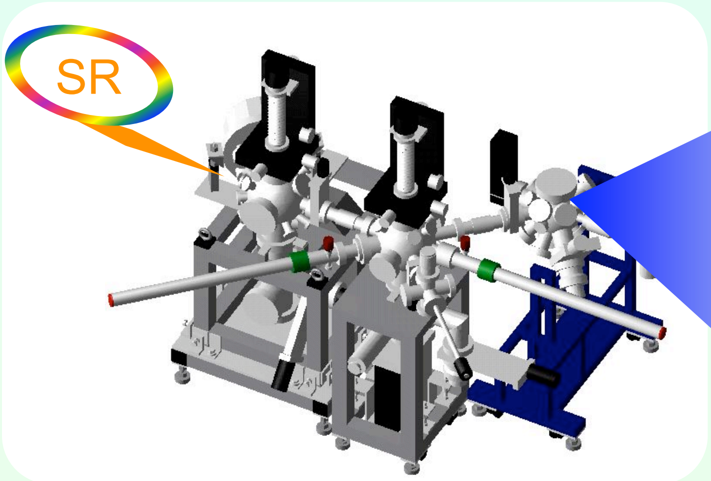
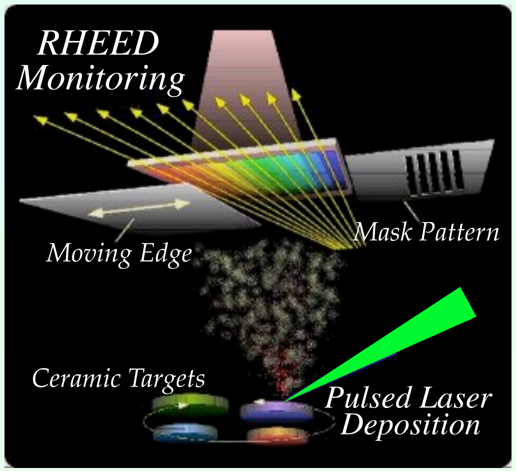
ISSP Workshop「東京大学アウトステーション(SPring-8 BL07LSU)での物性研究の新展開」 2011年3月8日@ISSP 6F第一会議室

放射光電子分光を用いた酸化物超構造の電子状態研究

東京大学大学院工学系研究科
JST-さきがけ
東京大学放射光連携研究機構

組頭 広志





共同研究者

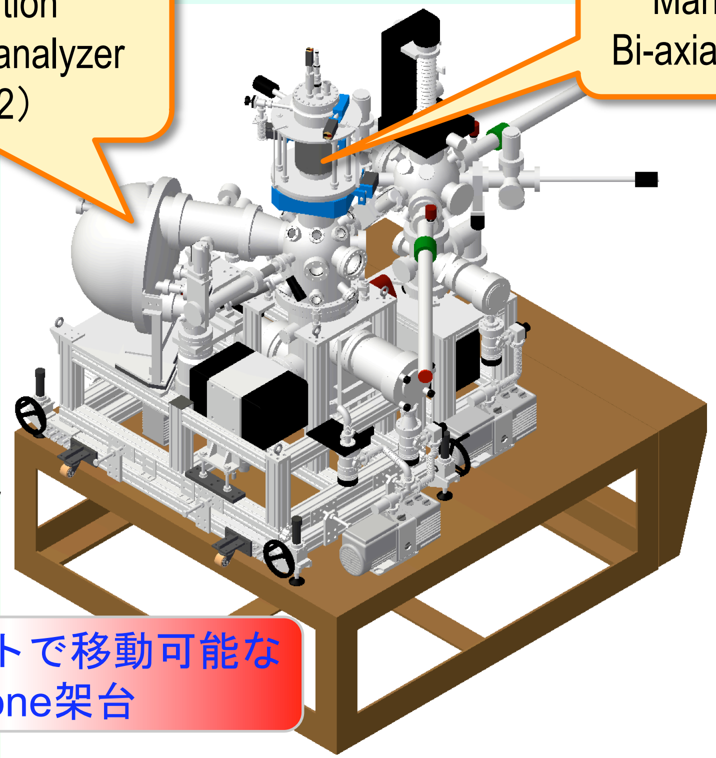
次元性制御$SrVO_3$&$LaNiO_3$薄膜@BL2C

東大院工
吉松公平、坂井延寿*,#、堀場弘司*,#、豊田智史*,#、尾嶋 正治*,#

東大院理
藤森淳

オークリッジ国立研
岡本敏史

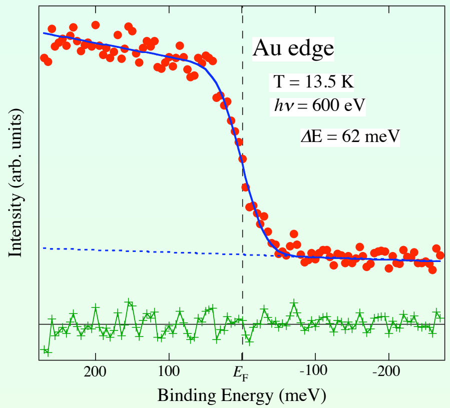
*JST-CREST、#東大放射光機構



BL2C
300–1500 eV

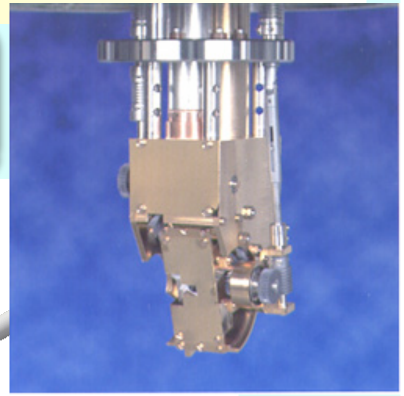
ホバークラフトで移動可能な
All-in-one架台

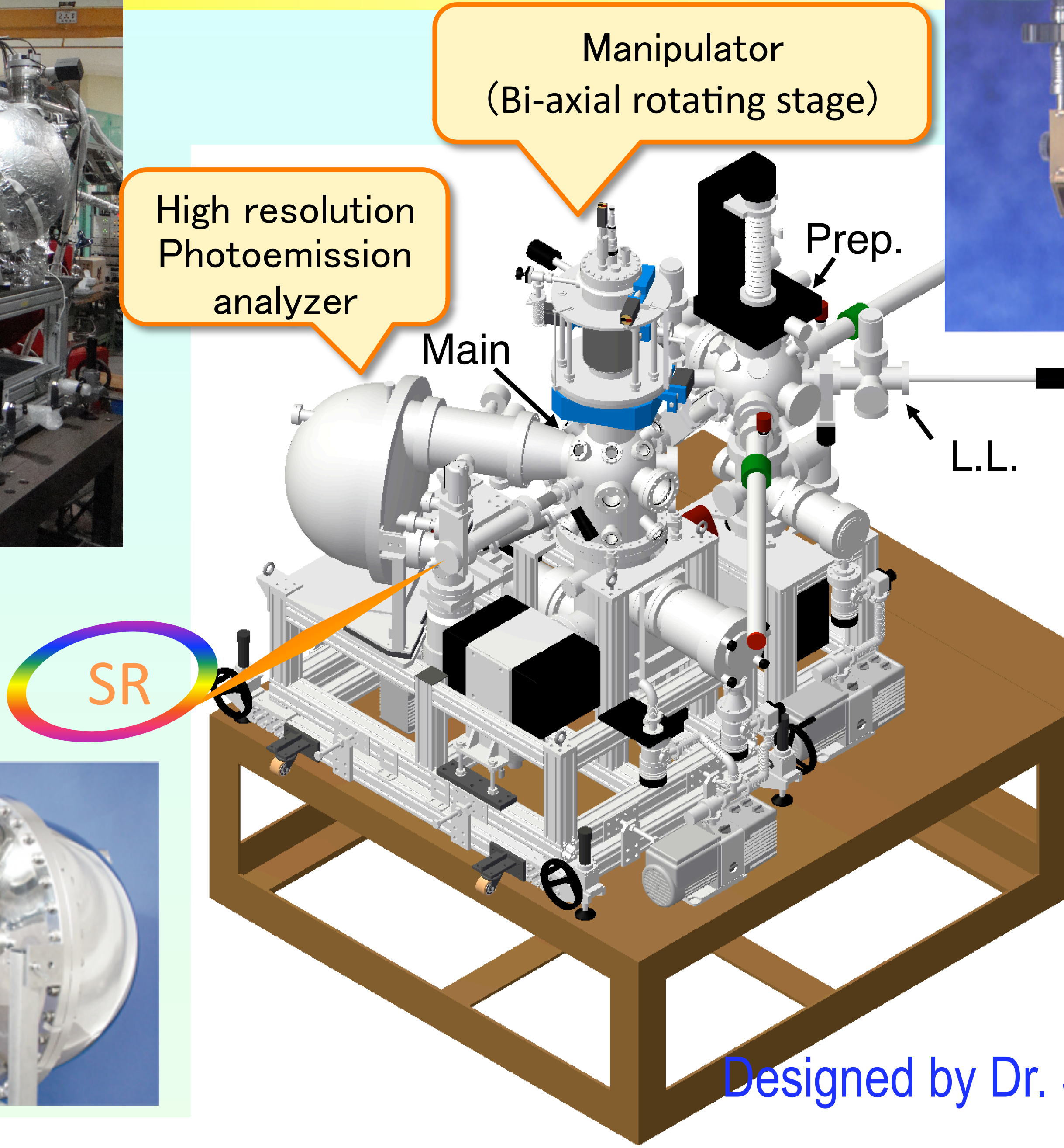
エネルギー分解能(Total)
: E/ΔE = 10,000
角度分解能:<0.1°
試料温度:10 ～400 K
二軸試料角度走査
フェルミ面mapping、LD-XAS



62 meV
@600 eV

Photoemission Chamber@PF BL2C

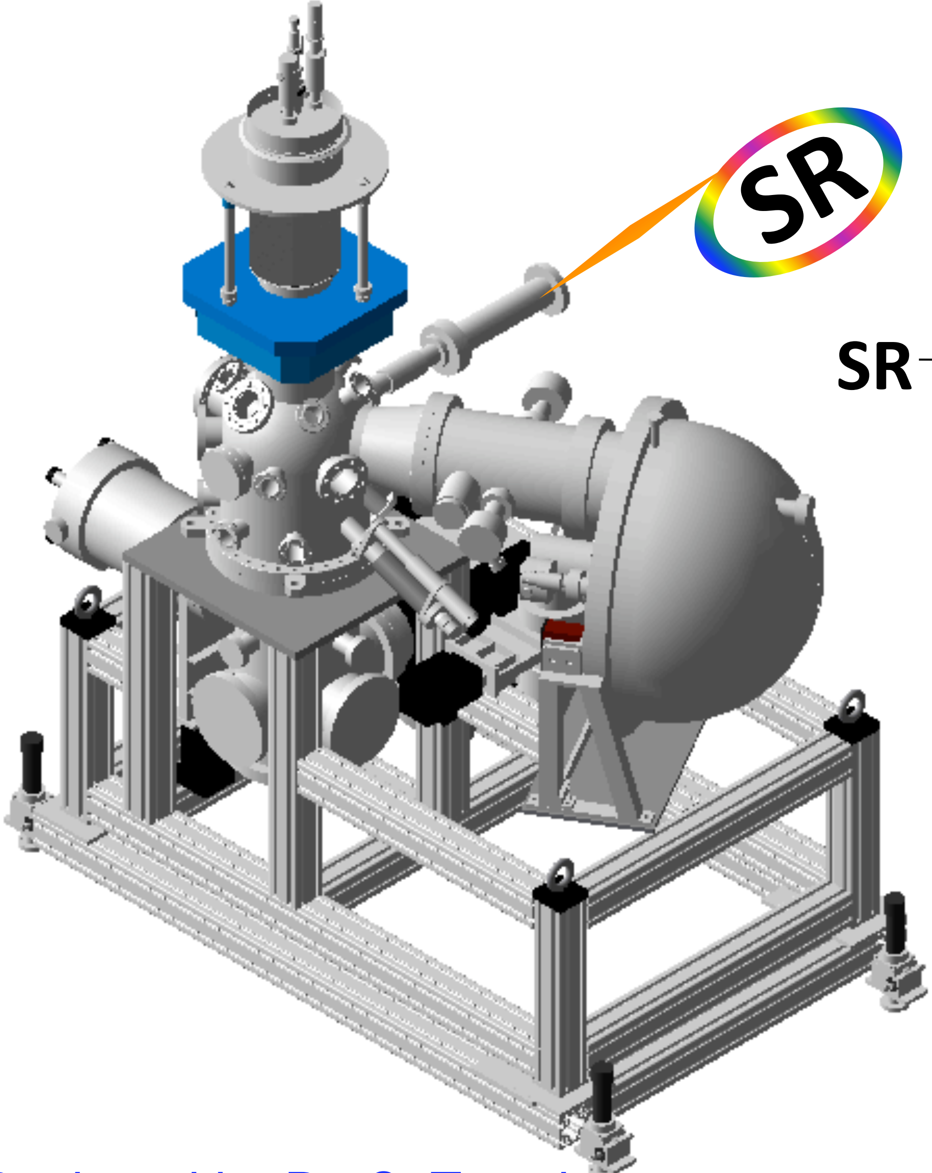


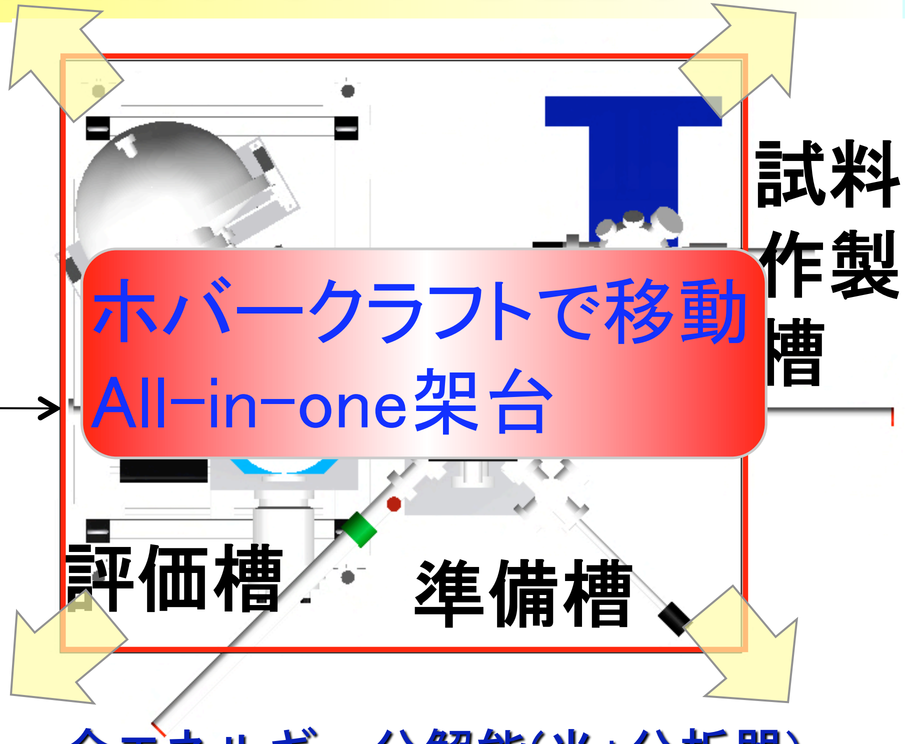


VGScienta SES2002

Designed by Dr. S. Toyoda

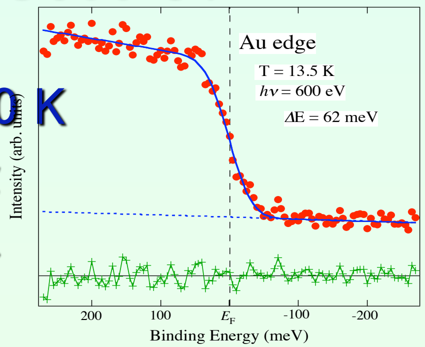
Photoemission Chamber@PF BL2C





全エネルギー分解能(光+分析器)
(E/ΔE)：10,000
：60 meV@600 eV

角度分解能：0.1°
試料温度：10 ～400 K
二軸試料角度走査
フェルミ面mapping、
LD-XAS

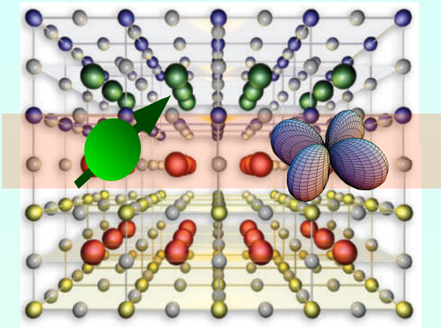


Designed by Dr. S. Toyoda

ARPES@BL2Cの研究展開

機能性遷移金属酸窒化物
（O, N, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn）

BL2C@PF (250-1400 eV)



Physics

強相関超構造

強相関酸化物ヘテロ構造による新しい量子相の研究

近年，世界的に界面が強相関系研究のフロンティアに

ARPES@BL2C
元素選択的分光

Chemistry

2次(Li)電池、燃料電池

省エネ・環境技術材料の評価・設計

Li_xFePO_4, Li_xCoPO_4, $LiCoO_2$

Ptフリーカーボン触媒

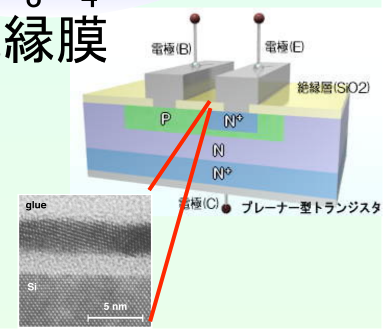
Devices

次世代不揮発性メモリ

元素戦略（レアメタルフリー）

ReRAM（Al/Fe_3O_4）

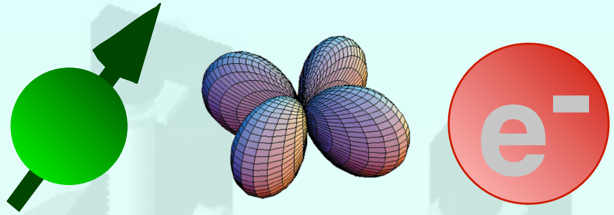
ULSIゲート絶縁膜

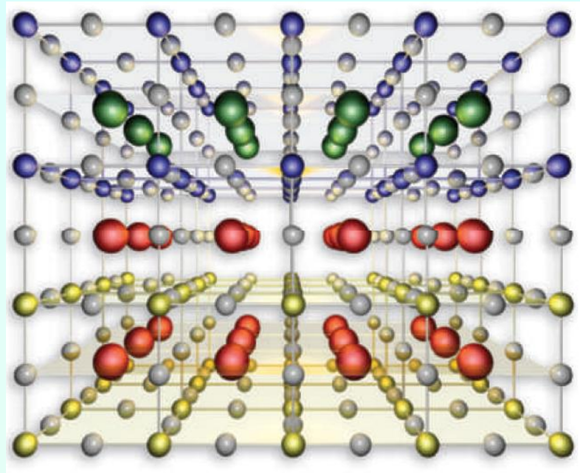


我々がパイオニアである*in-situ*ARPES+LaserMBEによる強相関酸化物ヘテロ構造の研究を重点的に進めると同時に、国家戦略材料の評価・設計のための産官学プラットフォームとしての場を提供する。

CONTENTS

SR





1. Introduction

   Oxide heterostructure is new frontier in strongly correlated physics.

2. Developments of *in-situ* PES + Laser MBE system

3. *In-situ* PES on thickness-dependent $SrVO_3$ films

   Dimensional-Crossover-Driven Metal-Insulator Transition in $SrVO_3$ Ultrathin Films

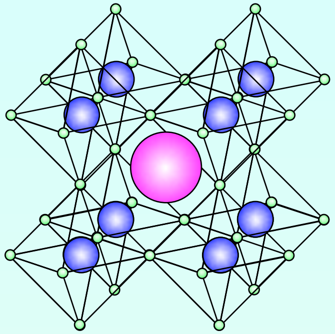
4. *In-situ* PES on $LaNiO_3$ ultrathin films

   High-Tc Cuprate-like 2D-Fermi Surface?

5. Summary & Outlooks

Introduction

Transition Metal Oxides

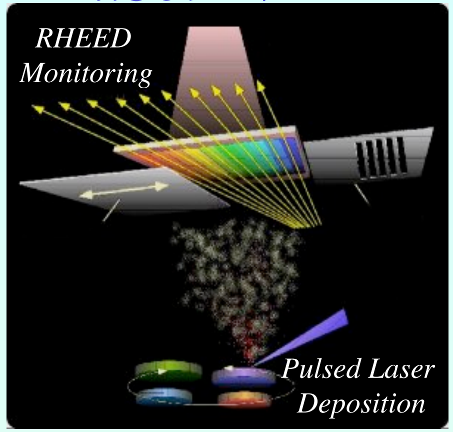


High-Tc
CMR
M-I Transiton

Controlling unusual physical properties

e^-

Laser MBE



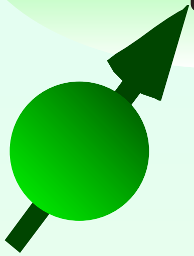
Charge

Charge Transfer

Heterostructure

Spin

Spin Exchange



Orbital

Epitaxial Strain

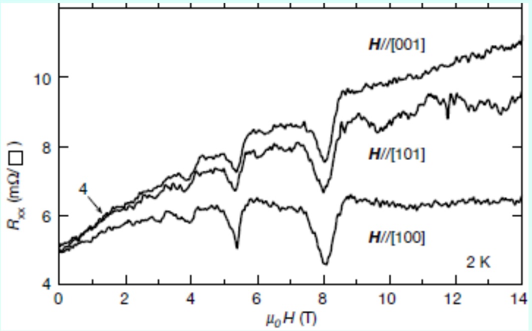
Explore new functional materials

"in-situ Photoemission"

Appearance of metallic conductivity at the interface between the band insulators $LaAlO_3$ and $SrTiO_3$

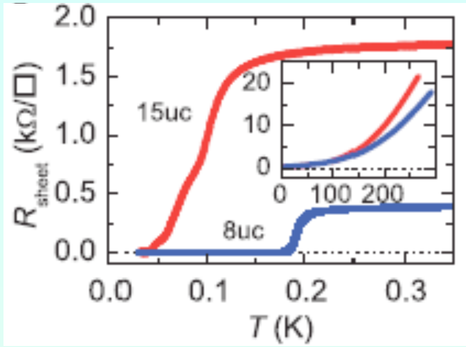
High-mobility electron gas

(A. Ohtomo *et al*, Nature 2004)



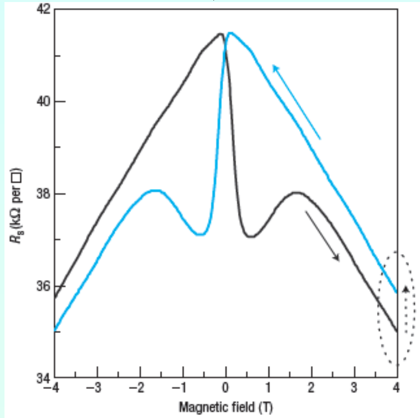
Superconductivity

(N. Reyren *et al*., Science 2007)



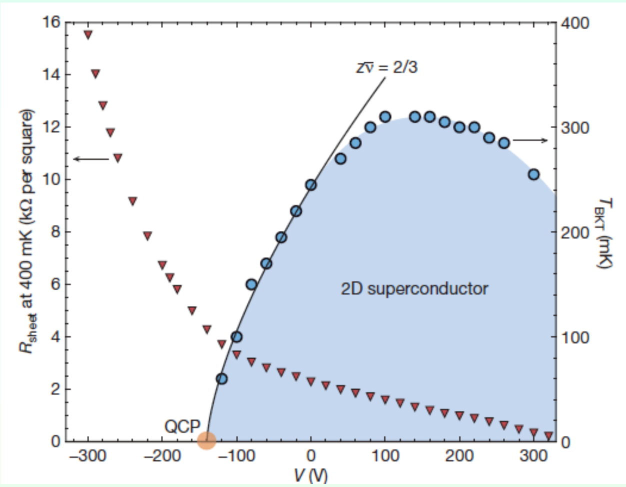
Ferromagnetism?

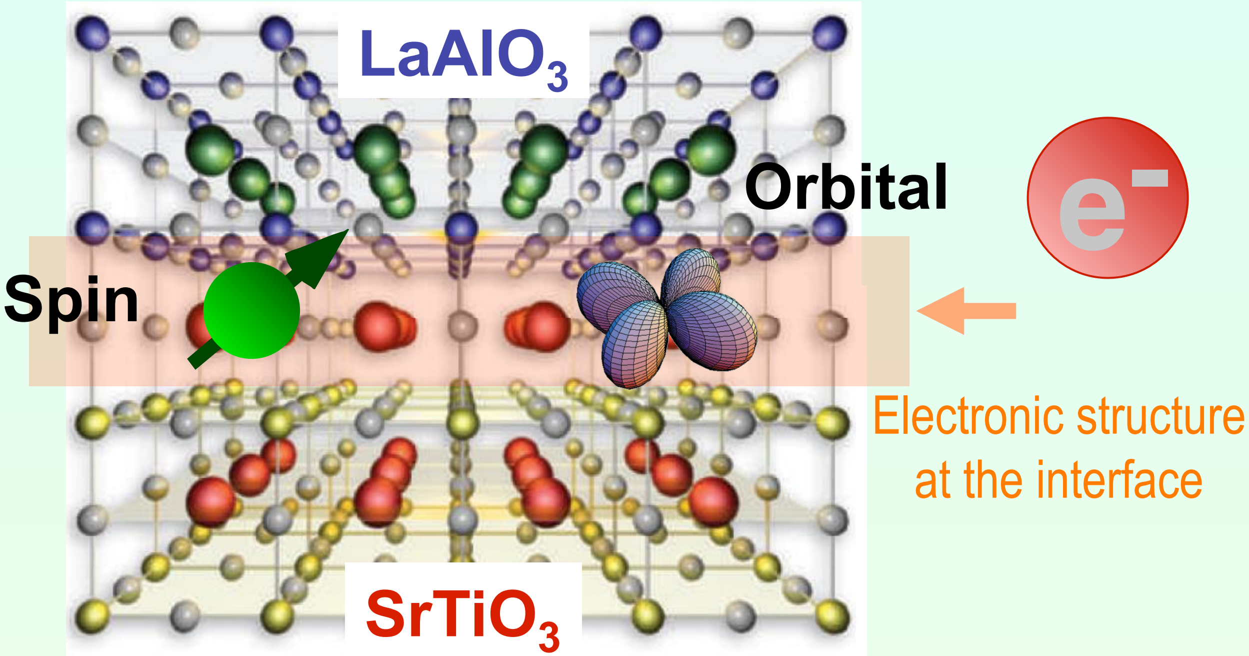
(A. Brinkman *et al*, Nat. Mater. 2007)



Electric field control of the superconductivity

(A.D. Caviglia *et al*, Nature 2008)





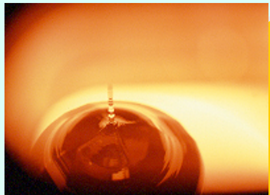
Road Map of Artificial Oxide Structures

Semiconductor (Si)

Searching materials (Bulk)

Growth of high quality single crystal

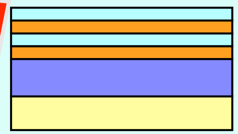
Characterization technique (Spectroscopy)



Understanding the semiconductor physics
(One electron picture)

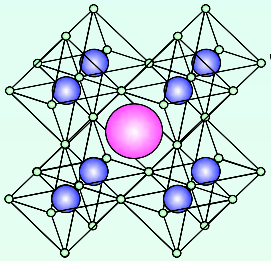
Heterostructuring

Controlling physical properties using artificial structures



New Functionalities
(Electric devices)
New Physics
(Quantum Hall effects)

Strongly correlated oxides



Searching materials (Bulk)

High-Tc
CMR
M-I Transiton

High quality single crystal

Spectroscopic technique

Understanding the underlying physics
(Many-body effects)

Artificial structure based on complex oxides

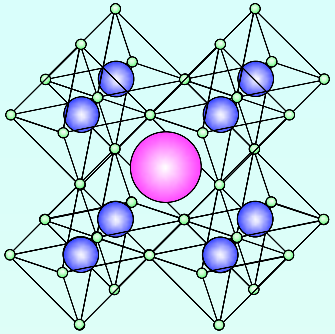
New Physics!

Controlling the anomalous physical properties of complex oxides

Oxide heterostructures are new frontier in strongly correlated physics.

Artificial TM-Oxide Structures

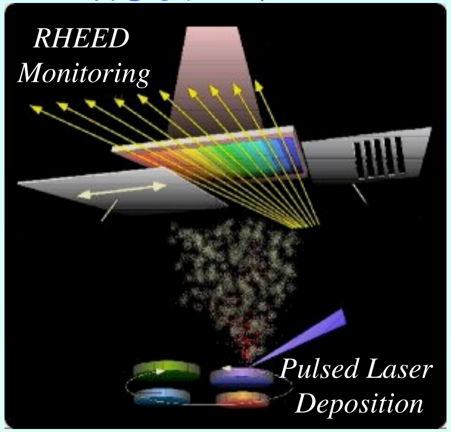
Transition Metal Oxides



High-Tc
CMR
M-I Transiton

Controlling unusual physical properties

Laser MBE



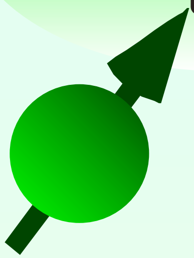
Charge

Charge Transfer

Heterostructure

Spin

Spin Exchange



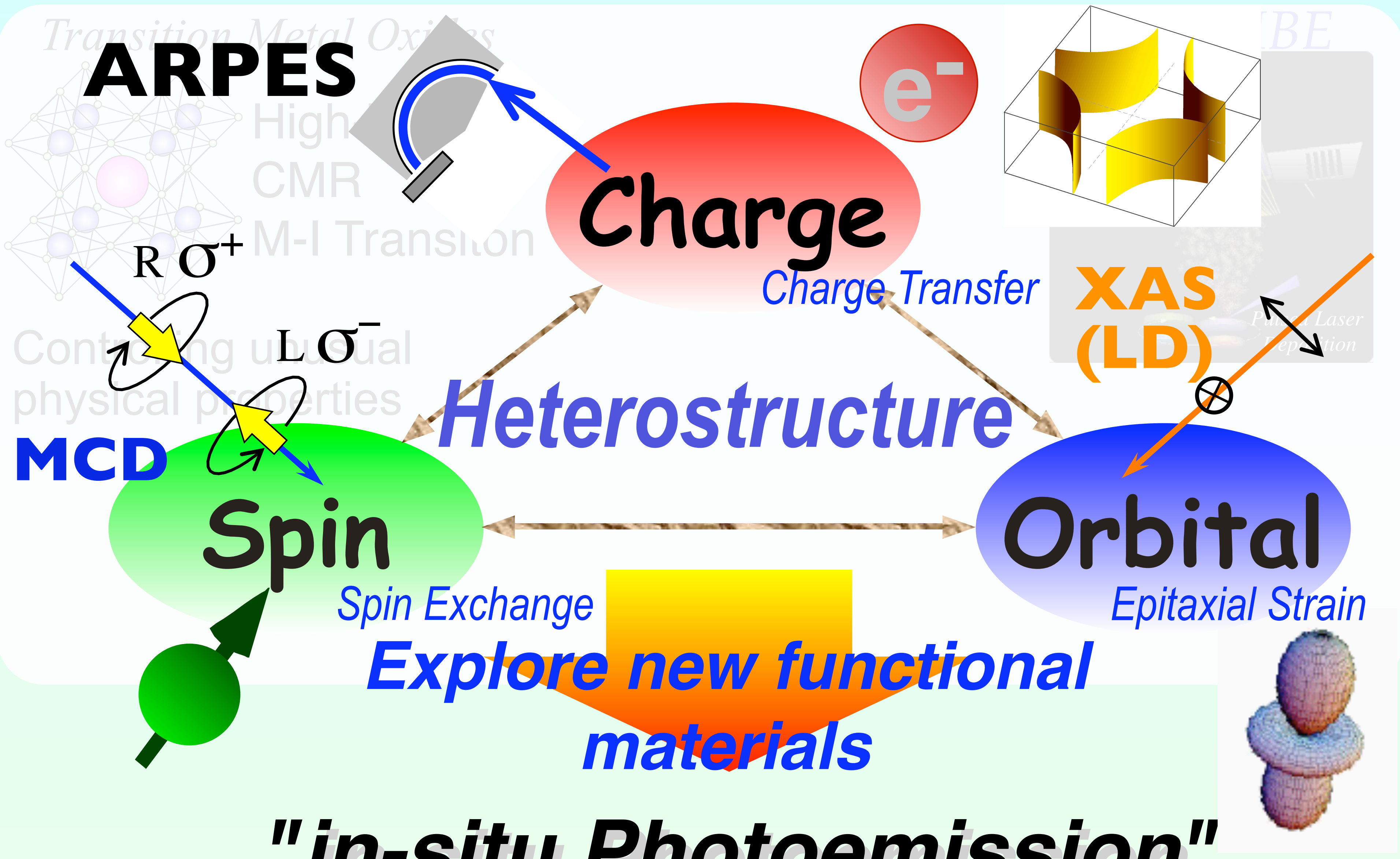
Orbital

Epitaxial Strain

Explore new functional materials

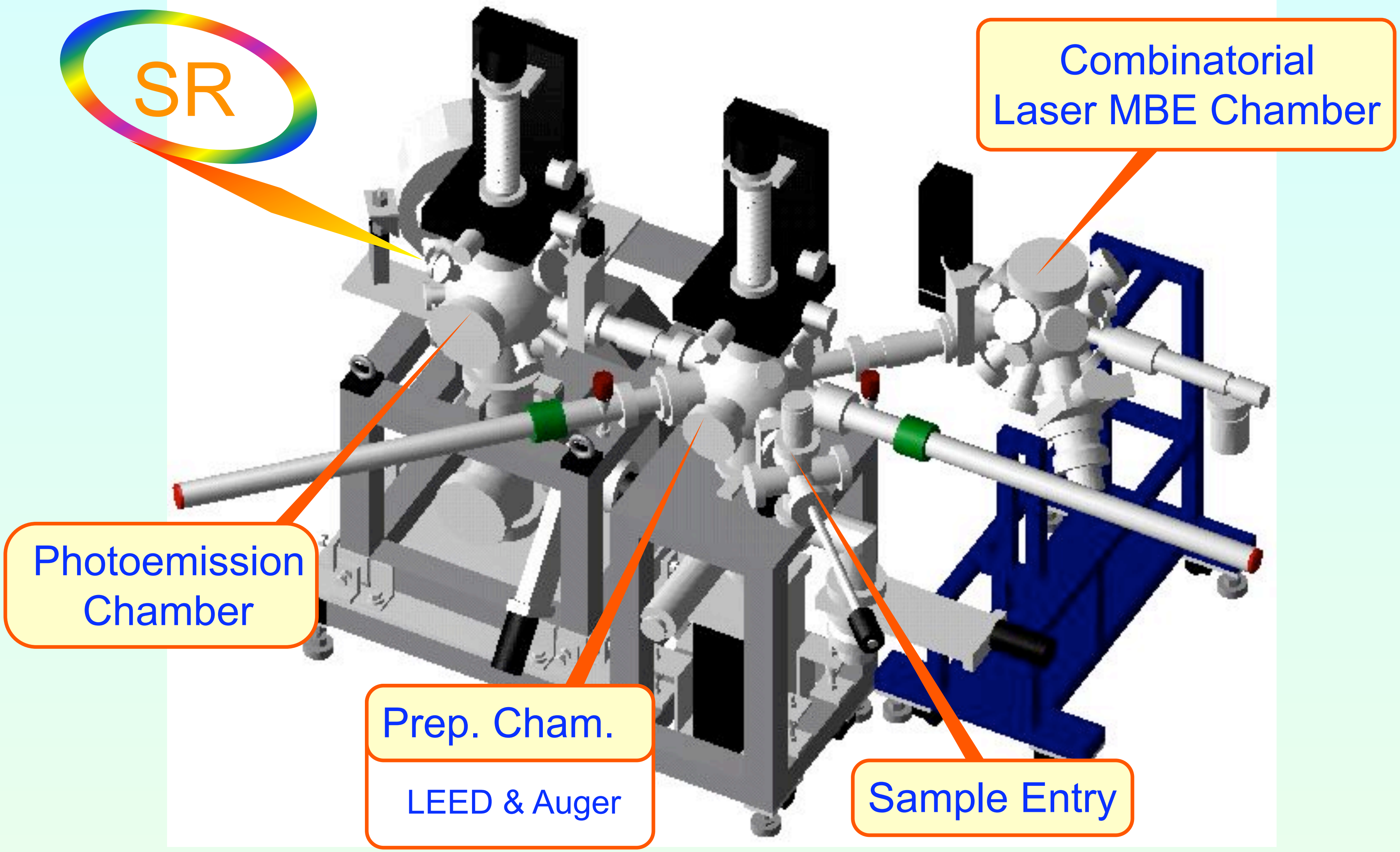
"in-situ Photoemission"

Artificial TM-Oxide Structures



"in-situ Photoemission"

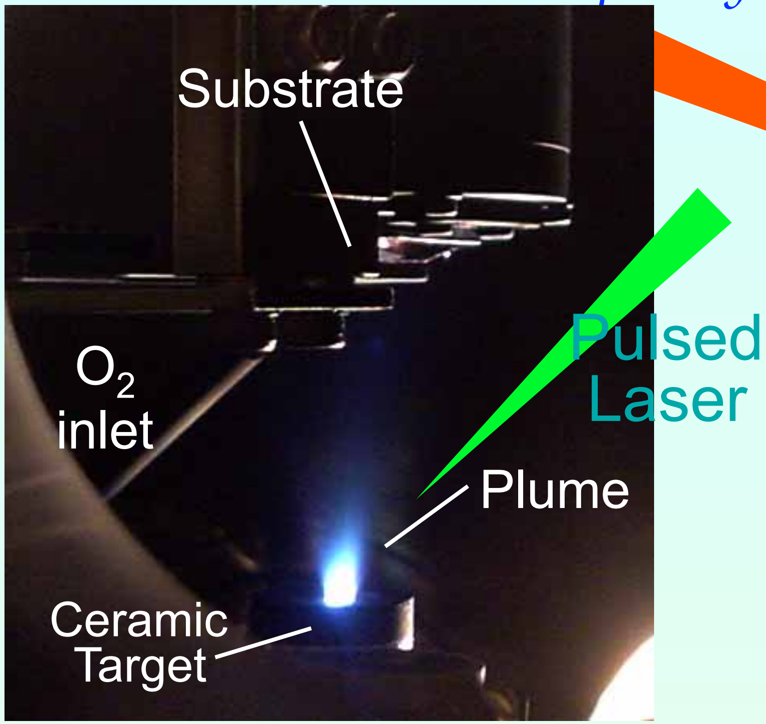
In-situ PES + Laser MBE system

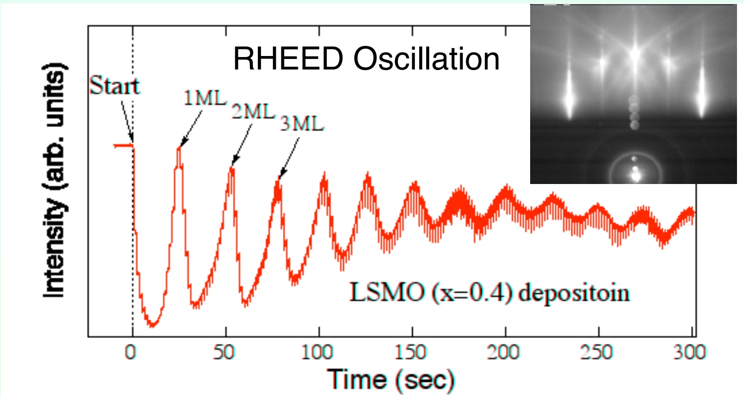


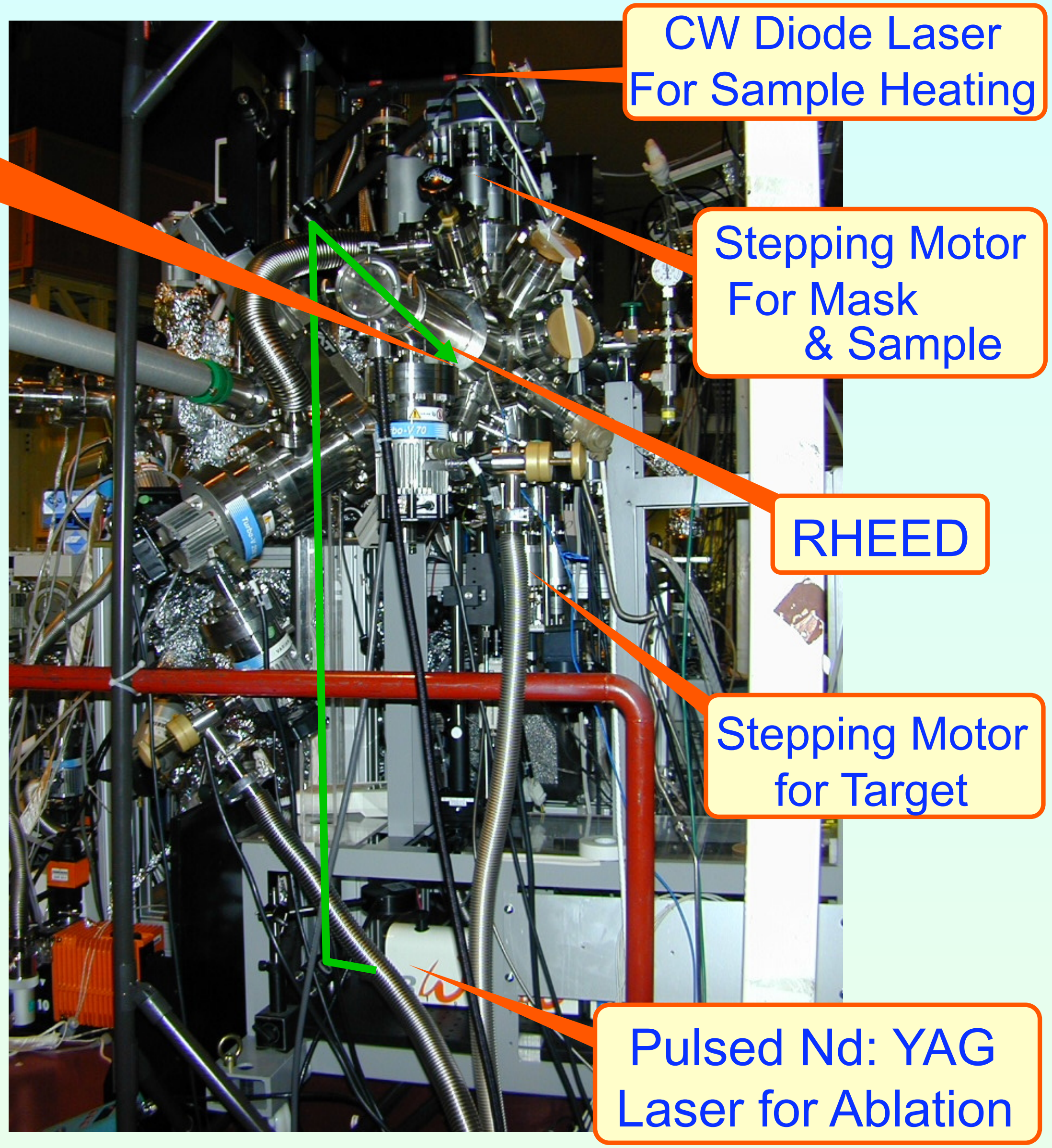
K. Horiba, HK *et al*., Rev. Sci. Instrum. **74**, 3406 (2003).

Combinatorial Laser MBE Apparatus

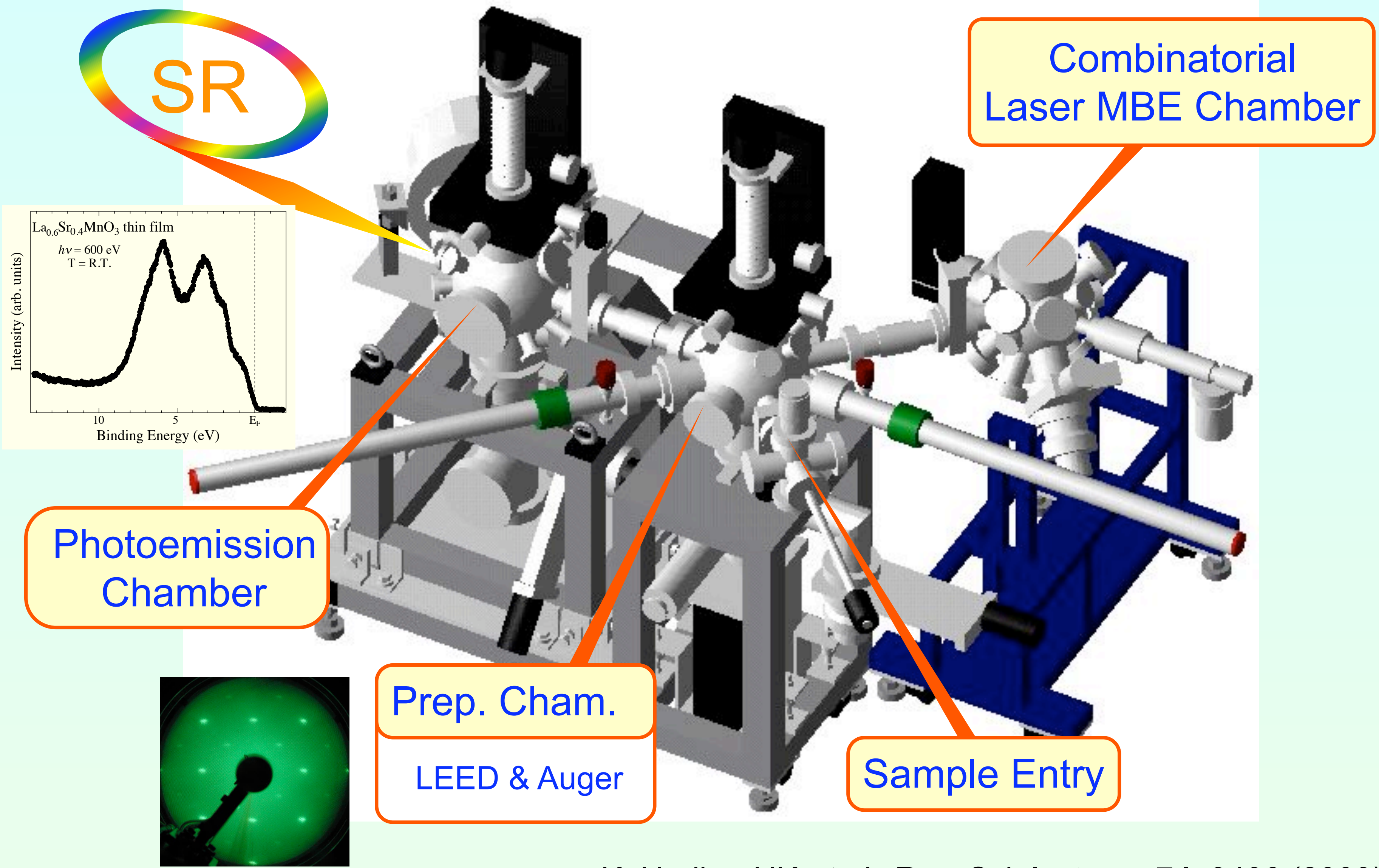
Laser Molecular Beam Epitaxy





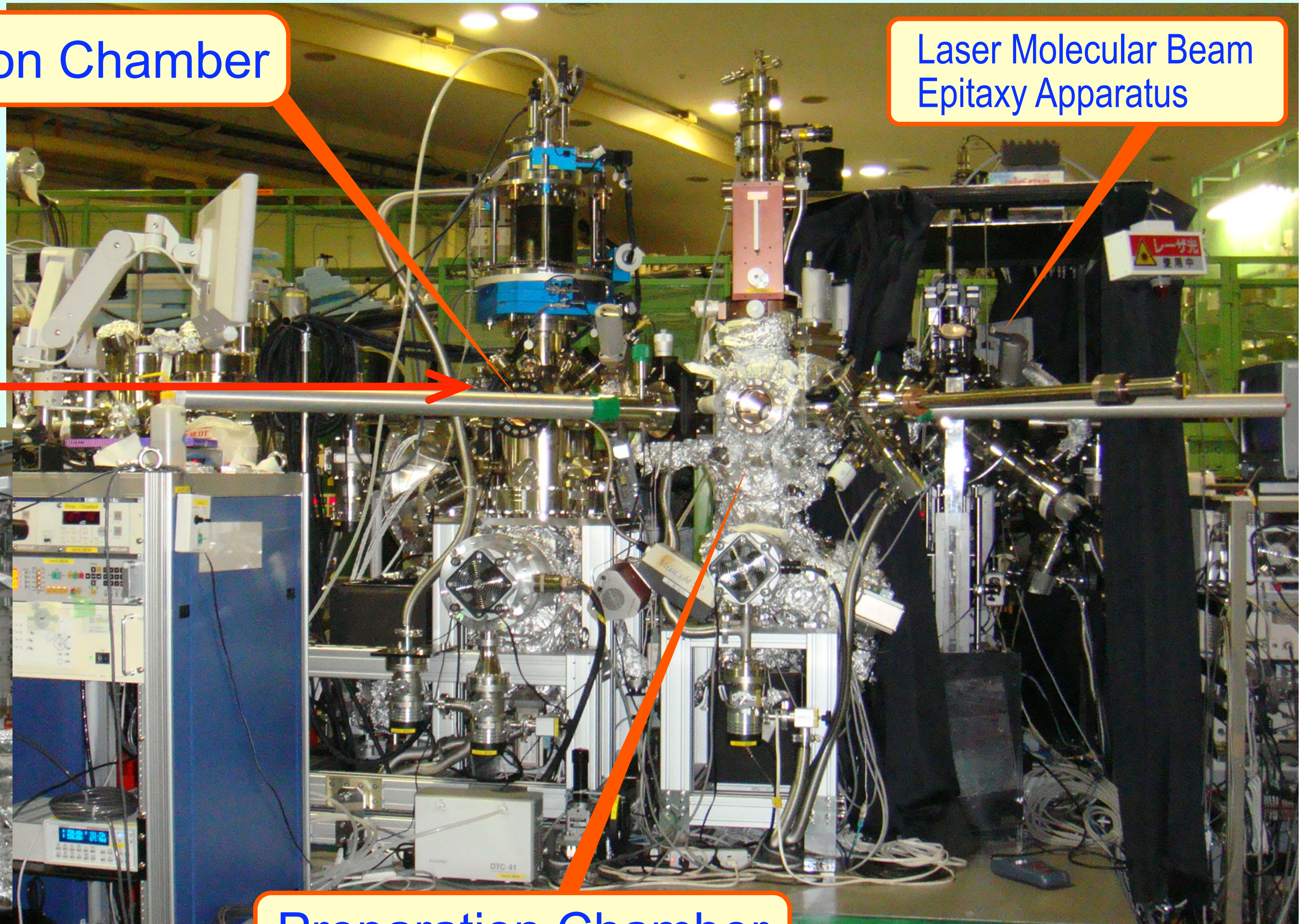


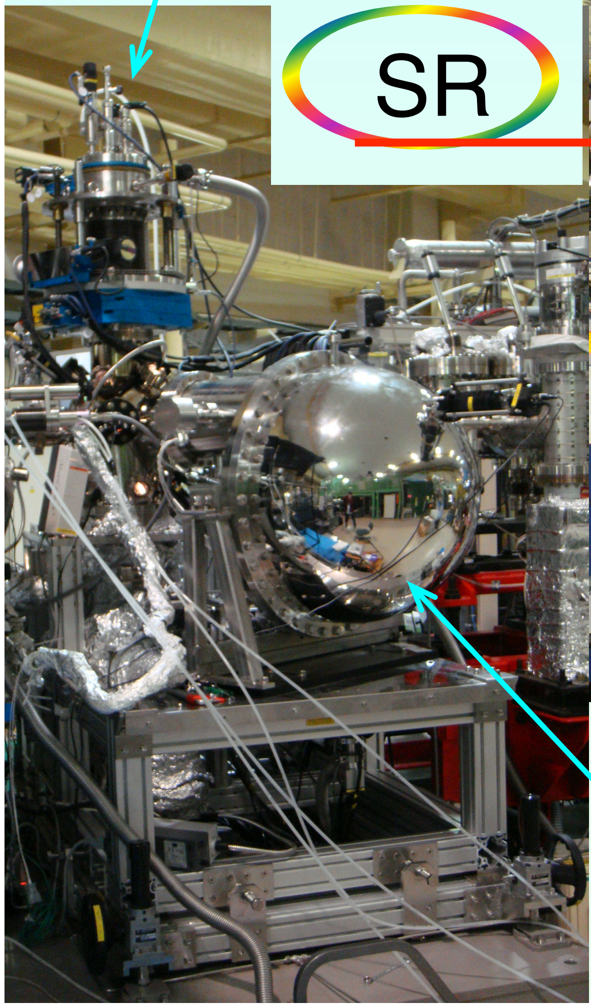
In-situ PES + Laser MBE system



K. Horiba, HK *et al*., Rev. Sci. Instrum. **74**, 3406 (2003).

New *in-situ* PES + Laser MBE system





@KEK-PF BL-2C

In-situ Photoemission Studies on Surface and Interface of Oxide Heterostructures

REVIEW ARTICLE

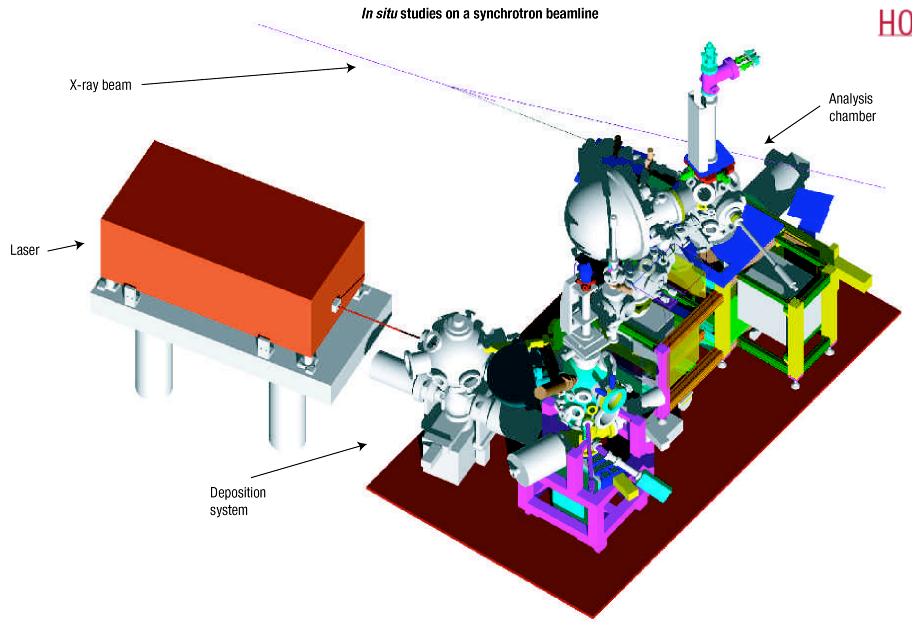


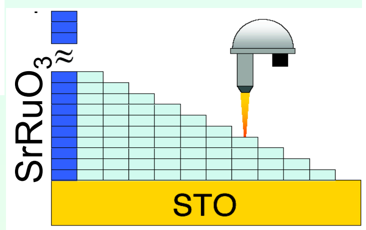
Figure 3 A schematic illustration of a thin-film deposition system (in this case a laser MBE system) that is attached to a synchrotron beamline. Such a system makes it easier to probe the electronic structure of surfaces and interfaces as the heterostructure is being grown. In the field of complex oxides, such *in situ* facilities are just emerging.

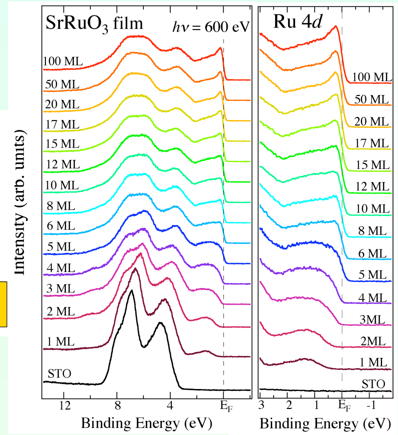
HORIZONTAL MULTILAYER HETEROSTRUCTURES

Finally, we mention that the field of horizontal heterostructure multiferroics is starting to benefit immensely from the use of a variety of surface-sensitive electronic probes such as angle-resolved photoemission (ARPES). An emerging area of research involves the probing of surface and near-surface interface electronic structure *in situ*. For this, the deposition process must be connected *in situ* to the probe; although this is common in semiconductor heteroepitaxy, it is only just evolving in complex oxide heteroepitaxy. Such systems, shown schematically in Fig. 3, are currently being designed in several laboratories around the world, and promising preliminary results are emerging[84].

Multiferroics: progress and prospects in thin films
R. Ramesh and N.A. Spaldin, *Nature Materials* **6**, 21 ('07)

Thickness dependent electronic structure of ultrathinfilm $SrRuO_3$ films studied by *in-situ* PES spectroscopy

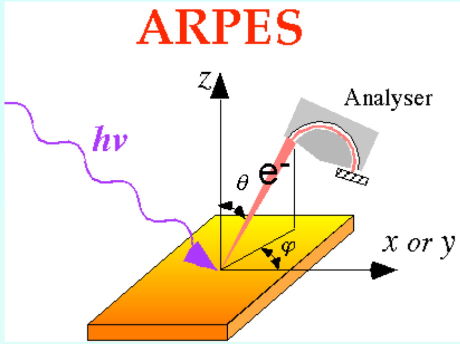




2001	2003	2005	2007	2009
PF		SPring8	ALS BESSY	SLS (Under construction)

D. Toyota *et al*, *Appl. Phys. Lett.* 87, 162508 ('05)

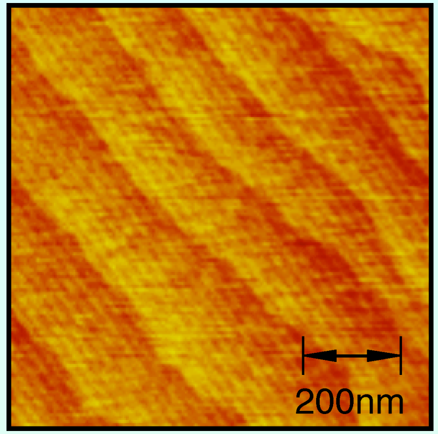
TM-Oxide Superstructures



Single crystal surface

Band Structure & Fermiology

Atomically flat LSMO thin film



"in-situ HR-PES"

+

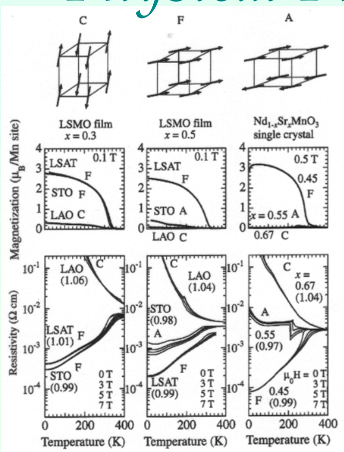
"Laser MBE"

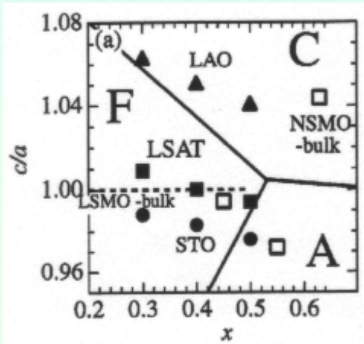
Epitaxial Strain

Physical Pressure

Superlattice

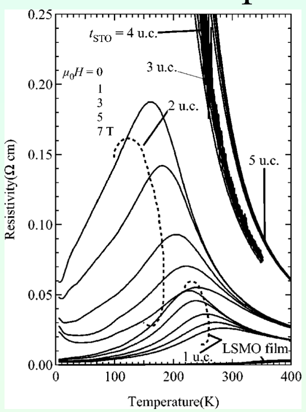
New Materials

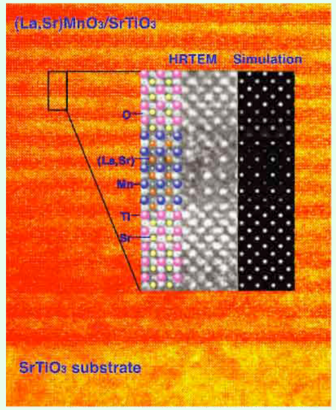




Y. Konishi *et al*., J. Jpn. Phys. Soc.**68**, 3790 (1999).

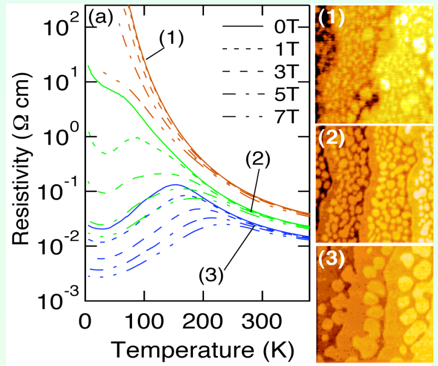
Superlattice



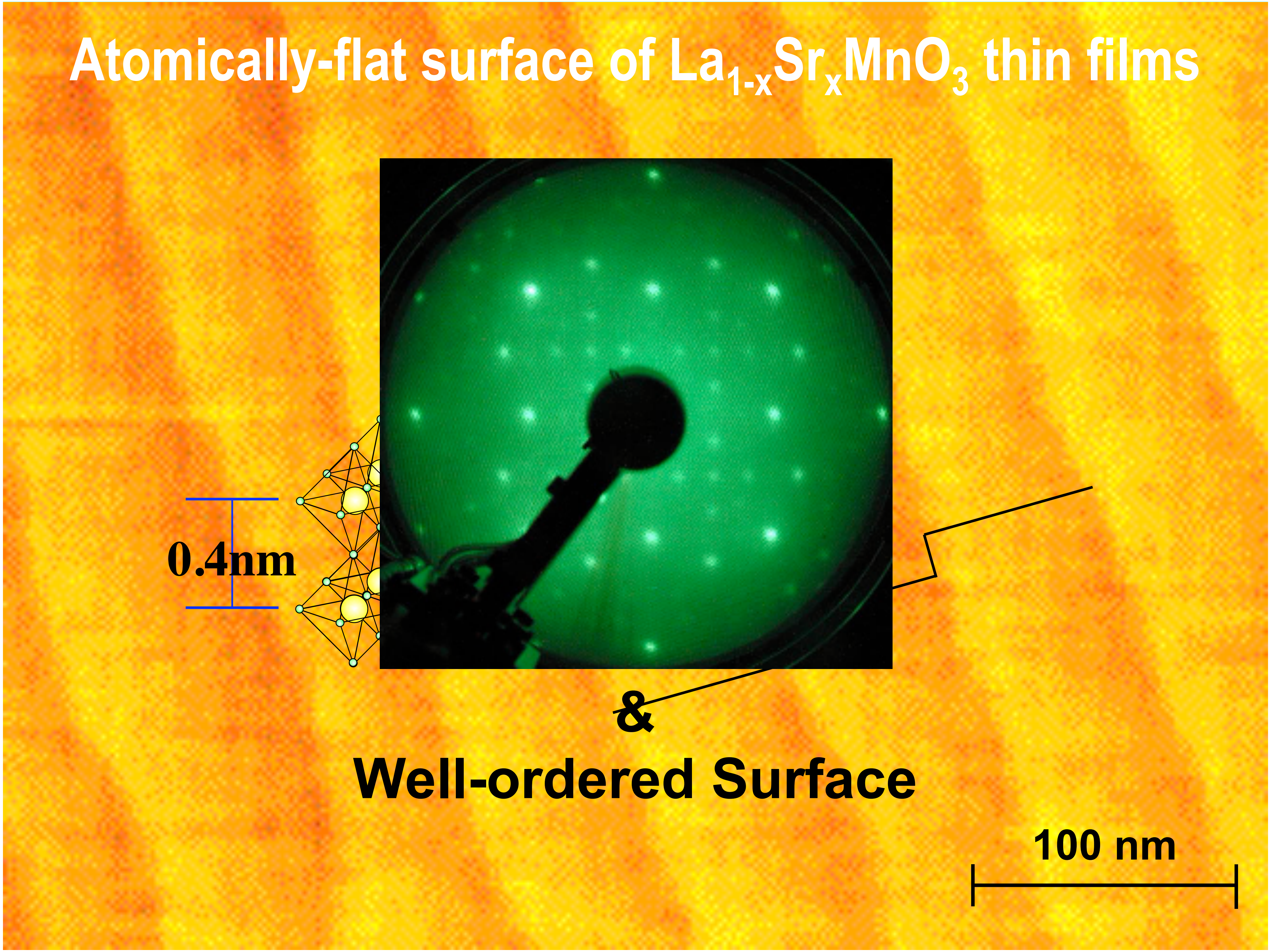


M. Izumi *et al*., Phys. Rev. B **64**, 064429 (2002).

Nanodots&Nanowires

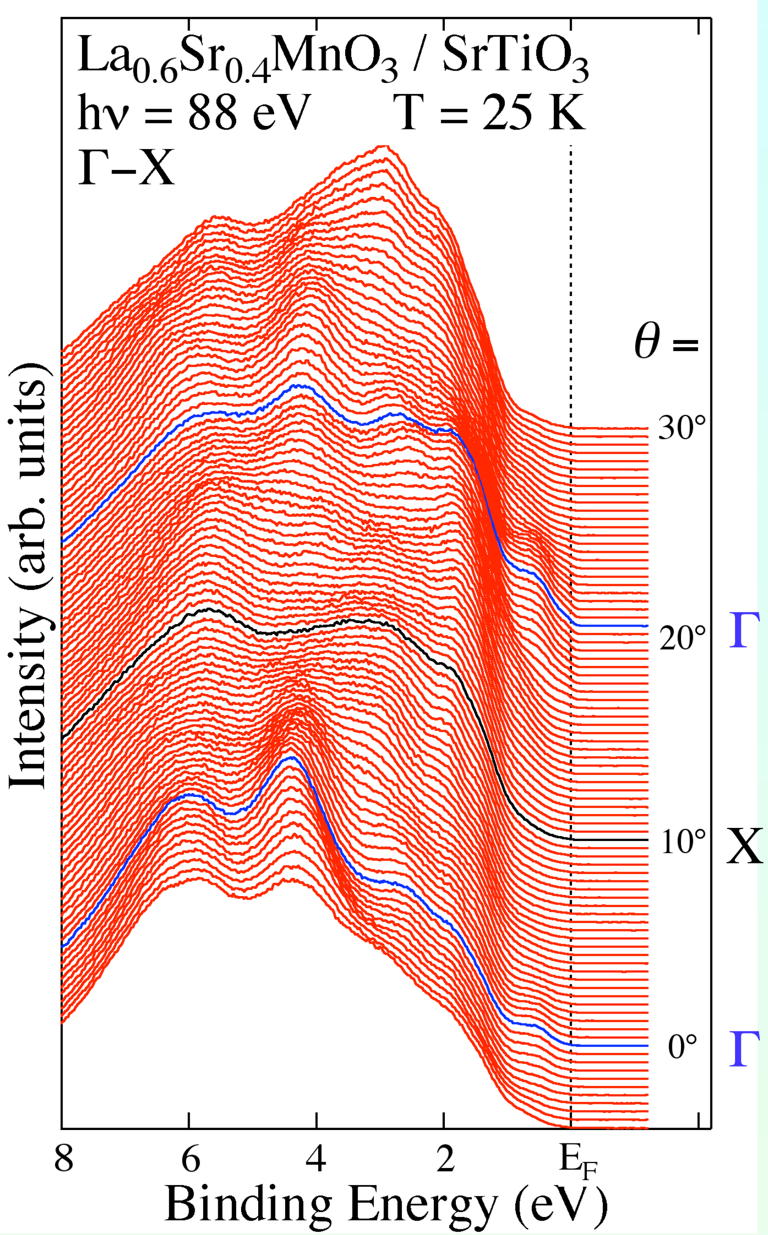


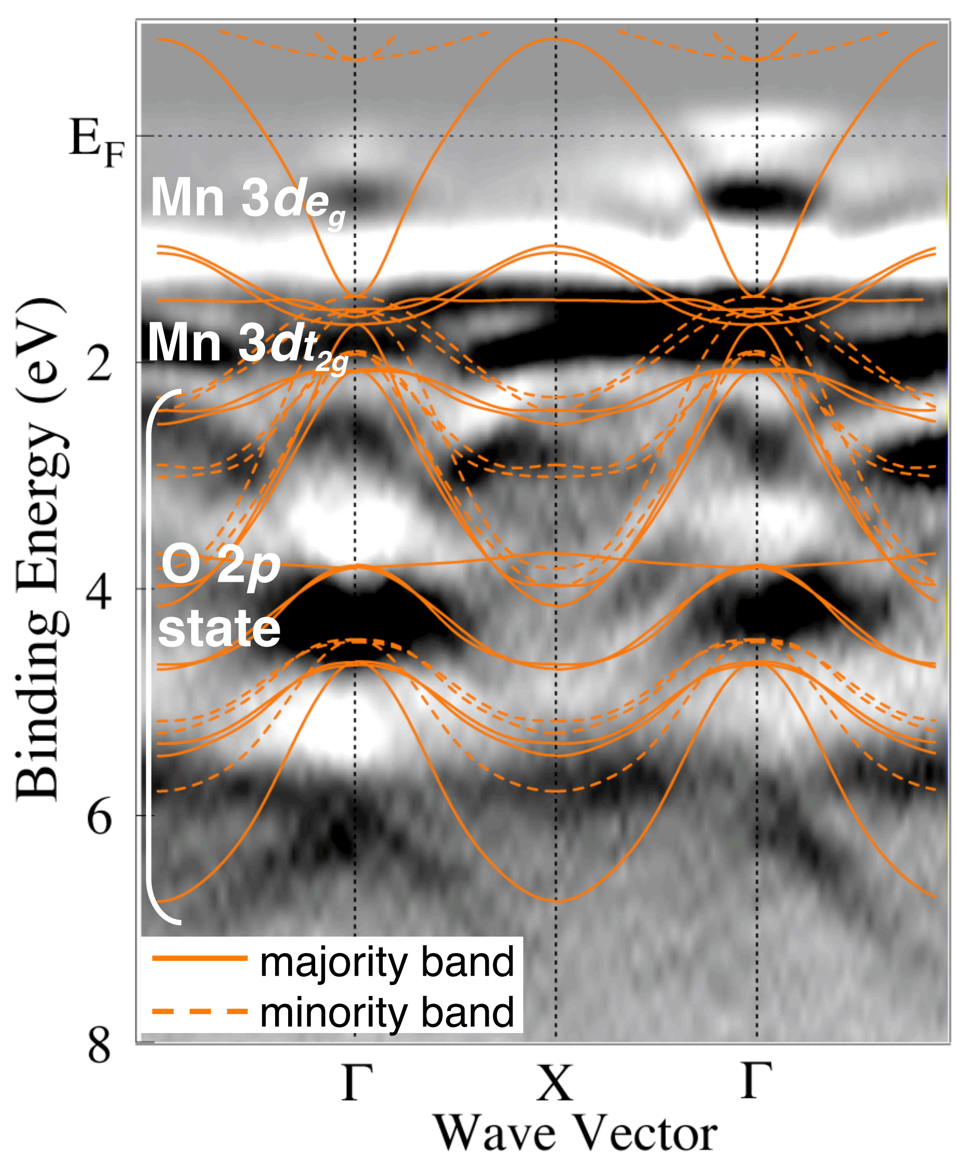
N. Nakagawa *et al*., Jpn. J. Appl. Phys. 41, L302 (2002)



Atomically-flat surface of $La_{1-x}Sr_xMnO_3$ thin films
0.4nm
&
Well-ordered Surface
100 nm

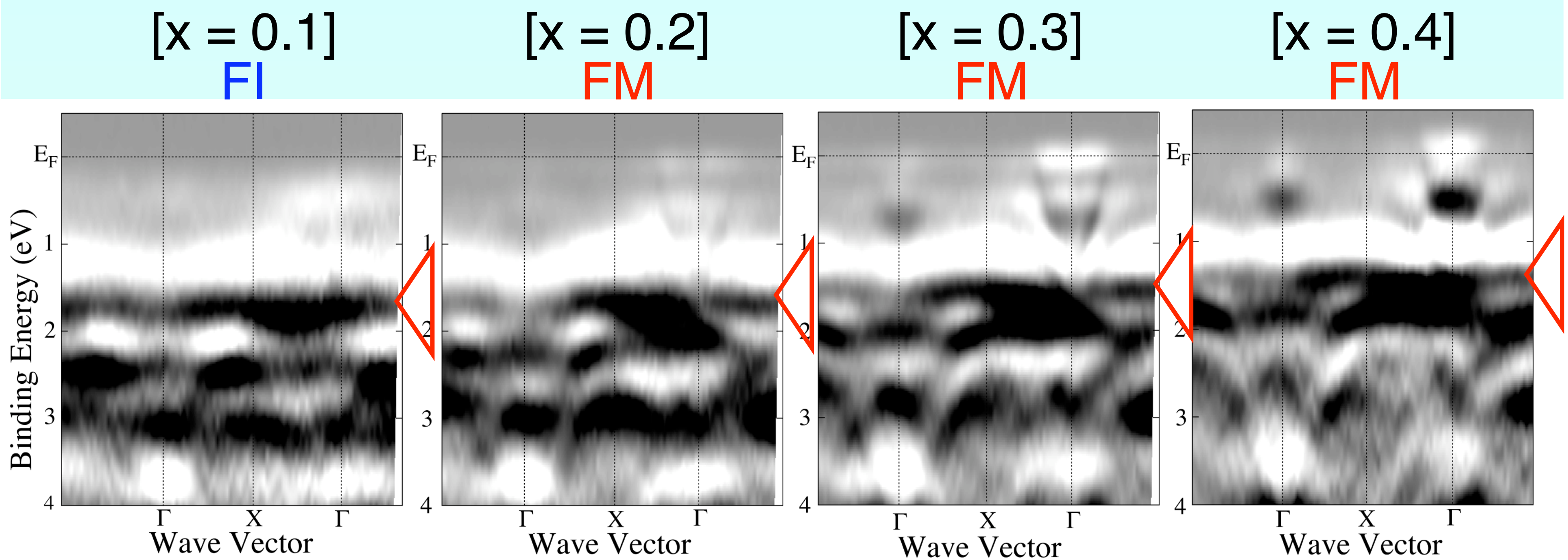
Band structure of LSMO determined by *in-situ* ARPES



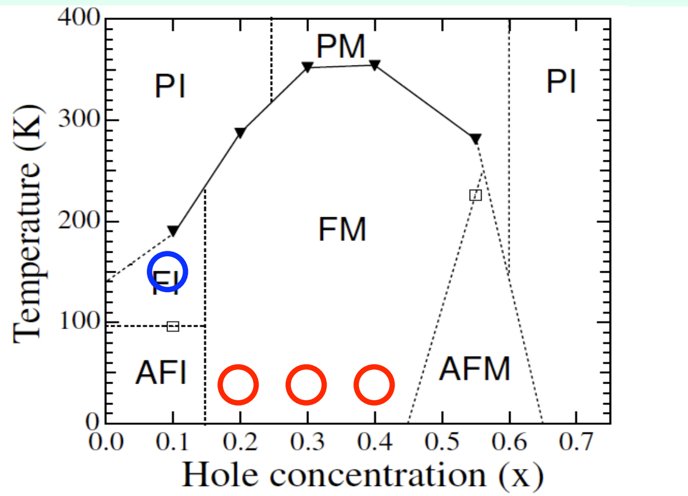


A. Chikamatsu, HK *et al*. *Phys. Rev. B* **73**, 195105 (2006).

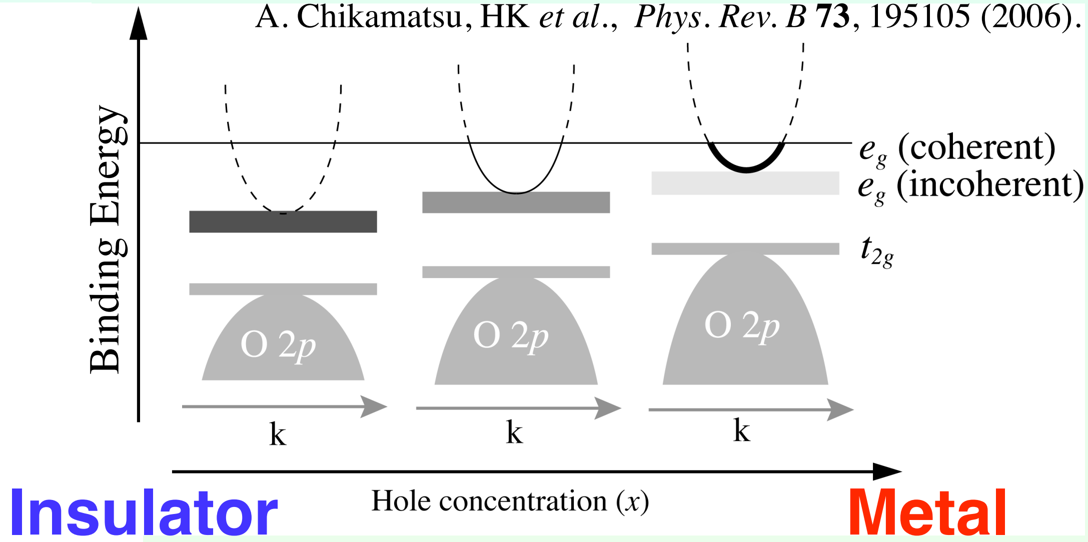
Composition dependence of Fermi surfaces



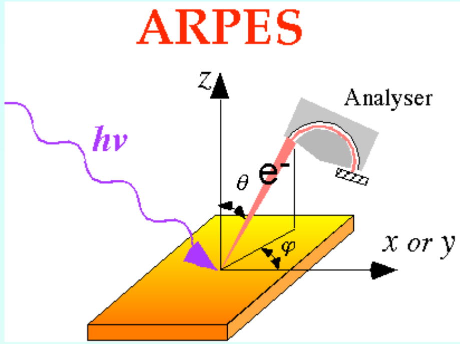
A. Chikamatsu, HK *et al*., *Phys. Rev. B* **73**, 195105 (2006).



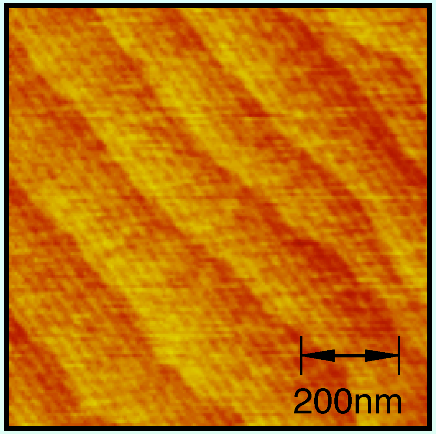
K. Horiba, HK *et al*., *Phys. Rev. B* **71**, 155420 (2005).



TM-Oxide Superstructures



Atomically flat LSMO thin film



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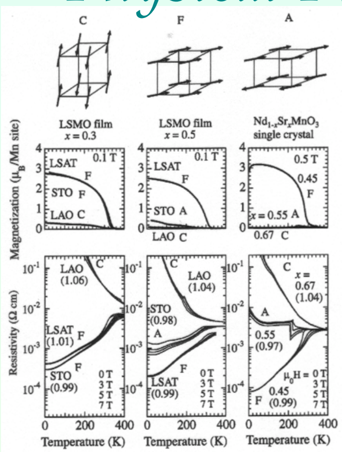
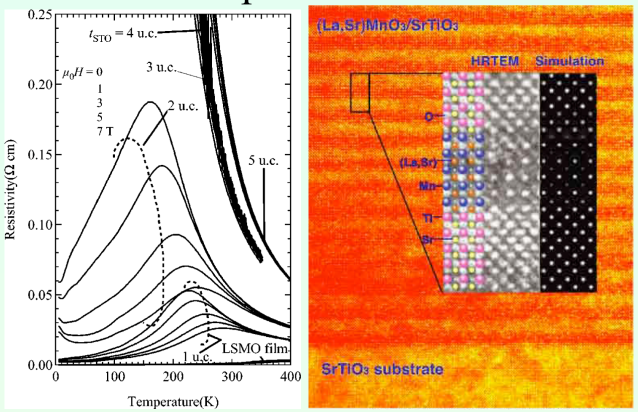
Superlattice

New Materials

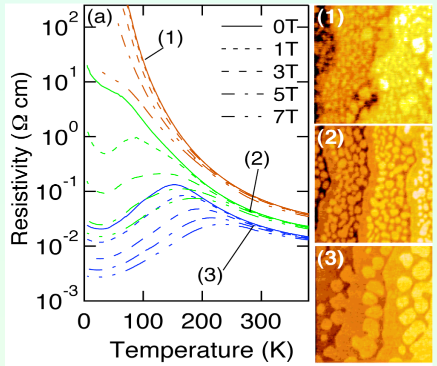


"Laser MBE"

Superlattice



Nanodots&Nanowires



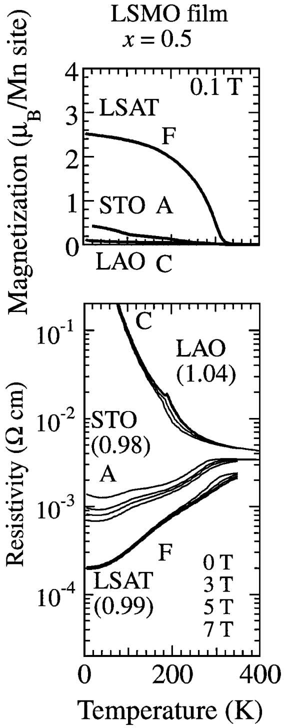
Y. Konishi *et al.*, J. Jpn. Phys. Soc.**68**, 3790 (1999).

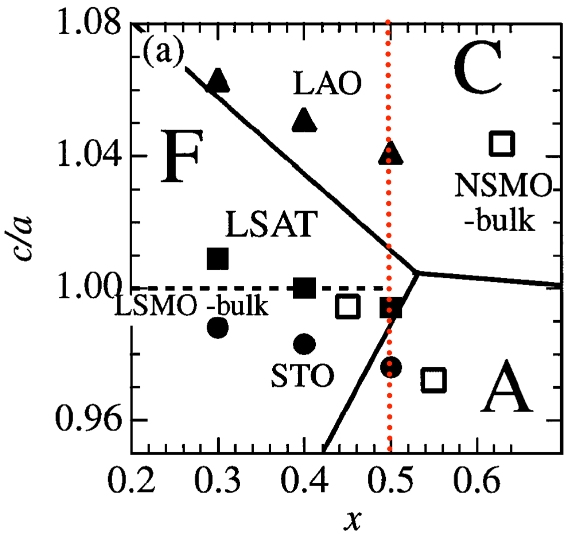
M. Izumi *et al.*, Phys. Rev. B **64**, 064429 (2002).

N. Nakagawa *et al.*, Jpn. J. Appl. Phys. 41, L302 (2002)

Physical Pressure Induced by Epitaxial Strain

Strain-controlled LSMO films

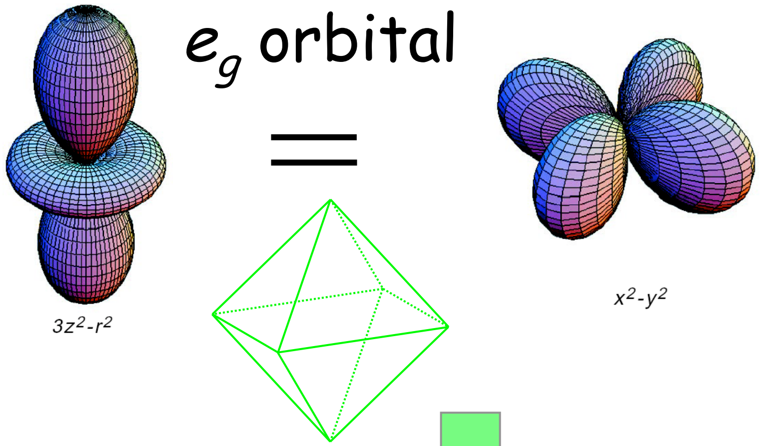




Y. Konishi *et al*., J. Phys. Soc. Jpn. 68, 3790 (1999).

LSMO x = 0.5

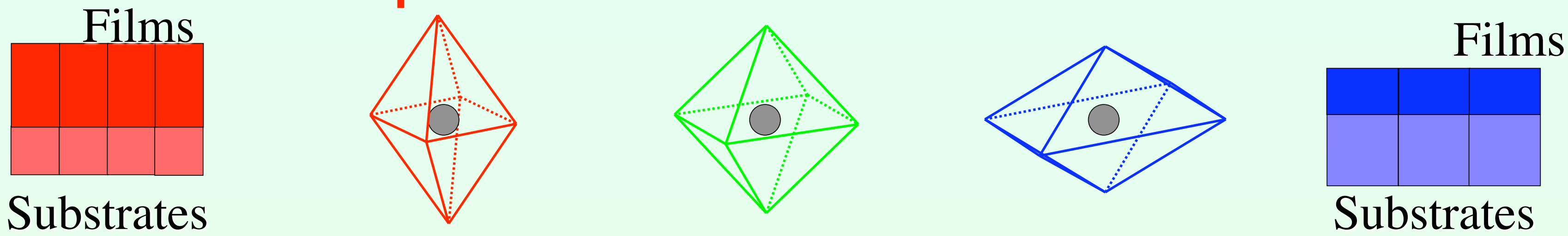
LSMO/LSAT (FM)



LSMO/LAO
(c-type AFI)

LSMO/STO
(A-type AFM)

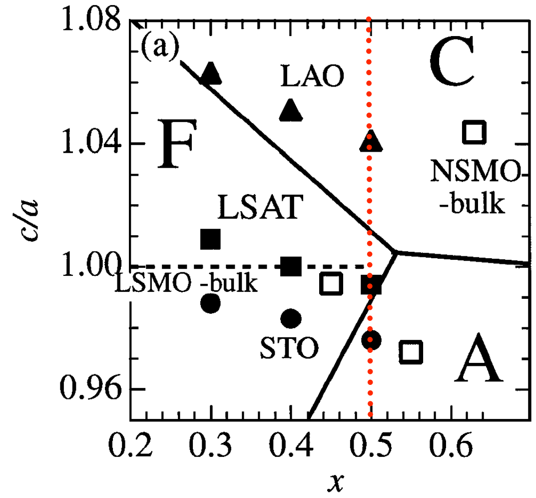
Compressive ⟷ **Tensile**



Change in electronic structure under physical pressure

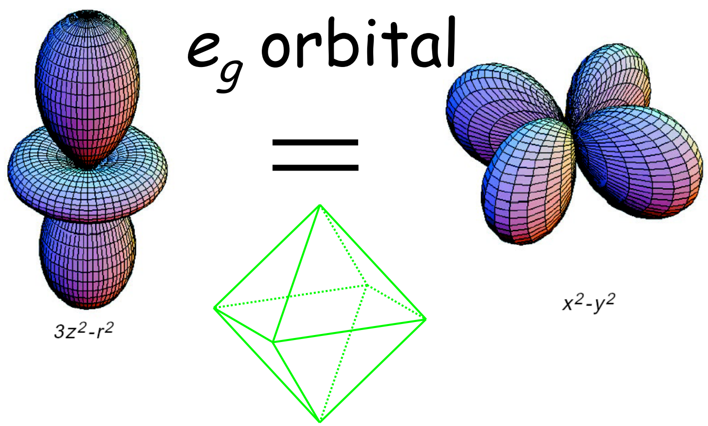
Phase Controlled LSMO films by Epitaxial Strain

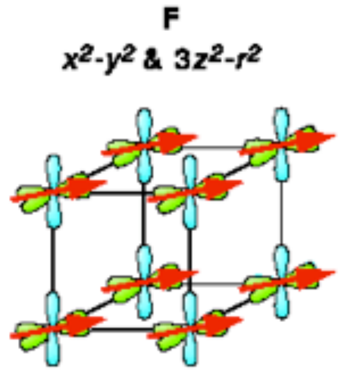
Strain-controlled LSMO films

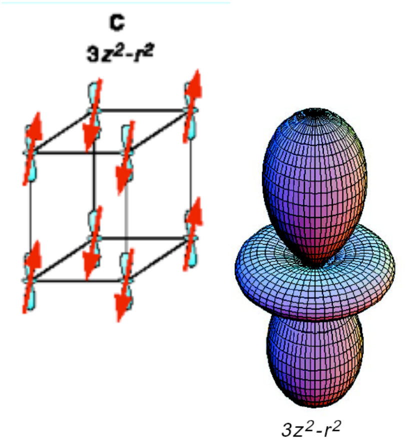


Y. Konishi *et al*., J. Phys. Soc. Jpn. 68, 3790 (1999).

LSMO/LSAT (FM)

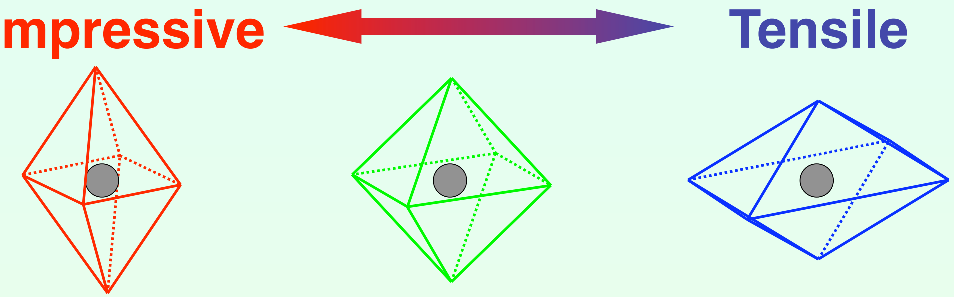


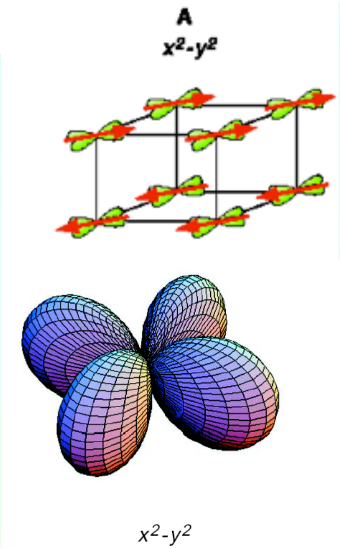




LSMO/LAO
(*c*-type AFI)

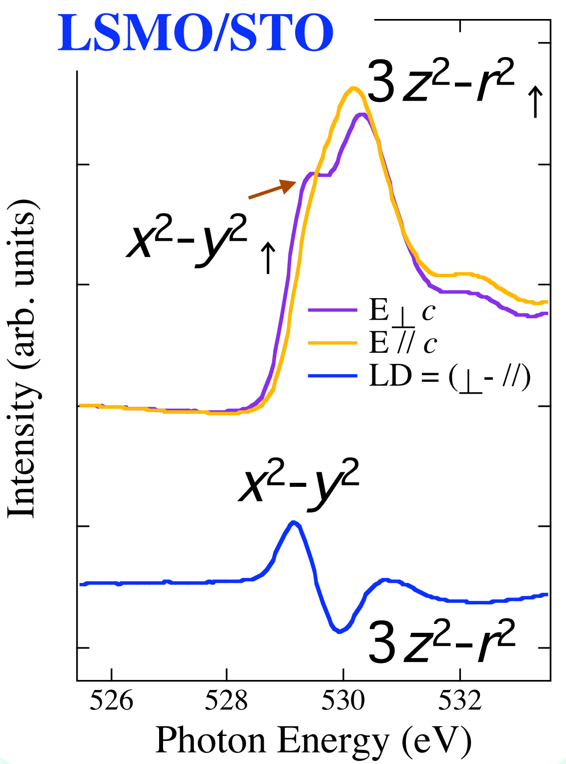
LSMO/STO
(A-type AFM)

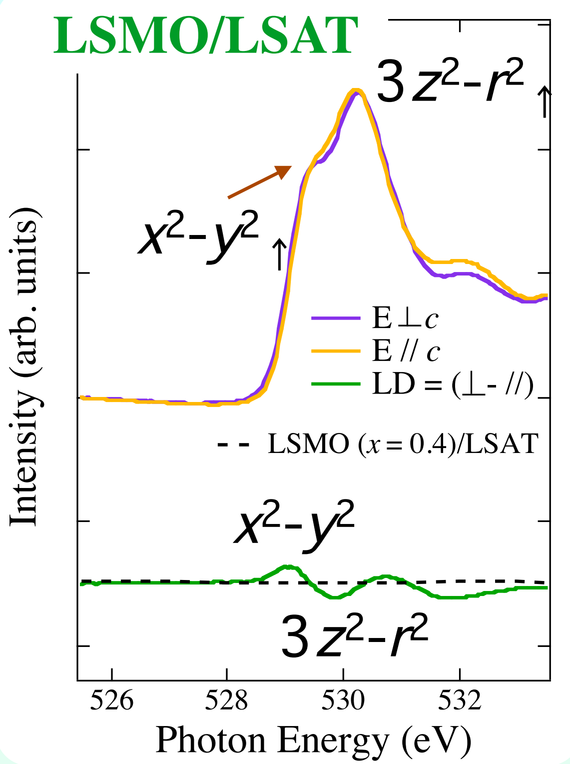


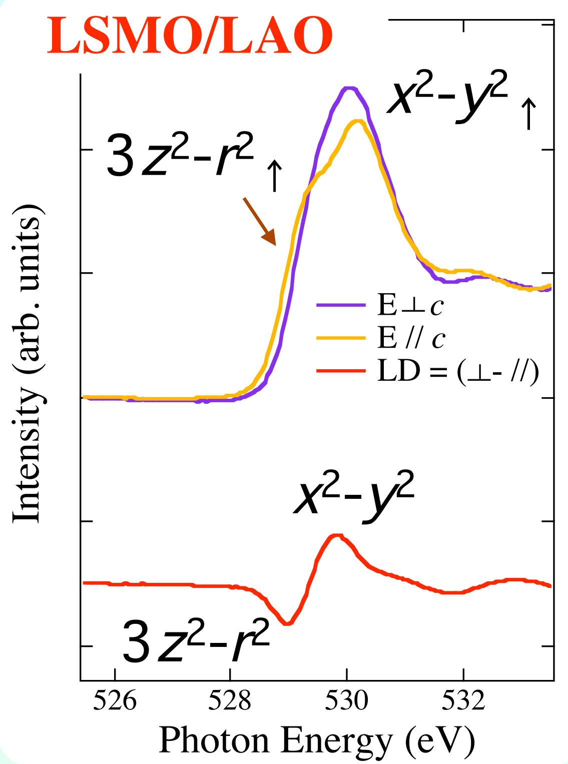


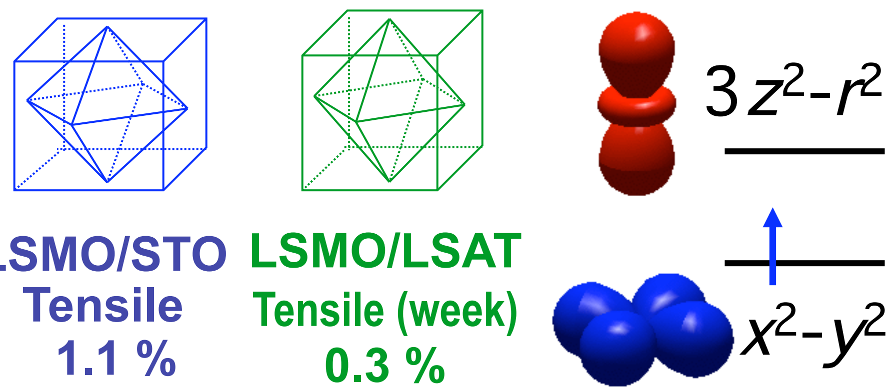
Photoemission Studies on Phase-Controlled LSMO Films

Linear Dichroism of XAS spectra



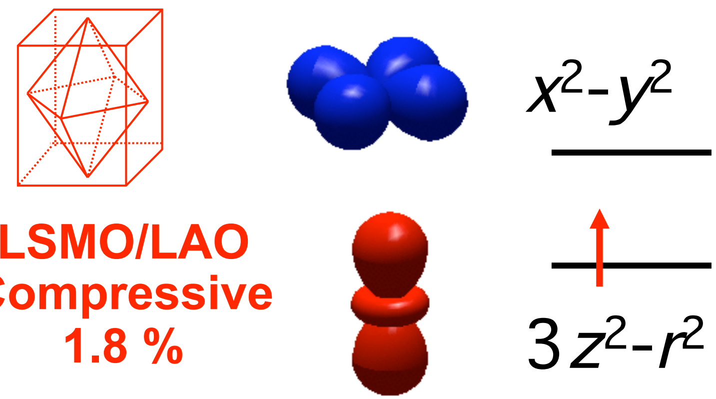






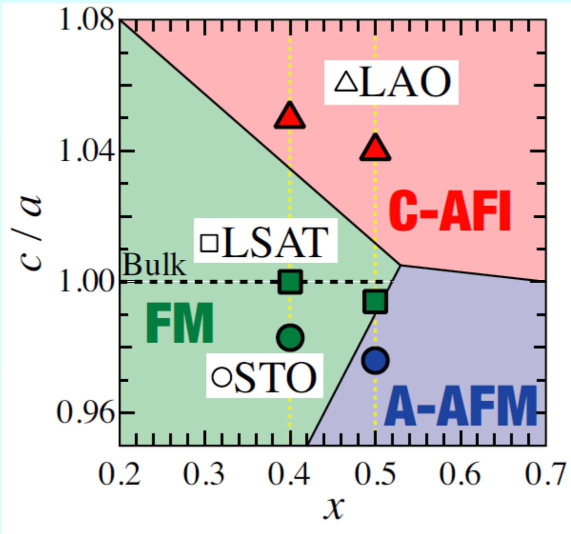
LSMO/STO
Tensile
1.1 %

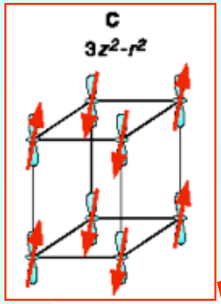
LSMO/LSAT
Tensile (week)
0.3 %

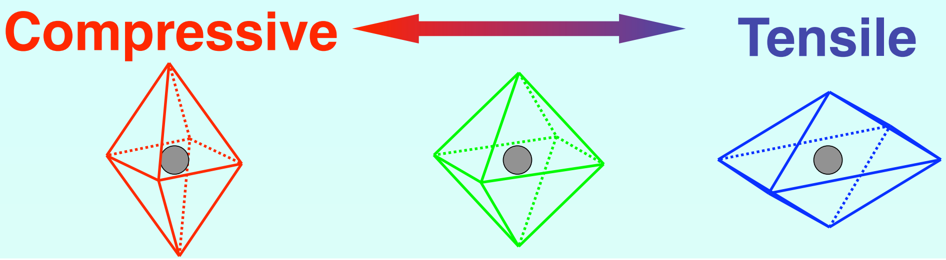


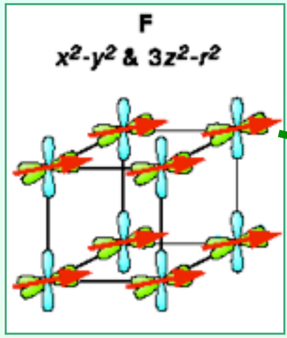
LSMO/LAO
Compressive
1.8 %

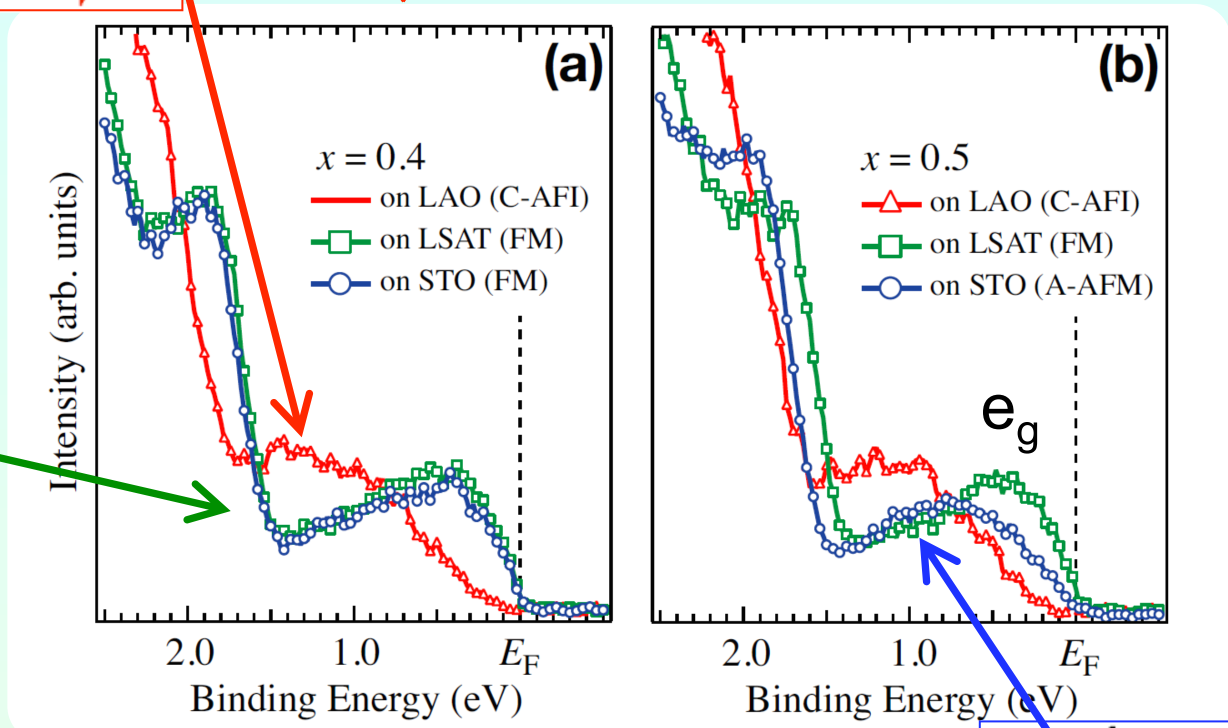
HXPES Spectra of Strain-controlled LSMO



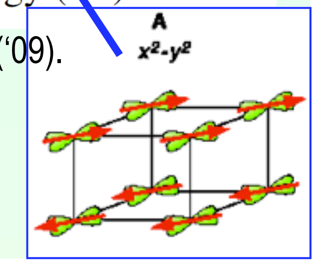






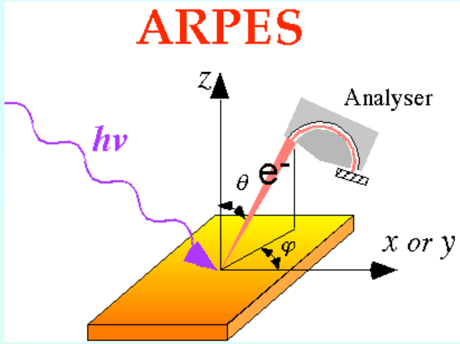


K. Horiba, HK *et al*., Phys. Rev. B **80**, 132406 ('09).



Energy Gap opens at E_F Associated with Pressure-Induced Metal-Insulator transition

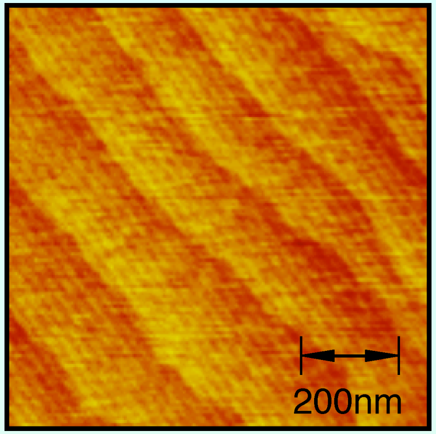
TM-Oxide Superstructure



Single crystal surface

Band Structure & Fermiology

Atomically flat LSMO thin film



"in-situ HR-PES"

+

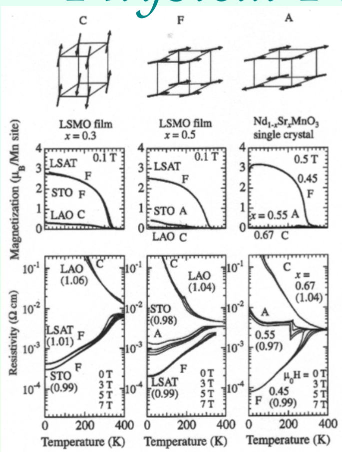
"Laser MBE"

Epitaxial Strain

Physical Pressure

Superlattice

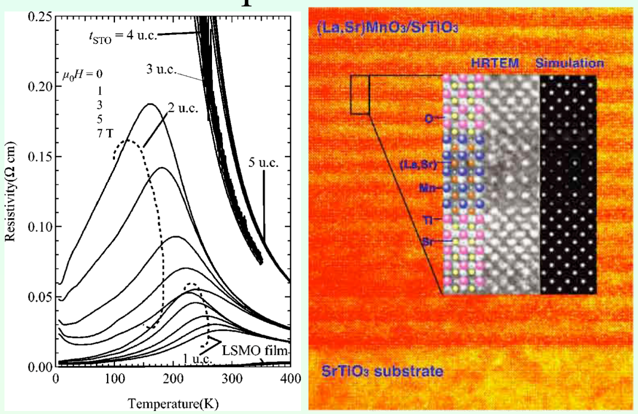
New Materials



"Laser MBE"

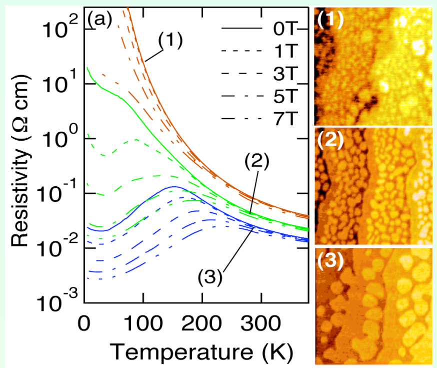
Y. Konishi *et al.*, J. Jpn. Phys. Soc.**68**, 3790 (1999).

Superlattice



M. Izumi *et al.*, Phys. Rev. B **64**, 064429 (2002).

Nanodots&Nanowires

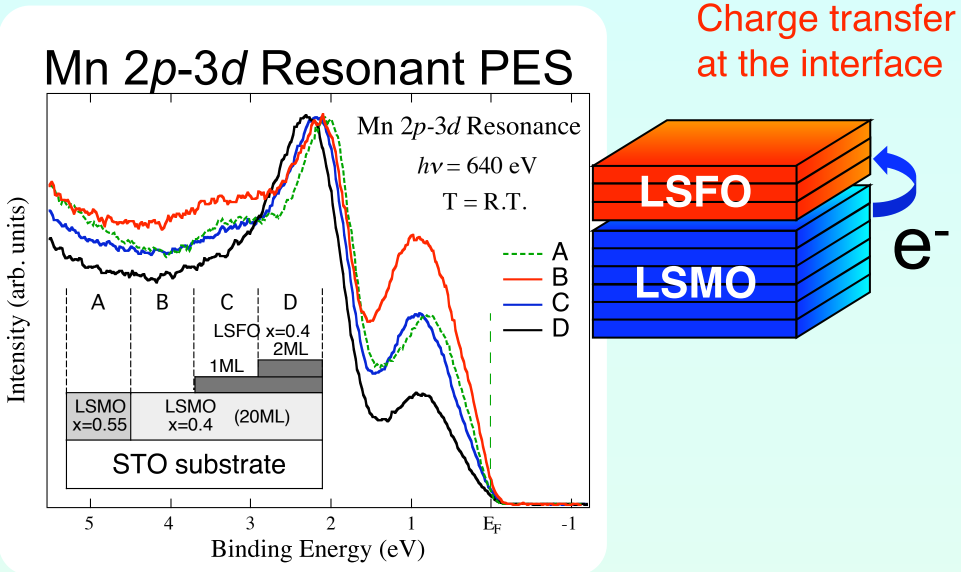


N. Nakagawa *et al.*, Jpn. J. Appl. Phys. 41, L302 (2002)

In-situ PES on Oxide Superstrucutres

Charge transfer at heterointerfaces

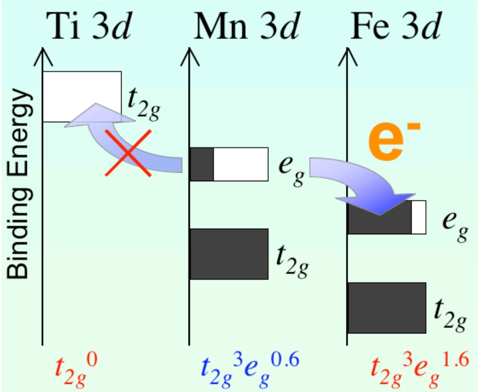
$La_{0.6}Sr_{0.4}FeO_3$/ $La_{0.6}Sr_{0.4}MnO_3$



H. Kumigashira *et al.*, *Appl. Phys. Lett.* **88**, 192504 (2006).

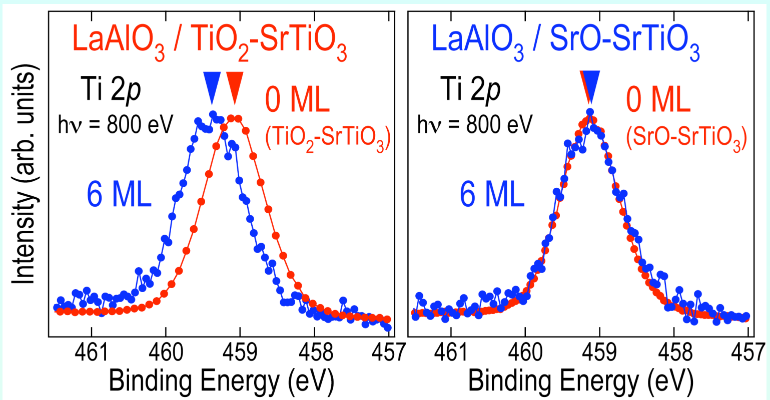
$SrTiO_3$/ $La_{0.6}Sr_{0.4}MnO_3$: No charge transfer

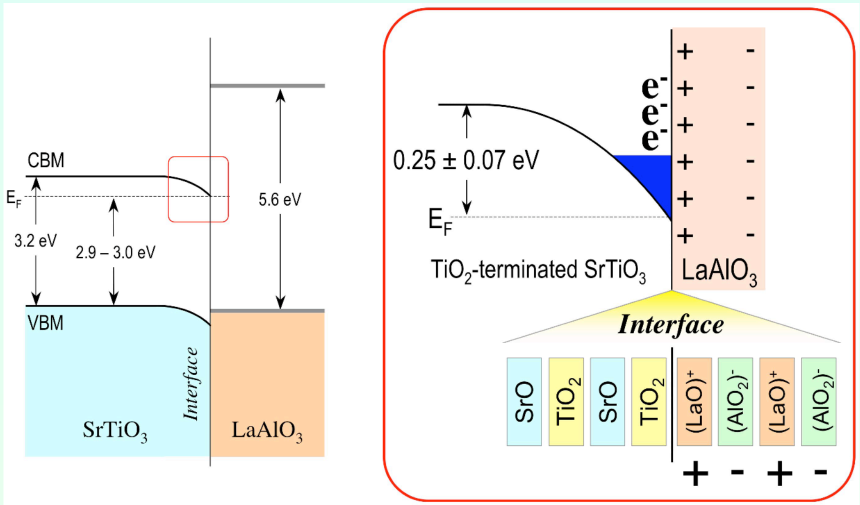
H. Kumigashira *et al.*, *Appl. Phys. Lett.* **84**, 5353 (2004).



Charge redistribution at the interface is dominated by the difference of 3*d* energy levels among transition metals.

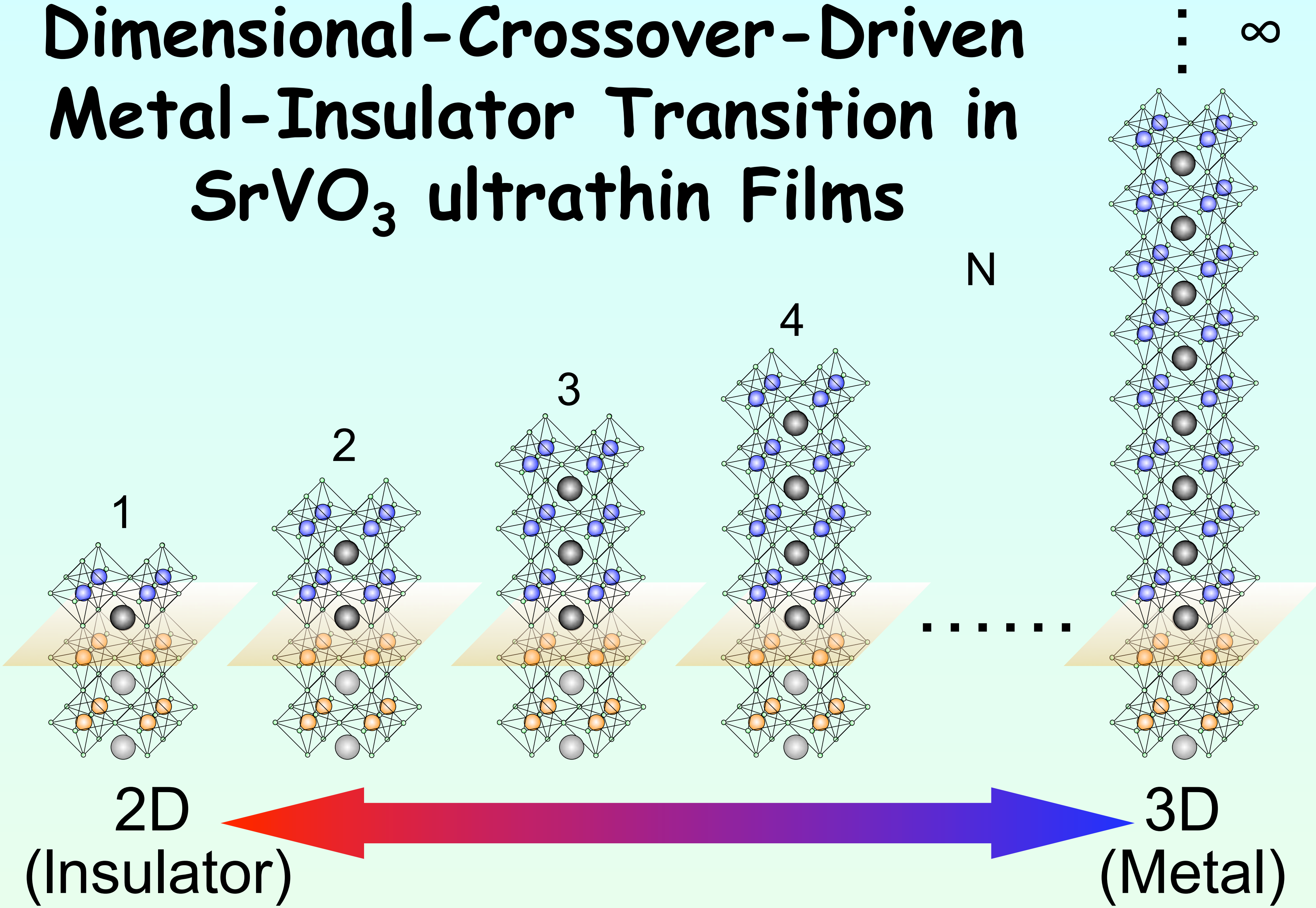
Origin of metallic conductivity at the $LaAlO_3/SrTiO_3$ interface





K. Yoshimatsu, H.K. *et al.*, *Phys. Rev. Lett.* **101**, 026802 (08); *ibid* **102**, 199704 (2009).

Dimensional-Crossover-Driven Metal-Insulator Transition in $SrVO_3$ ultrathin Films



K. Yoshimatsu, H.K., *et al*., Phys. Rev. Lett. **104**, 147601 ('10).

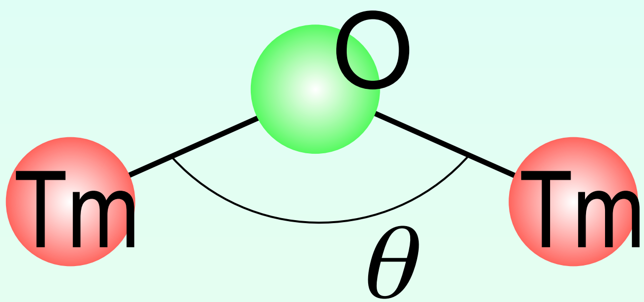
Metal Insulator Transition

Mott-Hubbard theory

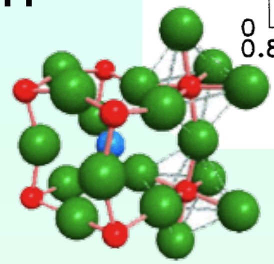
$U >> W$ Insulator

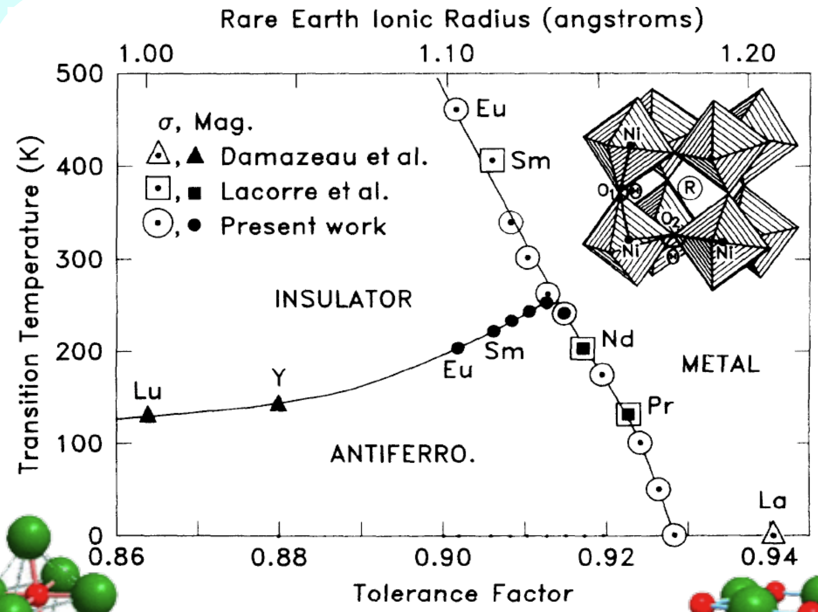
$U << W$ Metal

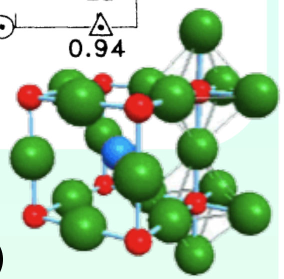
U : on-site Coulomb repulsion
W: one-electron band width



$W \propto \cos^2\theta$







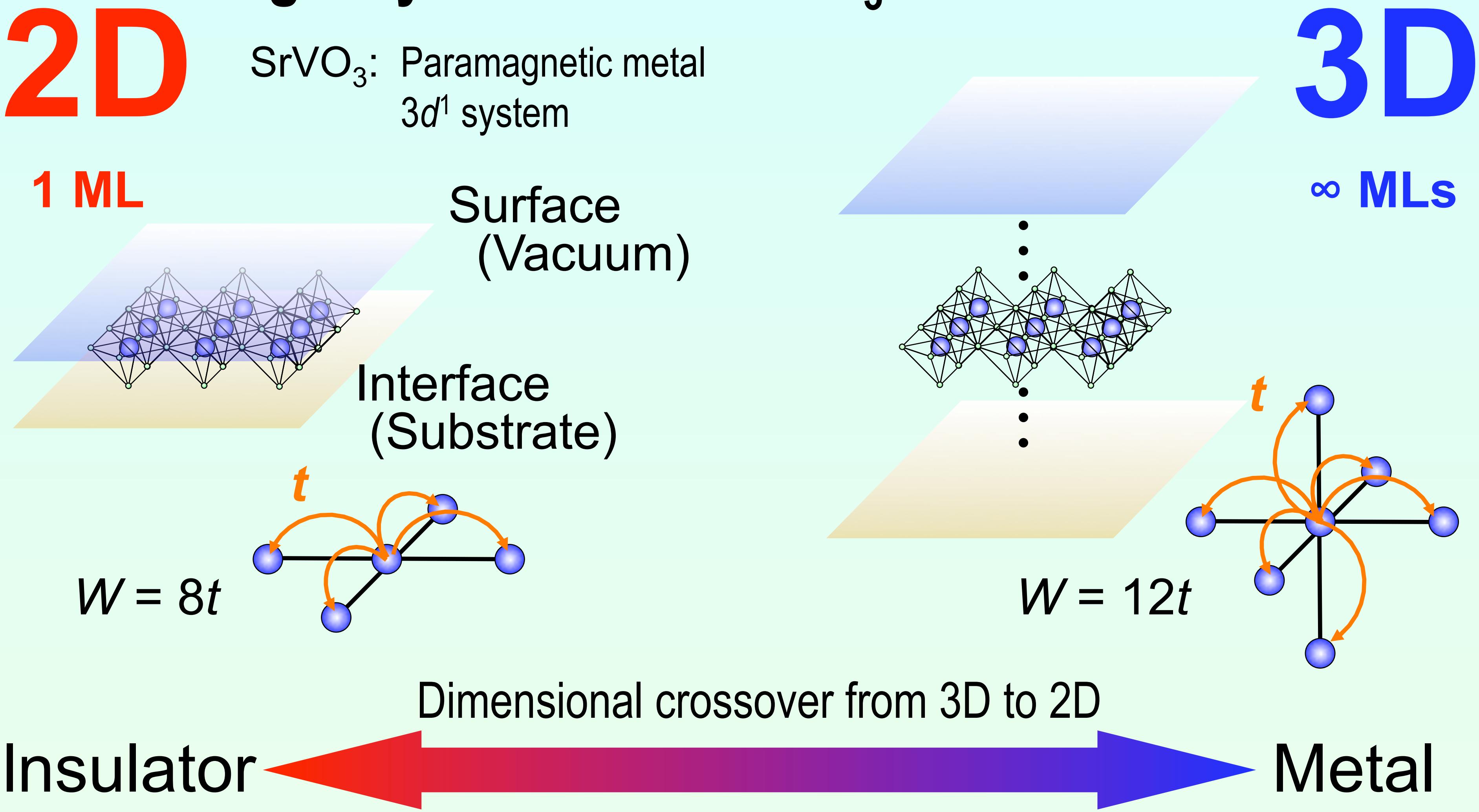
J.B. Torrance *et al*.,
Phys. Rev. B **45**, 8209 ('92)

For bulk materials, MIT has been intensively studied by chemical substitution of constituent ions with ones having a smaller ion radius. However, such chemical substitution always induce randomness in a solid.

Our Approach: Dimensional crossover occurring in an artificial structure

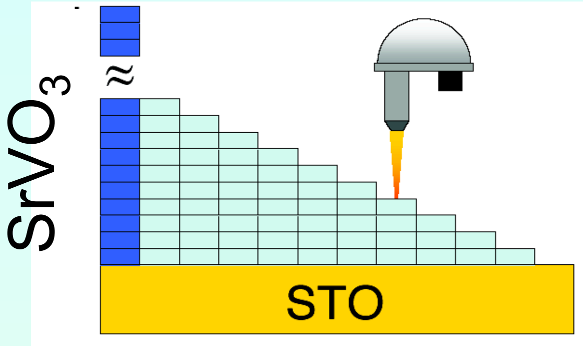
Digitally-controlled $SrVO_3$ ultrathin films

$SrVO_3$: Paramagnetic metal
$3d^1$ system

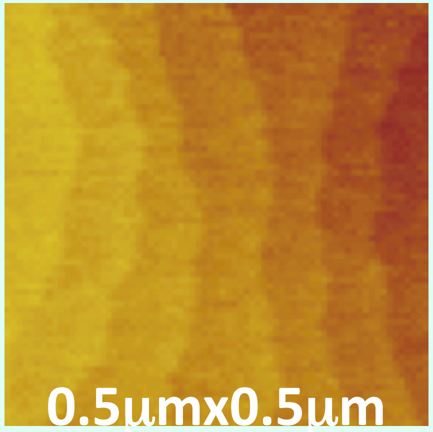


Atomically-flat Surface and Abrupt Interface

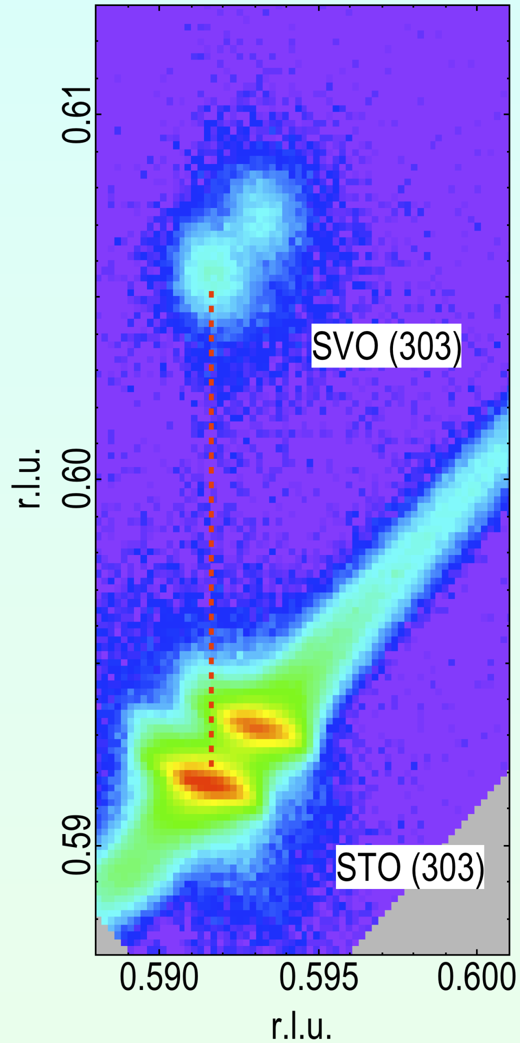
Preconditions to thickness dependent experiments



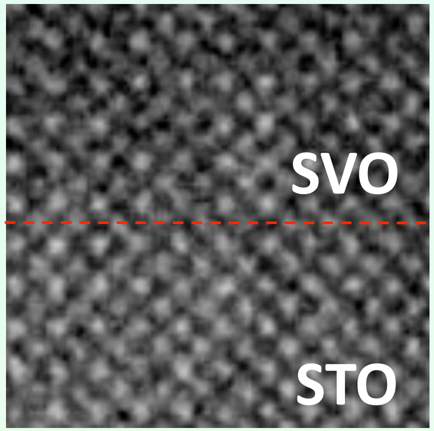
AFM image



4cXRD RSM around (303)

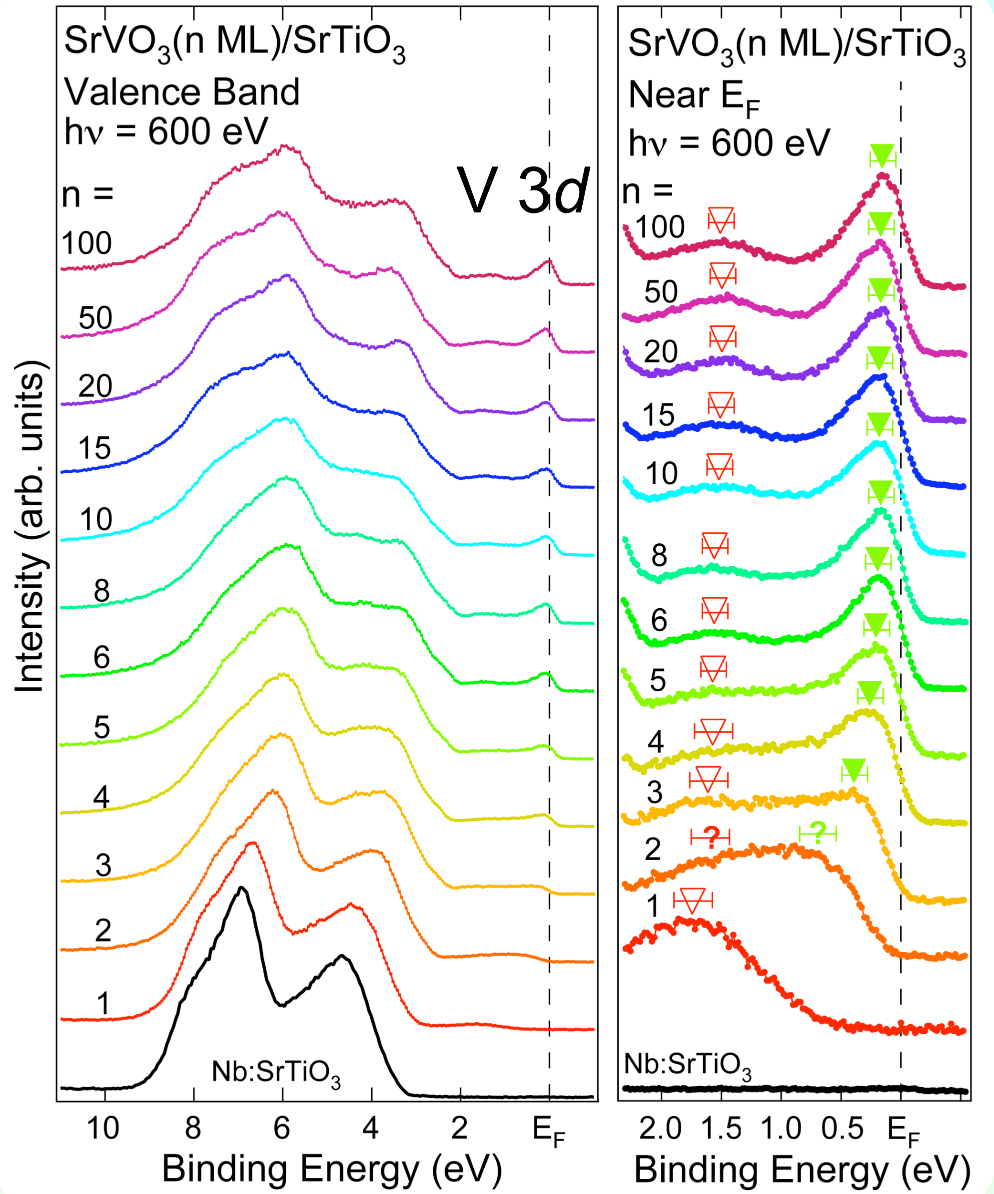


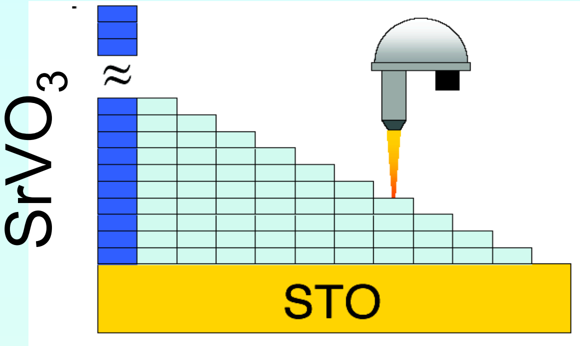
TEM image



- ✓ **Atomically flat surface (AFM image)**
- ✓ **Chemically abrupt interface (TEM image)**
- ✓ **Coherent growth of thin film (Reciprocal space mapping)**

In situ PES Spectra of $SrVO_3$ thin Films





Spectra remain unchanged down to 6–8 ML

Pseudogap formation at E_F

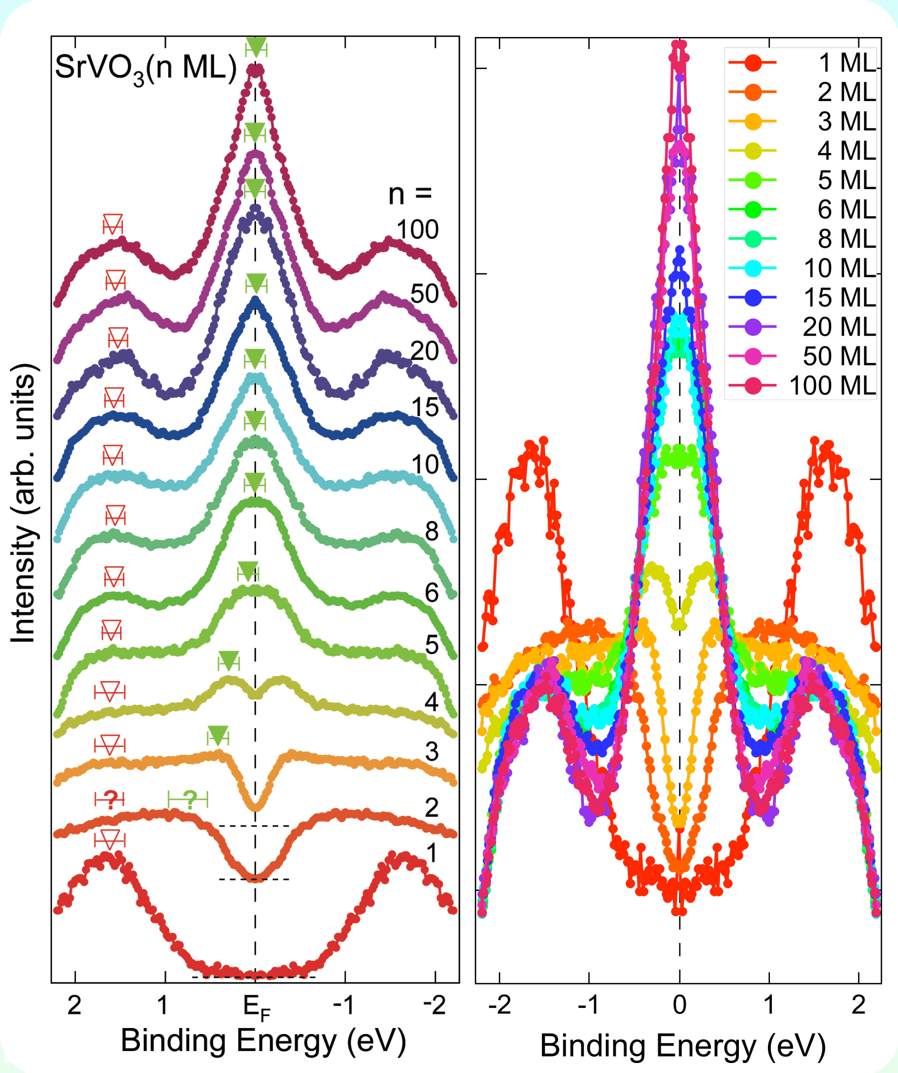
Disppearance of Fermi edge

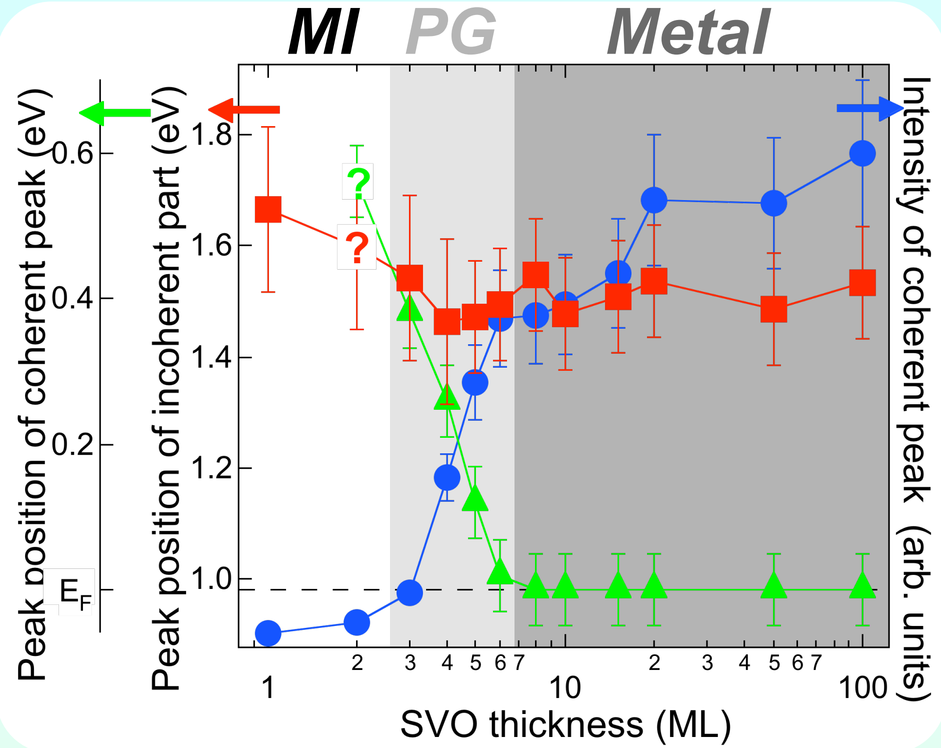
Gap at E_F

MIT@2-3 ML

Metal-insulator transition occurs in the SVO thickness of 2-3 ML.

Dimensional-Crossover-Driven MIT in $SrVO_3$ Films



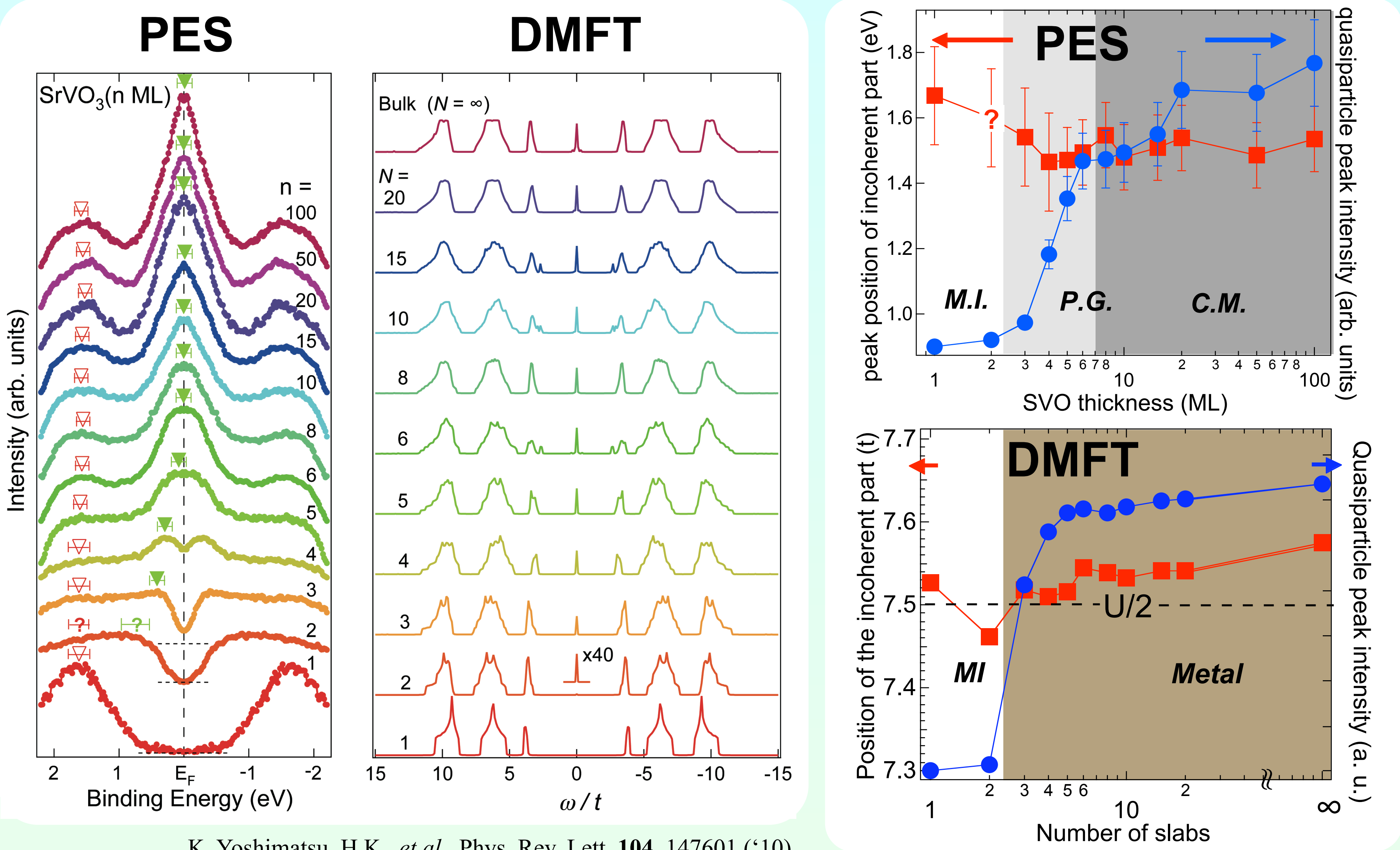


Quasiparticle peak intensity steeply increasing with increasing film thickness (*W* increasing).

Peak position of the incoherent peak remains unchanged (*U* is constant).

Dimensional-Crossover-Driven (from 3D to 2D) MIT in $SrVO_3$ Ultrathin Films

Comparison between PES and Layer DMFT Cal.

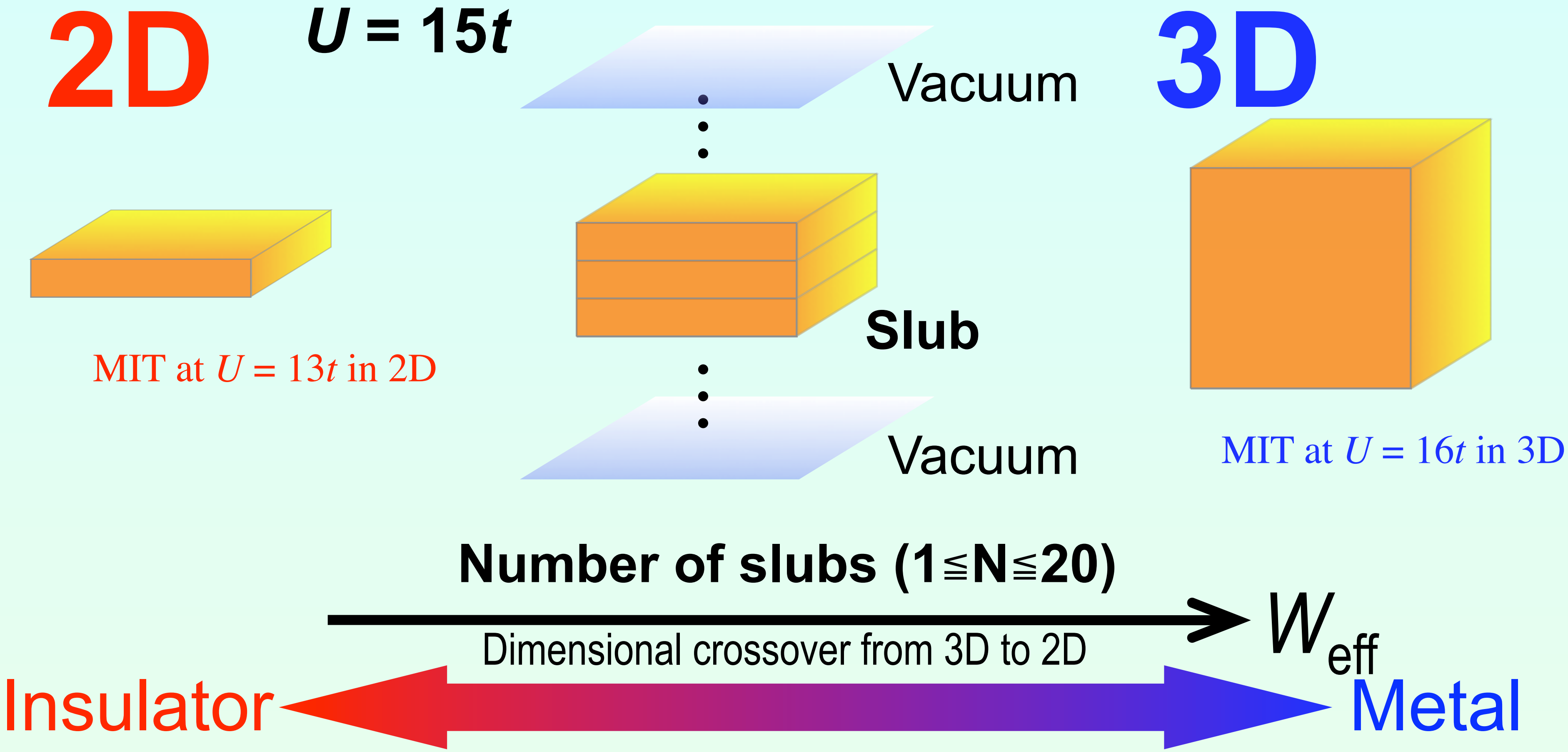


K. Yoshimatsu, H.K., *et al*., Phys. Rev. Lett. **104**, 147601 ('10).

Spectral behavior is well reproduced by layer DMFT calculation.

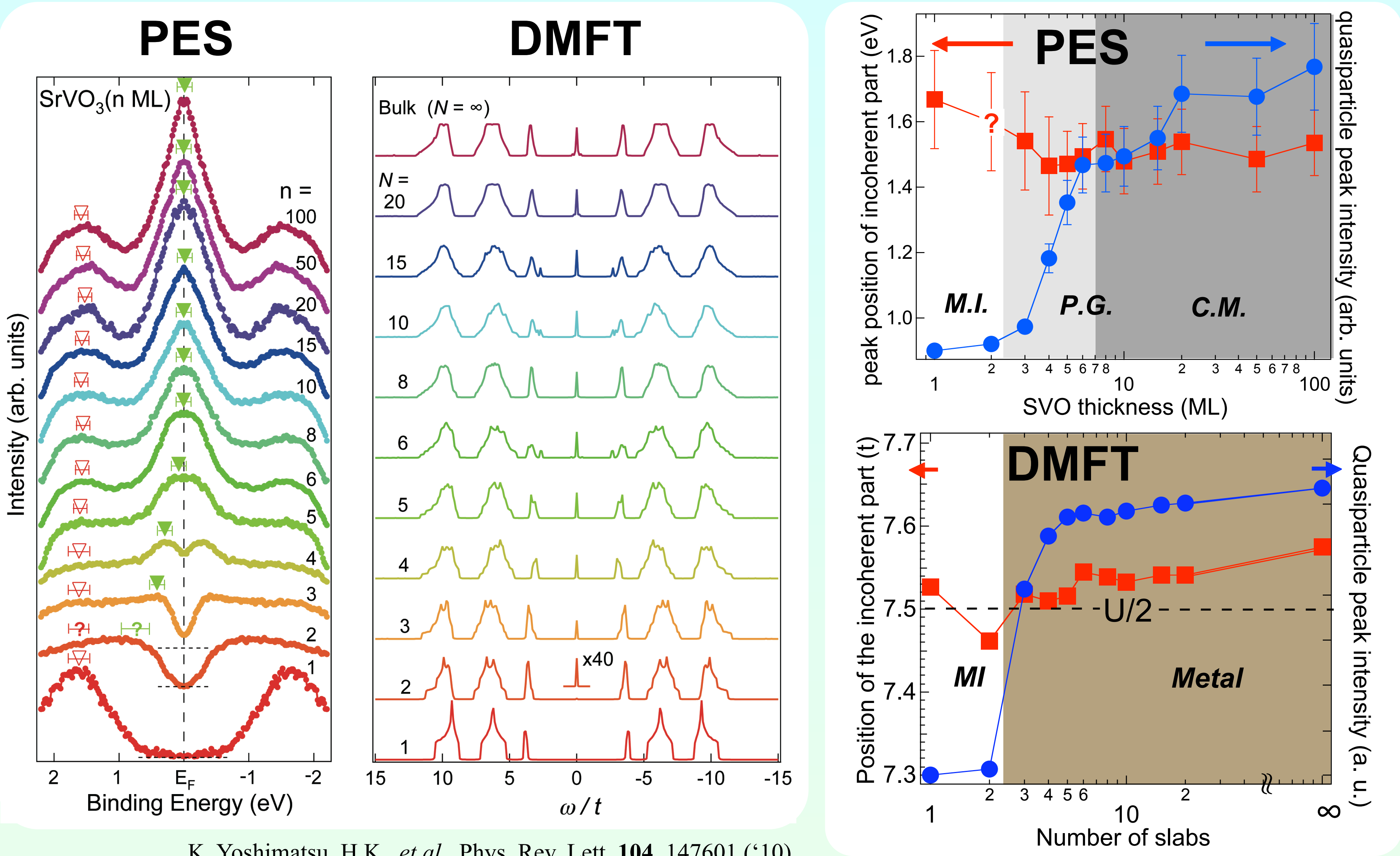
Layer DMFT Calculations for Simulating the Dimensional-Crossover-Driven MIT

Multilayered single-band Hubbard model



The system interpolates the two limits by changing the slab number corresponding to the change in the effective bandwidth (W_{eff}).

Comparison between PES and Layer DMFT Cal.

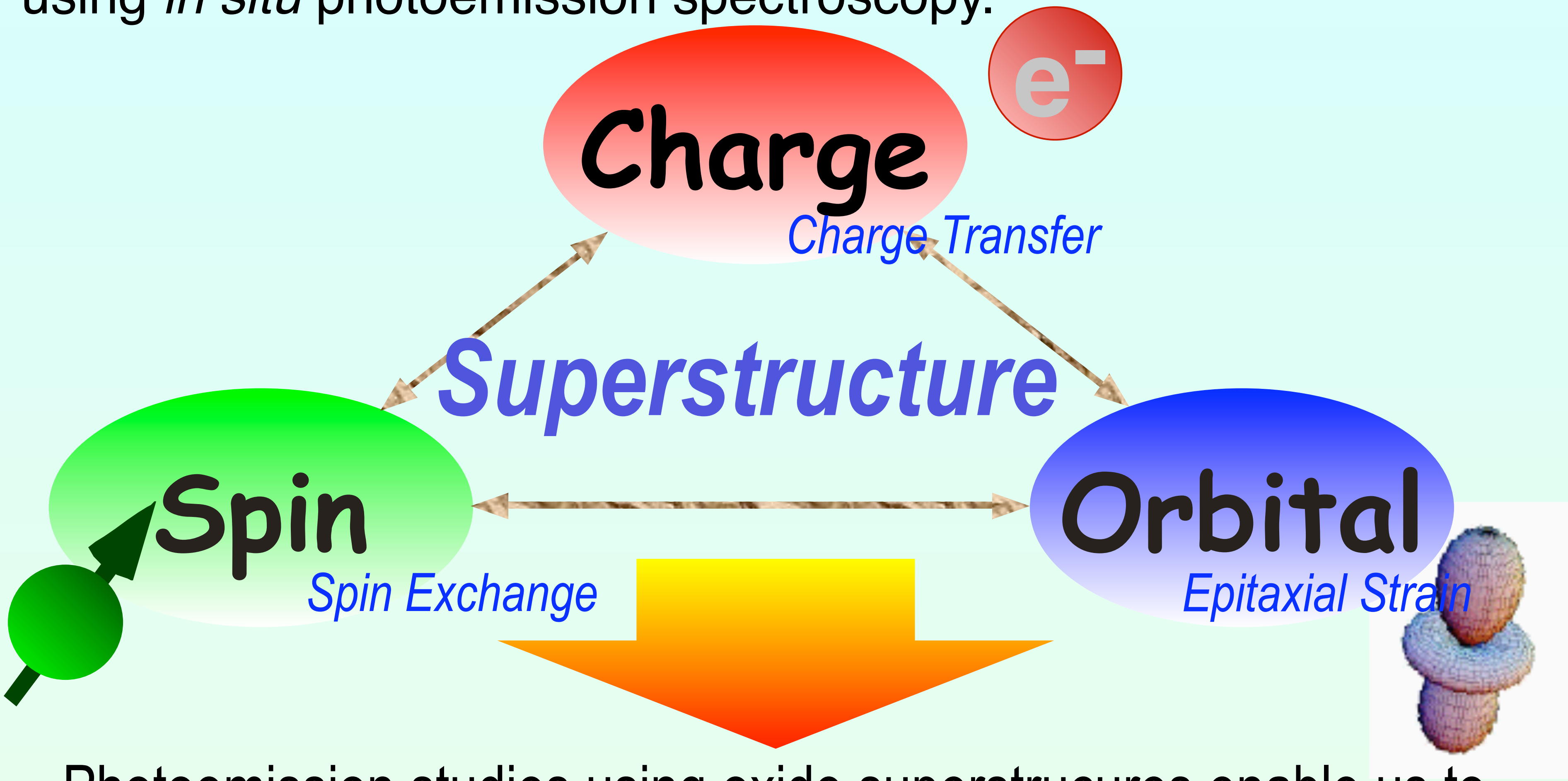


K. Yoshimatsu, H.K., *et al.*, Phys. Rev. Lett. **104**, 147601 ('10).

Dimensional-crossover-driven MIT in an $SrVO_3$ ultrathin films

Concluding Remarks

We studied the electronic states of oxide superstructures by using *in situ* photoemission spectroscopy.

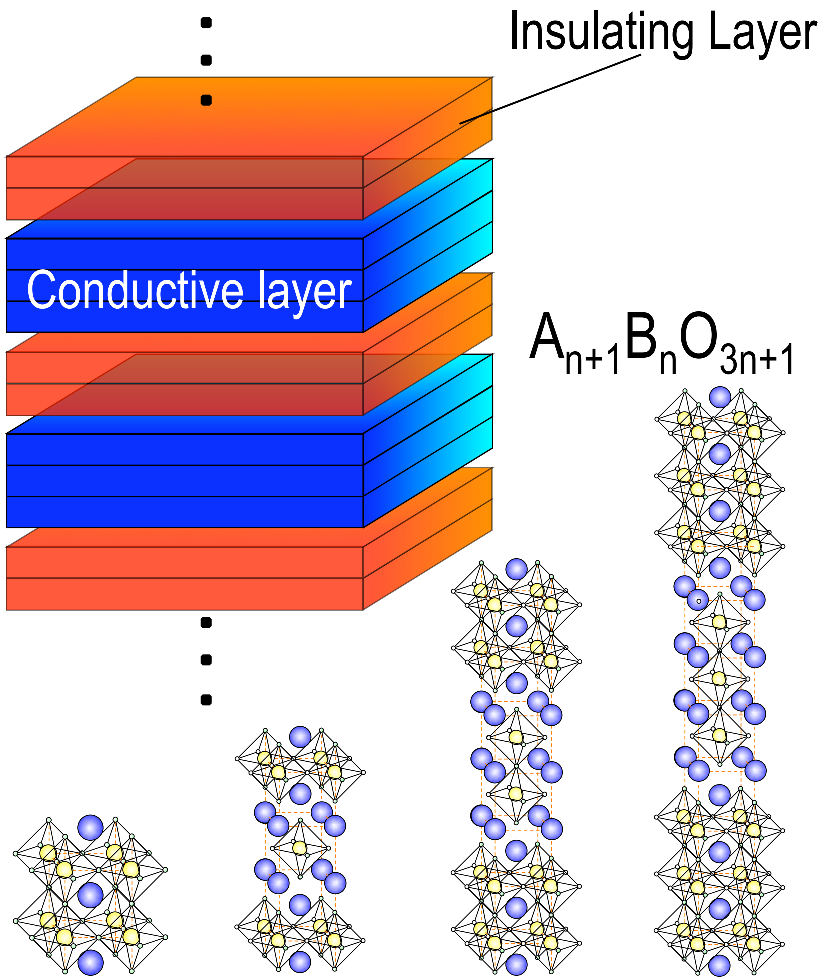


Photoemission studies using oxide superstrucures enable us to pave a new way for the better understanding of the physics of strongly correlated oxides.

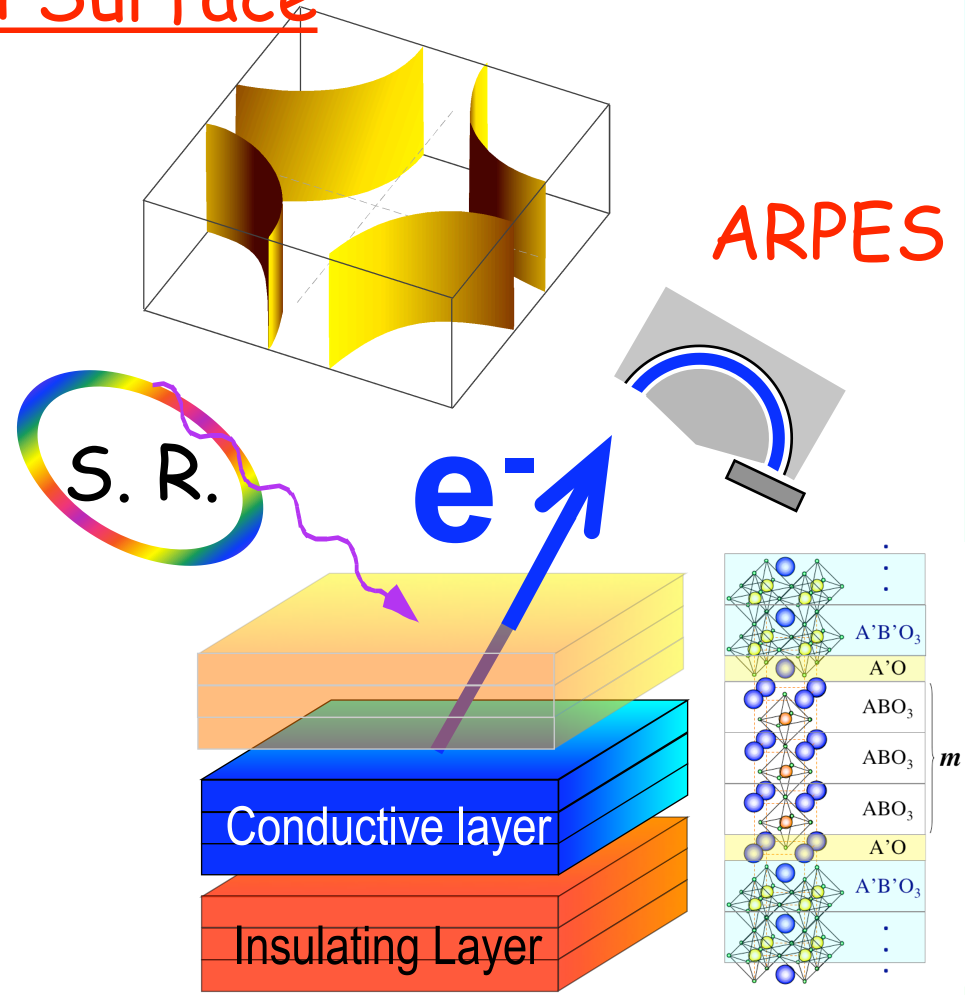
Outlooks

Fermiology of Quantum Well States in Artificial Structures
Based on Strongly Correlated Oxides

Layered Oxides



2D Fermi Surface



Oxide Quantum Well