Ultrafast Studies of Strong Correlated Electron Systems

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Outline

1. Strongly Correlated Electron Systems
   - What are they?
   - Why are they important?
2. Time-resolved, ultrafast studies
   - Why do pump-probe expts?
   - Why use the LCLS?
3. The metal-insulator transition
   - Manganites
4. The superconducting transition
   - Cuprates
5. Quiz

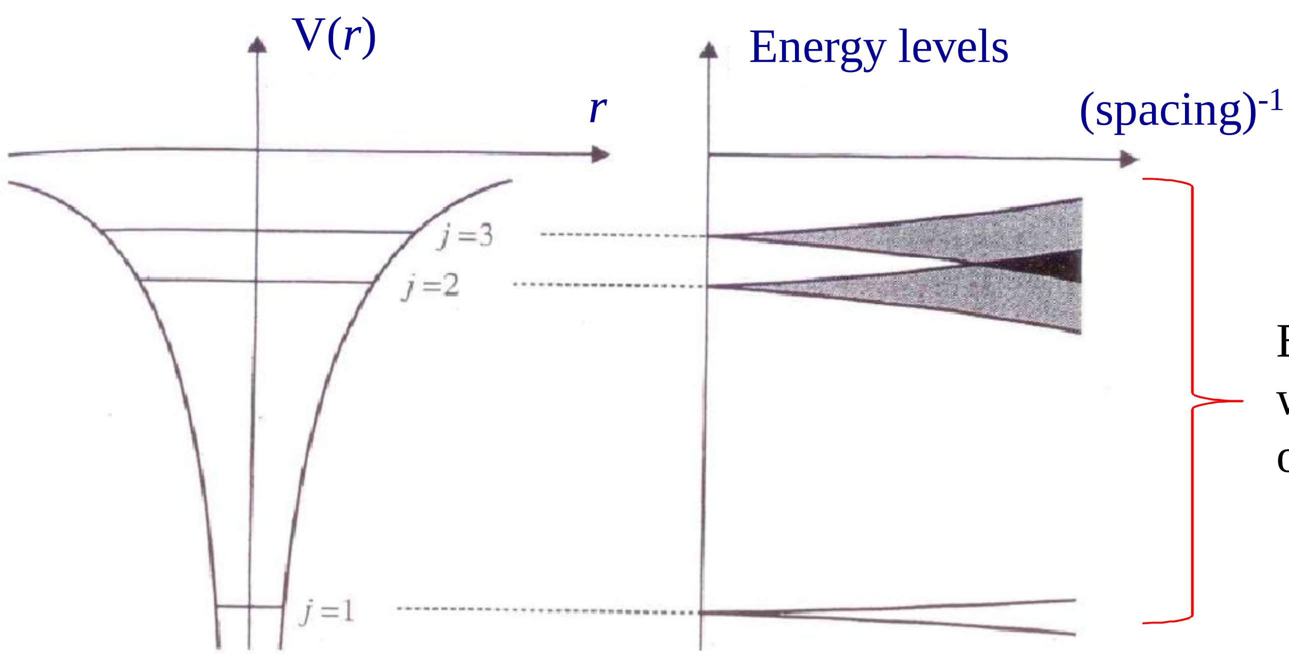
Introduction

Strongly Correlated Electron Systems

Conventional Solids

Start at the beginning: A solid is a collection of atoms bonded together. What happens to their electronic energy levels?

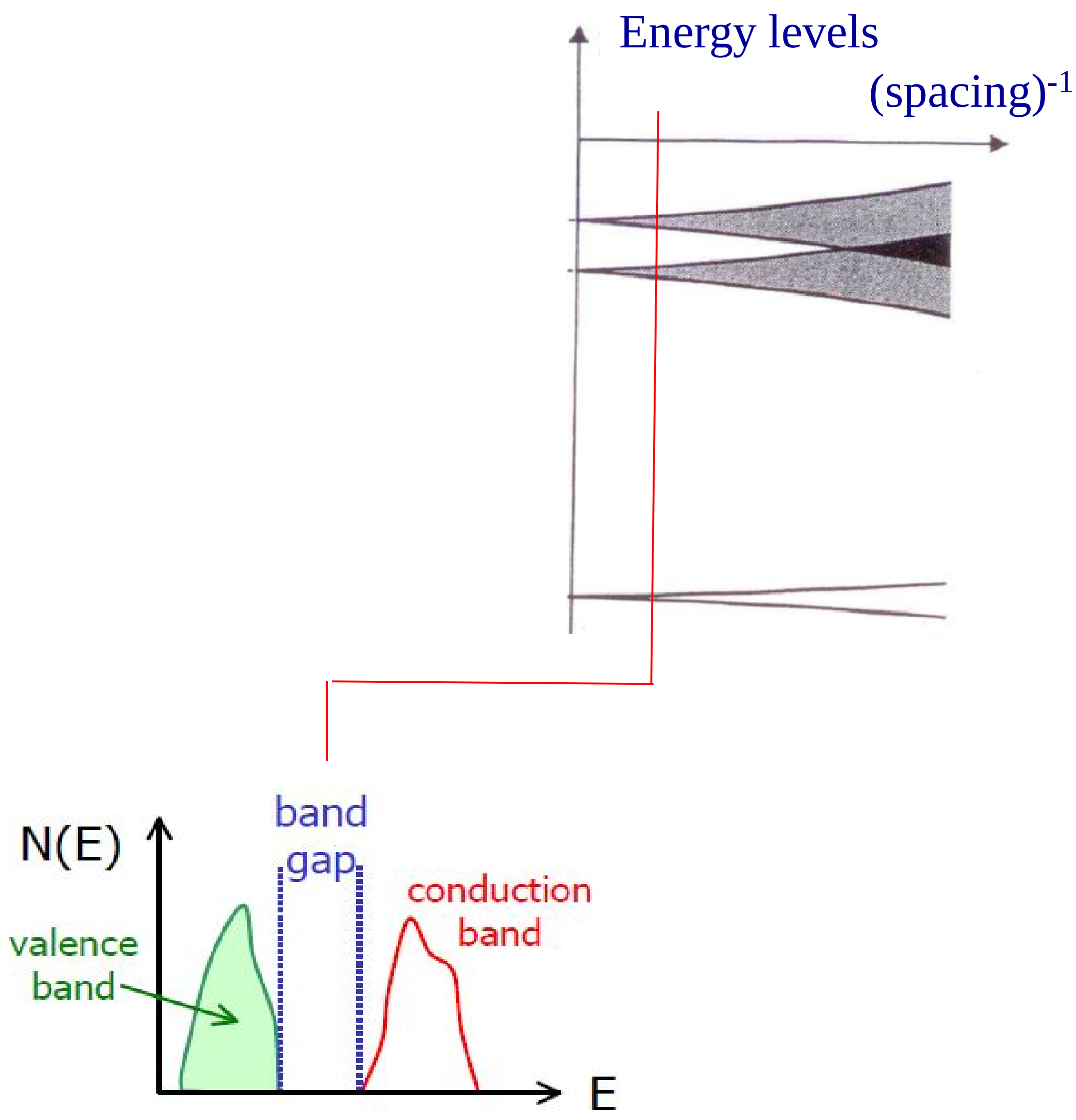
Individual Atoms → **Solid**



Bands, each with N values of *k*

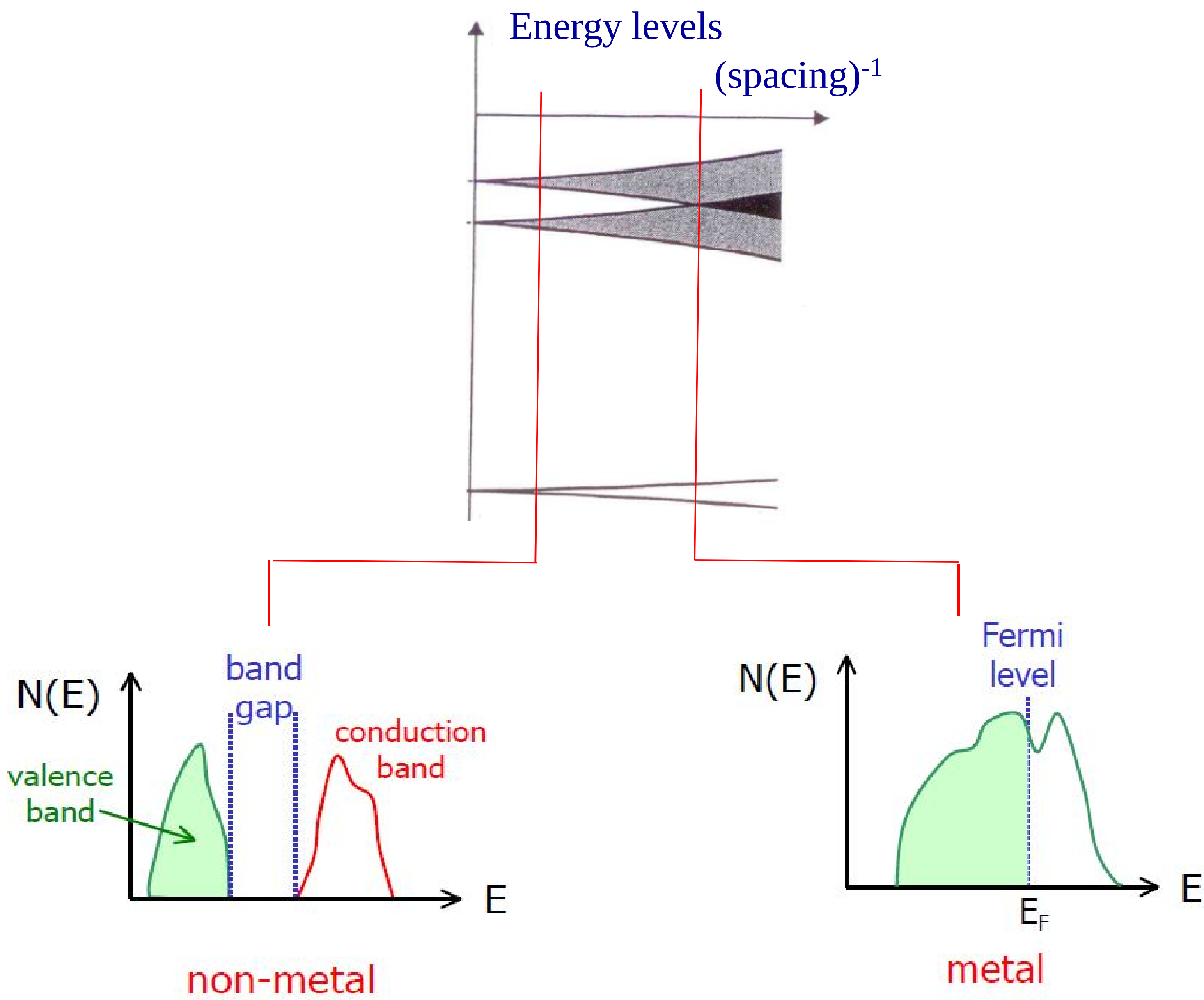
N atoms, with *j* discrete energy levels

Conventional Solids



non-metal

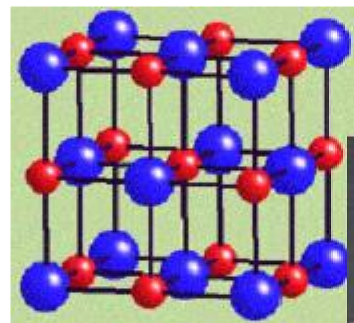
Conventional Solids



Conventional Solids

The electronic properties are determined by the crystal structure and the elements involved (electron count and orbitals). Materials for which such a single electron approach works include:

- Molecular
- Ionic
- Covalent
- Metallic



From M.S. Golden lecture notes www.science.uva.nl

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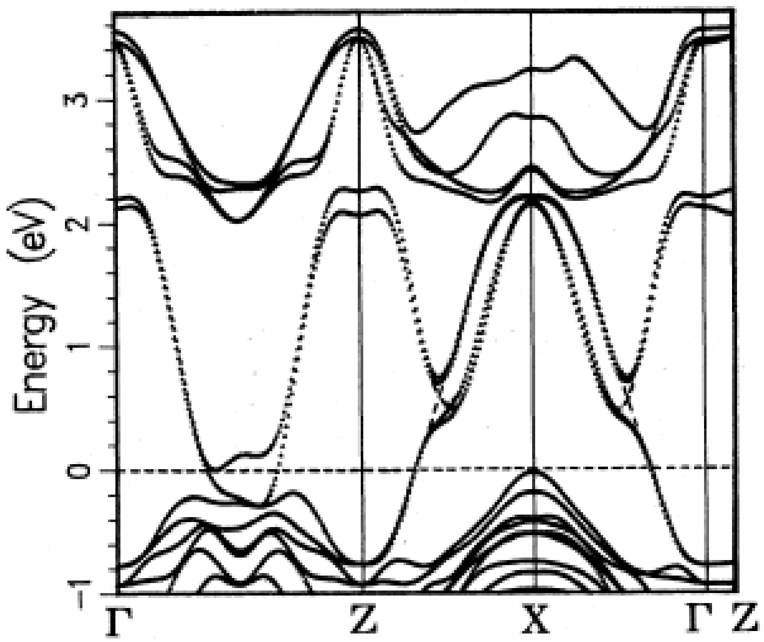
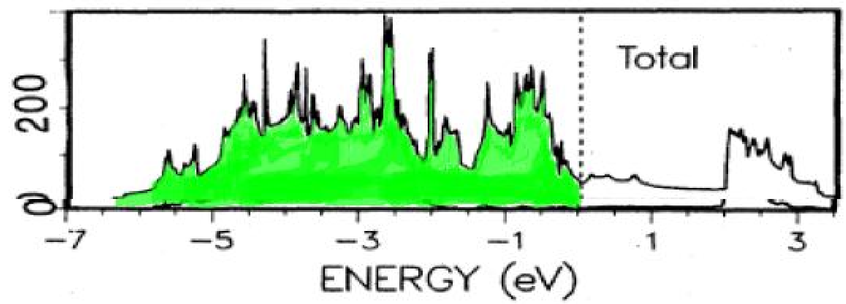
Strongly Correlated Solids

However, there is a class of systems for which this approach fails badly:

$Bi_2Sr_2CaCu_2O_8$



Krakauer and Pickett (1988)



Standard 1-electron bandstructure predicts a metal, but in fact it is an insulator with a several eV gap

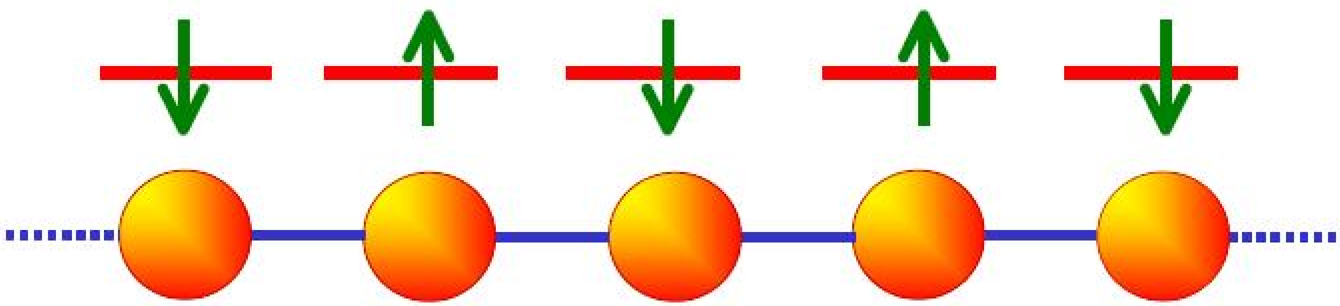
As we shall see, the reason for this is electron correlations

Strongly Correlated Solids

In the conventional picture we assume each electron acts independently of all the others. This fails when the bands are narrow and the electrons spend more time near the nucleus. Coulomb repulsion between them then becomes more significant and correlations cannot be ignored.

One moves away from a wave-like (k-space) picture of them and into a particle-like (real-space) picture.

Consider an array of atoms with 1 electron per site (Hubbard model):



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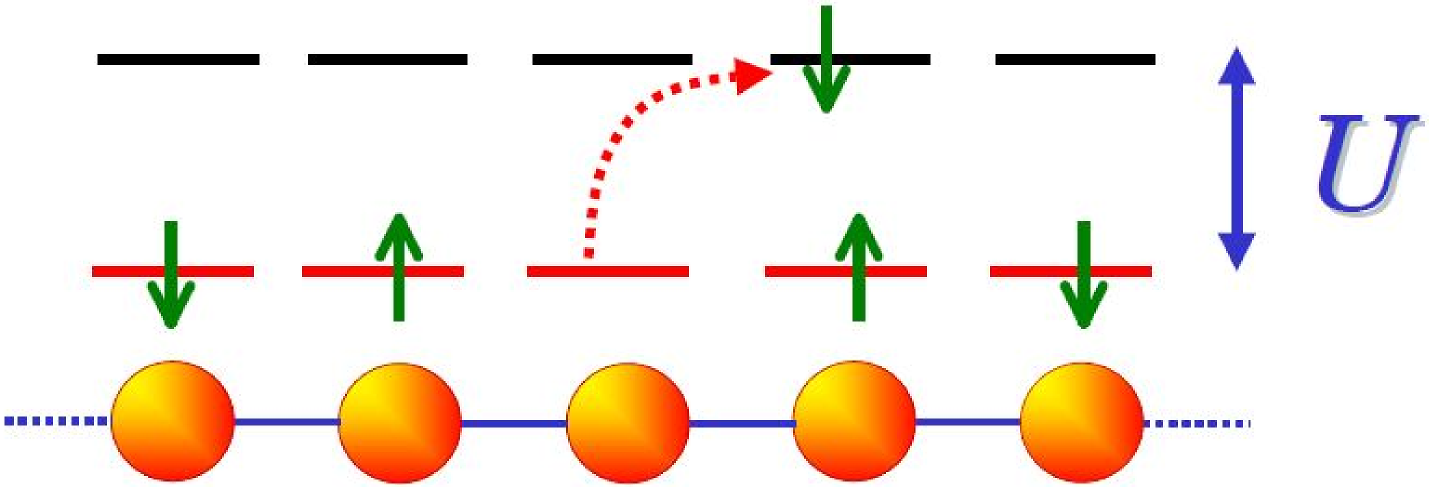
Strongly Correlated Solids



U is the energy required to move one electron from one site and place it on another:

$$\boxed{\text{U=Ionization Energy – Addition energy}}$$

Eg. If the atoms in the chain were hydrogen, then:

$$U = I - A = 13.6\ \text{eV} - 0.8\ \text{eV} = 12.8\ \text{eV}$$

This Coulomb energy wants to localize the electrons

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Strongly Correlated Solids

This is often modeled by the so-called single band "Hubbard" model:

$$H = -t \sum_{<ij>,\sigma} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

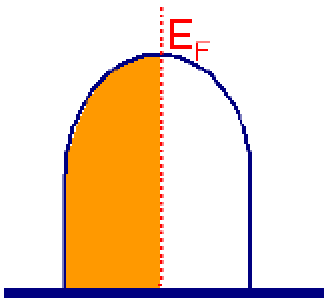
Transfer integral, t
wants to delocalize
electrons

"Hubbard" U,
wants to localize
electrons

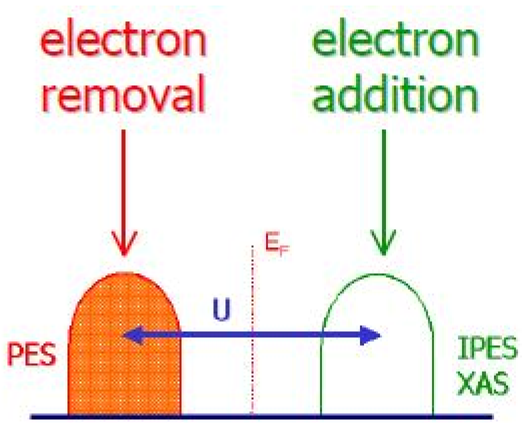
Whether a system is strongly correlated or not depends on the size of U compared to the bandwidth, W (=4t in two dimensions)…

Strongly Correlated Solids

U << W



U >W



If U is big enough (compared to the bandwidth), then a gap is opened up that is seen in spectroscopy and transport measurements.

Such effects are important when you have partially filled, narrow bands.

This is the case for transition metal elements because 3*d* orbitals are orthogonal to all n=1,2 orbitals (because of angular momentum) and therefore can be close into the nucleus and are more localized than *s* and *p* orbitals of the similar energy.

3d elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu

Examples:

Cuprates, manganites, nickelates, vanadates…

From M.S. Golden lecture notes www.science.uva.nl

Strongly Correlated Solids

Frequently in strongly correlated systems many of the energy scales are of similar size:

Hubbard interaction	U ~ 1-4 eV
Hopping integral	t ~ 0.5 eV
Magnetic Exchange	J ~ 0.15 eV
Charge-transfer energy	D ~ 2 eV
Jahn-Teller splitting	D_{JT} ~ 1 eV

The ground state is obtained by minimizing the total energy. Ground states include:

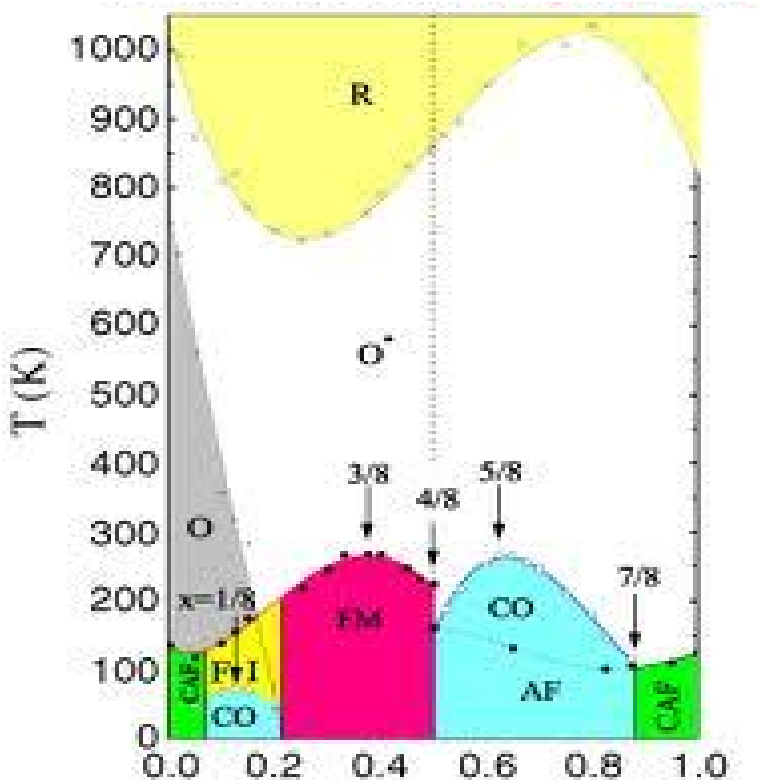
> Ferromagnetism, antiferromagnetism, metals, insulators, semiconductors, ferroelectrics, superconductors…

The fine balance of all the energy scales means that small changes can lead to switching ground states and large changes in the properties. These materials then exhibit extreme sensitivity to perturbations including:

> T, P, B-fields, E-fields, doping, defects…. and photons!

Manganites

$La_{1-x}Ca_xMnO_3$



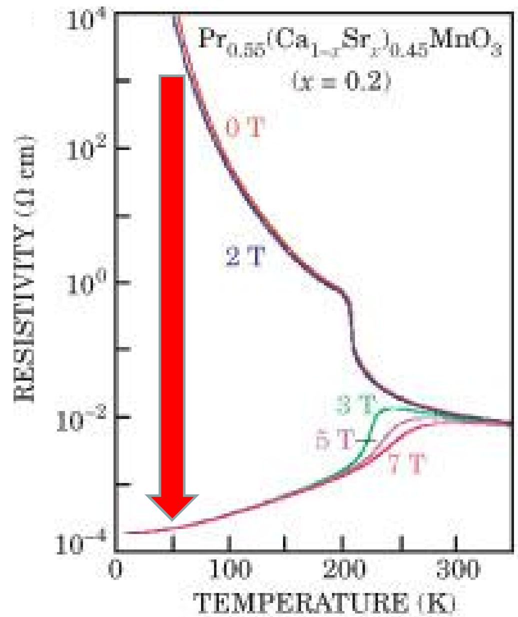
No. of holes per Mn

Mn^{3+} Mn^{4+}

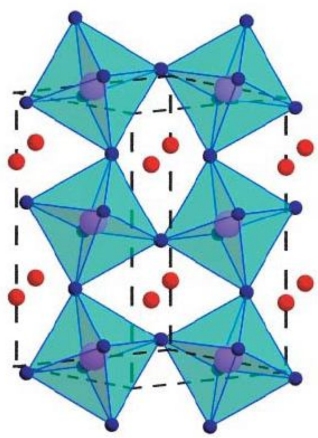
La^{3+} Ca^{3+}

From S.W. Cheong

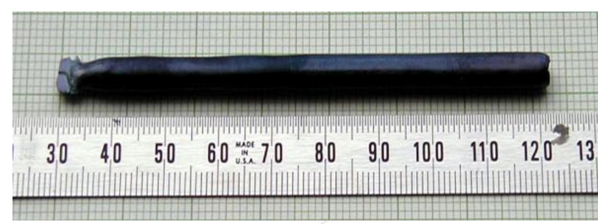
Metal-insulator transition



8 orders of magnitude decrease in resistivity in a magnetic field "colossal magnetoresistance" (CMR)



Perovskite crystal structure



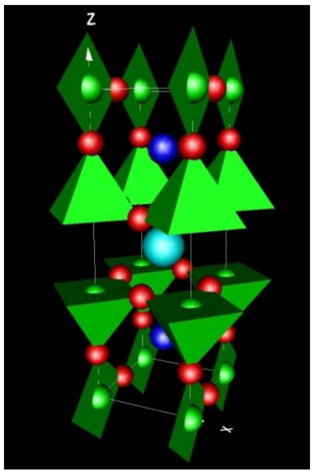
Cuprates

Discovered in 1986 (Bednorz and Muller)

Examples:

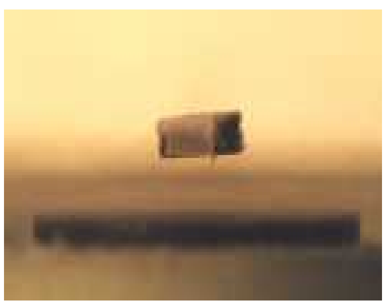
$La_{2-x}(Ba,Sr)_xCuO_4$ "214"

$YBa_2Cu_3O_{7-d}$ "123"

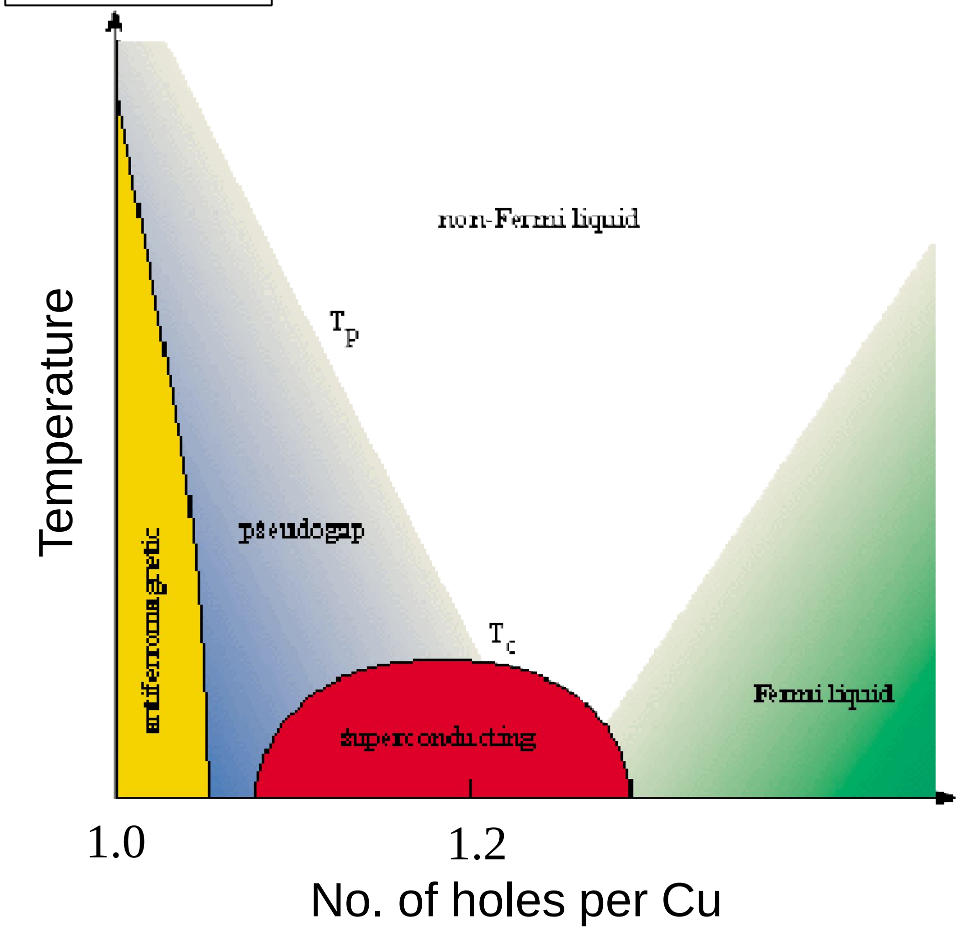


$YBa_2Cu_3O_7$

Highest Tc =130 K = -143 ^oC



Mott Insulator



From Batlogg and Varma, Physics World (2000)

Time-resolved Studies

Strongly Correlated Electron Systems

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Motivation

- New metastable states
- Photo-control of condensed matter
- Understanding the competing interactions through their different response in the time domain

- Time resolution required: sub-ps

Why LCLS?

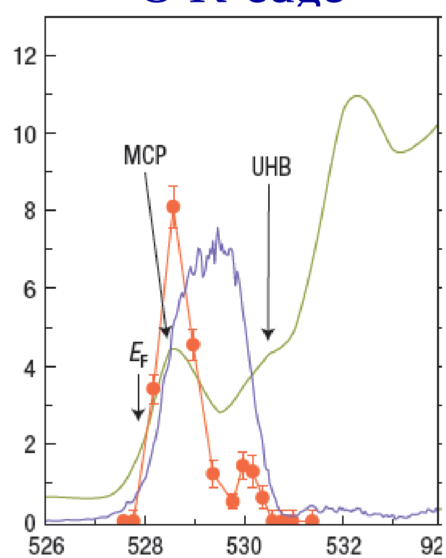
Soft Resonant Elastic X-ray Scattering with fs time resolution (see lecture by Maurits Haverkort.).

Reminder:

• By tuning the incident photon energy to absorption edges (K-edges, L-edges) the sensitivity to the relevant electrons (O 2*p*, TM 3*d*) is greatly enhanced.

• By choosing the scattering angle (Bragg condition) one picks out a particular wave-vector (order parameter); Spin, Orbital, Charge..

O K-edge

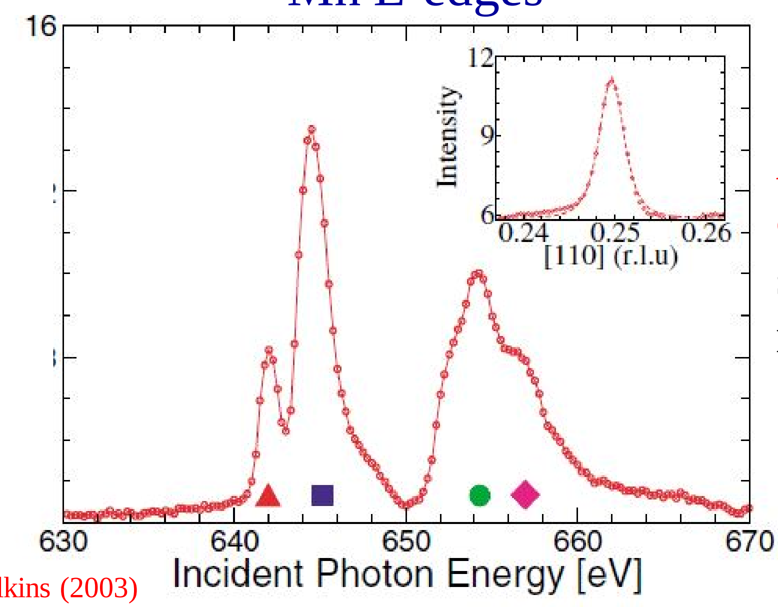


Abbamonte (2005)

Charge ordering of doped holes in a cuprate

1s $\leftrightarrow$ 2p

Mn L-edges



Wilkins (2003)

Antiferromagnetic ordering of Mn spins in a manganite

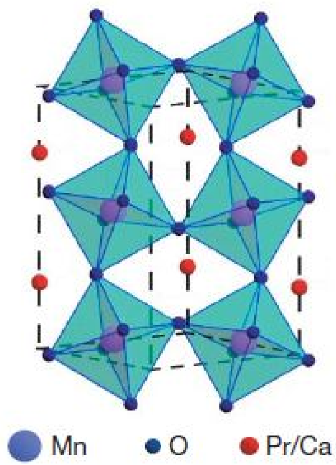
2p $\leftrightarrow$ 3d

Example 1: The Metal-Insulator Transition

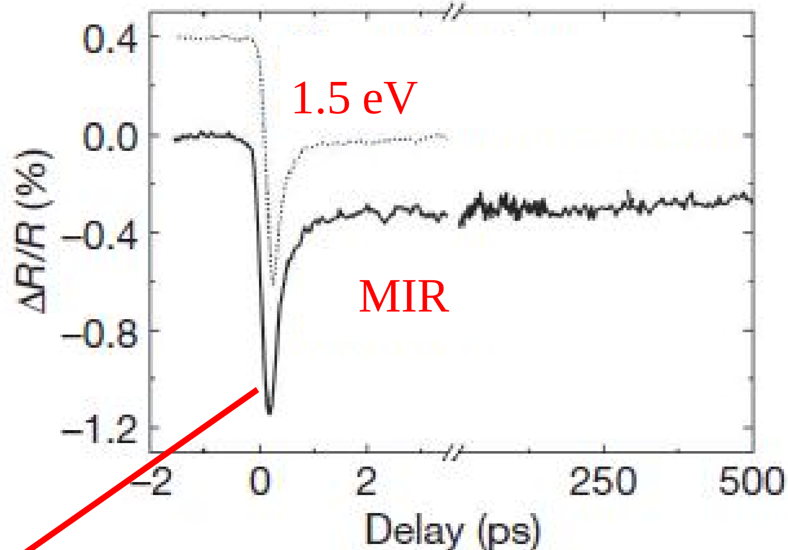
Manganites

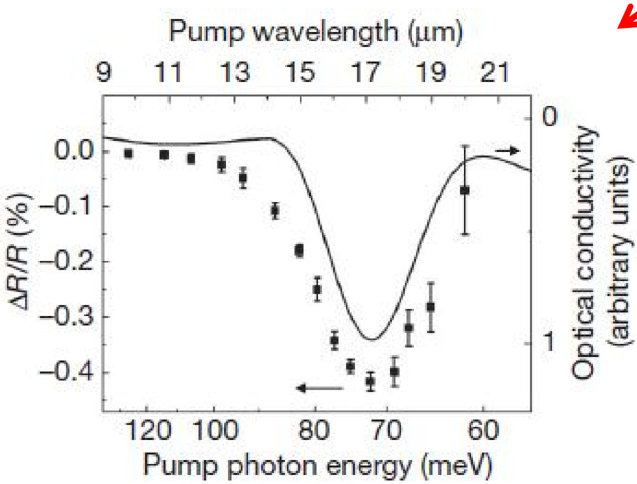
Photon Driven Metal-Insulator Transition

$Pr_{0.7}Ca_{0.3}MnO_3$

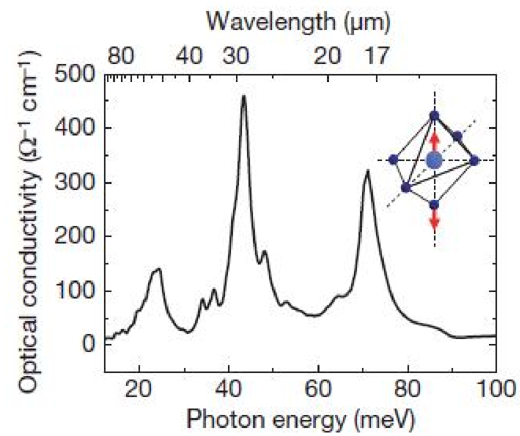


Big changes in reflectivity following photon pump:





MIR response is peaked at a Mn-O stretch phonon at 70 meV

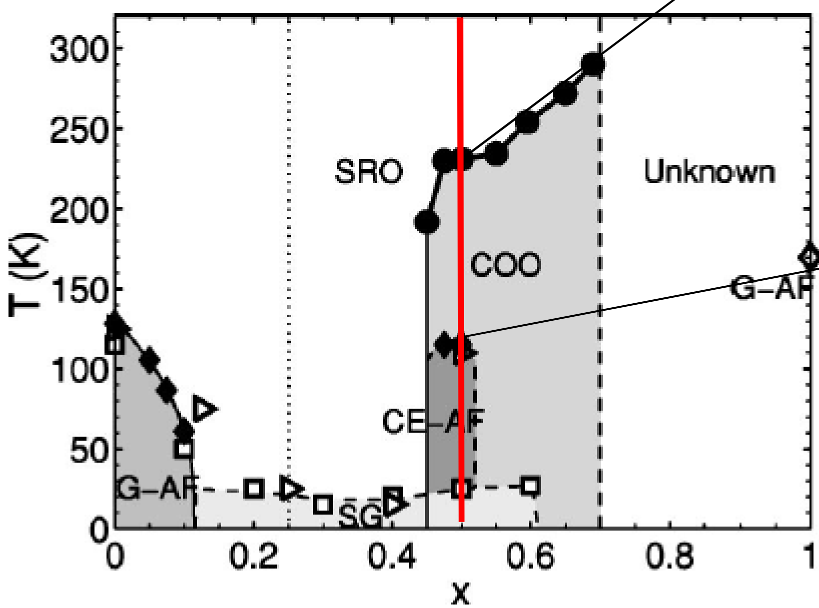


Rini *et al.* Nature **449** 72 (2007)

$La_{0.5}Sr_{1.5}MnO_4$

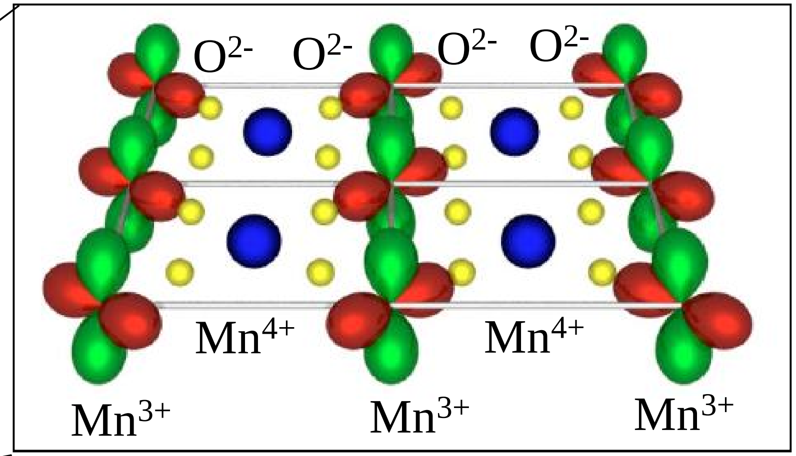
Phase Diagram

x=0.5



Larochelle *et al.* (2005)

$T_{OO/CO}$=220 K



Charge and orbital order

Three Order Parameters:

Q_{mag} = (0.25,0.25,0.5)
$Q_{orbital}$= (0.25,0.25,0)
Q_{charge}= (0.5,0.5,0)

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$La_{0.5}Sr_{1.5}MnO_4$

Phase Diagram

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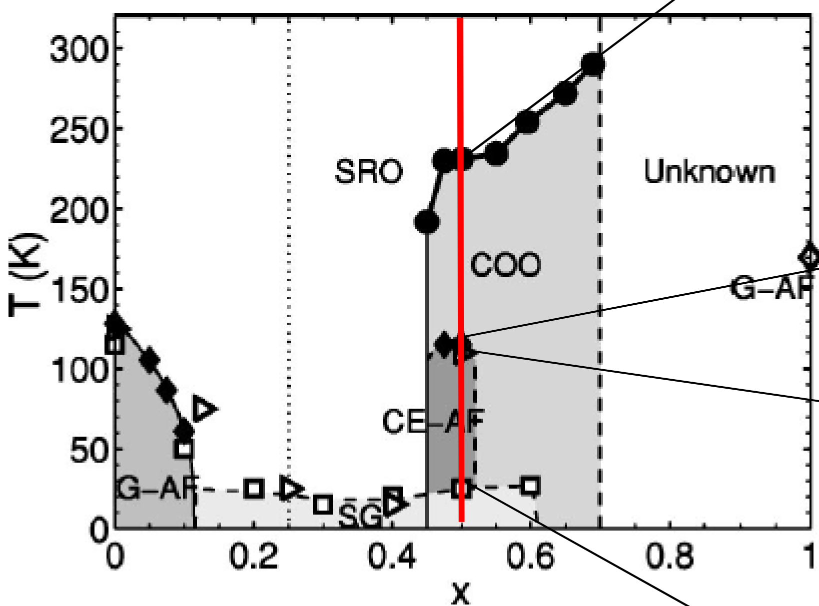

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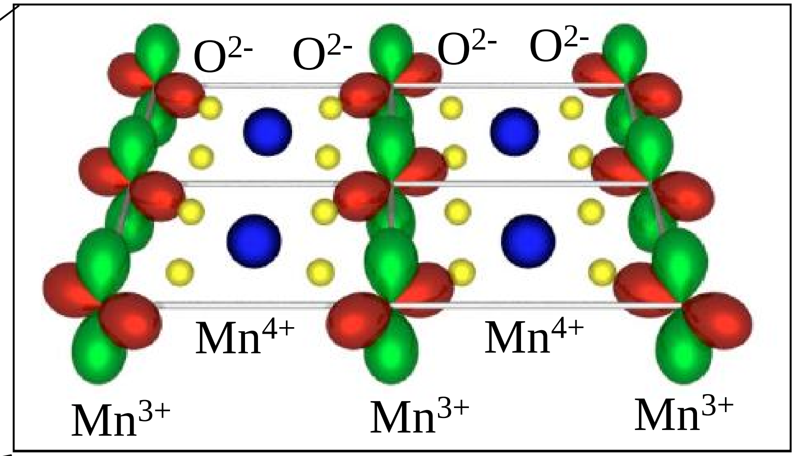
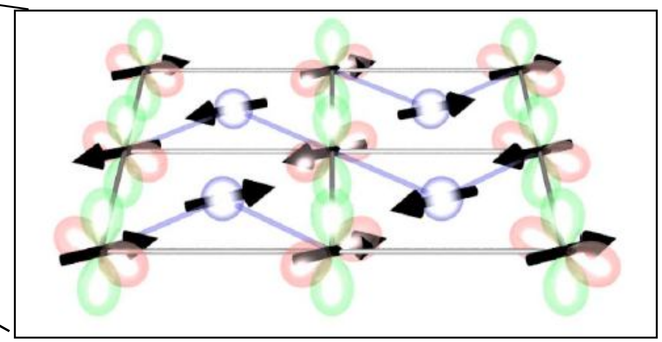


Charge and orbital order

T_N=110 K



Charge, orbital and spin order

Three Order Parameters:

Q_{mag} = (0.25,0.25,0.5)

$Q_{orbital}$= (0.25,0.25,0)

Q_{charge}= (0.5,0.5,0)

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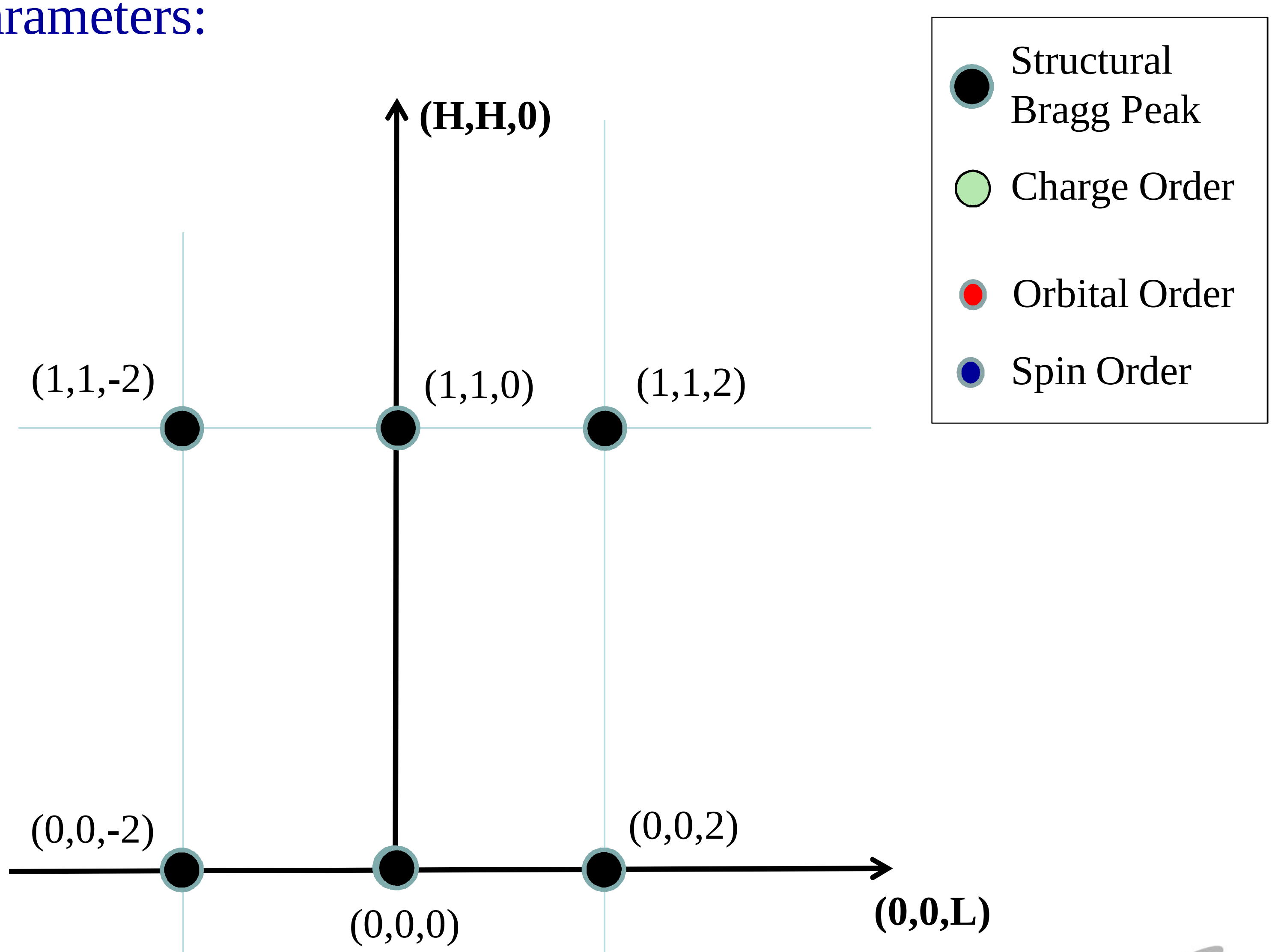
Reciprocal Space for $La_{0.5}Sr_{1.5}MnO_4$

Three Order Parameters:



Reciprocal Space for $La_{0.5}Sr_{1.5}MnO_4$

Three Order Parameters:

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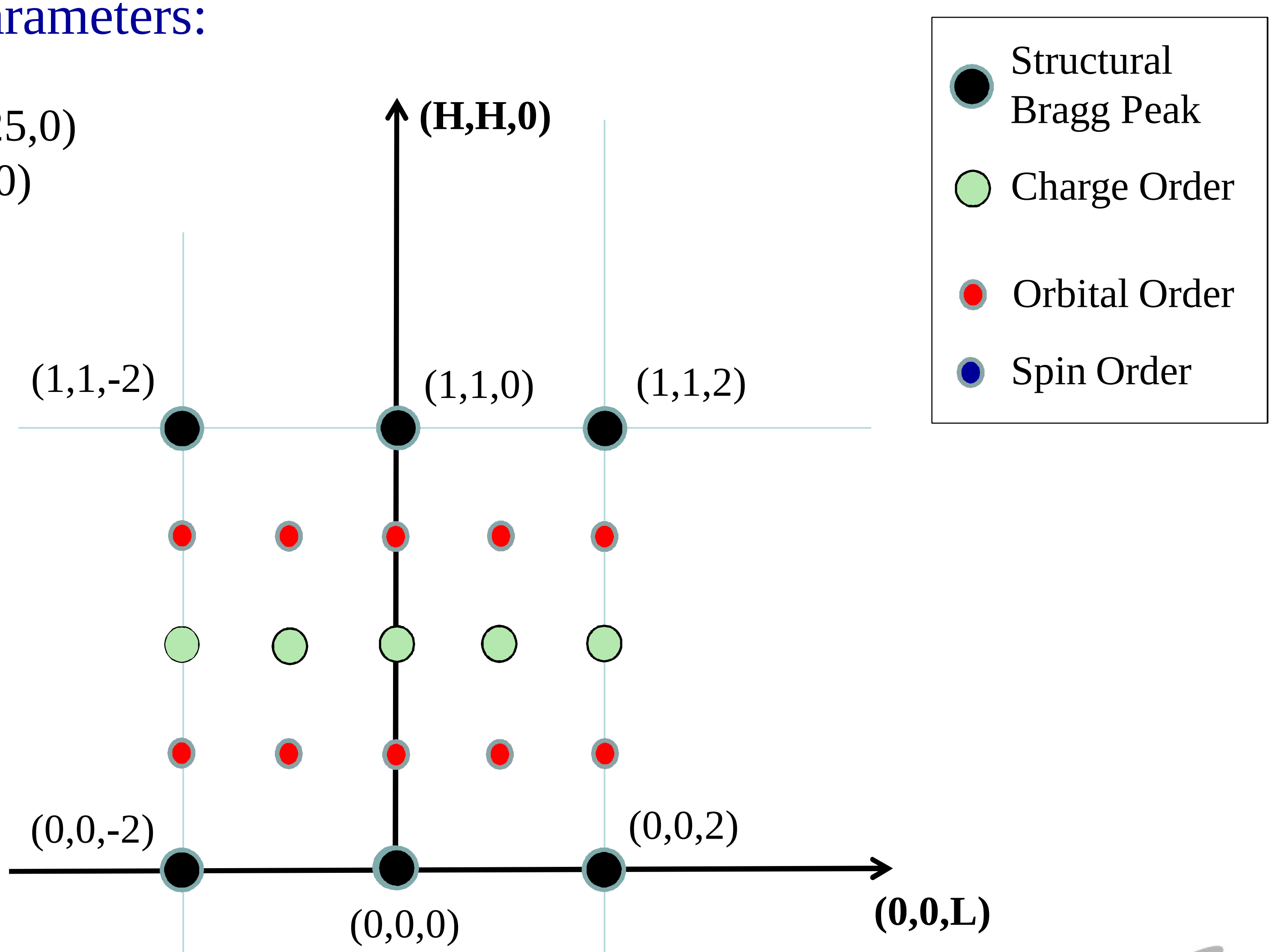
Q_{charge}= (0.5,0.5,0)



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Reciprocal Space for $La_{0.5}Sr_{1.5}MnO_4$

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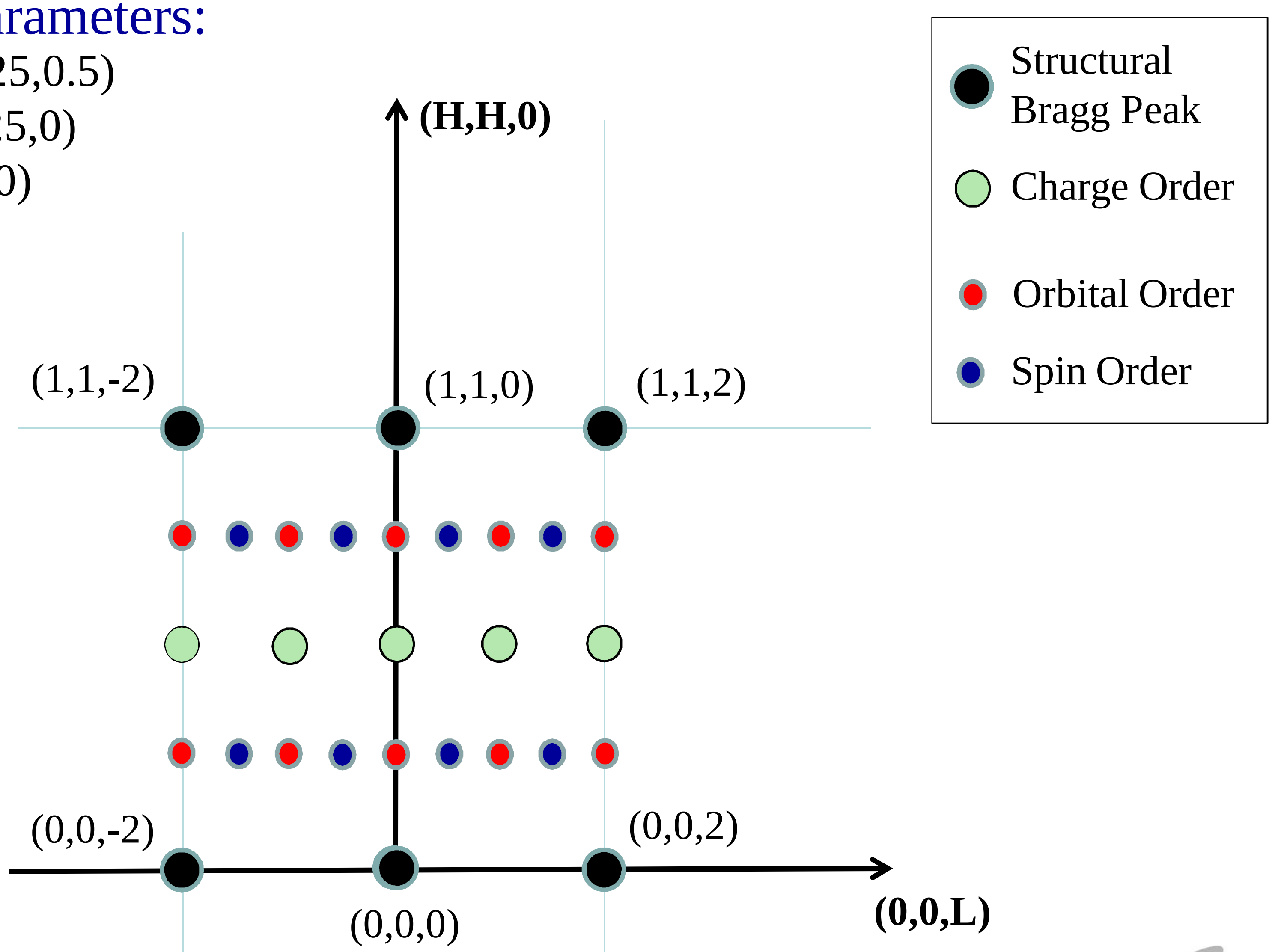

Reciprocal Space for $La_{0.5}Sr_{1.5}MnO_4$

Three Order Parameters:

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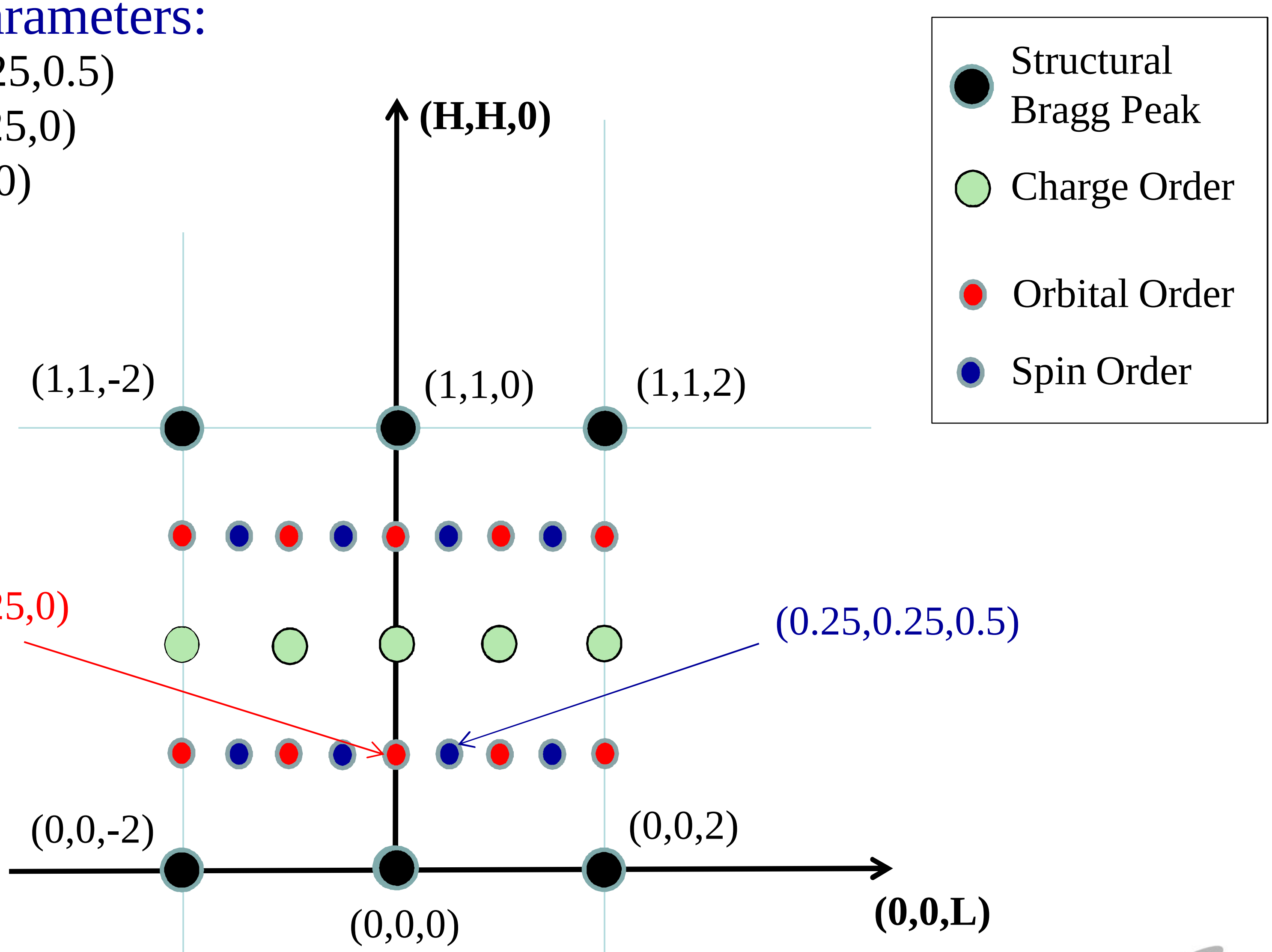

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Reciprocal Space for $La_{0.5}Sr_{1.5}MnO_4$

Three Order Parameters:

$Q_{mag} = (0.25,0.25,0.5)$

$Q_{orbital} = (0.25,0.25,0)$

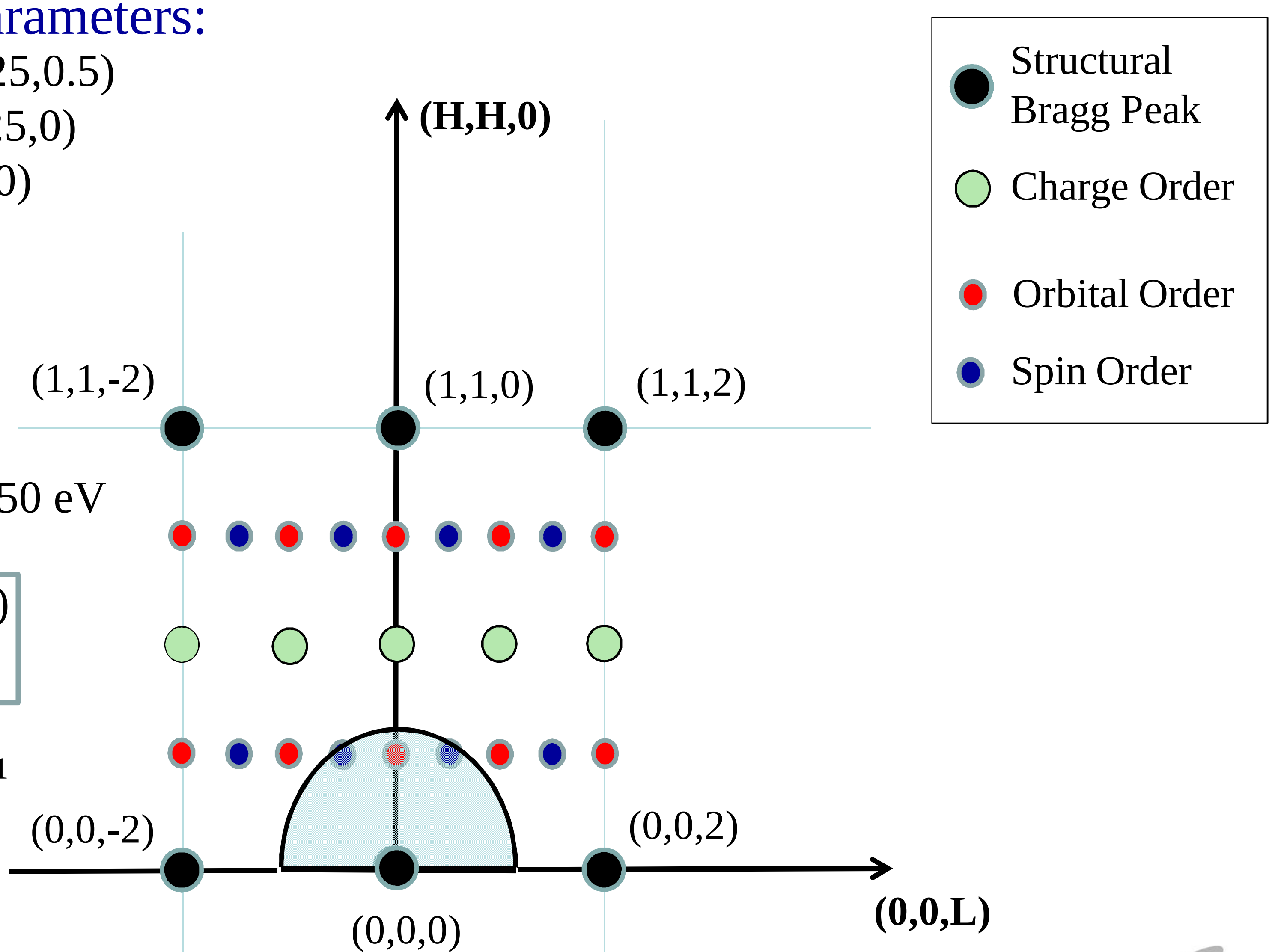
$Q_{charge} = (0.5,0.5,0)$

Mn L-edge E_i=650 eV

$Q = 2k \sin(2\theta/2)$

$2k = 4\pi/\lambda$

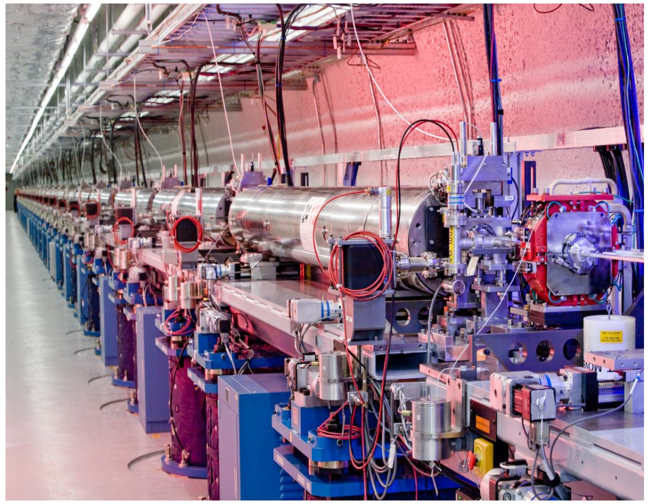
$Q_{max} = 2k = 0.6\ \text{Å}^{-1}$



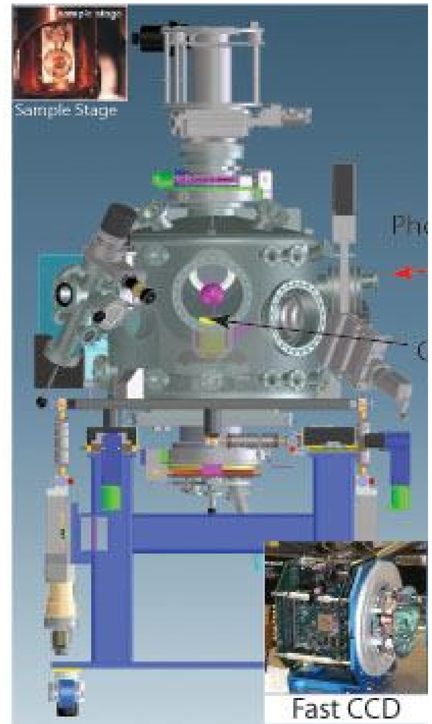
Linac Coherent Light Source (LCLS)

1km accelerator

100 m of undulator



Soft X-ray Chamber



D. Doering *et al.* RSI (2011)

P. Emma *et al.* Nature Photonics 4, 641 (2010)

Coherent radiation ~500 eV – ~25 keV.
Repetition rate 120 Hz
~ 10^{12} photons/pulse

We will use the very short pulse length, not the coherent properties of the beam:

X-ray pulse lengths as short as 10fs.
Temporal resolution ~200fs
(limited by laser-x-ray jitter)

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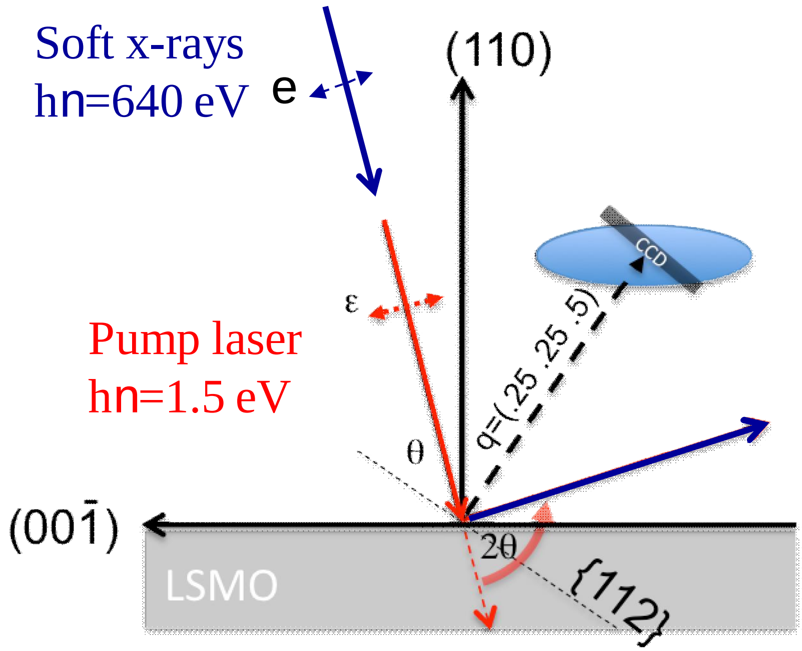
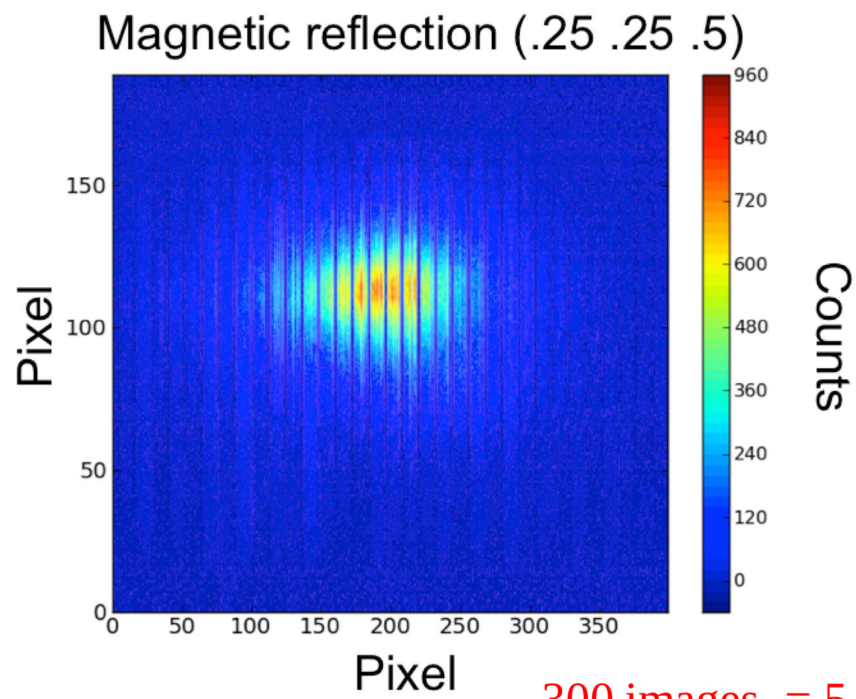
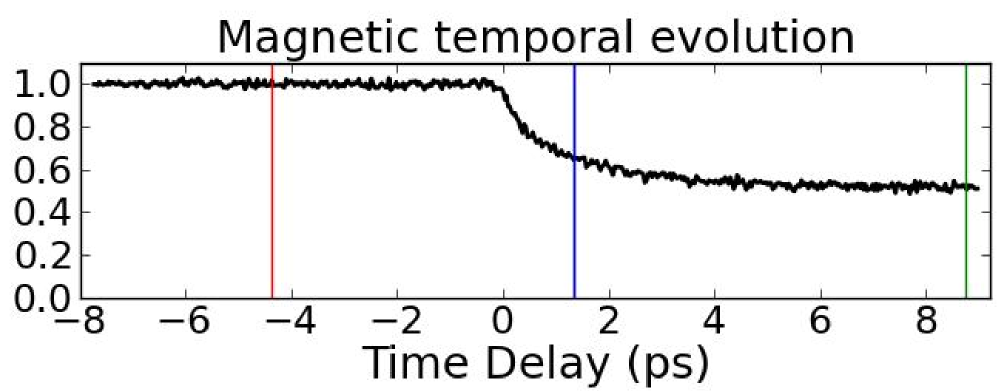
Spin Dynamics: Electronic Excitation



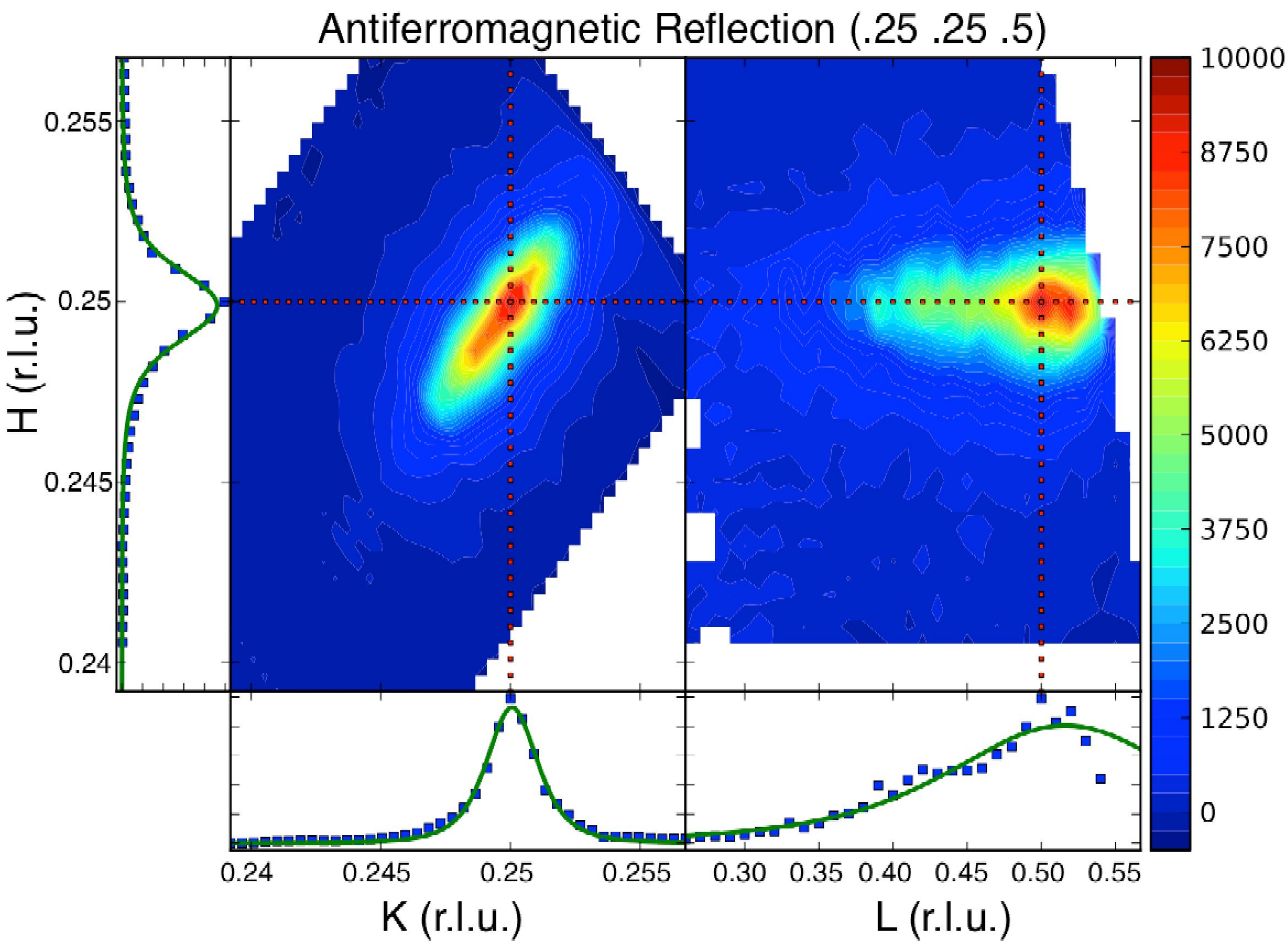


300 images = 5 s



R.I Tobey *et al.* (unpublished)

Three Dimensional Scattering Ellipsoid

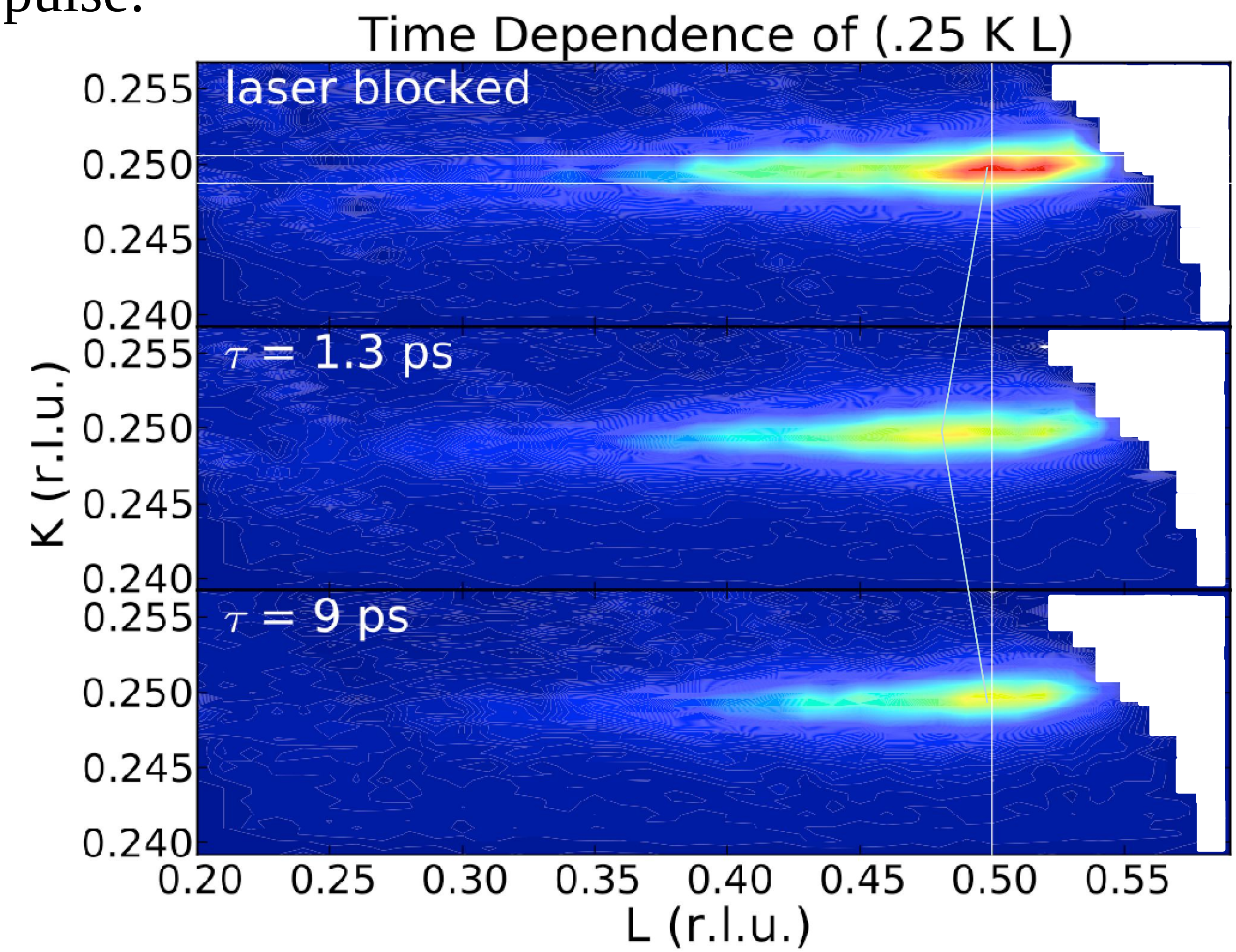


$\xi_a = \xi_b = 540$ Å
$\xi_c = 20$ Å

R.I Tobey *et al.* (unpublished)

Spin Correlations Following Laser Excitation

Measured the full scattering ellipse at two time delays following 1.5 eV pump pulse:



R.I Tobey *et al.* (unpublished)

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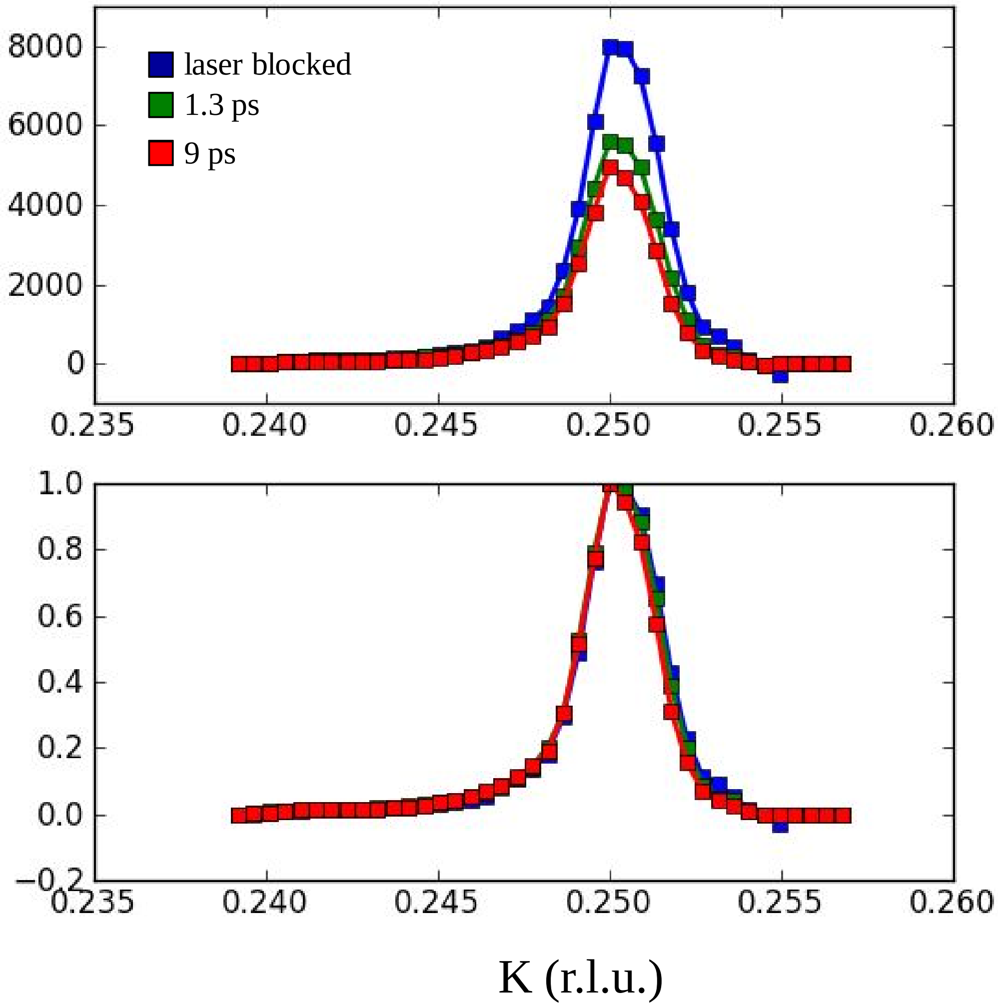
In-plane Correlations

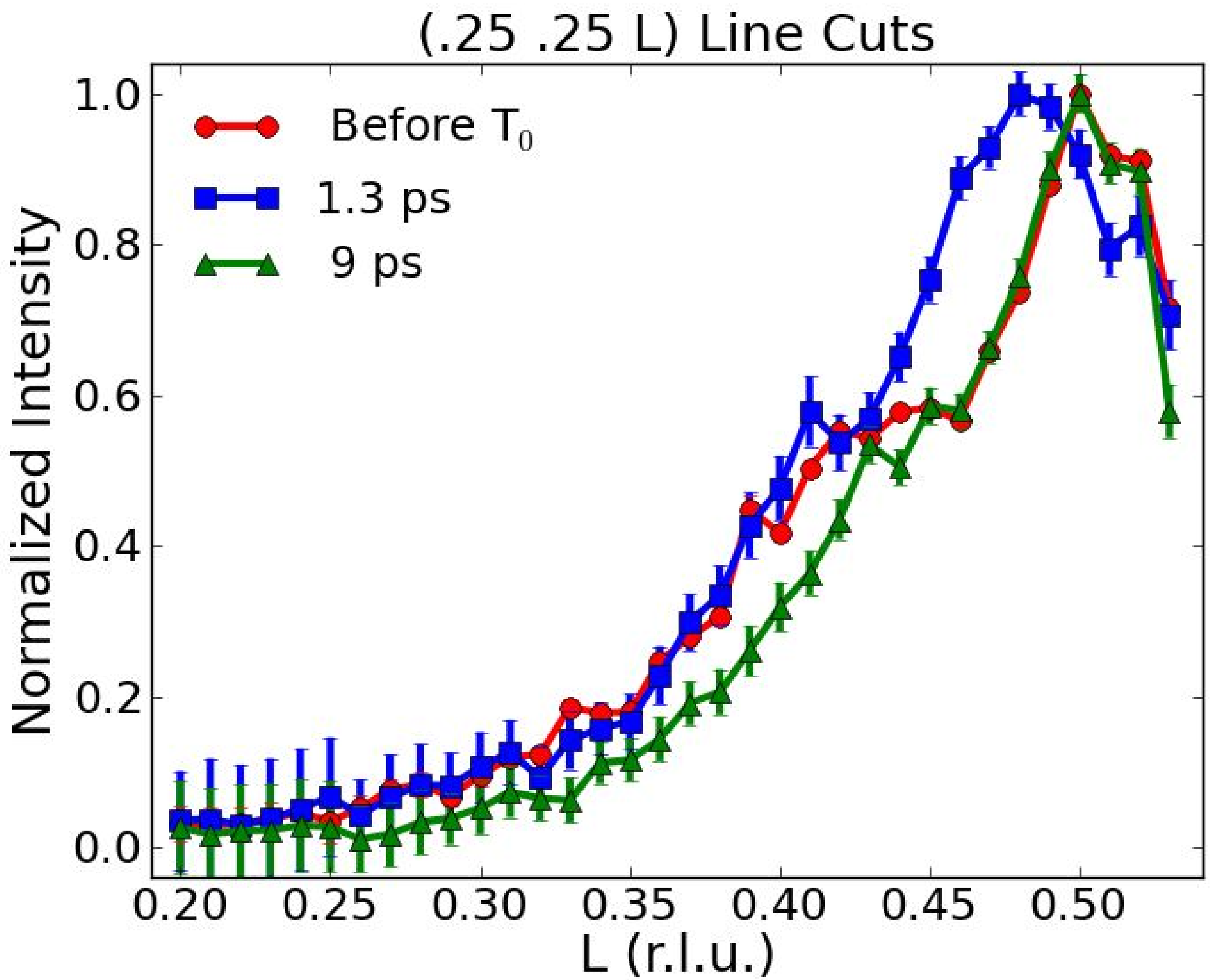


There is no measurable change in the in-plane lineshape.

In-plane correlations are unchanged during photo-melting process

R.I Tobey *et al.* (unpublished)

Out-of-plane Correlations



See small shift in peak position to smaller L at very short times, during the electronic melting process.

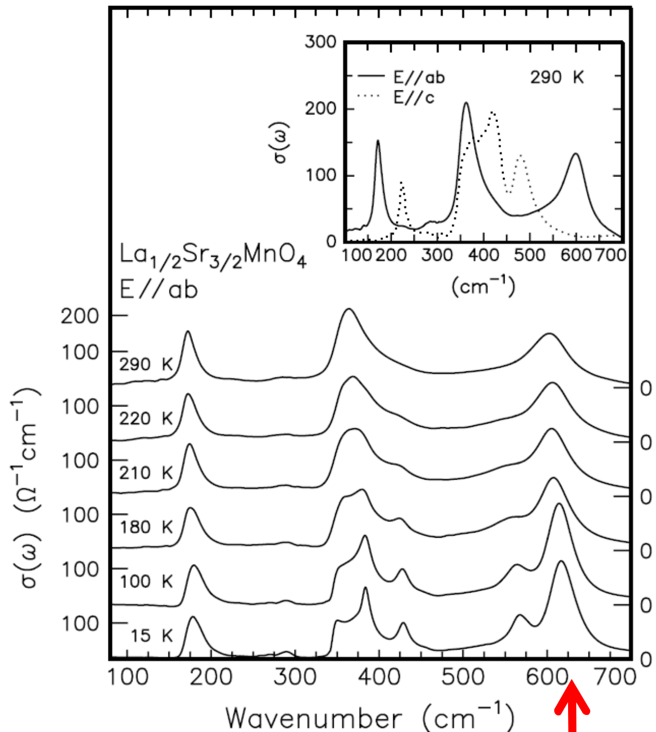
Suggests incommensurability?

Competition introduced by populating out-of-plane orbitals with hot electrons?

R.I Tobey *et al.* (unpublished)

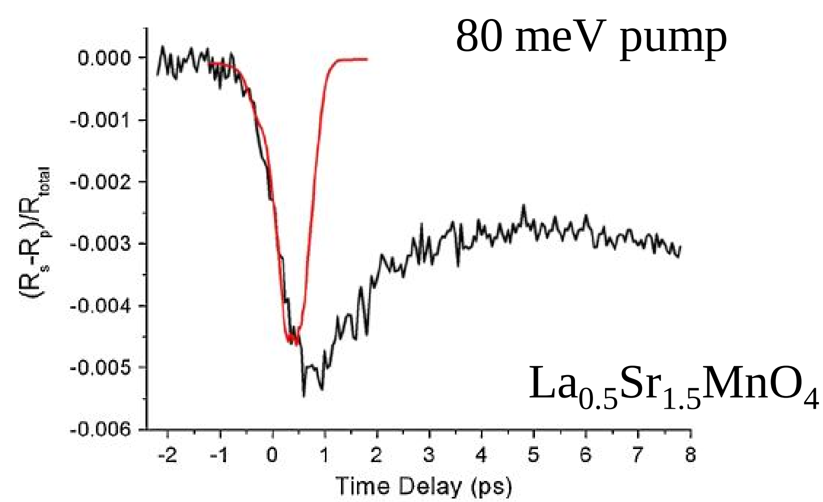
Spin Dynamics: Mid-IR Excitation

IR absorption



Jung *et al.* (2000)

Pumping this mode causes ultrafast loss of birefringence:



R.I Tobey *et al.* (2008)

16 mm=78 meV= 630 cm^{-1}

Mn-O in-plane stretch

Suggests loss of orbital order…

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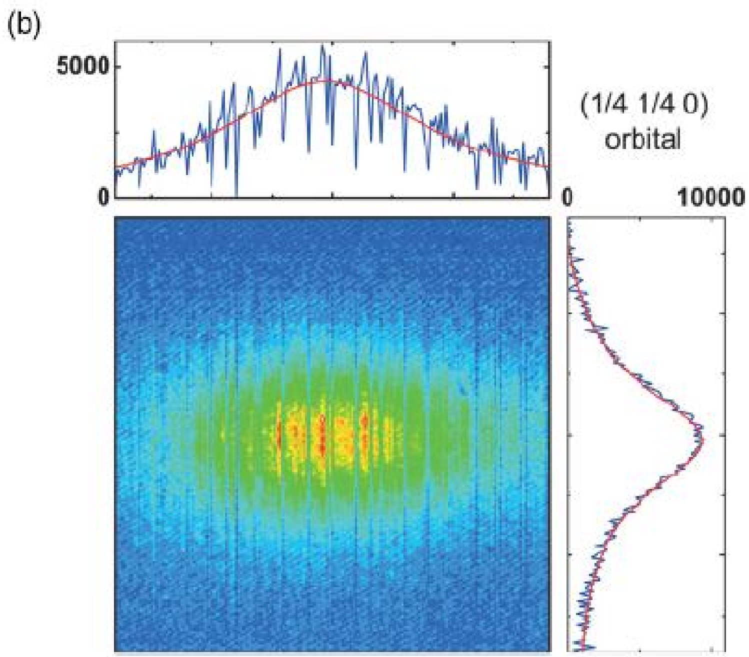
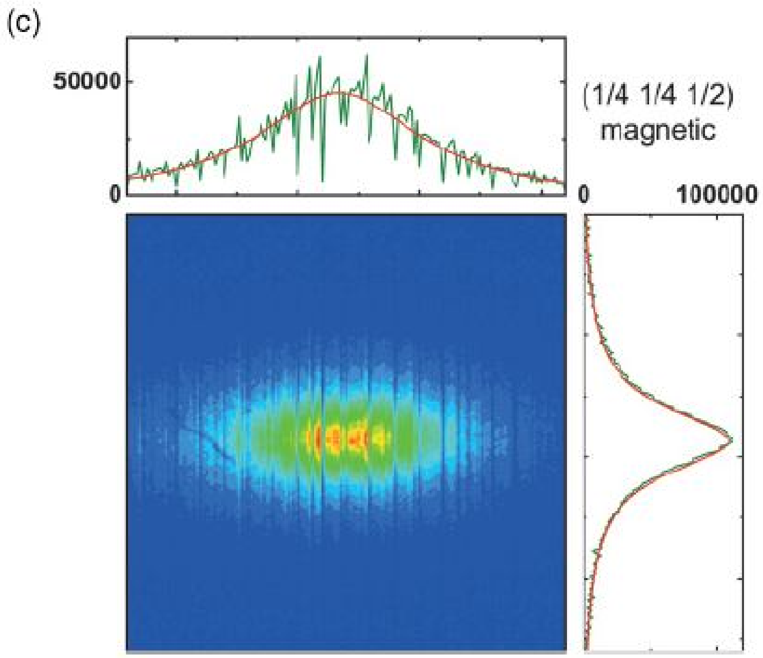
Soft X-rays Probe Both Magnetic and Orbital Order

Orbital Order

Magnetic Order





q_{OO}=(0.25,0.25,0)

q_{SO}=(0.25,0.25,0.5)

MIR pulses 130 fs, 1.2 mJ cm^{-2}
NIR pulses 130 fs, 5 mJ cm^{-2}

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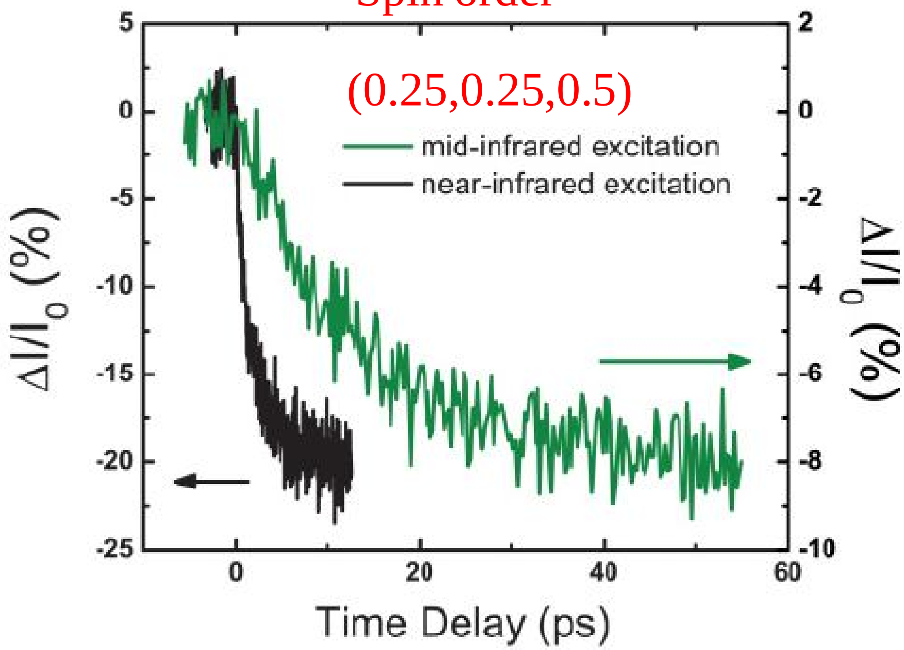
MIR Pump

MIR pulses do melt the magnetic order

Spin order



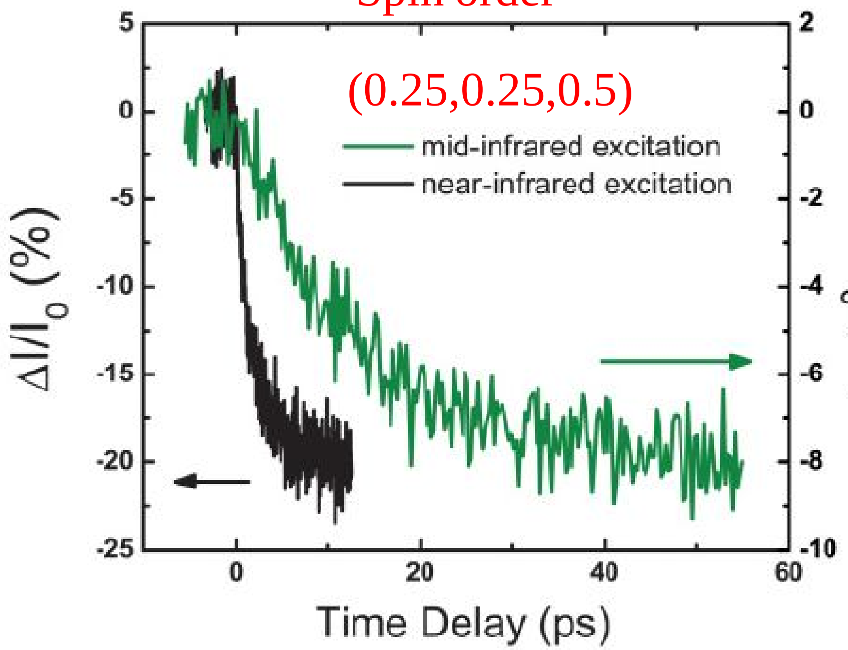
$t^{SO}_{NIR} < 250$ fs

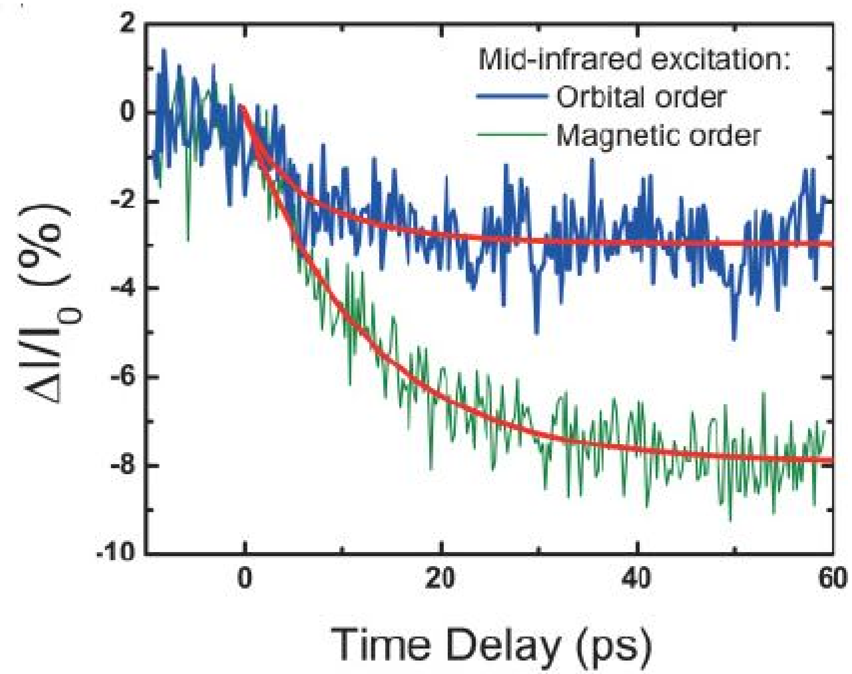
$t^{SO}_{MIR} = 12.2$ ps

MIR Pump

MIR pulses do melt the magnetic order and the orbital order:

Spin order





$t^{SO}_{NIR} < 250$ fs

$t^{SO}_{MIR} = 12.2$ ps

$t^{OO}_{MIR} = 6.3$ ps

Orbital order melts faster than the magnetic order

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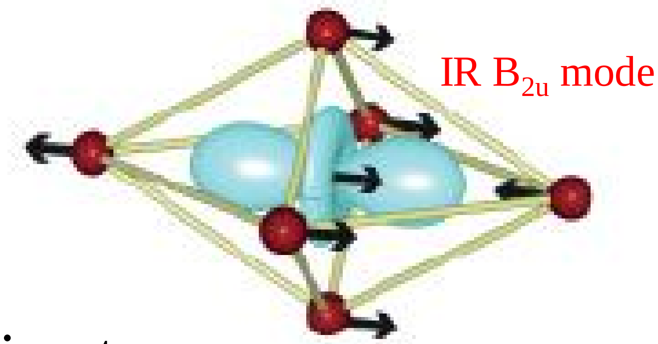
Possible Mechanism: Ionic Raman Scattering*

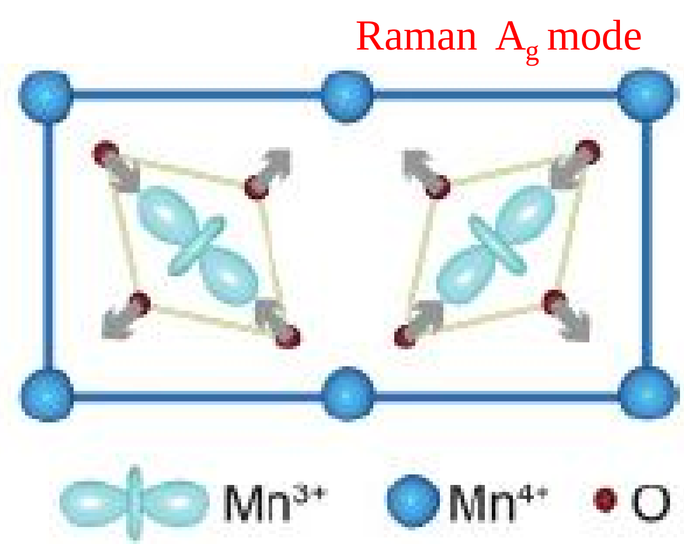


1. MIR pump pulse drives large amplitude IR-active B_{2u} mode (= 74 meV)

2. Non-linear lattice dynamics rectifies this vibration into a half-cycle of a mode belonging to the product group: $B_{2u} \otimes B_{2u} = A_g$

$$H_A = -NA\Omega_{RS}\Omega_{IR}^2$$

3. The Raman-active JT distortion mode at 77 meV has A_g symmetry and in this model this mode that is driven



4. This alters the crystal field splitting causing e_g electrons to rearrange, reducing the orbital order parameter and, on a slower time scale (spin inertia?), reduces the spin order parameter.

*Walls *et al.* (1971), Martin *et al.* (1974)

Summary: Manganites

•Insulating phase in manganites is a complicated phase of charge, orbital and spin order.

•When melted thermally, the spins disorder first, then the charge and orbital order melts.

•The insulating phase can be melted on ultrafast time scales with 1.5 eV photons and 70 meV photons – photo driven metal insulator transitions (temperature is constant).

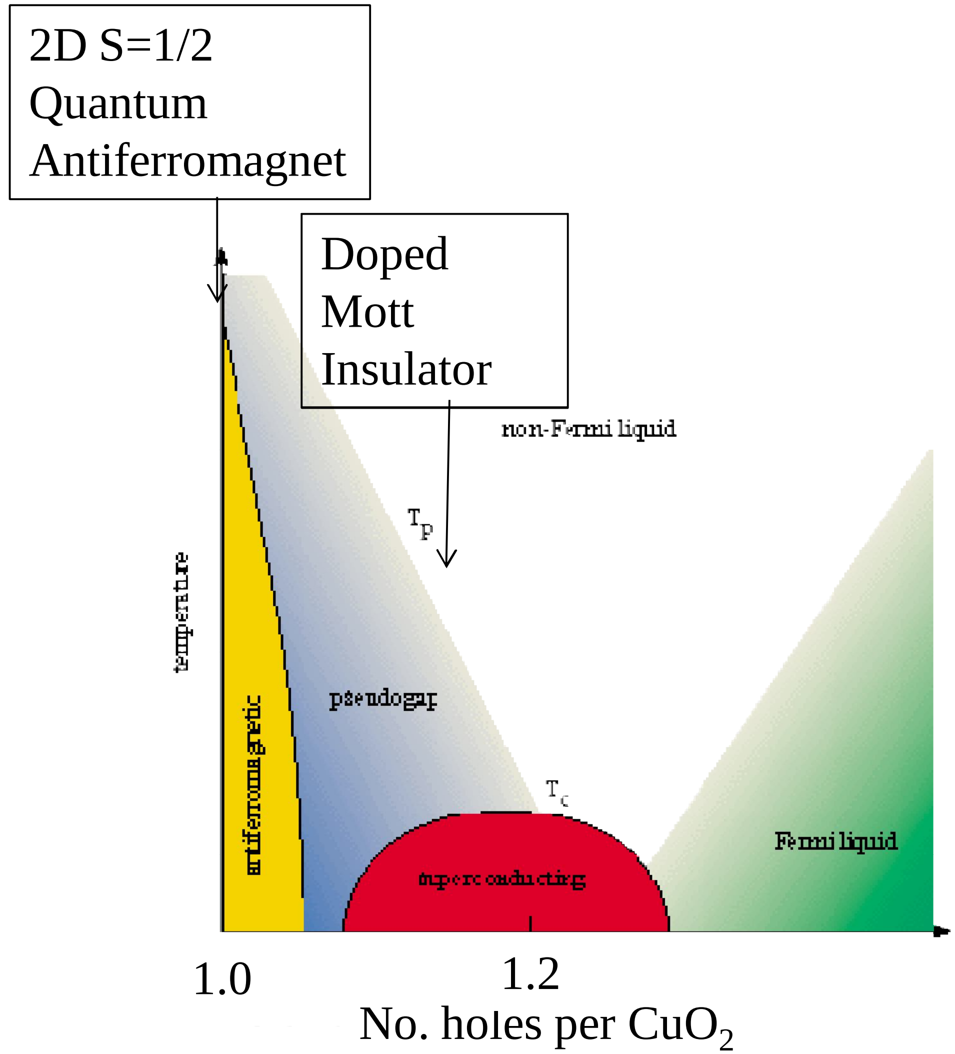
• Photo-melting is quite different from thermal melting. Do not see a change in (in-plane) correlation lengths

• When driven with MIR pulse, the orbital order melts first – the opposite to the thermal melting process.

Example 2: The Superconducting Transition

Cuprates

Cuprate Phase Diagram



underdoped

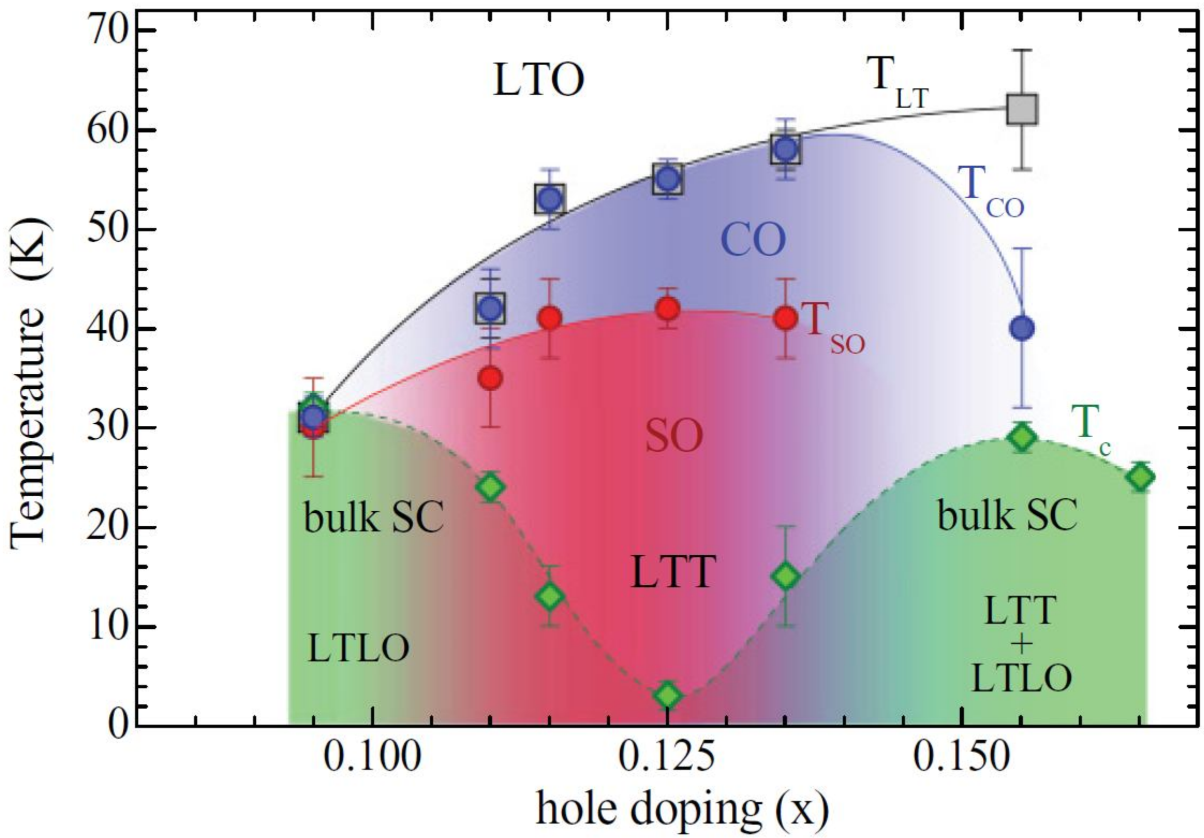
Optimal doped

overdoped

From Batlogg and Varma, Physics World (2000)

$La_{2-x}Ba_xCuO_4$

The "1/8th anomaly"– superconductivity is suppressed at x=0.125:



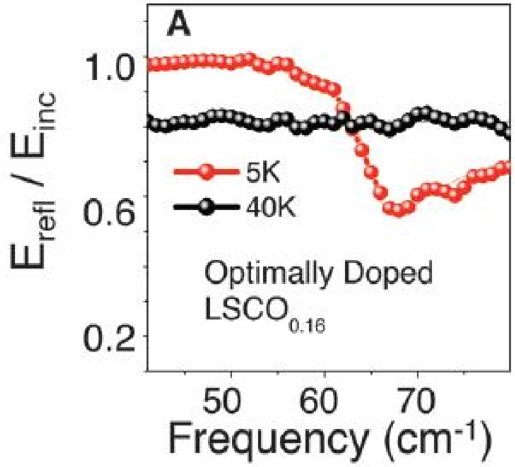
Also seen in
$La_{2-x-y}Nd_ySr_xCuO_4$
$La_{2-x-y}Eu_ySr_xCuO_4$

Huecker *et al.* PRB 83 104506(2011)

Photon-Driven Superconductivity

Josephson Plasma Resonance (JPR)

Superconductor



D. Fausti *et al.* Science (2011)

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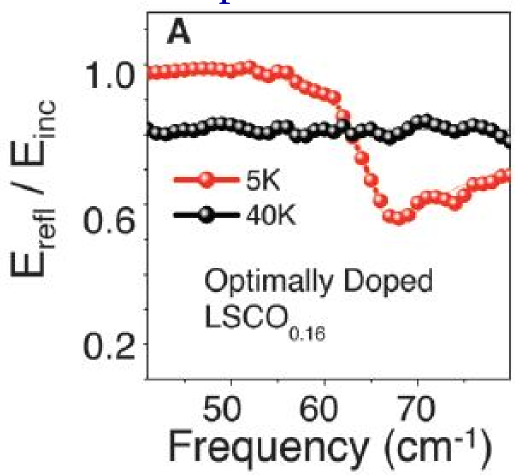
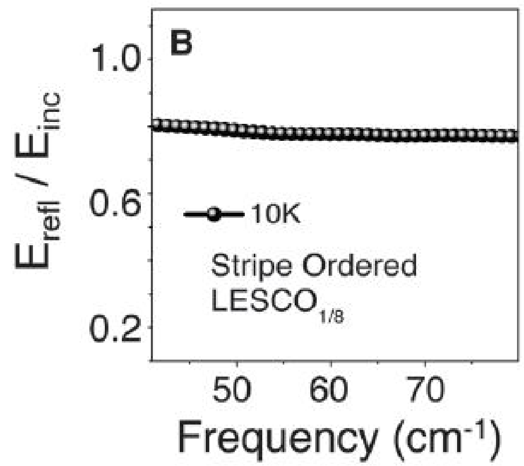
Photon-Driven Superconductivity

Josephson Plasma Resonance (JPR)

Superconductor



Non-Superconductor



D. Fausti *et al.* Science (2011)

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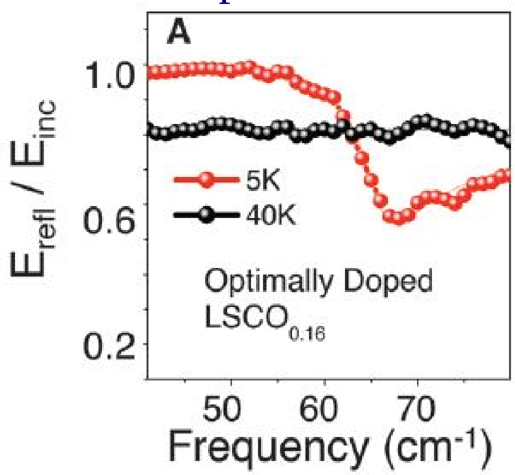
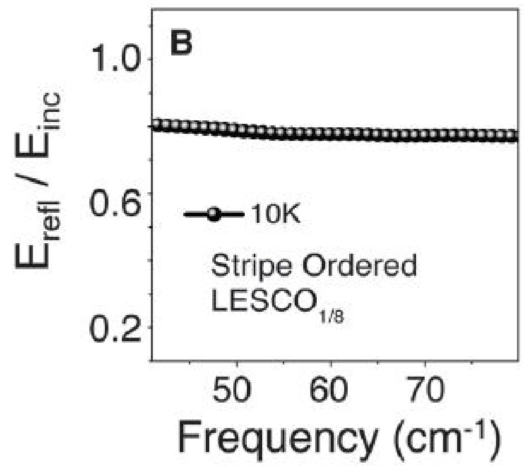
Photon-Driven Superconductivity

Josephson Plasma Resonance (JPR)

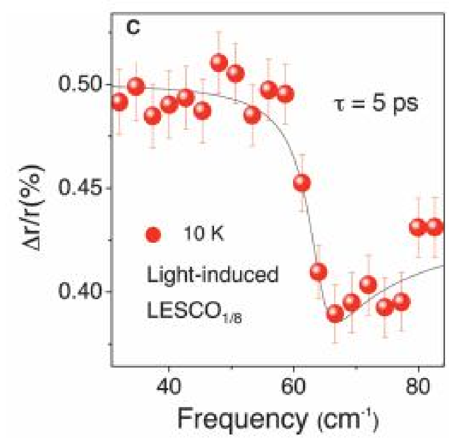
Superconductor

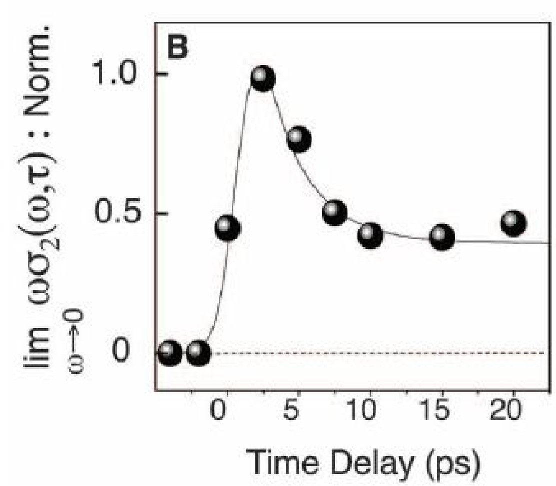


Non-Superconductor



LESCO following MIR pump





It appears that superconductivity is induced in a non-superconductor on a very short time scale following MIR excitation.

What is going on here?

D. Fausti *et al.* Science (2011)

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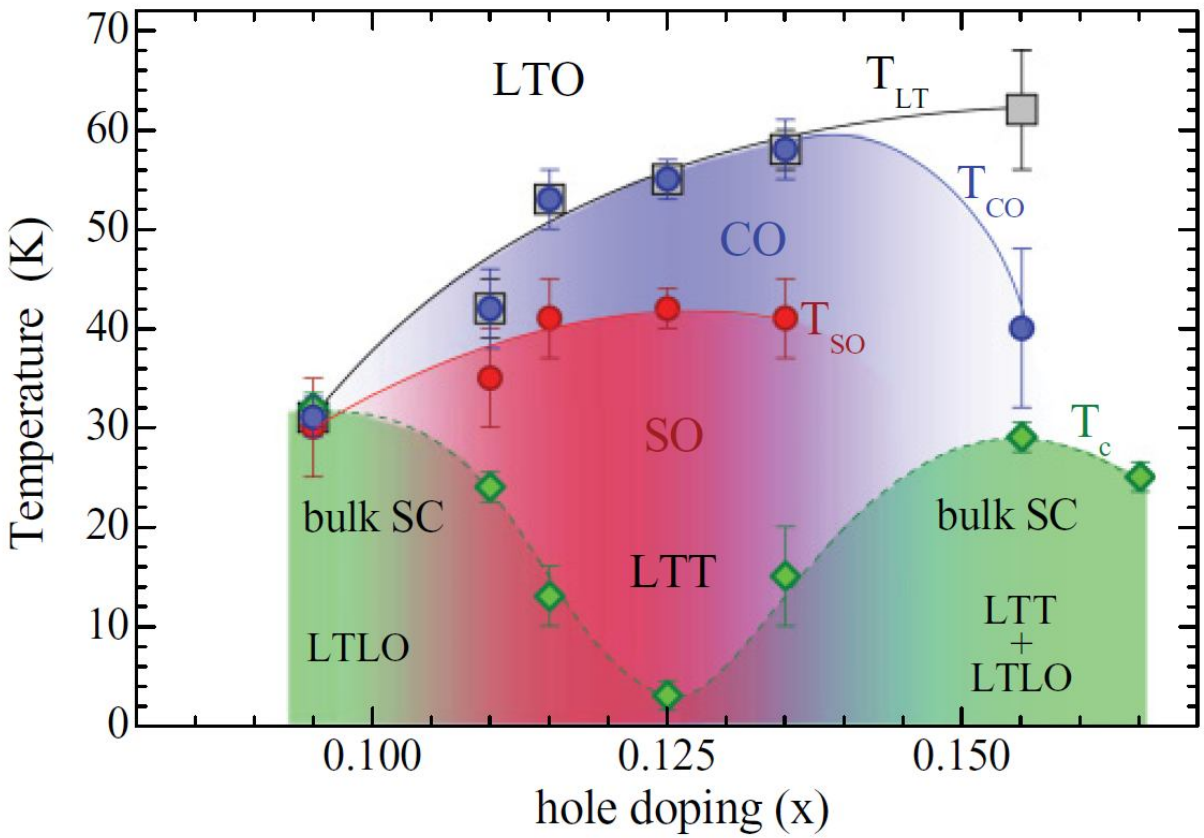
$La_{2-x}Ba_xCuO_4$

The "1/8[th] anomaly"– superconductivity is suppressed at x=0.125:



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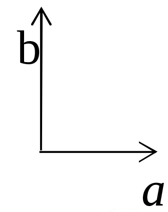
Huecker *et al.* PRB 83 104506(2011)

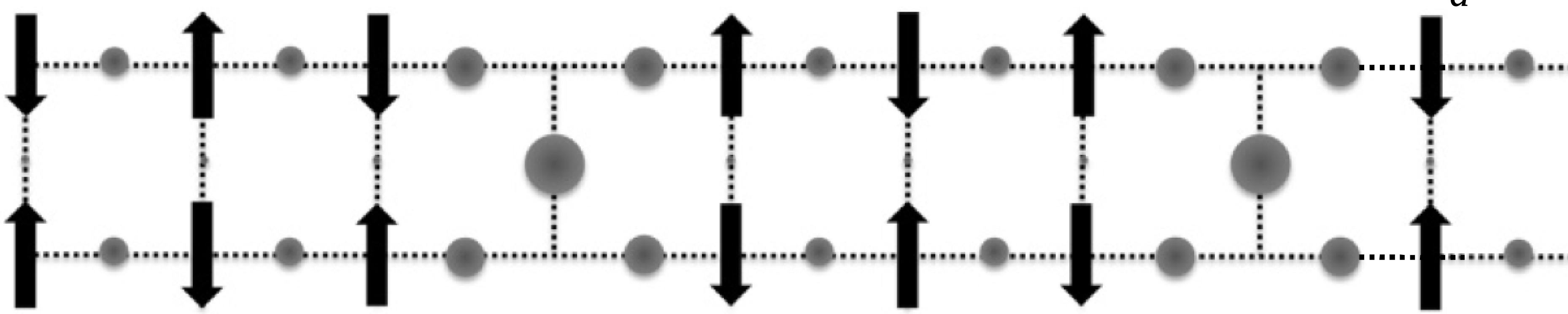
Charge and Spin Stripes

Modulation of the charge and spin density in the *a*-*b* plane:

Tranquada *et al.* (1995)



$\lambda_{charge} = 4a$

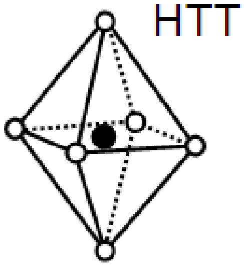


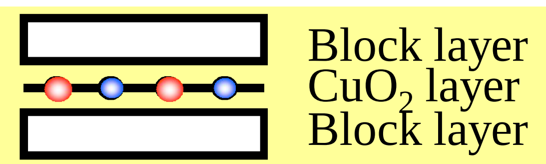
$\lambda_{magnetic} = 8a$

DFT+U calculation
Pesant and Cote PRB (2011)

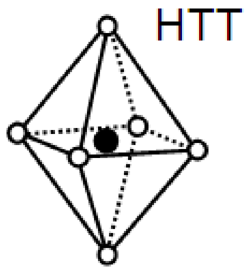
$Q_{charge} = (0.25,0,0.5)$
$Q_{mag} = (0.375,0.5,0)$

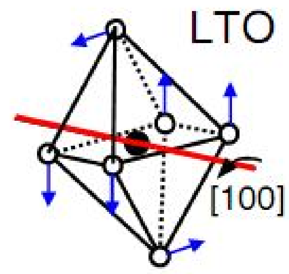
Octahedral Tilts

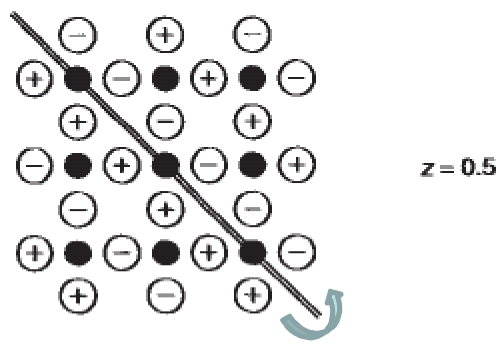


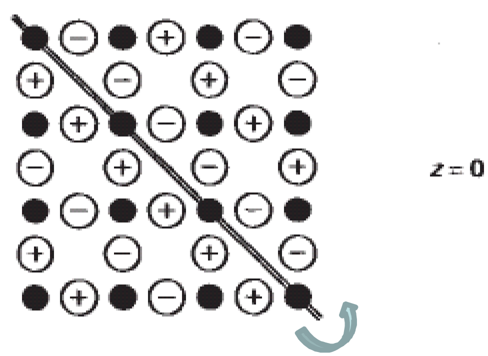


Octahedral Tilts



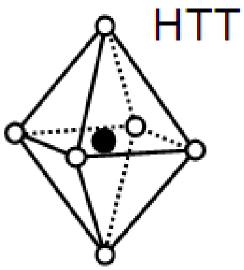


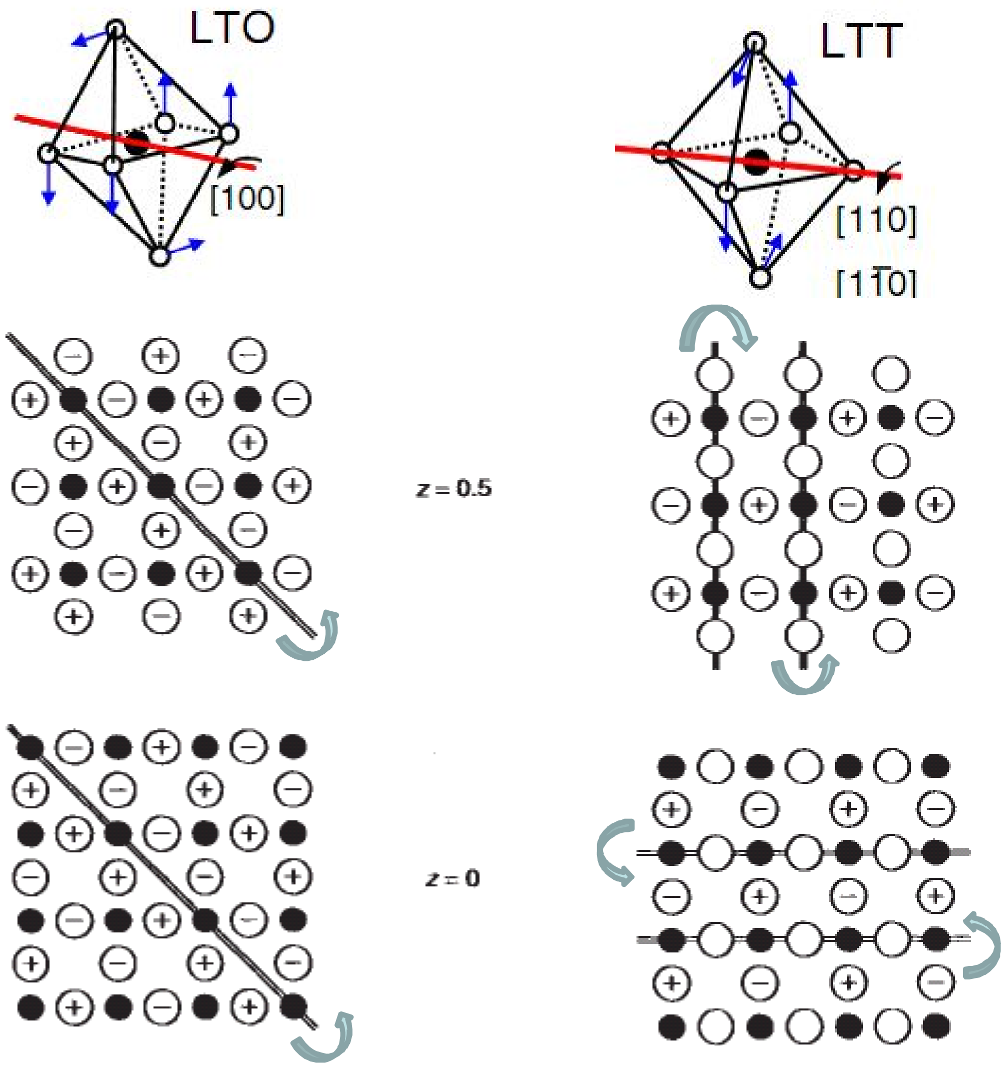




LTO

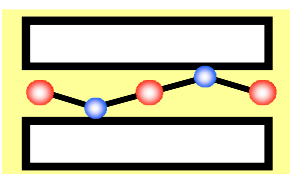
Octahedral Tilts





LTO

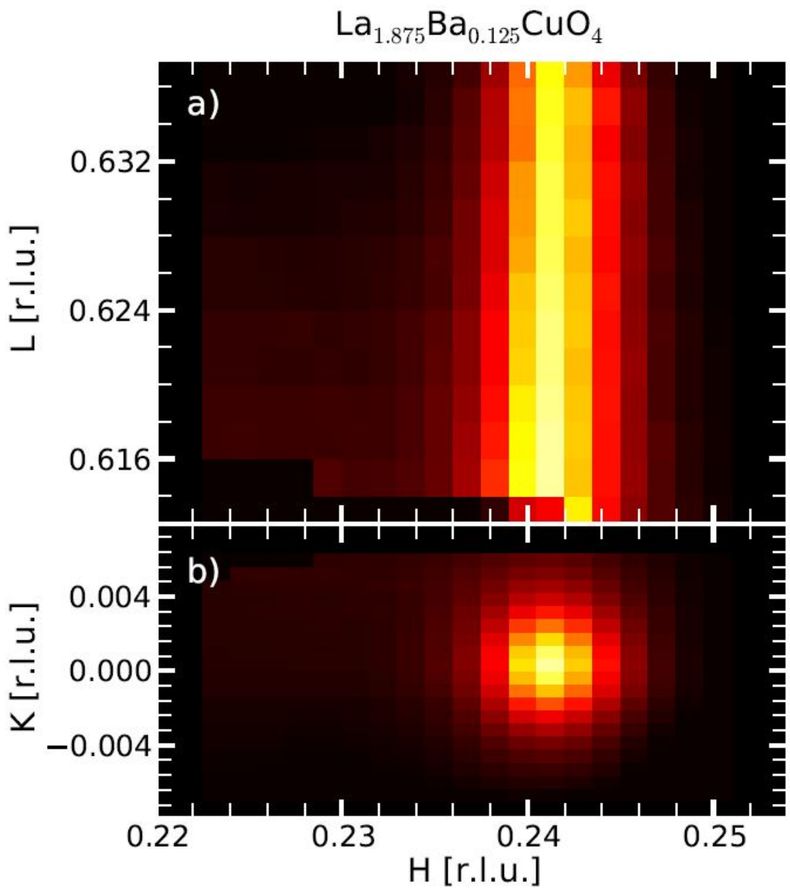
LTT

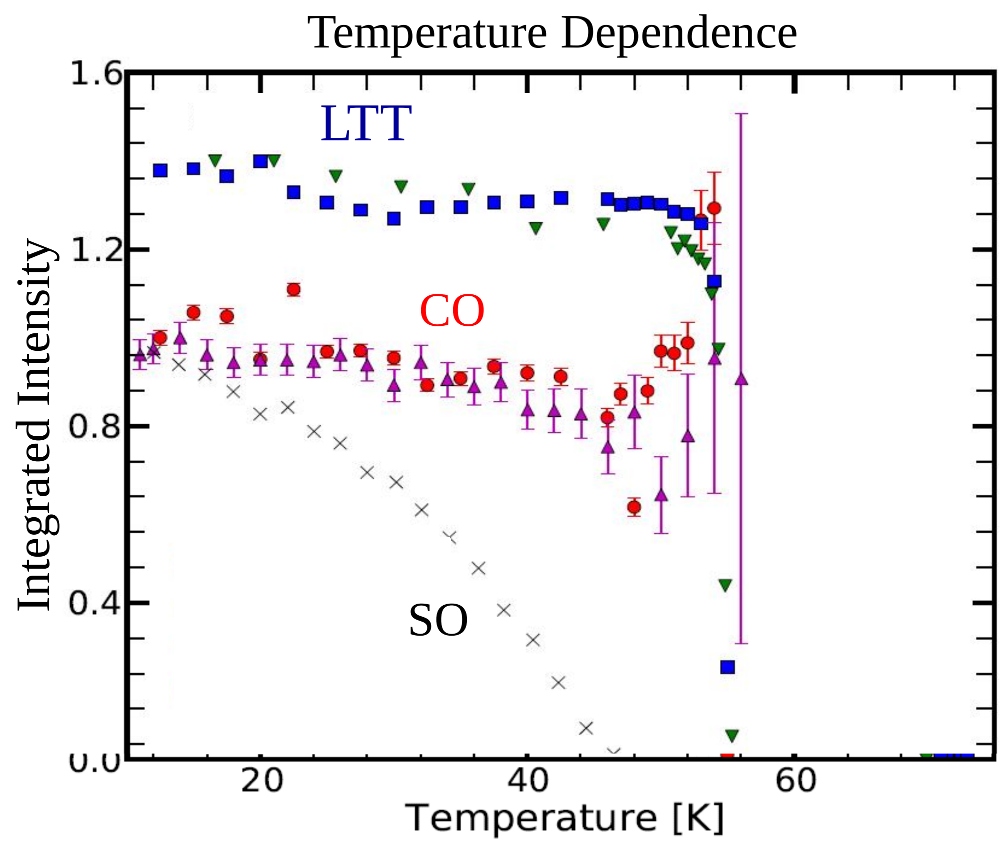


LTT phase stabilizes horizontal stripes

O K-edge Studies of Charge Stripe Order

With the incident x-ray energy tuned to the O K pre-edge, one is sensitive to the spatial modulation of the doped holes:





S. Wilkins *et al.* (2011)

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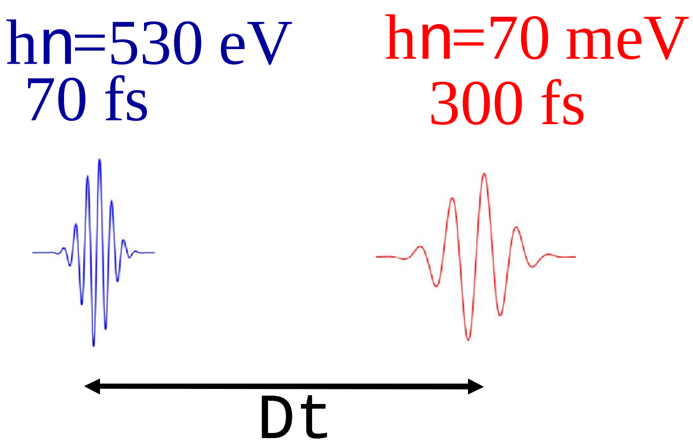
Ultrafast Soft X-ray Scattering

Pump with mid-IR photons, tuned to Cu-O bond stretching mode



Dt is varied with a mechanical delay stage from -40 ps to 40 ps

Probe with soft x-ray photons, tuned to the O K pre-edge

LTT structural Peak	q = (001)
Charge stripe ordering	q = (.25 0 .5)

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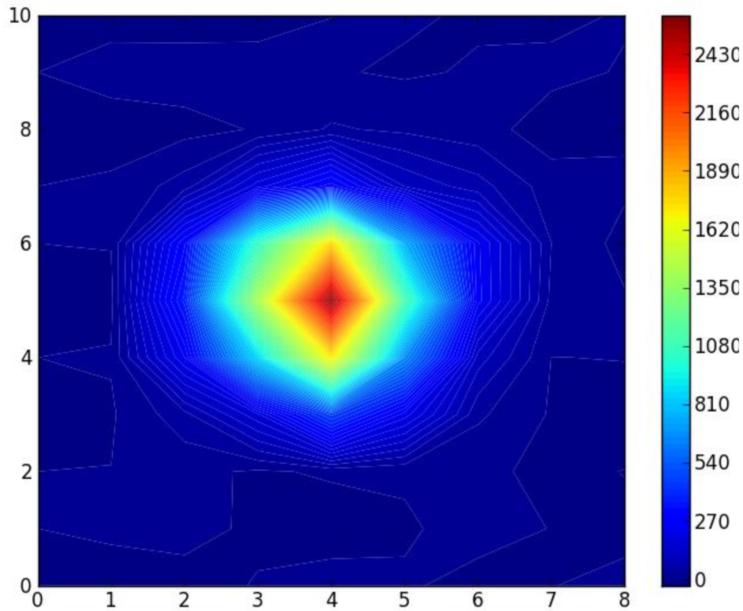
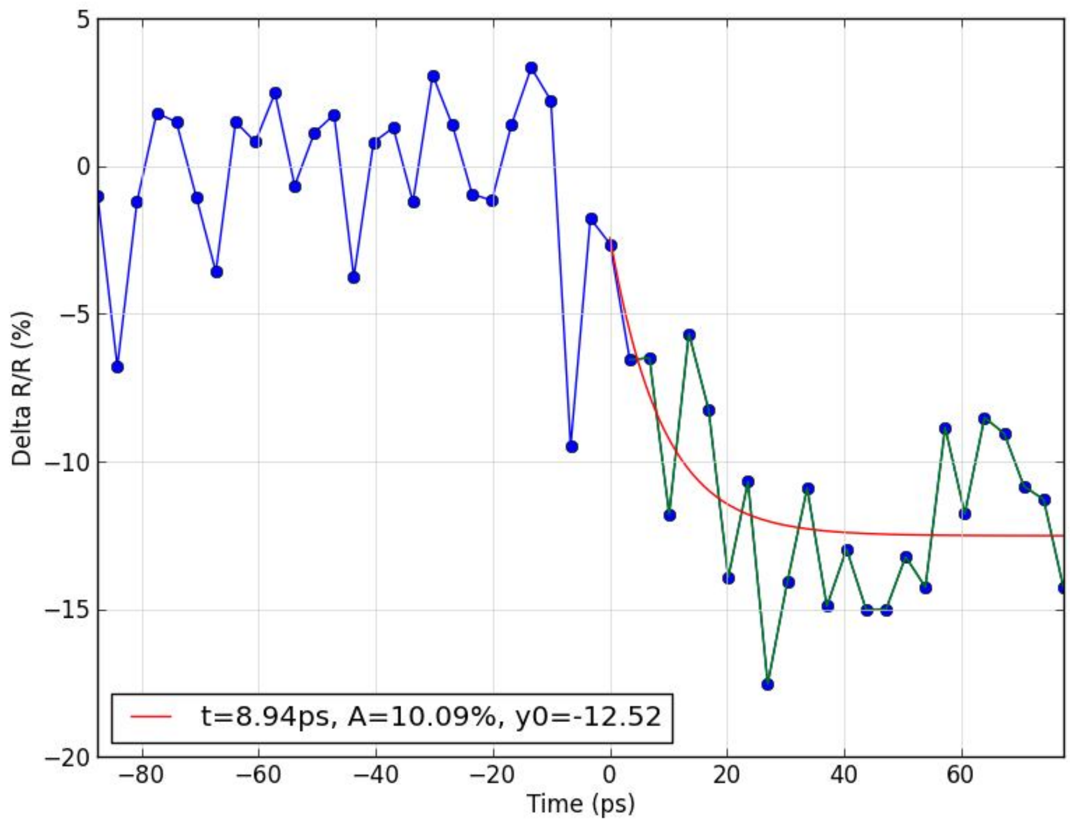
LTT Structural Peak

(001) T= 12 K

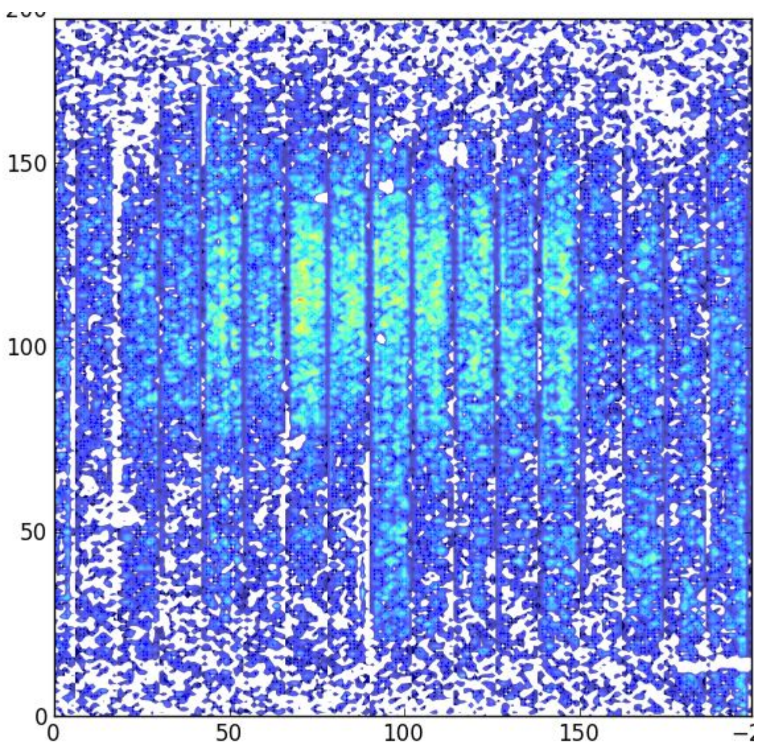




The (001) is suppressed following the MIR pulse with a ~ 10 ps time constant

Charge Stripe Peak

(0.25, 0, 0.65)

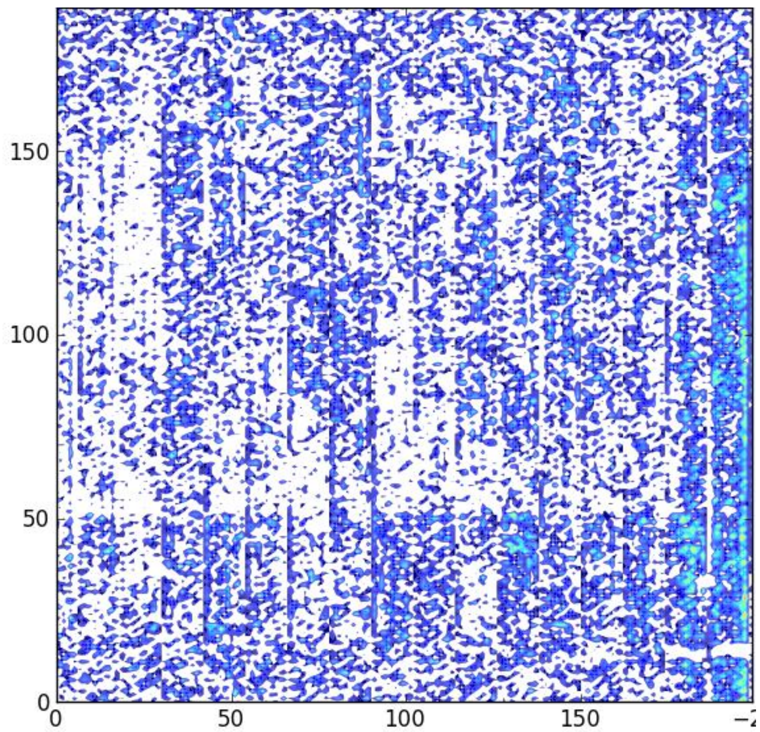


-ve time delay
(probe before pump)

700 frames, each 0.5 s integrating 30 FEL shots

Charge Stripe Peak

(0.25, 0, 0.65)

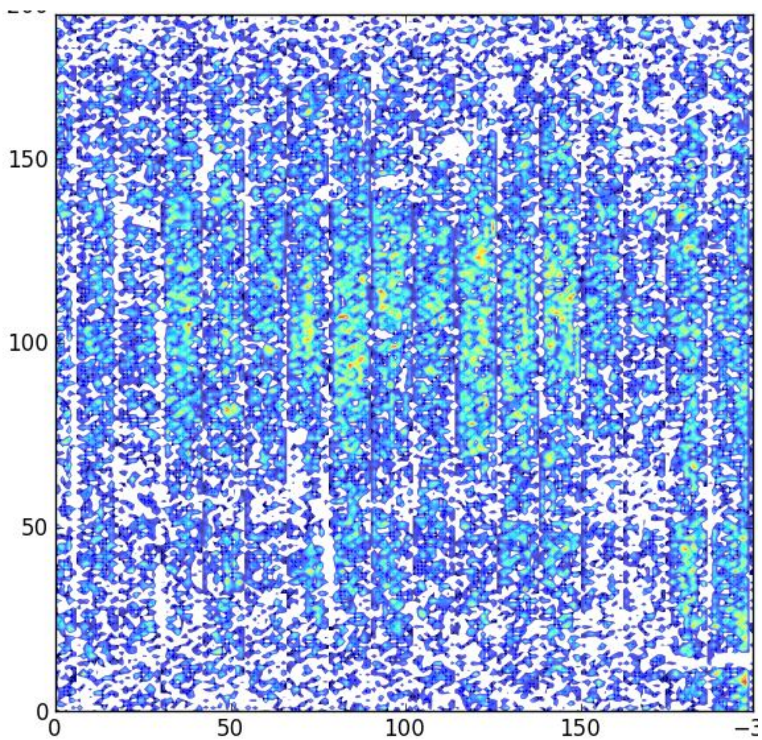


400 fs after pump

700 frames, each 0.5 s integrating 30 FEL shots

Charge Stripe Peak

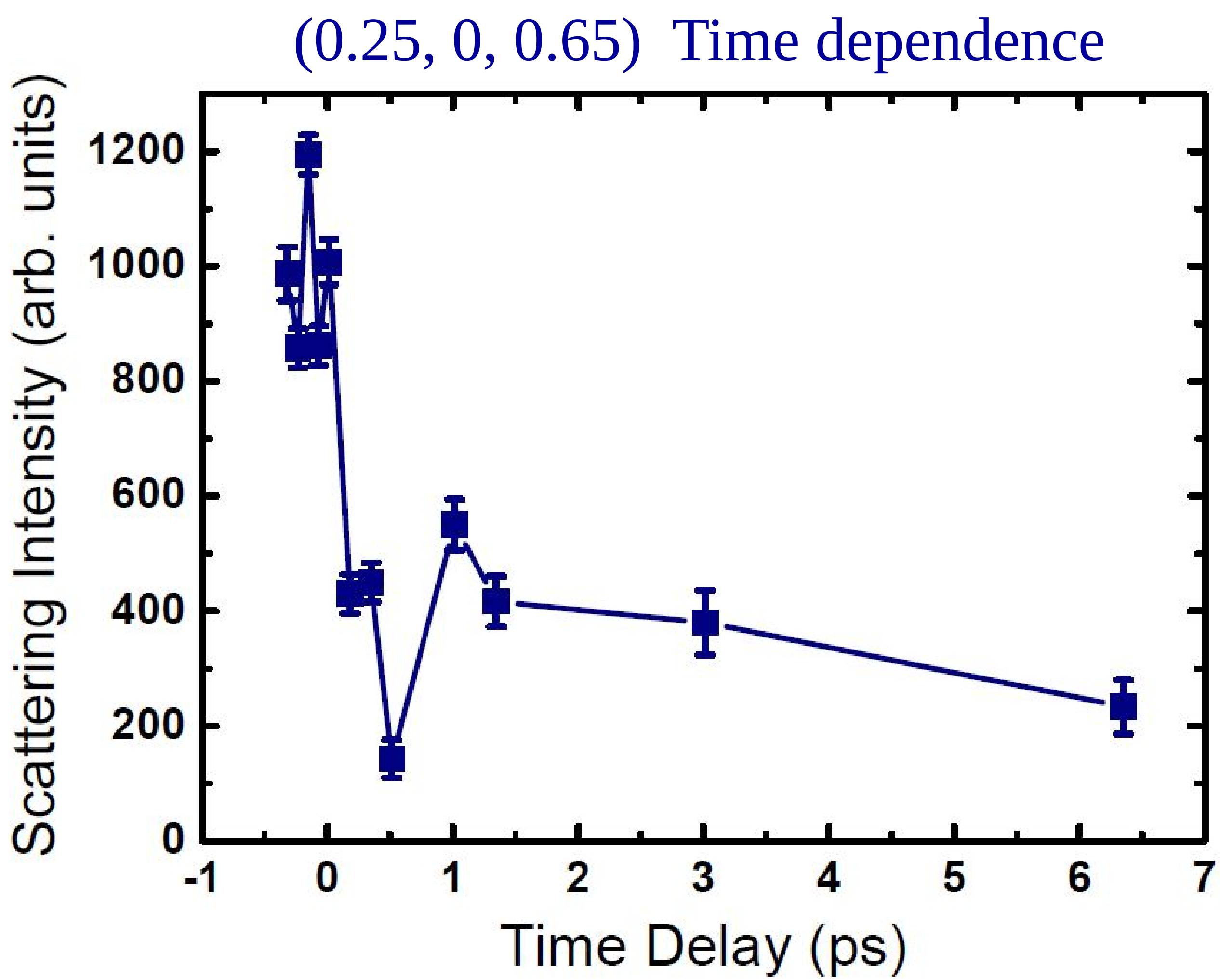
(0.25, 0, 0.65)



20 ps after pump

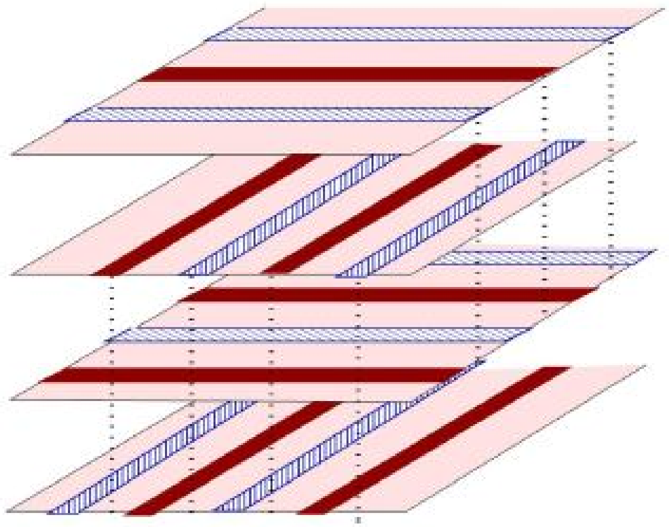
700 frames, each 0.5 s integrating 30 FEL shots

Charge Stripe Peak



Charge stripe peak is very rapidly suppressed (< 400fs)

Possible Hypothesis



(from Berg *et al.* PRL (2007))

Static charge modulations couple to superconducting order parameter and create "Pair Density Wave" state

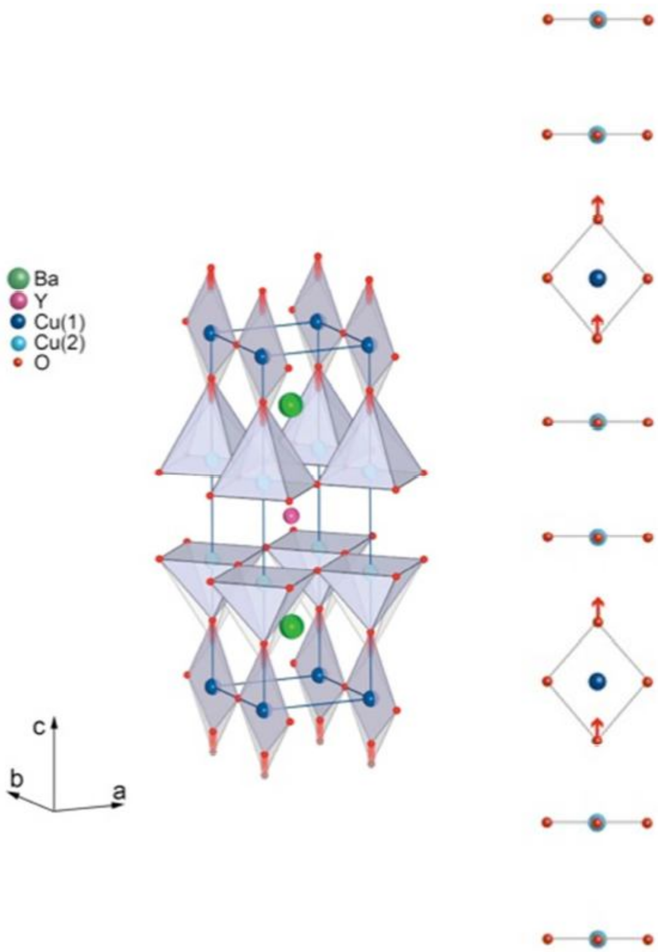
This creates a system of layered, striped, 2D superconductors that are exactly out of phase with their neighbors.

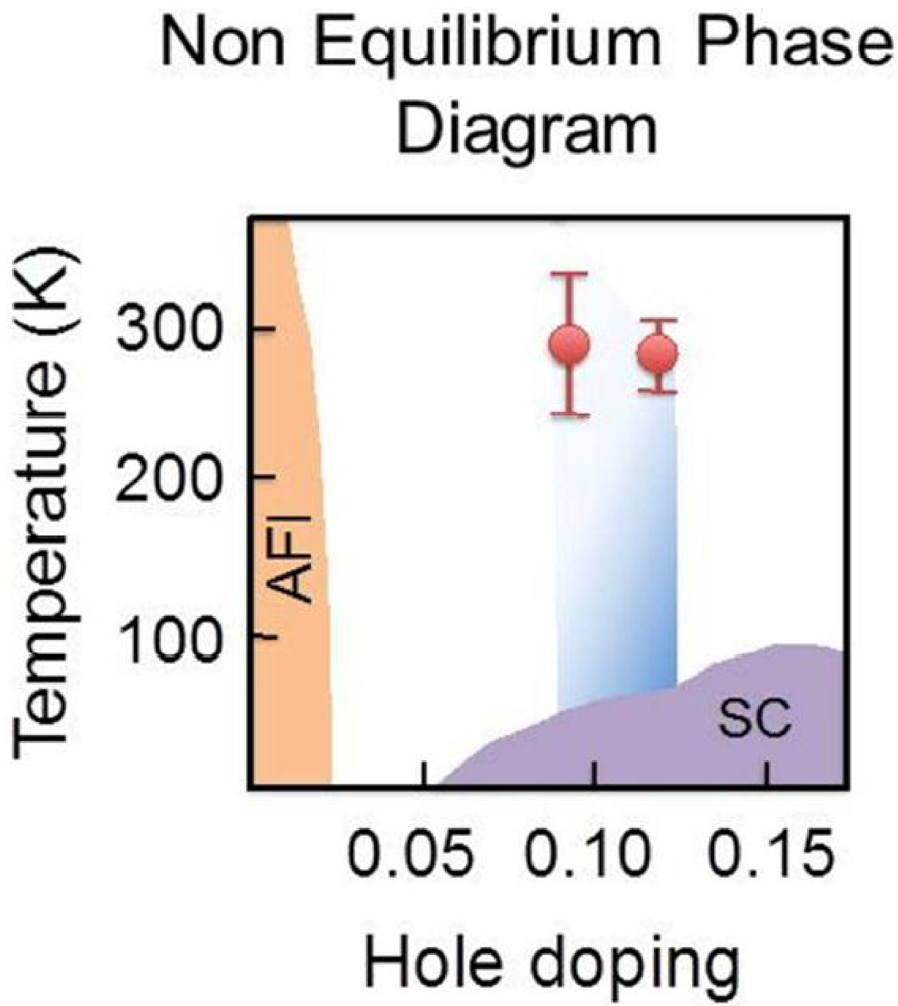
No long range phase coherence. No bulk superconductivity.

Melting the charge order removes this potential and allows the superconducting planes to recouple, giving bulk superconductivity.

Very Exciting, Very Recent Result

MIR pumping of YBCO above Tc





Kaiser et al. (2012)

Summary

• Strongly correlated electron systems have many useful properties and are characterized by strong responses to perturbations. Conventional theories fail in describing their electron dynamics and they are not well understood as a result.

• By knocking them out of equilibrium with various laser pumps, we can hope to tease out the role the various interactions play in determining their behavior – because the different degrees of freedom (spin, charge, orbital, lattice) have different characteristic time scales.

• We also have the possibility of creating transient states one cannot access in equilibrium and to the idea of photo-control of materials properties.

• The LCLS allows time-resolved studies of these systems with sufficient time-resolution (sub-ps) to see the electronic degrees of freedom. X-ray scattering techniques allow the different order parameters to be probed independently.

Quiz

1) Strongly correlated systems have which of these characteristics?

A. Large bandwidth, W
B. Large, transfer integral, *t*
C. Large Coulomb interaction, U
D. Filled bands

2) If you want to study the spin ordering on the manganese sites, the most appropriate absorption edge is:

A. O K-edge
B. Mn K-edge
C. Mn L-edge
D. Cu L-edge

3) A magnetic structure is well-correlated in the *a*-*b* plane. The magnetic scattering from this is elongated in the :

A. H-direction
B. K-direction
C. L-direction

4) The average Mn valence in $Pr_{0.7}Ca_{0.3}MnO_3$ is

A. $Mn^{3.5+}$
B. $Mn^{3.7+}$
C. $Mn^{3.3+}$

5) The time scale for a Josephson plasma oscillation (9 meV) is

A. 50 fs
B. 500 fs
C. 5 ps
D. 50 ps