Photoinduced structural dynamics investigated by pump-probe diffraction

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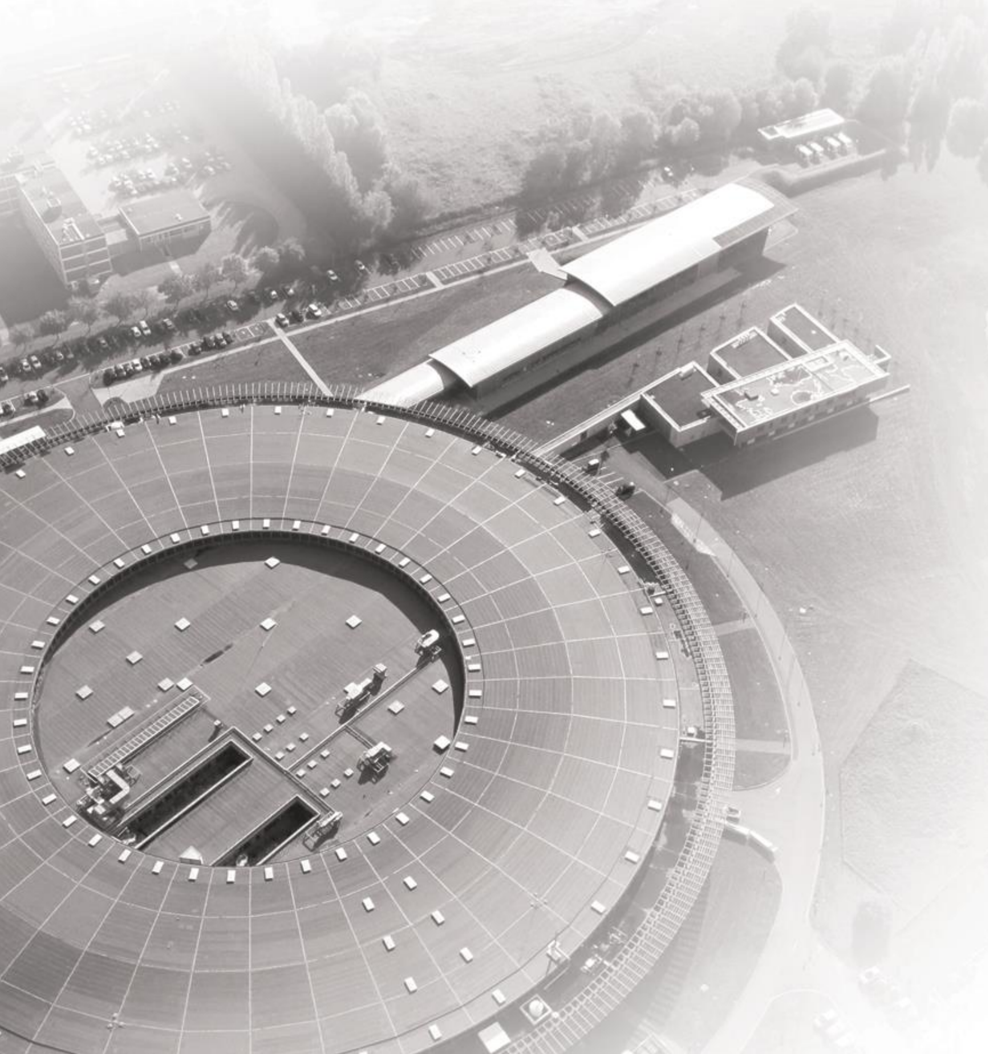


I. Scientific context

II. Pump-probe diffraction

- Pump-probe scheme
- Time resolution, synchronization
- Short X-ray pulse sources
- Specific geometrical constraints

III. Tracking structural dynamics with pump-probe diffraction

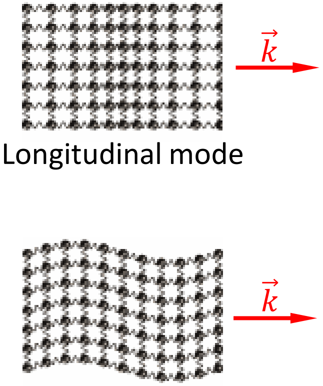
- Structural information brought by diffraction
- Coherent phonons
- Photoinduced phase transitions
- Photoinduced strain and temperature elevation

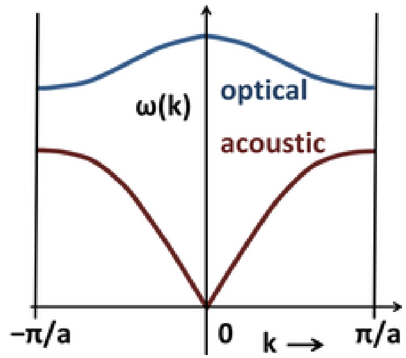
Photoinduced structural dynamics investigated by pump-probe diffraction
Part I. Scientific context

1- Crystals at thermodynamic equilibrium

Atomic displacements : sum of normal modes

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





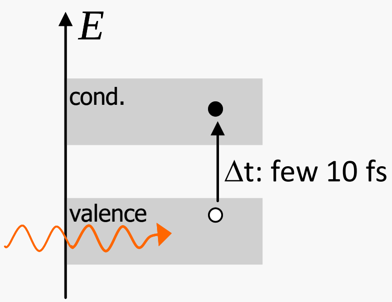
Phonon spectrum $(\omega,\vec{k})_\lambda$

→ **Experiments in the <u>frequency domain</u>: inelastic neutron scattering, Raman scattering…**

2- Photoinduced, out-of-equilibrium structural dynamics

- **Excitation of electronic transitions**

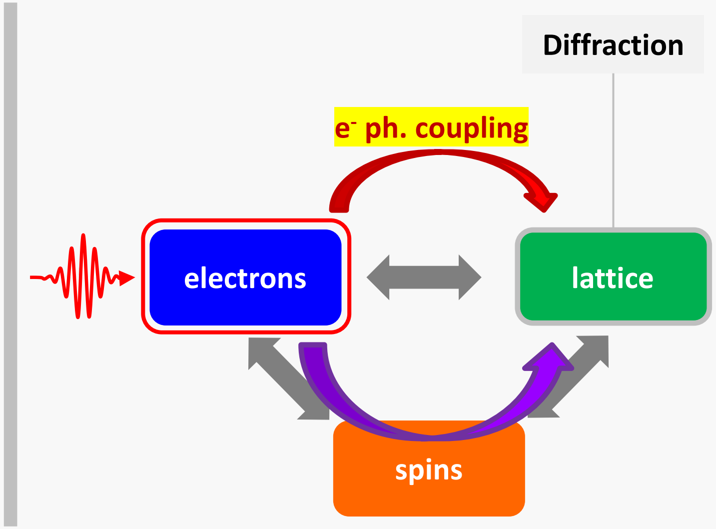
UV, optical and near-infrared photons [200 nm - 1.5 µm, 0.8 - 6.2 eV]
[Binding energies of the valence electrons]



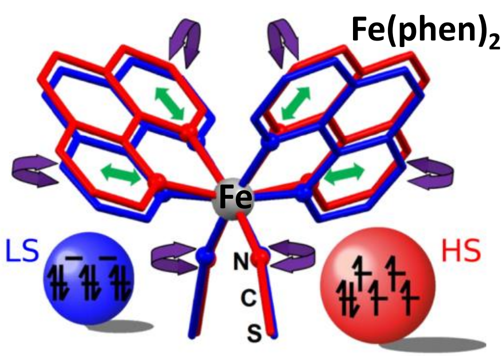
λ = 800 nm
E = 1.55 eV

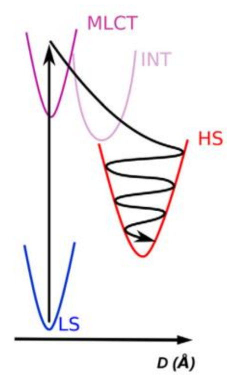
Within few 10 fs:
electronic transitions in a « frozen lattice »

→ Transiently decoupled electronic and lattice degrees of freedom
→ **Out-of-equilibrium dynamics**



Indirect e⁻ ph. coupling: **Spin crossover compounds** [Collet & Guionneau, CR Chim 21 1133 (2018)]
Angular momentum transfer from spins to lattice following ultrafast demagnetization [C. Dornes *et al.*, Nature **565**, 209 (2019)]





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

2- Photoinduced, out-of-equilibrium structural dynamics

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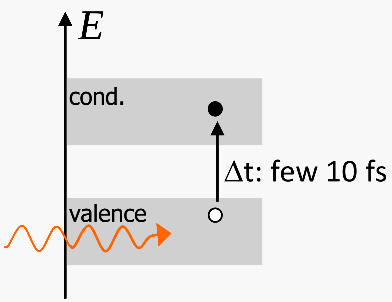
[Binding energies of the valence electrons]



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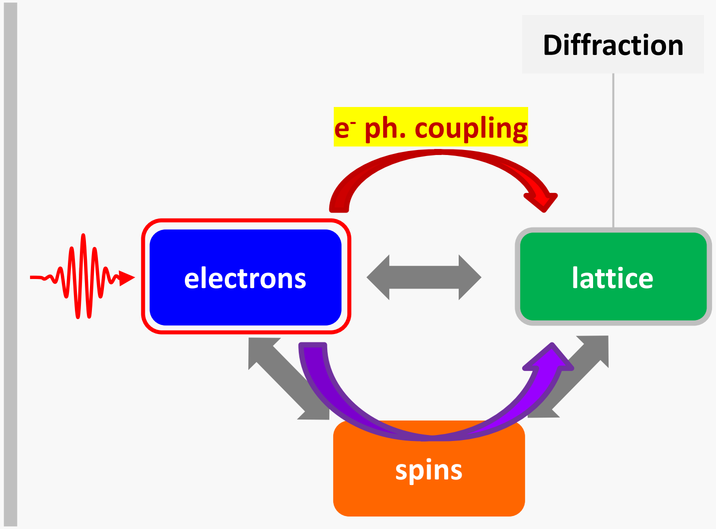

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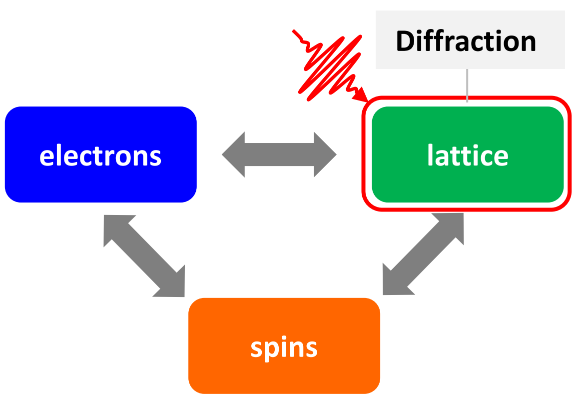
- **Excitation of vibrations**

Far-infrared photons [6 - 300 µm, 4 - 210 meV]

[Phonon energies]

→ **Direct excitation of a phonon mode**
→ **Indirect excitation of phonon modes via anharmonic couplings ("nonlinear phononics")**
Mankowsky *et al.*, Rep. Prog. Phys. **79**, 064503 (2016)



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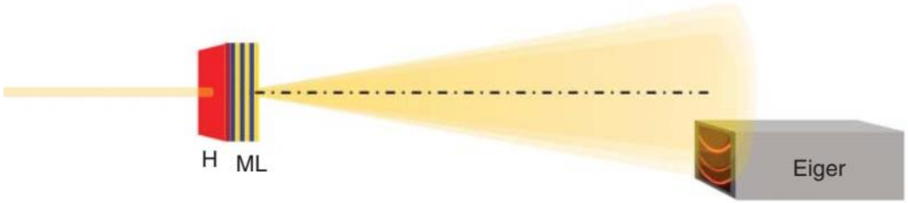
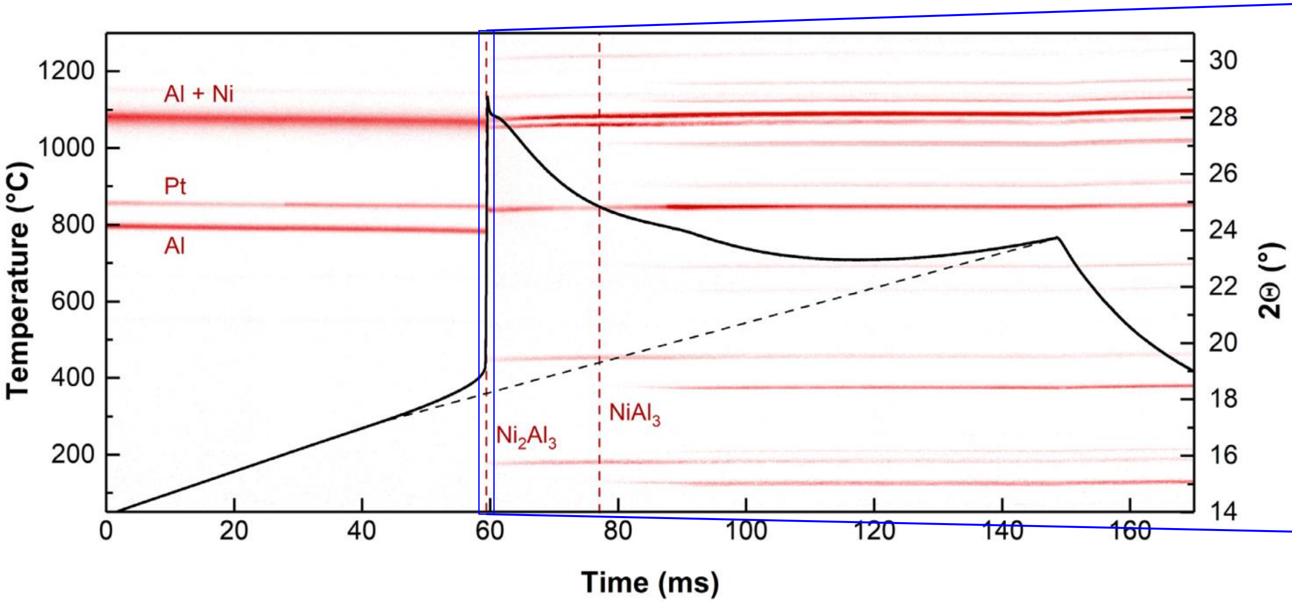
0- Real time experiments

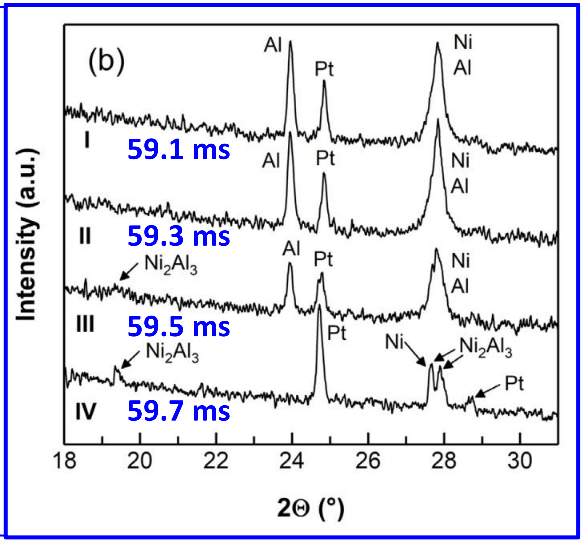
- **Example: study of the exothermic solid-state transformation [Ni+Al → $NiAl_3$]**



A 2 µm thick Ni/Al multilayer (ML) is heated at a rate of ~**5700 K/s** by using the heater H

T. Neuhauser et al. / Acta Materialia **195,** 579587 (2020)



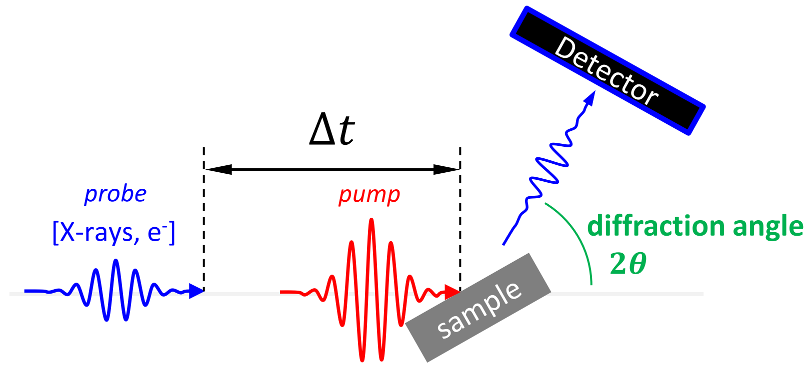


Several factors limit the time resolution in « real time » experiments:

- Limited detector frame rate
- Limited X-ray flux
- Need to scan sample angles to retrieve the relevant information

Photoinduced structural dynamics investigated by pump-probe diffraction
Part II. Pump-probe diffraction

1- Pump-probe scheme

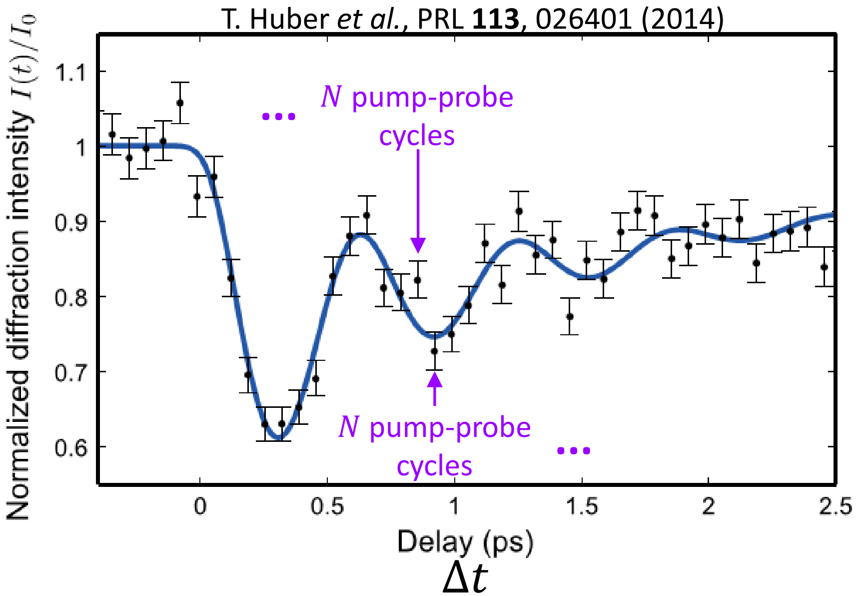


A pump-probe cycle with delay Δt

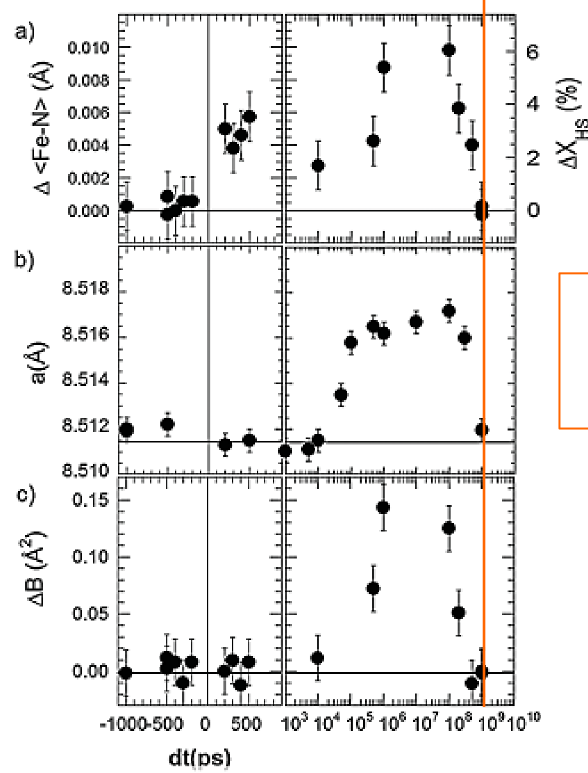
- **One pump-probe cycle ↔ diffraction signal usually too low!**

→ N pump-probe cycles needed for each Δt
→ Study of **reversible processes**

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



Typical relaxation time:
1 ms (or more)

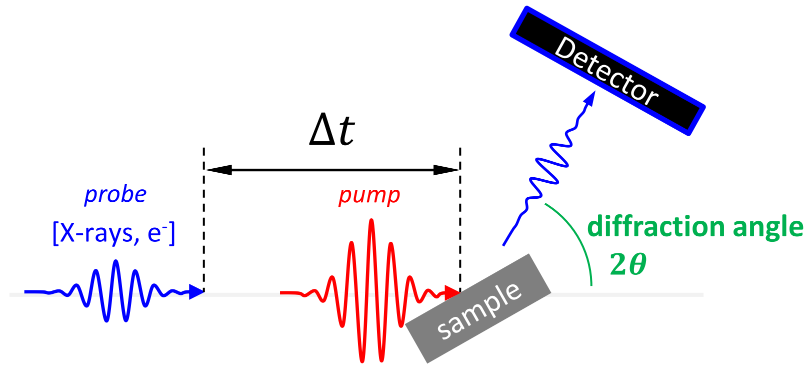


M. Lorenc *et al.*, PRL **103**, 028301 (2009)

Repetition rate of the pump-probe cycles:
1 Hz - 1kHz

Photoinduced structural dynamics investigated by pump-probe diffraction
Part II. Pump-probe diffraction

1- Pump-probe scheme

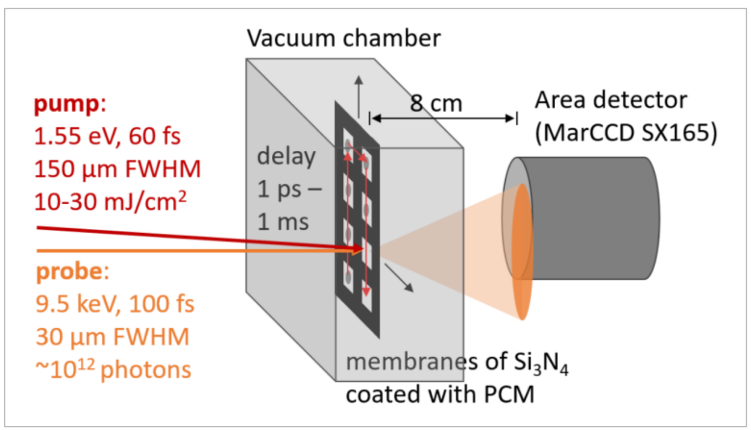


A pump-probe cycle with delay Δt

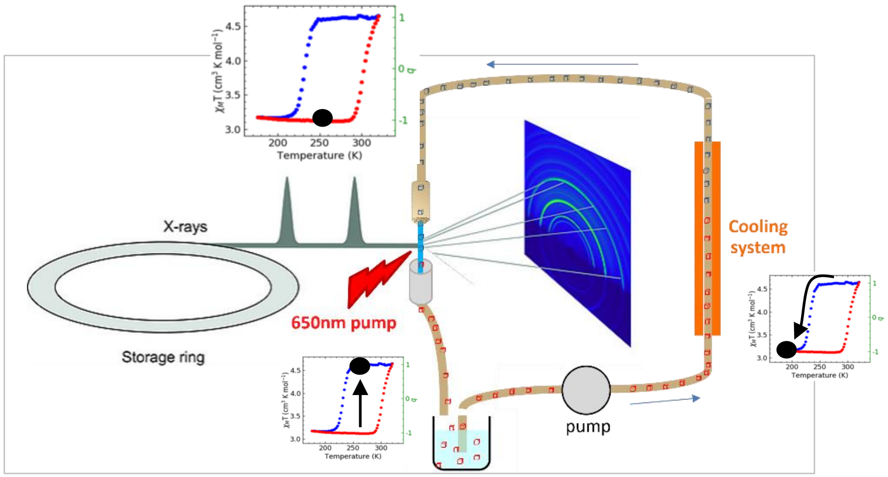
- **One pump-probe cycle ↔ diffraction signal usually too low!**

→ N pump-probe cycles needed for each Δt
→ Study of **reversible processes**

- **Irreversible processes : sample must be renewed between each pump-probe sequence ("single-shot" experiments)**



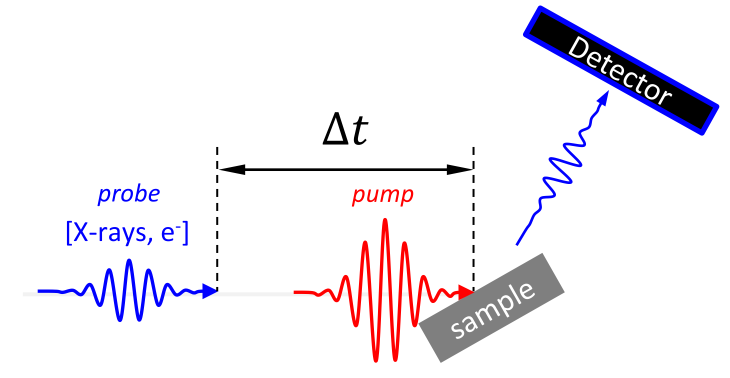
Study of an amorphous-to-liquid-to-liquid photoinduced phase transition. The sample is translated after each pump-probe sequence. [P. Zalden *et al.*, Science **364**, 1062-1067 (2019)]



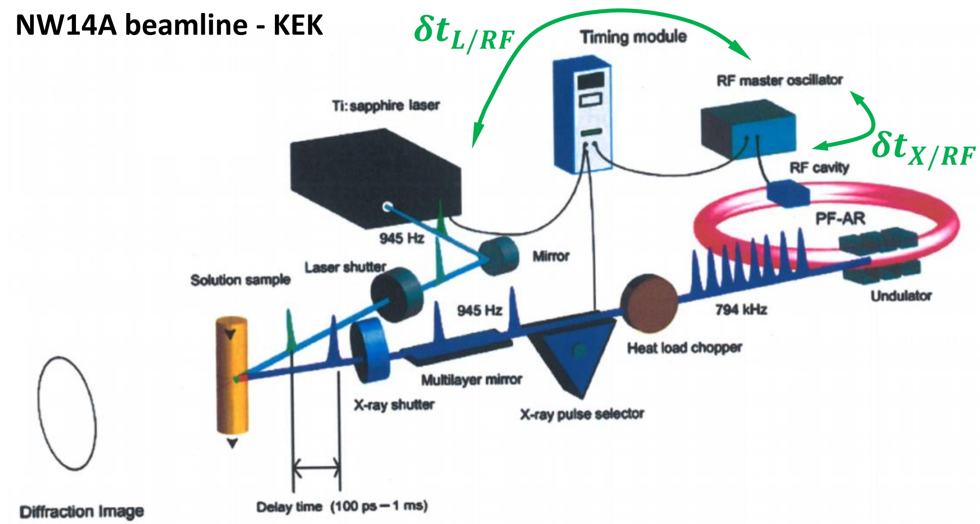
"Streaming crystallography", Eric Collet
M. Hervé et al, Nat Comm **15**, 267 (2024)

Photoinduced structural dynamics investigated by pump-probe diffraction
Part II. Pump-probe diffraction

2- Time resolution and relevant timescales

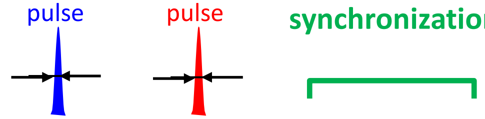


a pump-probe cycle with delay Δt



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

- **Time resolution**



$$\delta t^2 = \delta t_p{}^2 + \delta t_P{}^2 + \delta t_{jitter}{}^2$$

Time tools *were developed to retrieve δt_{jitter} on a shot-to-shot basis and correct the pump-probe delay accordingly.*

→ M. Harmand *et al.*, Nature Photonics **7**(3), 215 (2013).

- **Timescale of the fastest structural dynamics...**

Atomic vibrations:
$E_{ph} = \hbar\omega \sim 20$ meV $\Rightarrow$ **$T_{osc} \sim 200$ fs**

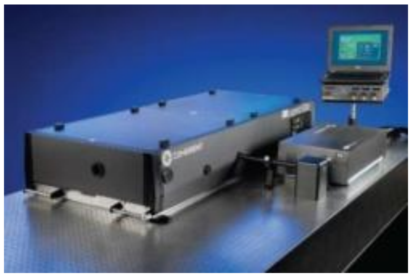
Need for < 100 fs time resolution, < 100 fs pump and probe pulses

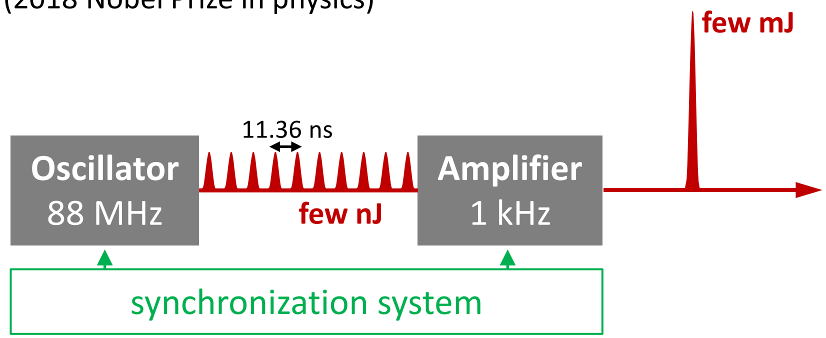
Photoinduced structural dynamics investigated by pump-probe diffraction
Part II. Pump-probe diffraction

3a- Sources of ultrashort pump pulses

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

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



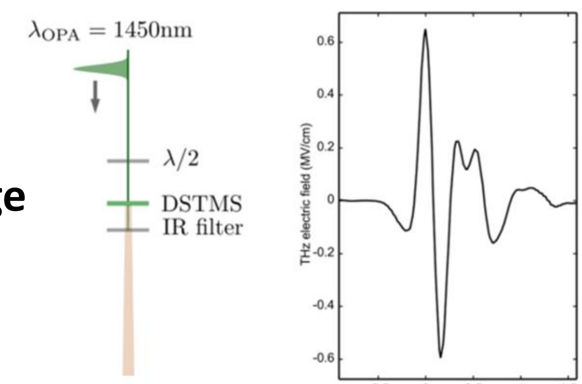


- **Optical parametric amplifiers: ~ 40 fs pulses in the UV to near-IR range**

J.-Y. Zhang, "Optical parametric generation and amplification", Routledge;CRC (2019)

- **Optical rectification: ~ ps pulses in the THz (far-infrared) range**

H. Hirori *et al.*, APL **98**, 091106 (2011)
C. P. Hauri *et al.*, APL **99**, 161116 (2011)

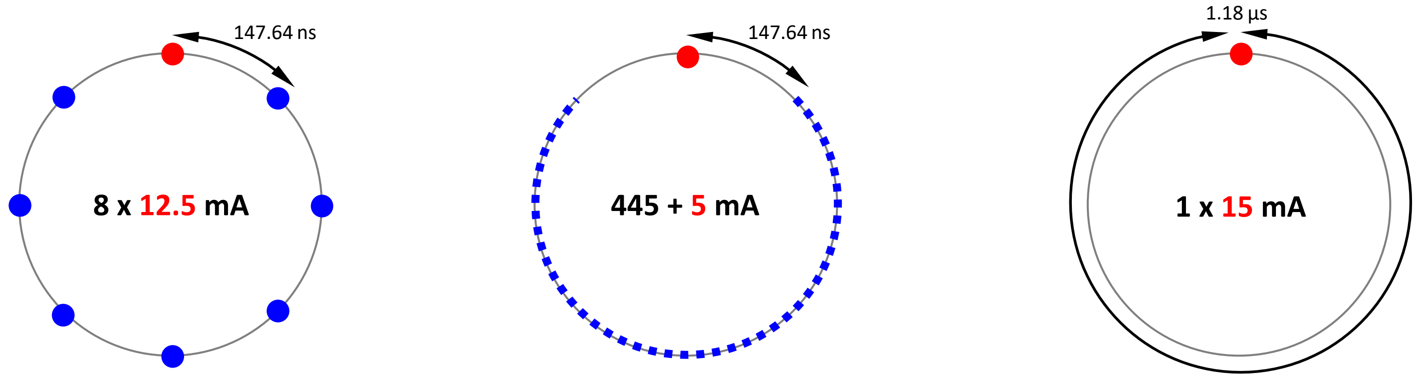


T. Huber *et al.*, APL **107**, 091107 (2015)

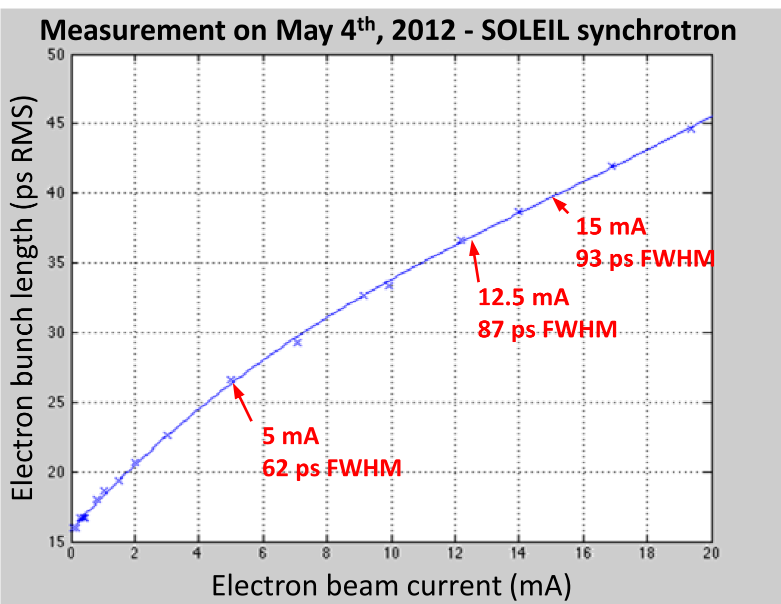
3b- Sources of (ultra)short, hard X-ray pulses [> 5 keV]

1982: first pump-probe diffraction experiment making use of single X-ray pulses (CHESS synchrotron)
→ B. C. Larson *et al.*, PRL **48**, 337-340 (1982)

- **100 ps pulses from synchrotrons**



Bunch modes for time-resolved experiments at SOLEIL



Modes dedicated to time-resolved experiments:

Isolated bunch with high current

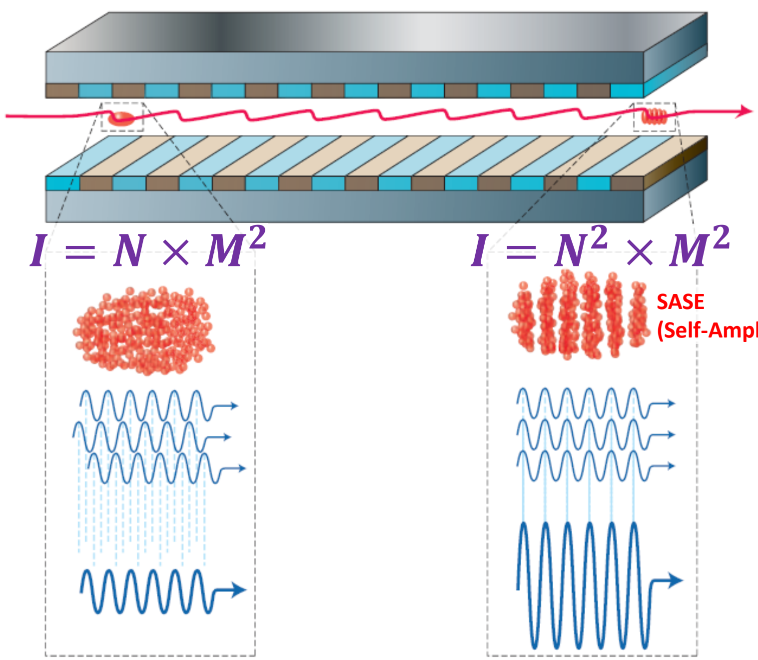
Isolated bunch → Enables pulse selection

High current → Optimized count rate from selected pulses

10^6 ph./pulse
@1kHz
100 ps duration

3b- Sources of (ultra)short, hard X-ray pulses [> 5 keV]

- **few 10 fs X-ray pulses: X-FELs (2009 →)**



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

- 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

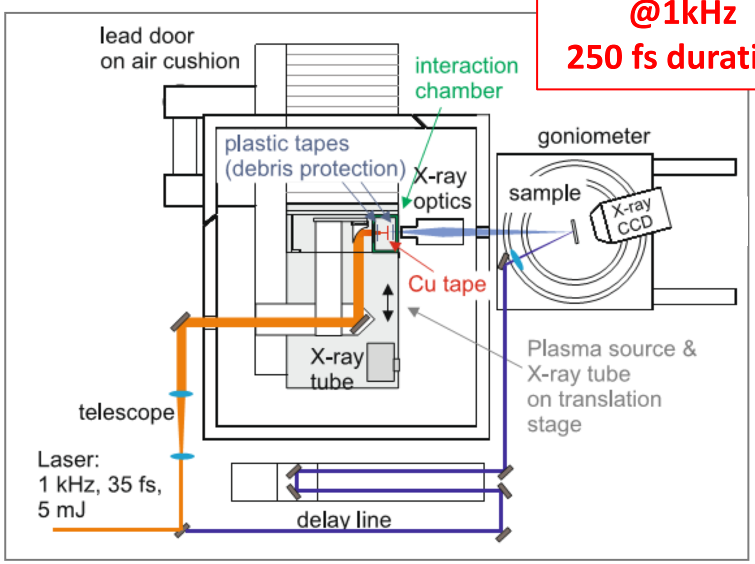
10^{11} ph./pulse
@100Hz
80 fs duration

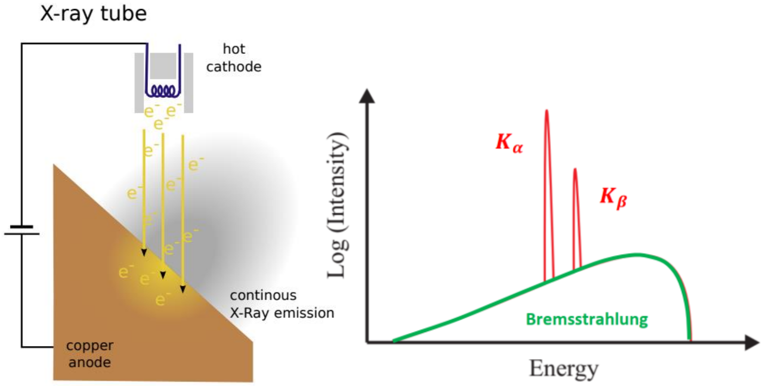
3b- Sources of (ultra)short, Å-wavelength pulses

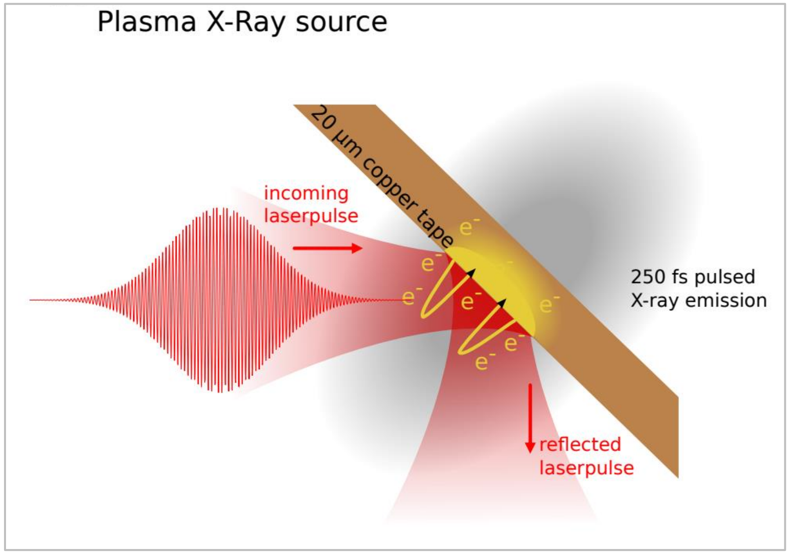
- **X-ray plasma sources (1994 →)**

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)

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







A. von Reppert: "Ultrafast Magnetostriction in Dysprosium studied by Femtosecond X-Ray diffraction" MSc thesis, Universität Potsdam (2015)

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

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Part II. Pump-probe diffraction

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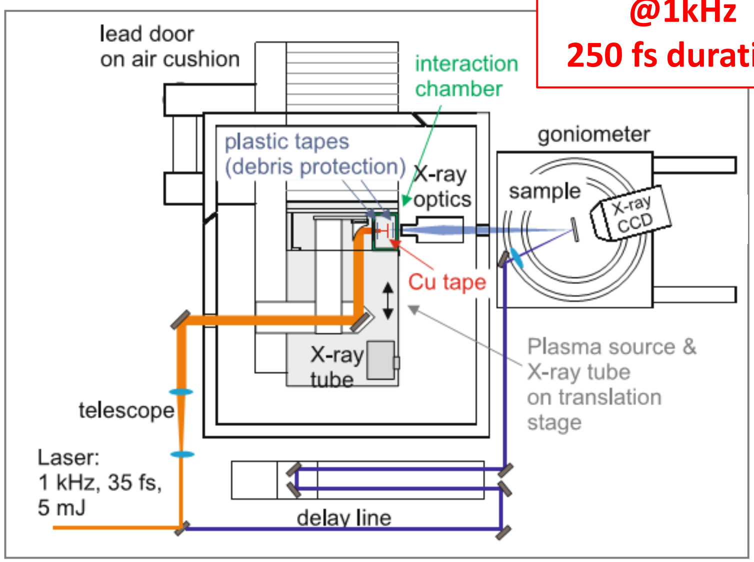

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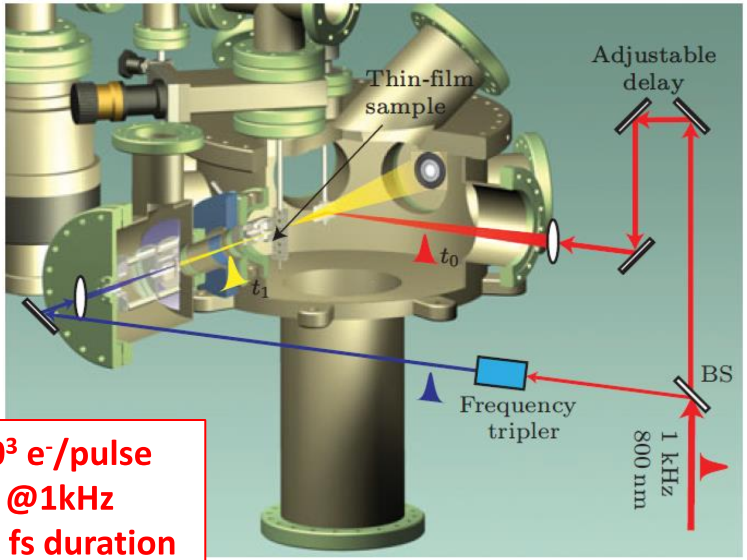
- Emission of X-rays with $K_\alpha(Cu)$ wavelength [λ= 1.54 Å]

• Ultrafast electron diffraction (2003 →)

W.-X. Liang *et al.*, Chinese Phys. Lett. **26**, 020701 (2009)

R. Srinivasan *et al.*, Helvetica Chimica Acta **86**, 1761-1799 (2003)



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

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

Photoinduced structural dynamics investigated by pump-probe diffraction
Part II. Pump-probe diffraction

3c- Available pump-probe diffraction setups for users [Europe]

X-ray free electron lasers
MID & FXE at Eu-XFEL, Bernina at SwissFEL

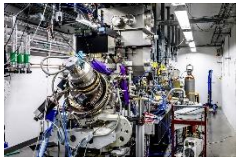
- < 100 fs X-ray pulses

~10^{12} photons/pulse
$\Delta E/E \sim 10^{-3}$

100 Hz [SwissFEL]
10 Hz/4.5 MHz [Eu-XFEL]

Short pulse facility, Lund (Sweden)
femtoMAX beamline

- < 160 fs X-ray pulses



10^{6} photons/pulse
$\Delta E/E \sim 10^{-2}$

10 Hz

Synchrotrons
ID09 at ESRF, KMC3-XPP at BESSYII

- 100 ps X-ray pulses

10^{6} photons/pulse
$\Delta E/E \sim 10^{-4}$

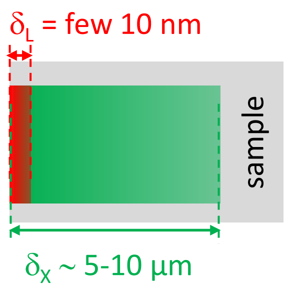
1 Hz to 3 kHz [ID09]
1 to 625 kHz [XPP]

- 10 ps X-ray pulses (low-α, BESSY)

~10^{3} photons/pulse
$\Delta E/E \sim 10^{-4}$

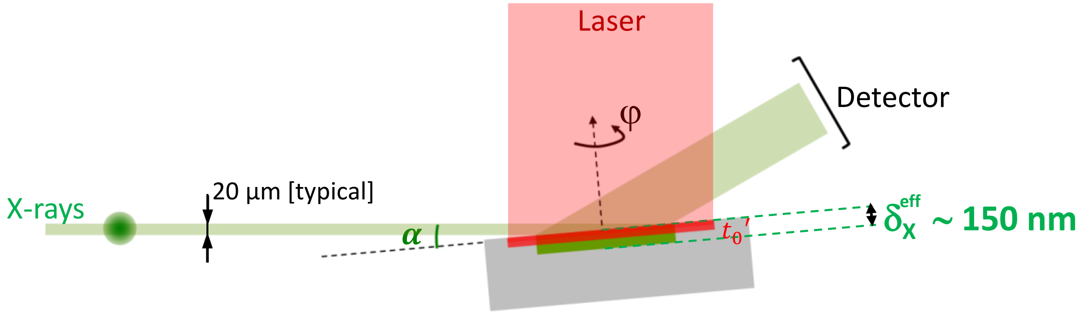
1 to 625 kHz [XPP]

4a- Methods specific to pump-probe X-ray diffraction : grazing incidence geometry



Normal (or large) incidence of X-rays and laser beams
!! $V_{probed} \gg V_{pumped}$!!

- **Nanocrystals (dilute) and thin-films can be studied using unconstrained diffraction geometries…**
- **Bulk crystals: a grazing incidence of the X-ray beam is required**



$$\delta_X^{eff} = \delta_X \sin\alpha$$

Beware - The grazing angle α should be small, but larger that the critical angle for total external reflection α_c:

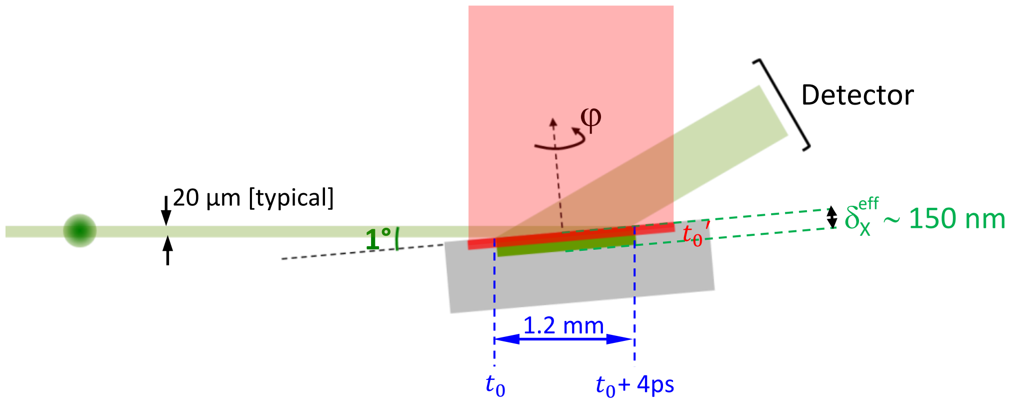
$$\alpha_c \approx \lambda\sqrt{\frac{\rho_{at}\, r_e}{\pi}}$$

r_e: classical radius of the electron ($2.818\ 10^{-15}$ m)

Orders of magnitude at 7 keV: $\alpha_c \sim 0.3 - 0.4°$ $\Longrightarrow$ $\alpha \sim 0.5 - 1°$

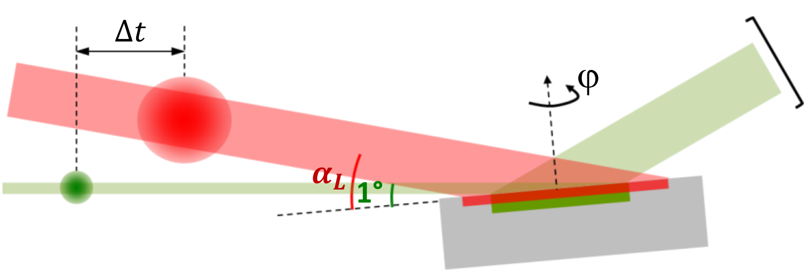
4b- Methods specific to pump-probe X-ray diffraction : collinear X-ray and laser beams

- **Grazing incidence geometry**

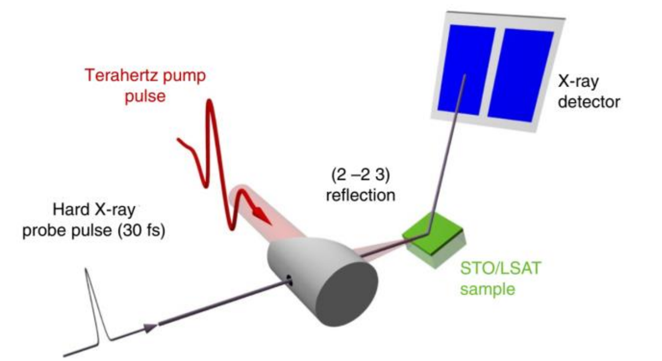


!! Loss of effective time resolution from the difference in relative arrival times between the pump and X-ray beams !!

- **Collinear pump & probe beams**



$\alpha_L < 10°$



Use of mirrors with through holes
XPP@LCLS [Kozina, Nature 2019]

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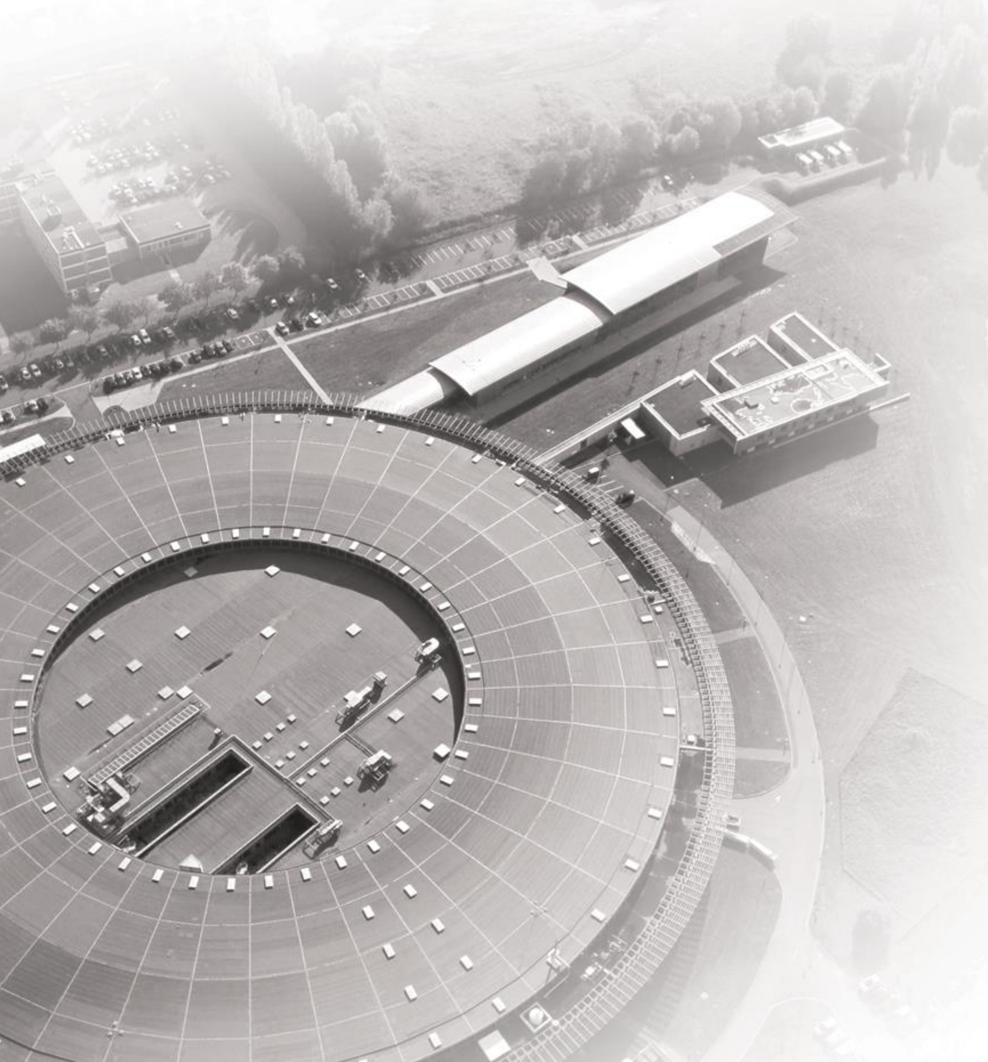

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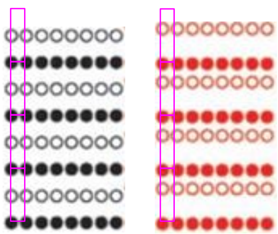
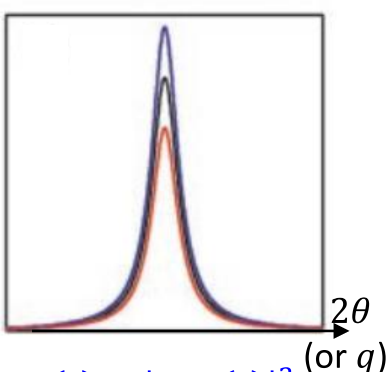
1- Structural information brought by the diffraction signals

M. Bargheer *et al.*, ChemPhysChem **7**, 783 – 792 (2006)

Change of the atomic motif
[coherent optical phonons]



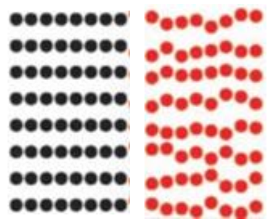
Intensity modulation



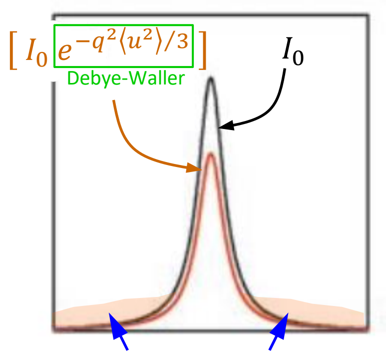
$$I(t) \propto |F_{hkl}(t)|^2$$

$\boldsymbol{F_{hkl}}$: structure factor
$\boldsymbol{q}$: scattering vector length
$\boldsymbol{2\theta}$: diffraction angle

Disorder
[non-coherent phonons]



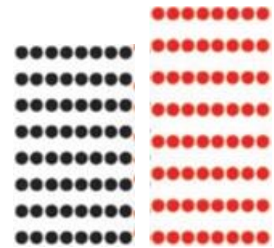
Intensity reduction



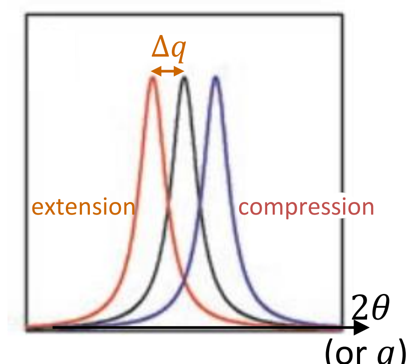
(Thermal) diffuse scattering

$\boldsymbol{\langle u^2\rangle}$: mean square displacement from ideal positions

Strain
[photostriction]



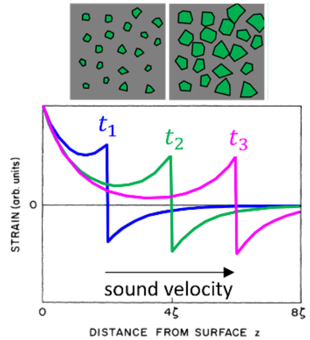
Peak shift



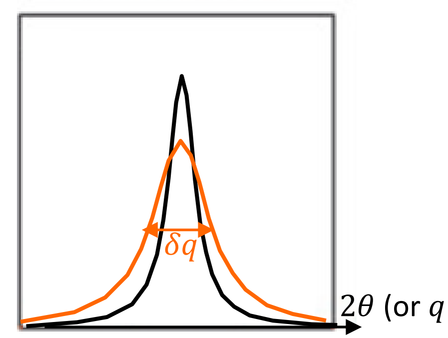
$$\varepsilon = \Delta q / q$$

$\boldsymbol{\varepsilon}$: strain

Limited correlation length or inhomogeneous strain
[Phase growth, strain wave propagation]



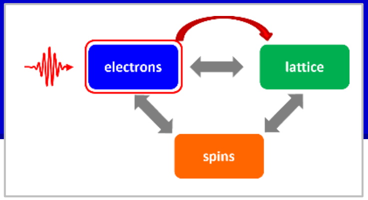
Broadening



$$\delta q \propto \delta\varepsilon \quad \text{or} \quad \delta q = \frac{2\pi}{\xi}$$

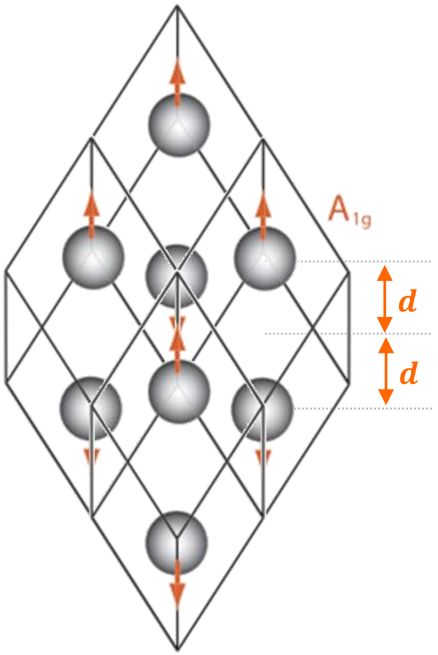
$\boldsymbol{\xi}$: correlation length or crystal size

Photoinduced structural dynamics investigated by pump-probe diffraction
Part III. Tracking structural dynamics with pump-probe diffraction



2- Coherent optical phonons

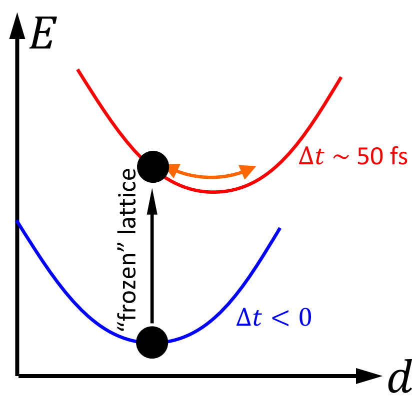
Coherent phonons give rise to atomic motions with a fixed phase relation between them, homogeneously in the sample



Example: coherent A1g phonon in bismuth
Atoms are moving in-phase from one unit cell to another

- **Displacive excitation of coherent phonons (DECP)**

Strong coupling between the initial/final electronic state and one particular vibrational mode
→ Shift of the local minimum of the potential energy along the vibrational mode coordinate



d: displacement along the normal coordinates of the A_{1g} mode

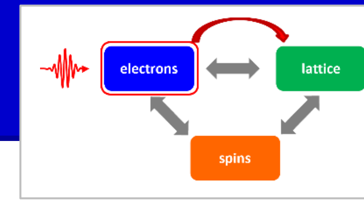
All the atoms of the excited volume are simultaneously significantly displaced with respect to the new quasi-equilibrium position: they start to oscillate in phase along the normal coordinate of the mode.

Further reading on coherent optical phonons:

R. Merlin, Solid State Commun. **102**, 207-220 (1997)
H.J. Zeiger *et al.*, Phys. Rev. B **45**, 768-778 (1992)
Y.-X. Yan *et al.*, J. Chem. Phys. **83**, 5391 (1985)
T. Stevens *et al.*, Phys. Rev. B **65**, 144304 (2002)

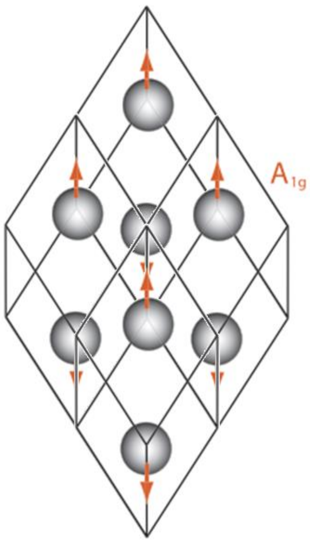
Photoinduced structural dynamics investigated by pump-probe diffraction

Part III. Tracking structural dynamics with pump-probe diffraction

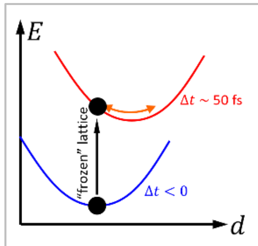


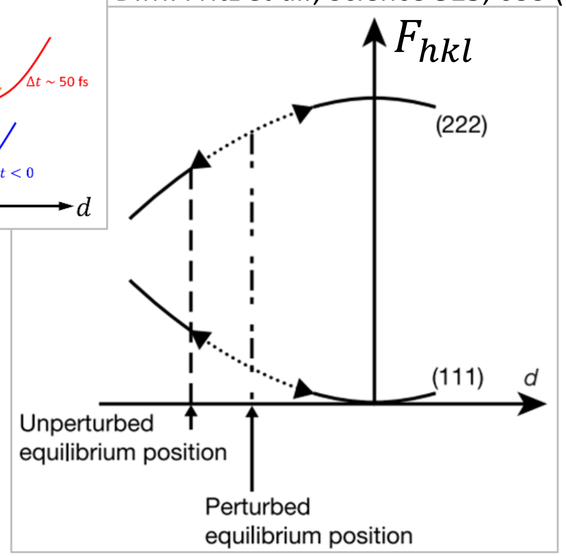
2- Coherent optical phonons

K. Sokolowski-Tinten *et al.*, Nature **422**, 287 (2003)
D.M. Fritz *et al.*, Science **315**, 633 (2007)



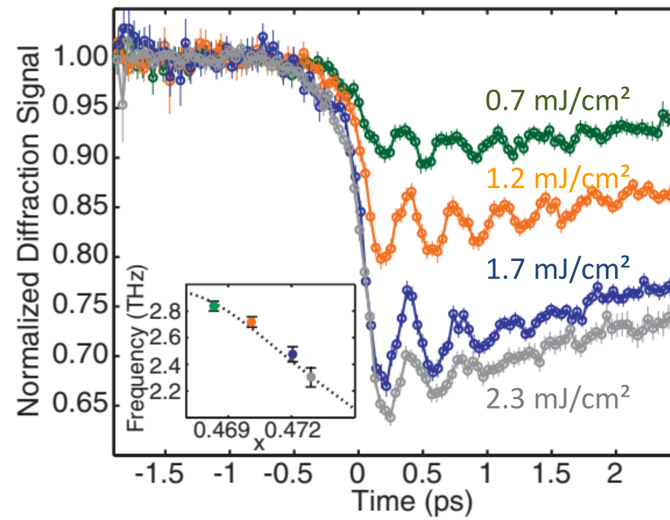
Coherent A1g phonon in bismuth
≡ a time-dependent motif in the unit cell



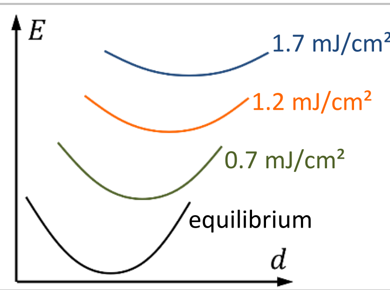


Time-dependent structure factor

Time-dependent (111) Bragg peak intensity

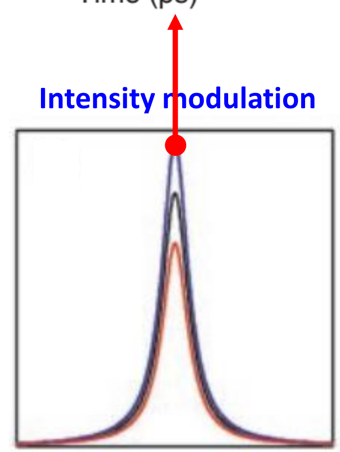


Photoinduced bond softening in Bismuth



$$E = C + \frac{1}{2}\mu\omega^2 d^2$$

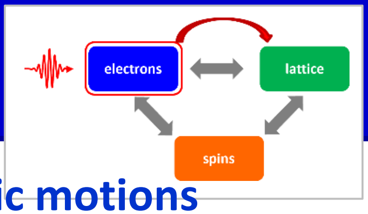
Intensity modulation



$$I(t) \propto |F_{hkl}(t)|^2$$

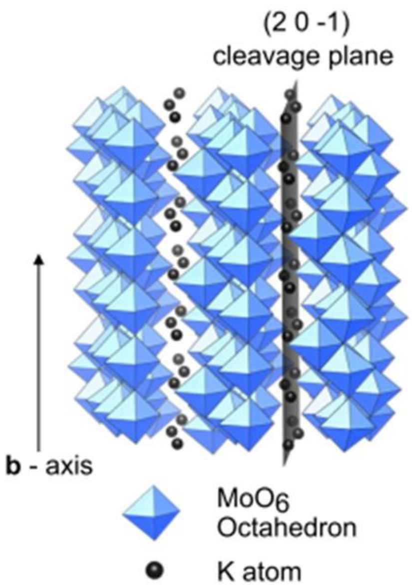
Coherent optical phonons:
exploration of the atomic potential in photo-excited states

Photoinduced structural dynamics investigated by pump-probe diffraction
Part III. Tracking structural dynamics with pump-probe diffraction

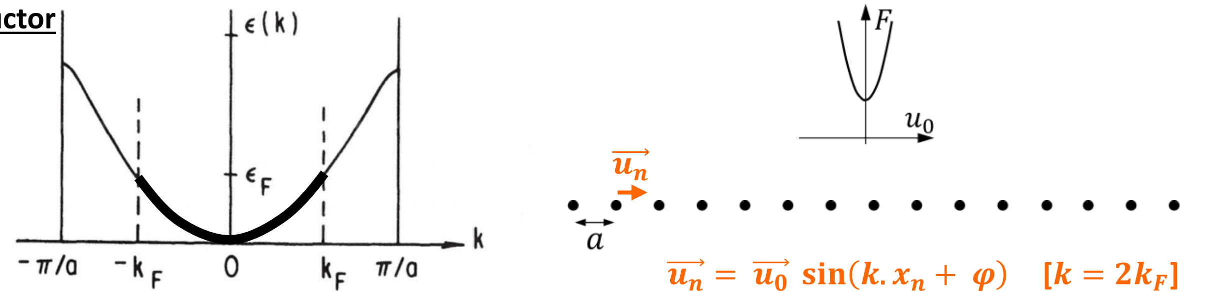


3a- Photoinduced phase transitions (PIPTs) achieved through coherent atomic motions

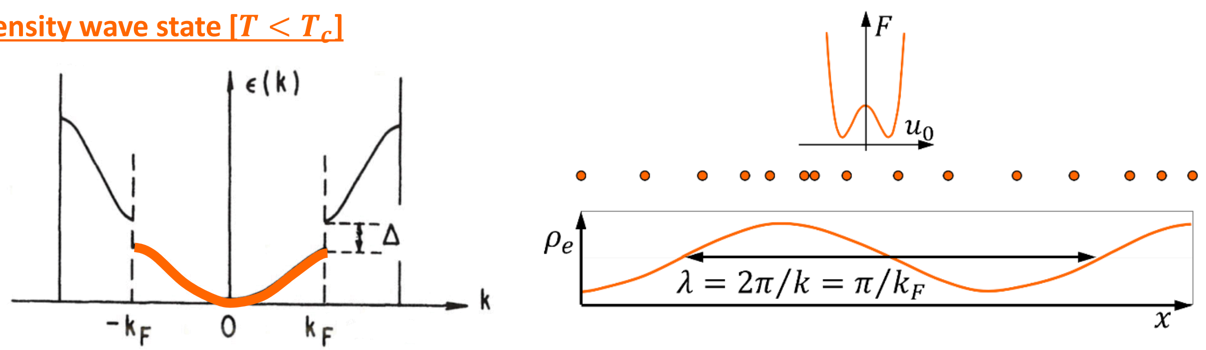
- **Blue bronze $K_{0.3}MoO_3$**



1D-conductor



Charge density wave state $[T < T_c]$ (CDW)

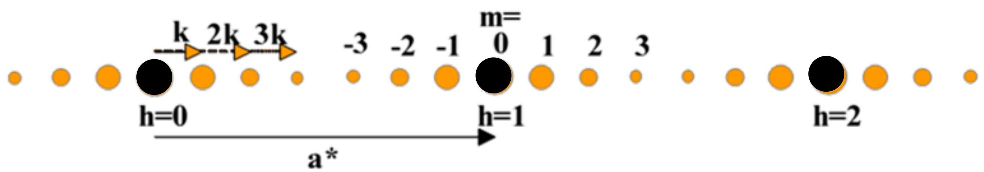


Gain in electronic energy

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

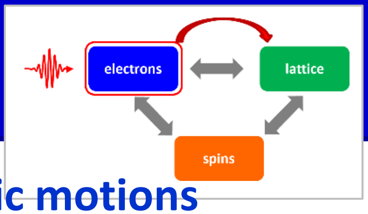
Strong e-ph coupling, CDW transition occurs along the coordinate u_0 of the vib. mode with $\vec{k} = 2\vec{k_F}$

- **Diffraction pattern: satellite peaks**



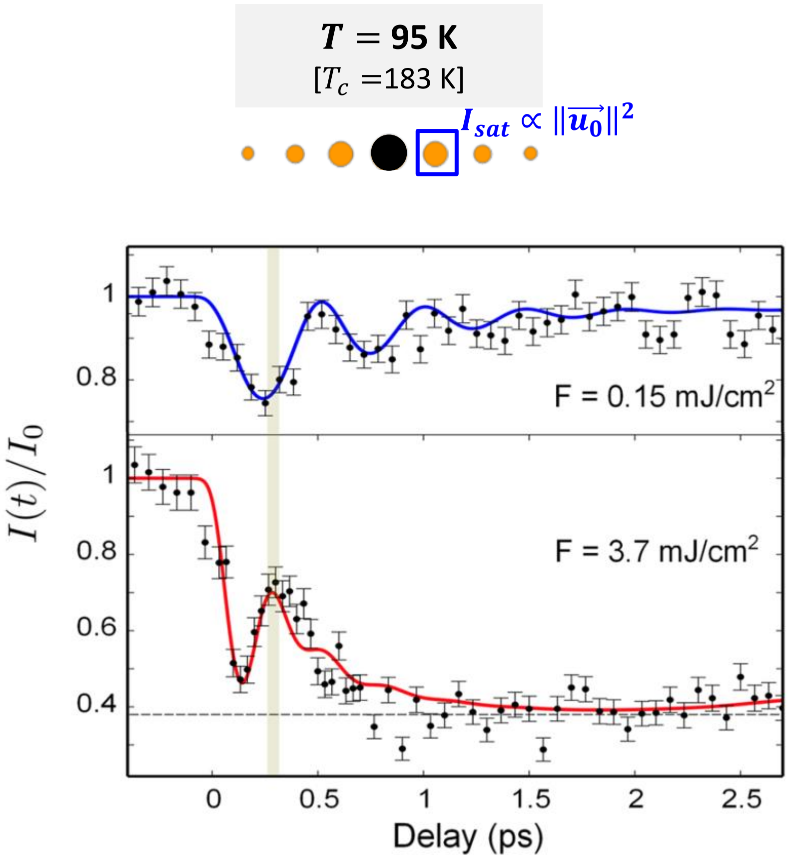
$$I_{sat} \propto \|\vec{u_0}\|^2$$

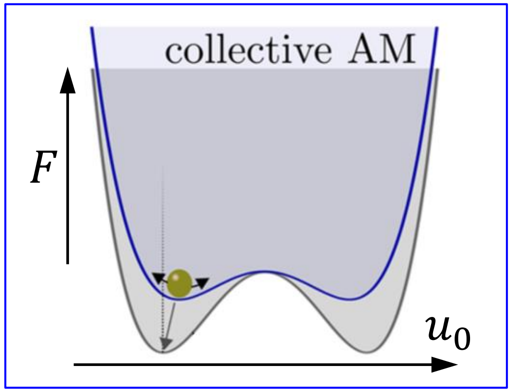
diffraction ⟷ CDW amplitude

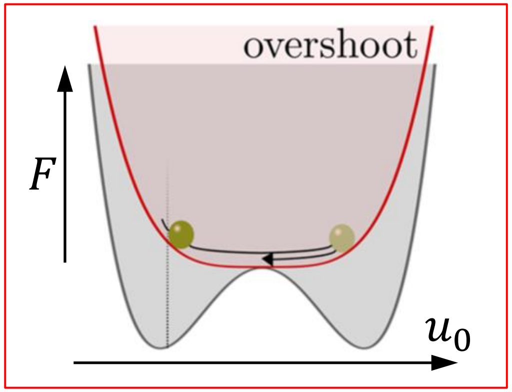


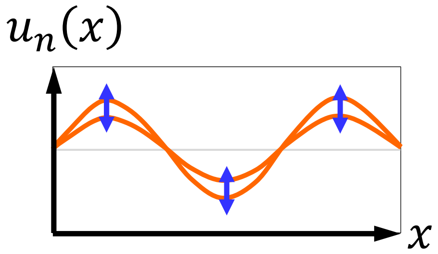
3a- Photoinduced phase transitions (PIPTs) achieved through coherent atomic motions

- **Ultrafast PIPT in Blue bronze $K_{0.3}MoO_3$**

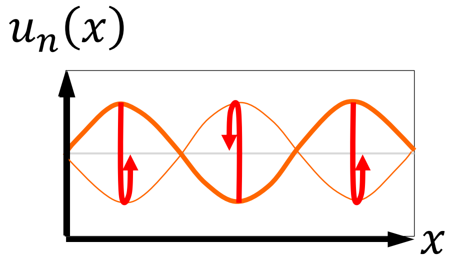








Oscillations of the CDW amplitude



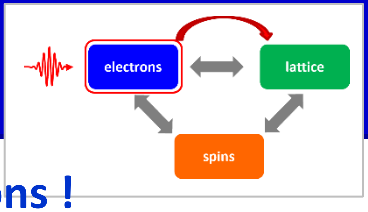
Coherent motion in the potential landscape of the unmodulated phase

Ultrafast optical switching

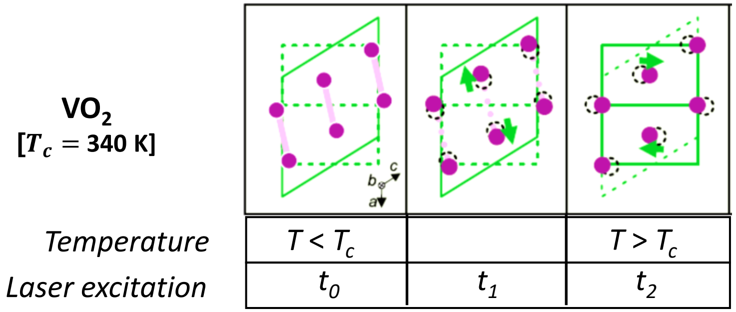
T. Huber *et al.*, PRL **113**, 026401 (2014)

See also [manganite $Pr_{0.5}Ca_{0.5}MnO_3$]: P. Beaud *et al.*, Nature Materials **13**, 923 (2014)

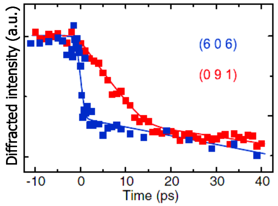
Photoinduced structural dynamics investigated by pump-probe diffraction
Part III. Tracking structural dynamics with pump-probe diffraction

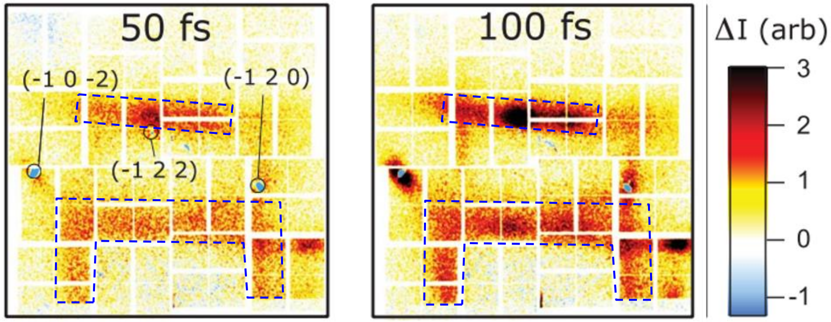


3b- Photoinduced phase transitions (PIPTs): non-fully coherent atomic motions !



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



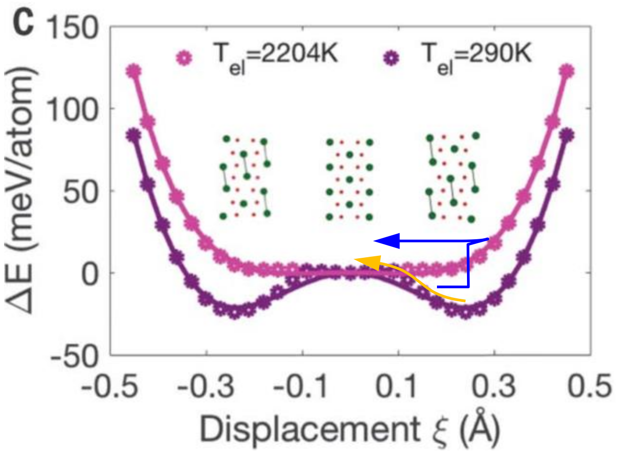


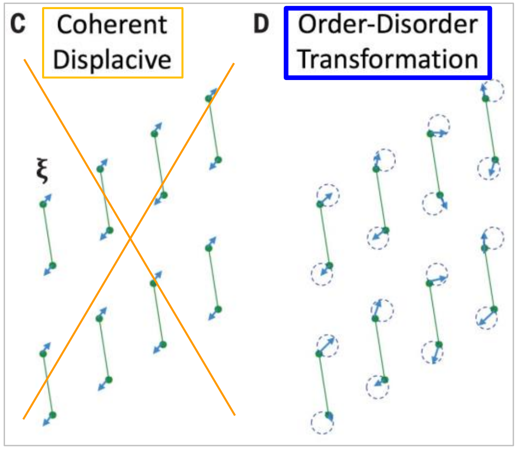
Detector images: $I(t) - I_0$

Insulator to metal transition revisited using an X-FEL (LCLS, Stanford):

→ Drop of diffracted intensity of the $\bar{1}0\bar{2}$, $\bar{1}20$ and $\bar{1}22$ reflections on the 100 fs timescale

→ Developement of a **diffuse scattering signal** on the 100 fs timescale



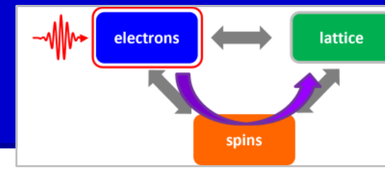


Non-fully coherent motion of atoms

The initial thermal distribution of velocities plays a role (inertial dynamics)

S. Wall *et al.*, Science **362**, 572-576 (2018)

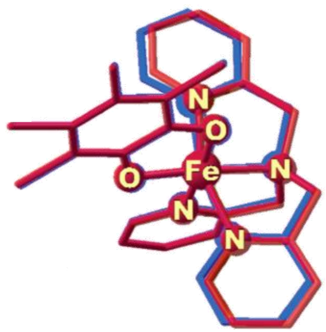
Photoinduced structural dynamics investigated by pump-probe diffraction
Part III. Tracking structural dynamics with pump-probe diffraction

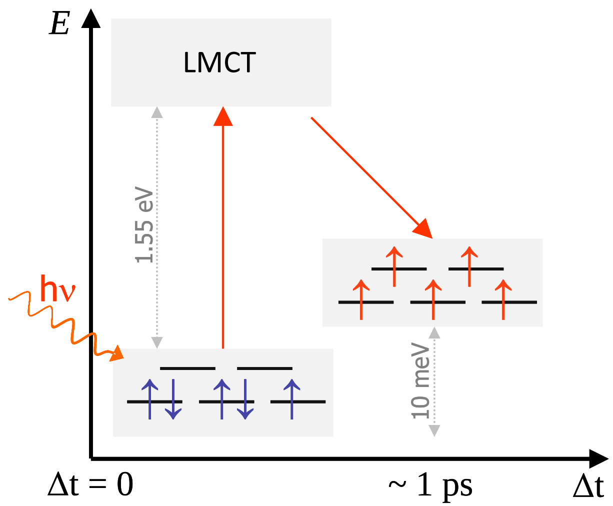


4- Photoinduced strain and temperature elevation (picosecond to microsecond timescales)

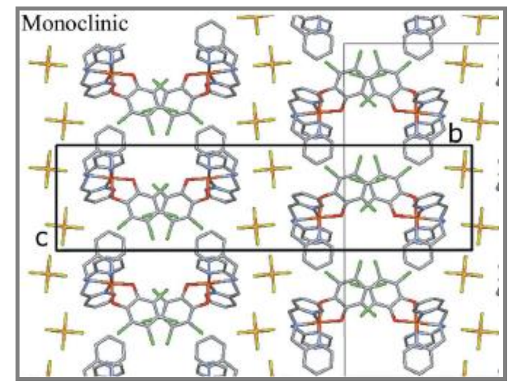
- **Spin state switching in a molecular crystal**

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

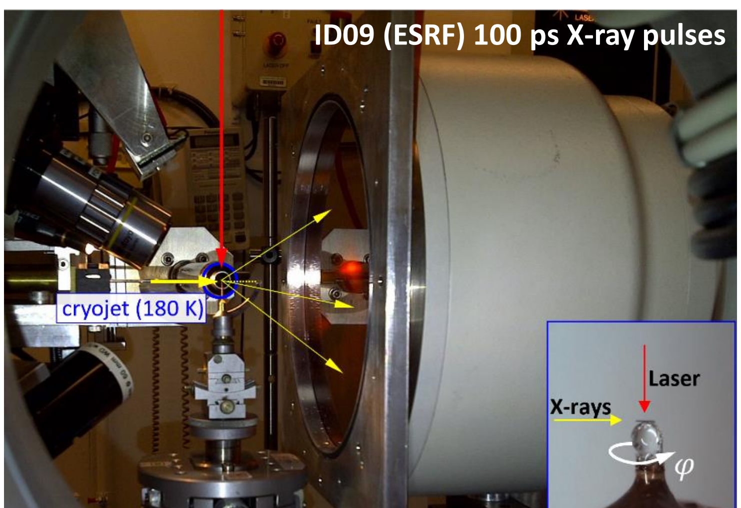




[TPA (FeIII) TCC] PF_6



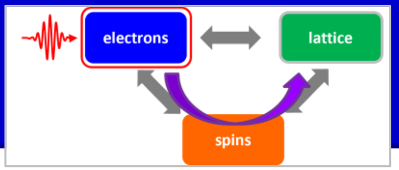
Lattice ↔ cooperative effects?



- 360° rotation in φ: ~ 3300 Bragg peaks
  → **Structural refinement**, starting from the structure observed at equilibrium
- Crystal thickness (15 µm) is chosen roughly equal to the penetration depth of 800 nm laser pulses
  → Near-homogeneous excitation
- Circularly polarized laser beam
  → Constant absorption probability of the 800 nm photons during φ rotations

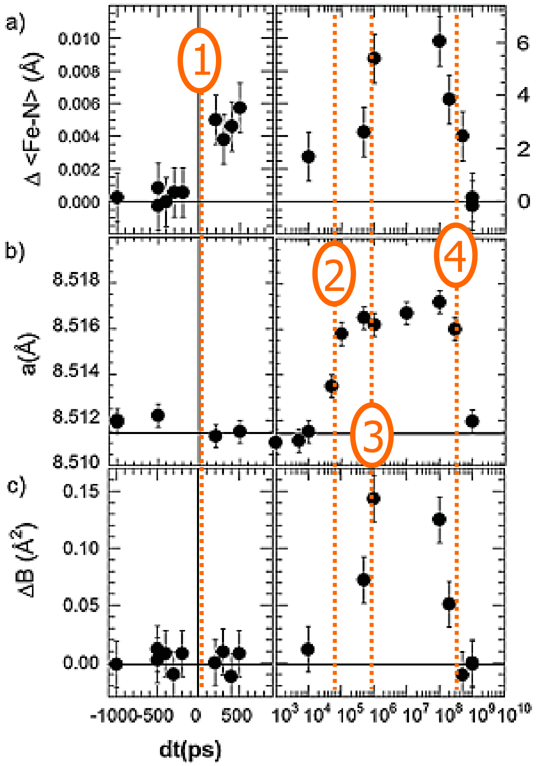
M. Lorenc *et al.*, PRL **103**, 028301 (2009)

Photoinduced structural dynamics investigated by pump-probe diffraction
Part III. Tracking structural dynamics with pump-probe diffraction



4- Photoinduced strain and temperature elevation (picosecond to microsecond timescales)

- **Spin state switching in a molecular crystal**



Δ<Fe-N> : fraction of molecules in the HS state

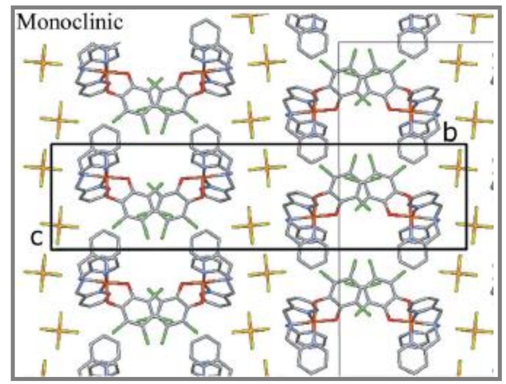
Unit cell parameter a : elastic deformations

Debye-Waller factor B: crystal temperature

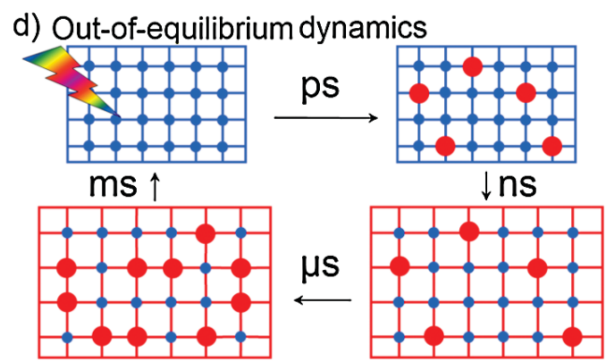
Photoinduced spin state switching in [TPA Fe(III) TPP] PF_6:

1) Laser-induced switching of molecules
2) Strain wave propagation
3) Heat diffusion + **additional spin state switching**
4) Relaxation

[TPA (FeIII) TCC] PF_6



Lattice ↔ cooperative effects?



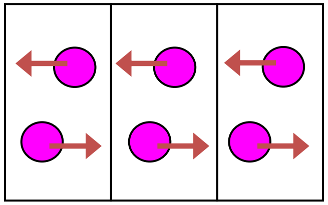
M. Lorenc *et al.*, PRL **103**, 028301 (2009)

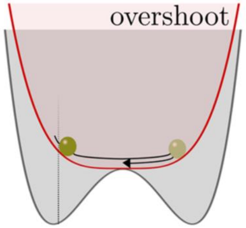
Switching due to strain waves (nanocrystals):
R. Bertoni *et al.*, Nat. Mater. **15**, 606 (2016)

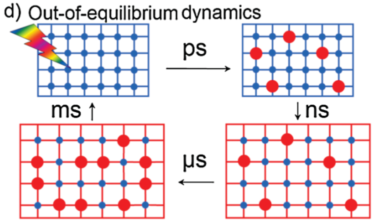
Photoinduced structural dynamics investigated by pump-probe diffraction

➢ Out-of-equilibrium structural dynamics:

- Coherent phonons
- Photoinduced phase transitions
- Strain wave propagation
- Heat diffusion





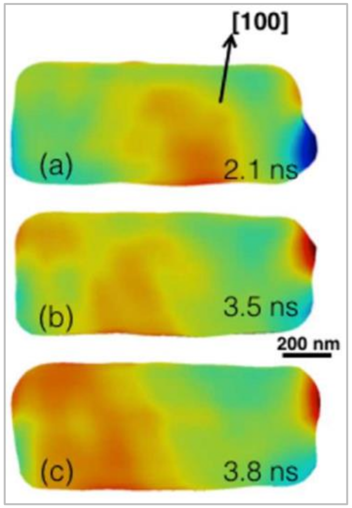


➢ Pump-probe diffraction

- **Bragg peak intensities:** time-dependent motif, volume fraction, average temperature (Debye-Waller factor)
- **Bragg peak positions:** transient strain
- **Bragg peak widths:** correlation length (up to 100 nm)
- **Diffuse scattering:** short range correlated atomic displacements

➢ Pump-probe diffraction at X-FELs:

- **μ-diffraction, coherent diffractive imaging, resonant scattering**



Strain pulse in a ZnO nanocrystal
M. J. Cherukara, Nano Lett. **17**, 1102-1108 (2017)