

## Anomalous Change of $y'$ and $z$ in $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ at $x \approx 0.33$

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### Abstract

We prepared some  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  with BLH single phase and examined the  $\text{Na}^+$  content ( $x$ ),  $\text{H}_3\text{O}^+$  content ( $z$ ) and  $\text{H}_2\text{O}$  content ( $y'$ ).  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  with BLH single phase and  $0.28 \leq x \leq 0.36$  were prepared by changing the amount of  $\text{Br}_2$  used. The drastical changes in the  $c$ -axis length and  $z$ , Co valence,  $y'$  around  $x=0.33$  were observed, strongly suggesting that there exists a phase transition here.

### Introduction

After the  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  was found to be superconductive with a  $T_c$  around 5 K<sup>1)</sup>, much attention has been paid to this compound because it is a superconductor that is prepared in solution, where  $\text{H}_2\text{O}$  is intercalated between the  $\text{CoO}_2$  layers after deintercalation of excess sodium. This compound, including 3d transition metal Co, can provide new insights into metal oxide superconductors such as copper oxides.

The compound has two-dimensional  $\text{CoO}_2$  layers separated by a  $\text{Na}^+$  ion and a  $\text{H}_2\text{O}$  molecule, which are analogous to that of copper oxide superconductors. Schaak et al.<sup>2)</sup> reported that there is an optimum sodium composition for the occurrence of superconductivity, namely  $x=0.30$ . This variation of  $T_c$  with the degree of electronic doping of the  $\text{CoO}_2$  planes is analogous with the behavior observed in the copper oxides.

It was reported that there is a magnetically ordered phase sandwiched by two superconducting phases<sup>3),4)</sup> and that  $\text{Na}^+$  content plays an important role in the occurrence of superconductivity. Takada et al.

<sup>5)</sup> discovered that partial dehydration brings about shrinkage of the interlayer distance to yield a monolayer hydrate, in which the superconductivity vanishes.

Many works<sup>2,6-9)</sup> show the possible ordered phases of  $\text{Na}_{0.3}\text{CoO}_2 \cdot y\text{H}_2\text{O}$  with water content  $y=0, 0.3, 0.6, 0.9, 1.3$ , or  $1.8$ , corresponding to the coordination number  $n = 0, 1, 2, 3, 4$ , or  $6$  with the sodium ion. In this case, the phases are transformed by only the change of water content, from 0 to 1.8 while keeping the  $\text{Na}^+$  content  $x$  at 0.3. Since the existence of oxonium ions in the material is reported<sup>10)</sup>, it is crucial to estimate the  $\text{H}_2\text{O}$  content considering an oxonium ion. In this case, the chemical formula of this compound is expressed as  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ , where  $y = z + y'$ .

Sakurai et al.<sup>11)</sup> had measured the contents of  $\text{Na}$  ( $x$ ),  $\text{H}_3\text{O}$  ( $z$ ), and  $\text{H}_2\text{O}$  ( $y'$ ) independently and found that the content of  $z$  is decreased, with the increasing of  $x$  from 0.331 to 0.351. The purpose of this study is to clarify the interactions between Co valence,  $y'$ ,  $z$ ,  $x$  and  $T_c$  for  $0.28 < x < 0.36$ .

## Experimental

The parent oxide  $\text{Na}_{0.7}\text{CoO}_2$  was prepared from powders of  $\text{Na}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$  by the conventional solid-state reaction method. Mixtures of the powders were calcined at  $600^\circ\text{C}$  for six hours, sintered at  $800^\circ\text{C}$  under oxygen gas flow for eight hours to prepare  $\text{Na}_{0.7}\text{CoO}_2$ , and ground in an agate mortar.

The obtained  $\text{Na}_{0.7}\text{CoO}_2$  was oxidized by an acetonitrile solution of  $\text{Br}_2$  for five days. The amount of acetonitrile was fixed at 100 ml, and that of  $\text{Br}_2$  was varied from 2.5 ml down to 0.1 ml. After rinsing the compound by the acetonitrile for stopping deintercalation of sodium,  $2.5\text{gNa}_x\text{CoO}_2$  was immersed in 100 ml water for a day to intercalate  $\text{H}_2\text{O}$  molecules between the  $\text{CoO}_2$  layers and to form

$\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ . After the intercalation, the compound was dried in an ambient atmosphere. To prevent deintercalation of  $\text{H}_2\text{O}$ , the prepared specimens were stored in a closed vessel at 70% relative humidity<sup>7)</sup>. The X-ray powder patterns were taken with  $\text{CuK}\alpha$  radiation and the reflections were indexed according to the assignment of Cmaidalka et al.<sup>12)</sup>. The content of  $\text{Na}^+$ ,  $x$  in the  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  was measured by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The  $\text{H}_2\text{O}$  content was studied by the thermogravimetric (TG) method. The specimen was weighed as a function of increasing temperature from  $20^\circ\text{C}$  to  $400^\circ\text{C}$  at a heating rate of  $8.0^\circ\text{C}/\text{min}$  under nitrogen gas flow. By measuring the difference of the weights at  $20^\circ\text{C}$  and  $400^\circ\text{C}$ , the amount of water,  $y$  was determined.

It was reported that the water in the  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  consists of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$ . Therefore, this compound is represented by  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ . The amounts of  $z$  and  $y'$  were estimated separately as follows. The oxidation state of Cobalt in the specimen was determined by the iodometric titration<sup>13),14)</sup>. The oxonium ion content was estimated by equation  $z = 4 - (\text{Co valence}) - x$ . Therefore, the amount of  $\text{H}_2\text{O}$ ,  $y'$  is calculated by  $y' = y - z$ .

## Results and Discussion

In Fig.1, XRD patterns of  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$  are shown for several values of the  $\text{Br}_2$  volume in the 100 ml acetonitrile. The data show that the patterns of the samples deintercalated in the acetonitrile solution with  $\text{Br}_2$  of 0.7 to 2.5 ml can be indexed as a single phase of  $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ . When the  $\text{Br}_2$  amount is smaller than 0.5 ml, not only Bilayer Hydrate (BLH) phase but also anhydrous (AH) phase,  $\text{Na}_x\text{CoO}_2$ , represented by the dark circles was formed,

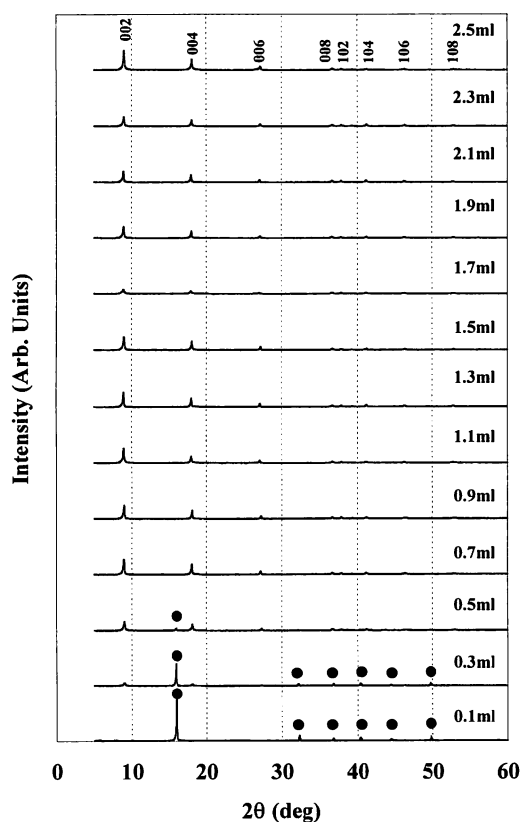


Fig.1 XRD patterns of  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  with various amounts of  $\text{Br}_2$ . Peaks of BLH phase are indexed. Solid circles represent peaks of the impurity phase, anhydrous  $\text{Na}_x\text{CoO}_2$ .

indicating that the samples are composed of the BLH and AH phases. The appearance of the AH phase with smaller amount of  $\text{Br}_2$  has also been reported by Takada et al.<sup>9)</sup>

The  $x$ ,  $y'$ , Co valence,  $z$ , and  $a$ - and  $c$ -axis length  $T_c$  of  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  are shown in table.1. Firstly, the relation between  $\text{Na}^+$  content ( $x$ ) and  $a$ -axis length and also,  $\text{Na}^+$  content and  $c$ -axis length are shown in Fig.2(a)

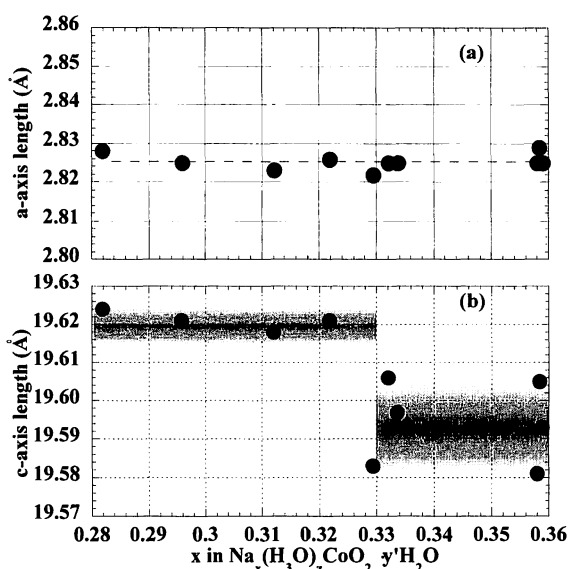


Fig.2.  $\text{Na}^+$  content ( $x$ ) vs.  $a$ -axis length (a) and  $c$ -axis length (b) in BLH single-phase  $\text{Na}_x\text{CoO}_2 \cdot y'\text{H}_2\text{O}$

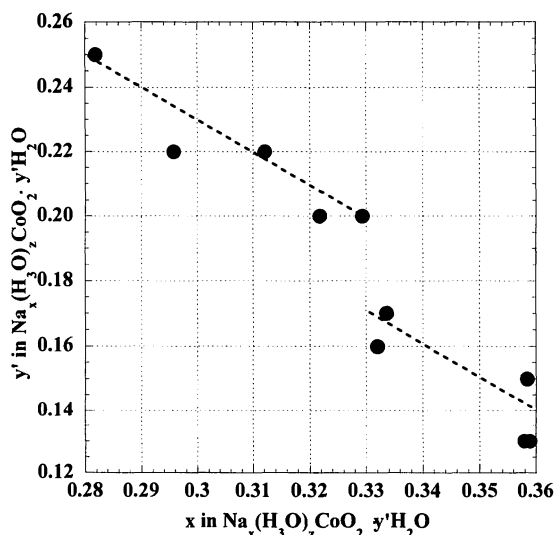


Fig.3.  $\text{Na}^+$  content ( $x$ ) in  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  vs.  $\text{H}_3\text{O}^+$  content ( $z$ ) in  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ .

and Fig.2(b) respectively. Compared with  $c$ -axis length, the change of  $a$ -axis length with different  $\text{Na}^+$  content is not so obvious. It may be due to the fact that  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  is a layered oxide, and the  $a$ -axis length of this compound is related to the direction of layer bonded. It is considered that  $\text{CoO}_2$  layer has strongest bonding in that compound, and  $\text{Co-O}$  bonding length is influenced for  $a$ -axis length of  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ . Besides, we examine the changes in Co valence. As shown in Table 1, the change of Co valence is varying from 3.47 to 3.51, which is less than 0.04. We estimate the change of  $a$ -axis length by considering the change in Co valence affected by the change in ionic radii between  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$ . The change in  $a$ -axis length estimated from ionic radii of  $\text{Co}^{3+}$  (0.545Å) and ionic radii of  $\text{Co}^{4+}$  (0.530Å) is estimated to be 0.008Å. There is  $\pm 0.005\text{Å}$  of error by XRD measurement, and in this work, it is difficult to reveal such a small change in  $a$ -axis length.

On the other hand, the change is revealed in  $c$ -axis length versus,  $\text{Na}^+$  content. Especially, the  $c$ -axis length drastically decreased from 19.62Å to 19.58~19.61Å at  $\text{Na}^+$  content around

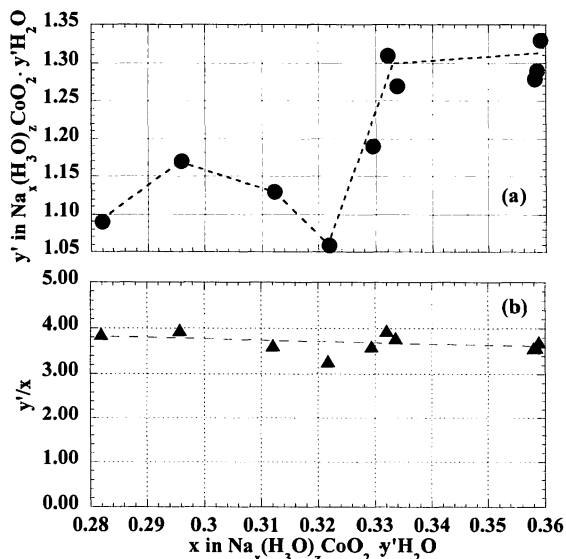


Fig.4.  $\text{Na}^+$  content ( $x$ ) vs.  $\text{H}_2\text{O}$  content ( $y'$ ) (a) and  $y'/x$  (b) in  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ .

0.33. It is to be noted that in  $x \geq 0.33$  region, the error of  $c$ -axis length in  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$  becomes large (Fig.2). Considering the stability of each phase affect the error of crystal parameters such as  $c$ -axis length, it may be suggest the existence of phase  $x \geq 0.33$  for  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ .

The  $c$ -axis length of layered compound generically changed by, (1) coulomb force between layers, and (2) the size of the ionic radius that enters between interlayer. As for (1), the change in Co valence,  $\text{Na}^+$ , and  $\text{H}_3\text{O}^+$  content were considered. However, because of the change in Co valence is very small as discussed in Fig.2 (a), therefore it is difficult to consider that the change in Co valence changed  $c$ -axis length. On the other hand,  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  content changes as they compensate each other. Since  $\text{H}_2\text{O}$  shields the coulomb force of  $\text{Na}^+$ <sup>15)</sup>, the Coulomb force is shielded as increasing of  $\text{Na}^+$  content, which will increase the  $c$ -axis length. Therefore, it is difficult to consider that Coulomb's force between layers originates the increase in the  $c$ -axis length. Secondly, We consider the change in ionic radii. In this system, it is reported that  $\text{H}_3\text{O}^+$  decreases with increase in  $\text{Na}^+$ . Therefore we examined whether a similar result could be seen in this study or not. In

Fig.3, the variation of  $\text{H}_3\text{O}^+$  content with  $\text{Na}^+$  content was shown. It clearly showed that  $\text{H}_3\text{O}^+$  content decreased with increasing of  $\text{Na}^+$  content. As shown in Table 1, the Co valence of  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$  was in range of 3.47~3.51. Hence, from the charge neutrality condition,  $\text{H}_3\text{O}^+$  content will decrease with increasing of  $\text{Na}^+$  content. We assume that the Co valence is not changed, since the plot of Fig.3 is nearly a straight line. By using the least-squared method, the line was simulated as the following two equations,

$$z = 0.53 - x \quad (x \leq 0.33) \quad (1)$$

$$z = 0.50 - x \quad (x \geq 0.33) \quad (2).$$

By separating the simulated equation into two parts at  $x \approx 0.33$ , standard deviations were drastically decreased, indicating that there is a jump among two equations at  $x \approx 0.33$ . This jump conforms to the relationship between  $c$ -axis length and  $x$ . Co valence calculated by (1) is  $V_{\text{Co}} = 4.00 - 0.53 = 3.47$ , and Co valence calculated by (2) is  $V_{\text{Co}} = 4.00 - 0.50 = 3.50$ . Therefore, it has been understood that there is a discrete change of Co valence at  $x \approx 0.33$ . The discrete changes of  $c$ -axis length,  $\text{H}_3\text{O}^+$ , and Co valence suggests a phase transitions.

Lastly, we consider the  $\text{H}_2\text{O}$  content. The relations between  $\text{Na}^+$  content and  $\text{H}_2\text{O}$  content (a), and  $\text{H}_2\text{O}$  content per one  $\text{Na}^+$  ion ( $y/x$ ) are

Table.1 The  $x$ , Co valence,  $z$ ,  $y'$ ,  $a$ - and  $c$ -axis length of  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y\text{H}_2\text{O}$ .

Amount of $\text{Br}_2$	$x$	Co valence	$z$	$y'$	$a$	$c$
2.5	0.33	3.47	0.20	1.19	2.822	19.583
2.3	0.36	3.51	0.13	1.28	2.825	19.581
2.1	0.31	3.47	0.22	1.13	2.823	19.618
1.9	0.32	3.48	0.20	1.06	2.826	19.621
1.7	0.28	3.47	0.25	1.09	2.828	19.624
1.5	0.33	3.50	0.17	1.27	2.825	19.597
1.3	0.33	3.51	0.16	1.31	2.825	19.606
1.1	0.30	3.49	0.22	1.17	2.825	19.621
0.9	0.36	3.51	0.13	1.33	2.825	19.593
0.7	0.36	3.49	0.15	1.29	2.829	19.605

shown in Fig.4. When  $x < 0.33$ ,  $\text{H}_2\text{O}$  content is in the range of 1.05~1.17. On the other hand, when  $x > 0.33$ ,  $y'$  is drastically increased to 1.30. And then,  $\text{H}_2\text{O}$  content remains constant. The change in  $\text{H}_2\text{O}$  content also suggests a phase transition at around  $x \approx 0.33$ . Besides  $\text{H}_2\text{O}$  per one  $\text{Na}^+$  is constant around 3.5~4.0. This result is similar to the previous report.<sup>6)</sup>

It is suggested that there are two phases in this system. We represent BLH- $\text{Na}_x\text{CoO}_2$ (I) as first phase and BLH- $\text{Na}_x\text{CoO}_2$ (II) as second phase, then the physical property of each phases are described in Table 2.

Although differences of  $c$ -axis length, composition and Co valence among these two phases could be identified, it is too difficult to determine which one is the origin. However other measurements for more detail structure determination and physical properties are needed.

## Conclusion

We prepared  $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$  with  $0.28 \leq x \leq 0.36$ ,  $1.05 \leq y' \leq 1.34$  and  $0.13 \leq z \leq 0.25$ , which were prepared by varying the  $\text{Br}_2$  content from 2.5ml to 0.7ml. The  $a$ -axis length is almost constant in all samples. On the other hand, the  $c$ -axis length changes with the change of  $\text{Na}^+$  content, Co valence and  $\text{H}_3\text{O}^+$  content. Relationship between  $\text{Na}^+$  and  $c$ -axis length drastically changes at  $x \approx 0.33$ . However, it is difficult to consider the change

in the Coulomb force determined by Co valence changes the  $c$ -axis length. Because the change of Co valence is too small to change the  $c$ -axis length. In addition, it is considered that  $\text{Na}^+$  content and  $\text{H}_3\text{O}^+$  content changes as they compensate each other.  $\text{H}_2\text{O}$  shields Coulomb force of  $\text{Na}$ , and the  $c$ -axis length increases linearly because Coulomb force is shielded by the increase of  $\text{Na}^+$  content but actually, that is inversely. Therefore it is difficult to consider that Coulomb's Force between layers originates the increase in the  $c$ -axis length. From the relation between  $x$  and  $z$ , the  $z$  decreases as the  $x$  increases and discrete change at  $x \approx 0.33$  is observed. It is approximated by two equations  $z = 0.53 - x$  ( $x \leq 0.33$ ) and  $z = 0.50 - x$  ( $x \geq 0.33$ ) up to and down to 0.33. Co valence  $V_{\text{Co}}$  calculated by that equations are 3.47 and 3.50, respectively. This drastic change also occurs in  $z$  and  $c$ -axis length. In addition, there is a discrete change of  $\text{H}_2\text{O}$  at  $x = 0.33$ . For  $x \geq 0.33$   $y'$  is 1.05~1.17, and for  $x \geq 0.33$   $y'$  is 1.30. These results suggest the existence of phase transition around  $x \approx 0.33$ .

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Table.2  $c$ -axis length,  $z$ ,  $y'$  and Co Valence of BLH- $\text{Na}_x\text{CoO}_2$ (I) and BLH- $\text{Na}_x\text{CoO}_2$ (II).

	$c$	$z$	$y'$	Co Valence
BLH- $\text{Na}_x\text{CoO}_2$ (I)	19.62	0.25-0.20	1.3	3.47
BLH- $\text{Na}_x\text{CoO}_2$ (II)	19.58-19.61	0.17-0.14	1.0.-1.20	3.50

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