

## Laser-excited ultrahigh-resolution photoemission spectroscopy of $\text{Na}_x\text{CoO}_2 \cdot y\text{H}_2\text{O}$ : Evidence for pseudogap formation

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We have studied the temperature ( $T$ )-dependent electronic structure near the Fermi level of the layered cobaltate superconductor,  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ , and related materials, using laser-excited ultrahigh-resolution photoemission spectroscopy. We observe the formation of a pseudogap (PG) with an energy scale of  $\sim 20$  meV in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  and  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ , which is clearly absent in  $\text{Na}_{0.7}\text{CoO}_2$ . The energy scale of the PG is larger than the expected value for the superconducting gap, suggesting an additional competing order parameter at low  $T$ . We discuss implications of the PG in relation to available transport and magnetic susceptibility results.

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After the discovery of the first cobalt oxyhydrate superconductor  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  (NCO13) (transition temperature  $T_c$  of  $\sim 4.5$  K) by Takada *et al.*,<sup>1</sup> extensive experimental and theoretical studies have been made in order to understand the superconductivity in this system. This is because the conductive two-dimensional (2D)  $\text{CoO}_2$  layers of NCO13 can be regarded as an electron-doped correlated  $S=1/2$  triangular network of frustrated Co spins,<sup>1</sup> where superconductivity emerging from a non-Fermi-liquid ground state has been proposed.<sup>2</sup> Theoretically, recent studies on the Co oxide superconductors have proposed superconducting (SC) order parameters depending on the model used.<sup>3</sup> And, in addition, several experimental studies have been performed to clarify the symmetry of the SC gap (SCG).<sup>4</sup> However, agreement on the order parameter has not been reached so far.

In the cuprate high-temperature superconductors (high- $T_c$ 's), whose electronic structure (ES) is often described in terms of a quasi-2D correlated system, understanding the unusual normal-state (NS) properties has led to deeper understanding of the superconductivity. Even for the layered Co oxides, recent studies have indicated a rich phase diagram in the nonhydrated (non-H)  $\text{Na}_x\text{CoO}_2$  system.<sup>5</sup> For SC samples, as has been also suggested from theoretical studies,<sup>6-8</sup> importance of well-separated  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  in the SC Co oxides has been reported experimentally very recently.<sup>9</sup> Coexistence of superconductivity and ordered states has been discussed in cuprate high- $T_c$ 's.<sup>10</sup> In this regard, NCO13 provides another opportunity to investigate charge and/or spin order competing or cooperating with superconductivity in these oxides.

Thus, it is essential to study the NS ES of the SC Co oxides using photoemission spectroscopy (PES), which provides direct information on the ES. Very recent PES studies<sup>9</sup> using hard x rays (escape depth of  $\sim 50$  Å) have provided bulk fundamental physical parameters that describe the su-

perconductor in terms of on-site Coulomb energy  $U_{dd}$ , charge transfer energy  $\Delta$ , and hybridization strength  $V$ . More importantly, the double-peak structure in the Co  $2p$  core-level spectra revealed charge disproportionation in  $\text{Na}_{0.7}\text{CoO}_2$  (NCO) and NCO13 samples, which suggest existence of remnant charge order in the SC samples. For the states near the Fermi level ( $E_F$ ), while angle-resolved PES (ARPES) studies<sup>11-13</sup> on non-H samples showed a large hole pocket around the  $\Gamma$  point in the Brillouin zone, and renormalization at the energy scale of  $J \sim 10$  meV,<sup>12</sup> no PES study on the ES near  $E_F$  of SC NCO13 is reported. Therefore, it is extremely important to study SC NCO13 and compare it with that of other related cobalt oxides to investigate the NS ES.

For investigating ES of samples having a very delicate surface, PES with a lower photon energy provided by a laser is found to be very powerful,<sup>14</sup> because of the very high energy resolution and expected large escape depth.<sup>15</sup> In this rapid communication, we report  $T$ -dependent ES near  $E_F$  of polycrystalline NCO,  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$  (NCO07), and NCO13 studied with PES using a laser as an excitation source. We succeeded in observing difference in ES between the mother compound and the H samples: absence and presence of a PG. We discuss the PG formation in the light of available transport and magnetic data to elucidate ES of the H superconductor.

Polycrystalline NCO13 are synthesized from NCO through a chemical oxidation process, by which a part of Na ions is removed and  $\text{H}_2\text{O}$  molecules are intercalated between  $\text{CoO}_2$  and Na planes, as described in Ref. 1. Magnetic measurements confirmed that the samples measured here have  $T_c$  of 4.5 K. PES under an ultrahigh vacuum condition requires special caution because SC NCO13 has a tendency to become non-SC NCO07 due to loss of  $\text{H}_2\text{O}$  molecules. Therefore, we carefully handled H samples as follows. We first covered the samples with silver paste and mounted them on

copper substrates to prevent loss of  $\text{H}_2\text{O}$  molecules under vacuum. Then, the prepared samples were cooled to  $\sim 180$  K and are fractured *in situ*. Immediately after the fracturing, they are transferred to a measurement chamber and measured without warming up above 180 K. We chose the temperature of 180 K because no loss of  $\text{H}_2\text{O}$  molecules occurs in NCO13 below 250 K.<sup>16</sup> In actual practice, the pressure did not change during the fracturing and measuring the H samples. We have also confirmed the existence of  $\text{H}_2\text{O}$  molecules in the H samples by measuring  $\text{O}1s$  core levels and valence band spectra using x rays.<sup>9</sup> We found that the  $\text{O}1s$  spectra of NCO13 show two peaks, which are derived from oxygen in the  $\text{CoO}_2$  planes and from oxygen in the chemically bonded  $\text{H}_2\text{O}$ . We also showed that the  $\text{H}_2\text{O}$  derived peak was not observed in the  $\text{O}1s$  spectrum of NCO. In addition, we have also measured valence-band spectra using x rays. The NCO spectrum was consistent with local-density approximation calculations, while the NCO13 spectrum showed a weak additional feature due to  $\text{H}_2\text{O}$  content present in the sample (Ref. 9). We have also confirmed reproducibility of the spectra with a spatial resolution of  $100 \mu\text{m}$  as determined by the incident laser beam spot size and found identical spectra were obtained for several samples as well as from region to region over a typical sample area of  $1.5 \times 1.5$  mm. Therefore, we believe that the  $\text{H}_2\text{O}$  molecule content is unchanged and the spectral changes are intrinsic to the samples even after fracturing and measuring them under vacuum.

All PES measurements were performed on a spectrometer built using a GAMMADATA-SCIENZA R-4000 electron analyzer and an ultraviolet laser ( $h\nu=6.994$  eV). The best energy resolution is  $360 \mu\text{eV}$ .<sup>14</sup> However, the energy resolution for all measurements was set to  $6.5$  meV in order to scan wide energy range and to get reasonable count rate. Samples are cooled using a flowing liquid He refrigerator with improved thermal shieldings. Sample  $T$  were measured using a silicon-diode sensor mounted below the samples. The base pressure of the measurement chamber was better than  $2 \times 10^{-11}$  Torr. The spectra were all reproducible during the measurement of 2 hours.  $E_F$  of samples was referenced to that of gold film evaporated onto the sample substrate. Its accuracy is estimated to be better than  $\pm 0.1$  meV. The advantage of the ultraviolet laser is the larger escape depth as expected from the literature ( $\sim 200 \text{ \AA}$ ) of emitted electrons,<sup>15</sup> enabling a probe of bulk electronic states.

Figure 1 shows the PES spectra near  $E_F$  of (a) NCO, (b) NCO07, and (c) NCO13 measured as a function of  $T$  from 3.5 K to 150 K. The spectra were normalized with the total intensity integrated from 64 meV to  $-56$  meV binding energy (BE). The similar intensity of measured spectra around 60 meV of each sample confirms the validity of the normalization we used. All the spectra show systematic  $T$  dependence with a clear Fermi edge structure at lower  $T$ s. However, we also found that there is a notable difference in the spectral shape near  $E_F$  at 3.5 K between NCO and the two H samples. While the spectrum of NCO has a nearly constant intensity with a smooth reduction close to  $E_F$ , the spectra of NCO07 and NCO13 show an additional decrease within 20 meV BE of  $E_F$ . Close look at the  $T$ -dependent intensity at  $E_F$  also shows a small but an important difference; while the

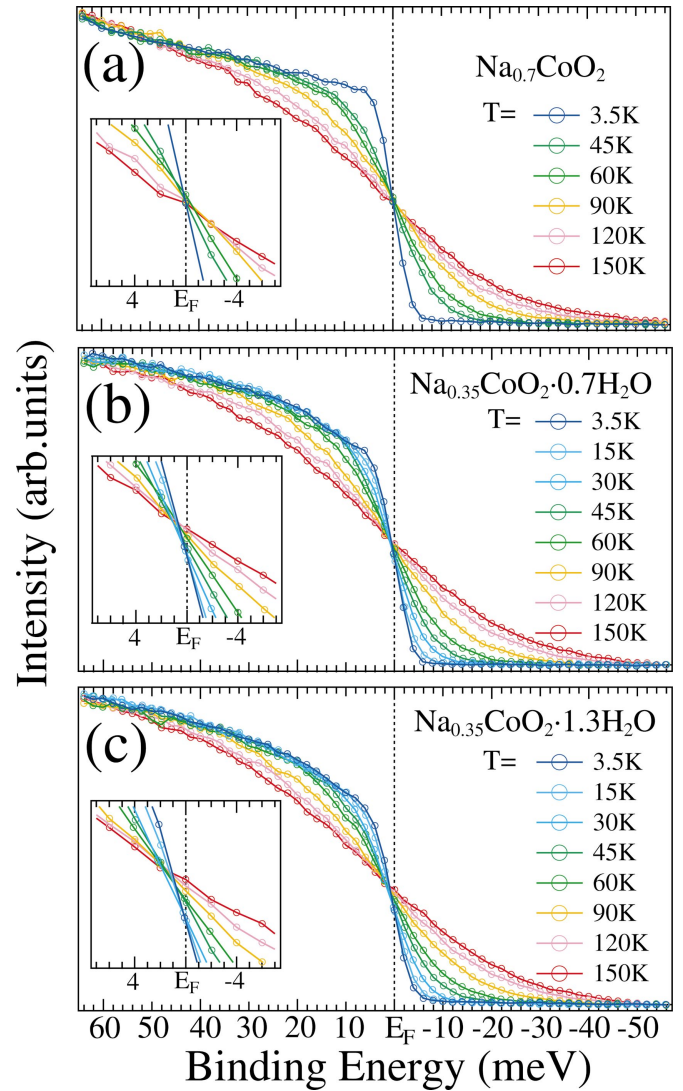


FIG. 1. (Color)  $T$ -dependent spectra of (a)  $\text{Na}_{0.7}\text{CoO}_2$ , (b)  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ , and (c)  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  measured with 6.994 eV photon energy. Insets are the enlargement of the near  $E_F$  region, which highlight the difference in  $T$ -dependent change at  $E_F$  between  $\text{Na}_{0.7}\text{CoO}_2$  and the hydrated samples.

intensity at  $E_F$  of NCO remains constant, the intensity at  $E_F$  of the two H samples decreases with lowering  $T$ . This is in sharp contrast to the  $T$  dependence of a normal metal, such as gold, where all the  $T$ -dependent spectra intersect with each other at  $E_F$  with the  $1/2$  value of the density of states (DOS) at  $E_F$ . This is clear from the insets where we show an enlarged view of intensities at  $E_F$  for the three samples. Thus, the raw spectra itself indicates that the two H samples exhibit an unusual NS ES near  $E_F$ .

In order to make the  $T$ -dependent change in DOS clearer, we have performed an analysis to extract the effect of the Fermi-Dirac (FD) function from the raw data as follows. The raw spectrum at each  $T$  was divided by the corresponding FD function convoluted with a Gaussian with the instrumental resolution. To see the  $T$ -dependent spectral changes, the divided spectra at all  $T$  were further divided with the smoothed spectrum at 150 K, as shown in Figs. 2(a)–2(c).<sup>17</sup> We also

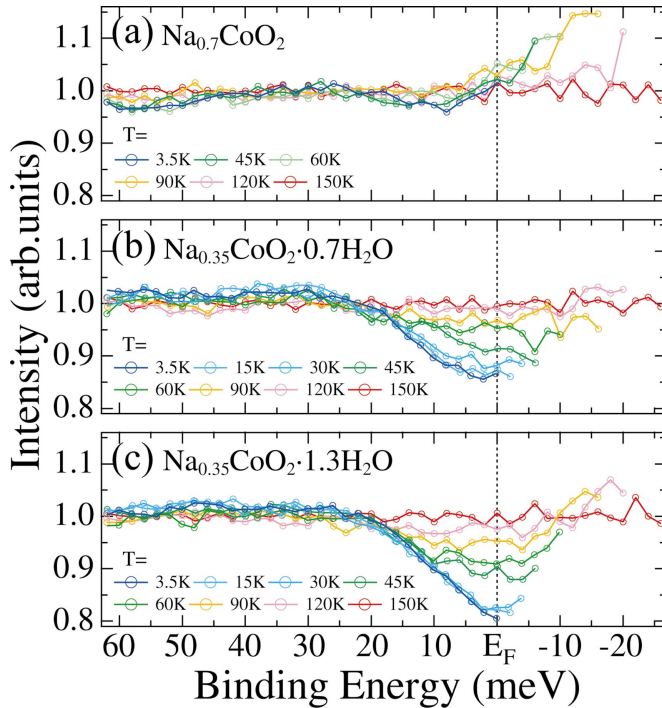


FIG. 2. (Color)  $T$ -dependent normalized DOS of (a)  $\text{Na}_{0.7}\text{CoO}_2$ , (b)  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$ , and (c)  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ . Note that clear formation of PG at lower  $T$  in the hydrated samples in (b) and (c).

plotted in Fig. 3 the  $T$ -dependent intensity at  $E_F$  (averaged from  $-2$  meV to  $2$  meV BE of the raw spectra in Fig. 1) normalized with that at  $150$  K of each sample. In Figs. 2(b) and 2(c), the normalized DOS of the H samples within  $\sim 20$  meV of  $E_F$  are gradually suppressed with decreasing  $T$ . The reduced spectral weight around  $E_F$  seems to be compensated by a slight increase beyond  $20$  meV BE, indicating that spectral weight is transferred from the near- $E_F$  region to the higher-BE region. Compared with the marked change in the H samples, the  $T$ -dependent change in NCO is smaller, though at lower  $T$  the normalized DOS shows a broad hump centered around  $30$  meV and a small upturn near  $E_F$ . Absence of the PG in NCO is consistent with the angle-integrated PES studies on  $\text{Na}_{0.6}\text{CoO}_2$ .<sup>18</sup> These qualitative differences in the spectra between NCO and the H samples are also seen in the  $T$ -dependent intensity at  $E_F$  as shown in Fig. 3. Relatively flat intensities in NCO and a decrease of the intensity with decreasing  $T$  in the H samples. It should be noted that the qualitative difference is not due to difference in inhomogeneity of samples, as we know that the quality is better for the H samples because of the narrower core levels.<sup>9</sup> This is also known from tunneling experiments which indicated less inhomogeneity in NCO13 than in NCO and which also observed a PG.<sup>19</sup> Thus, we conclude that appearance of the PG in the H samples and absence of the PG in NCO reflect the intrinsic difference in ES, highlighting unusual electronic states realized in the H samples.

More recently, evidence of  $T$ -dependent PG formation for non-H layered cobalt oxides  $\text{Na}_{0.25}\text{CoO}_2$  and  $\text{Na}_{0.5}\text{CoO}_2$  has been reported from optical spectroscopy (OS).<sup>20</sup> The energy scales of half of the PG measured from the OS are

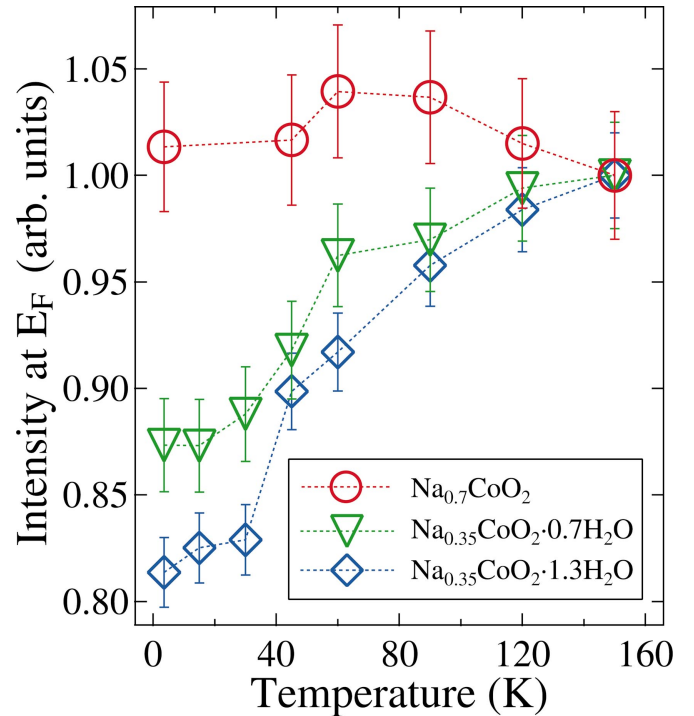


FIG. 3. (Color)  $T$ -dependent intensity at  $E_F$  (averaged from  $-2$  meV to  $2$  meV BE) of  $\text{Na}_{0.7}\text{CoO}_2$  (circles),  $\text{Na}_{0.35}\text{CoO}_2 \cdot 0.7\text{H}_2\text{O}$  (triangles), and  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  (diamonds). All intensities were normalized with that of  $150$  K.

$6$ – $25$  meV, depending on the Na concentration, consistent with the value obtained from the present study. However, the smaller reduction in the intensities (10%–20% reduction compared with that of  $150$  K) in the PES results compared with the OS results indicates that the PG formation in H samples is partly suppressed due to the difference in concentration of Na and/or inclusion of the  $\text{H}_2\text{O}$  molecules, suggesting parts of Fermi surface (FS) are gapped. This anticipation may have something to do with the resistivity data<sup>21,22</sup> not showing an anomaly around  $40$  K, where intensity at  $E_F$  of NCO13 shows a marked decrease (Fig. 3). One possibility is that the PG opens on the bands having little contribution to the transport properties, as described below. According to the band calculation,<sup>7</sup>  $\text{Na}_{0.33}\text{CoO}_2$  has two types of bands across  $E_F$  derived from mainly Co  $3d$  electrons. One has a dominant  $a_{1g}$  character providing light carriers and forming a large cylindrical FS centered around the  $\Gamma$  point. The other has a primarily  $e'_g$ -like character providing heavy carriers and forming a small pocket FS along the  $\Gamma$ -K direction. The  $e'_g$ -like band mainly contributes to the DOS at  $E_F$ . From these aspects, one may say that the PG forms on the small pockets but the large FS plays a dominant role for the transport. Moreover, recent theoretical studies have predicted that there is strong nesting tendencies for the small pockets that can induce charge or spin density waves (CDW or SDW).<sup>7</sup> It may be likely that the PG opens as a precursor of the CDW or SDW. Absence of PG in the DOS of NCO may be related to the disappearance of the small pockets in NCO due to the rigid band filling of electrons. Indeed, ARPES have reported the absence of the small pockets in  $\text{Na}_x\text{CoO}_2$  ( $x=0.7$ ).<sup>12</sup> To



check the presence of the small pocket, which plays a crucial role for the superconductivity, ARPES of the H samples is desired.

In relation to the superconductivity, the energy scale of the PG (20 meV) is larger than the expected SCG size ( $\sim 1$  meV as expected from the  $T_c$  and the known mean-field relation of  $2\Delta/k_B T_c = 3.54$ , where  $\Delta$  is the SCG value,  $k_B$  the Boltzmann constant). This indicates that the PG is different from the SCG, suggesting possible competing ground states at low  $T$ . A large energy scale PG has been also reported for the cuprate high- $T_c$ 's,<sup>23,24</sup> where the PG formation was found to be related to a development of magnetic correlations. On the other hand, a  $T$ -dependent PG has been observed in  $\text{Ba}_{0.67}\text{K}_{0.33}\text{BiO}_3$ ,<sup>25</sup> where the energy scale of the PG correlated with the energy of the breathing mode phonon. In the layered Co oxides, the energy scales of  $\sim 20$  meV is comparable to the nearest-neighboring magnetic coupling constant  $J = 10\text{--}20$  meV as predicted for  $U_{dd} \sim 5$  eV,<sup>7</sup> which has been also concluded from ARPES measurements.<sup>12,13</sup> This  $J$  value is smaller than the highest phonon energies.<sup>20</sup> It is interesting to note that  $T$ -dependent magnetic susceptibility shows deviations from a Pauli-like susceptibility beginning at the same  $T$  at which we see PG formation or intensity reduction at  $E_F$  more for NCO13. The comparative study of  $T$ -dependent susceptibility of NCO07 and NCO13 has shown an enlarged magnetic susceptibility in NCO13 compared to NCO07.<sup>26</sup> The NMR studies have also reported an existence of ferromagnetic fluctuation at lower  $T$ .<sup>27</sup> The additional sup-

pression in DOS at  $E_F$  (Figs. 2 and 3) in NCO13 compared to NCO07 also suggests further stabilization of the competing order. While these observed interesting physical properties in H- and non-H  $\text{Na}_x\text{CoO}_2$  need more systematic studies to be understood, the present results showing a PG may give an insight into the physics underlying the unconventional superconductivity observed in the H layered cobalt oxide superconductors.

In conclusion, we have studied the ES near  $E_F$  of NCO13 and related cobalt oxides using laser-excited ultrahigh-resolution PES. The obtained results show that, while the  $T$ -dependent spectra of the mother compound show no gap structure near  $E_F$ , those of H samples show PG with an energy scale of 20 meV in the occupied part with larger depletion at  $E_F$  in NCO13 compared in NCO07. The energy scale of the PG (20 meV) is larger than the expected SCG size ( $\sim 1$  meV), which indicates that the PG is a necessary but not sufficient condition for the superconductivity. These results suggest that the superconductivity in the H Co oxide occurs close to some ordered phase.

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