Chemical potential shifts in correlated electron systems: from titanates to cuprates

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Outline

- Introduction
- How to measure
- Dependence on carrier concentration
- Dependence on structural deformation
- Dependence on temperature
- Dependence on ……

Electron chemical potential

Electron chemical potential: $\mu \equiv F(N+1) - F(N) \approx F(N) - F(N-1)$

F: Helmholtz free energy

N: number of electrons

$$dF = \mu dN - SdT - pdV + fdD$$

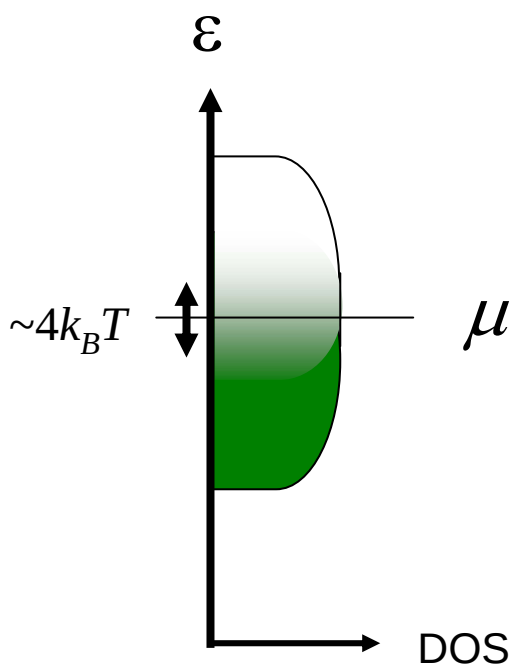
S: entropy

p: pressure

D: distortion

f: force/stress

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V,D}$$



Charge susceptibility - A basic physical quantity

Charge susceptibility: $\chi_c \equiv \frac{\partial n}{\partial \mu} = \left(\frac{\partial \mu}{\partial n} \right)^{-1}$

Chemical potential: $\delta\mu$ ⟶ Charge density: $\delta n = \delta n_{\uparrow} + \delta n_{\downarrow}$

n: electron density

n_σ: electron density of spin σ

cf: Magnetic susceptibility: $\chi \equiv 2\mu_B \frac{\partial m}{\partial H}$

Magnetic field: δH ⟶ Spin density: $\delta m = \delta n_{\uparrow} - \delta n_{\downarrow}$

m: spin density

μ_B: Bohr magneton

Deformation dependence of chemical potential

$$dF = \mu dN - SdT - pdV + fdD$$

D: distortion

f: force/stress

Uniform volume change:

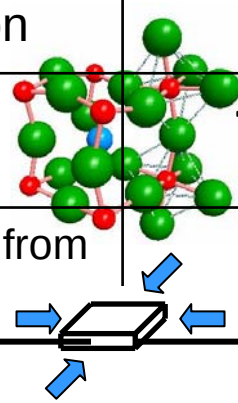
$$-\frac{\partial^2 F}{\partial V \partial N} = -\left.\frac{\partial \mu}{\partial V}\right|_N = \left.\frac{\partial p}{\partial N}\right|_V$$

perturbation	V	P
Hydrostatic pressure	volume	electronic pressure

Other structural deformation:

$$\frac{\partial^2 F}{\partial D \partial N} = \left.\frac{\partial \mu}{\partial D}\right|_N = \left.\frac{\partial f}{\partial N}\right|_D$$

perturbation	D	f
Chemical pressure	$\langle r_A \rangle$	electronic "force"
Epitaxial strain from substrate	c/a	electronic "force"



Temperature dependence of chemical potential

$$dF = \mu dN - SdT - pdV - fdD$$

Temperature change:

$$\frac{\partial^2 F}{\partial N \partial T} = \left.\frac{\partial \mu}{\partial T}\right|_N = -\left.\frac{\partial S}{\partial N}\right|_T$$

perturbation	S	T
Heat	entropy	temperature

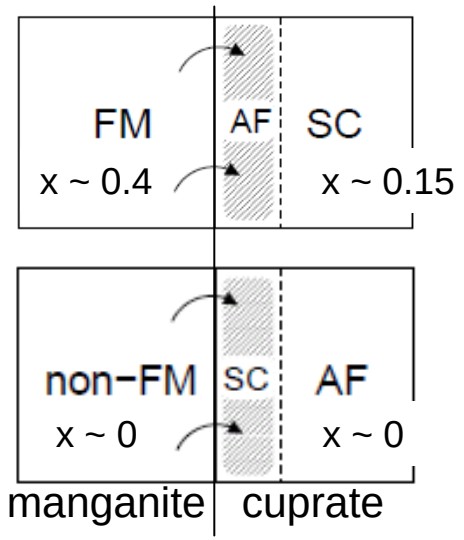
$$S \equiv \int_0^T \frac{d'Q}{T} = \int_0^T \frac{c}{T} dT$$

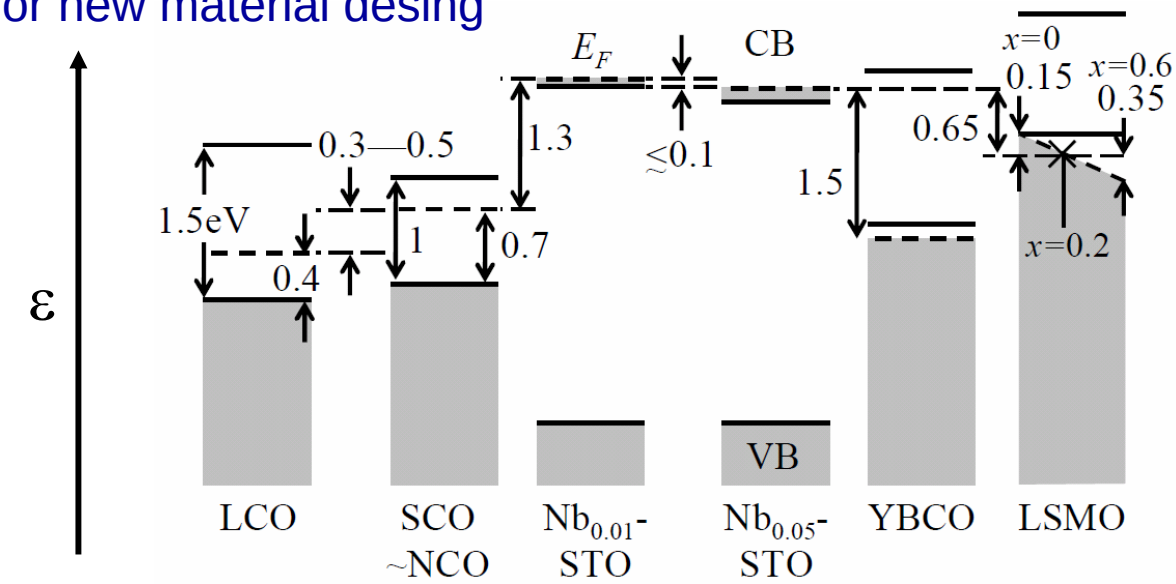
If $\frac{\partial \mu}{\partial T} > 0$, $-\frac{\partial S}{\partial N} > 0$: hole-like carriers

If $\frac{\partial \mu}{\partial T} < 0$, $\frac{\partial S}{\partial N} > 0$: electron-like carriers

New functionalities of oxide hetero-junctions controlled through chemical potential tuning

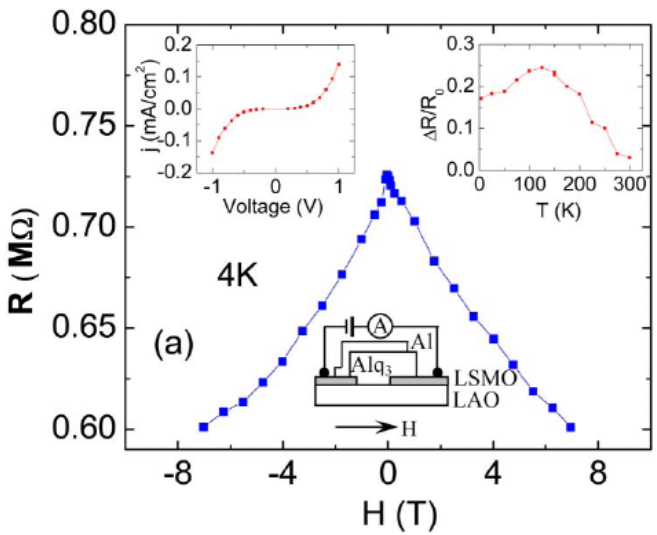
Self-doping at interfaces for new material desing





S. Yunoki et al., PRB, in press

Magnetic field-control of interfacial transport



D. Wu et al., PRL '05

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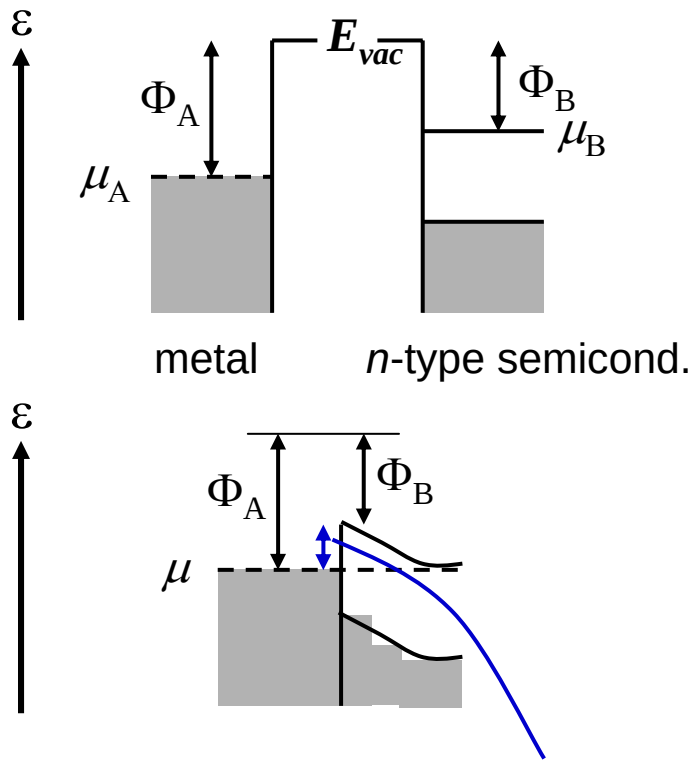
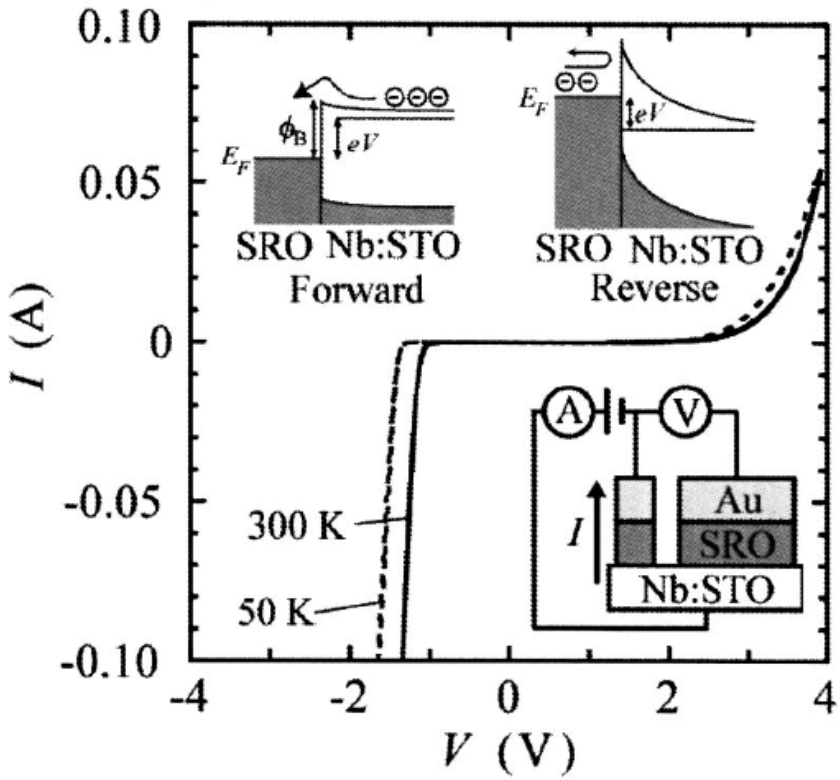
- Dependence on temperature
- Dependence on ……

To deduce chemical potential shift from *I-V* characteristics of junction

I-V characteristics of $SrRuO_3/SrTiO_3$



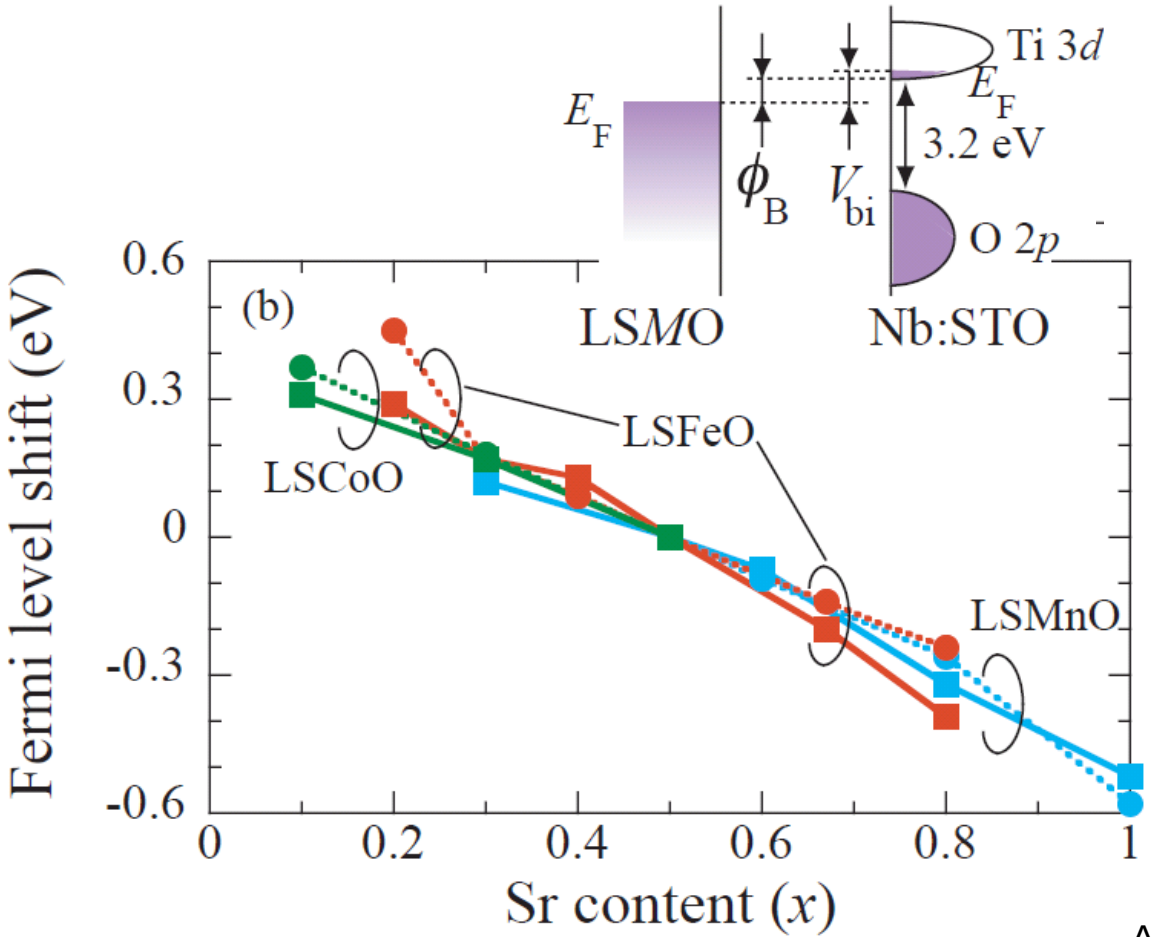


Schottky barrier height = $\Phi_A - \Phi_B = \mu_B - \mu_A$
(or built-in potential in *p-n* junction)

T. Fujii et al., APL '05

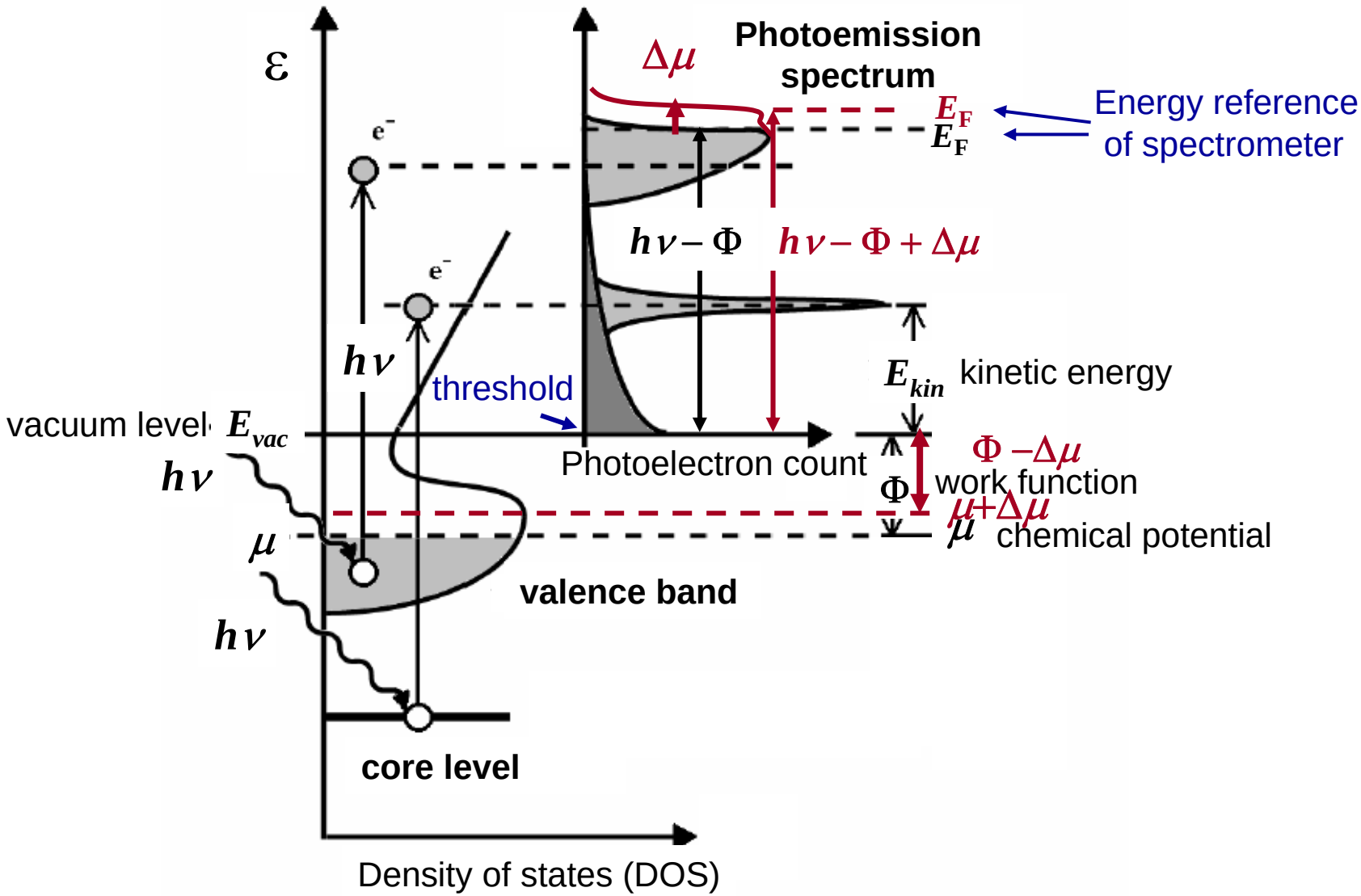
To deduce chemical potential shift from *I-V* characteristics of junction

Chemical potential shift from the built-in potential of $La_{1-x}Sr_xMO_3/SrTiO_3$ *p-n* (Schottky) junction

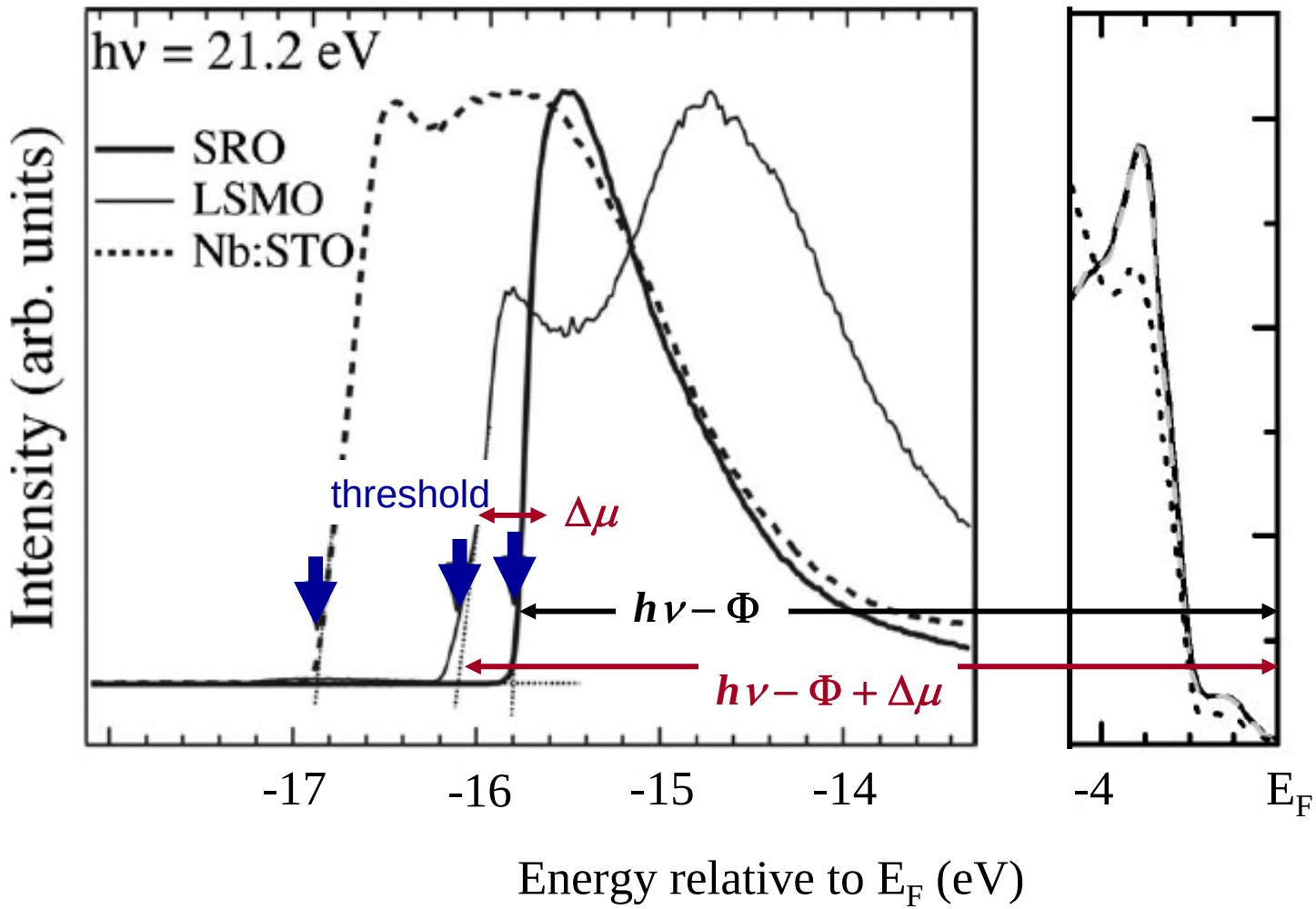


A. Sawa et al., APL '07

To deduce chemical potential shift from work function



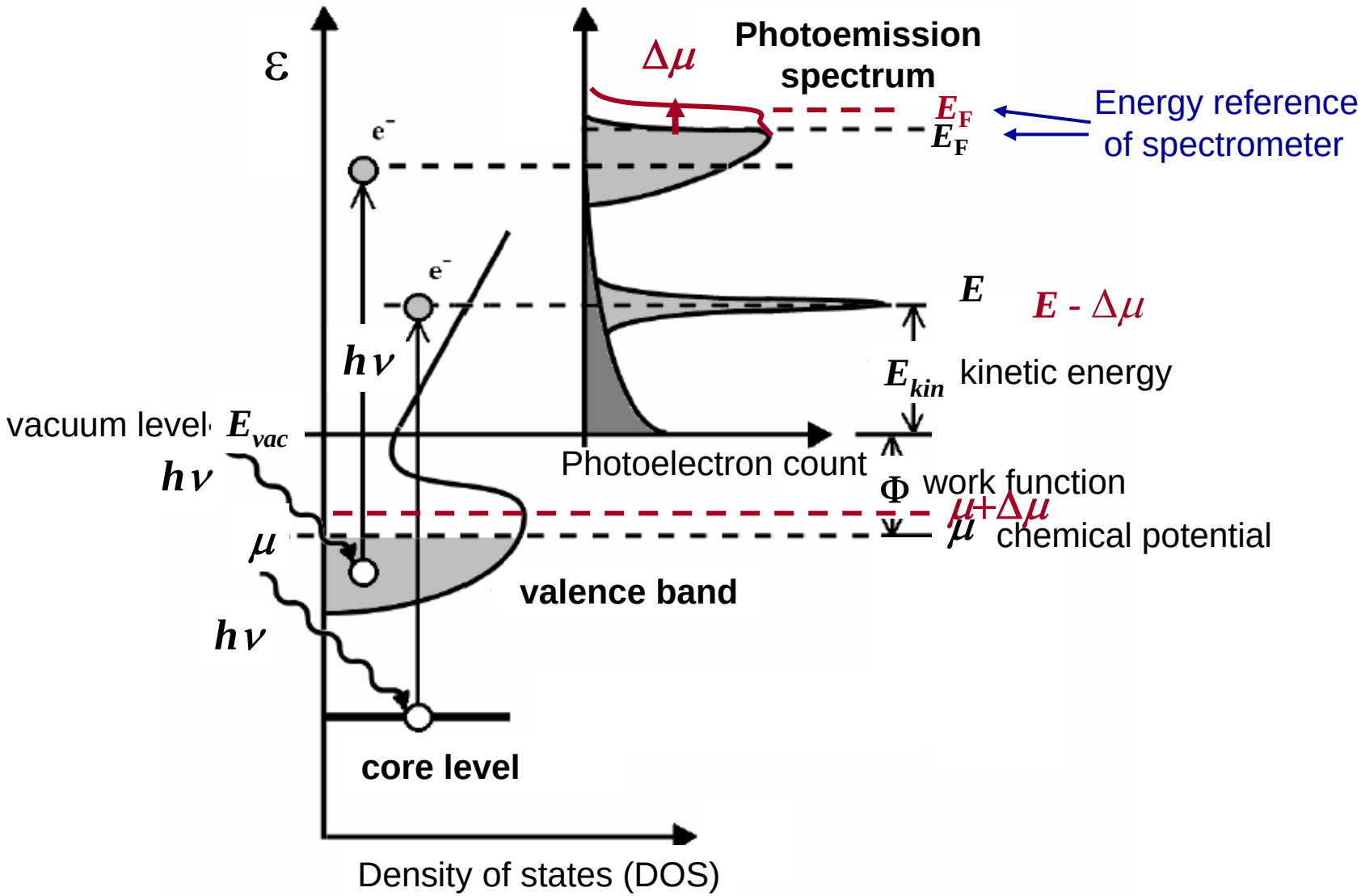
To deduce chemical potential shift from work function



M. Minohara et al., APL '07

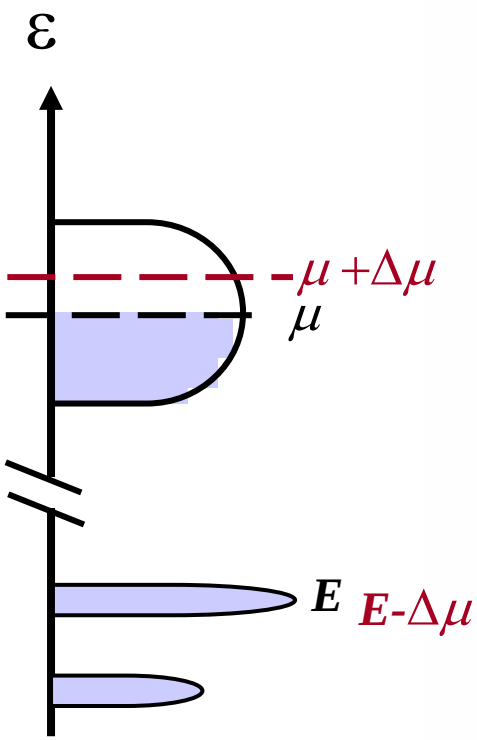
K. Schulte et al., PRB '01

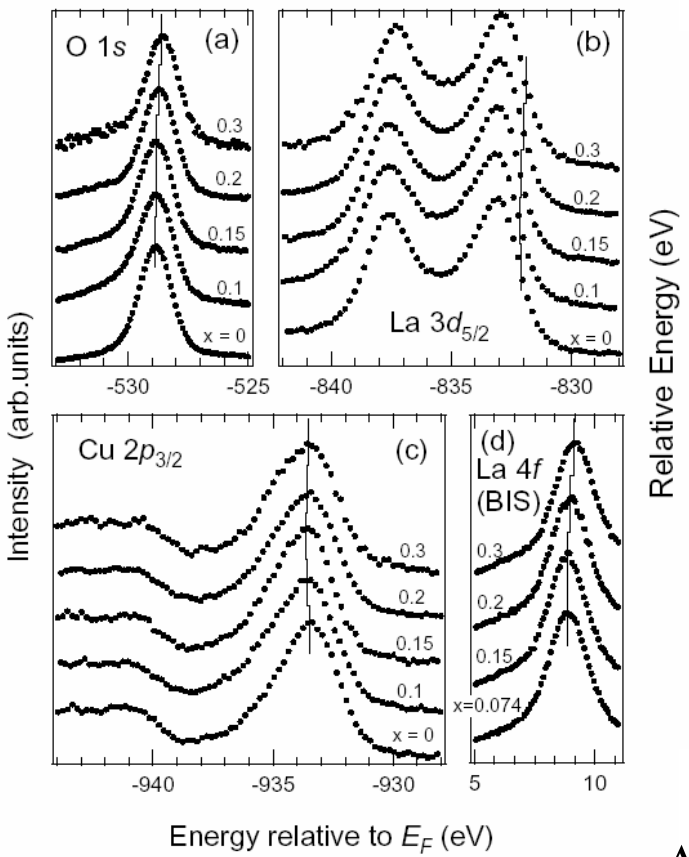
To deduce chemical potential shift from core-level photoemission

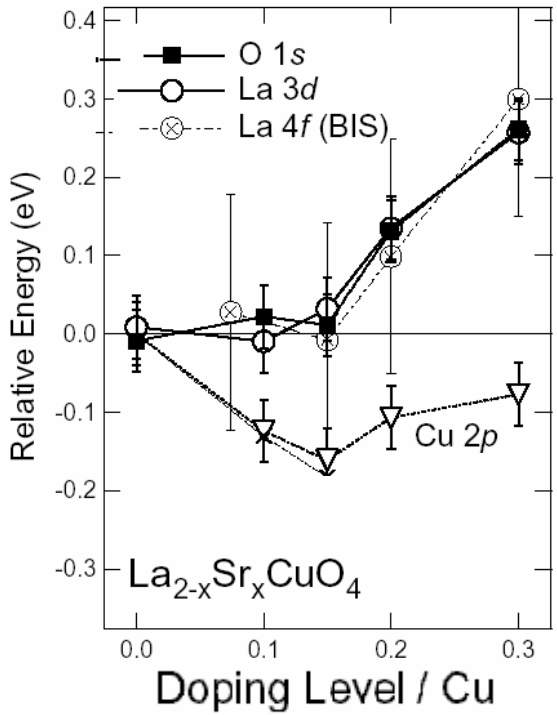


To deduce chemical potential shift from core-level photoemission

Core-level shifts







$$\Delta E = -\Delta\mu - K\Delta Q + \Delta V_M + \Delta E_R$$

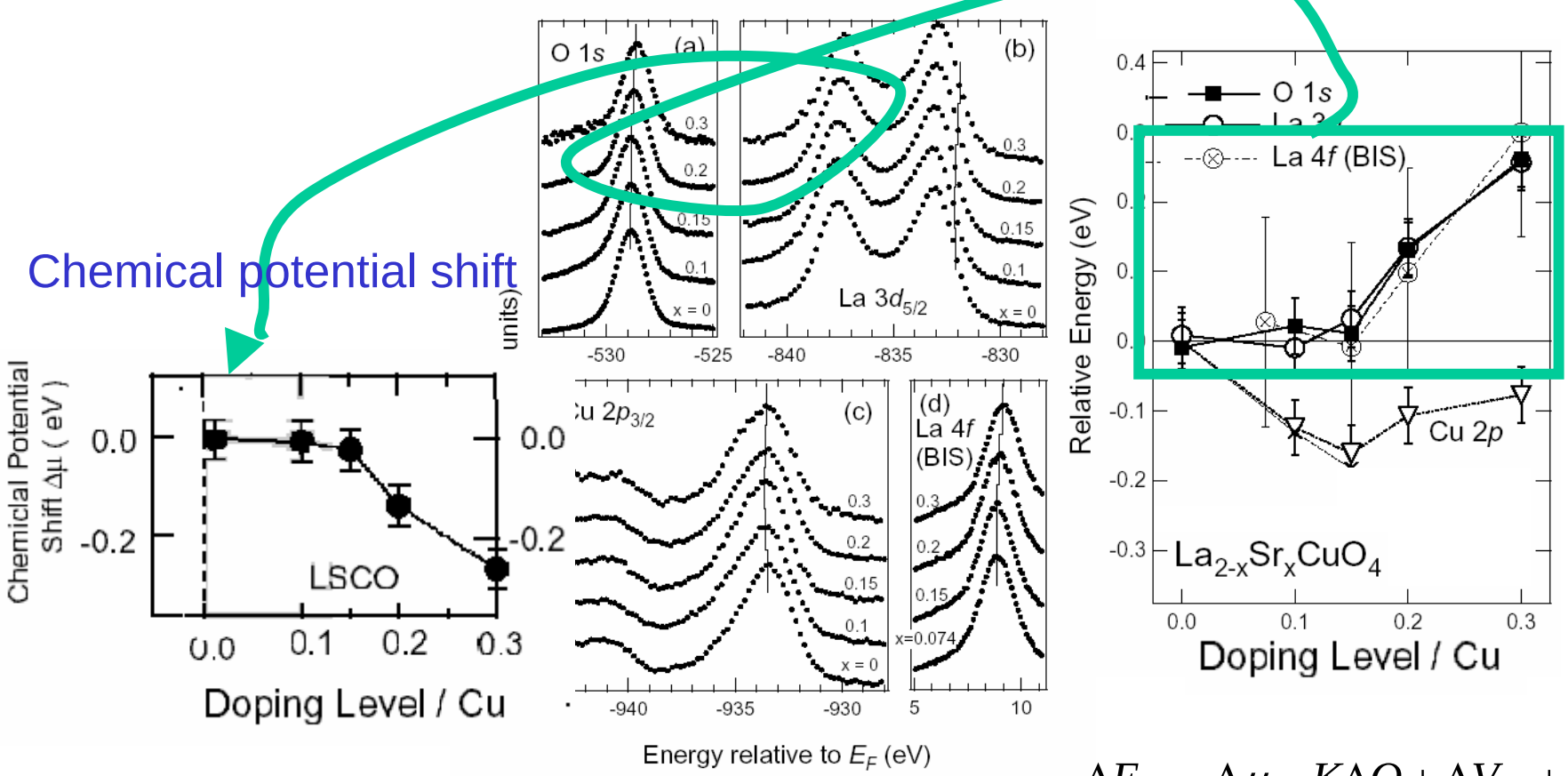
A. Ino et al., PRL '97

S. Huefner, Photoelectron Spectroscopy (Springer-Verlag, 1995)

To deduce chemical potential shift from core-level photoemission

Core-level shifts

Chemical potential shift



$$\Delta E = -\Delta\mu - K\Delta Q + \Delta V_M + \Delta E_R$$

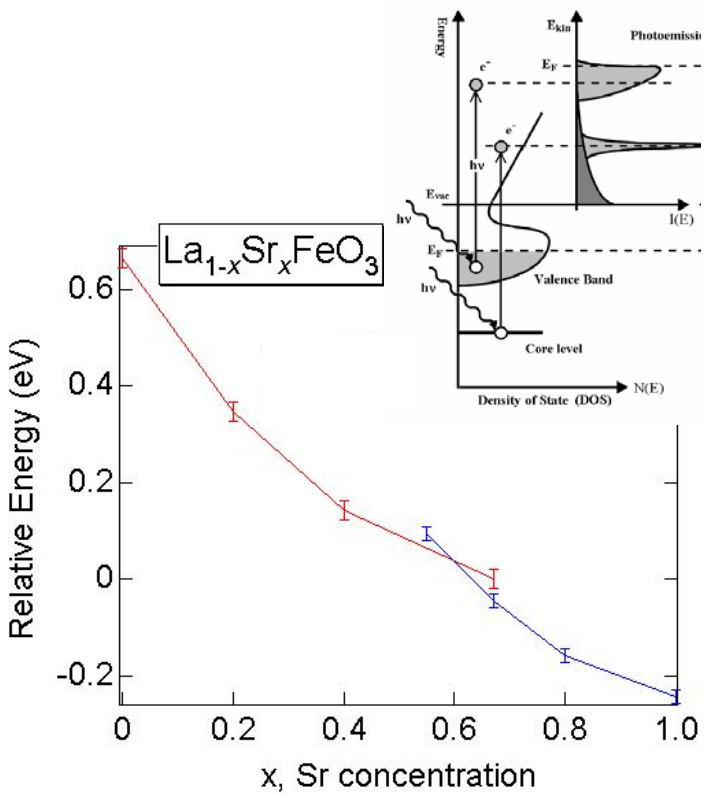
S. Huefner, Photoelectron Spectroscopy (Springer-Verlag, 1995)

N. Harima et al., PRB '01

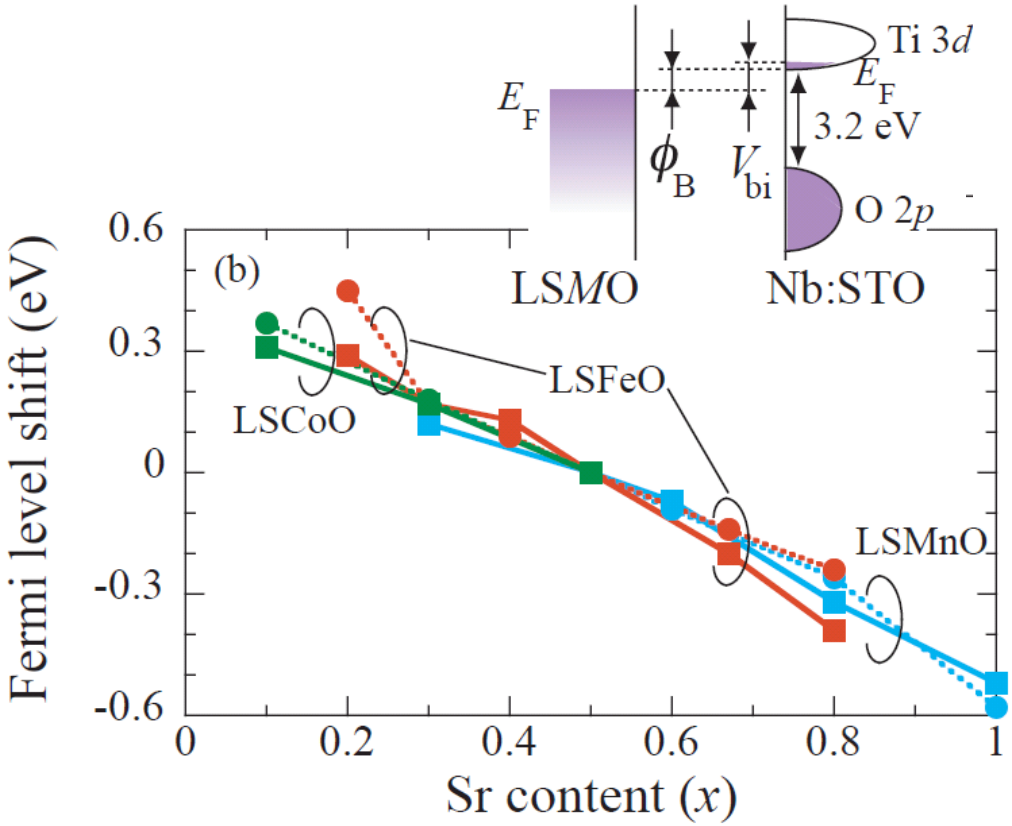
A. Ino et al., PRL '97

Consistency between different methods

Chemical potential shift from core-level photoemission



Chemical potential shift from junction *I-V* characteristics



J. Matsuno et al., PRB ‘99

A. Sawa et al., APL ‘07

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- Dependence on ……

Chemical potential shift in rigid-band Fermi-liquid systems

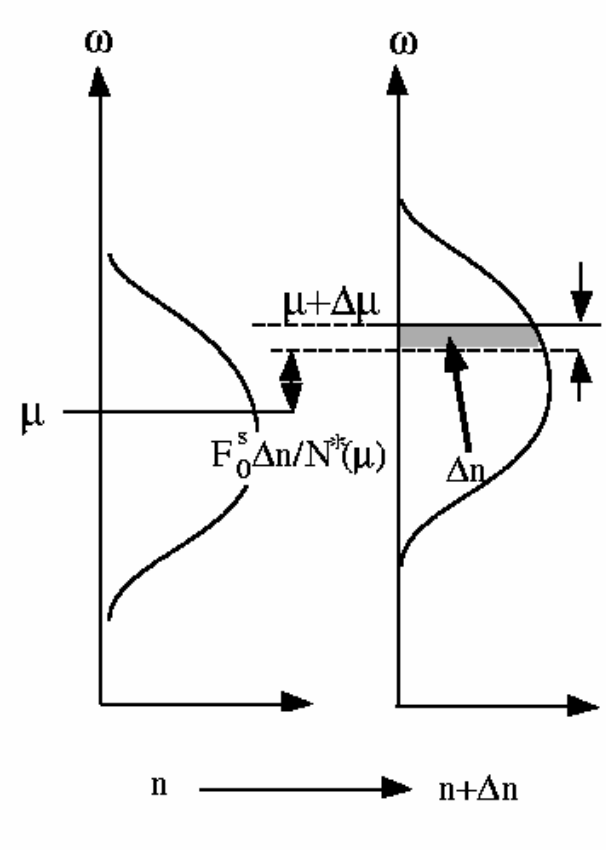
Charge susceptibility: $\chi_c \equiv \partial n / \partial \mu$

$$\frac{\partial \mu}{\partial n} = \frac{1 + F_s^0}{N^*(\mu)} \equiv \left(\frac{m_b}{m^*}\right) \frac{1 + F_s^0}{N_b(\mu)}$$

$N^*(\mu)$: QP density at μ

m^* : effective mass

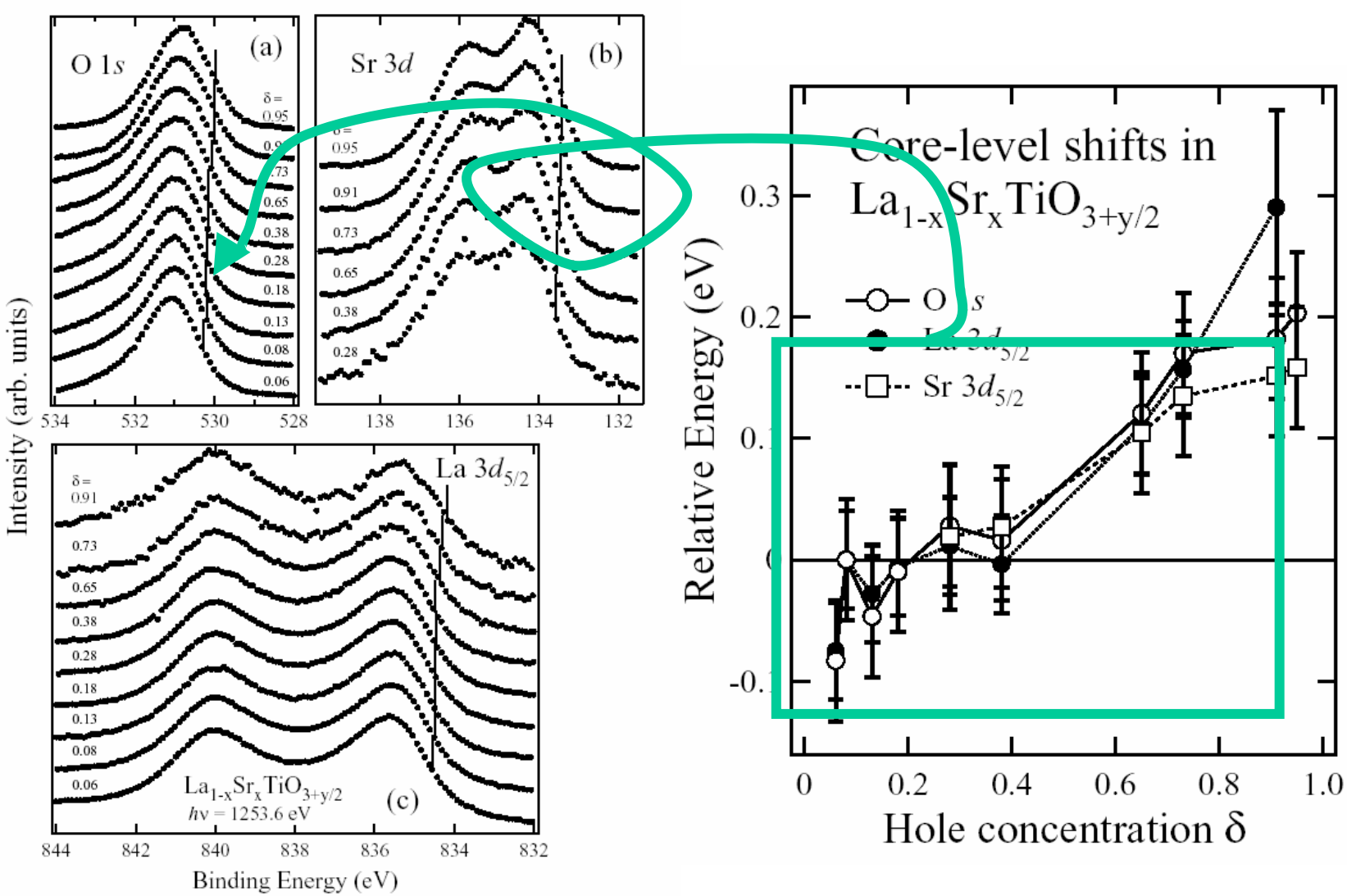
$F_s^0\,(>0)$: Landau parameter for e-e repulsion



$$\gamma = \frac{\pi^2 k_B^2}{3} N^*(\mu)$$: electronic specific heat coefficient

: QP density

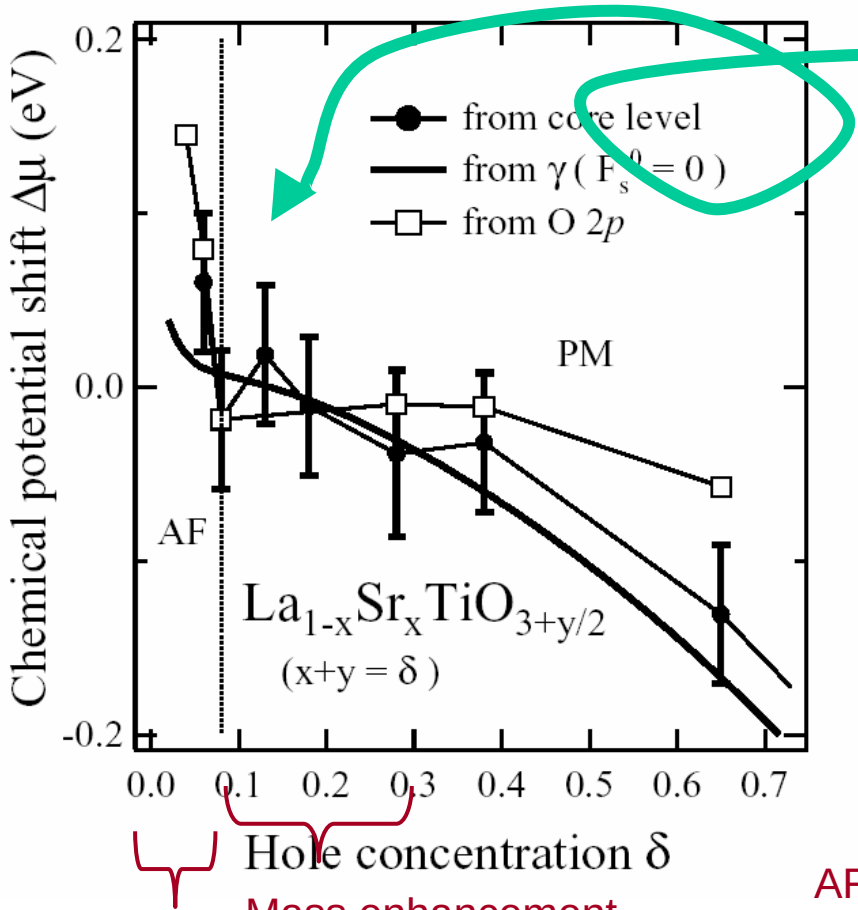
Core-level shifts in Fermi-liquid system $La_{1-x}Sr_xTiO_3$

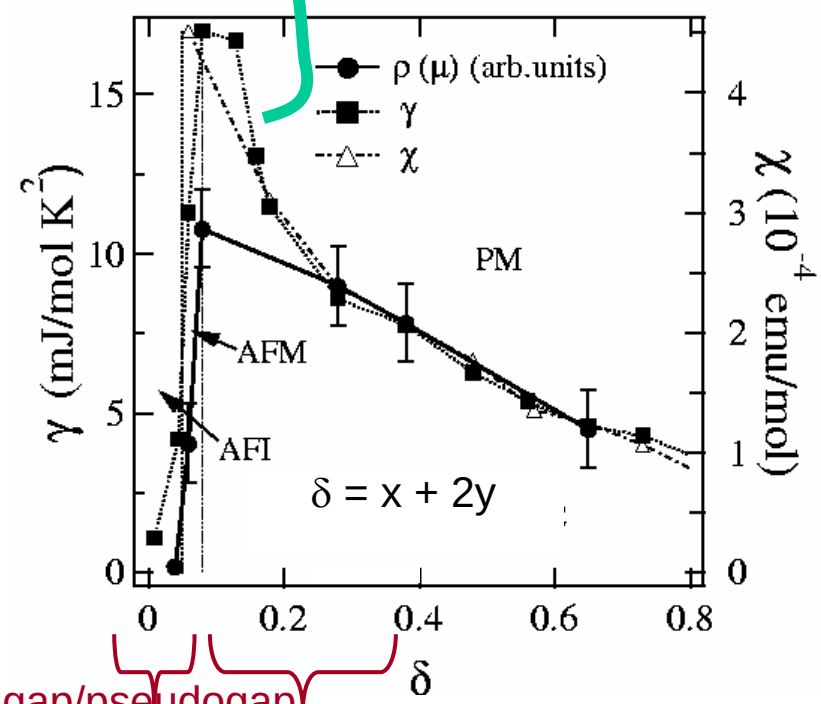


T. Yoshida et al.

Chemical potential shift in Fermi-liquid system $La_{1-x}Sr_xTiO_3$

γ: electronic specific heat coefficient
χ: Pauli susceptibility
ρ(μ): photoemission intensity at E_F





Mass enhancement

AF gap/pseudogap opening

$$\frac{\partial \mu}{\partial n} = \frac{1+F_s^0}{N^*(\mu)} \equiv \left(\frac{m_b}{m^*}\right)\frac{1+F_s^0}{N_b(\mu)}$$

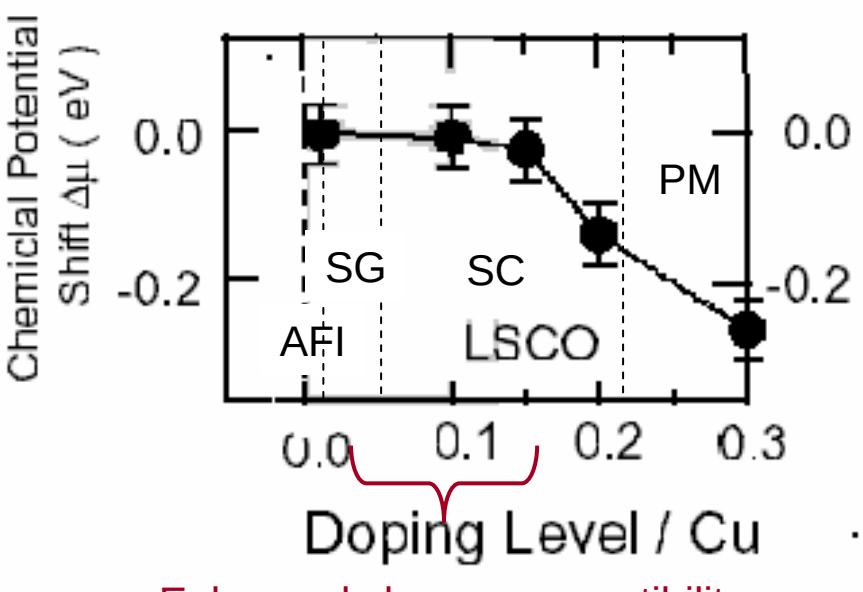
AF gap/pseudogap opening

Mass enhancement

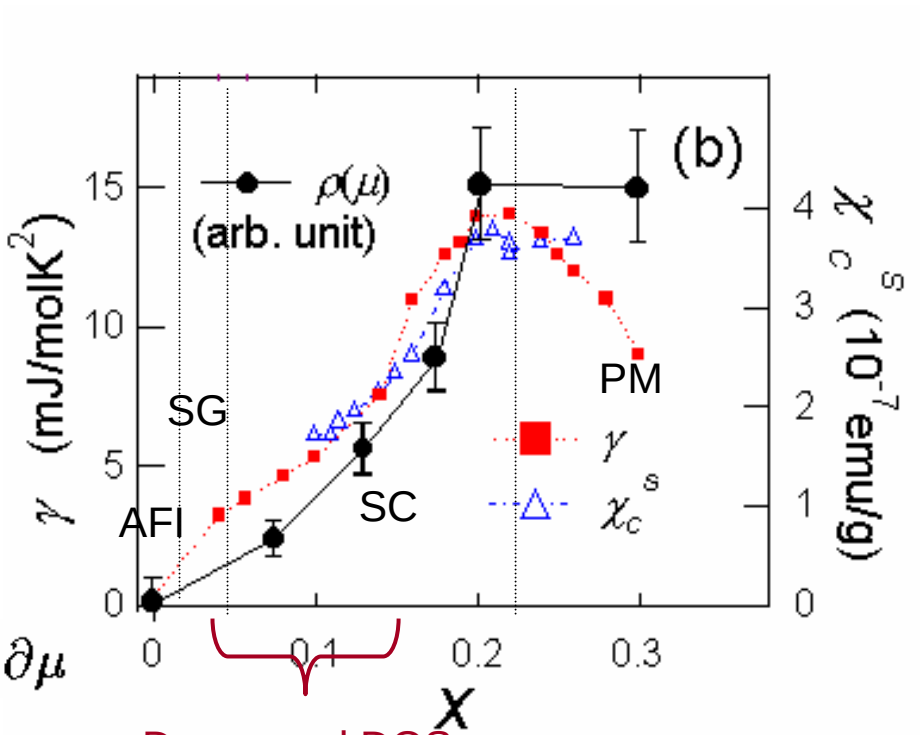
T. Yoshida et al., EPL '02

Non-rigid-band behavior in underdoped cuprates $La_{2-x}Sr_xCuO_4$

γ: electronic specific heat coefficient
χ: Pauli susceptibility
$\rho(\mu)$: photoemission intensity at E_F



Enhanced charge susceptibility



Depressed DOS

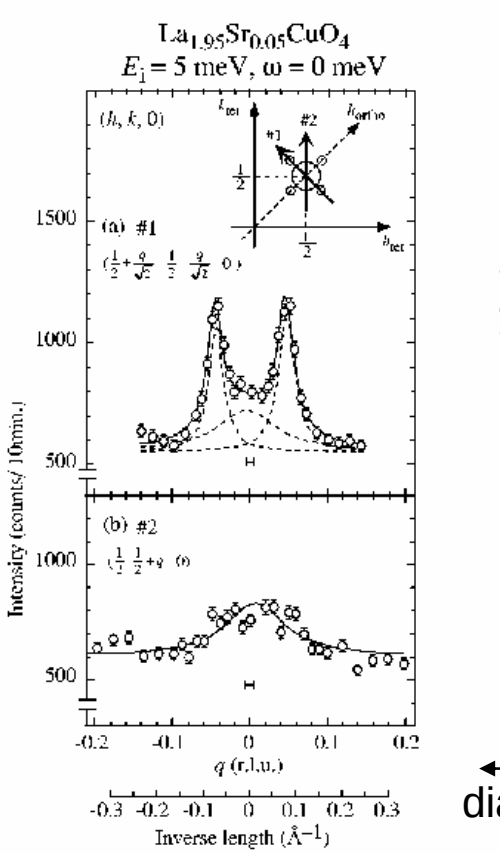
charge susceptibility: $\chi_c \equiv \partial n / \partial \mu$

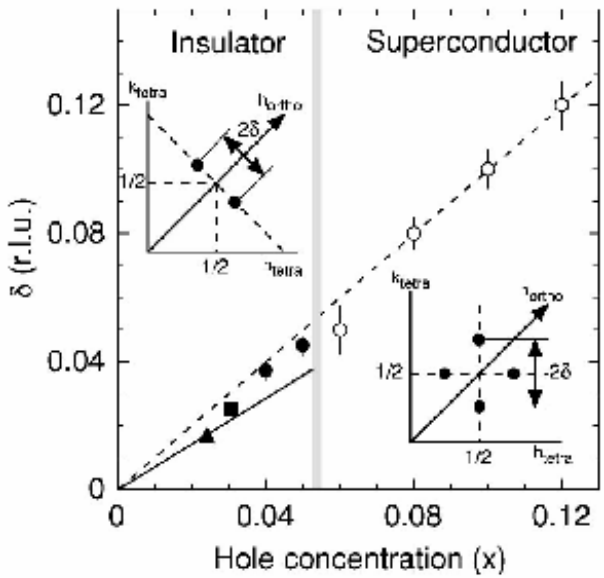
Rigid-band Fermi liquid

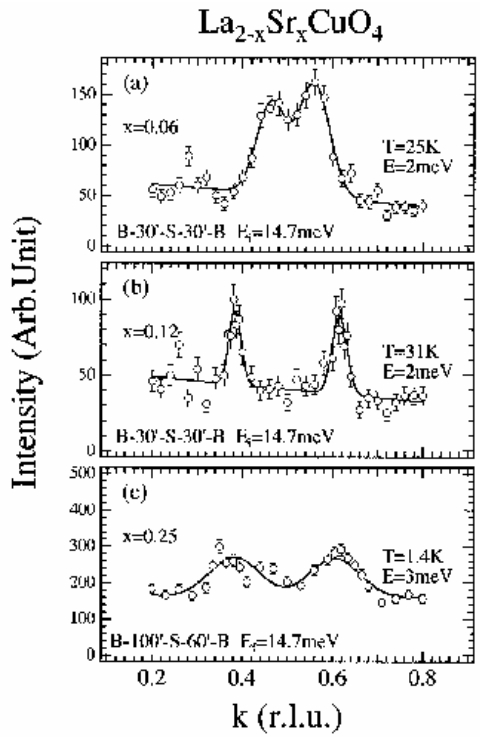
$$\frac{\partial \mu}{\partial n} = \frac{1+F_s^0}{N^*(\mu)} \equiv \left(\frac{m_b}{m^*}\right)\frac{1+F_s^0}{N_b(\mu)}$$

A. Ino et al., PRL '98

Incommensurate spin (and charge) fluctuations in $La_{2-x}Sr_xCuO_4$



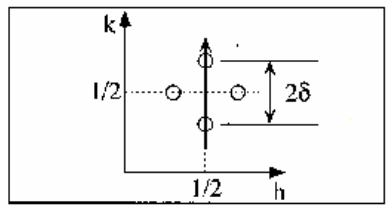




diagonal "stripes" ⟵ | ⟶ vertical "stripes"

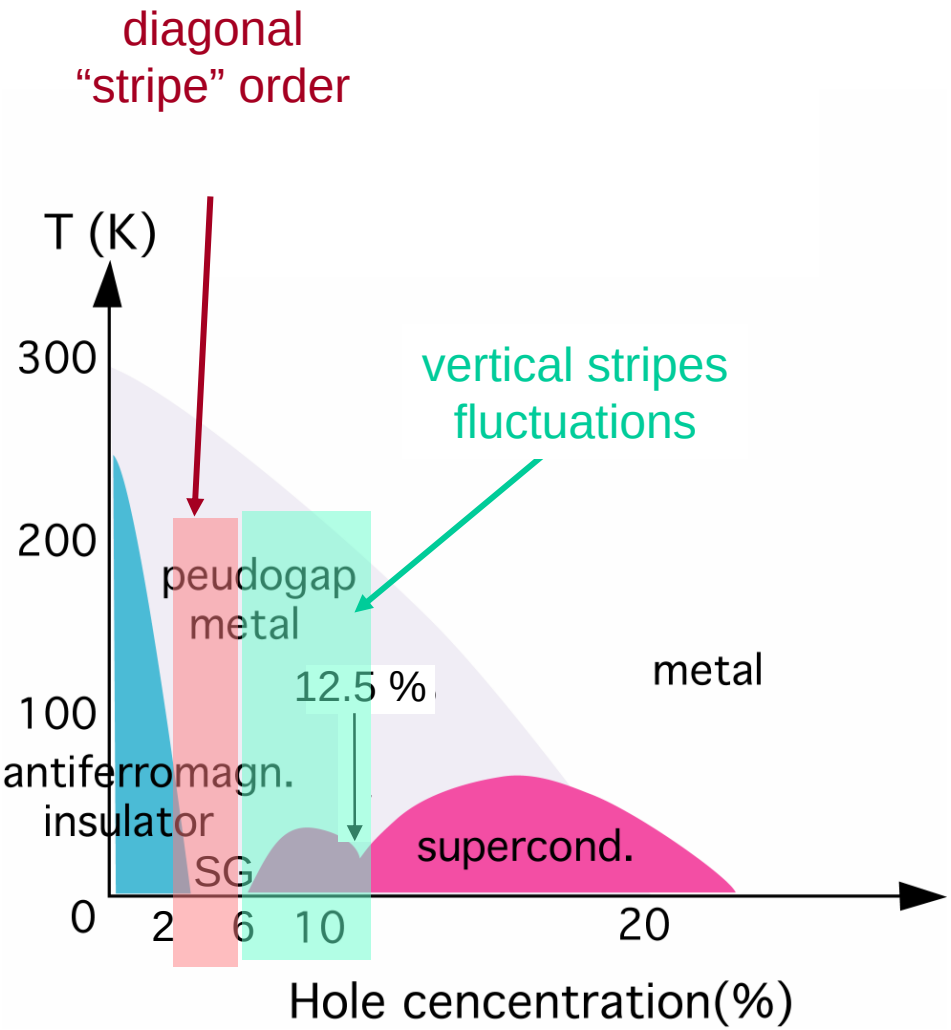
[static] [dynamical]

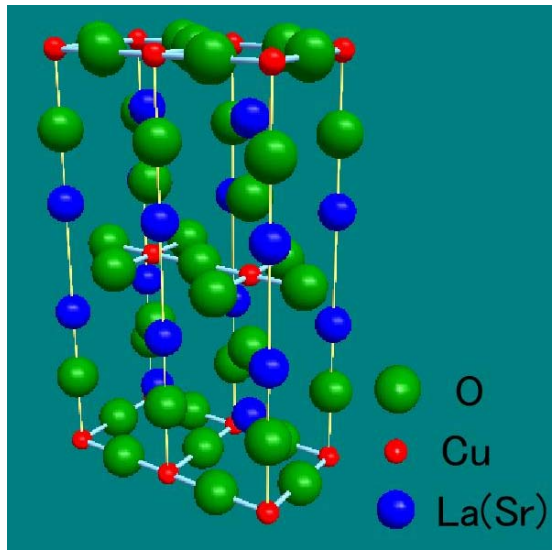
Nd subst. → static



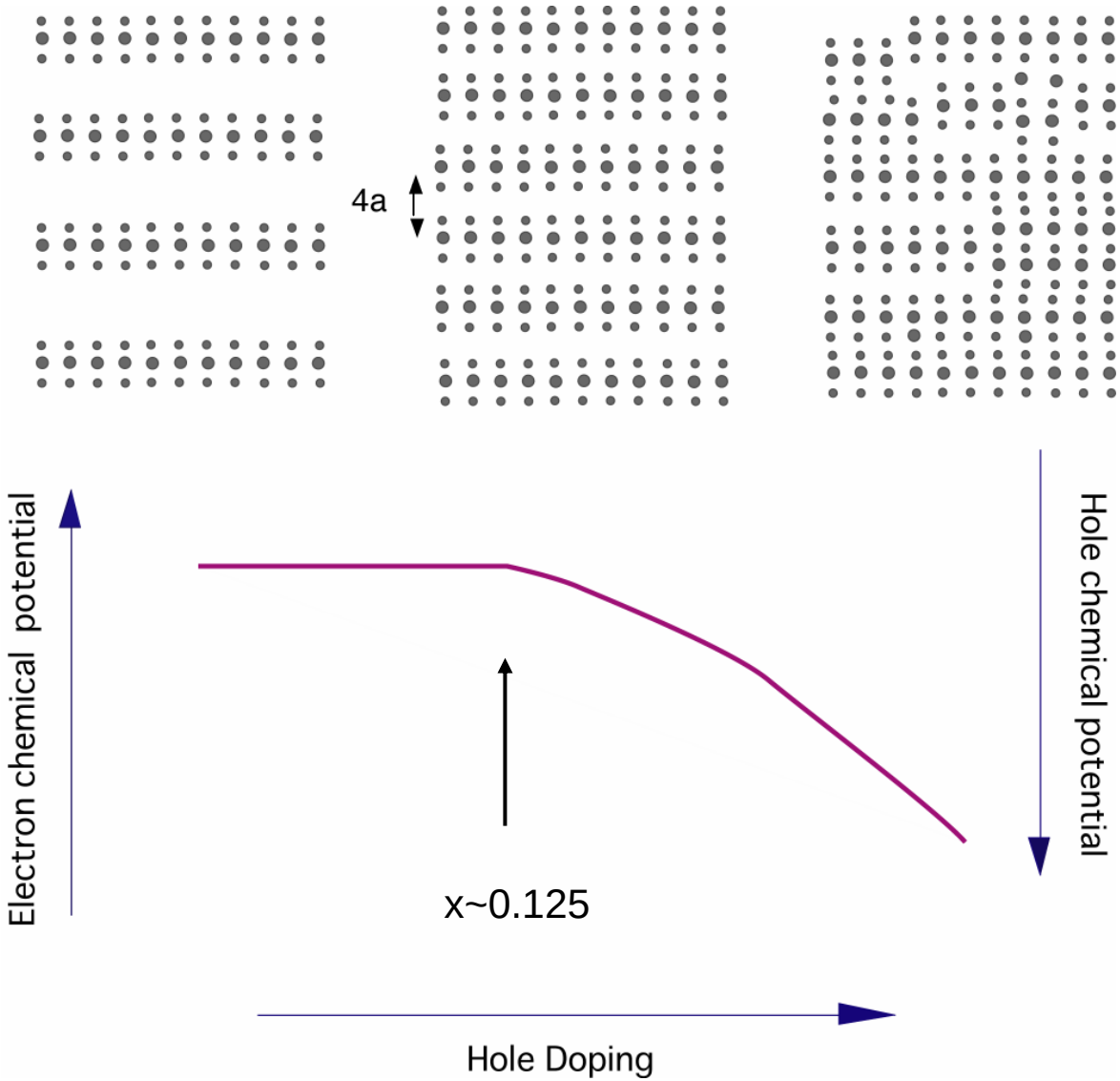
K. Yamada et al., PRB '97
S. Wakimoto et al., PRB '99, '00
M. Matsuda et al., PRB '00

Incommensurate spin (and charge) fluctuations in $La_{2-x}Sr_xCuO_4$





Chemical potential pinning in cuprates by incommensurate spin/charge fluctuations



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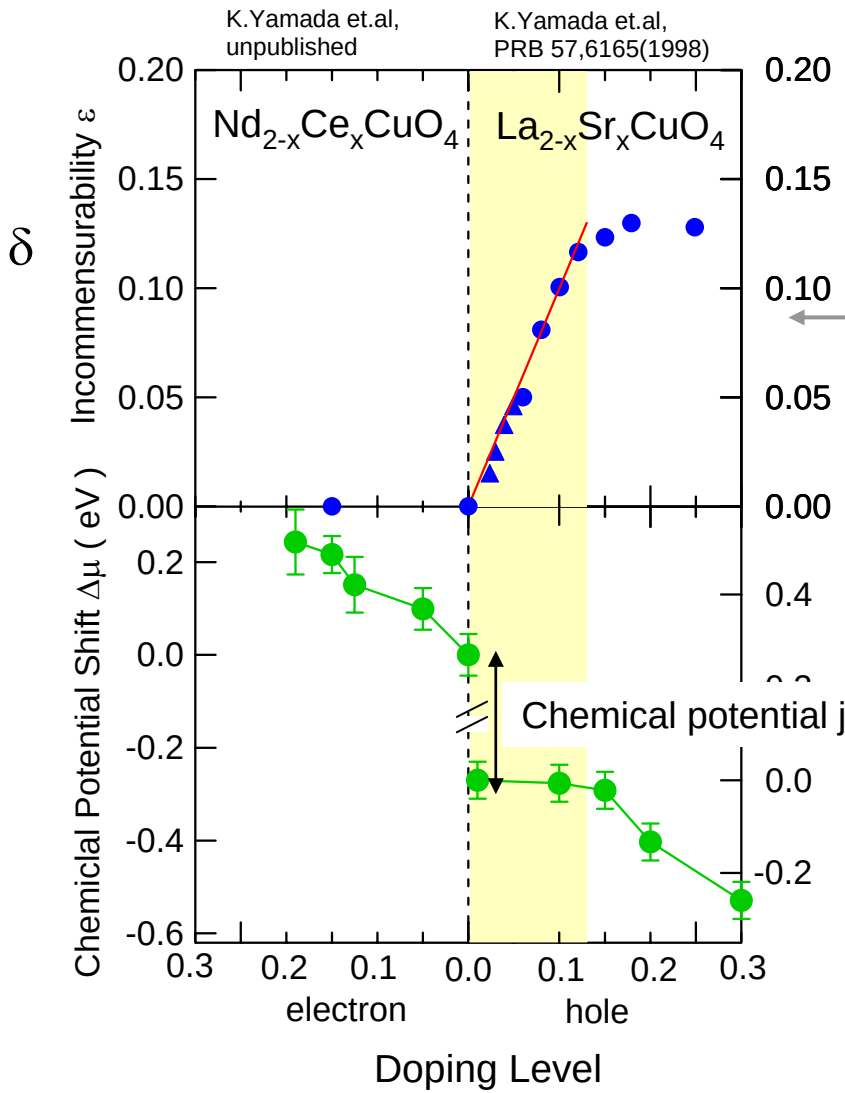


Incommensurate neutron peaks

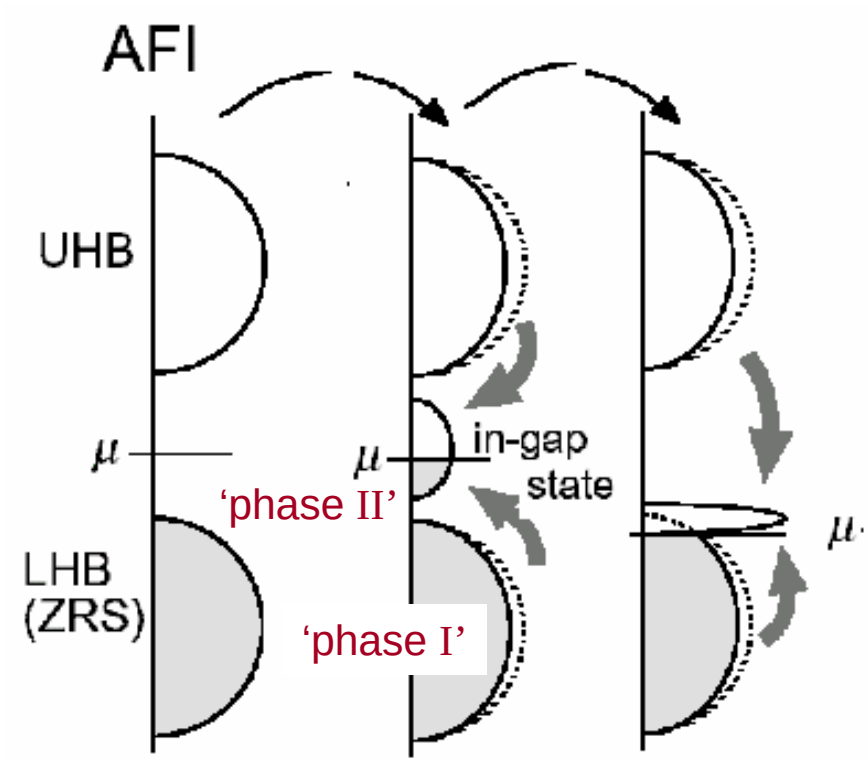
Chemical potential jump < 0.5 eV

<< Optical gap ~ 1.5 eV

A. Ino et al., PRL '97
N. Harima et al., PRB '00

Incommensurate spin/charge fluctuations ~ microscopic 'phase separation'

Chemical potential shift in high-T_c cuprates

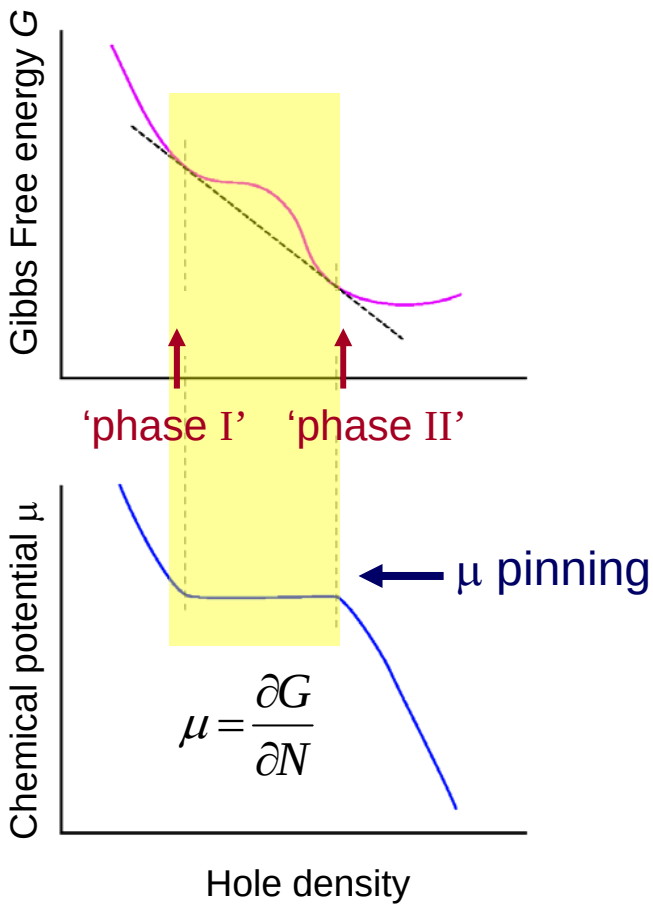


Mott insulator

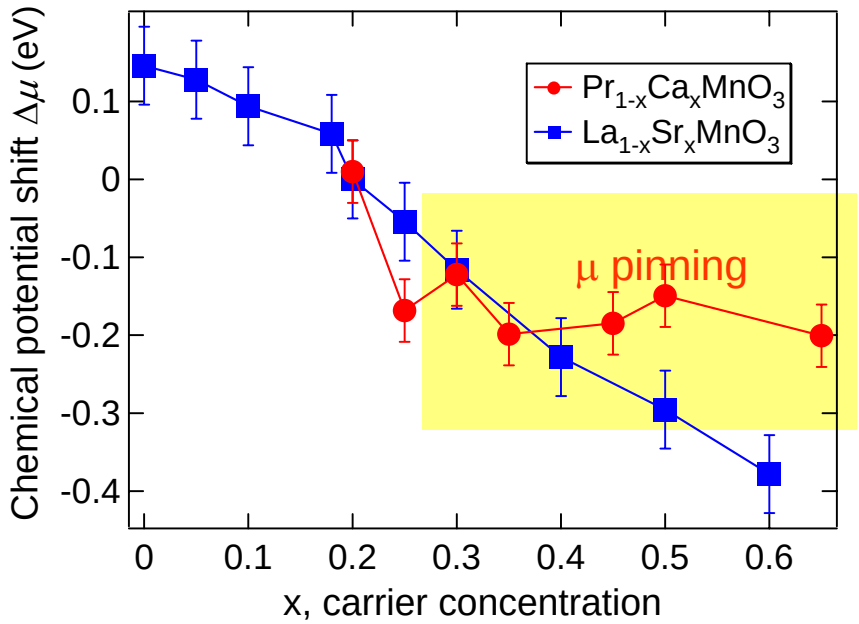
Pinning by incommensurate fluctuations

Rigid-band-like shift

"Phase separation" on a microscopic level

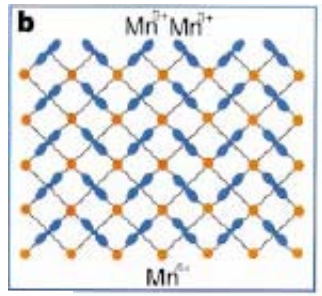


Chemical potential pinning in manganites by incommensurate spin/charge fluctuations

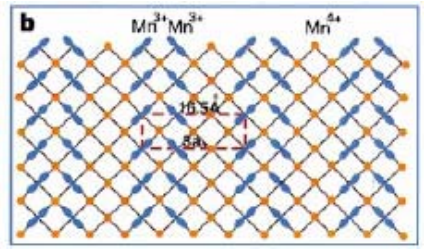


Stripe formation in $La_{1-x}Ca_xMnO_3$

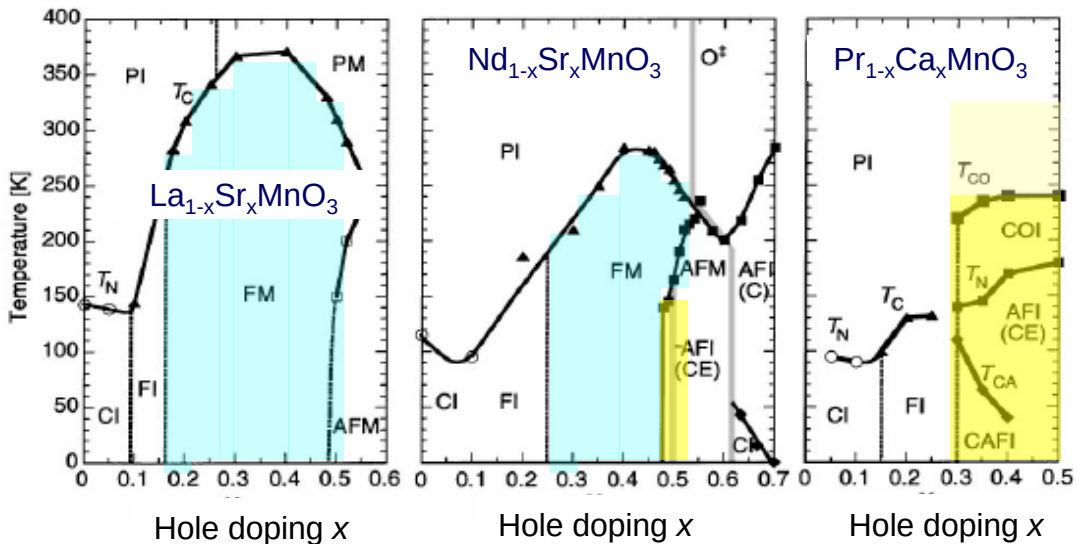
x = 0.5



x = 0.67



S.Mori et al., Nature '98



K. Ebata et al., PRB '06

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Deformation dependence of chemical potential

$$dF = \mu dN - SdT - pdV + fdD$$

D: distortion

f: force/stress

Uniform volume change:

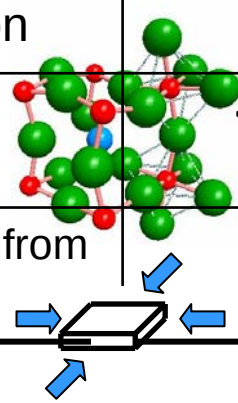
$$-\frac{\partial^2 F}{\partial V \partial N} = -\left.\frac{\partial \mu}{\partial V}\right|_N = \left.\frac{\partial p}{\partial N}\right|_V$$

perturbation	V	P
Hydrostatic pressure	volume	electronic pressure

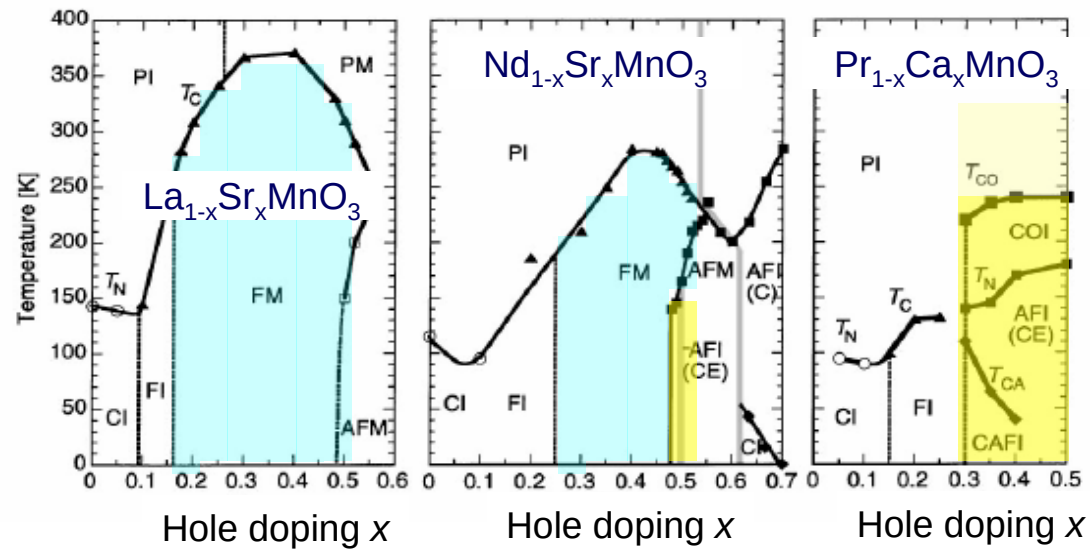
Other structural deformation:

$$\frac{\partial^2 F}{\partial D \partial N} = \left.\frac{\partial \mu}{\partial D}\right|_N = \left.\frac{\partial f}{\partial N}\right|_D$$

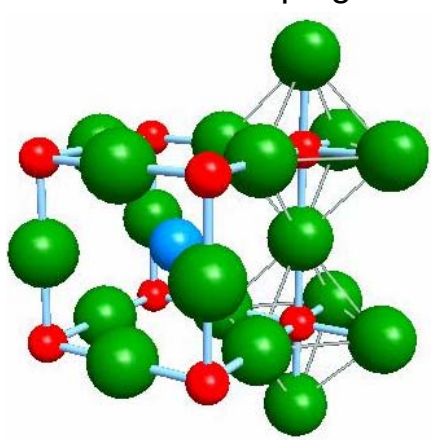
perturbation	D	f
Chemical pressure	$\langle r_A \rangle$	electronic "force"
Epitaxial strain from substrate	c/a	electronic "force"

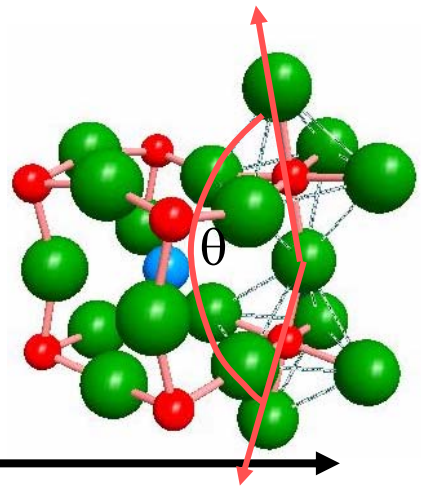


Band-width control in manganites



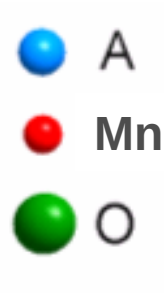
Y. Tomioka and Y. Tokura





Bandwidth:

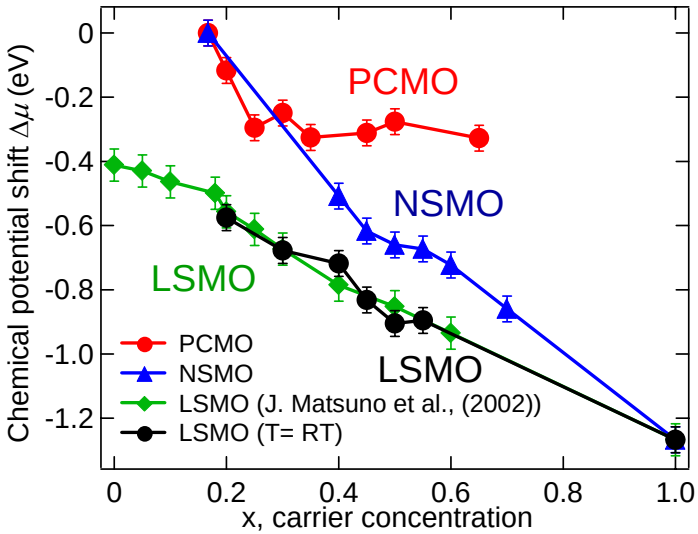
$W \propto \cos^2\theta$



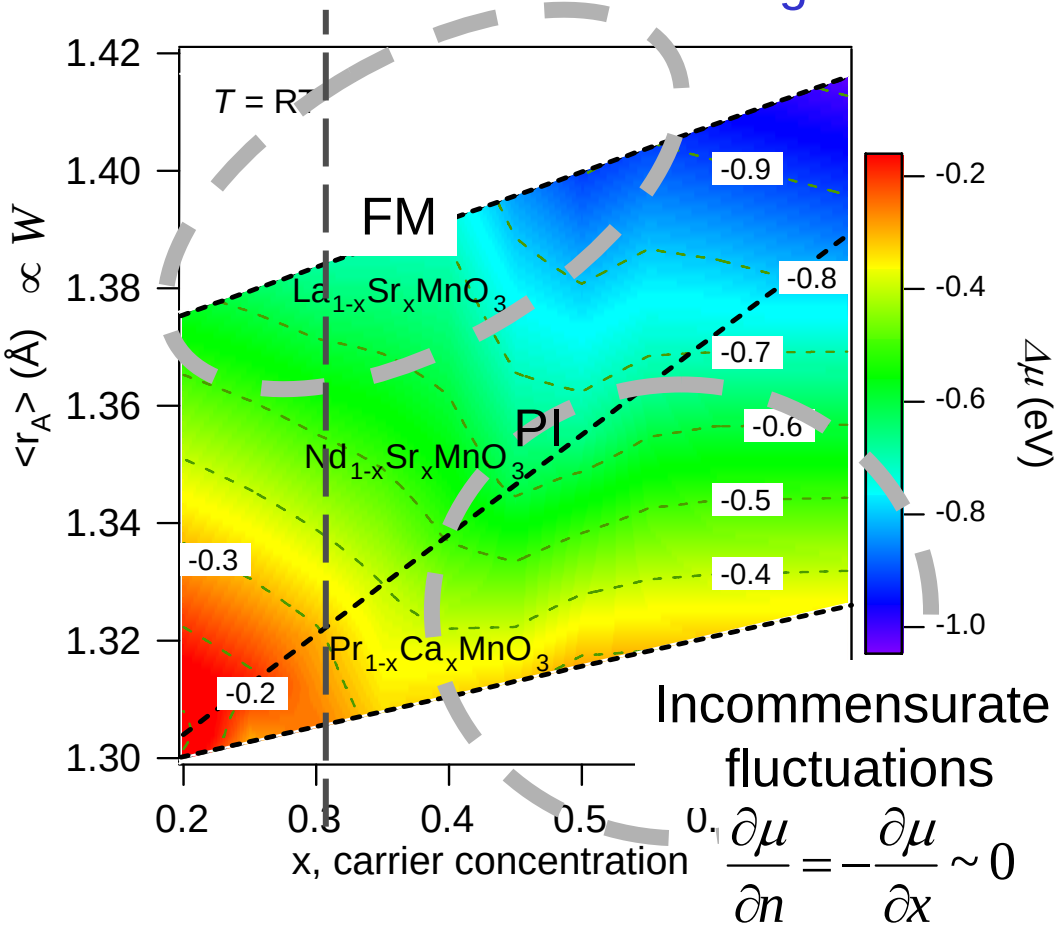
large ← $\langle r_A \rangle$ → small

large ← W → small

Bandwidth-dependent chemical potential shift in manganites



Chemical potential shift against bandwidth and band filling

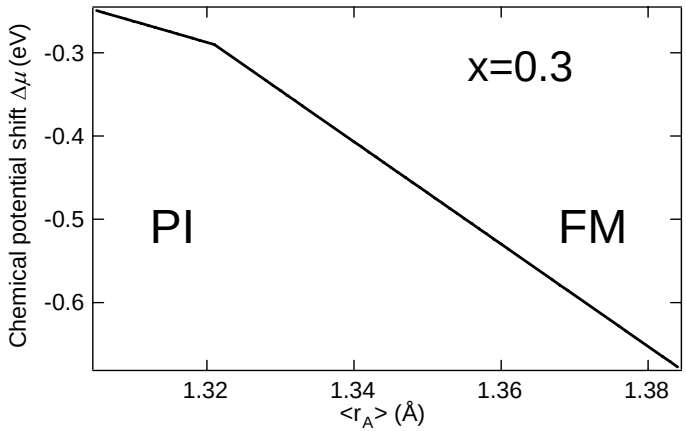


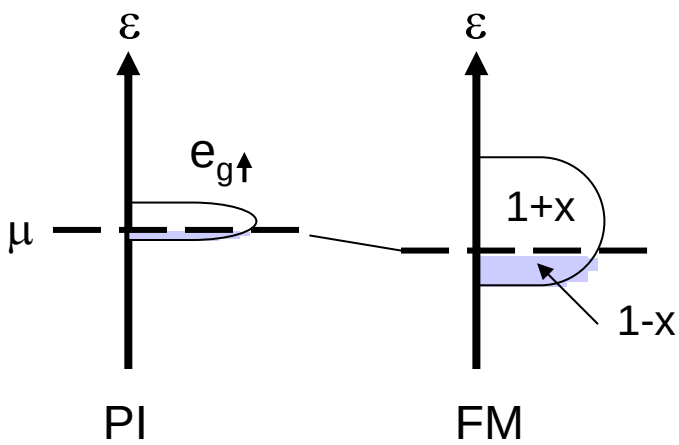
Incommensurate fluctuations

$$\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$$

K. Ebata et al.

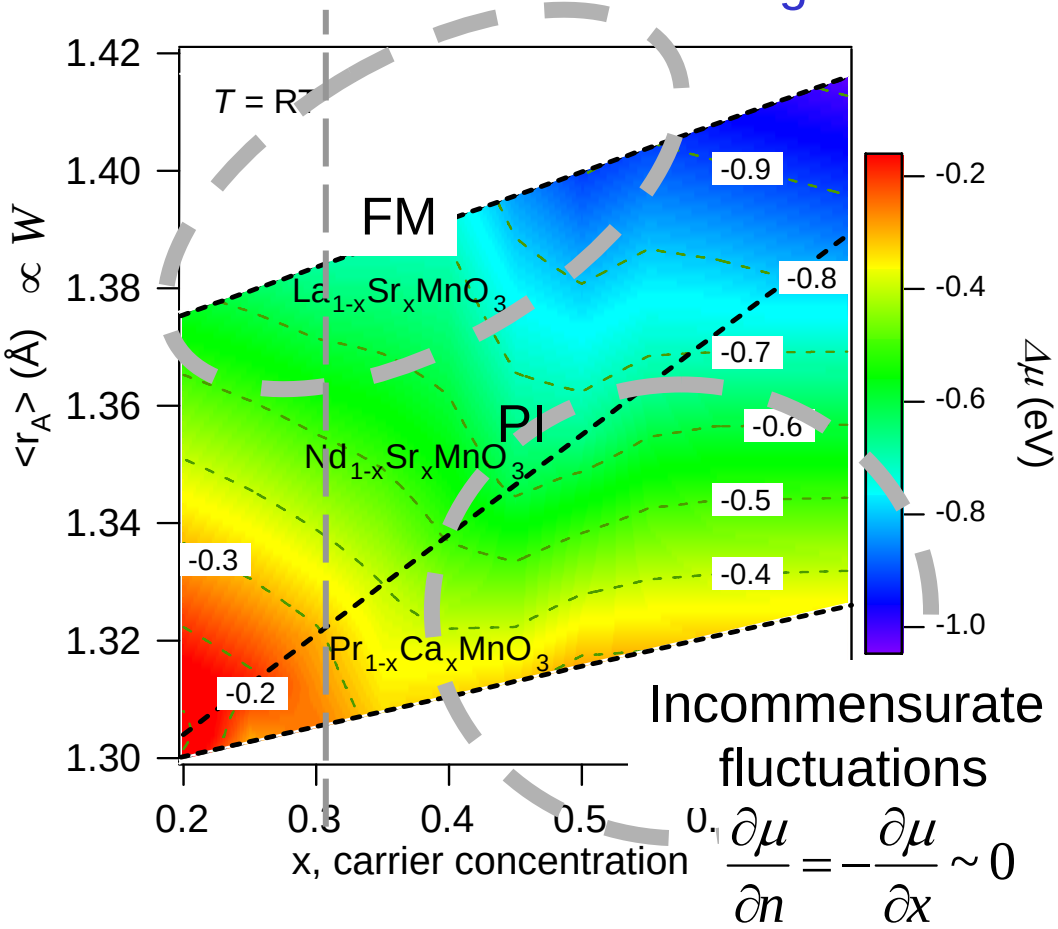
Bandwidth-dependent chemical potential shift in manganites





Theory: N. Furukawa, JPSJ '97

Chemical potential shift against bandwidth and band filling



Incommensurate fluctuations

$$\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$$

K. Ebata et al.

Deformation dependence of chemical potential

$$dF = \mu dN - SdT - pdV + fdD$$

D: distortion

f: force/stress

Uniform volume change:

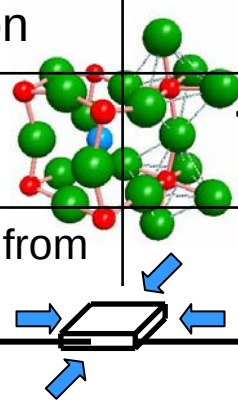
$$-\frac{\partial^2 F}{\partial V \partial N} = -\left.\frac{\partial \mu}{\partial V}\right|_N = \left.\frac{\partial p}{\partial N}\right|_V$$

perturbation	V	P
Hydrostatic pressure	volume	electronic pressure

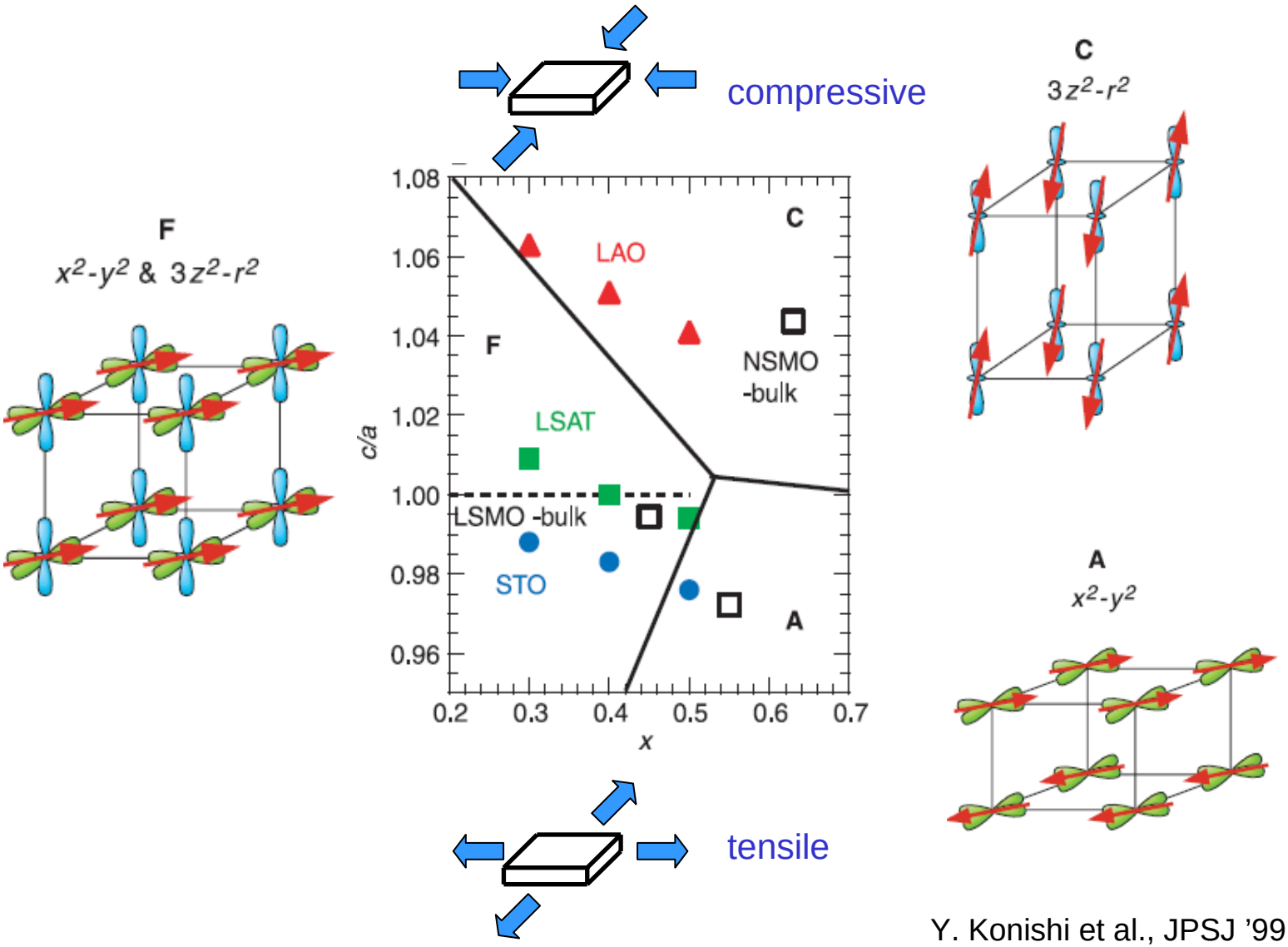
Other structural deformation:

$$\frac{\partial^2 F}{\partial D \partial N} = \left.\frac{\partial \mu}{\partial D}\right|_N = \left.\frac{\partial f}{\partial N}\right|_D$$

perturbation	D	f
Chemical pressure	$\langle r_A \rangle$	electronic "force"
Epitaxial strain from substrate	c/a	electronic "force"

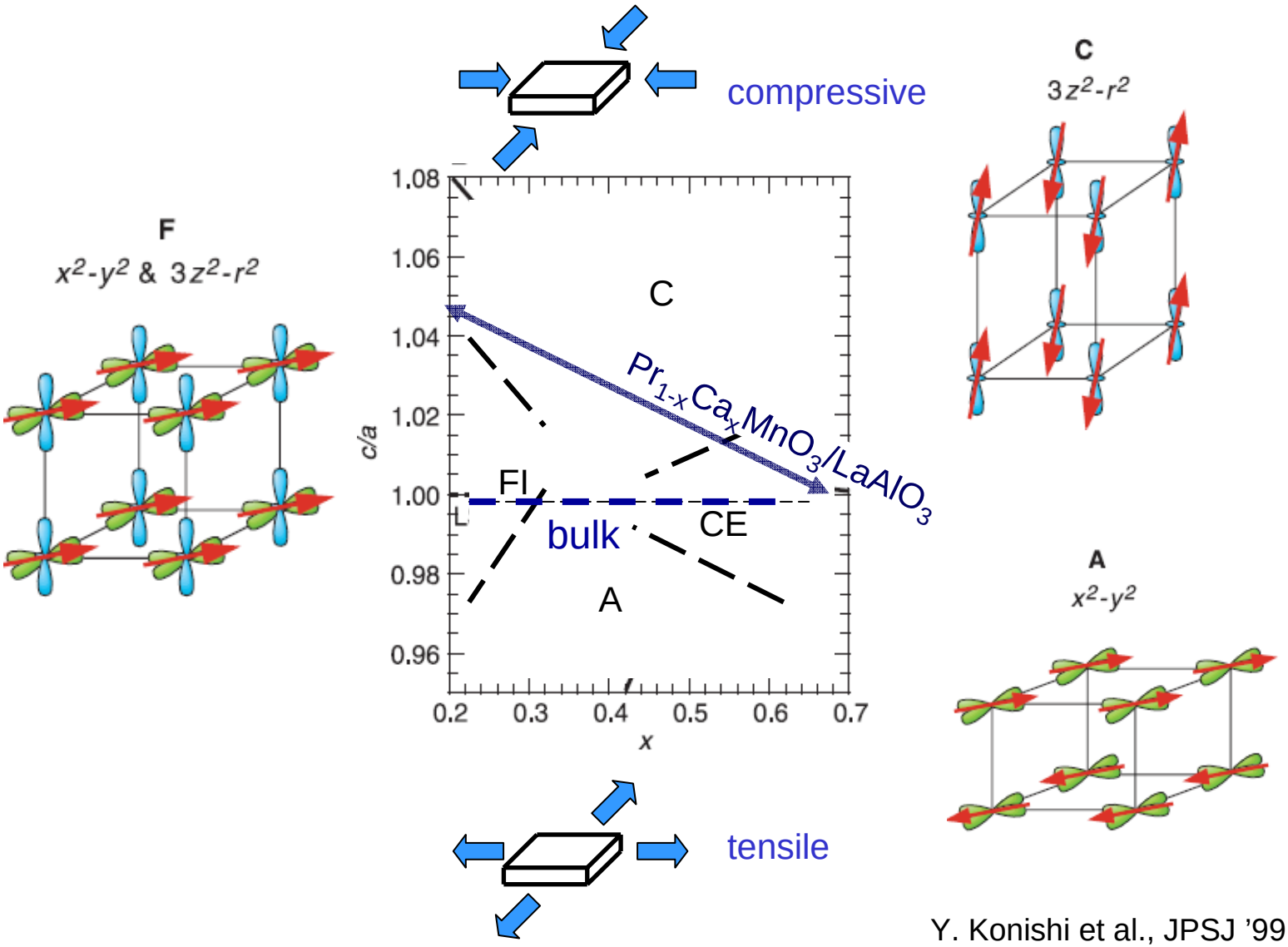


$La_{1-x}Sr_xMnO_3$ under epitaxial strain



Y. Konishi et al., JPSJ '99

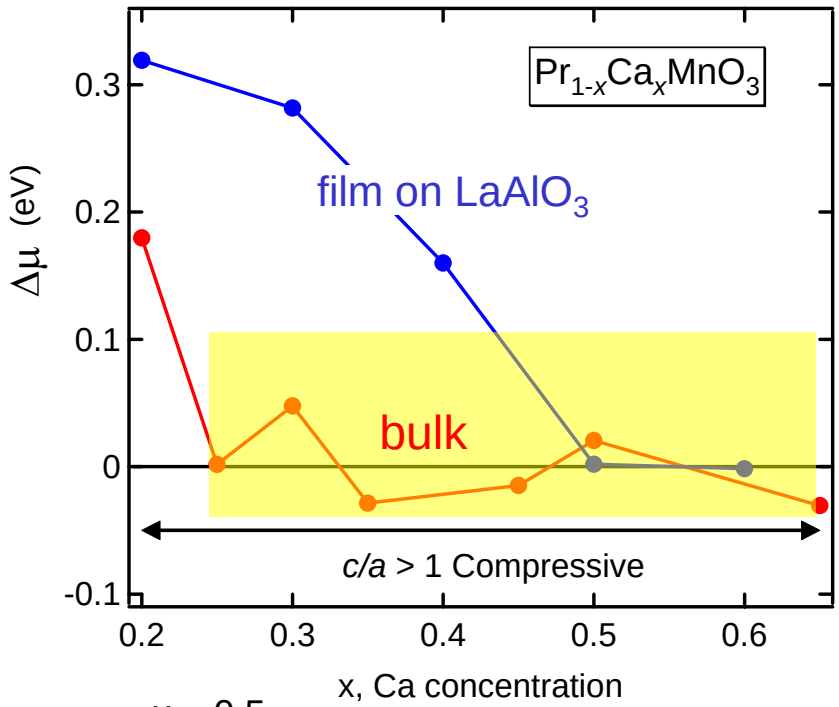
$Pr_{1-x}Ca_xMnO_3$ under epitaxial strain



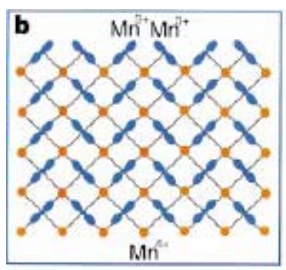
Y. Konishi et al., JPSJ '99

Chemical potential shift in $Pr_{1-x}Ca_xMnO_3$ under epitaxial strain

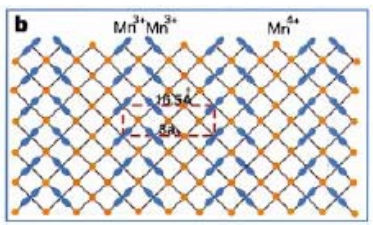
Chemical potential shifts as functions of hole concentration x



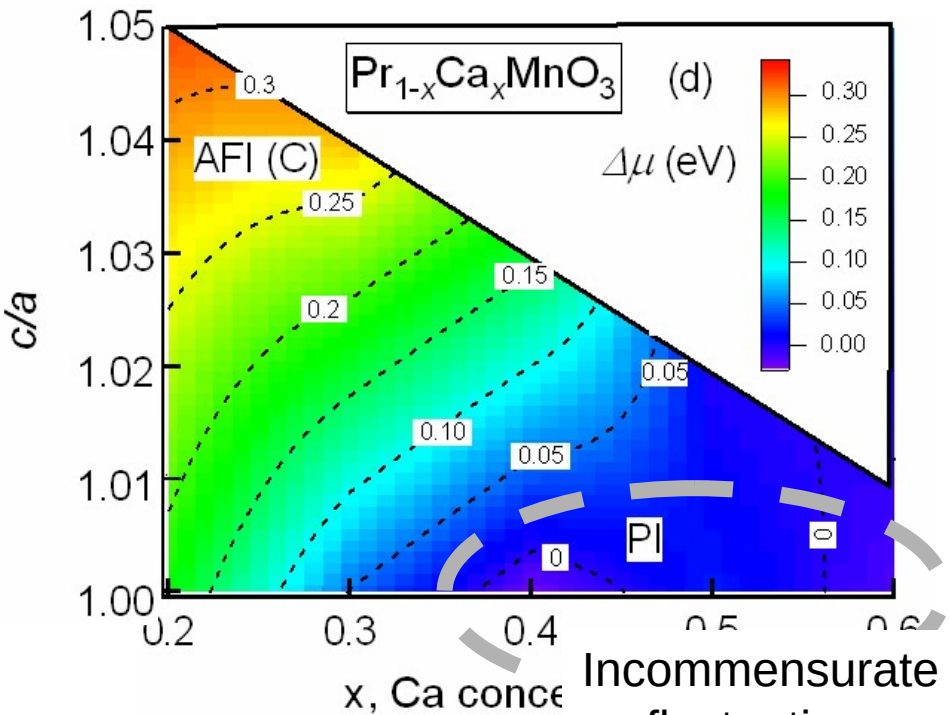
x = 0.5



x = 0.67



Chemical potential shift in *x-c/a* plane

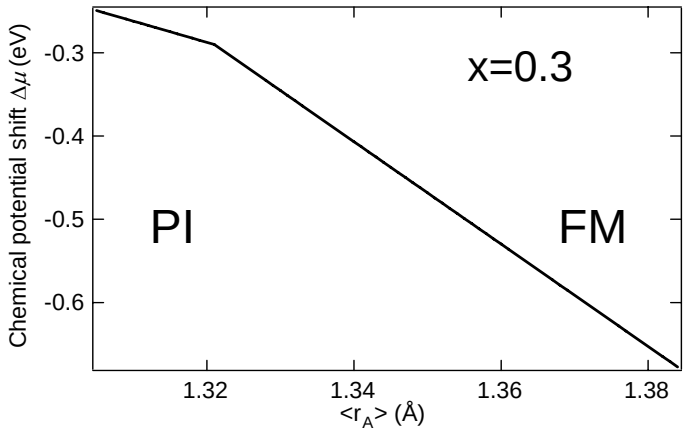


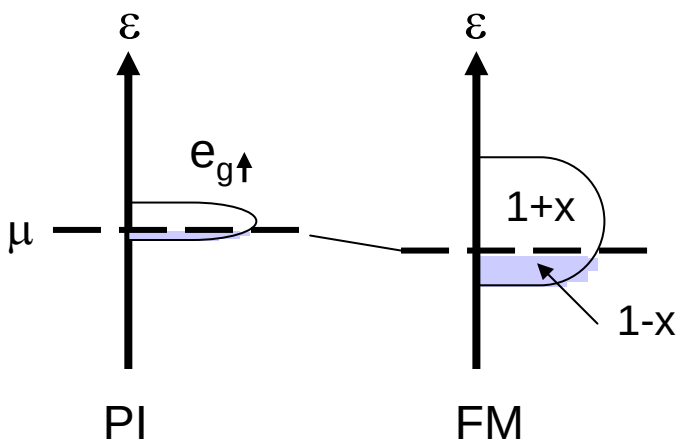
Incommensurate fluctuations

$$\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$$

H.Wadati et al., cond-mat/07

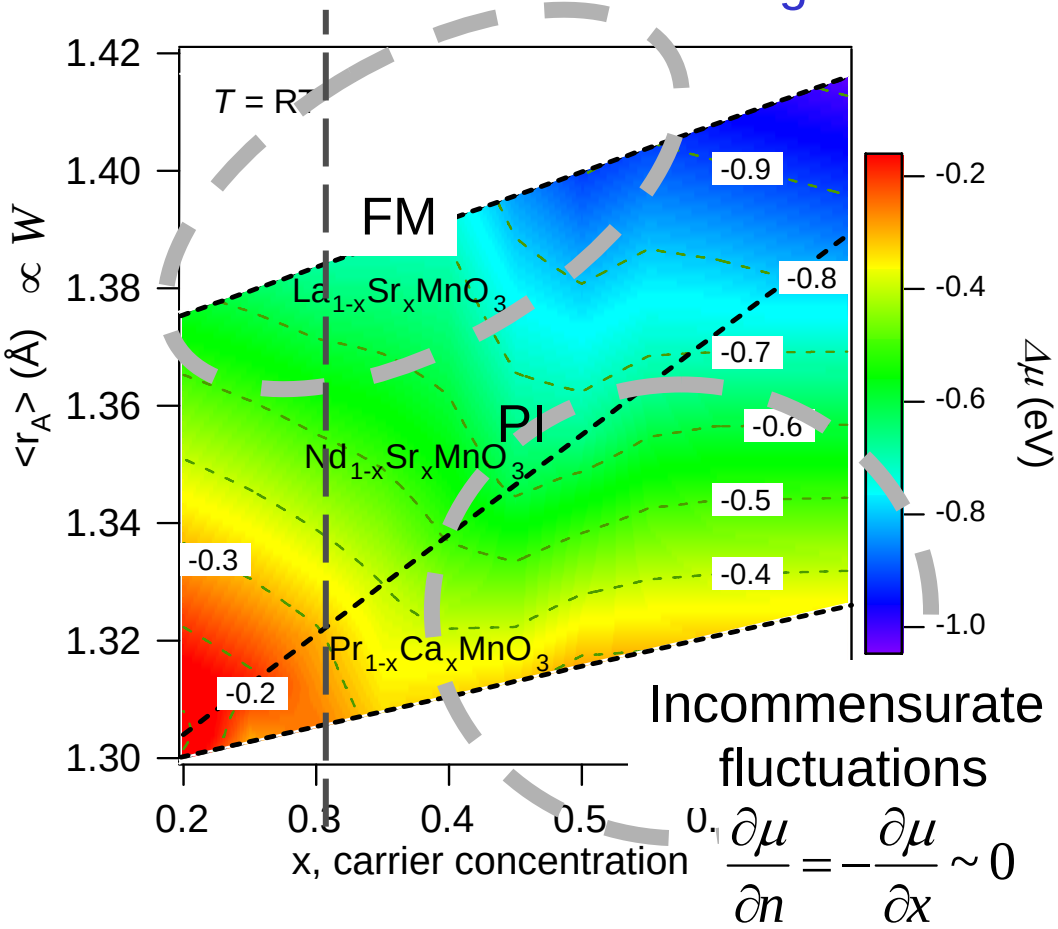
Bandwidth-dependent chemical potential shift in manganites





Theory: N. Furukawa, JPSJ '97

Chemical potential shift against bandwidth and band filling



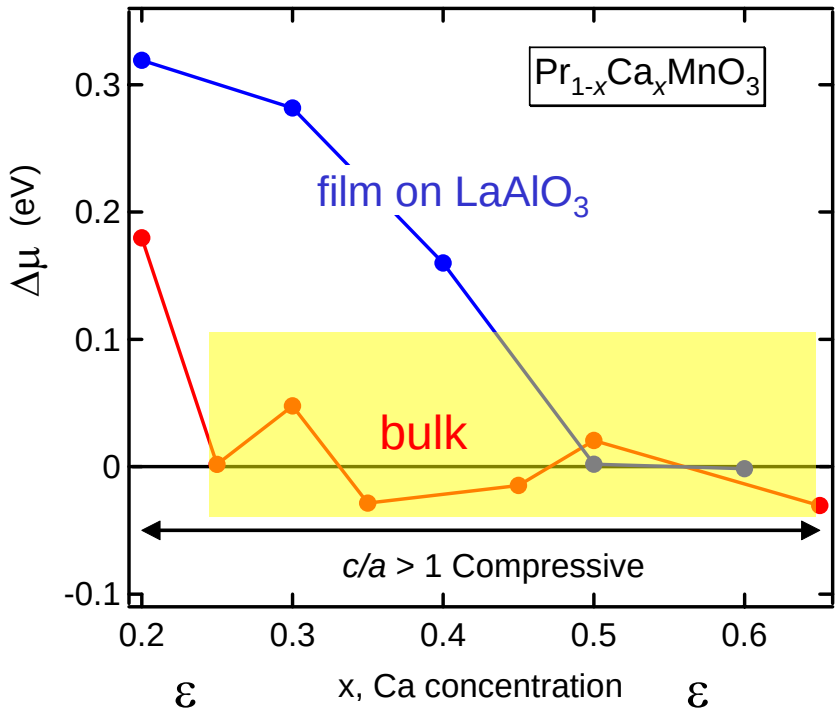
Incommensurate fluctuations

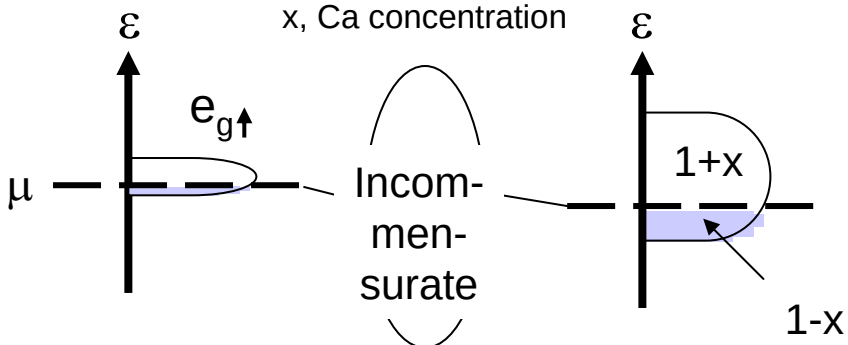
$$\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$$

K. Ebata et al.

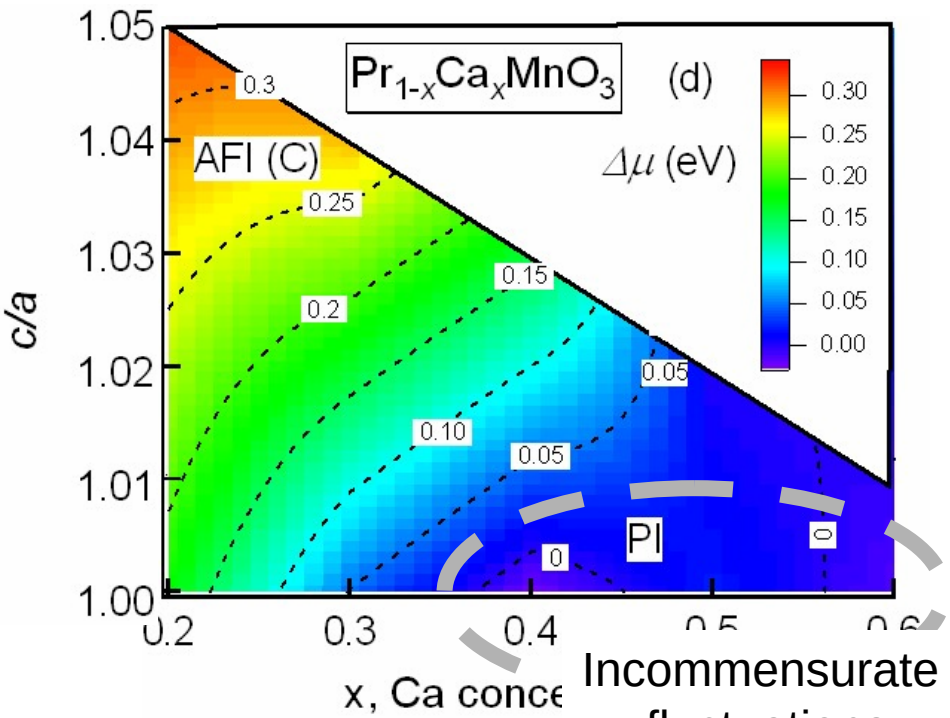
Chemical potential shift in $Pr_{1-x}Ca_xMnO_3$ under epitaxial strain

Chemical potential shifts as functions of hole concentration x





Chemical potential shift in *x-c/a* plane



Incommensurate fluctuations

$$\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$$

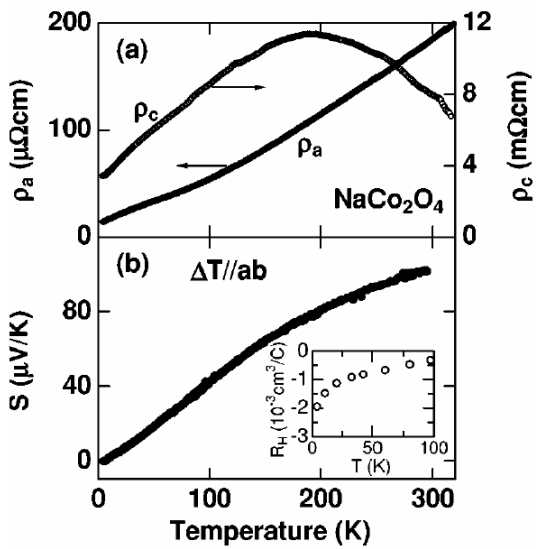
H.Wadati et al., cond-mat/07

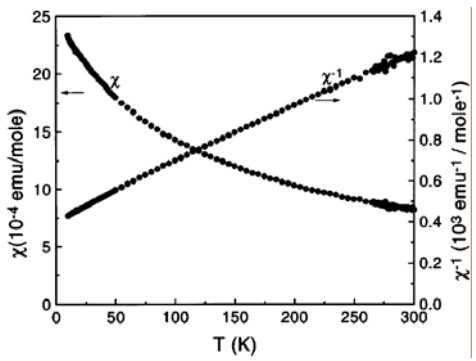
Outline

- Introduction
- How to measure
- Dependence on carrier concentration
- Dependence on structural distortion
- Dependence on temperature
- Dependence on ……

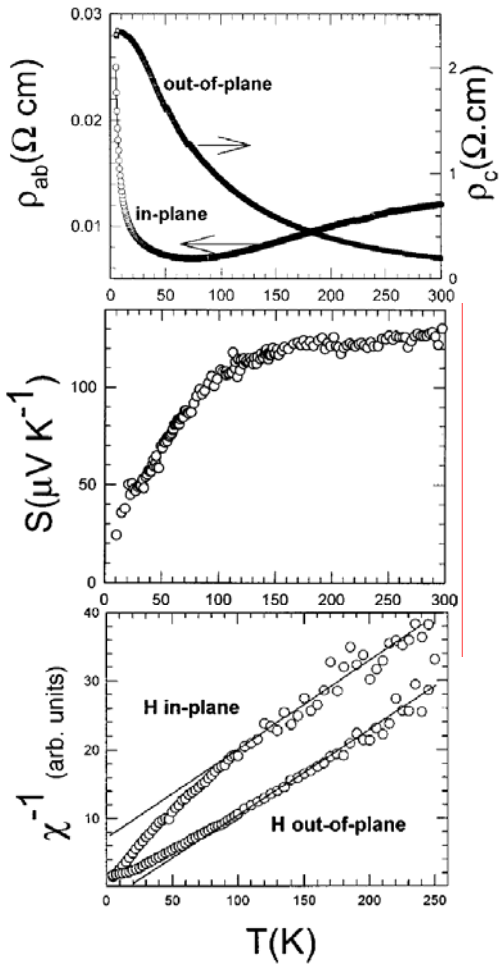
Large thermopower and metallicity in layered triangular Co oxides

$Na_{0.5}CoO_2$

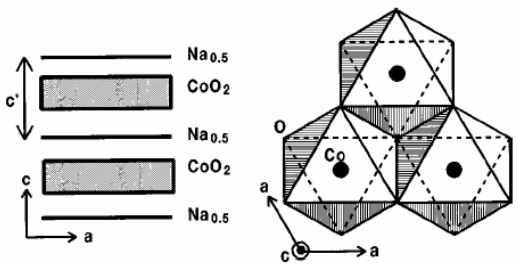




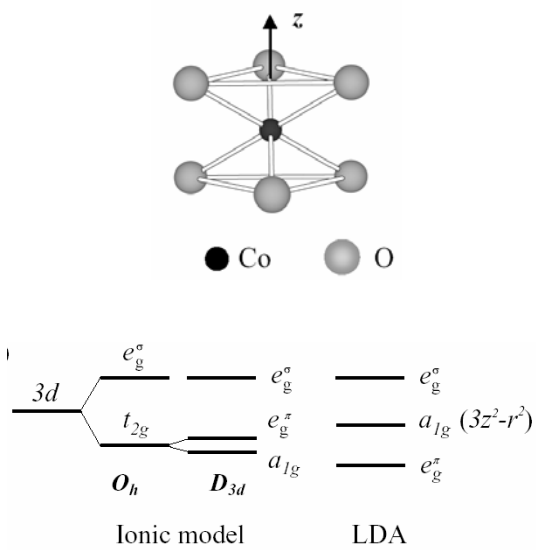
$Ca_3Co_4O_9$



layered triangular lattice



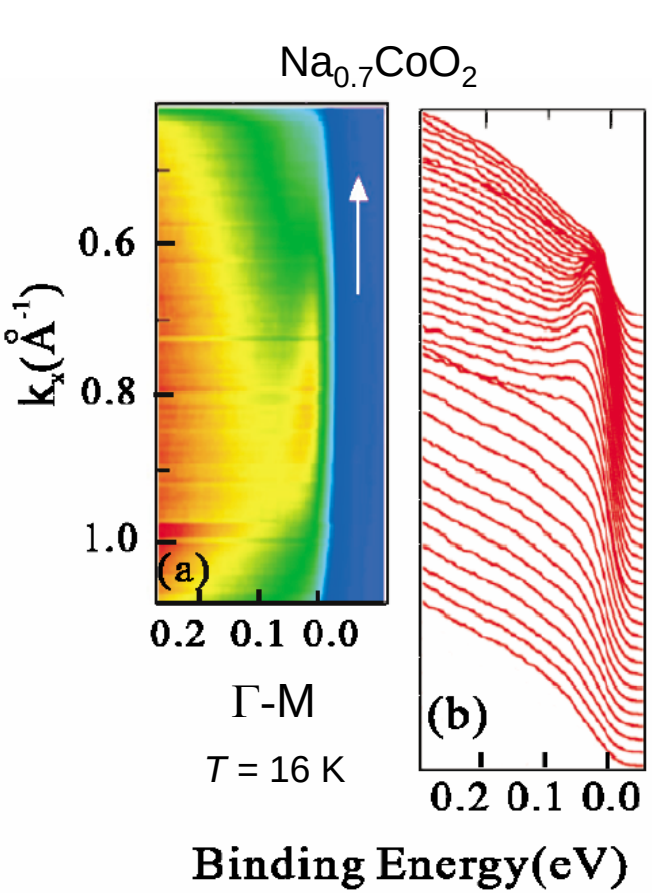
distorted octahedron

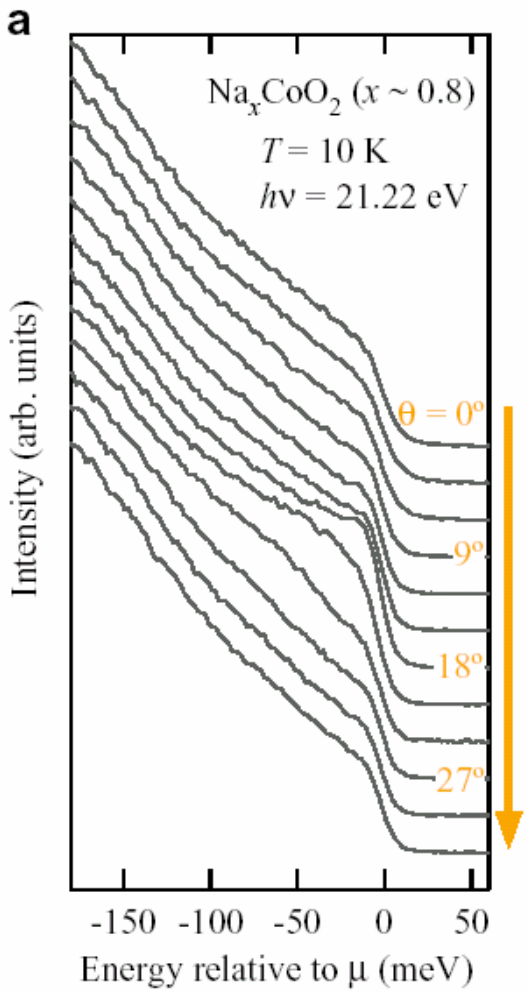


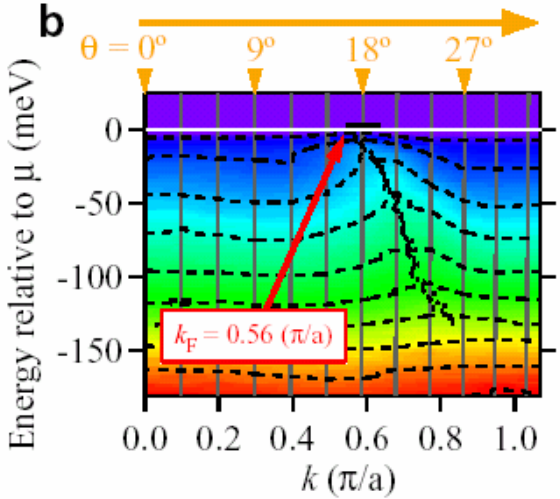
I. Terasaki et al., PRB '97

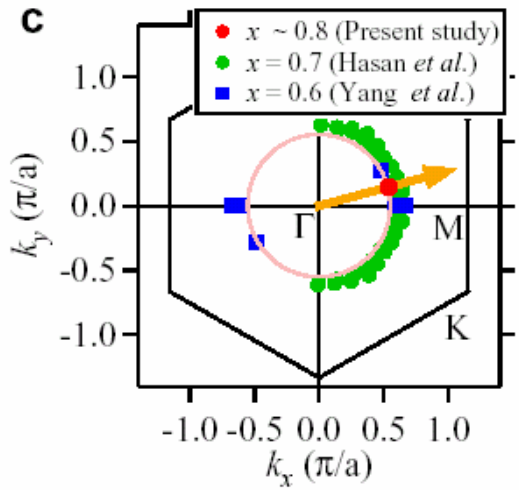
A.C. Masset et al., PRB '00.

Angle-resolved photoemission spectroscopy (ARPES) of Na_xCoO_2





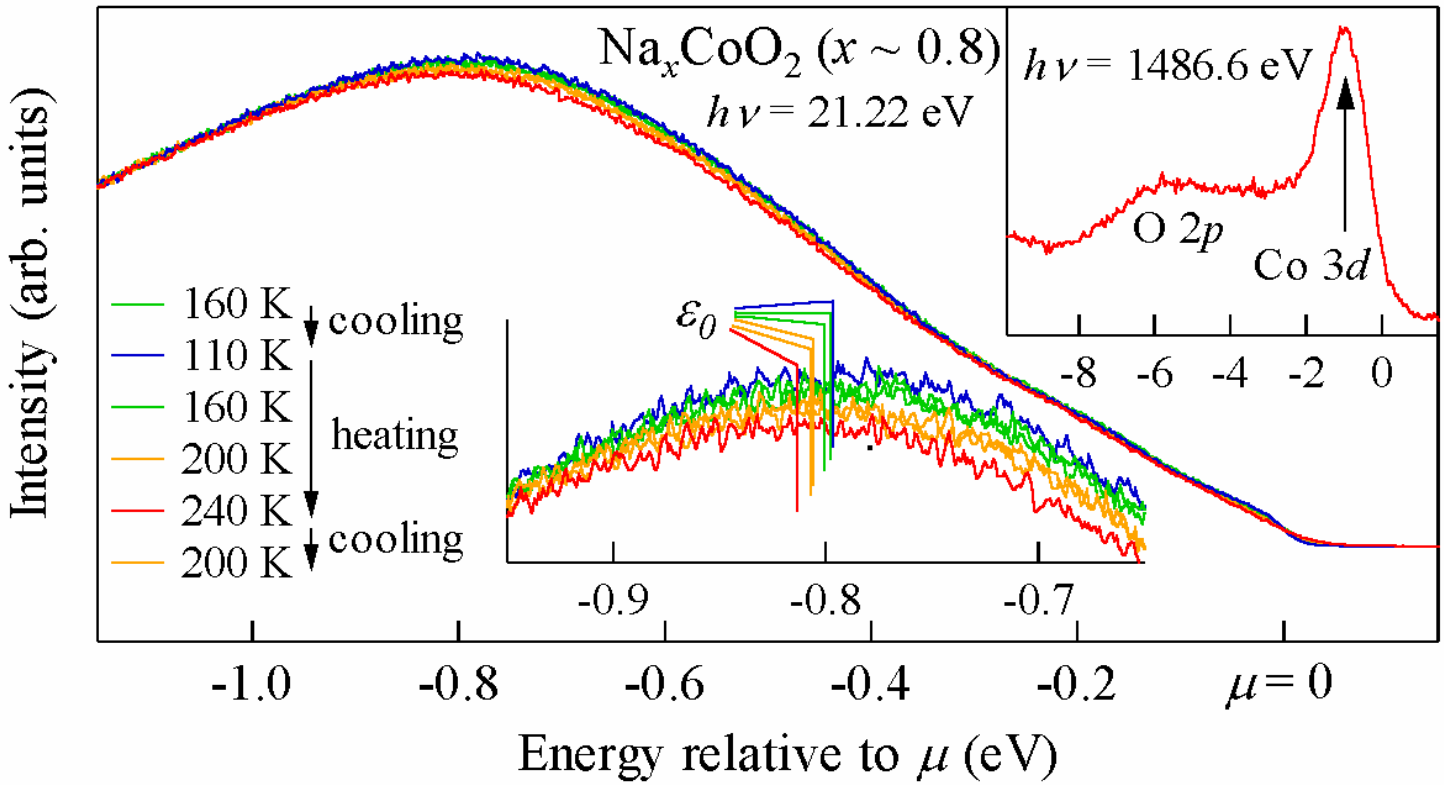




M.Z. Hasan et al., PRL 2004

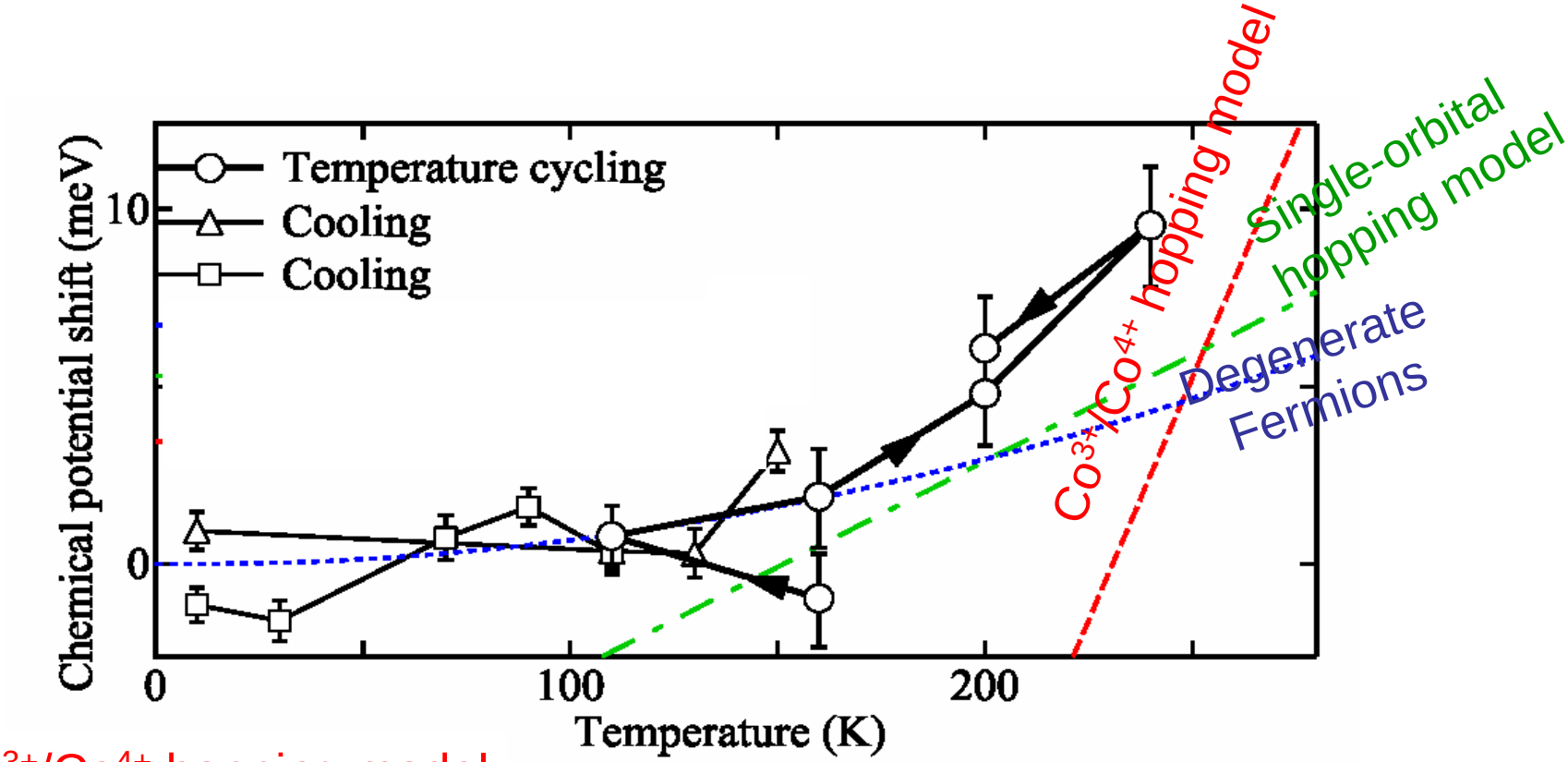
Y. Ishida et al., cond-mat/05

Temperature dependent shift of Co 3*d* peak



Y. Ishida et al., cond-mat/05

Cross-over from degenerate Fermions to ionic hopping in Na_xCoO_2



Co^{3+}/Co^{4+} hopping model

$$\frac{\partial \mu}{\partial T} = -k_B \ln\left(\frac{g_3}{g_4}\frac{1-x}{x}\right)$$

g_3 = 6 for LS Co^{4+}

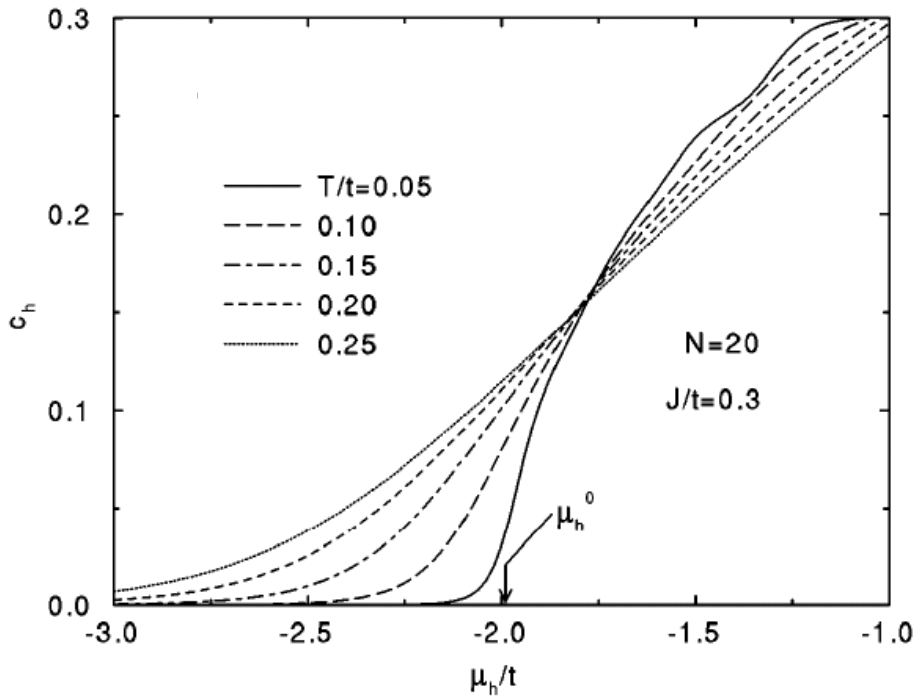
g_4 = 1 for LS Co^{3+}

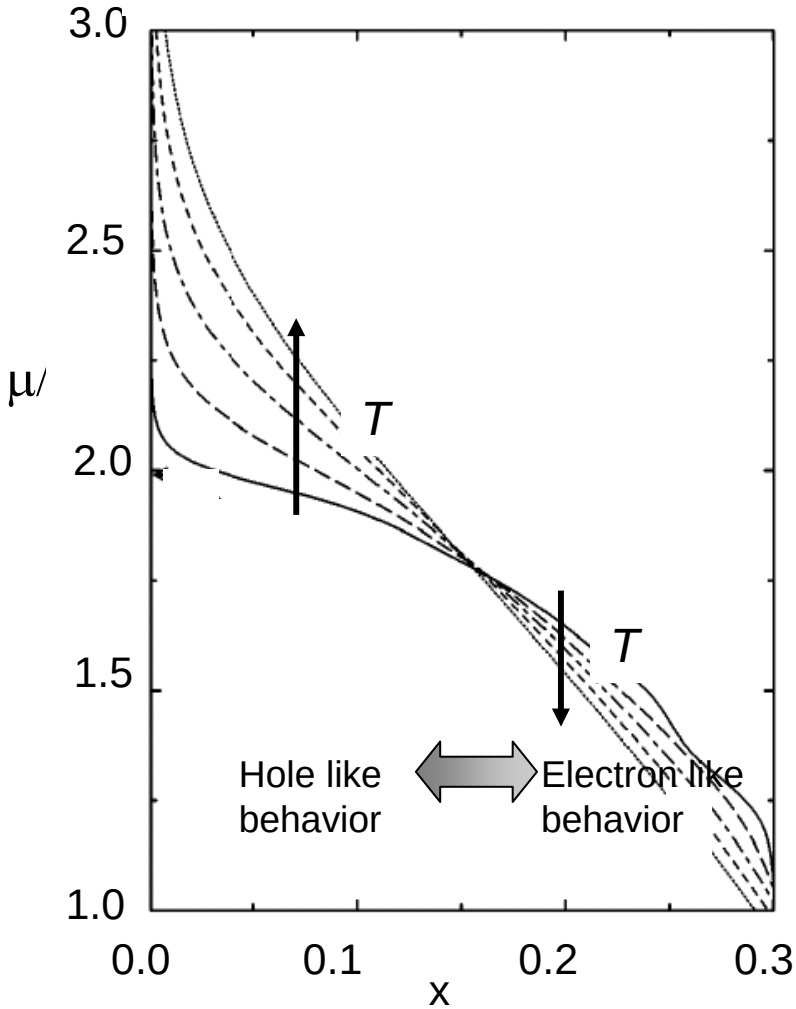
W. Koshibae et al., PRB '00

Y. Ishida et al., cond-mat/05

Temperature-dependence of chemical potential in cuprates

t-J model calculation

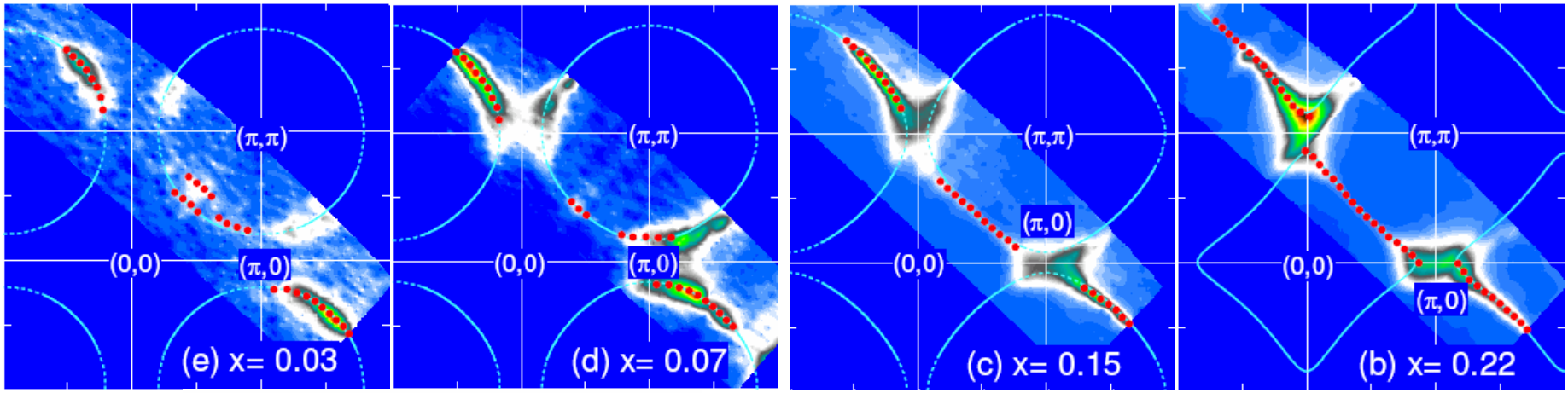


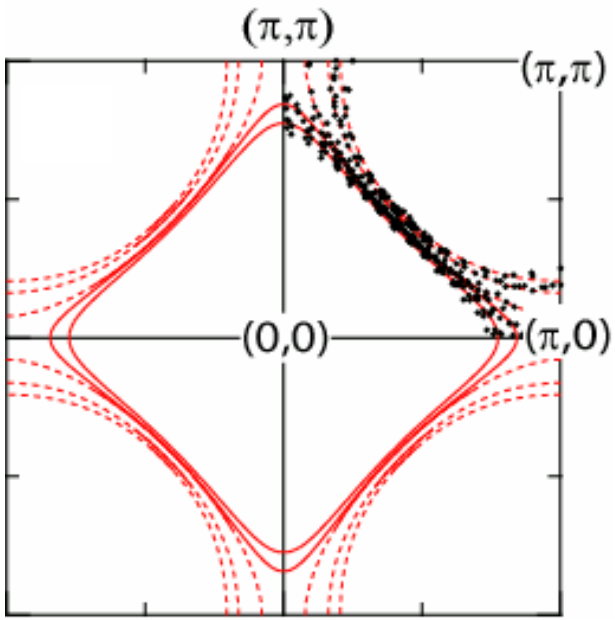


J. Jaklic and P. Prelovsek, PRL '96

Fermi surface in $La_{2-x}Sr_xCuO_4$

Hole-like ⟷ Electron-like





Tight binding fit: $E(\boldsymbol{k}) = -2t(\cos k_x a + \cos k_y a) - 4t'\cos k_x a \cos k_y a - 2t''(\cos 2k_x a + \cos 2k_y a)$

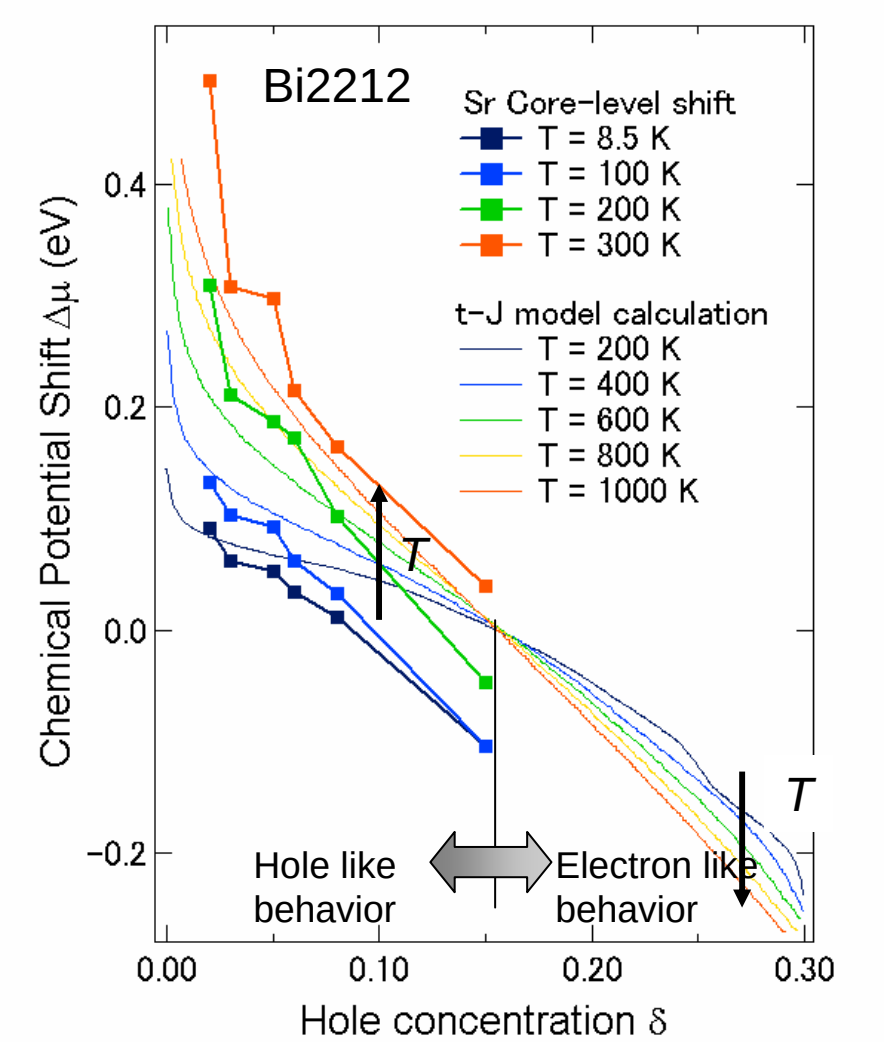
Tight-binding fit

"Remnant" Fermi surface

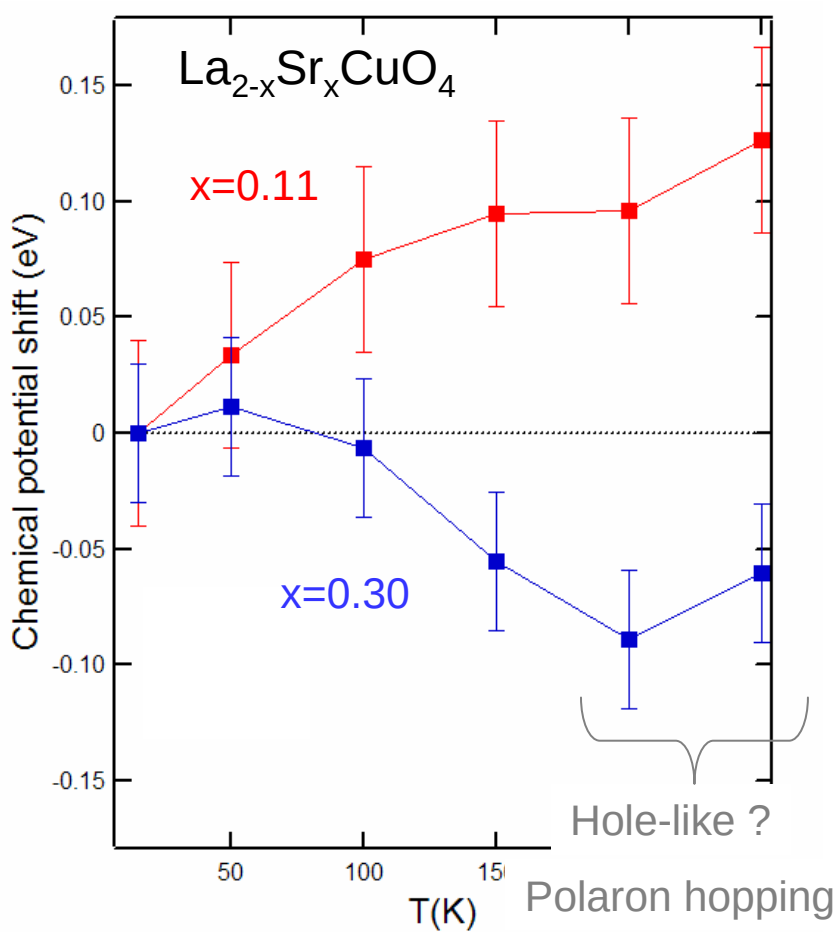
Intensity peak in k-space

T. Yoshida et al., PRB '06

Temperature-dependence of chemical potential in cuprates

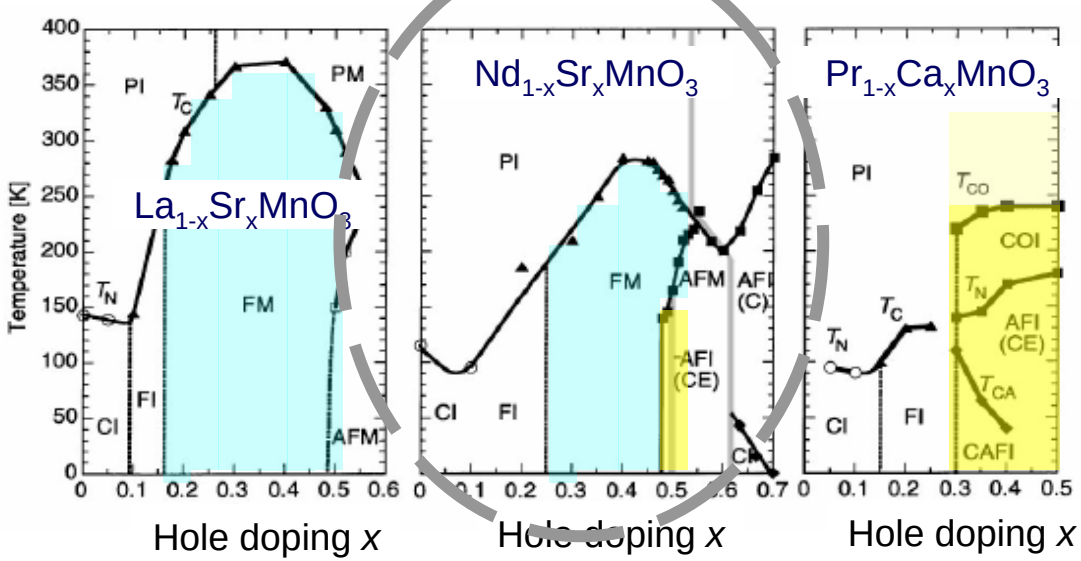


K. Tanaka et al., Thesis

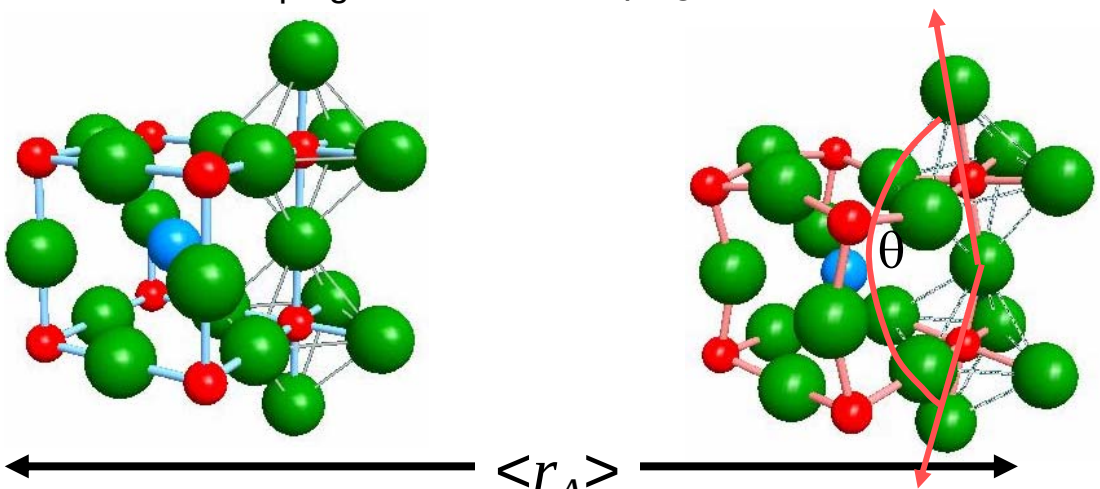


W. Malaeb et al

Band-width control in manganites



Y. Tomioka and Y. Tokura

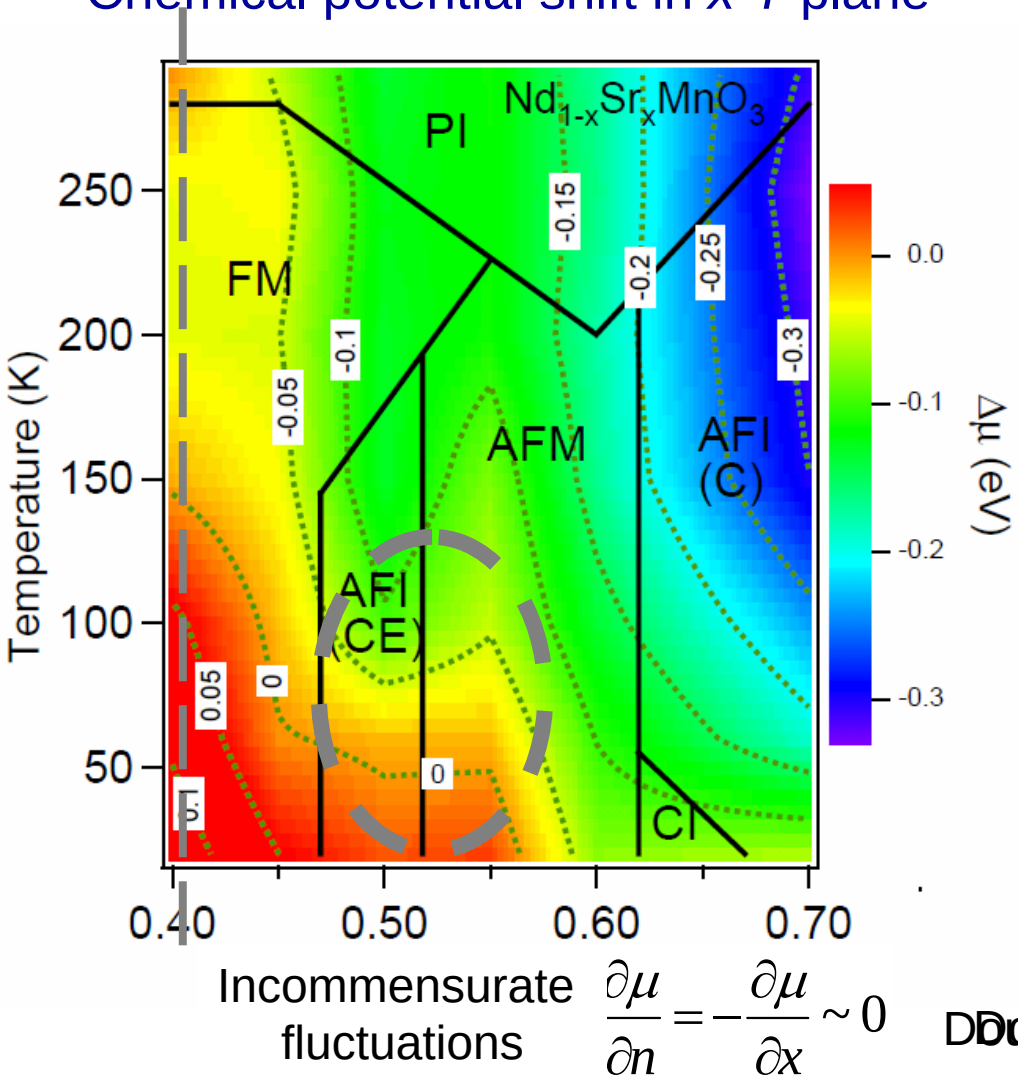


Bandwidth:

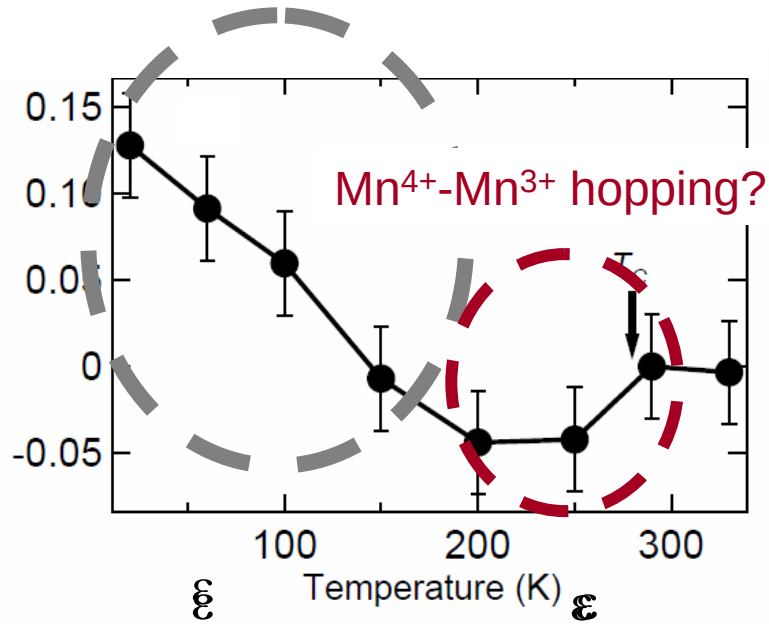
$W \propto \cos^2\theta$

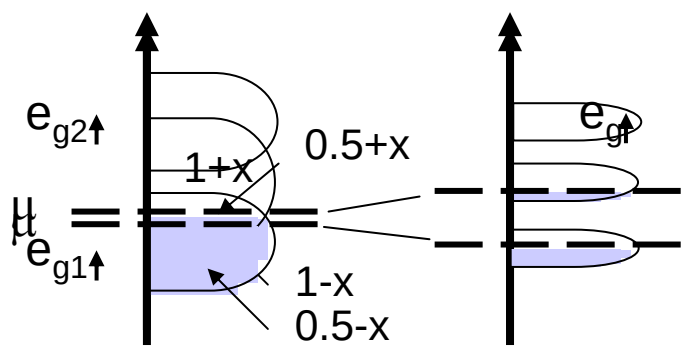
Temperature-dependent chemical potential shift due to double exchange?

Chemical potential shift in *x*-*T* plane



Incommensurate fluctuations $\frac{\partial \mu}{\partial n} = -\frac{\partial \mu}{\partial x} \sim 0$

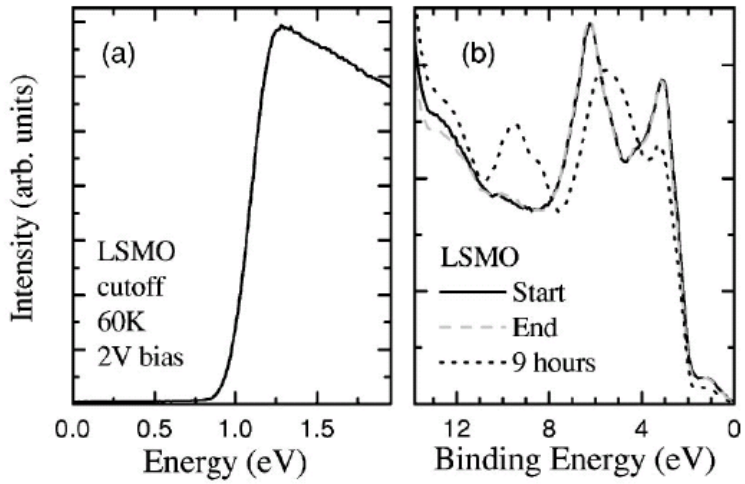


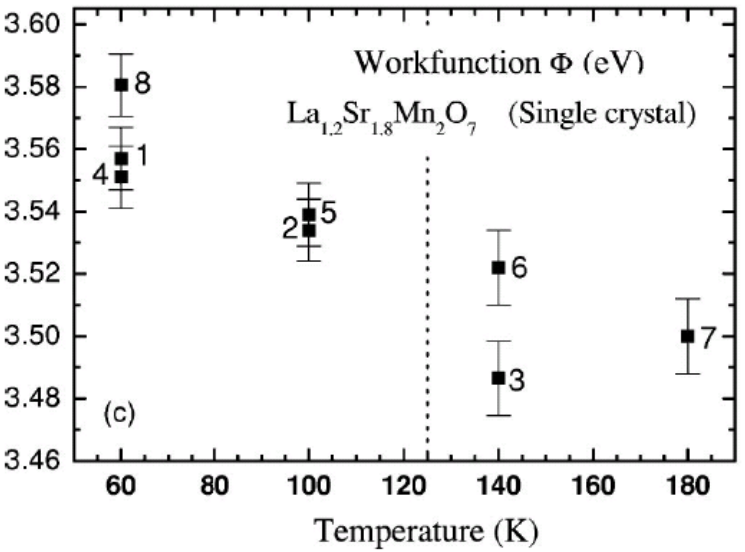


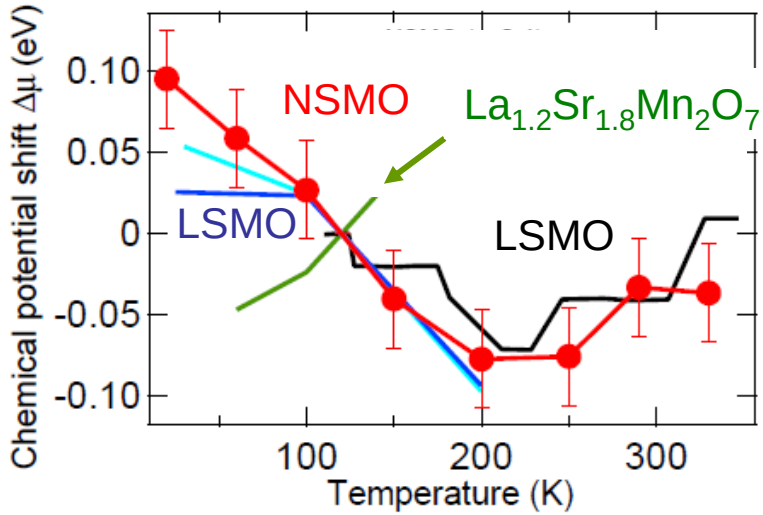
Double exchange in Jahn-Teller split e_g band

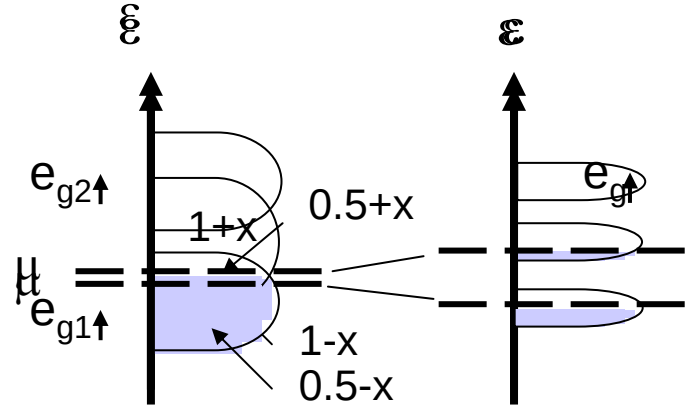
cf: pulsed neutoron, EXAFS

Temperature-dependent chemical potential shift in layered manganite $La_{1.2}Sr_{1.8}Mn_2O_7$









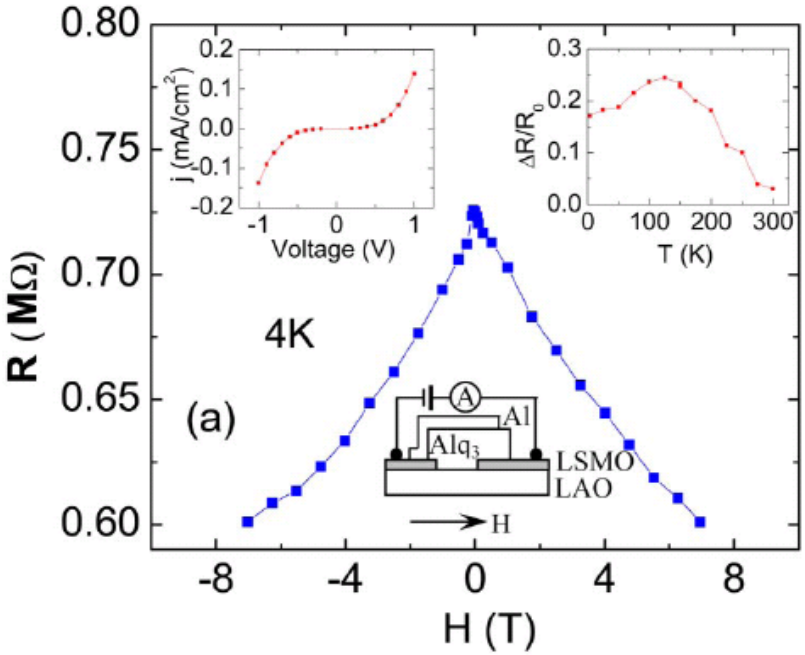
Double exchange in Jahn-Teller split e_g band

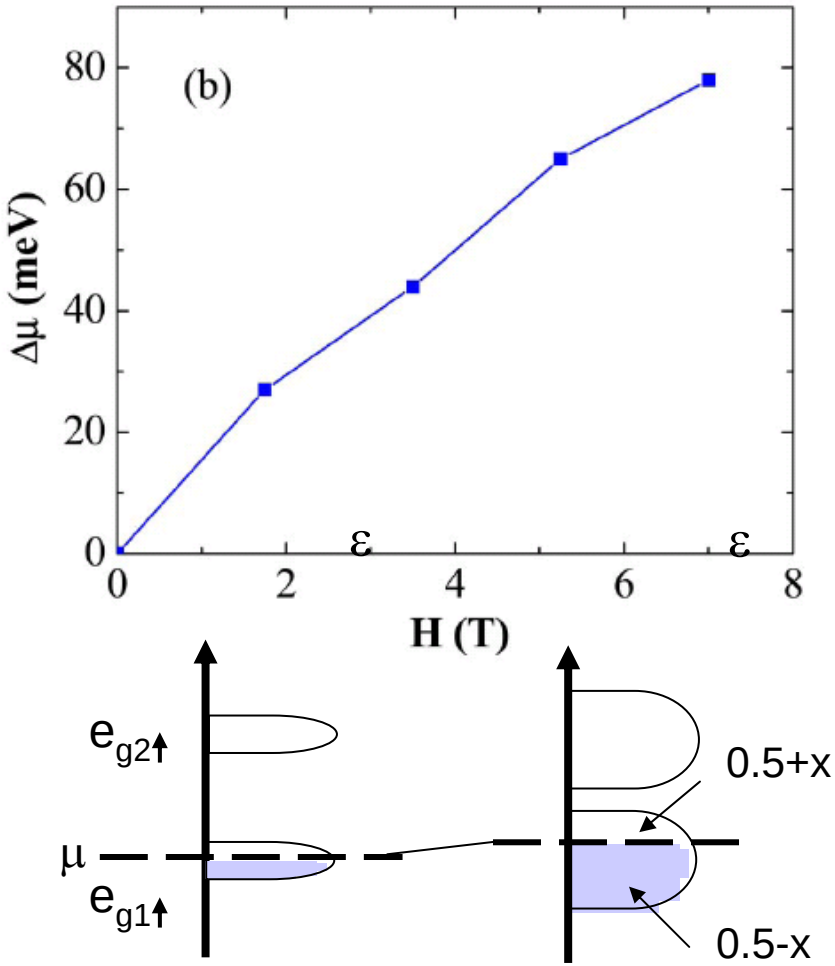
K. Shulte et al., PRB '01

Outline

- Introduction
- How to measure
- Dependence on carrier concentration
- Dependence on structural distortion
- Dependence on temperature
- Dependence on ……

Magnetic field-induced chemical potential shift in $La_{2/3}Sr_{1/3}MnO_3$/organic conductor junction

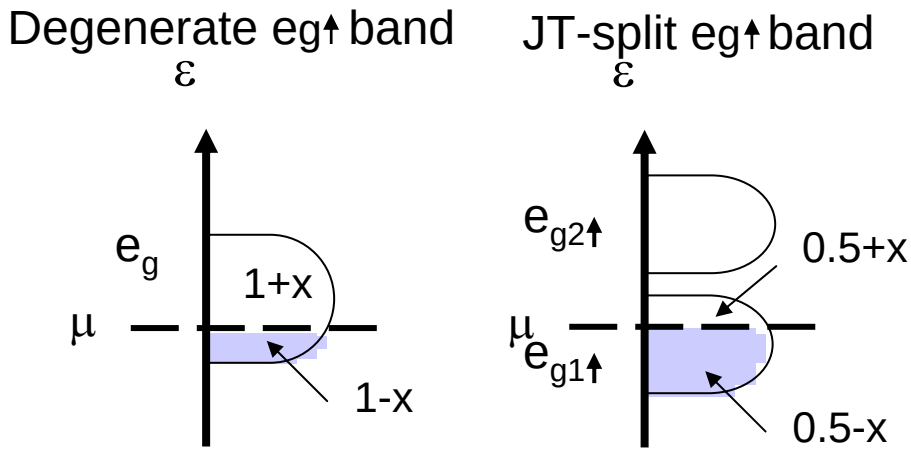




D. Wu et al., PRL '05

Double exchange in Jahn-Teller-split e_g band

Expt *vs* double-exchange model from chemical potential shift in manganites



Doping	OK	OK
Chemical pressure	OK	NG
Temperature		
cubic compound	NG	OK
layered compound	OK	NG
Magnetic field	NG	OK

Conclusion

- Chemical potential shift can be measured by several methods including photoemission spectroscopy and give the following unique information:
- Doping-dependent chemical potential shift
  - Fermi-liquid behavior
  - Magnitude of transport gap (< optical gap)
  - Incommensurate (“stripe”) fluctuation/order
- Pressure-dependent chemical potential shift
  - Double exchange in manganites?
- Temperature-dependent chemical potential shift
  - Degenerate Fermi liquid *vs* ionic hopping
  - Carrier sign and its change
  - Double exchange in manganites?

Previous review: A. Fujimori et al., J. Electron Spectrosc. Relat. Phenom.**124**, 127 (2002)