Scientific Applications of XFELs: strongly correlated materials

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Suggested readings

[1] V. Anisimov and Y. Izyumov, (2010). *Electronic Structure of Strongly Correlated Materials*. Springer Berlin Heidelberg. ISBN: 978-3-642-04825-8

[2] J. M. D. Coey, (2010). *Magnetism and Magnetic Materials.* Cambridge University Press.

[3] E. Beaurepaire, H. Bulou, L. Joly, and F. Scheurer, editors, (2013). *Magnetism and Synchrotron Radiation: Towards the Fourth Generation Light Sources*. Springer International Publishing.

[4] M. Buzzi, M. Först, R. Mankowsky, and A. Cavalleri, *Probing Dynamics in Quantum Materials with Femtosecond X-Rays*, Nature Review Materials **3**, 299 (2018). DOI: 10.1038/s41578-018-0024-9

[5] M. Imada, A. Fujimori, and Y. Tokura, *Metal-Insulator Transitions*, Review of Modern Physics **70**, 1039 (1998). DOI: 10.1103/RevModPhys.70.1039

Terminology

Strongly correlated materials: wide class of compounds that reveal collective electronic and magnetic properties, such as metal-insulator transitions, heavy fermion behavior, half-metallicity, and spin-charge separation. Their physical properties cannot be described effectively in terms of non-interacting entities (i.e. Fermi liquid description). The seminal example of such materials are **superconductors**.

Quantuum materials is a class of materials that reveal strong correlations (electronic, superconducting or magnetic) or non-generic quantum effects (**topological insulators, graphene, 2D materials**) as well as systems whose collective properties are governed by genuinely quantum behavior (**ultra-cold atoms, cold excitons, polaritons**).

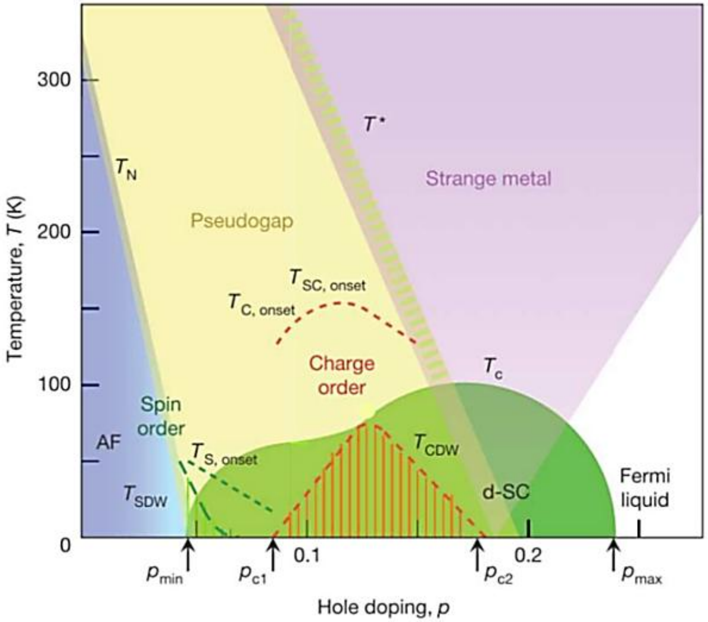
XMCD (X-ray Magnetic Circular Dichroism) is a phenomenon observed as a difference between two spectra or scattering patterns excited with circularly polarized light of opposite helicity. It is sensitive to projection of magnetic moment of the absorbing or scattering atom, respectively.

Outline

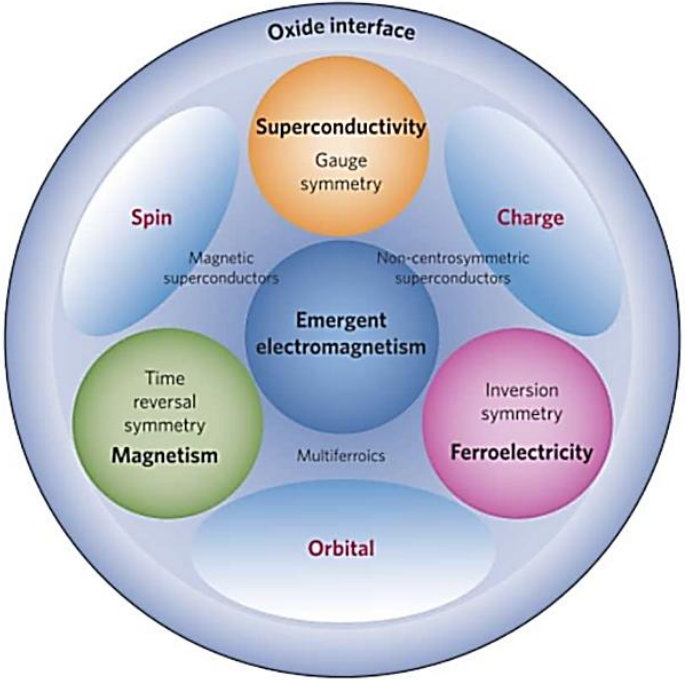
1. Strongly correlated materials
2. Examples of XFEL study of:
   - phonon and electron excitations
   - charge order
   - phase transitions
   - ultrafast demagnetization
3. Summary

Physics of strongly correlated materials

Interplay of lattice, charge, spin, and orbital degrees of freedom leads to extraordinary properties, e.g. ferromagnetism, ***superconductivity*** *and* ***multiferroicity***



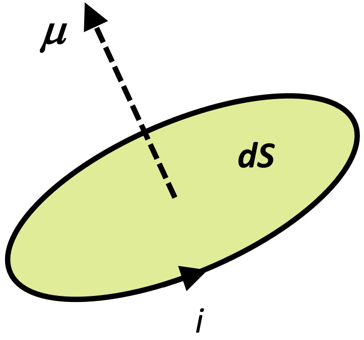
B. Keimer, *et al.*, *Nature* **518**, 179 (2015)



H.Y. Hwang, *et al.*, *Nature Materials* **11**, 103 (2012)

Spin and orbital moment

$$\boldsymbol{\mu} = \int i d\boldsymbol{S}$$

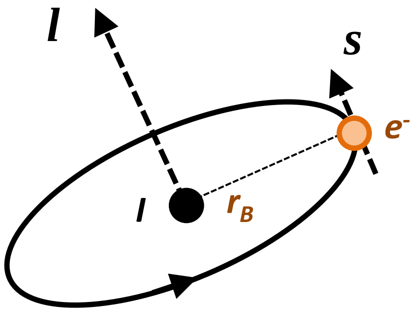


Effective magnetic moment:

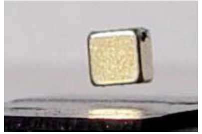
$$\mu_{eff} = g\sqrt{J(J+1)}\,\mu_B$$

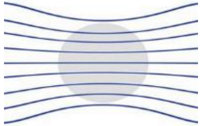
$$\mu_B = i\pi r_B^2 = \frac{e\hbar}{2m_e}$$

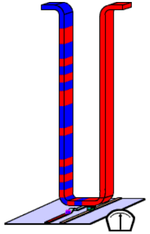
Bohr magneton

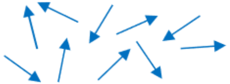
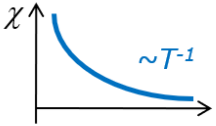
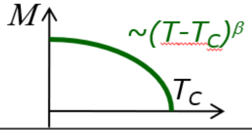
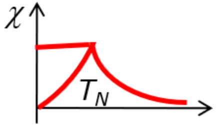
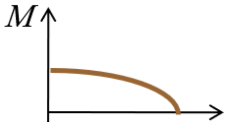


Magnetic materials





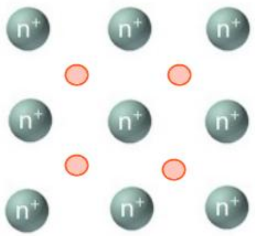


Type	Picture	*T* dependence
Dia-magnetic		
Para-magnetic		
Ferro-magnetic		
Antiferro(ferri)-		
Ferri-magnetic		

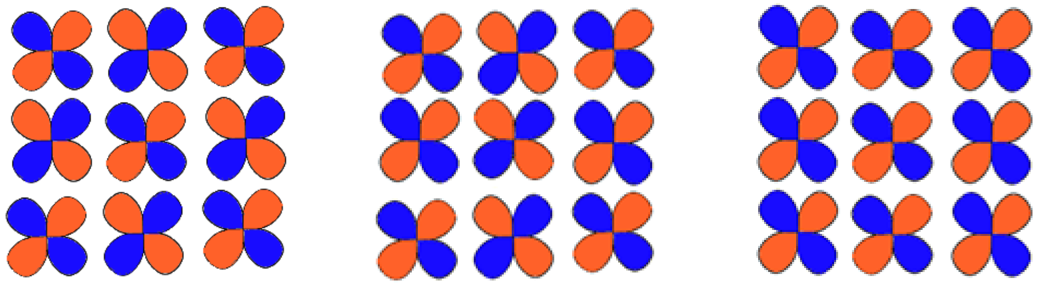
Correlation energy

A measure of how much the movement of one electron is influenced by the presence of all other electrons

charge order



orbital order

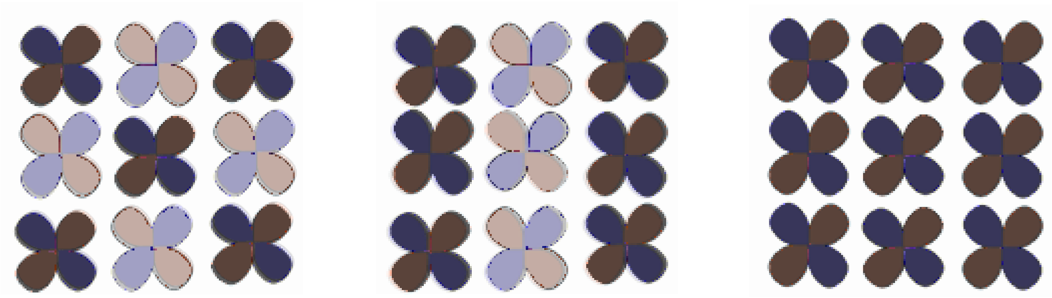


Electronic correlations are negligible in ionic crystals and significant in materials containing elements with open d and f electron shells as well as high Z elements

Correlation energy

A measure of how much the movement of one electron is influenced by the presence of all other electrons

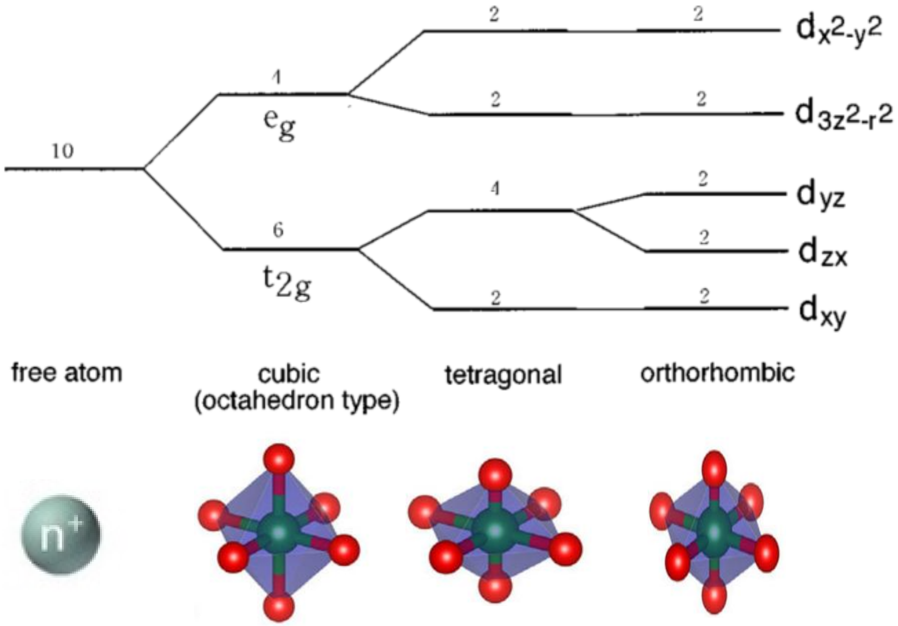
charge and orbital order

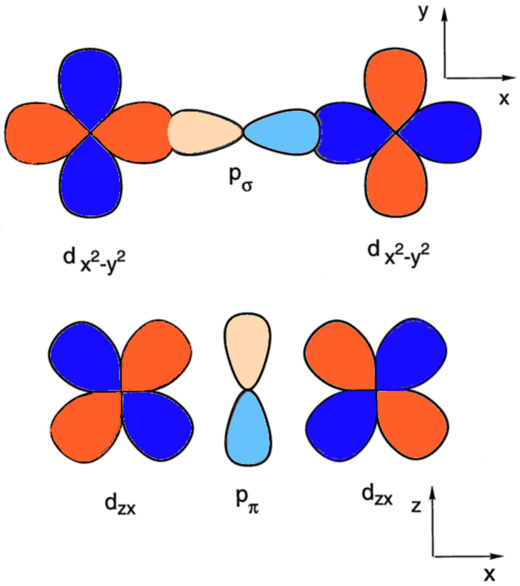


Electronic correlations are negligible in ionic crystals and significant in materials containing elements with open d and f electron shells as well as high Z elements

Electronic structure of d orbitals

Crystal-field splitting of 3d orbitals in different symmetries (the numbers indicate degeneracy)





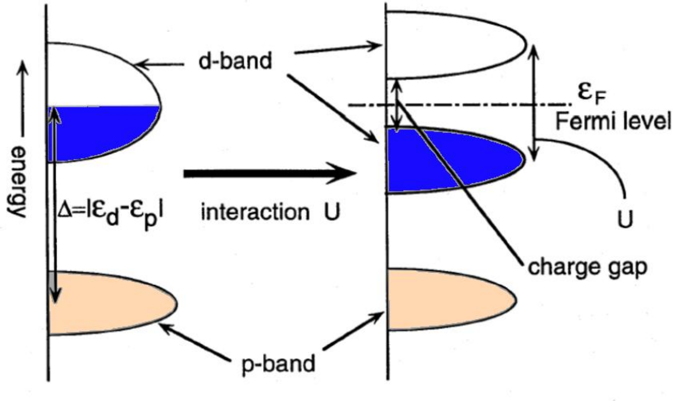
Examples of configurations for transition-metal 3d orbitals which are bridged by ligand p orbitals

source: [4]

Metal-insulator transitions

Hubbard model include inter-particle interactions
(e.g. Coulomb repulsion) as independent energy term

$$\hat{H} = -t \sum_{i,\sigma} \left(\hat{c}^\dagger_{i,\sigma} \hat{c}_{i+1,\sigma} + \hat{c}^\dagger_{i+1,\sigma} \hat{c}_{i,\sigma} \right) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$



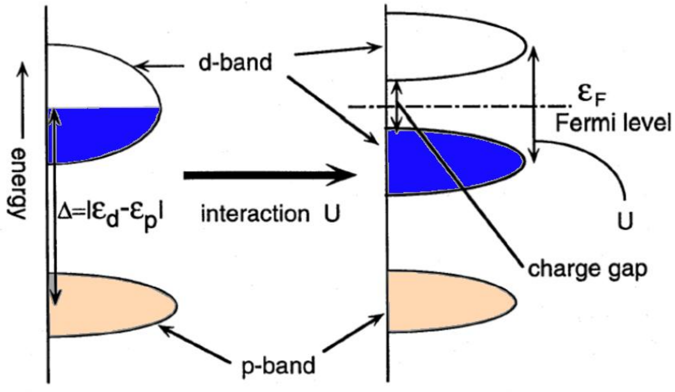
(a) Mott-Hubbard Insulator

source: [4]

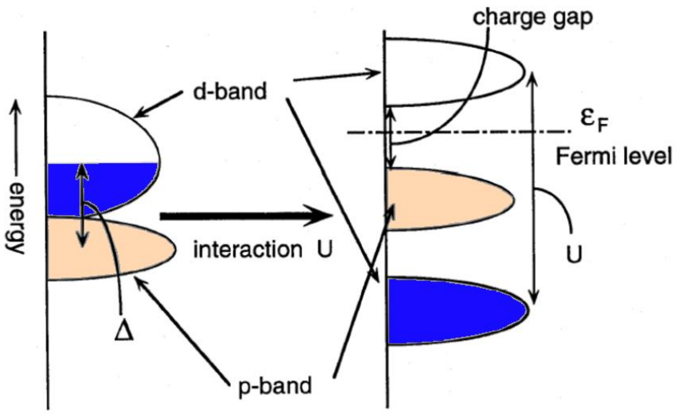
Mott-Hubbard vs. charge transfer

Mott-Hubbard insulator is due to electronic (orbital) interactions within single atom

Charge transfer insulator is due to electronic interactions between neighboring atoms



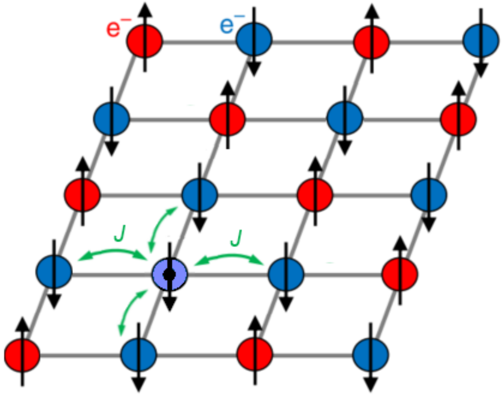
(a) Mott-Hubbard Insulator

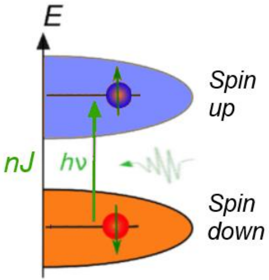


(b) Charge Transfer Insulator

source: [4]

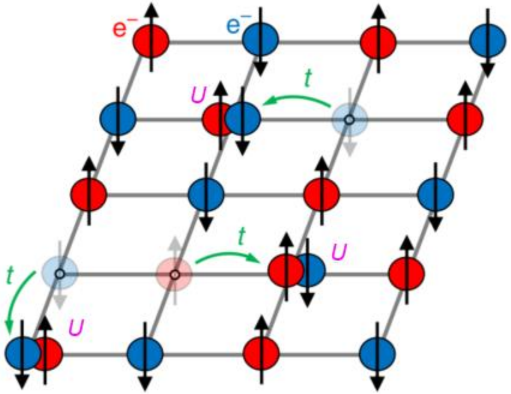
Electronic and magnetic excitations





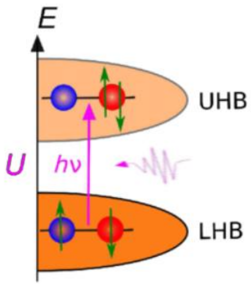
spin flip (dd)

$$\Delta S = 1$$
$$\Delta n = 0$$

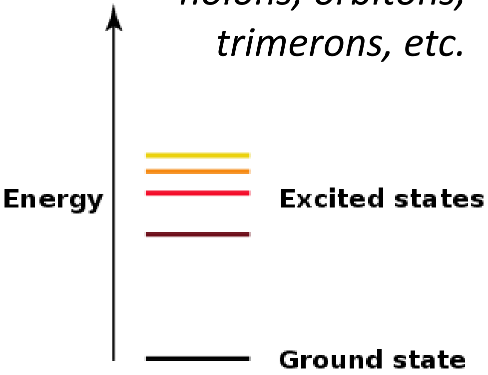


charge transfer

$$\Delta S = 0$$
$$\Delta n = \pm 1$$



Quasiparticles *and* ***collective excitations****:*
phonon, exciton,
plasmon, polariton
polaron, magnon
bimagnon, spinons,
holons, orbitons,
trimerons, etc.

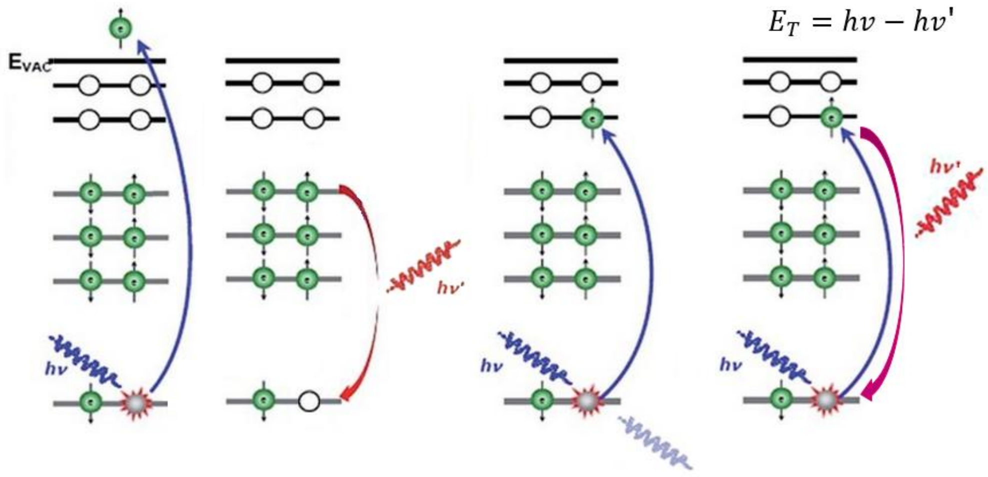


Core level X-ray spectroscopy

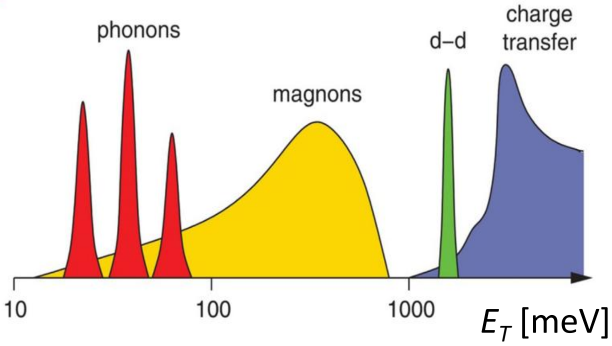
Empty orbitals (bands)

Valence orbitals (bands)

Core orbitals (levels)



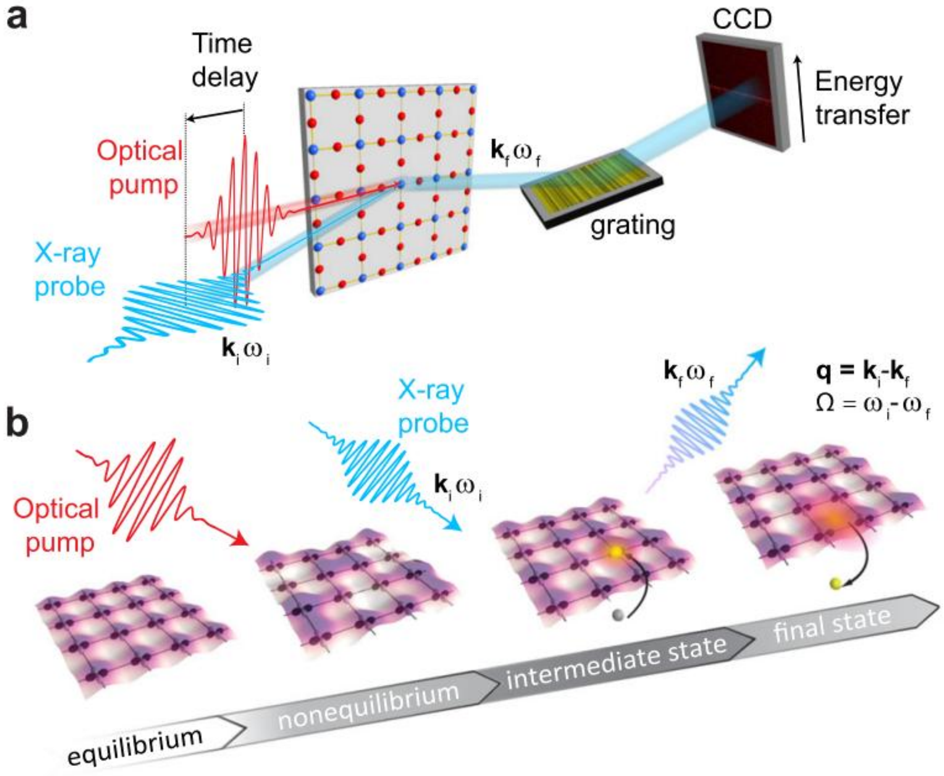
XPS **XES** **XAS** **(R)IXS**



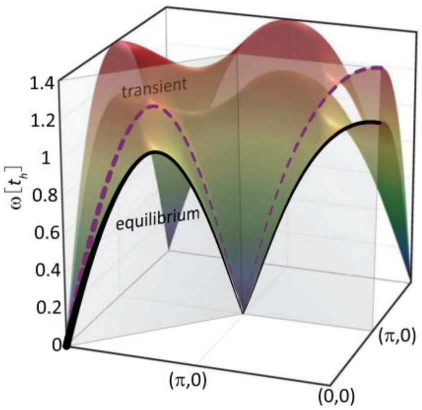
Element selective probe electronic structure of solids, including low energy excitations

Transient RIXS experiments (trRIXS)

Mitrano and Wang, *Communications Physics* **3**, 1 (2020)

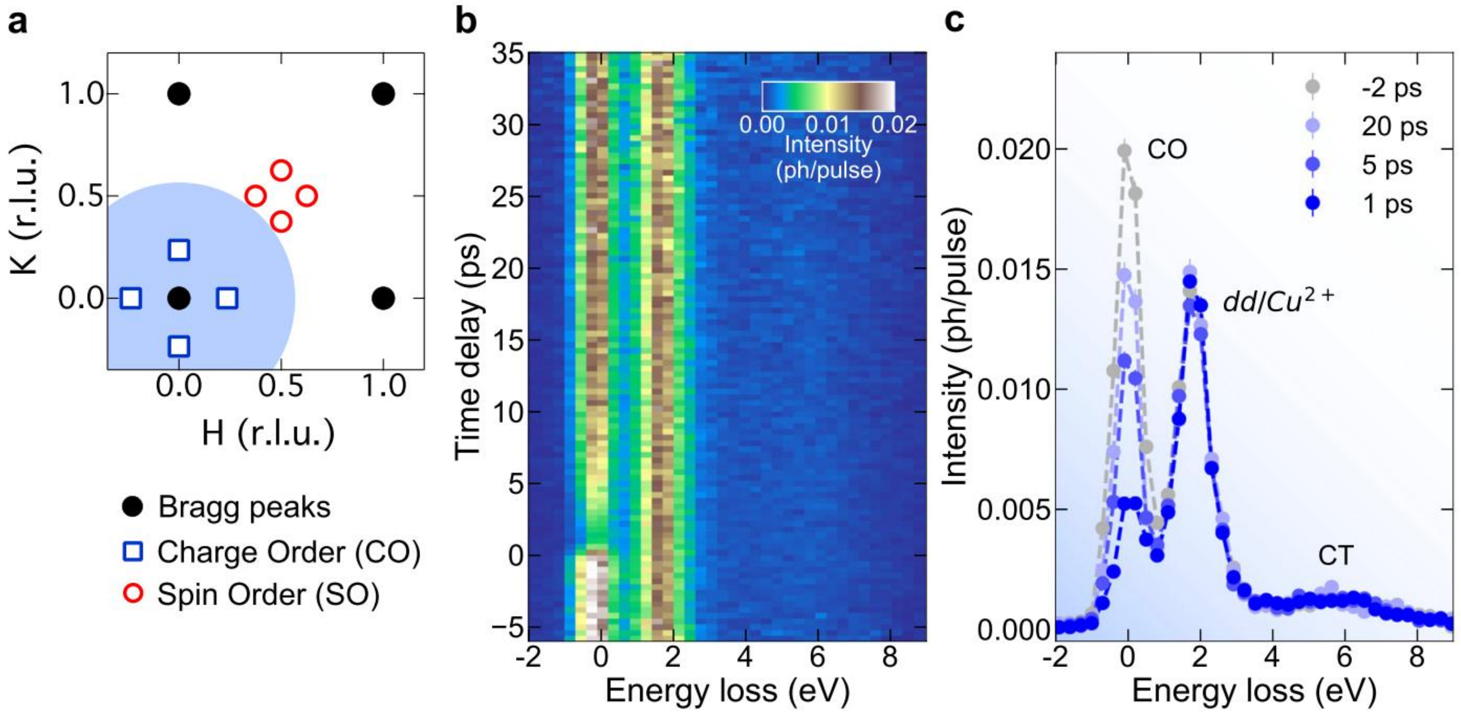


A material is driven out of equilibrium by an optical pump and probed with X-ray pulses with energy (ω_i) and momentum (k_i) resonantly tuned to a specific absorption edge



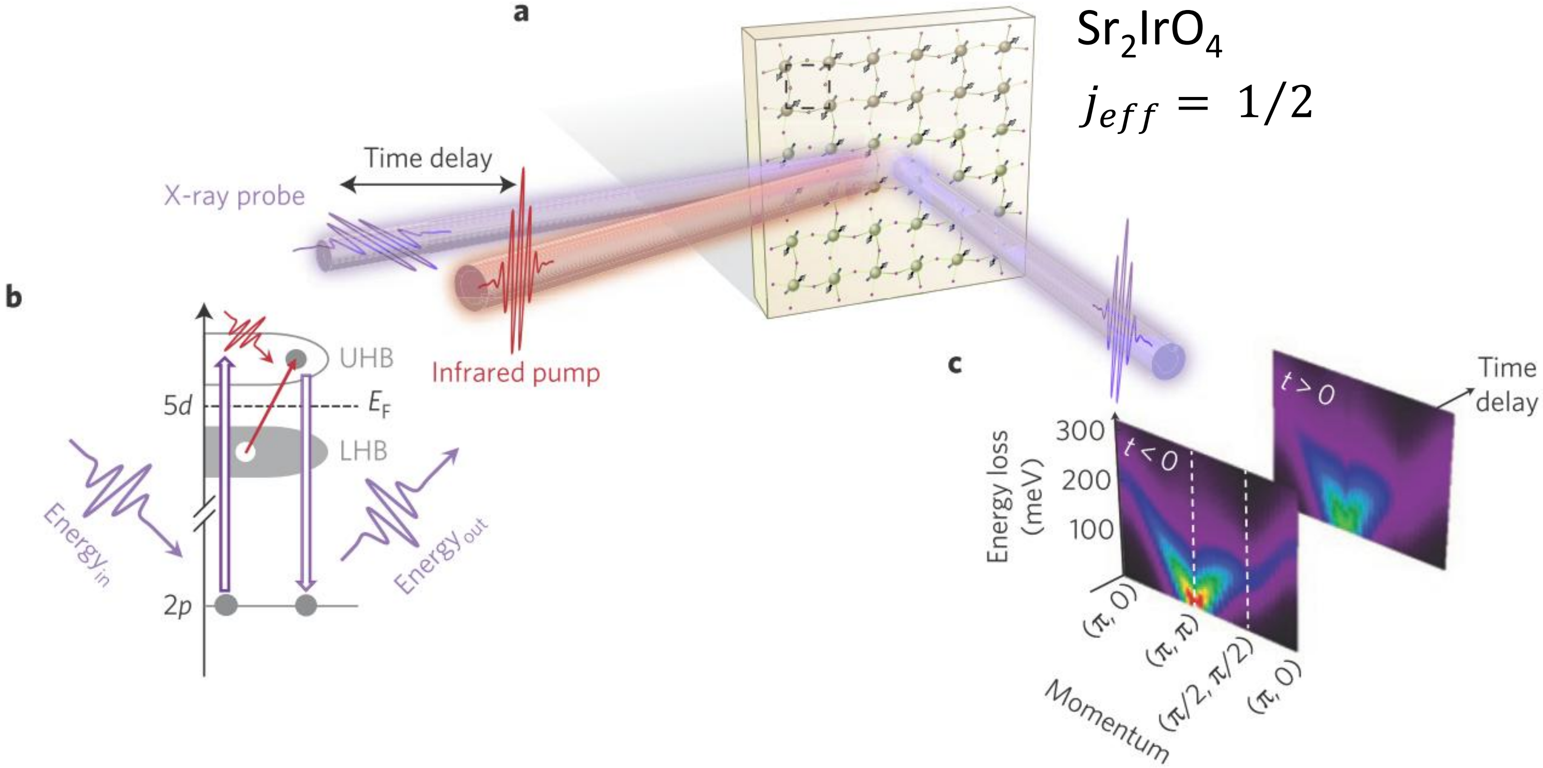
Charge order melting in cuprates

M. Mitrano, *et al.*, *Science Advances* **5,** eaax3346 (2019)



Magnetic correlations in iridates

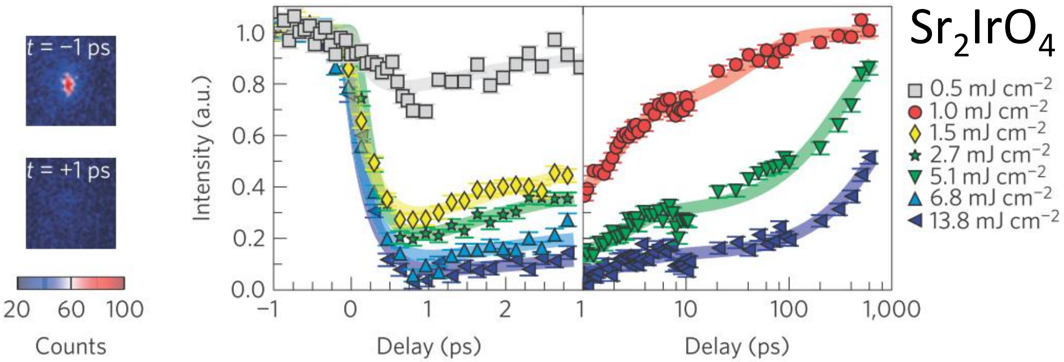
M.P.M. Dean, *et al.*, *Nature Materials* **15**, 601 (2016)



Sr_2IrO_4

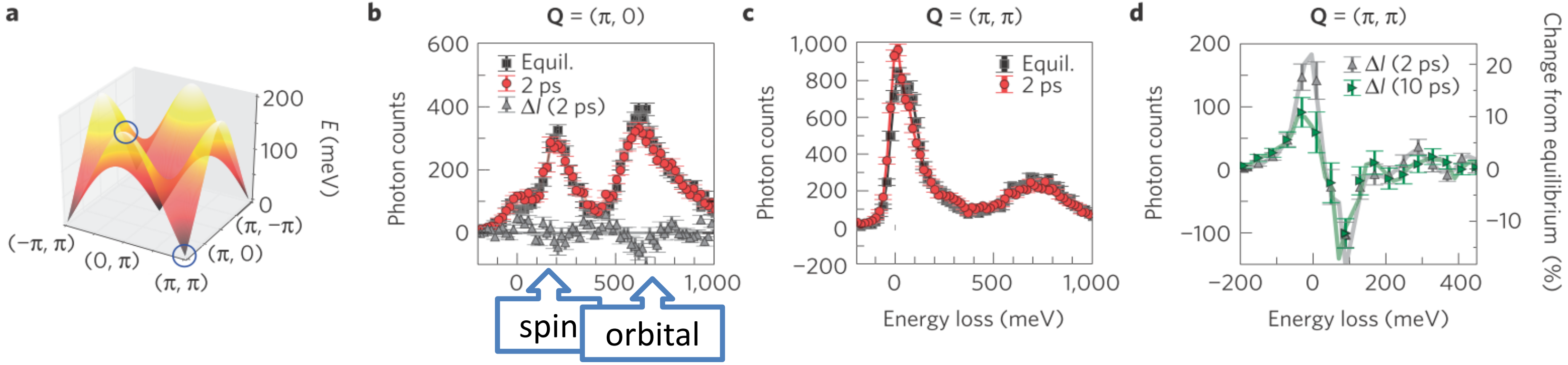
$j_{eff} = 1/2$

Dynamics of magnetic correlations



Destruction and recovery of 3D magnetic order

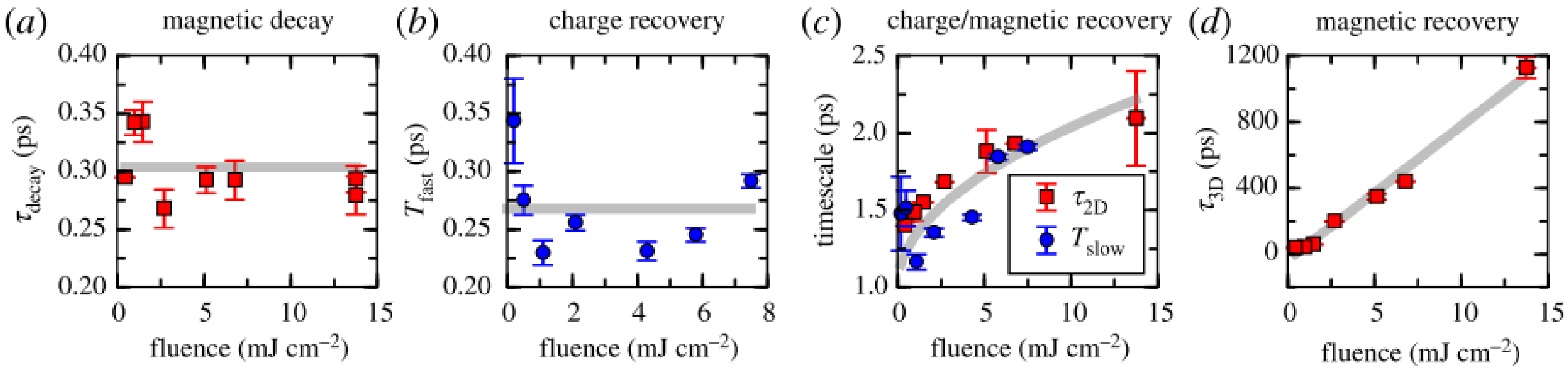
2D correlations before and after photo-excitation



M.P.M. Dean, *et al.*, *Nature Materials* **15**, 601 (2016)

Decay and recovery dynamics

M.P.M. Dean, *et al.*, *Nature Materials* **15**, 601 (2016)



Fluence dependence of the decay time that is required to destroy the ground state

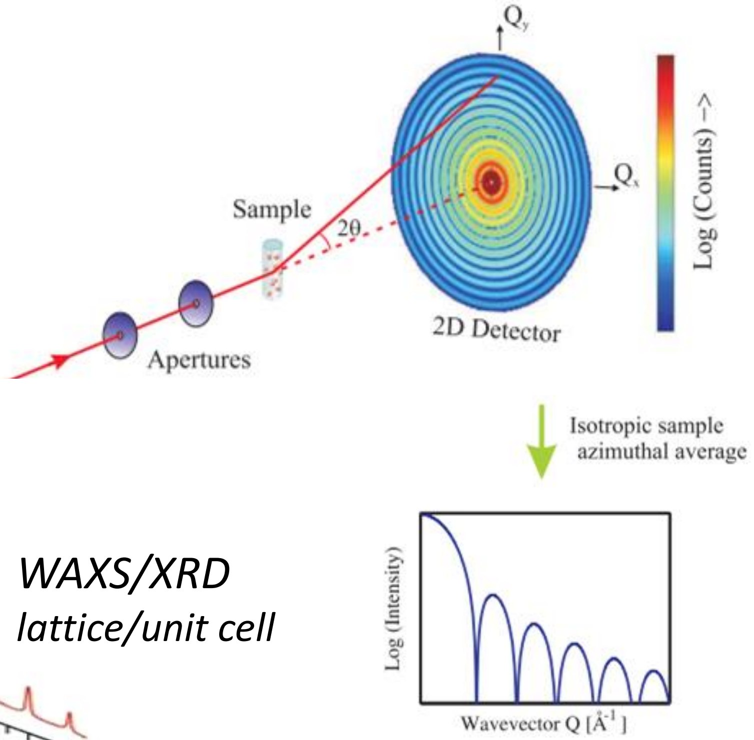
Fast recovery of the charge degree of freedom measured via optical reflectivity

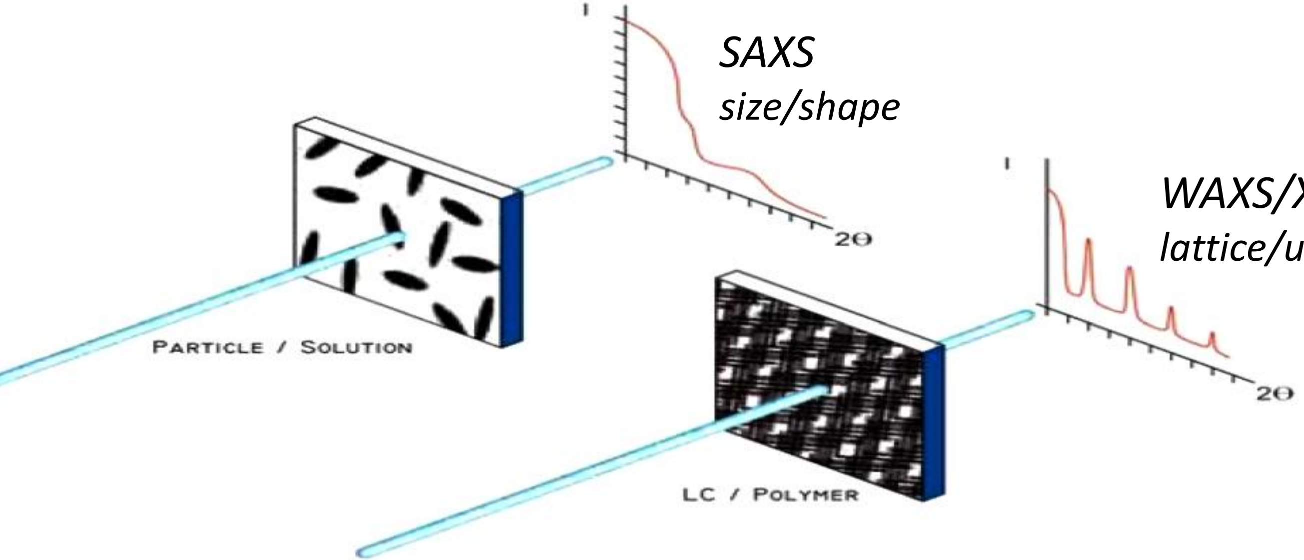
Slow recovery of the charge that matches that of 2D magnetic correlations

Slow recovery of 3D magnetic long-range order

Elastic X-ray scattering

J.A.Nielsen, D. McMorrow, Elements of Modern X-ray Physics, Wiley (2011)

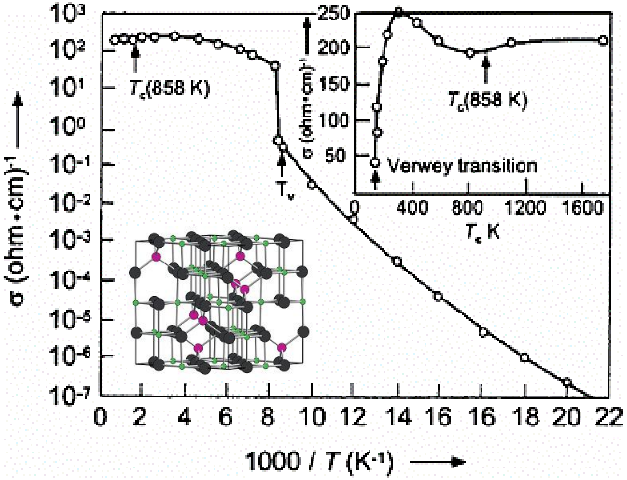


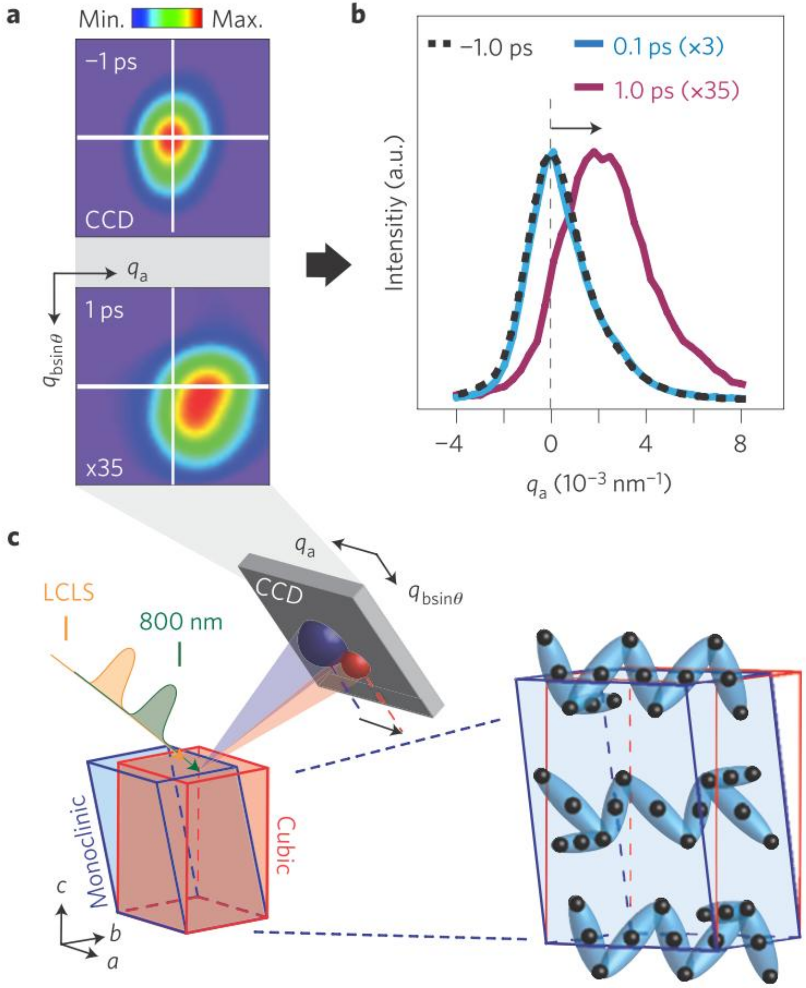


SAXS
size/shape

WAXS/XRD
lattice/unit cell

Dynamics of Verwey transition in Fe_3O_4



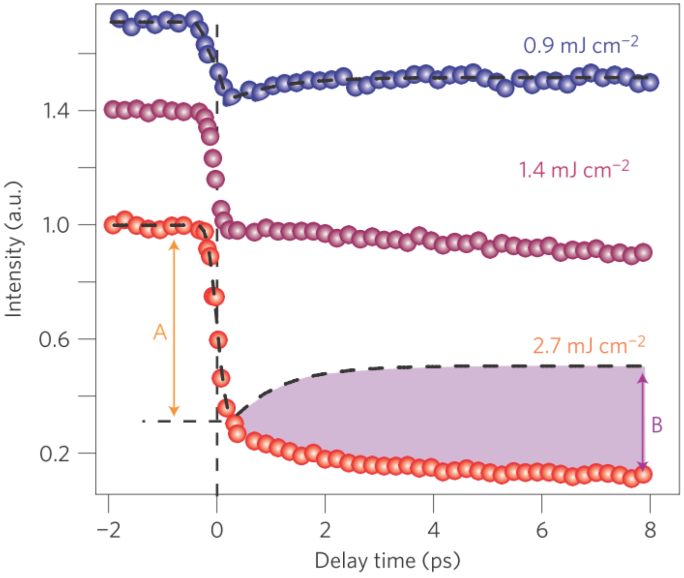


X-ray diffraction resonantly excited at Fe $L_{2,3}$-edge

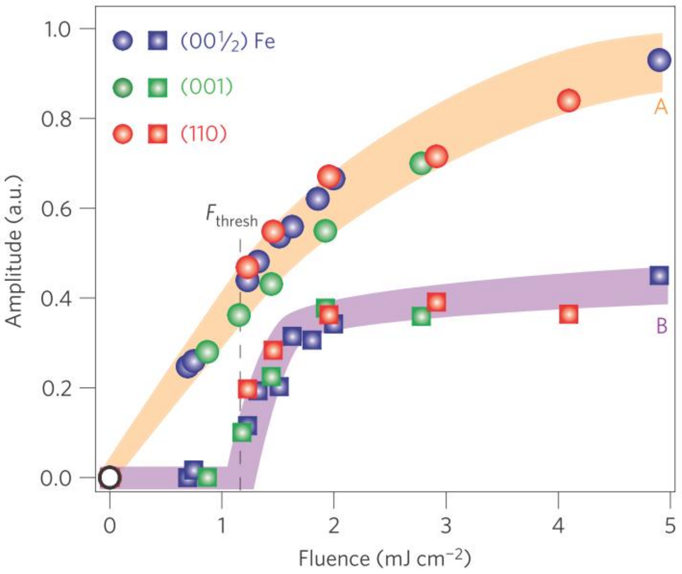
S. De Jong, *et al.*, *Nature Materials* **12**, 882 (2013)

Melting and recovery of trimerons

S. De Jong, *et al.*, *Nature Materials* **12**, 882 (2013)



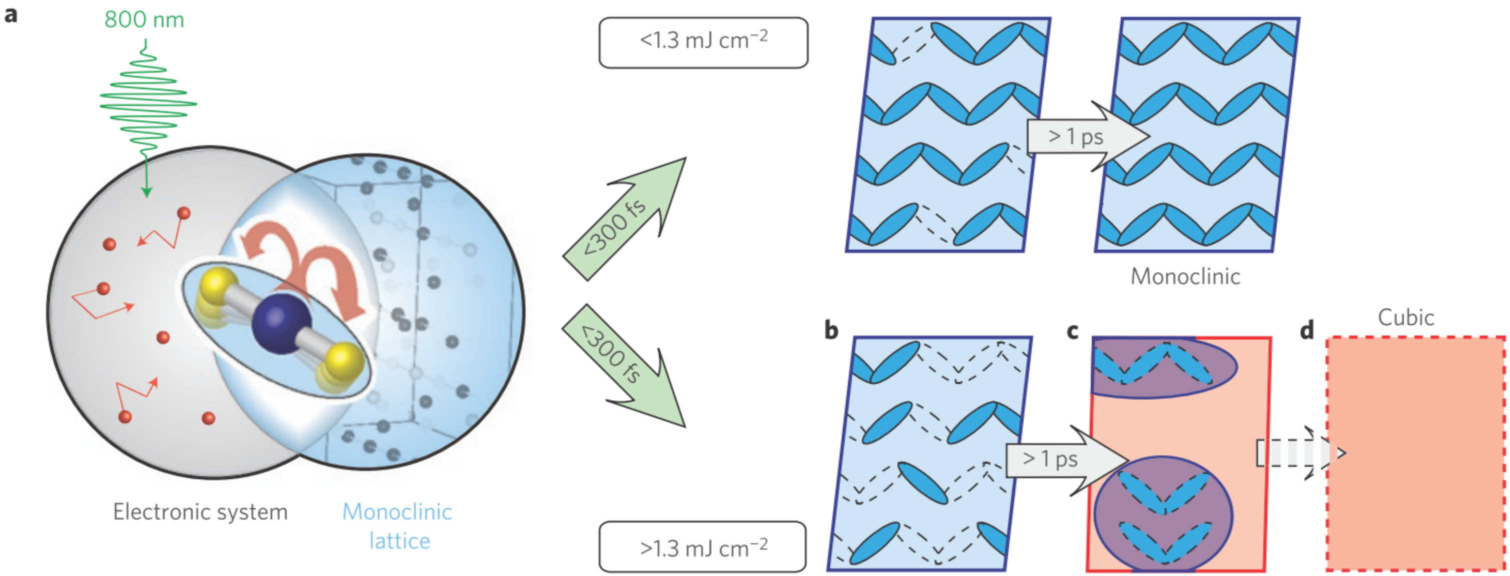
Normalized (001) diffraction intensity versus time delay for different pump fluences – two processes involved



Pump fluence dependence of the fast (t < 300 fs) intensity drop (A) and the slower intensity decay (B)

Fluence dependent recovery

S. De Jong, *et al.*, *Nature Materials* **12**, 882 (2013)



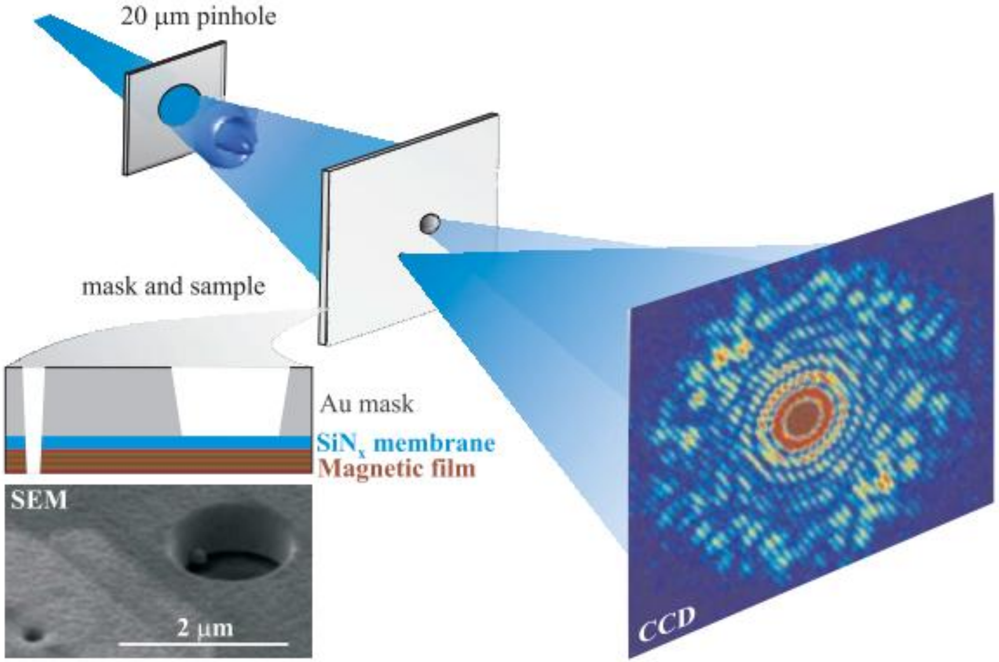
Ultrafast trimeron annihilation due to high fluence leads to metallic state (cubic) instead of recovering an insulating state (monoclinic)

X-ray holography

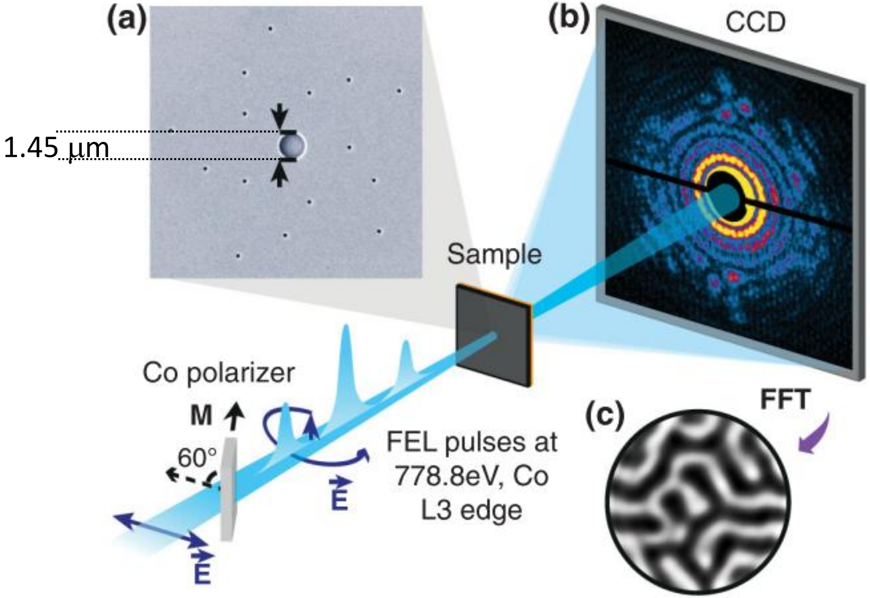
J.A.Nielsen, D. McMorrow, Elements of Modern X-ray Physics, Wiley (2011)

*A **hologram** is made by superimposing reference beam on the wavefront scattered from physical medium generating an interference pattern, which can be reconstructed into 3D image of the physical medium*

*Using ultra-brilliant coherent photon beam generated by **FEL** a hologram may be generated in **single shot** experiment*

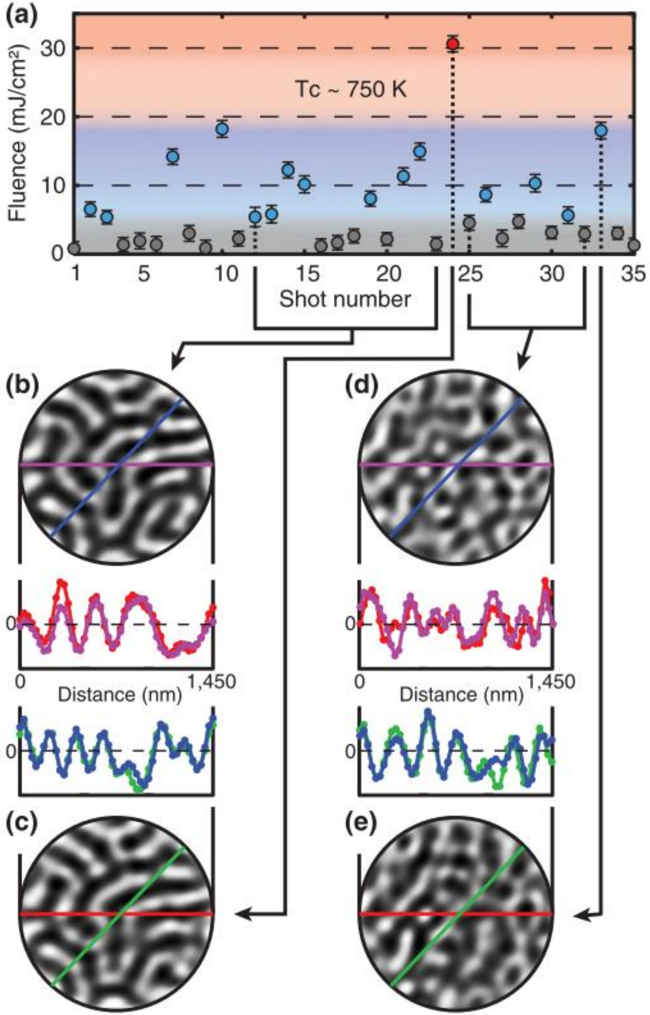


Melting of magnetic order



TaPd(CoPd)$_{40}$Pd multilayer on Si_3N_4 membrane

Magnetic domains vs. temperature (fluence)



T.Wang, et al., Physical Review Letters ***108****, 267403 (2012)*

X-ray magnetic circular dichroism

Atomic form factor:

$$f = f_0 + f'(E) + if''(E)$$

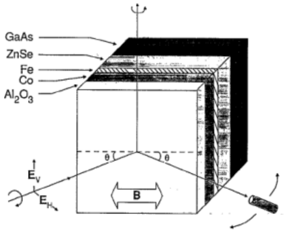
Elastic Reflection Absorption

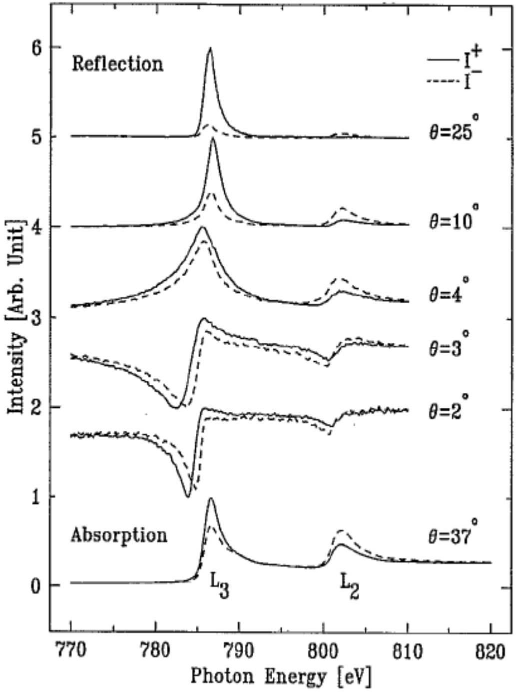
Magnetic scattering: $f_{magnetic} \sim \frac{f_{charge}}{10^{2\div4}} \sim \mathbf{A}\cdot\mathbf{L} + \mathbf{B}\cdot\mathbf{S}$

Orbital Spin

Magnetic scattering/absorption is strongly increased when probed with circularly polarised X-rays near spin-orbit split absorption edges

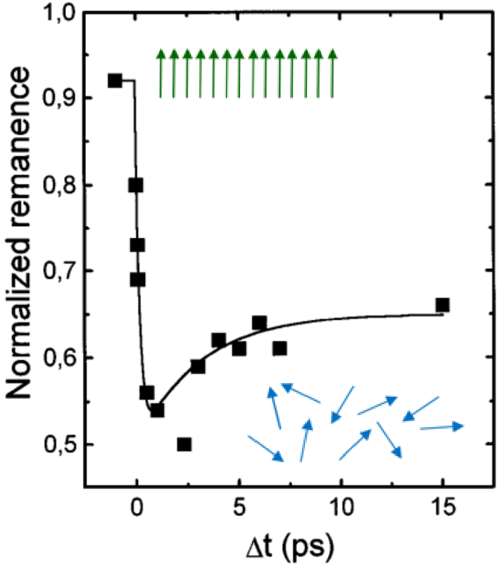
Magnetic dichroism (polarization dependence of scattering/absorption in magnetic materials) is sensitive to spin and orbital magnetic moments





C.C. Kao at al., Phys. Rev. B ***50****, 9599 (1994)*

Ultrafast demagnetization

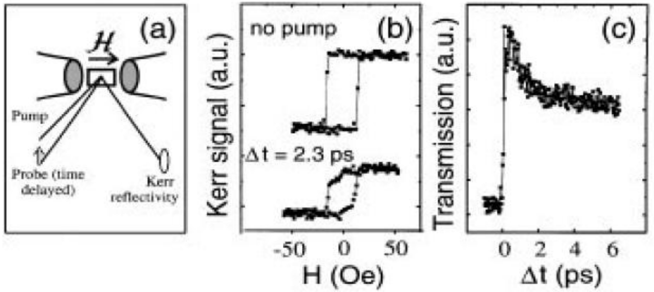


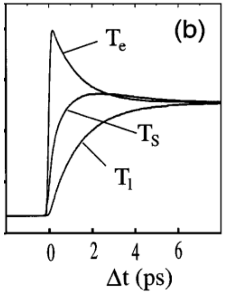
VOLUME 76, NUMBER 22 PHYSICAL REVIEW LETTERS 27 MAY 1996

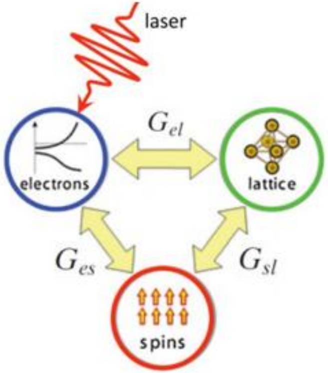
Ultrafast Spin Dynamics in Ferromagnetic Nickel

E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot

Institut de Physique et Chimie des Matériaux de Strasbourg, Unité Mixte 380046 CNRS-ULP-EHICS, 23, rue du Loess, 67037 Strasbourg Cedex, France







fast subpicosecond demagnetization induced using femtosecond optical pulses

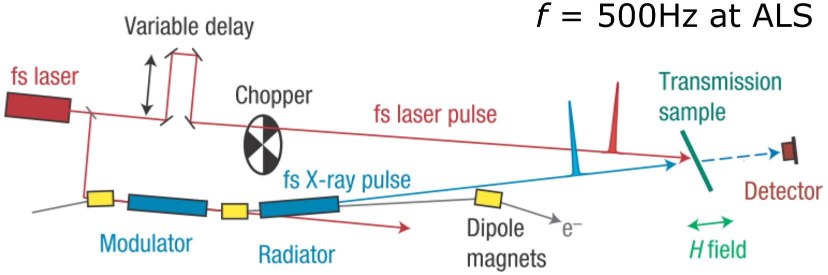
Three different dynamics are present

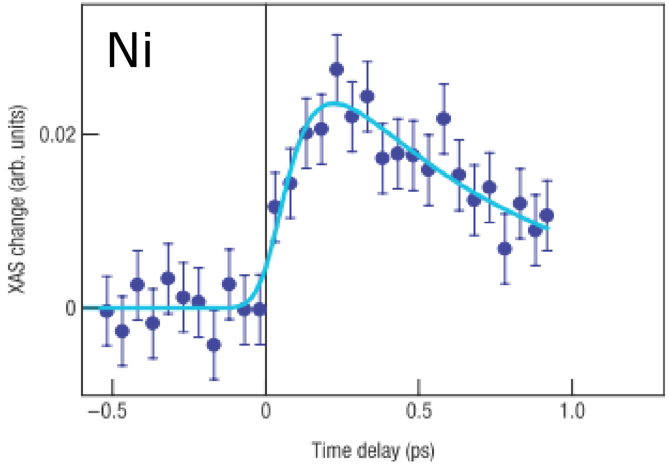
These are attributed to heat transfer between electron, spin and lattice

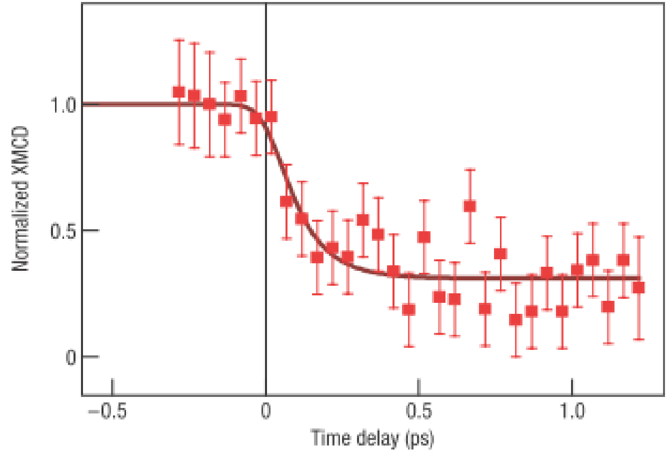
Ultrafast demagnetization (2)

*C. Stamm, et al., Nature Materials **6**, 740 (2007)*

Femtoslicing with
f = 500Hz at ALS





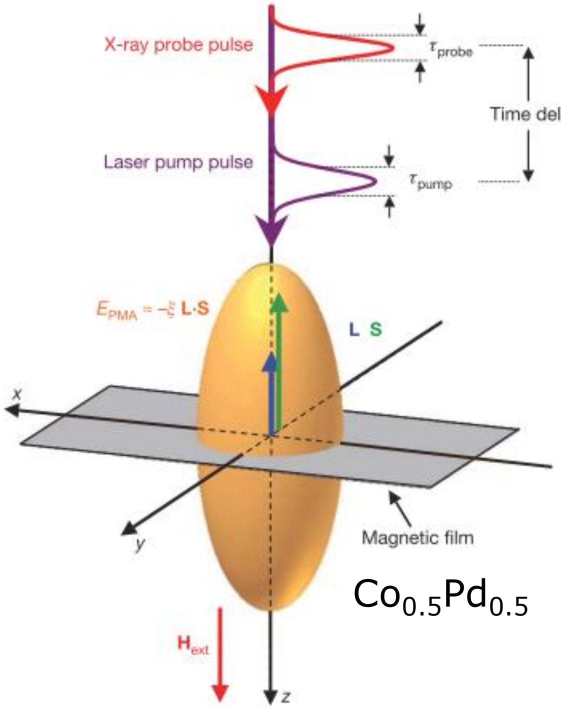


An increase in valence-electron localization on a timescale of 120 ± 50 fs

This mechanism is possibly related to the driving force for a spin–lattice relaxation that proceed on a timescale of 120 ± 70 fs

Ultrafast demagnetization (3)

*C. Boeglin, et al., Nature **465**, 458 (2010)*



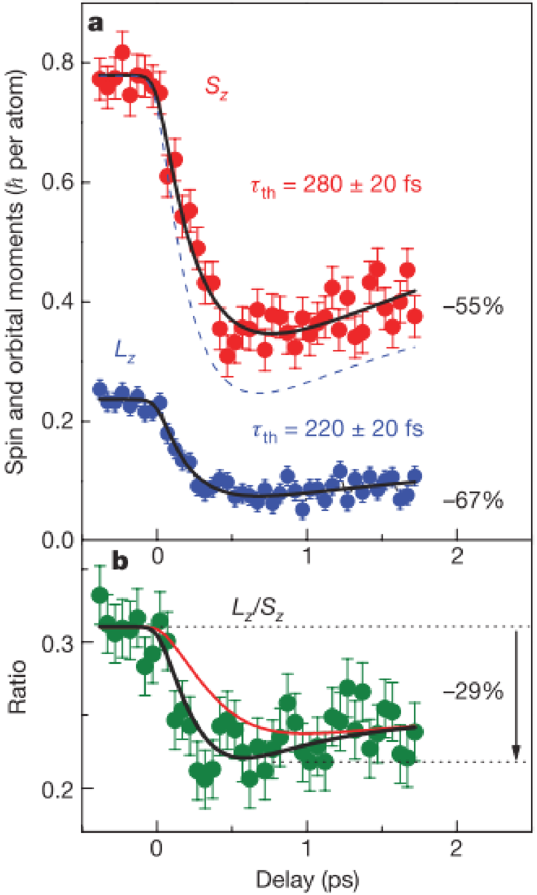
$Co_{0.5}Pd_{0.5}$

Femtoslicing at BESSY

Orbital momentum $L_z(t)$ of Co reveals ultrafast change in magneto-crystalline anisotropy (220 ± 20 fs)

spin momentum $S_z(t)$ decreases more slowly (280 ± 20 fs)

Spin-orbit decoupling

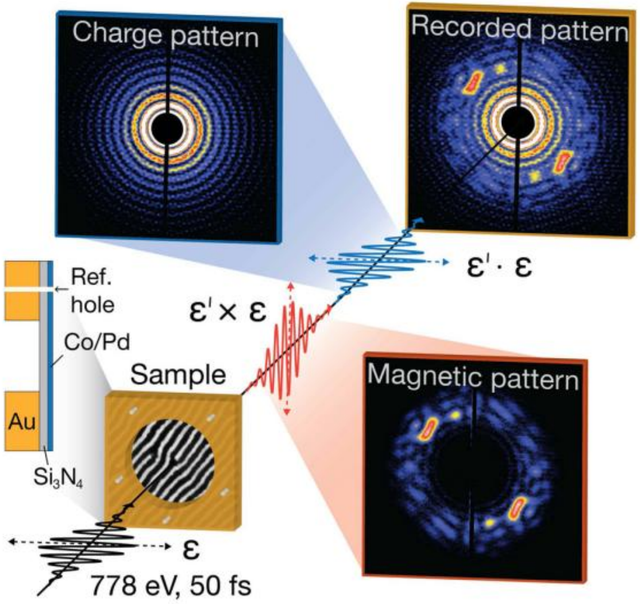


Ultrafast demagnetization (4)

B. Wu, et al., Phys. Rev. Lett. ***117****, 027401 (2016)*

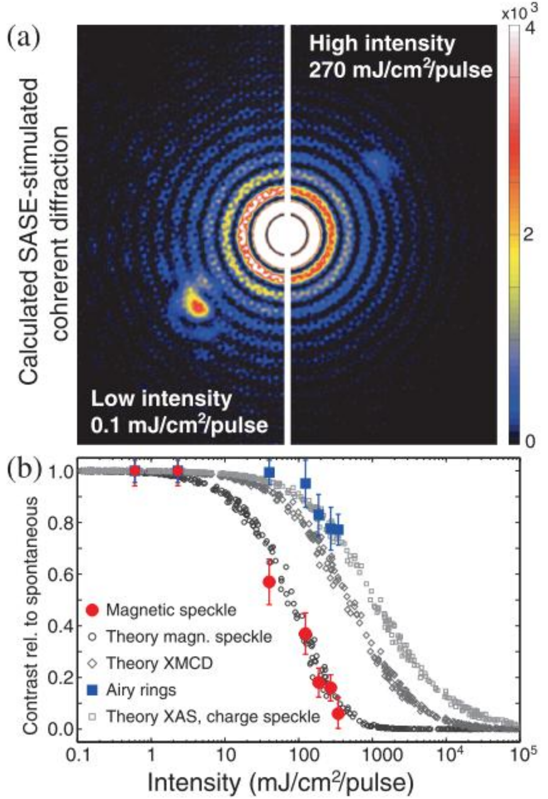
X-ray magnetic diffraction at LCLS

Full X-ray transparency confirmed by Z. Chen, et al., Phys. Rev. Lett. ***121****, 137403 (2018)*



Disappearance of both charge and magnetic contrast cannot be explained by ultrafast demagnetization

At an intensity of about 10 mJ/cm^2/pulse the coherent incident field

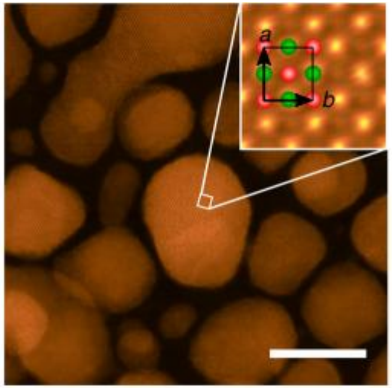


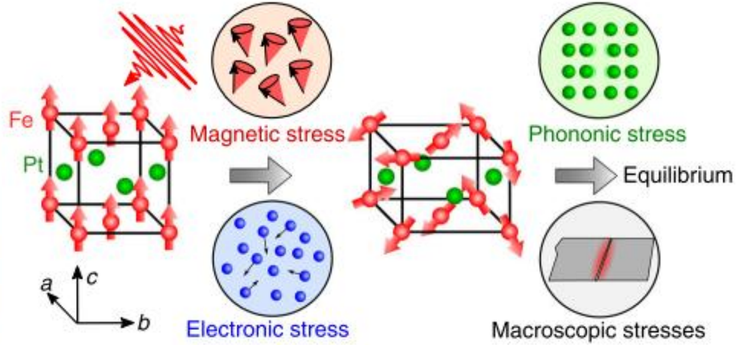
take control on the temporal evolution of the electronic core-valence transitions, and stimulated decays begin to dominate over spontaneous Auger and radiative decays

Ultrafast demagnetization (5)

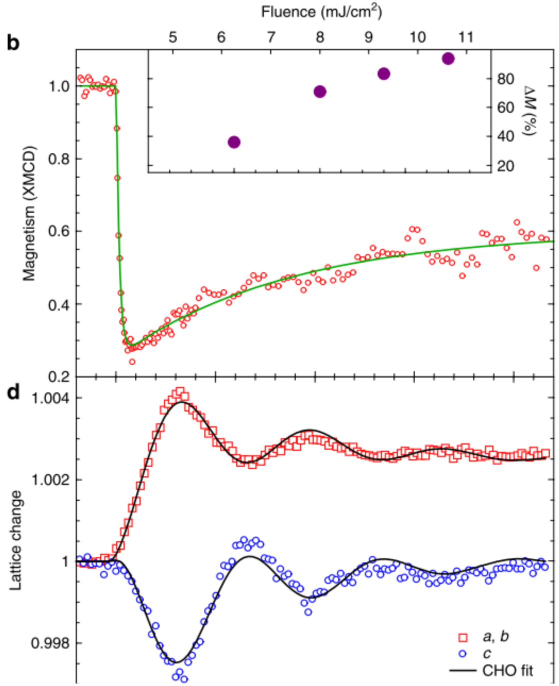
A.H. Reid, et al., Nature Commun. ***9****, 388 (2018)*

X-ray magnetic diffraction at LCLS



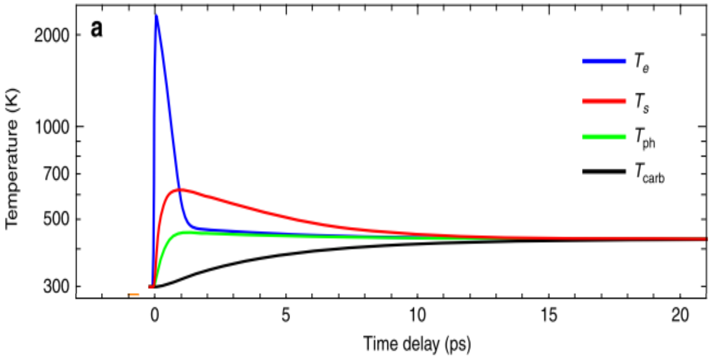


Unstrained samples: CoPt nanoparticles

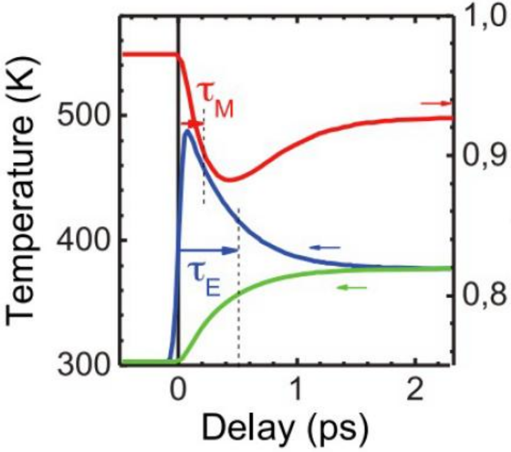


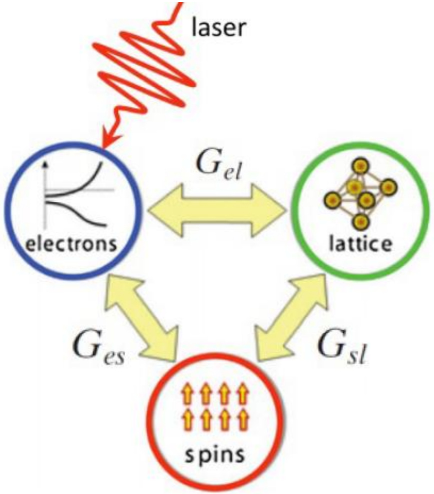
Magnetoelastic stress builds up on the sub-ps timescale, characteristic of ultrafast demagnetization

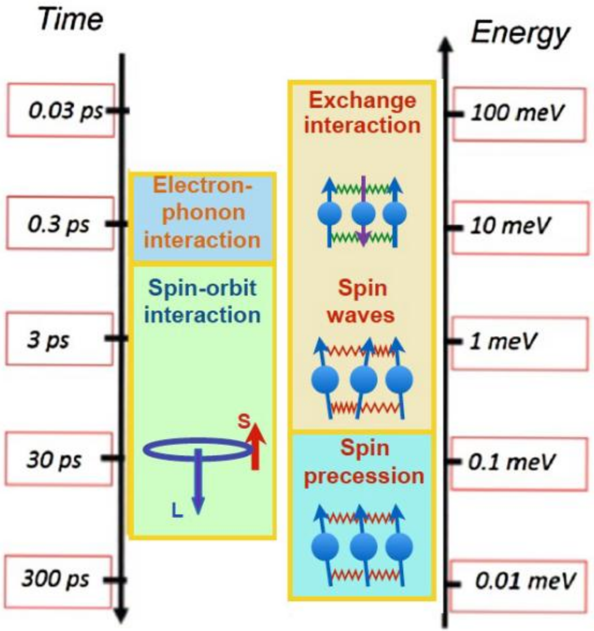
Stress from transiently populated phonons takes over on the ps timescale $\rightarrow$ reduced magn. anisotropy



Fundamental interactions and timescales







Hellman, et al., *Rev. Mod. Phys.* **89**, 025006 (2017)

Summary

What can we learn with XFELs regarding strongly correlated matter:

- What is the dynamics of chargé, orbital and spin excitations?
- What is the time scale of energy transfer between different degrees of freedom – spin, charge, orbitals and lattice?
- What is the domain shape and dynamics in photo-excited magnets?
- What is the dynamics of lattice, electrons and spins at phase transition?