5 March 2002, UVSOR研究会

1次元および2次元構造を持つ遷移金属酸化物の角度分解光電子分光（SSRLの利用）

東大新領域　溝川貴司

Outline

- Introduction
- ARPES and XAS study of transition-metal oxides

Electron-lattice coupling in strongly correlated electron systems

$PrBa_2Cu_3O_7$, $PrBa_2Cu_4O_8$ Cu-O chain

charge density wave, Tomonaga-Luttinger behavior

$Bi_2Sr_2Co_2O_9$ CoO_2 triangular lattice

small polaron, high-spin or low-spin?

$Ca_{2-x}Sr_xRuO_4$ RuO_2 square lattice

Jahn-Teller distortion, orbital switching

- Summary

Angle-resolved photoemission spectroscopy (ARPES)

(1) Band dispersion mapping

(2) Fermi surface mapping

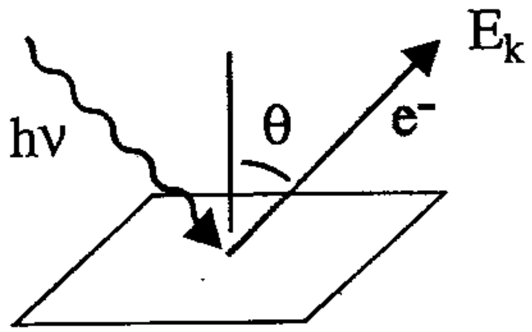
(3) Single-particle spectral function $A_k(\omega)$

Correlation effects manifest in $A_k(\omega)$

- 3d, 4 f, and 5f compounds
- diluted magnetic semiconductors
- nano-materials

Angle-resolved photoemission spectroscopy (ARPES)

SSRL BL-V3, Stanford

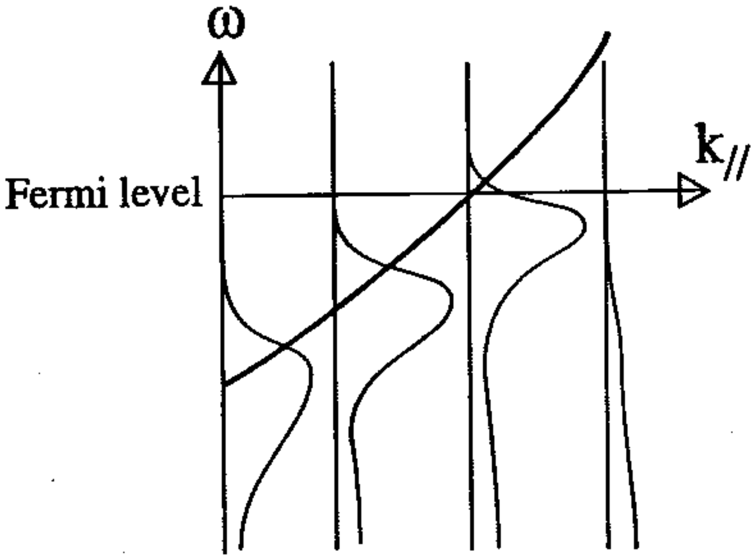


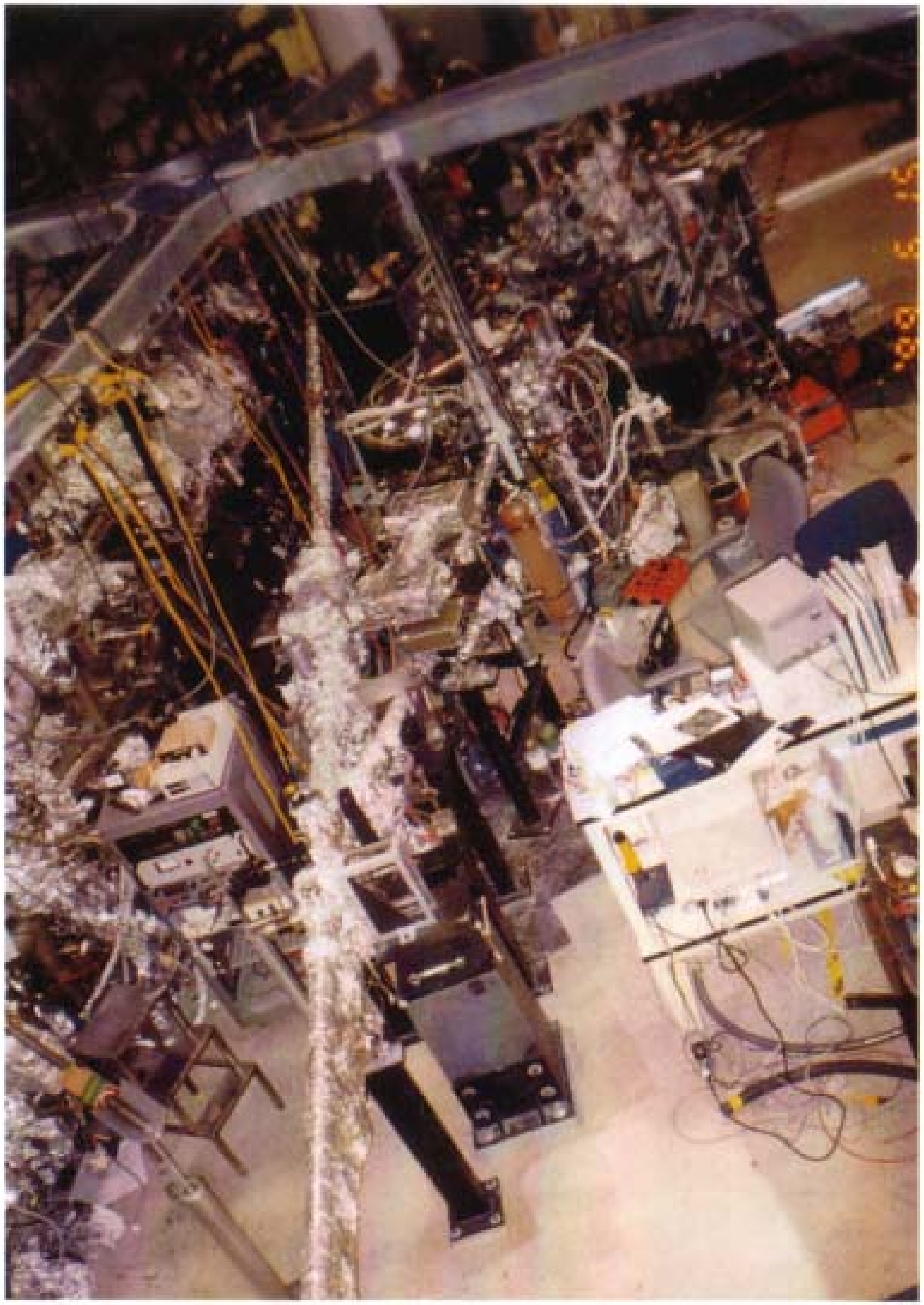
$$E_k = h\nu - \phi - E_B$$

$$k = (2mE_k)^{1/2}$$

$$k_{//} = (2mE_k)^{1/2} \sin\theta$$

Fermi surface
band dispersion





SSRL BL5-4
(multi-undulator)

6.65-m NIM

$h\nu$ = 10-30 eV

$E/\Delta E$ ~ 10,000

Flux (3.0GeV,100mA)
~ 10^{11} photons/s ?

Spot size (sample)
~ 0.5 x 1.0 mm

ARPES of $PrBa_2Cu_3O_7$ and $PrBa_2Cu_4O_8$

hole-doped Cu-O chain (1/4-filled chain)

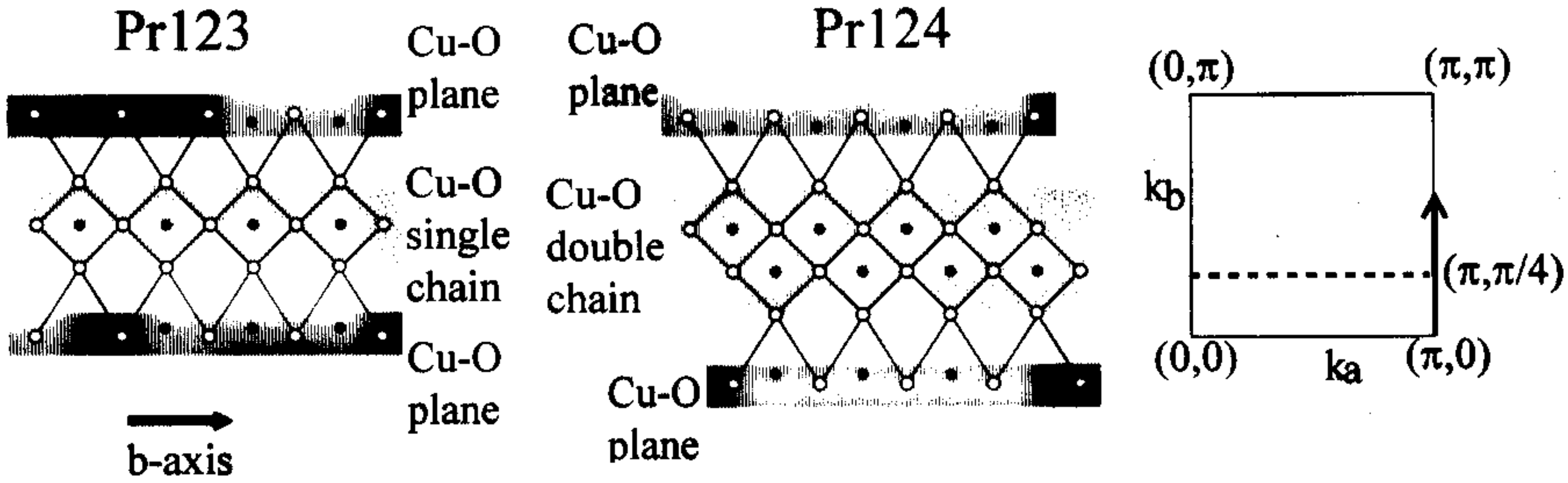
- Spin-charge separation ?
- Tomonaga-Luttinger (TL) liquid ?
- Charge density wave (CDW) ?

Collaborators:

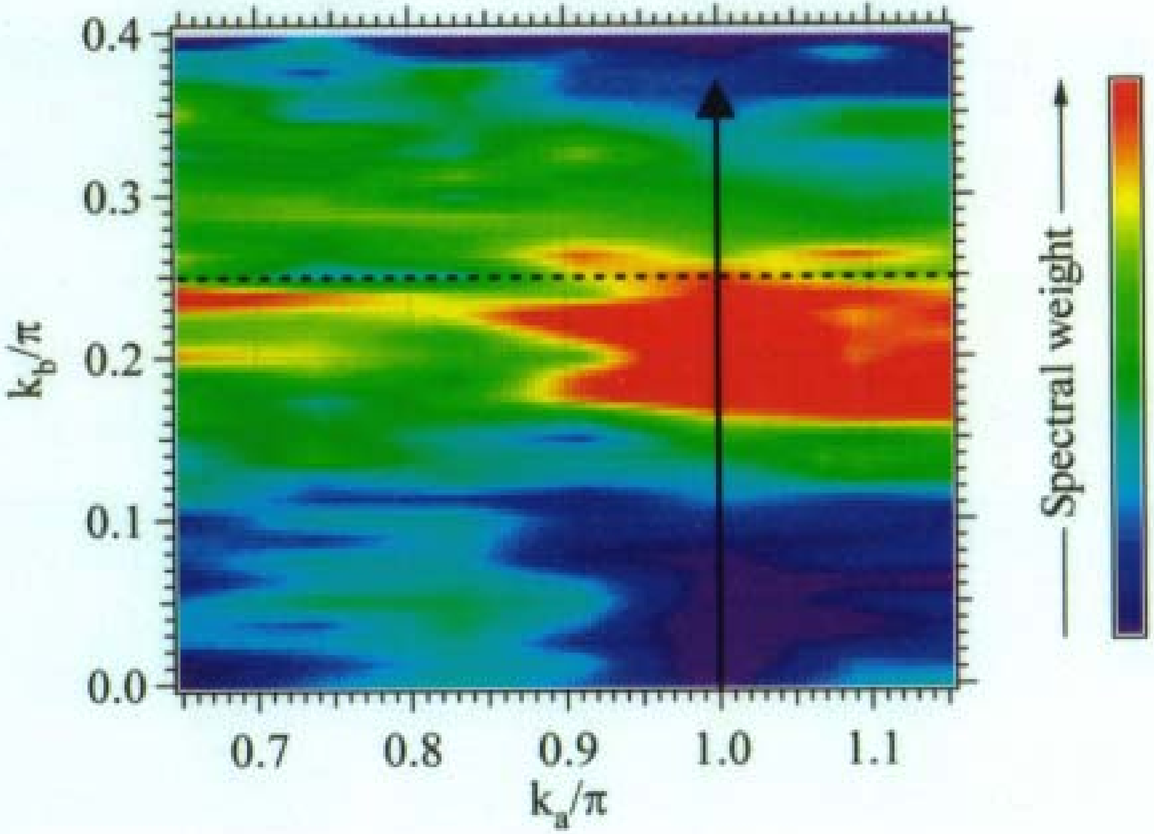
C. Kim, Z.-X. Shen, A. Ino, T. Yoshida, A. Fujimori, S. Horii, N. Yamada, Yasuji Yamada, I. Hirabayashi, Yuh Yamada, M. Goto, H. Eisaki, S. Uchida, M. Tagami, K. Yoshida, A. I. Rykov, Y. Shiohara, K. Tomimoto, S. Tajima, K. Nakata, H. Ikuta, U. Mizutani, N. Ueda

T. Mizokawa et al., PRL **85**, 4779 (2000)

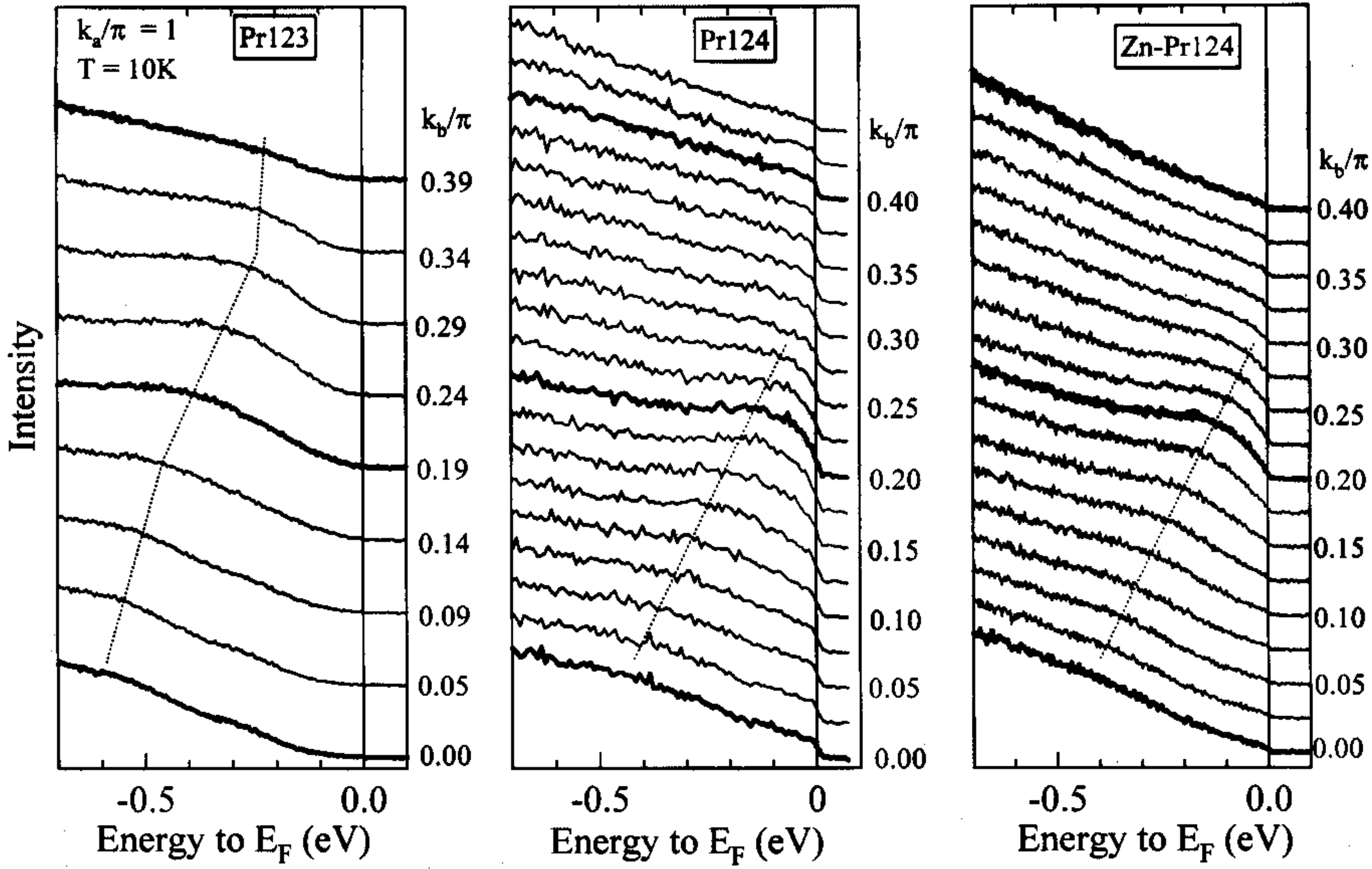
Cu-O chains in $PrBa_2Cu_3O_7$ (Pr123) and $PrBa_2Cu_4O_8$ (Pr124)



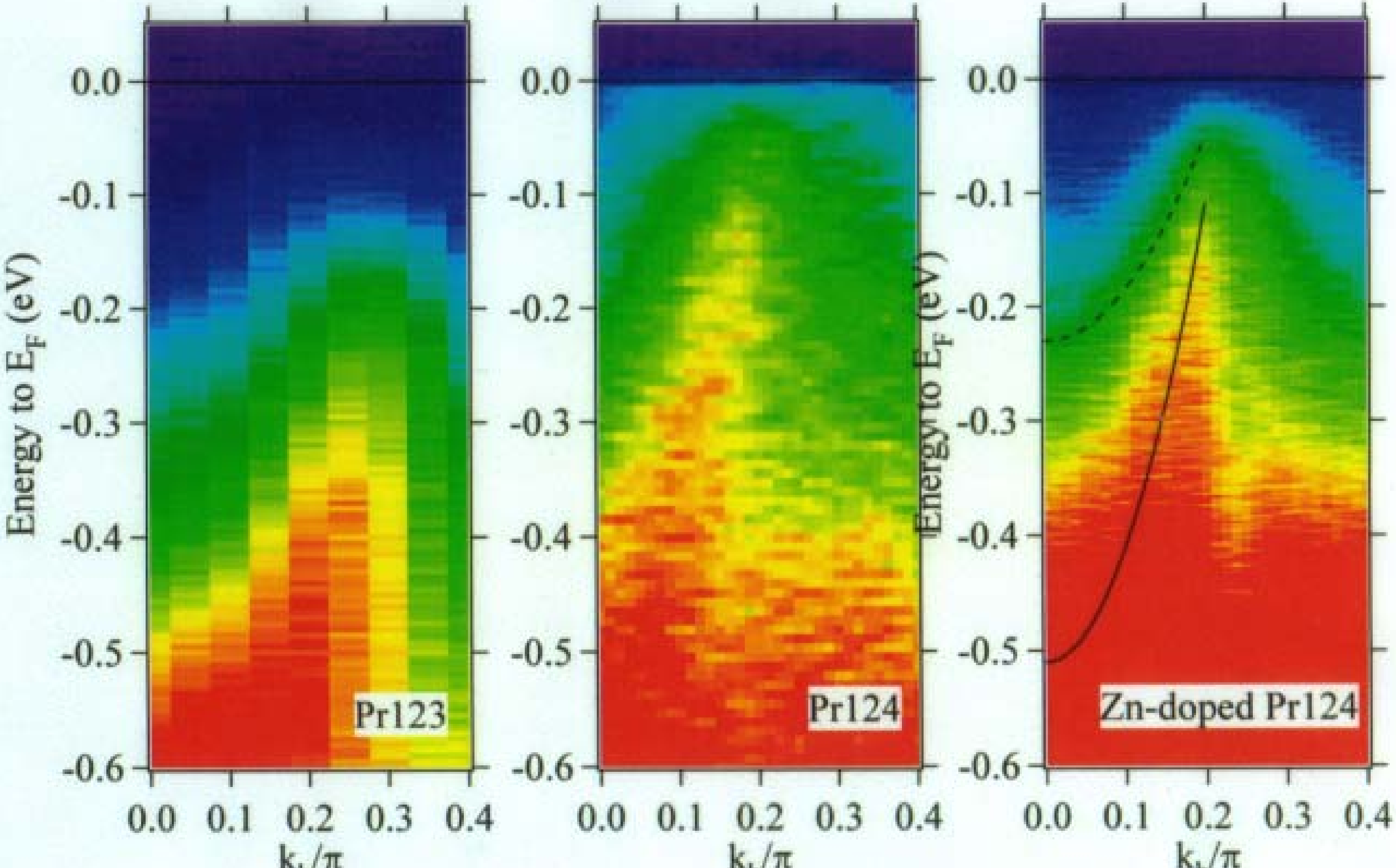
Fermi surface mapping for the Cu-O chain in Pr124



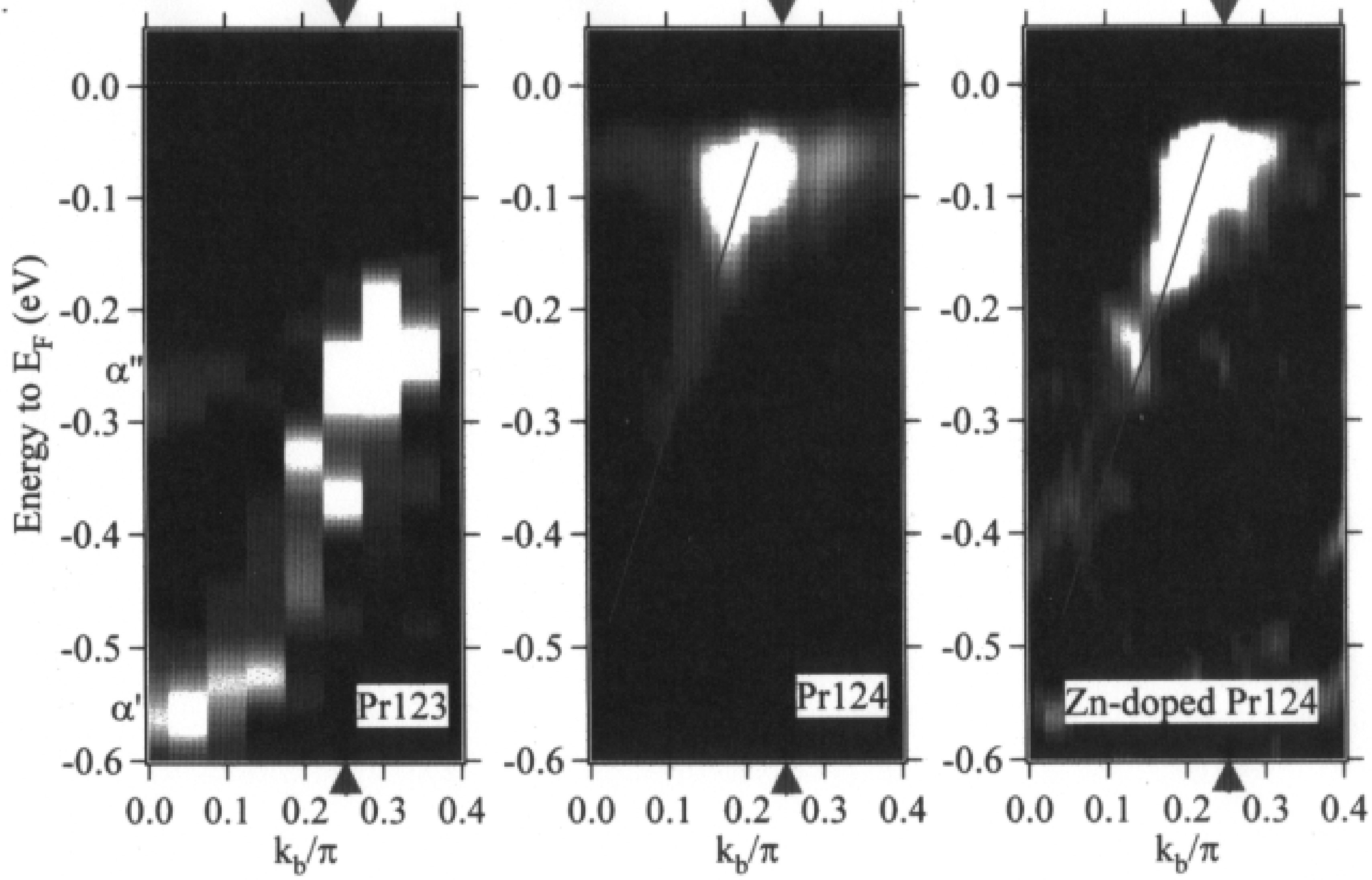
ARPES spectra of Cu-O chains



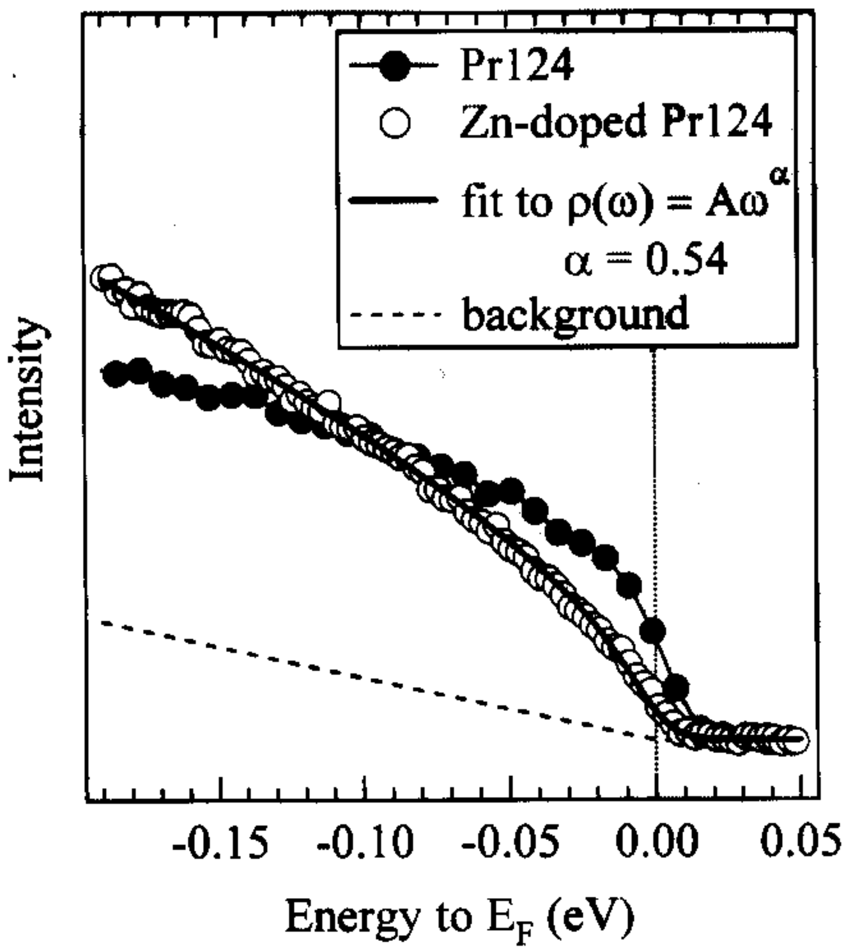
Band dispersion of Cu-O chains



Band dispersion of Cu-O chains (second derivative of the ARPES spectra)



Angle-integrated spectra of Cu-O chains



Pr124

Fermi liquid

Zn-Pr124

TL liquid

$\alpha \sim 0.6$

Exponent α in various 1D metallic systems

Hubbard model $\alpha < 0.125$, extended Hubbard model $\alpha < 0.56$

F. Mila and K. Penc, Synthetic Metals 70, 997 (1995).

- 1D organic conductors: $(TMTSF)_2X$, $(TMTTF)_2X$

  $\alpha > 1$ F. Zwick et al., PRL 79, 3982 (1997).
- Au chain on Si(111)

  $\alpha \sim 1$ P. Segovia et al., Nature 402, 504 (1999).
- $Li_{0.9}Mo_6O_{17}$

  $\alpha \sim 0.9$ J. D. Denlinger et al., PRL 82, 2540 (1999).
- Cu-O chain in Zn-doped Pr124

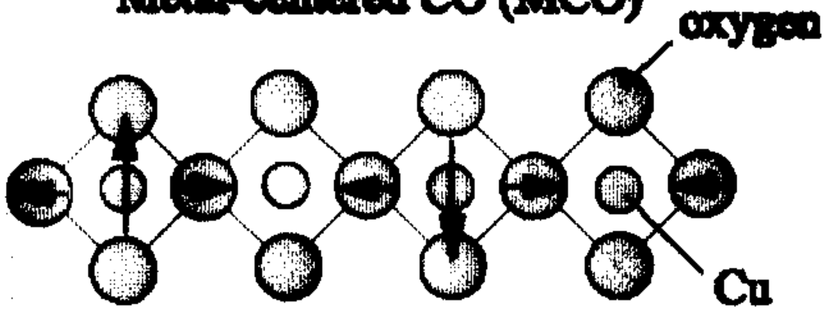
  $\alpha \sim 0.6$

Boundary effect? Electron lattice coupling?

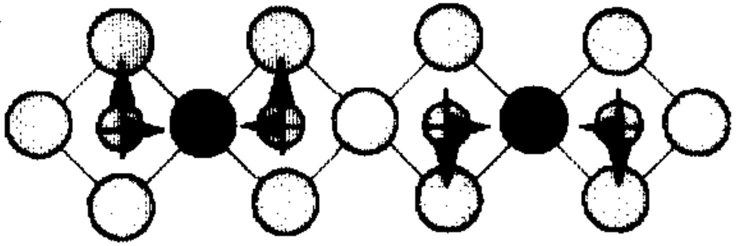
Single chain *versus* double chain

Single chain

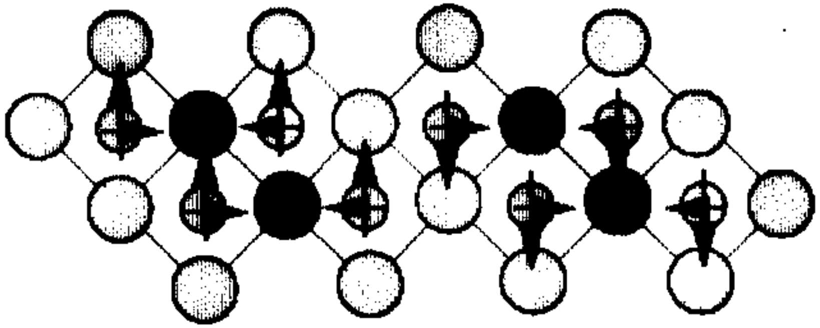
Metal-centered CO (MCO)



Oxygen-centered CO (OCO)

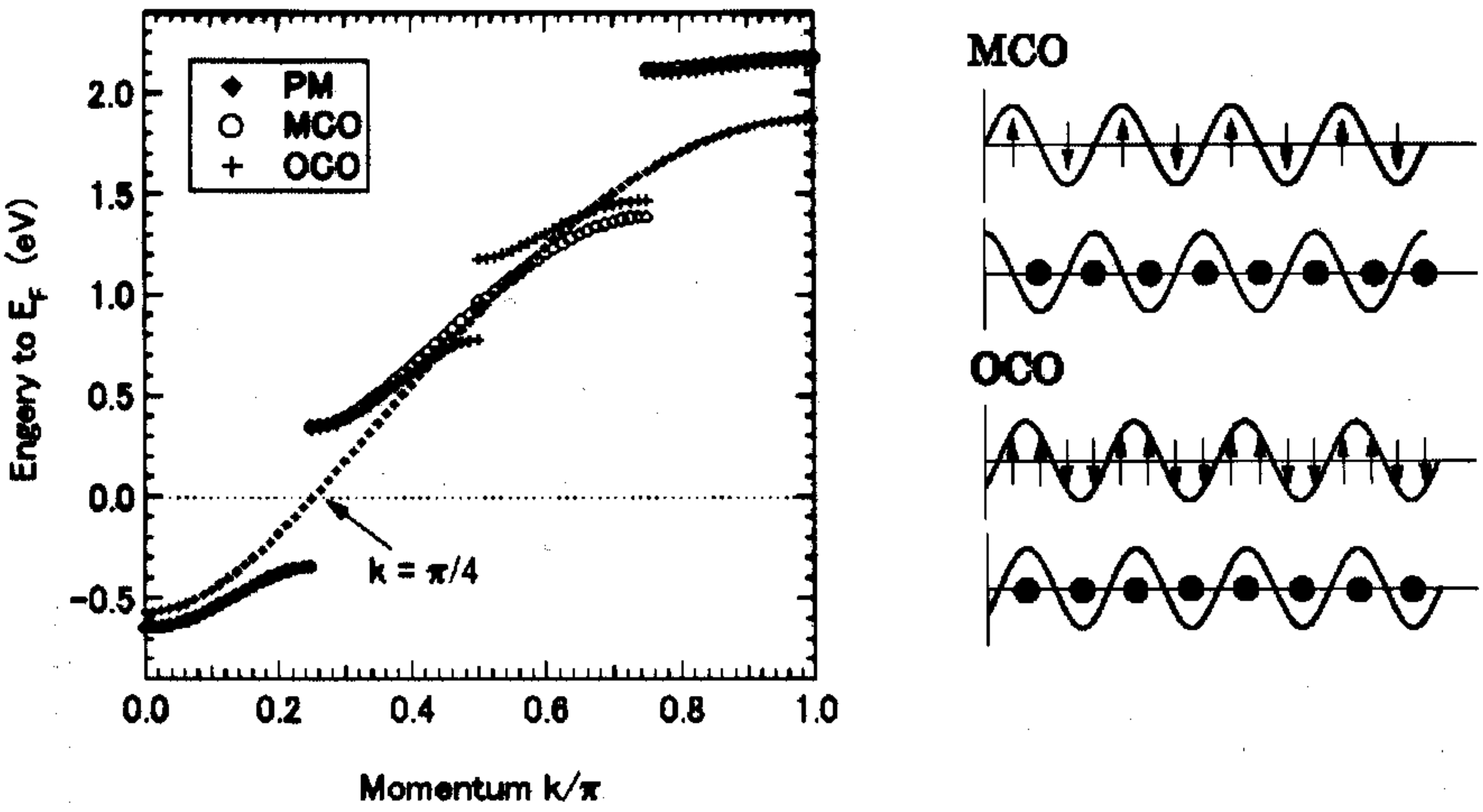


Double chain



This is unstable.

model Hartree-Fock calculation for a Cu-O single chain



ARPES and XAS of $Bi_2Sr_2Co_2O_9$

hole-doped CoO_2 triangular lattice

- Enhanced thermopower

  $NaCo_2O_4$ [I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B 56, 12685 (1997)]

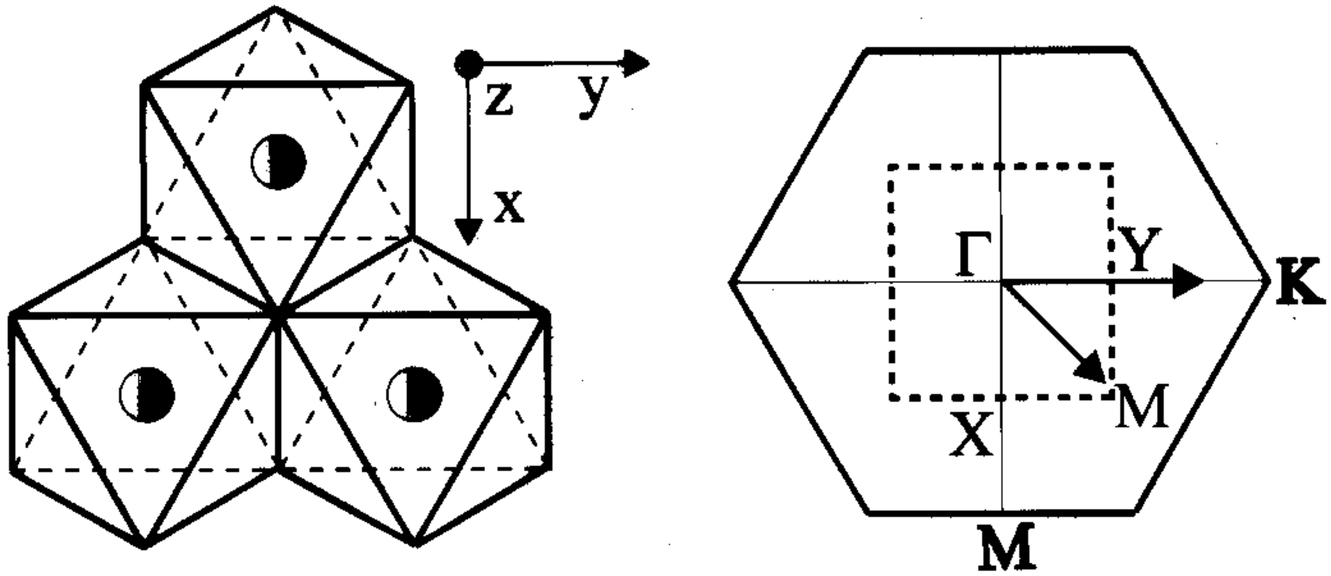
- Small polaron

Collaborators:

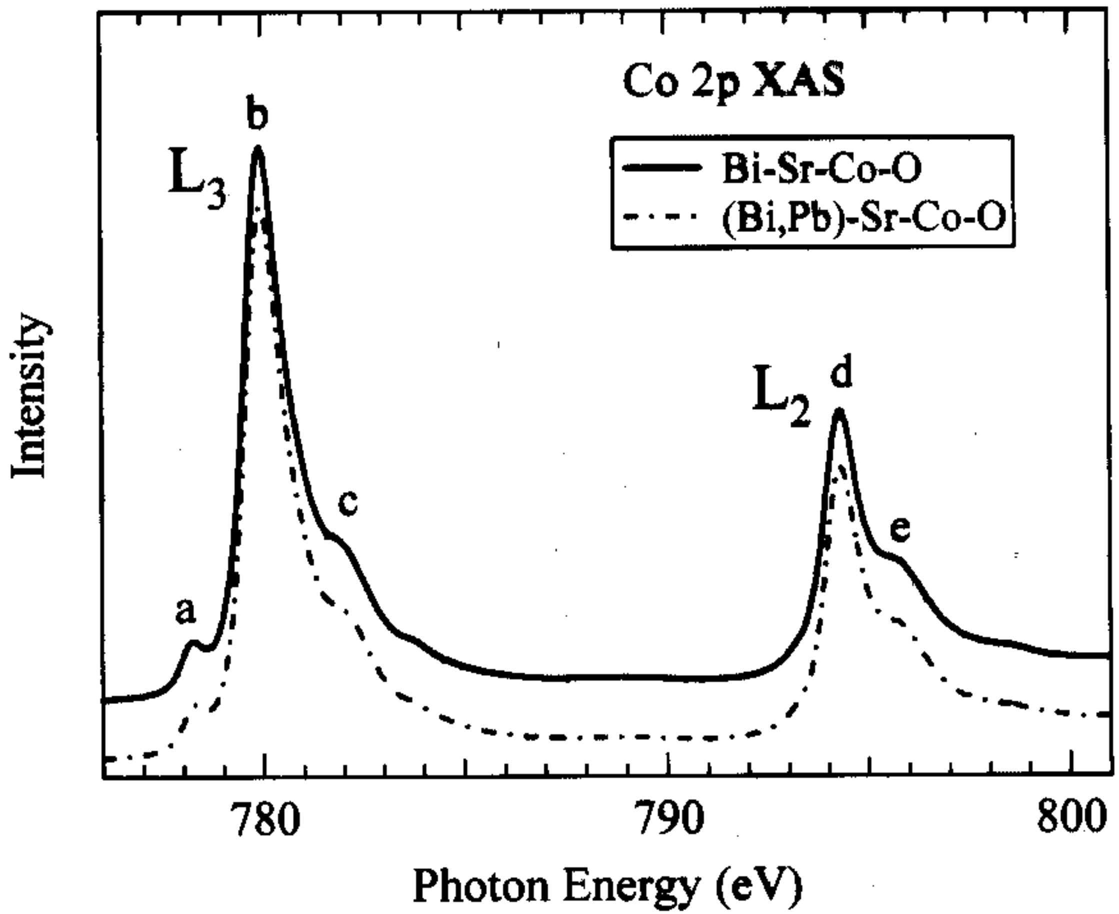
L. H. Tjeng, P. Steeneken, N. B. Brookes, I. Tsukada, T. Yamamoto, K. Uchinokura, Y. Hitsuda,

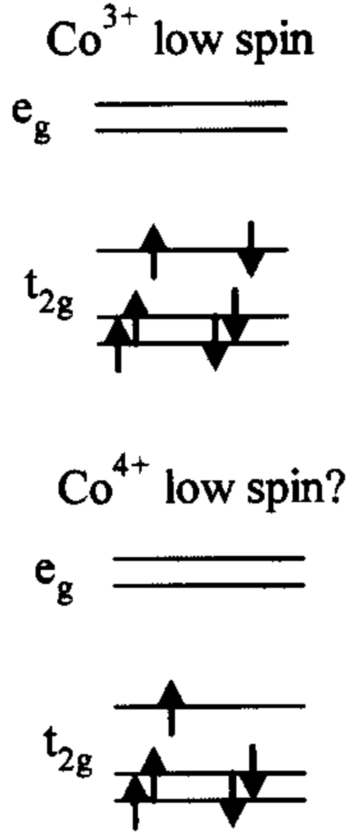
T. Mizokawa et al., PRB **64**, 024403 (2001).

CoO_2 triangular lattice

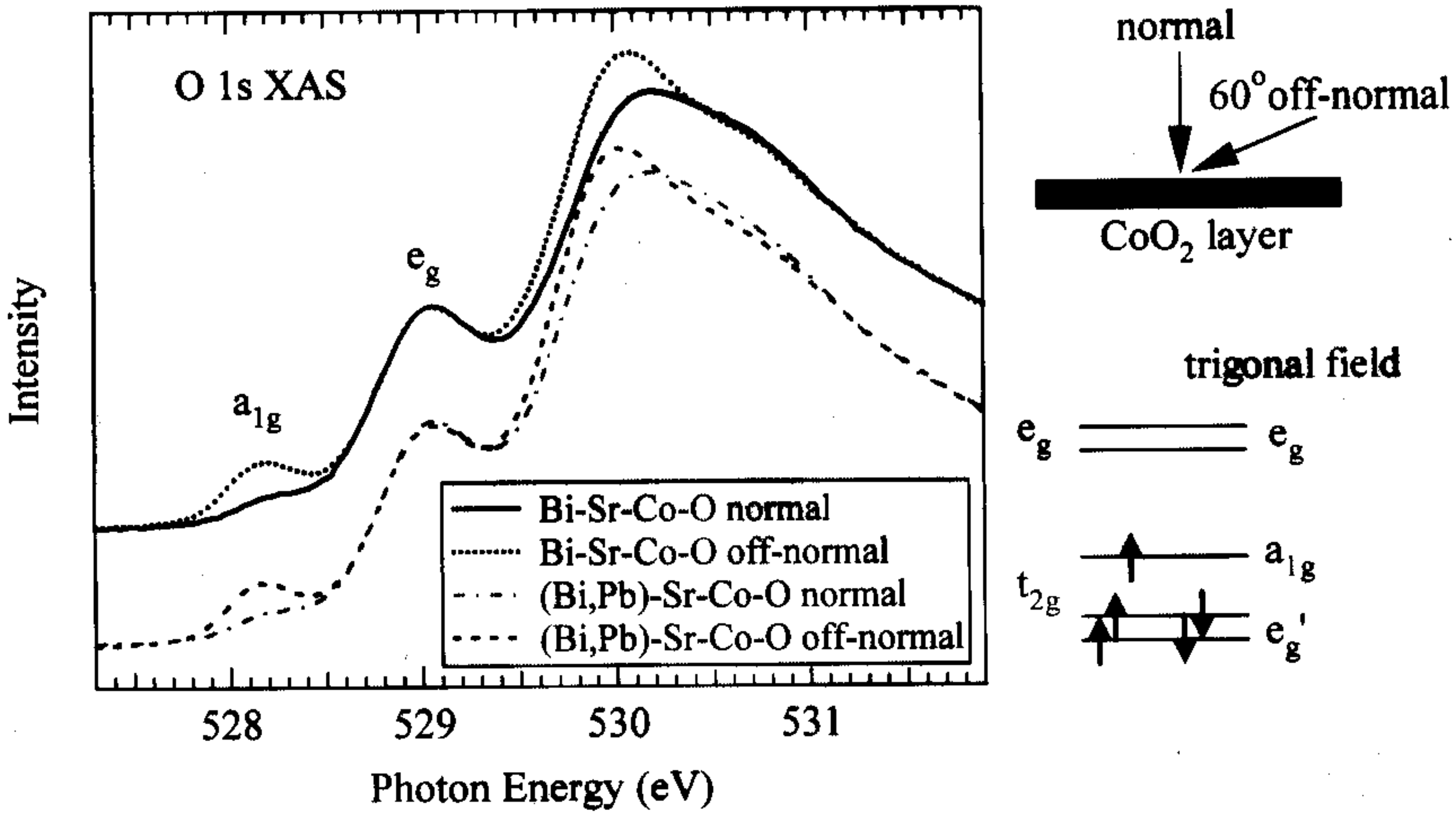


Co 2p XAS of (Bi,Pb)-Sr-Co-O

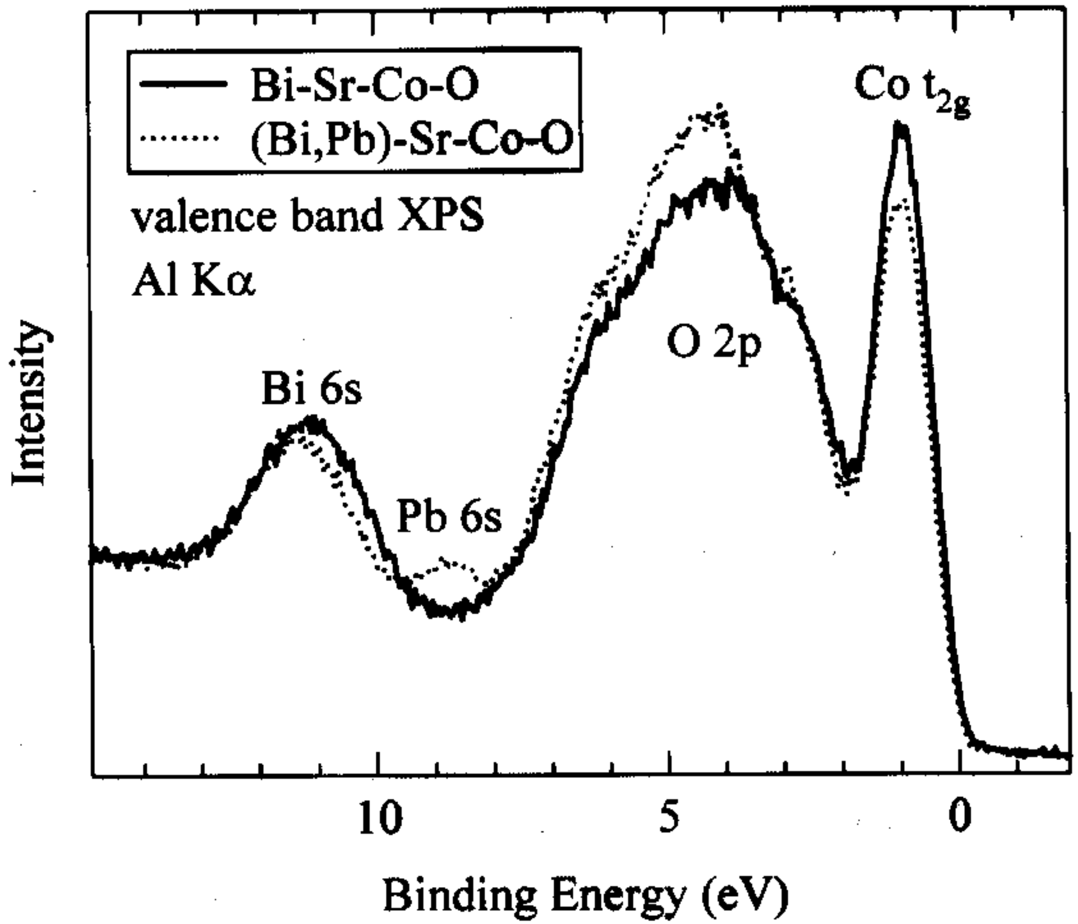




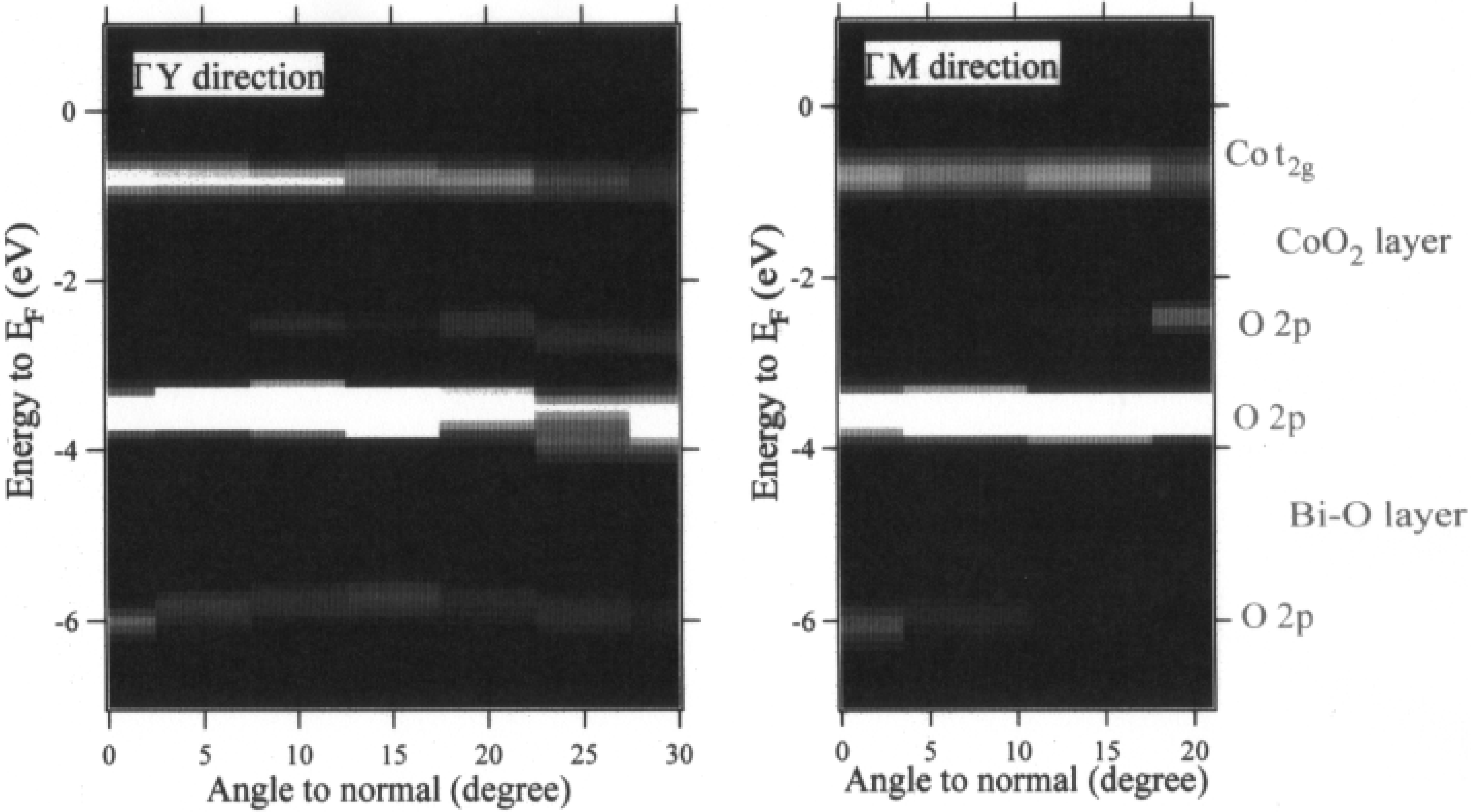
O 1s XAS of (Bi,Pb)-Sr-Co-O



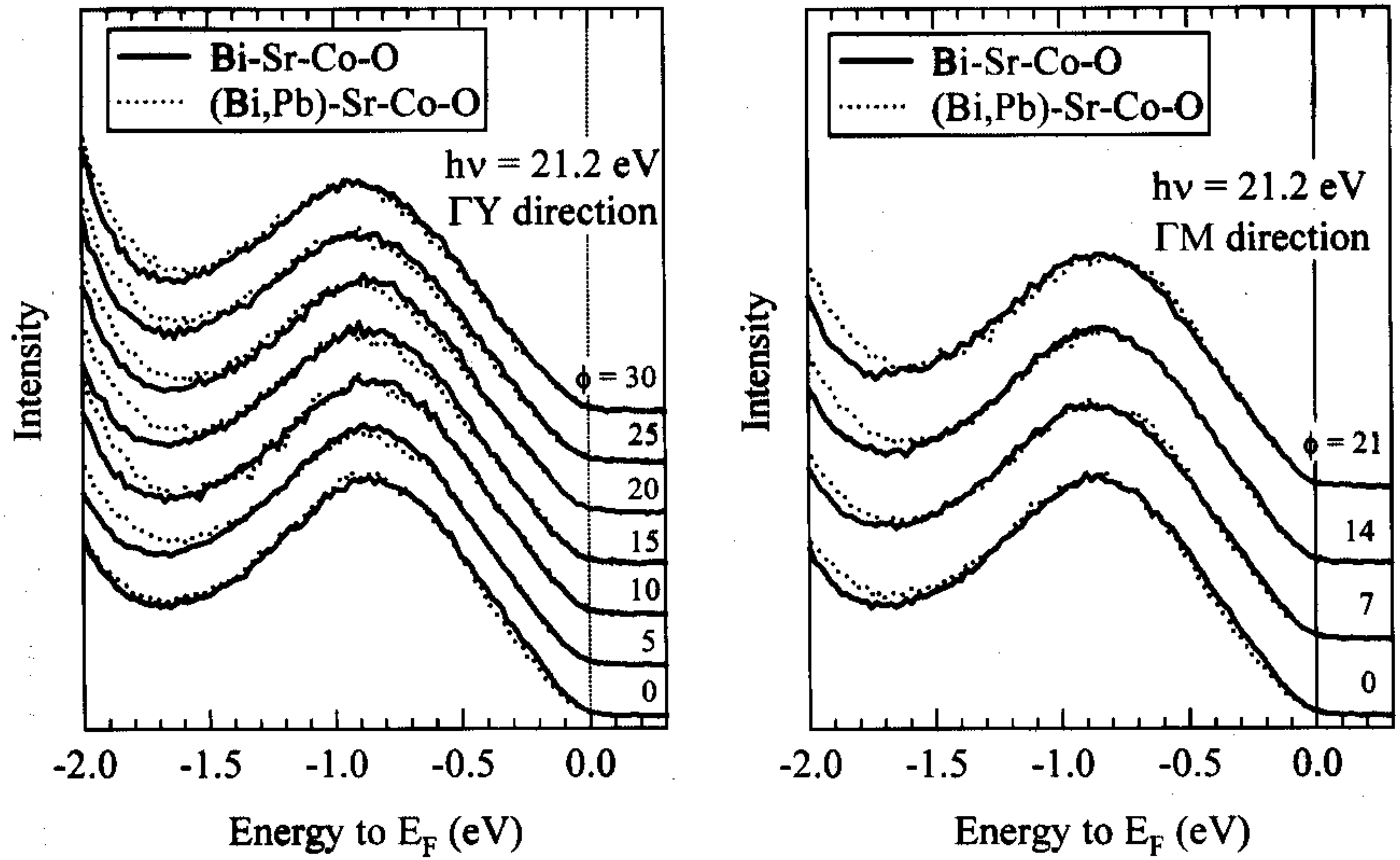
Valence-band XPS of (Bi,Pb)-Sr-Co-O



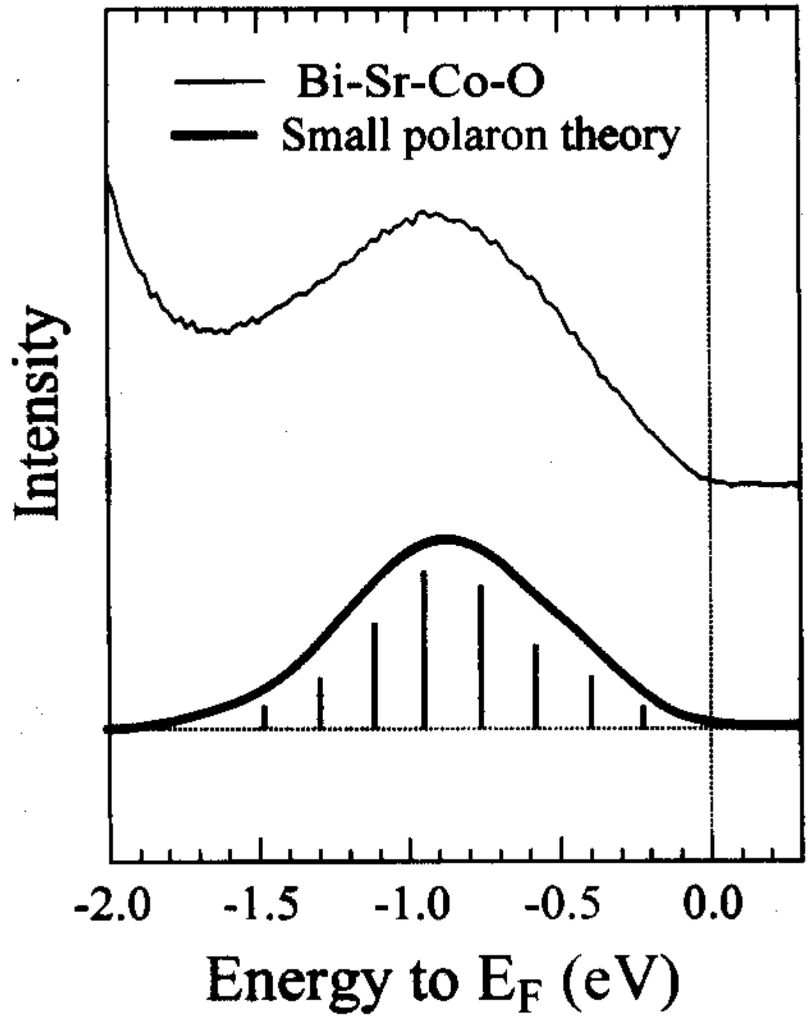
Band dispersion of (Bi,Pb)-Sr-Co-O



Spectral function near E_F (Bi,Pb)-Sr-Co-O



Electron spectral function of small polaron
(G. D. Mahan, "Many-particle Physics", Chap. 4)



Einstein model

optical phonon : ω_0

coupling constant : g

$$A(\omega) = \sum_{n=0} g^n/n!\ \delta(\omega-\varepsilon_c-\omega_0 n)$$

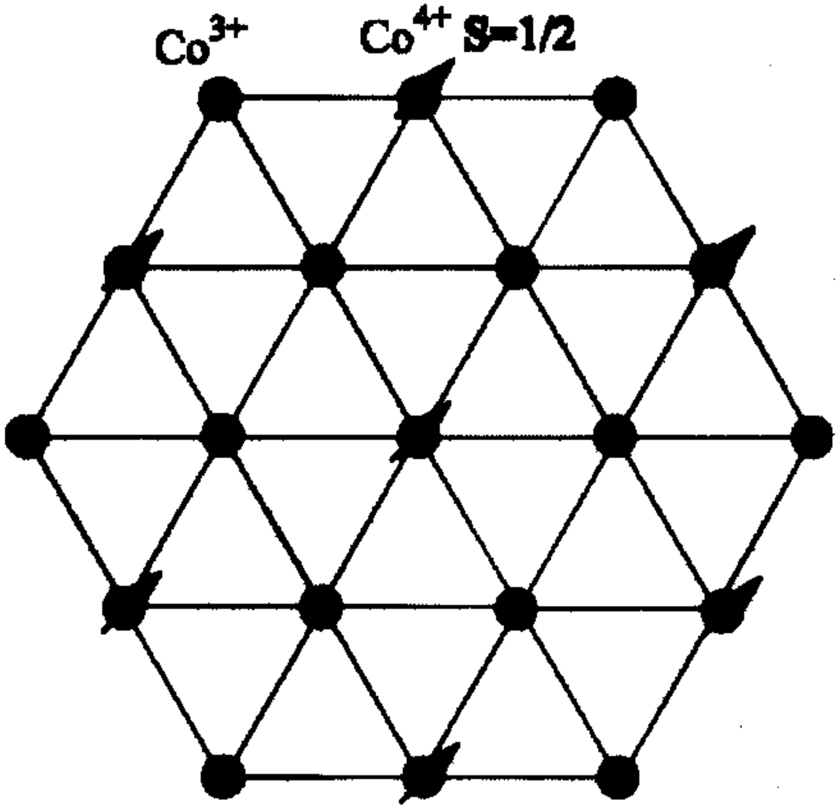
Small polaron and enhanced thermopower

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

- $S = -k_B/e \ln[x/6(1-x)]$ x: Co^{4+} concentration
  W. Koshibae, K. Tsutsui, S. Maekawa, PRB **62**, 6869 (2000)

- Repulsion between two polarons
  Bipolaron formation is suppressed?
  Charge ordering at $x = 1/3$?

Charge ordering in the triangular lattice (x =1/3)



$Co^{3+} : Co^{4+} = 2 : 1$

Ferromagnetic!

Y. Miyazaki et al.
to be published in JSPJ
$T_C \sim 20$ K for $Ca_3Co_4O_9$

ARPES and XAS of $Ca_{2-x}Sr_xRuO_4$

RuO_2 square lattice

- Orbital switching due to Jahn-Teller distortion
- Orbital disorder and metal-insulator transition

  Insulating region: orbital glass?

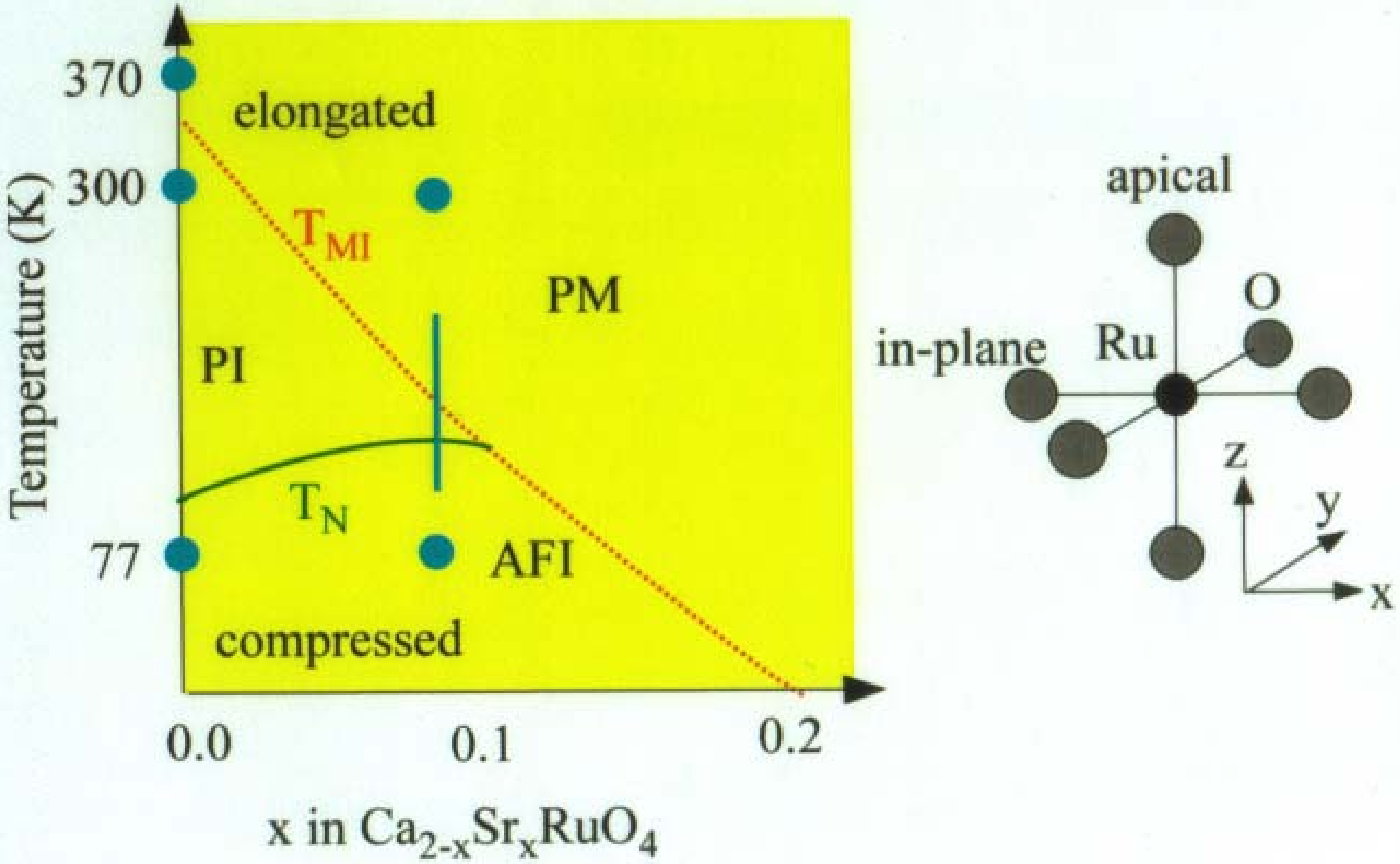
  Metallic region: orbital liquid?

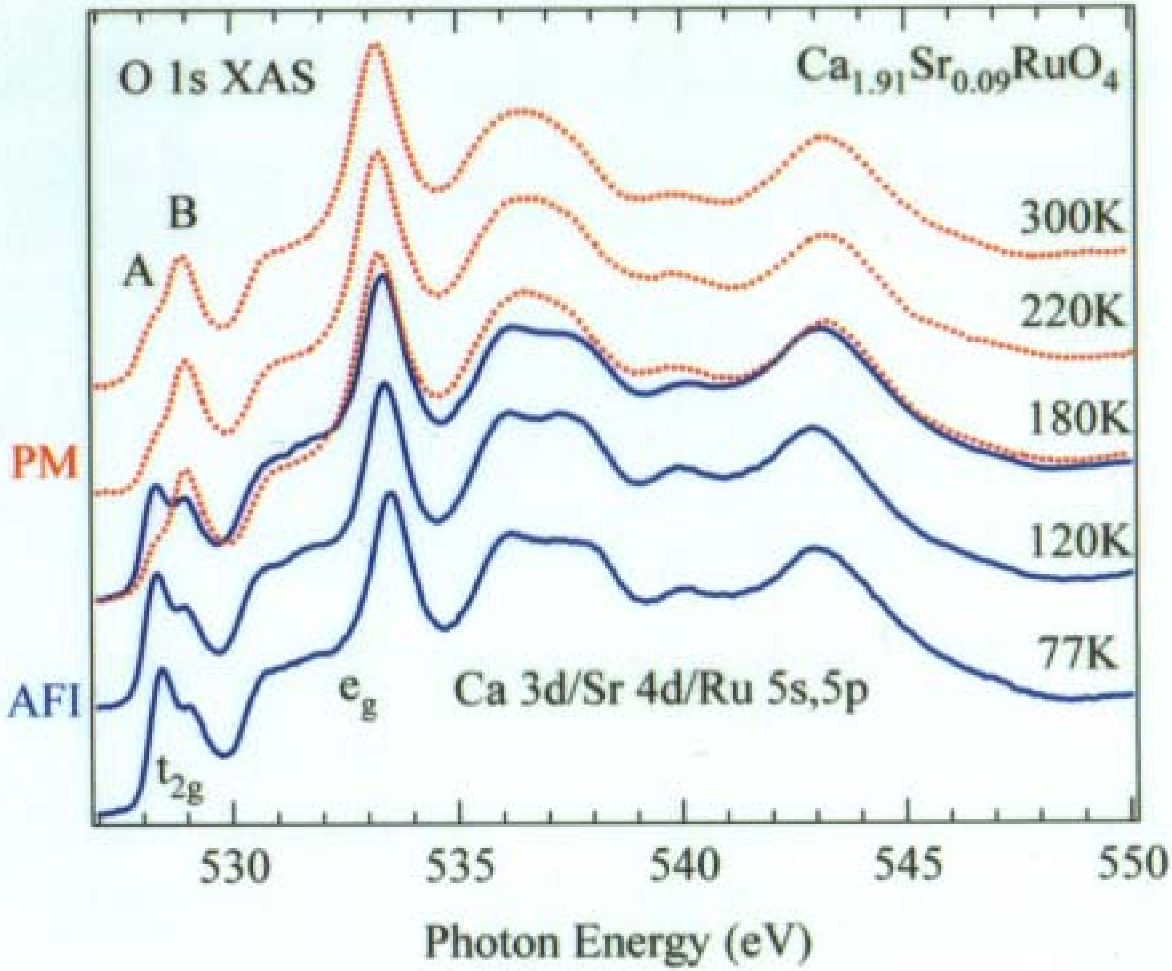
Collaborators:

L. H. Tjeng, G. A. Sawatzky, G. Ghiringhelli, O. Tjengberg, N. B. Brookes, S. Nakatsuji, H. Fukazawa, Y. Maeno, H.-J. Lin, C. T. Chen, A. Damachelli, K. M. Shen, Z.-X. Shen, M. Kurokawa

T. Mizokawa et al., PRL **87**, 077202 (2001)

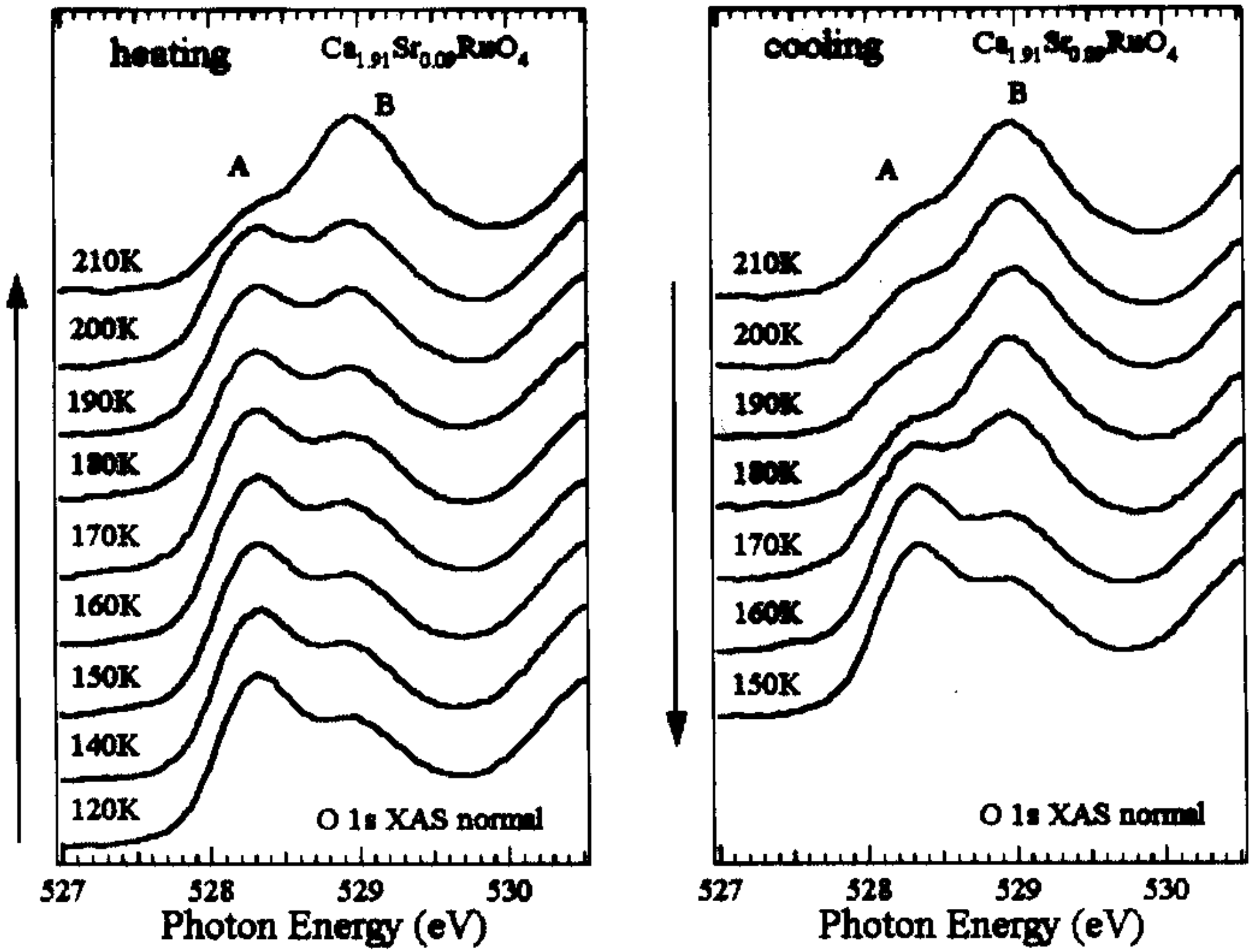
Phase diagram of $Ca_{2-x}Sr_xRuO_4$ (Nakatsuji and Maeno, 2000)



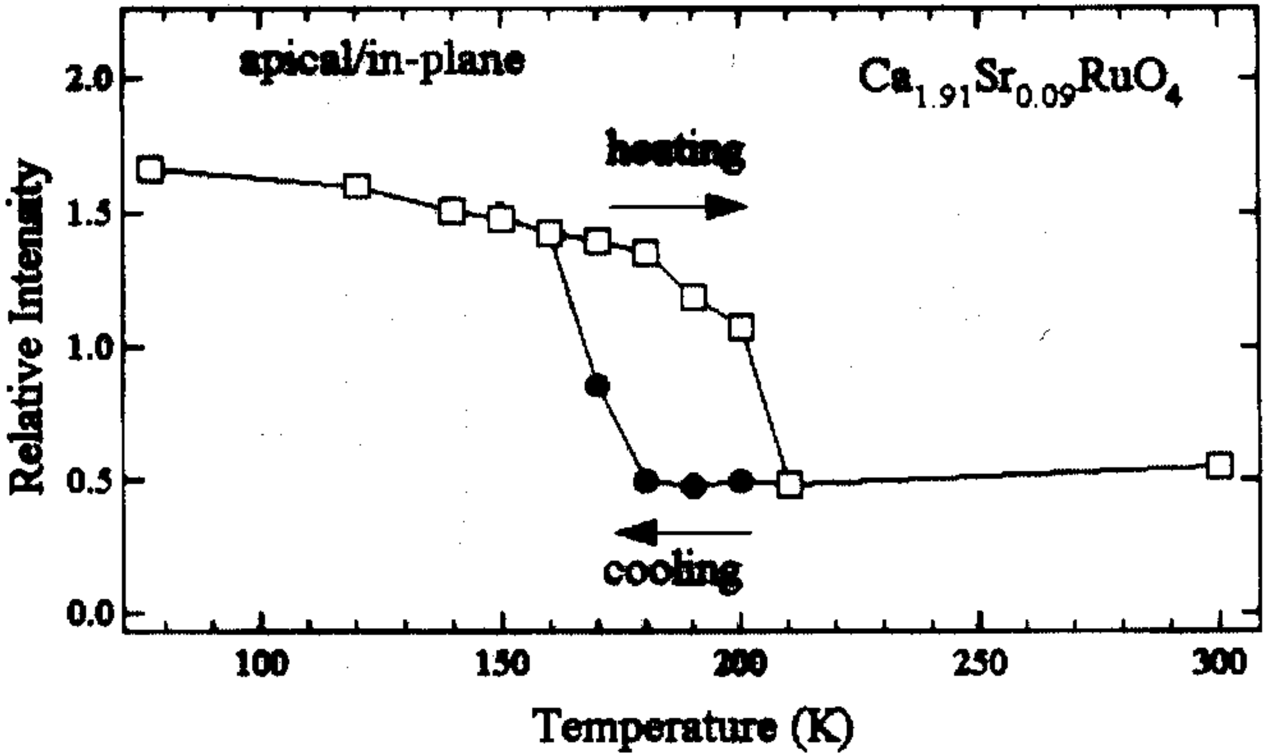

O 1s XAS
$Ca_{1.91}Sr_{0.09}RuO_4$
B
A
300K
220K
180K
PM
120K
77K
AFI
e_g
Ca 3d/Sr 4d/Ru 5s,5p
t_{2g}
530
535
540
545
550
Photon Energy (eV)

O 1s XAS across the MI transition

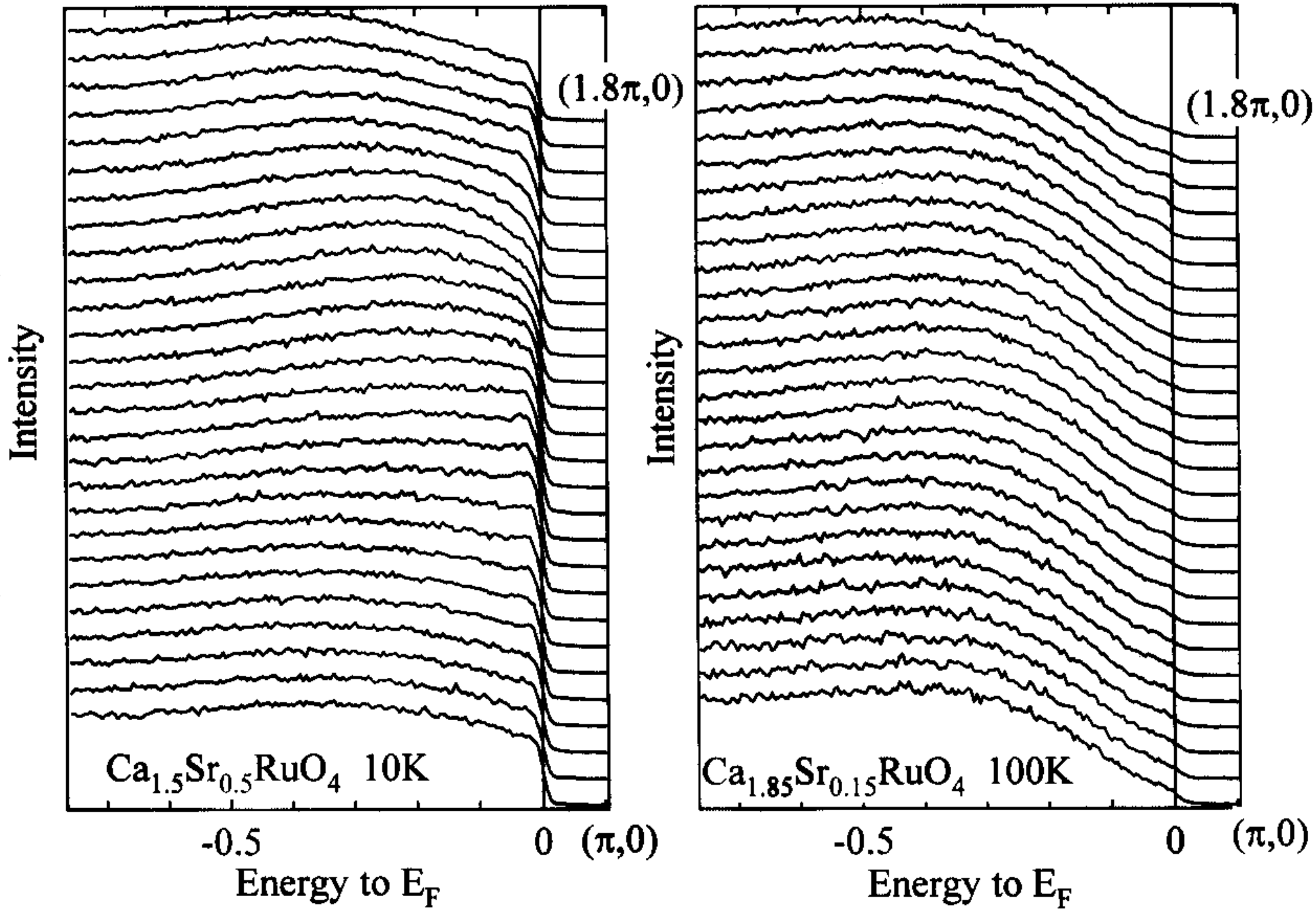
A: apical oxygen B: in-plane oxygen



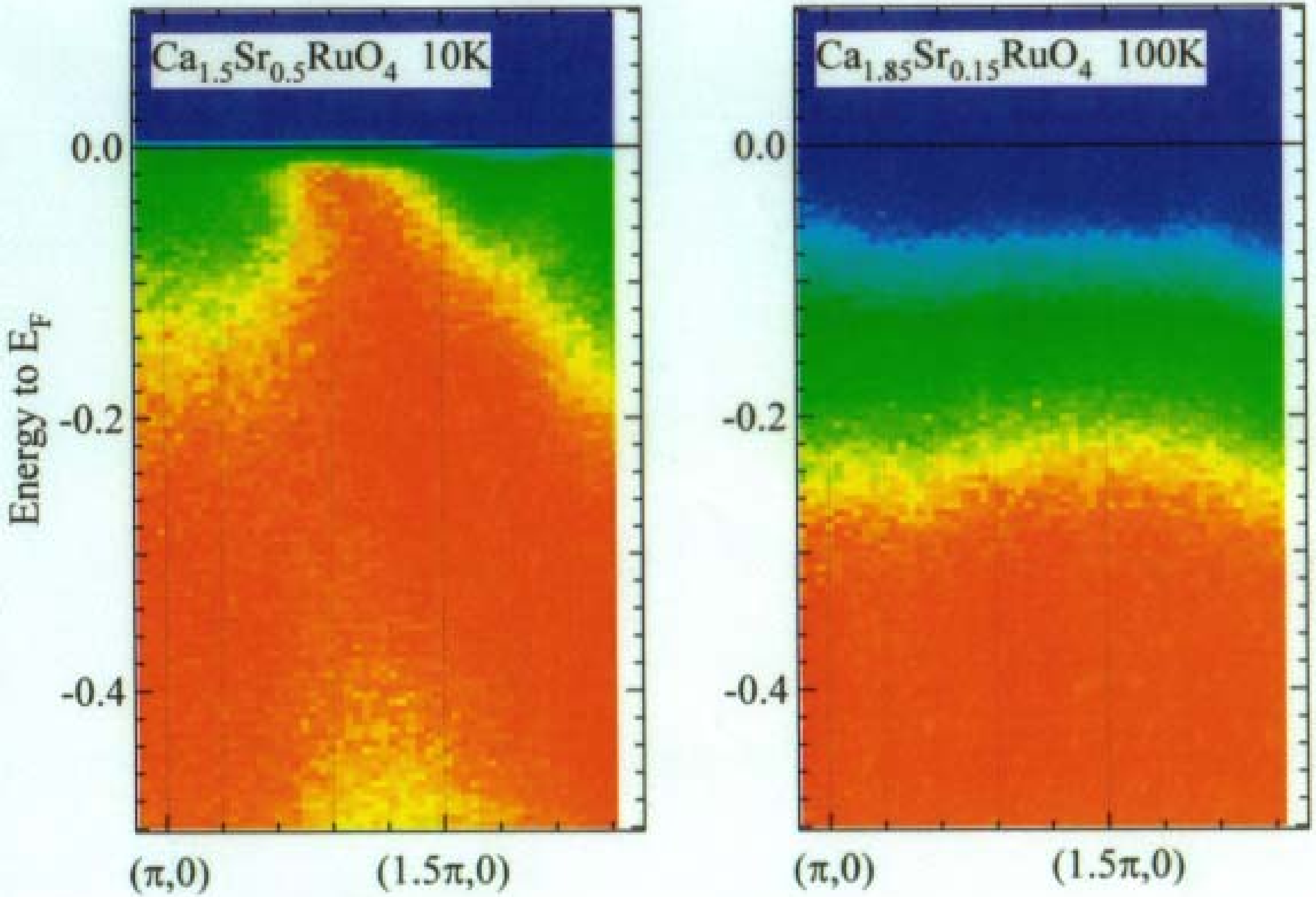
Orbital change across the MI transition

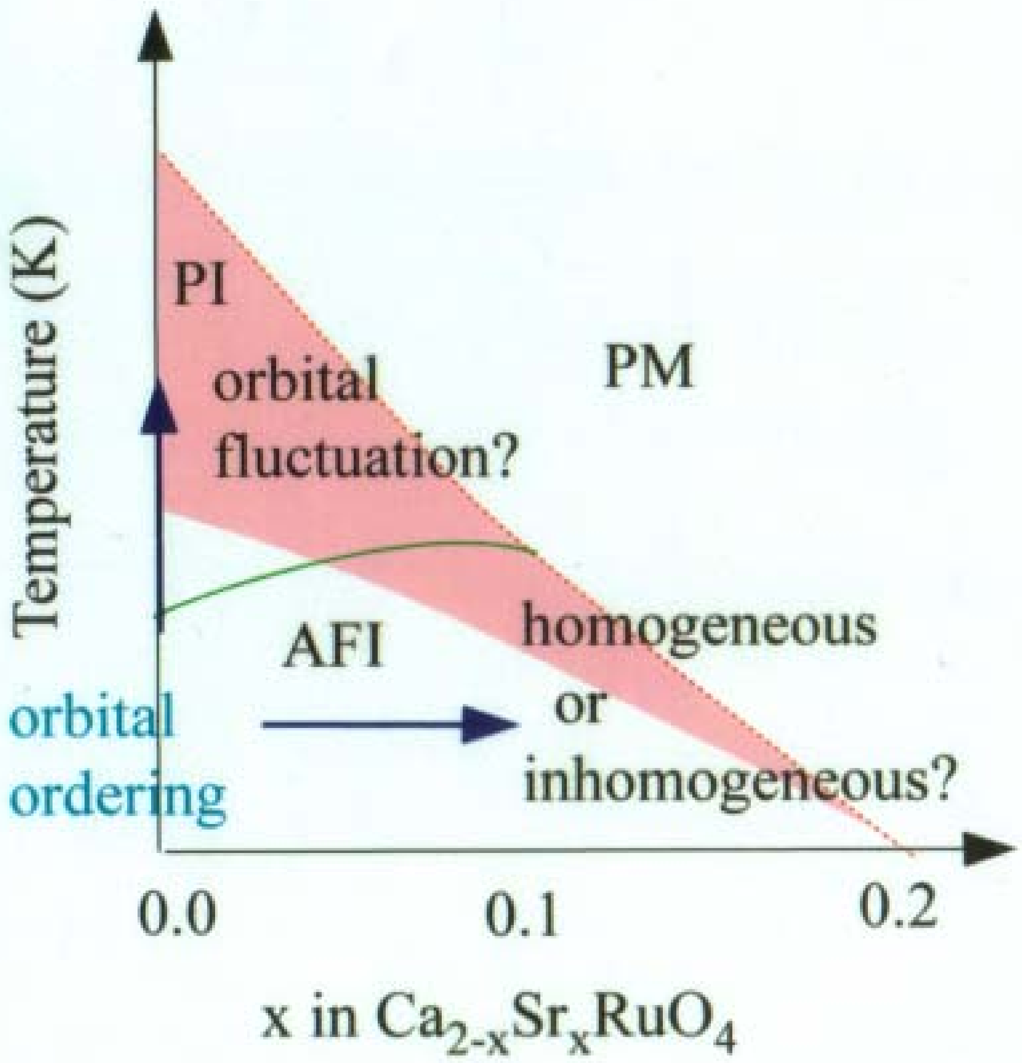


ARPES spectra of $Ca_{2-x}Sr_xRuO_4$



Band dispersion of $Ca_{2-x}Sr_xRuO_4$





Temperature (K)
PI
orbital
fluctuation?
PM
AFI
orbital
ordering
homogeneous
or
inhomogeneous?
0.0
0.1
0.2
x in $Ca_{2-x}Sr_xRuO_4$

Summary

ARPES and XAS can probe interesting electron-lattice coupled states in strongly-correlated electron systems (including bulk and surface of transition-metal oxides):

(1) Cu-O chain CDW and TL liquid

TL behavior is affected by electron-lattice coupling

(2) Bi-Sr-Co-O small polaron and enhanced thermopower

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

(3) $Ca_{2-x}Sr_xRuO_4$ orbital switching and Jahn-Teller distortion

orbital ordering => orbital glass => orbital liquid?