Disordered matter at high P and T: a challenge for X−ray Absorption Spectroscopy

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ESRF
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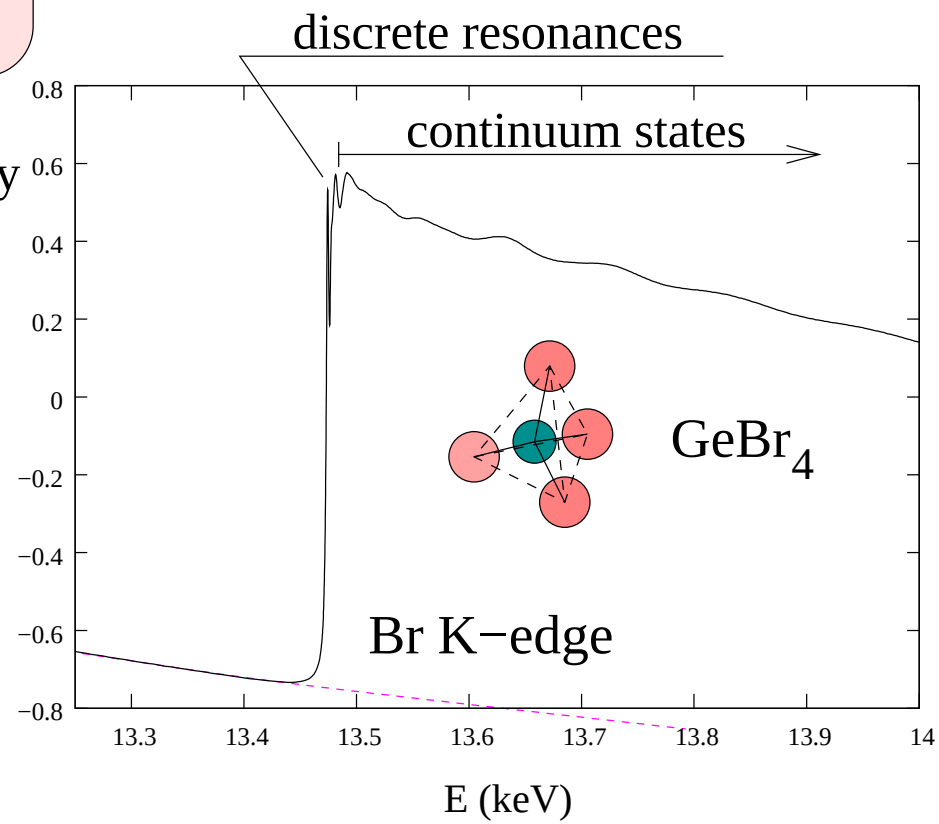
Paola D'Angelo
Univ. Roma "La Sapienza"

Talk Outline − main issues

- A role for X−ray Absorption Spectroscopy in condensed matter physics research
- X−ray beam requirements in terms of energy range, resolution, photon flux, etc.
- Current experimental station for HP−HT research at the ESRF − BM29
- Examples of current research and achievements.

X−ray Absorption Spectroscopy

- The phenomenon of X−ray absorption in mainly associated with core electron excitations
- The K, L ... threshold sequence suggestes it is mostly a one−electron phenomenon.
- Relevant matrix element $< \Psi_i | \varepsilon \cdot \hat{p} | \Psi_f >$
- Typical transition times 10^{-15} s (instantaneous with respect to atomic motion).



- A probe for average properties around the selected photoabsorber atomic species:
  unoccupied density of electronic states (projected + excitonic effect)
  short−range structure (partial radial distribution function)
- Can be indifferently applied to gas, liquid and solid (amorphous or crystalline) phases
- Suitable for investigations under extreme thermodynamic conditions (HP−HT)
- Full bulk sensitivity: typical sample thickness 0.01−10 mm

Where X−ray Absorption Spectroscopy is unique

- Crystalline structures: diffraction techniques tell almost everything, however XAFS can play a role when correlated local units exist.

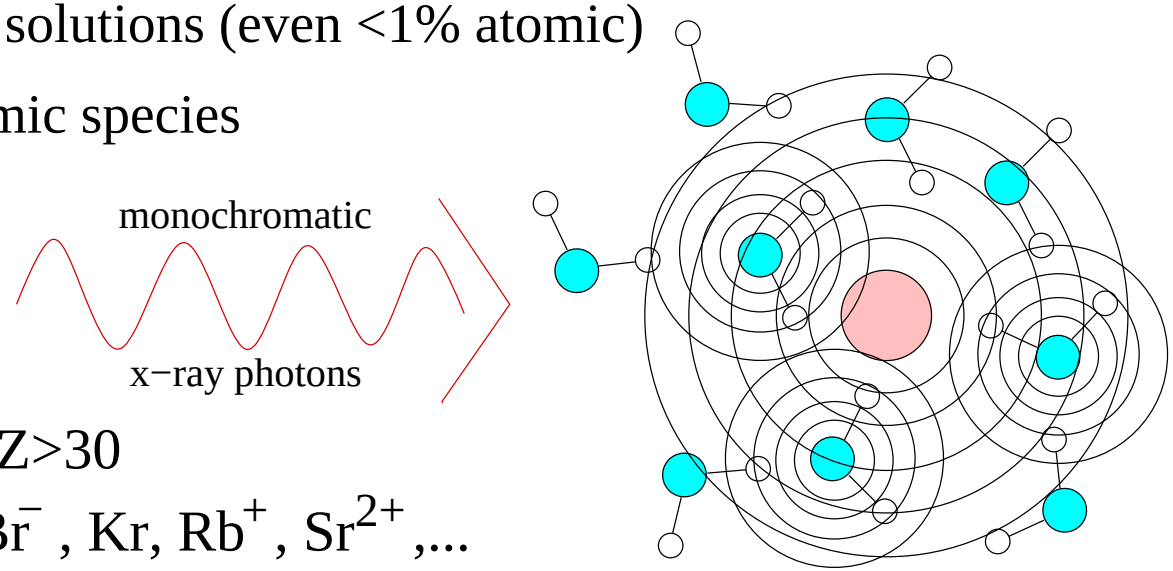
- Liquid or amorphous bulk structures: XAFS provide important complementary information on the short−range features of the partial radial distribution functions.

- Sensitivity to triplet correlations through MS (still largely unexploited)

- Electronic properties can be probed in many ways, but XAFS probes them simultaneously with the structure. Can be exploited in the case of I<−>M transitions or to probe the integrity of molecular strucutres.

- Diluted species (in low−Z environment) in disordered matter: impurities, diluted alloys, aqueous solutions (even <1% atomic)

XAS at the edge of the minority atomic species

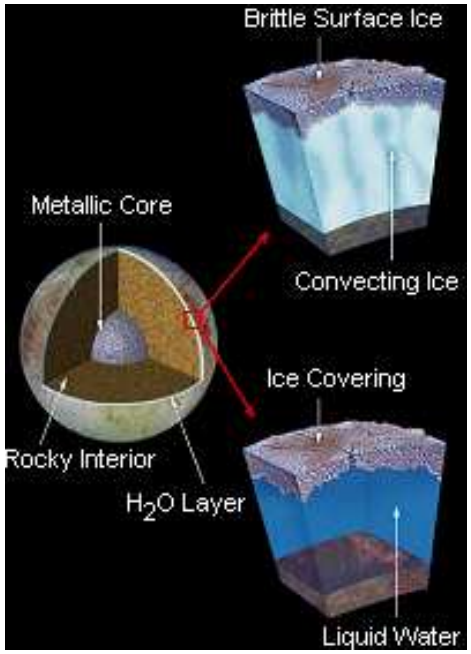


→ possible HP experiments for Z>30

Cu^{2+}, Zn^{2+} Ga, Ge, As^{3+}, Br^{-} , Kr, Rb^{+}, Sr^{2+},...

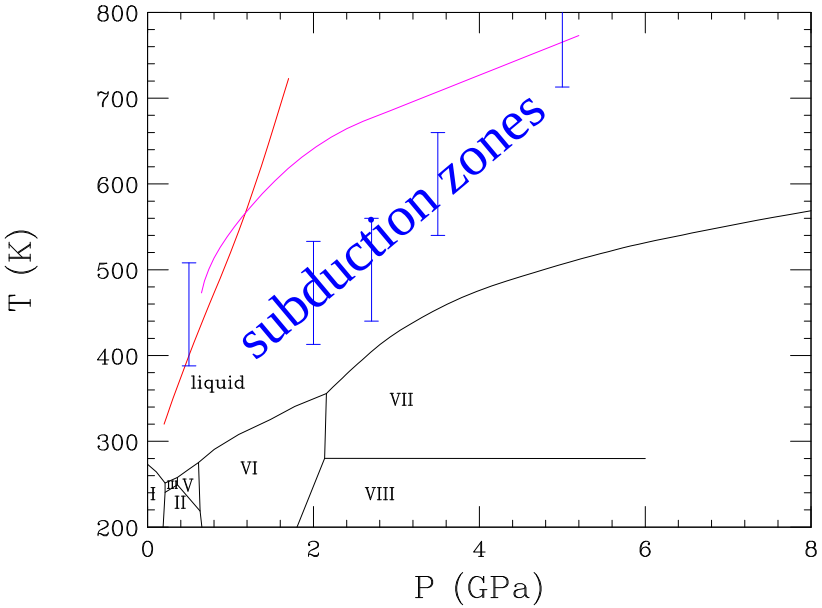
X−ray absorption spectroscopy study of aqueous solutions at High−Pressure

Scientific motivation:
Understanding the behaviour of water as a solvent at high−pressure



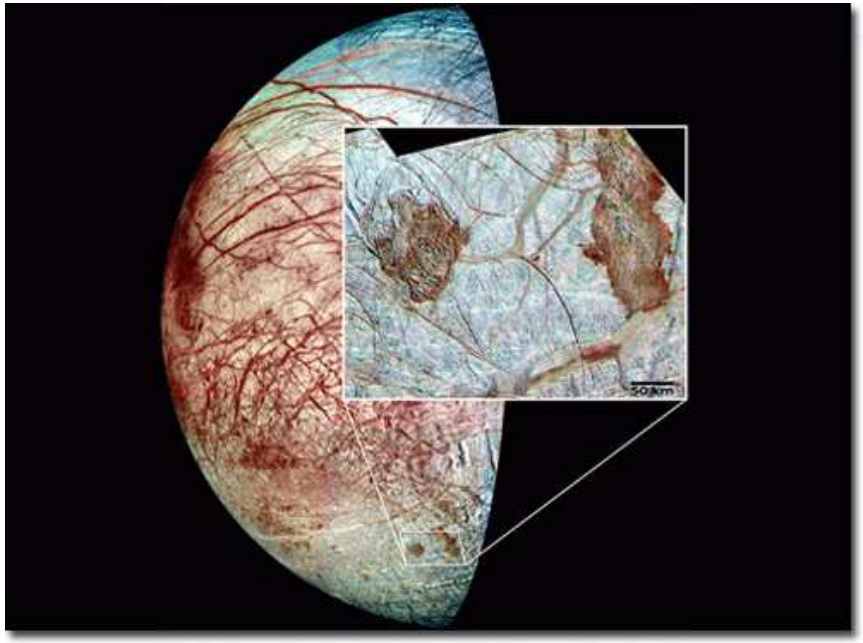
Relevant to:
- Basic chemical physics science
- Earth and Planetary science

Earth crust/upper mantle



H_2O phase diagram

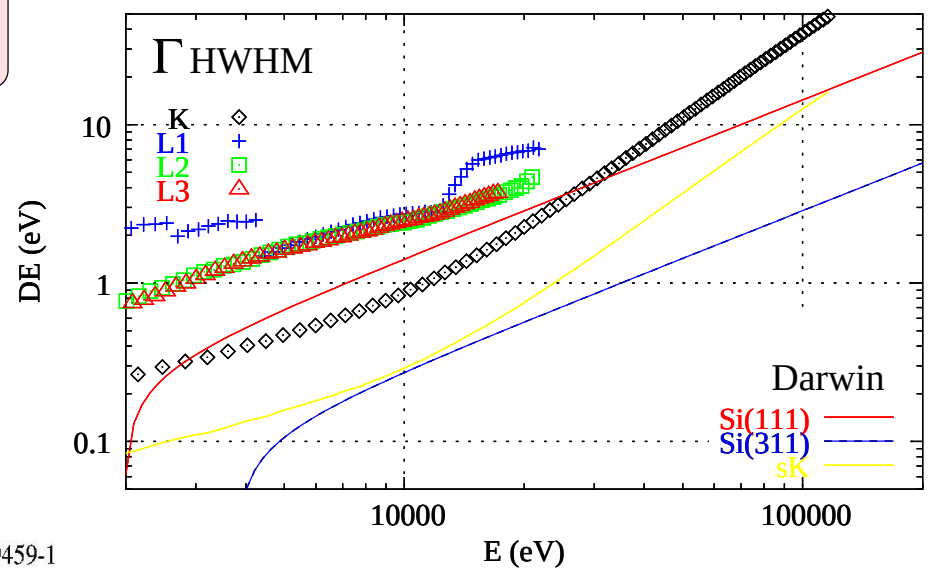
Europa buried ocean



What energy resolution is required?

Is it possible (and useful) to go beyond the core−hole lifetime broadening?

useful for secondary emission spectroscopy but also ... deconvolution ...



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Deconvolution of the lifetime broadening from x-ray absorption spectra of atomic and molecular species

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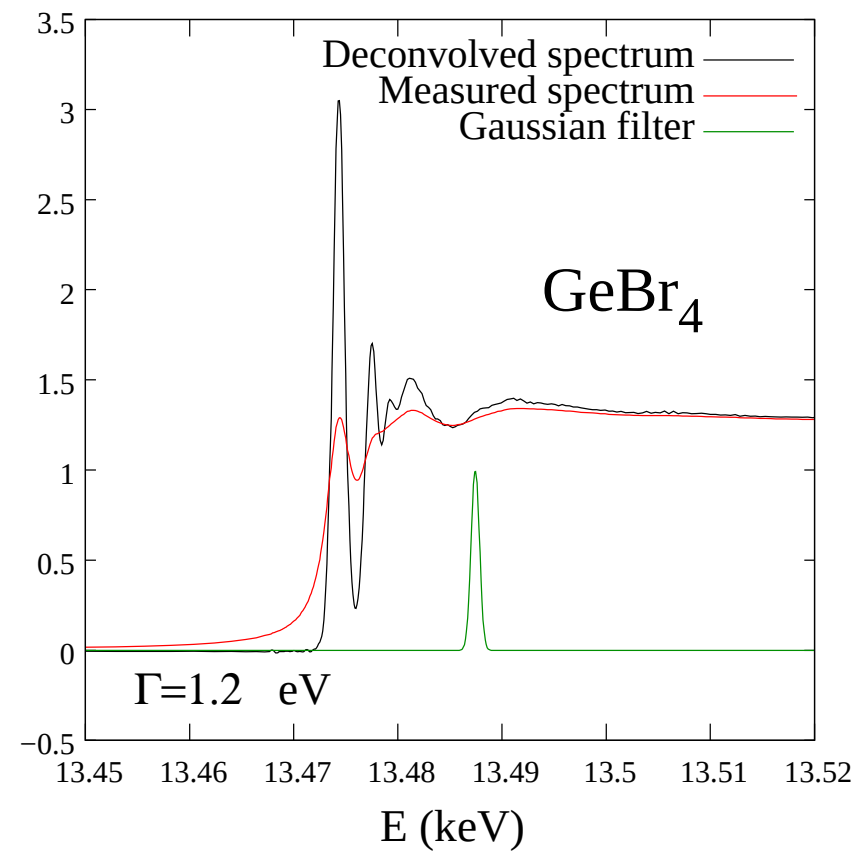
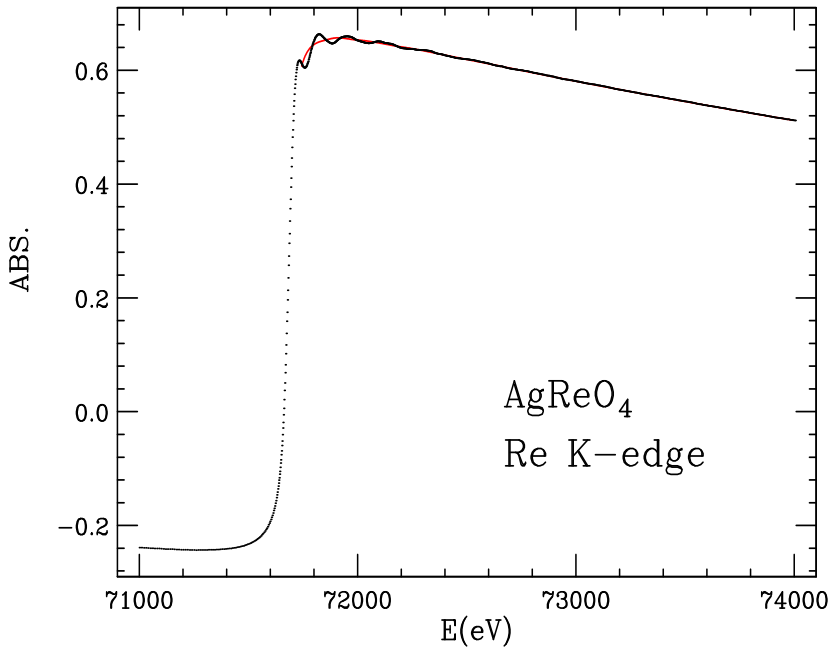
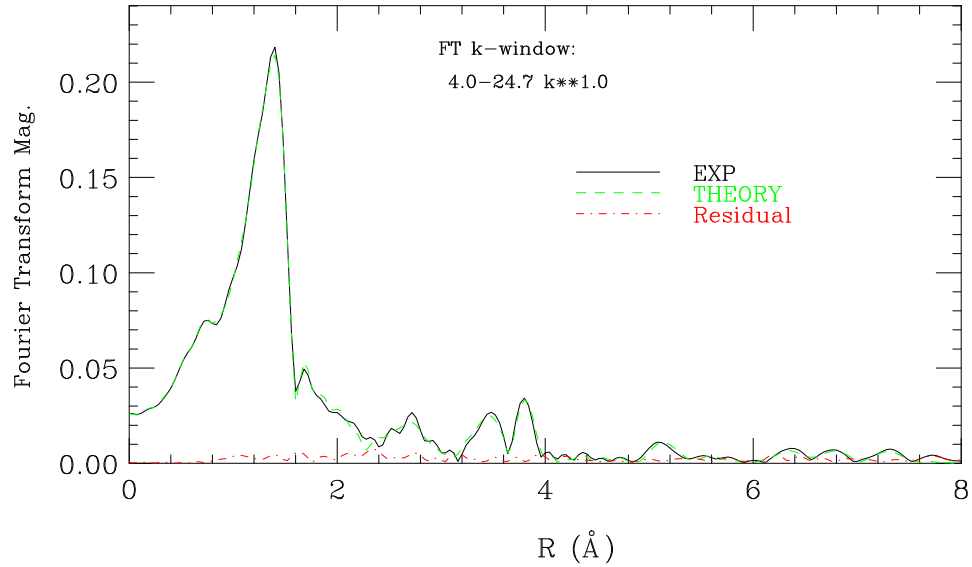
Abstract. An algorithm suitable to deconvolve the entire core-hole lifetime broadening from x-ray absorption spectra is described in detail. The algorithm is based on the convolution theorem in Fourier space and is implemented numerically for the treatment of typical spectra with an arbitrary energy sampling. The adoption of a Gaussian filter to avoid noise blow-up allows one to sharpen a Lorentzian profile of width Γ into a Gaussian with $\sigma \approx \Gamma/3$. The method is applied to previously published K-edge spectra of isolated atomic and diatomic molecular species such as Kr, Br_2 and I_2. In the Kr case the main Rydberg resonance is clearly separated from the continuum threshold. The region of the [1s4p] and [1s4s] double-electron excitation resonances is highlighted with an unprecedented resolution and is found to be very similar to the Ar K-edge [1s3p]–[1s3s] resonance region. In the diatomic molecular cases, a complete separation of the main resonance from the rest of the spectrum is achieved in Br_2, whereas the corresponding I_2 resonance, originally visible as a hump in the K-edge threshold, is highlighted.

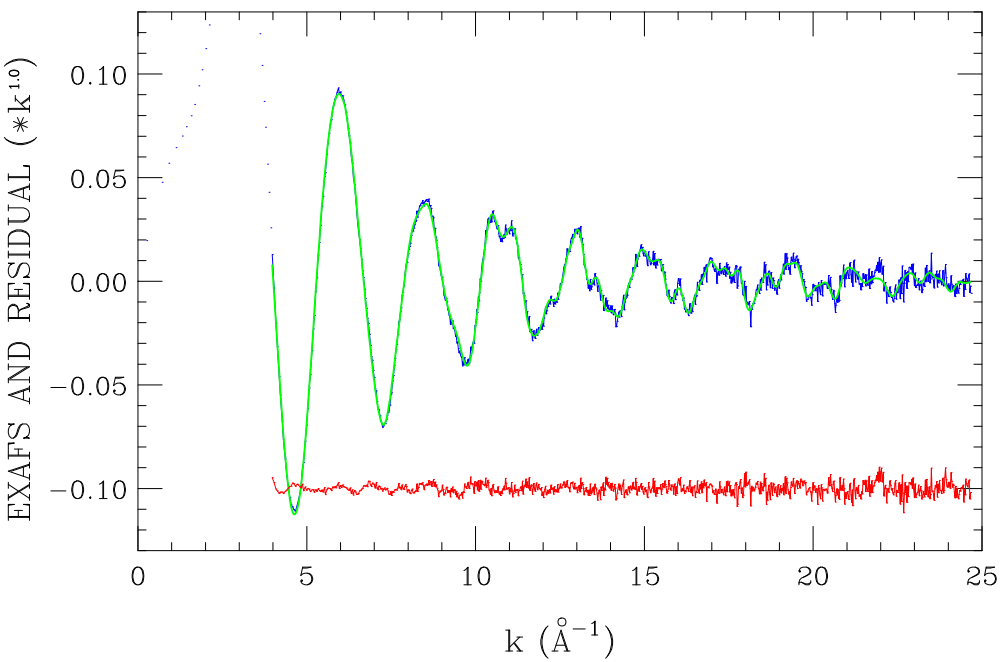


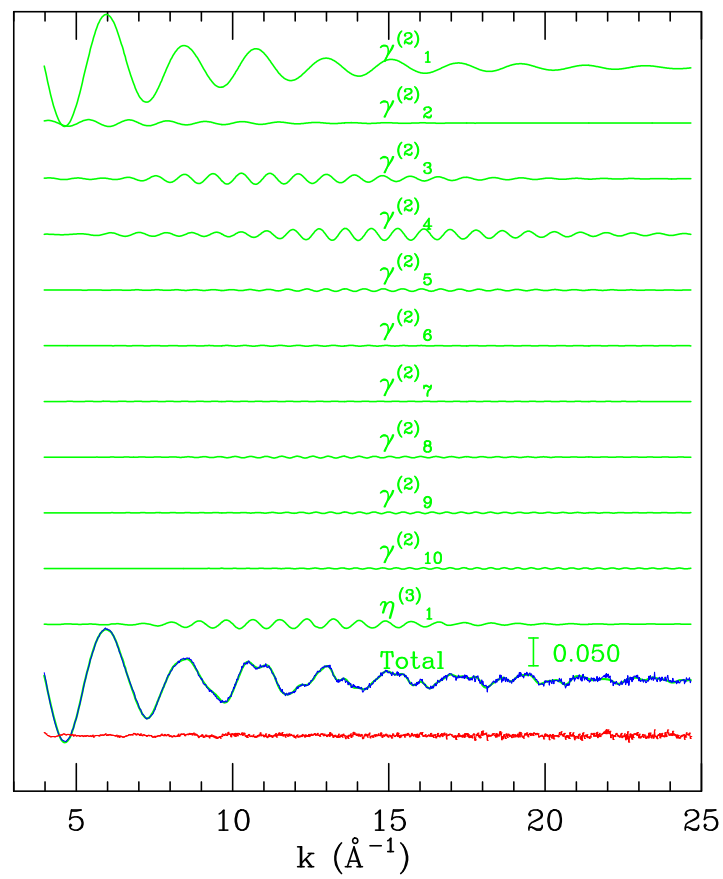
Is there any use of hard X−rays (E>50 keV) for XAS?

Silver perrhenate − 5 K ESRF−BM29

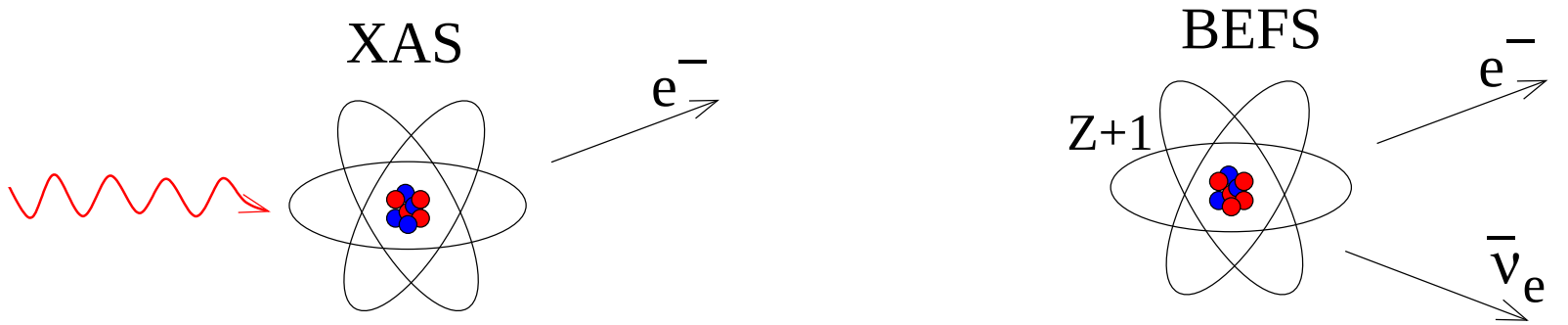








Beta Environmental Fine Structure the XAFS nuclear analogue

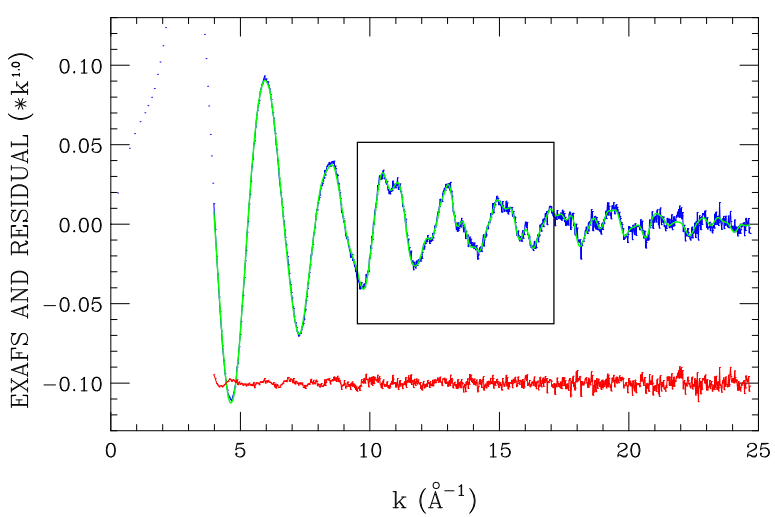


$$^{187}\mathrm{Re} \longrightarrow {}^{187}\mathrm{Os} + e^- + \bar{\nu}_e$$

PRL **96,** 042503 (2006) PHYSICAL REVIEW LETTERS week ending 3 FEBRUARY 2006

Measurement of the *p* to *s* Wave Branching Ratio of ^{187}Re β Decay from Beta Environmental Fine Structure

C. Arnaboldi,[1] G. Benedek,[2] C. Brofferio,[1] S. Capelli,[1] F. Capozzi,[1] O. Cremonesi,[1] A. Filipponi,[3] E. Fiorini,[1] A. Giuliani,[4] A. Monfardini,[5] A. Nucciotti,[1] M. Pavan,[1] M. Pedretti,[4] G. Pessina,[1] S. Pirro,[1] E. Previtali,[1] and M. Sisti[1]



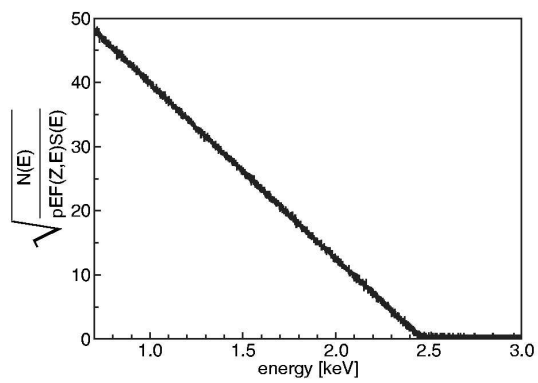


FIG. 1. Kurie plot obtained from the sum of all 8 detectors, where p is the electron momentum, E is the electron kinetic energy, $F(Z, E)$ is the Coulomb factor, and $S(E)$ is the shape factor.

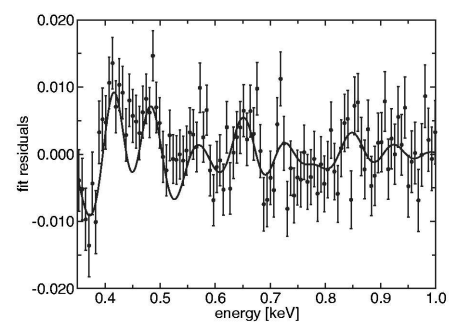
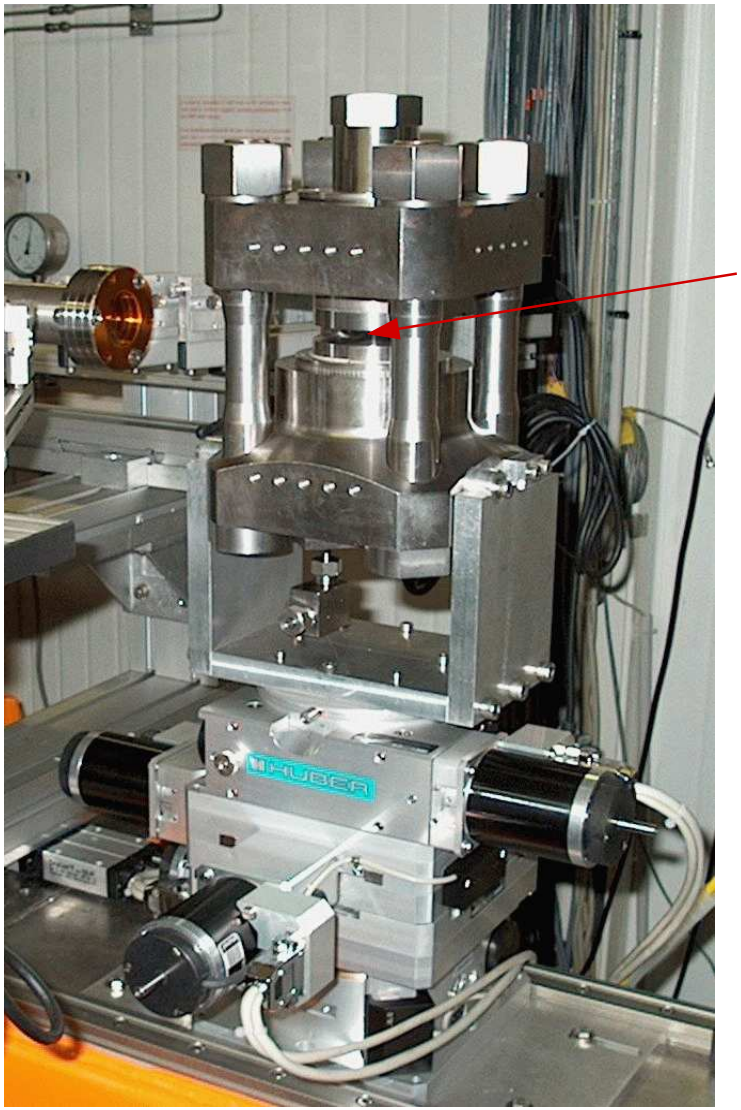


FIG. 2. The filled circles are the experimental fit residuals derived as the difference between the theoretical ^{187}Re β spectrum for free rhenium atoms and the measured one, as explained in the text. The BEFS oscillations appearing in the experimental residuals are fitted by using (1) with the backscattering amplitudes and phase shifts calculated with the Filipponi *et al.* theory [16] (solid line).

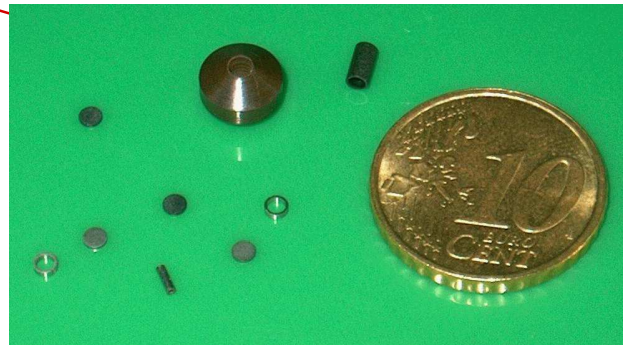
Paris−Edinburgh press and sample confinement

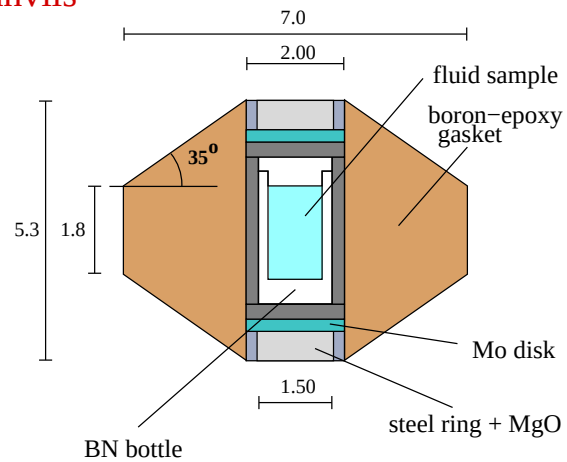
high−pressure large−volume technique

P: 0.2−8 GPa, T: 300−1000 K

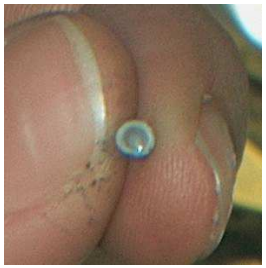


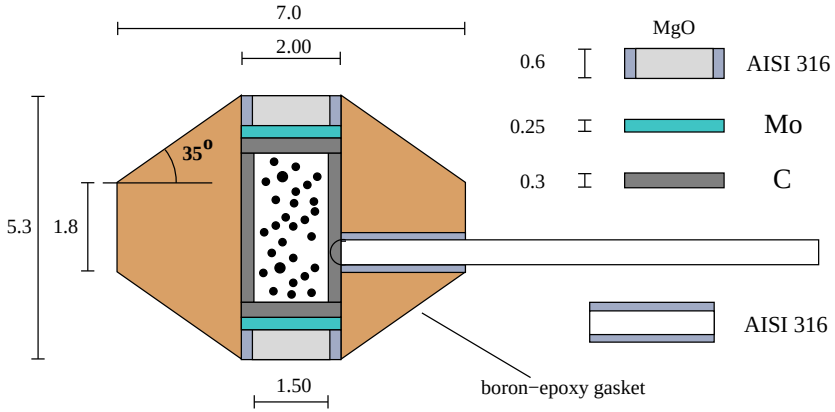
Sample mounting components



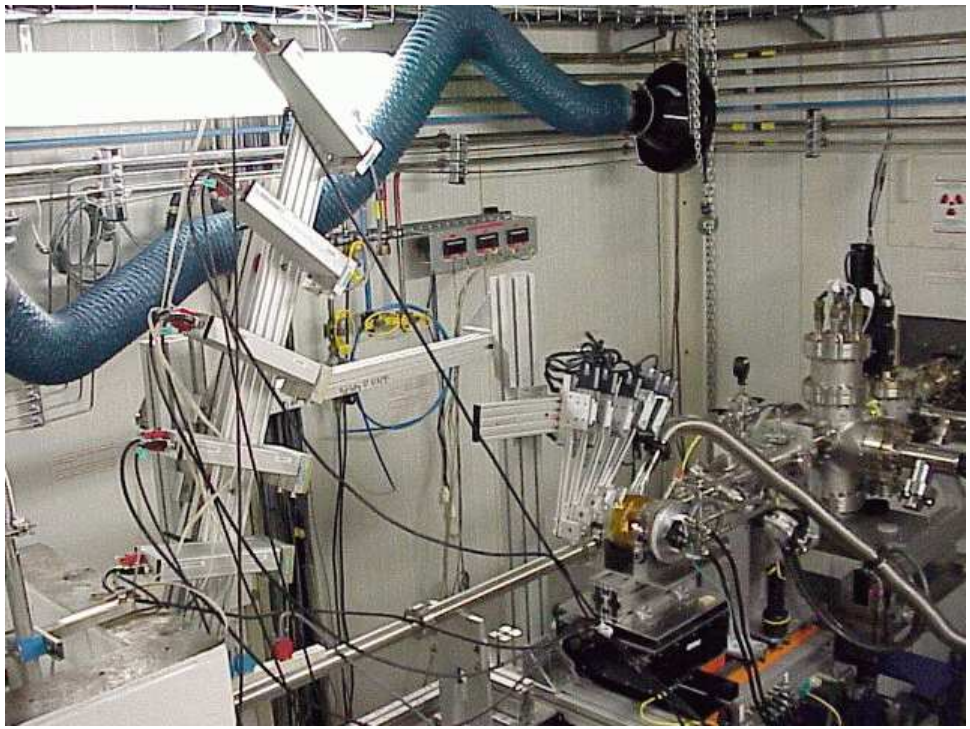


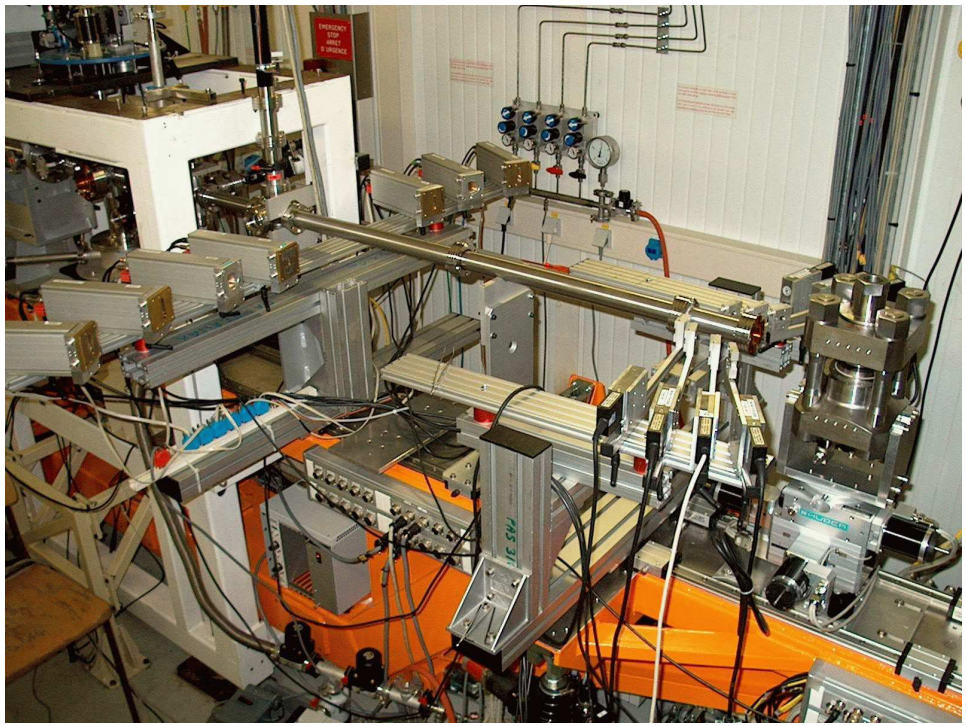
an aqueous solution sample





BM29: an experimental station for high−T, high−P experiments

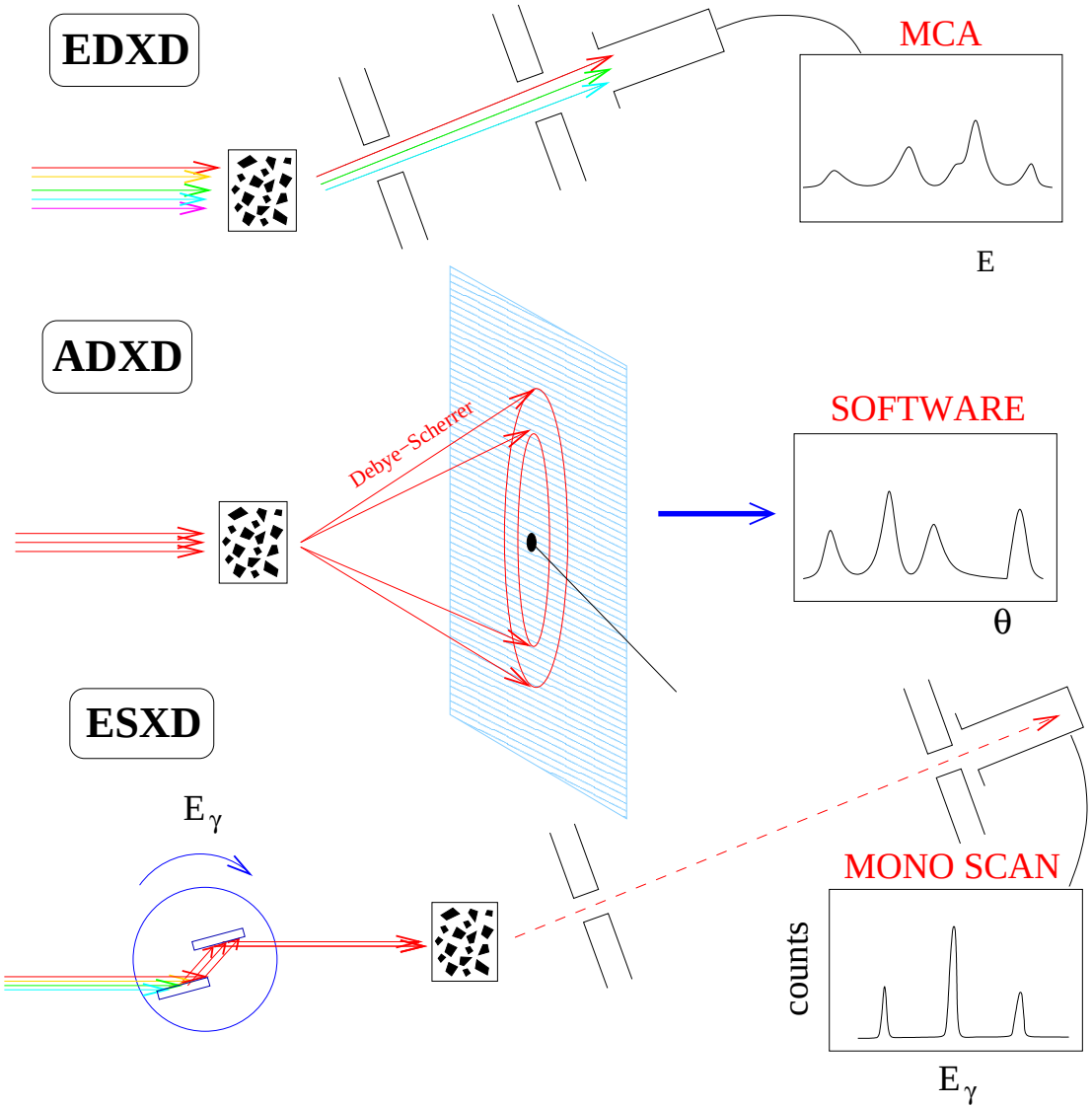




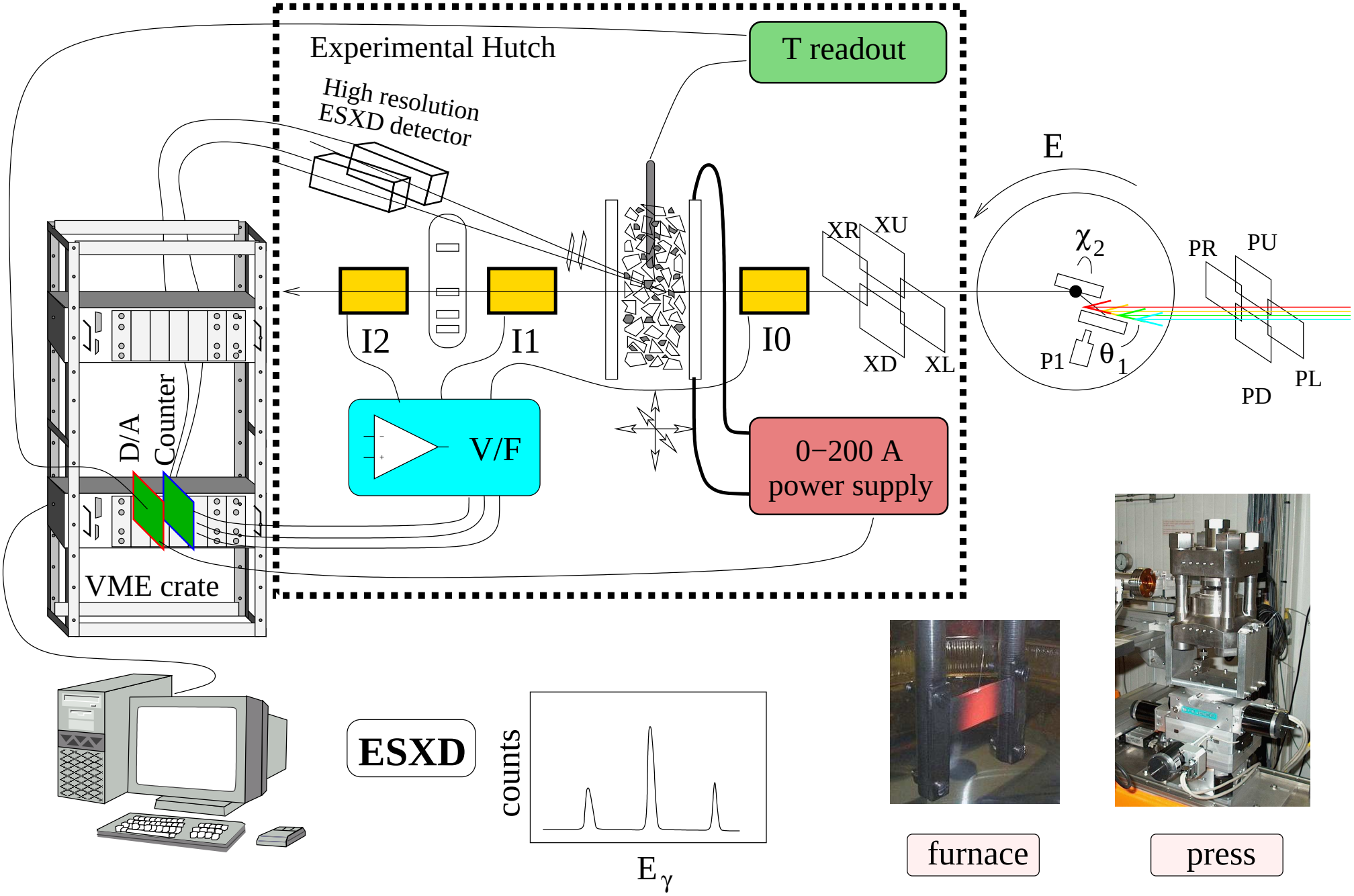
- X−ray absorption spectroscopy (XAS)
- Fixed energy X−ray absorption temperature scans (SEXAD, Tscan)
- Energy Scanning X−ray Diffraction (ESXD)

- A. Filipponi, M. Borowski, D. T. Bowron, S. Ansell, S. De Panfilis, A. Di Cicco, and J. P. Itie‘, ‘An experimental station for advanced research on condensed matter under extreme conditions at the ESRF − BM29 beamline.’. Rev. Sci. Instrum. 71, 2422−2432 (2000).
- A. Filipponi, V. M. Giordano, S. De Panfilis, A. Di Cicco, E. Principi, A. Trapananti, M. Borowski, and J. P. Itie, ‘Multichannel detector−collimator for powder diffraction measurements at energy scanning x−ray absorption spectroscopy synchrotron radiation beamlines for high−pressure and high−temperature applications.’ Rev. Sci. Instrum. 74, 2654−2663 (2003).

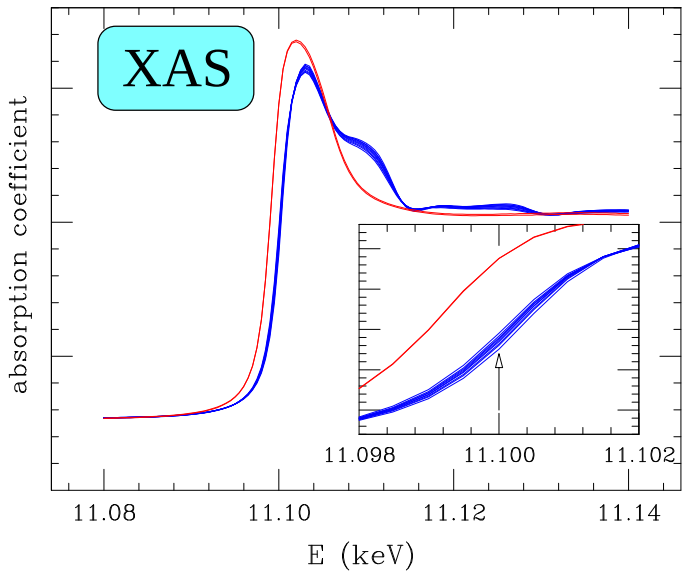
Alternative XRD detection methods

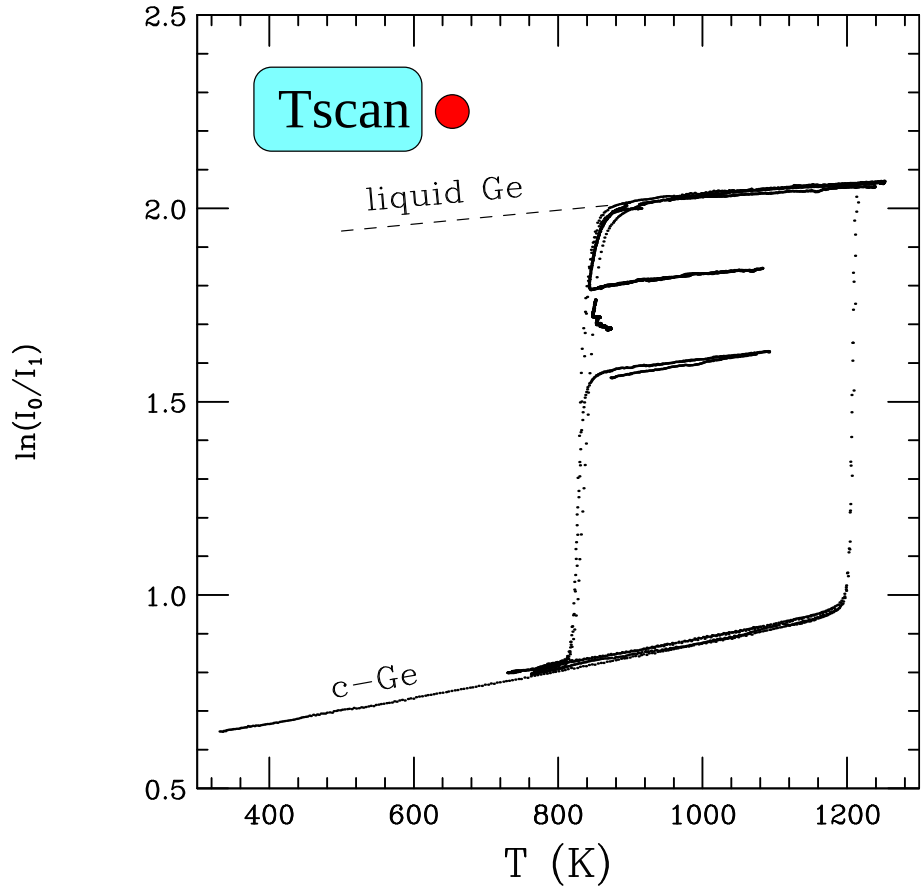


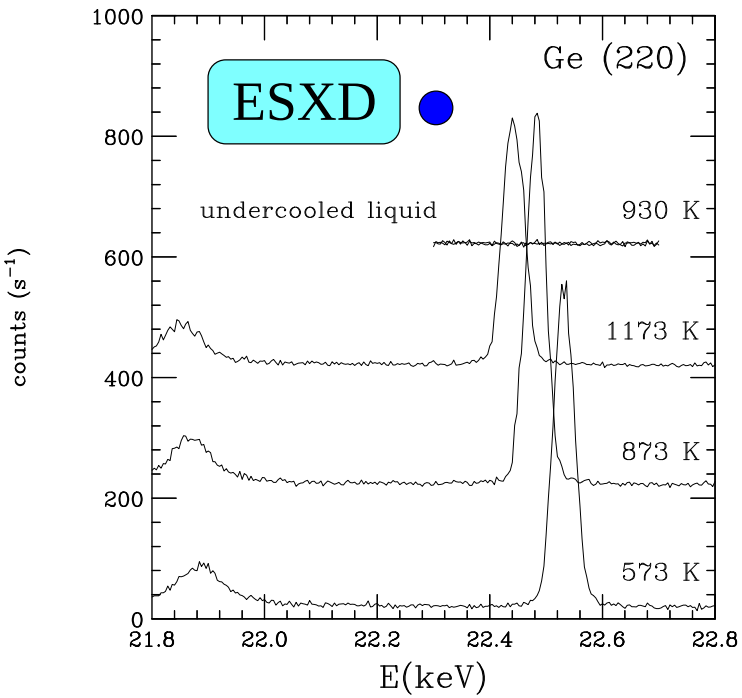
BM29 hardware for combined XAS−XRD−TSCAN experiments at HT−HP



X−ray absorption and diffraction measurements on Ge @P~0





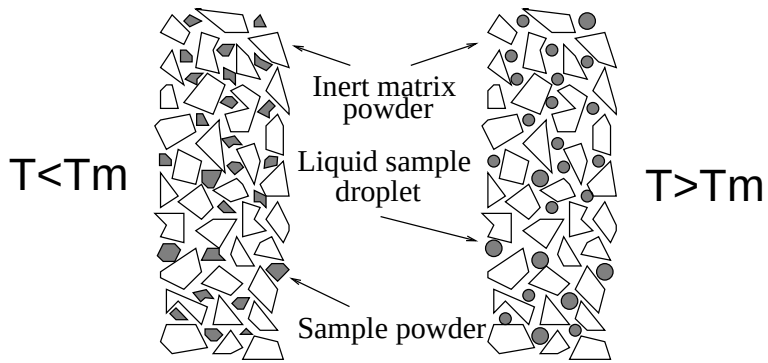


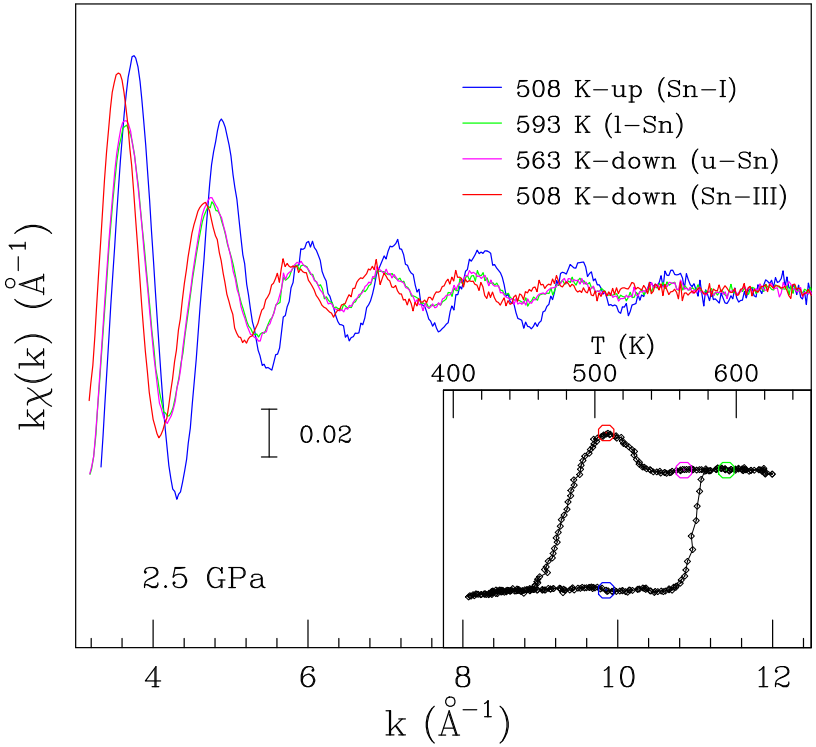
A. Filipponi, M. Borowski, P. W. Loeffen, S. De Panfilis, A. Di Cicco, F. Sperandini, M. Minicucci, and M. Giorgetti, ‘Single energy x−ray absorption detection: a combined electronic and structural local probe for phase transitions in condensed matter.’, J. Phys.: Condens. Matter 10, 235−253 (1998).

A. Filipponi, V. M. Giordano, S. De Panfilis, A. Di Cicco, E. Principi, A. Trapananti, M. Borowski, and J. P. Itie, ‘Multichannel detector−collimator for powder diffraction measurements at energy scanning x−ray absorption spectroscopy synchrotron radiation beamlines for high−pressure and high−temperature applications.’, Rev. Sci. Instrum. 74, 2654−2663 (2003).

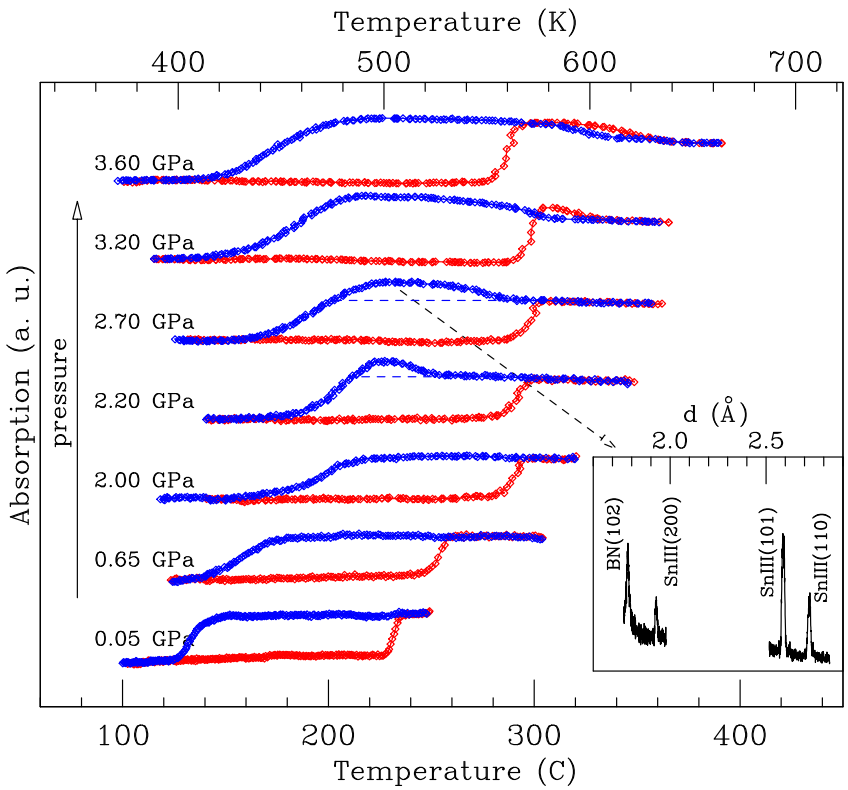
High−pressure investigation of Sn

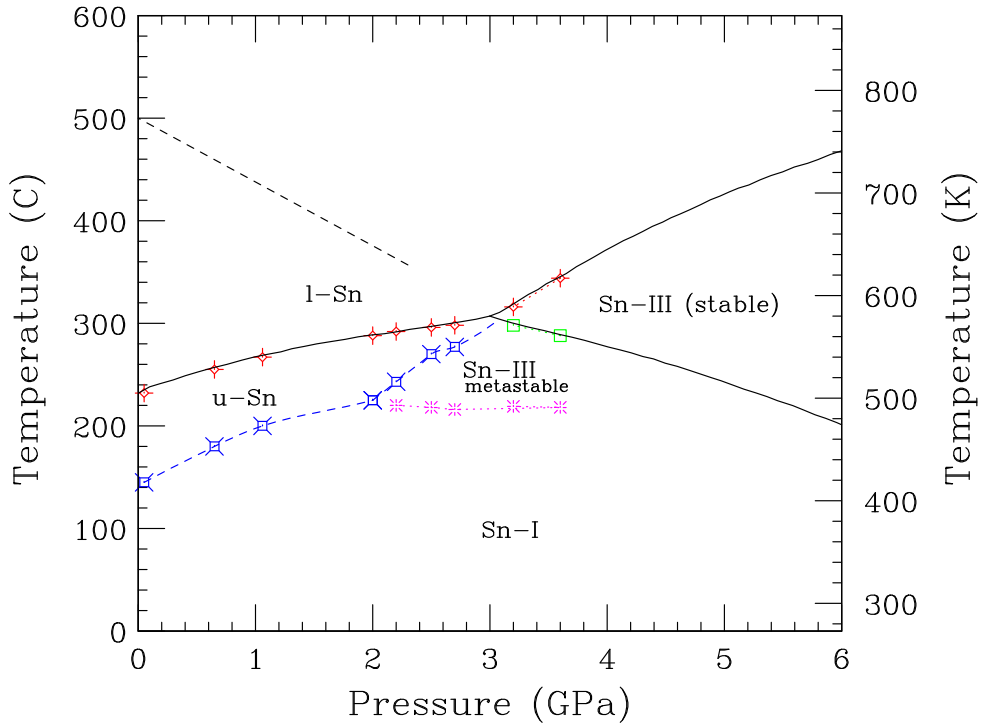
Samples for x−ray absorption spectroscopy
able to reach a deep undercooling



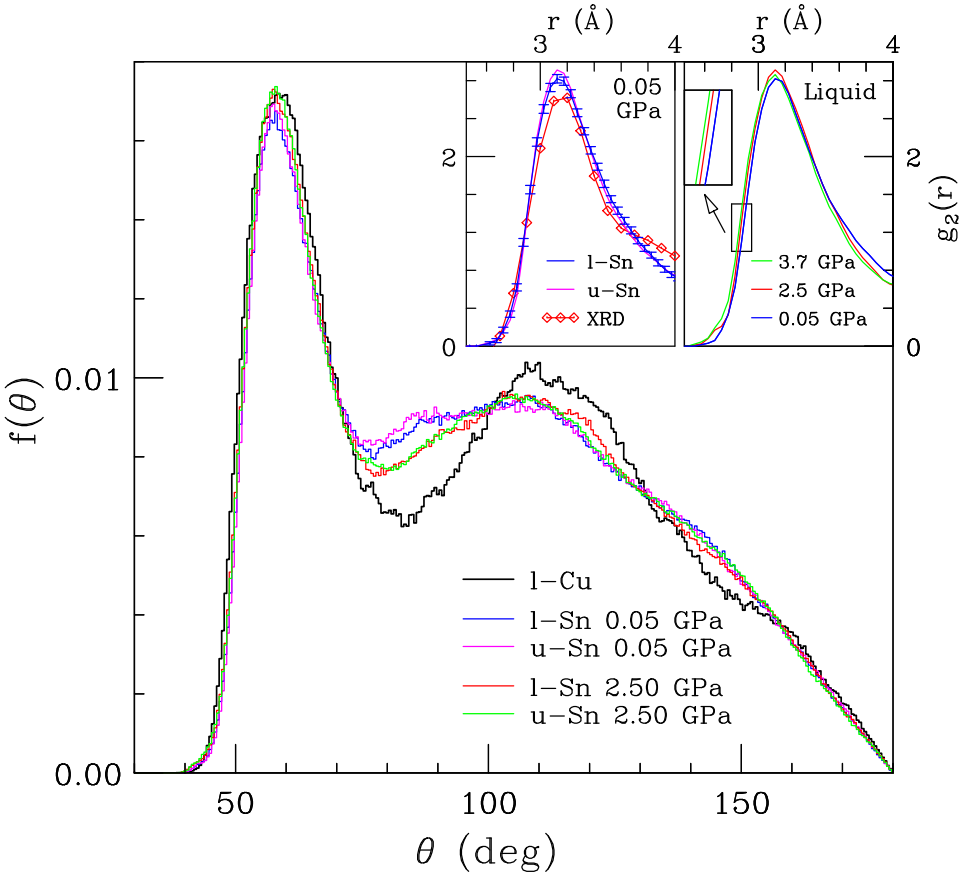


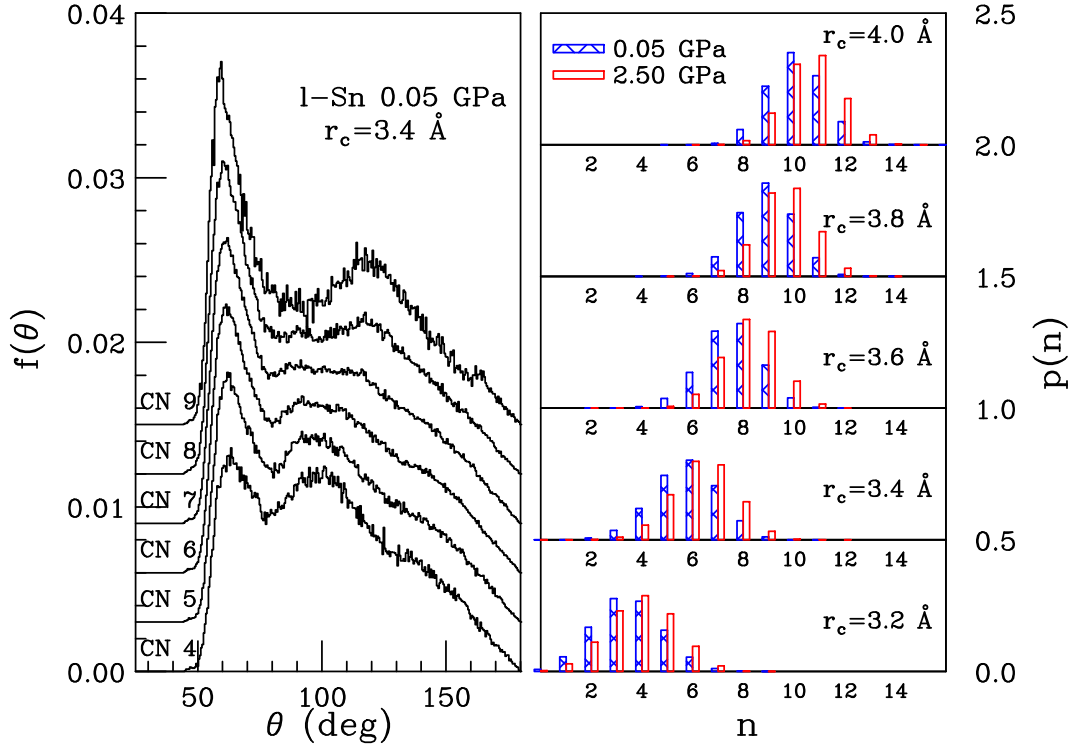
Powder samples (BN + Sn)





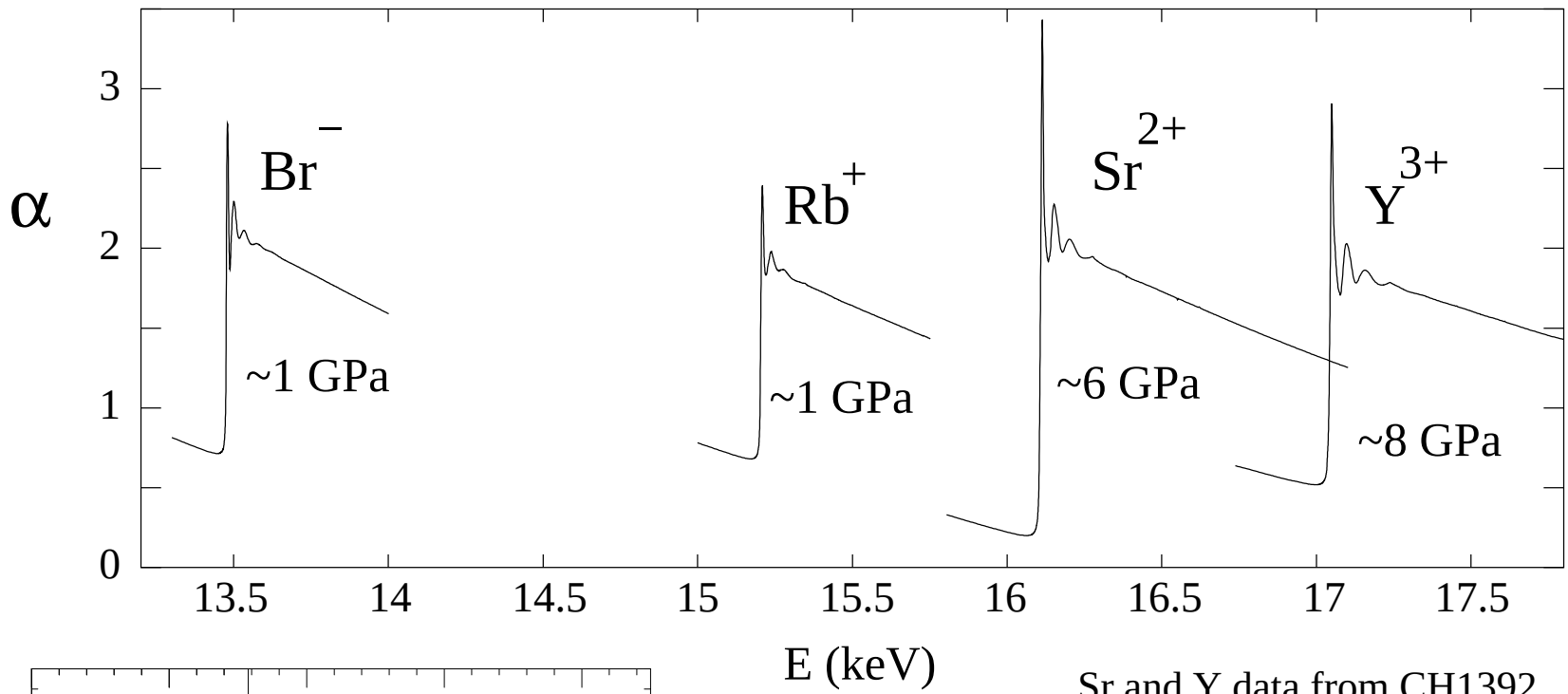
Liquid Sn at High pressure: RMC analysis and angular distributions



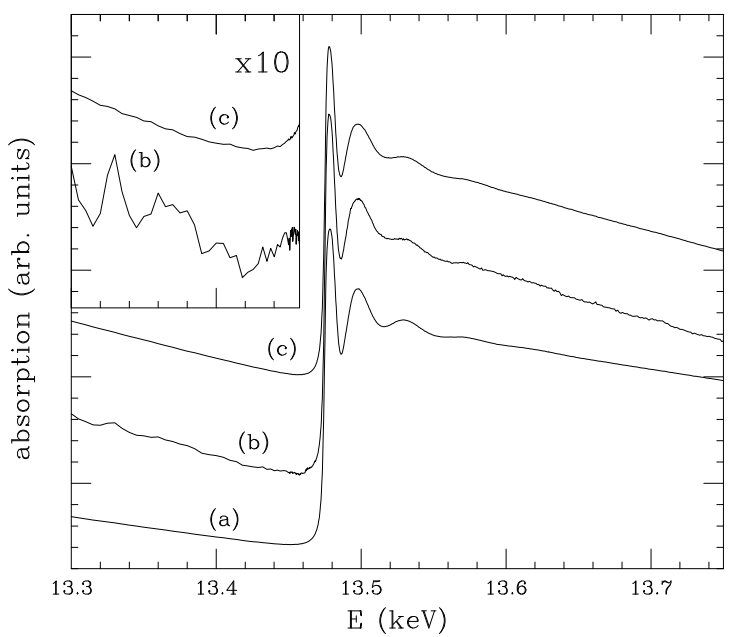


- A. Di Cicco, A. Trapananti, E. Principi, S. De Panfilis and A. Filipponi, ‘Polymorphism and metastable phenomena in liquid tin under pressure’, Appl. Phys. Lett. 89, 221912 (2006).

X−ray absorption spectra of aqueous solutions at HP

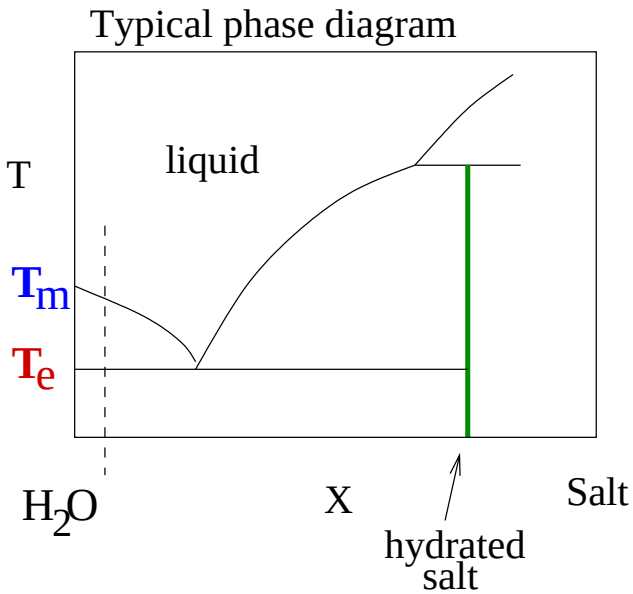


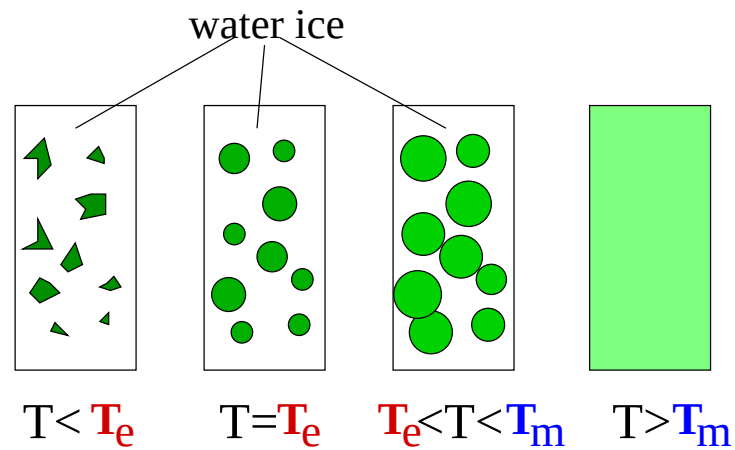
Sr and Y data from CH1392
(S. Ramos and A. Barnes)

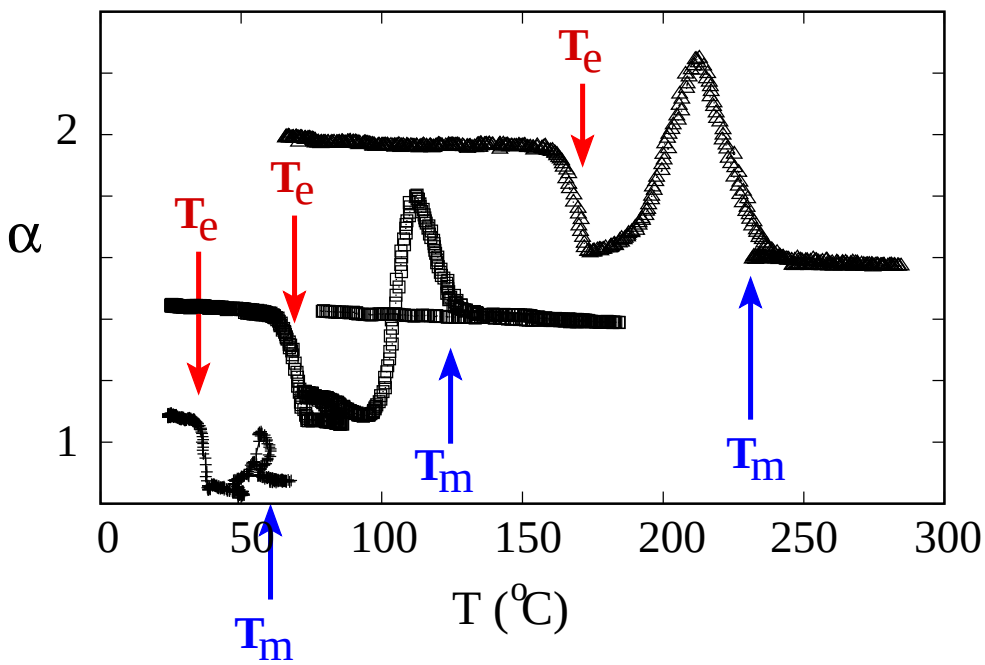


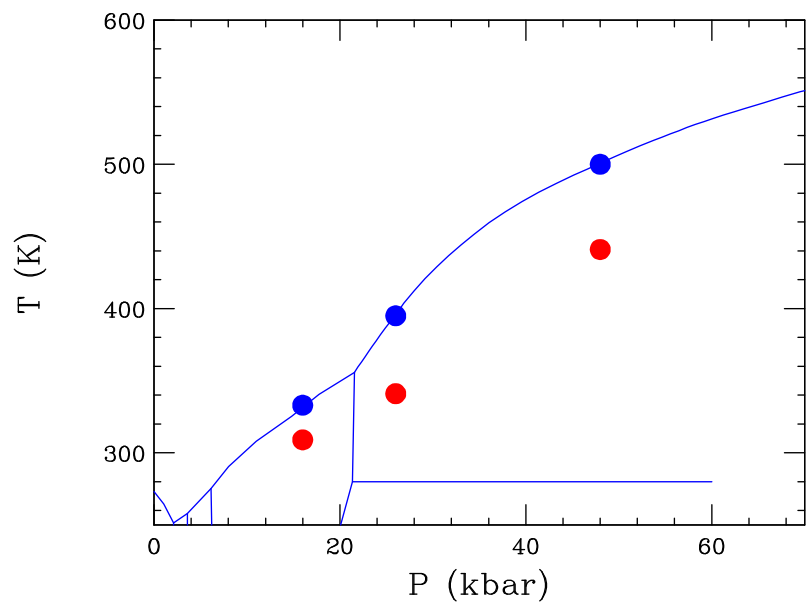
High quality x−ray absorption spectra can be collected also under extreme conditions of high pressure and temperature $\Delta\alpha / \alpha \sim 10^{-4}$

X−ray absorption temperature scans to investigate water−salt phase diagrams



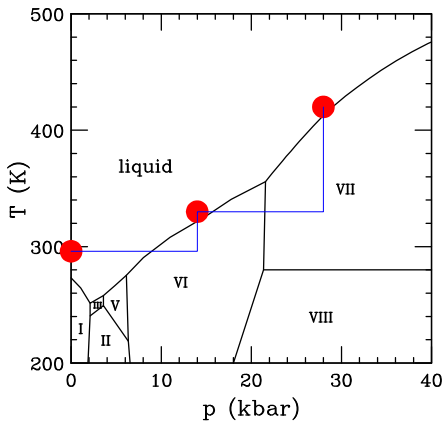




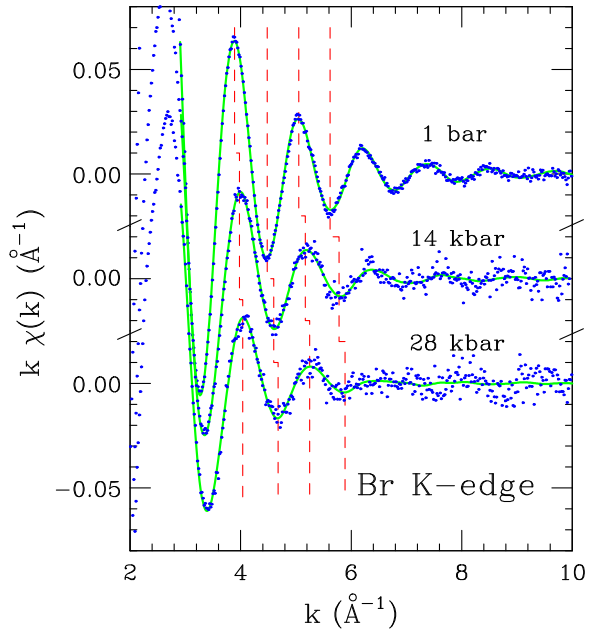


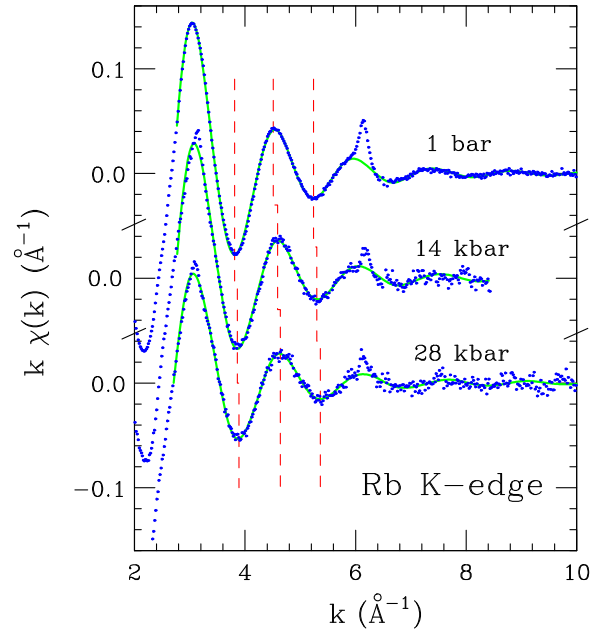
The hydration structure around Rb^+ and Br^- up to 2.8 GPa

P−T sample history

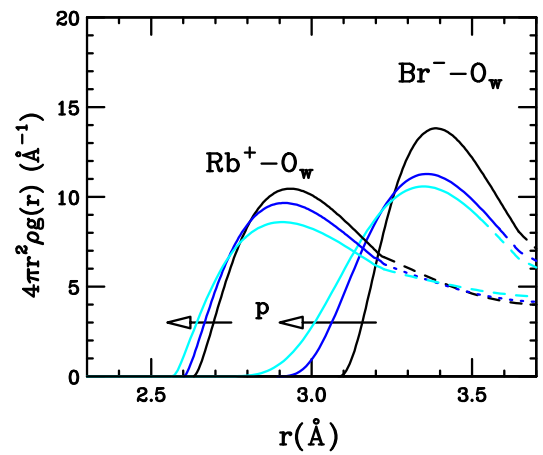


EXAFS of a RbBr aqueous solution





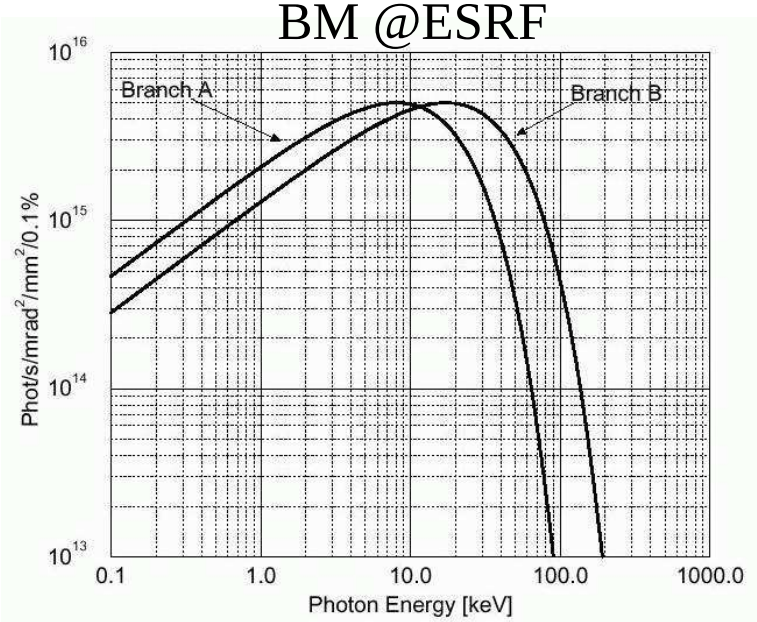
Pressure effect on the Ion−O distribution



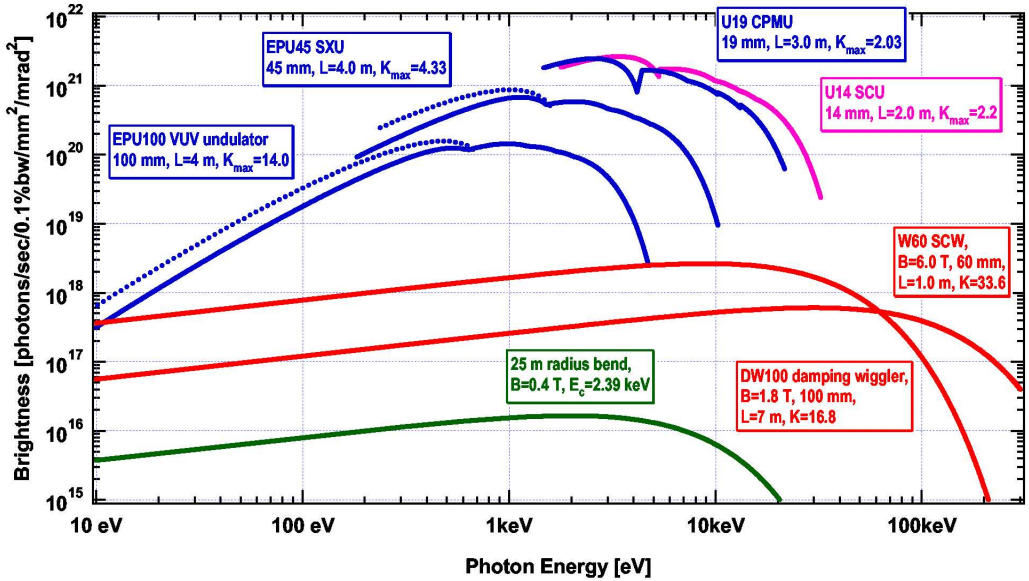
A. Filipponi, S. De Panfilis, C. Oliva, M. A. Ricci, P. D'Angelo, and D. T. Bowron, "Ion hydration under Pressure", Phys. Rev. Lett. 91, 165505 (2003).

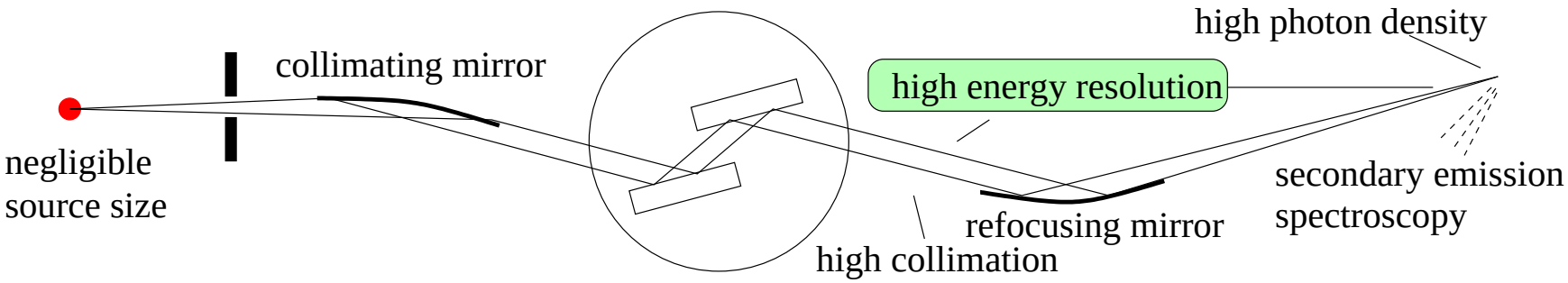
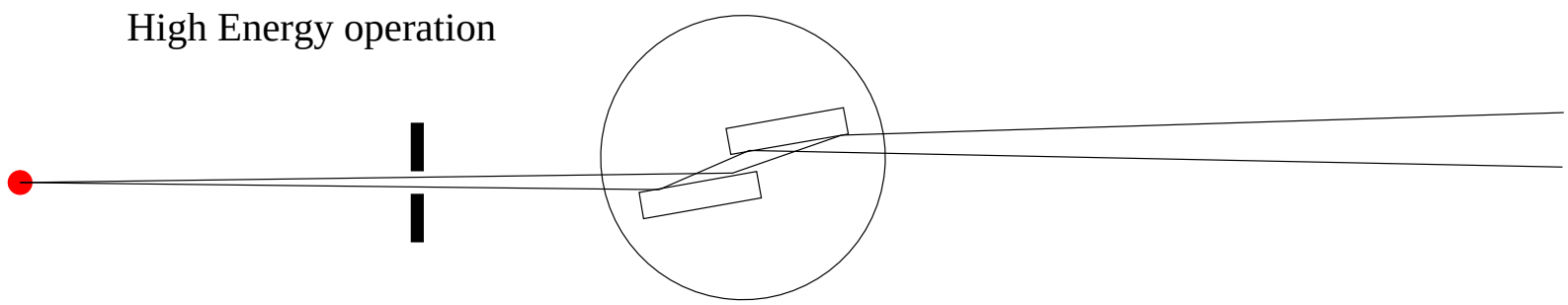
Why do we need a low emittance electron beam and a high brightness source?

BM @ESRF



NSLS−II





High Energy operation