Energy dispersive X-ray absorption Spectroscopy: scientific opportunities and technical challenges

ESRF user meeting 2009, 2-5 February 2009

EDXAS and melting in the DAC

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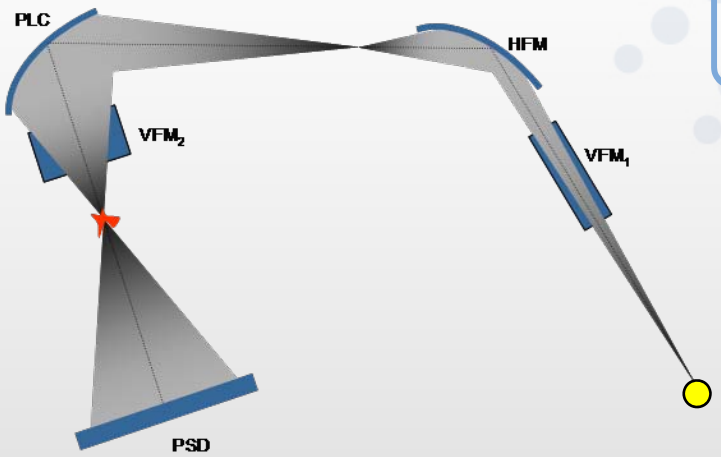
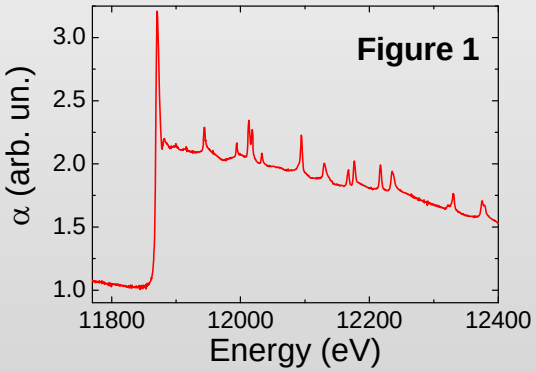
EDXAS: an instrument to go "small"

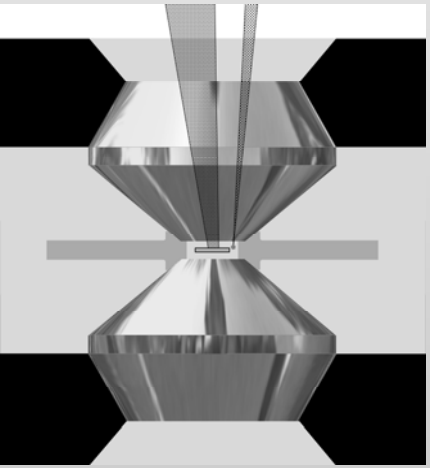


Small beam size

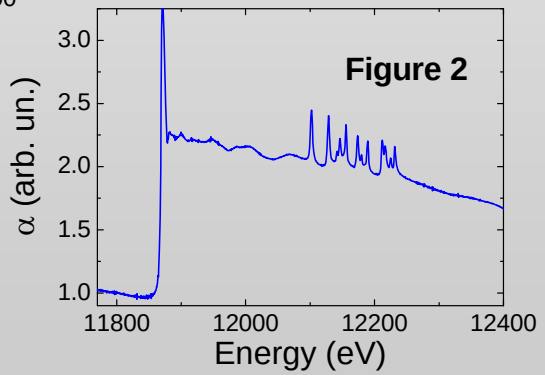
beam stability in energy and position

Studies at extreme conditions of pressure

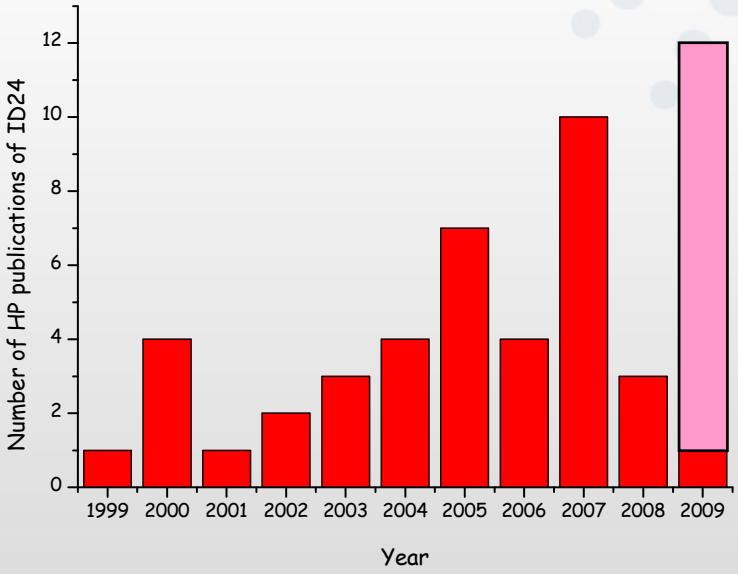




EDXAS: easy removal of the diamond Bragg peaks from the energy region of interest

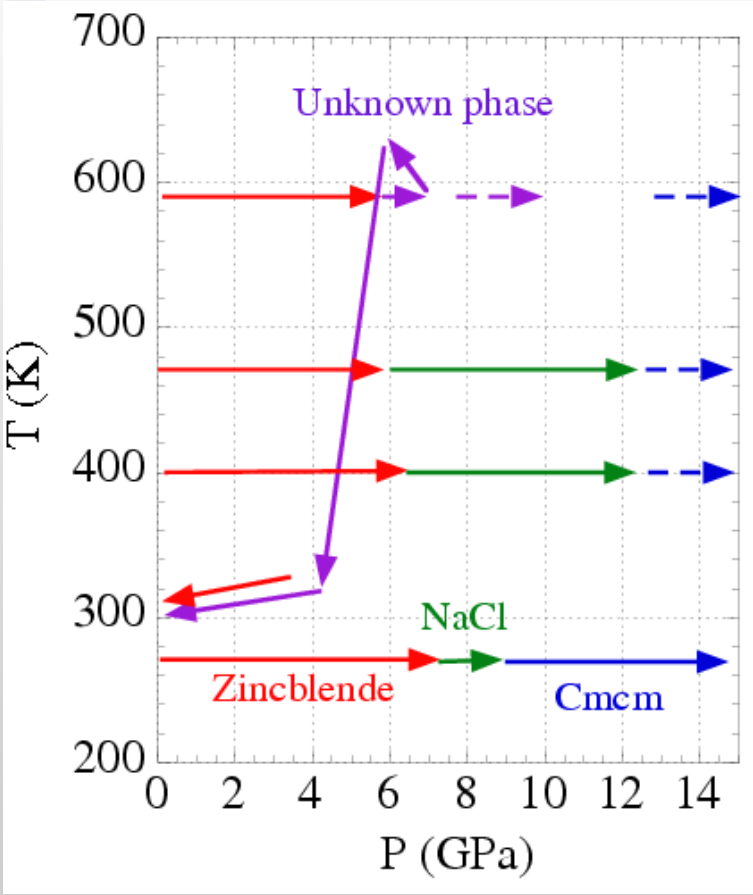


HP studies at ID24



From ESRF library database

Octect compounds - InAs at HP/HT



Pascarelli, Aquilanti, Munsch, Itié. NIM B **200**, 439 (2003)

Necessity of going "more extreme"

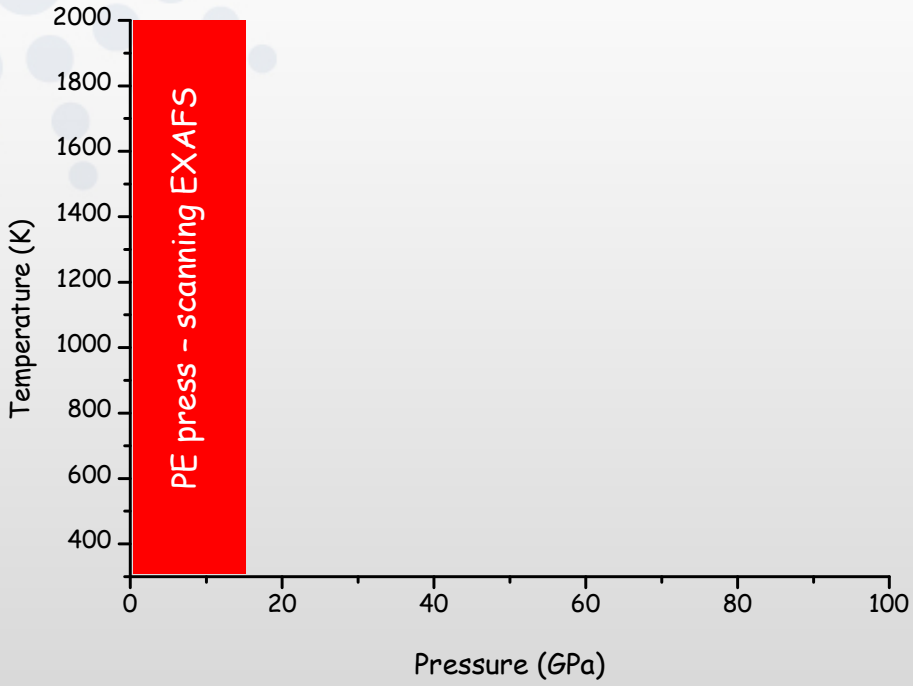
- P-T phase diagram largely inexplored
- Geoscience and planetary science
- *In situ* chemical reactions
- Synthesis of new materials
- Structure of melts at high pressure

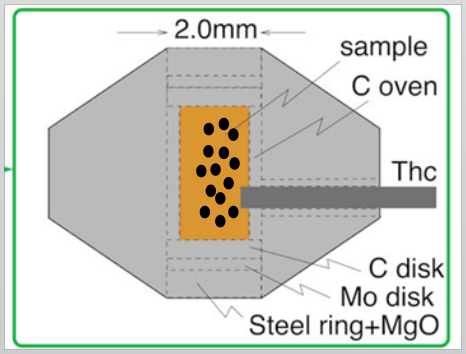
Melts at high pressure using XAFS

Liquid Ga
Poloni *et al.*, PRB 71, 184111 (2005)

Liquid Bi
Principi *et al.*, PRB 74, 64101 (2006)

Liquid Sn
Di Cicco *et al.*, APL 89, 19112 (2006)

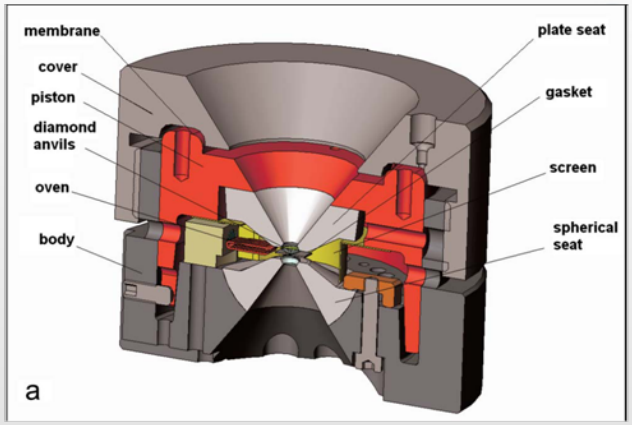


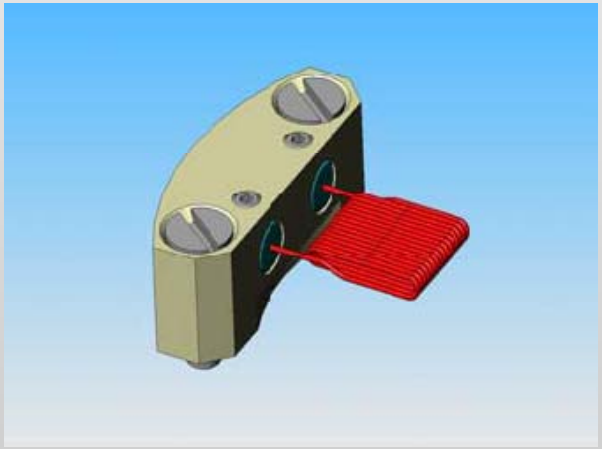


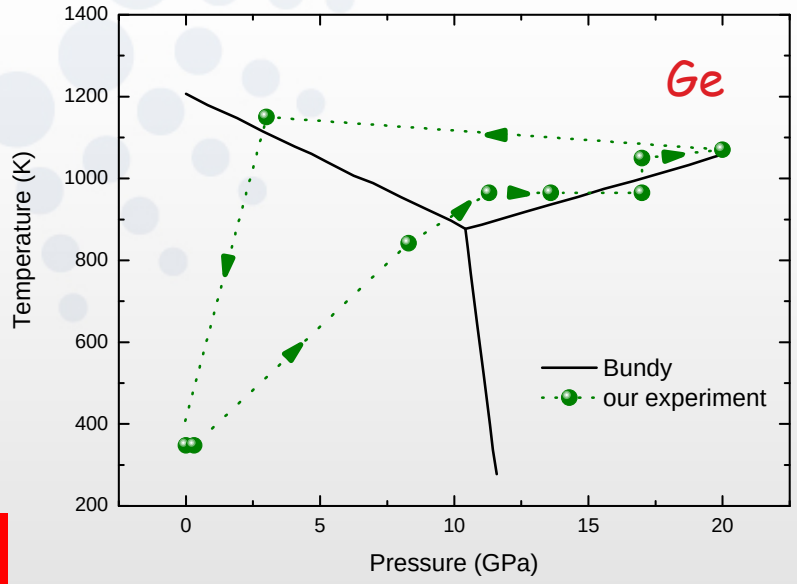
- Limited P-T space
- Unclean sample (chemical reactions)

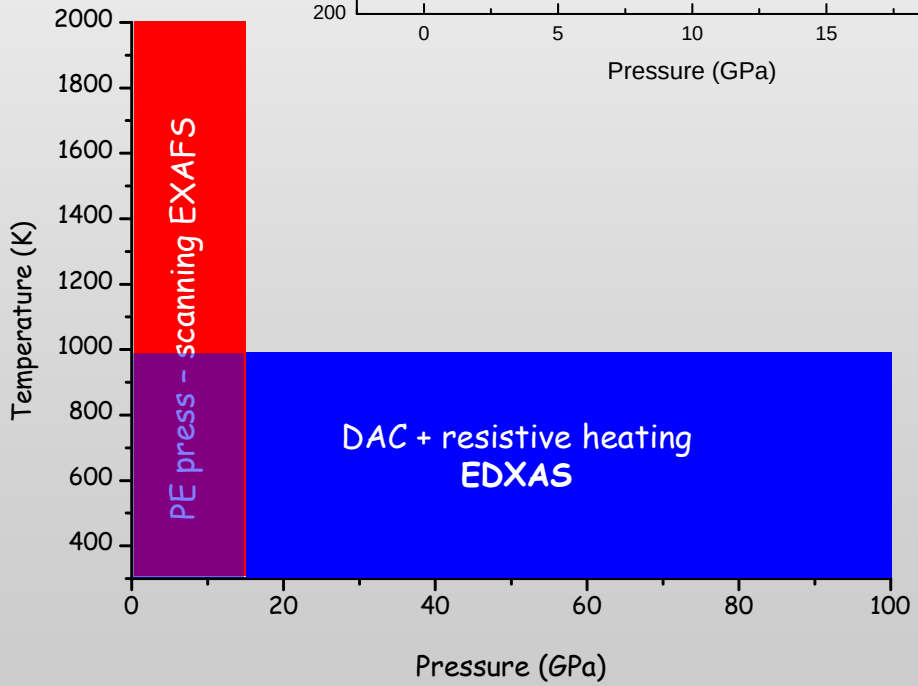
Resistive Oven

Poster of Sebastien Pasternak



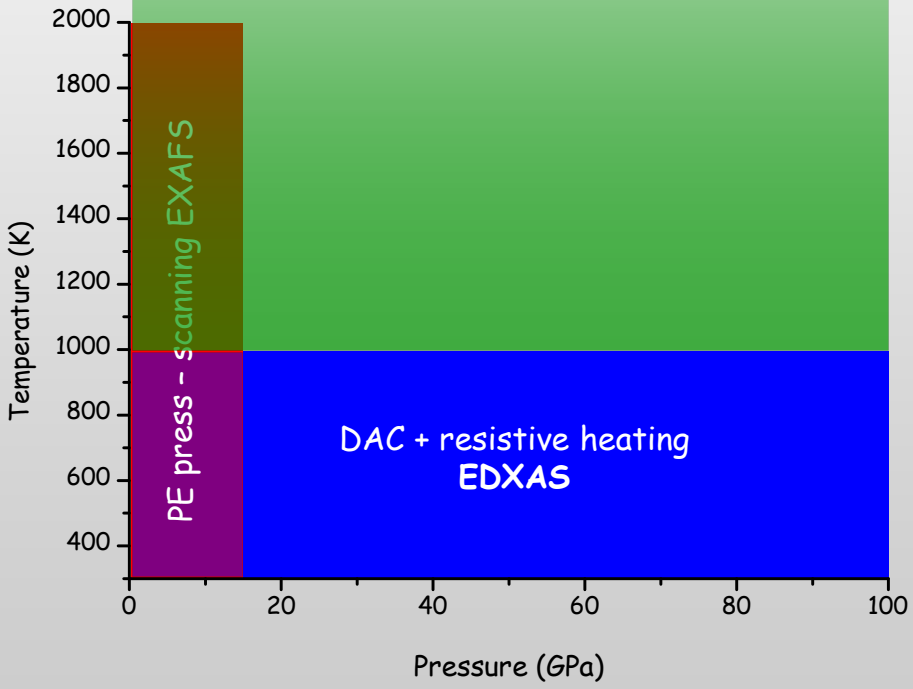






S. Pasternak *et al.*, RSI **79**, 85103 (2008)

Laser heated DAC



- LHDAC technology: 20 years old
- Today: simple and inexpensive devices

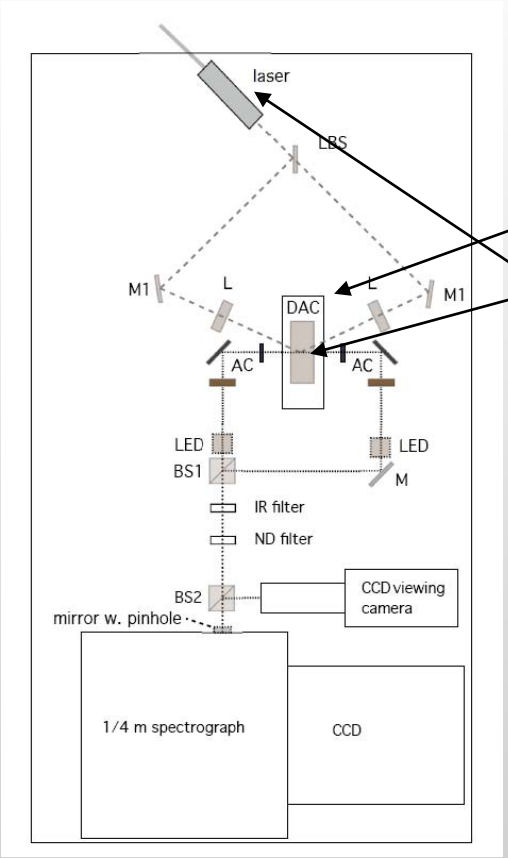
Applicable to:

- Mineral physics
- Material synthesis
- High pressure melting

In situ studies using LHDAC combined with SR have been done mainly using diffraction techniques

No *in situ* XAS studies using LHDAC

Portable laser heating stand (R. Boehler MPI-Mainz, Germany)

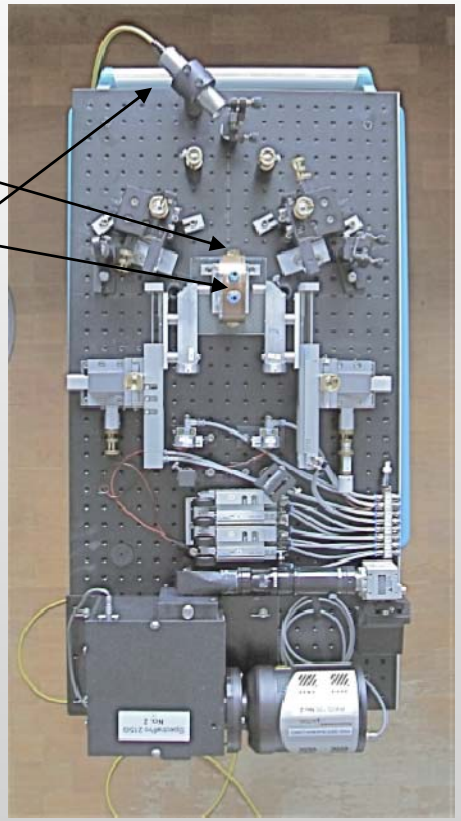


Cutout for goniometers

Cu cell holder

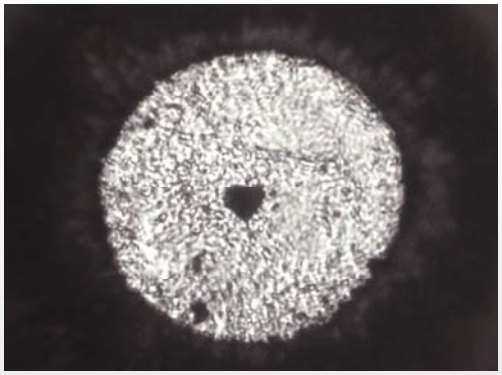
Fiber pumped near infrared laser
(P=110 W, λ=1070 nm)

Laser alignement and focusing:
off-axis incidence



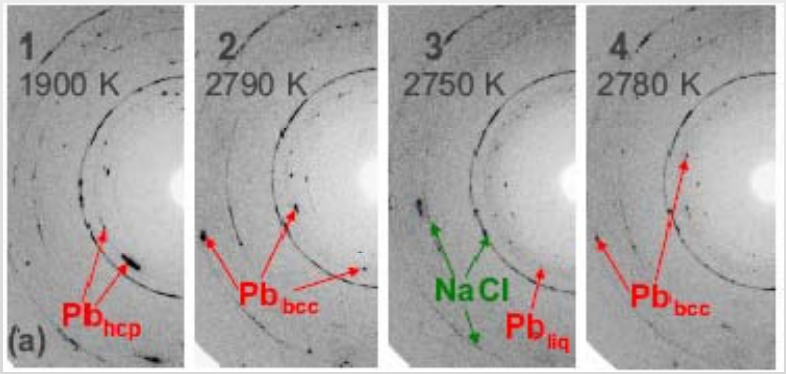
R. Boehler, H. G. Musshoff, R. Ditz, G. Aquilanti, and A. Trapananti, *submitted*

Melting in LHDAC



Spherical shape with a size commensurate with that of the laser beam (< 30 µm)

Smaller and smaller samples



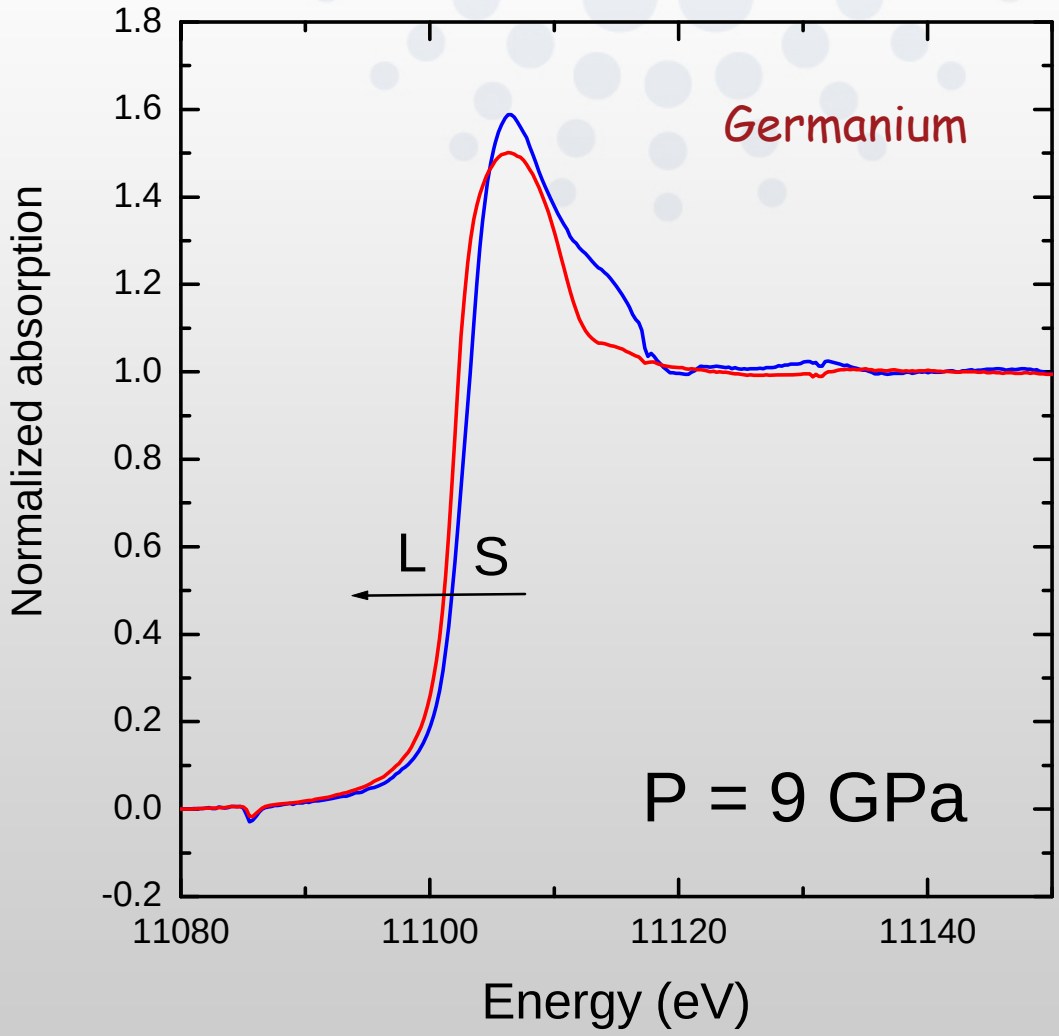
Dewaele, Mezouar, Guignot, Loubeyre, PRB **76**, 144106 (2007)

Time resolved XRD (1 pattern/s)

Short time scales

EDXAS

LHDAC melting at ID24



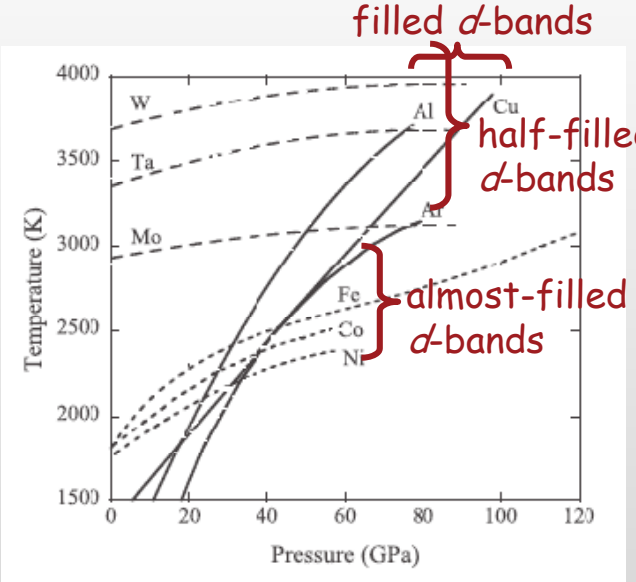
Melting of iron: geophysical implications

- Fe: major element of the Earth's core
- Need of better models and more precise measurements of the P-V-T EoS
- Melting temperature of Fe at HP constraints the temperature in the Earth's core
  - Earth's thermal gradient
  - Heat flow in the core and in the mantle
- Melting temperature of Fe at IOCB ranges from 5000 to 7000 K
  - Too big discrepancy for modelling the thermal history of the Earth
- Several melting detection techniques:
  - *ab initio* calculations for the solid-liquid equilibrium conditions
  - shock melting
  - LHDAC: laser speckle methods, XRD…

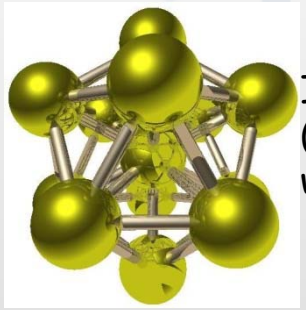
Can EDXAS + LHDAC provide an additional method to detect melting?

Melting of iron in a fundamental physics context

- Classic d-electron metal
- Systematic dependence of the electronic *d*-band occupancy and the melting slope



S. Japel et al., PRL 95, 167801 (2005)



It has been proposed that the liquid frustration (presence of icosahedral short range order - ISRO) would lower the freezing point in liquids

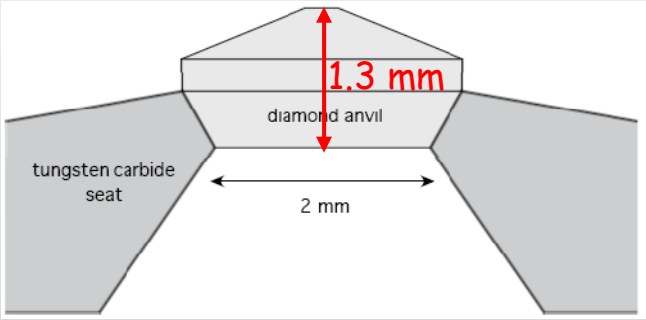
Theory predicts much steeper melting curve if the formation of icosahedral clusters is not taken into account

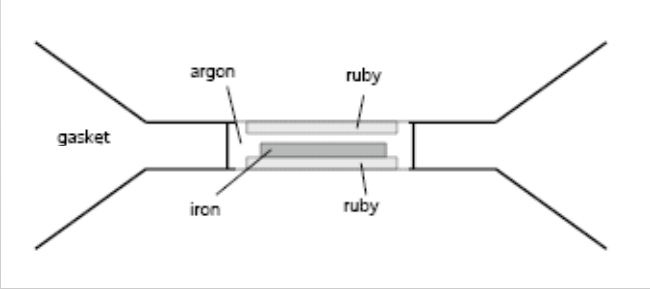
XAS is sensitive to 3-body distribution function through the presence of multiple scattering signals and together with RMC methods has evidenced ISRO in liquid metals
(A. Di Cicco et al., PRL **91**, 135505 (2003))

Can we provide evidence of preferred local ordering in liquid iron at HP ?

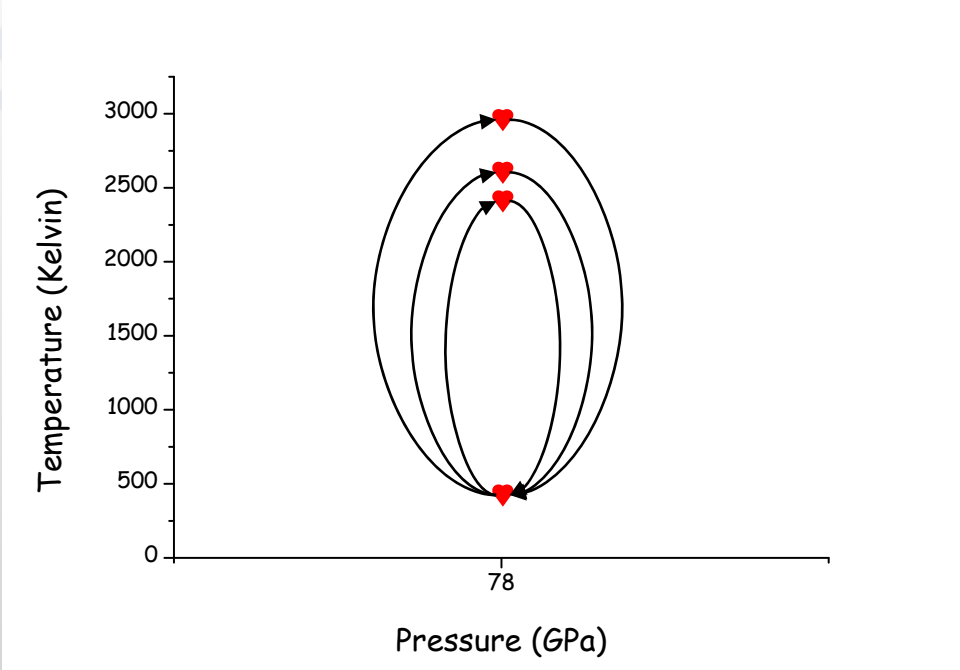
Melting of iron at ID24 - experiment

- 3 undulators
- Si(311) as polycromator
- Si mirror at 4 mrad
- Beam size 5x5 μm² FWHM

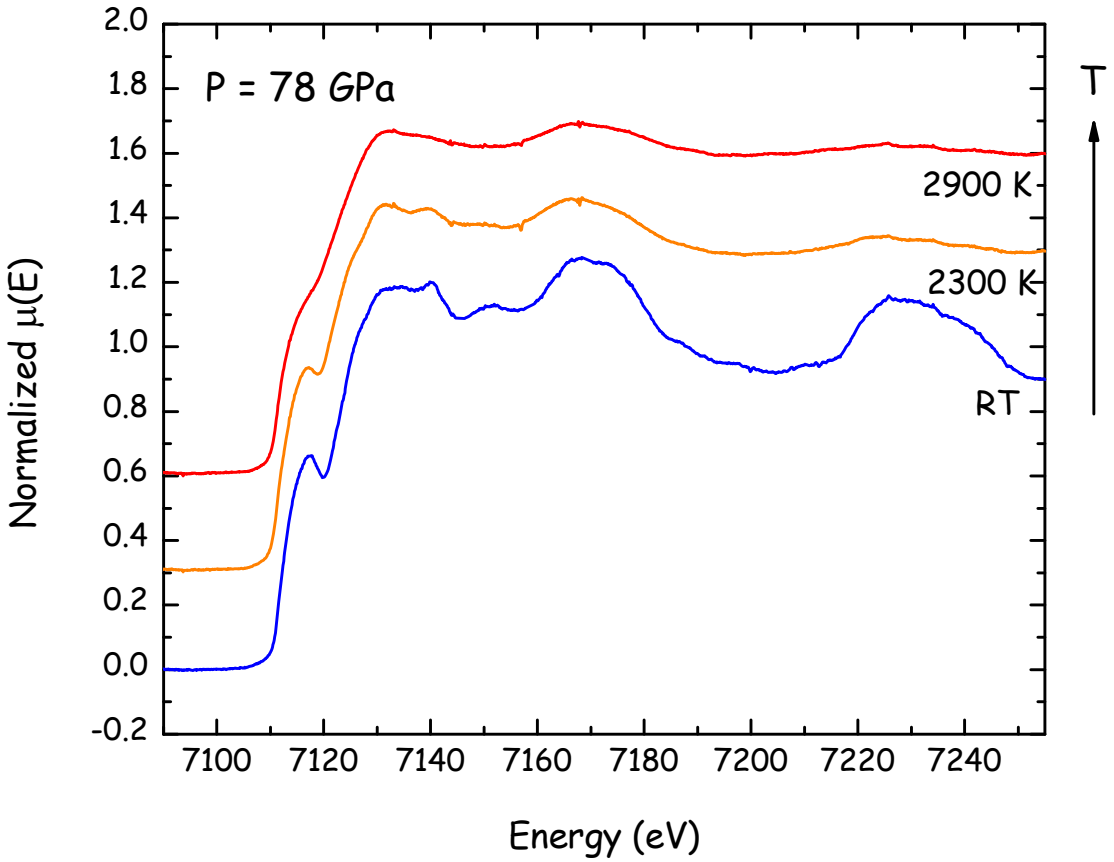




Sample pressurized to 78 GPa



Melting of iron at ID24 – experimental data



K-edge XANES: electronic DoS above the Fermi level with p symmetry

Prepeak:
3d-4p band hybridization

hcp features conserved at 2300 K

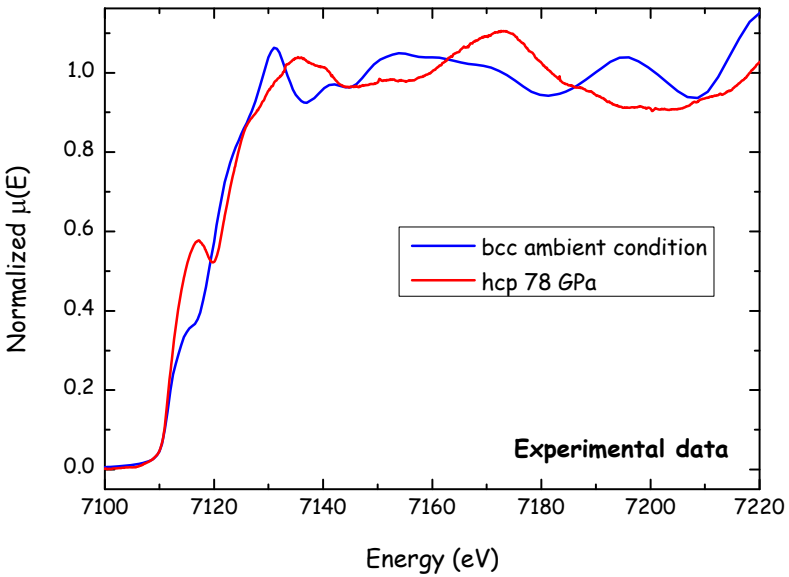
Oscillations damped with T

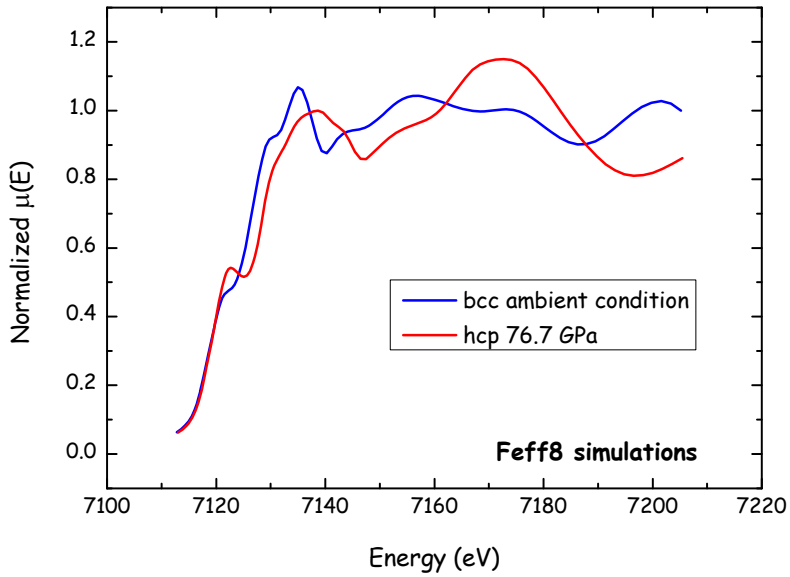
At 2900 K:
the prepeak disappears
double oscillations at 7130 eV

Preliminary analysis

- Can we detect melting of iron at HP ?
- What is the structure of the melt ?

We deal with the XANES → XANES simulations using Feff8





Simulations for the liquid

- ONE single cluster cannot describe the structure of the liquid
- Average over several configurations
- Configurations obtained using the EPSR method

EPSR* (Empirical Potential Structure Refinement)

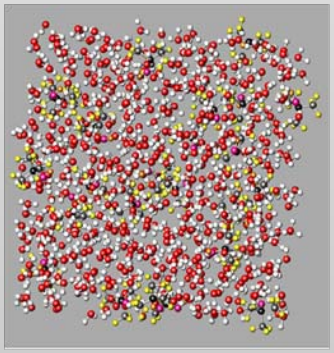
Computational method for building atomic and molecular structural models of disordered materials, such as liquids that are consistent with available structural data and known physical/chemical constraints

INPUT

experimental data (S(q))

Monte Carlo simulation
with an Empirical Potential
iteratively refined to reproduce
the experimental data

simulation box (known constraints such as density, atomic species, stoichiometry)

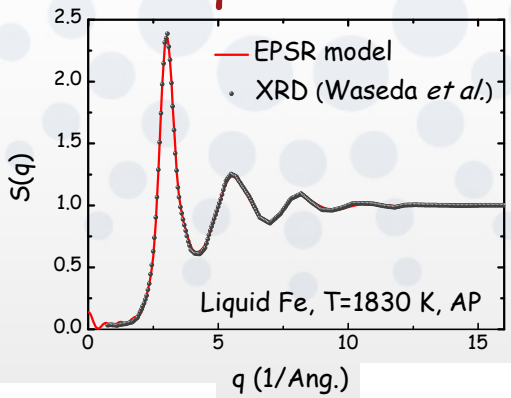


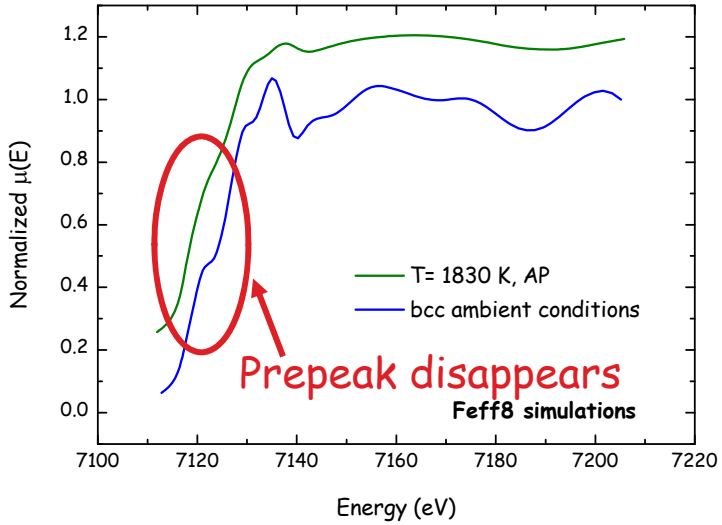
OUTPUT

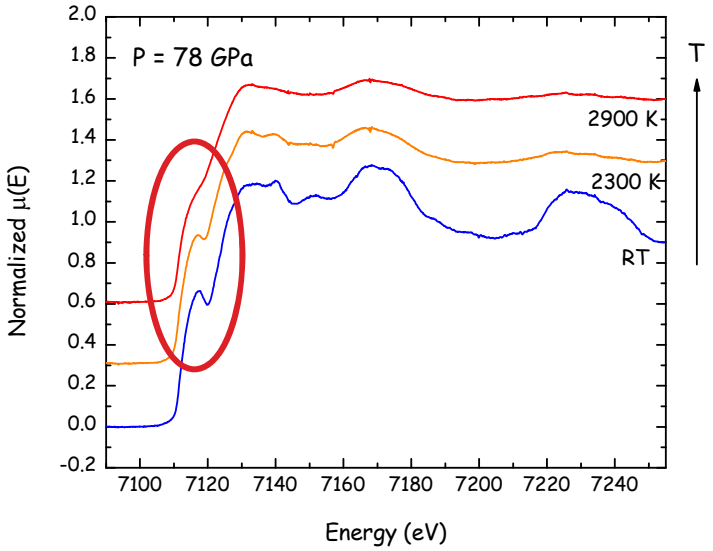
3-dimensional structural model

*A.K. Soper, J. Phys.: Condens. Matter **19**, 415108 (2007)

XANES simulation for the liquid iron - MELTING

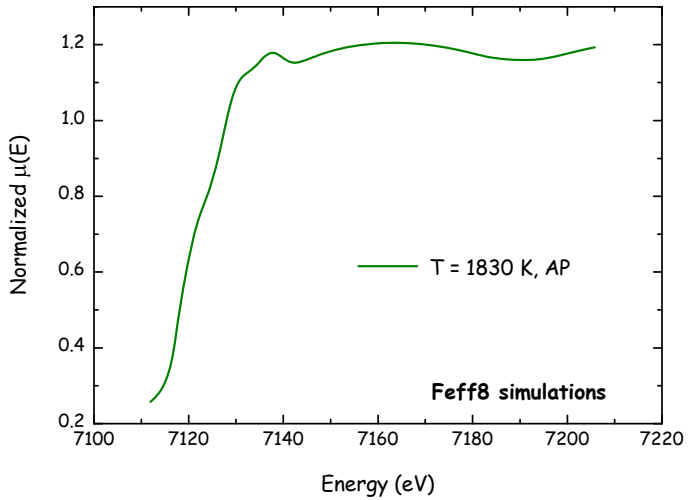




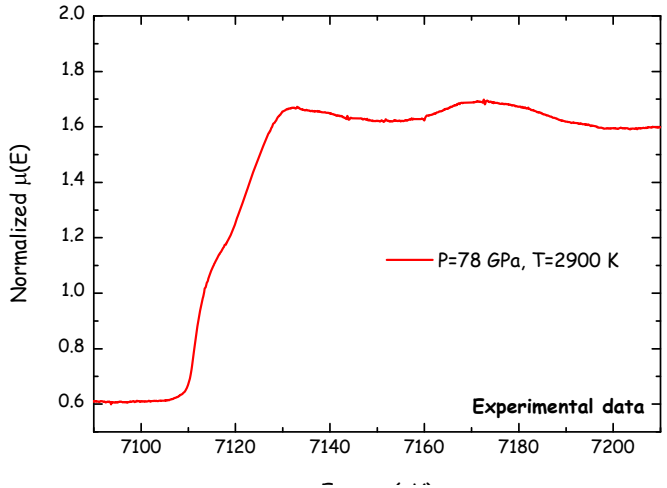


YES WE CAN detect melting in iron under pressure

XANES simulation for the liquid iron - STRUCTURE



Pressure is different

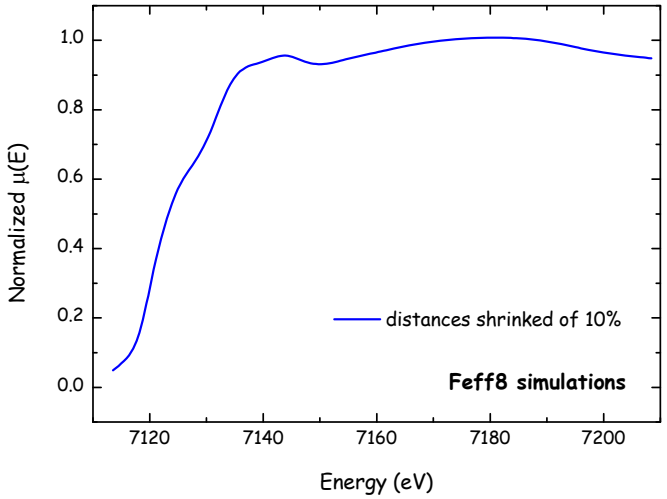


…more work to do…

- Average over more configurations
- To shrink the clusters with a different criterion

Other strategies:
- Fitting of the XANES
- Using models from ab initio calculations (R. Poloni)

… record Extended-XAFS data !



Summary

MELTING

- We have measured molten iron at 78 GPa using EDXAS combined with LHDAC
- EDXAS can be an additional method to detect melting temperature in iron
- Results compatible with previous determinations

LOCAL STRUCTURAL INFORMATION

- Different approaches (XANES fitting and/or *ab initio* calculations)
- EXAFS data

Perspectives – Things to do

Experimental point of view

1) Decrease the beam size

2) No compromise on the flux

3) Dedicated setup (possibly fixed)

4) Increase the energy range

Liquid Fe

1) Record melting data at other pressures

Thanks to

Sakura Pascarelli

Sebastien Pasternak

Florian Perrin

Marie-Christine Dominguez

Mohamed Mezouar