April 8, Dresden

Photoemission and Hartree-Fock study of some layered t_{2g}-electron systems

T. Mizokawa,[1] L.H. Tjeng,[2] T.T. Tran,[1] K. Takubo,[1] S. Hirata,[1] H.-J. Lin,[3] C.T. Chen,[3] K.M. Shen,[4] A. Damascelli,[4,5] Z.-X. Shen,[4] G. A. Sawatzky,[5] S. Nakatsuji,[6] H. Fukazawa,[6] Y. Maeno[6], Y. Miyazaki,[7] T. Kajimoto,[7] R. Kitawaki,[8] I. Terasaki,[8] S. Lambert,[9] C. Michel[9], N.B. Brookes,[10] S. Schuppler,[11] T. Yamamoto,[12] and K. Uchinokura[12]

[1] Department of Complexity Science and Engineering, University of Tokyo, Japan
[2] II. Physikalisches Institut, Universität zu Köln, Germany
[3] SRRC, Taiwan
[4] Department of Physics & Applied Physics, Stanford University, USA
[5] University of British Colombia, Canada
[6] Department of Physics, Kyoto University, Japan
[7] Department of Applied Physics, Tohoku University, Japan
[8] Department of Applied Physics, Waseda University, Japan
[9] ISMRA, France
[10] ESRF, France
[11] Karlsruhe, Germany
[12] Department of Applied Physics, University of Tokyo, Japan

Outline

$Ca_{2-x}Sr_xRuO_4$

XAS orbital symmetry

XPS spectral line shape and correlation effect

Hartree-Fock analysis

ARPES Fermi surface and the MI transition

CoO_2 triangular lattice in $Bi_2Sr_2Co_2O_9$, Na_xCoO_2 , $Ca_3Co_4O_9$

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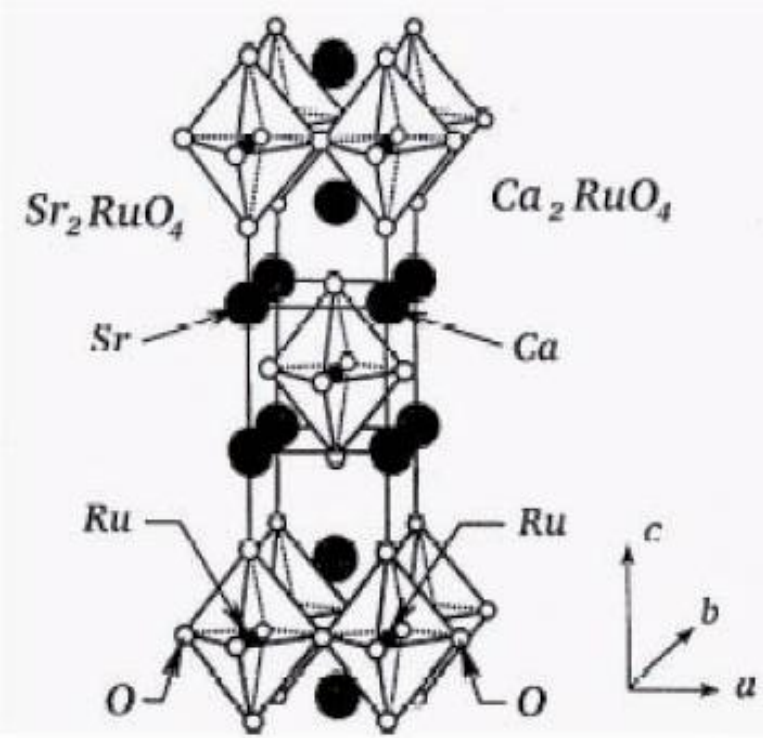
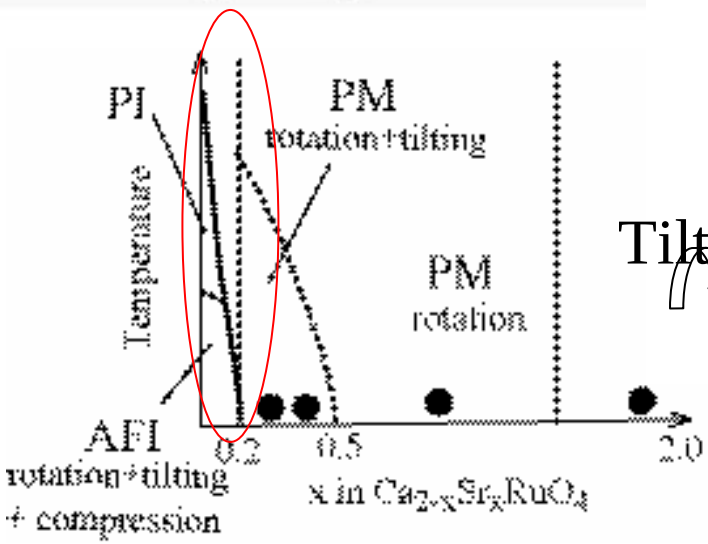
$Ca_{2-x}Sr_xRuO_4$

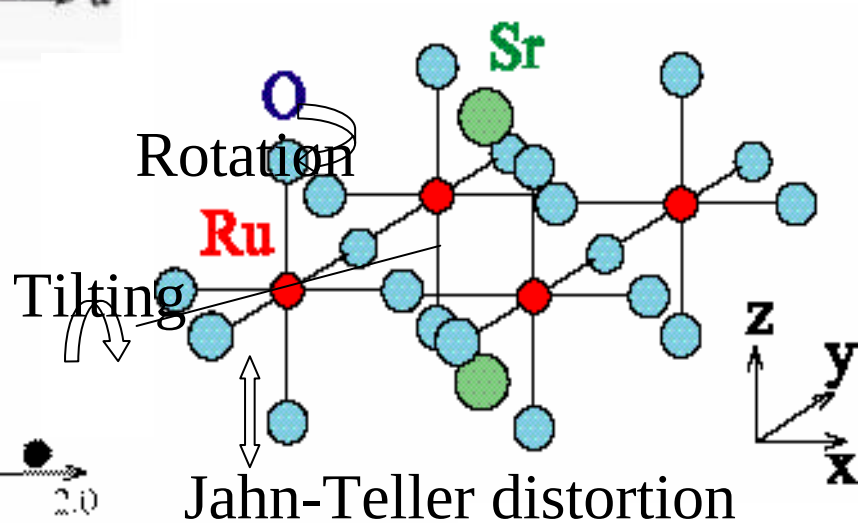
S. Nakatsuji and Y. Maeno,
Phys. Rev. Lett. 84, 2666 (2000)
O. Friedt *et al.*
Phys. Rev. B 63, 174432 (2001)



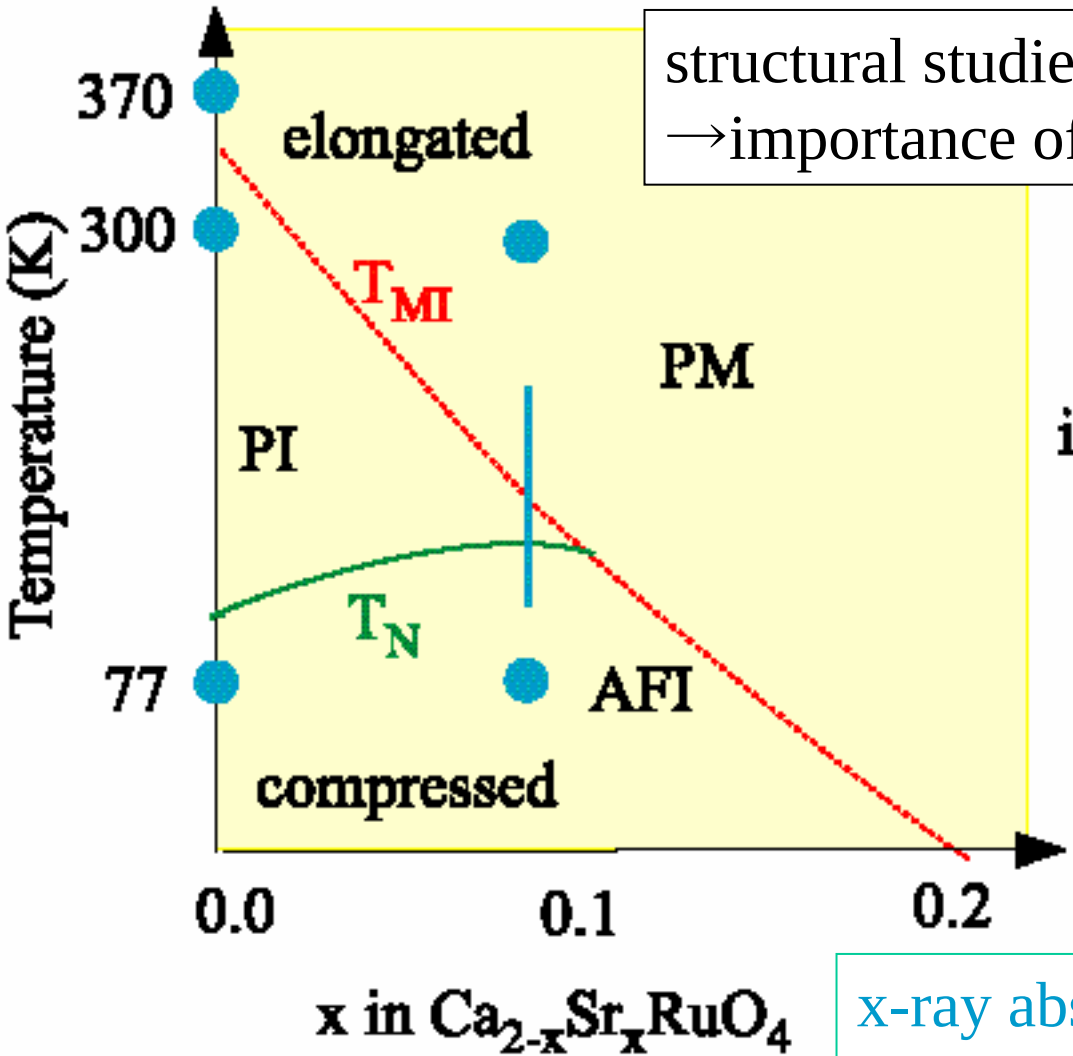
Layered Perovskite structure
With the substitution of Ca for Sr, the RuO_6 octahedron undergoes a series of structural distortions such as

- Jahn-Teller distortion
- Tilting
- Rotation

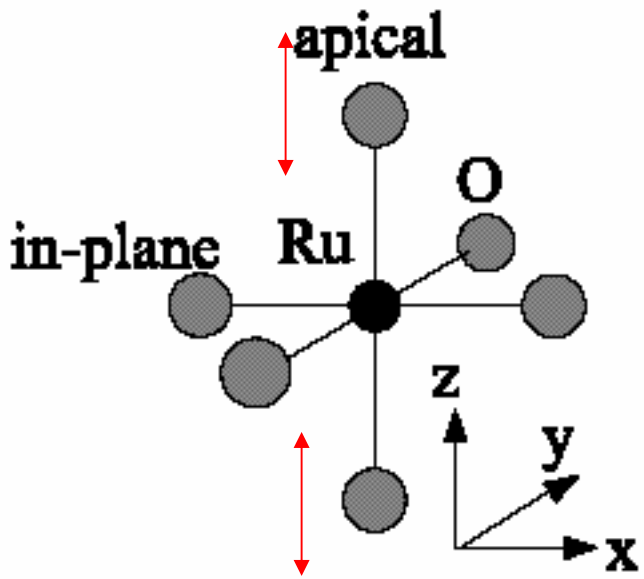




Phase diagram of $Ca_{2-x}Sr_xRuO_4$ (Nakatsuji and Maeno, 2000)



structural studies by Braden's group
→importance of electron-lattice coupling



compressed or **elongated**

x-ray absorption measurement
can probe the t_{2g} orbital symmetry

O 1s x-ray absorption spectroscopy of $Ca_{2-x}Sr_xRuO_4$

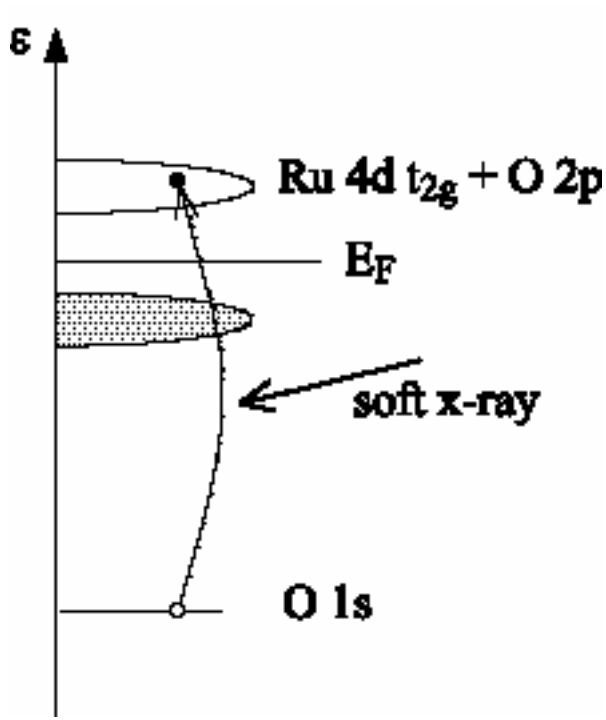
Dragon beamline at SRRC

Ca_2RuO_4 and $Ca_{1.91}Sr_{0.09}RuO_4$

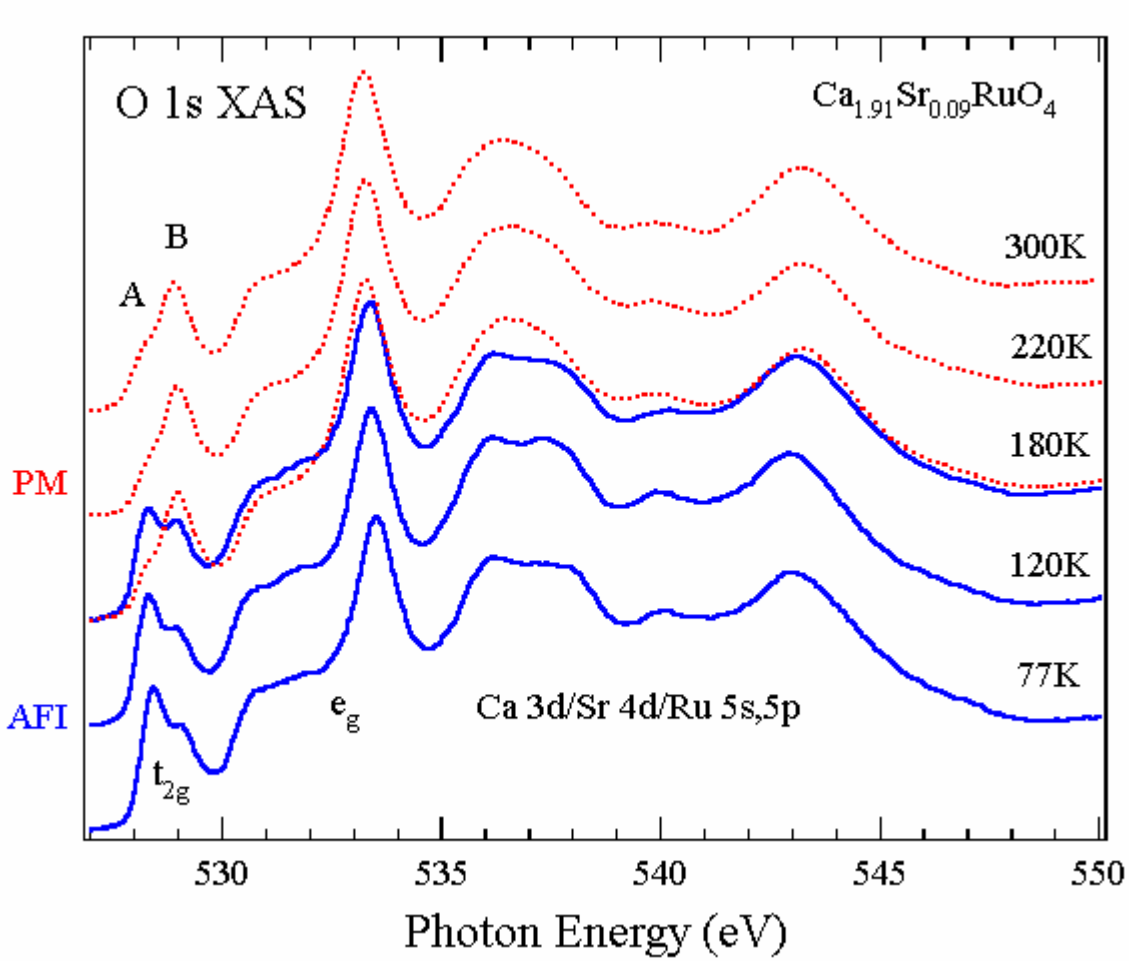
Single crystals were cleaved *in situ*

Total electron yield mode

t_{2g} orbital symmetry

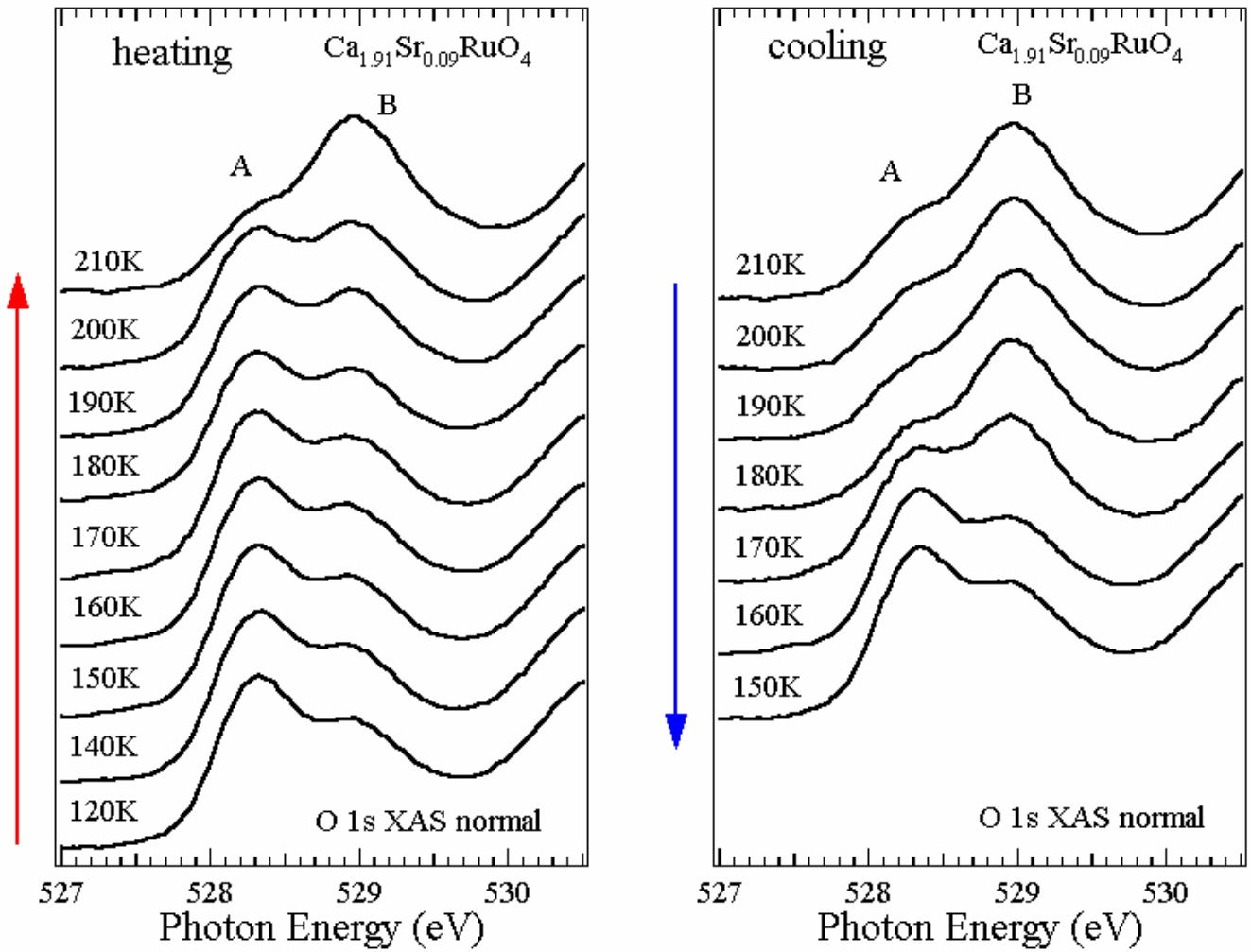


O 1s XAS of $Ca_{2-x}Sr_xRuO_4$

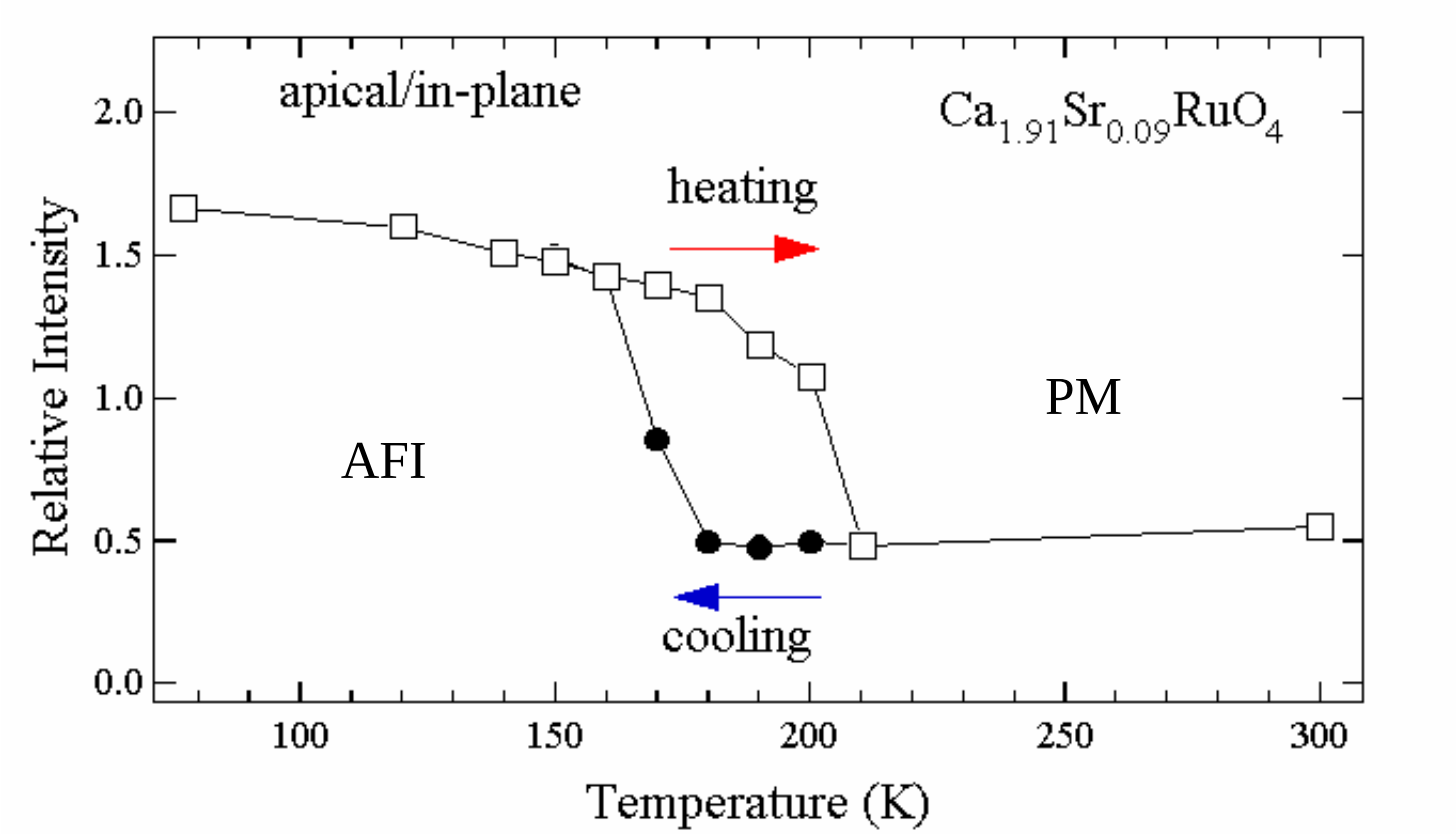


O 1s XAS across the MI transition

A: apical oxygen B: in-plane oxygen



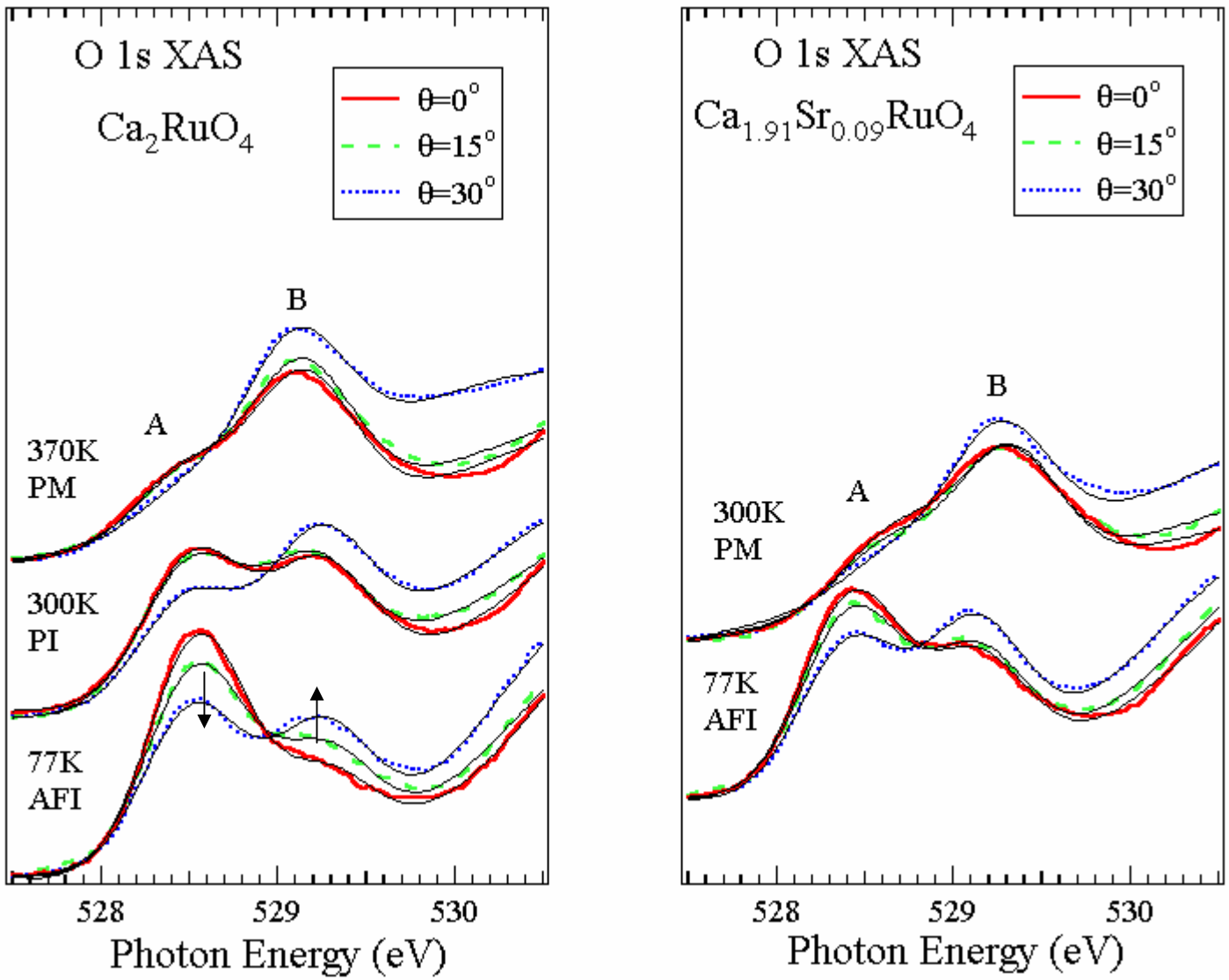
Orbital change across the MI transition



In the AFI phase, the amount of yz/zx holes decreases with temperature.
At the MI transition, the orbital occupation changes discontinuously.

T. Mizokawa, L. H. Tjeng *et al.*, PRB **69**, 132410 (2004)

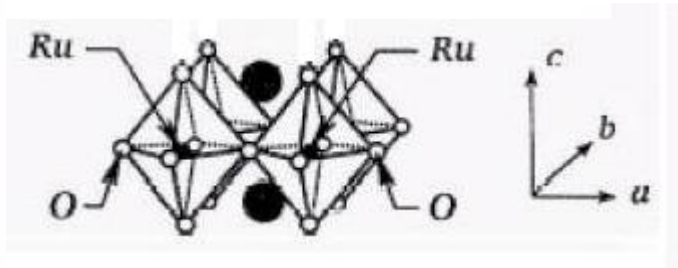
Angle dependence of the O 1s XAS spectra



Model Hartree-Fock calculation

$$H = H_p + H_d + H_{pd},$$

$$H_p = \sum_{\mathbf{k},l,\sigma} \epsilon_k^p p_{\mathbf{k},l\sigma}^\dagger p_{\mathbf{k},l\sigma} + \sum_{\mathbf{k},l>l',\sigma} V_{\mathbf{k},ll'}^{pp} p_{\mathbf{k},l\sigma}^\dagger p_{\mathbf{k},l'\sigma} + \text{H.c.},$$



$$\begin{aligned} H_d &= \epsilon_d^0 \sum_{i,m,\sigma} d_{i,m\sigma}^\dagger d_{i,m\sigma} + \sum_{m,m',\sigma,\sigma'} h_{m,\sigma,m',\sigma'} d_{i,m\sigma}^\dagger d_{i,m'\sigma'} \\ &+ u \sum_{i,m} d_{i,m\uparrow}^\dagger d_{i,m\uparrow} d_{i,m\downarrow}^\dagger d_{i,m\downarrow} \\ &+ u' \sum_{i,m\neq m'} d_{i,m\uparrow}^\dagger d_{i,m\uparrow} d_{i,m'\downarrow}^\dagger d_{i,m'\downarrow} \\ &+ j' \sum_{i,m\neq m'} d_{i,m\uparrow}^\dagger d_{i,m'\uparrow} d_{i,m\downarrow}^\dagger d_{i,m'\downarrow} \\ &+ (u'-j) \sum_{i,m>m',\sigma} d_{i,m\sigma}^\dagger d_{i,m\sigma} d_{i,m'\sigma}^\dagger d_{i,m'\sigma} \\ &+ j \sum_{i,m\neq m'} d_{i,m\uparrow}^\dagger d_{i,m'\uparrow} d_{i,m'\downarrow}^\dagger d_{i,m\downarrow}, \end{aligned}$$

$$H_{pd} = \sum_{\mathbf{k},l,m,\sigma} V_{\mathbf{k},lm}^{pd} d_{\mathbf{k},m\sigma}^\dagger p_{k,l\sigma} + \text{H.c.}$$

	(pdσ)	rotation	tilting	δ_{JT}	
Ca_2RuO_4	-2.8 eV	12.5°	10°	0.975	**compressed**
Sr_2RuO_4	-3.4 eV	0°	0°	1.025	**elongated**

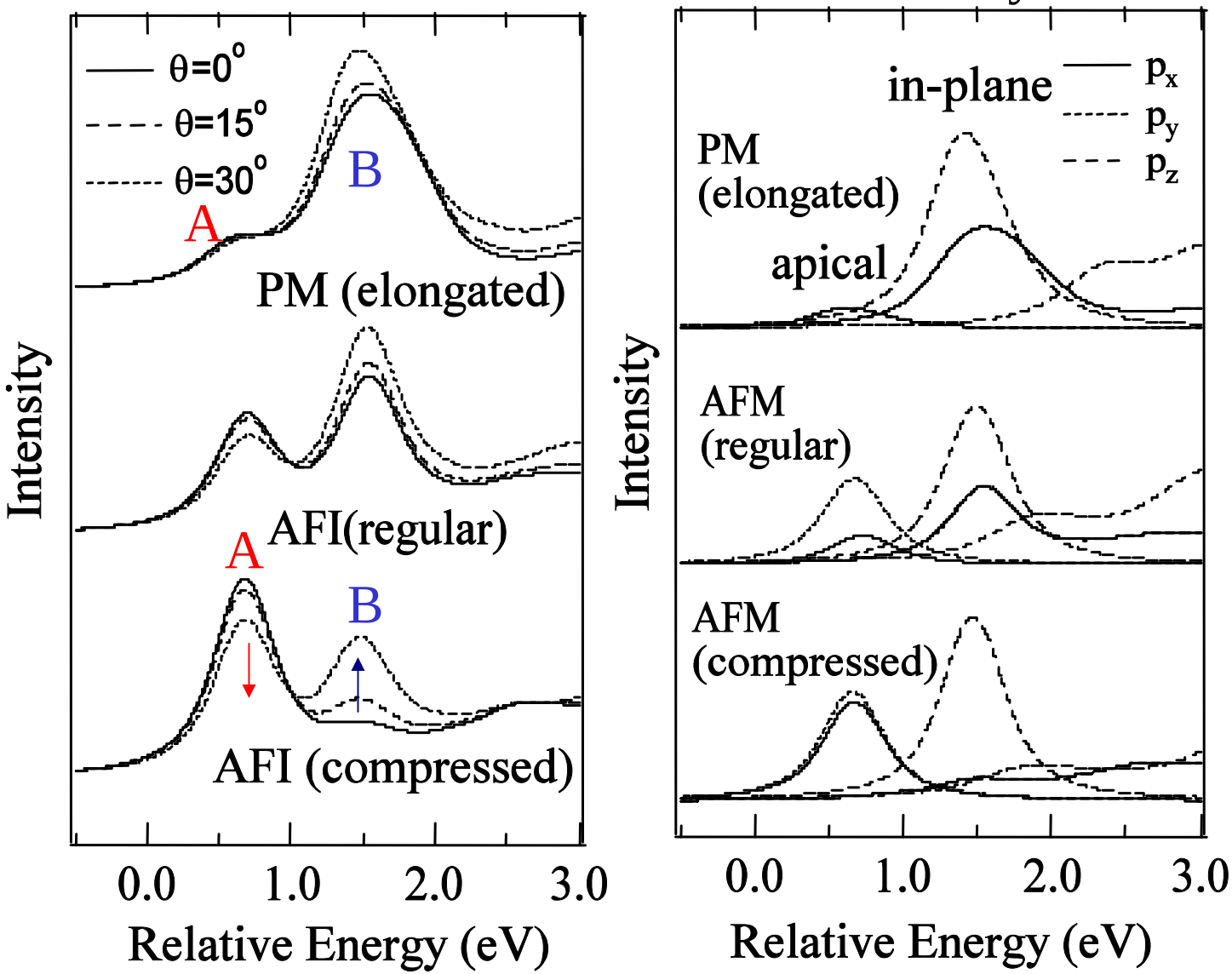
$\Delta = \varepsilon_d - \varepsilon_p + 4U = -0.4$ eV

u = 1.9 eV, u' = 0.9 eV, j = j' = 0.5 eV

(ppσ) = 0.6 eV, (ppπ) = -0.15 eV

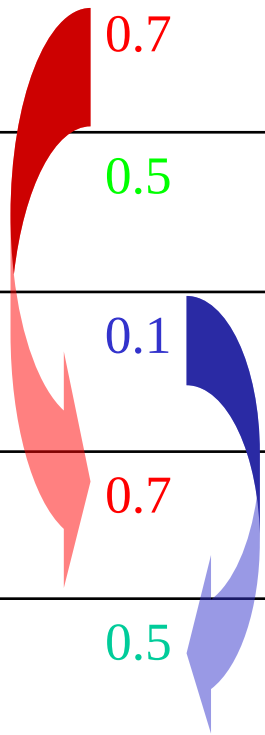
(pdπ)/(pdσ) = -0.45

Angle dependence and the orbital symmetry obtained from model Hartree-Fock analysis



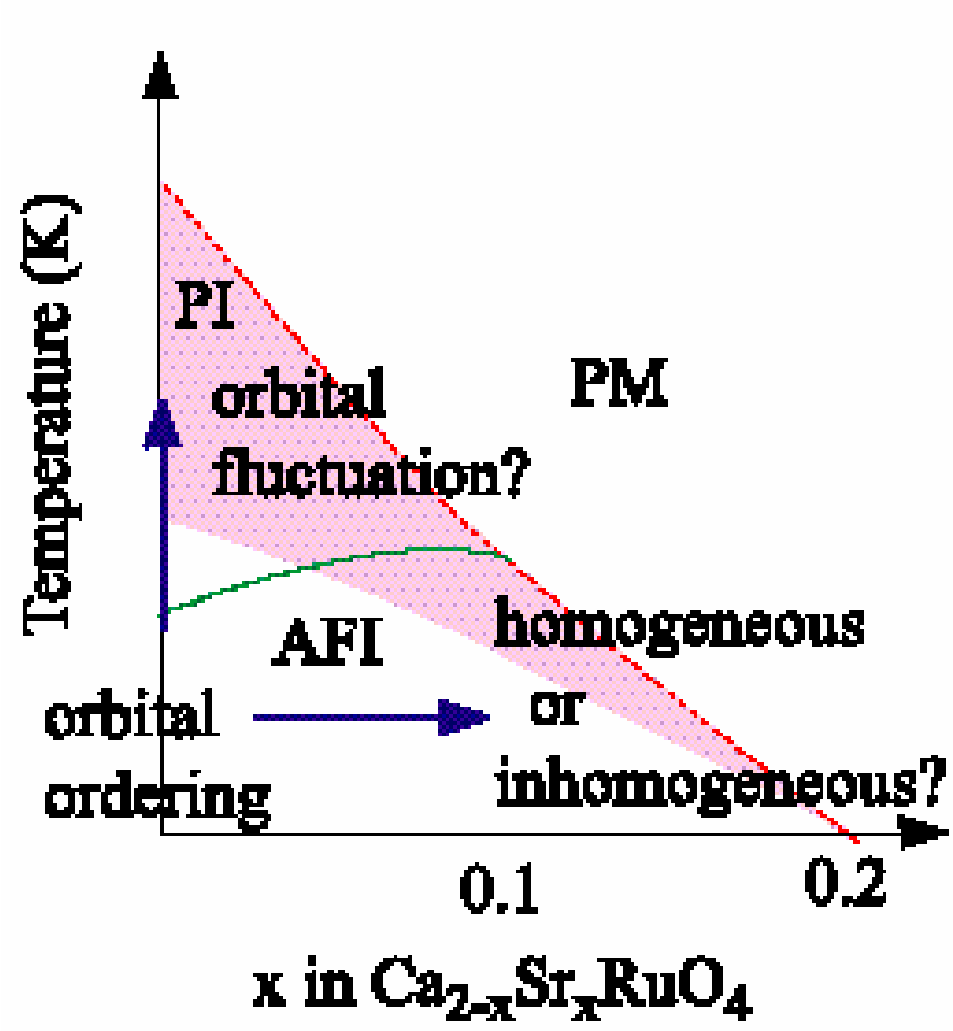
Orbital population of the unoccupied t_{2g} orbitals obtained from the Hartree-Fock analysis of O 1s XAS

	xy	yz/zx	O 2p
Ca_2RuO_4 370 K (PM)	0.7	0.35/0.35	0.6
Ca_2RuO_4 300 K (PI)	0.5	0.5/0.5	0.5
Ca_2RuO_4 77 K (AFI)	0.1	0.7/0.7	0.5
$Ca_{1.91}Sr_{0.09}RuO_4$ 300 K (PM)	0.7	0.35/0.35	0.6
$Ca_{1.91}Sr_{0.09}RuO_4$ 77 K (AFI)	0.5	0.5/0.5	0.5



T. Mizokawa, L. H. Tjeng *et al.*, PRB **69**, 132410 (2004)

Orbital disorder and the MI transition



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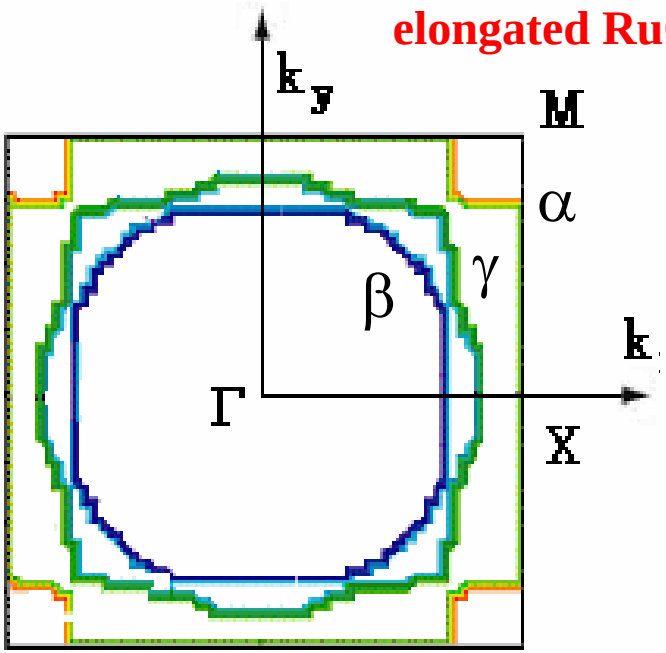
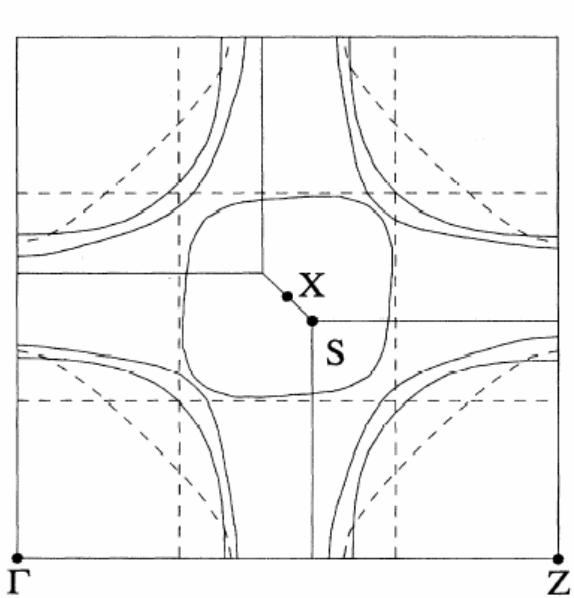
Hartree-Fock analysis

Model Hartree-Fock calculation for Sr_2RuO_4

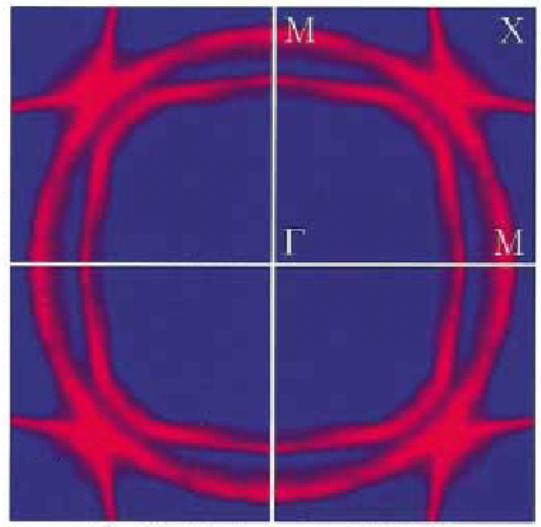
elongated RuO_6 octahedron



Calculated Fermi surface of Sr_2RuO_4

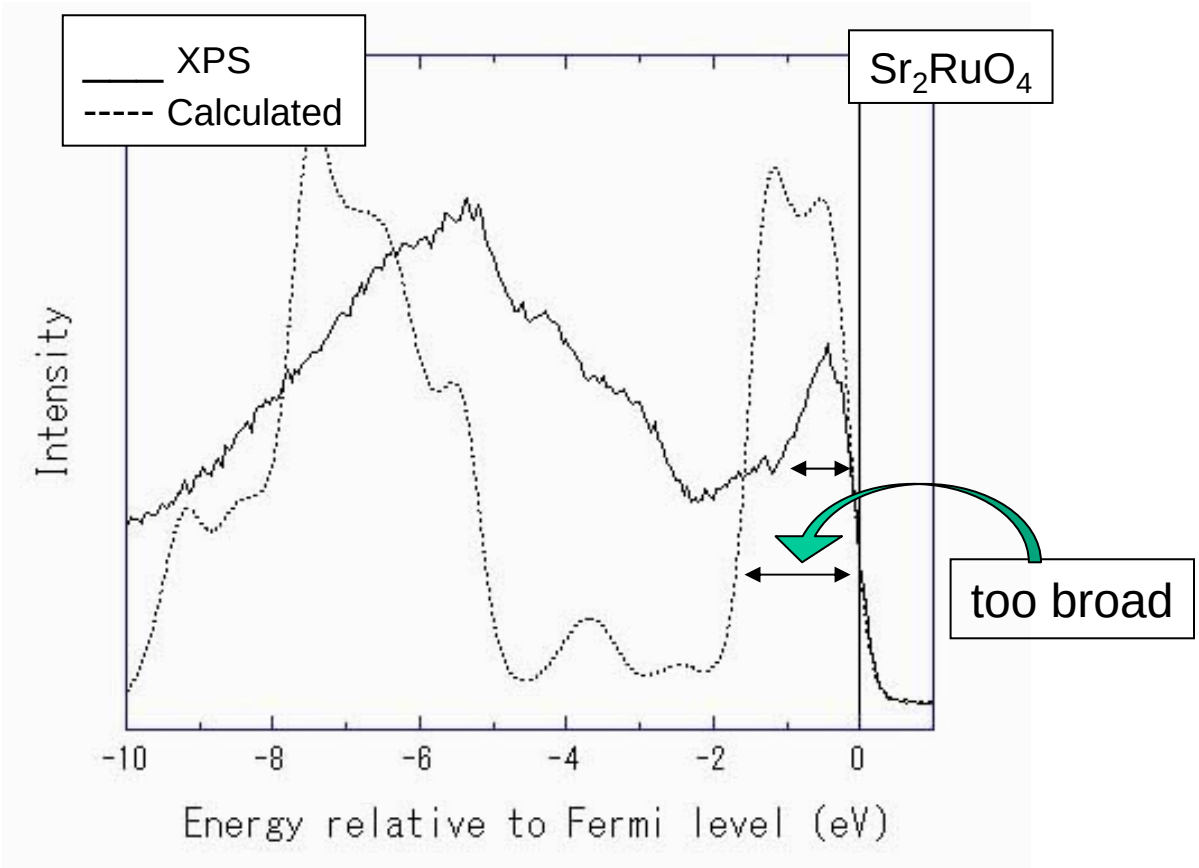


Calculated Fermi surface in the extended Brillouin zone scheme. (LDA)
T. Oguchi, PR B **51**, 1385 (1995)



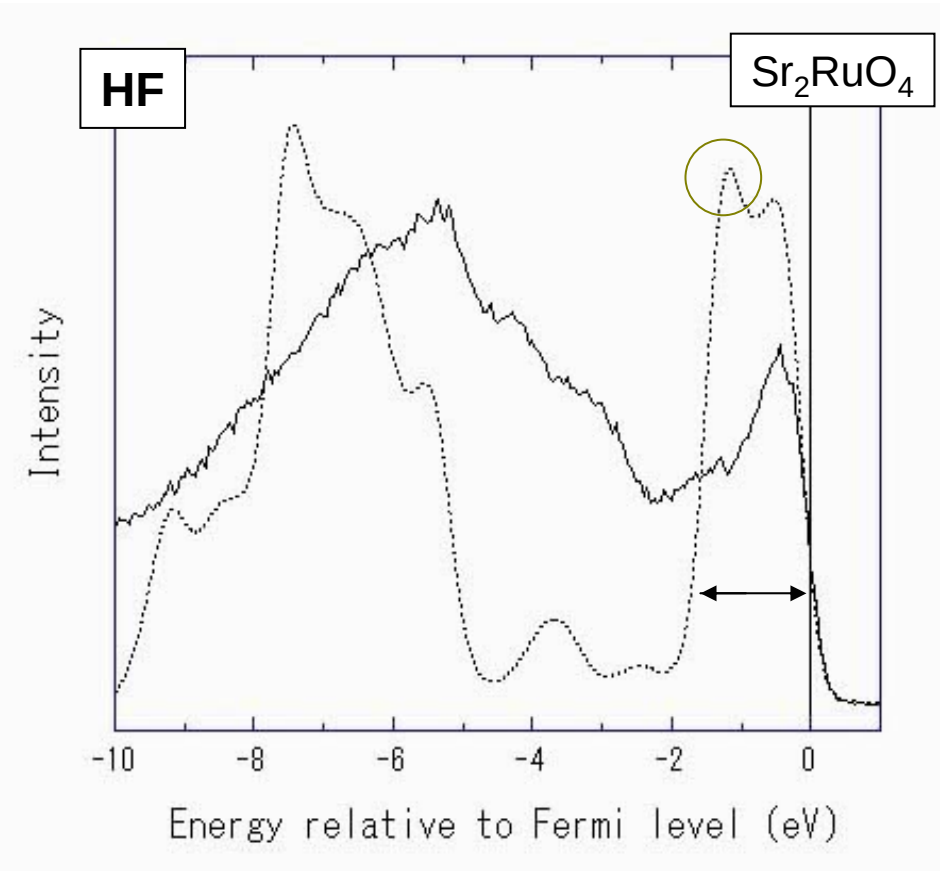
E_F intensity map from ARPES spectra
A. Damascelli *et al.*,
PR L **85,** 5194 (2000)

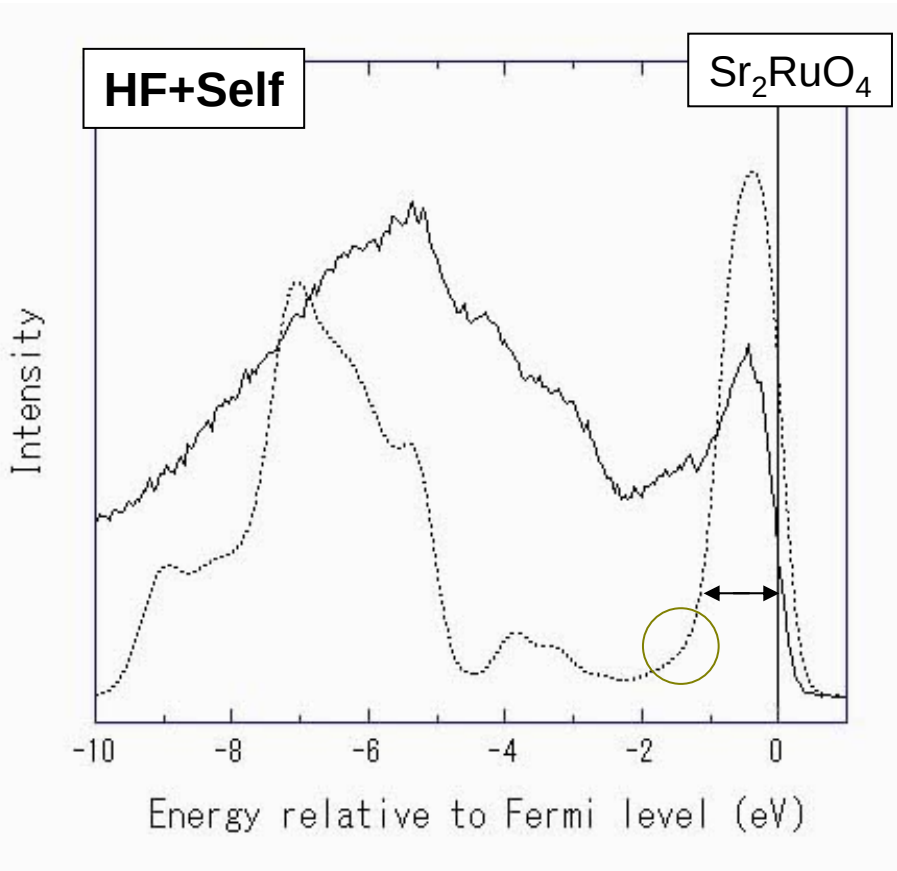
XPS and Hartree-Fock result for Sr_2RuO_4



The Ru t_{2g} band near the Fermi level is too broad.
The relative intensity of the two peaks near the Fermi level does not match the experimental result.

Second-order self-energy correction for Sr_2RuO_4





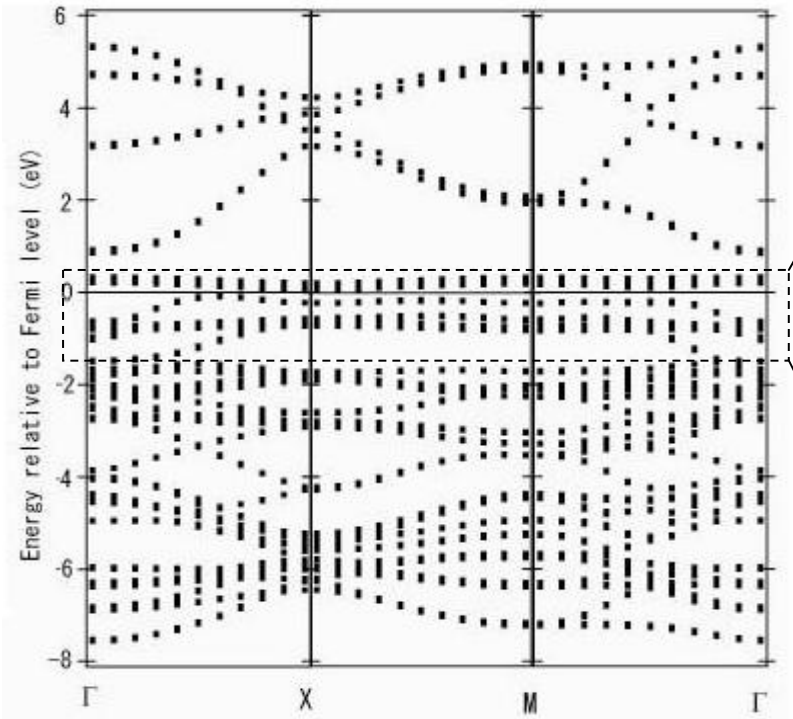
reduction of the band width

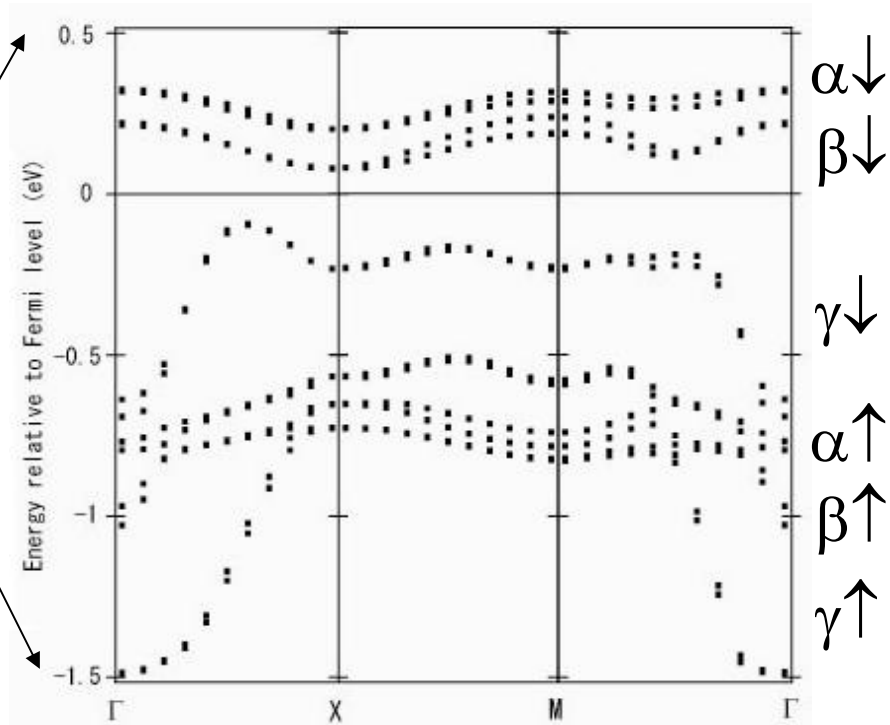
The overall spectral shape calculated with self-energy correction (second order in *u*, *u'*,*j*) shows a better agreement with the XPS spectrum.

T.T Tran, T. Mizokawa *et al.*, PRB **70**, 153106 (2004).

Model Hartree-Fock calculation for Ca_2RuO_4

compressed RuO_6 octahedron
AFI ground state

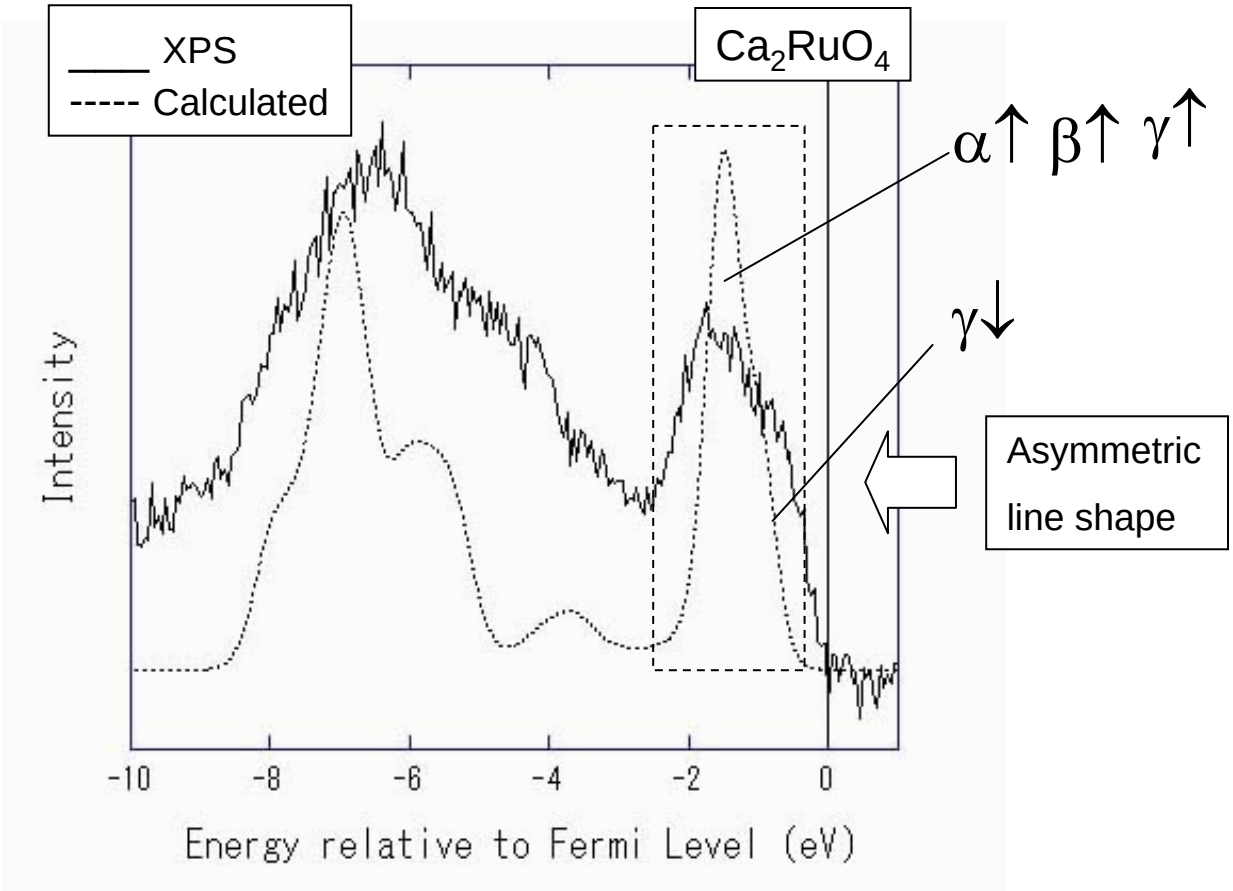




Energy band structure of Ca_2RuO_4 along high-symmetry lines.

Energy band structure of Ca_2RuO_4 in the region near the Fermi level.

Model Hartree-Fock calculation for Ca_2RuO_4



The HF result reproduces the spectrum of Ca_2RuO_4.

T. T Tran, T. Mizokawa *et al.*,
PRB **70**, 153106 (2004).

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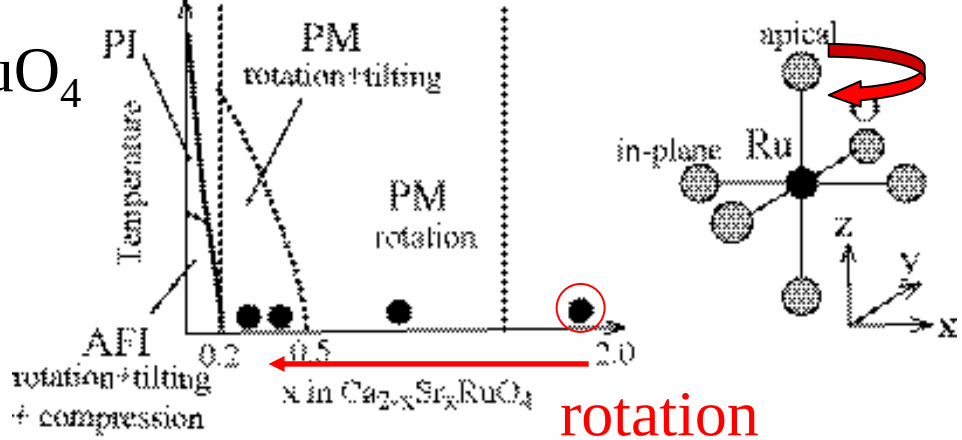
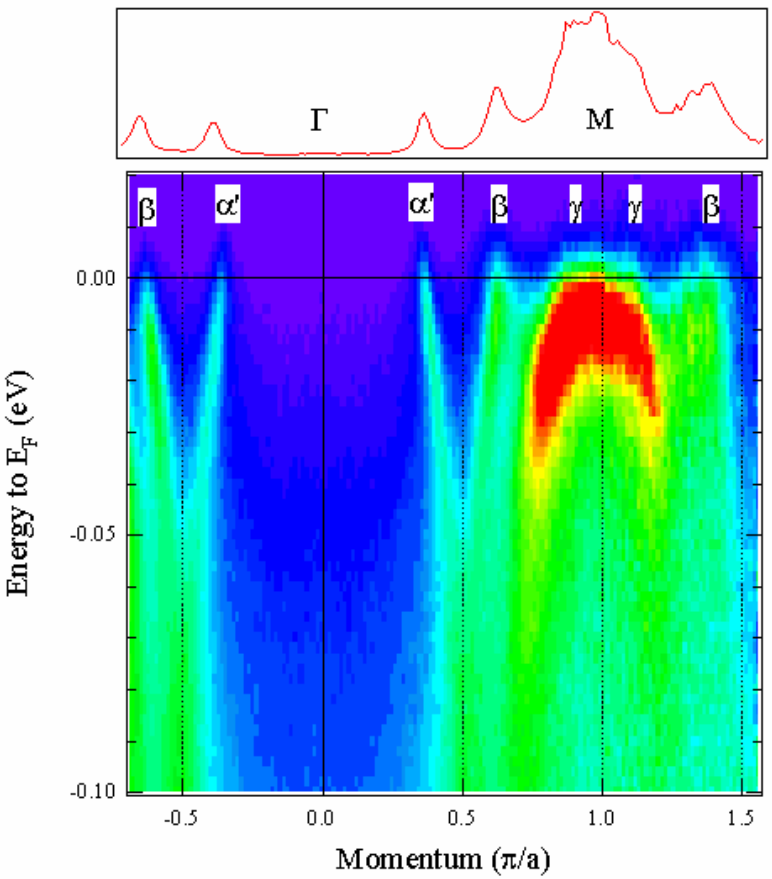
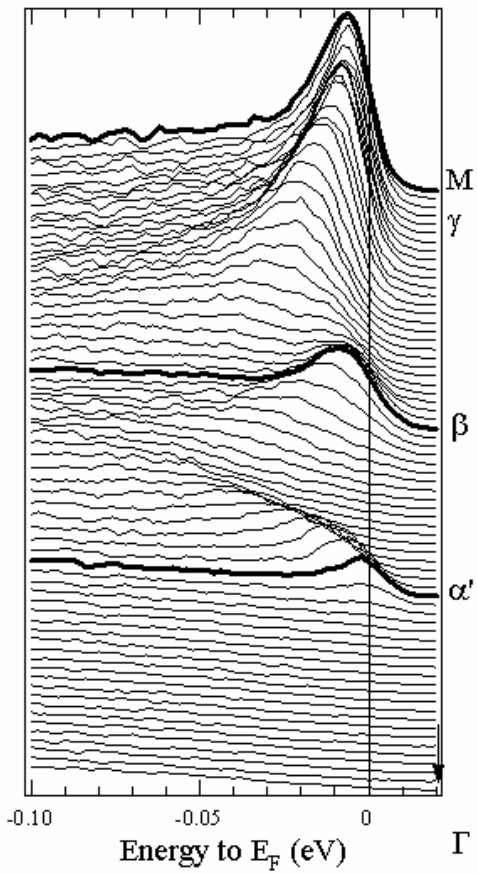
ARPES:metallic phase of $Ca_{2-x}Sr_xRuO_4$

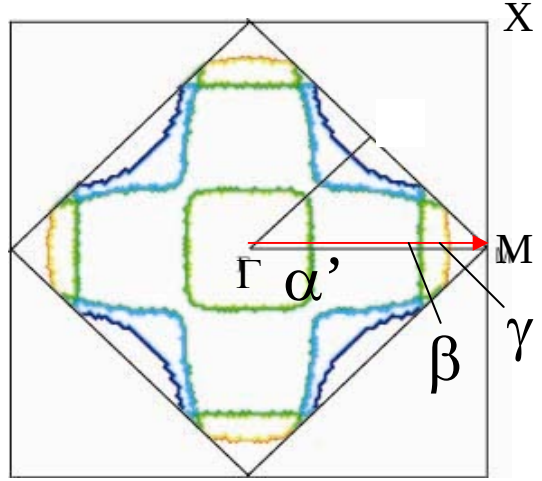
beamline 5-4 at SSRL
photon energy: 24eV
Energy resolution: 20 meV



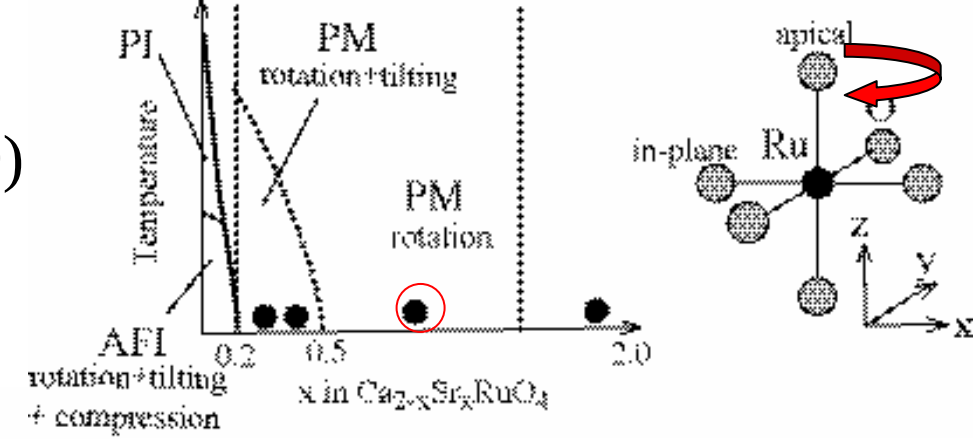
x=1.95 ΓM direction



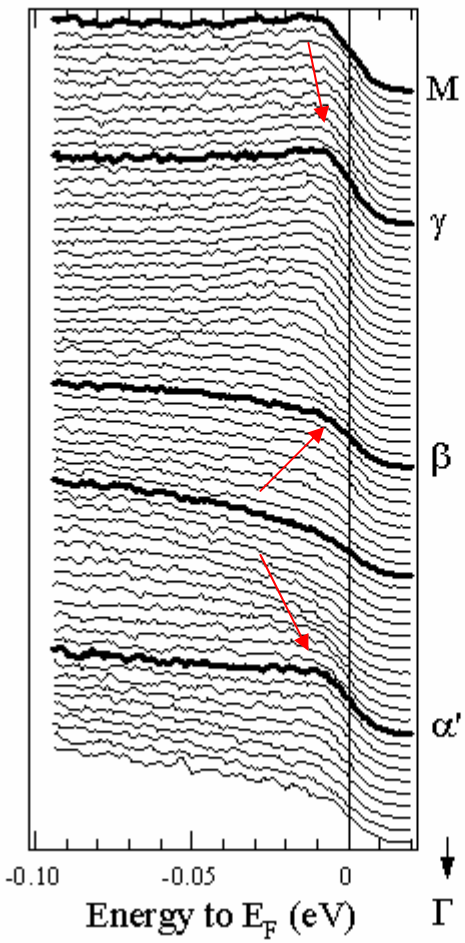




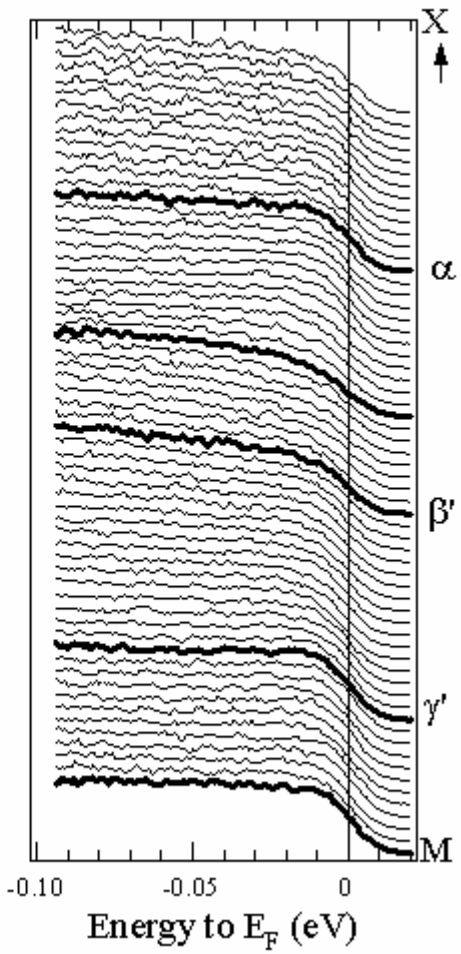
ARPES of $Ca_{2-x}Sr_xRuO_4$ (x = 0.9)

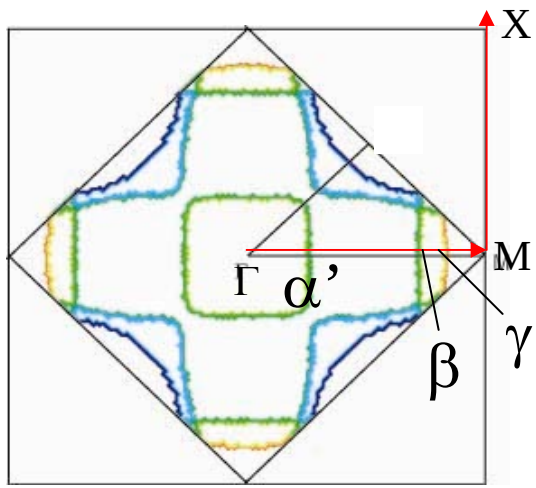


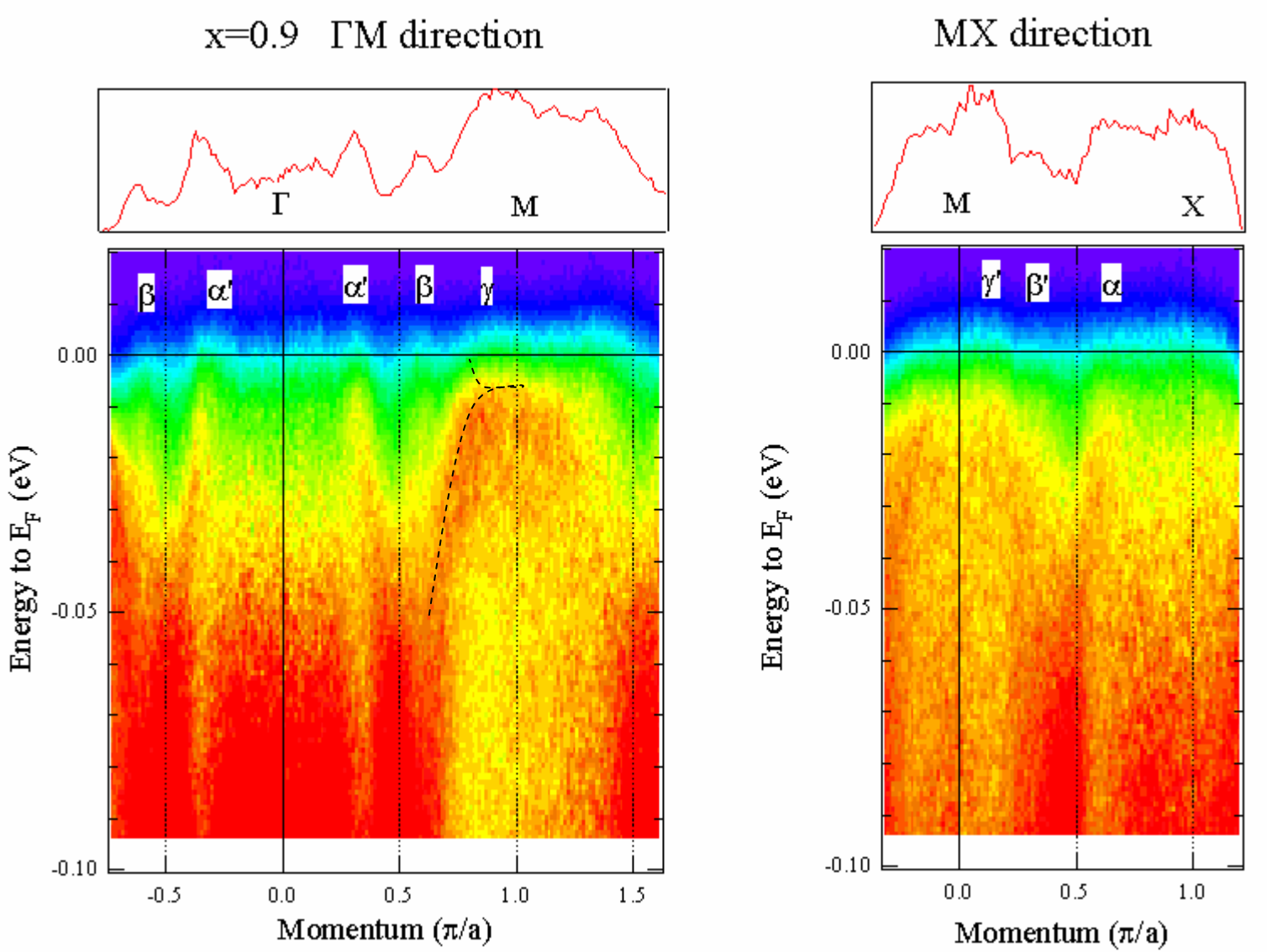
x=0.9 ΓM direction



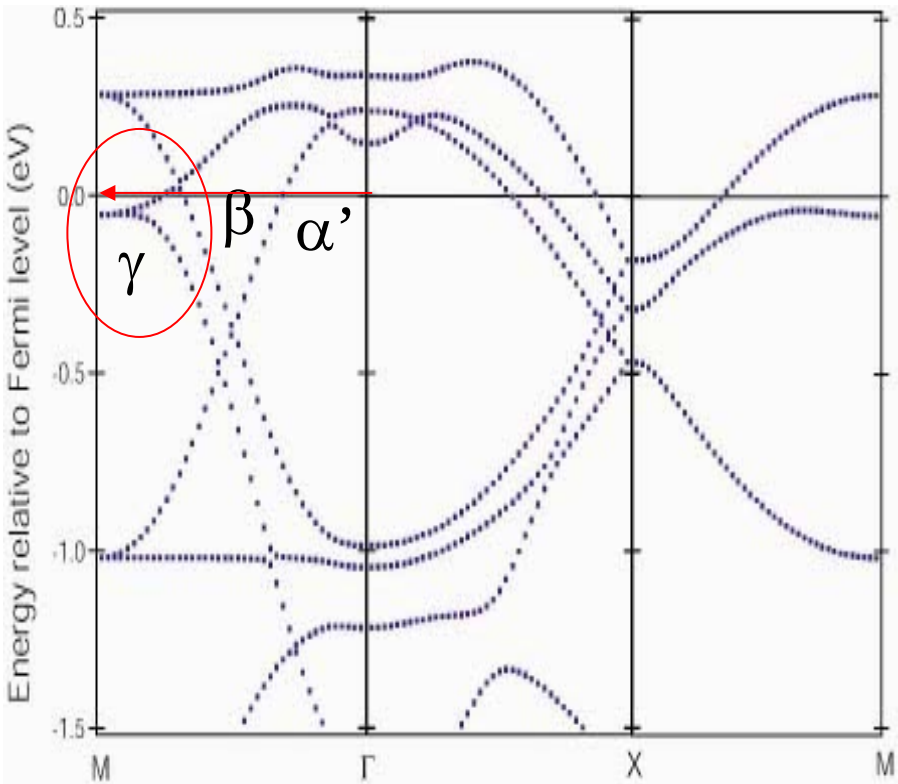
MX direction



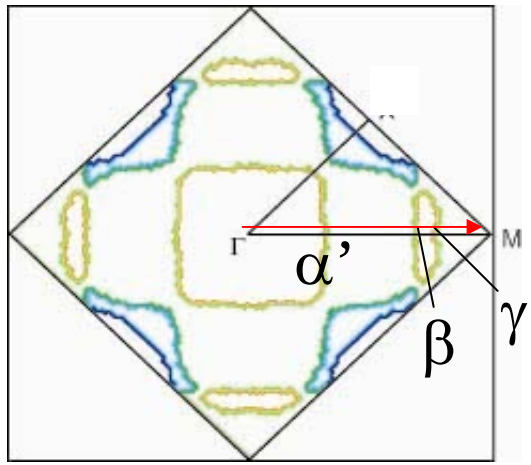



x=0.9 ΓM direction
Γ
M
β
α'
α'
β
γ
0.00
-0.05
-0.10
Energy to E_F (eV)
-0.5
0.0
0.5
1.0
1.5
Momentum (π/a)
MX direction
M
X
γ'
β'
α
0.00
-0.05
-0.10
Energy to E_F (eV)
0.0
0.5
1.0
Momentum (π/a)

rotation angle = 10^{o}



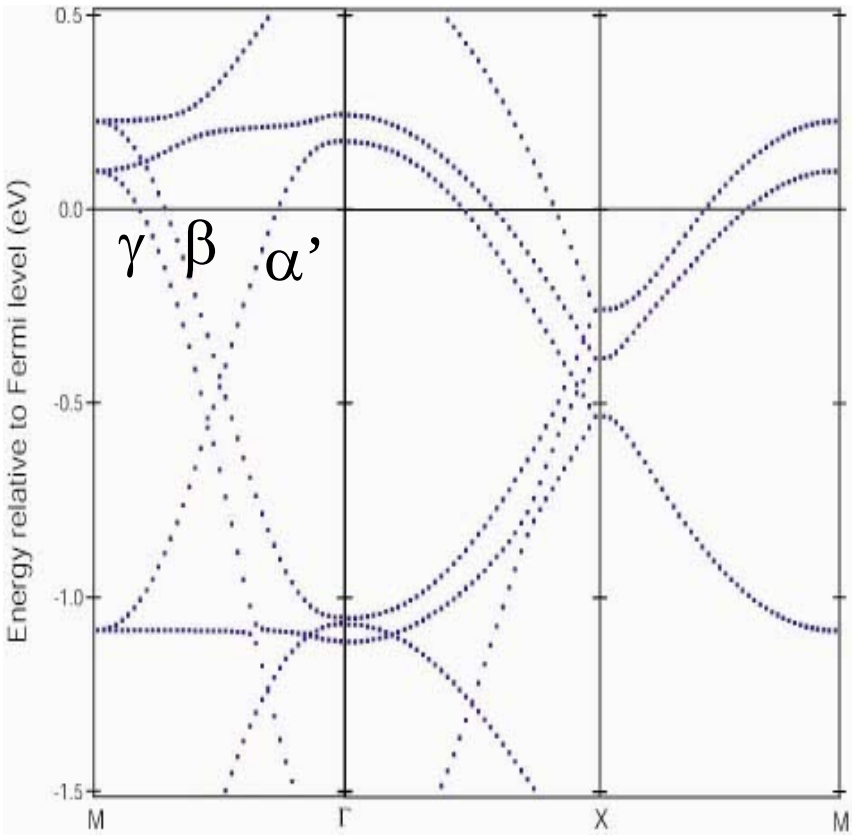
Energy band dispersion

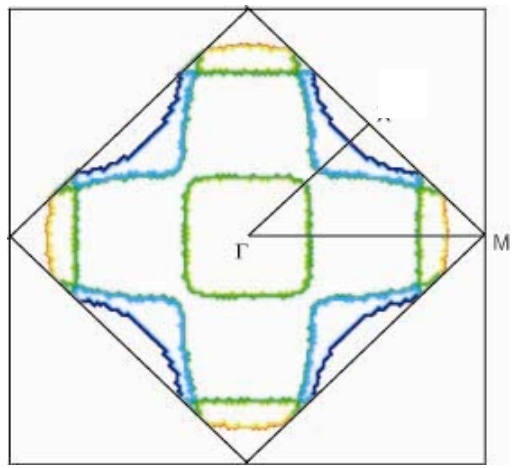


Orbital	xy	yz	zx
Occupation	0.75	0.86	0.86

Fermi surface and occupation number

rotation angle = 0°





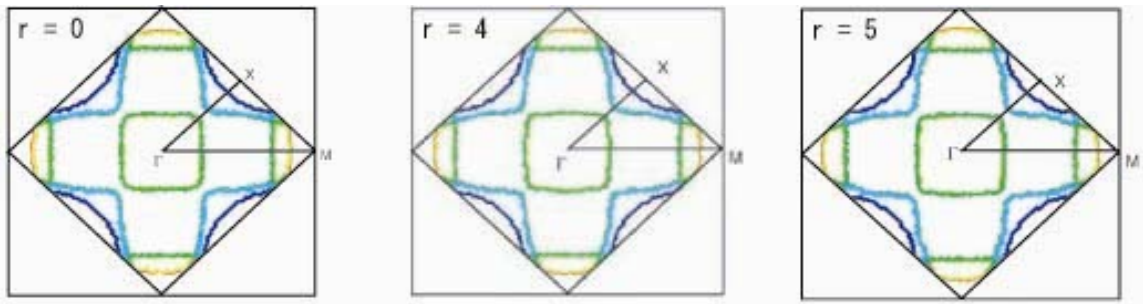
Orbital	xy	yz	zx
Occupation	0.78	0.87	0.87

Energy band dispersion

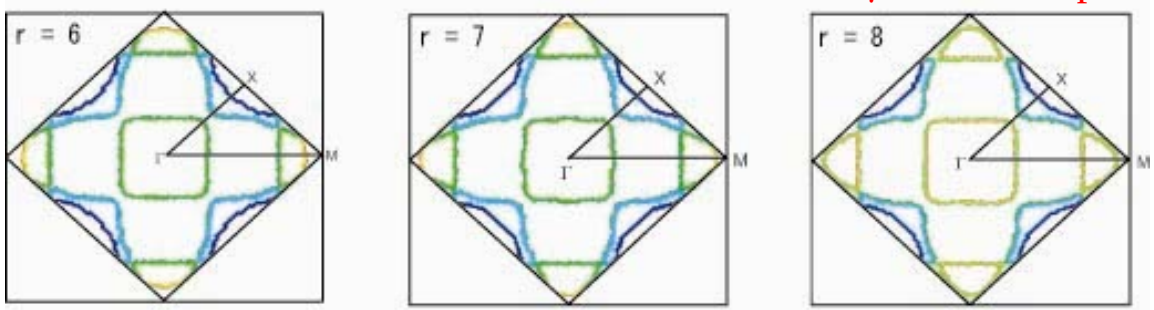
Fermi surface and occupation number

Fermi surface change as a function of rotation angle

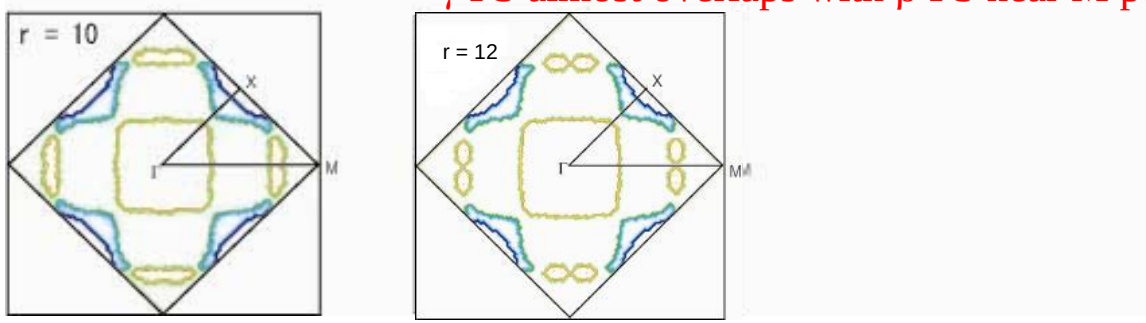
γ band at M point : above E_F



γ band at M point : below E_F

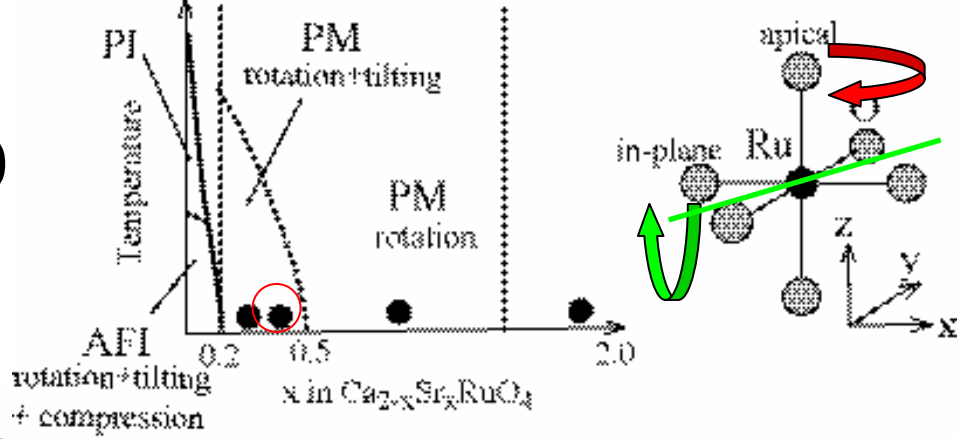


γ FS almost overlaps with β FS near M point

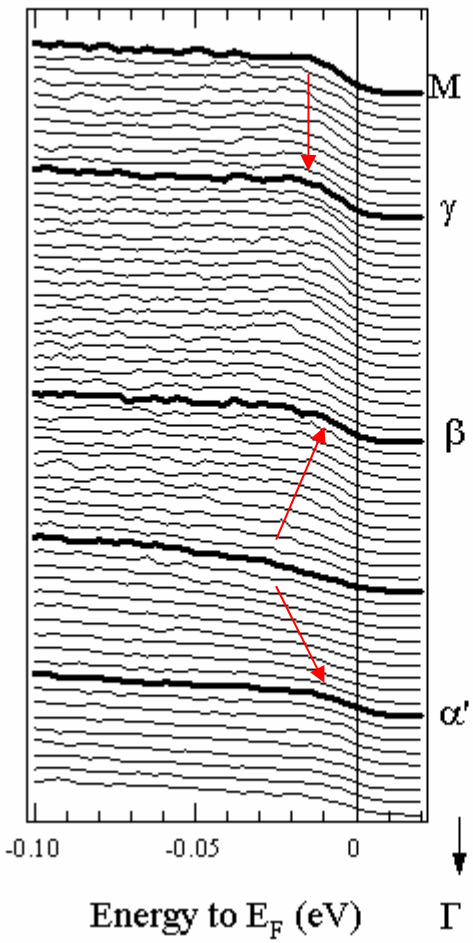


ARPES of $Ca_{2-x}Sr_xRuO_4$ (x = 0.4)

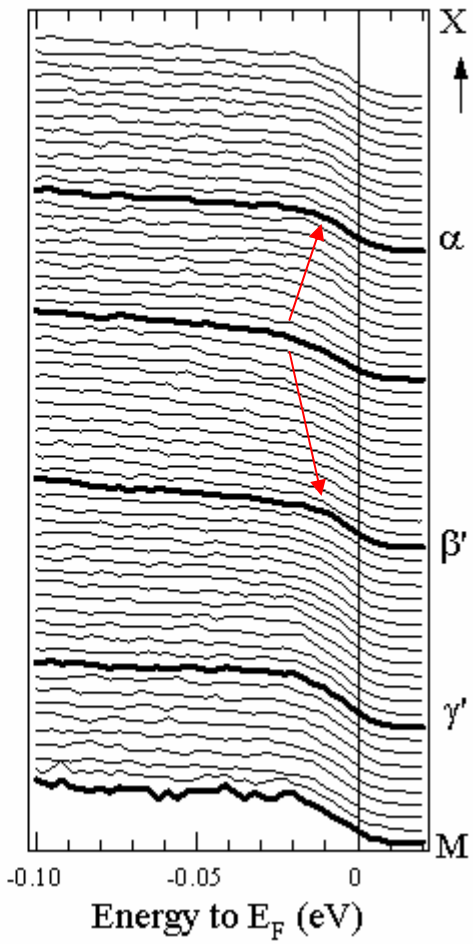
spectral weight at E_F is reduced

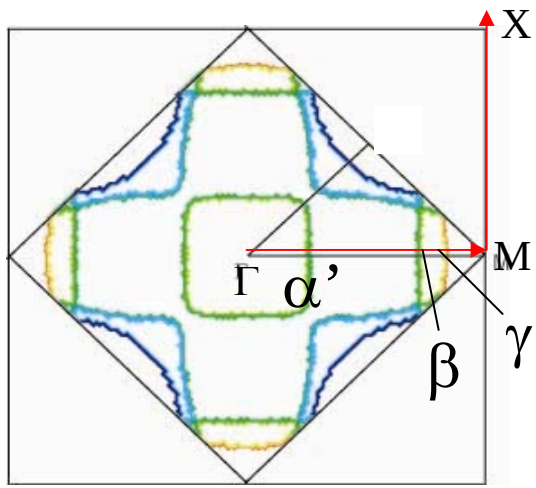


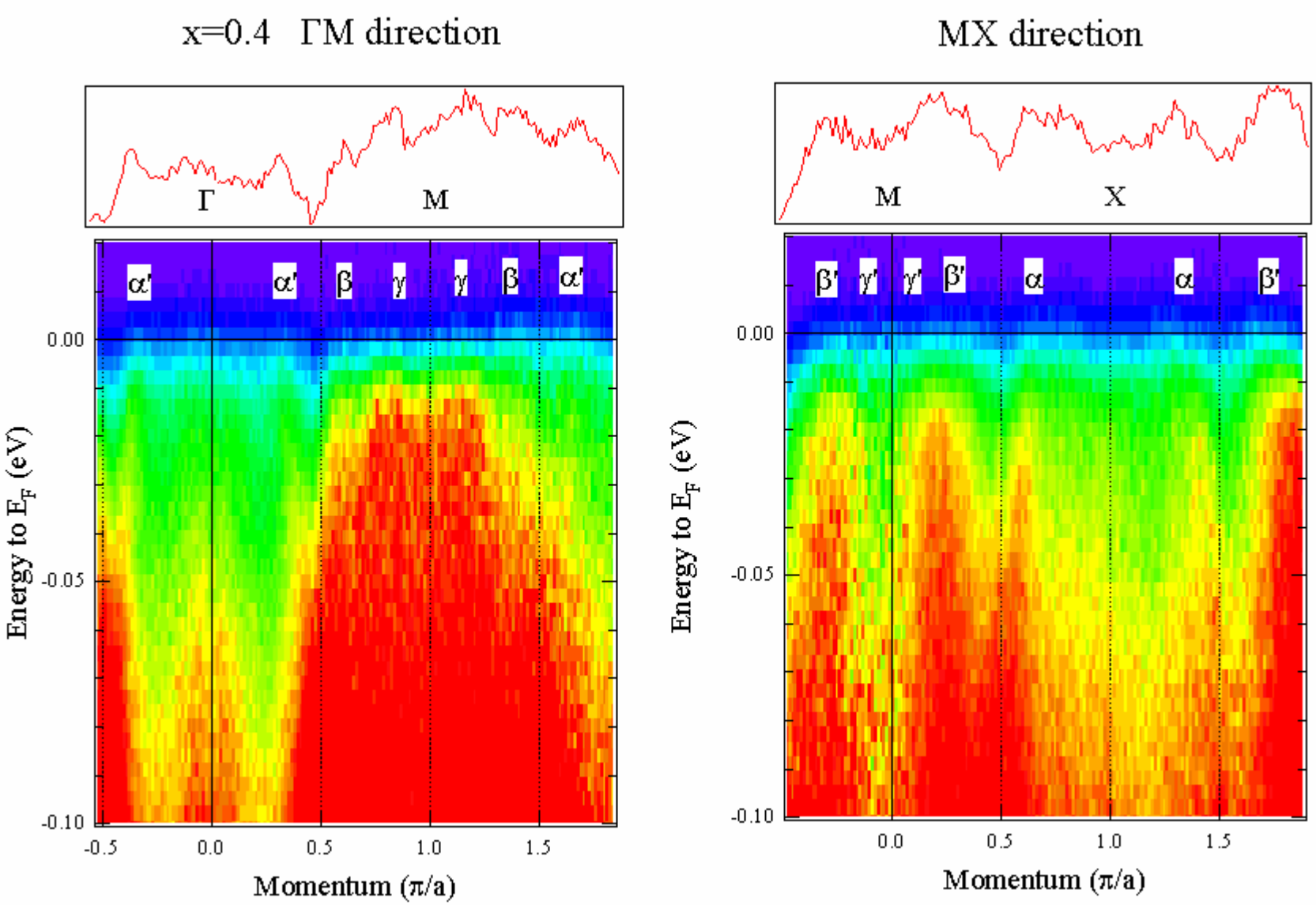
x = 0.4 ΓM direction



MX direction

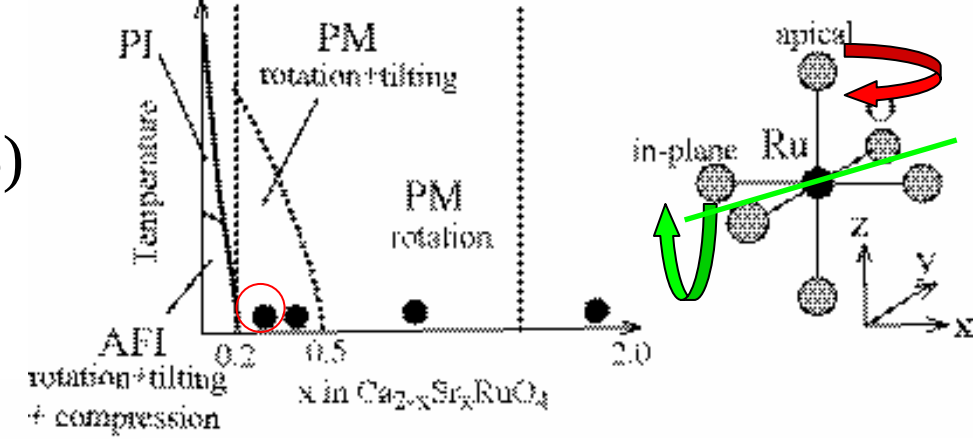




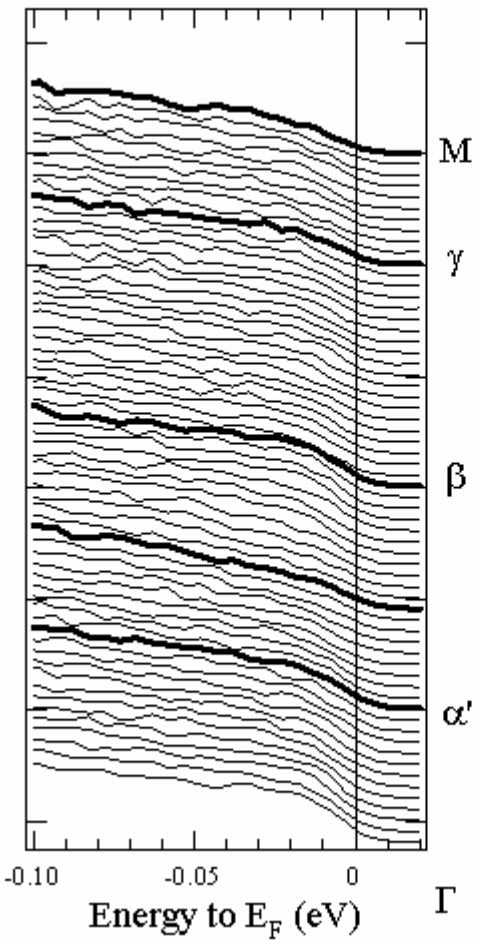

x=0.4 ΓM direction
Γ
M
α'
α'
β
γ
γ
β
α'
0.00
-0.05
-0.10
Energy to E_F (eV)
-0.5
0.0
0.5
1.0
1.5
Momentum (π/a)
MX direction
M
X
β'
γ'
γ'
β'
α
α
β'
0.00
-0.05
-0.10
Energy to E_F (eV)
0.0
0.5
1.0
1.5
Momentum (π/a)

ARPES of $Ca_{2-x}Sr_xRuO_4$ (x = 0.3)

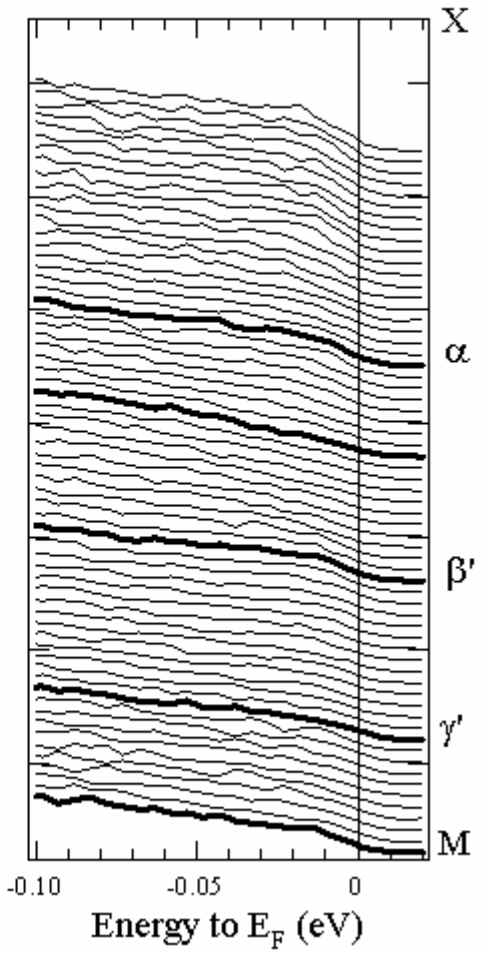
spectral weight at E_F is reduced

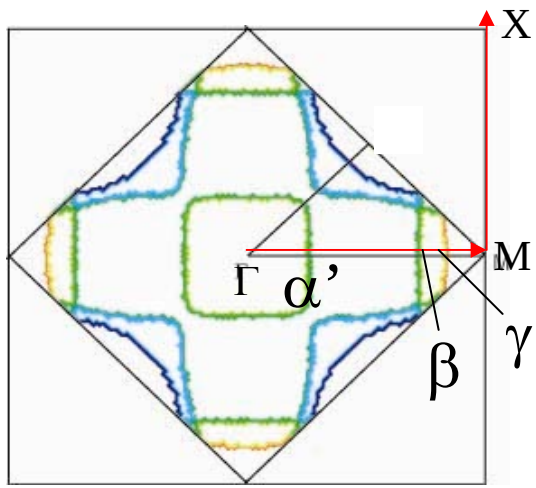


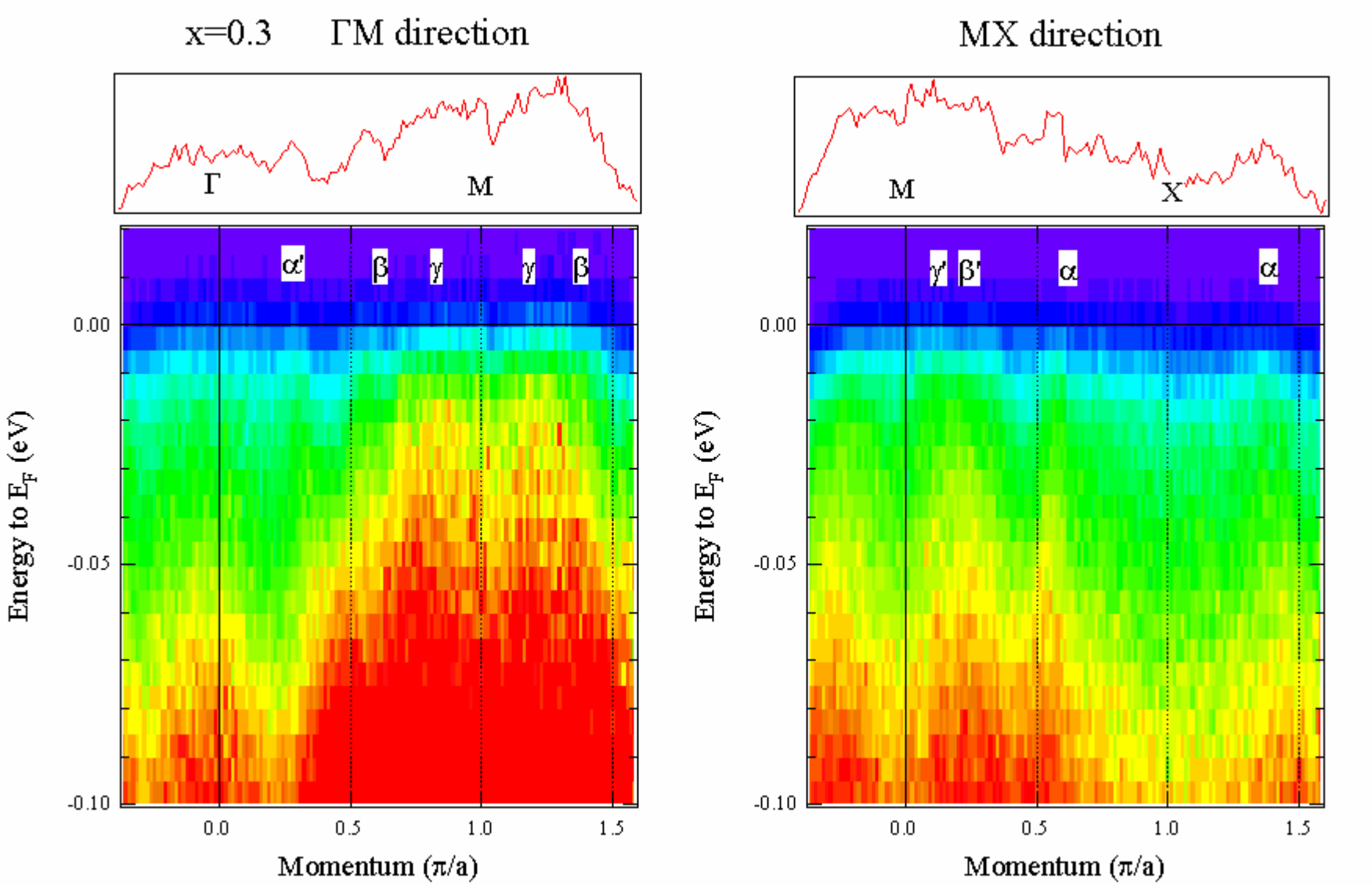
x = 0.3 ΓM direction



MX direction

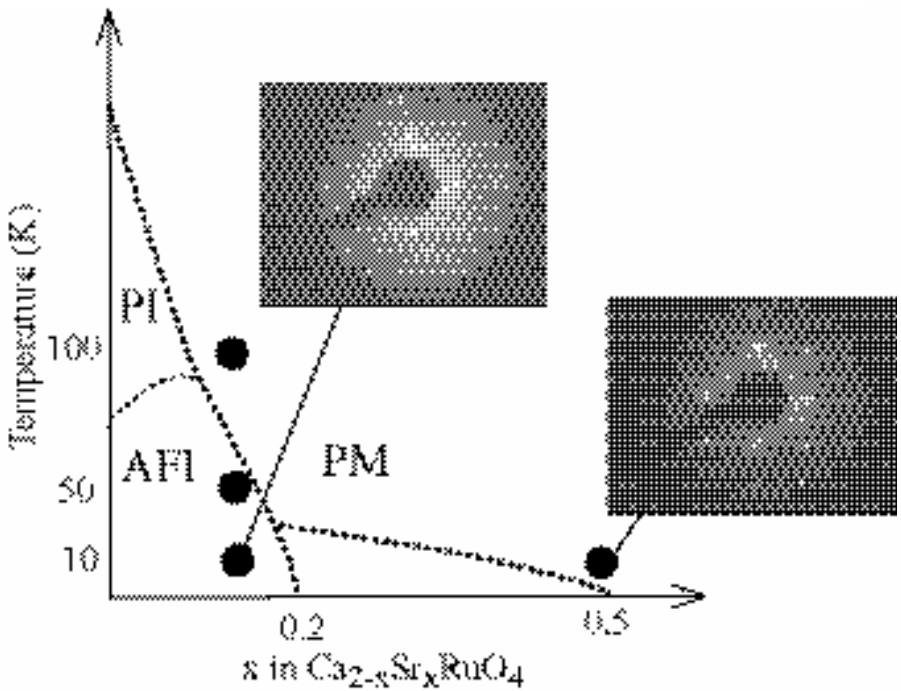


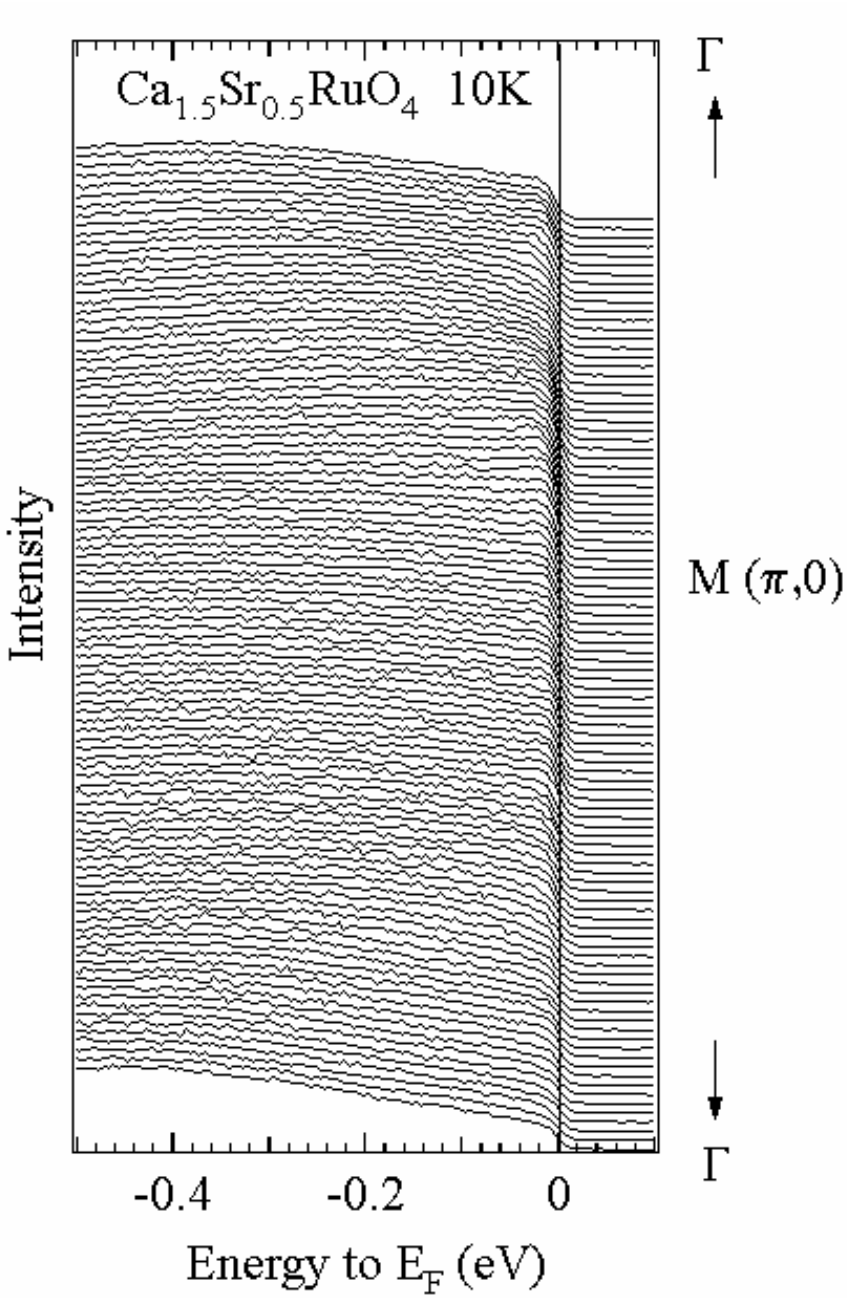



x=0.3 ΓM direction
Γ
M
α'
β
γ
γ
β
0.00
-0.05
-0.10
Energy to E_F (eV)
0.0
0.5
1.0
1.5
Momentum (π/a)
MX direction
M
X
γ'
β'
α
α
0.00
-0.05
-0.10
Energy to E_F (eV)
0.0
0.5
1.0
1.5
Momentum (π/a)

ARPES: insulating phase *vs* metallic phase

beamline 5-4 at SSRL
photon energy: 28eV
Energy resolution: 20 meV

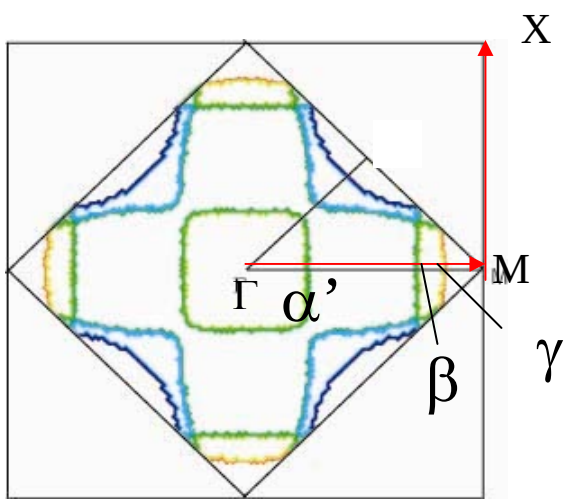


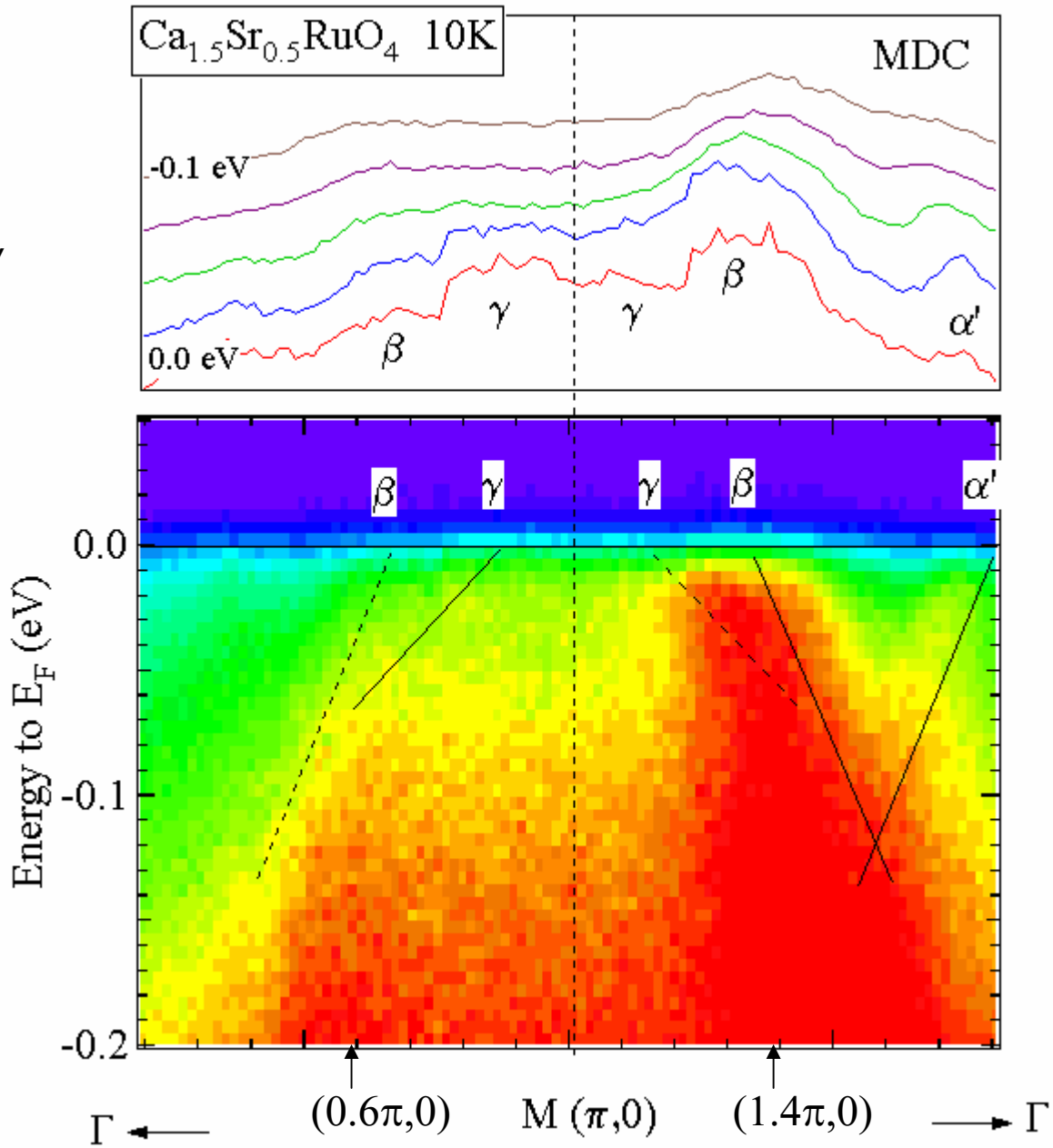


ΓM direction of x = 0.5

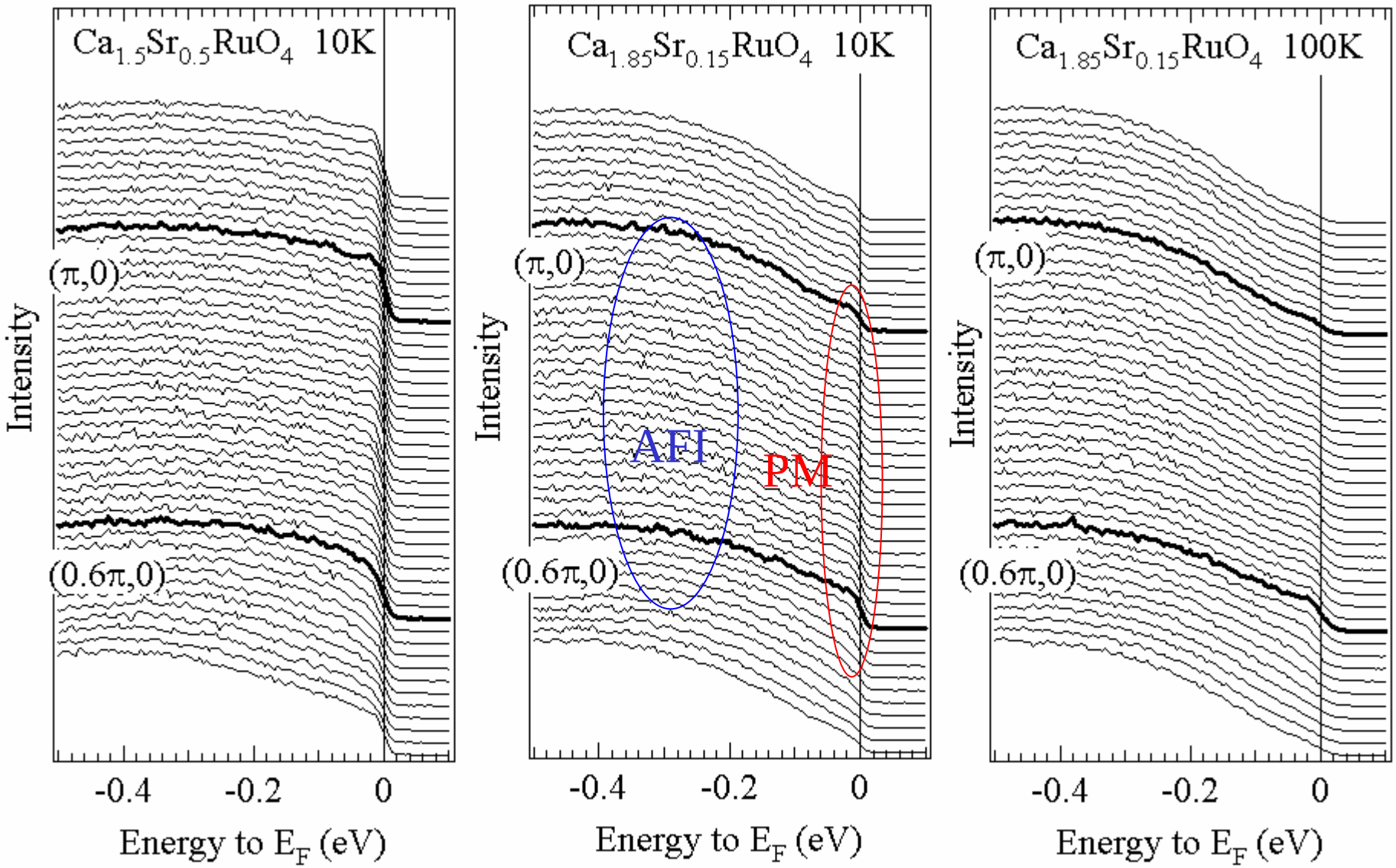
similar to x = 0.9

cf. Ding *et al.*, hole-like FS for γ



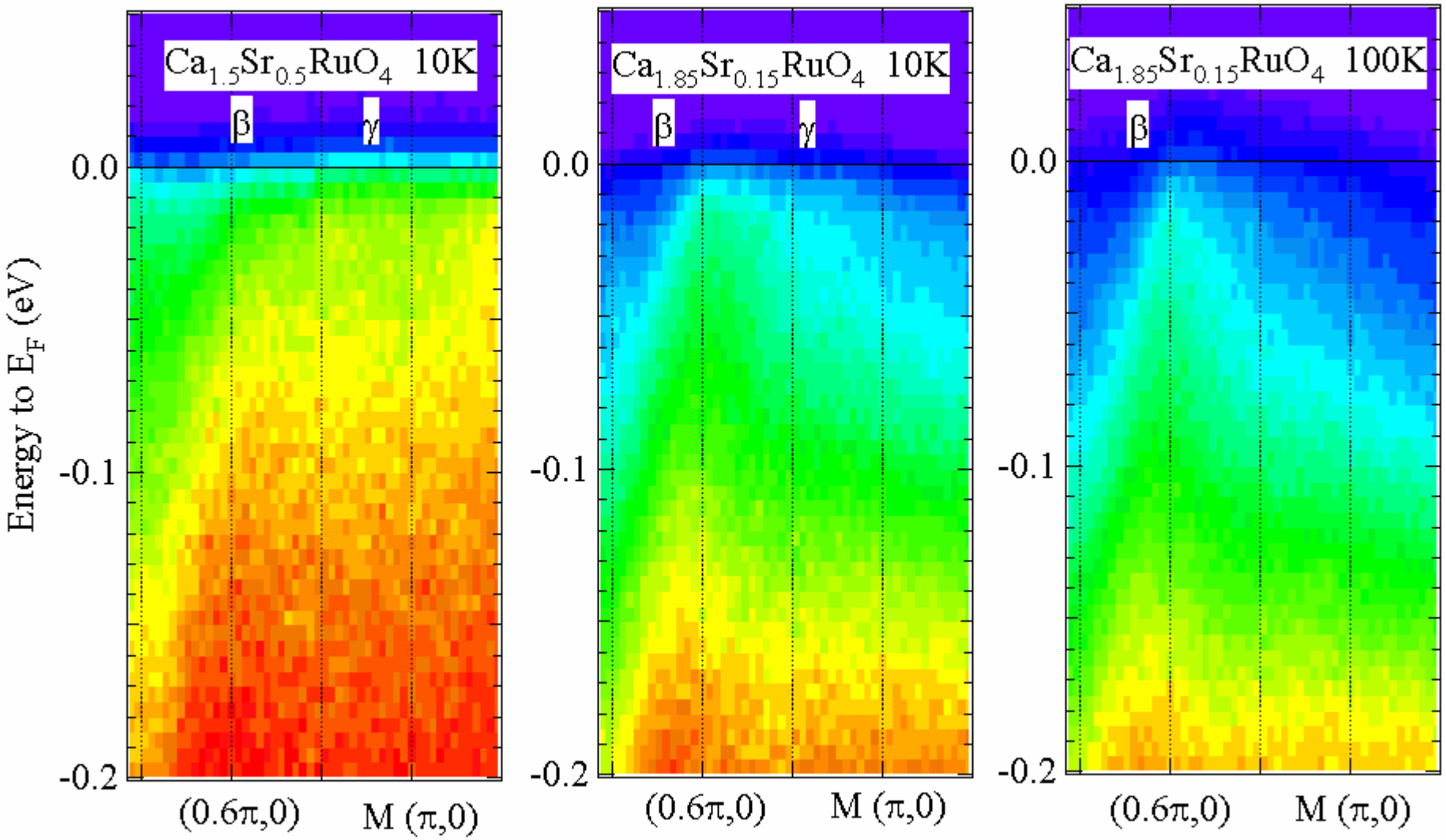


ΓM direction of x = 0.5 and 0.15



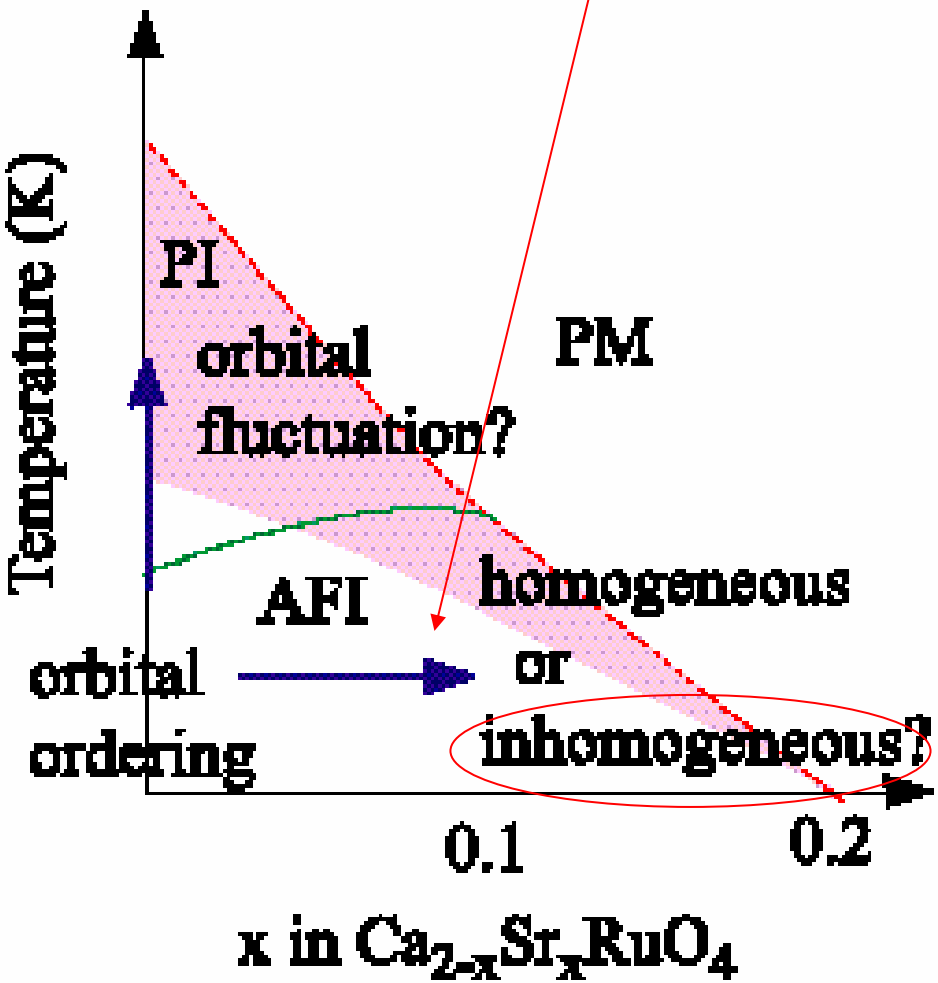
spectral weight at E_F in the insulating(non-metallic) phase

ΓM direction of x = 0.5 and 0.15



The spectral weight at E_F has some momentum dependence.

spectral weight at E_F
in the insulating(non-metallic) phase



VRH transport is observed for x=0.15
S. Nakatsuji et al., PRL 93, 146401 (2004).

The spectral weight at E_F can be attributed to the disorder-induced in-gap state that is responsible for the VRH transport.

Why does it show the nice momentum dependence?

The system is spatially (nano-scale?) separated into AFI region (compressed RuO_6 octahedron) and disorder-induced region (elongated RuO_6 octahedron).

Summary

In the AFI phase of x=0, 0.09 and 0.15:

- The amount of yz/zx holes decreases with temperature.
- Disorder (Sr doping) reduces the amount of yz/zx holes.
- Small spectral weight survives at E_F for Sr doped case (inhomogeneous state in the light of lattice distortion).

At the MI transition:

- Orbital occupation changes discontinuously.
- Disorder (Sr doping) does not affect the orbital change.

In the metallic phase of x = 0.3, 0.4, and 0.9:

- Orbital occupation is very similar to that of Sr_2RuO_4.
- γ FS becomes hampered in going from x=0.9 to 0.4.
- α, β, γ FS are observed even in x = 0.4, but spectral weight at E_F is considerably reduced for all α, β, γ FS.
  (inconsistent with the orbital-dependent Mott transition).

Outline

$Ca_{2-x}Sr_xRuO_4$

XAS orbital symmetry

XPS spectral line shape and correlation effect

Hartree-Fock analysis

ARPES Fermi surface and the MI transition

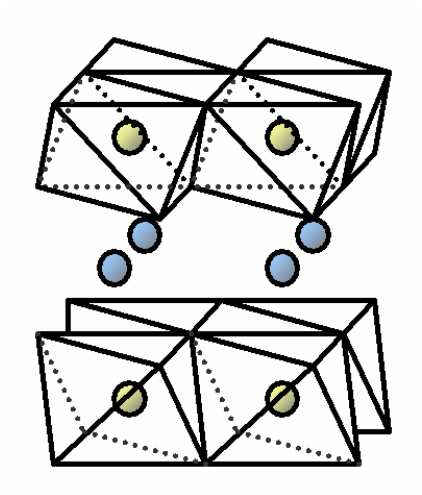
CoO_2 triangular lattice in $Bi_2Sr_2Co_2O_9$, Na_xCoO_2 , $Ca_3Co_4O_9$

XPS spectral line shape and correlation effect

XAS orbital symmetry

Hartree-Fock analysis

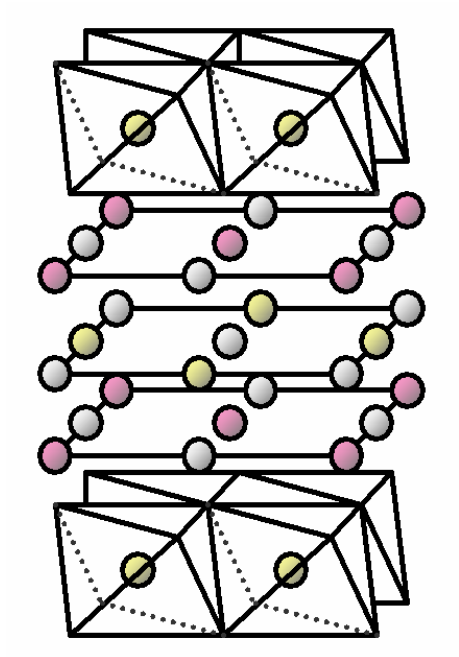
layered Co oxides with Co-O triangular lattice



Na_xCoO_2

Good metal

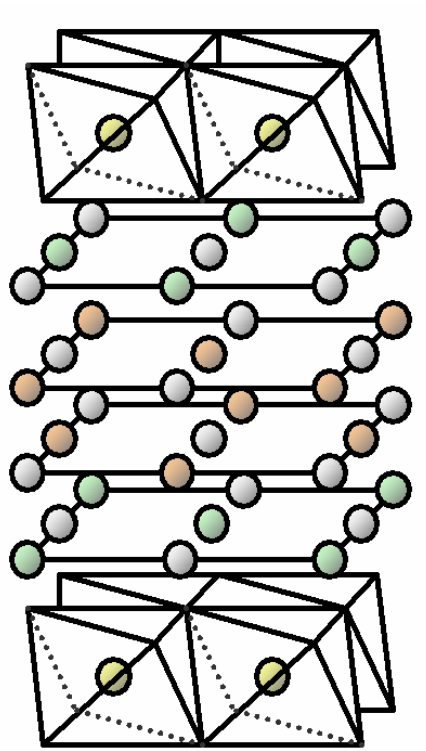
I. Terasaki *et al*., 1997.



$Ca_3Co_4O_9$

Insulating at low temperature

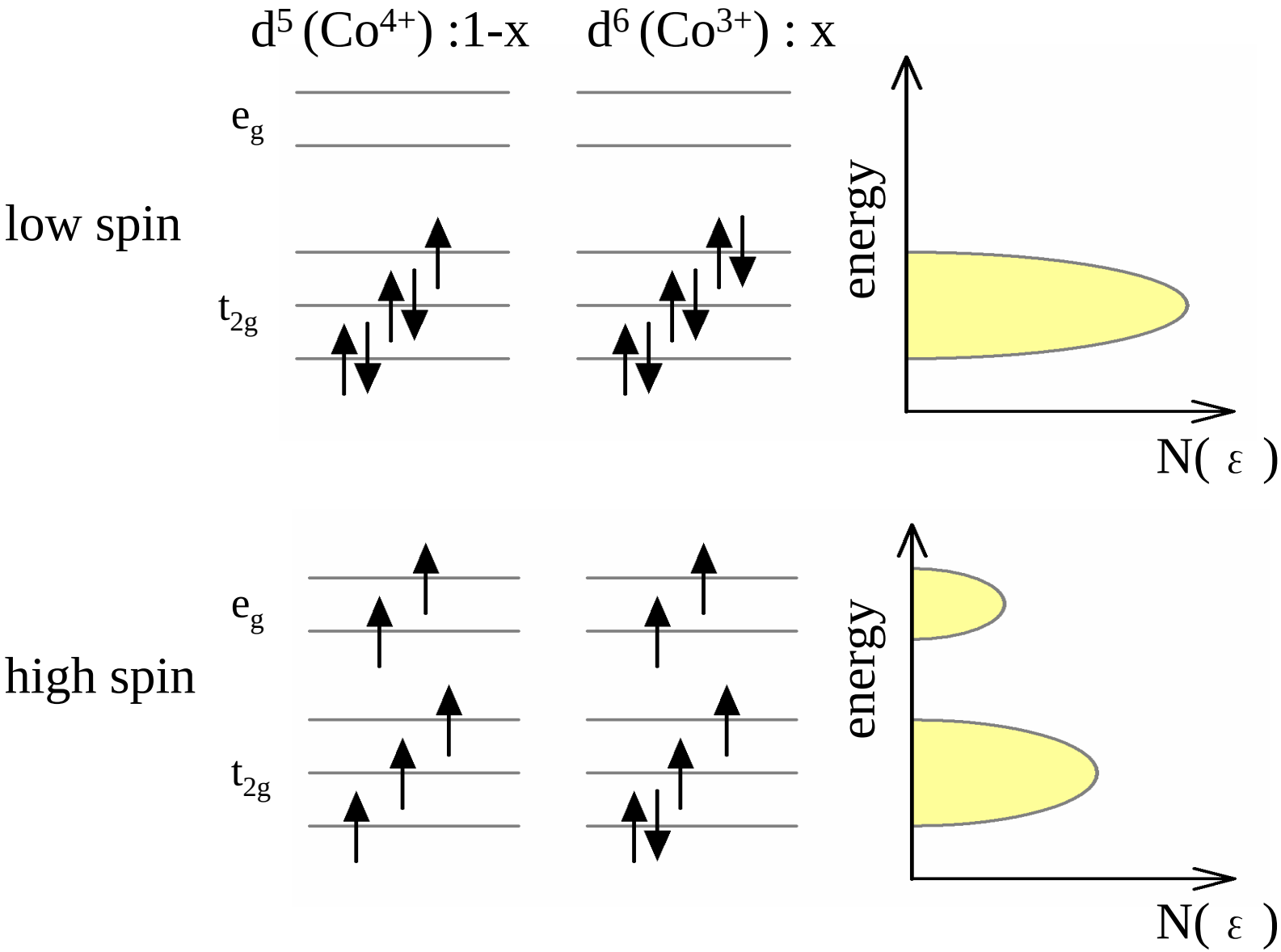
Y. Miyazaki *et al*., 2002



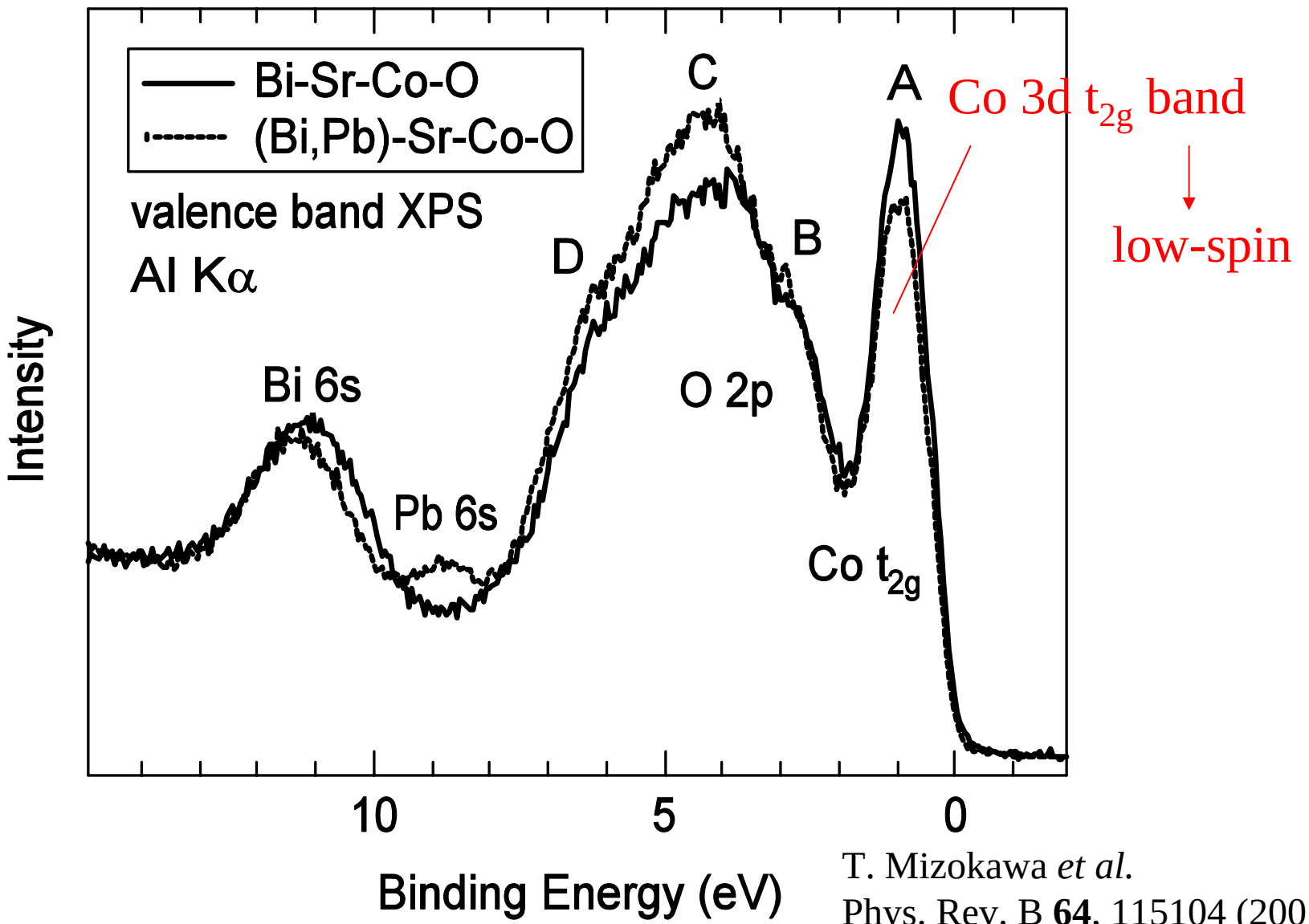
$Bi_2Sr_2Co_2O_9$

Bad metal

T. Yamamoto *et al*., 2000

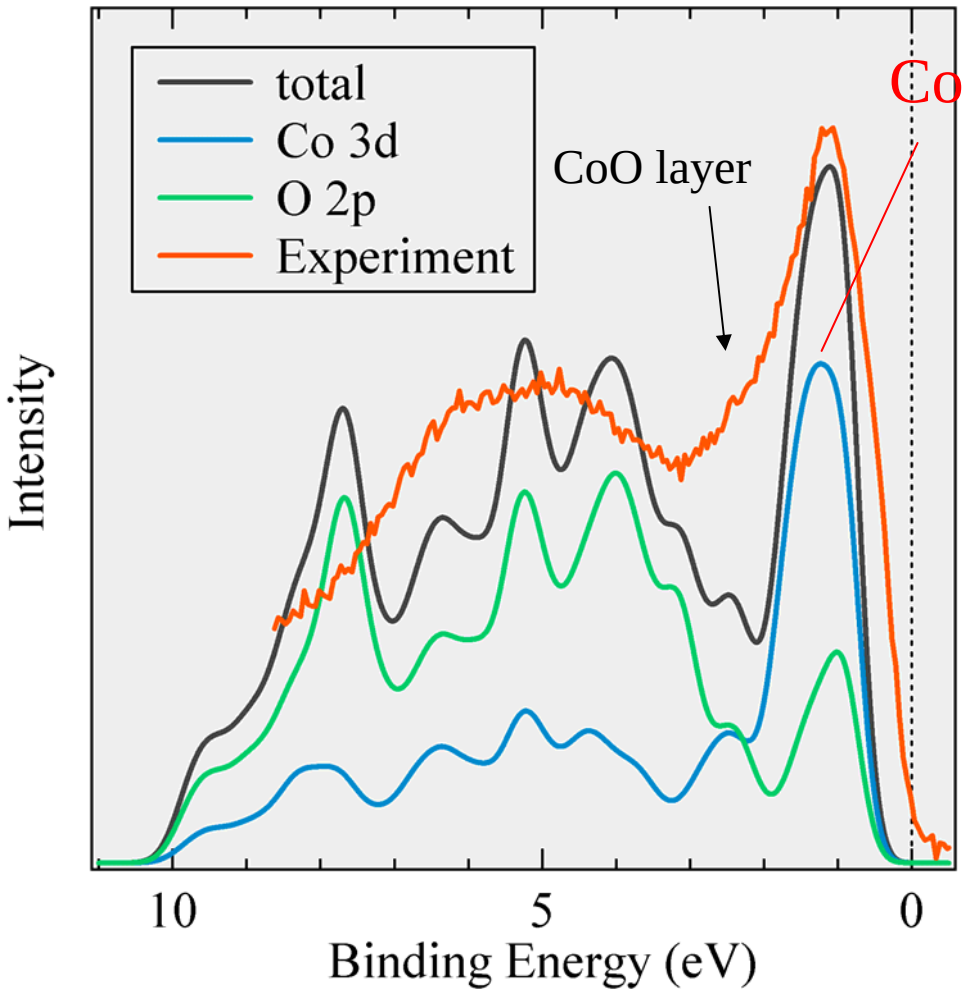

d^5 (Co^{4+}) :1-x
d^6 (Co^{3+}) : x
low spin
e_g
t_{2g}
energy
N(ε)
high spin
e_g
t_{2g}
energy
N(ε)

Valence-band XPS of (Bi,Pb)-Sr-Co-O



T. Mizokawa *et al.*
Phys. Rev. B **64**, 115104 (2001)

Valence-band XPS of $Ca_3Co_4O_9$



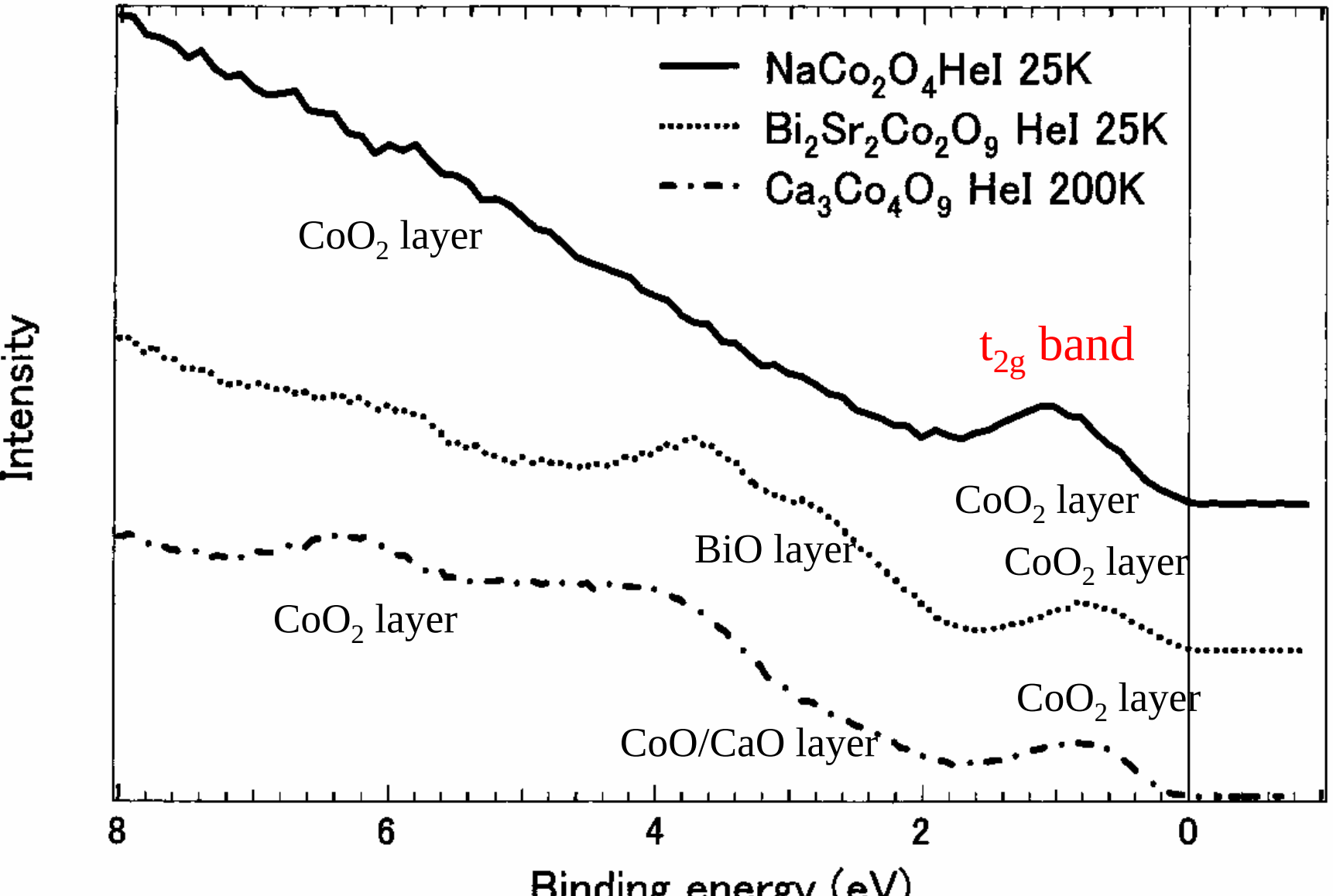
Co 3d t_{2g} band

↓

low-spin

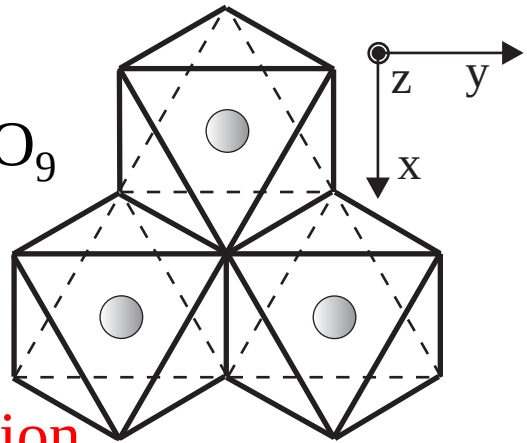
CoO_2 layer : low-spin Co^{3+} and Co^{4+}

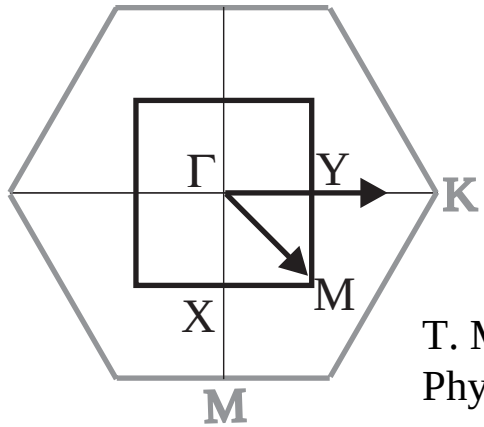
Valence-band photoemission spectra (hν = 21.2 eV)



ARPES

$Bi_2Sr_2Co_2O_9$



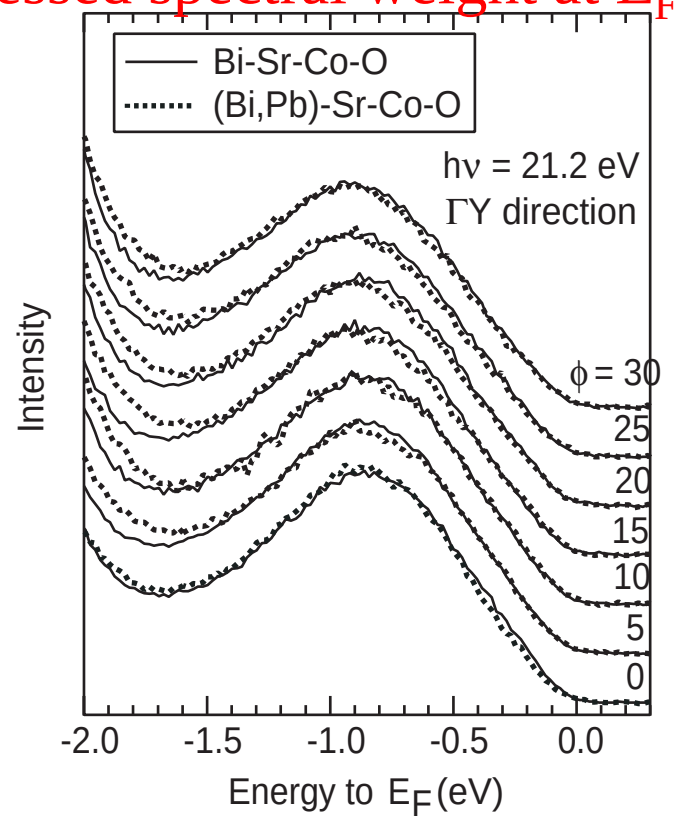


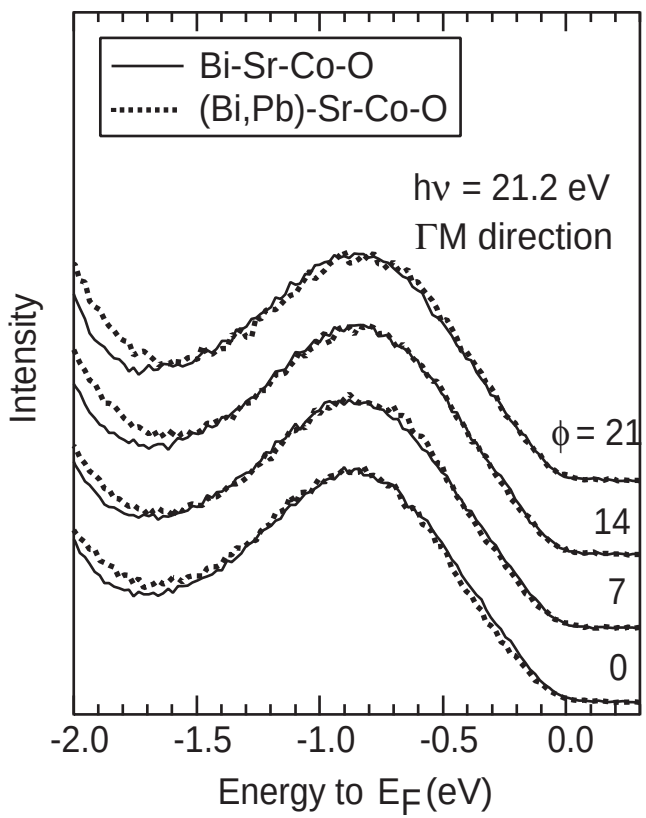
Structural study by Raveau's group and Uchinokura's group in 1999

T. Mizokawa *et al.*
Phys. Rev. B **64**, 115104 (2001)

Small dispersion

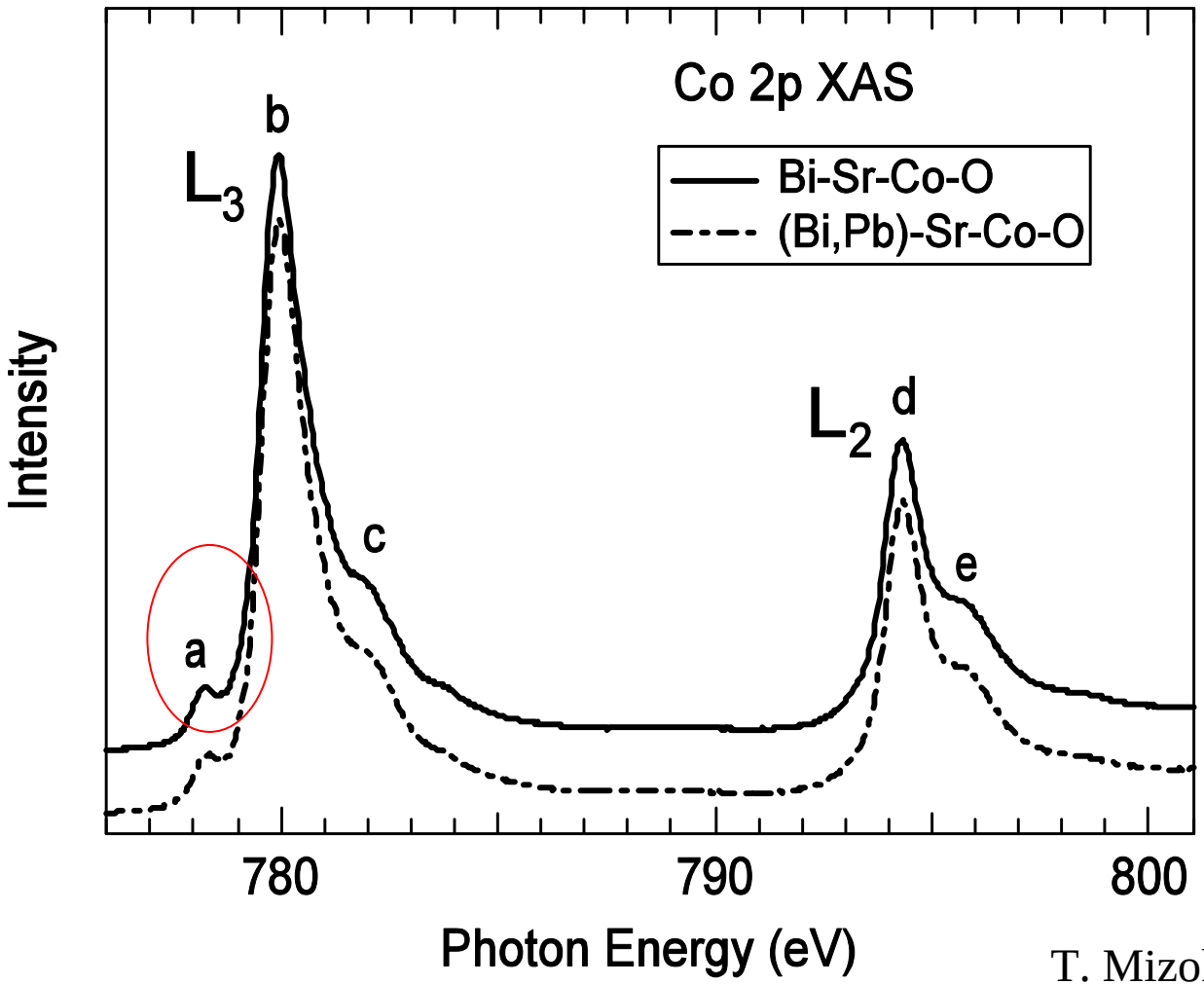
Suppressed spectral weight at E_F → Small polaron

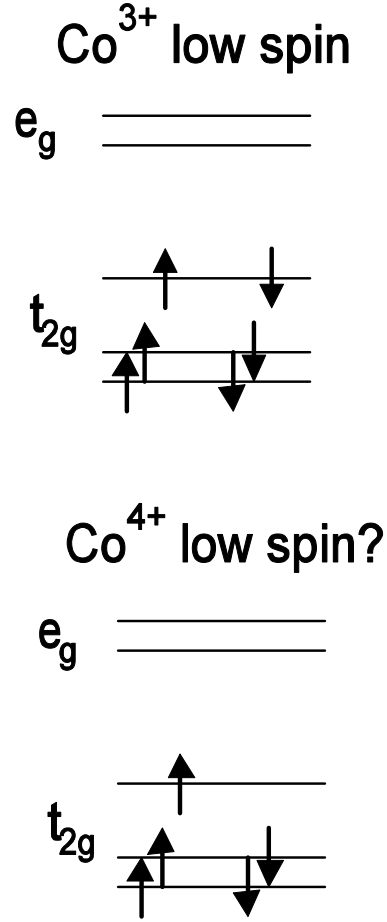




Co 2p XAS of $Bi_2Sr_2Co_2O_9$

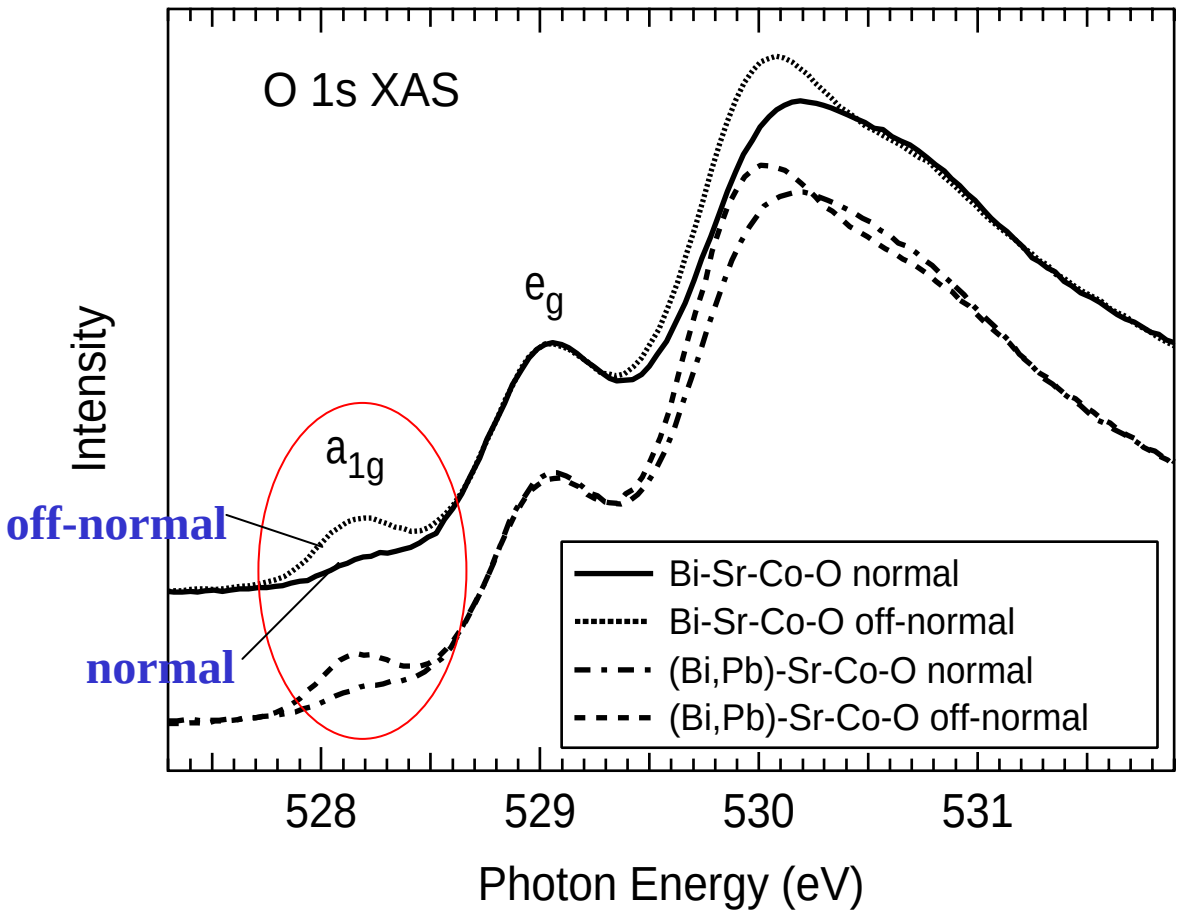
How about spin state?

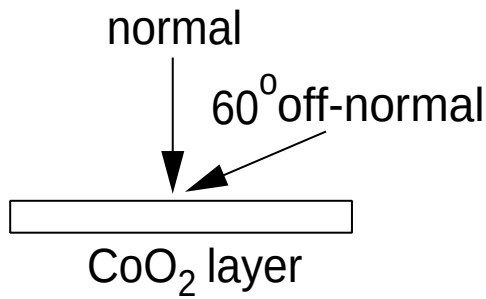


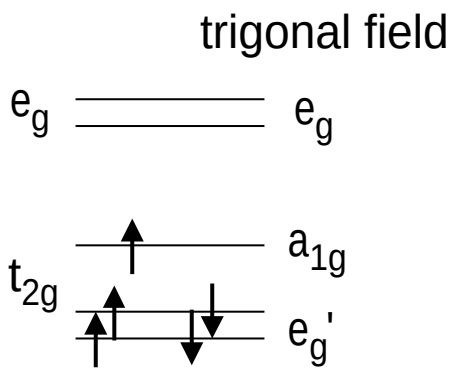


T. Mizokawa *et al.*
Phys. Rev. B **64**, 115104 (2001)

O 1s XAS of $Bi_2Sr_2Co_2O_9$ How about orbital state?



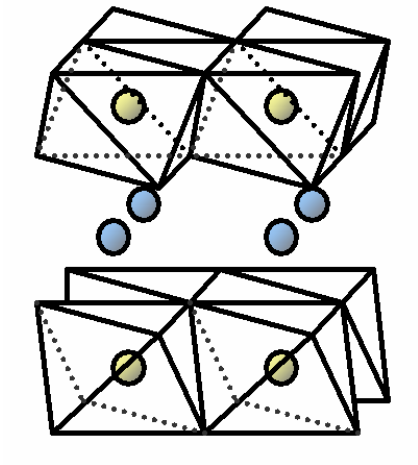




T. Mizokawa *et al.*
Phys. Rev. B **64**, 115104 (2001)

Orbial symmetry of the a_{1g} state

$$\phi_{a1g} = \frac{1}{\sqrt{3}} (\phi_{yz} + \phi_{zx} + \phi_{xy})$$



$$\phi_{yz} = \frac{i}{\sqrt{2}} (\phi_{321} + \phi_{32\text{-}1}) = \frac{\sqrt{15}}{\sqrt{4\pi}} yz/r^2 \, R_{32}(r)$$

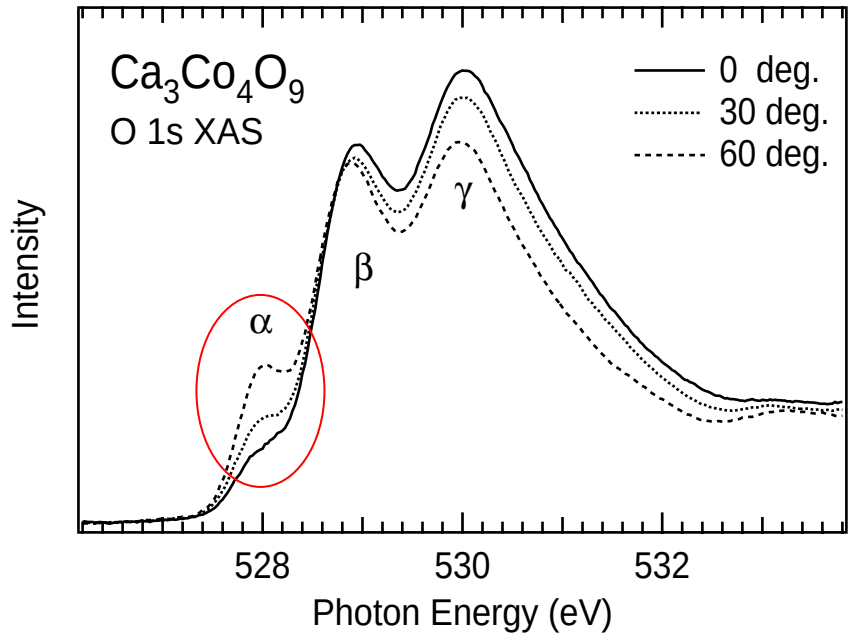
$$\phi_{zx} = -\frac{1}{\sqrt{2}} (\phi_{321} - \phi_{32\text{-}1}) = \frac{\sqrt{15}}{\sqrt{4\pi}} zx/r^2 \, R_{32}(r)$$

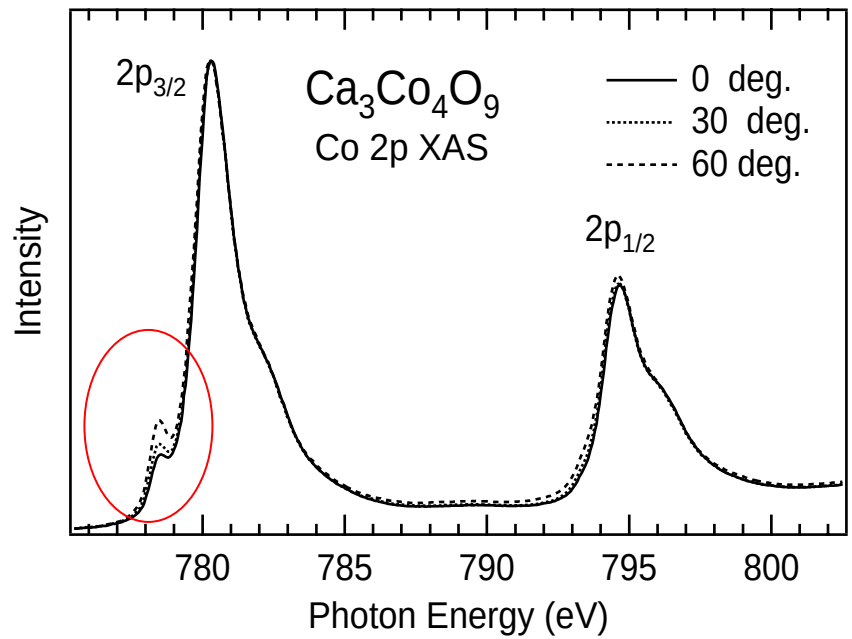
$$\phi_{xy} = -\frac{i}{\sqrt{2}} (\phi_{322} - \phi_{32\text{-}2}) = \frac{\sqrt{15}}{\sqrt{4\pi}} xy/r^2 \, R_{32}(r)$$

$$\phi_{3z2\text{-}r2} = \phi_{320} = \frac{\sqrt{15}}{\sqrt{16\pi}} (3z^2 - r^2)/r^2 \, R_{32}(r)$$

$$\phi_{x2\text{-}y2} = \frac{1}{\sqrt{2}} (\phi_{322} + \phi_{32\text{-}2}) = \frac{\sqrt{15}}{\sqrt{16\pi}} (x^2 - y^2)/r^2 \, R_{32}(r)$$

Co 2p and O1s XAS of $Ca_3Co_4O_9$

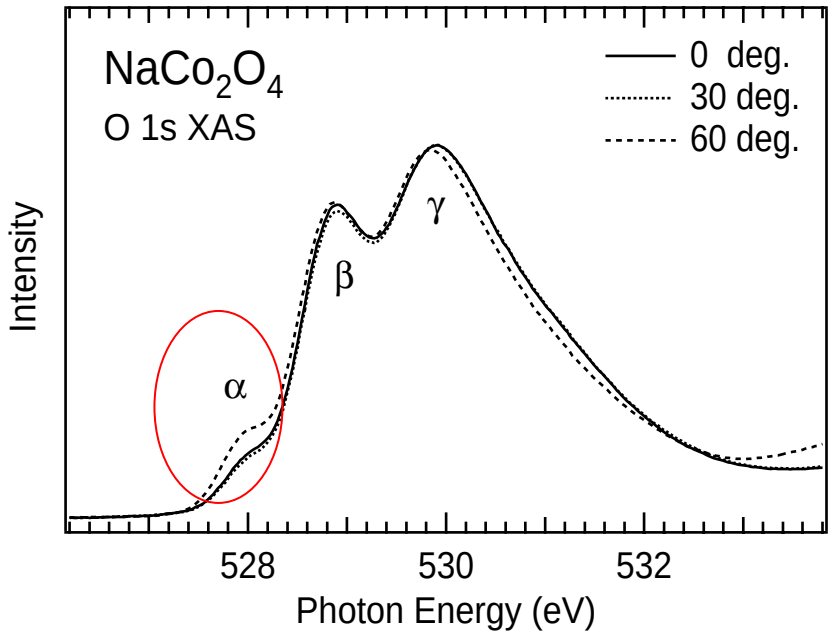


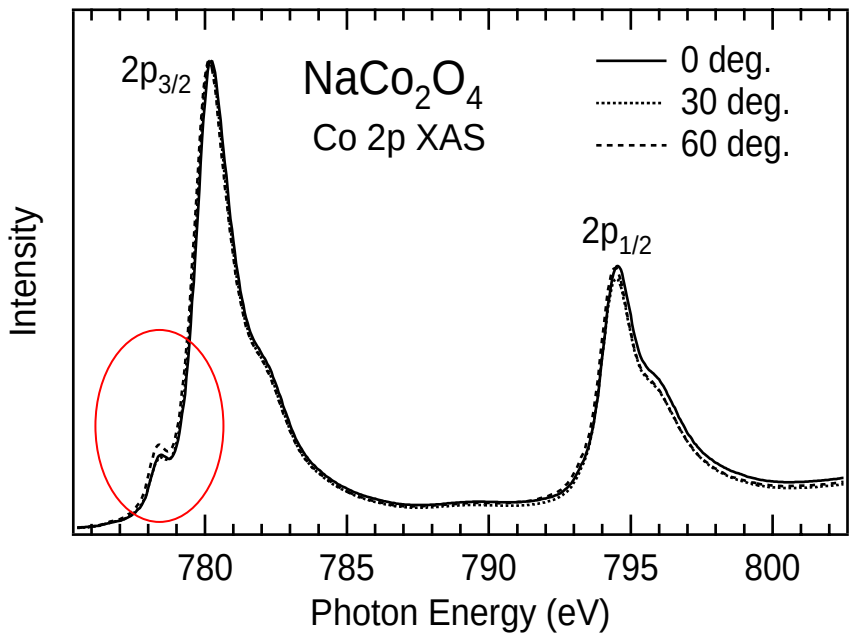


CoO_2 layer
low-spin Co^{3+}
low-spin Co^{4+}
a_{1g} hole

CoO layer
low-spin Co^{3+}

O 1s and Co 2p XPS of Na_xCoO_2





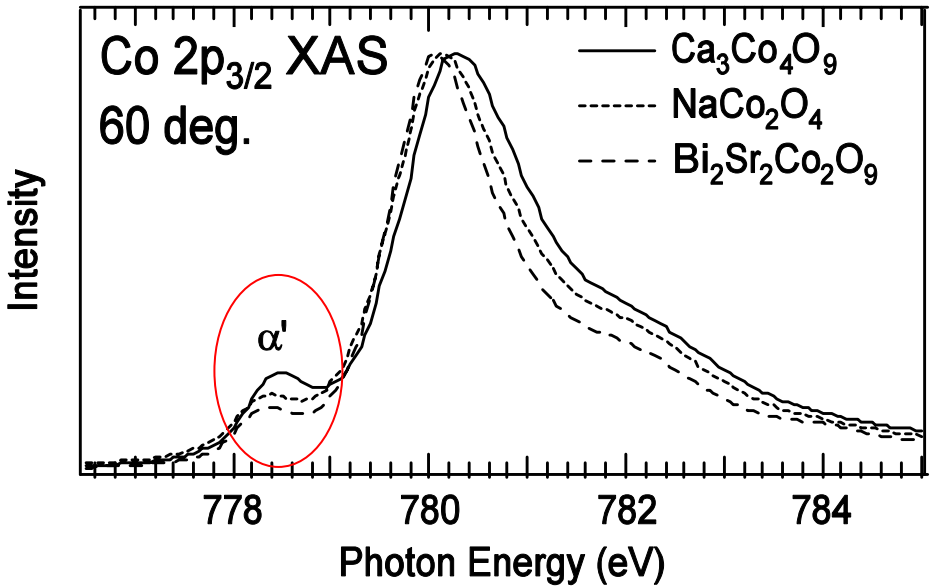
CoO_2 layer

low-spin Co^{3+}

low-spin Co^{4+}

a_{1g} + e_g‘ hole

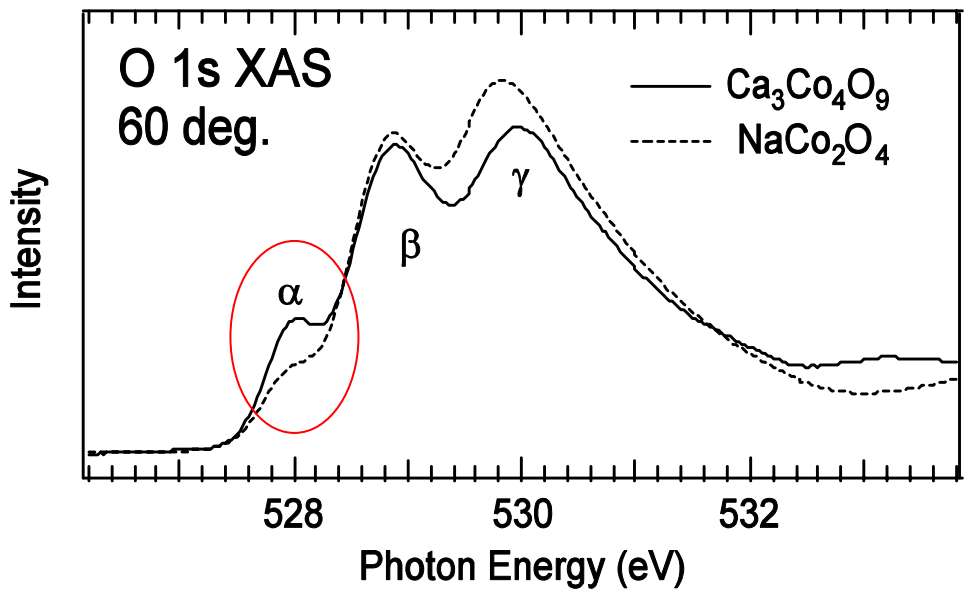
Hole concentration in the Co-O triangular lattice



Hole concentration x:

$Ca_3Co_4O_9 > Na_xCoO_2 > Bi_2Sr_2Co_2O_9$

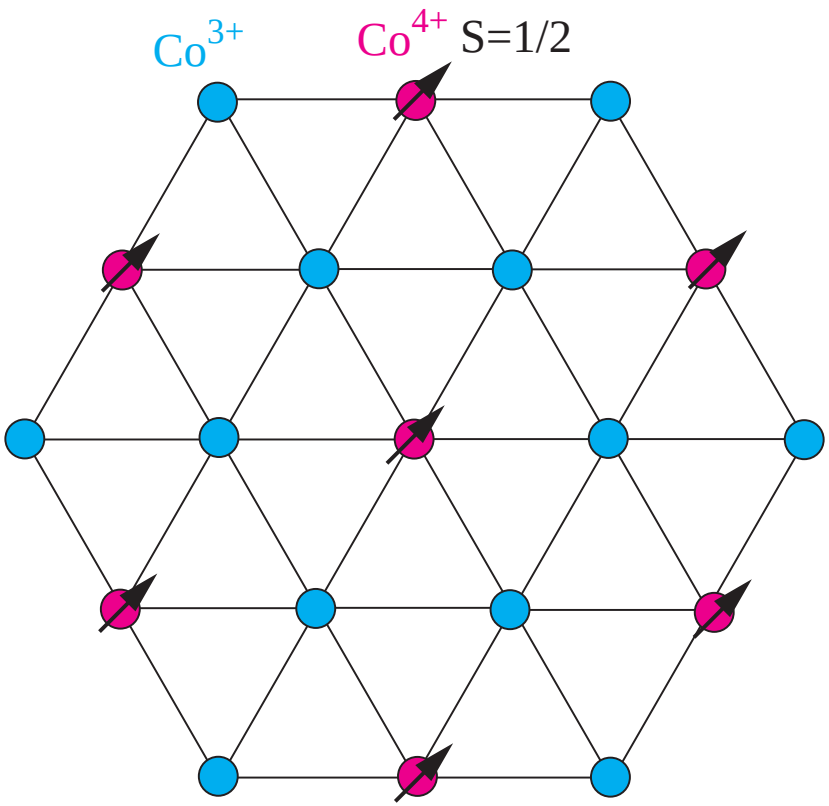
$x = 0.6$ 0.4 0.3



T. Mizokawa, L. H. Tjeng *et al.*

Phys. Rev. B in press.

Charge ordering in the triangular lattice



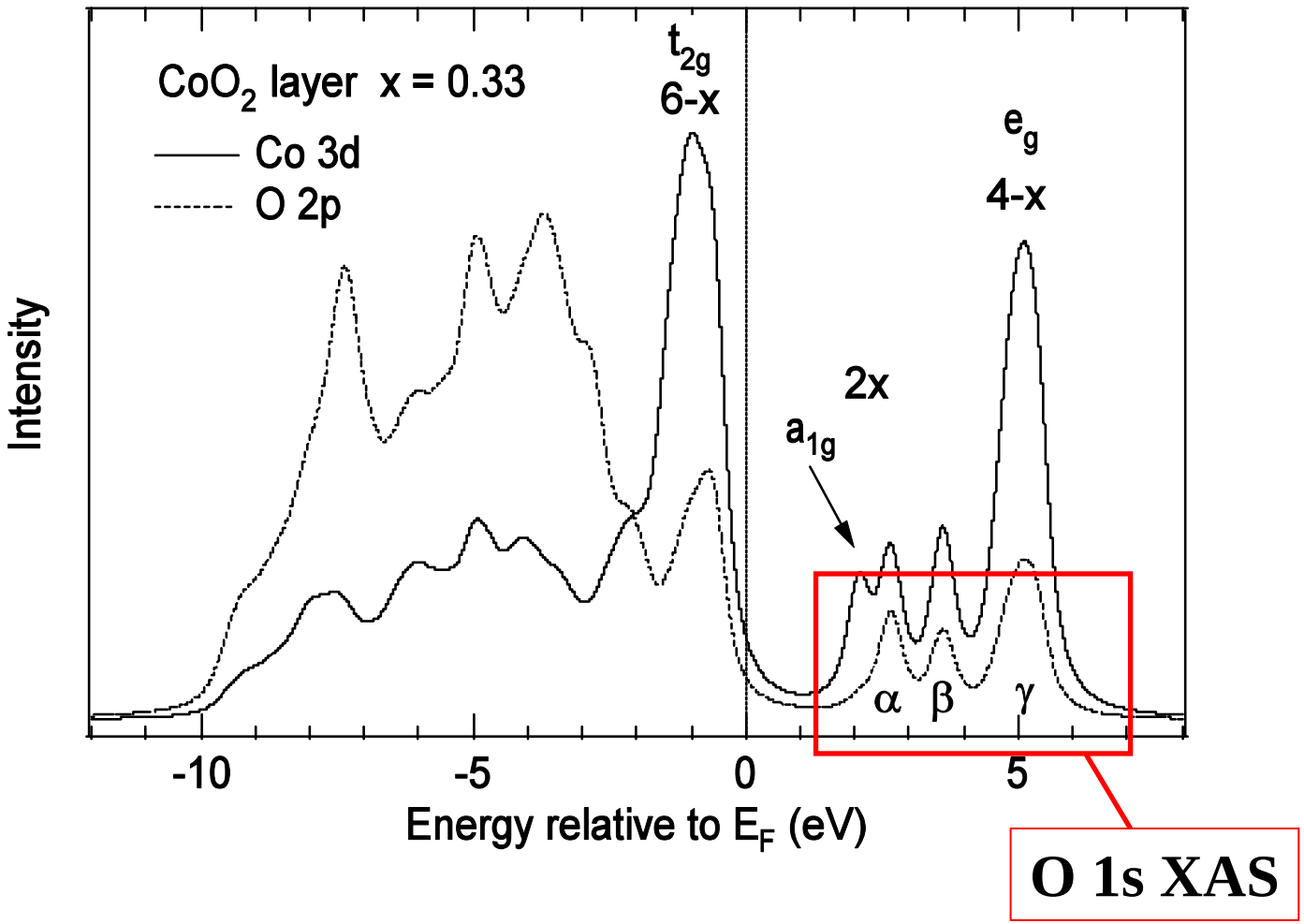
$Co^{3+} : Co^{4+} = 2 : 1$
Ferromagnetism due to frustration in the ring

$Co^{3+} : Co^{4+} = 1 : 2$
Anti-ferromagnetic due to the superexchange

T_C ~ 4 K for $Bi_2Sr_2Co_2O_9$
T_N ~ 20 K for $Ca_3Co_4O_9$

T. Mizokawa, New Journal of Physics **6**, 169 (2004)

Co 3d and O 2p PDOS for x = 0.33



Summary

low-spin Co^{4+} embedded in nonmagnetic Co^{3+} background

small polaron picture is OK

$S = -k_B/e \ln[x/6(1-x)]$ x: Co^{4+} concentration

W. Koshibae, K. Tsutsui, S. Maekawa, PRB **62**, 6869 (2000)

$Ca_3Co_4O_9$: charge ordering at $x = 2/3$ Antiferromagnetic

$Bi_2Sr_2Co_2O_9$: charge ordering at $x = 1/3$ Ferromagnetic

$Ca_3Co_4O_9 > Na_xCoO_2 > Bi_2Sr_2Co_2O_9$

x	0.6	0.4	0.3
orbital	a_{1g}	$a_{1g} + e_g'$	a_{1g}

Photoemission and x-ray absorption spectroscopy

can probe interesting strongly-correlated electron states

in the 2D t_{2g} electron systems:

$Ca_{2-x}Sr_xRuO_4$

relatively itinerant 4d t_{2g} electrons

atomic effect (spin-orbit interaction) is still important

orbital jump at the metal-insulator transition

metallic state at E_F in the insulating(non-metallic) phase

$Bi_2Sr_2Co_2O_9$, Na_xCoO_2 , $Ca_3Co_4O_9$

almost localized 3d t_{2g} electrons

low-spin Co^{4+} polaron in nonmagnetic Co^{3+} background

close to the charge ordered states at x= 1/3 and 2/3