3rd workshop on Studies of Dynamically Compressed Matter with X-rays

ESRF - Grenoble - France

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High pressure investigation of liquid and amorphous systems using X-ray absorption spectroscopy

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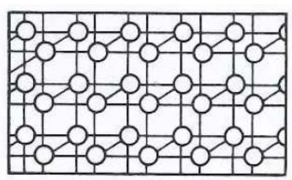
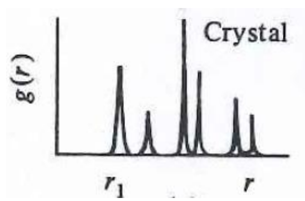
Liquids

Crystalline solids:

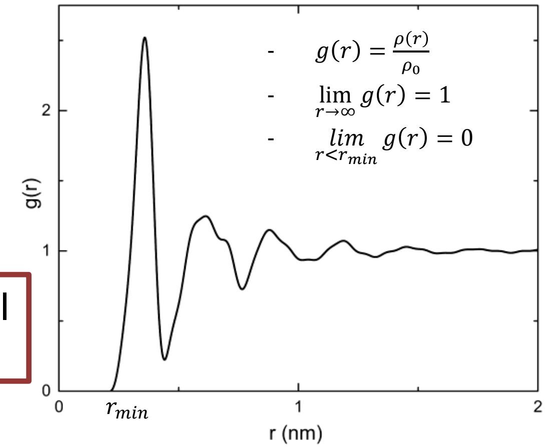
periodic structure





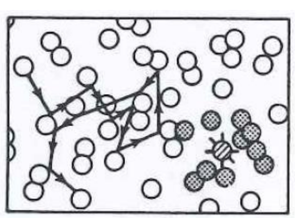
- Fixed atomic positions
- Short range order
- Long range order

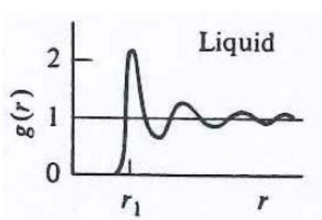
A liquid is described by a radial distribution function: g(r)



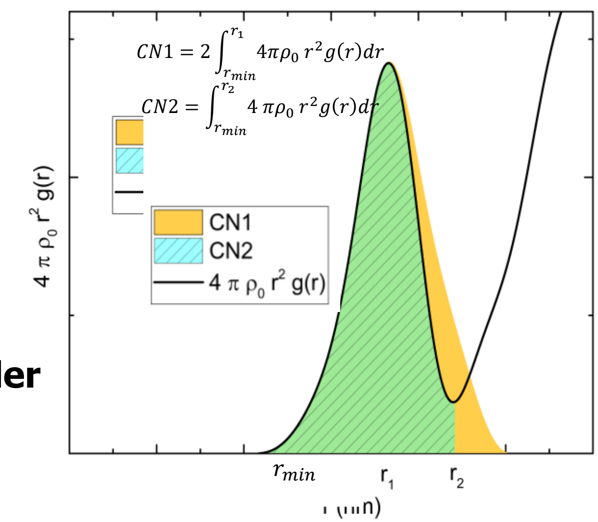
Liquids and amorphous solids:

continuous distribution of distances





- Fluctuations in the near-neighbor region
- **Short range order**
- **Absence of long range order**



The structure of liquid systems

- The structure of liquids and amorphous systems is characterized by the absence of long-range order which defines crystalline materials.

- Liquids, however, possess a rich variety of short to medium range order that steams from chemical bonding and intermolecular interactions.

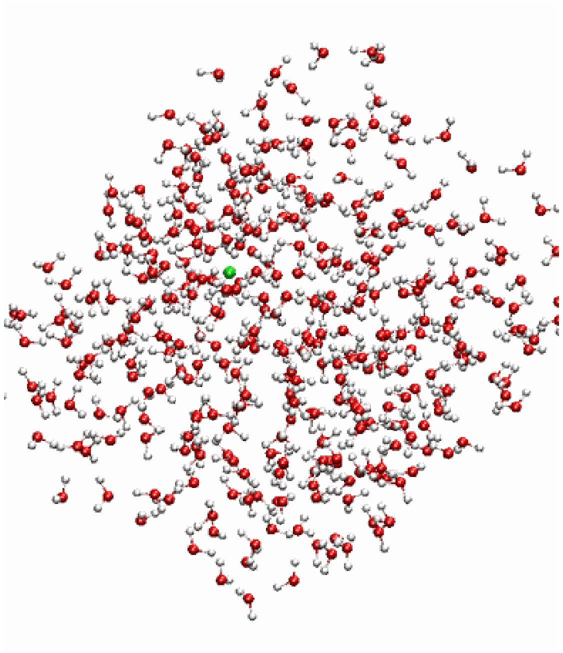
- The structure of liquids is a complex many body problem that has been historically solved by X-ray or neutron diffraction, NMR, Molecular dynamics, and Monte Carlo simulation techniques but none of these methods is able of providing unambiguous and definitive results.

- The complex problem of determining the structural properties of liquids can only be solved by combining different techniques.

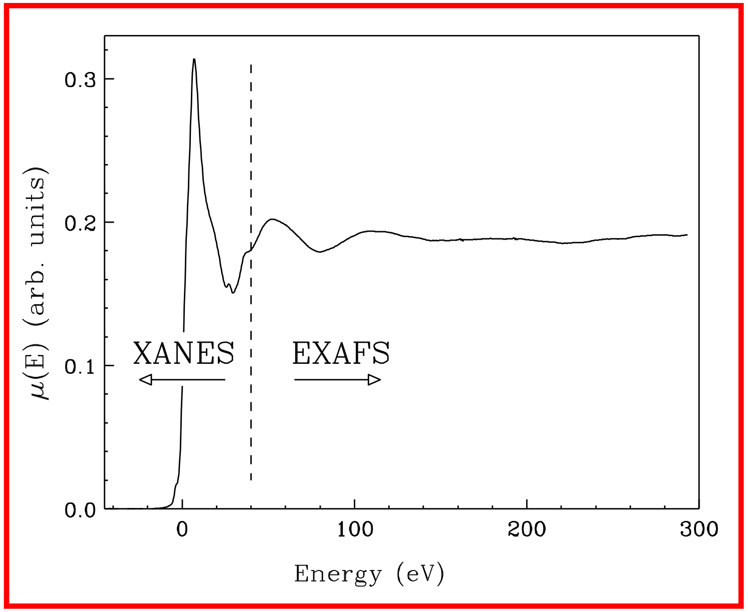
One possible solution to determine the structure of solutions is to combine:

Computational Methods

Molecular Dynamics simulations



X-ray Absorption spectroscopy (XAS)



EXAFS analysis of disordered systems

The XAS experiment probes the ensemble averaged cross-section over the possible instantaneous atomic configurations which are subject to atomic vibrations and possibly disorder.

For a monoatomic system described by a pair distribution function g(r) and a triplet distribution $g_3(r_1, r_2, f)$ (here r_1 and r_2 are the distances of two neighbors and f is the angle centered on the central atom) the ensemble averaged XAFS signal is given by:

$$\langle \chi(k) \rangle = \int_0^\infty dr\, 4\pi\, r^2 \rho\, g(r)\, \gamma^{(2)}\,(r,k)$$
$$+ \int dr_1\, dr_2\, d\phi\, 8\pi\, r_1^2 r_2^2 \sin(\phi) \rho^2\; g_3(r_1, r_2, \phi)\, \gamma^{(3)}(r_1, r_2, \phi, k)$$

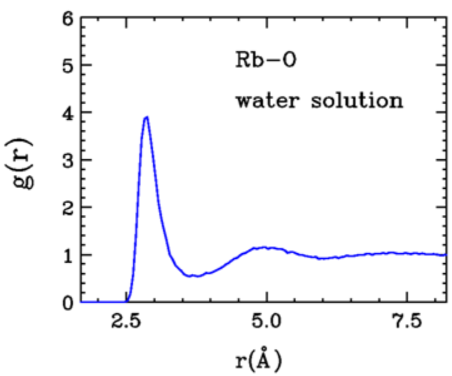
This equation has an analytical solution for a Gaussian function.

$$g^{GAU}\,(r) = \frac{N}{4\pi\rho\, r^2 \sigma \sqrt{2\pi}}\, e^{-\frac{(r-R)^2}{2\sigma^2}}$$

For disordered systems g(r) is always asymmetrical.

$$g^{GAM}\,(r) = \frac{2N}{\sigma\beta\,\Gamma(4\beta^{-2})} \left[4\beta^{-2} + \left(2\frac{r-R}{\sigma\beta} \right) \right]^{\left(4\beta^{-2}-1\right)} e^{-4\beta^{-2} - \left(2\frac{r-R}{\sigma\beta} \right)}$$

Where β gives the skewness of the distribution, and Γ(x) is the Euler's Gamma function for the parameter x.



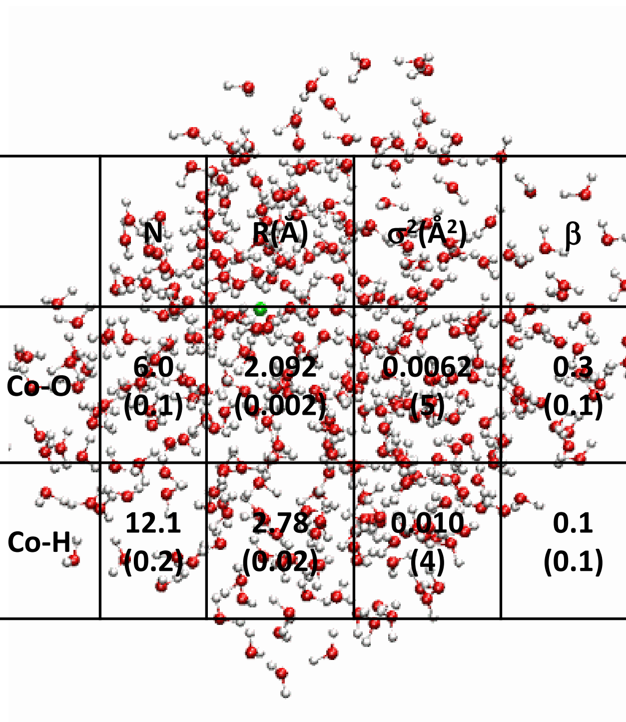
If an asymmetrical distribution is analyzed in the Gaussian approximation:

- the coordination numbers are too small (40%)
- the second cumulant is too small (40%)
- the mean bond length R is too short

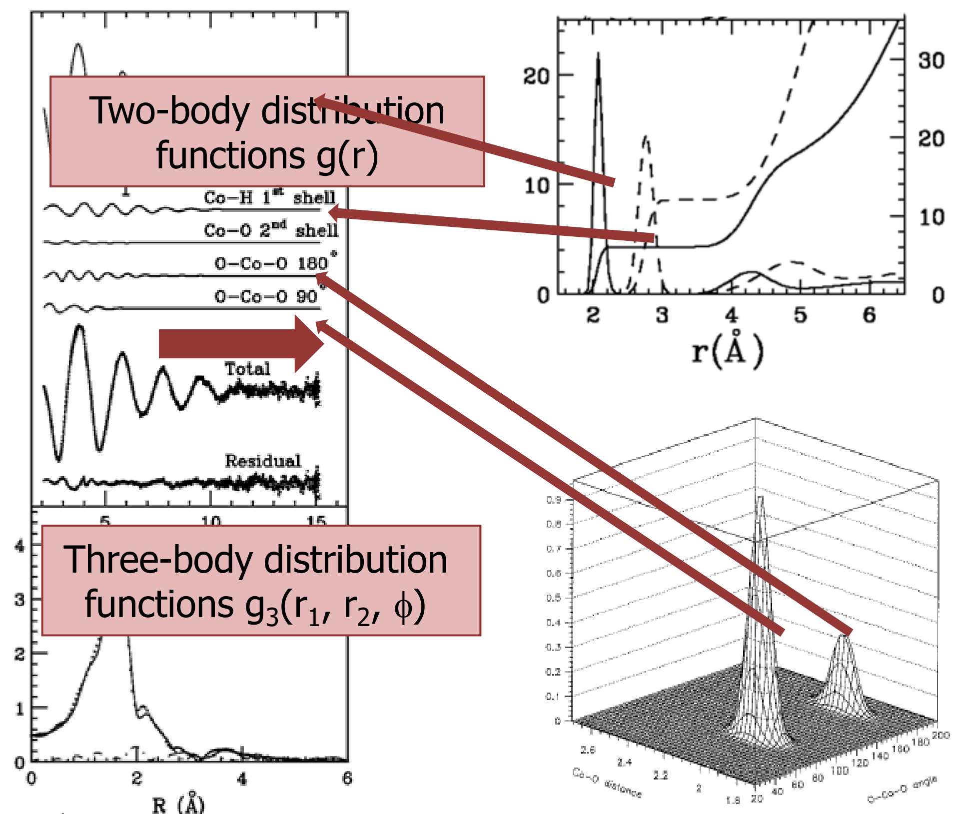
Combined Molecular Dynamics and EXAFS analysis

Radial distributions functions g(r) and triplet distributions $g_3(r_1, r_2, \phi)$ obtained from Molecular Dynamics simulations can be used in the EXAFS data analysis providing reliable short-distance structural information.

Co²⁺ in water



	N	R(Å)	σ^2(Å^2)	β
Co-O	6.0 (0.1)	2.092 (0.002)	0.0062 (5)	0.3 (0.1)
Co-H	12.1 (0.2)	2.78 (0.02)	0.010 (4)	0.1 (0.1)

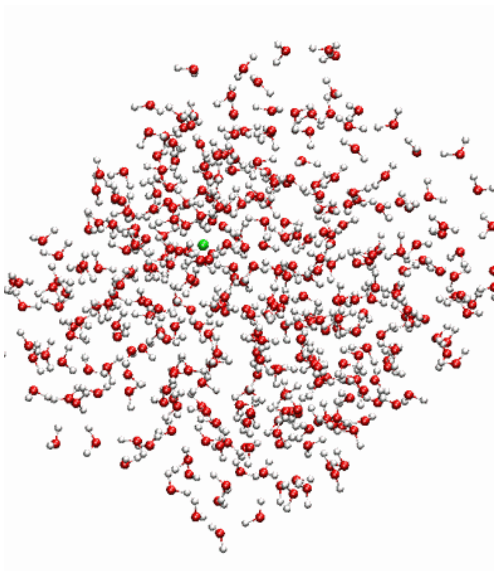


G. Chillemi, P. D'Angelo et al., *J. Am. Chem. Soc.* **124**, 1951 (2012)
P. D'Angelo, et al *J. Am. Chem. Soc.* **124**, 1951 (2012)

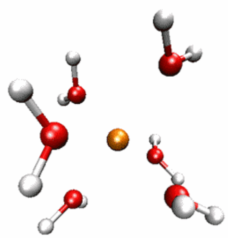
Combined Molecular Dynamics and XANES analysis

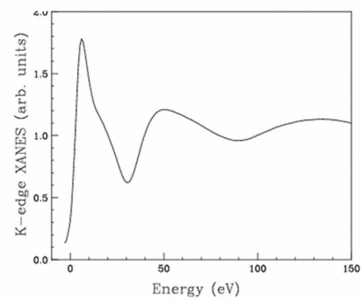
The structural and thermal disorder of a liquid can be reproduced from the MD simulation and XANES spectra can be calculated for each atomic configuration of the sampled ensemble

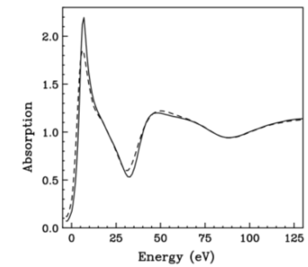
Ni^{2+} in water



1^{st} shell

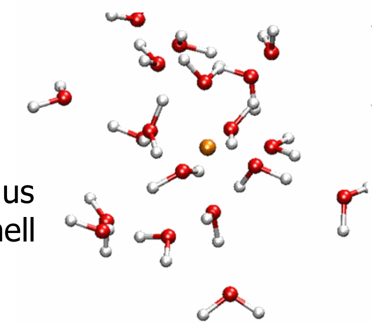


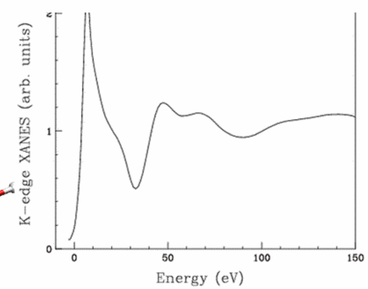


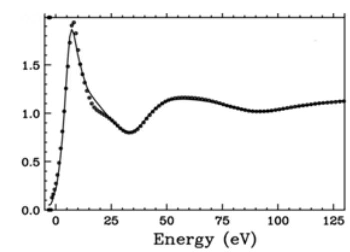


Average theoretical XANES spectra

1^{st} plus 2^{nd} shell



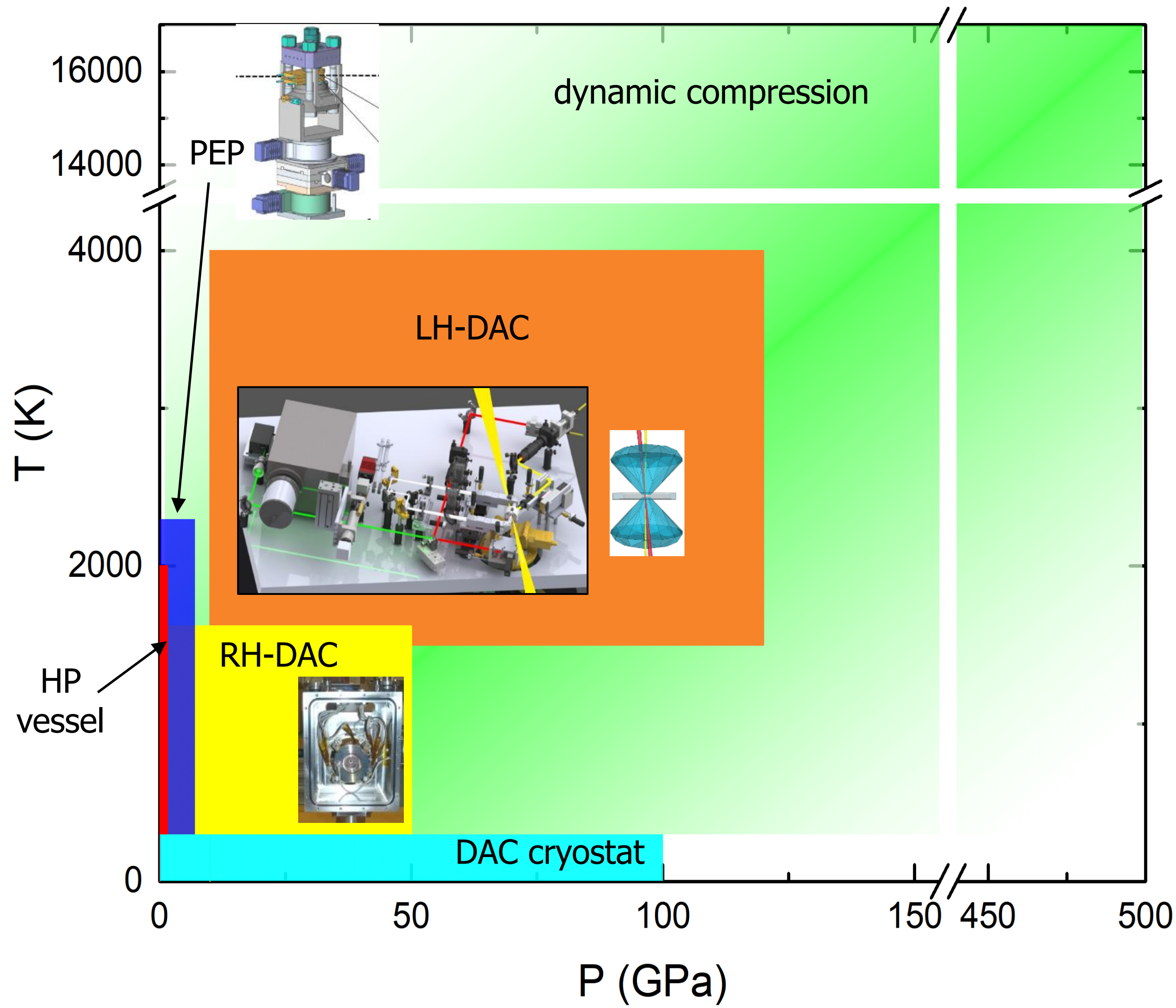




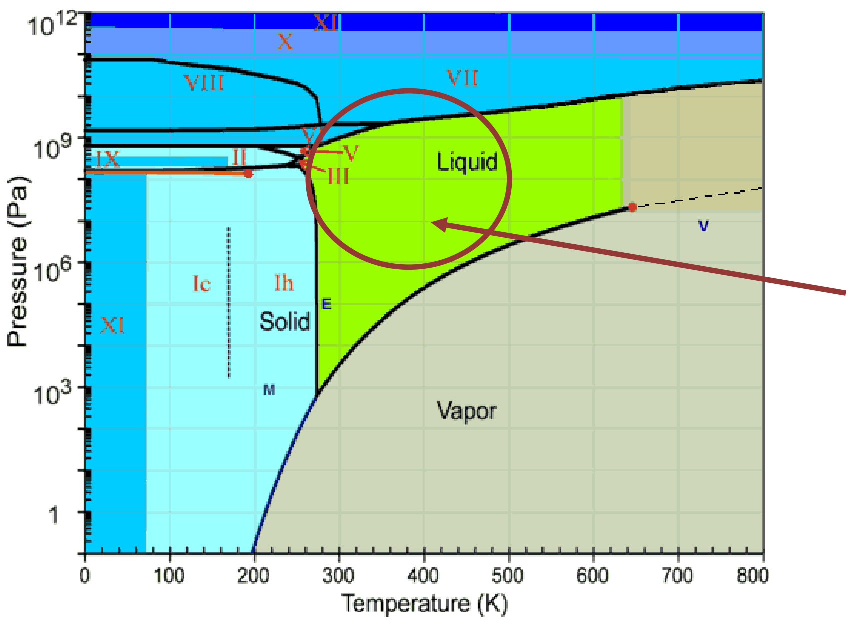
Comparison between experimental and theoretical spectra

P. D'Angelo, O. M.Roscioni, P. D'Angelo, G.Chillemi, S. Della Longa , M. Benfatto. *JACS*, **128**, 1853-1858 (2006).

Possibilities for XAS at high pressure



The phase diagram of water



• At high pressures (and temperatures) water exists in different liquid or solid phases whose properties are very different from those found at normal conditions.

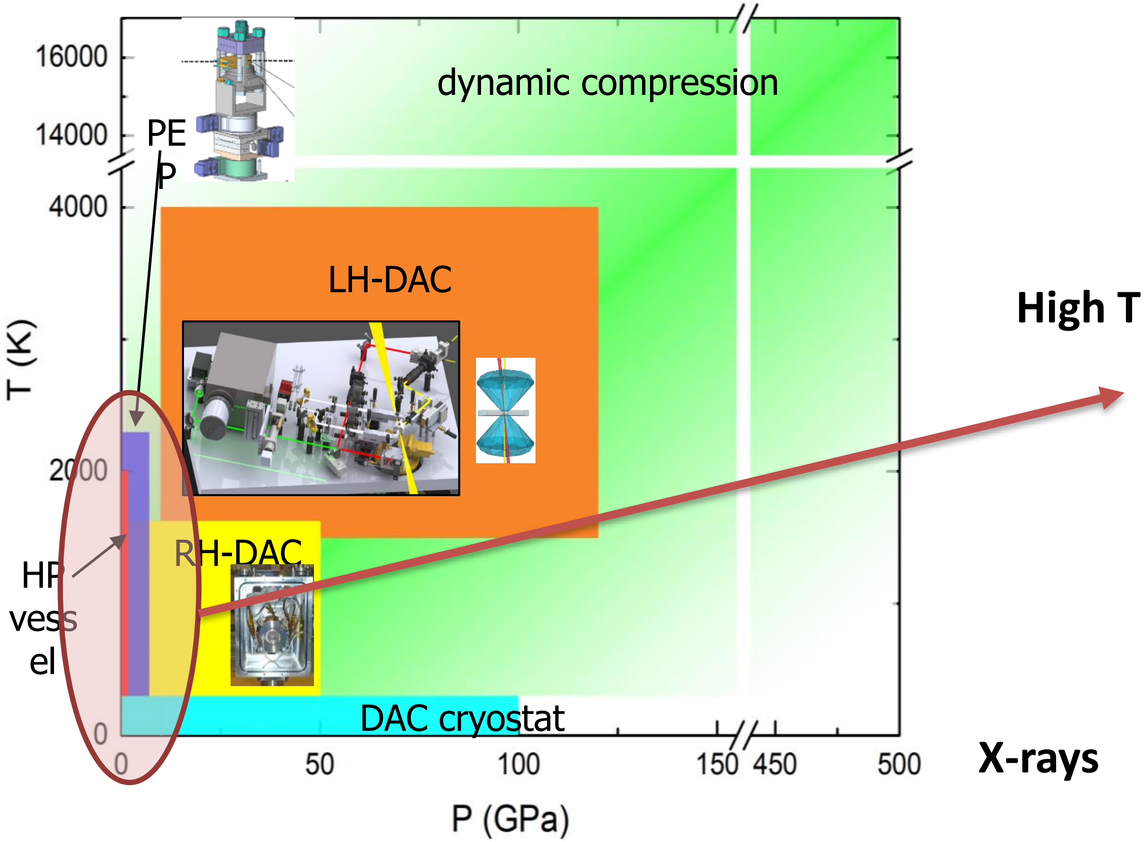
• At pressures between 0.1-10 GPa and temperature between 300 and 500 K liquid water is in equilibrium with several forms of ice and its phase in this region is called **compressed water.**

• In the literature it has been suggested the possible existence of a high-density state of water **(HDW)** for pressure below 0.4 GPa and T=268K with a collapsed second coordination shell, but the structural properties of water under high pressure are still the subject of intense debate.

• The properties of compressed water and compressed aqueous solutions are relevant for:

- Geoscience – Earth mantle
- Planetary modeling – Icy satellites
- Environmental science – High pressure chemical reactions

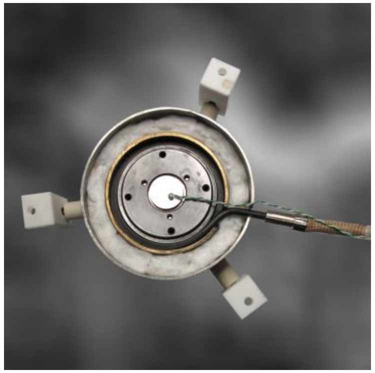
Experimental methods T=300-500 K P= 1MPa - 6.4 Gpa



High P

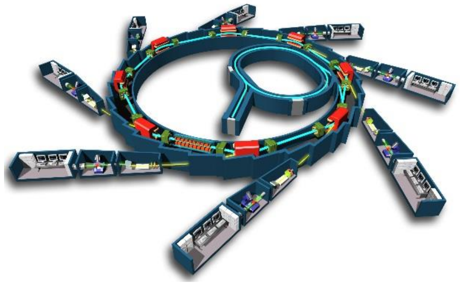
PARIS-EDINBURGH: Large Volume press

High T



Resistive Heating

X-rays



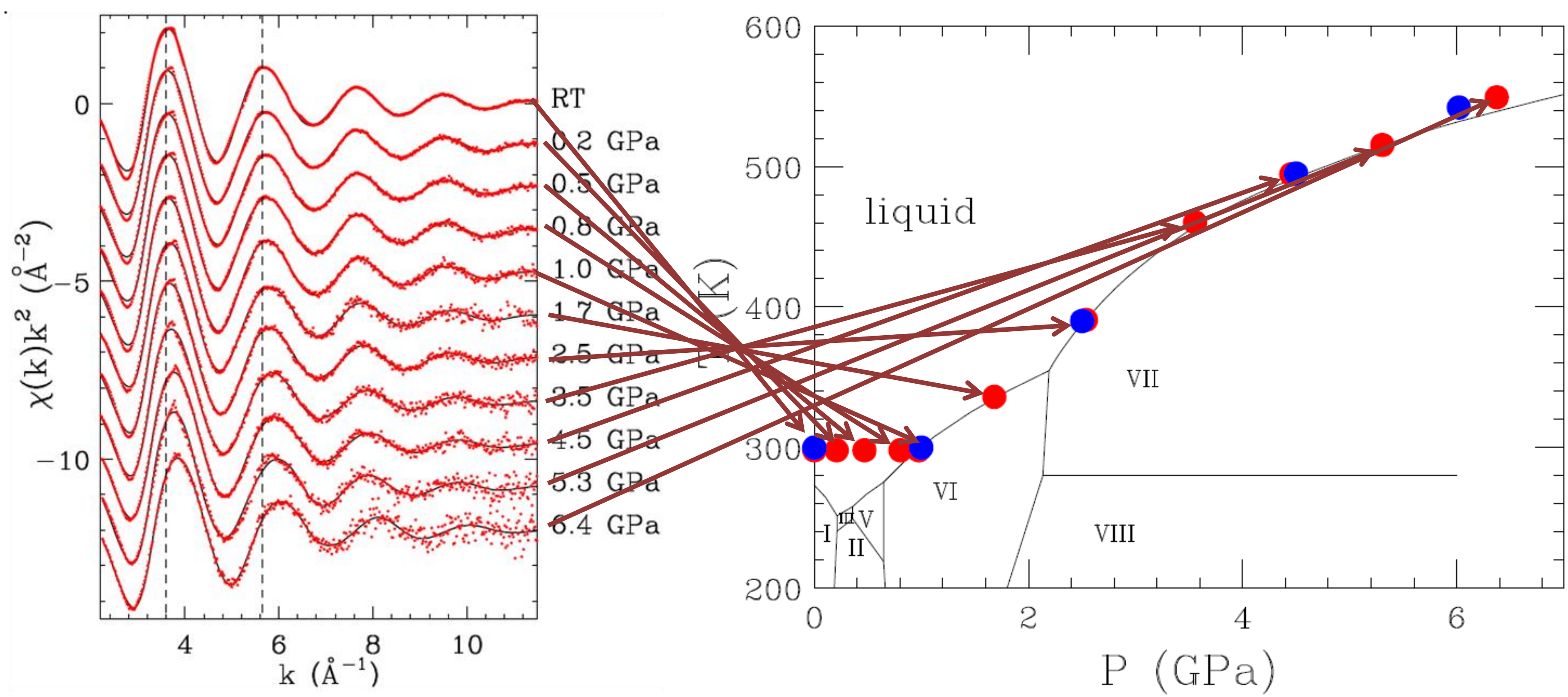
X-ray absorption spectroscopy (XAS)

EXAFS measurements of Zn^{2+} in water

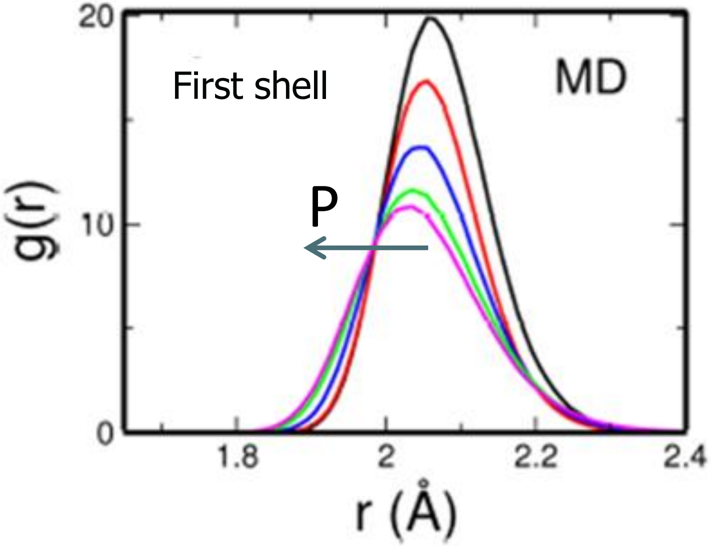
Data collected at
BM23 @ ESRF

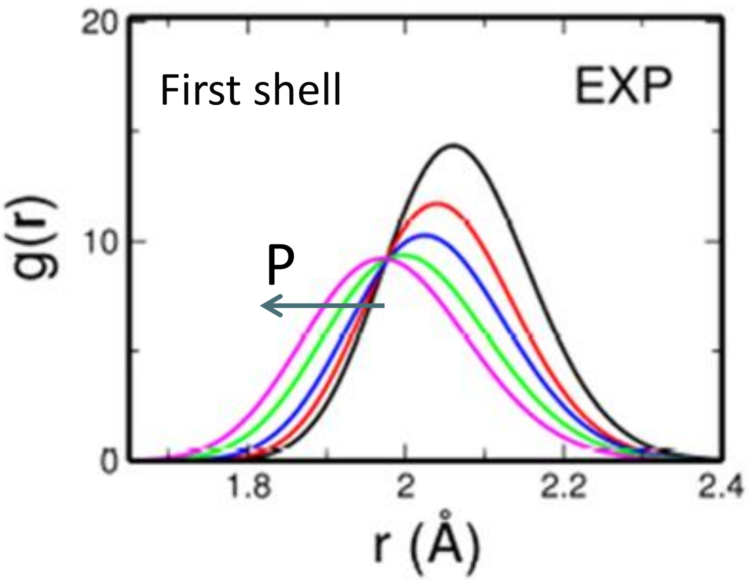
Large-volume high-pressure
set up Paris-Edinburgh press
MAR area detector for XRD spectra

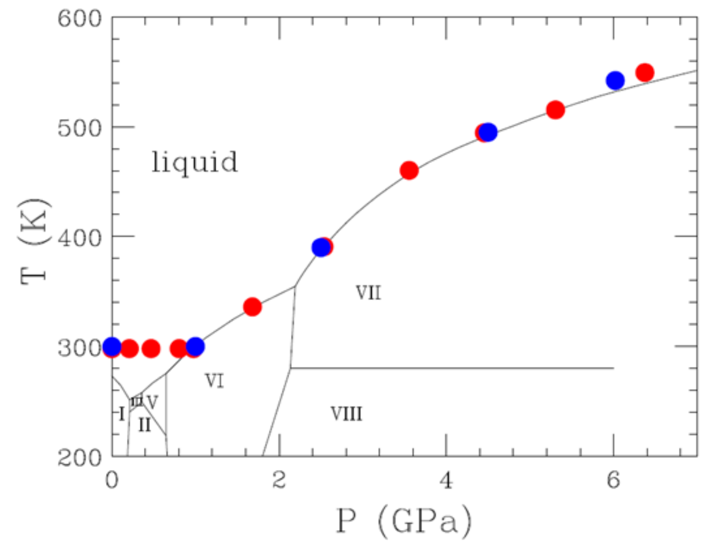
T between 300 and 560 K
P between 1MPa and 6.4 Gpa

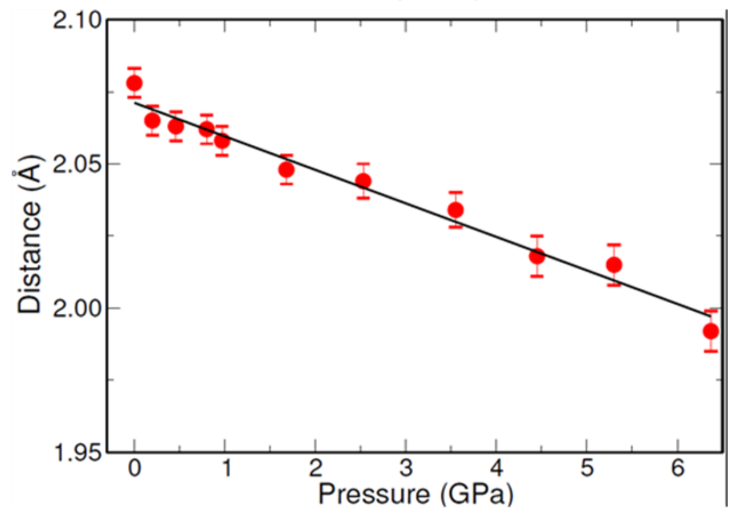


Comparison between EXAFS and MD results





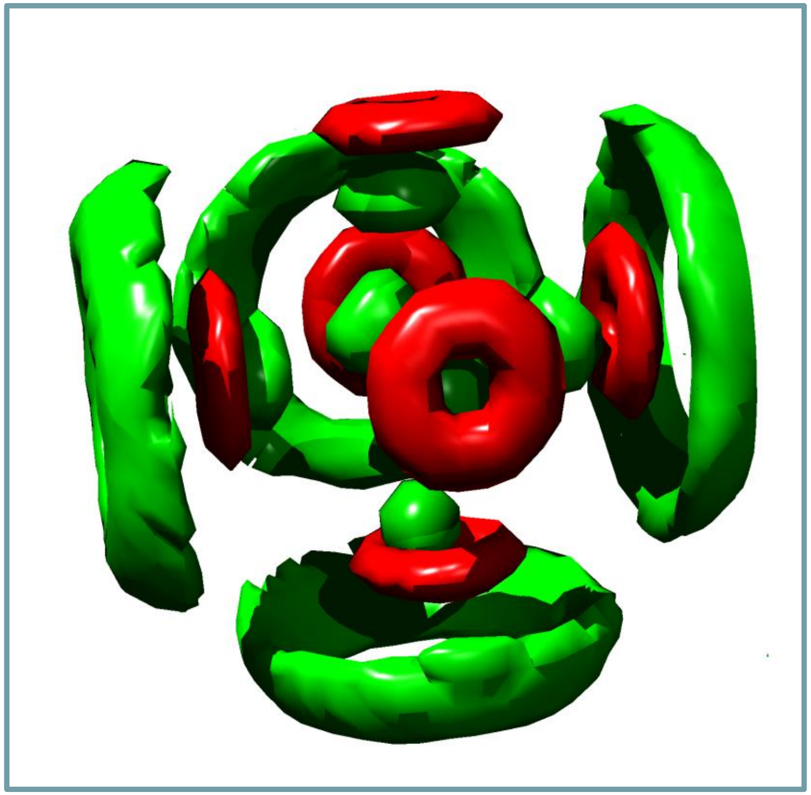




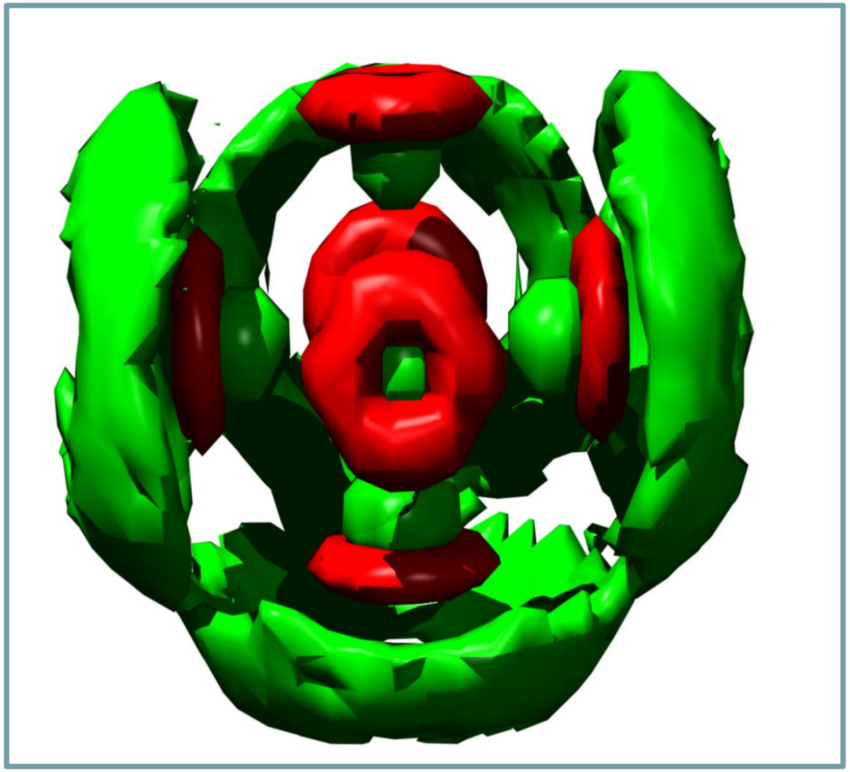
- The first hydration shell coordination number does not change.
- The octahedral cluster is conserved.
- The Zn-O distance undergoes a shortening of 0.09 Å.

Spatial distribution functions

0.1 MPa



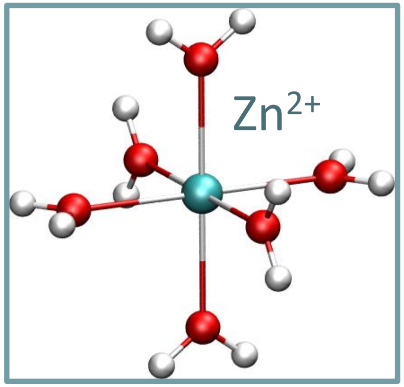
2.5 GPa

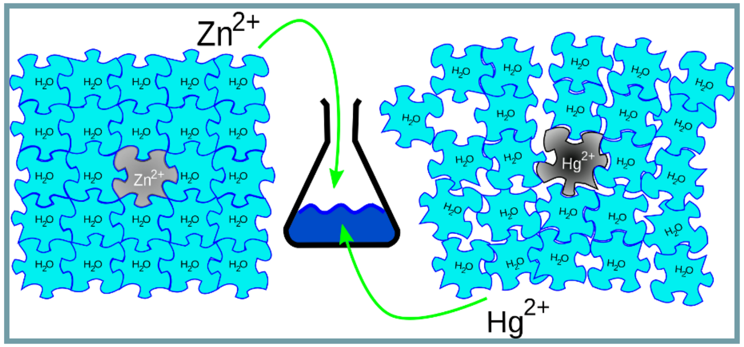


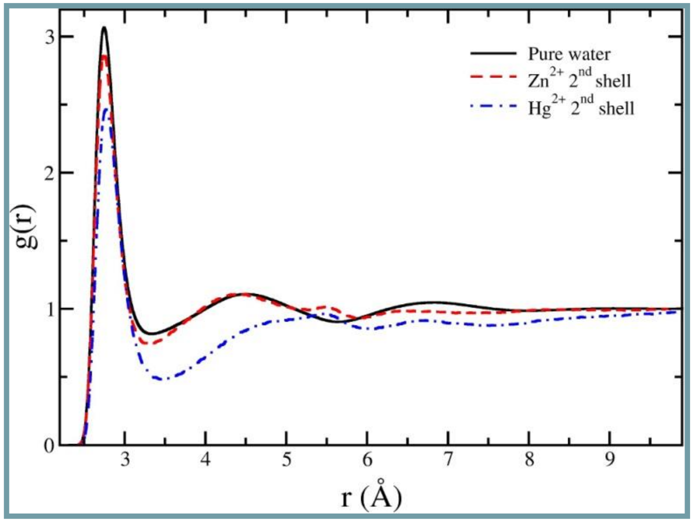
Both at ambient condition and in compressed water the O (green) and H (red) atoms of the first hydration shell have a clear octahedral symmetry. Moreover, the squeezing of hydration shells is clearly visible looking at the shift of isodensity levels towards the central Zn^{2+} ion.

Structural investigation of aqueous solution using XAS and MD

We have investigated the pressure effects on the hydration sphers of the Zn^{2+} ion, which is octahedral at ambient conditions.







The Zn^{2+} ion does not alter the tetrahedral structure of the HB network of water beyond the first hydration shell.

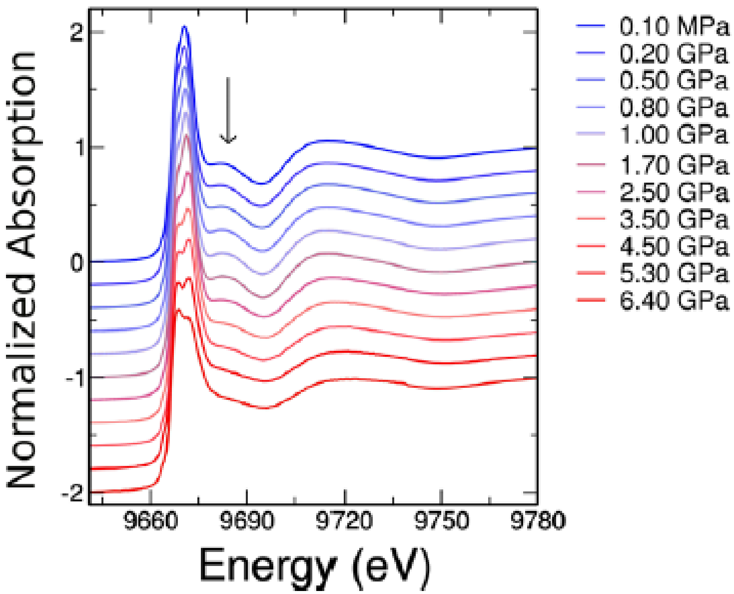
G. Chillemi. P. D'Angelo, N. V. Pavel, N. Sanna, V. Barone *J. Am. Chem. Soc.* 124, 1968 (2002).
V. Migliorati, G. Chillemi, P. D'Angelo, *Inorg. Chem*. 50, 8509 (2011).
V. Migliorati, A. Zitolo, G. Chillemi, P. D'Angelo, *ChemPlusChem* 77, 234 (2012).

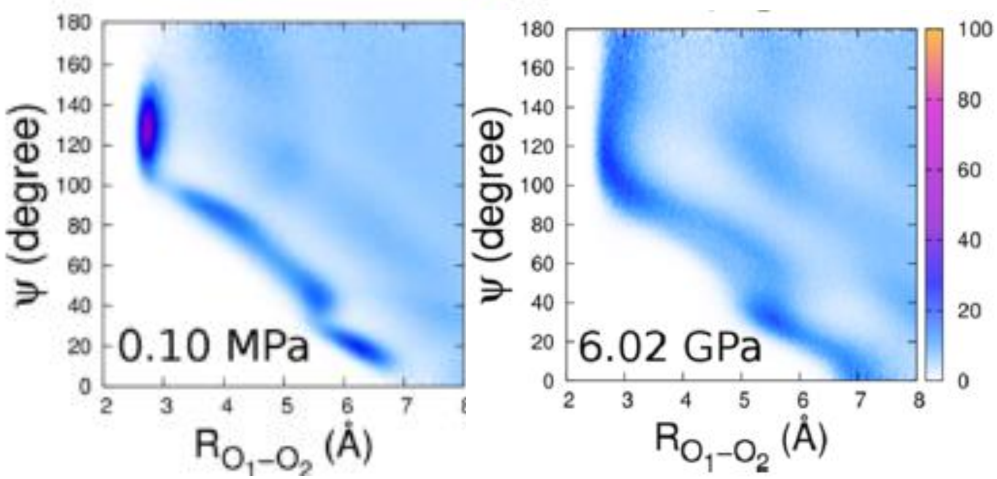
Comparison between XANES and MD results

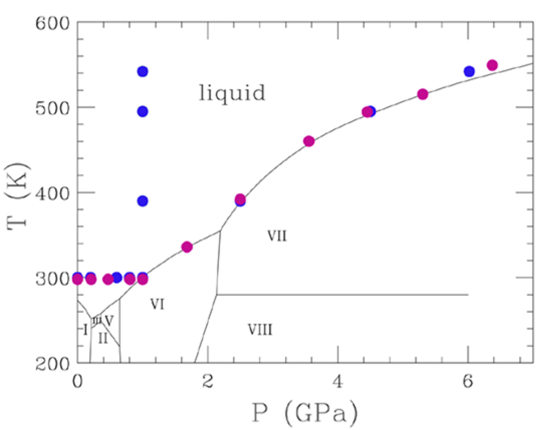
Inorg. Chem. 2017, 56, 14013-14022

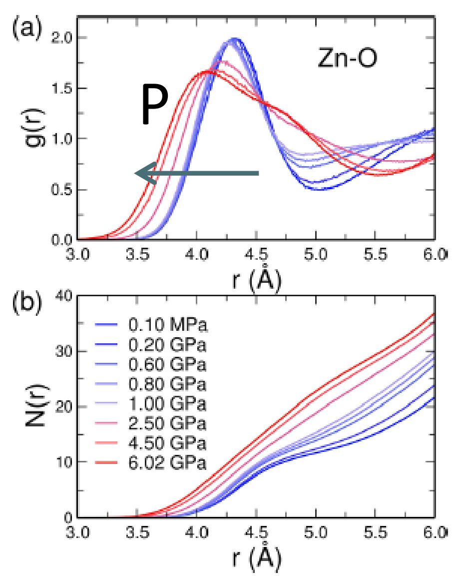
Structure of Water in Zn^{2+} Aqueous Solutions from Ambient Conditions up to the Gigapascal Pressure Range: A XANES and Molecular Dynamics Study

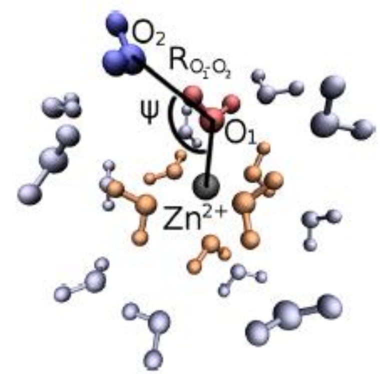
Valentina Migliorati,*[‡] Adriano Filipponi,[†] Andrea Di Cicco,[§] Simone De Panfilis,[#] and Paola D'Angelo*[‡]





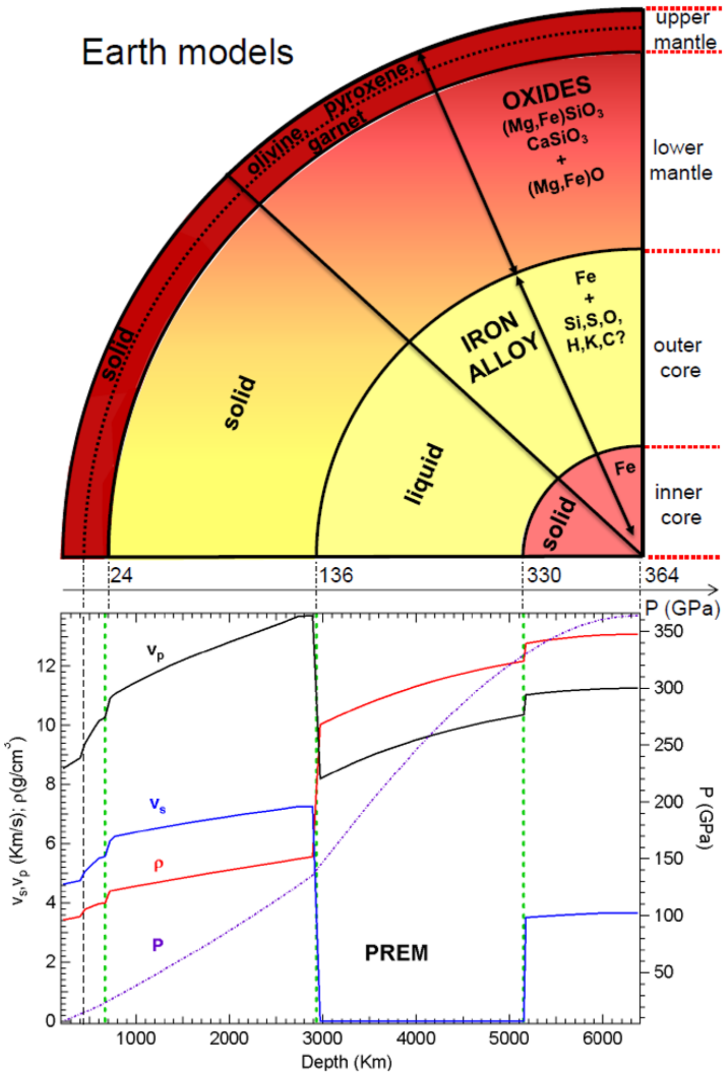




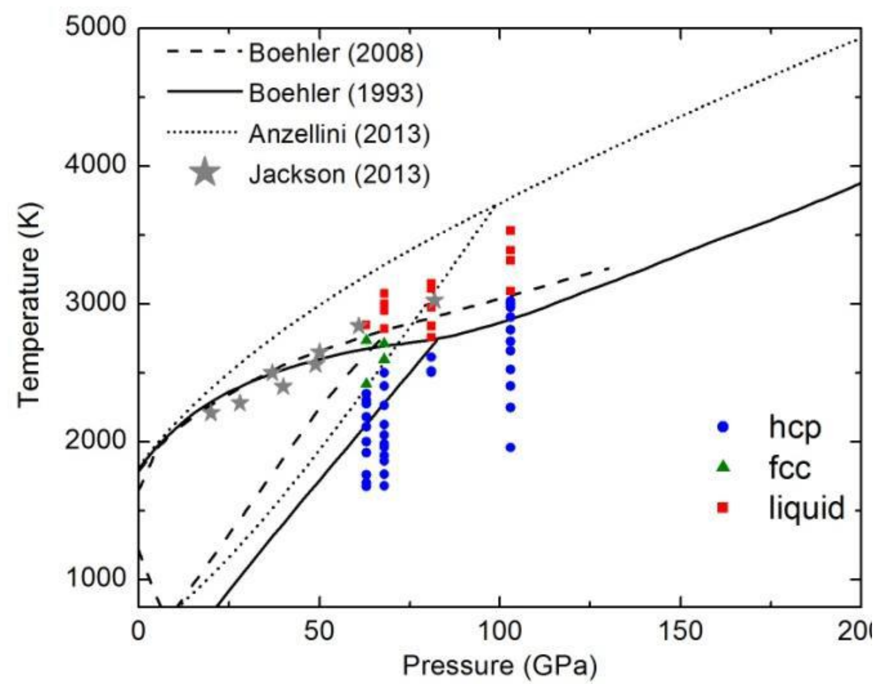


Second shell

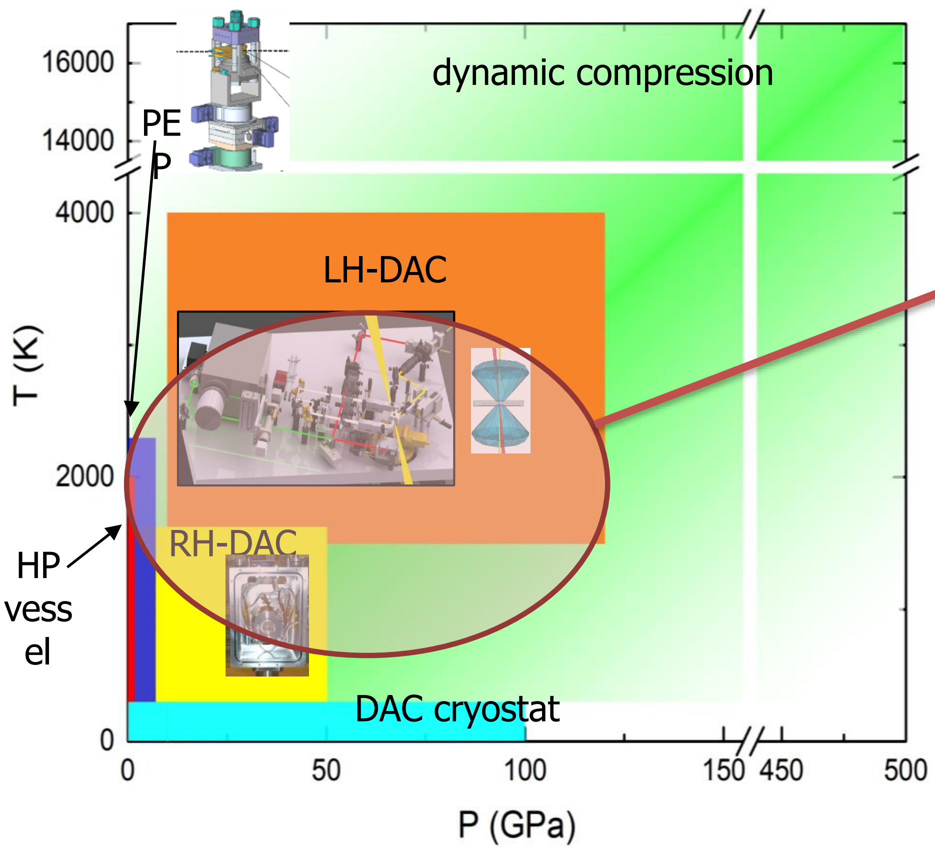
Melting of 3d metal alloyds



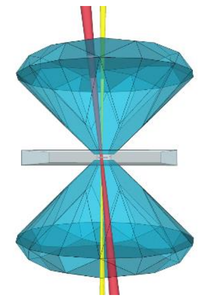
The temperature at the inner core boundary expected to be close to melting point of Fe at 330 GPa. Large controversy on melting temperature of Fe at these extreme pressures



Experimental methods T=300-3000 K P= 1MPa - 100 Gpa

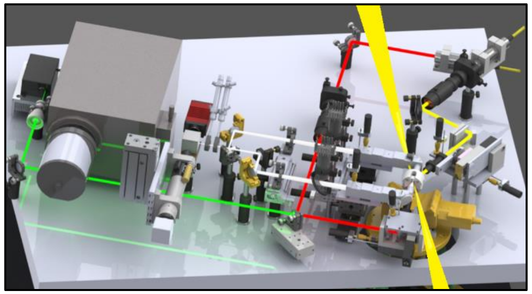


High P



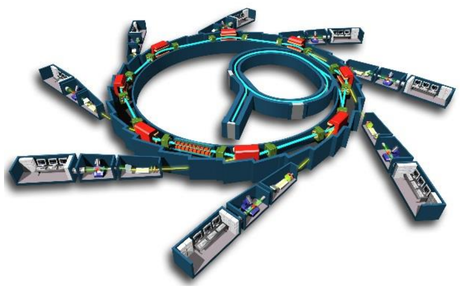
DAC

High T



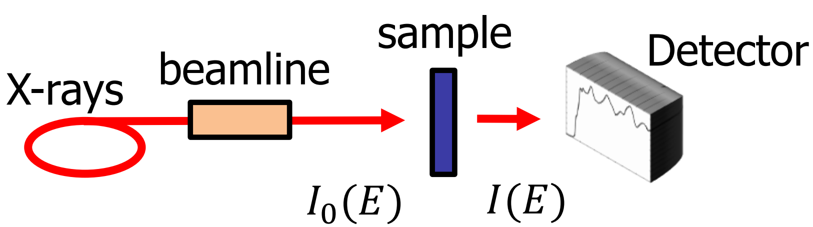
LH

X-rays



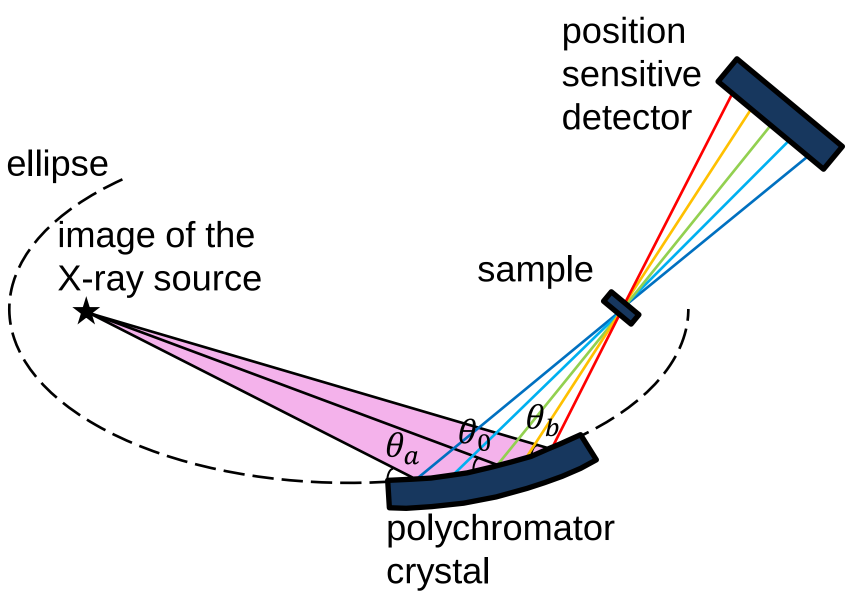
X-ray absorption spectroscopy (XAS)

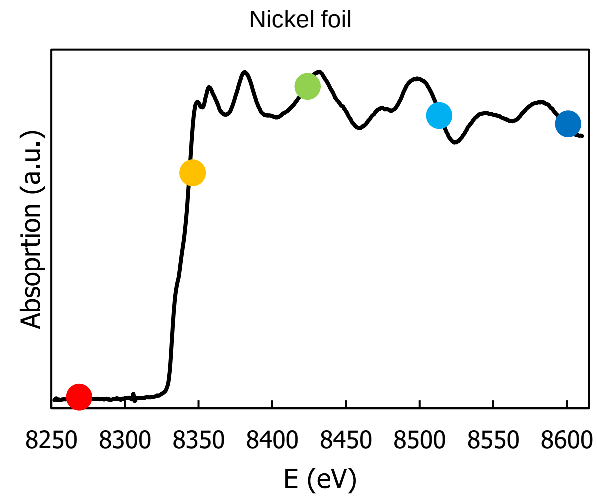
Experimental methods: Energy dispersive beamline ID24



$$2d\ sin\theta = \lambda = \frac{c \cdot h}{E}$$

$$\theta\uparrow \quad E\downarrow$$

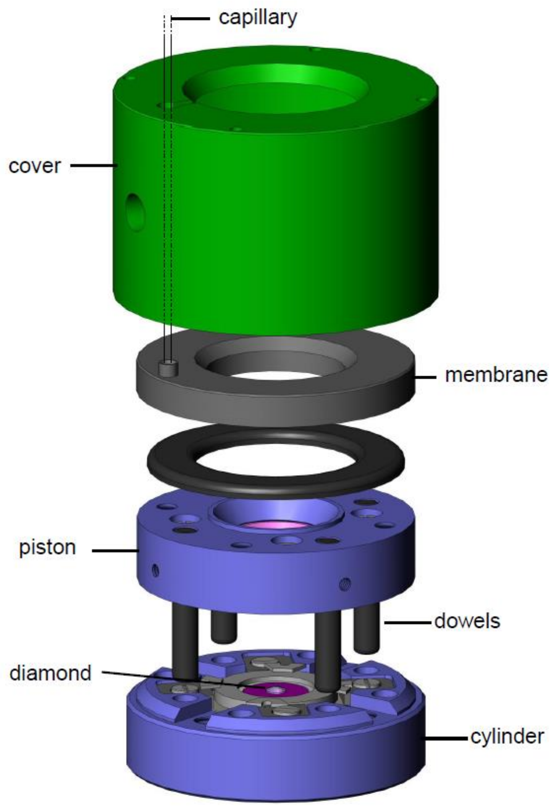




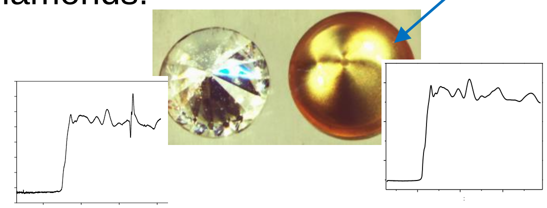
X-ray spot 5x5 µm on the sample
The dispersive geometry is ideal for time resolved measurements

Experimental methods: High pressure $P = F/S$

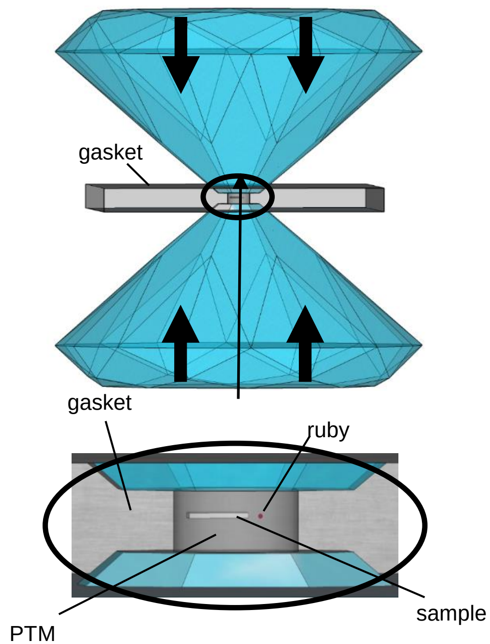
Diamond anvil cell:



Diamonds: T. Irifune, Ehime University, Japan

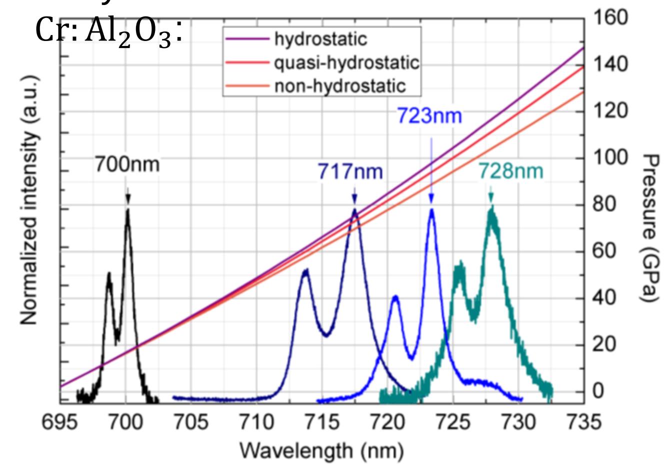


$d \sim 150 - 400\ \mu m \rightarrow P$ up to 130 GPa



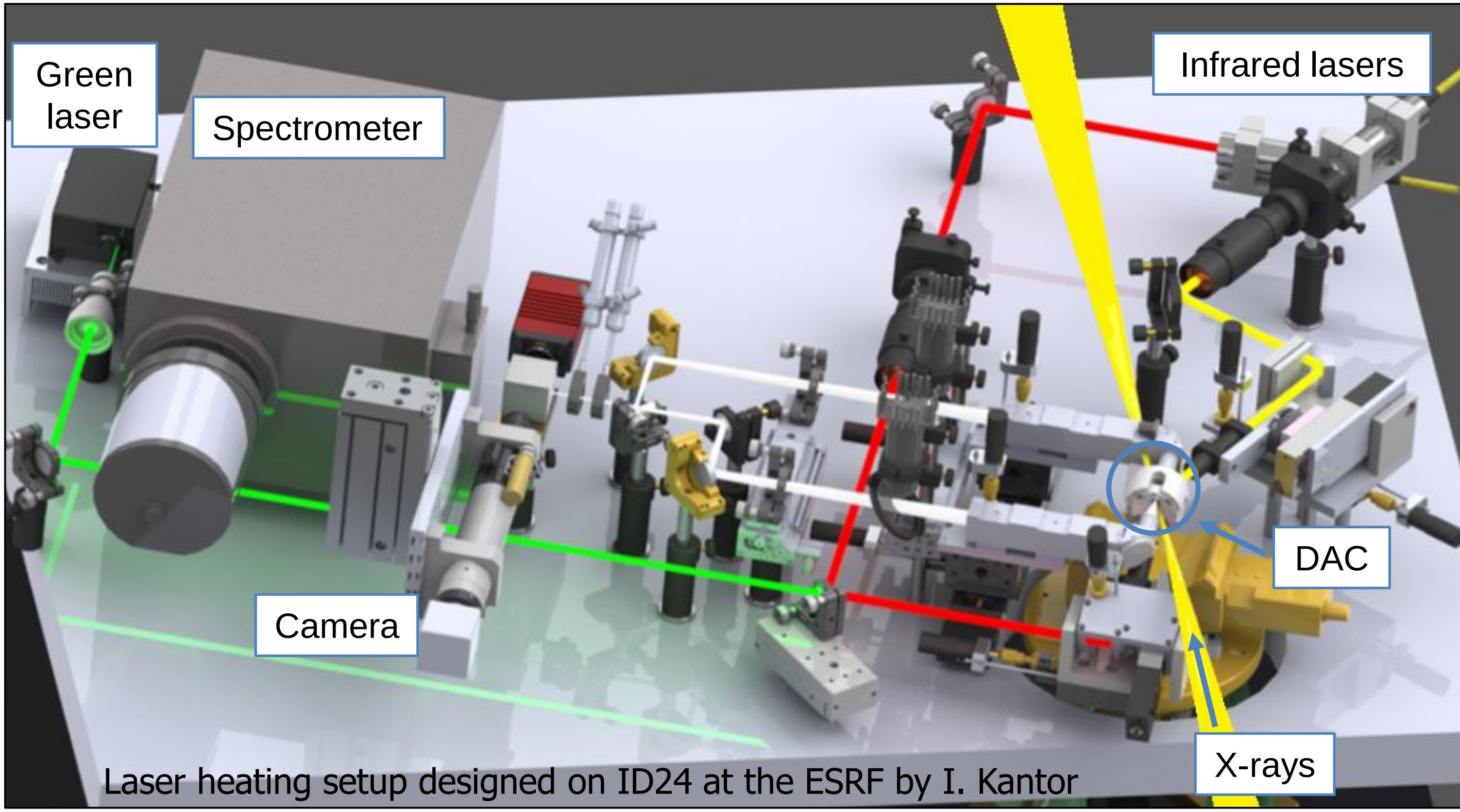
Ruby

$Cr: Al_2O_3$:

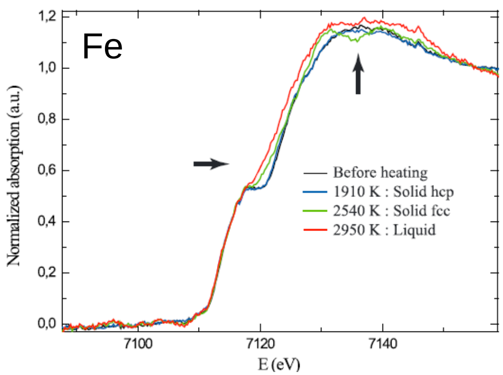


Experimental methods: High temperature – Laser heating system

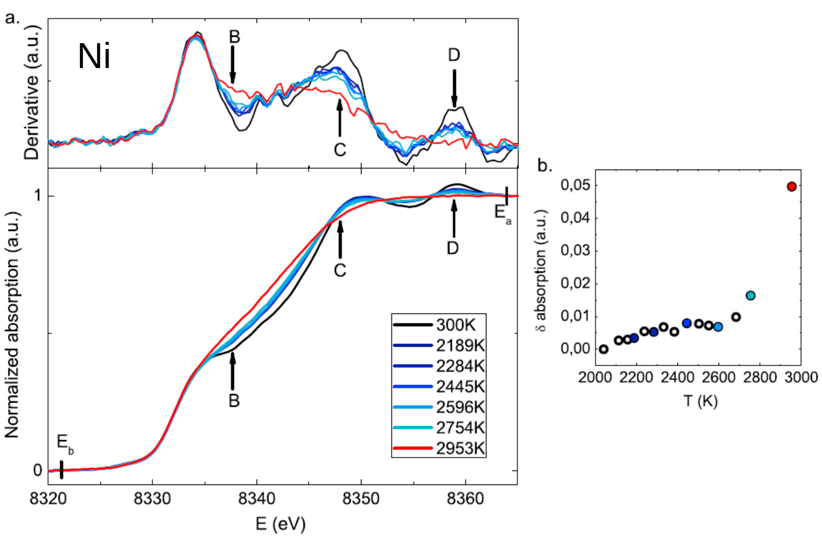
The only LH system coupled to XAS

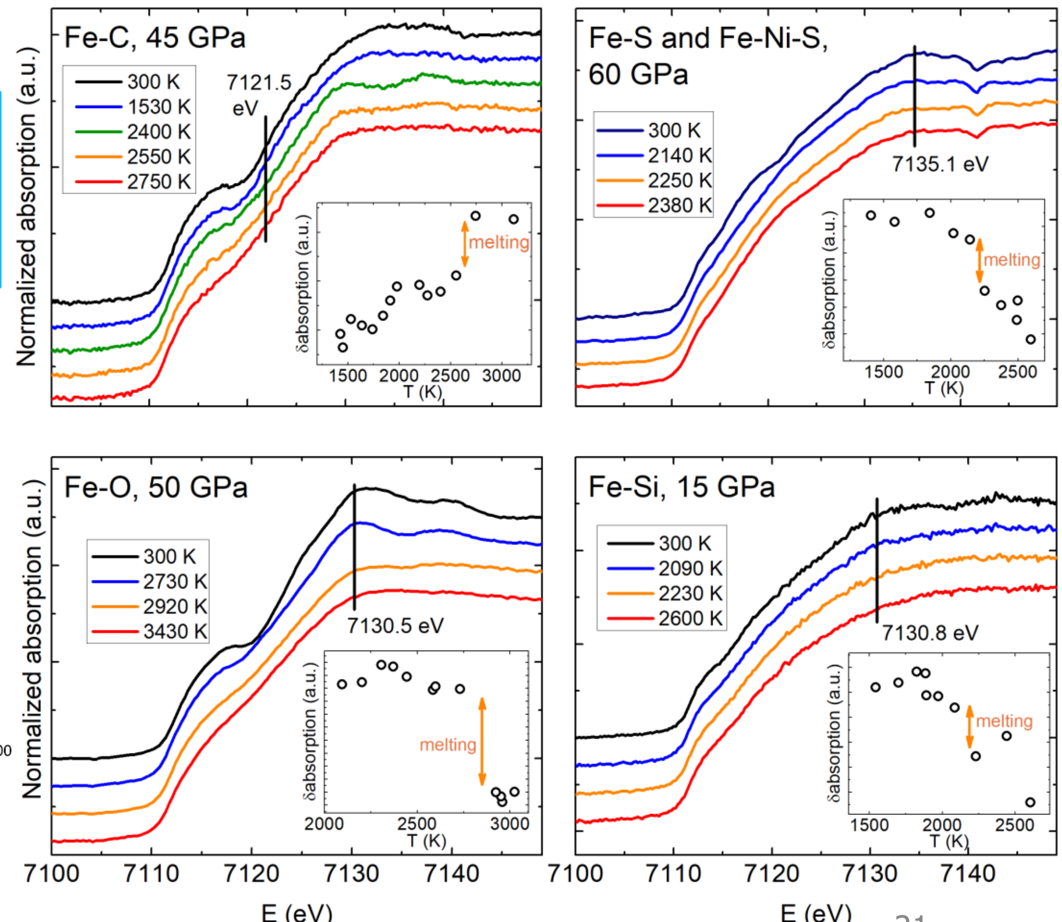


XAS melting criterion



Loss of features
Discontinuity in the T-scan

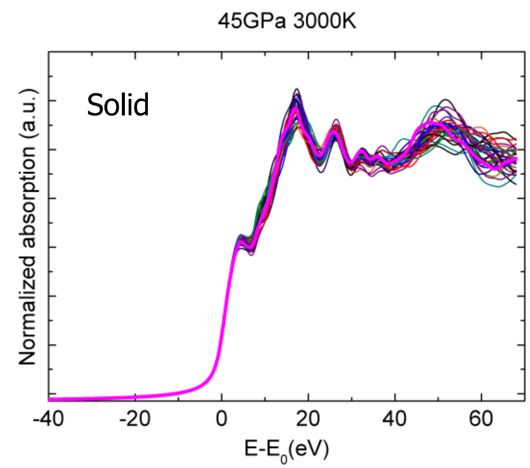




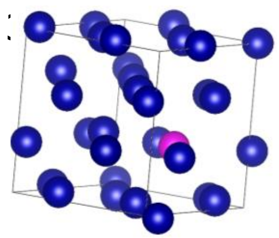
Ab-initio calculations

AIMD simulations

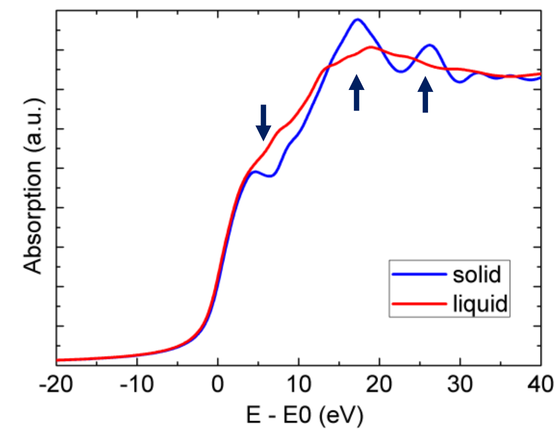
Atomic structure

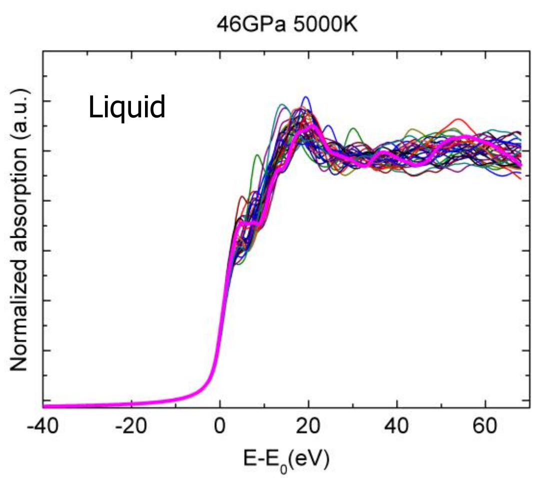


Solid: 45GPa

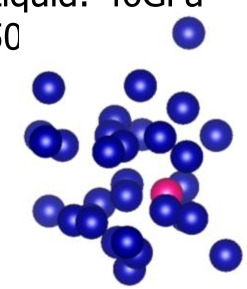


Calculations:

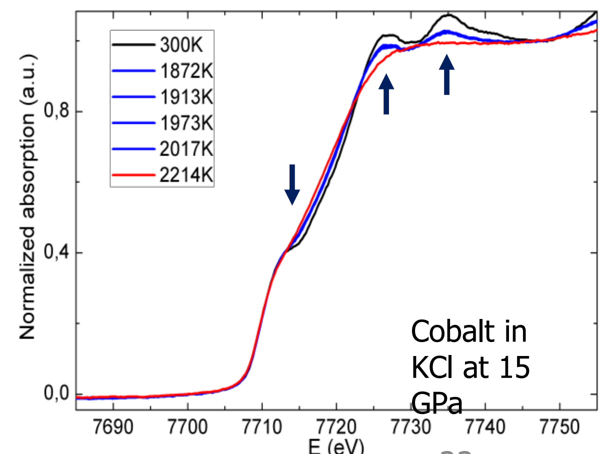




Liquid: 46GPa
50



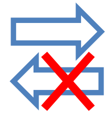
Experiment
al data:



Collaboration with Keith Gilmore, ESRF Vanina Recoules, CEA

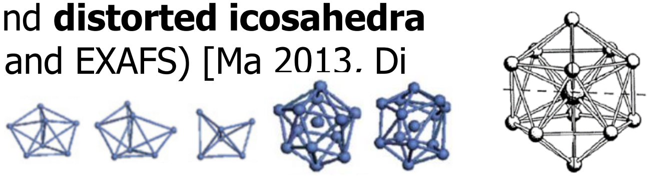
LOCAL STRUCTURE OF LIQUIDS: State of the art

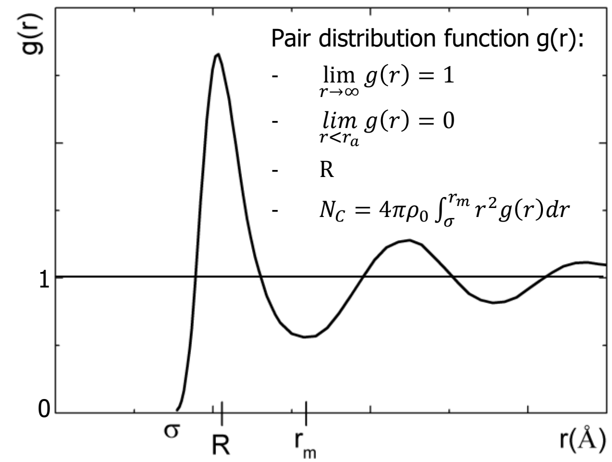
Structural model



Radial distribution function g(r)

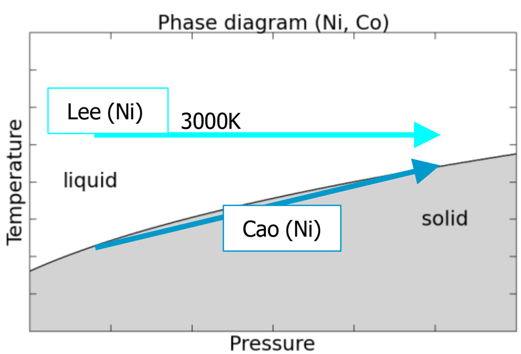
Ambient pressure, liquid nickel: predominance of **icosahedra** and **distorted icosahedra** (MD calculations and EXAFS) [Ma 2013, Di Cicco 2014]

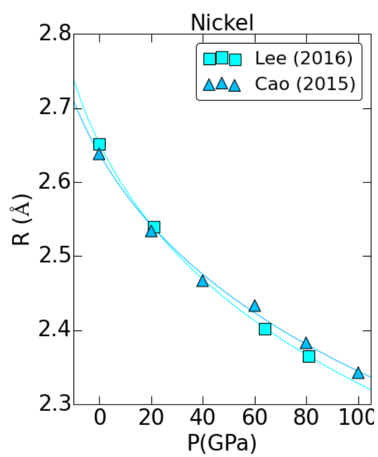




Distance of first neighbors

Under pressure: the structure does not change with pressure [Lee 2016]
Compression of liquid nickel calculated with MD [Cao 2015] and AIMD [Lee 2016]

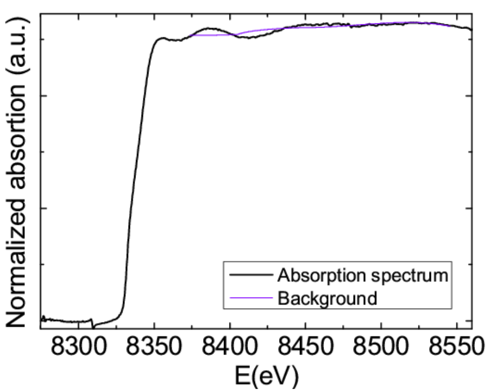


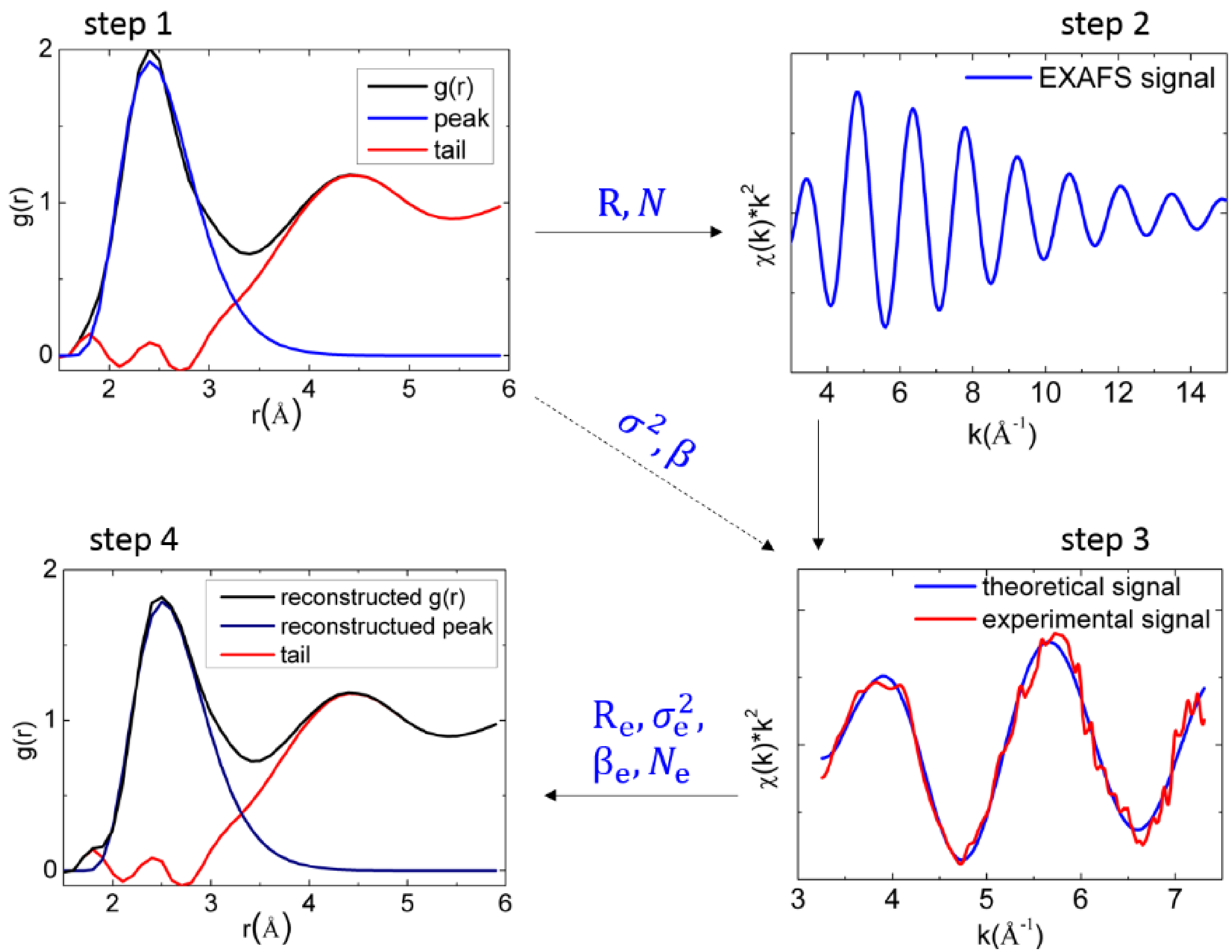


No experimental data for liquid nickel and cobalt under pressure

EXAFS analysis of melted metals $\chi(k) = \frac{\mu - \mu_0}{\mu_0}$

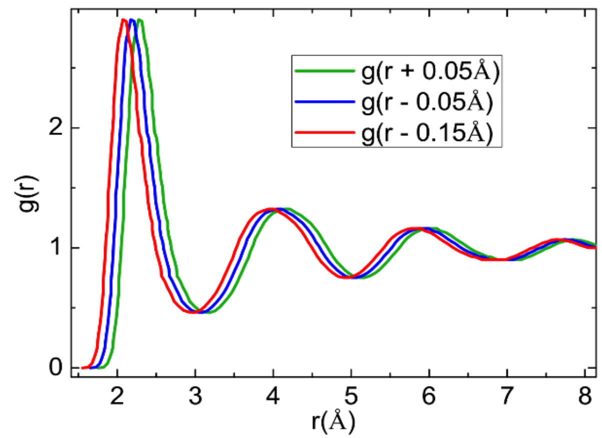
GNXAS analysis



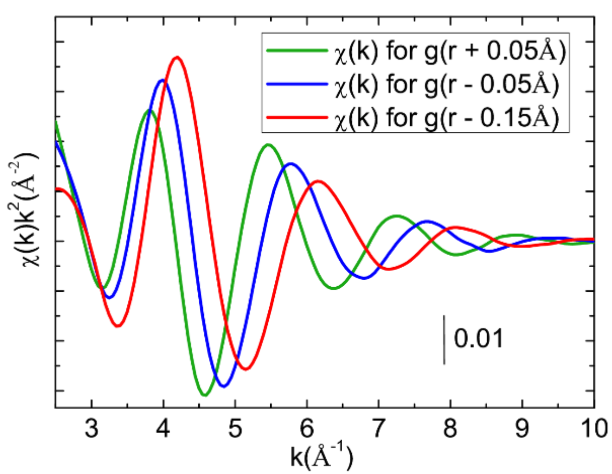


EXAFS analysis of melted metals

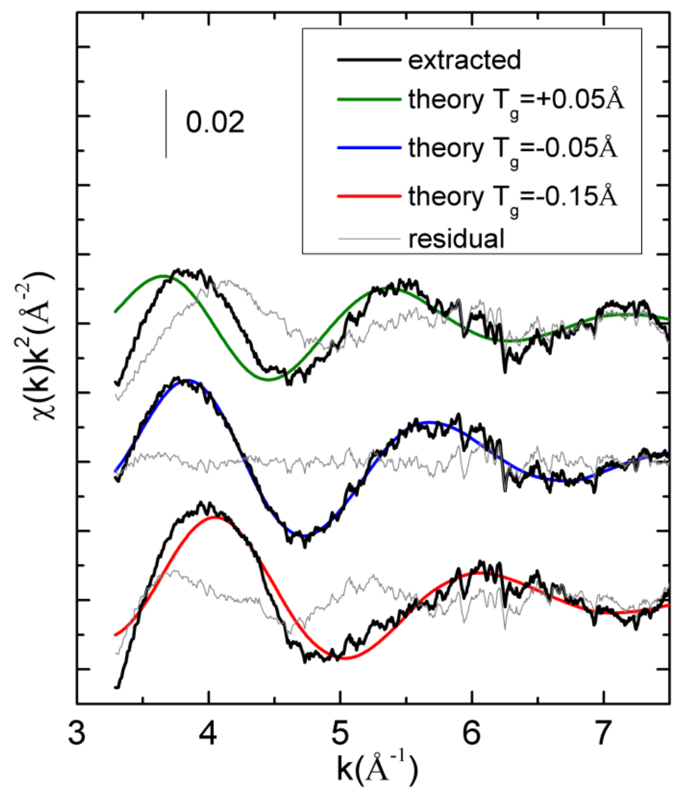
step 1



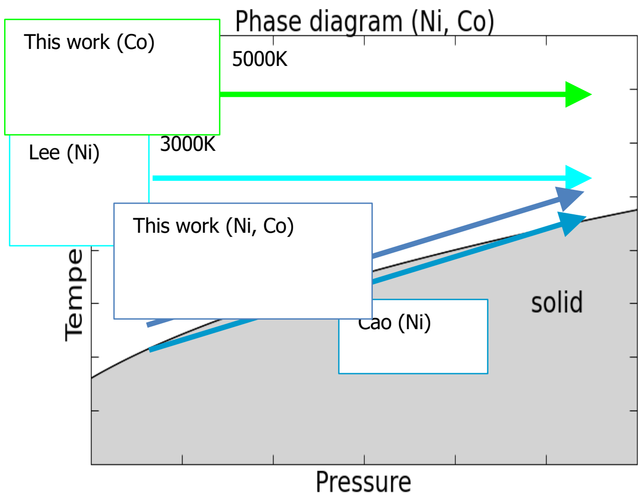
step 2

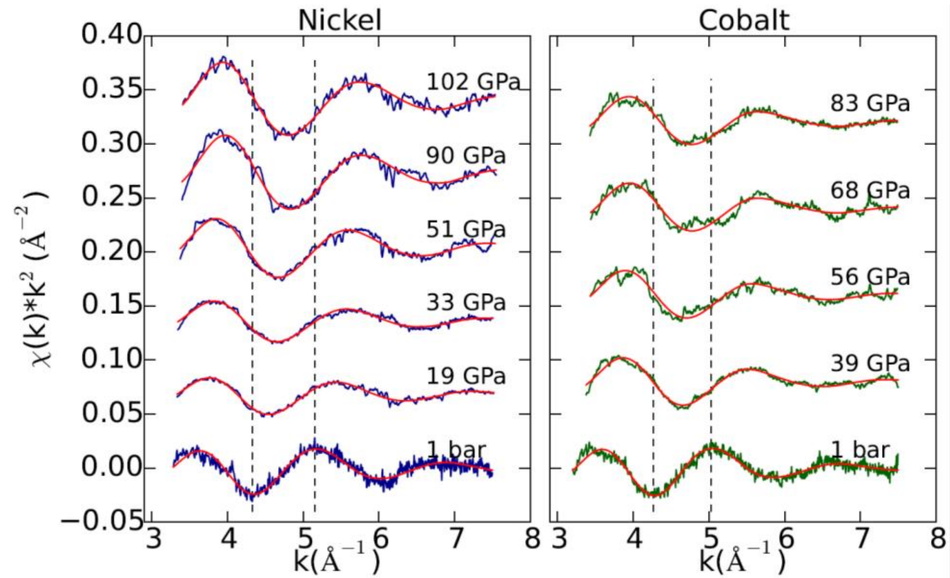


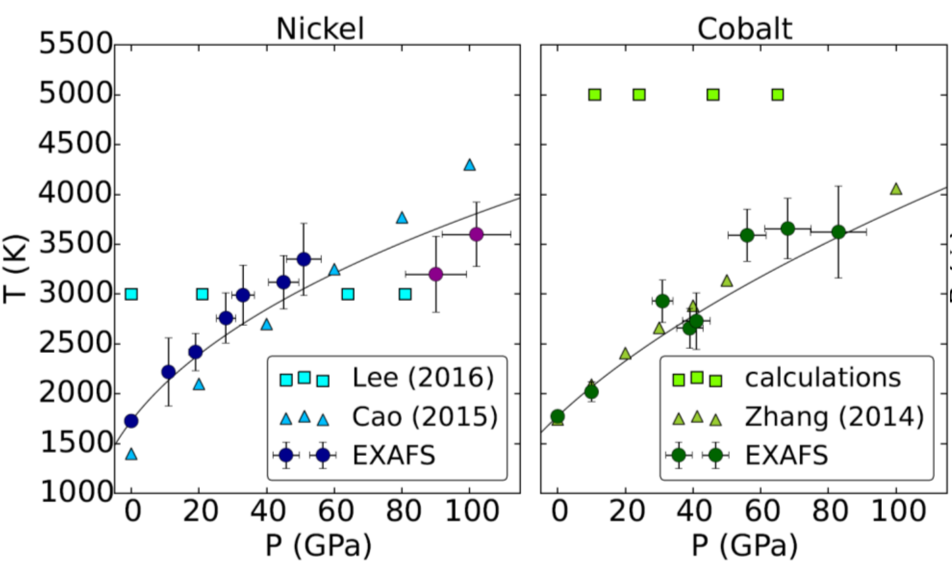
step 3

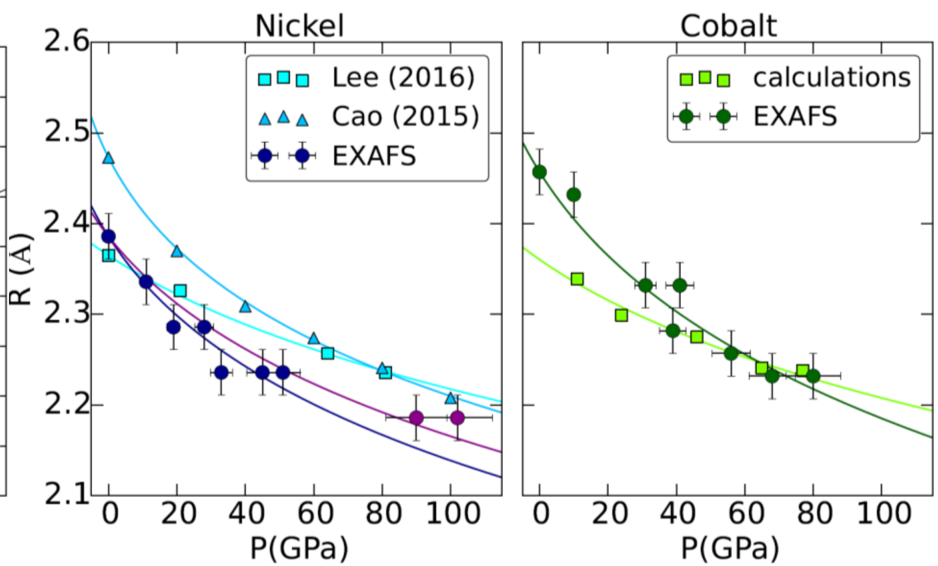


Compression of the first neighbours distance

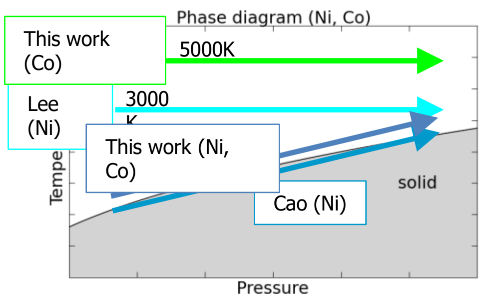


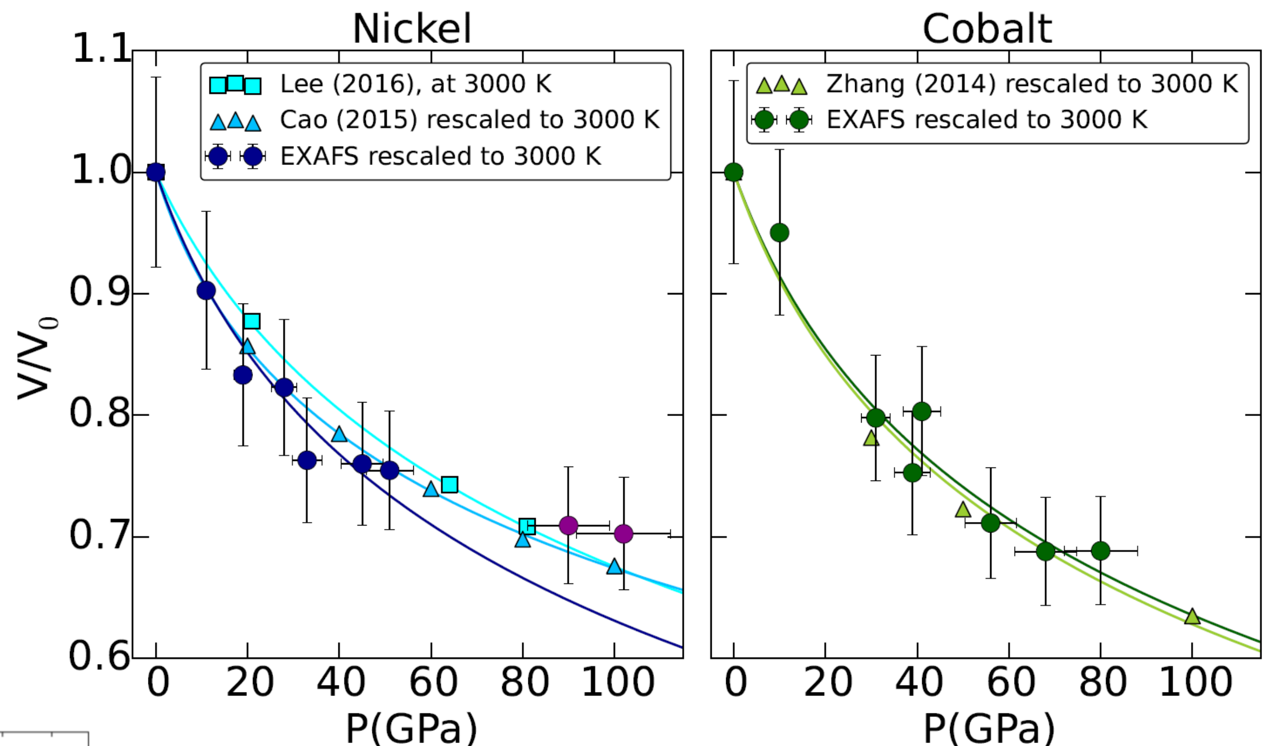


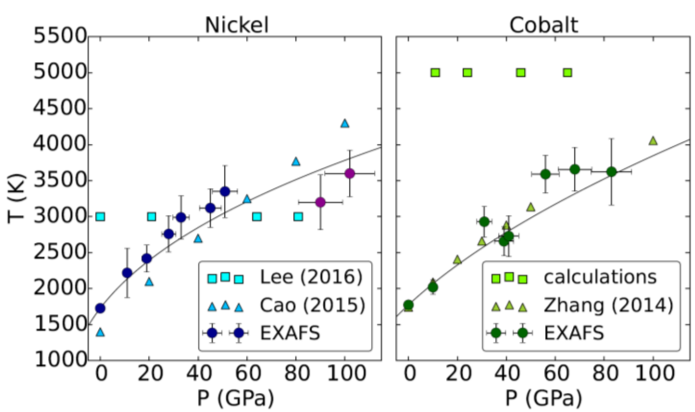




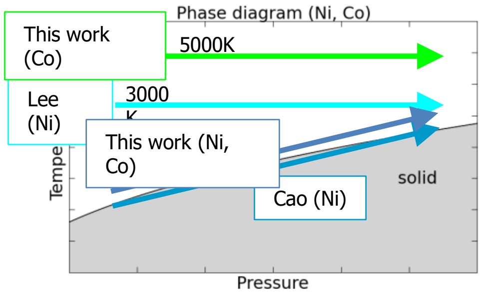
Volume normalized and rescaled at 3000 K

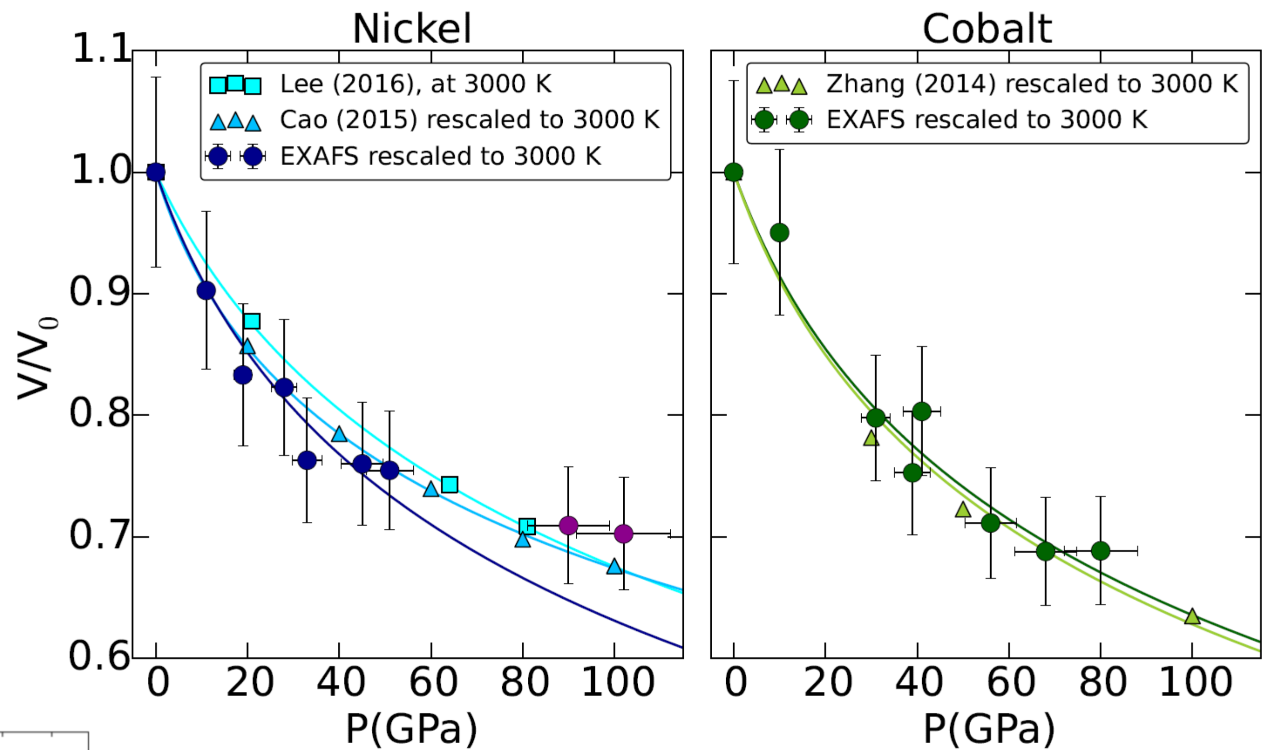


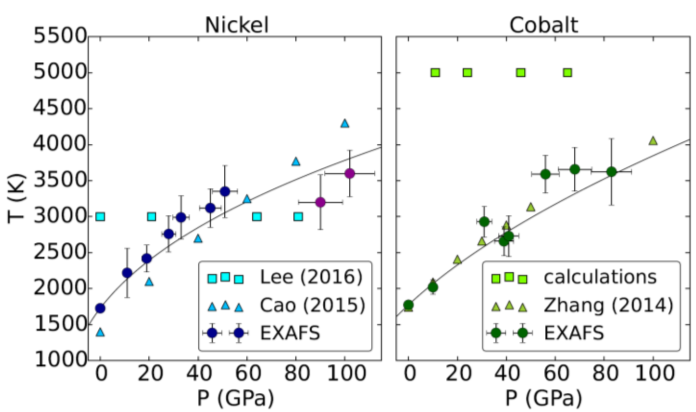




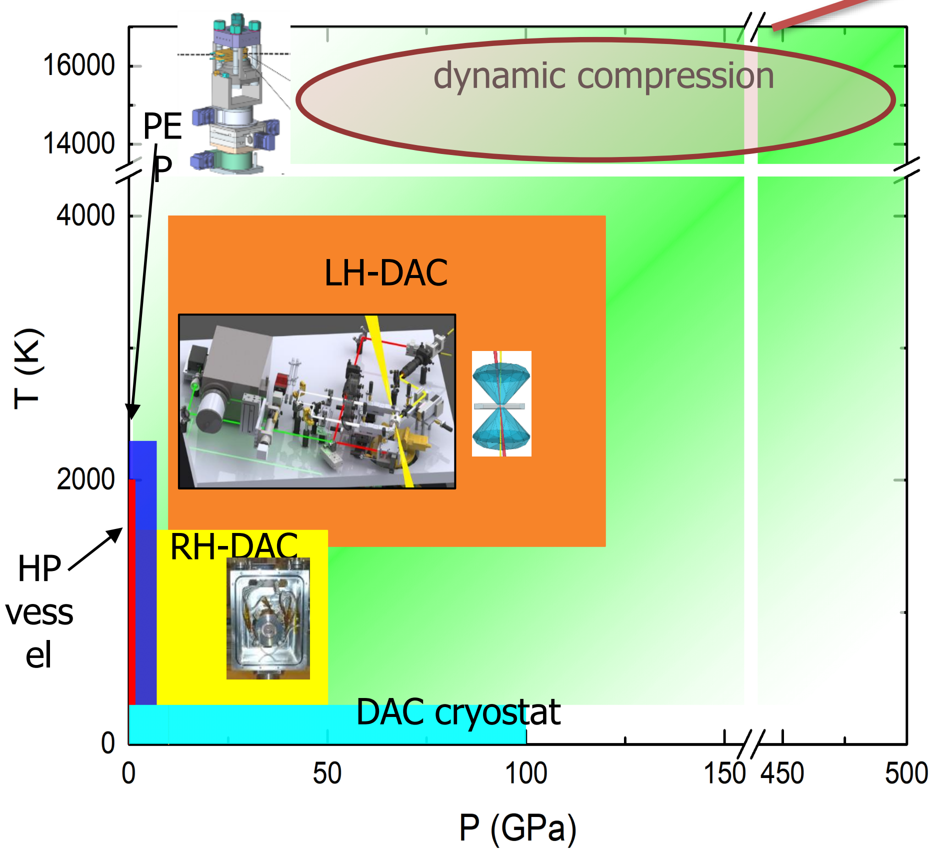
Volume normalized and rescaled at 3000 K







Experimental methods T=8000-16000 K P= 1MPa - 500 Gpa



SCIENTIFIC REPORTS

OPEN

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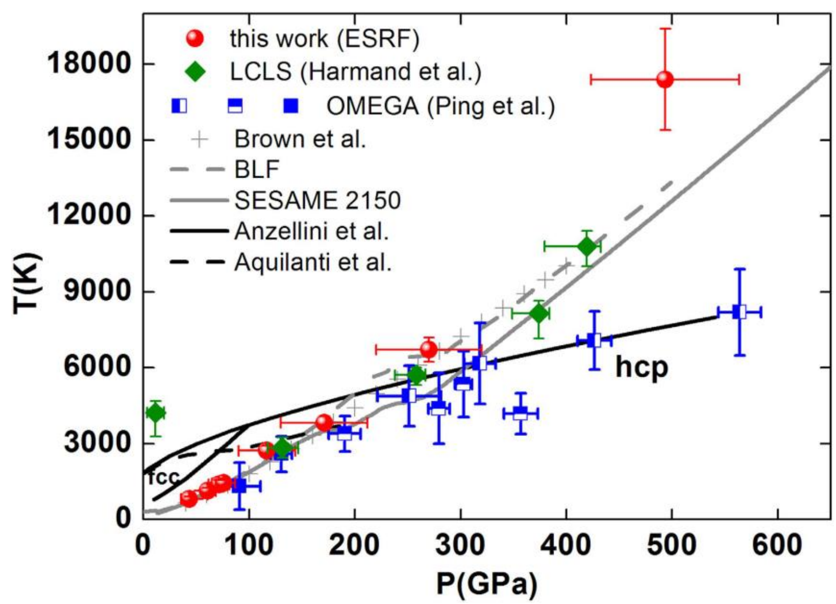
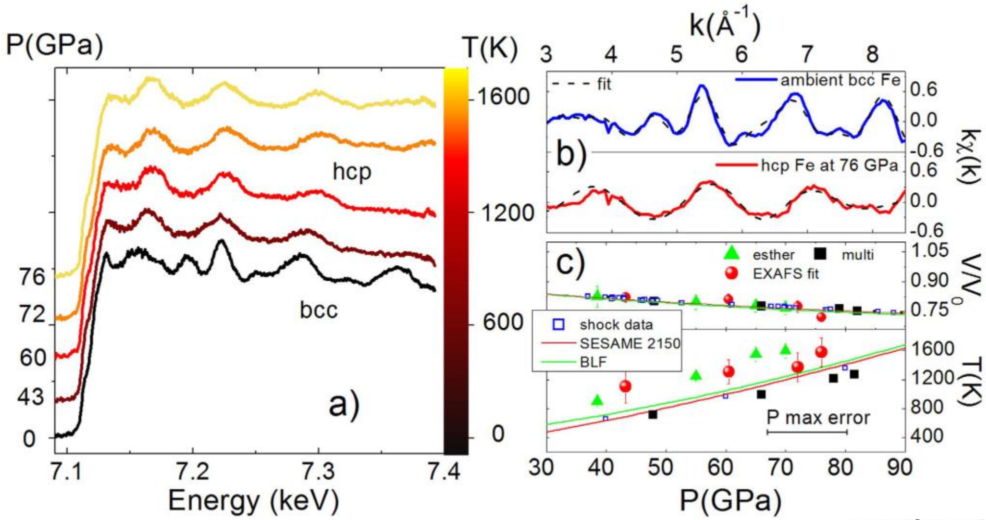
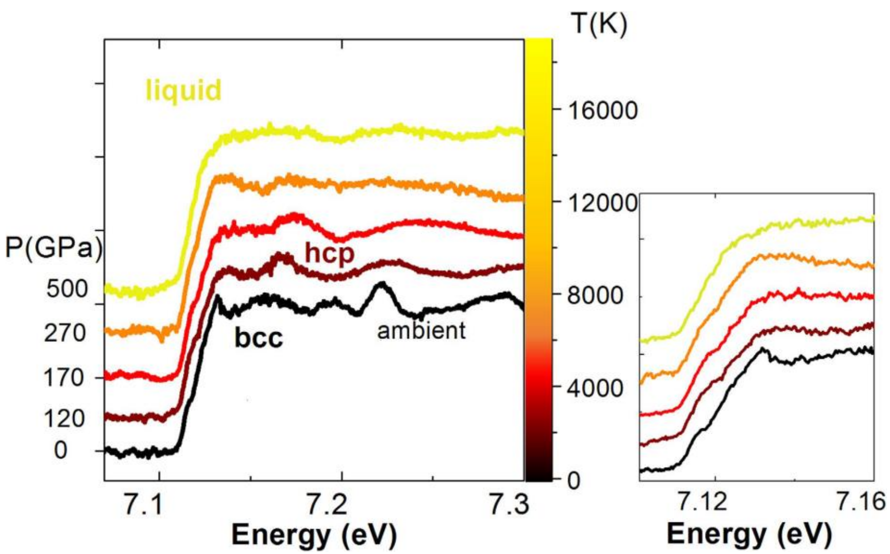
Probing local and electronic structure in Warm Dense Matter: single pulse synchrotron x-ray absorption spectroscopy on shocked Fe

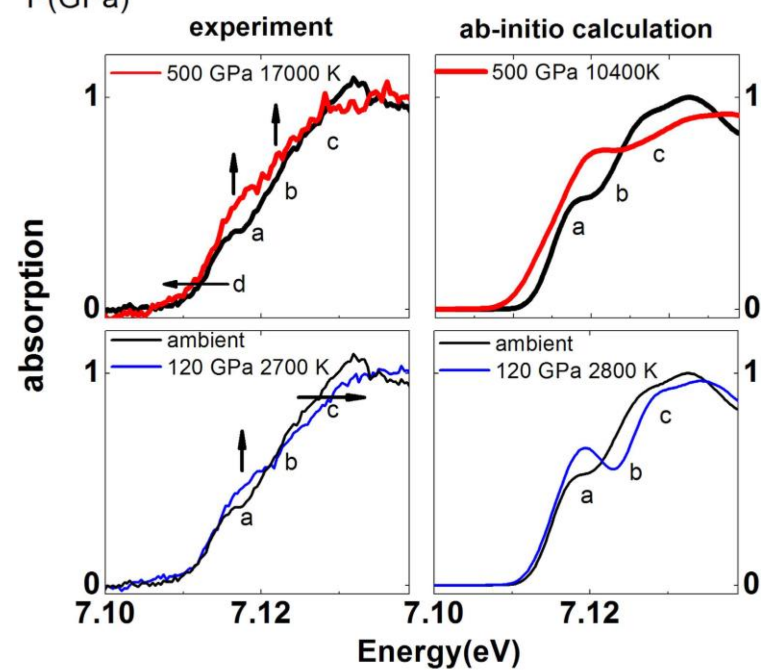
Raffaella Torchio[1,2], Florent Occelli[1], Olivier Mathon[2], Arnaud Sollier[1], Emilien Lescoute[1], Laurent Videau[1], Tommaso Vinci[3,4], Alessandra Benuzzi-Mounaix[3,4], Jon Headspith[5], William Helsby[5], Simon Bland[6], Daniel Eakins[5,6], David Chapman[6], Sakura Pascarelli[2] & Paul Loubeyre[1]



Experimental methods T=8000-16000 K P= 1MPa - 500 Gpa



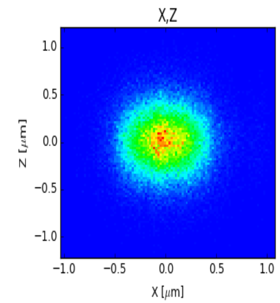




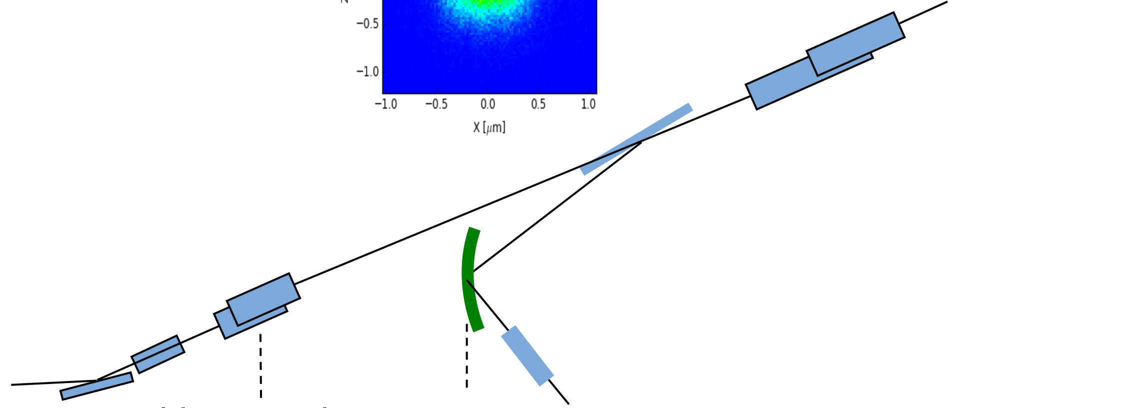
FUTURE PERSPECTIVES

EBS, new ID24:
Monochromator (fast scanning, longer *k* range)

- Focal spot down to 1 μm x 1 μm Full Width
- Flux between 10^{10} - 10^{14} ph/s
- Full EXAFS in 1s
- X-ray beam < 0.5 μm FWHM



Longer and nicer data of liquids
Higher pressures will be accessible



Improvement of the LH optics:

- Flat-top beam shaper
- New lenses with spatial resolution < 1 µm

Reduced temperature errors

High flux & small focal spot only possible with EBS

Quantitative analysis of the EXAFS spectra at extremely high T and P will be possible

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Olivier Mathon

Elettra Sincrotrone Trieste

Giuliana Aquilante

THE END

THANK YOU