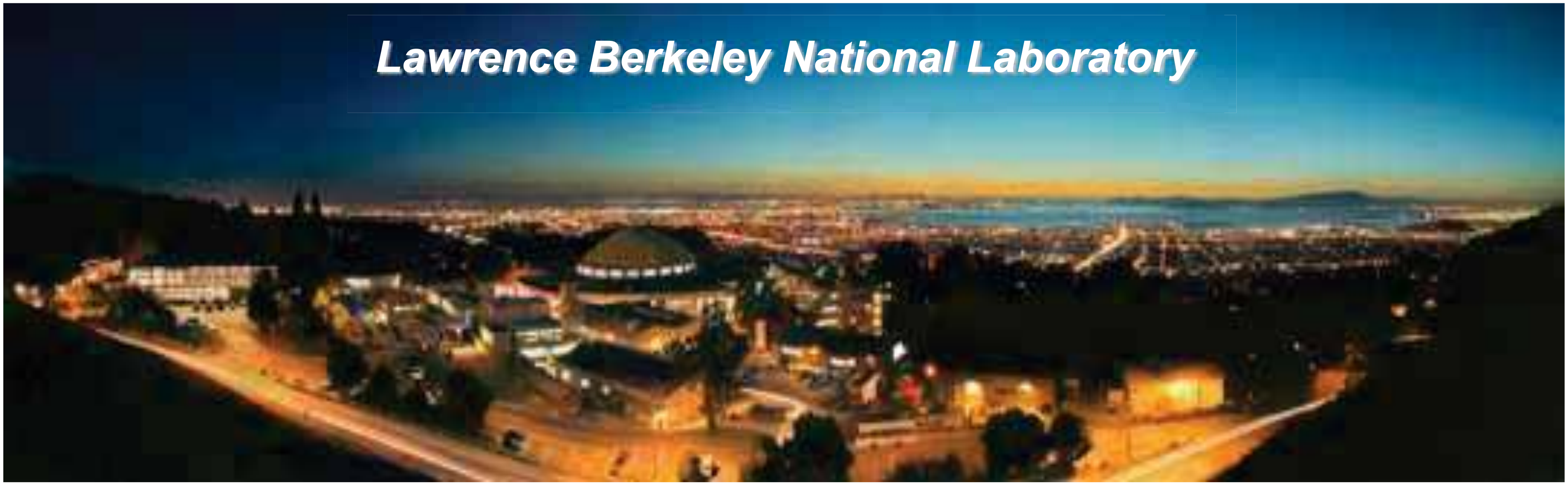
# Ultrafast X-ray Studies of Complex Materials: Science Challenges and Opportunities

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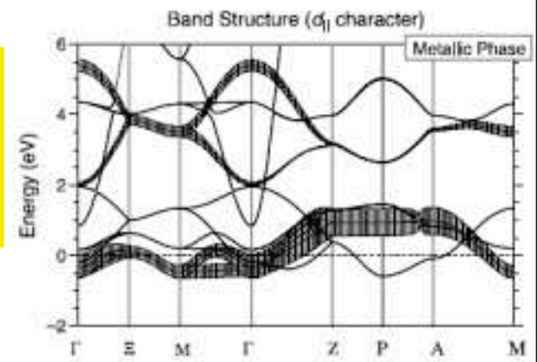
*Chemical Sciences Division – Ultrafast X-ray Sciences Laboratory*
*Next Generation Light Source*

**Cornell XDL 2011 Workshop – June 2011**

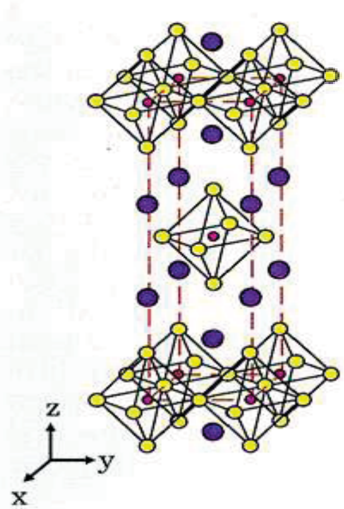
# Ultrafast Dynamics in Complex Materials - Beyond Bloch

**How do the properties of matter emerge from the:**
**correlated motion of electrons, and coupled atomic and electronic structure?**

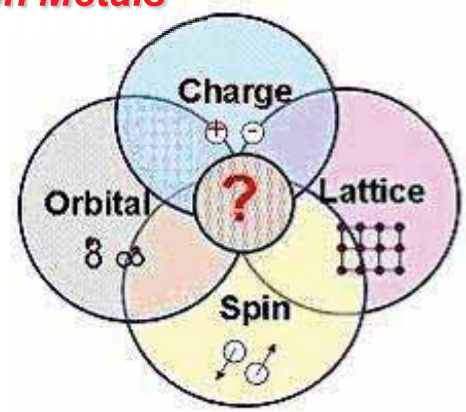
- *beyond single-electron band structure models, Bloch, Fermi Liquid Theory*
  - *complex materials exhibiting strong correlation among charges,*
    - *and between charge, spin, orbit, and lattice*

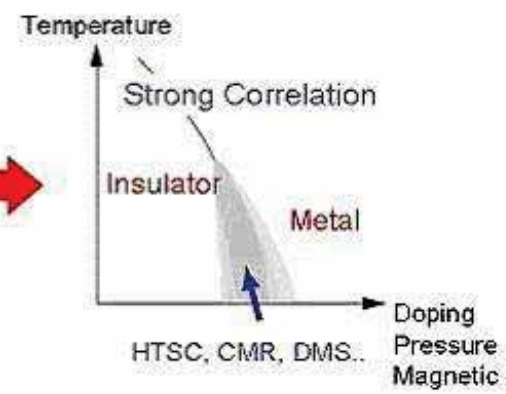



$T_{lifetime} \neq (E-E_F)^{-1/2}$




*Oxides of Transition Metals*
*(Cu, Mn, Ni, V…)*




## *Understand the Interplay between Atomic and Electronic Structure*

- *Valence electronic structure – energy levels, charge distribution, bonding, spin*
- *Atomic structure – coordination, atomic arrangements, bond distances*

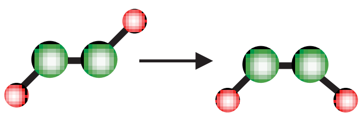
# *Fundamental Time Scales in Condensed Matter*

## Atomic Structural Dynamics

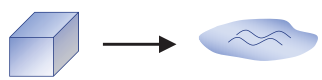
**atomic vibrational period: $T_{vib} = 2\pi(k/m)^{-1/2} \sim 100$ fs**

**$k \sim eV/a^2$  $m \sim 10^{-25}$ Kg**

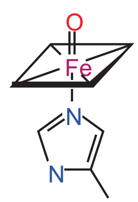
- **ultrafast chemical reactions**



- **ultrafast phase transitions**



- **ultrafast biological processes**




## Electronic Structural Dynamics

**electron-phonon interaction ~ 1 ps**

**e-e scattering ~10 fs**

**$e^-$ correlation time ~100 attoseconds ($a/V_{Fermi}$)**

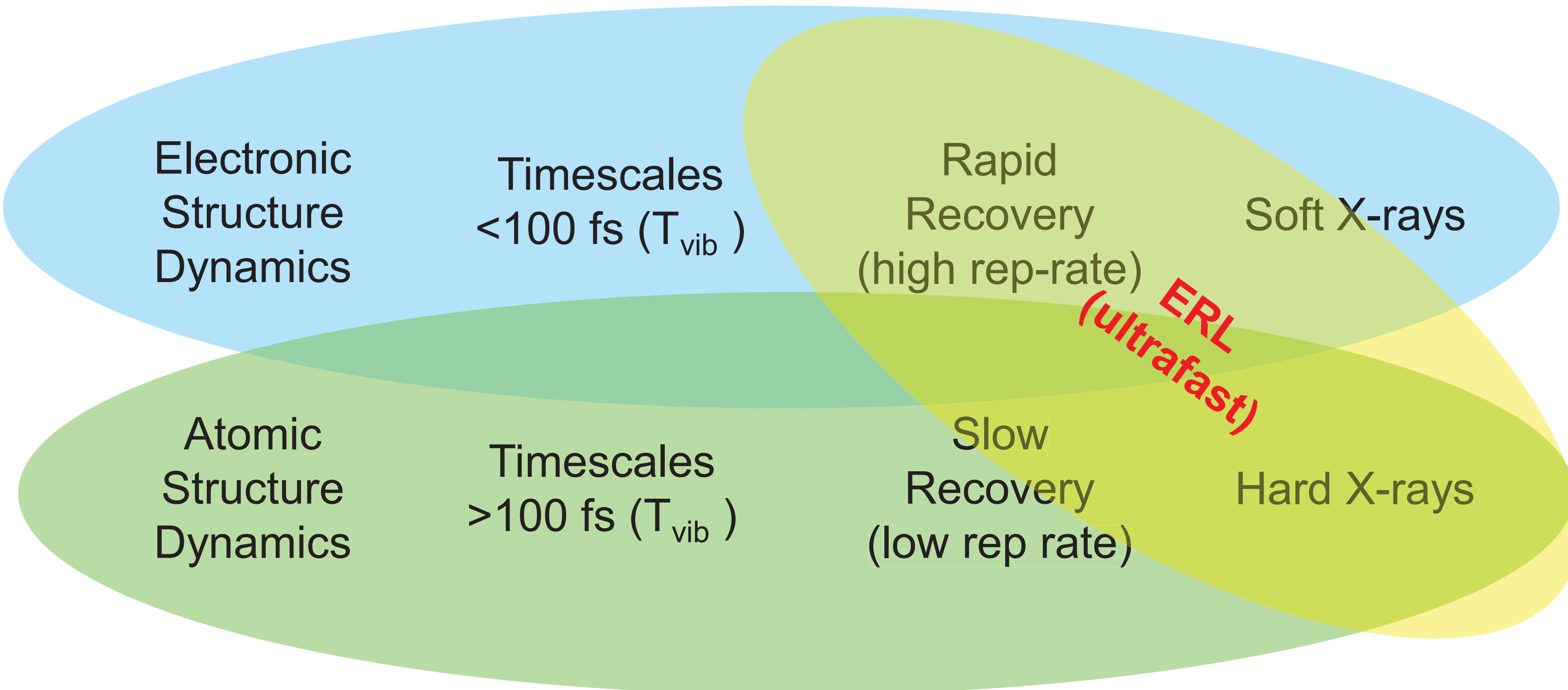
- **bond dynamics, valence charge flow**
- **charge transfer**
- **electronic phase transitions**
  - correlated electron systems

***Ultrafast Measurements:***

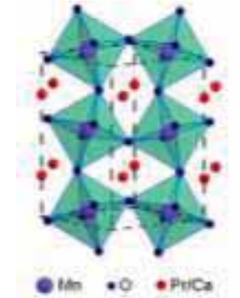
***- separate correlated phenomena in the time domain***

***- direct observations of the underlying correlations as they develop***

# Gross Generalizations – Workshop Discussion



# *Outline*

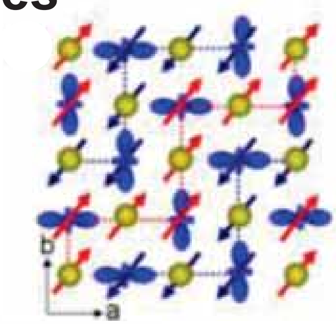



## Ultrafast Dynamics in Colossal Magnetoresistive (CMR) Manganites

- Ultrafast photo- and vibrationally-induced insulator-metal transition in $Pr_{1-x}Ca_xMnO_3$

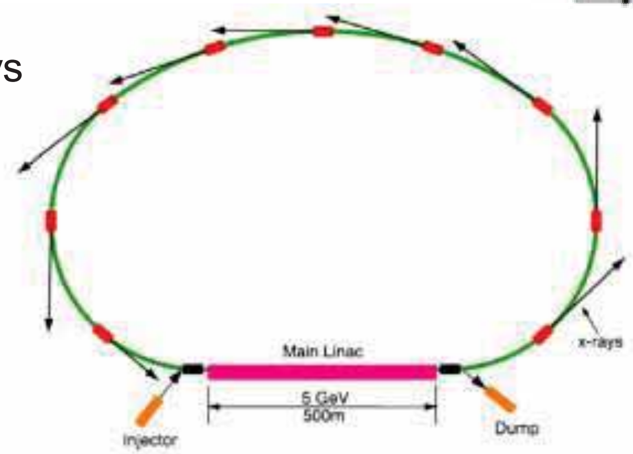
## Time-resolved X-ray Absorption, Scattering in CMR Manganites

- Electronic structure – time-resolved XANES (O K-edge, Mn L-edge)
- Dynamics of charge, orbital, and spin ordering




## Energy-Recovery Linac

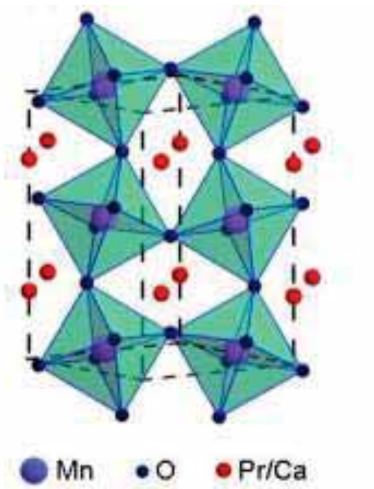
- Ultrafast, high-rep-rate, diffraction-limited hard X-rays
- Science challenges and opportunities

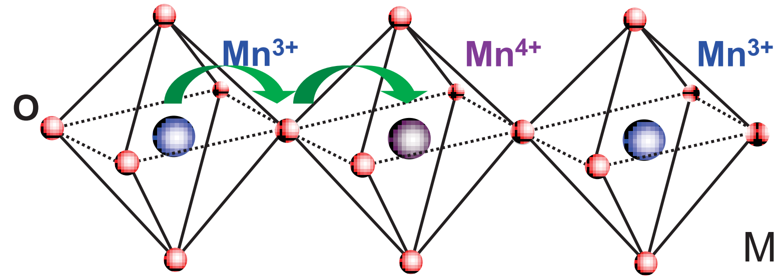


# Colossal Magnetoresistive Manganites

- magnetic control of electronic structure (magneto-transport)
- rich phase diagram – order/symmetry breaking
- new physics, correlation effects – other complex materials

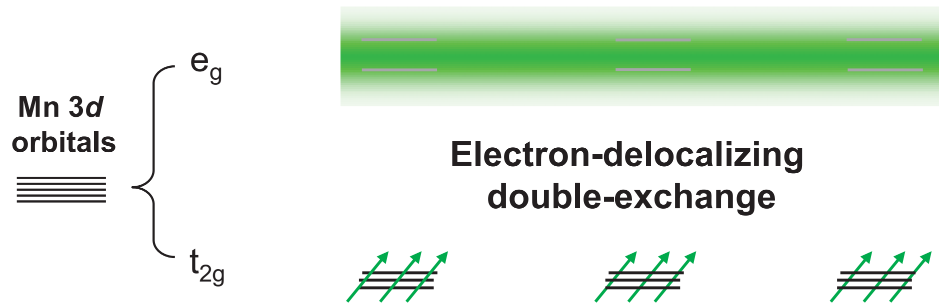
$Pr_{1-x}Ca_xMnO_3$



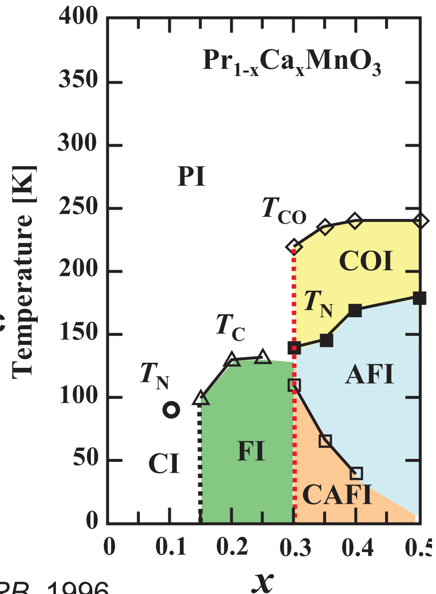

Metal

$Pr_{0.7}Ca_{0.3}MnO_3$

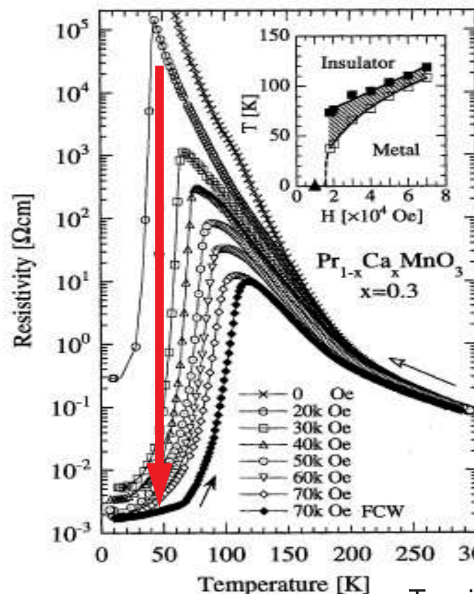



Electron-delocalizing double-exchange

COI - charge ordered ins.
PI – paramagnetic ins.
AFI – antiferromagnetic ins.
CA – canted antiferromagnetic




Tokura et al., *PRB*, 1996

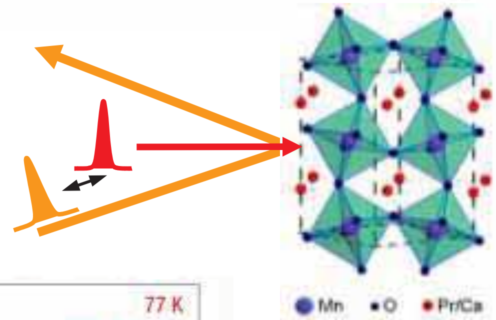


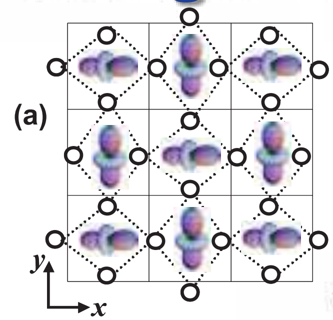

Tomioka et al., *JPSJ*, 1995

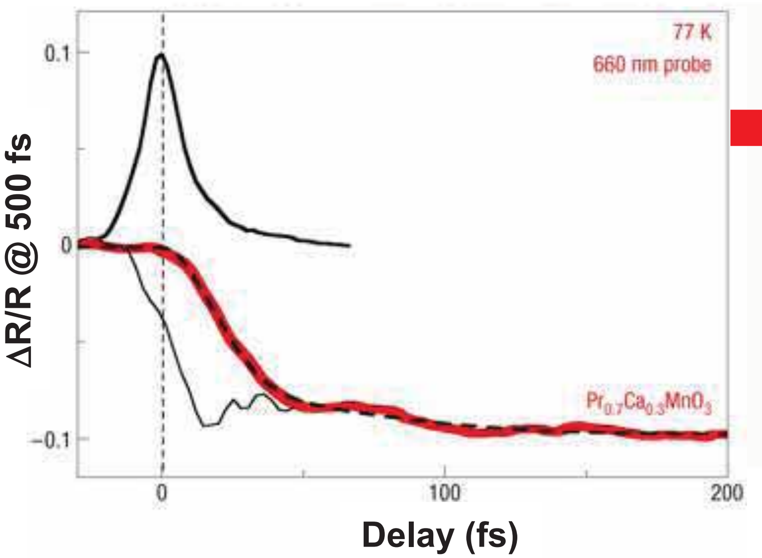
- applied magnetic field (CMR)
- pressure
- **ultrafast optical excitation**
- **coherent vib. excitation**
  **Mn-O stretch**

- practical applications
- fundamental physics
  atomic/electronic
  structural dynamics

# Photoinduced Melting of Charge-Ordered State?

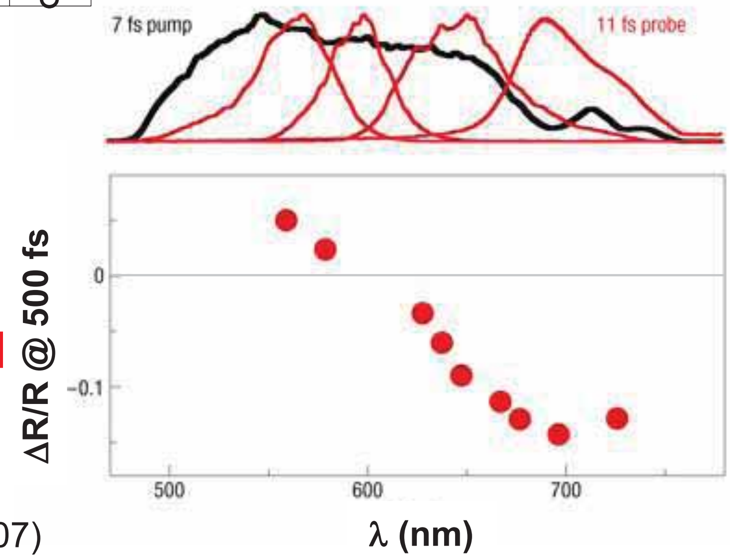



Timescale ~ 50 fs
- structural bottleneck ?

characteristic
ΔR/R spectrum
of the metallic phase

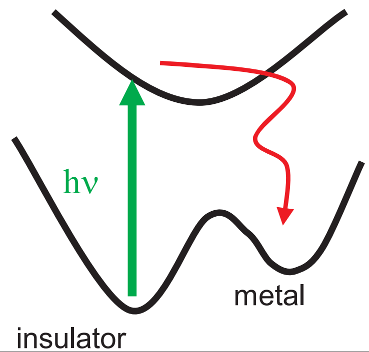



S. Wall et al. *Nature Materials* (2007)

- Sub-10 fs probing resolves phase-transition dynamics
- The IM phase transition does not occur promptly: $\tau_1 = 50$ fs, $\tau_2 = 150$ fs
  - the photo-induced metallic state is not driven directly by carrier injection
  - requires rearrangement in slower degrees of freedom of the system.
- Reflectivity changes are modulated at characteristic frequencies of the system
  - coherently excited vibrational modes 14 THz (low T) and orbital waves 30 THz (room T)

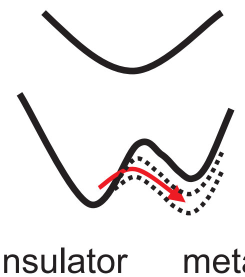
# Phase Control of Competing Ground States

Optical Pumping – Electronic Excited State




- doping – equilibrium /adiabatic
- photoexcitation - nonadiabatic

Electronic Ground State - Vibrational Pumping




- thermal equilibrium – temperature
- non-thermal – femtosecond IR pulses
- coherent vibrational excitation

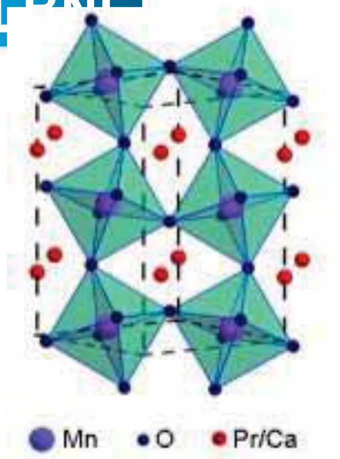
  specific lattice modes

Ground-state vibrational pumping $Pr_{0.7}Ca_{0.3}MnO_3$

- melting of charge ordering in electronic ground state – structural origin?

***Tailored excitation is essential – access physics of interest, recovery dynamics***

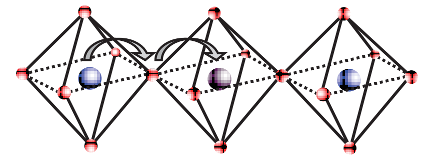
# The Tolerance Factor



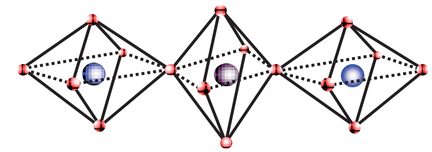

*Orthorhombic Distortion of Cubic Perovskite Structure*

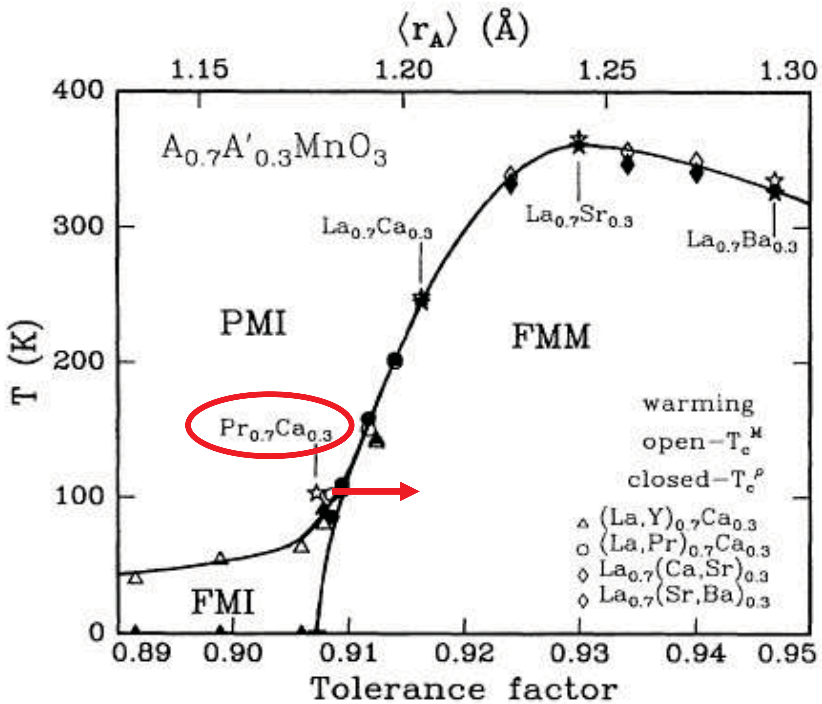
$$\Gamma = \frac{d_{Pr-O}}{\sqrt{2}\cdot d_{Mn-O}}$$

Related to the Mn-Mn electron hopping rate



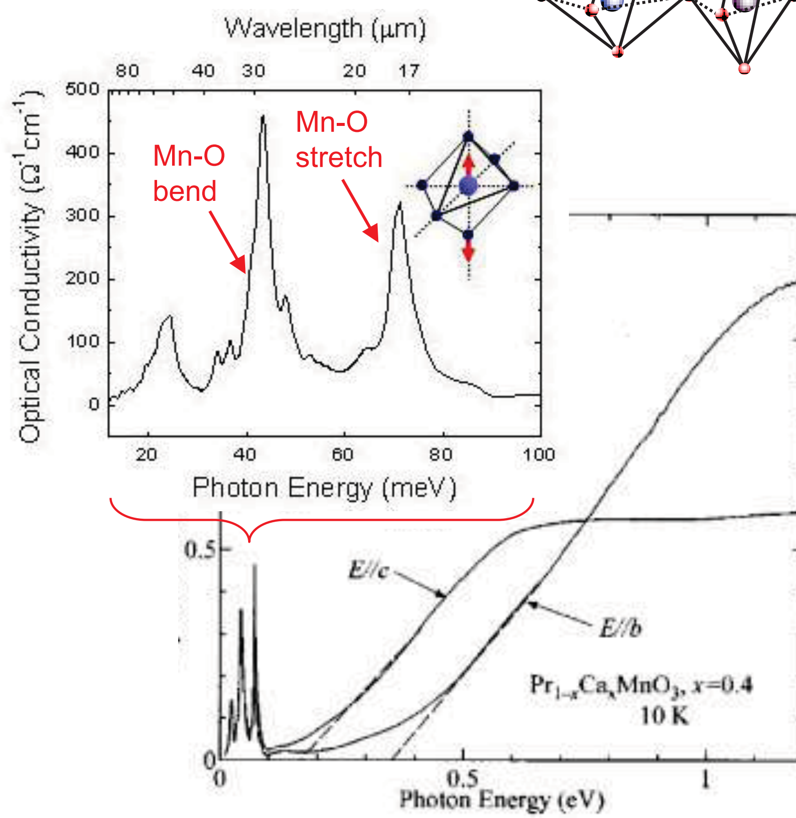
small tolerance factor ⟷ tendency to charge localization



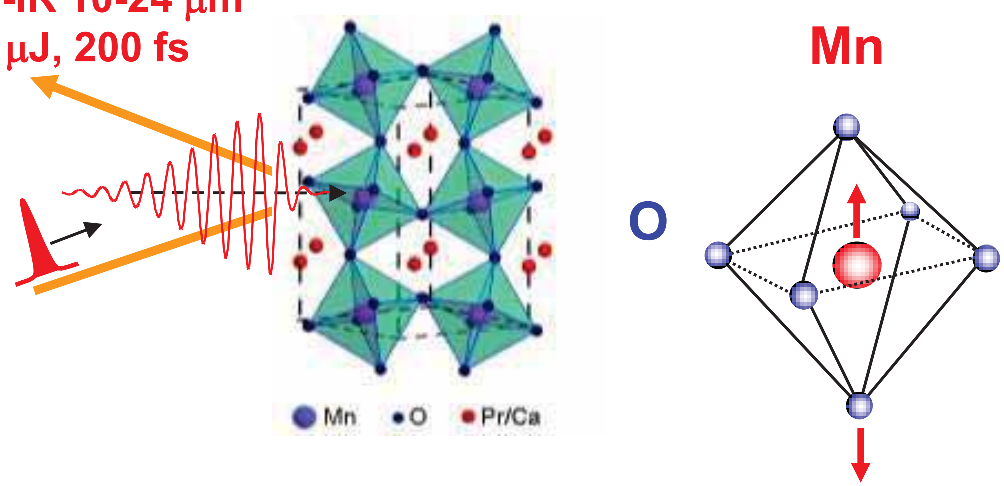


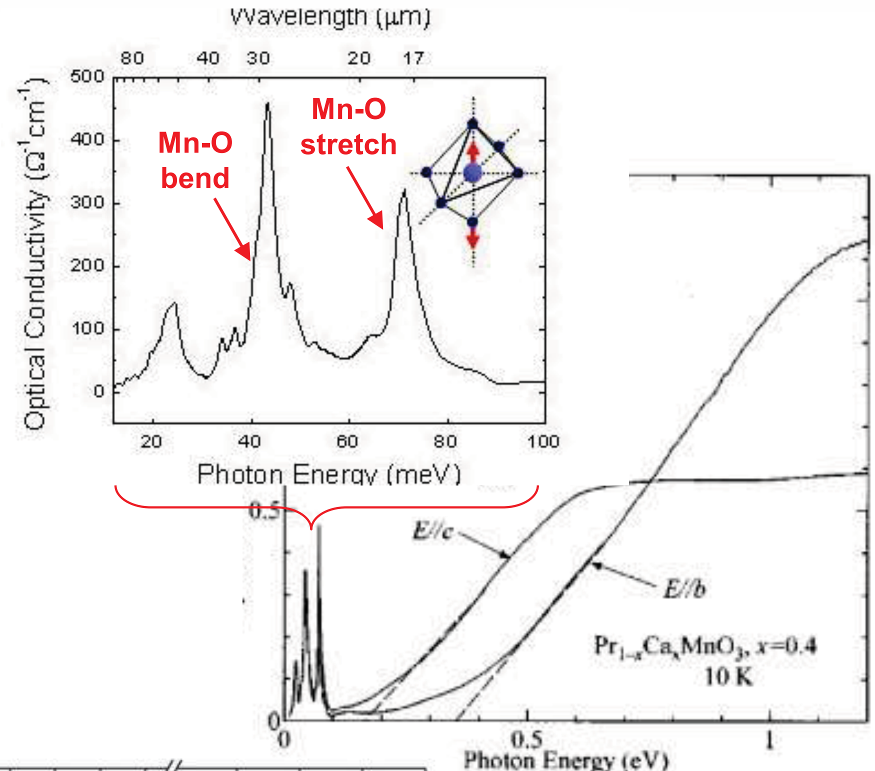

Generalized phase diagram for $A_{0.7}A'_{0.3}MnO_3$

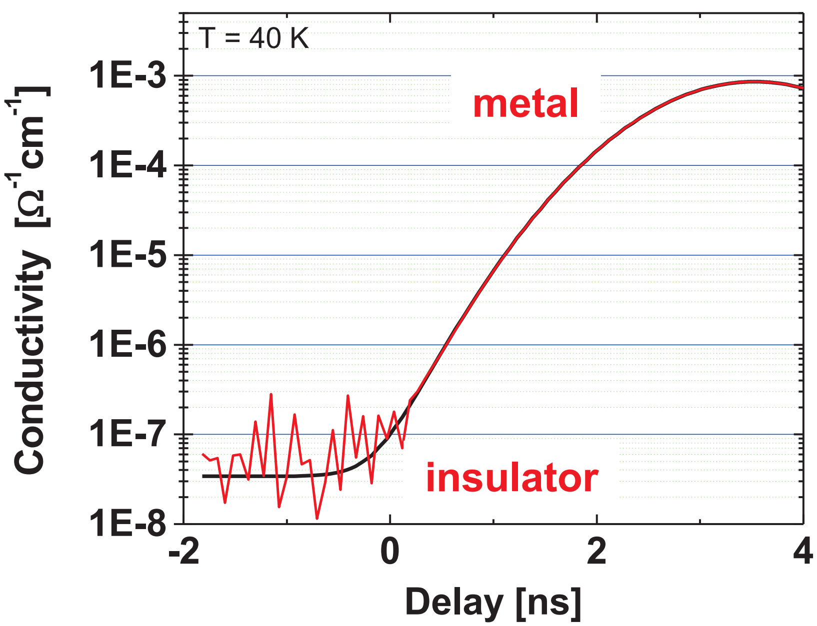
Hwang et al., *Phys. Rev. Lett.* 75 (1995) 914

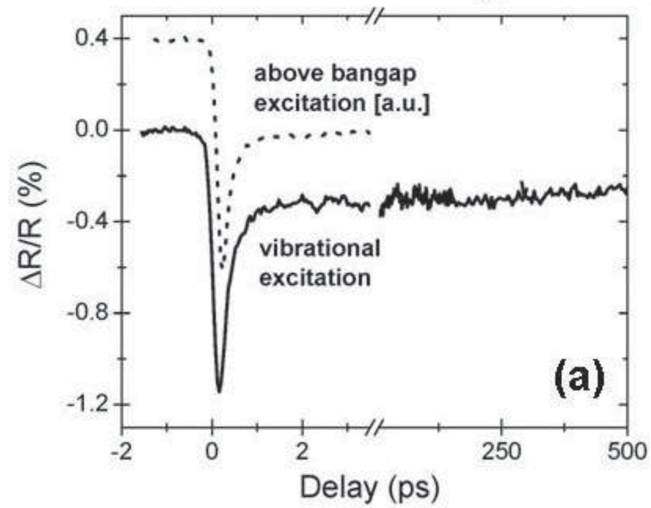


# Ultrafast Control: From Insulator to Metal in ~100 fs

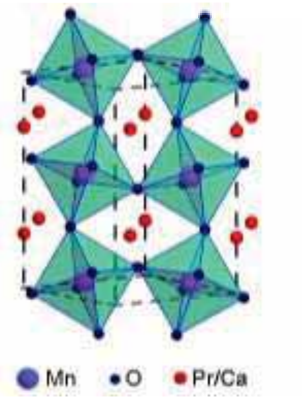


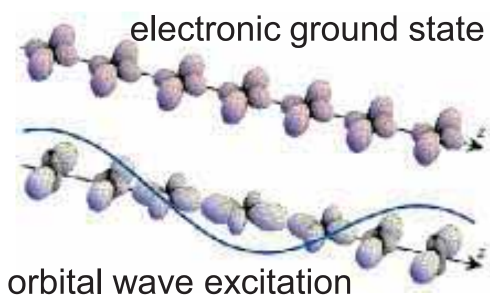



# Ultrafast X-rays - New Insight on Complex Materials

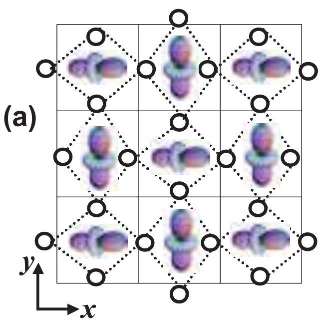



## Vibrationally Driven I-M Transition in a Manganite

- **THz vibrational control of correlated-electron phases**
  targeting specific vibrational modes - Mn-O stretch
- **Ultrafast I-M phase transition - electronic ground state**
  x$10^4$ resistivity change




## *Future Scientific Questions and Challenges:*




**Crystallographic distortion associated with electronic phase transitions?**
*ultrafast x-ray diffraction, EXAFS*

**Magnetic nature of the metallic phase – ferromagnetic?**
*ultrafast x-ray dichroism*

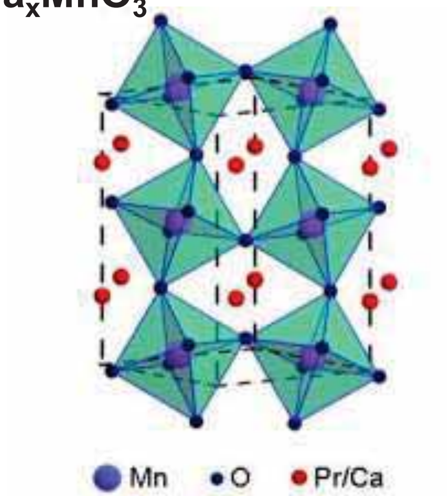
**Dynamics of electronic structure - charge/orbital ordering?**
*ultrafast resonant x-ray diffraction*
*time-resolved soft x-ray microscopy, XPCS (phase separation)*

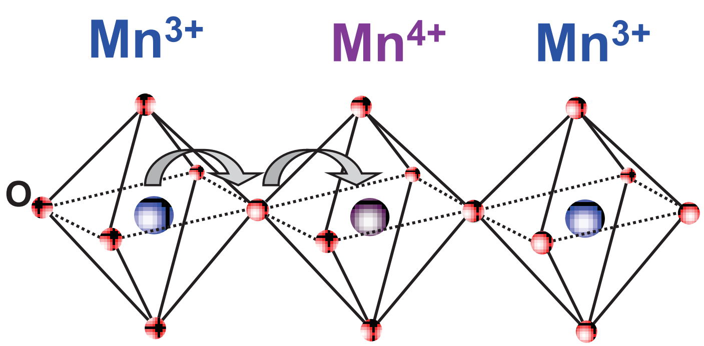
**Dynamics of electronic structure – charge localization/delocalization?**
*ultrafast XAS – 3d-2p hybridization*
*ARPES – dynamic band structure, valence charge distribution*

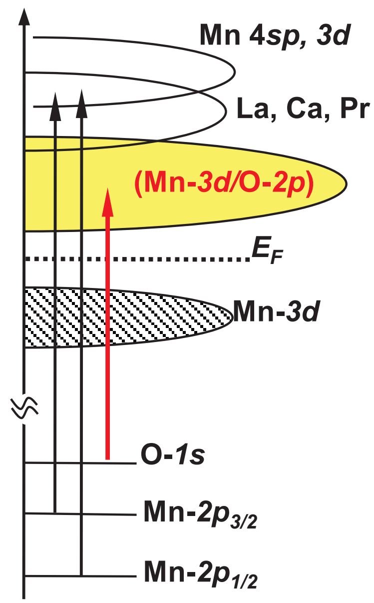
***Ultrafast x-ray techniques relevant for a broad range of complex materials***
(organics, multiferroics, novel superconductors…..)

# Static XAS - Insulator/Metal Transition in Manganites

$Pr_{1-x}Ca_xMnO_3$

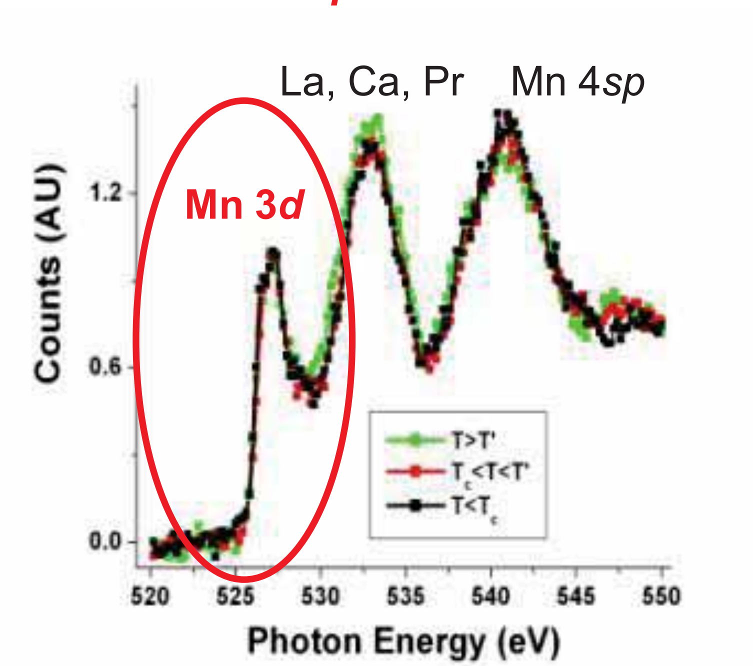


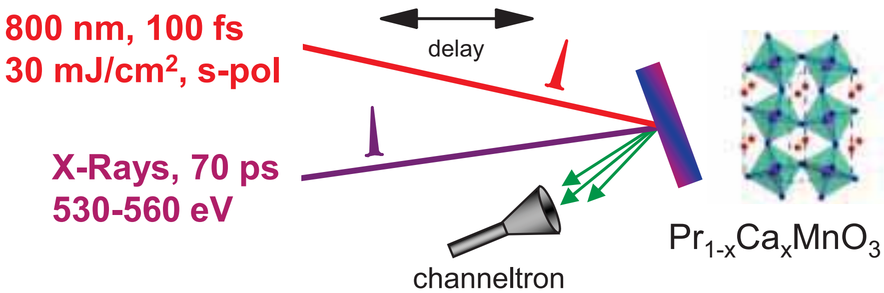

**O K-edge: 1$s \rightarrow$ 2$p$**

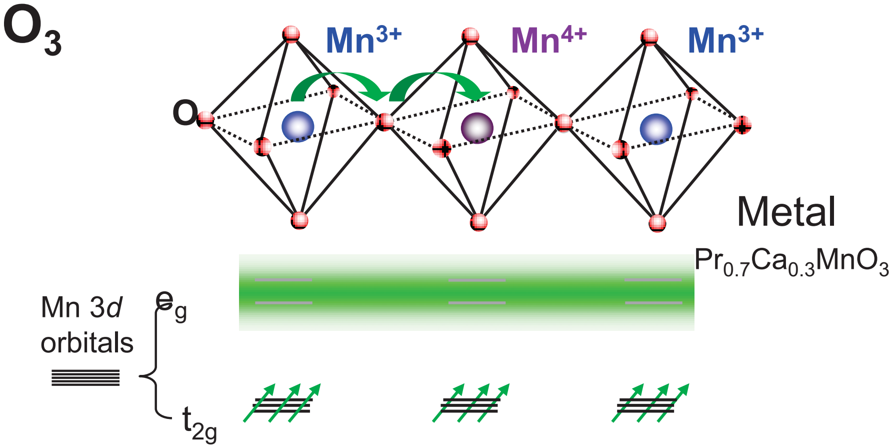
**Pre-edge: unoccupied states of mixed O-2*p* and Mn-3*d* character**

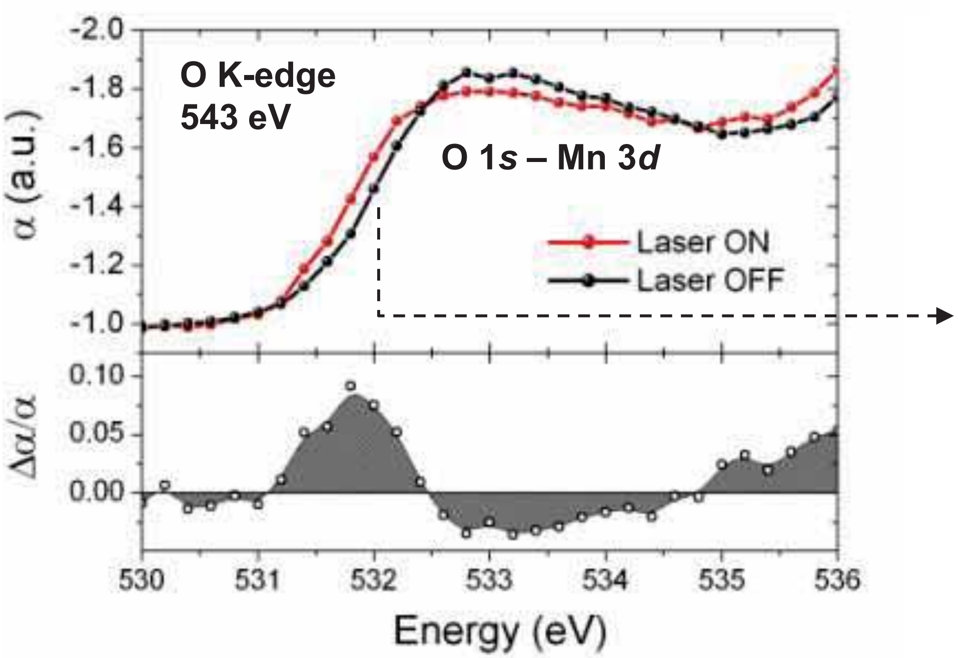


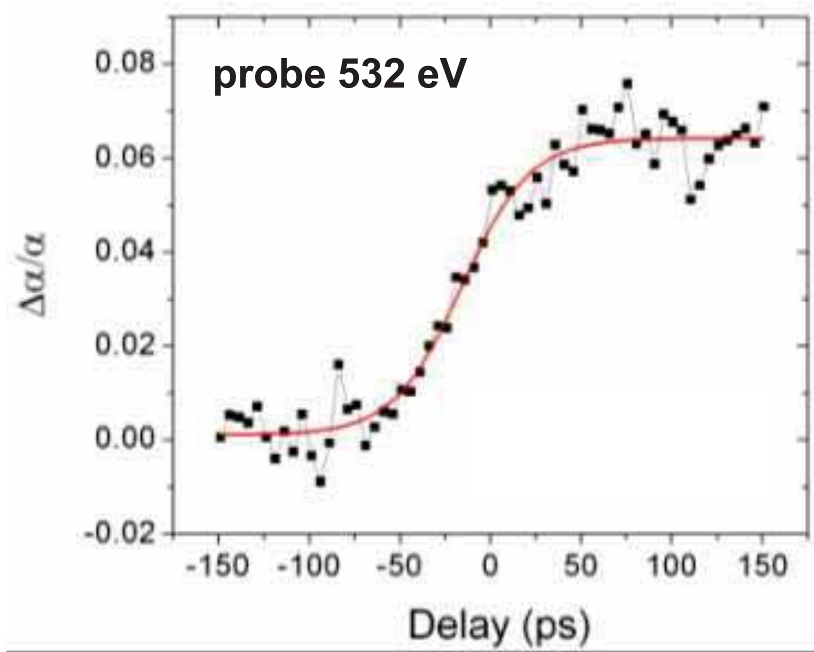

Mannella et al. PRB (2005)

# Time-resolved XAS: Insulator/Metal Transition in Manganite



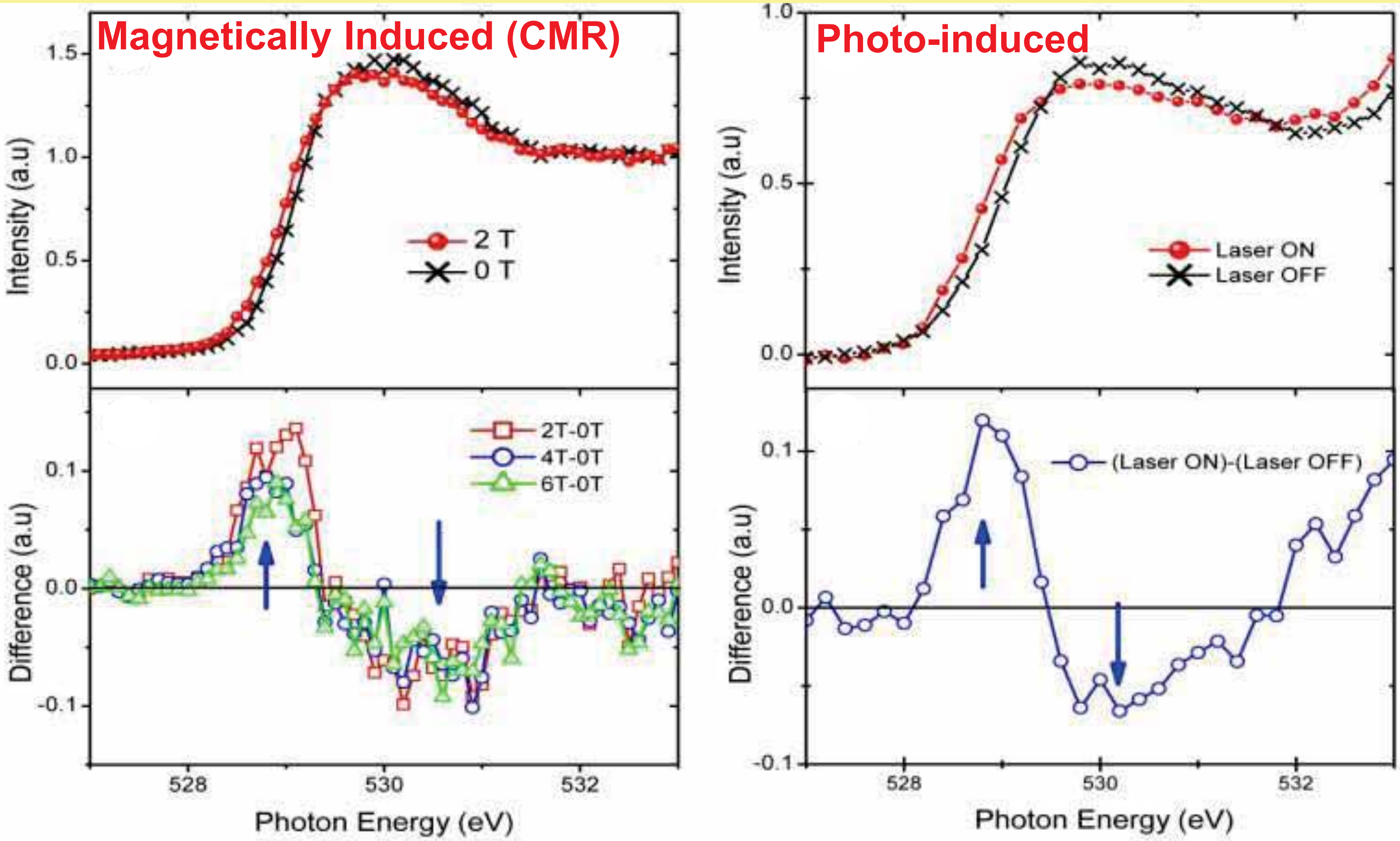




- XAS evidence of I-M transition, DOS spectral weight transferred to absorption threshold
- Mn-3*d*/O-2*p* hybridization
- Modification of 10*Dq* crystal field splitting

# Photoinduced XAS Changes - Evidence of IM Transition

***Photo-induced vs. Magnetically-induced Phase Transition:***

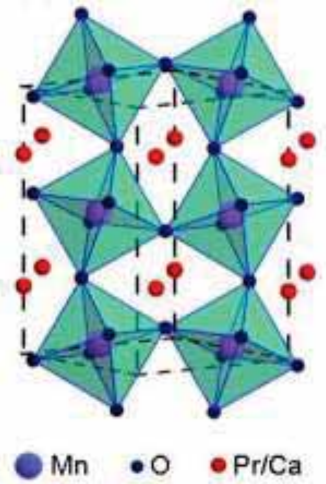
The DOS change in the conduction band appears in the O 1*s* XAS spectrum and spectral weight is transferred to the absorption threshold.

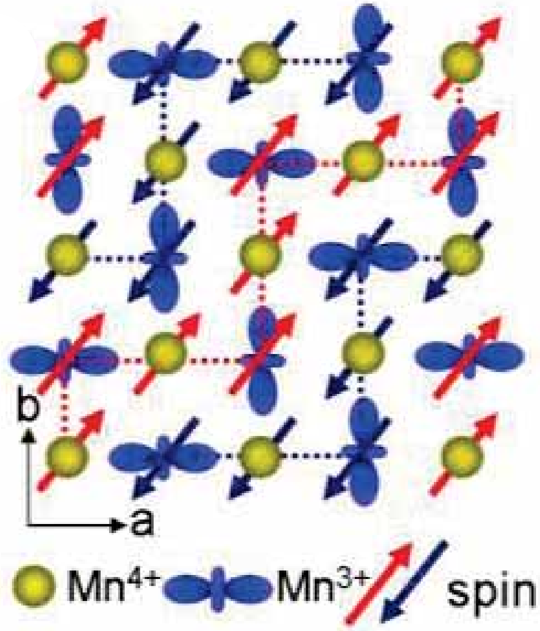



Magnetic measurements in collaboration with John Freeland - APS

# Charge/Orbital Ordering in Manganites

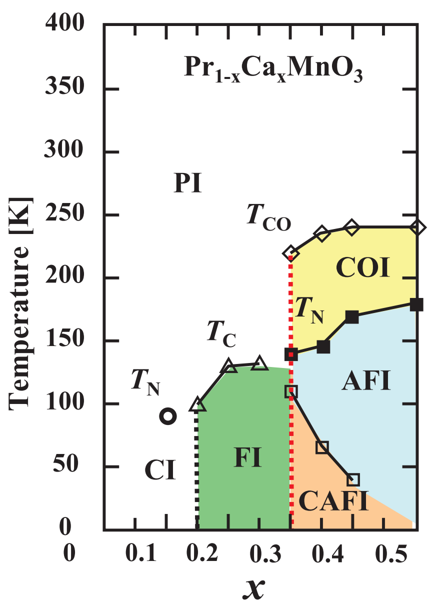
**Time-resolved resonant x-ray diffraction**



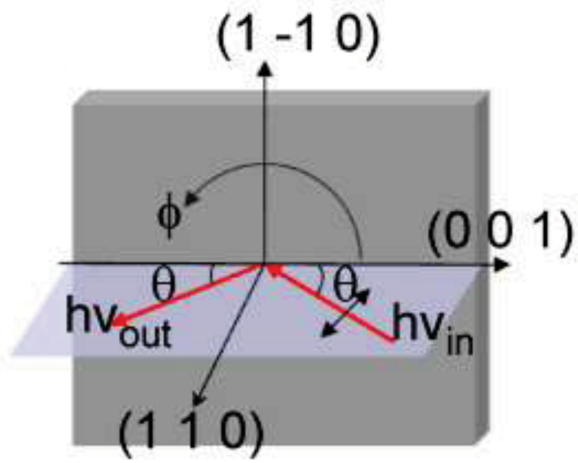



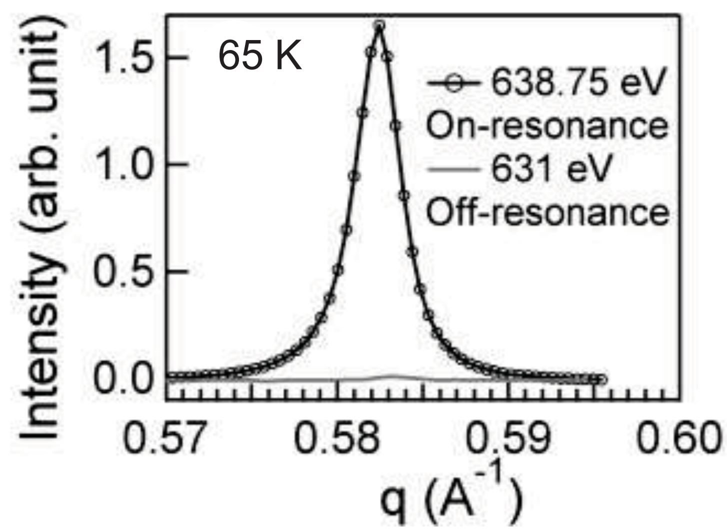

**$Pr_{0.5}Ca_{0.5}MnO_3$**

Mn L-edge (¼ ¼ 0)



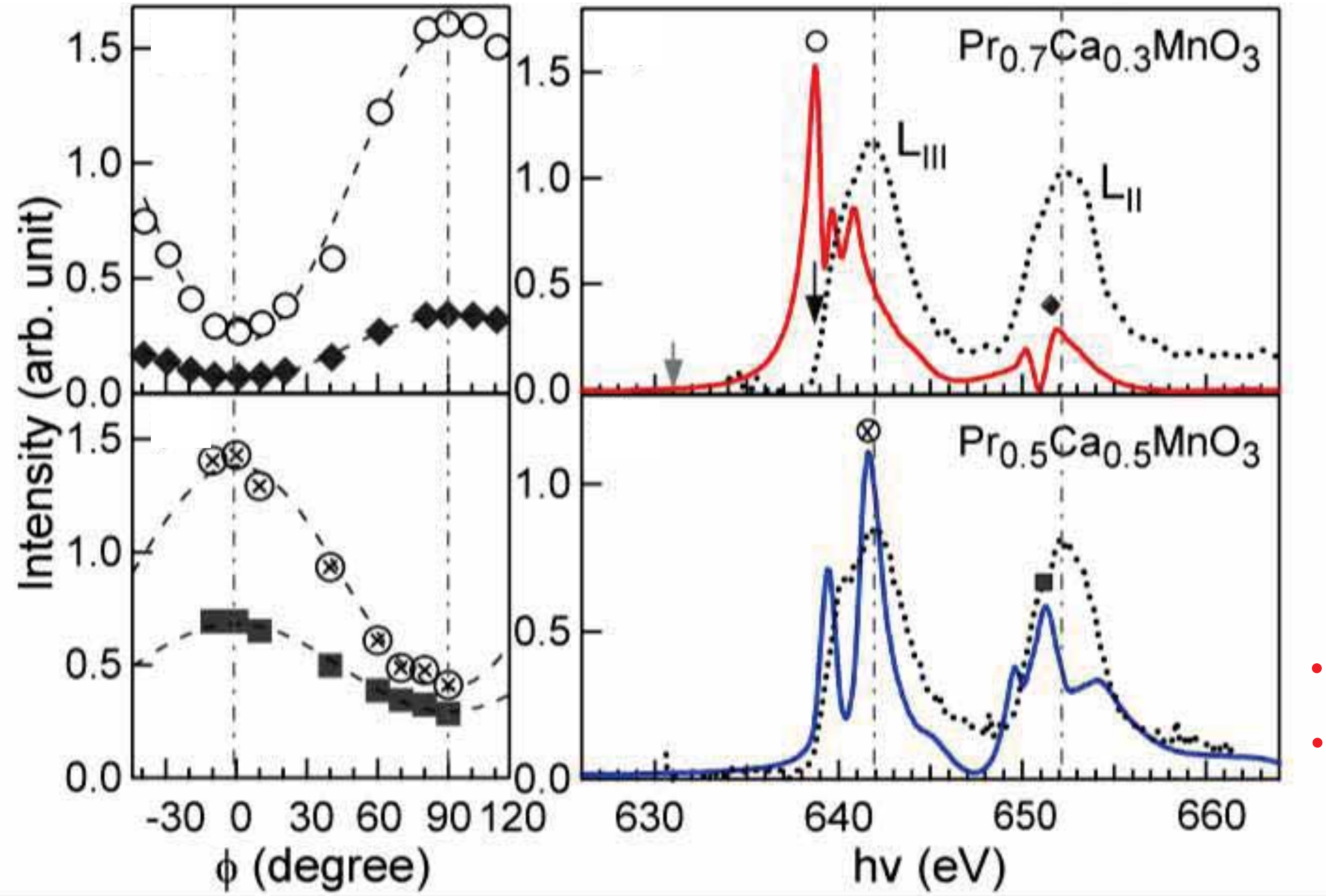

Tokura et al., *PRB*, 1996

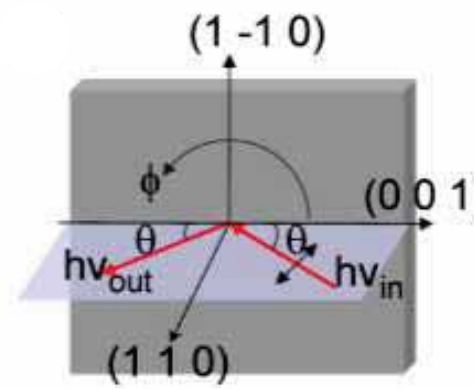


# Charge/Orbital Ordering in Manganites

## *resonant x-ray diffraction*



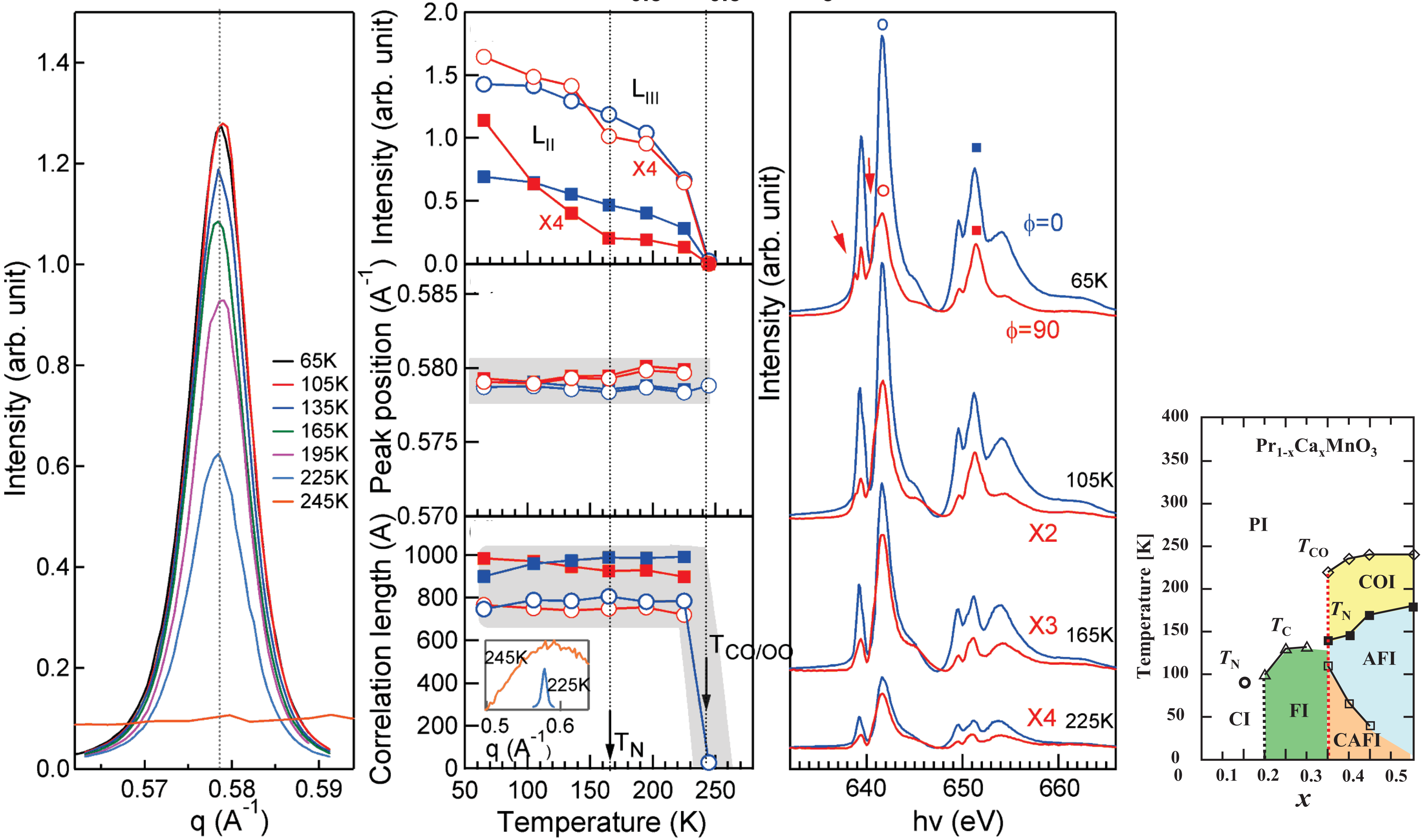

- different RXS profile
- different azimuthal angular dependence

S. Zhou et al. *Phys. Rev. Lett.*, (in press).

**Nature of the ordering is very different!**

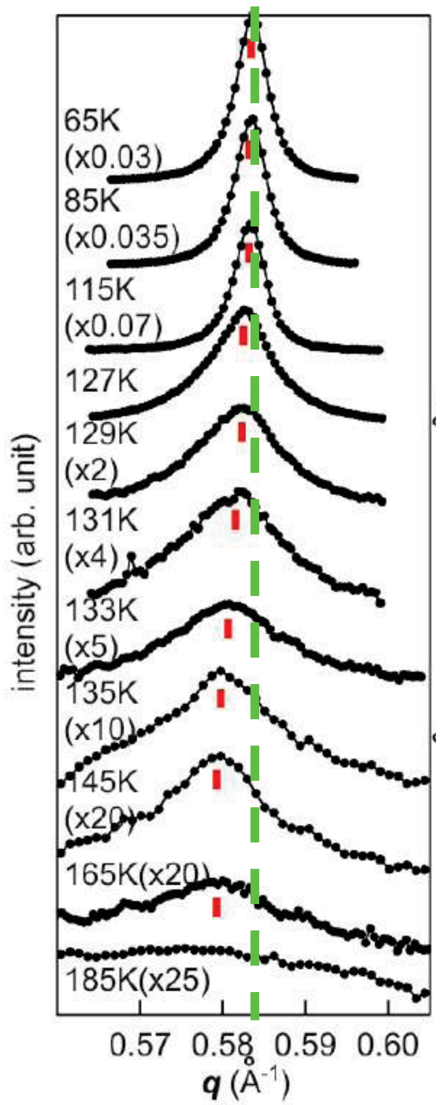
# Charge/Orbital Ordering in Manganites

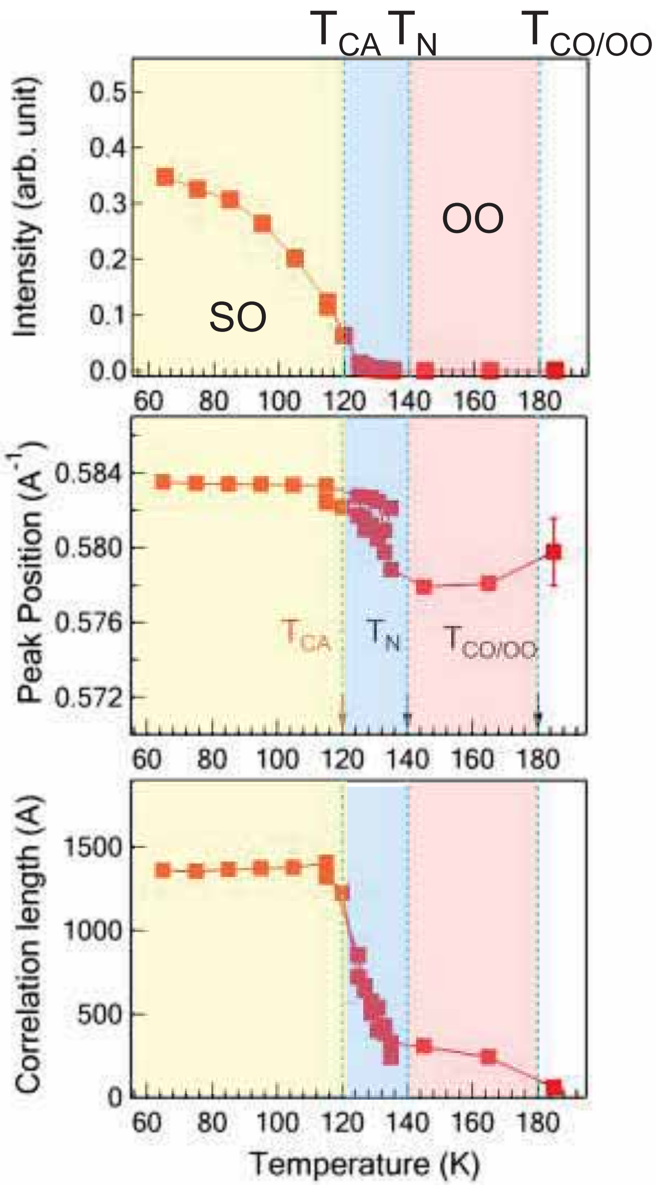
## $Pr_{0.5}Ca_{0.5}MnO_3$



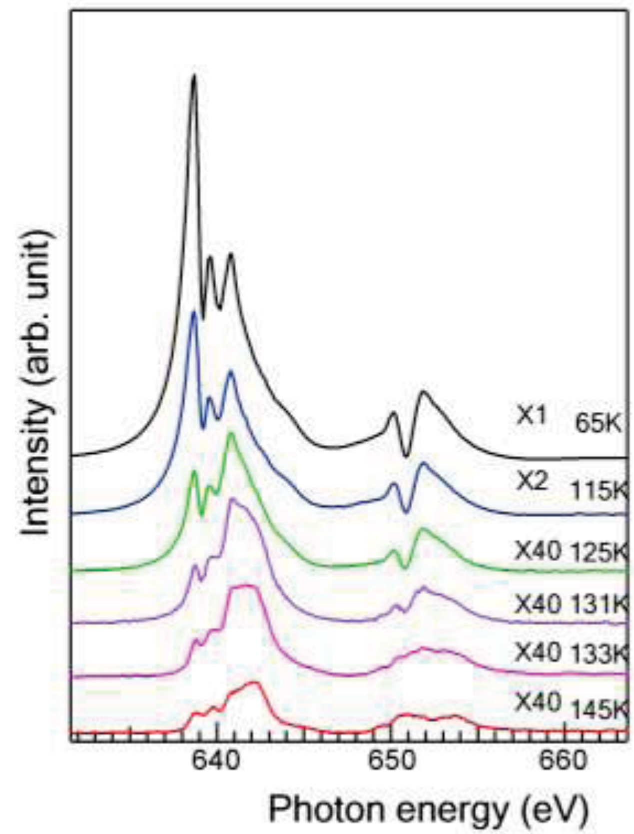
# Charge/Orbital Ordering in Manganites

## $Pr_{0.7}Ca_{0.3}MnO_3$



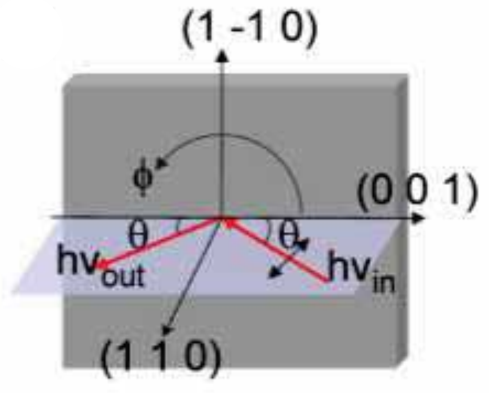

- SO stabilized only below $T_{CA}$
- OO is weak – disrupted by charge disproportionation

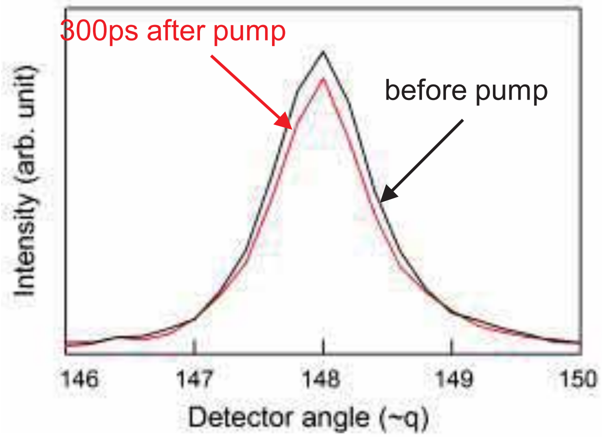


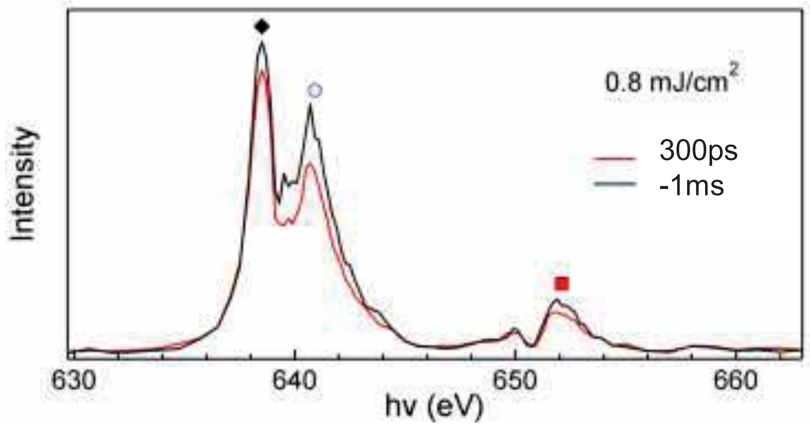

S. Zhou et al. *Phys. Rev. Lett.*, (in press).

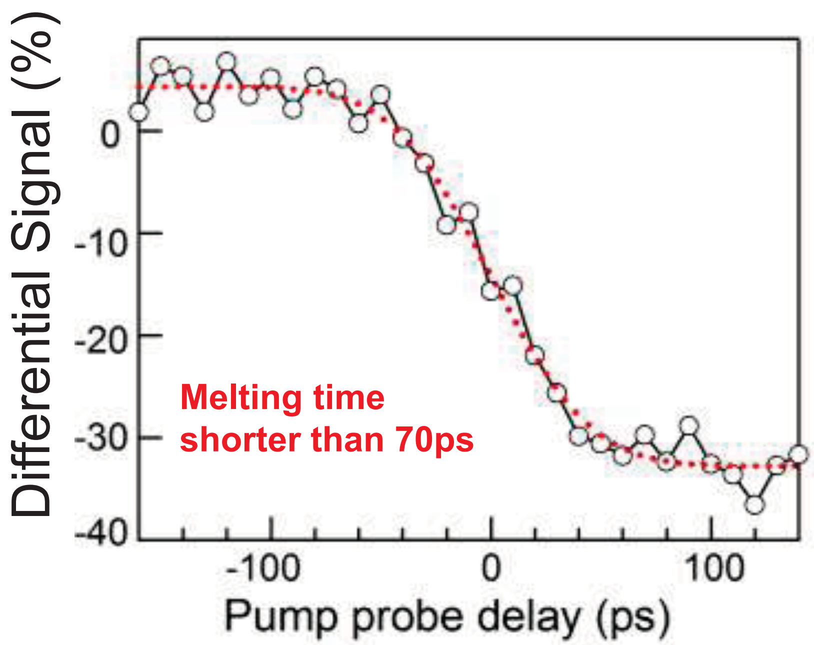
# Charge/Orbit/Spin Ordering Dynamics in Manganites

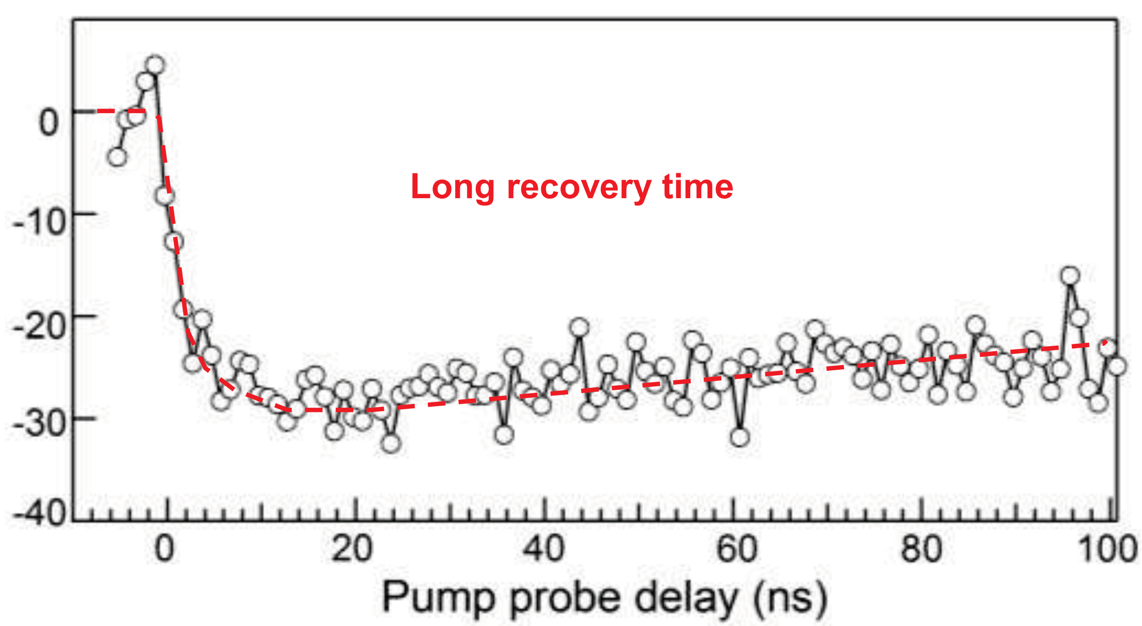
## Time-resolved Resonant X-ray Diffraction - $Pr_{0.7}Ca_{0.3}MnO_3$



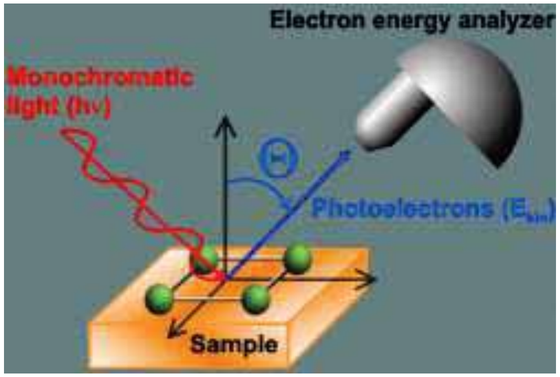



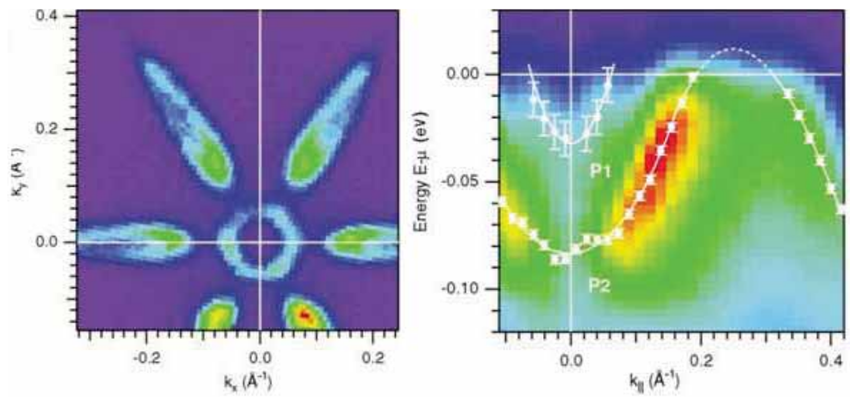



# Dynamic Probe of Electronic Structure - Time-resolved ARPES

(Angle-Resolved Photoemission Spectroscopy)

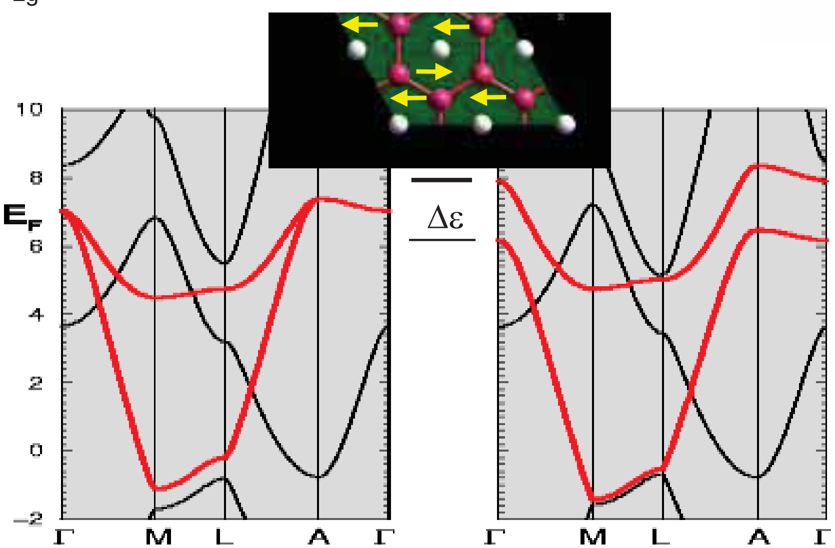



- Photoemission – *occupied* states, XAS – *unoccupied* states
- Time evolution of single-particle spectral density function A(***k***,*ω*)
- Dynamic band structure – response to tailored excitation
- Time-resolved – separation of correlated phenomena in time



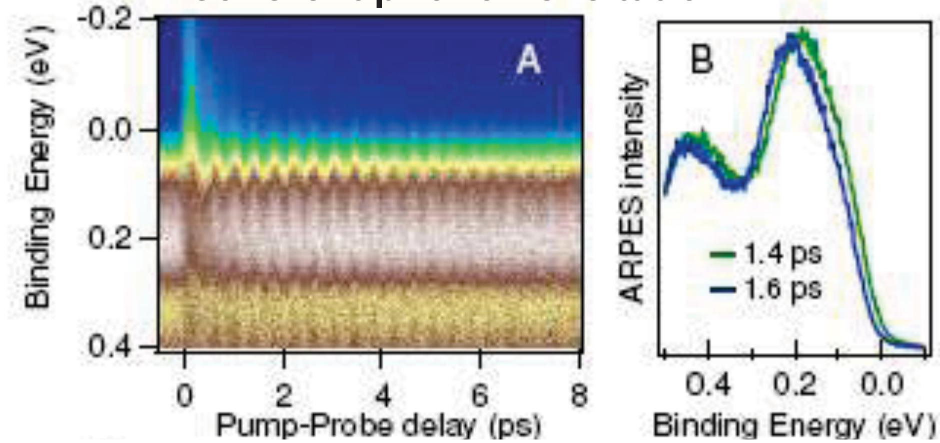

**Bi smuth occupied electronic density of states**

**$MgB_2$**
**Modulation of Electronic Structure**
$E_{2g}$ Mode (17 THz)



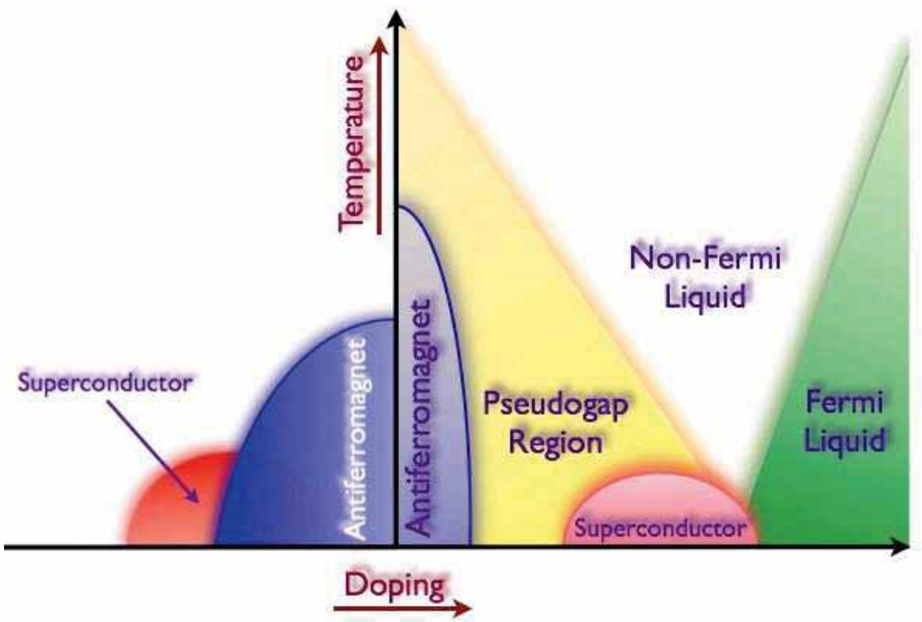

T. Yildrim et al., *PRL* (2001)

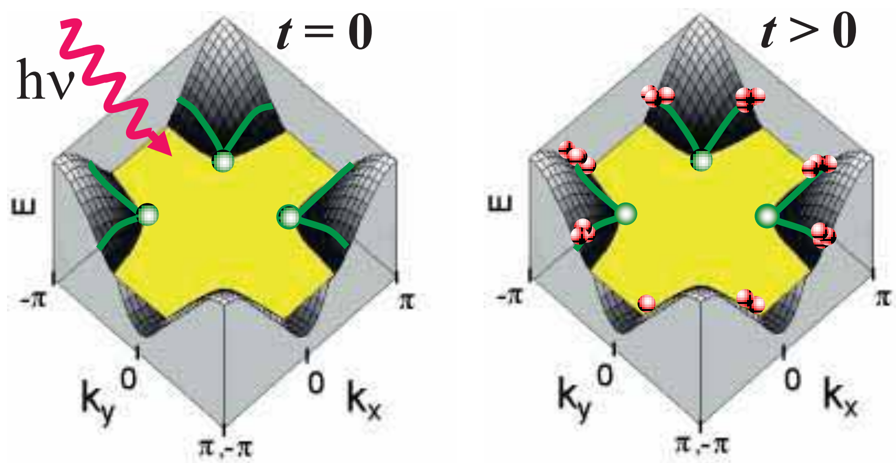
**$1T\text{-}TaS_2$ - Modulation of Hubbard Gap coherent phonon excitation**




Perfetti, et al. *PRL*, **97**, 067402 (2006)

# High-$T_c$ Superconductors (HTSC)




momentum-resolved quasiparticle dynamics

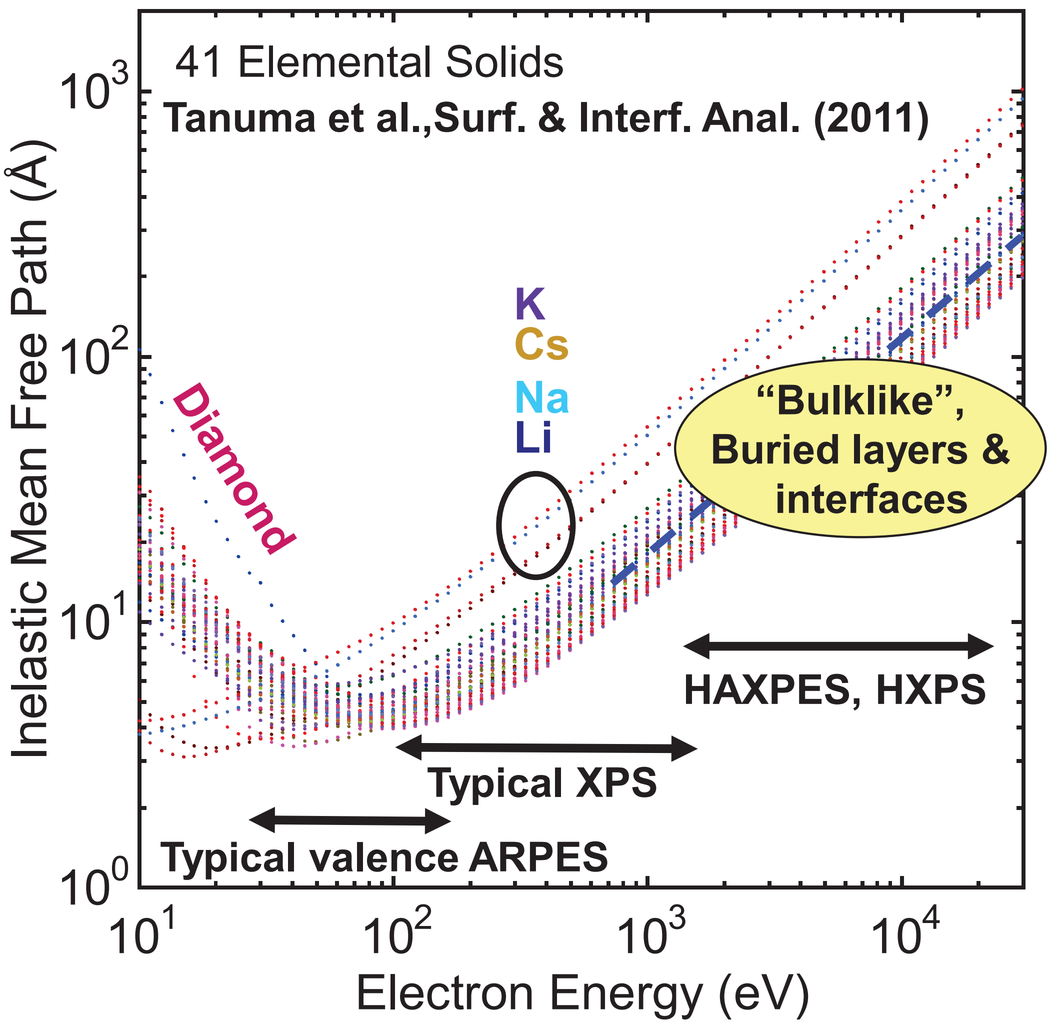
**Controlled perturbation of superconducting state (near-equilibrium)**

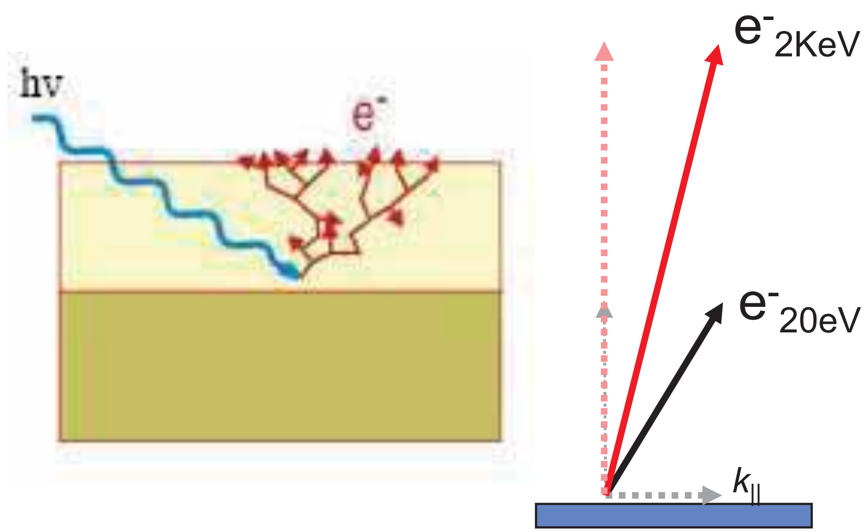
- Identify specific modes associated with superconducting state
- Observe re-establishment of SC from near-by states (e.g. transient pseudogap)
- Resolve this process with *time*, *energy*, *spin*, and *momentum* resolution

*Time and spin-resolved ARPES is a powerful now tool to understand a wide class of complex materials: topological insulators, CMR compounds, multiferroics, etc.*

# Time-resolved ARPES at KeV Energies

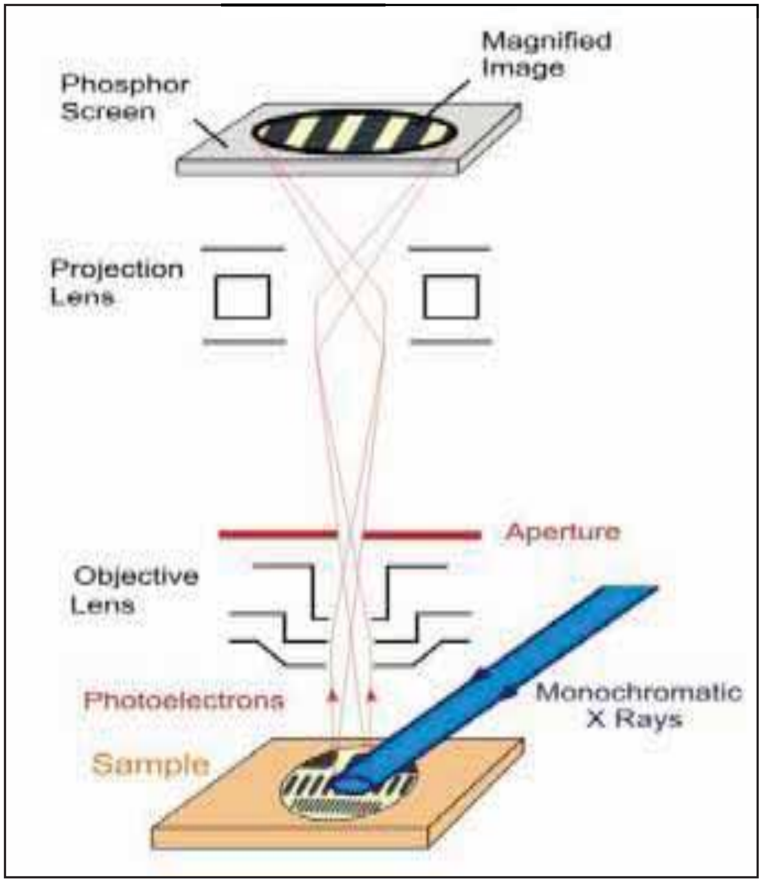
Electrons interact strongly
Surface Sensitivity – 5-20A

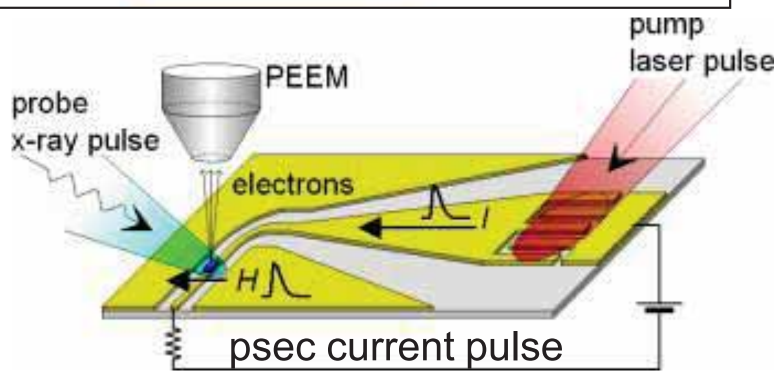


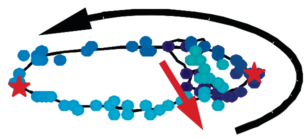

- KeV energy (10-100 meV res.)
  - bulk penetration (VUV sources)
- Space charge distortion of EDC
  low flux/pulse ⇔ high rep. rate
- Electron dynamics
  rapid recovery ⇔ high rep. rate

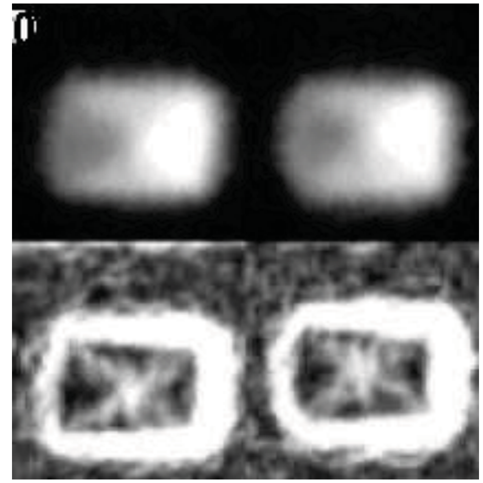
# X-ray Photoemission Electron Microscopy: XPEEM

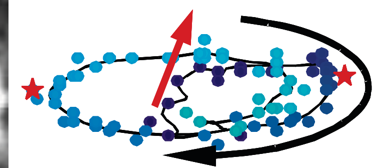



Vortex dynamics
micron-size Co
patterns

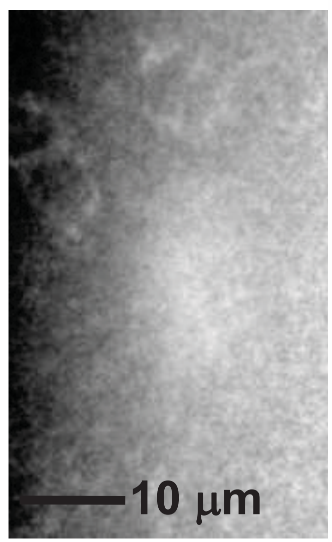


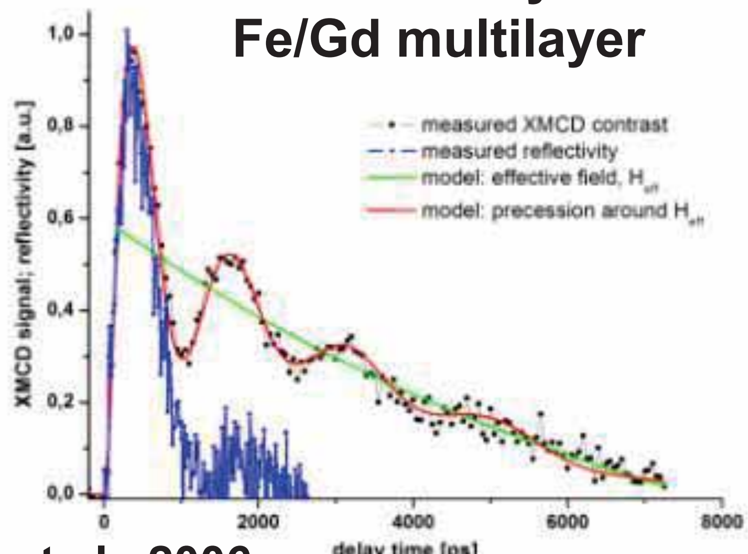




S.B. Choe et al.,
Science 2004

Reorientation Dynamics
Fe/Gd multilayer

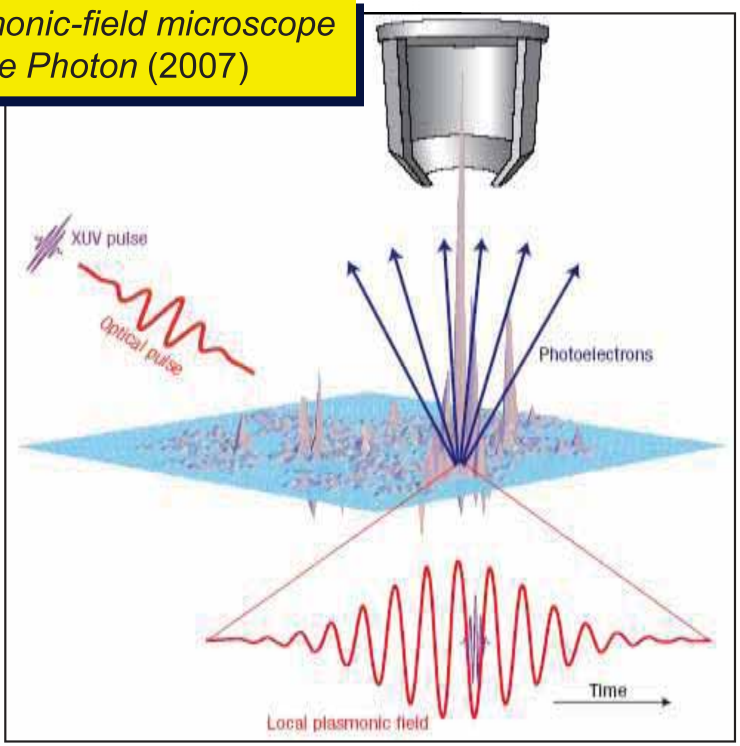



T. Eimüller et al., 2006

# Plasmonic Nanoscale Optical Manipulation

*Attosecond nanoplasmonic-field microscope*
Stockman, *Nature Photon* (2007)




***Why high-rep-rate ultrafast X-ray source?***

**Plasmonic systems:**

- **THz bandwidth and nm localization**
  **⇒ nm spatial and fsec temporal resolution**
- **Current optical and EUV methods lack both spatial and temporal resolution**

**ERL:**
**Time-resolved photoemission electron microscopy (PEEM)**

- **Energy resolved visible pump – x-ray probe PEEM**
  **- high x-ray photon energy ‘*freezes*’ the surface potential in the kinetic energy of the photo-electron**
- **Coulomb interaction dictates only a few electrons/shot**
  **high repetition rate is essential**

# Probing Electron Correlation in Solids

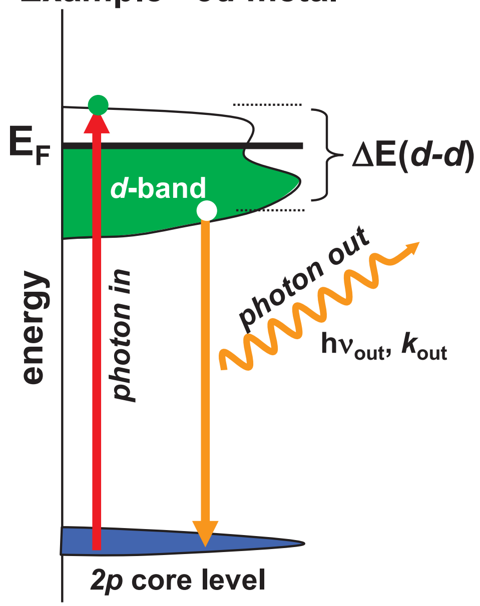
## Inelastic X-ray Scattering

**Electronic Structure:**

| | |
|---|---|
| **Photoemission (ARPES)** | **A($k$,ω) - single-particle spec.** |
| **Inelastic Neutron Scattering (INS)** | **S($q$, ω) - spin fluctuation spec.** |
| **Inelastic x-ray scattering (IXS)** | **S($q$, ω) - density-density *correlation*** |

**(X-ray Raman, q>0)**

**Example - 3*d* metal**

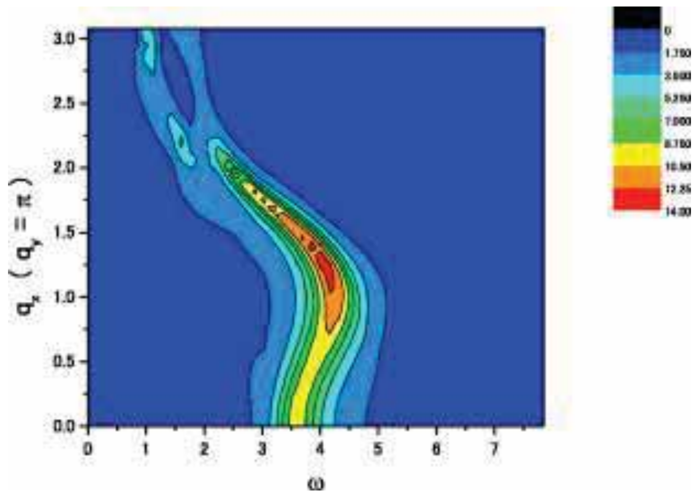



**Energy conservation:**

$\omega_{out} = \omega_{in} - \Delta E(d\text{-}d)$

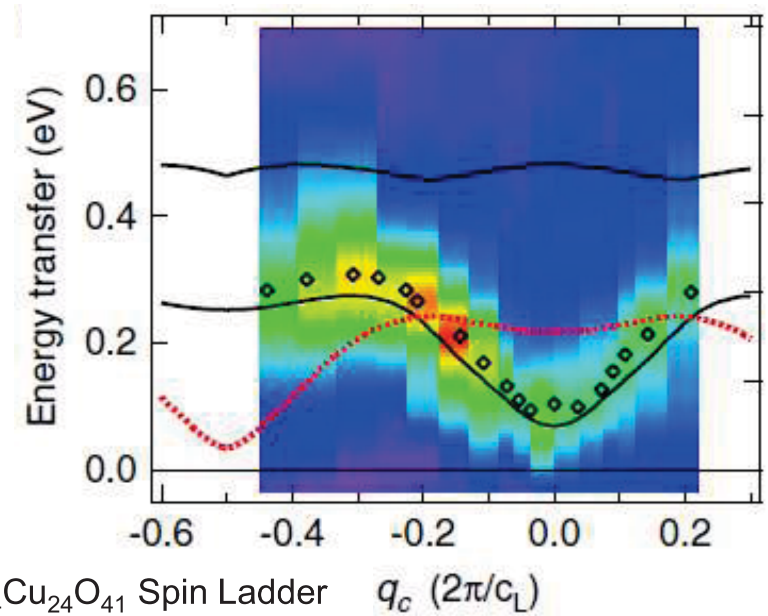
**Momentum conservation:**

$k_{out} = k_{in} - \Delta k(d\text{-}d)$




Density Correlation Function
Doped Mott Insulator

Lee et al. PRB, 2003




$Sr_{14}Cu_{24}O_{41}$ Spin Ladder
Schlappa et al., PRL (2009)

**Highly Optimized Photon Source – Scientific Impact**

- **High Average Flux – photons/sec/bandwidth**
- **High Resolution - throughput**

*Time-resolved RIXS: development of correlation S(q,ω) in response to tailored excitation*

## Time-resolved ARPES

- Follow charge correlations (in real time, with $k,\omega$ resolution) as they develop
- Evolution of electronic structure in response to tailored excitations
- Probe $A(k,\omega)$ for states above EFERMI (nominally un-occupied)
- Separate correlated phenomena in the time domain

## Hard X-ray Photoemission

- Bulk sensitive
- Map entire Brillioun zone
- Interface sensitivity
- Electron holography

## Time-resolved Photoemission Electron Microscopy (XPEEM)

- Real-space imaging of electronic structure + time resolution + element specific
- Phase separation, magnetic domains, plasmonics

**ERL Advantages:**

- ➢ Short pulses (~100 fs)
- ➢ High rep-rate (space charge)
- ➢ Hard X-rays

**ERL Challenges:**

- ➢ Few femtosecond (sub-fs) pulses?
- ➢ ~1 MHz (GHz?)
- ➢ Soft X-rays (<1 keV)

# Resonant X-ray Scattering – Electronic Structure

## Elastic:

- Evolution of charge/orbital/spin ordering phenomena
- Long-range (Bragg)
- Short-range (X-ray photon correlation spectroscopy – correlation time/length)
  (see: XDL 2011 Workshops 1, 5, 6)

## Inelastic (X-ray Raman)

- Density-density correlation function $S(q,\omega)$
- Follow charge correlations (in real time, with $k,\omega$ resolution) as they develop

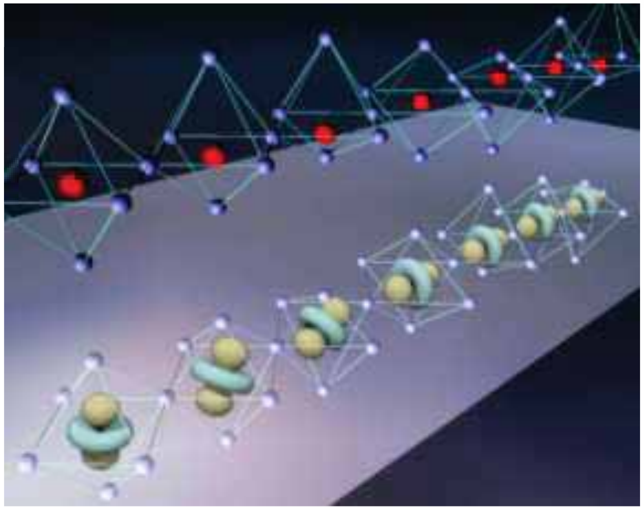
**ERL Advantages**

- ➢ Short pulses (~100 fs)
- ➢ High rep-rate
- ➢ Hard X-rays

**ERL Challenges**

- ➢ Higher energy resolution (RIXS)
  (10 meV ⇔ 200 fs, transform limit)
- ➢ Rep rate: ~100 kHz to 1 MHz, (GHz?, average flux)
- ➢ Soft X-rays (<1 keV)

# Acknowledgements



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