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

Véronique Brouet, Alessandro Nicolaou

*Laboratoire de Physique des Solides d'Orsay*


M. Zacchigna (Elettra), A. Tejeda (Nancy)
A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran (SOLEIL)

Samples : S. Hébert, W. Kobayashi, H. Muguerra, D. Grebille (CRISMAT Caen, France)

# Experiments carried out at :

## Swiss Light Source

SIS : L. Patthey
M. Shi

## Elettra

APE : I. Vobornik
BACH : M. Zacchigna

## SOLEIL

CASSIOPEE :
A. Taleb-Ibrahimi,
P. Le Fèvre, F. Bertran

# Outline

$Na_xCoO_2$ and misfit cobaltates

Counter-intutive evolution of the correlation strength with doping

Nature of low energy excitations in cobaltates ?

Study of ARPES lineshapes

=> Consistent with strong correlations (Z = 0.15 at x=0.7).

=> Increasing correlations near x=1, towards the band insulator.

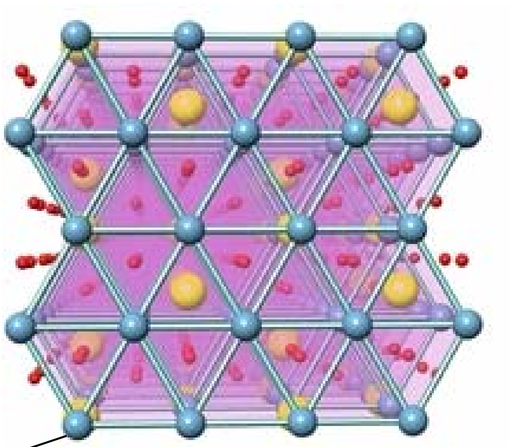
Influence of the 3D environment on electronic orderings in $CoO_2$ planes ?

=> Deviation from the rigid band filling picture at high x

=> Consistent with partial electronic localization induced by the Na or misfit potentials

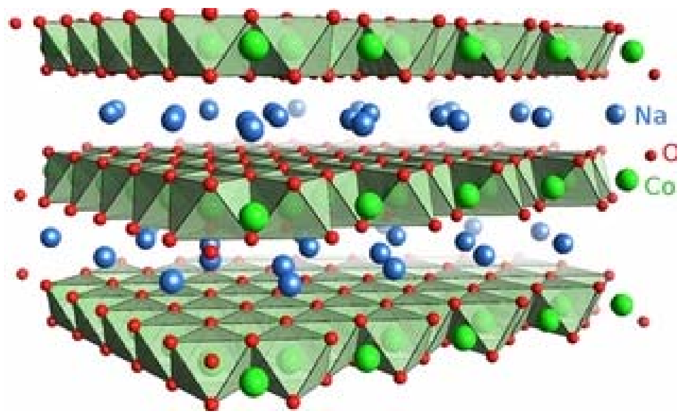
# Cobaltates : triangular planes of Co filled by a variable number of electrons

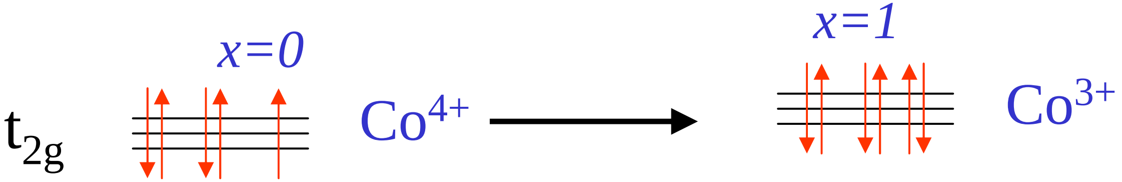
$CoO_2$ slabs



Co

$Na_xCoO_2$

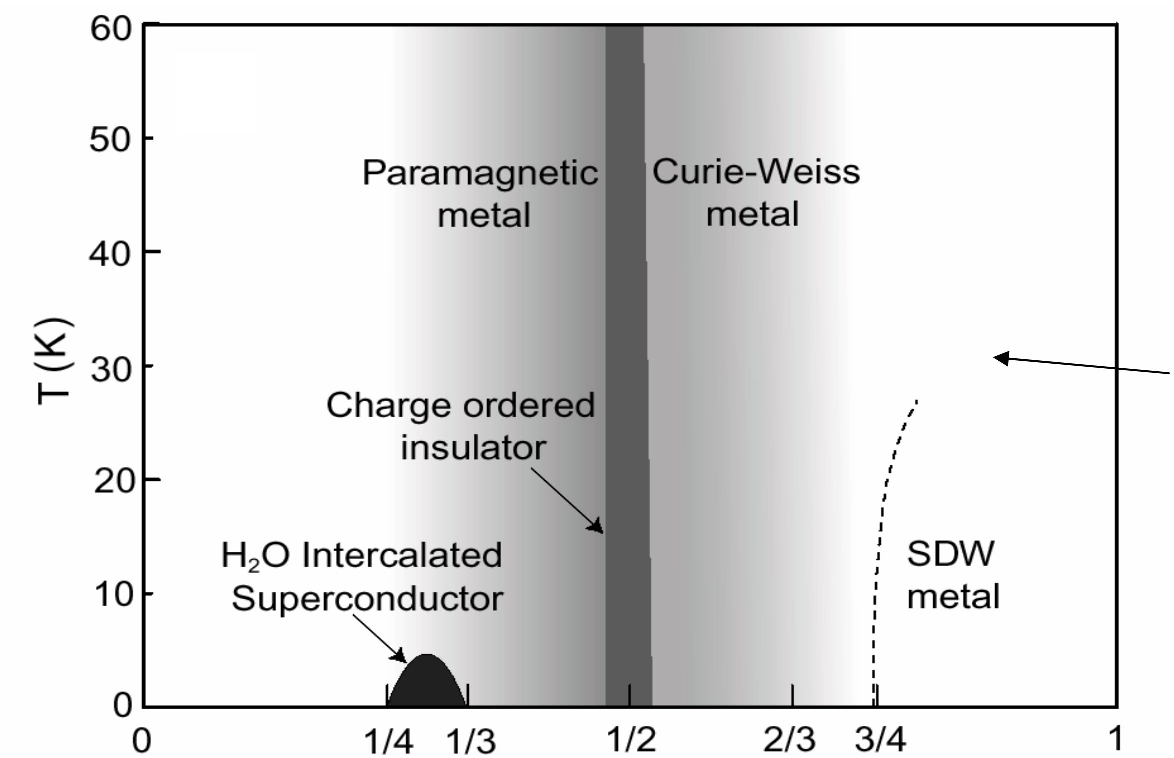



Metallic phases with charge, spin, orbital degrees of freedom…
How do they interact ? Does Na plays a role ?

# From Mott insulator to band insulator…

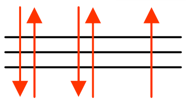
$Na_xCoO_2$




Foo *et al.*, PRL **92,** 247001 (04)

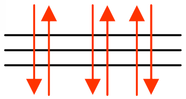
High TEP

$t_{2g}$



$Co^{4+}$

$Co^{3+}$



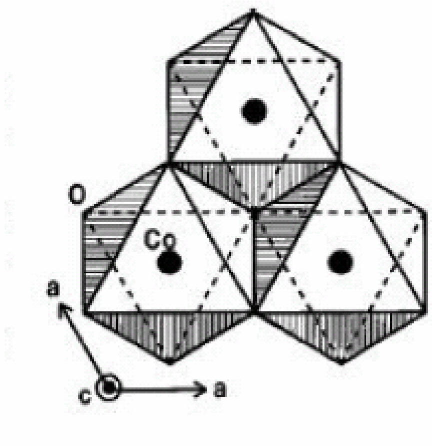
*Mott insulator ?*

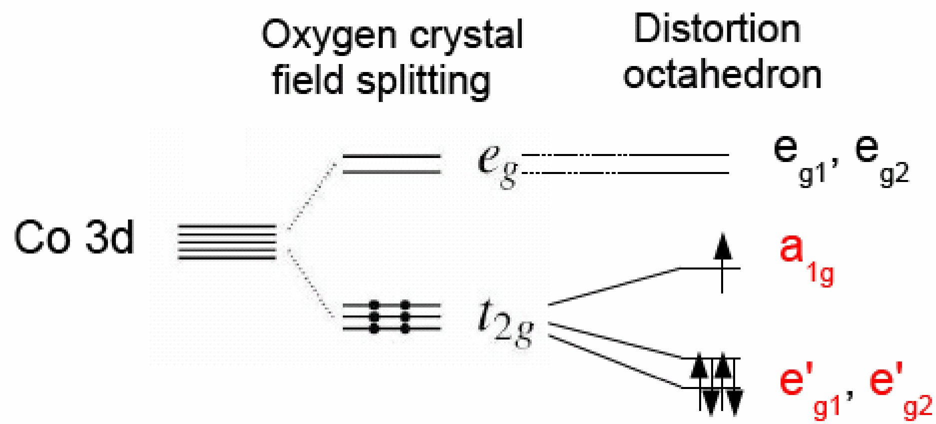
*Band insulator*

*Magnetic correlations seem to appear near the band insulator !*

# Competing degrees of freedom

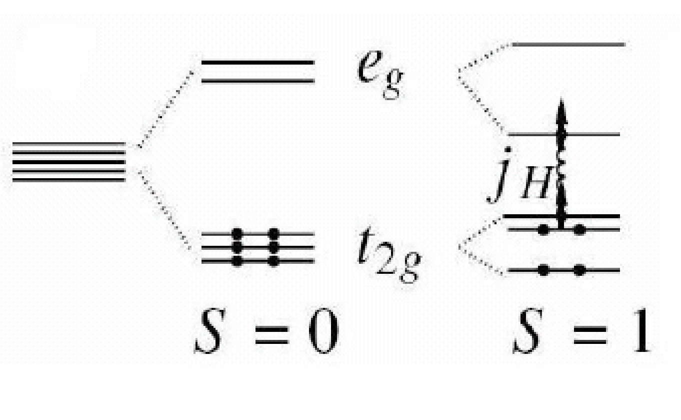
Triply degenerate band, hybridization with oxygen, triangular geometry may frustrate AF correlations…




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

$Co^{3+}$



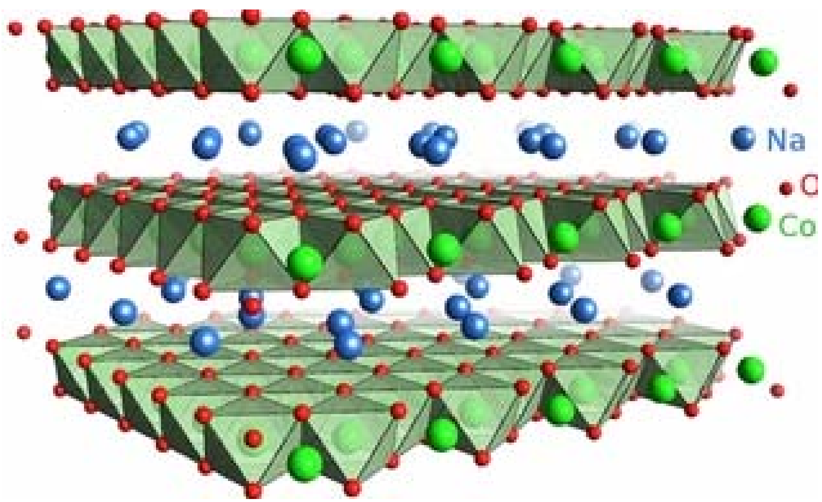

« The low-lying magnetic states of $Co^{3+}$, accessible for electrons via the intersite hopping, provide an extra dimension in physics of $Na_xCoO_2$. »

Khaliullin and Chaloupka PRB 77, 104532 (2008)

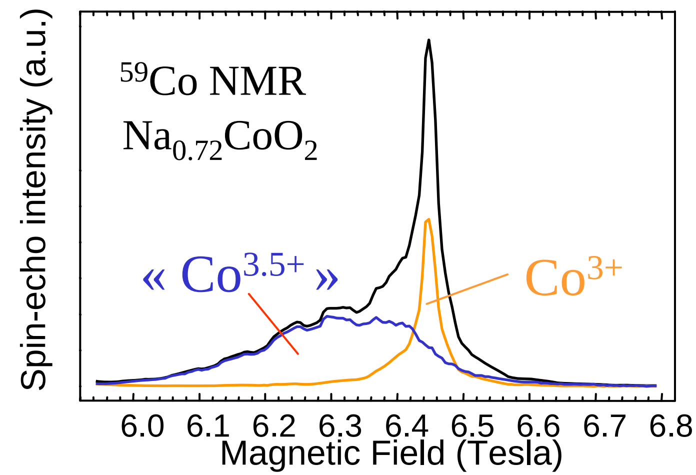
# An additional degree of freedom : role of Na ?

Na induced correlations ?

Marianetti and Kotliar
PRL **98**, 176405 (2007)

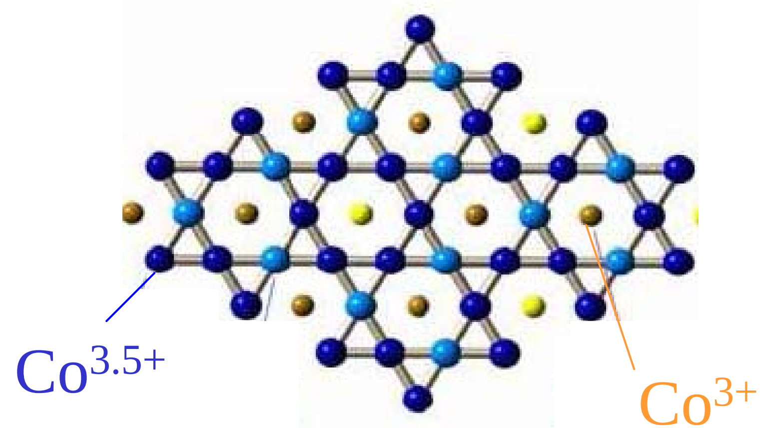



NMR detects inequivalent Co sites at high *x*




I.R. Mukhamedshin *et al.*, PRL 2005

The charge order is induced by Na order

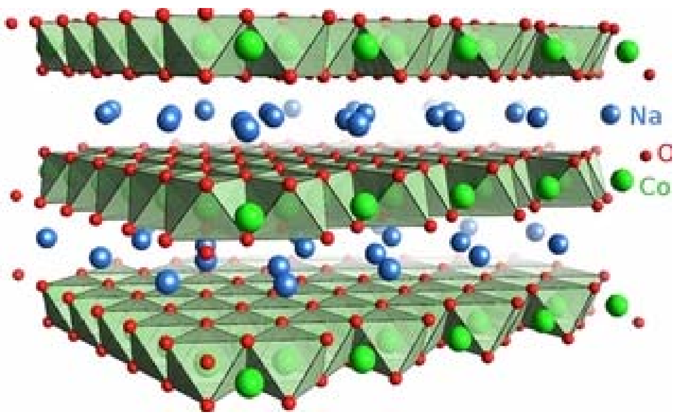


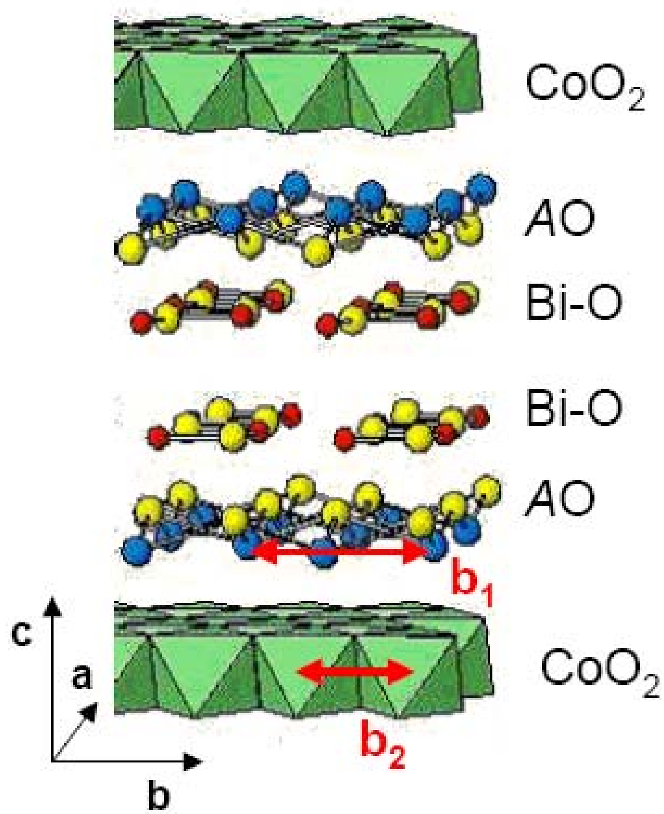

H. Alloul *et al.*, EPL 2009

# Two families of cobaltates : Na and misfits

$[Bi_2A_2O_4][CoO_2]_{b1/b2}$

$Na_xCoO_2$

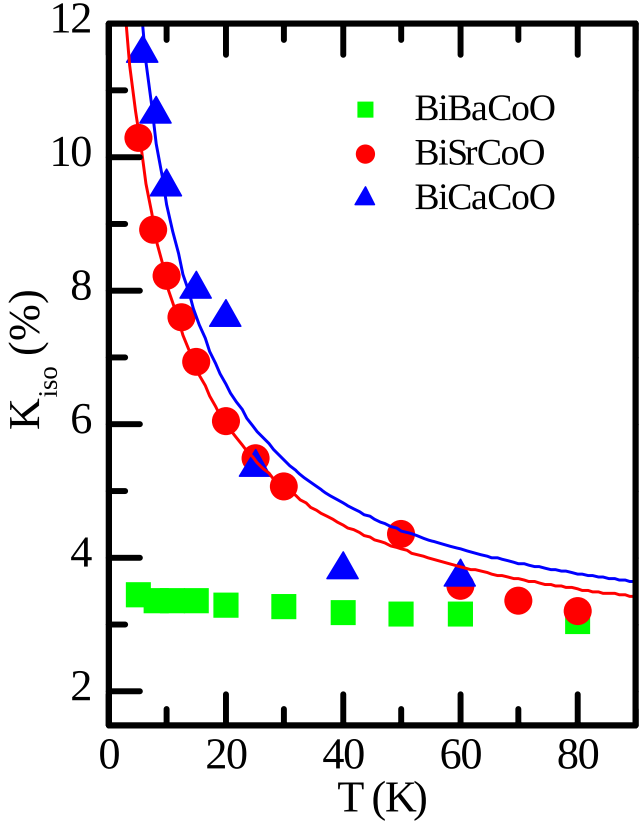



- Charge transfer from Rock-Salt planes to $CoO_2$ planes
- Doping equivalent to x=0.7-0.9
- Different 3D environment (better surface quality for ARPES)

# Electronic properties of misfit cobaltates

Pauli to Curie-Weiss susceptibilities

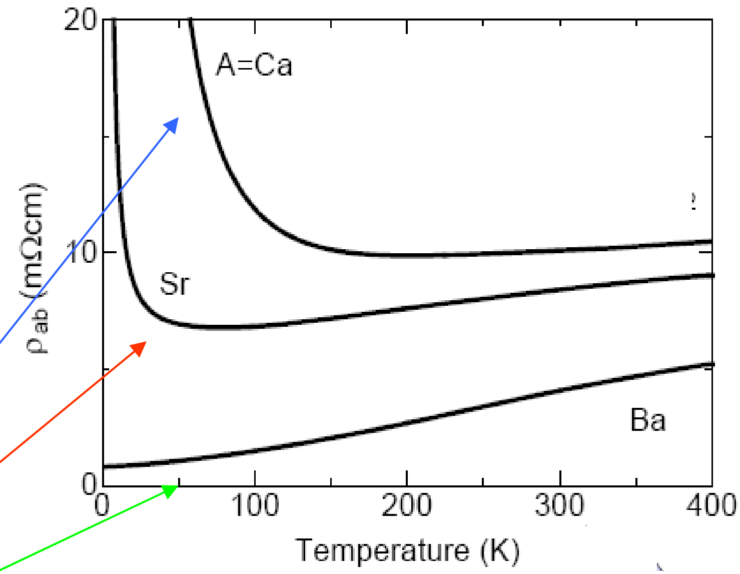



J. Bobroff *et al.* PRB 2007

Resistivity vs Temperature

High TEP values

*x*=0.85
*x*=0.75
*x*=0.7

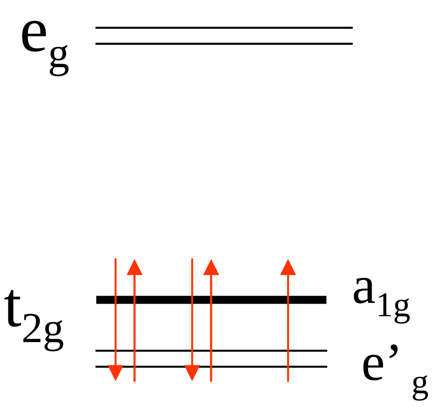



W. Kobayashi *et al.*

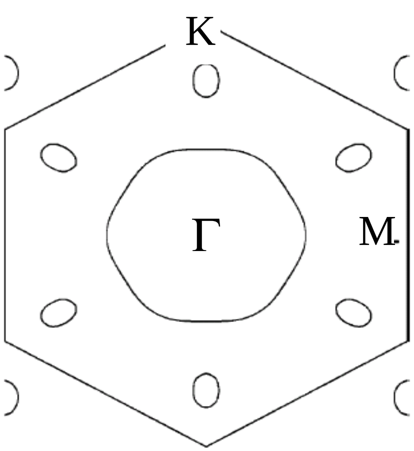
Same magnetic interactions
& different charge order / disorder ?

# Electronic structure as seen from ARPES

# Band structure of a $CoO_2$ plane (from LDA)

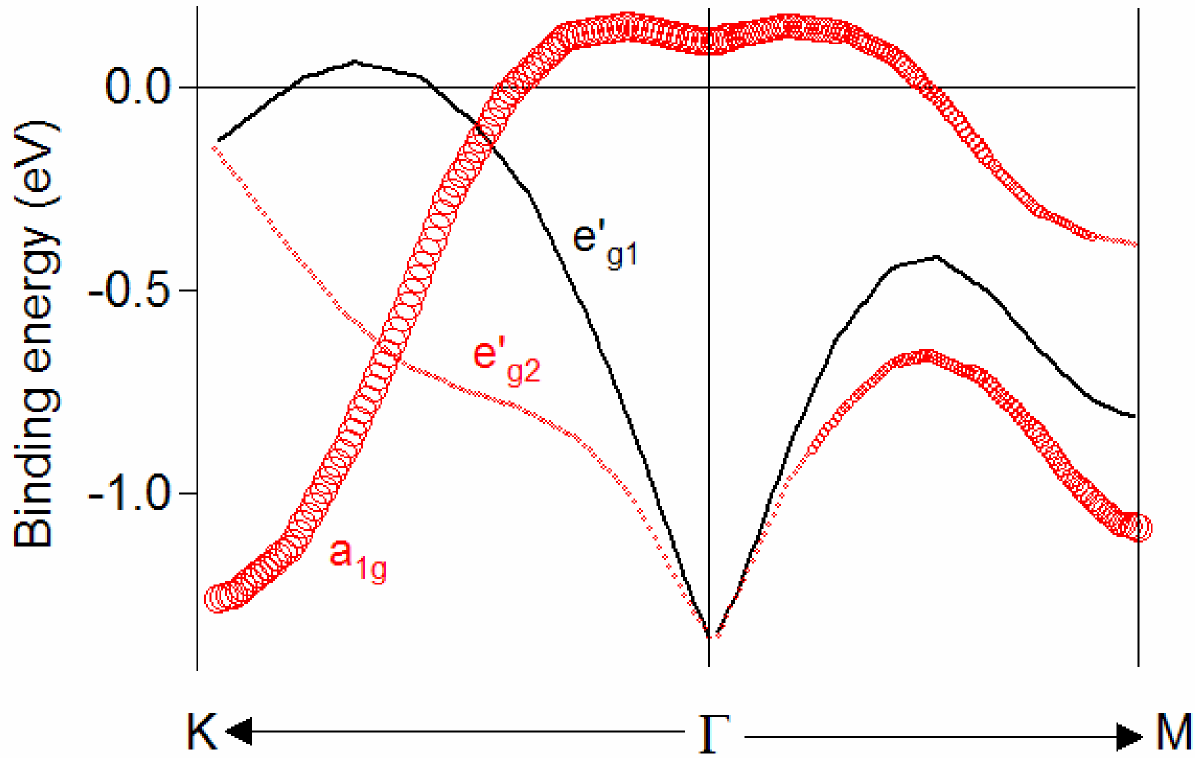



$Co^{4+}$ + *x* electrons
on a triangular lattice




Surface de Fermi

$Na_{0.5}CoO_2$

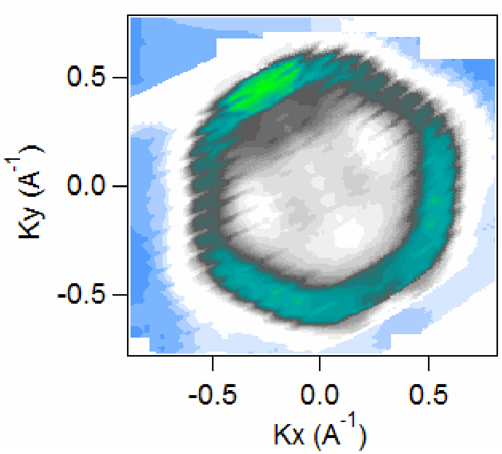



Singh *et al.*, PRB 2000; Lee *et al.*, PRB 2004

# Same low energy electronic structure in Na and misfit cobaltates (BiBaCo)

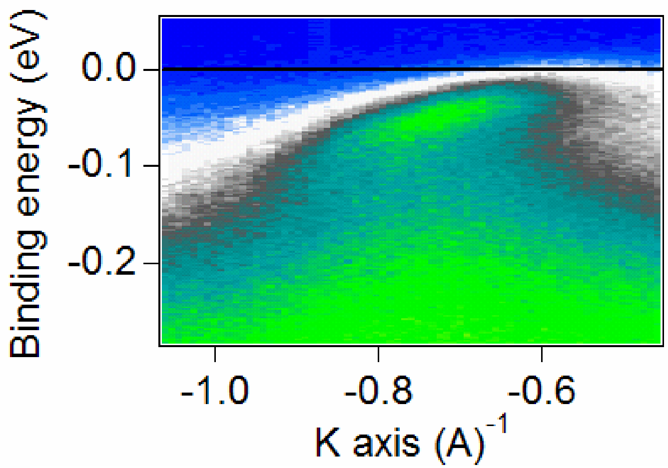
ARPES in $Na_xCoO_2$ : M.Z. Hasan *et al.*, PRL2004, D. Qian *et al.*, PRL2006
H.B. Yang *et al.*, PRL 2004, 2005

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




- No $e'_g$ pockets

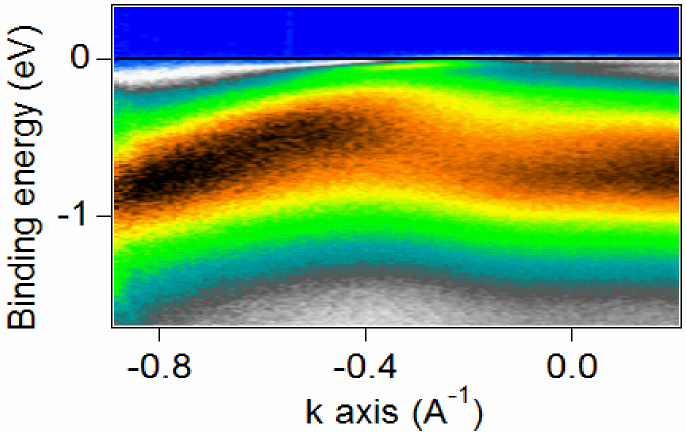
High effective mass




- Narrow band near the Fermi level

$V_F = 0.3eV.Å$

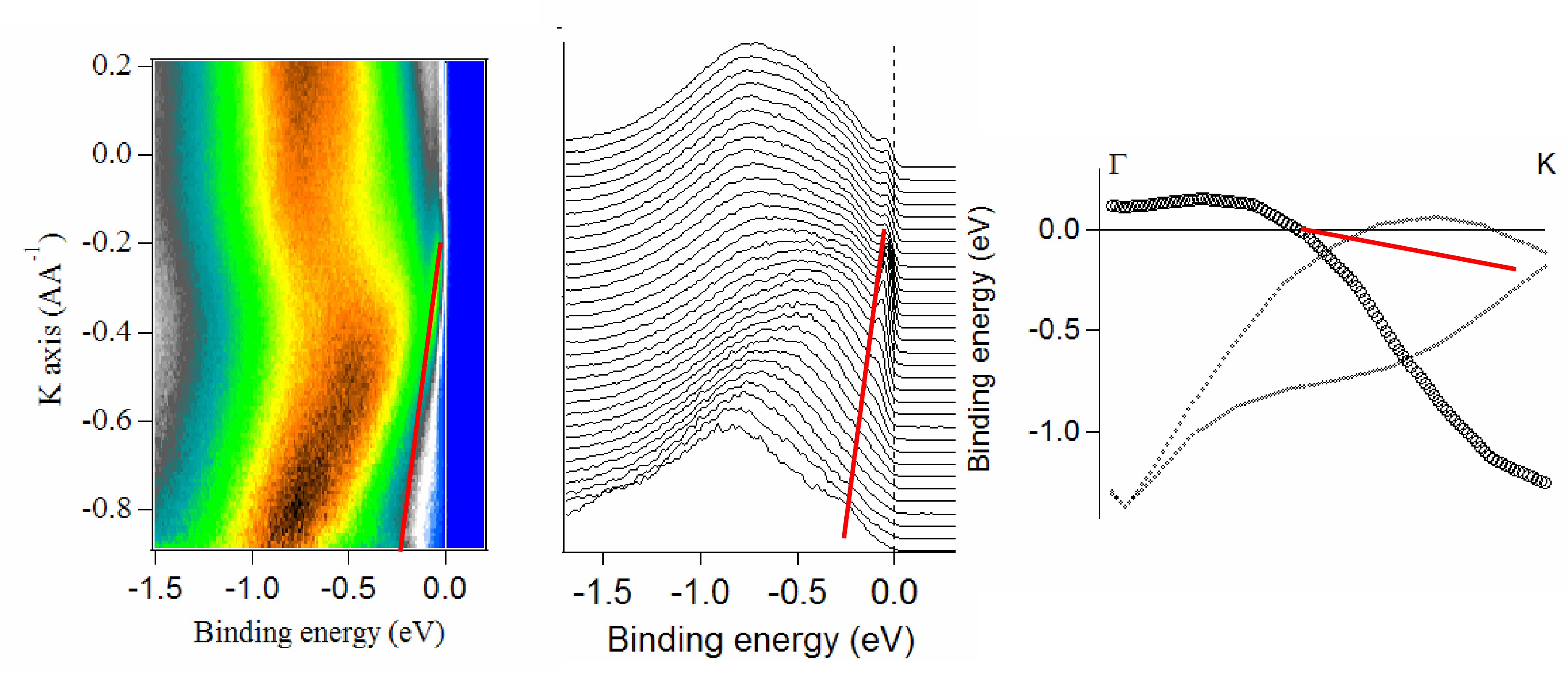
Peculiar lineshape




- Two dispersing components

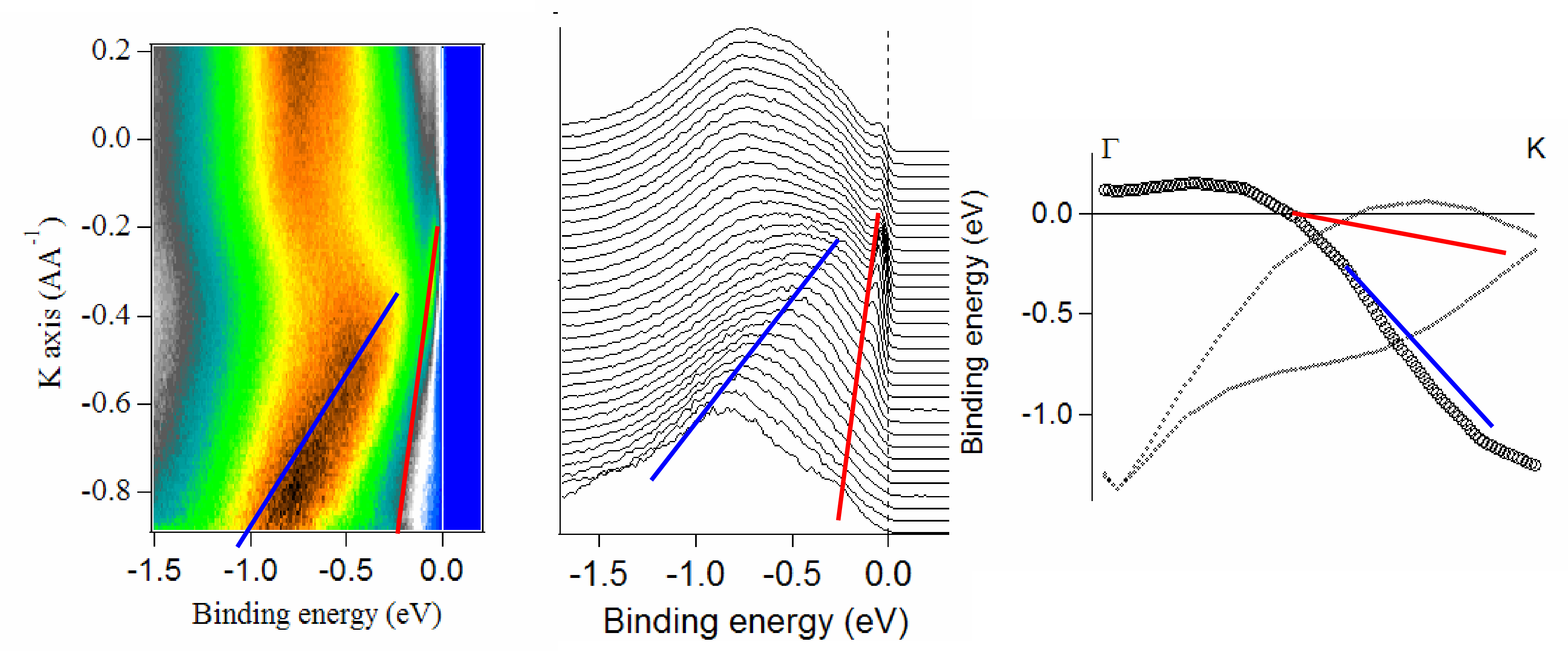
V. Brouet et al., PRB2007

# How to interpret the lineshape in BiBaCo ?




- Strongly renormalized $a_{1g}$ band

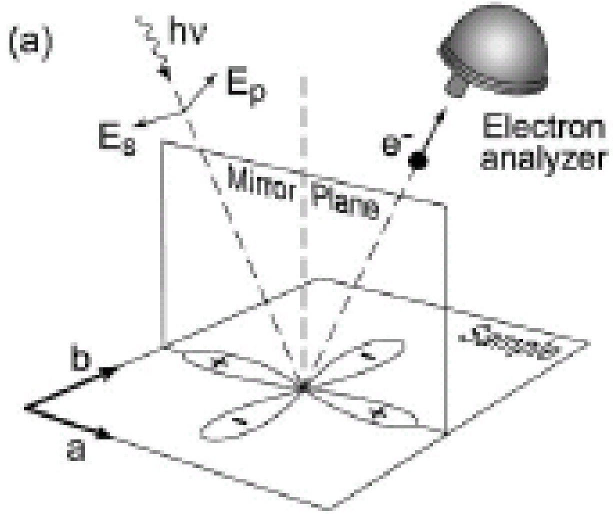
# How to interpret the lineshape in BiBaCo ?




- 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*

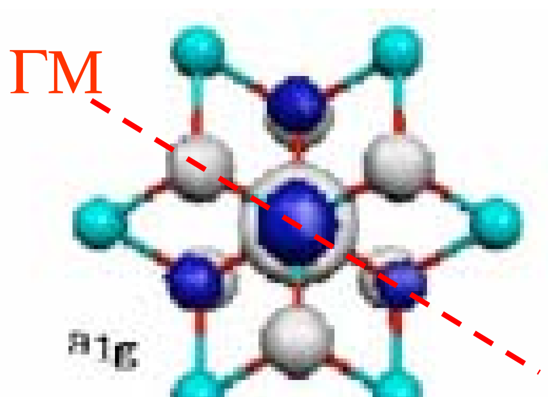
# Using light polarization to observe different orbitals



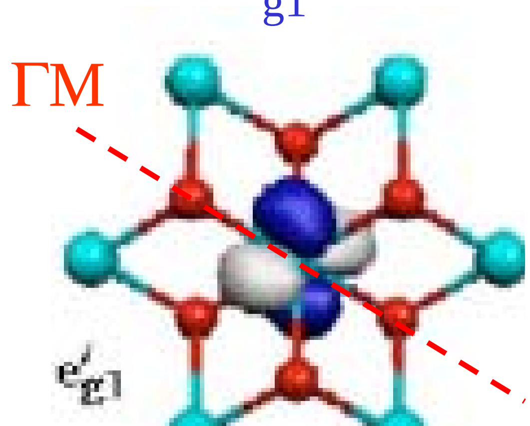

ARPES intensity proportional to :

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

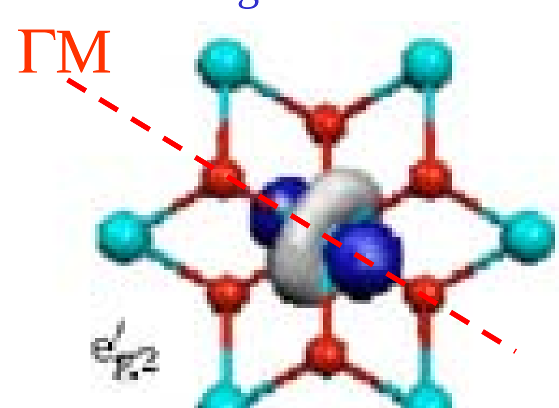
$a_{1g}$ : even




$e'_{g1}$ : odd



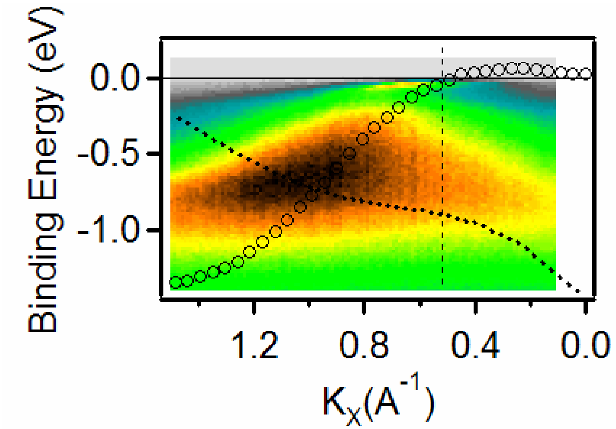

$e'_{g2}$ : even



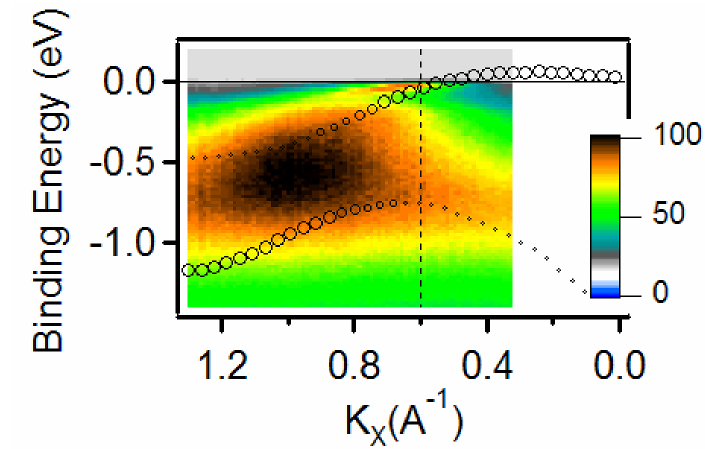
# The structure of $a_{1g}$ is not due to interaction with $e'_g$

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

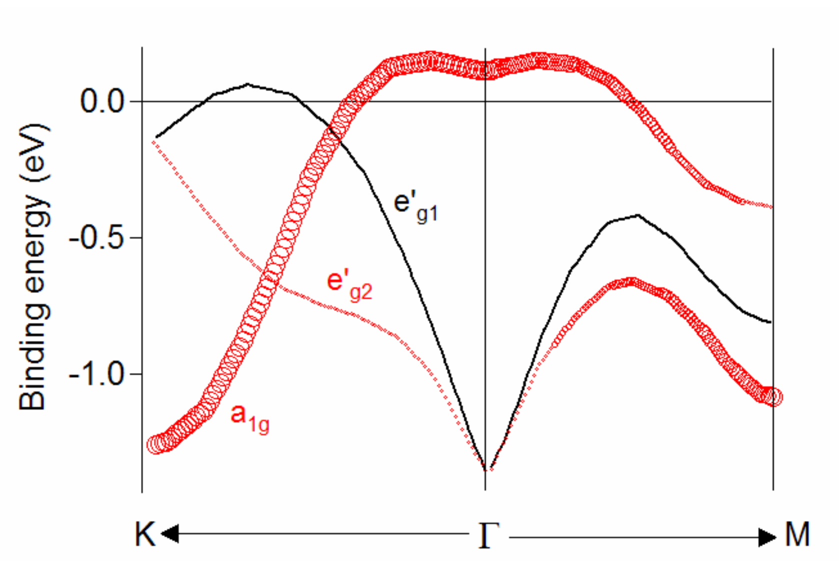
ΓK



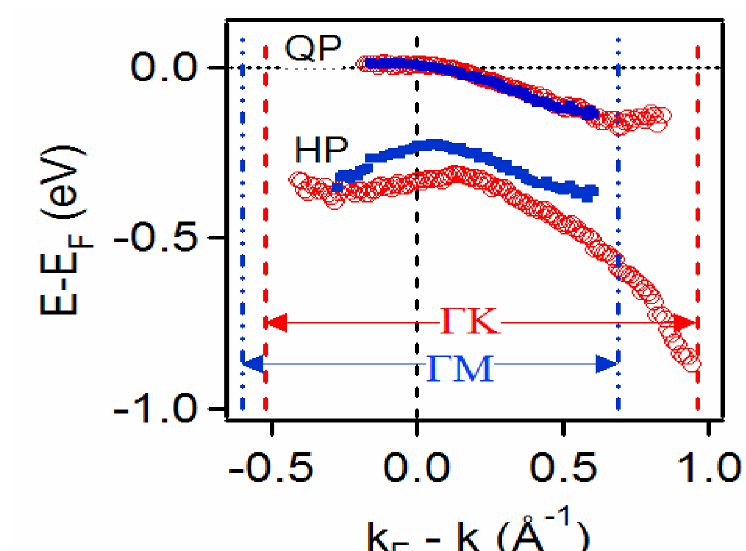

ΓM




LDA bands




Experimental dispersion

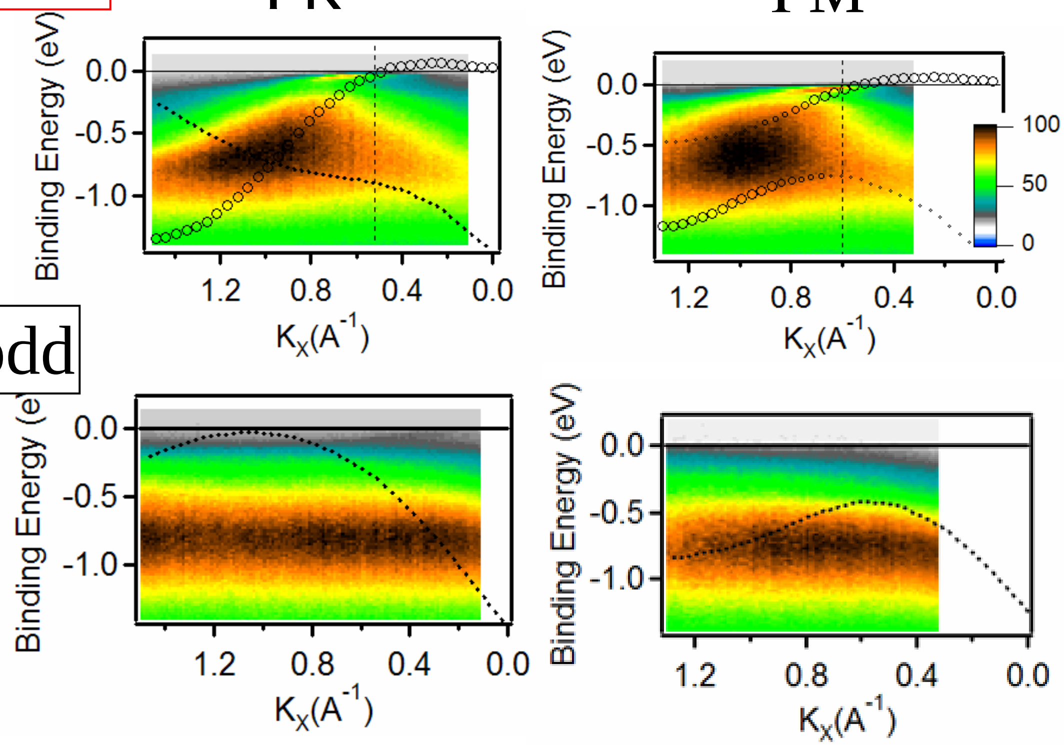


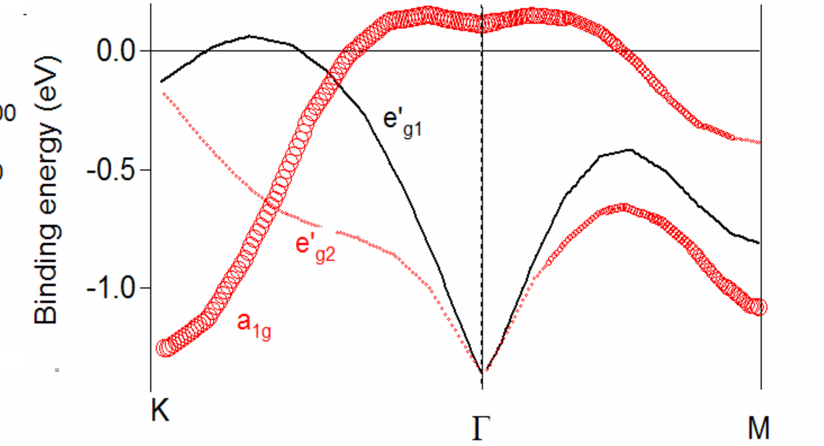
# Intrinsic peak-dip-hump structure of $a_{1g}$

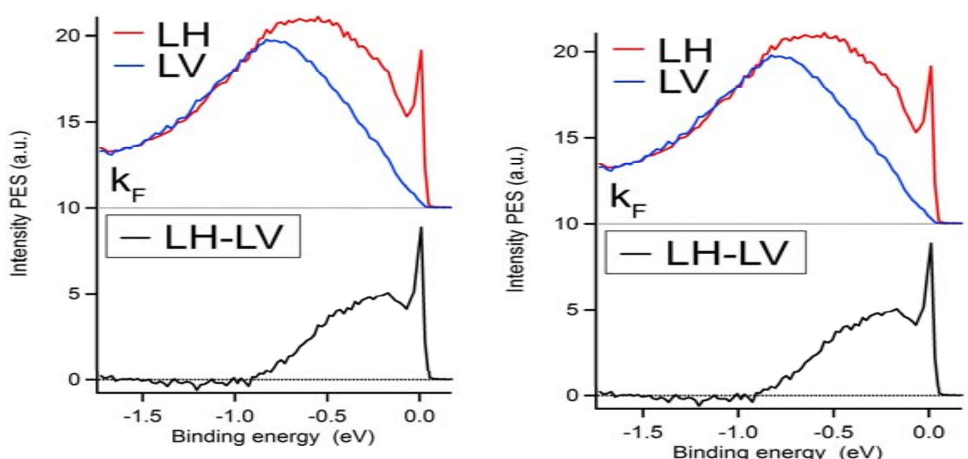
even

ΓK ΓM

odd

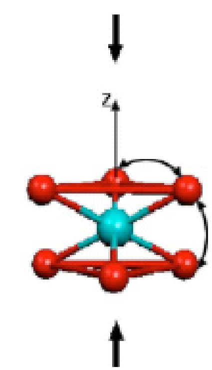



$a_{1g}/e'_g$ splitting sensitively depends on the octahedra distortion

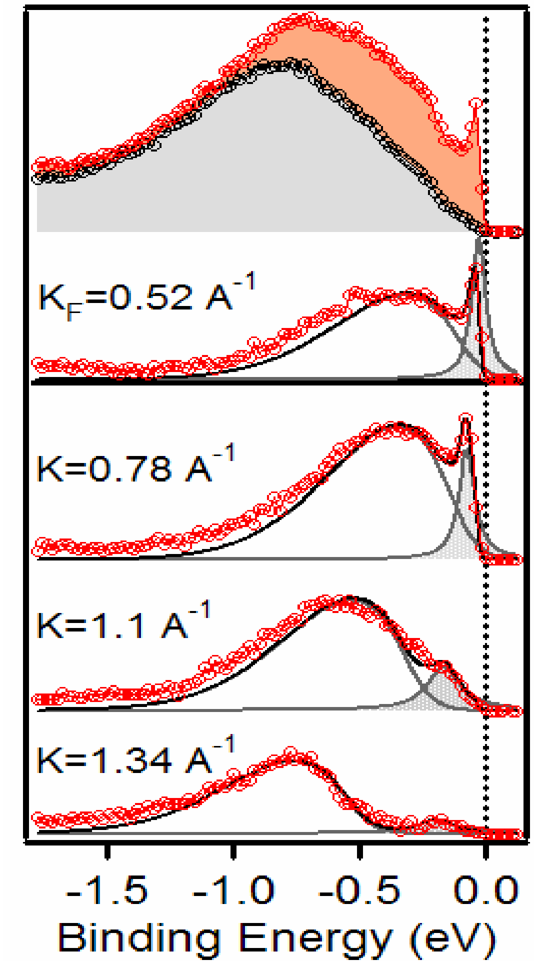
M.B. LePetit, PRB2007




=> Subtracting LV spectrum from LH isolate the PDH of $a_{1g}$

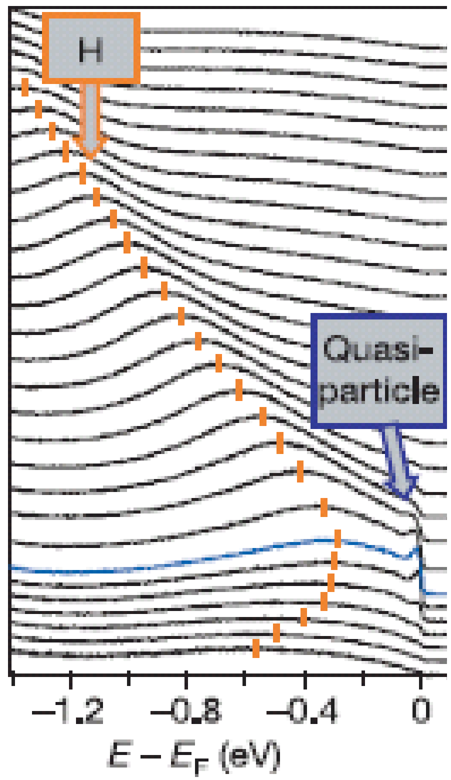
# Intrinsic peak-dip-hump structure of $a_{1g}$

BiBaCo




Manganites

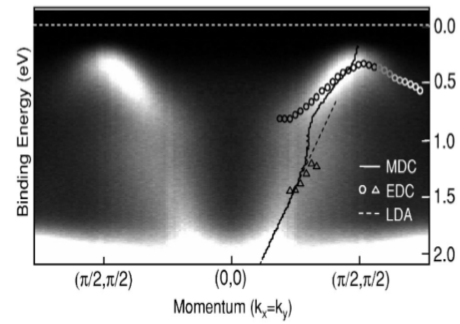
$La_{1.2}Sr_{1.8}Mn_2O_7$




N. Mannella *et al.*, Nature **438**, 474 (2005)

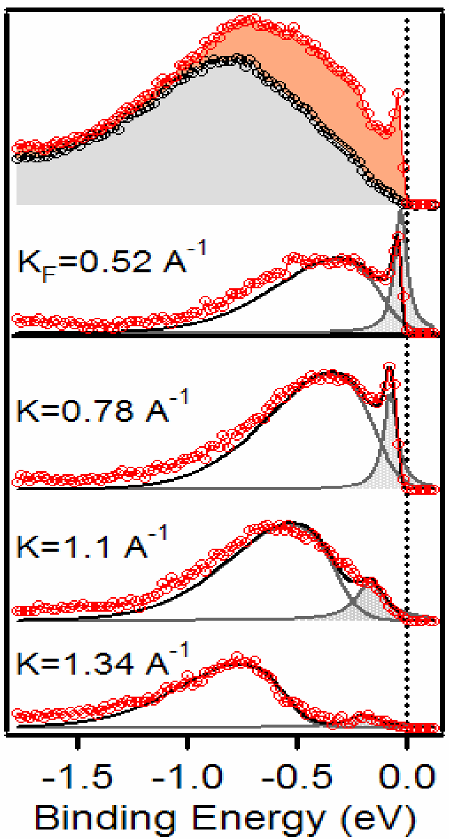
« Waterfall » in cuprates

$Ca_2CuO_2Cl_2$

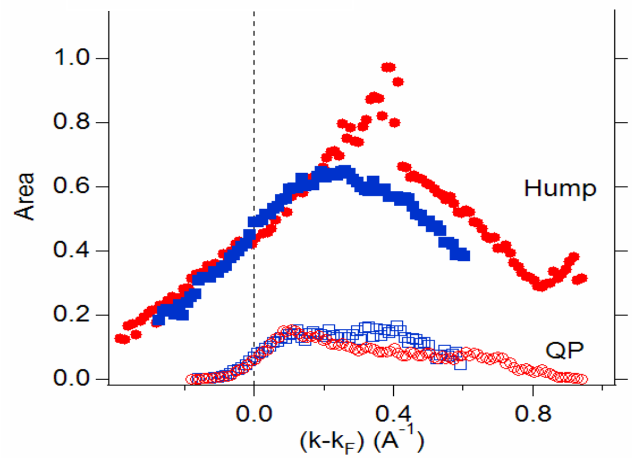


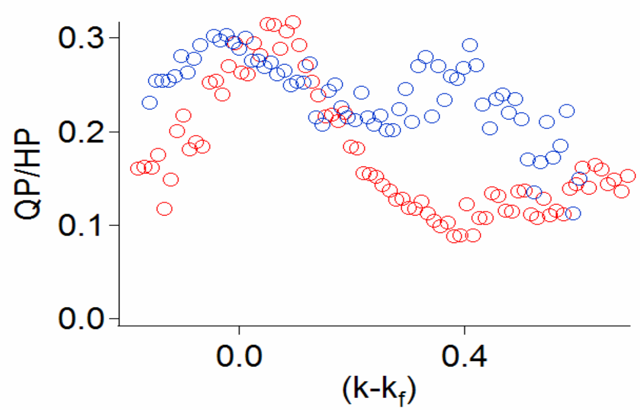

F. Ronning et al. PRB 2005

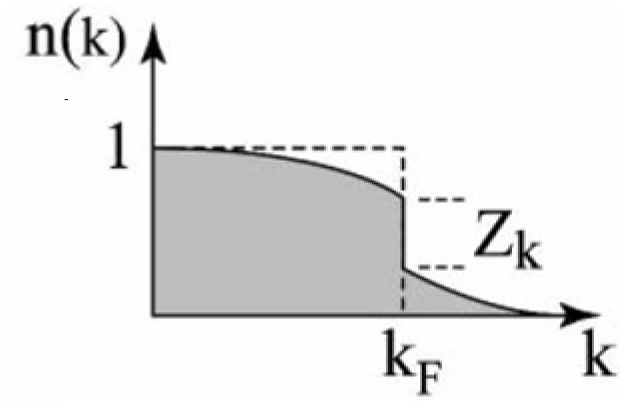
# The distribution of spectral weight imply strong many-body effects




Area vs k




=> Z=0.15±0.05

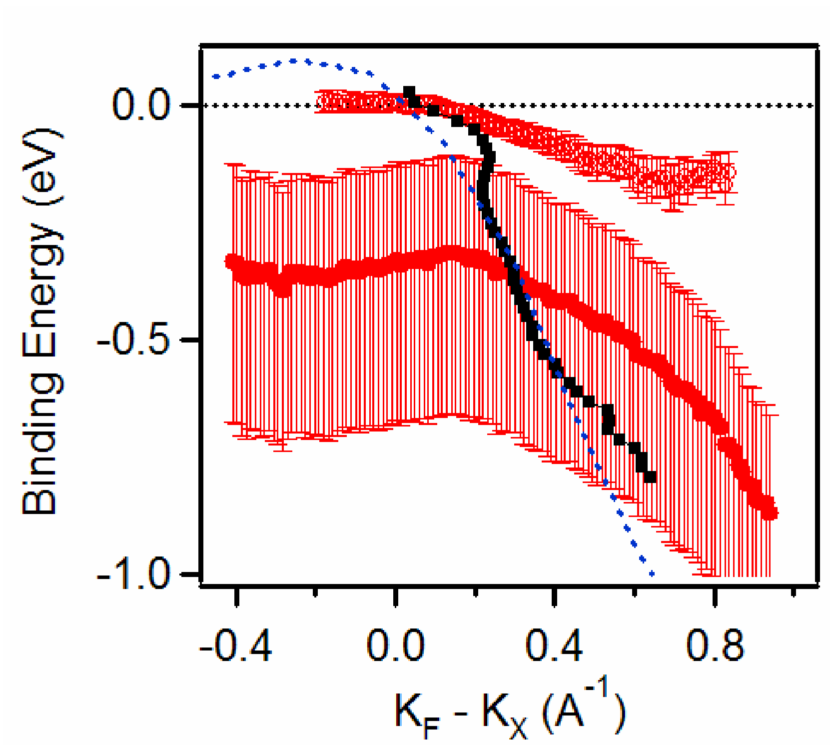
Z * (LDA bandwidth) = 0.2eV

=> 0.2eV is the QP energy scale

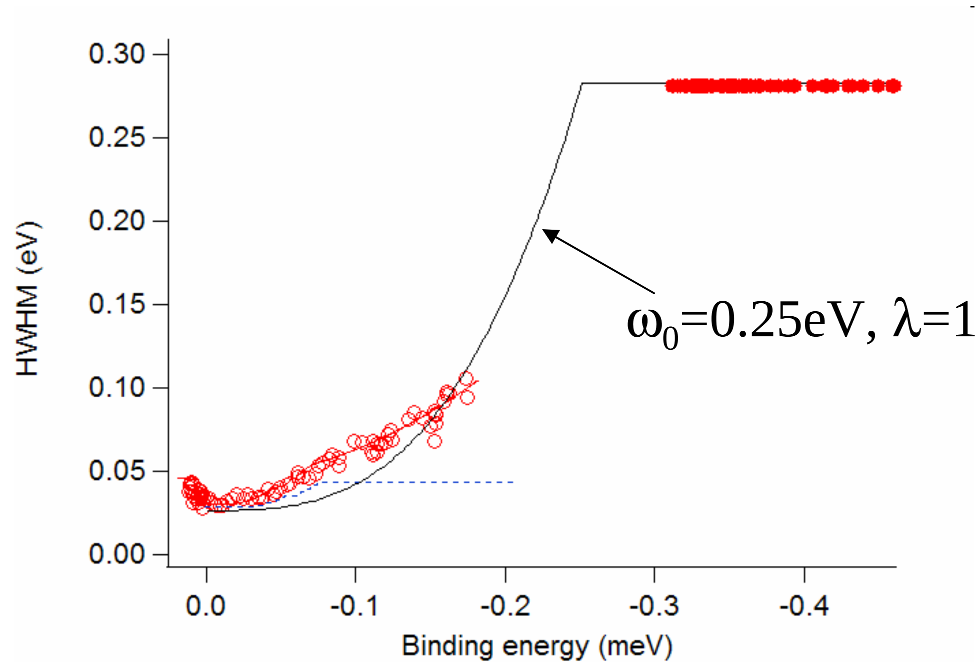
A. Nicolaou *et al.*, PRL 2010

# In this case, spectral weight information is more direct than self-energy fits

Dispersion - Σ'(ω)



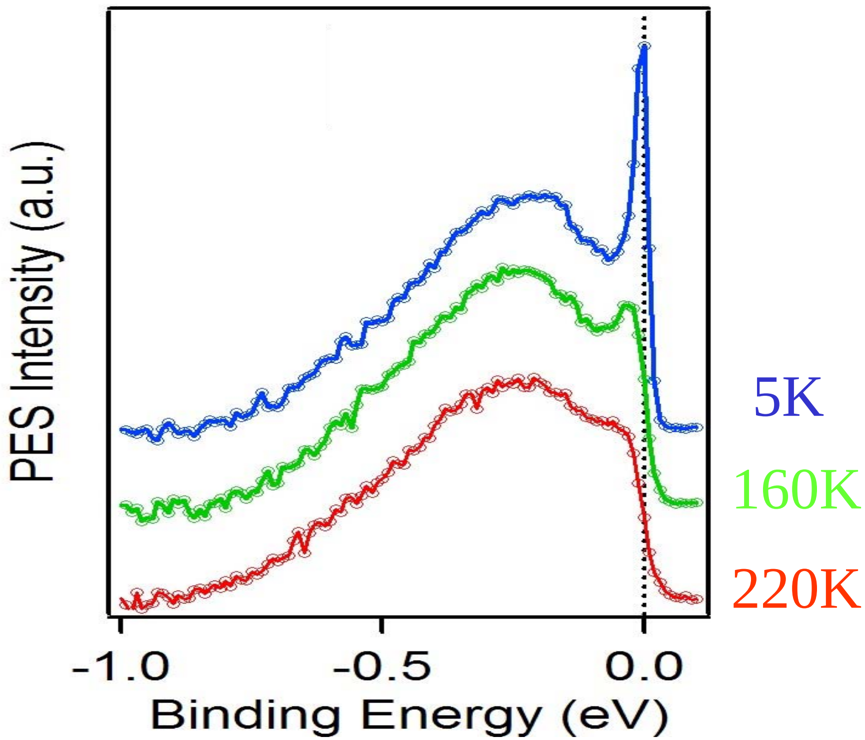

Width - Σ''(ω)

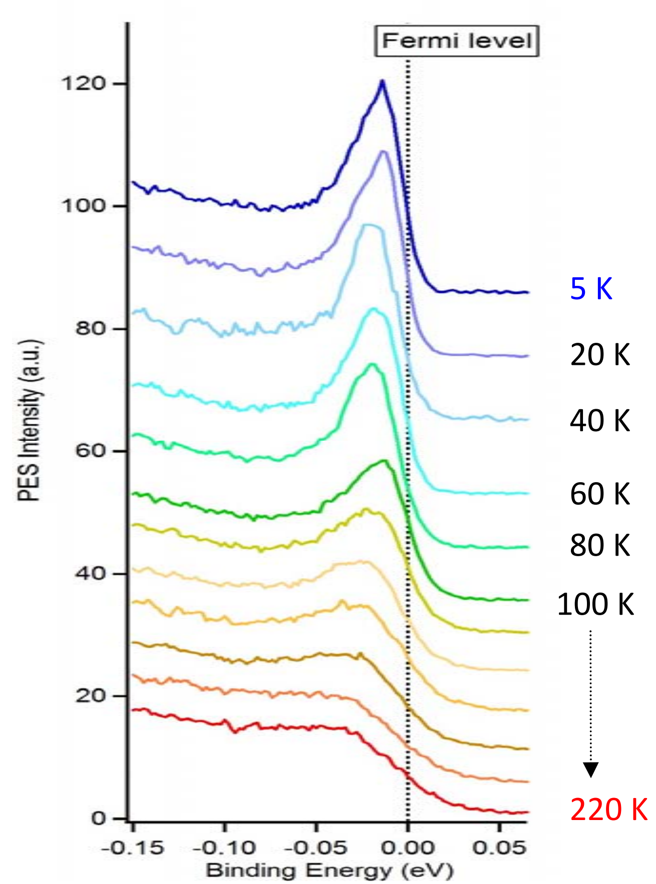



Typical fits of width increase and dispersion renormalization fail to reproduce the HP weight at $E_F$

A. Nicolaou *et al.*, PRL 2010

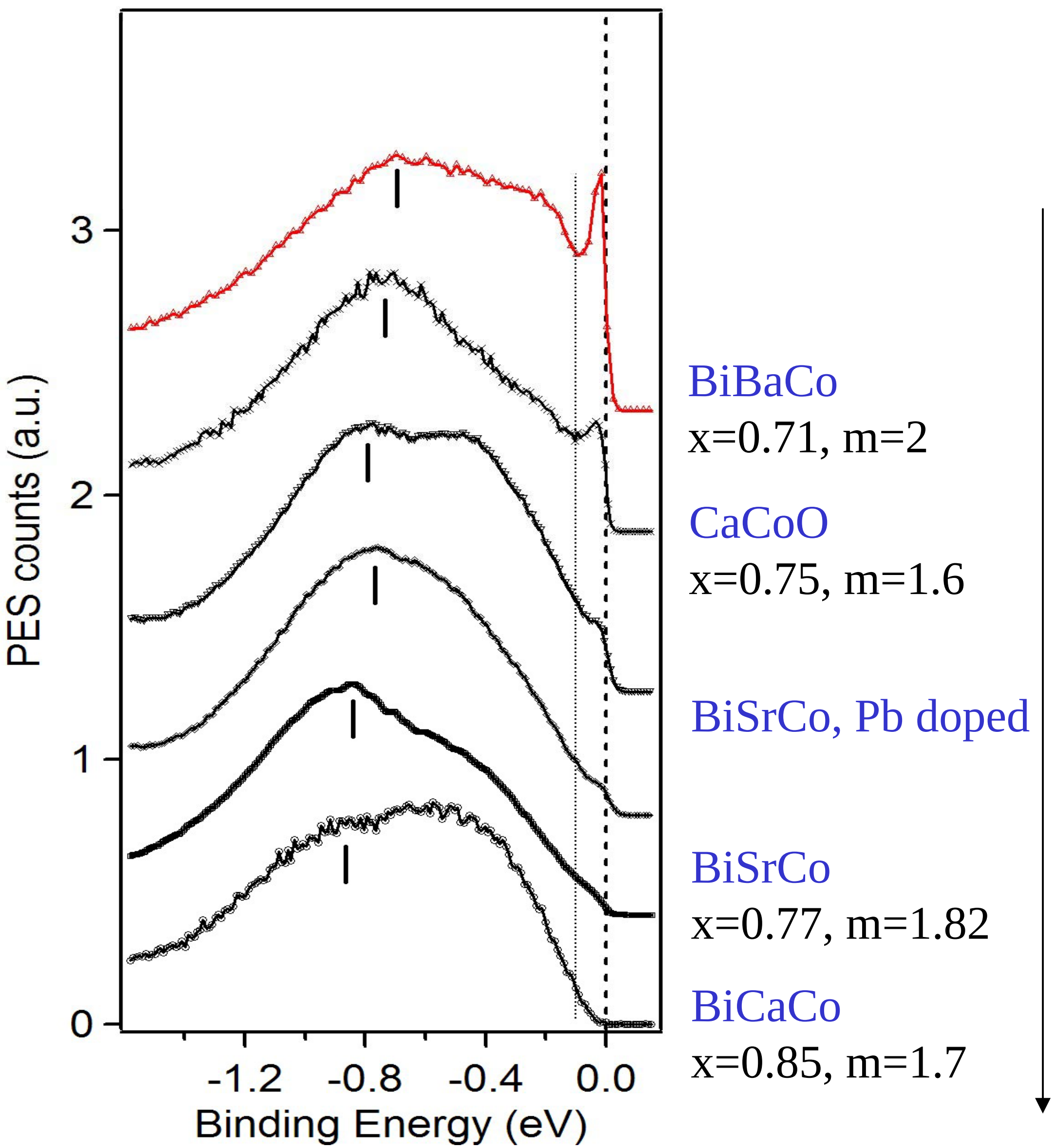
# The QP « disappears » at high temperature




Typical behavior of a strongly correlated system

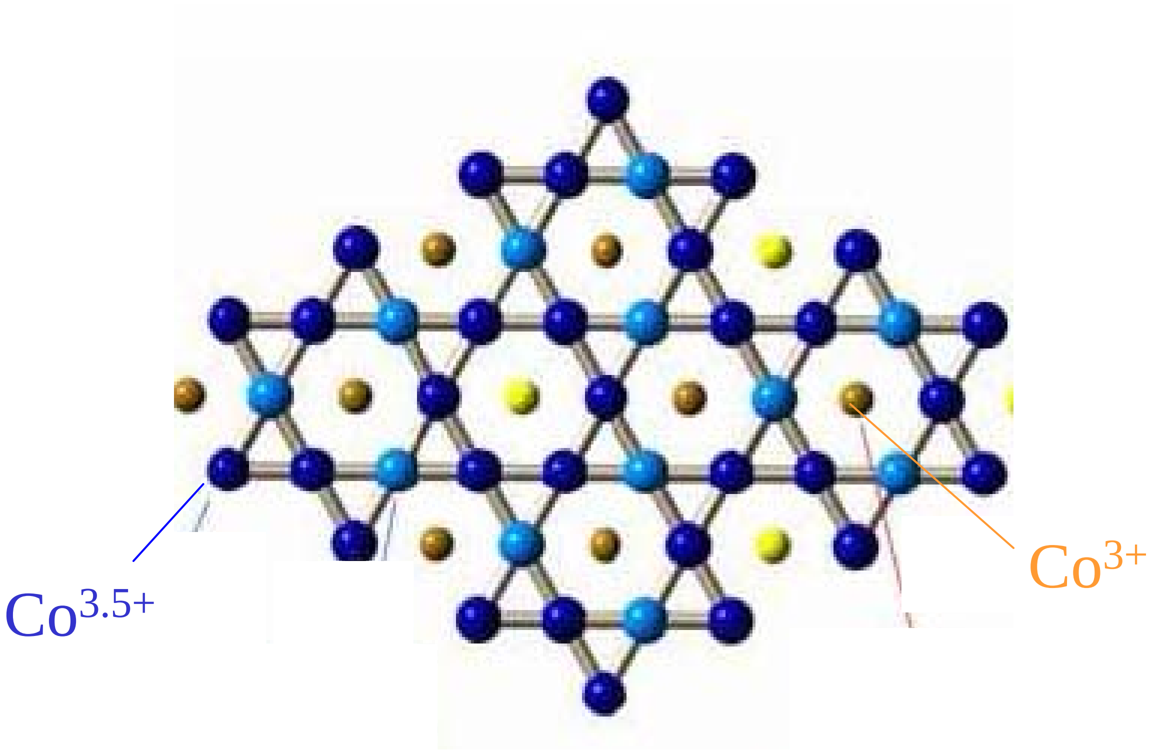
# The QP « disappears » when doping increases




- The correlations seem to increase near the band insulator.

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

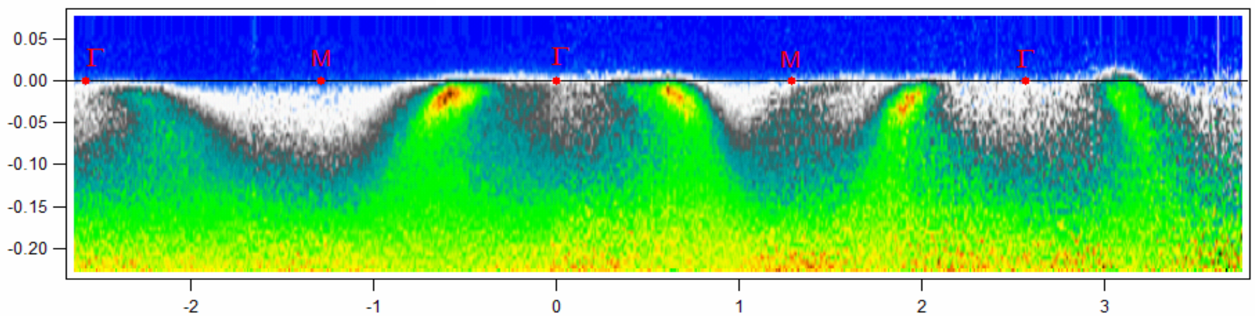
# Electronic orderings at high dopings ?

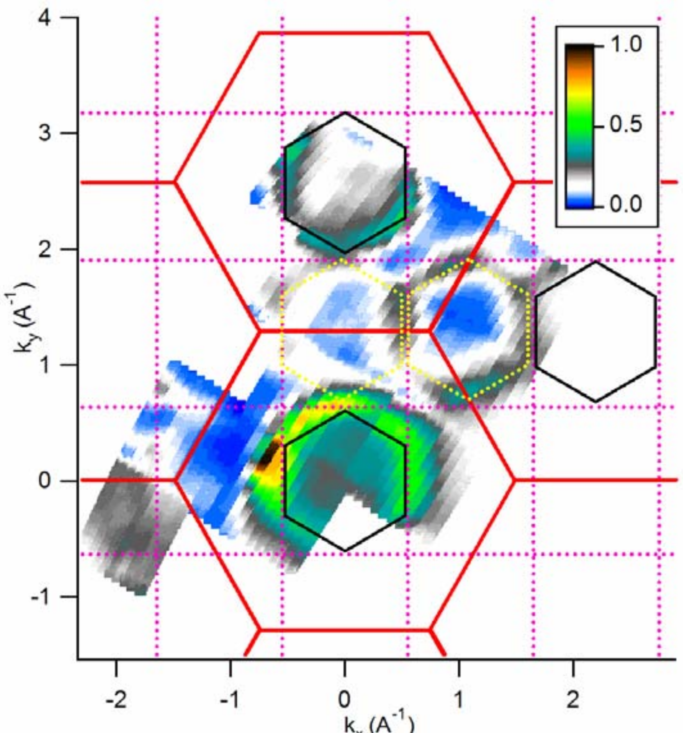



H. Alloul *et al.*, EPL 2009

# Misfit cobaltates : Evidence for coupling between Rock-Salt and $CoO_2$ planes

$[Bi_2Ba_2O_4]_2CoO_2$

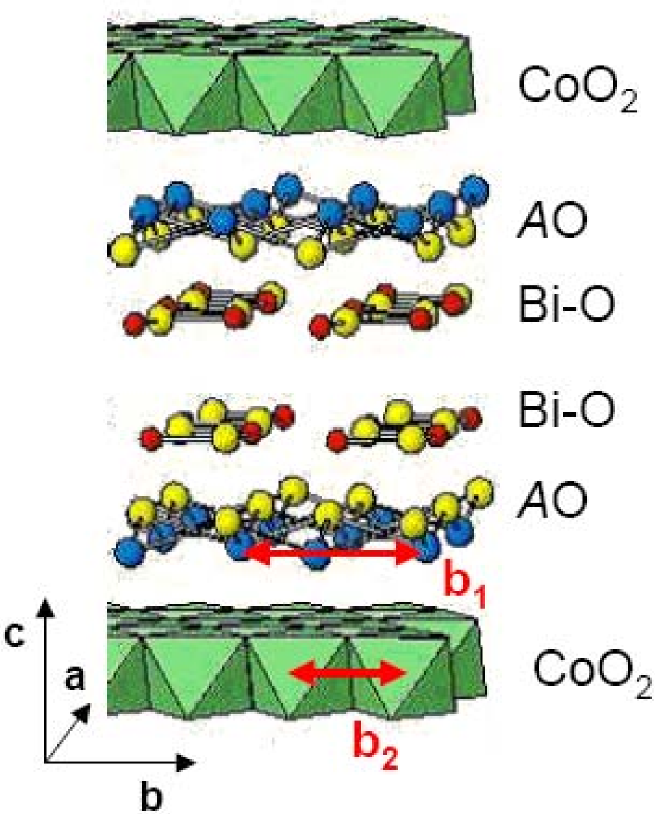


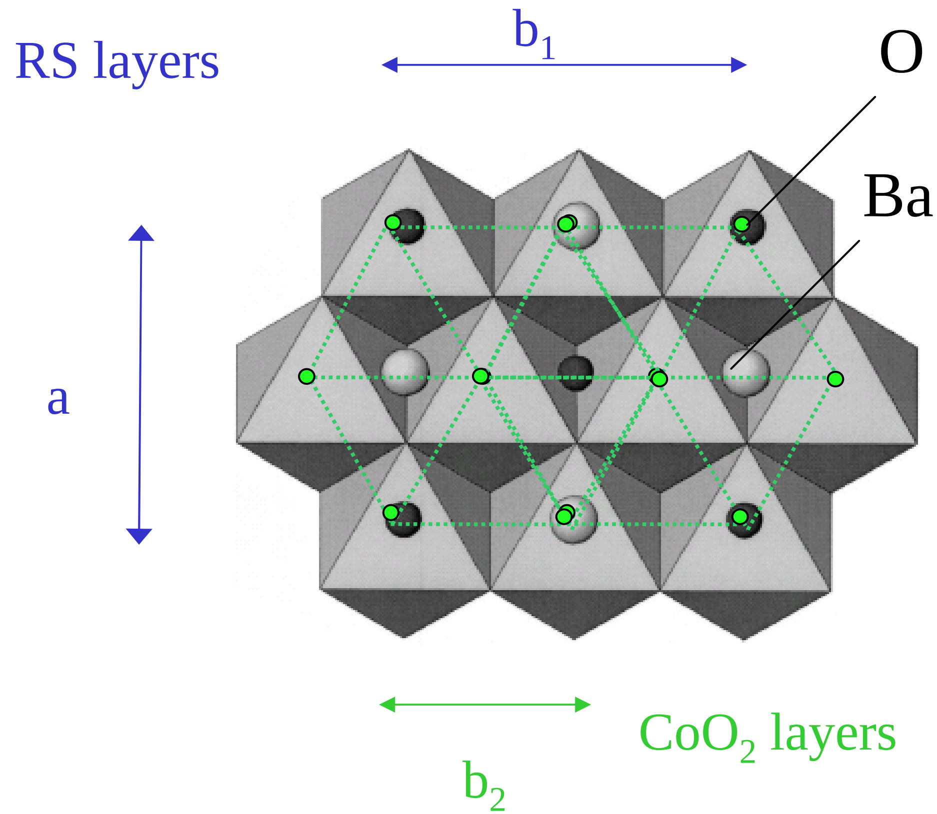




=> Replica appear with RS periodicity

What is the effect of the RS potential on the electronic motion in the $CoO_2$ plane ?

# Rock-Salt structure



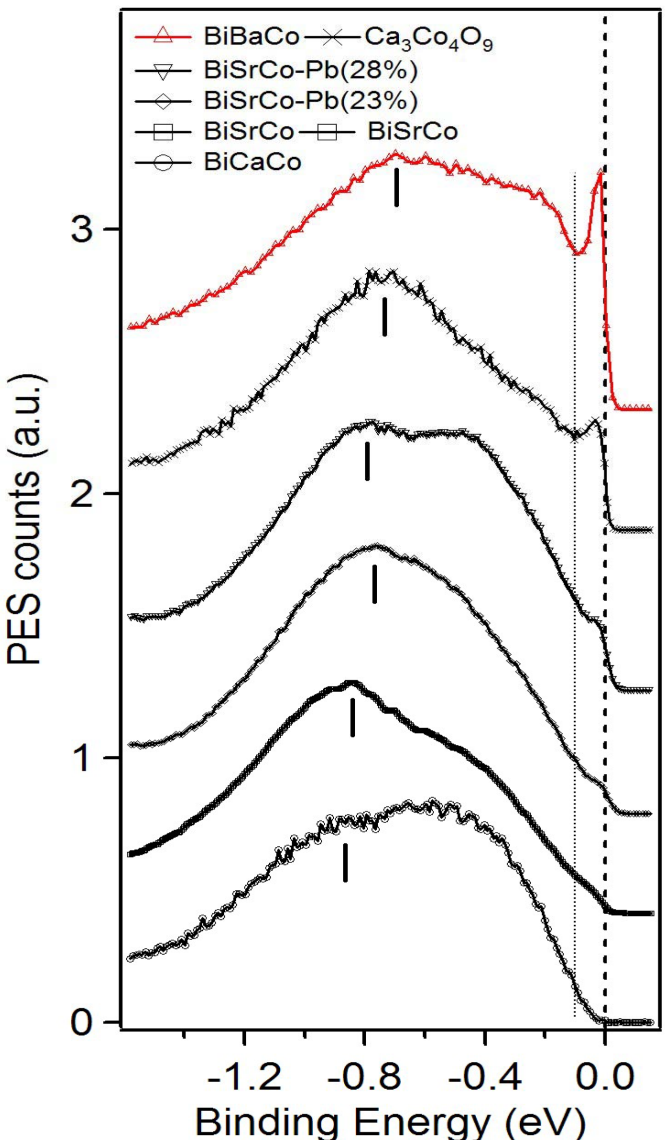




Inequivalent Co sites with respect to $Ba^{2+}$ positions.

=> Situation may be analogous to $Na_xCoO_2$

=> $Co^{3+}$ may form directly below a $Ba^{2+}$

# The number of metallic holes in the band can be deduced from the FS area




BiBaCo
x=0.71, m=2

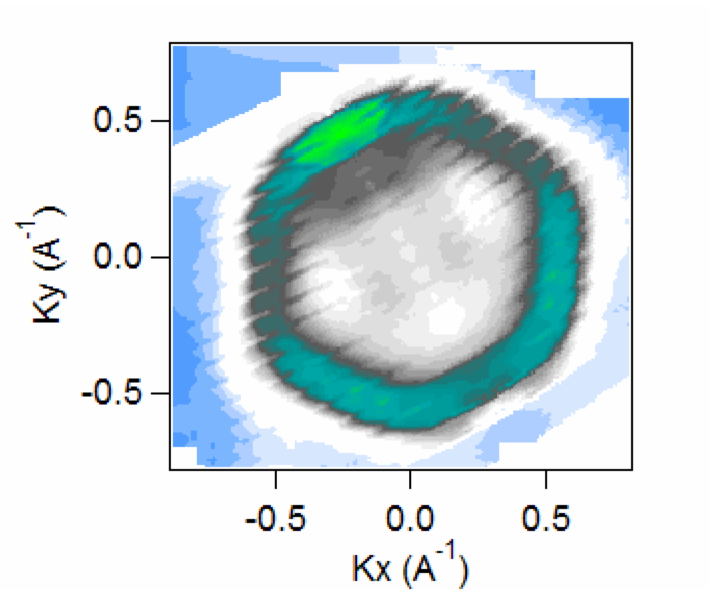
CaCoO
x=0.75, m=1.6

BiSrCo, Pb doped

BiSrCo
x=0.77, m=1.82

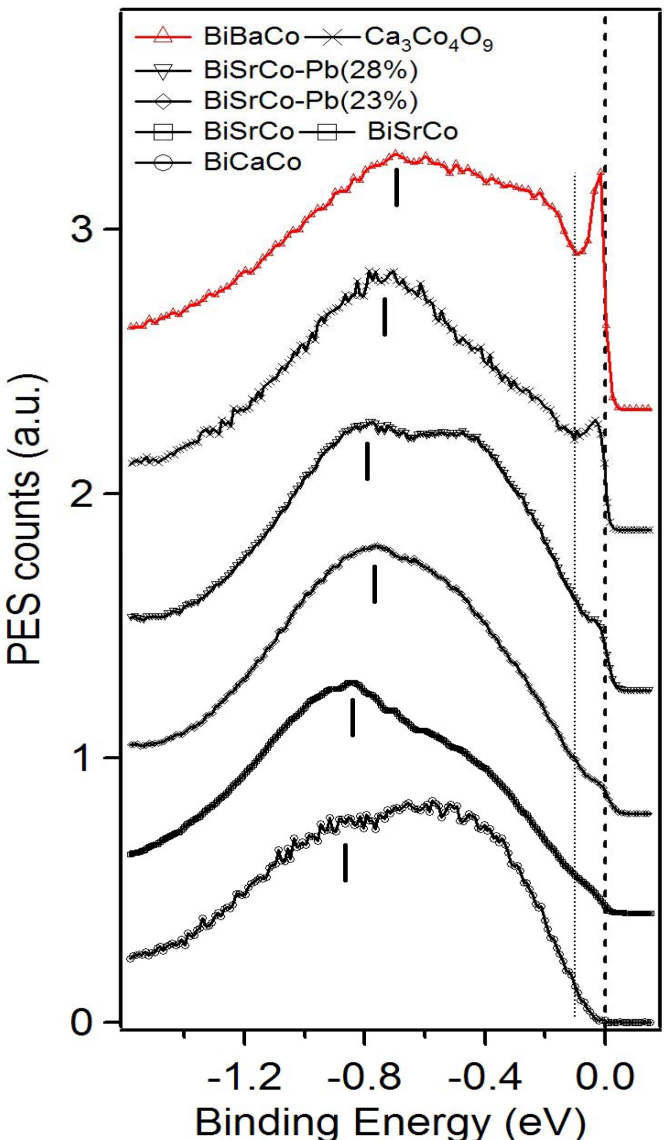
BiCaCo
x=0.85, m=1.7

Fermi Surface of BiBaCo




… $k_F$=0.6 => x=0.7

# The number of metallic holes in the band can be deduced from the FS area




BiBaCo
x=0.71, m=2

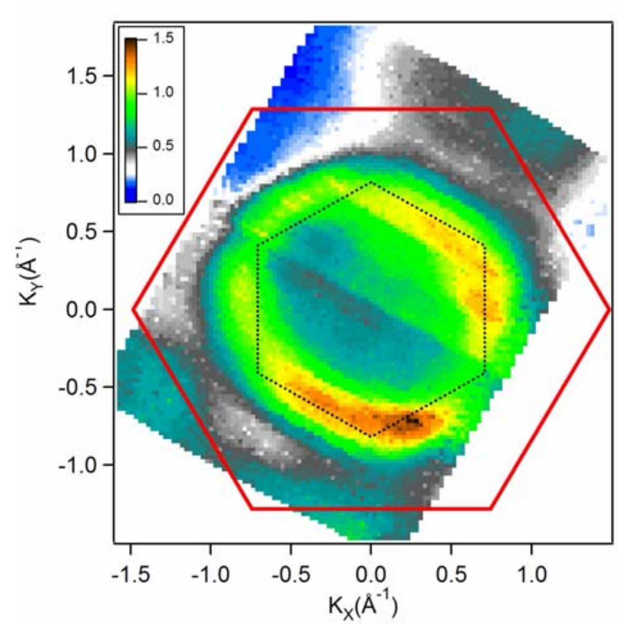
CaCoO
x=0.75, m=1.6

BiSrCo, Pb doped

BiSrCo
x=0.77, m=1.82

BiCaCo
x=0.85, m=1.7

Fermi Surface of CaCoO

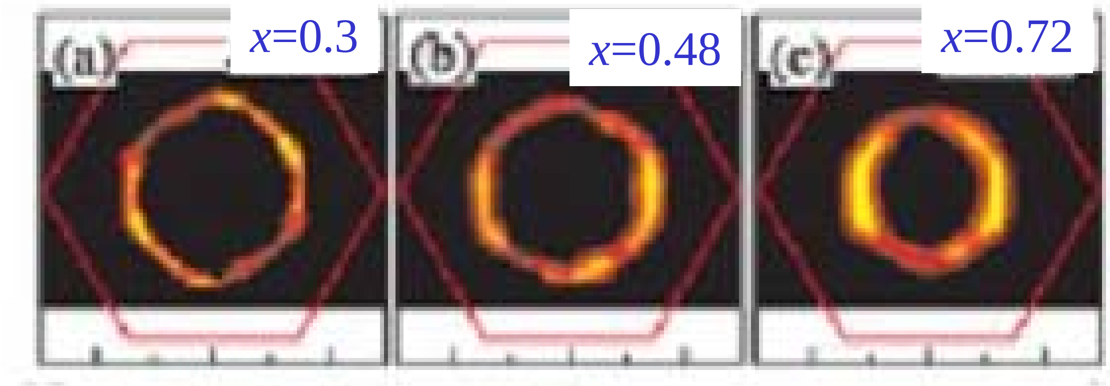


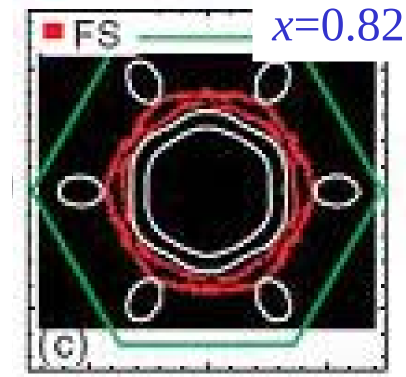

… larger than in BiBaCo
$k_F$=0.75 instead of $k_F$=0.6
=> x=0.5

# Deviation from Luttinger theorem in cobaltates

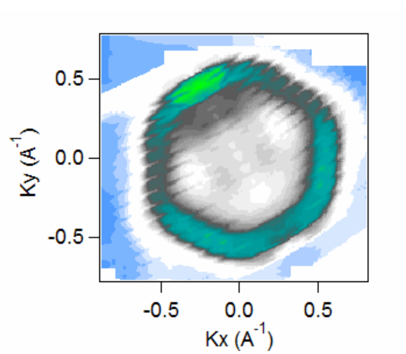
Yang, Ding *et al.*

Qian, Hasan *et al.*

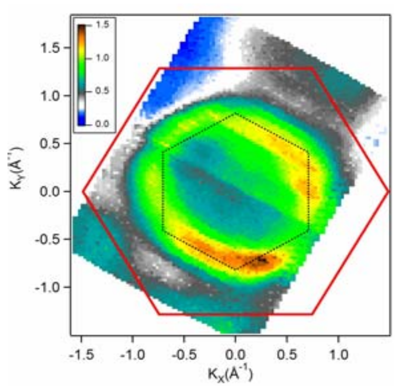


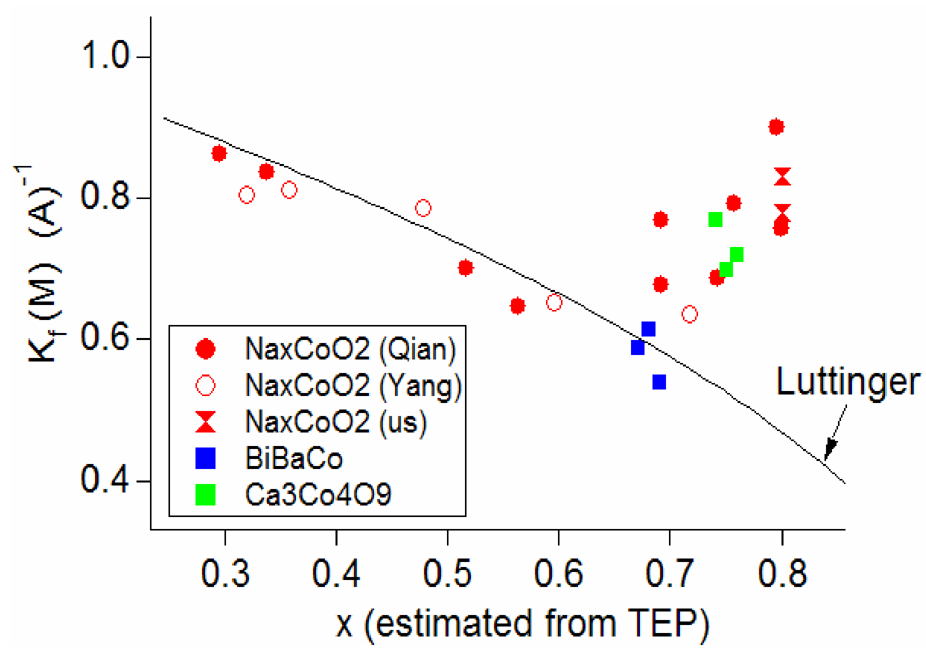




BiBaCo, x=0.7




CaCoO, x=0.75

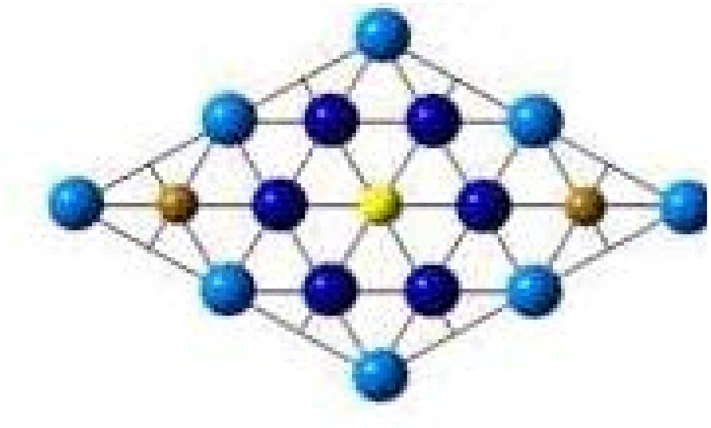


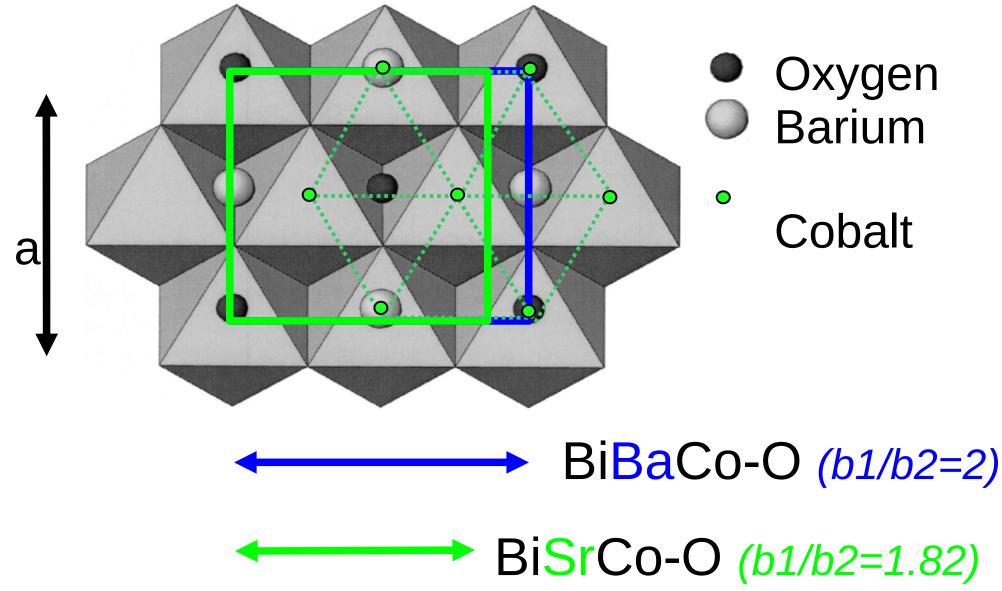

- Deviation from the rigid band filling at high *x*.
- More holes than expected = consistent with presence of $Co^{3+}$.

# Localization with structure depending on the potential inprinted by neighboring planes

$Na_{2/3}CoO_2$
=> Kagomé



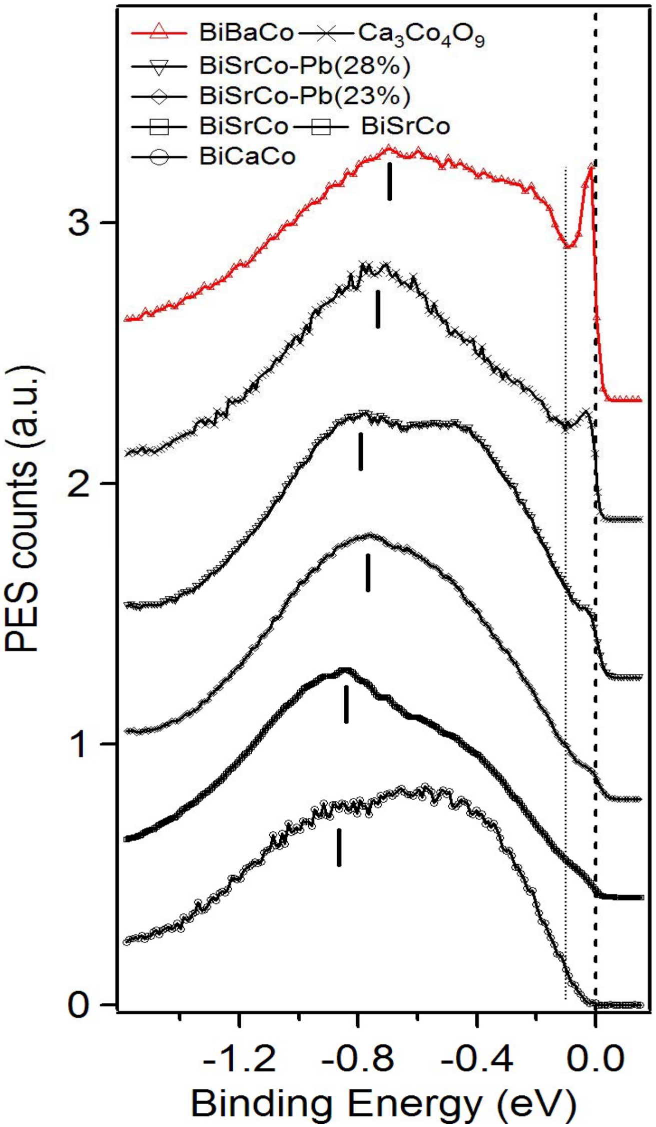
Misfits => « striped » structures




Different metallic structure may explain different evolution of metallicity

A. Nicolaou et al., EPL 2010

# New electronic orderings ?



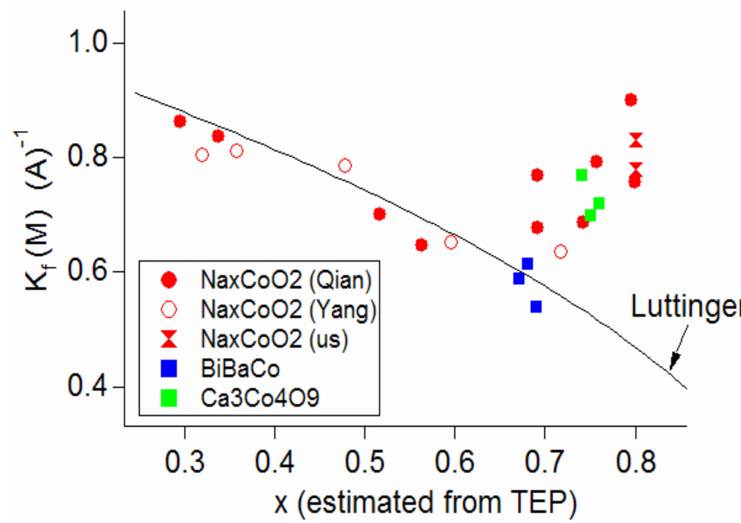

BiBaCo
x=0.71, m=2

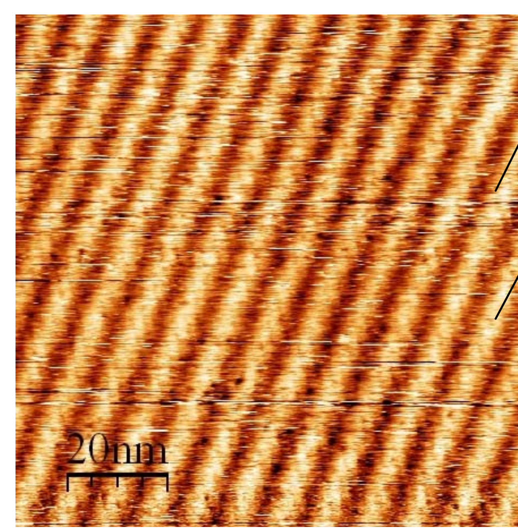
CaCoO
x=0.75, m=1.6

BiSrCo, Pb doped

BiSrCo
x=0.77, m=1.82

BiCaCo
x=0.85, m=1.7




80Å

STM,
coll.
Soleil.

# 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 ?*