Femtosecond X-ray studies of strongly correlated electron systems

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Outline

- Ultrafast X-Ray experiments (BL 5.3.1)
  - **Time-resolved <u>NEXAFS studies</u> of the insulator-to-metal phase transition in VO_2**
  - **Time-resolved <u>X-ray diffraction</u> studies of polariton dynamics in ferroelectrics**
  - **Time-resolved <u>X-ray absorption</u> spectroscopy of a photoinduced spin crossover reaction in solution**
- Planned X-Ray experiments (BL 6.0)
  - **Structural dynamics and photoinduced phase transitions in Manganites**

Fundamental Scientific Challenge in Condensed Matter:

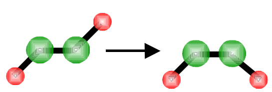
Understanding the interplay between atomic and electronic structure
- beyond single-electron band structure model – correlated systems (charge, spin, orbit, lattice)
- beyond simple adiabatic potential energy surfaces

Fundamental Time Scales in Condensed Matter

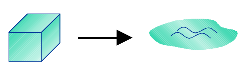
Atomic Structural Dynamics

fundamental time scale for atomic motion
vibrational period: T_{vib} ~ 100 fs

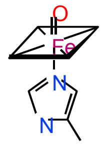
- ultrafast chemical reactions



- ultrafast phase transitions



- surface dynamics
- ultrafast biological processes



Electronic Structural Dynamics

fundamental time scales for electron dynamics
electron-phonon interaction times ~ 1 ps
e-e scattering times ~10 fs
correlation time ~100 attoseconds (a/V_{Fermi})

- charge transfer
- electronic phase transitions
- correlated electron systems
  - charge/orbital ordering
  - CMR
  - high T_c superconductivity

Ultrafast X-ray Science
Rapidly emerging field of research - Physics, Chemistry and Biology

Femtosecond X-ray Science

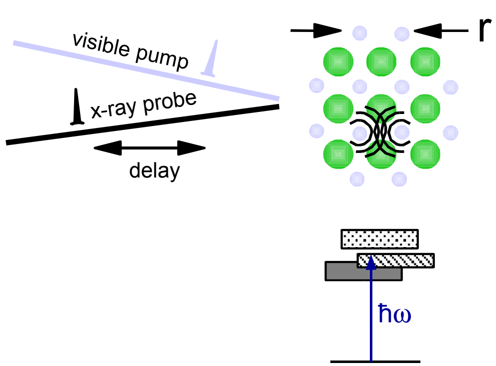
time-resolved x-ray spectroscopy

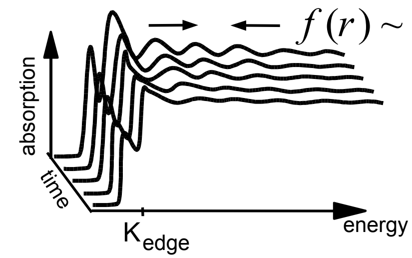
EXAFS – local atomic structure and coordination
(extended x-ray absorption fine structure)

NEXAFS – local electronic structure, bonding geometry, magnetization/dichroism
(near-edge x-ray absorption fine structure)

element specific
molecular systems and reactions
complex/disordered materials

surface EXAFS, µEXAFS ….

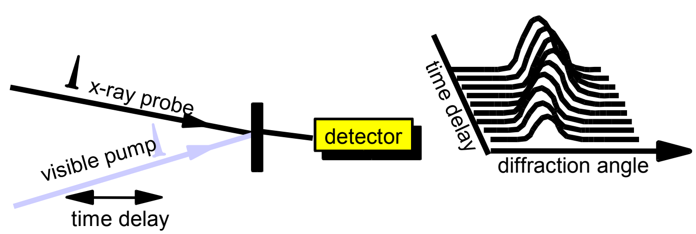


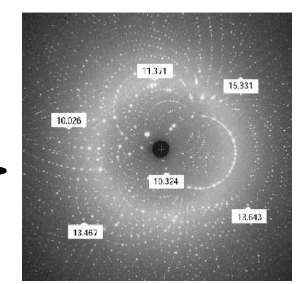


$$f(r) \sim \frac{\sin(2kr + \phi(k))}{kr^2}$$

time-resolved x-ray diffraction

atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons

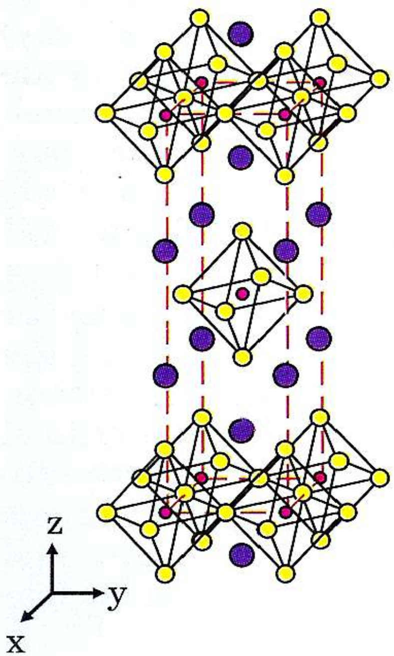




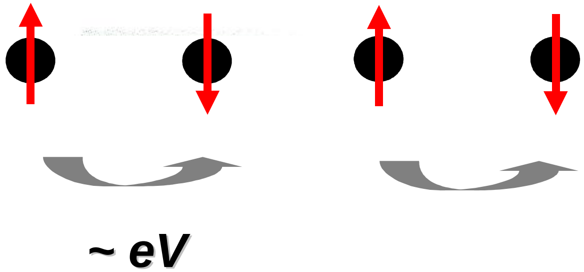
Strongly Correlated Materials

Oxides of Transition Metals

(e.g. Cu, Mn, Ni, V…)



Electrons are strongly interacting

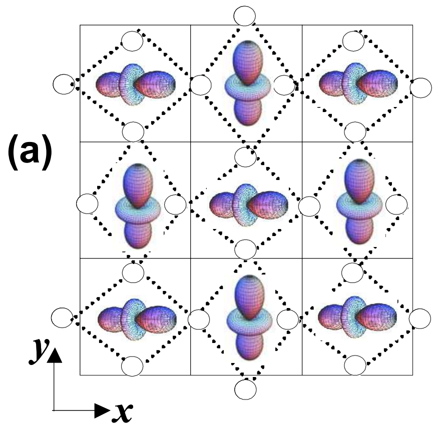


1) Unconventional Phenomena (e.g. Mott Insulator, High-T_c superconductivity, Colossal Magnetoresistance, Metal-Insulator transitions,…….)

2) Interesting phenomena and phase transitions at high temperatures

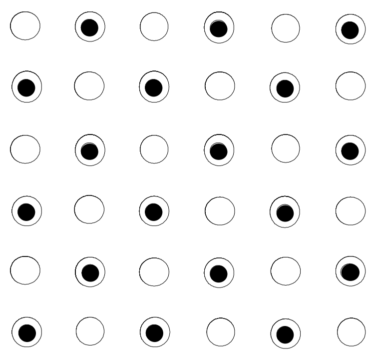
Exotic Ground States in Complex Solids

Jahn-Teller Instability
Orbital order

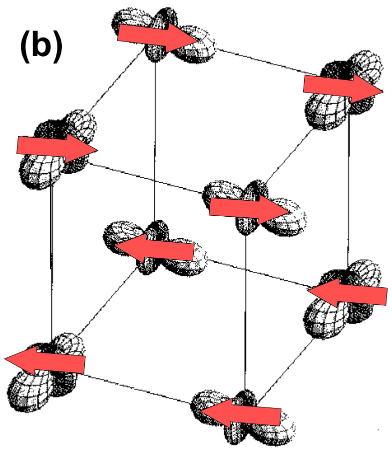


Charge order

Manganites

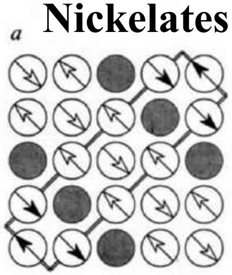


Spin order



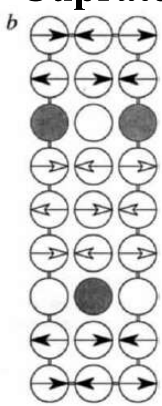
Stripes

Nickelates



NiO_2: $n_h = 0.25$

Cuprates



CuO_2: $n_h = 0.125$

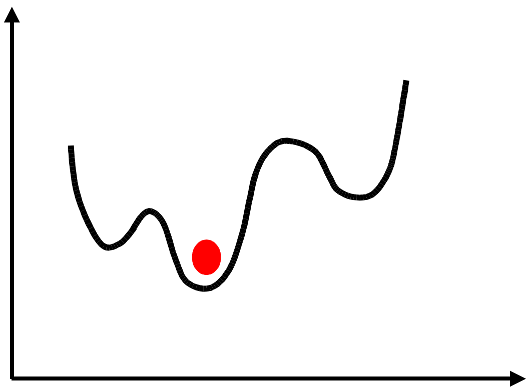
Understand interactions between

- ✓ Atomic arrangements
- ✓ Carrier doping/ordering
- ✓ Magnetic ordering

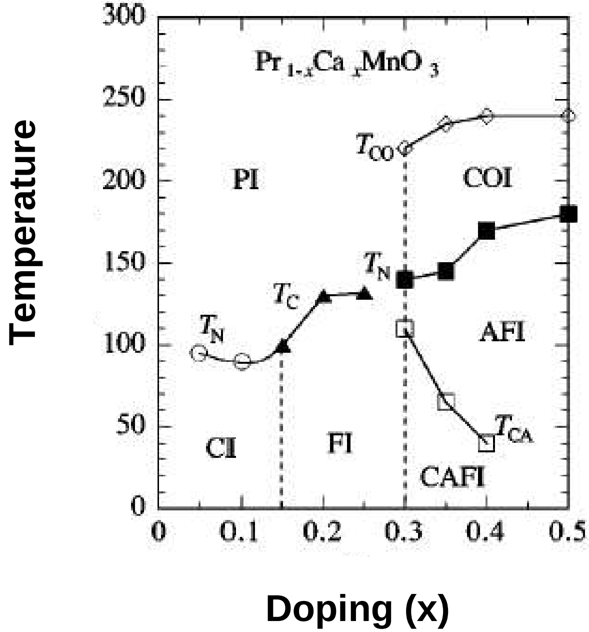
Multi-stability and Phase Competition

Many competing ground states

F (T, H, x, hν, P, E…)



e.g. Manganese Oxides



Phase Control :

Magnetic Field

Photo-excitation

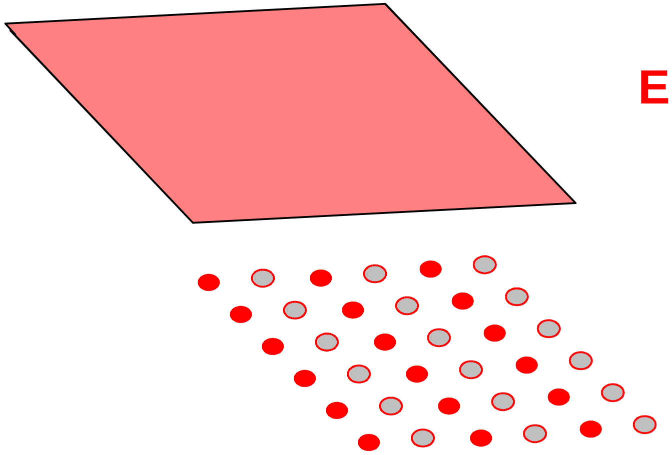
Electric Field

Pressure

………..

Phase of a solid

The “stiffness” of a phase is strongly affected by charge arrangements



The phase of a solid can be controlled by chemical doping or by photo-excitation

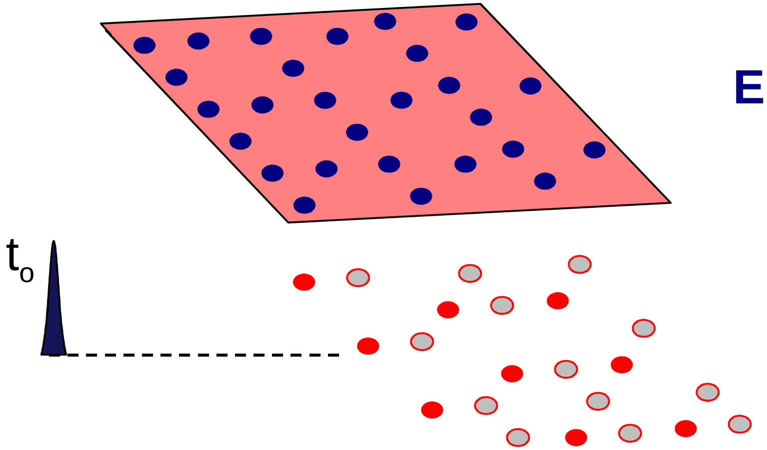
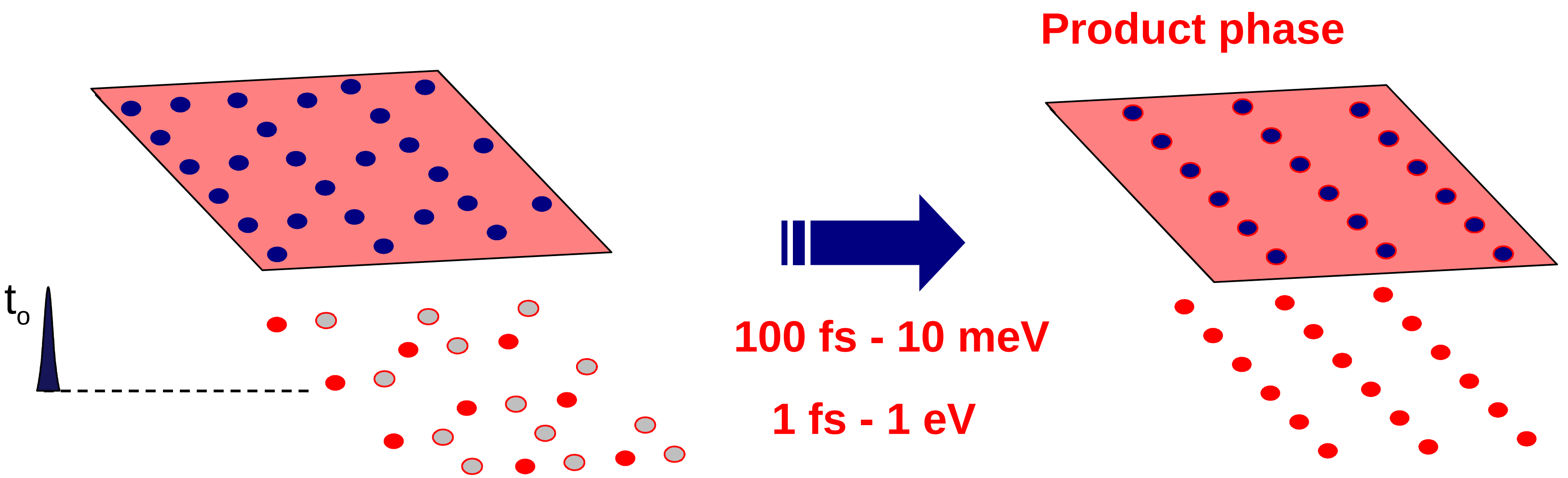


Photo-excitation

✓ Exotic transient phases can be created and controlled

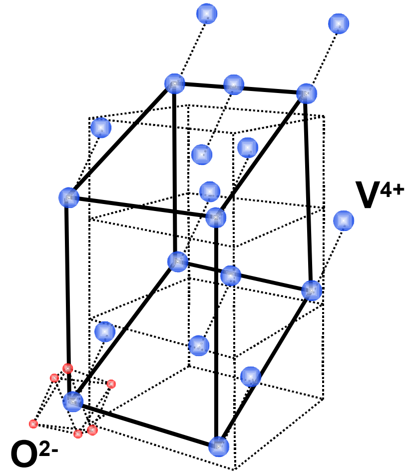
✓ Fundamental correlation mechanisms can be revealed

✓ Giant, ultrafast manipulation of the system's parameters

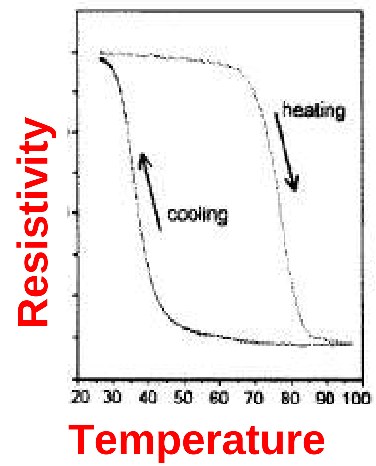


Ultrafast Structural and Electronic Transitions in VO_2

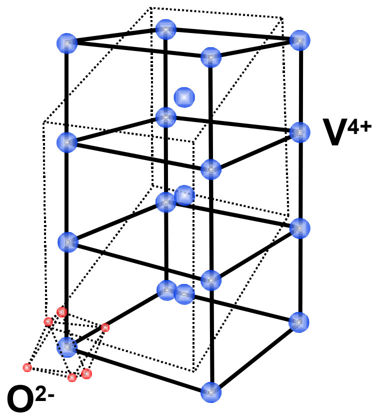
T < 340 K
Monoclinic



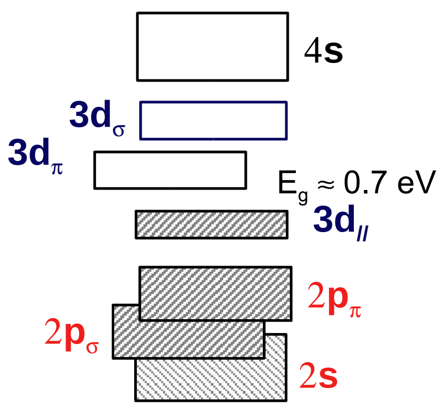
VO_2

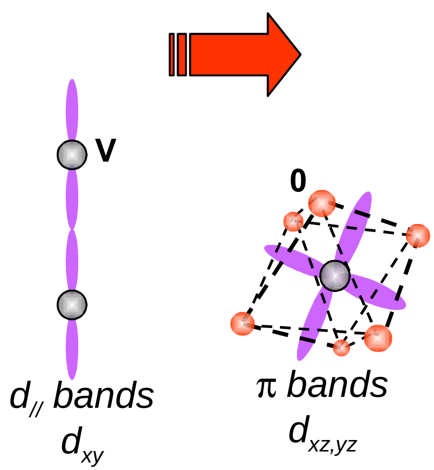


T > 340 K
Rutile

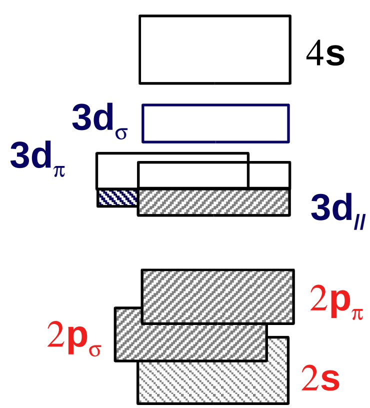


Insulator
low T





Metal
high T



Ultrafast Structural and Electronic Transitions in VO_2

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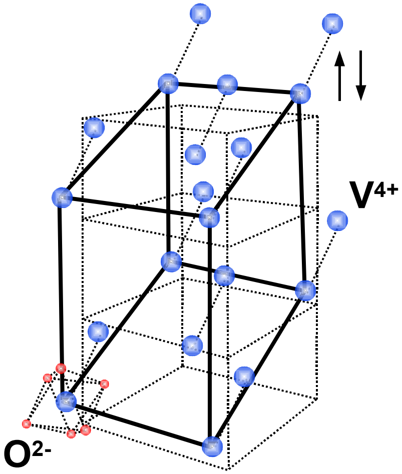
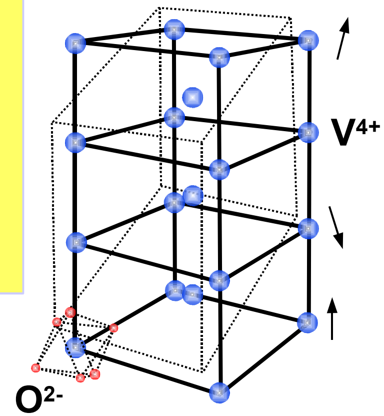
T < 340 K
Monoclinic



VO_2

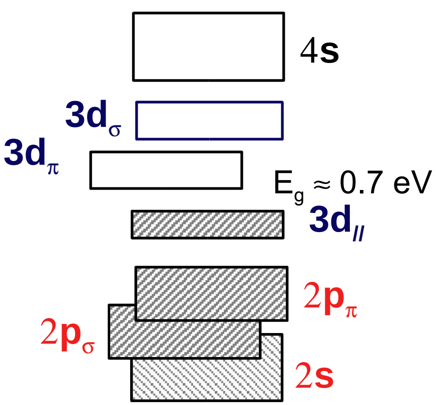
T > 340 K
Rutile

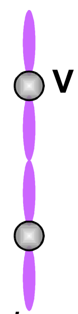


Mott-Hubbard insulator – e-e correlation ?
- Zylberstein and Mott, *PRB* (1975)
- Pouget et al., *PRB* (1974), *PRL* (1975)

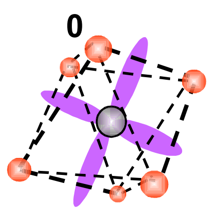
Band insulator – structural component ?
- Goodenough, *Phys. Rev.* (1960)
- Wentzcowitch, *PRL* (1994)

Insulator
low T



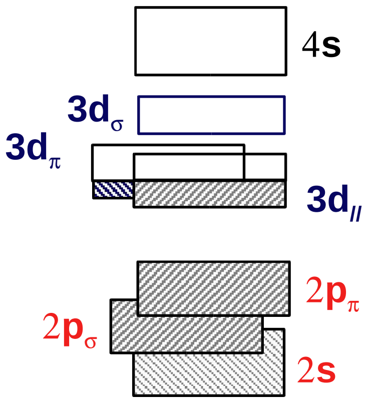


$d_{//}$ *bands*
d_{xy}



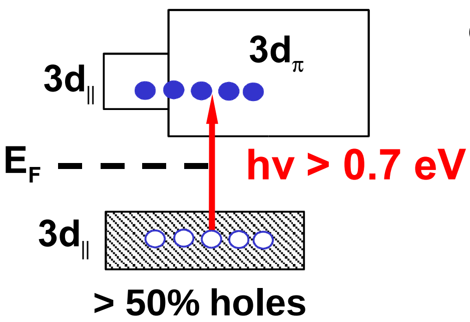
π *bands*
$d_{xz,yz}$

Metal
high T

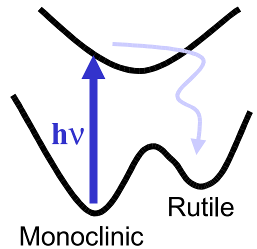


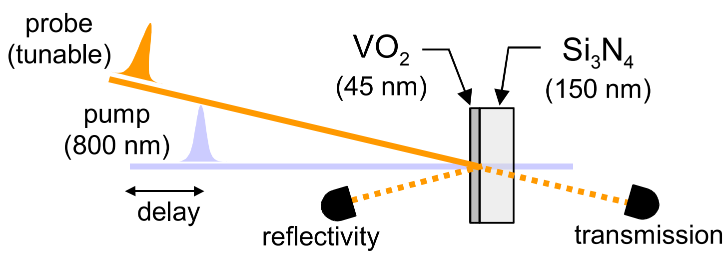
Optical Measurements of VO_2 I-M Transition

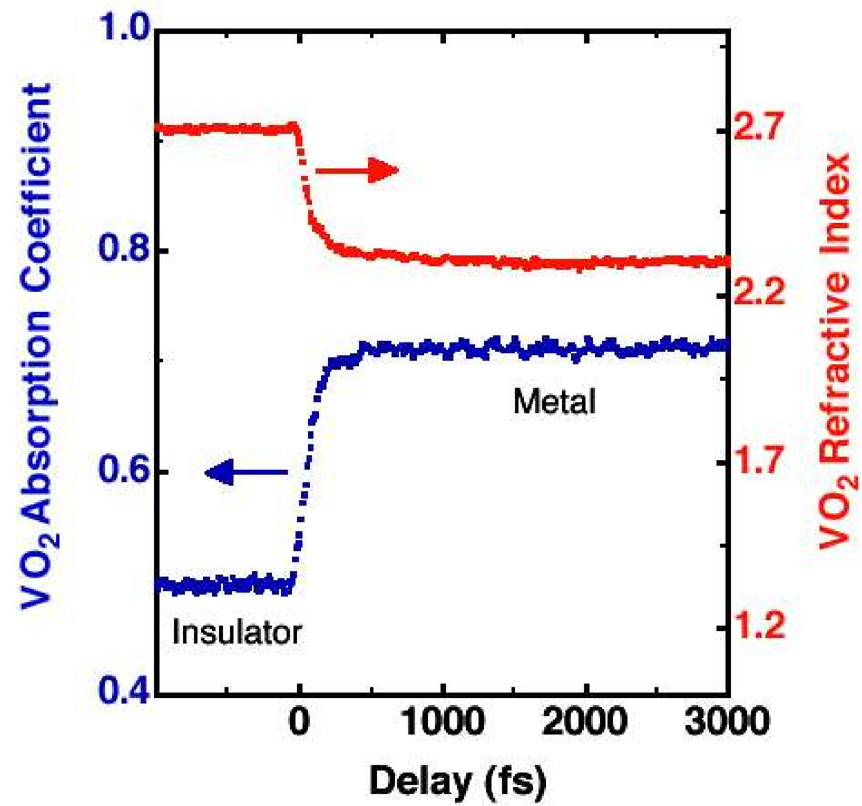
Transient photo-doping - new information compared to adiabatic changes in doping, pressure, temperature, etc.



Optical Pumping – excited state







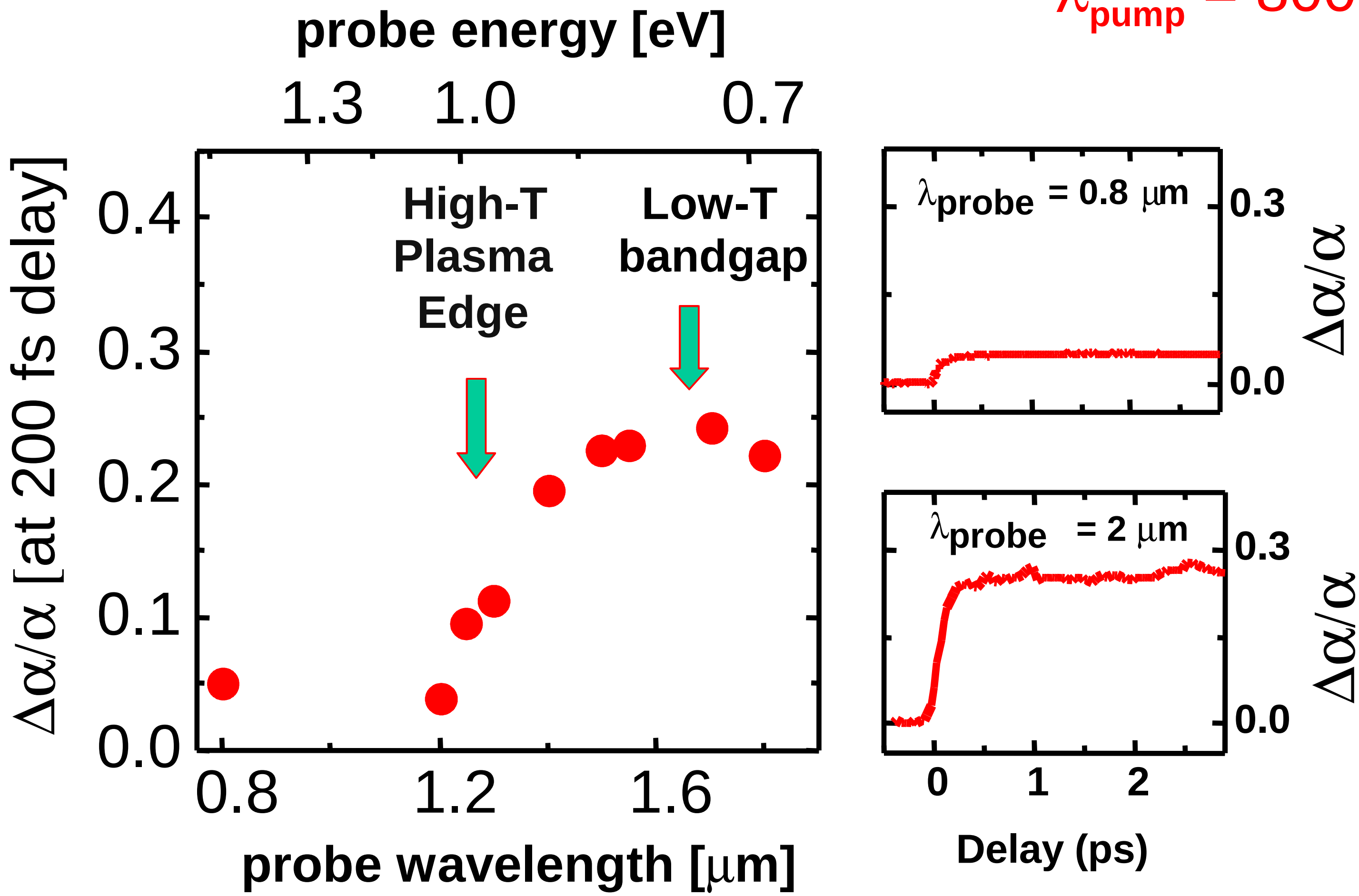
Time scales:
structural ~100 fs (T_{vib})
electronic <1 fs (a/V_{Fermi})

Cavalleri et al. *Phys. Rev. B* **70**, 161102(R) (2004)

Rini et al *Optics Letters* **30**,1,(2005)

IR Spectroscopy: Bandgap Collapse

λ_{pump} = 800 nm



Rini et al *Optics Letters* **30**,1,(2005)

Mott-Hubbard or Band-like?

What causes the formation of the metallic state?

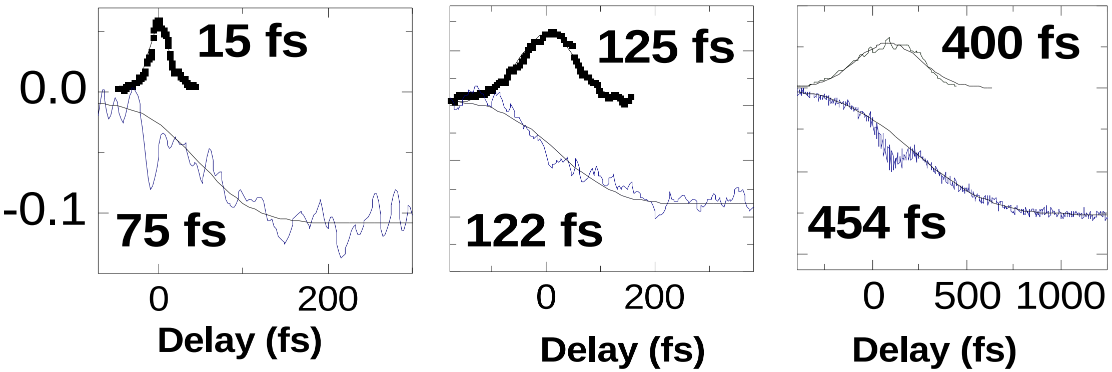
Mott-Hubbard insulator: e-e correlation

⇨ Prompt collapse of the bandgap

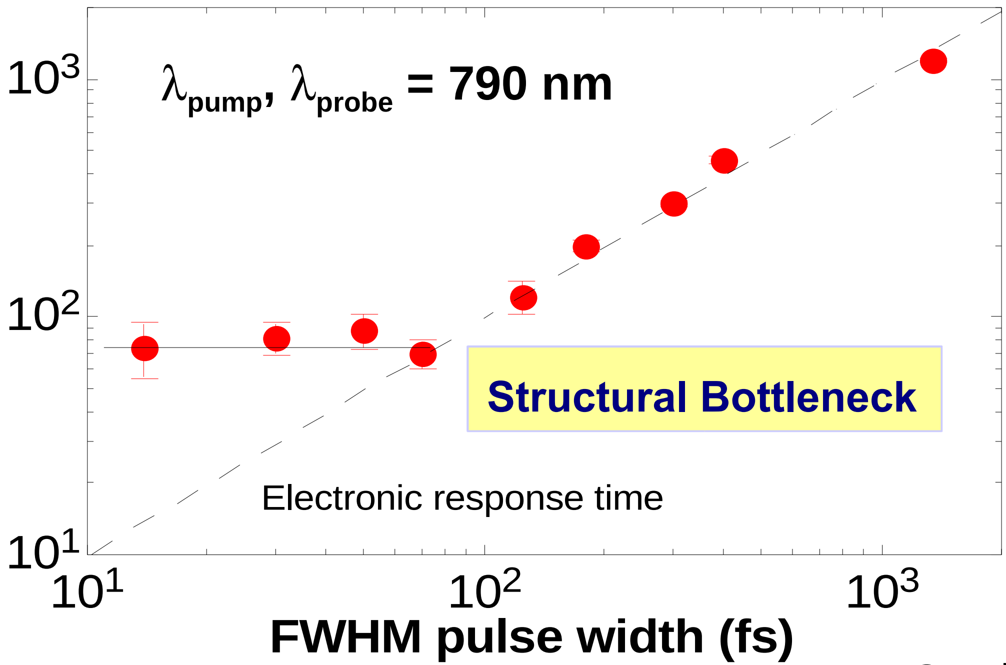
Band-like insulator: change of symmetry

⇨ Structurally driven transition

Pump-probe for different pulse durations



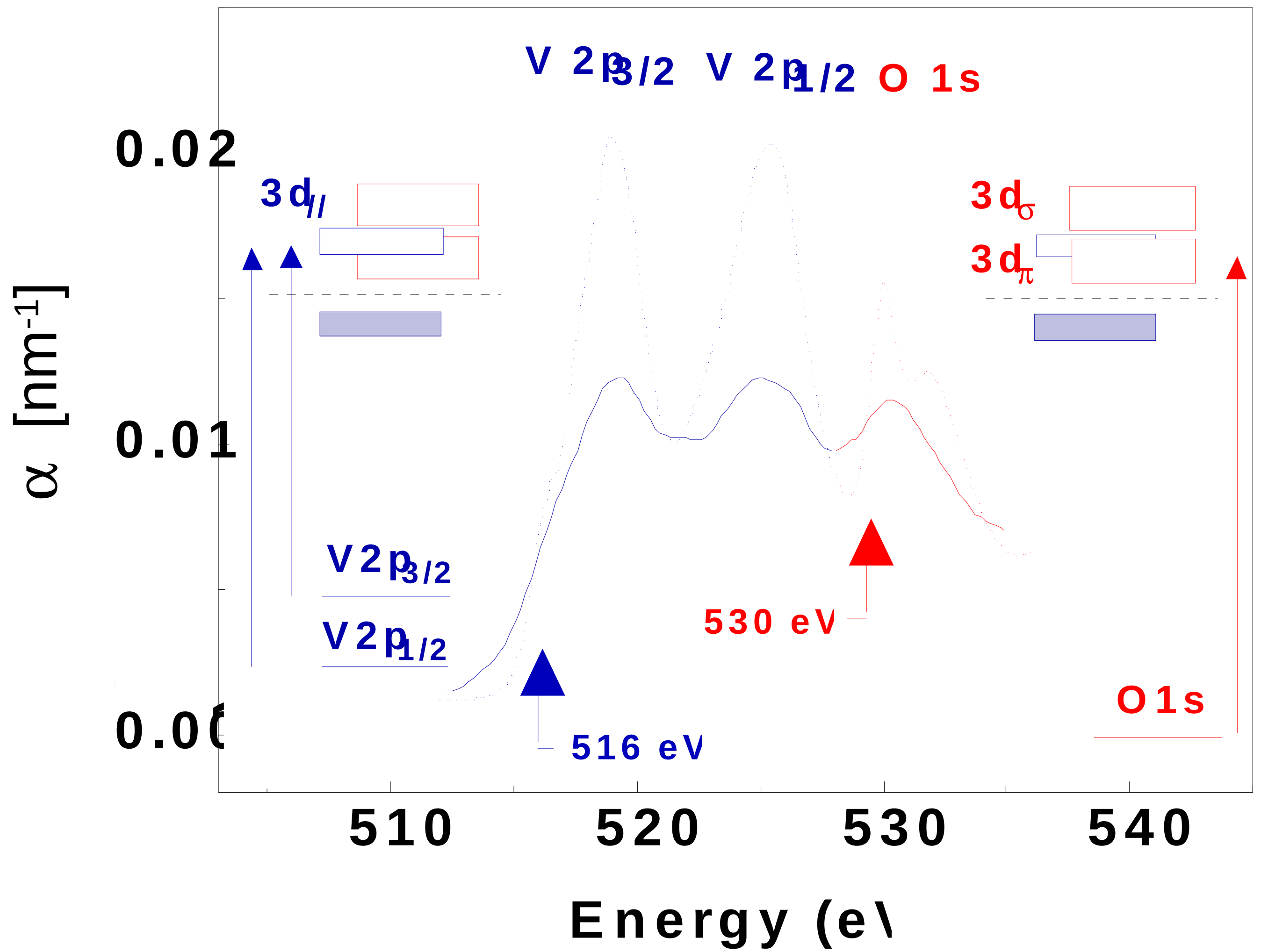
Question: is the system metallic immediately after photo-doping?



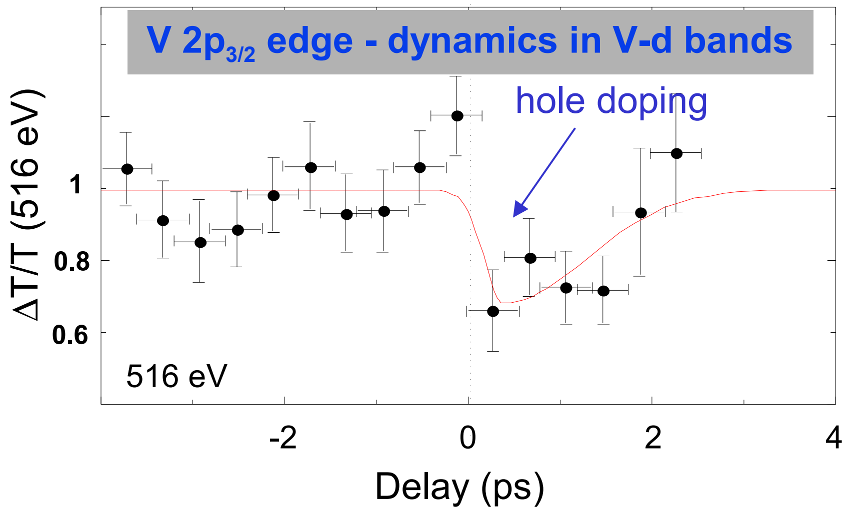
Answer: The phase transition timescale is 80 fs, also for 10-fs photo-doping

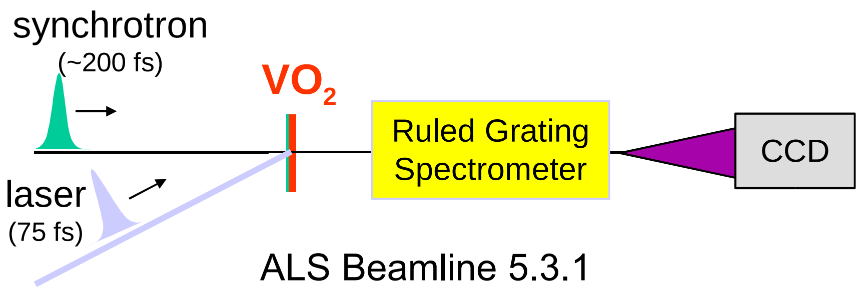
Cavalleri et al. *Phys. Rev. B* 70, 161102 (2004)

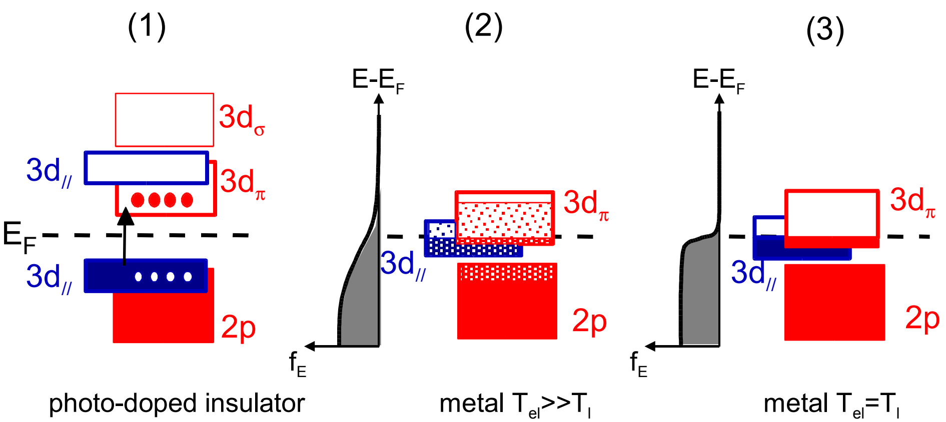
NEXAFS: Band Selective Spectroscopy



Femtosecond NEXAFS Measurements in VO_2

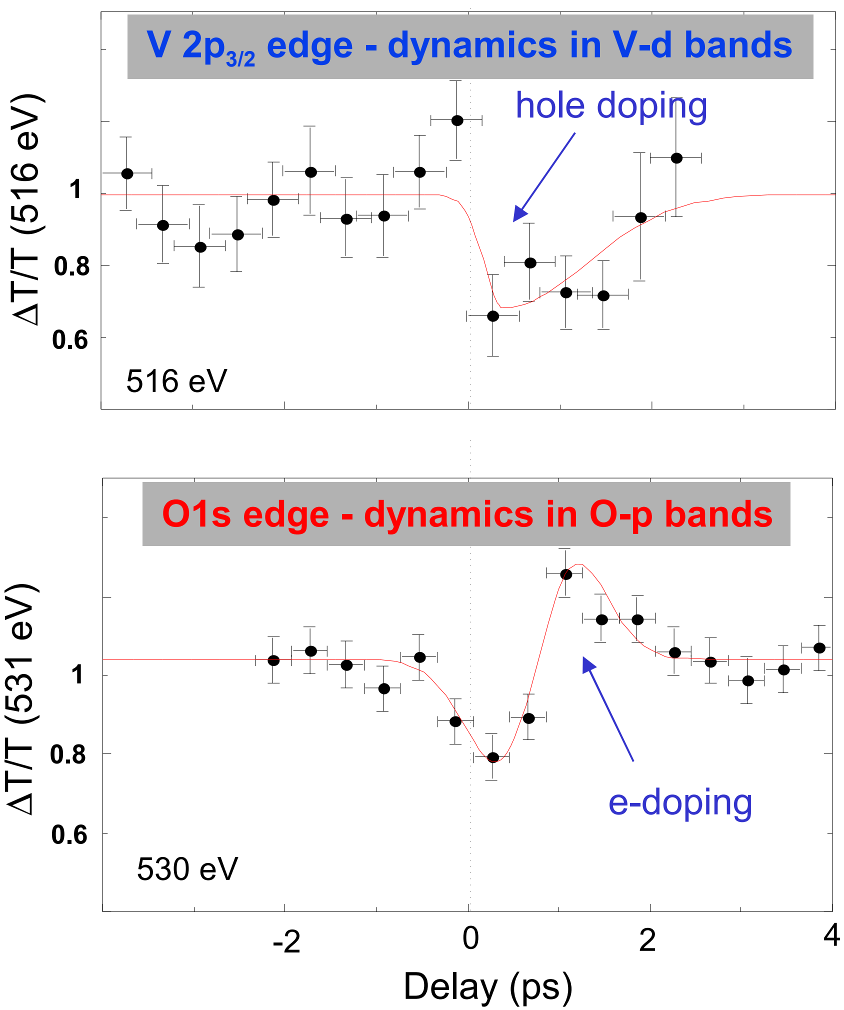


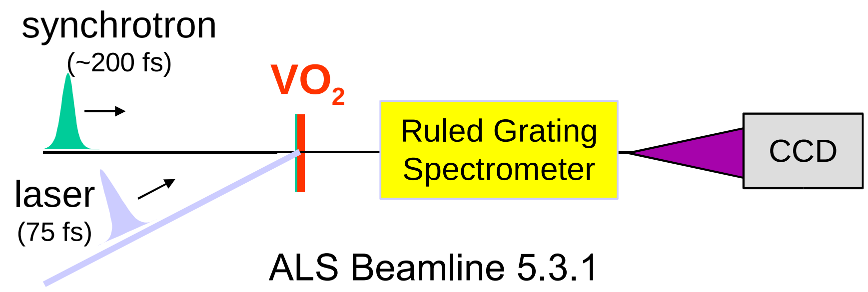


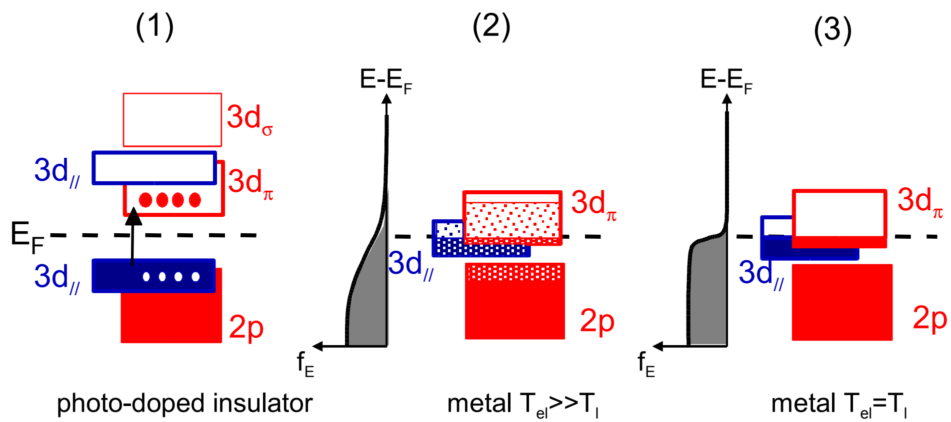


A.Cavalleri et al., *Phys. Rev. Lett.*, **95**, 067405, (2005).

Femtosecond NEXAFS Measurements in VO_2







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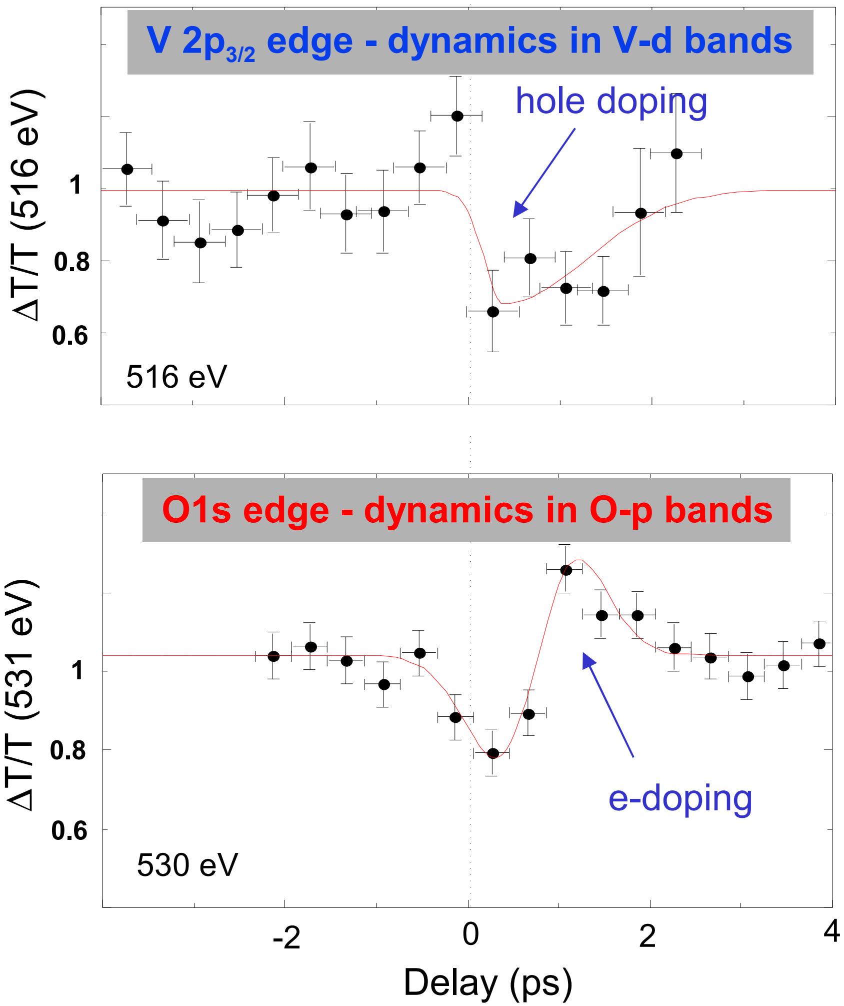
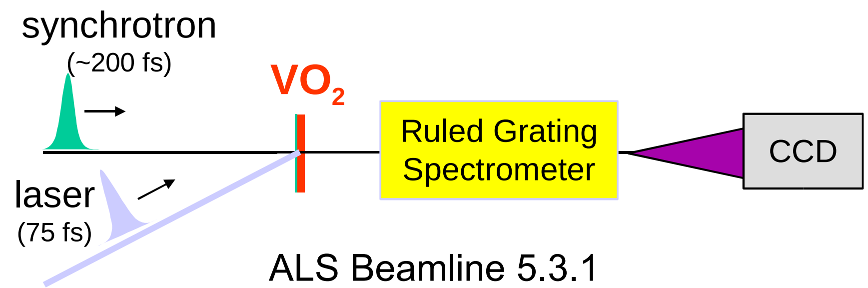
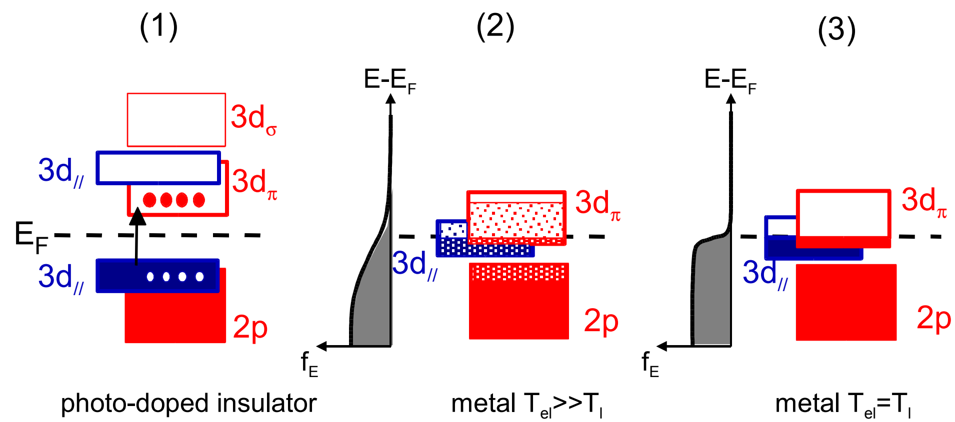
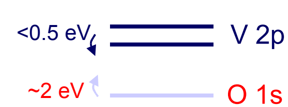








valency change ⇒ chemical edge shift

$O^{2-} \Rightarrow O^{2.25-}$ $V^{4+} \Rightarrow V^{4.5+}$

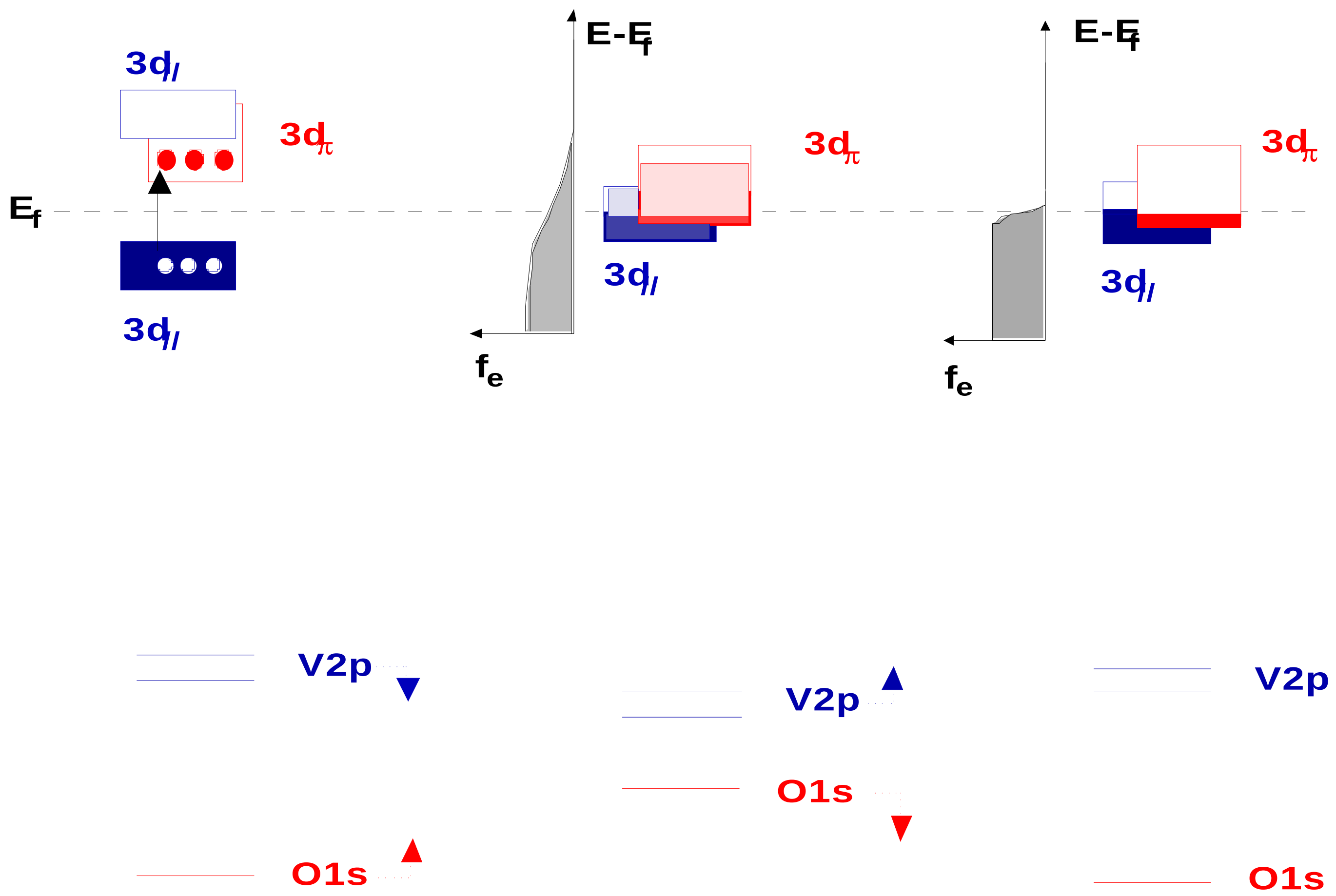
A.Cavalleri et al., *Phys. Rev. Lett.*, **95**, 067405, (2005).

Valency Change: Dynamic Chemical Shift

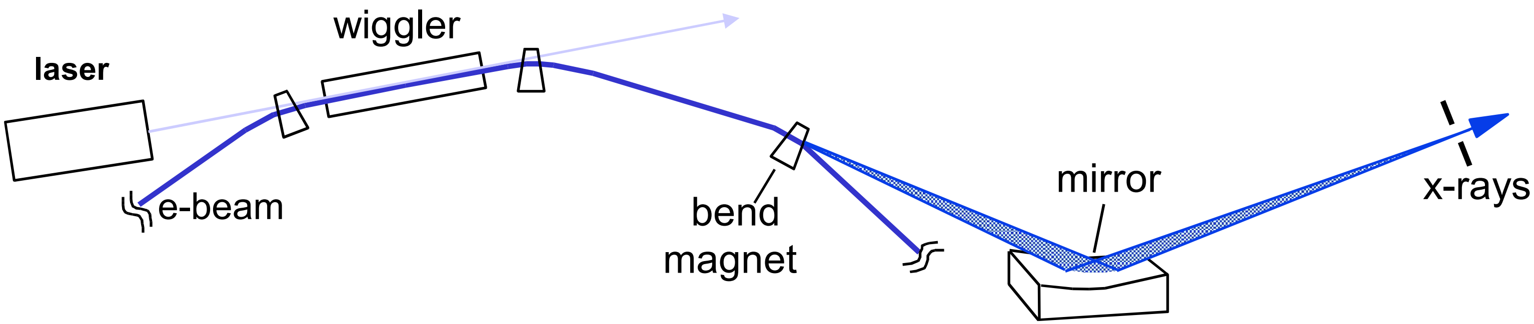
(1) Insulating pha
Photo-dopin

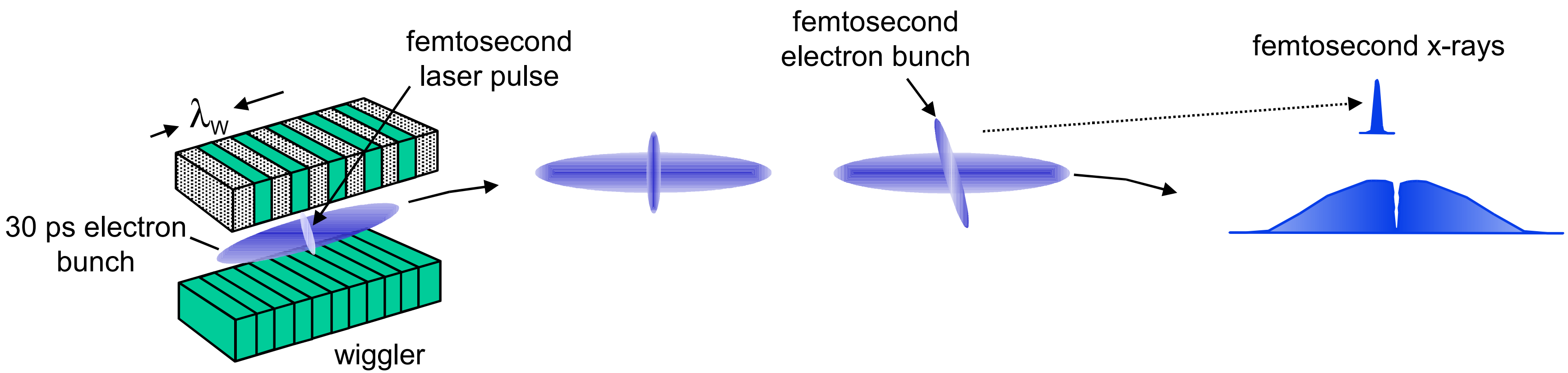
(2) Metallic pha
$T_{electr} >> T_{latt}$

(3) Metallic pha
$T_{electr} = T_{latt}$



Tunable femtosecond X-rays at the ALS



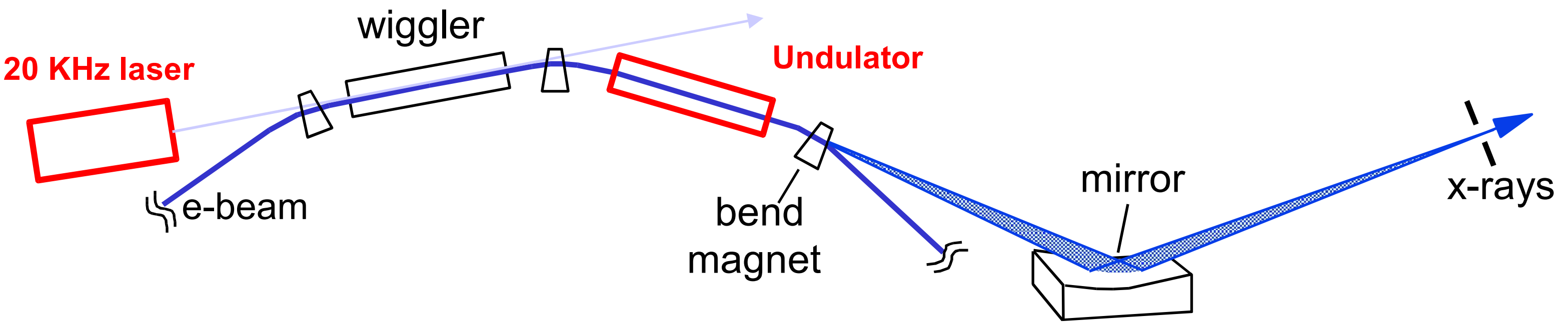


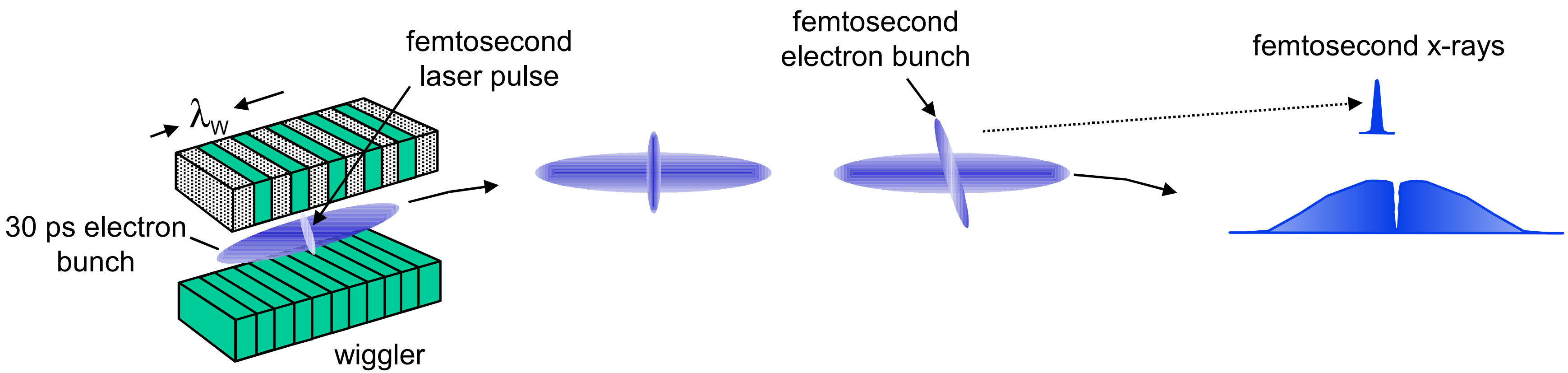
electron-photon
interaction in wiggler

Zholents and Zolotorev, *Phys. Rev. Lett.*, 76, 916,(1996).

Schoenlein et al., *Science*, 287, (2000)

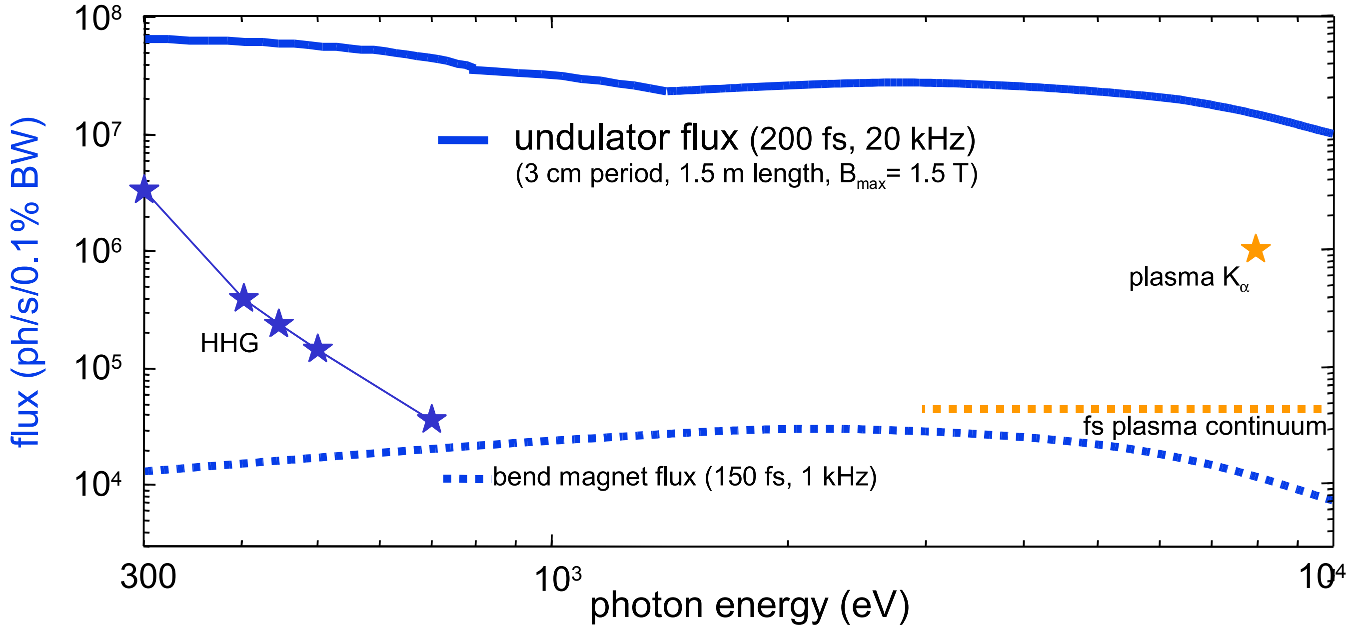
Upcoming Undulator Beamline





electron-photon
interaction in wiggler

Femtosecond X-ray Flux



★ HHG flux from F. Krausz, laser: 10 fs, 3 mJ/pulse, 30 W

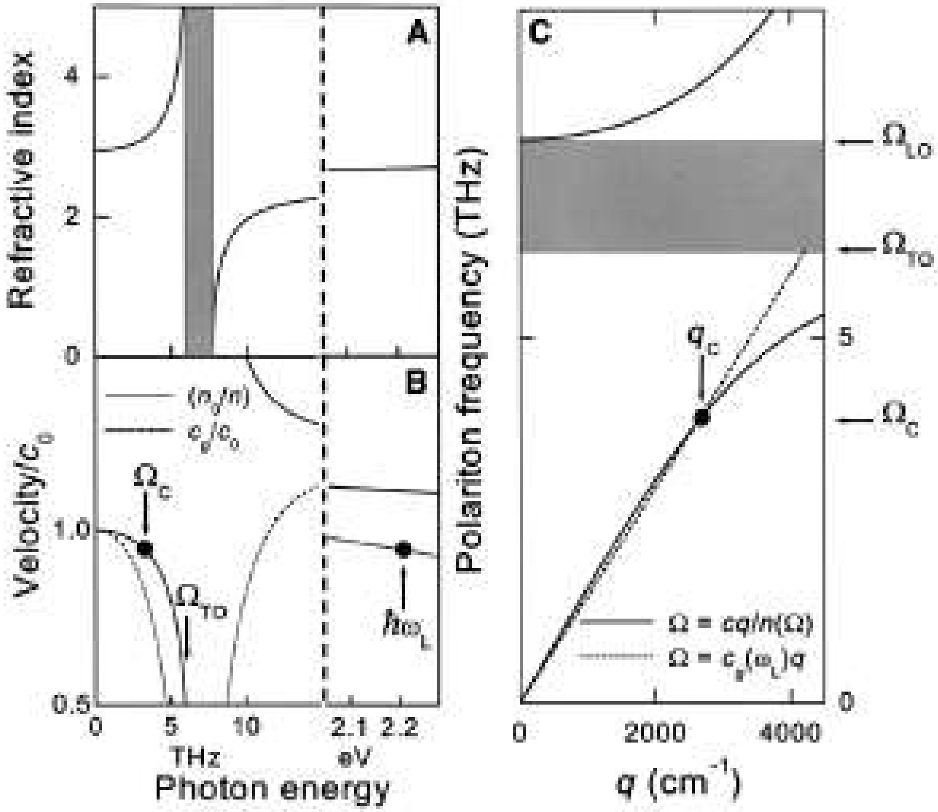
★ Plasma source flux in mrad² laser: 40 fs, 1 mJ/pulse, 30 W (continuum includes projected 10^5 improvement)

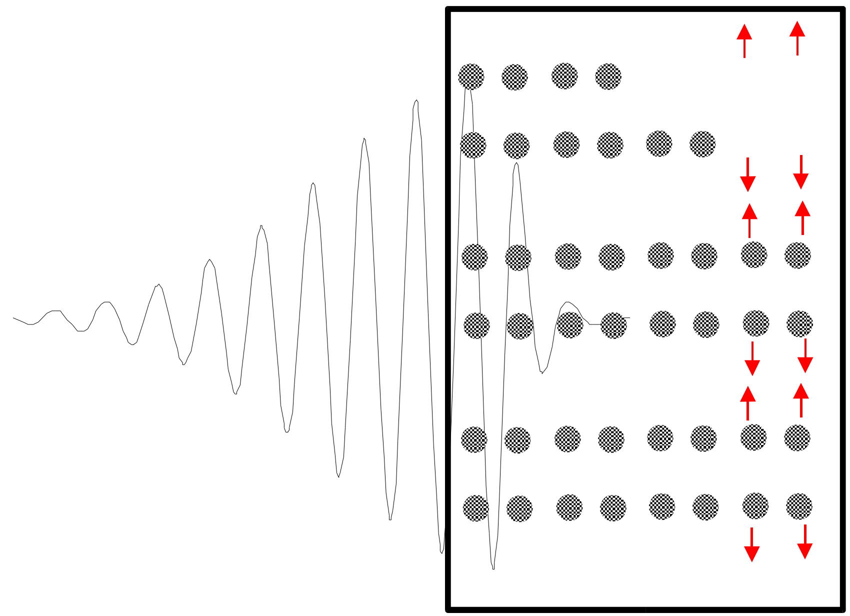
Cu K_α - 10^{10} ph/s/4π (proj. 10^{12} with Hg target)

cont. $6x10^7$ ph/s/4π (integ. from 7-8 keV)

ALS typical average x-ray flux
undulator ~10^{15} ph/s/0.1% BW
bend-magnet ~10^{13} ph/s/0.1% BW

Phonon-Polaritons in $LiTaO_3$

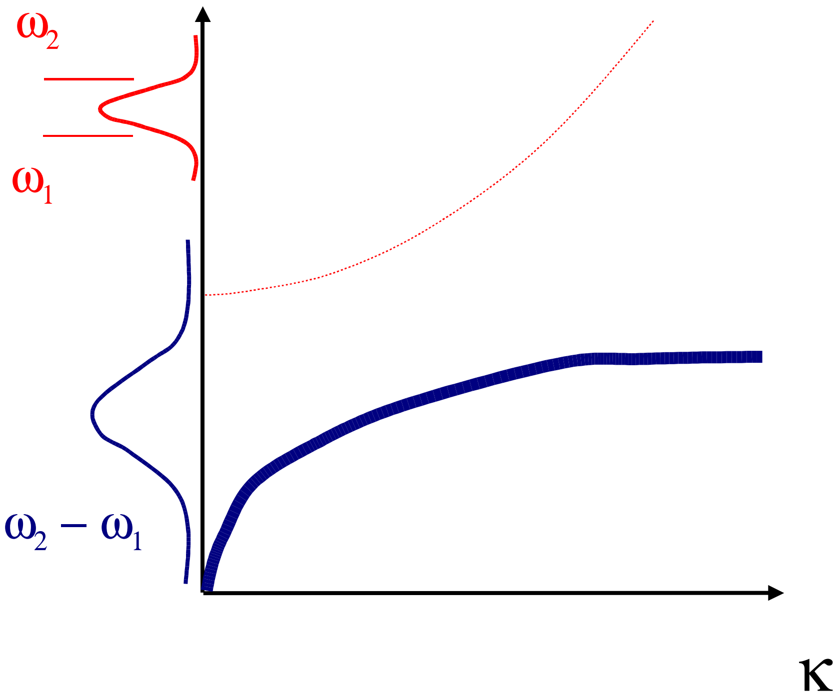




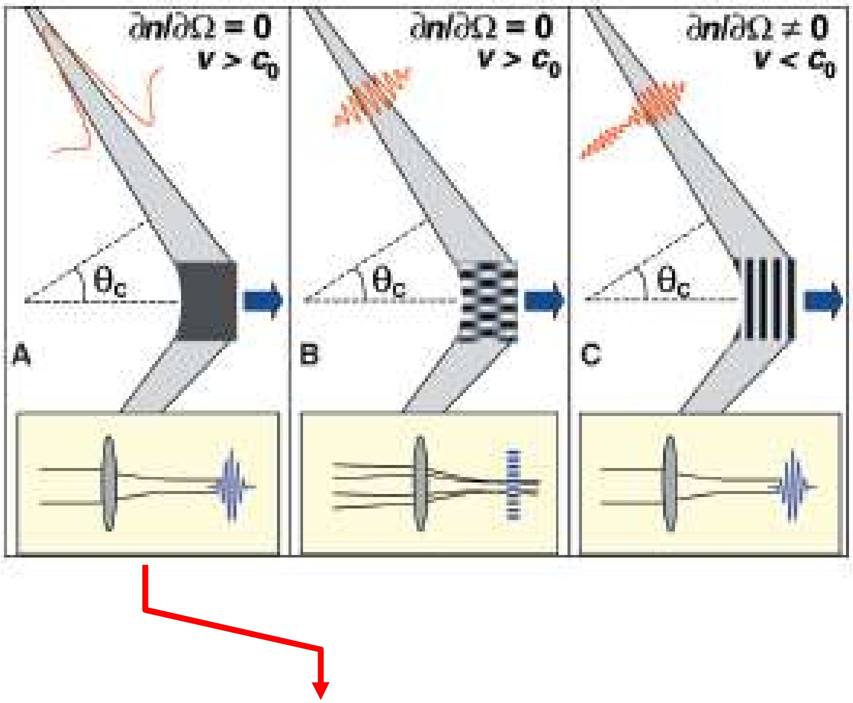
Stevens et al, *Science* **291** (2001) 627

Excitation of Coherent Phonon-polaritons

Difference Frequency

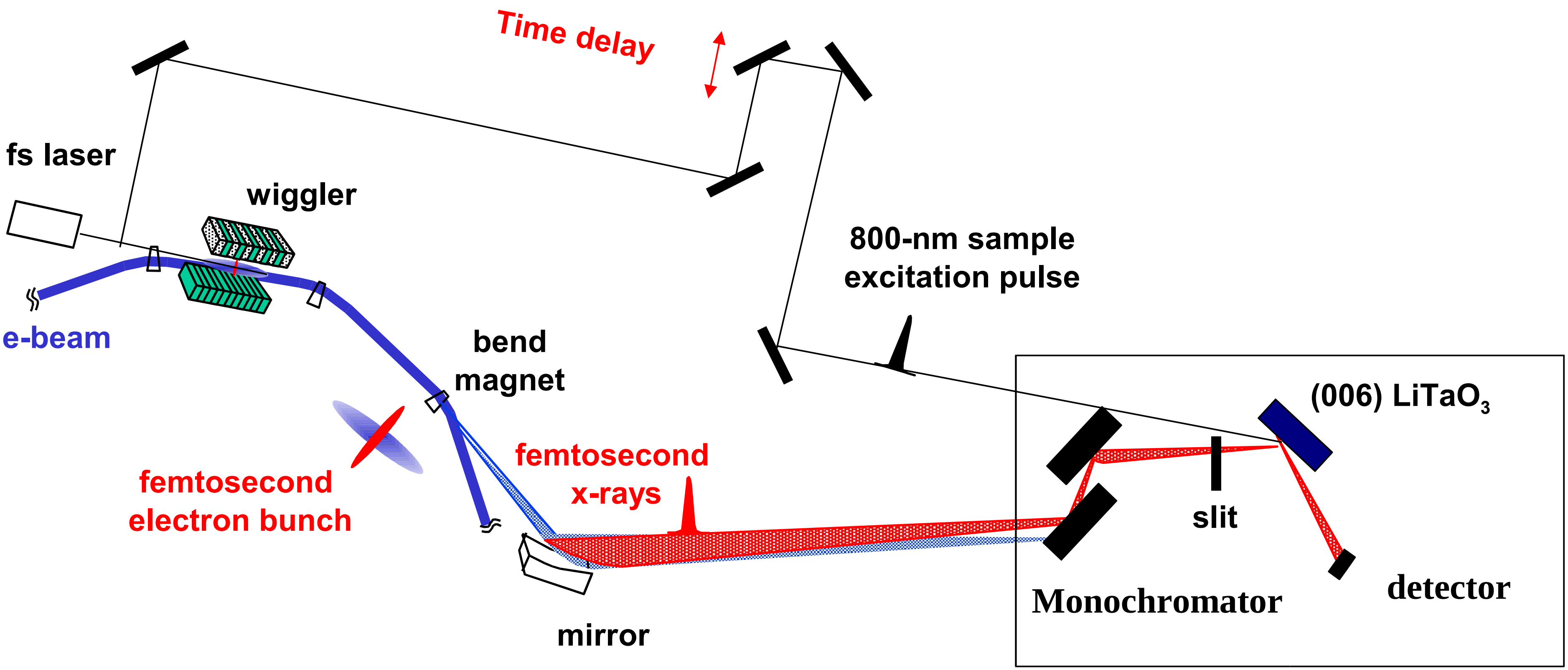


Cherenkov Radiation

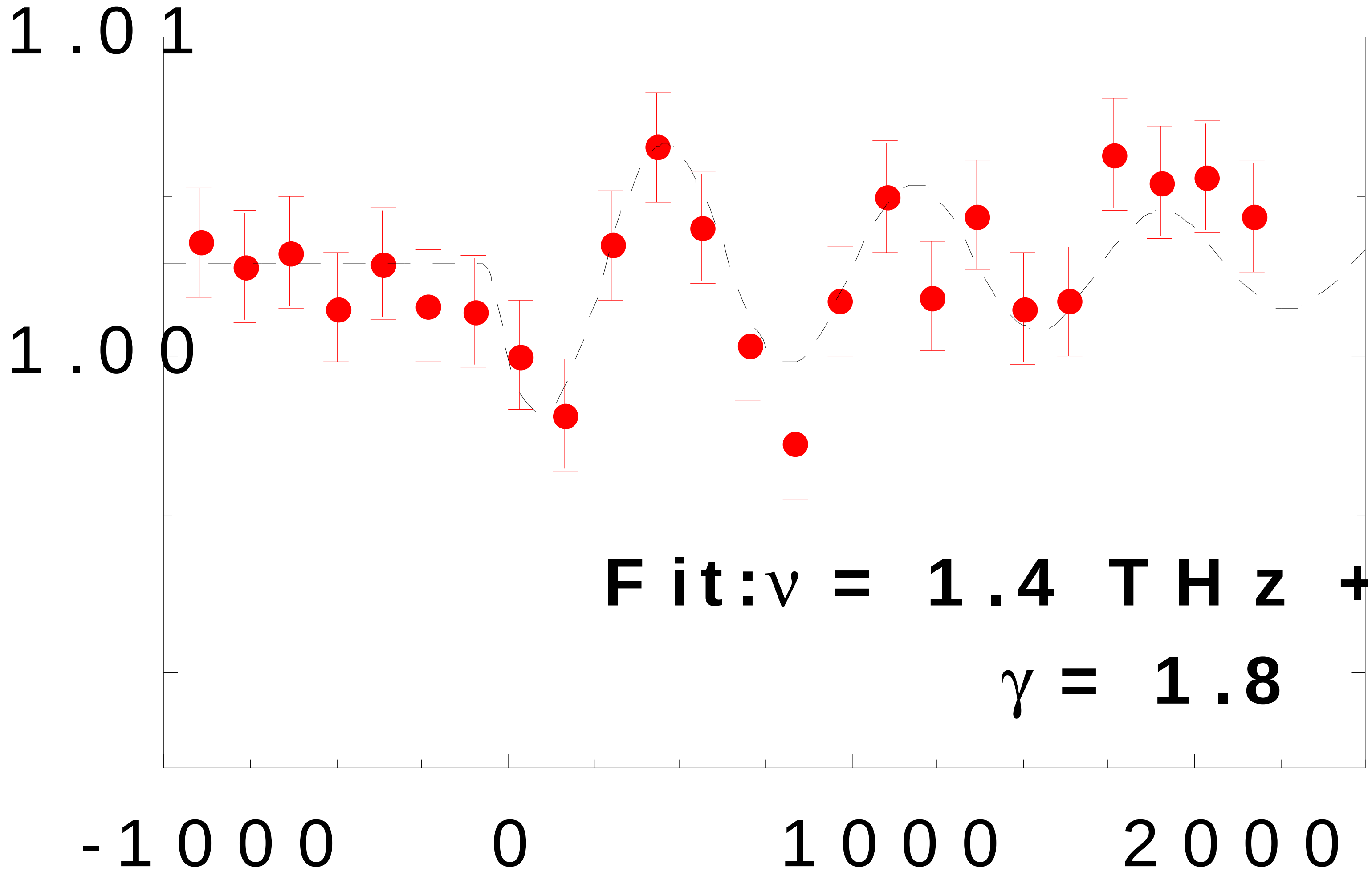


Austen et al., PRL (1984)

Ultrafast X-ray Diffraction

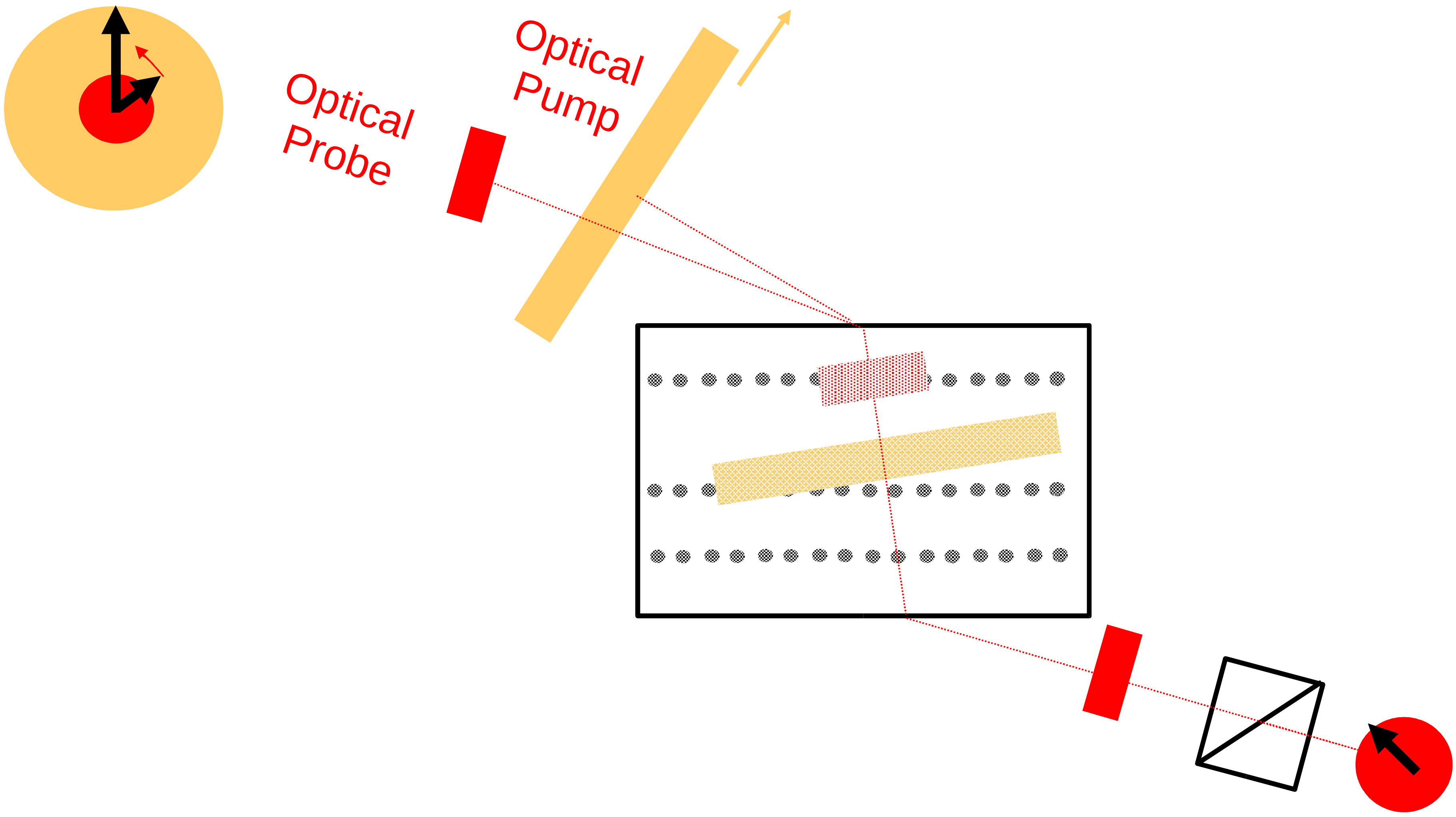


Time-resolved 006 Structure Factor

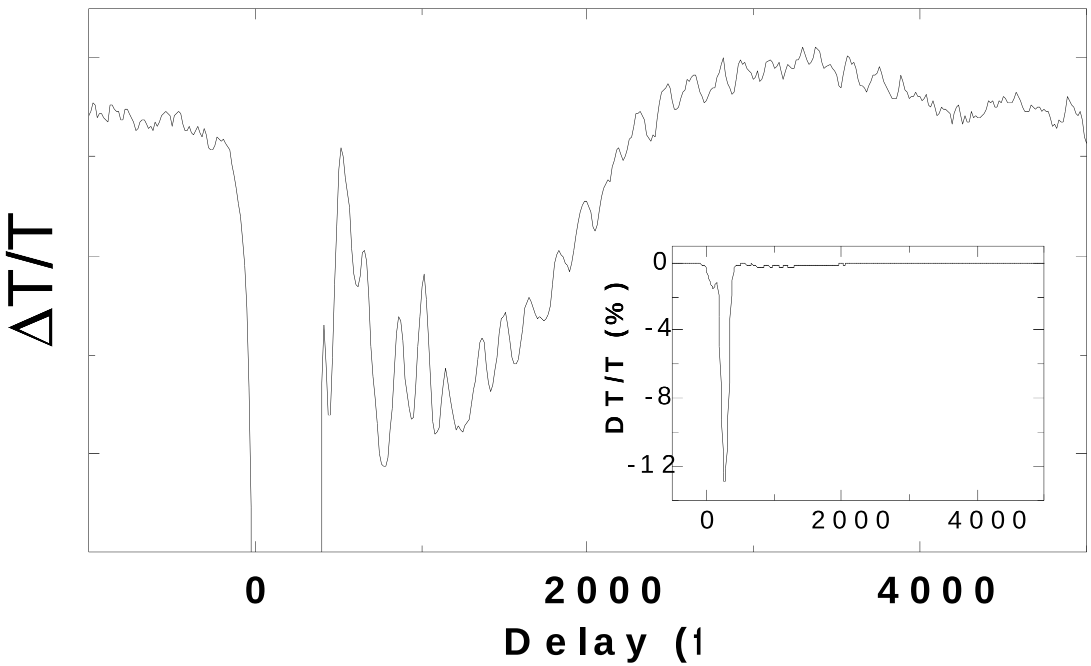


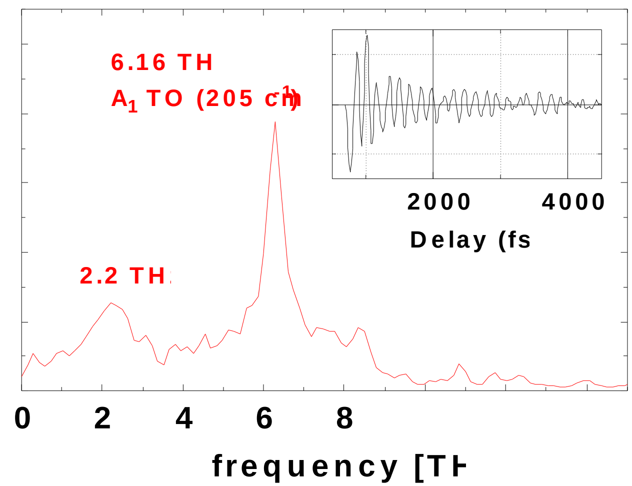
Optical Exp: time-resolved Pockels effect

Front view

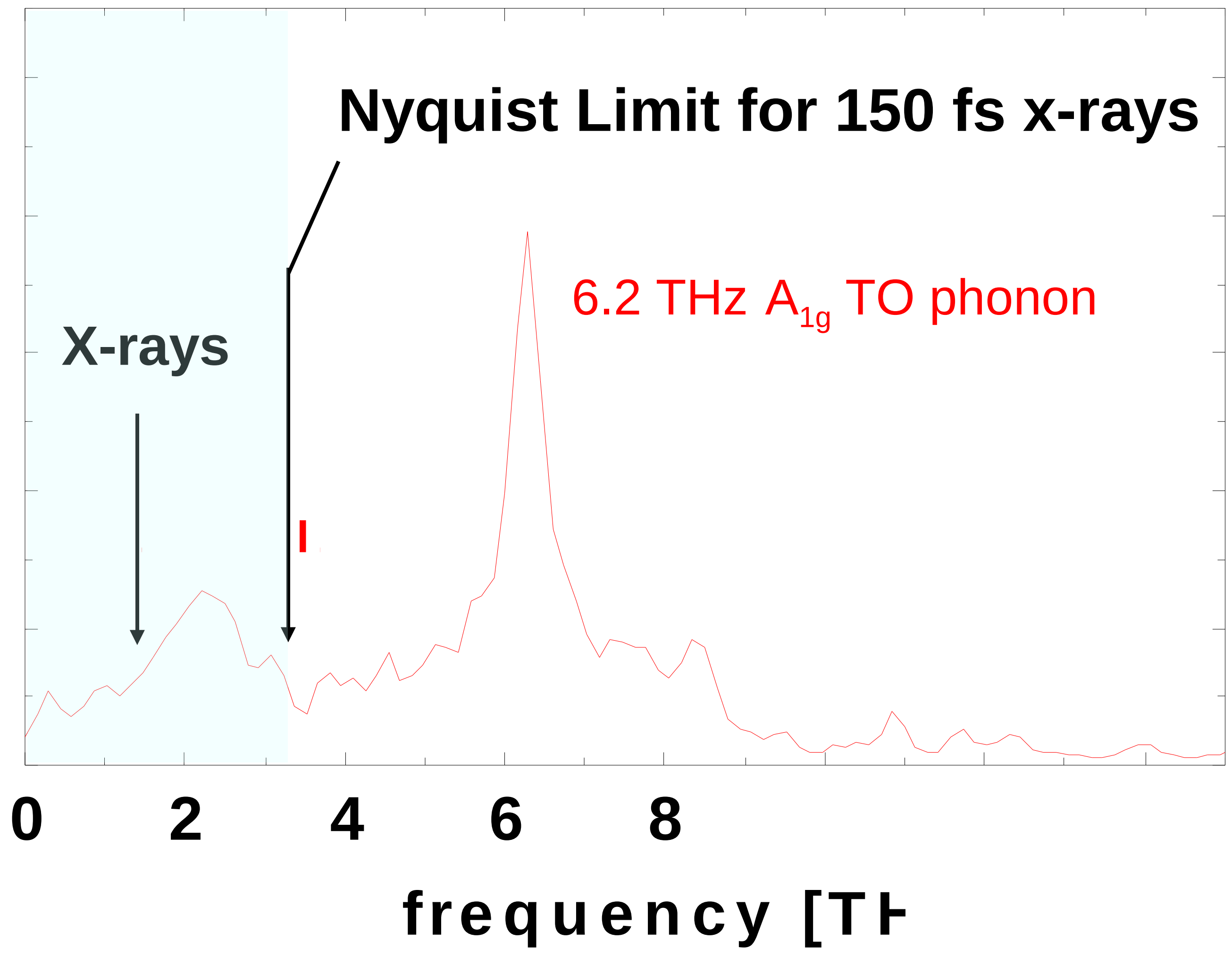


Time-resolved Pockels effect

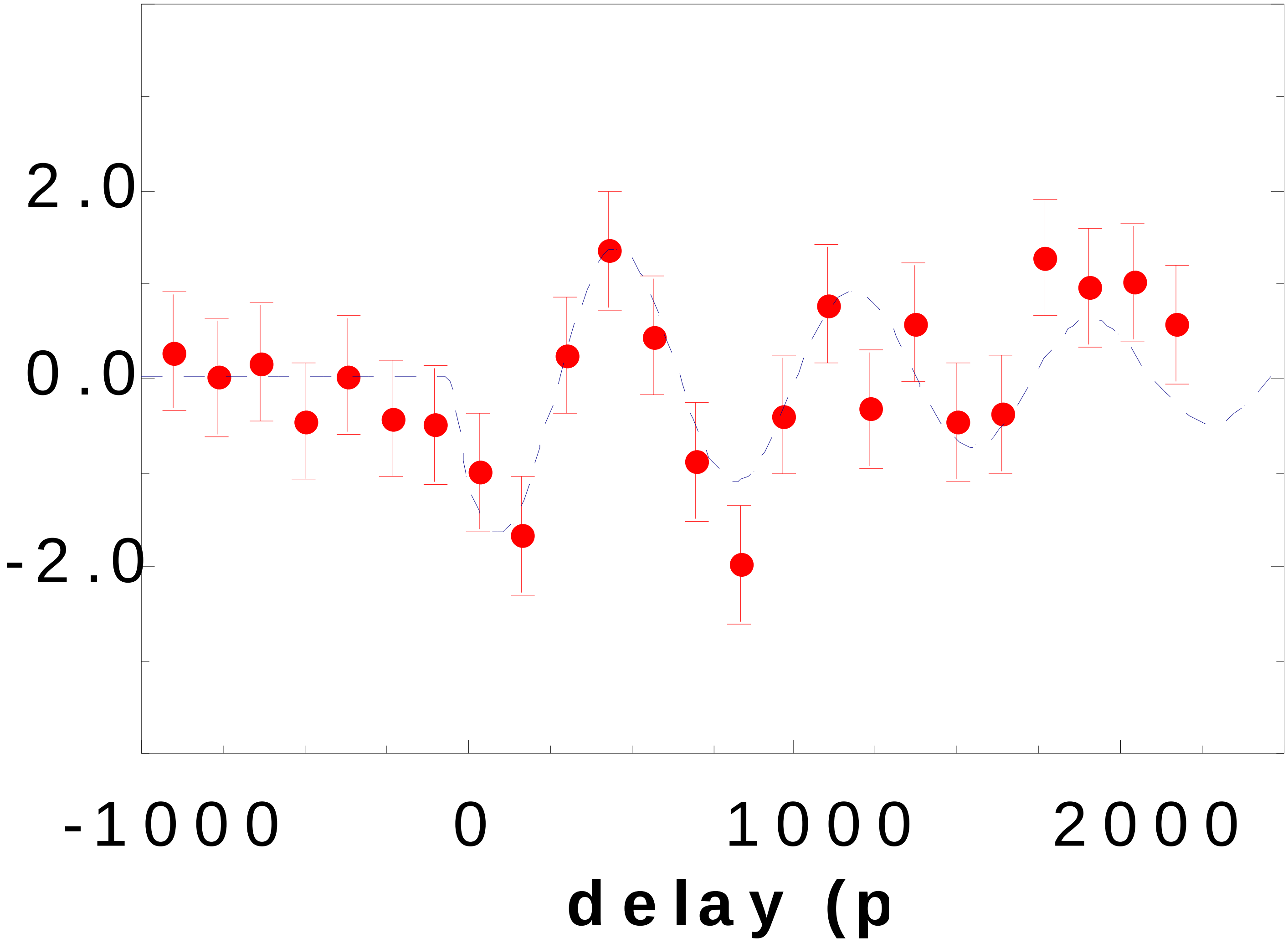




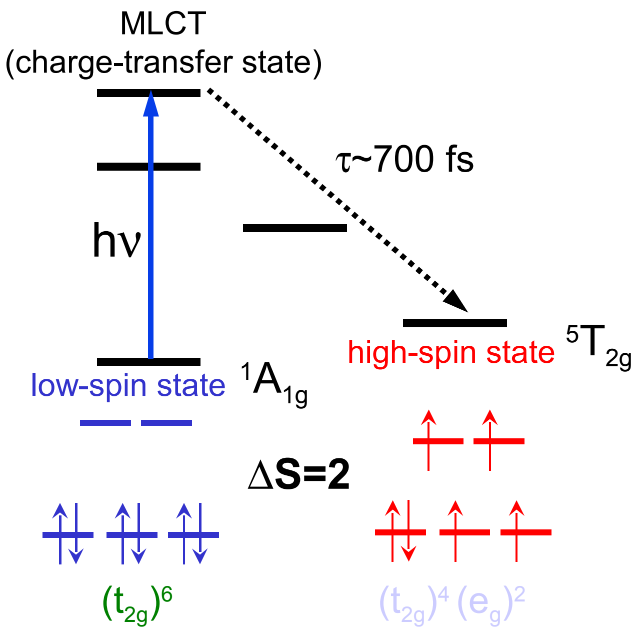
Comparison with Optical data

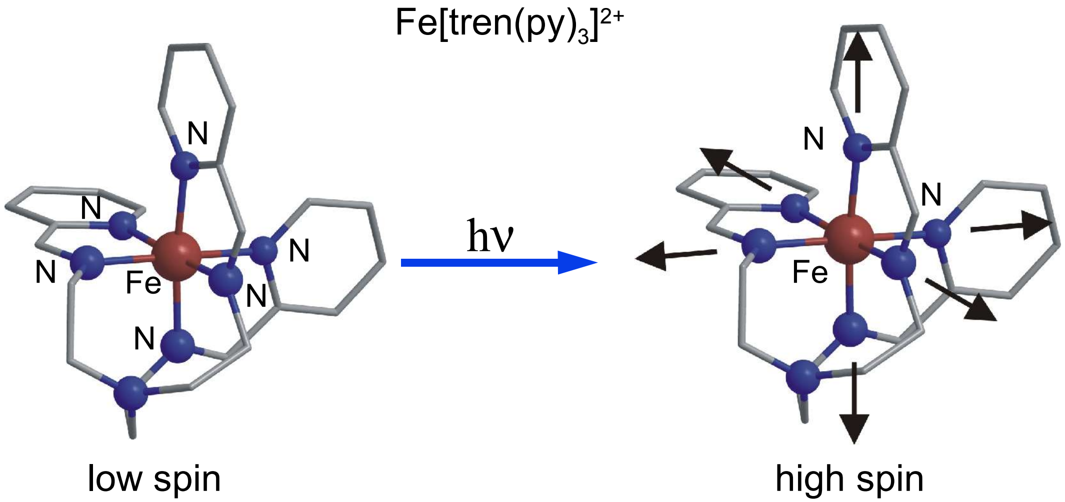


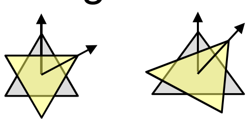
Ta-O displacement along the c axis



Fe^{II} Spin-Crossover Molecules





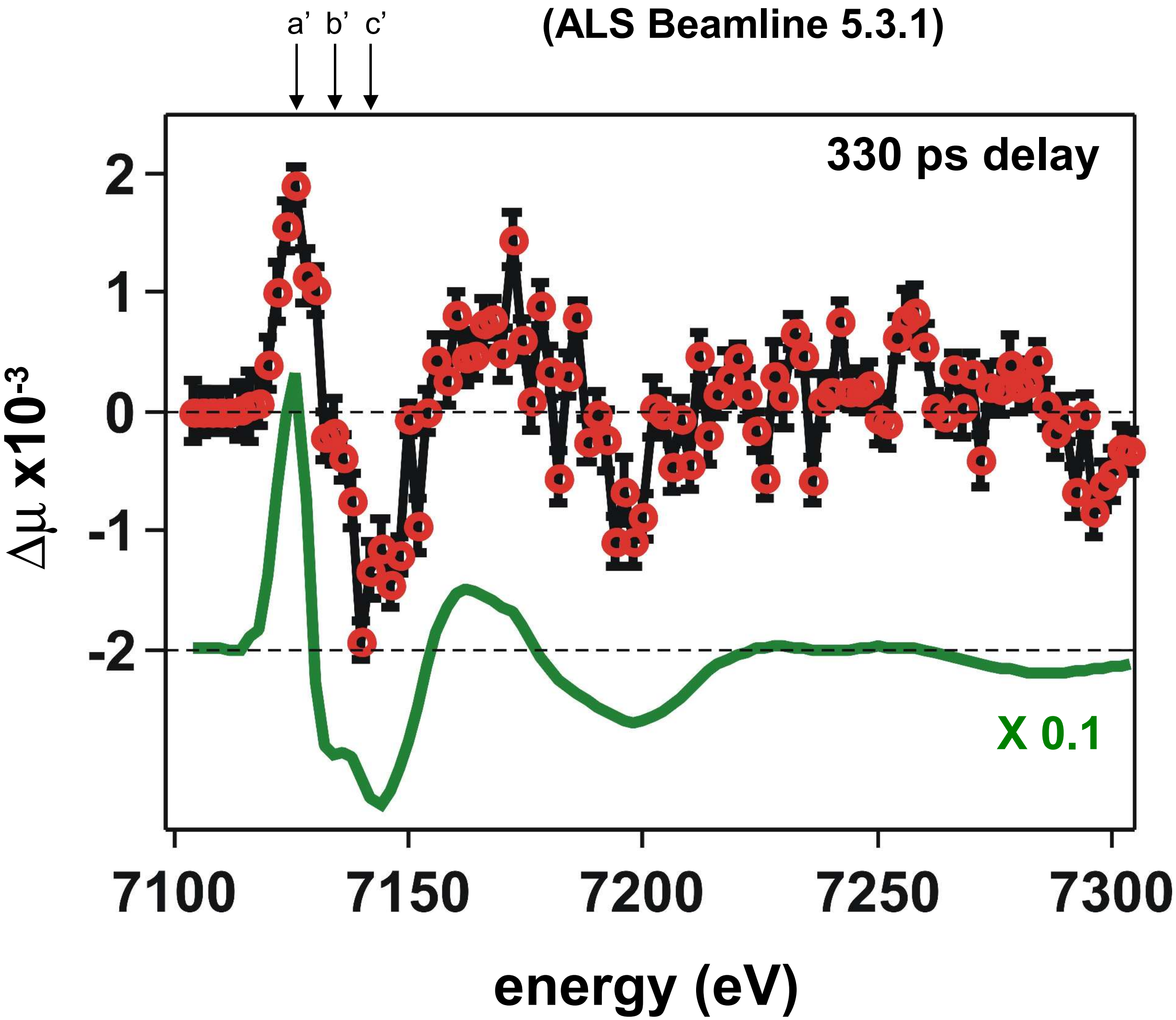
- ~10-15% increase in metal-ligand bond distances
- trigonal cage distortion? 

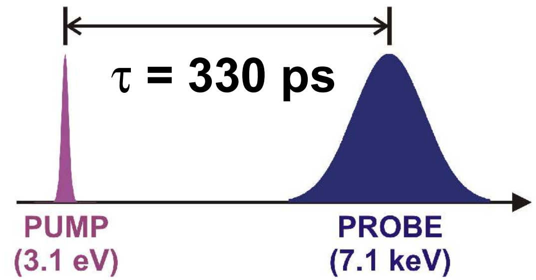
Motivation:

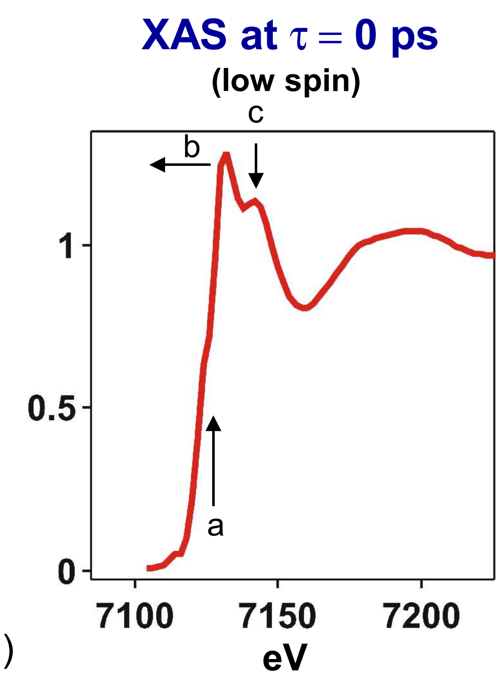
- relationship between structure, electronic, and magnetic properties

  Do the structural distortions facilitate the spin-crossover reaction?
- electron transfer mechanistic role in biochemical processes (cytochrome P450)
- magnetic and optical storage material

Fe^{II} Time-resolved XAS





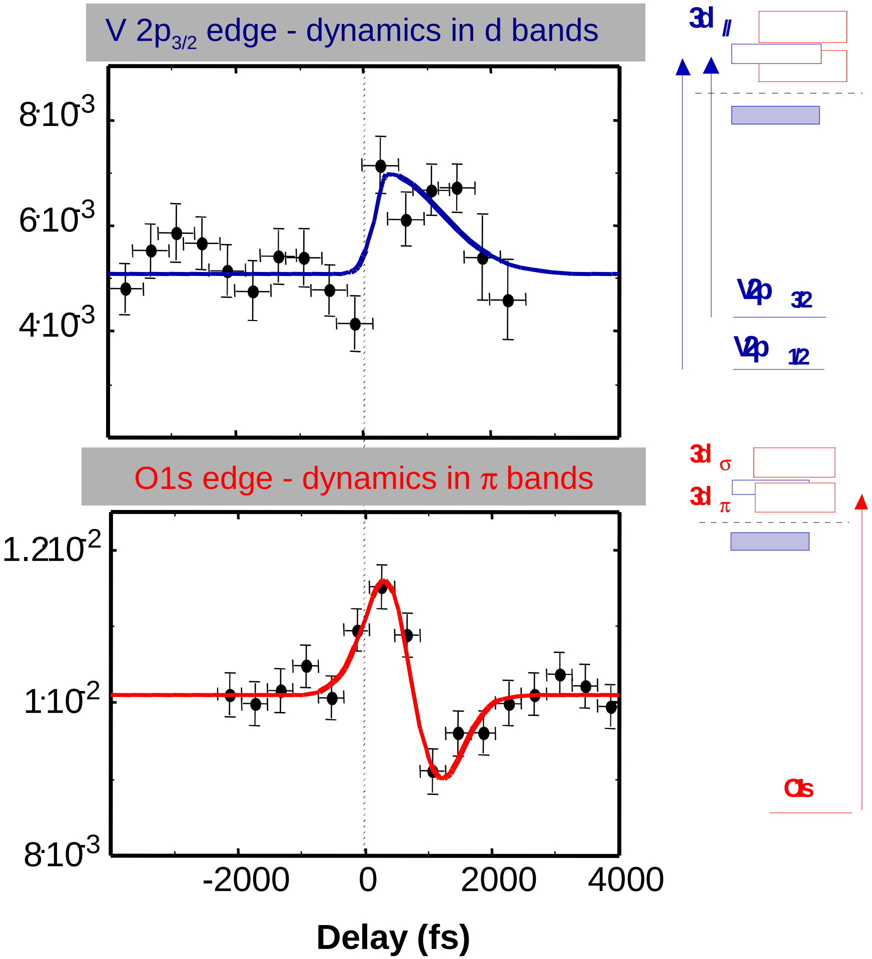


M. Khalil et al., *J. Phys. Chem.* (in press)

Fs X-ray Diffraction and Absorption at the ALS

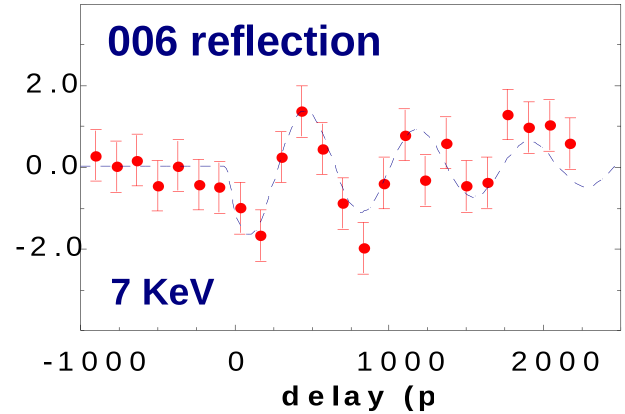
Femtosecond X-ray Absorption

VO_2 Insulator-metal Transition



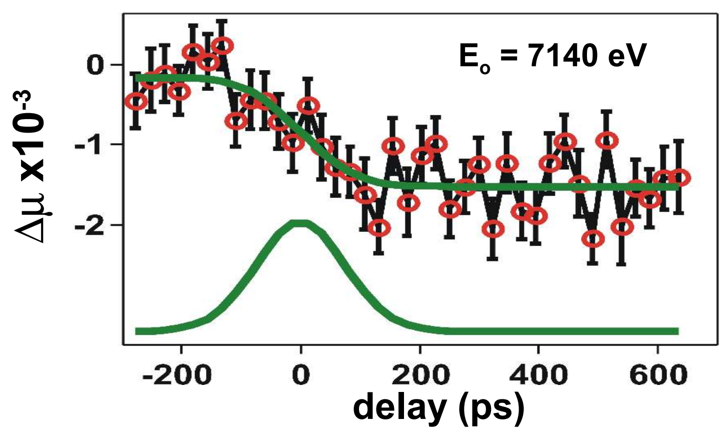
Femtosecond X-ray Diffraction

Phonon Polaritons in $LiTaO_3$



Picosecond X-ray Absorption

Spin-crossover phase transition

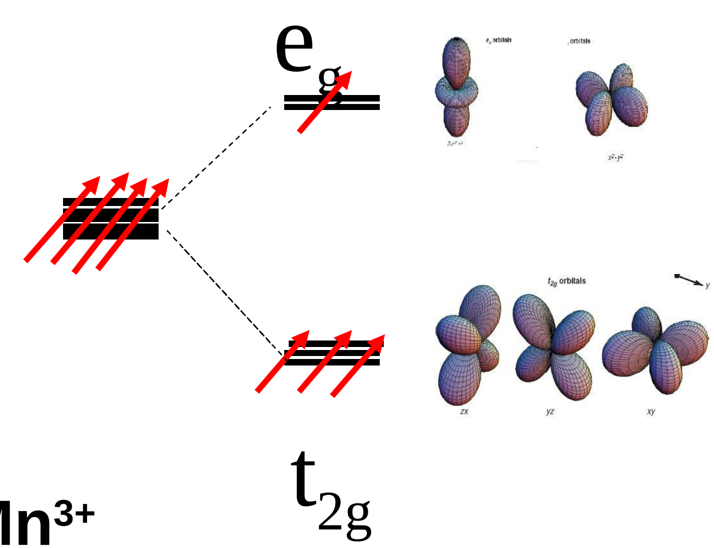


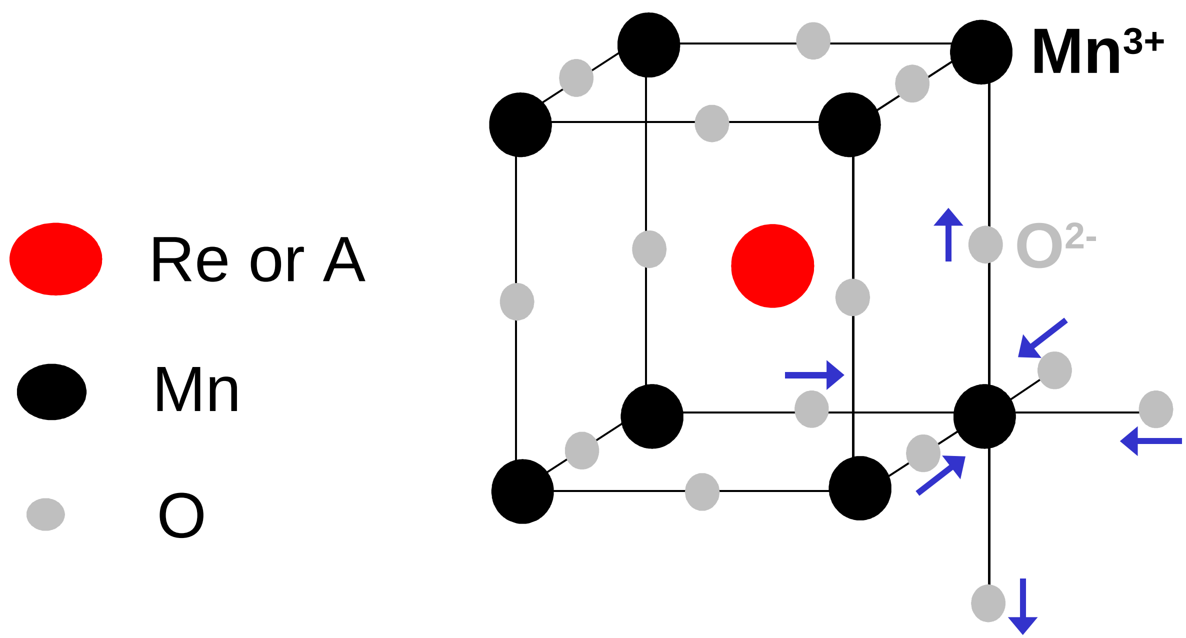
Perovskite Manganites

$Re_{1-x}A_xMn\,O_3$

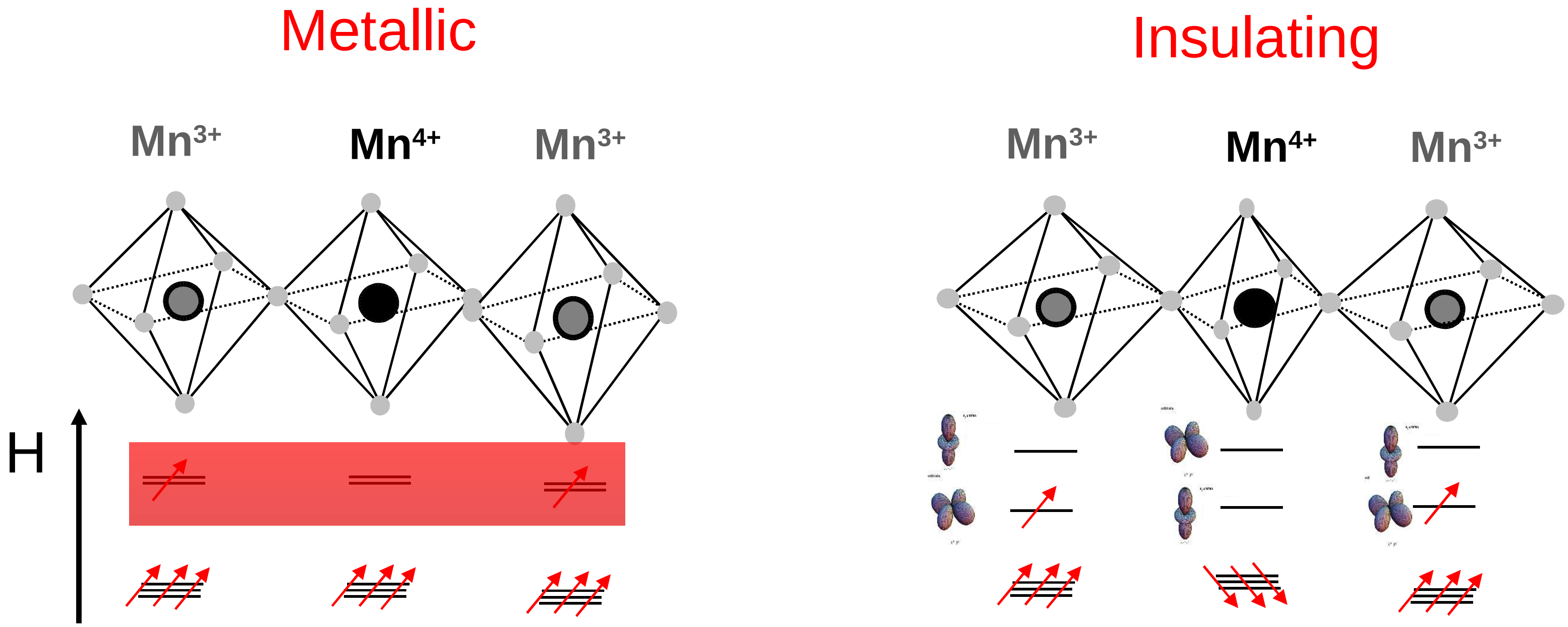
[Ar] $3d^5\,4s^2$

$1s^2\,2s^2\,2p^4$



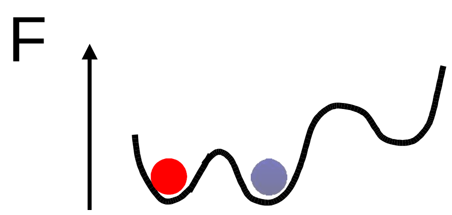


Two competing states



Electron-delocalizing double-exchange

Charge-localizing real-space ordering



Phase competition

Delicate balance

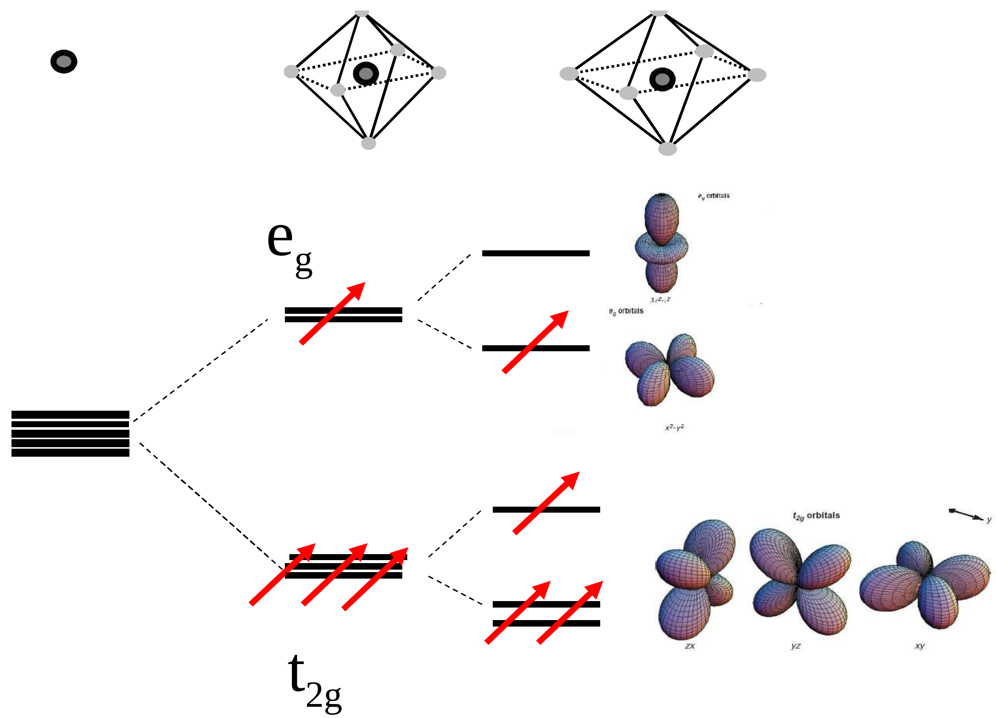
Lattice Effects?

VOLUME 74, NUMBER 25 PHYSICAL REVIEW LETTERS 19 JUNE 1995

Double Exchange Alone Does Not Explain the Resistivity of $La_{1-x}Sr_xMnO_3$

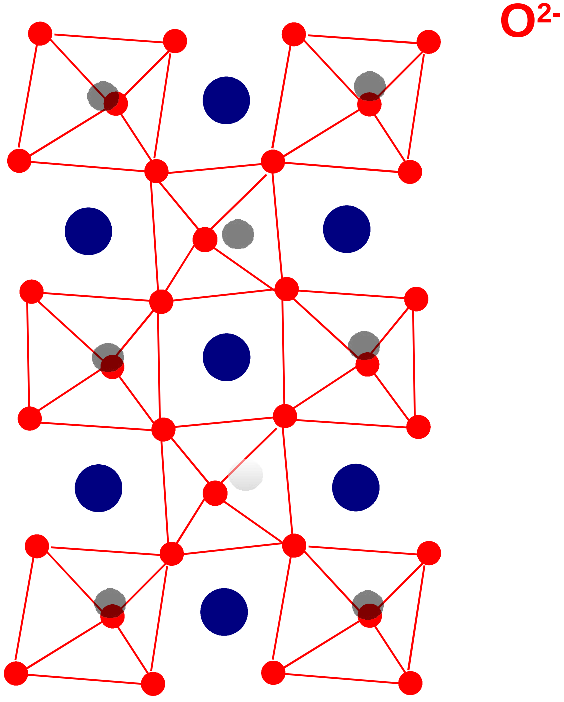
A. J. Millis, P. B. Littlewood, and B. I. Shraiman
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 12 January 1995)

The $La_{1-x}Sr_xMnO_3$ system with $0.2 \lesssim x \lesssim 0.4$ has traditionally been modeled with a "double-exchange" Hamiltonian in which it is assumed that the only relevant physics is the tendency of carrier hopping to line up neighboring spins. We present a solution of the double-exchange model, show it is incompatible with many aspects of the data, and propose that in addition to double-exchange physics a strong electron-phonon interaction arising from the Jahn-Teller splitting of the outer Mn d level plays a crucial role.



$Pr_{(1-x)}Ca_x MnO_3$: Statically Distorted

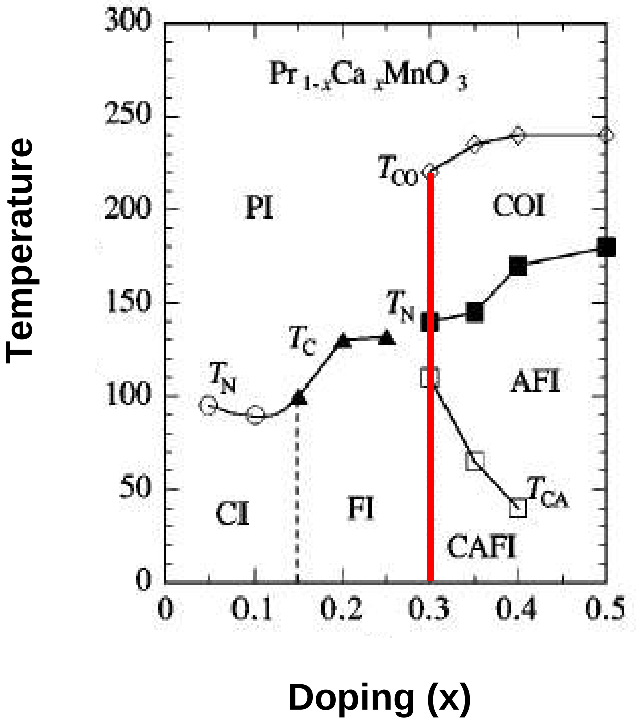
Not quite cubic



Z(Pr)=59

Z(Ca)=20

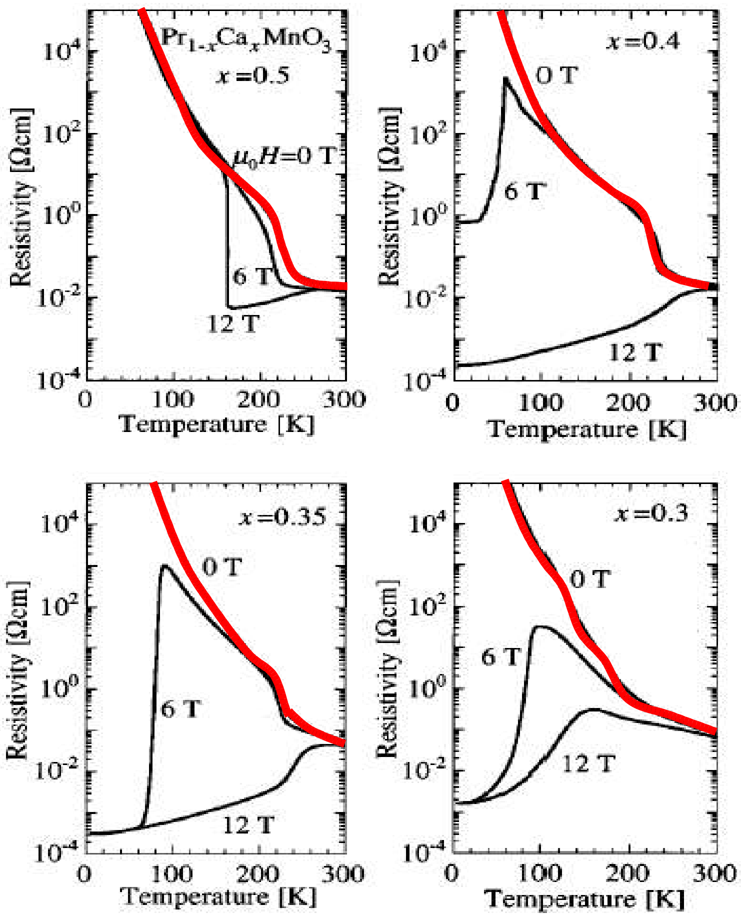
Always Insulating for zero field



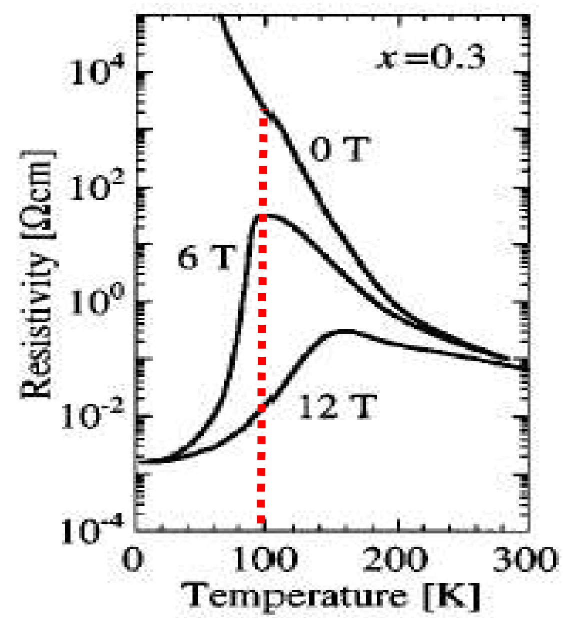
Y. Tomioka et al. Phys Rev. B 53 R1689 (1996)

CMR in $Pr_{(1-x)}Ca_x MnO_3$

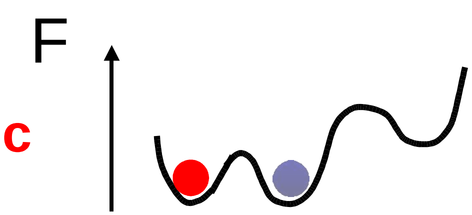
Always Insulating at 0 field
dR/dT < 0



CMR



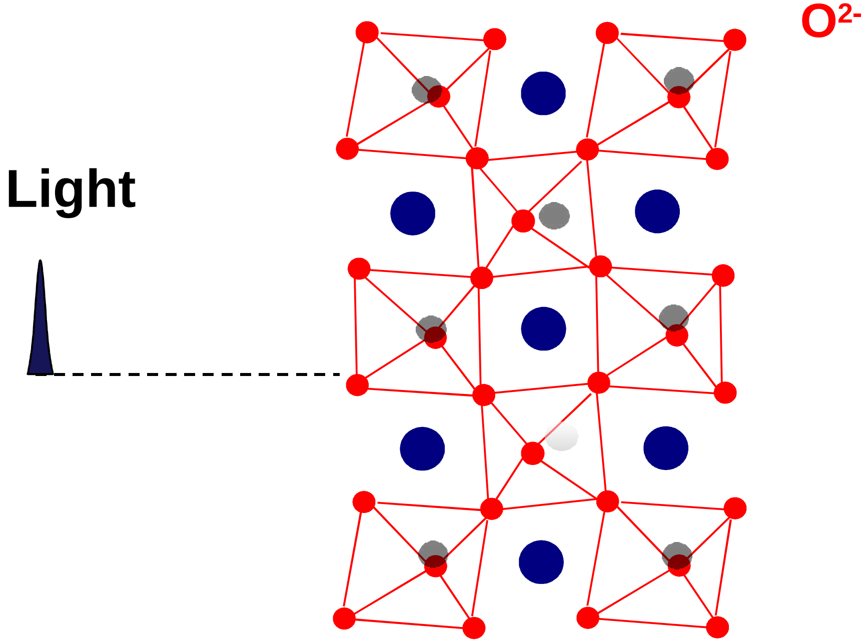
Hidden metallic phase



Y. Tomioka et al. *Phys Rev. B* **53** R1689 (1996)

Colossal Photo-resistance: $Pr_{(1-x)}Ca_x MnO_3$

Colossal photo-resistance

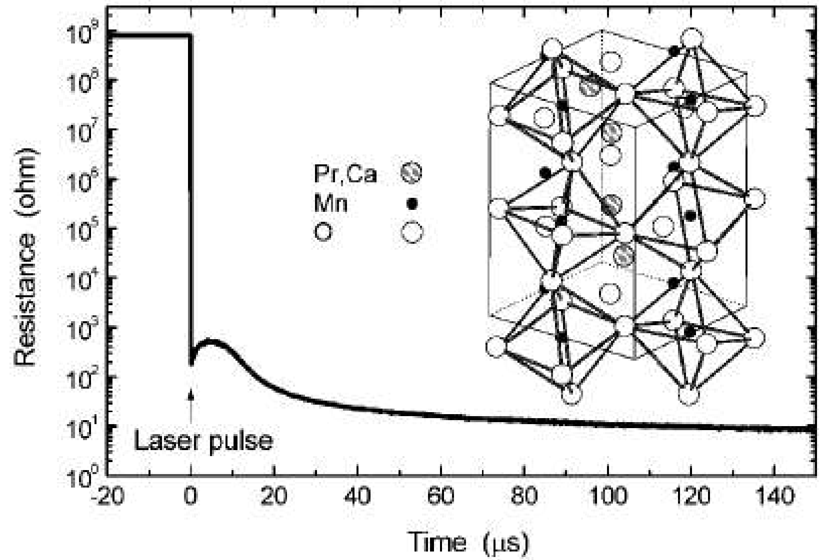


timescale: ~ 230 fs

Visualization of the Local Insulator-Metal Transition in $Pr_{0.7}Ca_{0.3}MnO_3$

Manfred Fiebig,* Kenjiro Miyano, Yoshinori Tomioka, Yasuhide Tokura

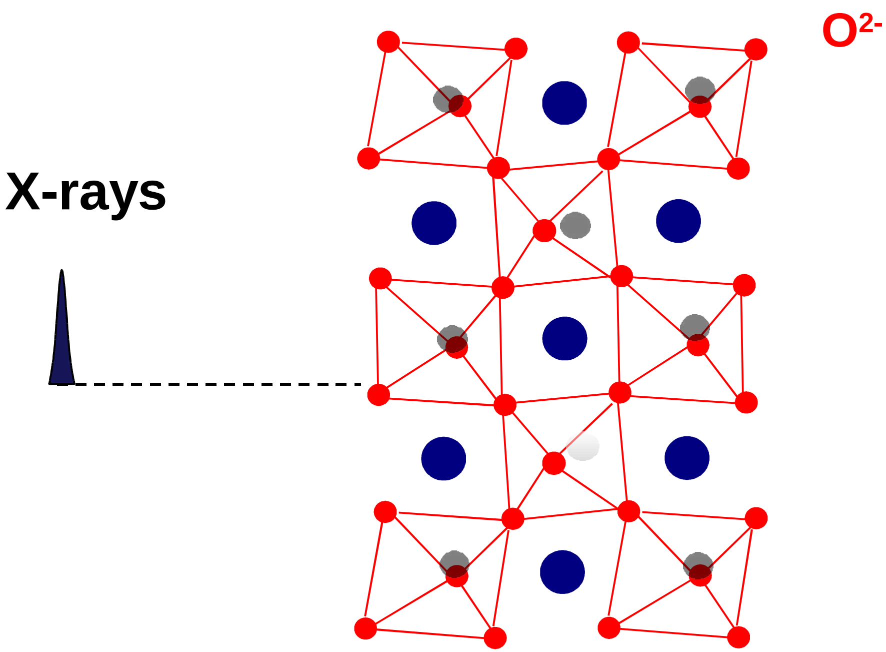
The light-induced insulator-metal transition in the "colossal magnetoresistance" compound $Pr_{0.7}Ca_{0.3}MnO_3$ is shown to generate a well-localized conducting path while the bulk of the sample remains insulating. The path can be visualized through a change of reflectivity that accompanies the phase transition. Its visibility provides a tool for gaining insight into electronic transport in materials with strong magnetic correlations. For example, a conducting path can be generated or removed at an arbitrary position just because of the presence of another path. Such manipulation may be useful in the construction of optical switches.



Fiebig et al. *Science* **280**, 1925 (1998)

X-ray Induced IMT: $Pr_{(1-x)}Ca_x MnO_3$

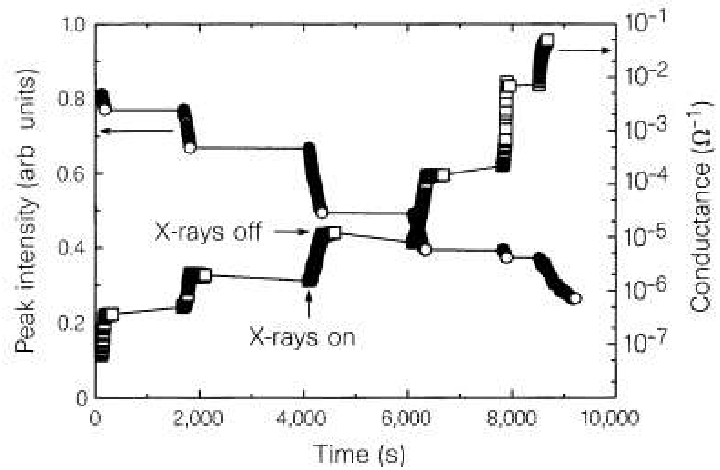
Colossal photo-resistance



An X-ray-induced insulator–metal transition in a magnetoresistive manganite

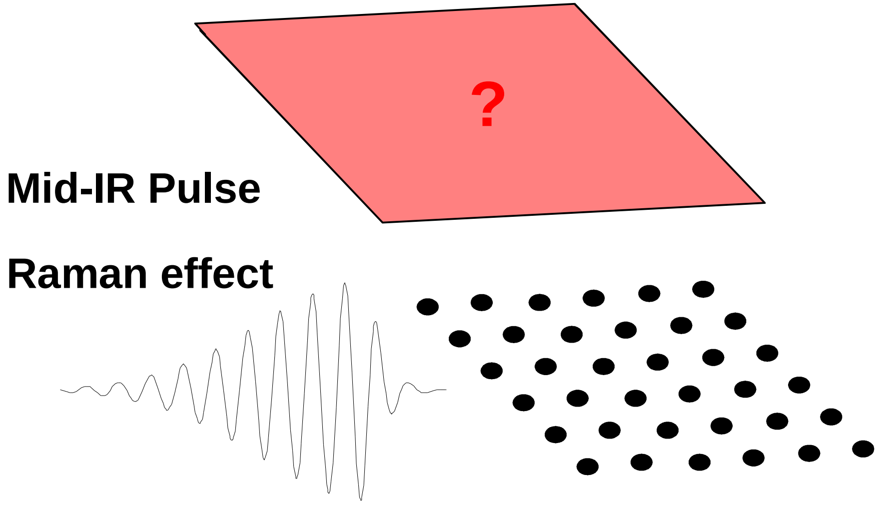
V. Kiryukhin*, D. Casa*, J. P. Hill†, B. Keimer*, A. Vigliante†, Y. Tomioka‡ & Y. Tokura‡§

* *Department of Physics, Princeton University, Princeton, New Jersey 08544, USA*
† *Department of Physics, Brookhaven National Laboratory, Upton, New York 11973, USA*
‡ *Joint Research Center for Atom Technology (JRCAT), Tsukuba, Ibaraki 305, Japan*
§ *Department of Applied Physics, University of Tokyo, Tokyo 113, Japan*



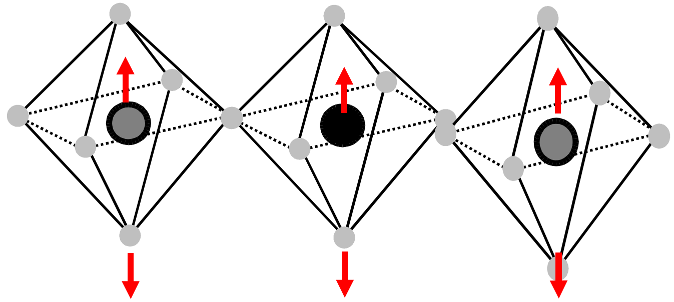
Kiryiukin et al. Nature 386, 813 (1997)

Phase Transitions Occur in the Electronic Ground State

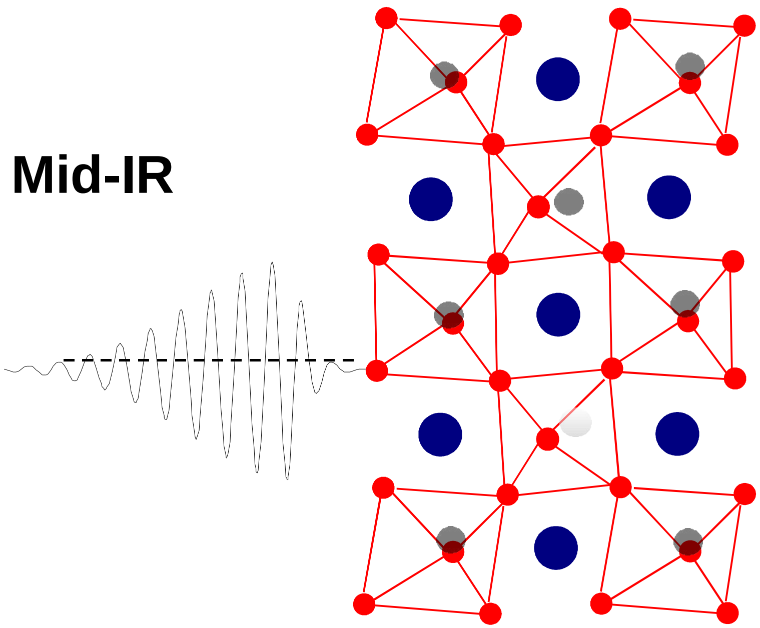


Atomic motion in the electronic ground state

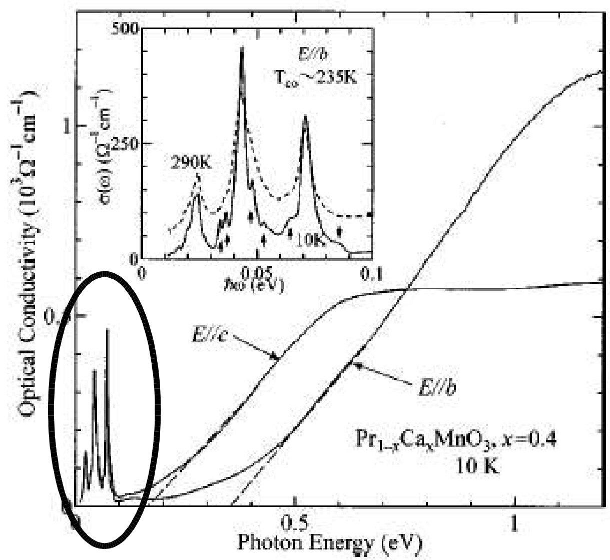
Mn-O Excitation: electronic ground state



Mid-IR



Absorption



Photon Energy

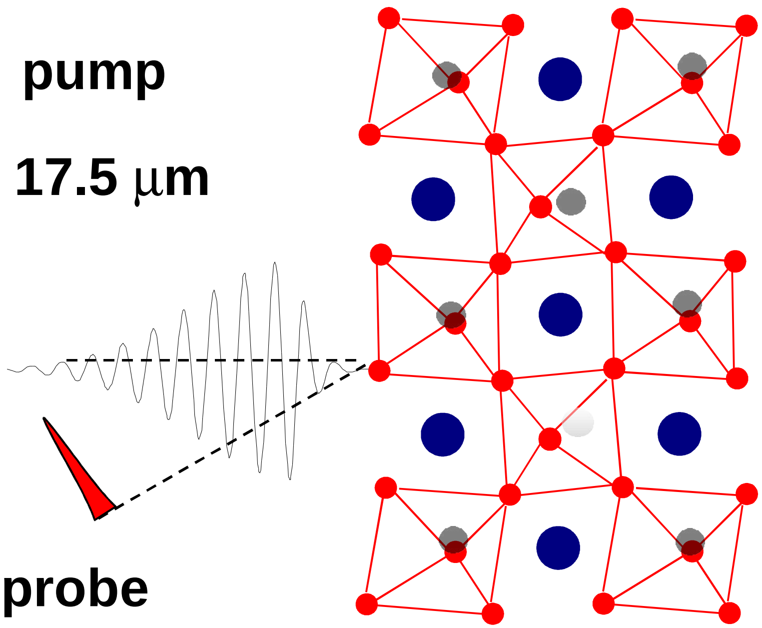
Change in Phase?

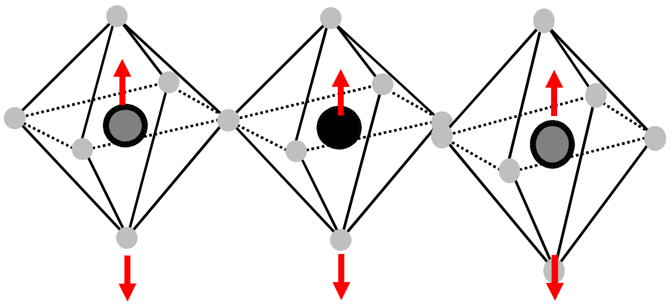
pump

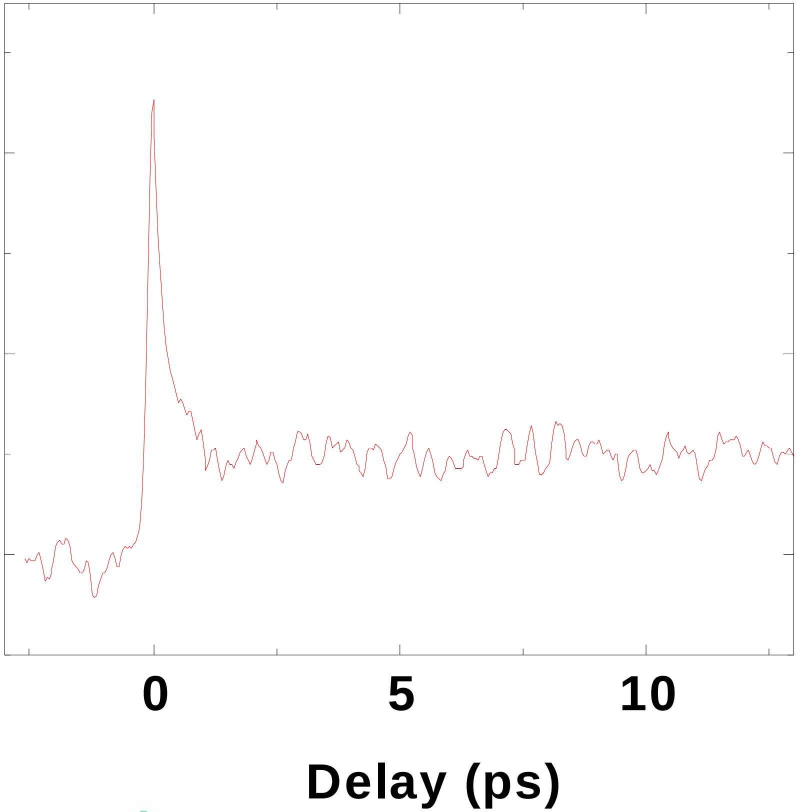
17.5 μm

probe

800 nm

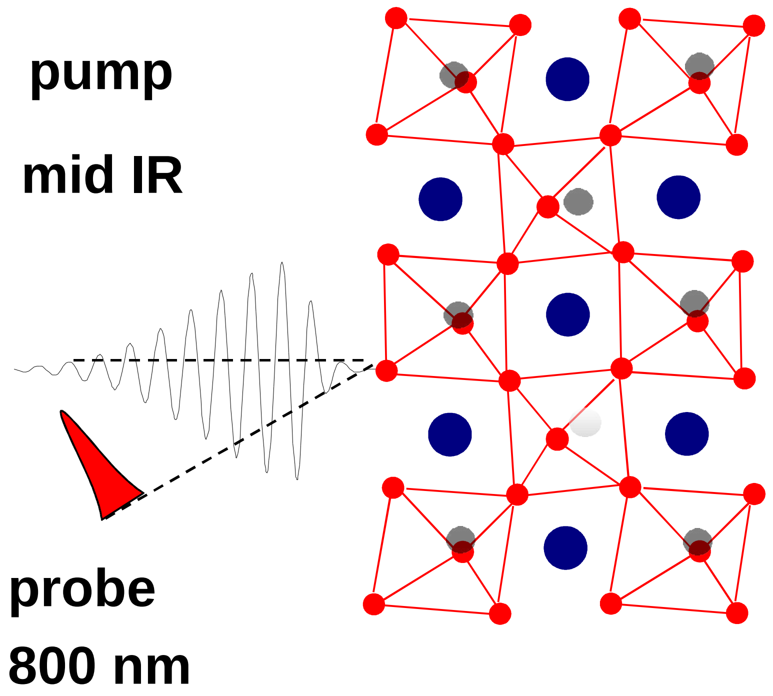


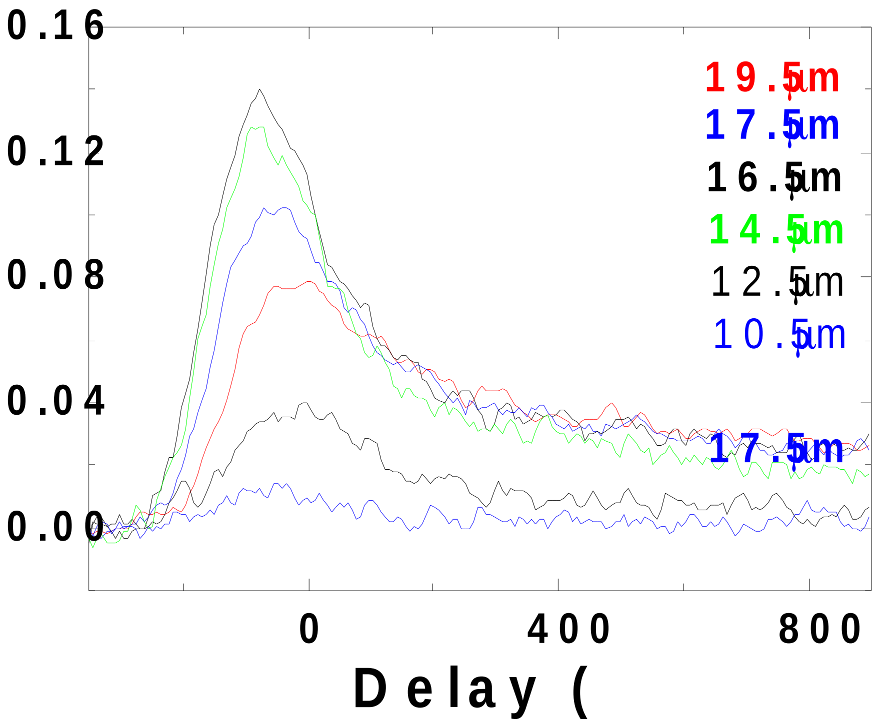




Vibrational Excitation Experiments

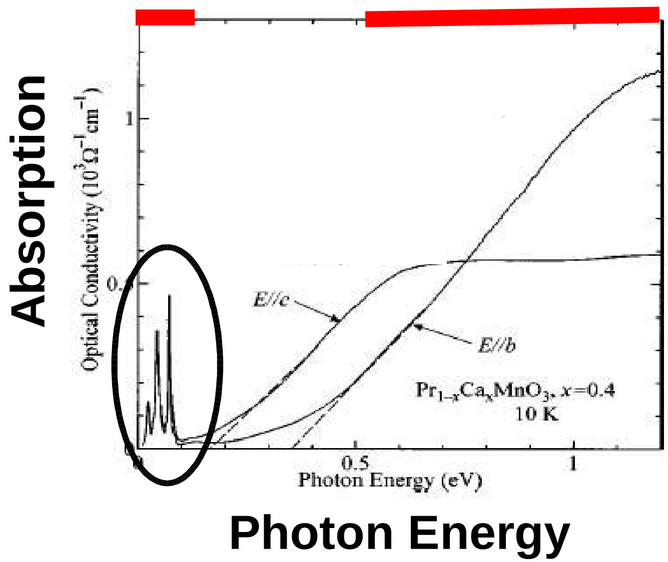
Maximum response by pumping at 16.5 μm

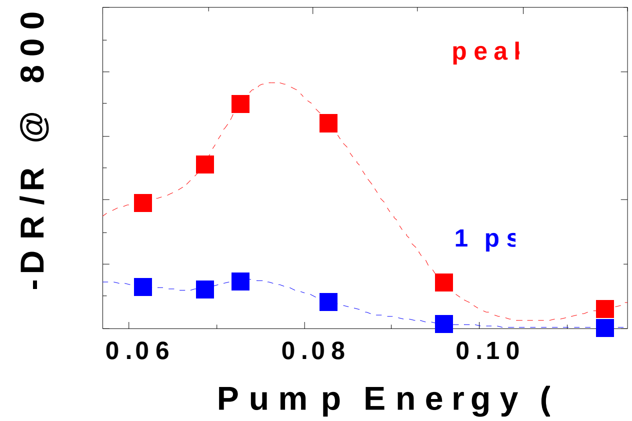


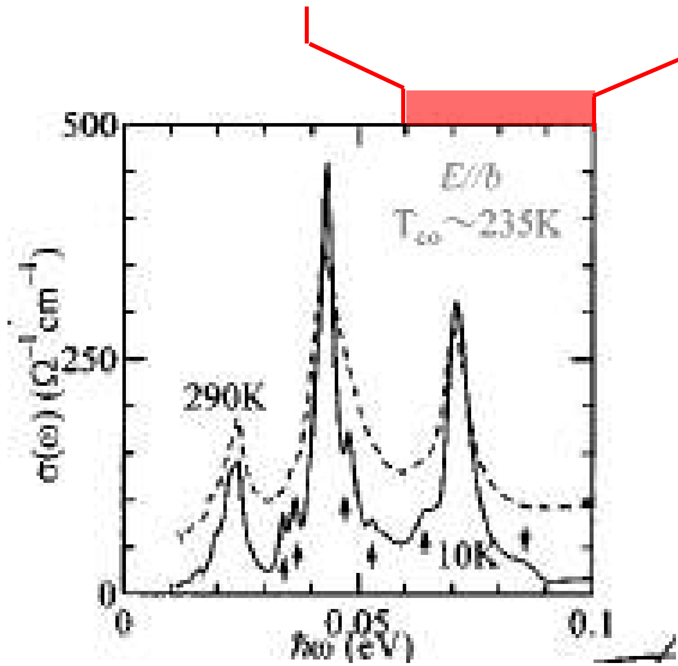


Vibrational Excitation

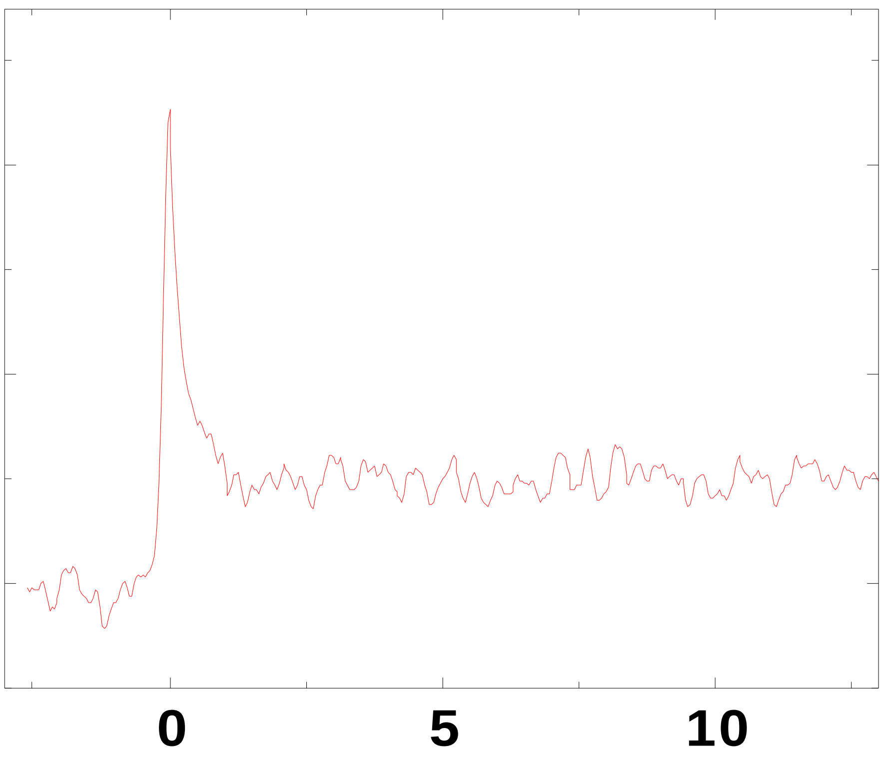
phonons **bandgap**





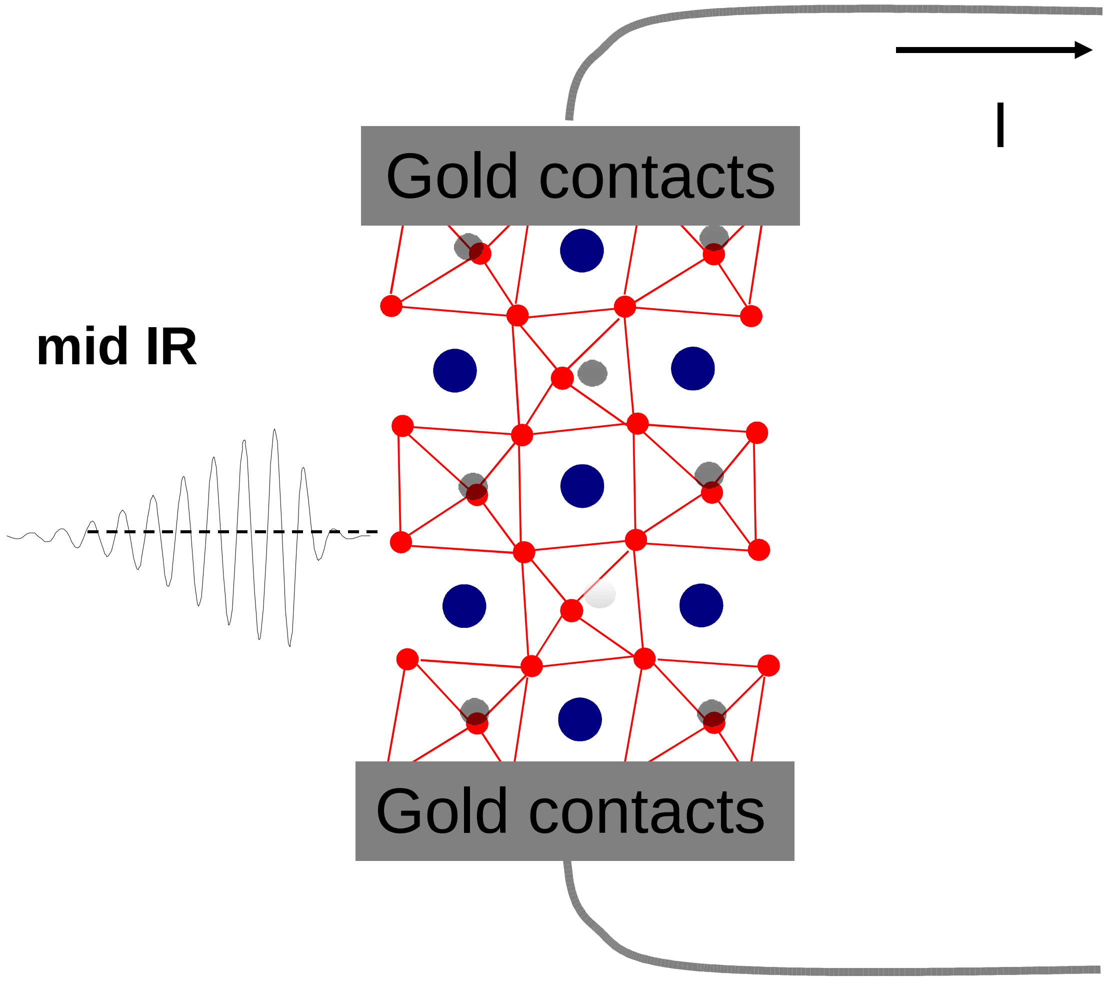


What is the long-lived state?

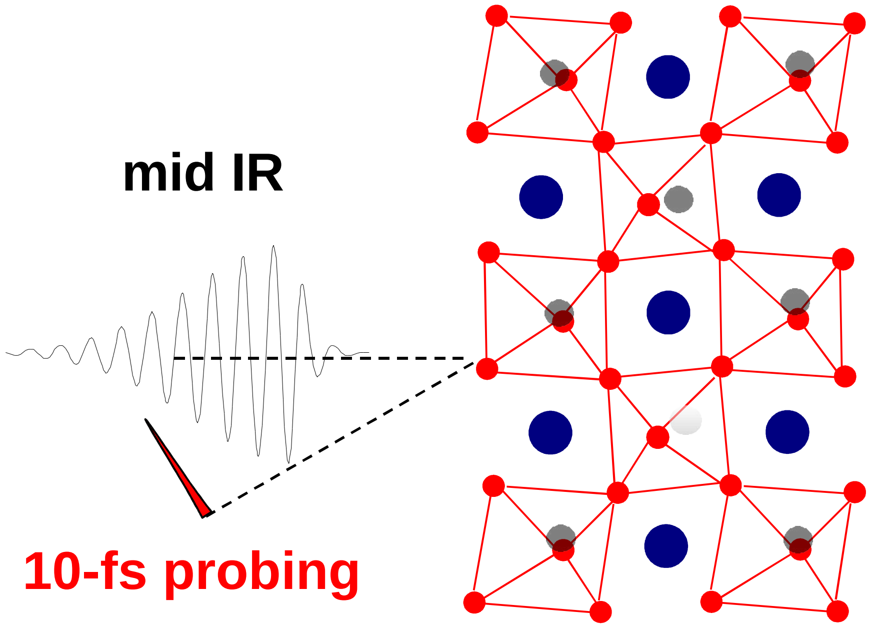


Is this a new phase ?

Next Step: probe quasi-DC conductivity



Necessary: sub-vibrational probing



Can you do this in CuO_2 - High T_c ?

Can we drive spin-crossover in Co oxides?

Can we coherently control the phase of a solid in the Electronic ground state?

Future Experiments – Vibrational Excitation

- **Are we driving a first-order phase transition?**
  - ⇨ Measuring persistent changes in the sample conductivity
  - ⇨ Time-resolved THz/Visible probing of the formation of the metallic phase

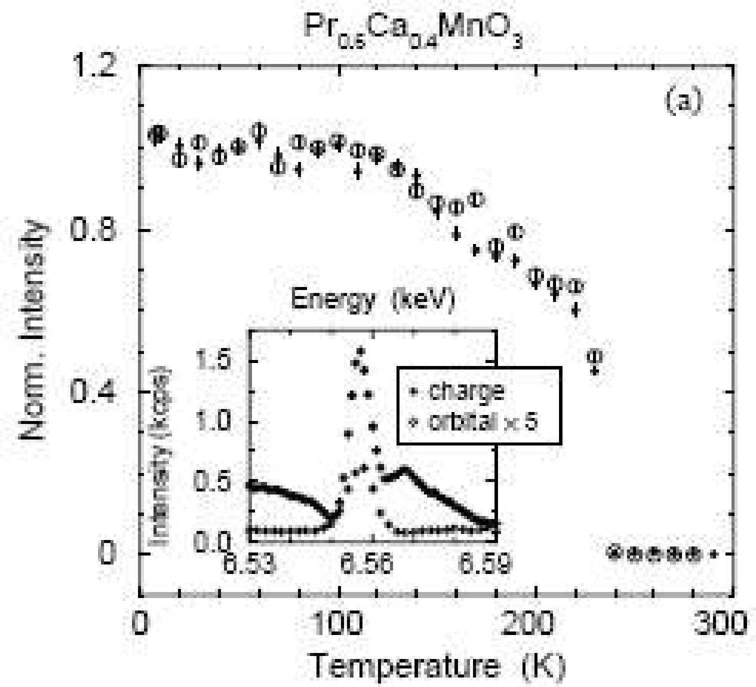
- **Time-resolved X-ray experiments:**
  - ⇨ Resonant x-ray diffraction: role of charge/orbital ordering
  - ⇨ XANES: investigate Mn-O complex, Mn-*3d* hybridization with O-*2p* states

Future Experiments – Excited Electronic State

- **Origin of the photoinduced phase transition:**

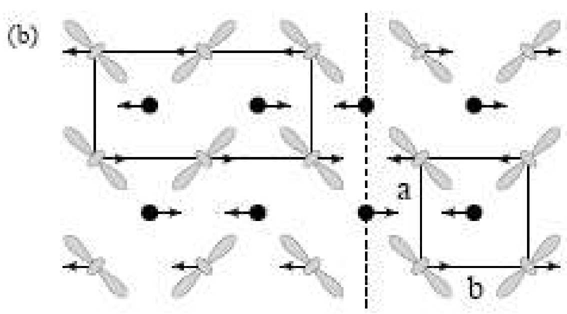
  melting of the charge-ordering by photoexcited carriers?

  ⇨ Resonant fs x-ray diffraction at the Mn K-absorption edge



Resonant x-ray diffraction is an effective probe of charge and orbital ordering in manganites

Zimmerman et al., *Phys. Rev. Lett* (1999)



Future Experiments – Excited Electronic State

- **Valence and conduction bands in CMR manganites are comprised of hybridized Mn-*3d* and O-*2p* states**

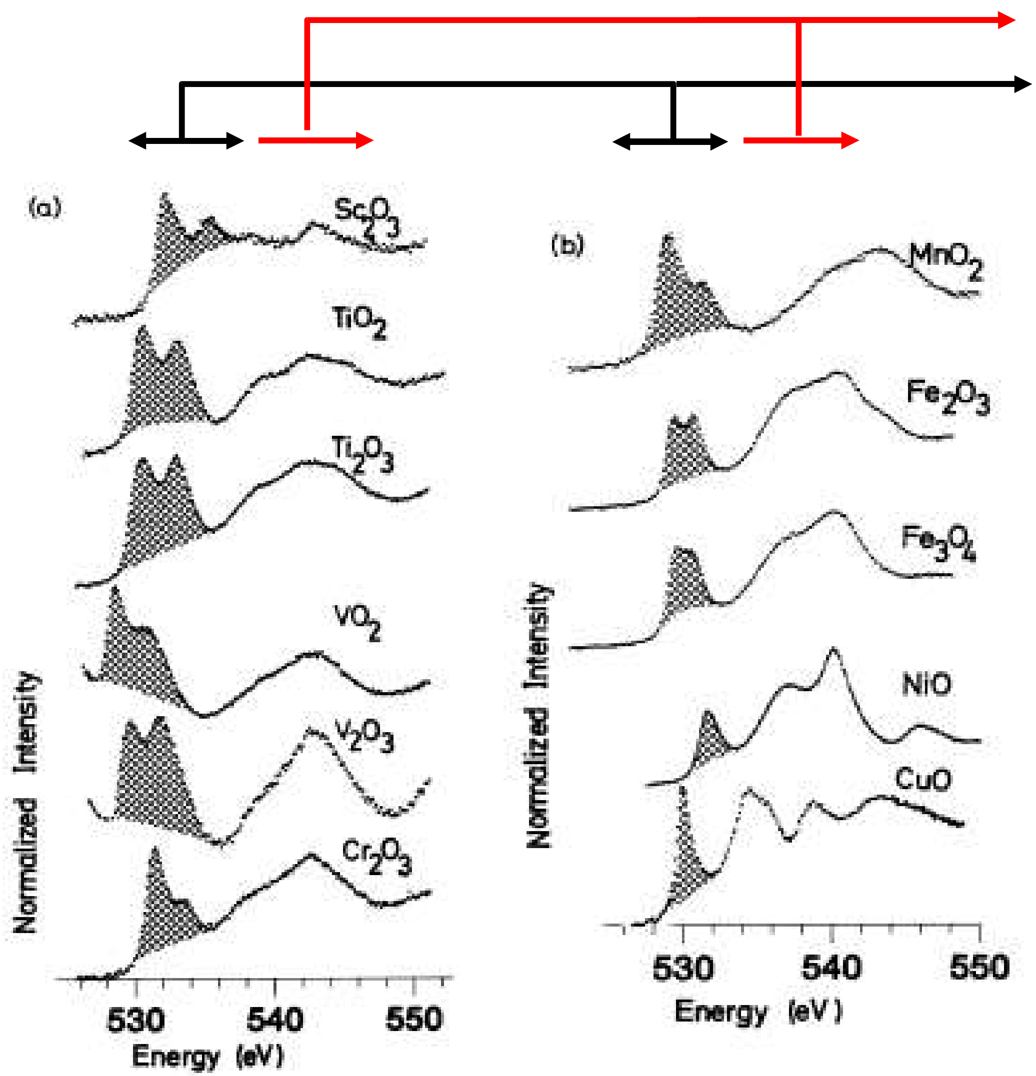
time-resolved XANES at the O K-edge and Mn $L_{II,III}$-edge

⇩

Measuring local structural distortion of the Mn-O complex resulting from the photo-excitation:

- Polaron effects
- Ionization of the Jahn-Teller instability
- Changes of the Mn-O-Mn bond angle (influencing the double-exchange mechanism)

Oxygen K-edge

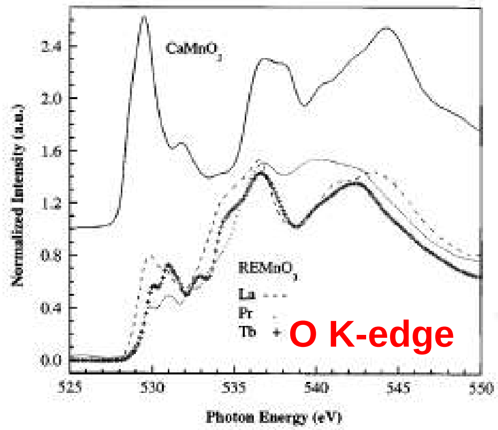


Sensitivity to changes in the hybridization for unoccupied states of mixed O-2p and metal-3d character

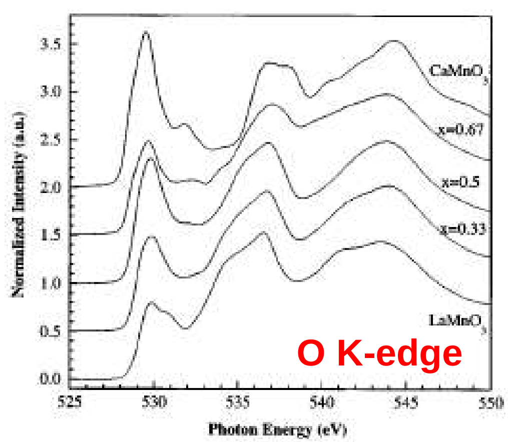
Subias et al., *Surf. Rev. Lett* (2002)

O K-edge, Mn L-edge

Sensitivity to the rare-earth cation

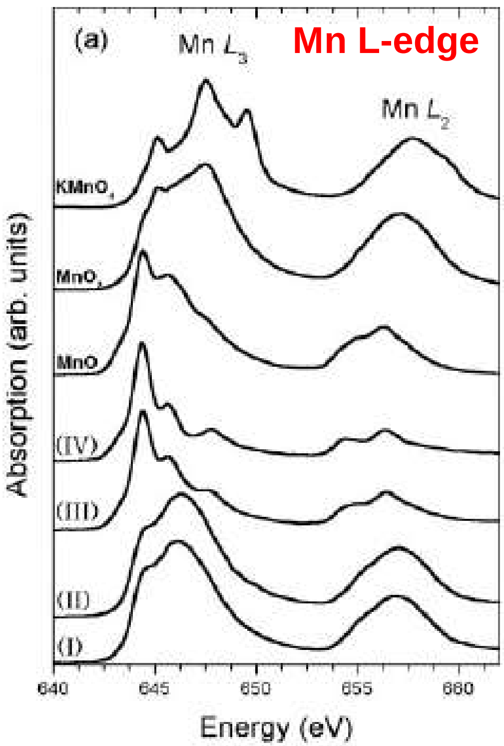


Sensitivity to the doping ratio



De Groot et al., *Phys. Rev. B* (1989)

Mn L-edge XANES: probes unoccupied states of metal-3d character
Chemical shift: changes in the Mn oxidation state



Lee et al., *Phys. Stat. Sol. A* (2003)

Topics and People

Fs NEXAFS
I-M Transition in VO_2

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Universite' du Quebec

R. Lopez, R. Haglund
Vanderbilt University

T. Dekorsy
Univ. Konstanz

Vibrational Excitation in CMR

Y. Tomioka, Y. Tokura
University of Tokyo

Fs XRD in $LiTaO_3$

K.A. Nelson
MIT

J. Itatani, S. Koshihara
KEK and Tokyo Tech.

M. Khalil (Fe II)
A. Cavalleri
R.W. Schoenlein
Materials Sciences LBNL