ENGINEERING ELECTRONIC AND MAGNETIC INTERACTIONS AT COMPLEX OXIDE INTERFACES

Divine P Kumah

North Carolina State University

NSF DMR1751455

Our Research Group

Graduate Students:

Sanaz Koohfar, Physics

Tongjie Chen, Physics

Athby Al-Tawhid, Physics

Undergraduate Students:
- Jacob Mauthe, Sophomore, Engineering
- Caroline Kirkland, Sophomore, Engineering
- Sayam Patel, Physics

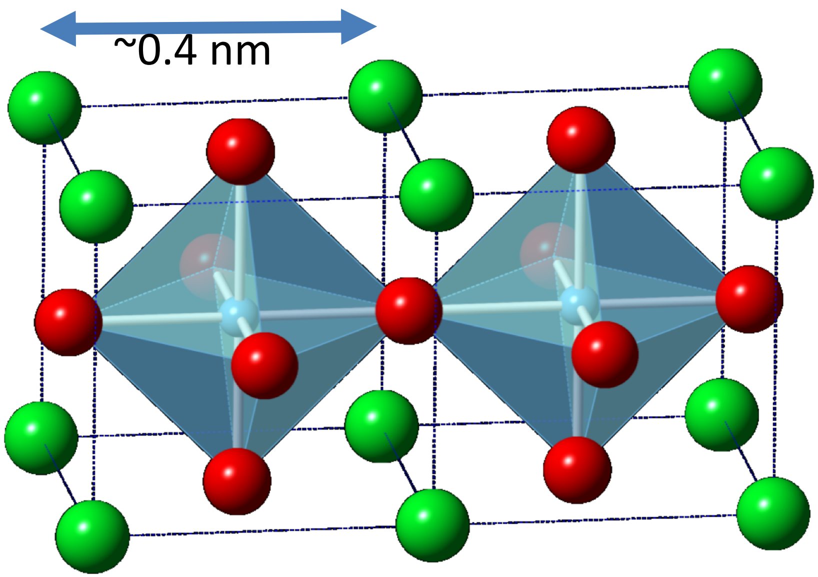
High School Students
- Mason Farasay, Senior, Broughton High School

Collaborators

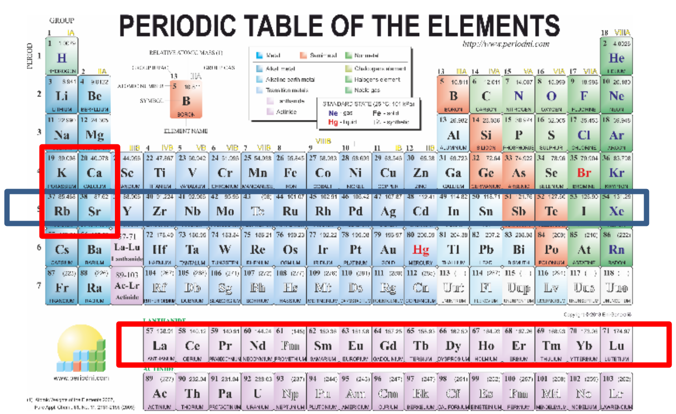
Elke Arenholz, LBNL
Alexandru Georgscu, Flatiron Institute
James Lebeau, NCSU MSE/ MIT
Aubrey Penn, NCSU MSE

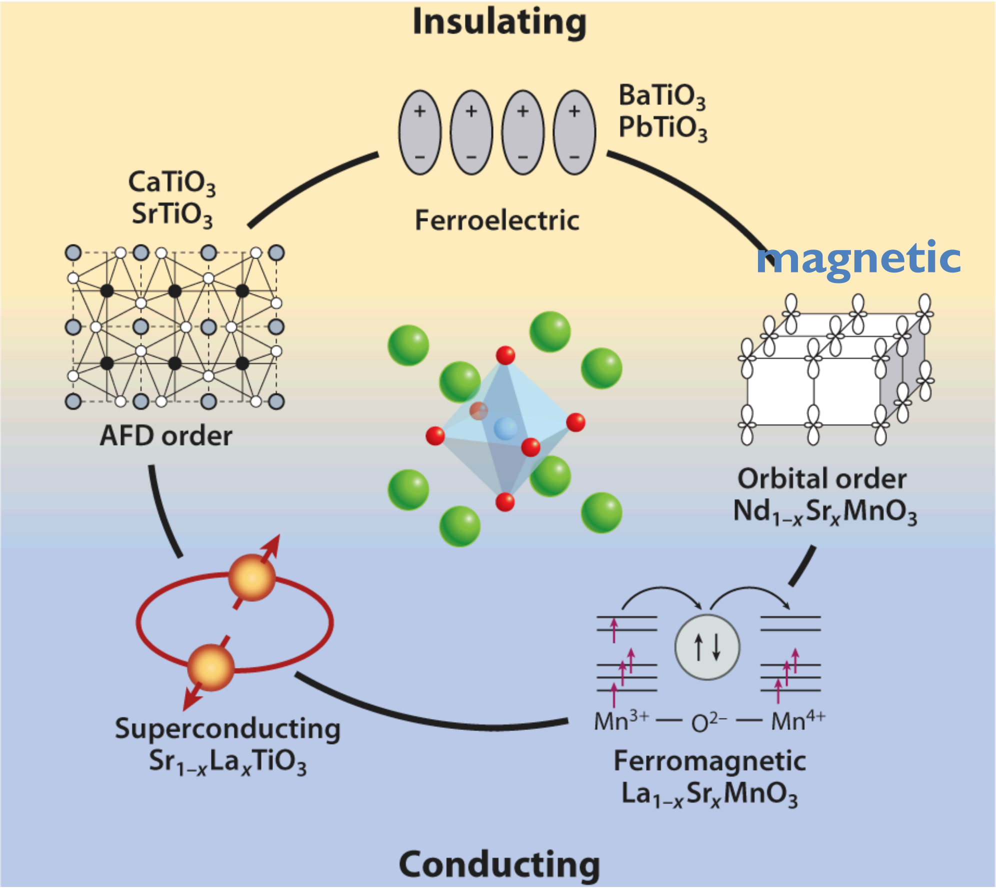
NSF DMR1751455

Complex Oxide Materials



basic formula ABO_3

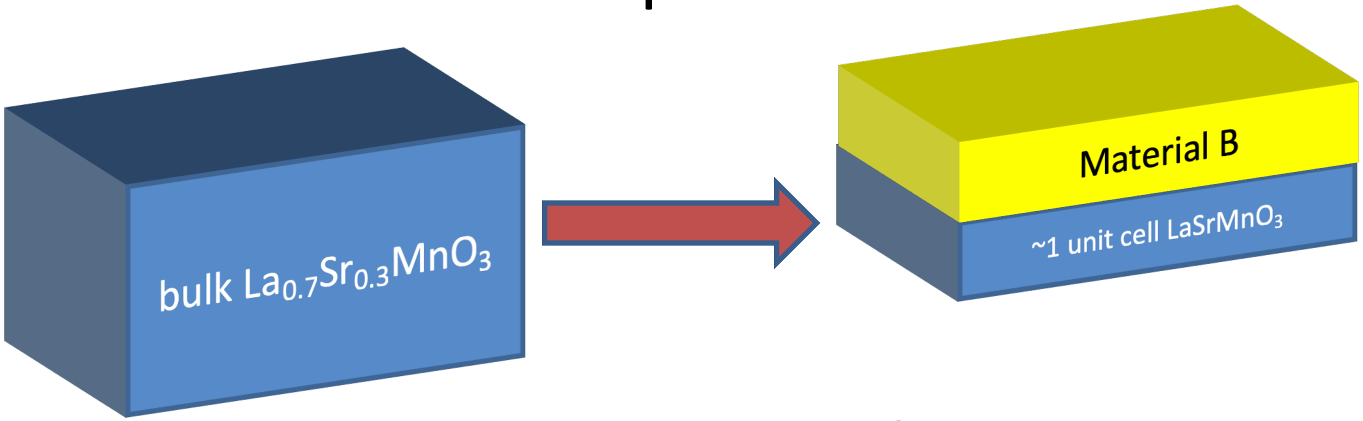




Zubko, Ann. Rev of Condensed Matter Physics, 2, **141**

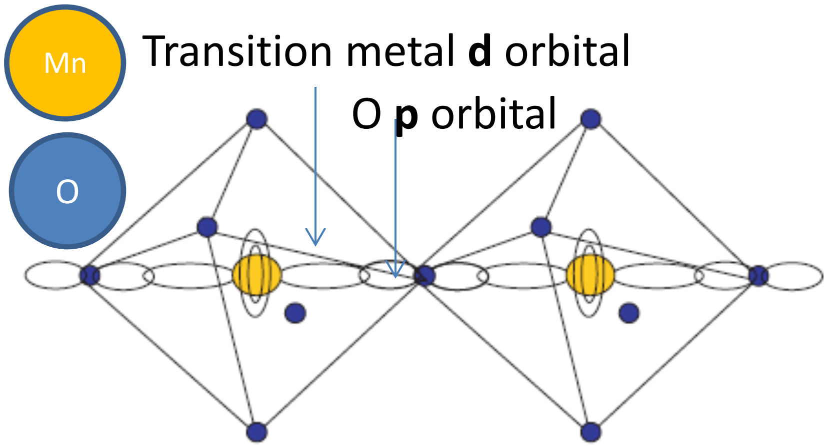
Talk Outline

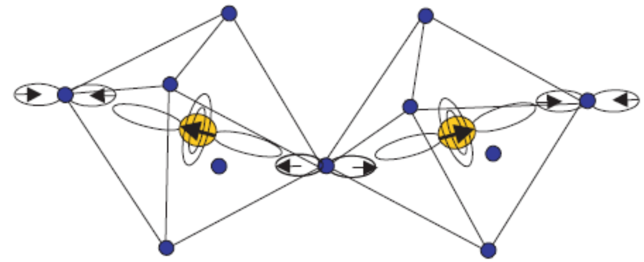
- Two Dimensional complex oxides and interfaces



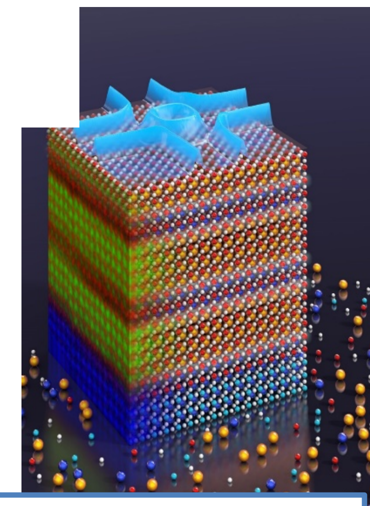
- Structural and Magnetic Interfacial interactions
  - Synthesis → Molecular beam epitaxy
  - Characterization → SQUID, synchrotron diffraction and spectroscopy, electron microscopy, theory
- Application→ Understanding thickness-dependent transitions

Tuning parameters





- Magnetic and electronic ordering depends on **TM d-O p** orbital interactions

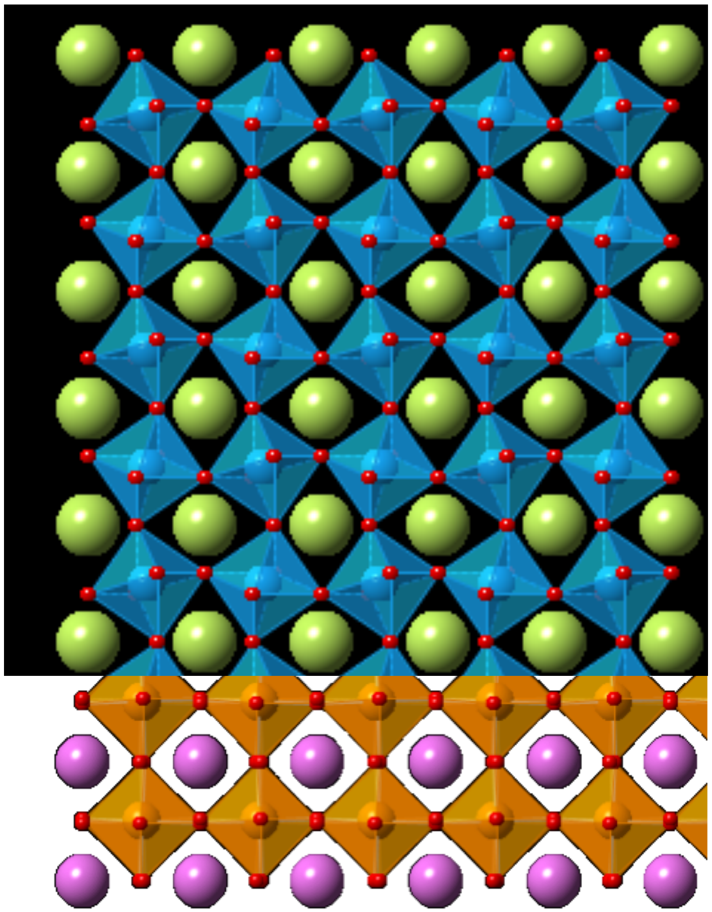


- Rotate octahedra
- Stretch/compress unit cell
- Electronic/Chemical doping

- Atomic layer heterostructuring

Hwang, Phys. Rev. B, 52, **15046**, (1995).
Millis, Nature, 392, **147**,

Going beyond epitaxial strain



$[La^{3+}\ O^{2-}]^{+1}$
$[Al^{3+}\ O_2^{4-}]^{-1}$
$[La^{3+}\ O^{2-}]^{+1}$
$[Al^{3+}\ O_2^{4-}]^{-1}$

$[La^{3+}\ O^{2-}]^{+1}$
$[Al^{3+}\ O_2^{2-}]^{-1}$
$[La^{3+}\ O^{2-}]^{+1}$
$[Ti^{4+}\ O_2^{4-}]^{0}$
$[Sr^{2+}\ O^{2-}]^{0}$

$LaAlO_3$: Band Insulator
$SrTiO_3$: Band Insulator

$LaAlO_3$/$SrTiO_3$ interface
- High mobility electron gas
- Ferromagnetic
- Superconducting

- Charge transfer
- Ionic intermixing
- Structural re-arrangements

Polar Oxide interfaces and surfaces

Ohtomo, Hwang, *Nature* 427, 423 (2004)

A new route to tune functionality

- Can polar discontinuities be used to tune structure and functionality in thin oxide films?

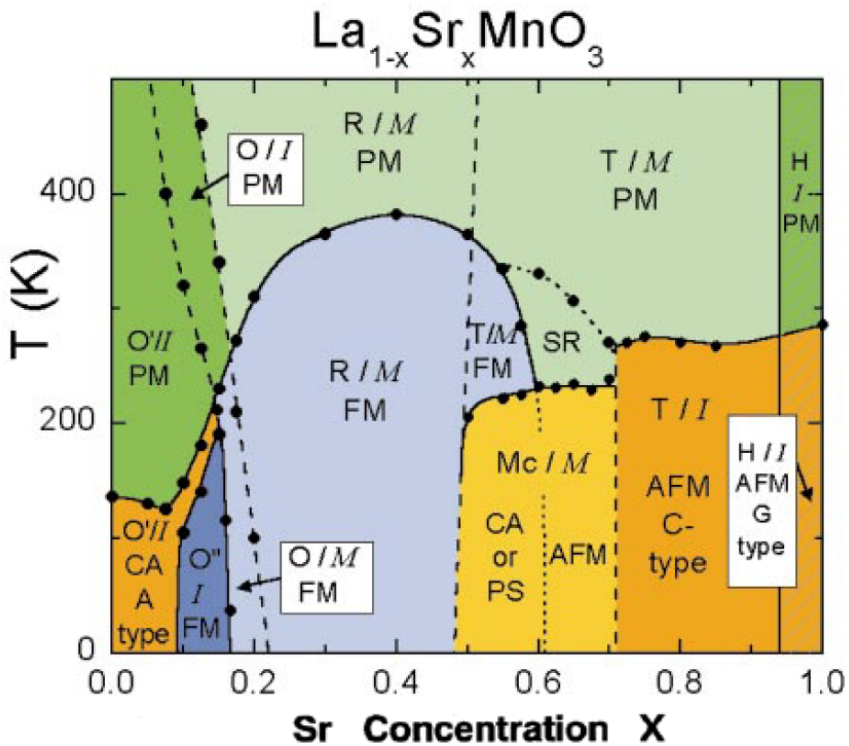
- How are thickness-dependent properties related to polar interfaces?
  - **Magnetic transitions in $LaSrMnO_3$**

S. Koohfar et al. Phys. Rev. B 96, 024108 (2017)
Koohfar et al, npj Quantum Materials 4, 25(2019) arXiv:1710.07592
Koohfar, et al. Phys. Rev B 101, 064420 (2020)

THICKNESS-DEPENDENT MAGNETIC TRANSITIONS IN LSMO

Phys. Rev. B 96, 024108 (2017)

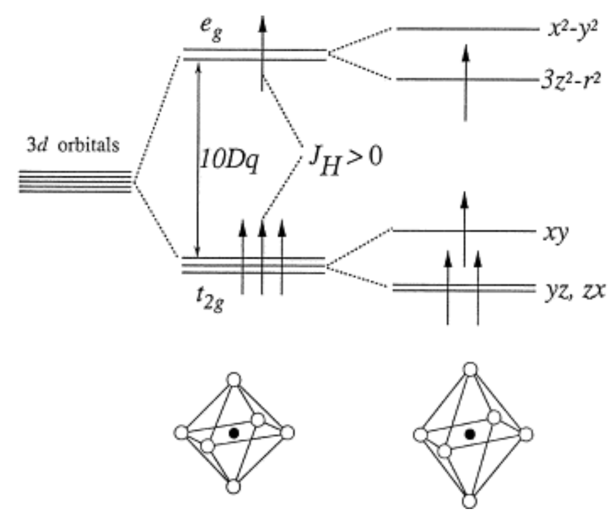
Bulk Rare Earth Manganites



FM-M→ Ferromagnetic Metal
AFM-I→ Antiferromagnetic Insulator

Properties

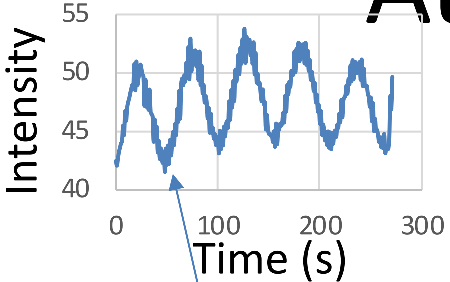
- x=0.3, Tc ~ 350 K
- Colossal Magnetoresistance
- Spin polarized half-metal

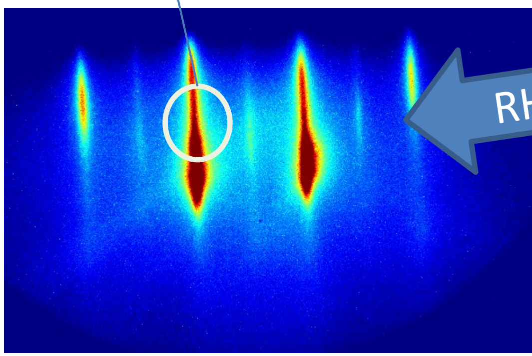


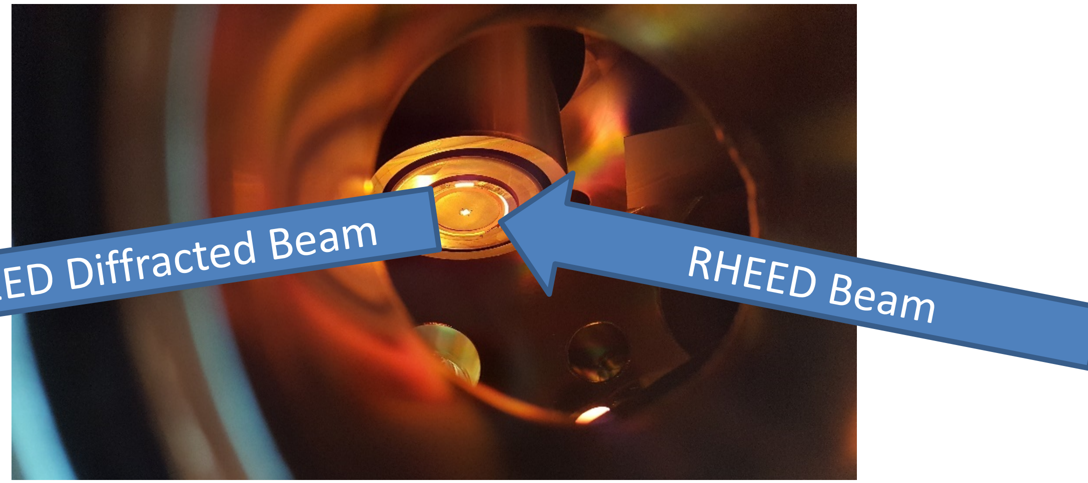
Hemberger, PRB **66**, 094410 (2002)

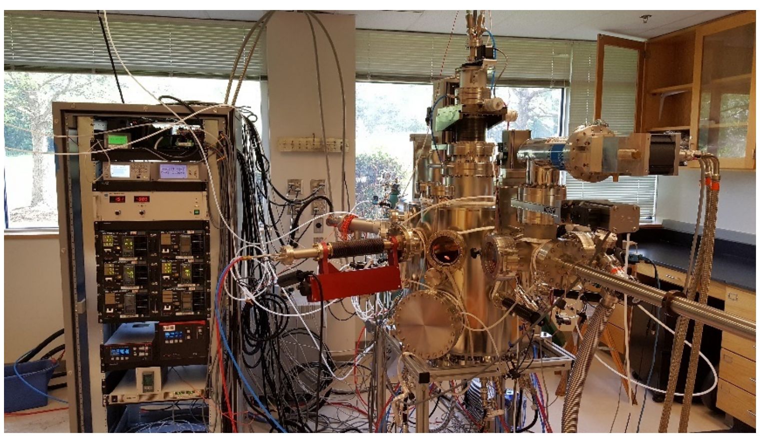
Tokura, Reports on Progress in Physics 69, 797 (2006)

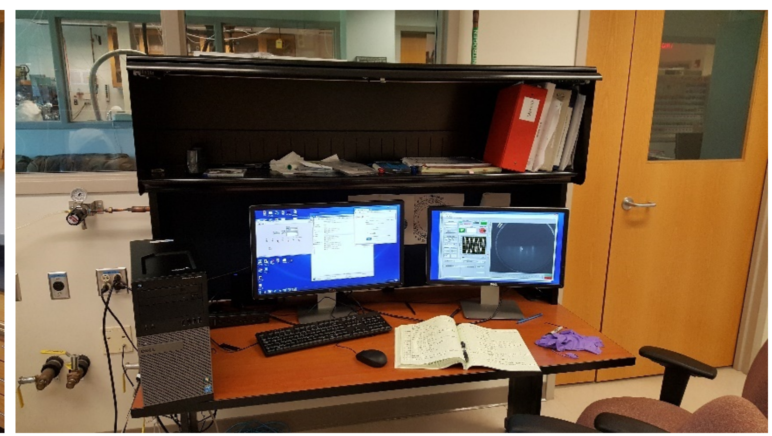
Atomic Layer Synthesis











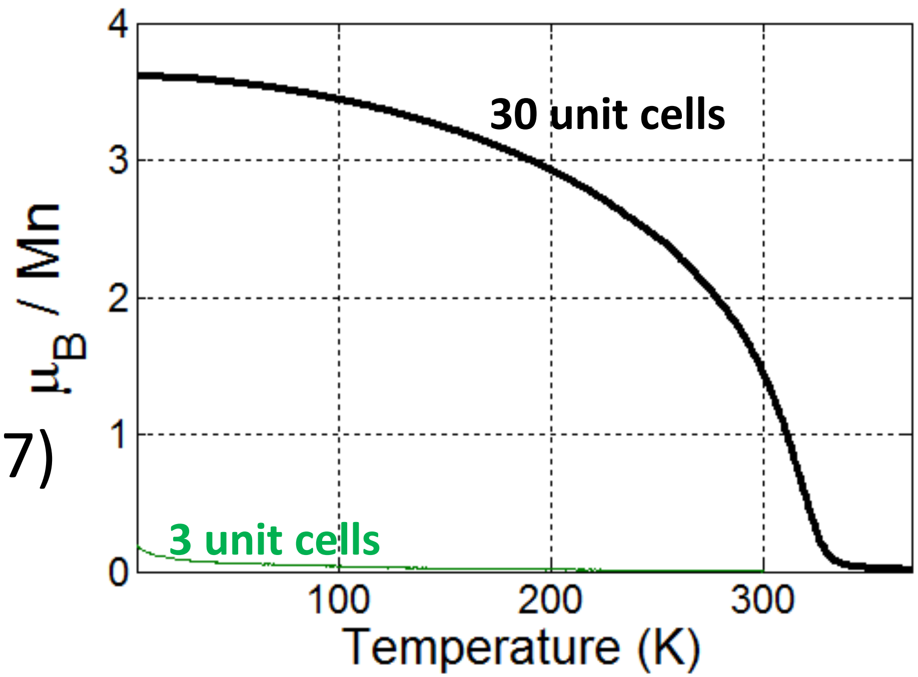
Custom Oxide Molecular beam epitaxy system with in-situ reflective high energy electron diffraction

Magnetic Properties

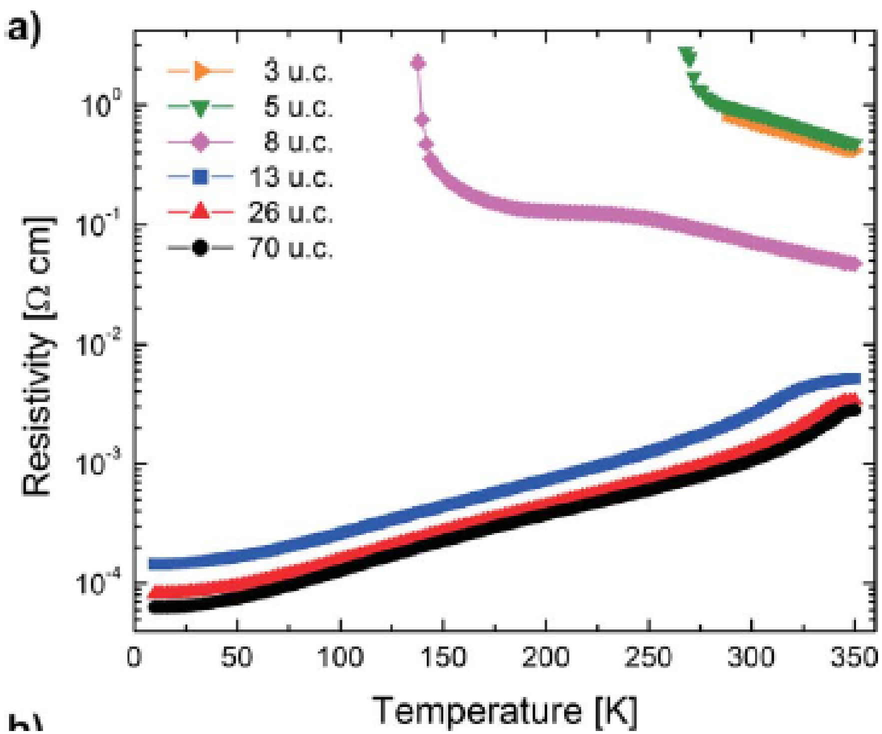
- SQUID measurements

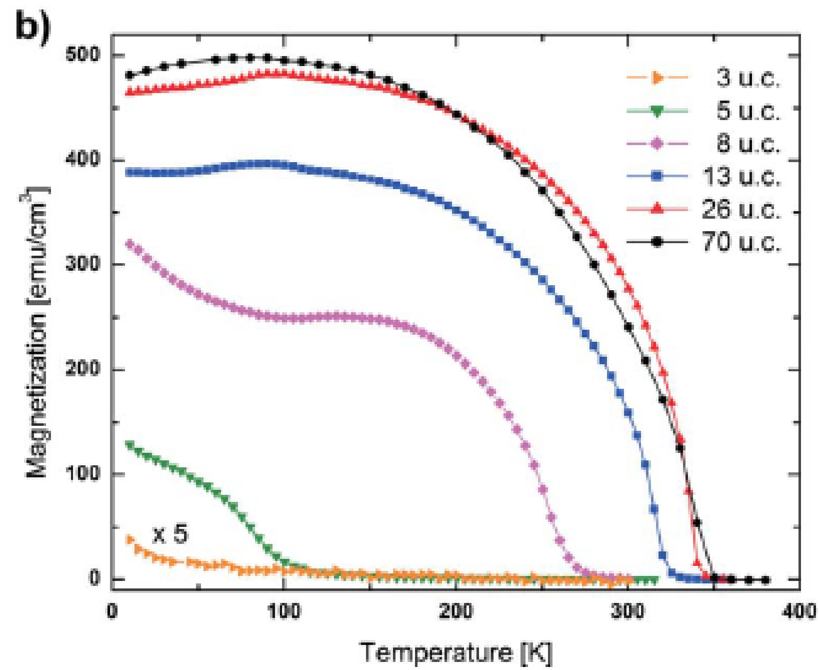
- 30 unit cells(1uc ~.4nm)
  - M_S=3.6 μ_B/Mn (bulklike 3.7)
  - T_C = 331 K (bulk 350 K)

- < 5 unit cells
  - Non-magnetic
  - Insulating



Dead Layer Effects in LSMO

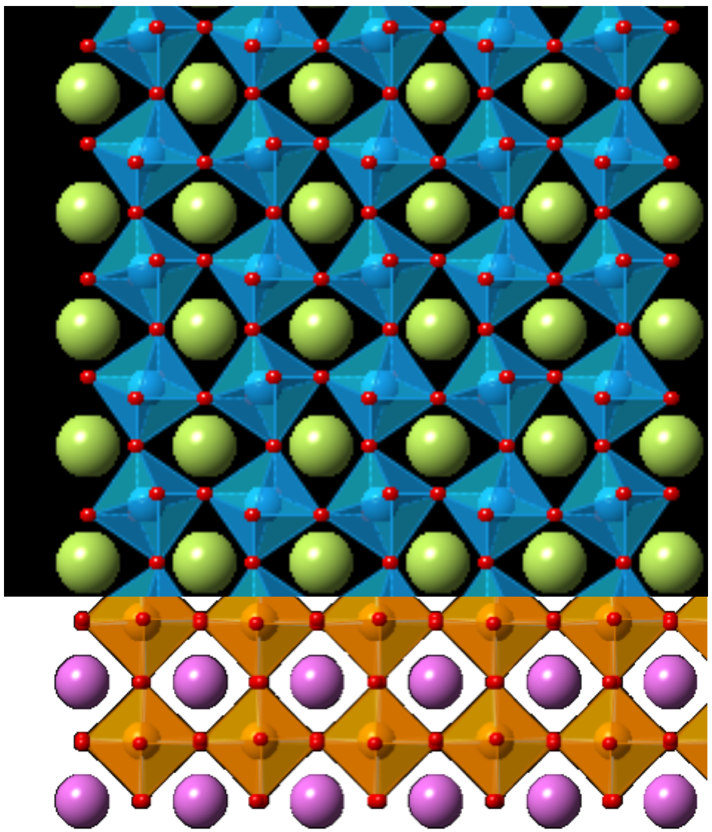




- PLD grown LSMO films (300 mTorr O_2) insulating below 10 unit cells
- Non-magnetic below 5 unit cells

Huijben, PRB **78**, 094413
Sun, *APL*, 74, **3017**, (1999)

The polar LSMO/STO interface



$[Mn^{3+} Mn^{4+} O_2^{4-}]^{-0.7}$

$[La^{3+} Sr^{2+} O^{2-}]^{+0.7}$

$[Mn^{3+} Mn^{4+} O_2^{4-}]^{-0.7}$

$[La^{3+} Sr^{2+} O^{2-}]^{+0.7}$

$[Mn^{3+} Mn^{4+} O_2^{4-}]^{-0.7}$

$[La^{3+} Sr^{2+} O^{2-}]^{+0.7}$

$[Ti^{4+} O_2^{4-}]^{0}$

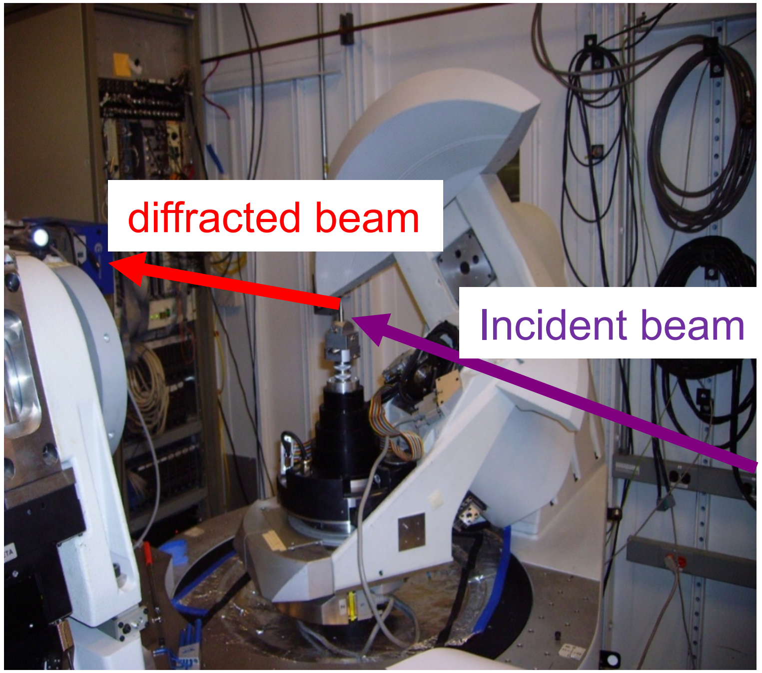
- Polar surface
- Polar Interface

[S. Koohfar, Phys. Rev. B 96, 024108](#) **(2017)**

Boscheker, *Adv. Func. Mat*, 22, **2235**, (2012)

Kourkoutis, PNAS 107, 11682 (2010)

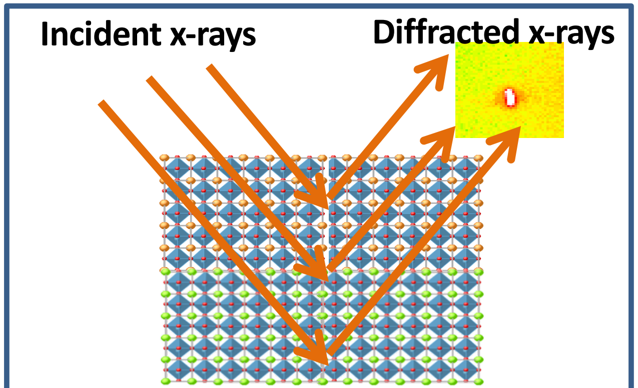
Synchrotron X-ray diffraction



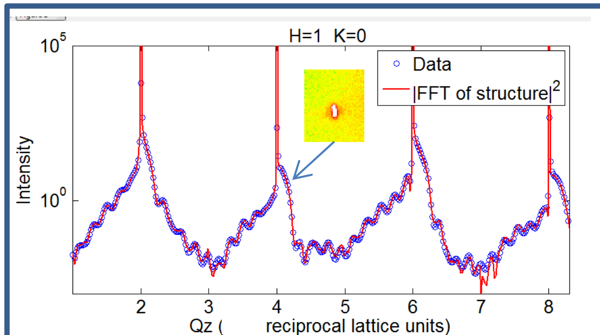
- Direct quantitative determination of atomic-scale structure from x-ray intensities along crystal truncation rods

Kumah et al. PRL116 (10), 106101

Atomic-Scale Structure Determination from Synchrotron Diffraction

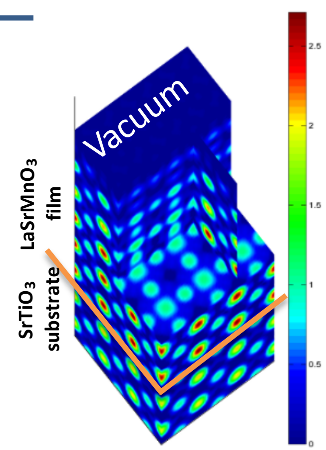


- Sample with unknown structure



-Measured crystal truncation rod intensities
-Phases determined with COBRA phase retrieval technique

Inverse Fourier transform (measured intensities + COBRA phases)

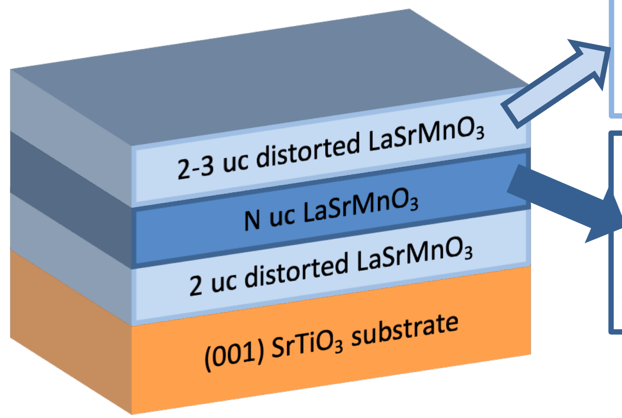


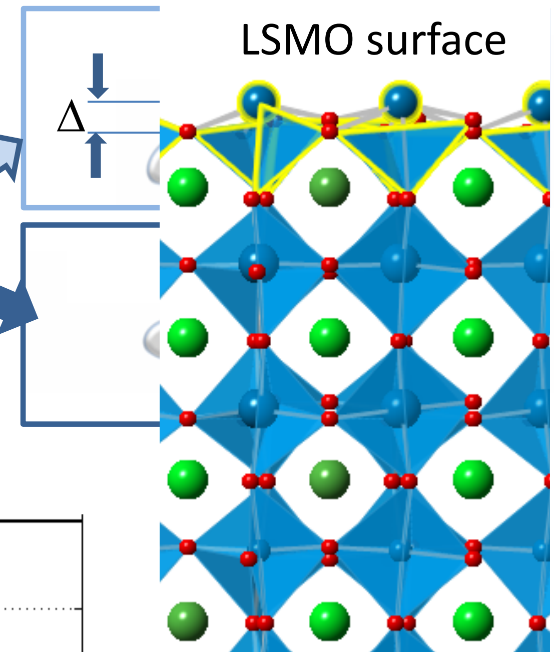
- Electron density map of real atomic structure

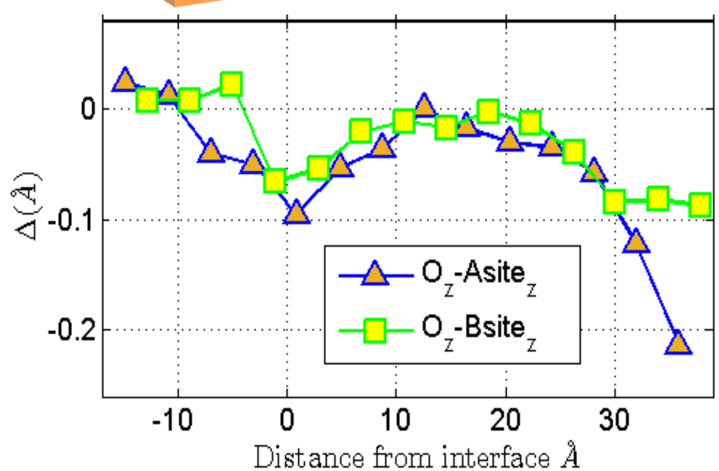
[S. Koohfar et al. Phys. Rev. B 96, 024108](#) (2017)

Ferrodistortive surface and interfacial instabilities

- Interfacial and surface lattice out-of-plane dilation
- Interfacial and surface out-of-plane polar distortions
- Distortions extend into nominal $SrTiO_3$ substrate (2-3 unit cells (0.8-1.2nm)

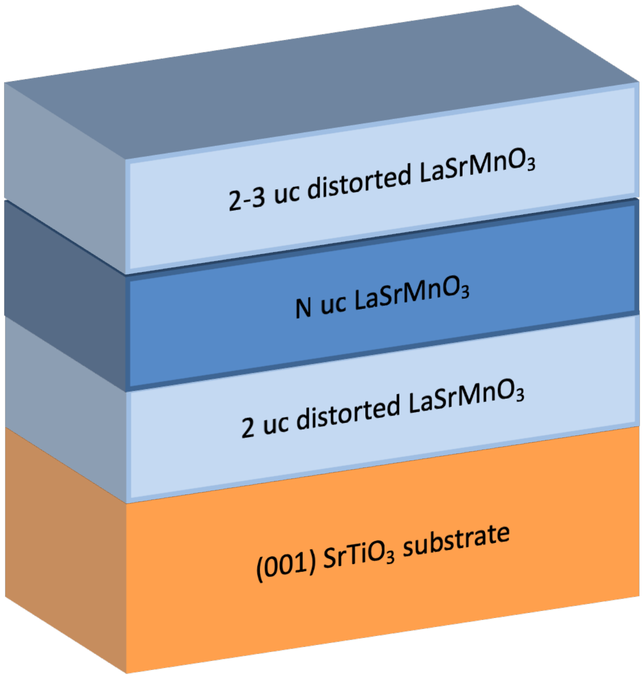






Pruneda, PRL 99, **226101 (2007)**
Burton, *PRB*, 82, **161407**, (2010)
Herger, PRB, 77 , 085401(2008)

S. Koohfar et al. Phys. Rev. B 96, 024108 **(2017)**



Structural changes → **Paramagnetic Insulator**

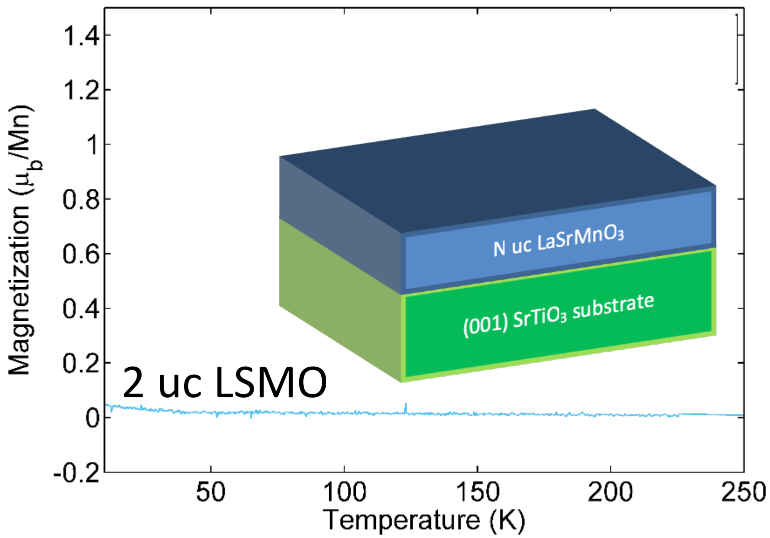
Bulk-like structure/composition→ **FM-Metal**

Compositional+Structural → **Paramagnetic Insulator**

- If t<4
  - Nonmagnetic, Insulating
- If t>4
  - Interface, non-magnetic
  - Middle layers, magnetic

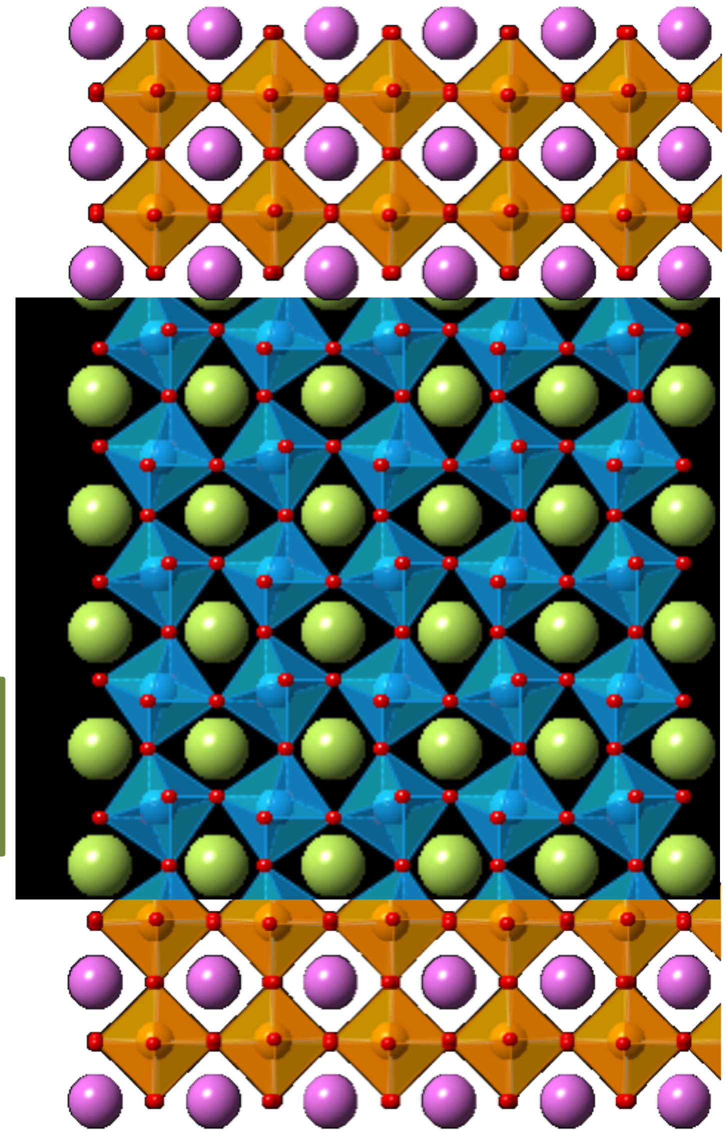
S. Koohfar et al. Phys. Rev. B 96, 024108 **(2017)**

Interface-Engineered 2D magnetism



Modify Interface/Surface to remove polar discontinuity!

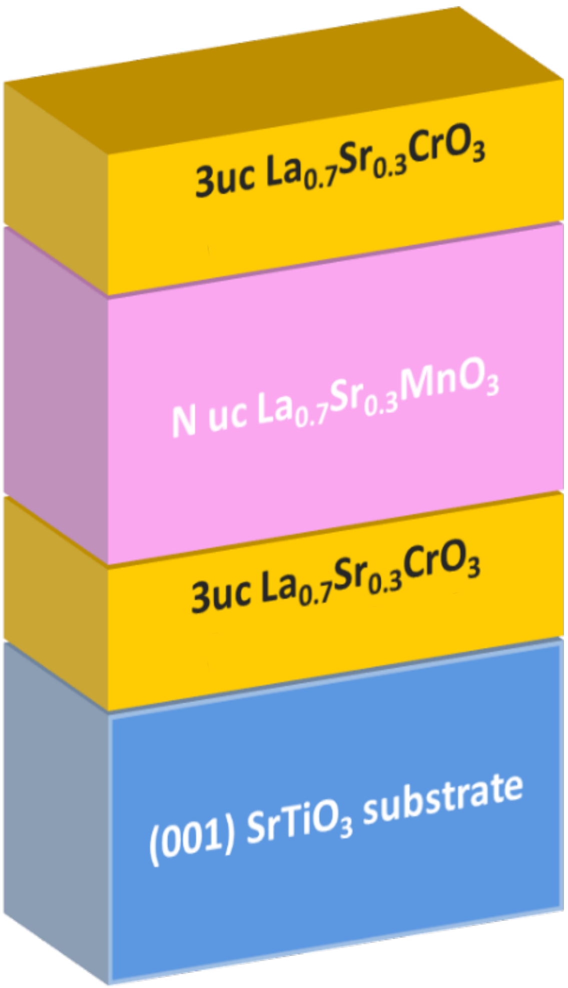
Guo et al. Adv. Func. Mat. **1800922**, (2018)
Peng, Appl. Phys. Lett. 104, **081606 (2014)**
Boscheker, *Adv. Func. Mat*, 22, **2235**, (2012)
Kourkoutis, PNAS 107, 11682 (2010)
Li, APL 105, **202401**, (2014).
Kumigashira, APL, 84, **5353**, (2004)

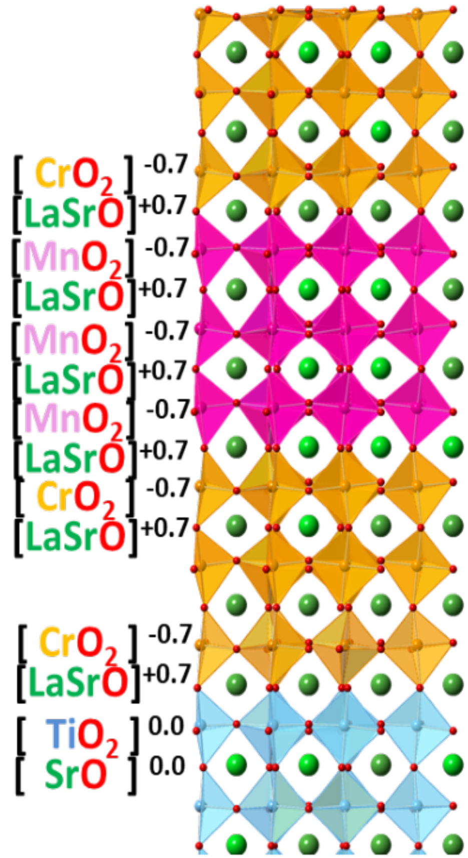


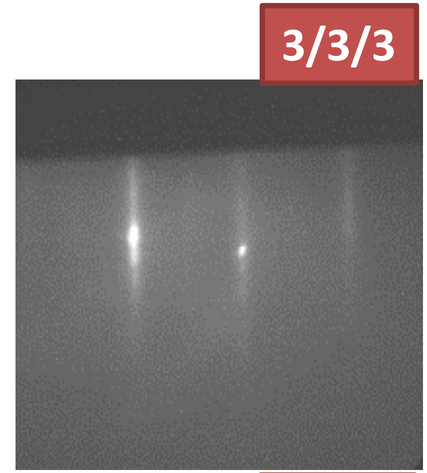
[La^{3+} $Sr^{2+}O^{2-}$] $^{+0.7}$
[X^{3+} $X^{4+}O_2^{4-}$]$^{-0.7}$
[La^{3+} $Sr^{2+}O^{2-}$] $^{+0.7}$
[Mn^{3+} $Mn^{4+}O_2^{4-}$]$^{-0.7}$
[La^{3+} $Sr^{2+}O^{2-}$] $^{+0.7}$
[Mn^{3+} $Mn^{4+}O_2^{4-}$]$^{-0.7}$

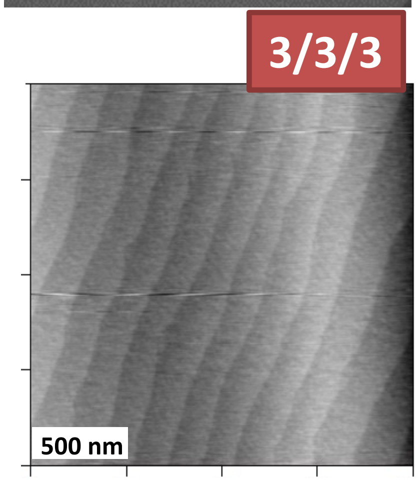
[La^{3+} $Sr^{2+}O^{2-}$] $^{+0.7}$
[Mn^{3+} $Mn^{4+}O_2^{4-}$]$^{-0.7}$
[La^{3+} $Sr^{2+}O^{2-}$] $^{+0.7}$
[X^{3+} $X^{4+}O_2^{4-}$]$^{-0.7}$

LSCO/LSMO/LSCO heterostructures









LSCO Structure: G-AF, $R3^{-}c$ symmetry with a-a-a- rotations (160^{o} Cr-O-Cr bond angle)

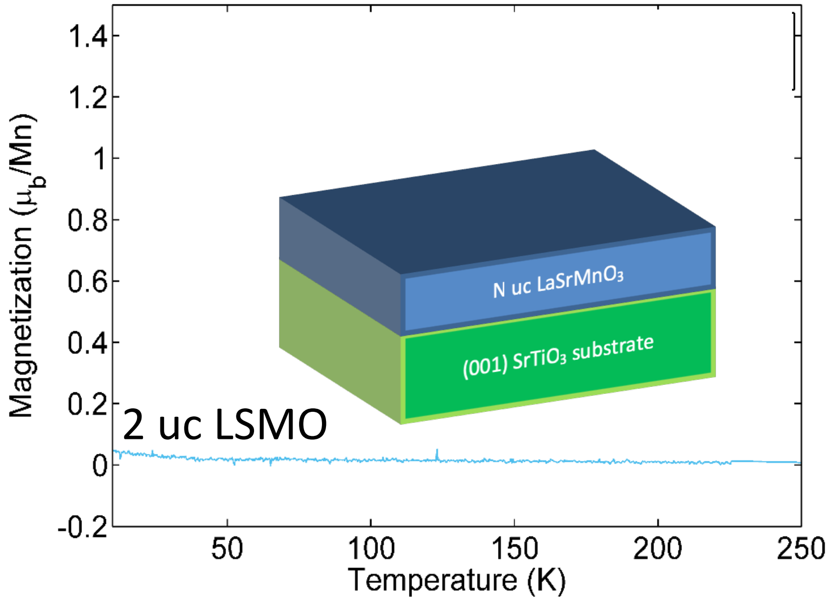
Tezuka, J. of Solid State Chemistry, 141, **404**, (1998)

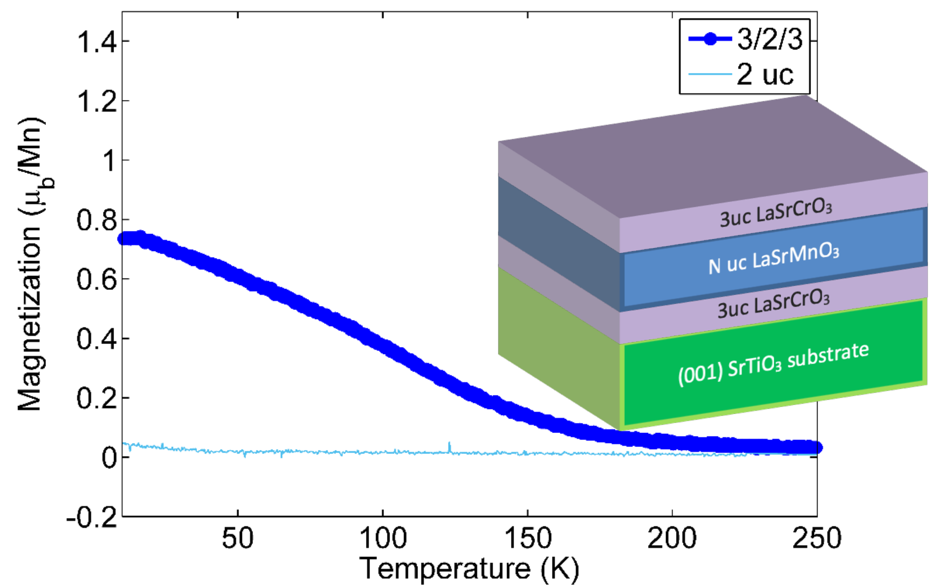
Why $LaSrCrO_3$

- **Valence –matched to $LaSrMnO_3$**
  - Tune La/Sr ratio
- **Lattice matched to LSMO**
  - Pseudocubic lattice constant LSCO ~3.88 A
- **Oxygen-octahedral rotations matched to LSMO**
  - Cr-O-Cr bond angles ~160^o (166^o for LSMO)
- **Suspress Interfacial charge transfer**

Kumigashira, APL, 84, **5353**, (2004)

Interface-Engineered 2D magnetism

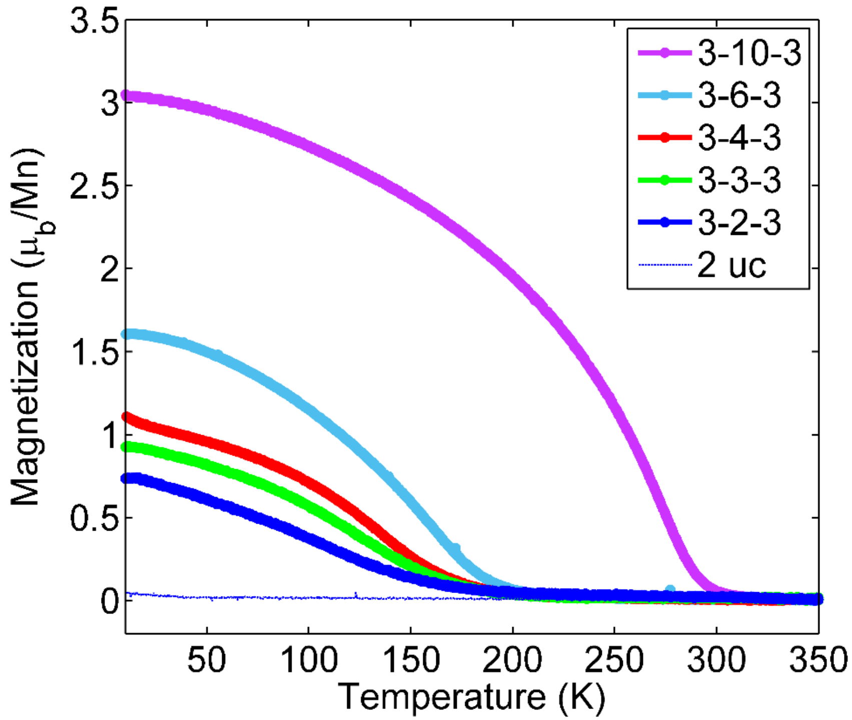


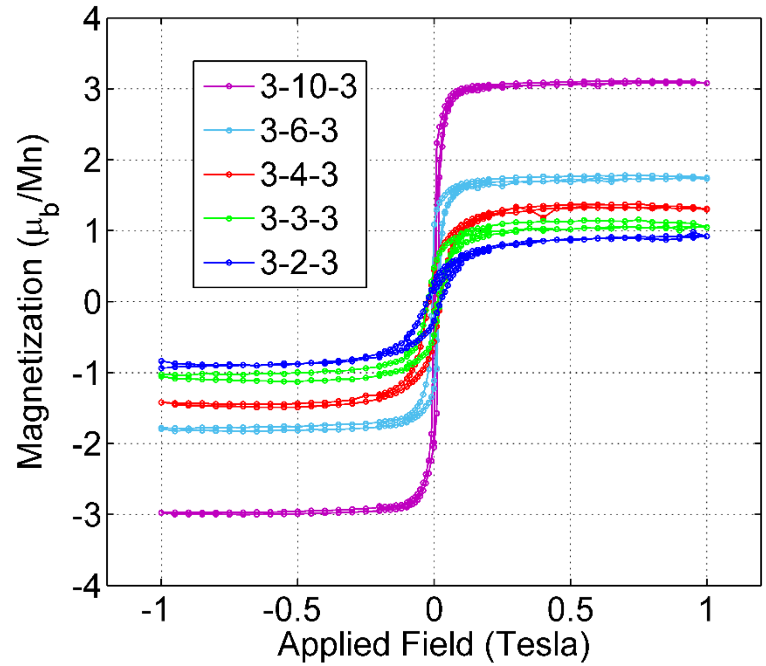


Magnetic properties controlled by interfacial structural engineering!

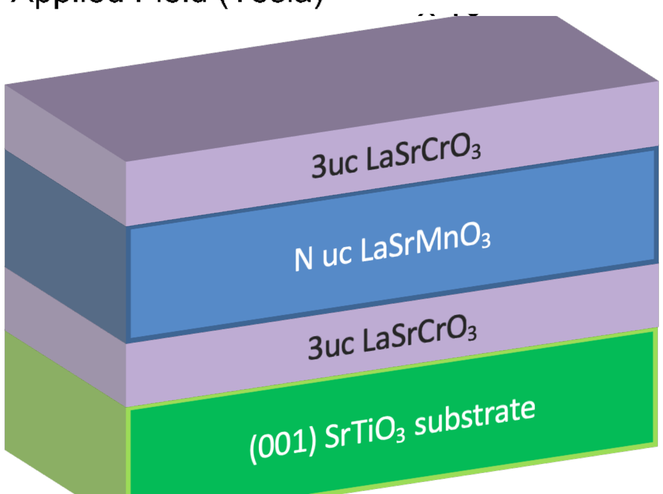
[Koohfar et al, npj Quantum Materials 4, 25(2019)]

Interface-Engineered 2D magnetism



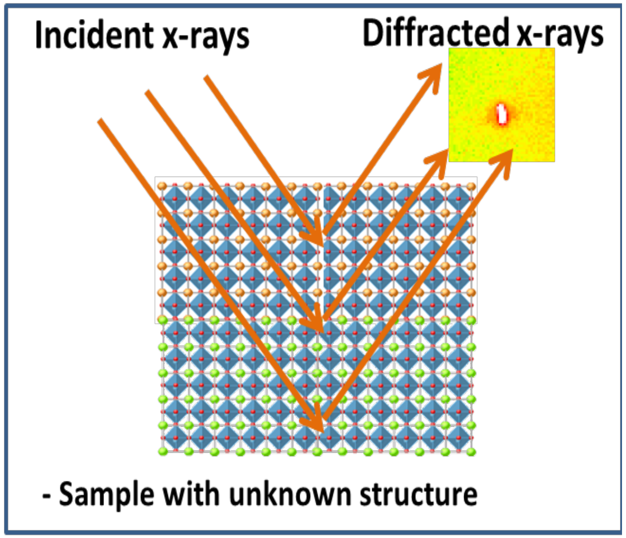


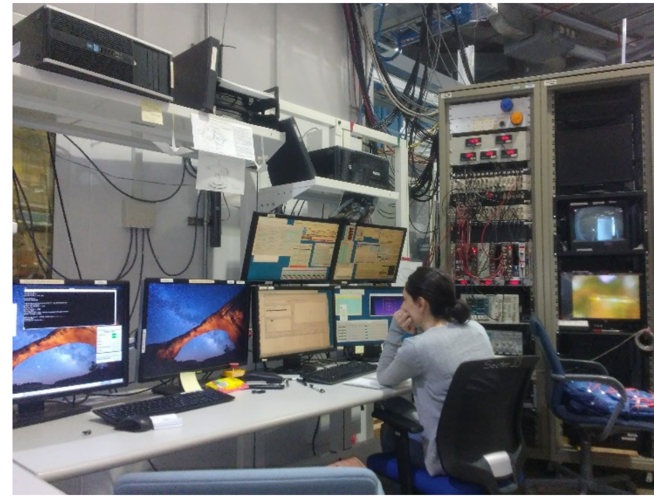
- Ferromagnetism in 2 uc LSMO!



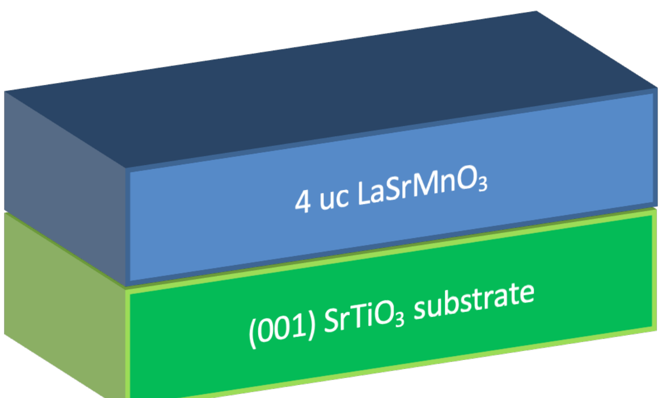
Are we removing polar distortions?

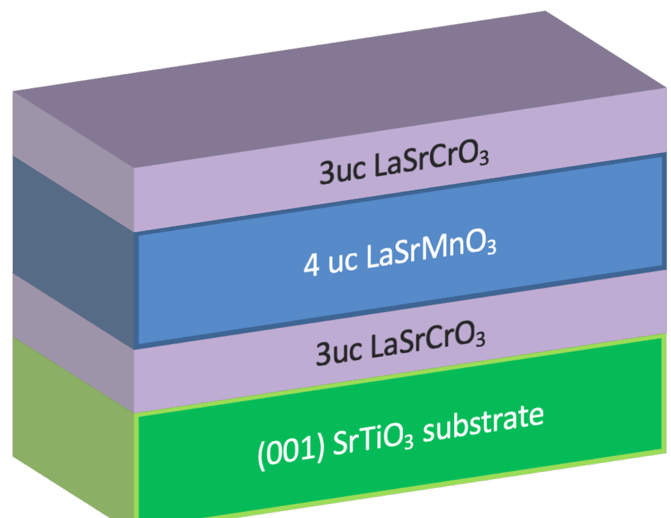
Argonne NATIONAL LABORATORY





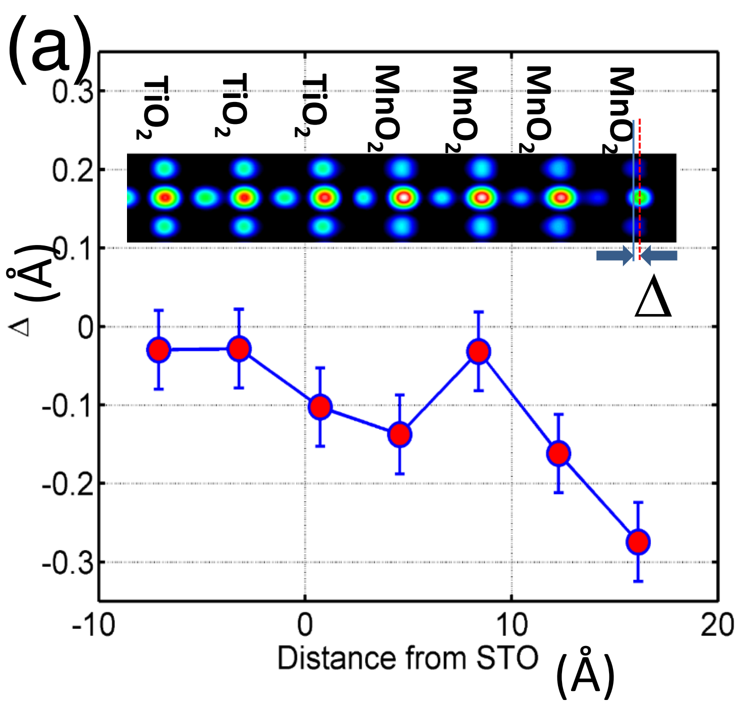
Compare atomic structures of **4uc LSMO** and **3LSCO/4LSMO/3LSCO**



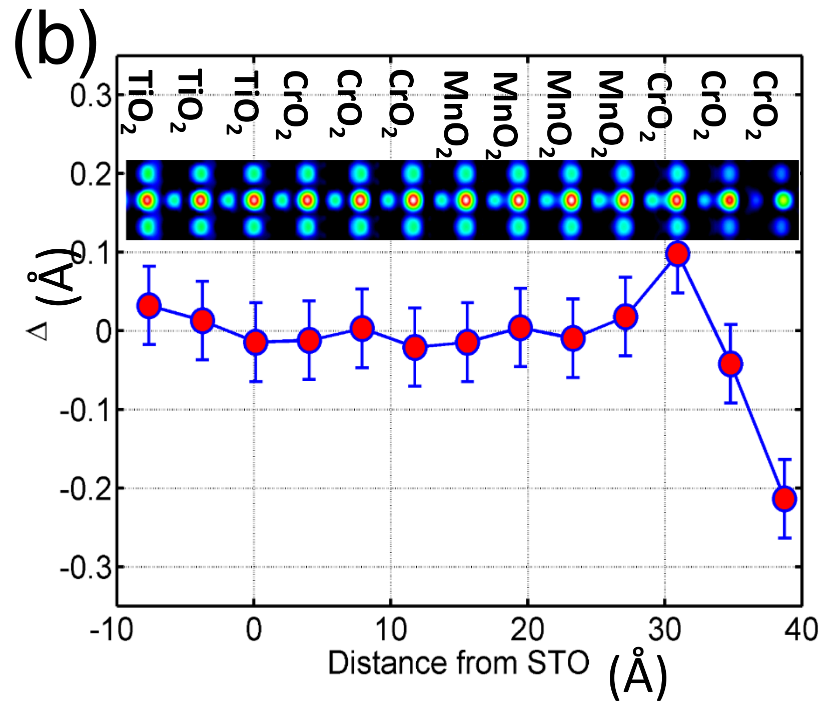


Are we removing polar distortions?

4uc LSMO/$SrTiO_3$



3uc LSCO \4uc LSMO/3uc LSCO

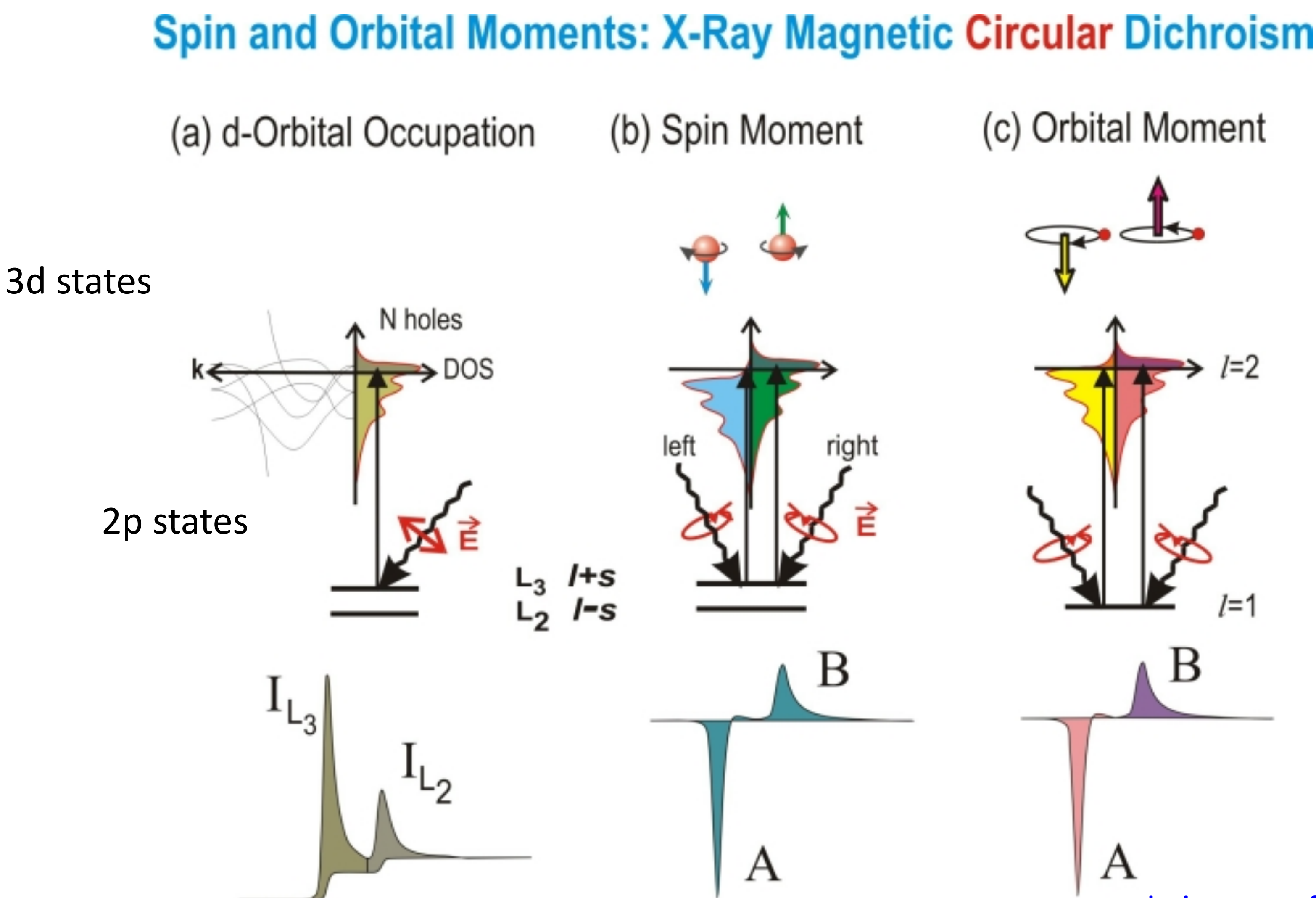


No polar distortions in LSMO layer!

- Bulk-like Mn-O bonds in 3/4/3 heterostructure

Koohfar et al, npj Quantum Materials 4, 25(2019)

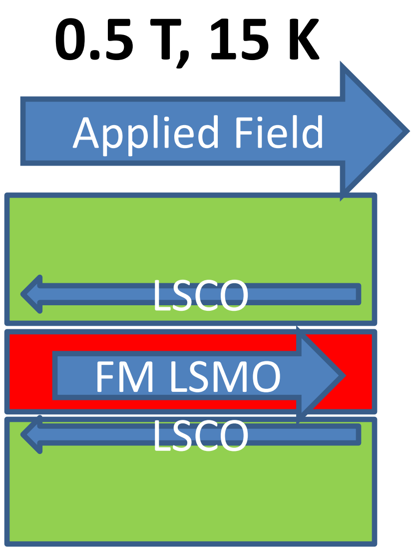
Verifying Magnetism by XMCD



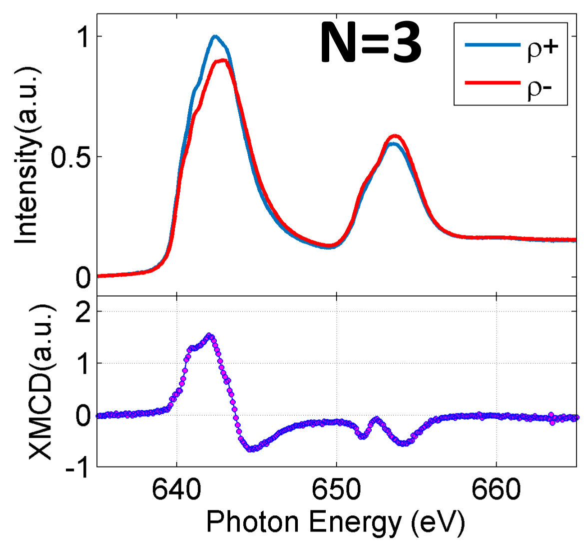
www-ssrl.slac.stanford.edu

Element-Specific Magnetic Measurements

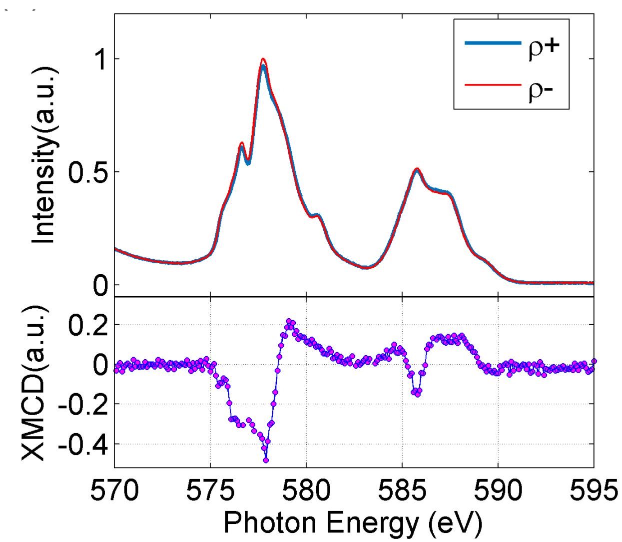
- XMCD indicates Ferromagnetic LSMO



Mn L edge

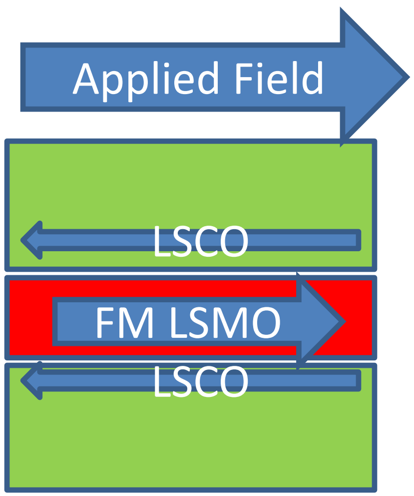


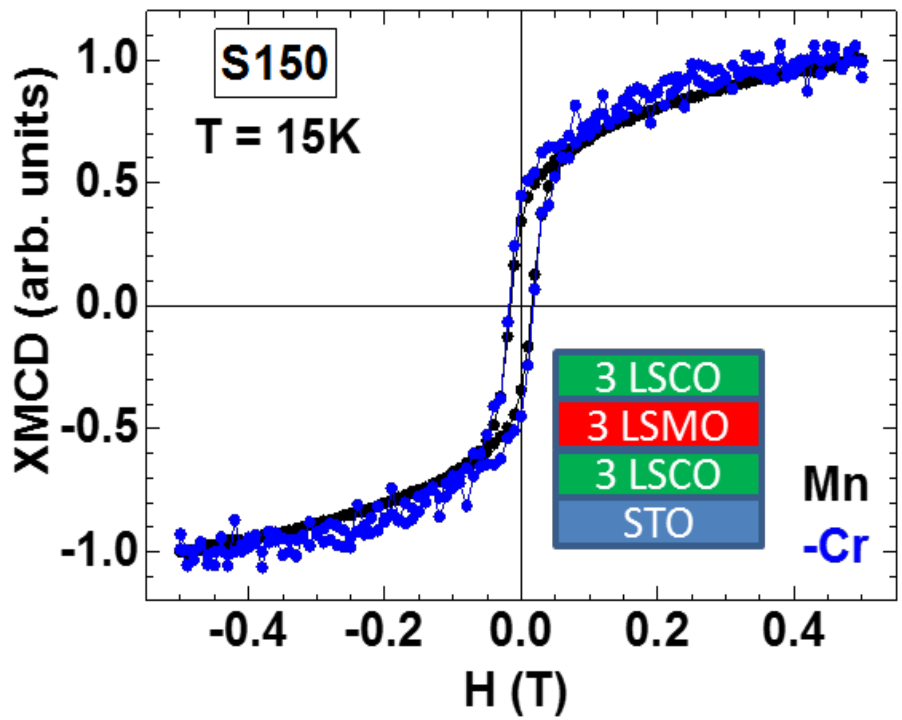
Cr L edge



Element-Specific Magnetic Measurements

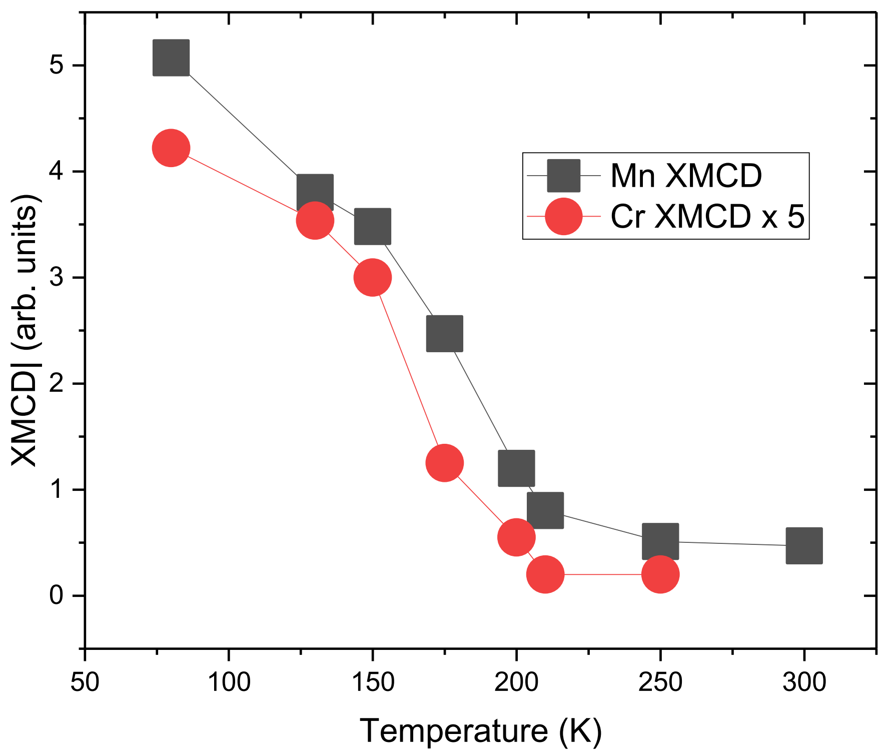
- XMCD indicates Ferromagnetic Mn ions

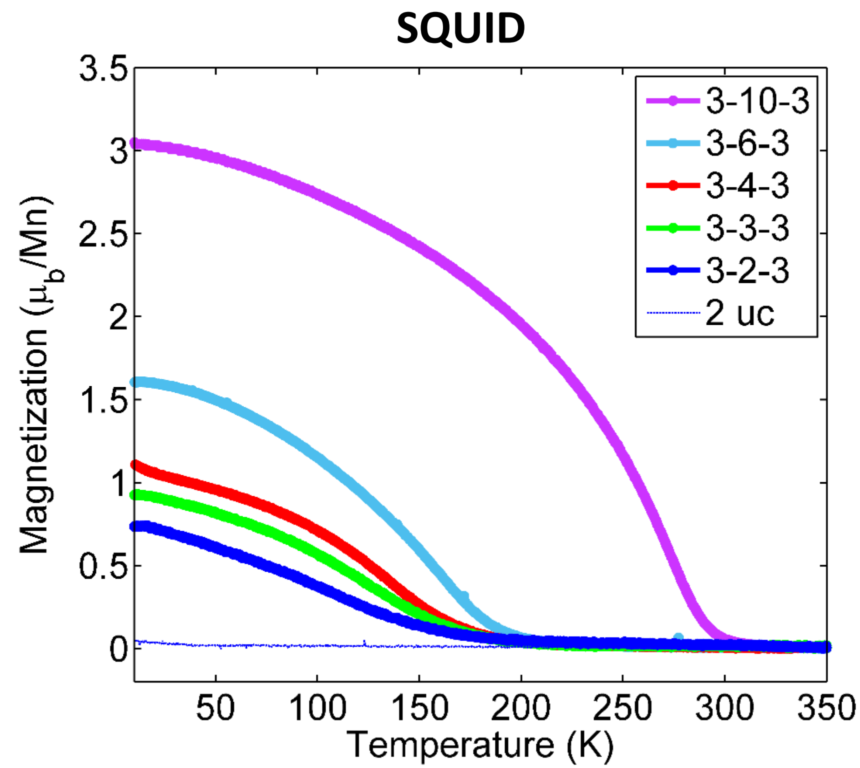




- Anti-Ferromagnetic exchange interaction between Cr and Mn at interface

Temperature dependence of Cr and Mn XMCD



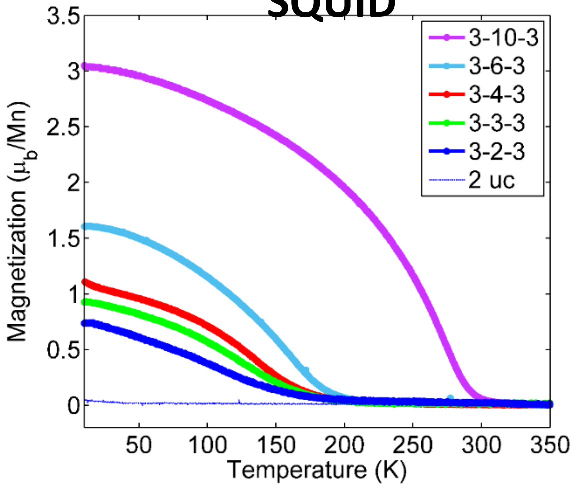


- SQUID measures net magnetization
- Theory predicts -2.0 μ_B /Cr and 3.4 μ_B /Mn

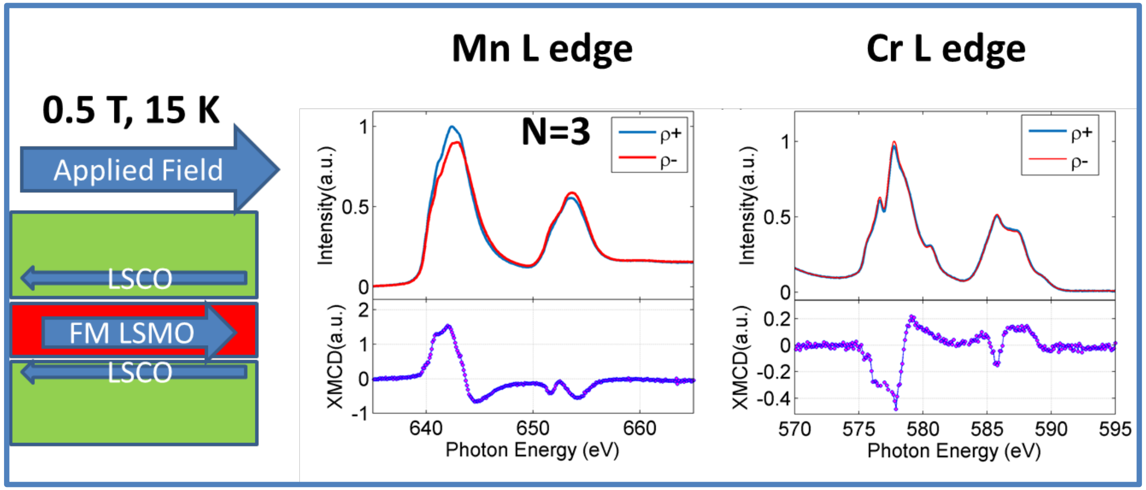
Koohfar et al, npj Quantum Materials 4, 25(2019)

Determining LSMO and LSCO moments

SQUID

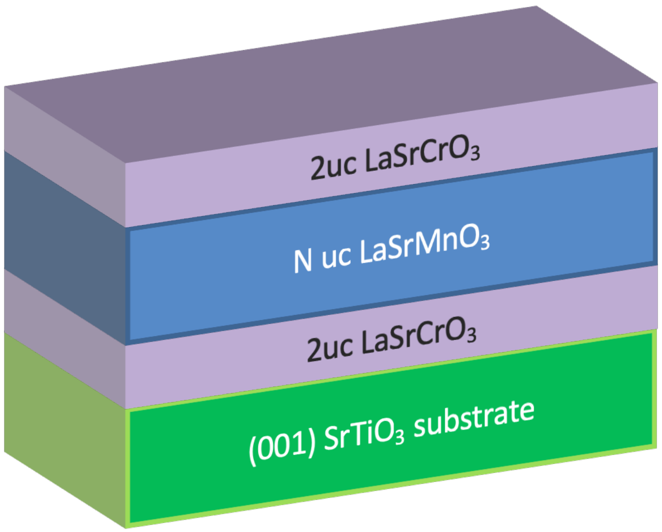


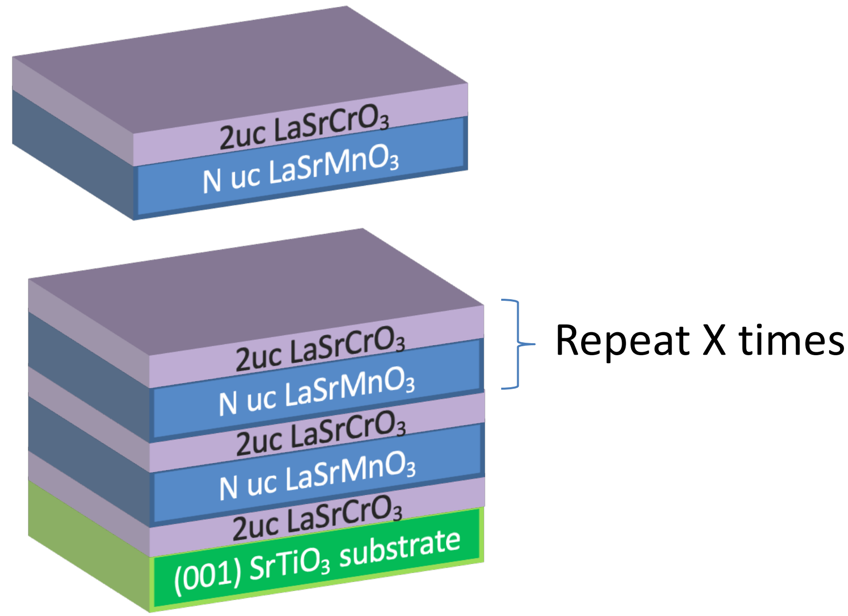
XMCD



- Squid measures total (LSMO+LSCO) magnetization
- XMCD shows LSCO has a negative magnetization
- Can we determine LSMO and LSCO moments separately?

Determining LSMO and LSCO moments





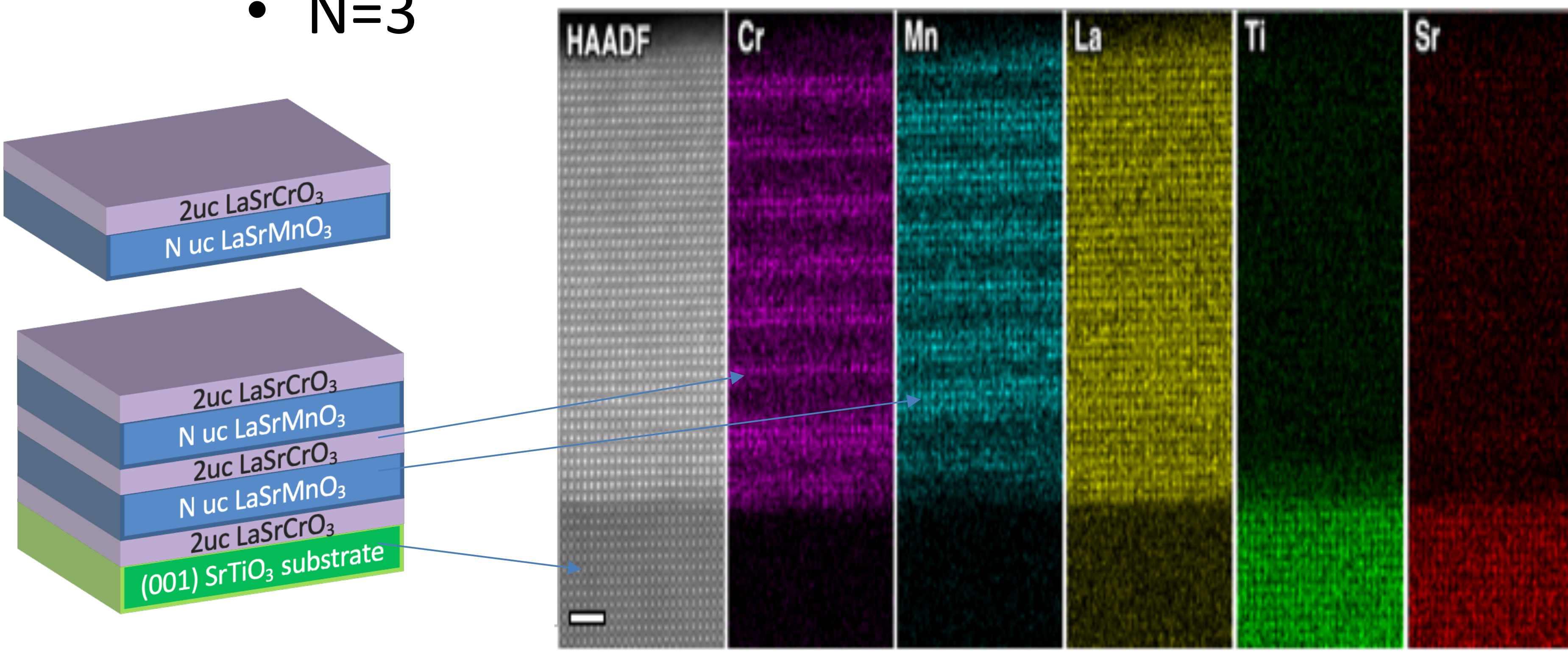
- Create repeats of LSMO/LSCO bilayers
- Determine magnetization as a function of ratio of LSMO/LSCO thickness

$$m^* = \text{total SQUID magnetization}/N_{LSMO} = m^{Cr}\; M_{LSCO}/N_{LSMO} + m^{Mn}$$

$m^{Mn} \rightarrow$ magnetization per Mn ion
$m^{Cr} \rightarrow$ magnetization per Cr ion

High-Resolution Electron Microscopy

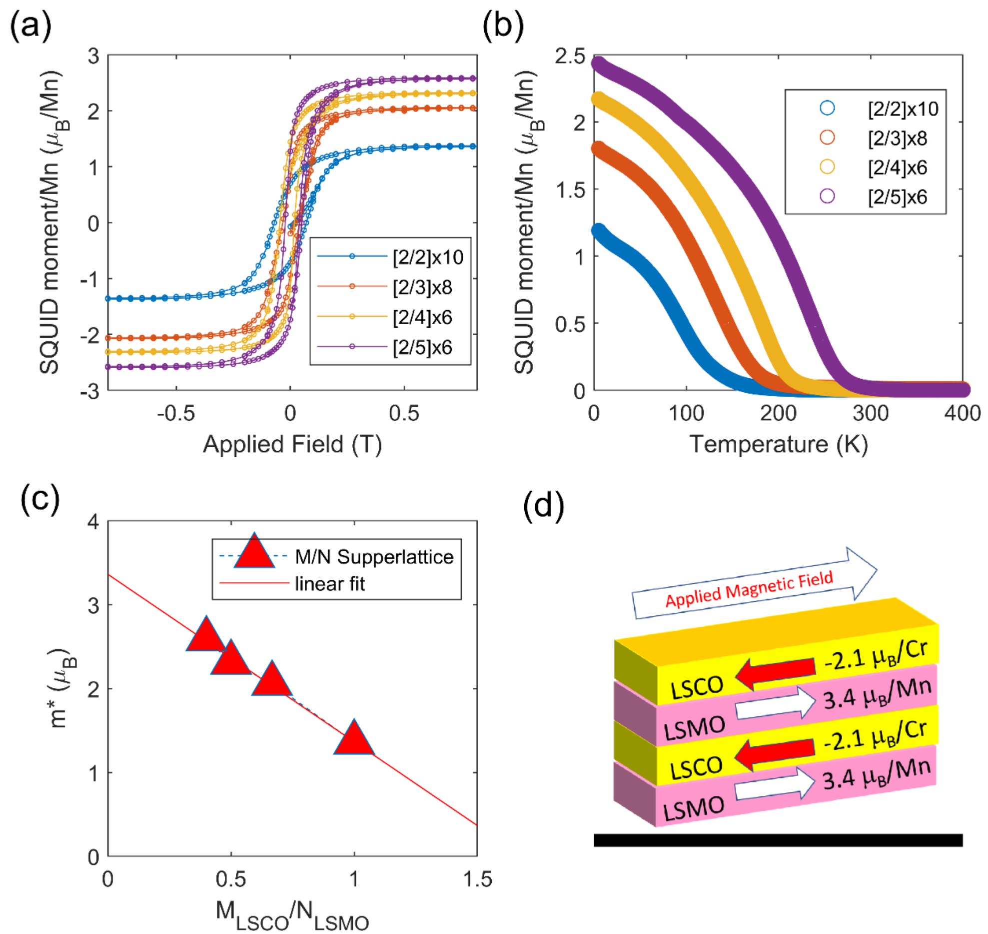
- N=3



Koohfar et al, npj Quantum Materials 4, 25(2019)

[M LSCO/N LSMO] superlattices

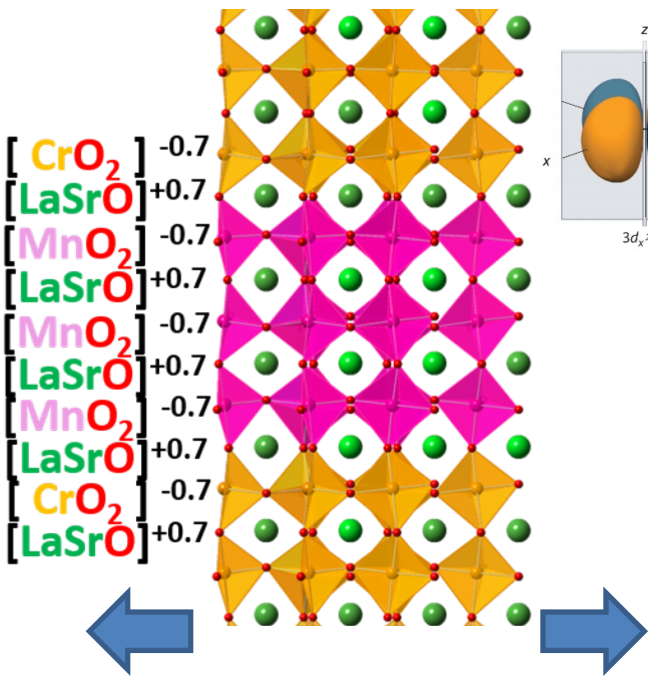
- Determine Cr and Mn spins from fitting SQUID magnetization as a function of LSCO thickness/LSMO thickness
- Extract from linear fit Mn (3.4 uB/Mn) and Cr(-2.1 uB/Mn) moments.
- Moments agree with DFT predictions

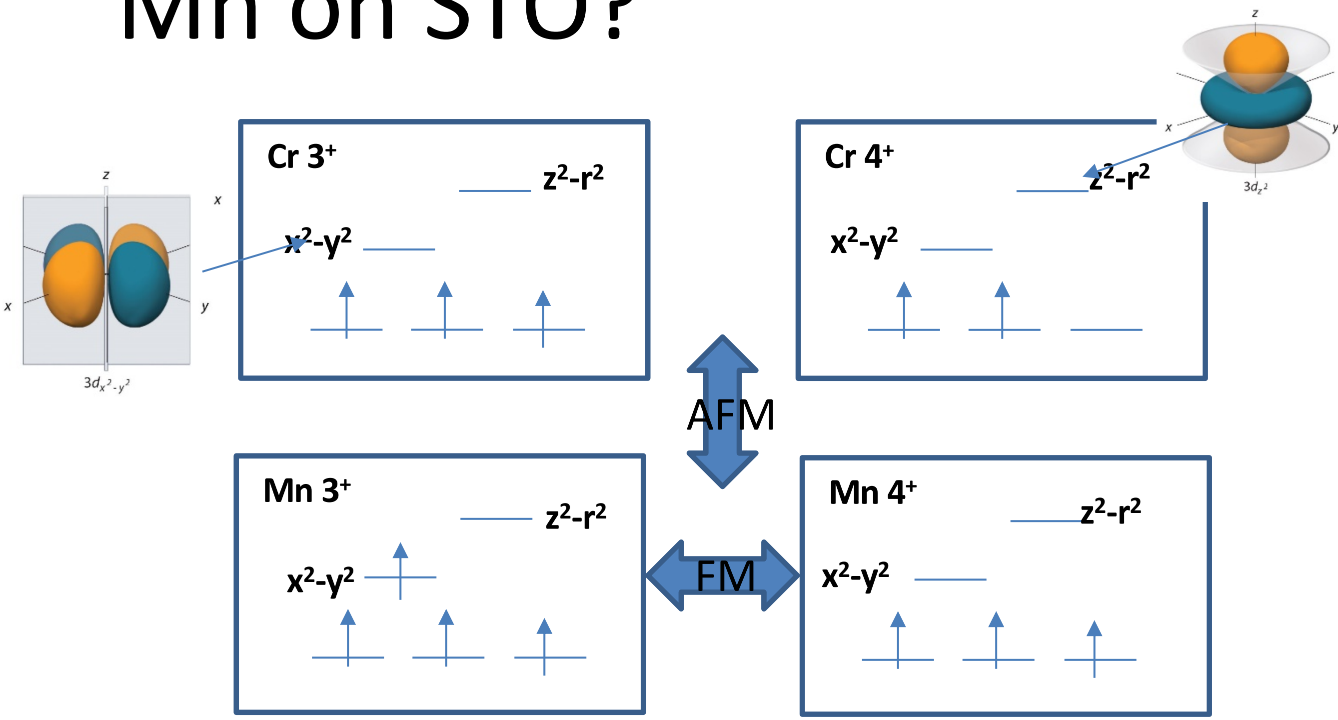


$\mathbf{m^*}$=total SQUID magnetization/N_{LSMO} $= \mathbf{m^{Cr}}\ M_{LSCO}/N_{LSMO} + \mathbf{m^{Mn}}$

$m^{Mn} \rightarrow$ magnetization per Mn ion
$m^{Cr} \rightarrow$ magnetization per Cr ion

Why AFM coupling between Cr and Mn on STO?





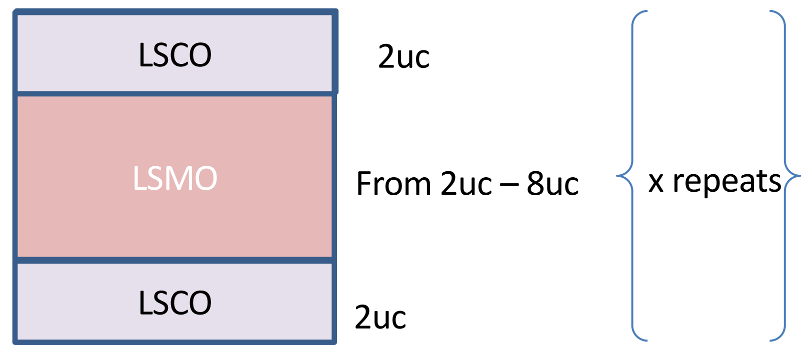
Tensile strain on STO

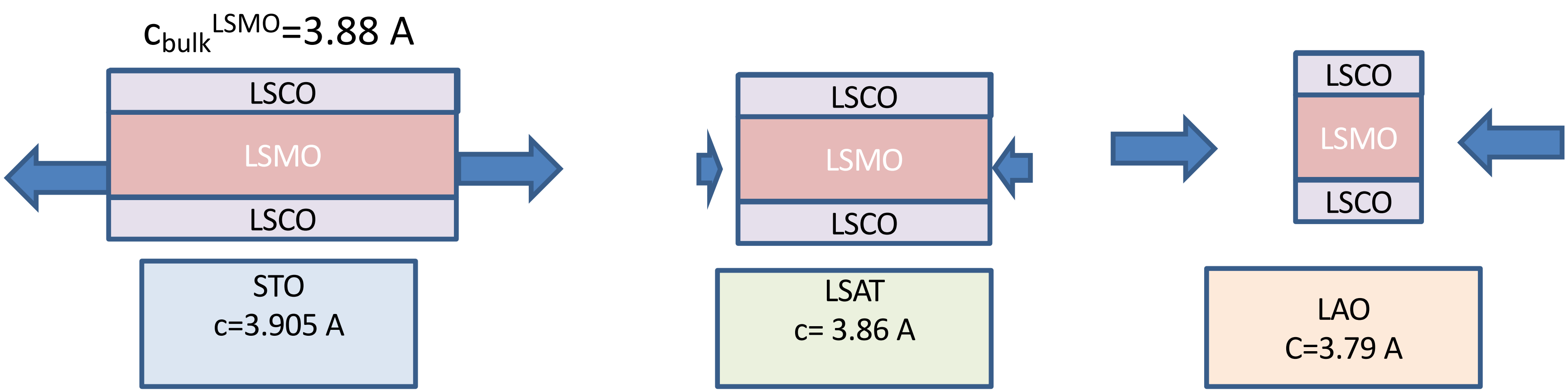
–Tensile strain lowers x^2-y^2 orbitals. In-plane FM Mn^{3+}-Mn^{4+} coupling

- AFM coupling between empty Mn z^2-r^2 and Cr ions – Goodenough-Kanamori rules
- What happens for compressive strain on LAO? FM Cr-Mn coupling??

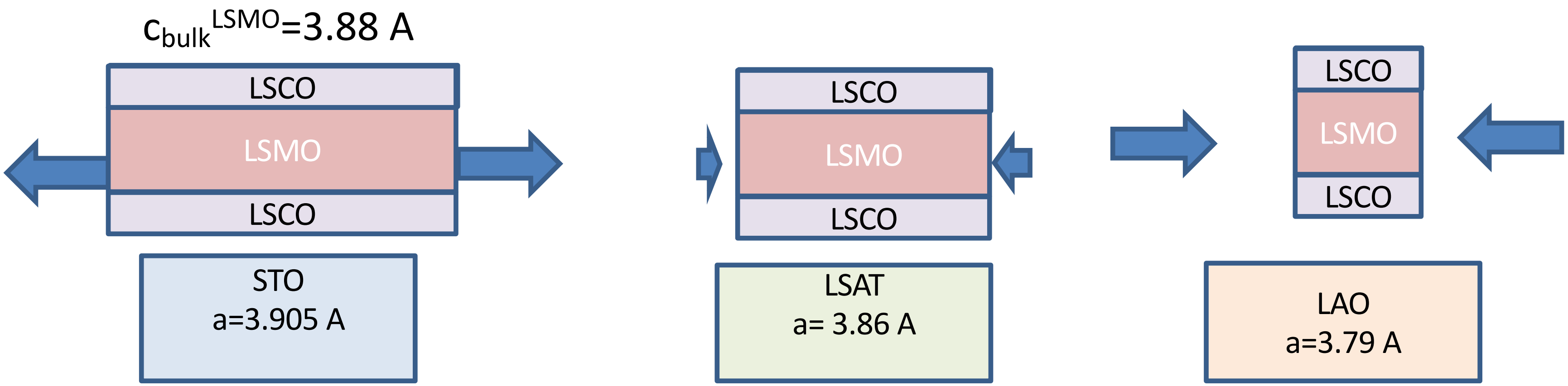
Kanamori, J. of Phys. Chem. Solids, 10, **87**, (1959)

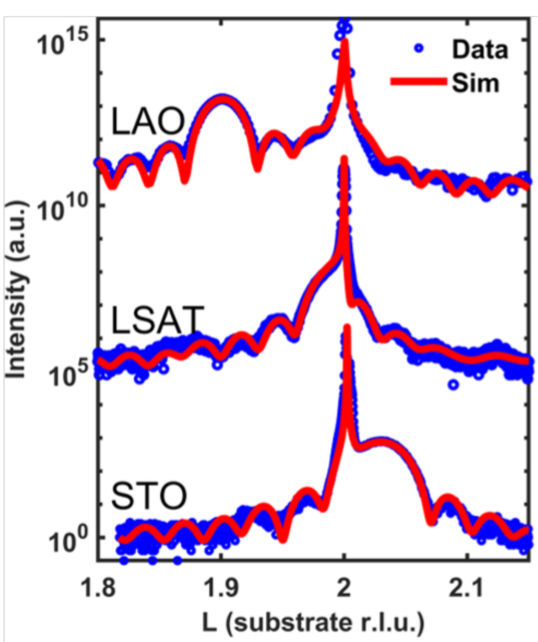
Effect of Epitaxial Strain

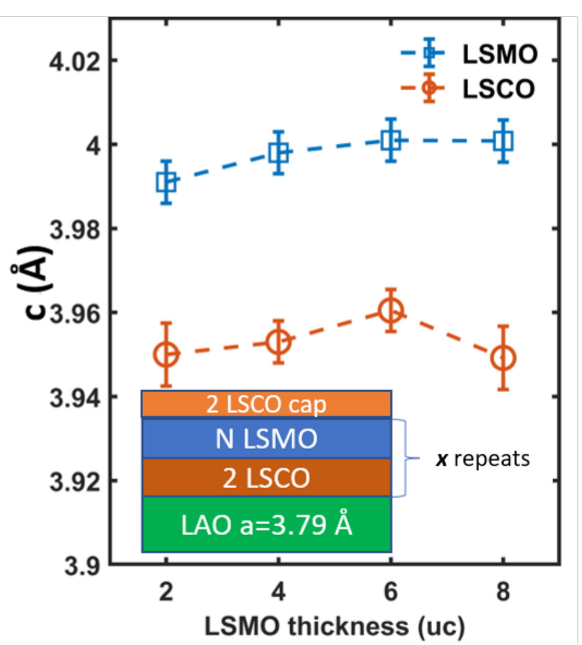


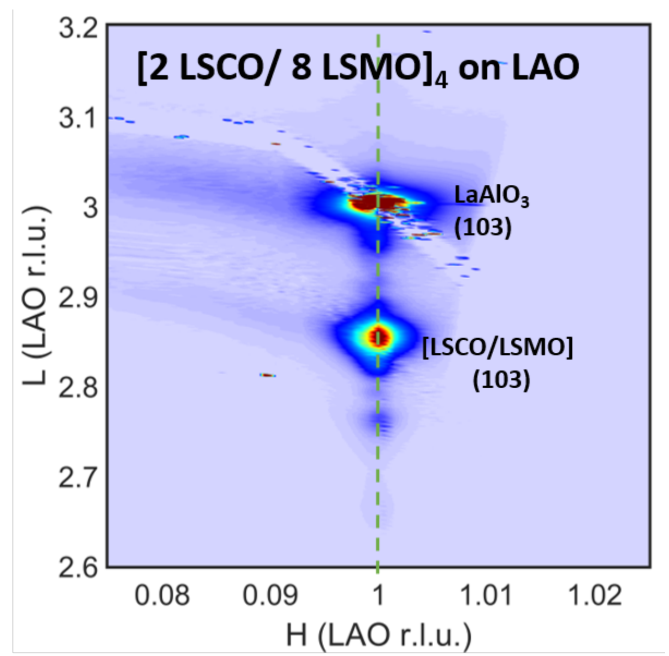


Strain Engineering

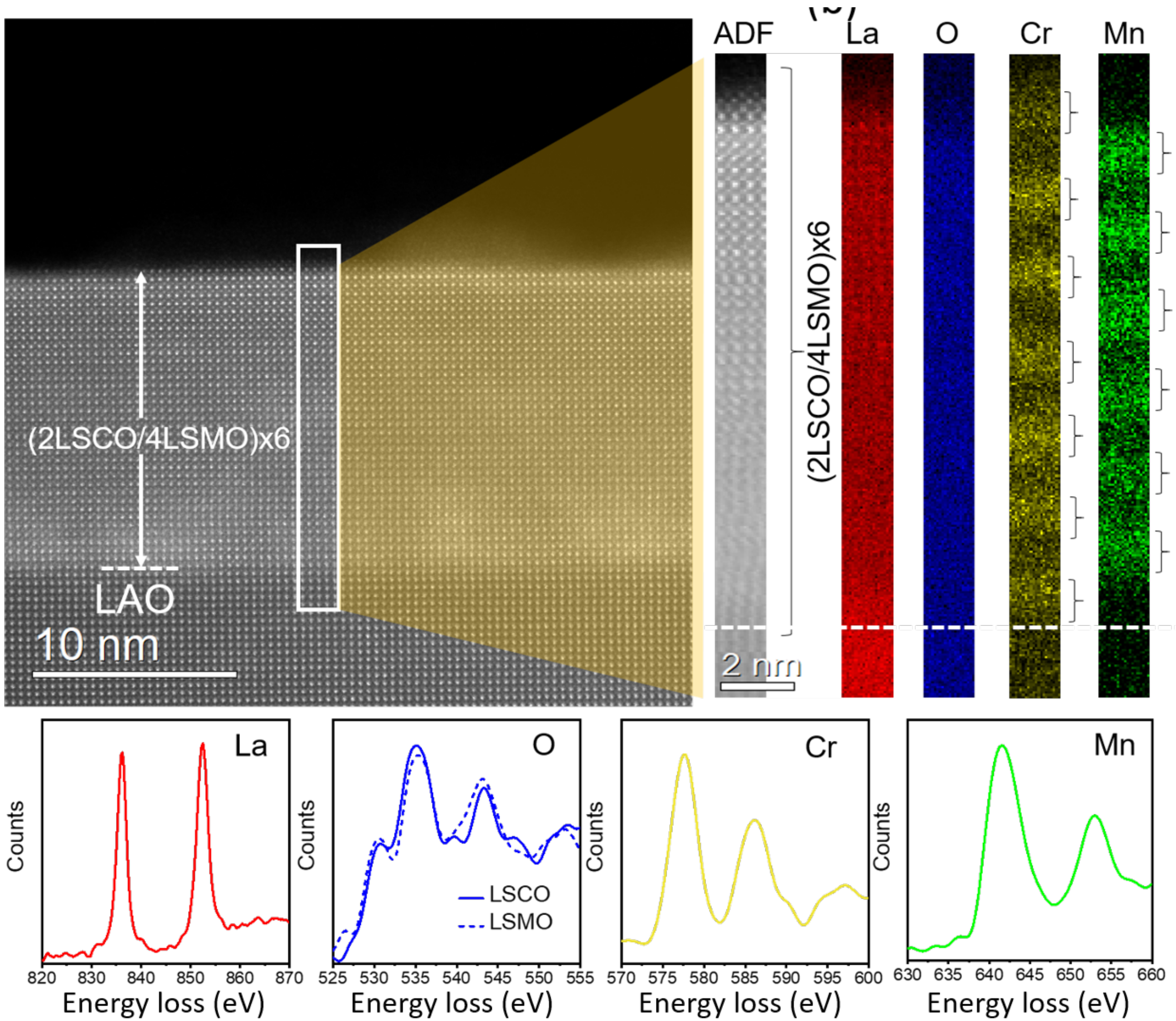




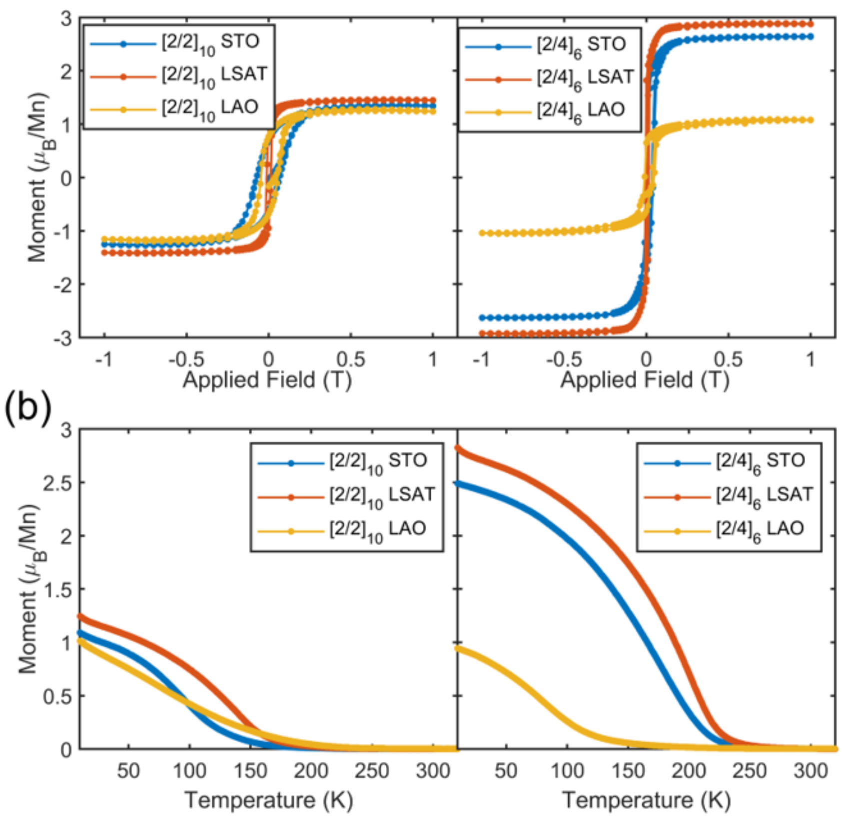


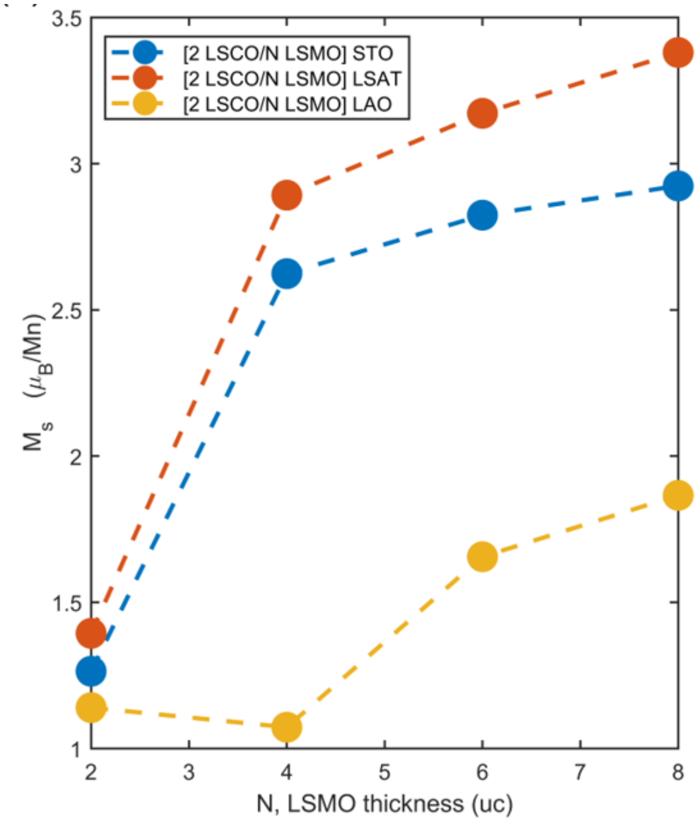


Compresively strained LSCO/LSMO



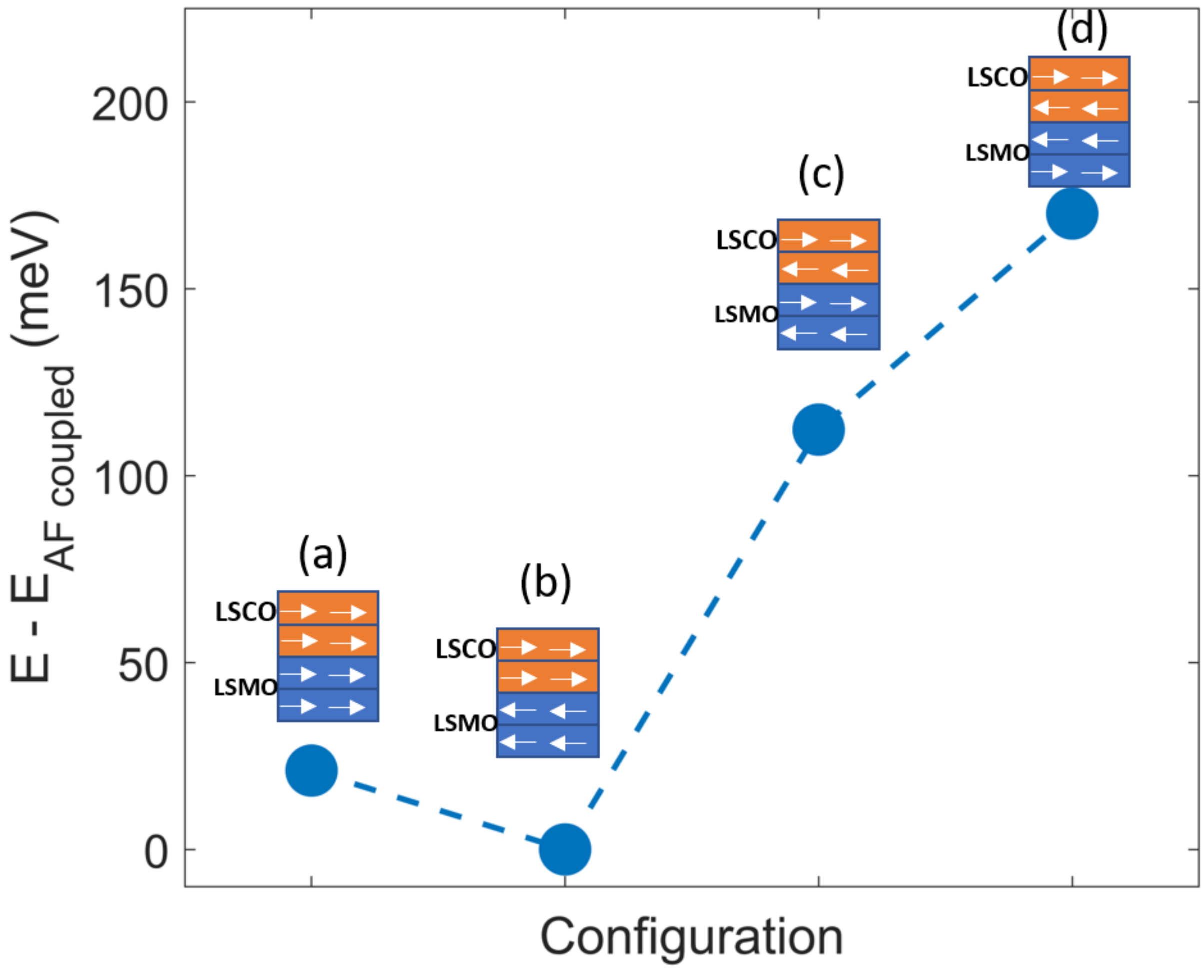
FM ground state independent on strain

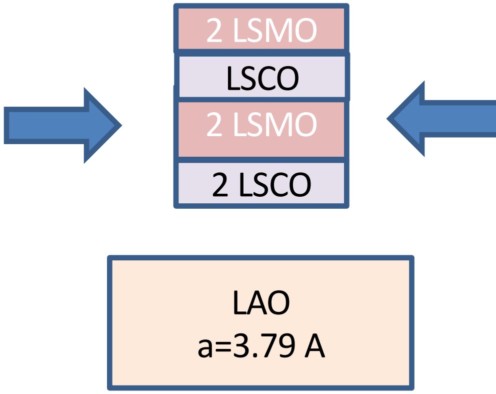




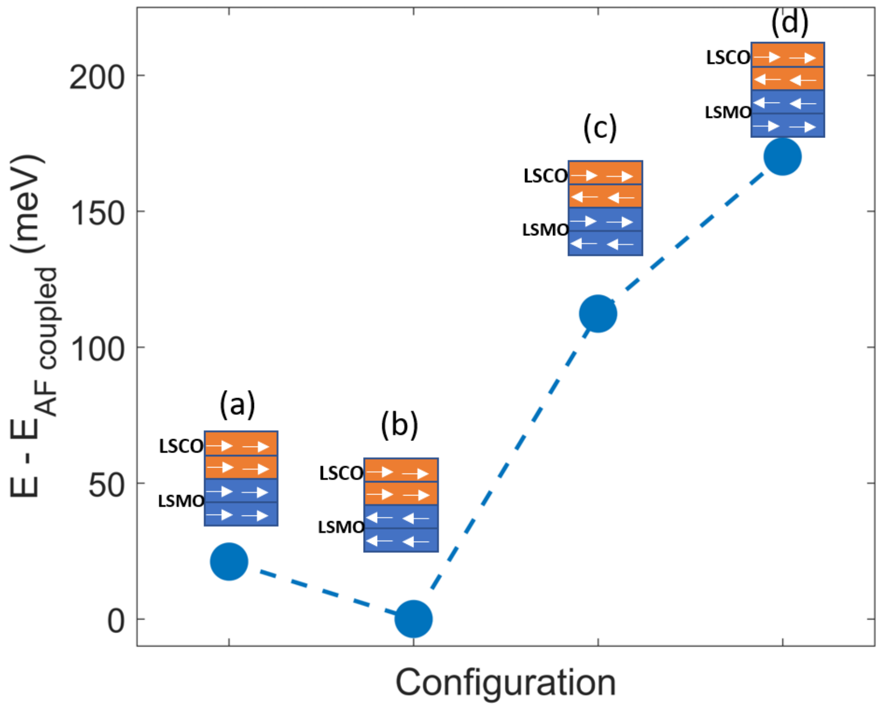
[Koohfar, et al. Phys. Rev B 101, 064420 (2020)]

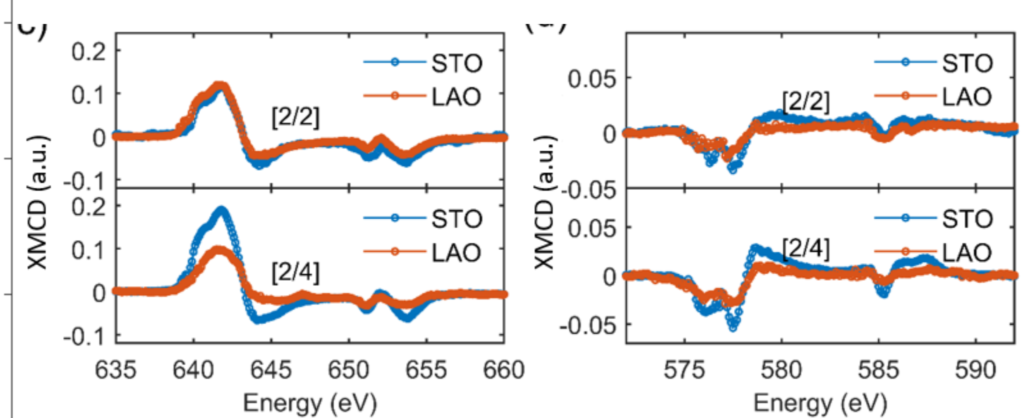
DFT Magnetic ground states





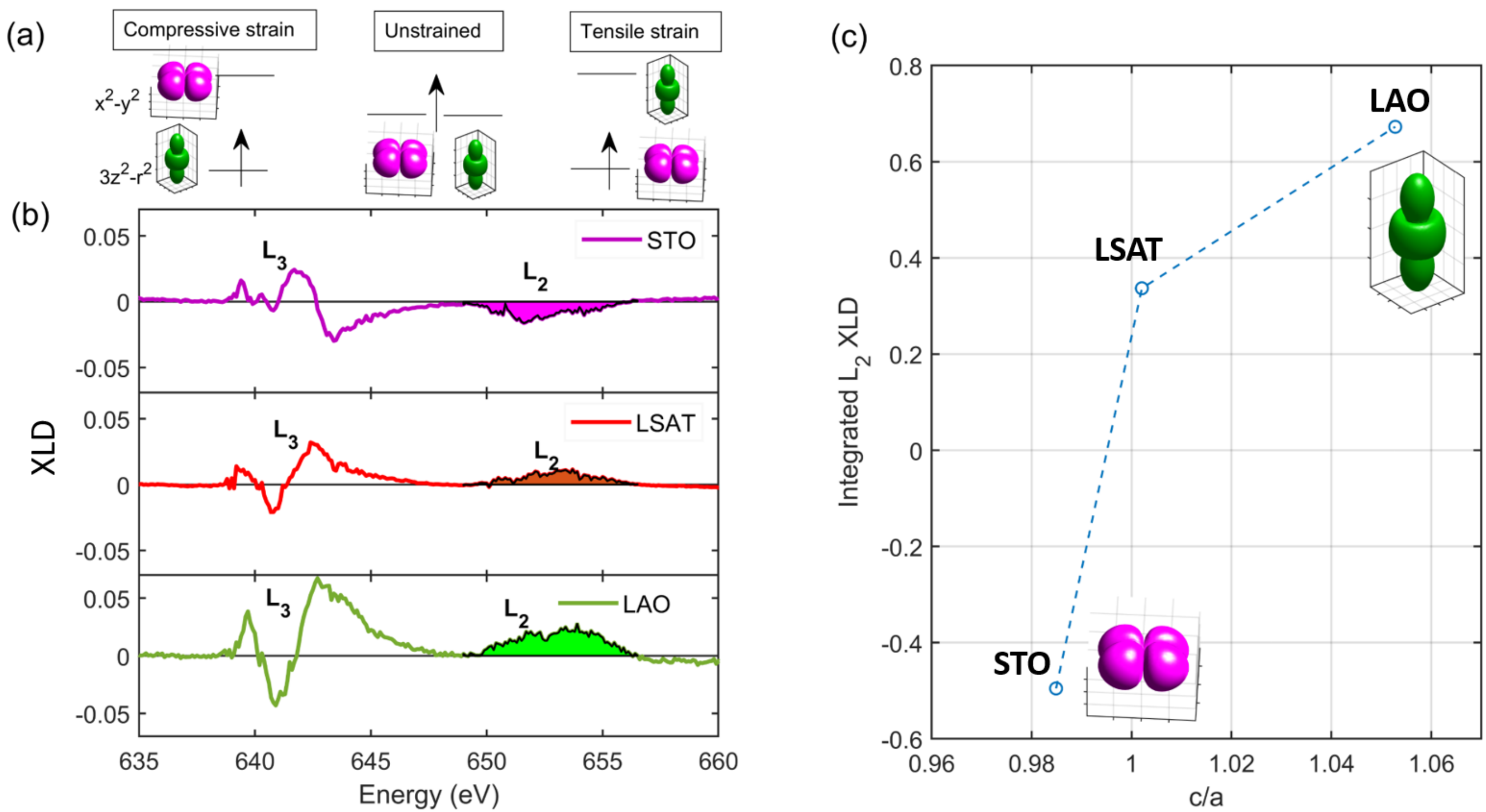
Cr-Mn AF coupling



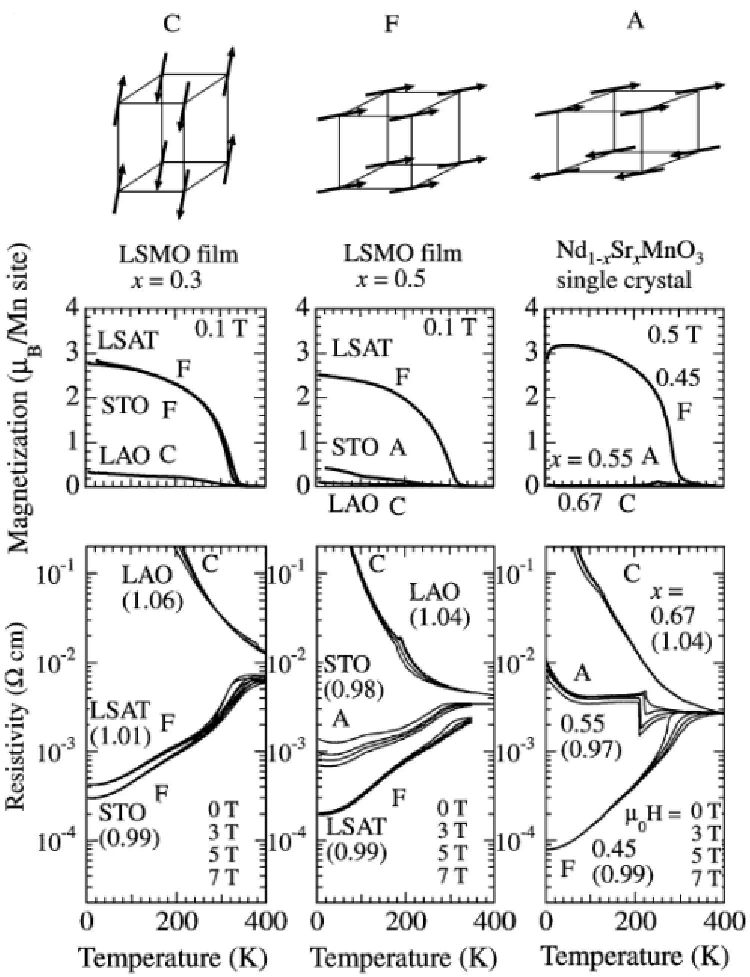


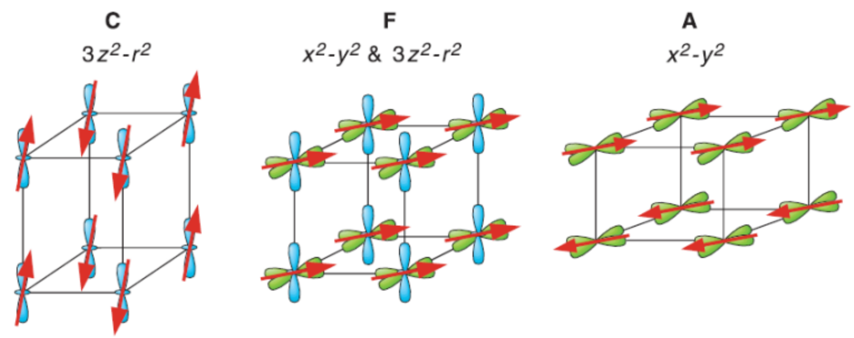
- AF Mn-Cr exchange confirmed for both compressive (LAO) and tensile (STO) strain

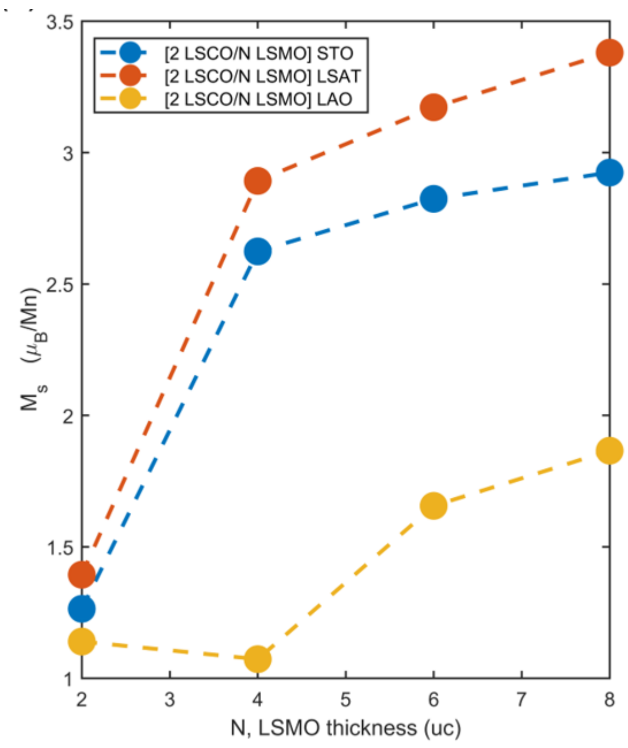
Strain-dependent Orbital ordering



Strain dependent orbital polarization







Millis, Phys. Rev. B **55**, 6405 (1997)
Konishii,..Tokura, J Phys Soc. Japan, 68, 3790 (1999)
Tokura, Nagaosa, Science, 288, 462 (2000)

Summary

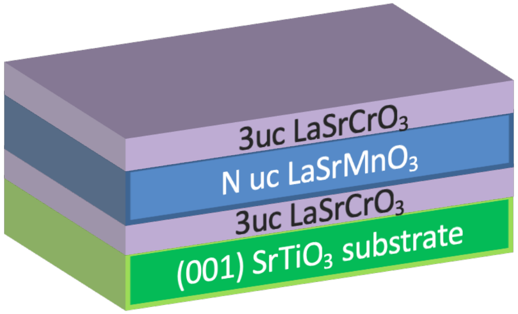
- Demonstrated atomic scale control of magnetism in 2D oxide films

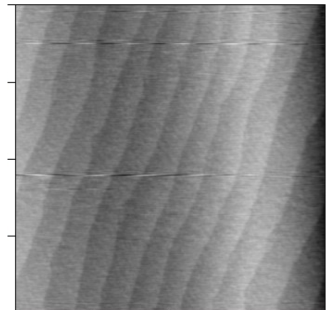
- Strong interplay of electronic/magnetic properties with atomic scale structural distortion in thin $LaSrMnO_3$ films .

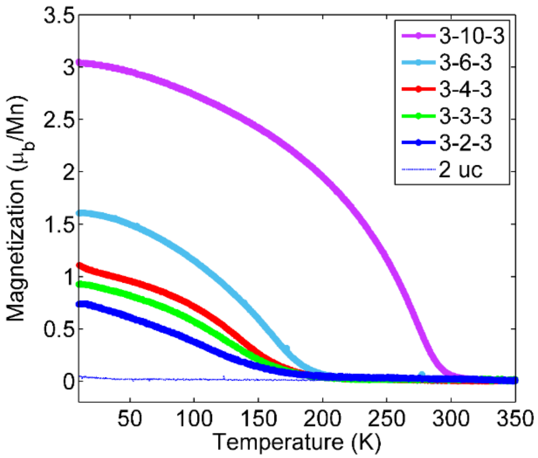
- Important implications for the design of optimized complex oxide materials

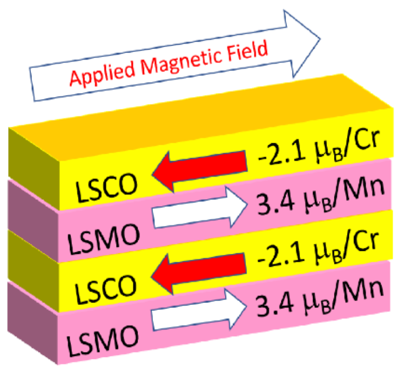
Koohfar, et al. Phys. Rev B 101, 064420 (2020)

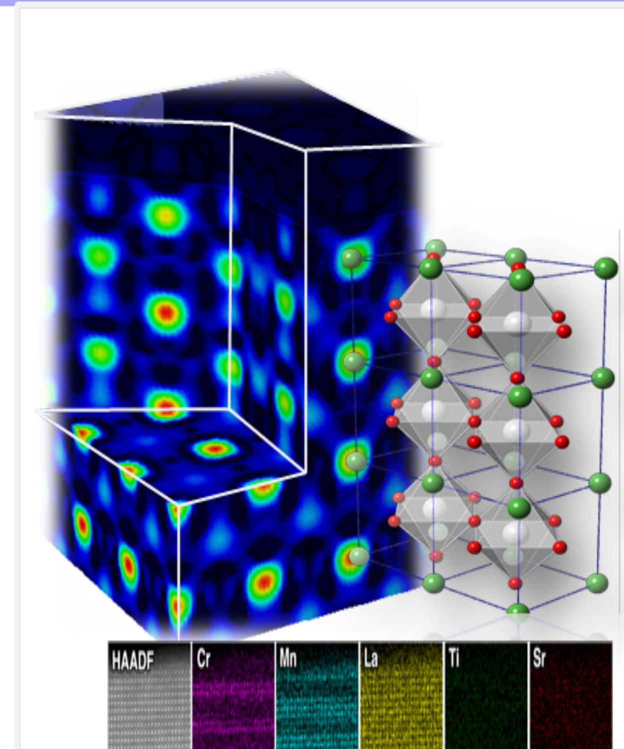
Summary

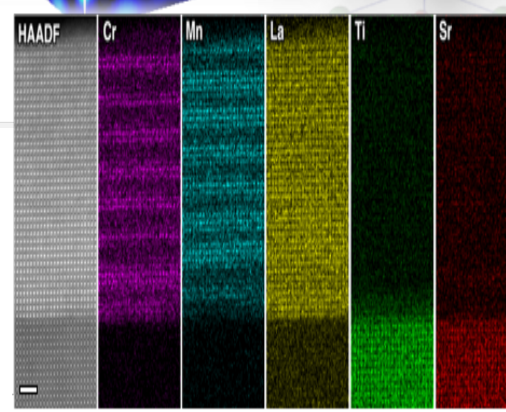








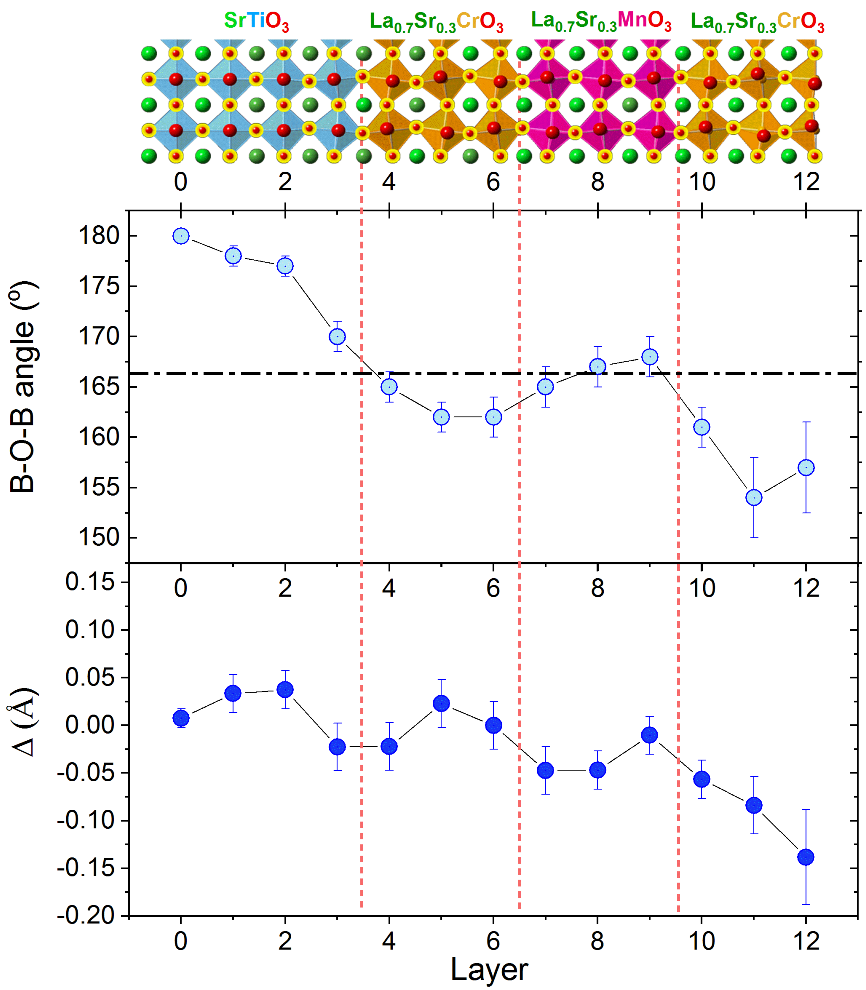


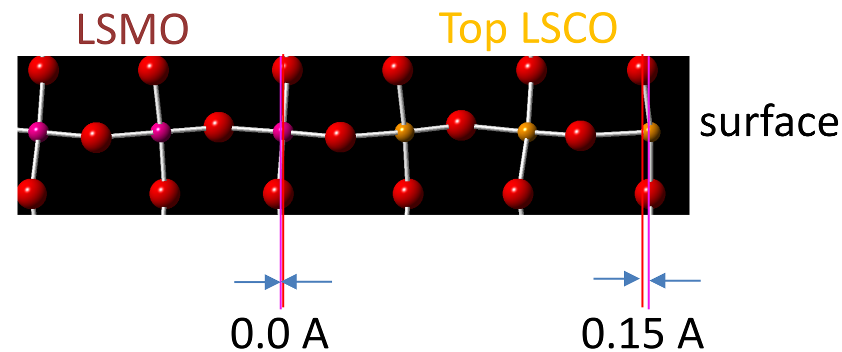


- Ferromagnetism in quasi-2D $LaSrMnO_3$ with bulk-like Mn moments
- Magnetic ground state related to interfacial orbital and structural interactions

NSF DMR1751455

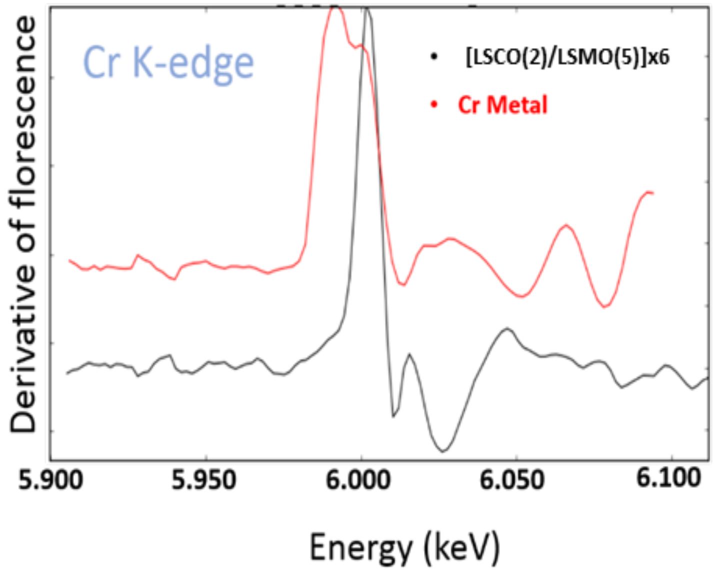
Atomic structure of 3/3/3

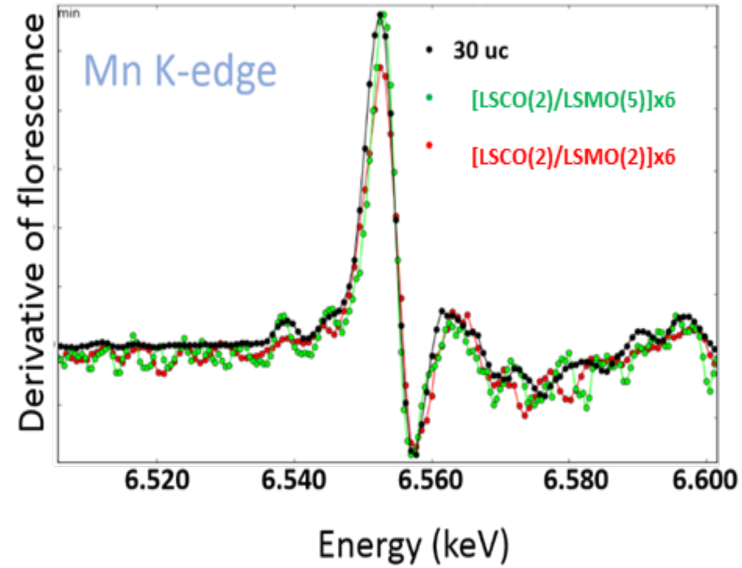




- ❑ LSMO bond-angles close to bulk (166°)
- ❑ Suppressed polar distortions in LSMO

Suppression of Charge Transfer





The absorption edges (first peak for each curve) occur at 5.9922 +/-0.0005 keV for Cr metal and 6.0035 +/-0.0005 keV for the superlattice. The energy shift of ~12 eV corresponds to a Cr valence of +3.3+/- 0.1eV

The absorption edges for the 3 samples occurs at ~6.5526+/-0.0005 keV.
- No chemical shift observed.