

Valence and Na content dependences of superconductivity in $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ Hiroya Sakurai,^{1,*} Naohito Tsujii,² Osamu Suzuki,² Hideaki Kitazawa,² Giyuu Kido,² Kazunori Takada,¹ Takayoshi Sasaki,¹ and Eiji Takayama-Muromachi¹¹National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan²National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0044, Japan

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In order to acquire knowledge of the general superconducting phase diagram of sodium cobalt oxyhydrate, various samples with relatively large amounts of Na^+ ions were synthesized by a modified soft-chemical process in which a NaOH aqueous solution was added in the final step of the procedure. From these samples, a superconducting phase diagram was determined for a section of cobalt valence of $\sim +3.48$, which was compared with a previously obtained one of $\sim +3.40$. In addition, it was proven that the superconductivity was significantly affected by the isovalent exchange of Na^+ and H_3O^+ , implying that the e'_g bands play an important role in the superconductivity. Furthermore, the high-field magnetic susceptibility measurements for one sample indicated an upper critical field much higher than 8 T.

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Sodium cobalt oxyhydrate $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ has been studied intensively since the discovery of a superconducting transition below about 5 K.¹ Superconductivity can be induced in a CoO_2 layer having a triangular lattice of Co and this superconductivity is considered to be of an unconventional type.^{2,3} Supporting the existence of this exotic superconductivity, it has recently been discovered that, in this system, a magnetically ordered phase is located just next to the superconducting phase,^{4,5} implying that the superconductivity has some magnetic origin.

However, there are still serious discrepancies in some experimental results even for properties that are critical for understanding superconductivity. One such case of discrepancies is among superconducting phase diagrams, although the diagram is very important for the study of the superconductivity. Two kinds of x dependence of T_c have been reported,⁶⁻⁸ which is probably due to the fact that the Co valence is not determined by the Na content alone; the oxyhydrate includes a significant amount of oxonium ions and the rigorous chemical formula is $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$, rather than $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$, which has often been used previously.⁹ Thus, we have to consider three compositional parameters x , z , and y' , although the variation of water content is not significantly large. Milne *et al.* have reported a revised T - s (s is the Co valence) phase diagram with consideration of the oxonium ion.¹⁰ Their phase diagram is, however, still far from sufficient because it is not obvious that the properties of the system are governed only by s . Indeed, it has been recently elucidated that the ratio of z/x is a crucial parameter governing the phase diagram.⁵ Furthermore, their range of Co valence is much lower than those reported by other groups.^{9,11-14}

The H - T phase diagram (H is the magnetic field) is also an issue of disagreement because the upper critical fields H_{c2} reported thus far show very large variation. $H_{c2}(T=0)$ perpendicular to the c axis, which was estimated from electrical resistivity measurements, is about 8 T, as determined for samples with $T_c=4.2$ (Ref. 15) and 4.5 K.¹⁶ This value may look reasonable because it is close to the Pauli limit of $1.84T_c$.^{17,18} However, much higher H_{c2} values have also been

reported from magnetic and thermal measurements, such as 15.6 T for a sample with $T_c=3.7$ K,¹⁹ 17.1 T for $T_c=4.7$ K,²⁰ 28 T for $T_c=4.3$ K,²¹ and 61 T for $T_c=4.6$ K.²² These values were obtained by extrapolating the data under lower magnetic fields using the Werthamer-Helfand-Hohenberg (WHH) model.²³ However, it is not obvious whether the WHH model and the Pauli limit are adequate for the present system because they are applicable only for weakly coupled spin-singlet superconductivity. Indeed, a theoretical calculation for the compound has predicted spin-triplet superconductivity with T_c negligibly reduced by the magnetic field.²⁴

In the previous study, we drew the phase diagram for the $\text{Na}_x(\text{H}_3\text{O})_z\text{CoO}_2 \cdot y'\text{H}_2\text{O}$ system taking z/x as a parameter and keeping the Co valence constant at $s=+3.40$, i.e., the $s=+3.40$ cross section of the three-dimensional T - x - z phase diagram.⁵ Considering the aforementioned progress of research, it is highly desired at present to determine the phase relations for a different Co valence to obtain an overview of the entire three-dimensional phase diagram. Furthermore, high-field magnetic susceptibility measurements for a well-characterized sample are desired to elucidate the phase relationships in the H - T diagram. In the present study, we systematically synthesized samples by soft-chemical processes while controlling their composition, and the magnetic susceptibility of one sample was measured up to an extremely high field of 30 T.

The samples were obtained by a method similar to that previously reported.⁵ In the previous study, we added HCl aqueous solution to the system in the final step of the procedure to obtain samples with various z/x values depending on the volume of HCl solution but with the constant s value of $+3.40$ (HCl series of samples). In the present study, a NaOH aqueous solution was added in the final step of the procedure (NaOH series of samples). First, 1 g of $\text{Na}_{0.7}\text{CoO}_2$ precursor was immersed in $\text{Br}_2\text{-CH}_3\text{CN}$ for 5 days at room temperature, and filtered samples were immersed in 400 ml of distilled water for 3 days. Then, v_{NaOH} ml of 0.1M NaOH aqueous solution was added to the water (instead of $v_{\text{NaOH}}=100$ and 500 ml, 10 and 50 ml of 1M NaOH solution were used)

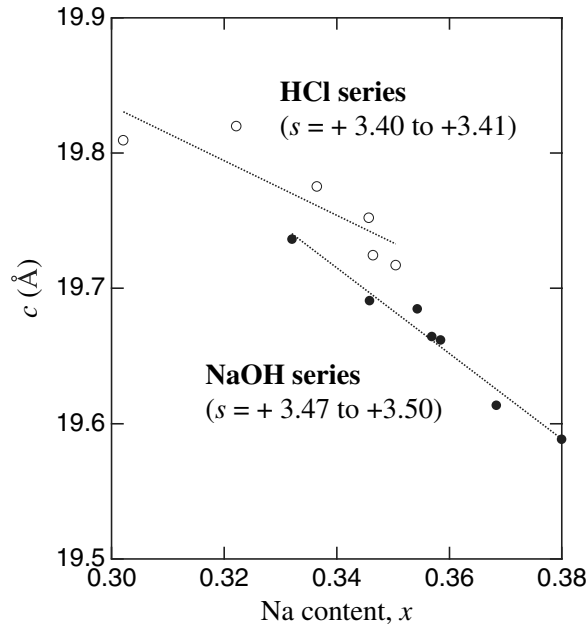
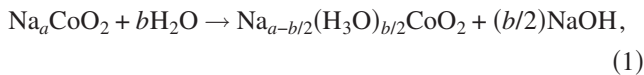


FIG. 1. Lattice parameter c of NaOH (full circles) and HCl (open circles) series of samples. The dotted lines are guides.

and then the samples were kept for 3 more days before performing a final filtration. The samples were characterized⁹ and measured after being stored in air with 70% humidity for more than 3 weeks.

The sample with $v_{\text{NaOH}}=500$ ml had the largest Na content and a very small amount of the secondary phase of anhydrous Na_xCoO_2 was detected in its x-ray diffraction (XRD) pattern (the ratio of the peak intensities of the secondary phase and the main phase was about 0.08%). This suggests that the solid solution terminates near this composition. All other NaOH samples were identified as being of a single phase by XRD analysis. The c -axis length decreases with increasing Na content as shown in Fig. 1, confirming the substitution of the smaller Na^+ ion for the larger H_3O^+ ion.

As discussed previously, the following two side reactions should be considered for the hydration process in addition to the intercalation of the water molecules.



According to reaction (1), the sodium ion content (the oxonium ion content) of the final product is expected to increase (decrease) with increasing v_{NaOH} . On the other hand, reaction (2) suggests a decrease in the Co valence with increasing v_{NaOH} .⁹ In Table I, results of the chemical analysis for the NaOH series of samples are shown in comparison with the data for the previous HCl series of samples.⁵ As can be seen in the table, the Na content increases systematically as a function of v_{NaOH} in accordance with reaction (1).

On the other hand, the analytical data of the Co valence are not fully understandable. First, there is a significant dif-

TABLE I. Na content and Co valence of the NaOH and HCl series of samples as determined by chemical analyses. The v value represents the volume of added NaOH or HCl aqueous solution.

v (ml)	Na content x	Co valence s
NaOH series		
0	0.332	+3.48
10	0.346	+3.48
20	0.354	+3.49
30	0.357	+3.50
40	0.358	+3.47
100	0.368	+3.47
500	0.380	+3.49
HCl series		
0	0.350	+3.41
2	0.346	+3.40
4	0.346	+3.41
6	0.336	+3.40
8	0.322	+3.40
10	0.302	+3.36

ference in Co valence (and in sodium content though the difference is much smaller) between samples of the two series with $v_{\text{HCl}}=0$ ml and $v_{\text{NaOH}}=0$ ml. These samples were from different batches but were prepared by essentially the same procedure and should have the same analytical values. The difference in Co valence is not negligible and it may suggest that there are still unknown factors in the hydration process and we have not fully controlled the process. Second, the Co valence is kept almost constant at $\sim +3.48$ in the NaOH series of samples independent of v_{NaOH} . Reaction (2) proceeds under alkaline conditions⁹ and, thus, a systematic decrease in Co valence is expected with increasing v_{NaOH} . This is not really the case, which implies that a more complicated situation exists. In spite of these uncertainties, the analytical data for the NaOH series of samples are quite favorable for our further experiments because from this new series of samples we can obtain a different cross section of the T - x - z phase diagram with $s = \sim +3.48$.

All of the NaOH series of samples show superconductivity with T_c depending on x as seen in Fig. 2(a). From these results, the phase diagram is depicted as shown in Fig. 3. It should be stressed again that the Co valence is kept almost constant at $\sim +3.48$ and the change in T_c is caused by the isovalent substitution between the Na^+ and H_3O^+ ions. The superconductivity appears even for $0.33 \leq x \leq 0.35$, where the magnetic phase is located in the cross section for the HCl series of samples as shown in the inset of Fig. 3.⁵ This remarkable difference should be caused by the difference in Co valence between the two series of samples; namely, the region of the SC1 phase obtained for the HCl series seems to extend to the lower x direction when the Co valence increases from +3.40 to +3.48.

The superconductivity of the system depends strongly on the substitution between Na^+ and H_3O^+ (the z/x ratio) as seen in both cross sections of Fig. 3 and this suggests that the

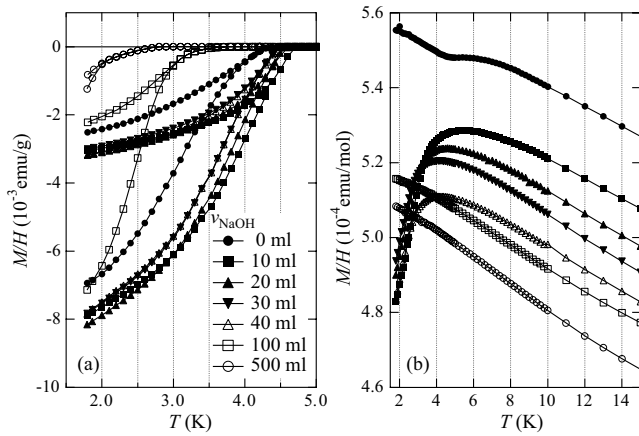


FIG. 2. Magnetic susceptibility of the NaOH series measured under 0.001 (a) and 7 (b) T. The data were collected under zero-field-cooling and field-cooling (FC) conditions, although only FC data are shown in (b).

electronic band structure of the present compound is substantially affected by the substitution. Band calculations have led to the proposal of the presence of small holelike pockets of the e'_g bands near the K points as well as a large cylindrical Fermi surface around the Γ point.²⁵ Although it is still unclear whether the bands really reach the Fermi level, their energy is expected to be quite sensitive to the thickness of the CoO_2 layer.^{26,27} With increasing H_3O^+ content, the oxygen ions in the CoO_2 layer will be attracted less strongly to the Na^+ and H_3O^+ ions, moving toward the Co ions due to

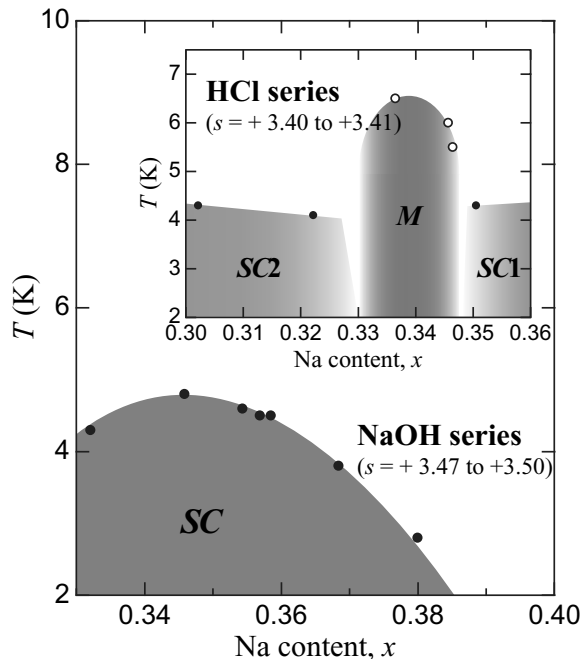


FIG. 3. Superconducting phase diagram determined from Fig. 2(a), which is a cross section of the three-dimensional x - z - T phase diagram at $s \approx +3.48$. The inset shows the cross section at $s \approx +3.40$ obtained from the HCl series of samples.⁵ SC and M denote the superconducting and magnetically ordered phases, respectively.

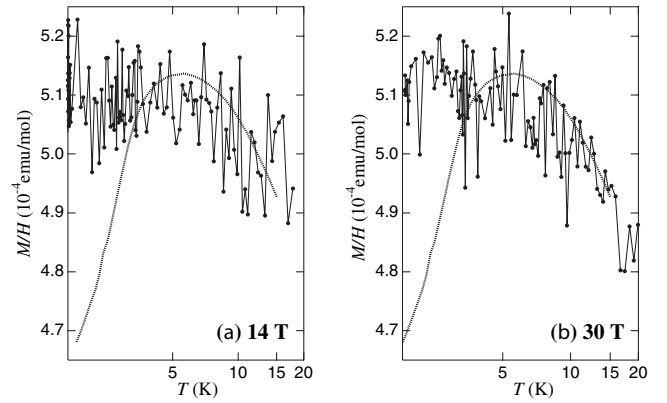


FIG. 4. Magnetic susceptibility of the $v_{\text{NaOH}} = 10$ ml sample measured under 14 (a) and 30 (b) T. The T axis is on a logarithmic scale. The dotted lines denote the magnetic susceptibility of the samples under 7 T.

the expansion of the distance between the oxygen atoms and the Na^+ - H_3O^+ plane, as in the case of the pressure effect reported by Jorgensen *et al.*²⁸ Thus, the substitution of H_3O^+ for Na^+ is expected to make the CoO_2 layer thinner and the e'_g bands pushed up. Quite recently, it was shown that, depending on the thickness, a small pocketlike Fermi surface centered at the Γ point, instead of the hole pockets near the K points, appears,²⁹ which can cause an unconventional superconductivity.³⁰ These effects may be the origin of the diagram reported here.²⁹

In the previous study, we found that the superconducting phase is transformed into the magnetic phase under a high magnetic field when it is located in the vicinity of the magnetically ordered M phase in the phase diagram.^{5,31} The $v_{\text{NaOH}} = 0$ ml sample with $x = 0.332$ exhibits the transformation in question at ~ 4 K under ~ 4 T, and indeed its susceptibility has a bend at 6–7 K under 7 T as seen in Fig. 2(b), indicating magnetic ordering. On the other hand, the $v_{\text{NaOH}} = 100$ and 500 ml samples do not show the anomaly at 7 T which is characteristic of the magnetic transition. The present results support the idea that the SC1 phase region extends in the lower x direction with increasing Co valence from $+3.40$ to $+3.48$. It is not clear at present whether the M phase exists under no or low magnetic field in the $s = +3.48$ section of the diagram. The SC1 and SC2 phases are possibly combined with each other under a low magnetic field in the high-Co-valence section and the M phase may appear only under a high magnetic field in this section.

High-field magnetic susceptibilities up to 30 T were measured for the $v_{\text{NaOH}} = 10$ ml sample having the highest T_c among the present samples by an extraction method under the field generated by a hybrid magnet (Gama) at the Tsukuba Magnet Laboratory (the field below 15 T was generated using only a Gama superconducting magnet). As can be seen in Fig. 4(a), in spite of the rather large dispersion of the data, the susceptibility under 14 T shows a downturn below about 4 K indicating the superconducting transition. It should be noted that this field is much higher than the Pauli limit of $1.84T_c = 8.6$ T.^{17,18} The superconducting transition seemed to survive under 20 T though it became unclear under 30 T [see Fig. 4(b)] because of reduction of the super-

conducting volume fraction by the field. In addition, as seen in Fig. 2(b), T_c of the sample under 7 T is much higher than ~ 2 K or ~ 2.6 K, which were reported for the samples having $H_{c2} = \sim 8$ T.^{15,16} Thus, it is clear that H_{c2} can become higher than the Pauli limit depending on the sample. Our aforementioned results indicate that a compound located close to the magnetic phase in the phase diagram has a low H_{c2} due to the transformation to the magnetic phase under a high magnetic field while one located far from the magnetic phase has a much higher H_{c2} .

In conclusion, in order to investigate the general T - x - s phase diagram, the x - T phase diagram for $s = \sim +3.48$ was determined using well-characterized samples and was compared with the previous diagram drawn for $s = \sim +3.40$. The $s = +3.48$ section of the diagram was different from the $s = +3.40$ section, and the region of the SC1 phase seen in the latter section seemed to extend to the lower x direction in the former section. The M phase was not detected under a low

magnetic field. In addition, it was proven that the superconductivity is very sensitive to the ion exchange between Na^+ and H_3O^+ (the x/z ratio) in both sections. We proposed that the thickness of the CoO_2 layer is changed by the exchange, which can have a significant influence on the electronic band structure. Furthermore, high-field magnetic susceptibility measurements for one sample indicated the survival of superconductivity up to at least 20 T, which is much higher than the Pauli limit.

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