Femtosecond dynamics of long-range order: coupling of the lattice, spins, charge and orbitals

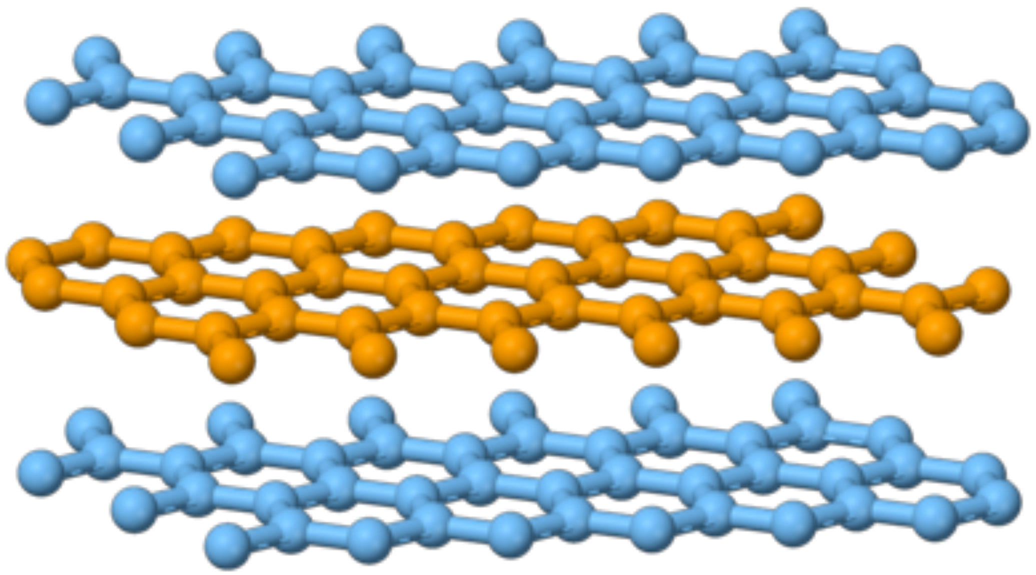
Steve Johnson

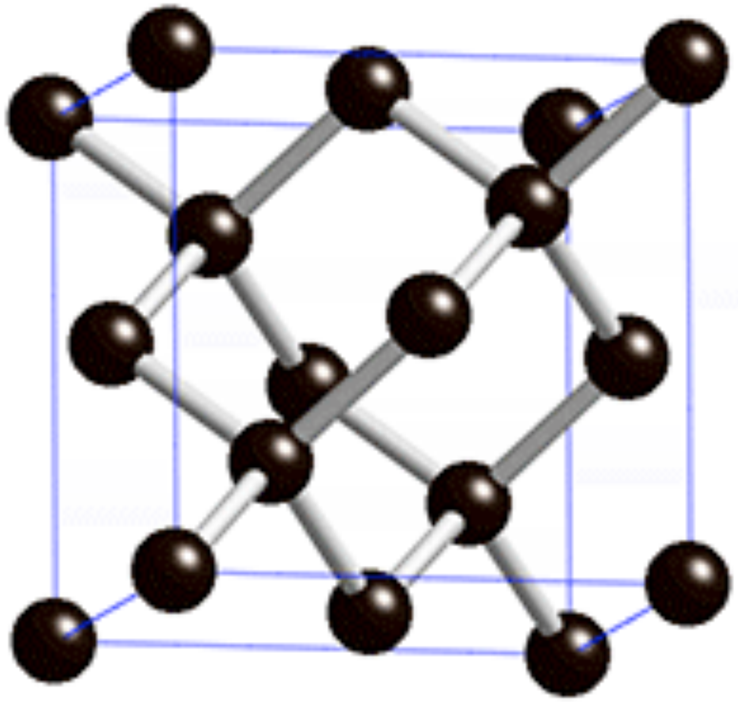
ETH Zurich

Outline

- Overview: dynamics as pathway to control
- X-rays as a selective probe of structure in condensed matter
- Indirect control: coupled lattice, orbital and charge in PCMO
    - Aside: a first look at x-ray "control" in a solid
- Direct control: coherent electromagnon in $TbMnO_3$
- Outlook

Structure and function





Graphite

Diamond

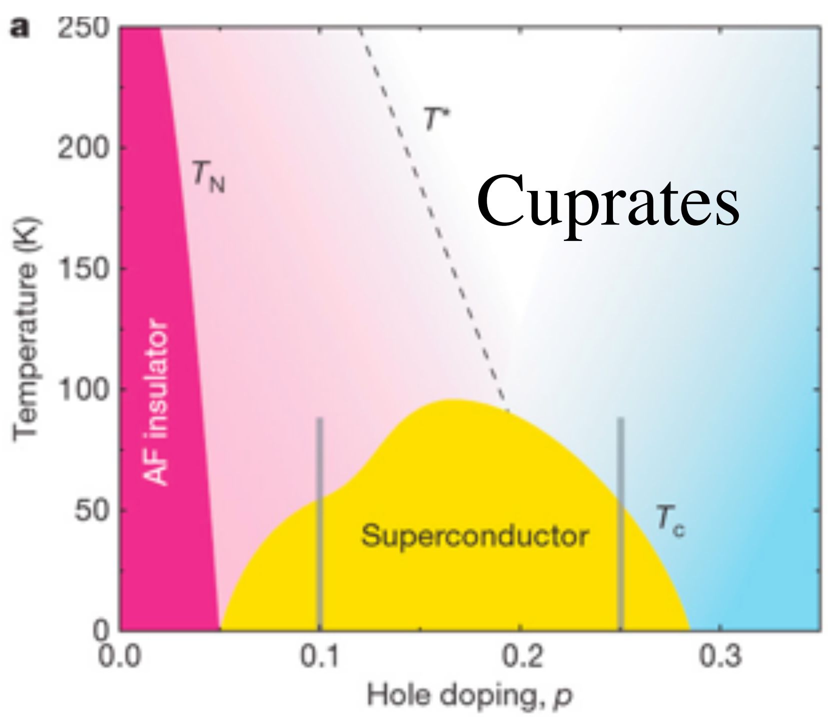
Conventional: adiabatic/stochastic

Temperature, pressure, static fields...

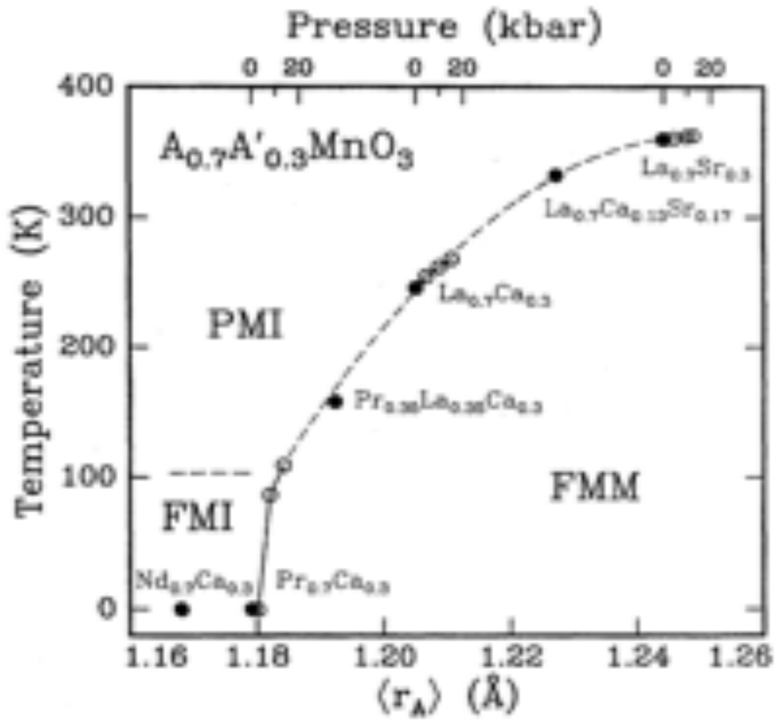
...works, but slow.

Can we do this faster, more efficiently?

Dynamics of symmetry changes

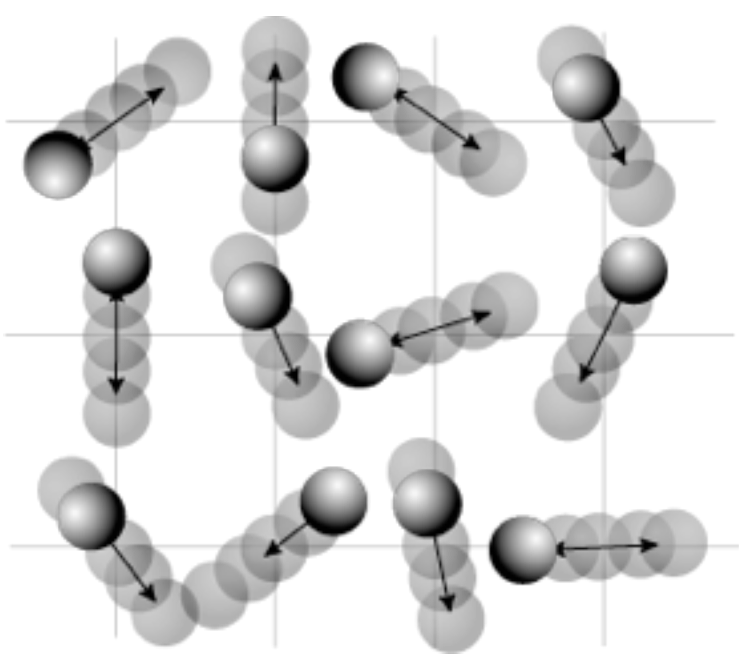


[Doiron-Leyraud et al. Nature 447, 565 (2007)]



[Hwang et al. PRB 52, 15046 (1995)]

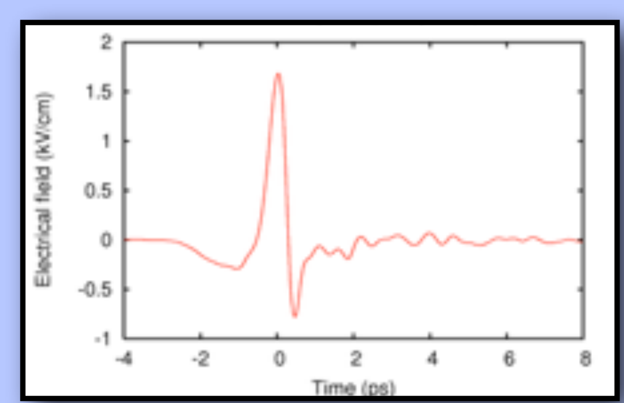
Equilibrium thermodynamics powerful: Critical phenomena, RG theory

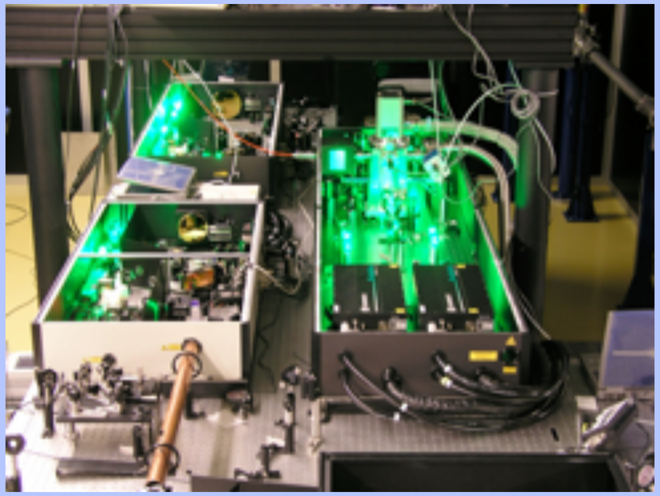


Time scales ≲ interaction times (~ 1-1000 fs): breakdown of conventional thermodynamics

Experimental concept

Intense light pulses to perturb structure





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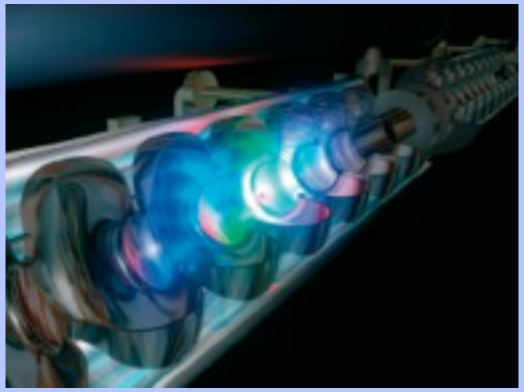
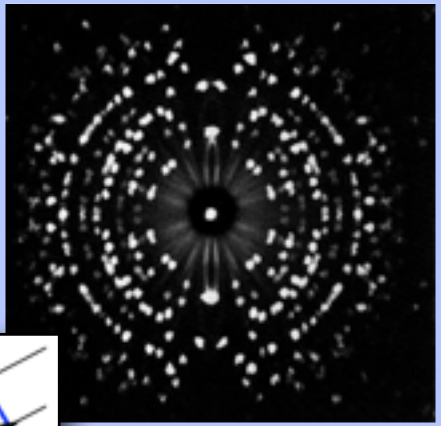
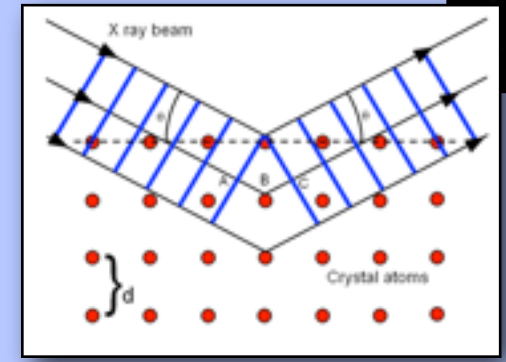
Femtosecond-resolved x-ray probes of structure changes

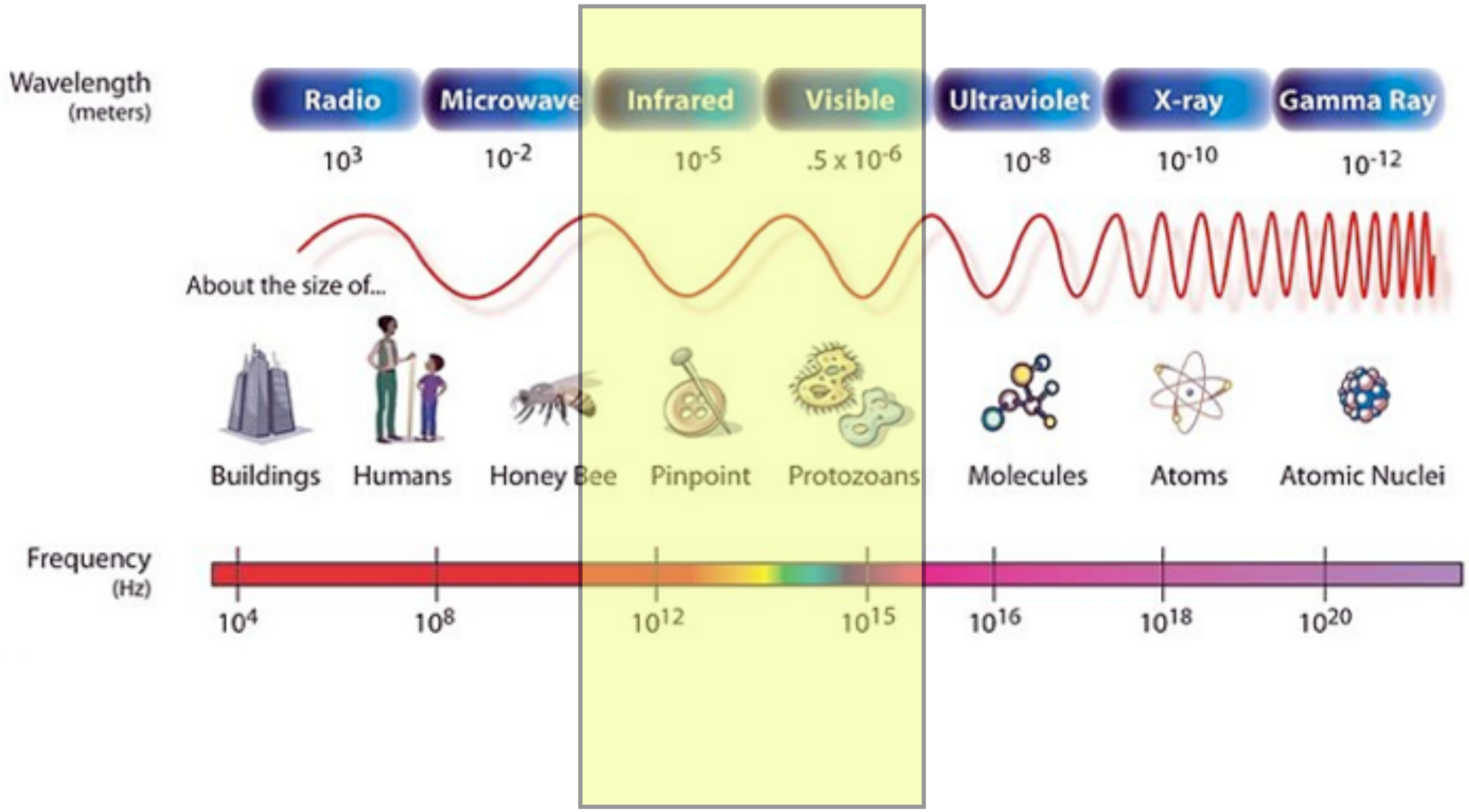






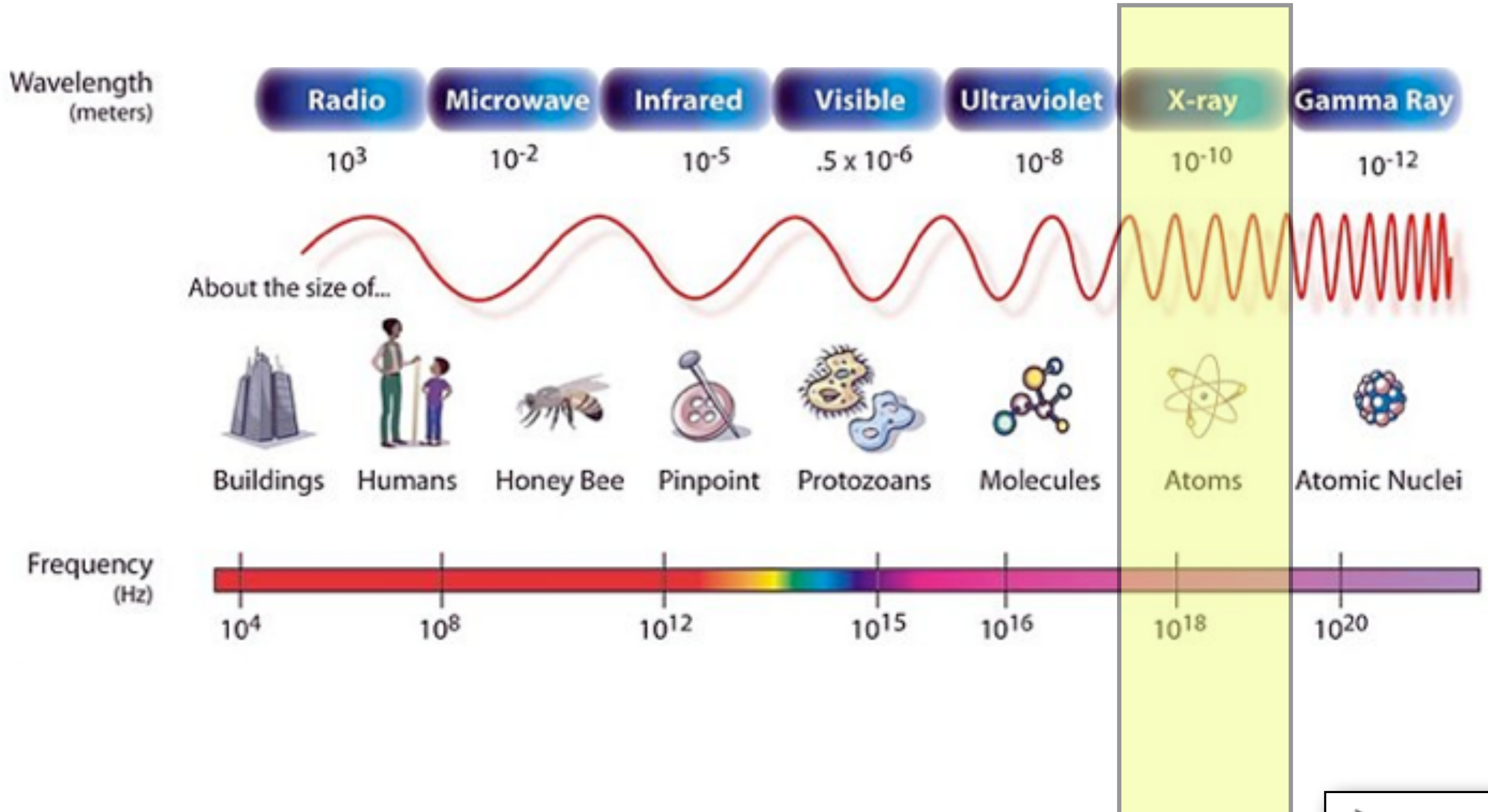
Understand & control of atomic-scale structural dynamics

Light as a control knob

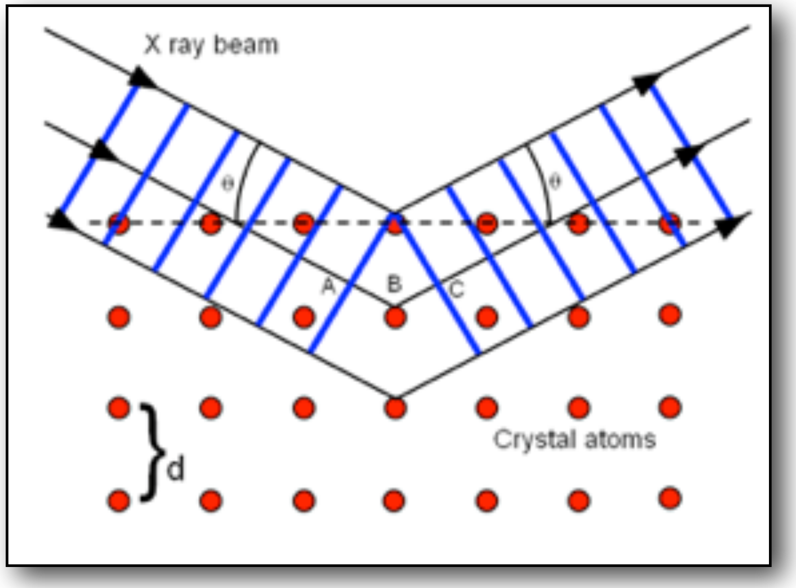


- Mature technology for creating / shaping pulses at near-optical frequencies
- Recent advances at lower frequencies make direct resonant excitation of IR active modes possible

X-ray pulses as a fast probe

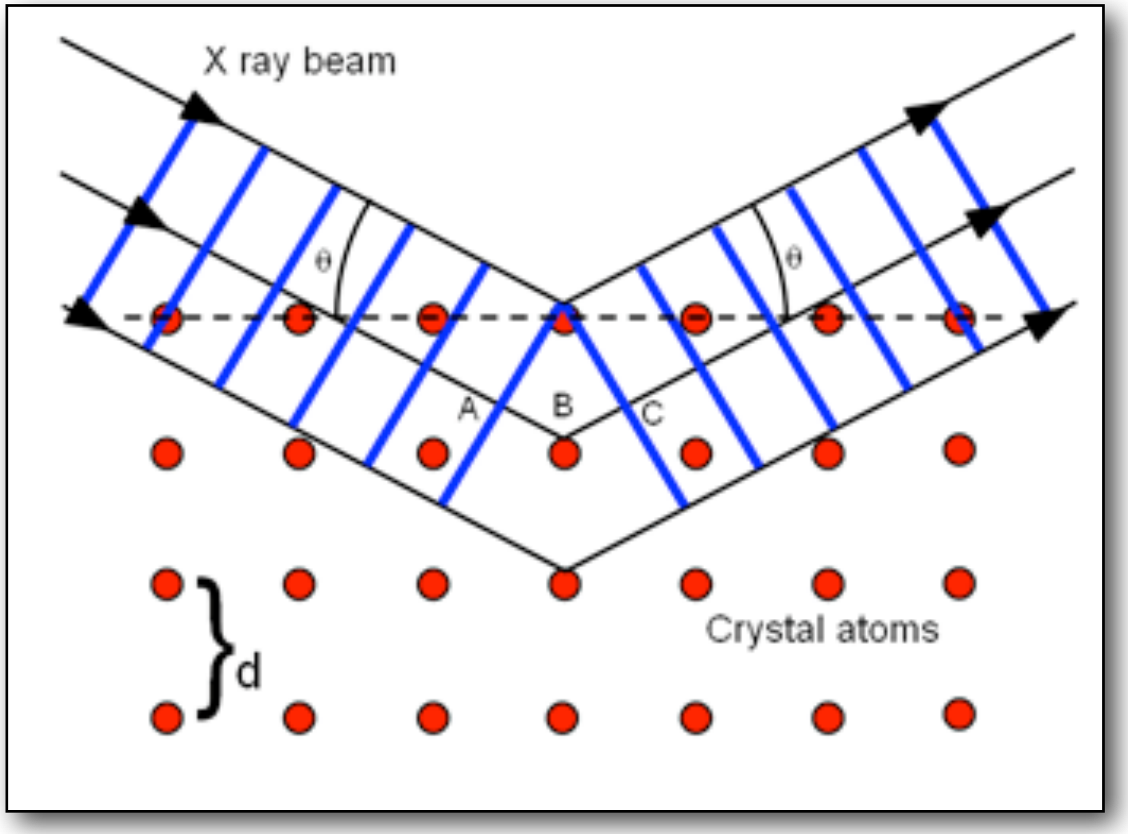


- X-ray diffraction: access to long-range atomic-scale order
- Sources for short pulses
  - Electron-beam slicing at Swiss Light Source (PSI)
  - X-ray free electron lasers



X-ray pulses as a fast probe

- Non-resonant: first-order elastic scattering dominated by $|A|^2$ term in H_{int}
- Intensity related to FT of electron density



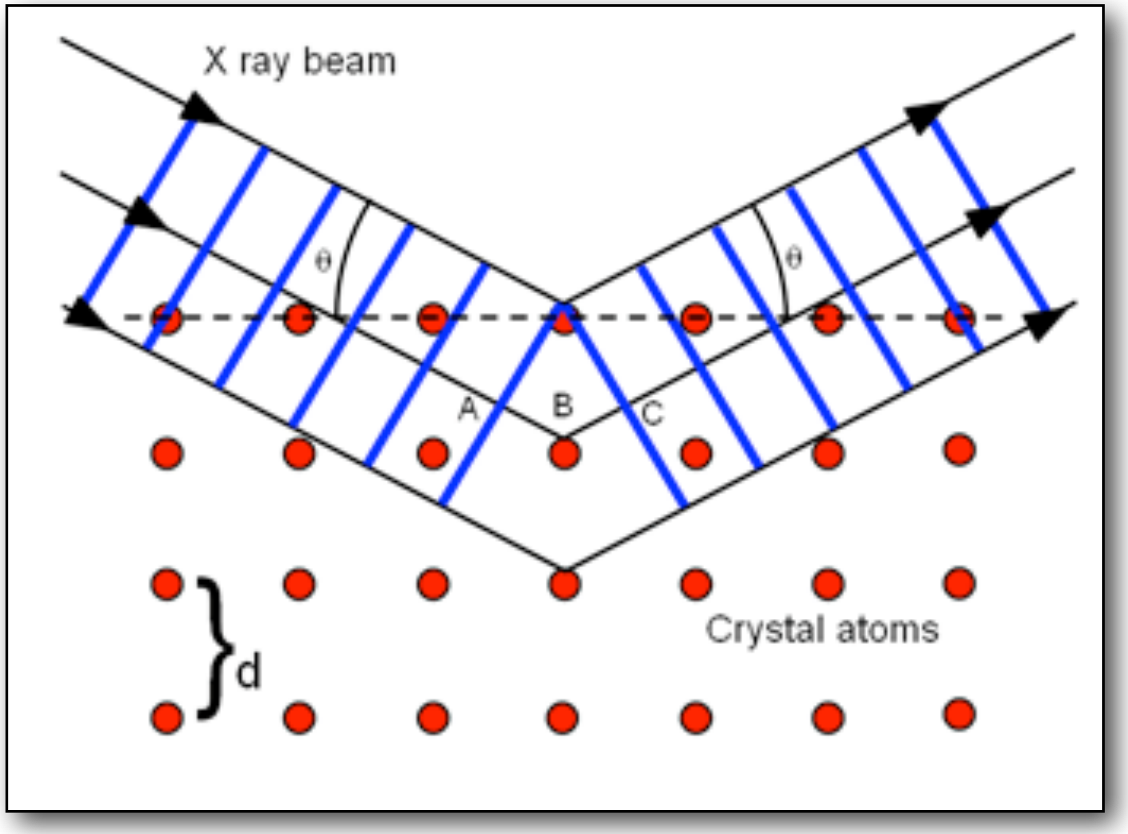
$$H_{\mathrm{int}} = -\frac{q}{mc}(\mathbf{A}\cdot\mathbf{P}+\mathbf{P}\cdot\mathbf{A}) + \frac{q^2|\mathbf{A}|^2}{2mc^2}$$

(non-relativistic, spin ignored)

$$I(Q) \propto |F(Q)|^2 = \left|\sum_j f_j e^{i\mathbf{r}_j\cdot\mathbf{Q}}\right|^2$$

X-ray pulses as a fast probe

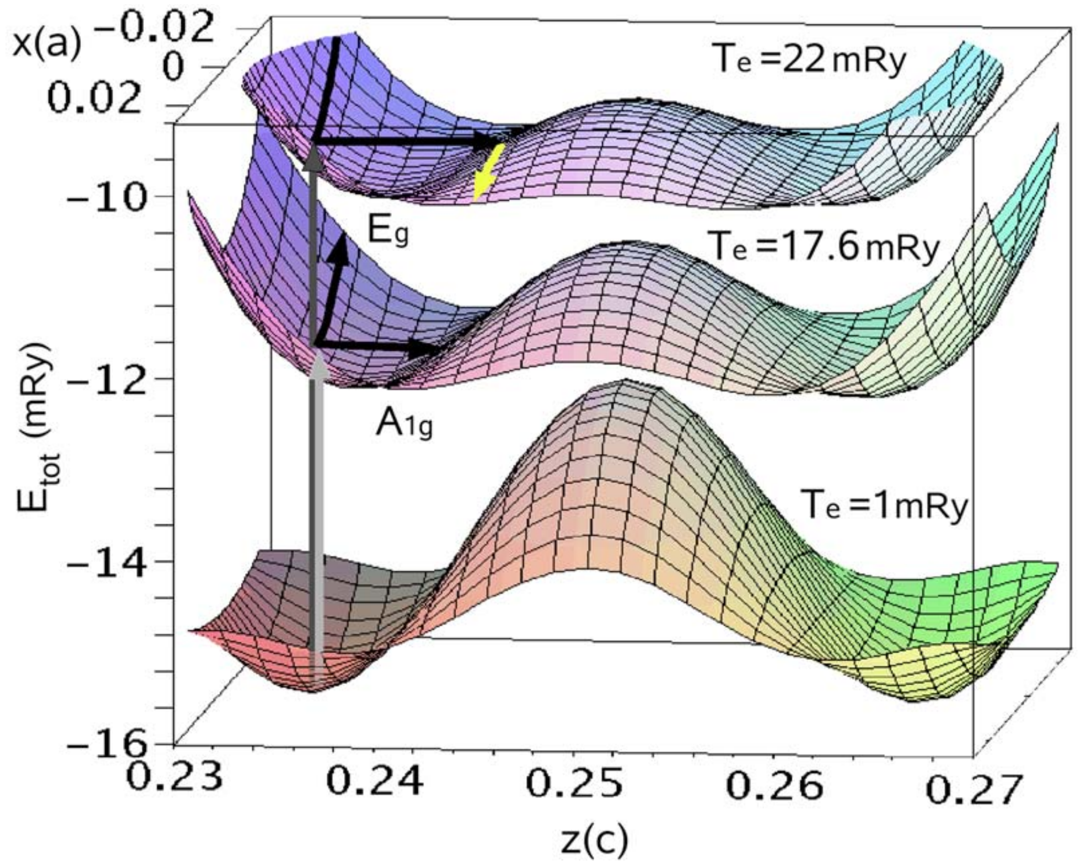
- Near core-level resonance: large second-order scattering
- Enhanced contributions from valence states



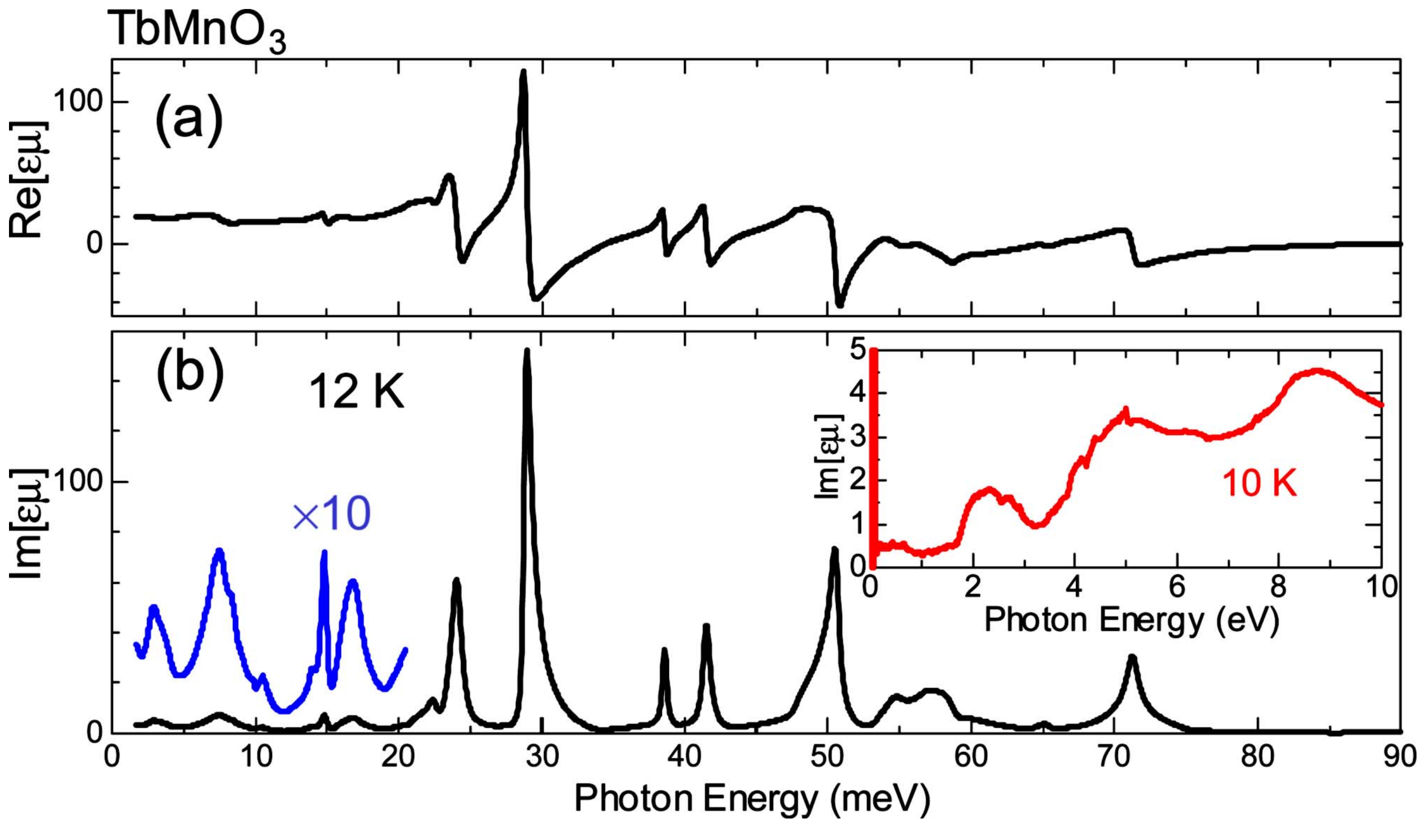
$$H_{\text{int}} = -\frac{q}{mc}(\mathbf{A}\cdot\mathbf{P}+\mathbf{P}\cdot\mathbf{A}) + \frac{q^2|\mathbf{A}|^2}{2mc^2}$$

$$\Delta f = \sum_j \frac{\langle\psi_i|\,H_{\text{int}}\,|\psi_j\rangle\,\langle\psi_j|\,H_{\text{int}}\,|\psi_i\rangle}{h\omega - (E_j - E_i) + i\Gamma/2}$$

"Indirect" vs. "Direct" control



[Zijlstra, Tatarinova & Garcia, PRB 74, 220301 (2006)]



[Kida et al., JOSAB 26 A35 (2009)]

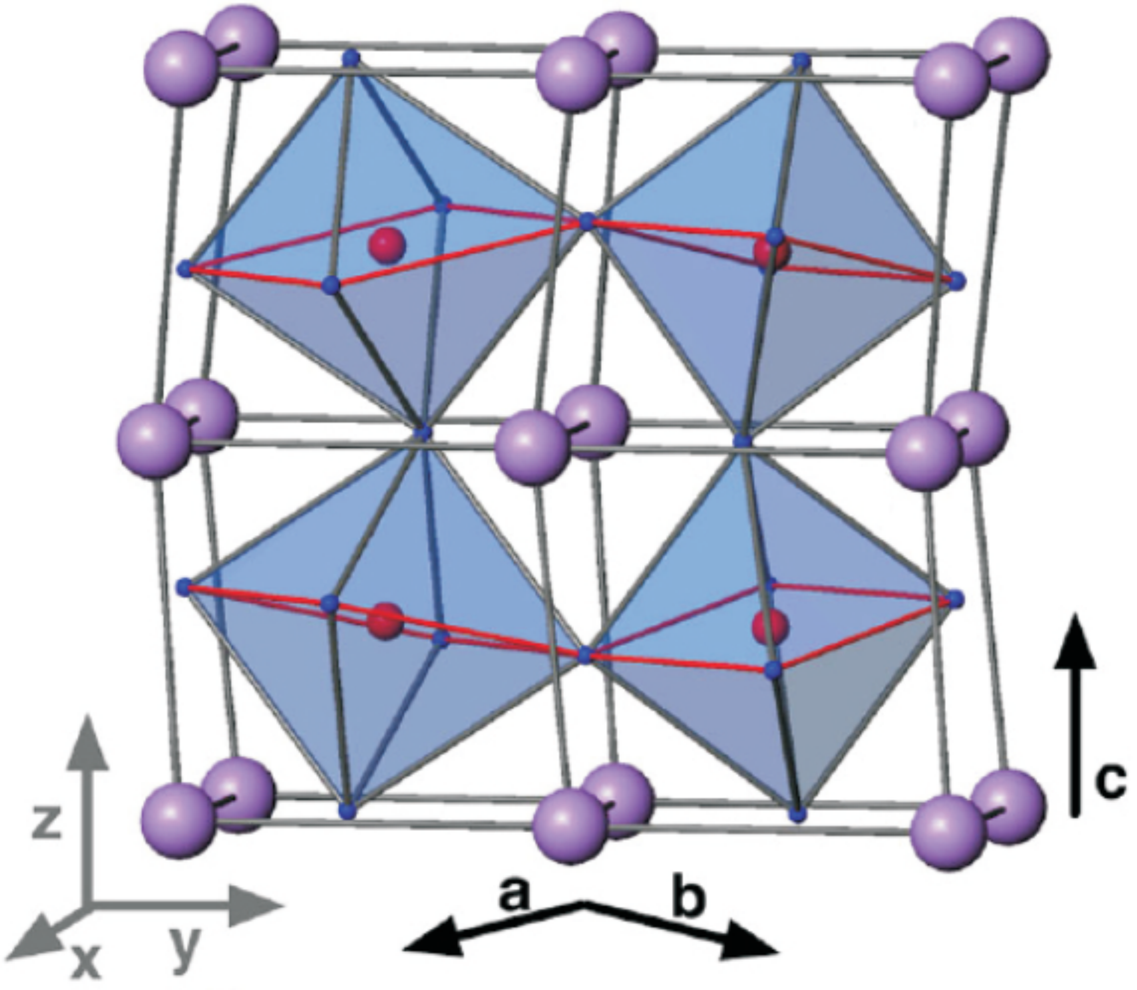
- "Indirect" control of order parameters
  - Excitation of other DOF, couples to order
- "Direct" control
  - Drive order directly with EM pulse

“Indirect” control:

Electronically induced structure changes

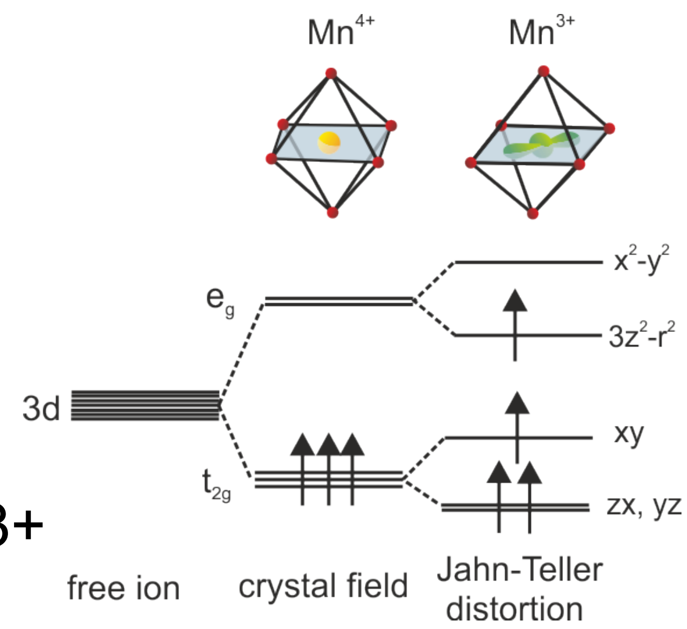
$Pr_{0.5}Ca_{0.5}MnO_3$: mixed-valence manganite

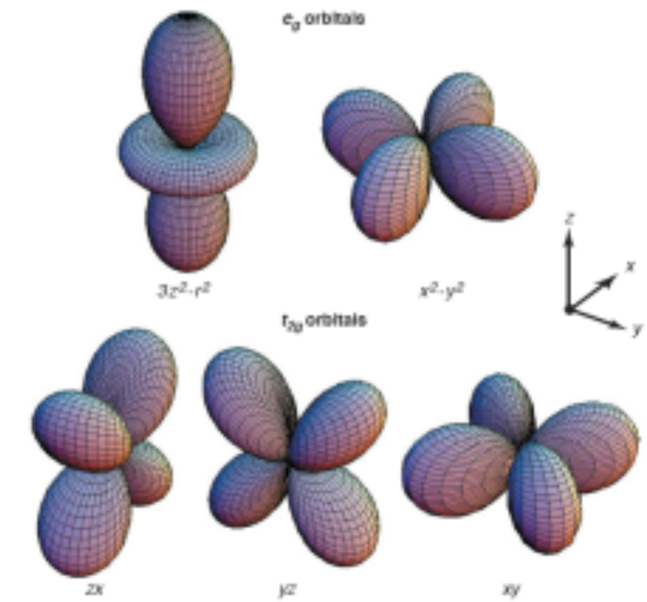
- Distorted perovskite
- Charge and orbital ordering below 240 K
- Strong lattice distortion due to Jahn-Teller interaction

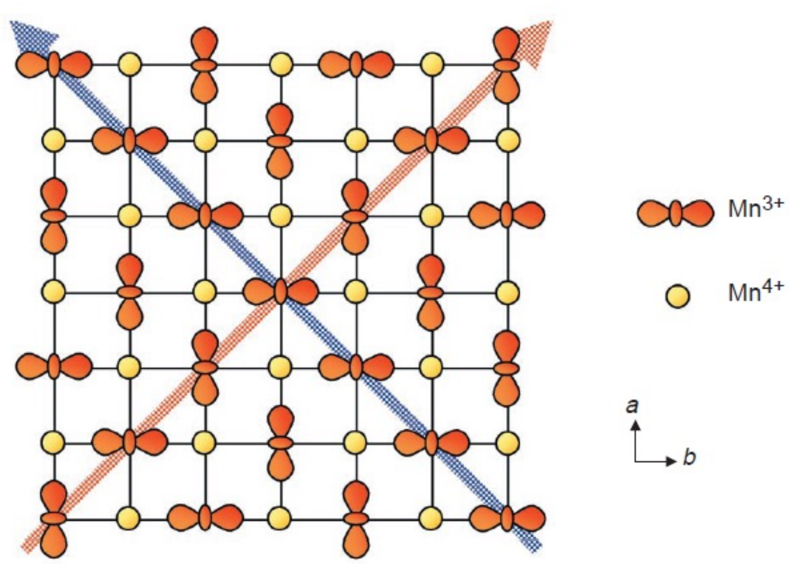


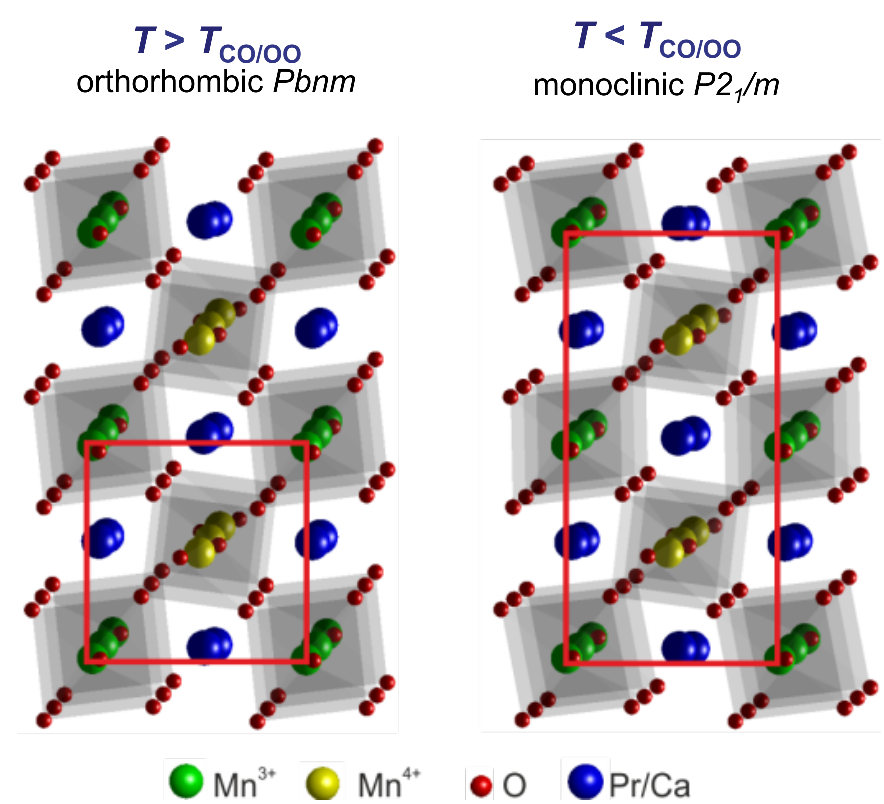
$Pr_{0.5}Ca_{0.5}MnO_3$: mixed-valence manganite

- CE-type charge & orbital order
- Jahn-Teller distortion at Mn^{3+} sites doubles unit cell



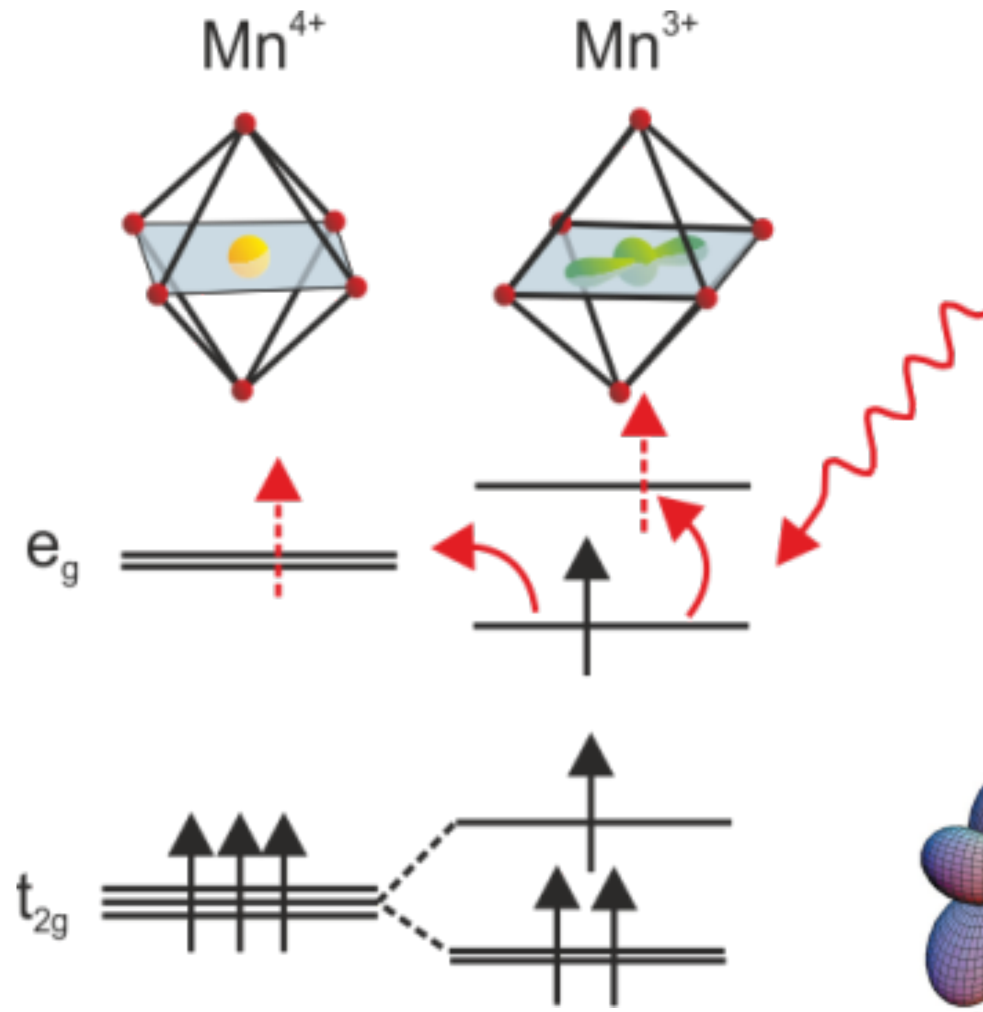


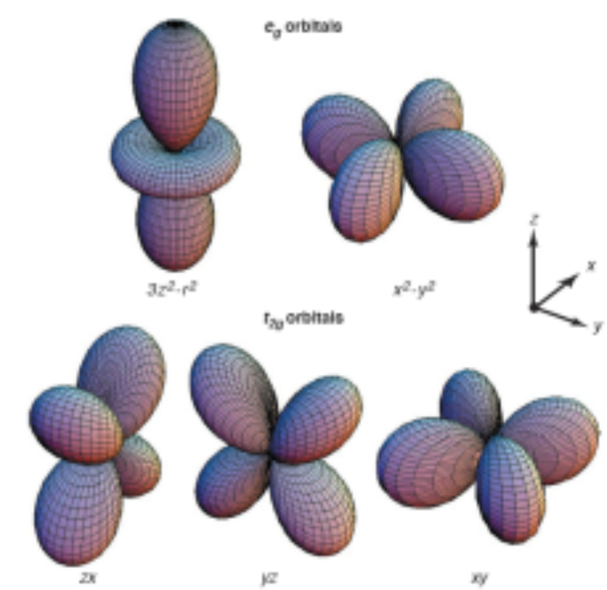




Photoexcitation drives transition

- Photoexcitation: perturbation of charge and orbitals
- Forces system to higher symmetry state
- How does this couple to structure?





ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Experiment team: $Pr_{0.5}Ca_{0.5}MnO_3$

PAUL SCHERRER INSTITUT
PSI

P. Beaud
U.Staub
S.-W. Huang
J. Johnson
C. Vicario
G. Ingold
S. Gruebel
S. Mariager
L. Patthey

SLAC:

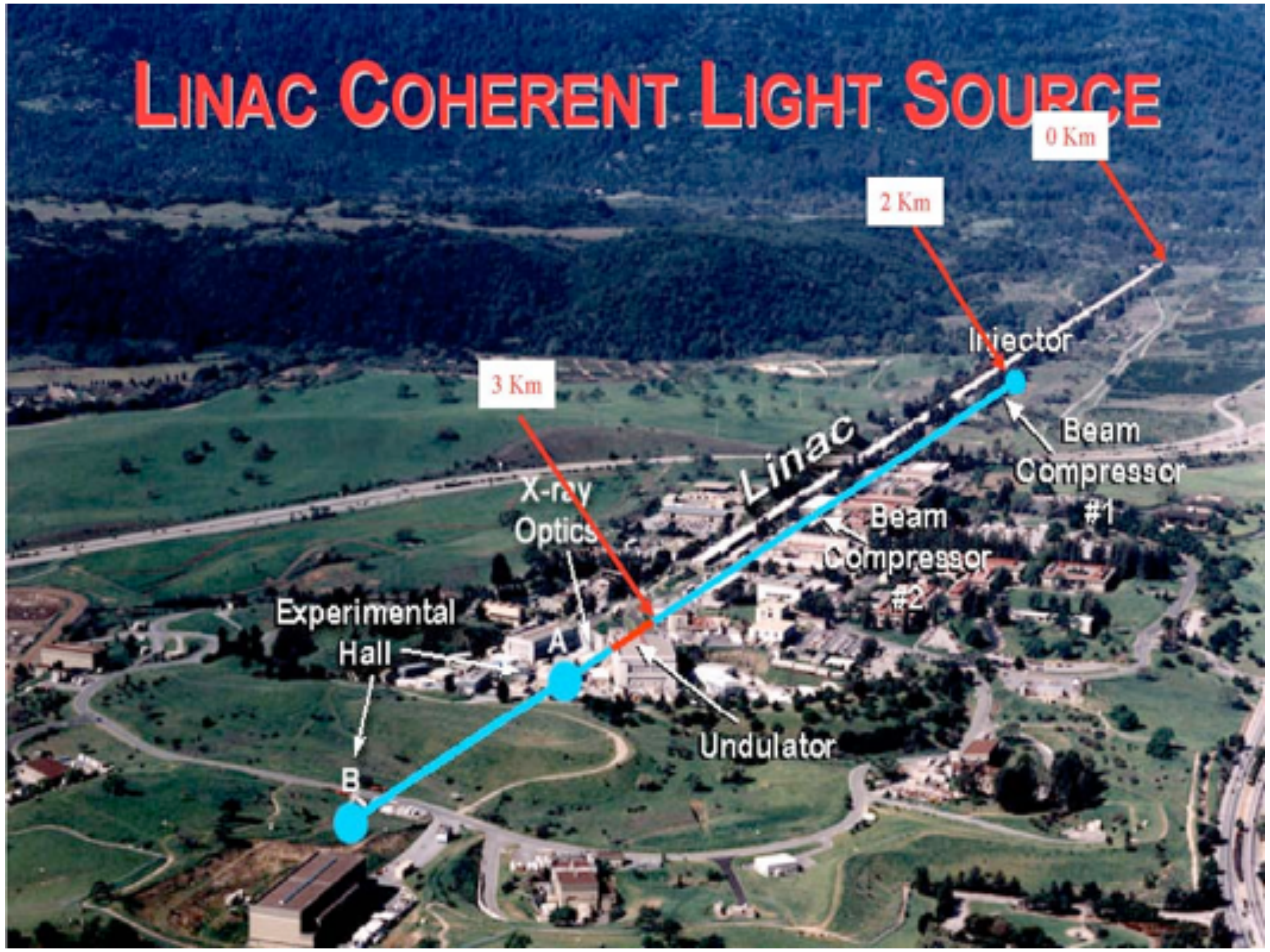
J. Glownia
H. Lemke
M. Chollet
A. Robert
D. Fritz
D. Zhu

ETHZ:

A. T. Huber
A. Ferrer
T. Kubacka
L. Huber
C. Dornes
V. Scagnoli

RIKEN/U. Tokyo:

M. Nakamura
H. Wadati
M. Kawasaki
Y.Tokura



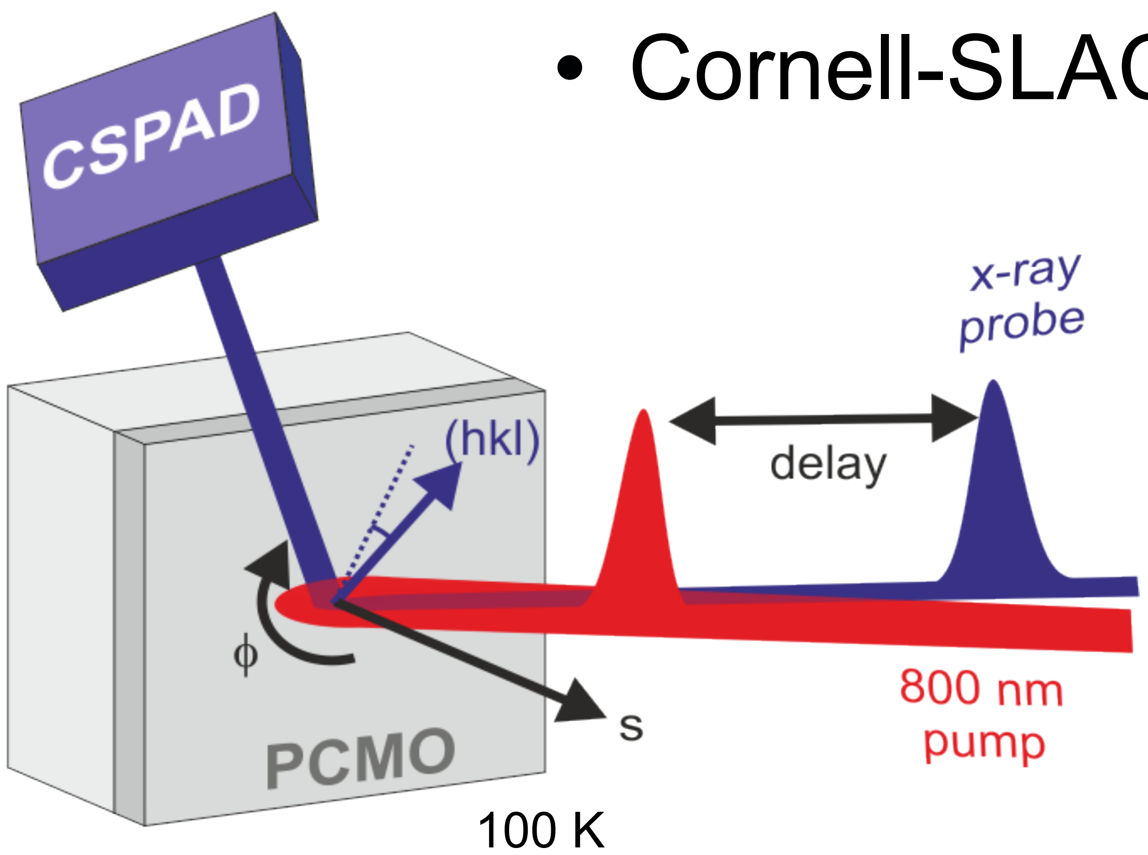
xmust

LCLS

FNSNF
SWISS NATIONAL SCIENCE FOUNDATION

Experiment

- 40 nm film sample of $Pr_{0.5}Ca_{0.5}MnO_3$
- $(011)_c$ orientation
- Pumped at 1.55 eV, 50 fs pulses
- Probed with ~ 6.55 keV, ~50 fs
- Cornell-SLAC Pixel Array Detector



Resonant diffraction at Mn K-edge

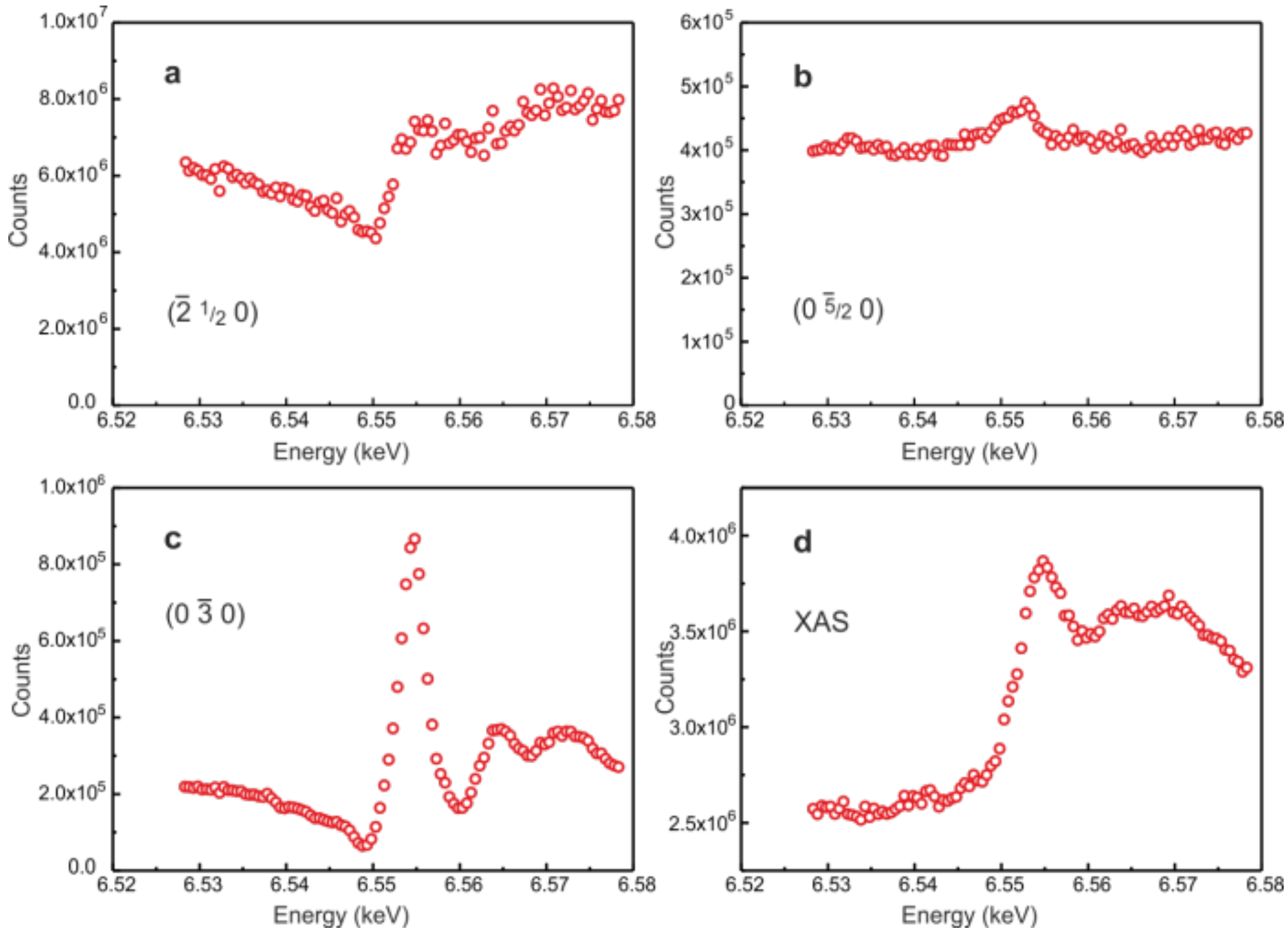
- From hybridization of Mn 3d and O 2p states [Zimmermann et al. PRL 83, 4871 (1999)]

for k odd…

(h k/2 0): structural distortion

(0 k/2 0): orbital order & Jahn-Teller

(0 k 0): charge order



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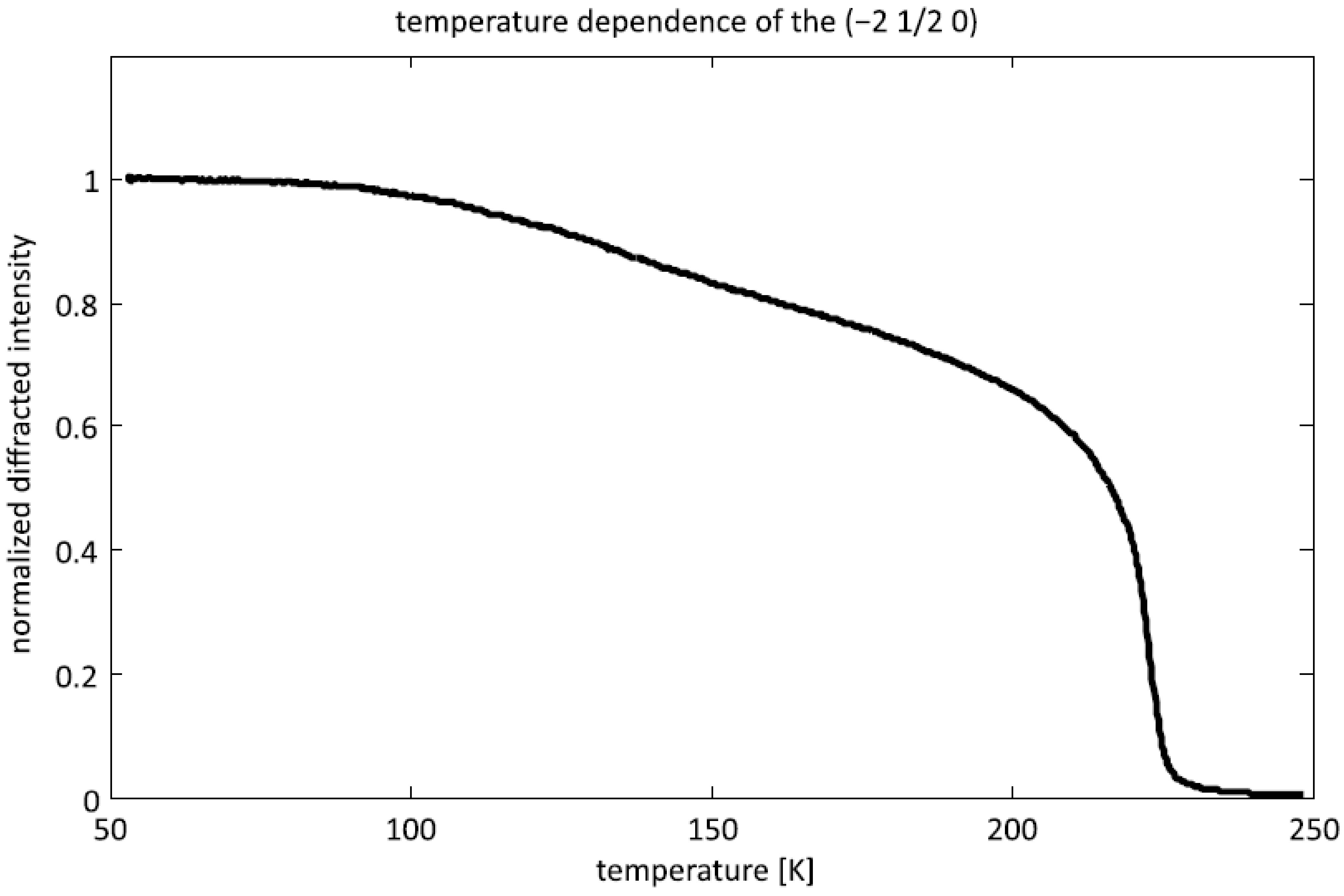
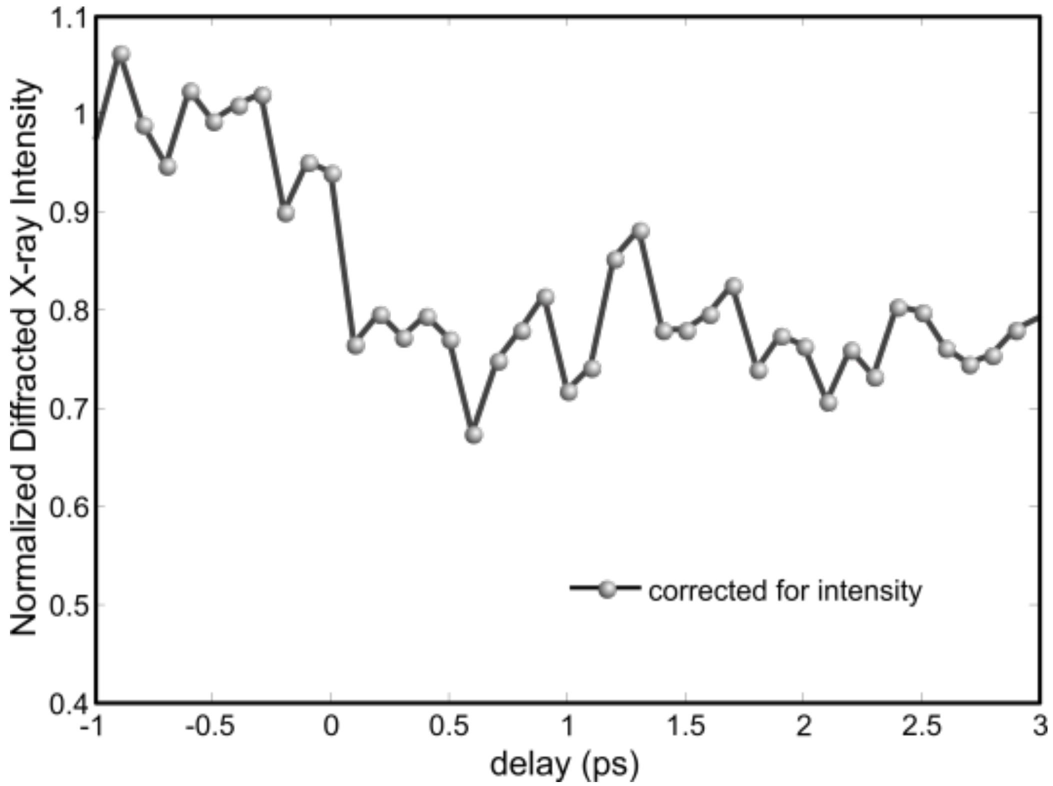
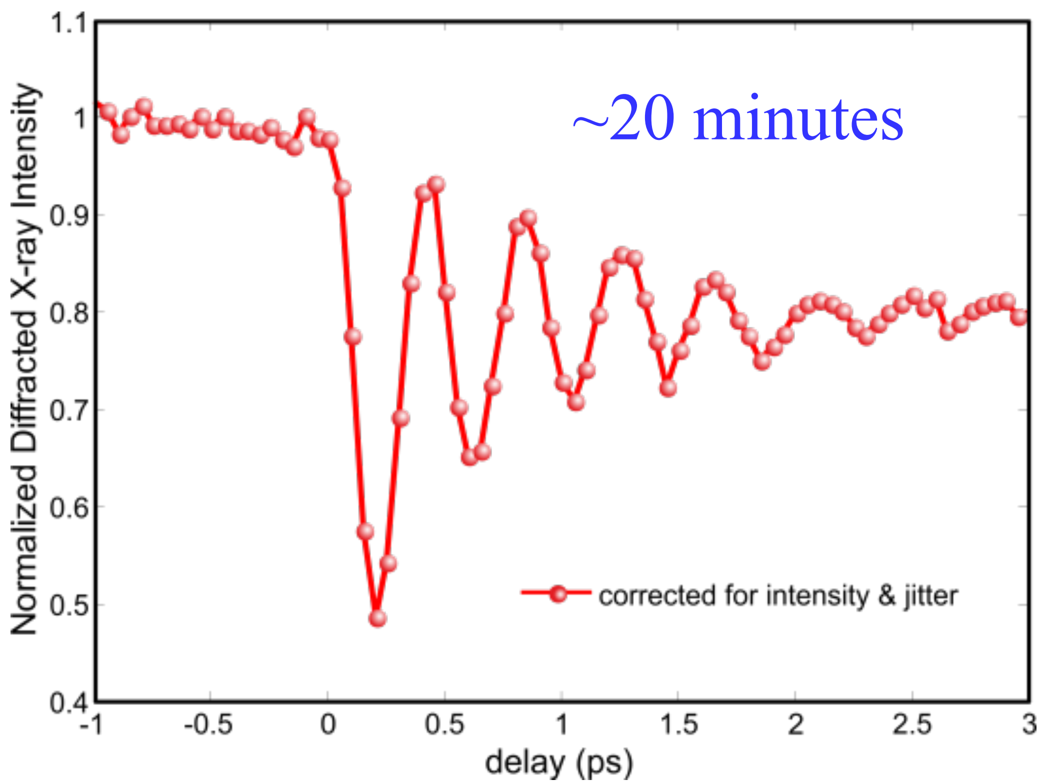
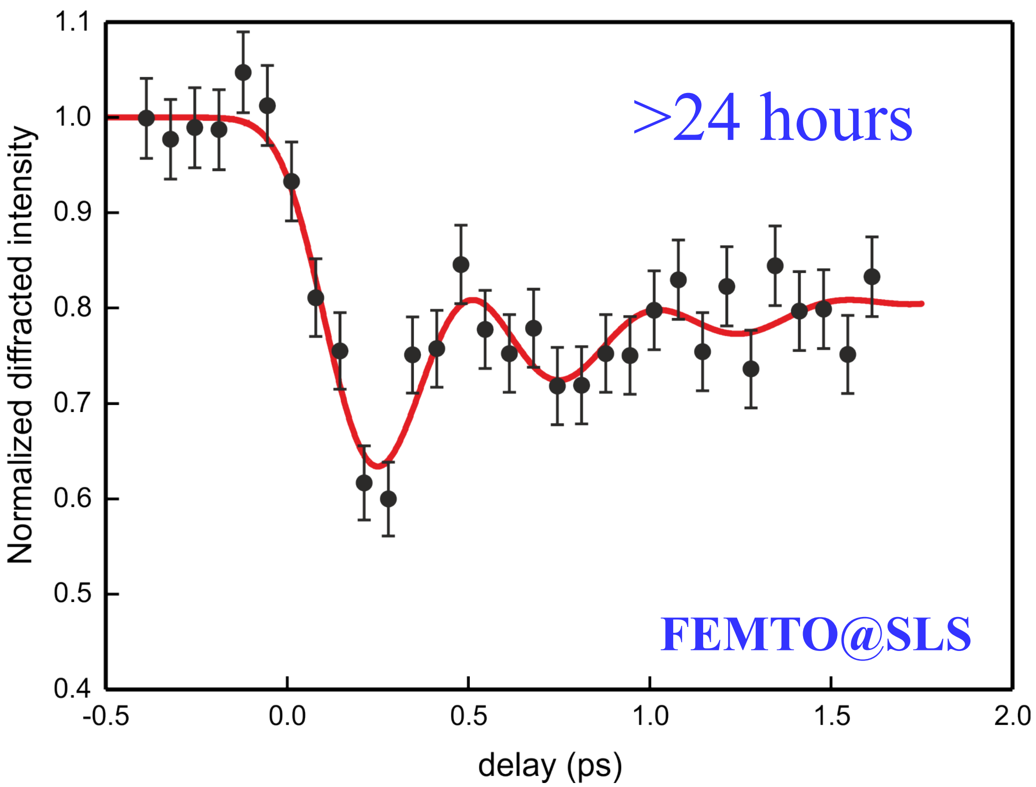


Time resolution



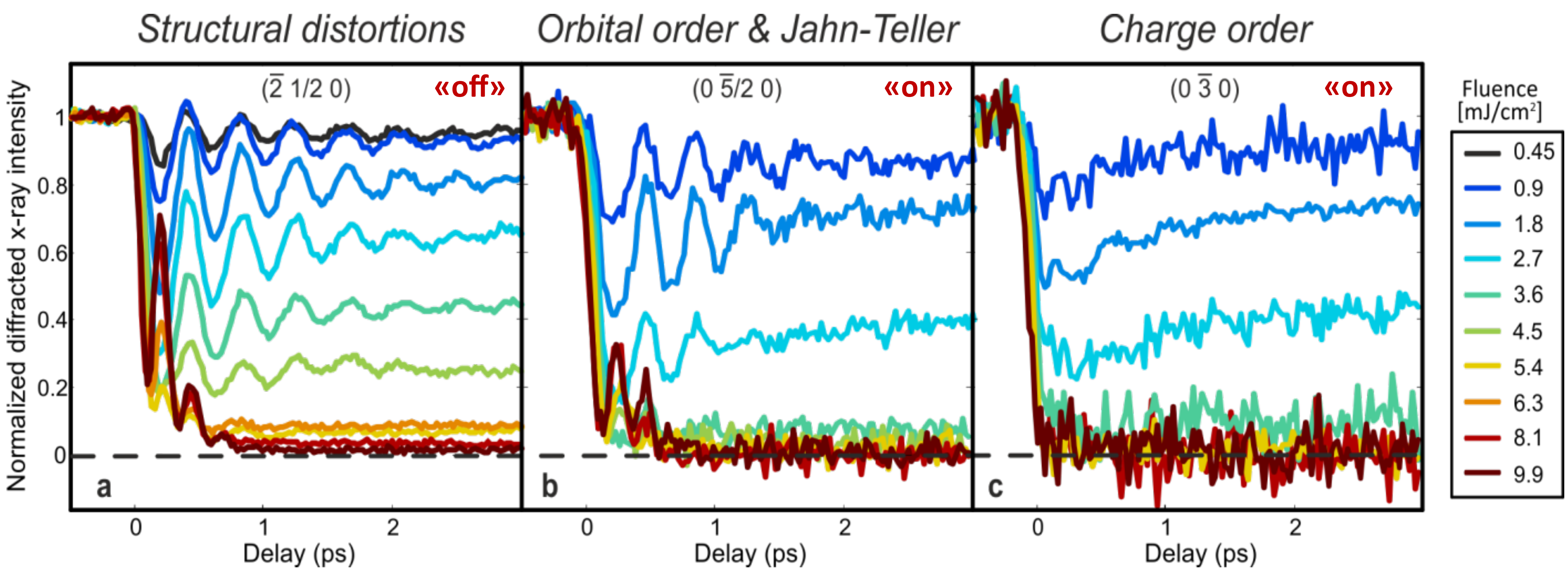
- Per-shot arrival time monitor essential [spectral encoding method, Harmand et al. Nat. Photon. 7, 215 (2013)]
- Dramatic improvement over previous measurements





[P. Beaud et al., Nature Mater. 13, 923 (2014)]

Overview: coupled motions

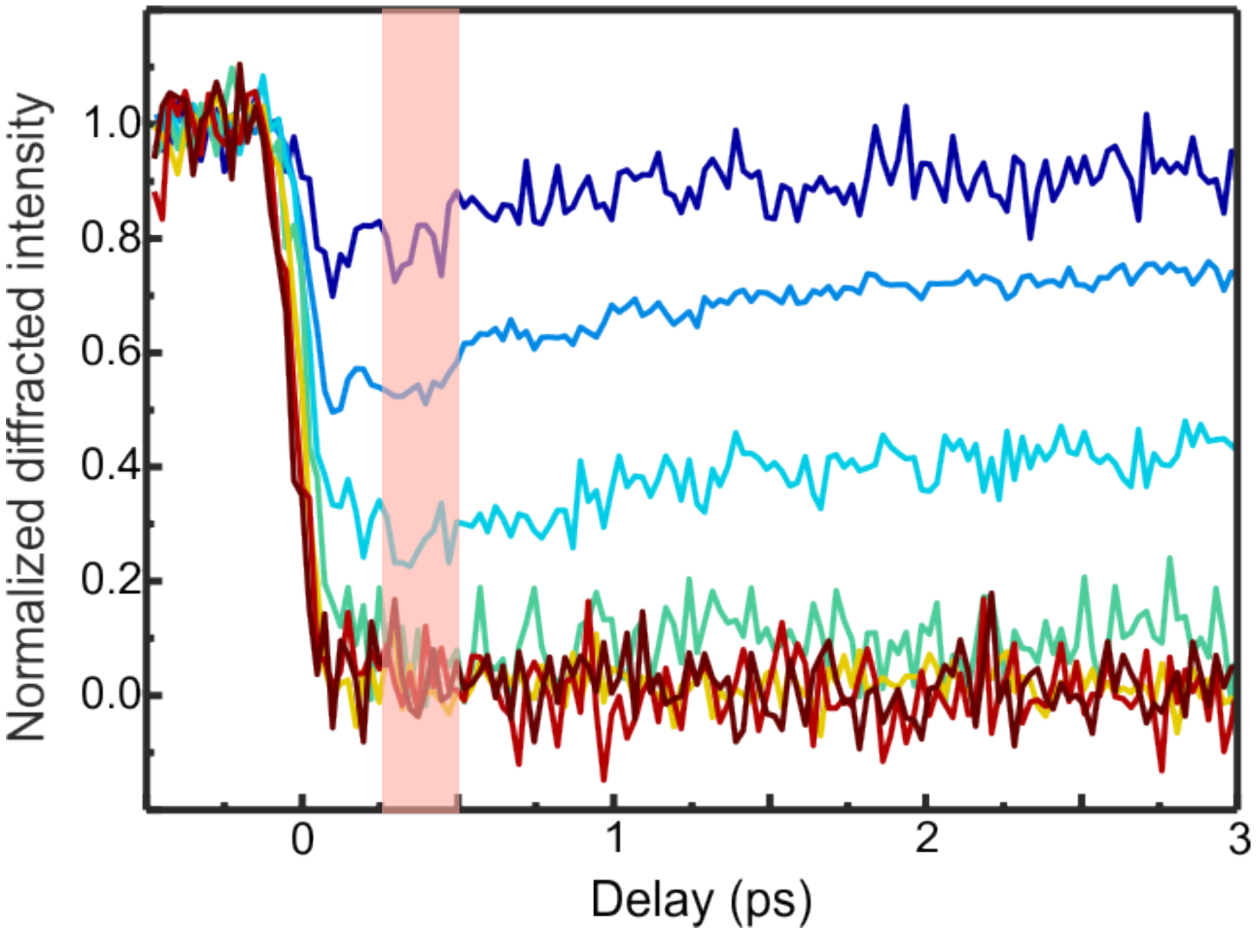


- Different reflections in & out of resonance gives access to different types of long-range order
- Above a certain excitation density, all go to zero at t > 1 ps
- Charge order melting fastest
- Other peaks see strong coherent vibration contribution

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

“Time-dependent" order parameter

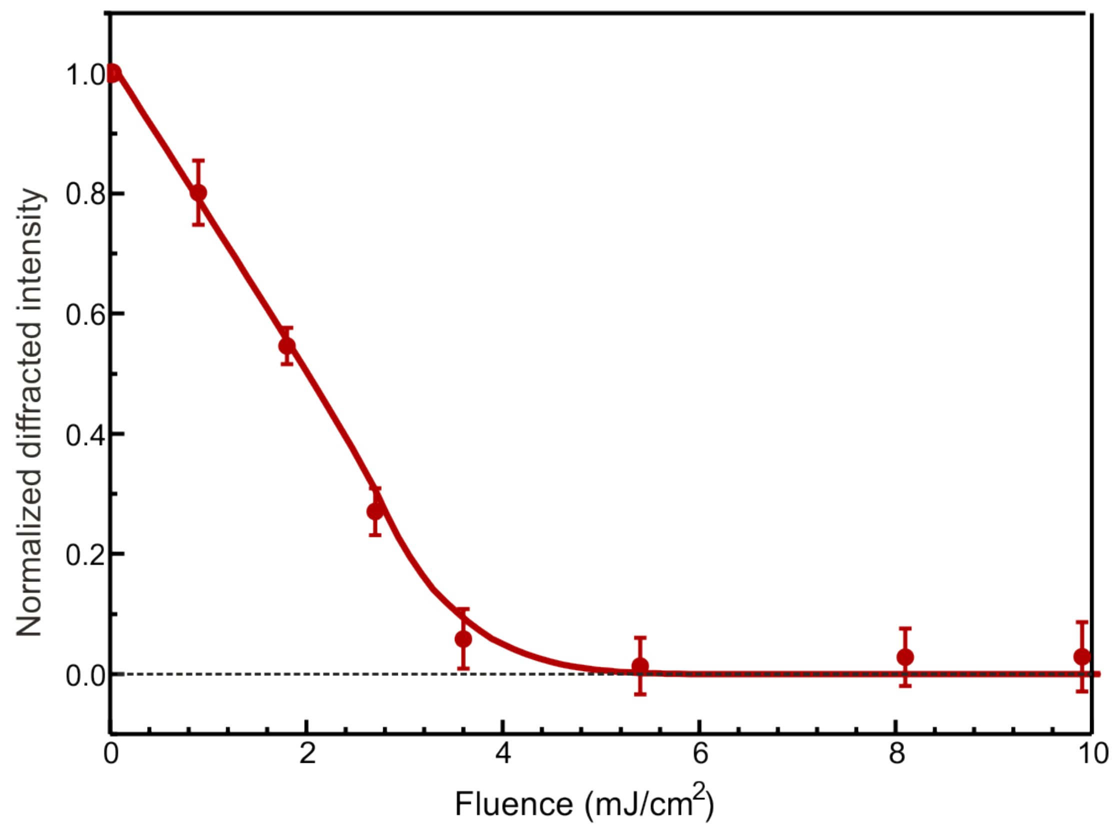
- Use (0 -3 0) intensity as a measure of charge order
- Intensity gives square of Mn charge modulation amplitude
- Identify charge modulation amplitude as a transient order parameter η_t
- Order parameter varies with time (and depth)



[P. Beaud et al., Nature Mater. 13, 923 (2014)]

"Time-dependent" order parameter

(0 -3 0) at t = 250-500 fs



- Early time excitation fluence dependence well described by

$$\eta_t = \begin{cases} \sqrt{1 - \frac{n_0}{n_c}} & n_0 < n_c \\ 0 & n_0 \geq n_c \end{cases}$$

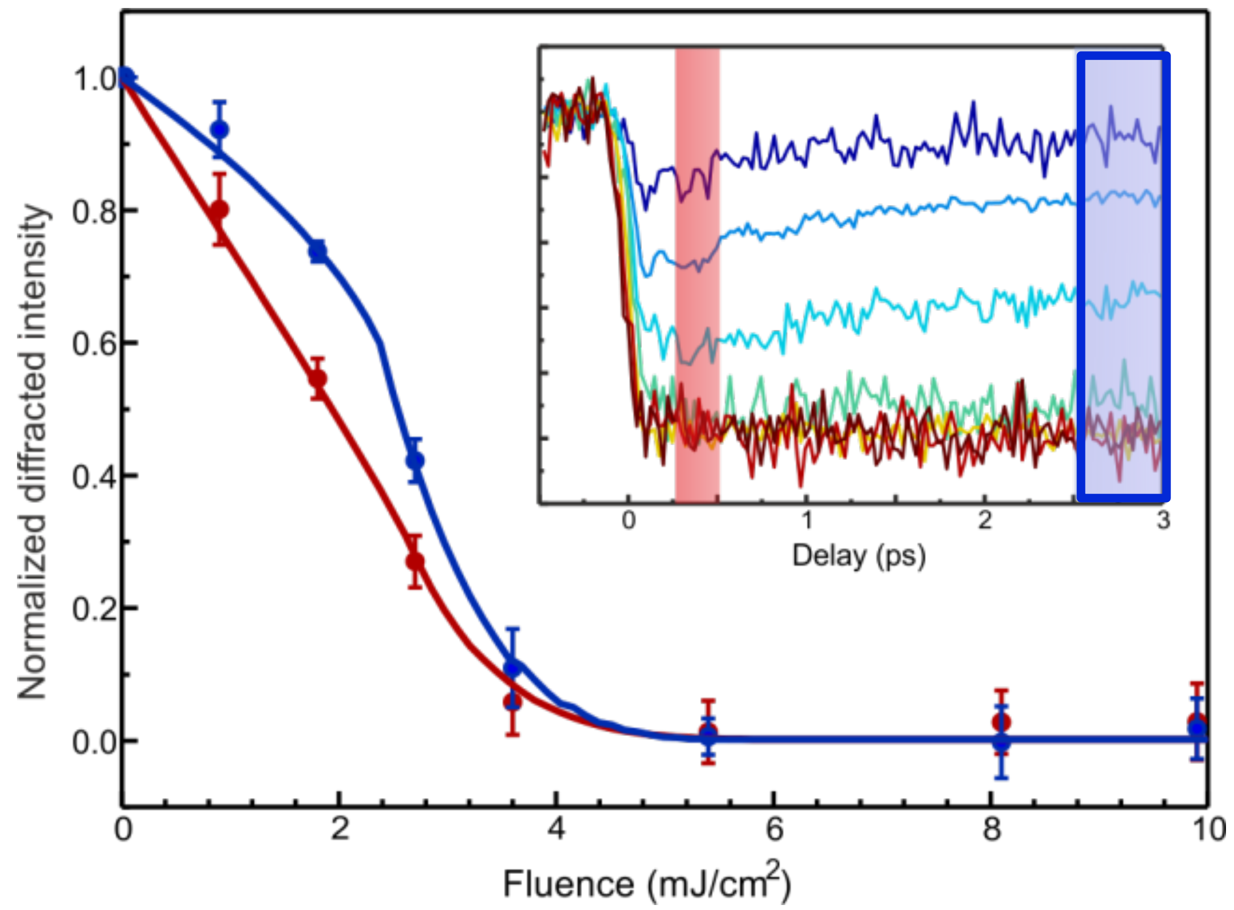
n_0 = initial electronic energy density, proportional to fluence

n_c = 350 meV/Mn site

- Very similar to Landau mean-field result for 2nd order phase transitions

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

Time evolution of order parameter



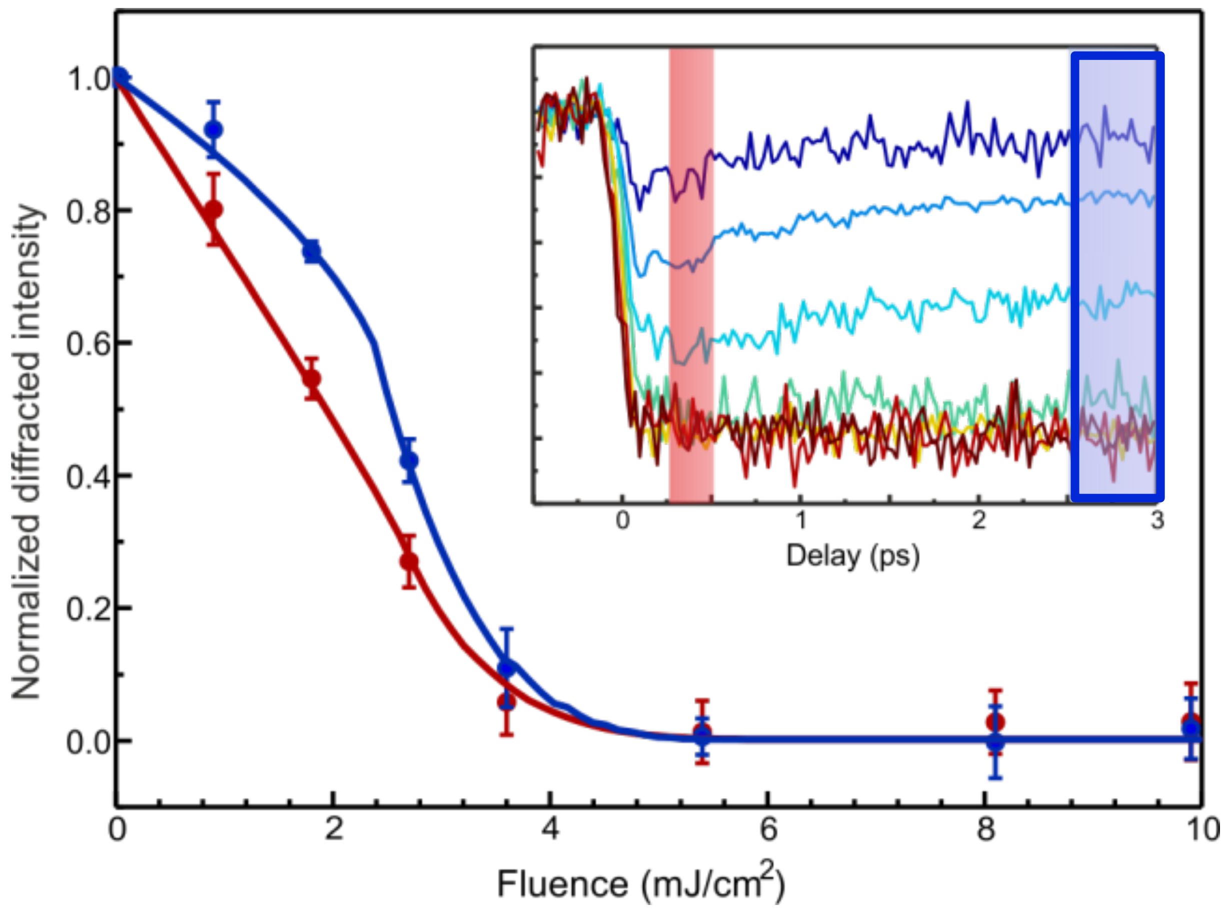
- Later times, after e-ph interaction:

$$\eta_t(t_{\text{late}}) = \left(1 - \frac{n_0}{n_c}\right)^{\gamma} \qquad \gamma = 0.20 \pm 0.02$$

Change of exponent: onset of long-range correlations?

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

Time evolution of order parameter



- Represent as an evolving *n*(*t*):

$$\eta_t = \begin{cases} \sqrt{1 - \frac{n}{n_c}} & n < n_c \\ 0 & n \geq n_c \end{cases}$$

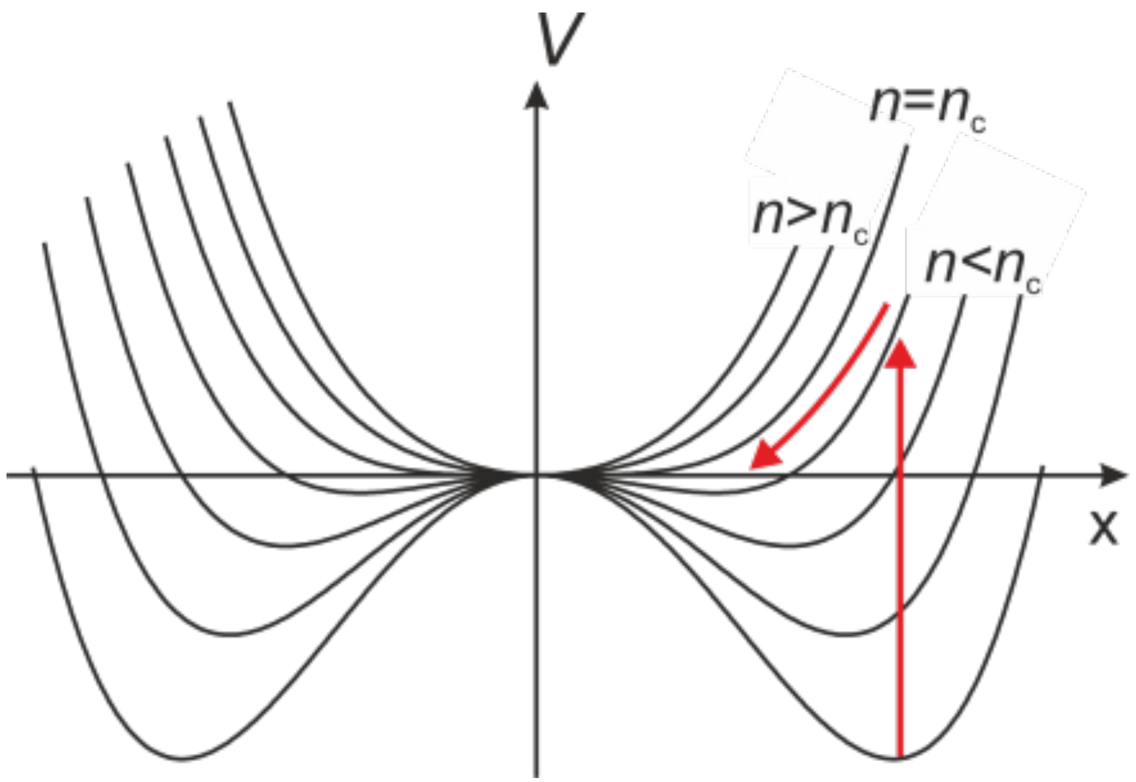
$$n(t) = (n_0 - an_c)e^{-t/\tau} + an_c$$

$$a = 1 - \left(1 - \frac{n_0}{n_c}\right)^{2\gamma}$$

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

Coupled dynamics of structure

- Coupling to structure via a time-dependent interatomic potential
- For quasi 1-D systems with one transition coordinate, Landau form has worked

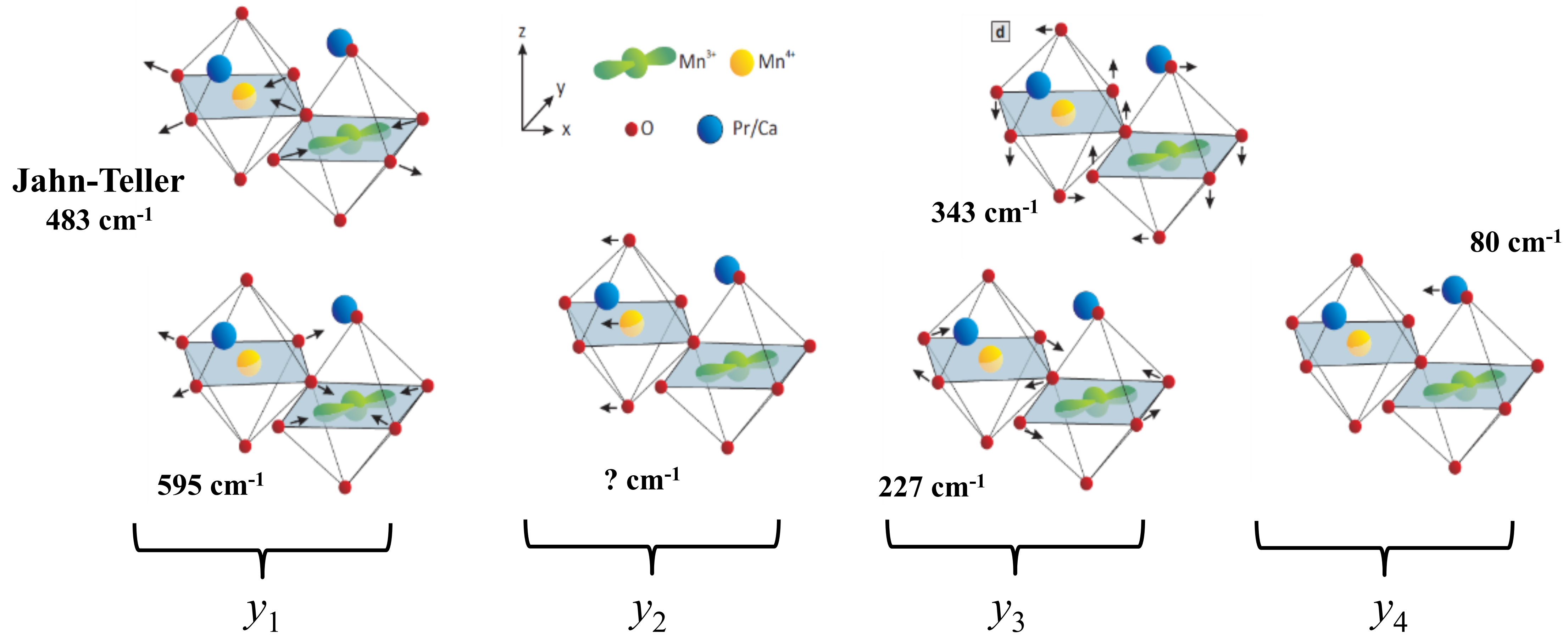


[Yusupov et al. Nat. Phys. 6, 681 (2010)]

[Huber et al. Phys. Rev. Lett. 113, 026401 (2014)]

$$V(x,t) = V_0 + a\left[n(t) - n_c\right] x^2 + b x^4$$

Coupled dynamics of structure



- In PCMO, multiple independent vibrational modes contribute
- Simplify as only four groups of modes

$$V(y_1, y_2, y_3, y_4, t) = V_0 + \underbrace{a\,[n(t) - n_c]\,y_1^2 + by_1^4}_{\text{driven motion}} + \underbrace{c_{21}(y_2 - y_1)^2 + c_{32}(y_3 - y_2)^2 + c_{43}(y_4 - y_3)^2}_{\text{chain of coupled motions}}$$

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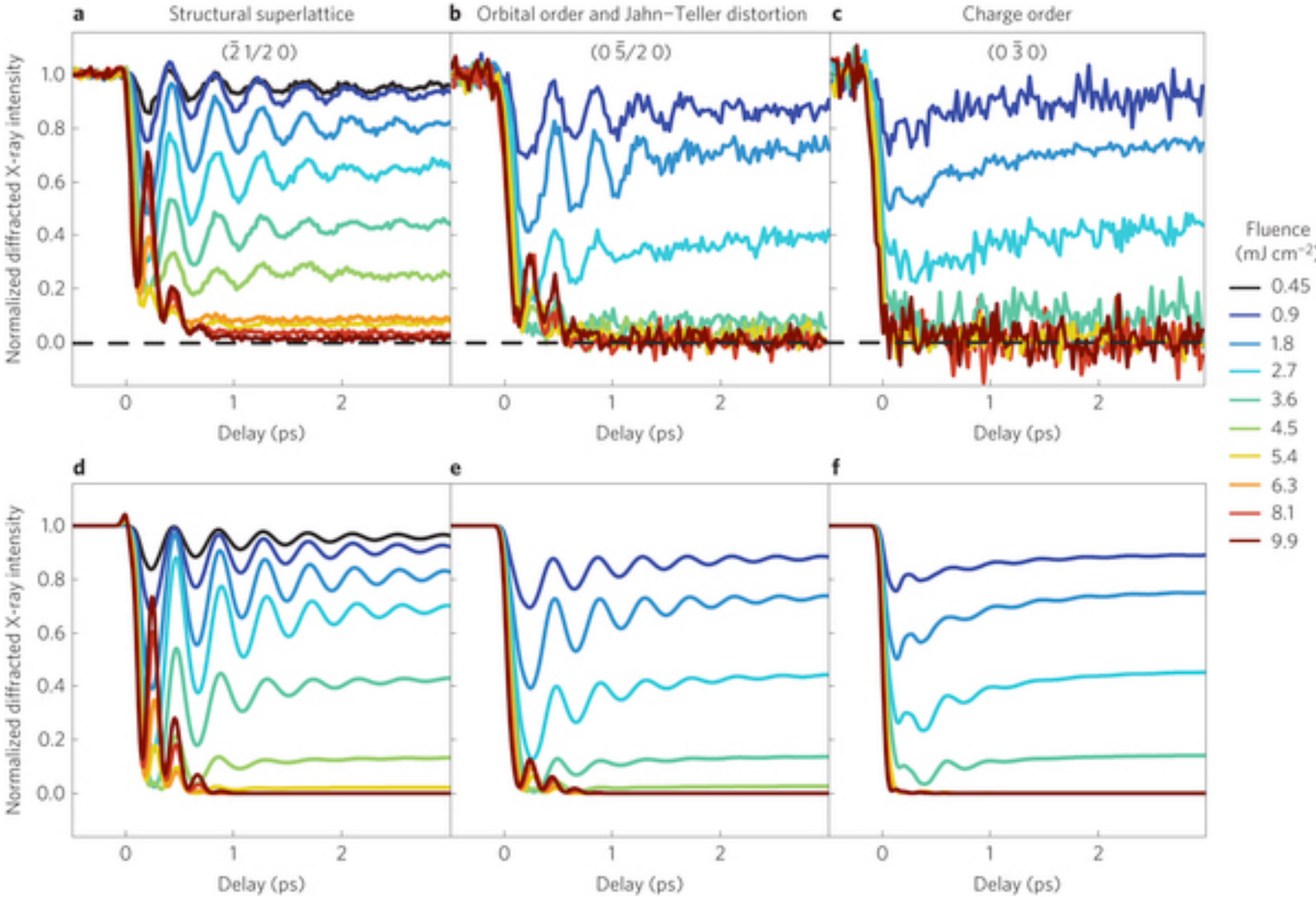
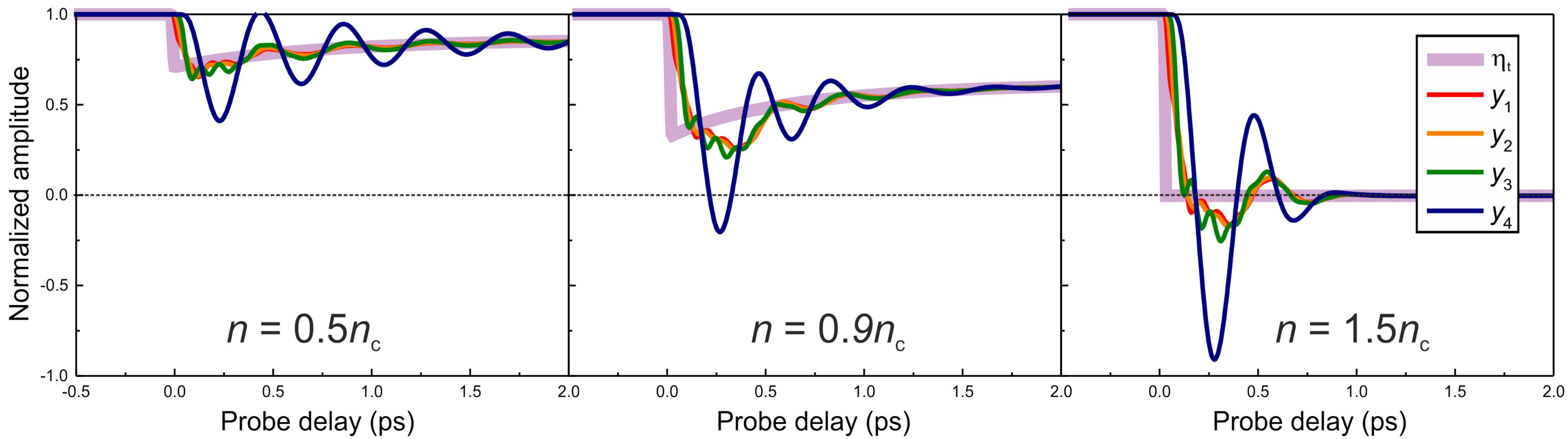
Coupled dynamics of structure



- Use time-dependent potential to construct equations of motion (linear damping added)

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

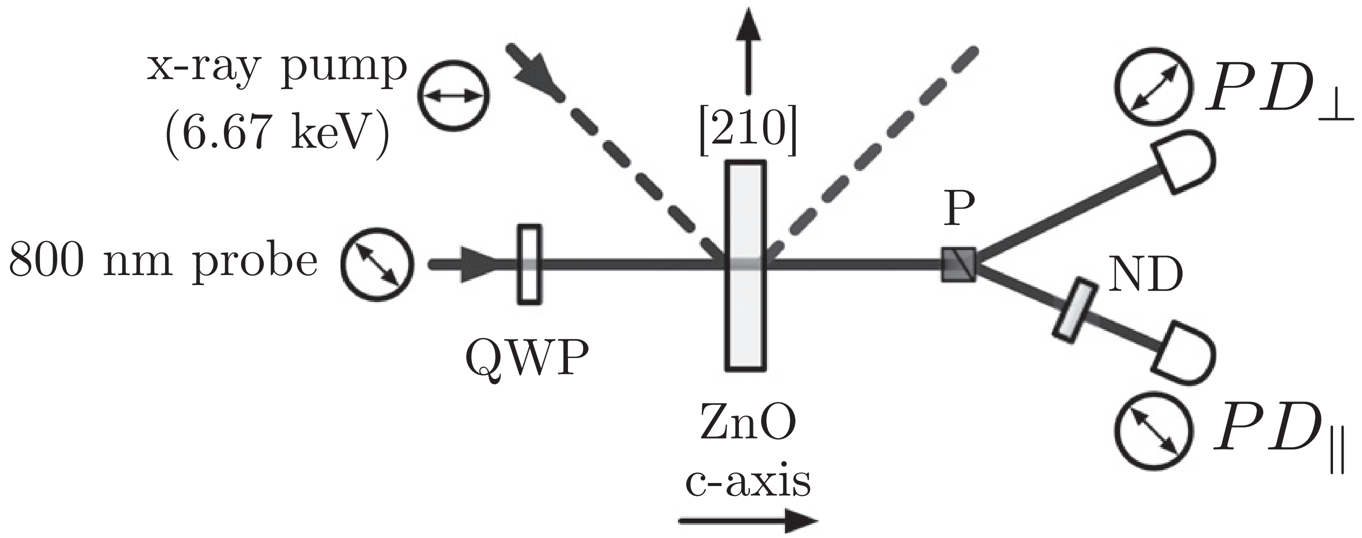
Coupled dynamics of structure



- Strong coupling: lowest frequency dominates at late times
- High fluence: overshoot of high symmetry point leads to doubling in measured diffraction signal

[P. Beaud et al., Nature Mater. 13, 923 (2014)]

Aside: X-rays as driver?



- X-ray pump to drive electronic and possible structural motion (tuned to diffraction peak)
- Detection channel: change in polarization of transmitted optical light

[A. Ferrer et al., Appl. Phys. Lett. 106, 154101 (2015)]

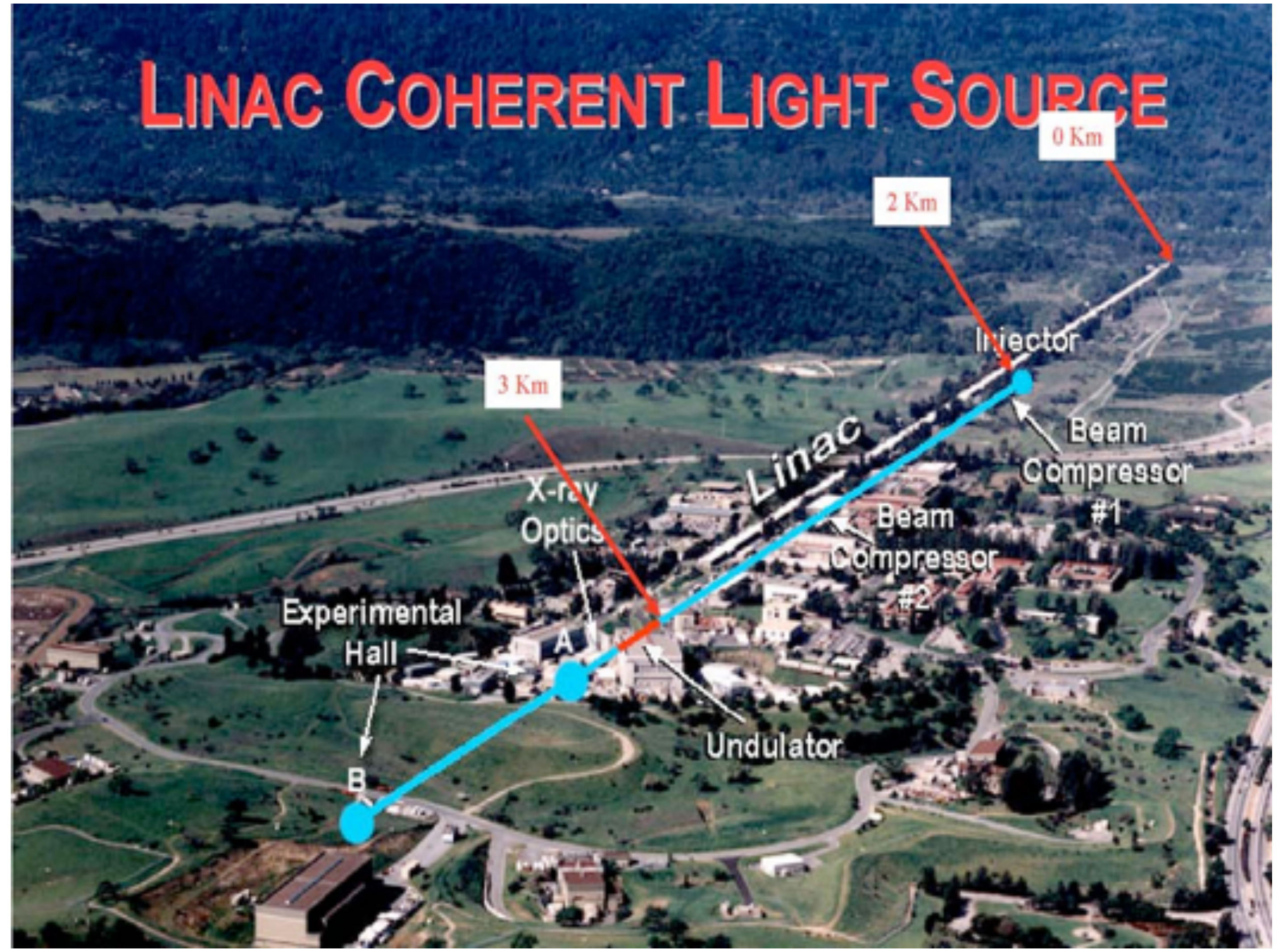
Experiment team: ZnO

ETHZ:

A. Ferrer
T. Huber
V. Scagnoli
M. Trant

SLAC:

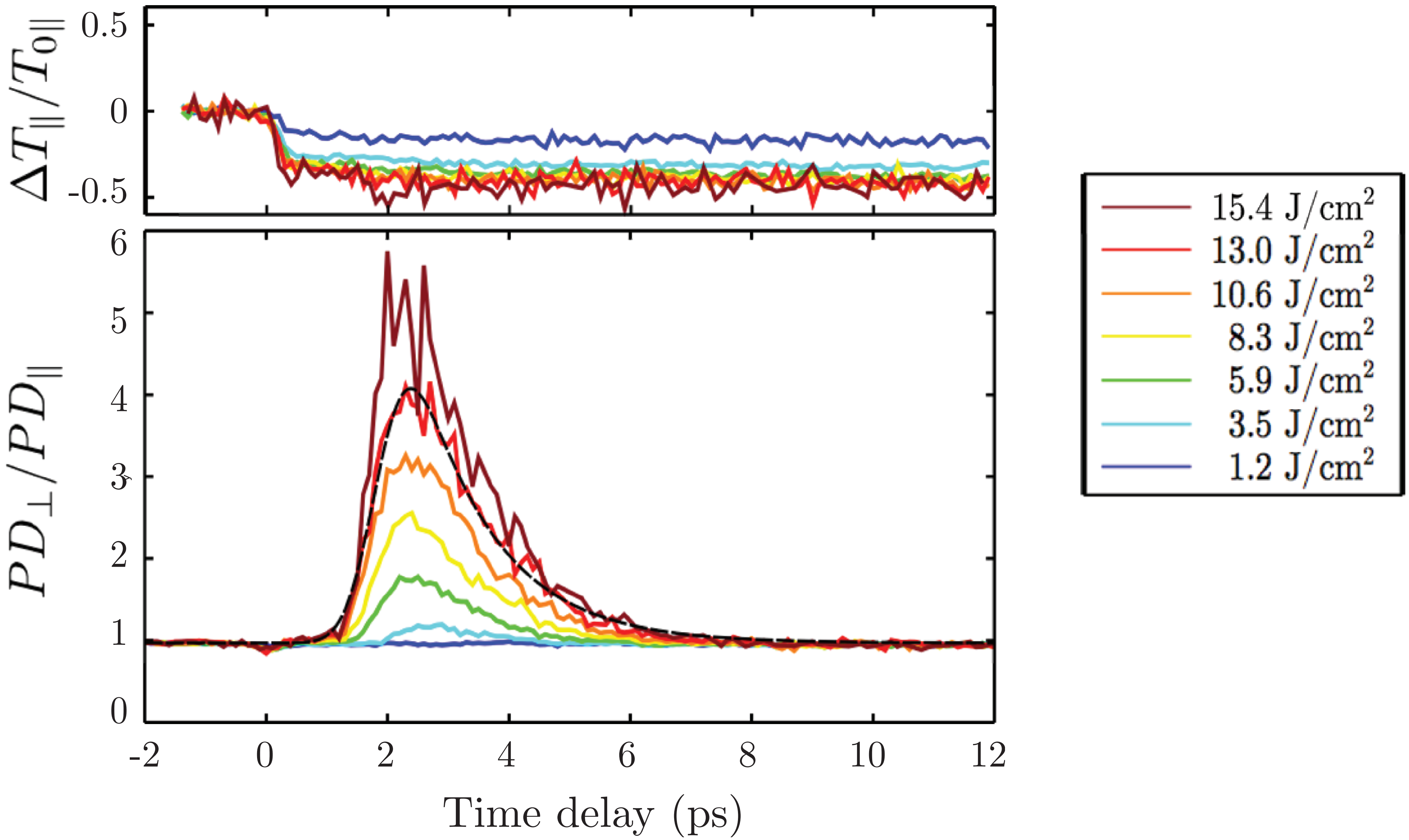
D. Zhu
M. Chollet
H. T. Lemke



J. A. Johnson
U.Staub
S. O. Mariager
G. Ingold

C. Milne
S. Gruebel
P. Beaud
L. Patthey

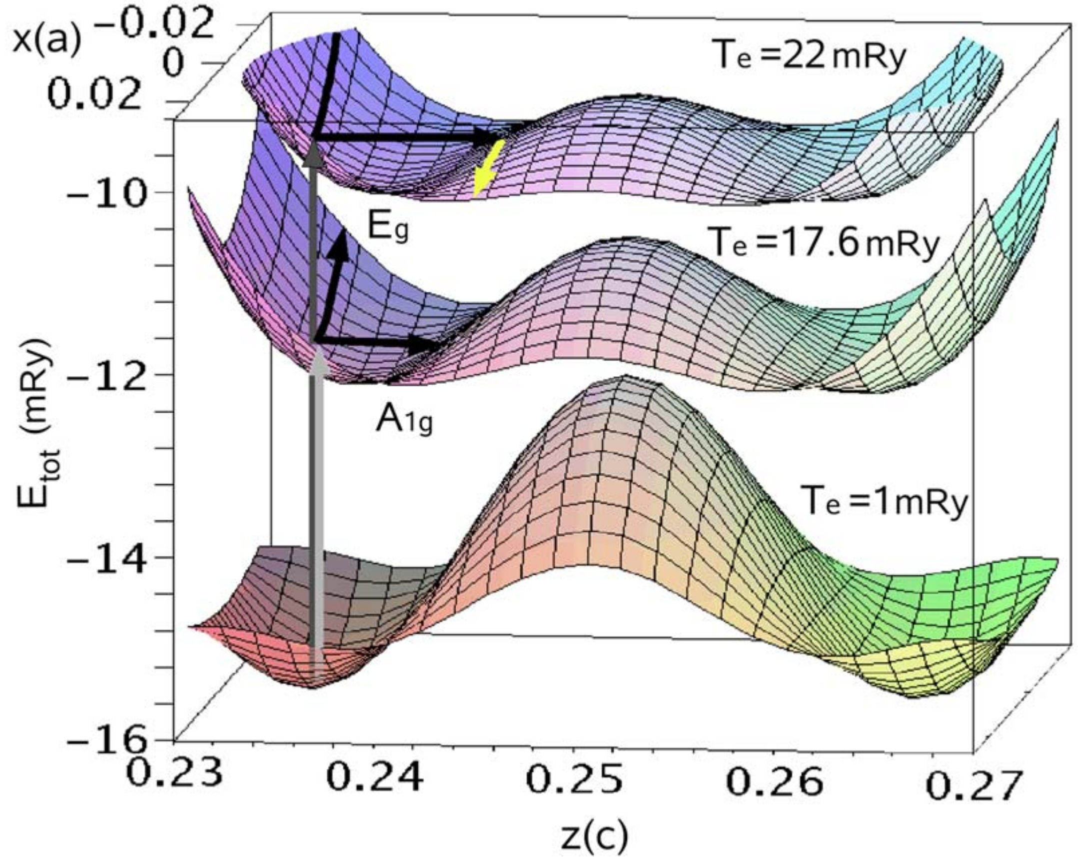
Persistent induced anisotropy



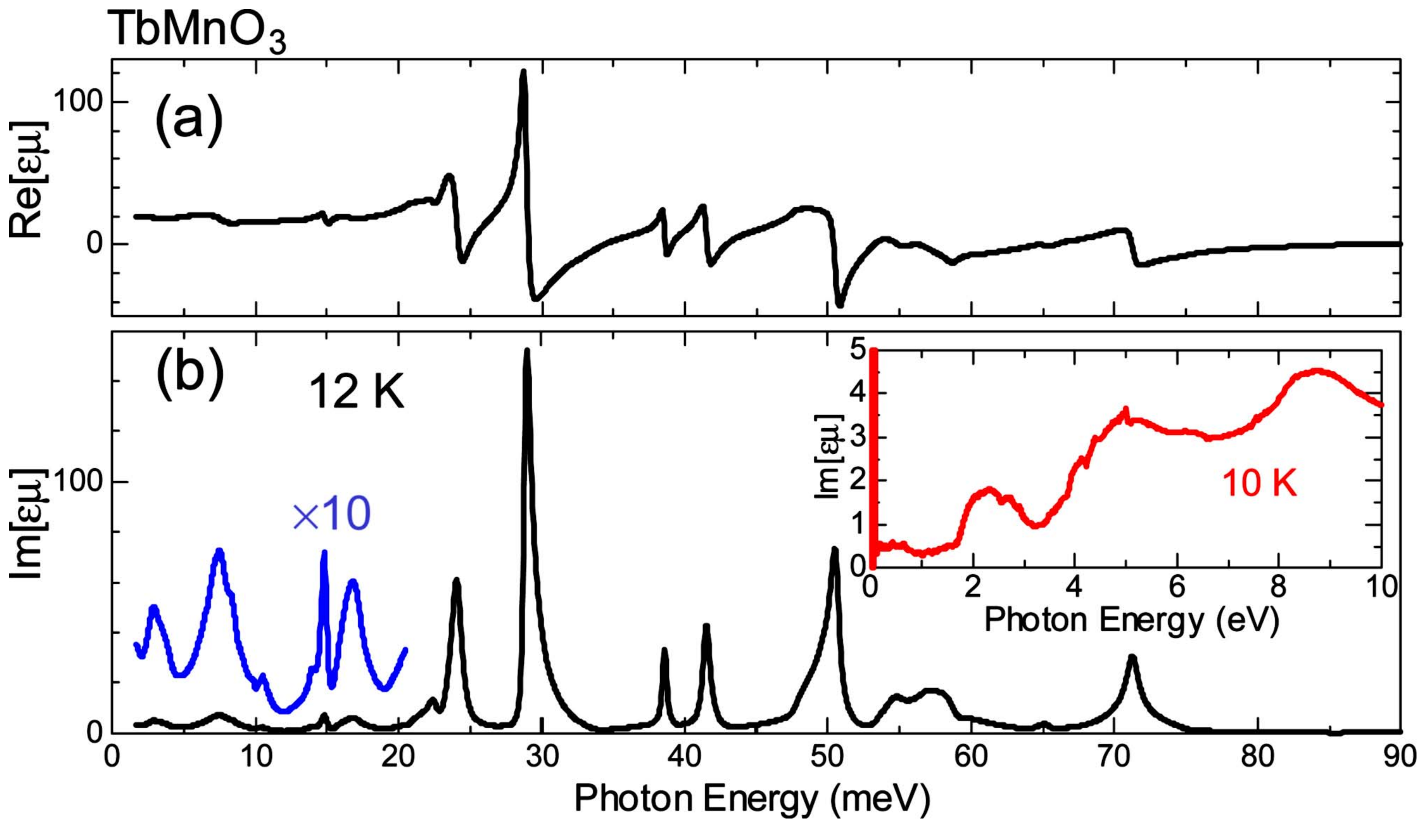
- Nonlinear increase in optical anisotropy from electronic excitation
- Delayed onset, signal persists to ~ 6 ps!!

[A. Ferrer et al., Appl. Phys. Lett. 106, 154101 (2015)]

"Indirect" vs. "Direct" control



[Zijlstra, Tatarinova & Garcia, PRB 74, 220301 (2006)]



[Kida et al., JOSAB 26 A35 (2009)]

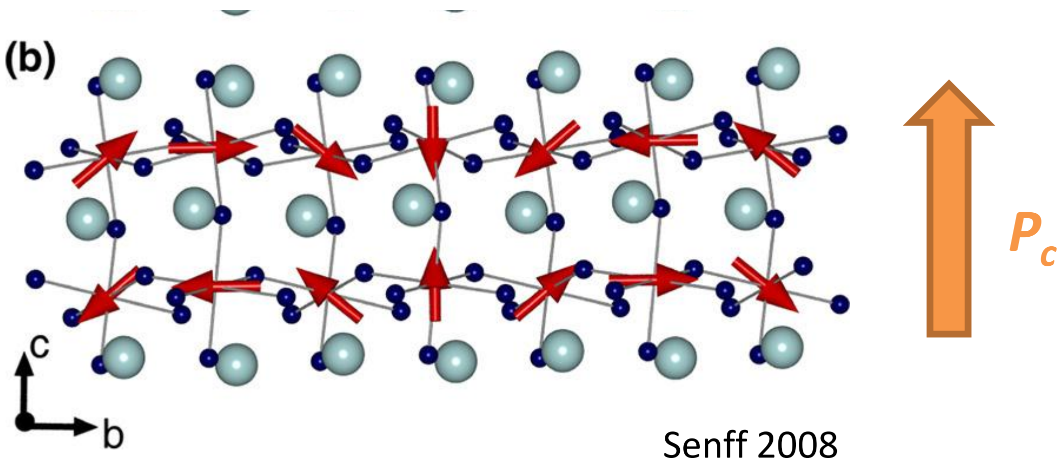
- Indirect works, but some significant disadvantages:
  - Competing channels (especially for electronic excitation)
  - Upscaling limited in potential
  - Often irreversible

“Direct” control:

Resonant THz excitations

THz excitation: path to fast control of multiferroics?

$TbMnO_3$

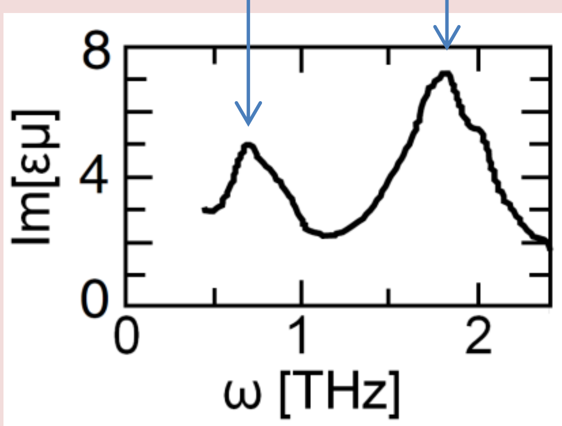


Senff 2008

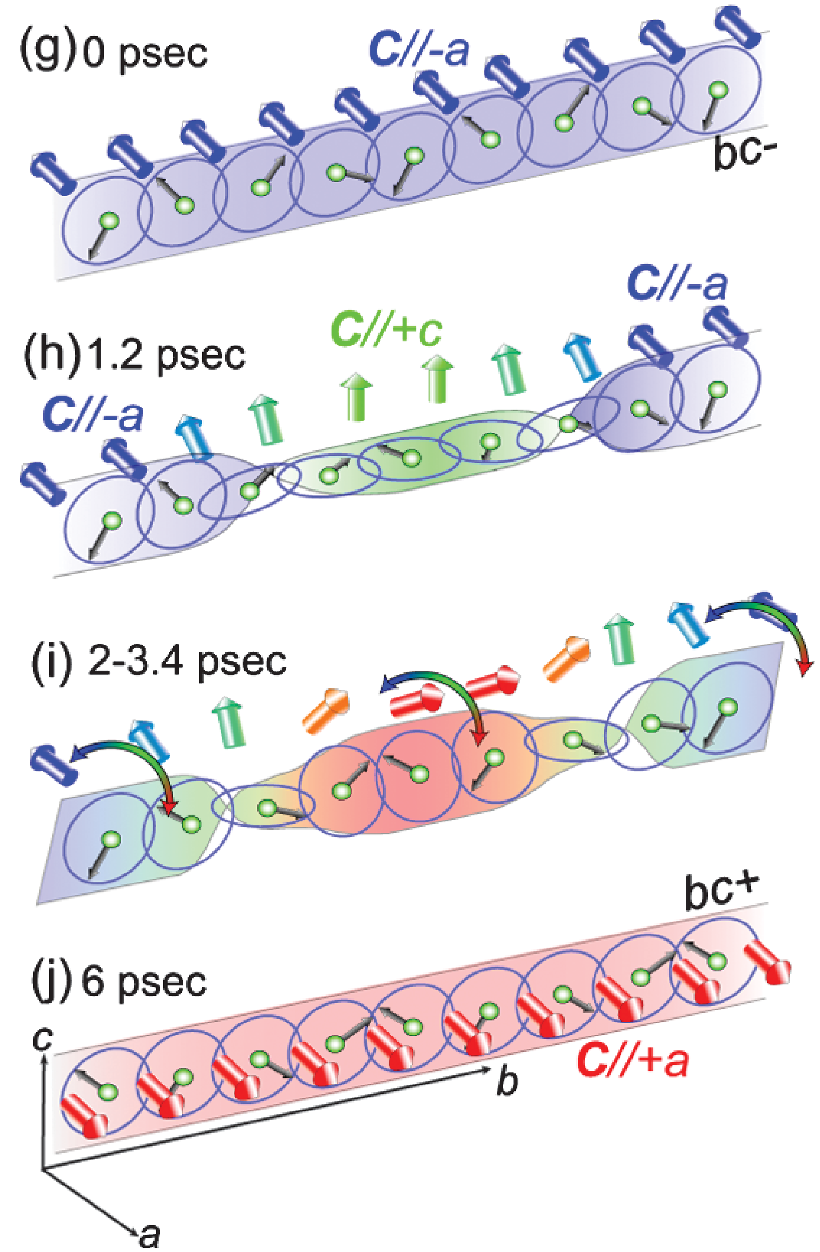
excitations due to the electromagnetic coupling:

higher-harmonic, ellipticity, phonons 0.7 THz

spin-spiral excitation, 1.8 THz

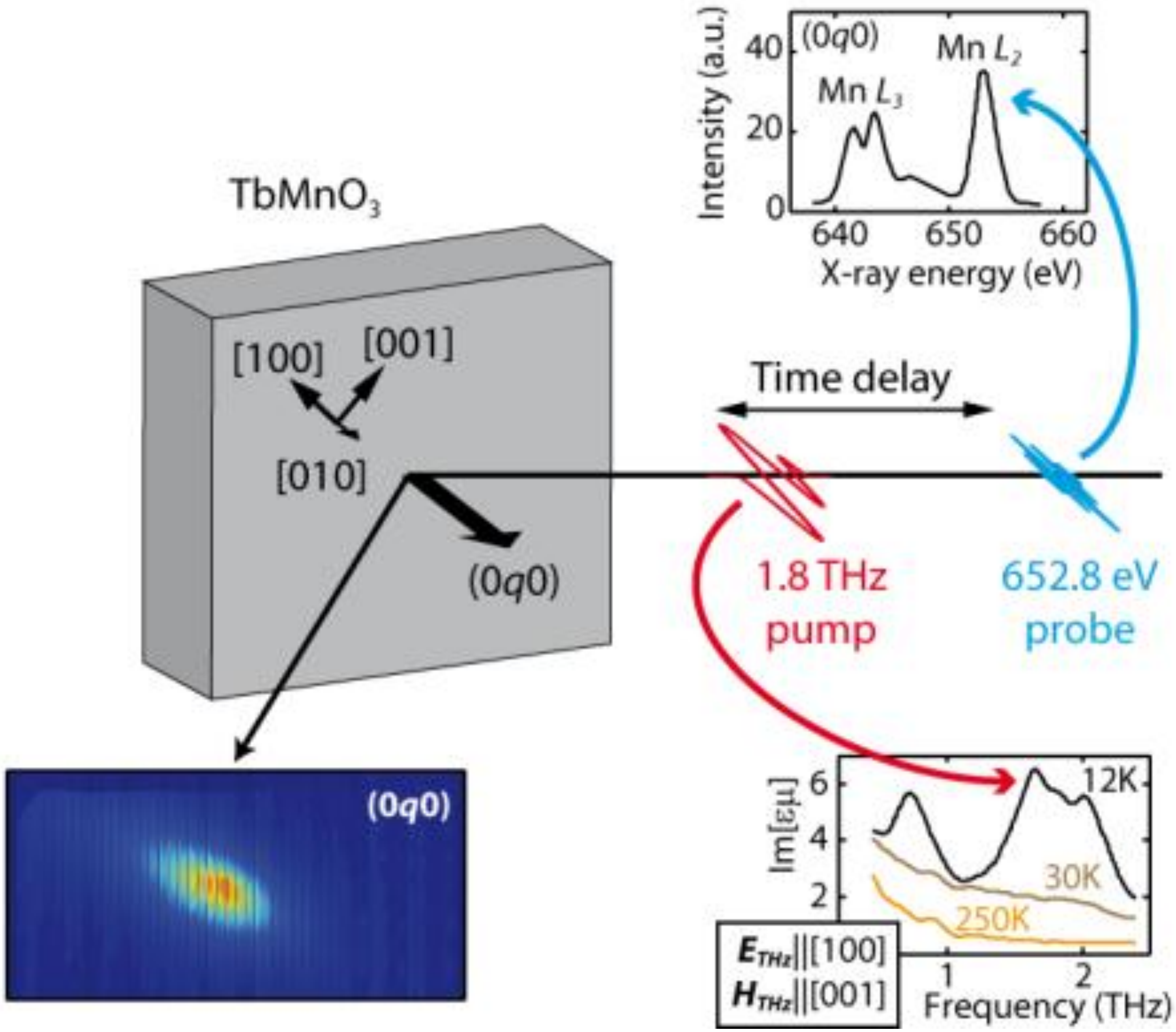


[Y. Takahashi et al., PRL **101**, 187201 (2008)]



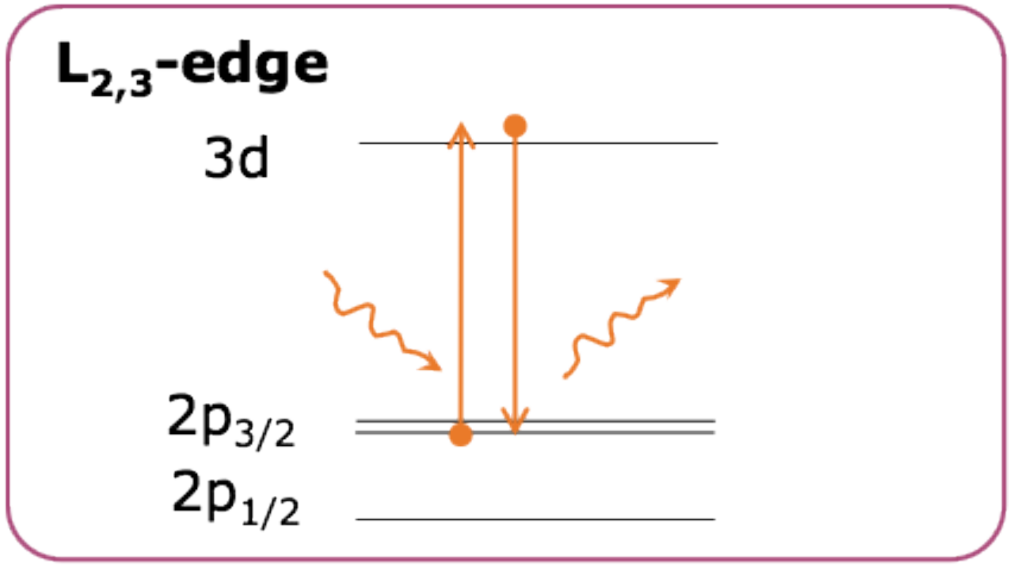
[Mochizuki & Nagaosa, PRL **105**, 147202 (2010)]

Experiment concept

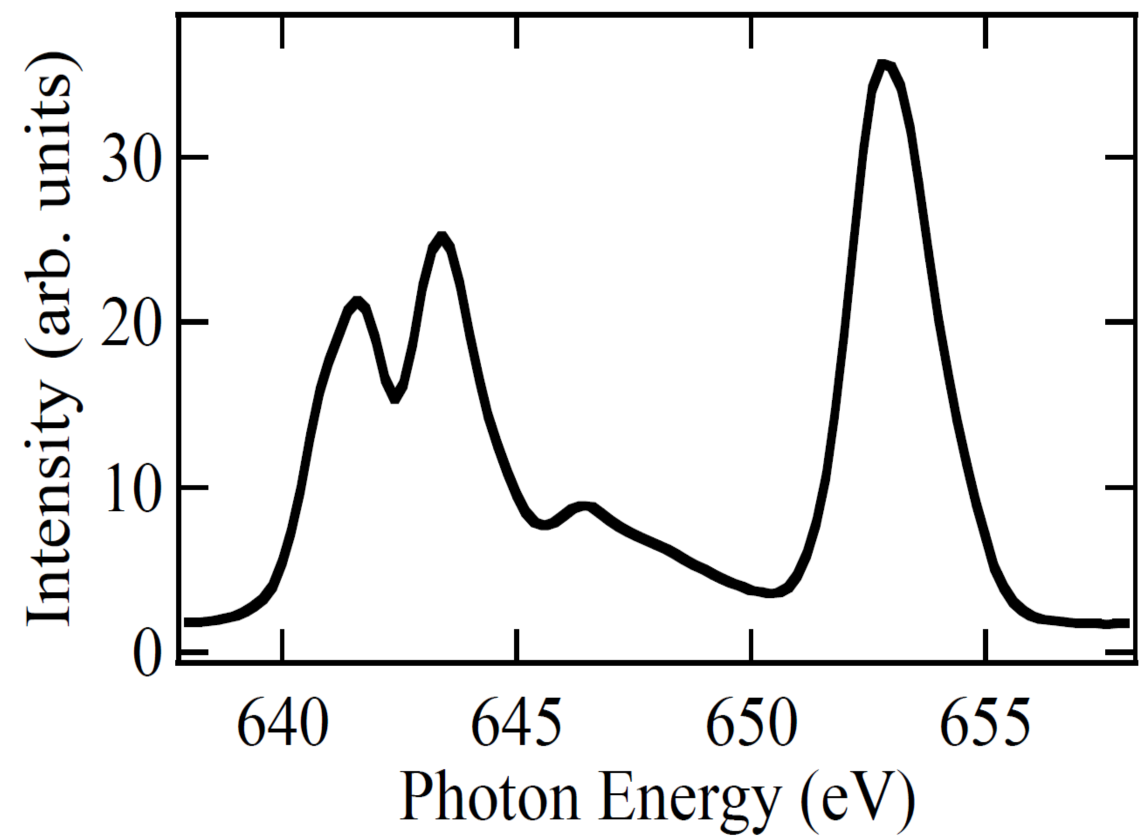


Pump electromagnon with THz, watch spins with resonant x-ray diffraction

X-ray pulses: probe spin order



- (0q0) reflection at Mn L-edges: only magnetic order



$$\left\langle \mathbf{T}_q^k \right\rangle \propto \sum_n \frac{\langle g|\, O\, |n\rangle \langle n|\, O^*\, |g\rangle}{E_n - E_g - \hbar\omega + i\Gamma}$$

- Experiment at LCLS
- Pulses of < 80 fs duration
- Time-stamping for < 250 fs resolution

[Beye et al. Appl. Phys. Lett. 100, 121108 (2012)]

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Experiment team: $TbMnO_3$

ETHZ:

T. Kubacka
L. Huber
V. Scagnoli

SLAC:

M. Hoffmann
S. de Jong
J. Turner
W. Schlotter
G. Dakovski

LBNL:

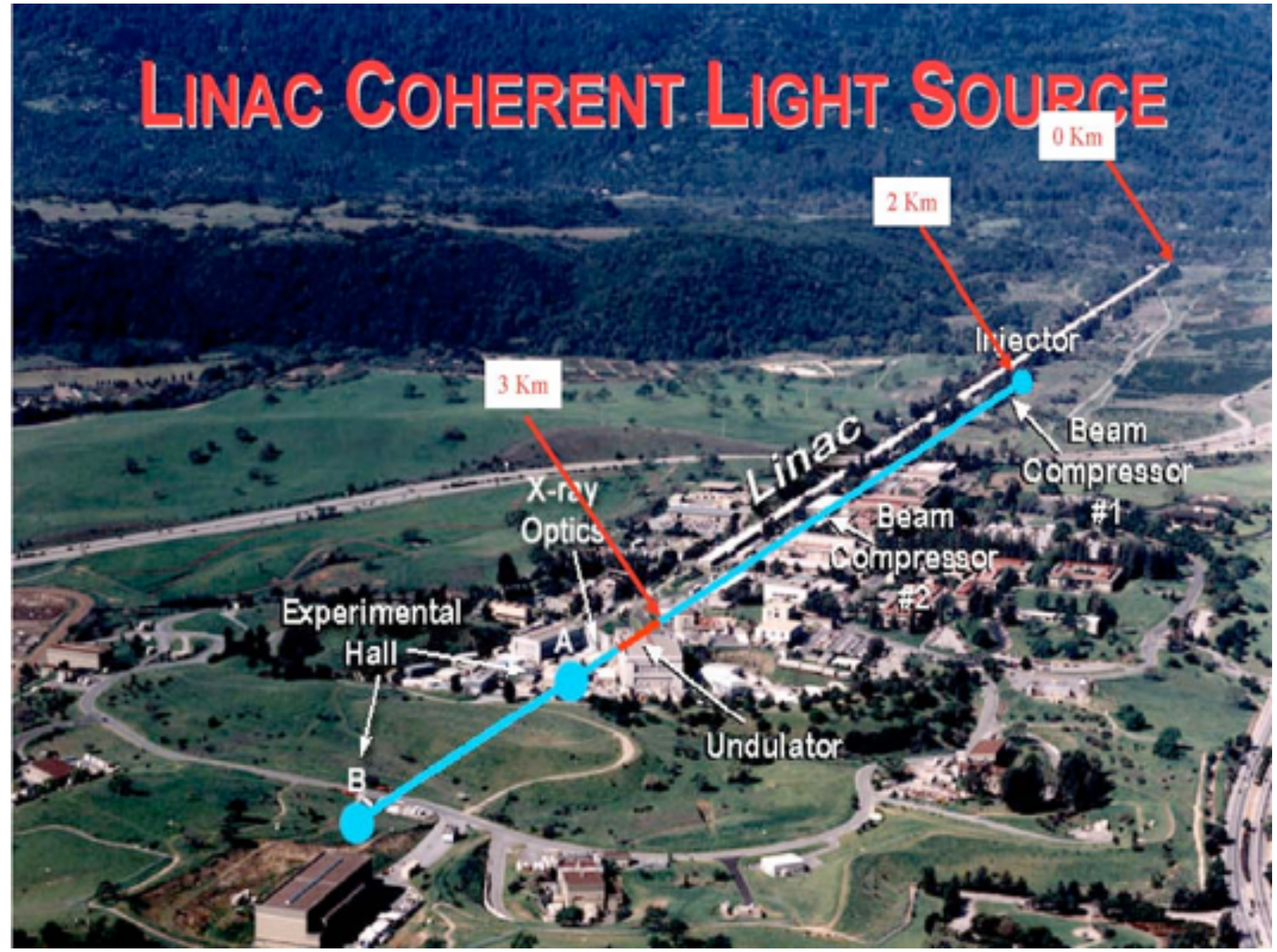
Y.-D. Chuang

Stanford:

W.-S. Lee
R. G. Moore

Johns Hopkins:

S. M. Koohpayeh



PAUL SCHERRER INSTITUT
PSI

U.Staub
S.-W. Huang
J. Johnson
C. Vicario
G. Ingold

Ch. Hauri
S. Gruebel
P. Beaud
L. Patthey

must

LCLS

FNSNF
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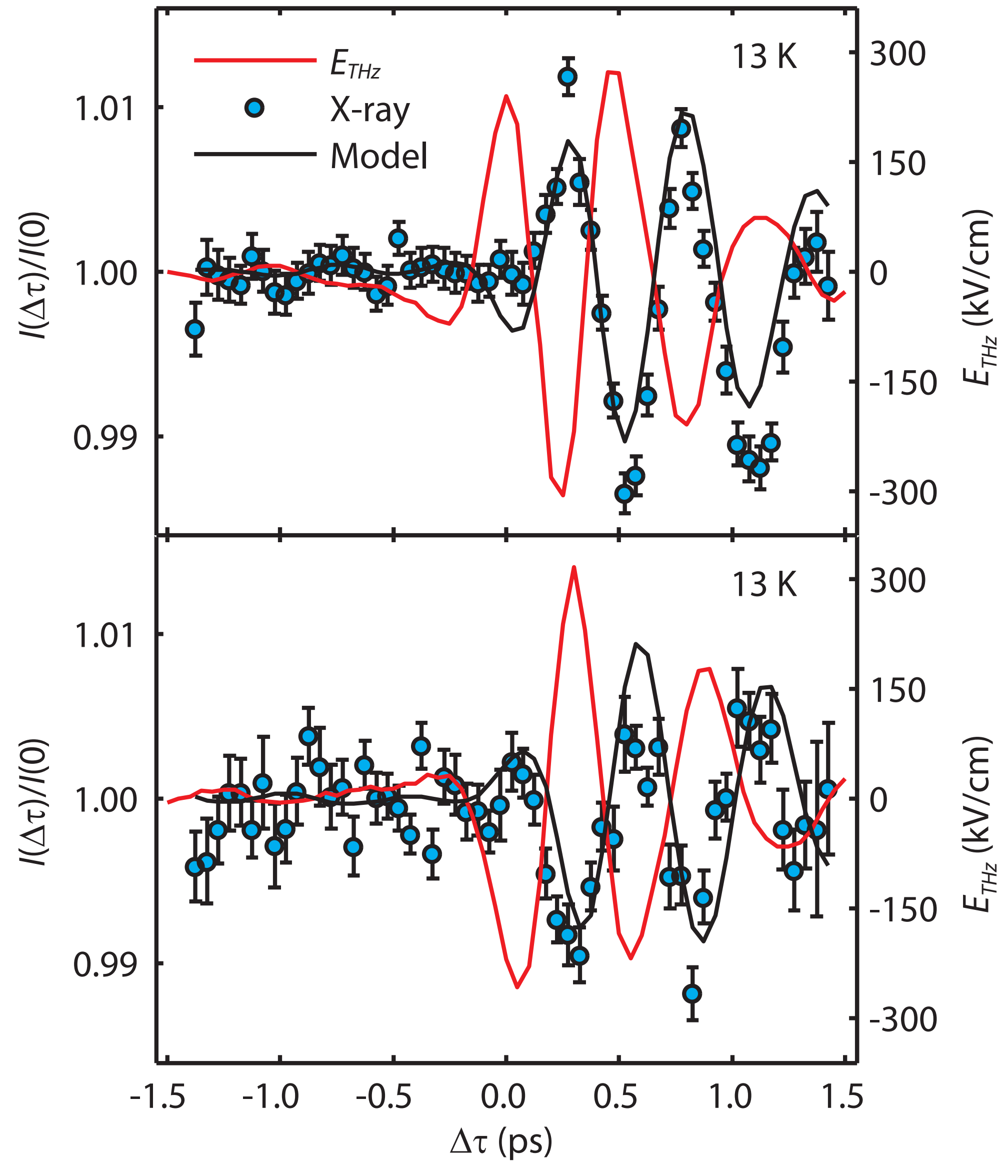
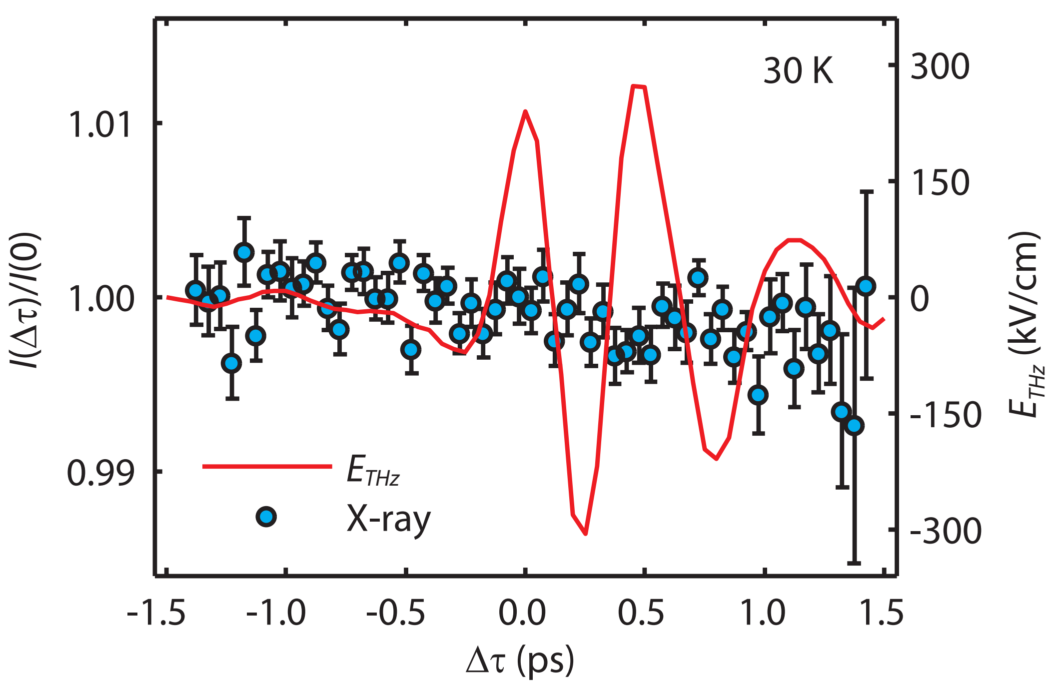
Results: coherent electromagnon

- E-field of THz → coherent spin response
- Measured spin response delayed by half cycle
- Response suppressed in non-multiferroic phase





[T. Kubacka et al., Science **343**, 1333 (2014)]

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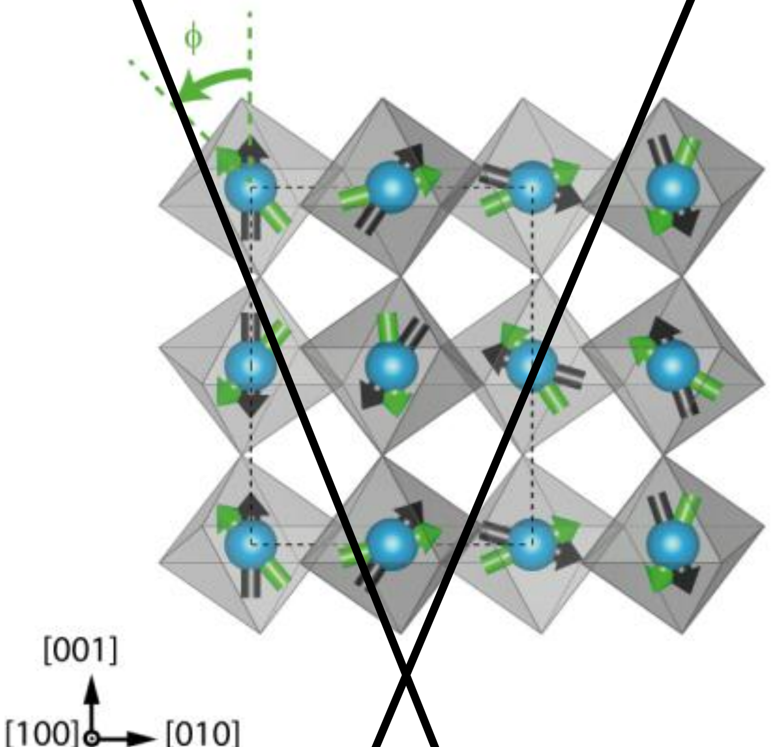
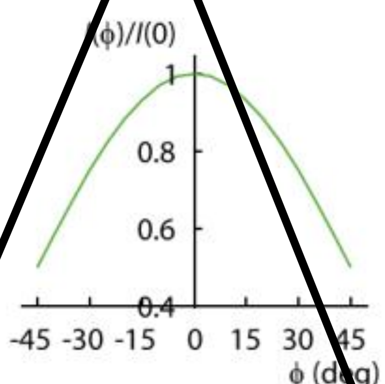
Analyzing the motion

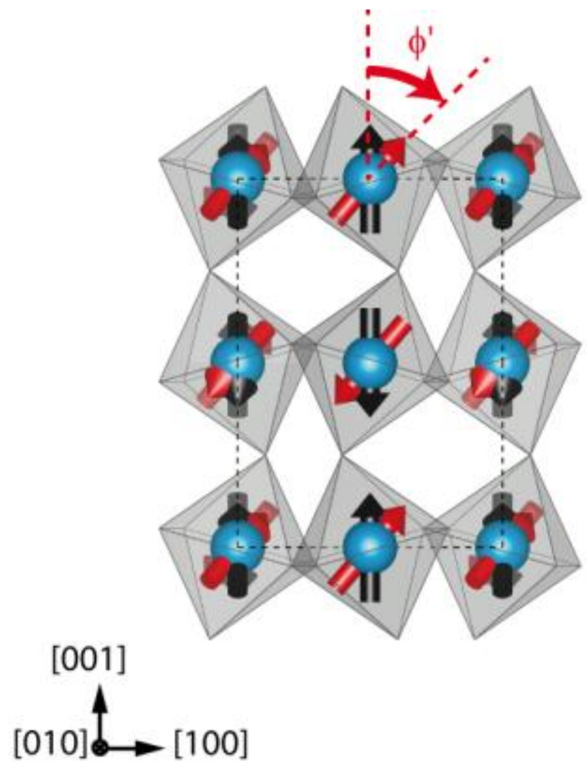
In-plane rotation

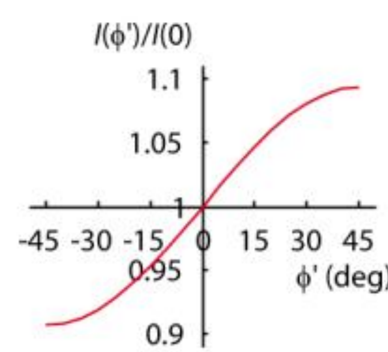




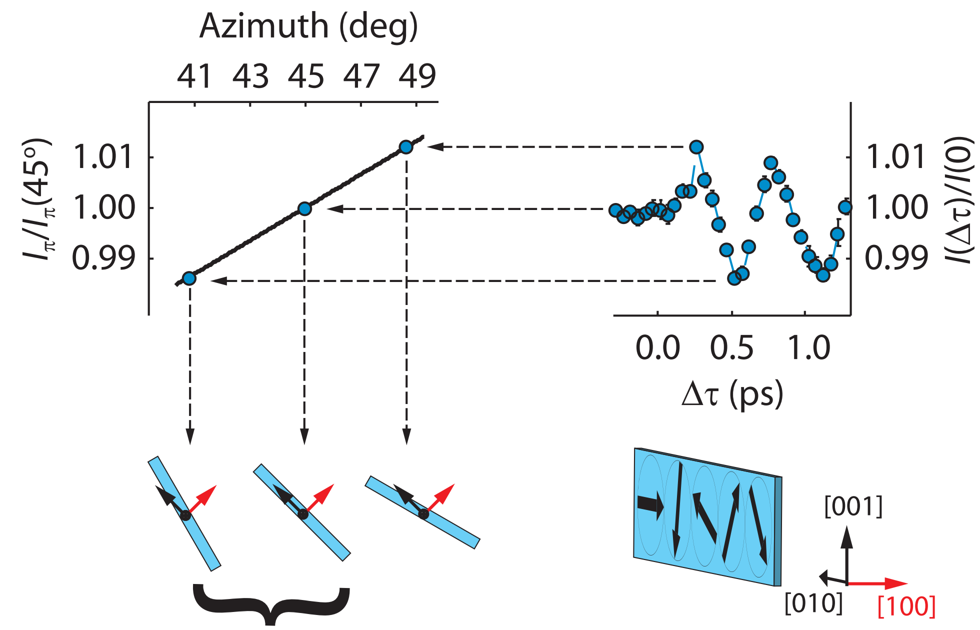
Even function

Rotation of spin planes





Odd function

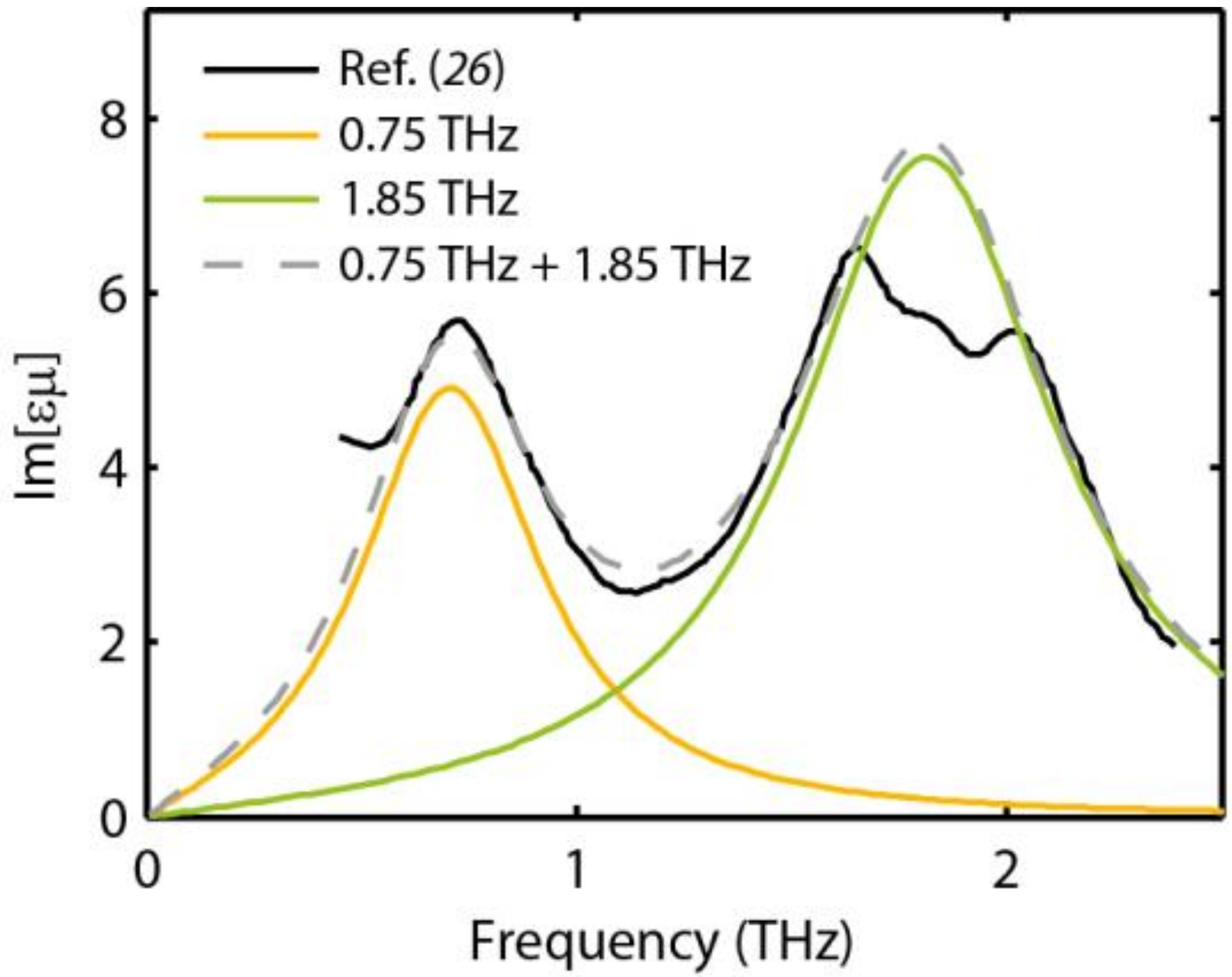


4.2°±0.4°

⇒ 4.2 ± 0.4 degree rotation of spin planes

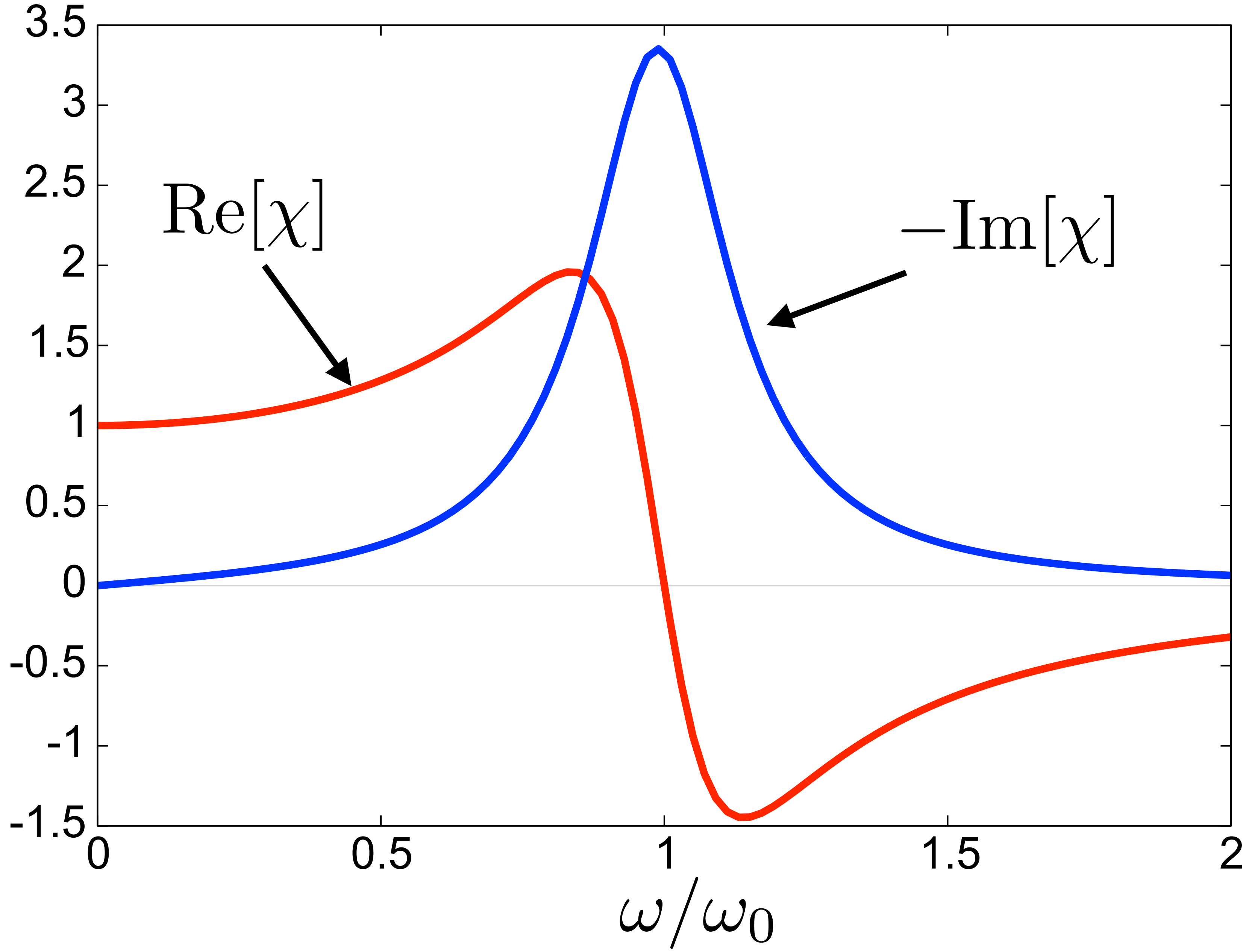
[T. Kubacka et al., Science **343**, 1333 (2014)]

Analyzing the motion



- What about time response?
- Approximate electromagnons as damped harmonic oscillators

Analyzing the motion

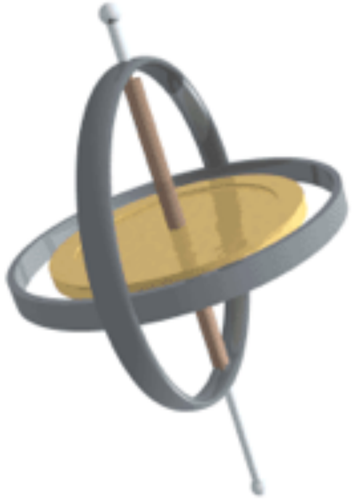


- Susceptibility vs. frequency: phase lag of 90 degrees at resonance
- …but data shows lag of 180 degrees!?!

Analyzing the motion

$$H = \sum_{<i,j>} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + D\sum_i S_{\zeta i}^2 + E\sum_i (-1)^{i_x+i_y}(S_{\zeta i}^2 - s_{\eta i}^2)$$

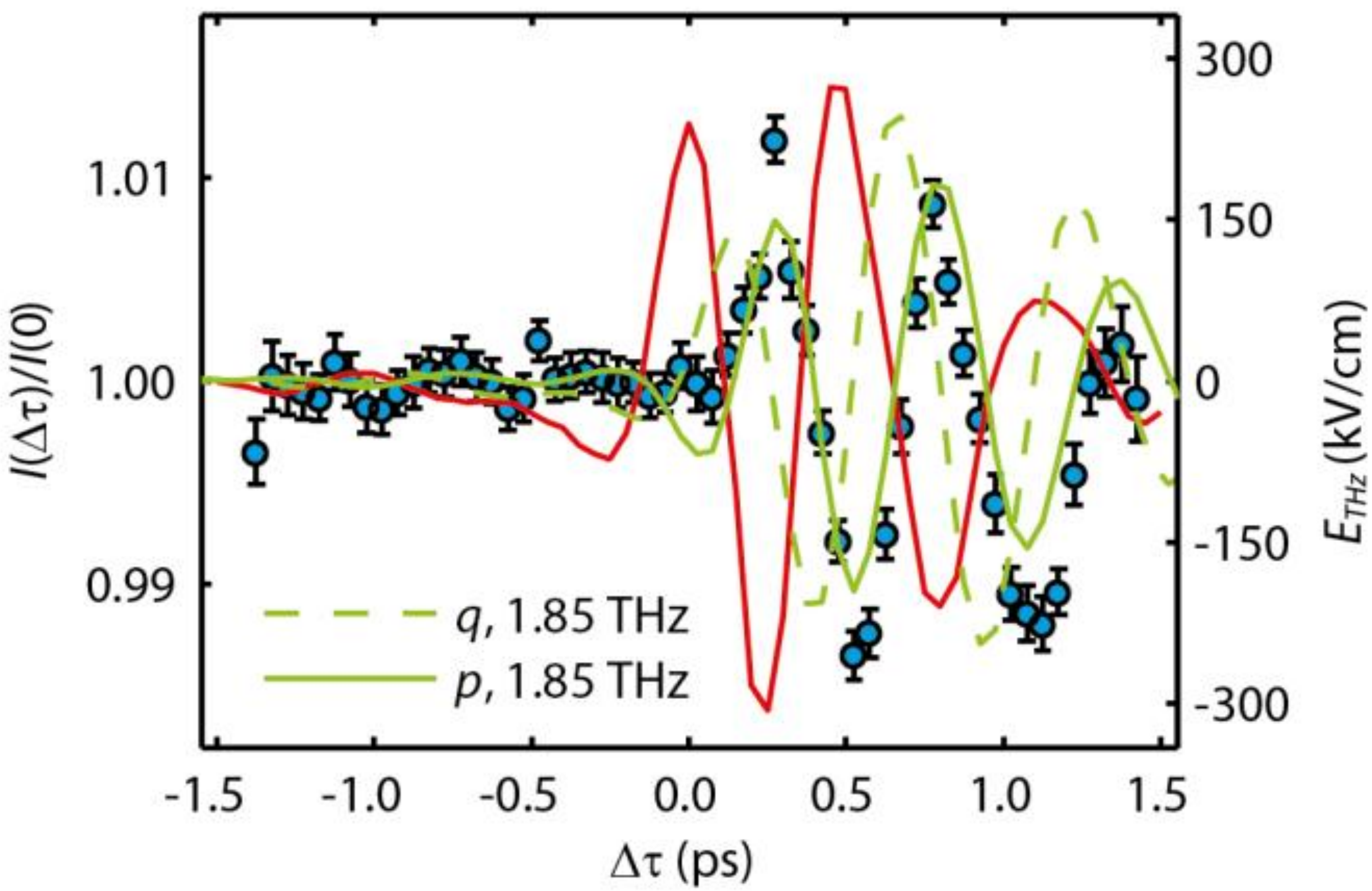
$$+ \sum_{<i,j>} \mathbf{d}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) - B_{\mathrm{biq}} \sum_{<i,j>}^{ab} (\mathbf{S}_i \cdot \mathbf{S}_j)^2$$



- Dynamics dominated by spin interaction
- One component of spin motion (in-plane) coupled to polarization
- No "kinetic energy": role of momentum played by another spin component (similar to precession)

[Michizuki & Nagaosa, Phys. Rev Lett. 105, 147202 (2010)]

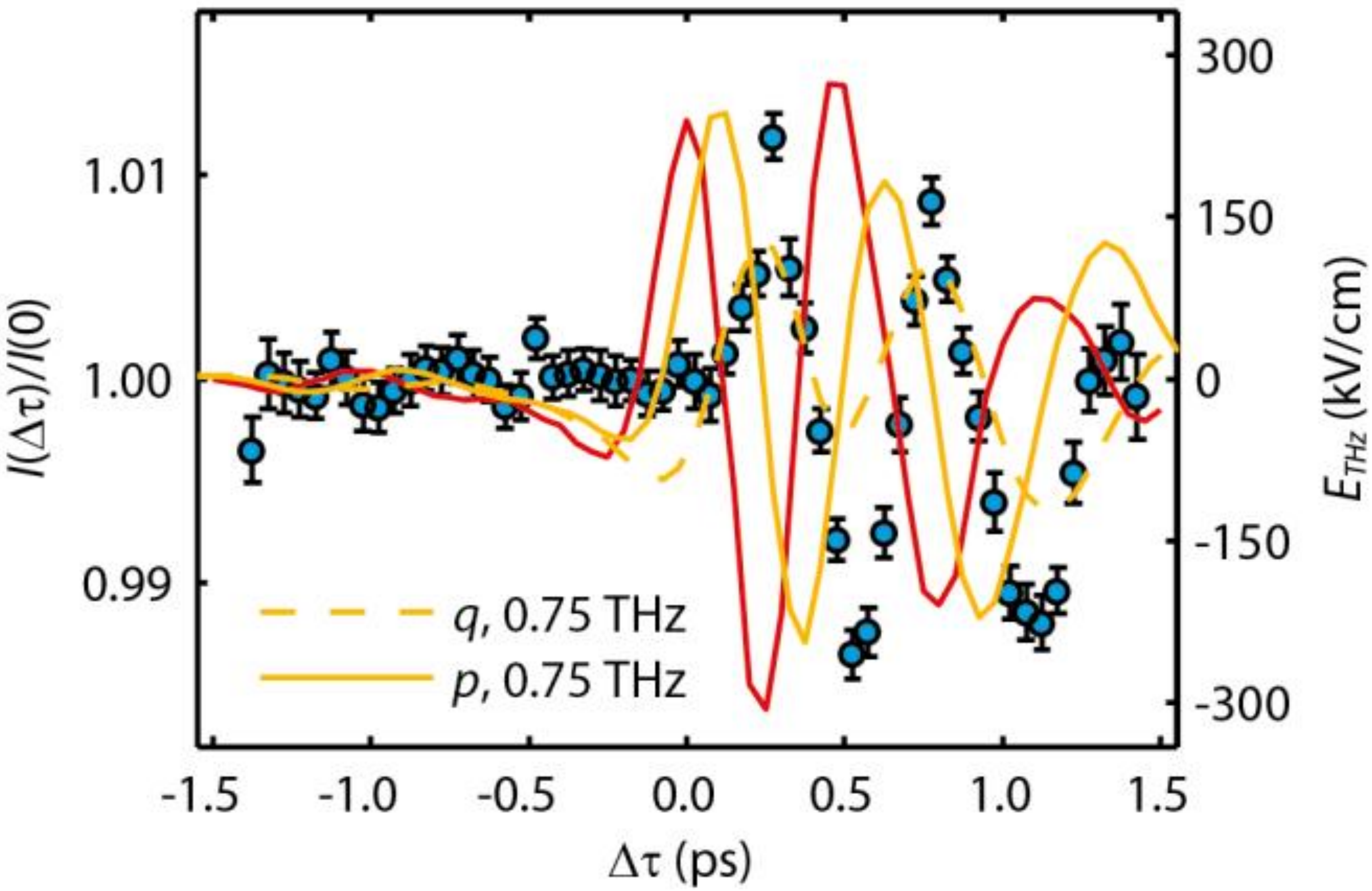
Analyzing the motion



- X-ray response corresponds to the "momentum" of a harmonic oscillator driven by E-field
- Rotation of spin planes fills this role

[T. Kubacka et al., Science **343**, 1333 (2014)]

Analyzing the motion

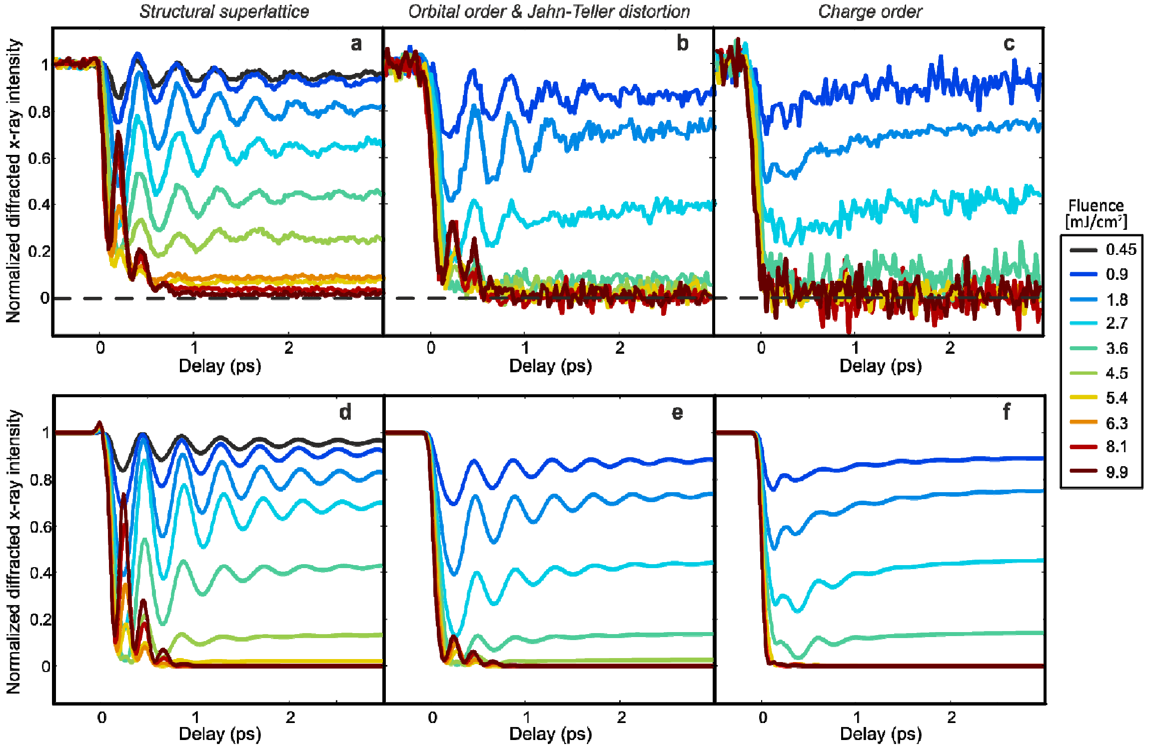


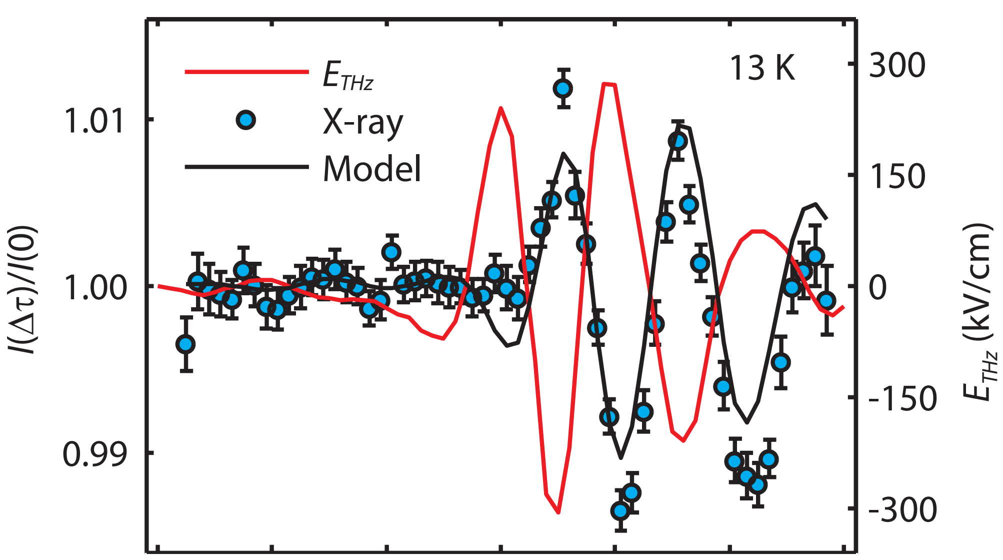
- Similar analysis assuming lower-frequency resonance is poorer match to data

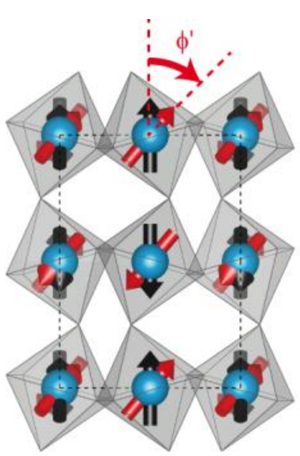
[T. Kubacka et al., Science **343**, 1333 (2014)]

Summary

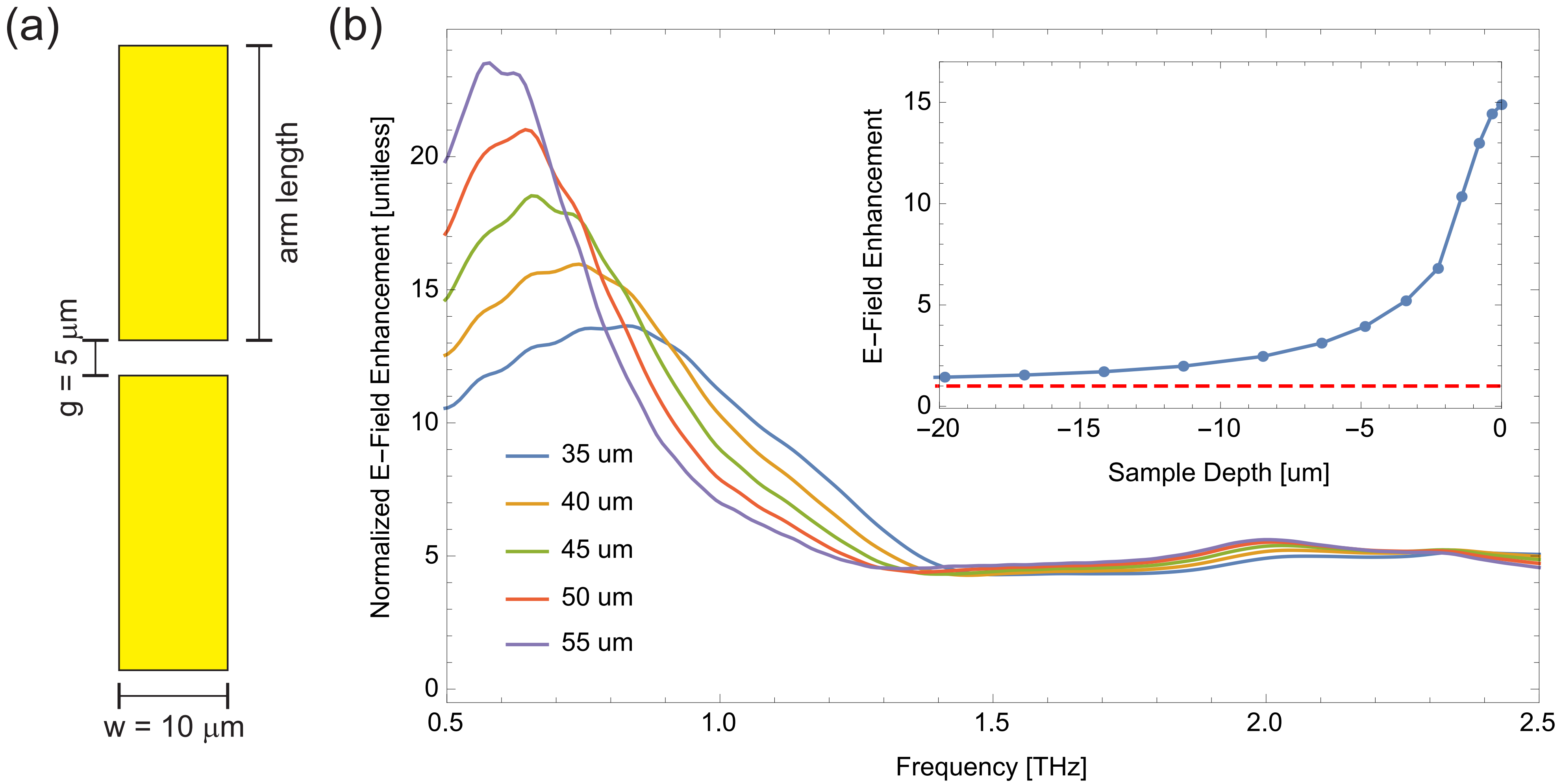
- Indirect control via e-ph coupling
  - Entropy in electron system couples to other DOFs
- Direct control with THz
  - Drive spin structure changes with E-field, switching expected at ~ 10 MV/cm







Outlook



[Calculations from M. Savoini]

- Way forward: micro-antennas
  - Enhancement factors of > 10 with large volumes

ETH UDG Group (January 2015)