The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

**2332-4**

**School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications**

*19 - 30 March 2012*

# Time resolved and high pressure science

S. Pascarelli
*ESRF (France)*

# Outline

## XAS, XANES, EXAFS, and XMCD

- X-ray Absorption
- X-ray Absorption Fine Structure
- Simple Theoretical Description
- XANES
- Major historical EXAFS breakthroughs
- Examples of applications at ELETTRA
- EXAFS data analysis
- Introduction to XMCD

yesterday

## Energy Dispersive XAS

- X-ray Absorption Spectrometers
- EDXAS
  - Basic principles, historical evolution
  - Examples of applications at ESRF
  - Future opportunities for studies of matter at extremes
- Probing laser induced extreme states of matter

today

# Laser-induced extreme states of matter

- out-of-equilibrium states of matter
- matter at local thermal equilibrium (LTE)

# Out-of-equilibrium states of matter

- short-pulsed laser (~ fs): heat deposited at rate faster than the thermal expansion rate
- possible to prepare extreme states of solid matter at temperatures well above the normal melting point (strongly driven limit)

  - Visible or near visible laser light absorbed by e- → very hot e- in cool lattice
  - Nuclear response determined by rate of energy transfer from excited e- to nuclei (~ ps)
  - Very high heating rates. $T \gg T_{melt}$ in few ps. Highly metastable state.

→ interatomic forces can be altered

probe instantaneous effect of change in e- distribution on interatomic potential energy

# Out-of-equilibrium states of matter

Phenomena for which the temperature of the electrons differs from that of the ions

- Can learn about how $e^-$-$e^-$ , $e^-$-ion and ion-ion interactions are altered
  - covalent systems: strong electronic excitation → lattice instabilities
  - metals: changes in screening → bond weakening or hardening

- Experimental requirements
  - short laser pulses (~ fs)
  - fast probe (sub-ps)
  - thin samples (10-100 nm)

- Structural probes
  - mostly e- diffraction
  - some X-ray diffraction: sample thickness limitations, reflection geometry
  - soft X-ray XANES

# Matter at local thermal equilibrium (LTE)

- Long laser pulse (~ ns): allows energy transfer between e- and ions

- Heating occurs simultaneously to density changes: dynamic excitation used to generate equilibrium thermodynamical state along a Hugoniot equation

- Very high pressures can be generated (10-100 TPa possible)

| P | Internal energy $\Delta E \sim - P \Delta V$ | Response |
|---|---|---|
| 100 GPa | ~ 1 eV outer bonding electrons | chemical bond profoundly changed |
| 100 TPa | ~ 1 keV core-electrons | new type of chemistry becomes accessible |

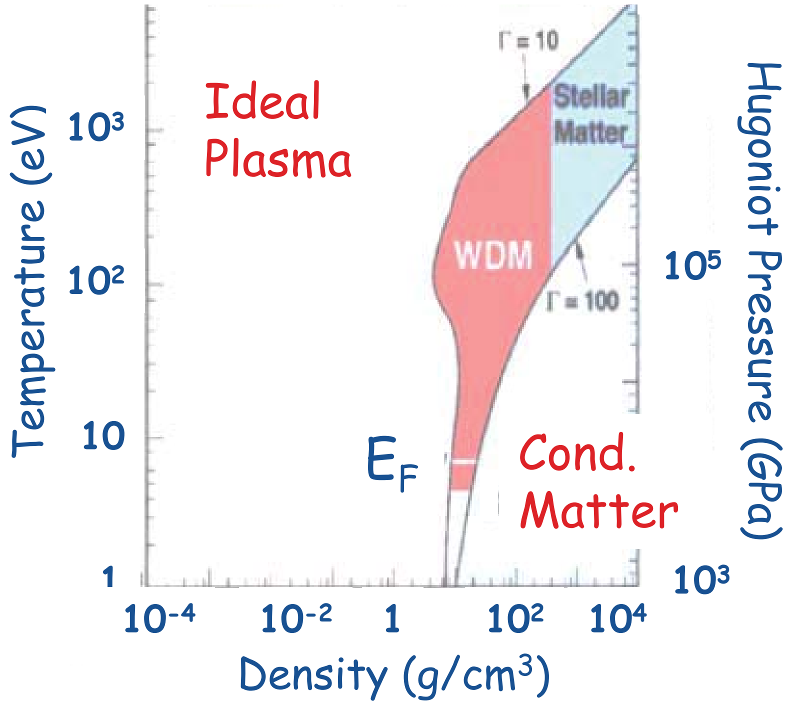
study formation and properties of high density plasma

# Warm Dense Matter

Zone in ρ, T space where standard theories for condensed matter physics and statistical physics of plasmas are no longer valid

- Internal structure of giant planets (Jupiter, Saturn, Uranus, Neptune) determined by EoS of dense plasmas
- Radiative transfer in stars governed by opacities of transition metals (Fe)
- Applications in fusion reactions, extreme materials, ..

Equation of state regimes for Fe



# Warm Dense Matter: theoretical challenges

| | Coupling $\Gamma = \frac{Z^2 e^2}{akT}$ | Degeneracy $\theta \equiv \frac{kT}{\varepsilon_F}$ | |
|---|---|---|---|
| ideal plasma<br>high T, low ρ | Γ << 1 | θ >> 1 | Non-degenerate electrons<br>$E_{coulomb} \ll E_{thermal}$ |
| warm dense matter | Γ ~ 1 | θ ~ 1 | Ions strongly coupled<br>Collective behaviour of particles<br>Electrons partially degenerate |
| condensed matter | Γ >> 1 | θ << 1 | Degenerate electrons<br>$E_{thermal} \ll E_F$ |

→ No obvious small quantity to be used as perturbation parameter

- Accurate experimental data required to test validity of models

# Investigating Warm Dense Matter by XAS

- Electronic structure
  - changes in electronic shielding of inner shells due to ionization
  - continuum lowering depression (neighbour atoms getting closer)
  - electron degeneracy

- Local structure
  - loss of structural order
  - modifications of ion-ion correlation

- Experimental requirements
  - laser energy density ~ 1 $J/mm^3$ $H_2O$ $B_0$ ~ $10^3$ $J/cm^3$
    ~ 100 $J/mm^3$ Fe $B_0$ ~ $10^5$ $J/cm^3$
  - sample thickness: nm (out-of-equil) → μm (LTE)
  - time resolution: ps (out-of-equil) → ns (LTE) (speed of sound in Fe ~ 5 μm /ns)

## Ultrafast XAS

- ❑ laser driven shock + laser driven X-ray source
  - Bradley et al. PRL 1987
  - Davidson et al. APL 1988
  - Da Silva et al. PRL 1989
  - Hall et al. EPL 1998
  - Mancic et al. PRL 2010
- ❑ laser driven shock + synchrotron source
  - Cho et al. PRL 2011

+ MEC @ LCLS …

# Probing laser-induced extreme states of matter

- out-of-equilibrium states of matter

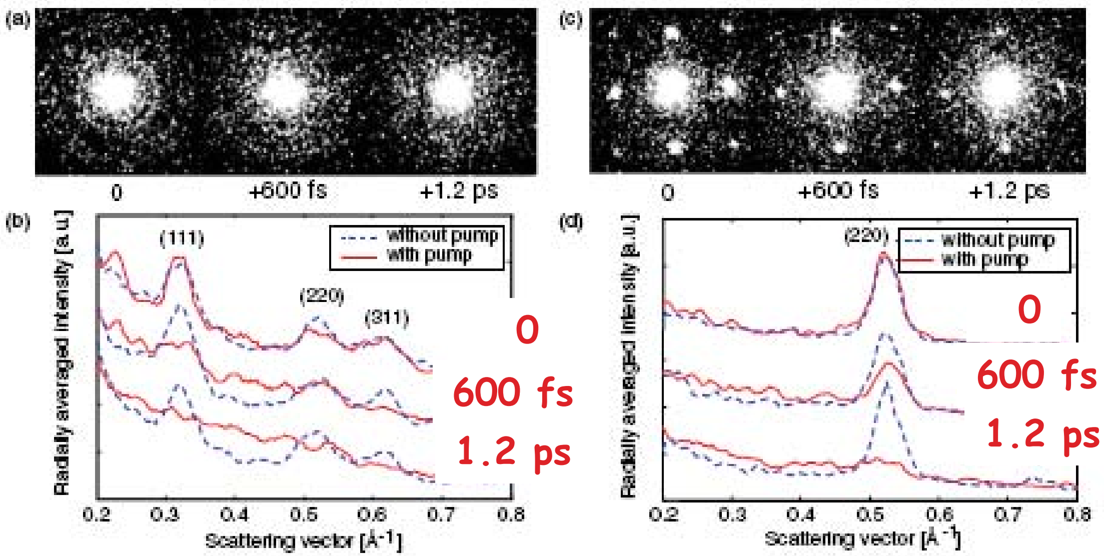
- matter at local thermal equilibrium (LTE)

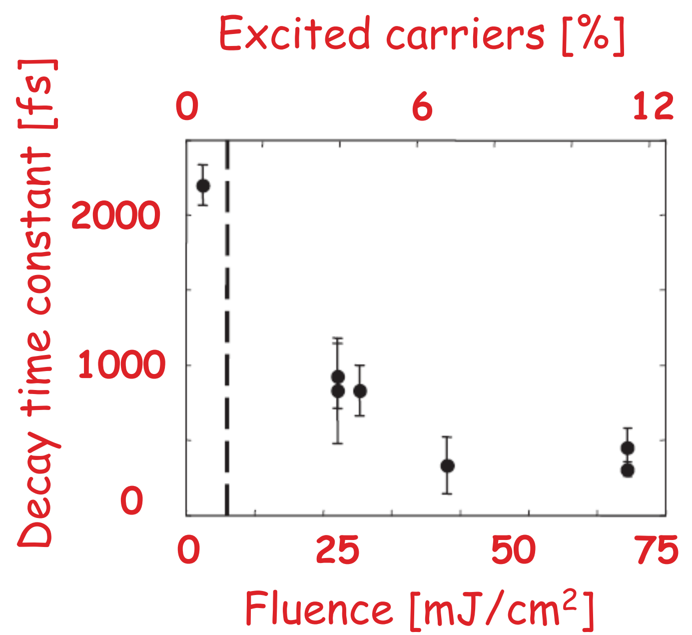
# Examples: out-of-equilibrium studies

| SAMPLE | PUMP<br>Optical laser | PROBE | Subject |
|---|---|---|---|
| 30nm<br>Si Xtal<br>Si polyXtal | 387 nm<br>150 fs<br>65 mJ/cm$^2$ | Electron diffraction<br>200 fs | dynamics of melting |
| 20nm<br>Al polyXtal | 775 nm<br>120 fs<br>70 mJ/cm$^2$ | Electron diffraction<br>600 fs | dynamics of melting |
| 20nm<br>Au polyXtal | 387 nm<br>200 fs<br>110 mJ/cm$^2$ | Electron diffraction<br>40 fs | dynamics of melting |
| 70 nm<br>Cu polyXtal | 387 nm<br>150 fs<br>330 mJ/cm$^2$ | ALS undulator XANES<br>2 ps | electronic structure in warm dense Cu |

# Laser induced melting in Si

Si polyXtal | Si Xtal




- at high fluence dynamics not explained by thermal relaxation mechanism

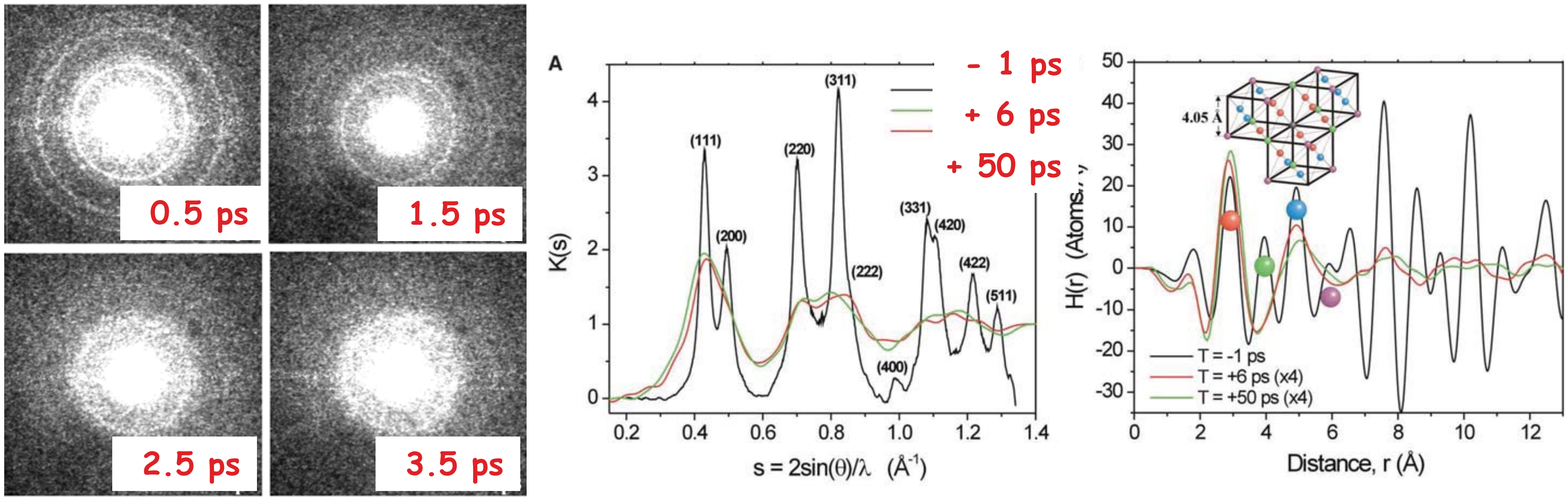
- possible mechanism: large portion of valence e- promoted by single photon absorption across direct band gap (~ 11 % at 65 mJ/cm$^2$)

→ covalent bond weakens

→ electronically induced phase transition

Harb PRL 2008

# Laser induced melting in Al




- transition complete at 3.5 ps, melting dynamics compatible with thermal disordering

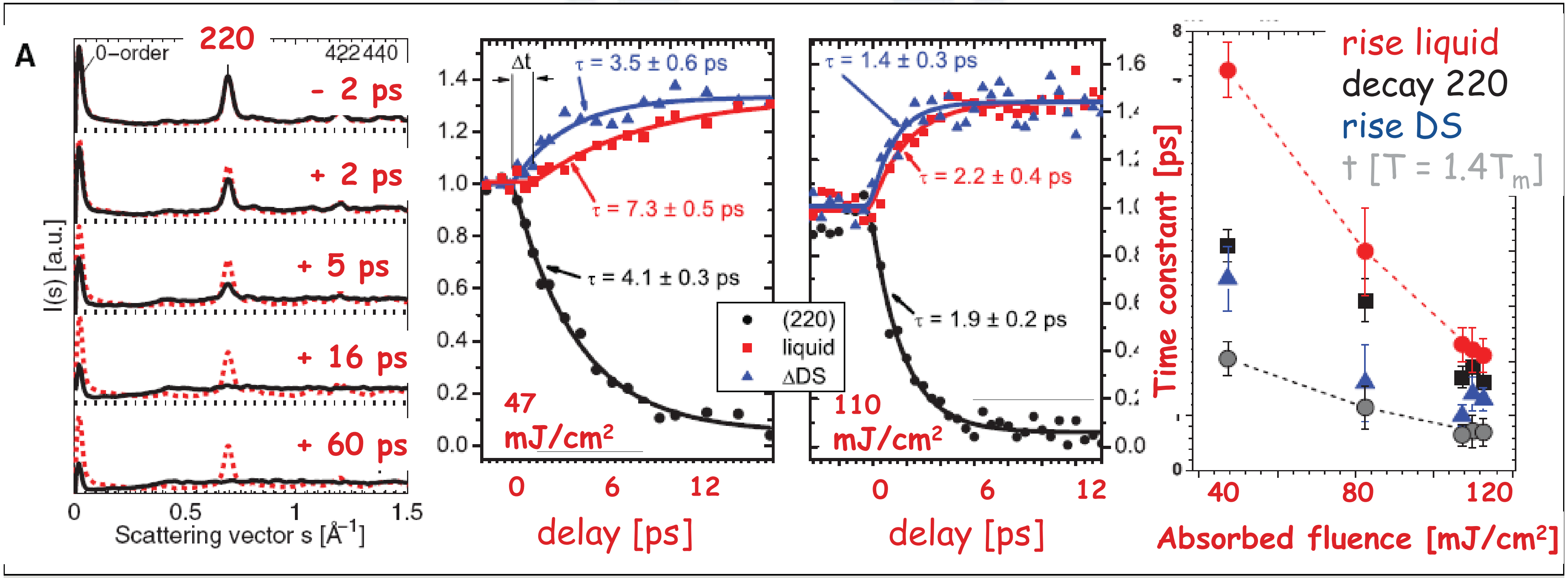
→ thermally induced phase transition

- fast hot electron energy redistribution into phonons: $T_{melting}$ reached in < 0.8 ps
- at 1.5 ps, $T_{lattice}$ ~ 1.5 $T_{melting}$

→ superheated metastable state

Siwick Science 2003

# Laser induced melting in Au




- rise of liquid structure factor is delayed Δt = 1.4 ps compared to DS and 220 dynamics

→ thermally induced phase transition

- rate of disordering retarded w/respect to degree of lattice heating

→ superheated metastable state

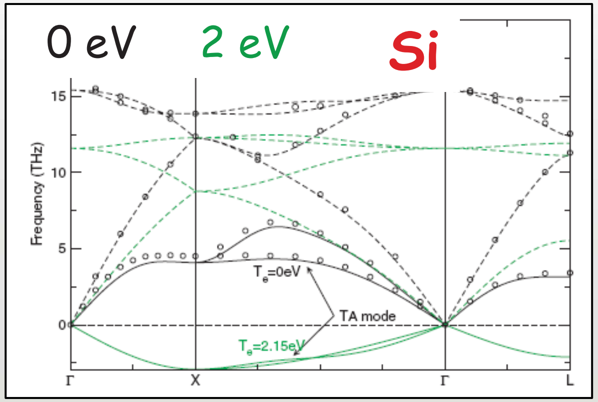
- results can be explained with $T_e$ - dependent Debye Temperature → lattice hardening

Ernstorfer Science 2009

# Laser induced melting: DFT calculations

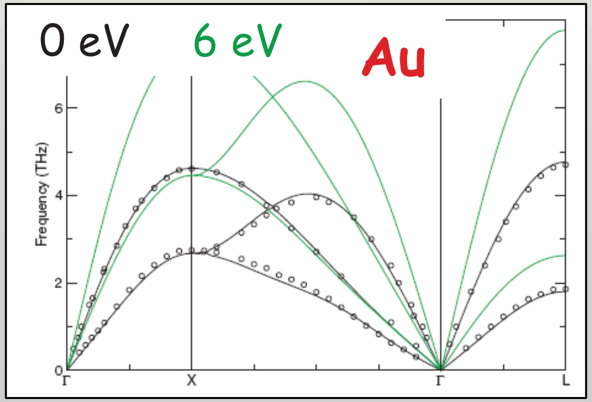
- Effect of laser illumination on structural stability of lattice
  - few fs after illumination immediately after electrons have reached their equilibrium $T_e$
  - ions not yet responded to T increase → density unchanged

phonon spectrum



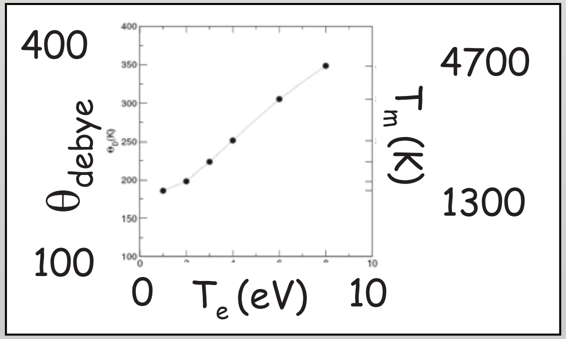

covalent bonding

- TA mode becomes unstable for $T_e$ > 1.5 eV
- lattice instability induced by $e^-$ thermal excitation




metallic bonding

- Au: steepening of phonon dispersion, hardening of lattice
- Al: ion-ion interaction unaffected by $T_e$




Recoules PRL 2006

# Investigating laser induced melting by XAS ?

What additional information can XAS provide ?

- Fully resolve the relative atomic motions during the melting process
- Local structure in the superheated and in the liquid phase

- Covalent systems (non-thermal melting)
  - effects of valence electron promotion on electronic structure
  - dynamics of electronically driven phase transition

- Metals (thermal melting)
  - electronic structure in highly superheated metastable phase
  - force constants from mean square relative displacements

- Experimental difficulties
  - thickness limitations (some work with soft x-rays)
  - transmission vs reflection geometry

# XANES on Warm Dense Cu (out-of-equil)

PRL 106, 167601 (2011) PHYSICAL REVIEW LETTERS week ending 22 APRIL 2011

**Electronic Structure of Warm Dense Copper Studied by Ultrafast X-Ray Absorption Spectroscopy**

B. I. Cho,[1] K. Engelhorn,[1] A. A. Correa,[2] T. Ogitsu,[2] C. P. Weber,[3] H. J. Lee,[4] J. Feng,[1] P. A. Ni,[5] Y. Ping,[2] A. J. Nelson,[2] D. Prendergast,[6] R. W. Lee,[2] R. W. Falcone,[1,7] and P. A. Heimann[1]
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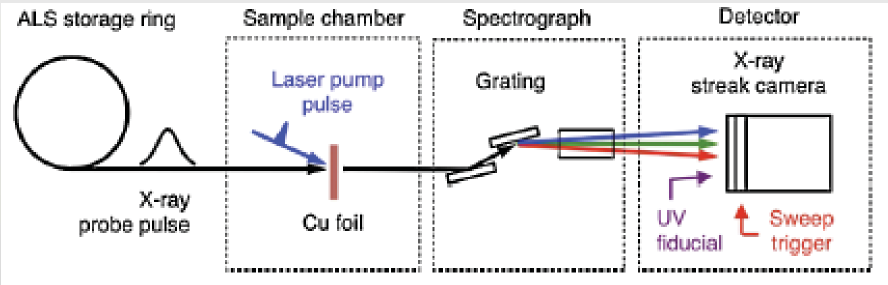
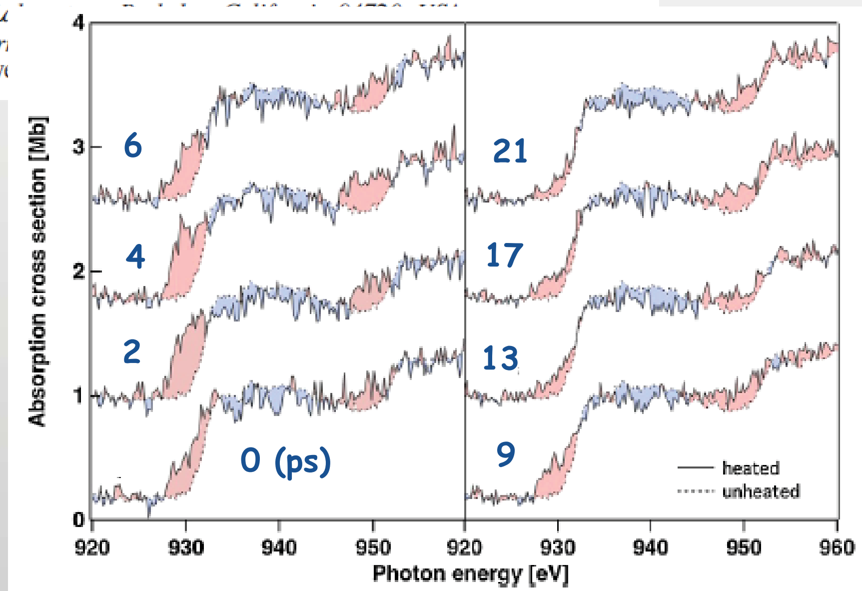
[7]*Department of Physics, University of Califor*
(Received 1 September 2010; revised manuscript receiv




- probe: broadband 70 ps x-ray pulse from ALS undulator
- VLS grating spectrometer → streak camera (2ps)

- ❑ $T_e$ quickly increased to ~ 1eV (from DFT)
- ❑ $L_3$ and $L_2$ edges shift to lower E
- ❑ $T_e$ (t) → e-phonon coupling in non-equil Cu

# Probing laser-induced extreme states of matter

- out-of-equilibrium states of matter
- matter at local thermal equilibrium (LTE)

# XANES on Warm Dense Al (LTE)

PRL 104, 035002 (2010) PHYSICAL REVIEW LETTERS week ending 22 JANUARY 2010

**Picosecond Short-Range Disordering in Isochorically Heated Aluminum at Solid Density**

A. Mančić,[1] A. Lévy,[2] M. Harmand,[2] M. Nakatsutsumi,[1] P. Antici,[3,4] P. Audebert,[1] P. Combis,[5] S. Fourmaux,[6] S. Mazevet,[5] O. Peyrusse,[2] V. Recoules,[5] P. Renaudin,[5] J. Robiche,[1,*] F. Dorchies,[2] and J. Fuchs[1,†]

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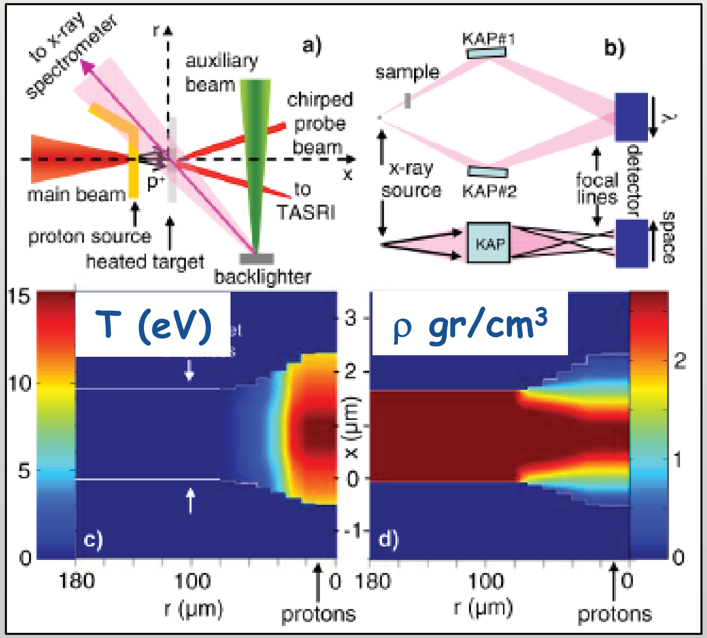
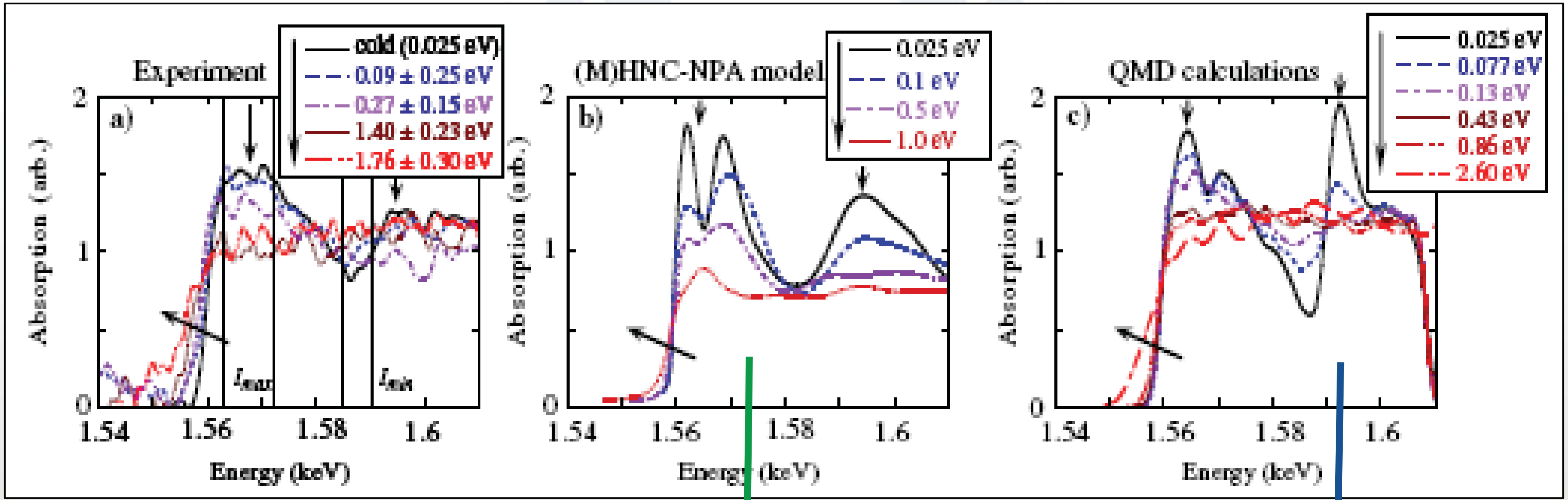
[6]*INRS-Energie et Matériaux, 1650 BD. L. Boulet, J3X1S2 Varennes, Québec, Canada*
(Received 5 October 2009; published 20 January 2010)

First combination of XANES and ab-initio calculations on warm dense Al

- Pulsed proton beam heats isochorically and uniformly 1.6 μm Al foil over 25 ps
- Ultrashort (~ 4 ps) X-ray pulse backlights sample
- X-ray spectrometer (2 diffractive crystals) allows simultaneous measurement of $I_0$ and $I_1$



# XANES on Warm Dense Al (LTE)




MHNC-NPA (DFT):

- produce TD averaged structural quantities, ie. g(r)
- select atomic configurations compatible with g(r)
- calculate XANES for each and average all

- decrease of slope around the edge + red shift
- progressive smoothing of XANES structures
- very fast dynamics: loss of order < 10 ps

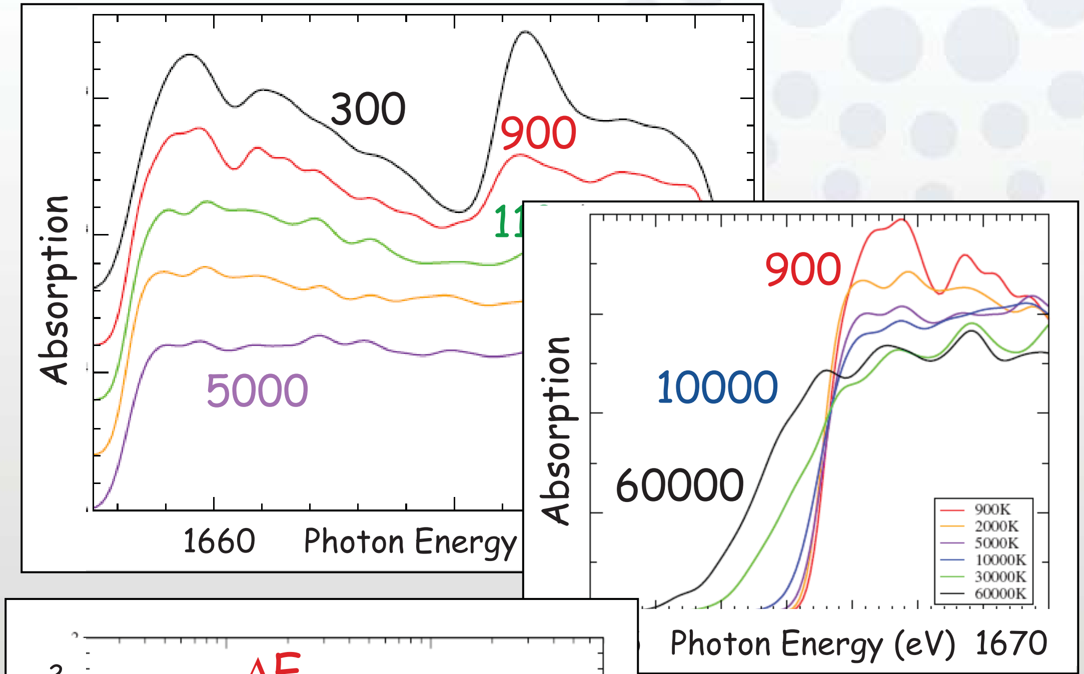
QMD (DFT):

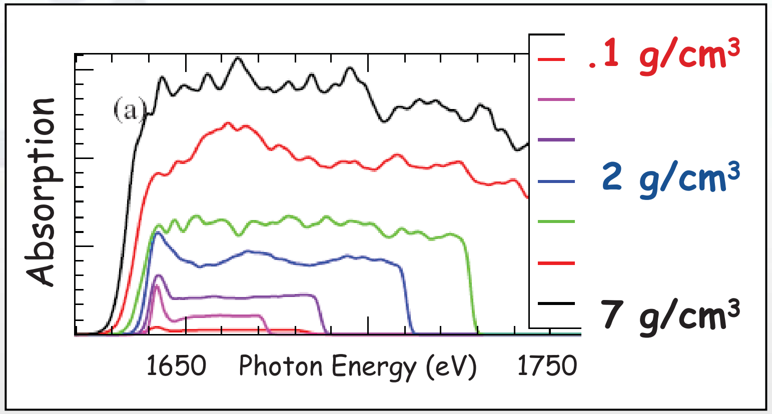
- large supercells (108 → 32 atoms)
- ab-initio electronic structure and thermodynamical state

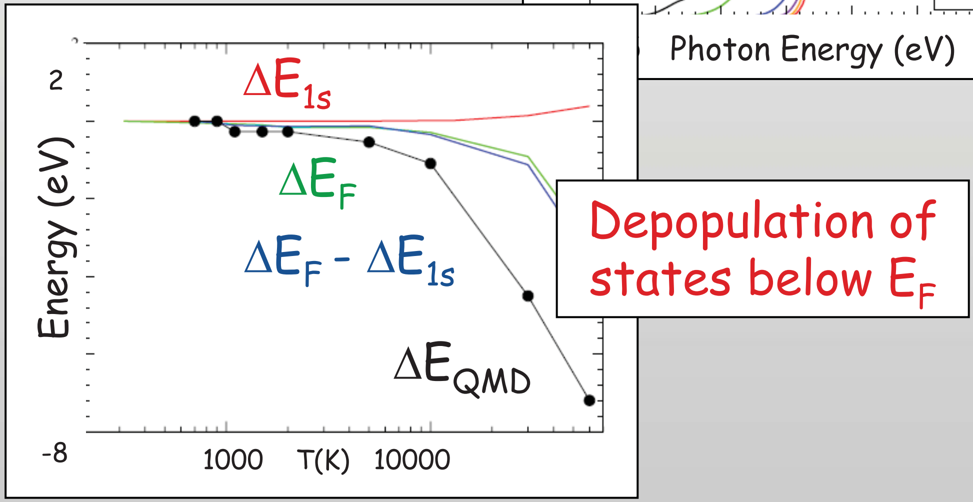
# QMD + DFT on Al

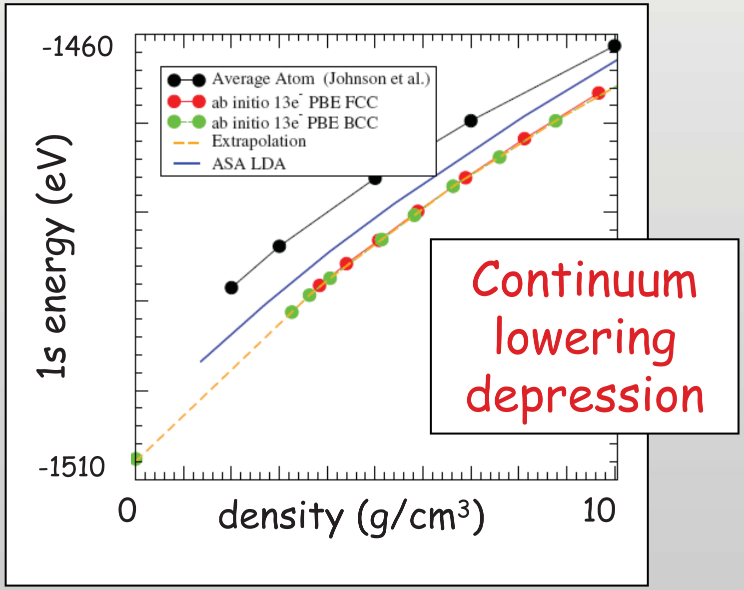
$\rho = \rho_0$

T = 1.5 eV



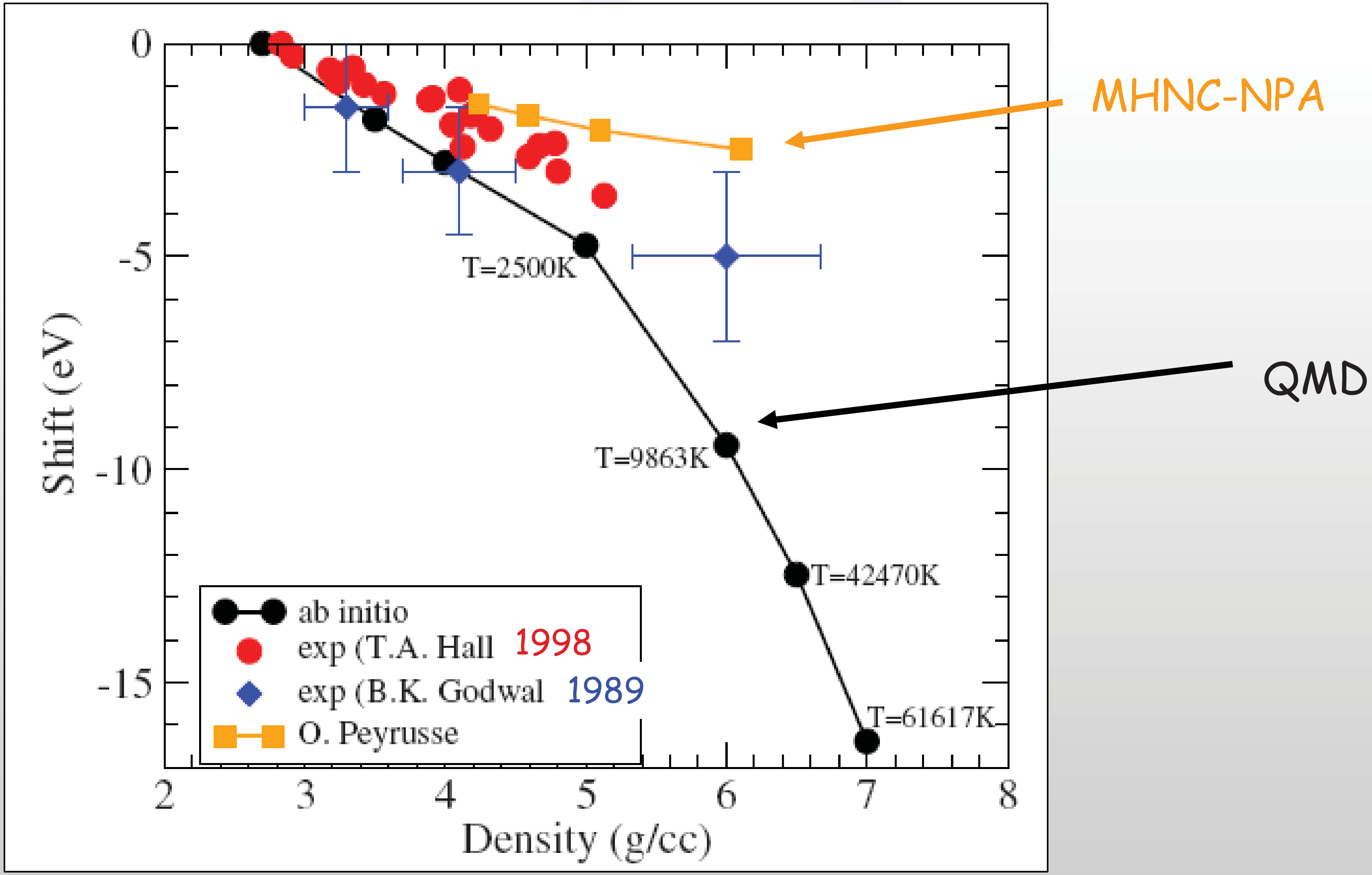




Recoules PRB 2009

# QMD + DFT on Al: along the Hugoniot




Experimental data falls in-between theoretical predictions at high density

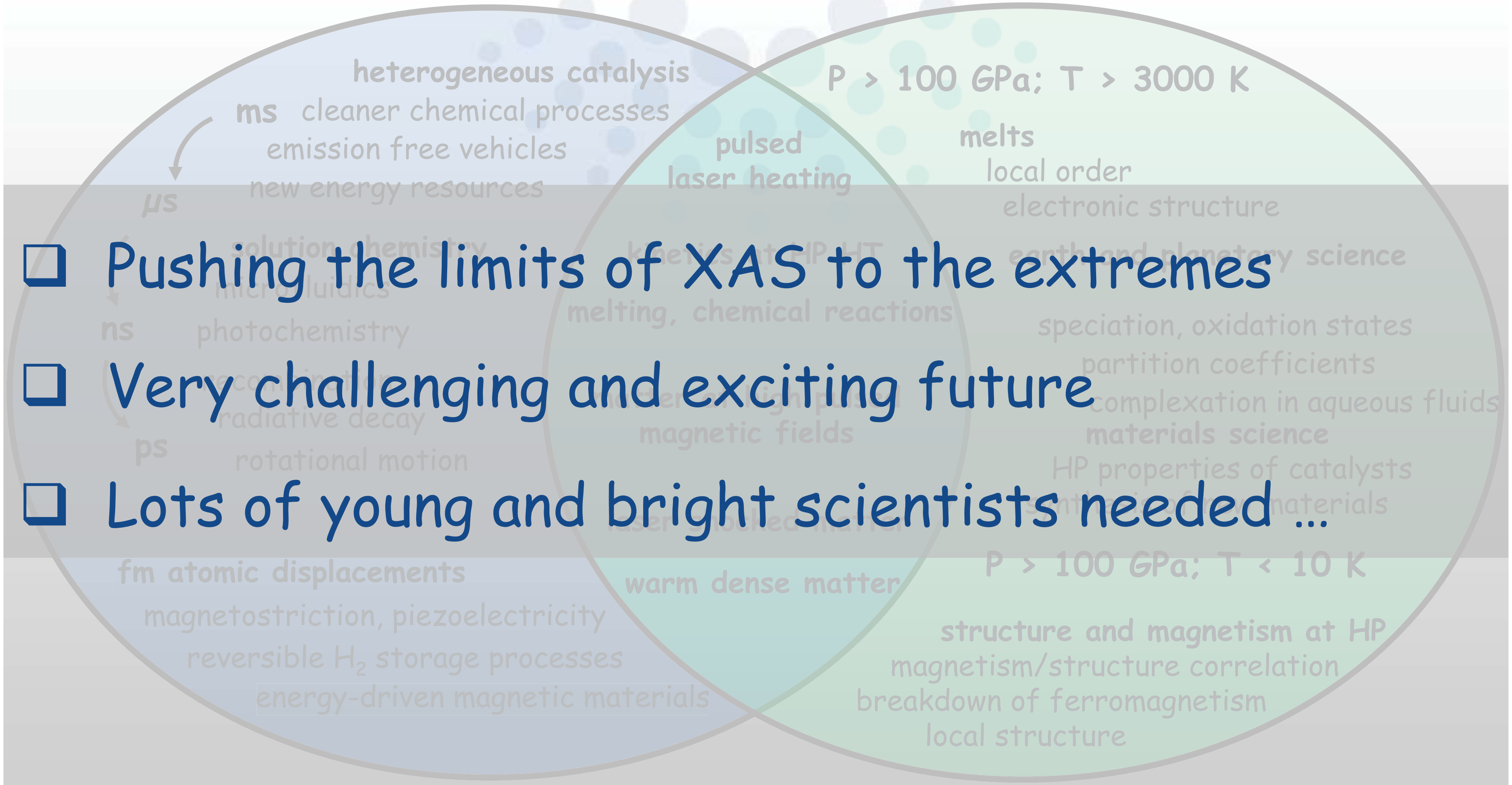
Mazevet PRL 2008

# UPBL11: perspectives for WDM studies

| X-ray source | UPBL11 parameters | New experimental capacity |
|---|---|---|
| Brightness | $10^6$ - $10^7$ photons / 100ps bunch<br>3 x 3 $\mu m^2$ (FWHM) | sample volume: $10^{-6}$ $cm^3$<br>i.e. warm dense Fe: laser power < 1 J |
| Energy tunability | 5 - 30 keV | K-edges between Ti and In<br>L-edges between Te and U |
| Bandwidth of polychromatic beam | DE/E > 10 % | Absorption edges<br>XANES<br>EXAFS |

- X-ray-optical laser interfacing using table-top transportable lasers (1 J)
- Access to large portion of periodic table (i.e. all 3d, 4d and 5d metals)

# Outlook




- Pushing the limits of XAS to the extremes
- Very challenging and exciting future
- Lots of young and bright scientists needed …