

# Superconductor Cobaltites

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In this paper electronic and structural properties of Superconductor Cobaltite  $Na_xCoO_2 \cdot H_2O$  and its parent compound  $Na_xCoO_2$  will be summarized.

## INTRODUCTION

Since the discovery of high transition-temperature (high  $T_c$ ) superconductivity in layered copper oxides [1], they have held the pole position in the race for achieving higher  $T_c$  [2]. In this race many different compounds which contain copper oxide layers has been examined. Although there are reports of  $T_c$  s up to 185K for very rare phases of complex compounds like  $(Sn_{1.0}Pb_{0.5}In_{0.5})Ba_4Tm_5Cu_7O_{20+}$  [3] the highest  $T_c$  record for a single phase material belongs to  $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$  [4]. Even though the highest  $T_c$  reported is higher than the coldest temperature ever measured on earth it is still far below the room temperature.

As a result of the success of layered copper oxides, many researchers have searched for similar behavior in other layered metal oxides. Most of the attempts involving 3d-transition metals, such as nickel and cobalt have failed. But Takada et. al. [5] have reported that  $Na_xCoO_2 \cdot yH_2O$  ( $x \sim 0.35, y \sim 1.3$ ) is a superconductor with a  $T_c$  of about 5K. Despite its low  $T_c$  this material has attracted considerable attention because of the similarities and contrasts between it and copper oxides.

## PHASE DIAGRAMS

### Structure and Phase Diagram of $Na_xCoO_2$

Similar to its sister  $Li_xCoO_2$  which is commercially used in lithium-ion batteries,  $Na_xCoO_2$  ( $x \leq 1$ ) have been of interest for many years as battery cathodes. It has also been investigated for thermoelectric applications [7].  $Na_xCoO_2$  is composed of  $CoO_2$  layers which have a triangular lattice structure (Fig. 2) and Na ions which are sandwiched between  $CoO_2$  layers. (Fig. 1).

In this material the amount of Na can easily be changed, allowing the electronic and other properties to be chemically tuned over a wide range. The hole density in  $Na_xCoO_2$  may be increased by reducing the Na content  $x$ . In principle with  $x=1$  there are no holes on the lattice and they occupy every lattice site at  $x=1$ . Vary-

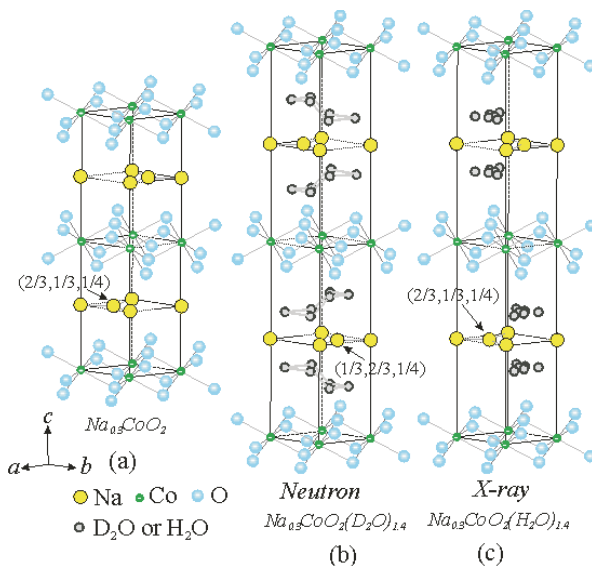


FIG. 1: Crystal structures [6].

ing the Na amount results with a phase diagram given in Fig. 3 [8] [9].

The most dominant feature of the phase diagram of nonhydrated  $Na_xCoO_2$  is the narrow insulating state at  $x=0.5$ . Below 0.5 the material is a paramagnetic metal with high conductivity. Samples with  $x$  close to  $2/3$  also have metallic resistivity. On the other hand their magnetic susceptibility displays a profile different than many metals. In a metal a very small fraction of electron spins can be aligned with a magnetic field and this fraction steadily goes to zero with decreasing temperature [10]. But in  $Na_xCoO_2$  the susceptible spin population is equal to the number of holes ( $\sim(1-x)$ ) and stays unchanged even at very low temperatures. Such a phase - metallic-like in charge conduction and insulator-like in spin alignment - is called 'Curie-Weiss metal' [8] [9] [11]. Figure 4 gives the susceptibility  $\chi$  and in-plane resistivity  $\rho$  of single crystals of  $Na_xCoO_2$  with different  $x$  values. In these figure it can be seen that for  $x \sim 2/3$ ,  $\chi$  vs T follows the Curie-Weiss law given as

$$\chi = \frac{C}{T + \Theta} \quad (1)$$

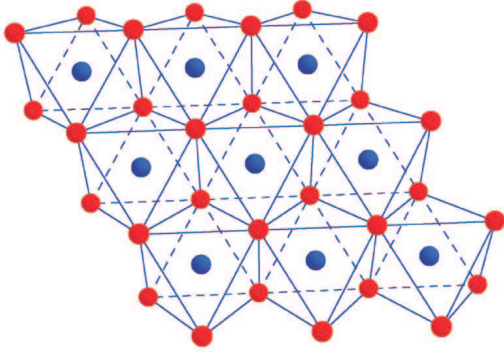


FIG. 2: Top-down view of a single  $CoO_2$  layer found in the cobalt oxide superconductor and related sodium cobalt oxide bronzes. In this hexagonal lattice blue represents the cobalt and red represents the oxygen atoms [2].

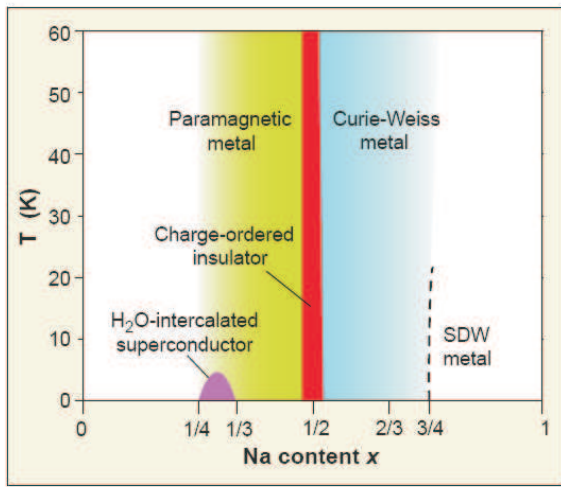


FIG. 3: Phase diagram of  $Na_xCoO_2$ . [9]

where  $\Theta \sim 70$  K. Furthermore, the metallic behavior of  $T$  dependence of  $\rho$  can be observed in this figure.

When the doping density is increased to  $3/4$  magnetic susceptibility shows a different character.  $\chi$  is slightly rounded below 20 K, consistent with the weak magnetization ( $M \sim 0.03 \mu_B$  per Co where  $\mu_B$  is the Bohr magneton). This phase is suggested to be a spin density wave metal [8].

In contrast to these metallic states, an insulating behavior abruptly appears at  $x=0.5$ . At this doping level  $\rho$  rises rapidly to reach  $\sim 20 m\Omega cm$  at 4 K which is 3 orders of magnitude larger than its neighboring metallic states. In order to accommodate both the strong Coulomb forces and geometric frustration caused by the triangular lattice, the holes firmly localize and cannot carry a current anymore. Electron-diffraction studies show that (Fig. 5) in this phase the Na ions order as a superstructure with lattice vectors  $a\sqrt{3}\hat{x}$  and  $2a\hat{y}$  (where  $a$  is the hexago-

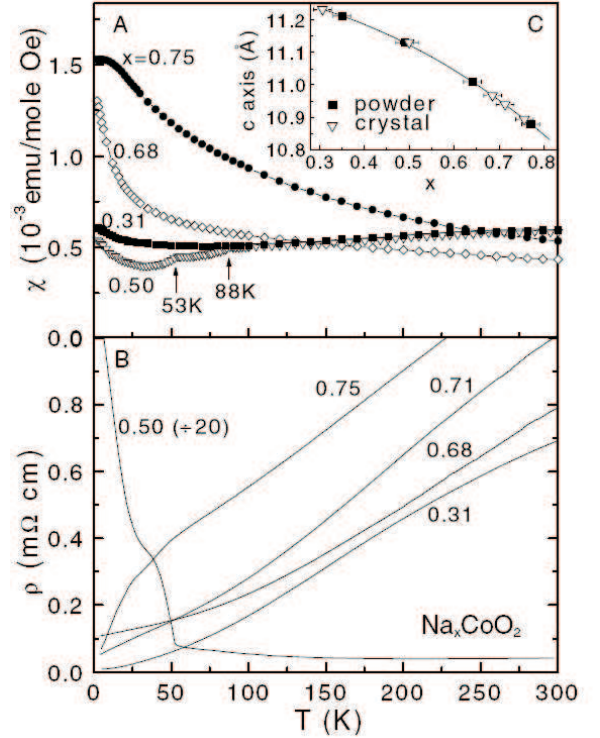


FIG. 4: The susceptibility  $\chi$  (a) and in-plane resistivity  $\rho$  (b) of single crystals of  $Na_xCoO_2$  with  $x$  determined by ICP (c) [8].

nal lattice parameter) in the basal plane. Also, polarized and unpolarized neutron scattering measurements of the magnetic order in single crystals of  $Na_{0.5}CoO_2$  indicates that below  $T = 88$  K the spins form a novel antiferromagnetic pattern within the  $CoO_2$  planes, consisting of alternating rows of ordered and non-ordered Co ions [12]. In this "charge-ordered insulator" phase Na ions order with a very long range correlation, confirmed with thermal conductivity and Hall resistance measurements, even at  $T \sim 300$  K.

Roger et. al [13] [9] have used single crystal neutron diffraction supported by numerical simulations to determine the long range three dimensional structures of these ions. They found stable phases at  $x=1/3$  and at  $x=1/2$  which is in agreement with the experimental observations [8] [6].

### Superconductivity in two dimensional $CoO_2$ layers

Superconductivity in the layered sodium cobalt oxyhydrate,  $Na_{0.35}CoO_2 \cdot 1.3H_2O$  was first reported by Takada et al. [5]. This compound consists of two dimensional  $CoO_2$  layers separated by a thick insulating layer of  $Na^+$

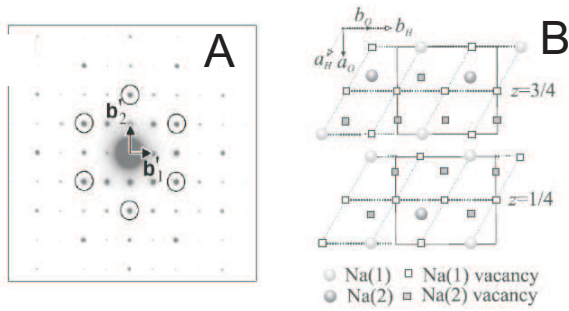


FIG. 5: room temperature electron diffraction pattern of non-hydrated  $Na_xCoO_2$  crystal with  $x = 1/2$  (A), and the Na superstructure lattice (B).

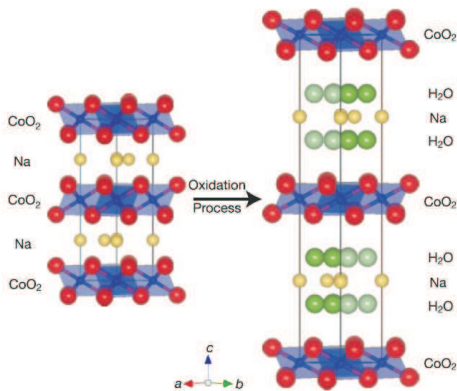


FIG. 6: Structural views of  $Na_{0.7}CoO_2$  (left) and  $Na_xCoO_2 \cdot yH_2O$  (right), where Na and  $H_2O$  sites are partially occupied [5]

ions and  $H_2O$  molecules (see Fig. 6). Similar to the cuprates  $CoO_2$  layers are electronically active while  $Na^+$  and  $H_2O$  layers act as charge reservoirs and provides quasi two-dimensionality of  $CoO_2$  layers.

$Na_xCoO_2 \cdot yH_2O$  is obtained through a chemical oxidation process from a parent compound of  $Na_{0.7}CoO_2$ . X-ray diffraction (XRD) patterns of the materials showed that the distance between succeeding  $CoO_2$  layers increased dramatically from 10.9628(8) to 19.6207(14). The marked increase in lattice constant  $c$  indicates the intercalation of  $H_2O$  molecules in the oxidation process in addition to the de-intercalation of  $Na^+$  ions. The water molecules in the structure play an essential role in the superconductivity both by enhancing the 2D character of the cobalt oxide planes and also by screening the strongly fluctuating electrostatic potential of Na ions from the charge carriers in the  $CoO_2$  layers.

A detailed study [14] of phase diagram of  $Na_xCoO_2 \cdot yH_2O$  showed that the superconducting phase is restricted to the narrow interval  $0.25 < x < 0.33$  (Fig.4). In

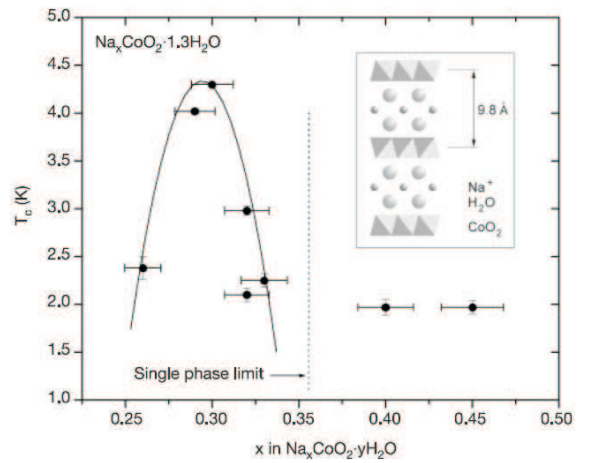


FIG. 7: The superconducting phase diagram for  $Na_xCoO_2 \cdot 1.3H_2O$ . Main panel,  $T_c$  as a function of  $x$  as determined from the a.c. susceptibility measurements. Inset, schematic representation of the layered crystal structure of  $Na_xCoO_2 \cdot 1.3H_2O$ . Triangular layers of  $CoO_6$  edge-shared octahedra are shown in a polyhedral representation. [14]

order to determine the  $T_c$  Schaak et al [14] have used a.c. susceptibility measurements which are more sensitive to weakly superconducting samples. They have found that  $x=0.3$  is the optimal sodium composition for the occurrence of superconductivity (see Fig. 7). They have also observed that the in-plane  $CoO_2$  dimensions ( $a=2.82 \text{ \AA}$ ) and the interlayer 'crystal water' content remains essentially constant (at  $\sim 1.3$  per formula unit) regardless of the sodium content.

Although  $Na_xCoO_2 \cdot yH_2O$  is a superconductor only below 5 K, it is an important material for better understanding high  $T_c$  superconductors. In parallel to its similarities with cuprates such as having transition metal oxide layers that have very weak inter-planar coupling, it also have many dissimilarity. The major differences in lattice geometry and the electronic structures ( especially the strength of mixing between the oxygen and transition metal levels ) may be pointing us that superconductivity is not restricted to very special cases. Recent discovery of iron based layered transition metal-oxide superconductors [15] also supports the idea that superconductivity is not a very rare property in materials world.

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- [1] J. G. Bednorz and K. A. Mller, Z. Phys. B **64**, 189 (1986).
- [2] J. V. Badding, Nature Materials **2**, 208 (2003).
- [3] a, [http://www.superconductors.org/185k\\_p.at.htm](http://www.superconductors.org/185k_p.at.htm).
- [4] P. Dai, B. C. Chakoumakos, G. F. Sun, K. W. Wong, Y. Xin, and D. F. Lu, Physica C:Superconductivity **243**, 201 (1995).
- [5] K. Takada, H. Sakurai, E. T. Muromachi, F. Izumi, R. A.

- Dilanian, and T. Sasaki, *Nature* **422**, 53 (2003).
- [6] Q. Huang, M. L. Foo, J. W. Lynn, H. W. Zandbergen, G. Lawes, Y. Wang, B. H. Toby, A. P. Ramirez, N. P. Ong, and R. J. Cava, *J. Phys. Condens. Matter* **16**, 5803 (2004).
- [7] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev B* **56**, 12865 (1997).
- [8] M. L. Foo, Y. Wang, S. Watauchi, H. W. Zandbergen, T. He, R. J. Cava, and N. P. Ong, *Phys. Rev. Lett* **92**, 247001 (2004).
- [9] N. P. Ong and R. J. Cava, *Science* **305**, 52 (2004).
- [10] H. Kojima, R. S. Tebble, and D. E. G. Williams, *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **260**, 237 (1961).
- [11] Y. Wang, N. S. Rogado, R. C. Cava, and N. P. Ong, *Nature* **423**, 425 (2003).
- [12] G. Gasparovic, R. A. Ott, J.-H. Cho, F. C. Chou, Y. Chu, J. W. Lynn, and Y. S. Lee, *Physical Review Letters* **96**, 046403 (2006).
- [13] M. Roger, D. J. P. Morris, D. A. Tennant, M. J. Gutmann, J. P. Goff, J.-U. Hoffmann, R. Feyerherm, E. Dudzik, D. Prabhakaran, A. T. Boothroyd, et al., *Nature* **445**, 631 (2007).
- [14] R. E. Schaak, T. Klimczuk, M. L. Foo, and R. J. Cava, *Nature* **424**, 527 (2003).
- [15] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, *J. AM. Chem. Soc.* **130**, 3296 (2008).