ARPES study of many-body effects and electronic reconstructions in misfit cobaltates

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Outline

$\text{Na}_x\text{CoO}_2$ and misfit cobaltates

Counter-intuitive evolution of the correlation strength with doping

Nature of low energy excitations in cobaltates?

Study of ARPES lineshapes

$\Rightarrow$ Consistent with strong correlations ($Z = 0.15$ at $x=0.7$).

$\Rightarrow$ Increasing correlations near $x=1$, towards the band insulator.

Influence of the 3D environment on electronic orderings in CoO$_2$ planes?

$\Rightarrow$ Deviation from the rigid band filling picture at high $x$

$\Rightarrow$ Consistent with partial electronic localization induced by the Na or misfit potentials
Cobaltates: triangular planes of Co filled by a variable number of electrons

Metallic phases with charge, spin, orbital degrees of freedom...
How do they interact? Does Na play a role?
From Mott insulator to band insulator…

Na$_x$CoO$_2$

Mott insulator ?

Band insulator

Magnetic correlations seem to appear near the band insulator!

Foo et al., PRL 92, 247001 (04)
Competing degrees of freedom

Triply degenerate band, hybridization with oxygen, triangular geometry may frustrate AF correlations…

Possibility of coupled spin-orbital-lattice excitations
=> spin-orbital-polarons ?

« The low-lying magnetic states of Co$^{3+}$, accessible for electrons via the intersite hopping, provide an extra dimension in physics of Na$_x$CoO$_2$. »

Khaliullin and Chaloupka PRB 77, 104532 (2008)
An additional degree of freedom: role of Na?

Na induced correlations?
Marianetti and Kotliar
PRL 98, 176405 (2007)

NMR detects inequivalent Co sites at high $x$

$^{59}\text{Co NMR}$
$\text{Na}_{0.72}\text{CoO}_2$

I.R. Mukhamedshin et al., PRL 2005

The charge order is induced by Na order

H. Alloul et al., EPL 2009
Two families of cobaltates: Na and misfits

- Charge transfer from Rock-Salt planes to CoO$_2$ planes
- Doping equivalent to $x=0.7-0.9$
- Different 3D environment (better surface quality for ARPES)
Electronic properties of misfit cobaltates

Pauli to Curie-Weiss susceptibilities

Resistivity vs Temperature

High TEP values

$\rho_{ab} (\text{m} \Omega \text{cm})$

$A=\text{Ca}$

Sr

Ba

W. Kobayashi et al.

Same magnetic interactions & different charge order / disorder?

J. Bobroff et al. PRB 2007

$K_{\text{iso}}(\%)$

$T (K)$

$\times=0.7$

$\times=0.75$

$\times=0.85$
Electronic structure as seen from ARPES
Band structure of a CoO\textsubscript{2} plane (from LDA)

Co\textsuperscript{4+} + \( x \) electrons on a triangular lattice

Singh et al., PRB 2000; Lee et al., PRB 2004
Same low energy electronic structure in Na and misfit cobaltates (BiBaCo)

ARPES in $\text{Na}_x\text{CoO}_2$ : M.Z. Hasan et al., PRL2004, D. Qian et al., PRL2006
H.B. Yang et al., PRL 2004, 2005

Hexagonal FS from Co $a_{1g}$ band

- No $e'_{g}$ pockets

High effective mass

- Narrow band near the Fermi level
$V_F = 0.3\text{eV.Å}$

Peculiar lineshape

- Two dispersing components

V. Brouet et al., PRB2007
How to interpret the lineshape in BiBaCo?

- Strongly renormalized $a_{1g}$ band
How to interpret the lineshape in BiBaCo?

- Strongly renormalized \( a_{1g} \) band
- Or kink? (of what origin?)
- Or interactions between \( a_{1g} \) and \( e'_{g} \) bands? (hybridization gap)

=> Depending on the interpretation: \( 1.5 < m^*/m < 6 \)
Using light polarization to observe different orbitals

ARPES intensity proportional to:

\[
\langle \phi_f^k | A \cdot \mathbf{p} | \phi_i^k \rangle \begin{cases} 
\phi_i^k \text{ even } & \langle + | + | + \rangle \Rightarrow A \text{ even } \\
\phi_i^k \text{ odd } & \langle + | - | - \rangle \Rightarrow A \text{ odd. }
\end{cases}
\]

- \text{\textit{a}}_{1g} : \text{even}
- \text{\textit{e}}'_{g1} : \text{odd}
- \text{\textit{e}}'_{g2} : \text{even}
The structure of $a_{1g}$ is not due to interaction with $e'_{g}$

Horizontal polarization:
- even bands $a_{1g} + e'_{g2}$

LDA bands
- Experimental dispersion
Intrinsic peak-dip-hump structure of $a_{1g}$

\[ \Gamma \rightarrow K \rightarrow \Gamma \rightarrow M \]

even

\[ \Gamma K \]

odd

\[ \Gamma M \]

$\Gamma K$ and $\Gamma M$ diagrams show the peak-dip-hump structure of $a_{1g}$.

$\Gamma K$ and $\Gamma M$ diagrams illustrate the binding energy distribution.

\[ e'_{g1} \quad e'_{g2} \quad a_{1g} \]

$e'_{g1}$ and $e'_{g2}$ are distinct energy levels, with $a_{1g}$ being another level.

$a_{1g}/e'_{g}$ splitting sensitively depends on the octahedra distortion.

M.B. LePetit, PRB 2007

$\Rightarrow$ Subtracting LV spectrum from LH isolates the PDH of $a_{1g}$.
Intrinsic peak-dip-hump structure of $a_{1g}$

BiBaCo

Manganites $La_{1.2}Sr_{1.8}Mn_2O_7$

« Waterfall » in cuprates $Ca_2CuO_2Cl_2$


F. Ronning et al. PRB 2005
The distribution of spectral weight imply strong many-body effects

\[ Z = 0.15 \pm 0.05 \]

\[ Z \times \text{(LDA bandwidth)} = 0.2 \text{eV} \]

\[ \Rightarrow 0.2 \text{eV is the QP energy scale} \]

A. Nicolaou et al., PRL 2010
In this case, spectral weight information is more direct than self-energy fits.

Typical fits of width increase and dispersion renormalization fail to reproduce the HP weight at \( E_F \)

\[ \omega_0 = 0.25 \text{eV}, \lambda = 1 \]

A. Nicolaou et al., PRL 2010
The QP « disappears » at high temperature

Typical behavior of a strongly correlated system
The QP « disappears » when doping increases

- The correlations seem to increase near the band insulator.

- Why are there strong correlations in this limit?
  - => Polaronic lineshape?
  - => Electronic orderings?

BiBaCo
x=0.71, m=2

CaCoO
x=0.75, m=1.6

BiSrCo, Pb doped

BiSrCo
x=0.77, m=1.82

BiCaCo
x=0.85, m=1.7

x increases towards band insulator
Electronic orderings at high dopings?

H. Alloul et al., EPL 2009
Misfit cobaltates: Evidence for coupling between Rock-Salt and CoO$_2$ planes

$[\text{Bi}_2\text{Ba}_2\text{O}_4]_2\text{CoO}$

$\Rightarrow$ Replica appear with RS periodicity

What is the effect of the RS potential on the electronic motion in the CoO$_2$ plane?
Rock-Salt structure

Inequivalent Co sites with respect to Ba\(^{2+}\) positions.

\[ \Rightarrow \] Situation may be analogous to Na\(_x\)CoO\(_2\)

\[ \Rightarrow \] Co\(^{3+}\) may form directly below a Ba\(^{2+}\)
The number of metallic holes in the band can be deduced from the FS area.

For BiBaCo:
- \(x=0.71, m=2\)

For CaCoO:
- \(x=0.75, m=1.6\)

For BiSrCo, Pb doped:
- \(x=0.77, m=1.82\)

For BiCaCo:
- \(x=0.85, m=1.7\)

The Fermi Surface of BiBaCo:

- \(k_F=0.6 \Rightarrow x=0.7\)
The number of metallic holes in the band can be deduced from the FS area

- BiBaCo, \(x=0.71, m=2\)
- CaCoO, \(x=0.75, m=1.6\)
- BiSrCo, Pb doped
- BiSrCo, \(x=0.77, m=1.82\)
- BiCaCo, \(x=0.85, m=1.7\)

... larger than in BiBaCo
\(k_F=0.75\) instead of \(k_F=0.6\)

\(\Rightarrow x=0.5\)
Deviation from Luttinger theorem in cobaltates

- Deviation from the rigid band filling at high $x$.
- More holes than expected = consistent with presence of $\text{Co}^{3+}$. 

BiBaCo, $x=0.7$  
CaCoO, $x=0.75$
Localization with structure depending on the potential inprinted by neighboring planes

\[ \text{Na}_{2/3}\text{CoO}_2 \Rightarrow \text{Kagomé} \]

Misfits \(\Rightarrow\) « striped » structures

Different metallic structure may explain different evolution of metallicity

A. Nicolaou et al., EPL 2010
New electronic orderings?

- BiBaCo
  - $x=0.71$, $m=2$

- CaCoO
  - $x=0.75$, $m=1.6$

- BiSrCo, Pb doped
  - $x=0.77$, $m=1.82$

- BiSrCo
  - $x=0.85$, $m=1.7$

STM, coll. Soleil.

80Å
Conclusions

- Misfit cobaltates offer an alternative opportunity to study CoO$_2$ slabs. Na$_{0.7}$CoO$_2$ and BiBaCo show a very similar electronic structure.

- Excitations have a strong many-body character (« peak-dip-hump » structure).

  => *The QP energy scale is 0.2eV.*

- There is a systematic deviation from Luttinger theorem, suggesting inhomogeneous charge order in CoO$_2$ plane. Its periodicity might depend on the intercalated structure.

  => *Role on CW susceptibilities and high TEP?*