钙钛矿氧化物超晶格及异质界面的研究进展

A highly conducting layer forms at the interface between thin films of the insulators $LaAlO_3$ and $SrTiO_3$.

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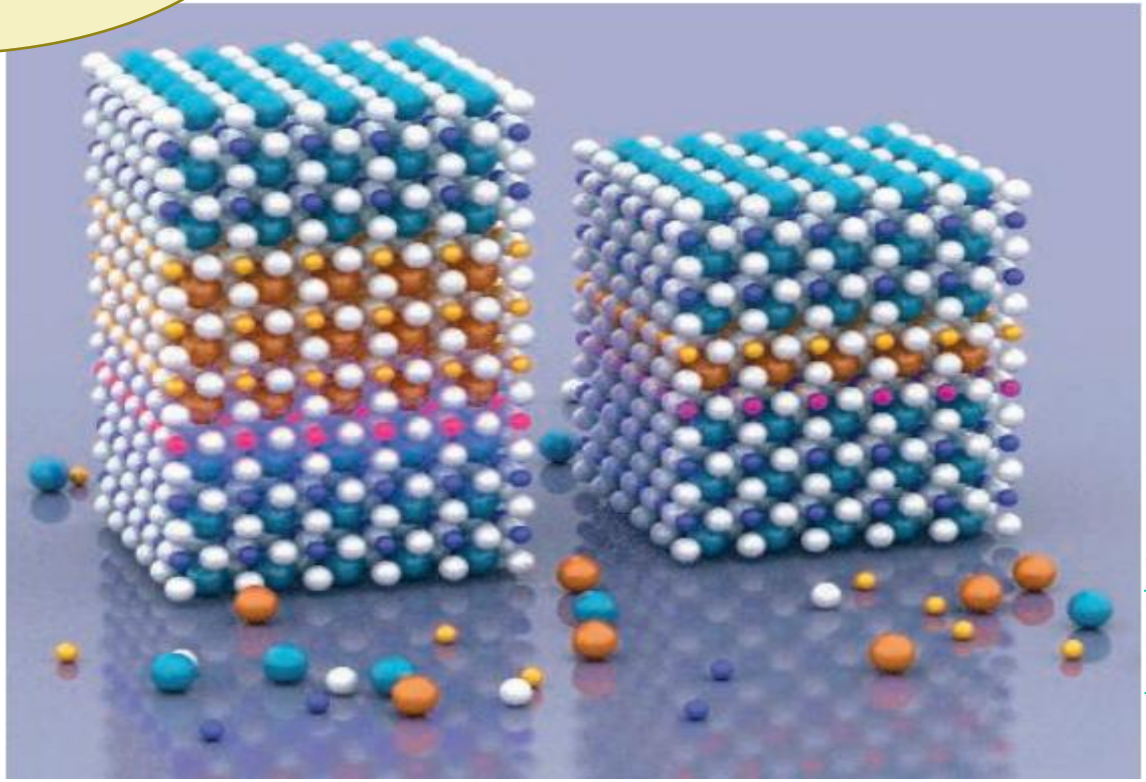
A story about oxide heterostructures

Sir, I want to grow oxide heterostructures!

Harold Y. Hwang

1996-2004: 8 years!!!!

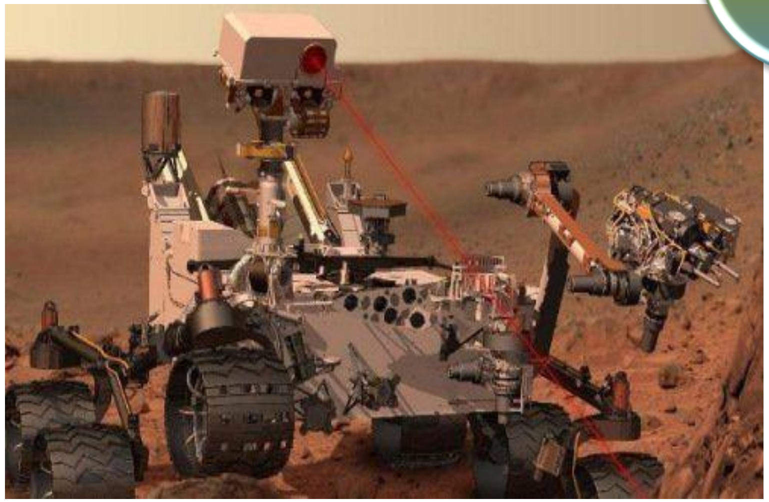
Story from: Nature 459, 28 (2009)
By: Joerg Heber



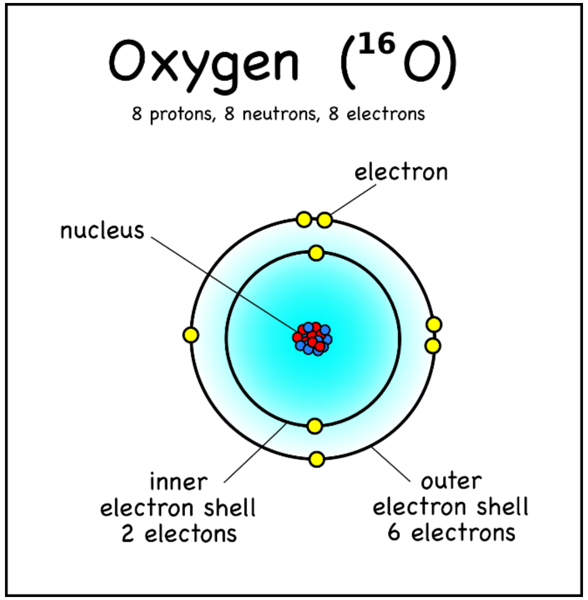
"Have you ever grown a thin film in your life?"
— Horst Störmer

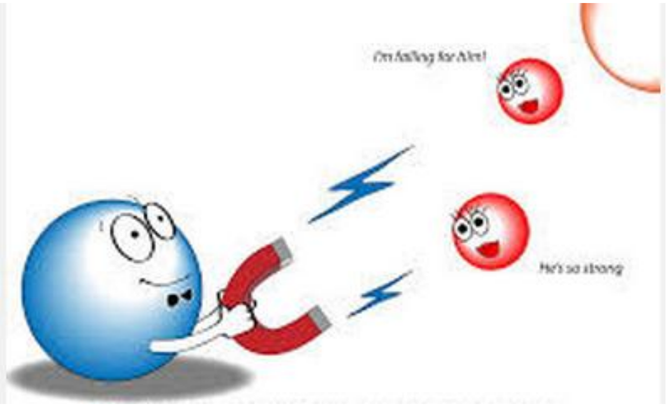
Nobel Prize (1998)
with Daniel Tsui and Robert Laughlin "for their discovery of a new form of quantum fluid with fractionally charged excitations"

Why choose Oxides?



Why oxides so interesting?→power of Oxygen





Strong negativity

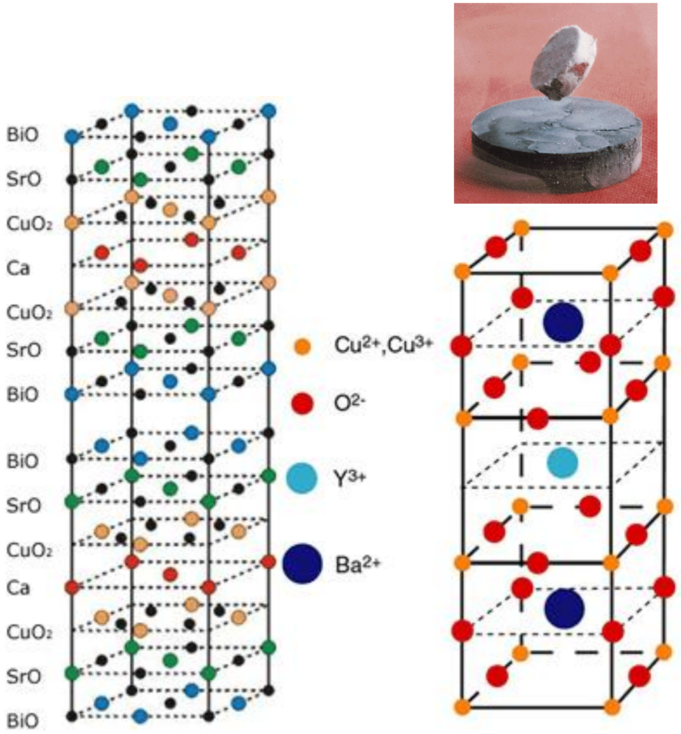
→strong internal electric field

→correlation effect

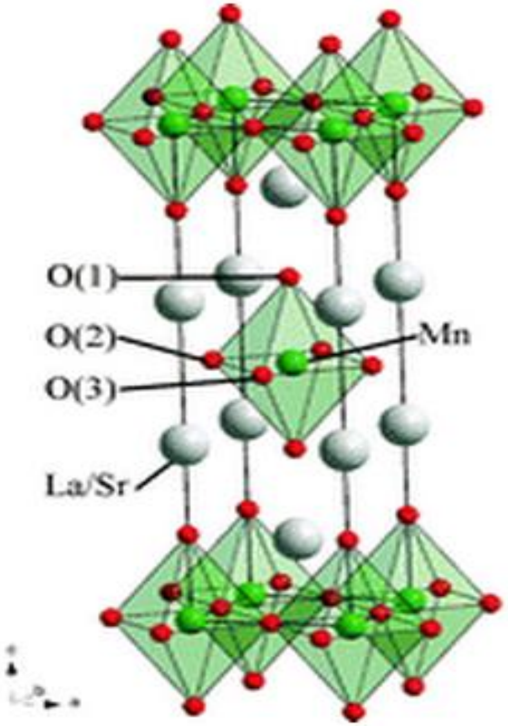
H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	Lu	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

History of oxides study

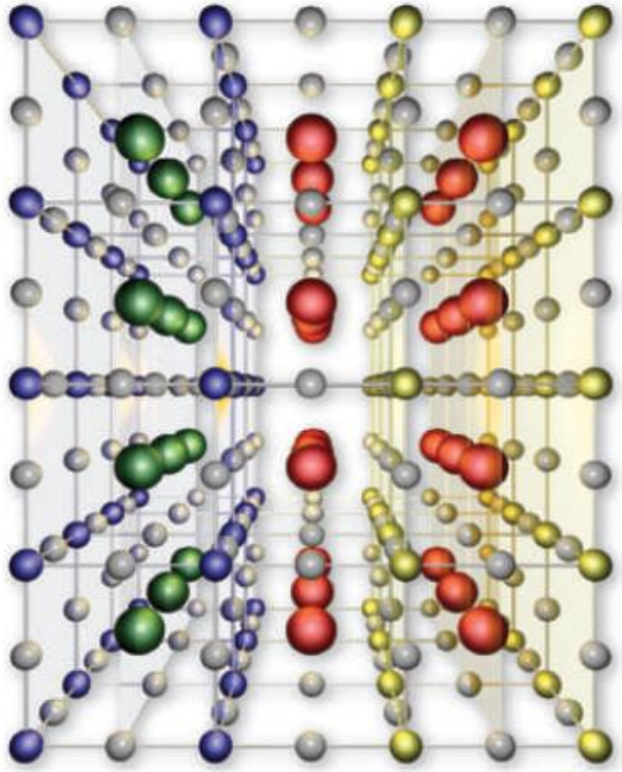
Far more difficult to fabricate than metals and semiconductors



YBCO (late 80s)
high-temperature superconductivity

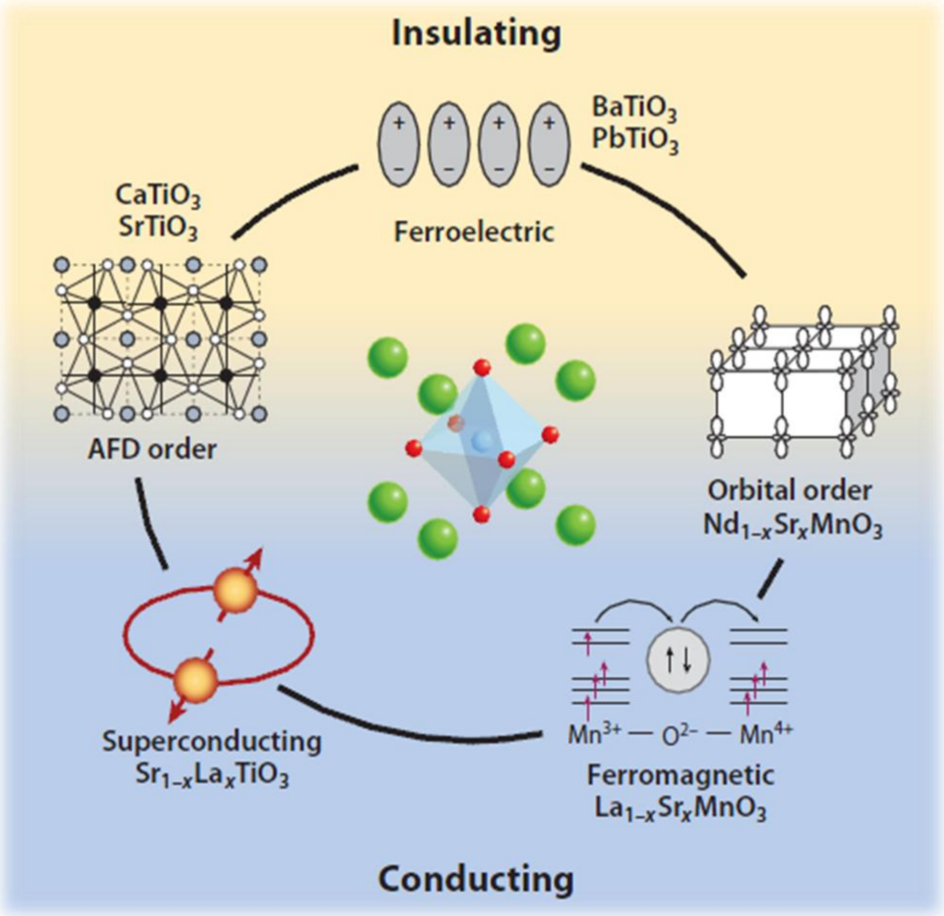


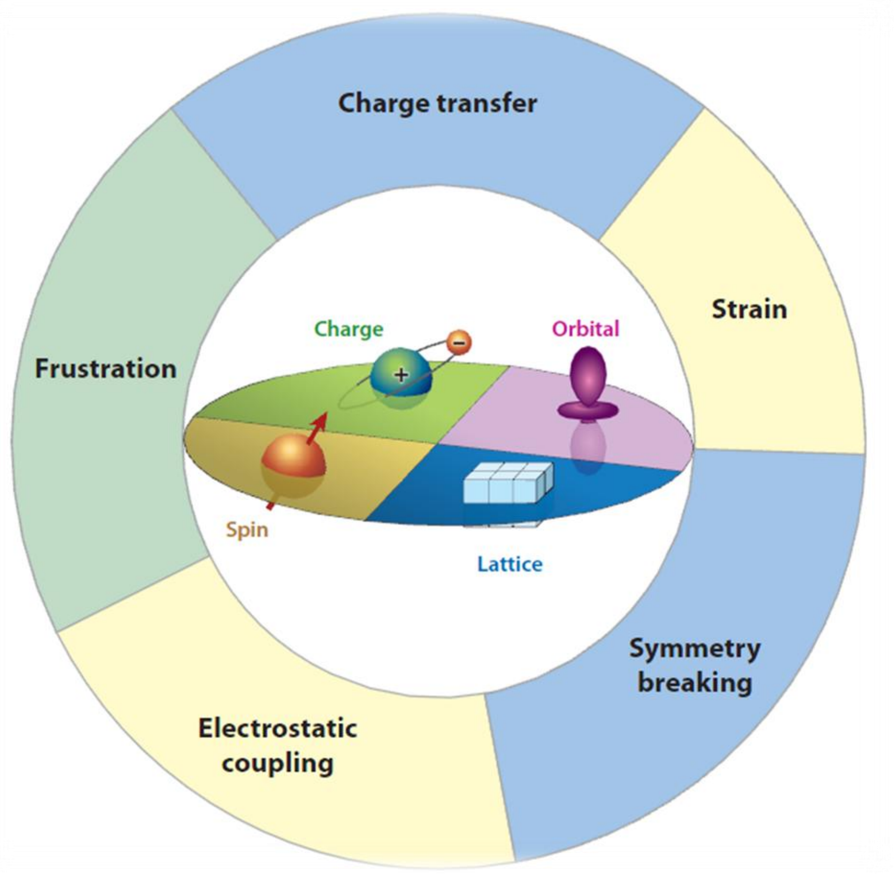
LSMO (early 90s)
CMR



LAO/STO(early 00s)
2-D electron gas

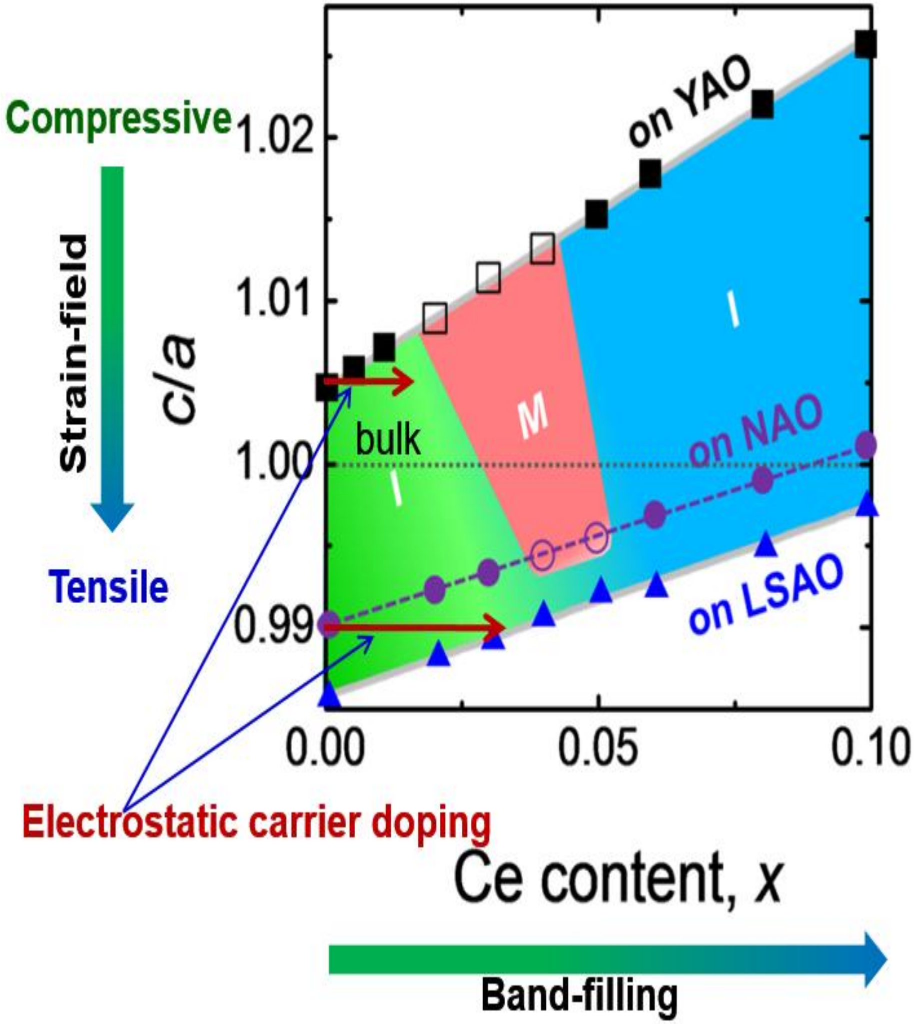
Oxides interface/surface



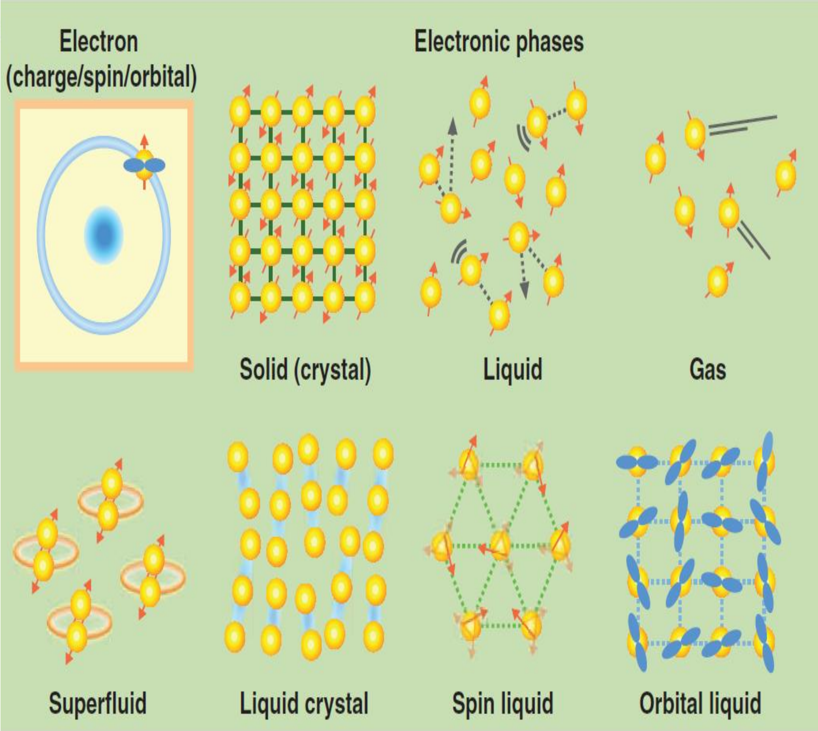


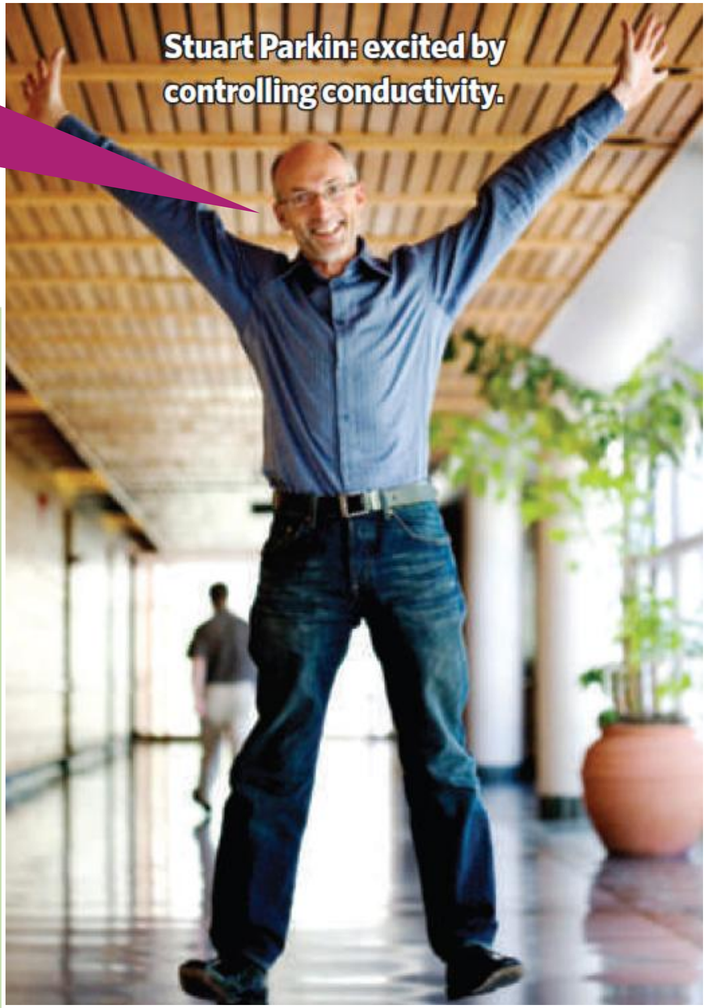
P. Zubko, *et al*. Interface Physics in Complex Oxide Heterostructures. Annual Review of Condensed Matter Physics **2**, 141-165 (2010).

How to control?

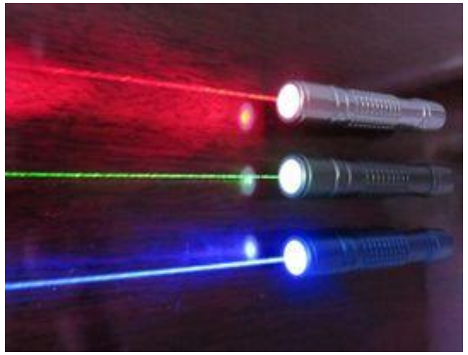


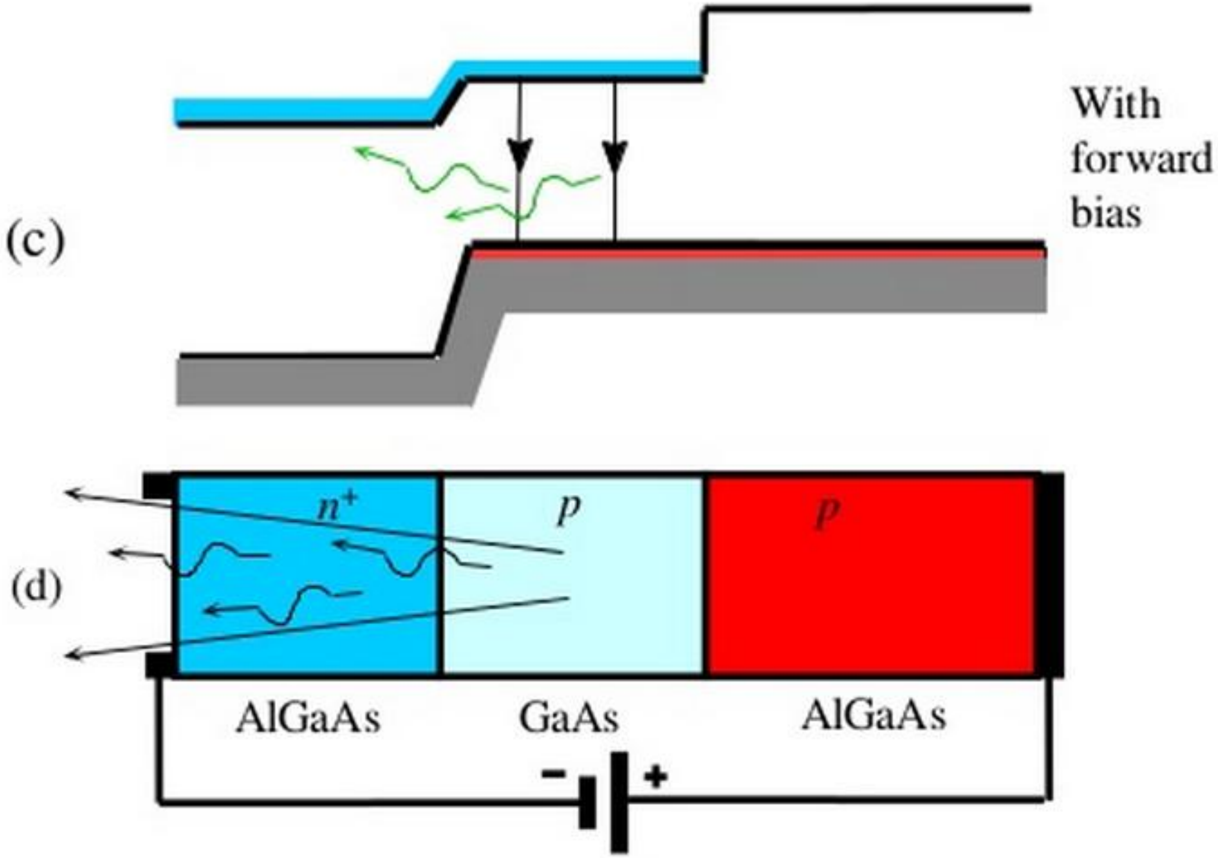
"You can imagine controlling the states at phase boundaries by making small modifications."

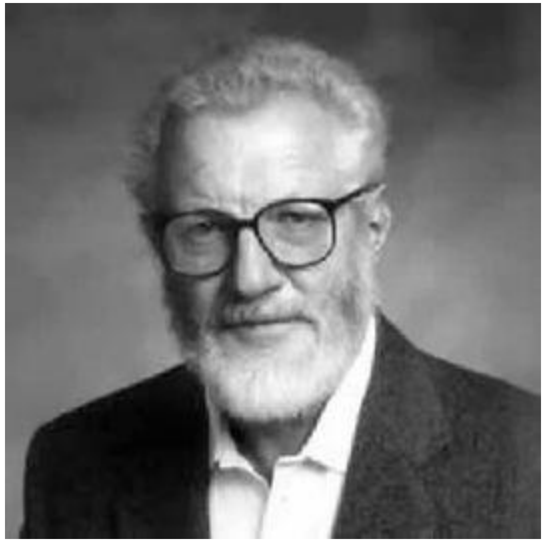




The interface is the device



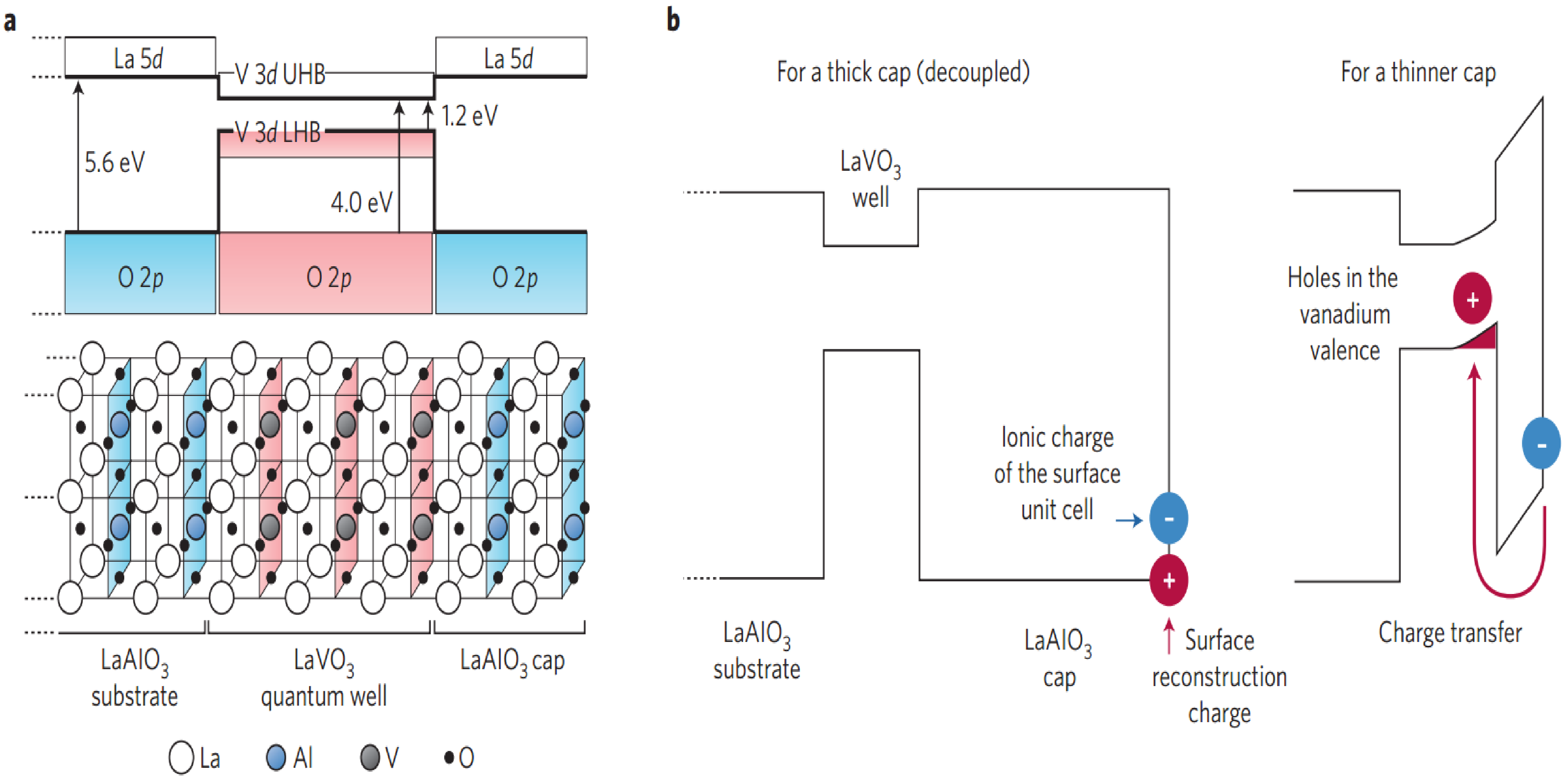




Herbert Kroemer (8/25, 1928-) Nobel Prize in Physics (2000) along with Zhores I. Alferov, for developing semiconductor heterostructures used in high-speed- and opto-electronics

double semiconductor heterostructures

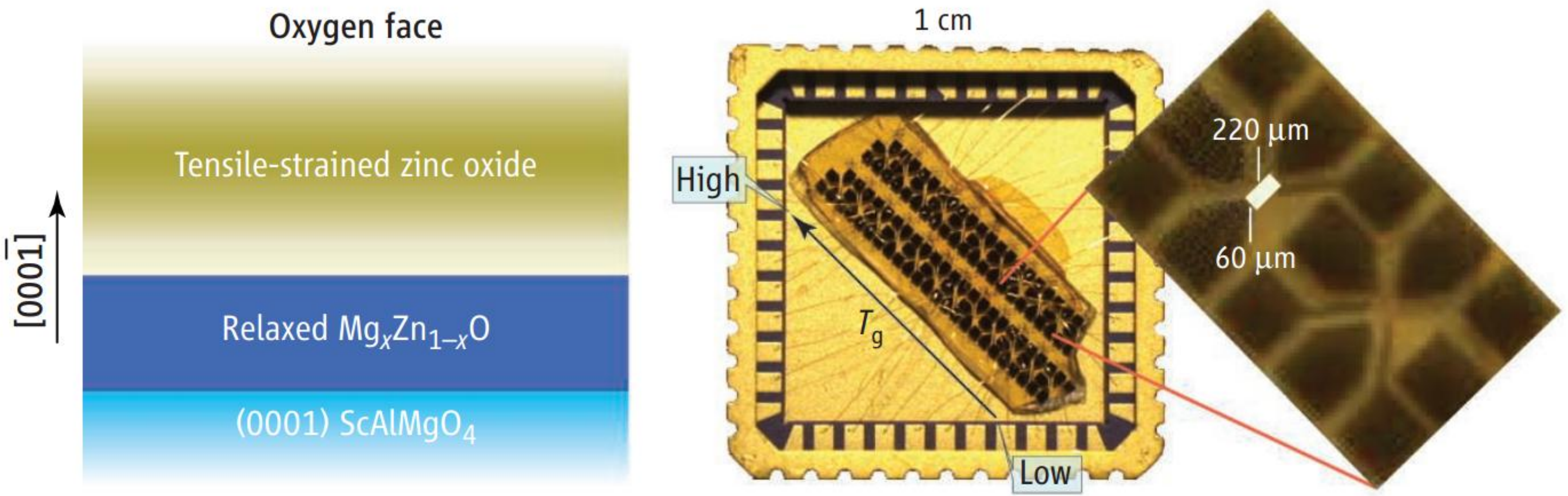
The interface is still the device



Hwang, H. Y. *et al. Nature Mater.* **11,** 103–113 (2012).

Oxide Electronics Emerge

Oxide Electronics: Oxidetronics

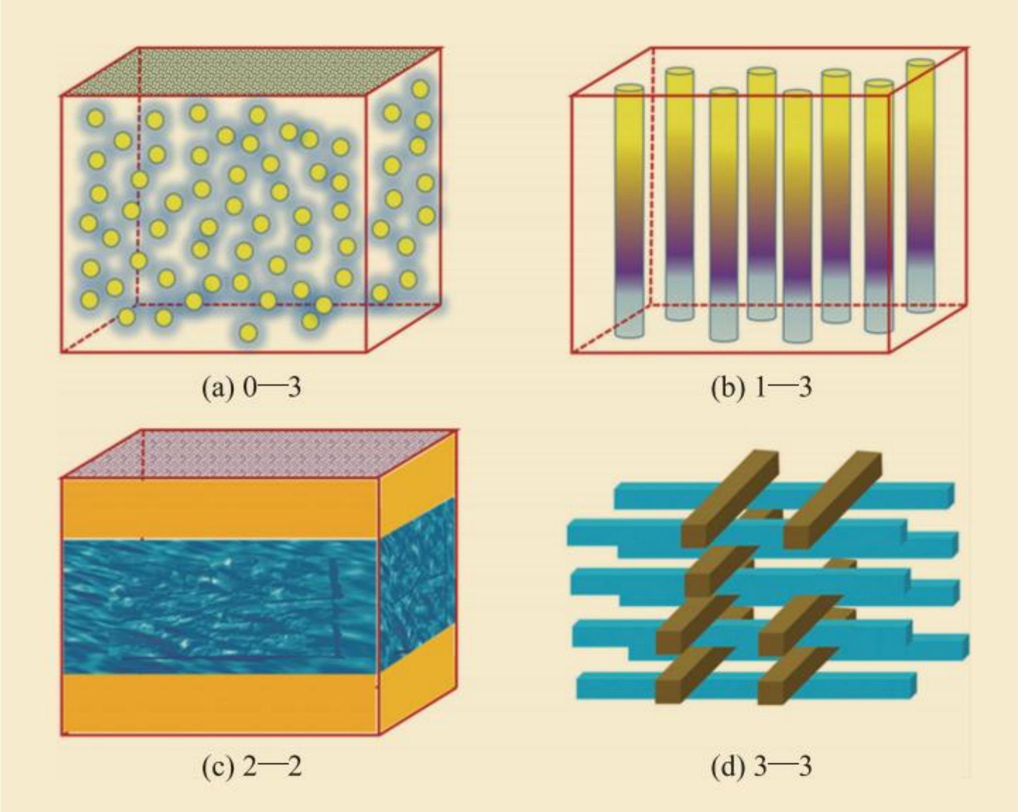


Tsukazaki et al., Science 315, 1388 (2007)
Introduced by Ramirez, Science 315, 1377-1378 (2007).

Emergent Phenomenon

Emergent phenomena:

new properties arise from the interactions of many particles in a complex system



多铁性异质结：1+1≠2*

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(1 华东师范大学极化材料与器件教育部重点实验室　上海　200241)

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Multiferroic heterojunctions：1+1≠2

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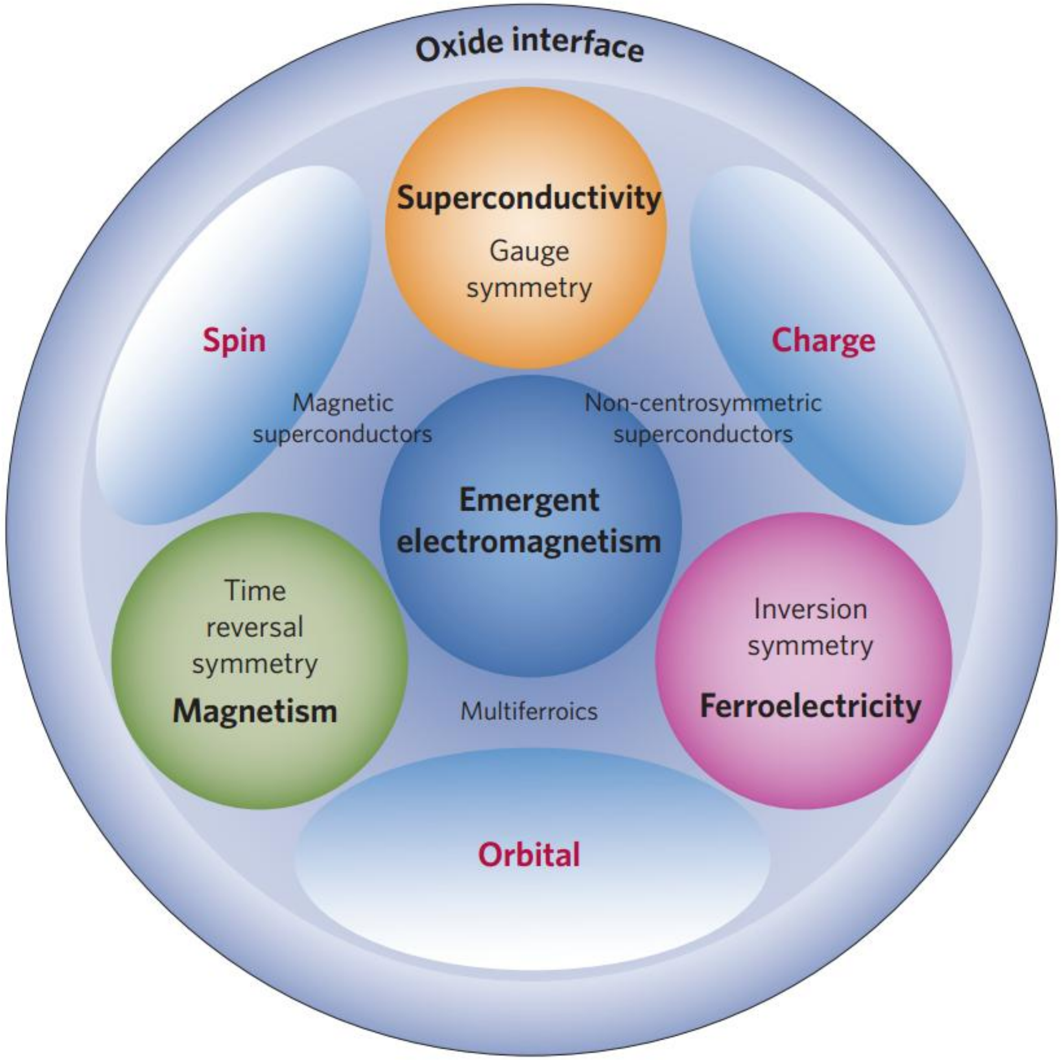
(2 Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics，Tsinghua University，Beijing 100084，China)

Physics 43, 99 (2014), **invited paper** in Chinese.

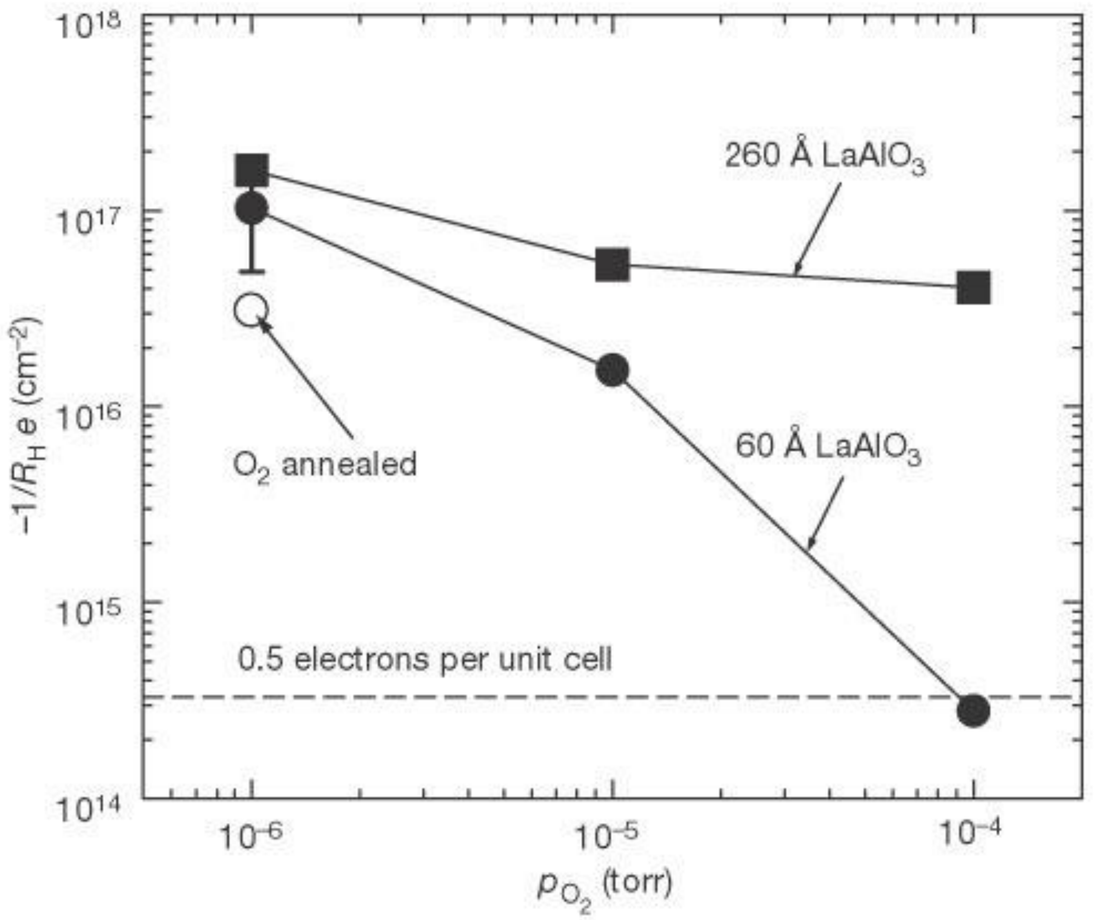
Emergent phenomena at oxide interfaces

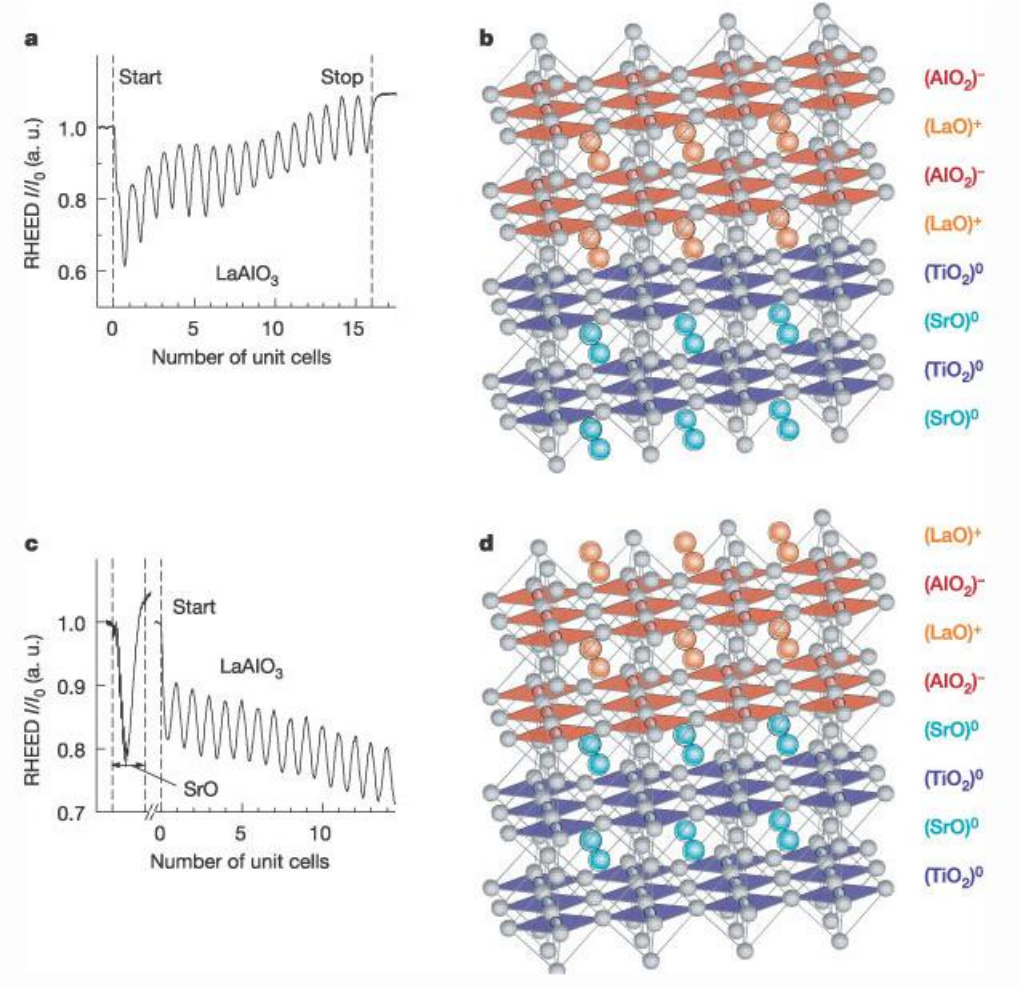


- Mott insulators
- various charge
- spin and orbital orderings
- metal–insulator transitions
- multiferroics
- superconductivity

Hwang, H. Y. *et al. Nature Mater.* **11,** 103–113 (2012).

2D electron gas with high mobility

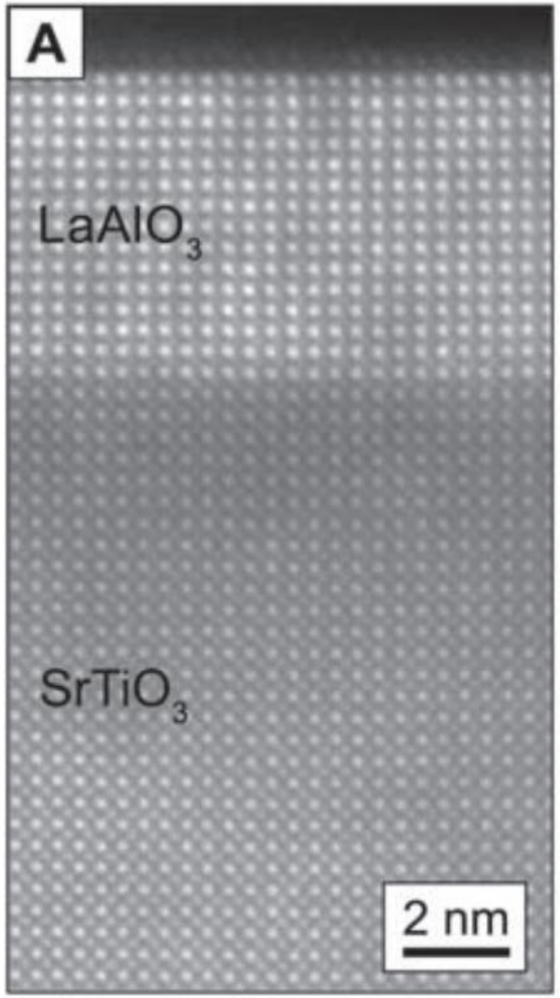


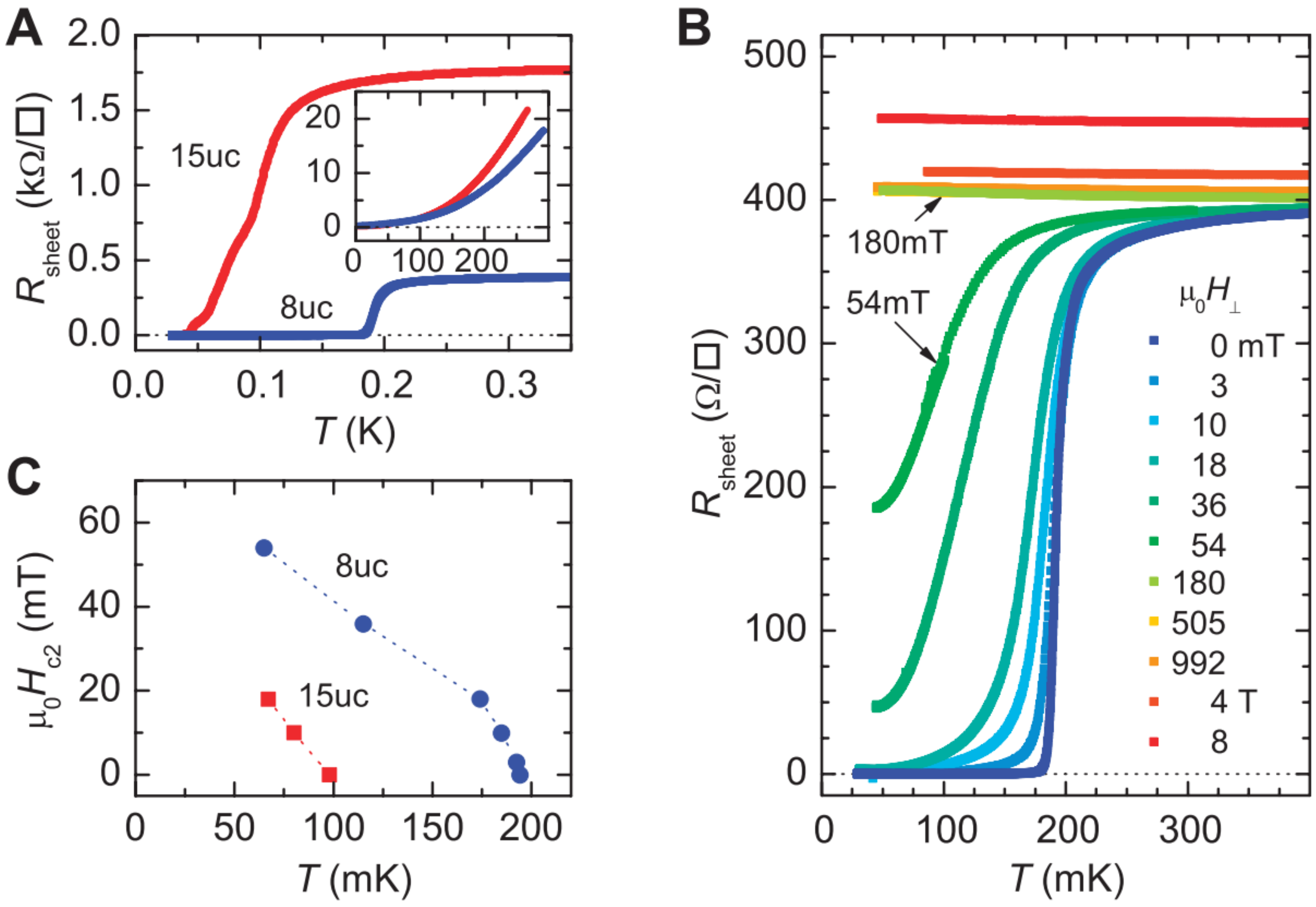


A. Ohtomo, H. Y. Hwang, Nature 427, 423 (2004)

10^4 cm^2 V^{-1} s^{-1} (4.2 K)

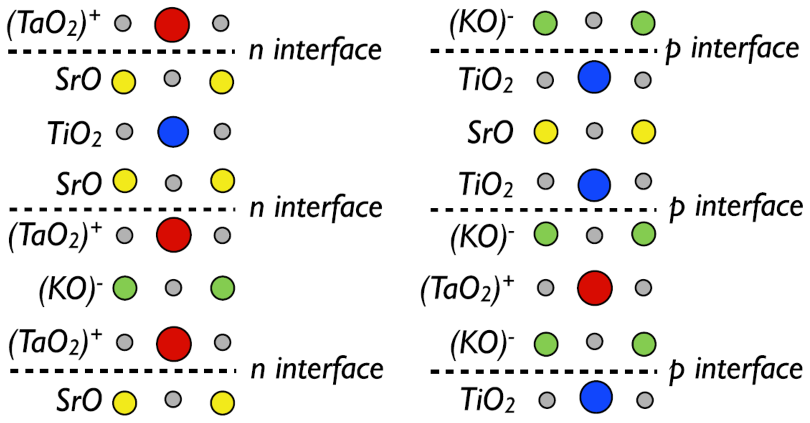
Superconducting Interfaces Between Insulating Oxides

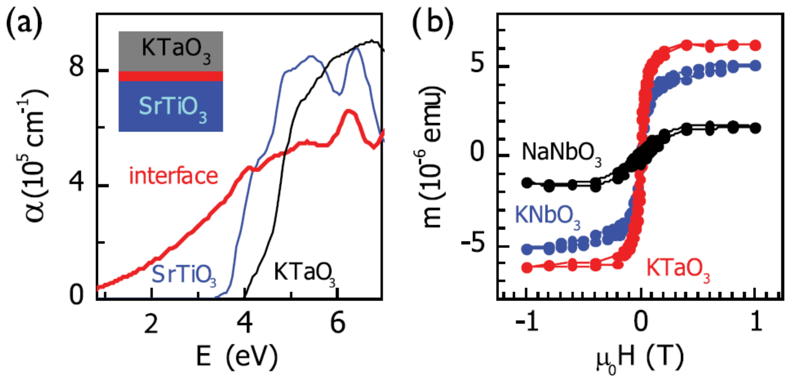


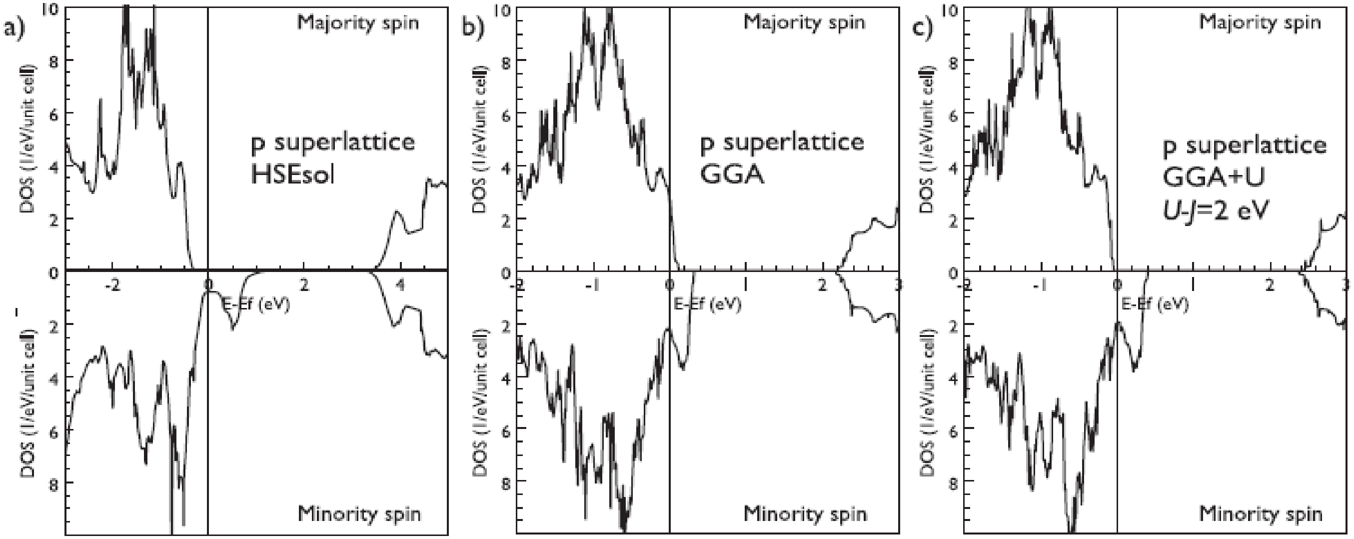


N. Reyren, et al. ***Science*** 317, 1196-1199 (2007)

d^0 Ferromagnetic Interface between Nonmagnetic Perovskites



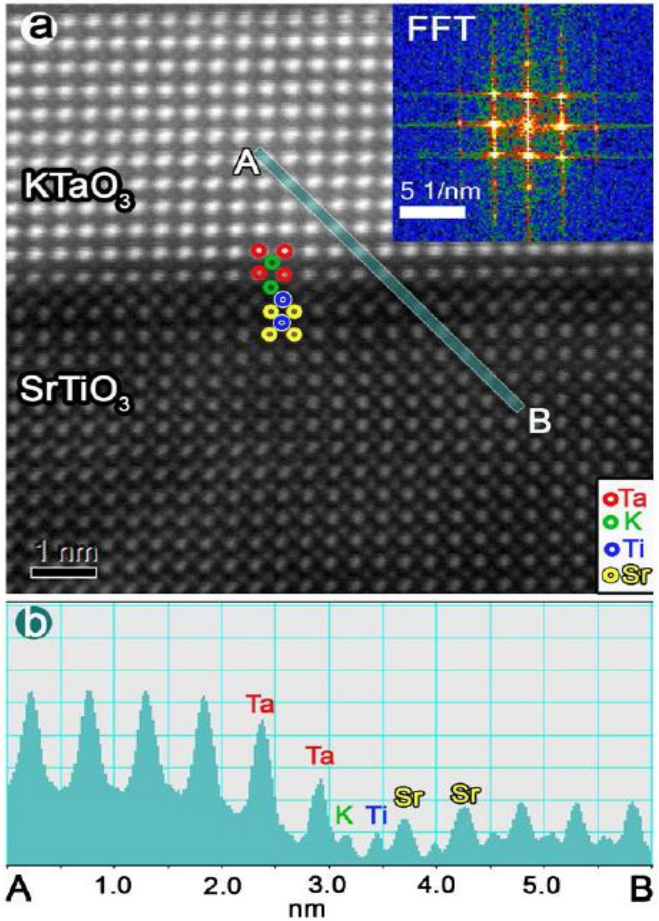




2D gas

+

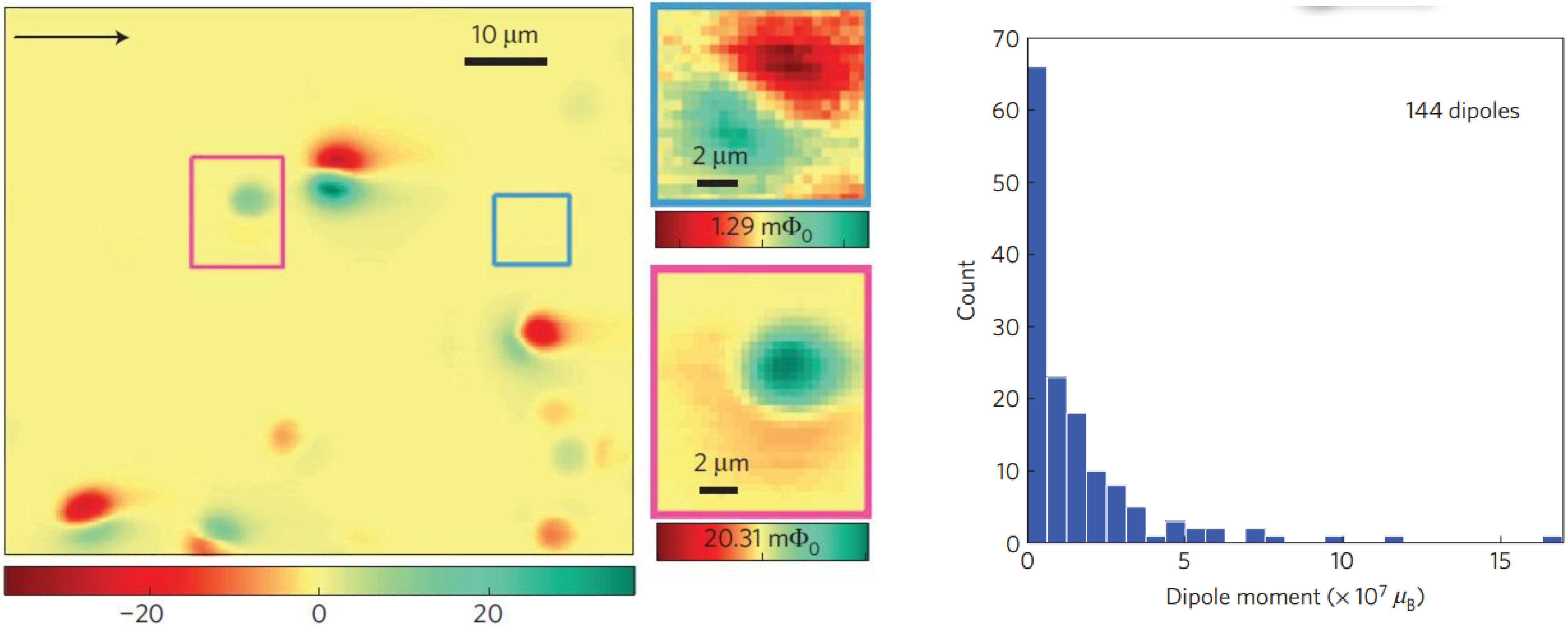
Stoner



$SrTiO_3/KTaO_3$ superlattice

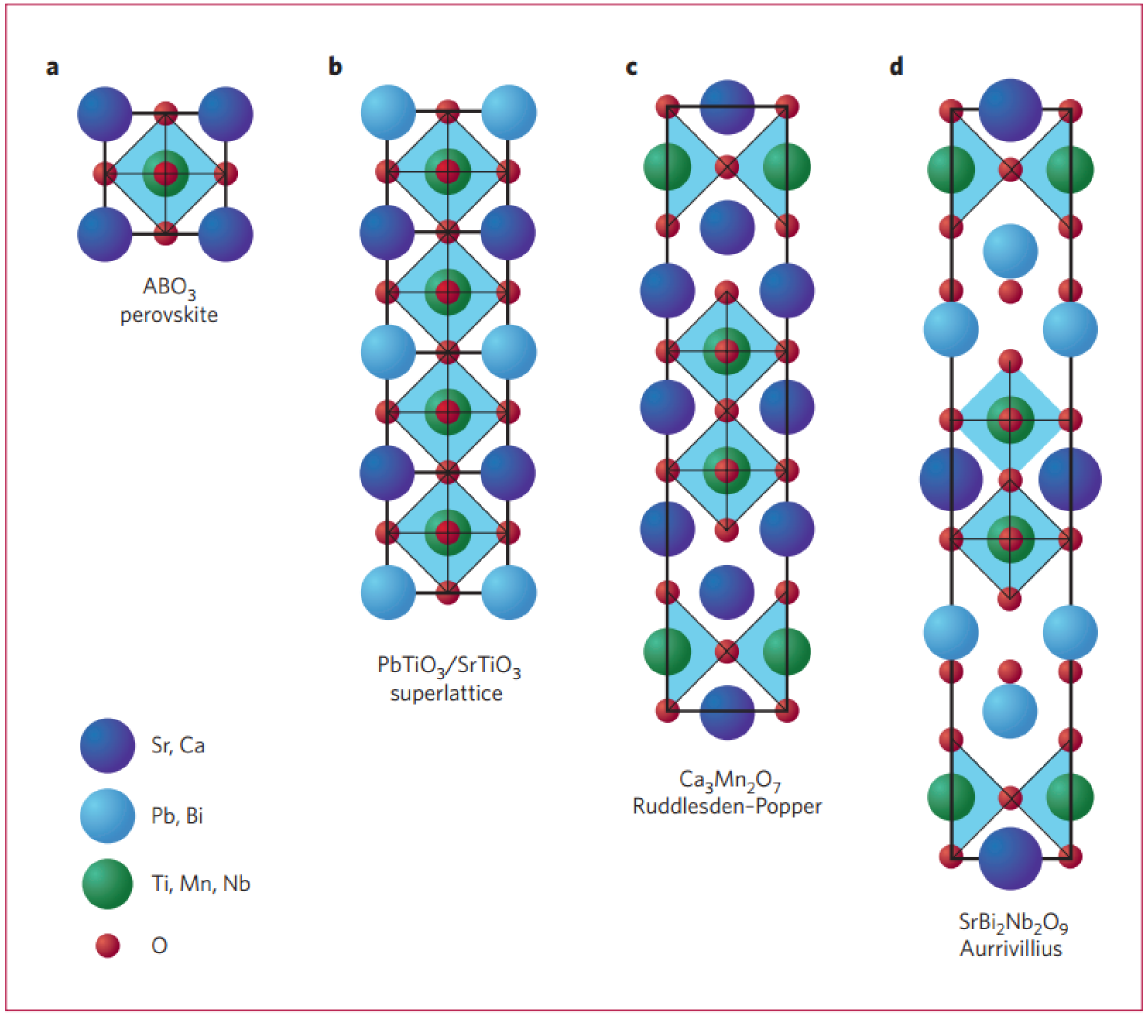
Phys. Rev. Lett. 109, 127207 (2012)

Coexistence of ferromagnetism and superconductivity (LAO/STO)



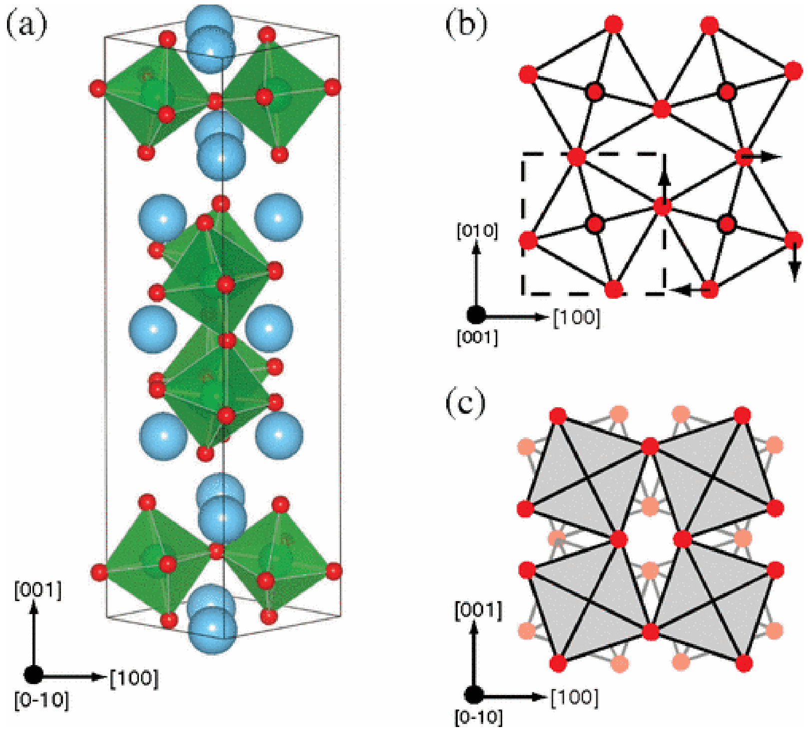
Bert,.. Hwang,Moler, Nature Physics**7**, 767-771 (2011).

Improper ferroelectricity



Ghosez, & Triscone, "MULTIFERROICS: Coupling of three lattice instabilities".***Nat. Mater.*** 10, 269-270, (2011).

a polar ferroelectric instability, and non-polar instabilities related to rotations and tilts of the oxygen octahedra



Phys. Rev. Lett. 106, 107204 (2011)

Electric Field Tuning of the Rashba Effect in Perovskite Structures

PRL 112, 086802 (2014) PHYSICAL REVIEW LETTERS week ending 28 FEBRUARY 2014

Electric Field Tuning of the Rashba Effect in the Polar Perovskite Structures

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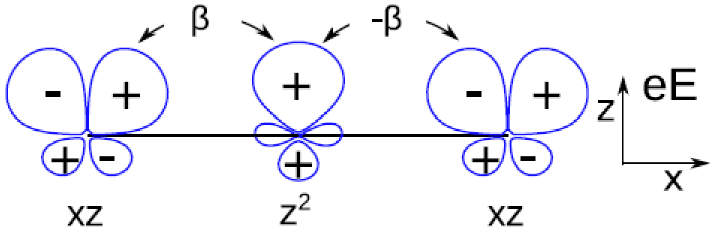
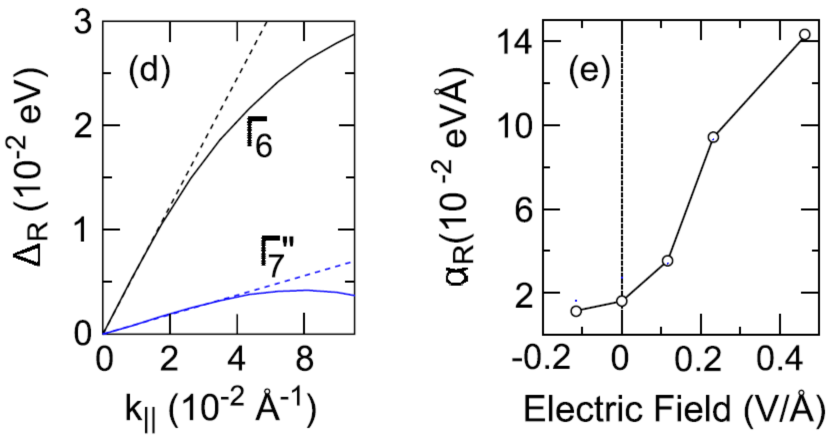
Department of Physics, University of Missouri, Columbia, Missouri 65211, USA
(Received 27 June 2013; published 25 February 2014)

We show that the Rashba effect at the polar perovskite surfaces and interfaces can be tuned by manipulating the two-dimensional electron gas by an applied electric field, using it to draw the two-dimensional electron gas out to the surface or push it deeper into the bulk, thereby controlling the surface-sensitive phenomenon. These ideas are illustrated by a comprehensive density-functional study of the recently discovered polar $KTaO_3$ surface. Analytical results obtained with a tight-binding model unravel the interplay between the various factors affecting the Rashba effect such as the strengths of the spin-orbit interaction and the surface-induced asymmetry. Our work helps interpret the recent experiments on the $KTaO_3$ surface as well as the $SrTiO_3/LaAlO_3$ interface.

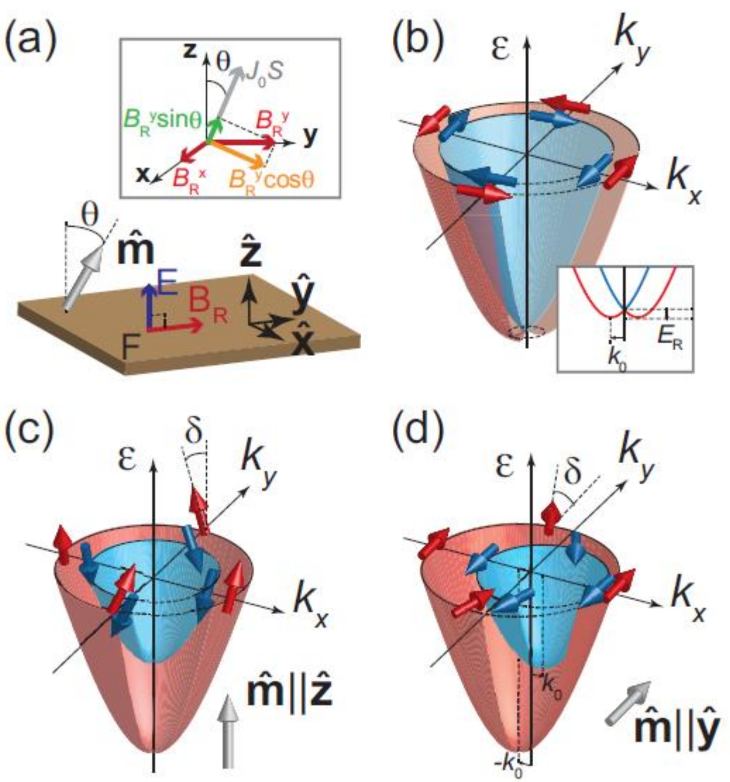


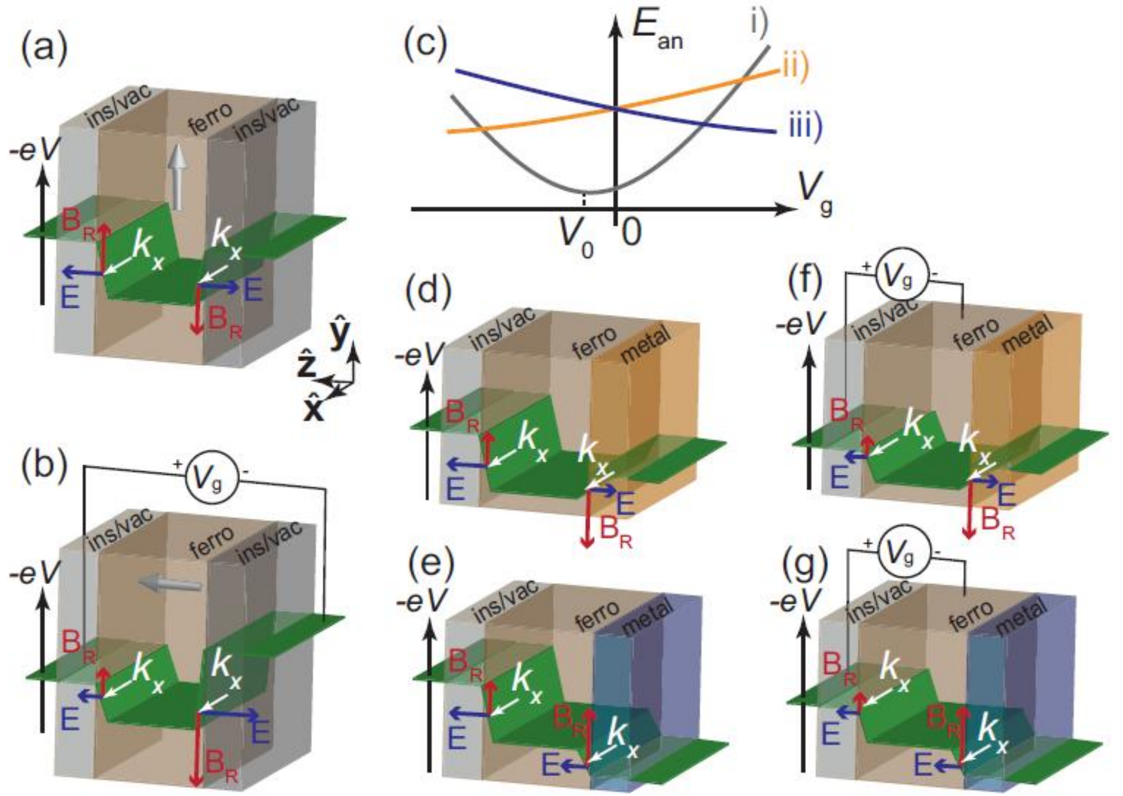


Rashba effect can be tuned in the polar perovskite oxides by manipulating the 2DEG profile by an external electric field

Rashba Spin-Orbit Anisotropy

$$H=\frac{p^2}{2m}-J_0\,\mathbf{S}\cdot\boldsymbol{\sigma}+\frac{\alpha_R}{\hbar}\left(\sigma_x p_y-\sigma_y p_x\right)$$





$$E_{an}=E_R\left[1-\frac{2T}{J_0 S}\right]\cos^2\theta,\qquad T=\frac{\hbar^2}{2m}\left(\langle k_x{}^2\rangle_{\uparrow}-\langle k_x{}^2\rangle_{\downarrow}\right)$$

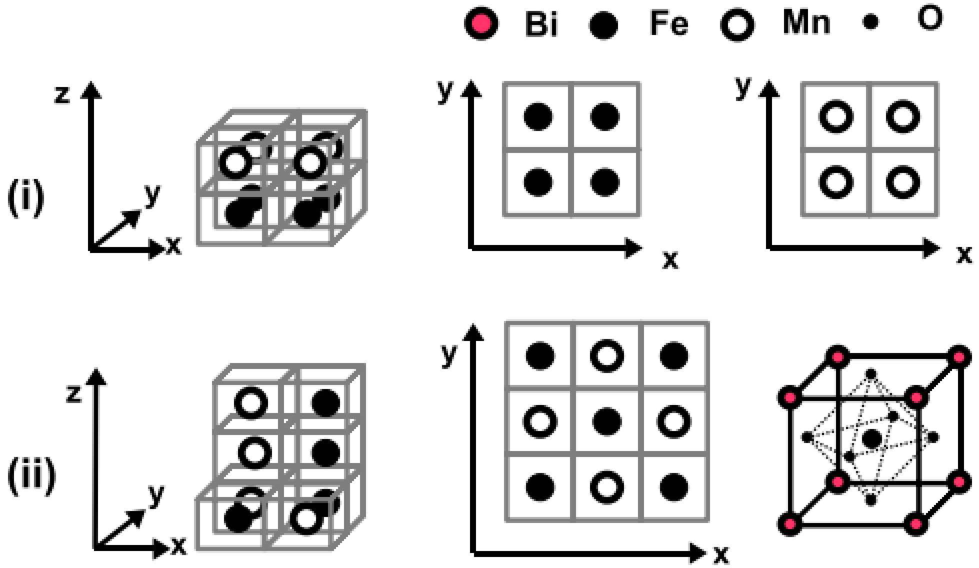
S. E. Barnes, J. i. Ieda, and S. Maekawa, Sci. Rep. 4, 4105 (2014)

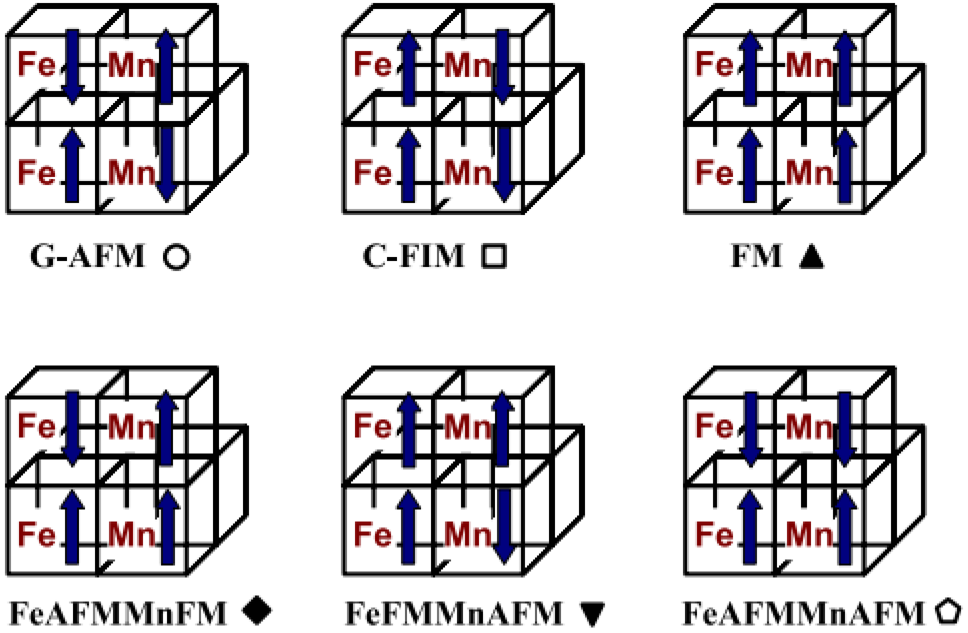
人工结构:BFMO（棋盘型)

PRL 104, 037202 (2010) PHYSICAL REVIEW LETTERS week ending 22 JANUARY 2010

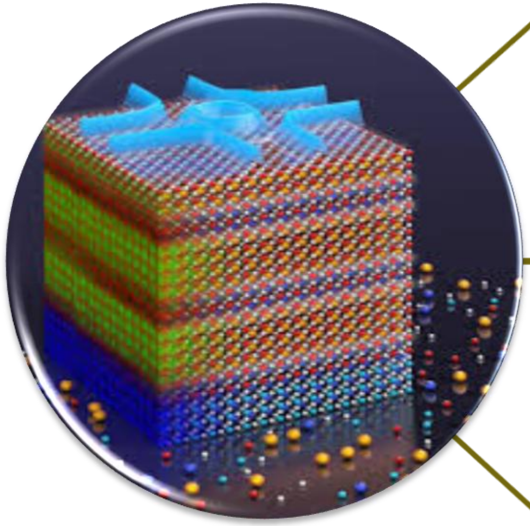
Magnetostructural Effect in the Multiferroic $BiFeO_3$-$BiMnO_3$ Checkerboard from First Principles

L. Pálová, P. Chandra, and K. M. Rabe





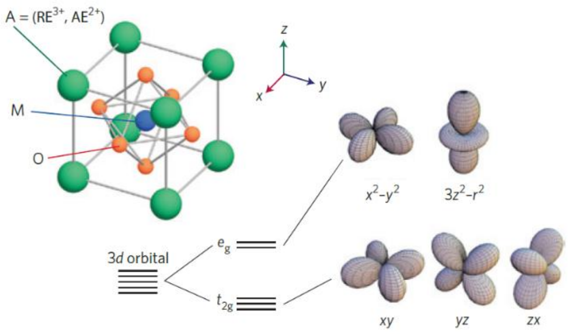
Powerful tools to study oxides interface

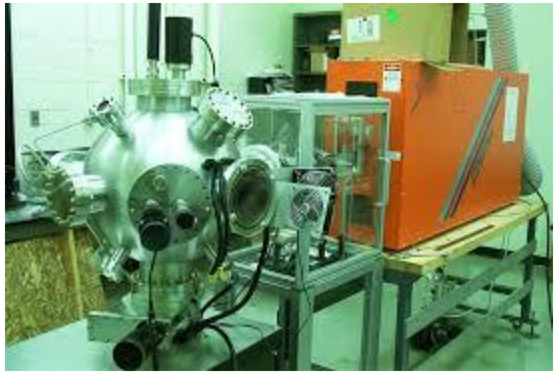


First principles calculation

Cutting edge film growth technology

Atomic scale Observation





第一性原理计算手段（不断增加中）

第一性原理计算

晶体性质

能带，态密度，结构优化，弹性模量，杨氏模量，硬度，韧性

材料物性

磁学特性：
磁矩，磁交换关联，磁有序

电学特性：
极化，介电

光学特性：
介电函数，反射，折射率

动力学性质

结合热力学原理进行分子动力学模拟：
温度相关性质

低维及微结构

表面、界面：
表面能，界面能，吸附能，功函数

微结构：
纳米管，纳米线，掺杂，渗透

PLD薄膜制备系统（一托二）

铁电/铁磁/半导体外延制备平台

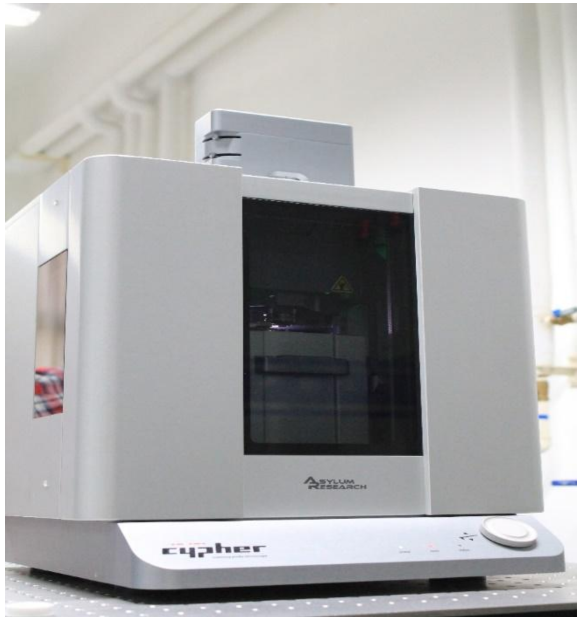
氧化物铁电体/多铁体分子束外延制备

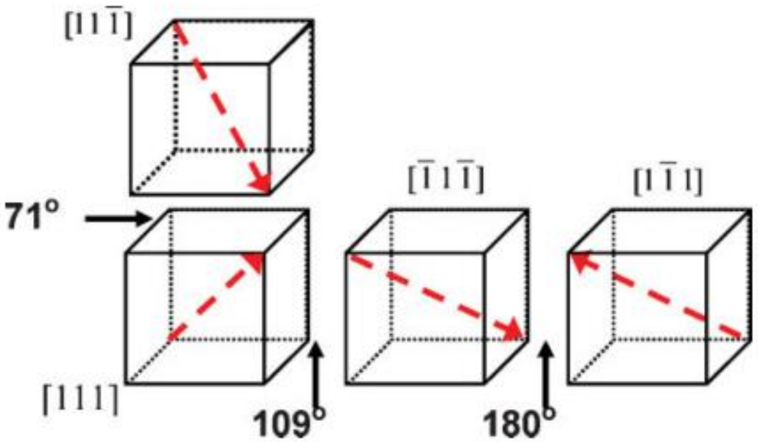
- 氧化物单晶铁电薄膜
- 氧化物铁电/铁磁复合多铁性体系
- 铁磁/铁电薄膜的界面控制

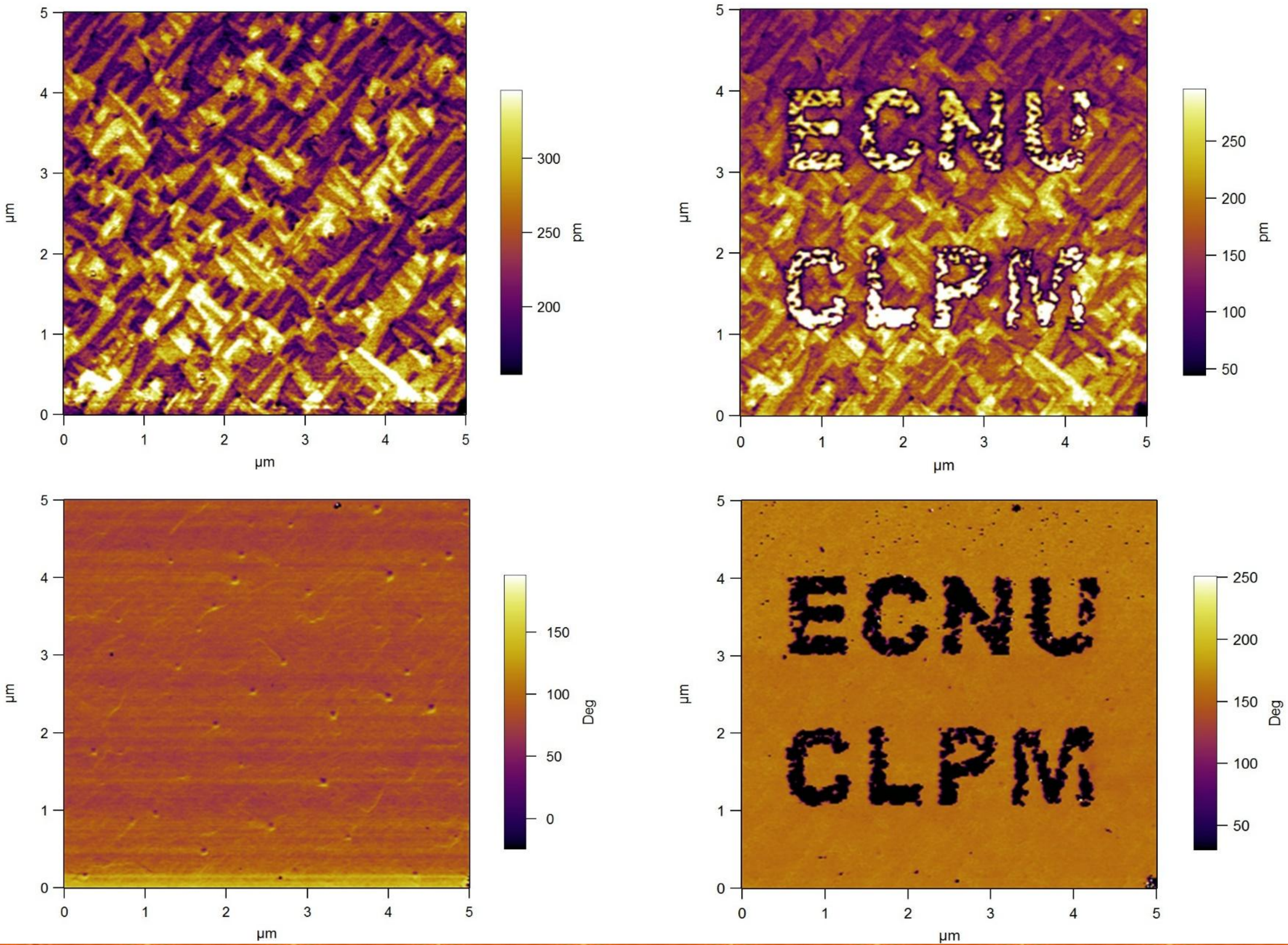
窄禁带半导体材料分子束外延制备

- 窄禁带半导体材料（MCT）
- 窄禁带半导体低维结构（异质结、量子阱）
- 磁性窄禁带半导体材料

压电原子力显微镜对自制BFO薄膜的电畴操作

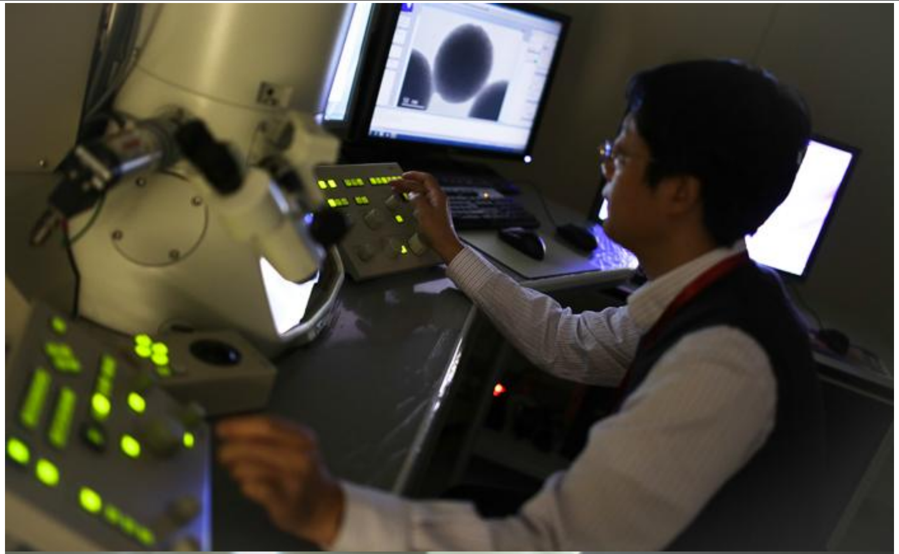
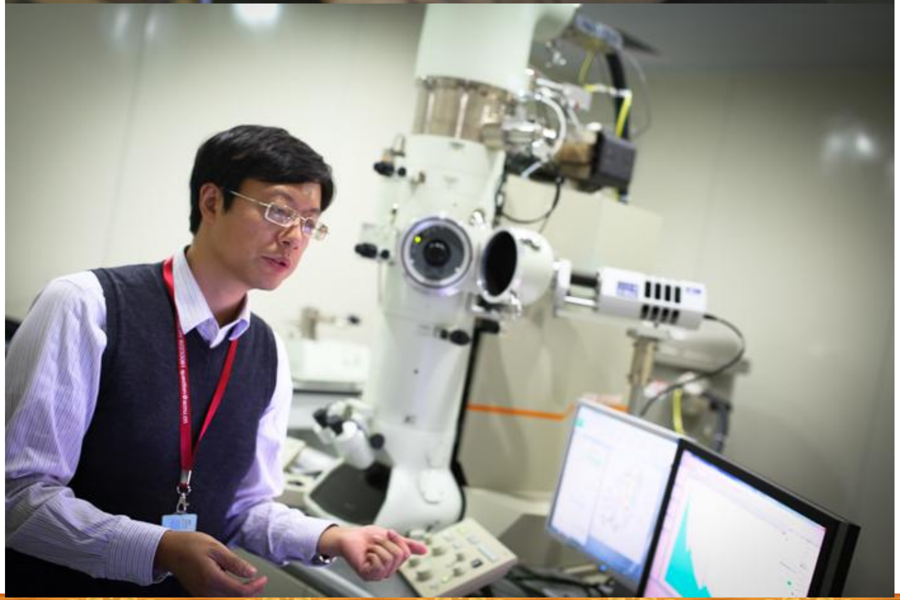






透射电镜实验室（和设备处合建）

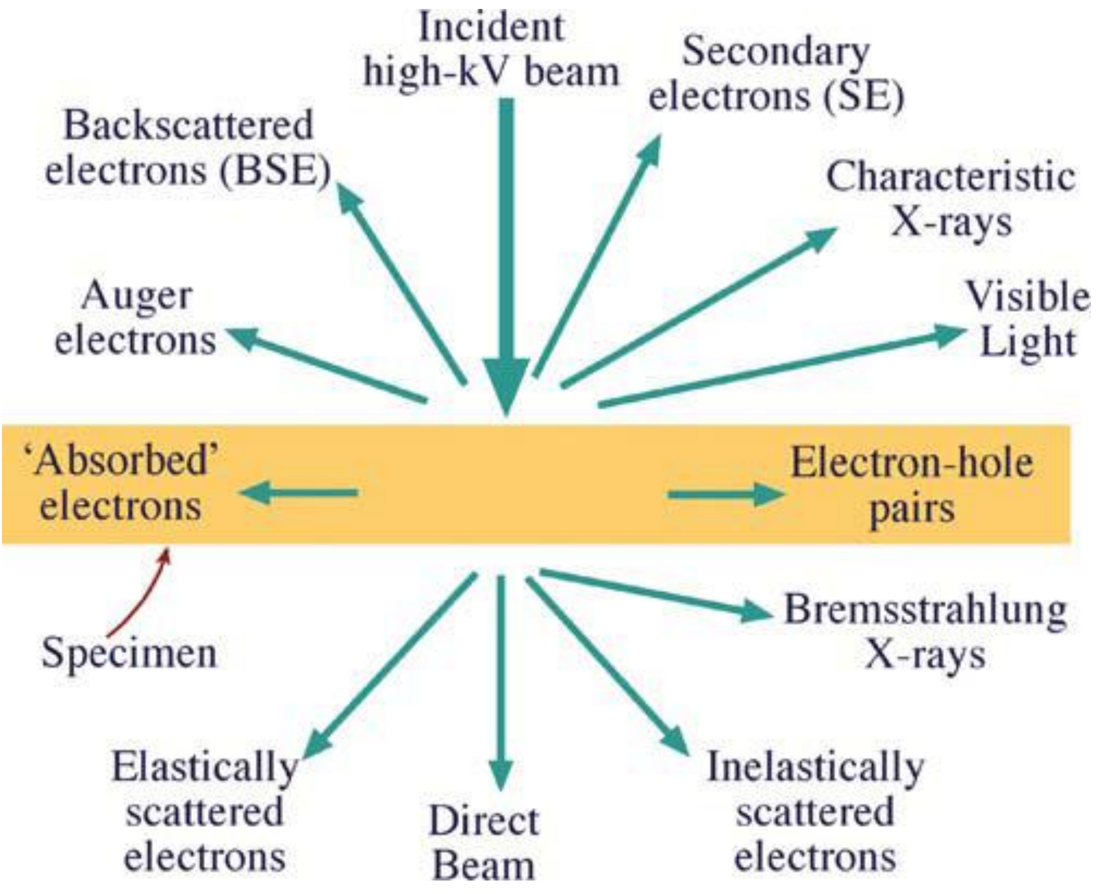
- 透射电镜(200kV场发射 + STEM + EDS + EELS）
- 扫描电镜（冷场发射）
- 材料样品透射电镜制样平台（切割、研磨、抛光、凹坑、离子减薄等全套仪器设备）
- 透射电镜图像模拟分析平台（基于Mac平台进行SADP、HRTEM、STEM等图像模拟）





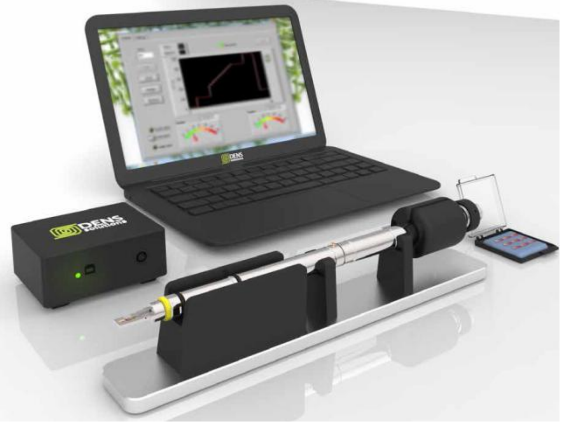

已经具备的分析手段和能力

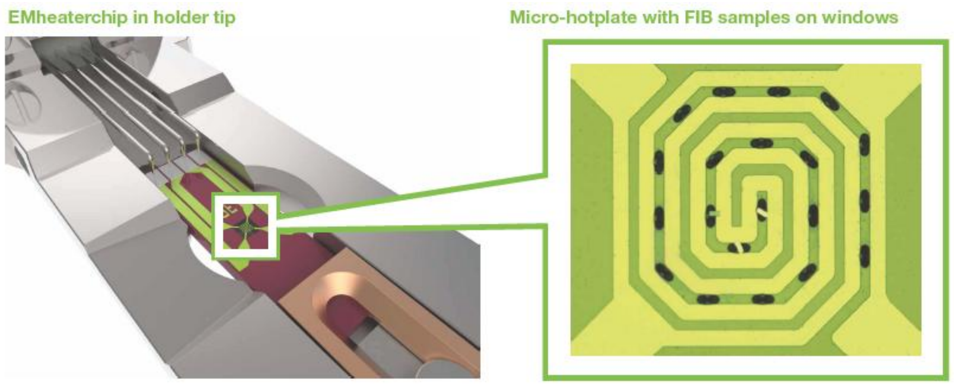


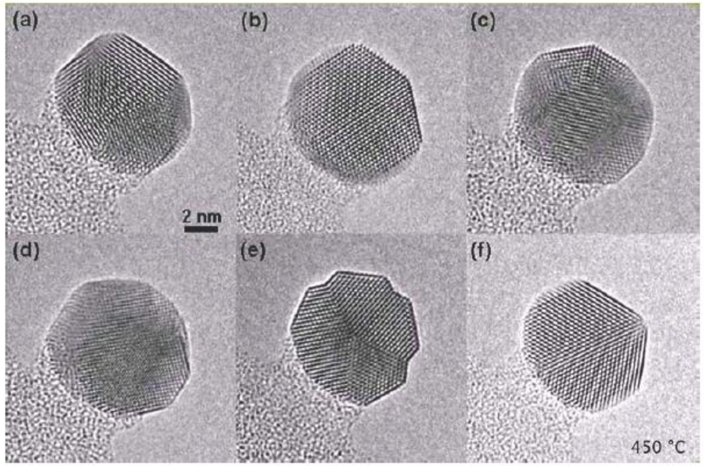
- 电子衍射（SAD）
  晶体结构
- 明场（BF）像、暗场（DF）像
  形貌
- 高分辨成（HRTEM）像
  原子结构、晶体缺陷
- Z衬度像（HAADF）
  原子结构、晶体缺陷、成分
- X射线能谱（EDS）
  化学成分、元素分布
- 电子能量损失谱（EELS）
  化学键、价态、配位

原位加热/电学测量双倾样品杆

荷兰DENS solution DH30-4M-JU

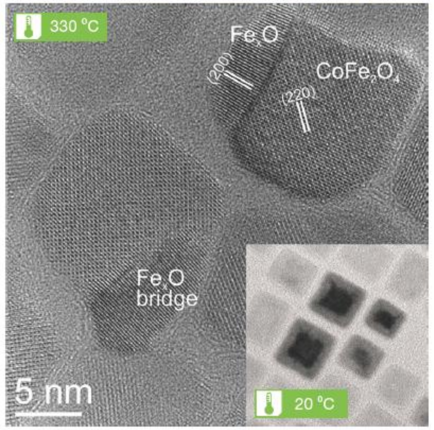






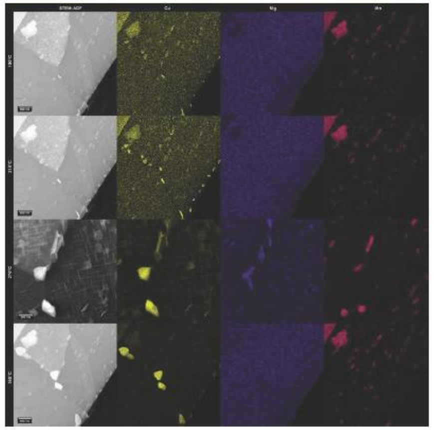
Morphological transformations of a Au nanoparticle at 450 °C
N.P. Young et al., Ultramicroscopy, 2010, 110/5

1. Imaging of structure evolution of core-shell particles



In situ HREM imaging of FexO/CoFe$_2$O$_4$ core shell particles at elevated temperatures. 'Initially' core shell NC arrays at RT, shown in the inset, start reconfiguration at 330 °C. FexO left the shell of CoFe$_2$O$_4$, segregated at the exterior of the shells, forming "snow-man-type" particles.
Anil O Yalcin et al. 2014 *Nanotechnology* 25 055601

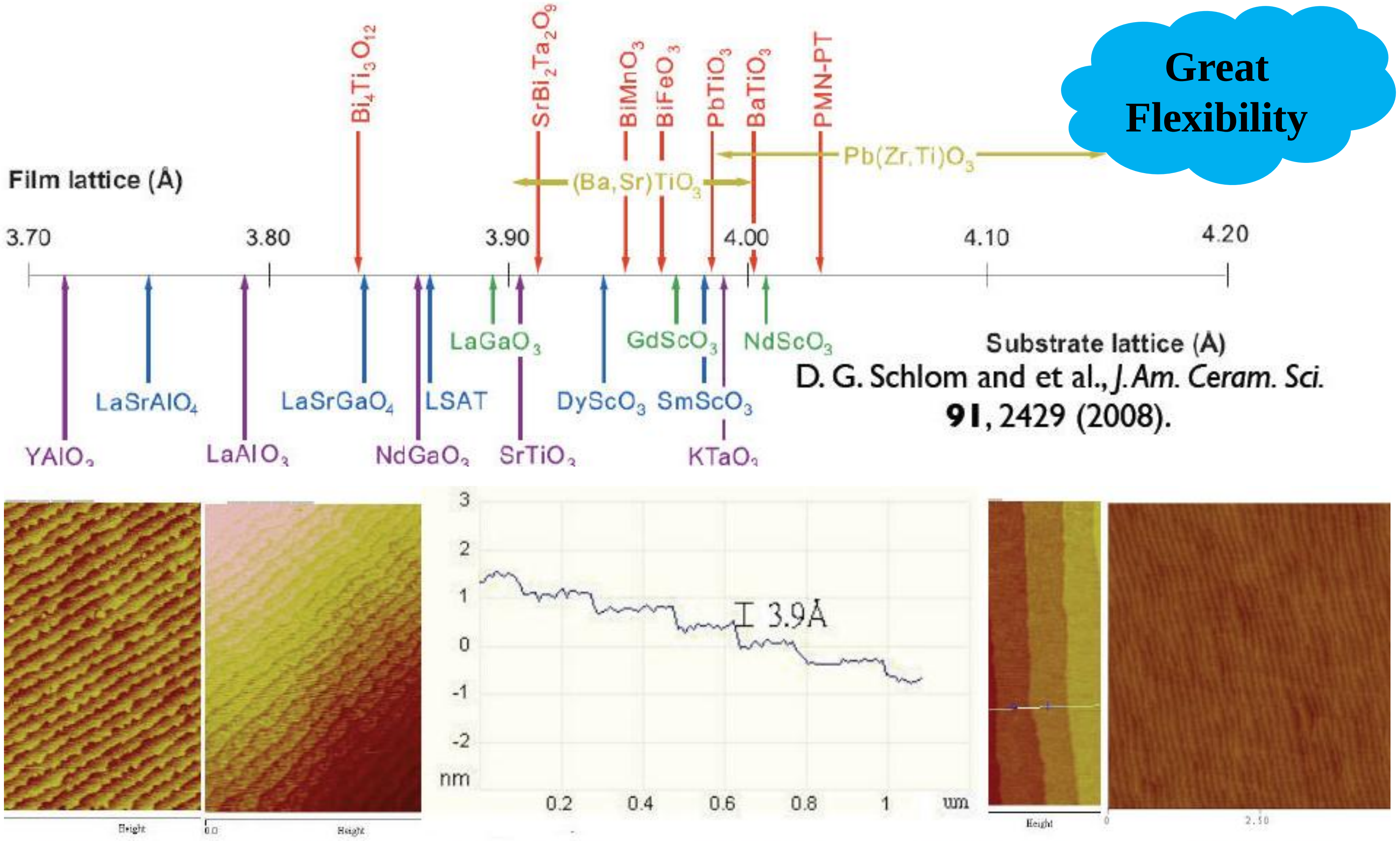
2. Structure & chemical mapping of Al alloy annealing



STEM imaging and chemical mapping of in-situ temperature annealing of Al alloys. It shows the structure and composition evolution during the growth and dissolve of lath-like S-type of precipitates at varies of temperatures.
Sairam K. Malladi *Nano Lett.*, 2014, 14 (1), pp 384–389

Advanced Experimental Technique

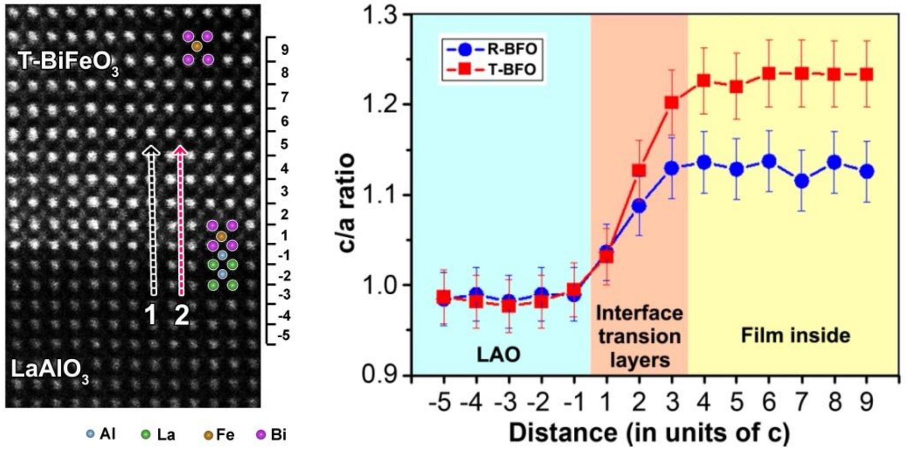
Courtesy of Y.-H. Chu

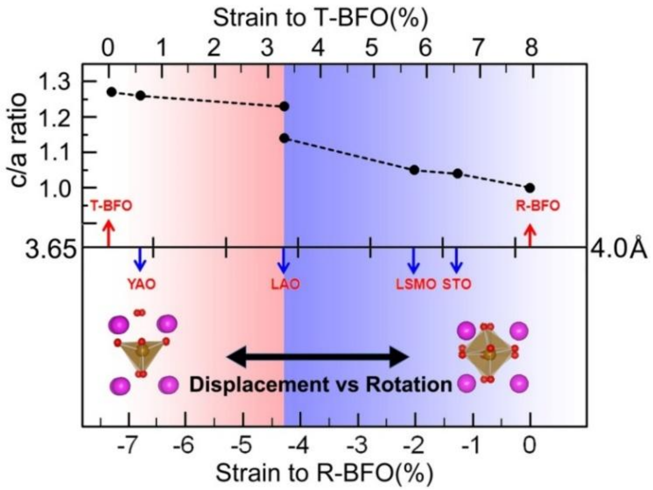


Great Flexibility

$YAlO_3$ $LaAlO_3$ $NdGaO_3$ $SrTiO_3$ $DyScO_3$ $NdScO_3$

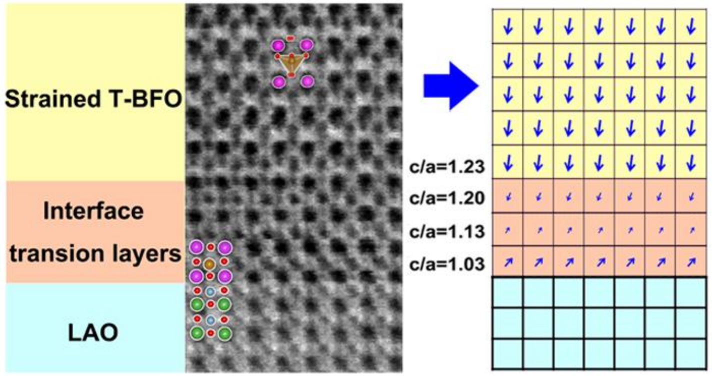
$BiFeO_3/LaAlO_3$界面处极化钉轧及弛豫





界面处存在2-3个单层的过渡层（上图）

新的界面极化钉轧及弛豫现象（下图）



相稳定性

T-BFO ⟷ R-BFO

↓ ↓

Fe离子位移 vs FeO_6八面体倾转

↓ ↓

压应力 拉应力

R. Huang *et al*., Adv. Funct. Mater. 24, 793-799 (2014)

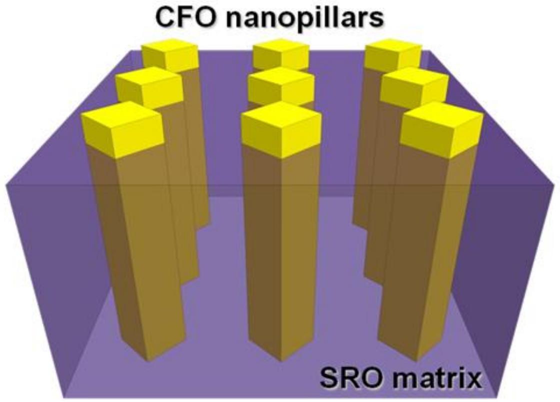
揭示了磁耦合$SrRuO_3$-$CoFe_2O_4$ 自组装纳米结构中Fe的扩散

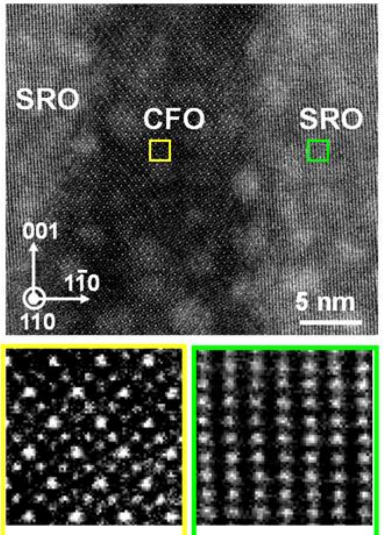
$SrRuO_3$ + $CoFe_2O_4$

（钙钛矿）　　（尖晶石）

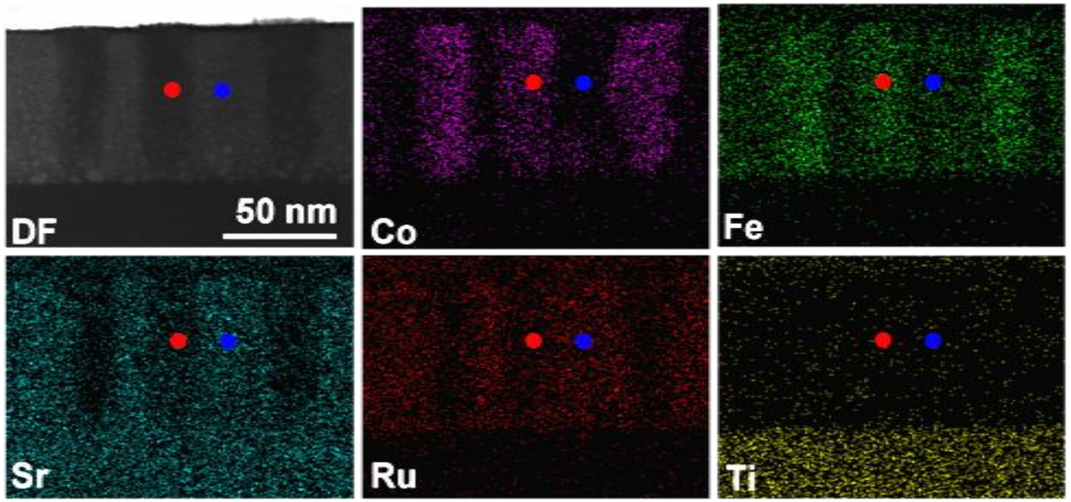
低场磁阻效应（LFMR）

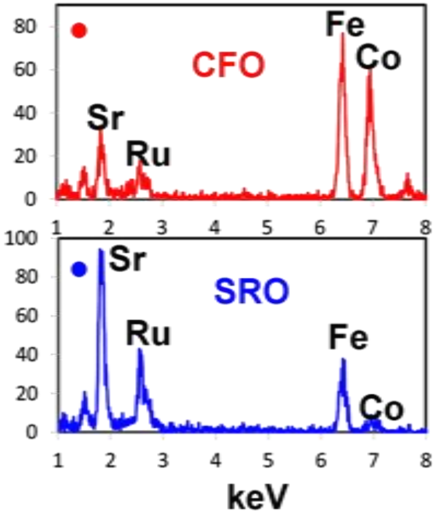
电阻率降低~40%@0.5T





CFO　SRO





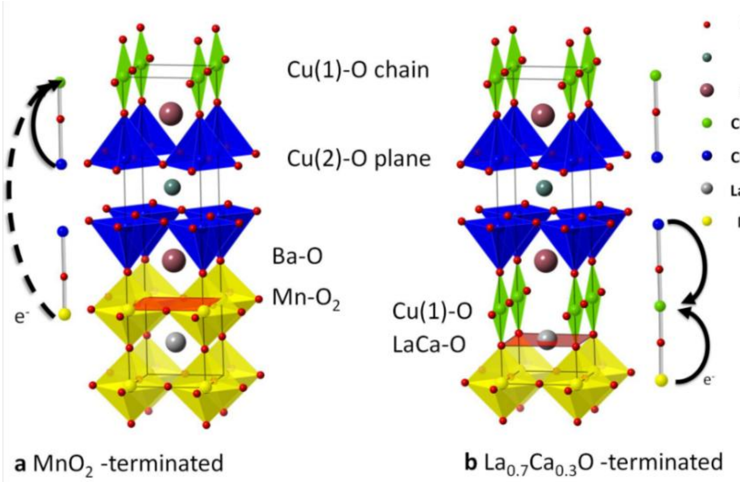
✓Fe扩散进入SRO中并取代Ru位

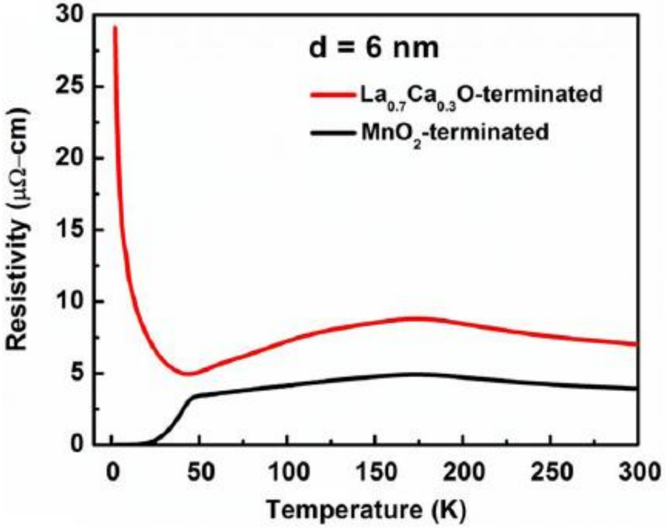
✓Fe掺杂SRO与CFO纳米柱相互作用

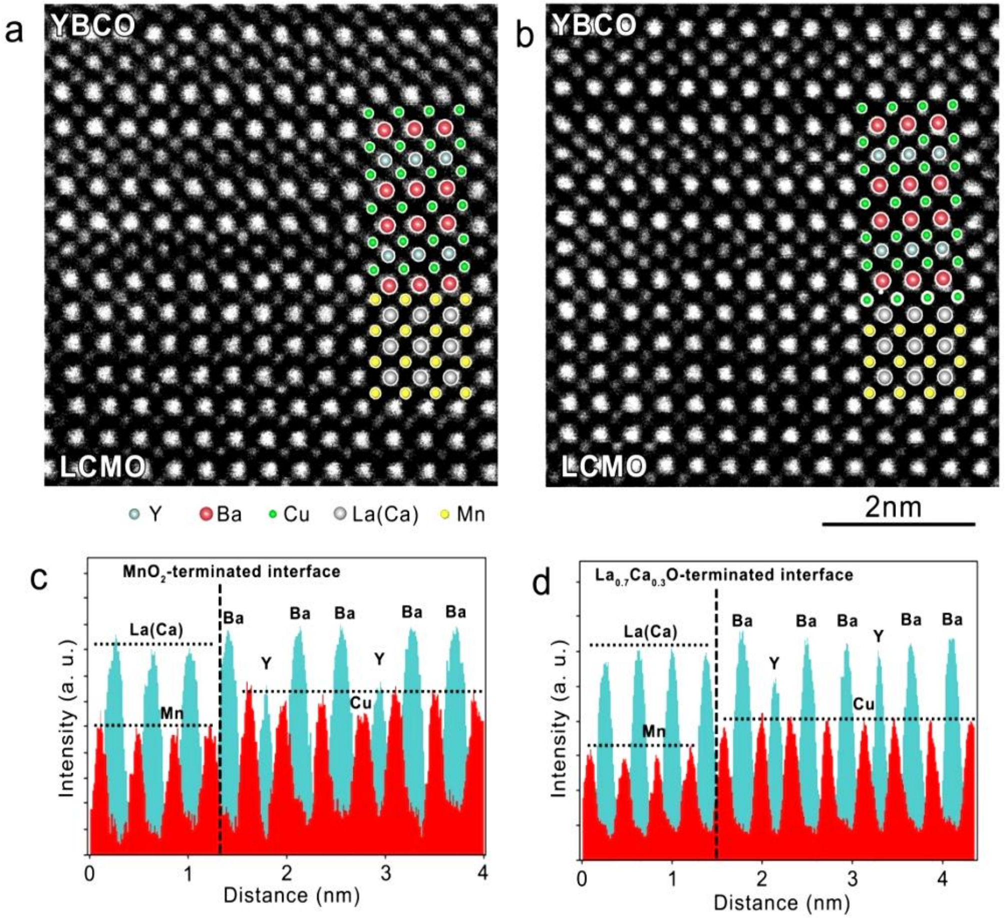
✓增强电子散射和自旋局域化

Adv. Mater. 25, 4753-4759 (2013)

$YBa_2Cu_3O_{7-x}/La_{0.7}Ca_{0.3}MnO_3$ 界面结构

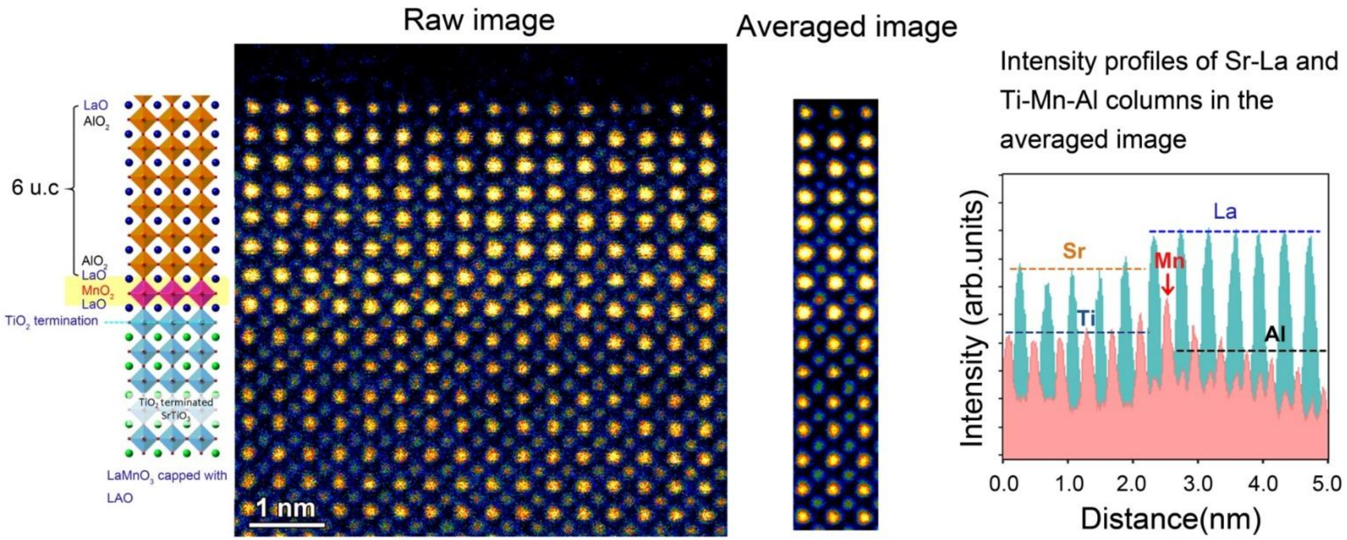


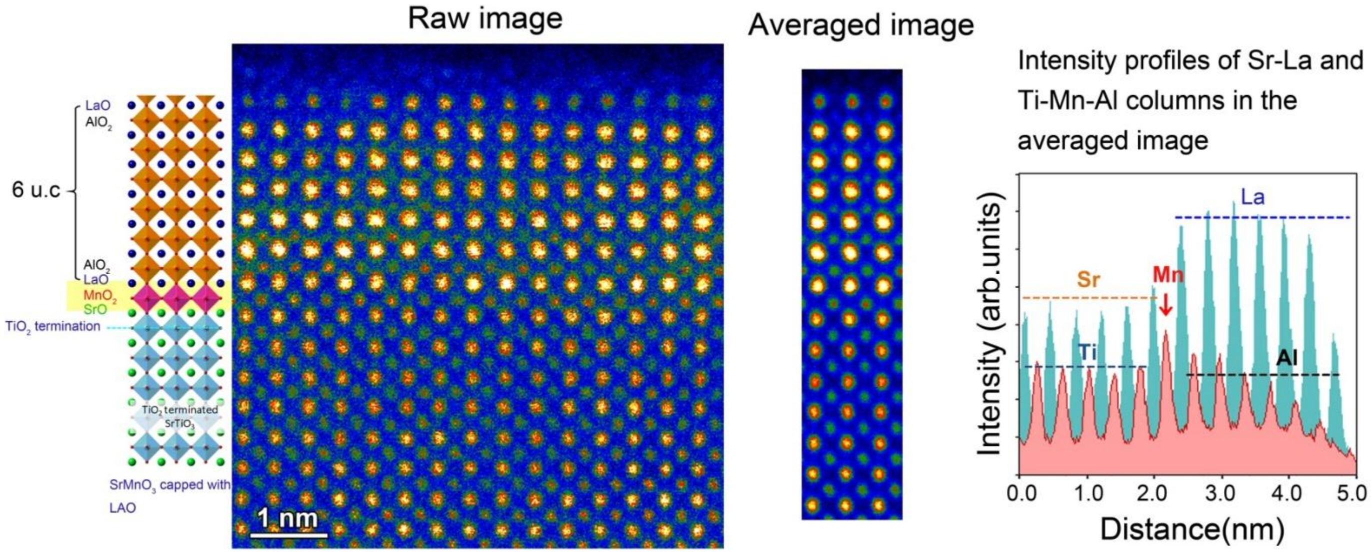




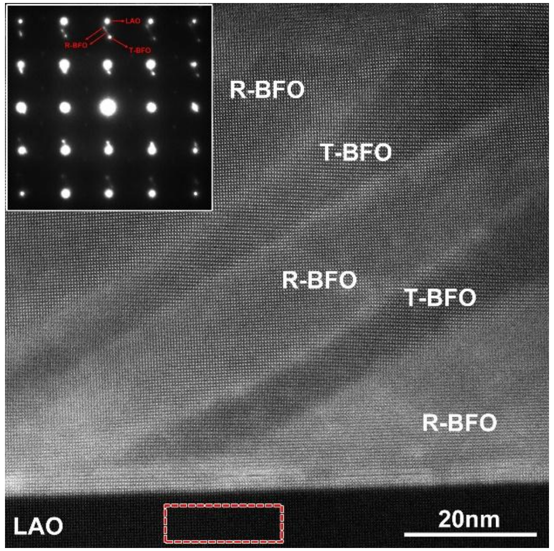
Atomic number：Y(39)、Ba(56)、Cu(29)、La(57)、Ca(20)、Mn(25)

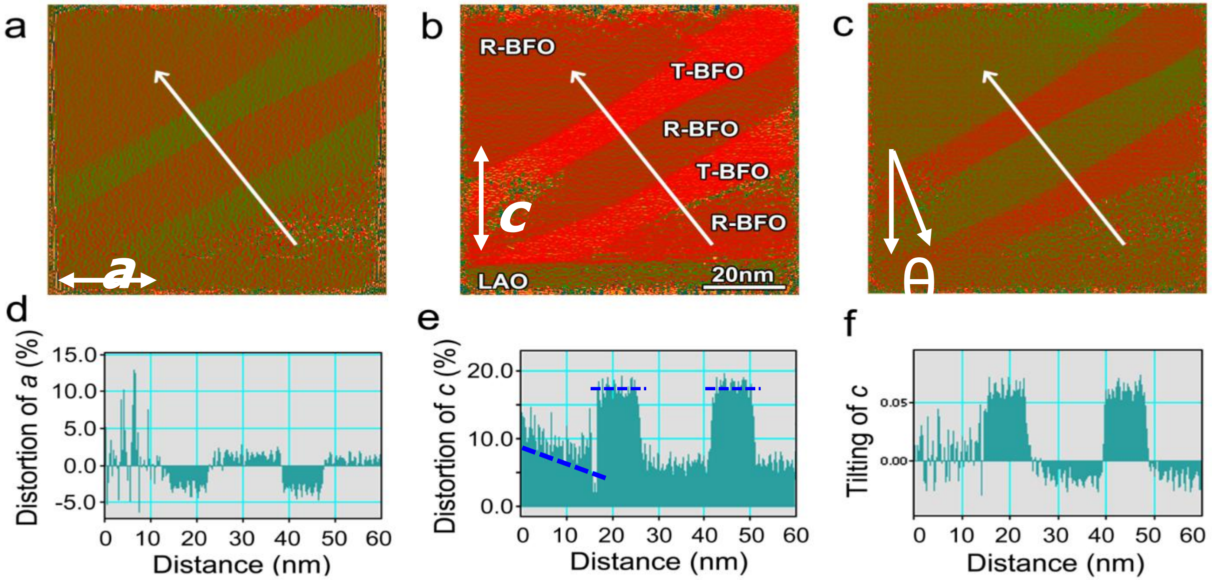
MnO_2单层结构的观察——挑战HAADF原子序数（Z）的分辨极限

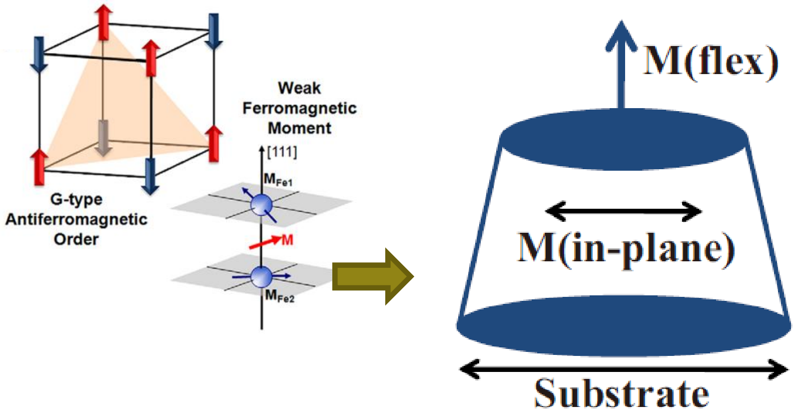




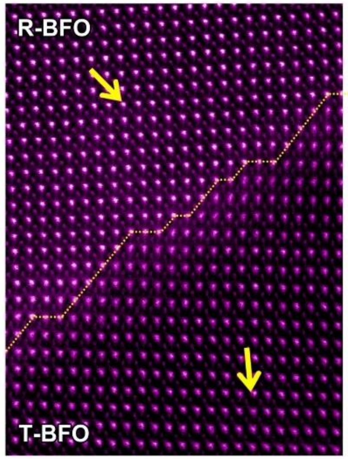
BFO薄膜中R/T相界面结构及相关性质

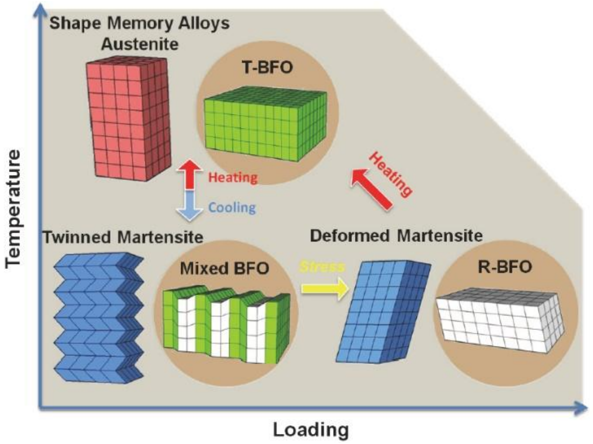




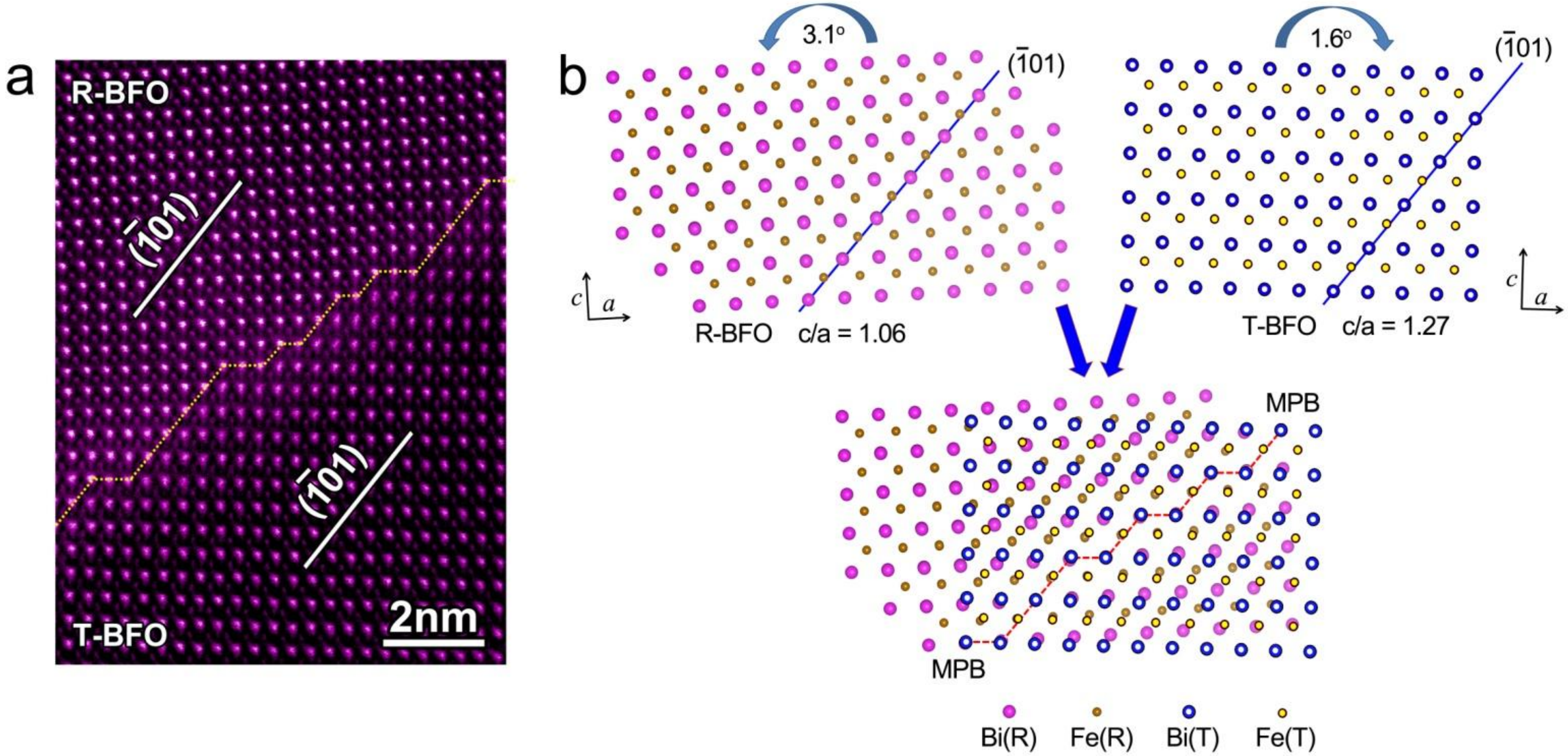


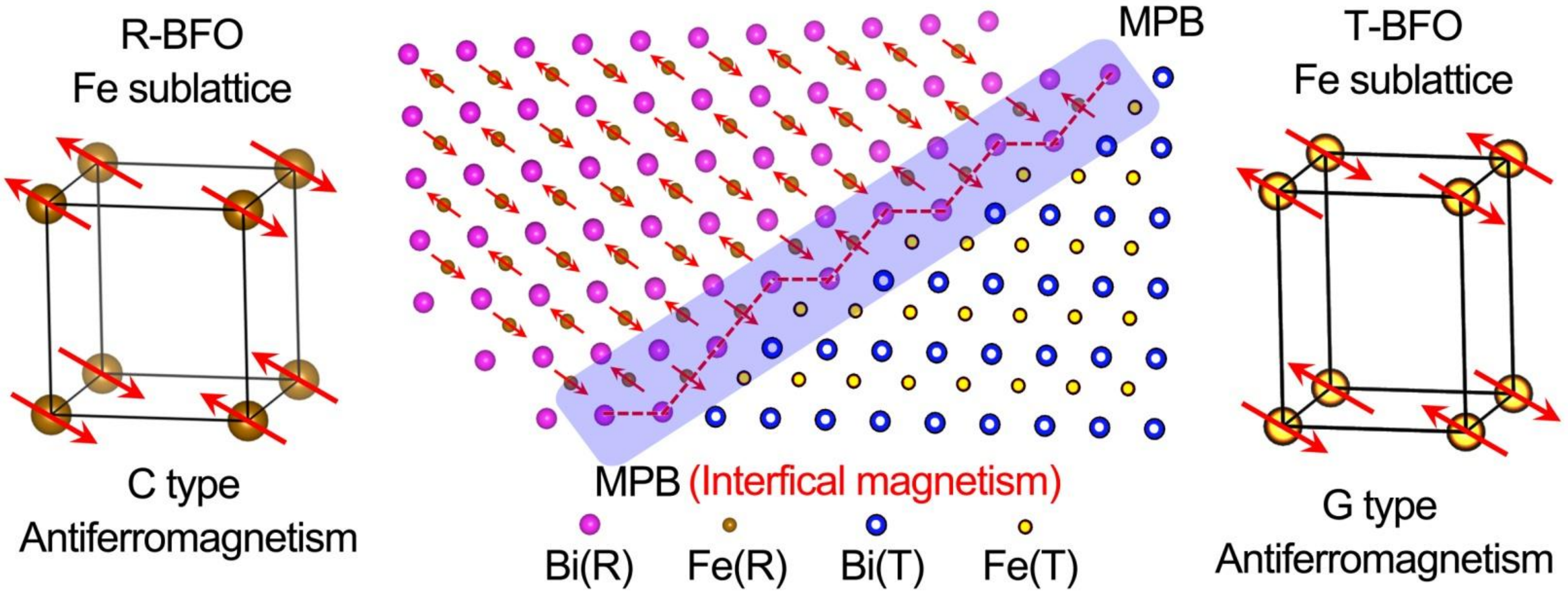
弯磁效应

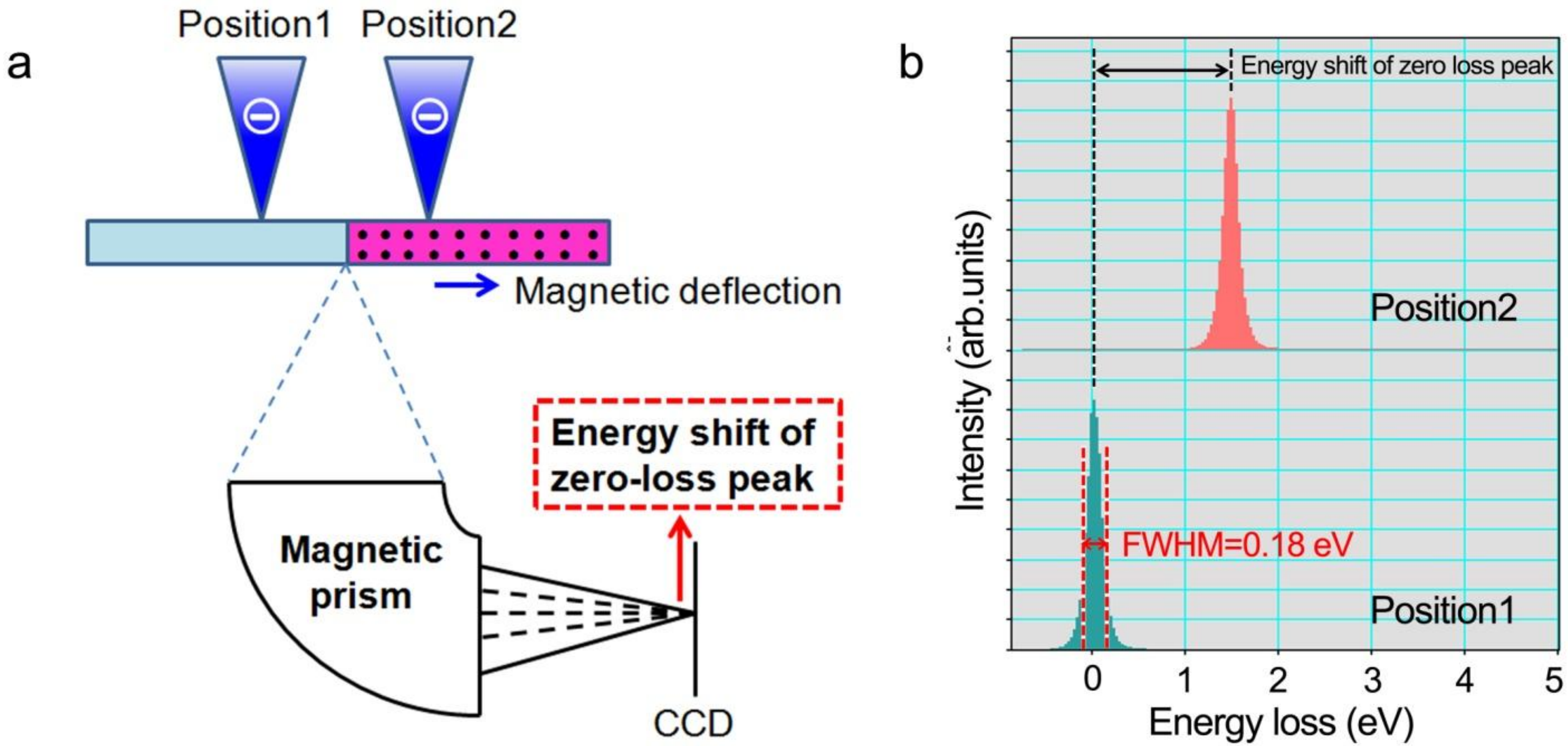


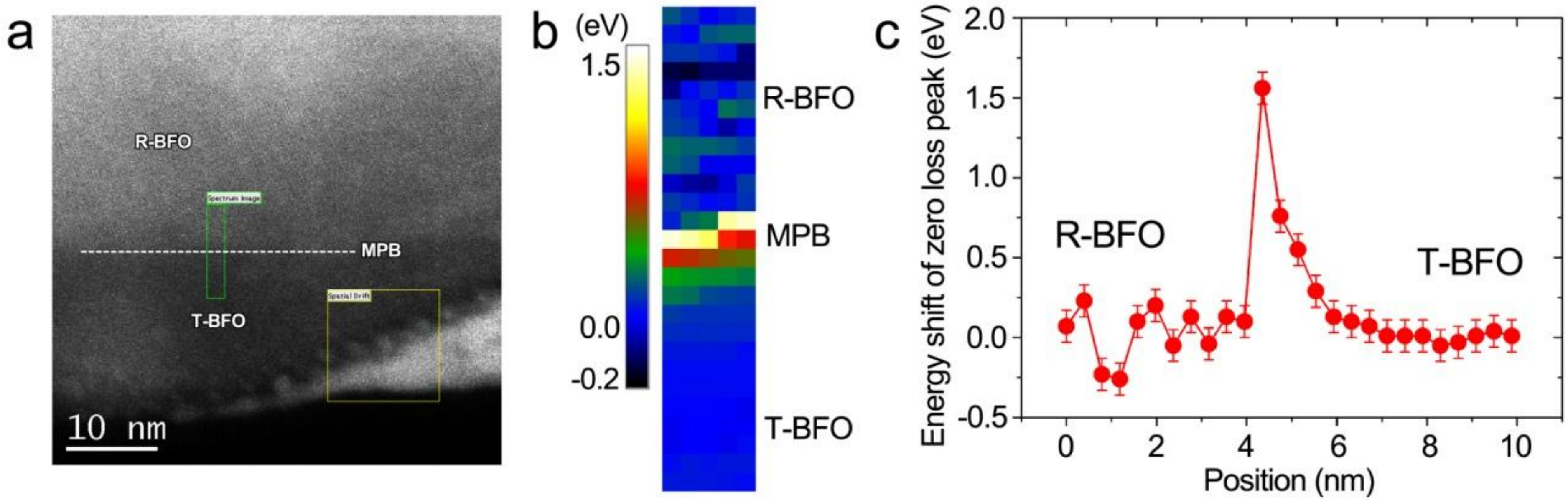


马氏体相变——形状记忆效应

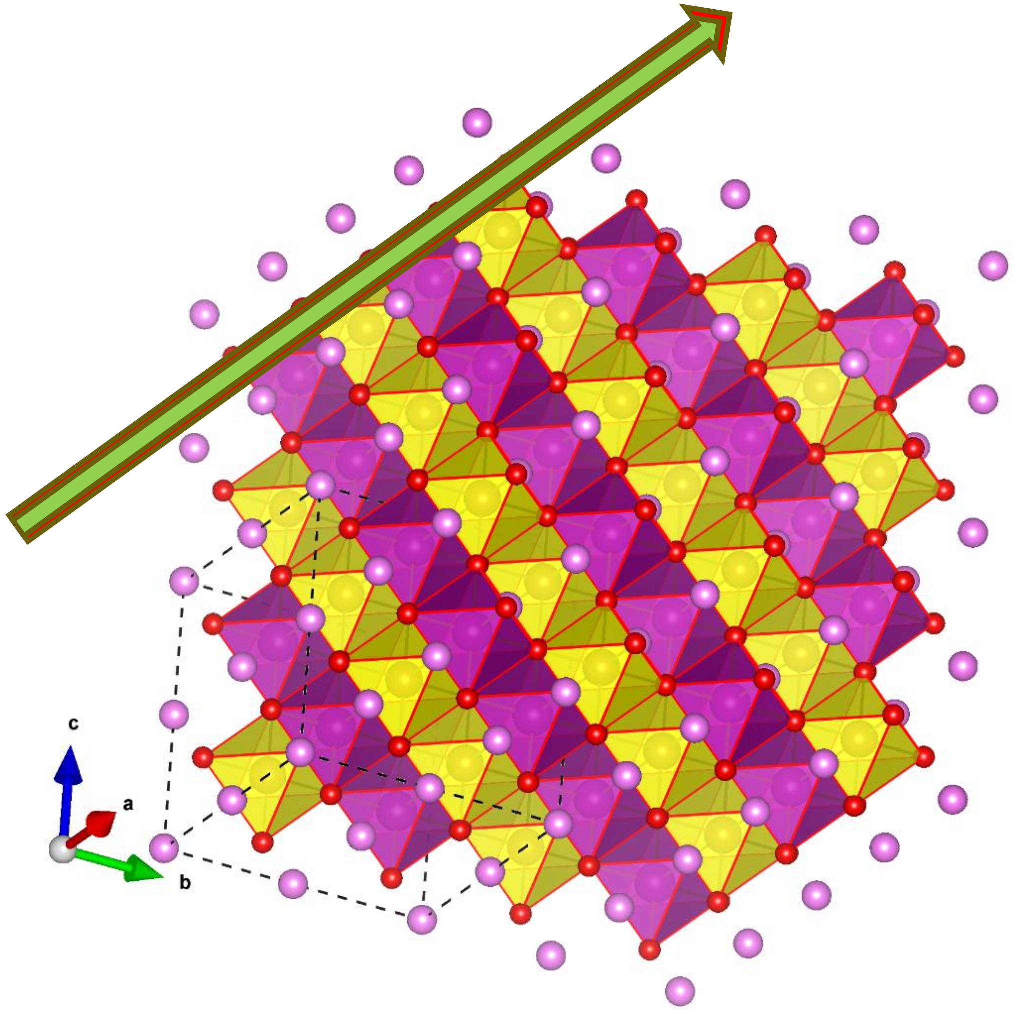

a
R-BFO
($\bar{1}$01)
($\bar{1}$01)
T-BFO
2nm
b
3.1°
($\bar{1}$01)
1.6°
($\bar{1}$01)
c
a
R-BFO c/a = 1.06
T-BFO c/a = 1.27
c
a
MPB
MPB
Bi(R) Fe(R) Bi(T) Fe(T)


R-BFO
Fe sublattice
C type
Antiferromagnetism
MPB
MPB (Interfical magnetism)
Bi(R)
Fe(R)
Bi(T)
Fe(T)
T-BFO
Fe sublattice
G type
Antiferromagnetism


a
Position1
Position2
Magnetic deflection
Energy shift of zero-loss peak
Magnetic prism
CCD
b
Energy shift of zero loss peak
Position2
FWHM=0.18 eV
Position1
Intensity (arb.units)
0
1
2
3
4
5
Energy loss (eV)


a
R-BFO
MPB
T-BFO
10 nm
b
(eV)
1.5
0.0
-0.2
R-BFO
MPB
T-BFO
c
Energy shift of zero loss peak (eV)
2.0
1.5
1.0
0.5
0.0
-0.5
0
2
4
6
8
10
Position (nm)
R-BFO
T-BFO

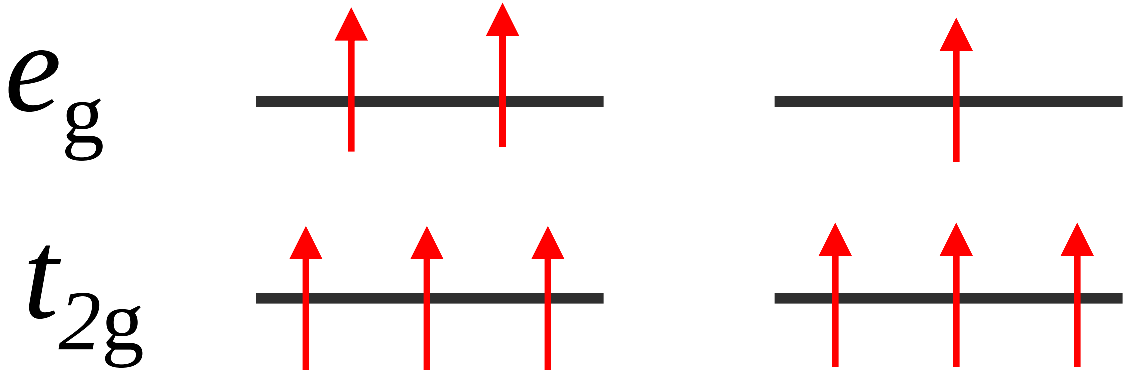
(111) BFMO superstructure



For G-type AFM of BFO:

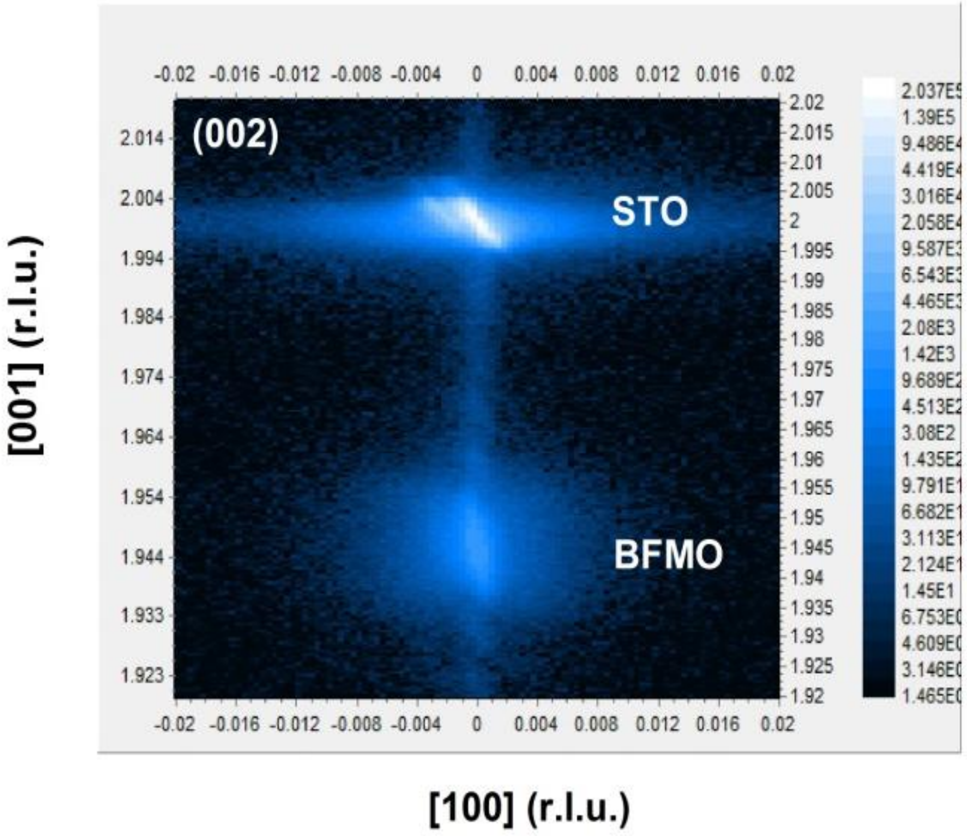
(111) plane is ferromagnetic plane!!!

Fe^{3+}: $3d^5$ Mn^{3+}: $3d^4$

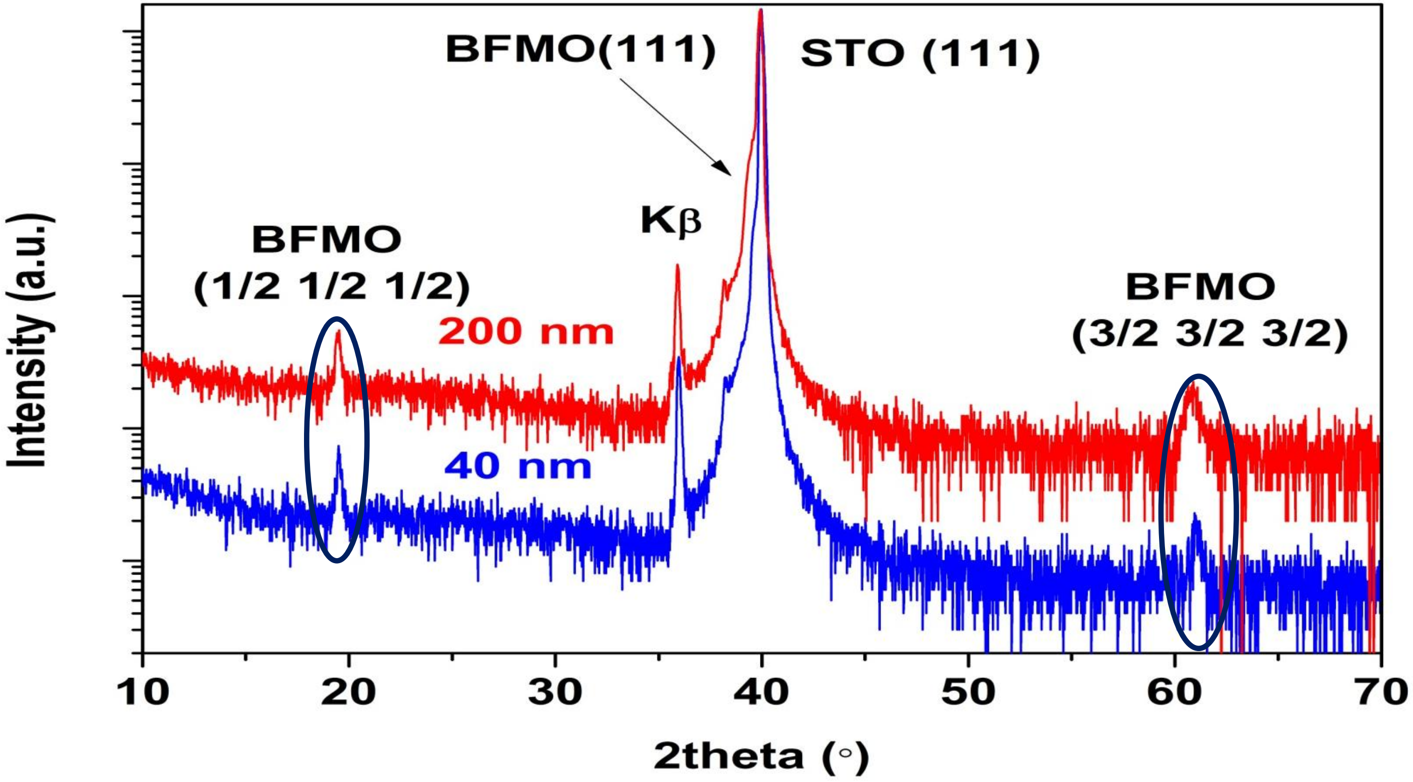


~5 μ_B ~4 μ_B

Double Perovskite: BFMO on STO(001)

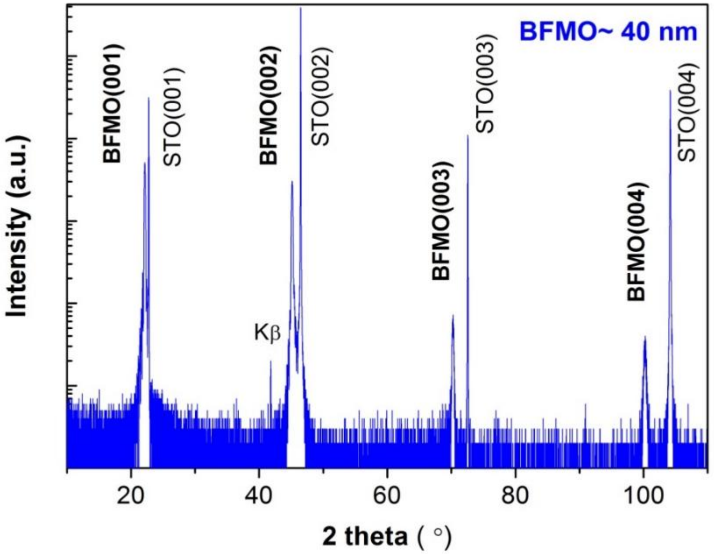


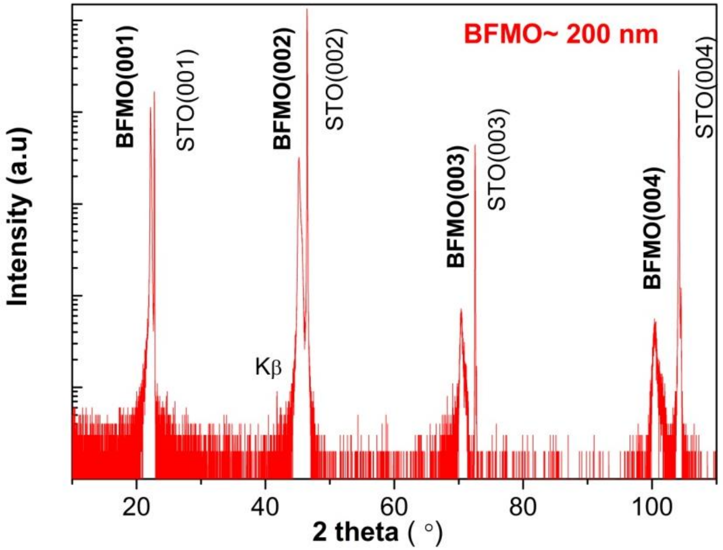
Reciprocal space mapping of (002) reflection
(40 nm-thick BFMO/STO substrate)

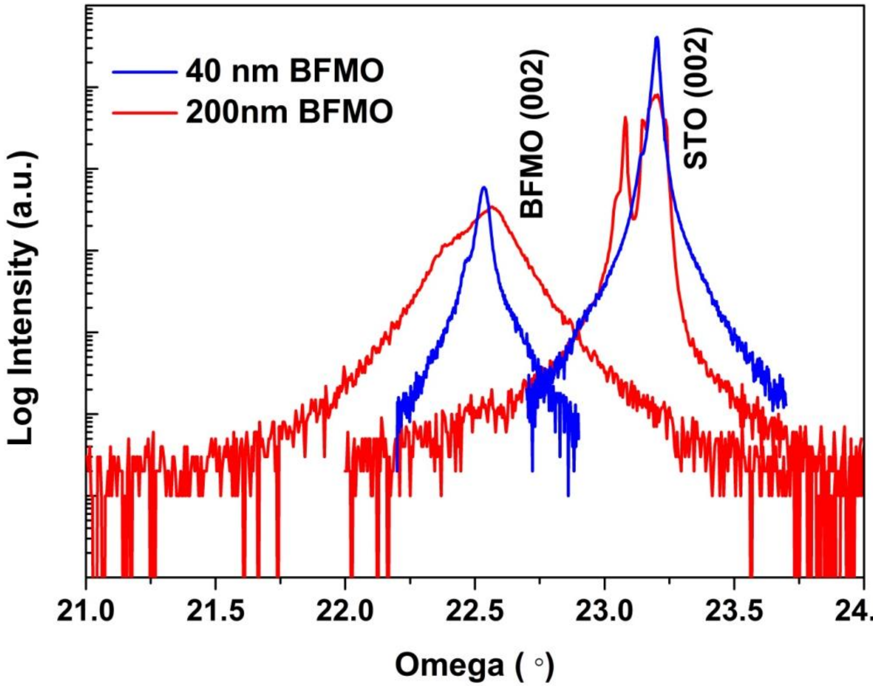


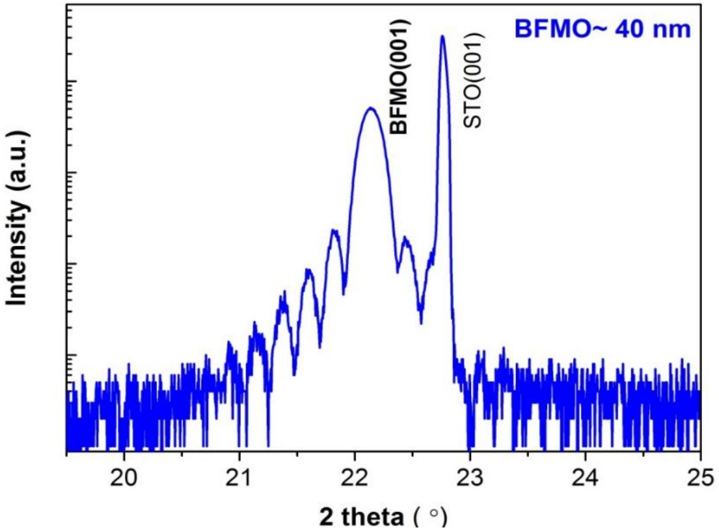
Asymmetric (111) 2theta-Omega XRD scan

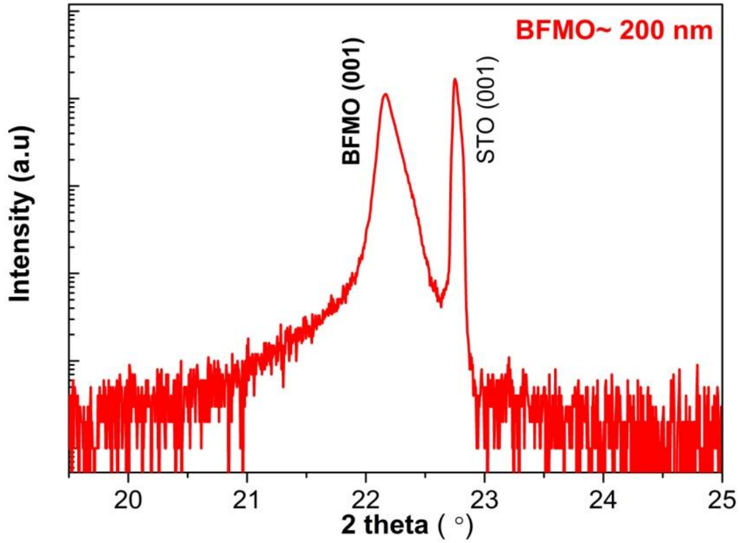
BFMO of different thickness









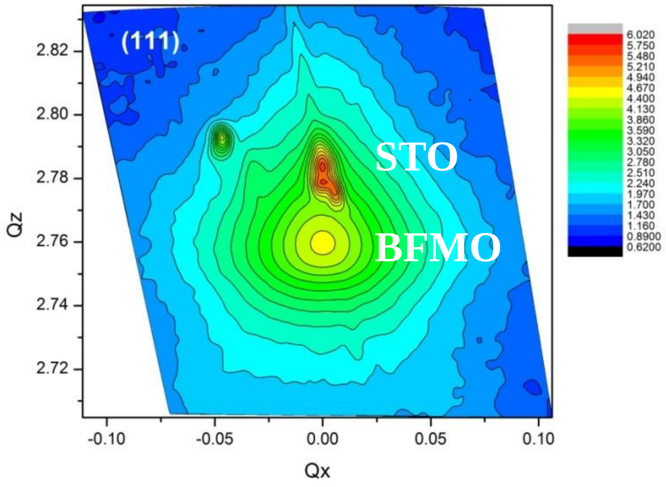


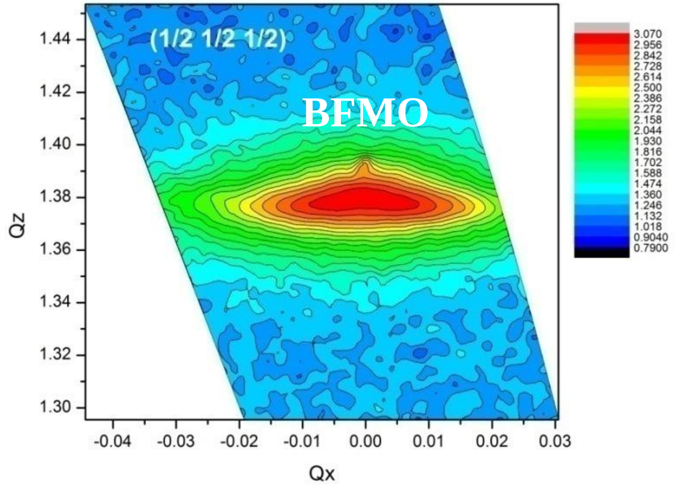
40 nm BFMO/STO (001)

200 nm BFMO/STO (001)

Certification of Fe and Mn ordering along [111] direction

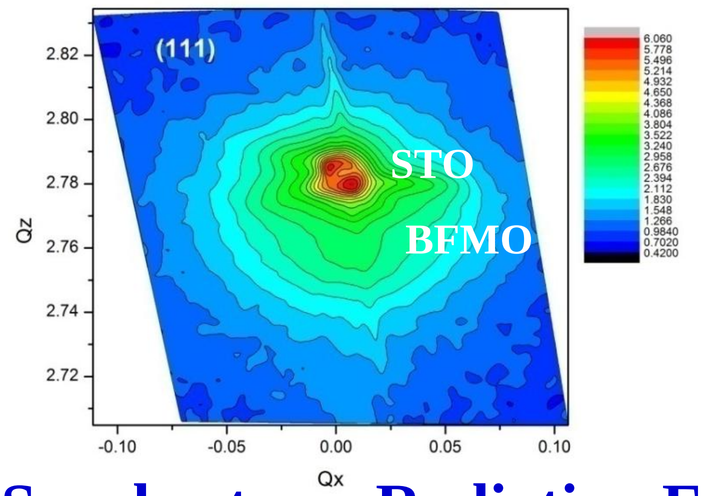
200 nm
BFMO

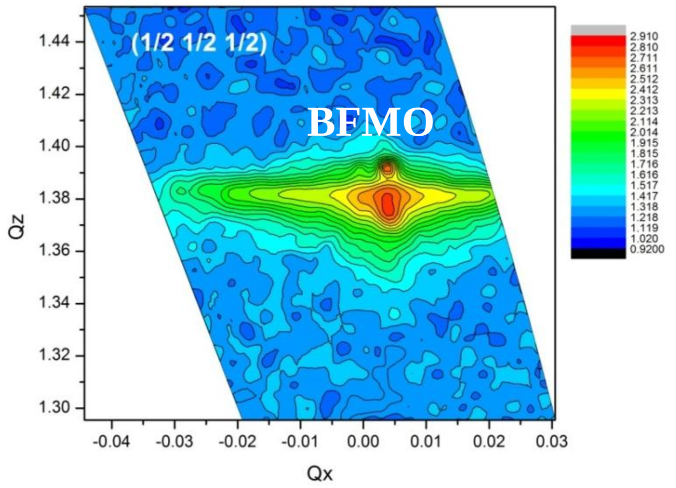




a=3.905Å
c=4.000Å

40nm
BFMO

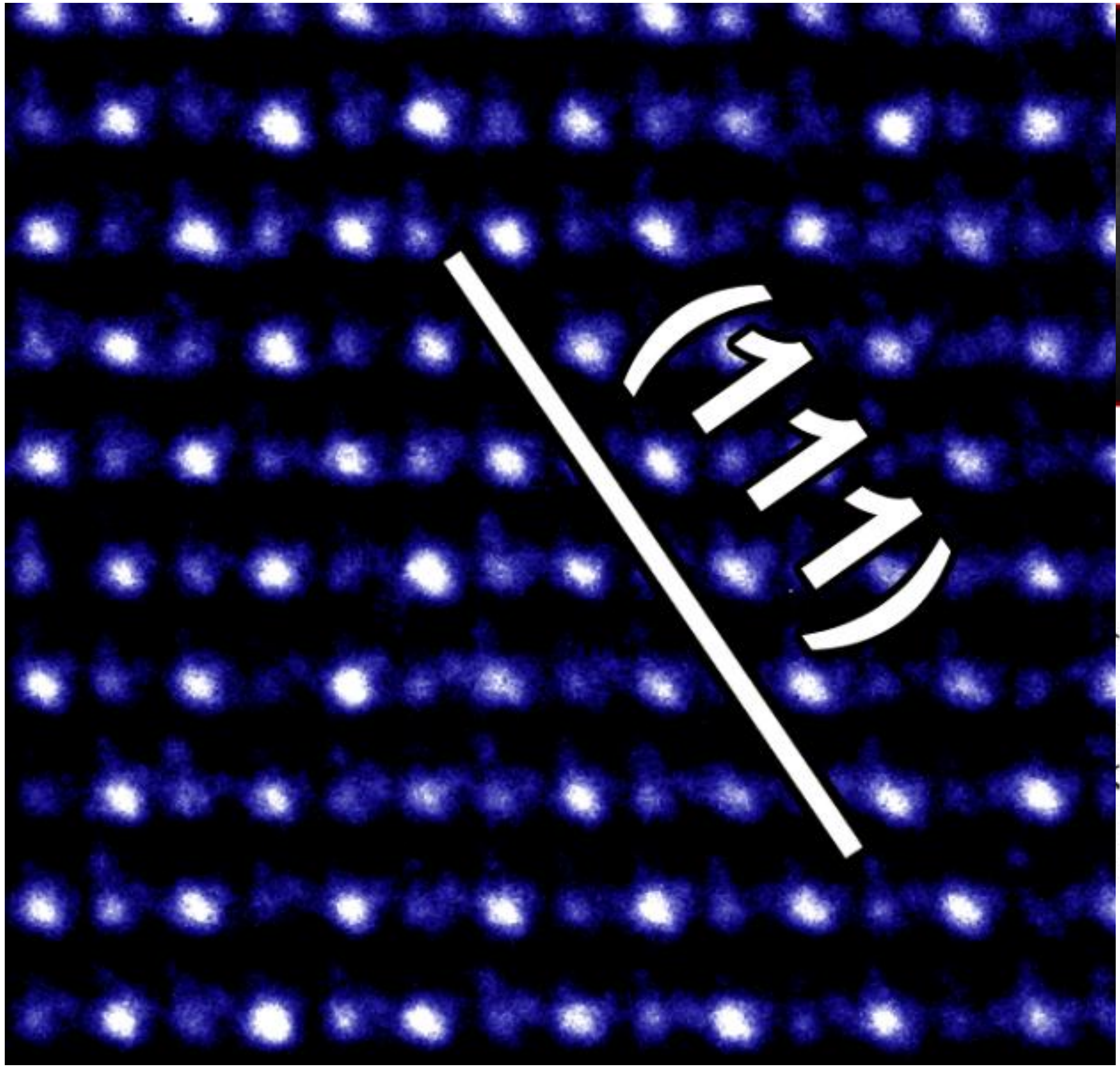


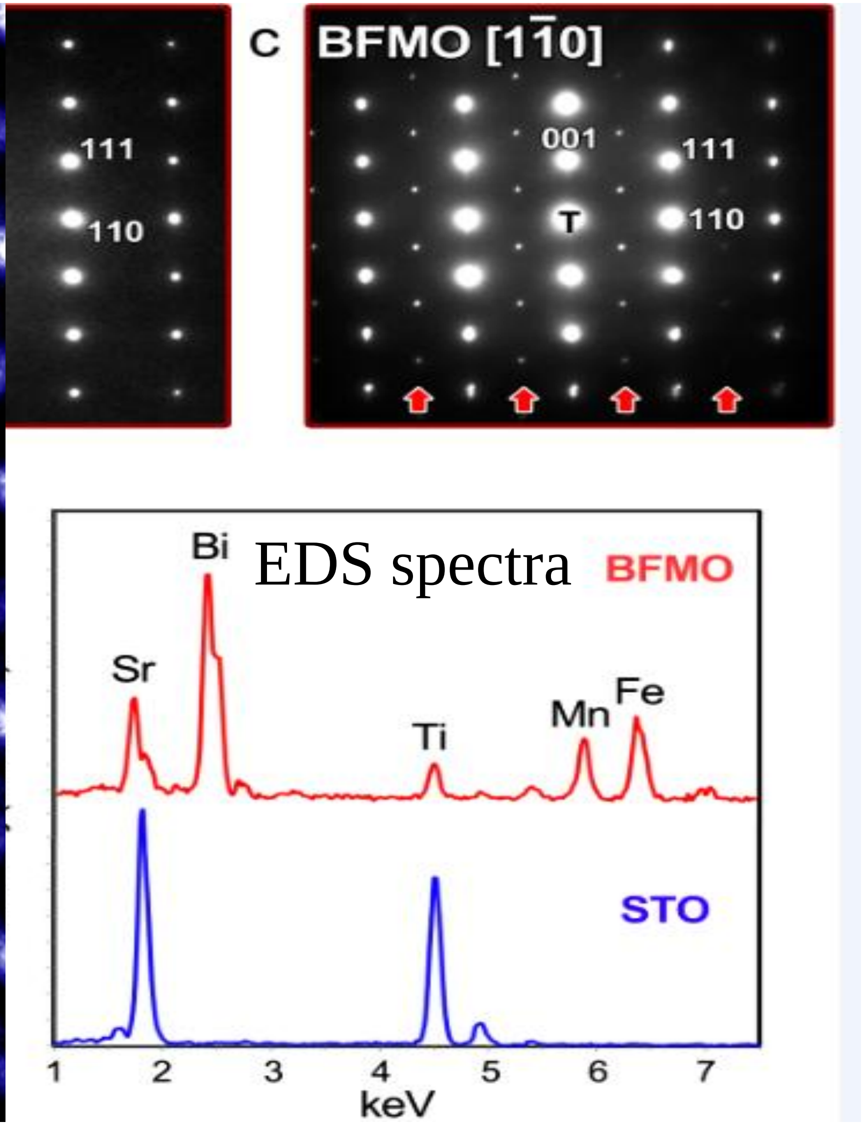


a=3.905Å
c=4.015Å

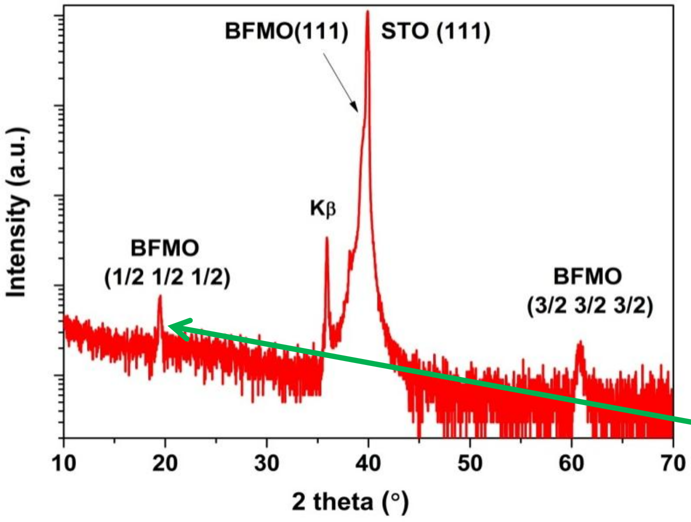
Shanghai Synchrotron Radiation Facility –X-ray Reciprocal Space Mapping

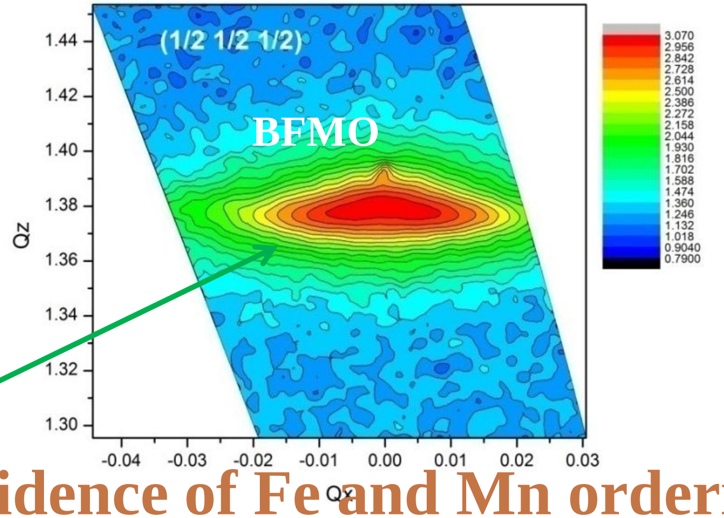
TEM support


(111)

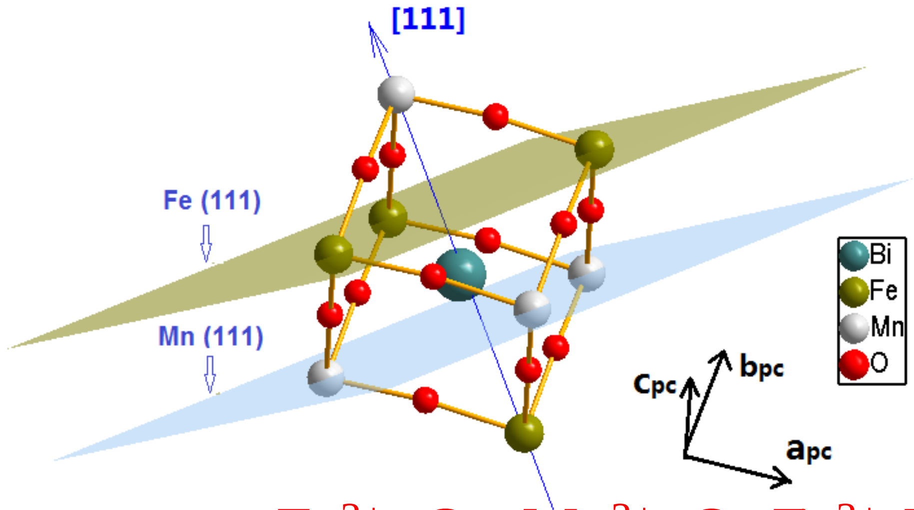

c
BFMO [1$\bar{1}$0]
111
110
001
111
T
110
Bi
EDS spectra
BFMO
Sr
Fe
Mn
Ti
STO
1
2
3
4
5
6
7
keV

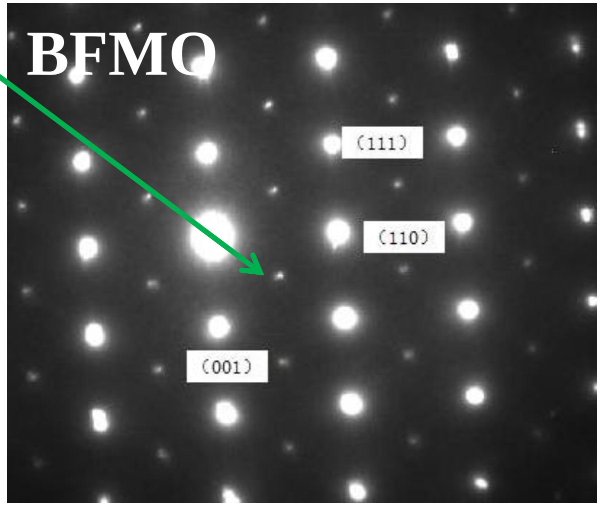
Structure analysis: Asymmetric XRD, RSM and TEM-SEAD





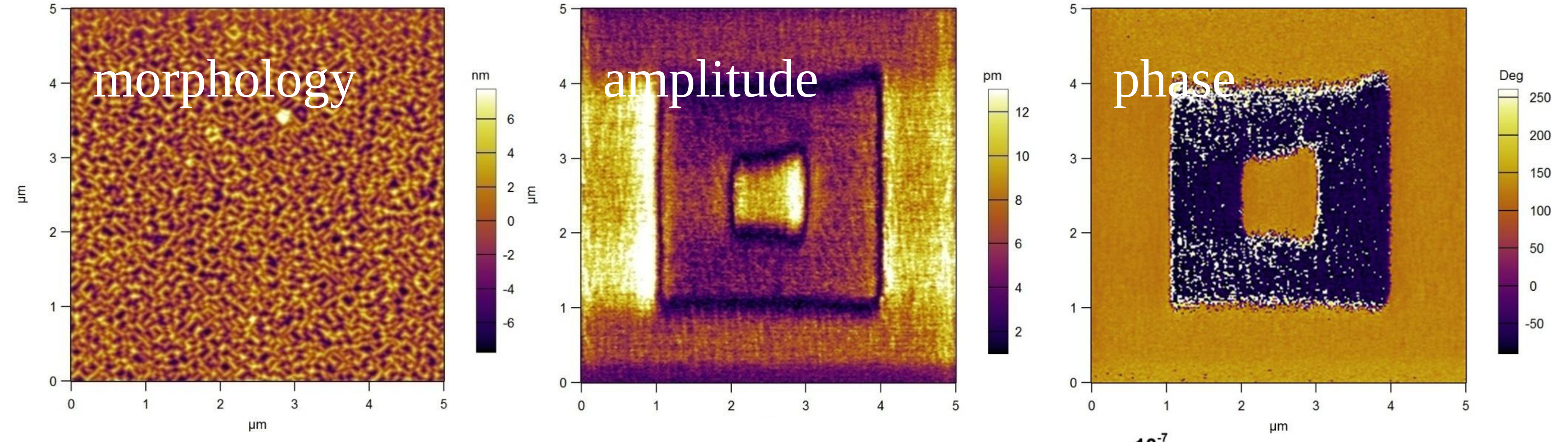
Evidence of Fe and Mn ordering

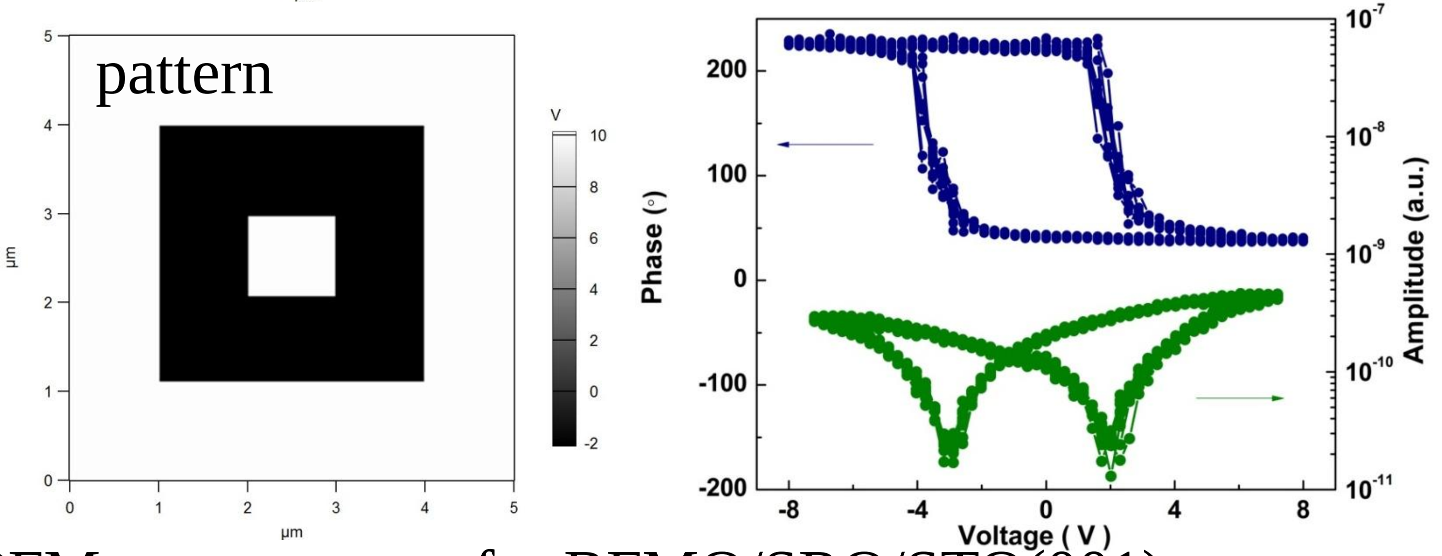




-Fe^{3+}- O - Mn^{3+} -O -Fe^{3+}-Mn^{3+} -

Ferroelectricity characterization



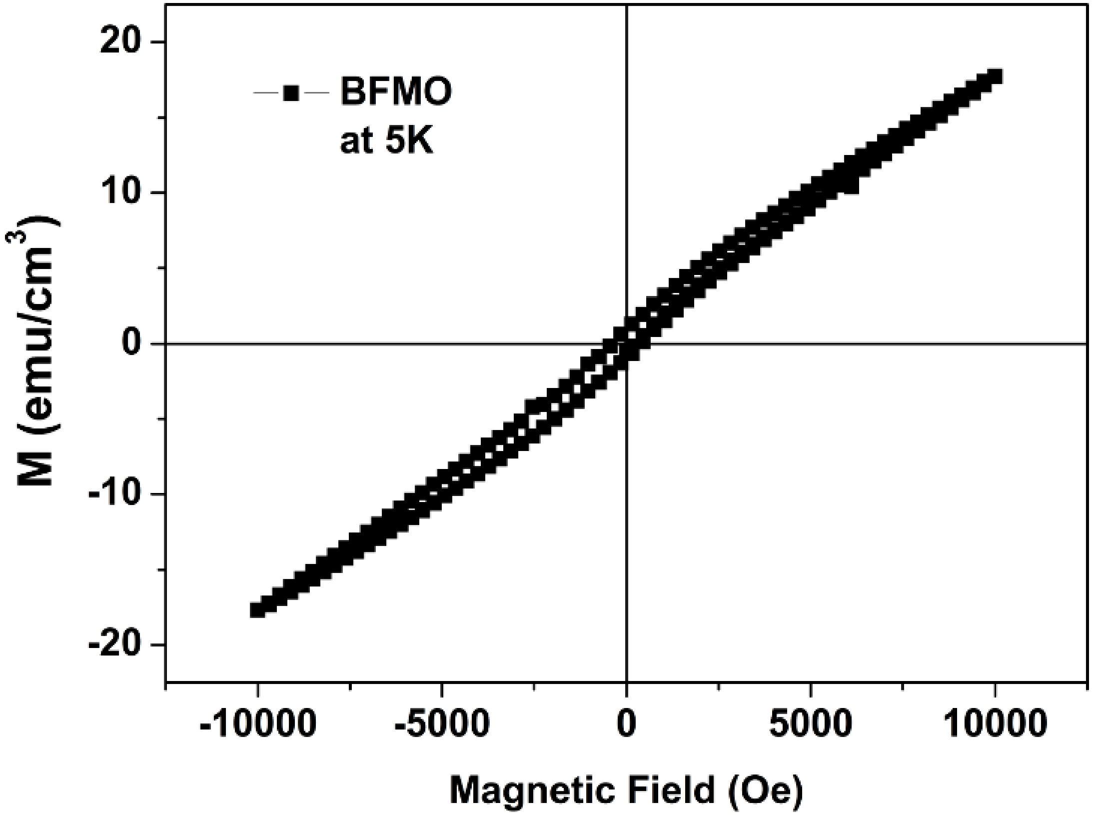


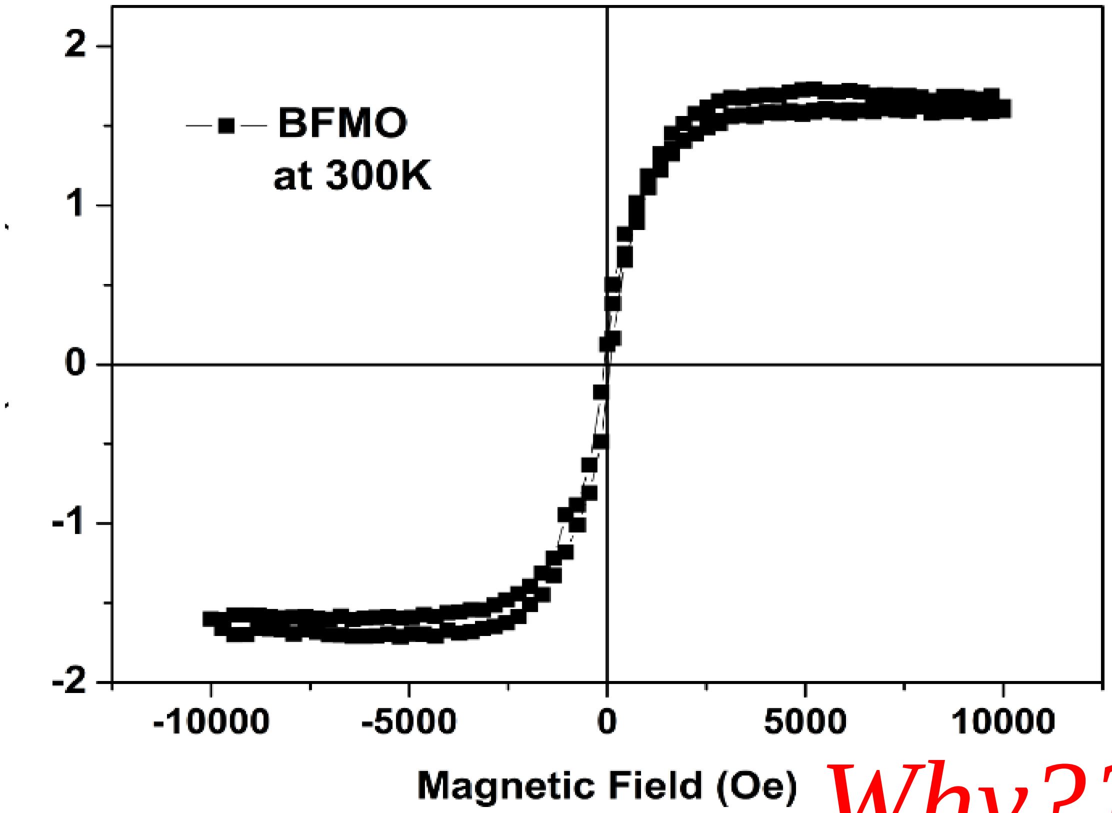
Room-temperature

Ferroelectricity

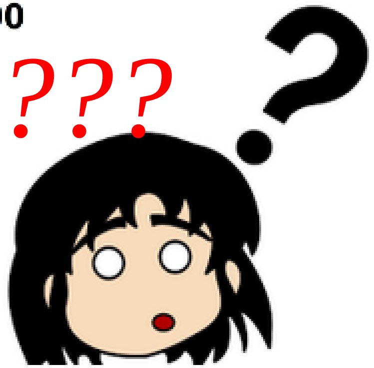
PFM measurement for BFMO/SRO/STO(001) at room temperature

SQUID measurement





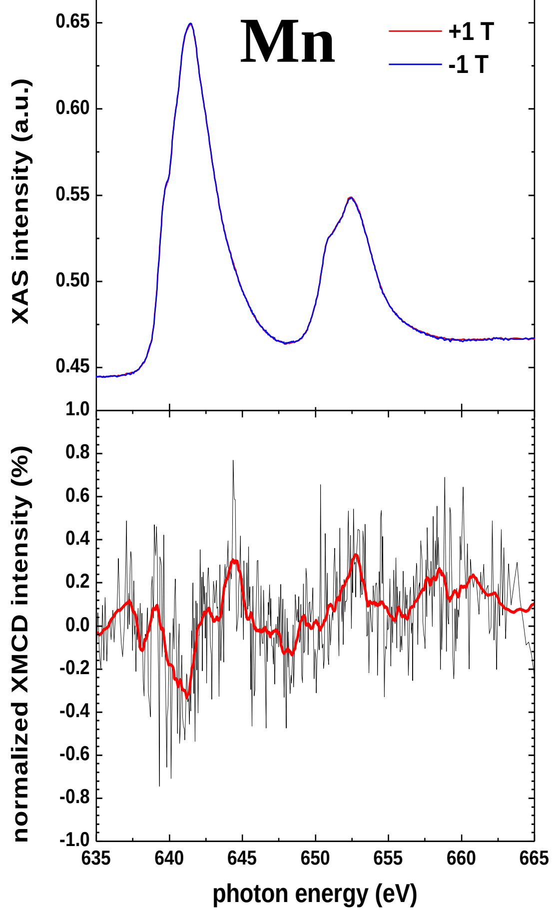
Why???

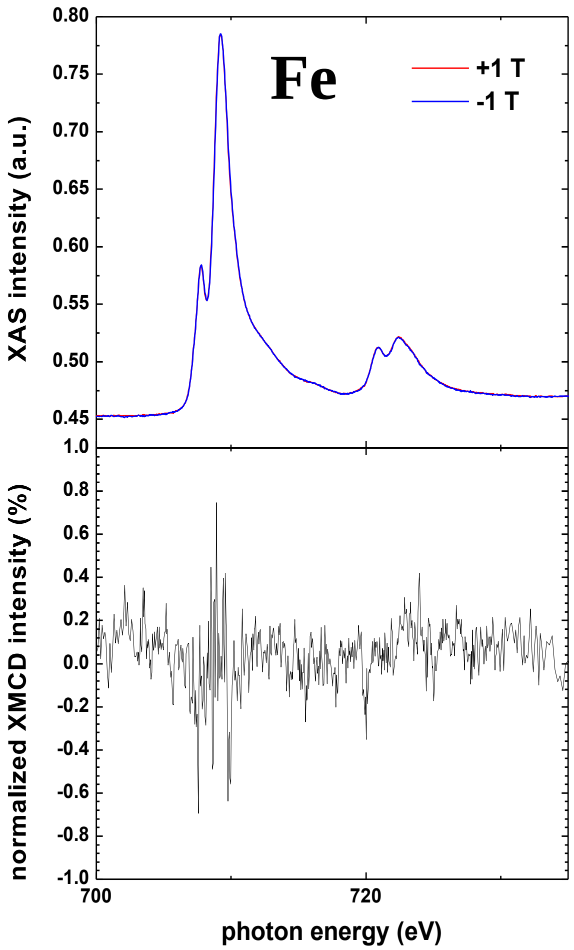


M_s of BFMO film:

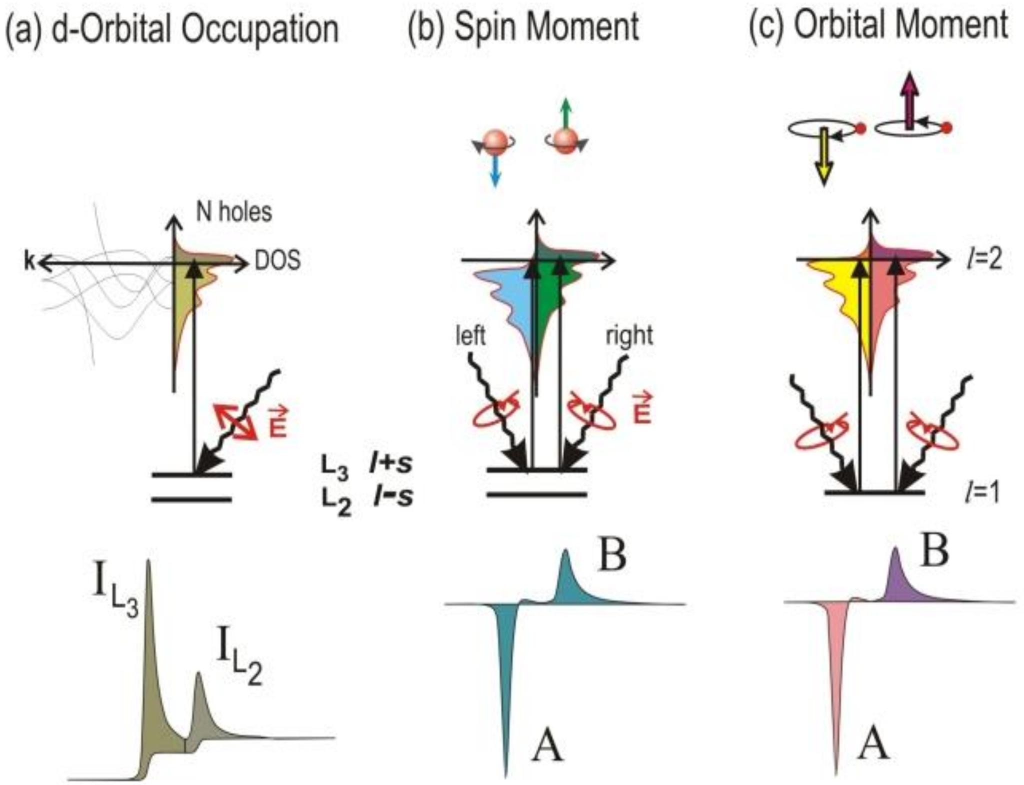
~ 0.02(300k) -0.24μ_B (5k,1T,~200nm) per Fe-Mn pair

XMCD on Mn and Fe L edges for Bi_2FeMnO_6



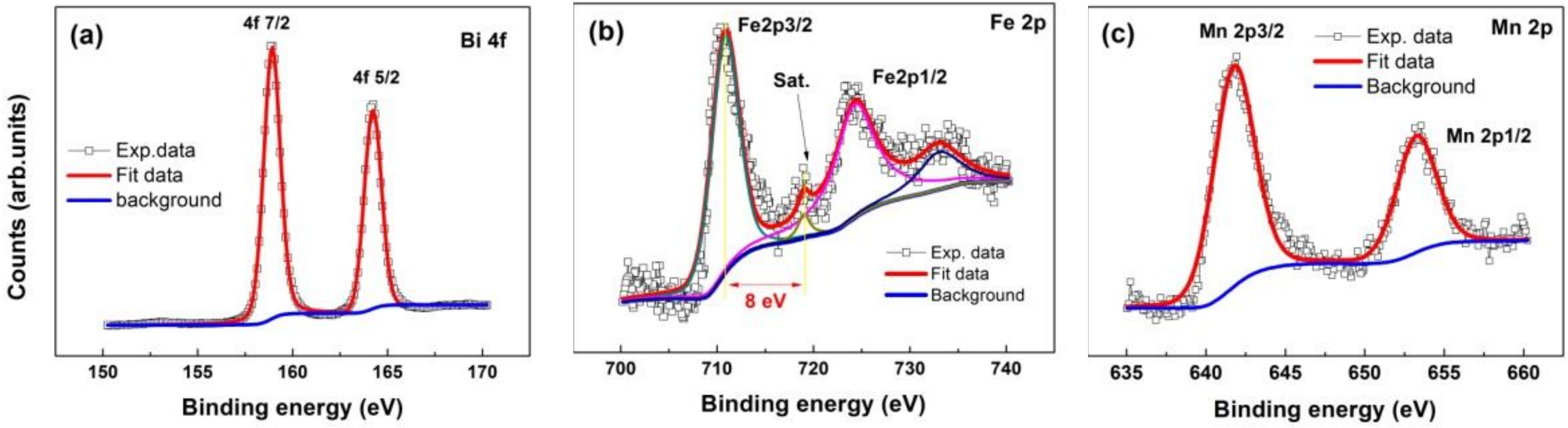


X-Ray Magnetic Circular Dichroism



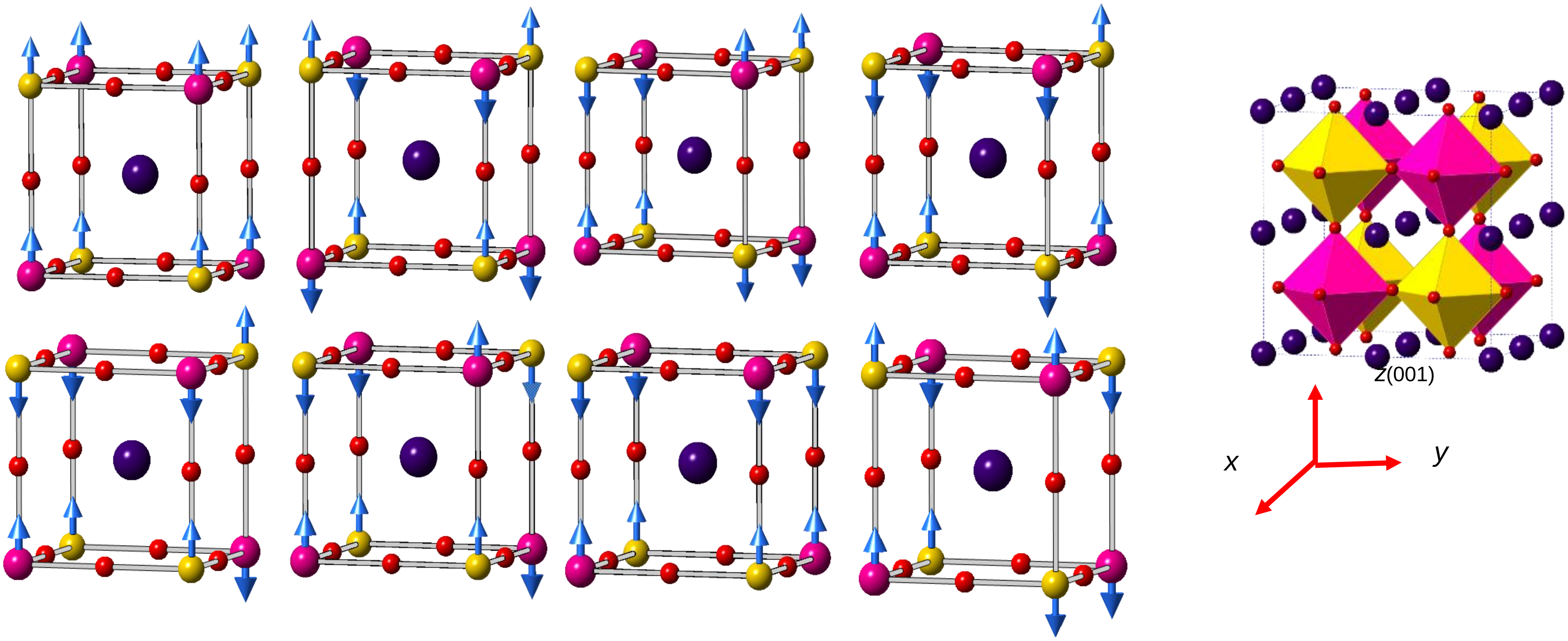
These are NO measurable XMCD from either Mn or Fe L edges.

XPS: Determination of the valence of Fe and Mn in BFMO



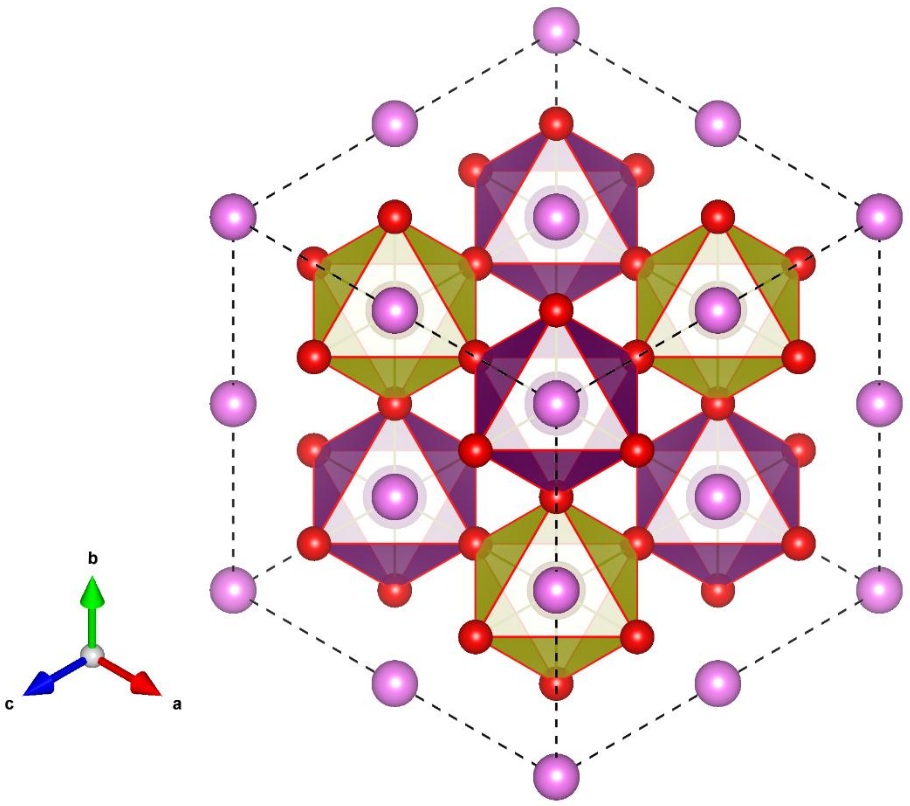
∗ Fe and Mn are 3+ ions

Origin of weak magnetism of BFMO

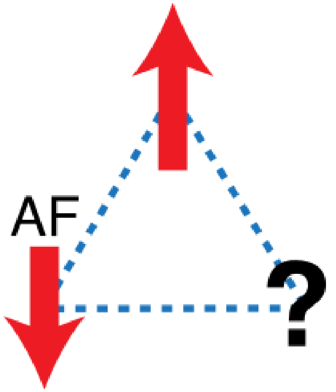


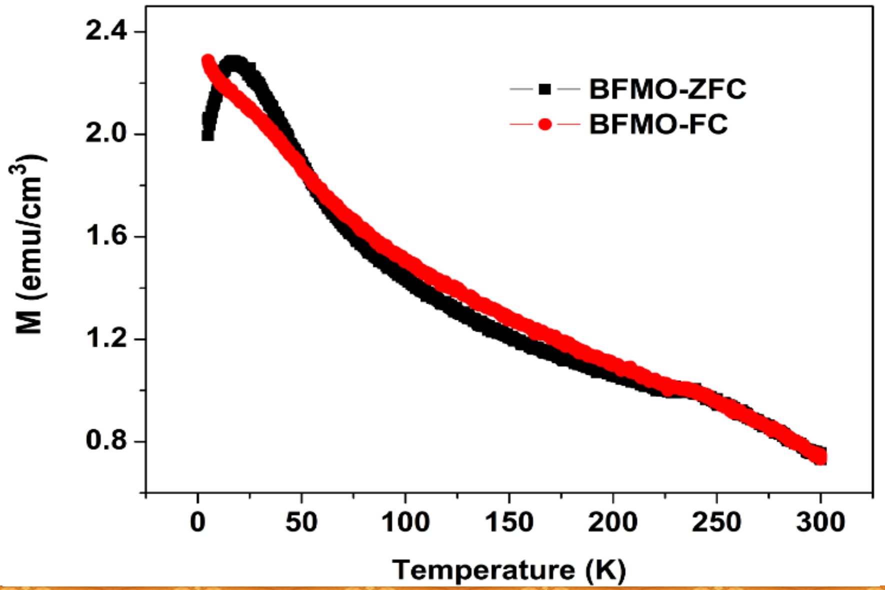
Various kinds of spin configurations to conduct DFT+*U* calculations.

Spin Glass???

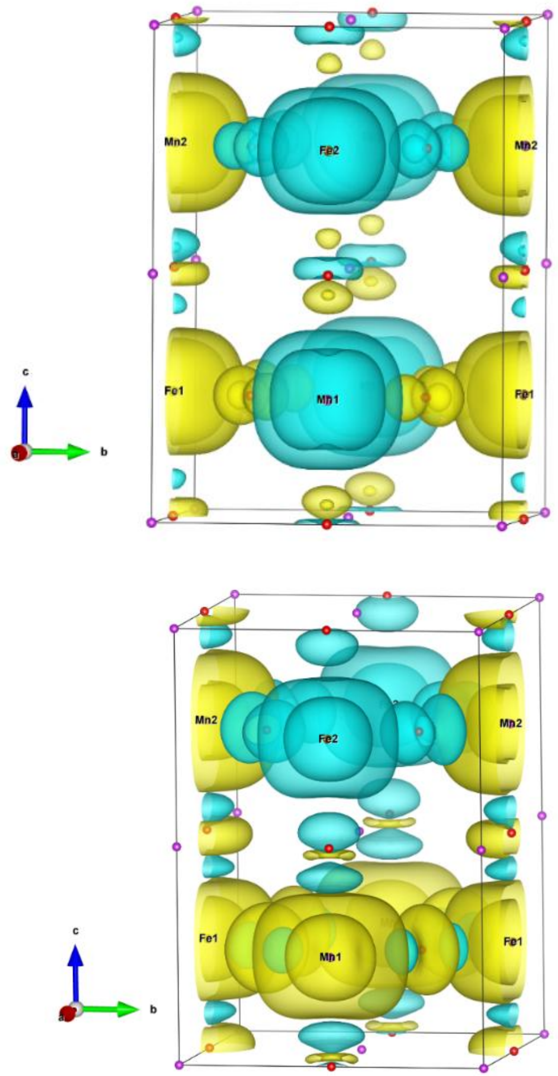


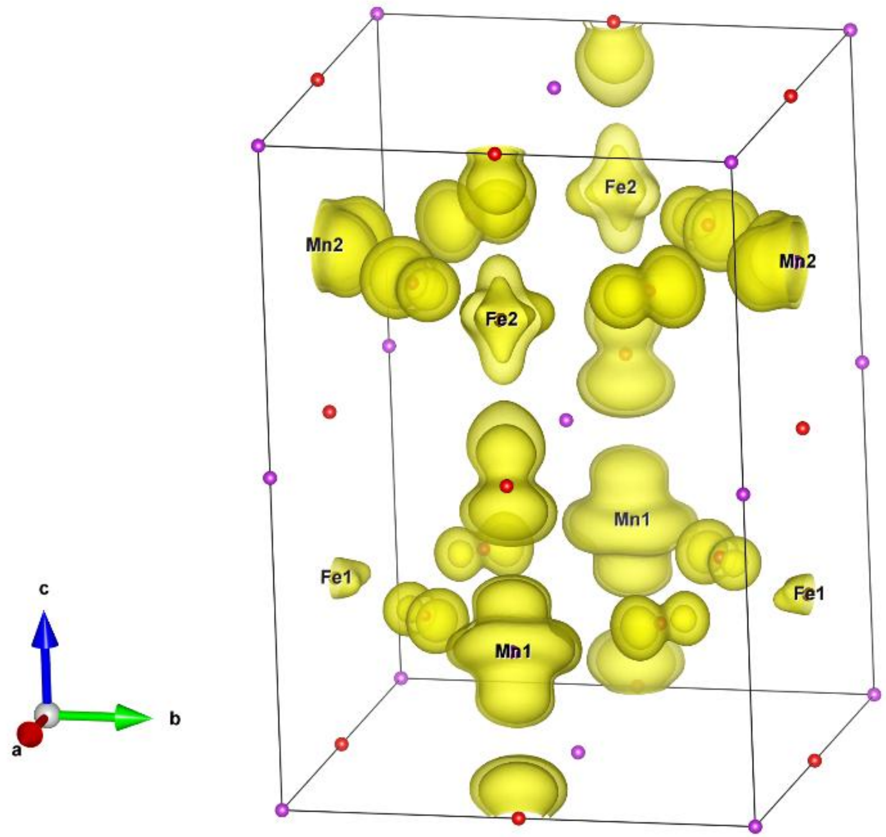
Possible spin frustration in (111) Fe or Mn ion plane

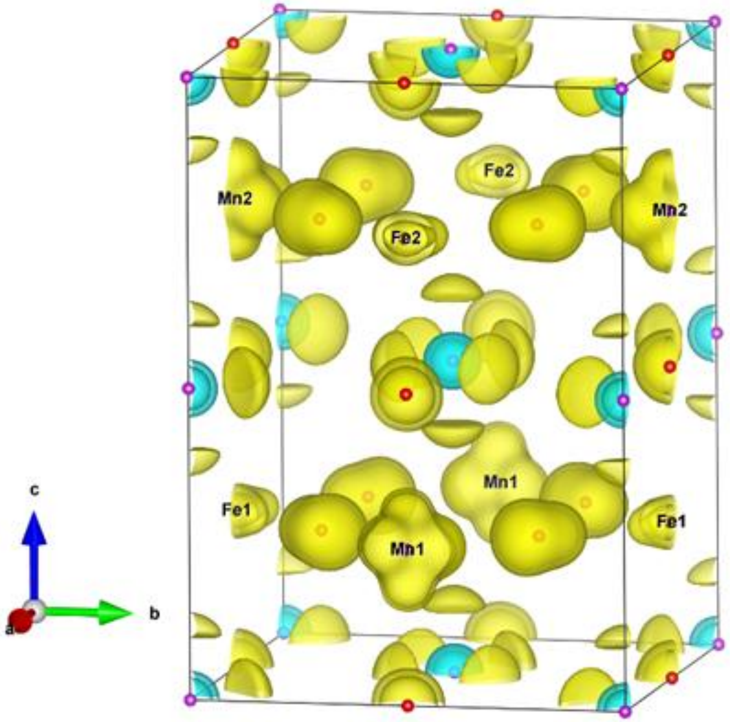




轨道有序？


Mn2
Fe2
Mn2
Fe1
Mn1
Fe1
c
b
Mn2
Fe2
Mn2
Fe1
Mn1
Fe1
c
b


c
a
b
Fe2
Mn2
Mn2
Fe2
Mn1
Fe1
Fe1
Mn1


c
b
Fe2
Mn2
Mn2
Fe2
Mn1
Fe1
Fe1
Mn1

微加工平台

双面光刻机 H94-30，去胶机 RIE-601B，离子束刻蚀 MRIBE-150，磁控溅射镀膜 MSP-300B，湿法刻蚀清洗操作台，去离子水机，蒸发镀膜机 KCDL-1、原子层沉积系统 KMSQ-150A、台阶仪 DektakXT、引线键合机 Westbond 7KE

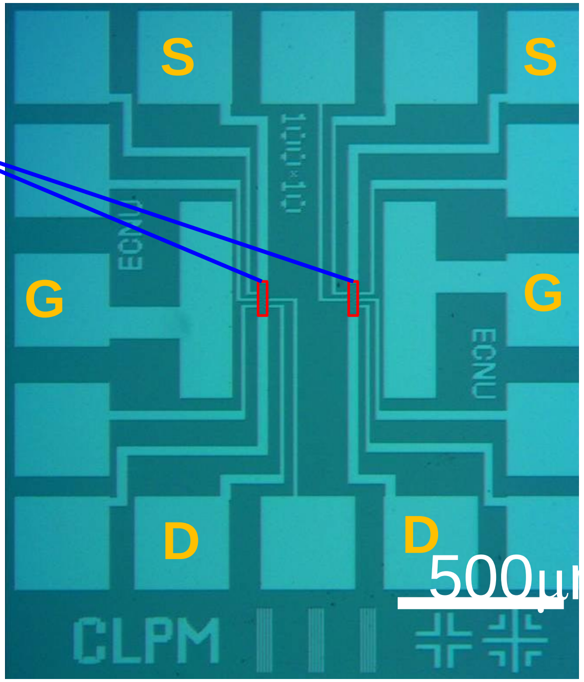
器件进展

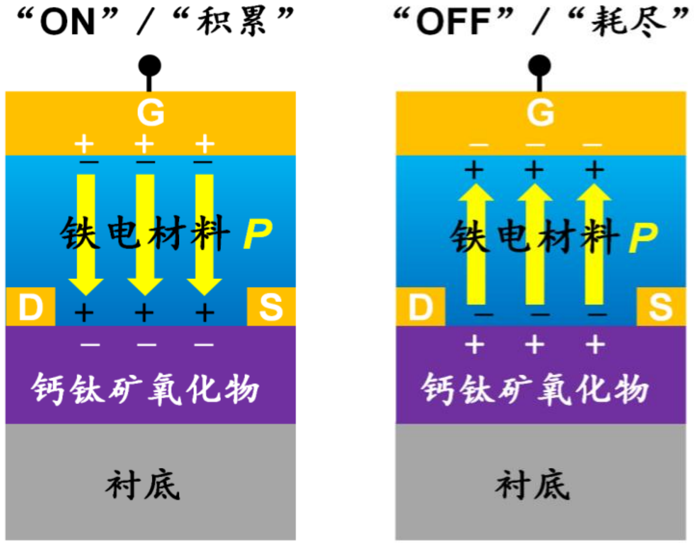
采用“固态”离子凝胶膜为栅极，实现物性的电场调控，研制“全固态”双电层晶体管。

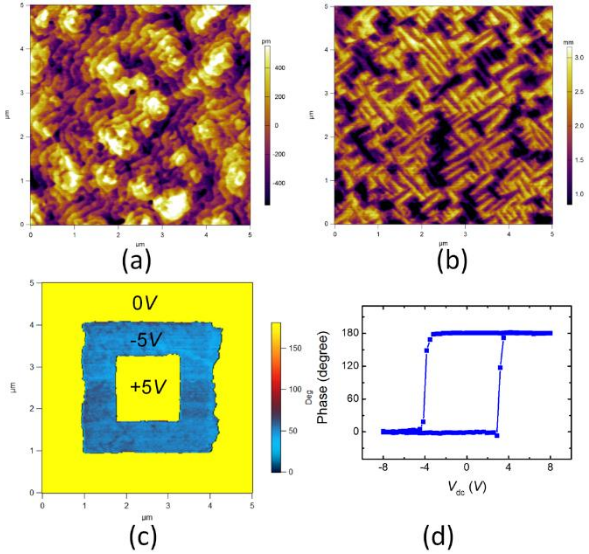
铁电场效应调控物性

沟道
100μm×10 μm

双电层晶体管
（CLPM_EDLT1）



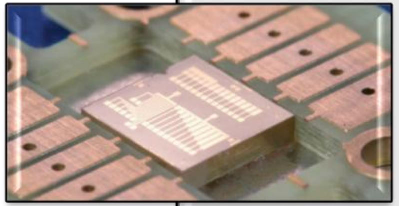




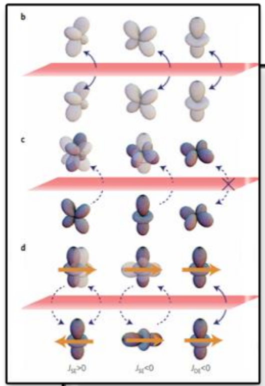
- ◆ 室温下金属-绝缘体相变的电场调控
- ◆ 电控磁性

P = 50 μC·cm^{-2}，表面束缚电荷可高达3×10^{14} cm^{-2}

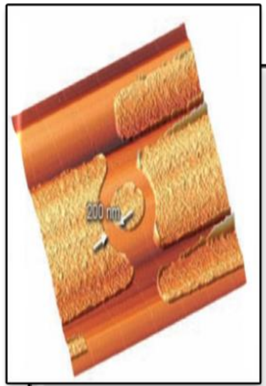
未来挑战



Working Temperature



Dealing Strongly Correlated System



Compete Silicon Industry

Thank You !

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ECNU, Key Laboratory of Polar Materials and Devices, Ministry of Education

Key Laboratory of Polar Materials and Devices

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