

Structure and Dynamics of Na_xCoO_2 and the Hydrated Superconductor

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ABSTRACT

The properties of the Na_xCoO_2 class of materials are of interest from a number of viewpoints. These compounds are based on a triangular lattice of spin- $1/2$ ions—prototype RVB system—where a high thermoelectric-power Curie-Weiss metallic paramagnet is found for $\text{Na}_{0.7}\text{CoO}_2$, a charge ordered insulator at $x=0.5$, and a paramagnetic metal where superconductivity is induced in $\text{Na}_{0.3}\text{CoO}_2$ when it is intercalated with water. Here we briefly review our neutron diffraction and inelastic scattering measurements characterizing the crystal structure and lattice dynamics, and relate these to the observed physical properties. The basic structure of Na_xCoO_2 is hexagonal and consists of robust layers of CoO_2 interspersed by Na layers with two inequivalent sites. Two special cases are $x=1$ where one of these sites is fully occupied and the other empty, and $x=1/2$ where both sites have equal occupancies of $1/4$ and the system is a charge ordered insulator. For general x the site occupancies are inequivalent and vary systematically with x . In the regime of $x=0.75$ we find a first-order transition from a high symmetry Na site at low T to a three-fold split site (with lower symmetry) at high T . This transition is first order and varies with x . For the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.4(\text{H/D})_2\text{O}$ superconductor, the water forms two additional layers between the Na and CoO_2 , increasing the c -axis lattice parameter of the hexagonal $P6_3/mmc$ space group from 11.16 \AA to 19.5 \AA . The Na ions are found to occupy a different configuration from the parent compound, while the water forms a structure that replicates the structure of ice to a good approximation. We find a strong inverse correlation between the CoO_2 layer thickness and the superconducting transition temperature (T_C increases with decreasing thickness). The phonon density-of-states for $\text{Na}_{0.3}\text{CoO}_2$ exhibits distinct acoustic and optic bands, with a high-energy cutoff of $\sim 100 \text{ meV}$. The lattice dynamical scattering for the superconductor is dominated by the hydrogen modes, with librational and bending modes that are quite similar to ice, supporting the structural model that the water intercalates and forms ice-like layers in the superconductor.

INTRODUCTION

Cobalt oxide systems are now a focus of materials researchers because of their interesting magnetic and thermoelectric properties, as well as for possible analogies to colossal magnetoresistive manganite materials or high superconducting transition temperature cuprate oxides. For the Na_xCoO_2 system of particular interest here, the spin entropy has been found to play an essential role [1] in the dramatically enhanced thermopower [2] for large sodium content ($x \sim 0.7$), and magnetic order and spin fluctuations have been observed in this regime [3-7]. At lower Na content the recent discovery of superconductivity in hydrated Na_xCoO_2 has been of particular interest with regard to the superconducting cuprates [8-9]. This is a layered system where the Co^{4+} ions are in the low-spin state and carry $S=1/2$ so that quantum effects are maximal,

while the underlying lattice is triangular rather than square like the cuprates. These observations suggest that this may be the first new class of “high- T_C ” superconductors since the discovery of the cuprates over 18 years ago, but of course the nature and mechanism of superconducting pairing is in the early stages of being addressed. The appropriate underlying model may be a Mott insulator in two-dimensions, with $S=1/2$, where quantum fluctuations are optimal. The Co spins would then play a critical role in forming Cooper pairs that might have triplet symmetry as in Sr_2RuO_4 or d -wave symmetry as in the cuprates. On the other hand, the traditional electron-phonon interaction may be establishing conventional s -wave pairing, with the possibility that the anharmonic motion of the hydrogen and oxygen ions might be playing a role in enhancing the superconducting properties, in a manner similar to MgB_2 [10]. In recent studies we have investigated the crystal structure of Na_xCoO_2 as a function of doping x [11-14], and related the structure to the observed physical properties [15-18]. We have also determined the lattice dynamics for the superconducting hydrate, and compared the behavior with the related non-superconducting $\text{Na}_{0.3}\text{CoO}_2$ compound [11].

STRUCTURE OF SODIUM COBALTATE

The crystal structures for the Na_xCoO_2 series were investigated by refinements of powder neutron diffraction data [11-14]. The basic structures are shown schematically in Fig. 1. The compounds over the composition range from $0.34 < x < 0.74$ (with the exception of $x=0.5$) are well described by a structure in which both sodium sites are partially occupied and the Na(2) ions are displaced from the ideal centers of the NaO_6 triangular prisms, i.e., in the Na(2)' sites [19]. When a particular Na(2)' site (or Na(2) site at higher concentrations) is occupied, then its nearest-neighbor Na(1) sites are excluded from occupancy, as they are too close together to both accommodate Na ions simultaneously. This structure type covers a large fraction of the phase diagram, and is designated as the H1 phase. A different structure type is found for $0.76 < x < 0.82$. This phase, designated as H2, has all the Na(2) ions (when this site is occupied) directly in the center of the ideal Na(2) triangular prism, as well as Na ions on the (partially occupied) Na(1) site. The H1 and H2 phases are separated by a narrow two-phase region, and samples of nominal Na stoichiometry $x \sim 3/4$ are mixtures of the H1 and H2 phases and clearly exhibit two-phase coexistence. The change in position from Na(2)' to Na(2) sites is abrupt, indicating that at a critical Na layer filling the system suddenly favors on-center Na(2) ion occupancy. The reason for this behavior is not yet understood.

In the H1 and H2 phases both Na sites are fractionally occupied, and for general x the site occupancies are inequivalent and vary systematically with x ; detailed quantitative results are given elsewhere [11, 13-14]. However, there are two cases where the crystal structure is well ordered. One is for Na half filling ($x=1/2$), where both Na sites have equal occupancies of $1/4$ and form zigzag chains, and the material is a charge ordered (antiferromagnetic) insulator at low temperatures [12]. The other case is for $x=1$, where a distinct phase, designated H3, is found (composition NaCoO_2) after another two-phase coexistence region. In this compound, all the Na(1) sites are empty and all the Na(2) sites are fully occupied; the Na are all in ideal trigonal prismatic sites that share only edges with the CoO_6 octahedra [13]. The crystal structure of H3 is distinctly different from that of the thermodynamically stable phase NaCoO_2 , which has all the Na in octahedral coordination with oxygen [20].

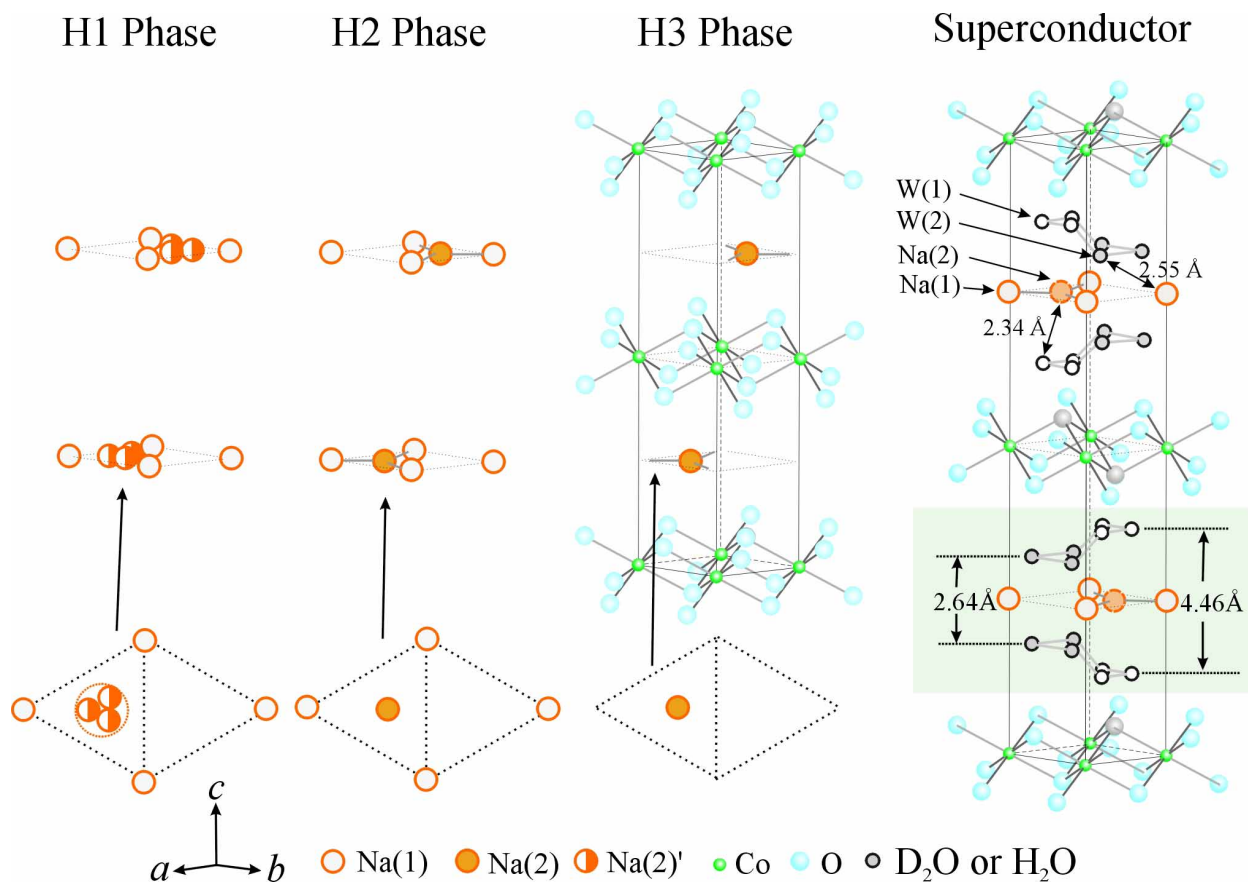


Fig. 1. Three different structures (designated H1, H2, and H3) that are controlled by the Na ions in Na_xCoO_2 . At lower Na concentrations the Na(2) ions are randomly located at one of three positions that are symmetrically shifted off-center (designated Na(2)'), while at higher Na content the Na(2) occupancy is at the centered position. There is an anti-correlation between the Na(1) and Na(2) sites in that when a particular Na(2) site is occupied then its nearest-neighbor Na(1) sites are excluded from occupancy, as they are too close together to both accommodate Na ions simultaneously. The structure on the right is for the superconductor, where we note that the Na ions shift to the other side of the unit cell to accommodate the ice-like layers of water. (after references [11, 13, 14])

Each Na ion nominally donates an electron to the CoO_2 plane, but the phase diagram [9] (shown in Fig. 2) and the behavior of the Na is much more complicated than this simple picture would suggest [13]. In particular, the Na ions fractionally occupy two different sites over a wide range of x , while the CoO_2 layer is structurally robust. The system is a paramagnetic metal for $x < 1/2$, with both the Na(1) and Na(2) sites being partially occupied, and the Na(2) being further split into a threefold site that is again randomly occupied, designated the H1 structure as shown in Fig. 1. At $x = 1/2$ the system exhibits a special charge/orbitally ordered structure that is insulating in the ground state, with the Na ions occupying ordered positions that form one-dimensional zigzag chains [12]. For $x > 1/2$ the system returns to the H1 structure and is again

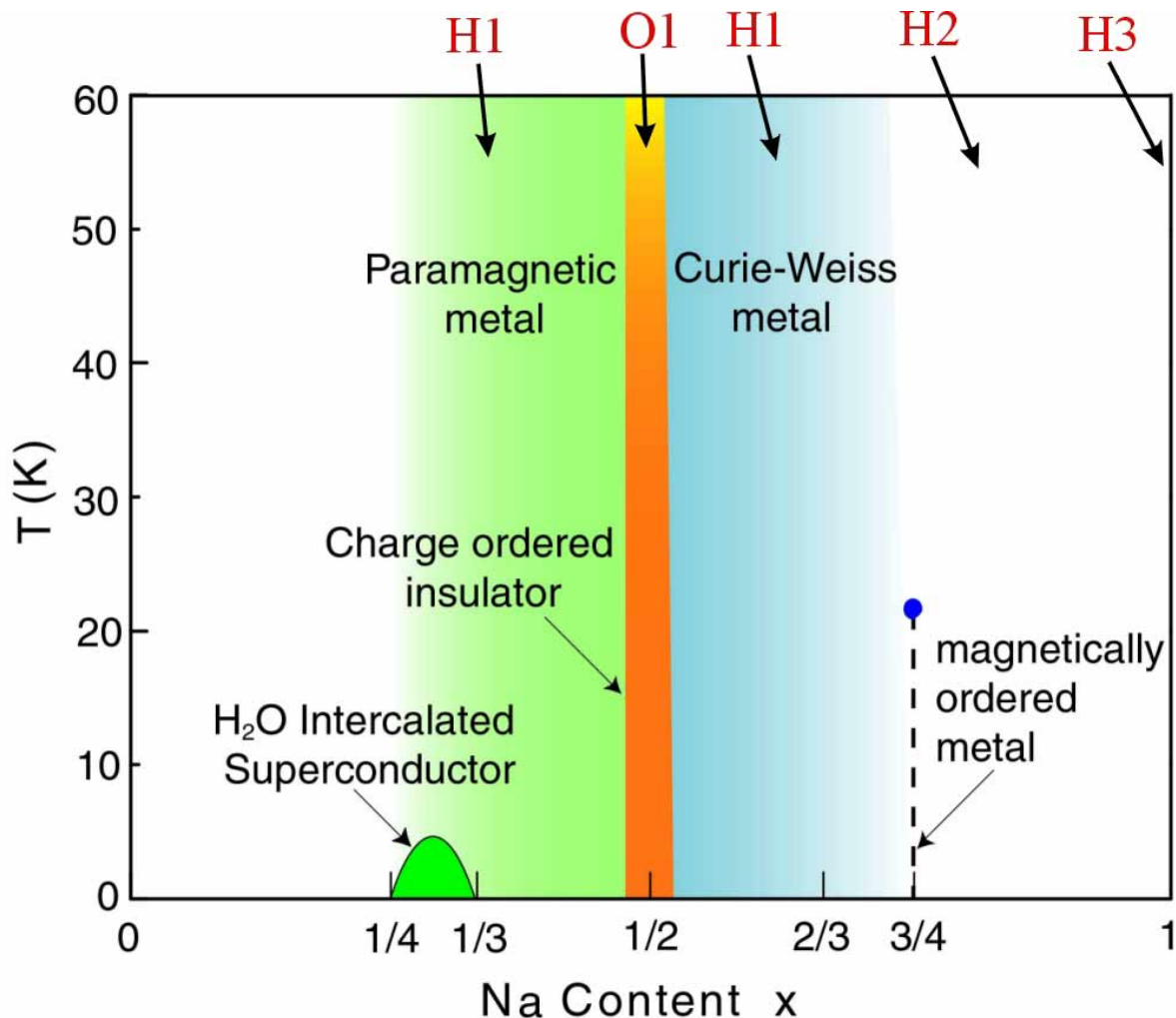
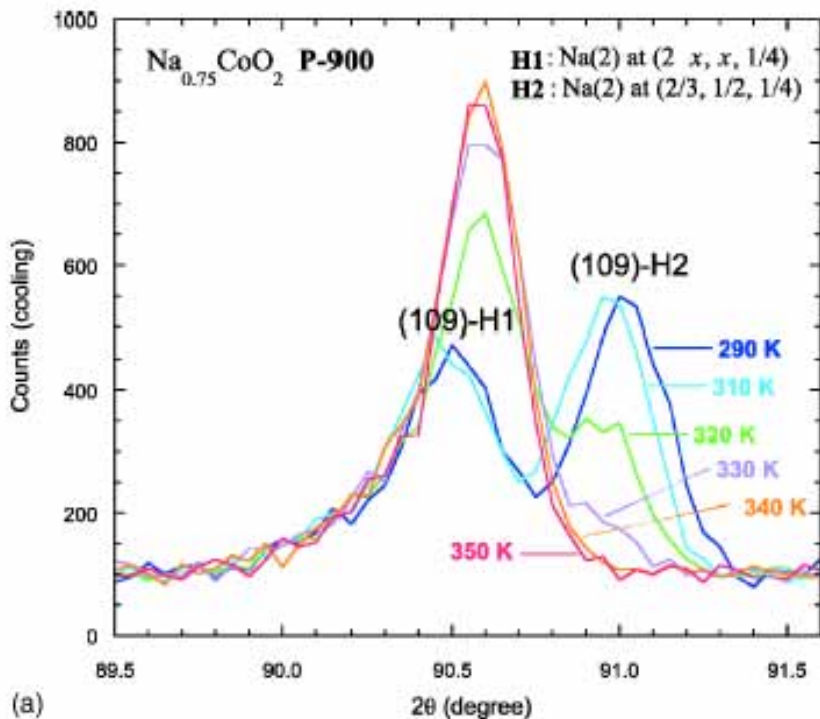


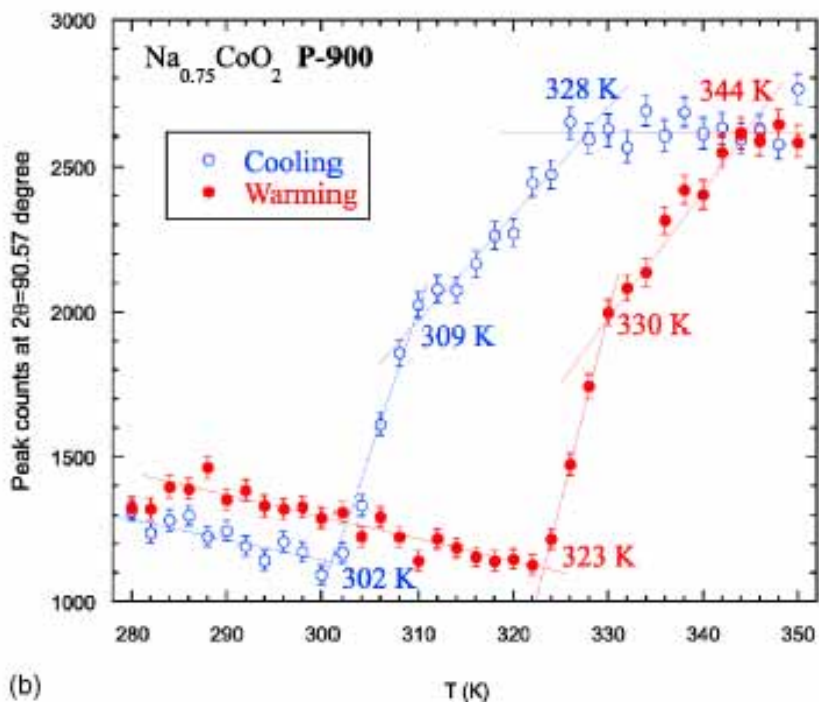
Fig. 2. Phase diagram for Na_xCoO_2 showing the different structural phases associated with the Na positions and ordering. At $x=1/2$ the system is a charge-ordered insulator and at $x=1$ one Na site is empty and the other completely occupied. Away from these concentrations the system is a metal. Superconductivity develops around $x=0.3$ by the introduction of water layers in the structure [13].

metallic, but the magnetism exhibits Curie-Weiss behavior [9]. Around $x \sim 3/4$ the structure transforms to the more ordered H2 structure, where the randomness in the Na(2) site is absent. Finally, with further increase of the Na composition we realize the H3 structure, where the Na(2) site is fully occupied and the Na(1) site is completely vacant [13]. The transition from the H2 to the H3 structure as a function of composition is also discontinuous in nature.

There are a number of differences between the H1 and H2 phases in addition to the symmetry of the N(2) sites, as there are changes in the lattice parameters, bond distances and angles. One of the interesting aspects of the system is that in the range of $x \sim 3/4$ the transition



(a)



(b)

Fig. 3. a) Scans through the (109) Bragg peaks for the high temperature H1 phase and the low temperature H2 phase at various temperatures. The peaks are well separated due to the different a and c lattice parameters of these two phases. b) Temperature dependence of the peak intensity of the (109)-H1 peak. These data demonstrate that at high temperatures (above 340 K), H1 is the stable structure. The transition is hysteretic, indicating that it is first order [14].

between the H1 and H2 structures can be driven thermally [14]. The identification of $x=0.75$ as the critical concentration is confirmed by studies on a variety of samples of Na_xCoO_2 in this composition range. We note that in the H1 structure the a axis is significantly shorter and the c axis is significantly longer than for the H2 structure, which in fact allows these two structures to be readily distinguished from each other in diffraction, as indicated in the top panel of Fig 3. In order to characterize this structural phase transition in detail, we measured the (109) Bragg peak over a range of temperatures as shown in the top panel of Fig. 3 [14]. At a temperature of $T=290$ K there are two diffraction peaks, (109)-H1 and (109)-H2, signifying the coexistence of the H1 and H2 structures, respectively. Moreover, with increasing temperature the intensity for the H1 peak increases as the intensity for the H2 peak decreases, as is evident from the figure. This behavior can be followed in detail by measuring the peak intensity as a function of temperature, as shown in the bottom panel of Fig. 3. As the temperature is raised, the H1 phase fraction suddenly begins to increase above 323 K and reaches a maximum near 344 K. Above this temperature the sample is single phase, possessing only the H1 structure. Upon cooling, the intensity begins to decrease suddenly below 328 K and levels off below 302 K. The distinct hysteresis (around 20 K) indicates that the transformation from structure H2 to H1 is a first-order transition. Thus the transition is first-order in nature in both temperature and composition. We note that it is quite unusual to transform from a high-symmetry Na occupancy at low temperature to a lower-symmetry Na occupancy at higher temperature, and the discovery that this transition can be driven thermally affords us the opportunity to directly determine the changes in the physical properties associated with these two structures. The structural phase transition resembles an order-disorder phase transition in that Na atoms shift from a random occupation of the $6h$ sites (H1 structure) to a configuration in which every Na(2) atom occupies a $2c$ position (H2 structure), but the transition is unusual in that it is first-order rather than continuous like a conventional order-disorder transition, and it is the lower temperature (H2) phase which has the higher site symmetry for the Na(2) ions. However, we note that both structures have the same *average* space group symmetry, $P6_3/mmc$, as measured by neutron powder diffraction. There is a sharp increase in the resistance and decrease in susceptibility that is observed near 340 K upon warming [14], and the sudden expansion of the c -axis lattice constant at the transition from the H1 to H2 structure may explain this behavior. We note that the transport properties of Na_xCoO_2 are highly anisotropic, with the resistivity within the ab planes being several hundred times lower than that perpendicular to the planes. The resistance of such an anisotropic material measured using the four-probe technique usually contains an out-of-plane component due to non uniform current flow across the sample. Since the c -axis resistivity should increase for a larger c -axis lattice constant, this may explain the observed jump in the resistance. Alternatively, or in combination, the jump in resistivity may be related to enhanced scattering due to the disorder in the H1 structure originating from the randomly occupied Na(2) site.

SUPERCONDUCTIVITY

One of the amazing characteristics of this system is the discovery of superconductivity when the material is hydrated [8]. Initially water goes into the Na layer, but then the water forms its own layer between the Na and CoO_2 layers, with the c -axis expanding from 11.2 Å to 19.5 Å and the material becoming a 5 K superconductor. Both the structure and lattice dynamics indicate that this separate water layer has the basic structure of ice as shown on the right-hand

side of in Fig. 1 [11]. Note in particular that the structure of the Na is different than in the parent compound, with the Na shifting to the other side of the unit cell to accommodate the water. The neutron data also determine the water positions, which are well established in the neutron refinements by the oxygen. The positions of the hydrogen are randomized as they are in ice (leading to the famous excess entropy problem of ice) and specific hydrogen occupancies could not be determined. The small fractional occupancies of these sites make these determinations challenging, but we have found that the crystallographic structure of the (H/D)₂O parallels the structure of ice, as shown in Fig. 1. Both the Na and H sites are fractionally occupied, but the refinements suggest that the oxygen in the water has a tendency to shift toward the Na when the sodium site is occupied, with the hydrogen tending to bond to the oxygen in cobalt layer.

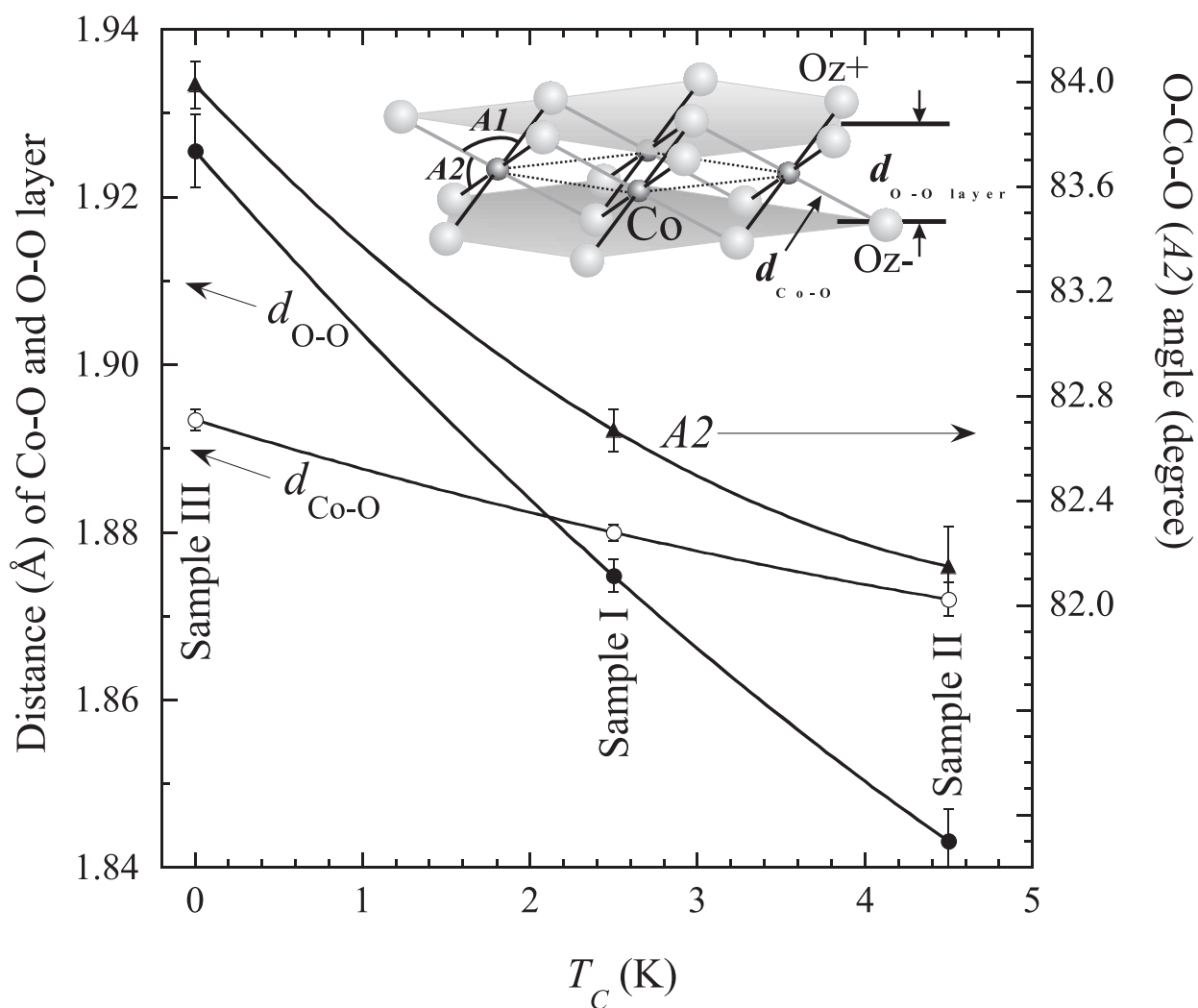


Fig. 4. Interatomic distances for Co–O in the CoO₂ layer, and the O–Co–O bond angle, as a function of the superconducting transition temperature T_c . Note the strong dependence of T_c on the bond angle A2 (defined in the inset), which determines the CoO₂ layer thickness [11].

The CoO_2 layer, on the other hand, is robust, and the diffraction results reveal an interesting correlation between the structure of this layer and the superconducting transition temperature. The Co-O distance is shown in Fig. 4 (open circles), and there is a modest decrease with increasing T_C , which from a crystal chemistry point of view would suggest some electron transfer off the cobalt [11]. The bond angle for O-Co-O, on the other hand, varies quite substantially with T_C . This means that the layer thickness (or alternatively, the bond angle) exhibits a large change, from 1.93 Å for $T_C = 0$ K to 1.84 Å for $T_C = 4.5$ K. A central question is whether the water is playing an active role in the superconducting pair formation, or is simply expanding the lattice and making the system more two-dimensional in nature. So far, however, only water has been found to render this system superconducting, both in the two-layer material under discussion here, and for the three-layer system [21]. Previous to the Na_xCoO_2 system, there was only one other known superconductor that contains water [22].

Inelastic neutron scattering measurements were carried out to determine the generalized phonon density-of-states for the “parent” $\text{Na}_{0.3}\text{CoO}_2$, and the hydrated superconductor. For $\text{Na}_{0.3}\text{CoO}_2$, in the low energy range we have the acoustic phonons that band in the energy range from 0-40 meV, and then the optic modes that band in the range from 50-100 meV. For the superconductor, both hydrated and deuterated samples used for the inelastic measurements were those without free ice, prepared by freeze drying. Similar features are observed for the hydrated samples, indicating that the phonons associated with the CoO_2 layer and the Na layer are similar in the two materials, as might be expected. For the $\text{Na}_{0.3}\text{CoO}_2$ material the one-phonon density of states cuts off at ~ 100 meV, with the additional scattering observed at higher energies originating from multiphonon scattering.

For the H_2O superconducting sample, the scattering is much stronger in the energy range from 50–120 meV than for the parent compound, indicating that this scattering is dominated by the very strong proton scattering; protons have one the largest neutron scattering cross sections. The features in this scattering are in fact quite similar to the scattering observed in free H_2O [23], which originates in this energy range from the librational modes of the water. This is confirmed by the results for the deuterated sample, whose scattering in this energy range closely follows the scattering for the protonated sample after scaling the energies by $(m_{\text{H}}/m_{\text{D}})^{1/2}$ to account for the change in isotopic mass. Note in particular the rather strong peak in the scattering at 37 meV for the deuterated sample. This sharp peak is in excellent agreement with the peak observed in D_2O ice [23]. The rather remarkable similarities between the lattice dynamical density-of-states of the superconducting compounds measured here and ice strongly support our structural model, where the intercalated ice in the superconductor forms a structure that mimics the ice structure.

CLOSING REMARKS

The structure and lattice dynamics results briefly reviewed here have elucidated the basic crystal structure for the Na_xCoO_2 as a function of sodium content, and the lattice dynamics and crystal structure for the hydrated superconductor. There are both systematic changes in the bonding and structure as the electron count is varied, combined with first order transitions to new structures. This class of materials represents a highly correlated electron system that exhibits a wide range of interesting physical properties, such as charge ordering, orbital ordering, magnetic ordering, thermoelectricity, and superconductivity. There are certainly important

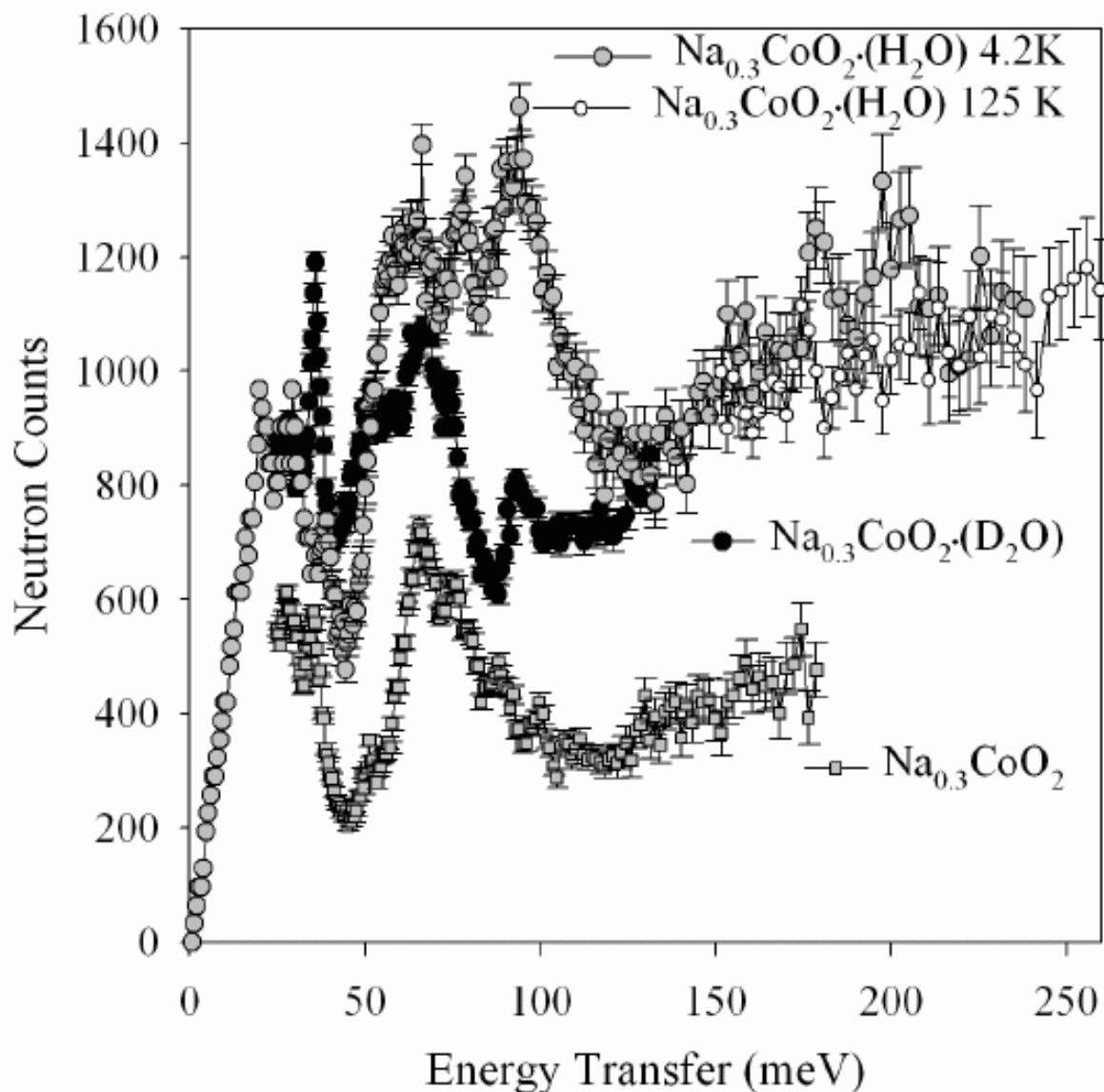


Fig. 5. Measurements of the generalized phonon density of states for the parent compound, the deuterated superconductor, and the protonated superconductor. For $\text{Na}_{0.3}\text{CoO}_2$ the excitations divide into an acoustic band and an optic band, with a one-phonon density-of-states cutoff around 100 meV; at higher energies the scattering is multiphonon in origin. For the protonated superconducting sample there is additional strong scattering in the 50–120 meV range, which matches relatively well to the librational modes of ice [23], while at higher energies there are bending modes. The intensities of these bending modes have a significant temperature dependence due to Debye Waller effects. For the deuterated sample the positions of the hydrogen modes scale with the mass. In particular, the sharp peak at 37 meV agrees very well with the peak position from ice, indicating that the dynamics of the water in the superconductor is quite similar to the dynamics (and structure) of ice. [11].

analogies between the sodium cobalt oxides and perovskite-based oxides such as relaxor ferroelectrics and cuprate superconducting that suggest commonalities in the underlying physics. The clear differences observed between these different classes of materials, however, suggests that conducting triangular lattice systems exhibit their own distinct type of structural and electronic phases, that will no doubt provide a rich variety of new physical phenomena to explore for both fundamental and technological purposes.

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