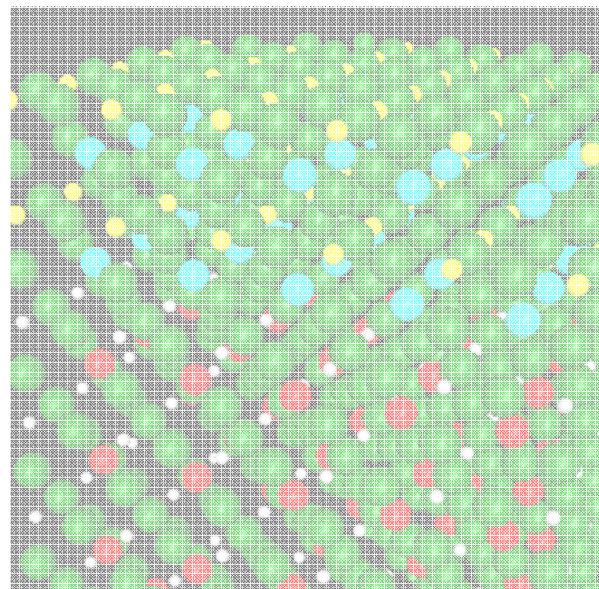


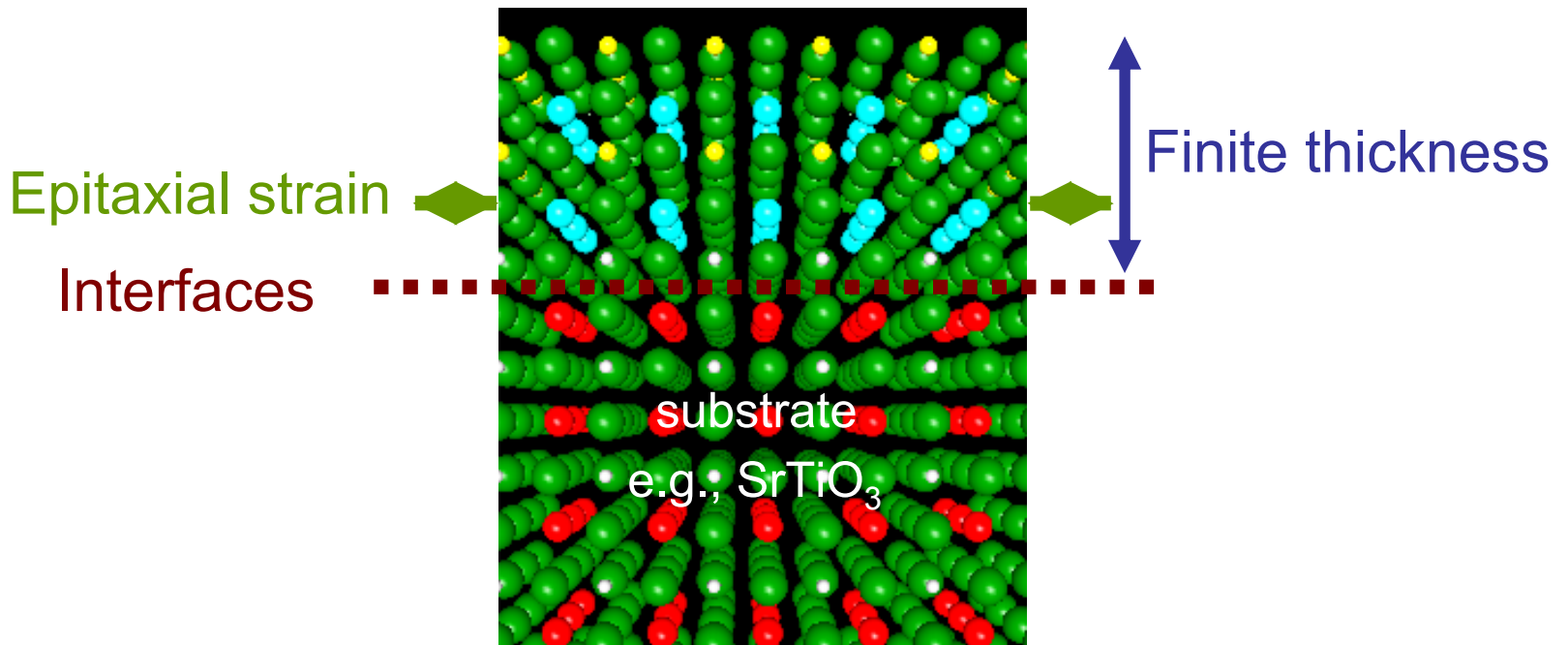
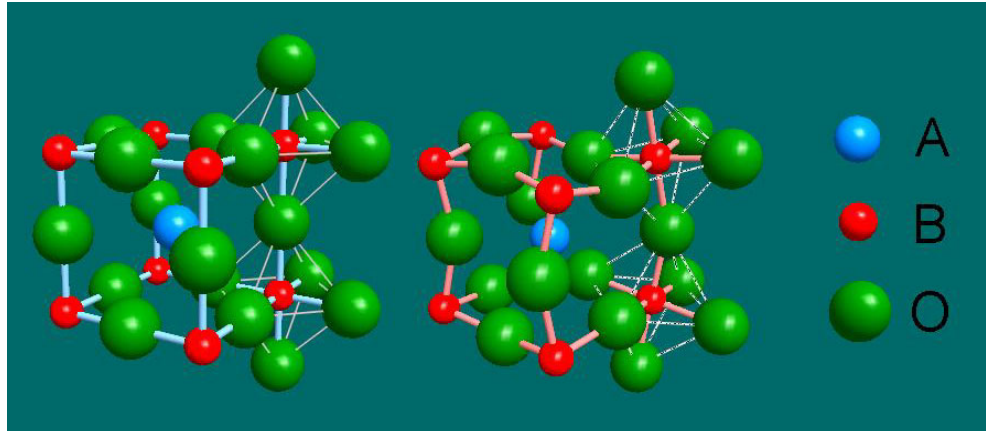
Heterostructures of transition-metal oxides

- Experiment, mainly spectroscopy -

Atsushi Fujimori
University of Tokyo

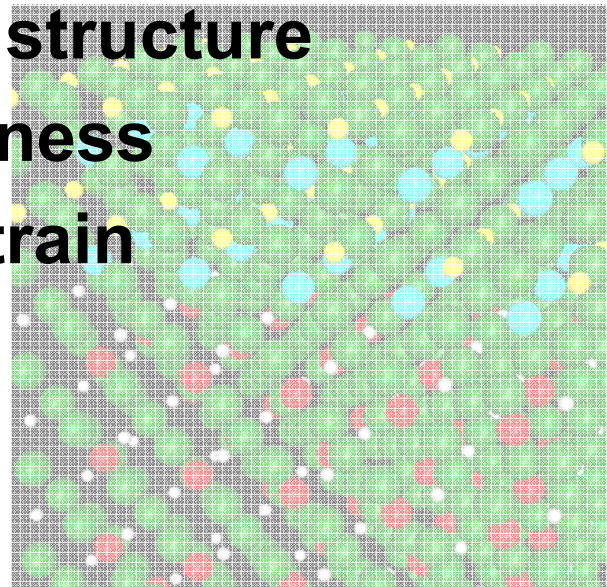


New opportunities with oxide thin films

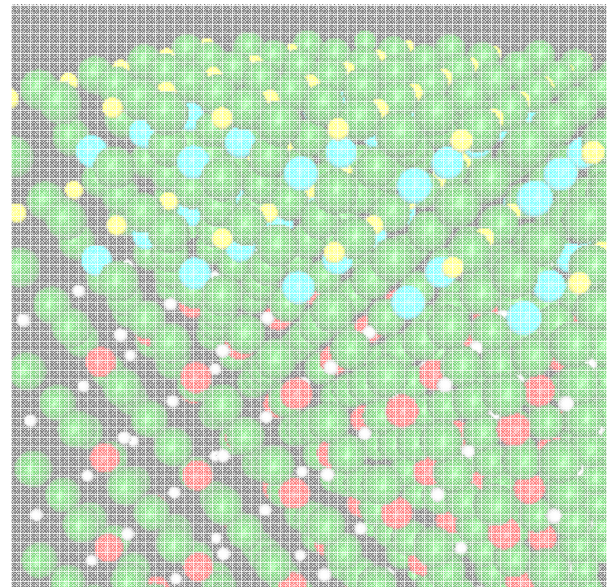


Outline

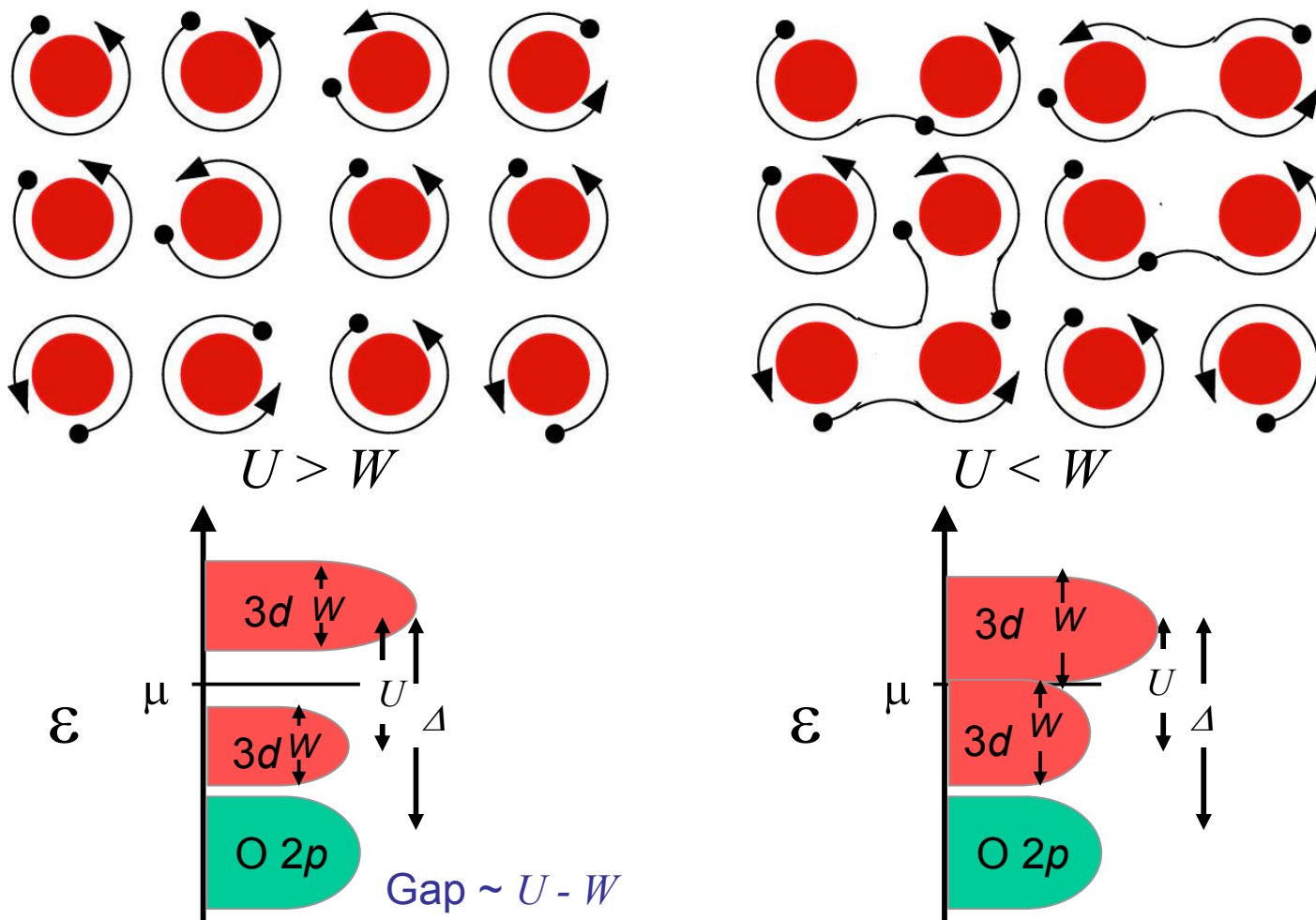
- **Electronic structure of transition-metal oxides**
- **Fabrication and characterization**
- **Interfacial electronic structure**
- **Effects of finite thickness**
- **Effects of epitaxial strain**



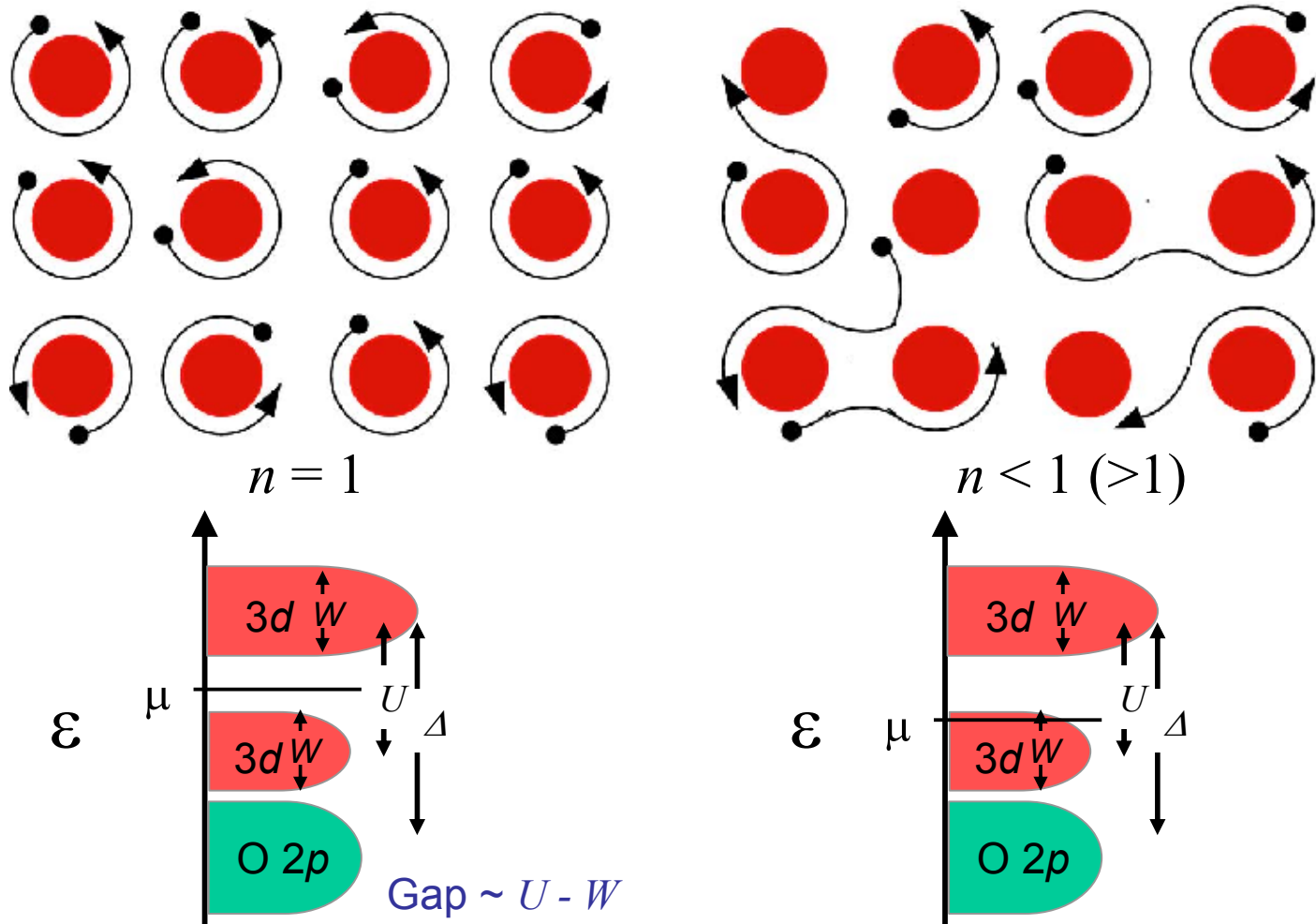
Electronic structure of transition-metal oxides



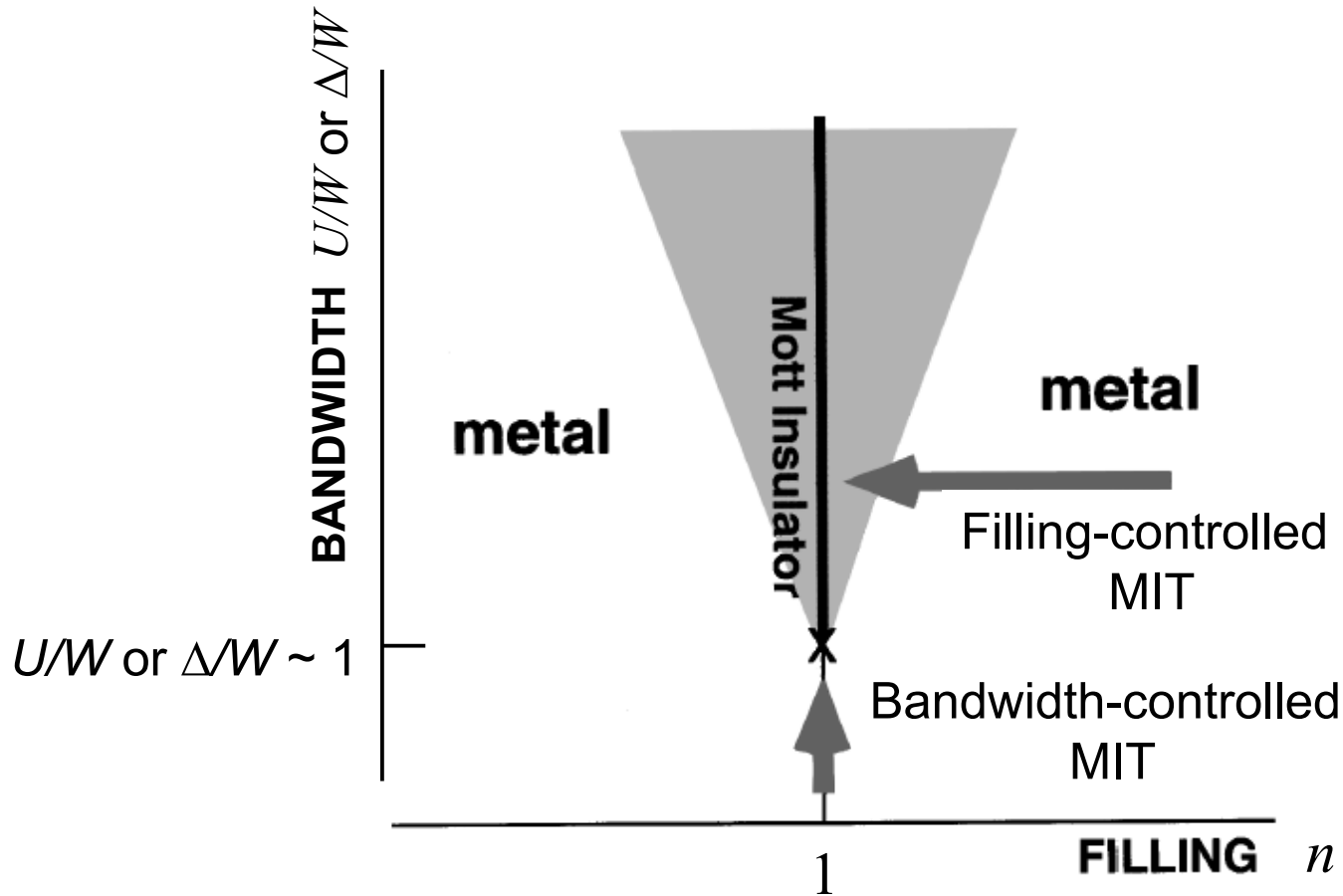
Metal-insulator transition through collapse of Mott gap – Bandwidth control



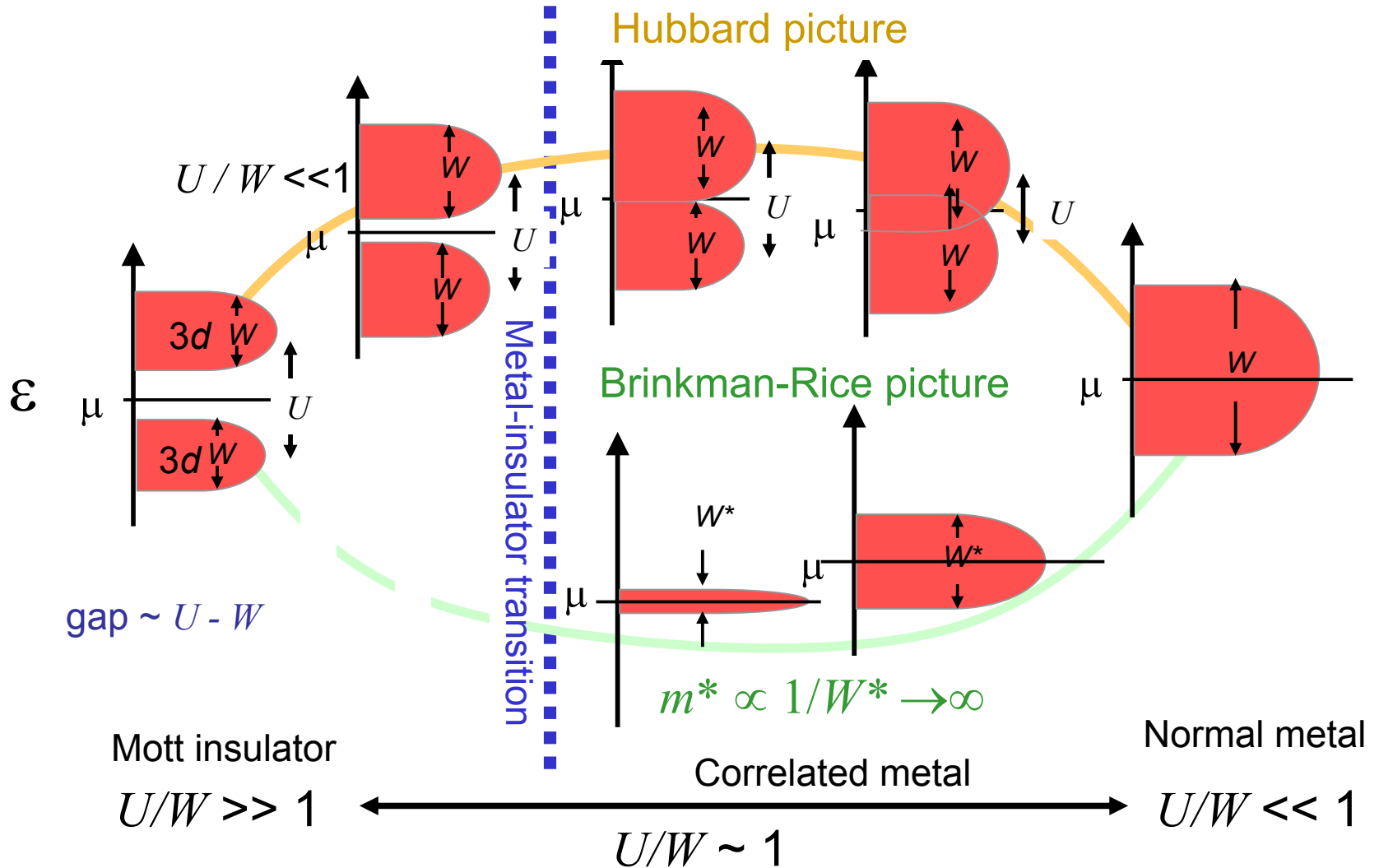
Metal-insulator transition through carrier doping into Mott insulator – Filling control



Bandwidth- versus filling-controlled metal-insulator transition

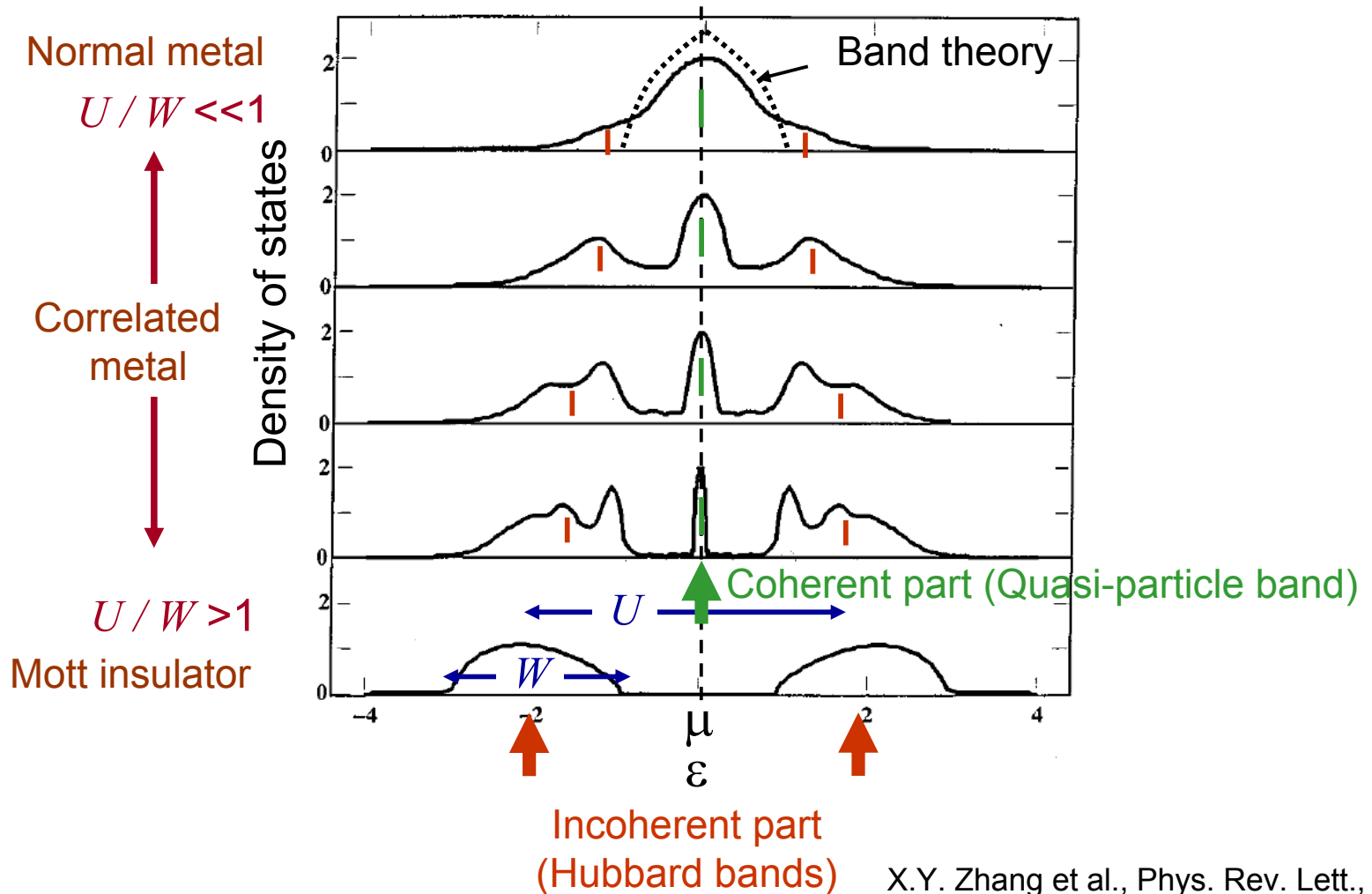


Electronic structure change across bandwidth-controlled metal-insulator transition



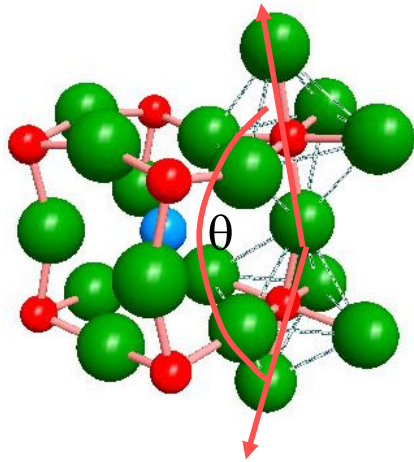
Electronic structure change across bandwidth-controlled metal-insulator transition

Dynamical mean-field theory (DMFT) calculation

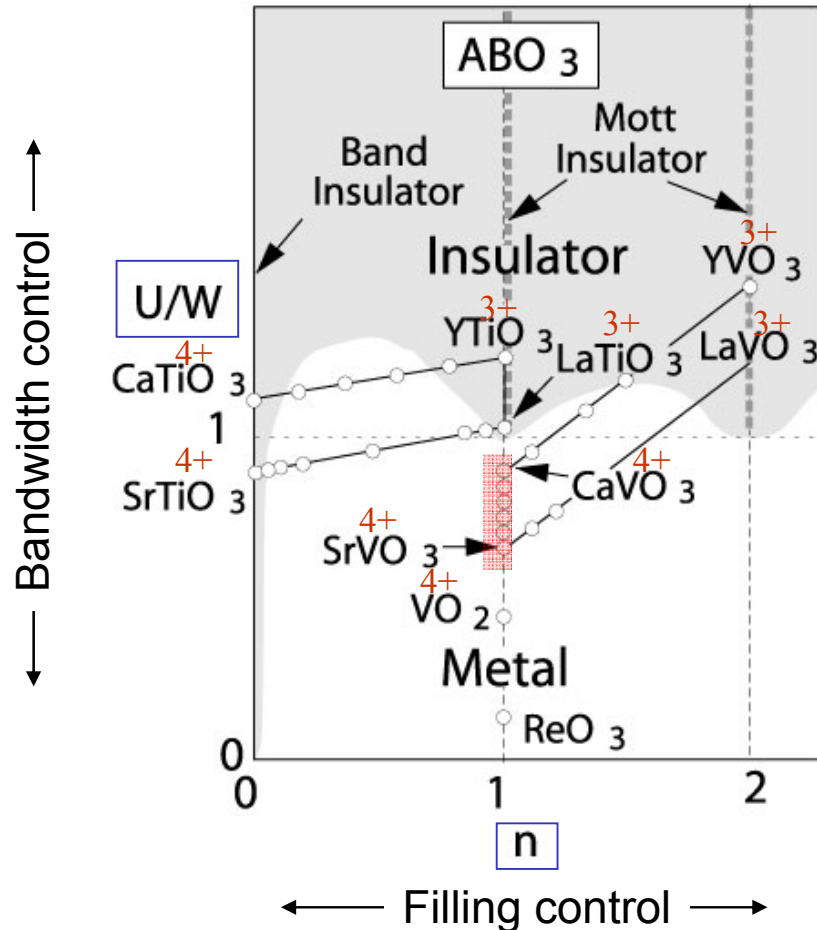
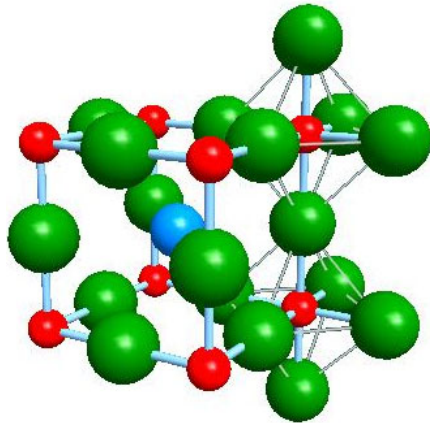


Bandwidth- versus filling-controlled in Mott-Hubbard systems

Perovskite structure

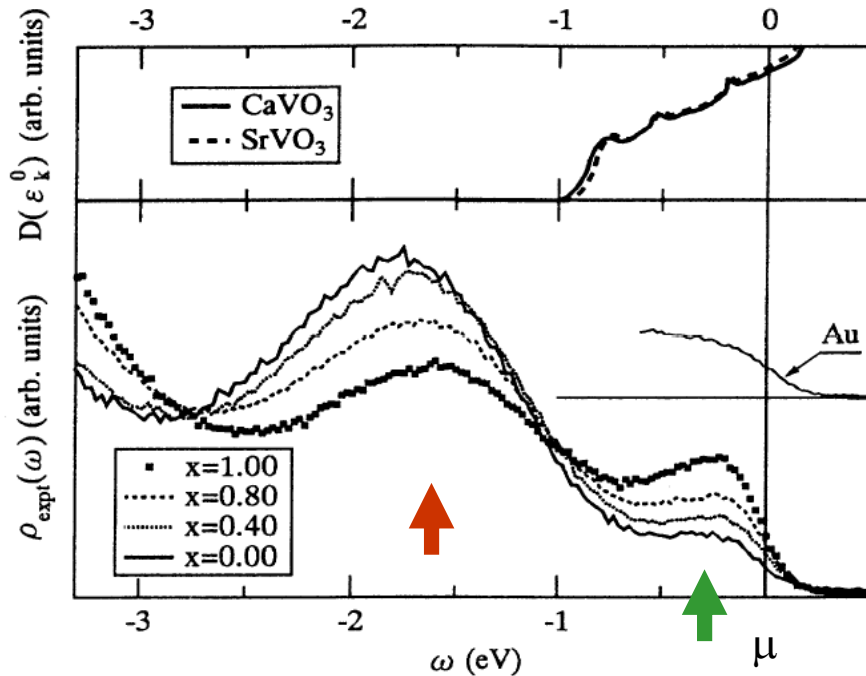


$$W \propto \cos^2\theta$$



Electronic structure change across bandwidth-controlled metal-insulator transition

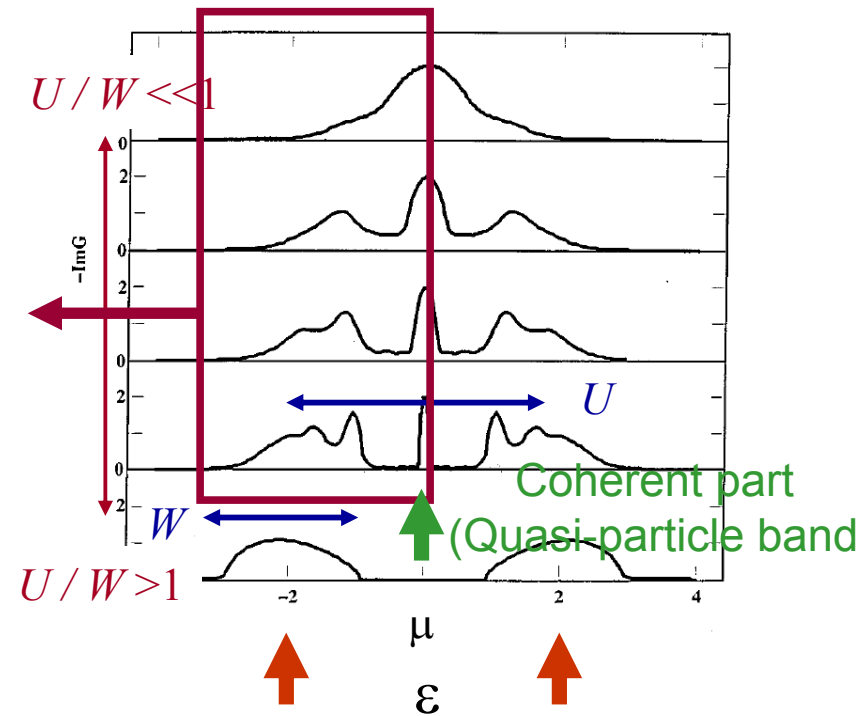
Photoemission spectra of $\text{Ca}_{1-x}\text{Sr}_x\text{VO}_3$ (d^1)



Incoherent part

Coherent part

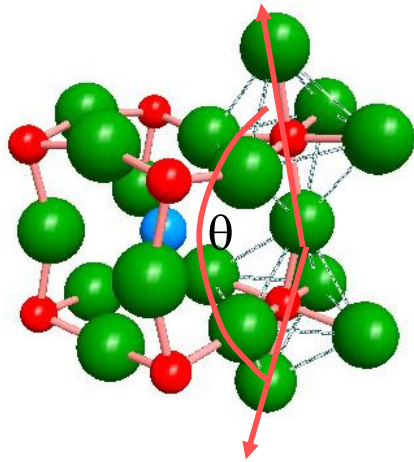
DMFT calc.



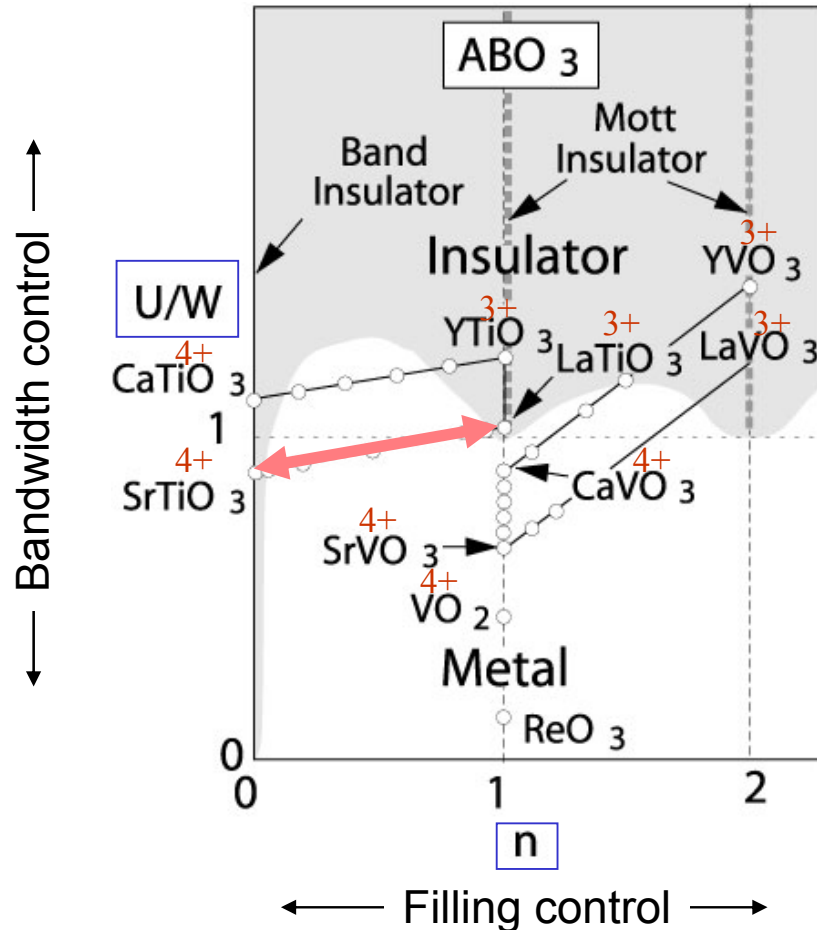
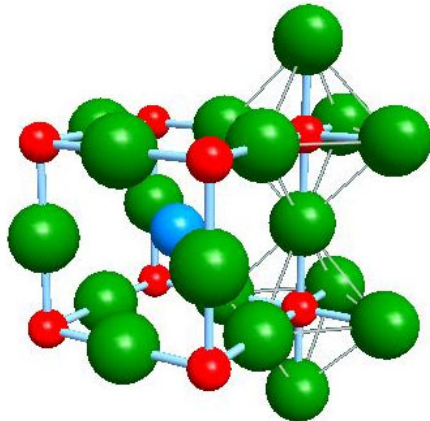
Incoherent part
(Hubbard bands)

Bandwidth- versus filling-controlled in Mott-Hubbard systems

Perovskite structure



$$W \propto \cos^2\theta$$

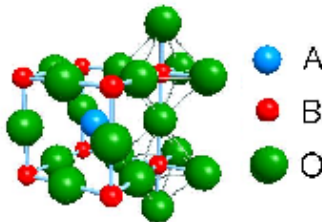
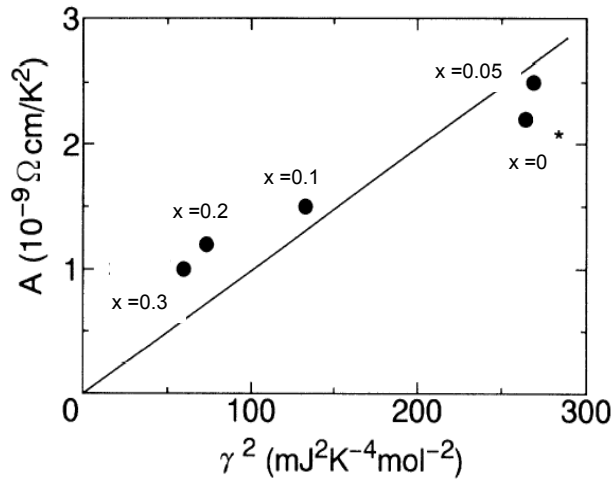


Filling-controlled Mott-Hubbard system

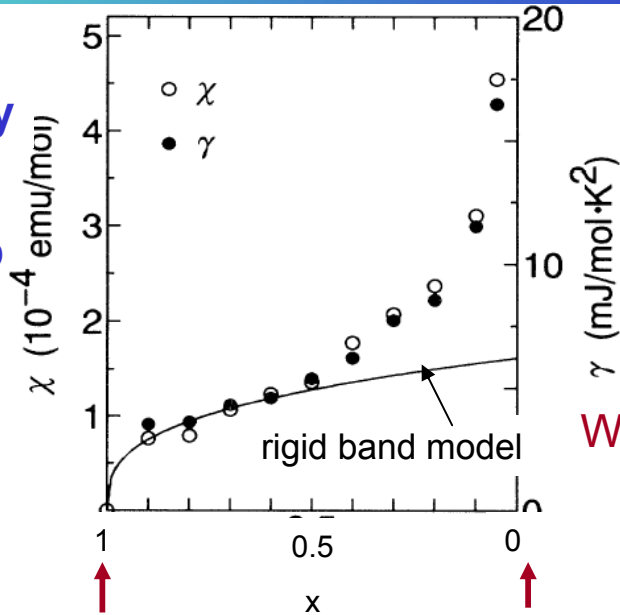
$\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$

Electronic specific heat & Pauli-paramagnetic susceptibility

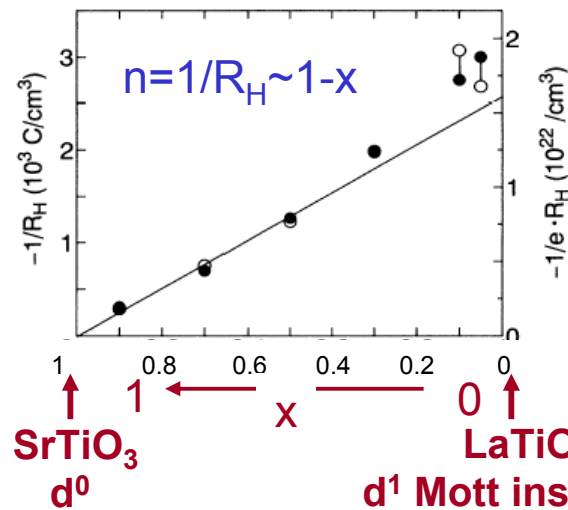
Kodowaki-Woods relationship



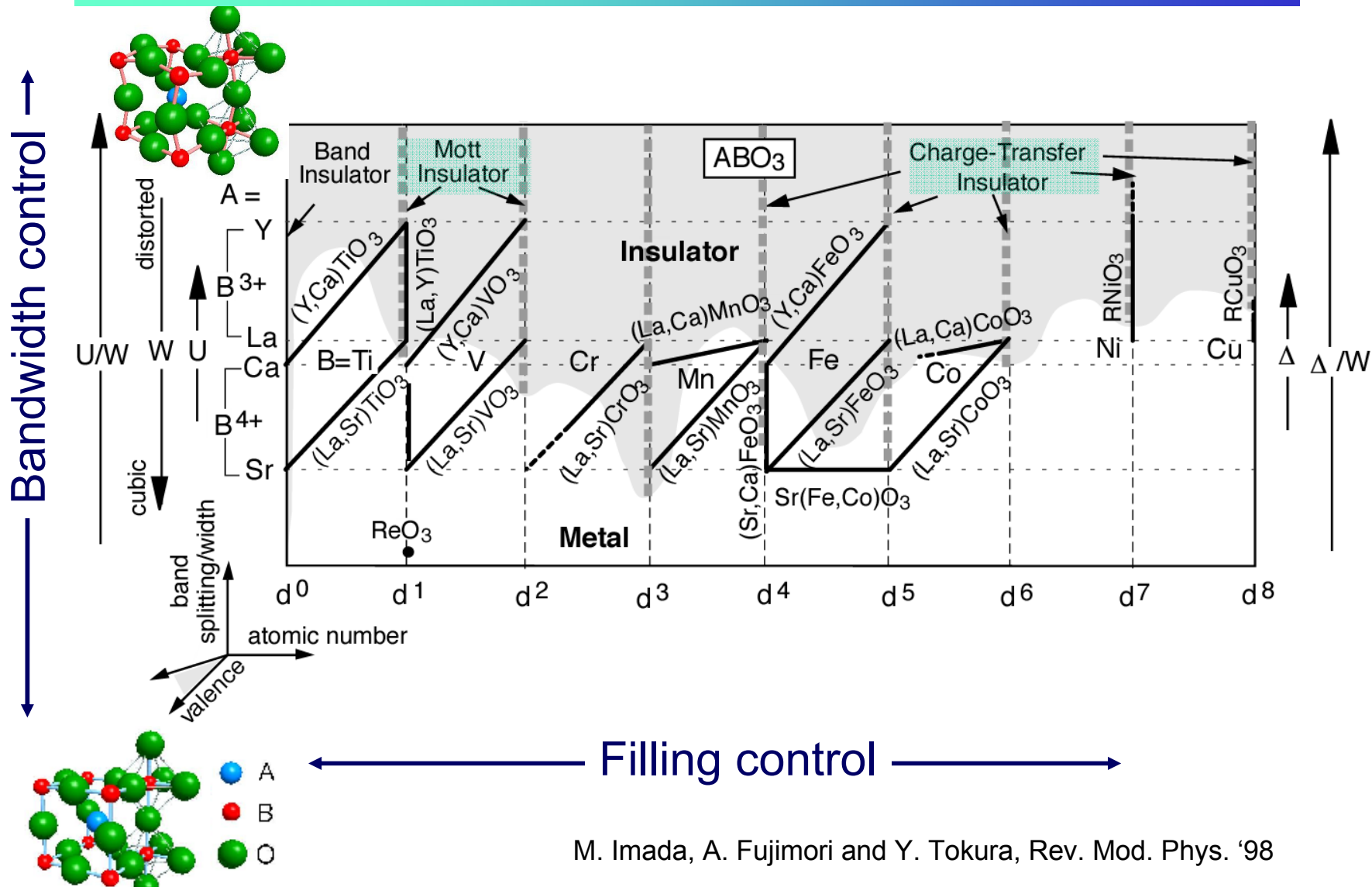
Y. Tokura et al. PRL '93



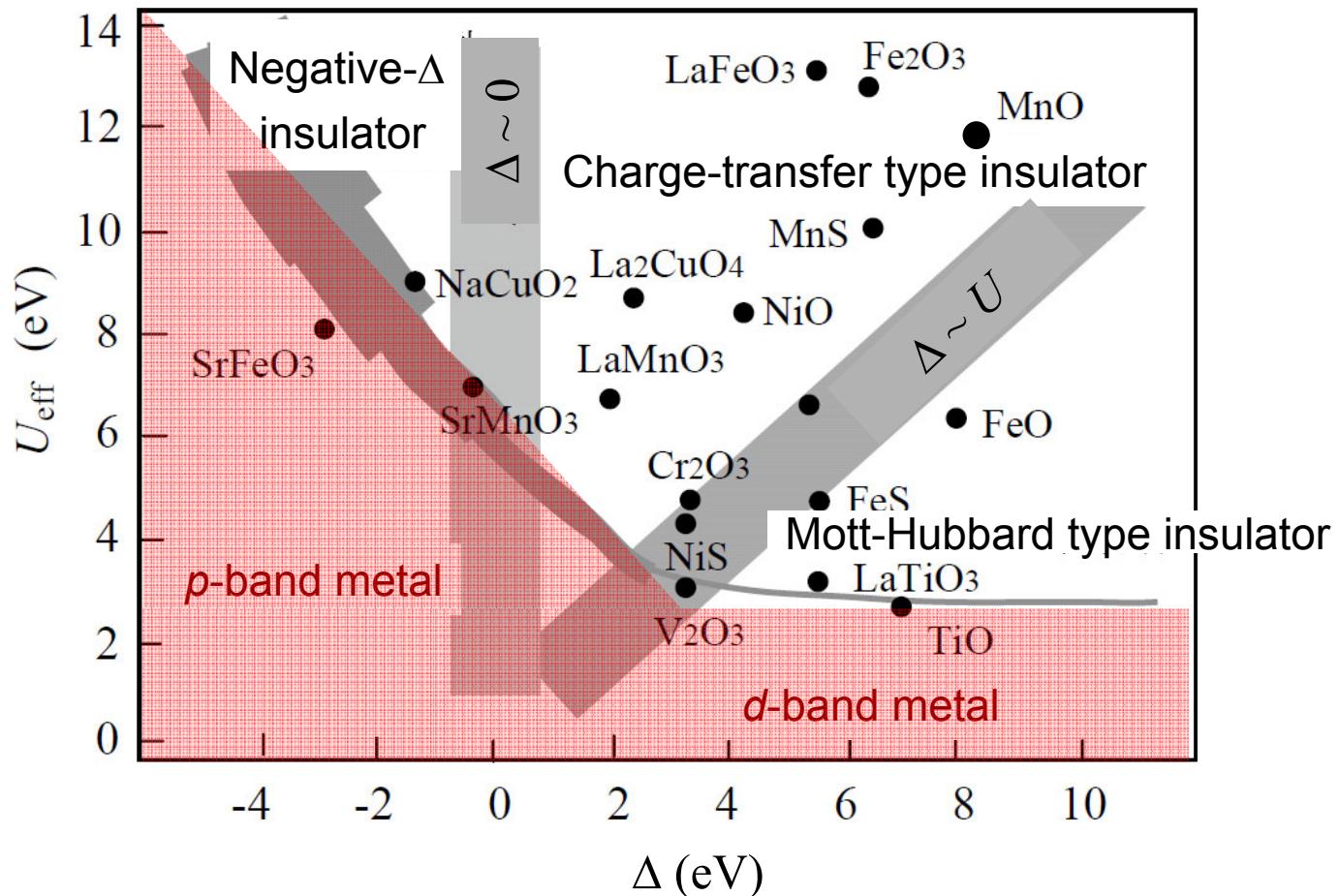
Wilson ratio:
 $\chi/\gamma \sim 2$



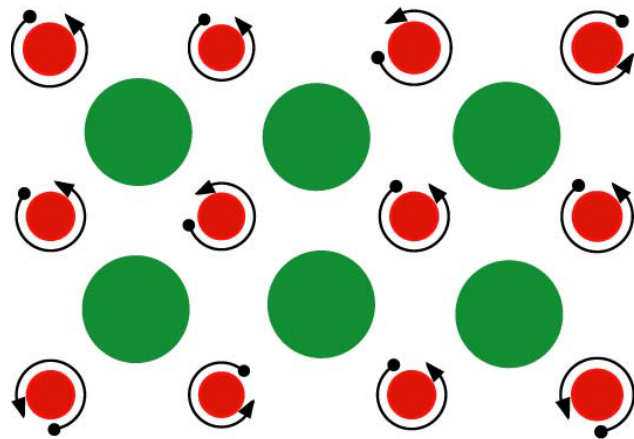
Perovskite-type transition-metal oxides



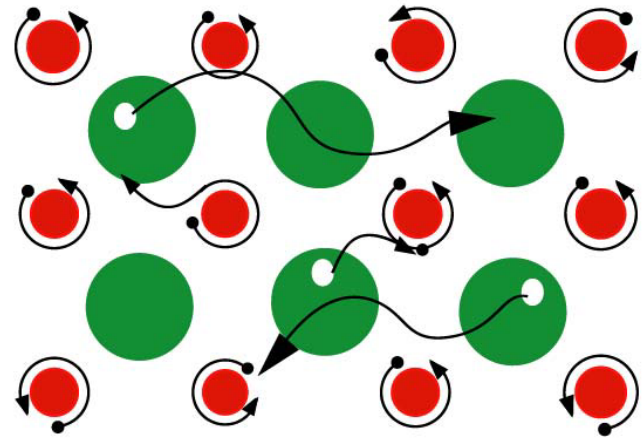
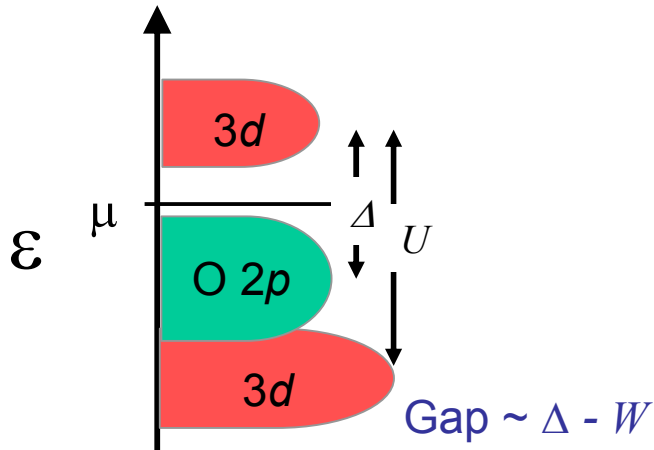
Zaanen-Sawatzky-Allen diagram



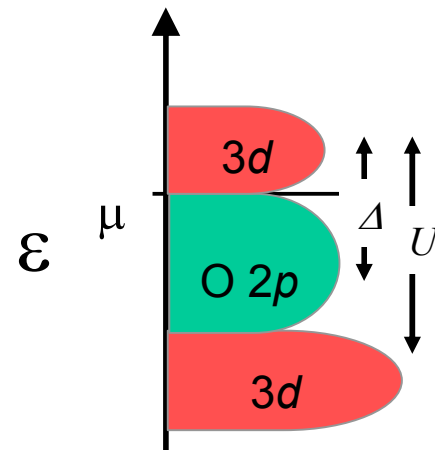
Metal-insulator transition through collapse of charge-transfer gap – Bandwidth control



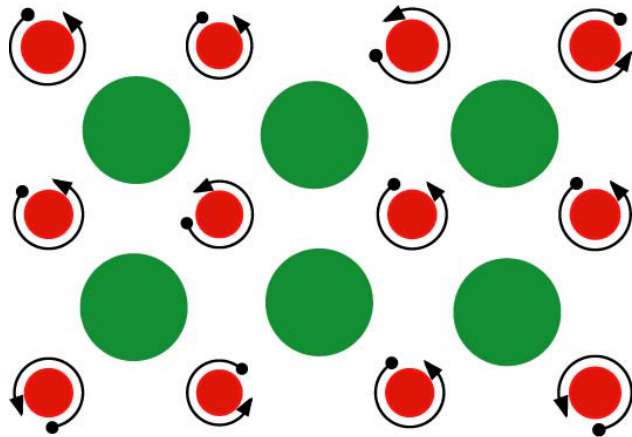
$$\Delta > W$$



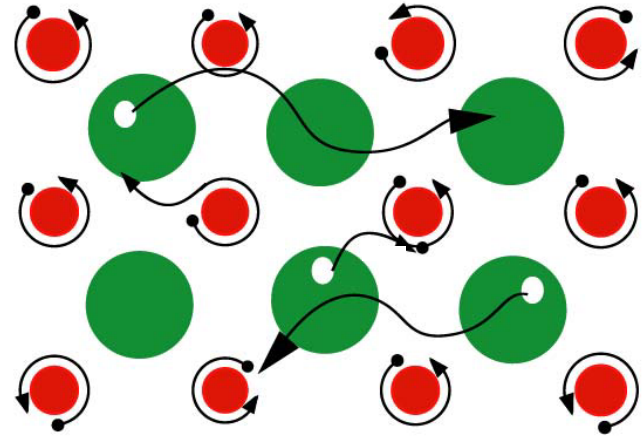
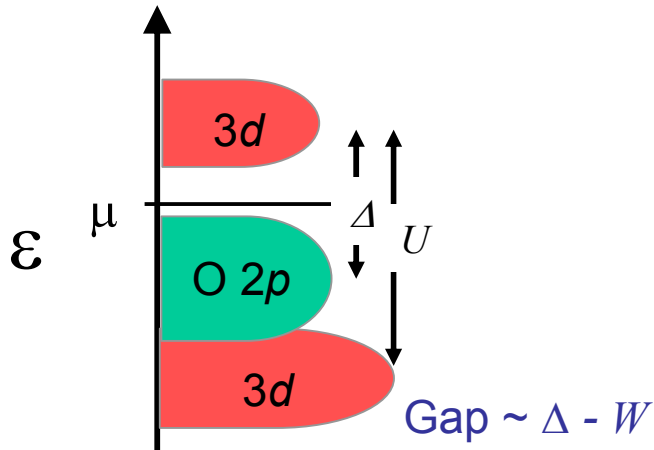
$$\Delta < W$$



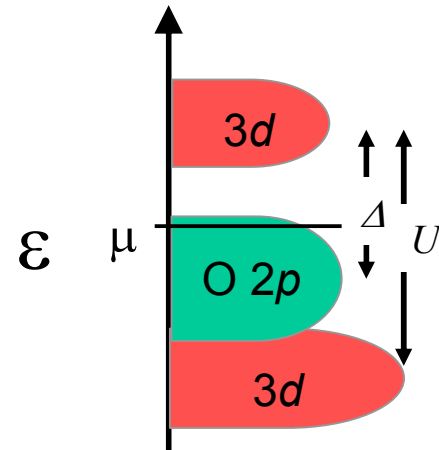
Metal-insulator transition through carrier doping into charge-transfer insulator



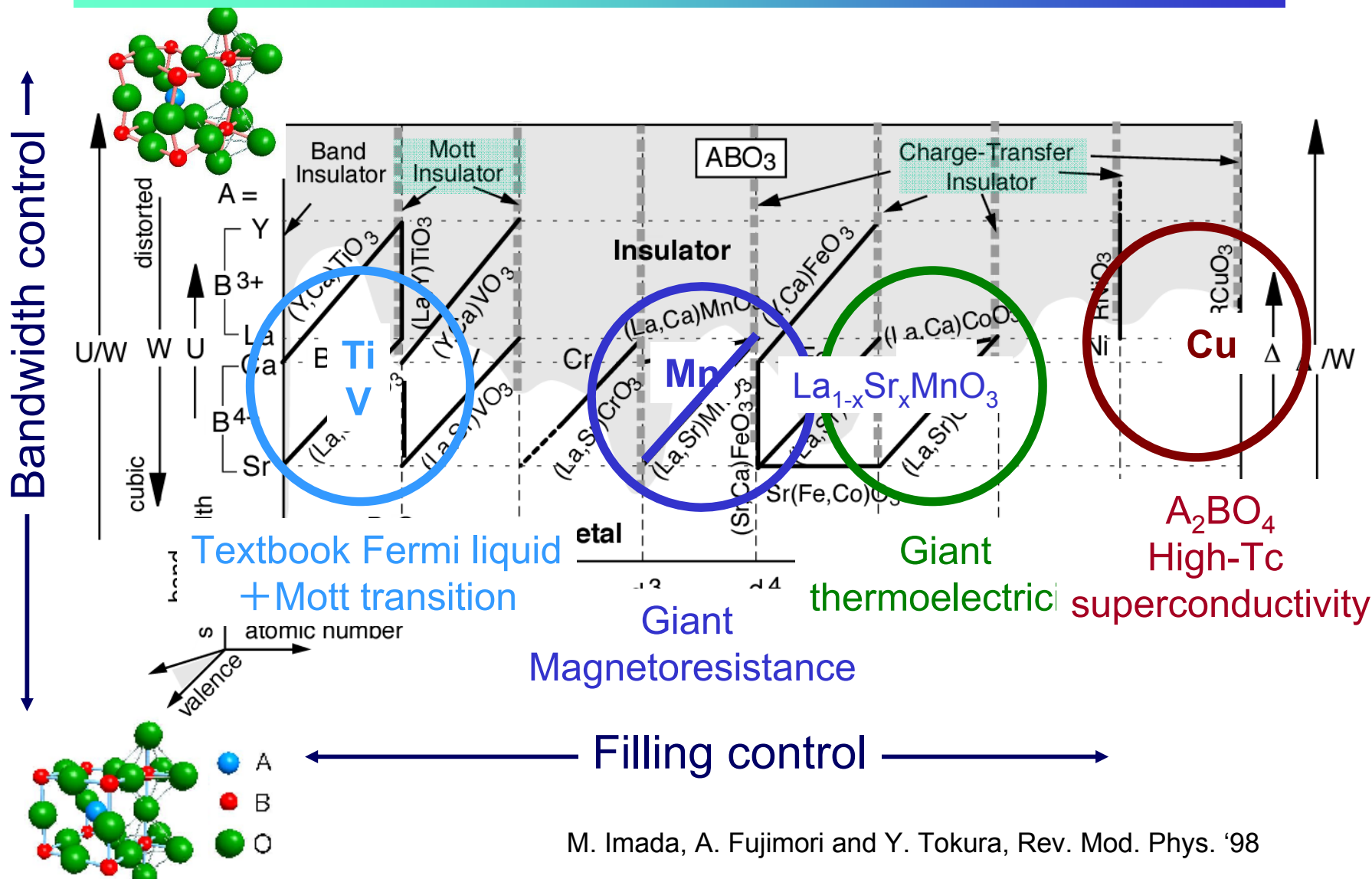
$n = 1$



$n < 1$

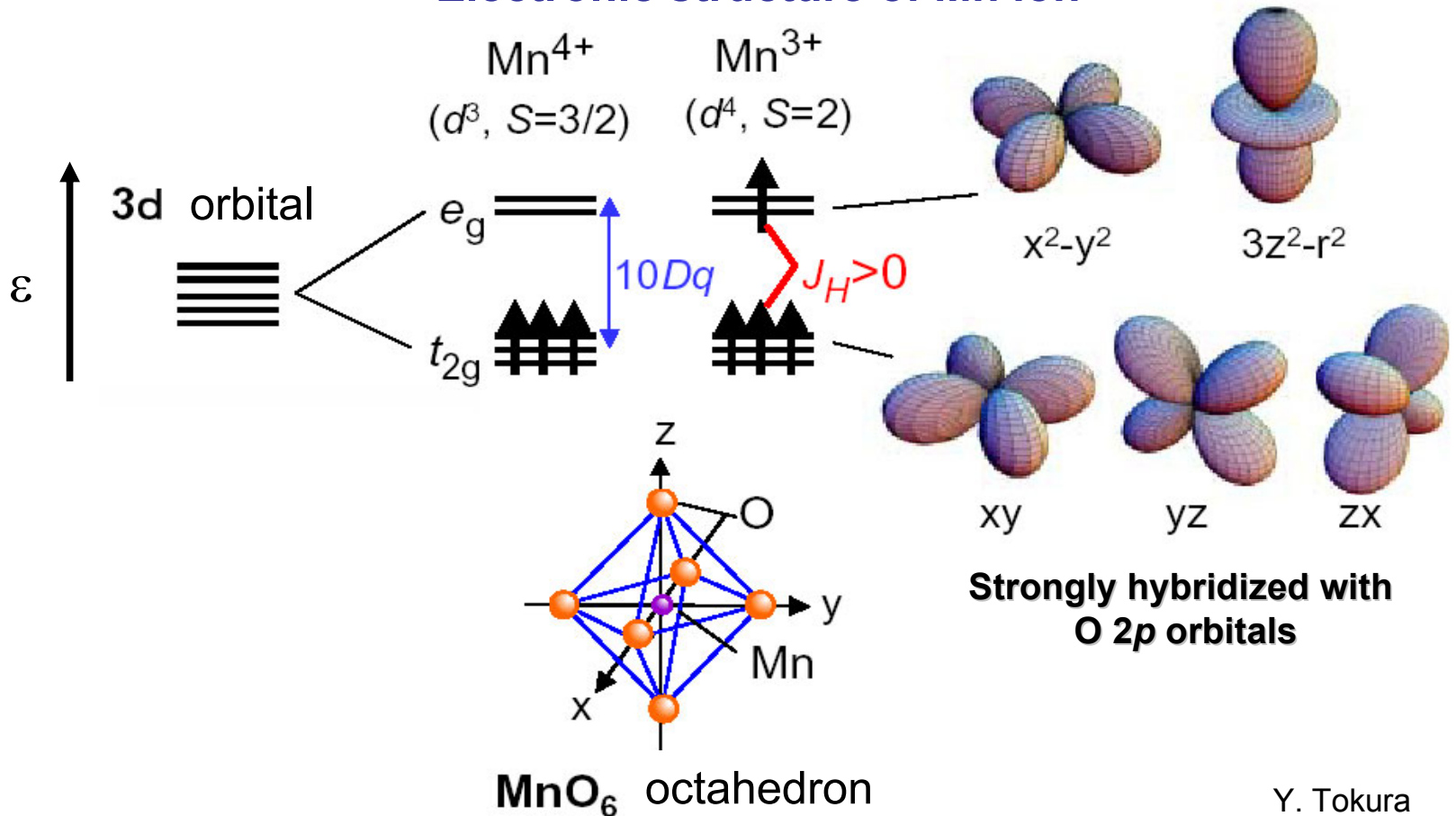


Perovskite-type transition-metal oxides



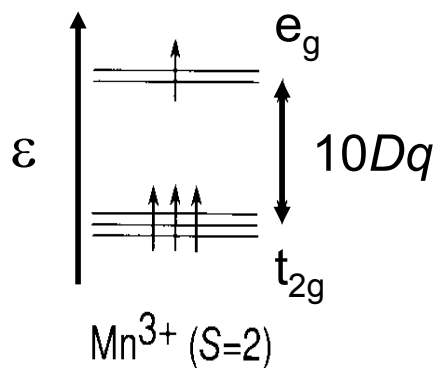
Perovskite-type Mn oxides

Electronic structure of Mn ion



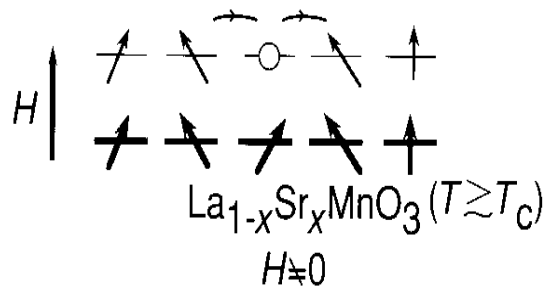
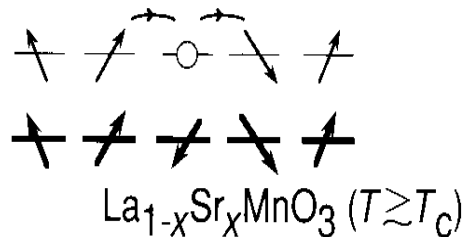
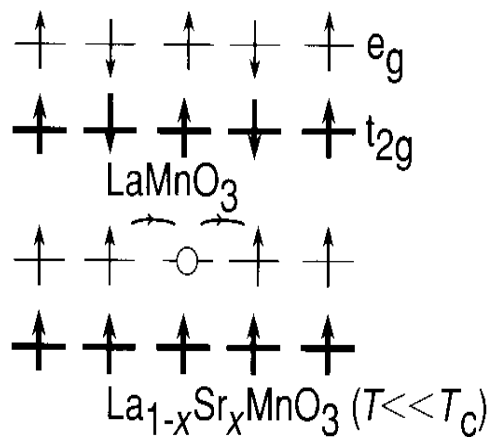
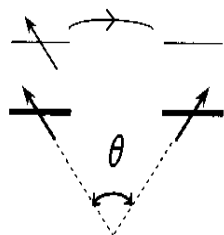
If Hund coupling $3J_H >$ Cryst. field $10Dq \rightarrow$ high-spin state

Double exchange model for magnetoresistance in Mn oxides



$$t = t_0 \cos(\theta/2)$$

Mn^{3+} Mn^{4+}



$$\mathcal{H}_{DE} = \mathcal{H}_t + \mathcal{H}_{Hund},$$

$$\mathcal{H}_t = -t \sum_{\langle ij \rangle} \sum_{\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + \text{H.c.}),$$

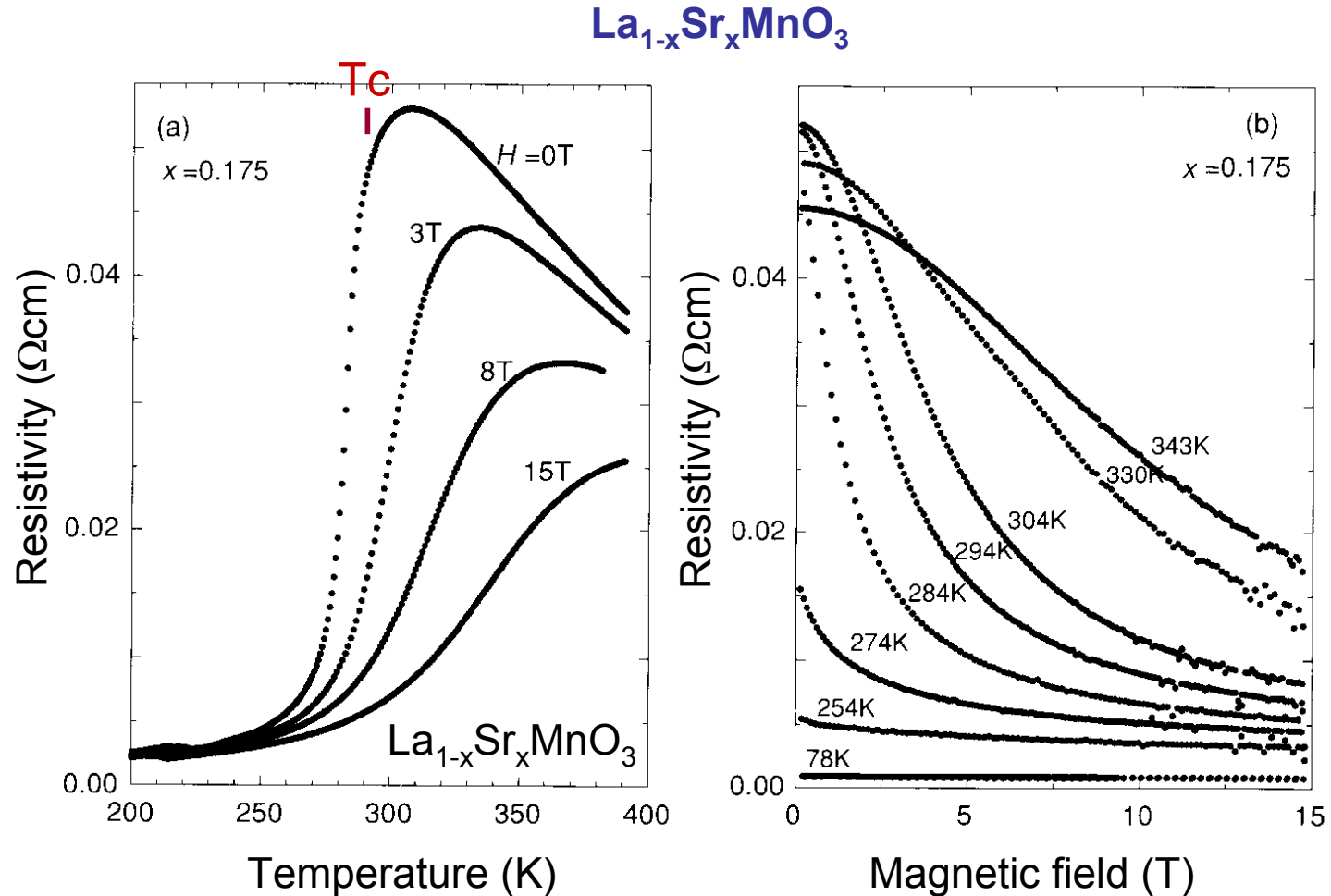
$$\mathcal{H}_{Hund} = -J_H \sum_i \vec{S}_i \cdot \vec{\sigma}_i,$$

\vec{S}_i ; e_g spin

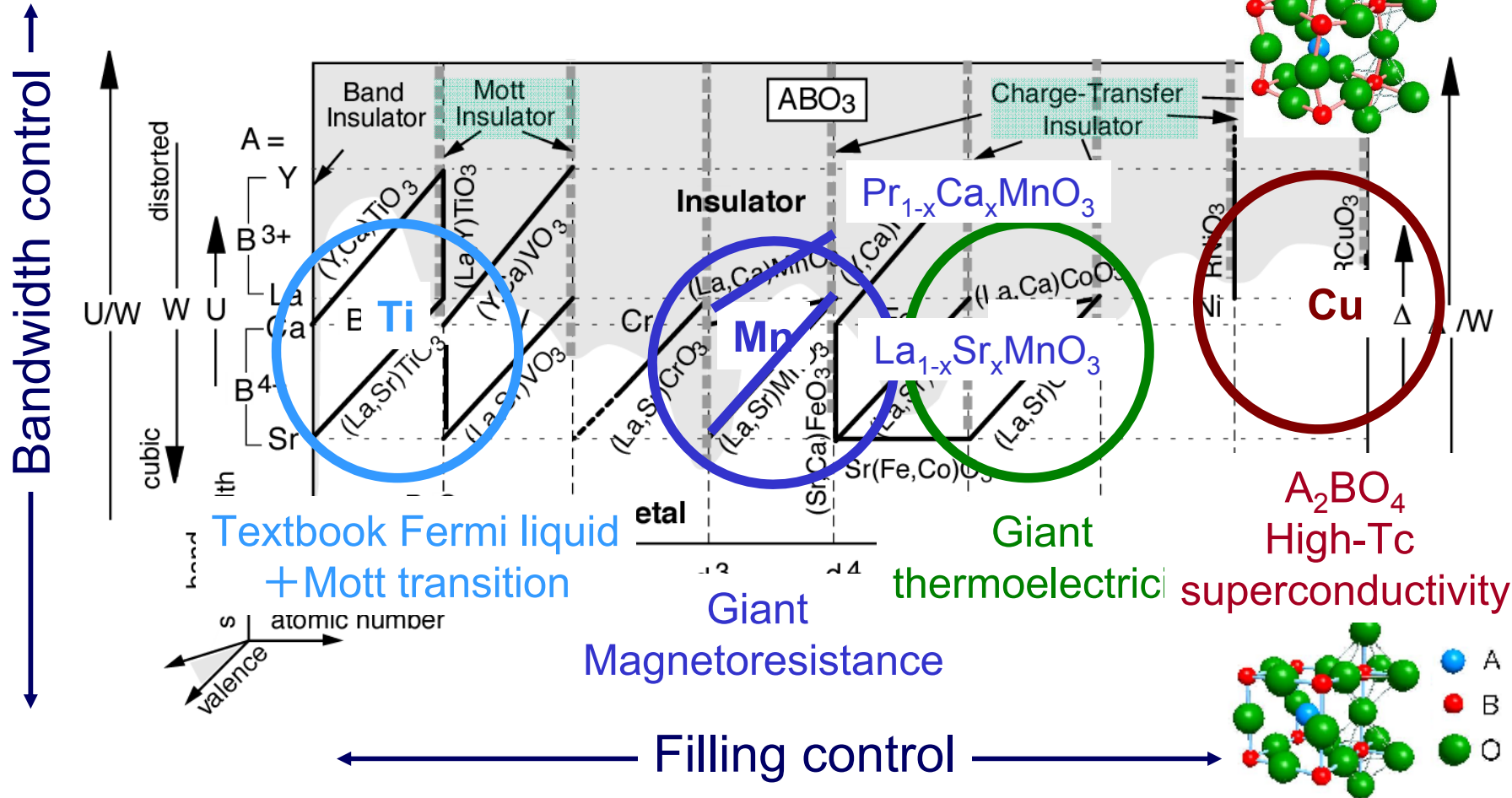
$\vec{\sigma}_i$; t_{2g} spin

J_H : Hund coupling constant

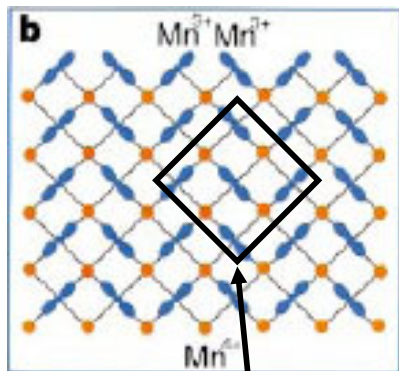
Colossal magnetoresistance of Mn oxides



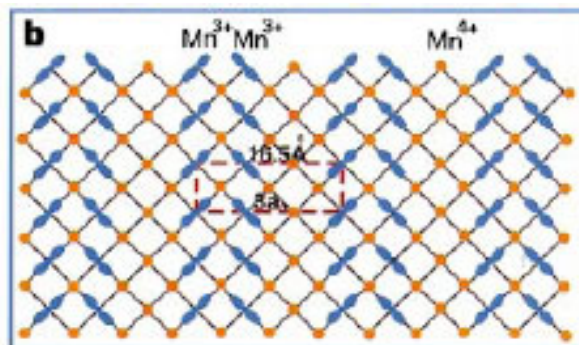
Perovskite-type transition-metal oxides



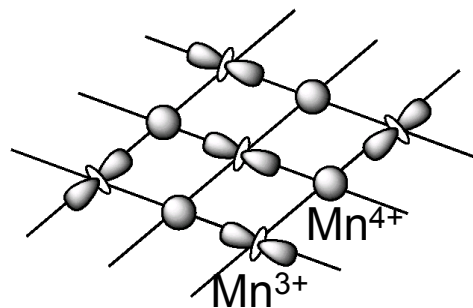
Spin-charge-orbital ordering in perovskite-type Mn oxides



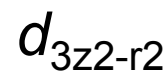
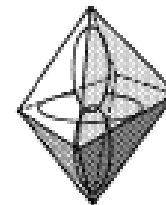
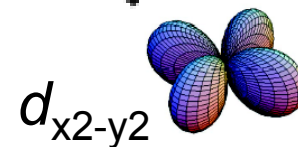
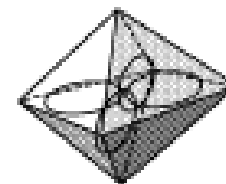
$x=0.5$



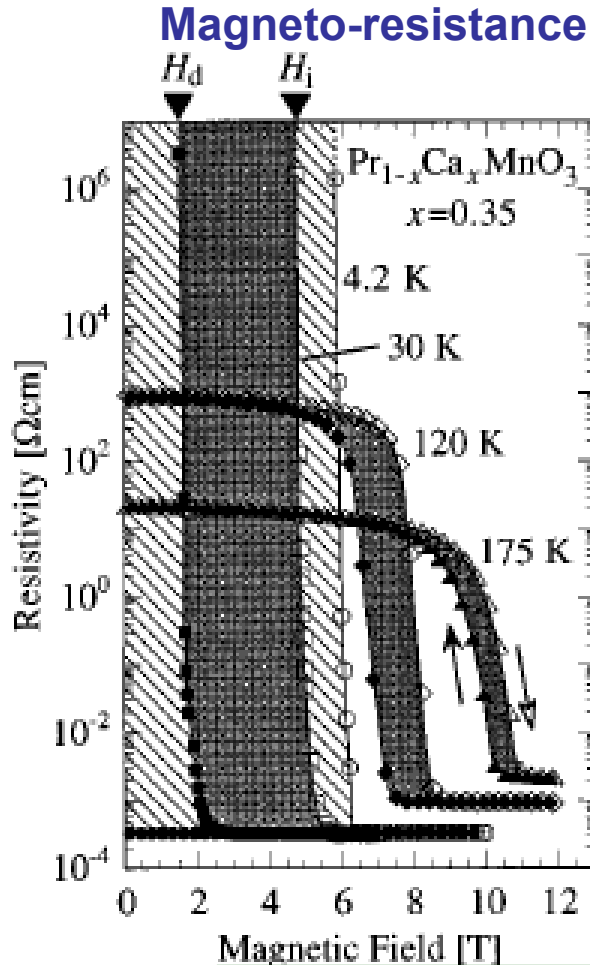
$x=0.67$



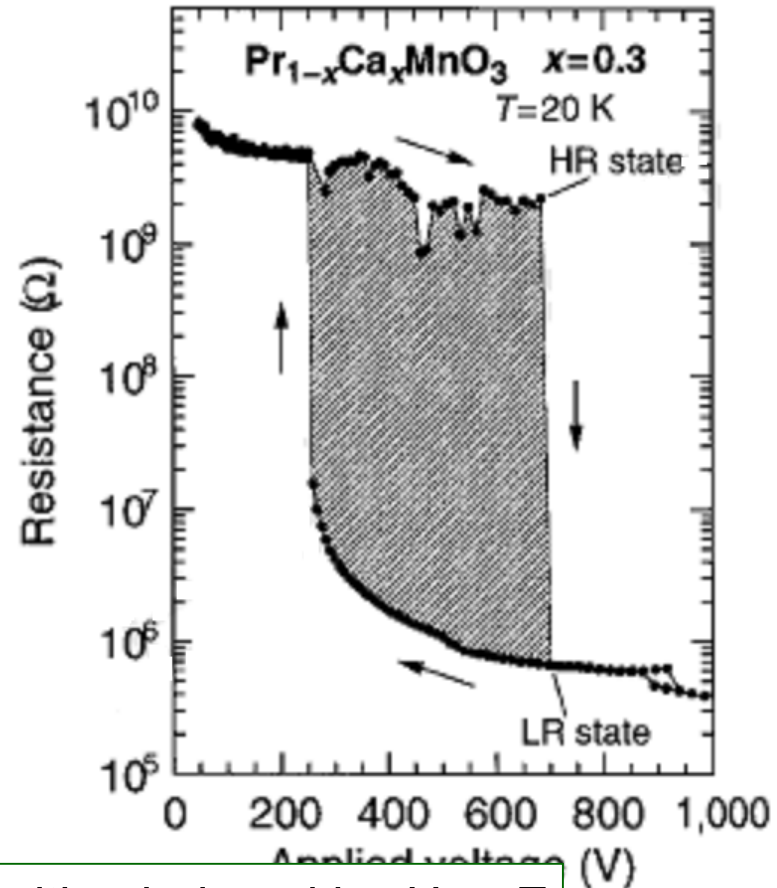
Jahn-Teller distortion of MnO_6 octahedron



Even bigger magnetoresistance in narrow-band Mn oxides

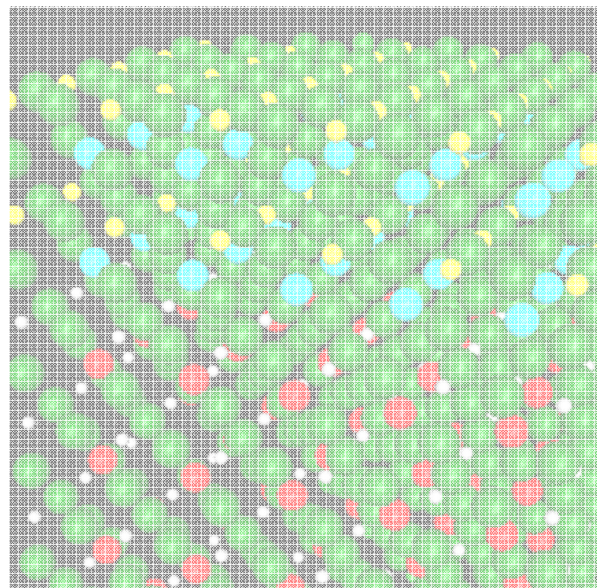


Resistance drop by electric field



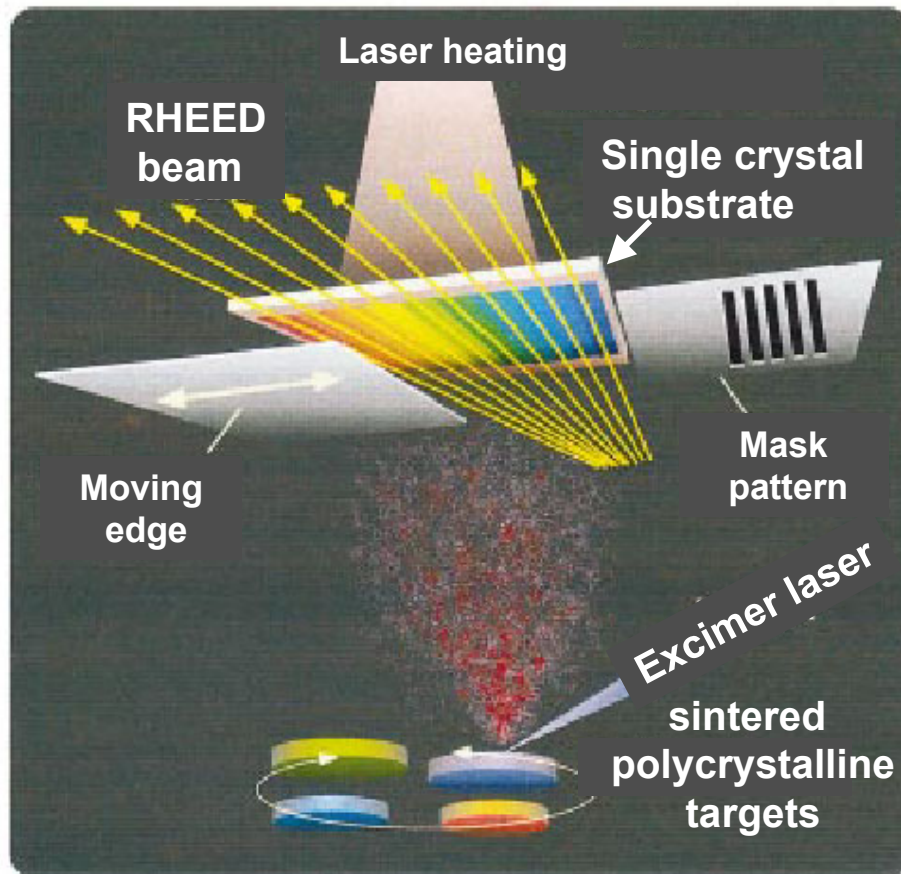
Metal-insulator transition induced by H or E

Fabrication and characterization

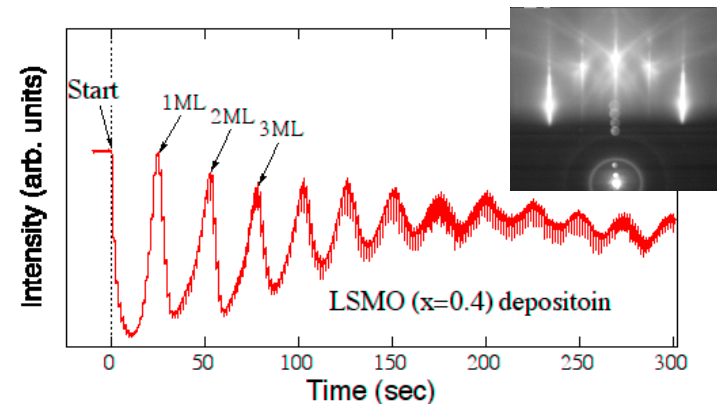


MBE using pulsed laser deposition (PLD)

PLD system



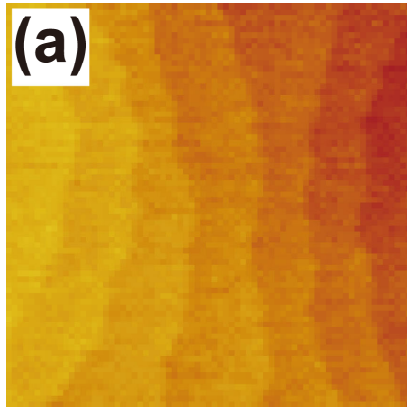
Monitoring RHEED oscillations



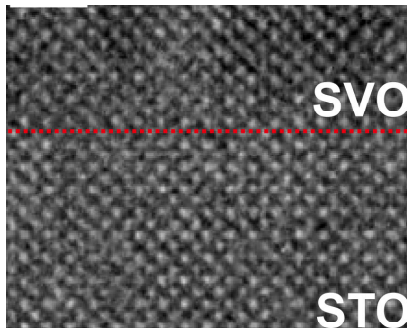
T. Ohnishi et al., APL '01.

Characterization of epitaxially grown thin film on SrTiO₃(001) substrate

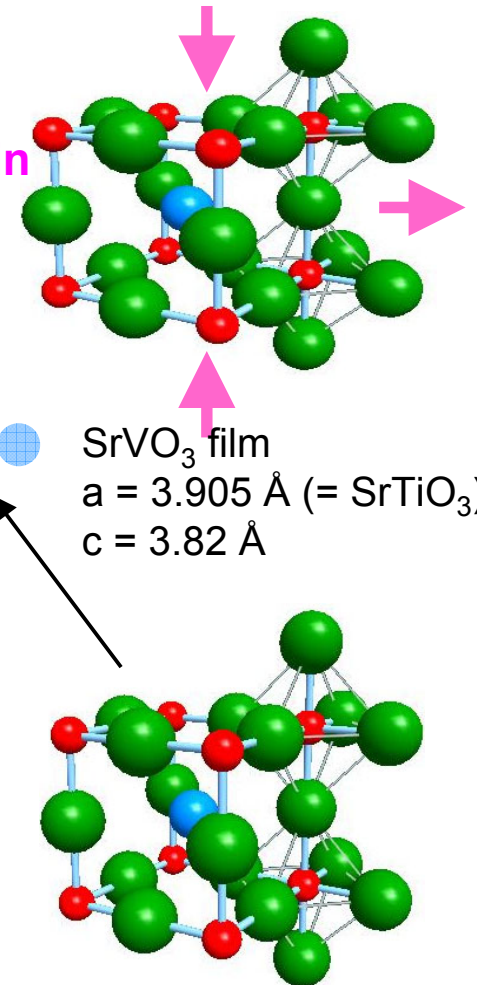
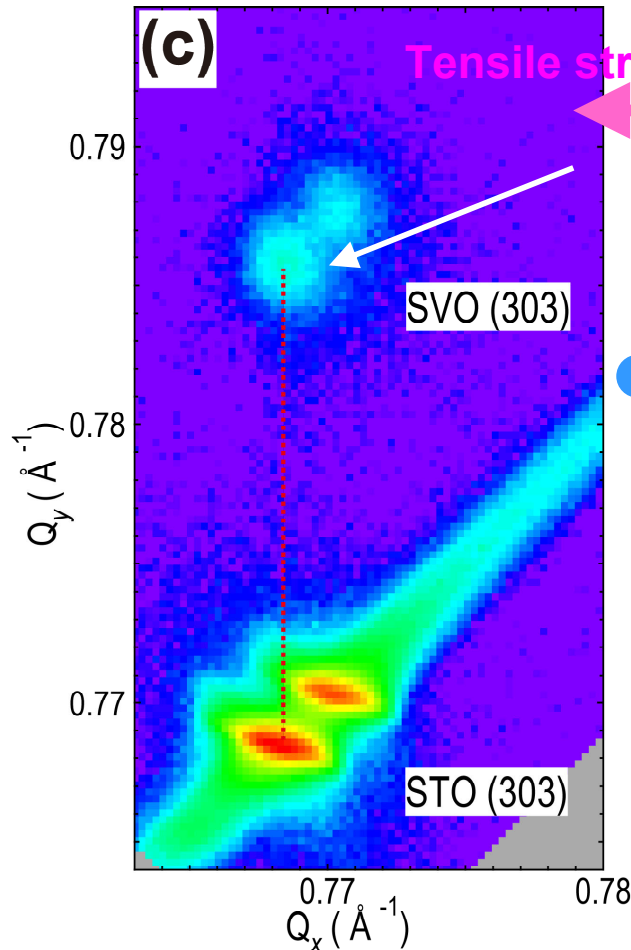
Atomic force microscope (AFM)



Transmission electron Microscopy (TEM)



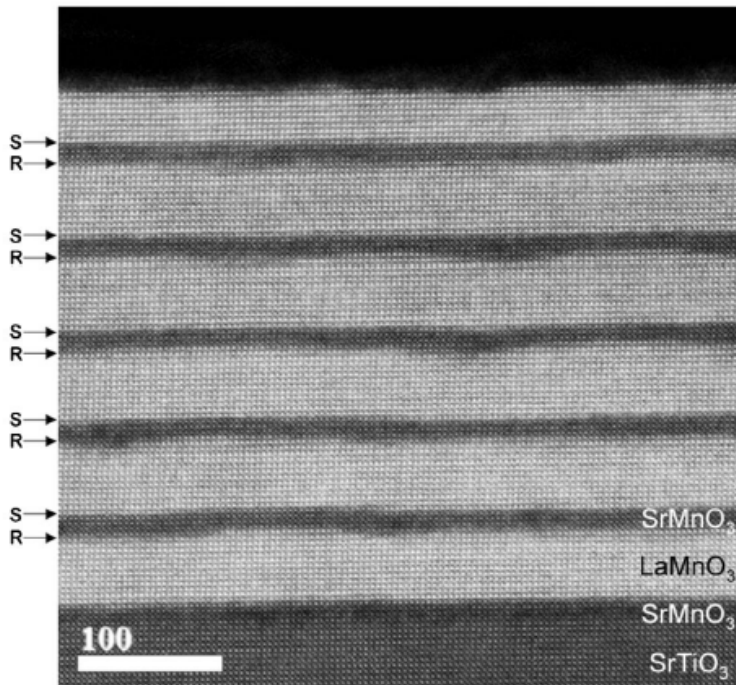
Reciprocal space mapping of XRD pattern



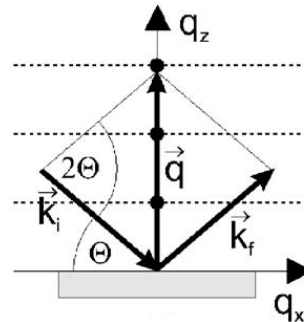
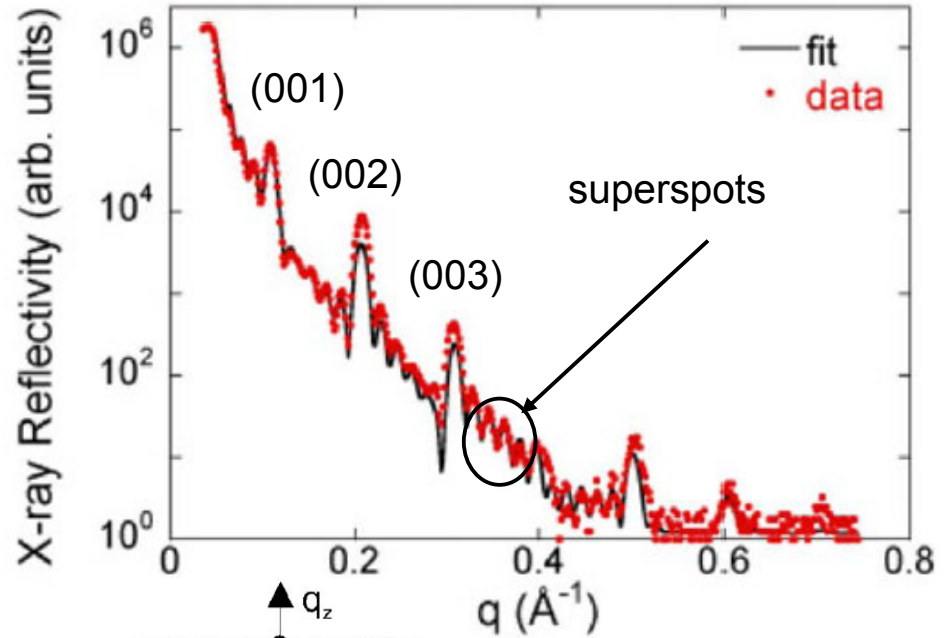
Characterization of epitaxially grown superlattice on SrTiO₃(001) substrate

$[(\text{LaMnO}_3)_{11.8} / (\text{SrMnO}_3)_{4.4}]_6$ superlattice

TEM image

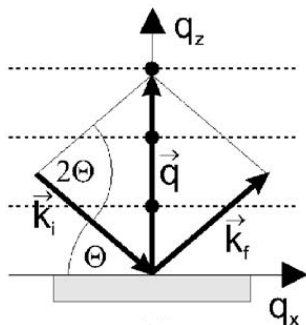
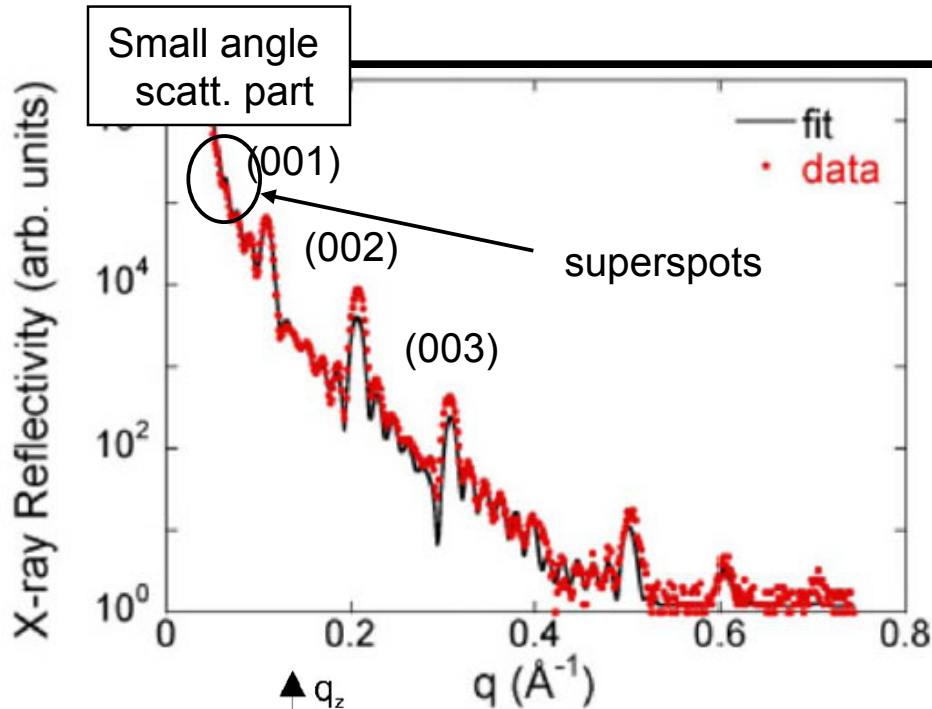


X-ray reflection

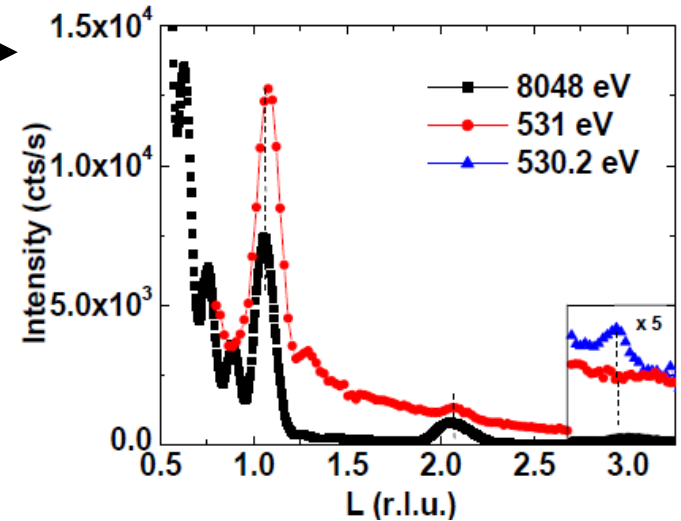


Soft x-ray scattering from $[(\text{LaMnO}_3)_m/(\text{SrMnO}_3)_{m'}]_n$ superlattice

X-ray scattering (reflectivity)



Soft X-ray scattering



$$S(003) = 2f_{\text{int}} - f_{\text{LMO}} - f_{\text{SMO}}$$

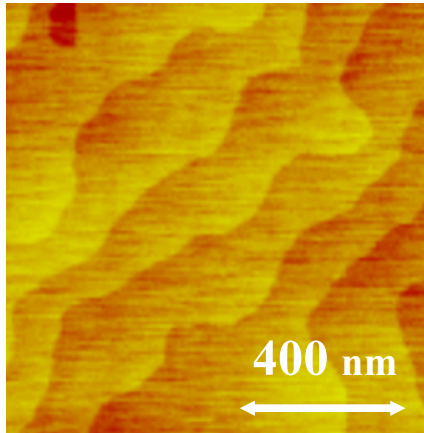
(003) (in units of $1/m+m'$):

visible only at O 1s edge

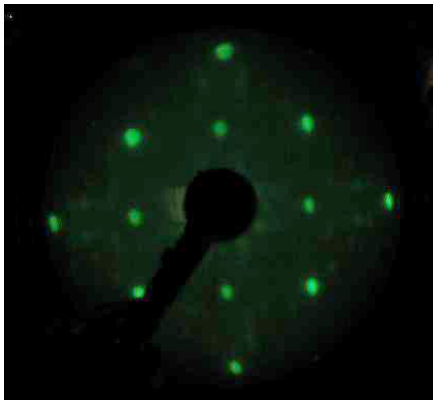
→ O 2p hole doping only at interface.

In-situ ARPES measurement system of PLD-grown oxide thin films

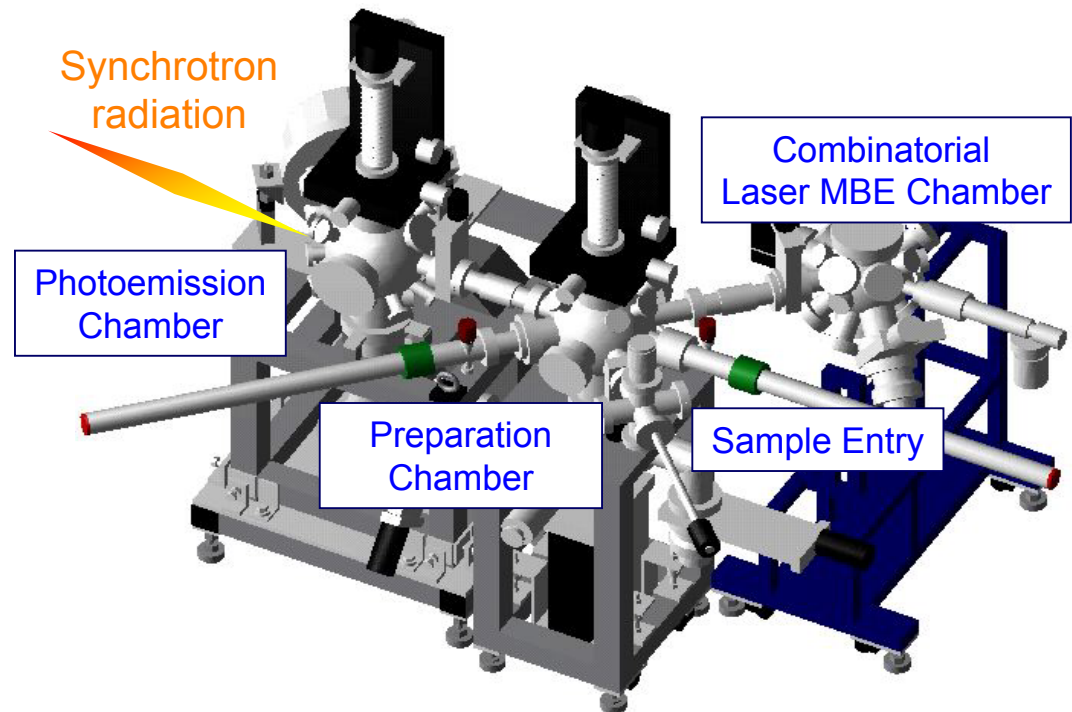
AFM image



LEED

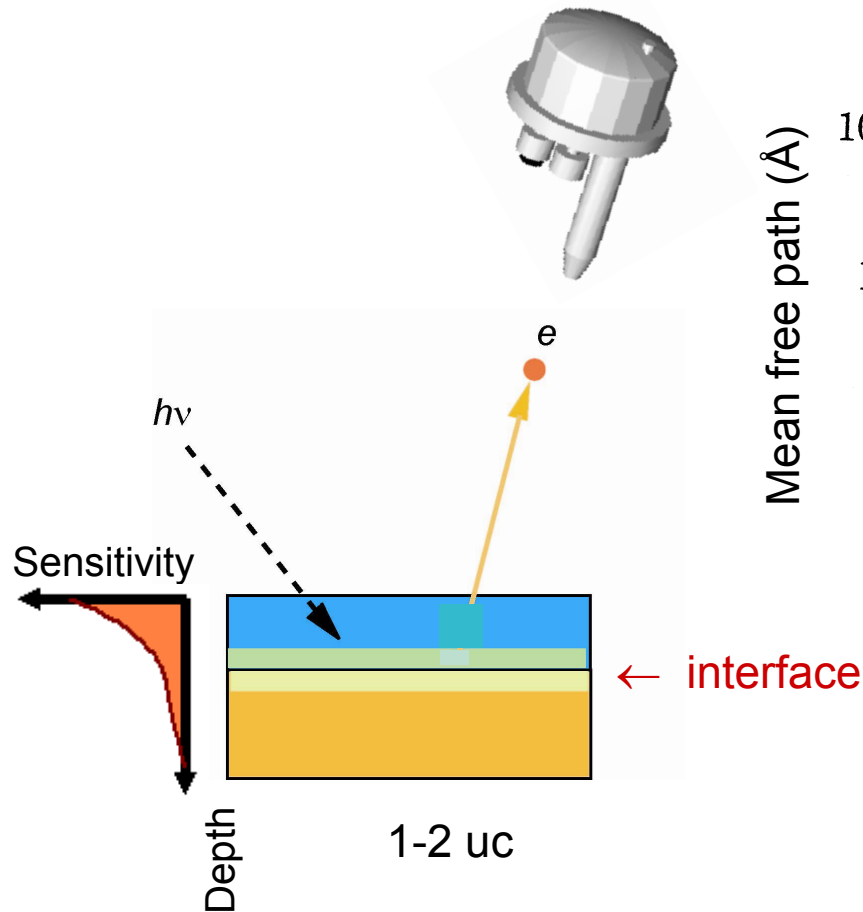


Combined photoemission-laser MBE system
Oshima-Kumigashira group

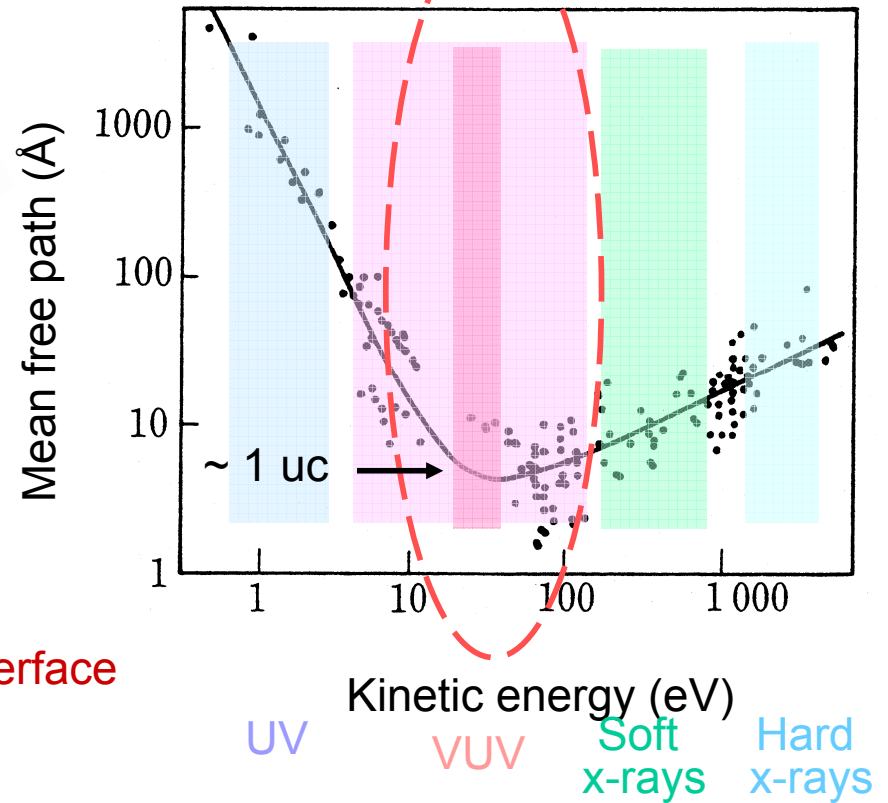


Photon Factory BL-1c, BL2c, BL-28

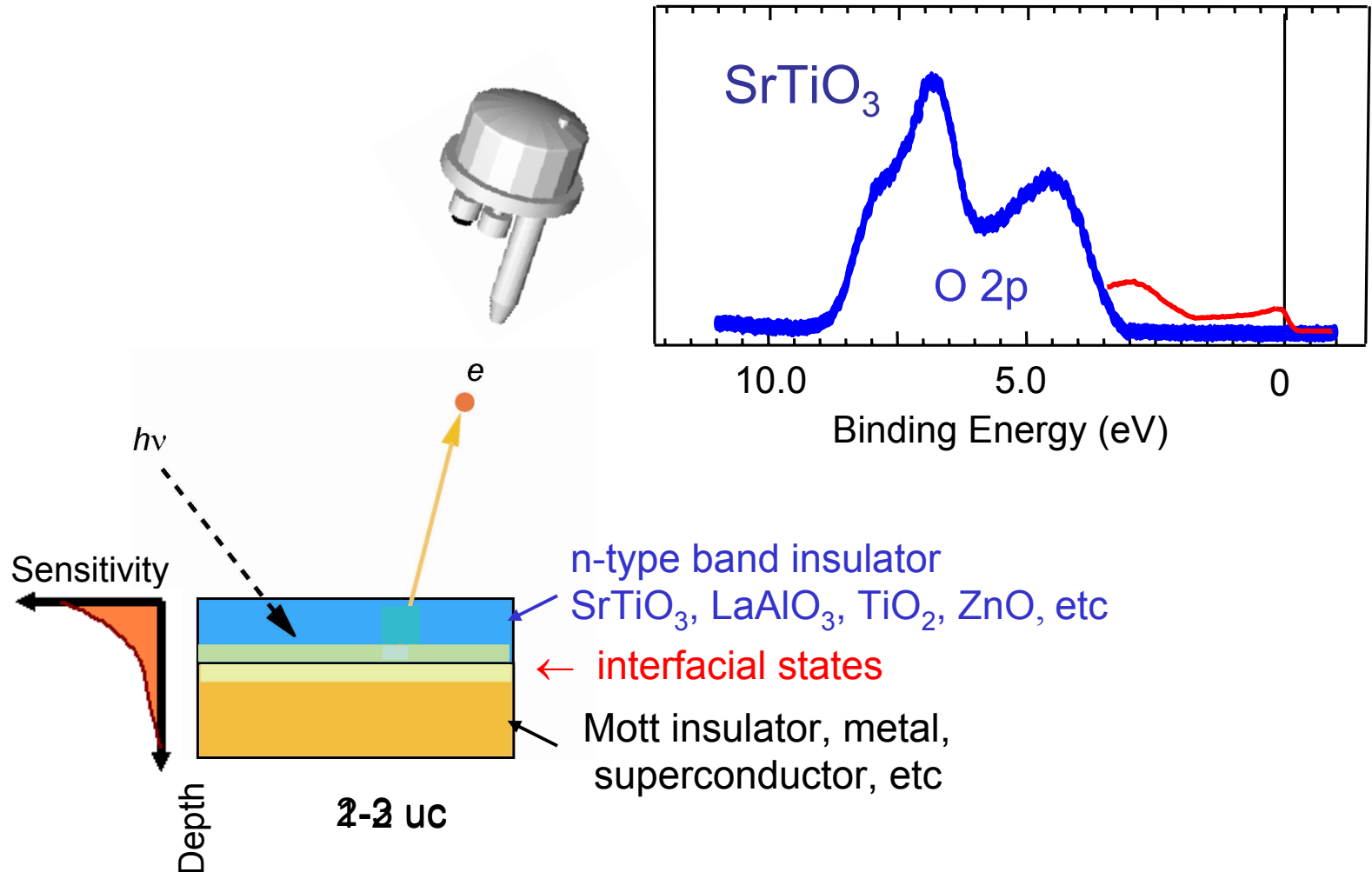
Photoemission spectroscopy of buried interfaces



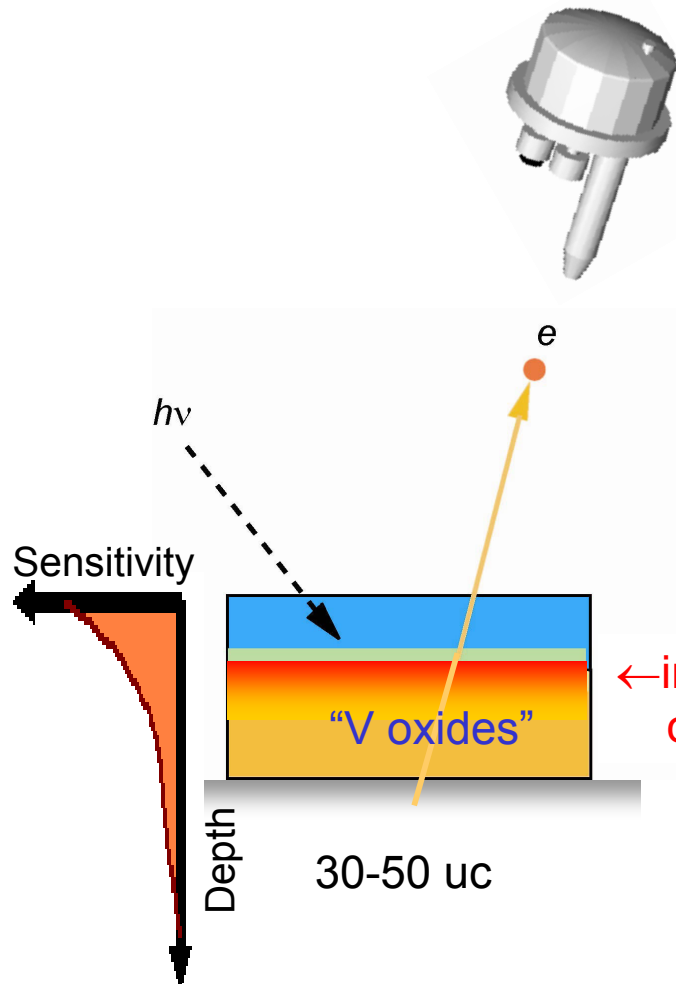
Probing depth of photoelectrons



Photoemission spectroscopy of buried interfaces



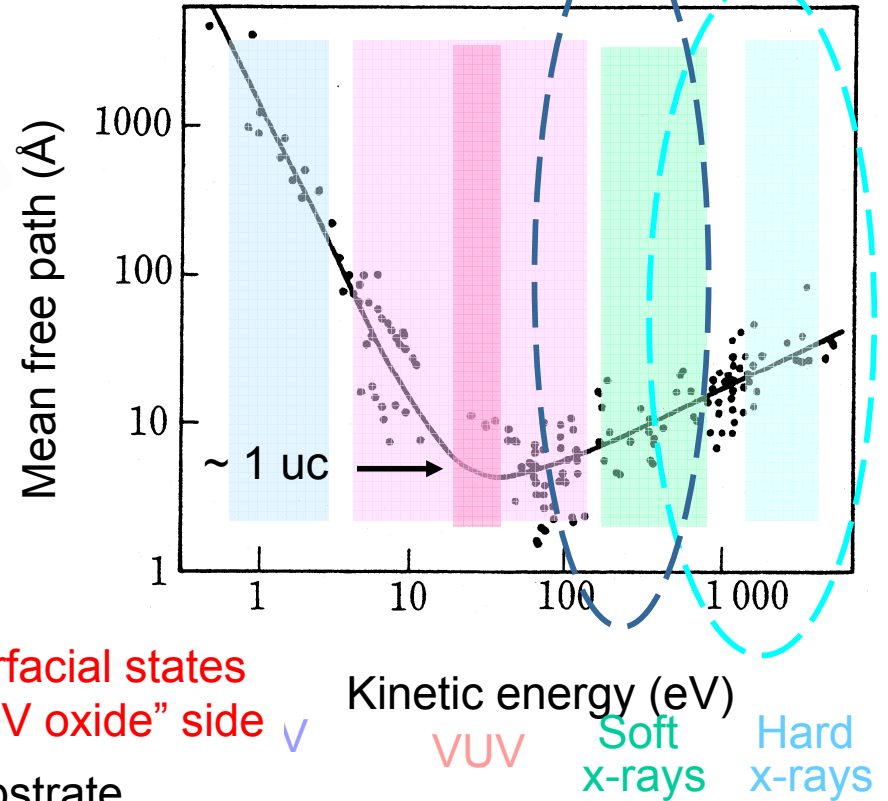
Photoemission spectroscopy of buried interfaces



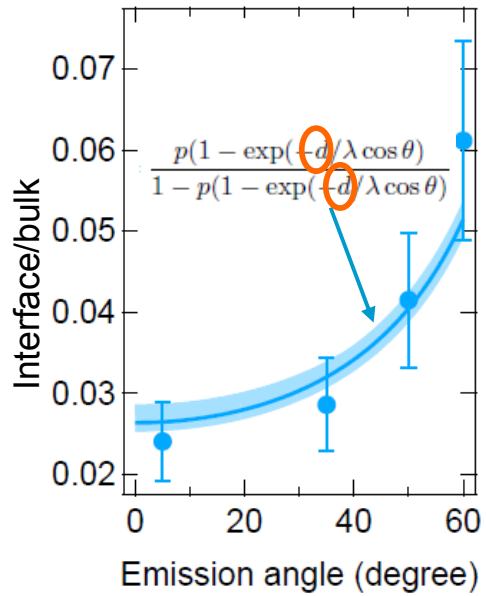
← interfacial states on "V oxide" side
 substrate

30-50 uc

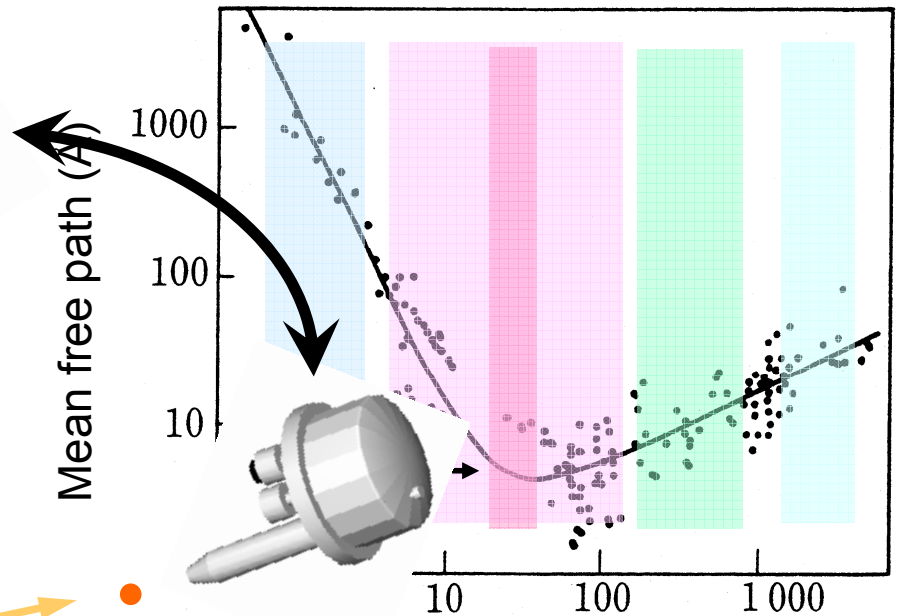
Probing depth of photoelectrons



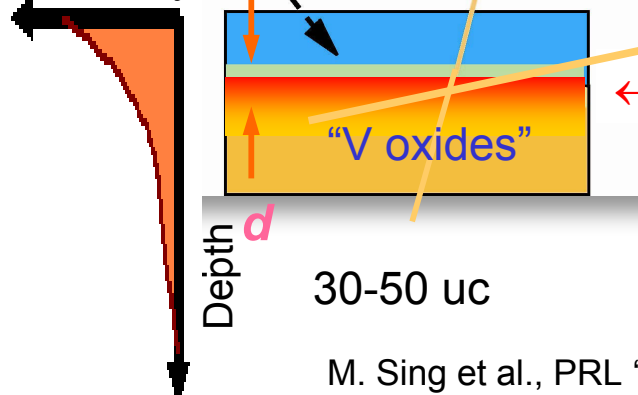
Photoemission spectroscopy of buried interfaces



Probing depth of photoelectrons



Sensitivity

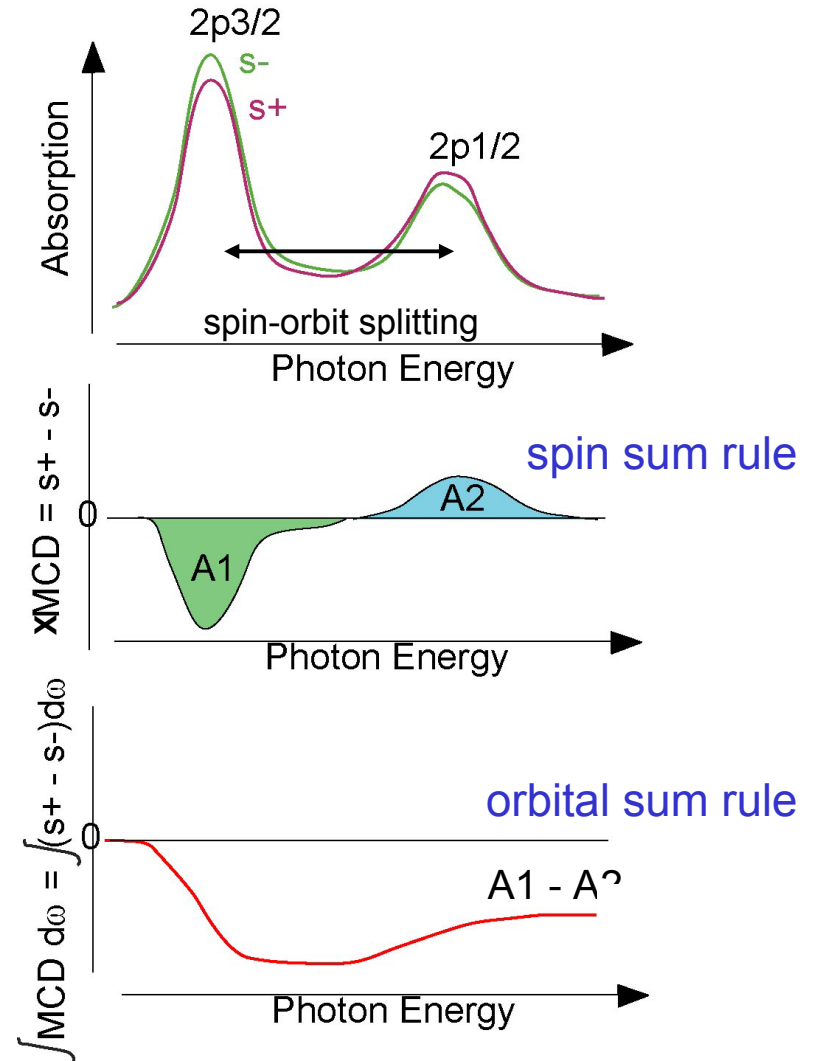
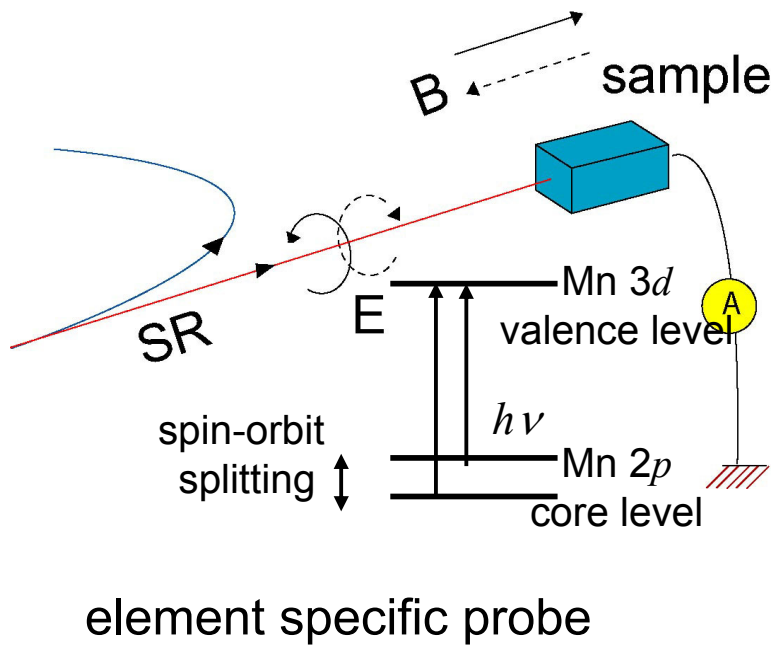


30-50 μc

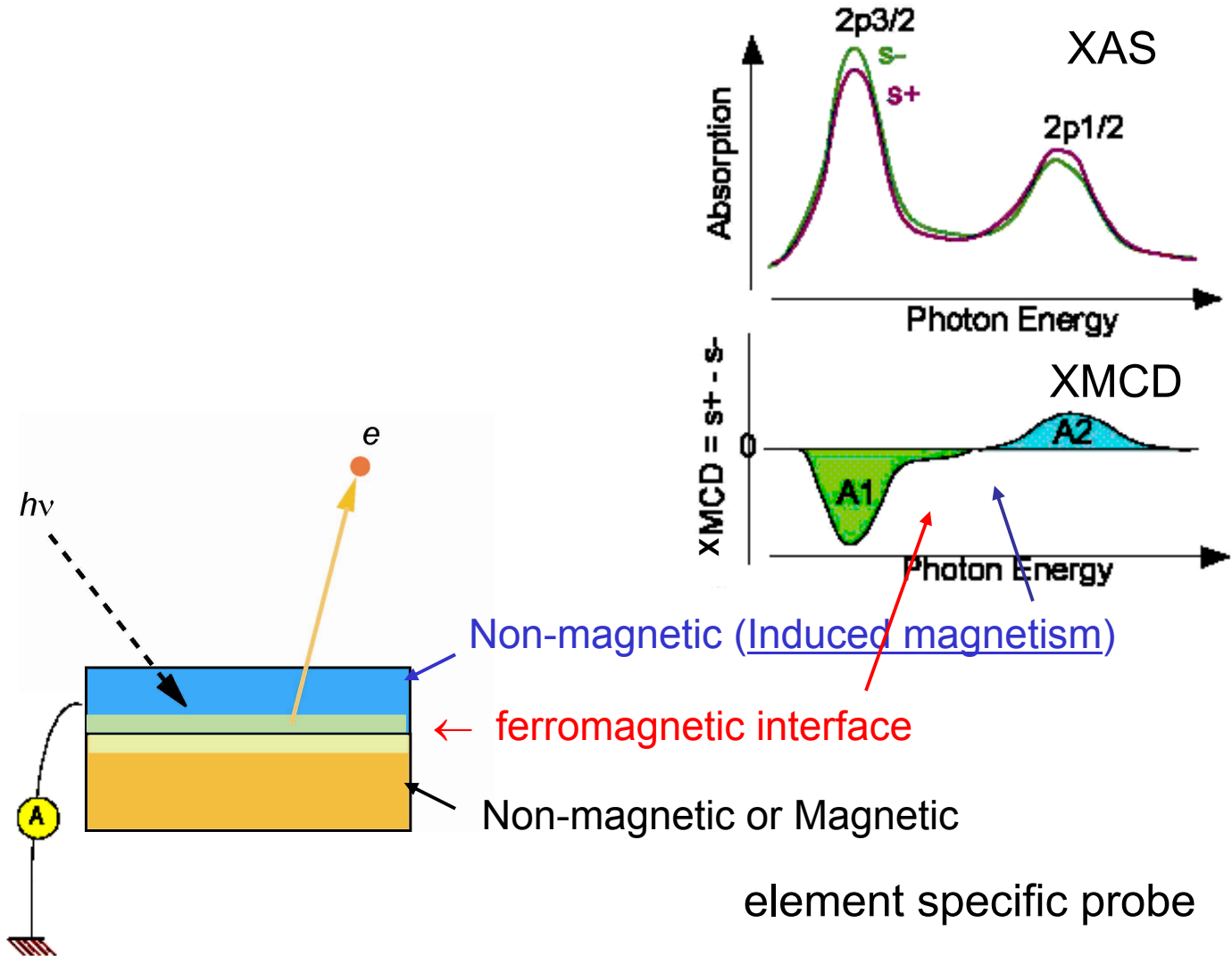
M. Sing et al., PRL '09

Polarized soft x-ray absorption spectroscopy (XAS)

Magnetic circular x-ray dichroism (XMCD)



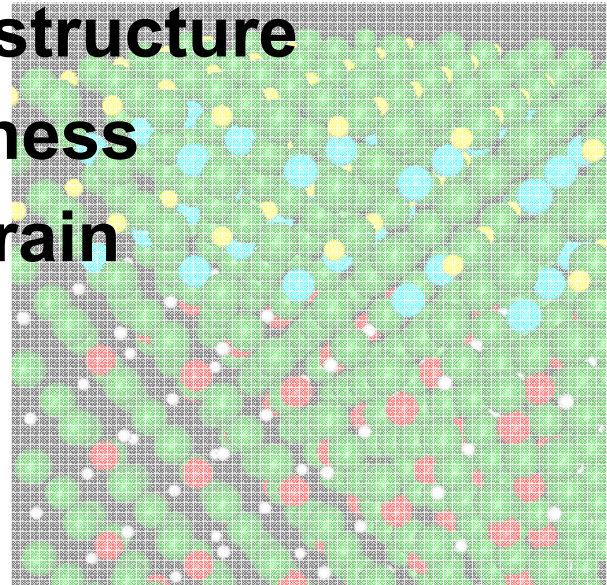
XMCD of buried interfaces



element specific probe

Outline

- **Electronic structure of transition-metal oxides**
- **Fabrication and characterization**
- **Interfacial electronic structure**
- **Effects of finite thickness**
- **Effects of epitaxial strain**

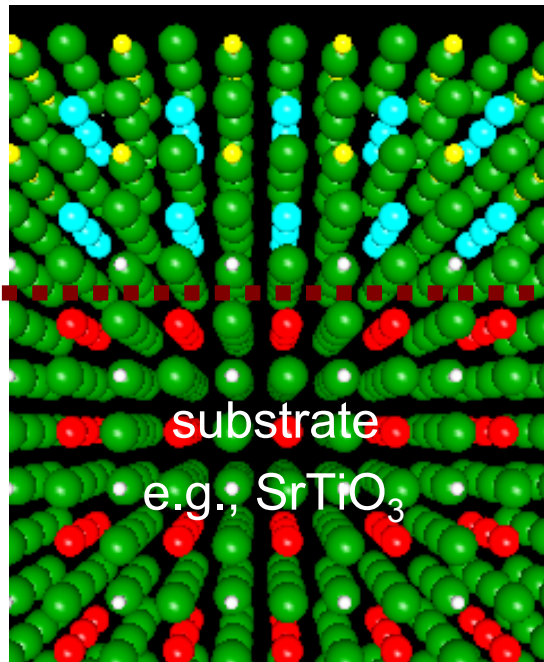


Interfacial electronic structure

Metallic states between two insulators

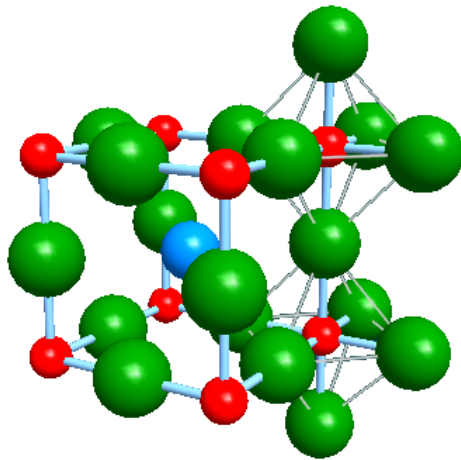
-States near the Fermi level-




Interfaces



Metallic behavior of interfaces between Mott insulator and band insulator

Perovskite-type oxides ABO_3

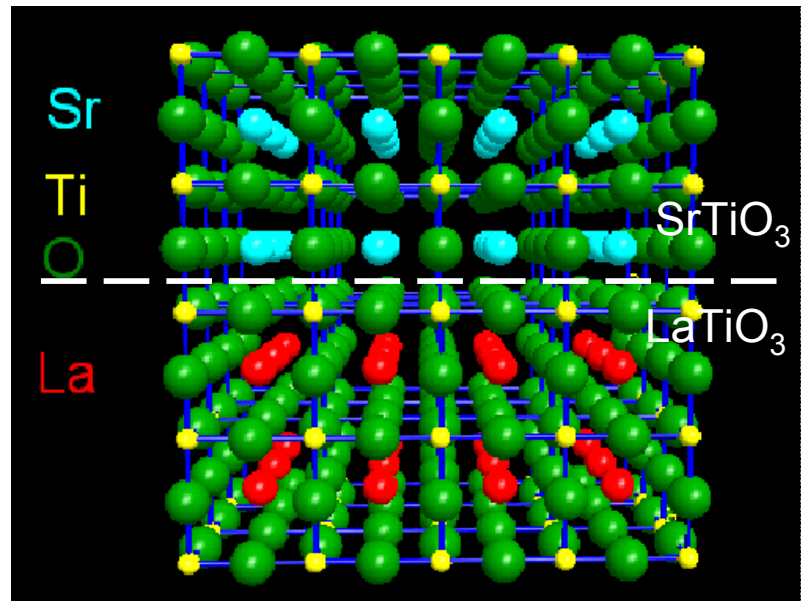


	A	Sr^{2+}	La^{2+}
	B	$Ti^{4+} (d^0)$	$Ti^{3+} (d^1)$
	O	O^{2-}	O^{2-}

$SrTiO_3$: d^0 (Ti^{4+}) band insulator

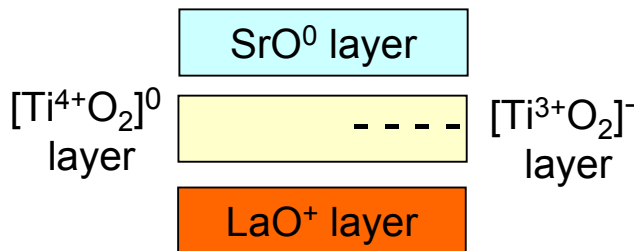
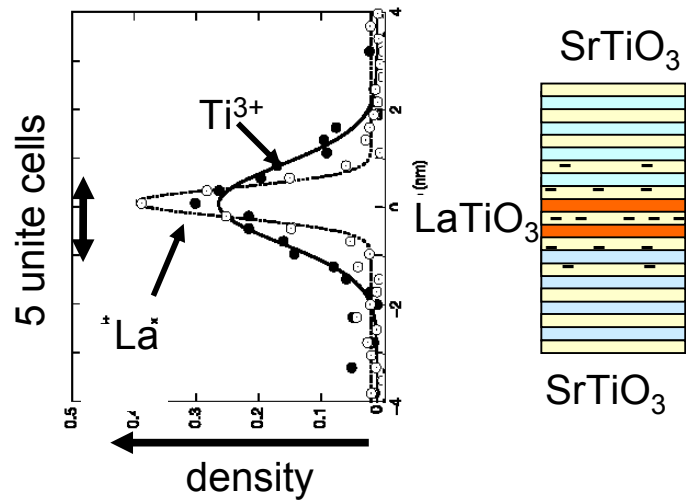
Metallic interfaces !

$LaTiO_3$: d^1 (Ti^{3+}) Mott insulator

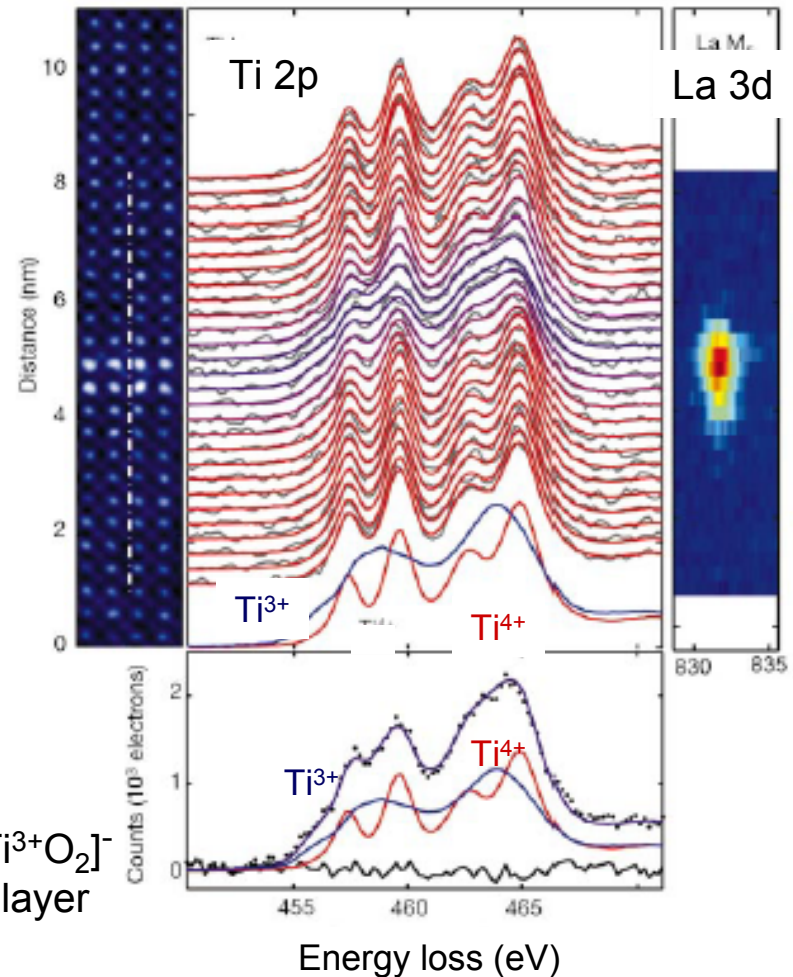


LaTiO₃ layers embedded in SrTiO₃: Penetration of Ti 3d electrons into SrTiO₃

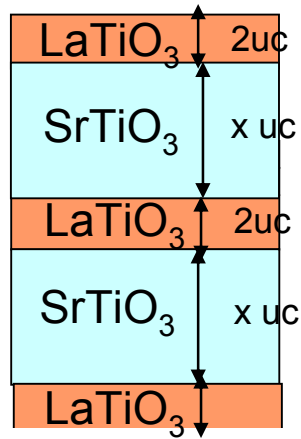
LaTiO₃: d^1 (Ti³⁺) Mott insulator
SrTiO₃: d^0 (Ti⁴⁺) band insulator



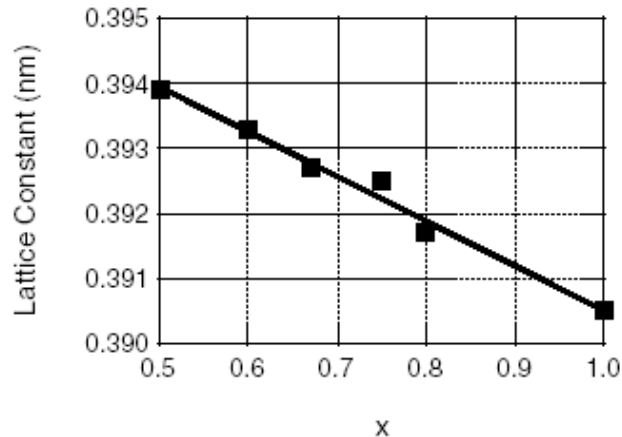
Atomically resolved EELS



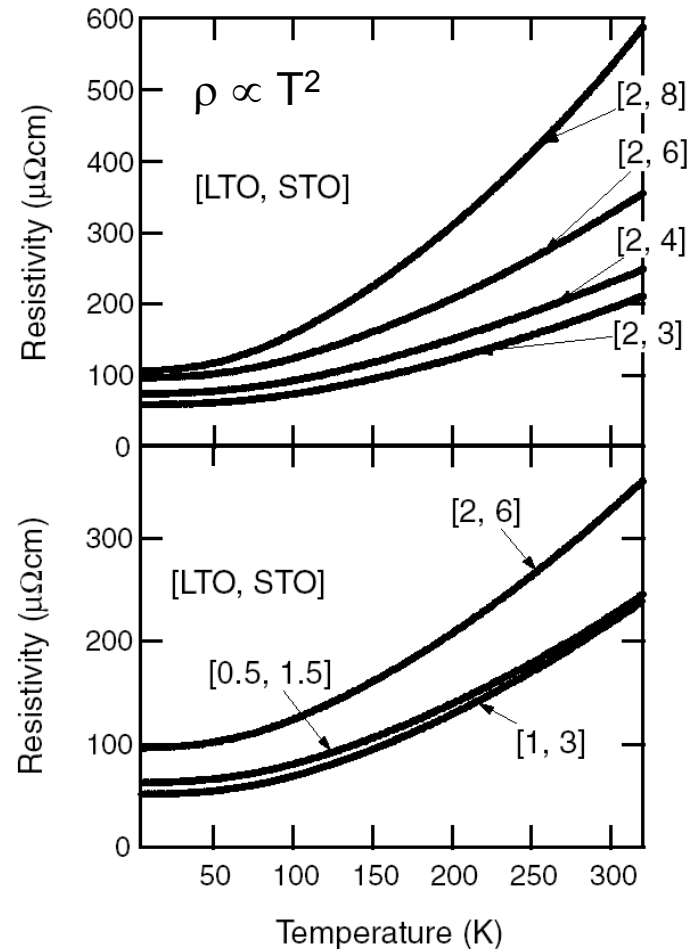
Metallic transport of SrTiO₃/LaTiO₃ superlattices



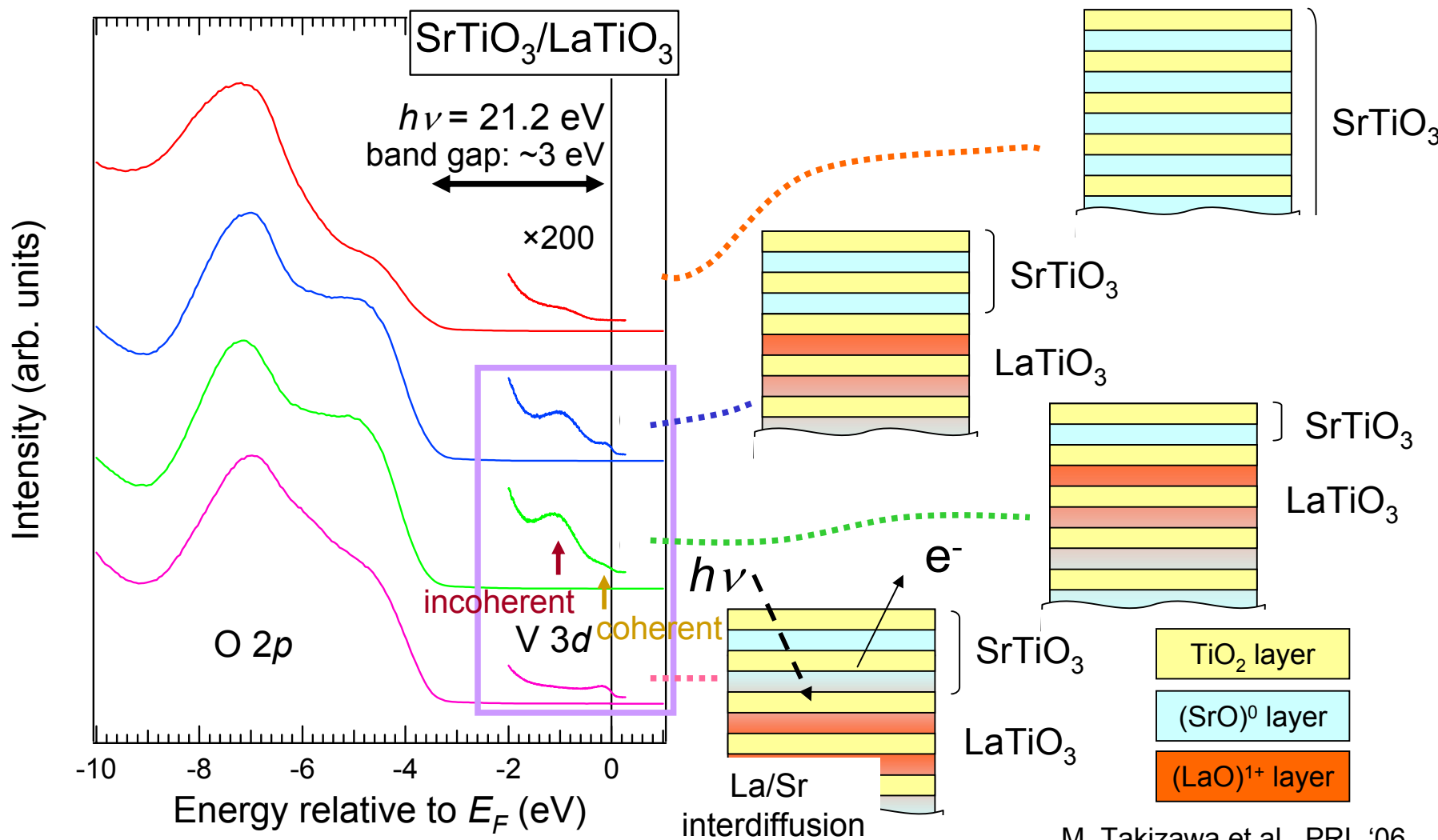
Lattice constant



Electrical resistivity

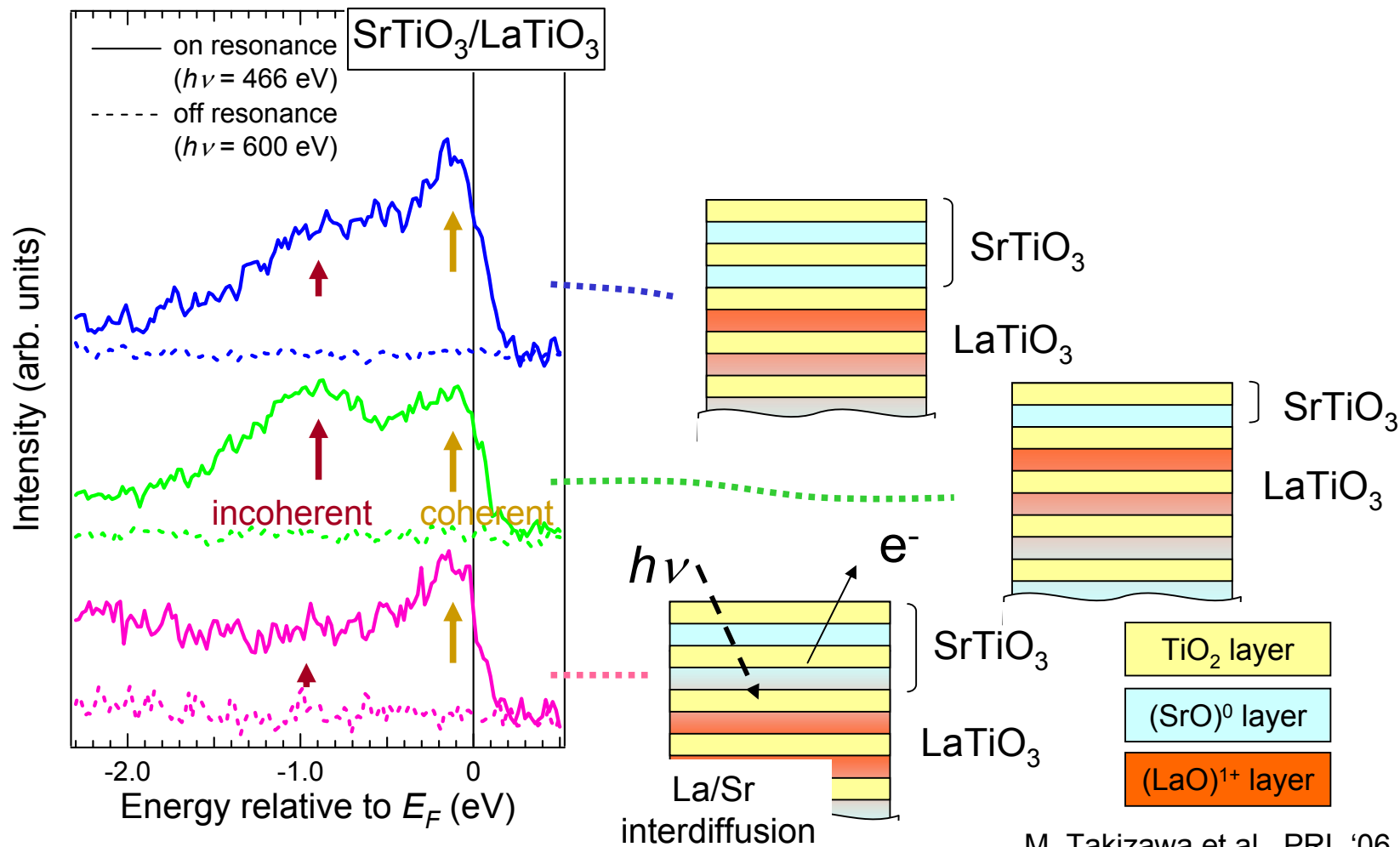


Photoemission spectra of SrTiO₃/LaTiO₃ interfaces

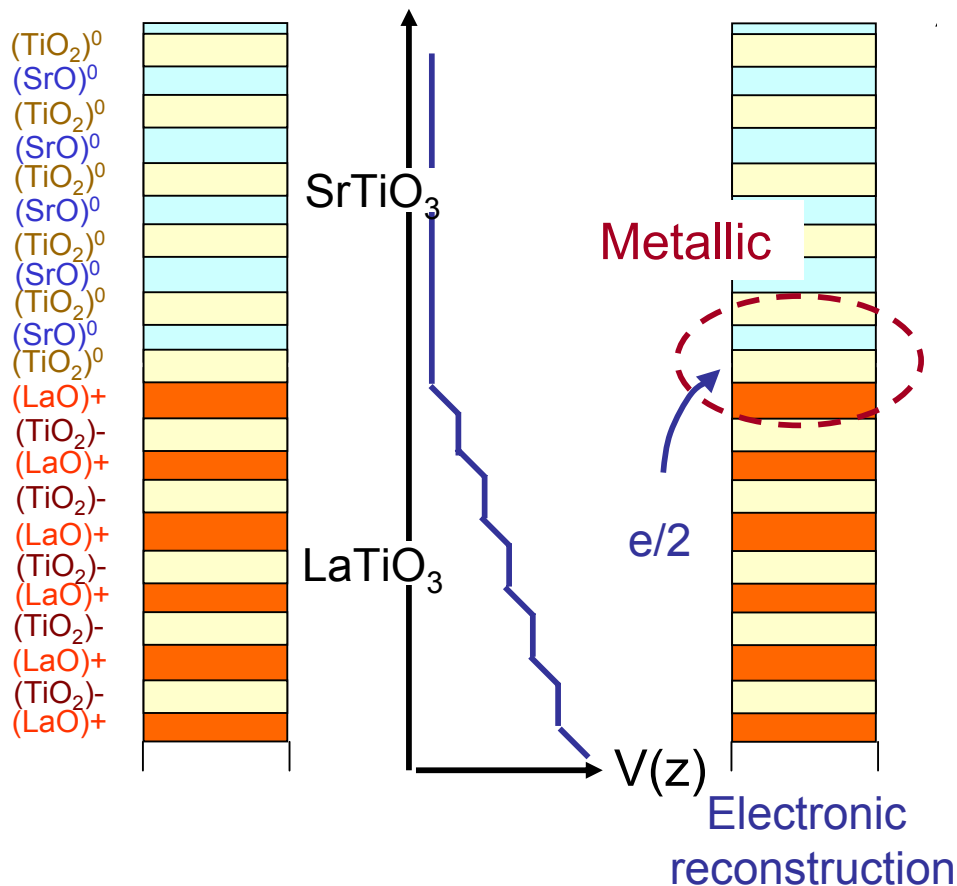


Photoemission spectra of SrTiO₃/LaTiO₃ interfaces

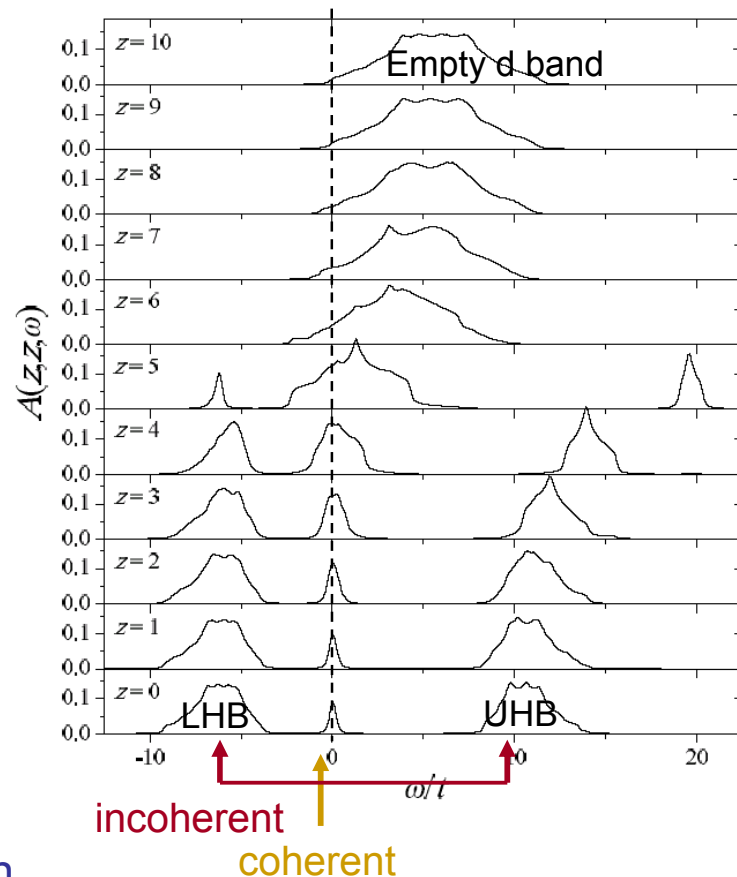
Ti 2p-3d resonant photoemission



Metallicity at SrTiO₃/LaTiO₃ interfaces resulting from electronic reconstruction



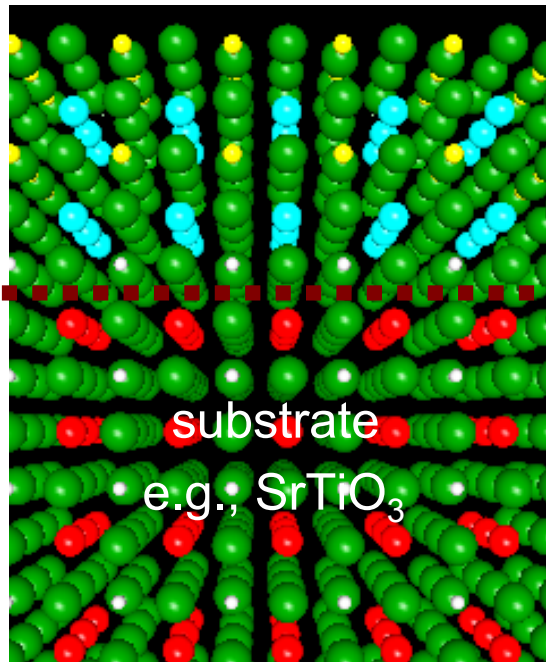
Layer DMFT calculation including long-range Coulomb interaction



Interfacial electronic structure

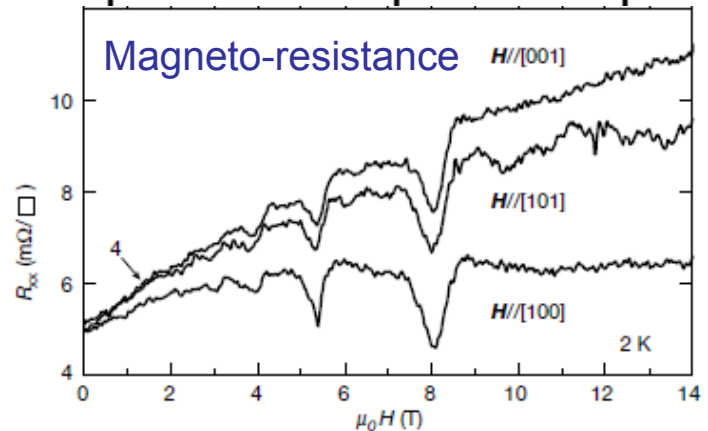
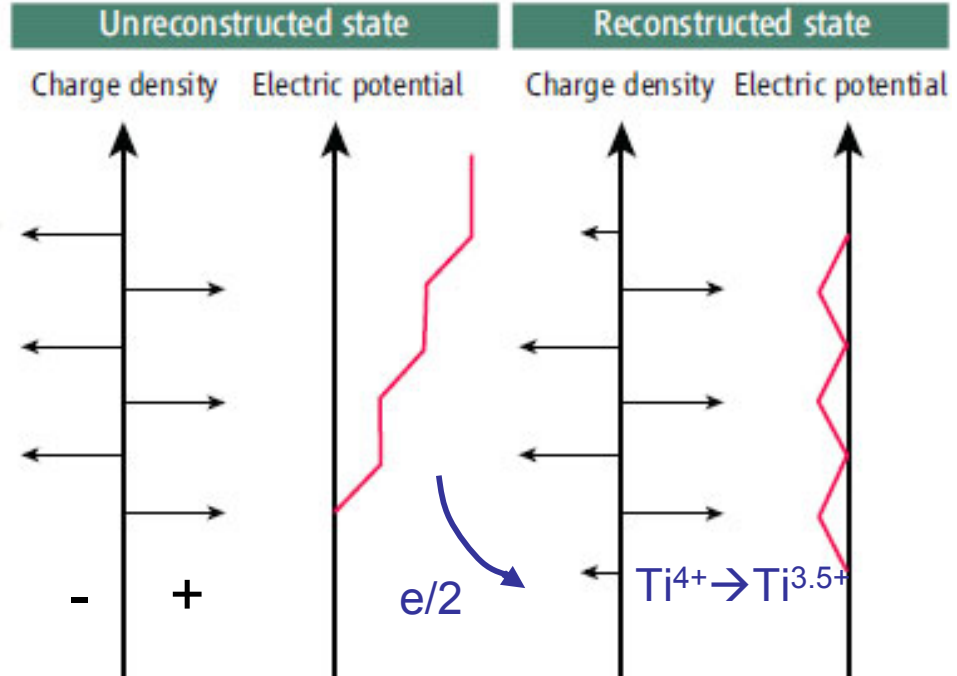
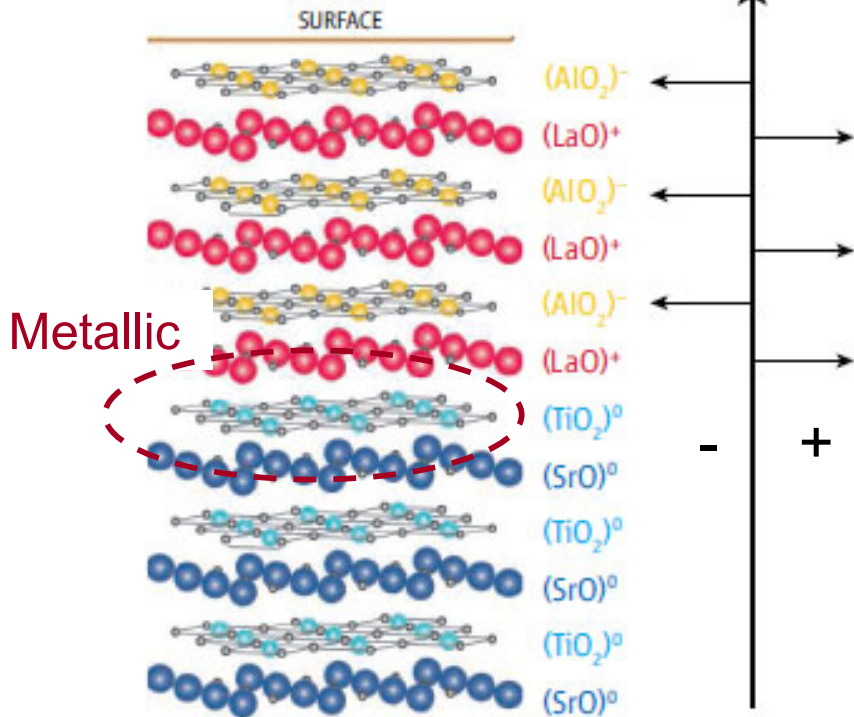
Metallic states between two insulators
-Charge transfer in electronic reconstruction-

Interfaces



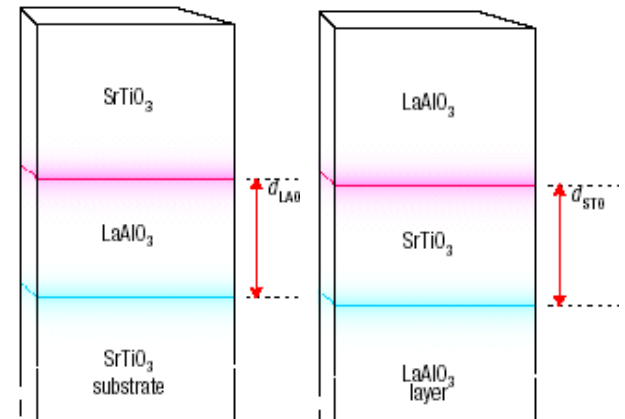
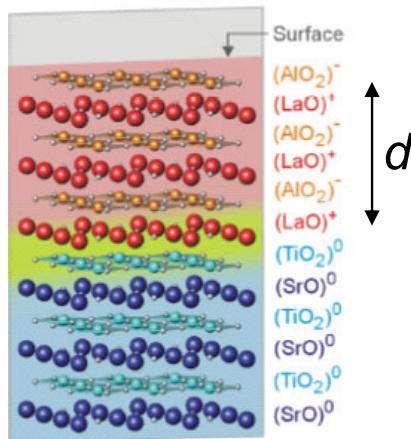
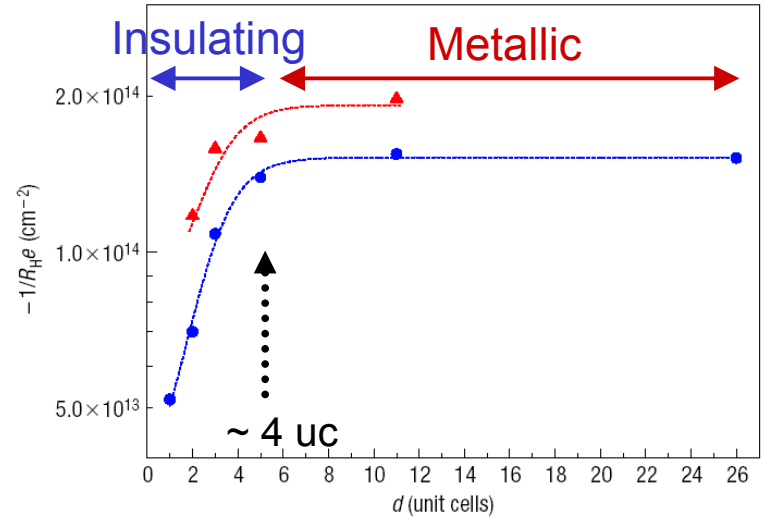
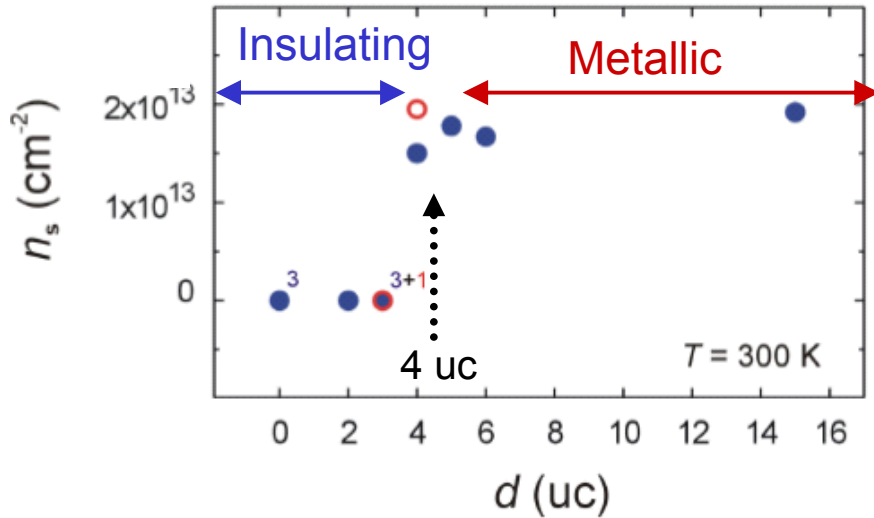
High mobility of *n*-type carriers at interfaces between two band insulators

LaAlO₃: band insulator
SrTiO₃: band insulator

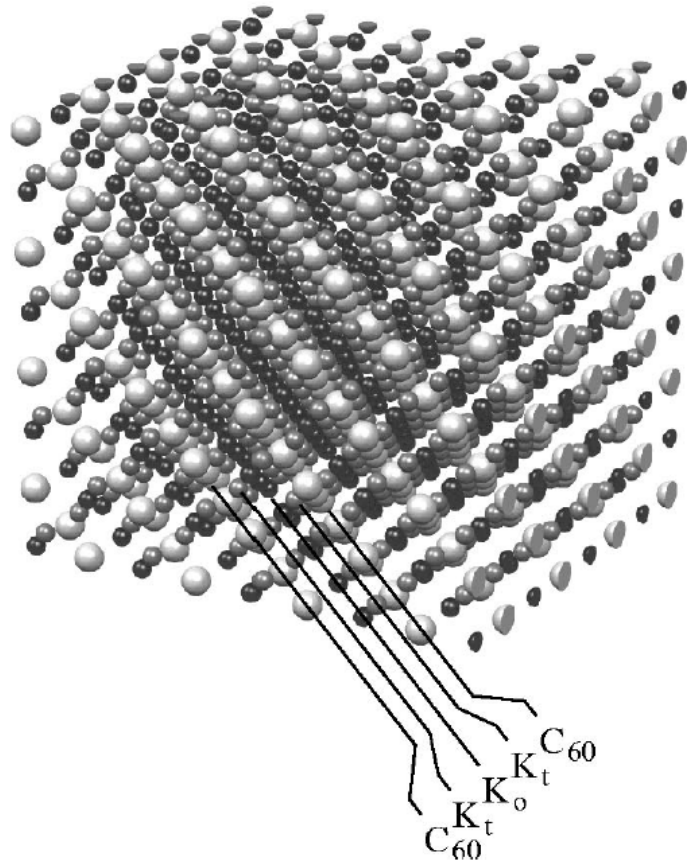


A. Ohtomo and H.Y. Hwang, Nature '04
H.Y. Hwang, Science '07

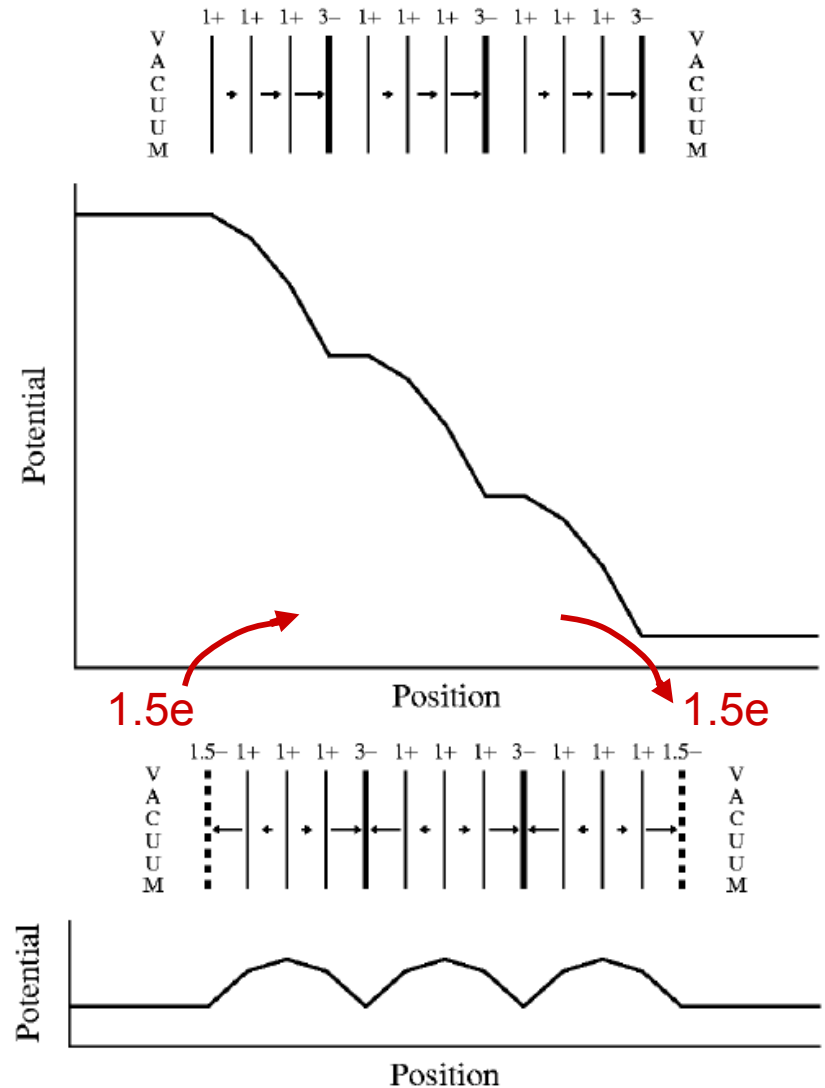
Critical thickness of ~ 4 uc for conductivity transition at $\text{LaAlO}_3/\text{SrTiO}_3$ interface



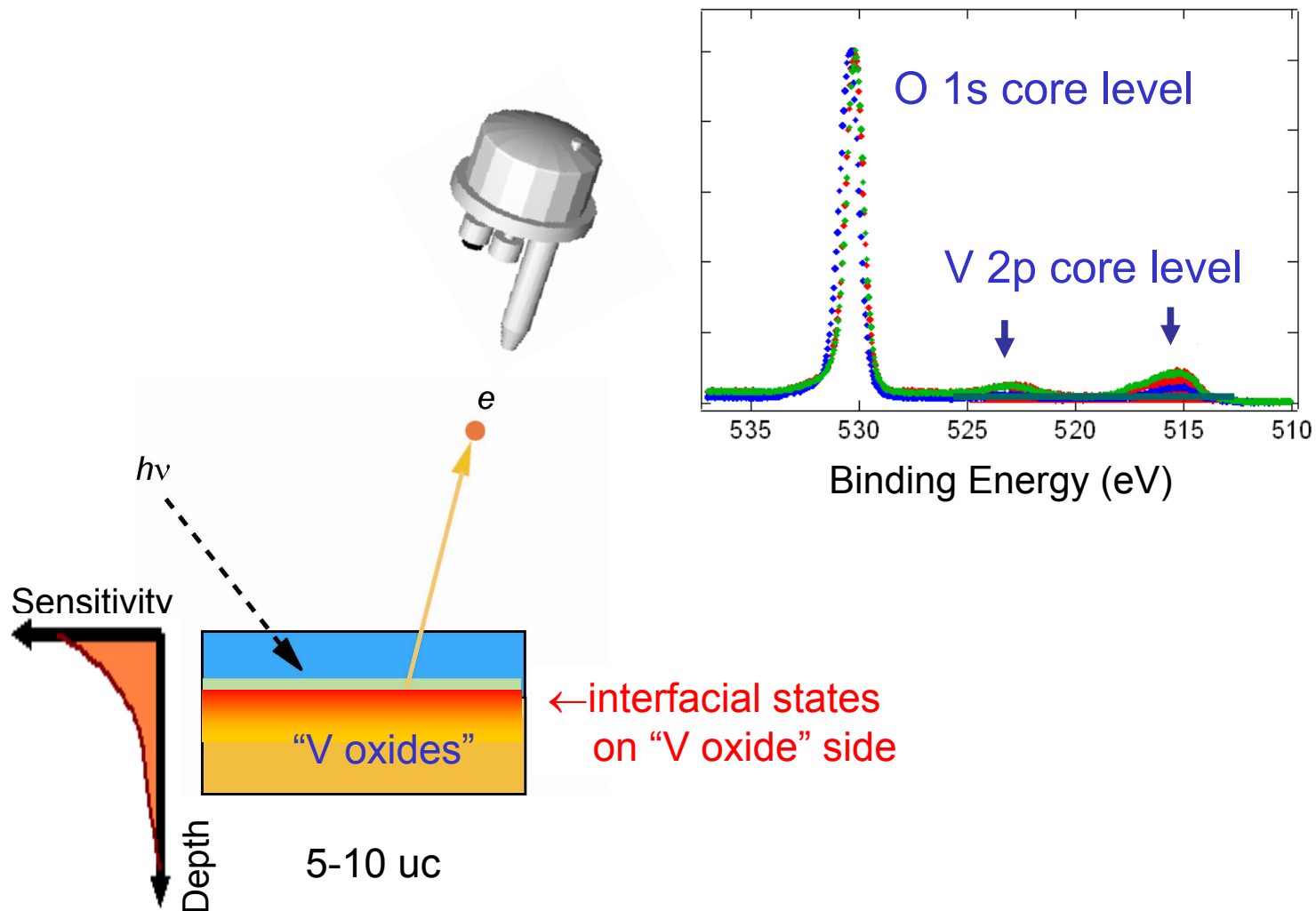
Polar (111) surface of K_3C_{60} and its electronic reconstruction



R. Hepster et al., PRB '00

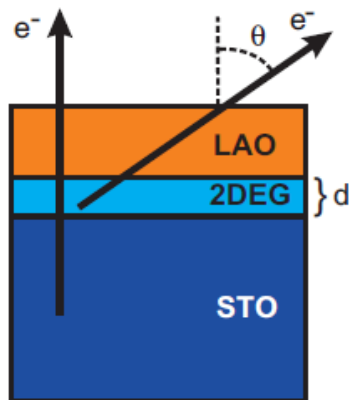
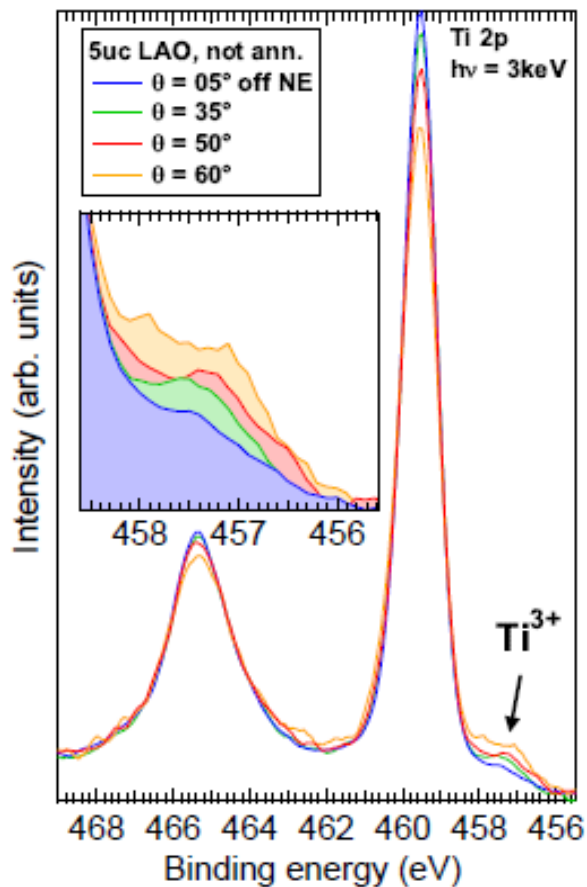


Photoemission spectroscopy of buried interfaces

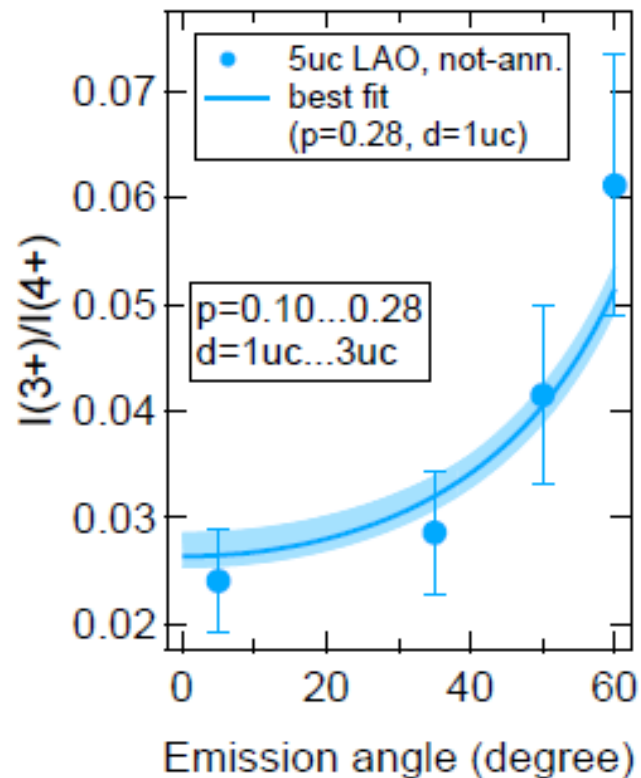


Evidence for Ti^{3+} states at the n -type $LaAlO_3/SrTiO_3$ interface

Ti 2p core-level spectra

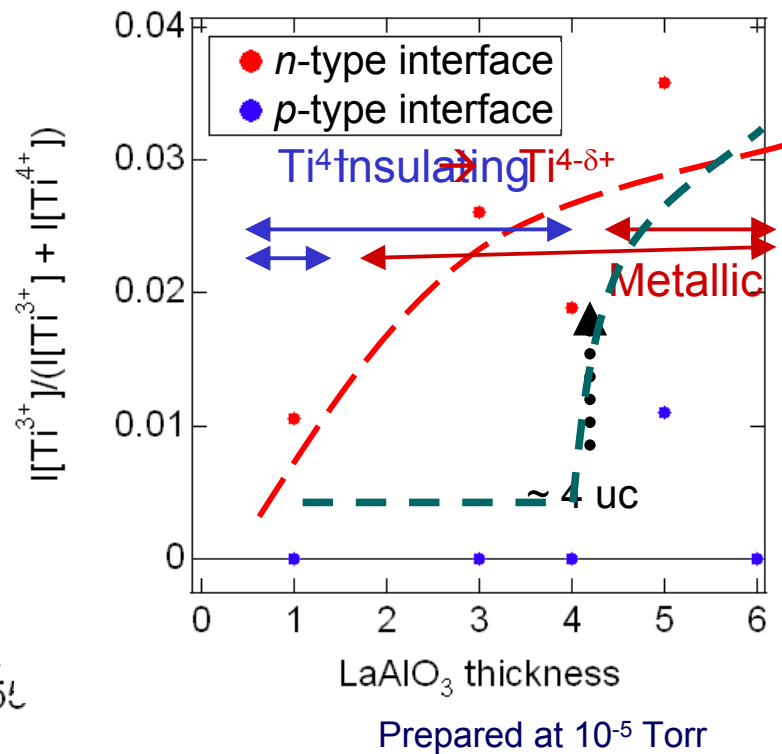
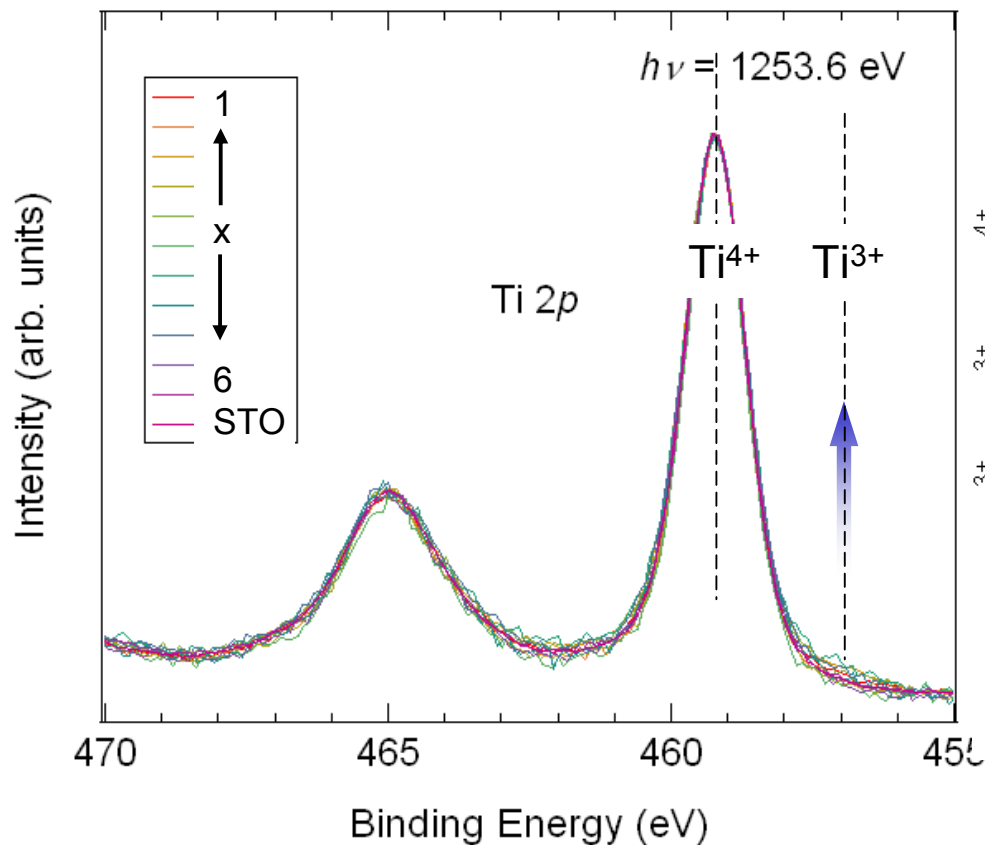


Ti^{3+} intensity

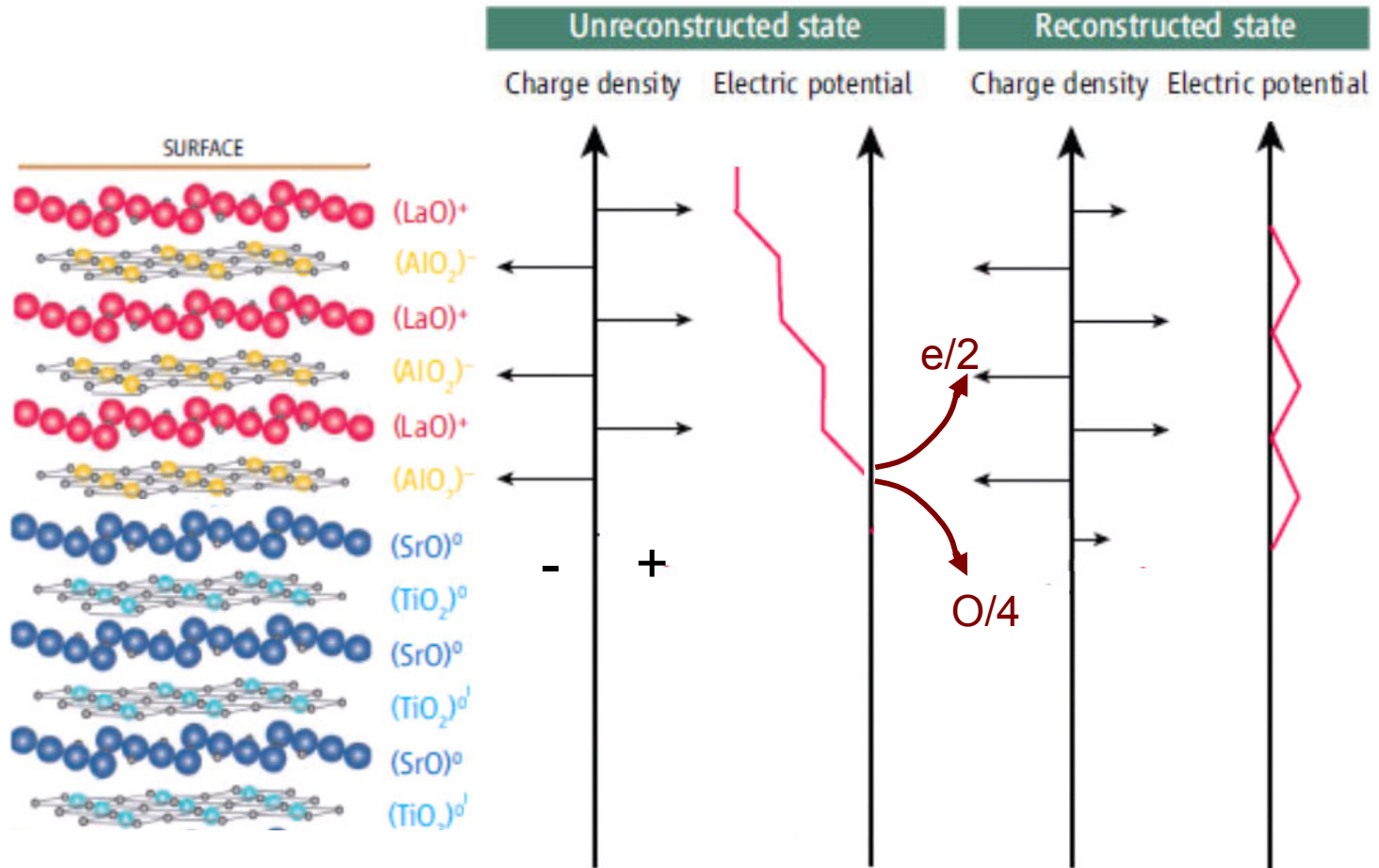


LaAlO₃ overlayer thickness dependence of Ti³⁺ concentration at LaAlO₃/SrTiO₃ interface

LaAlO₃(*x* uc)/SrTiO₃



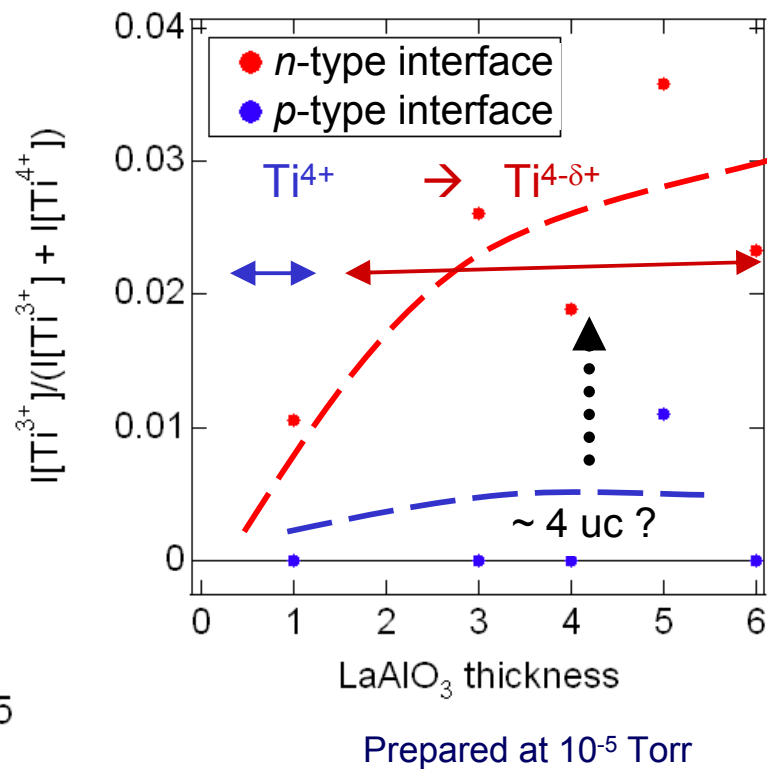
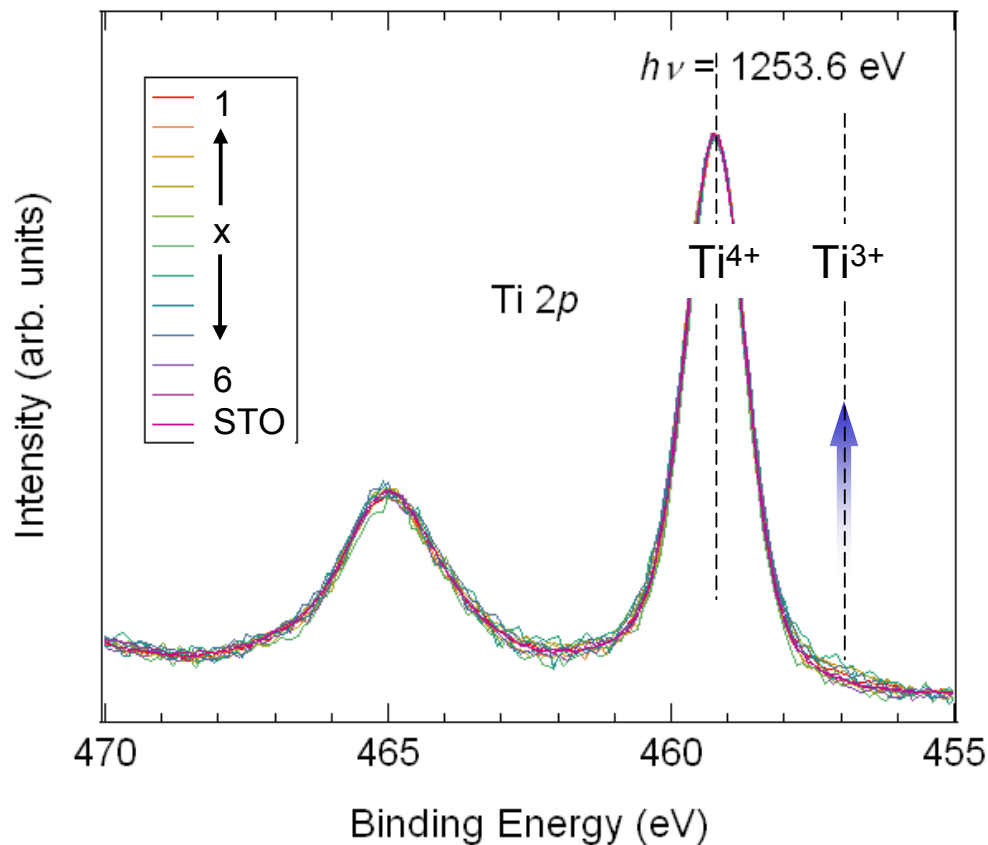
p-type $\text{LaAlO}_3/\text{SrTiO}_3$ interface



A. Ohtomo and H.Y. Hwang, Nature '04; N. Nakagawa et al, Nat. Mater. '06
 H.Y. Hwang, Science '07

LaAlO₃ overlayer thickness dependence of Ti³⁺ concentration at LaAlO₃/SrTiO₃ interface

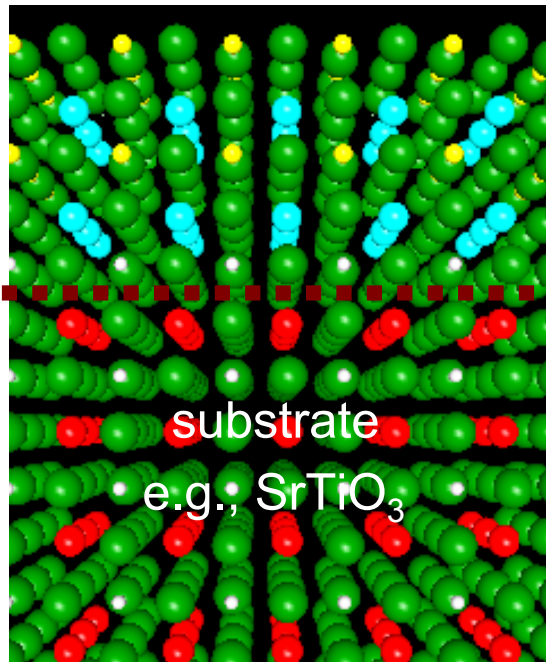
LaAlO₃(*x* uc)/SrTiO₃



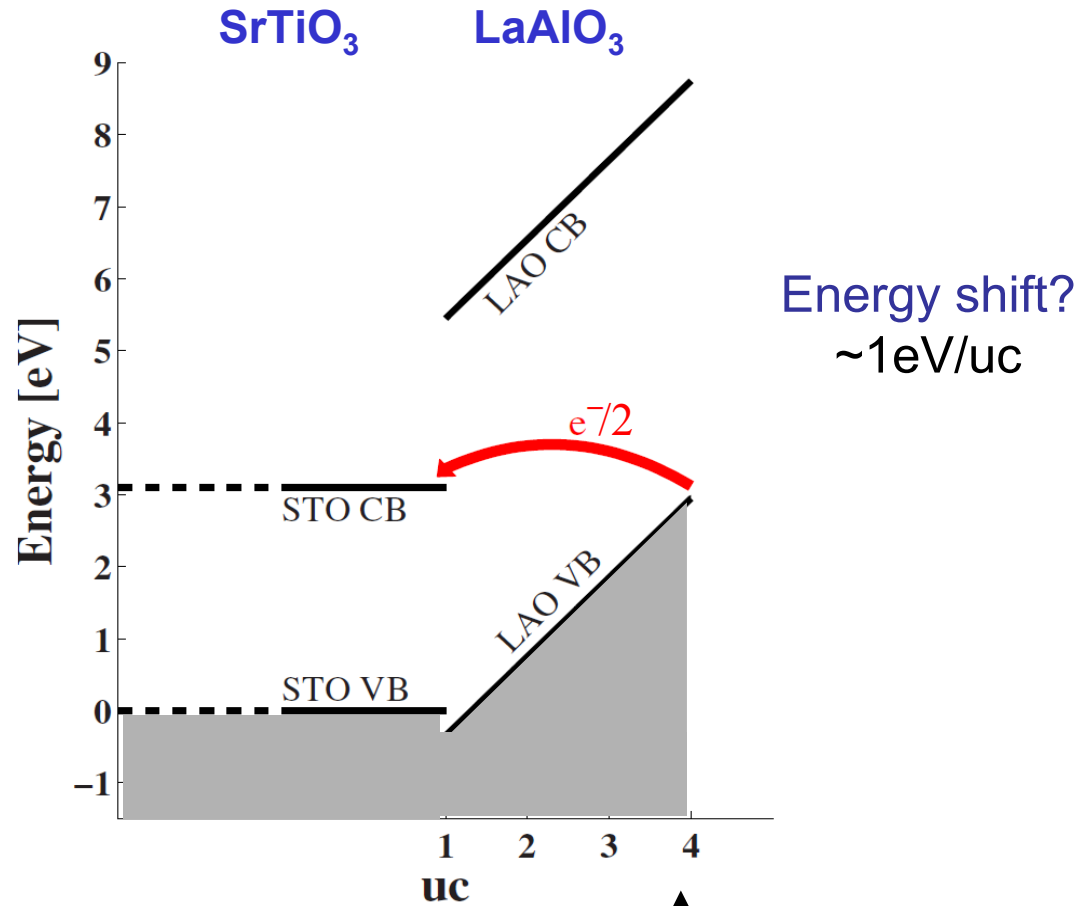
Interfacial electronic structure

Metallic states between two insulators
-Potential change in electronic reconstruction-

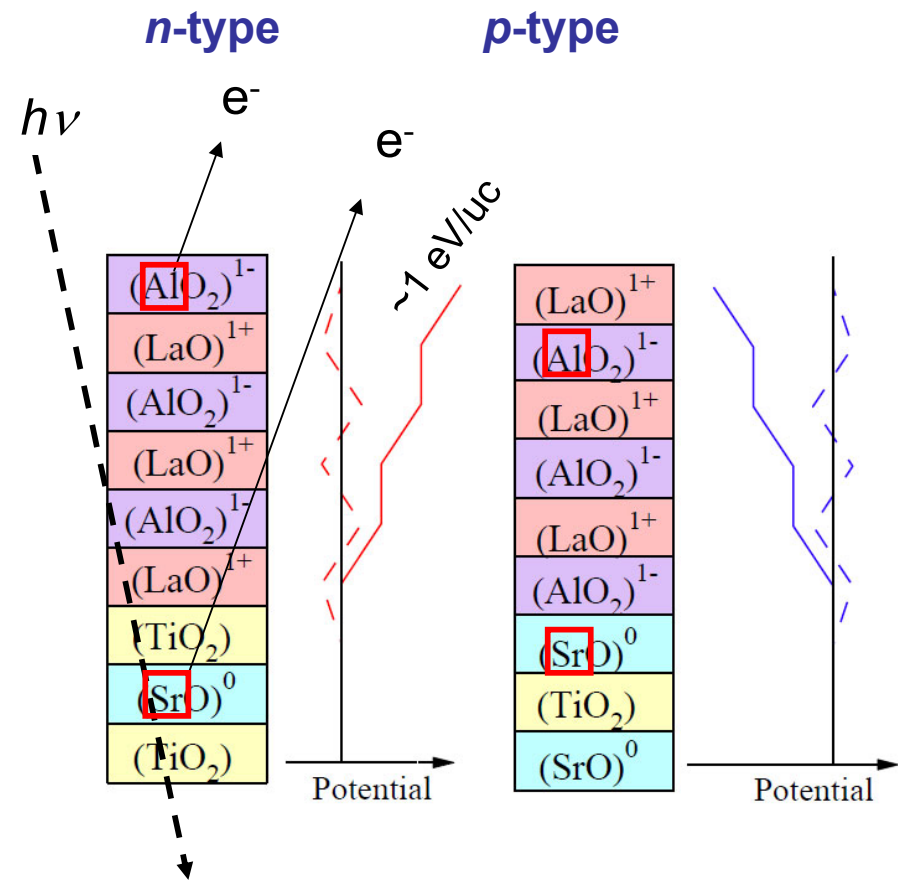
Interfaces



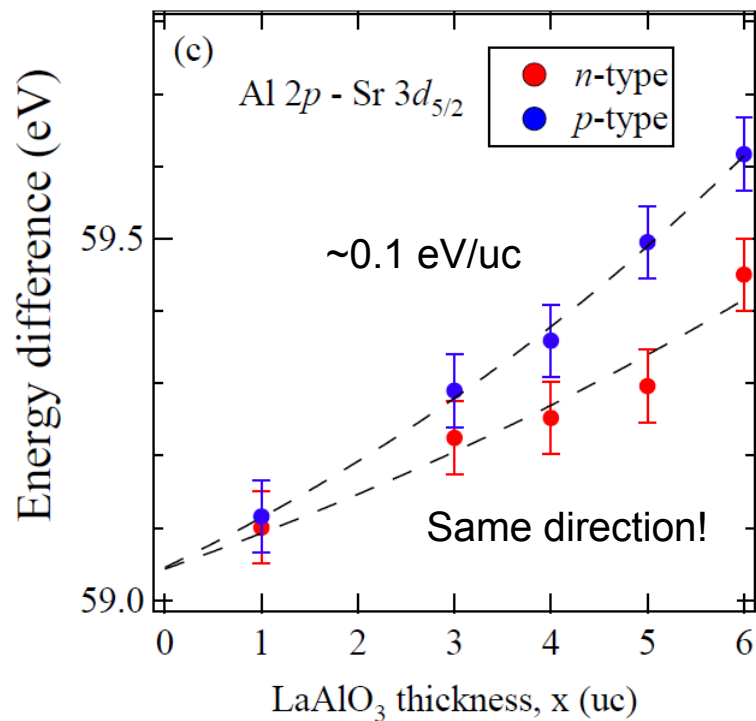
Polar catastrophe model of $\text{LaAlO}_3/\text{SrTiO}_3$



Probing the potential slope in the LaAlO₃ layer of LaAlO₃/SrTiO₃



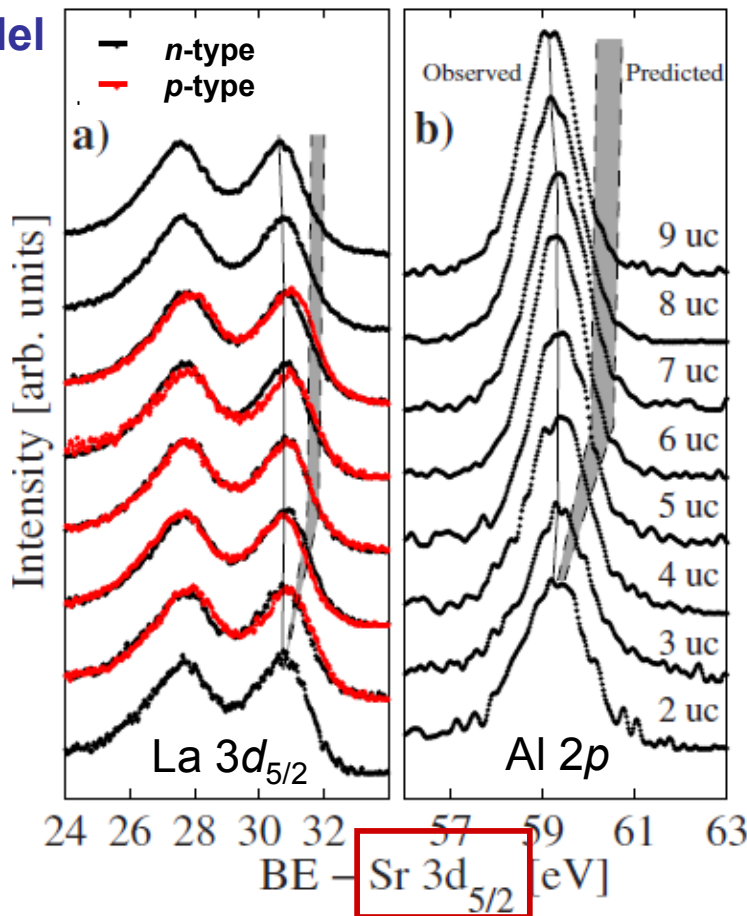
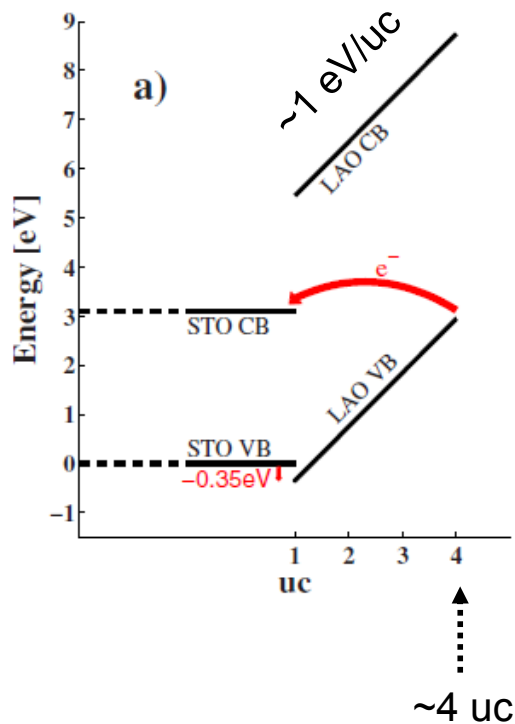
Al 2p – Sr 3d relative core-level shifts



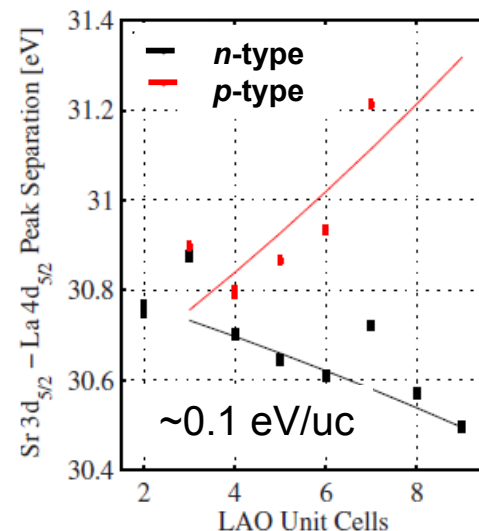
Probing the potential slope in the LaAlO_3 layer of $\text{LaAlO}_3/\text{SrTiO}_3$

La 3d and Al 2p core levels
referenced to Sr 3d

Polar catastrophe model



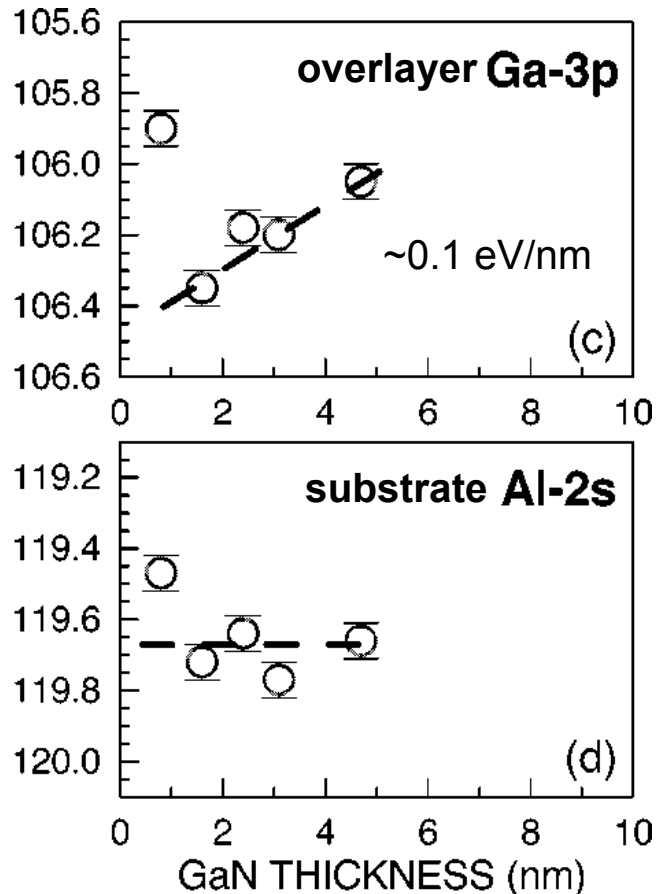
Sr 3d – La 4d relative
core-level shifts



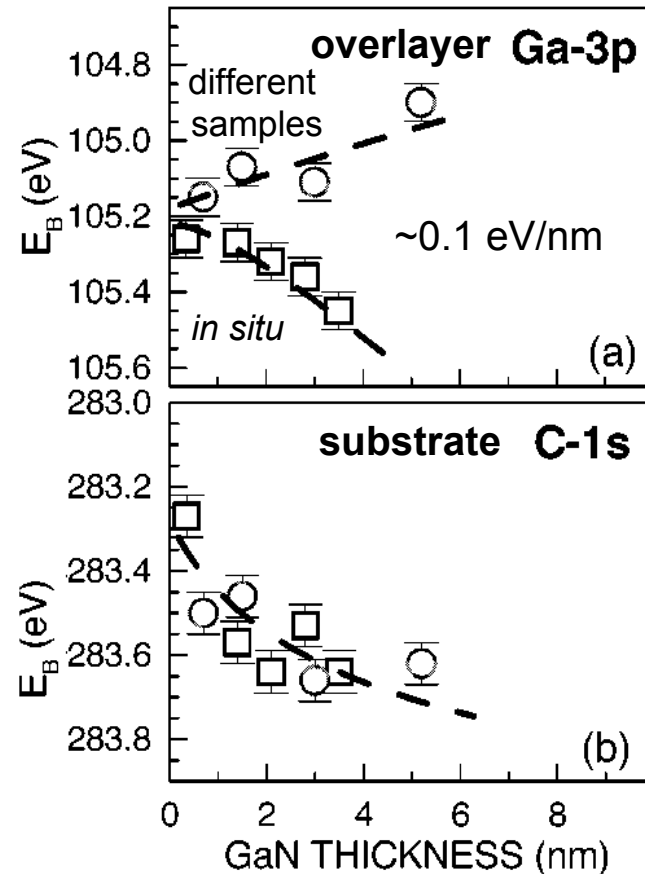
Opposite to the model!

Probing the potential slope in GaN (0001) layers

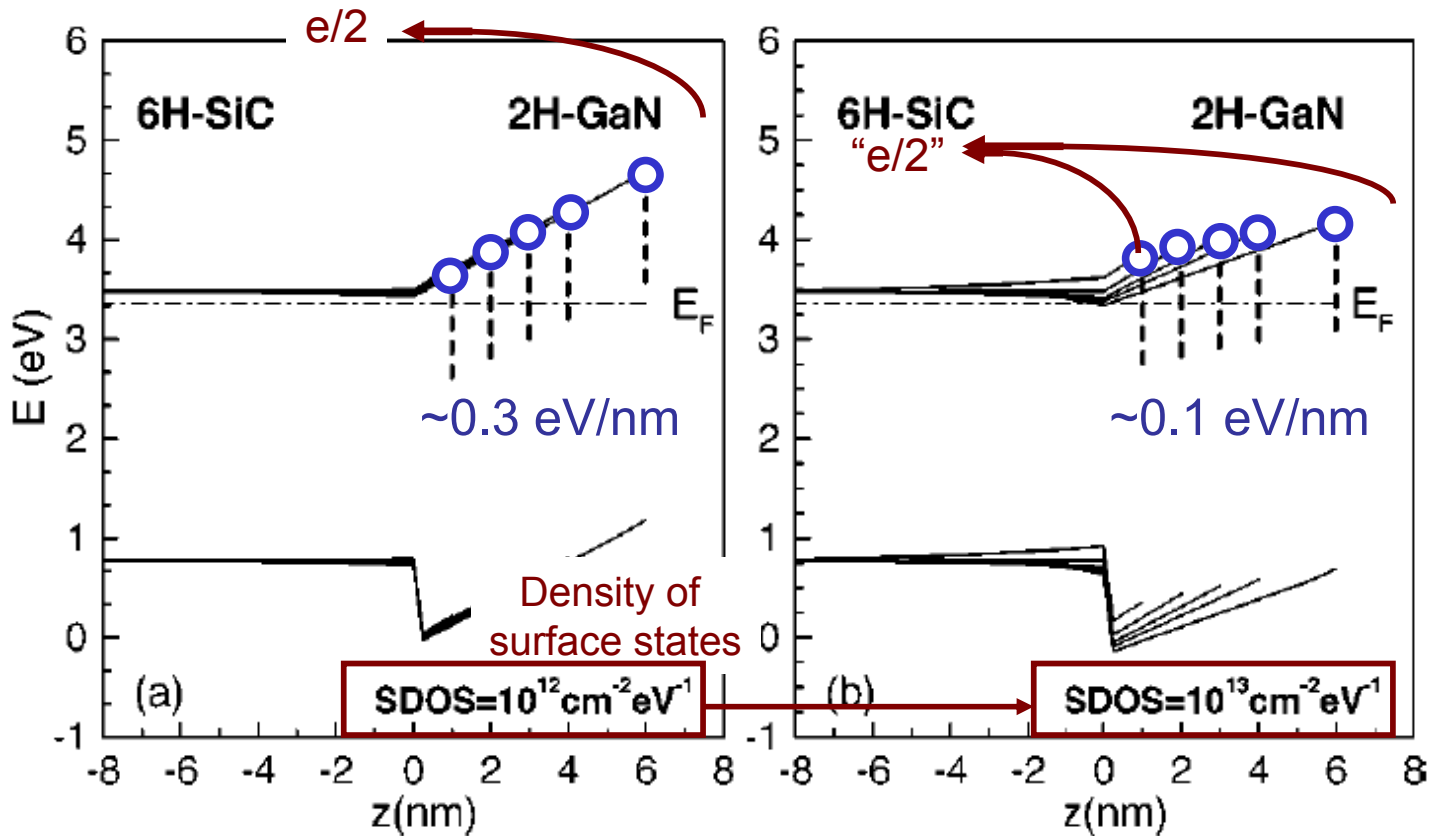
GaN/AlN(0001)



GaN/SiC(0001)



Calculated potential in polar GaN/SiC(0001)

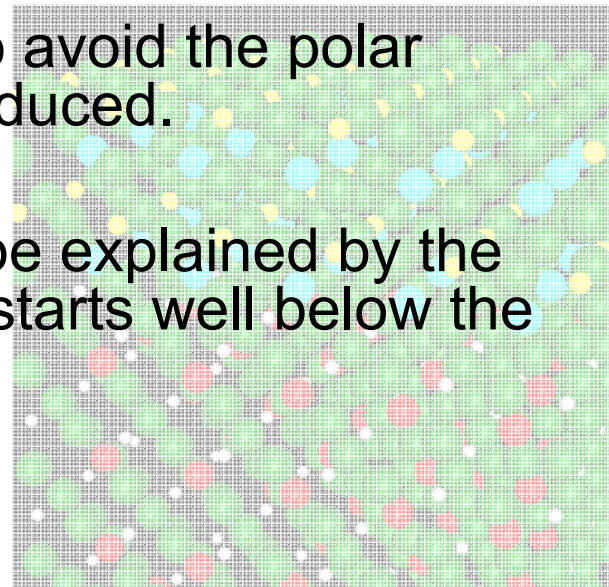


Short summary

- Metallic states between two insulators -

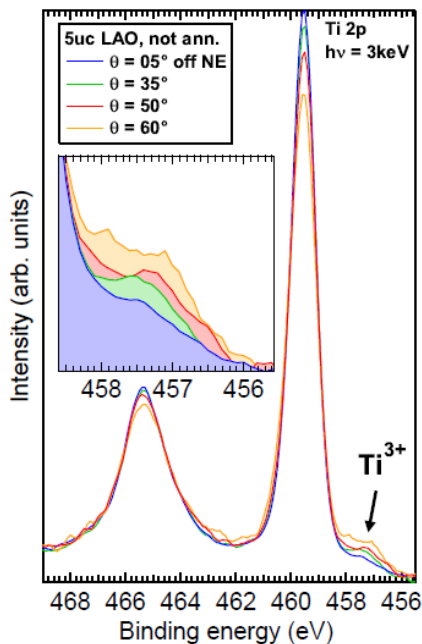
Electronic reconstruction at insulator-insulator interfaces:

- ✓ Charge transfer occurs as expected to avoid the polar catastrophe, but the charge transfer starts well below the critical thickness of transport.
- ✓ Potential slope as expected to avoid the polar catastrophe model is much reduced.
- ✓ The above observations can be explained by the gradual reconstruction which starts well below the critical thickness.

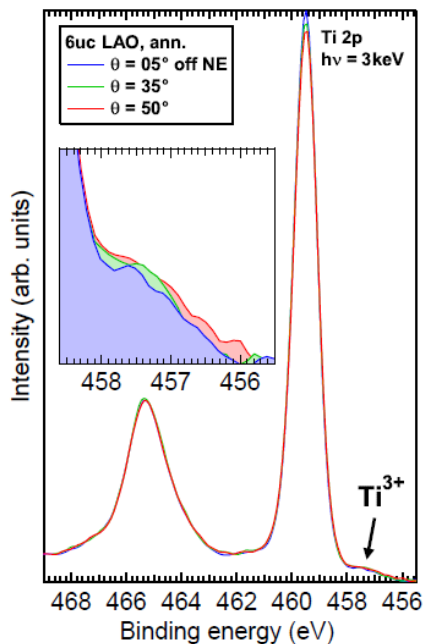


Preparation dependence of carrier distributions at the n -type $\text{LaAlO}_3/\text{SrTiO}_3$ interface

Core-level photoemission



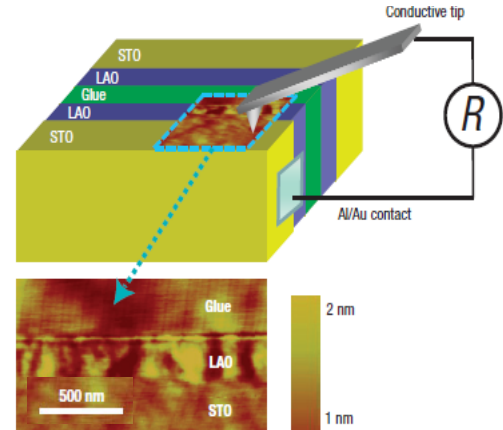
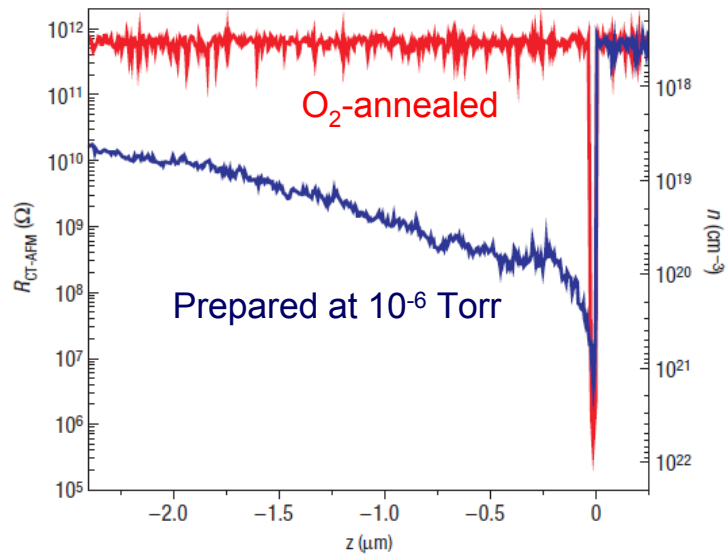
Prepared at 10^{-6} Torr



O_2 -annealed

M. Sing et al., PRL '09

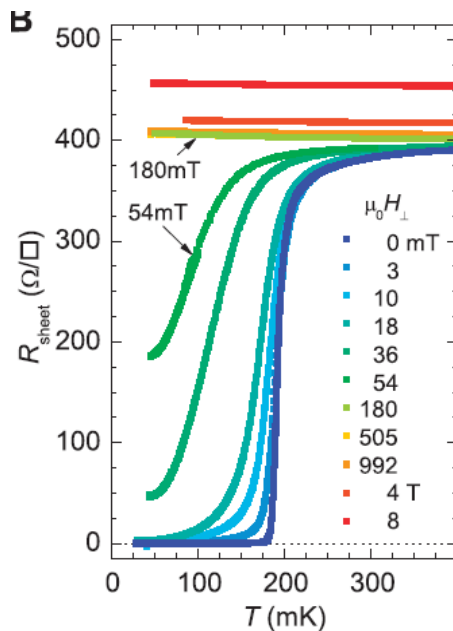
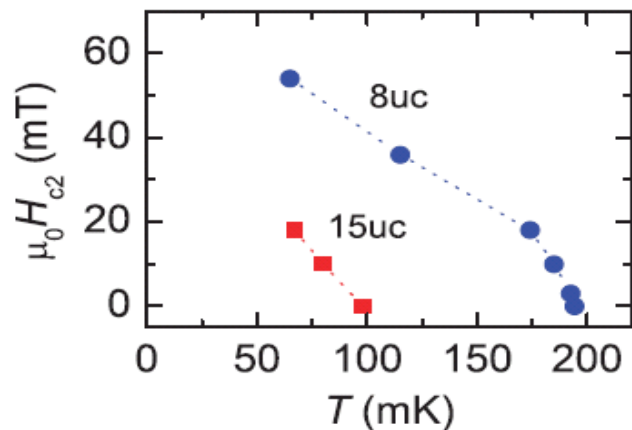
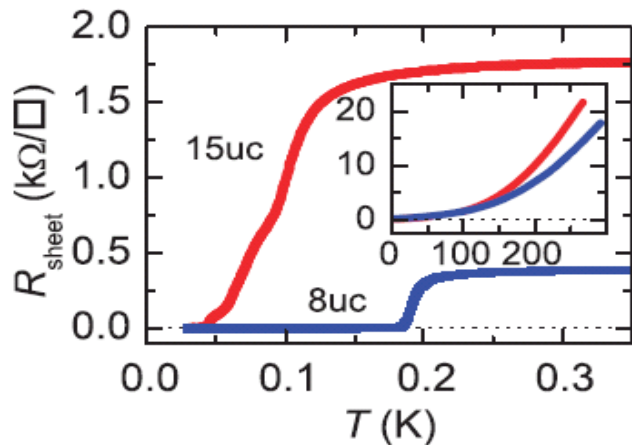
Cross-sectional AFM



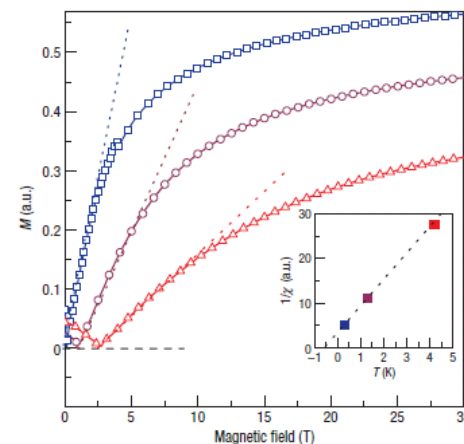
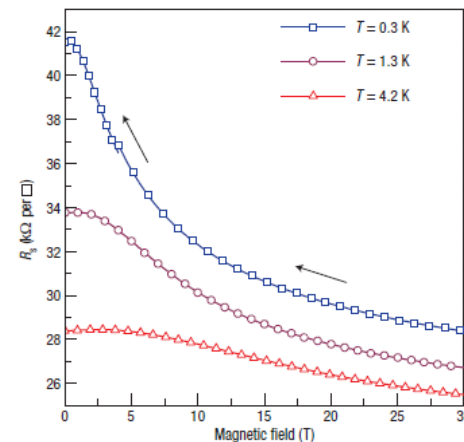
M. Basletic et al., Nat. Phys. '08

Novel physical properties of $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces

Superconductivity



Ferromagnetism

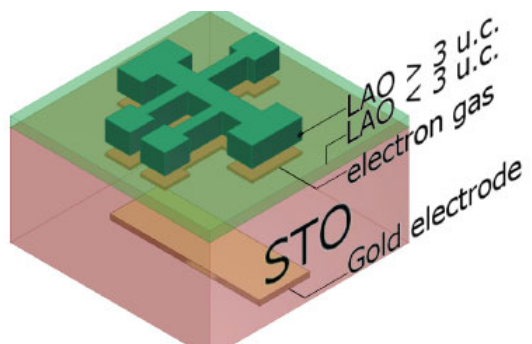
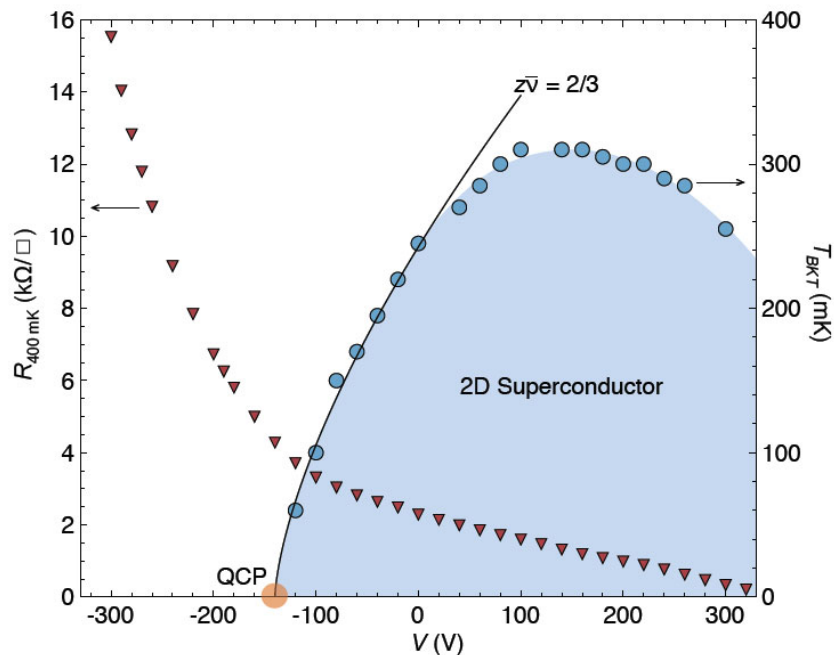
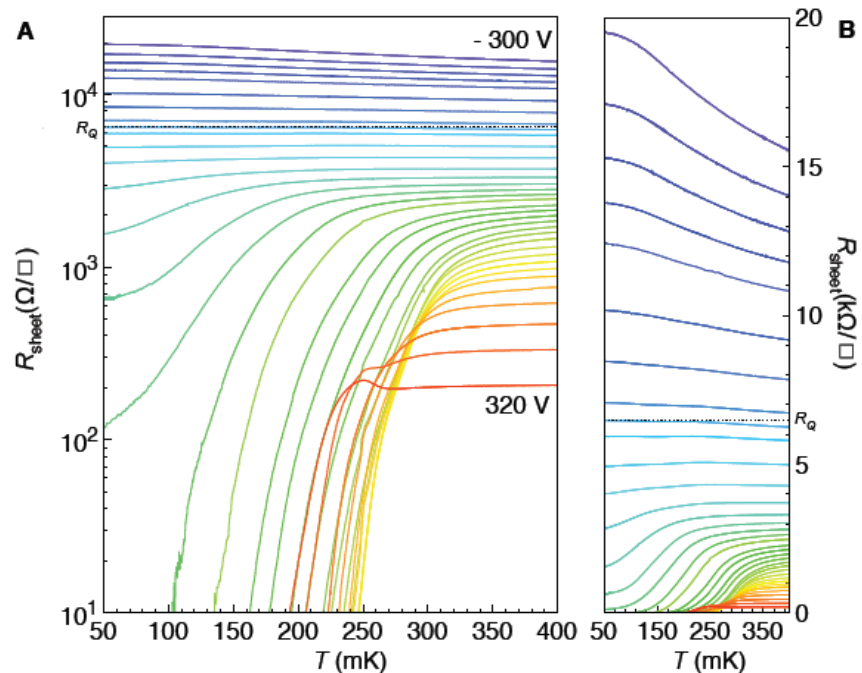


N. Reyren et al. Science '07

A. Brinkman et al. Nat. Mater. '07
cf: MR by M. B. Shalom et al., PRB '09

Gate-voltage control of superconductivity at LaAlO₃/SrTiO₃ interface

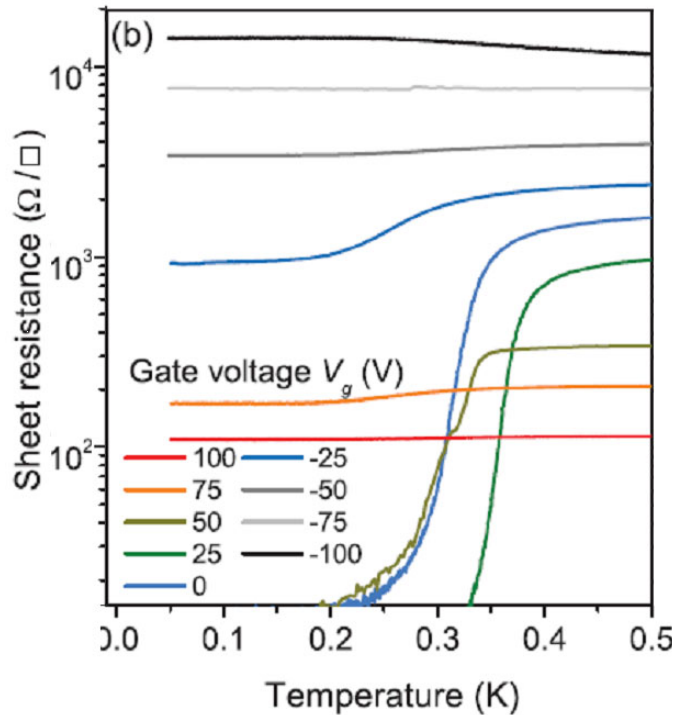
Resistivity for various gate voltages



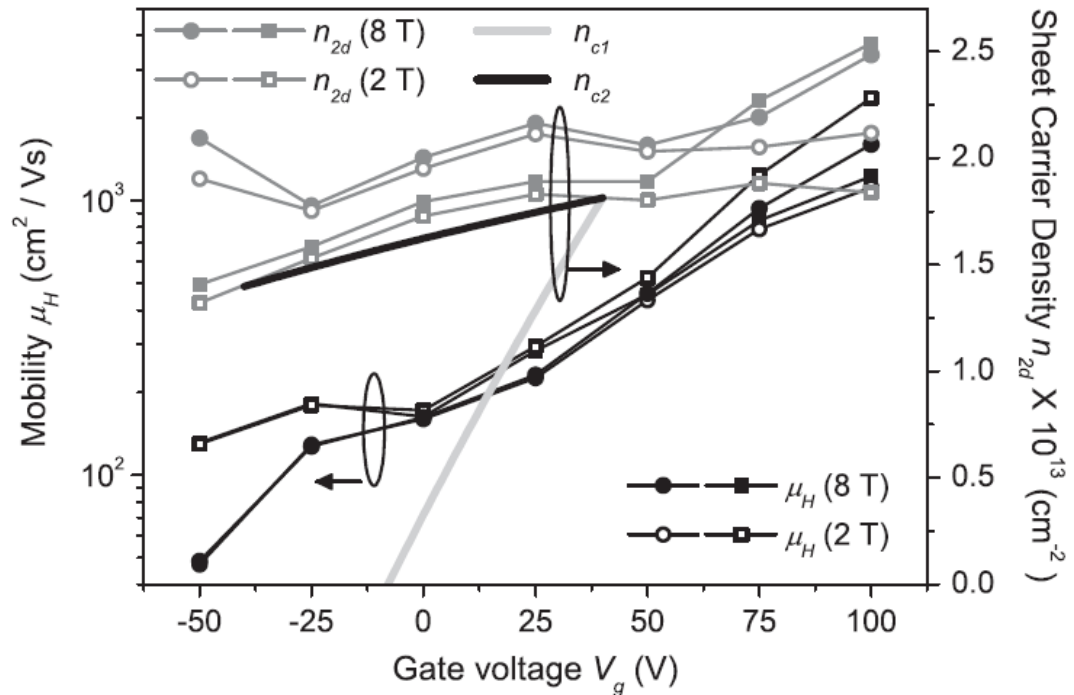
$$T_{\text{BKT}} \propto (V - V_c)^{z\bar{\nu}}, \text{ with } z\bar{\nu} = 2/3.$$

Gate-voltage-controlled LaAlO₃/SrTiO₃ interface: Filling control or mobility control?

Resistivity for various gate voltages



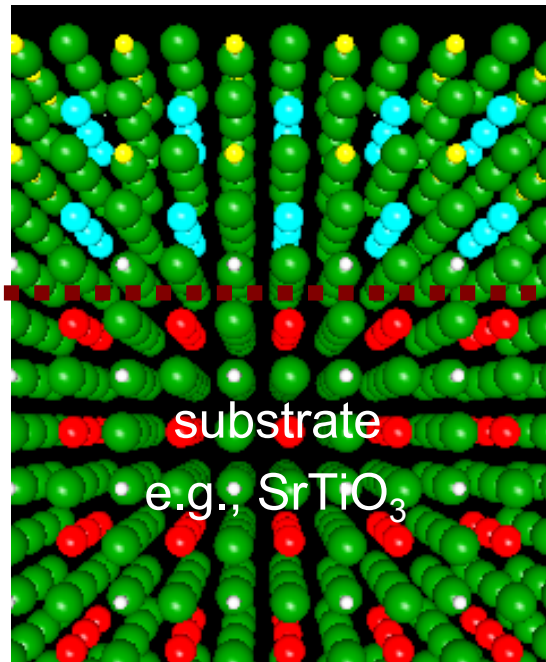
Gate-voltage dependence of carrier density and mobility



Interfacial electronic structure

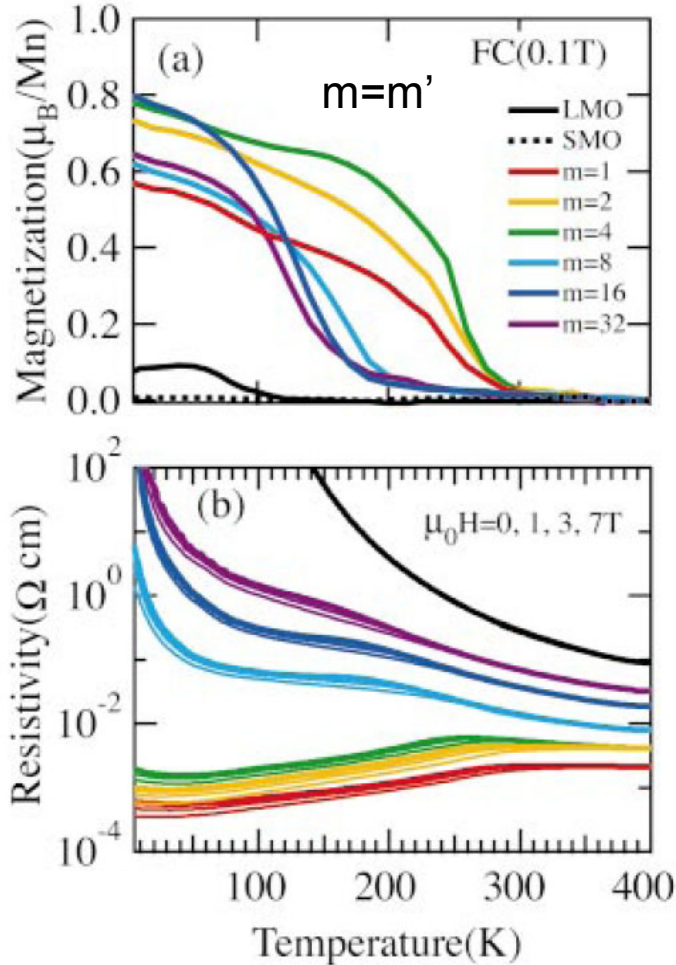
Ferromagnetism between non-magnetic materials

Interfaces



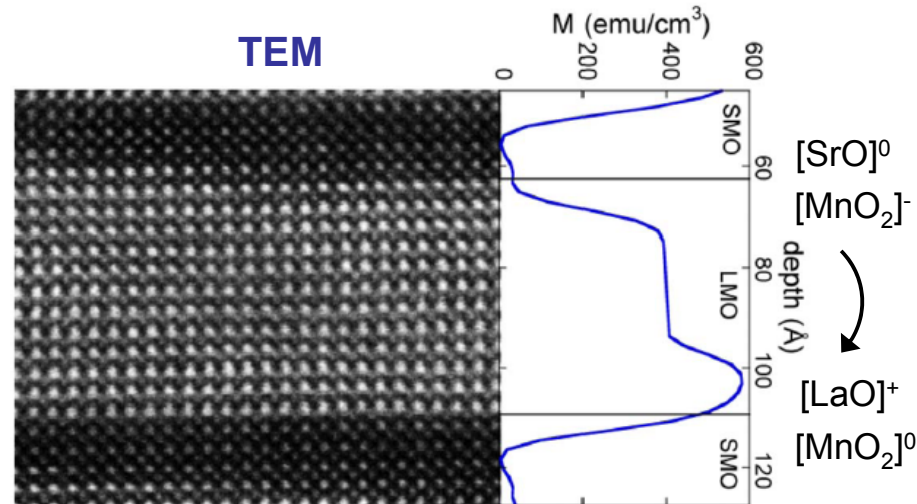
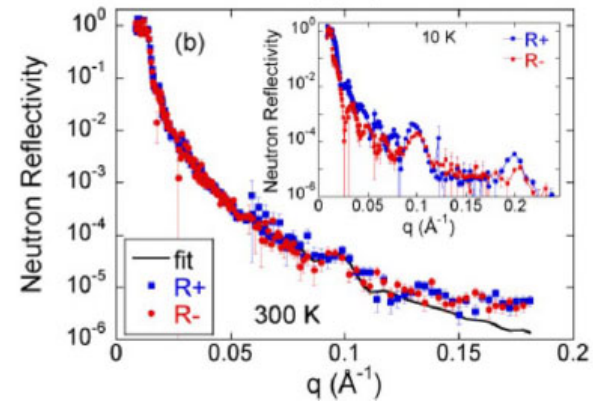
Ferromagnetism in $[(\text{LaMnO}_3)_m/(\text{SrMnO}_3)_{m'}]_n$ superlattices

Magnetization, resistivity



T. Koida et al., PRB '02

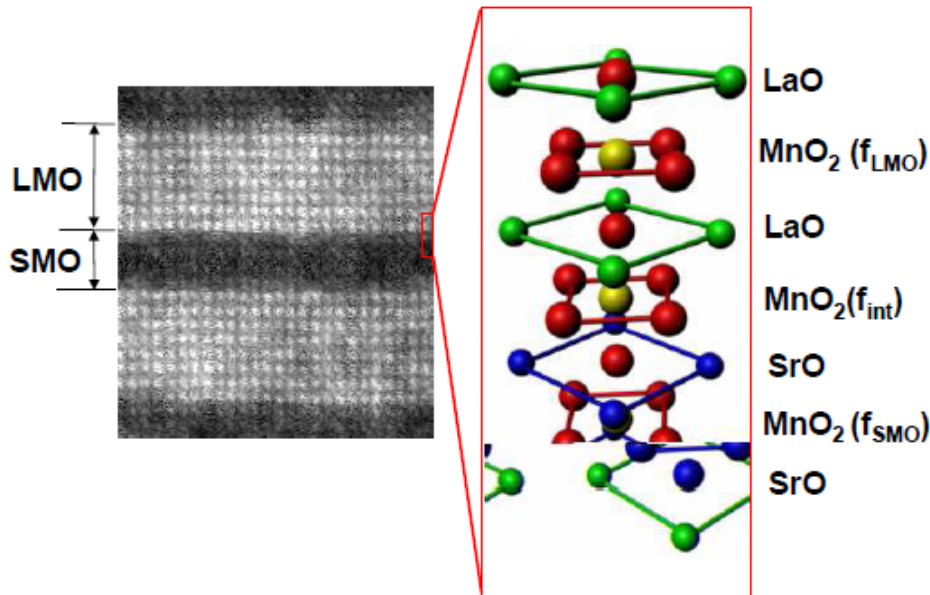
Polarized neutron reflectivity



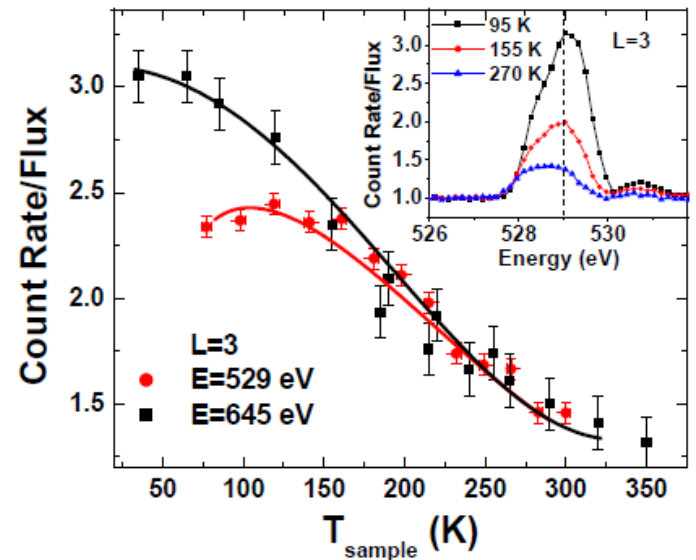
S.J. May et al., PRB '08

Soft x-ray scattering from $[(\text{LaMnO}_3)_8/(\text{SrMnO}_3)_4]_7/\text{SrTiO}_3(001)$

STEM image



Temperature dependence



(003) resonance

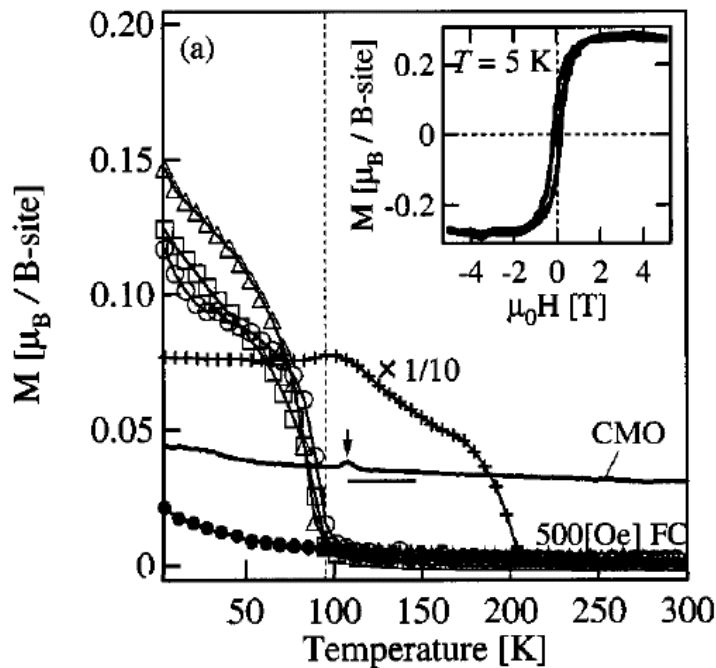


Metallic behavior

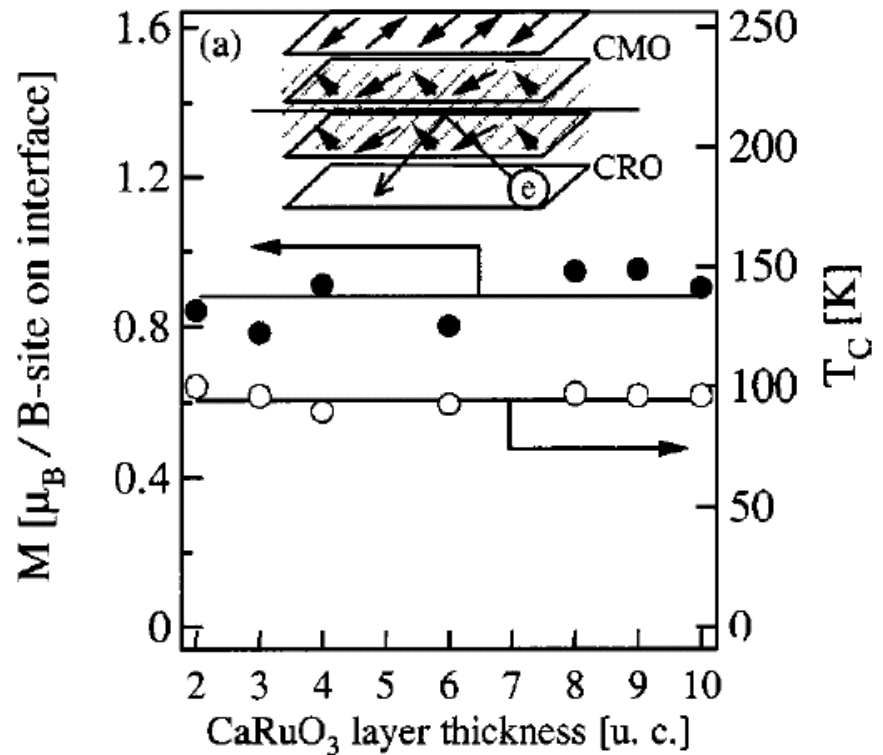
Ferromagnetism in AF insulator-paramagnetic metal interfaces

CaMnO₃: AF insulator
 CaRuO₃: PM metal

Magnetization

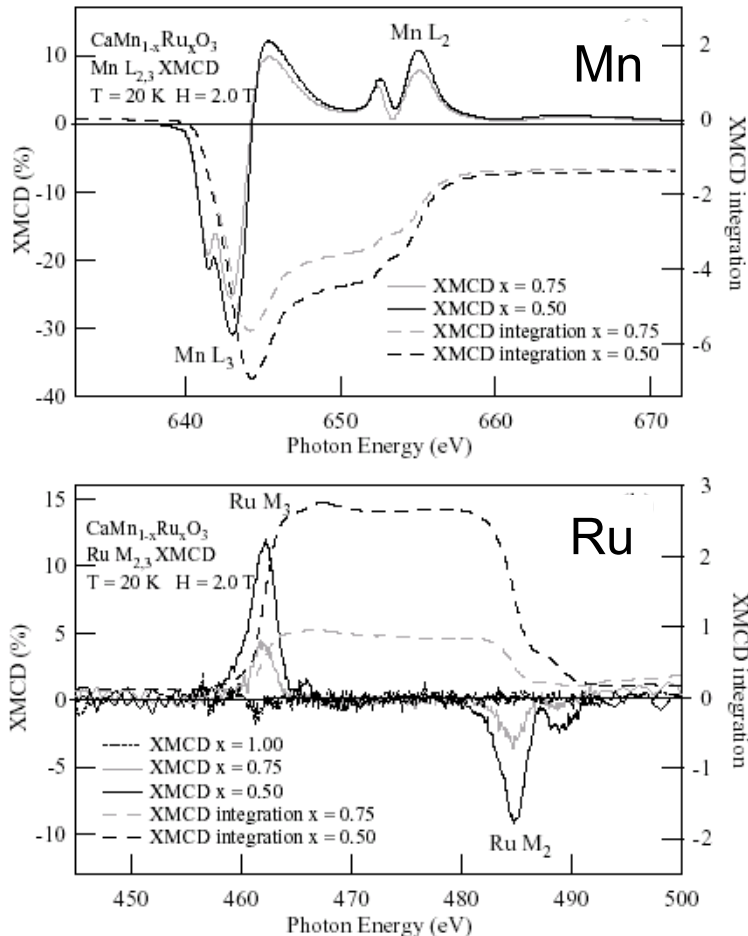


Magnetization and T_c

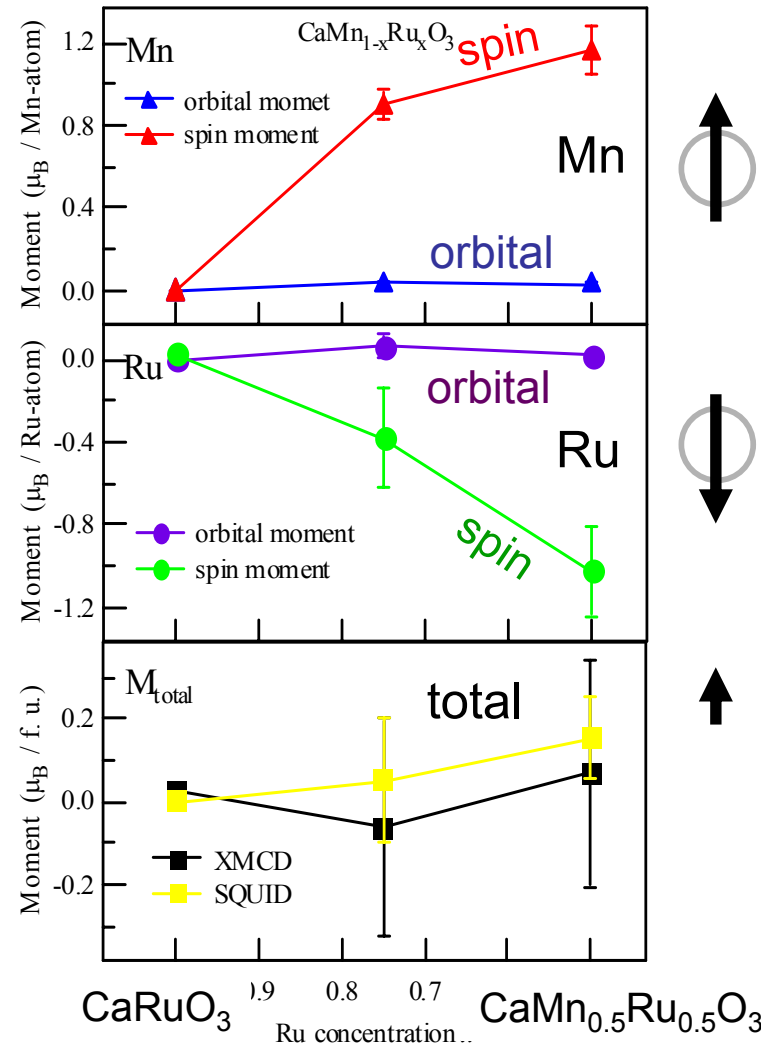


Mn 2p and Ru 3p XMCD for $\text{CaMn}_{1-x}\text{Ru}_x\text{O}_3$ thin films

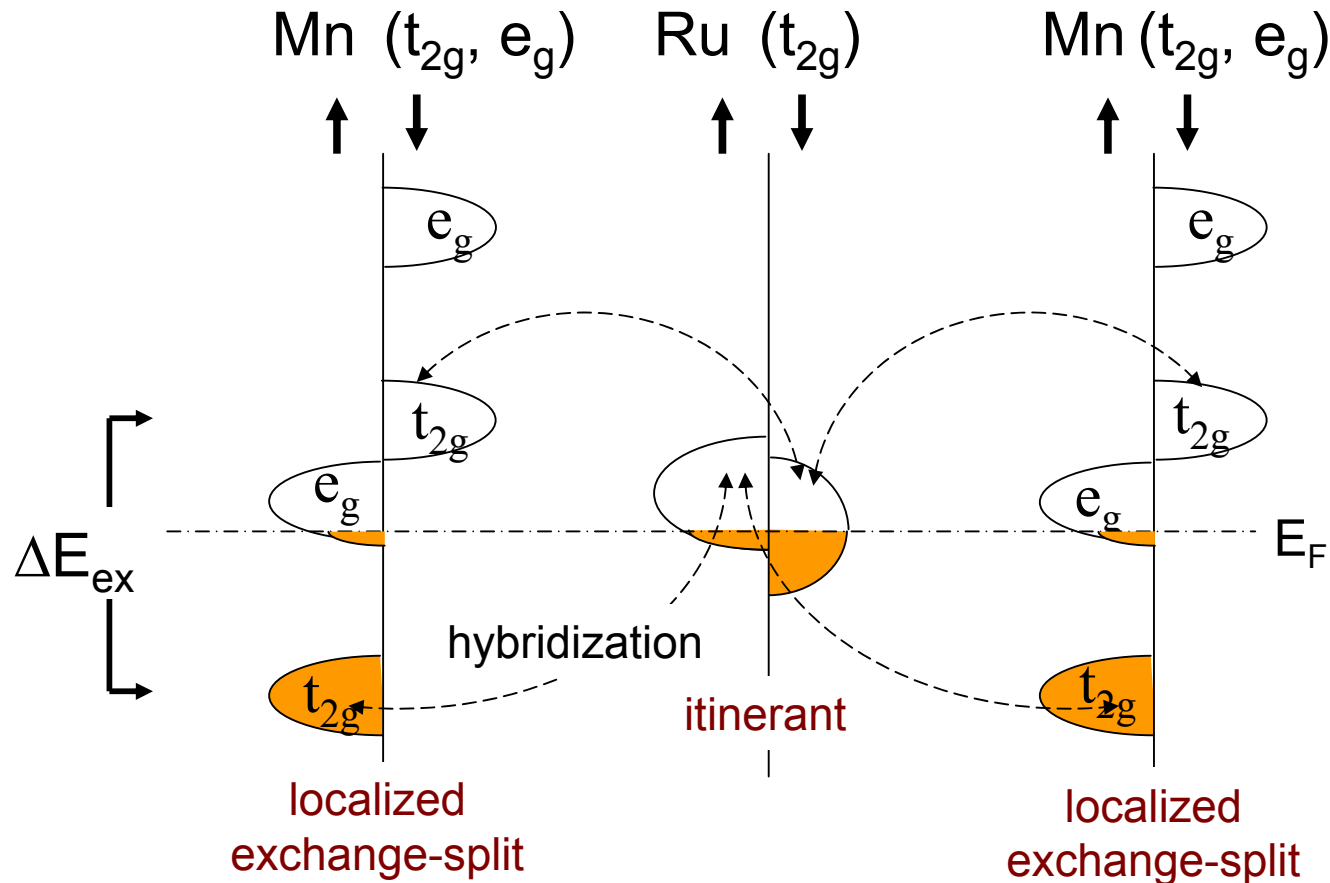
XMCD spectra



Magnetic moments on Mn and Ru



Mechanism for ferromagnetism in $\text{CaMn}_{1-x}\text{Ru}_x\text{O}_3$ – $\text{CaMnO}_3/\text{CaRuO}_3$, too ?

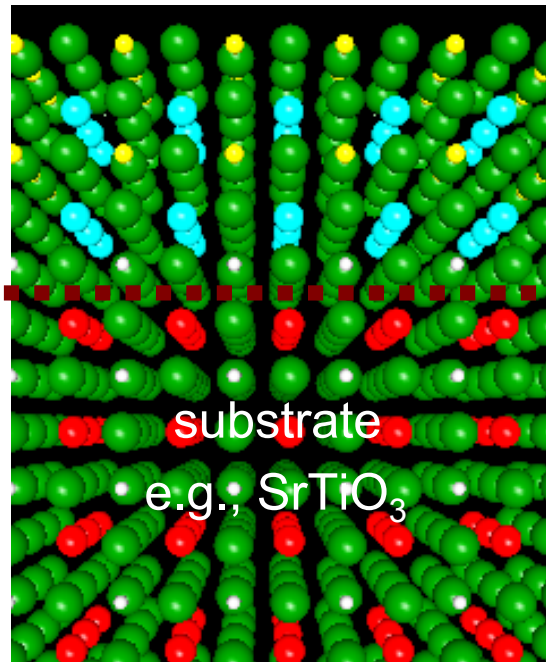


cf.) Double perovskite $\text{Sr}_2\text{FeMoO}_6$ D.D. Sarma et al., PRL '00, Z. Fang et al., PRB '01

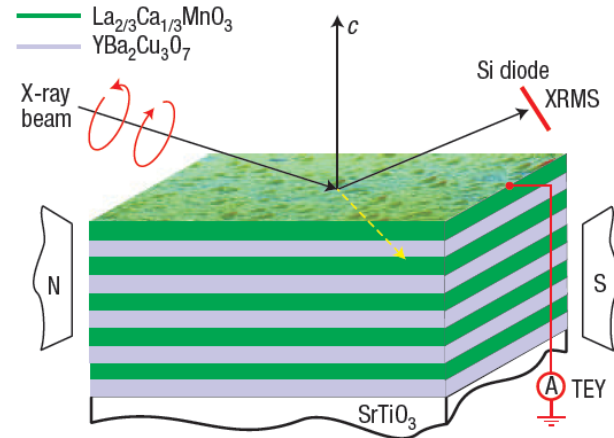
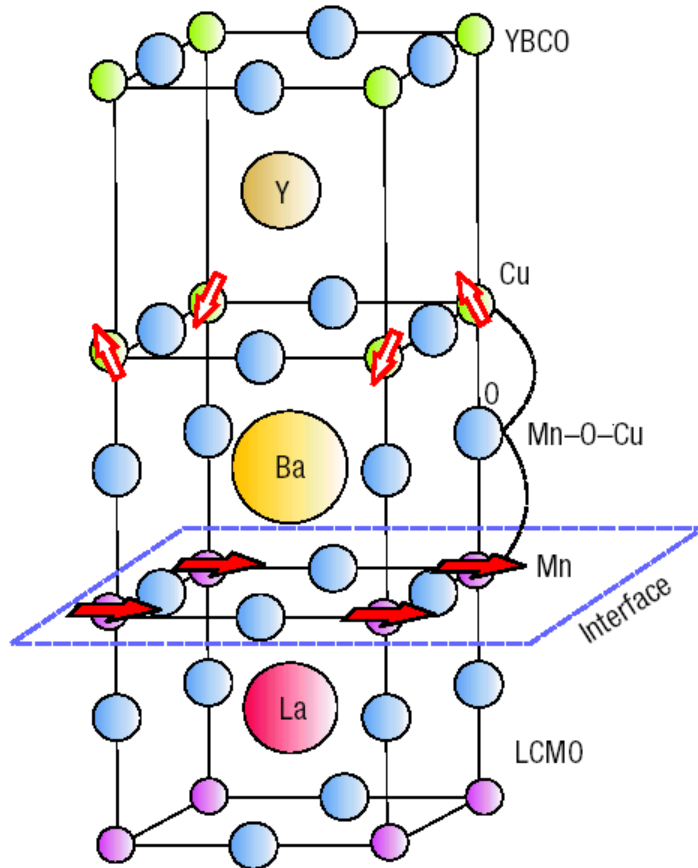
Interfacial electronic structure

Interface between different ground states

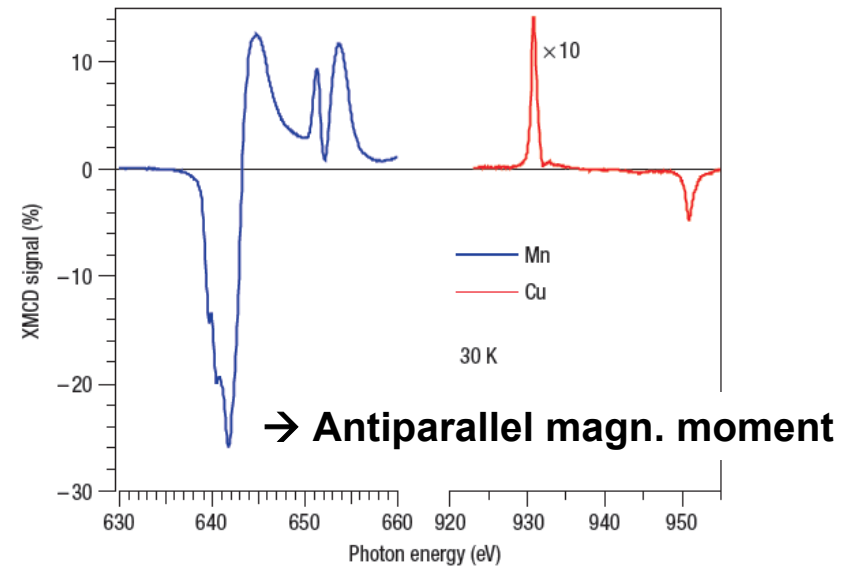
Interfaces



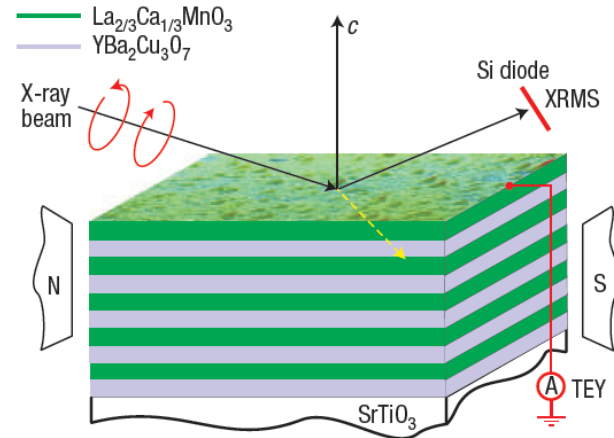
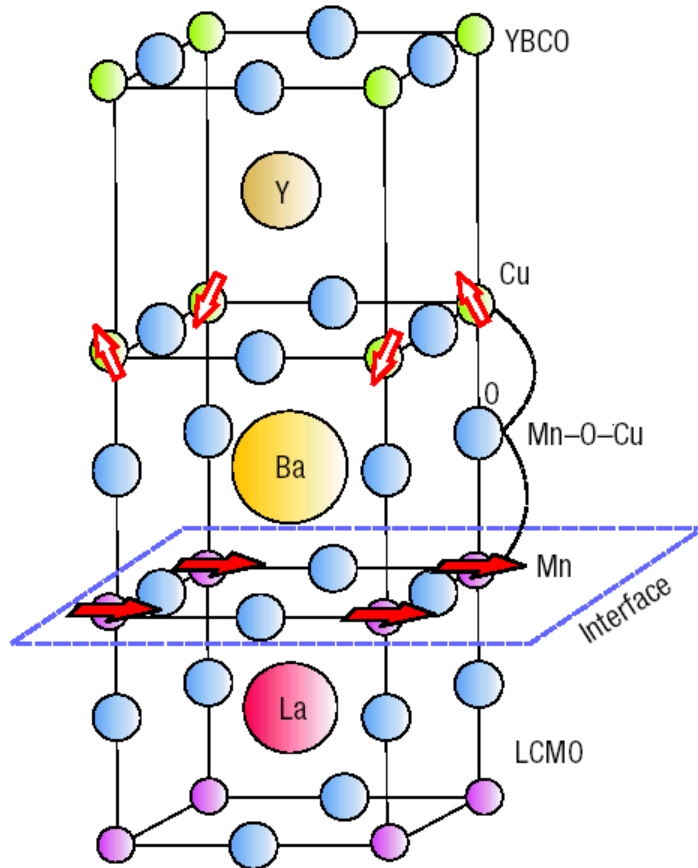
Interface between superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ and ferromagnet $(\text{La,Ca})\text{MnO}_3$



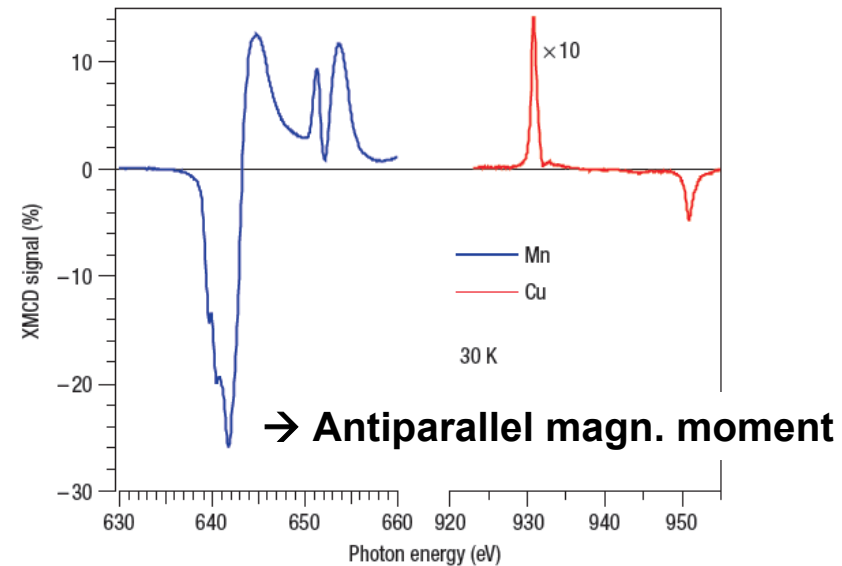
XMCD of Cu and Mn



Interface between superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ and ferromagnet $(\text{La,Ca})\text{MnO}_3$



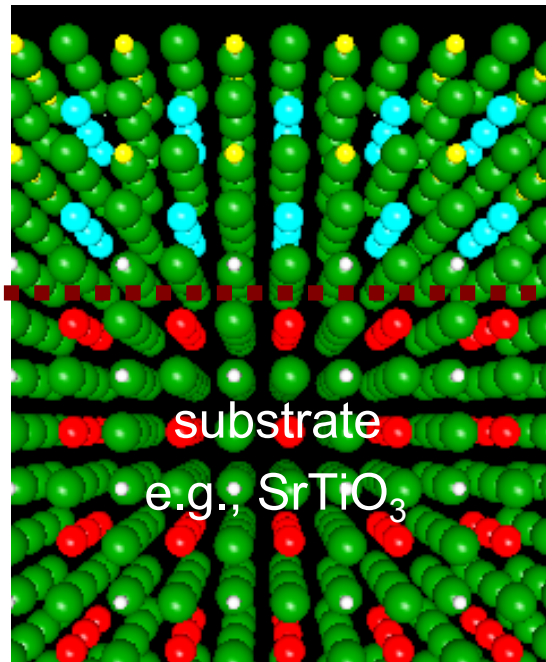
XMCD of Cu and Mn



Interfacial electronic structure

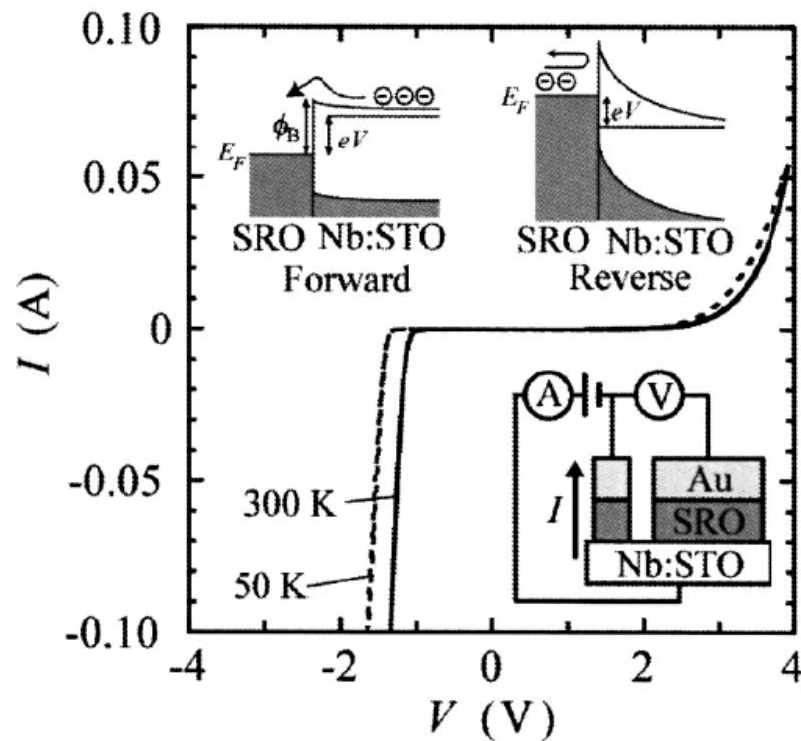
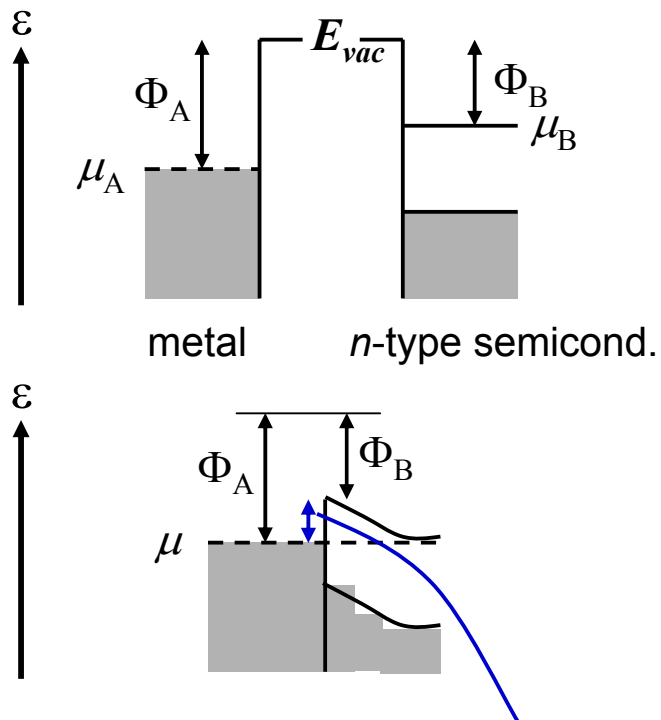
Chemical potential

Interfaces



To deduce chemical potential from I - V characteristics of junction

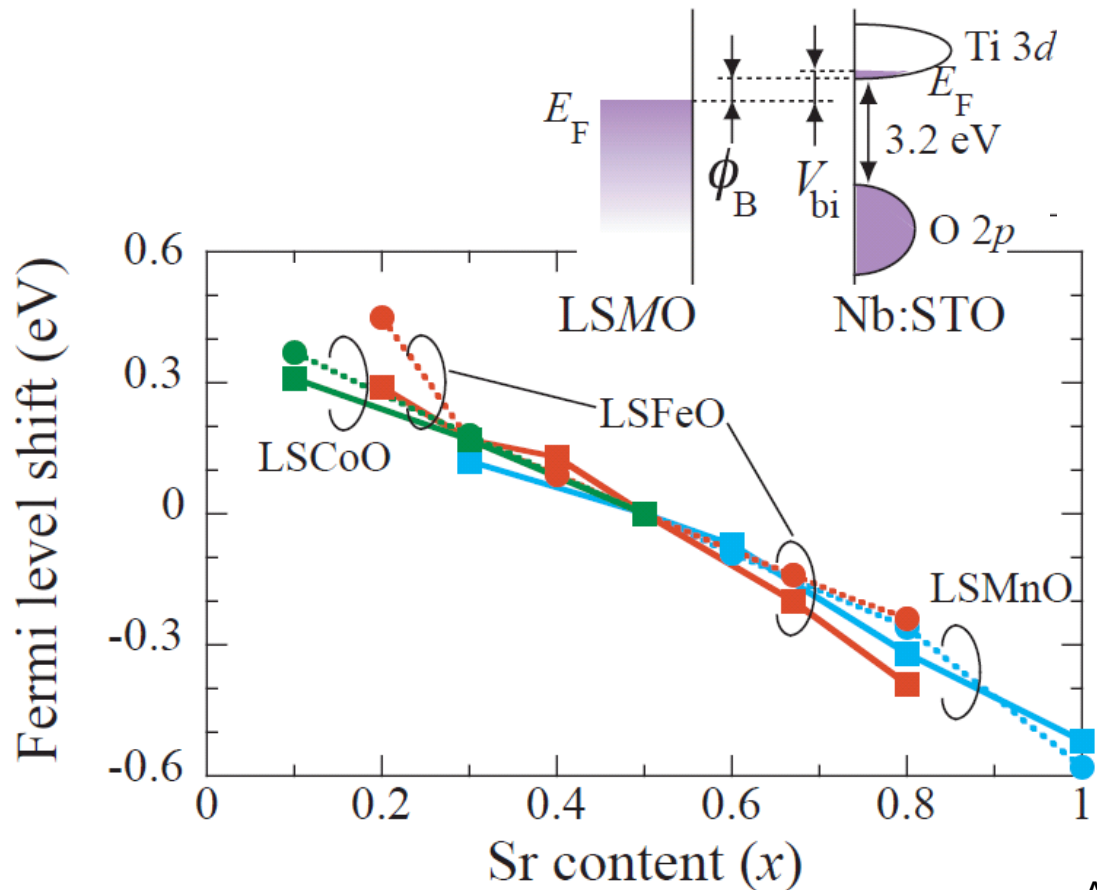
I - V characteristics of SrRuO₃/SrTiO₃



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

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

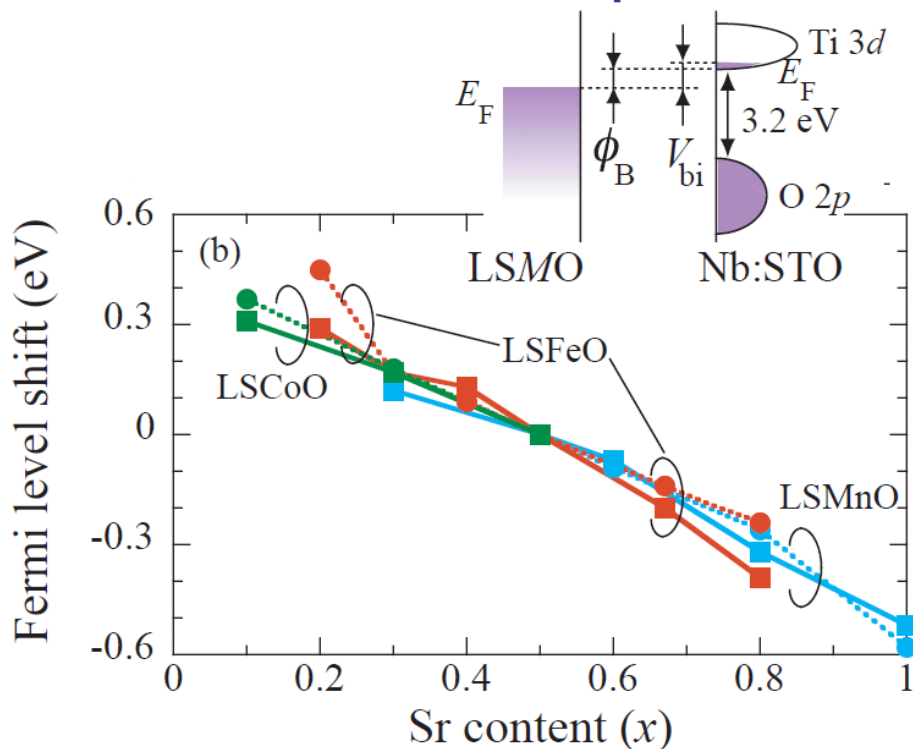
Chemical potential shift from the built-in potential of $\text{La}_{1-x}\text{Sr}_x\text{MO}_3/\text{SrTiO}_3$ p - n (Schottky) junction



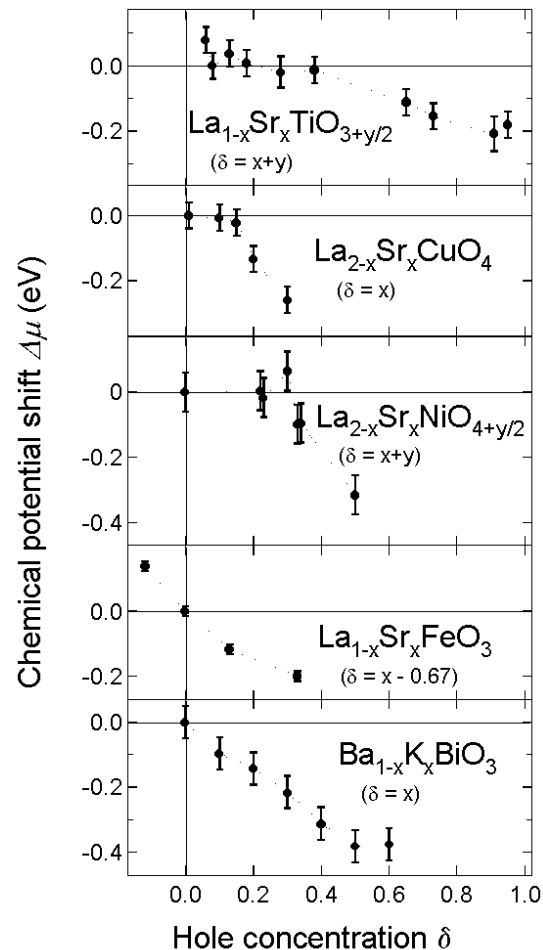
To deduce chemical potential shift from I - V characteristics of junction

Chemical potential shift from core-level XPS

Chemical potential shift from the built-in potential

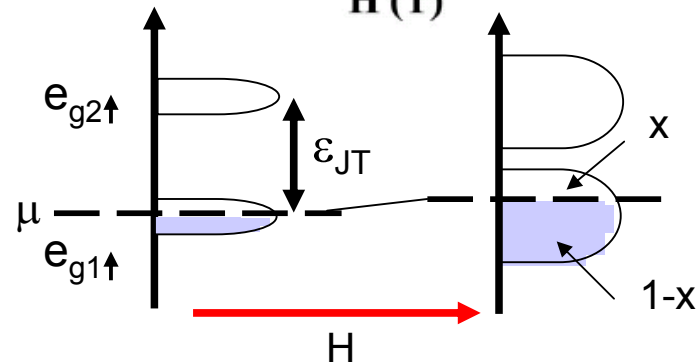
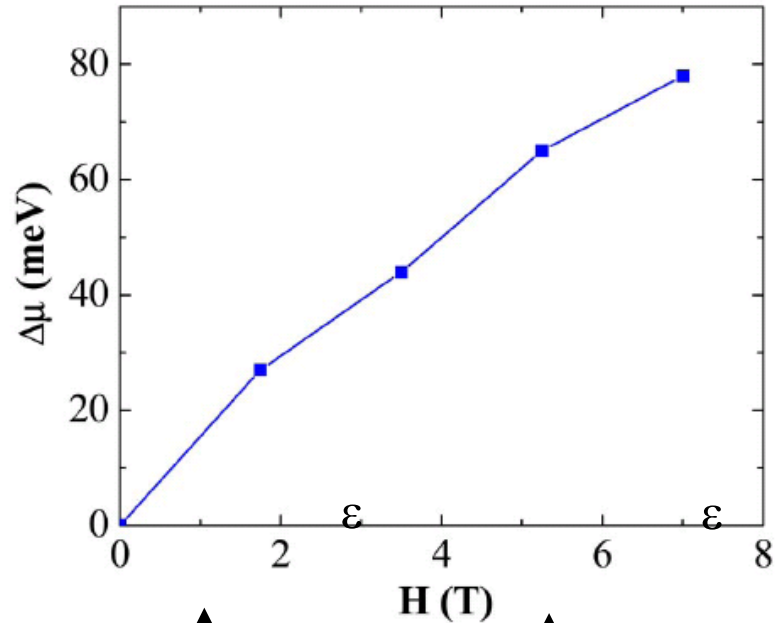
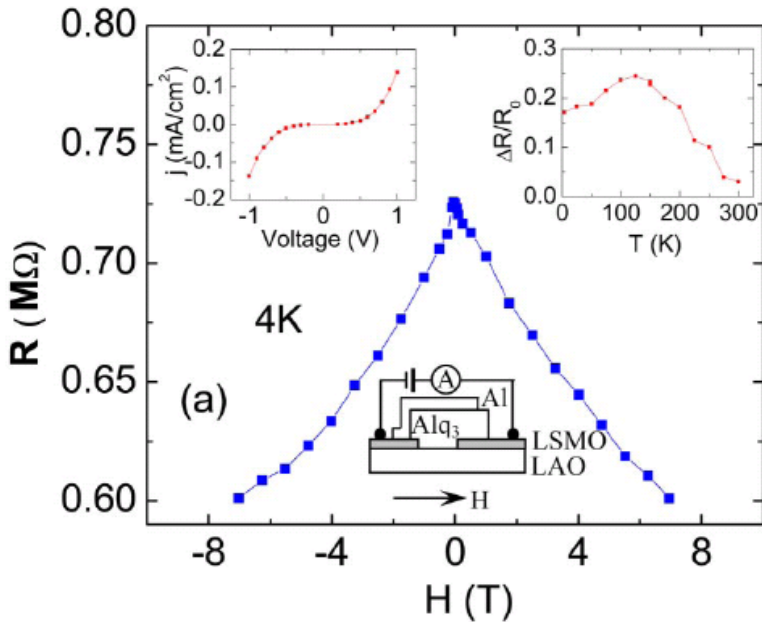


A. Sawa et al., APL '07

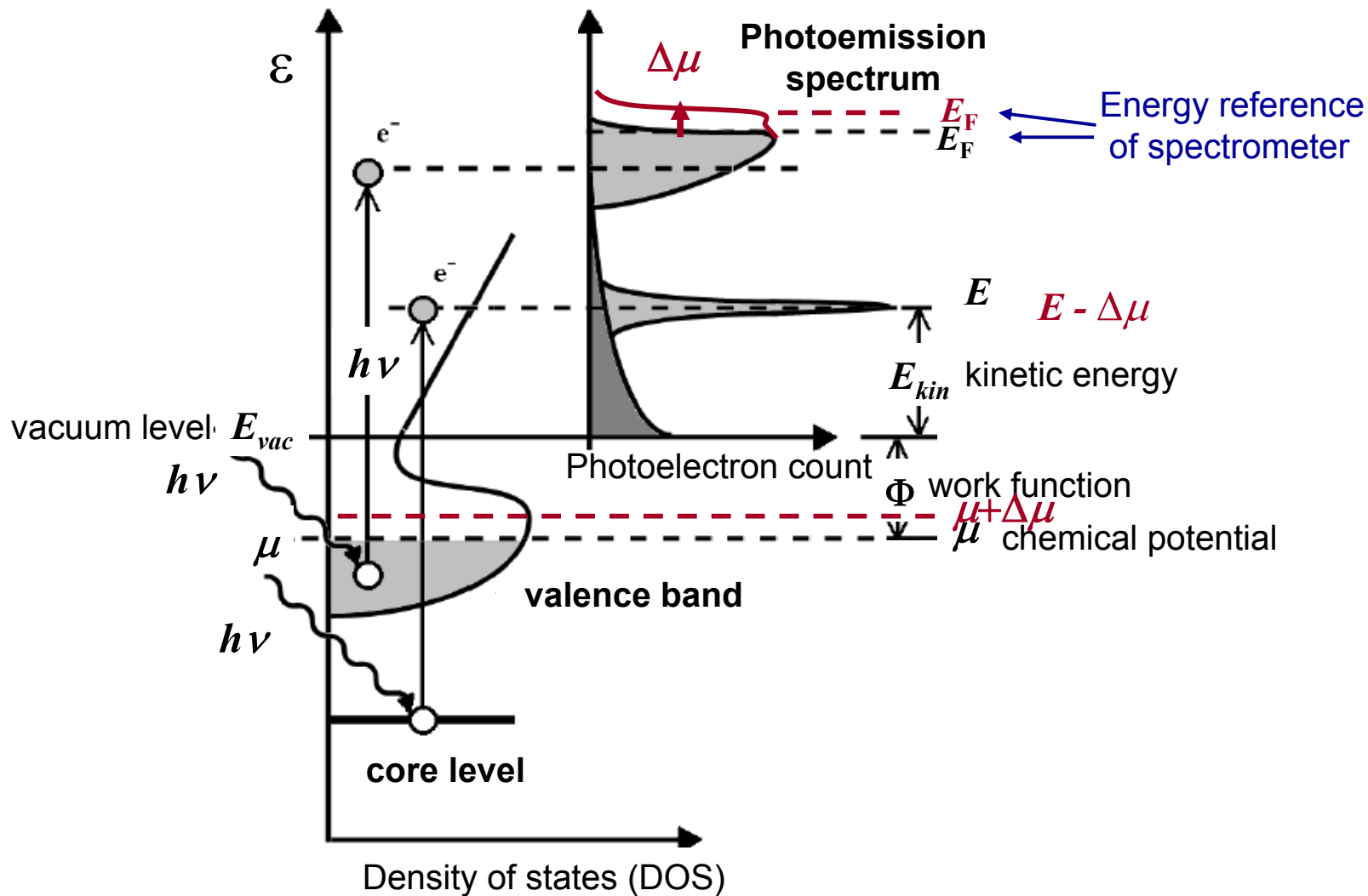


A. Fujimori et al.,
J. Electron Spectrosc. '02

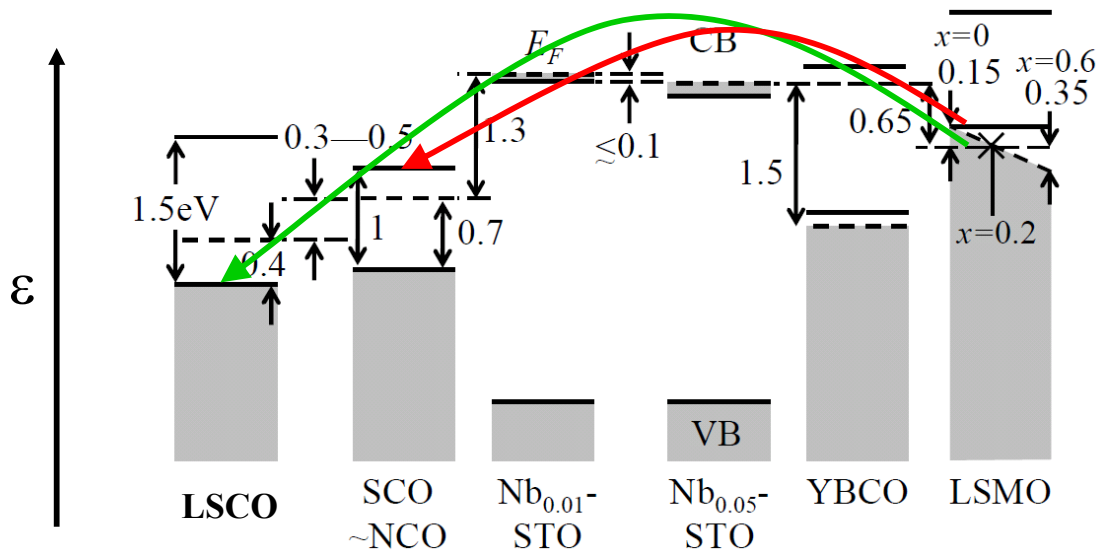
Magnetic field-induced chemical potential shift in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ /organic conductor junction



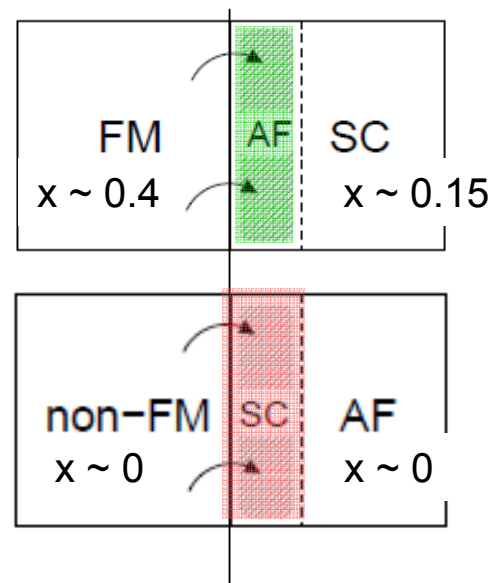
To deduce chemical potential shift from core-level photoemission



Carrier doping utilizing chemical potential differences



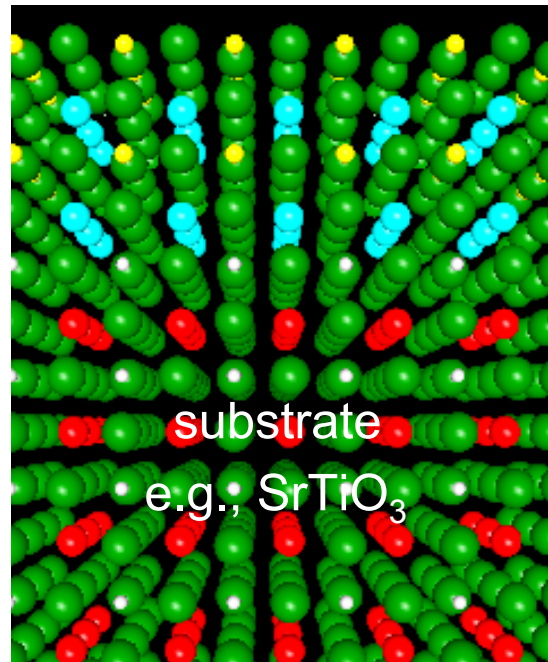
Manganite Cuprate



Superconducting

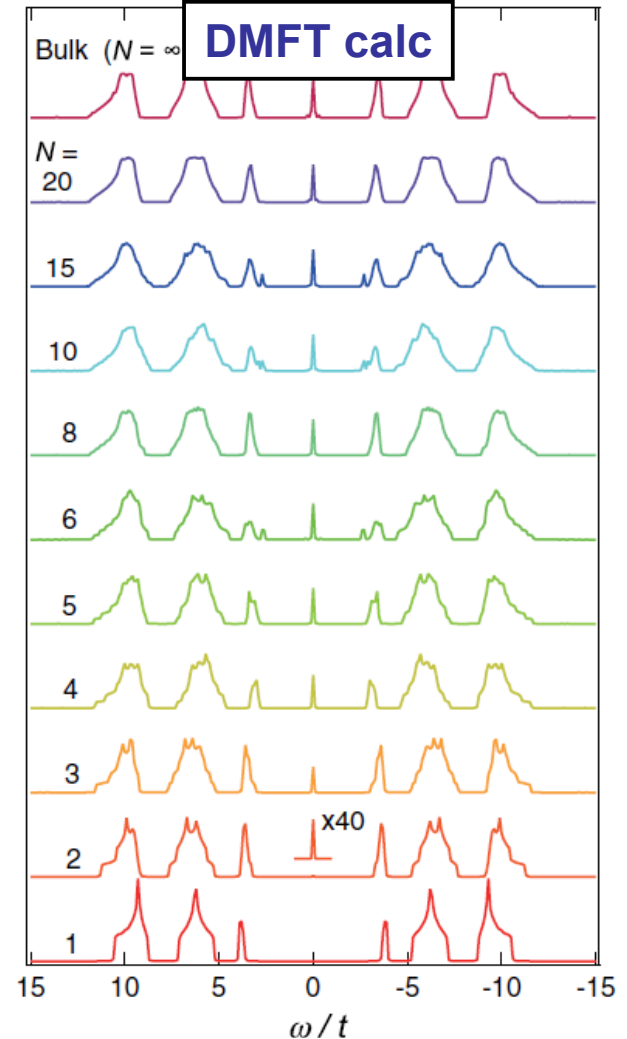
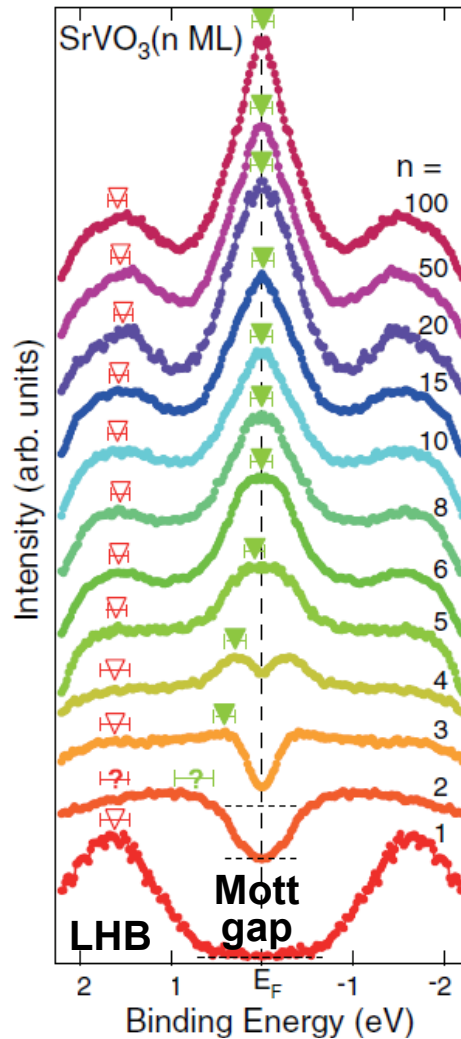
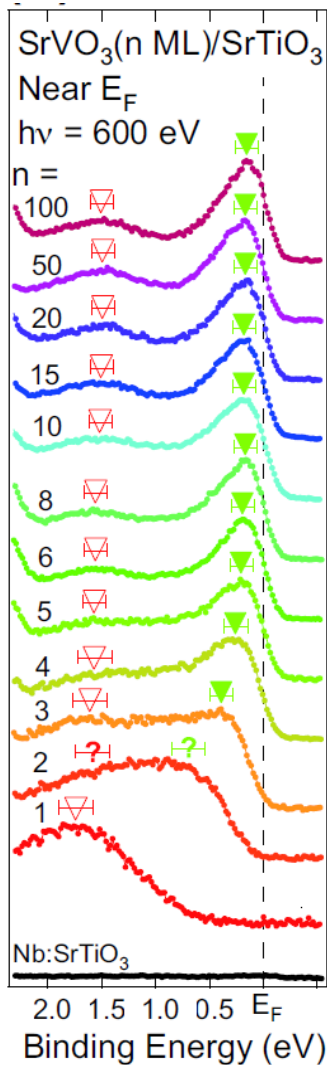
Effects of finite thickness

Metal-insulator transitions



Finite thickness

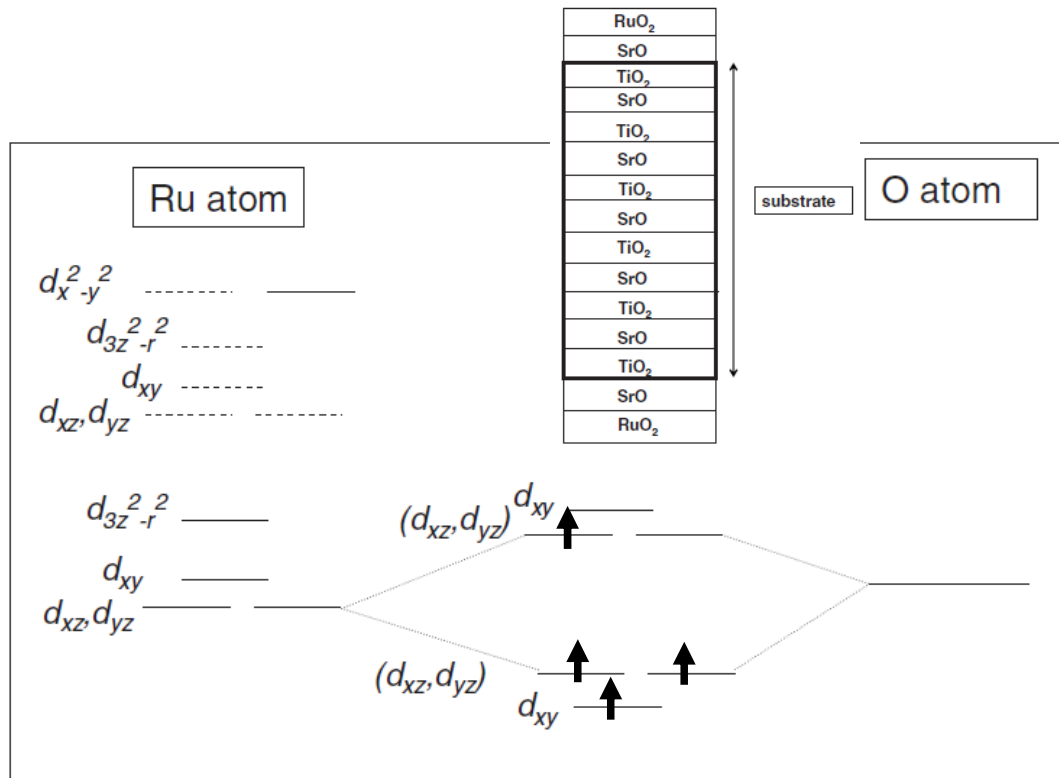
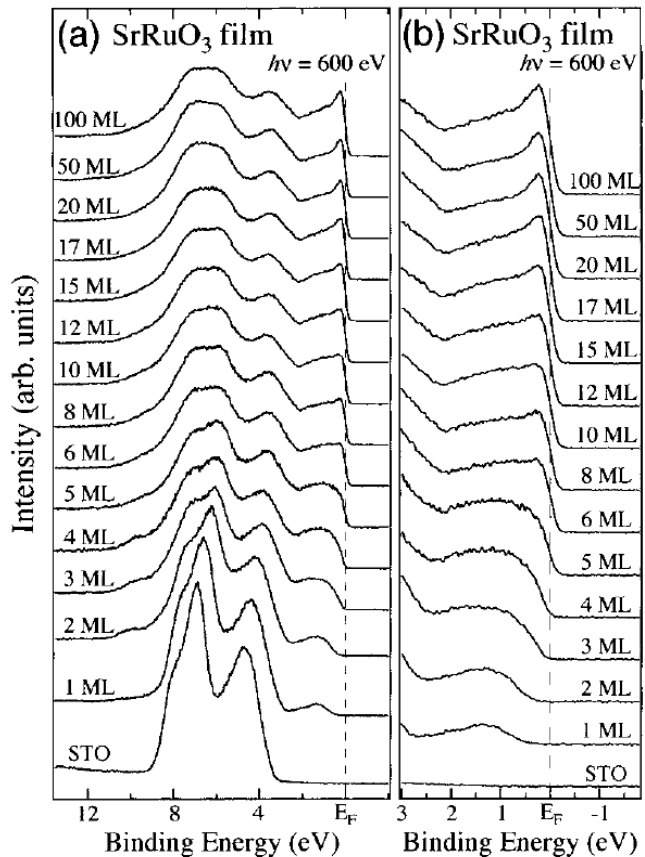
Metal-to-insulator transition in SrVO₃ with decreasing film thickness of



K. Yoshimatsu et al., PRL '10,
Orbital ordering? (P. Mahadevan)

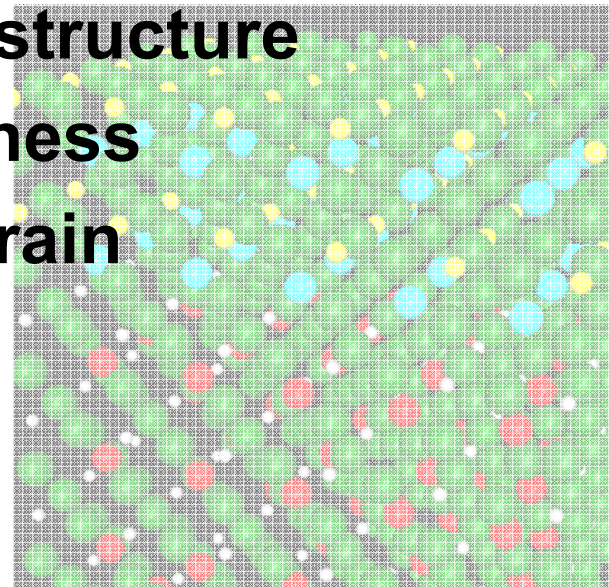
Metal-to-insulator transition in SrRuO₃ with decreasing film thickness of

- Small $W \rightarrow$ large U/W ?
- Orbital-ordering \rightarrow AFMI ?



Outline

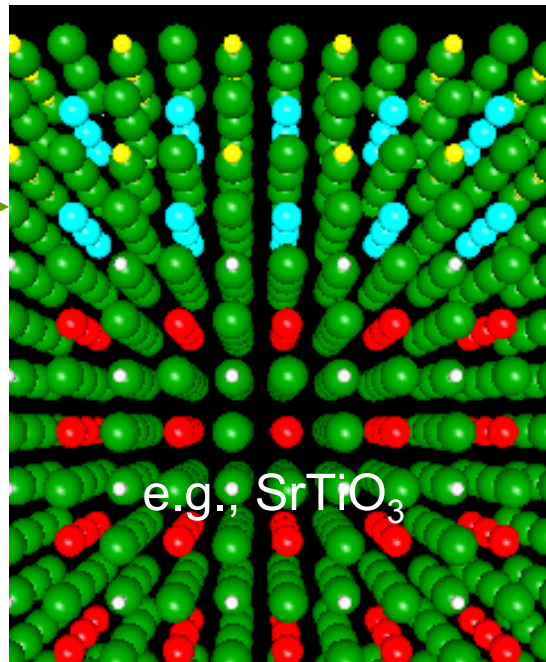
- **Electronic structure of transition-metal oxides**
- **Fabrication and characterization**
- **Interfacial electronic structure**
- **Effects of finite thickness**
- **Effects of epitaxial strain**



Effects of epitaxial strain

Superconductivity

Epitaxial strain



Band structure of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.15$) under compressive strain studied by ARPES

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4/\text{SrLaAlO}_4(001)$

Bulk

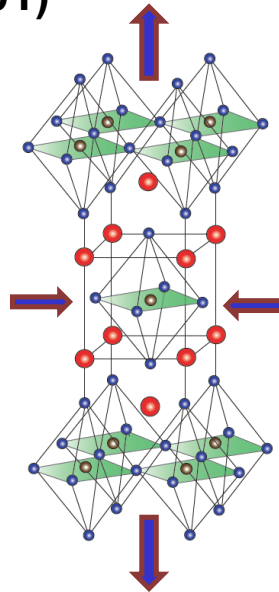
$$a = 3.784 \text{ \AA}$$

$$c = 13.23 \text{ \AA}, d_{\text{AP}} = 2.43 \text{ \AA}$$

Thin film

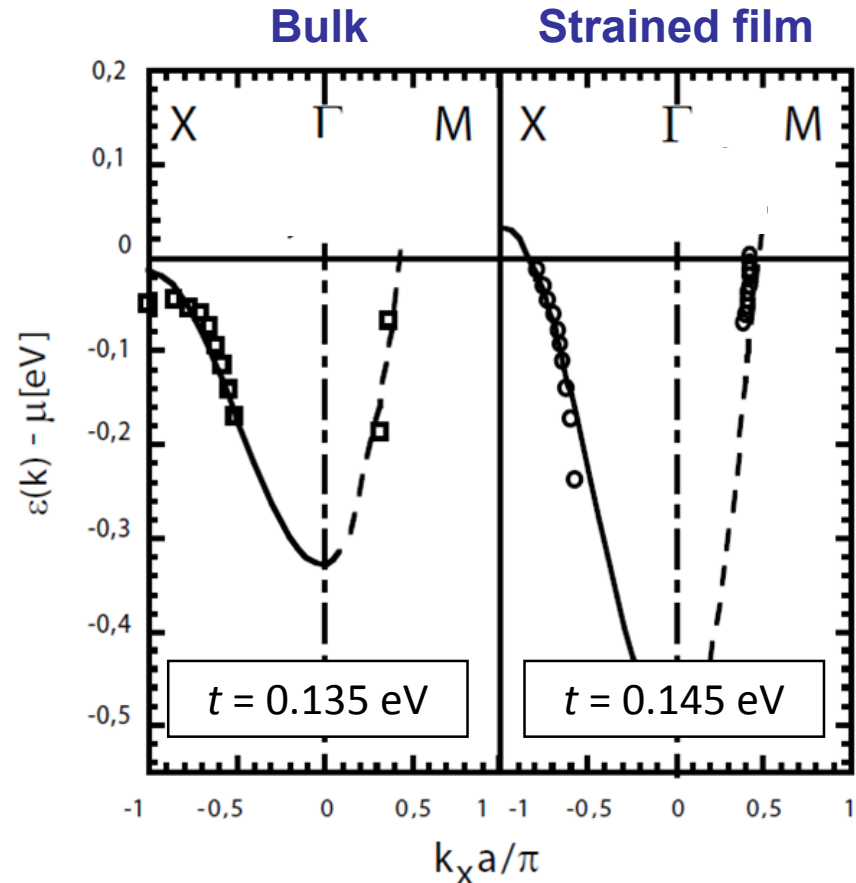
$$a = 3.754 \text{ \AA} (= \text{SrLaAlO}_4)$$

$$c = 13.29 \text{ \AA}, d_{\text{AP}} = 2.50 \text{ \AA}$$

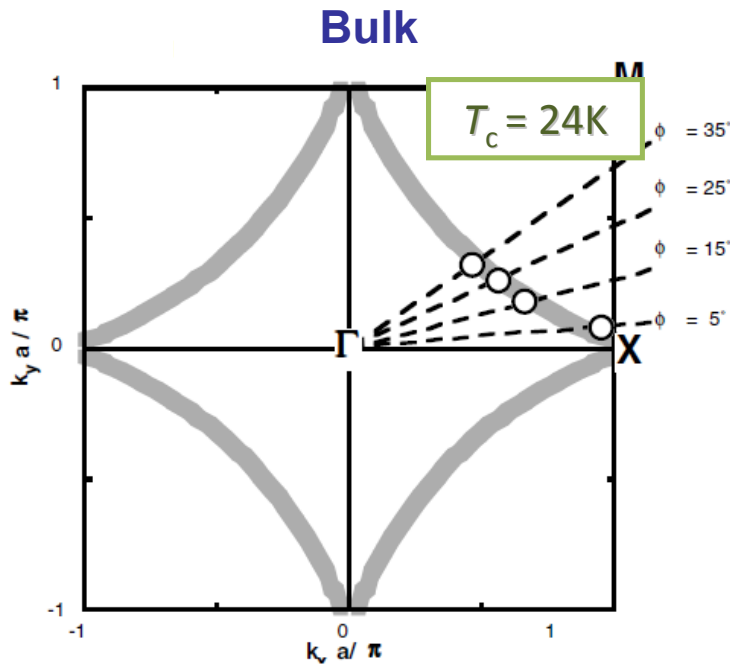


Tight-binding model

$$\xi_k = -2t[\cos(k_x a) + \cos(k_y a)] + 4t' \cos(k_x a) \cos(k_y a) - \mu$$

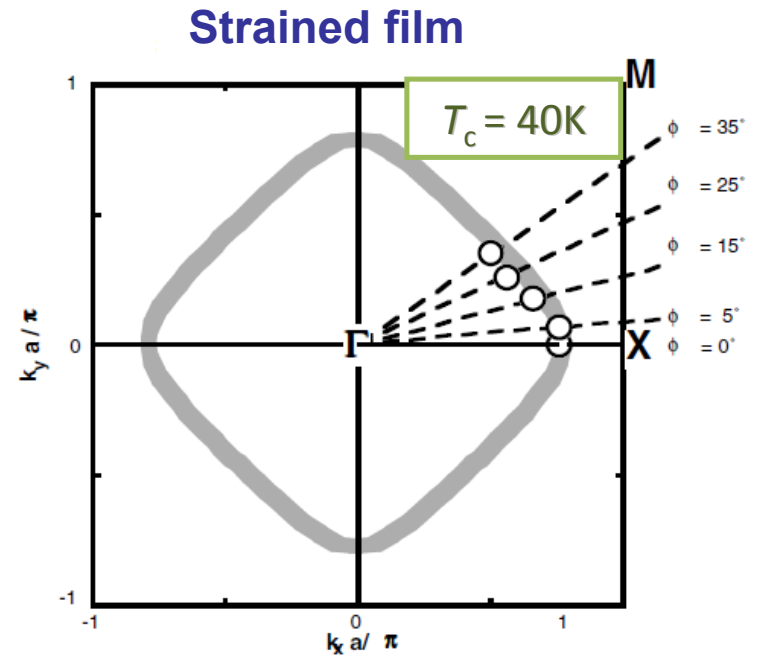


Fermi surface of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.15$) under compressive strain studied by ARPES



$$t = 0.135 \text{ eV}, t' = 0.036 \text{ eV}$$

Large t'



$$t = 0.145 \text{ eV}, t' = 0.0052 \text{ eV}$$

Small t'

M. Abrecht et al., PRL '91

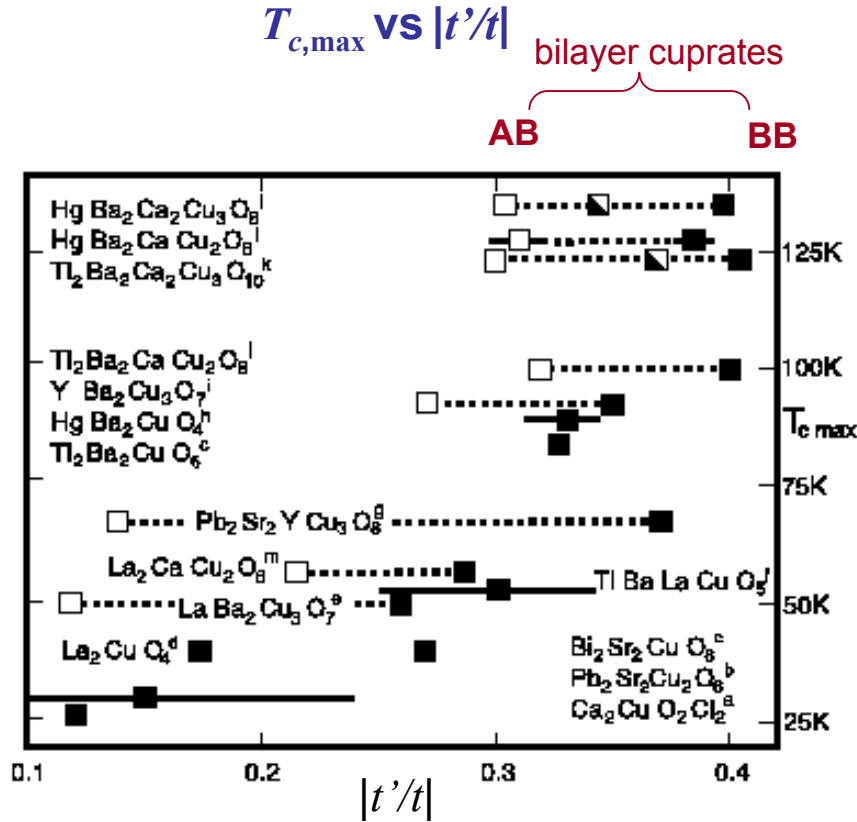
Tight-binding model

$$\xi_k = -2t[\cos(k_x a) + \cos(k_y a)] + 4t' \cos(k_x a) \cos(k_y a) - \mu$$

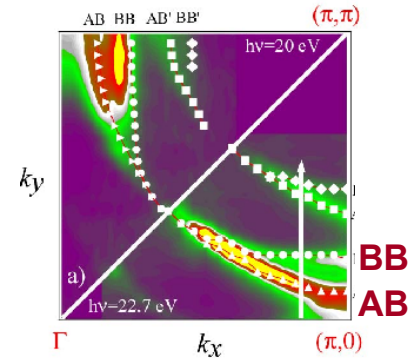
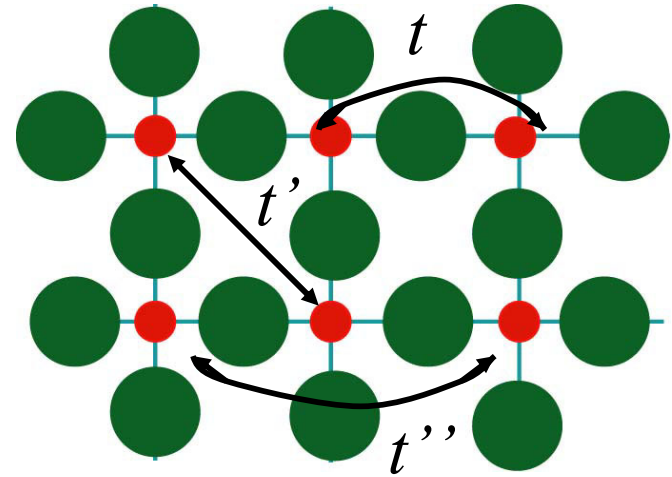
cf: Tensile strain: $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4/\text{SrTiO}_3(001)$

D. Coleta et al., PRB '06

Empirical correlation between $T_{c,max}$ and next-nearest-neighbor hopping t'



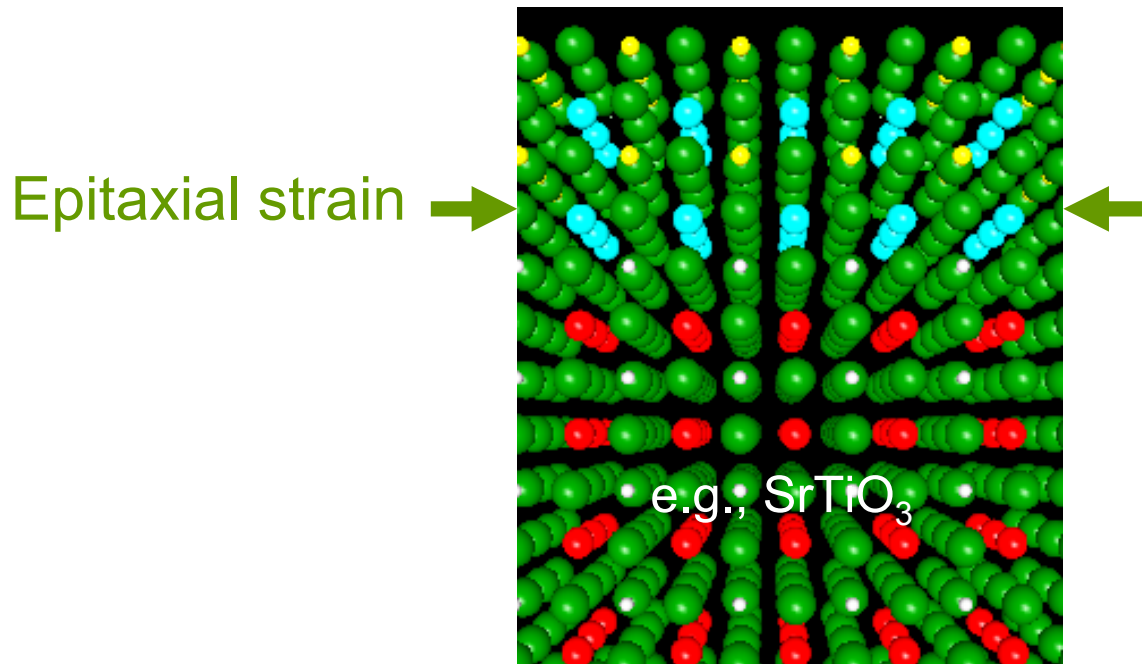
E. Pavarini et al., PRL '01



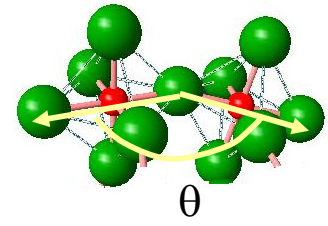
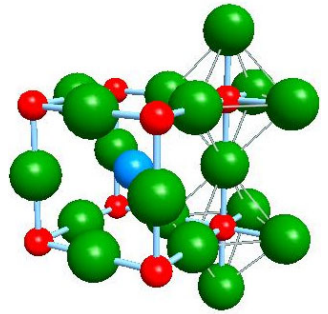
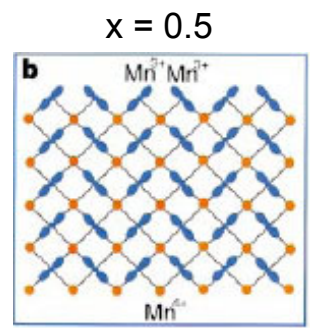
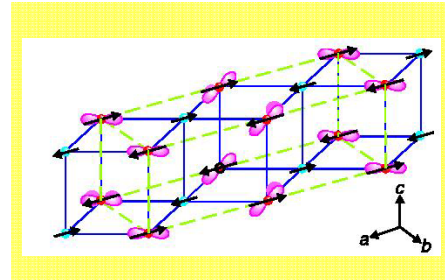
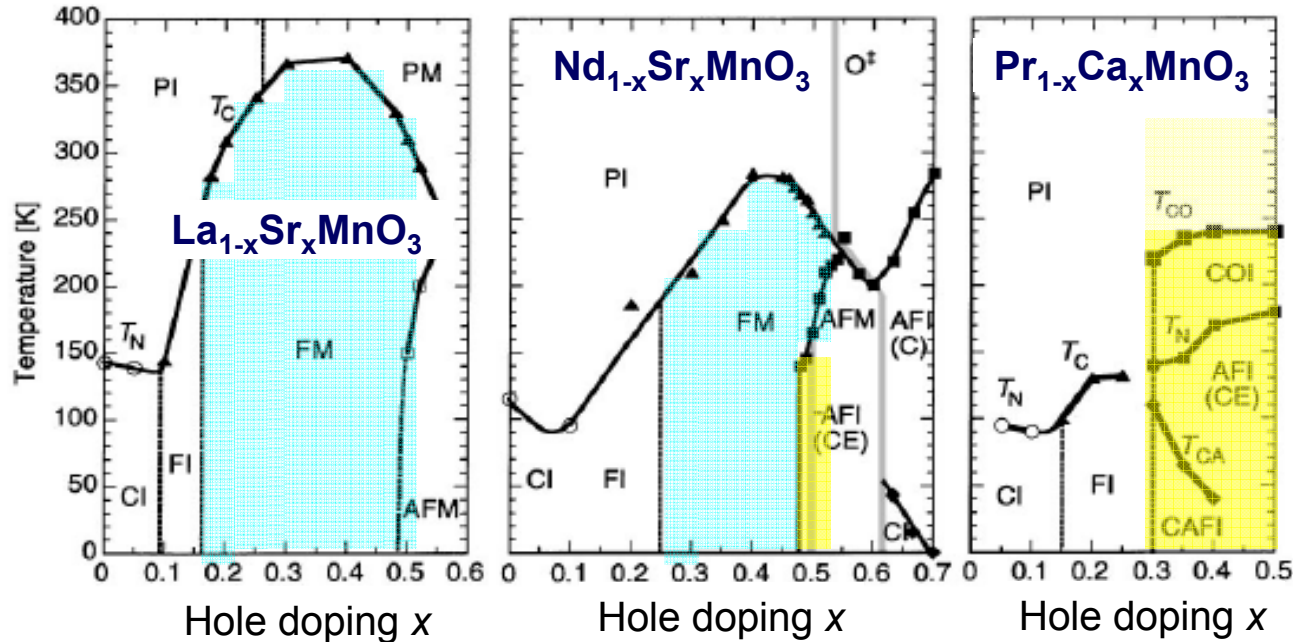
D. Feng et al., PRL '01

Effects of epitaxial strain

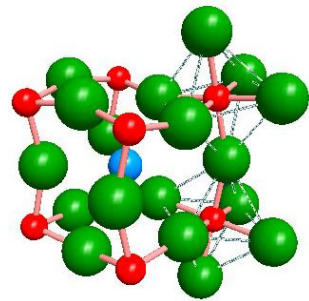
Metal-insulator transitions



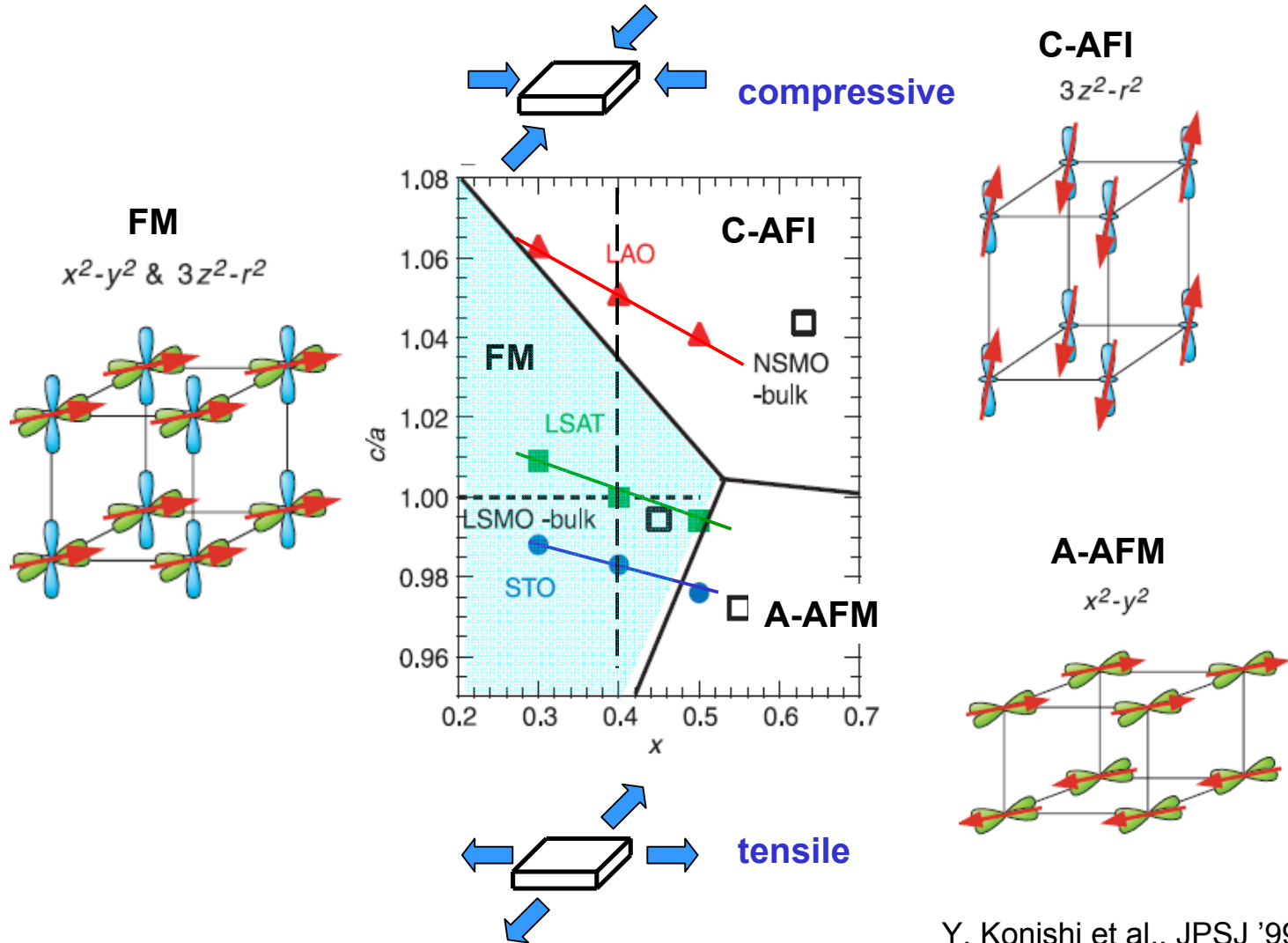
Electronic phase diagram of $R_{1-x}A_x\text{MnO}_3$



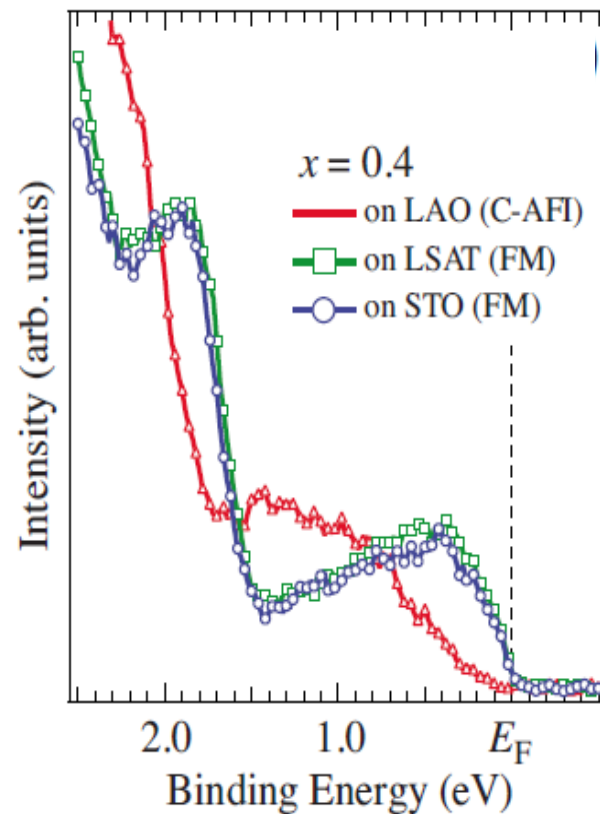
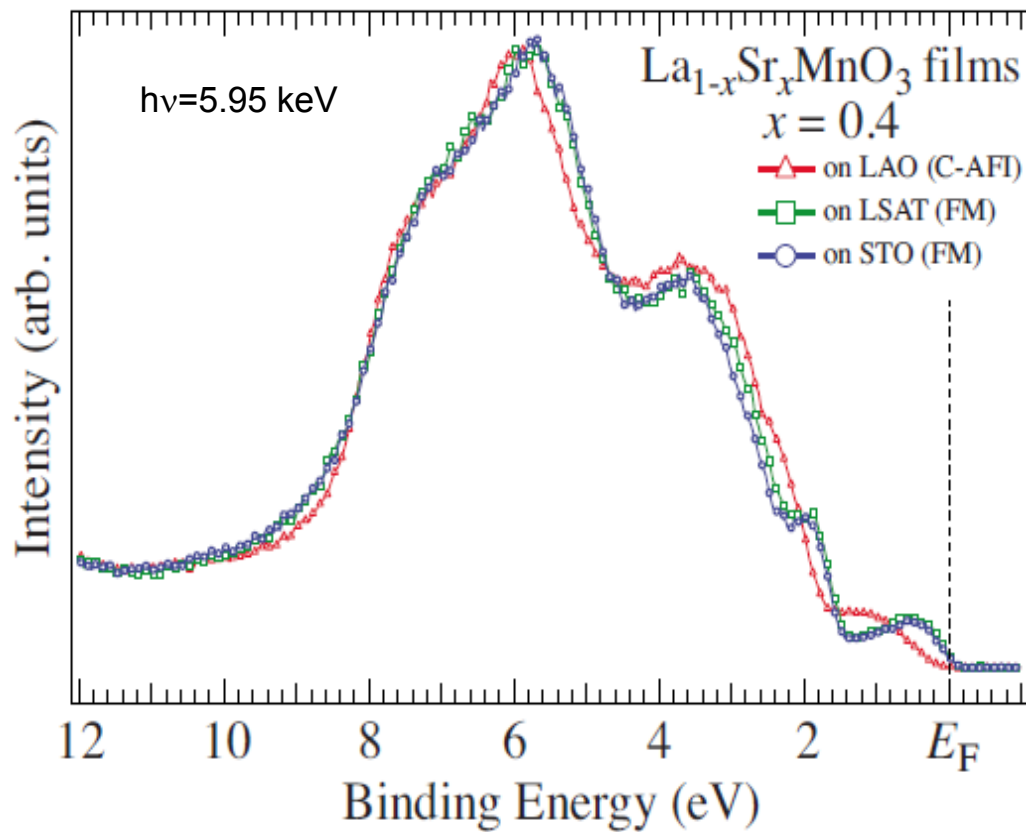
$W \propto \cos^2\theta$



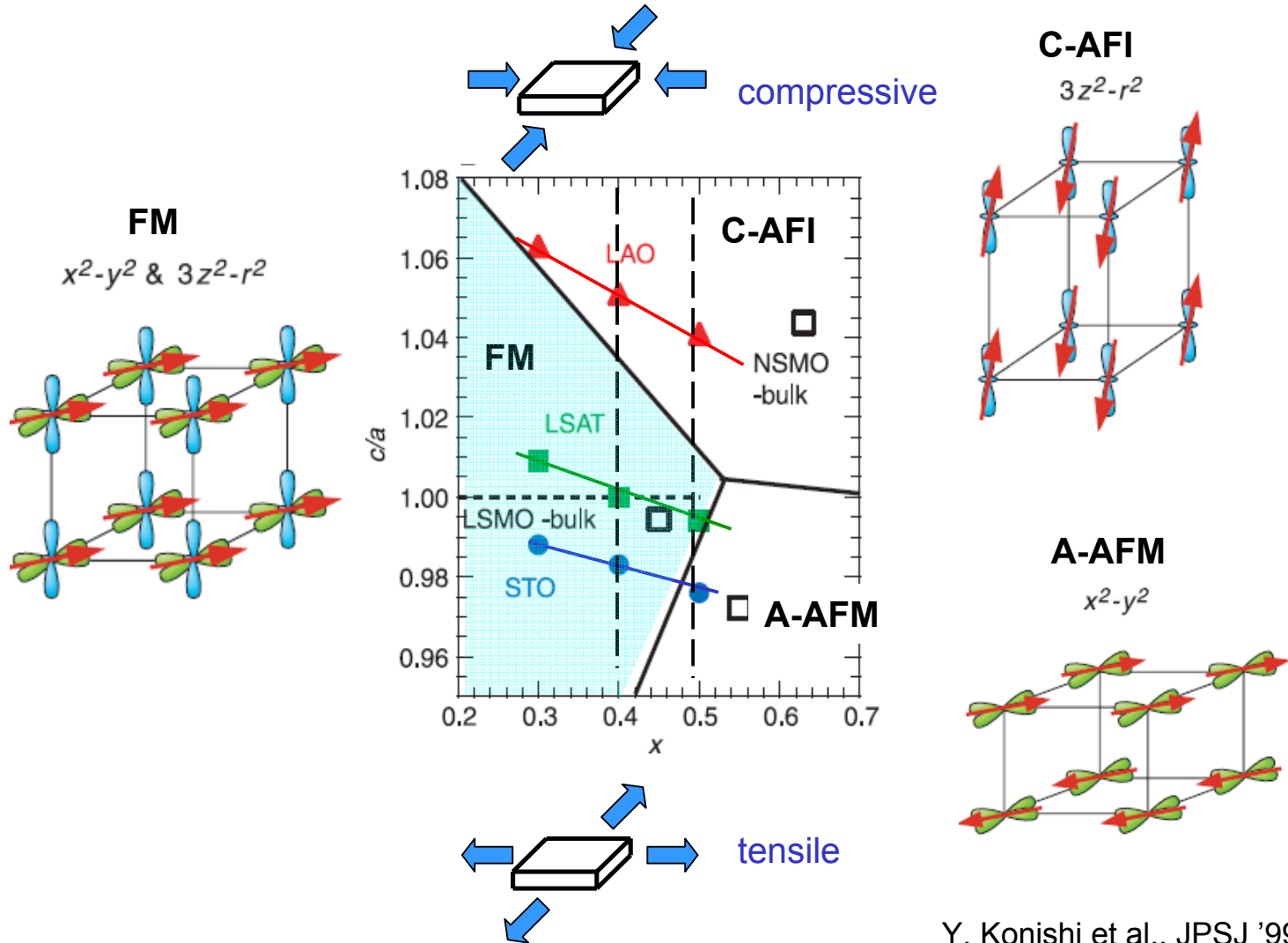
Electronic phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ under epitaxial strain



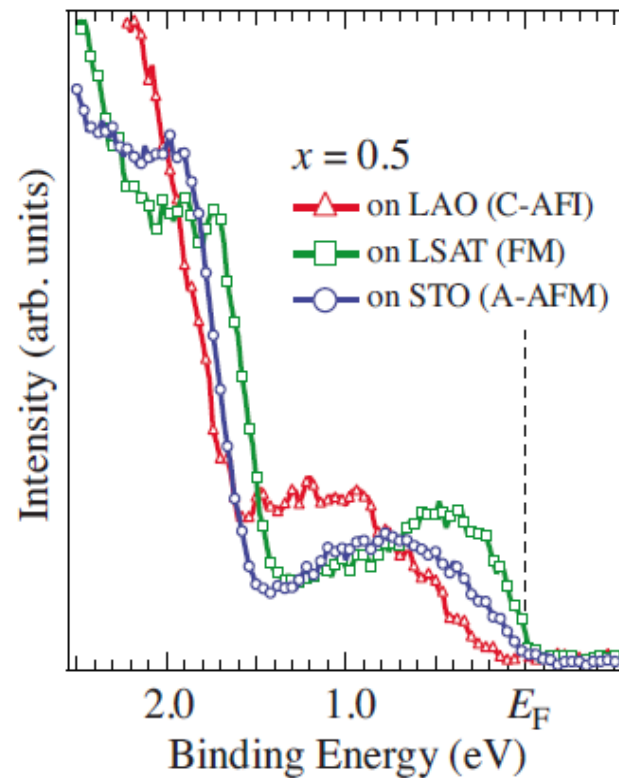
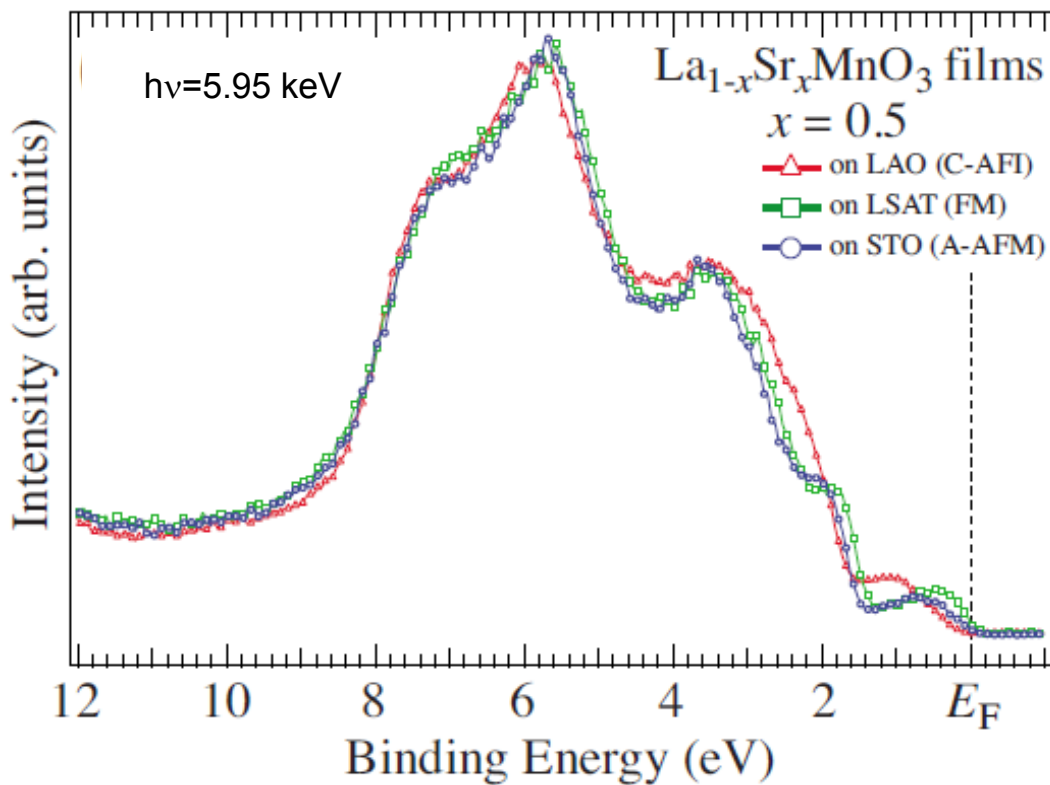
HX-PES spectra of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.4$) under epitaxial strain



Electronic phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ under epitaxial strain

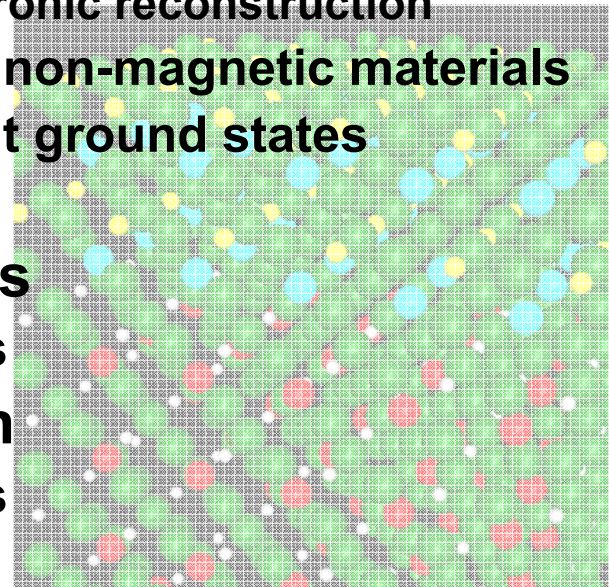


HX-PES spectra of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.5$) under epitaxial strain



Summary

- **Electronic structure of transition-metal oxides**
- **Fabrication and characterization**
- **Interfacial electronic structure**
 - **Metallic states between two insulators**
 - States near the Fermi level
 - Charge transfer in electronic reconstruction
 - Potential change in electronic reconstruction
 - **Ferromagnetism between non-magnetic materials**
 - **Interface between different ground states**
 - **Chemical potential**
- **Effects of finite thickness**
 - **Metal-insulator transitions**
- **Effects of epitaxial strain**
 - **Metal-insulator transitions**
 - **Madelung potential shifts**
 - **Changes in chemical potential shift**



Acknowledgement

VUV, soft x-ray photoemission

M. Takizawa, H. Wadati, M. Takizawa, T. Yoshida, K. Maekawa (U of Tokyo)
H. Kumigashira, K. Horiba, K. Yoshimatsu, T. Okabe, M. Oshima,
A. Maniwa, M. Minohara (U of Tokyo)

Hard x-ray photoemission

S. Shin, Y. Takata, K. Horiba, M. Matsunami, M. Yabashi,
K. Tamasaku, Y. Nishino, D. Miwa, T. Isikawa (SPring-8, RIKEN)
E. Ikenaga, K. Kobayashi (JASRI)

Materials synthesis

H.Y. Hwang, Y. Hotta, S. Tsuda, T. Higuchi, T. Susaki (U of Tokyo)
M. Lippmaa, K. Shibuya, N. Mihara (ISSP)
M. Kawasaki (Tohoku U), H. Koinuma (U Tokyo, JST)
Y. Muraoka (Okayama U), Z. Hiroi (ISSP)

Supported by: a Grant-in-Aid for Scientific Research, JSPS
& Quantum Beam Technology Development Program, JST

