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Competing Magnetism and Superconductivity in Na_xCoO_2 at Half Doping

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Na_xCoO_2 is a classic material that has been intensively investigated in the past as a potential cathode for solid-state batteries and as a thermoelectric system.[1,2] The discovery in 2003[3] of superconductivity (SC) in the hydrated $x = 0.3$ phase renewed the interest in the basic properties of this compound and challenged our understanding of the phenomenon of SC. For example, although H_2O is essential for the achievement of SC, its precise role is still the subject of strong debate. The same occurs with the mechanism of electron pairing, in which magnetic fluctuations have been speculated to be very important.

Here we show that superconductivity can be induced in $Na_{0.51}CoO_2$ after suppression of the magnetic order by topotactic $H_3O^+-Na^+$ exchange. This finding not only suggests that the development of superconductivity in hydrated Na_xCoO_2 competes with the development of a magnetic phase but also makes an interesting link with the properties of the recently discovered superconducting Fe oxypnictide.[4]

The two metallic states characteristic of Na_xCoO_2, one at high x ($x = 0.7$) and the other at low x ($x = 0.3$), are separated at 0 K by a singular point at around half doping in which a spin density wave (SDW) develops.[5] On the other hand, it was proposed that water insertion into the $x = 0.3$ composition results in a partial reduction of the $Co^{3+/4+}$ redox couple[6−8] and hence that SC could be occurring closer to half doping (and to the magnetically ordered phase) than normally thought. Of importance in regard to this point is the report by Sakurai et al.[8,13] that topotactic replacement of Na^+ by H_3O^+ results in a constant Co^{3+}/Co^{4+} ratio but produces a strong variation of the magnetic susceptibility. This shows that water plays a combined role of stabilizing the Co oxidation state while reducing the effective dimensionality of the system. Inspired by these works, we carried out a direct replacement of H_3O^+ by Na^+ in the magnetically ordered phase at $x = 0.5$.

Figure 1 shows the temperature dependence of the absolute electrical resistance and the zero-field-cooled−field-cooled (ZFC−FC) magnetization curves in $Na_{0.51}CoO_2$. The results are similar to those reported by Shu et al.[9] for electrochemically deintercalated crystals. We would like to emphasize that we did not perform any additional annealing of the samples after Na^+ extraction and before the transport/magnetic experiments. This was done in order to prevent any possible rearrangement of Na^+, oxygen loss, etc., after the synthesis and to make the results similar to the process followed in single-crystals as much as possible. Thus, only the relative changes in the resistance should be considered, not its absolute value. The increase in the electrical resistance is reminiscent of a charge-ordering (CO) effect below ~45 K, similar to the one reported in single crystals.[5] The increase in the resistance below T_{CO} is very modest compared with that in single crystals, probably because of the extrinsic effect of intergrain boundary scattering.

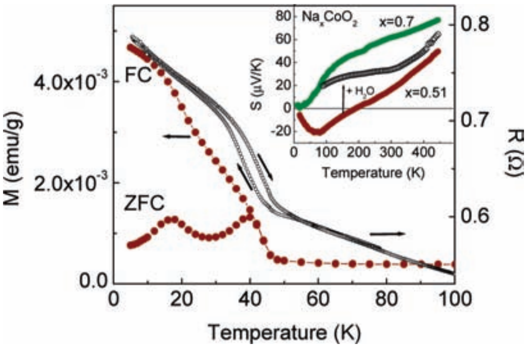

Figure 1. ZFC−FC magnetization curves at $H = 100$ Oe (brown ●) and electrical resistance of $Na_{0.51}CoO_2$ (black ☐). Inset: Temperature dependence of the Seebeck coefficient for various x. At $x \approx 0.5$, the thermopower becomes negative below ~200 K. Partial hydration at 25 °C results in a composition $Na_{0.41}(H_3O^+)_{0.1}CoO_2 \cdot 0.8H_2O$, which recovers the positive Seebeck coefficient.

On the other hand, intrinsic transport properties can be proved through the Seebeck coefficient, whose magnitude is not sensitive to intergrain scattering as no current flows through the sample. The results show a crossover toward negative values that is absent at larger concentrations of Na^+ (Figure 1 inset). This is consistent with a local change in the curvature of the $N(E_F)$ close to $x = 0.5$ due to partial gapping of the density of states that develops gradually as the temperature is reduced.

The increase in the electronic resistance is accompanied by a magnetic transition, indicating a partial spin polarization. Two additional magnetic transitions are observed at ~18 and ~86 K (the latter not visible on the scale of Figure 1), consistent with previous reports.[10] We also observed that none of the magnetic and electronic transitions discussed in this paper are influenced by fast quenching of the sample from room temperature to liquid He temperature. This observation discards any link between these transitions and a particular Na^+ arrangement, as has been discussed for other magnetic transitions at higher doping.[11] Also, room-temperature Na^+ deintercalation/intercalation in the $x = 0.51$ precursor has a clear effect on the magnetic phase transitions: the peak at ~45 K is partially lost and that at ~17 K decreases progressively (Figure 2). Both transitions are completely erased for $0.40 > x > 0.60$. Thus, the combination of these results indicates that the magnetic/electronic transitions observed at half-doping are intrinsic to the ratio $Co^{3+}/Co^{4+} \approx 1$.

On the other hand, Takada et al.[12] proposed that apart from intercalation of water molecules, the process of hydration involves the following chemical reaction:

$$Na_xCoO_2 + yH_2O \rightarrow Na_{x-y/2}(H_3O^+)_{y/2}CoO_2 + \frac{y}{2}NaOH$$

Keeping the medium slightly acidified results in an ionic exchange of Na^+ by H_3O^+. Since the hydronium ions occupy the same

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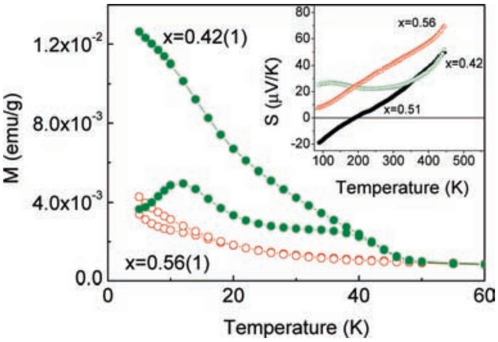

Figure 2. ZFC−FC magnetization curves at $H = 100$ Oe after subsequent Na^+ deintercalation (●) and intercalation (○) from $Na_{0.51}CoO_2$. Inset: Evolution of the Seebeck coefficient for Na^+-deintercalated/intercalated samples, showing the recovery of the positive values.

position as Na^+ between the layers,[11] the substitution occurs topotactically. Sakurai et al.[13] demonstrated that it is possible to go from a superconducting to a nonsuperconducting phase just by changing the H_3O^+/Na^+ ratio, without modifying the Co valence. Thus, the right formula to express the superconducting phase would be $Na_x(H_3O^+)_zCoO_2 \cdot yH_2O$.

In view of these results, we should be able to force the topotactic replacement of Na^+ by H_3O^+ in $Na_{0.51}CoO_2$. Because of the relevance of the $x = 0.5$ phase for a global understanding of the phase diagram of the system, it could be very important to verify whether a superconducting phase can condense directly from it after suppression of the SDW phase.

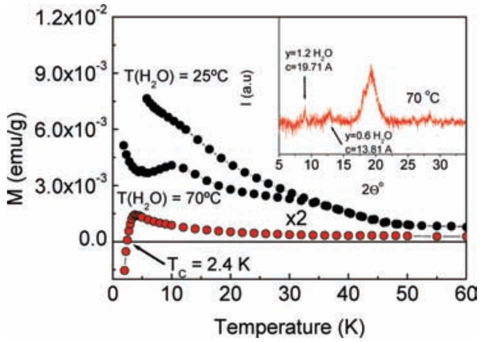

Figure 3. Magnetic response of the $Na_{0.51}CoO_2$ sample after water insertion at 25 and 70 °C. The susceptibility of the superconducting phase was rescaled (2×) for clarity. Inset: X-ray patterns of the superconducting sample. The *c* axis and water content are indicated for two different phases.

A sample of $Na_{0.51}CoO_2$ was stirred in water for 4 days at room temperature. After this process, the magnetic transitions were weakened and displaced toward lower temperatures relative to those for $x = 0.51$ (Figure 3). The Na^+ and total H_2O content was determined by ICP-OES and TGA. This data, along with the dependence of the *c* axis on *y*, was used to determine a chemical composition (assuming the electrical neutrality of the samples) of $Na_{0.41}(H_3O^+)_{0.1}CoO_2 \cdot 0.8H_2O$. The fact that the magnetic response was very similar to that of dry $Na_{0.42}CoO_2$ (Figure 2) and that the Seebeck coefficient recovered positive values (Figure 1 inset) supports this composition. These results demonstrate that topotactic exchange of Na^+ by H_3O^+ keeps the valence of the $Co^{4+/3+}$ redox pair unchanged but weakens the SDW phase, probably through decreasing the interlayer coupling.

Iincreasing the time of hydration did not result in complete suppression of the magnetic transitions. Then, the sample of $Na_{0.51}CoO_2$ was kept in water at 70 °C for 4 days. In some cases, the magnetic transitions were completely erased after reaching the composition $Na_{0.38}(H_3O^+)_{0.13}CoO_2 \cdot 1.0H_2O$. But in other cases, the material underwent a superconducting transition at ~2.4 K (Figure 3). The combined TGA and X-ray analysis showed that the composition in the superconducting samples was approximately $Na_{0.38}(H_3O^+)_{0.13}CoO_2 \cdot 1.2H_2O$.

In any case, we have observed a mixture of phases with different degrees of hydration ($y = 0.6, 1.2$; Figure 3 inset), which makes difficult a more reliable determination of the amount of intercalated/substituted water in the superconducting phase. This was previously observed also in hydrated samples with lower Na content.[14] In view of our results, the phase diagram for this system should probably consider an SDW phase at an [electron]/[hole] ratio of ~1 that is progressively suppressed by a decrease of dimensionality (we never observed coexistence of the magnetic and superconducting phases). It also follows from our results that the right place to look for superconductivity through the introduction of neutral, nonaqueous spacers (e.g., supercritical CO_2) is probably $Na_{0.5}CoO_2$ rather than $Na_{0.3}CoO_2$. We hope to stimulate further studies in this direction.

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Supporting Information Available: Details of the synthesis of the polycrystalline samples of γ-$Na_{0.7}CoO_2$, X-ray pattern for Na_xCoO_2 ($x = 0.51, 0.7$) (Figure S1), details of the X-ray patterns for all of the samples (Figure S2) and the lattice parameters derived from their fits (Figure S3), TGA curves for hydrated samples (Figure S4), evolution of the X-ray patterns with hydration (Figure S5), and magnetization curves (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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