Resonant X-Ray Scattering (RXS) on Layered Manganites: Observing the Orbital Ordering Effect

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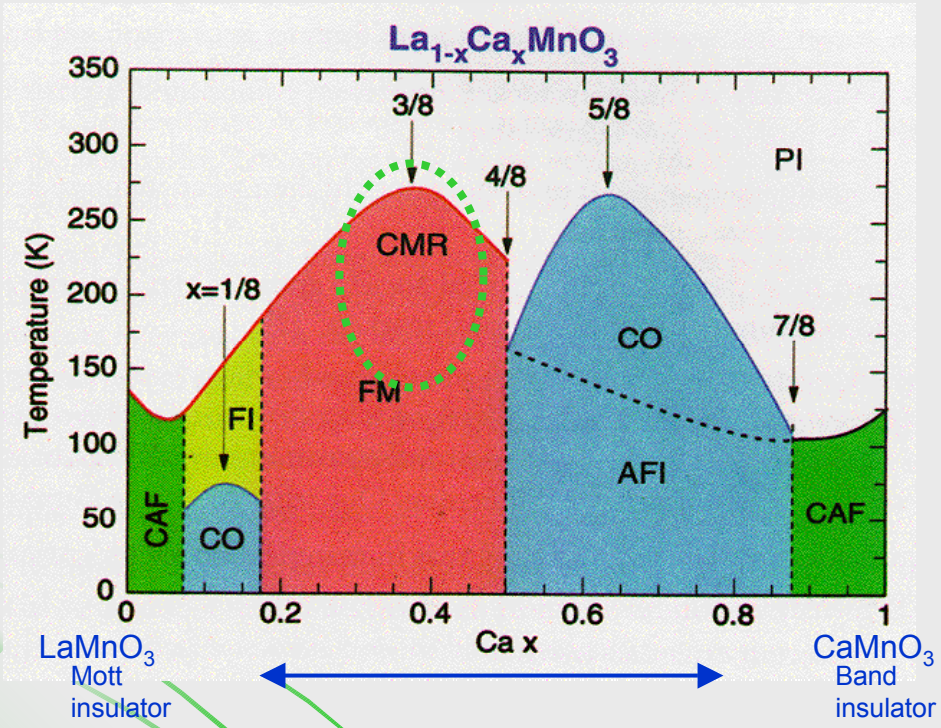
Strong Electronic Correlation Effect

Complex phase diagram in 3*d* Transition Metal Oxides

Novel electronic phase diagram



$LaMnO_3$
Mott insulator

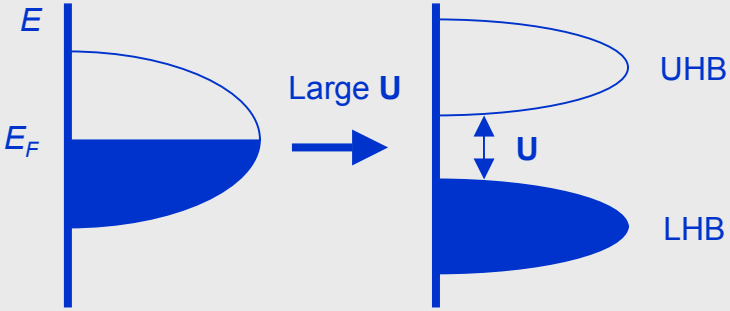
$CaMnO_3$
Band insulator

CO: charge-ordering
FM: ferromagnetic metallic
CAF: canted anti-ferromagnetic insulating
PI: paramagnetic insulating

Mott insulator

Half-filled *d* band
"metallic"

Mott insulator



"One electron / site"

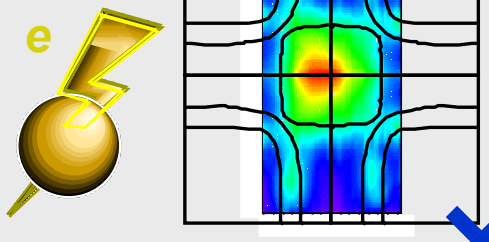
Proximity in energy scale is likely to be the cause of complex phase diagram

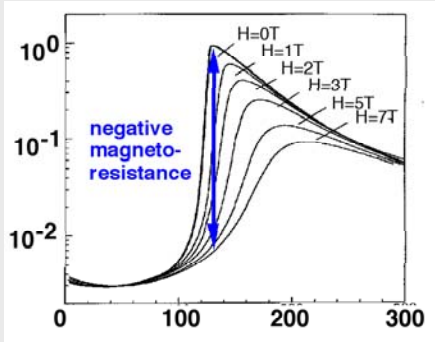
Strong correlation effect makes manganite physics extremely complicated!

Intimate Interplay Between Various Degrees of Freedom

Competition/cooperation between *spin, charge, lattice and orbital* degrees of freedom

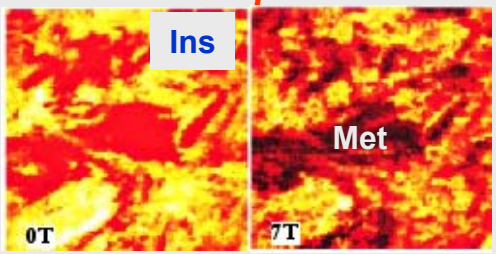
Electronic, Charge Transport



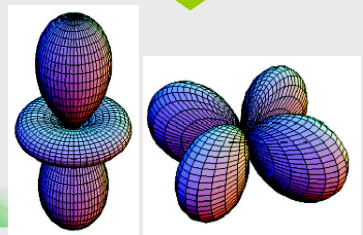


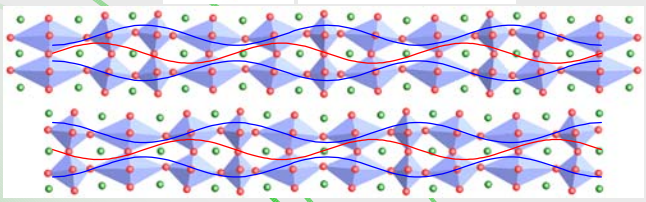
Spin, Magnetic

Phase separation

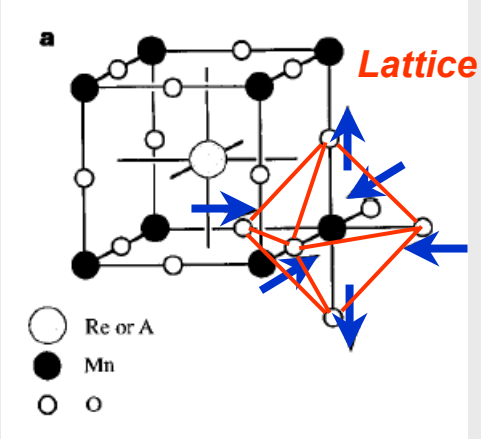


Orbital





Lattice



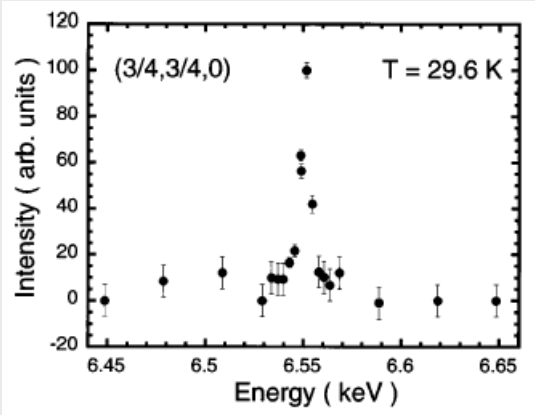
Strong interplay results in **phase separation (nm~μm)**, percolation induces "colossal" effect

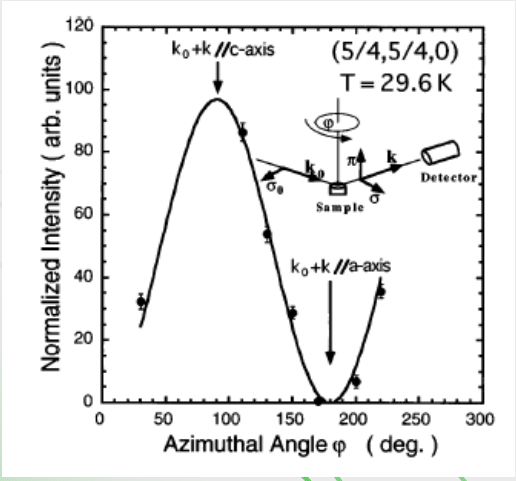
Yi-De Chuang *et al.*, *Science* **292**, 1509 (2001).
B. Campbell *et al.*, *PRB* **65**, 014427 (2002).
S. Mori *et al.*, *Nature* **392**, 473 (1998).
M. Uehara *et al.*, *Nature* **399**, 560 (1999).
M. Fath *et al.*, *Science* **285**, 1540 (1999).

How to Study Orbital Physics? Resonant X-ray Scattering

Hard X-ray scattering

$La_{0.5}Sr_{1.5}MnO_4$, 6.5keV, ~30K





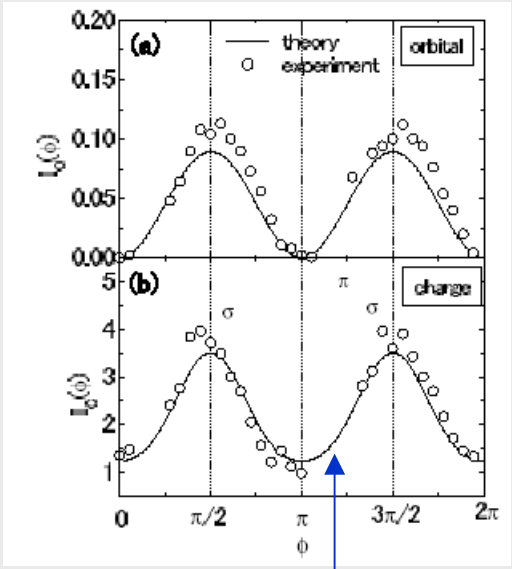
- Strong resonance enhancement
- Azimuth scan suggests either ($3y^2$-r^2 : $3x^2$-r^2) or (y^2-z^2 : x^2-z^2) orderings
- Need to measure other orbital superlattice reflection to uniquely determine the ordering states

Atomic Scattering Factor (ASF) is sensitive to **charge / orbital** arrangement (overlap between Mn 4*p* orbital and O 2*p*-Mn 3*d* hybridization via **Coulomb interaction**), as well as local lattice distortion (**Jahn-Teller effect**).

$$I \propto \left| \Delta f_{3x^2-r^2} - \Delta f_{3y^2-r^2} \right|^2$$

Predict to have ***sin²φ*** dependence

$LaSr_2Mn_2O_7$, ~6.5keV

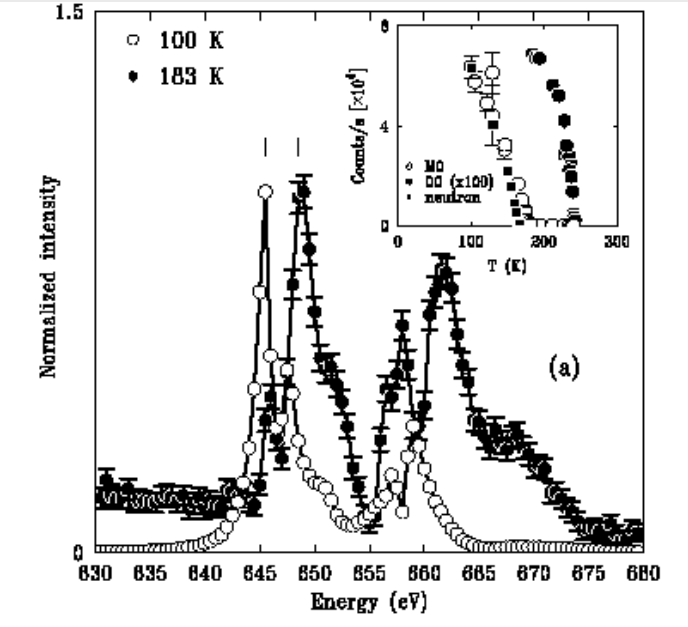


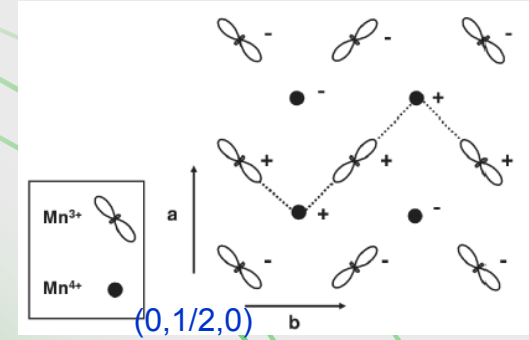
($3y^2$-r^2 : $3x^2$-r^2)

Y. Murakami *et al.*, *PRL* **80**, 1932 (1998)
Y. Wakabayahi *et al.*, *J. Phys. Soc. Japan* **69**, 2731 (2000)
S. Ishihara and S. Maekawa, *Rep. Prog. Phys.* **65**, 561 (2002)

Ordering in Charge and Orbital Channels

$Pr_{0.6}Ca_{0.4}MnO_3$, Mn L edge





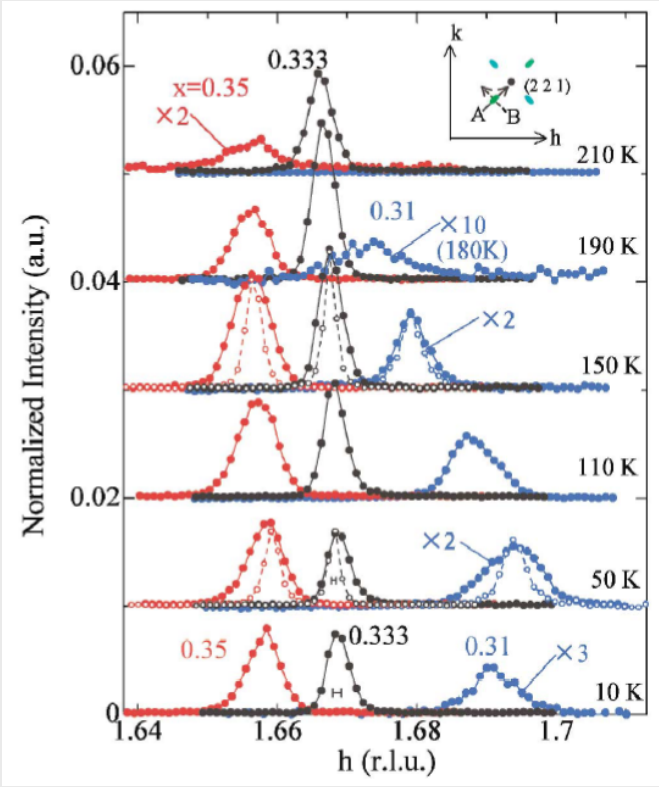
(1/2,0,0) spin

(0,1/2,0) orbital

Spin and orbital orderings as function of temperature

Other material systems are currently been investigated

~1/3 stripe ordering in $(La,Sr)_2NiO_4$ (**charge**)

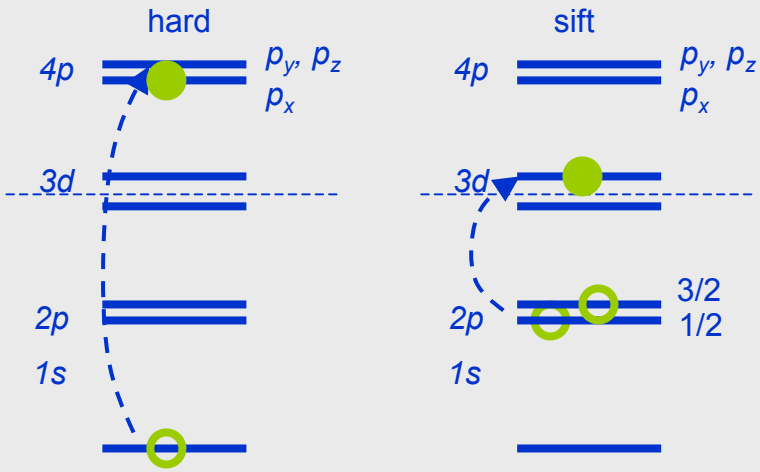


Evolution of charge stripe ordering as function of temperature and doping can be nicely tracked in RXS spectra

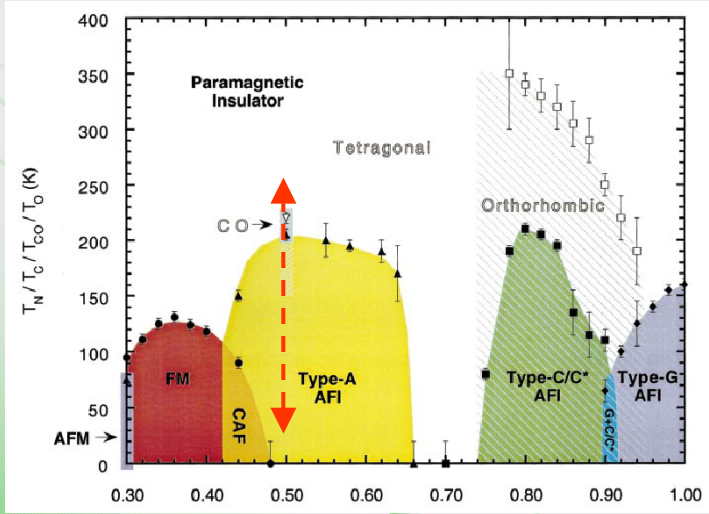
K. Ishizaka *et al. PRL* **92**, 196404 (2004)
K.J. Thomas *et al*, *PRL* **92**, 237204 (2004)

OK, What Do We Want to Work on Layer Manganites?

I. Hard X-ray is different from soft X-ray

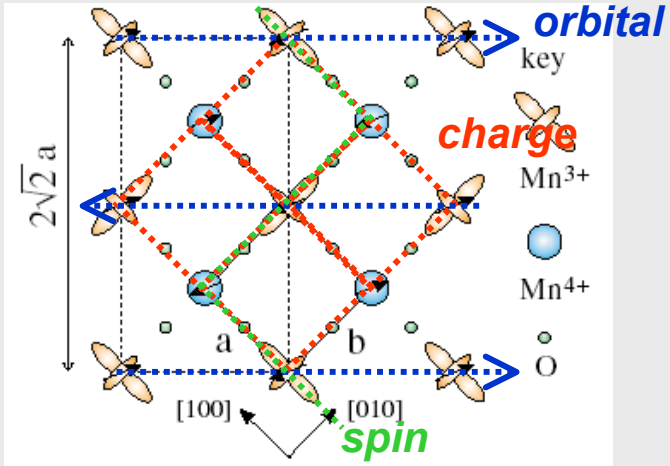


II. Single layer manganite is different from double layer manganite: no CMR effect

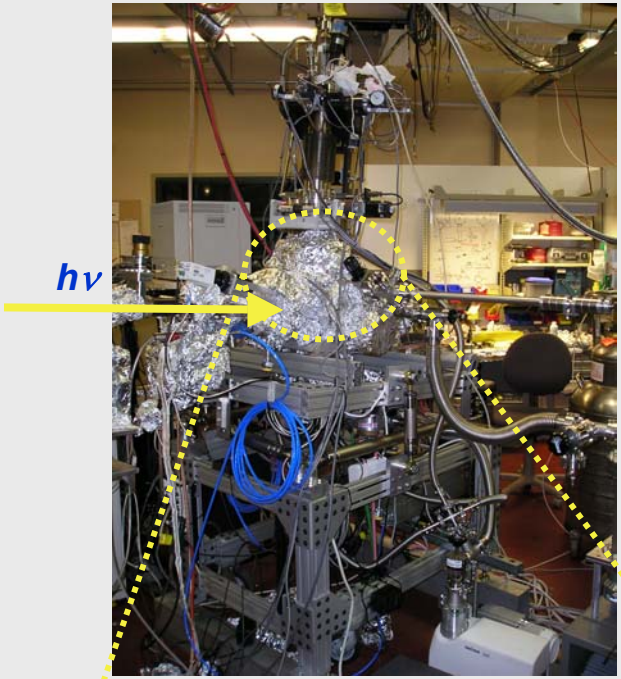


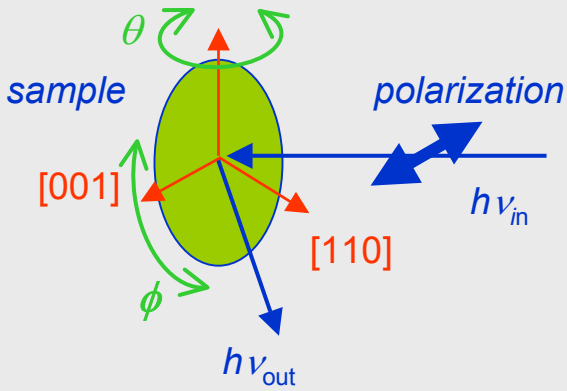
"Simple strategy: pick the easy target first before working on something hard"

At commensurate doping, ordering phenomena can be observed in charge, orbital or spin channel: ***CE ordering***



Experimental Details





On resonance:

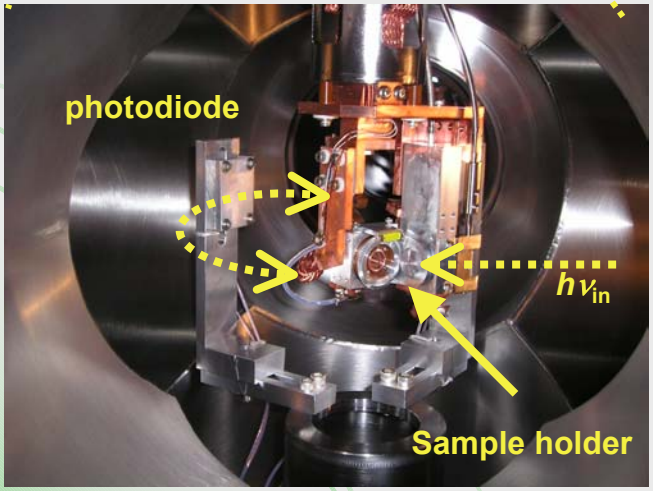
$$|\vec{q}_{out}| \sim |\vec{q}_{in}|$$

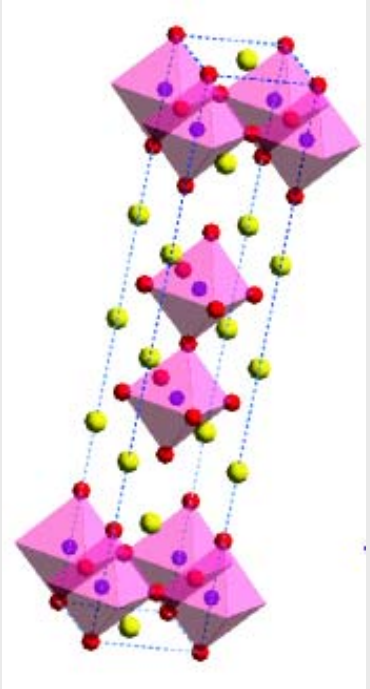
$$\Delta q = |\vec{q}_{out} - \vec{q}_{in}| = 2 \times |\vec{q}_{in}| \times \sin\theta$$

or

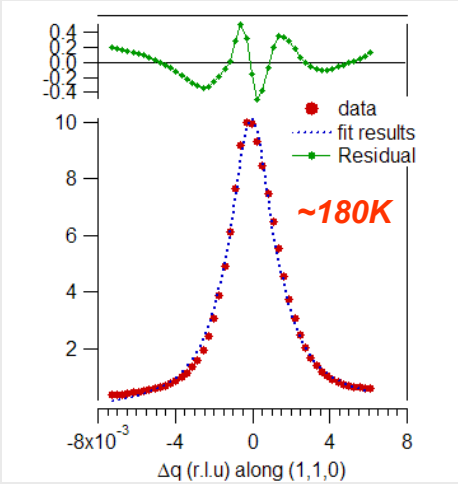
$$\Delta q = \frac{4\pi}{\lambda} \times \sin\theta$$

$$= 1.013 \times E(keV) \times \sin\theta$$



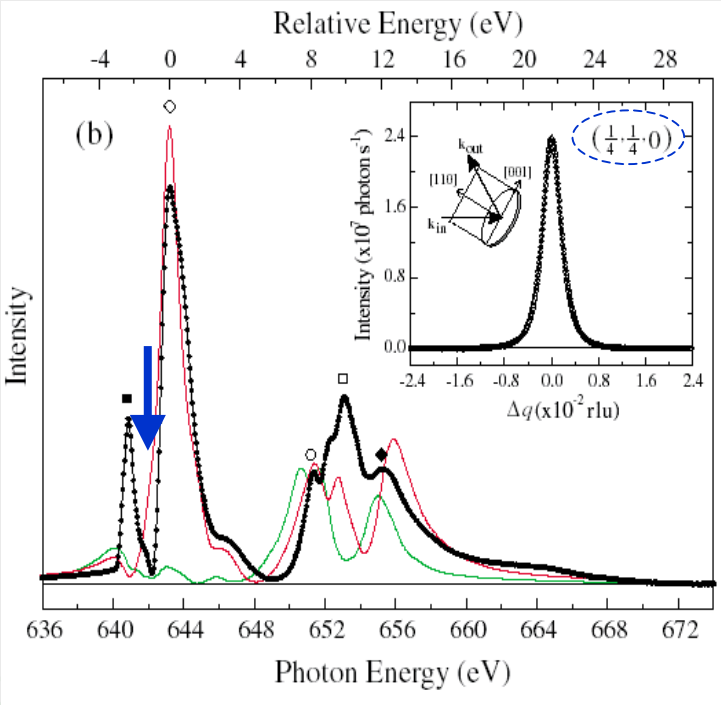


Row data (θ-2θ scan) fitted with single Lorentzian function and a linear background

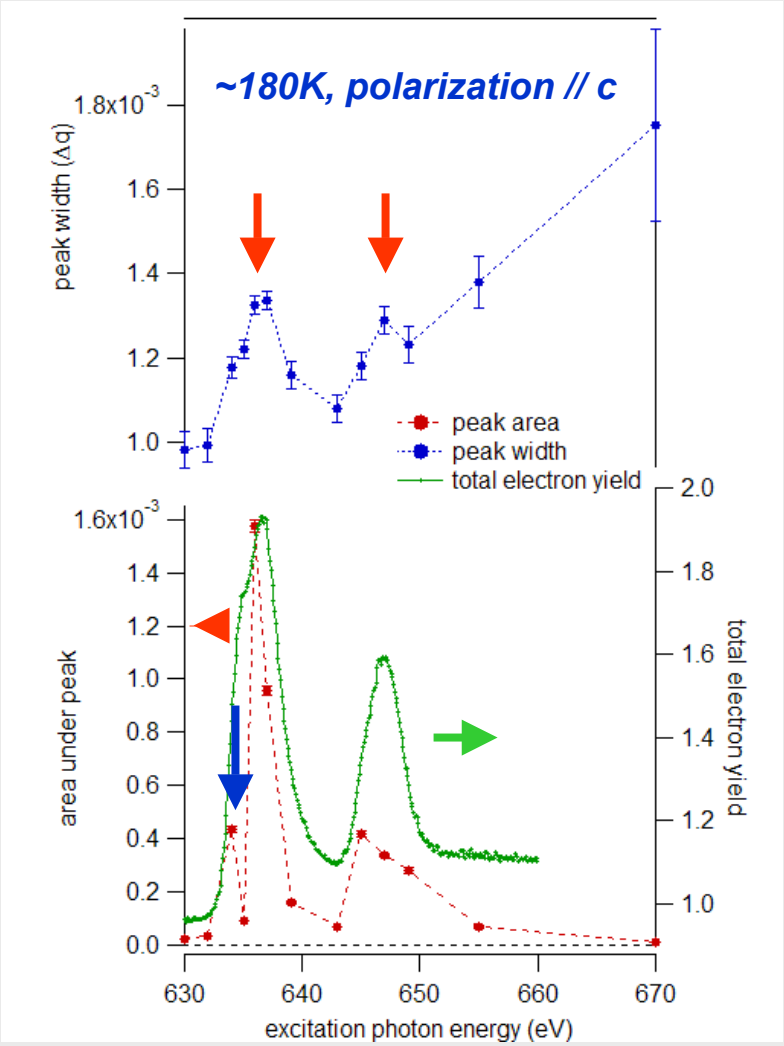


Resonance Enhancement of Superlattice Reflection

$La_{0.5}Sr_{1.5}MnO_4$ (single layer)



Experimental data on $LaSr_2Mn_2O_7$ (double layer)

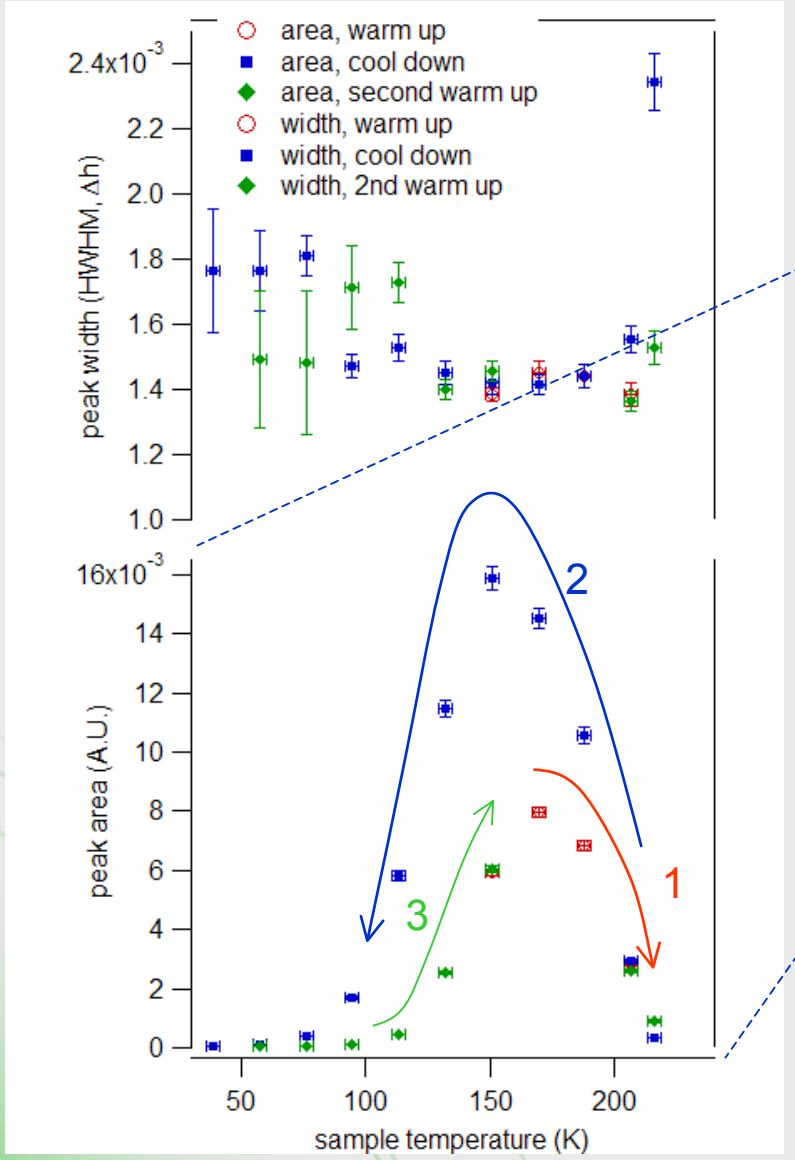


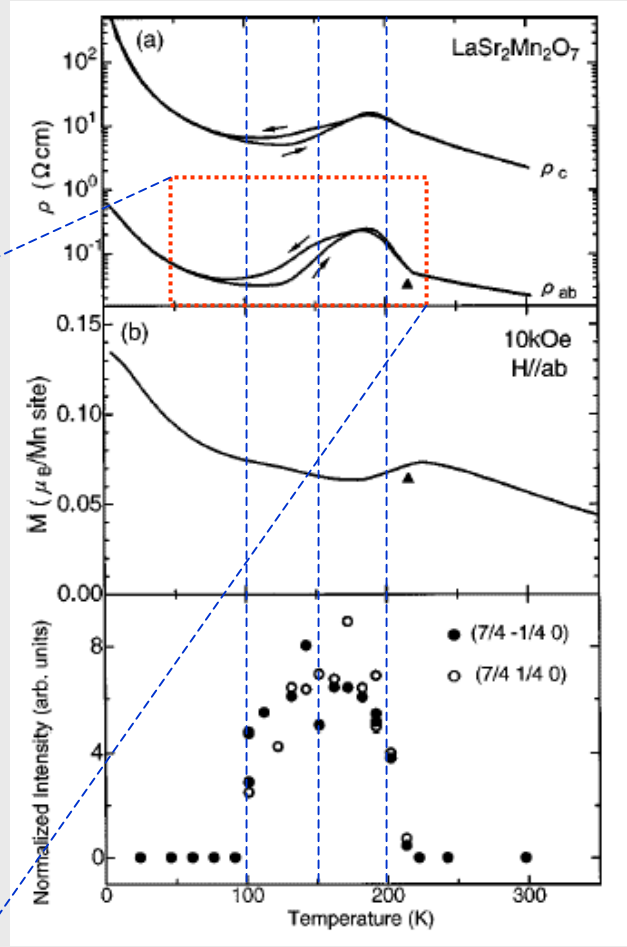
- Novel spectral feature (dip) observed
- Anomalous width behavior correlates to resonance enhancement

Strong photon energy dependence, showing large resonance enhancement both in single and double layer manganites

S.S. Dhesi *et al. PRL* **92**, 056403 (2004)
S.B Wilkins *et al. PRL* **91**, 167205 (2003)

Temperature Effect

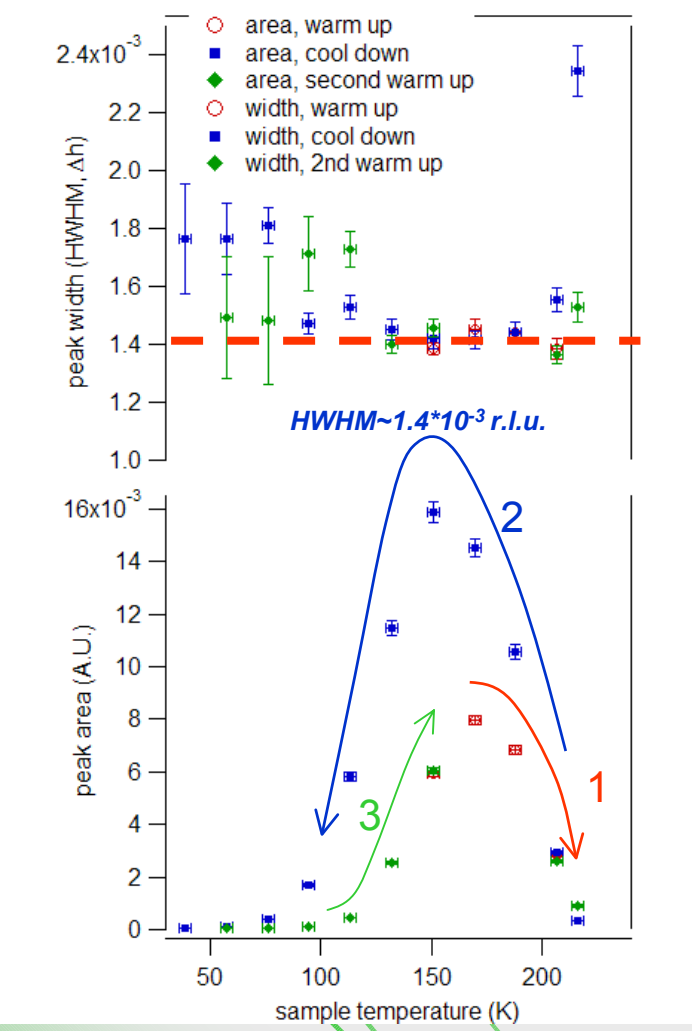




- Strong hysteresis loop observed in scattering intensity
- No noticeable width change throughout transition
- Orbital ordering is indeed closely related to resistive behavior of the sample

T. Kimura *et al.*, *PRB* **58**, 11081 (1998)

Correlation Length vs. Temperature



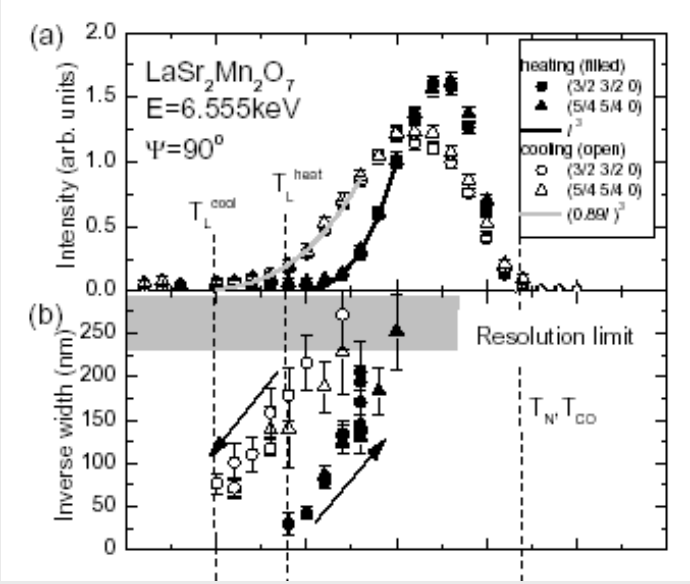
Correlation length of orbital ordering is around

$(2*\pi/3.87Å)*1.4*10^{-3}=2.3*10^{-3}$ $Å^{-1}$ (HWHM)

This gives real space length ~***440Å***

In single layer manganite $La_{0.5}Sr_{1.5}MnO_4$, HWHM is around $2.6*10^{-3}$ Å implying a length ~***400 Å***

Soft X-ray



Hard X-ray

Y. Wakabayashi *et al.*, *J. Phys. Soc. Japan* **72**, 618 (2003)

- Correlation length of orbital ordering is insensitive to layer number
- Orbital ordering is unlikely the only factor for insulating behavior
- No significant change in coherence length through phase transition. Favors phase separation scenario.

Summary and Future Direction

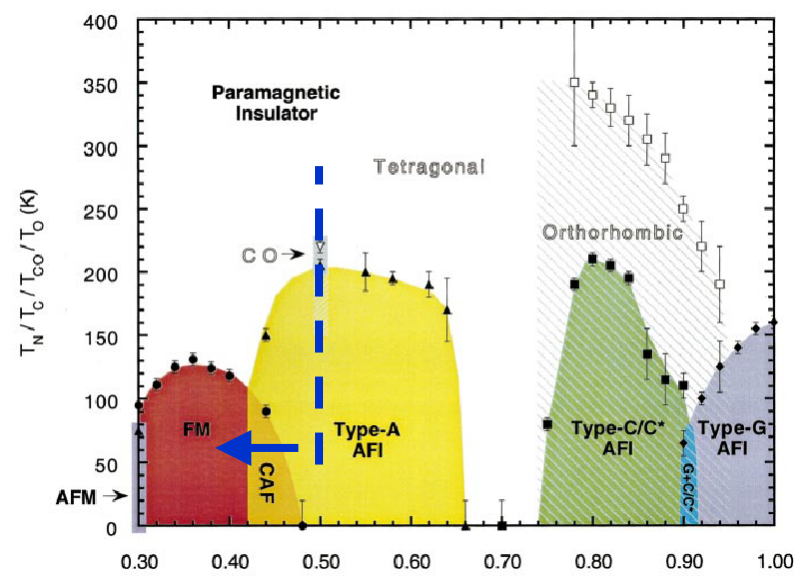
We observed the orbital superlattice reflection in bilayer manganite $LaSr_2Mn_2O_7$:

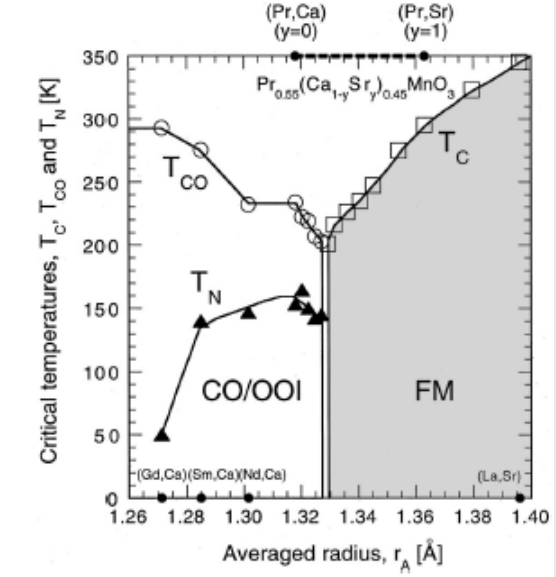
- Strong resonance enhancement at Mn L edge
- Strong temperature dependence with large hysteresis loop similar to resistivity curve

The correlation length of superlattice reflection:

- No noticeable change across phase transition (*)
- Nearly identical to the correlation length observed in hard X-ray, as well as single layer manganite $La_{0.5}Sr_{1.5}MnO_4$
- Insensitive to layer structure

What's next? CMR effect and the influence of charge / orbital orderings





Competition between FM and CO/OO phases

C.D. Ling *et al*, *PRB* **62**, 15096 (2000)
Y. Tomioka, Y. Tokura, *PRB* **66**, 104416 (2002)