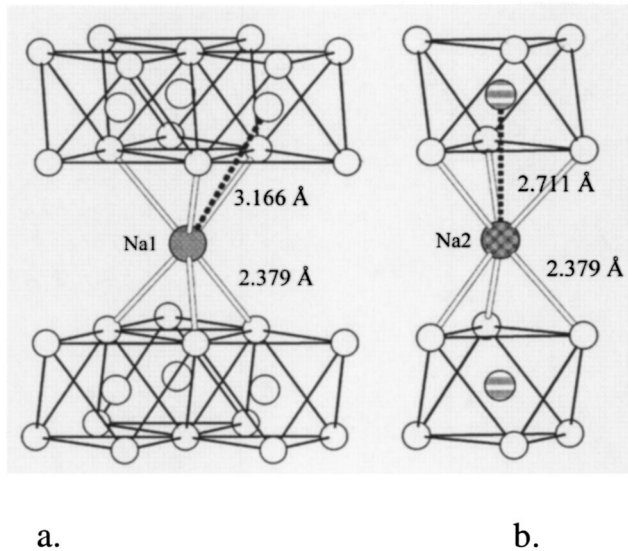
a.   **b.**

FIG. 5. Coordination of the Na1 and Na2 sites in $Na_{0.61}CoO_2$ to nearby oxygen atoms in the CoO_2 layers. Na1 is coordinated to six oxygen atoms (three above and three below), which are coordinated to six different Co atoms. Na2 is also coordinated to six oxygen atoms, but these oxygen atoms are associated with two Co atoms (one directly above and one directly below the Na ion). The average Na–O bond lengths (2.379 Å at 12 K) are the same for the two Na sites, but the Na–Co distances are significantly different. Atom symbols are the same as for Fig. 4. Note that the Na1–O bond length shown here is the average bond length, i.e., the bond length to the average Na1 site, rather than to the displaced site used in the refinement (Table I).

rigid-body constraints being used to maintain the expected molecule geometry; i.e., a D–O distance of 0.99 Å and a D–O–D angle of 109°. This constraint is thought to be justified based on the configurations seen for water molecules in a wide range of hydrated compounds and ices.[15] In this model, the refinement gives the best-fit position for the oxygen atom of the D_2O molecule and the orientation of the molecule. The resulting refined structural parameters and selected bond lengths for the deuterate superconducting compound are given in Table II. This refinement model gives a composition of $Na_{0.31(3)}CoO_2 \cdot 1.25(2)D_2O$ (based on the 12 K data where correlations between temperature factors and site occupancies are the smallest). The refined 1:4 ratio of Na to D_2O (within one esd) suggests that the synthesis method used here, including the careful adjustment of the D_2O content to the conditions for the most stable phase, has produced a compound with four D_2O molecules coordinated to each Na ion. While sixfold coordination is common for Na ions, fourfold coordination is observed in many oxides and hydrated compounds, including Na_2O.[16] The refined average Na–O distance (2.31 Å) is also consistent with that expected for a four-coordinated Na hydrate[16,17] and is remarkably similar to the Na–O distance for Na ions in water (2.4 Å), where the average coordination is 4.9.[18] (Note that when static displacement of the Na ions is considered, the resulting inequivalent Na–O distances vary from 2.18 to 2.42 Å.) The refined composition also falls within the range of values re-

TABLE II. Refined structural parameters for $Na_{0.31}CoO_2 \cdot 1.25D_2O$ based on Rietveld refinement using neutron powder diffraction data for various temperatures. The structure is refined in hexagonal space group $P6_3/mmc$ with Co at $2a(0,0,0)$, O at $4f(1/3,2/3,z)$ and Na1 at $6h(2x,x,1/4)$. The Na1 ion position is refined at the displaced $6h$ site, rather than its average, high-symmetry site $2d(1/3,2/3,3/4)$, in order to better model the static and dynamic displacements seen for this ion.. The D_2O molecule, consisting of O_w, D1, and D1 all in general positions $24l(x,y,z)$, is refined using rigid body constraints with D–O distances of 0.99 Å and a D–O–D angle of 109°. Site occupancies are expressed in terms of the chemical formula unit to simplify understanding the refined composition.

Temperature, K	12	295
a, Å	2.81693(5)	2.82166(5)
c, Å	19.6449(6)	19.7681(6)
$z(O)$	0.0473(1)	0.0469(1)
$n(Na1)$	0.31(3)	0.35(3)
$2x(Na1)$	0.52(2)	0.525(5)
$U(Co)$, Å^2	0.0001(6)	0.0040(6)
$U_{11}=U_{22}=2U_{12}(O)$, Å^2	0.0027(2)	0.0046(2)
$U_{33}(O)$, Å^2	0.0146(7)	0.0226(8)
$x(O_w)$	−0.260(6)	−0.263(4)
$y(O_w)$	−0.091(7)	−0.073(9)
$z(O_w)$	0.1750(6)	0.1706(2)
$x(D1)$	−0.479(6)	−0.421(3)
$y(D1)$	−0.204(10)	−0.159(10)
$z(D1)$	0.1321(3)	0.1240(3)
$x(D2)$	−0.098(4)	−0.112(7)
$y(D2)$	0.312(6)	0.325(9)
$z(D2)$	0.1819(5)	0.1801(3)
$n(D_2O)$	1.25(2)	1.43(2)
$U_{11}(O_w)=U_{11}(D1)=U_{11}(D2)$	0.080(5)	0.105(6)
$U_{22}(O_w)=U_{22}(D1)=U_{22}(D2)$	0.12(1)	0.24(2)
$U_{33}(O_w)=U_{33}(D1)=U_{33}(D2)$	0.012(2)	0.019(2)
$U_{12}(O_w)=U_{12}(D1)=U_{12}(D2)$	−0.08(6)	0.10(1)
$U_{13}(O_w)=U_{13}(D1)=U_{13}(D2)$	−0.027(3)	−0.031(3)
$U_{23}(O_w)=U_{23}(D1)=U_{23}(D2)$	−0.019(4)	−0.065(6)
$U(Na1)$	0.014(4)	0.018(5)
Co–O $(x6)$, Å	1.8727(10)	1.8744(9)

ported for the composition of the optimized superconducting compound.[1,5,6]

STRUCTURE MODEL FOR THE DEUTERATE PHASE

Refinement of this structural model in the fundamental hexagonal unit cell leads to partially occupied symmetry-equivalent sites for D_2O that cannot be simultaneously occupied in the actual structure because of impossibly close O–O distances, incorrect orientations of D_2O with respect to Na (i.e., orientations in which D, rather than O, is oriented toward the Na ion), and energetically unfavorable D–D repulsions. A plausible picture for the actual structure can be readily constructed by considering logical rules for chemical bonding and coordination. All symmetry-equivalent D_2O
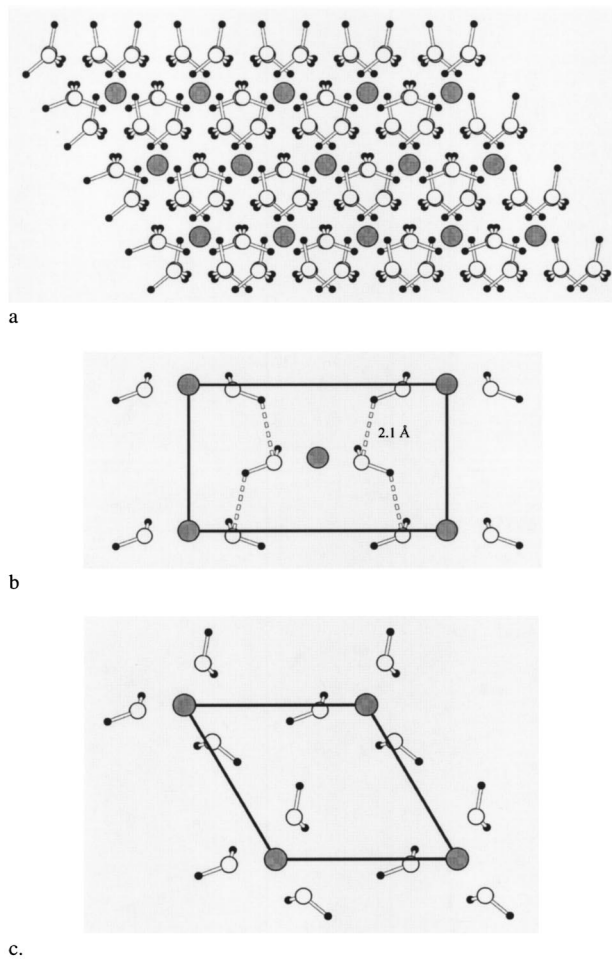
a

b

c.

FIG. 6. (a) View of one layer of Na ions and D_2O molecules in the structure of $Na_{0.31}CoO_2 \cdot 1.25D_2O$ showing all symmetry-equivalent sites, as determined from Rietveld refinement using neutron powder diffraction data. Note that all symmetry-equivalent oxygen atoms are at the same z coordinate even though the structure-drawing program shows one above the other for overlapping pairs. Shown at (b) and (c) are two two-dimensional ordered structures that result in a straightforward by applying logical rules about bonding and coordination (discussed in the text). The supercell at (b) has an ideal composition of $Na_{1/3}CoO_2 \cdot (4/3)D_2O$, with fourfold coordination of Na by D_2O, that agrees with the 1:4 Na to D_2O ratio from the Rietveld structure refinement. It can be expressed as a rectangular supercell of dimensions $3a \times \sqrt{3}a$. Hydrogen bonding in the plane links neighboring D_2O molecules to form zigzag $D–O\cdots D–O\cdots D–O\cdots$ chains, as shown by the dotted lines. The supercell at (c) has an ideal composition of $Na_{1/4}CoO_2 \cdot (3/2)D_2O$ with sixfold coordination of Na by D_2O. It can be expressed as a hexagonal supercell of dimensions $2a \times 2a$. Atom symbols are the same as for Fig. 4.

molecules have the same coordination to oxygen atoms in the CoO_2 plane. Hence, the actual structure can most easily be visualized by considering only one layer of D_2O molecules and the associated Na ions. Figure 6(a) shows all symmetry-equivalent Na and D_2O sites in one of these layers. If all such sites were occupied (including the D_2O layers above and below Na), the composition would be

$NaCoO_2 \cdot 12D_2O$. However, it is straightforward to see that all of these sites cannot be simultaneously occupied. Three bonding/coordination rules can be applied to construct plausible structures from Fig. 6(a). First, to minimize D–Na repulsion, D_2O molecules strongly prefer to be oriented with the deuteron "pointing" away from, not toward, an occupied Na site. Second, impossibly close oxygen–oxygen distances cannot occur. Third, each Na ion should be coordinated by four D_2O molecules (two above and two below) in agreement with the refined composition and consistent with known Na oxide and hydrate compounds.[16,17]

The application of these rules leads in a straightforward way to the ordered structure shown in Fig. 6(b). [The interested reader can sequentially mark Na and D_2O sites in Fig. 6(a) following the three rules above and see how this solution is obtained.] Both the Na ions and the D_2O molecules are ordered into a two-dimensional supercell. This structure has 1/3 of the Na sites occupied with four oxygen atoms (two above and two below) coordinated to each Na ion, giving an ideal composition of $Na_{1/3}CoO_2 \cdot (4/3)D_2O$. The D_2O molecules are arranged in a way that hydrogen bonds can form between neighboring molecules in the plane to give zigzag $D–O\cdots D–O\cdots D–O\cdots$ chains, as shown in Fig. 6(b). In the basal plane, this supercell is rectangular with dimensions $3a \times \sqrt{3}a$. Note that there are three equivalent choices for the orientation of D_2O molecules around each Na ion, leading to three equivalent directions for these chains. One would not expect the orthorhombic supercell to have lattice parameters that so accurately match the fundamental hexagonal cell unless the three equivalent choices for forming ordered layers occur with equal populations. Thus, if there is ordering (i.e., translational symmetry of a particular stacking sequence) along the c axis, the c axis must also be tripled. Hence, the smallest supercell that can manifest the Na and D_2O ordering while preserving the hexagonal symmetry of the fundamental cell is orthorhombic with dimensions $3a \times \sqrt{3}a \times 3c$.

This orthorhombic $3a \times \sqrt{3}a \times 3c$ supercell can describe all of the major features of the scattering from shorter-range ordering seen in neutron and x-ray powder diffraction data, as shown in Fig. 7. The broad scattering feature extending from ~ 2.8 to 2.5 Å in the neutron diffraction data can be explained equivalently as a $(30l)$ rod of scattering with its intensity strongly modulated along l or as scattering from a series of $(30l)$ peaks [i.e., (300), (301), (302), (303), etc.] whose peak broadening increases with l, causing them to overlap [Fig. 7(a)]. Maxima in the intensity are observed around the (303) and (309) peaks. The scattering from this $30l$ zone is characteristic of short-range ordering in which the coherence length along the c axis is shorter than in the basal plane. Since this scattering feature is observed much more strongly in neutron diffraction than in x-ray diffraction, one might conclude that it comes from short-range ordering of D_2O molecules (because D has a comparatively large scattering cross section for neutrons). In the x-ray diffraction data, the (30.12) peak in this series, seen at 2.45 Å, is stronger than for neutron diffraction and is resolved from the nearby peaks from the fundamental hexagonal cell by the high resolution [Fig. 7(b)]. The width of this supercell peak defines a coherence length of about 500 Å, which is longer
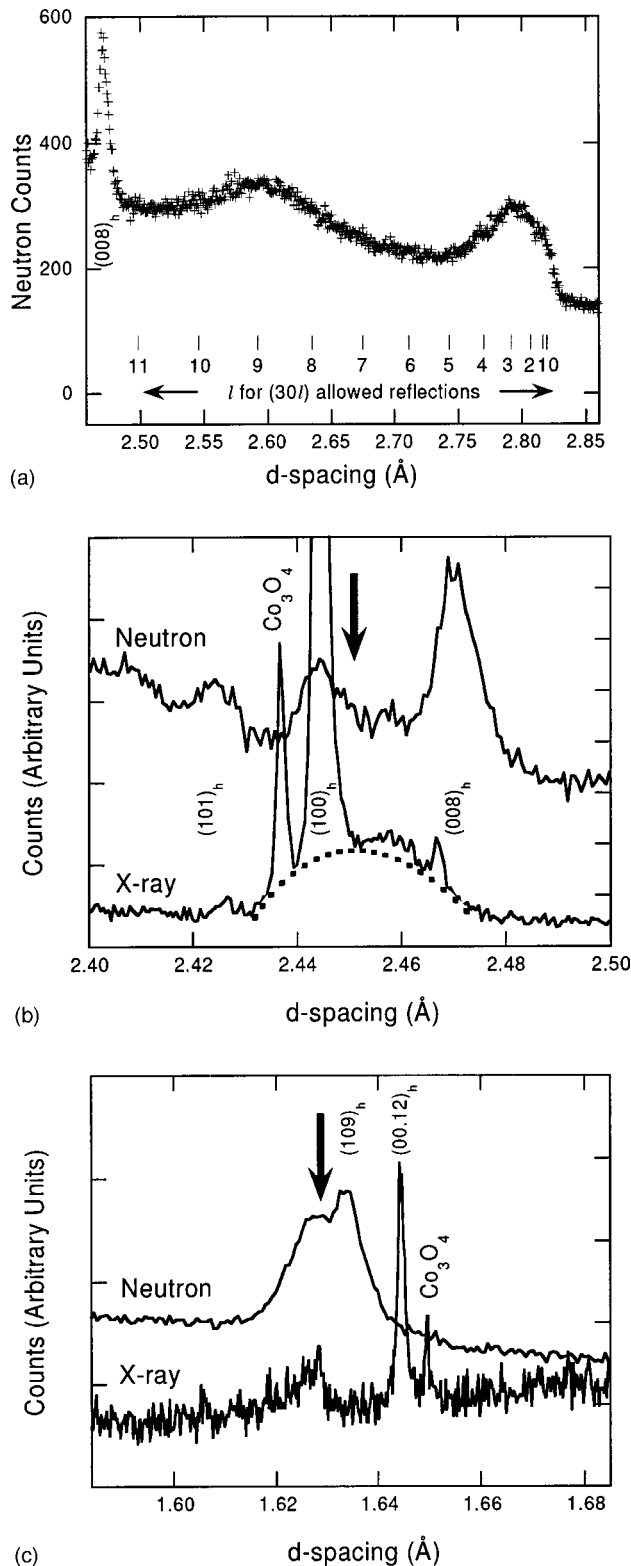
FIG. 7. Major features of the scattering from ordering on shorter length scales that can be explained by a $3a \times \sqrt{3}a \times 3c$ orthorhombic supercell. (a) The broad scattering extending from 2.8–2.5 Å can be indexed as a series of $(30l)$ peaks whose broadening increases with increasing l. The l index is given below the tick marks that mark the positions of these peaks. Equivalently, this scattering can be viewed as a $(30l)$ rod that is strongly modulated as a function of 1. The sharp feature below 2.5 Å is the (008) peak from the fundamental hexagonal cell shown for comparison. (b) The (30.12) peak (marked by the arrow and dotted line) is seen in high-resolution x-ray diffraction, but not in neutron diffraction. Its width defines a coherence length of ~500 Å. (c) The (030) peak (marked by the arrow) is very strong in neutron diffraction and is also seen in x-ray diffraction. Its width defines a coherence length of ~1000 Å in the basal plane. In (b) and (c), the other sharper features are peaks from the fundamental hexagonal unit cell, plus small peaks from Co_3O_4 in the x-ray data. All allowed peaks of the fundamental hexagonal cell are marked and indexed as $(hkl)_h$. (Data shown here are all at room temperature; thus, d spacings are slightly different from those in Fig. 3 for data at 12 K.)

than the out-of-plane coherence length implied by the neutron diffraction data for the $(30l)$ series [Fig. 7(a)]. Thus, taken together, the neutron and x-ray diffraction data suggest that there may be two different length scales for supercell ordering along the c axis. A possible explanation is that Na site occupancies and/or displacements (and perhaps corresponding distortions of the CoO_2 layers) are ordered over a

~500 Å length scale while D_2O orientations are ordered over a shorter length scale. The supercell peak at 1.629 Å, which is very strong in neutron diffraction and is also seen in x-ray diffraction, can be indexed as a (030) peak [Fig. 7(c)]. The width of this peak defines an in-plane coherence length of about 1000 Å, which is assumed to apply to both Na and D_2O in-plane ordering. The supercell peak at ~1.41 Å [seen

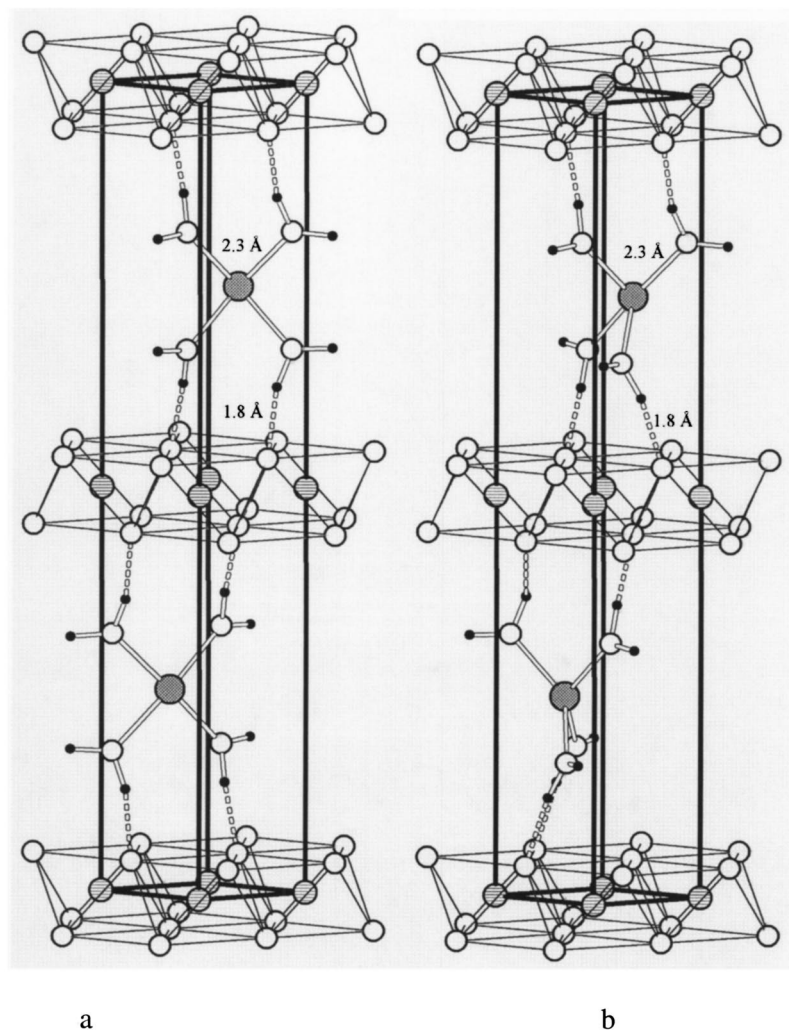FIG. 8. View of the structure of the hydrated compound $Na_xCoO_2 \cdot 4xD_2O$ ($x \approx 1/3$) showing two possible local configurations for the four D_2O molecules coordinated to each Na ion. The CoO_2 layers are held apart by $2D_2O-Na-2D_2O$ "pillars" that are hydrogen bonded to oxygen atoms in the CoO_2 layers. The D_2O molecules can assume either the *cis* (planar) (a) or the *trans* (twisted by 60°) arrangement (b). The view of the structure shown here is a partial unit cell that ignores the supercell ordering in which $2D_2O-Na-2D_2O$ "pillar" locations are only $\sim 1/3$ occupied according to the two-dimensional ordering pattern shown in Fig. 6(b). Atom symbols are the same as for Fig. 4.

in the difference plot in Fig. 3(b)] can be indexed as the (060)/(330) peak and may have additional scattering from (06*l*)/(33*l*) peaks extending to smaller *d* spacings as for the (30*l*) series. Many other weaker features can also be indexed in the same supercell, but, because the supercell is so large, the assignments are not unique. A full interpretation of the scattering from ordering on shorter length scales will certainly come in the future from studies of single crystals, which are now reported to have been grown.[19,20] For that reason, and given the complexity resulting from the very large supercell involved, a more complete analysis of the scattering from shorter-range ordering has not been pursued using the present data.

The proposed structure model of the ordered superconducting deuterate compound $Na_xCoO_2 \cdot 4xD_2O$ ($x \approx 1/3$) is illustrated in Fig. 8. The diffraction experiment done here cannot differentiate between the *cis* (planar) and *trans* (twisted by 60°) arrangements of the pairs of D_2O molecules above and below a particular Na ion; both arrangements are shown in Fig. 8. Based on O–O and D–D repulsions, the *trans* configuration would perhaps be energetically preferred. Local probes of the Na coordination will be needed to determine which configuration exists in the actual structure.

DISCUSSION

The structure shown in Figs. 6(b) and 8 satisfies several criteria expected to be obeyed for a hydrate compound containing Na.[15-18] The Na ions are coordinated by four D_2O molecules, which is a common coordination for oxygen around Na.[16,17] The average Na–O distance (2.31 Å) is typical of such compounds and is, additionally, close to the average Na–O distance in the anhydrous compound $Na_{0.61}CoO_2$ (2.41 Å). The D_2O molecules are oriented to minimize Na–D repulsion and achieve an Na–D distance in the acceptable range.[15] All D_2O molecules achieve positions that allow hydrogen bonding involving both deuterons [as shown in Figs. 6(b) and 8].[15] The hydrogen bonding in the plane between neighboring D_2O molecules leads to the formation of zigzag D–O··D–O··D–O··· chains. The bending angle and D–D distance (2.44 Å) of these chains is typical of hydrogen bonded systems in which the donor and acceptor atoms are of the same type.[15] These many examples of agreement with the literature for hydrate compounds lead to the conclusion that $Na_xCoO_2 \cdot 4xD_2O$ ($x \approx 1/3$) is a typical sodium hydrate (deuterate) compound. There are no exotic features of the structure, although the layering is somewhat uncommon.

The sodium cobaltate hydrate phases exhibit a striking similarity to $M_x TaS_2 \cdot y H_2O$ ($M_x = Na_{1/3}, Mn_{1/6}, Y_{1/9}, La_{1/9}, Gd_{1/9}; 0 \leqslant y \leqslant 2$) layered compounds studied by Johnston *et al.* in the early 1980's.[21] In particular, in those compounds there was thermodynamic evidence for the existence of specific hydrate phases and the incorporation of water led to superconductivity with T_c as high as 5 K. The detailed crystal structures were never solved.

The results presented here show that the highest onset T_c ($=4.5$ K) reported in $Na_x CoO_2 \cdot y D_2O$ is achieved in an ordered deuterate structure in which each Na ion is coordinated to four D_2O molecules and both Na ions and D_2O molecules are ordered into a superlattice. This ordered structure has the ideal composition $Na_x CoO_2 \cdot 4x D_2O$ with $x = 1/3$ when all Na and D_2O sites are occupied. The refined composition, $Na_{0.31(3)} CoO_2 \cdot 1.25(2) D_2O$, suggests that the maximum T_c is achieved at a composition slightly off the ideal composition, in agreement with other reports for the composition at maximum T_c.[1,5,6] In the sample studied here, which was made in a way that places the composition at a plateau in partial pressure of D_2O in equilibrium with the sample, the ideal 1:4 Na to D_2O ratio is maintained, even though the sample is slightly deficient in both Na and D_2O compared to the ideal model. Other reports[1,5,6,19] indicate that a higher water content can be achieved for an Na content of $x \approx 0.3$. It is perhaps possible that additional water could be accommodated using the space made available by Na vacancies for the $x \approx 0.3$ composition [see Fig. 6(b)]. One can visualize a hydrogen-bonded network of D_2O molecules occupying the available space in a way consistent with the pattern of symmetry equivalent positions shown in Fig. 6(a). Alternatively, additional D_2O could perhaps be accommodated in the Na plane, as must occur in the structure of the lower deuterate phase, $Na_{0.3} CoO_2 \cdot 0.6 D_2O$, where the elongation of the c axis is much shorter and the water cannot be coordinated to Na as in the higher deuterate structure. Thus, reports of water contents higher than 4/3 are not necessarily inconsistent with the model presented here, especially in the case where the Na content is below 1/3. However, the incorporation of two water molecules per formula unit, as reported by Jin *et al.*[19] seems unlikely in light of the structure. Perhaps reports of water concentrations higher than 4/3 should be viewed with suspicion until it is shown that all of the water is actually in the lattice. Surface adsorbed water could easily cause errors in bulk measurements of water content. The data presented here for the partial pressure of D_2O in equilibrium with the hydrated material (Fig. 1) argue that the water content does not depart far from the ideal 1:4 ratio of Na to D_2O molecules. Even if extra water can be accommodated in the space made available by Na vacancies, as the ideal Na content of 1/3 is approached the ability to accommodate extra water would be expected to decrease. Additionally, for Na contents greater than 1/3, the compound must either generate "Na interstitial" defects in the Na ordering, where the extra Na ions could not achieve the fourfold coordination to D_2O molecules, or phase separate. The data of Schaak *et al.*[5] for T_c vs Na concentration are consistent with phase separation for Na contents above $x = 1/3$. T_c remains constant at ~ 2 K,

while the superconducting fraction decreases, for increasing Na contents above 1/3.

It is important to speculate about what happens for Na concentrations below $x \approx 0.3$. Baskaran[10] has presented a theory based on the idea that the highest T_c in this system occurs between the compositions $Na_{1/3}$ and $Na_{1/4}$ that would be expected to give ordered phases. He argues that charge ordering in the CoO_2 layers, especially at the special compositions 1/3 and 1/4, suppresses superconductivity but that the incorporation of water as "ice" layers introduces screening that weakens the ordering. Thus, the ordered phases at the ideal compositions $x = 1/3$ and 1/4 are unfavorable for superconductivity and the highest T_c is achieved between these special compositions. In agreement with these ideas, the maximum T_c is achieved at a Na concentration below $x = 1/3$.[5] However, the present results show that the optimal superconducting composition displays ordering of Na ions and D_2O molecules, over an in-plane coherence length of ~ 1000 Å, the same as for the ideal $x = 1/3$ composition. Since the ordered D_2O molecules are hydrogen bonded into the CoO_2 layers, there is also likely to be an ordered distortion pattern in these layers, which could provide a template for charge ordering. In such a case, the screening may not be as effective as proposed by Baskaran. The increase of T_c upon decreasing the Na content from $x = 1/3$ could simply be a doping effect, as proposed by Schaak *et al.*[5] To better understand this behavior, it is important to understand what happens when the Na concentration is further reduced toward the composition $x = 1/4$, which corresponds to a different ordered structure in Baskaran's model. Figure 6(c) shows a possible ordered structure with this Na concentration. At this Na concentration, each Na ion can achieve sixfold coordination to D_2O molecules. This is also the most common coordination for Na oxide and hydrate structures.[16] The present data give no evidence for the occurrence of this ordered compound. However, if it does form at the Na composition $x = 1/4$, the data of Schaak *et al.* for T_c vs composition may have a different interpretation. The drop in T_c from 4.5 K to 2 K upon decreasing the Na concentration from 0.30 to 0.26 may result from a transition from the $Na_{1/3}$ to the $Na_{1/4}$ phase. If this is the case, the conclusion that the domelike behavior of T_c mimics the behavior seen in the layered cuprates[5] may be premature. Clearly, a careful structural study of a composition near $x = 1/4$ must be pursued.

CONCLUSIONS

In conclusion, we have shown that the highest reported T_c ($=4.5$ K) in the $Na_x CoO_2 \cdot y D_2O$ system is achieved in a hydrate phase with well-defined composition and ordering of both Na ions and D_2O molecules. The deuteration of Na leads to the formation of $2D_2O-Na-2D_2O$ "pillars" extending between the CoO_2 planes. This interesting "pillar" structure is further stabilized by hydrogen bonding within the planes of the D_2O molecules to form zigzag $D-O\cdots D-O\cdots D-O\cdots$ chains. These structural results are in contrast to initial reports that implied that the material could be viewed a solid solution that could intercalate both Na and D_2O in varying amounts. The ideal composition of the superconduct-

ing phase is $Na_xCoO_2 \cdot 4xD_2O$ ($x \approx 1/3$). The sample studied here has a refined Na composition of $x = 0.31(3)$ and a perfect 1:4 Na to D_2O ratio (within one esd) consistent with the ideal structure, but with vacancy defects on both the Na and D_2O sites; i.e., entire $2D_2O$–Na–$2D_2O$ "pillar" sites are vacant. This hydrated phase would be expected to exist only within rather narrow composition limits. For $x \geq 1/3$, fourfold coordination of Na by D_2O molecules cannot be achieved. As x approaches 1/4, a different ordered phase, involving sixfold coordination of the Na, could be formed. Thus, mea-

surements of physical properties, such as T_c, vs composition should be viewed with caution until it is confirmed that all samples in a particular study are in the same phase.

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