Superconductivity, charge ordering and structural properties of 
\( \alpha, \beta\)-Na\(_x\)CoO\(_2\)·y(H\(_2\)O, D\(_2\)O)

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Two series of \( \alpha\)- and \( \beta\)-Na\(_x\)CoO\(_2\) materials have been prepared by means of Na deintercalation from the parent \( \alpha\)-NaCoO\(_2\) and \( \beta\)-Na\(_0.6\)CoO\(_2\) phases, respectively. The \( \alpha\)-Na\(_x\)CoO\(_2\) materials undergo a clear phase transition from the hexagonal to the \( \beta\)-phase like monoclinic structure along with Na deintercalation. Measurements of resistivity and magnetization demonstrated the presence notable charge ordering transitions in both \( \alpha\)- and \( \beta\)-Na\(_x\)CoO\(_2\) with 0.4 < x < 0.5 below 100K. Bulk Superconductivity has been observed in the hydrated \( \alpha\)-Na\(_x\)CoO\(_2\)·1.3H\(_2\)O at ~4.5K and in \( \beta\)-Na\(_x\)CoO\(_2\)·1.3H\(_2\)O at ~4.3K. Intercalation of D\(_2\)O in \( \alpha\), \( \beta\)-Na\(_{0.33}\)CoO\(_2\) also yields superconductivity at slightly lower temperatures. It is worthy to note that, despite of the structural difference, the \( \alpha\)-, \( \beta\)- and \( \gamma\)-Na\(_x\)CoO\(_2\)·yH\(_2\)O materials show up notable commonalities in their essential physical properties, e.g. superconductivity and charge ordering transitions.

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Layered $\gamma$-Na$_x$CoO$_2$ system have been investigated systematically in the past years due to its particular properties of large thermoelectric power coexisting with low electric resistivity [1-4]. Recently, superconductivity in the water intercalated Na$_{0.3}$CoO$_2$·1.3H$_2$O ($\gamma$-phase) and complex charge-ordering (CO) transitions in $\gamma$-Na$_{0.5}$CoO$_2$ has been extensively investigated and discussed in connection with the strong electron correlation in present system [5-12]. Actually, there are three distinctive structural series of Na$_x$CoO$_2$ materials corresponding with the CoO$_6$ octahedra stacking differently along c-axis direction, so called $\alpha$-, $\beta$- and $\gamma$-phase respectively. In order to know the structural and physical properties, especially the superconductivity in $\alpha$, $\beta$-Na$_x$CoO$_2$ phases, we have performed an extensive study on samples with a variety of Na contents. Actually, a few works, concerning superconductivity in the hydrated $\alpha$- and $\beta$-Na$_x$CoO$_2$·yH$_2$O samples, have reported that $\alpha$-phase is a superconductor with $T_c \sim 4.6$ K [13] and, on the other hand, the water-intercalated $\beta$-Na$_x$CoO$_2$·yH$_2$O compound is likely to be not a superconductor [14]. In this paper, we will perform a systematical study on the $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials, certain notable properties are specially analyzed in comparison with the results obtained from $\gamma$-phase, i.e. structural transformation induced by Na-deintercalation, CO phenomenon at $x \cong 0.5$, and superconductivity in the hydrated $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials.

Polycrystalline samples of $\alpha$-NaCoO$_2$ were prepared by a conventional solid-state reaction [15]. Powdered cobalt (Co) metal (99.5%) and anhydrous NaOH pellets (Aldrich) in 10 molar excess (Na : Co = 1.1 : 1) were ground together under inert atmosphere and placed in an alumina boat under flowing O$_2$ for approximately 6 days at 500°C with one intermittent grinding. The parent material with nominal composition of $\beta$-Na$_{0.6}$CoO$_2$ was prepared by a similar process as described above for the $\alpha$-NaCoO$_2$: Co powder and NaOH pellets were mixed in a molar ratio of
Na : Co = 0.7 : 1 and ground together under flowing O₂ for approximately 5 days at 550°C with one intermediate grinding. Materials with lower Na contents were prepared by the sodium deintercalation [10]. Superconducting samples were synthesized by means of the Na-deintercalation to x ~ 0.3 and then the water intercalation as reported for the preparation of superconducting γ-NaₓCoO₂·1.3H₂O materials [5]. X-ray diffraction (XRD) measurements were carried out with a diffractometer in the Bragg-Brentano geometry using Cu Ka radiation. The compositions of all materials have been measured by inductively coupled plasma (ICP) analysis technique. Low-temperature magnetization measurements as a function of temperature were performed using a commercial Quantum Design SQUID. Transmission-electron microscopy (TEM) observations were performed on a H-9000NA TEM operating at the voltage of 300kV.

We first focus our attention on the structural evolution of the two series of samples prepared respectively from α-NaCoO₂ and β-Na₀.₆CoO₂ by the Na-deintercalation then the water intercalation for samples at around x = 0.3. Fig. 1(a) shows XRD patterns of the α-NaₓCoO₂ samples for several typical Na contents of x = 1.0, 0.48, 0.43 and 0.33. The diffraction pattern from the hydrated superconducting phase α-Na₀.₃₁CoO₂·1.3H₂O is also shown to illustrate an evident upsurge of c-axis parameter from H₂O intercalation. The parent α-NaCoO₂ phase has the O₃ structure containing three CoO₂ layers in an unit cell as reported in ref [13, 15, 16, 17], all diffraction peaks in its XRD pattern shown in fig. 1a can be well indexed on an hexagonal cell with the lattice parameters of a= 2.89Å and c= 15.59 Å (space group of R₃m). The strike structural feature noted in our XRD analysis is a remarkable structural transformation arising from Na-deintercalation; Actually, the well-defined hexagonal α-NaₓCoO₂ phase is found to be stable only for the Na content of 0.9 < x <1, and a monoclinic structural distortion appears
evidently in the Na-deintercalated materials as illustrated for the products with lower Na contents (table 1). In order to study the CO phenomenon in the α-NaxCoO2 system, we have made certain attempts to obtain samples with x ≈ 0.5 by using either I2 or Br2 in the Na deintercalation, ICP analysis indicated that the products have the compositions of Na0.46CoO2 and Na0.43CoO2, they both show up clear CO transitions at low temperatures as discussed in the following context. The XRD patterns of α-Na0.48CoO2, different apparently from that of α-NaCoO2 in XRD peak positions, corresponds a P’3 structure with the space group of C2/m and lattice parameters of a= 4.92Å, b= 5.63 Å, c= 17.36 Å and β= 105.98°. Another product α-Na0.43CoO2 has the same average structure with slightly different lattice parameters as demonstrated in the XRD pattern in fig. 1a. The Na deintercalated material α-Na0.31CoO2 is found to be highly sensitive to moisture and shows up visible hydrated feature quickly at the ambient atmosphere as illustrated in fig. 1a; the addition peaks as indicated by asterisks arise actually from the hydrated phase Na0.31CoO2·0.7H2O. This material was further washed in water and stored in a humidified atmosphere for about two days, we finally obtained the superconducting phase α-Na0.31CoO2·1.3H2O. This phase has a P’3-type structure (space group of R3m) with the lattice parameters of a= 2.82 Å, and c= 29.57 Å [13].

Fig. 1(b) shows the XRD patterns for the β-NaxCoO2 series of samples with different Na contents and H2O intercalations. The parent sample β-Na0.6CoO2, as reported in the previously literatures [14, 15, 18], has a P’3 structure (space group: C2/m). Systematical analysis on the XRD patterns for the β-NaxCoO2 materials, and also in comparison with our above investigation on the α-NaxCoO2 materials, suggest that materials prepared from the either α-NaCoO2 or β-Na0.6CoO2 have an identical structural properties for x < 0.5. Hence, our experimental results
directly suggest that the $O_3$-type hexagonal structure for the parent $\alpha$-NaCoO$_2$ phase is only stable in the high Na content range in agreement with the previous reported data [15]. In order to facilitate our analysis in present paper, we will still separately discuss the two series of samples obtained respectively from the $\alpha$-NaCoO$_2$ and $\beta$-Na$_{0.6}$CoO$_2$. In fig. 2b, we show the XRD patterns for two typical samples of $\beta$-Na$_{0.41}$CoO$_2$ and $\beta$-Na$_{0.29}$CoO$_2$, it can be clear recognized that the chief reflection peaks in the XRD patterns correspond perfectly with the known monoclinic structure (C2/m). The $\beta$-Na$_{0.29}$CoO$_2$ sample, as illustrated above for $\alpha$-Na$_{0.31}$CoO$_2$, is also easily hydrated at the ambient condition and gives rise to clear peaks from the hydrated phase as indicated by asterisks in fig. 1b.

In order to study the CO phenomenon in $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials, we have carefully prepared a number of samples with $x \sim 0.5$ by the Na-deintercalation, our experimental results demonstrated that all samples of $\alpha$- and $\beta$-Na$_x$CoO$_2$ with $0.4 < x < 0.5$ undergo a series of low-temperature phase transition as reported for the CO phase $\gamma$-Na$_{0.5}$CoO$_2$ [10]. Fig. 2(a) shows the XRD patterns taken respectively from the $\alpha$-Na$_{0.48}$CoO$_2$ phase in comparison with that of the $\gamma$-Na$_{0.5}$CoO$_2$ phase which was extensively discussed in previous literatures [19]. The $\alpha$-Na$_{0.48}$CoO$_2$ compound has a monoclinic unit cell ($P3$ structure) and $\gamma$-Na$_{0.5}$CoO$_2$ sample has an orthorhombic lattice ($P2$ structure), these structural distinctions therefore are clearly recognizable on the XRD peaks appearing at the diffraction angles of larger than $30^\circ$. In order to examine the microstructure feature, in particular the Na ordering in the CO phase of $\alpha$- and $\beta$-Na$_x$CoO$_2$, we have performed TEM observations on several typical samples with notable CO transitions. Fig. 2 (b) shows the [001] zone-axis diffraction pattern taken from the $\alpha$-NaCoO$_2$ sample, illustrating the well-defined hexagonal structure of basic plane. Electron diffraction
pattern obtained on the \( \beta-\text{Na}_{0.6}\text{CoO}_{2} \) crystal is the same as fig.2 (b) in which no clearly superstructure spots are observed. On the other hand, careful TEM observations on either \( \alpha-\text{Na}_{0.5}\text{CoO}_{2} \) (0.4 < x < 0.5) or \( \beta-\text{Na}_{x}\text{CoO}_{2} \) (0.4 < x < 0.5) samples reveal very similar systematic satellite spots within the a*-b* plane. Fig. 3 (c) shows an electron diffraction pattern taken from the sample of \( \alpha-\text{Na}_{0.48}\text{CoO}_{2} \), exhibiting the presence of superstructure spots. This superstructure in general appears as an incommensurate structural modulation with the wave vector of \( q = \langle 110 \rangle / 4 + \delta \) (0 ≤ \( \delta \) < 0.2). This kind of structural modulation as previously reported in the \( \gamma-\text{Na}_{0.5}\text{CoO}_{2} \) material can be well understood by the zigzag type of Na ordering among the CoO\(_2\) sheets [19].

We now proceed to discuss the electric transport and magnetic properties of \( \alpha-\) and \( \beta-\text{Na}_{x}\text{CoO}_{2} \) materials in connection with CO transitions that were systematically discussed at low temperatures in the \( \gamma-\text{Na}_{0.5}\text{CoO}_{2} \) sample [10, 19]. Fig. 3(a) and (b) show respectively the temperature dependences of resistivity (\( \rho \)) and magnetic susceptibility for \( \alpha-\text{Na}_{0.43}\text{CoO}_{2} \) samples. The \( \alpha-\text{NaCoO}_{2} \) phase is a semiconductor with a remarkable resistance increase below 50K [10]. Experimental measurements of resistivity and magnetic susceptibility suggest that all samples of \( \alpha-\text{Na}_{x}\text{CoO}_{2} \) (0.4 < x < 0.5) show up the similar low-temperature anomalies as discussed \( \gamma-\text{Na}_{0.5}\text{CoO}_{2} \). Fig. 3(c) shows the resistivity \( \rho \) of \( \beta-\text{Na}_{0.6}\text{CoO}_{2} \) and \( \beta-\text{Na}_{0.4}\text{CoO}_{2} \). The \( \beta-\text{Na}_{0.6}\text{CoO}_{2} \) sample is metallic, its resistivity decreases linearly with lowering temperature. The \( \beta-\text{Na}_{0.41}\text{CoO}_{2} \) sample, similar with the other x≈0.5 materials, shows up a sharp upturn in resistivity at the temperature of around 53 K, a notable saturation just below 25 K following by another increase of the slope. In general, magnetization measurements (see fig. 3b and fig. 3d) on either \( \alpha-\) or \( \beta-\text{Na}_{x}\text{CoO}_{2} \) samples with 0.4 < x < 0.5 clearly revealed the presence of three phase transitions at
the temperatures of around 25 K, 50 K and 90 K respectively. The 53K-transition was proposed to be associated with a notable magnetic ordering of two distinctive Co sites, and, therefore, an remarkable upturn of resistivity appears in general accompany this transition [10]. This fact also demonstrates that the correlated alternations of CO and magnetic structure indeed exist in present materials at low temperatures. The transition at 90 K is proposed in connection with certain kind of structural changes [19]. It is also noted the CO materials of α- and β-Na₅CoO₂, in contrast with the known CO γ-Na₀.₅CoO₂ phase, often have a notable antiferromagnetic (AFM) background as seen in fig.3b and d. We firstly considered this kind of AFM signal arises from an impurity phase, we therefore make a lot of effort to increase the sample quality, however, this AFM background remains visible in the samples in which TEM and XRD structural analysis cannot detect any impurity phases. Another possible original of this AFM background arises from the phase separation commonly appearing in the sample with x ~ 0.5 [19], i.e. certain fraction of materials in the CO materials with different Na content possibly produce complex AFM property.

Superconductivity in the α- and β-Na₅CoO₂ materials are another key issue concerned in present study. Structural investigation on the hydrated samples demonstrated the presence of certain typical hydrated phases with nominal compositions of α- and β-Na₀.₃CoO₂·yH₂O (y=0.7, and 1.3) similar with what observed in the γ-Na₀.₃CoO₂·yH₂O. The supercomputing phase, with the nominal compositions of α- and β-Na₀.₃CoO₂·1.3H₂O, have a distance of ~9.9Å between two adjacent CoO₂ sheets in consistence with the data of the known γ-Na₀.₃CoO₂·1.3H₂O superconductor. Figure 4 (a) shows the zero-field cooling (ZFC) magnetization data measured in a field of 20Oe for α- and β-Na₀.₃CoO₂·1.3H₂O samples. The presence of strong diamagnetic
signals for both samples provides direct evidence for bulk superconductivity in these two hydrated phases. The superconducting transitions, changing slightly from one sample to another, occurs at around $T_{\text{onset}} \approx 4.2$ K for $\alpha$-Na$_{0.3}$CoO$_2$·1.3H$_2$O and $T_{\text{onset}} \approx 4.3$ K for $\beta$-Na$_{0.3}$CoO$_2$·1.3H$_2$O. In previous literatures, the bulk superconductivity was observed in the hydrated $\alpha$-Na$_{0.3}$CoO$_2$·1.3H$_2$O at about $T_c \approx 4.6$ K [13]. On the other hand, no bulk superconductivity was detected in the hydrated $\beta$-phase [14]. Careful analysis on $\alpha$- and $\beta$-Na$_{0.3}$CoO$_2$·1.3H$_2$O materials suggests that the existence of a small fraction of impurity phases often totally destroy superconductivity in this kind of system. Hence, the acquisitions of superconducting phases in either $\alpha$- or $\beta$-Na$_x$CoO$_2$·yH$_2$O materials are found to be more difficult than that in the $\gamma$-Na$_{0.3}$CoO$_2$·1.3H$_2$O phase.

Alternations of intercalated layers among the CoO$_2$ sheets are expected to have certain effects on the structure as well as superconductivity as discussed in the $\gamma$-Na$_{0.3}$CoO$_2$·1.3H$_2$O and $\gamma$-Na$_{0.3}$CoO$_2$·1.3D$_2$O superconducting phases [7]. In $\alpha$, $\beta$-Na$_x$CoO$_2$ systems, we have prepared a series of the D$_2$O-intercalated samples with nominal composition of $\alpha$-Na$_{0.3}$CoO$_2$·1.3D$_2$O. X-ray diffraction result as shown in the insert of Fig. 4 (b) demonstrates that this phase has a similar hexagonal structure with the H$_2$O-intercalated superconducting phase, the only recognizable change is the decrease of c-axis parameter from 29.56 Å to 29.42 Å. Fig. 4 (b) shows the temperature dependence of the magnetic susceptibility of a $\alpha$-Na$_{0.3}$CoO$_2$·1.3D$_2$O sample showing a superconducting transition at around 3.7 K, the data for the $\alpha$-Na$_{0.3}$CoO$_2$·1.3H$_2$O is also shown for comparison. Our systematic analysis on the D$_2$O intercalated samples suggests that the substitution of D$_2$O for H$_2$O is likely to lower the superconducting transition. However, considering the structural complexity in this kind of
materials, numerous factors, such as the Na content, the H$_2$O (D$_2$O) layer structures and small fraction of impurities, might have notable effects on superconductivity. Hence, we cannot conclude the essential role of the D$_2$O substituting for H$_2$O on superconductivity ($T_c$) based on present experimental data, a further study performing on several high quality samples are still in progress.

In summary, we have successfully prepared two series of $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials by means of Na deintercalation from the parent $\alpha$-NaCoO$_2$ and $\beta$-Na$_{0.6}$CoO$_2$ phases, respectively. The $\alpha$-Na$_x$CoO$_2$ materials undergo a clear phase transition from the hexagonal to the $\beta$-phase like monoclinic structure along with Na deintercalation, as a result, $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials is likely to have the identical crystal structure for sample with $x < 0.5$. Measurements of resistivity and magnetization demonstrated the presence notable CO transitions in all $\alpha$- and $\beta$-Na$_x$CoO$_2$ materials with $0.4 < x < 0.5$, these transitions is very similar with those observed in the $\gamma$-Na$_{0.5}$CoO$_2$ phase. Bulk superconductivity has been found in the hydrated $\alpha$-Na$_{0.3}$CoO$_2$·1.3H$_2$O at $\sim$4.2K and in $\beta$-Na$_x$CoO$_2$·yH$_2$O at $\sim$4.3K. Intercalation of D$_2$O in $\alpha$, $\beta$-Na$_{0.33}$CoO$_2$ also yields superconductivity at 3.7K. Despite of the structural difference, the $\alpha$-, $\beta$- and $\gamma$-Na$_x$CoO$_2$ materials show up notable commonalities in superconductivity and CO transitions.
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**Figure and Table Captions**

Table 1. Structural properties and ICP results for the typical α- and β-Na₅CoO₂·yH₂O materials.

Figure 1. XRD patterns for (a) α-Na₅CoO₂, (b) β-Na₅CoO₂, illustrating the structural alternations along with Na content and H₂O intercalation.

Figure 2. (a) Comparison of the XRD patterns between the charge-ordered α-Na₀.₄₈CoO₂ and γ-Na₀.₅CoO₂, the structural distinction can be clearly recognized. The [001] zone axis electron diffraction pattern taken from (b) α-NaCoO₂ and (c) α-Na₀.₄₈CoO₂, the presence of superstructure spots in the charge ordered phase is evident.

Figure 3. Temperature dependence of magnetic susceptibility (χ) and resistivity (ρ) for (a, b) the α-Na₀.₄₃CoO₂ and (c, d) the β-Na₀.₄₁CoO₂ materials, clearly demonstrating the low-temperature charge-ordering transitions.

Figure 4. (a) The magnetic susceptibilities for the α- and β-Na₀.₃CoO₂·1.₃H₂O superconducting samples. (b) The magnetic susceptibilities for the α-Na₀.₃CoO₂·1.₃D₂O, shwing the superconducting transition at 3.₇ K. The data from α-Na₀.₃CoO₂·1.₃H₂O are cited for comparison.
Table 1

| Samples                     | ICP data (Na : Co) | Space group | Lattice Parameters (Å)          |
|-----------------------------|--------------------|-------------|---------------------------------|
| α-parent sample             | 0.99               | R3m         | Hexagonal  
                        |                    |                          | $a=2.89$, $c=15.59$  |
|                            |                    |             | Monoclinic                      |
| α-CO samples                | 0.48               | C2/m        | $a=4.92$, $b=5.63$, $c=17.36$, $\beta=105.98$ |
|                            | 0.43               | C2/m        | Monoclinic  
                        |                    |                          | $a=4.92$, $b=5.64$, $c=17.39$, $\beta=105.76$  |
| α-superconducting sample    | 0.31               | R3m         | Hexagonal  
                        |                    |                          | $a=2.82$, $c=29.57$  |
| β-parent sample             | 0.63               | C2/m        | Monoclinic                      |
|                            |                    |             | $a=4.89$, $b=5.65$, $c=17.14$, $\beta=106.18$ |
| β-CO sample                 | 0.41               | C2/m        | Monoclinic                      |
|                            |                    |             | $a=4.92$, $b=5.65$, $c=17.39$, $\beta=106.10$ |
| β- superconducting sample   | 0.29               | R3m         | Hexagonal  
                        |                    |                          | $a=2.82$, $c=29.56$  |
Figure 1

(a) X-ray diffraction patterns for superconducting phases at various dopant concentrations:
- **x=0.31**
- **x=0.43**
- **x=0.48**
- **x=0.99**

(b) X-ray diffraction patterns for superconducting phases at various dopant concentrations:
- **x=0.29**
- **x=0.41**
- **x=0.63**

Intensity (a.u.) vs. 2θ
Figure 2
Figure 3

(a) X-ray diffraction patterns of α-Na$_{0.48}$CoO$_2$ and γ-Na$_{0.5}$CoO$_2$. The peaks at specific 2θ values correspond to the crystal structures of these compounds.

(b) Schematics showing the crystallographic orientations and reflections for α-Na$_{0.48}$CoO$_2$.

(c) Zoomed-in view of the crystallographic unit cells for γ-Na$_{0.5}$CoO$_2$, highlighting the positions of atoms and the lattice parameters.
$\chi(10^{-3} \text{ emu/g})$ vs $T(\text{K})$

- **a**

- **b**

- $\alpha$-phase
- $\beta$-phase

**Figure 4**

- Hexagonal $\alpha$Fm
- $a = 2.82 \text{Å}, c = 29.42 \text{Å}$