Ultrafast Dynamics in Complex Materials

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Workshop on "Scientific Potential of High Repetition-Rate, Ultra-short Pulse ERL X-Ray Source"
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Why use ultrafast optics to study complex materials?

~10-100 fs optical pulses are short enough to resolve processes at the fundamental timescales of electronic and nuclear motion allowing for the temporal discrimination of different dynamics.

Time

electron-electron (fs) electron-phonon (ps) spin-lattice (many ps)

Understanding the interplay between atomic and electronic structure

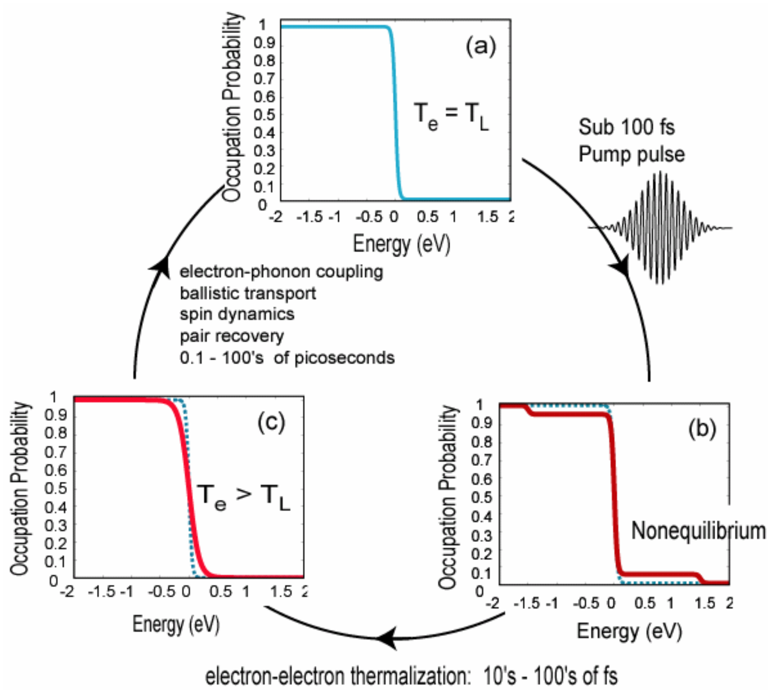
- Beyond single-electron band structure model: correlated systems (charge, spin, orbit, lattice)
- Beyond simple adiabatic potential energy surfaces

Understanding the nature of quasiparticles

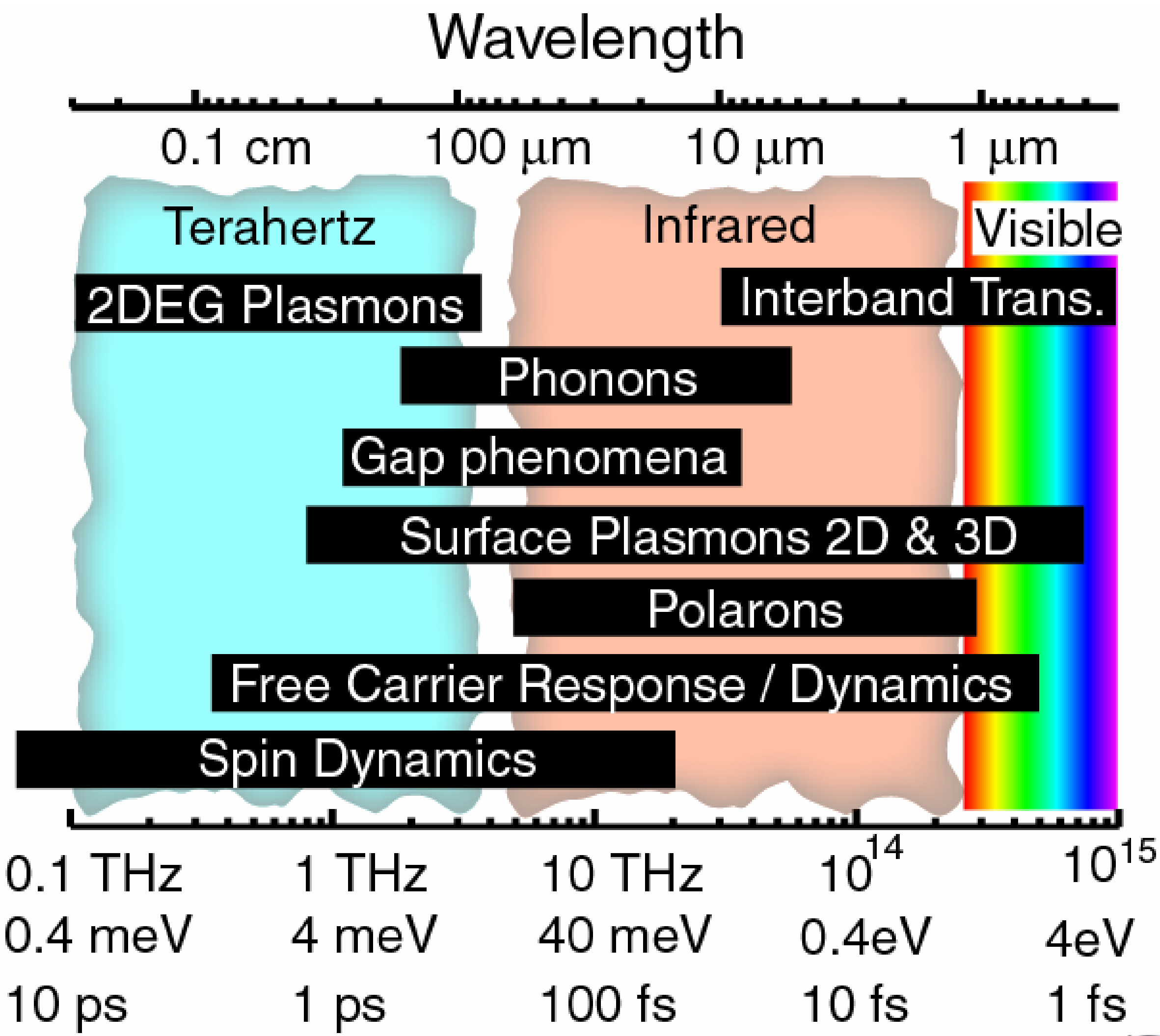
- Formation dynamics, scattering processes, relaxation channels and dynamics

Creating new states of matter

Photoinduced phase transitions—fast switching, probing dynamics where the order parameter has been perturbed, creating nonthermally accessible phases.



Why investigate dynamics from 0.001 to 5 eV?



Ultrafast X-ray Science

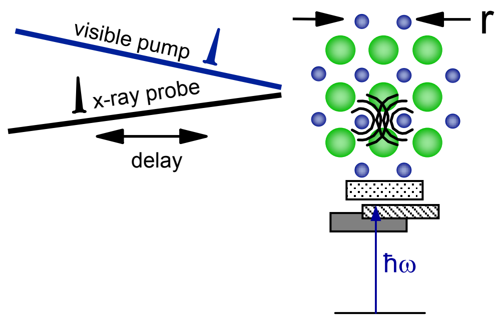
Time-resolved x-ray spectroscopy

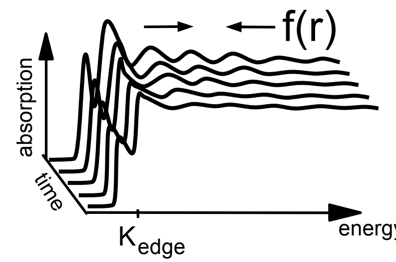
EXAFS (extended x-ray absorption fine structure) **– local atomic structure and coordination**

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

surface EXAFS, μEXAFS, ….

complex/disordered materials, molecules,chemical reactions, element specific

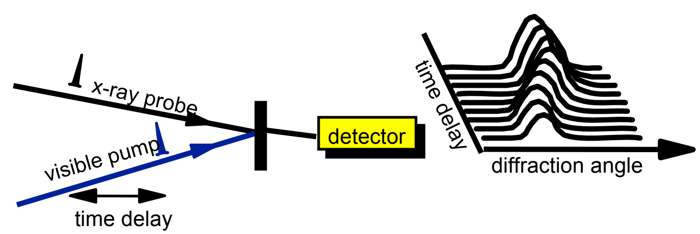


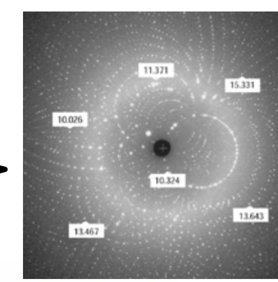


R.W. Schoenlein

Time-resolved x-ray diffraction

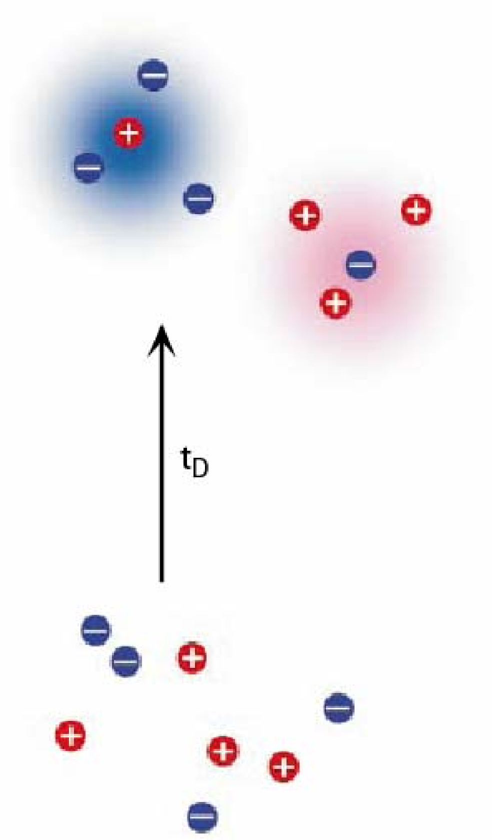
atomic structure in systems with long-range order/periodicity
phase transitions, coherent phonons, polarons



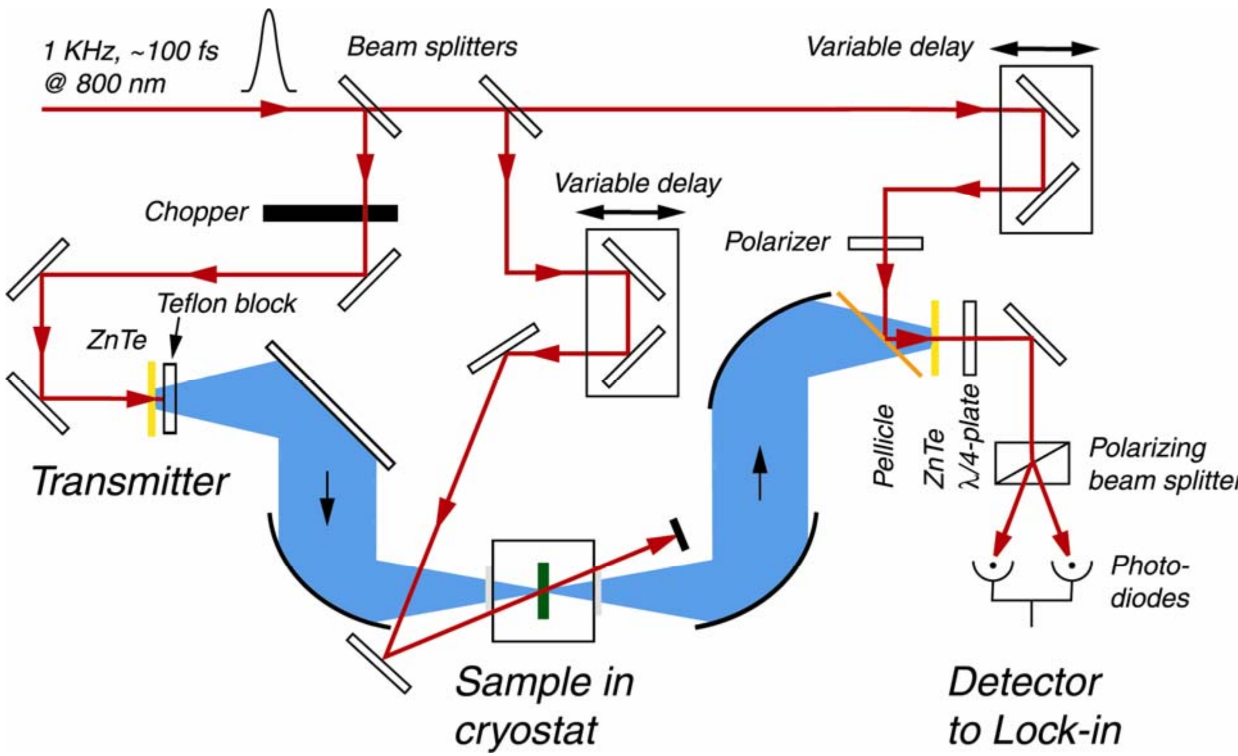


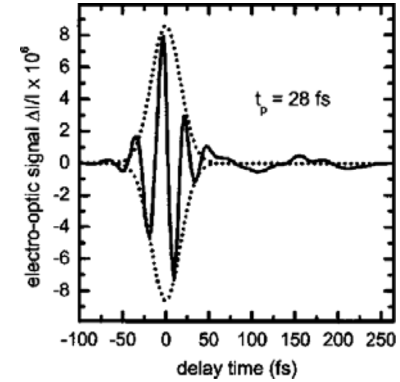
Formation of the many-body state in an electron-hole plasma

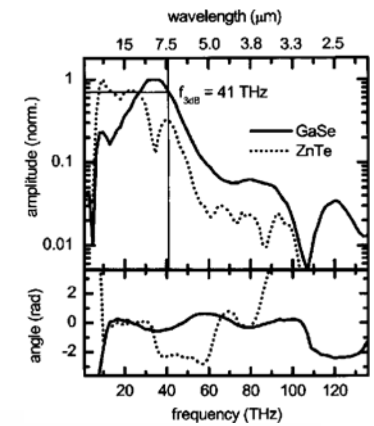
- Following photoexcitation in a semiconductor, the electrons and holes form a collective state governed by a screened interaction potential, renormalized by the dielectric function: $V_C(q)/\varepsilon_q(\omega,t_D)$
- The modified coulomb potential produces 'dressed' quasiparticles: electrons with a screening cloud of positive charges and vice versa.
- Quantum kinetic theories predict a delayed formation of these quasiparticles, with a broadened plasmon resonance following excitation.
- Drude theory should describe the long-time limit of the dielectric function/conductivity of these quasiparticles.
- Can ultrafast optical techniques be used to observe the formation of these quaisparticles?

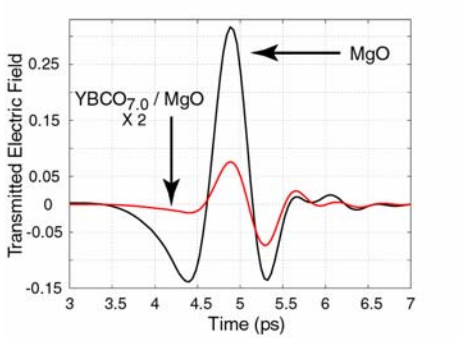


Optical pump/ terahertz probe spectroscopy dynamically probes low lying excitations



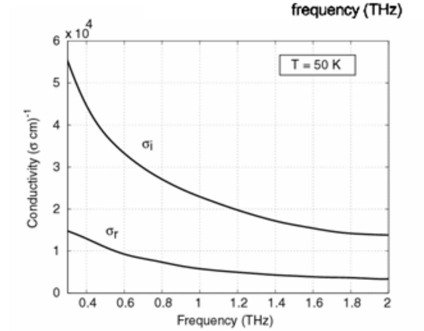






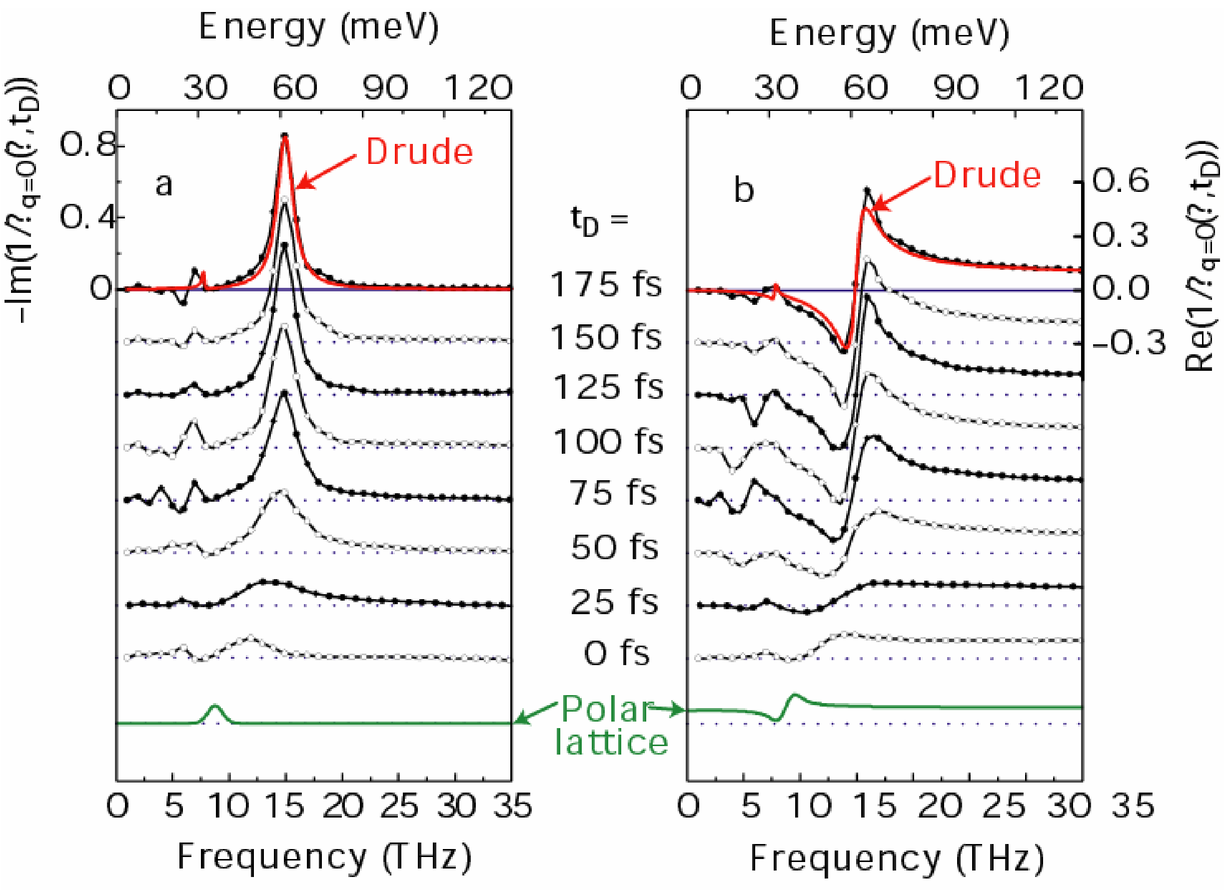
$$\Phi(\omega) = FT\{E_{sample}(t)\}/FT\{E_{ref}(t)\}$$

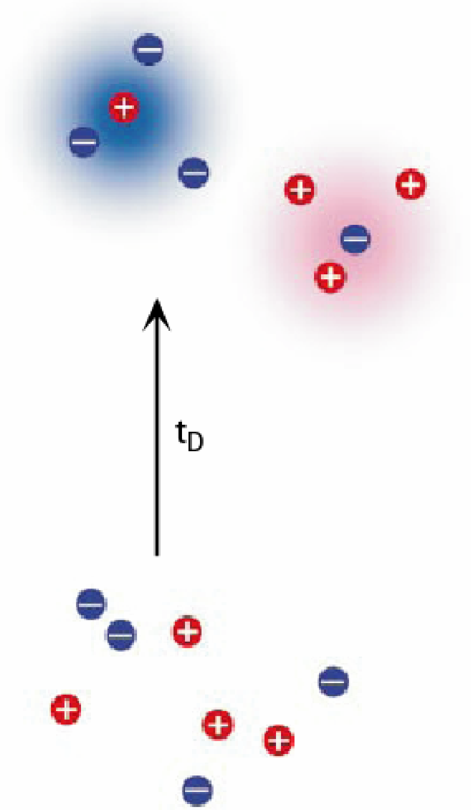
$$\Phi(\omega) = \frac{1+n_3}{1+n_3+Z_0\sigma(\omega)d}\exp(i\frac{\omega}{c}\Delta L)$$



Kubler et al, Appl. Phys. Lett. **85**, 3360 (2004)

The formation of dressed quasiparticles in GaAs supports quantum kinetic theories





- Delayed build up of screening and a broadened plasma pole following photoexcitation
- Good agreement with Drude fits for delays >75 fs with τ increasing from 20 fs to 80 fs.

N=2x10^{18} cm^{-3}
ω_p = 15 THz (70 fs)

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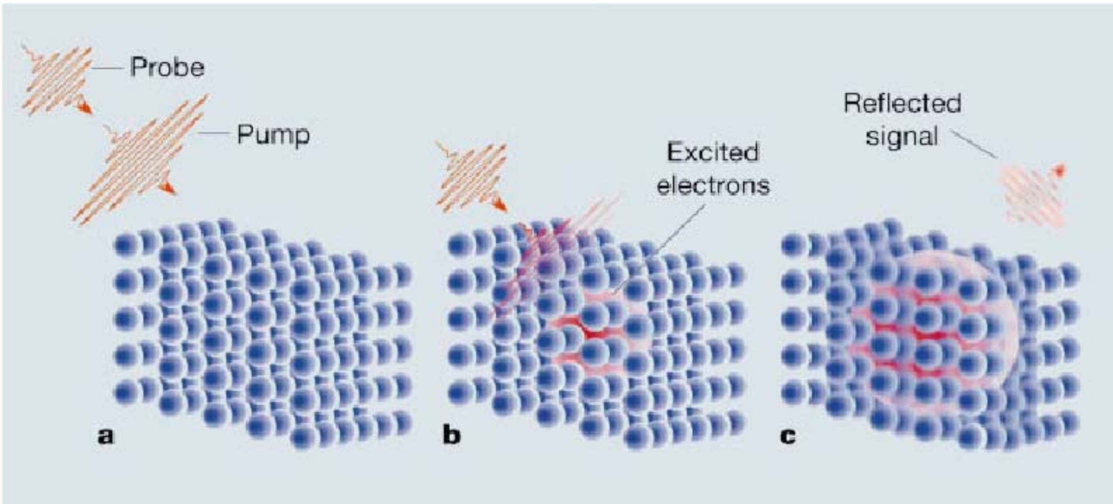
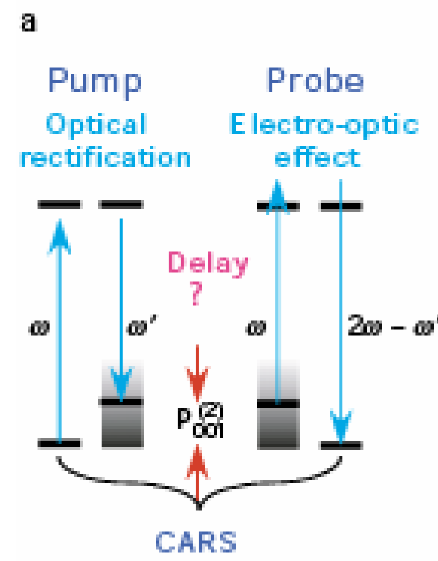
Huber et al, Nature **414**, 286 (2001).

The response of the coupled carrier-lattice system in Si—formation of the coherent phonon

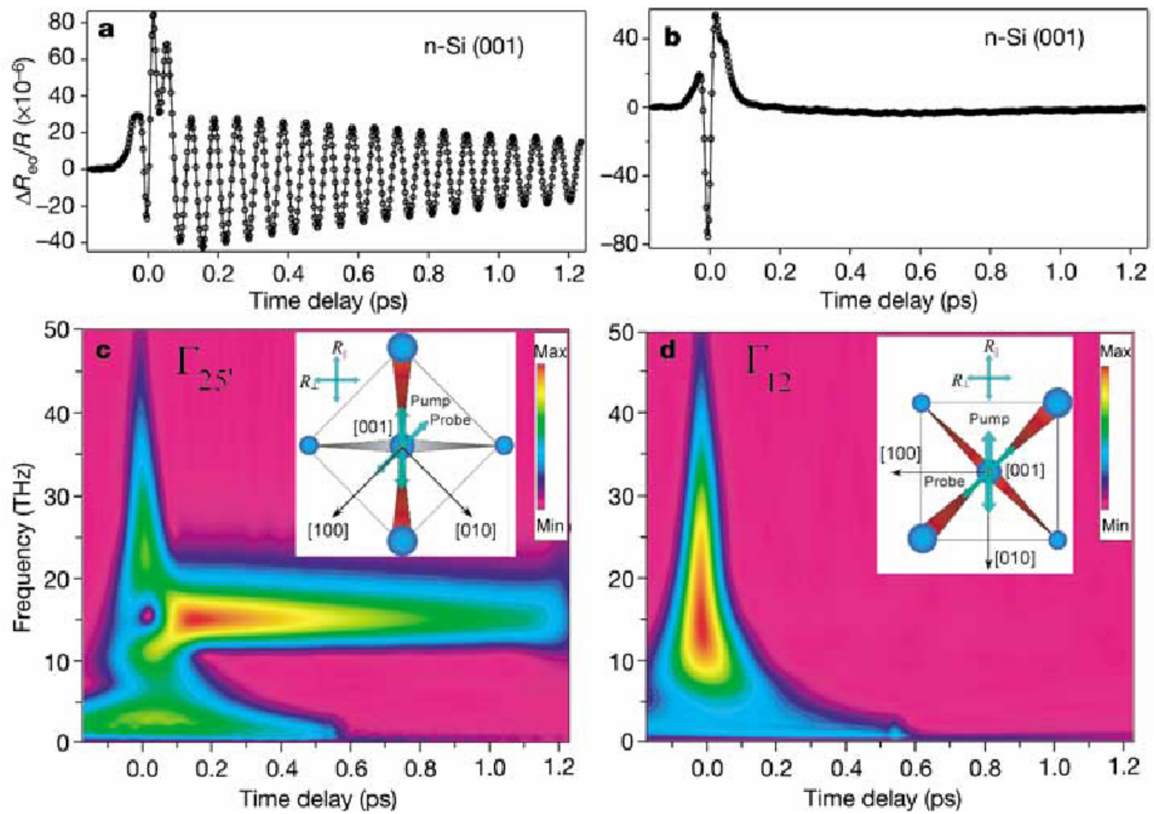




- Optical pump pulses interacts with the sample via a χ^2 process to generate a force on the lattice and drive a coherent phonon oscillation.
- The coherent response following 10-fs excitation reveals the dynamics of formation of the 15-THz coherent LO phonon in Si and its dressing through interaction with the electron-hole plasma.
- Differential detection of the reflected electro-optic signal in orthogonal polarizations enables detection of the coherent response.

The response of the coupled carrier-lattice system in Si—formation of the coherent phonon

$$\Delta R \sim \exp(-t/1.30)\cos[(15.24t+.016t^2+0.064)2\pi]$$



- Coherent phonon response only seen when pump pulse polarized to drive excitation.
- Delayed (~100 fs) coherent phonon response observed after electronic coherences have dephased
- Coherent phonon frequency (15.24 vs 15.6 THz and dephasing time (1.3 vs 3.5 ps) changed by density-dependent coherent phonon self-energy.
- Antiresonance with Fano lineshape observed at 15.3 THz, 22 fs (overlap between electronic and coherent phonon response).
- Results from coupling of the LO phonon and electron-hole continuum amplitudes via χ^3 scattering and electron-phonon coupling.

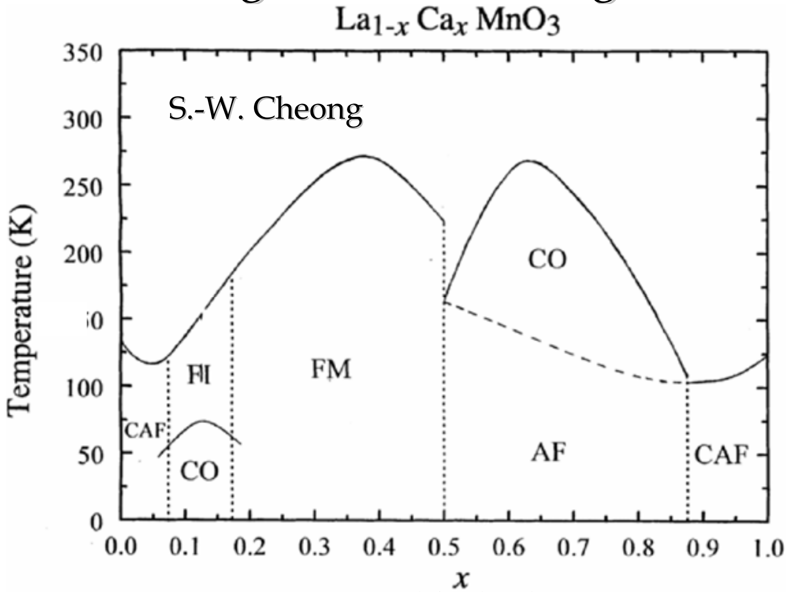
ERL experiment: Ultrafast x-ray diffraction (need short pulses)

Hase et al, Nature **426,** 51 (2003).

Mixed Valence Manganites

Strong coupling of the charge, spin, lattice, and orbital degrees of freedom
(at metallic carrier densities i.e. ~ 10^{22} cm $^{-3}$)

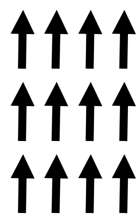
Magnetic Phase Diagram

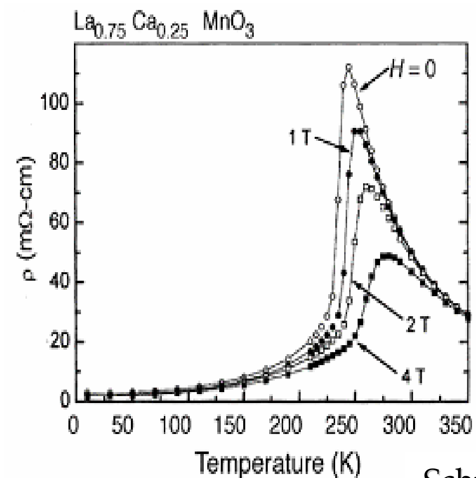


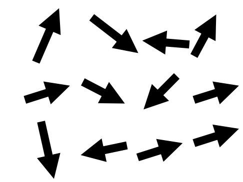
Increased hole doping

$La^{3+}Mn^{3+}(O^{2-})_3$ $Ca^{2+}Mn^{4+}(O^{2-})_3$

Colossal Negative Magnetoresistance

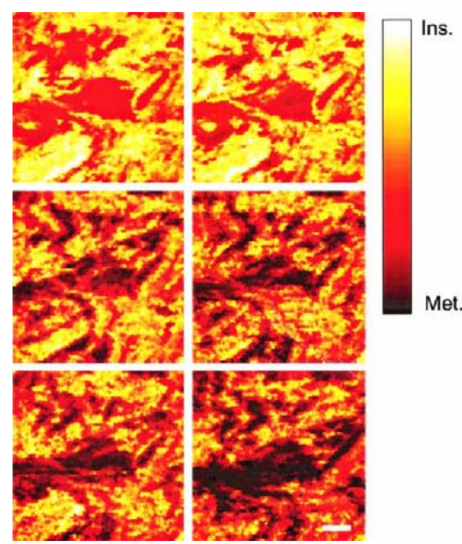






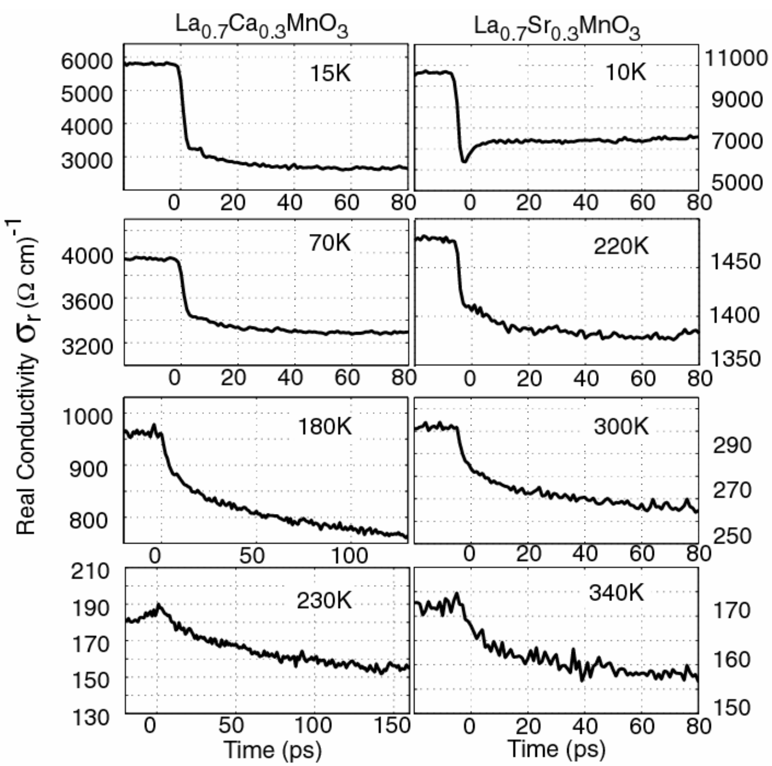
Schiffer, et al., PRL **75**, 3336 (1995)

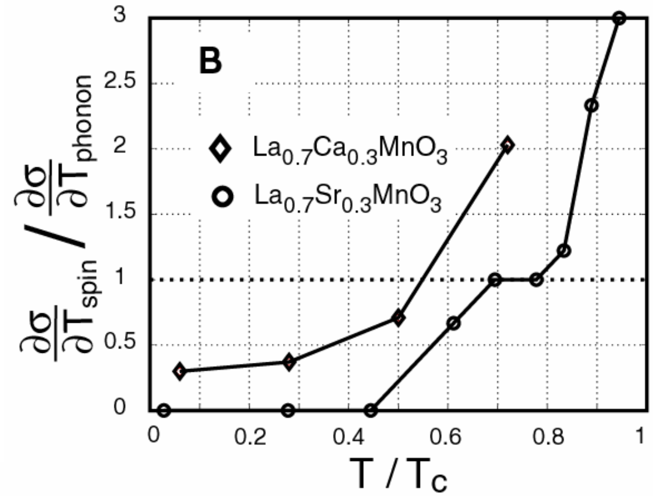
Electronic Phase Separation



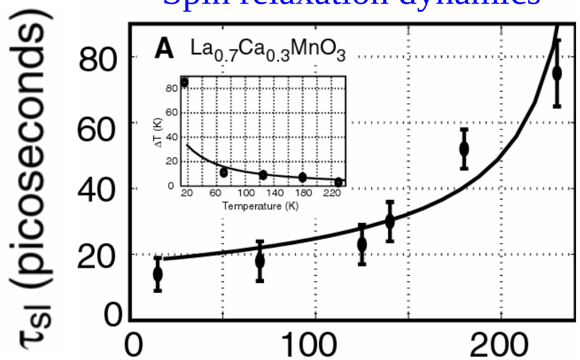
M. Fath, et al., Science **285**, 1540 (1999).

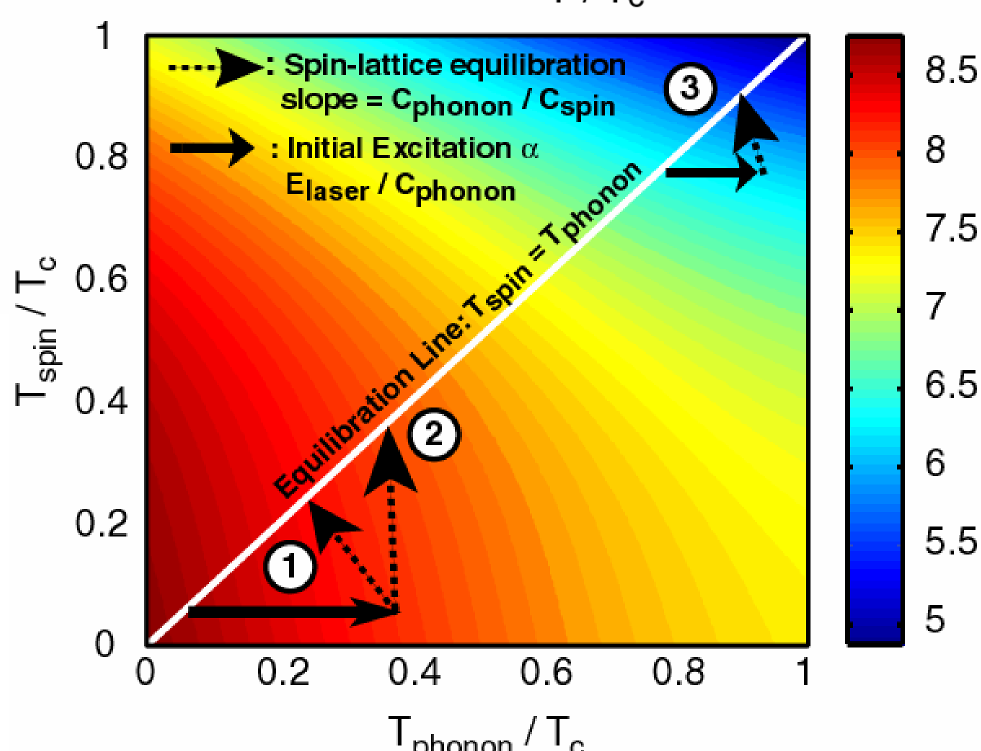
Ultrafast measurements separate spin and phonon dynamics





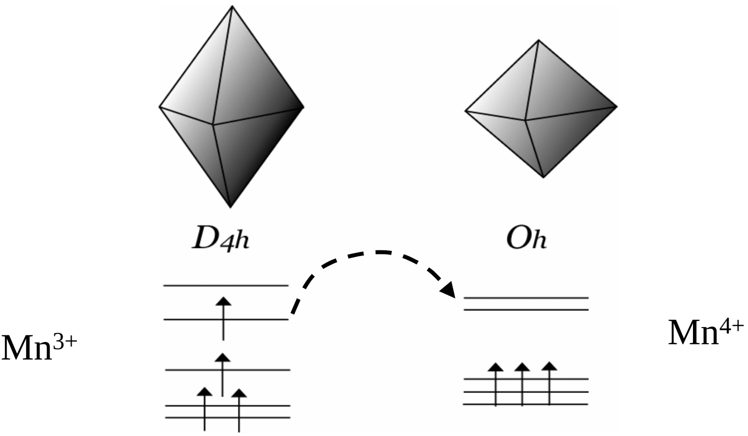
Spin relaxation dynamics

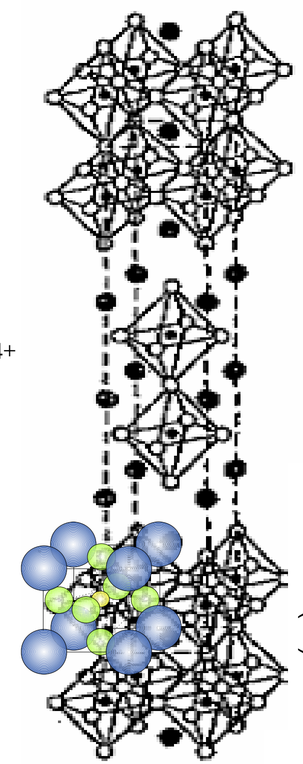




R. D. Averitt, et al, Phys. Rev. Lett. **87**, 017401 (2001).

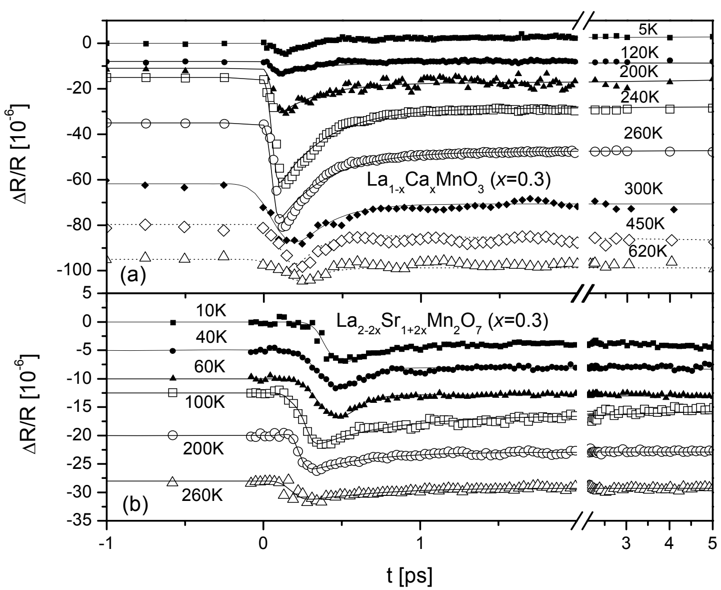
Polaron Formation: 3-D Perovskite vs 2-D Bilayered Manganites

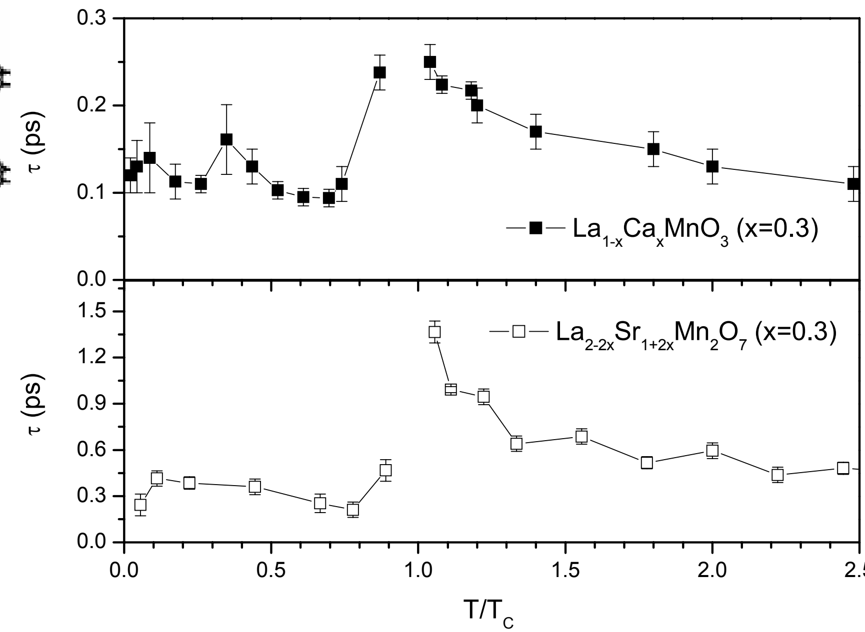




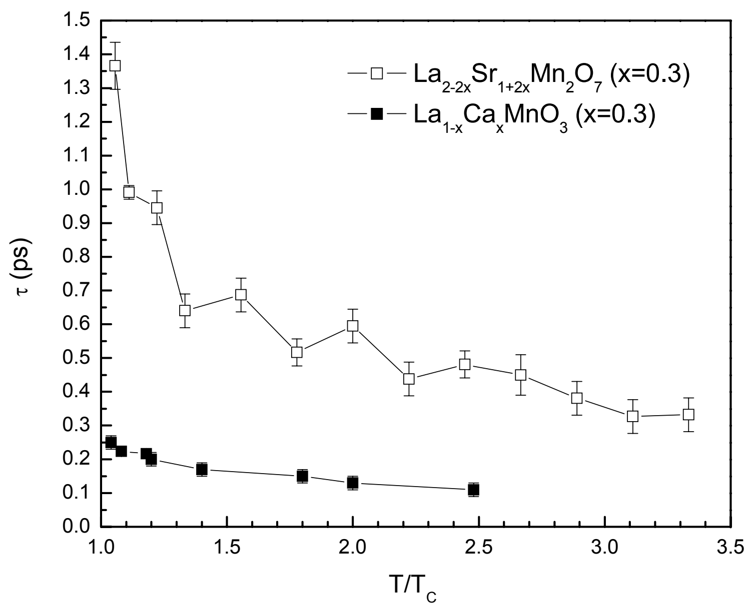
$La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.3, T_C ~ 90 K)

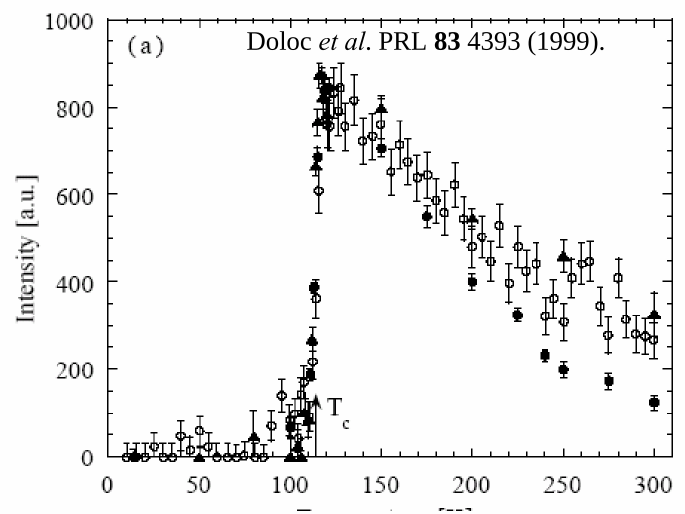
$La_{1-x}Ca_xMnO_3$ (x=0.3, T_C ~ 240 K)

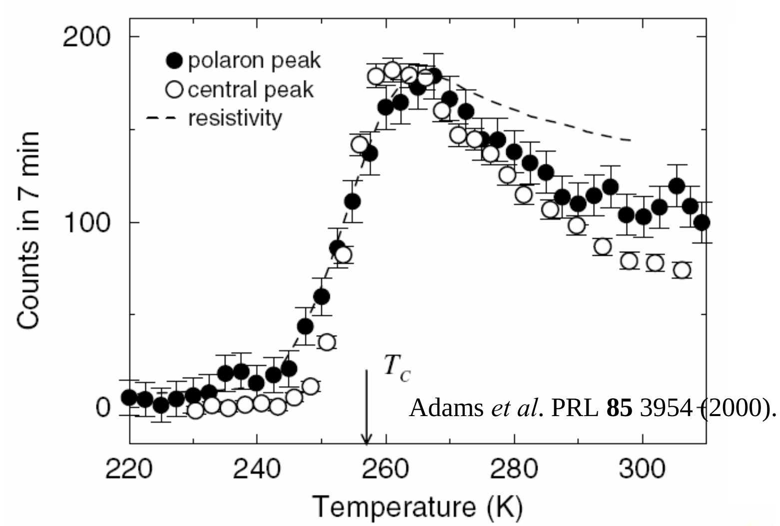




Polaron Dynamics: Ultrafast Optics and Neutron Scattering Data







ERL experiment: 1) Ultrafast x-ray diffraction and/or EXAFS to directly observe polaron dynamics. 2) Spatially resolve experiment on ~100 nm scale.

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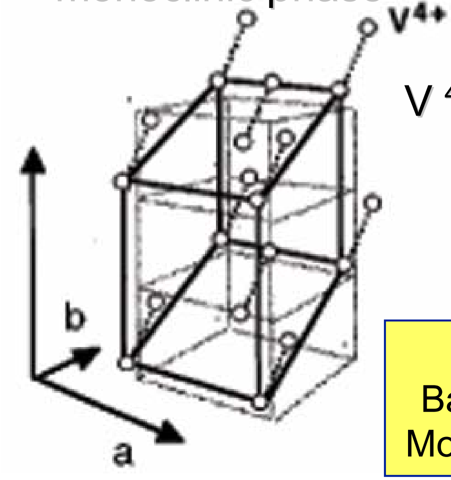
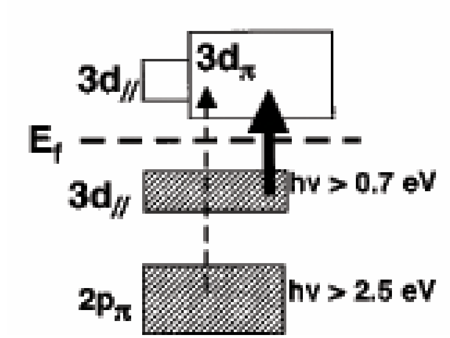
Ultrafast Structural and Electronic Transitions in VO_2

Semiconductor

Low temperature (T<340 K)
monoclinic phase

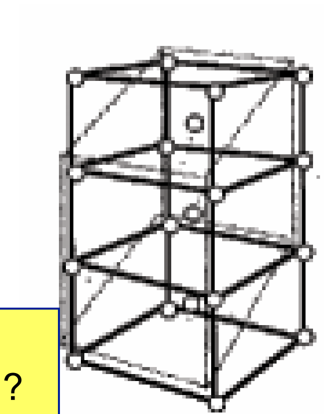


V^{4+} pairing and tilting

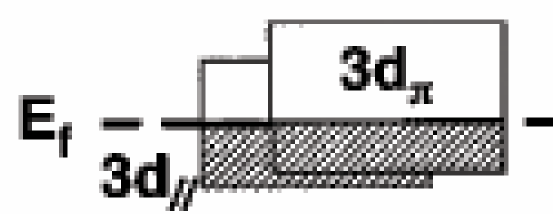


Metal

High temperature (T>340 K)
rutile phase

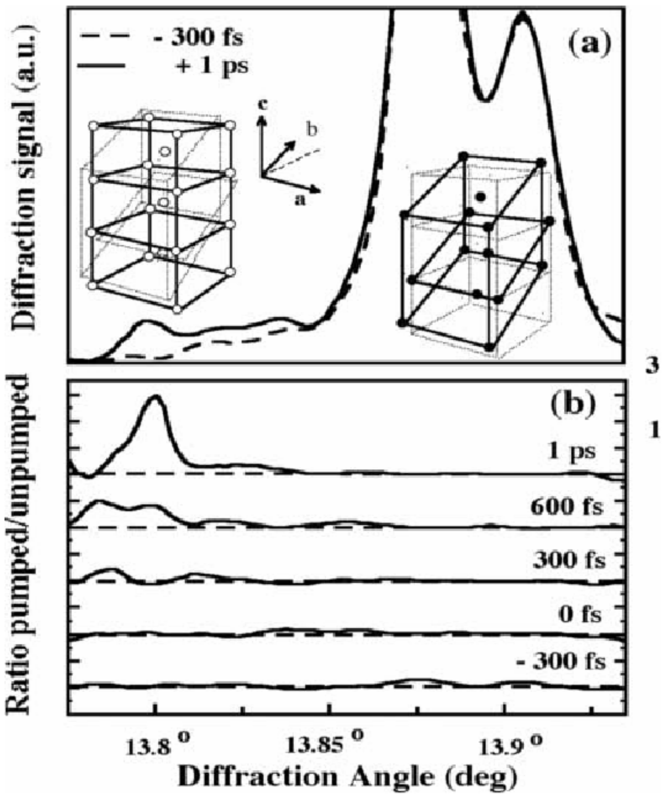


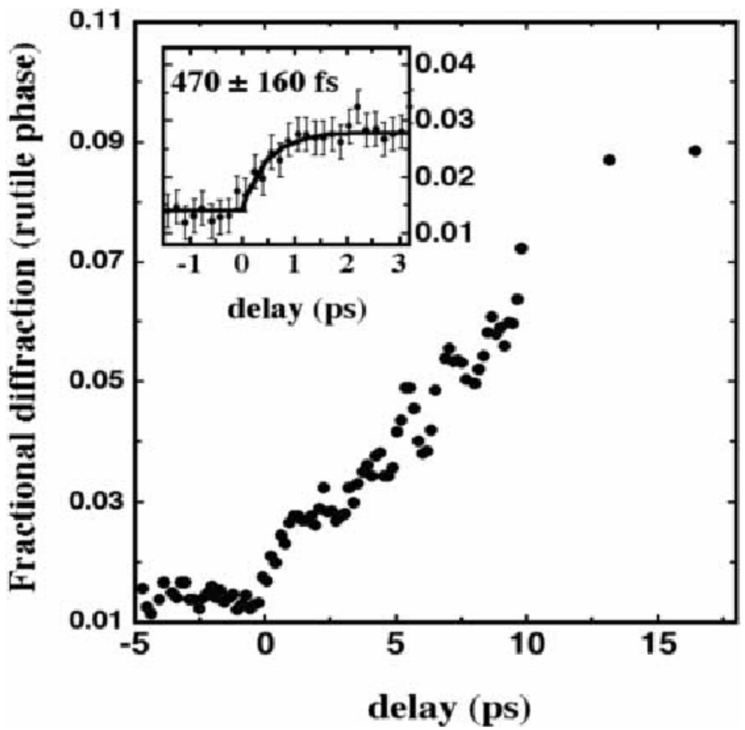
Origin of insulating phase:
Band insulator – structural component ?
Mott-Hubbard insulator – e-e correlation ?



Ref: Goodenough, J. Solid State Chemistry, **3**, 490 (1971)

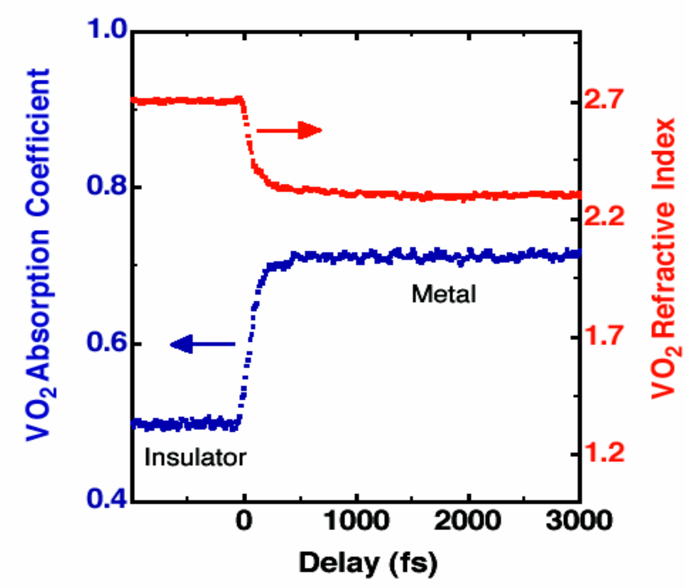
Previous ultrafast x-ray diffraction measurements of the VO_2 Insulator-Metal Transition reveal a resolution-limited formation time





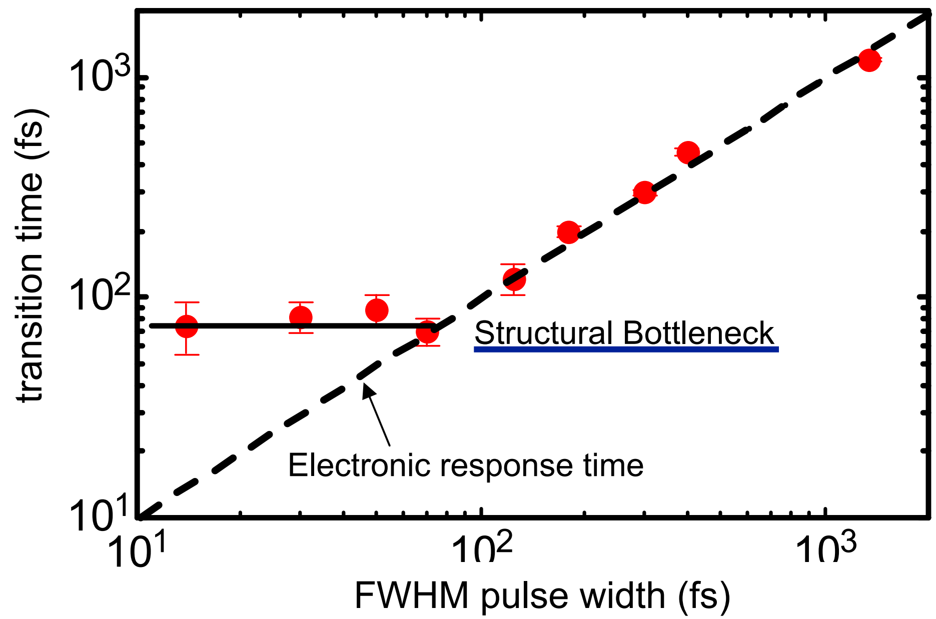
Cavalleri et al, *Phys. Rev. Lett.* **87**, 237401, (2001).

Optical Measurements of VO_2 Insulator-Metal Transition indicate a structural transition drives the insulating phase



V-V distortion

($T_{optical\text{-}phonon}$~150 fs)

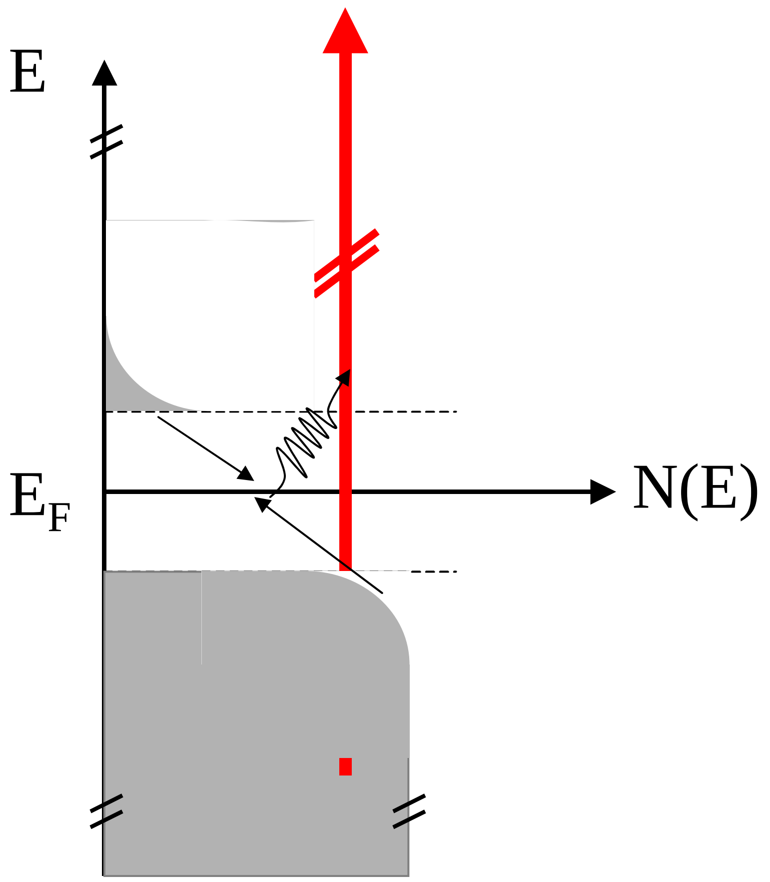


⇒ band (Peierls) type insulator

ERL experiment: Ultrafast x-ray diffraction to definitively measure the timescale of the structural change. Spatially resolved experiment also of interest.

Cavalleri, Dekorsy, Chong, Kieffer, Schoenlein, Shank, *Phys. Rev. B,* **70**, 161102, (2004).

Carrier relaxation dynamics in superconductors



1) PHOTO-EXCITATION: ***Short pulse ~100 fs excites quasiparticles.***

(n_{PE}/n_C $\approx 10^{-3}$-10^{-2})

2) INITIAL RELAXATION: ***via QP scattering, phonon emission, and in the case of superconductors the condensate fraction is reduced - i.e. pair-breaking. This results in a distbn. of QP's at the gap.***

3) RECOMBINATION: ***A small energy gap near E_F creates a bottleneck in the QP recombination.***

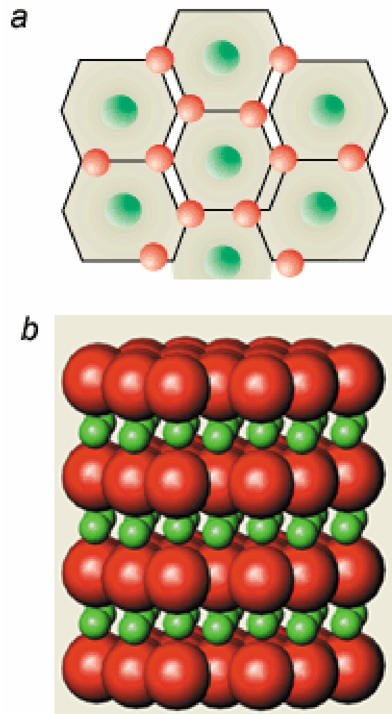
$$\omega > 2\Delta$$

Superconducting recovery dynamics

τ_r ~ 0.5 – 1000 ps

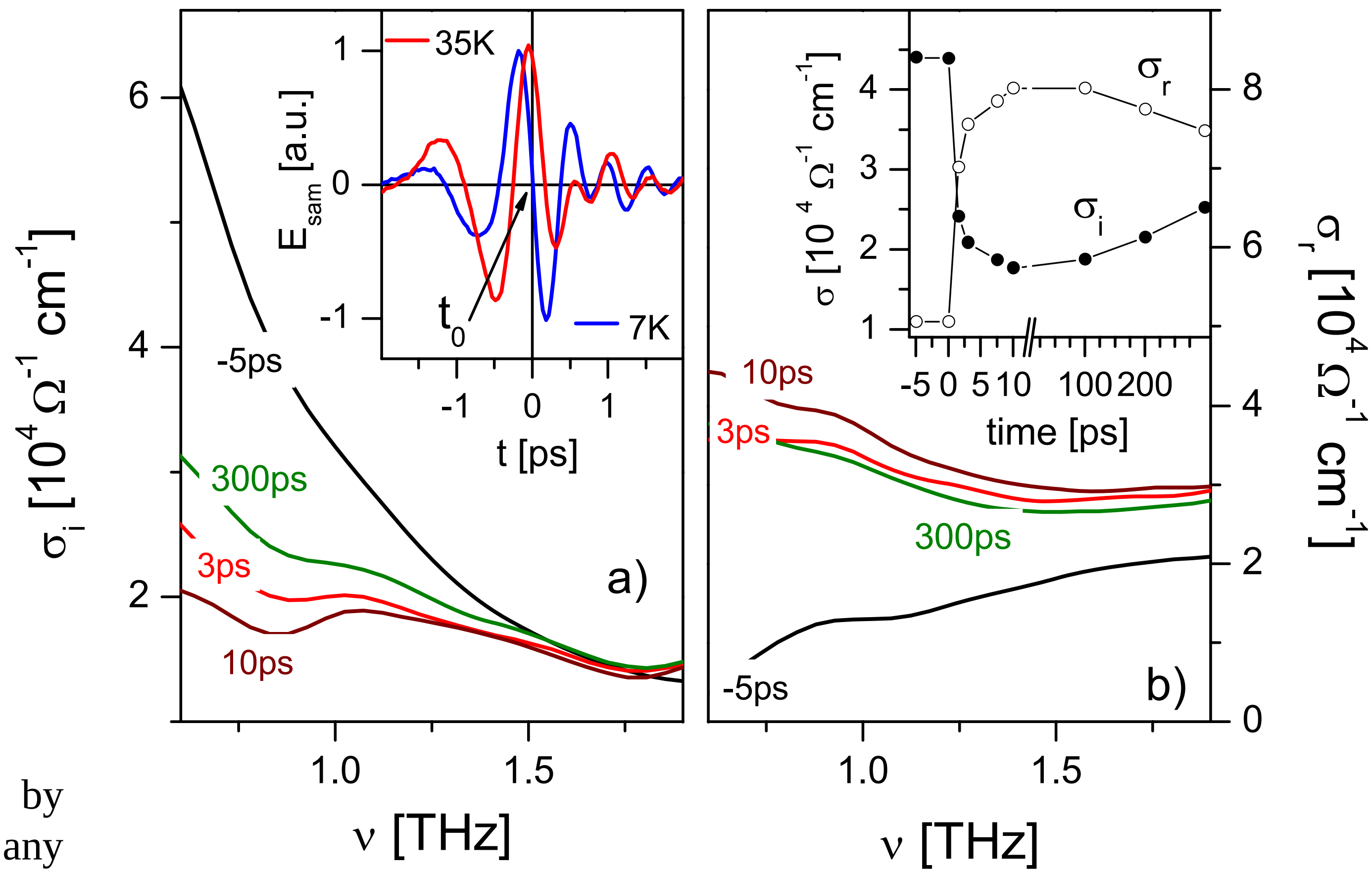
V.V.Kabanov et al., *Phys. Rev. B 59, 1497 (1999)*

Conductivity Dynamics in MgB_2



MgB_2: T_c = 39K

MgB_2 has the highest T_c, by nearly a factor of two, of any simple intermetallic superconductor.



7K, ~4 mJ/cm2

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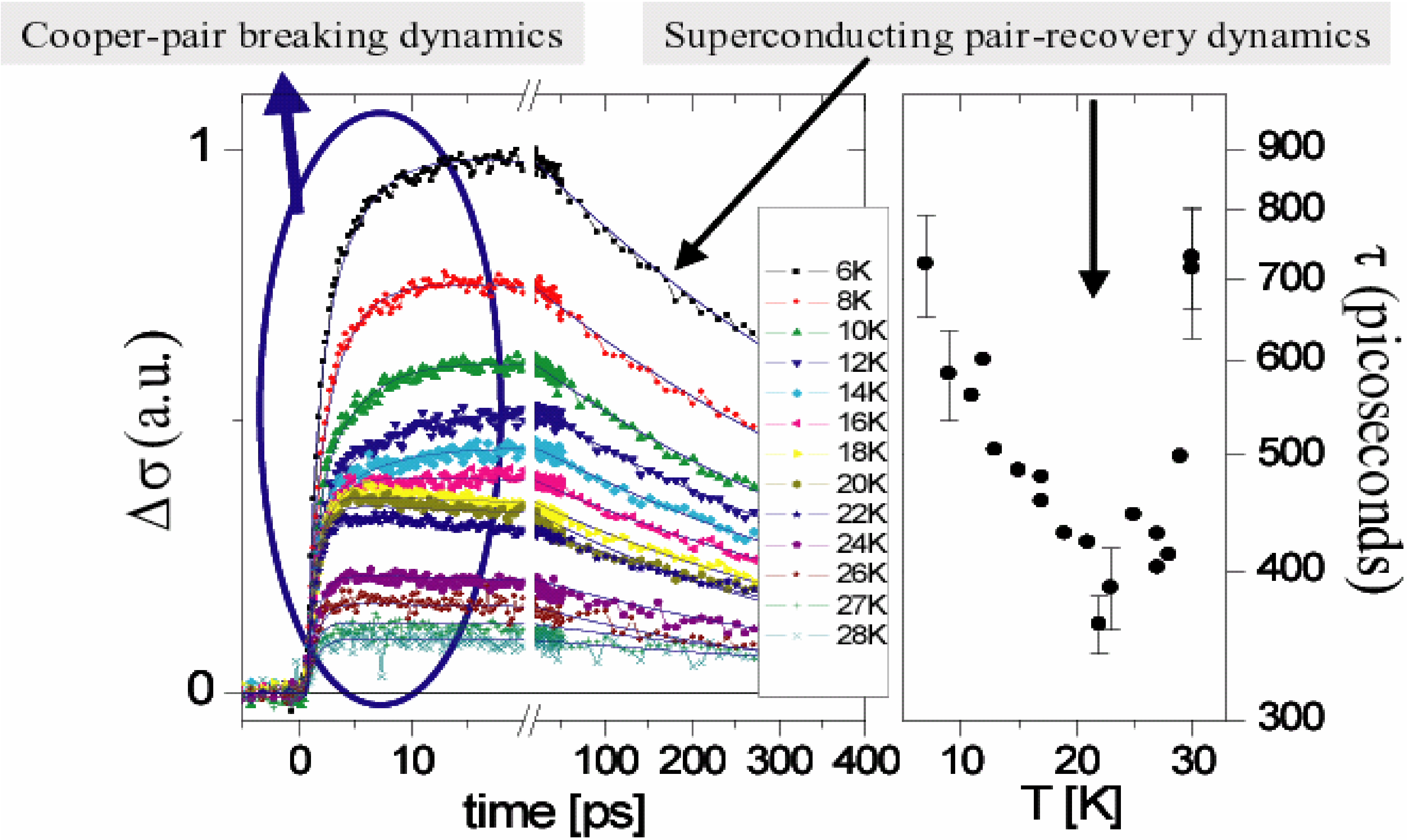
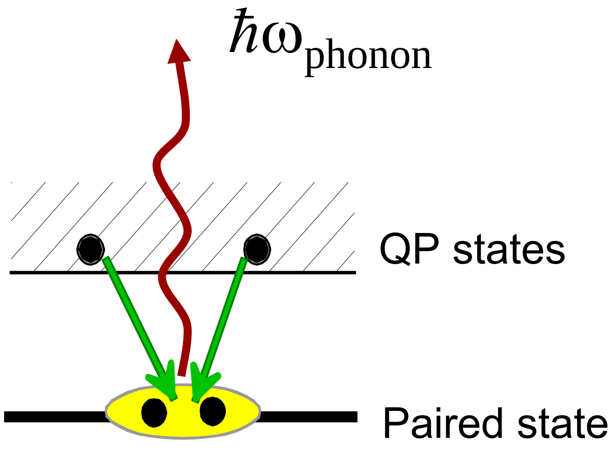
80 nm MgB_2 film on sapphire, T_c = 34K

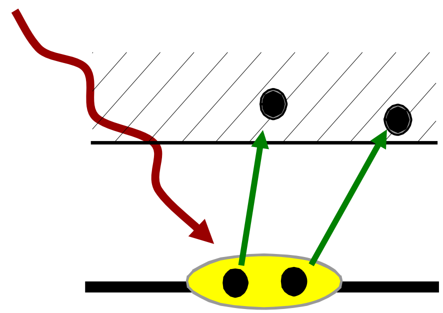
The Cooper-pair breaking and recovery dynamics



J. Demsar et al., Phys. Rev. Lett. 91, 267002 (2003).

Phenomenological Rothwarf-Taylor model





1. Emission of a phonon with $\hbar\omega_{phonon} > 2\,\Delta$

2. Re-absorption of a phonon with $\hbar\omega_{phonon} > 2\,\Delta$

A. Rothwarf, B.N. Taylor, Phys. Rev. Lett. 19, 27 (1967).

Phenomenological Rothwarf-Taylor model

Rothwarf-Taylor equations[1]

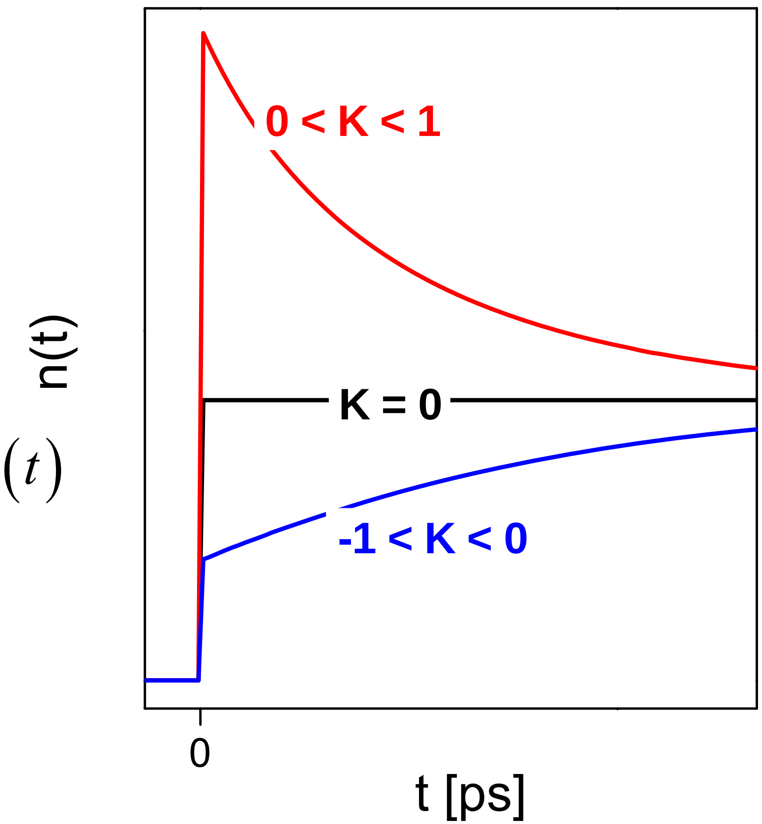
n : quasiparticle density

N : density of high frequency (ω>2Δ) phonons

$$\frac{dn}{dt} = \beta N - R n^2 + n_0 \delta(t)$$

$$\frac{dN}{dt} = +\frac{1}{2}\left[R n^2 - \beta N \right] - \cancel{\frac{(N - N_0)}{\tau_\gamma}} + N_0 \delta(t)$$

$$n(t) = \frac{\beta}{R}\left[-\frac{1}{4} - \frac{1}{2\tau} + \frac{1}{\tau}\frac{1}{1-K\exp(-t\beta/\tau)} \right]$$



K and τ are dimensionless parameters uniquely determined by initial conditions

$$\tau^{-1} = \sqrt{\frac{1}{4} + \frac{2R}{\beta}\left(n_0 + 2N_0\right)}$$

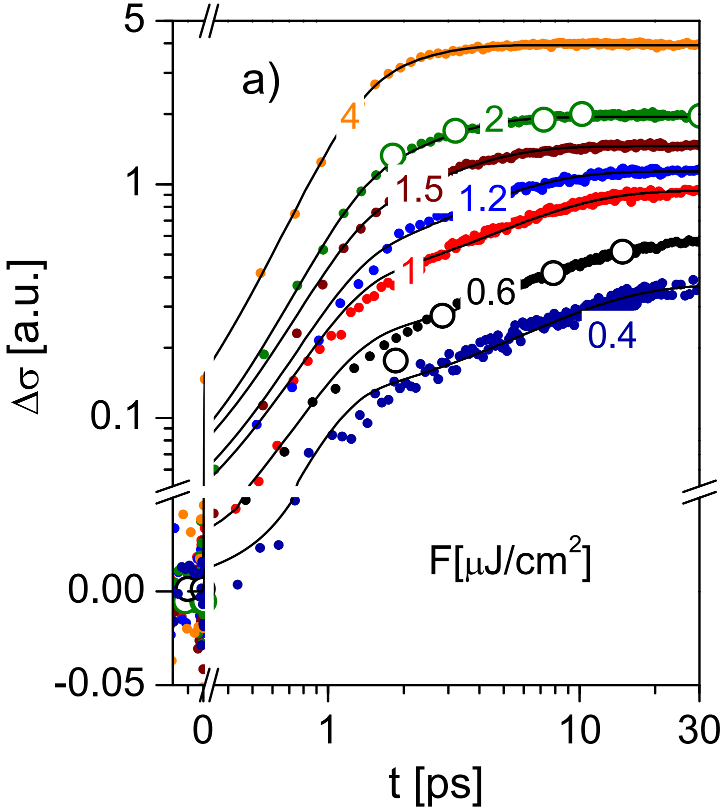
$$K = \frac{\frac{\tau}{2}\left(\frac{4Rn_0}{\beta} + 1\right) - 1}{\frac{\tau}{2}\left(\frac{4Rn_0}{\beta} + 1\right) + 1}$$

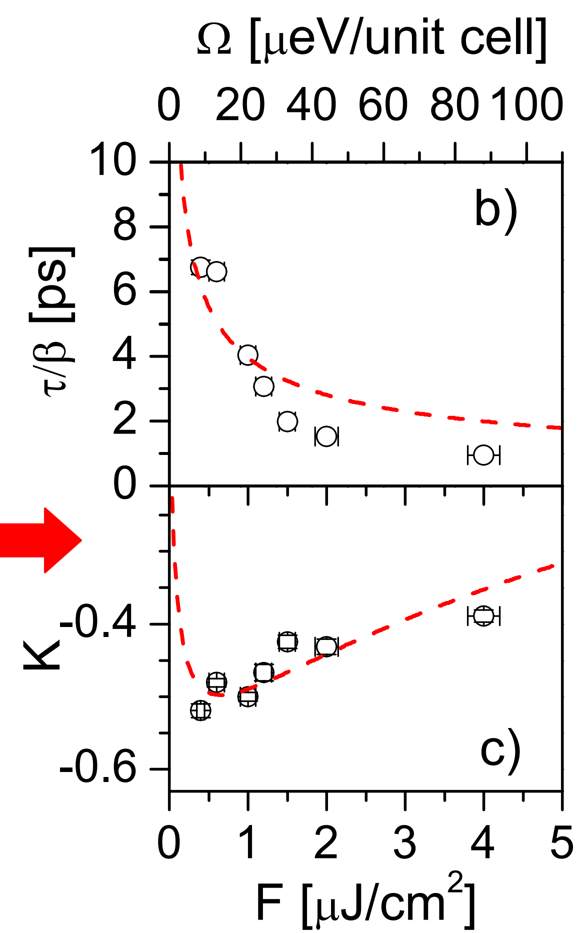
[1] A. Rothwarf, B.N. Taylor, Phys. Rev. Lett. 19, 27 (1967).

[2] J. Demsar et al., Phys. Rev. Lett. 91, 267002 (2003).

Analysis of pair – breaking dynamics yields quasiparticle characteristics

$$n(t) = \frac{\beta}{R}\left[-\frac{1}{4} - \frac{1}{2\tau} + \frac{1}{\tau}\frac{1}{1-K\exp(-t\beta/\tau)} \right]$$





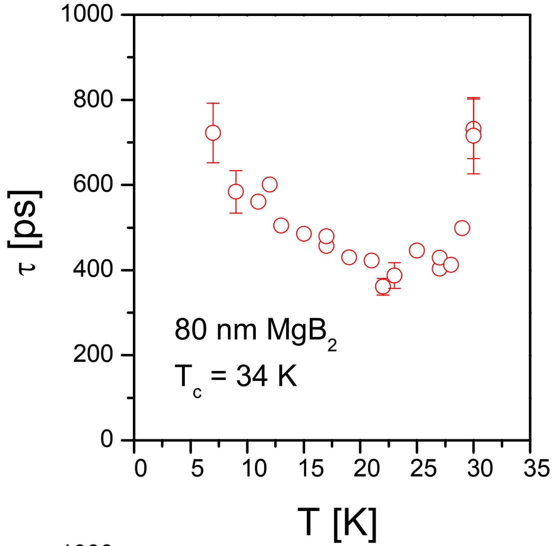
$$\tau^{-1} = \sqrt{\frac{1}{4} + \frac{2R}{\beta}\left(n_0 + 2N_0\right)}$$

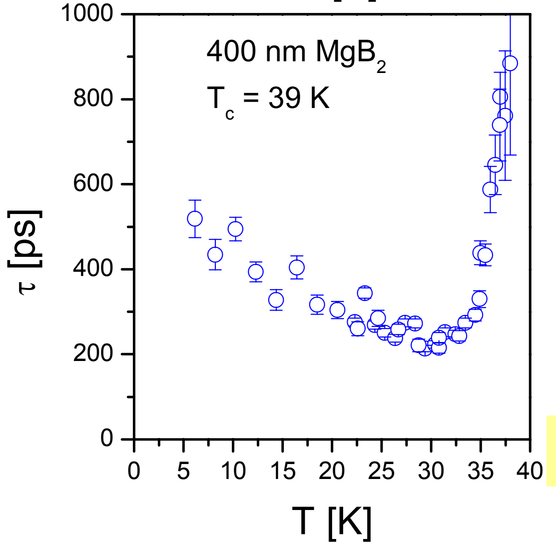
$$K = \frac{\tau/2\left(4Rn_0/\beta + 1\right) - 1}{\tau/2\left(4Rn_0/\beta + 1\right) + 1}$$

R = 100 +/- 30 ps^{-1} unit cell^{-1} ; β^{-1} = 15 +/- 2 ps

6% of energy goes to QP initially

Superconducting state recovery dynamics





Phonon bottleneck (Rothwarf-Taylor)

$$\frac{dn}{dt} = \beta N - Rn^2 + n_0 \delta(t)$$

$$\frac{dN}{dt} = +\frac{1}{2}\left[Rn^2 - \beta N\right] - \frac{(N - N_0)}{\tau_\gamma} + N_0 \delta(t)$$

τ_γ (decay of high frequency phonon population) governed by either:

a) escape of 2Δ phonons out of the probed volume (substrate)

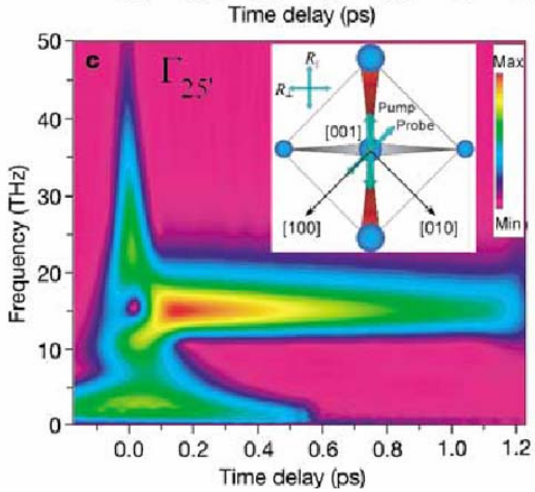
b) anharmonic decay of 2Δ phonons

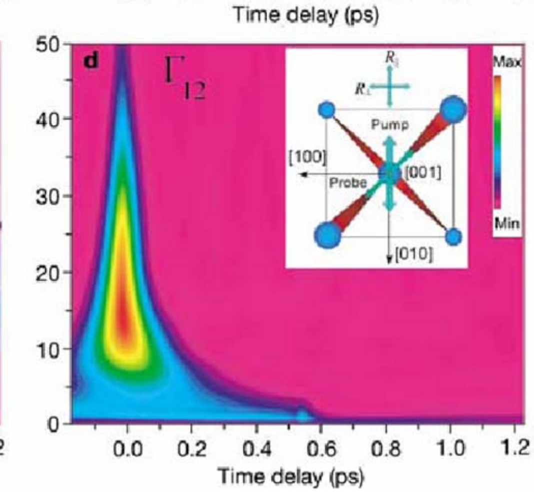
- τ does not depend on film thickness (80, 100, 300, 400 nm)
- τ shows $\tau \propto 1/\Delta(T)$ near T_c expected for anharmonic phonon decay[1] model.
- anharmonic decay time of 10 meV LA phonon is estimated to be ~ 1 ns at 10 K, consistent with the observed timescale.

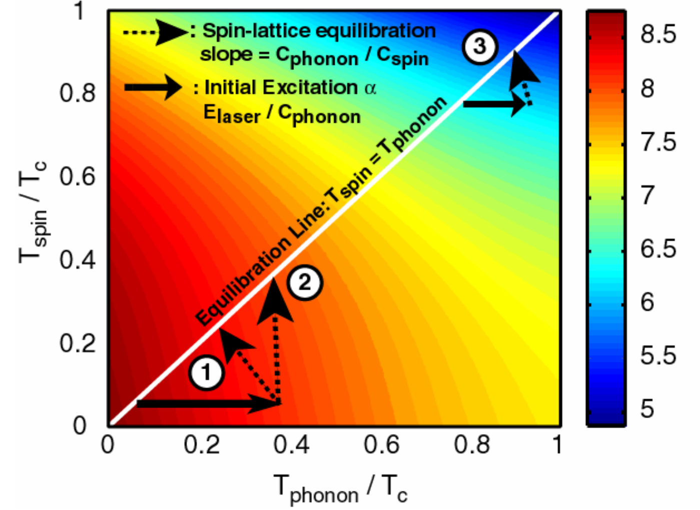
SC recovery governed by anharmonic decay of 2Δ acoustic phonons

ERL experiment: Ultrafast x-ray scattering to clarify role of phonons

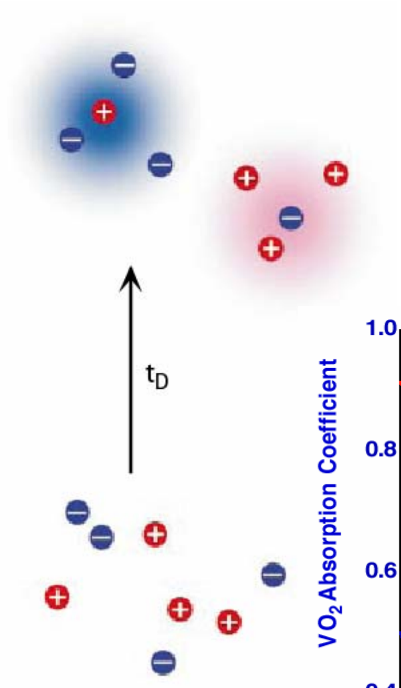
[1] V.V.Kabanov et al., *Phys. Rev. B 59, 1497 (1999)*

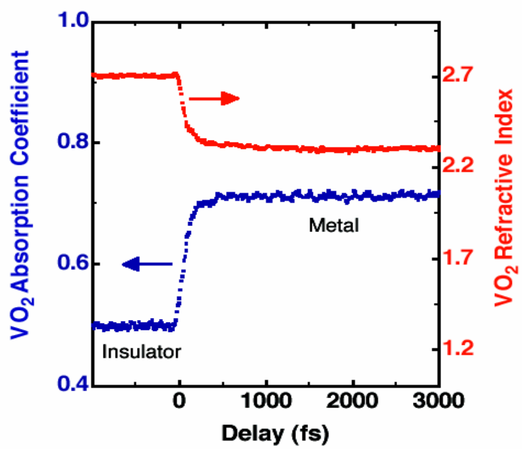


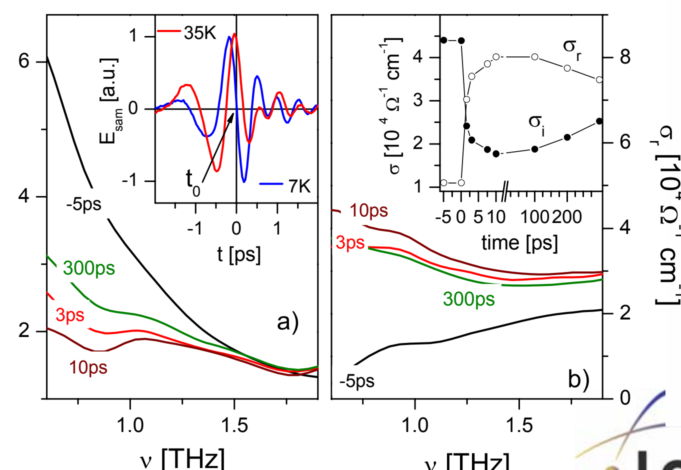


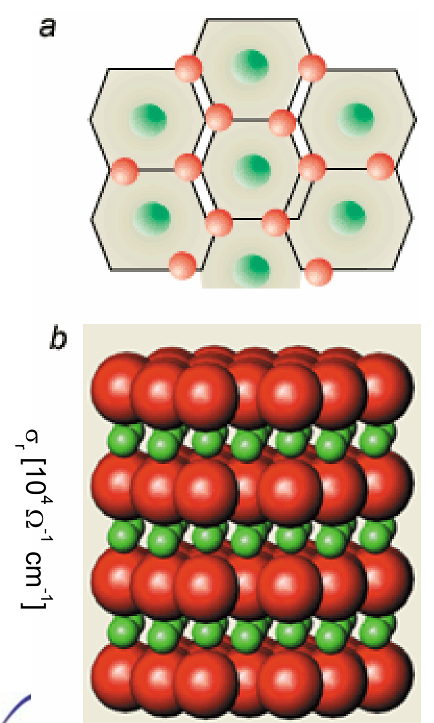


Ultrafast spectroscopic techniques provide a sensitive probe of dynamics in complex materials. Routine use of x-ray probes could significantly enhance this capability.

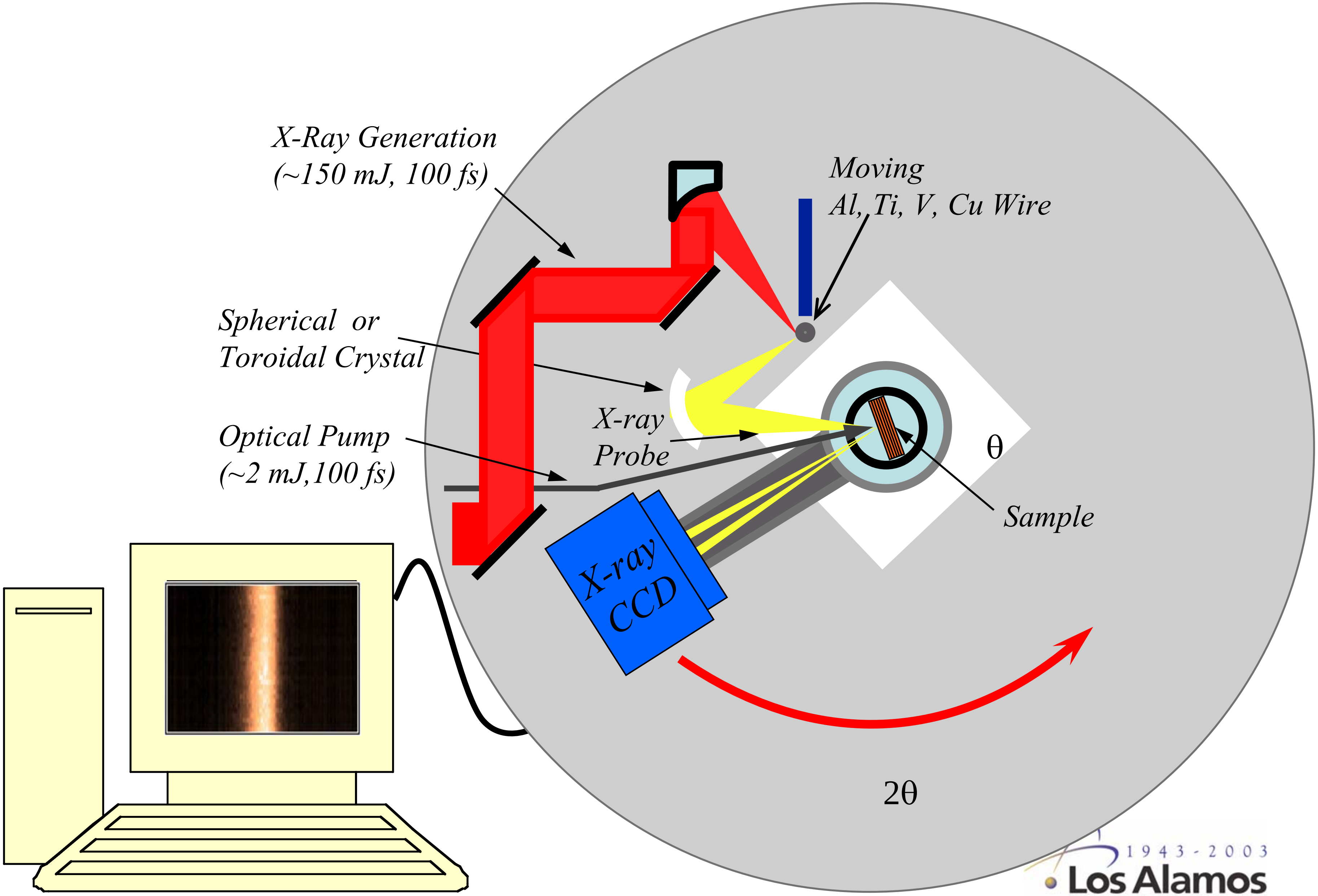




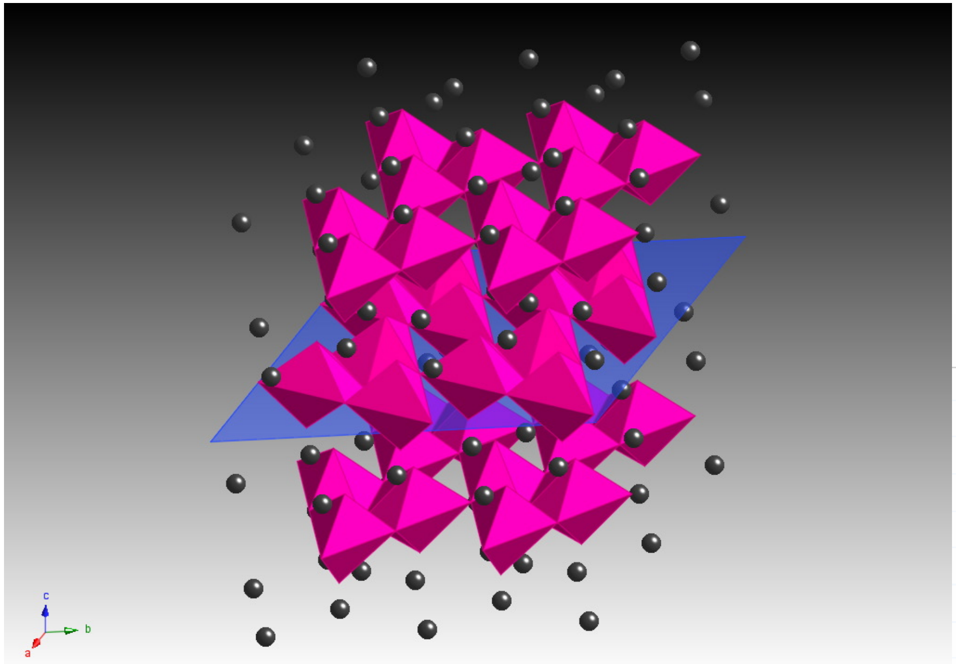




Ultrafast X-ray Diffraction

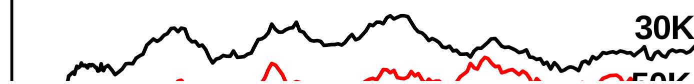


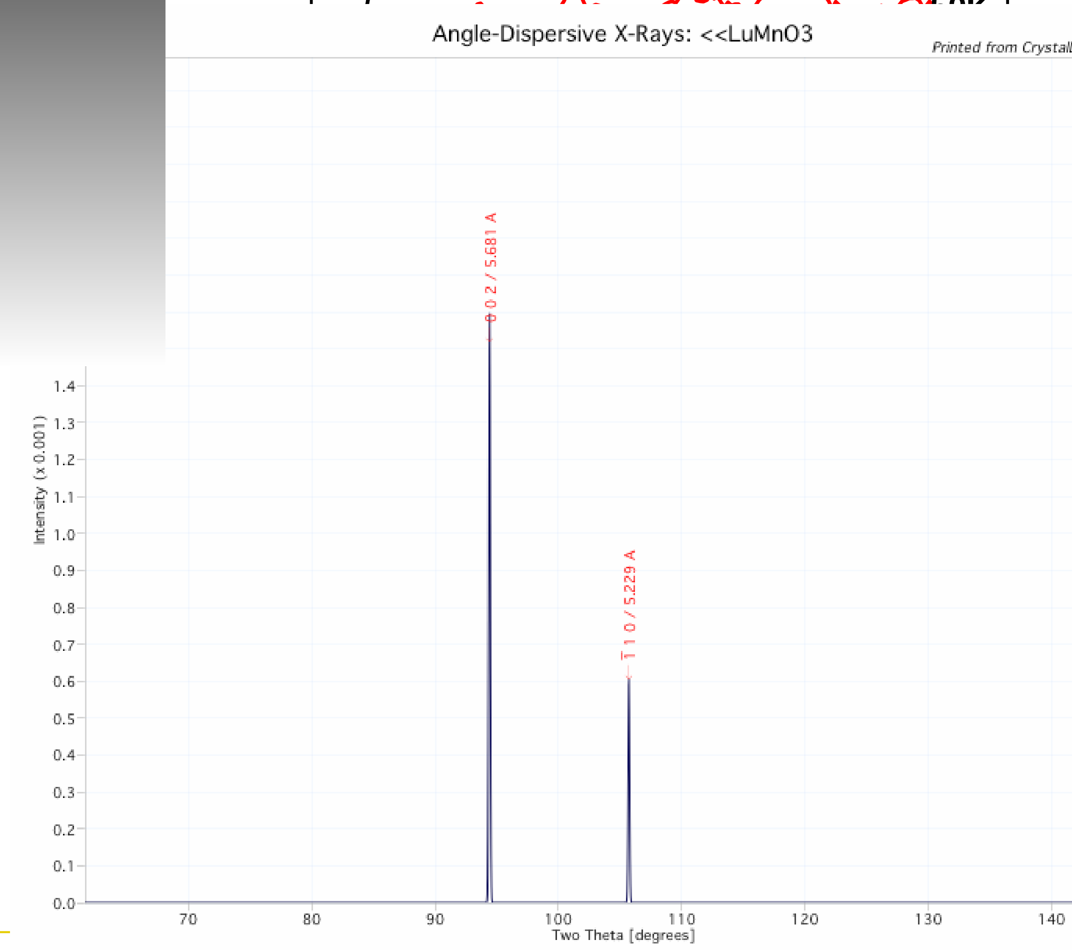
Structure and x-ray diffraction of $LuMnO_3$



Al K_α can be used to observe two diffractic

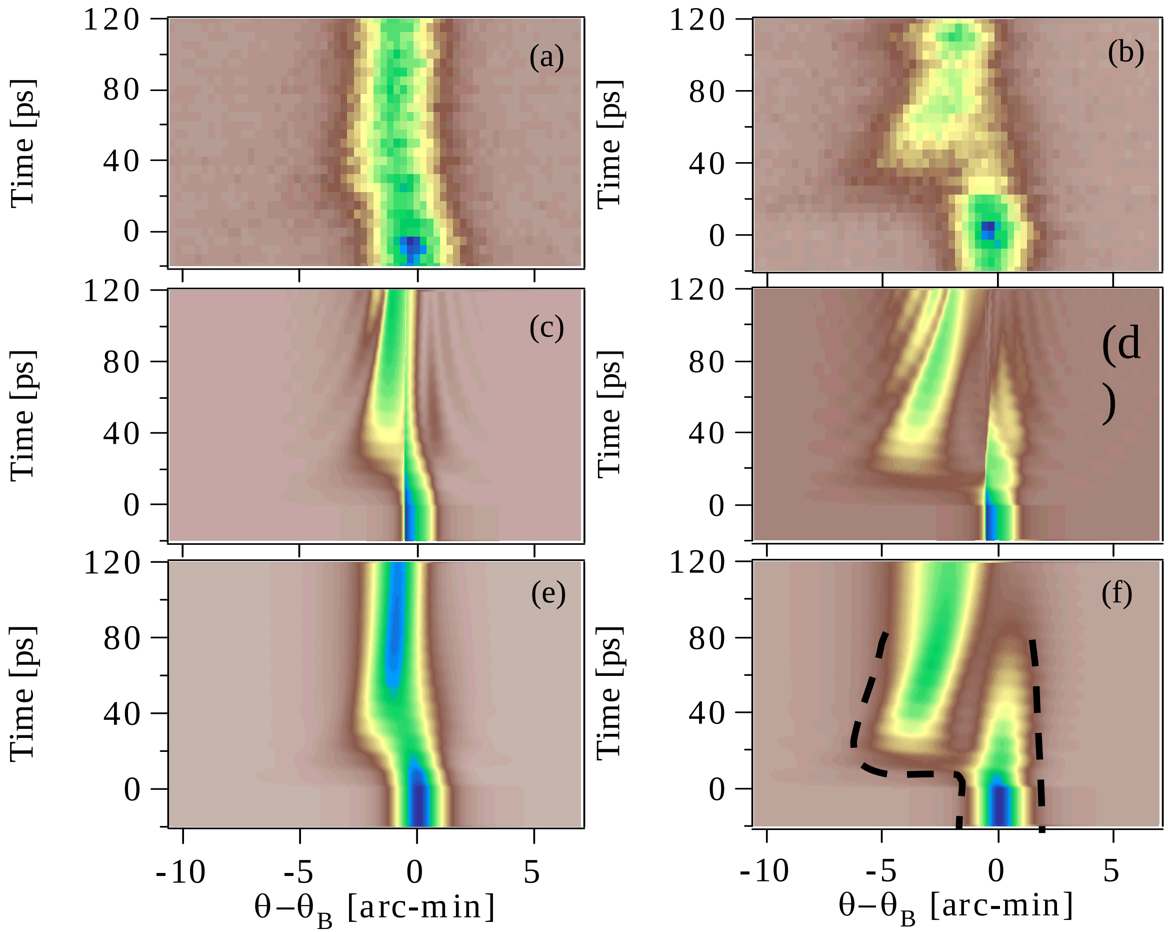
planes [002], [-110]

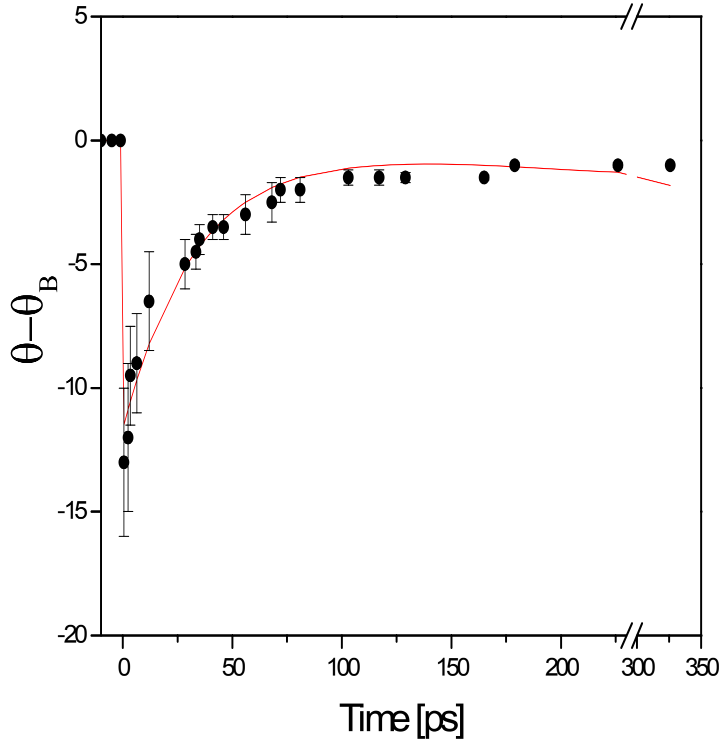




Observation of atomic scale lattice dynamics (coherent acoustic phonons) in $LuMnO_3$.

Ultrafast X-ray Diffraction





Modeling of x-ray diffraction data reveals a coupling of the strain wave between the ab plane and c axis.

The propagating strain pulse from the surface occurs by means of acoustic phonon generation and relaxation. The thermally generated stress launches a bipolar strain wave which travels into the crystal, yielding the periodic modulation of the optical properties and changes in the location and broadening of the diffraction peak.

H.-J. Lee, et al., submitted to PRB