The electronic structure of single crystals \( \text{Na}_{0.6}\text{CoO}_2 \), which are closely related to the superconducting \( \text{Na}_{0.3}\text{CoO}_2 \cdot \text{yH}_2\text{O} \) \( (T_c \sim 5 \text{ K}) \) [1] has generated great interest in the condensed matter physics community. Over the past 17 yr, the study of high-\( T_c \) superconductivity has focused on copper oxide compounds (cuprates). The unexpected finding of superconductivity in cobalt oxide (cobaltates) raises the hope that it may help solve the Fermi Surface and Unusual Band Dispersion problem. Similar to the cuprates, \( \text{Na}_{0.6}\text{CoO}_2 \) has the same electron filling level \( (\text{Co}) \), which is believed to be a \( p \)-wave superconductor. The two materials have similar behaviors in transport and magnetic susceptibility [5,6]. In addition, both materials exhibit ferromagnetic fluctuations at low temperatures [7,8], which are believed to be responsible for the \( p \)-wave pairing in the ruthenate. Indeed a \( p \)-wave triplet superconducting state has been suggested for the cobaltate [9]. In addition, we note that both materials have the same electron filling level \( (\frac{2}{3}) \) for the maximum superconductivity. This is further away from half-filling than in the cuprates, where the filling number of \( 1 \pm 0.16 \) is usually regarded as the optimal doping level.

Band structure and Fermi surface (FS) topology are known to be important in understanding unconventional superconductivity. Different electronic structures may induce different fluctuation, which can lead to different pairing symmetry. In this Letter, we report an angle-resolved photoelectron spectroscopy (ARPES) study on \( \text{Na}_{0.6}\text{CoO}_2 \) single crystals. Although \( \text{Na}_{0.6}\text{CoO}_2 \) is not a superconductor, a reduction of the Na concentration and proper hydration can turn this material into a superconductor [1]. It is worth mentioning that \( \text{Na}_{0.5}\text{CoO}_2 \) has a large thermoelectric power \( (S \sim 100 \text{ mV/K at 300 K}) \), which is 1 order of magnitude larger than in typical metals and high-\( T_c \) cuprates [5]. In our ARPES study, we observe clear band dispersion and FS crossings in \( \text{Na}_{0.6}\text{CoO}_2 \). While the observed FS location agrees with the large FS predicted by local-density approximation (LDA) band theory [10], the predicted small FS pockets near the \( K \) points are not observed. The observed Fermi velocity for the near-\( E_F \) band is renormalized and anisotropic along the two principal axes \((\Gamma-M, \Gamma-K)\). The Fermi velocity is reduced by a factor of 3 along \( \Gamma-M \), and 5–10 along \( \Gamma-K \). In addition, we observe an unusual band splitting along \( \Gamma-M \), which is however absent along \( \Gamma-K \).
High-quality Na$_x$CoO$_2$ single crystals are grown using the floating-zone method. The Na composition $x = 0.6$ is determined by inductively coupled plasma atomic emission spectroscopy [11]. ARPES experiments are performed at the Synchrotron Radiation Center, Wisconsin. The energy resolution is $\sim 10–20$ meV, and the momentum resolution $0.02 \, \text{Å}^{-1}$. Samples are cleaved and measured in situ in a vacuum better than $8 \times 10^{-11}$ Torr at low temperatures (20–40 K) with a flat (001) surface. The sample is stable and shows no sign of degradation during a typical measurement period of 12 h. The sample is oriented according to its Laue diffraction pattern.

In ARPES, a sign for a good surface is a clear valence band dispersion, which is observed in this material, as shown in Fig. 1. We measure the valence band at a number of photon energies, ranging from 16–110 eV. The band dispersion is clearly visible, as shown in Fig. 1(a), where a set of energy distribution curves (EDCs) along $\Gamma$-$K$ are measured with 22 eV photons. In Fig. 1(b), we plot the intensity of the second derivatives of the measured EDCs to display the band dispersion. It can be seen in Fig. 1(b) that the extracted band dispersion has some similarities to the calculated band structure [10]. In Fig. 1(c), we integrate spectra over a large $k$ space to mimic the density of states (DOS) for two different photon energies (22 and 70 eV). Four peaks can be identified at binding energies of 5.9, 4.6, 2.8, and 0.7 eV, respectively, matching well with the calculated band structure [10]. In Fig. 1(c), we integrate EDCs along $\Gamma$-$K$ using 22 eV (red) and 70 eV (blue) photons. The dashed line is the total DOS from band theory [10]. (d) Near-E$_F$ EDCs at $k_F$ along $\Gamma$-$K$ using 22 eV (red) and 70 eV (blue) photons.

Figure 2 shows dispersing spectra along a principal axis $\Gamma$-$K$, or (0,0)-(0,\frac{1}{2}) in the hexagonal reciprocal lattice. The unit of $k$, used throughout this article, is $\pi/a$, where $a$ (2.84 Å) is the nearest Co-Co distance. As seen in Fig. 2(a), a “shoulderlike” peak centered around $-65$ meV starts to emerge at $k \sim (0,0.67)$. With decreasing $k$, this peak disperses toward $E_F$, and seems to cross $E_F$ at $\sim (0,0.5)$. Note that another broad peak around 160–200 meV emerges at $k_x > 0.8$, which has no smooth connection to the $A_{1g}$ band. A careful examination of the spectra indicates that there is a “break” in the dispersion, as shown in Fig. 2(b). Comparing to the calculated band dispersion along $\Gamma$-$K$, this break occurs at almost the same $k$ location where the $A_{1g}$ band intersects with another $t_{2g}$ band, usually called the $E'$ band. The $E'$ band is predicted to cross $E_F$ and form a small FS pocket near the $K$ point. However, no evidence of this FS crossing is
observed in our experiment, which may result from a shift in the chemical potential due to electron correlations or other many-body interactions. A possible explanation for the break in dispersion is that the electron band interacts with a collective mode. Not that three phonon modes, with an energy of \( \sim 55-75 \) meV, have been observed by a Raman experiment [13].

To see the low-energy excitations more clearly, we subtract the large background from the EDC. One example of the subtraction is demonstrated in Fig. 2(c), where an almost straight line is used for the background. The background-subtracted EDCs along \( \Gamma - K \) are plotted in Fig. 2(d). One can clearly see that an asymmetrical peak disperses toward \( E_F \) while its line shape sharpens up. At \( k = (0, 0.5) \), the peak experiences a substantial reduction in its intensity, indicating that the peak is crossing \( E_F \) and the sharp Fermi function removes most of the spectral weight above \( E_F \). After the crossing, a small peak near \( E_F \) persists for an extended range of \( k \), from \( \sim (0, 0.5) \) to \( (0,0) \). This indicates that there is an extended flatband just above the \( E_F \). The small peak is the leftover intensity from the Fermi function cutoff. We note that there is an extended flatband in both the cuprates (i.e., \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \)) and the ruthenate \( \text{Sr}_2\text{RuO}_4 \). While the influence of the flatband to superconductivity is still under debate, the enhanced DOS near \( E_F \) would certainly enhance spin and charge fluctuations, which are found to be strong in all three materials.

ARPES spectra along another principal axis \( \Gamma - M \), or \( (0,0) - [(2/\sqrt{3}), 0] \), are plotted in Fig. 3. Symmetric dispersion can be observed along a long cut in \( k \) over different Brillouin zones (BZs). We observe some differences for spectra between \( \Gamma - M \) and \( \Gamma - K \). One major difference is that there is a band splitting along \( \Gamma - M \). This splitting can be easily seen if we zoom in at the band crossing, as shown in Figs. 3(c) to 3(e), where we plot the intensity plot, EDCs, and momentum distribution curves (MDCs) in the vicinity of the band splitting. From these three displays, we observe two nearly parallel bands in the vicinity of \( k_F \) with an energy separation of \( \sim 60 \) meV and a momentum separation of \( \sim 0.1 \pi/\alpha \).

We summarize our ARPES results in Fig. 4. In Fig. 4(a), we plot the FS crossings (FSCs) in the hexagonal BZ. For comparison, the calculated FS [10] of \( \text{Na}_0.5\text{CoO}_2 \) is also plotted in Fig. 4(a). We have measured many samples with several photon energies; the results are consistent. All the FSCs shown in Fig. 4(a) are extracted directly from measurements, and no symmetry operations have been applied here. Note that the FSCs with the same symbols over different BZs are obtained from the same sample during a short time interval. This eliminates potential problems from sample misalignment and surface contamination, and helps accurately determine the size of the FS. As seen from Fig. 4(a), the size of the measured FS in \( \text{Na}_0.6\text{CoO}_2 \) is somewhat larger than the calculated one in \( \text{Na}_0.5\text{CoO}_2 \). We also noted that in a recent ARPES study [14] for a more Na-doped sample (\( \text{Na}_0.7\text{CoO}_2 \)), the observed holelike FS appears larger than the one observed here. The observation of a smaller occupied area with more doped electrons apparently violates the Luttinger theorem. It is possible that some electron carriers become localized at higher Na doping levels,
resulting in a reduction in the number of itinerant electrons that contribute to the area of the FS. This might also explain the unusual ferromagnetic transition observed in highly Na-doped samples [15,16].

We extract the band dispersion from peak positions in MDCs. The extracted band positions along \( \Gamma - M \) and \( \Gamma - K \) are plotted in Figs. 4(b) and 4(c). Reliable values of the dispersion can be obtained from \( E_F \) to \( \sim 70 \) meV since beyond this energy the spectral linewidth becomes so broad that its position is ill defined. As seen in Fig. 4(b), the measured band dispersion along \( \Gamma - M \) is nearly linear in the 70-meV range, with a Fermi velocity \( v_F \sim 0.41 \) eV \( \AA \). We use a simple tight binding band on the triangular lattice to fit the measured band dispersion for the outer band:

\[
e_k = -2t \left( \cos k_x + 2 \cos \frac{k_x}{2} \cos \frac{\sqrt{3} k_y}{2} \right) - \mu,
\]

where \( t \) is the nearest neighbor hopping integral, and \( \mu \) is the chemical potential. The fitting yields \( t \sim 44 \) meV (with a negative sign) along \( \Gamma - M \). The measured dispersion along \( \Gamma - K \) is more complicated, as shown in Fig. 4(c). In addition to the “flat dispersion” around 70 meV due to the break, the dispersion changes its slope at \( \sim 20 \) meV. This slope change may be a consequence of the flatband observed in this material [3].

Another surprising finding from this study is a relatively large band splitting along \( \Gamma - M \). In addition to the “flat dispersion” around 70 meV due to the flatband observed in the 70-meV range, with a Fermi velocity \( v_F \sim 41 \) eV \( \AA \). We use a simple tight binding model or LDA band theory. This small value of \( t \sim 12 \) meV and \( v_F \sim 0.12 \) eV \( \AA \) indicates a strong overlap with oxygen orbitals. In support of this, we note that the tight binding model or LDA band theory shows no discernible gap at the zone boundary of the doubled unit cell [10]. This suggests that the band can be unfolded to yield a c-axis dispersion rather than a splitting. (iii) No band splitting is observed along \( \Gamma - K \), which is not consistent with a simple bilayer splitting, although different \( k_y \) may modify the size of splitting. It is known that other phenomena, such as itinerant ferromagnetism or surface state, can also cause band and FS splitting. More studies are necessary in order to resolve this issue.

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