

Observation of two O-H covalent bonds of water in the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ superconductor by inelastic neutron spectroscopy

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The vibrational dynamics of pure H_2O and isotopically substituted HDO water in a $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ layered compound was studied using neutron spectroscopy. The obtained results showed that water in the *ab* plane of the hexagonal structure exhibits intermolecular translational vibrations and intramolecular O-H stretching modes similar to those in bulk water, but the vibrations along the *z* direction are different—the corresponding hydrogen bond between the water molecule and the CoO_2 layer is much weaker than between water molecules in the water layer. These data revealed two O-H covalent bonds for water in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ superconductor which differ in strength by about 18%.

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Layered hydrated sodium cobalt oxide materials ($\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$) have attracted significant interest since the discovery of their superconductivity¹ in a narrow range of Na concentration ($0.25 < x < 0.35$). The basic crystal structure of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ has been considered to consist of electronically active planes (edge sharing CoO_6 octahedra) separated by H_2O -Na- H_2O layers which act as charge reservoirs. The presence of water is the key to the material's superconductivity; however, it is still not yet clear whether the water is playing an active role in the superconducting state or is simply expanding the lattice and making the system more two-dimensional in nature. However, so far, only water has been found to render the system superconductive.

Numerous efforts have been made to understand the structure of water in the compound using neutron diffraction techniques for the deuterated materials, since x rays are incapable of revealing the positions of water molecules in the hydrate. The first neutron diffraction work done by Lynn *et al.*² proposed that the intercalated water forms a structure that replicates the structure of hexagonal ice-Ih between Na and CoO_2 layers. In the same year, Jorgensen *et al.*, also using neutron diffraction, came to a different conclusion.³ They proposed that the compound should be viewed as a specified layered hydrate, in which four D_2O molecules coordinate with each Na ion (two above and two below the Na layer). Recently, Argyriou *et al.*, using neutron diffraction, suggested⁴ that $\text{Na}_x\text{CoO}_2 \cdot y\text{D}_2\text{O}$ is a homogeneous solid solution in a wide range of Na concentrations, with the Na average coordination close to 6.

Recently, diffusion of water in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ was studied by Garcia Sakai *et al.*⁵ in a wide temperature range from 3.5 to 315 K using high resolution ($0.85 \mu\text{eV}$) quasi-elastic neutron scattering (QENS). It was shown on a time scale of the measurements (10^{-9} s) that at temperatures below 235 K, water in the hydrate is immobile; then at higher temperatures (235–310 K), 5%–15% of water (depending on the temperature) exhibit highly constrained diffusive motion, which can be described as localized jumps between the Na sites, while the rest of the water is still immobile. Another

QENS study of the $\text{Na}_{0.28}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ compound was done by Jalarvo *et al.*⁶ at room temperature with resolutions of 93 and $32 \mu\text{eV}$. Due to higher energy transfer covered, they were able to identify the rotational motion corresponding to reorientation of water molecules.

More experimental work is clearly required to gain a better understanding of the structure and dynamics of the hydrated sodium cobalt oxide compound, in particular, with regard to the local environment of water in this material. Inelastic neutron scattering (INS) is a technique particularly suited for this study, because the vibrational spectrum of water is highly sensitive to subtle structural modifications and is very intense due to the much larger incoherent neutron scattering cross section of hydrogen (~ 80 b) compared to other atoms in the material (about 5 b). On the other hand, all vibrational modes are neutron active because the nuclear interactions are not subject to dipole or polarizability selection rules as IR and Raman spectra do, therefore all vibrations can be observed, in principle. Thus, high-quality INS data can be used to deduce information on the local structure and bonding of the intercalated water in the hydrates.

Up to now, INS spectra of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.4\text{H}_2\text{O}$ and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.4\text{D}_2\text{O}$ (at 4.2 K) were measured only by Lynn *et al.*² The vibrational spectrum of water in the hydrate in the energy transfer range of 0.5–260 meV was found to be similar to the spectrum of hexagonal ice-Ih.⁷ This result was rather unexpected, because due to the two-dimensional water-water interaction in the hydrate (with only two water-originated hydrogen bonds per water molecule) and three-dimensional water-water interaction in ice-Ih (with four hydrogen bonds per water molecule) one would expect a big difference in their vibrational spectra. In this Brief Report, we report the INS study of the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$ in the energy transfer range of 2–500 meV, compare the results with the spectrum for ice-Ih, and show the difference between the spectra of confined water and ice-Ih.

The samples used in the present study were $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$. The supercon-

ducting materials were synthesized as reported in Ref. 8. The water contents in the samples were measured by the thermogravimetry method. The samples were characterized by x-ray diffraction and low-temperature magnetization measurements, which confirmed their good quality. The lattice constants $a=2.821(1)$ Å and $c=19.807(9)$ Å (at room temperature) obtained with the space group $P6_3/mmc$ were in good agreement with the literature data.³

INS data were measured using time of flight neutron scattering spectrometer HRMECS at IPNS.⁹ The spectrometer is a direct geometry machine: the incoming neutrons have a fixed energy E_i , selected by a rotating chopper, and the energy analysis is made on neutron time of flight. Under optimum conditions (large E_i and small scattering angles), the neutron momentum transfers at high energy transfers are relatively small, which made it possible to measure good quality INS spectra up to the highest excitation energies of around 450 meV. Experiments were carried out at low temperature, $T=4$ K, to reduce multiphonon contribution and the effect of the Debye-Waller factor. Due to sufficiently long neutron flight paths between sample and detectors (~ 4 m), the spectrometer provides a good energy resolution, $\Delta E/E_i \approx 2\% - 3\%$, in the range of interest.

The INS spectra for $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ are shown in Fig. 1 (curves 2). According to neutron diffraction study³ of $\text{Na}_{0.31}\text{CoO}_2 \cdot 1.25\text{D}_2\text{O}$, the oxygen atoms of the D_2O molecules are located in layers between the CoO_2 layers and the Na layers; and deuterium atoms occupy two sites: one approximately in the same plane as the oxygen atoms (with water O-D covalent bond in the ab plane) and one closer to the CoO_2 layers (with water O-D covalent bond out of the ab plane). In the ab plane, D_2O molecules form hydrogen bonds between neighboring molecules to give zigzag D-O \cdots D-O \cdots D-O \cdots chains.³ The spectrum of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ in the range of translational vibrations of water molecules (<40 meV) shows a small peak around 8 meV, similar to the first acoustic peak for ice-Ih [Fig. 1(a), curve 5], a large peak at ~ 21 meV (much bigger than a similar peak in ice-Ih), and a broad high energy peak around 35 meV (also present in the spectrum for ice-Ih). In the range of the librational band of water molecules (50–120 meV), there are three peaks at energies 57, 71, and 92 meV [Fig. 1(b)]. The peaks are rather sharp in comparison to those in ice-Ih,⁷ indicating weak dispersion of the corresponding librational modes. The low-energy cutoff of the librational band is at very low energy (~ 50 meV) compared to ice-Ih and to all other known crystalline and amorphous ice phases.¹⁰ This is probably a consequence of the two-dimensional water layer in the hydrate with only two water hydrogen bonds per water molecule.

The spectrum measured with $E_i=600$ meV [Fig. 1(c)] clearly shows a peak at about 200 meV due to intramolecular bending H-O-H modes, and a split peak with two maxima at 405 and 440 meV due to water intramolecular stretching O-H modes. The lower energy peak is close to that in ice-Ih (406 meV), which indicates the existence of a strong hydrogen bond between water molecules in the layer similar to that in ice-Ih (a strong hydrogen bond between water molecules stretches and weakens the water intramolecular O-H covalent bond). The peak at higher energy (440 meV) is

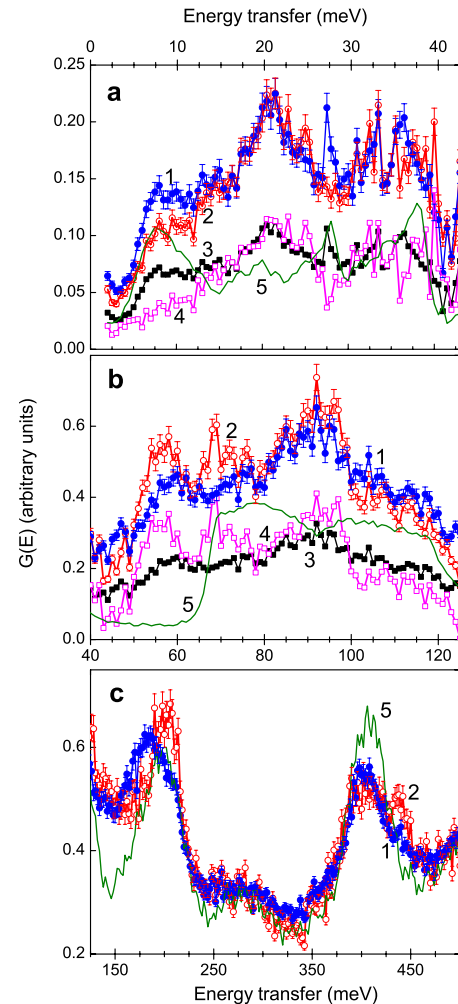


FIG. 1. (Color online) INS spectra for $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$ (blue curves 1 with filled circles) and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ (red curves 2 with open circles) measured at 4 K with HRMECS; the spectra normalized for the same amount of hydrogen. Black curves 3 with filled squares are half the intensity of spectra 1; pink curves 4 with open squares are differences between spectra 2 and 3. According to our model, curves 3 and 4 represent vibrations of water hydrogens placed in the ab plane and out of the ab plane (close to the CoO_2 layer), respectively. Thin solid green curves 5 show the spectra of ice-Ih measured at similar conditions, for comparison. The spectra in (a), (b), and (c) were measured with incident neutron energies of 50, 140, and 600 meV, respectively.

characteristic of a very weak hydrogen bond (a strong O-H covalent bond), which is probably related to the stretching mode of the O-H covalent bond directed out of the ab plane. The peak at 405 meV is about three times broader than the peak at 440 meV (their full widths at half maximum are 50 and 17 meV, respectively), which can be explained by the large dispersion of the corresponding modes of the low-energy peak, caused by the collective character of the vibrations in the ab plane, and the localized origin of the high-energy peak (nondispersive modes). Due to the large difference in the stretching mode energies (35 meV), there is a possibility that, in the sample with isotopically substituted HDO water, deuterium atoms will reside in the positions cor-

responding to the stronger covalent bond and hydrogen atoms will occupy the positions related to the weak covalent bond. This is because the HDO molecule tends to have a minimum total energy, and for the covalent bond of the same strength in the harmonic approximation, O-D stretching mode is about $\sqrt{2}$ smaller than O-H stretching mode.

Curves 1 in Figs. 1(a)–1(c) show the INS spectra for the sample with HDO water. The stretching mode peak now consists of only one peak at 405 meV. Because the neutron scattering cross section of the deuterium atom is much smaller than that of hydrogen, the O-D stretching peak is invisible in the INS spectrum. The disappearance of the high-energy stretching mode peak (at 440 meV) proves that deuterium and hydrogen atoms really occupy the positions corresponding to the strong and weak covalent bonds, respectively. As long as the force constant of the vibrating particle is proportional to the square of the corresponding frequency, the observed difference in the water stretching modes should correspond to about 18% difference in the strength of the corresponding covalent bonds, $(440/405)^2=1.18$. The intramolecular H-O-H bending mode peak shifts to lower energy, and its position (at ~ 185 meV) corresponds to the known bending mode peak in the HDO molecule (see, e.g., Ref. 11).

At low energies, there is a strong increase in intensity of the peak at 8 meV. Assuming that in $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$ hydrogen occupies the position corresponding to the weak covalent bond, its INS spectrum will correspond to the partial vibrational density of states in the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ sample for a hydrogen atom with a weak covalent bond. The partial density of vibrational states for hydrogen with a strong covalent bond can be estimated by subtracting half of the spectrum for $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$ (curves 3 in Fig. 1) from the spectrum for the $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ sample. This difference [curve 4 in Fig. 1(a)] does not show the peak at 8 meV. We suppose that the strong water covalent bond relates to the hydrogen atom positions out of the *ab* plane (with the corresponding weak hydrogen bond due to interaction with oxygen in the CoO_2 layer), and the weak covalent bond relates to the water O-H bond in the *ab* plane (due to

the relatively strong hydrogen bond with another water molecule in the water layer, similar to that in ice-Ih). As a result, the vibrations involving the water molecules in the *ab* plane exhibit an acoustical peak similar to that in ice-Ih. The acoustical vibrations involving water molecules out of the *ab* plane reflect mainly the vibrations of the entire lattice, and have an acoustical peak around 20 meV. In the range of the librational band, the peaks corresponding to the strong covalent bond (out of the *ab* plane hydrogen) are sharper (like local modes) due to the absence of hydrogen bonds between this kind of O-H groups, while the librations involving weak water O-H covalent bonds (and, consequently, strong hydrogen bonds) are more featureless due to the collective character of vibrations of $\text{H-O} \cdots \text{H-O} \cdots \text{H-O} \cdots$ chains in the *ab* plane (more like in ice-Ih).

To summarize, the vibrational spectra of water molecules in the hydrated sodium cobalt oxide superconductor were studied by inelastic neutron scattering in the entire range of possible one phonon excitations, up to 500 meV. The INS spectra of $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and $\text{Na}_{0.3}\text{CoO}_2 \cdot 1.3\text{HDO}$ compounds revealed two different covalent bonds in the water molecule: a strong one for hydrogen placed close to the CoO_2 layer, and a weak one in the O-H layer, with a strong hydrogen bond between water molecules. The observed strong asymmetry of the water molecule in the hydrated sodium cobalt oxide should correspond to the strong asymmetry of charge distribution around the water molecule. A proper reproduction of this picture in *ab initio* simulations will be a guarantee of their validity; these simulations can then be used for a description of the superconductivity of the material.

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