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Modulation Doping of Ferromagnetism in Manganite Superlattices

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FOR WOMEN IN SCIENCE
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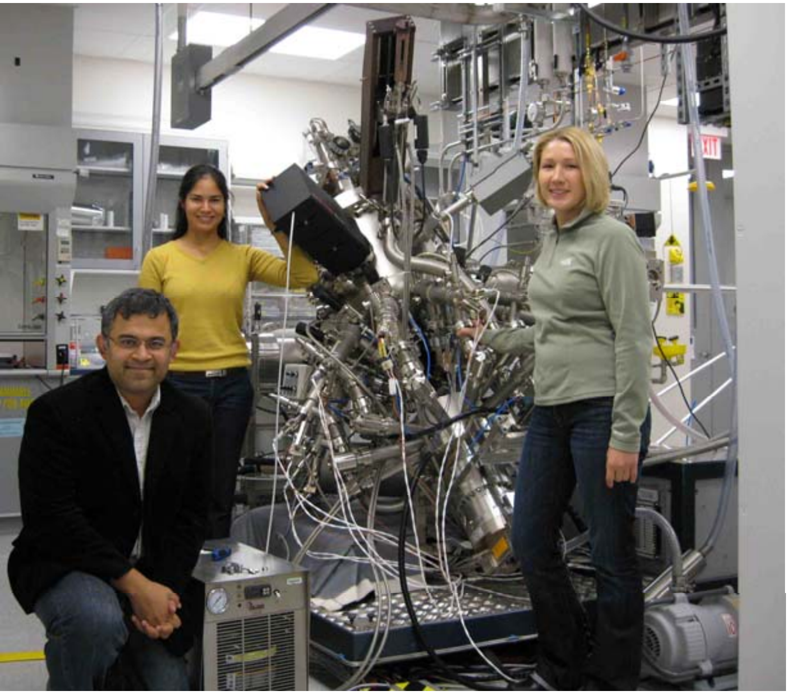
U.S. DEPARTMENT OF ENERGY

Ozone-MBE Team



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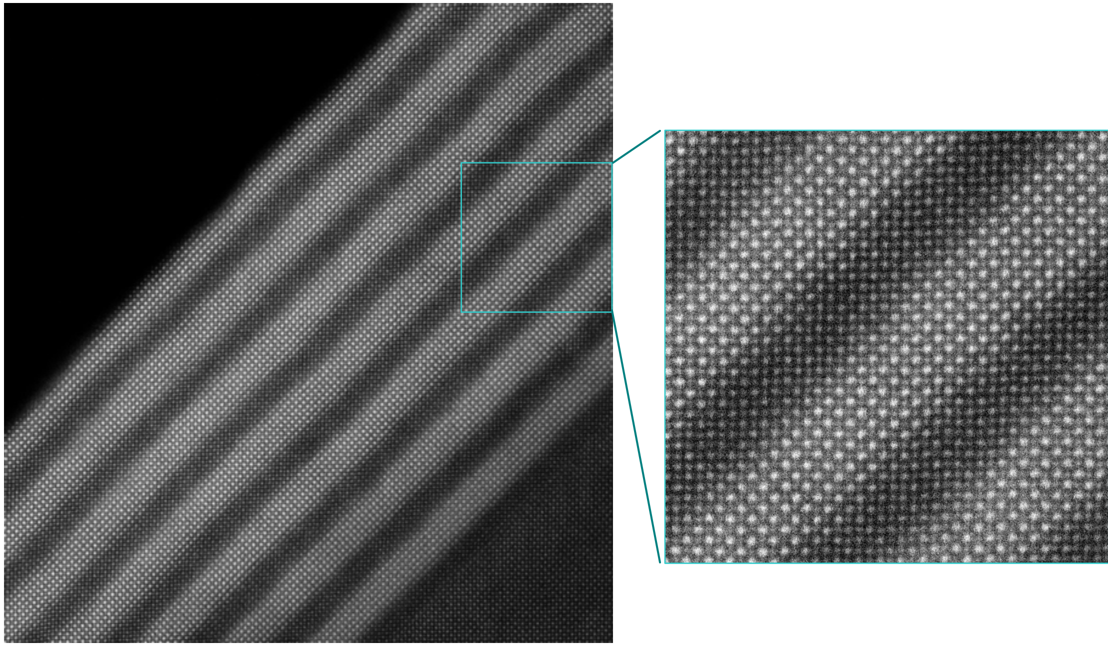

$LaMnO_3/SrMnO_3$ superlattice

STEM: Amish Shah, J.-M. Zuo, UIUC

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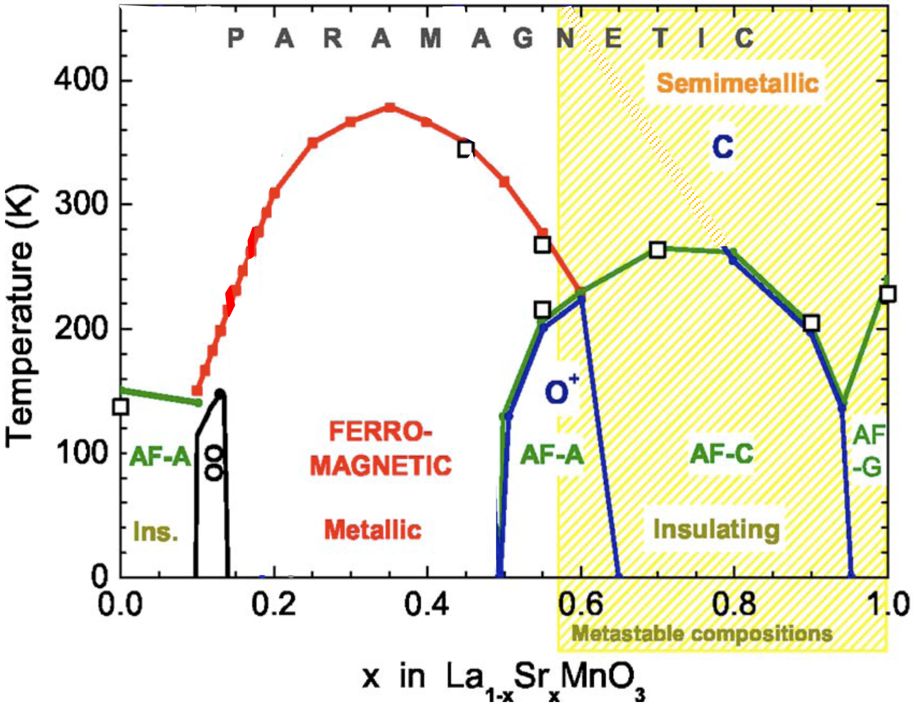
Talk Outline

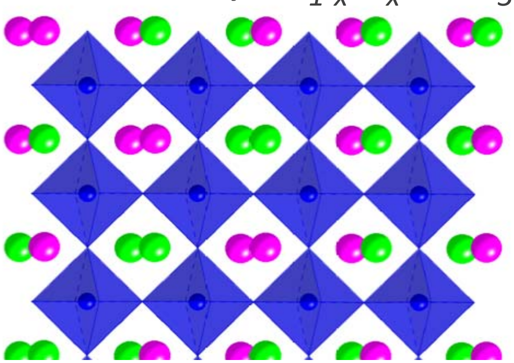
- Tuning across the F/AF phase transition at x=0.5 by digital synthesis

- Delta-doping of ferromagnetism into the antiferromagnetic state

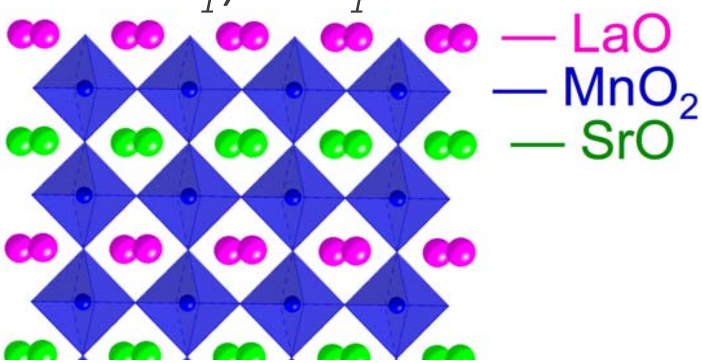


O. Chmaissem, *et al.*, PRB 2003

Disordered La/Sr
Random Alloy $La_{1-x}Sr_xMnO_3$



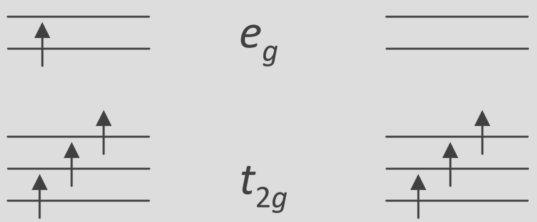
Ordered La/Sr
SMO_1 / LMO_1



Manganites ($La_{1-x}Sr_xMnO_3$): Magnetic Ordering

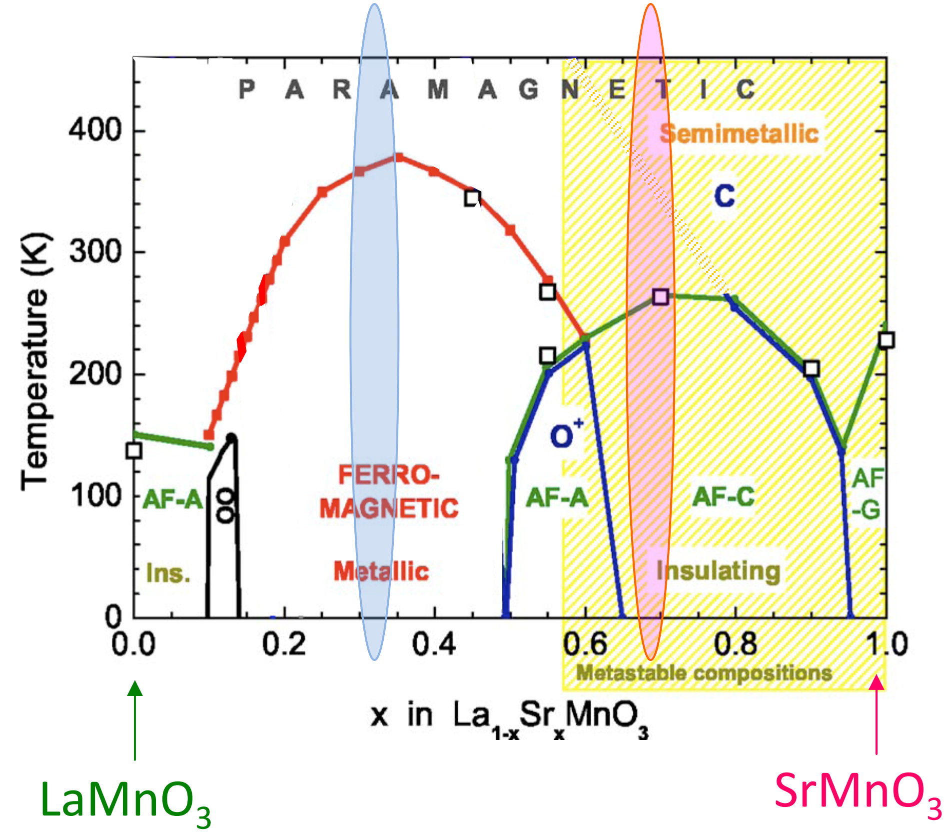
- Exhibit wide variety of ordering phenomena (magnetic, orbital)
- Magnetic ordering related to Mn valence state

Mn 3*d* states



LMO, d^4 — *Mott insulator*

SMO, d^3 — *band insulator*

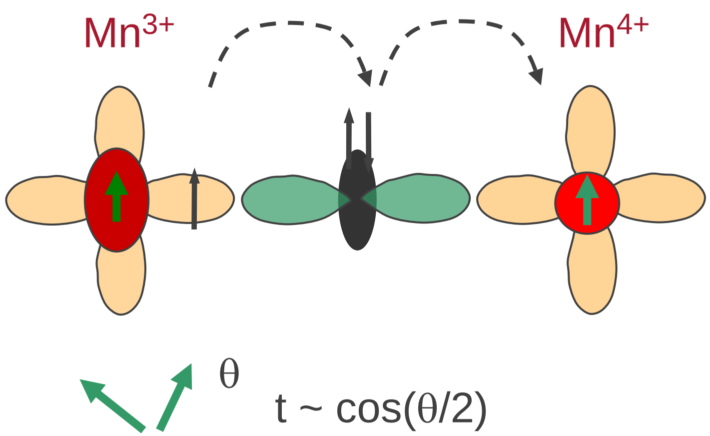


$La_{2/3}Sr_{1/3}MnO_3$: half-metal, CMR effect, T_C > RT

$La_{1/3}Sr_{2/3}MnO_3$: insulating AFM

Competition between double exchange and superexchange

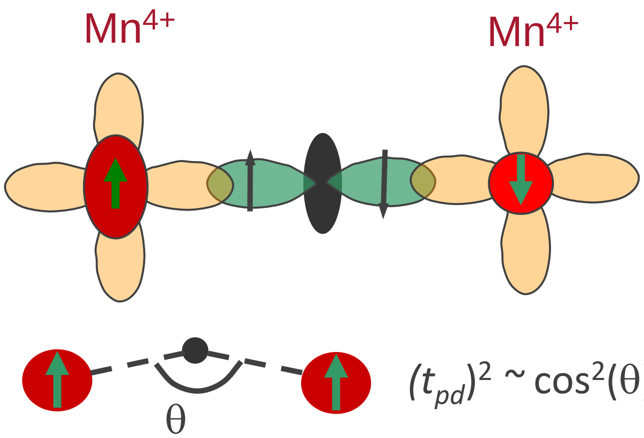
Double exchange



Ferromagnetic, metallic

C. Zener, PRB (1951)

Superexchange

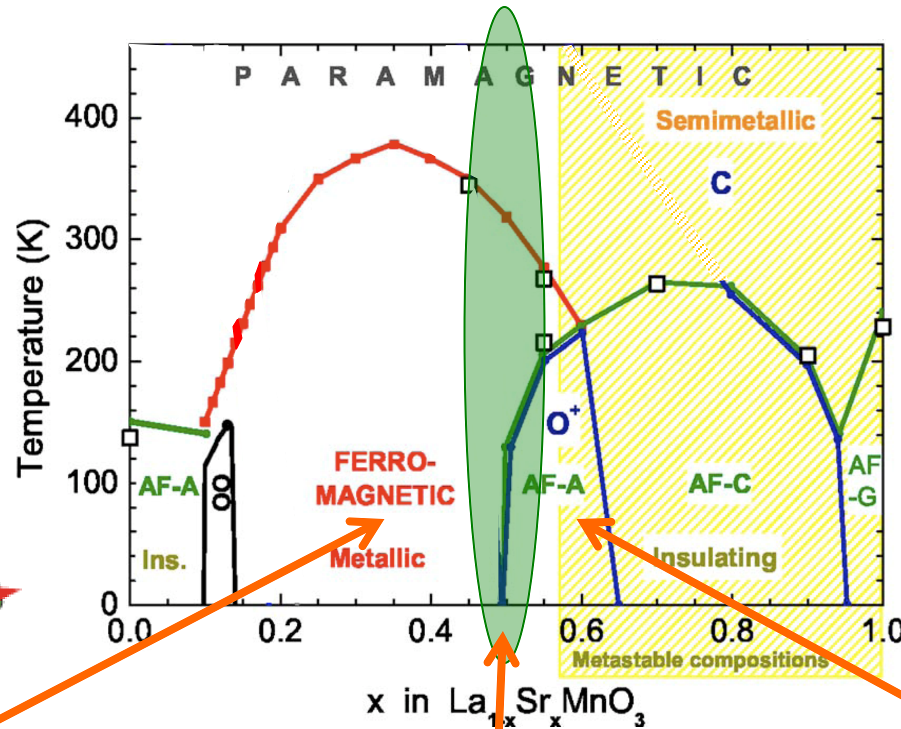


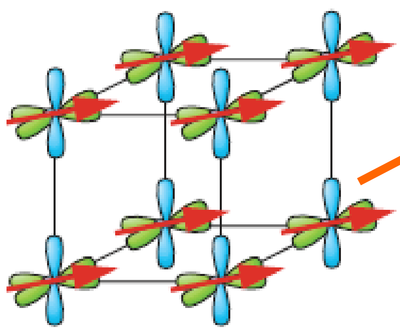
Antiferromagnetic, insulating

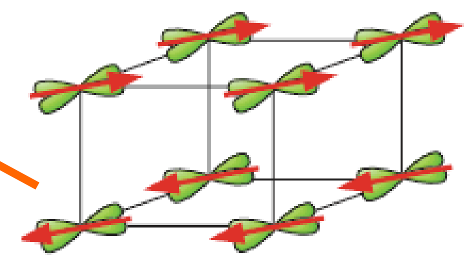
J. B. Goodenough, Phys. Rev. (1955)

→ Determines the magnetic properties across the phase diagram

F-AF Phase Transition at x ~ 0.5







Has T_N and T_C

F state

- orbital disorder

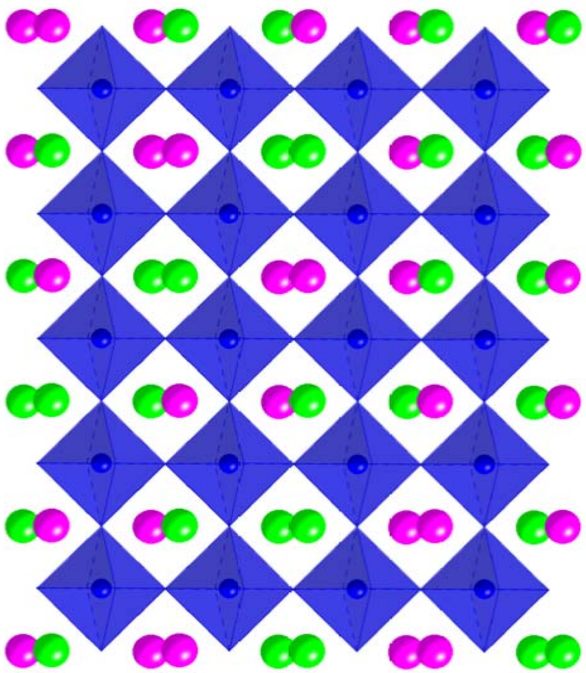
A-type AF order

- x^2-y^2 lie in MnO_2 sheets
- F double exchange in plane
- AF superexchange along *c*

Previous x=0.5 studies: Koida et al, PRB (2002); P. K. Muduli et al, JPCM (2007); M. Izumi et al, PRB (2000); Y. Konishi et al, J. Phys. Soc. Jpn. (1999)

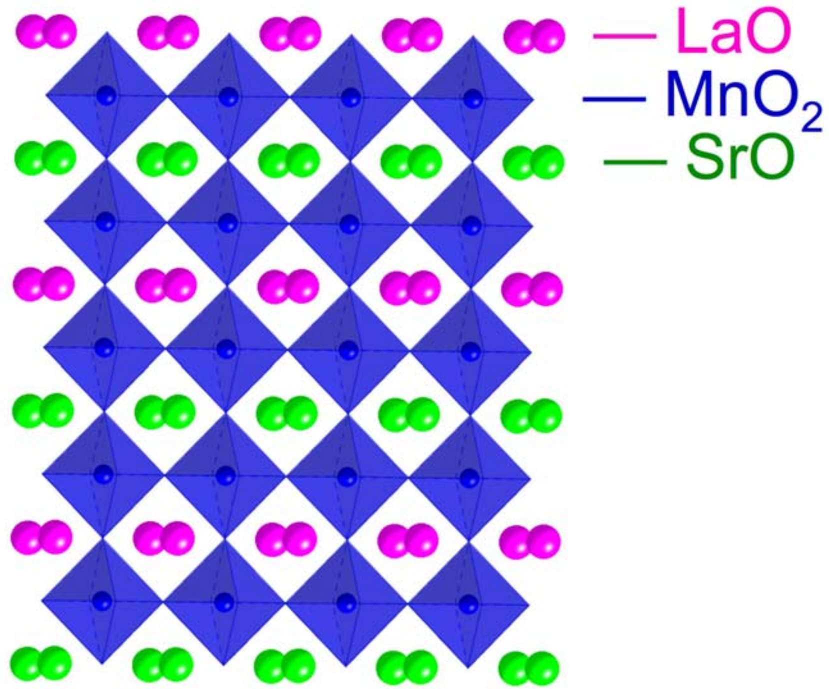
Order vs Disorder of Sr/La on A-sites

Disordered La/Sr
Random Alloy $La_{1-x}Sr_xMnO_3$



vs

Ordered La/Sr
SMO_1 / LMO_1



Why study order ?

$(R_{0.7}M_{0.3})MnO_3$: Suppressed T_C with A-site Disorder

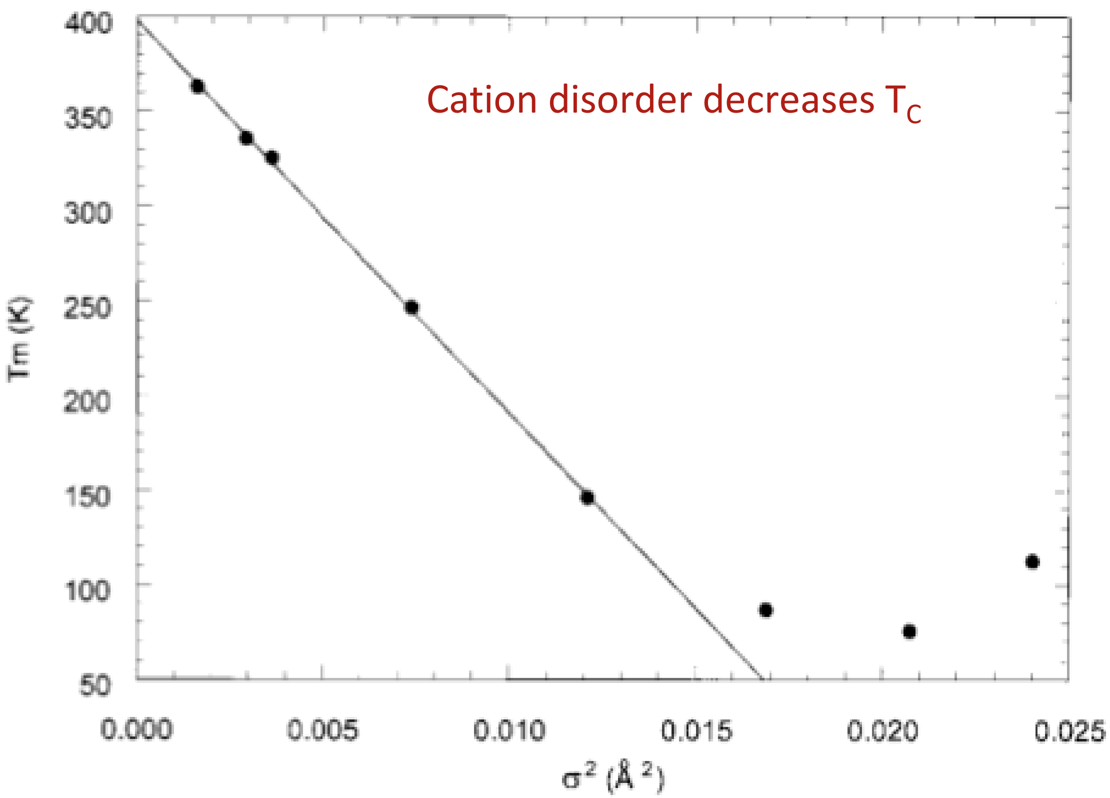
Rodriguez-Martinez and Attfield, PRB (1996)

$\sigma^2 (r_A) = <r_A^2> - <r_A>^2$

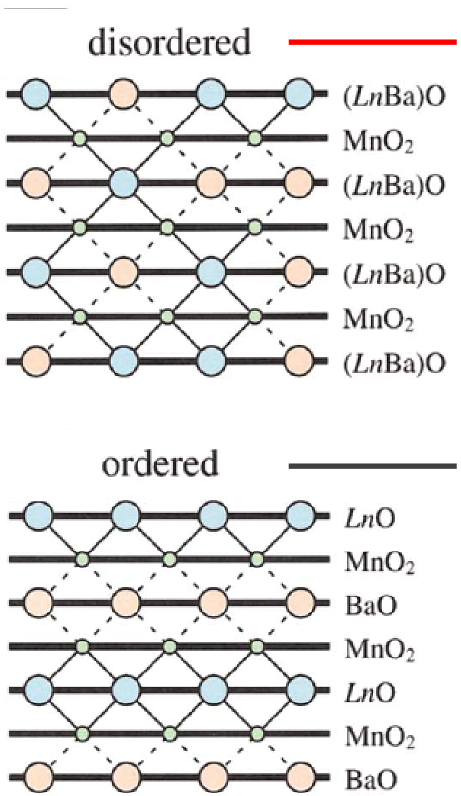
Variance in local tolerance factor $t = \dfrac{<A-O>}{\sqrt{2}<Mn-O>}$

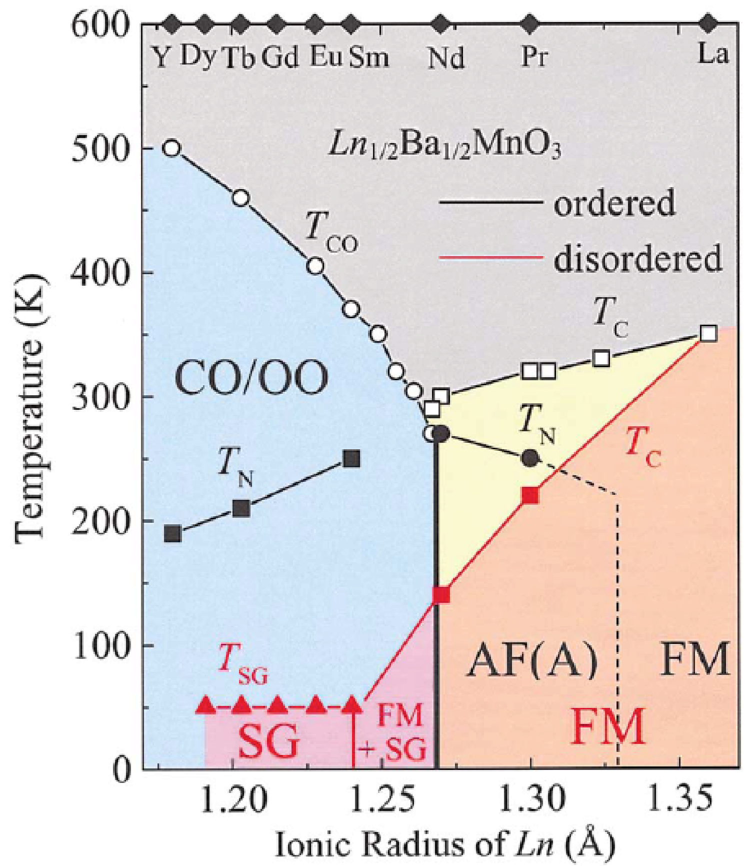
avg. cation radius $<r_A>$ = 1.23 Å
doping level x = 0.30

A-site composition	σ^2 (Å^2)
$La_{0.70}Ca_{0.11}Sr_{0.19}$	0.0016
$La_{0.32}Pr_{0.38}Sr_{0.30}$	0.0029
$La_{0.53}Sm_{0.17}Sr_{0.30}$	0.0036
$Pr_{0.70}Sr_{0.23}Ba_{0.07}$	0.0074
$Nd_{0.70}Sr_{0.16}Ba_{0.14}$	0.0123
$Nd_{0.41}Sm_{0.29}Ba_{0.20}Sr_{0.10}$	0.0169
$Nd_{0.15}Sm_{0.55}Ba_{0.25}Sr_{0.05}$	0.0207
$Sm_{0.70}Ba_{0.30}$	0.0240



$Ln_{0.5}Ba_{0.5}MnO_3$: New Ground States with Ordered Analogs

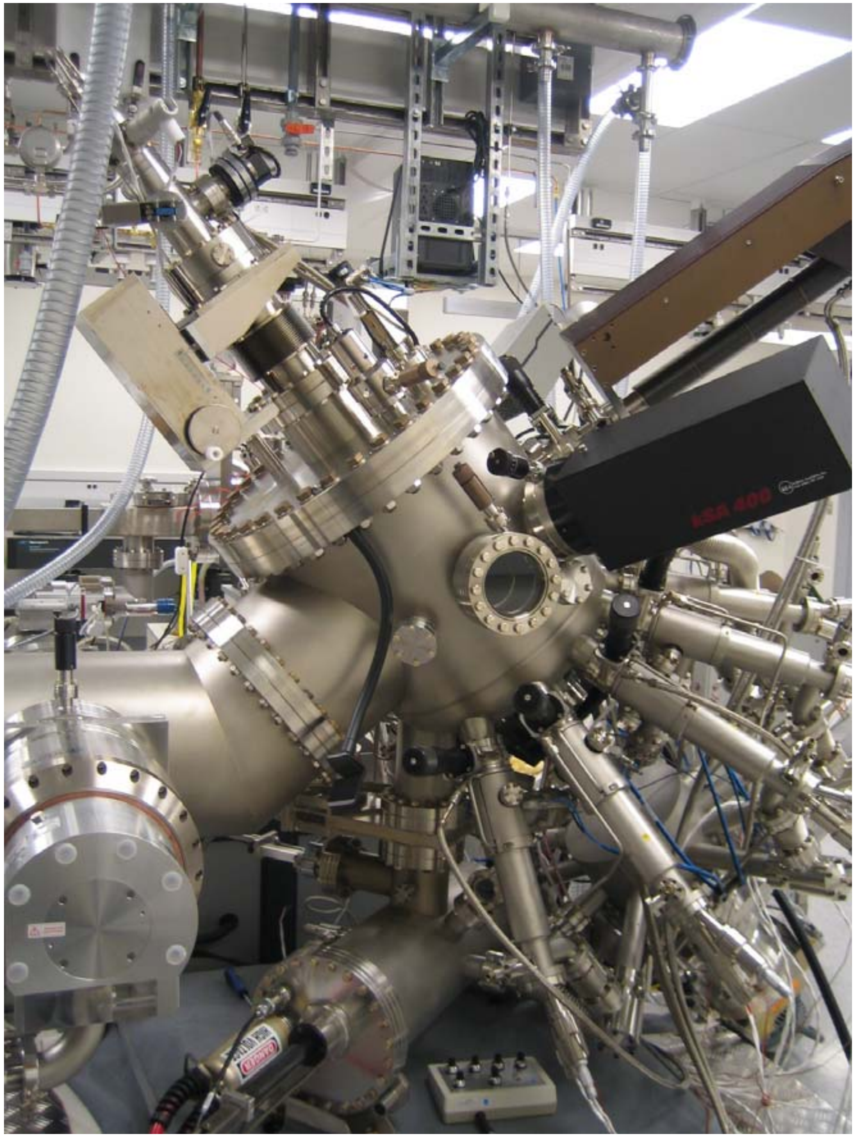




D. Akahoshi *et al.*, PRL (2003)

A-site disorder drastically changes the ground state

Ozone-Assisted Molecular Beam Epitaxy



This is a user facility !

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- Pure ozone
- 10 differentially-pumped K-cells
- 3 e-beam sources
- *in situ* RHEED
- Rate measured by QCM
- Composition calibrated by RBS
- Atomic absorption in progress

Ozone-Assisted Molecular Beam Epitaxy

This is a user facility !

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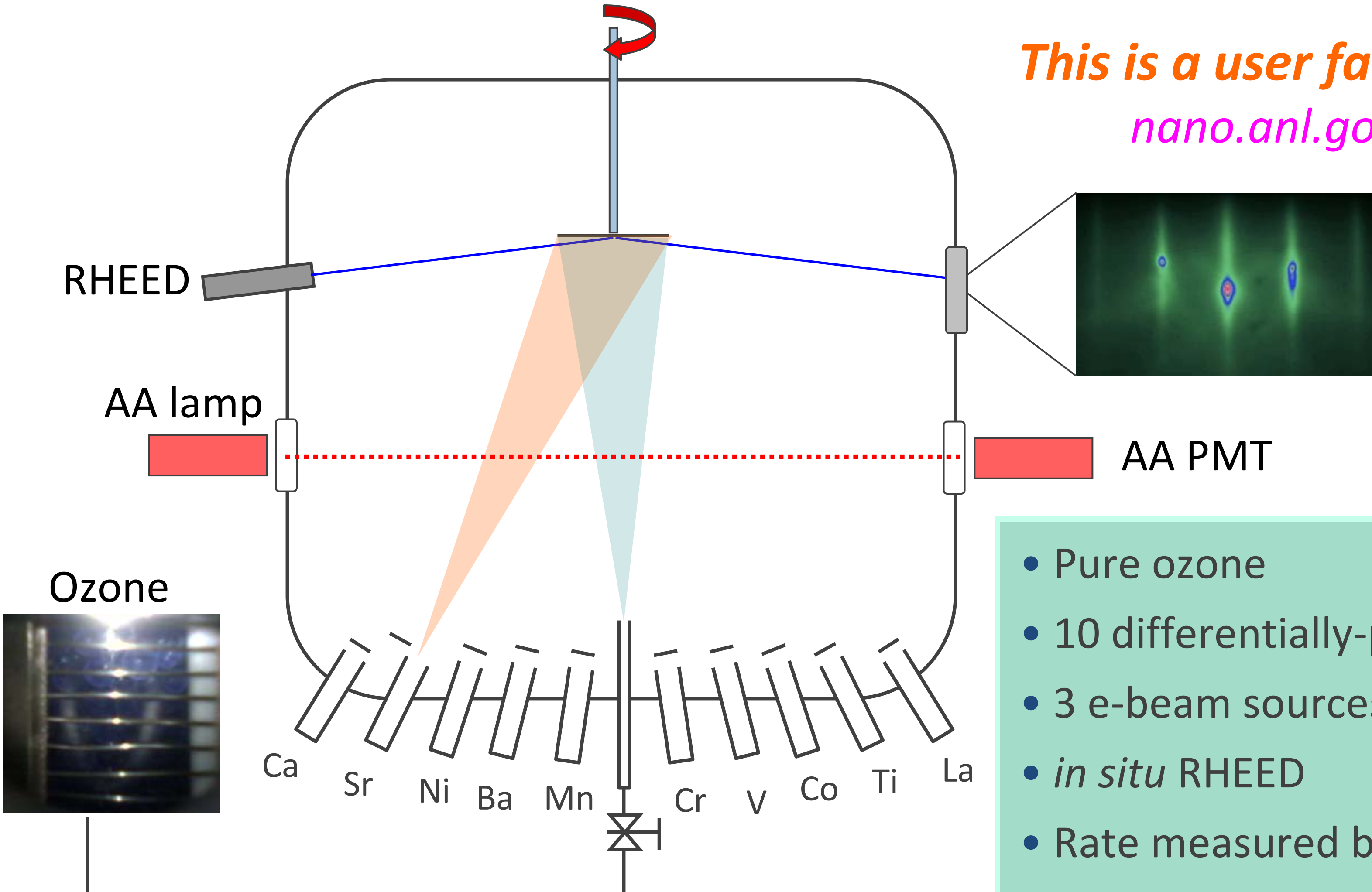
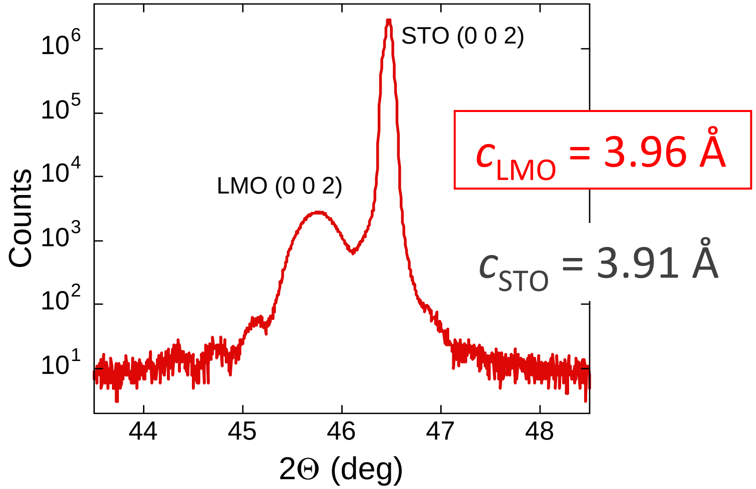


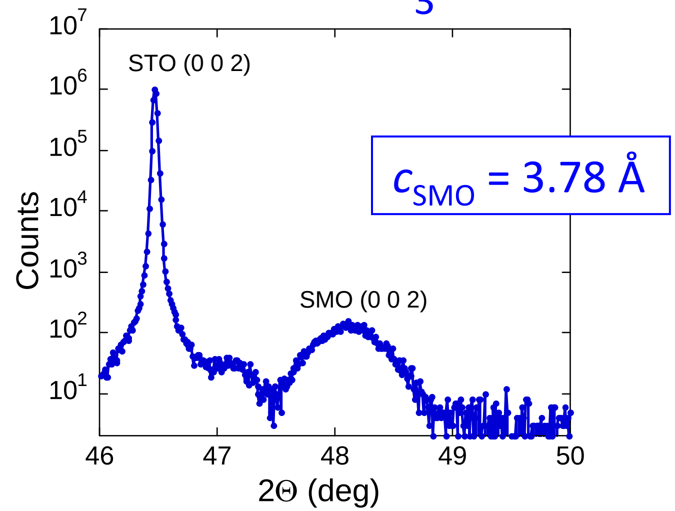
- Pure ozone
- 10 differentially-pumped K-cells
- 3 e-beam sources
- *in situ* RHEED
- Rate measured by QCM
- Composition calibrated by RBS
- Atomic absorption in progress

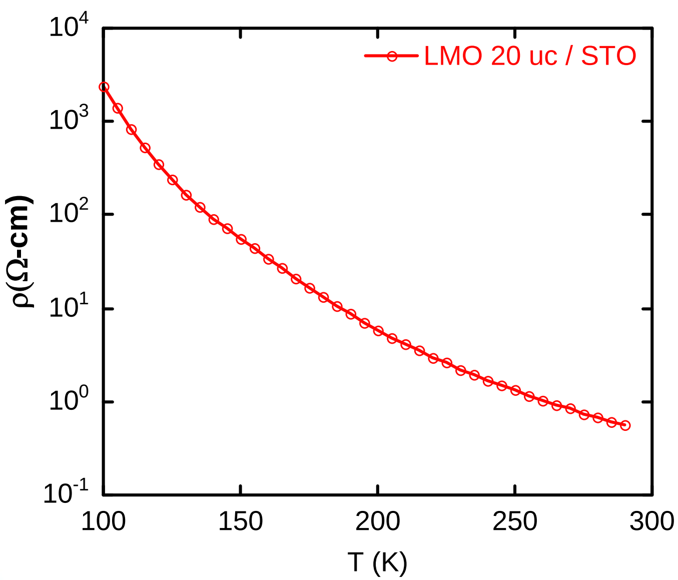
$LaMnO_3$, $SrMnO_3$ on $SrTiO_3$

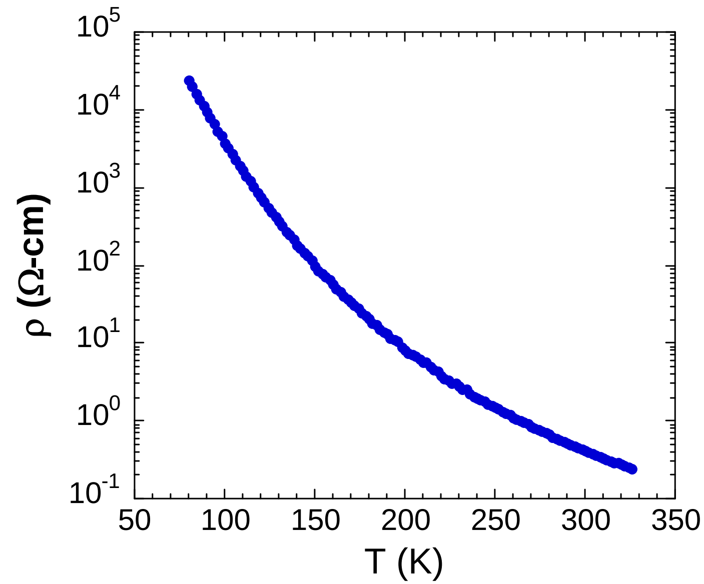
$LaMnO_3$



$SrMnO_3$

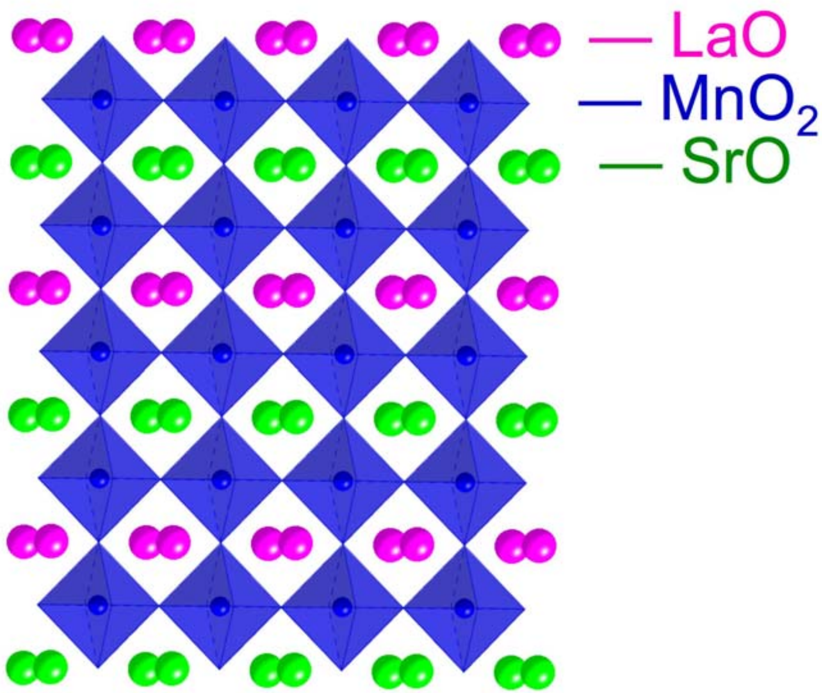




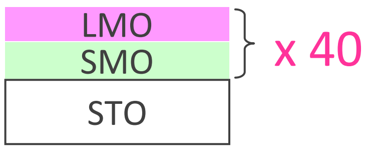


Digital Synthesis

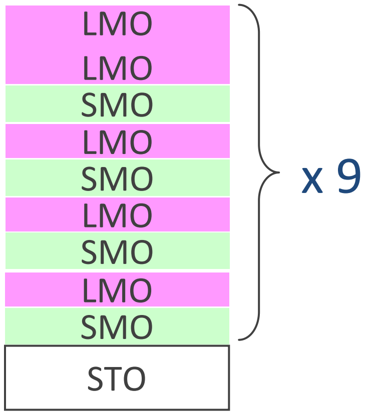
SMO_1 / LMO_1 superlattice



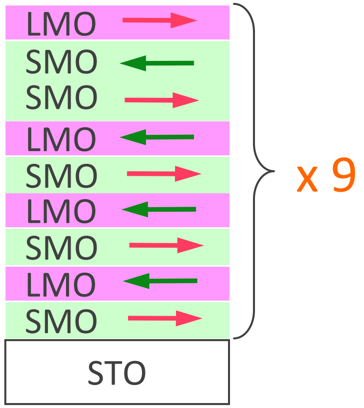
x = 0.50



x = 0.44



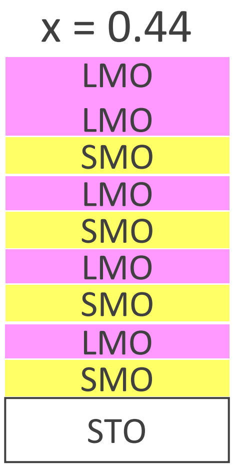
x = 0.55

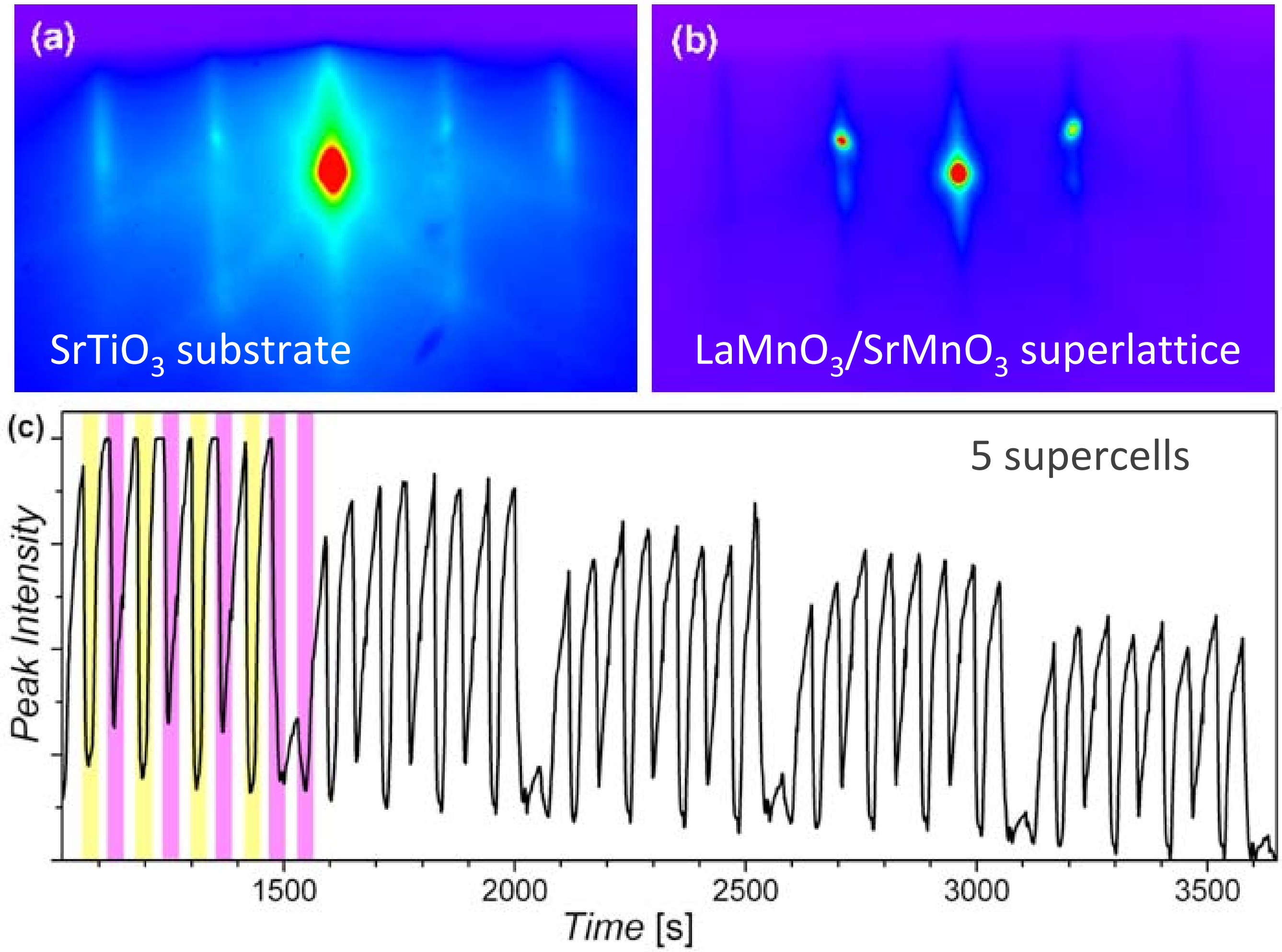


total thickness ~ 30 nm

compare with alloys of equivalent composition…

Reflection High Energy Electron Diffraction



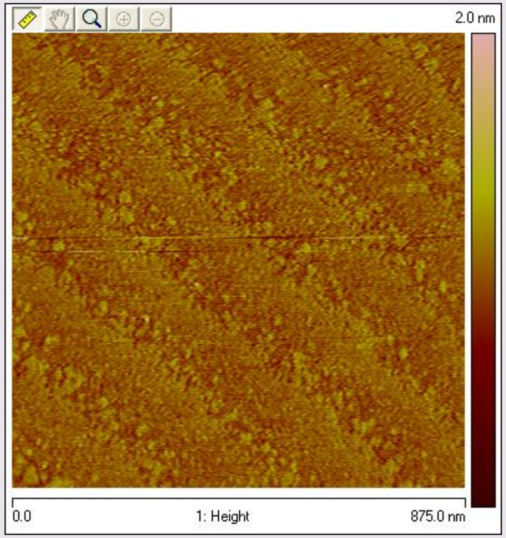


- oscillations of specular peak
- layer-by-layer growth

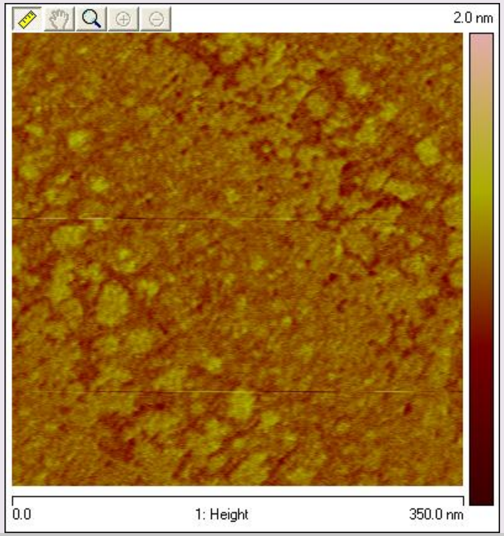
Smooth Surfaces: AFM and STM of x=0.50 SL

AFM

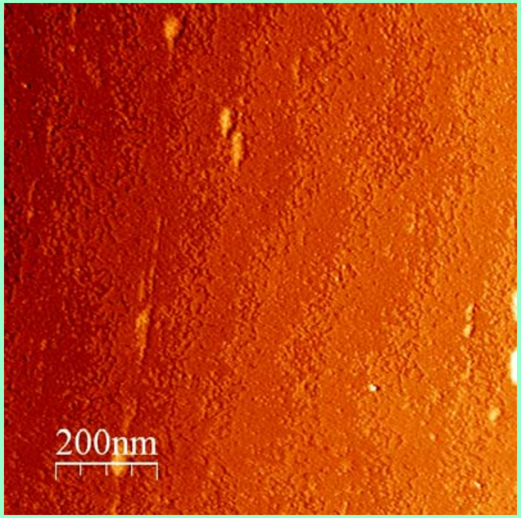
875 nm
x 875 nm

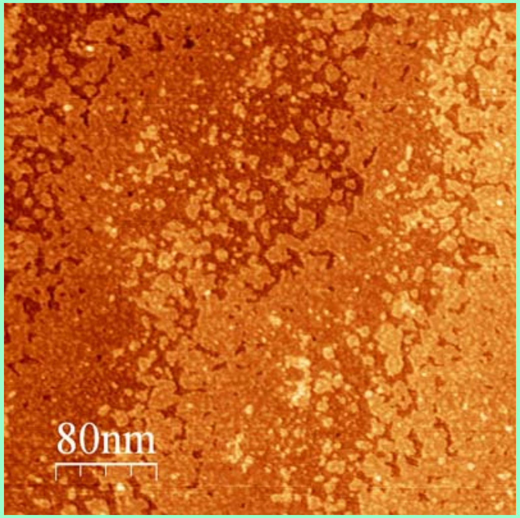


350 nm
x 350 nm



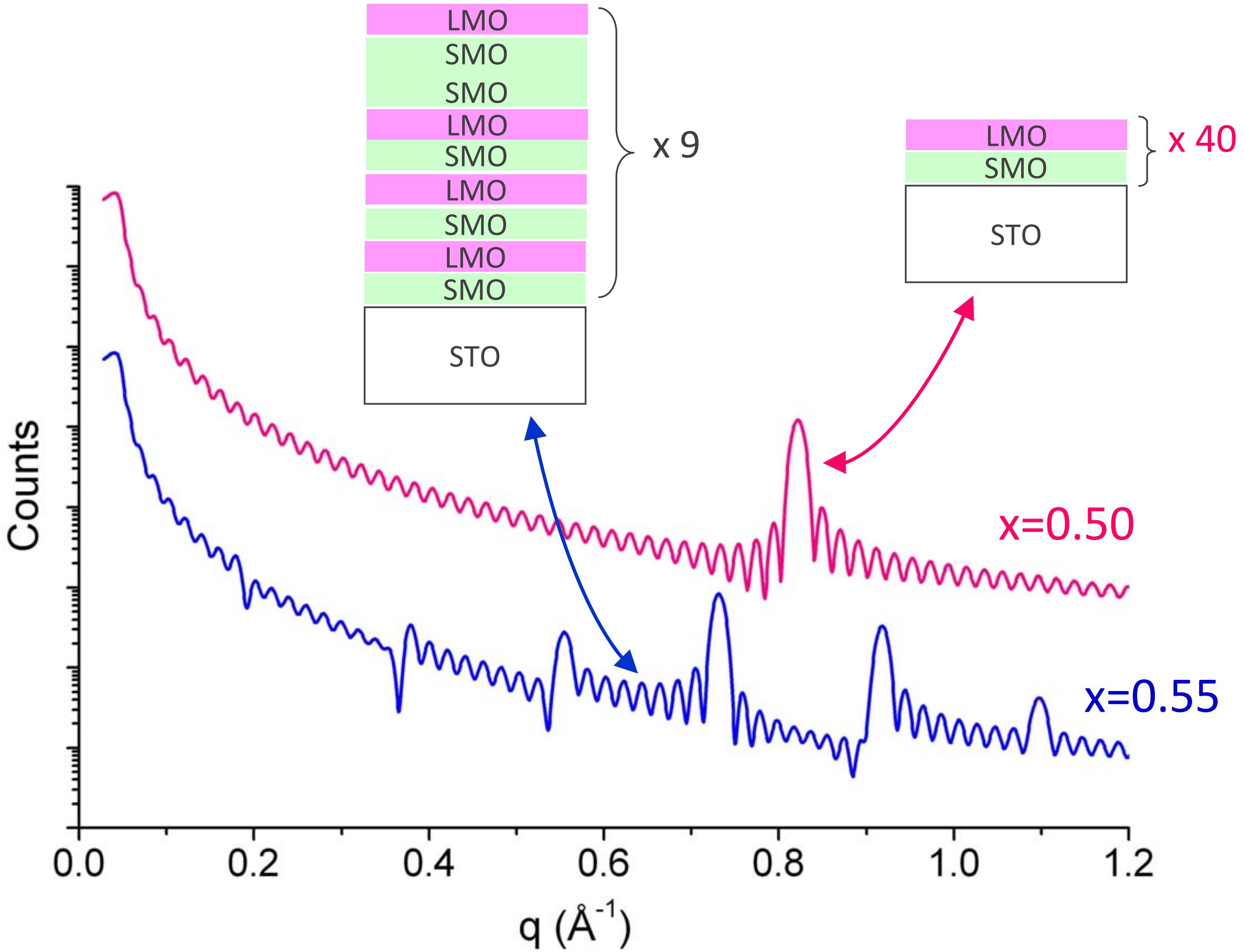
STM



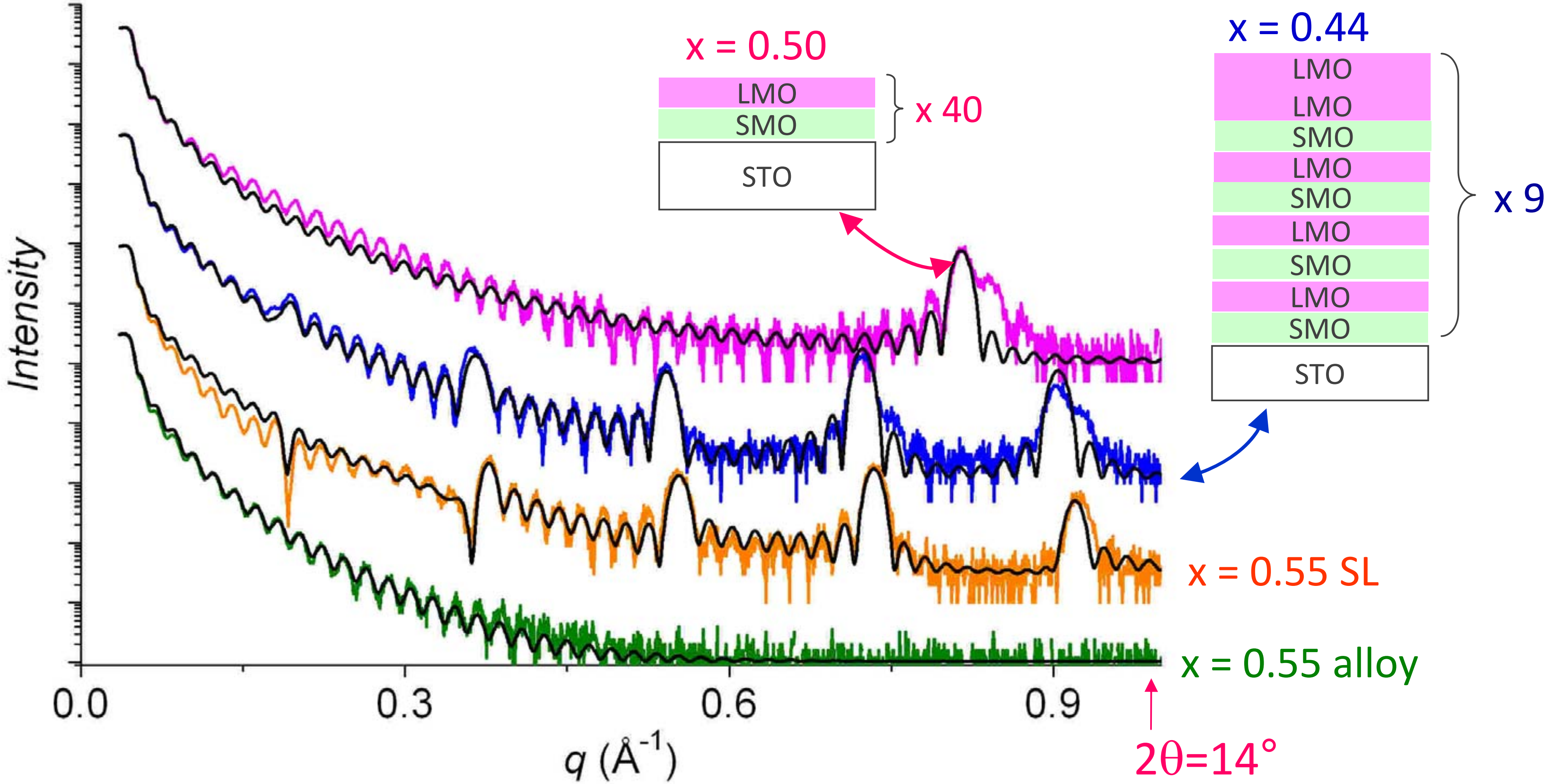


In collaboration with Matthias Bode, CNM

X-Ray Reflectivity: Simulation



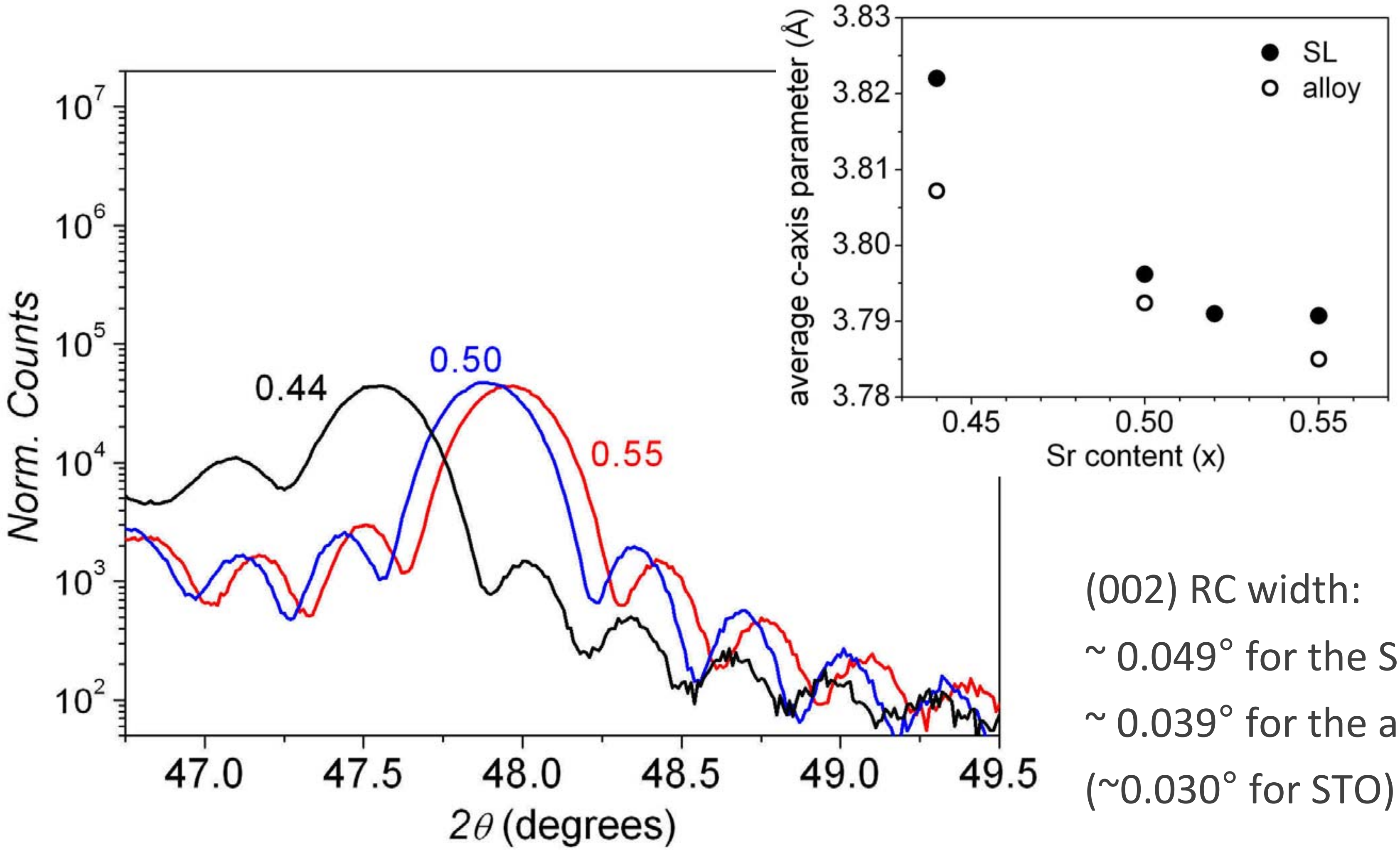
Single Layer Control: X-Ray Reflectivity



SL peaks not possible with layer roughness of a single unit cell

X-ray Diffraction

(002) peak of the $SrMnO_3/LaMnO_3$ superlattices



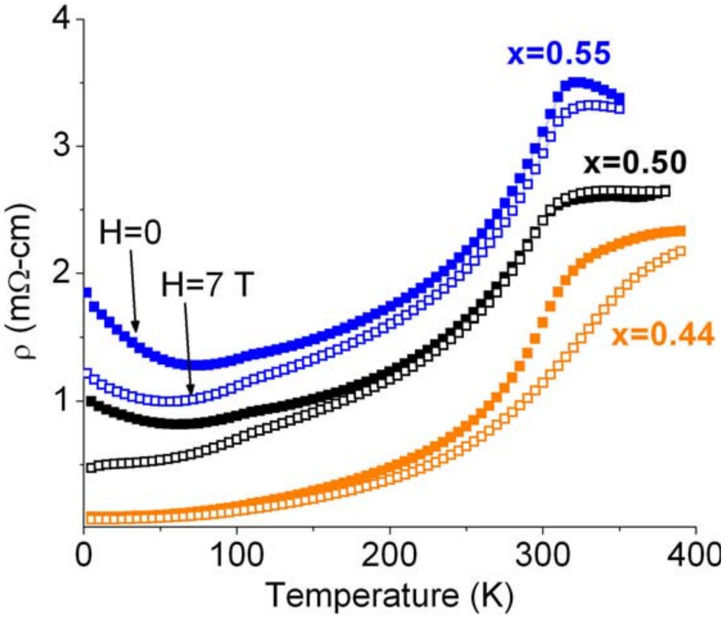
(002) RC width:

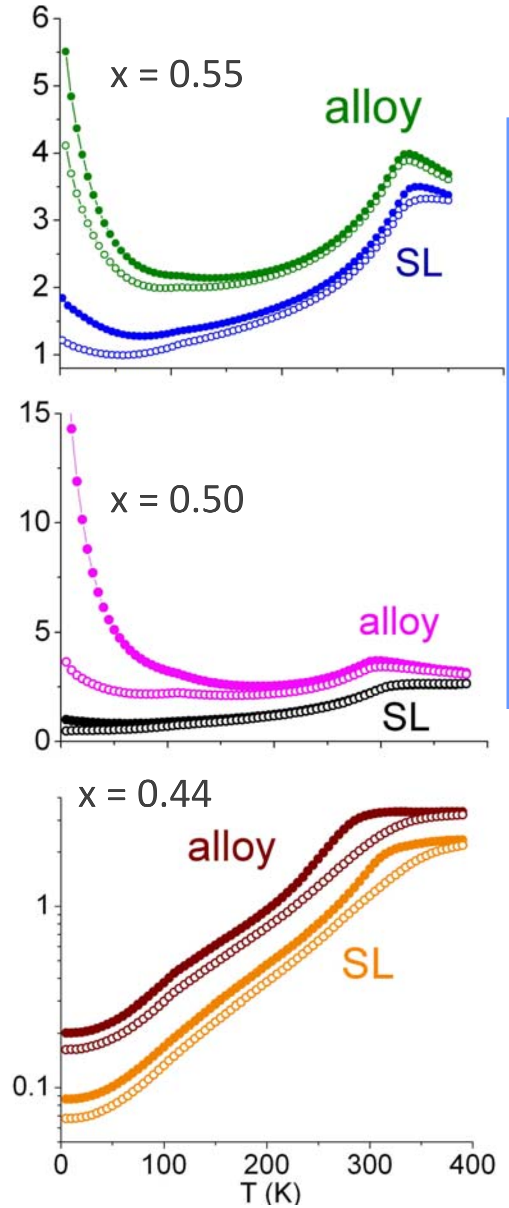
~ 0.049° for the SLs

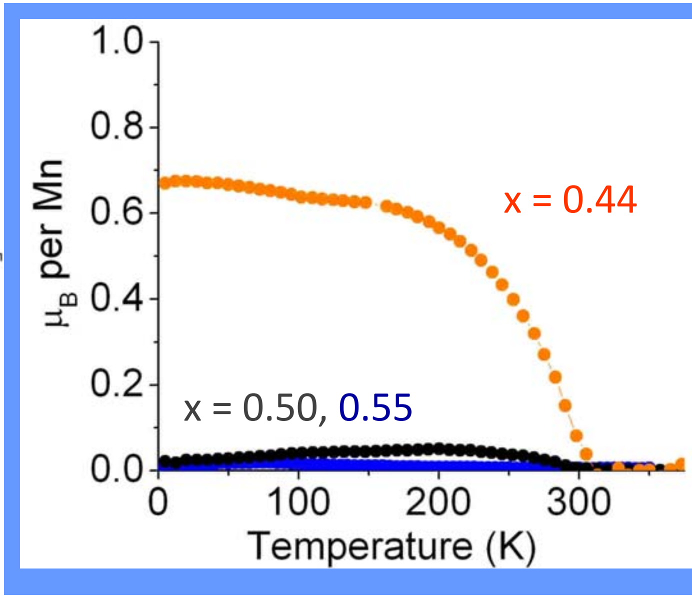
~ 0.039° for the alloys

(~0.030° for STO)

Enhanced Metallicity with A-site Order





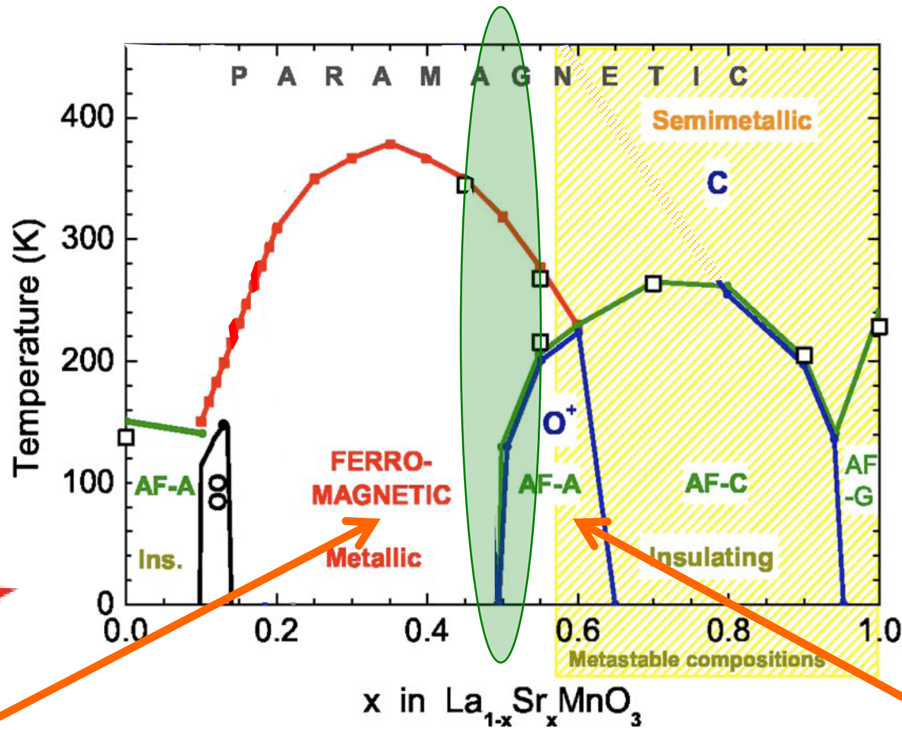


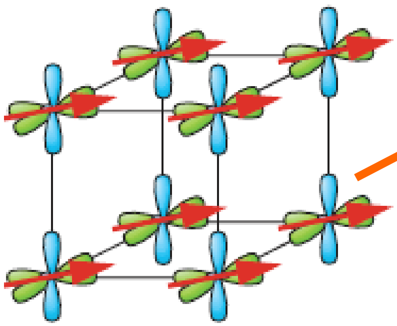
- metal-like behavior

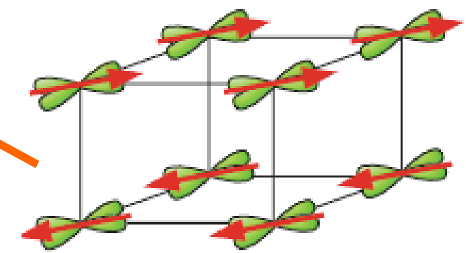
  ρ < 3 mΩ-cm

- disorder raises resistivity

Metal-like behavior near x=0.5







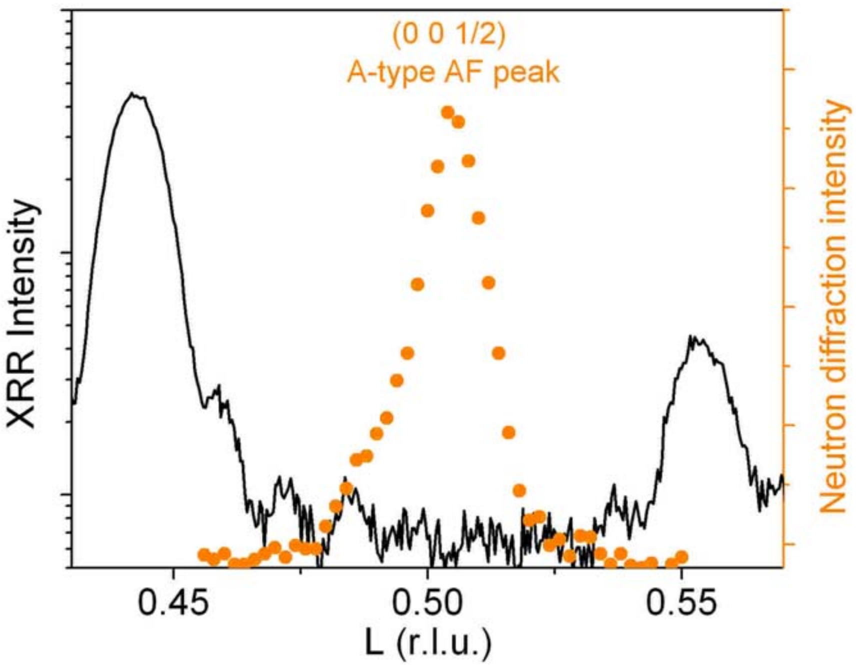
F state

- orbital disorder
- double exchange in 3D

A-type AF order

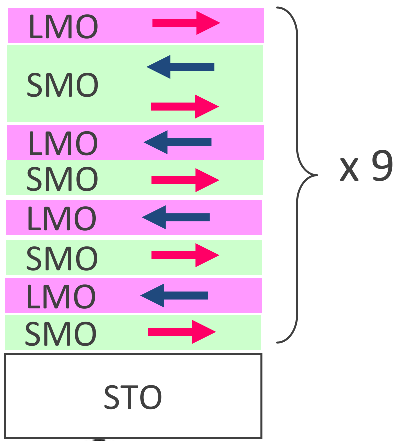
- x^2-y^2 lie in MnO_2 sheets
- F double exchange in plane
- AF superexchange along *c*

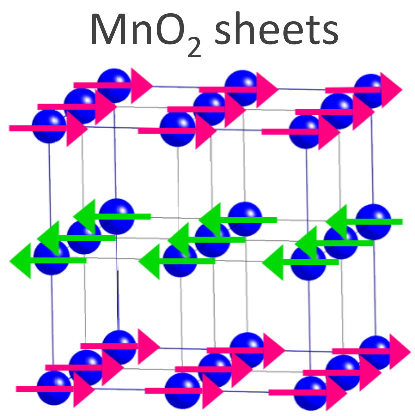
A-type AF order: Neutron Diffraction, x = 0.55

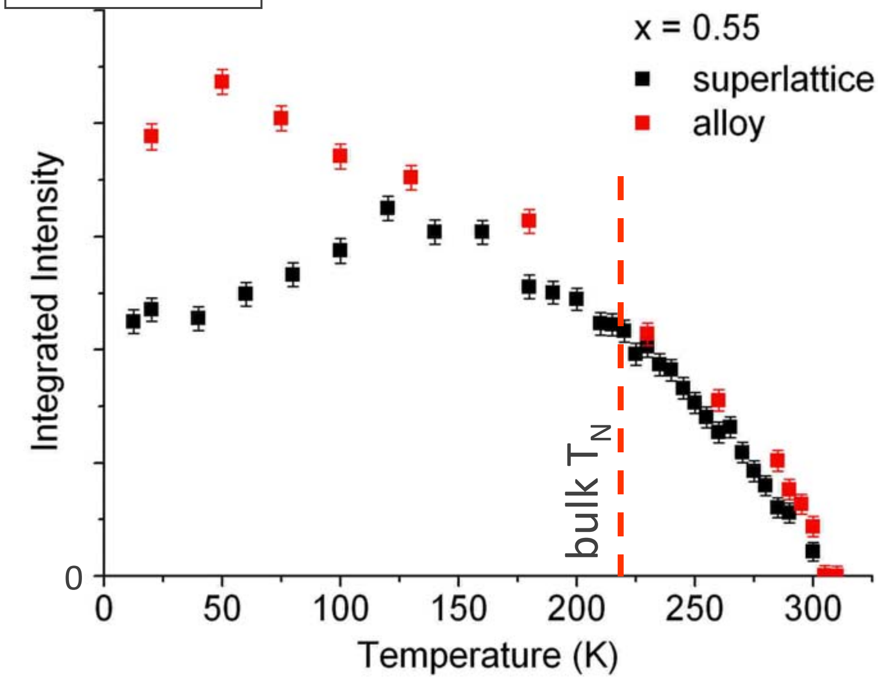


- Structurally forbidden (0 0 ½) diffraction peak below T_N
- coherence length ξ ~ film thickness
- T_N enhanced from bulk T_N=220 K

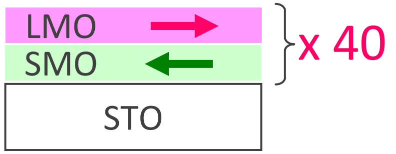
Measured at HFIR, ORNL
Collaboration with Lee Robertson, Jerel Zarestky

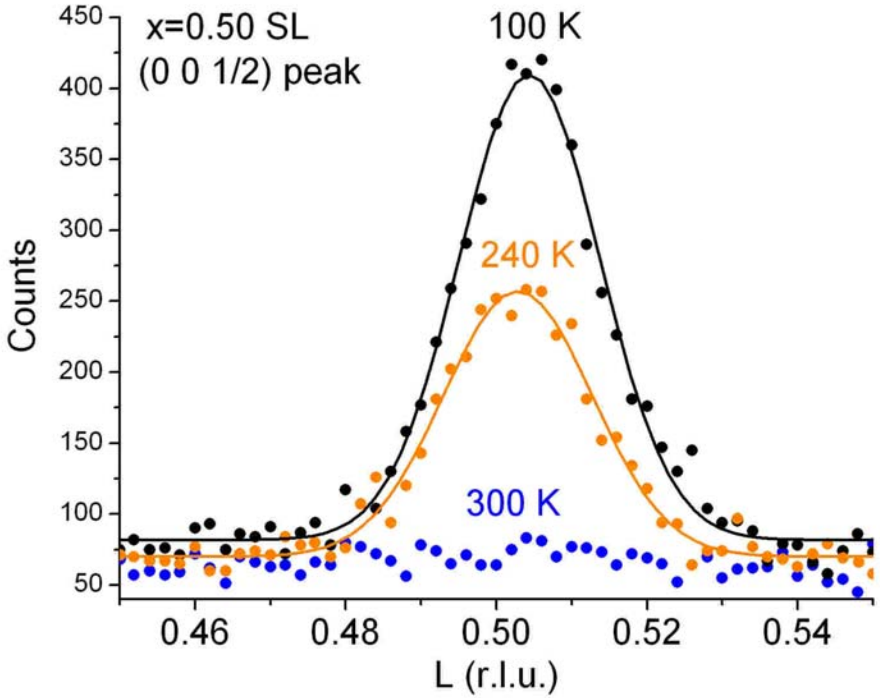


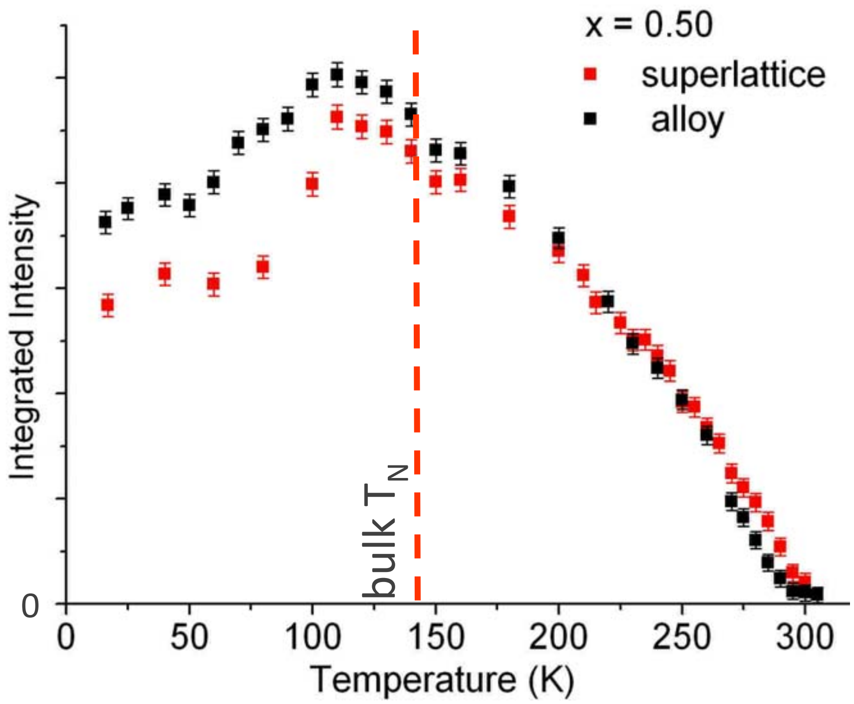




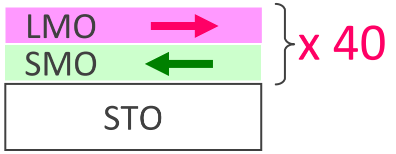
A-type AF order, x=0.50

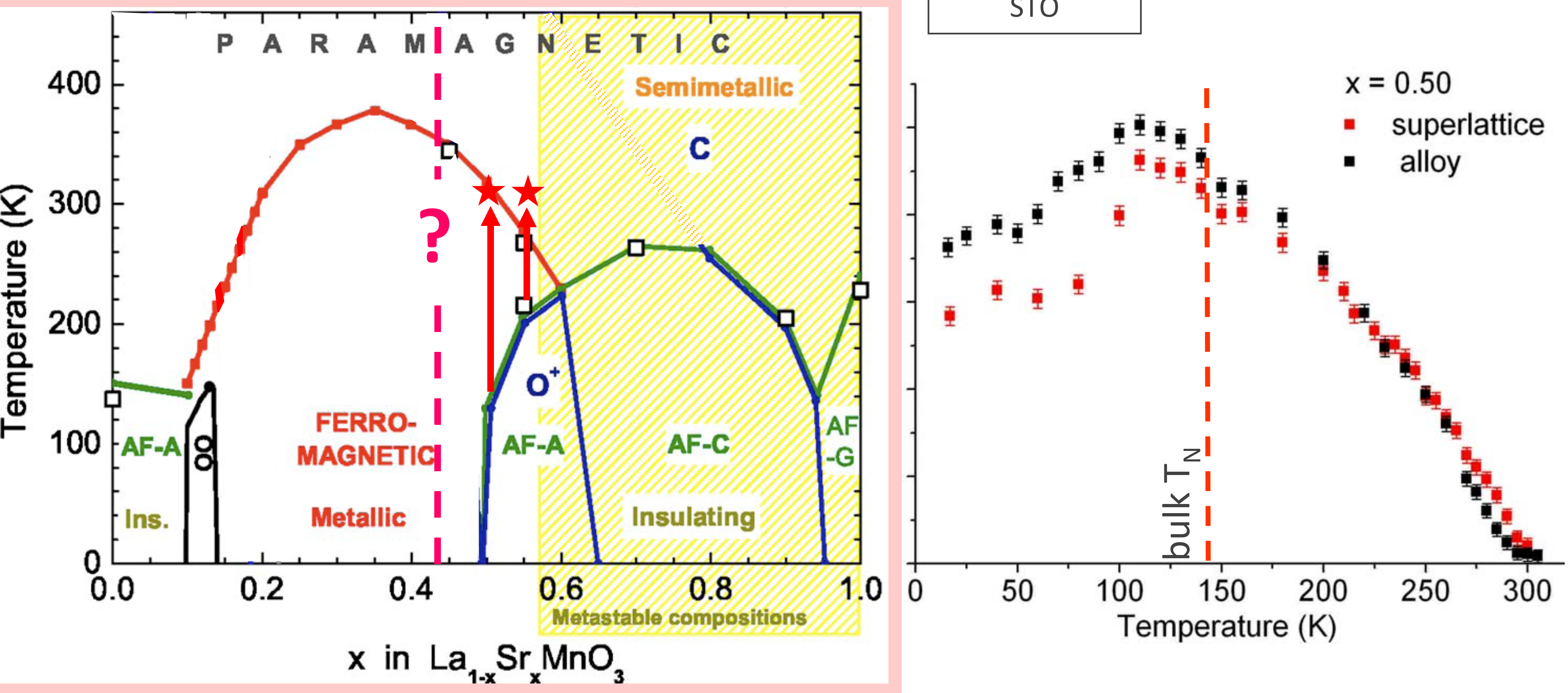






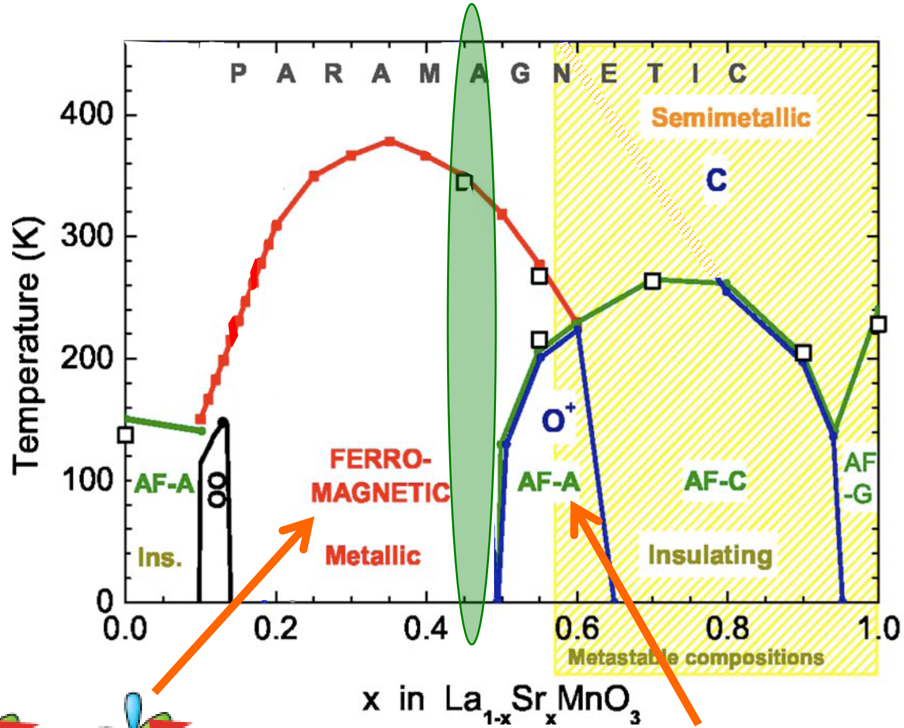
Enhanced Néel Temperature





- T_N greatly increased over bulk T_N
- No F phase at high T
- Strain, rather than A-site order, leads to enhanced T_N:
  compression of c-axis → stronger superexchange

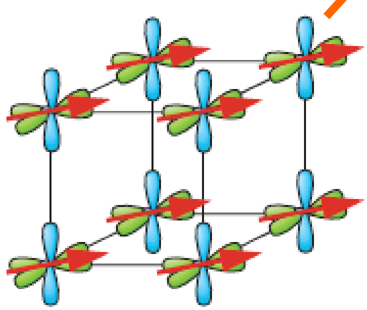
$La_{1-x}Sr_xMnO_3$ on the Verge of Ferromagnetism: *x*=0.44, 0.47



Adding mobile carriers to AF

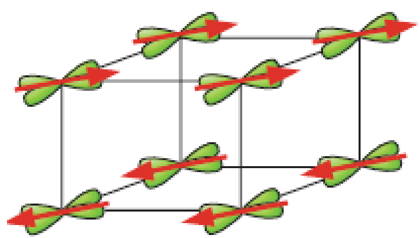
→ *Canting due to double exch.*

(single orbital model by de Gennes, Phys. Rev. 1960;
degenerate orbital model by van der Brink & Khomskii, PRL '99)



F state

- double exchange 3D
- orbital disorder

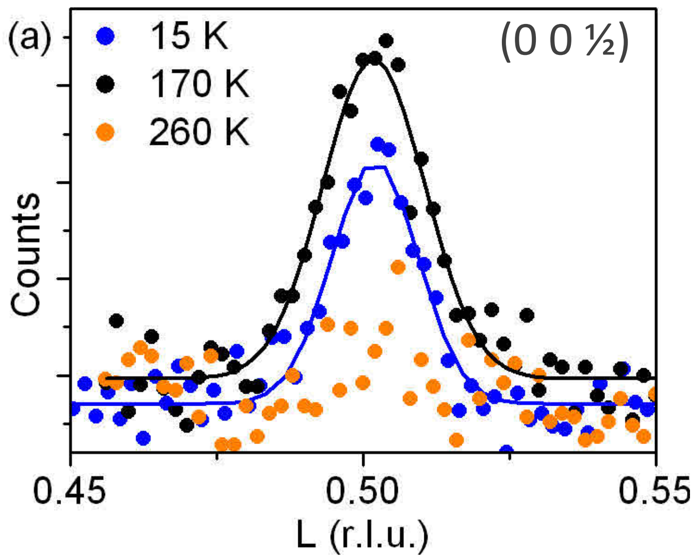


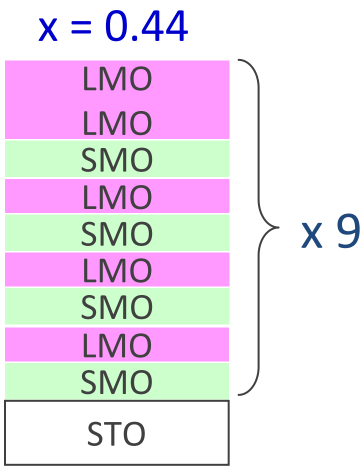
A-type AF metal

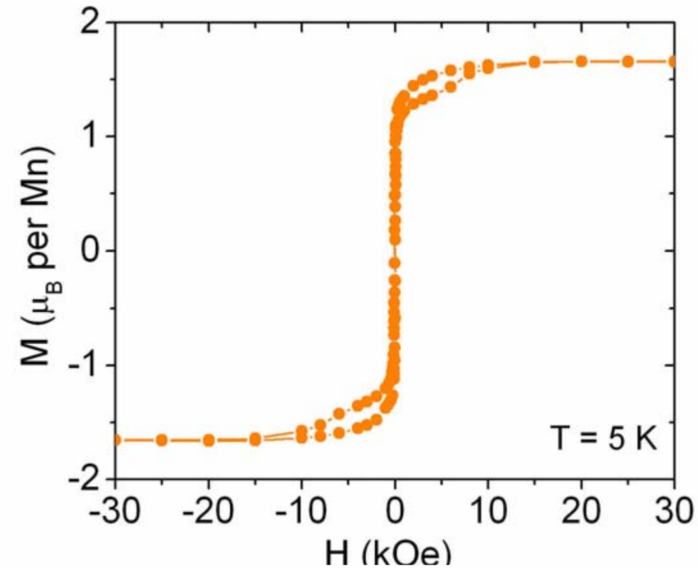
- x^2-y^2 lie in MnO_2 sheets
- F double exchange in plane
- AF superexchange along *c*

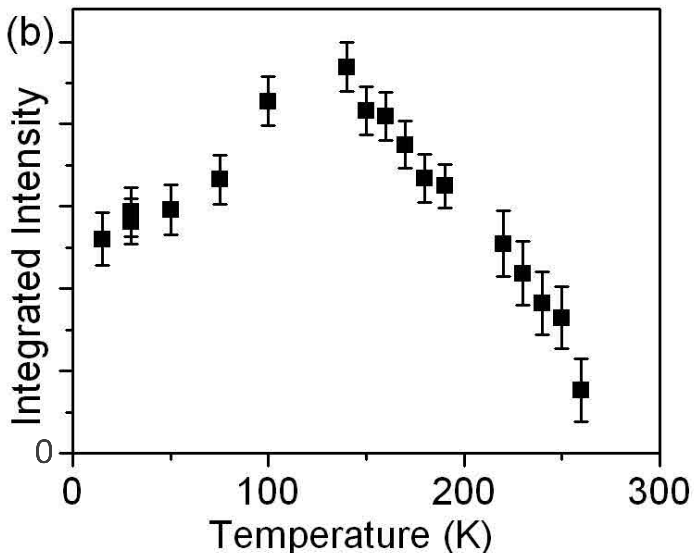
This study:
The transition from an anisotropic AF to an isotropic F ?

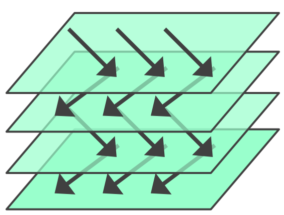
x = 0.44 : *Canted AF ? Modulated Behavior ?*

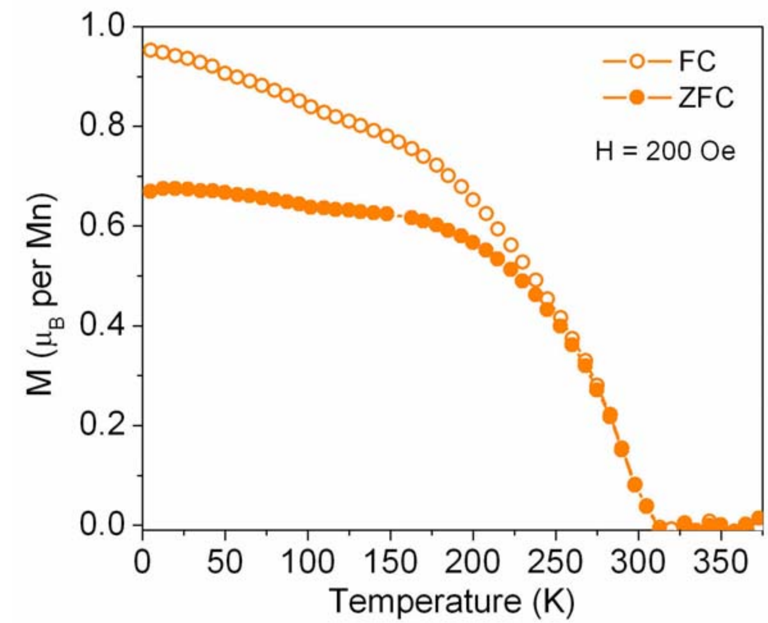






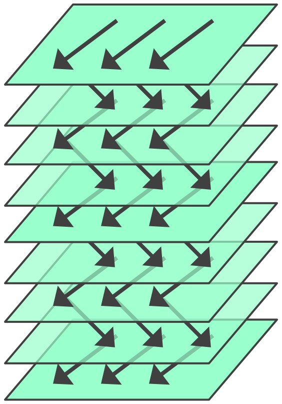


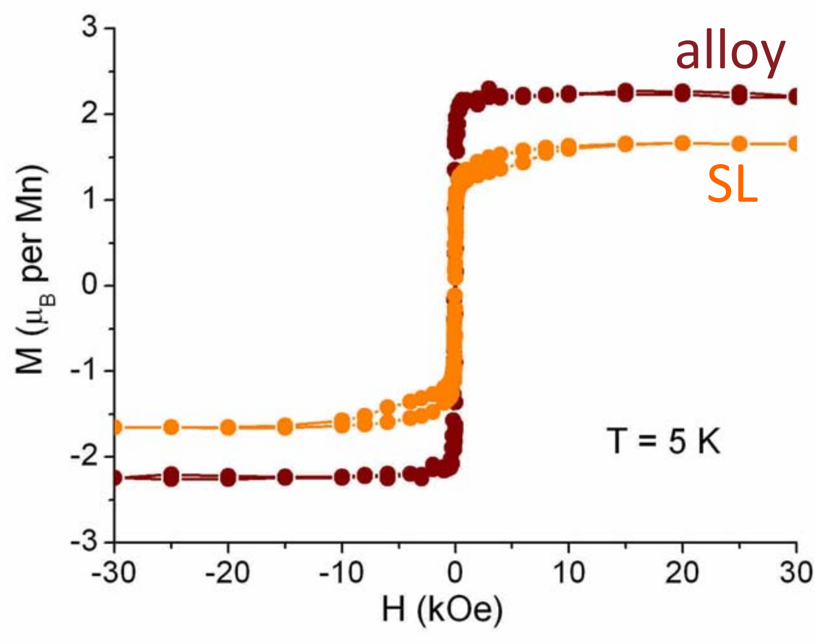


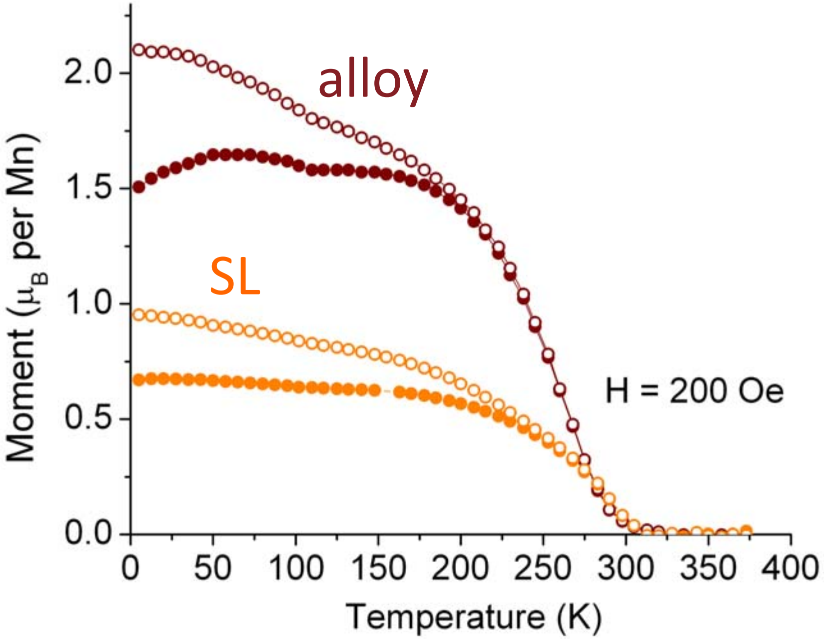


Compare x=0.44 SL and alloy

- Alloy has higher moment than SL, but still < (4 – x) μ_B
- *Canted ?*

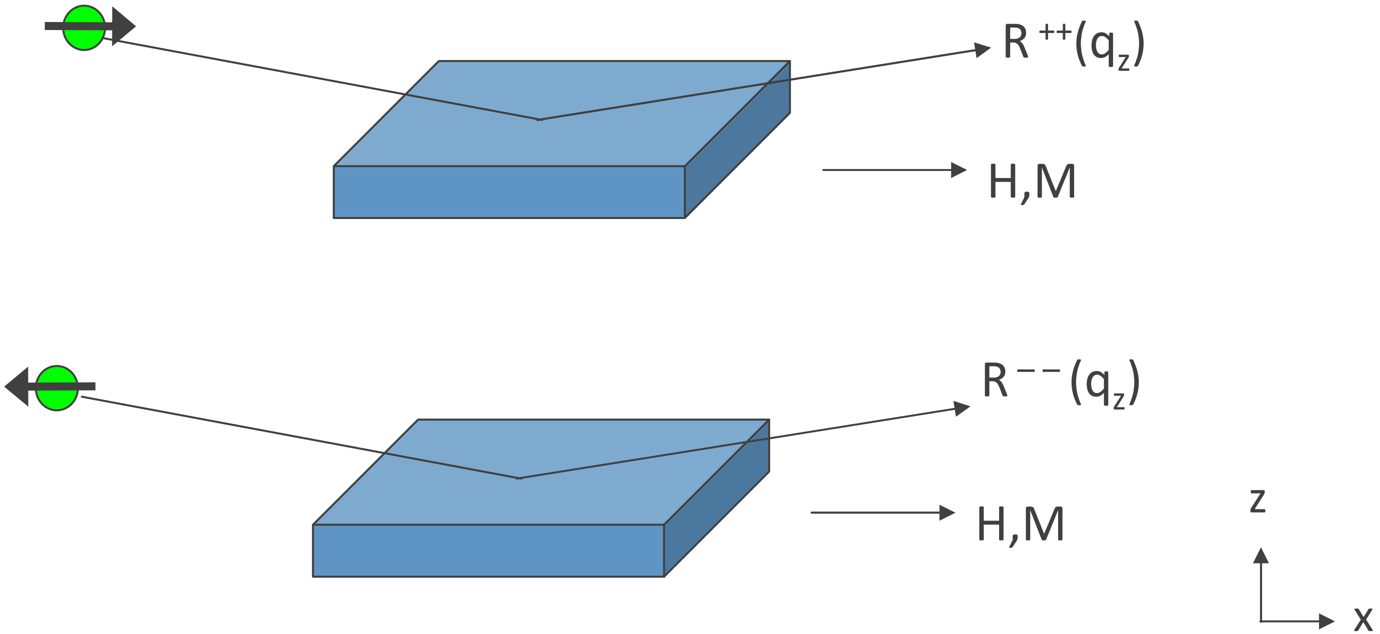




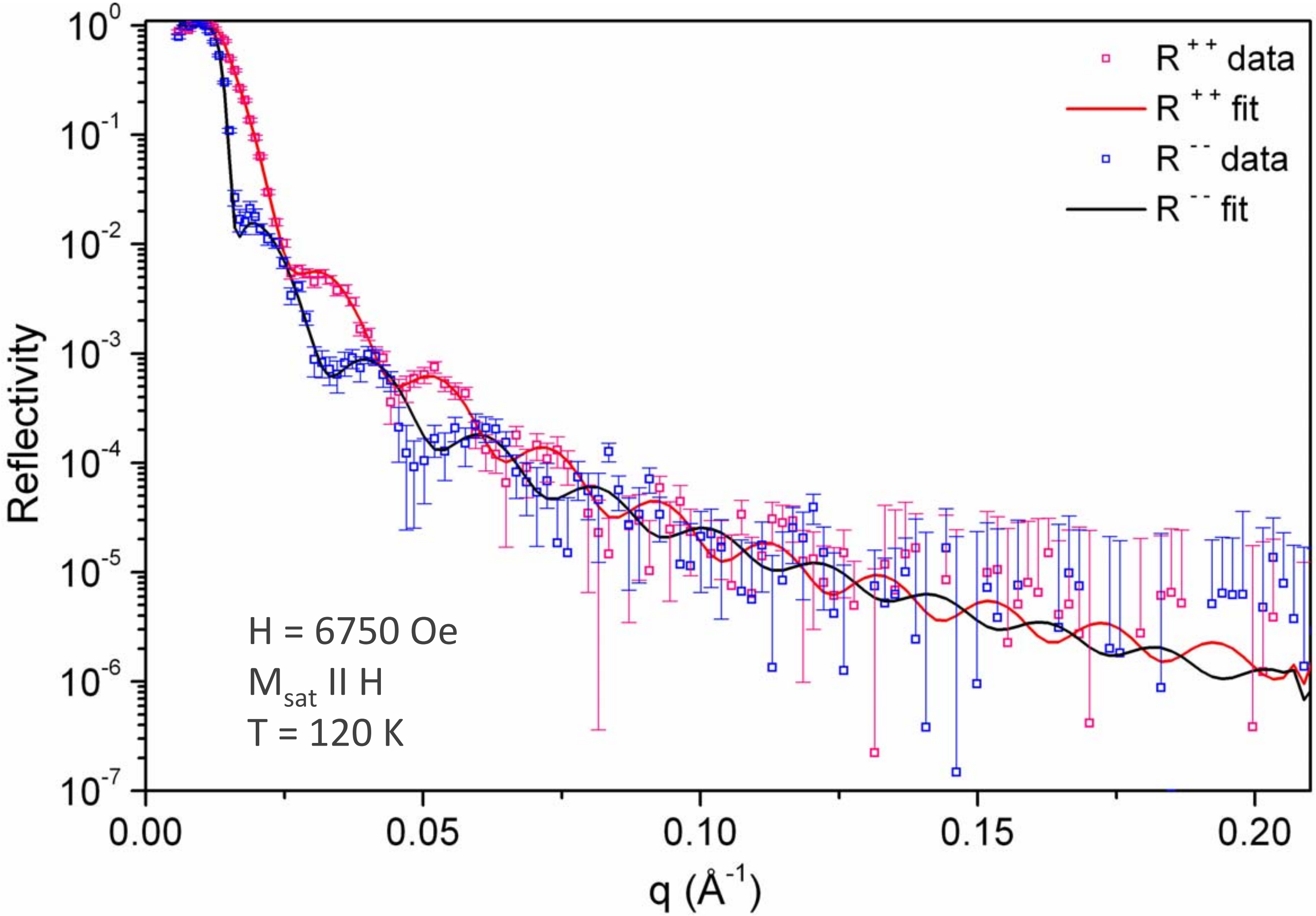


Polarized Neutron Reflectometry

- Study magnetic depth profiles with sub-nm resolution
- Sensitive to the in-plane component of magnetization
- Measurement at NIST Center for Neutron Research
  - *NG1 and AND/R, Brian Kirby and Brian Maranville*
  - *Suzanne te Velthuis, Argonne*

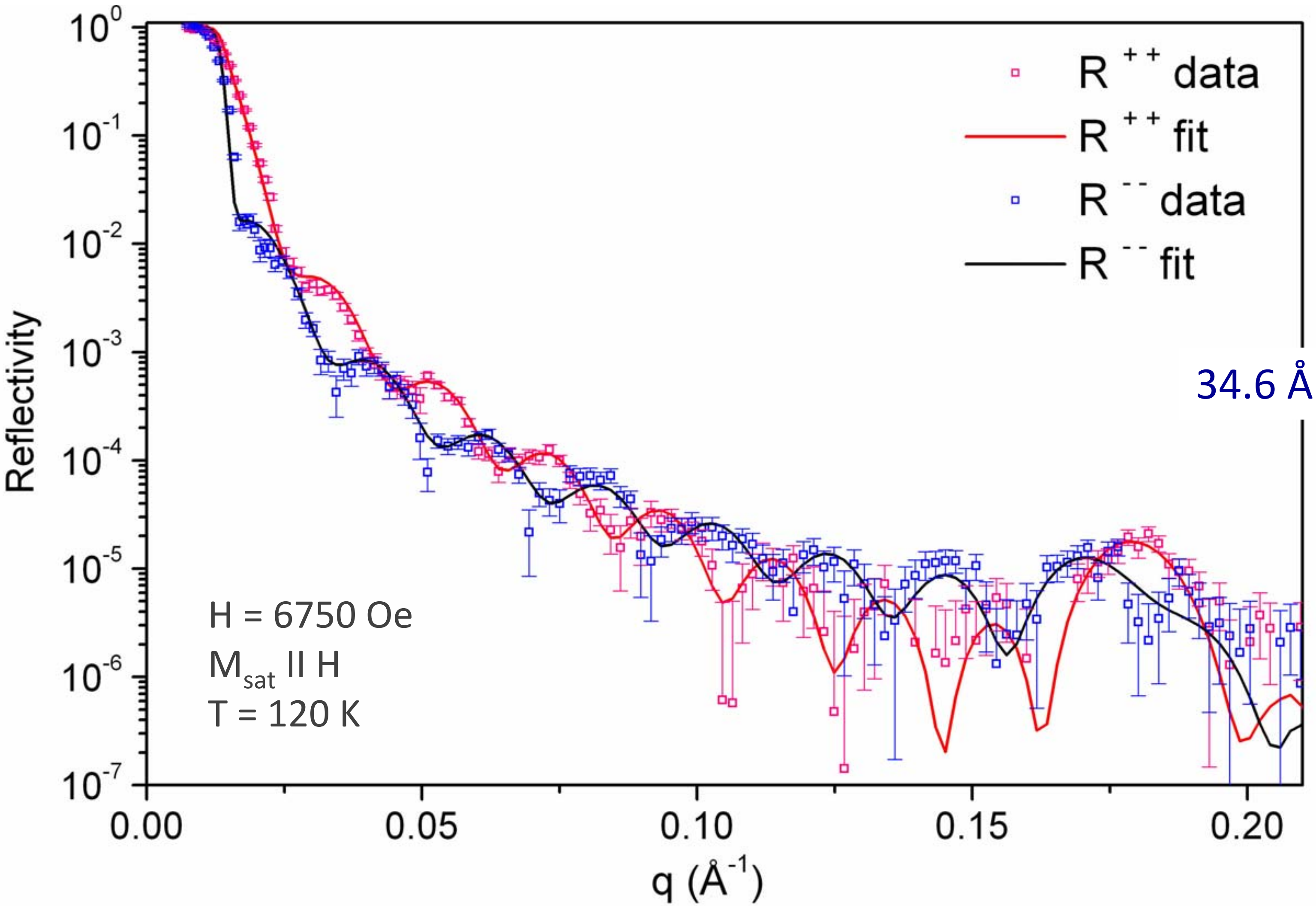


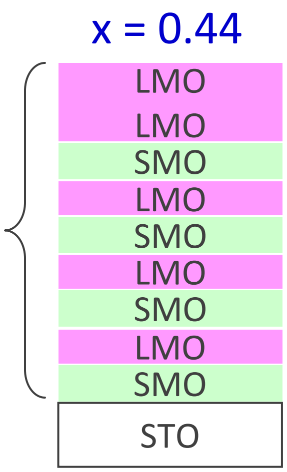
x=0.44 Alloy: Polarized Neutron Reflectivity



Alloy has no Bragg peak → no modulation

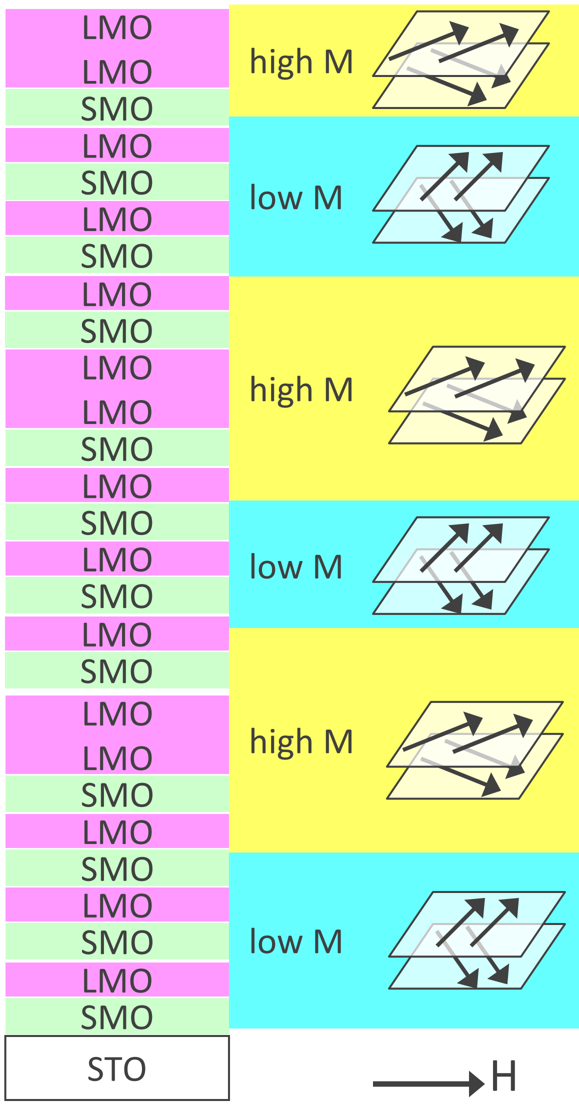
PNR: Modulated Moment in x=0.44 SL

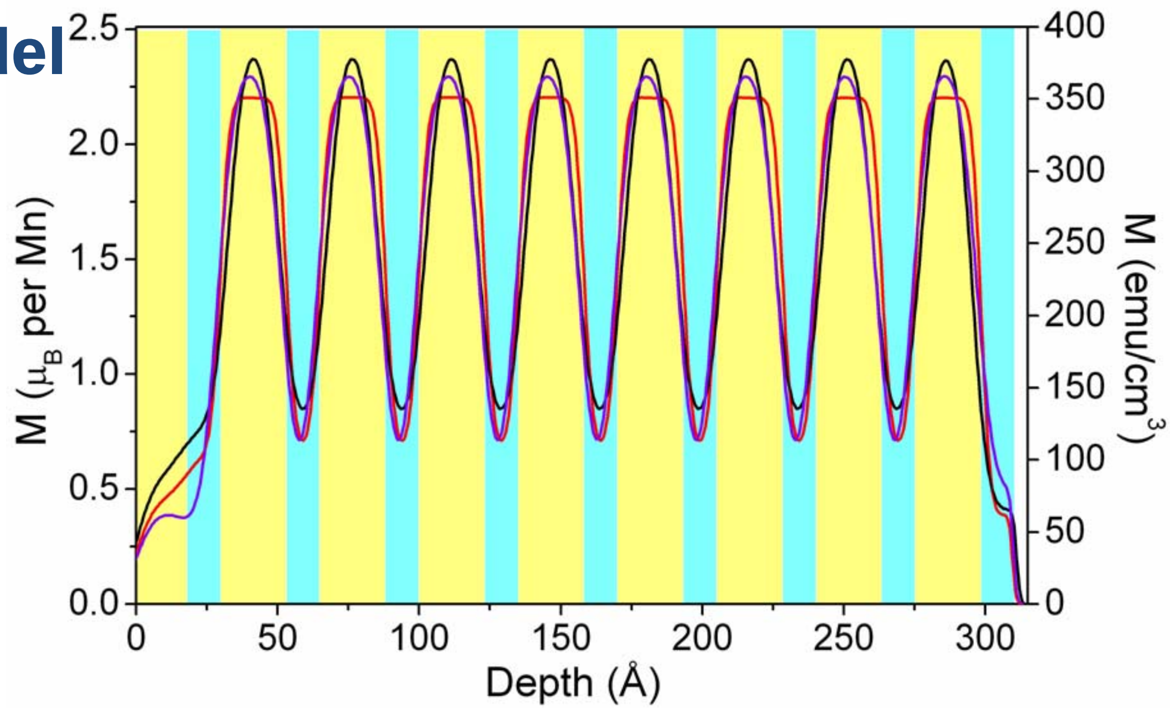




Bragg peak at q = 0.18 $Å^{-1}$ → ***modulated moment*** commensurate with SL structure

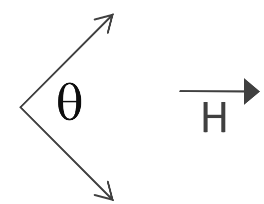
x=0.44: PNR fitting model





Butterfly spin structure

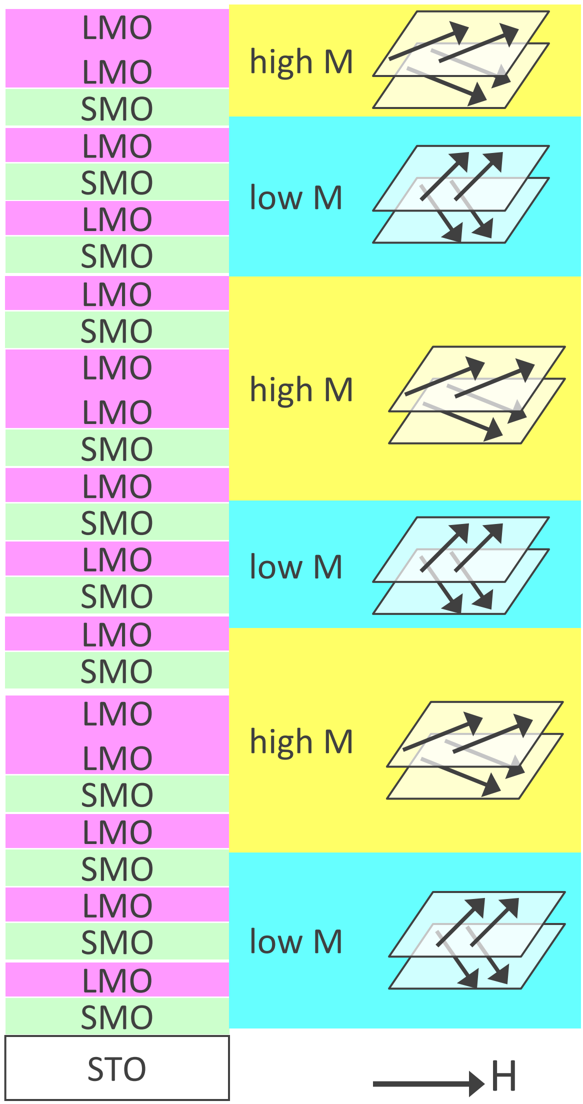
- canted, modulated



High M layer: 2.2 μ_B, 6 u.c., $\theta = 102°$

Low M layer: 0.7 μ_B, 3 u.c., $\theta = 157°$

Delta-Doping of Ferromagnetism



- Inserting a single layer of electrons *enhances double-exchange* along the c-axis → canting → higher moment
- Tuning the strength of the ferromagnetic exchange interactions
- Locally change the property of the material, without introducing *disorder* or *frustration*

Compare with:

$La_{0.6}Sr_{0.4}FeO_3$ (I)
$La_{0.45}Sr_{0.55}MnO_3$ (M) — **AF**

$La_{0.60}Sr_{0.40}MnO_3$ — **F**

Izumi, Tokura, et al PRB '99,'00

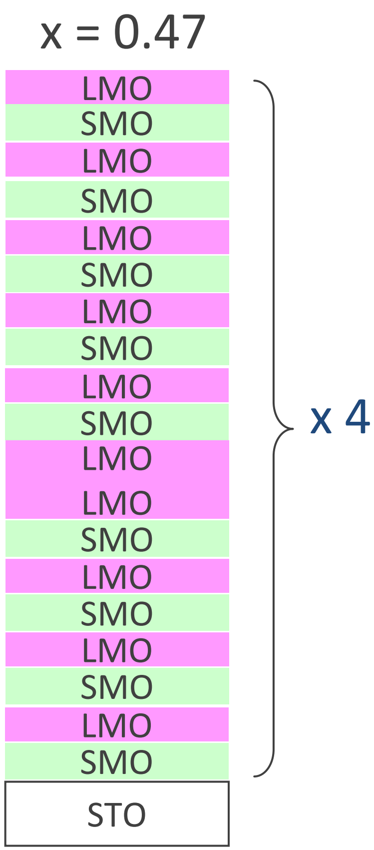
➢What is the magnitude of the induced moment?

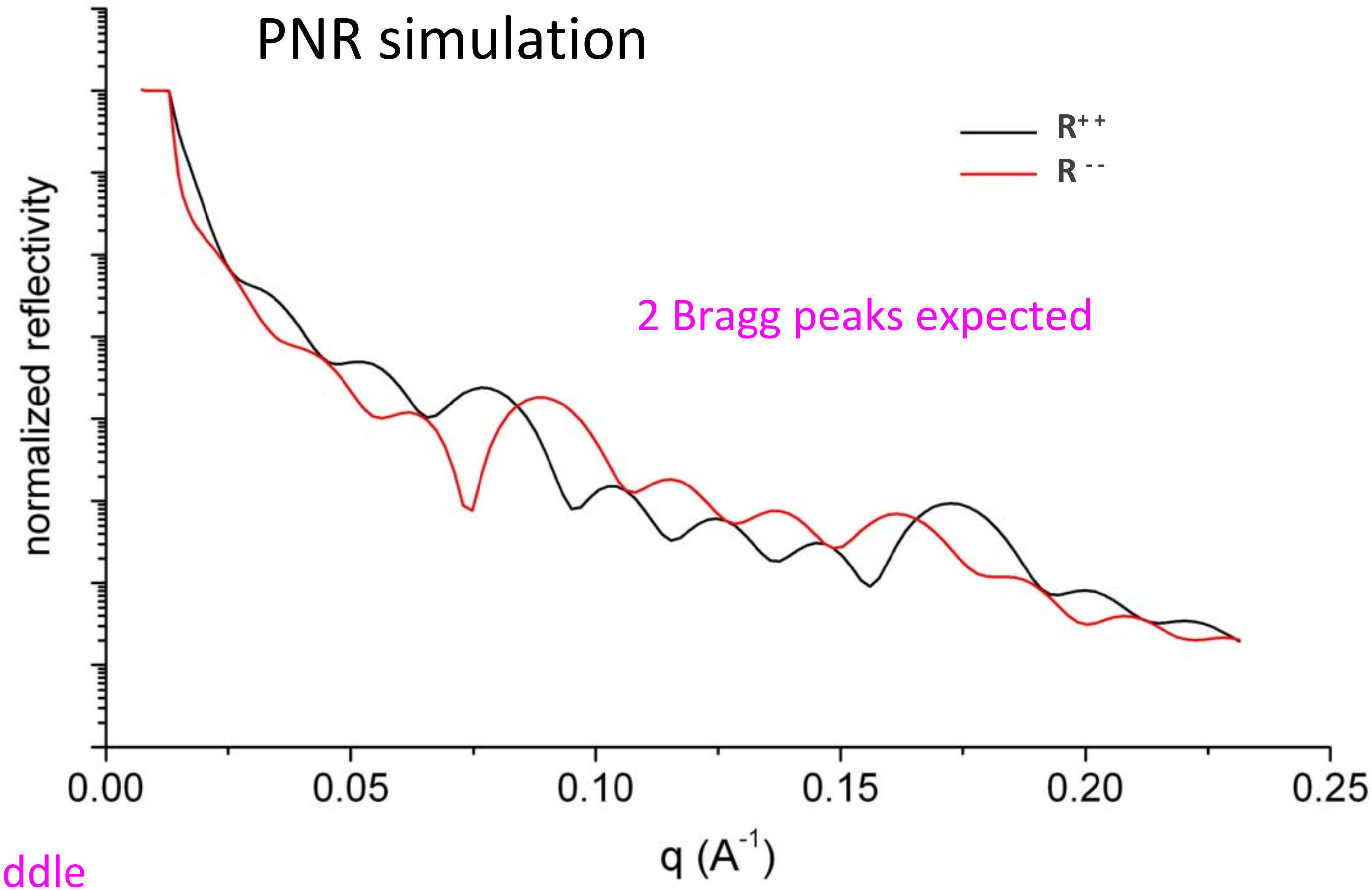
➢How far does the delta-doped charge extend?

➢Can we design a modulated profile with a different periodicity?

x=0.47 superlattice

On the verge of ferromagnetism

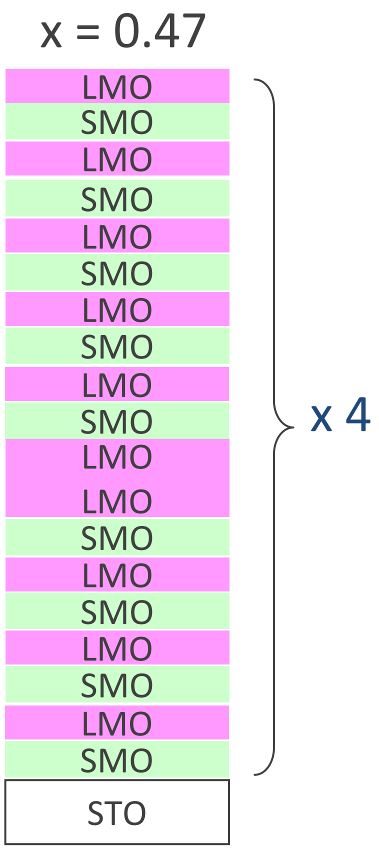


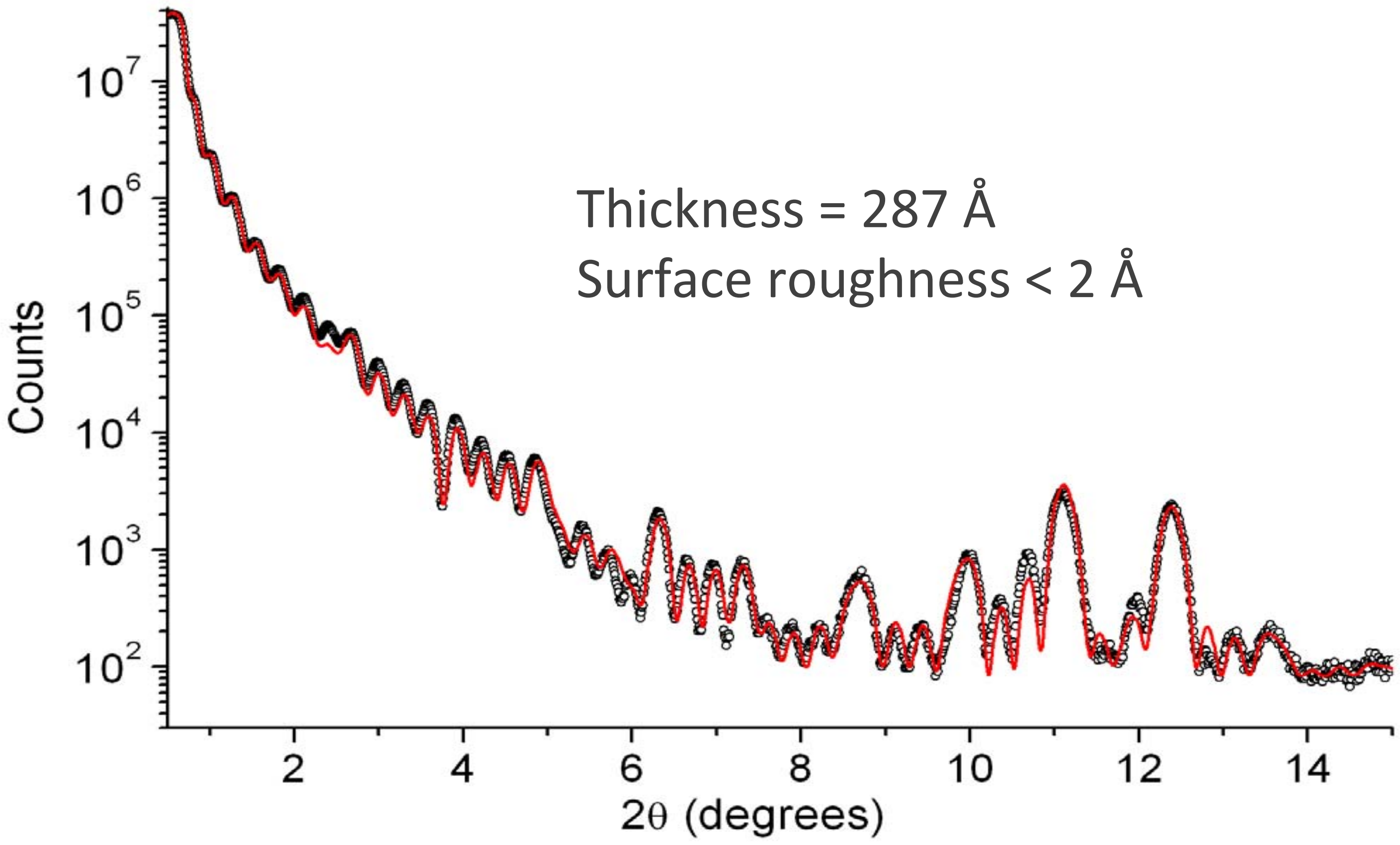


Double $LaMnO_3$ in middle

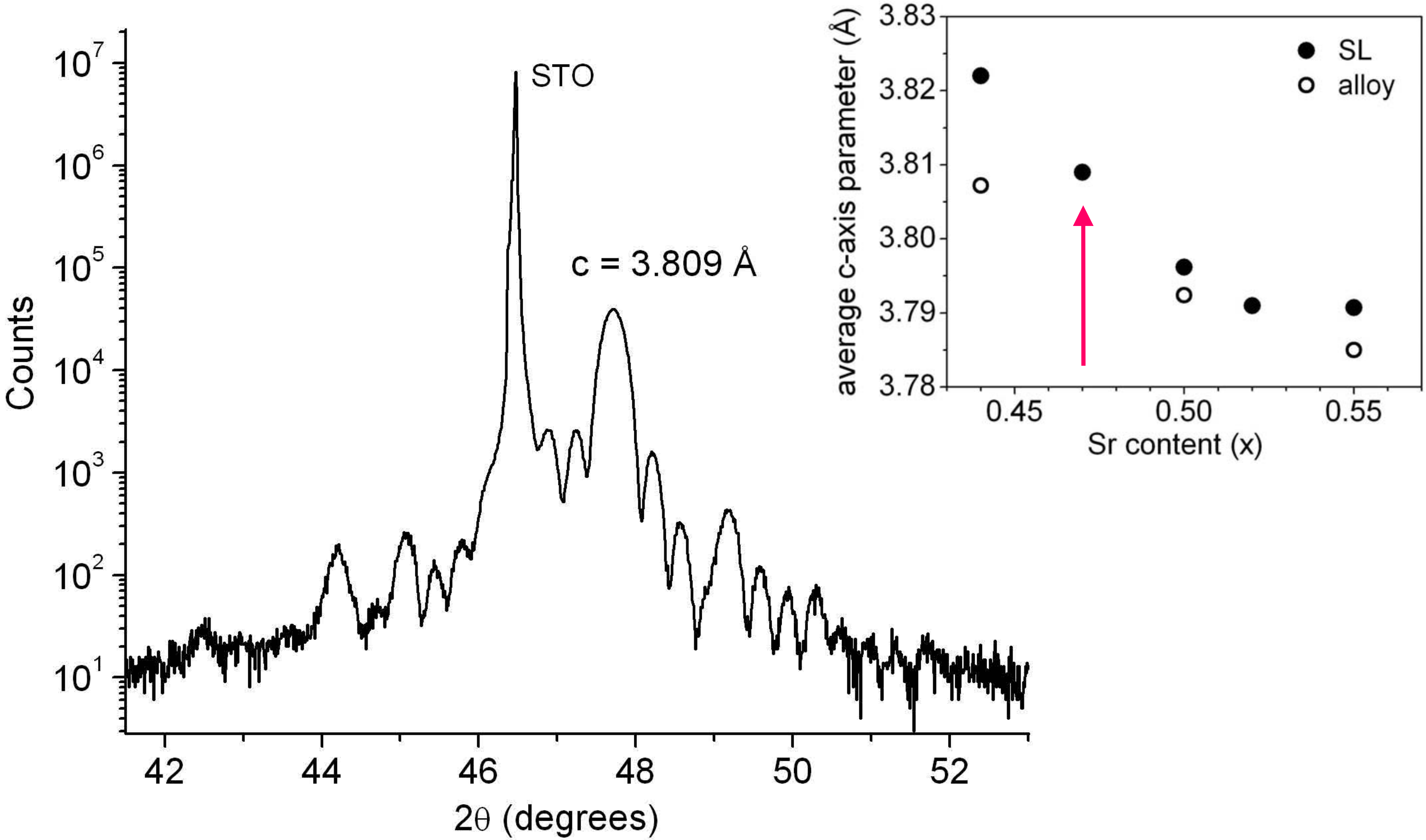
x = 0.47 superlattice: SL x 4 / L / SL x 5

X-ray reflectivity

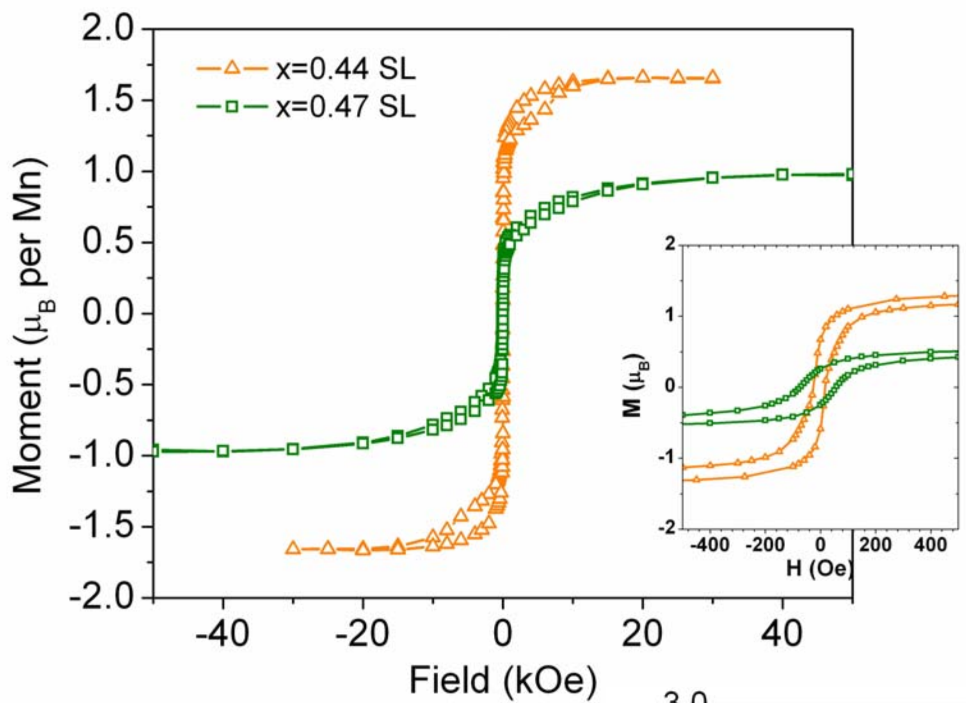


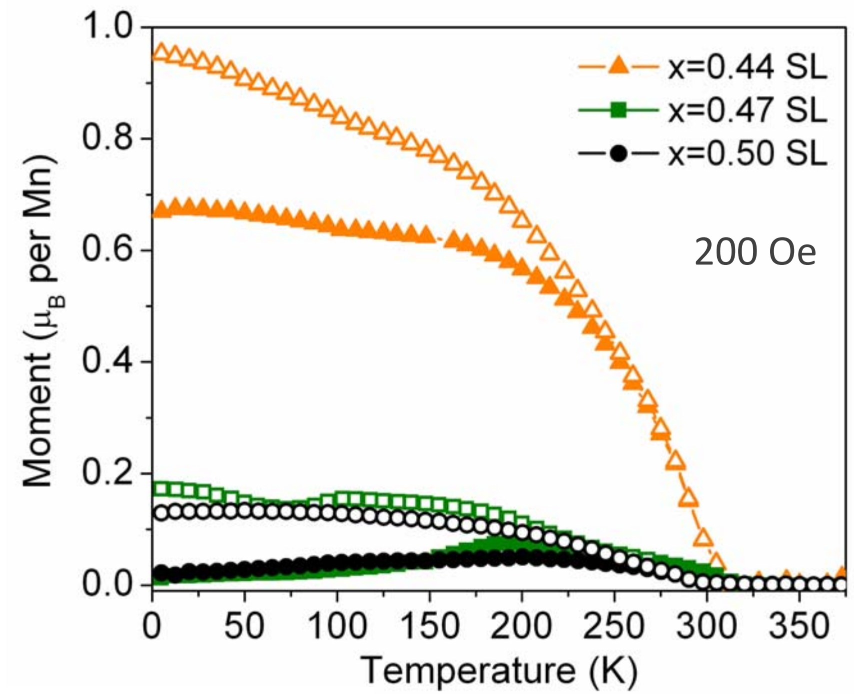


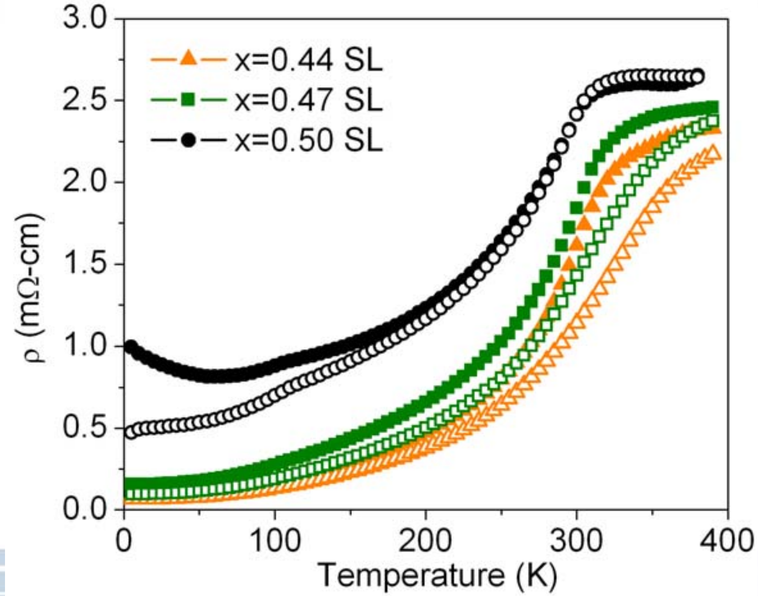
x = 0.47 superlattice – X-Ray Diffraction



X = 0.47 SL - Magnetization & Resistivity

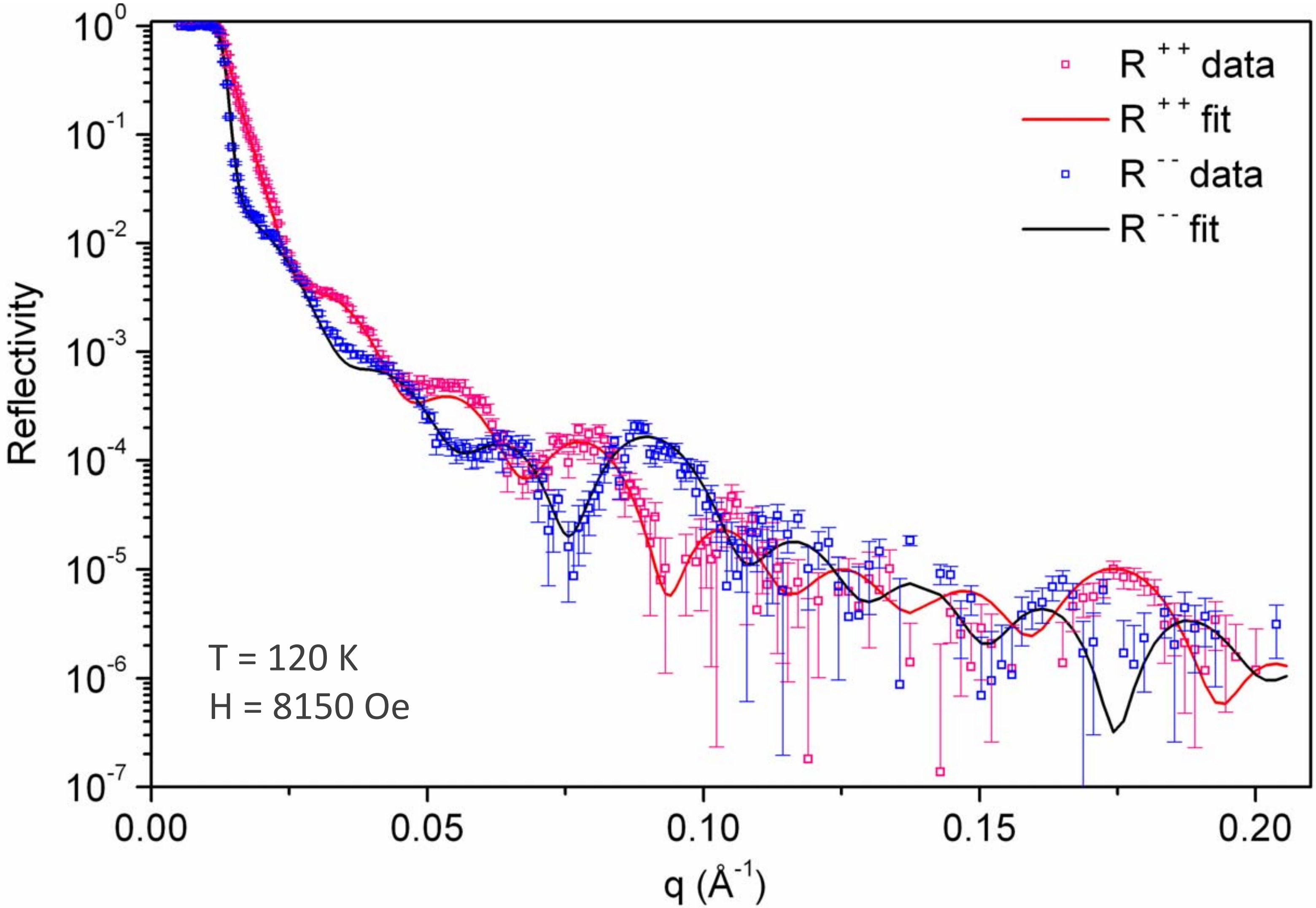




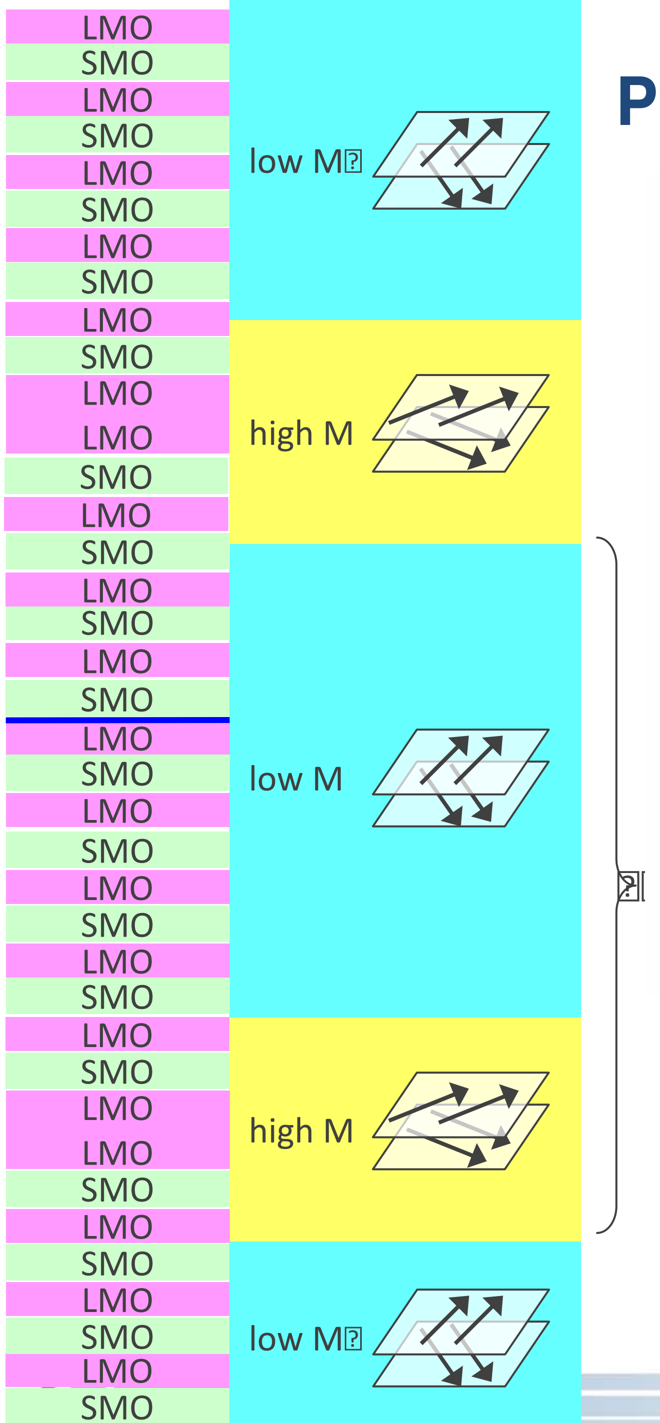


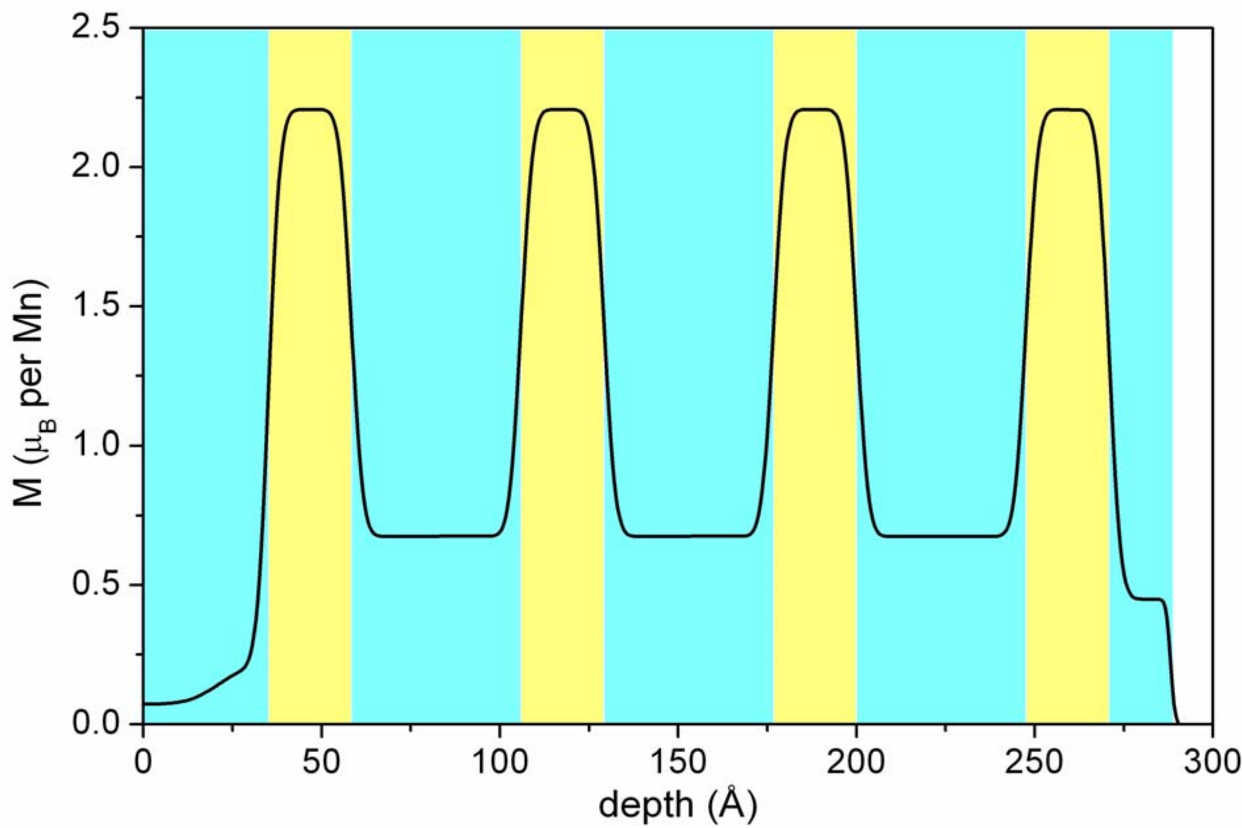
- properties follow trend with other SL compositions

PNR: x = 0.47 SL – Modulation here too!



PNR fitting model: x=0.47 SL





Induced moment

Length scale for carrier confinement

High M layer: 2.2 μ_B, 6 u.c., θ = 102°

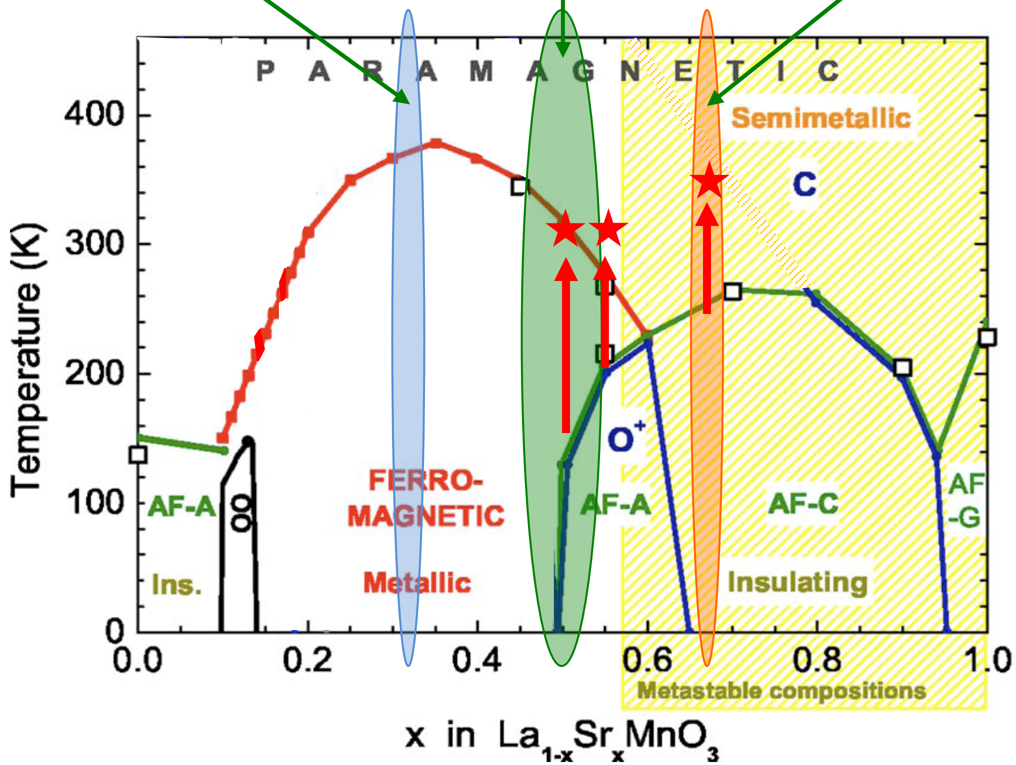
Low M layer: 0.7 μ_B, 13 u.c., θ = 158°

$La_{1-x}Sr_xMnO_3$ Ordered Analogs

Salvador *et al.* APL '99;
C. Adamo *et al* APL '08; many others
A. Bhattacharya *et al* PRL '08

Koida *et al,* PRB (2002);
T. Santos *et al* PRB '09

S. May et al, Nat. Mat. '09



Conclusions

- Tuning across F-AF phase boundary using digital synthesis
- Enhanced T_N over bulk $La_{1-x}Sr_xMnO_3$, measured by neutron diffraction
- Canted, modulated magnetic profile revealed by PNR
  - Delta-doping of ferromagnetism *without disorder*
  - *Solved the magnetic structure:*
    - Magnitude of the induced moment
    - Length scale for spreading of charge