Low-lying electronic structure of doped triangular cobaltites

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We report detailed Fermi surface topology and quasiparticle dynamics of the host cobaltate Na$_{0.7}$CoO$_2$. A direct mapping of the Fermi surface is carried out by angle-resolved photoemission spectroscopy (ARPES). Fermi surface at 16 K is a hole-pocket centered around the Γ-point. The highly correlated nature of the electron liquid in this system is evidenced from strong on-site Coulomb interaction seen through a valence satellite and via renormalization of the quasiparticle dispersion. The quasiparticle exhibits spectral coherence only below 150K which includes the non-Fermi liquid regime.

INTRODUCTION

The family of sodium cobalt oxyhydrates or oxides (cobaltites) Na$_x$CoO$_2$ (with x varying from 0.7 to 0.3) attracted a great deal of attention recently after the discovery of superconductivity around 5 K in the x=0.3 compound. Though there are several clear differences in crystal structure and electronic structure between cobaltites and high-T$_c$ cuprates both systems have layered structure with electronic two-dimensionality, and typical strong electron correlations of a doped Mott insulator. Moreover, the triangular lattice of cobaltites induces spin frustration and hence may lead to Anderson’s RVB state that can also result in a non-s-wave order parameter. Low temperature ferromagnetic fluctuations observed in cobaltites may lead to a p-wave superconducting state. In addition, the cobaltite with x = 0.7, being the host compound for the family of lower x, demonstrates its own unusual physical properties like linear rise of resistivity with temperature up to 100 K, no saturation of the anomalous Hall signal up to 500 K, and extraordinary high and magnetic field dependent thermopower. Hence, the details of complete Fermi surface topology and of quasiparticle dynamics are highly desirable for understanding the unconventional physics of this promising class of materials. This work reports such direct measurements performed by the angle-resolved photoemission spectroscopy (ARPES) on the host compound Na$_{0.7}$CoO$_2$.

Single crystals of Na$_{0.7}$CoO$_2$ prepared by the flux method were kept under dry nitrogen gas and screened by x-ray diffraction in Laue geometry. ARPES experiments were carried out with Scienta analyzers at the Advanced Light Source Beamlines 7.0.1 and 12.0.1. Photon energy covered 30 eV - 90 eV range with energy resolution better than 30 meV. The complete Fermi surface topology was measured in the image mode of the programmable three-axis goniometer at the “Electronic structure Factory” endstation of Beamline 7.0.1. Fermi surface areas close to principal symmetry points were also obtained independently from a set of energy spectra for different angles of incidence and emission. Multi-angle mode allowed acquisition of energy spectra in 9.5’ wide emission angle window with an angular resolution better than 1% of the Brillouin zone (BZ). To obtain clean and flat surface, samples were cleaved under ultra-high vacuum of 5 × 10$^{-11}$ torr or better at 16 K.

ELECTRONIC STRUCTURE

The valence band dispersions along Γ - K and Γ - M principal symmetry lines follow the general trends of LDA calculations including energy positions, widths, and dispersion of recognized features at binding energies around 0.7 eV, 3.0 eV, 4.1 eV, 6.0 eV, and the width of the density of states of about 7 eV as shown in Fig-1(a) and Fig-1(b) respectively. Some bands may be less visible due to photon energy and polarization dependence of the matrix elements. A well defined peak is also observed at higher binding energies around 11 eV as shown in Fig-1(c). Its resonant enhancement near 3p → 3d excitation together with the photon energy dependence of the Fano-type interference are shown in Fig-2 and al-

![FIG. 1: Valence band of Na$_{0.7}$CoO$_2$: (a) and (b) intensity plots along Γ - M and Γ - K lines respectively; both images obtained with 65 eV photons, curves are the LDA results from (c) averaged energy dispersion curve (EDC) for Γ - K orientation obtained with 90 eV photons showing correlation satellite at around 11 eV.](image-url)
FIG. 2: Resonant enhancement of the correlation satellite at 11 eV: (a) EDCs taken at different photon energies around Co 3p → 3d transition at ~ 63 eV, and shifted for clarity. (b) Background subtracted integrated intensity of the 11 eV feature shows Fano-type interference resonance.

FIG. 3: The energy integrated k-resolved intensity map. Fermi surface of Na$_{0.7}$CoO$_2$ is the inner edge of the k-resolved intensity map (a hexagonal hole pocket).

low to identify it as a correlation satellite that arises from strong on-site Coulomb interaction and is consistent with cluster calculations with strong Hubbard - U(∼5eV), providing strong evidence for the electron’s highly correlated nature.

Quasiparticle features were found near the Fermi crossing along all direction from zone boundary towards Γ point. By tracing the crossing point in the whole Brillouin zone, we get the Fermi surface. The shape of the Fermi surface at 16 K is established to be an anisotropic hexagonal-like hole-pocket centered around the Γ - point as shown in Fig-3 $\text{[8]}$, in agreement with LDA calculations $\text{[7]}$ by integrating spectral weight from 75 meV below Fermi level ($E_F$) to 25 meV above it with 90 eV photons. In disagreement with these calculations, no small satellite pockets are observed around the central one. This may reflect strong electron correlations that may drive the minority bands out of $E_F$. The size of the central pocket is 0.65 ± 0.1 Å$^{-1}$. Intensity plot and energy dispersive curves (EDCs) near $E_F$ crossing along Γ - M and Γ - K symmetry lines are presented in Fig-4. These images were collected from the very same sample during the same experimental run and conditions following only 30° azimuthally rotation. The quasiparticle feature strongly depends on the momentum ($k$). Its spectral weight being well defined only in the limited area of the BZ may be explained by drastic lifetime shortening on departure from Fermi level similar to the case of cuprates and other correlated systems. For both principal orientations this quasiparticle feature disperses only slightly, overall hardly more than 100 meV. Thus, it is at least five times narrower than for the cuprates which is an order of magnitude renormalization from the mean field calculations $\text{[3, 7]}$ and hence may be responsible for an order of magnitude enhancement of thermopower $\text{[8]}$ and electronic specific heat $\text{[10]}$. Along both principal symmetry lines it crosses Fermi surface in the same direction - from the BZ boundary toward Γ - point, giving the negative sign of the nearest neighbor single particle hopping $t$. The quasiparticle (occupied) bandwidth is about 100 ± 30 meV. The value of $t$ can be estimated from tight-binding approximation and for the lattice with hexagonal symmetry (bandwidth = 9$t$) leads to 11 ± 3 meV. Such small values imply a very small fermion degeneracy temperature in comparison with normal metals. It is worth mentioning that these values are of the same order as exchange coupling $J ∼ 10$ meV for the compounds of this family $\text{[3]}$ and hence, charge motion might be strongly perturbed by the spin fluctuations. Na$_{0.7}$CoO$_2$ has small Fermi velocity less than ∼ 0.3 eV·Å, which can be estimated from EDC and momentum distribution curve (MDC) as well. This value is almost 6 times smaller than the nodal Fermi velocity for the cuprates of 1.8 eV·Å, which is in agreement with much wider dispersion of the cuprate quasiparticle bands $\text{[8]}$.

TEMPERATURE DEPENDENCE OF QUASIPARTICLE

We performed temperature dependent measurements of the spectral weight near $E_F$ presented in Fig-5. On raising temperature quasiparticle weight steadily decreases up to about 120 K, where it becomes indistinguishable from the background. Extrapolation to zero places the temperature value to around 150K. Similar behavior is observed by cooling the samples. This temperature roughly matches the crossover region where re-
FIG. 4: Quasiparticle feature near \( E_F \) along \( \Gamma - M \) and \( \Gamma - K \) cuts.

FIG. 5: Temperature scale for \( \text{Na}_0.7\text{CoO}_2 \): (a) \( T \)-dependence of quasiparticle weight along \( \Gamma - M \) line, (b) integrated spectral weight after background subtraction, and (c) in-plane resistivity.

 resistivity changes its temperature dependence from linear at lower temperatures to a much steeper one shown in Fig-5(c). Quasiparticle transport property may be connected to the inherently frustrated nature of local antiferromagnetic interactions in a triangular lattice as the strength of the exchange interactions \( J \) and single-particle hopping \( t \) are of the same order. It is interesting to note that this temperature scale is also relevant to peculiarities of Hall coefficient and thermopower. Such a low energy scale present in a variety of physical properties of this compound still lacks proper theoretical explanation. It is desirable to carry out inelastic x-ray scattering to study the collective charge dynamics in this system which would be complementary to the ARPES study.

CONCLUSIONS

In summary, we observed a number of electronic features that indicate the existence of strong Coulomb correlations in \( \text{Na}_0.7\text{CoO}_2 \): intense valence band satellites, a highly renormalized quasiparticle band near Fermi level and the existence of quasiparticle coherence only below 150K. The small low energy scales for the effective single-particle hopping \( t \), magnetic exchange coupling \( J \) and non-Fermi liquid behavior observed opens the way for unconventional physics in the cobaltates.

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Note added : Subsequent to our work H.B. Yang et.al. [12], reported a new measurement of FS on a sample with similar doping-level as ours. In this study, only one Fermi surface is found which is reported to be of size \( K_f \sim 0.6 \text{ Å}^{-1} \) [12]. This is in agreement with our reported value within the error bar.

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