

Fermi Surface and Quasiparticle Dynamics of $\text{Na}_{0.7}\text{CoO}_2$ Investigated by Angle-Resolved Photoemission Spectroscopy

M. Z. Hasan,^{1,2,3,*} Y.-D. Chuang,^{1,3} D. Qian,¹ Y.W. Li,¹ Y. Kong,¹ A. Kuprin,³ A.V. Fedorov,³ R. Kimmerling,³ E. Rotenberg,³ K. Rossnagel,³ Z. Hussain,³ H. Koh,³ N. S. Rogado,^{2,4} M. L. Foo,^{2,4} and R. J. Cava^{2,4}

¹Joseph Henry Laboratories, Department of Physics, Princeton University, Princeton, New Jersey 08544, USA

²Princeton Center for Complex Materials, Princeton Materials Institute (PMI), Princeton, New Jersey 08544, USA

³Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

⁴Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

(Received 23 August 2003; published 18 June 2004)

We present the first angle-resolved photoemission study of $\text{Na}_{0.7}\text{CoO}_2$, the host material of the superconducting $\text{Na}_x\text{CoO}_2 \cdot n\text{H}_2\text{O}$ series. Our results show a hole-type Fermi surface, a strongly renormalized quasiparticle band, a small Fermi velocity, and a large Hubbard U . The quasiparticle band crosses the Fermi level from M toward Γ suggesting a *negative* sign of effective single-particle hopping t_{eff} (about 10 meV) which is on the order of magnetic exchange coupling J in this system. Quasiparticles are well defined only in the T -linear resistivity (non-Fermi-liquid) regime. Unusually small single-particle hopping and unconventional quasiparticle dynamics may have implications for understanding the phase of matter realized in this new class of a strongly interacting quantum system.

DOI: 10.1103/PhysRevLett.92.246402

PACS numbers: 71.20.-b, 73.20.At, 74.70.-b, 74.90.+n

Since the discovery of cuprate superconductivity [1], the search for other families of superconductors that might supplement what is known about the superconducting mechanism of doped Mott systems has been of great interest. The recent report of superconductivity near 5 K in the triangular lattice, layered sodium cobalt oxyhydrate, $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$, suggests that such materials may indeed be found [2]. The crystal structure of this material, and its precursor hosts, consists of electronically active triangular planes of edge sharing CoO_6 octahedra separated by Na (and hydration) layers that act as spacers, to yield electronic two dimensionality, and also as charge reservoirs [2–4]. It has been argued that Na_xCoO_2 is probably the only system other than cuprates where a doped Mott insulator becomes a superconductor, although the fully undoped system has not yet been realized [5,6]. $\text{Na}_{0.7}\text{CoO}_2$ is the host compound for these materials from which Na_x is varied to achieve superconductivity.

Despite some similarities with the cuprates, cobaltates show their own unique set of anomalous properties. For $\text{Na}_{0.7}\text{CoO}_2$, the anomalous Hall signal shows no saturation to 500 K [7], the thermopower is anomalously high and magnetic field dependent [8], there is linear- T resistivity (deviation from Fermi-liquid behavior) from 2 to about 100 K [7], and there is strong topological frustration [5,6,9]. This class of systems may potentially contain new fundamental many-body physics and may as well be the realization of Anderson's original triangular lattice resonating valence bond system [10]. Therefore it is of interest to have a detailed look at the charge dynamics, starting with the host material. In this Letter, we report results of an angle-resolved photoemission (ARPES) study of $\text{Na}_{0.7}\text{CoO}_2$. A direct measurement of detailed Fermi surface topology and quasiparticle dynamics is of significant interest as it would provide a microscopic

basis for understanding the complex electron behavior. We observe a hole-type Fermi surface generated by the crossings of an extremely flat quasiparticle whose spectral weight decreases on raising the temperature to around 120 K and correlated with the non-Fermi-liquid behavior.

Single crystals of $\text{Na}_{0.7}\text{CoO}_2$ were grown by the flux method [7]. Measurements were performed at the Advanced Light Source Beamlines 12.0.1 and 7.0.1 using a Scienta analyzer. The data were collected with 30 or 90 eV photons with better than 20 or 30 meV energy resolution, and an angular resolution better than 1% of the Brillouin zone. The chamber pressure was better than 5×10^{-11} torr. Cleaving the samples *in situ* at 16 K resulted in shiny flat surfaces, characterized by optical (laser-reflection) and electron diffraction methods to be flat, clean, and well ordered with the same symmetry as the bulk. No signs of surface aging were seen for the duration of the experiments. Instead of cleaving several crystals to map the complete Fermi surface topology, we have worked on an image mode with fully motorized manipulator at BL7.0.1 ARPES end station [11]. The entire Fermi surface topology could be mapped out within several hours after the cleavage.

Figure 1(a) shows the full valence band spectrum taken at 90 eV photon energy. It shows five prominent features: 0.7 eV, 3 eV (No. 2), 4.1 eV (No. 3), 6 eV (No. 4), and 11 eV (No. 5). The width of the main valence density of states being on the order of 7 eV is consistent with local-density approximation (LDA) calculations [13]. To account for the valence satellite, one needs to consider the on-site Coulomb interaction (U), and cluster calculations provide a measure of U . Such calculations, with a strong Hubbard U , suggest that the valence band has predominantly 1A_1 character (low-spin configuration $t_{2g}^x e_g^0$) and account for the 11 eV feature. We identify the 11 eV feature as a

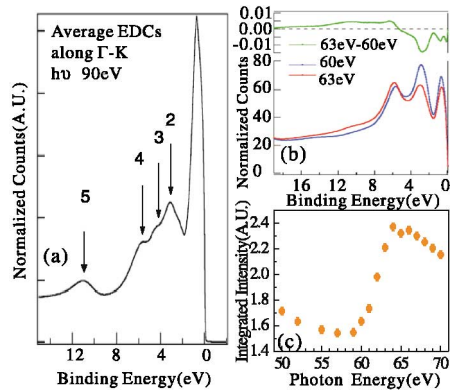


FIG. 1 (color). Valence excitations and resonance behavior: (a) Full valence band spectrum of $\text{Na}_{0.7}\text{CoO}_2$ taken at 90 eV photon energy. It shows five prominent features; the feature at 0.7 eV arises from Co t_{2g} states. (b) Valence band near Co: $3p \rightarrow 3d$ resonant excitation (~ 63 eV, red curve) compared with off-resonant excitation (~ 60 eV, blue curve). Resonance behavior of valence excitations shows the enhancement of the 11 eV feature (green curve), a correlation satellite. (c) Incident energy dependence of the 11 eV feature. It shows a Fano-type interference [12]

correlation satellite analogous to that seen in LaCoO_3 [14], an indication of strongly correlated behavior with a Hubbard $U \sim 5$ eV. The major low-energy feature is a broad band centered around 0.7 eV. Its resonance and photon-energy dependent behavior suggest that it consists of Co t_{2g} derived states, consistent with LDA and cluster calculations. Resonance behavior near $3p \rightarrow 3d$ excitation is shown in Fig. 1(b). Valence band near Co: $3p \rightarrow 3d$ resonant excitation (~ 63 eV) is compared with off-resonant excitation (~ 60 eV) by normalizing the area under both spectra to unity. Resonance behavior of valence excitations shows the enhancement of the broad 11 eV feature — a correlation satellite. Figure 1(c) shows the detail resonance behavior (Fano-type interference) of the correlation satellite. We also observe enhancements of the valence satellites under $2p \rightarrow 3d$ resonance (not shown here), supporting the identification of the 11 eV feature as a correlation satellite. Existence of such features and the resonance behavior are strong evidences for the system's highly correlated nature with large Hubbard U similar to the cuprates [15,12].

Much lower in energy near the Fermi level we observe a highly momentum (\mathbf{k})-dependent quasiparticle feature. Figure 2(a) shows this feature near the Fermi level crossing from M toward the Γ point in the Brillouin zone. Figure 2(b) shows part of the energy dispersion curves (EDCs) corresponding to Fig. 2(a). This feature is well defined in momentum and energy and only weakly dispersive, hardly dispersing more than 100 meV. Beyond 70 meV, the feature gets so broad (much broader than resolution) that the quasiparticle is not defined anymore in the sense that its lifetime is extremely short. To give a measure of bandwidth, we first make a dispersion plot using the following procedure: Take each EDC and sub-

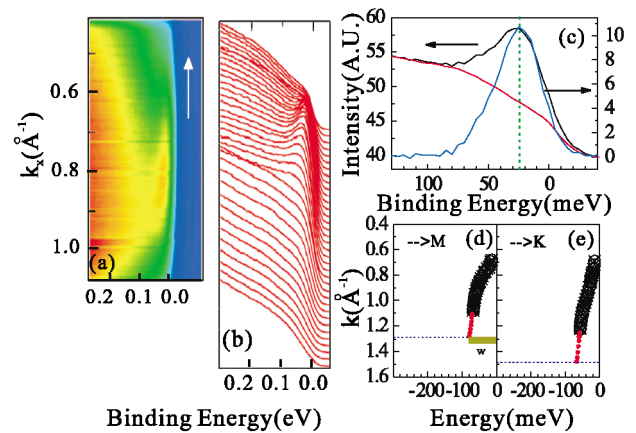


FIG. 2 (color). Quasiparticle dispersion: (a) $\Gamma \rightarrow M$ Fermi crossing. The color red reflects the highest intensity; yellow to green to blue is in the order of decreasing intensity. (b) EDCs corresponding to the image plot in (a). (c) A single EDC for $k = 0.78 \text{ \AA}^{-1}$. To extract the peak position a background is subtracted. A constant steplike background is best seen in 2(a). Based on the extracted peak positions E vs k plots are made and shown in (d) for $\Gamma \rightarrow M$ and in (e) for $\Gamma \rightarrow K$ directions.

tract a background as shown in Fig. 2(c). Note that a steplike background is observed for all k as evident from Fig. 2(a). After background subtraction, we take the centroid of the peak for its energy value [Fig. 2(c)]. Based on these peak positions, we make dispersion plots [Figs. 2(d) and 2(e)]. To get a measure for bandwidth, we extrapolate the band to the zone boundary as shown in Figs. 2(d) and 2(e). Since the band is narrow its extrapolation to the zone boundary is within the error bars of the measurement. This gives a value between 70 to 100 meV. Just looking at the raw data [Fig. 2(a)], one could argue that the band is narrower than 100 meV. It is interesting to note that this band is not well defined over the full Brillouin zone — a case similar to the cuprates and other correlated systems (strong correlation can lead to significant lifetime shortening away from Fermi level). This can also be due to strong scattering by bosonic collective modes such as phonons around 70 meV as a kink in dispersion [16]. A bandwidth of about 300–400 meV for cuprates is argued in a similar manner [16]. Note that the cobaltate band is about a factor of 5 narrower than the cuprates.

Figure 3 shows the experimentally measured $n(k)$ indicating a shape of the Fermi surface of $\text{Na}_{0.7}\text{CoO}_2$ over the complete Brillouin zone measured at a temperature of 16 K with a photon energy of 90 eV. The frequency-integrated spectral distribution, the $n(k)$ image, has been taken by integrating spectral weights within 75 meV below the Fermi level (and 25 meV above the Fermi level). It reveals a large hole pocket centered around the Γ point. The Fermi surface assumes a weak hexagonal character with an average radius of $k_f \sim 0.65 \pm 0.1 \text{ \AA}^{-1}$. Because of the unusually flat character of the band, there is larger uncertainty in the extracted value of k_f . This average k_f is calculated based on half of

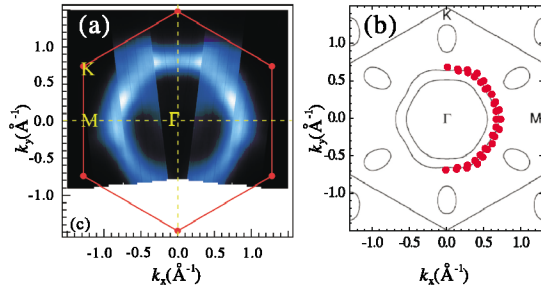


FIG. 3 (color). The $n(k)$ plot and Fermi surface of $\text{Na}_{0.7}\text{CoO}_2$: (a) $n(k)$ plot generated by integrating within 75 meV of Fermi level. A hole pocket is centered around the Γ point. The Fermi surface, exhibiting weak hexagonal anisotropy, is the inner edge of the pocket as shown over the complete Brillouin zone. (b) Comparison with LDA calculation on NaCo_2O_4 [13]. Red dots indicate the locations of measured Fermi crossings in $\text{Na}_{0.7}\text{CoO}_2$.

the Brillouin zone measured [Fig. 3(a)]. Based on the electron count assuming CoO_2 is a half-filled (completely) two-dimensional band, $x = 0.7$ doping would suggest a Fermi surface with $k_f \sim 0.54 \text{ \AA}^{-1}$. A larger 2D Fermi surface could be due to several different reasons. It can be due to some 3D coupling since in that case one needs to count the full 3D Fermi surface (noncylindrical) to satisfy the electron (Luttinger) count. This could also be due to the possibility that, although most of the doped electrons are in the Fermi sea, a small fraction is presumably localized and form local moments as seen in various experiments [7,17,18]. Note this could also be due to deviation from nominal (in-plane) doping level or magnetic ordering on the surface. However, it is interesting to note that the measured Fermi surface shape is similar to the one calculated for the related compound NaCo_2O_4 ($\text{Na}_{0.5}\text{CoO}_2$) using LDA [13]. A comparison is presented in Fig. 3(b). However, we do not observe any of the small satellite pockets predicted by LDA calculations around this large hexagonal Fermi surface (at least for the excitation photon energy of 90 eV where the search has been most extensive). This could be due to strong correlation effects, which can push the minority bands away from the Fermi level or wash out their relative intensity. It could also be due to the fact that one cannot shift the chemical potential with doping in a trivial way as commonly observed in doped Mott systems, so a straightforward rigid shift picture of the chemical potential for comparison may not be appropriate.

Along the $\Gamma \rightarrow M$ Fermi crossing, the quasiparticle band crosses the Fermi level from M toward Γ [Fig. 2(a)] as opposed to Γ to M . Such a dispersion behavior is consistent with the *negative* sign of single-particle hopping (t) and the first direct identification of the sign. This direct identification of the sign of (t) is important in constructing the relevant low-energy Hamiltonian of the system [5,6,9]. Based on several EDC cuts, we estimate the total bandwidth of this system which is between 70 to 100 meV (less than 100 meV). For a tight-binding hexagonal lattice

total bandwidth $W = 9t$, where t is the nearest neighbor single-particle hopping. This gives a value of the effective single-particle hopping, t_{eff} of about 10 ± 2 meV. It is interesting to note that this value is on the order of exchange coupling J (~ 10 meV) [17,18] in this system. The observed bandwidth is an order of magnitude renormalization compared to mean field calculations, which suggest a bandwidth of the order of 1 to 1.4 eV [5,6,13]. Such enhancement of effective mass is in agreement with electronic specific heat measurements [19,20]. Bandwidth suppression is likely to be responsible for enhancing the thermopower by an order of magnitude [8]. Single-particle hopping being on the order of exchange coupling suggests that the charge motion would be significantly affected by the spin dynamics of this system. Also a small value of t_{eff} suggests that this system has an unusually small fermion degeneracy temperature compared to conventional metals.

Momentum distribution curves (MDCs) could be fitted with a single Lorentzian function, on top of a linear background, except along $\Gamma-M$ where a weak double peak is seen in some crystals. The MDC fitting is known to produce reasonable results, especially when features are close to Fermi level E_f [21,16] though not without controversies. Lorentzian line shapes indicate that the quasiparticle self-energy is weakly dependent on the momentum normal to the Fermi surface [16]. We can then estimate the quasiparticle velocity normal to the Fermi surface. Such *MDC based* Fermi velocity is found to be less than 0.3 eV \AA . This value is much smaller than the nodal Fermi velocity of the cuprates ($\sim 1.7 \text{ eV \AA}$). This is consistent with the fact that the cuprate bands are more dispersive [16].

We further studied the quasiparticle spectral weight near the Fermi level as a function of temperature (Fig. 4). The quasiparticle weight decreases to almost zero (background level) on raising the temperature to around 120–150 K [Fig. 4(b)]. This roughly coincides with the temperature where the T -linear behavior in resistivity gives way to a stronger T dependence [Fig. 4(b)]. Apparently, quasiparticles exist in this system only in the temperature regime where resistivity is linear in T and transport behavior is non-Fermi-liquid-like. This is in contrast with the conventional expectation that well-defined quasiparticles are signatures of good Fermi-liquid behavior. We also note that this temperature scale coincides with our scale of effective single-particle hopping $t_{\text{eff}} \sim 10 \text{ meV} \sim 120 \text{ K}$. The Hall coefficient takes an upturn toward a linear- T dependence around this temperature scale [7]. This is also the temperature range when thermopower starts to deviate from linearlike behavior [7]. We argue that this is an important energy scale to describe the physics of these systems. A strong lack of quasiparticle weight at higher temperatures is also reminiscent of the lack of quasiparticles in the high temperature normal state of cuprates [16]. But in cuprates it is difficult to study the normal state over a large temperature range as

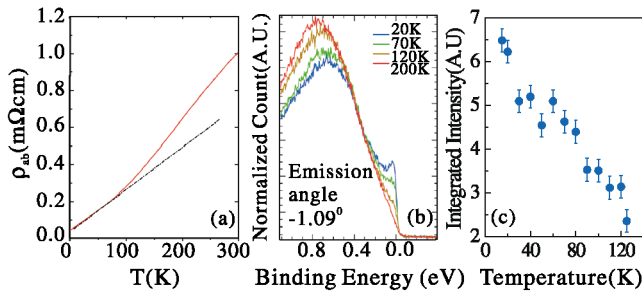


FIG. 4 (color). Temperature dependence: (a) In-plane resistivity in $\text{Na}_{0.7}\text{CoO}_2$ is linear up to 100 K [7] and then gradually crosses over to a stronger T dependence. (b) Temperature dependence of quasiparticles near the $\Gamma \rightarrow M$ Fermi crossing. The quasiparticle spectral weight ceases to exist above 120–140 K, close to the temperature where the T -linear behavior of the resistivity disappears. (c) Background subtracted integrated quasiparticle spectral weight is plotted as a function of temperature.

it enters the superconducting state at a fairly high temperatures. Also, cuprates cannot be too heavily overdoped. Cobaltates may offer the unique opportunity to study the normal state behavior of a heavily doped Mott system. This class of cobaltates has its own uniqueness and, hence, is interesting in its own rights. For the quasiparticle behavior, it may be that the transport in $\text{Na}_{0.7}\text{CoO}_2$ becomes incoherent well before a dimensional crossover (two- to three-dimensional charge transport, [17]) is reached. Such behavior could be related to the highly frustrated nature of the antiferromagnetic interactions in a triangular lattice.

Previously studied layered cobaltates structurally similar to the cuprate family of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, such as $\text{Bi}_2\text{Sr}_{2.1}\text{Co}_2\text{O}_y$ and $\text{Bi}_{1.5}\text{Pb}_{0.5}\text{Sr}_{2.1}\text{Co}_2\text{O}_y$, were not reported to exhibit a quasiparticle state [22]. Cobaltates such as $(\text{Bi}_{0.5}\text{Pb}_{0.5})_2\text{Ba}_3\text{Co}_2\text{O}_y$ or NaCo_2O_4 exhibit quasiparticles and Fermi surfaces that were found to be roughly rounded [23]. Recent studies rather suggest that $\text{Na}_{0.5}\text{CoO}_2$ is not even a metal [24]. A low temperature phase transition has been reported for $\text{Na}_{0.75}\text{CoO}_2$ —an indication that higher (commensurate) doping drives the system towards an ordering instability [25]. Despite the possibilities of kinematic nesting associated with the observed Fermi surface, the ordering in $\text{Na}_{0.75}\text{CoO}_2$ may be more complex due to the strongly correlated nature and the frustrated interactions in the system.

In conclusion, we report the first angle-resolved photoemission study of $\text{Na}_{0.7}\text{CoO}_2$. Resonant scattering of valence excitations indicates the existence of a large Hubbard U supporting the strongly correlated nature of the system. The low-energy results reveal a hole-type (negative t_{eff}) Fermi surface and an extremely narrow quasiparticle band (~ 100 meV), an order of magnitude renormalization from the mean field value. Such bandwidth suppression may be the key toward understanding the colossal thermopower and electronic specific heat.

Effective single-particle hopping being on the order of exchange coupling suggests that charge motion is significantly influenced by spin fluctuations in these systems. Quasiparticles are well defined only in the T -linear resistivity (non-Fermi-liquid) regime. The system's strongly correlated nature as manifested from an extremely narrow band and small Fermi velocity may shed clues toward understanding the broad spectrum of unusual properties. It would be interesting to study the doping evolution of the Fermi surface and quasiparticle behavior of these systems by combining ARPES and newly developed momentum resolved inelastic x-ray scattering [26]. Furthermore, any comprehensive theory for cobaltates needs to account for the unconventional quasiparticle dynamics observed.

The authors thank P.W. Anderson, N. P. Ong, S. Shastry, P. A. Lee, D. A. Huse, P. M. Chaikin, D. Singh, G. Baskaran, M. Johannes, and Y. Wang for valuable discussions and B. Mesler for technical assistance. The experiment was performed at the ALS of LBNL, which is operated by the U.S. DOE's BES with Contract No. DE-AC03-76SF00098. M. Z. H. acknowledges partial support through the NSF-MRSEC (DMR-0213706) grant and R. H. Dicke Grant by Princeton University Materials synthesis supported by DMR-0213706 and the DOE, Grant No. DE-FG02-98-ER45706.

*Electronic address: mzhasan@Princeton.edu

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