

Determination of the Co Valence in Bilayer Hydrated Superconducting $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ by Soft X-Ray Absorption Spectroscopy

H. Ohta,^{1,*} K. Yoshimura,^{1,†} Z. Hu,² Y. Y. Chin,² H. -J. Lin,³ H. H. Hsieh,⁴ C. T. Chen,³ and L. H. Tjeng²

¹*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

²*Max-Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany*

³*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

⁴*Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan*

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We addressed the so-far unresolved issue concerning the Co valence in the superconducting bilayer hydrated $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x \sim 0.35$, $y \sim 1.3$) using soft x-ray absorption spectroscopy at the Co- $L_{2,3}$ and O-K edges. We find that the valence state of the Co lies in a narrow range from +3.3 to +3.4 for all studied $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ samples and their deuterated analogue with T_c 's ranging from 3.8 to 4.7 K. These valence values are far from the often claimed +3.7, the number based on the Na content only. We propose to modify the phase diagram accordingly, where the basic electronic structure of the superconducting phase is very close to that of the $\text{Na}_{0.7}\text{CoO}_2$ system, suggesting that the presence of in-plane spin fluctuations could play an important role for the superconductivity.

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The bilayer hydrated $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ ($x \sim 0.35$, $y \sim 1.3$) (BLH) is one of the exotic superconductors with a superconducting transition temperature (T_c) of about 5 K [1]. BLH has attracted tremendous research interest since this compound was discovered as the first Co-based superconducting oxide. It has two-dimensional Co-oxygen planes analogous to the Cu-oxygen planes in the high- T_c cuprate superconductors. It was found that varying the Na content in BLH results in the same type of out-of-plane chemical doping control of the in-plane electronic charge as found in the high- T_c cuprates [2].

Since the existence of an optimal doping for a maximum T_c is thought to be an important characteristic of the cuprate superconductors, the relationship between doping and T_c has also been examined intensively for the BLH system [1–3]. At the time of discovery, the BLH was regarded as an electron-doped system in which a low spin Co^{4+} lattice would acquire an electron density of about 0.35 per Co atom on the basis of the Na content. In other words, the Co valence state V_{Co} would be close to +3.65 [1,2]. In the BLH phase diagram, the superconductivity was then found to lie in the narrow region from $V_{\text{Co}} = +3.65$ to +3.75, with an optimum T_c for $V_{\text{Co}} = +3.7$ [2].

Within 1 yr from the discovery, however, chemical analysis studies using redox titration methods claimed that the value of V_{Co} must be in the +3.3 to +3.4 range [3–7]. It was proposed that the charge compensation is achieved by the intercalation of oxonium ions (H_3O^+) along with the water. Yet, spectroscopic studies in the same period and afterwards, provide the standard Na doping picture. Electron energy loss [8], high-energy photoemission [9], NMR [10], hard x-ray absorption [11,12], and angle-resolved photoemission [13] all conveyed the

message that the superconducting BLH has a Co valence of about +3.7 consistent with the Na content. Also a more recent study using a chemical postreduction method [14] found a similar value. This message is in clear conflict with the earlier chemical titration results, and this issue has not yet been resolved to the best of our knowledge.

The debate about the Co valence causes considerable uncertainty about the size and shape of the Fermi surface and has, in turn, far reaching consequences for the modeling of the superconductivity in this system. A Co valence of about +3.7 would lead to the existence of six e'_g hole pockets in addition to the large a_{1g} cylindrical Fermi surface according to standard band structure calculations [15,16]. This then leads to multiorbital models claiming the superconductivity driven by magnetic spin correlations with even the possibility of triplet pairing [17–20]. A scenario with a Co valence of +3.3 on the other hand, does not have the six e'_g hole pockets and requires quite different approaches for the superconductivity, e.g., involving electron-phonon mechanisms and unconventional s -wave pairing [21–24].

The confusion about the Co valence and the Fermi surface has not been settled yet. An angle-resolved photoemission study did not find the presence of the six e'_g hole pockets [13], but there is also considerable debate whether this due to correlation effects [15,25] or surface effects [26]. By contrast, a more recent study using Compton scattering claimed to have observed these pockets [27]. Also a recent specific heat experiment has been interpreted as to support the existence of two types of hole pockets [28].

Here we utilize soft x-ray absorption (XAS) spectroscopy at the Co- $L_{2,3}$ ($2p \rightarrow 3d$) and O-K ($1s \rightarrow 2p$) edges as the preferred method to determine the valence state of

the Co ions. The Co ($2p \rightarrow 3d$) transitions involve directly the relevant valence shell, and are extremely sensitive to the charge state: not only do the energy positions depend on the valence but also the spectral line shape can be used as finger prints for the valence [29–31]. In addition the O $1s \rightarrow 2p$ transitions reach final states which are directly hybridized with the empty Co $3d$ orbitals. We have explicitly proven recently that this method is suitable for the cobaltates [32–34]. In particular, we have shown that soft XAS provides not only element specific information but also quantitative information on how much of the Co ions are in the $4+$, $3+$ or $2+$ states as they are present in the material. This is obviously more specific than obtaining only the average charge number for entire multicomponent system when using chemical titration methods.

We synthesized powder samples of the BLH and their deuterated analogue (BLD) from the $\text{Na}_{0.7}\text{CoO}_2$ powders. Detailed synthesis conditions are described in our previous report [35]. The powders of BLH and BLD were then put in a high humidity atmosphere (43–75%) and kept there for several days to condition their electronic states by the “duration effect” [36,37]. From powder x-ray diffraction measurements, we confirmed that the obtained BLH and BLD samples were single phase. We determined the T_c of the samples by measuring the magnetization at $H = 20$ Oe down to 1.9 K.

The ^{59}Co nuclear quadrupole resonance (NQR) is also used for characterizing the BLH samples [38,39], since ^{59}Co NQR can detect small local differences of the arrangement of surrounding oxygen ions and of the number of the unpaired electrons on Co ions through the interaction between nuclear spin of Co nucleus and the electric field gradient at Co nucleus. NQR spectra were recorded at 77 K to extract ν_{Q3} , which is associated with the transition of $I_z = \pm 5/2 \leftrightarrow \pm 7/2$ [35,36]. The ν_{Q3} and T_c values of the samples BLH1–BLH5 and BLD1–BLD3 are inserted in the phase diagram displayed in Fig. 1. The envelope in the figure is reconstructed from Ref. [35]. Here, the “SC-I” phase is the superconducting phase reported in Ref. [1], “SC-II” is also the superconducting phase discovered later, and “M” the magnetic ordering phase [38,39]. Similar phase diagrams were reported in other experimental and theoretical studies [23,40–44].

The XAS experiments were performed at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The Co- $L_{2,3}$ and O-K XAS spectra were taken in the total electron yield with a photon energy resolution of 0.25 and 0.15 eV, respectively. Since the BLH samples deteriorate easily above 0°C in dry air or vacuum, we kept each sample frozen in carbon containers using dry ice during transport to the NSRRC and using liquid nitrogen during transfer into the ultra high vacuum system. These carbon containers remained at 77 K and were cut open *in situ* just before the data taking. In this manner we have succeeded in preventing the sample from

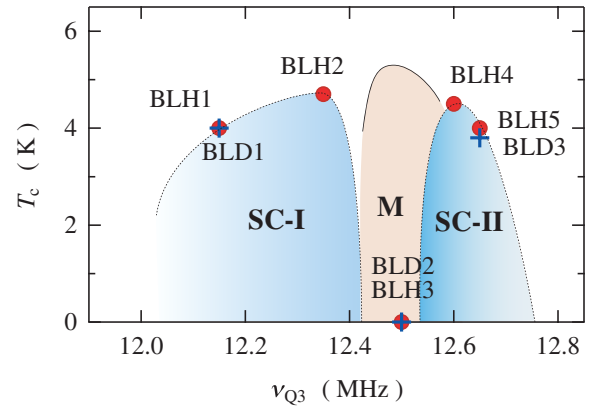


FIG. 1 (color online). T_c vs ν_{Q3} phase diagram of the BLH and BLD samples, after Ref. [35]. SC-I and SC-II are superconducting phases and M is the magnetic ordered phase. The closed circles and “+” symbols represent our data of the BLH and BLD, respectively.

losing water and in getting clean surfaces for the XAS measurements.

Figure 2 shows the Co XAS spectra of our BLH4 and BLD3 samples. The inset displays the complete $L_{2,3}$ range in which the spectra are dominated by the Co $2p$ core-hole spin-orbit coupling which splits the spectrum roughly into two parts, namely, the L_3 ($h\nu \approx 779\text{--}783$ eV) and L_2 ($h\nu \approx 794\text{--}798$ eV) white lines regions. In order to see more clearly the changes upon water intercalation, we plot in the main panel of Fig. 2 a blow-up of the Co- L_3 region of samples BLH4 and BLD3 together with those of the $\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$ reference samples. For comparison, we also include the spectrum of the BLH sample from an earlier work (green line) [45] and of CoO (black dash-dotted line). One can see that our results are quite different from the earlier work [45]. In the latter, the

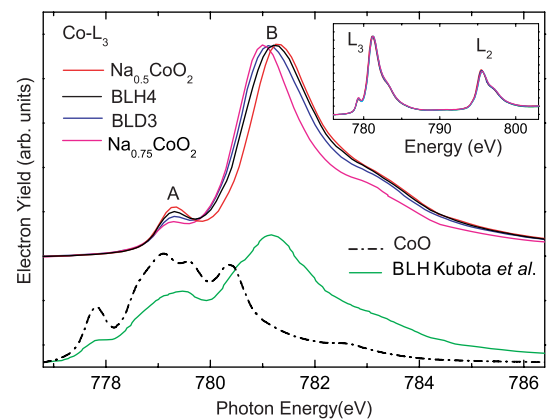


FIG. 2 (color online). The Co- L_3 XAS spectra of the BLH4 and BLD3 samples together with $\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$, as well as $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ from Ref. [45], and CoO for comparison. Inset: complete view of the Co- $L_{2,3}$ edges of the samples studied.

spectral feature at 777.8 eV is characteristic for the presence of a Co^{2+} component as demonstrated by the CoO spectrum in Fig. 2 [33]. The absence of this 777.8 eV feature in all of our the BLH, BLD and Na_xCoO_2 samples indicates that our data are free from Co^{2+} impurity phases and that our samples have not lost oxygen under our experimental conditions.

More important is that our BLH and BLD samples have the same distinct Co- L_3 main (B) and satellite (A) peaks as the Na_xCoO_2 single crystals [32,34]. The satellite peak A at 779.3 eV has been identified in our recent Na_xCoO_2 studies [32,34] as due transitions from the Co $2p_{3/2}$ core level into the t_{2g} orbitals of mainly a_{1g} character for a Co^{4+} ion in D_{3d} point group. Therefore, the intensity of peak A relative to the main peak B provides direct information about the $\text{Co}^{4+}/\text{Co}^{3+}$ ratio. Moreover, it has been established that this $\text{Co}^{4+}/\text{Co}^{3+}$ ratio as deduced from the XAS spectra agrees very well with the nominal Na concentration in Na_xCoO_2 [34]. The Co valence for the Na_xCoO_2 samples is then given by $V_{\text{Co}} = 3 + (1 - x)$: $V_{\text{Co}} = 3.50$ for $\text{Na}_{0.5}\text{CoO}_2$ and 3.25 for $\text{Na}_{0.75}\text{CoO}_2$.

We now can estimate the V_{Co} of the BLH and BLD samples by comparing their spectra with those of the $\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$ samples, without the need to do detailed line shape calculations. We can directly see from Fig. 2 that the relative spectral weight of the peak A for the BLH4 and BLD3 samples lies between $\text{Na}_{0.75}\text{CoO}_2$ and $\text{Na}_{0.5}\text{CoO}_2$. This implies that the V_{Co} of BLH4 and BLD3 is between +3.25 and +3.5. In fact, from all our BLH and BLD samples studied here, the highest and the lowest peak A intensity is found for BLH4 and BLD3, respectively. This means that BLH4 has the highest V_{Co} and BLD3 the lowest, and that all the other samples have V_{Co} values in between. With the intensity ratio of peak A and B being proportional to the $\text{Co}^{4+}/\text{Co}^{3+}$ ratio, we found that V_{Co} lies in a narrow range from +3.33 to +3.41 for our BLH and BLD samples. See Table I.

Figure 3 shows the O- K edge XAS spectra of the BLH4 and BLD3 samples together with those of $\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$ for comparison. Peaks α_1 and α_2 correspond to the transition from the O $1s$ core level to the unoccupied O $2p$ states which are hybridized with the a_{1g} and e_g states of Co^{4+} ions, respectively [32]. Peak β is due to a transition to the empty O $2p$ states which are mixed with e_g state of the Co^{3+} ions. The spectral weight of peaks α_1 and α_2 relative to that of peak β thus provides information about the Co^{4+} content in the samples. Using the

TABLE I. Co valence (± 0.02 .) in BLH and BLD as determined from the Co- L_3 and O- K edges.

	BLH1	BLH2	BLH3	BLH4	BLH5	BLD1	BLD2	BLD3
Co	3.33	3.35	3.40	3.42	3.41	3.39	3.40	3.33
O	3.28	3.30	3.33	3.36	3.35	3.31	3.33	3.28

$\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$ reference spectra, we arrive at V_{Co} values between +3.28 and +3.35. An overview of the results is given in Table I. We note that the V_{Co} values obtained from the O- K edge are slightly smaller than those from the Co- $L_{2,3}$, probably due to the fact that we have neglected in the O- K analysis the appearance of a broad spectral feature centered around 532 eV upon intercalation of water and oxonium.

Our main result is that V_{Co} of the superconducting BLH and BLD system lies in a narrow range between +3.28 and +3.41. This provides strong support for the chemical analysis using redox titration methods [3,4]. Yet, our result is very much in disagreement with the earlier spectroscopic studies all claiming a V_{Co} of +3.7 [8–13]. We attribute this to the fact that the energy resolution in the electron energy loss spectroscopy is not sufficient to detect the characteristic peak A in the L_3 spectrum, that core level photoemission and hard x-ray absorption spectroscopy do not show sufficiently distinct features for the different valence states, and that angle-resolved photoemission has insufficient probing depth to obtain numbers representative for the bulk material.

At the moment we have not enough accurate data to establish a correlation between V_{Co} and the properties of the BLH/BLD system in the narrow regime of V_{Co} between 3.3 and 3.4 (see Table I). Yet we now know already that there is a clear correlation between $\nu_{\text{O}3}$ and the lattice parameter c [35,43,44,46]. We now propose to connect the phase diagrams of the Na_xCoO_2 and BLH systems as follows. In Fig. 4 we first reproduce the results for Na_xCoO_2 from Ref. [47], where one can identify a Curie-Weiss like paramagnetic metallic phase (CW metal), a Pauli paramagnetic metallic phase (PP metal), a charge ordered insulating phase (CO insulator), and an antiferromagnetic metallic phase (AFM). Important is that on the horizontal axis we no longer put the Na content x , but rather the Co valence V_{Co} . We then can link the phase diagram of the BLH system of Fig. 1 to this V_{Co} axis at the

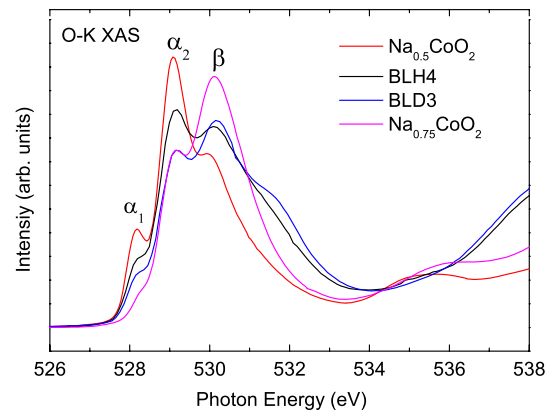


FIG. 3 (color online). The O- K XAS spectra of the BLH4 and BLD3 samples together with those of $\text{Na}_{0.5}\text{CoO}_2$ and $\text{Na}_{0.75}\text{CoO}_2$.

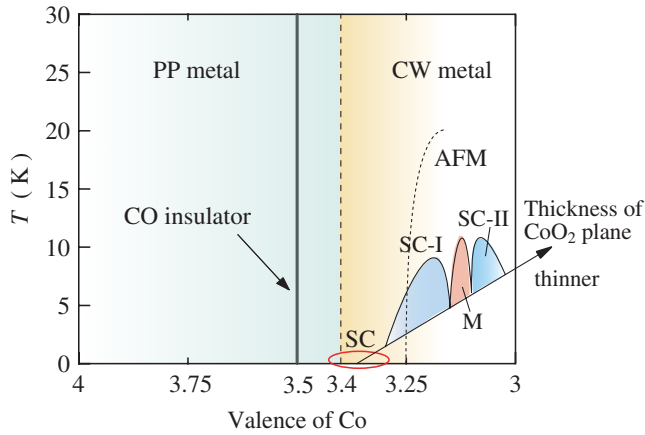


FIG. 4 (color online). Electronic phase diagram of the Na_xCoO_2 against both the Co valence (V_{Co}) and the Na content x , reproduced from Ref. [47]. The BLH lies within the CW metal phase of the Na_xCoO_2 (circled area).

+3.4 value as indicated by the ellipse in Fig. 4. The ν_{Q3} axis is set orthogonal to the V_{Co} axis. We also propose to replace this variable by the thickness of the CoO_2 plane, following the finding of Mochizuki and Ogata that there is a one-to-one correspondence between ν_{Q3} and the thickness [23].

With the detailed information about the Co valence state, now we can discuss the presence of spin fluctuations in Na_xCoO_2 and the possible consequences for the BLH system. In neutron diffraction measurements, the A-type, i.e., in-plane ferromagnetic and interplane antiferromagnetic spin fluctuations were observed for the Na_xCoO_2 in the CW metallic phase for $x \sim 0.6$ [48] with a Co valence state of +3.4, whose electronic state is comparable to the BLH as found from our experiments. The intercalation of water molecules makes the distance of CoO_2 planes twice larger in the BLH than in Na_xCoO_2 . One could envision that the interplane antiferromagnetic spin fluctuations will be strongly reduced while the in-plane ferromagnetic spin fluctuations will survive through the expansion by the water intercalation. It is then quite tempting to speculate that such in-plane ferromagnetic spin fluctuations may support the scenario of the spin-triplet superconducting pairing, which seems to be not inconsistent with the symmetry of the crystal structure.

In summary, we have prepared a series of BLH and BLD samples with T_c ranging from 3.8 to 4.7 K. Using soft x-ray absorption at the Co- $L_{2,3}$ and the O- K edges we have determined the Co valence state in these BLH and BLD samples. We found surprisingly that the Co valence of all studied BLH and BLD samples lies in the narrow range from +3.3 to +3.4, which is far from that estimated from the Na content. We pointed out the possibility for the presence of in-plane ferromagnetic spin fluctuations, which could be of help to realize a spin-triplet superconducting pairing scenario.

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*shioshio@kuchem.kyoto-u.ac.jp

†kyhv@kuchem.kyoto-u.ac.jp

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