Angle-resolved photoemission study of the doping evolution of a three-dimensional Fermi surface in $\text{Na}_x\text{CoO}_2$

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Abstract. We have performed angle-resolved photoemission spectroscopy of layered cobalt oxide $\text{Na}_x\text{CoO}_2$ for a wide doping range ($0.35 \leq x \leq 0.85$) with synchrotron radiation, and determined the doping dependence of the Fermi surface and band structure. The two-dimensional (2D) cylindrical $a_{1g}$ Fermi surface at $x = 0.35$ gradually increases the dimensionality upon Na doping and eventually transforms into a 3D-like Fermi surface at $x = 0.77$, indicating the strong inter-layer coupling between adjacent CoO$_2$ layers in the highly doped region. We found that the characteristic shape of the top of the $a_{1g}$ band is closely related to the various anomalies of physical properties in $\text{Na}_x\text{CoO}_2$.

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1. Introduction

Sodium cobalt oxide Na\textsubscript{x}CoO\textsubscript{2} has attracted much attention because the hydration transforms it into a superconductor with the superconducting transition temperature $T_c$ of 4.5 K [1]. Na\textsubscript{x}CoO\textsubscript{2} shares some similarities with copper oxide (cuprate) high-$T_c$ superconductors, such as the presence of a two-dimensional (2D) conduction plane and the rich electronic and magnetic phase diagram as a function of carrier doping. The interplay between magnetism and superconductivity, and the comparison between the antiferromagnetically ordered square lattice (CuO\textsubscript{2} plane) and the geometrically frustrated triangular lattice (CoO\textsubscript{2} plane), have also been debated intensively [2, 3]. Among the various fascinating physical properties of Na\textsubscript{x}CoO\textsubscript{2}, superconductivity, the magnetic order and the metal–insulator transition have been paid considerable attention [4]–[6]. It is inferred that these physical properties are closely linked to the dimensionality of the system. For instance, the superconductivity emerges at the low-doped region of $x \approx 0.35$ by inserting the hydrogen atoms between CoO\textsubscript{2} layers to enhance the two dimensionality. In contrast, in the highly doped region of $x > 0.75$, the 3D spin density wave (SDW) appears at low temperature [7]–[13], which is possibly caused by 3D Fermi-surface nesting [14, 15]. This contrasting behavior of the physical properties between the low- and high-doped regions highlights the importance of experimental determination of the precise 3D electronic structure in a wide doping range. However, such a systematic investigation has not been reported in previous angle-resolved photoemission spectroscopy (ARPES) papers because they were mainly focused on clarifying the 2D electronic states [16]–[22].

In this paper, we report the results of our ARPES study of Na\textsubscript{x}CoO\textsubscript{2} over a wide doping range ($0.35 \leq x \leq 0.85$) by utilizing synchrotron radiation. We clarify the systematic doping dependence of the Fermi surface and band dispersions in the 3D Brillouin zone, and reveal a significant change in the dimensionality of the observed electronic states upon band filling. We discuss the implications of the present ARPES results for some physical properties, such as thermal and transport measurements.

2. Experiments

High-quality single crystals of Na\textsubscript{x}CoO\textsubscript{2} ($x = 0.35$–0.85) were grown by the floating-zone and flux methods. In this paper, we label samples like Na0.35 for Na\textsubscript{0.35}CoO\textsubscript{2}. ARPES measurements were carried out with VG-SCIENTA SES2002 and R4000 analyzers at the beamline BL28A at Photon Factory (KEK) and the PGM beamline at the Synchrotron Radiation Center, Wisconsin. Energy and angular resolutions were set at 15–40 meV and 0.2°, respectively. Clean sample surfaces were obtained by in situ cleaving in an ultrahigh vacuum.
better than $1 \times 10^{-10}$ torr. All the measurements were carried out within 12 h after cleaving. The Fermi level ($E_F$) of the sample was referenced to that of a gold film evaporated onto the sample substrate.

### 3. Results and discussion

Figure 1 shows the plot of ARPES intensity at $E_F$ as a function of in-plane wave vectors $k_x$ and $k_y$ for $x = 0.35$–0.85 measured with 60 eV photons at $T = 25$ K. In all the samples, we clearly identify a single large $a_{1g}$ hole-like Fermi surface centered at the $\Gamma$$(A)$ point, whereas a small $e'_g$ Fermi surface predicted by the local-density-approximation band calculation [23] is absent, consistent with previous ARPES reports [16, 17, 19]. To compare the absolute volume of the Fermi surface, we determined the Fermi wave vectors ($k_F$) for each doping levels by tracing the local maxima of the momentum distribution curves (MDCs) at $E_F$ and show the obtained $k_F$ points by red open circles in figures 1(a)–(d). Figure 1(e) shows a comparison of all dopings. As can be seen in figure 1(e), the hole-like $a_{1g}$ Fermi surface systematically shrinks on increasing the Na content, consistent with the electron doping into the CoO$_2$ plane from Na atoms.

Figure 2 displays the doping dependence of energy distribution curves (EDCs) in the vicinity of $E_F$ measured at $T = 25$ K with two different photon energies $\hbar\nu = 55$ and 70 eV. ARPES measurements with $\hbar\nu = 55$ and 70 eV photons trace the AL and $\Gamma M$ high-symmetry
Figure 2. Doping dependence of EDCs near $E_F$ of Na$_x$CoO$_2$ measured at $T = 25$ K with (a–d) 55 eV and (e–h) 70 eV photons. EDCs at the high-symmetry point (A or $\Gamma$) are indicated in black. Dashed curves are a guide to the eye to trace the peak position. The upper panel shows the 3D Brillouin zone and the $k_x$–$k_z$-plane (blue shade).

lines, respectively (see figure 2). To determine the absolute momentum location in the 3D Brillouin zone, we have estimated the inner potential value by the periodicity of the band dispersion along the momentum perpendicular to the crystal surface ($k_z$) [14]. Along the AL line (figures 2(a)–(d)), the $a_{1g}$ band (shown in dashed line) gradually disperses toward $E_F$ on approaching the A point from the $\Gamma$ point and crosses $E_F$ near the A point. Along the $\Gamma$M line (figures 2(e)–(h)), we find a similar band-crossing behavior in the Na0.35 and Na0.65 samples, while we also identify a less-dispersive band near $E_F$ for the Na0.77 and Na0.85 samples around the $\Gamma$ point. The flat band smoothly connects the highly dispersive $a_{1g}$ band. This result unambiguously demonstrates a sizable band dispersion along the $k_z$-direction in the highly doped Na0.77 and Na0.85 samples. It is noted here that the flat band of the Na0.85 sample slightly disperses downward around the $\Gamma$ point as is seen in figure 2(h), producing a characteristic local minimum structure at the $\Gamma$ point.

To highlight the variation of the band dispersion along the $k_z$-direction, we show in figure 3 the photon energy dependence of the ARPES intensity measured at $h\nu = 50$–90 eV for Na0.85 and Na0.35 samples. In the Na0.35 sample, the highly dispersive band simply crosses $E_F$
Figure 3. Photon energy dependence of the ARPES intensity near $E_F$ plotted as a function of the wave vector and binding energy measured at $T = 25$ K for (a–e) $x = 0.85$ and (f–j) $x = 0.35$. (k, l) Schematic view of the 3D Brillouin zone and the Brillouin zone in the $k_x$–$k_z$-plane (ΓALM plane), respectively.

irrespective of the measured photon energies, suggesting the essentially 2D nature of electronic states. On the other hand, in the Na0.85 sample, the intensity at $E_F$ around $k_x = 0$ systematically increases from $h\nu = 50$ eV to $h\nu = 70$ eV, and then decreases at higher photon energies. At $h\nu = 70$ eV the highly dispersive $a_{1g}$ band appears to be smoothly connected to the intense feature around $k_x = 0$, showing a characteristic M-shaped dispersion with a local minimum at $k_x = 0$. These experimental results indicate a sizable 3D component of the electronic states in the Na0.85 sample.

To accurately determine the 3D band dispersion and the $E_F$-crossing point, it is important to follow the band dispersion above $E_F$. Since the EDCs are cut off by the Fermi–Dirac (FD) distribution function, it is necessary to remove this effect. For this purpose, we measured EDCs at a relatively high temperature ($T = 100$ K) for the Na0.77 and Na0.85 samples, and divided them by the FD function convoluted with a Gaussian reflecting the instrumental resolution. The results at $h\nu = 70$ eV (the ΓM cut) for each doping level are displayed in figures 4(a)–(d). In the low-doped Na0.35 and Na0.65 samples, the $a_{1g}$ band appears to simply cross $E_F$ without any anomaly. On the other hand, in the highly doped Na0.77 sample, the $a_{1g}$ band disperses toward $E_F$ on approaching the Γ point from the M point, and crosses $E_F$ between the two points. This band has a peak of dispersion at 10 meV above $E_F$ and disperses backward to $E_F$ again and then gives a local minimum structure at 15 meV below $E_F$ at the Γ point [14]. A similar trend is also observed in the Na0.85 sample, while the energy position of the band appears to be slightly different: the local maximum of the $a_{1g}$ band merges or touches $E_F$ and the $E_F$ crossing of the band is not clearly seen within the experimental uncertainty. In figures 4(e) and (f), we display the doping dependence of the band dispersion at $h\nu = 70$ eV (ΓM cut) and 55 eV (AL cut) as determined by tracing the peak position in EDCs after removing the effect of the FD function. As visible in figure 4(e), the $a_{1g}$ band crosses $E_F$ at $k_x \approx -0.6$ Å$^{-1}$ in the Na0.35 sample, and the wave vector of the crossing point gradually shifts toward the zone center on increasing the doping. In the Na0.77 and Na0.85 samples, we identify a characteristic local minimum.
structure in the band dispersion at the \( \Gamma \) point. This local minimum structure is likely situated at the unoccupied side in the Na0.35 and Na0.65 samples, whereas it is lifted downward into the occupied side owing to the chemical potential shift caused by the additional electron doping from the Na atom. We note that the chemical potential shift and the resultant band shift are also well recognized along the AL cut, as shown in figure 4(f).

To see the out-of-plane Fermi-surface shape more clearly, we show in figure 5 the doping dependence of the ARPES intensity at \( E_F \) as a function of \( k_x \) and \( k_z \). As shown in figure 5(a), the Fermi surface of the Na0.35 sample is nearly straight with a very small wiggling along the \( k_z \)-direction, indicating its strong 2D nature. The 2D character of the Fermi surface remains in the Na0.65 sample (figure 5(b)), whereas the wiggling amplitude looks much more pronounced than that in the Na0.35 sample. As also seen in figures 5(c) and (d), the wiggling amplitude of the Fermi surface is systematically enhanced upon Na doping, indicating the doping-induced enhancement of the inter-plane electron hopping, consistent with the shorter \( c \)-axis length in the higher-doped region [24]. The most important aspect in figure 5 is the observation of a sizable ARPES intensity around the \( \Gamma \) point in the Na0.77 and Na0.85 samples, indicative of the appearance of a new Fermi surface originating from the flat band, as is seen in figures 4(c) and (d).
Figure 5. (a–d) Doping dependence of ARPES intensity at $E_F$ plotted as a function of $k_x$ and $k_z$. To calculate the $k_z$-value, we estimate the inner potential value to be 8.0 eV from the periodicity of the band dispersion along the $k_z$-direction.

Figure 6. Comparison of experimentally determined $k_F$ points in the $k_x$–$k_z$ ($\Gamma$MLA) plane for $x = 0.35$–0.85. Error bars originate from the experimental uncertainty in determining the peak position of MDCs or EDCs.

To evaluate quantitatively the doping evolution of the Fermi-surface topology, we compare in figure 6 the estimated $k_F$ positions in the $k_x$–$k_z$-plane. We again confirm that the straight portion of the cylindrical Fermi surface around the $\Gamma M$ line in the Na0.35 sample gradually transforms into a concaved shape, and a new segment emerges near the $\Gamma A$ line in the Na0.77
and Na0.85 samples, demonstrating the transition of Fermi-surface topology upon the band filling.

The doping-induced evolution of the Fermi surface is schematically illustrated in figure 7. Since the local maximum structure is situated at $E_F$ along the $\Gamma M$ cut (see figure 4(c)), it is inferred that the neck of the cylindrical Fermi surface seen in the Na0.77 sample (marked by an arrow in figure 7(a)) gradually shrinks upon the band filling and finally disappears at $x > 0.85$. As a result, the 3D electron pocket disappears and the quasi-2D cylindrical hole-like Fermi surface becomes 3D-like. In this sense, the Na concentration of $x \approx 0.85$ can be regarded as a critical doping level where the outer $a_{1g}$ Fermi surface undergoes the 2D–3D transition. All these results suggest that the Fermi surface of Na$_x$CoO$_2$ has a two-step transition upon band filling at the critical doping levels of $x \approx 0.77$ and $x \approx 0.85$. The former transition is accompanied by the emergence of a small 3D electron pocket, while the latter is characterized by the 2D–3D transition of the large hole-like $a_{1g}$ band and the disappearance of a small 3D electron pocket. Such an evolution of the Fermi-surface topology is understood essentially by the rigid-band picture, as shown in figure 7(b).

Now we discuss the present ARPES results more quantitatively by comparing them to those of other experiments. In figure 8(a), we plot the observed bandwidth ($W_z$) along $k_z$, estimated from the energy difference of the band dispersion along the $\Gamma M$ and AL lines, as shown in the inset. Apparently, the $W_z$ value is enhanced at the highly doped region of $x = 0.77$ and 0.85, owing to the prominent 3D nature of electronic states. In figure 8(b), we plot the doping dependence of the chemical potential relative to the Na0.35 sample ($\Delta \mu$), estimated from the experimental results of figures 4(e) and (f). The $\Delta \mu$ value monotonically increases on doping and becomes $\approx 50$ meV in the Na0.85 sample. This value is in agreement with the value reported from the band calculation based on the local spin density approximation [25] where $\Delta \mu$ is about 30 meV. It is noted that the systematic change in the Fermi-surface volume, as estimated from the experimental 3D band dispersion [14] (33 $\pm$ 3, 24 $\pm$ 3, 13 $\pm$ 4 and 8 $\pm$ 4% of the first BZ for the Na0.35, Na0.65, Na0.77 and Na0.85 samples, respectively), is consistent with the monotonic shift of the chemical potential.

In figure 8(c), we show the doping dependence of the Fermi velocity ($v_F$) estimated from the band dispersion along the $\Gamma M$ and AL cuts. In the Na0.35 sample, the obtained $v_F$ values
Figure 8. (a) Bandwidth of the $a_{1g}$ band along the $k_z$-direction ($W_z$) as a function of the Na doping ($x$). (b) Doping dependence of chemical–potential shift relative to the value of $x = 0.35$. (c) Doping dependence of the Fermi velocity ($v_F$) along the $\Gamma M$ (AL) line measured at $h\nu = 55$ eV (pink curve) and 70 eV (red and orange curves). (d) Doping dependence of the specific heat coefficient $\gamma$ estimated from the present ARPES result. The red curve shows the contribution of both the outer hole and inner electron pockets ($\gamma_{PES(e+h)}$), whereas the black curve represents the contribution only from the outer hole Fermi surface ($\gamma_{PES(h)}$). The results of bulk thermodynamic measurements are also plotted by a pink shaded curve and red dots ($\gamma_{el}$). Error bars reflect experimental uncertainty in determining the peak position of EDCs/MDCs.

along the two directions (0.3–0.35 eV Å) are essentially similar, indicative of a small anisotropy along the $k_z$-direction, whereas the $v_F$ value of the outer Fermi surface along the $\Gamma M$ cut is reduced down to 0.1 eV Å, showing in the highly anisotropic $v_F$ value along $k_z$. Moreover, the $v_F$ value of an inner electron pocket ($\approx 0.05$ eV Å) is smaller than that of the outer hole pocket, indicating that the electron pocket contributes significantly to the density of states at $E_F$. We have estimated the electronic specific heat coefficient $\gamma_{PES}$ by using the equation $\gamma_{PES} = \pi N_A k_B^2 a_0^2 / 3h \sum m^*$ [26]. We calculated the value $\sum m^*$ by averaging the observed quasiparticle mass $m^* = \hbar k_F / v_F$ over the 3D Fermi surface by assuming the in-plane isotropy of the $k_F$ and $v_F$ values and also neglecting the $v_F$ component along $k_z$. In figure 8(d), we compare the $\gamma_{PES}$ value with the $\gamma_{el}$ from the specific-heat measurement [27]. When we do not consider the presence of an electron pocket in the highly doped region (black circles), the $\gamma$ value does not show a discernible doping dependence and always keeps a value of 10–15 mJ mol$^{-1}$ K$^2$. On the other hand, when we take into account the contribution from the electron pocket, the $\gamma$ value...
is significantly enhanced up to 30 mJ mol\(^{-1}\) K\(^2\) at the highly doped region in accordance with the jump of \(\gamma_{\text{el}}\). Remarkably, the \(\gamma_{\text{PES}}\) shows quantitative agreement with the \(\gamma\) from the specific-heat measurement, demonstrating that the enhancement of \(\gamma\) is due to the appearance of the electron pocket. Figure 8(d) suggests that about 60\% of the total \(\gamma\) is from the electron pocket in the Na0.77 sample. The present ARPES experiment is also consistent with the presence of the previously reported Lifshitz transition [28, 29] and the theoretical prediction of the enhancement of thermo-power caused by the pudding mold band [30].

Finally, we discuss the present ARPES result in relation to iron pnictides. A recent ARPES study of the parent compound of iron pnictide CaFe\(_2\)As\(_2\) [31] reported that one of 2D Fermi surfaces in the normal state transforms into a 3D-like Fermi surface below the SDW transition, which is interpreted in terms of the SDW-driven reconstruction of the Fermi surface. In Na\(_x\)CoO\(_2\), on the other hand, we observe the 2D–3D transition of the Fermi surface in the non-SDW normal state upon the band filling. While the dimensional crossover of electronic states is certainly related to the SDW order in both pnictides and cobaltates, the involved physics may be different between the two. Namely, the 2D–3D transition of the Fermi surface is a consequence of the SDW in pnictides, while it is a cause of SDW in cobaltates. The origin of such an interesting difference should be further investigated by the comprehensive ARPES measurements of both systems, which cover the wide temperature and doping range.

4. Summary

We have performed photon-energy-dependent ARPES measurements of Na\(_x\)CoO\(_2\) with a wide range of Na concentration (0.35 \(\leq\) \(x\) \(\leq\) 0.85). We clarified that the \(a_{1g}\) Fermi surface exhibits a 3D character in the highly doped region, whereas it is 2D in the low-doped region, demonstrating that the dimensional crossover takes place upon band filling. These characteristic variations in the electronic states are ascribed to the presence of a local minimum structure in the \(a_{1g}\) band, as well as the rigid-band-like chemical potential shift. We also found good agreement of the present ARPES result with reported physical properties, such as the specific-heat coefficient, and suggested a close connection between the appearance of the 3D electron pocket and the anomalous physical properties in the highly doped region.

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