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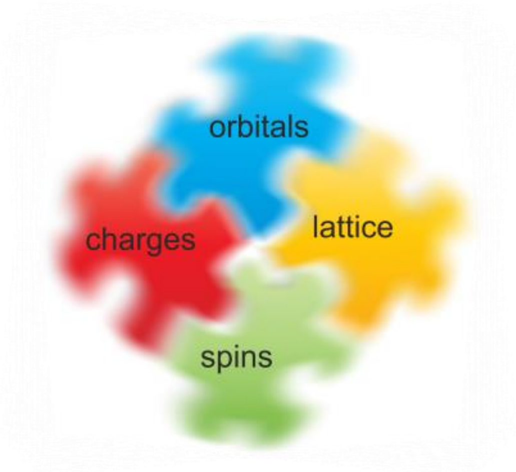
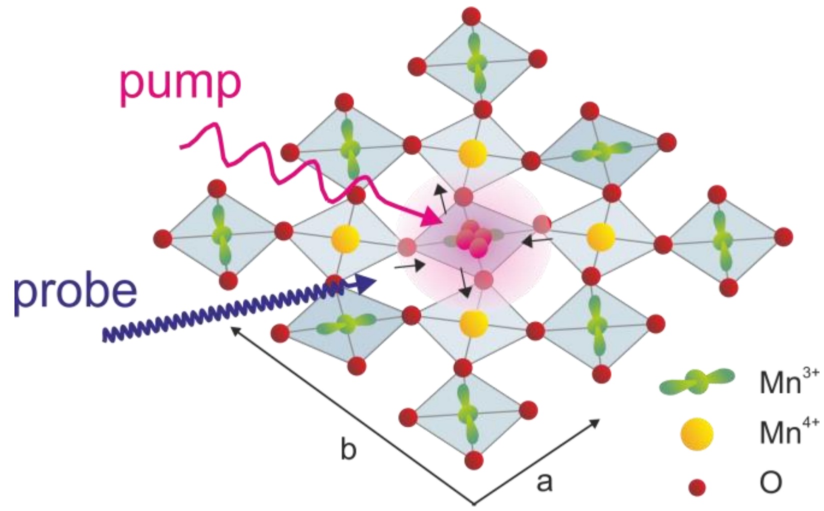
Paul Scherrer Institut
P. Beaud

Resonant X-ray diffraction to study ultrafast phase changes in solid matter

Motivation of ultrafast x-ray studies





Understand how materials work

→ Study dynamic interplay between structural and electronic degrees of freedom on their relevant time and length scales.

Electron dynamics:	Structural dynamics:	Spin dynamics:
electron correlations <1 fs	optical phonons: 10 - 500 fs	spin waves < 1ps
e-e scattering ~10 fs	acustic phonons: 1 - 100 ps	magnetization: ps-ns

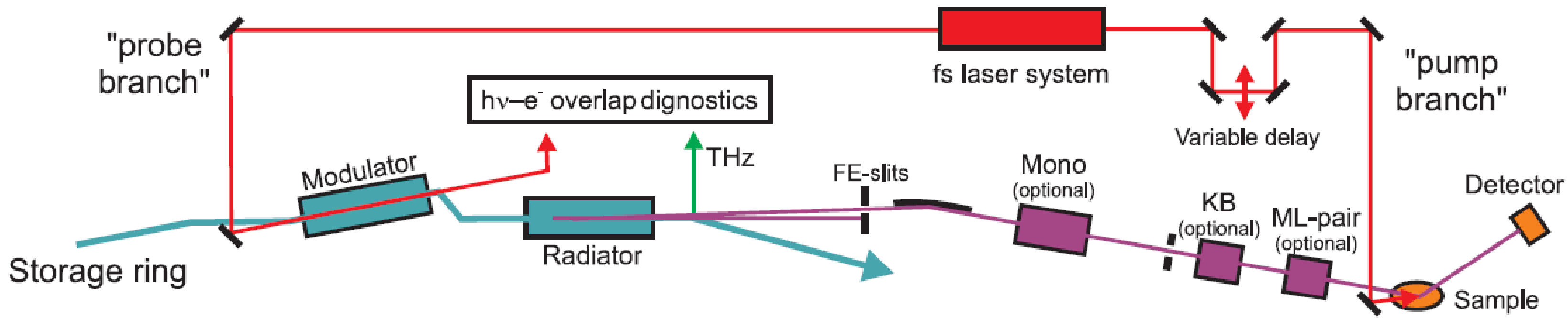
e-ph scattering ~1ps

Manipulation of material properties

→ access to highly excited electronic states

→ ultrafast phase transitions

Sources of tunable femtosecond x-rays



P. Beaud *et al.* PRL 99, 174801 (2007)

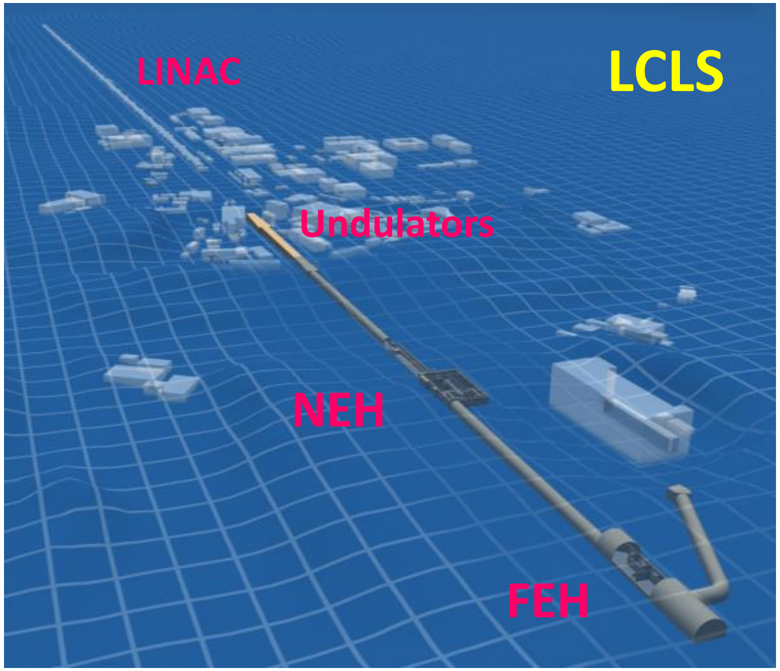
'Slicing' in storage rings

- Very low flux, 20-500 ph/p, 2kHz
- Time resolution ~160 fs

Free Electron Lasers

- High photon flux, ~10^{12} ph/p, 100Hz
- Time resolution <10 fs - 100 fs

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



Main experimental technique: X-ray diffraction – resonant XRD

Team

FEMTO (SLS)
Gerhard Ingold
Paul Beaud
Steven Johnson (-2010)
Faton Krasniqi (2004-2007)
Simon Mariager
Jeremy Johnson (
Ekaterina Vorobeva (PhD 2011)
Andrin Caviezel (PhD 2014)
Sebastian Grübel (PhD 2011 -)
Vincent Esposito (PhD 2014 -)
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ETHZ
Steven Johnson
Tim Huber
Teresa Kubacka
Andres Ferrer
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Christian Dornes
Lukas Huber
Martin Kubli
Matteo Savoini

EPFL **Chris Milne** (EPFL, now SwissFEL)
Jochen Rittmann (EPFL)

RESOXS Team (SLS)
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Elisabeth Botschafter

microXAS-beamline (SLS)
Daniel Grolimund
Camilla Borca

Science

Simple systems, coherent phonon dynamics (Bi, Te)

Johnson, PRL **100** 155501 (2008); Johnson, PRL **102** 175503 (2009);
Johnson, PRL **103** 205501 (2009); Johnson, PRB **87** 054301 (2013)

Ultrafast structural phase transition in manganites (FEMTO & LCLS)

P. Beaud, PRL **103** 155702 (2009); A. Caviezel, PRB **86**, 174105 (2012);
A. Caviezel et al. PRB **87**, 205104 (2013); P. Beaud, Nat. Mater. **13**, 923 (2014).

Charge density waves

E. Möhr-Vorobeva, PRL **107**, 036403 (2011); T. Huber, PRL **113**, 026401 (2014).
C. Laulhé, *Physica B*, online (2015).

Magneto-structural transitions (FeRh, Ni_2MnGa))

S. Mariager, PRL **108**, 087201 (2012); S. Mariager, PRB **90**, 161103(R) (2014).

Structural dynamics in $BaFe_2As_2$

L. Rettig *et al.* PRL **114**, 067402(2015).

Ultimate speed of antiferromagnetic phase transition in CuO (LCLS)

S. Johnson, PRL **108**, 037203 (2012).

Electro-magnon in a multiferroic using intense THz fields (LCLS)

T. Kubacka, Science **343**, 1333 (2014).

PRL 114, 067402 (2015) PHYSICAL REVIEW LETTERS week ending 13 FEBRUARY 2015

Ultrafast Structural Dynamics of the Fe-Pnictide Parent Compound $BaFe_2As_2$

L. Rettig,[1,*] S. O. Mariager,[1] A. Ferrer,[2,1] S. Grübel,[1] J. A. Johnson,[1] J. Rittmann,[3,1] T. Wolf,[4] S. L. Johnson,[2] G. Ingold,[1,5] P. Beaud,[1,5] and U. Staub[1]
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[2]*Institute for Quantum Electronics, Physics Department, ETH Zürich, CH-8093 Zürich, Switzerland*
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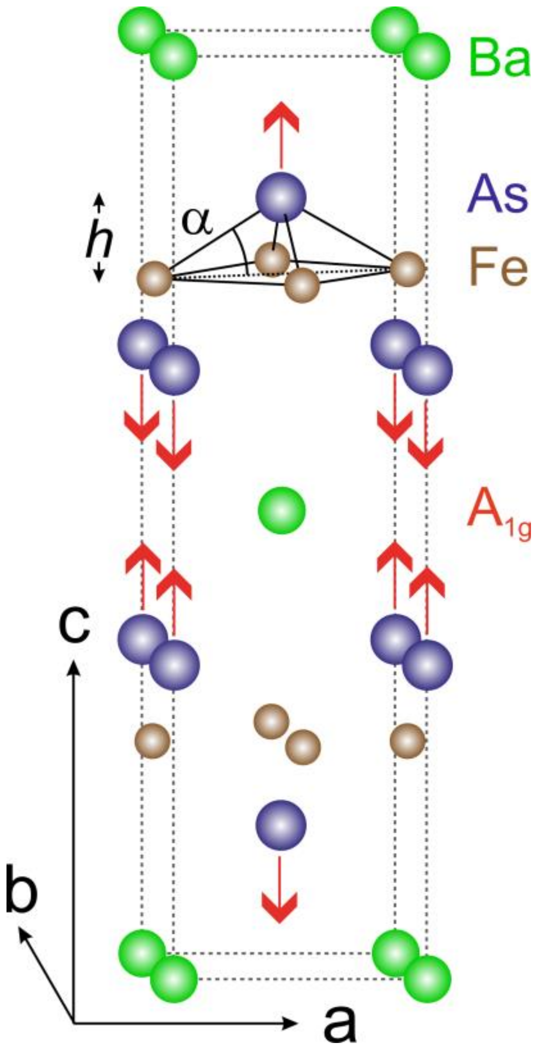
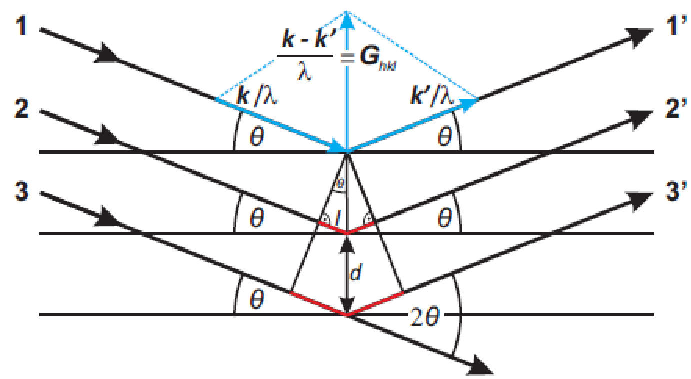
(Received 3 November 2014; published 13 February 2015)



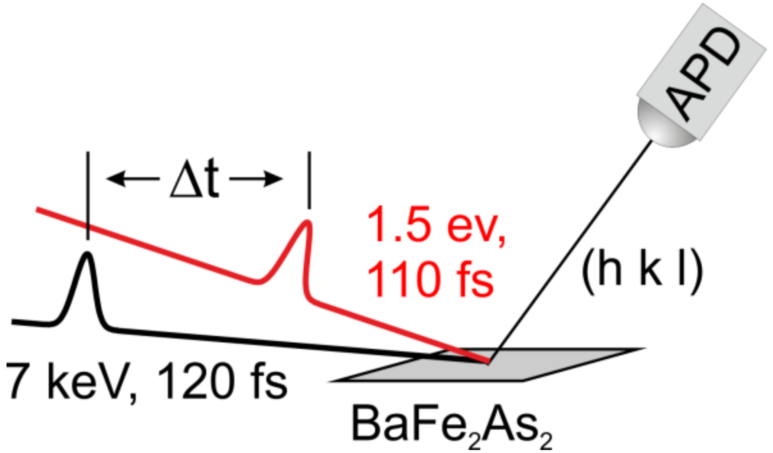
- Ultrafast displacive excitation of coherent A_{1g} phonon (5.5THz).
- Tetrahedra angle α important tuning parameter for superconductivity and Fe magnetic moments.
- Coherent excitation of A_{1g} mode:
  Transient resurrection of SDW ordering above T_N proposed to interprate THz probe experiment
  (K.W. Kim *et al.*, Nat. Mater. 11, 497, 2012).

Time-resolved x-ray diffraction

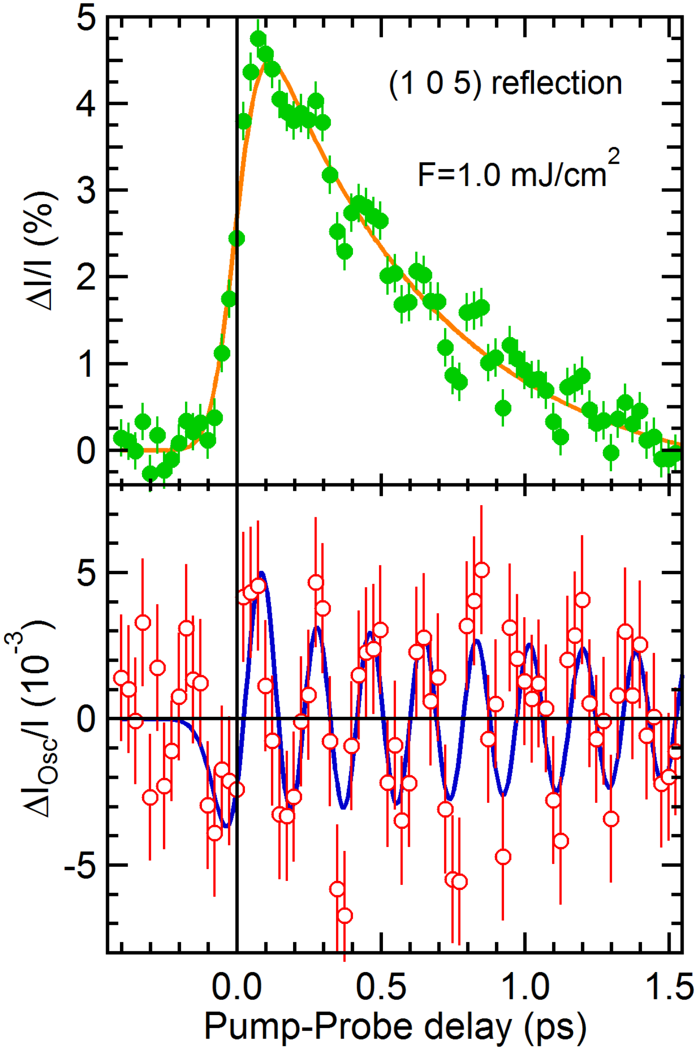
- Time-resolved x-ray Bragg diffraction to determine transient crystal structure
- Optical pump laser:
  - Ti:Sapphire
  - 800nm, ~100 fs
- X-ray probe:
  - Femtosecond sliced beam at FEMTO beamline (microXAS)
  - 7 keV, ~3 x 10^5 photons/sec
  - ~ 100 fs pulse duration
- Overall time-resolution ~160 fs
- Grazing incidence of x-rays ~0.45° to match penetration depth of optical pump laser
- Diffracted x-rays detected with Pilatus pixel detector and avalanche photodiode (APD)

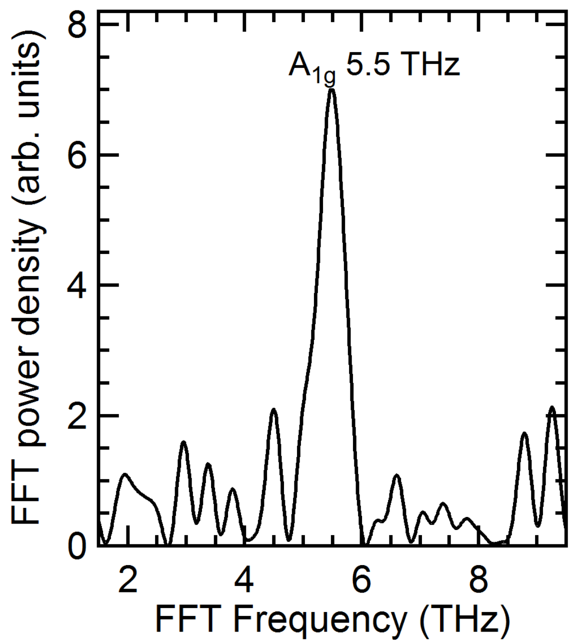


$$I(\mathbf{q}) \propto |F(\mathbf{q})|^2 = \sum_{j=1}^{N} f^{q} e^{-i\mathbf{G_q r_j}}$$



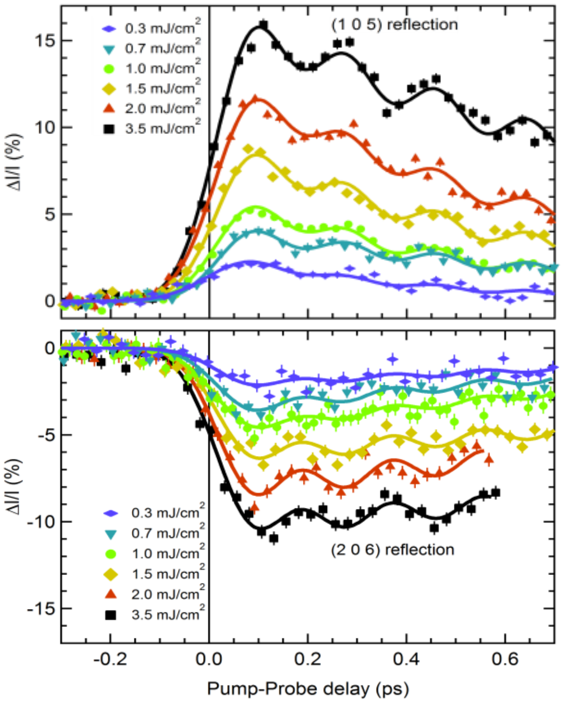
Displacive excitation of A_{1g} mode

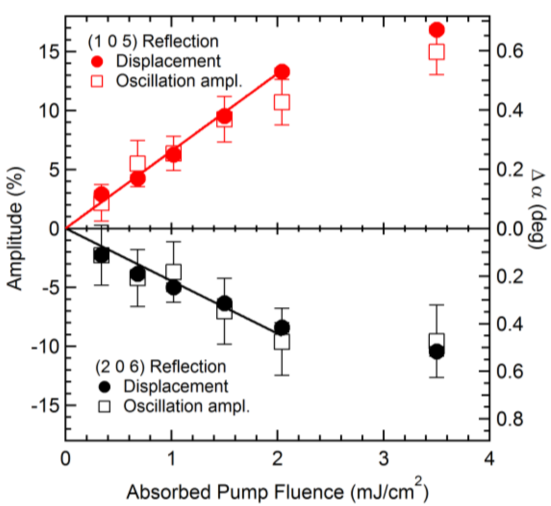




- Step-like increase of intensity within the time-resolution
- Coherent oscillations at 5.5 THz, A_{1g} phonon mode
- Cosine-like oscillation phase agrees with displacive excitation

Fluence dependence





- Linear behavior up to ~2 mJ/cm^2
- Saturation effects for fluence >3 mJ/cm^2
- Determination of As oscillation amplitude by structure factor calculations.
- Displacement towards larger α
- Maximal displacement amplitude of >0.6 pm, >5% of Fe-As distance

Comparison to trARPES yields

- A_{1g} electron-phonon **deformation potential**

$$\Delta\mu/\Delta z = -(1.0 - 1.5)\,\mathrm{eV}/\mathrm{\mathring{A}}$$

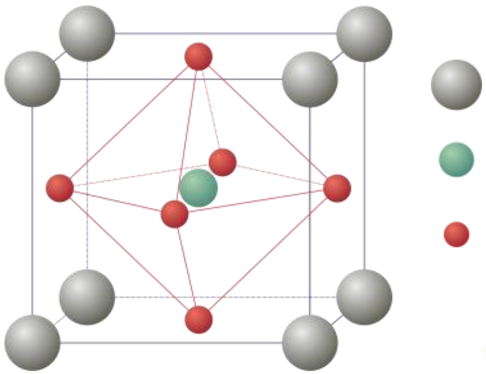
- **Electron-phonon coupling constant** ($\lambda_{tot} \leq 0.35$)

$$\lambda_{A_{1g}} = 0.05 - 0.30$$

- Displacement towards *larger* $\alpha \rightarrow$ transient *increase* of Fe magnetic moments.
- Increase too small to explain resurrection of SDW phase.

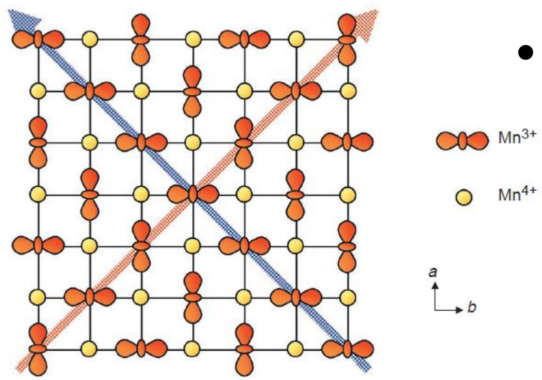
L. Rettig *et al.* PRL **114**, 067402 (2009);

Manganese Oxides: $R_{1-x}A_xMnO_3$



R: 3^+ rare earths
A: 2^+ cation
Mn: 3^+,4^+
O: 2^- anions

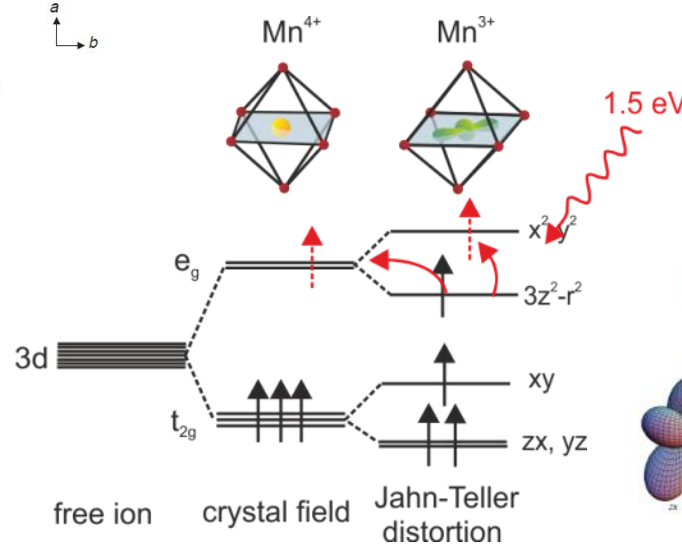
- Transition metal oxides, with perovskite structure.
- Prototype of strongly correlated electron system.
- Exhibit colossal magnetoresistance & insulator-metal transitions.
- Many types of ordering patterns.

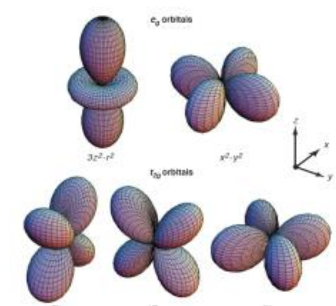


Tokura & Nagaosa, Science (2000)

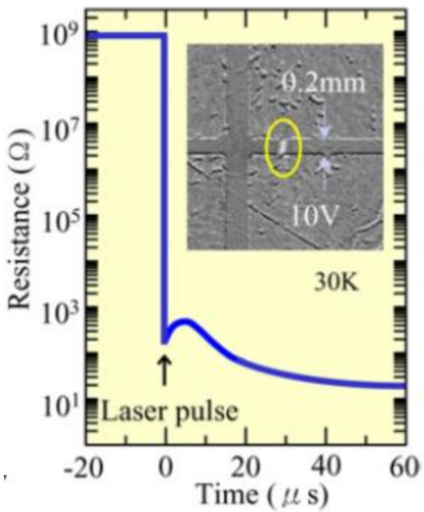
Ground state (x ≈ 0.5)

- CE-type charge & orbital order
  Goodenough, Phys. Rev. 100, 555 (1955).
- Jahn-Teller distortion at Mn^{3+} sites leading to a doubling of the unit cell.
- Strong electron-phonon coupling
  → sensitive to optical excitation.



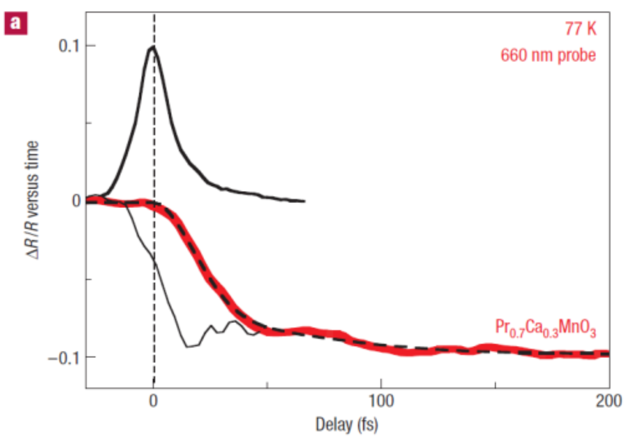


Ultrafast insulator-metal transition



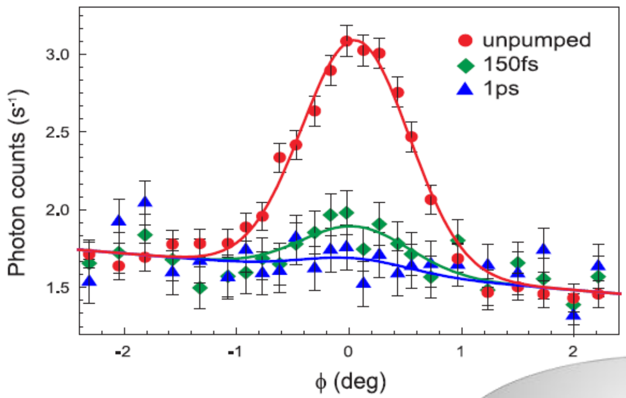
M. Fiebig et al., Science 280, 1925 (1998)

Optical reflectivity

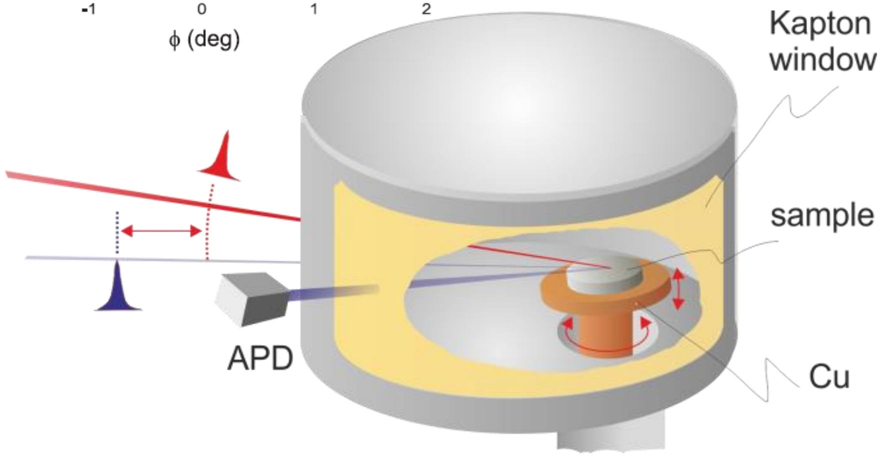


Polli et al., Nat. Mater. 6, 643 (2007)

XRD experiment at SLS slicing source



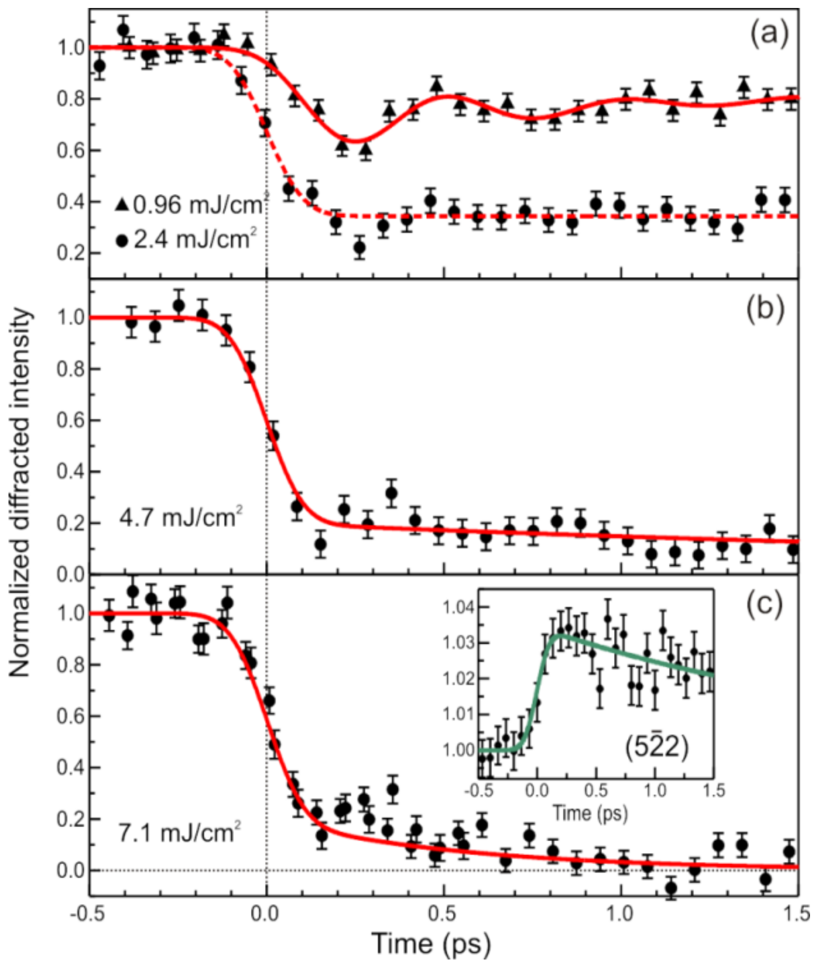
(5 -5/2 2)
superlattice peak



- At high fluence dissapearance of superlattice peak
- Evidence of ultrafast structural transition driven by melting of charge and orbital order

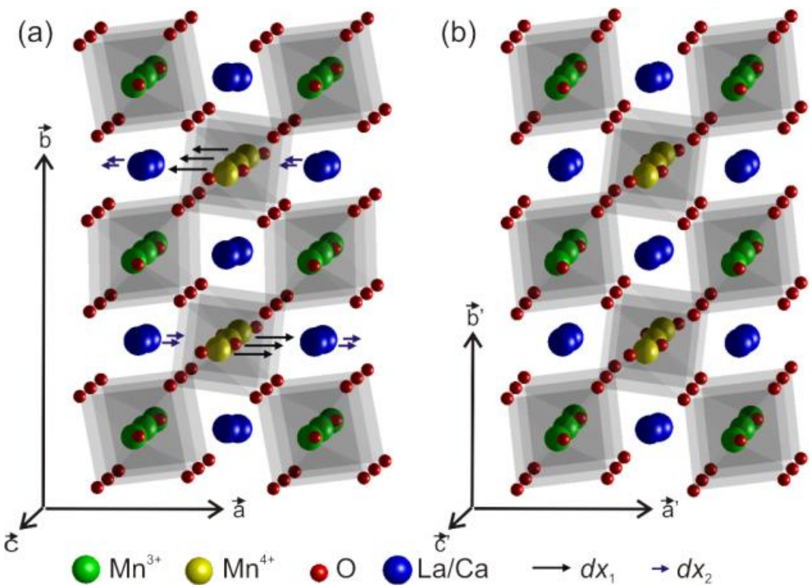
Beaud *et al.* PRL 103 155702 (2009);

Time evolution of phase transition



Low fluence

Displacive excitation of coherent optical phonon.



Discrepancy:

Phonon assigned *to rare earth cation* motion, but induced coherent phonon must include motion of Mn^{4+} sites.

A. Caviezel *et al.* PRB 86, 174105 (2012).
A. Caviezel *et al.* PRB 87, 205104 (2013).

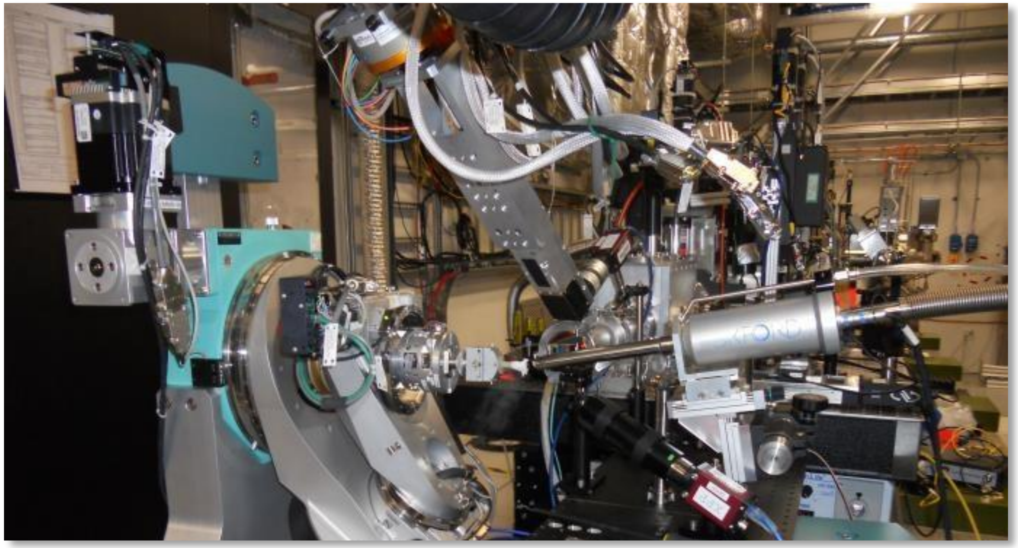
FEL experiment (XPP instrument at LCLS)

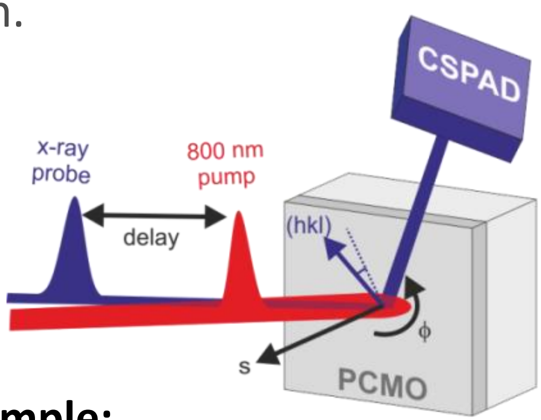
Questions:

1. Understand different time scales and role of phonon in structural transition.
2. Time scales of CO&OO melting?
3. How do electronic states modulate in the presence of a phonon?

→ Measure orbital and charge order dynamics with resonant diffraction.

→ requires higher photon flux & better time resolution.

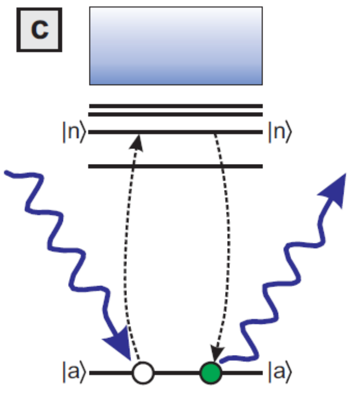




Sample:

- $Pr_{0.5}Ca_{0.5}MnO_3$,
- thin film (d ≈ 40 nm), $(011)_c$-orientation
- Sample cooled to 100 K (nitrogen cryo blower)

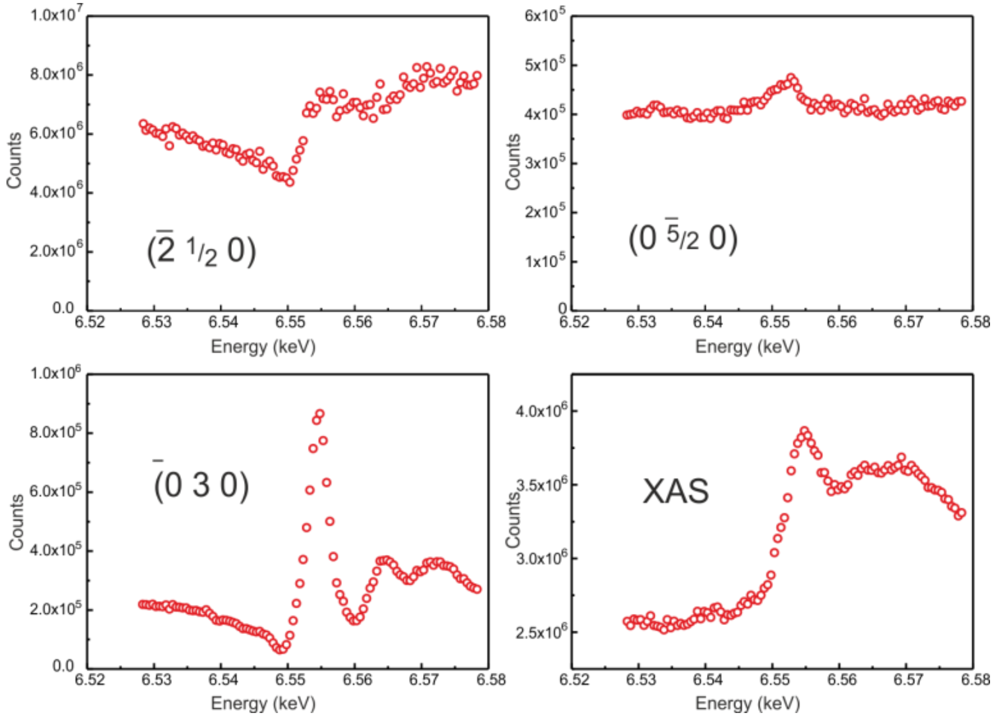
Resonant x-ray diffraction



Resonant scattering

Combines diffraction and element specific absorption, unique site specific probe.

Measures charge, orbital & magnetic order.



Resonant XRD at Mn K edge

Possible at Mn *K* edge due to hybridization of Mn 3d and O 2p states

Zimmermann et al. PRL 83, 4872,1999

(h k/2 0) → structural distortion
(0 k/2 0) → orbital order & Jahn-Teller
(0 k 0) → charge order

Static experiment at 100 K (SLS Material Science beamline)

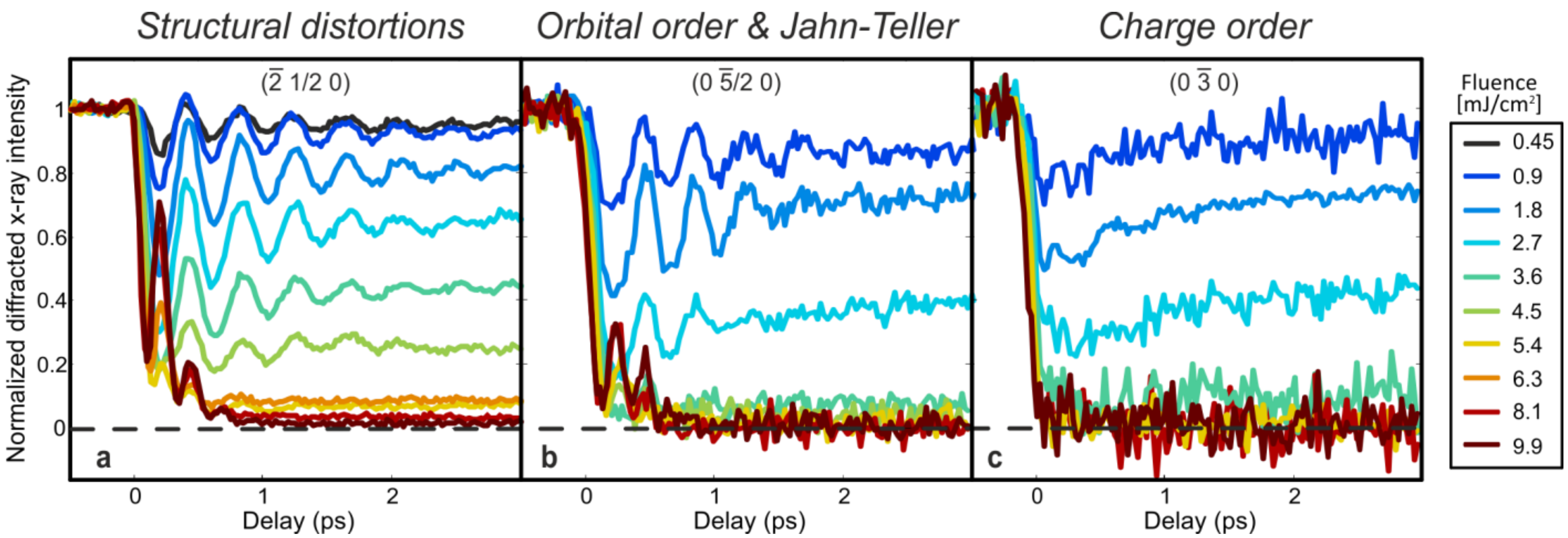
nature materials

LETTERS

PUBLISHED ONLINE: 3 AUGUST 2014 | DOI: 10.1038/NMAT4046

A time-dependent order parameter for ultrafast photoinduced phase transitions

P. Beaud[1,2]*, A. Caviezel[1], S. O. Mariager[1], L. Rettig[1], G. Ingold[1,2], C. Dornes[3], S-W. Huang[1], J. A. Johnson[1], M. Radovic[1,2], T. Huber[3], T. Kubacka[3], A. Ferrer[1,3], H. T. Lemke[4], M. Chollet[4], D. Zhu[4], J. M. Glownia[4], M. Sikorski[4], A. Robert[4], H. Wadati[5,6], M. Nakamura[7], M. Kawasaki[5,7], Y. Tokura[5,7], S. L. Johnson[3] and U. Staub[1]



- No threshold behavior,.
- Atoms overshoot at high fluence.

- Ultrafast onset of structural and electronic transition.
- Partial recovery of charge order within ~2-3 ps.

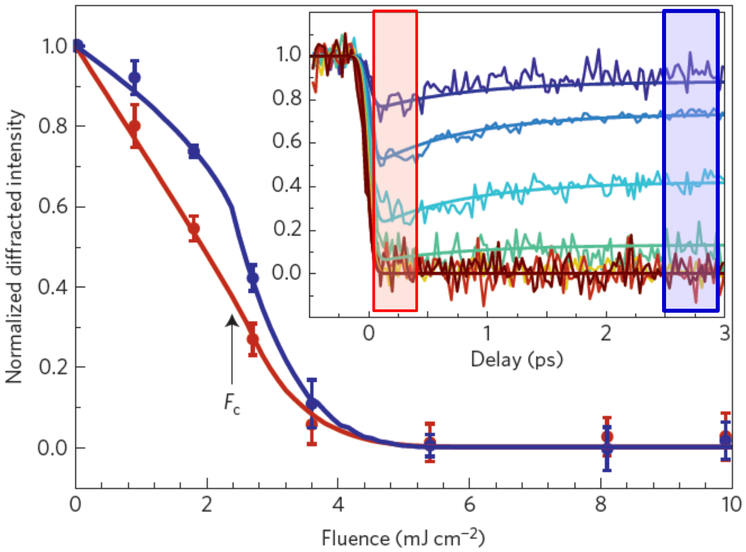
Order parameter

- Structure factor of a superlattice reflection is direct measure of the order parameter (η):

$$I^{0\bar{3}0} = \left|F^{0\bar{3}0}\right|^2 = |\eta|^2$$

- Initially intensity drops linearly with excitation density, transition occurs for $n_0 > n_c$

$$\eta_0 = \sqrt{1 - n_0/n_c}$$



- After electron-lattice thermalization (τ≈1ps):

$$\eta_{th} = (1 - n_0/n_c)^{\gamma}$$

Time dependent order parameter

$$\boldsymbol{\eta(t) = \sqrt{1 - n(t)/n_c}}$$

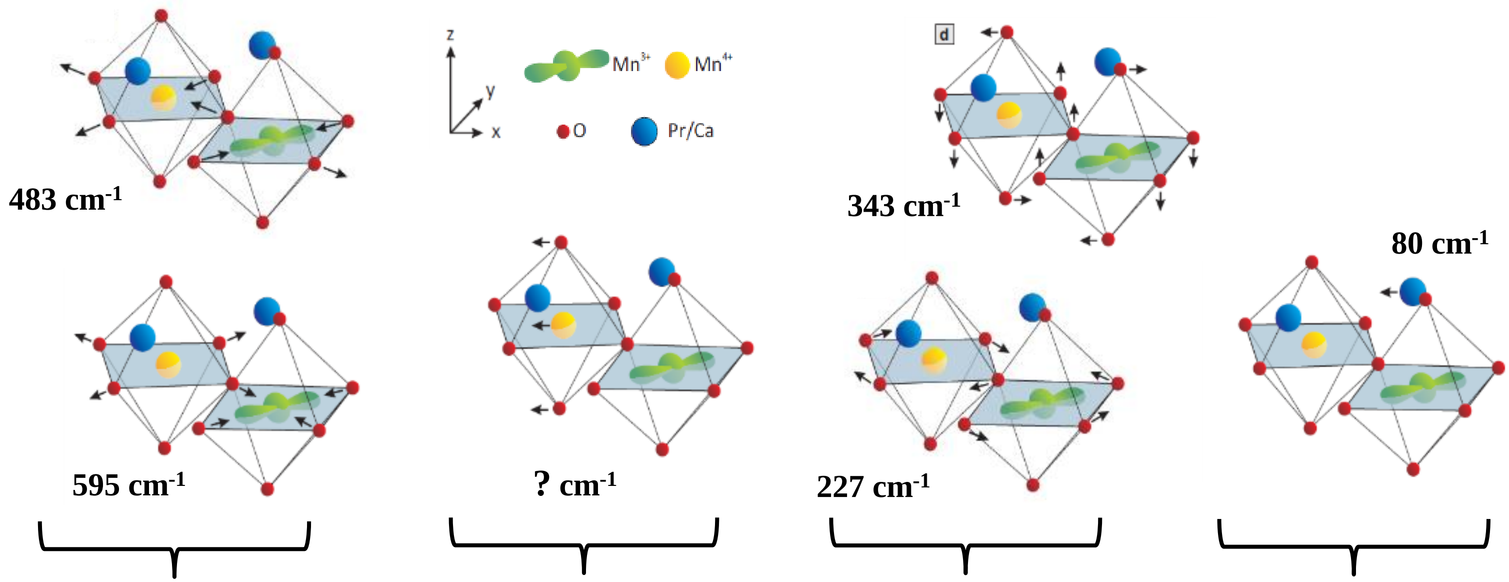
- Striking ressemblence to $\sqrt{1 - T/T_c}$ the Landau result for 2nd order phase transitions.

- Mean Field Theory including long range correlations: $(1 - T/T_c)^{\beta}$, to $\sqrt{1 - T/T_c}$

(**Universality:** critical exponent β depends on dimension and symmetry, but not on microscopic details of the system)

Lattice dynamics

- Unit cell with 40 atoms, multiple coordinates.
- Simplified model of atomic motion to derive time dependent atomic potential:

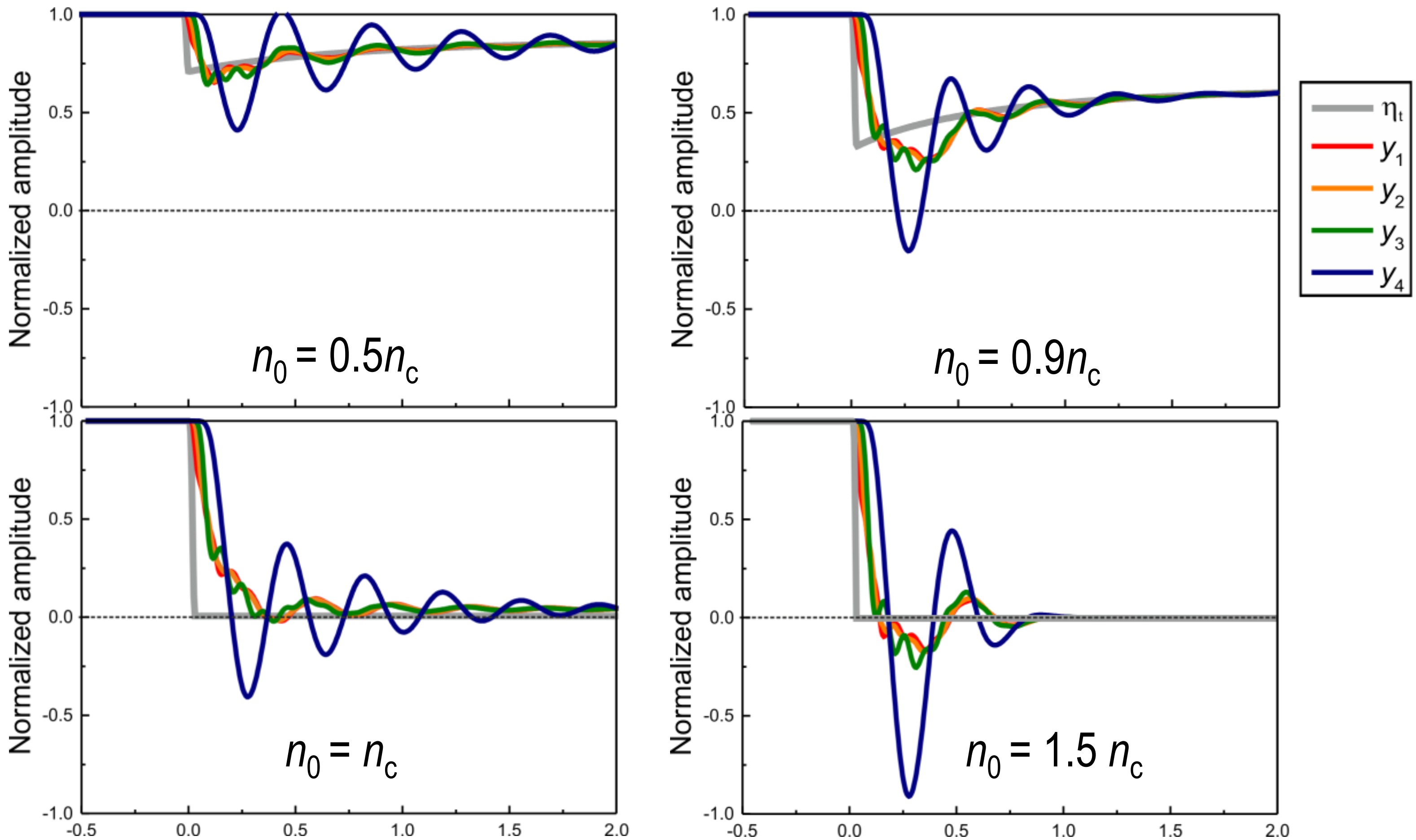


Jahn-Teller | Mn^{4+} translation | O_6 rotations | Pr/Ca translation

$$V(t)=V_0+\underbrace{a(n-n_c)\,y_1^{\,2}+b\,y_1^{\,4}}_{\text{Driven 'mode'}}+\underbrace{c_{21}(y_2-y_1)^2+c_{32}(y_3-y_2)^2+c_{43}(y_4-y_3)^2}_{\text{Chain of coupled 'modes'}}$$

Ultrafast collapse of Jahn-Teller distortion → chain reaction rearranging the unit cell.

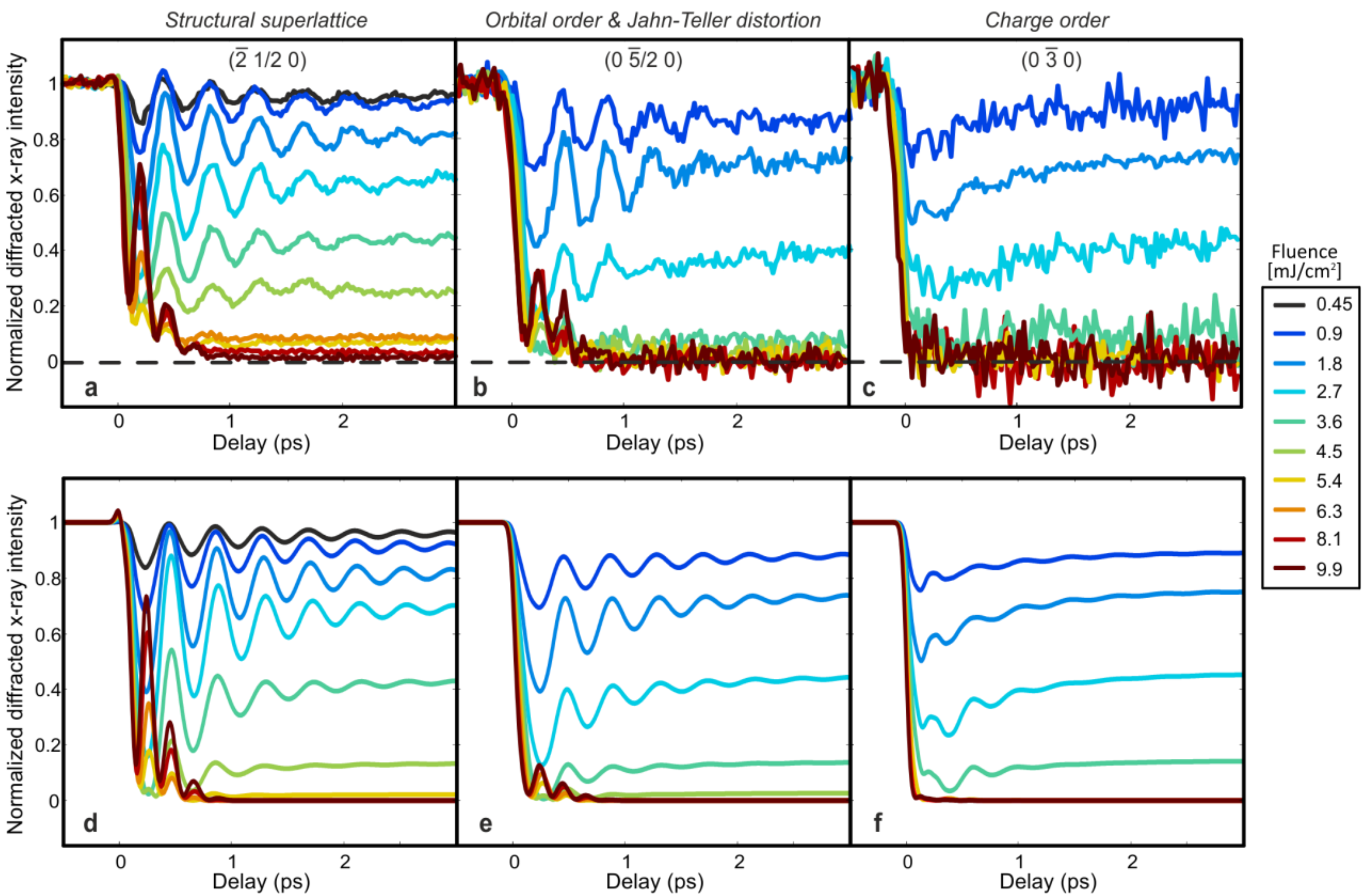
Time evolution



- Fast loss of long range order, partially recovers within 2-3 ps for $n_0 < n_c$.
- Strong coupling → lowest frequency in chain dominates late dynamics.
- Atoms are slower, overshoot → frequency doubling in diffracted signal.

Simulation (structural response only)

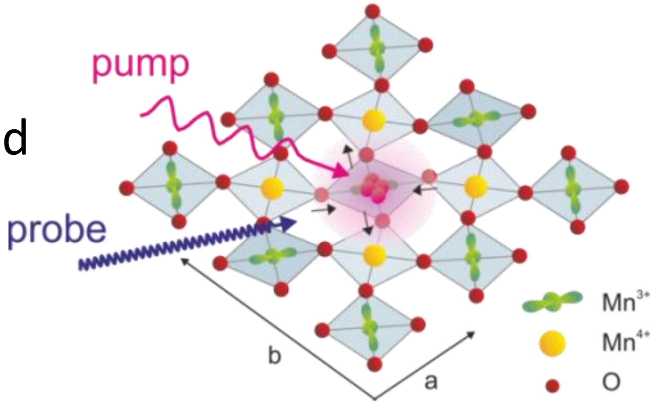
Beaud et al., Nat. Mater. **13**, 923 (2014).



Fairly simple description relying on a single time-dependent order parameter captures the essential dynamics down to ~80 fs.

Summary & outlook

- Femtosecond XRD useful tool to study correlated materials.
- Resonant XRD only possible at FELs.
- Time dependent order parameter concept proposed to describe ultrafast phase transitions.



$$\boldsymbol{\eta(t) = \sqrt{1 - n(t)/n_c}}$$

- Universal description of phase transitions in the time domain?

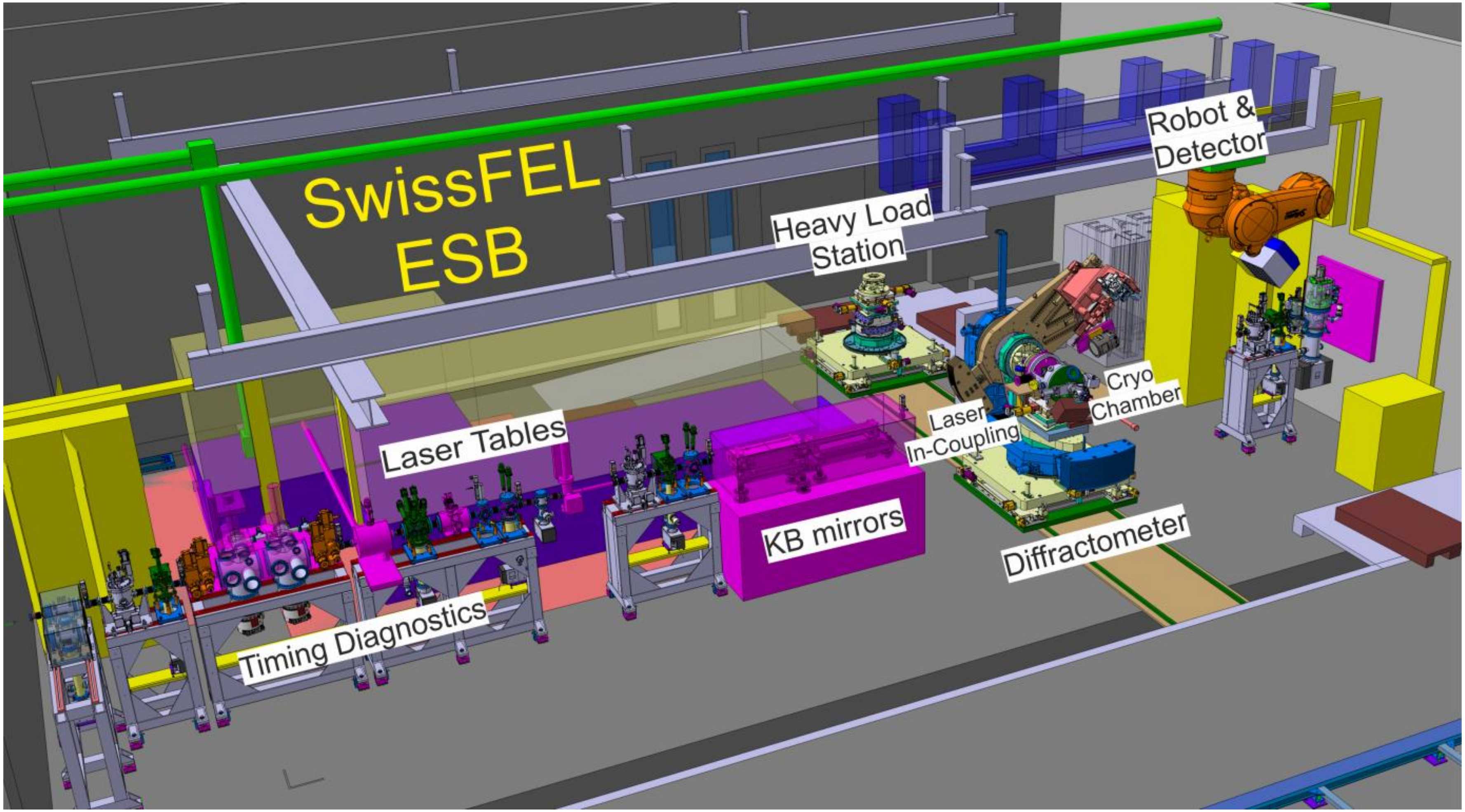
- Our wish list for the future includes:

  → Improved time resolution
  → Polarization control & analysis
  → Controlled sample environment (temperature, pressure, magnetic fields …)
  → **Theory**

- At SwissFEL we currently build an instrument dedicated to dynamic studies on strongly correlated electron systems.

ESB Instrument Layout

Gerhard Ingold, Jochen Rittmann, Paul Beaud



1. **Dedicated diffractometer** for resonant XRD (with polarization control & analysis).
2. **Flexible station** for diverse x-ray scattering geometries (with 16M pixel detector).

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1. Diffraction endstation

must

Dedicated diffractomter for dynamic studies on strongly correlated electron system

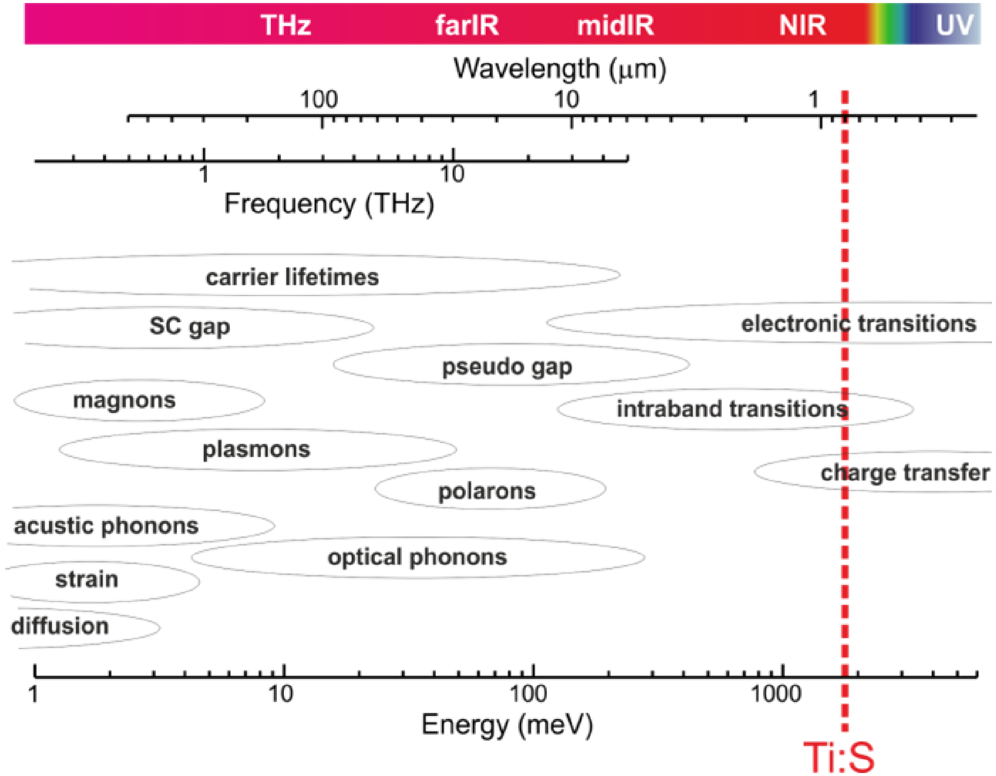
- Diffractometer arm with polarization analysis
- Control of x-ray polarization
- Controlled sample environment (low T, high B, …)
- Extension to include RIXS (phase II)

Selective excitations

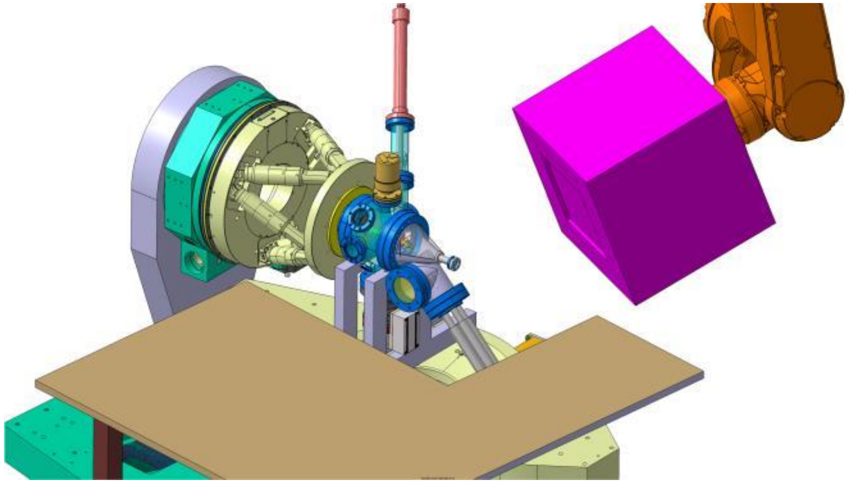
Laser system covering UV to THz:

1 – 100 mJ/cm^2

10 - 100 fs or ‘ps-narrowband’



2. General purpose station



Open for various other techniques & user setups

- Heavy load manipulator
- 16M 2-D pixel detector mounted on a robot arm

Techniques - diffuse scattering, SAXS, WAXS, XAS, nonlinear x-ray pump, …

Science - Condensed matter
- Planetary science (matter under high pressure)
- Crystallography (Bio), crystals on solid support

Thank you for your attention!