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An order parameter concept for ultrafast phase transitions

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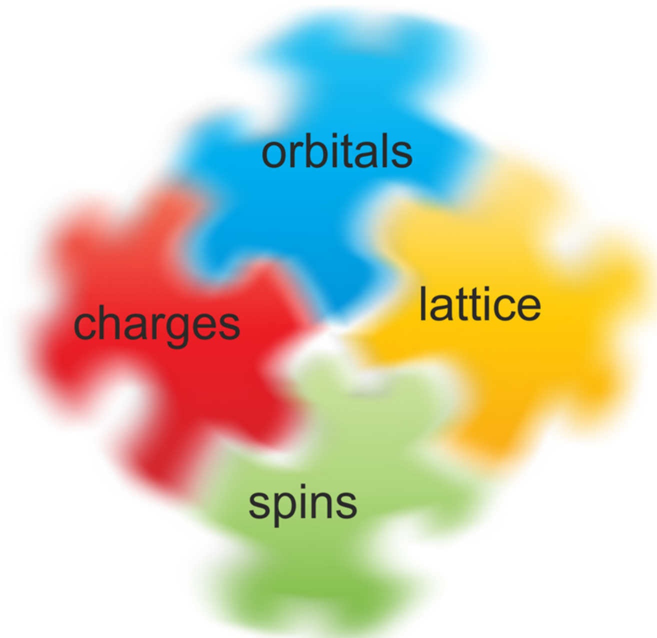
Strongly correlated electron systems

Dynamic interplay between structural
and electronic degrees of freedom.

Complex phase diagrams with exciting properties,
sensitive to external stimuli (*T*, *p*, *B*, *E*, h*ν* …).



Motivation of ultrafast x-ray studies

- Study correlations on their relevant time and length scales

- Manipulation of material properties → ultrafast phase transitions

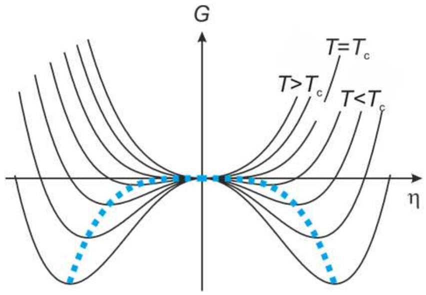
Continuous phase transitions

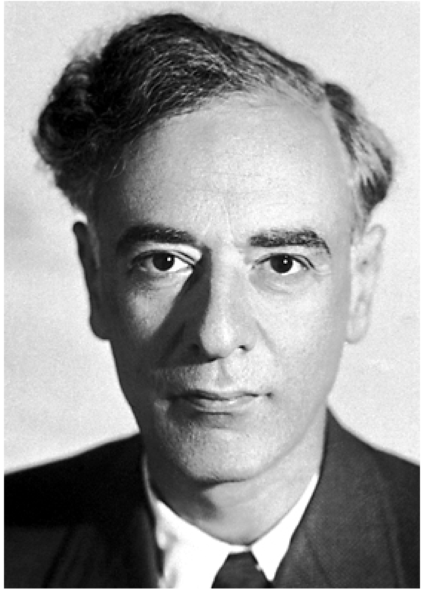
Order parameter concept introduced by Landau (1937):

- η is a measure of symmetry breaking in the equilibrium state.
- phase transition characterized by change from η=0 to η≠0 as a function of thermodynamic state variable.

$$G(\eta) = G_0 + a(T - T_c)\eta^2 + b\eta^4$$

$$\eta \propto \sqrt{1 - T/T_c}$$





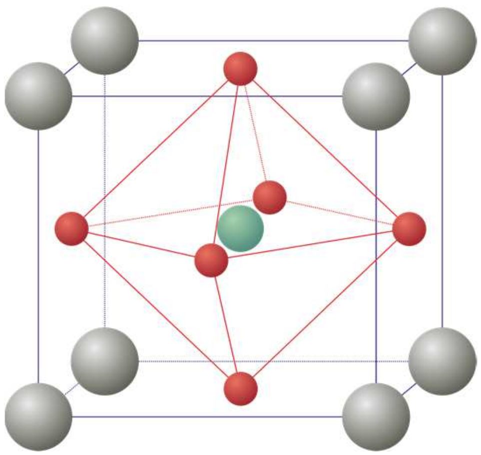
Including long range correlations → $\eta \propto (1 - \alpha/\alpha_c)^\beta$

- Universality: critical exponents depend on dimension and symmetry, but not on microscopic details of the system.
- Applications in Cosmology, Biology, Economy …

Thermodynamic concept, breaks down in non-equilibrium.

How to describe ultrafast phase transitions?

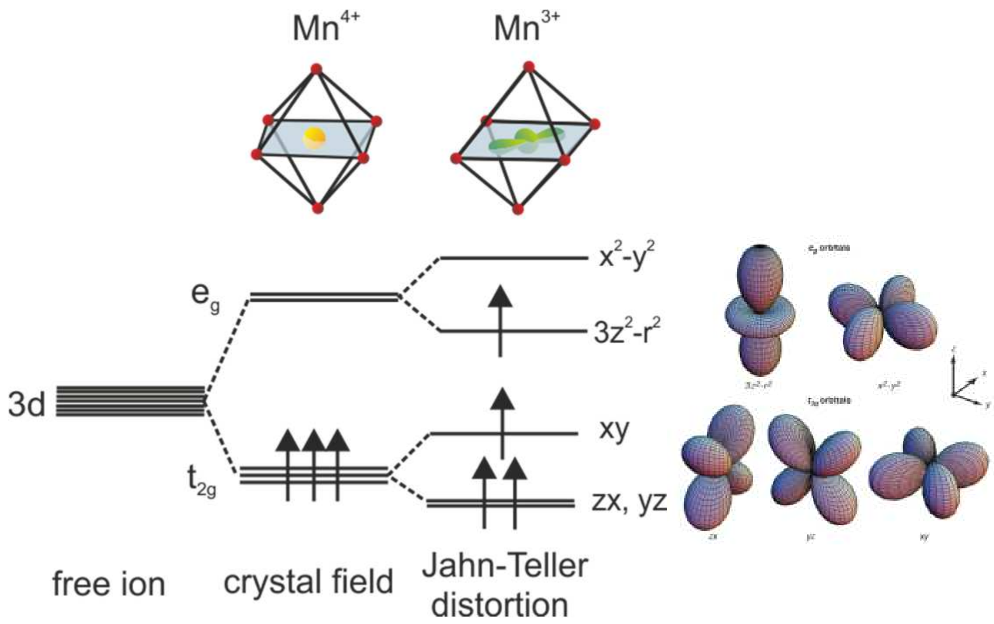
Manganese Oxides: $R_{1-x}A_xMnO_3$



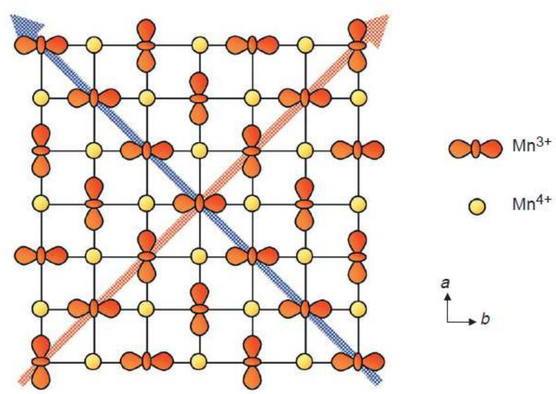
R: 3^+ cation as rare earths (La, Pr,…)
A: 2^+ cation as Ca, Na, Sr
Mn: 3^+,4^+ cations
O: 2^- anions

- Transition metal oxides with perovskite structure, prototype of strongly correlated electron systems
- Exhibit colossal magnetoresistance & insulator-metal transitions.
- Many types of ordering patterns
  - Changes of structural symmetry
  - Modulation of Mn valence
  - Modulation of orientation of occupied e_g orbitals in Mn^{3+}
  - Magnetic order

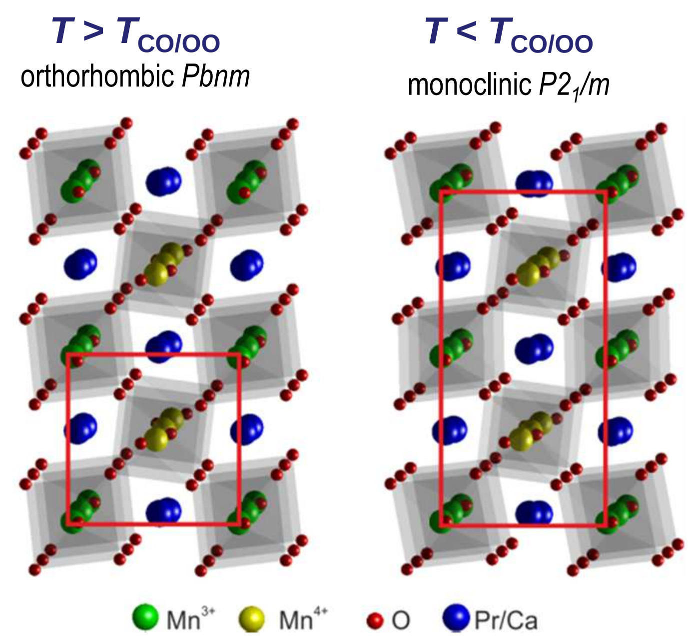
Ground state ($x \approx 0.5$)



- 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.

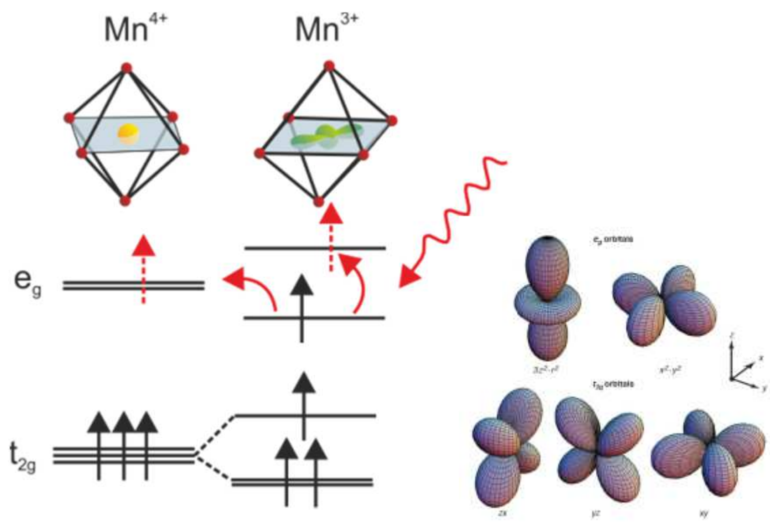


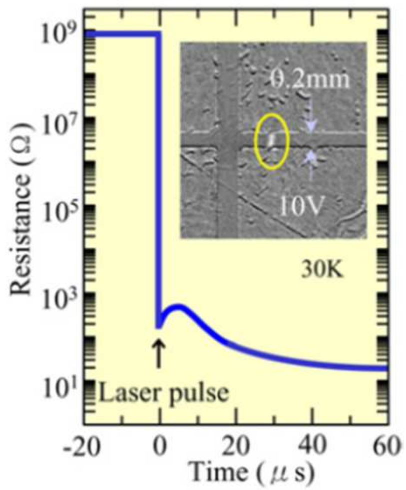
Tokura & Nagaosa, Science (2000)



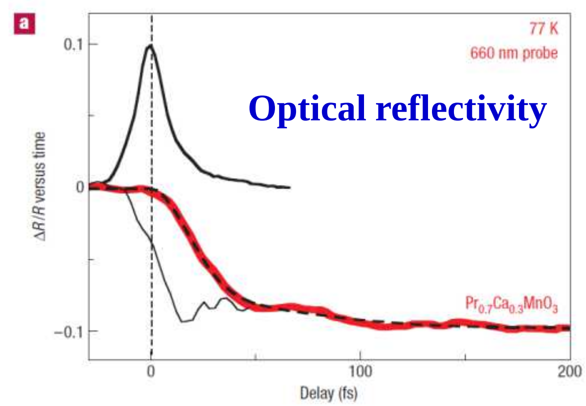
Photoinduced phase transition

Excitation of Mn^{3+}/Mn^{4+}system drives insulator-to-metal transition:



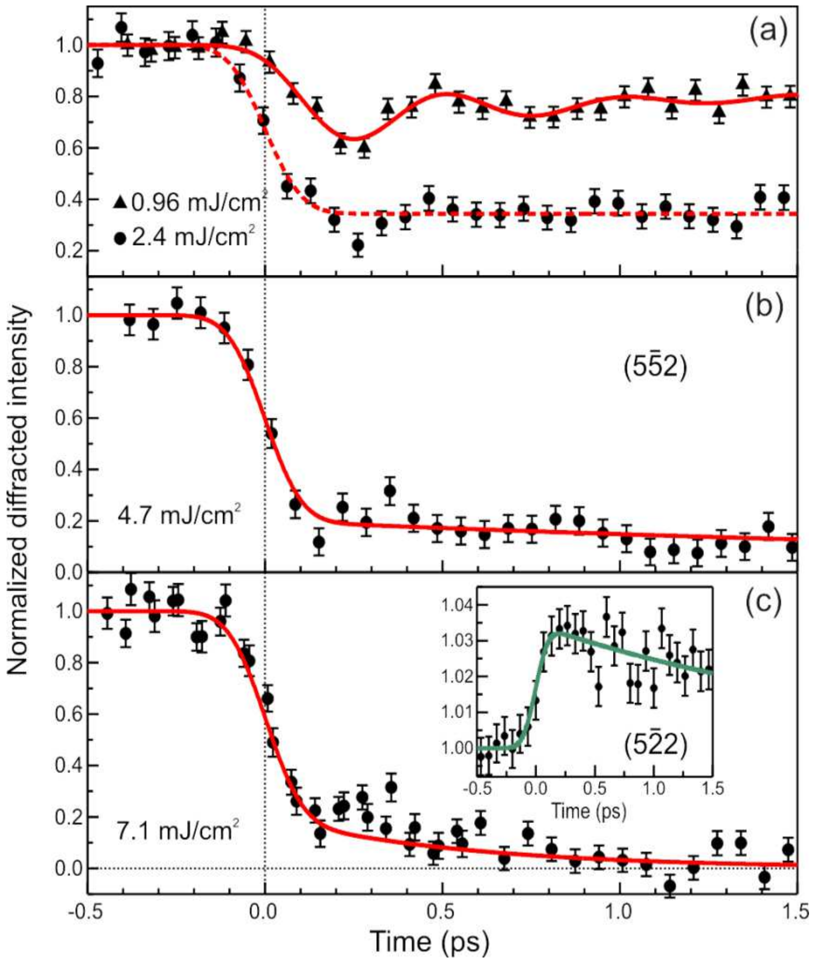


Fiebig et al., Science 280, 1925 (1998)



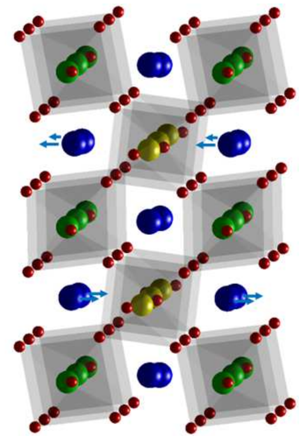
Polli et al., Nat. Mater. 6, 643 (2007)

Ultrafast structural phase transition (LCMO)



Low fluence

Displacive excitation of coherent optical phonon.



High fluence

Dissapearance of SL peak within 1 ps

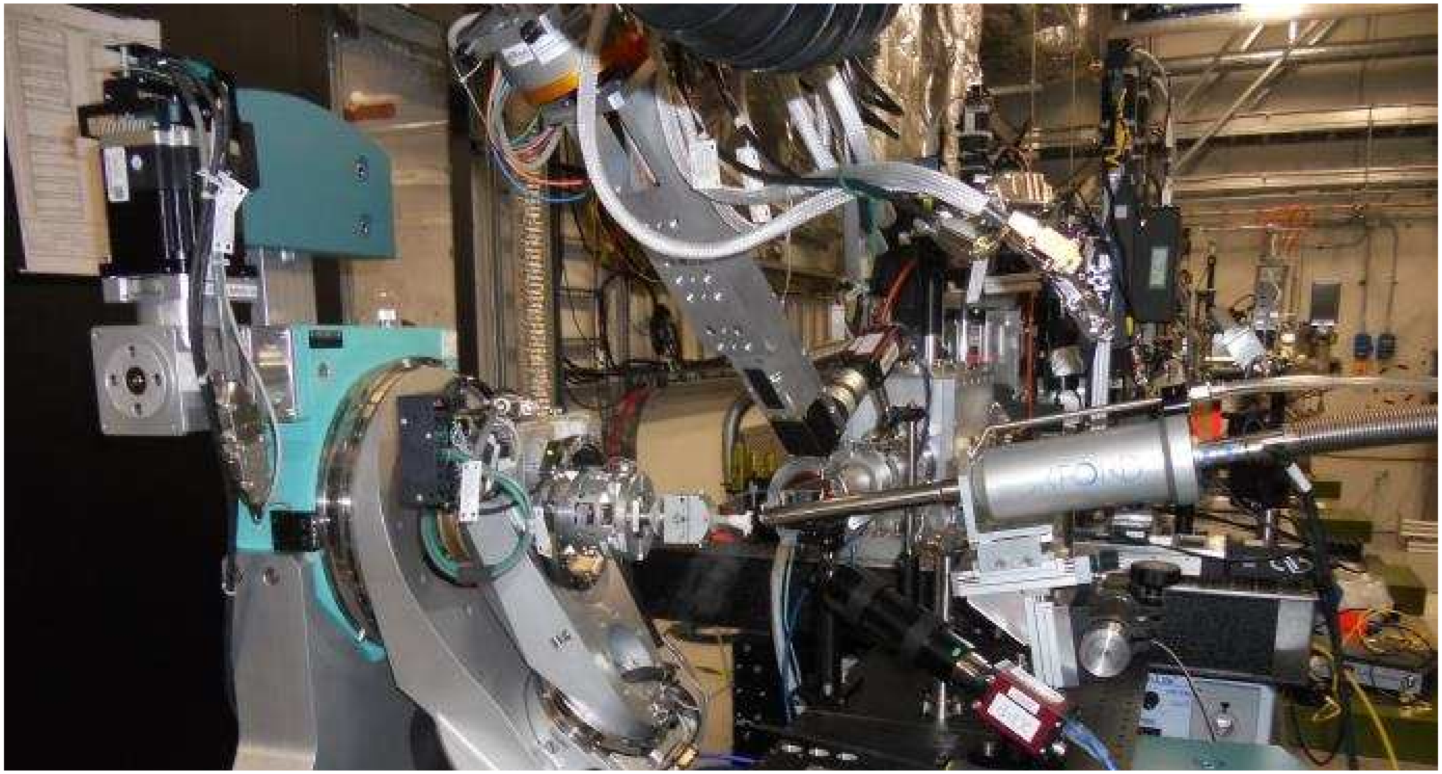
→ Evidence of ultrafast structural transition.

Beaud *et al.* PRL 103 155702 (2009); A. Caviezel *et al.* PRB 87, 205104 (2013).

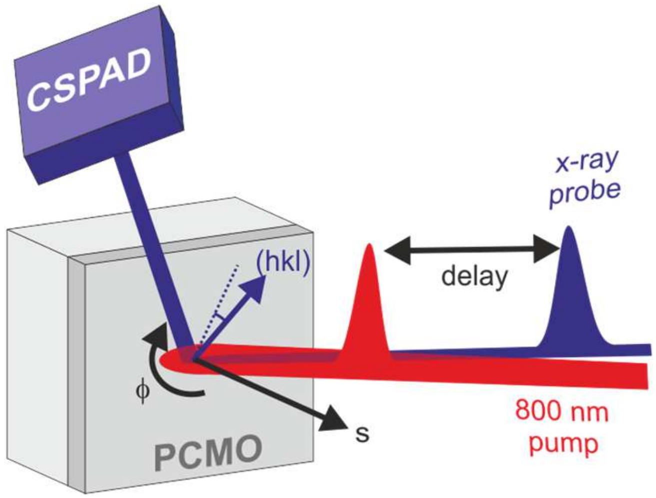
More detailed dynamics→ FEL

1. **Better time resolution** → understand structural dynamics.
2. **High photon flux** → time scales of CO & OO melting with **resonant** XRD.

XPP-instrument (5 x 12h, Feb 2013)



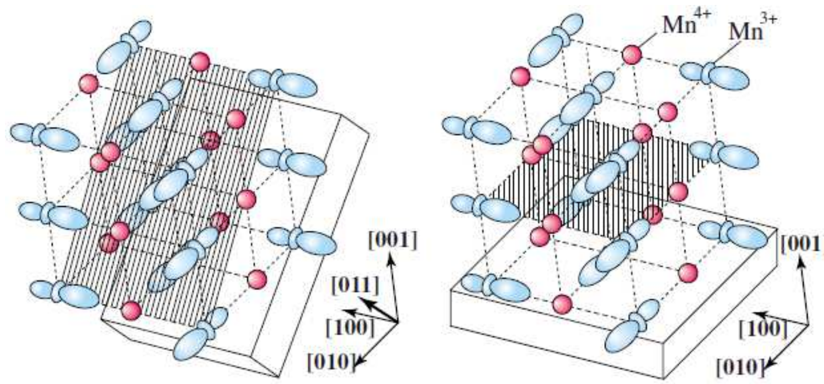
Experimentals



Sample

Okuyama *et al*. APL 95, 152502 (2009)

- $Pr_{0.5}Ca_{0.5}MnO_3$, thin film (*d* ≈ 40 nm)
- $(011)_c$-orientation → access to CO & OO peaks
- 100 K (nitrogen cryo blower)



Optical pump

- Ti:Saphhire
- 50 fs, 800 nm

X-ray probe

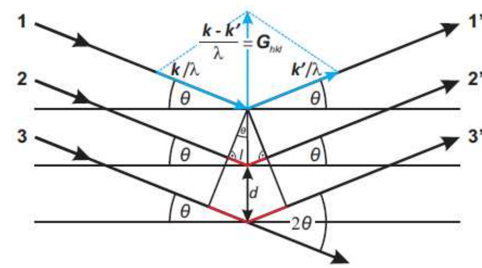
- 50 fs, ~6.55 keV, Si(111) monochromator
- Cornell-SLAC hybrid Pixel Array Detector

Herrmann *et al*. NIM A 718, 550 (2013)

Resonant X-ray diffraction

Site specific information

Diffraction → probes long range order
Absorption → probes electronic system



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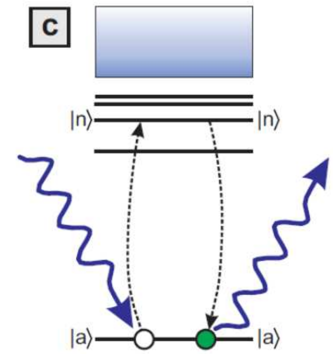
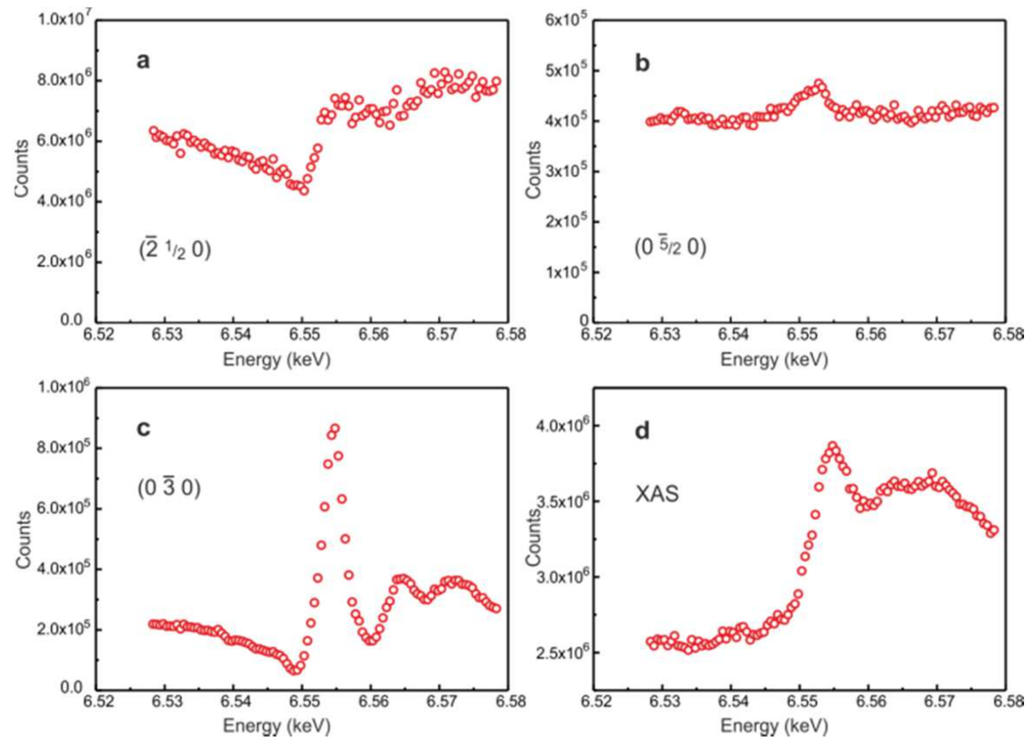


Resonant scattering

Resonant XRD at Mn *K* edge

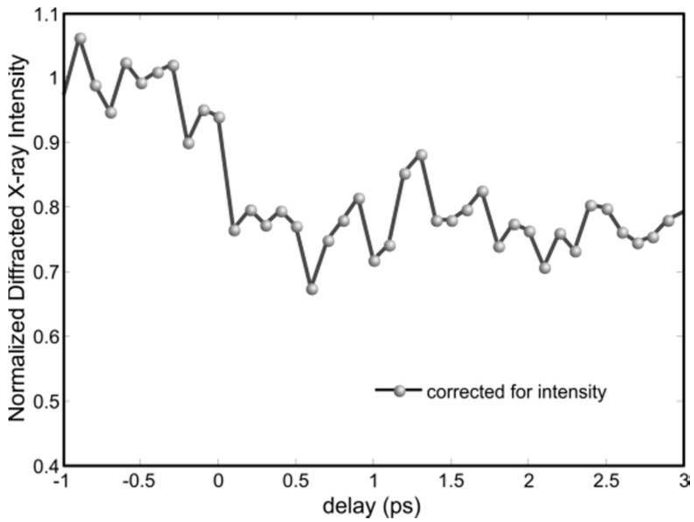
Possible due to hybridization of
Mn 3d and O 2p states
Zimmermann et al. PRL 83, 4872,1999

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

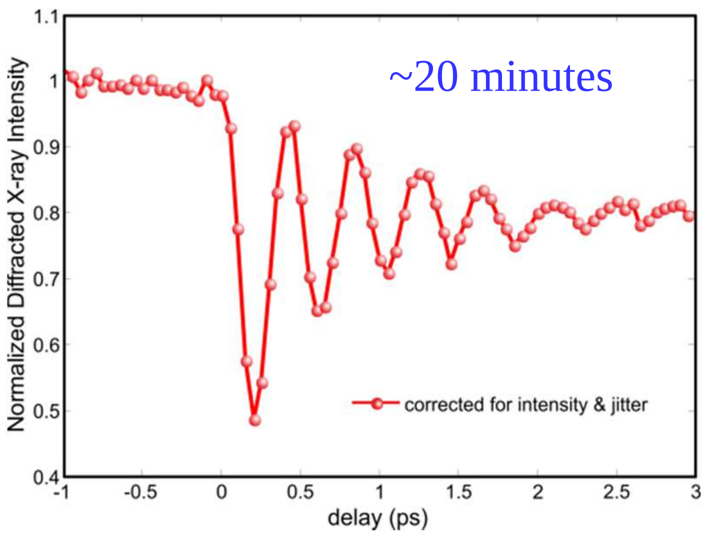


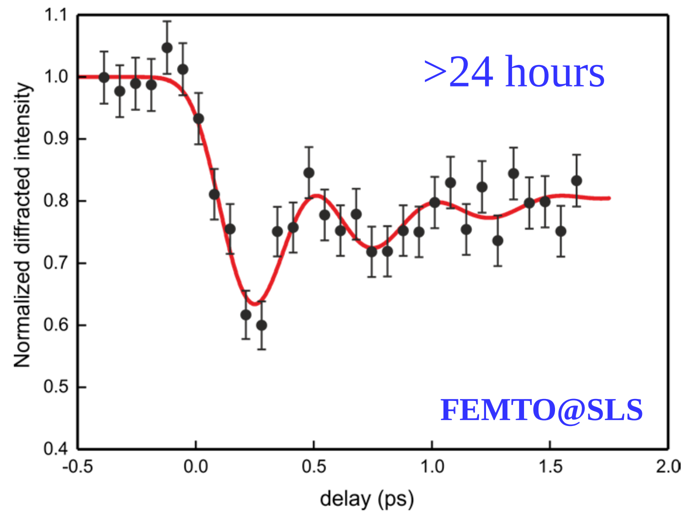
Static experiment at 100 K
(SLS Material Science beamline)

Time resolution

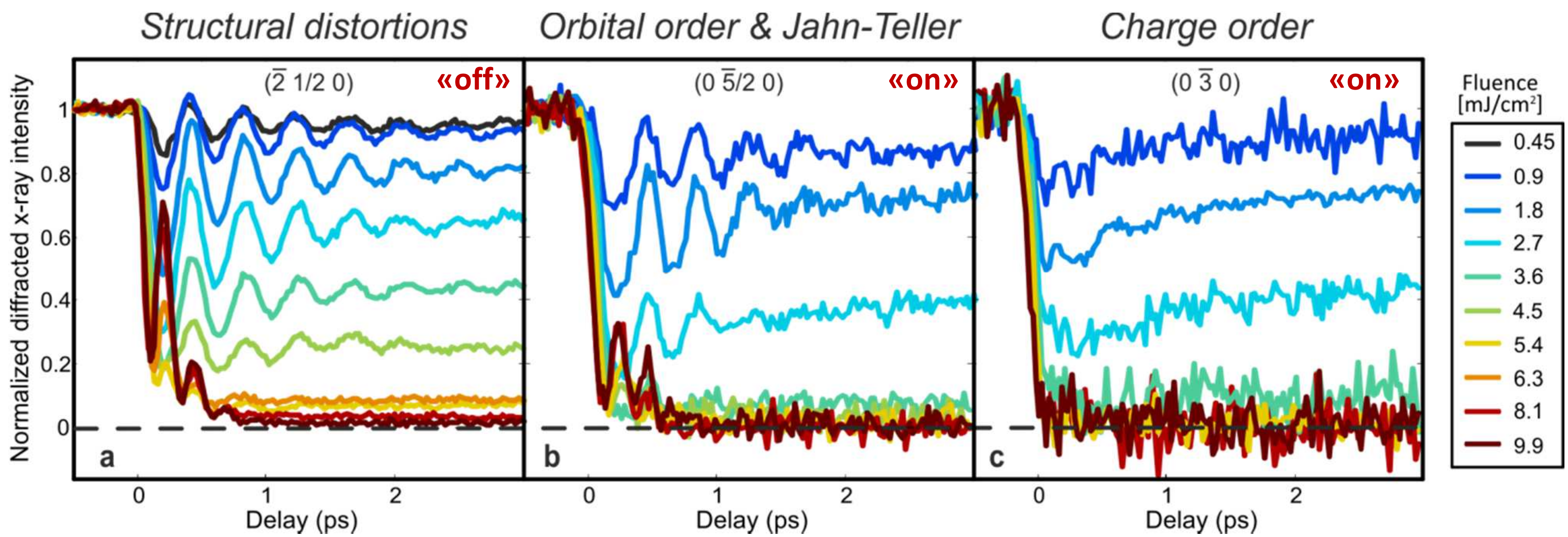


- Laser/FEL arrival time jitter measured with spectral encoding.
  Harmand *et al.* Nat. Photon. 7, 215, 2013
- Tremendous improvement in time resolution and data acquisition efficiency.





Overview of experimental data

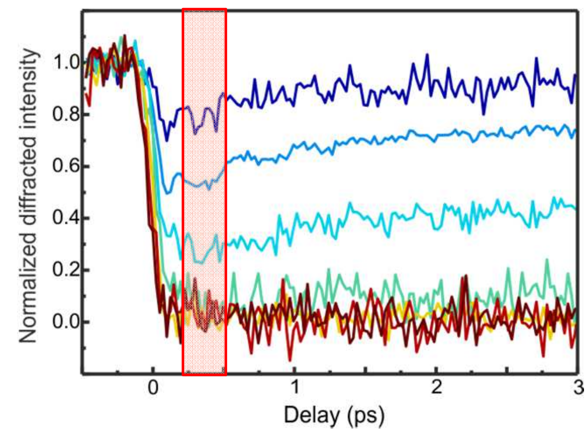


- Superlattice reflections vanish at high fluence, no threshold behavior.
- Different fluence dependence due to optical birefringence.
- Very fast onset of structural and electronic transition .
- Later dynamics dominated by ~2.5 THz mode,
  no softening but frequency doubling at high fluence.

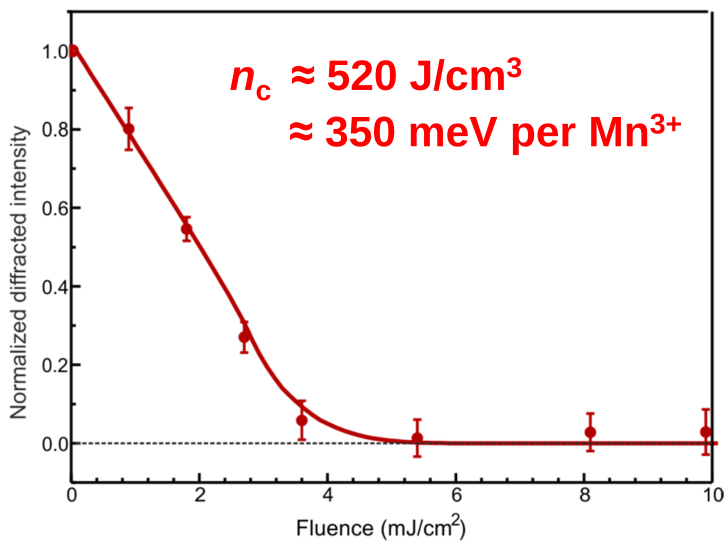
Charge order

- By definition the structure factor of a superlattice reflection is a direct measure of the order parameter:

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



- At early times intensity drops linearly with fluence.



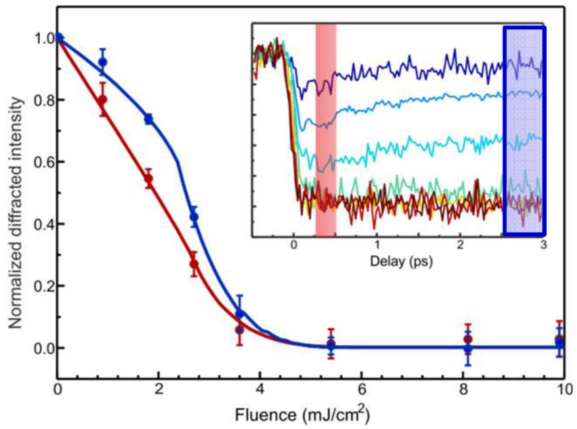
$$\Rightarrow \quad \eta_{\text{early}} = \sqrt{1 - \frac{n_0}{n_c}}$$

- n_0 is the initial excitation density.
- phase transition occurs for $n_0 > n_c$.

- To quantitatively determine n_c we must account for pump gradient ($\sigma_{800nm} \approx 1/d$):

$$\left|F^{0\bar{3}0}\right|^2 = \frac{1}{N^2}\left|\sum_i \sqrt{1 - n_0(z_i)/n_c}\right|^2$$

Time evolution of order parameter



Late times:

$$\eta_{\text{late}} = \left(1 - n_0 / n_c\right)^{\gamma}$$

$n_c \approx 470(6)$ J/cm^3
$\gamma \approx 0.20(2)$

Electron-phonon coupling cools electronic system leading to a partial recovery of CO for $n_0 < n_c$.

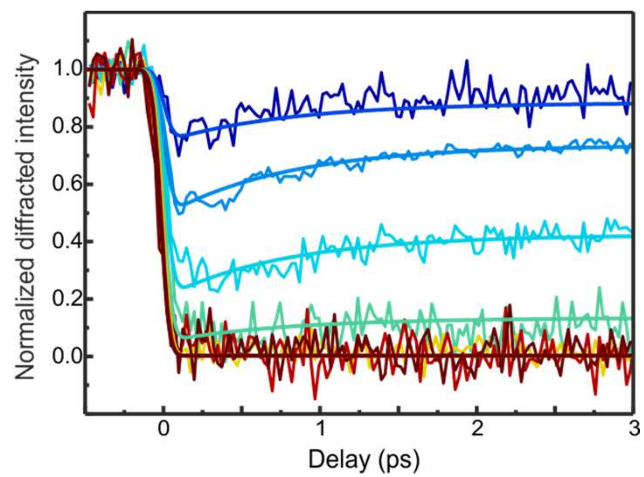
→ ***Time dependent order parameter***

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

Empirically we get:

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

$$\alpha = 1 - (1 - n_0/n_c)^{2\gamma}$$



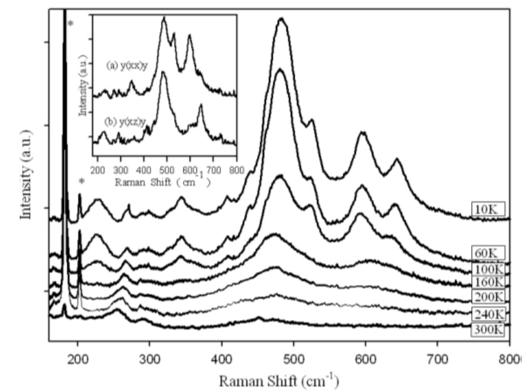
$n_c = 477(7)$ J/cm^3
$\gamma = 0.21(1)$
$\tau = 0.81(4)$ ps.

→ ***Striking similarity to Landau result for second order phase transitions.***

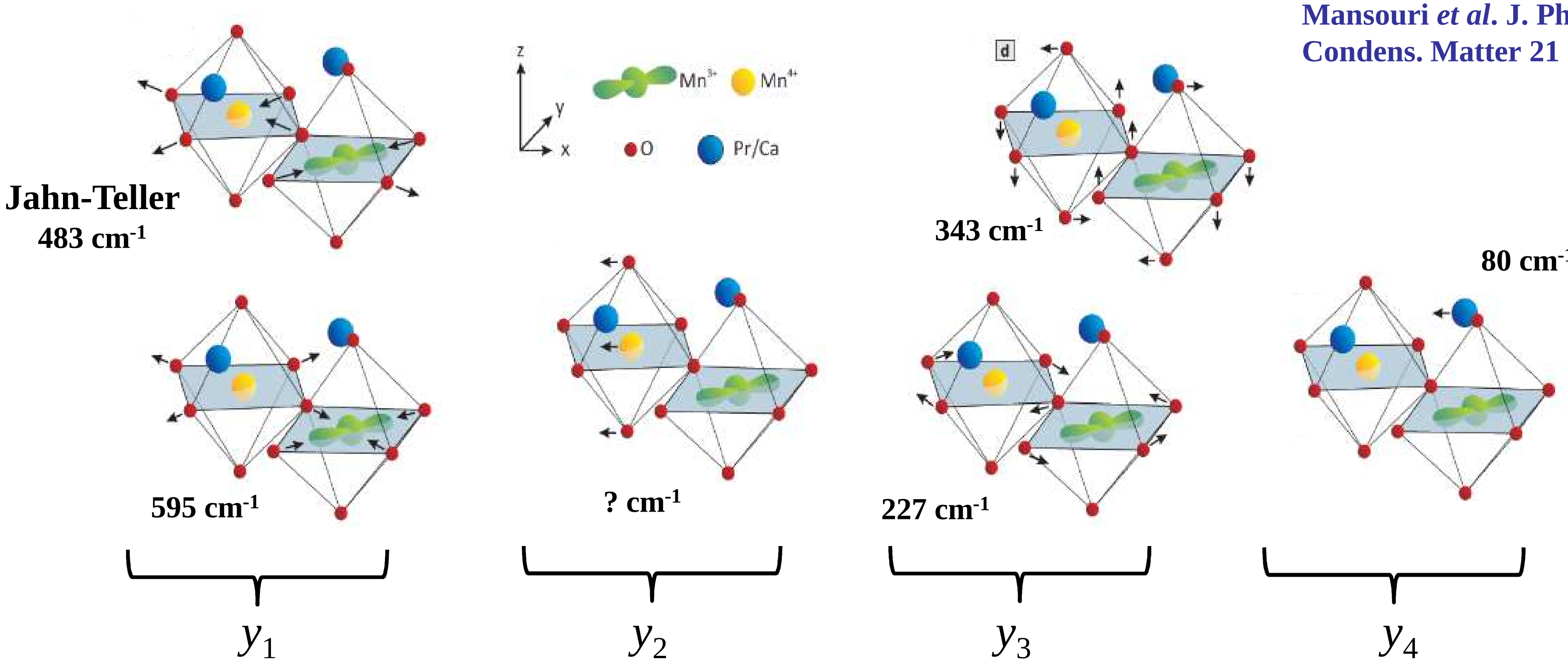
→ ***Must also describe structural dynamics.***

Structural dynamics

- Unit cell with 40 atoms, multiple coordinates.
- Excitation at Mn^{3+} sites
  - → fast collapse of Jahn-Teller distortion
  - → chain reaction rearranging the unit cell.



Mansouri *et al.* J. Phys.: Condens. Matter 21 (2009)



Simplified model of atomic motion using four groups of effective modes.

Time dependent atomic potential

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

Similar Landau-type potentials have been used to describe single coordinate systems.

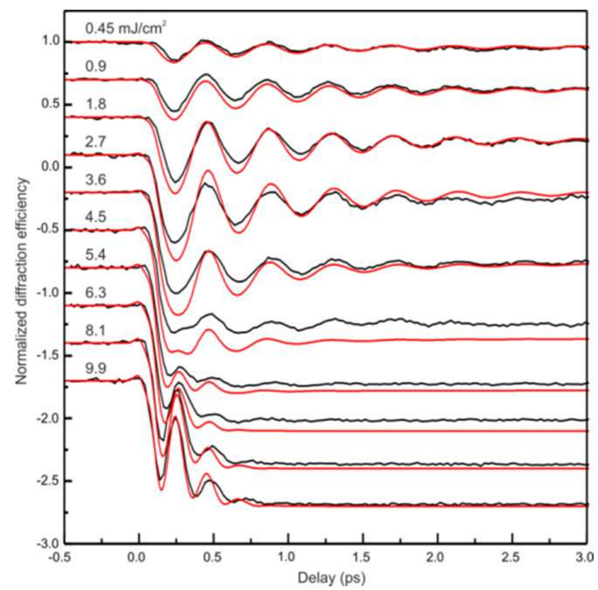
Yusupov *et al.* Nat. Phys. 6, 681 (2010); Van Veenendaal, PRB 87, 235118 (2013); Huber *et al.* PRL 113 026401 (2014);.

Solve: $\ddot{y}_i = \dfrac{1}{m_i}\dfrac{\partial V}{\partial y_i} - \Gamma_i \dot{y}_i$

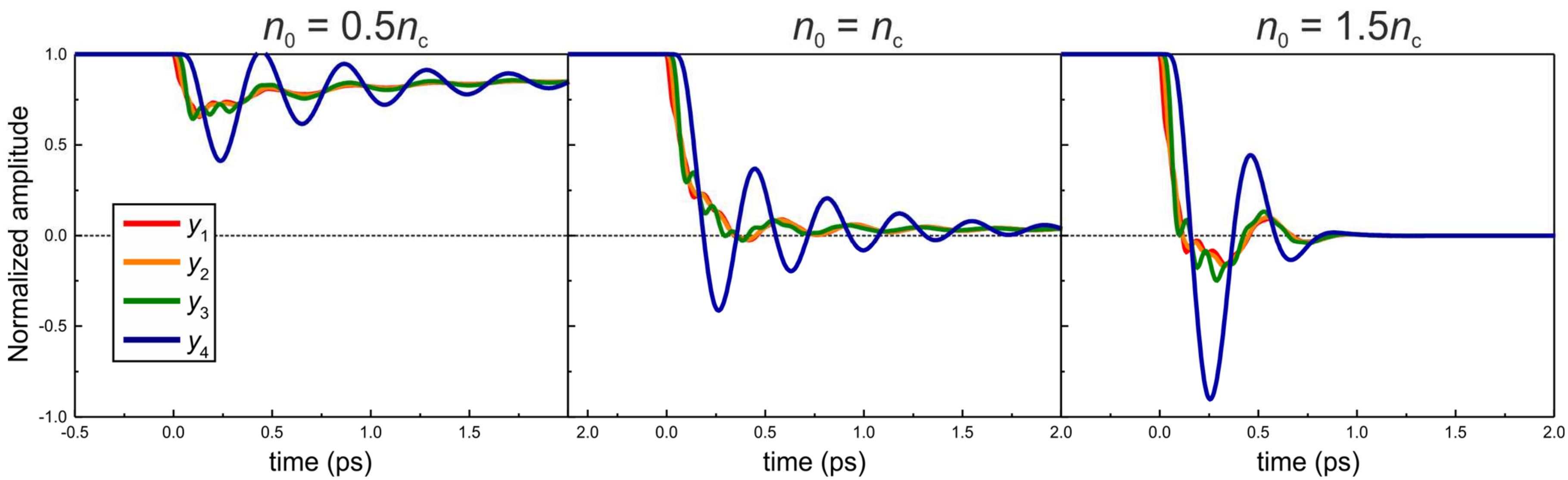
$$F^{hkl}(z,t) = \sum_{1}^{40} f_j e^{i\mathbf{G}\cdot\mathbf{r}_j(z,t)}$$

$$\frac{I^{hkl}(t)}{I_0^{hkl}} = \frac{1}{N^2}\left|\sum_{i=1}^{20} \frac{F^{hkl}(z_i,t)}{F_0^{hkl}}\right|^2$$

compare to experiment



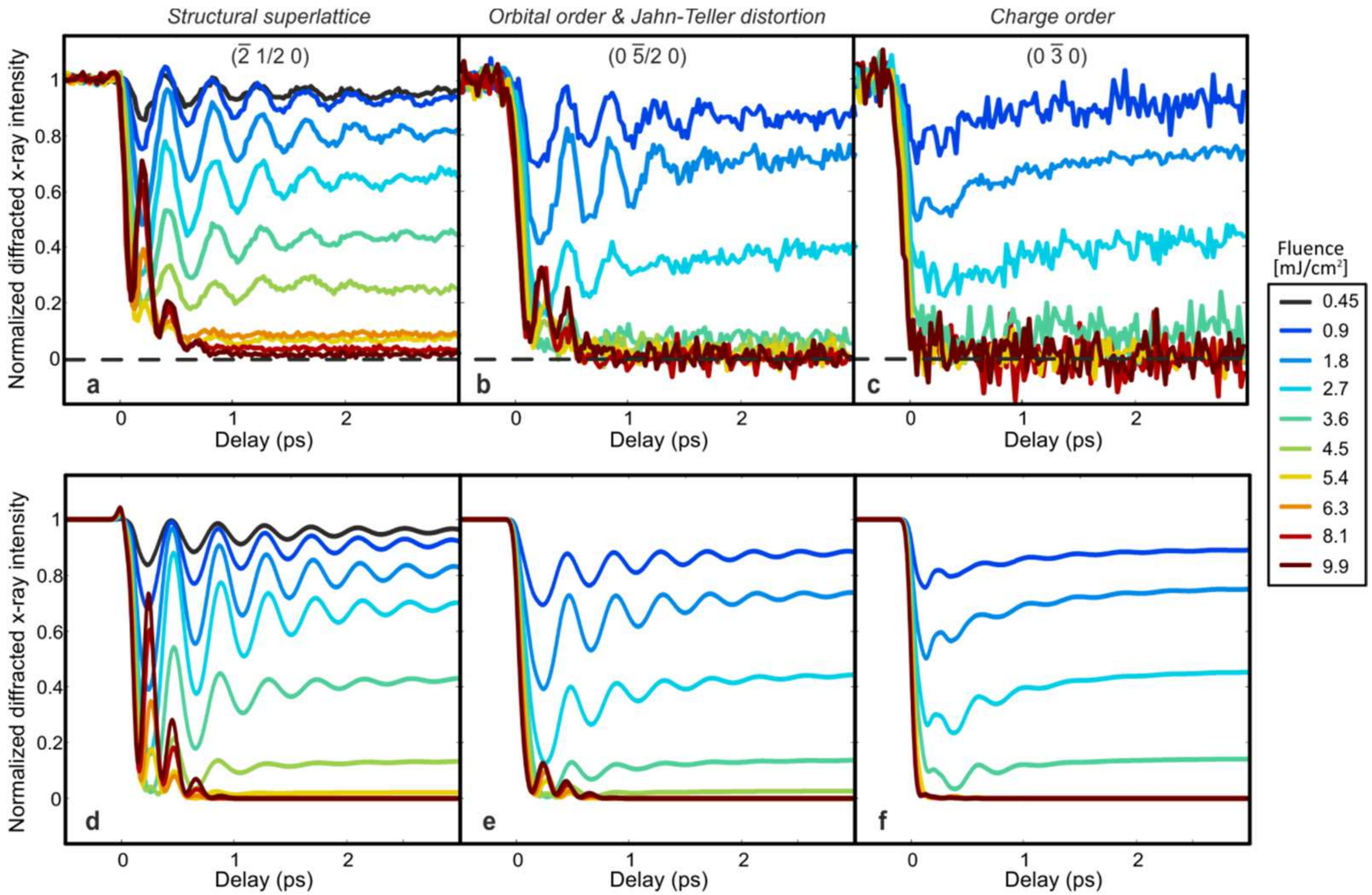
Time evolution of structural modes



- Strong coupling → lowest frequency in chain dominates late dynamics.

- Atoms overshoot → frequency doubling in diffracted signal.

Simulation (structural response only)

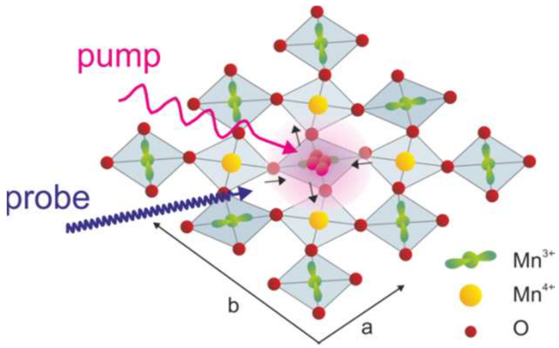


Fairly simple description relying on a single time-dependent order parameter captures the essential dynamics down to ~80 fs.

Nat. Mater. **13**, 923 (2014).

Summary & outlook

- Time dependent order parameter concept proposed.



$$\eta_t(t) \propto (n_c - n)^{\beta} \quad \text{with} \quad \beta = \tfrac{1}{2}$$

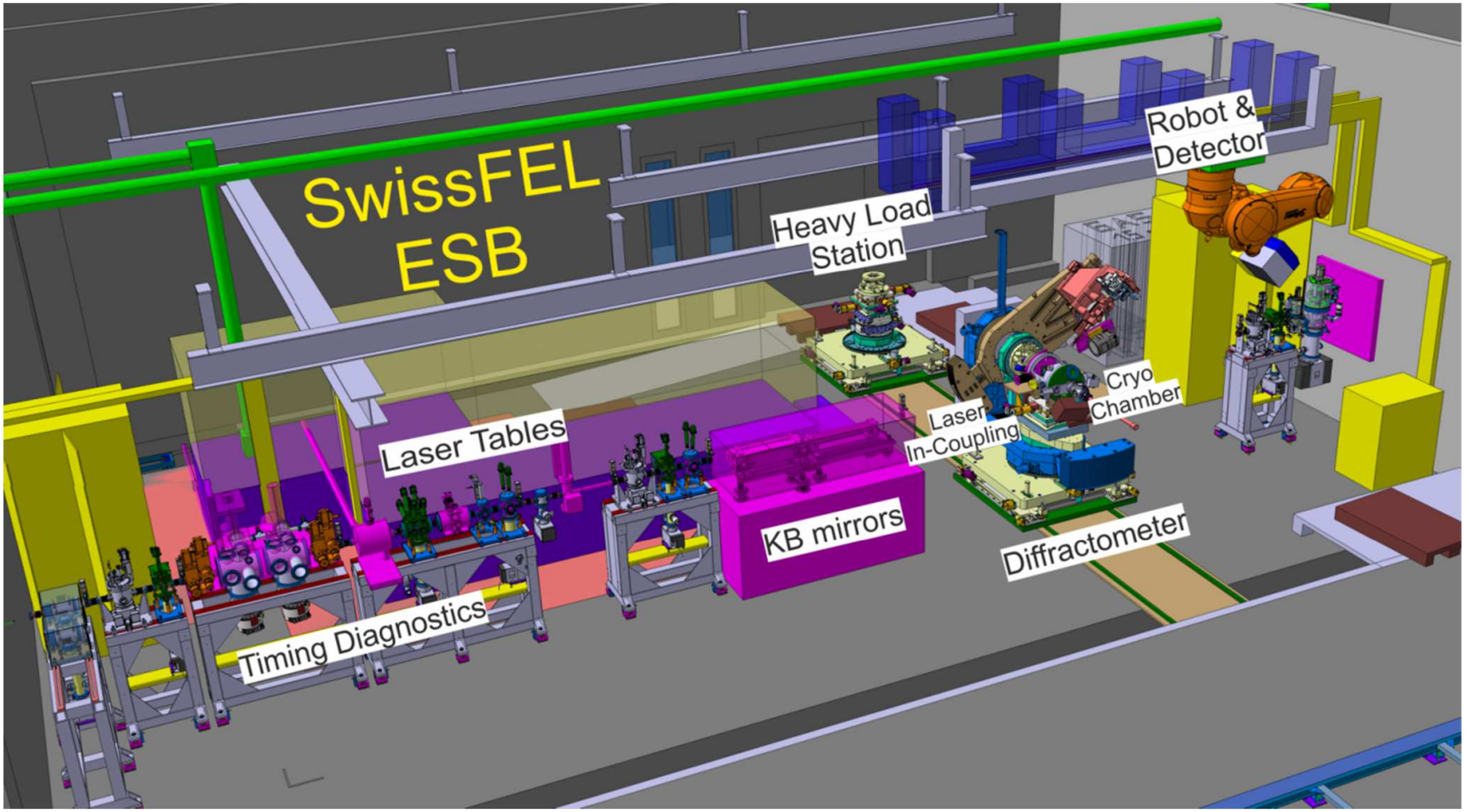
- Universal classification of phase transition dynamics in the time domain?

Decision of SNB to lift enforced € – CHF exchange rate.

- Our wish list for the future includes:
  - → Improved time resolution
  - → Polarization control & analysis
  - → Controlled sample environment

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

G. Ingold, Poster #81



Thank you for your attention!