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Revised Superconducting Phase Diagram of Hole-Doped $Na_x(H_3O)_z CoO_2 \cdot yH_2O$

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We have studied the superconducting phase diagram of $Na_xCoO_2 \cdot yH_2O$ as a function of electronic doping, characterizing our samples both in terms of Na content x and the Co valence state. Our findings are consistent with a recent report that intercalation of H_3O^+ ions into Na_xCoO_2, together with water, acts as an additional dopant, indicating that Na substoichiometry alone does not control the electronic doping of these materials. We find a superconducting phase diagram where optimal T_C is achieved through a Co valence range of 3.24–3.35, while T_C decreases for materials with a higher Co valence. The critical role of dimensionality in achieving superconductivity is highlighted by similarly doped nonsuperconducting anhydrous samples, differing from the superconducting hydrate only in interlayer spacing.

A characteristic feature of the cuprate superconductors is the existence of an optimal electronic doping that gives a maximum superconducting transition temperature, T_C. This composition separates the underdoped and over-doped regimes in which T_C decreases from the optimal value. This behavior is thought to be a universal characteristic of cuprate superconductors that arise from the fundamental origin of superconductivity in these systems. This feature of the cuprates has recently been tested for the layered intercalated cobaltate $Na_xCoO_2 \cdot yH_2O$ ($x \sim 0.35$ and $y \sim 1.3$) [1], which exhibits superconductivity below 5 K [2]. The structure of these layered cobaltates is significantly different from the cuprates, in that super-conductivity is thought to occurs in CoO_2 sheets that have quasi-2D triangular symmetry, analogous to that of geo-metrically frustrated systems. An initial superconducting phase diagram of $Na_xCoO_2 \cdot 1.3H_2O$ was drawn as a function of Na content x [1]. Schaak *et al.* demonstrated that such a phase diagram resembles the characteristic phase diagram of the cuprates in that an optimum $T_C = 4.5$ K is found for a material of Na content $x = 0.3$, with T_C rapidly decreasing for lower or higher Na contents [1].

The stoichiometry of this superconductor has recently been revised by Takada *et al.* [3] to account for a lower Co valence than that expected if the system is doped purely by Na nonstoichiometry. This work showed that charge neutrality is reached by the intercalation of oxonium ions (H_3O^+) along with water, giving a composition of the superconducting phase of $Na_{0.337}(H_3O)_{0.234}CoO_2 \cdot yH_2O$ [3]. Our examination of the superconducting phase dia-gram of $Na_x(H_3O)_z CoO_2 \cdot yH_2O$, where we determine the Co valence via redox titrations, demonstrates that the optimal T_C for this superconductor is obtained over a wide Co valence range, 3.24–3.35, while T_C decreases for samples with a Co valence >3.35. Although x-ray absorption and photoemission spectroscopy [4,5] have been applied to probe the electronic states of both the anhydrous and hydrated layered cobaltates and have identified Co^{3+} and Co^{4+} species, quantitative data are not attainable. In the absence of angle-resolved photo-emission spectroscopy data, to map the Fermi surface, simple titrations are an accurate and reliable technique to determine the Co valence. Similar methods have been applied to determine the valence of Cu in the cuprates [6].

The fundamental electronic and magnetic interactions in the parent compounds of the superconducting phase are tuned by the doping of $1 - x$ charge carriers on formation of substoichiometric Na_xCoO_2. In the stoichiometric $x = 1$ compound Co is in the Co^{3+} state with $S = 0$ in a low spin (LS) t_{2g}^6 configuration. For $x < 1$ the result is a mixed valence system $Na_xCo_x^{3+}Co_{1-x}^{4+}O_2$, where Co^{4+} has a LS $S = 1/2$ configuration with holes doped into a t_{2g}^5 state. This provides control for both the electronic and mag-netic properties of these materials in a natural way, where Na content x controls both the charge carrier concentra-tion and the amount of magnetic LS Co^{4+} ions. For example, the $x = 0.75$ compound has attracted attention due to its unusual thermoelectric properties [7–10], and it has recently been viewed as a correlated electron system with correlations driving coincident magnetic and elec-tronic transitions.

We have synthesized a series of samples with varying Na content x and have chemically characterized them in terms of both x, using neutron activation analysis, and the Co valence, using redox titrations. This has allowed us to accurately determine the parameters that control elec-tronic doping in these materials and draw the supercon-ducting phase diagram in terms of Co valence. Our measurements indicate that the amount of H_3O^+ that is intercalated into the lattice has an approximate inverse relationship with respect to the Na content x. We find that optimum T_C is achieved over the cobalt valence range of 3.24–3.35, while T_C decreases for valence states >3.35. Measurements of the c/a ratio of the lattice constants indicate that the separation between CoO_2 sheets in-
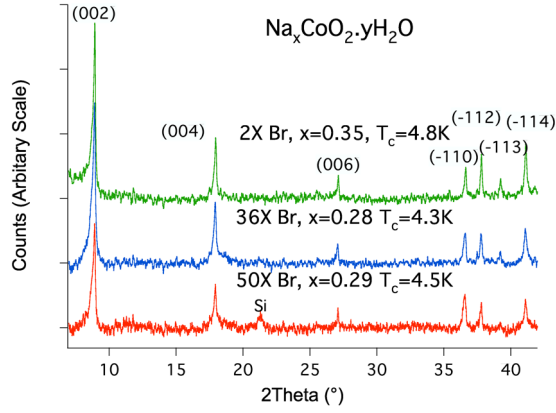
FIG. 1 (color online). XRD measurements of three hydrated samples prepared for this work. These measurements are typical of all the sample prepared in this work. The Si peak from the sample holder is indicated for the last diffraction pattern.

creases as the Co valence is tuned into the optimal region. This suggests that optimum T_C is achieved as the electronic interlayer coupling between CoO_2 sheets becomes more 2D-like.

Polycrystalline samples of Na_xCoO_2, $x \sim 0.70$, were first prepared by mixing appropriate amounts Na_2CO_3 and Co_3O_4 with a 10% molar excess of Na. These materials were heated to 850 °C in flowing oxygen for 36 h with two intermediate regrindings. This method yielded x-ray pure phases of $Na_{0.72}CoO_2$ (for determination of x, see below). In order to move from $x = 0.72$ to Na contents where superconductivity is observed, powder samples were immersed in a bromine-acetonitrile solution with a 2, 5, 36, and 50 times bromine excess as compared to Na. Samples were stirred in the solution for 24 h, after which they were washed with acetonitrile and then H_2O or D_2O. A time dependence study of the deintercalation process showed that it reaches completion within a few hours, as opposed to 5 d as suggested previously [1,2]. The Na/Co ratio of the products was measured using neutron activa-

tion analysis (NAA) to establish x [11]. To achieve superconductivity the Na deintercalated materials were placed in a sealed container with either H_2O or D_2O and evacuated to a pressure of ~ 20–30 mbar. Sample containers were kept at a constant temperature of 26 °C to produce a $p(H_2O)$ of ~ 40 mbar. Samples were left in a humid atmosphere for at least two weeks before final characterization measurements were made.

The valence of Co was measured directly by redox titration as described in Ref. [3]. As a check of the accuracy of this method, the Co valence of an anhydrous sample of $Na_{0.66(1)}CoO_2$ was measured to be 3.35, in excellent agreement with the $4 - x$ value determined from NAA. The error in the measurement of the Co valence is estimated to be 0.01. The crystal structure of these materials was probed using a Guinear x-ray diffractometer (XRD) with $CuK\alpha$ source and confirmed that all samples crystallized in a hexagonal structure as described by Takada *et al.* [2] and free of intermediate hydrate phases. Typical diffraction patterns from these samples are shown in Fig. 1. A Rietveld analysis of the XRD measurements was used to determine lattice constants for our samples. The Na/Co ratio of each sample was determined using NAA. The error in x from these measurements is estimated to be 5%. Superconducting properties were characterized using a quantum design SQUID magnetometer. In Table I we show the summary of our results from the characterization of our samples in terms of Na content x, Co valence, lattice constants, and superconducting transition temperatures.

As suggested by the results shown in Table I, there is a significant discrepancy between the expected valence of Co based purely on Na content and that given by redox titration. These observations are consistent with the revised composition of the superconducting phase where H_3O^+ accounts for the missing charge. From our measurements of x and the Co valence, we can determine the amount of H_3O^+ present in our samples. We find that there is a relationship between x and the Co valence, indicating

TABLE I. Details of the preparation, hydration medium, and characterization of the samples used in this work. The oxidation state of Co was determined for most samples used in this work from redox titrations. The superconducting transition temperatures, T_C, were determined using a SQUID magnetometer defining T_C as the onset of diamagnetism in ZFC and $H = 50$ Oe.

Br excess	x	Co^α	H_2O/D_2O	a (Å)	c (Å)	c/a	T_C
2	0.41	3.38	D_2O	2.8278(14)	19.561(2)	6.917(10)	2.8
2	0.37	$\cdots$	H_2O	2.8249(8)	19.657(2)	6.959(6)	4.5
5	0.37	3.45	$(H, D)_2O$	2.8257(8)	19.578(7)	6.928(6)	2.5
5	0.35	3.32	D_2O	2.8244(7)	19.656(6)	6.959(5)	4.8
5	0.35	3.33	H_2O	2.8231(6)	19.668(2)	6.967(4)	4.8
5	0.35	3.24	D_2O	2.8253(11)	19.676(8)	6.971(8)	4.7
36	0.32	3.27	D_2O	2.8231(10)	19.784(7)	7.008(7)	4.5
36	0.28	$\cdots$	H_2O	2.8251(9)	19.677(7)	6.965(7)	4.3
36	0.28	3.35	D_2O	2.8245(5)	19.726(9)	6.975(5)	4.3
50	0.29	$\cdots$	D_2O	2.8261(7)	19.653(7)	6.954(6)	4.5
50	0.29	3.26	D_2O	2.8233(4)	19.855(7)	7.033(4)	4.4

that Na poor samples tend to contain larger amounts of H_3O^+ [see inset of Fig. 3(b)]. This is consistent with recent structural measurements suggesting that Na^+ and H_3O^+ may reside on the same crystallographic site [3]. Our results show that, as Na is deintercalated from the lattice to values of $x < \frac{1}{2}$, a cobalt valence >3.5 is reached; the intercalation of H_3O^+, however, reduces the cobalt valence to values of <3.5 [3]. To determine the properties of this novel superconductor as a function of electronic doping, we have produced a series of samples with varying cobalt valence. By controlling the amount of Na chemically and measuring directly the Co valence, we have drawn a phase diagram using a series of samples over the broad range of cobalt valence 3.24–3.45.

Typical magnetization measurements of our samples are shown in Fig. 2(a). Here the zero field cooling (ZFC) dc magnetizations at 1.8 K are in the range of $M_{dc} = 0.7–1.6 \times 10^{-3}$ (emu/g/Oe) very similar to those obtained by other workers for similar T_C samples [1.8–5.5 $\times$ 10^{-3} (emu/g/Oe)] [1,2]. An estimation of superconducting volume fractions was performed using both field cooling (FC) and ZFC measurements as well as measurements of M versus H [see Fig. 2(b)]. Overall, we found values of the superconducting volume fraction to be in the range of 20% to 30%, indicative of bulk superconductivity for samples with cobalt valence states between 3.24 and 3.35. However, these values are only estimates, as there is a significant error in the measurement of the mass of the samples due to unbound intergranular water. This would tend to underestimate the superconducting volume fraction. Overall, the T_C values obtained in this work are relatively high (≥ 4.3 K), with the exception of two samples (see Table I) with $T_C = 2.5$ and 2.8 K. These two samples exhibited a low diamagnetic signal, and T_C

was measured using magnetic susceptibility measurements. In agreement with the measurements of Jin *et al.* [12], no clear difference is found between the T_C of hydrated and deuterated samples. Finally, we comment that the diamagnetic transitions of all samples are relatively broad in temperature, suggesting an appreciable degree of inhomogeneity. This behavior appears to be typical of these materials [1,12] and is understandable in view of the synthesis method of these superconductors.

The superconducting phase diagram of $Na_x(H_3O)_zCoO_2 \cdot yH_2O$ determined from our measurements is shown in Fig. 3(a). From these data, we find that optimal T_C is reached over the region of cobalt valence 3.24–3.35, while for cobalt valence states >3.35, T_C decrease to values of <3 K. In the optimal cobalt valence region, T_C differs from 4.3 to 4.8 K values close to the maximum values of T_C reported for this material [2].

The cobalt valence is a reflection of the electronic doping in the material. We can consider the cobalt valence range 3.0–3.5 as hole doped with respect to Co^{3+}, with the number of holes, n, equal to (valence state) $- 3$. Holes are doped in by removal of electrons from the upper lying, fully occupied, two electron t_2g band of Co in trigonally distorted CoO_2 sheets [see Fig. 3(a)]. Conversely, the cobalt valence range 3.5–4.0 can be con-
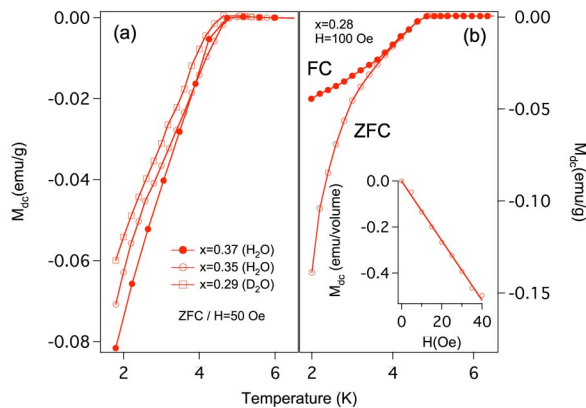
FIG. 2 (color online). Typical dc magnetization measurements of samples investigated in this work. (a) ZFC dc magnetization measurements in $H = 50$ Oe. (b) FC and ZFC measurements in $H = 100$ Oe for the $x = 0.28$ (D_2O) sample. The inset shows an M versus H measured from the $x = 0.35$ (D_2O) sample at 1.8 K. The data without corrections for pinning, shape, or excess water indicate a superconducting volume fraction of ~ 20%.
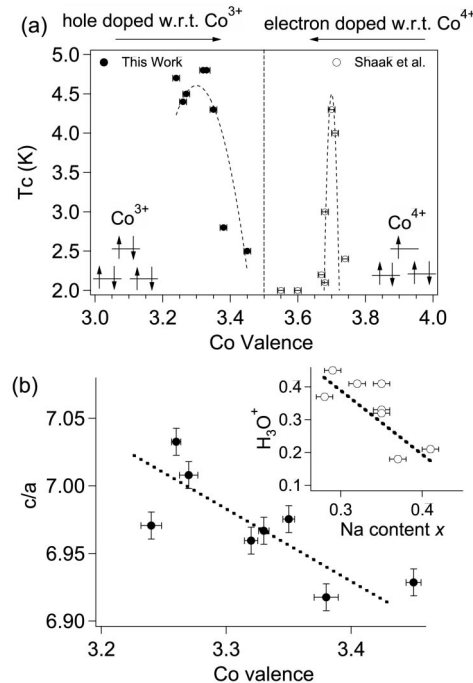
FIG. 3. (a) T_C as a function of the Co valence state given in Table I. The left curve was obtained from our titration data, while the right hand curve describes oxidation states based solely on Na content from Schaak *et al.* [1]. (b) The variation of the c/a ratio as a function of the cobalt oxidation state. In the inset, we show the variation of the H_3O^+ content of our samples as determined from measurements of the Na content and the Co oxidation state. Dashed lines are guides to the eye.

sidered as electron doped with respect to Co^{4+}, with the number of electrons determined as $4 -$ (valence state), with doped electrons entering the upper lying, half filled, two electron t_2g band.

The phase diagram that we draw here, by measuring the Co valence directly, demonstrates that superconductivity in these layered cobaltates occurs for hole-doped compositions and is in sharp contrast to the phase diagram of Schaak *et al.* [1], where the Co valence was thought to be controlled by Na content alone. The width of the superconducting region cannot be defined at this stage, as we have not been able to obtain underdoped samples; however, from the present data, we estimate it to be $\Delta n \sim 0.15$–0.2, a value actually similar to that found for hole-doped cuprate superconductors such as, for example, in $La_{1-x}Sr_xCuO_{4-\delta}$ [13]. Although our data suggest similarities with the band filling model of the cuprates, superconductivity in this system is observed on hole doping of a fully occupied band, as opposed to the hole doping of a half-filled band as found in the cuprates.

In Fig. 3(b) we show the variation of the ratio of the lattice constants (c/a) with Co valence, which suggests that the interlayer separation of CoO_2 sheets increases as the hole doping is varied through the optimal superconducting region [14]. The origin of these structural changes is not clear at this point, but, irrespectively, these data do suggest that the electronic interlayer coupling between CoO_2 sheets becomes more 2D-like as the hole doping is varied into the optimal doping region. This trend mirrors the overall behavior of these materials in that superconductivity is achieved only for a hydrated phase with $c \sim 19.8$ Å, while intermediate hydrate phases ($c \sim 12$ Å) [15] and anhydrous phases with a smaller interlayer spacing are not superconducting. We note here that the Co valence that we obtain here for superconducting compositions is similar to that of the nominally parent phase $Na_{0.7}CoO_2$ ($Co^{3.3+}$). This parent phase exhibits correlated electron behavior and may suggest that superconductivity arises by the modification of electronic correlations that are directly present in that phase. That T_C is found to be optimized for increasing interlayer separation we believe highlights the role of dimensionality and possibly a dimensionality crossover in these materials, as recently suggested by density-functional theory calculations [16]. Here the hydration of layered Na_xCoO_2 is suggested to result in a reduction in the local-density approximation band splitting as the interlayer coupling is reduced.

Finally, we suggest that it is possible that the broad plateau observed around optimal T_C may result from extrinsic effects arising from the standard method of preparation of these samples. In particular, the presence of compositional gradients due to the deintercalation of Na and intercalation of H_2O can result in samples containing a range of T_C's. We believe that the relative invariance of the superconducting volume fraction in our samples over the plateau region (see above) argues against the formation of a single point compound [17] with a single optimal T_C as the origin of this plateau region.

The measurements that we report in this Letter are critical in gaining a deeper understanding of the physics of this unusual superconductor. By measuring directly the Co valence of our samples, we have established the variation of T_C with electronic doping, considering both Na^+ and H_3O^+ contributions. We find a superconducting phase diagram where optimal T_C is obtained for a hole-doped Co^{3+} system, over the wide region of Co valence states 3.24–3.35, while T_C decreases for overdoped samples. These measurements suggest a band filling behavior similar to that of hole-doped cuprate superconductors may also be applicable here, although the electronic configurations are quite different. The key role of dimensionality in these layered cobaltates is highlighted by the increase of the separation between CoO_2 layers, as the cobalt valence is varied into the optimal T_C region. Our measurements show that hydrated superconductors and the anhydrous higher sodium content parent phases are similarly doped; however, the change of dimensionality on hydration appears to be critical in obtaining superconductivity. This points to a strong lattice coupling to the electronic degrees of freedom and makes the understanding of the physical properties of the anhydrous compounds more pressing.

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