Probing Electronic Structure in Novel Engineered Quantum States of Matter

In situ ARPES Studies of Epitaxial Novel Oxides Thin Films

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Cornell University

– The design and set-up of OMBE/ARPES systems at Cornell and most work on $SrRuO_3$ epitaxial thin films

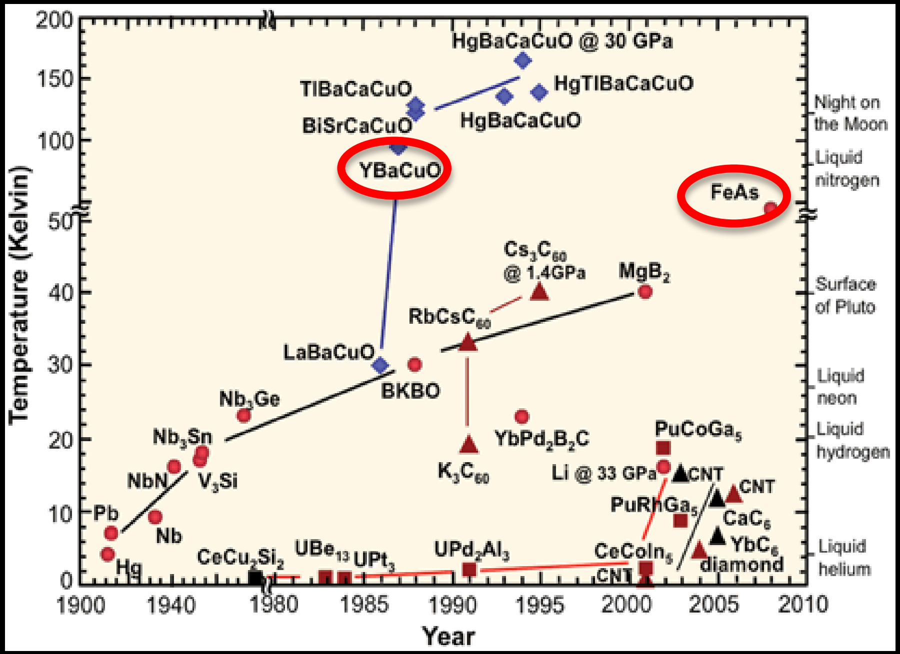
❖ Rui Peng, Haichao Xu, Miao Xia, Xin Xie, Prof. Binping Xie, and Prof. Donglai Feng
Fudan University

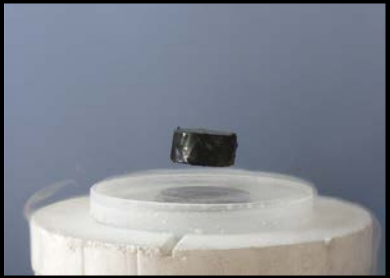
– The work on the dead-layer of LSMO/STO interface

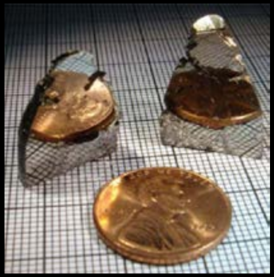
The Trend: Discovering and Engineering Novel Quantum Matters

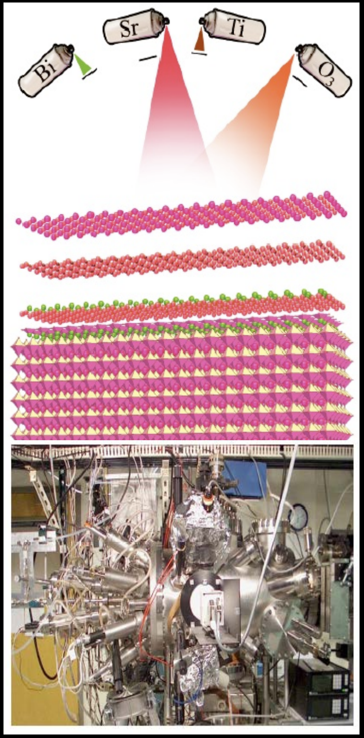
"At the extreme forefront of research in supercon-ductivity is the empirical search for new materials"

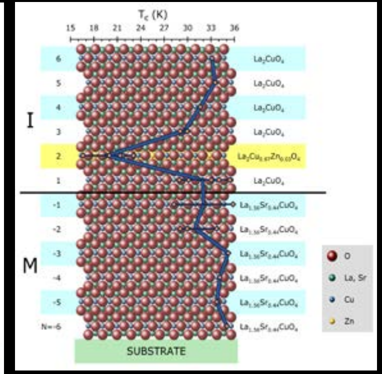
Bednorz and Mueller ('86)

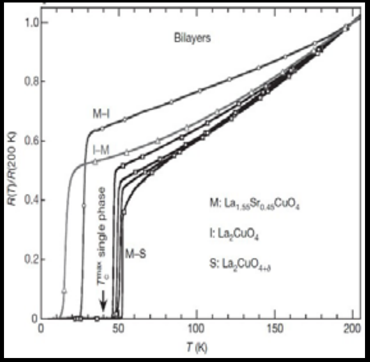








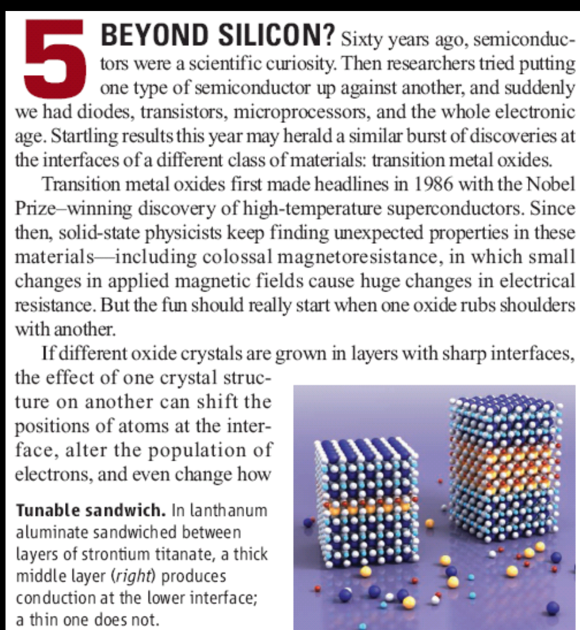




Atomic-scale layer-by-layer growth

G. Logvenov et al., Science 326, 699 (2009)
A. Gozar et al., Nature 455, 782 (2008)

Rational Materials Design: Desired Correlated-electron properties



5 **BEYOND SILICON?** Sixty years ago, semiconductors were a scientific curiosity. Then researchers tried putting one type of semiconductor up against another, and suddenly we had diodes, transistors, microprocessors, and the whole electronic age. Startling results this year may herald a similar burst of discoveries at the interfaces of a different class of materials: transition metal oxides.

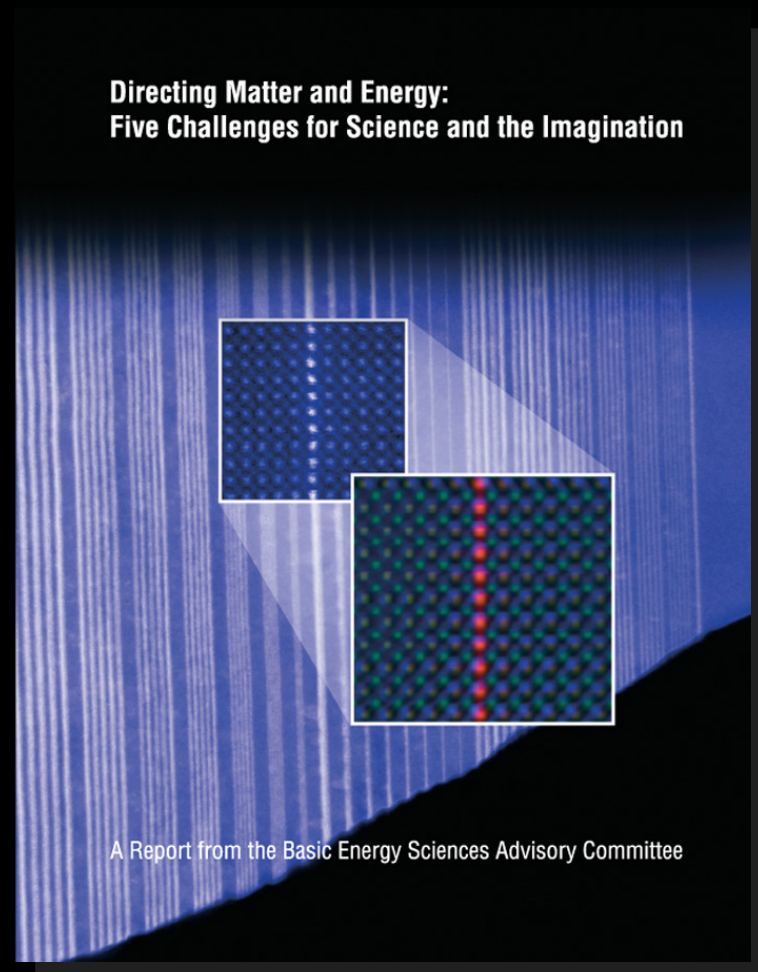
Transition metal oxides first made headlines in 1986 with the Nobel Prize–winning discovery of high-temperature superconductors. Since then, solid-state physicists keep finding unexpected properties in these materials—including colossal magnetoresistance, in which small changes in applied magnetic fields cause huge changes in electrical resistance. But the fun should really start when one oxide rubs shoulders with another.

If different oxide crystals are grown in layers with sharp interfaces, the effect of one crystal structure on another can shift the positions of atoms at the interface, alter the population of electrons, and even change how

Tunable sandwich. In lanthanum aluminate sandwiched between layers of strontium titanate, a thick middle layer (*right*) produces conduction at the lower interface; a thin one does not.

The Cover of Science, Vol . 318 (2007)

Rational Materials Design: How can we control the properties of matter emerging from complex correlations **by design**?



Ohtomo, Muller, Grazul, Hwang, Nature, 419;

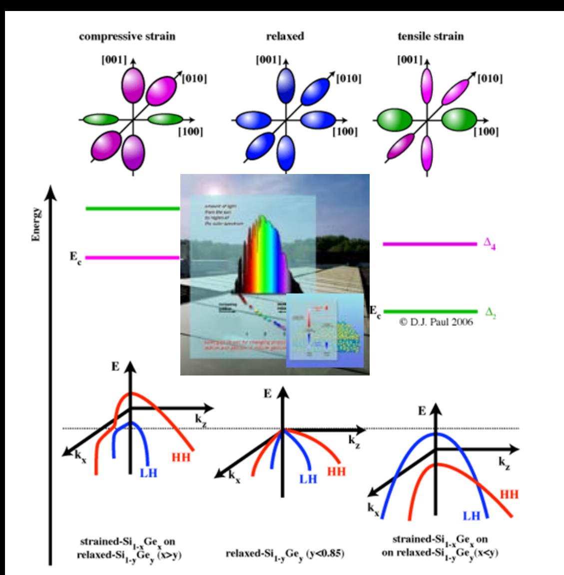
DOE BESAC Report (2008)

Great Success of Band-gap engineering in conventional semiconductors

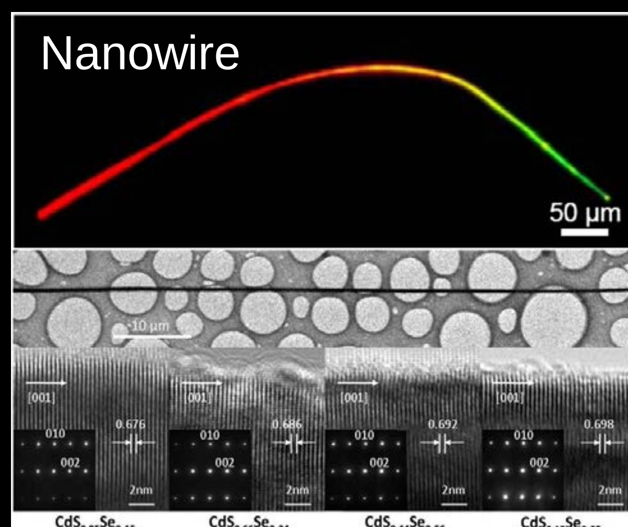
Calculation of physical properties

Construction of desired materials

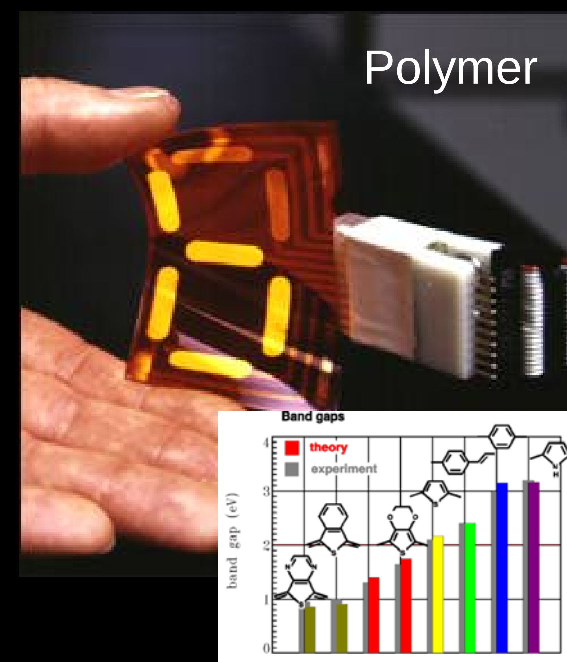
Control of properties through epitaxial strain & chemical doping etc.



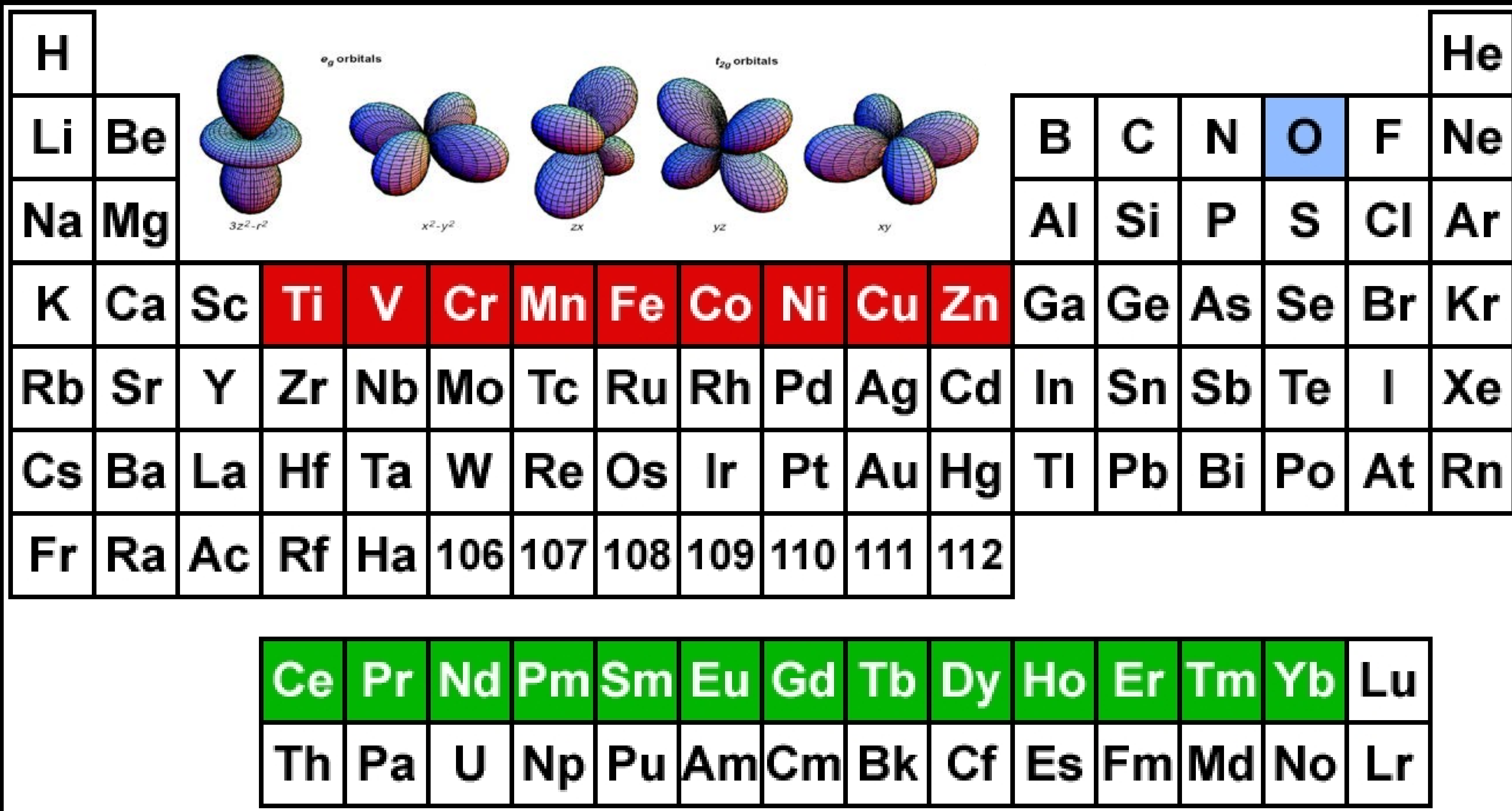
Strain band gap engineering



Quantum confinement effects



Correlated Transition Metal Oxides

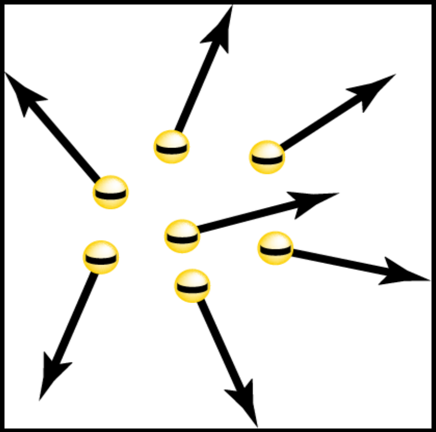


$$\mathcal{H} = -\sum_{j}^{N_e} \frac{\hbar^2}{2m} \nabla_j^2 - \sum_{\alpha}^{N_i} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 - \sum_{j}^{N_e}\sum_{\alpha}^{N_i} \frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_{j \ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} + \sum_{\alpha \ll \beta}^{N_j} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

e^- KE | Nuclei KE | e^- / Nuclei Int. | e^- / e^- Int. | Nuclei / Nuclei Int

Innovation in the design of correlated quantum matters is needed!

Non-Interacting



We understand well:

- Systems of non-interacting or weakly interacting particles;
- Interaction energy is smaller than the kinetic energy, perturbation theory works well.
- DFT do nice predictions.

Correlated

Calculation of physical properties

Construction of desired materials

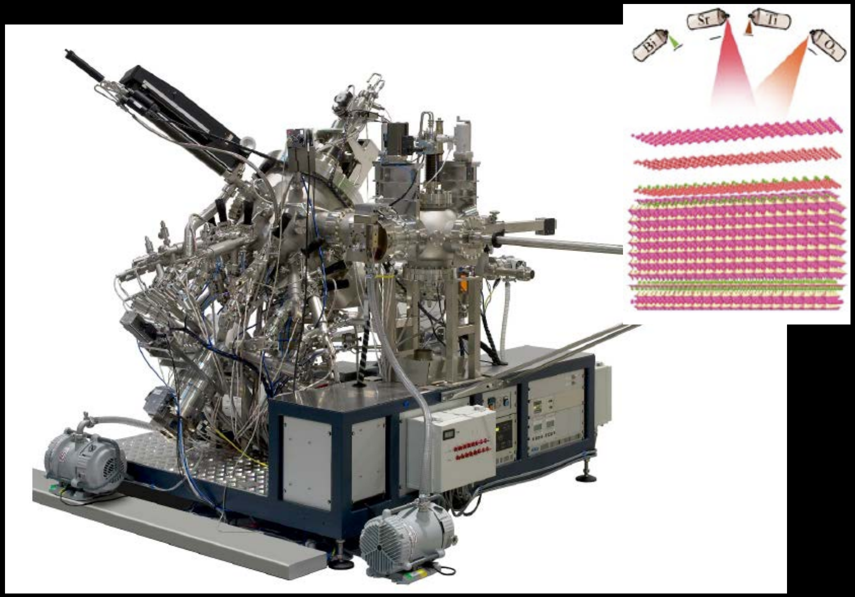
Characterization of microscopic interactions by high-resolution experiments

Control of properties through epitaxial strain & chemical doping

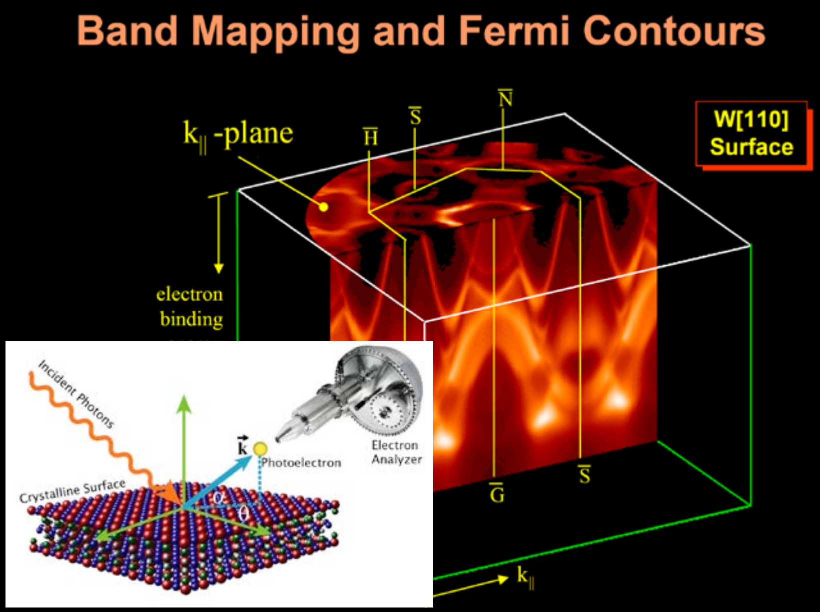
Courtesy of Prof. Kyle. M Shen

Outline

1. **New tools for investigating novel quantum electronic states**
2. **Correlation in epitaxial Ruthenate Thin Films**
3. **Dead-layer at the $La_{1-x}Sr_xMnO_3/SrTiO_3$ interface**



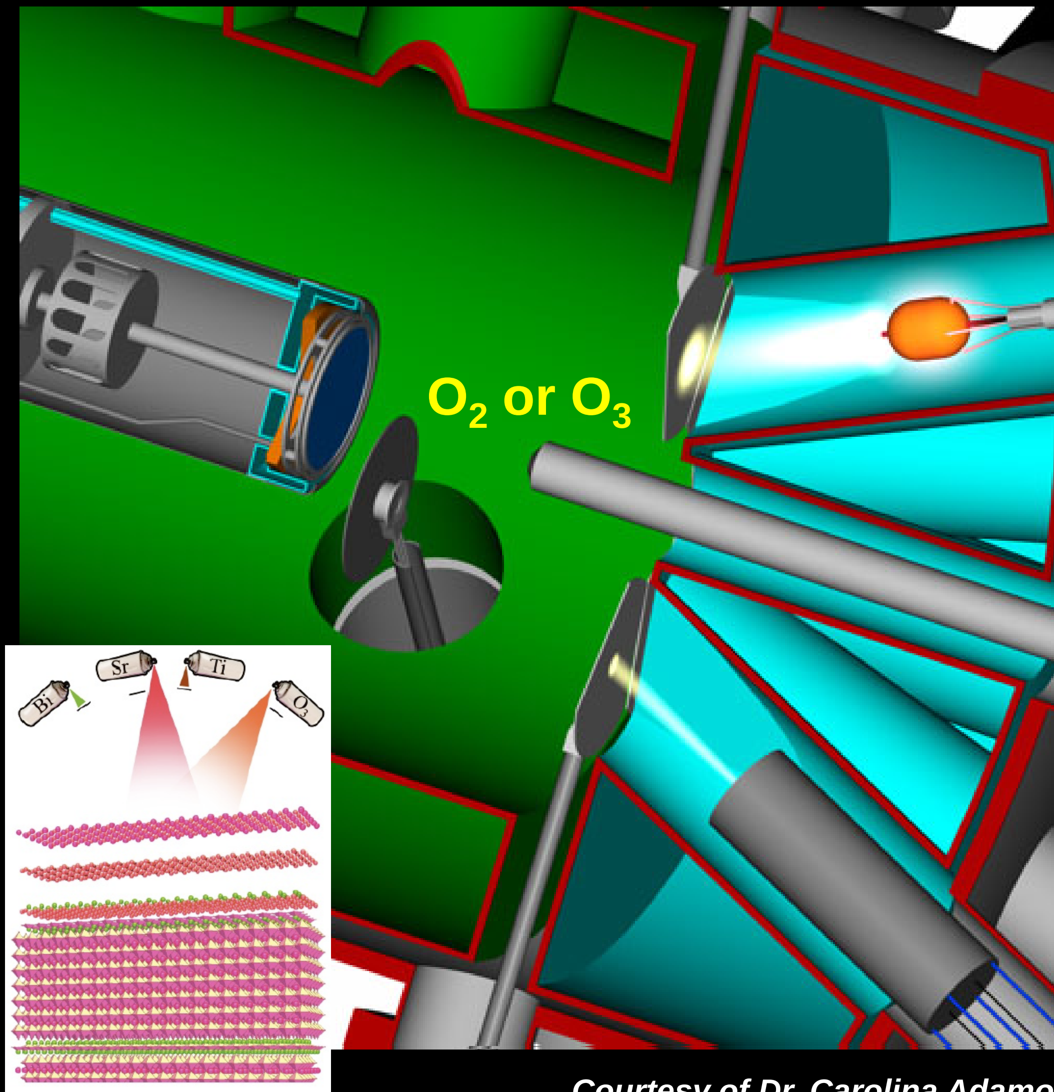
Oxide Molecular Beam Epitaxy



Angle-Resolved Photoemission Spectroscopy

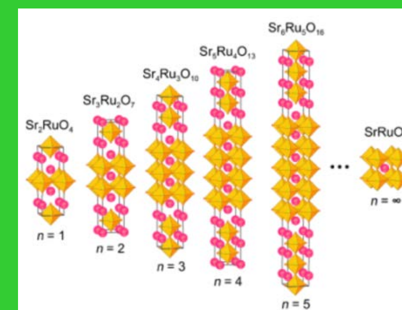
Oxide *Molecular Beam Epitaxy : "Atomic Spray Painting"*

Shuttered growth **utilizes alternating molecular beams so that each element is evaporated separately.**

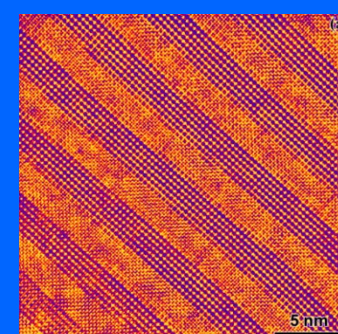


Courtesy of Dr. Carolina Adamo

RHEED oscillation (<1%)

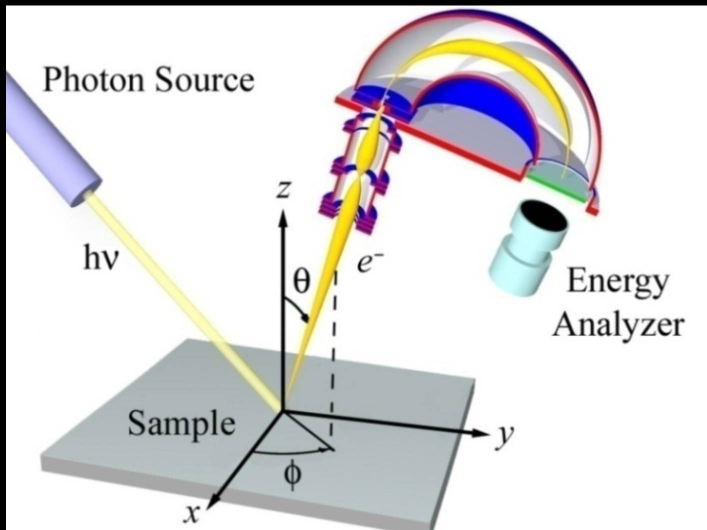


New Phase



Superlattice, Interface

Characterization by Angle-Resolved Photoemission Spectroscopy

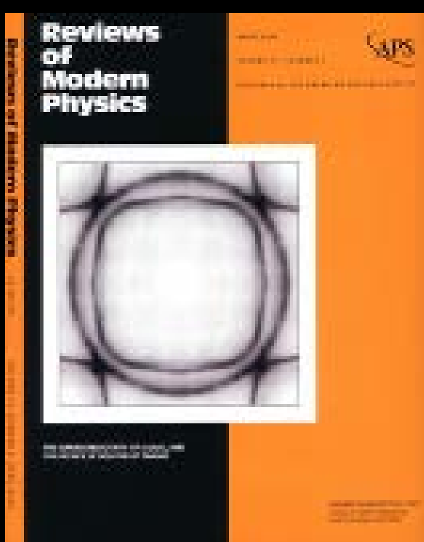


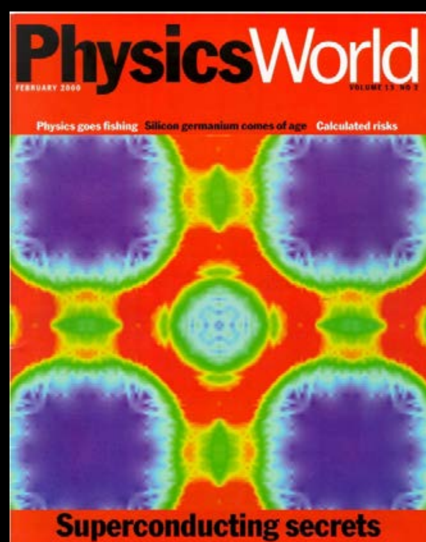
http://en.wikipedia.org/wiki/ARPES

From momentum/energy conservation rules:

$$k_{pe} = -k_{N-1}$$

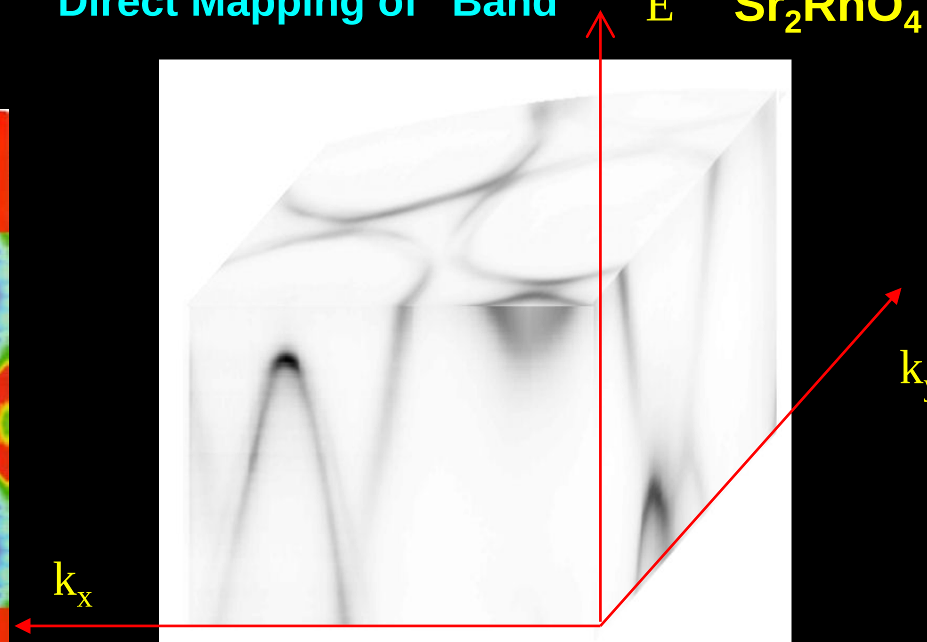
$$h\nu - E_{pe} = E_{N-1} - E_N$$





Direct Mapping of "Band"

Sr_2RhO_4



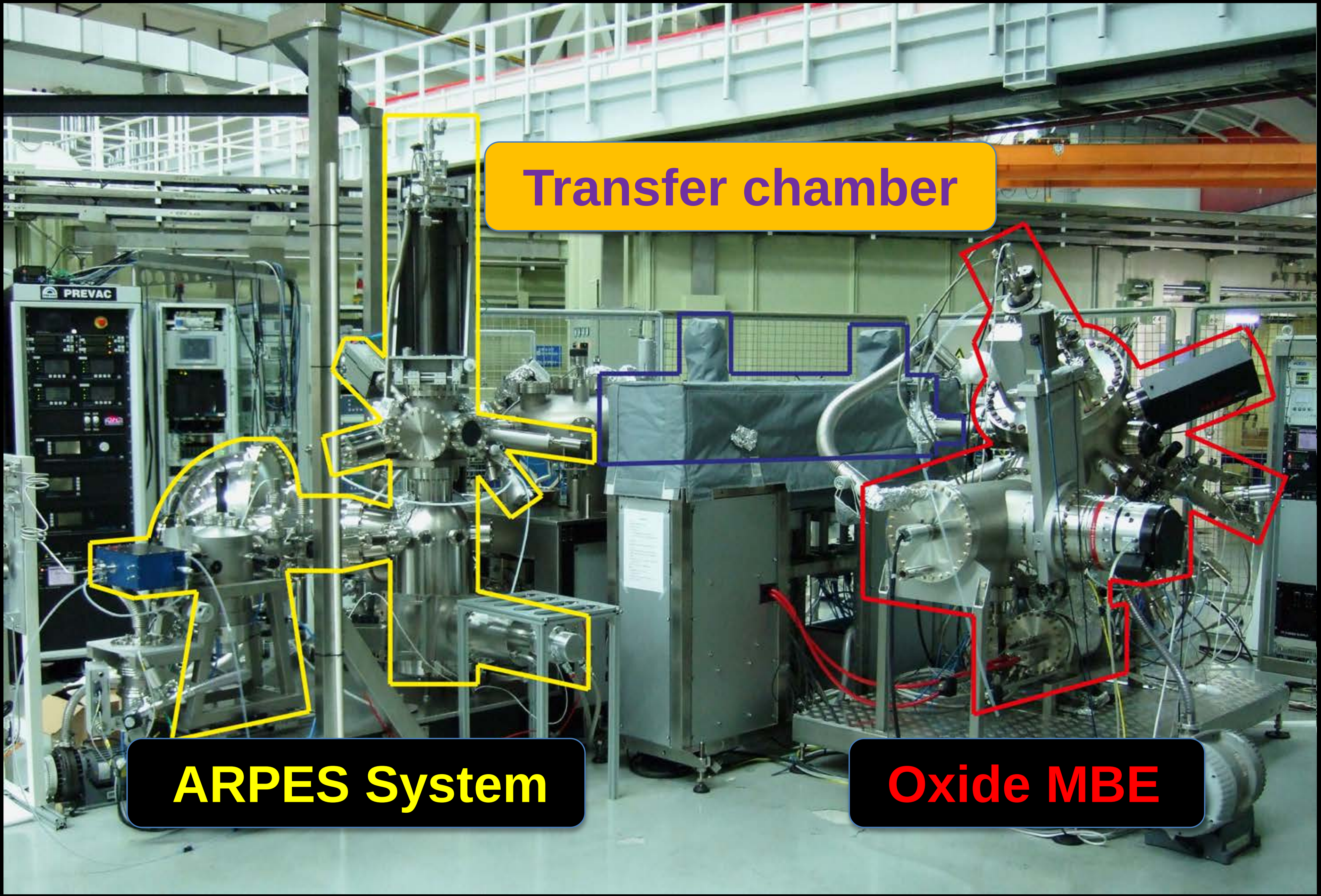
Courtesy of Prof. Donglai Feng

http://arpes.stanford.edu/research_strontium_ruthnates.html

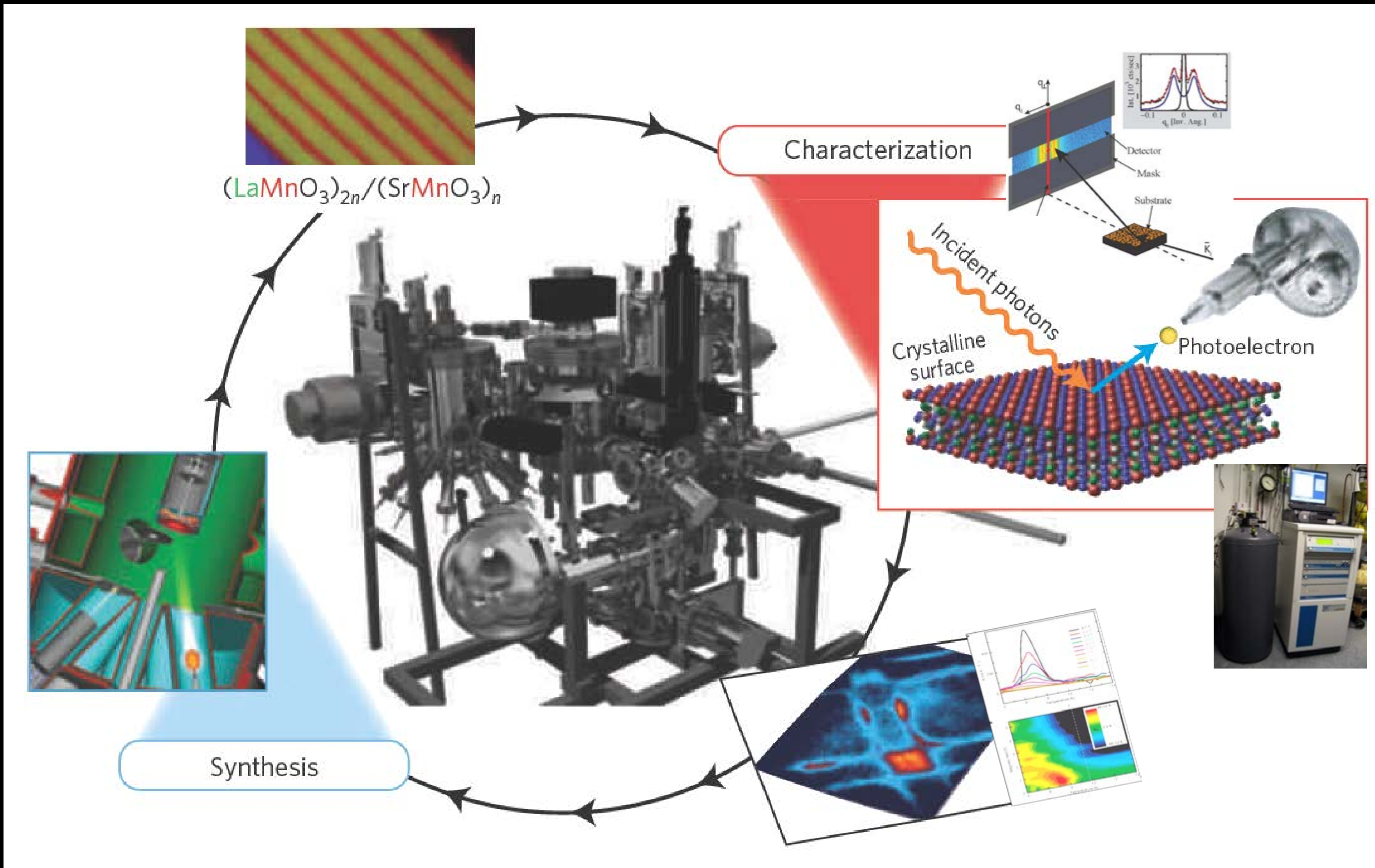
The necessity and possibility of synergistic collaborations

Limitations of ARPES	Advantages of OMBE
Highly surface sensitive (atomically clean surfaces)	Films grown under ultra-high vacuum conditions, not energetic deposition
Mostly restricted to cleavable samples (need well-defined layer-structured crystals)	Epitaxial growth allows for study of "uncleavable" materials
Requires sizable single crystals ~ mm-sized	Allow for growth of "artificial" materials : heterostructures, interfaces, epitaxially strained materials

Integrated Oxide MBE + ARPES at SIMIT



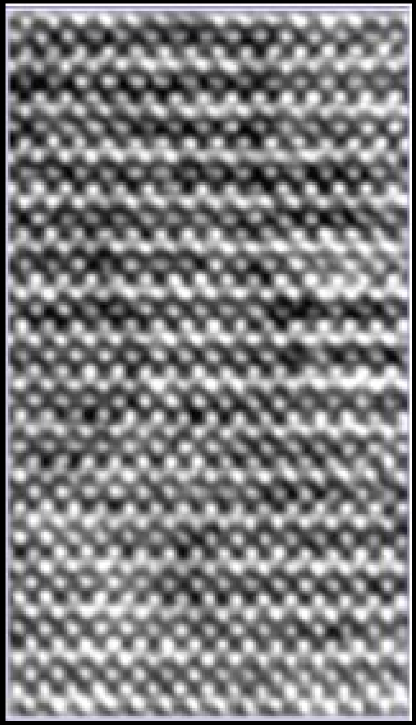
The mode of rational materials design for complex quantum matters

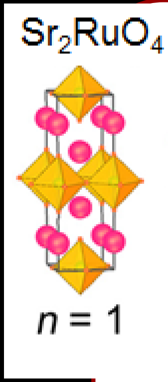


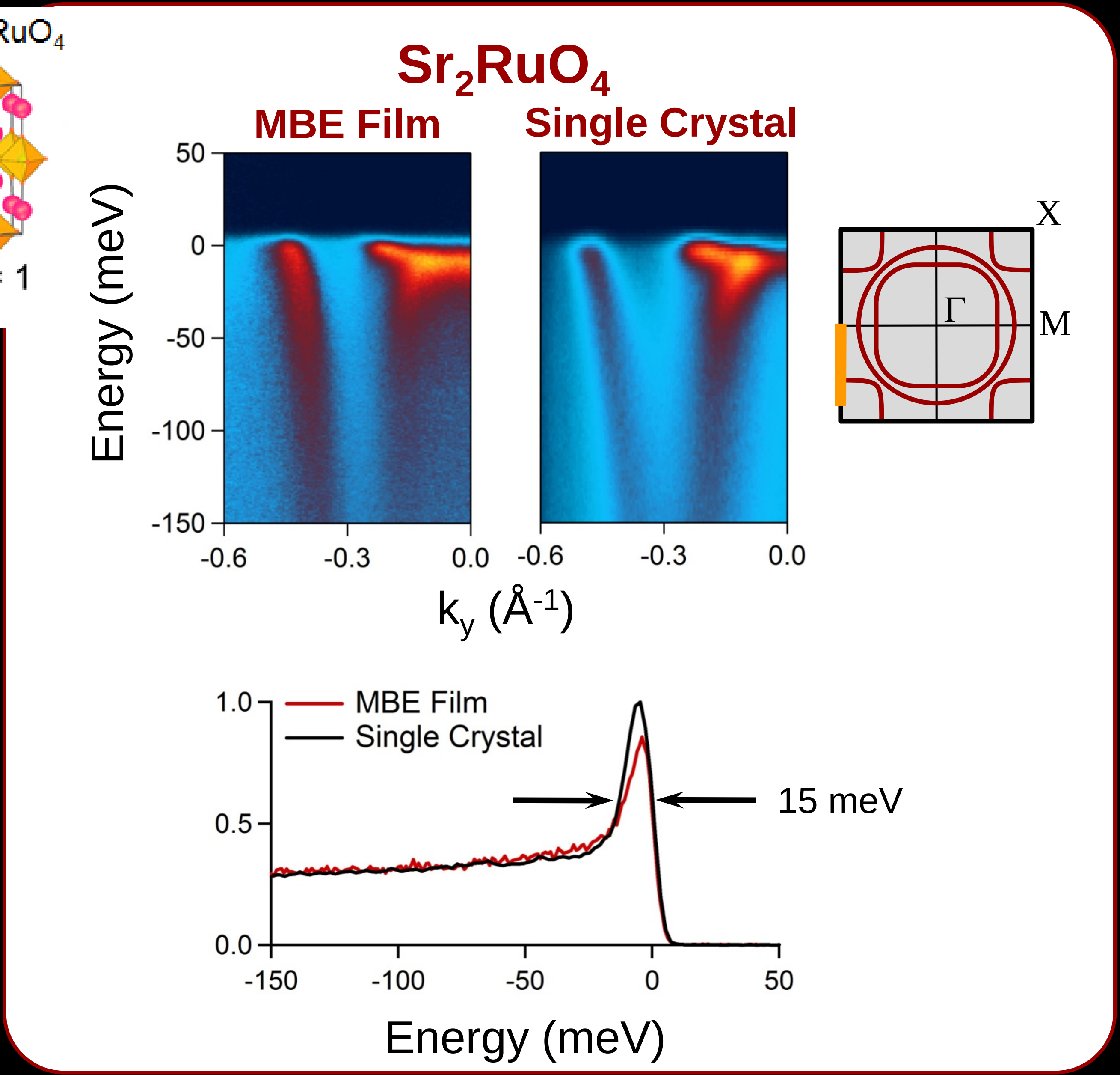
J. M. Rondinelli and S. J. May, Nature materials, 11, 833 (2012)

Preliminary reliability testing of the integrated OMBE/ARPES

High-resolution transmission electron microscopy (HRTEM) image of Sr_2RuO_4 films







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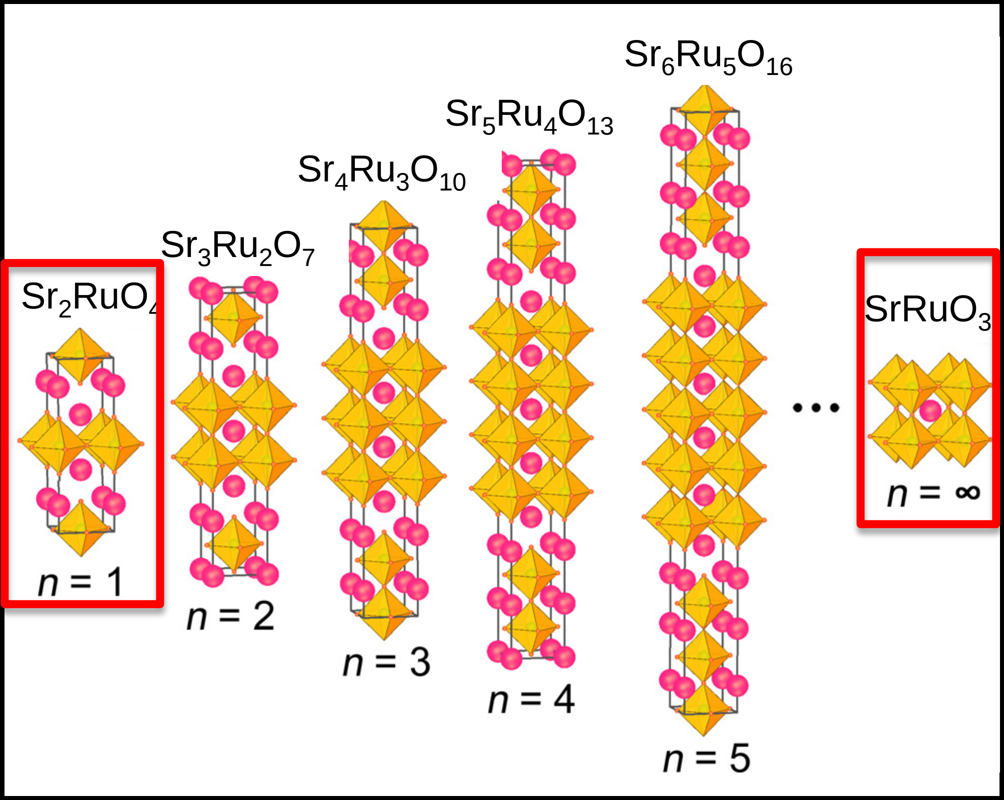
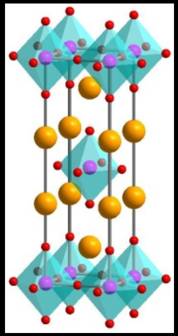


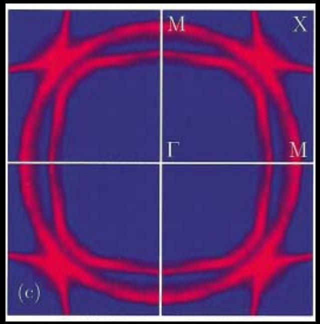
Sr-based Ruthenates $SrO(SrRuO_3)_n$: Rich physics

N=1



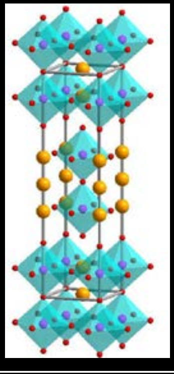
Sr_2RuO_4

Spin triplet super-Conductivity, possible topological SC



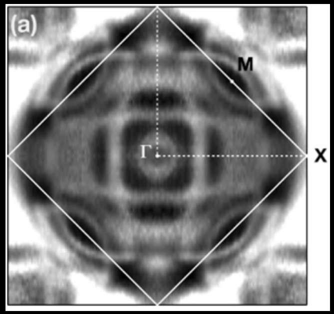
Damascelli et al., PRL (2000)

N=2



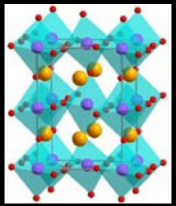
$Sr_3Ru_2O_7$

Electronic nematic phase



Tamai et al., PRL (2008)

N=∞



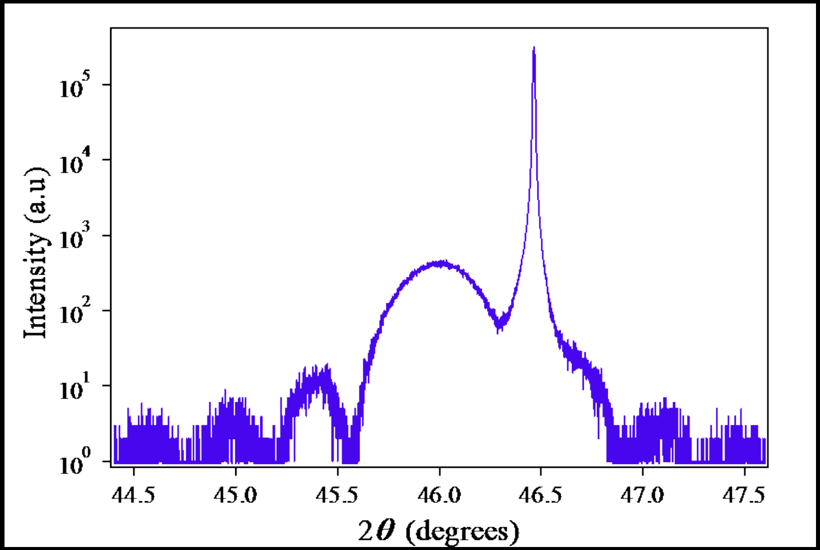
$SrRuO_3$

Significant correlations, Ferromagnetism (origin?)

http://www.phys.psu.edu/~liu/

Characterization of $SrRuO_3$ Epitaxial films

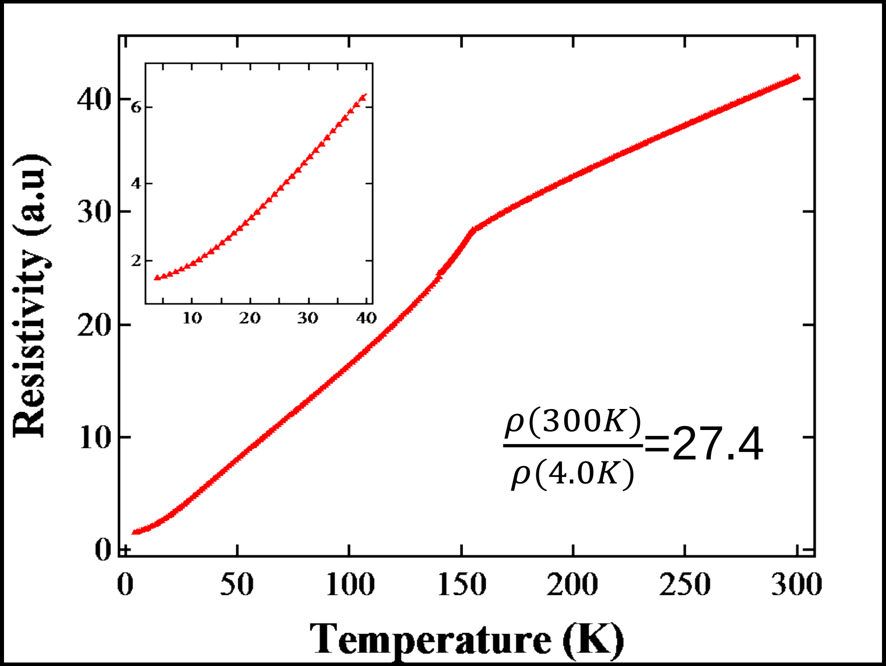
X-ray diffraction



- The fringes indicate good crystalline quality of the films
- Right 2θ value of the (002) peak for stained $SrRuO_3$ films

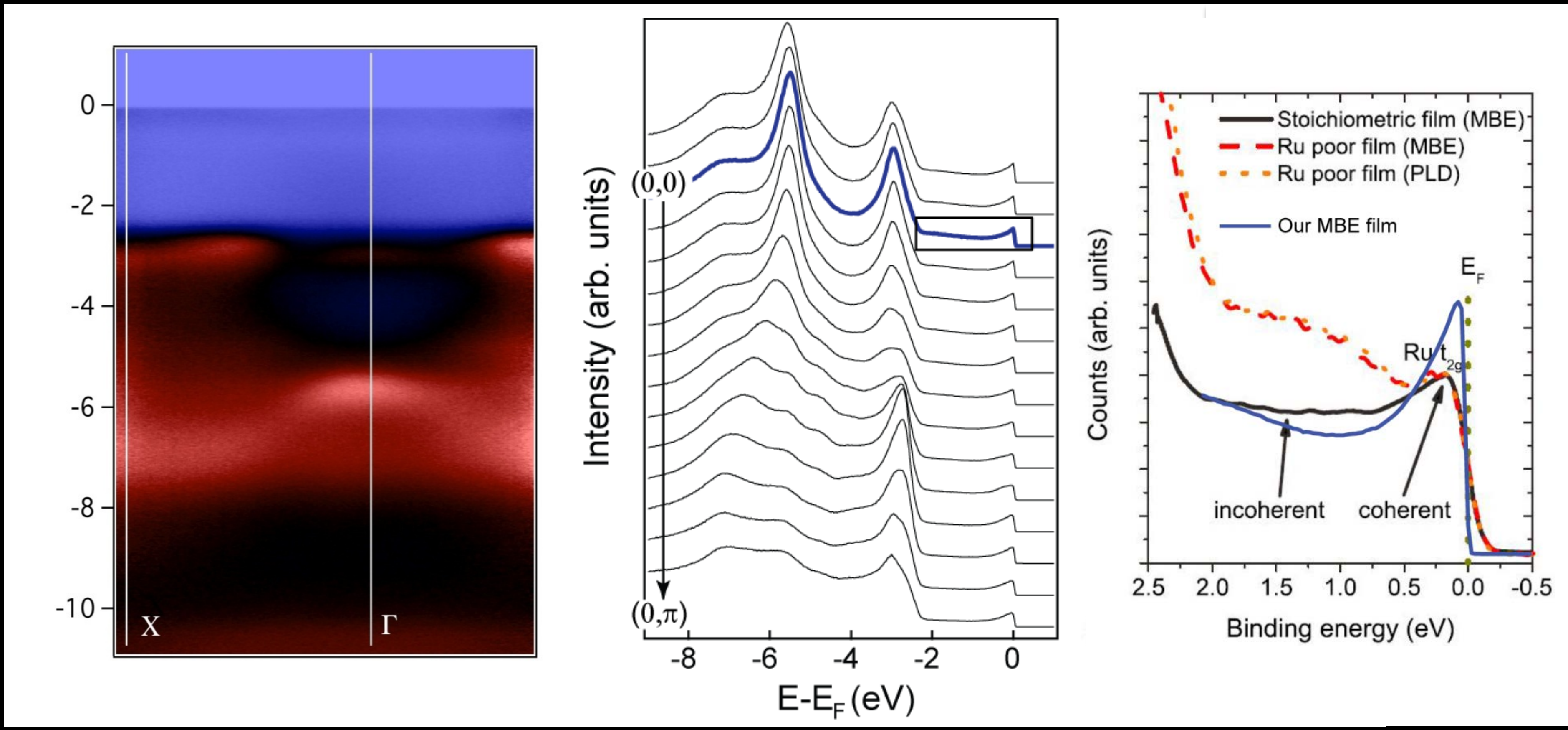
Transport measurements

Residual resistivity ratio RRR ~27.4, the record high quality of $SrRuO_3$ thin film



So far the best $SrRuO_3$ thin films (~20nm) reported

What does the electronic structure look like?

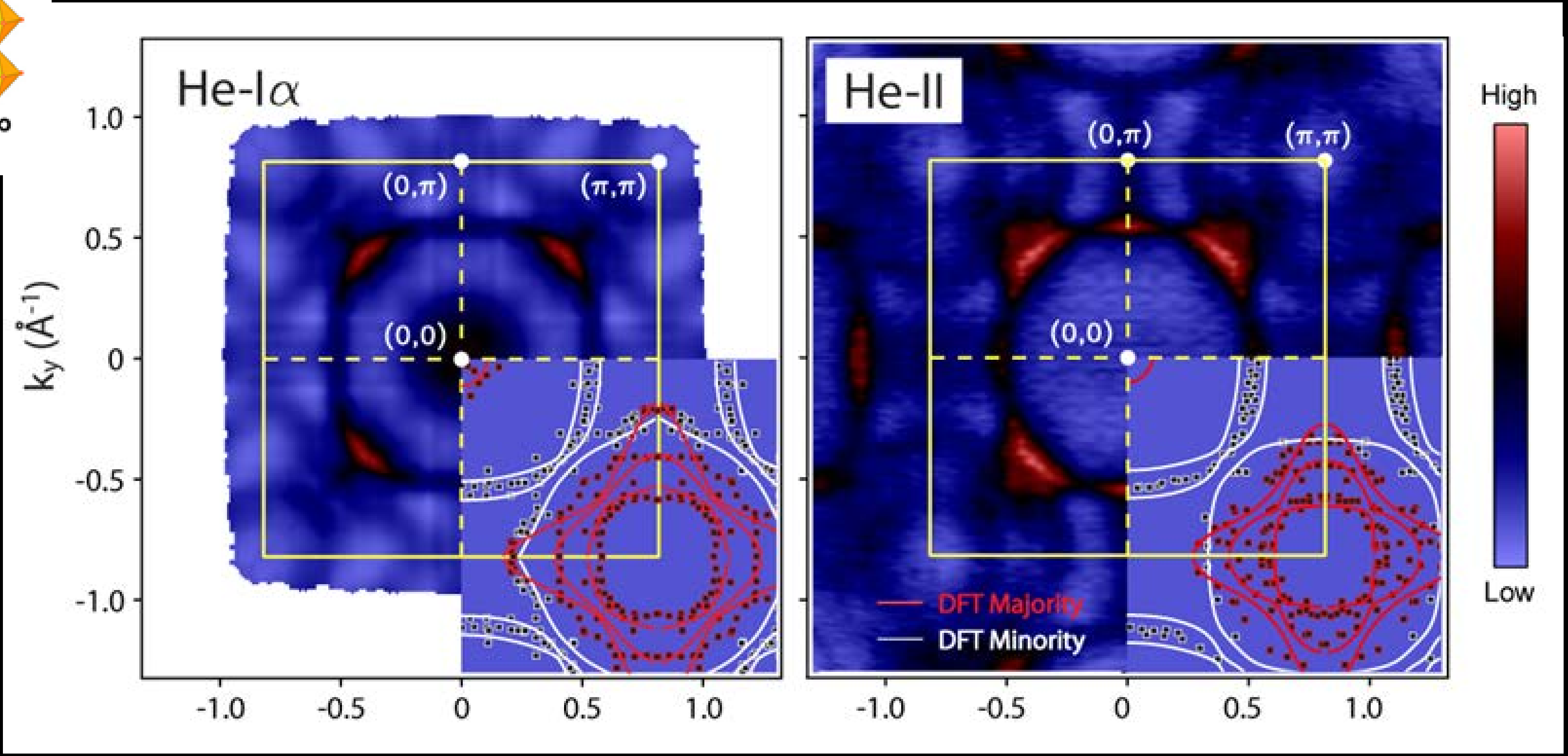


*Siemons et al., PRB **76**, 075126(2007)*

Photoemission spectra are sensitive to the stoichiometry

The first probe of the k dependent electronic structure

Fermi Surface Topology Maps (4-fold symmetrized)
T=10K, FM phase

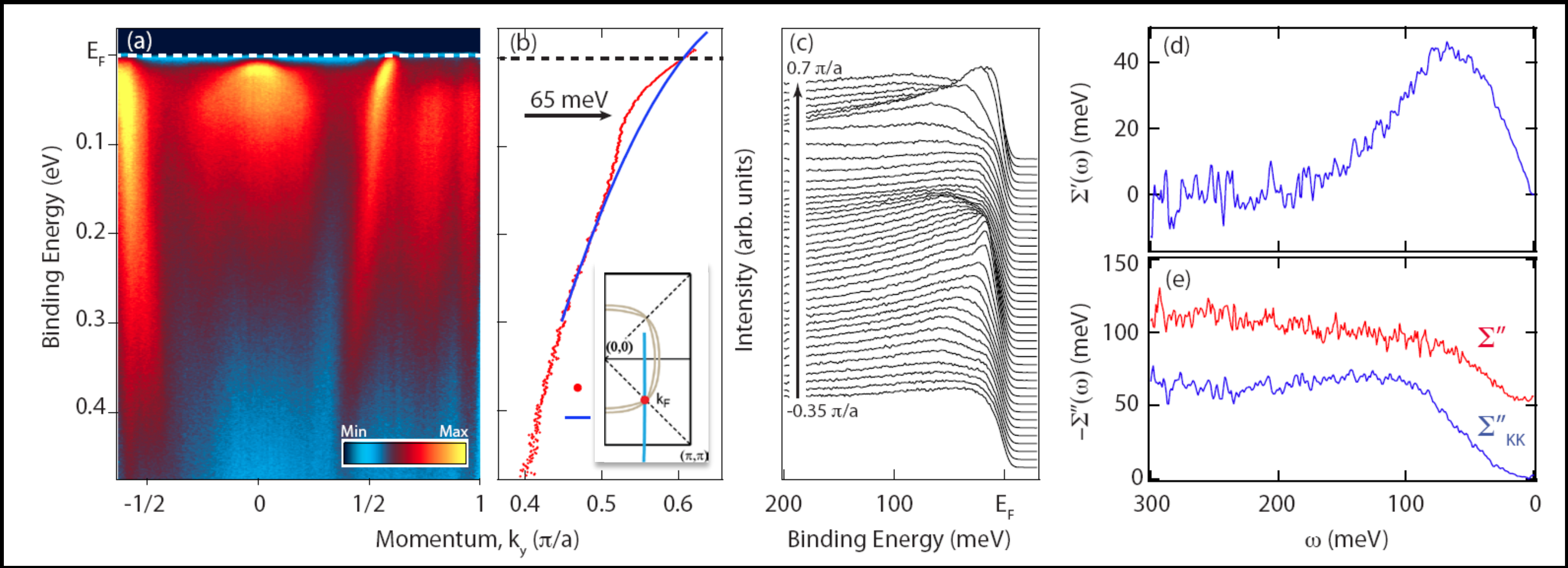


HeIα (21.2eV) **HeII (40.8eV)**

k_F's are consistent with both DFT prediction and previous bulk sensitive quantum oscillation measurements on $SrRuO_3$.

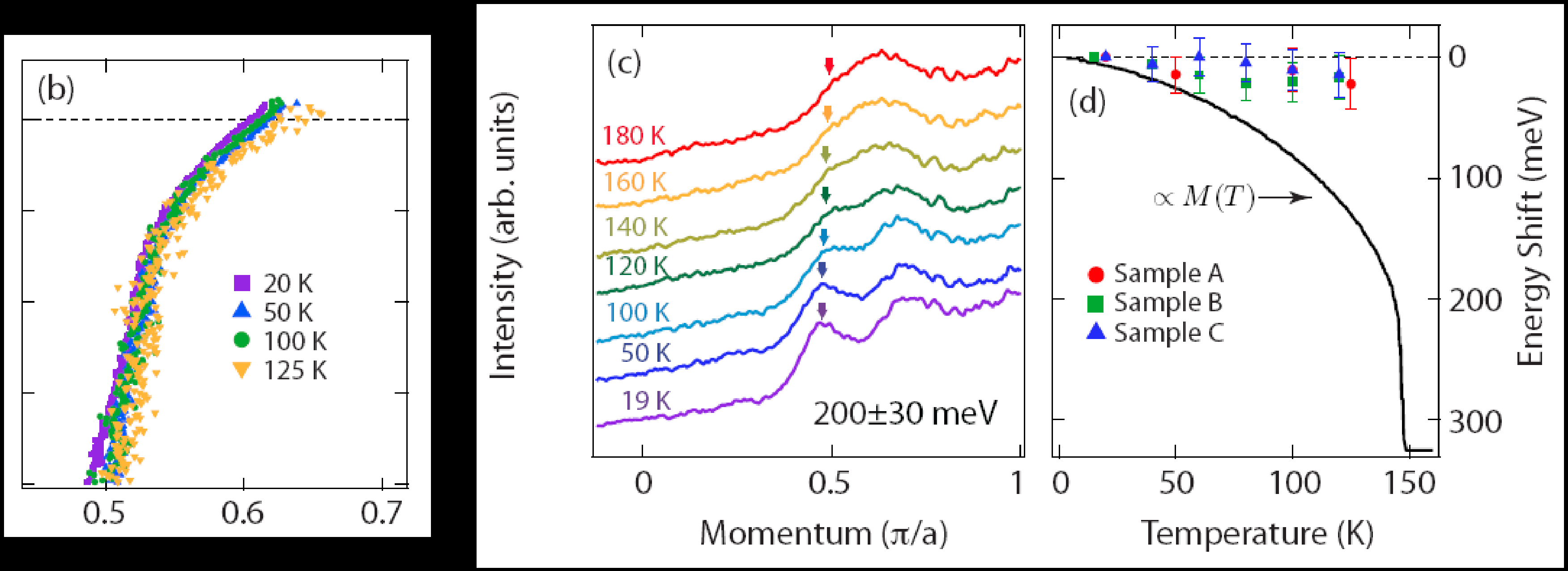
A. P. Mackenzie et al., PRB (1998) and C. S. Alexander et al., PRB (2005)

What is the origin of the strong correlation?



- **Evident 'kink' at ~65meV: signature of a strong coupling to some bosonic modes:**
  - **Low binding energy: heavily dressed QP ($M^* = 4.5\ M_{LDA}$), in good agreement with dH-vA oscillations;**
  - **High binding energy: similar slope as DFT, *weak e-e correlation*.**
- **Naturally explain the long-standing puzzle about the strong correlation effects.**

What is the origin of the ferromagnetism in $SrRuO_3$?



- **The Stoner model: the exchange splitting of an itinerant FM should decrease from its saturation value at low temperatures to zero at Tc.**
- **A strong deviation of the band dispersion from the Stoner model.**
- **The magnetism has a strong local character and cannot be explained in a simple picture of itinerant Stoner FM.**

Strong correlation in $SrRuO_3$ thin films

- ***For the first time*, high resolution ARPES is conducted on epitaxial $SrRuO_3$ thin films to extract the electronic structure:**
  - High accuracy Fermi surface maps, in agreement with DFT calculation;
  - Strong kink structure in QPs' dispersion

- **Many-body interactions in $SrRuO_3$ thin films are anatomized:**
  - Strong coupling to some bosonic modes, e-ph? Magnons?
  - Relatively weak e-e correlations.
  - The magnetism has a strong local character.

Naturally explain the long-standing puzzle about the strong correlation effects.

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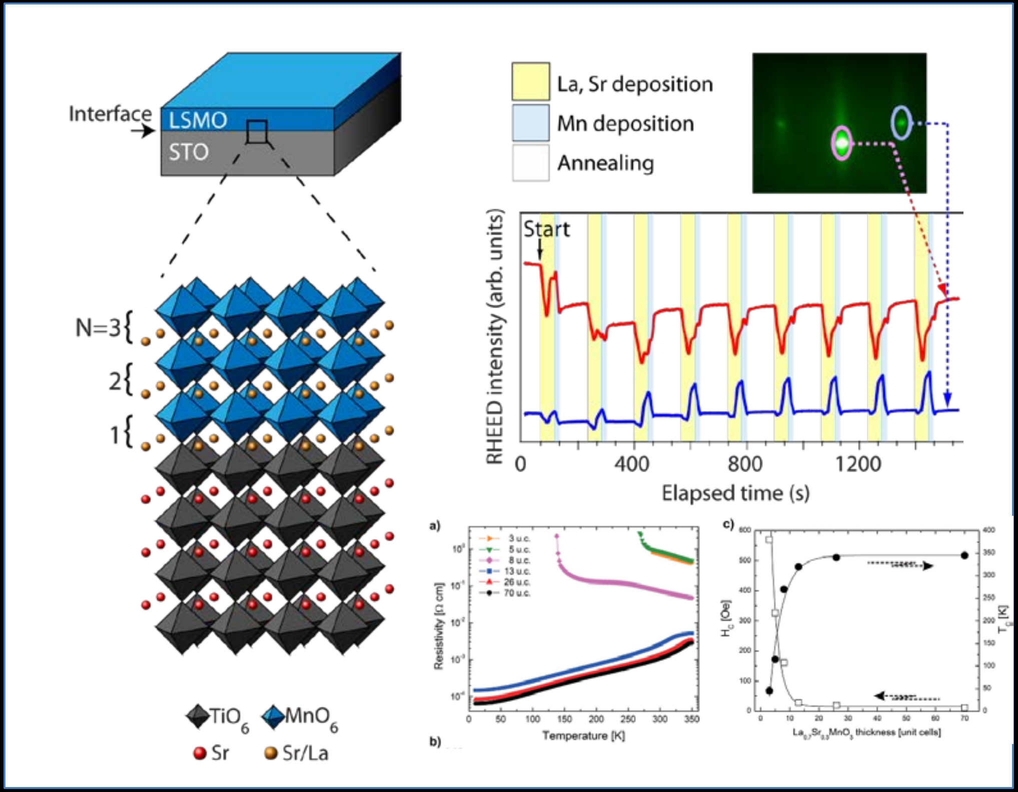
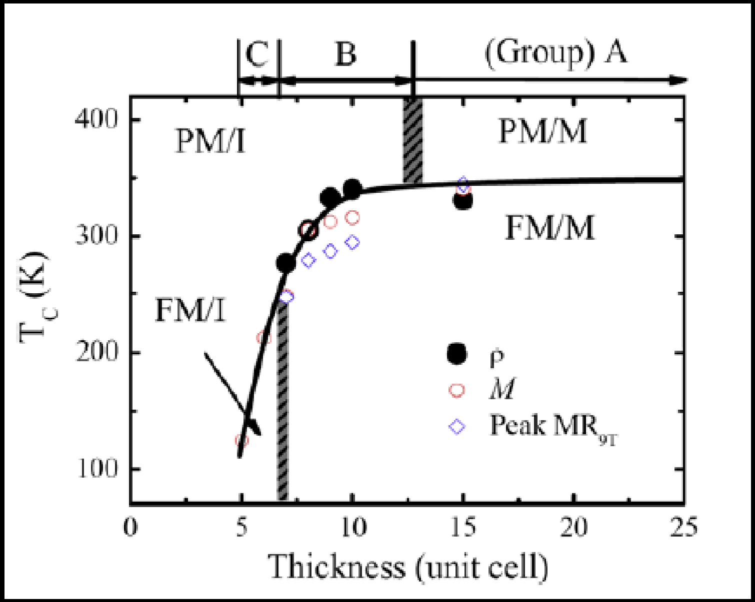


Dead-layer phenomenon at $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$ interfaces



7 unit cells on LSMO/STO

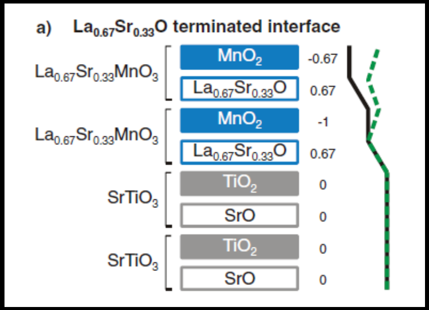
Dead layer—strongly affected by defects

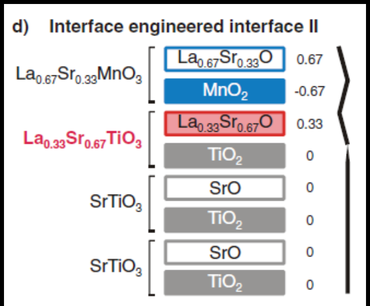
Oxide MBE:
- ➢ Sharp interface, low energy
- ➢ low defect densities

Nakagawa, Nature materials (2006)
Tebano et al., PRL 100, 137401 (2008)
Kim et al., Solid State Communications 150(13–14): 598-601
H. Boschker et al., AdFuncMat 22,2235 (2012)

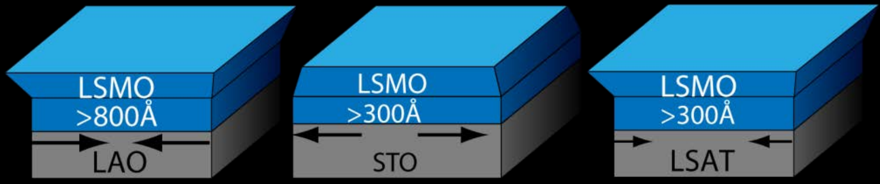
Possible mechanisms:

- Charge redistribution

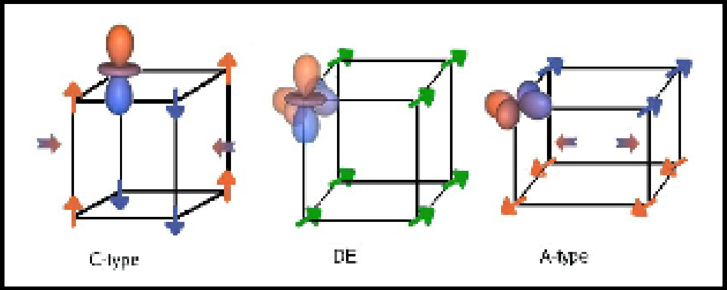




- Strain effect

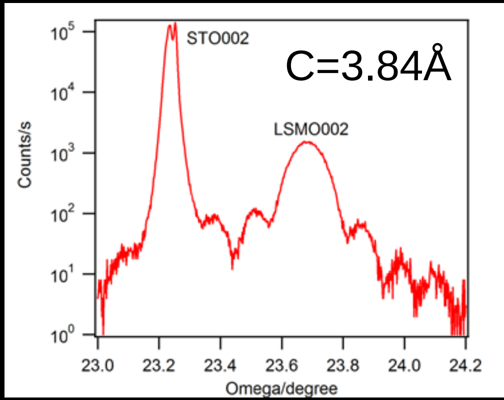


- Magnetic and orbital reconstruction

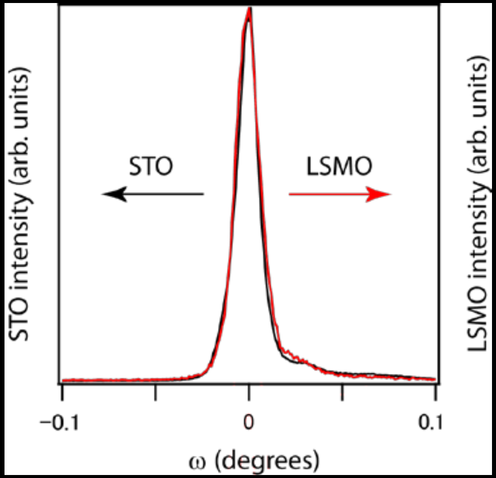


Characterization of $La_{0.67}Sr_{0.33}MnO_3$ thin films

Fine scan around (002)

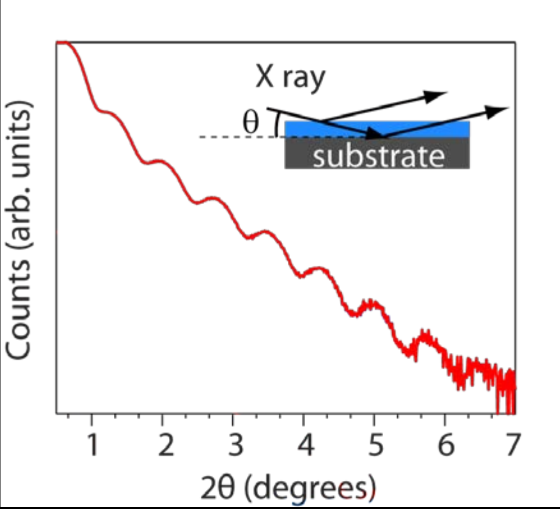


Rocking around (002)



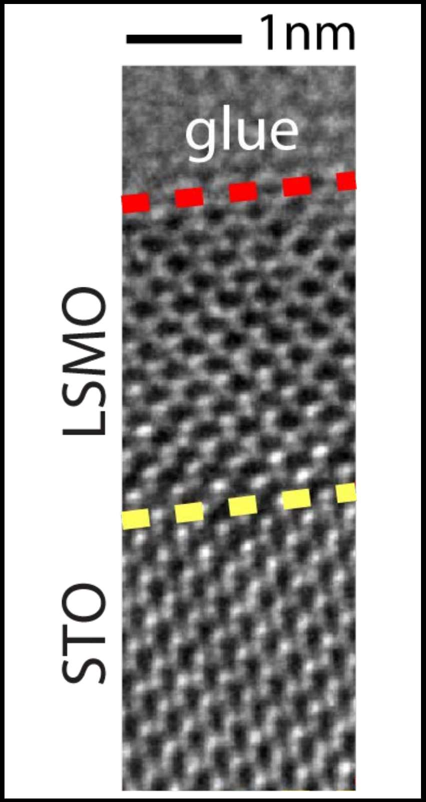
FWHM=0.015, limited by the substrate

X-ray refection



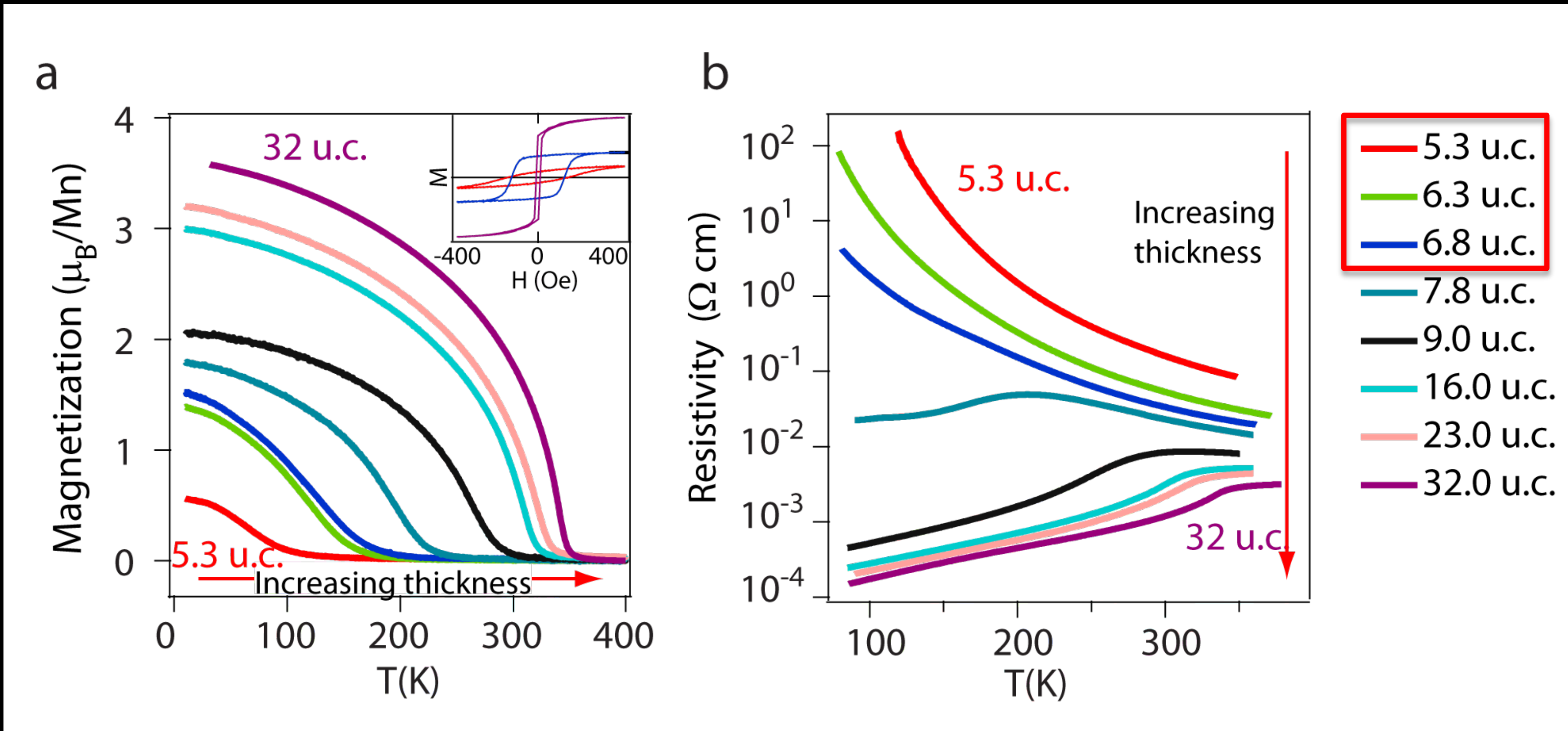
Absolute thickness error within 2%

Cross-sectional TEM image



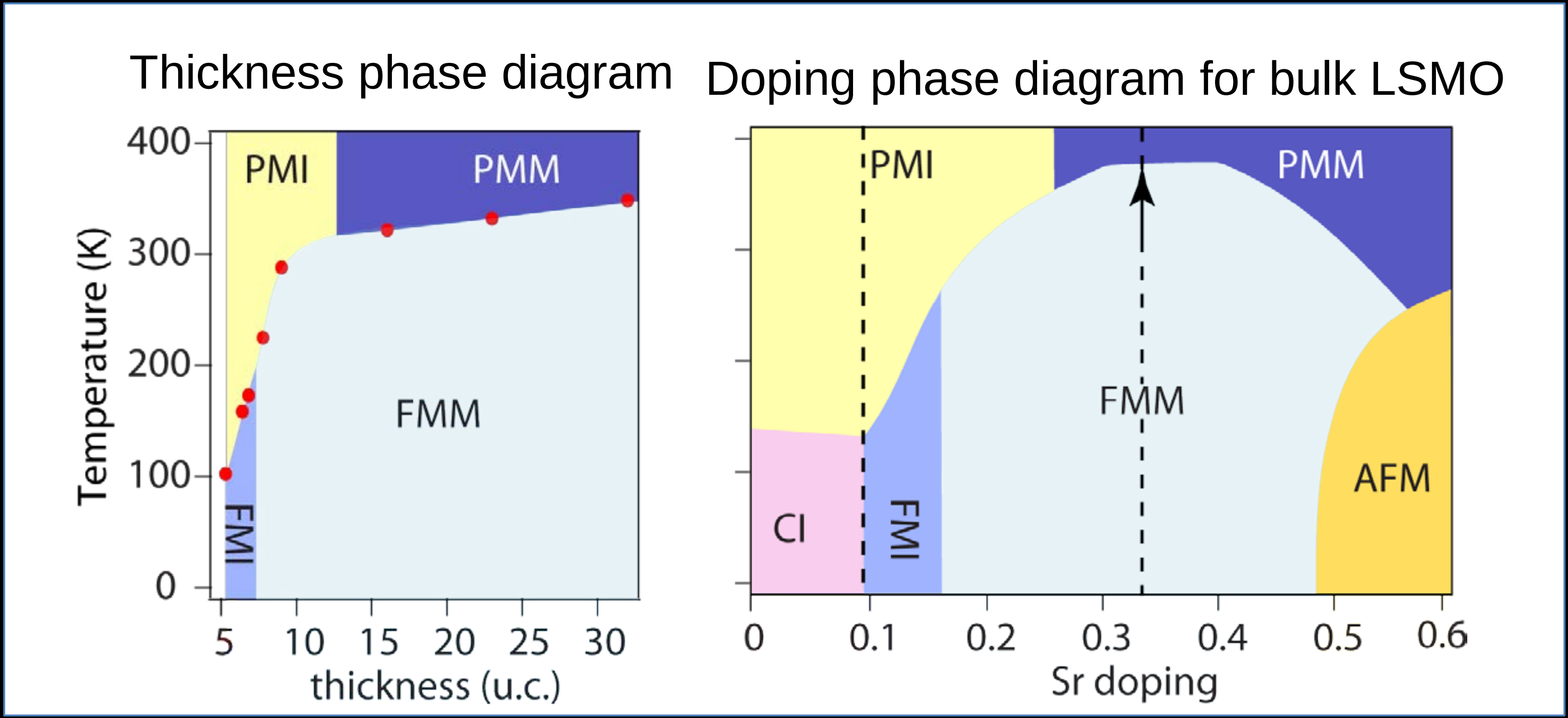
Confirm the 7uc thickness

Transport properties v.s. thickness



- 32 u.c. ~ bulk;
- Both of Curie temperature and conductivity drop upon decreasing thickness;
- Below 7u.c., the films are insulating below Tc, as a typical dead-layer behavior.

Remarkable similarity in the phase diagram to the doped bulk



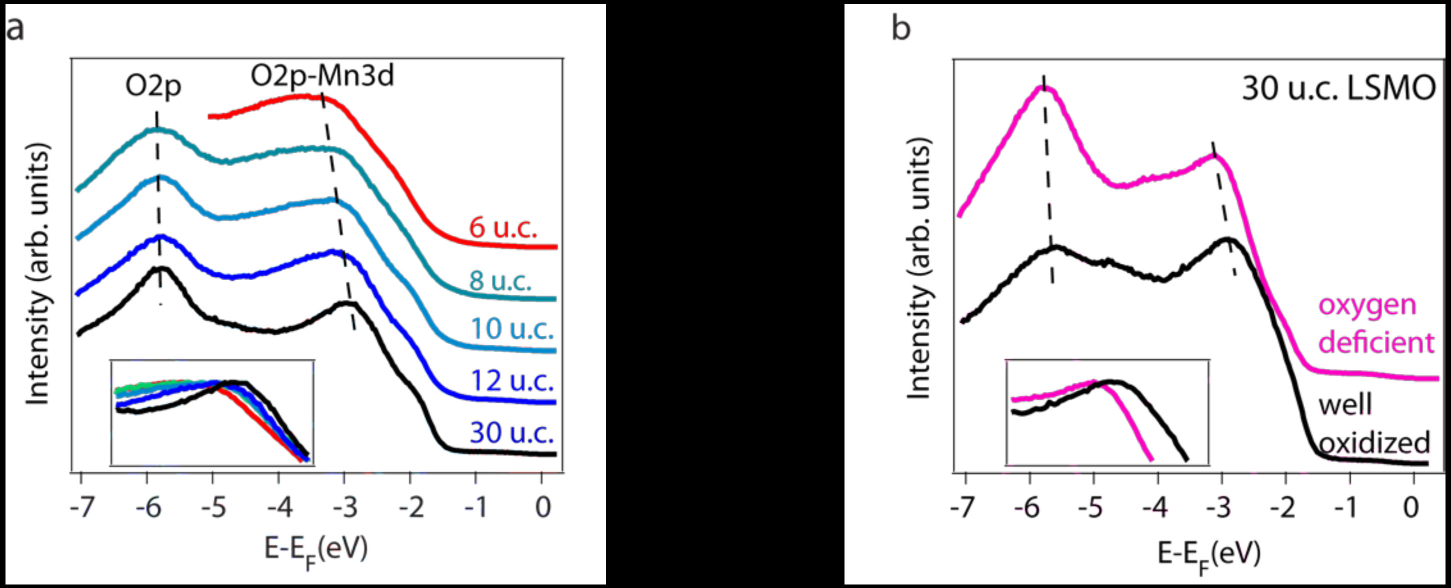
In bulk: double-exchange is suppressed → metal-insulator transition

Suppressed double exchange
- Decreased hole concentration
- Change of Mn-O bond angle

The same mechanism for ultrathin films?

Moreo, A., et al., Science 283, 2034 (1999).

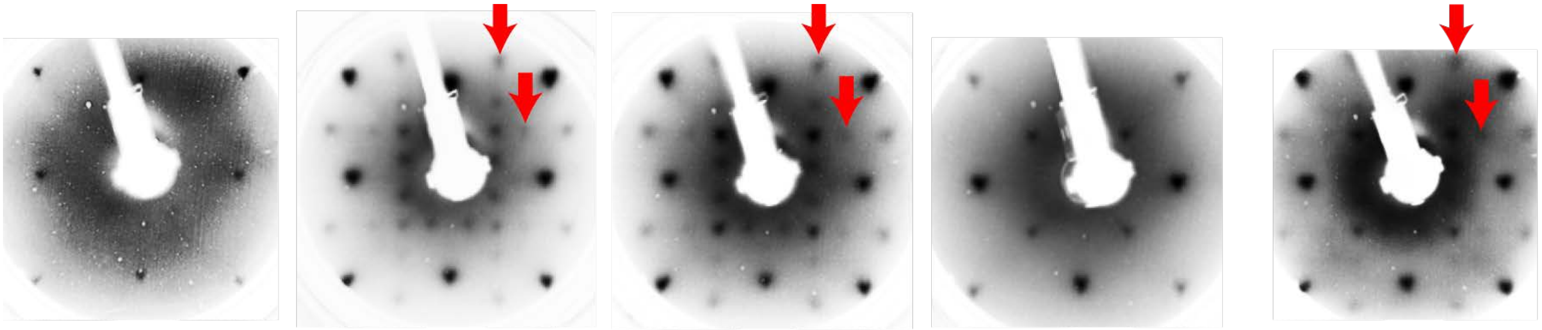
Oxygen vacancies → hole concentration and bond angle change



- The Mn-O hybridized band, shifts towards higher binding energy with decreasing thickness.
- Similar shift is observed in the 30 u.c. film intentionally grown under oxygen deficient condition
- **This valence band shift closely related to the oxygen deficiency**

Picozzi, S., et al., Phys. Rev. B. 75, 094418 (2007).
Schlueter, C., et al. Phys. Rev. B. 86, 155102 (2012).

Other evidence from LEED



substate

6 u.c.
well oxidized

15 u.c.
well oxidized

30 u.c.
well oxidized

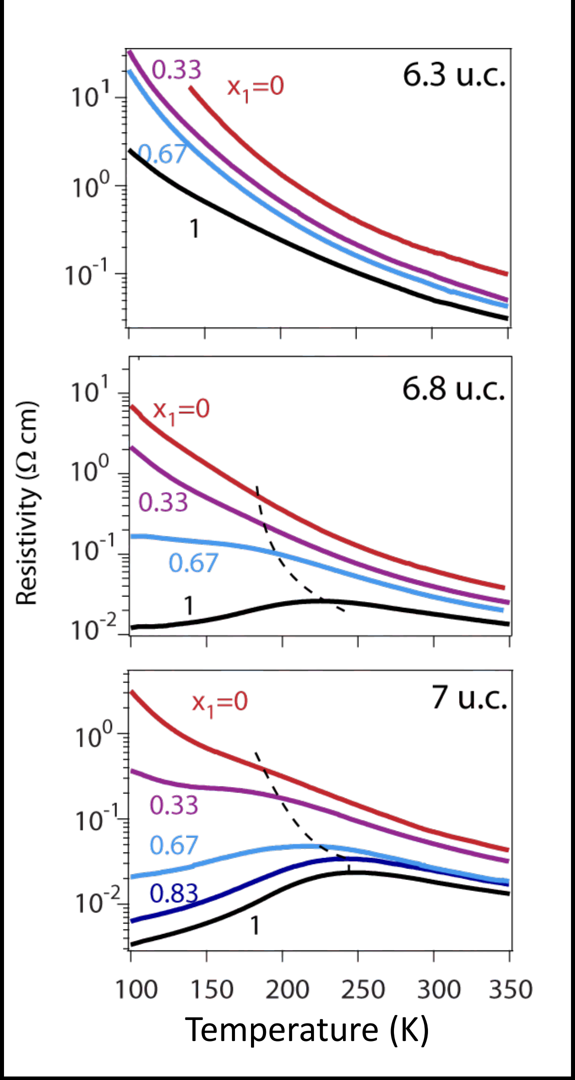
30 u.c.
oxygen deficient

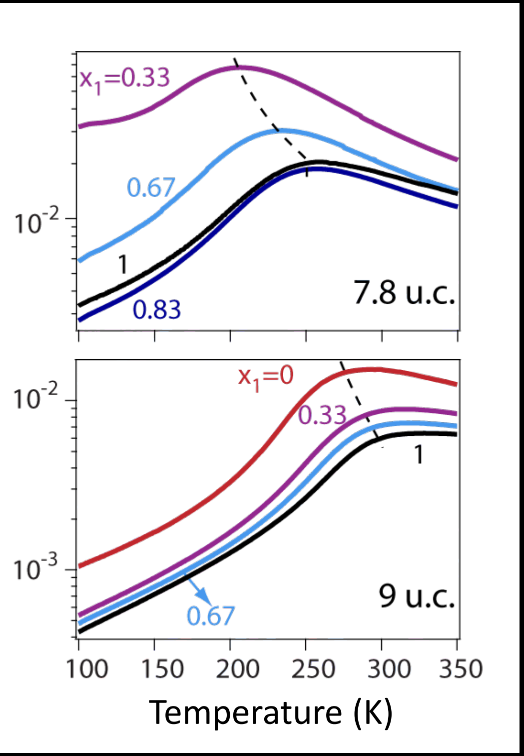
- Both the ultra-thin films and the intentionally oxygen deficient thick film show an additional surface reconstruction.

- Further annealing in ozone did not cause any variation in the valence band or LEED patterns of the ultra-thin films.

Intrinsic oxygen vacancy formation appear in ultra-thin films ----- change the carrier concentration, and suppress the double exchange

Interface engineering based on this model





The deteriorated metallicity and ferromagnetism with decreased thickness can be compensated by higher interfacial Sr doping.

The dead-layer is successfully reduced to 6 u.c.

Summary and Outlook

- ARPES is a powerful tool to study the strongly interacting solid state materials; BUT, it is greatly limited to the cleavable samples.
- MBE+ARPES technique can greatly extend our research scope to originally unachievable materials phase;
- It also provides a great tool to customize and characterize the oxide thin films with desired functions.

Thanks for your attention!