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Synthesis and high-pressure behavior of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ and related phases

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We have prepared powder samples of $Na_xCoO_2 \cdot yH_2O$ using an alternative synthesis route. Superconductivity was observed in $Na_{0.3}CoO_2 \cdot 1.3H_2O$ between 4 and 5 K as indicated by the magnetic susceptibility. The bulk compressibilities of $Na_{0.3}CoO_2 \cdot 1.3H_2O$, $Na_{0.3}CoO_2 \cdot 0.6H_2O$, and $Na_{0.3}CoO_2$ were determined using a diamond anvil cell and synchrotron powder diffraction. Chemical changes occurring under pressure when using different pressure-transmitting media are discussed and further transport measurements are advocated.

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The observation of superconductivity in $Na_{0.3}CoO_2 \cdot 1.3H_2O$ below 5 K (Ref. 1) has sparked interest in this system since this is the second known case where superconductivity arises from doping a Mott insulator. The CoO_2 lattice is such a frustrated triangular spin system and provided the initial line of reasoning for Anderson's resonating valence bond model.[2] A number of authors propose a d-wave-type pairing based on these ideas,[3] while others argue that the proximity to a ferromagnetic state favor a p-wave-pairing mechanism.[4] The crystal structures of the $Na_xCoO_2 \cdot yH_2O$ family are built up of hexagonal layers composed of x nonmagnetic Co^{3+} and $1-x$ low-spin Co^{4+} $(S=1/2)$ ions that are separated by a "charge reservoir" of $Na_x(H_2O)_y$. The role of this "charge reservoir" is not at all clear and further chemical and physical modifications are required to probe the stability field of this superconducting family. We show here that pressure-induced intercalation can be used to alter and distort the hexagonal structure, thus providing us an opportunity to probe the structural prerequisites for superconductivity in this family of compounds.

Early on it was realized that these materials are extremely sensitive to variations of their water content when handled without special precautions in the atmosphere.[5,6] Furthermore, the original synthesis[1] of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ relies on the deintercalation of Na using Br_2 in acetonitrile (flash point$=42\,°F$). In attempts to scale up the amounts of product and avoid the associated environmental hazards when manipulating large amounts of high concentrations of bromine, alternative synthetic routes are called for. Chou *et al.*[7] used an electrochemical route for the deintercalation step that allows better control of the Na content. We report here that superconducting powder samples of large quantities can be made by using $Na_2S_2O_8$ for the oxidation and deintercalation step: the precursor material $Na_{0.7}CoO_2$ was obtained by heating a mixture of Na_2CO_3 with a 10 mol % excess (Alfa & Fischer, 99.5% pure) and Co_3O_4 (Alfa, 99.7% pure) at 850 °C for 8 h under $O_2(g)$ flow. $Na_xCoO_2 \cdot yH_2O$ was then made using $Na_2S_2O_8$ in aqueous solution using an equimolar ratio with $Na_{0.7}CoO_2$ by stirring for 22 h in a beaker covered with a Parafilm™. For more mechanistic details see Refs. 8 and 9. Using 4–5 drops of $1N$ NH_4OH in 20 ml deionized (DI) water (pH$\sim$10.5) allowed us to reproducibly obtain $Na_{0.3}CoO_2 \cdot 1.3H_2O$. Figure 1 shows that the variation of pH is crucial for obtaining the superconducting phase. An optimal pH to obtain the superconducting $Na_{0.3}CoO_2 \cdot 1.3H_2O$ phase was found to be close to 10.5. The advantages of this synthesis are that large amounts of sample can be made; it is environmentally benign and uses only water as a solvent. All samples were placed in humidified containers and characterized by x-ray powder diffraction. For comparison we also prepared samples using bromine for the deintercalation/oxidation step. A SQUID magnetometer (Quantum Design) was used to determine the magnetic susceptibility as a function of temperature. Figure 2 compares a sample of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ made (a) via the $Na_2S_2O_8$ route with one made (b) using the bromine/acetonitrile route. We observe a slightly earlier onset of superconductivity in the latter and attribute this to minute variations of the Na content.[8]

All samples used for the high-pressure x-ray powder diffraction studies were made using the $Na_2S_2O_8$ synthesis route. *In situ* high-pressure powder diffraction experiments were performed using a diamond anvil cell (DAC) at beamline X7A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The detailed setup is

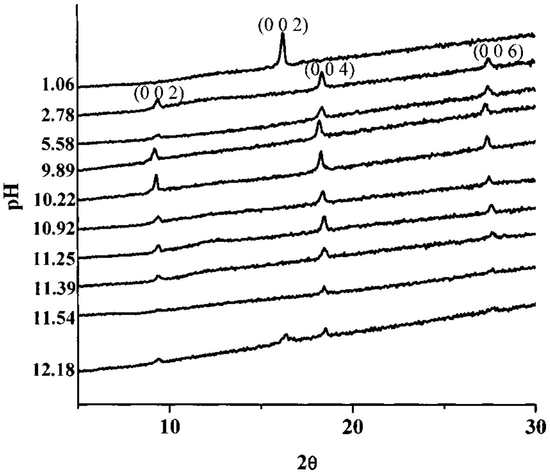

FIG. 1. Powder x-ray diffraction patterns (Cu $K\alpha$ radiation) for $Na_xCoO_2 \cdot yH_2O$ phases prepared using $Na_2S_2O_8$ as a function of pH.

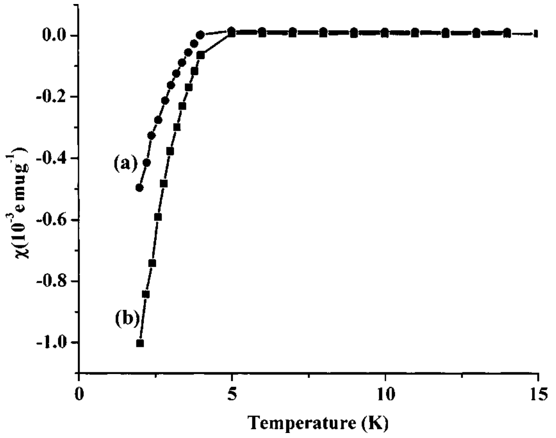

FIG. 2. Magnetic susceptibility of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ prepared (a) via the $Na_2S_2O_8$ synthesis route and (b) using Br_2/acteonitrile.

described elsewhere.[9] Due to the extreme moisture sensitivity of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ it was necessary to contain the sample in a wet environment prior to loading in the diamond anvil cell. Furthermore, care was taken to minimize the exposure time to the atmosphere during loading. Initially a methanol:ethanol:water mixture of 16:3:1 by volume was used as a pressure-transmitting fluid to ensure hydrostaticity. However, we noticed a phase transition from the hexagonal to a monoclinic phase already at very low pressures ($\sim$0.15 GPa) (Fig. 3) as well as an initial increase of the a axis of the monoclinic cell. When changing the pressure-transmitting fluid to Fluorinert™ no phase transition or intercalation under pressure is observed. It is noteworthy that this intercalation affects the basal plane of the monoclinic distorted hexagonal unit cell and not the c axis. This could be related to an increase of the Na coordination number from six to seven within the charge reservoir as is frequently observed in Na-containing zeolites under conditions where pressure-induced hydration occurs.[10] The pressure on the sample was measured by detecting the shift of the $R1$ emission line of the included ruby chips.[11] In our experiments, no evidence of nonhydrostatic behavior or pressure anisotropy was detected, and the $R1$ peaks of 3 to 4 included ruby chips remained strong and sharp with deviations less than ± 0.1 GPa. The hydrostatic limit for Fluorinert™ is generally quoted to be ca. 1.5 GPa,[12,13] but others report extended hydrostaticity when the samples are softer than the glass that Fluorinert forms under pressure.[14] Flourinert™ was also used in the determination of the effect of hydrostatic pressure on the superconducting transition temperature $d \ln T_c/dp$ by Lorenz *et al.*[15] Bulk moduli were determined by fitting the normalized volumes to a second-order Birch-Murnaghan equation of state[16] using a fixed pressure derivative of 4.

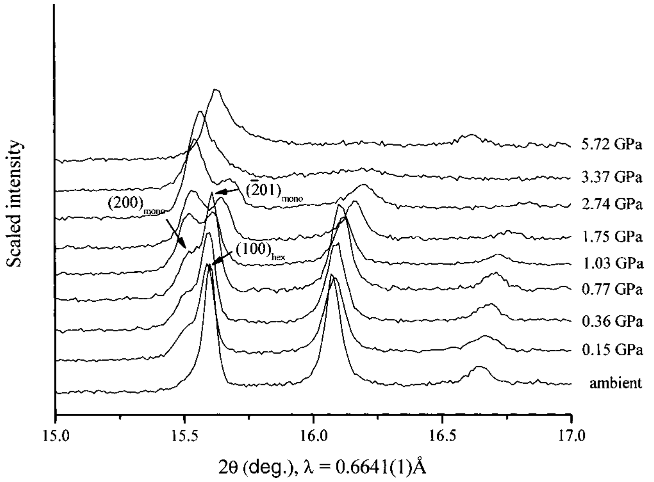

FIG. 3. Pressure-induced changes of the x-ray powder diffraction patterns of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ when using an alcohol/water mixture as a pressure-transmitting fluid.

The derived bulk compressibilities of 43(2) GPa, 90(6) GPa, and 101(3) GPa for $\{x=0.3, y=1.3\}$, $\{x=0.3, y=0.6\}$, and $\{x=0.3, y=0\}$, respectively, show the expected higher compressibility of the superconductor compared to the doped metal oxide $\{x=0.3, y=0\}$ as well as the intermediate $\{x=0.3, y=0.6\}$ oxyhydrate (Fig. 4). Lorenz *et al.*[15] showed that dT_c/dp is negative and nonlinear up to 1.6 GPa. Interestingly enough $d \ln T_c/dp \sim -0.07$ GPa is, as was pointed out, similar to values observed in electron-doped cuprates.[15] Despite the low T_c $Na_{0.3}CoO_2 \cdot 1.3H_2O$ appears to behave according to the universal relationship[17] between $d \ln T_c/dp$ and T_c established for high-T_c superconductors. The structures show a very strong anisotropy under pressure: in all cases the c axis is the most compressible direction, whereas the a axes show only a marginal decrease with pressure (see Fig. 4 for details). However, when intercalating extra molecules under pressure (alcohols or water), the structure distorts and the former hexagonal basal plane expands slightly under pressure in both $Na_{0.3}CoO_2 \cdot 1.3H_2O$ and $Na_{0.3}CoO_2 \cdot 0.6H_2O$. The bulk moduli of the monoclinic phases measured when using the methanol:ethanol:water mixture as the pressure-transmitting fluid are about 15–30 % higher than those obtained for the hexagonal phases using Flourinert™ [Figs. 4(a) and 4(b)]. This is in contrast to other observed framework structures altered by intercalation under pressure.[10,14] The linear compressibilities along the CoO_2 layers, however, indicate that the monoclinic phases are more compressible than the corresponding hexagonal phases [Figs. 4(a) and 4(b)]. Full release of pressure and subsequent exposure of the $Na_{0.3}CoO_2 \cdot 1.3H_2O$ sample to the laboratory humidity conditions ($\sim$25% relative humidity) resulted in a gradual deintercalation, and after 1 day of exposure to air a $Na_{0.3}CoO_2 \cdot 0.6H_2O$ phase formed. We encourage repeating the measurements of the pressure dependence on T_c using methanol:ethanol:water as the pressure-transmitting medium to probe if the observed monoclinic phase is also superconducting and to understand how the expansion of the (a,b) plane influences the electronic properties.

In summary, we have found an alternative environmentally benign synthesis route for the superconductors of the $Na_xCoO_2 \cdot yH_2O$ family ($x \sim 0.3$). Furthermore, we have determined the intrinsic bulk compressibilities of $Na_{0.3}CoO_2 \cdot 1.3H_2O$, $Na_{0.3}CoO_2 \cdot 0.6H_2O$, and $Na_{0.3}CoO_2$. A monoclinic distortion of $Na_{0.3}CoO_2 \cdot 1.3H_2O$ was found to occur at very low pressures when using an alcohol:water mixture as a pressure-transmitting fluid. Magnetic suscepti-

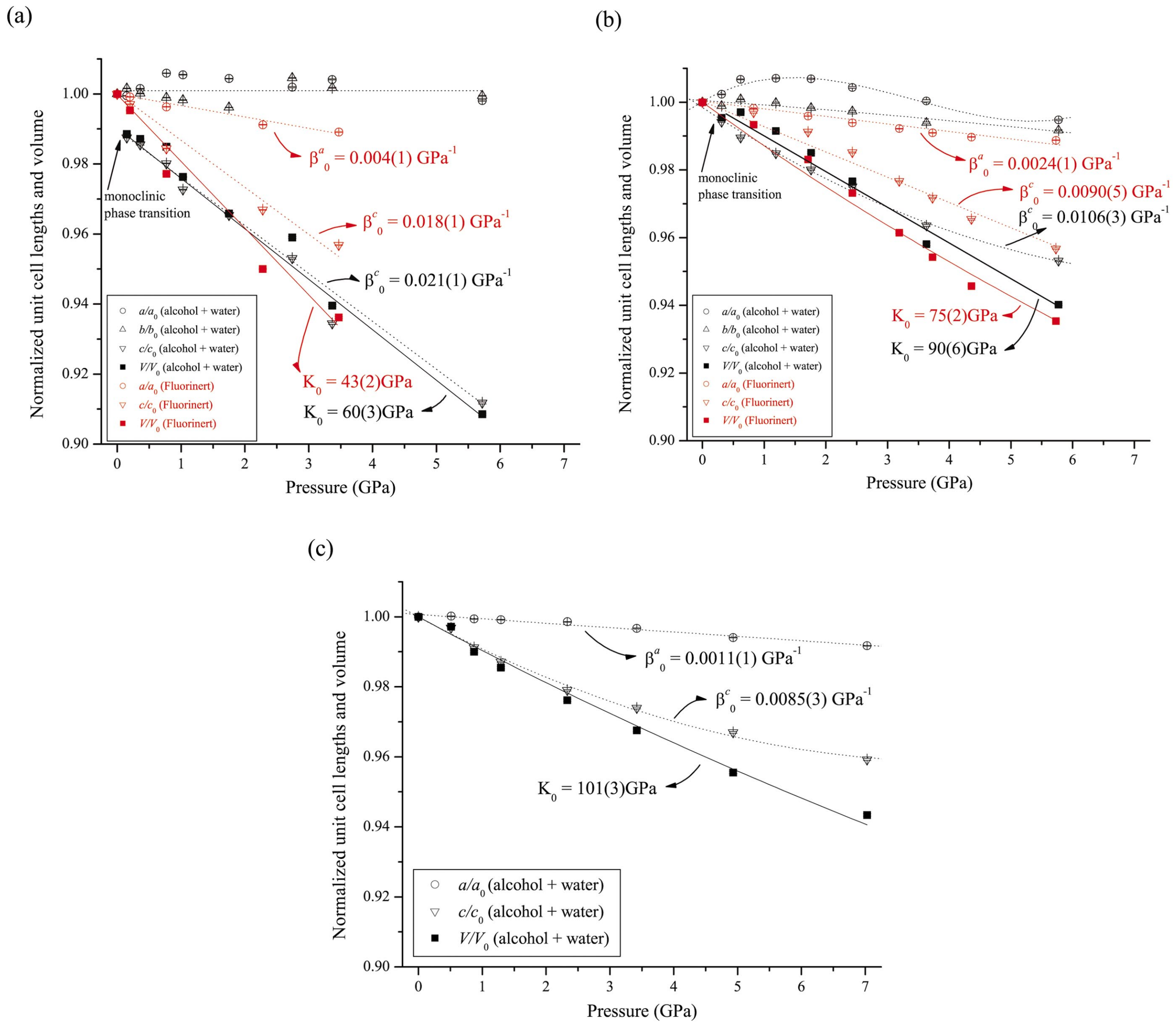

FIG. 4. (Color) Unit cell volume and axis compressibilities of (a) $Na_{0.3}CoO_2 \cdot 1.3H_2O$, (b) $Na_{0.3}CoO_2 \cdot 0.6H_2O$, and (c) $Na_{0.3}CoO_2$. The hydrates were measured using Flourinert™ (data in red) and an alcohol/water mixture as the pressure-transmitting fluid (data in black).

bility and resistivity measurements of this pressure-stabilized phase could provide valuable information about this fascinating new family of superconductors and its stability field.

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