Role of Doping and Dimensionality in the Superconductivity of Na_xCoO_2

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We report a complete analysis of the formal $Co^{3+/4+}$ oxidation state in Na_xCoO_2, in the interval $0.31 \leq x \leq 0.69$. Iodometric titration and thermoelectric power confirm that a direct relationship between the Na content and the amount of Co^{3+} cannot be established in this system. Creation of a significant amount of oxygen vacancies accompanies Na-ion deintercalation, keeping the formal Co valence at 3.45+ for $x \leq 0.45$. In light of new thermoelectric power data which reveals important differences between the hydrated (superconducting) and nonhydrated (nonsuperconducting) samples, we propose here that water plays an important "chemical" role beyond that of a spacer between the CoO_2 layers.

Introduction

Superconductivity remains one of the most attractive and challenging areas of research in materials science. In this line, the recent report of superconductivity by Takada et al.[1] in hydrated Na_xCoO_2 has generated a huge activity and given an unprecedented impulse to the investigation of the fundamental properties of this system. However, an explanation of the role of the water in the occurrence of superconductivity in this material has remained elusive. Superconductivity was found after Na-ion deintercalation below $x \approx 0.42$ and subsequent hydration.[1,2] H_2O intercalates between the CoO_2 layers, increasing dramatically the lattice spacing and reducing the electronic dimensionality of the structure (the *c*-axis increases more than 50% over its original value). The proximity to a nonmetallic phase establishes a possible comparison to the hole-doped cuprates, but the CoO_2 planes in Na_xCoO_2 adopt a 2D hexagonal symmetry to give the first example of a superconductive system with such geometry. On the other hand, the dome-shaped T_C vs x curve reported by Schaak et al.[2] is now being challenged in a series of works[3,4] in which dimensionality is argued to have a strong influence on the appearance of superconductivity.

A systematic and extensive study of the formal valence state of Co versus Na and H_2O contents is lacking. Here we report that in the nonhydrated samples, the Co valence is much lower than that expected from the Na content. Both thermoelectric power and iodometric titration indicate that oxygen is progressively removed from the structure accompanying Na deintercalation. Our data point to an active role of H_2O in the determination of the number of carriers in the CoO_2 layers, and the removal of the oxygen vacancies that strongly perturb the periodic potential.

Experimental Section

Polycrystalline Na_xCoO_2 was prepared by a conventional solid-state reaction. Dried Na_2CO_3 and Co_3O_4 were thoroughly mixed in a molar ratio Na/Co = 0.7 in an Al_2O_3 crucible that was placed directly in a preheated furnace at 850 °C to avoid Na evaporation and fired for 12 h in air. A second heat treatment at 900 °C was carried out for 12 h in air. After each heat treatment the sample was slowly cooled to room temperature and reground. Na was chemically deintercalated from $Na_{0.67}CoO_2$ by stirring the powder in a Br_2/CH_3CN oxidizing solution for 5 days at room temperature. Different Br_2 excesses ($\times 1 - \times 100$) with respect to the stoichiometric amount needed to remove all of the Na were used in order to get a wide range of compositions. The products were washed several times with CH_3CN and acetone, and then dried under vacuum. The Na and Co contents of the phases were determined by inductively coupled plasma optical emission spectroscopy (ICP−OES). The analysis confirms that the amount of Na decreases systematically as the excess of Br_2 increases (Table 1).

The oxidation state of cobalt was determined for all the samples with the iodometric titration method. Superconducting samples were obtained by stirring Na_xCoO_2, $x < 0.45$, in water for 2 days at room temperature. Thermoelectric power was measured from 85 to 450 K in a homemade setup. Lattice parameters were calculated from the X-ray patterns after indexing all the reflections with Rietica.[5]

Results and Discussion

Na_xCoO_2 is a highly hygroscopic material which makes it very unstable under ambient conditions. This, and the

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Table 1. Results of the Chemical Analysis of Na_xCoO_2[a]

Na content, x	%Co^{3+}	oxygen content, $2 - \delta$	Br_2 excess
0.690(1)	89.0(1)	1.90(1)	
0.673(7)	77.3(7)	1.95(4)	
0.450(4)	61.0(4)	1.92(2)	×1
0.429(6)	58.9(6)	1.92(4)	×5
0.402(5)	56.6(5)	1.91(3)	×10
0.381(6)	58.1(6)	1.90(4)	×20
0.369(5)	53.8(5)	1.92(3)	×30
0.362(4)	54.2(4)	1.91(2)	×40
0.322(4)	52.2(4)	1.90(2)	×50
0.310(3)	57.0(3)	1.87(2)	×100

[a] The first two samples correspond to the parent phase synthesized in slightly different conditions of temperature.

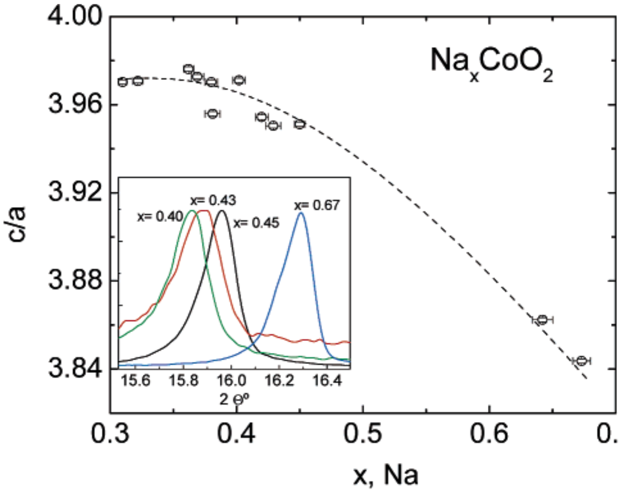

Figure 1. Evolution of the c/a lattice parameters in Na_xCoO_2, for the majority phase $P6_3/mmc$. Inset: Displacement of the (002) reflection in $P6_3/mmc$ with Na content.

unavoidable Na evaporation during the high-temperature synthesis, reduces control over the final stoichiometry and prevents a good characterization of the intrinsic and structural properties for a wide range of x. So, although the unit cell for the most stable phase, $x \approx 0.67$, is considered hexagonal with space group $P6_3/mmc$ (No. 184), hexagonal $R3m$ (No. 160) and monoclinic $C2/m$ (No. 12) have been reported for nearly the same composition.[6] Moreover, ordering of Na vacancies may change the symmetry. In the case of superconducting samples the complexity and controversy are even bigger because a mixture of fully and partially hydrated phases normally coexist in the same specimen.[3]

We confirmed that the best fits of our powder diffractograms of the parent phase, $x = 0.67$ and 0.69, were achieved on the basis of a single phase with space group $P6_3/mmc$. On the other hand, to get a good fitting of the diffractograms corresponding to the Na-deintercalated samples, two new minority phases of the hexagonal space groups, $P6_3/m$ (No. 176) and $P6/m$ (No. 175), must be considered in addition to the $P6_3/mmc$ majority phase. The ratio of the c/a lattice parameters as a function of the Na content are shown in Figure 1 for the majority phase. A significant increase of the c-axis lattice parameter is observed with decreasing Na content (see the displacement of the (002) reflection in the inset of Figure 1) while the a-axis parameter decreases slightly, but continuously over all the sodium content range. This appreciable expansion of the unit cell along the c-axis is due to the decrease in bonding between the CoO_2 layers as Na is removed. Surprisingly, the expansion of the c-axis parameter is less marked below $x \approx 0.4$, leading to an approximately constant c/a ratio down to $x \approx 0.3$. A similar effect was reported in the related material Li_xCoO_2 and was ascribed to the growing amount of oxygen vacancies that accompanies Li^+ deintercalation.[7] It is of fundamental relevance for the understanding of the magnetic/transport properties of this material to know whether a significant amount of vacancies are also present in this case.

Some groups recently reported the presence of an oxygen content less than stoichiometric in both hydrated[8,9] and nonhydrated[8,10] samples of Na_xCoO_2. However, just a few, very specific compositions were studied in these works, and in the case of the hydrated samples the amount of water present which is not inserted between the layers is difficult to determine, and this introduces an important source of error. So, to determine the presence and extent of oxygen vacancies in this material, we have first carried out a meticulous determination of the Co oxidation state in the nonhydrated samples in a wide compositional range. Then, we have related the oxidation state (and hence their actual doping level) with the experimentally determined thermopower, which is very sensitive to the effective charge carrier concentration. This allowed us to infer an active role of H_2O in the superconducting samples beyond that of a simple lattice spacer.

We have determined the oxidation state as a function of Na for the nonhydrated samples in the range $0.310(3) \leq x \leq 0.690(1)$. The samples were dried, all the solutions were previously bubbled with Ar, and the volumetric titration was carried out quickly to avoid any ambient oxidation of I^-. Reproducible iodometric titrations were consistent with an oxidation state of $Co^{3+/4+}$ that is considerably lower (a larger amount of Co^{3+} and a smaller amount of Co^{4+}) than expected from the Na content determined by ICP−OES. The percentage of Co^{3+} determined experimentally is plotted in Figure 2 versus the Na content determined by ICP−OES.

The compound is always oxygen deficient, even at the largest doping probed in this work ($x = 0.69$), although the amount of oxygen vacancies increases very much below $x \approx 0.5$. In fact, deintercalation of Na below $x \approx 0.4$ has almost no effect in the final oxidation state of Co, which remains close to $\approx 3.45+$, down to at least 0.3, the lowest Na content probed in this work. The creation of an important number of oxygen vacancies below $x \approx 0.4$ and the consequent reduction of the expected charge of the metallic ions is also consistent with an almost constant c/a ratio (see Figure 1).

The loss of oxygen is made possible by a pinning of the $Co^{3+/4+}$:t_{2g} band at the top of the O^{2-}:$2p^6$ band. In this case,

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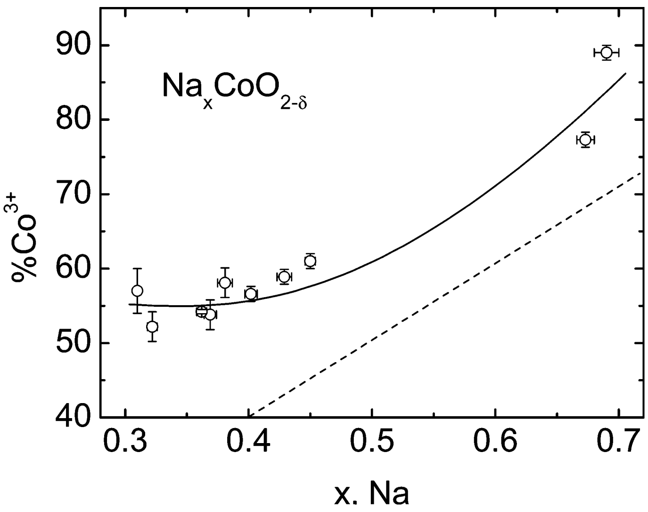

Figure 2. Actual Co^{3+} percentage as a function of the Na content. The solid line is a guide to the eye and the dotted line is the %Co^{3+} expected on the basis of the Na content, supposing a perfect oxygen stoichiometry of 2.00.

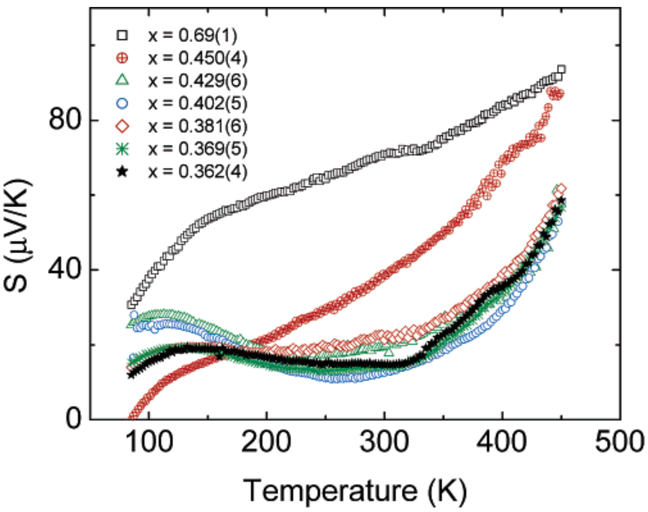

Figure 3. Evolution of the temperature dependence of the thermopower with Na content. Below $x \approx 0.42$, the thermopower does not show a strong dependence on the Na/Co ratio due to the invariance of doping at the CoO_2 planes in this range of x.

a redox process between the pairs $Co^{3+/4+}$ and O^{2-}/O_2 can occur when holes are actually introduced into the oxygen band. Marianetti et al.[11] proposed an alternative mechanism in which hole-doping at the t_{2g} band rehybridizates the e_g and O:2p orbitals, which produces an effective hole transfer to the oxygen band and hence the same global redox process described above.

This redox process $Co^{3+/4+} \leftrightarrow O^{2-}/O_2$ makes it extremely difficult to reach a good control over doping of the CoO_2 layers through variation of the Na content.

Similar results of oxygen migration were reported in Li_xCoO_2, where Venkatraman and Manthiram demonstrated that the maximum oxidation state for Co is also around 3.5 + even after all the Li^+ was removed from the structure.

To confirm our results we have carried out systematic measurement of the thermoelectric power in the same samples analyzed chemically. Thermopower is the most sensitive electronic transport property of a metal: it is very susceptible to variations in the number of carriers and gives direct information of the asymmetry of the density of states around the Fermi energy. The results for the system $Na_xCoO_{2-\delta}$ are shown in Figure 3.

The samples with high Na content present a thermoelectric power behavior similar to that previously reported by several authors.[12,13] The thermopower increases with temperature, but the value and the temperature dependence deviates from what in principle should be expected in a metal with such a low resistivity. As Na is removed, the thermopower decreases and becomes less temperature dependent, and in the low doping range it remains practically insensitive to variations in Na content. These measurements are fully consistent with the results obtained previously from iodometric titration analysis. The thermopower in the powder is dominated by the *ab*-plane[12] due to its higher conductivity; the influence of the dimensionality is low, so we are testing the variations in the number of charge carriers available for scattering in the electronically active CoO_2 planes (provided that the material remains metallic).[14] Hence, the invariance of the thermopower in the low doping region corroborates the inefficiency of Na removal to introduce charge carriers in the CoO_2 layers due to the oxygen loss process. Therefore, our results show unambiguously through two completely independent methods that a direct relationship between the Na content and the number of holes introduced into the CoO_2 planes does not exist in Na_xCoO_2. This effect is particularly dramatic at low doping ranges, where superconductivity is found after hydration. The parallelism with the cuprates in terms of out-of-plane doping control of the in-plane electronic charge is not completely valid in Na_xCoO_2, unless water plays an active role in the doping of the CoO_2 planes.

This opens two possibilities for the role of H_2O in the superconductivity. (1) *Structural role*: H_2O is a passive lattice spacer. Hydrated samples with lower Na content accept more H_2O and become more 2D than those with higher Na content, favoring superconductivity. However, Schaak et al.[2] found that although the *c*-axis expands in the superconducting samples when lowering the Na content, the amount of intercalated H_2O remains constant, about 1.3 molecules per formula unit, independent of *x*. Moreover, Shi et al.[15] reported a decreasing T_C with an increasing *c*-axis lattice parameter, reflecting the strong controversy among the results.

(2) *Chemical role*: H_2O plays an active role in the doping of the CoO_2 planes. If the oxygen of the intercalated H_2O enters the oxygen vacancies of the CoO_2 planes (as occurs for bound H_2O on the surface of an oxide particle), it gives its proton to the free interstitial water to create $(H_3O)^+$-ions, which reduce the CoO_2 sheets like the Na^+ ions. On the other hand, the bound O^{2-} ions from the water decrease the strong perturbations of the periodic potential created by the vacan-

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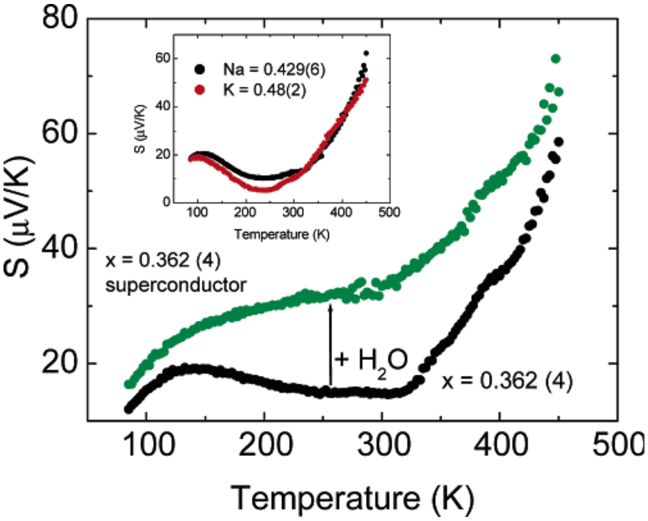

Figure 4. Variation in the thermopower due to water intercalation. The $Na_{0.36}CoO_{2-\delta}$ was stirred in water for 2 days, after what was found to be superconductor below 4 K. Inset: Temperature dependence of the thermopower of $Na_{0.429(6)}CoO_{2-\delta}$ and $K_{0.48(2)}CoO_{2-\delta}$.

cies, oxidizing at the same time the CoO_2 sheets. In fact, Karppinen et al.[8] reported a net increase in the oxidation state of Co as the hydrated superconducting phase is obtained from the corresponding nonhydrated one. If we assume that the water molecules intercalated between CoO_2 layers are electrically neutral and that the $(H_3O)^+$ ions are counterbalanced by the O^{2-} ions, a reduction of the oxygen vacancies and an increase of the oxidation state of Co would explain the continuous increase in the *c*-axis lattice parameter that it is observed in the hydrated samples as *x* is reduced, despite the constant amount of water introduced.[2]

To check this active role of intercalated H_2O in controlling the oxidation state of the CoO_2 planes, we have monitored the evolution of the thermopower as a nonsuperconductive sample is hydrated to render the superconductive phase. The results are plotted in Figure 4. We have measured the susceptibility of this hydrated sample, becoming superconductive below $T_C = 4$ K. It is important to note that the thermoelectric power only probes variations in the electronic structure of the material, and so any amount of water that is not introduced between the layers is not a source of error for this experiment. From the results previously obtained in dried samples (Figure 3) an increase of the thermopower in the superconducting sample (Figure 4) is consistent with a substantial change in the oxidation of the CoO_2 planes due to H_2O intercalation. Alternatively, the anisotropic expansion of the structure introduces the possibility of a change in the density of states at the Fermi energy, $N(E_F)$, due to the overlapping of the e^T and $a_1{}^T$ bands at E_F,[16,17] which could also contribute to the thermopower. To distinguish between these two possibilities, we have synthesized K_xCoO_2 (with structure identical to Na_xCoO_2 except for the interlayer space which is larger in the K sample) and compared the thermopower for two samples with almost identical composition (inset of Figure 4). The thermopower presents identical behavior in both materials irrespective of whether the interlayer spacer is Na^+ or K^+.

It is true that the increase in the *c*-axis parameter in the K samples with respect to the Na phase is much lower than in the hydrated superconductors, but the thermopower remains practically insensitive to the lattice spacer. This result makes us believe that a change in the oxidation state of the CoO_2 planes and the elimination of oxygen vacancies that strongly perturb the periodic potential by the introduction of H_2O is a realistic explanation of the role of the water in stabilizing the superconducting state.

After comparing Figures 3 and 4, the increase in the thermopower after water insertion could in principle be interpreted as a signature of reduction instead of oxidation. However, a conclusion like that could be completely erroneous, especially in a system where the population of more than one band crossing the Fermi energy is changing continuously. For this reason we do believe the change in the thermopower can be only indicative of the variation in the Co oxidation state but not of its sign, until a more complete study is performed to confirm this.

From our results it seems that the key for superconductivity is in a delicate balance between doping and dimensionality. Small variations in the doping and/or interlayer spacing will surely modify dramatically the $N(E_F)$ through the narrowing and relative position of the antibonding a^T band with respect to the E_F. The narrowing of this band will surely increase the Pauli susceptibility in the hydrated samples with respect to the nonhydrated ones.

Conclusions

We have demonstrated that below $x \approx 0.4$ in Na_xCoO_2, the formal oxidation state of Co remains constant around 3.45+, which indicates oxygen loss from the $CoO_{2-\delta}$ layers. We have argued that the water insertion allows the introduction of oxygen into the oxygen vacancies and that the acidic character of a Co^{4+}/Co^{3+} oxide would release hydrogen from OH^- groups on the $CoO_{2-2\delta}(OH)_{2\delta}$ layers to the interstitial H_2O to create H_3O^+ ions in the Na layers between CoO_2 layers. In this way the water removes the perturbation of the periodic potential in the CoO_2 layers and oxidizes them more deeply than is possible by Na^+-ion removal alone.

The role of lattice dimensionality is probably important in the occurrence of superconductivity in the hydrated samples by a modification of $N(E_F)$, but our experiments point to H_2O molecules playing a role other than a passive lattice spacer, with a direct implication in the control of the effective doping at the CoO_2 planes.

Note: Since first submission of this paper, Chen et al. [January 10, 2005 in cond-mat/0501181][18] reported the change of the formal valence of CoO_2 planes by oxonium ions.

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