Orbital correlations in doped manganites

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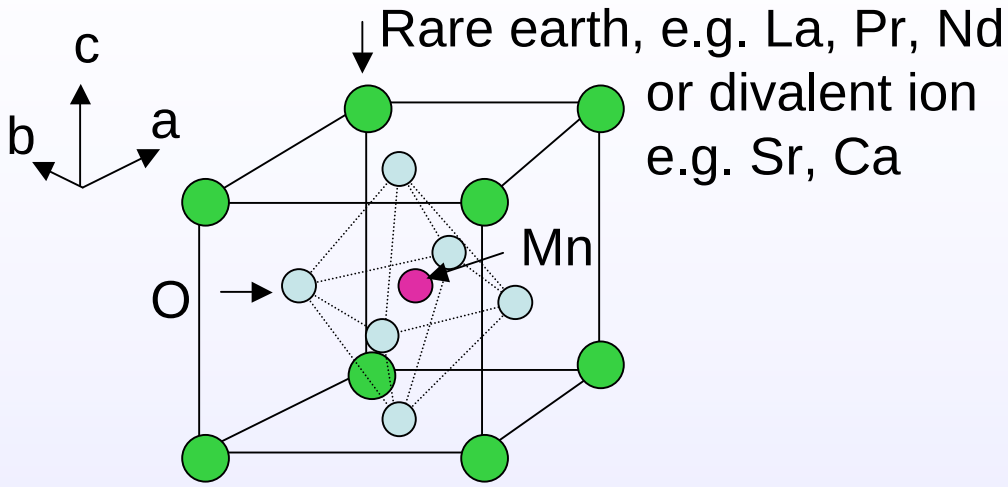
Outline

- The questions that motivate the experiments
  (and the experiments that motivate the questions)

- Resonant x-ray scattering
  - Direct comparison of orbital and magnetic order
  - The oxygen contribution to orbital order
  - Orbital domain dynamics

- Summary of open questions

Cubic Perovskite Manganites

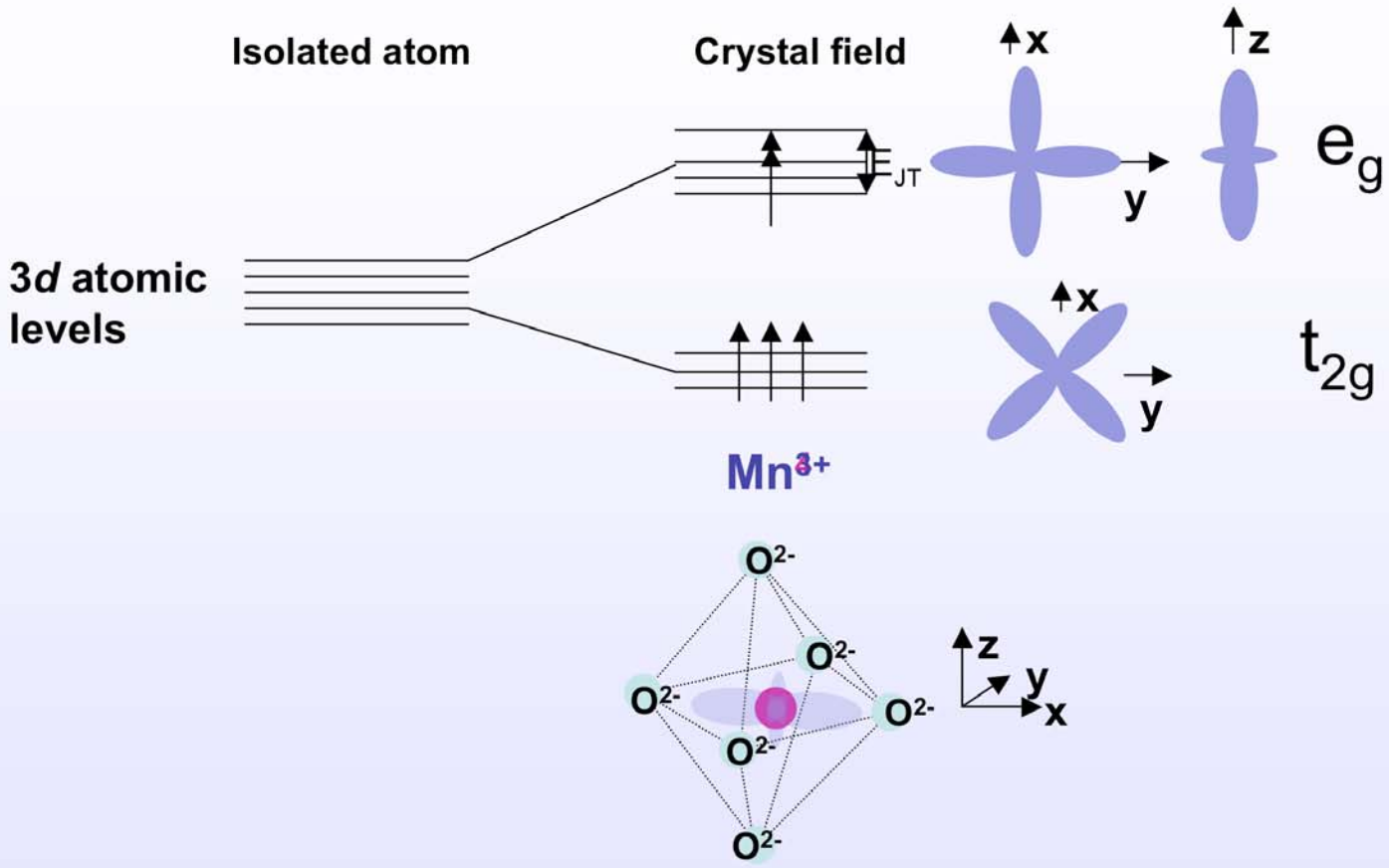


$RE_{1-x}A_xMnO_3$ (e.g. $La_{1-x}Sr_xMnO_3$)

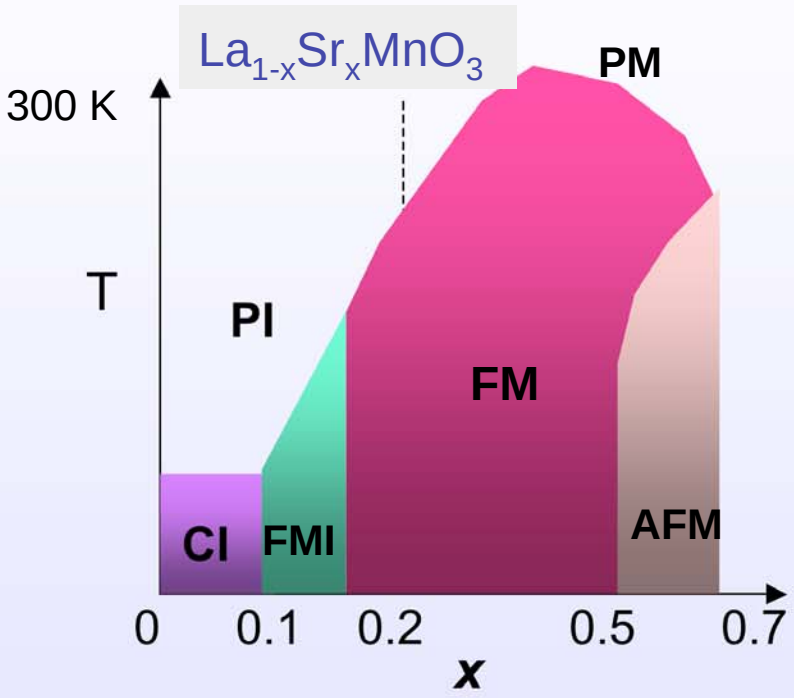
$(1-x)RE^{3+} + xA^{2+} + Mn^{v} + 3(O^{2-}) = 0$

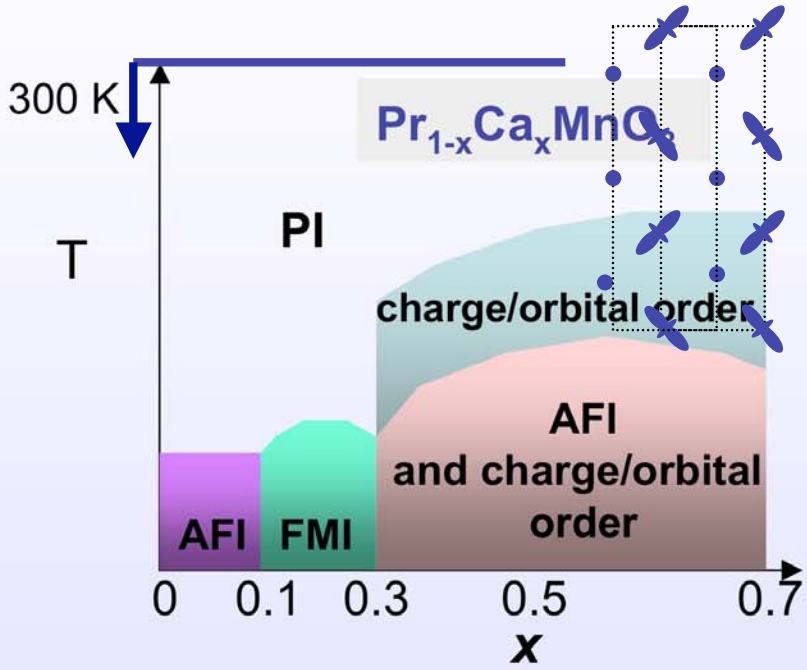
$v = 3 + x$

Jahn-Teller effect and orbital ordering



Phase diagrams of two different manganites



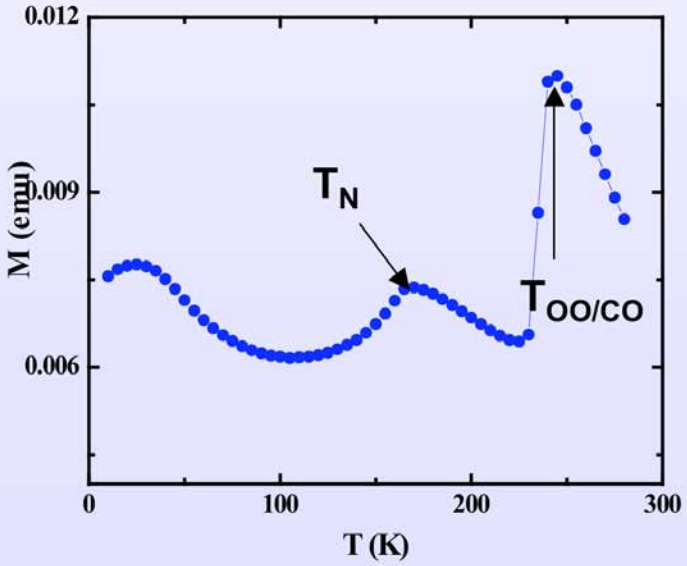


Important questions

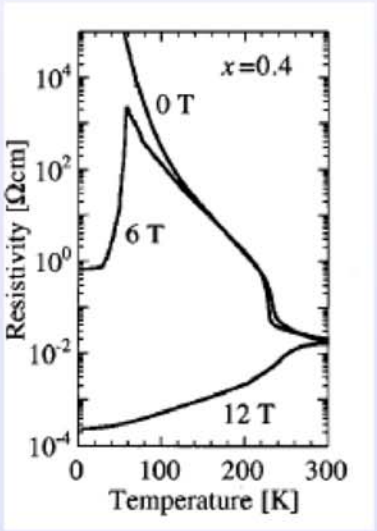
- Are sublattices separated by unit valence?
- What drives charge/orbital order?
- Dynamics associated with orbital order?
- Coupling between orbital and magnetic correlations?

$Pr_{0.6}Ca_{0.4}MnO_3$

χ(T)



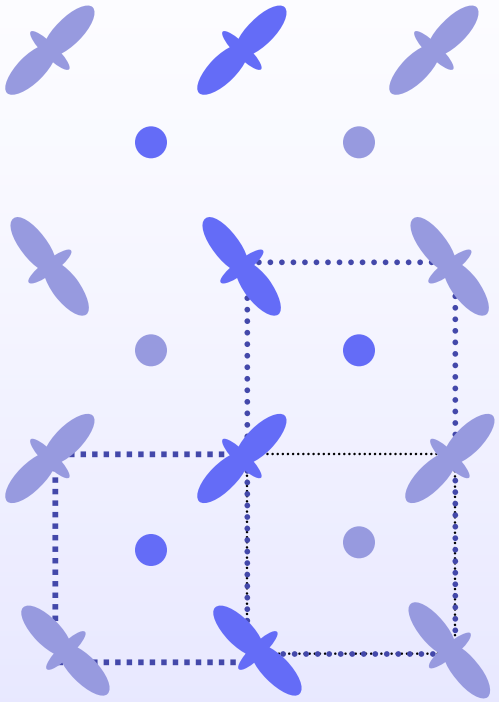
R(T)

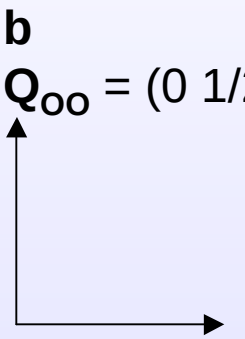


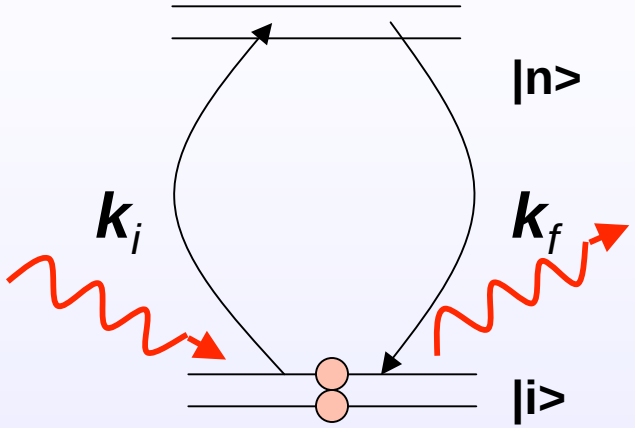
Y. Tomioka *et al*.,
PRB **53** R1639 (1996)

Resonant x-ray scattering

Orbital order in the a-b plane







$$f_{\text{res ion}} \sim \sum_n \frac{\langle i|\boldsymbol{\varepsilon}|n\rangle\langle n|\boldsymbol{\varepsilon}|i\rangle}{E - E_{res} + i\Gamma/2}$$

Mn^{4+}, spin up

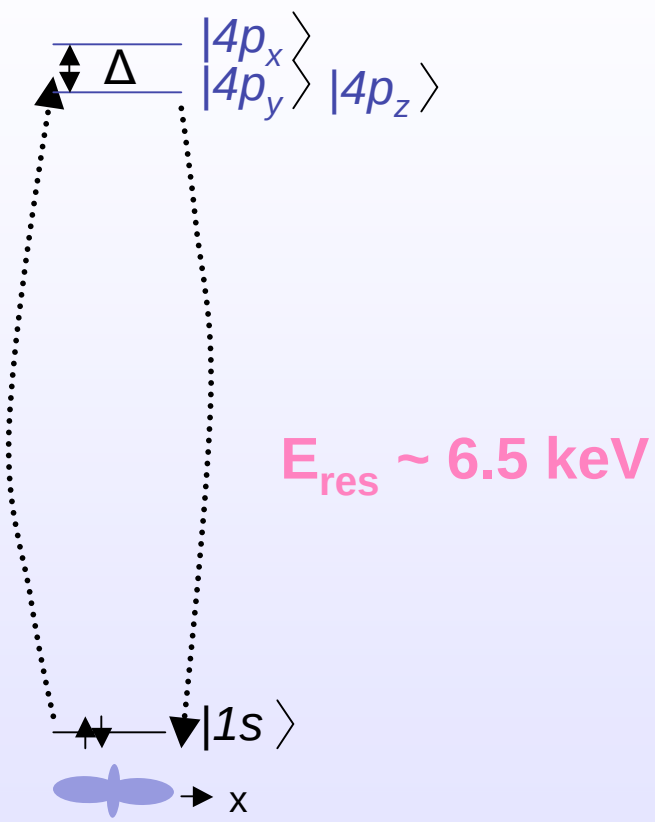
Mn^{3+}, spin down

$$f_{ion} = f(Q) + f'(E) + if''(E)$$

$$\text{Bragg peak intensity} = |\Sigma\, f_{ion} e^{(i\mathbf{Q}\cdot\mathbf{r})}|^2$$

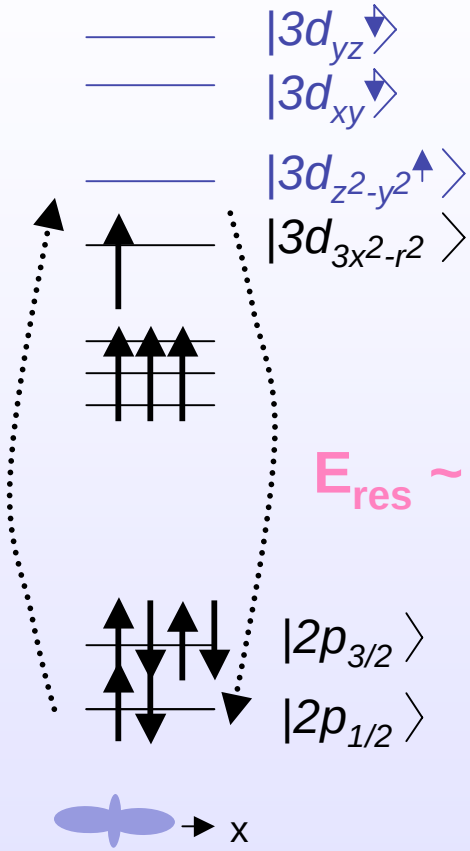
Mn absorption edges

K-edge (1s to 4p)



E_{res} ~ 6.5 keV

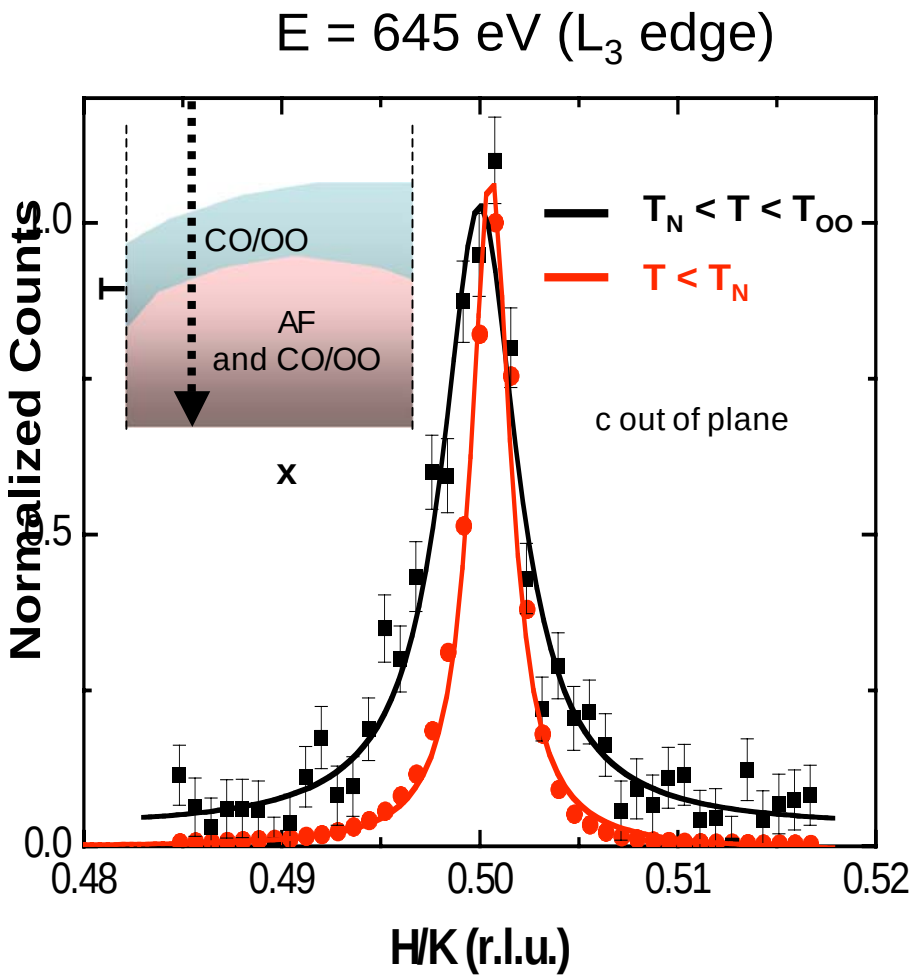
L-edge (2p to 3d)

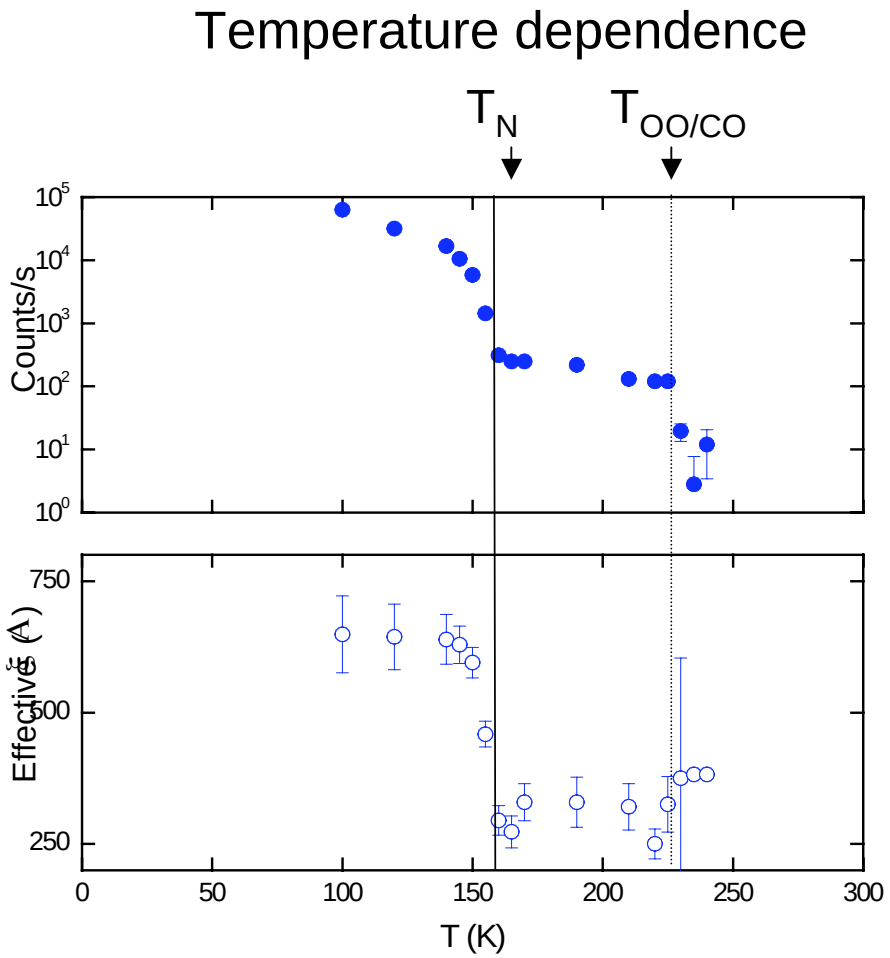


E_{res} ~ 650 eV

C. Castleton and M. Altarelli,
Phys. Rev. B 62 1033 (2000)

Direct comparison of orbital and magnetic superlattice reflections

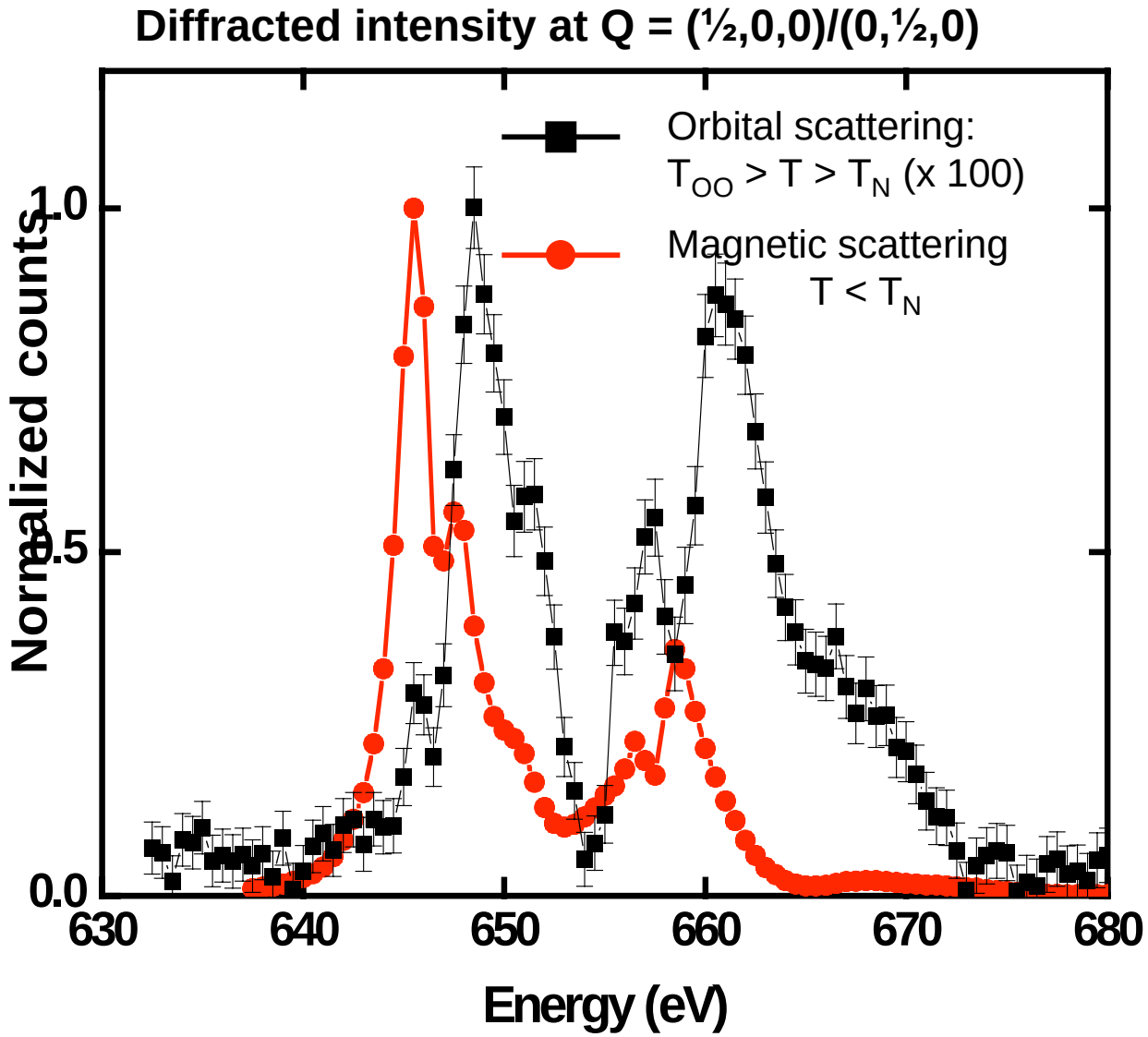


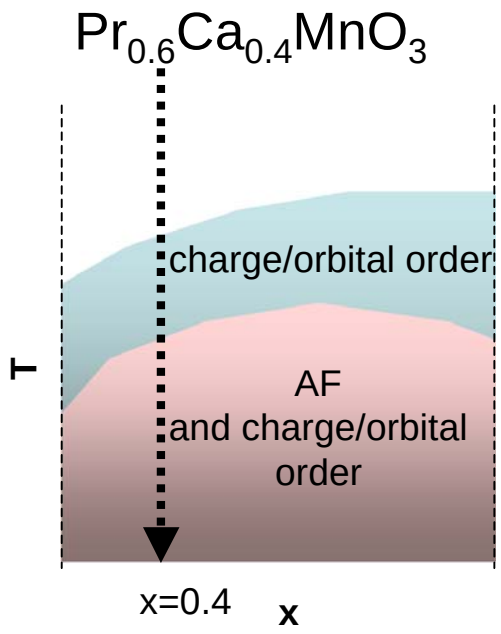


Orbital order correlated over a shorter length scale than magnetic order

K. J. Thomas, J. Hill, S. Grenier, P. Abbamonte, M. v. Veenendaal, G. Sawatzky *et al*. PRL **92**, 237204 (2004).

Magnetic and orbital resonant line shapes: direct comparison

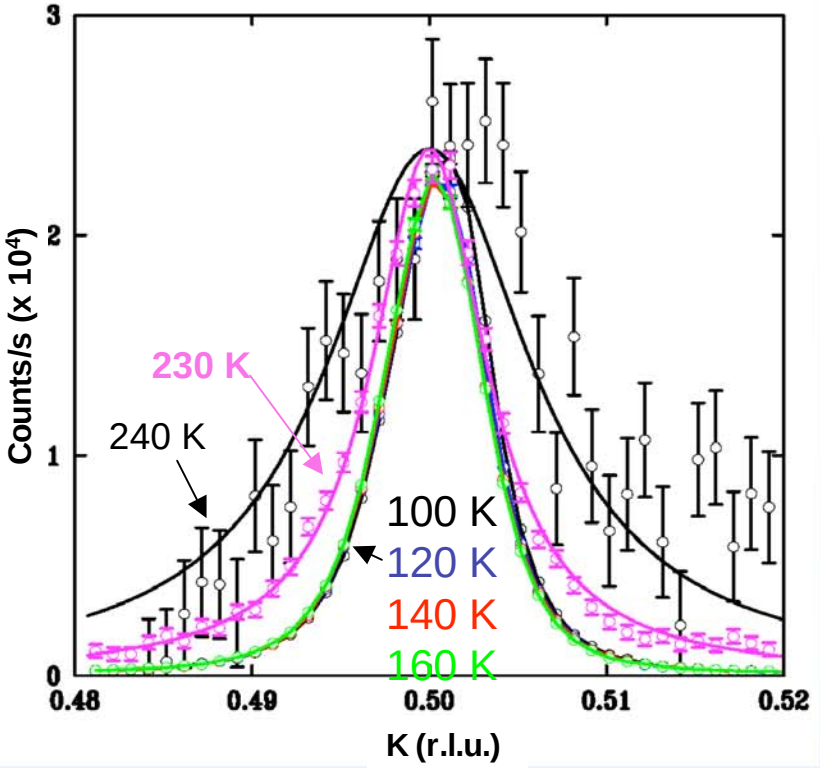




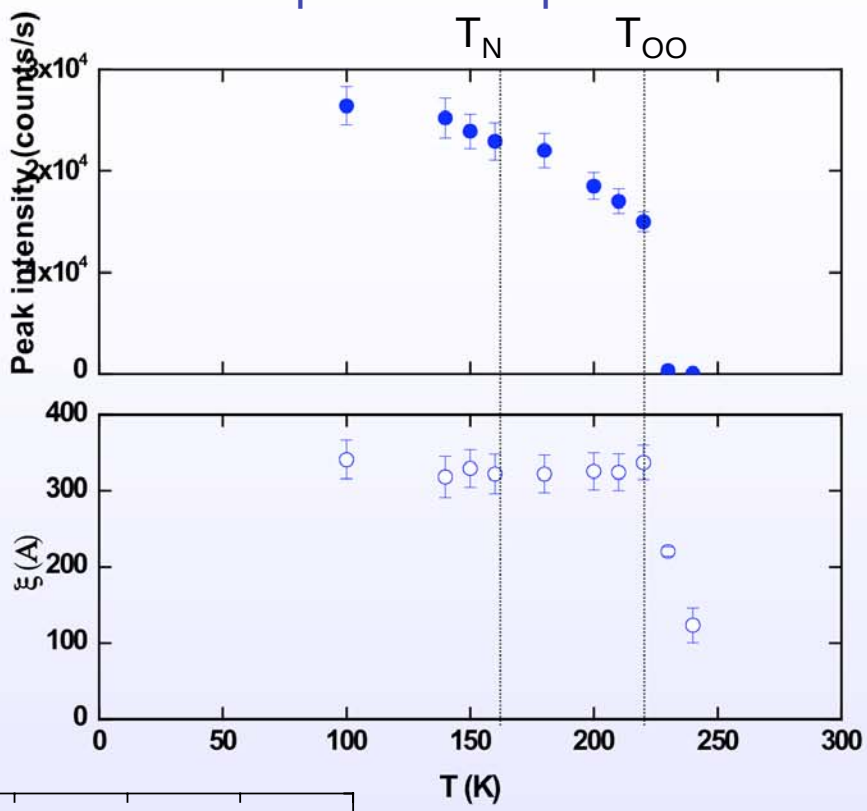
K. J. Thomas *et al*. PRL **92**, 237204 (2004).

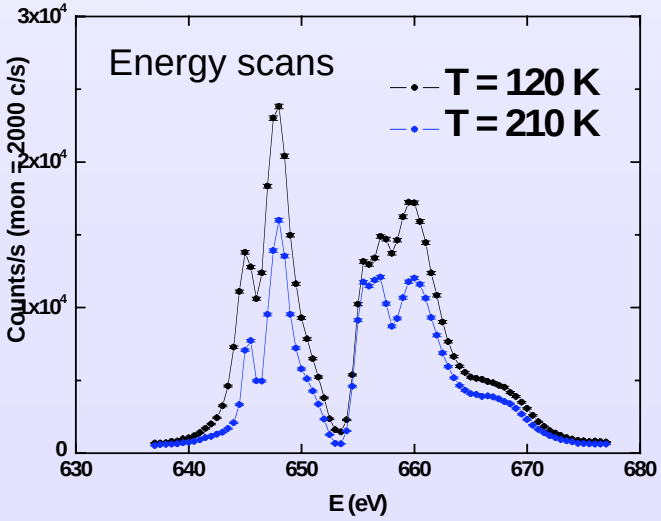
Pure orbital scattering

Orbital reflection at different T



Temperature dependence



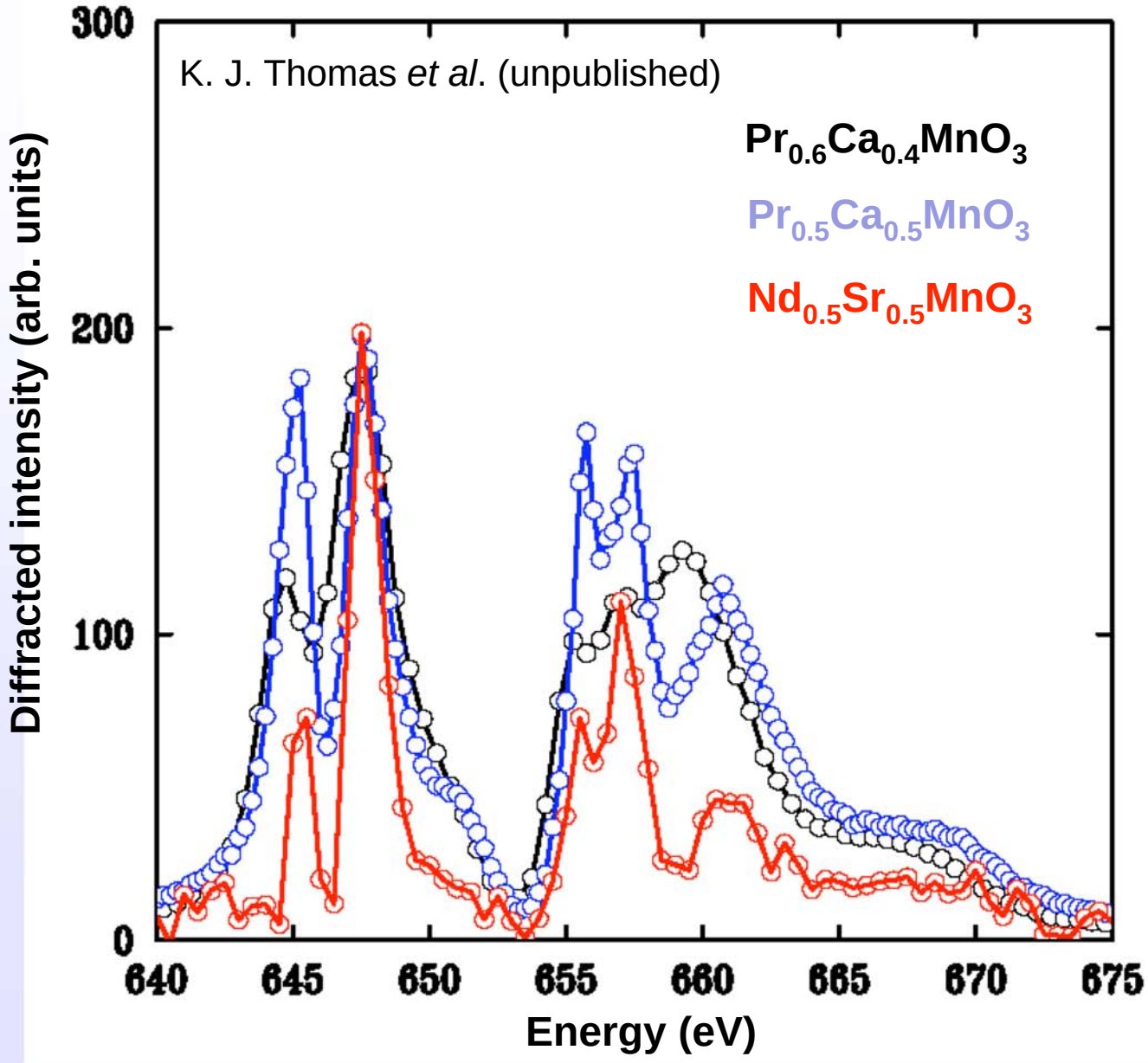


- **Understanding the line shape associated with orbital order**

- **The role of oxygen**

- **What sets the length scale for the orbital domains?**

Characteristic orbital scattering in half-doped manganites

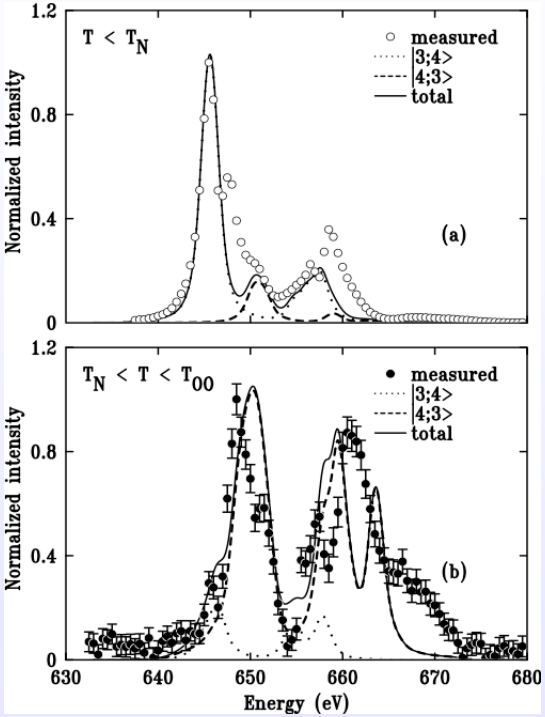


- Similarity of spectra suggest a “thumbprint” on orbital order

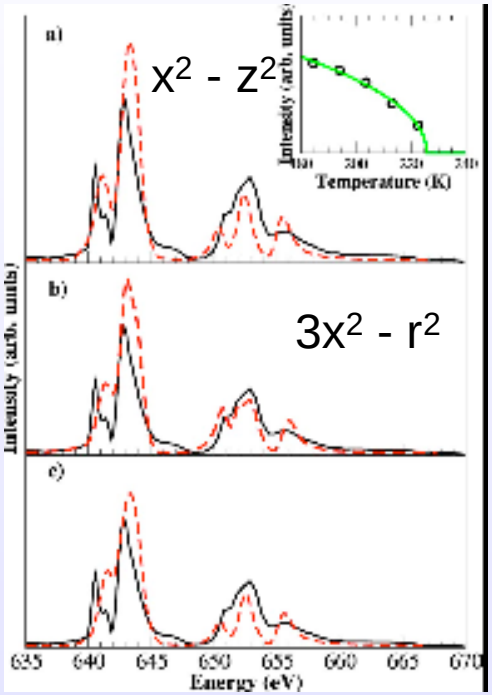
- Improve calculations to isolate features in the spectra (crystal field and hybridization effects)

Understanding the line shape associated with orbital order

Explain difference between magnetic and orbital lineshapes
(K. J. Thomas *et al*. PRL **92**, 237204 (2004))

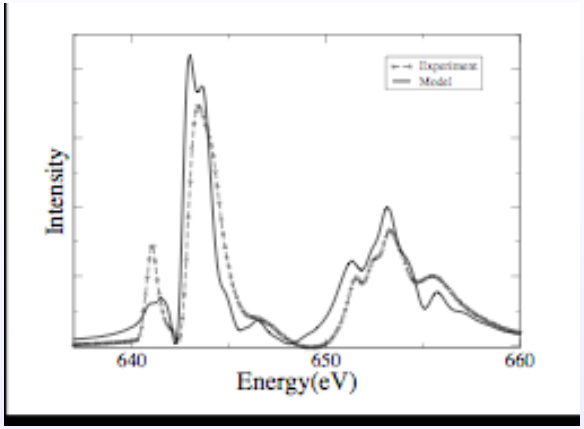


$Pr_{0.6}Ca_{0.4}MnO_3$



Explain the change in the OO diffraction spectrum below T_N and parametrize the JT distortion (C. W. M. Castleton and M. Altarelli, PRB **62**, 1033 (2000); S. B. Wilkins *et al*. PRB, 71 245102 (2005))

Treat contribution from oxygen sites and role of spin exchange
A. Mirone *et al*., The European Physical Journal B **53**, 23-28 (2006).

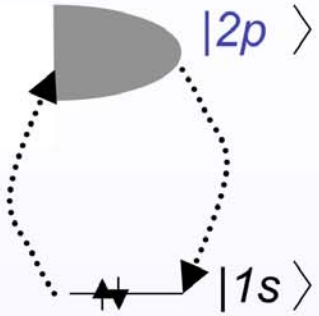


← $La_{0.5}Sr_{1.5}MnO_4$

Oxygen contribution to orbital order

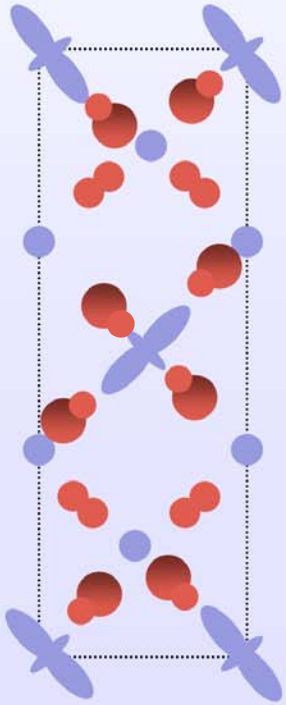
- Figure out where the charge is sitting and the degree of hybridization between the metal 3*d* and oxygen 2*p*

- Separate ‘electronic’ and ‘structural’ contributions to the orbital order



O K-edge (540 eV) probes
2*p* unoccupied states
(hybridization with Mn 3d)

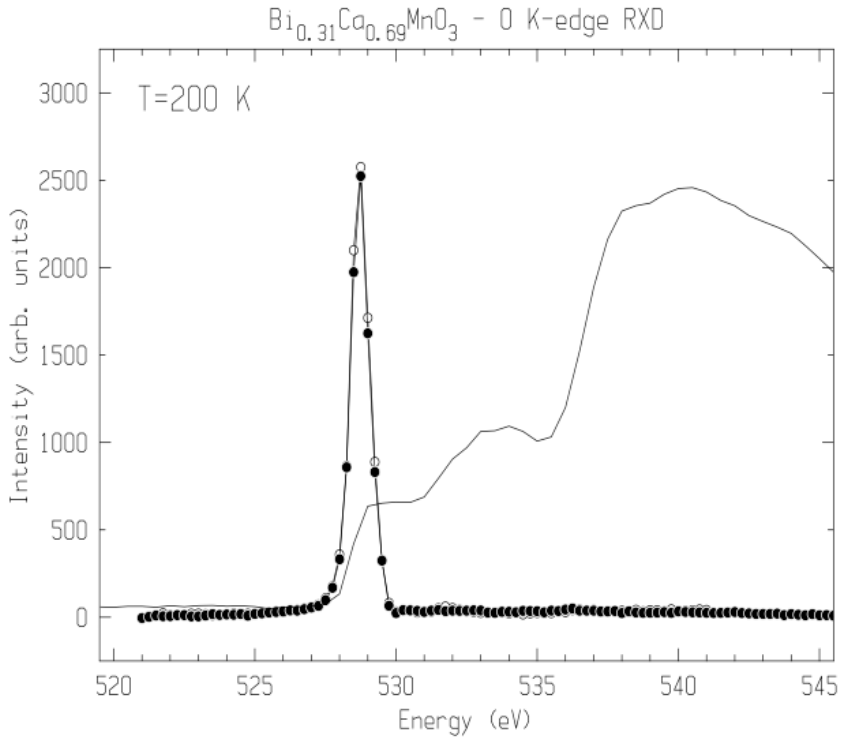
$Bi_{0.31}Ca_{0.69}MnO_3$ (~ 2 holes per 3 Mn sites)

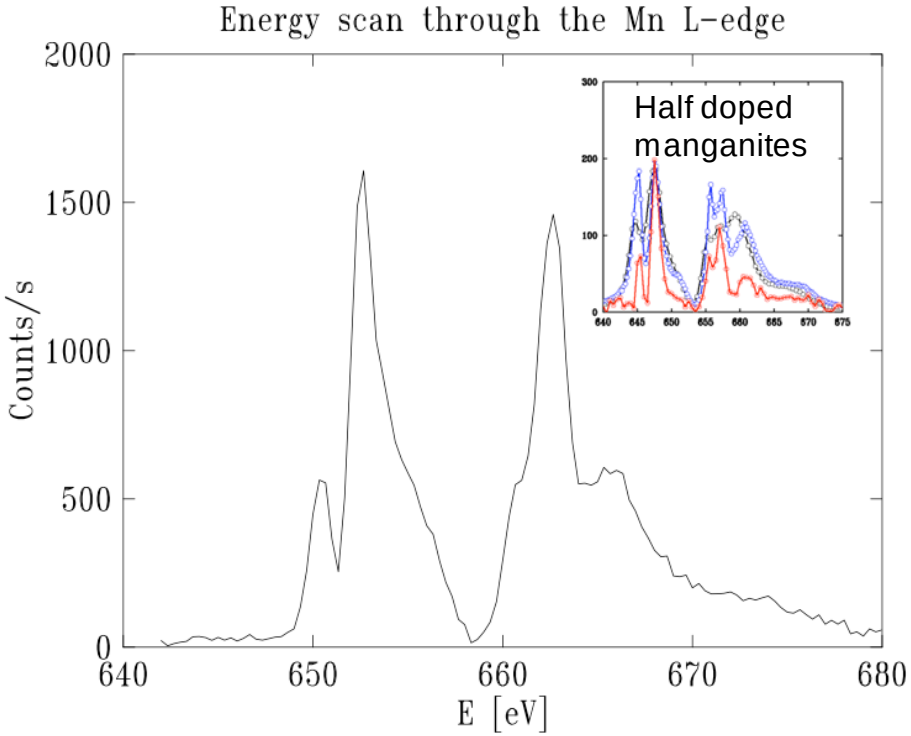


Q_{OO} = (0, 0.31, 0)

S. Grenier *et al*. PRB 75, 085101 (2007)
Confirms ‘Wigner crystal’ mode with
K-edge resonant diffraction

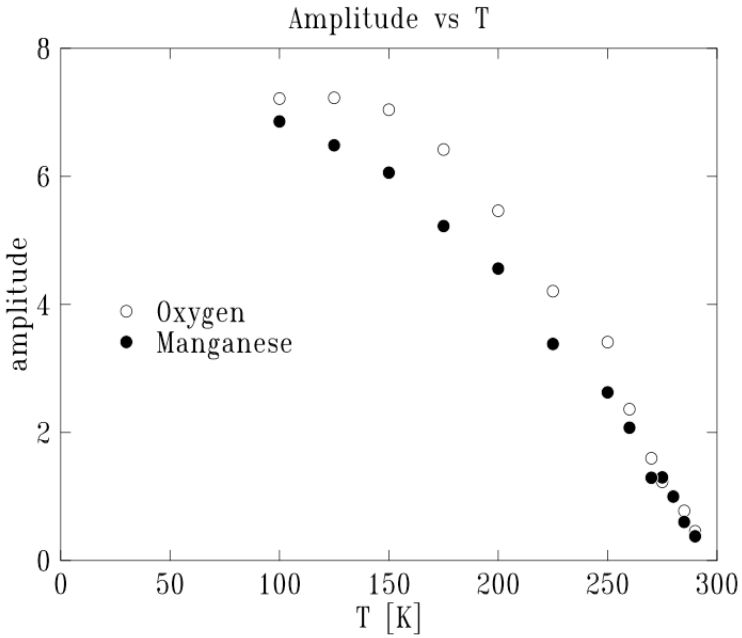
Orbital order diffraction peak in $Bi_{0.31}Ca_{0.69}MnO_3$ at the O K-edge and Mn L-edge

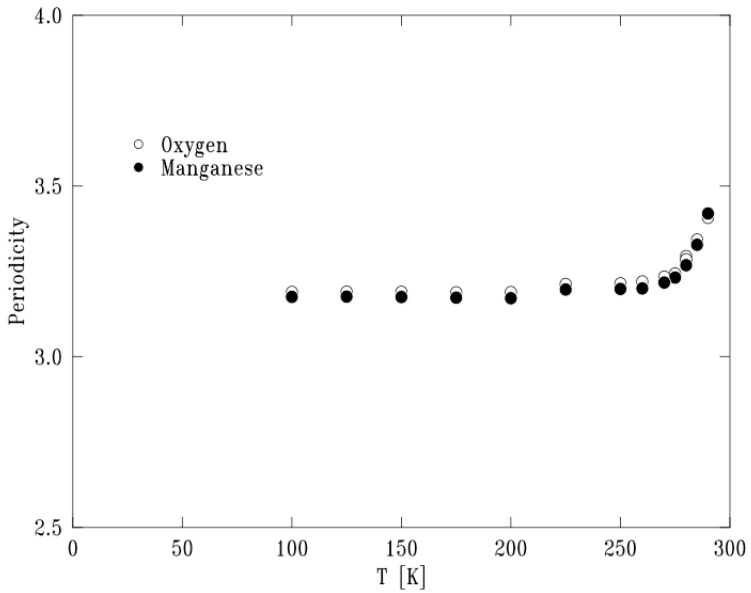


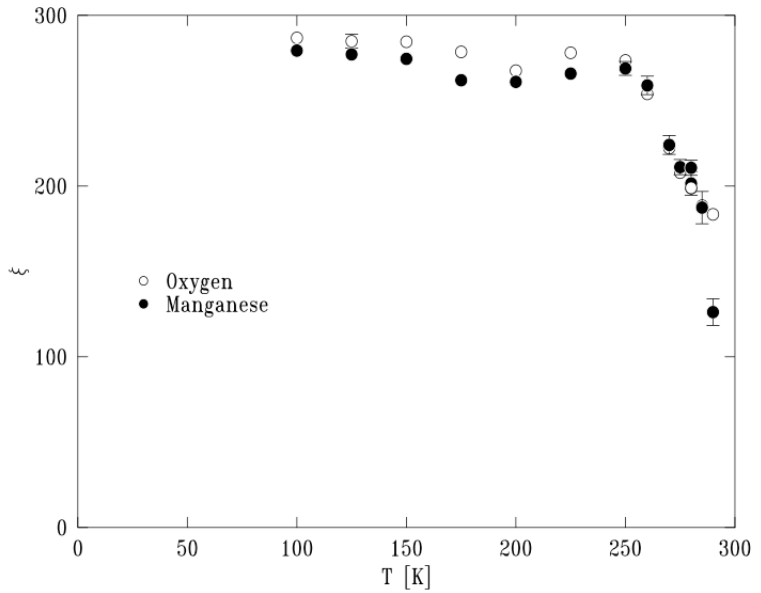


S. Grenier et al. arXiv:0707.4388v1

Temperature dependence at the Mn and O edges



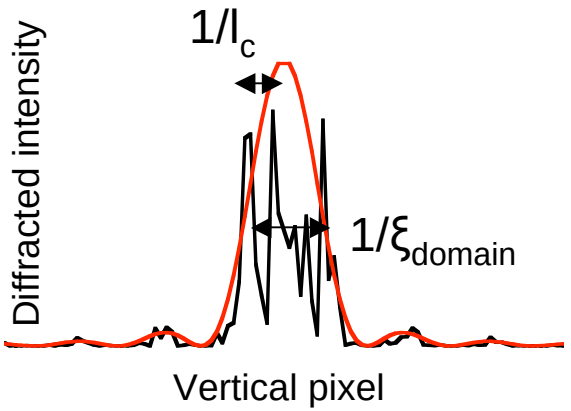


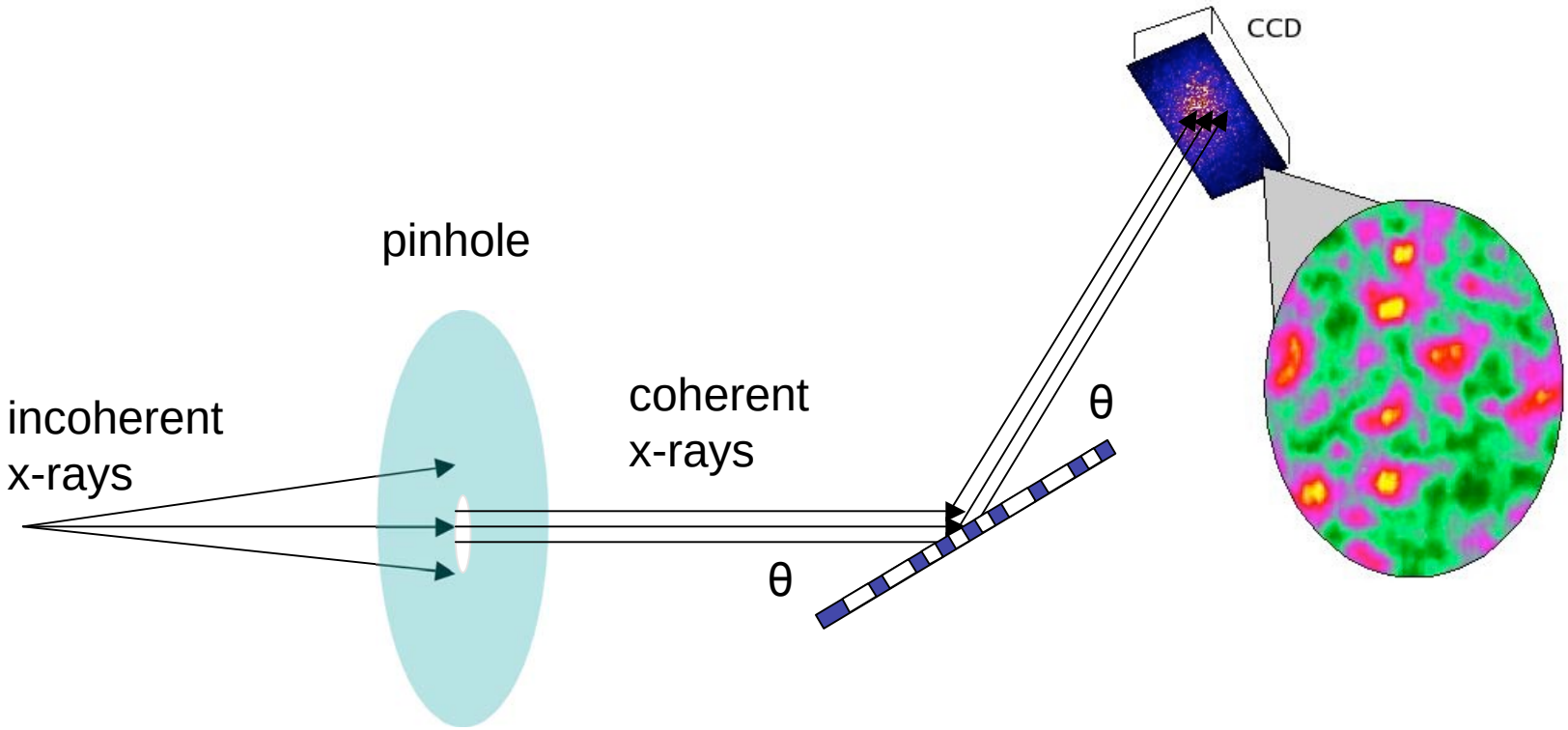


What sets the orbital domain size?

- Correlation length appears to be half that of the magnetic state
- But, it is still large, suggesting it is limited by a macroscopic ‘field’ (disorder, strain)
- 100-300 Å appears to be a general result (i.e. not about the sample)

Track OO domain dynamics with coherent x-rays





J. Turner, K. Chesnel, J. Thomas, M. Pfeifer, J. Hill, S. Kevan (ALS, BL 12)

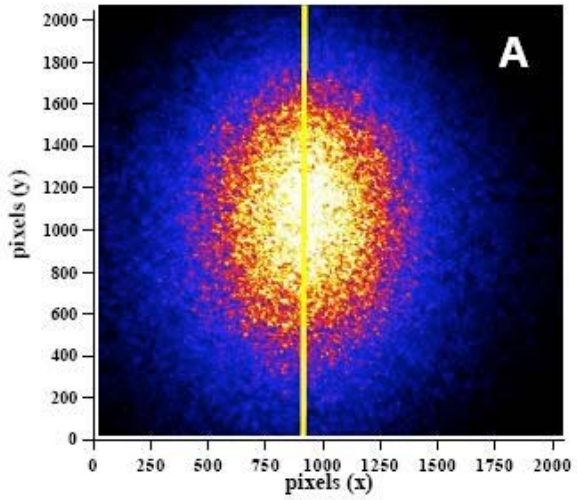
Orbitals are essentially static

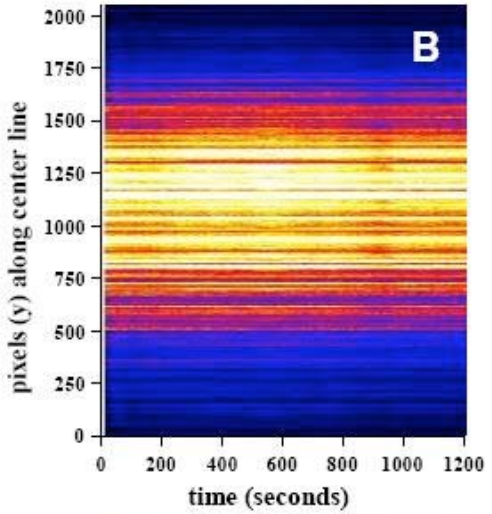
$Pr_{0.5}Ca_{0.5}MnO_3$

Speckle of the (0 1/2 0) OO diffraction peak

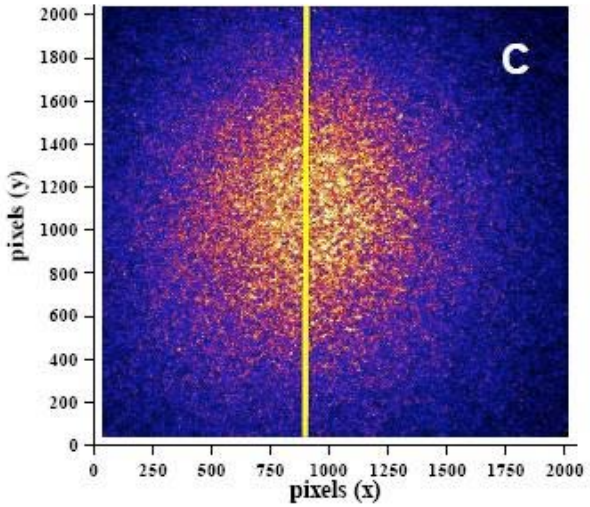
Time evolution of a vertical slice through the speckle

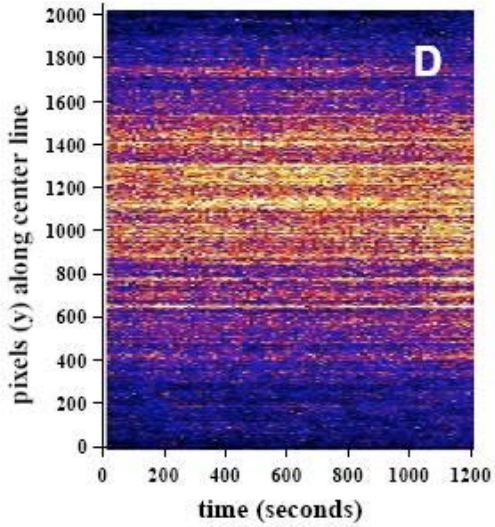
$T = T_{oo} - 17$ K





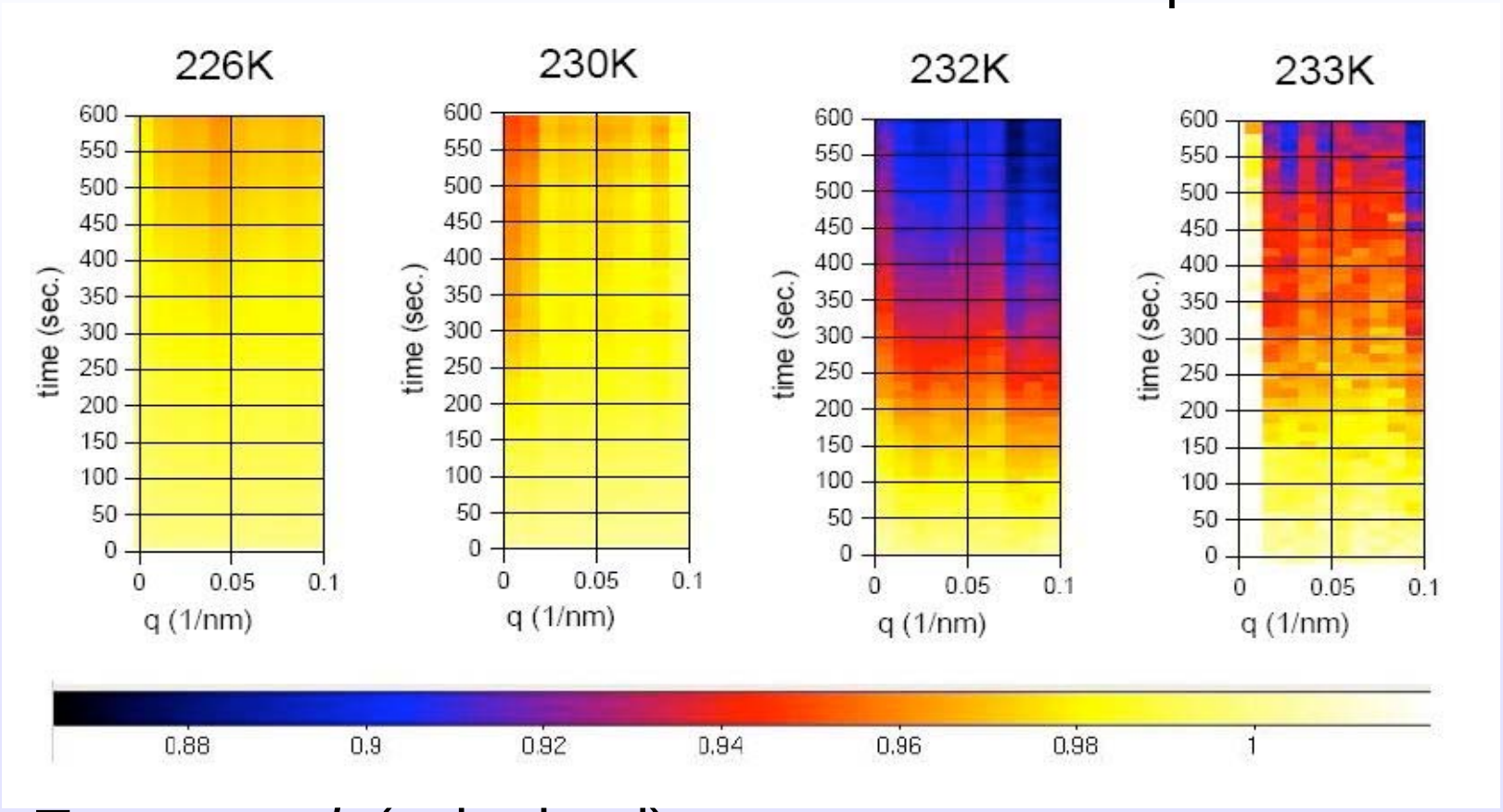
$T \sim T_{oo}$



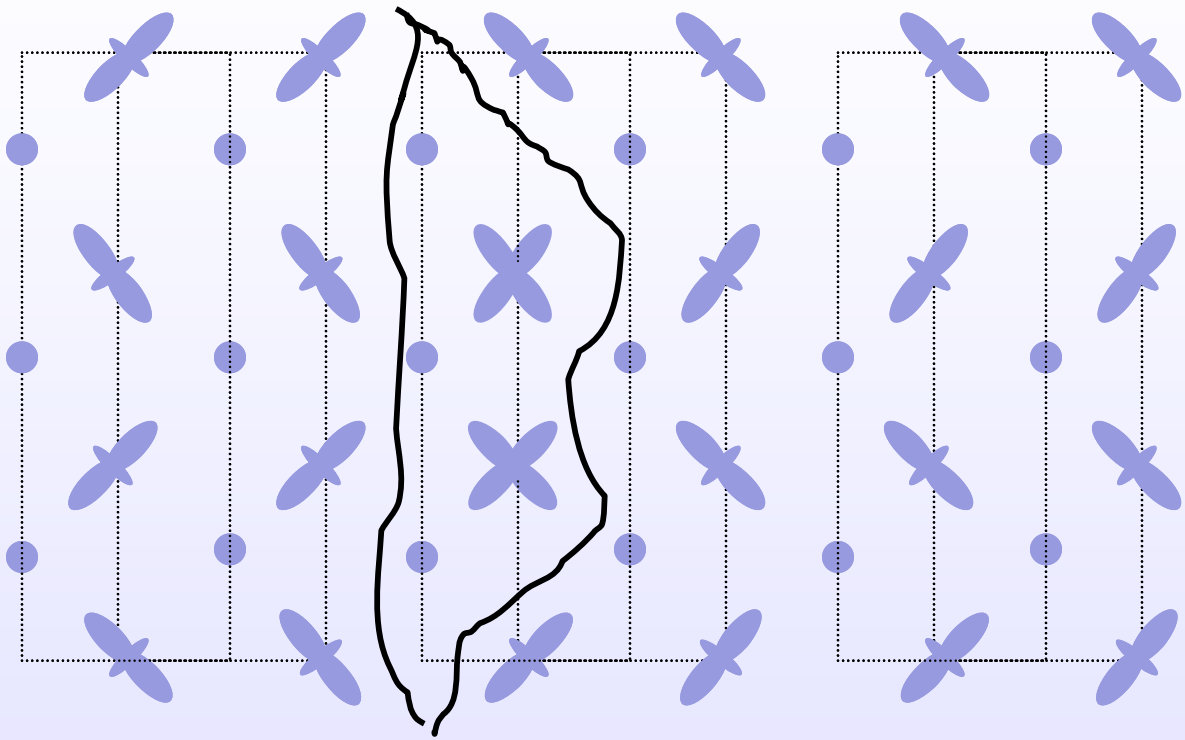


Coherent scattering:
But, there is a small fluctuating component

Cross-correlation coefficient maps



J. Turner *et al*. (submitted)



Summary of open problems

- General model to explain the resonant diffraction curves

- On the basis of the OO diffraction peaks at the O and Mn absorption edges, can the hole concentration on the oxygen sites/hybridization be calculated?

- What do the slow dynamics of the OO domains tell us about how domain walls form and what pins them?

Collaborators

John Hill *Brookhaven National Lab*
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Urs Staub *Swiss Light Source PSI*

V. Kiryukhin *Rutgers University*

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Steve Kevan *The University of Oregon*
Josh Turner *The University of Oregon*
Mark Pfeifer *La Trobe University, Australia*

Peter Abbamonte *University of Illinois, Urbana-Champaign*
Andrivo Rusydi *University of Hamburg*
Serban Smadici *UIUC/BNL*

Y. Tokura *University of Tokyo, Japan*
Y. Tomioka *AIST, Japan*

George Sawatzky *University of British Columbia*
Michel van Veendendaal *Argonne National Lab*