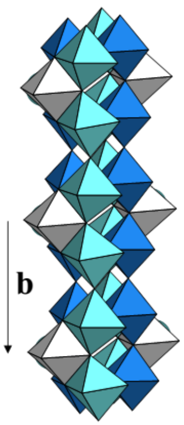
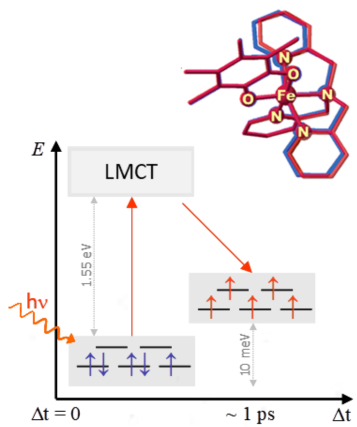
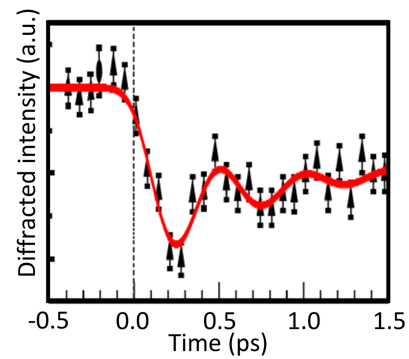
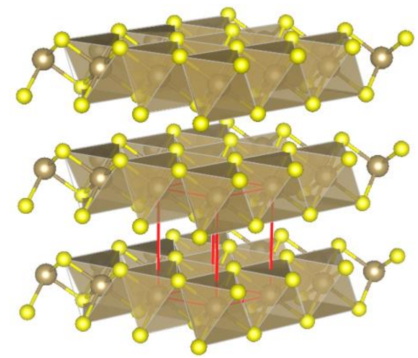
(Ultra)fast structural dynamics:

a view from time-resolved X-ray diffraction









Claire Laulhé

SOLEIL synchrotron - CRISTAL beamline

Paris-Saclay University (Psud)

(Ultra)fast structural dynamics:

a view from time-resolved X-ray diffraction

I. Scientific motivations

II. Pump-probe diffraction

- Principle
- Time resolution & synchronization
- Short X-ray pulse sources
- Specific geometrical constraints

III. Example

- Photo-induced phase transition in $K_{0.3}MoO_3$

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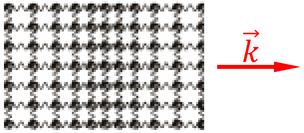
SOLEIL SYNCHROTRON

Structural dynamics in physics

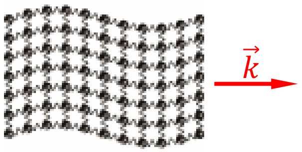
• Crystals at thermodynamic equilibrium

Atomic displacements : sum of normal modes

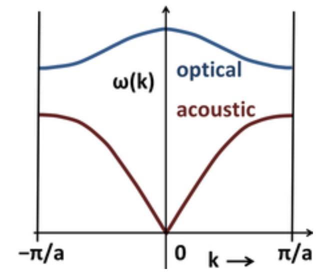
$$\overrightarrow{u_n}(\vec{r},t) = \sum_{\lambda,\|\vec{k}\|} u_n(\lambda,\vec{k})\, \vec{e}_{\lambda,\vec{k}}\, e^{i[\omega(\lambda,\vec{k})t - \vec{k}.\vec{r}]}$$



Longitudinal mode



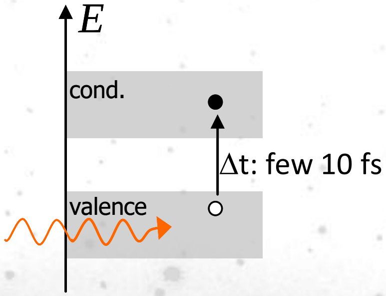
Transverse mode



Phonon spectrum $(\omega,\vec{k})_\lambda$

→ **Experiments in the frequency domain: inelastic neutron scattering, Raman scattering…**

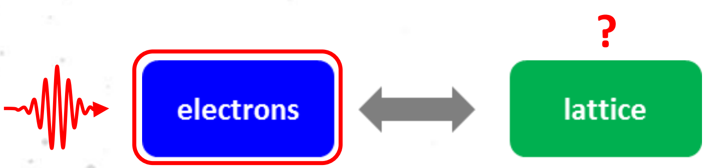
• Photo-induced structural dynamics



Within few 10 fs: electronic transitions in a « Frozen lattice »

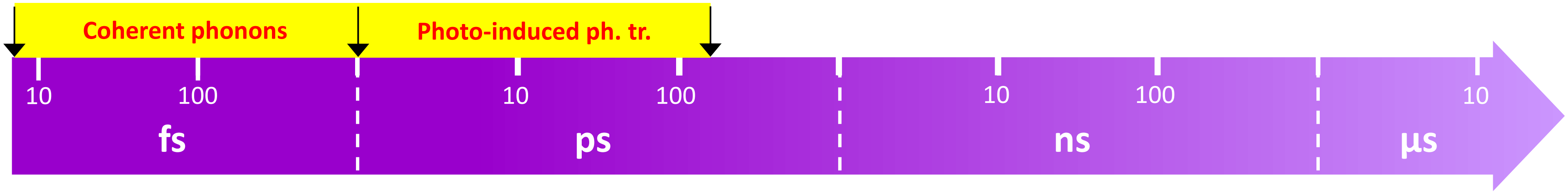
→ Decoupled electronic and lattice degrees of freedom

→ Out-of-equilibrium dynamics



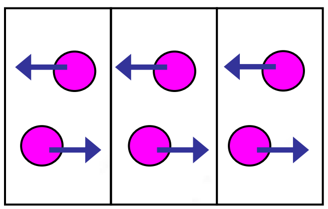
→ **Experiments in the time domain: time-resolved pump-probe diffraction**

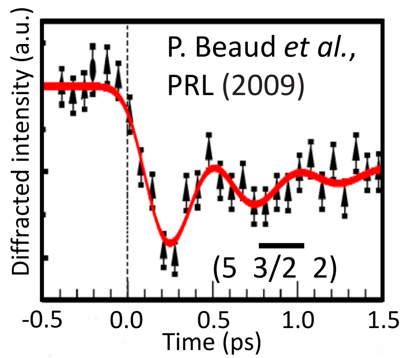
Structural dynamics in physics (1/2)

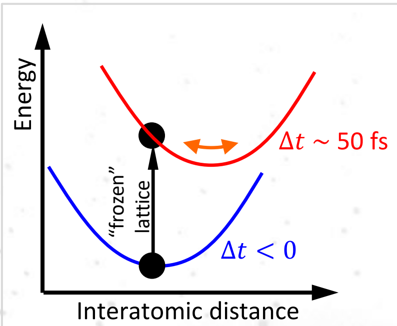


t < few ps : coherent phonons

$La_{0.42}Ca_{0.58}MnO_3$







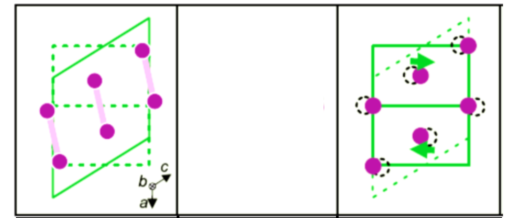
Sudden shift of the quasi-equilibrium atomic positions:

Displacive excitation

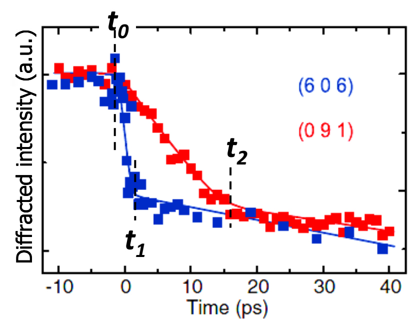
H.J. Zeiger *et al.*, PRB **45**, 768 (1992)

t < few 100 ps : ultrafast phase transitions

VO_2



Temperature	$T < T_c$		$T > T_c$
Laser excitation	t_0	t_1	t_2

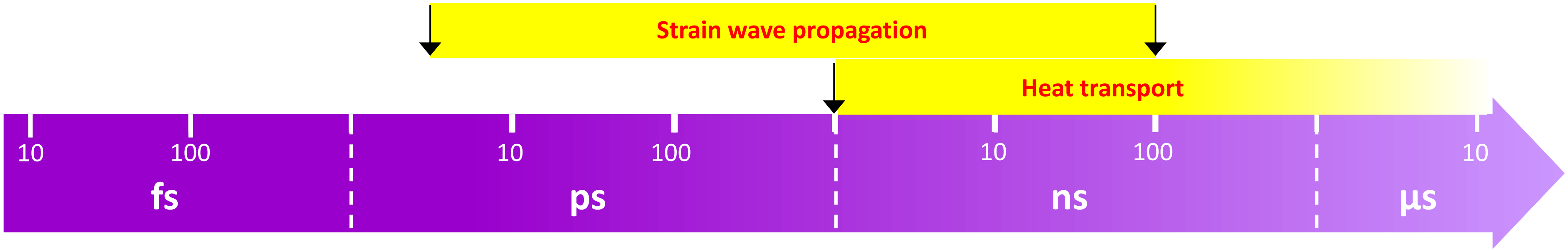


P. Baum *et al.*, Science (2007)

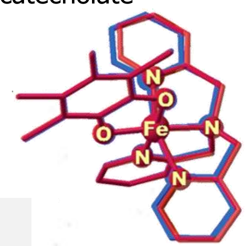
Exploration of the potential in photo-excited states

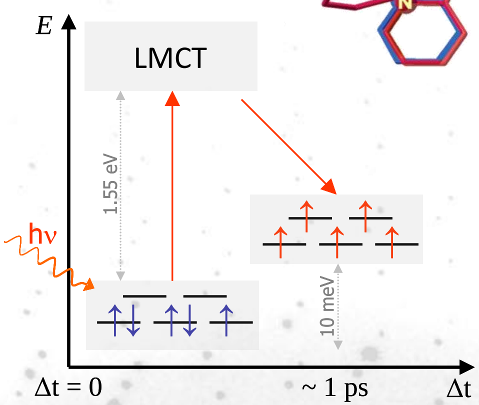
Novel states of matter
Ultrafast control of the physical properties

Structural dynamics in physics (2/2)

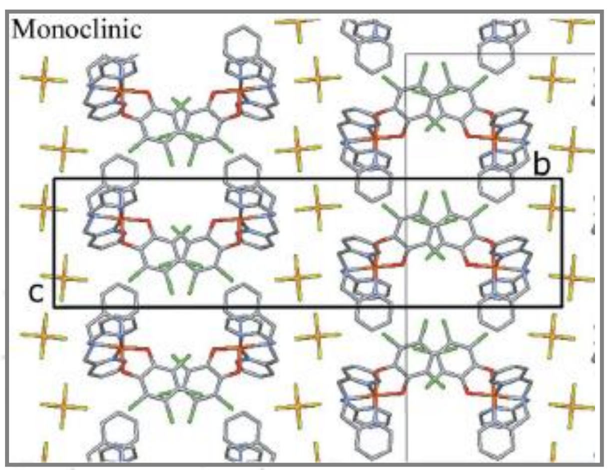


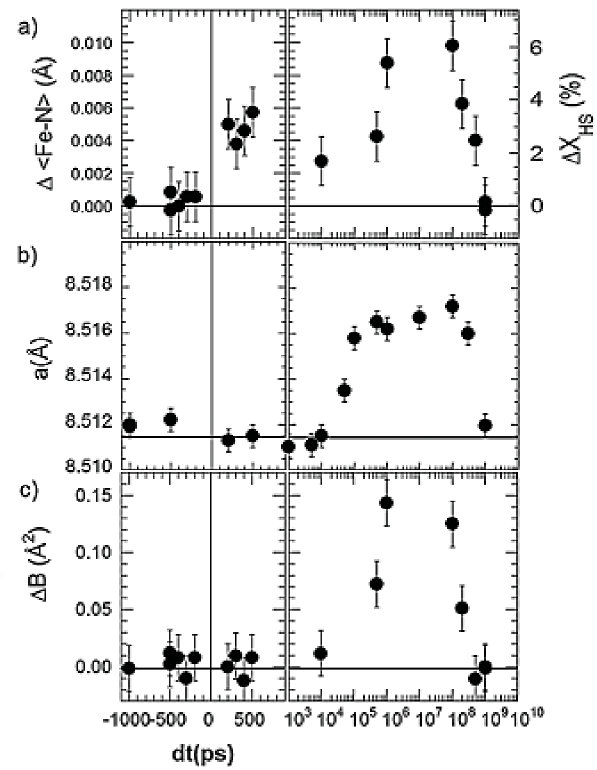
[TPA (FeIII) TCC]
Tris(2-pyridylmethyle)
3,4,5,6-tetrachlorocatecholate





[TPA (FeIII) TCC] PF_6





M. Lorenc *et al.*, PRL **103**, 028301 (2009)

SOLEIL SYNCHROTRON

Cooperative effects in molecular crystals
Light control of ferroelectric and magnetic materials

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a view from time-resolved X-ray diffraction

I. **Scientific motivations**

II. **Pump-probe diffraction**

- Principle
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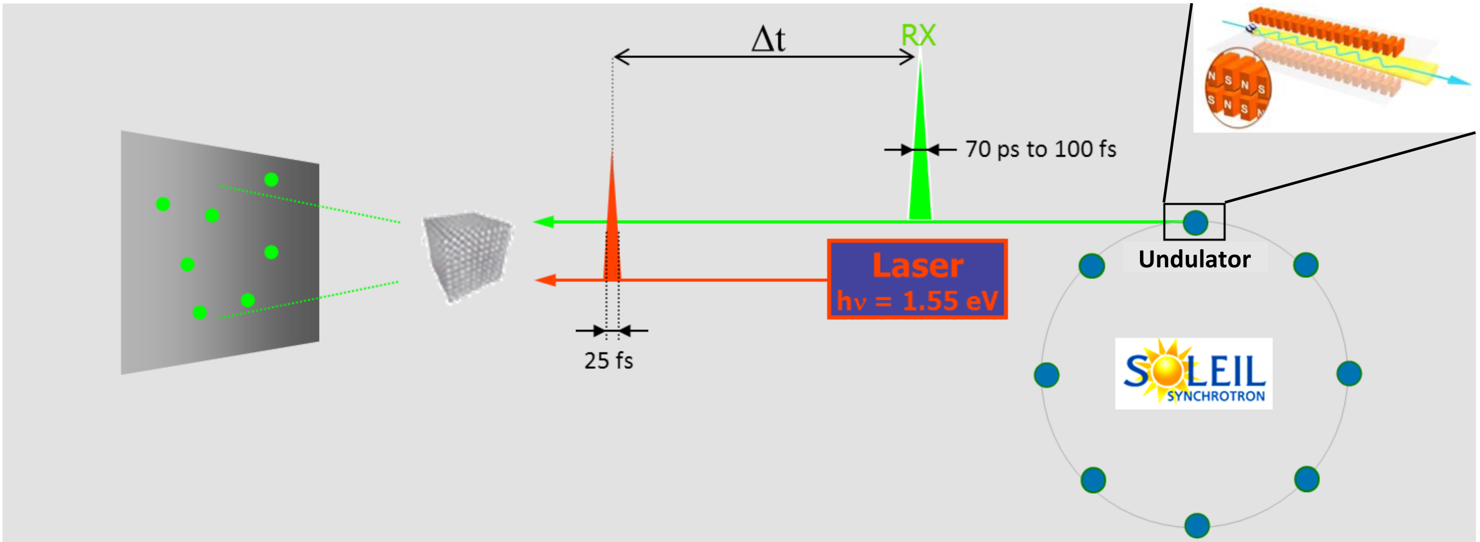
Time-resolved pump-probe diffraction

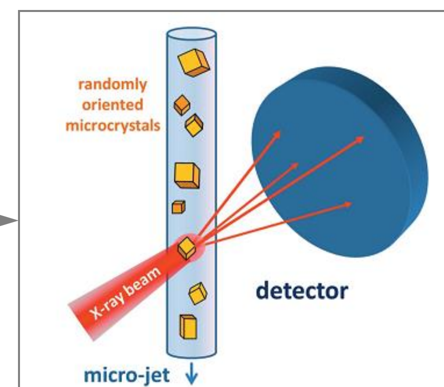
Following photo-induced structural changes as a function of time



- **One pump-probe cycle ↔ diffraction signal too low !**

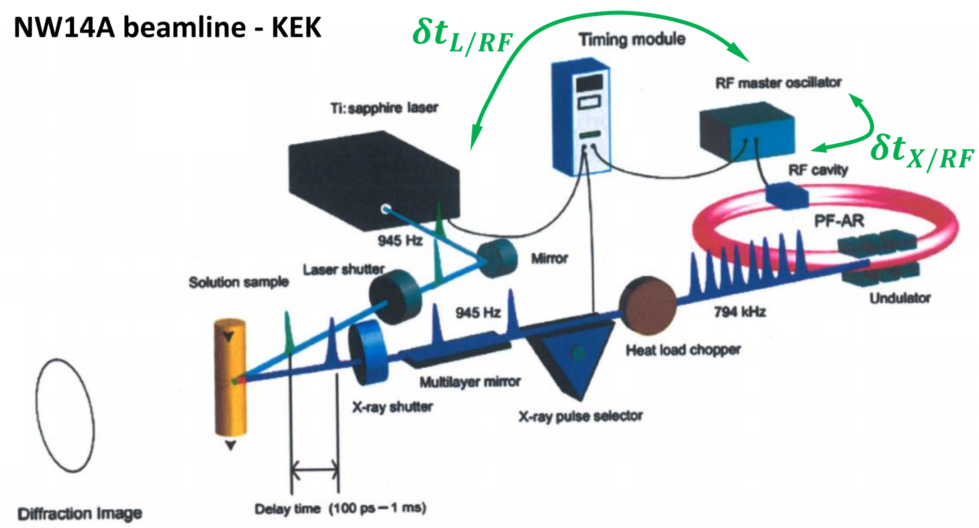
→ N pump-probe cycles needed for each Δt: study of reversible processes

→ Irreversible processes : liquid jets / serial crystallography at X-FELs

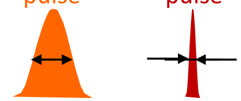


I. Schlichting, IUCrJ **2**, 246–255 (2015)
V. Panneels *et al.*, Structural Dynamics **2**, 041718 (2015)
T. R. M. Barends, Science **350**, 445 (2015)

Typical layout for pump-probe diffraction



H. Ihee, Int. Rev. Phys. Chem. **29**, 453-520 (2010)

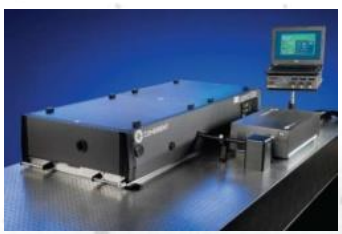


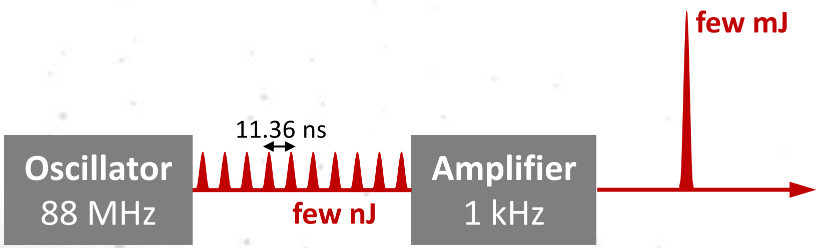
$$\delta t^2 = \delta t_X{}^2 + \delta t_L{}^2 + \underbrace{\delta t_{X/RF}{}^2 + \delta t_{L/RF}{}^2}_{\text{jitter terms (few ps)}}$$

- **Atomic vibrations: $E = \hbar\omega \sim$ 20 meV $\Rightarrow$ $T_{osc} \sim$ 250 fs**

  → Need for time resolutions of few 10 fs

- **Commercially available Ti:Sa lasers (1990 →): ~ 40 fs pulses @ 800 nm [1.55 eV]**





Chirped pulse amplification
G. Mourou, D. Strickland (2018 Nobel Prize in physics)

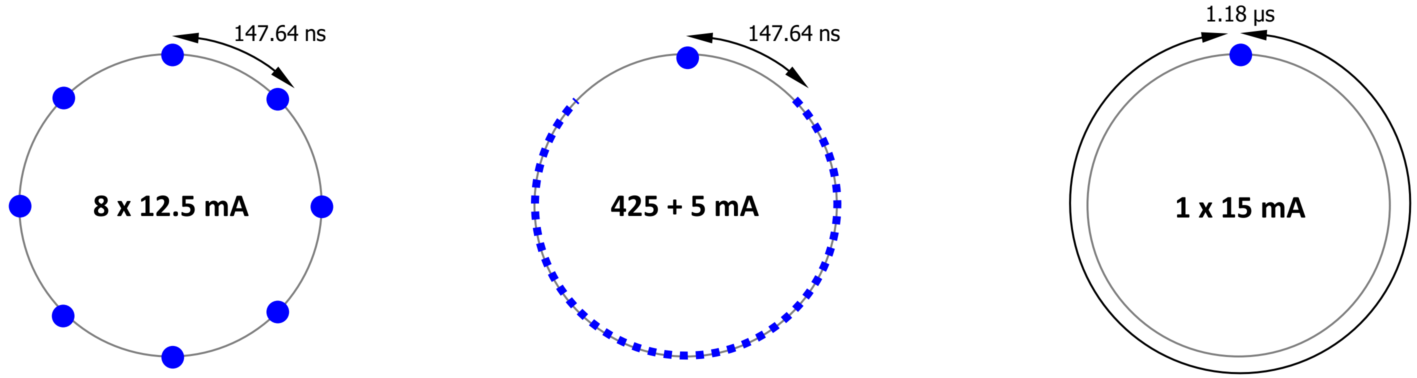
Non-linear optics:

far-infrared ↔ ultraviolet
(20 µm, 60 meV) **(60 eV, 20 nm)**

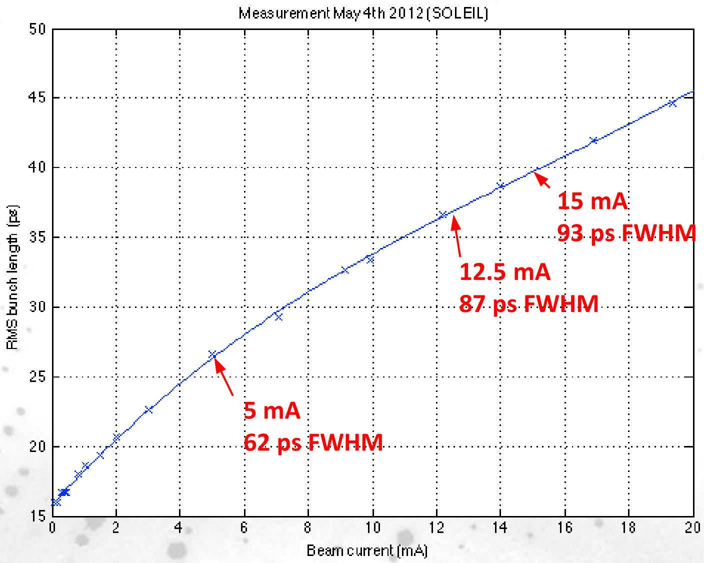
SOLEIL SYNCHROTRON

X-ray pulse sources

- **Few 10 ps pulses from synchrotrons**



Bunch modes for time-resolved experiments at SOLEIL



Modes dedicated to time-resolved experiments:

Isolated bunch with high current

Isolated → Enables pulse selection

high current → Optimized count rate from selected pulses

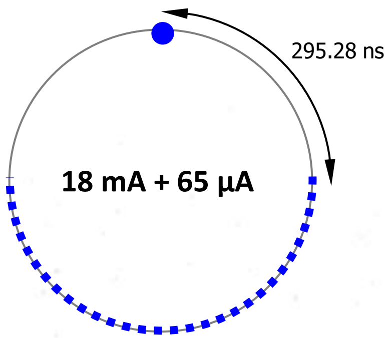
X-ray pulse sources

- **Few ps pulses from synchrotrons: low-α mode**

<u>Normal operation</u>:
- Optics optimized for a low-emittance electron beam
- Dispersion of E_{e^-} $\Longrightarrow$ dispersion of e^- revolution period
- Elongated e^- bunches, longer X-ray pulses

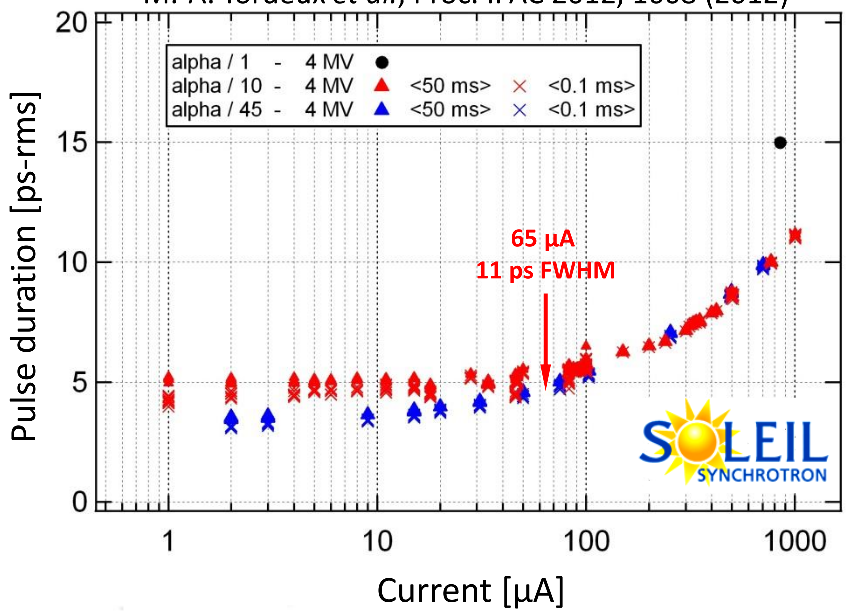
<u>**Quasi-isochronous ring:**</u>

- **Electron revolution period independent of ΔE_{e^-}**
- **Shorter e^- bunches**
- **Lower bunch currents!**



Hybrid mode
Low-α operation at SOLEIL

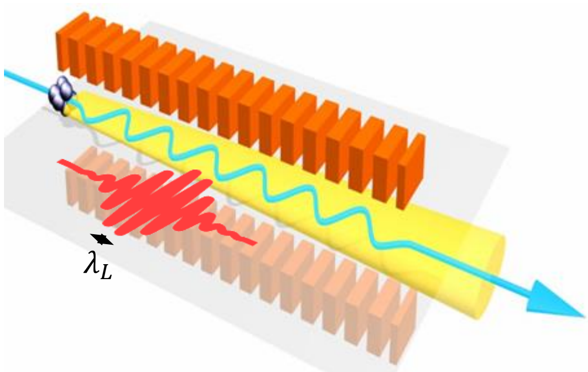
M.-A. Tordeux *et al.*, Proc. IPAC 2012, 1608 (2012)



→ **User operation at BESSY, SOLEIL, DIAMOND**

SOLEIL SYNCHROTRON

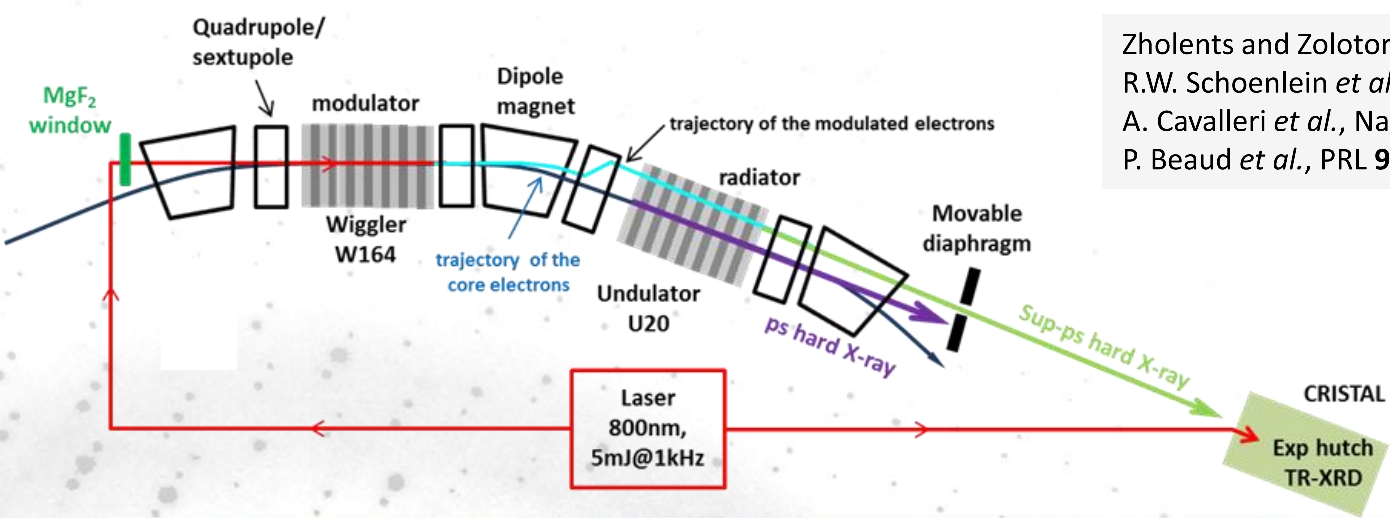
- **100 fs X-ray pulses from synchrotrons: femto-slicing sources (1995 →)**



Co-propagation of an electron bunch and a laser pulse in a wiggler

- $\vec{E}.\vec{v} \neq 0$
- $\lambda_w = \lambda_L$

→ Modulation of electron energies in the overlap zone

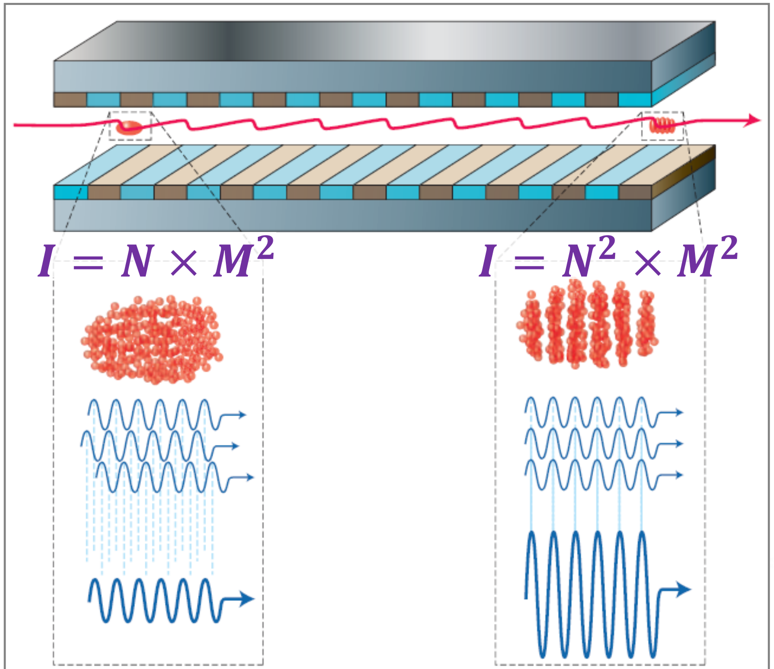


Zholents and Zolotorev, PRL **76,** 912 (1996)
R.W. Schoenlein *et al.*, Science **287**, 2237 (2000)
A. Cavalleri *et al.*, Nature **442**, 664 (2006)
P. Beaud *et al.*, PRL **99** 174801 (2007)

10^3 ph./pulse @1kHz 100 fs duration

→ **BESSY (soft X-rays), ALS, SLS & SOLEIL (hard X-rays)**

- **100 fs X-ray pulses: X-FELs (2009 →)**



B.W.J. Mc Neil and N.R. Thompson
Nature Photonics **4,** 814 (2010)

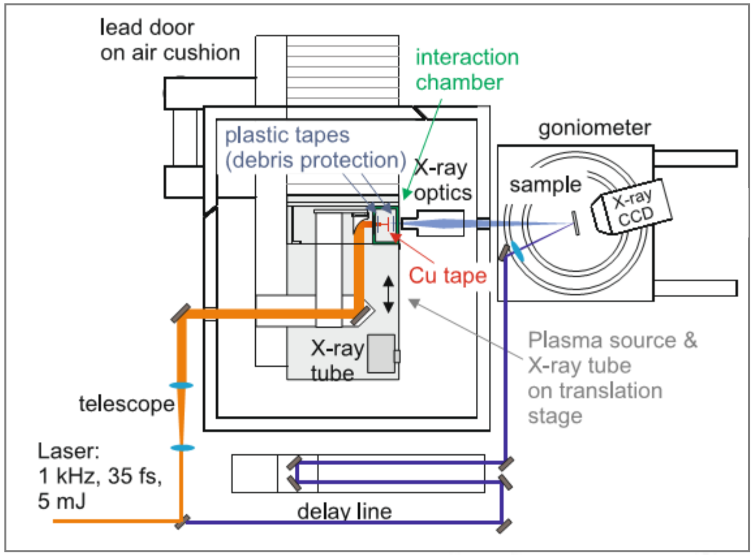
10^{11} ph./pulse
@100Hz
80 fs duration

- Short electron pulses produced by a laser-driven electron gun [N electrons]
- Propagation in long undulators (100 m) [M poles]
- Electron beam bunching
  → Coherent emission of all the electrons

$I \propto N^2 \times M^2$: very high flux
80 fs hard X-ray pulses

Time-resolved pump-probe diffraction: laser-based sources

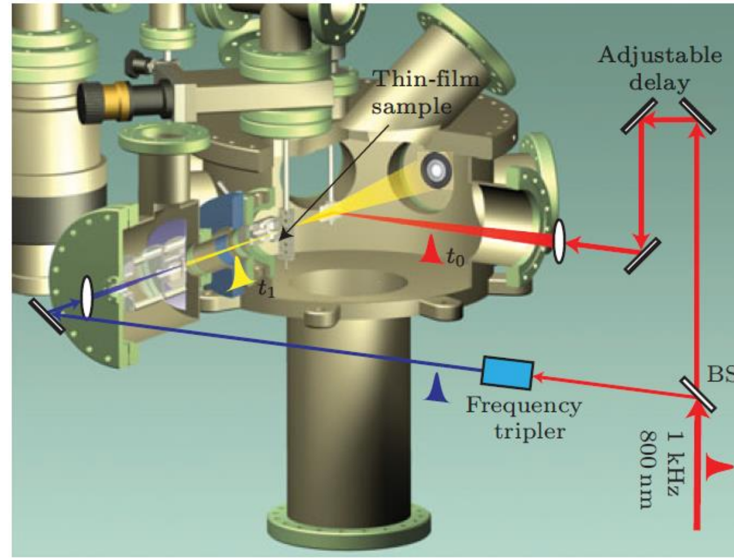
- **X-ray plasma sources (1994 →)**



- Laser pulse onto a copper target
- Indirect ionization of Cu atoms
- Emission of X-rays with $K_\alpha(Cu)$ wavelength [λ= 1.54 Å]

10^3 ph./pulse
@1kHz
100 fs duration

- **Ultrafast electron diffraction (2003 →)**



- Frequency-tripled Ti:Sa laser pulse (λ =266 nm)
- Pulse-driven photocathode → photoemission
- Acceleration to ~ 60 keV [λ~ 0.05 Å]

10^3 e^-/pulse
@1kHz
300 fs duration

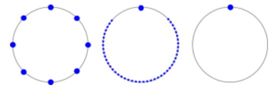
F. Zamponi, Appl. Phys. A **96**, 51-58 (2009)
A. Rousse *et al.*, PRE **50**, 2200 (1994)
A. Rousse *et al.*, Nature 410, **65** (2001)

W.-X. Liang *et al.*, Chinese Phys. Lett. **26**, 020701 (2009)
R. Srinivasan *et al.*, Helvetica Chimica Acta **86**, 1761-1799 (2003)

Pump-probe diffraction : typical photon or electron fluxes

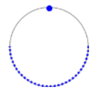
Synchrotrons [repetition rate 1 kHz]

- **80 ps X-ray pulses**



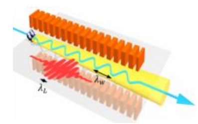
10^6 photons/pulse $\Delta E/E \sim 10^{-4}$ — **10^9 ph/s**

- **Few ps X-ray pulses (low-α)**



10^4 photons/pulse $\Delta E/E \sim 10^{-3}$ — **10^7 ph/s**

- **100 fs X-ray pulses (femto-slicing)**



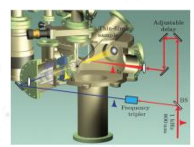
10^3 photons/pulse $\Delta E/E \sim 8.10^{-3}$ — **10^6 ph/s**

Laser-based sources [repetition rate 1 kHz]

- **100 fs X-ray pulses (plasma source)**

10^3 photons/pulse $\Delta E/E \sim 10^{-4}$ — **10^6 ph/s**

- **300 fs electron pulses**



10^3 electrons/pulse — **10^6 e$^-$/s**

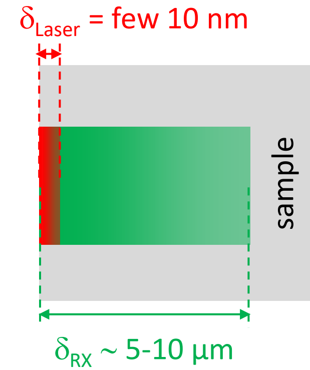
X-ray free electron lasers [repetition rate 100 Hz]

- **80 fs X-ray pulses**

10^{11} photons/pulse $\Delta E/E \sim 10^{-3}$ — **10^{13} ph/s**

Time resolved X-ray diffraction: experimental facts

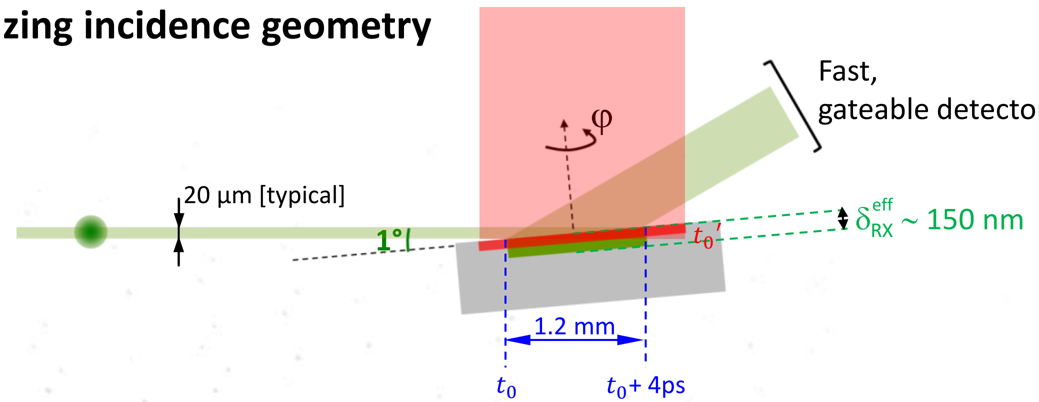
- **X-rays and IR photons: differing penetration depths !**



!! $V_{probed} \gg V_{pumped}$!!

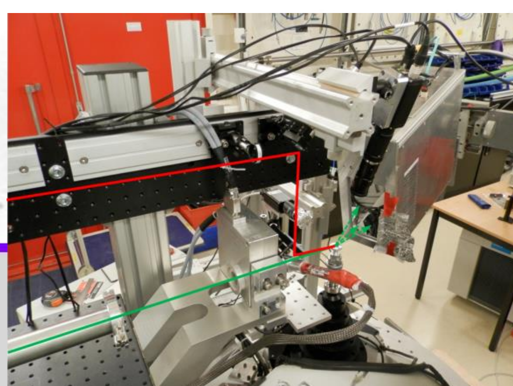
[Typical values for hard condensed matter, 7 keV X-ray photons]

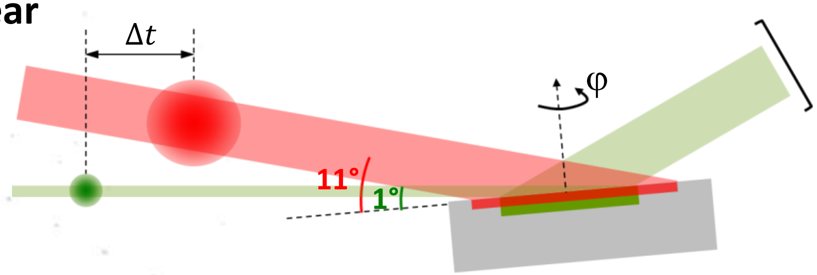
- **Grazing incidence geometry**



!! Loss of effective time resolution from the difference in relative arrival times between the pump and X-ray beams !!

- **Grazing incidence geometry, pump & probe beams collinear**





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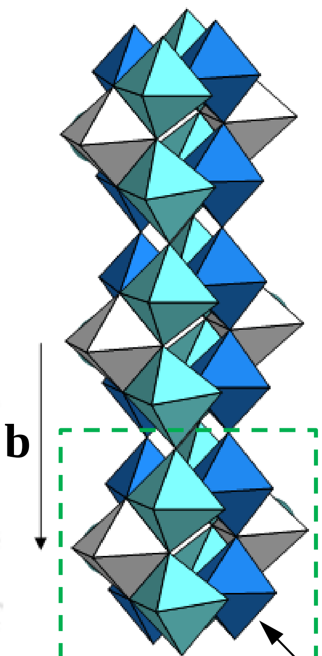
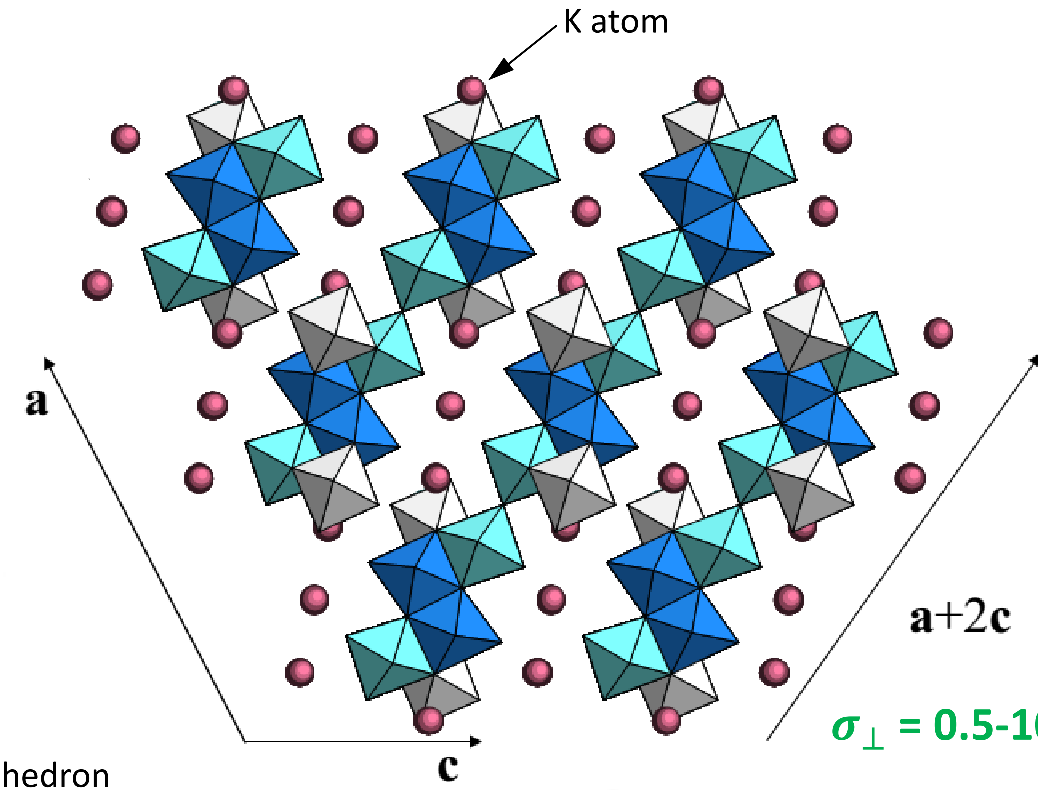
Atomic structure of blue bronze ($K_{0.3}MoO_3$)

- **A quasi-one-dimensional conductor…**





$\sigma_{\perp}$ **= 0.5-10 [Ω.cm]$^{-1}$**

σ_b **= 3 10^2 [Ω.cm]$^{-1}$**

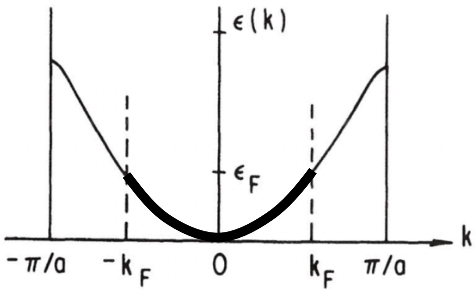
…which undergoes a transition to a charge density wave phase at 183 K

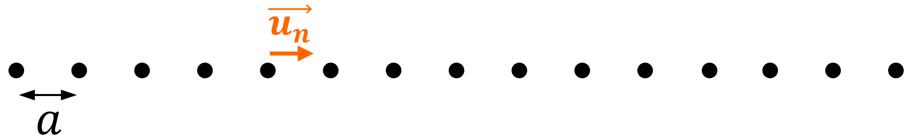
J. Graham and A.D. Wadsley, Acta Cryst. **20**, 93 (1966)
G. Grüner, "Density waves in solids"

Formation of a charge density wave - Peierls model

- **A metal-insulator transition driven by a periodic lattice distortion**

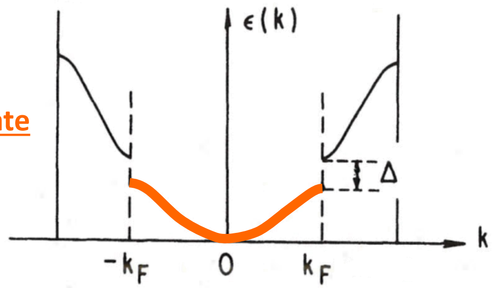
Metallic state

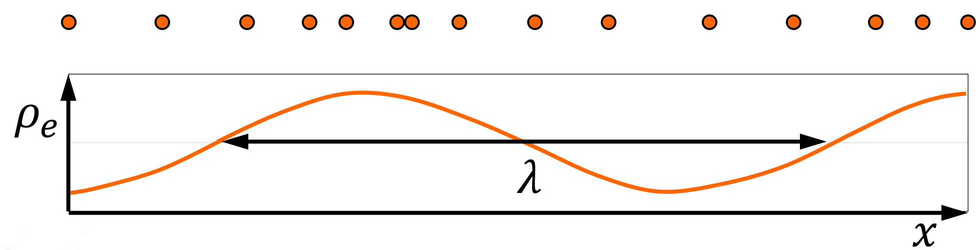




$\overrightarrow{u_n} = \overrightarrow{u_0}\ \sin(\vec{k}.\overrightarrow{R_n} + \varphi)$ $\quad \vec{k} = 2\overrightarrow{k_F}\ ,\ \lambda = \frac{2\pi}{k} = \frac{\pi}{k_F}$

Charge density wave state (CDW)



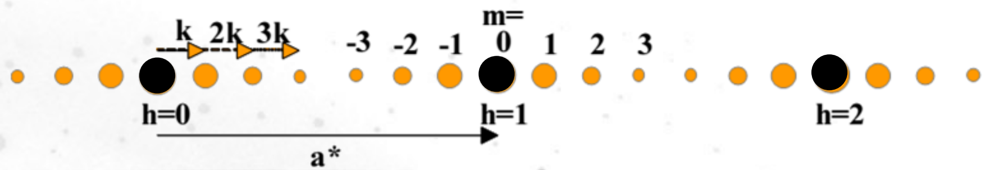


Gain in electronic energy

...At the expense of a moderate cost in elastic energy

CDW systems: strong e-ph coupling

- **Diffraction pattern: satellite peaks**



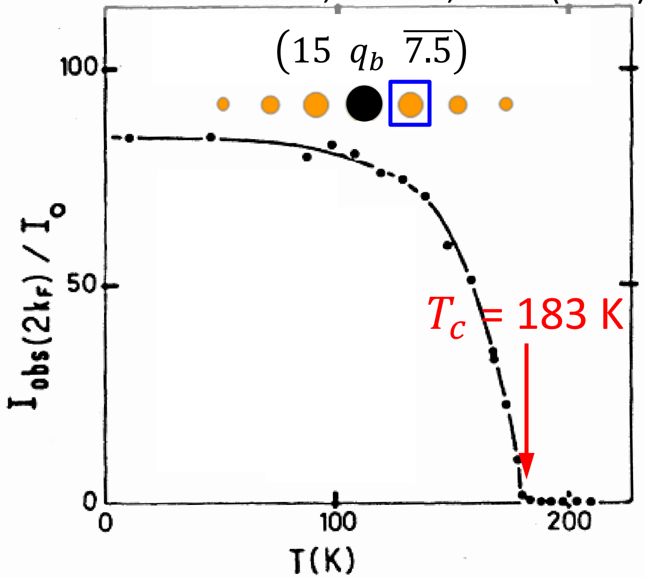
$I_{sat} \propto \|\overrightarrow{u_0}\|^2$

SOLEIL SYNCHROTRON

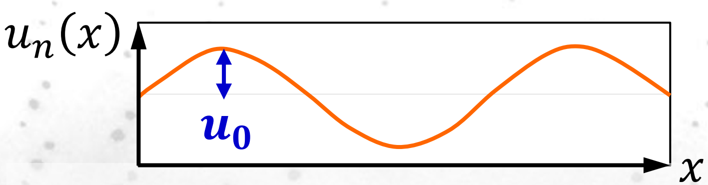
Appearance of a charge density wave in blue bronze ($K_{0.3}MoO_3$)

- **$K_{0.3}MoO_3$: satellite peaks @ $(h\ k\ l) + \left(1\ q_b\ \frac{1}{2}\right)$**

S. Girault *et al.*, PRB **39**, 4430 (1989)



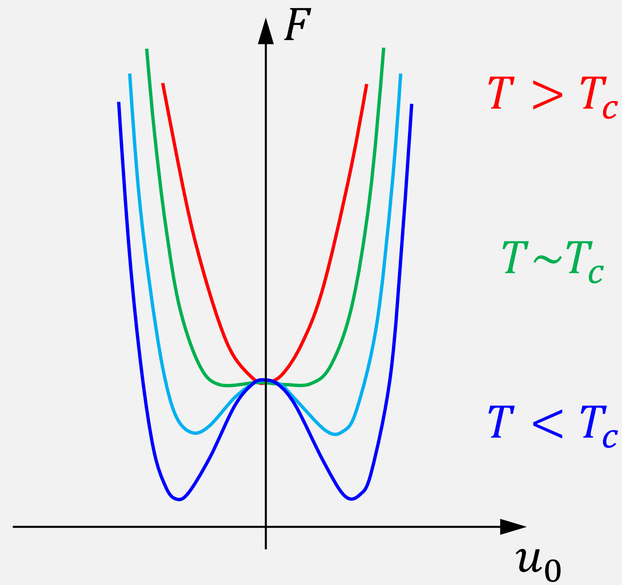
$$I_{sat} \propto \|\overrightarrow{u_0}\|^2$$



u_0: order parameter of the transition

Free energy

$$F = C + \frac{1}{2} r_0 (T - T_c)\, {u_0}^2 + \frac{1}{4} {u_0}^4$$



SOLEIL SYNCHROTRON

Ultrafast light control of the physical properties of CDW compounds ?

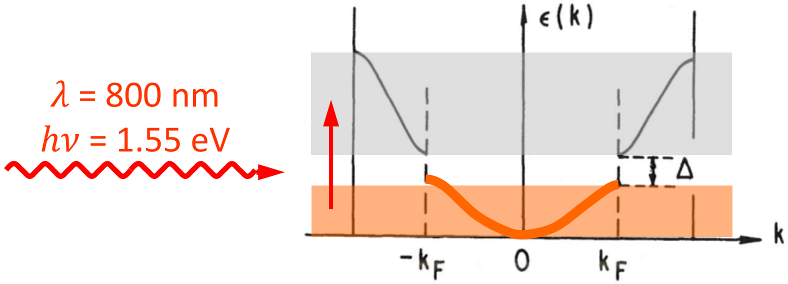
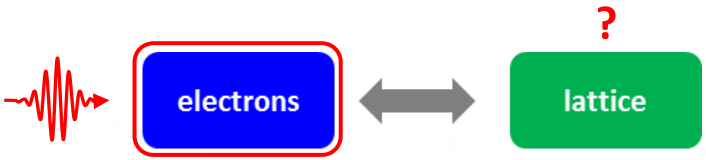


Photo-excitation @ 800 nm

↕

Electronic transitions across the CDW gap

[timescale : few 10 fs]

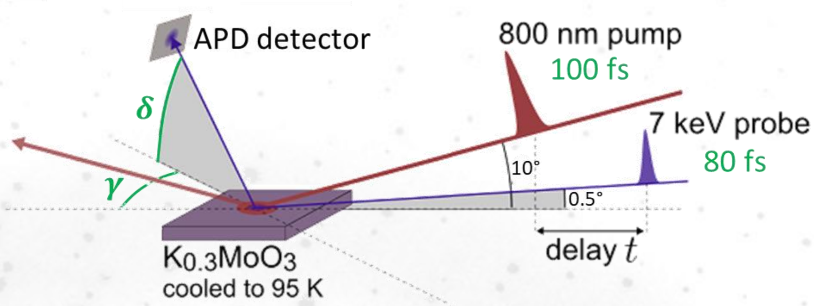


e-ph coupling…

Does photo-excitation affect the CDW structural modulation ?

On which timescale ?

- **Femto-slicing source @ SLS:**



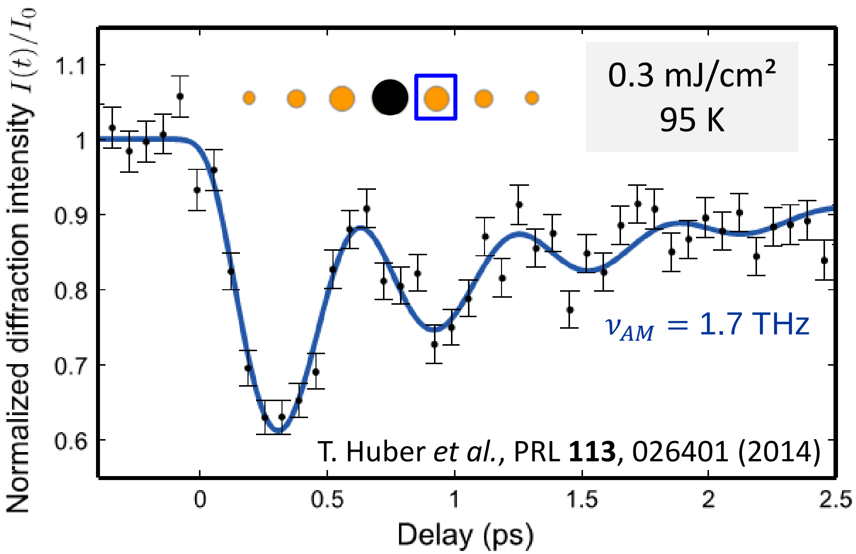
Count rate: 2 ph/s…

T. Huber *et al.*, PRL **113**, 026401 (2014)

SOLEIL SYNCHROTRON

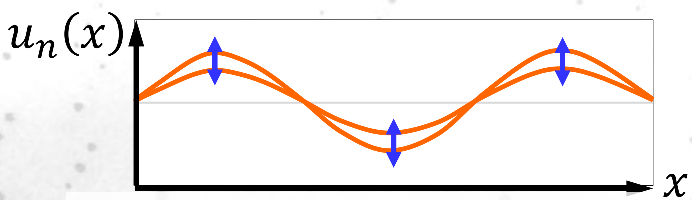
Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1 \;\; [4 - q_b] \;\; \bar{\tfrac{1}{2}}\right)$ - Low fluence**



$$I_{sat} \propto \|\overrightarrow{u_0}\|^2$$

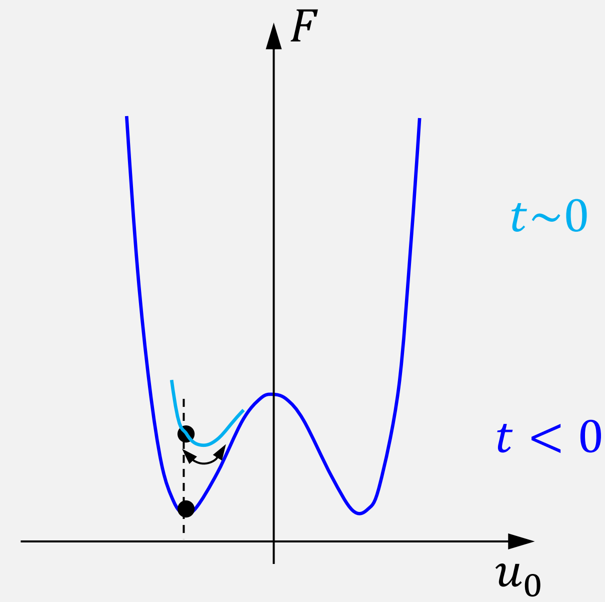
Oscillations of the order parameter u_0 in time



Amplitude mode (AM) of the CDW

Displacive excitation of the AM:

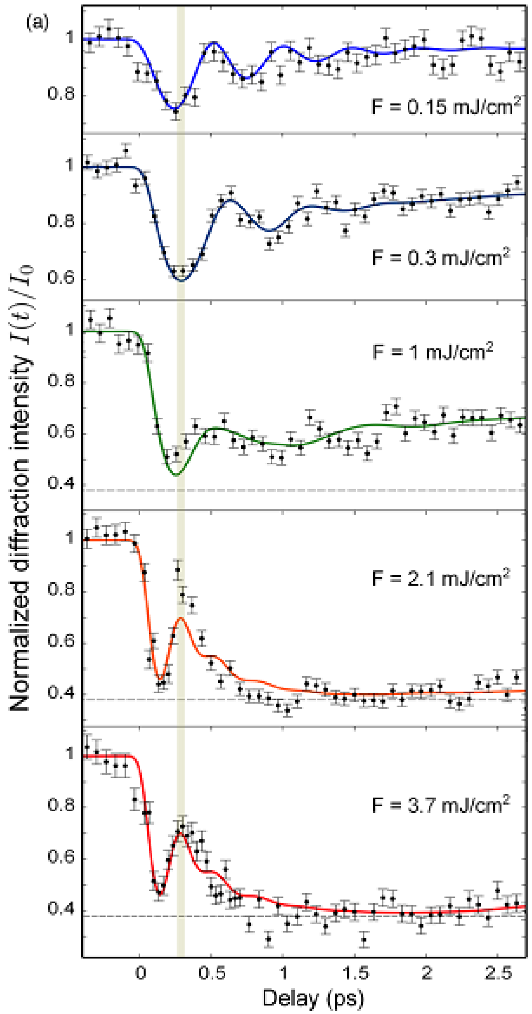
$$\frac{u_0(t)}{u_0(t<0)} = A_{disp}\left[\cos 2\pi\nu_{AM}(t)\; e^{-t/\tau_{AM}} \; - \; e^{-(t)/\tau_{disp}}\right]$$



Coherent harmonic motions of atoms in their quasi-equilibrium potential

Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1\ \ [4-q_b]\ \ \bar{\frac{1}{2}}\right)$ - Higher fluences**



- $F =$ **1mJ/cm²**

→ The recovery time of satellite peak intensity increases

→ Coherent oscillations: hardly observable

- $F >$ **1mJ/cm²**

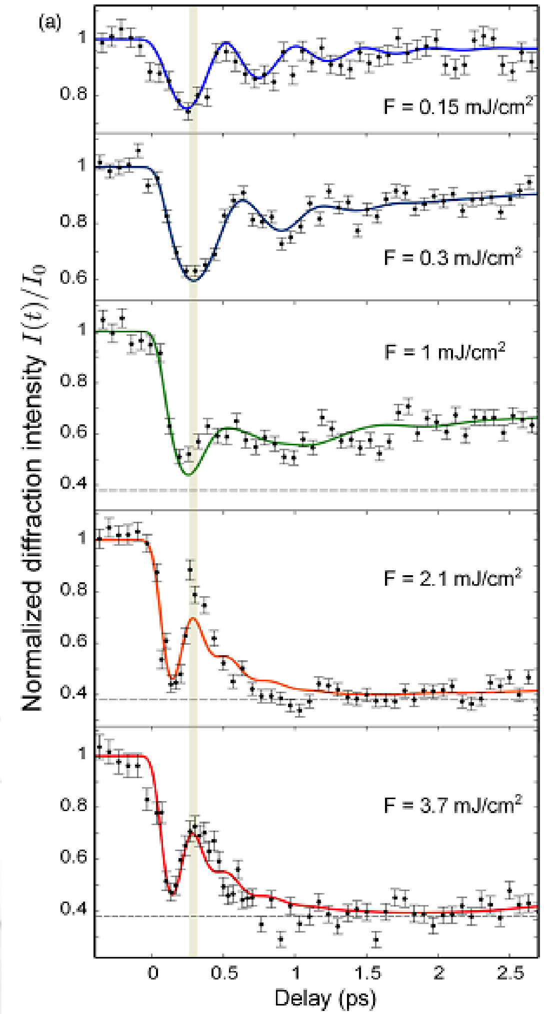
→ No recovery of satellite peak intensity within 10 ps

→ Oscillation frequency doubled w/r to the low fluence case

Significant changes of the atomic potential surface

Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

- **Time-dependence of the satellite $\left(1\ \ [4-q_b]\ \ \frac{\bar{1}}{2}\right)$ - Higher fluences**



- **Free energy vs laser excitation** [$\eta \propto$ laser fluence]

$$F = F_0 + \frac{1}{2}\left[\eta e^{-\frac{t}{\tau}} - 1\right] u_0{}^2 + \frac{1}{4} u_0{}^4$$

- **Equation of motion to be solved:**

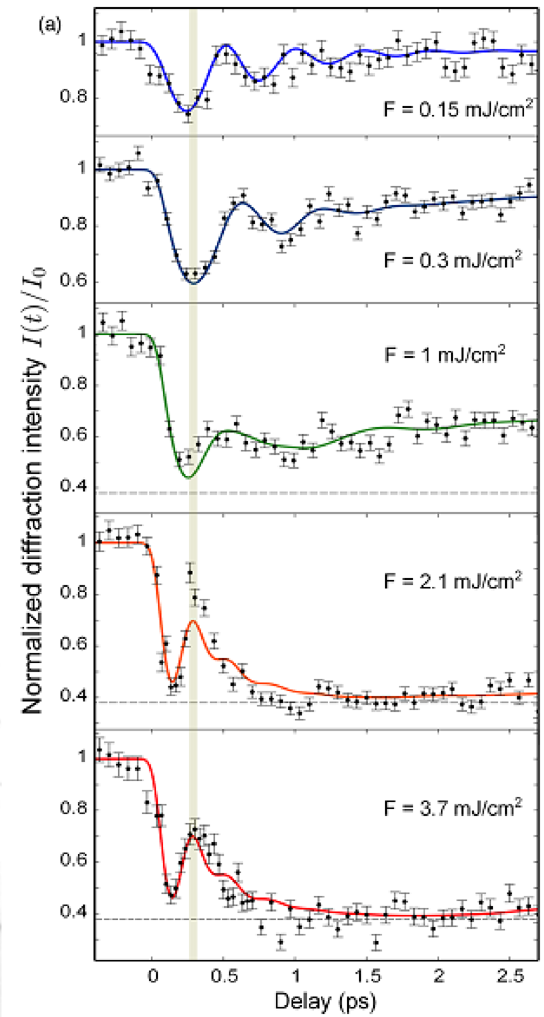
$$C_1 \frac{\partial^2 u_0(t)}{\partial t^2} = -\frac{dF}{du_0} - C_2 \gamma(t) \frac{\partial u_0(t)}{\partial t}$$

Non-harmonic motions of atoms

T. Huber *et al.*, PRL **113**, 026401 (2014)

Coherent structural dynamics in blue bronze ($K_{0.3}MoO_3$)

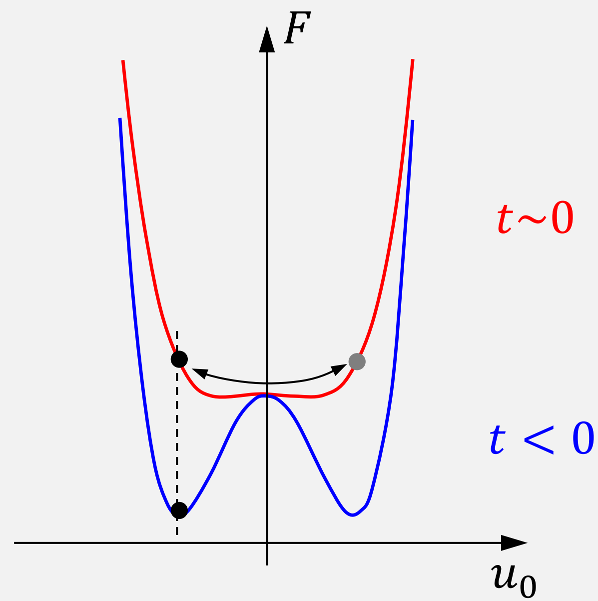
- **Time-dependence of the satellite $\left(1\ [4-q_b]\ \frac{\bar{1}}{2}\right)$ - Higher fluences**

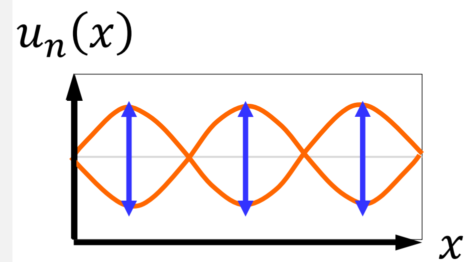


- **Origin of the fast oscillations above 1 mJ/cm² ?**

Free energy

$$F = F_0 + \frac{1}{2}\left[\eta e^{-\frac{t}{\tau}} - 1\right] {u_0}^2 + \frac{1}{4}{u_0}^4$$





Ultrafast change of atomic potential symmetry

Thank you !