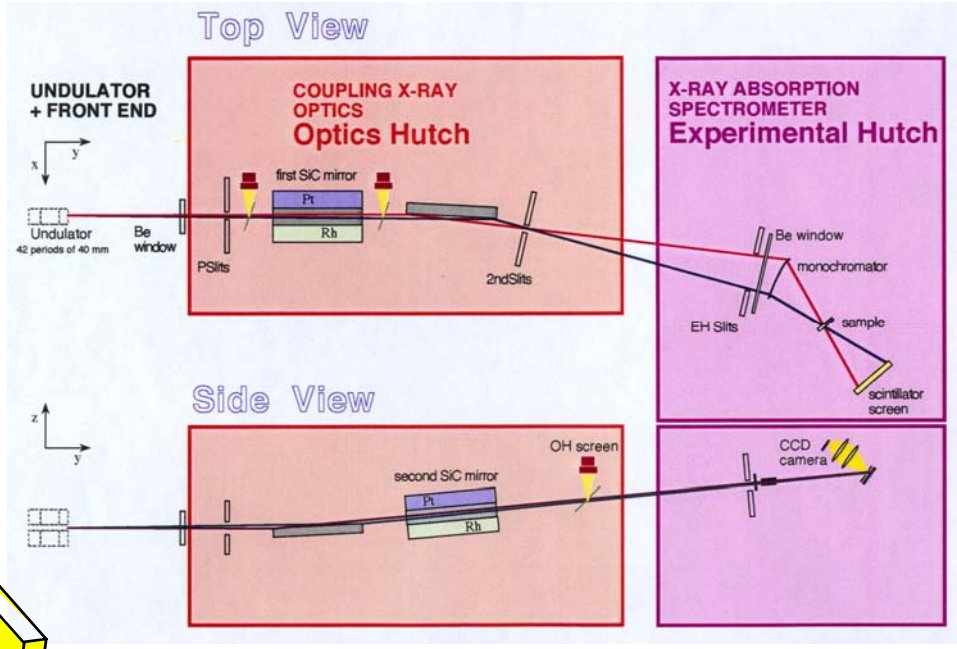
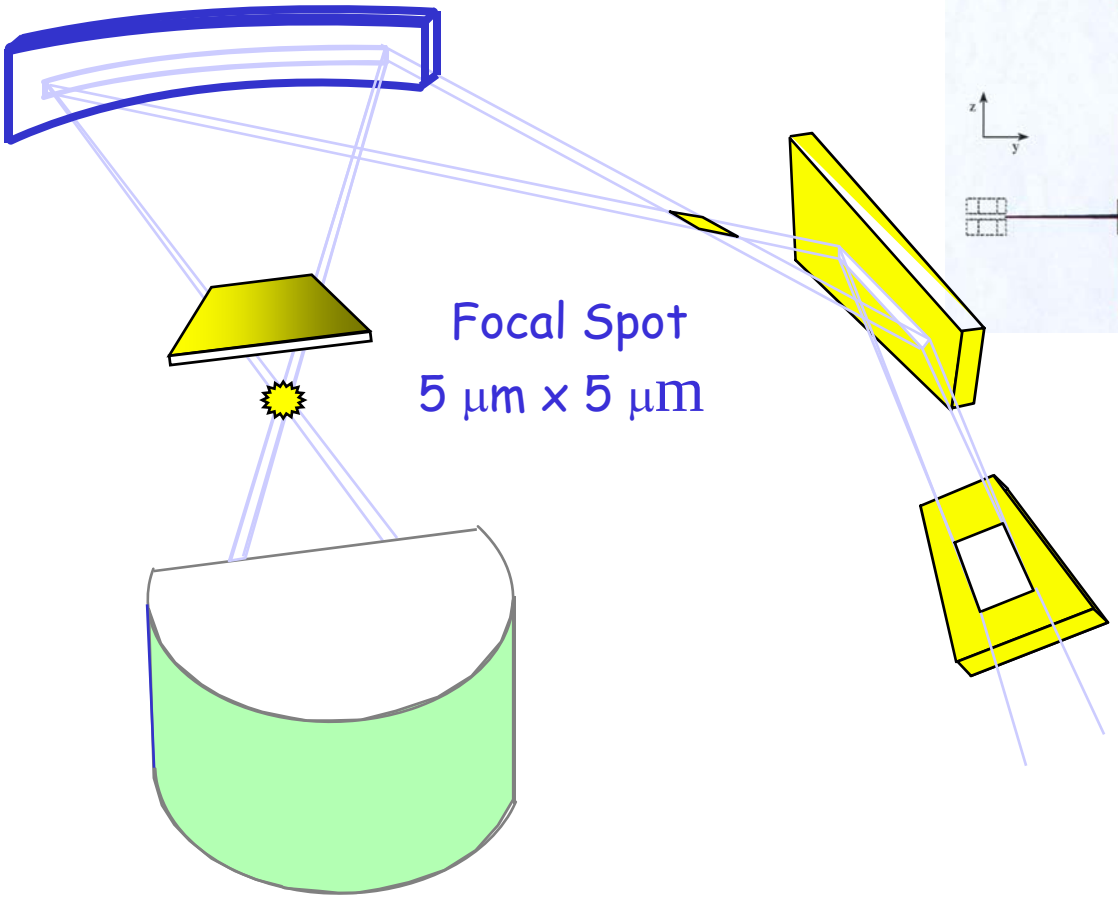
High Pressure Studies using EDXAS

Alfonso San Miguel

University of Lyon and CNRS

High pressure XAS @ ID24





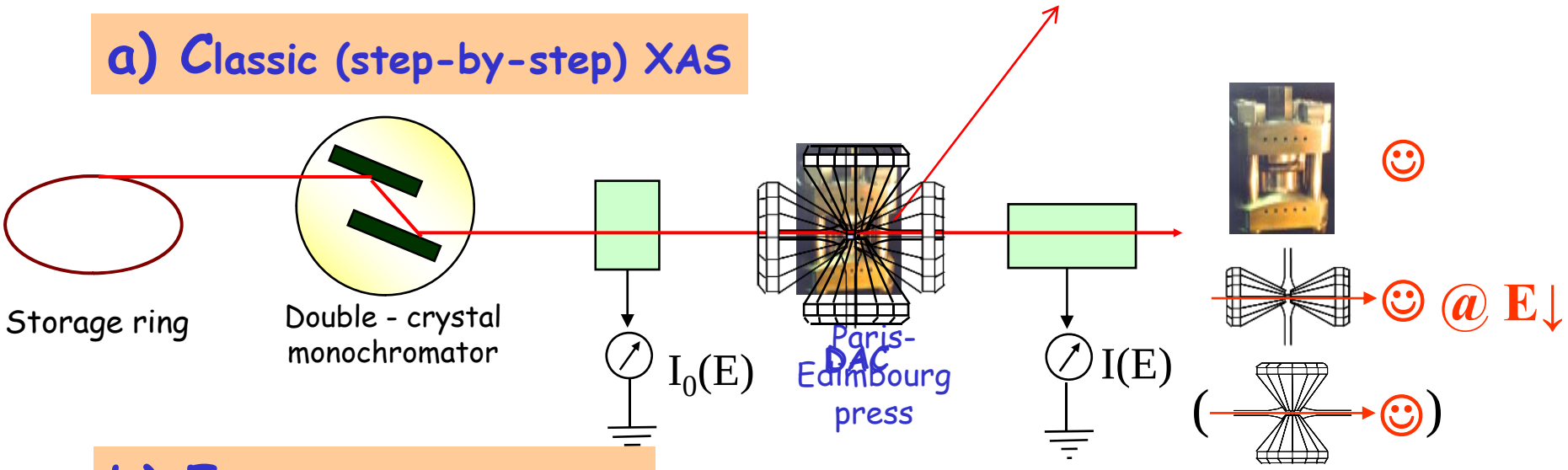
The 3 KEY elements For HP XAS:

- Focus
- Time resolution
- Mechanical stability

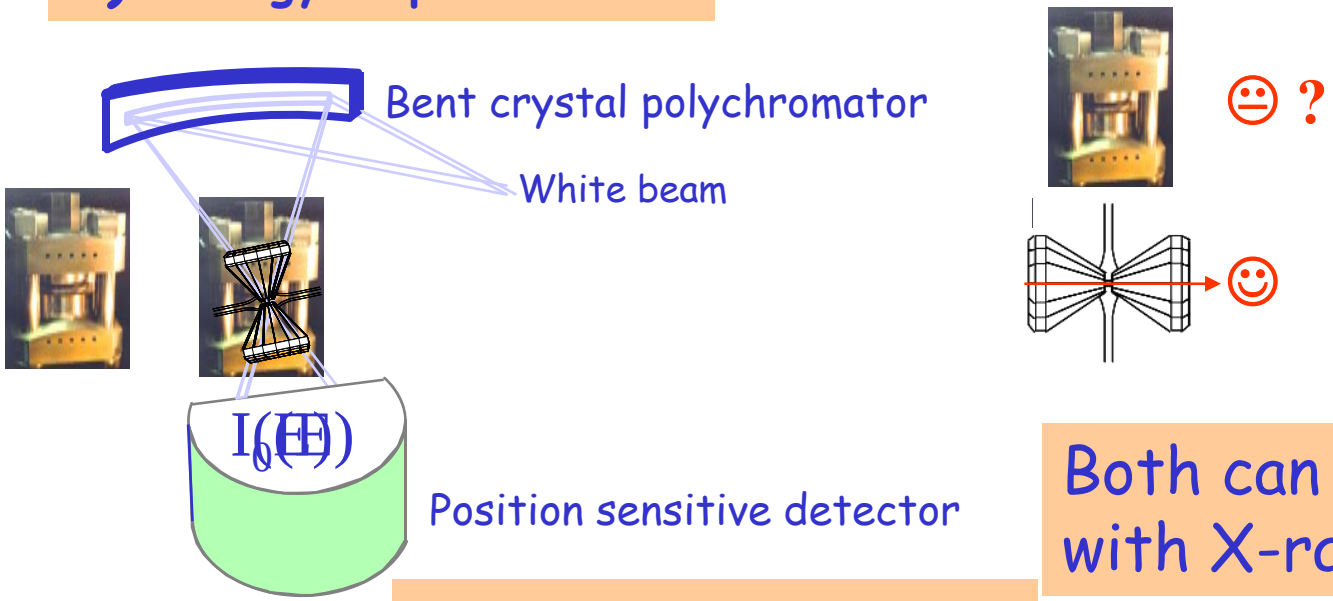
"The beamline ID24 at ESRF for energy dispersive x-ray absorption spectroscopy"
M. Hagelstein, A. San Miguel, T. Ressler, A. Fontaine and J. Goulon
J. de Physique IV, 7, C2, *C2-303* (1997).

XAFS at high pressure

a) Classic (step-by-step) XAS



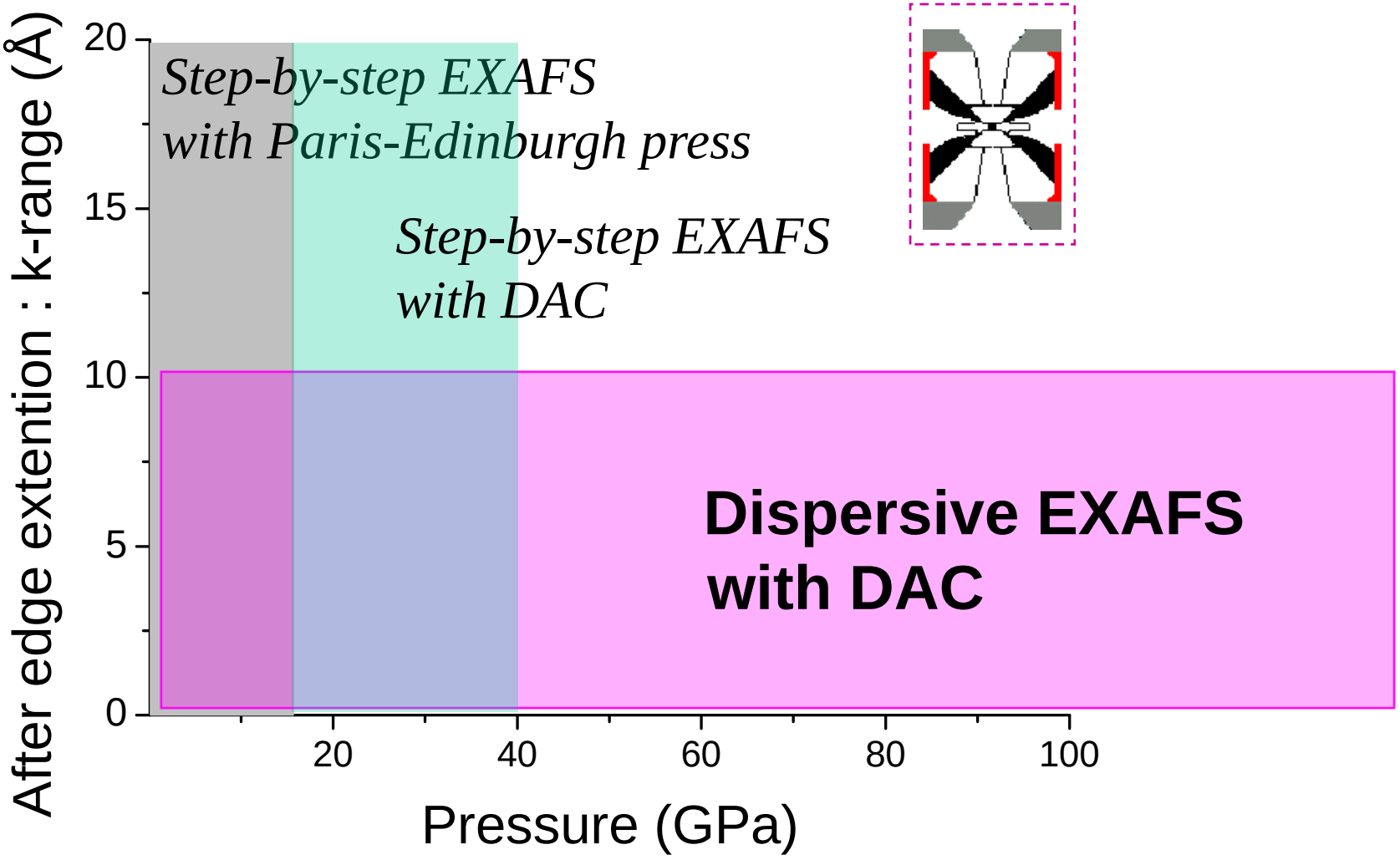
b) Energy dispersive XAS



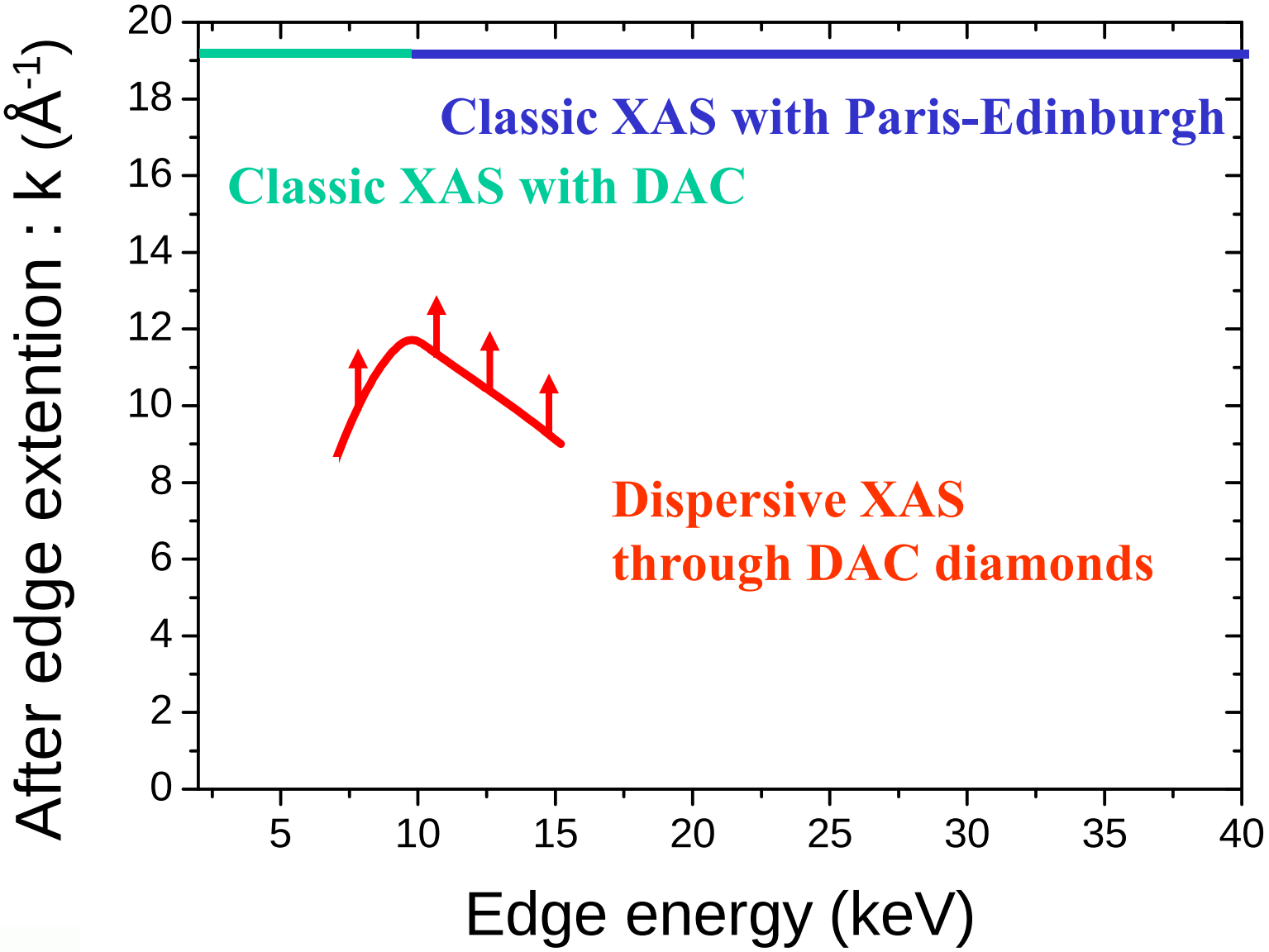
Both can be combined with X-ray diffraction !

c) X-ray Raman spectroscopy

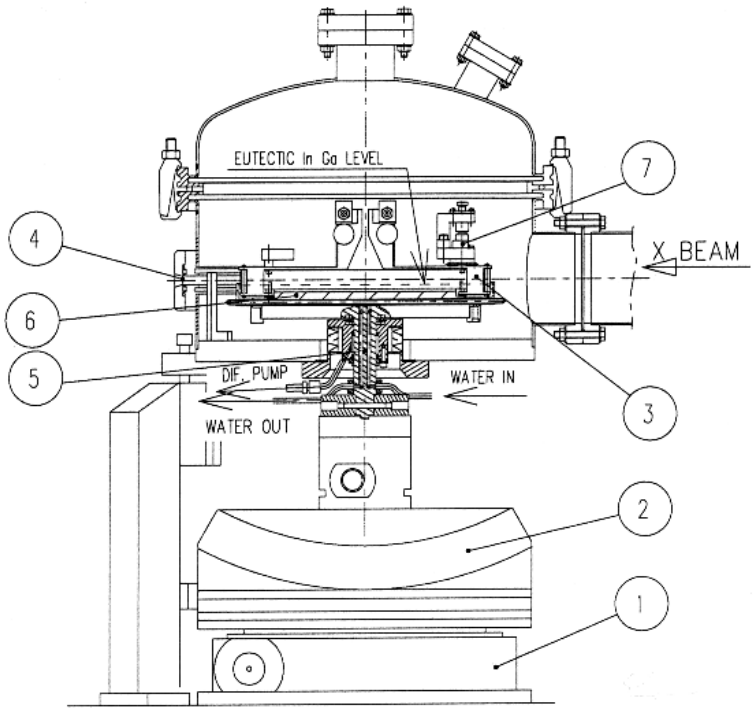
High pressure XAS

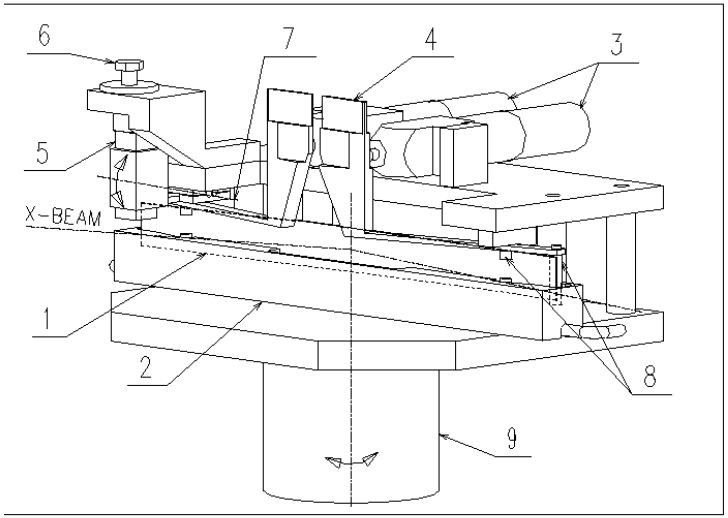


High pressure XAS : present limitations



ID24: an Energy Dispersive Optics on an Ondulator



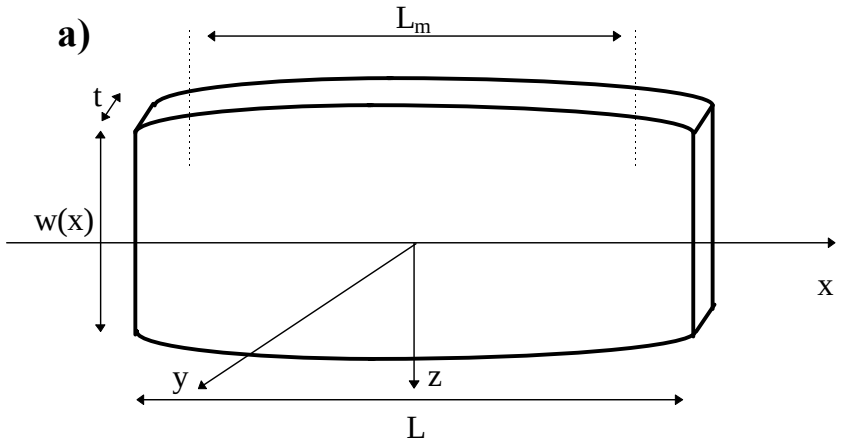


Polychromator vessel

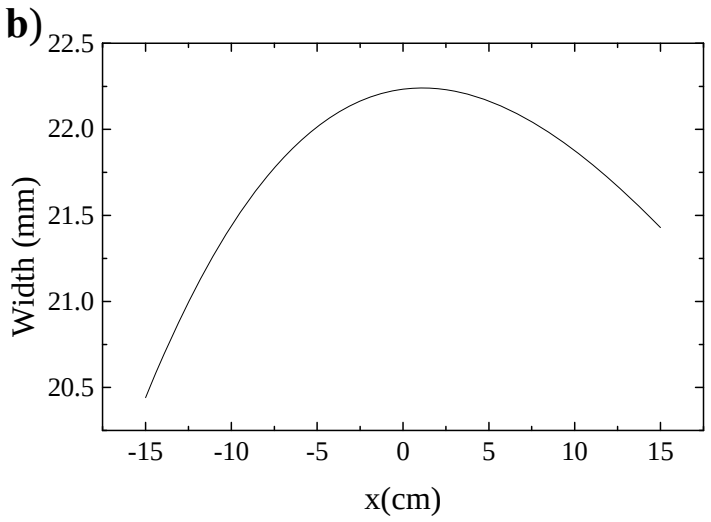
Bragg Bender

A. SAN MIGUEL, M. HAGELSTEIN, J. BORREL, G. MAROT AND M. RENIER
Journal of Synchrotron Radiation **5,** 1396-1397 (1998)

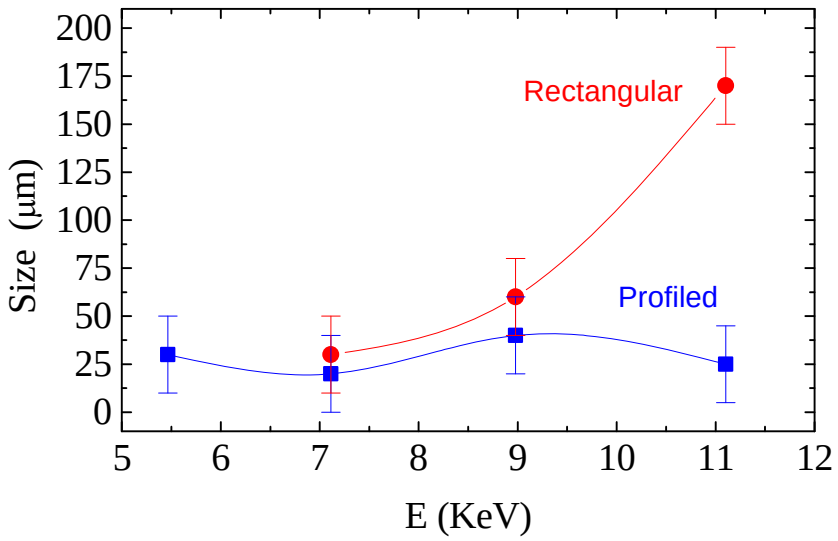
Crystal profiling

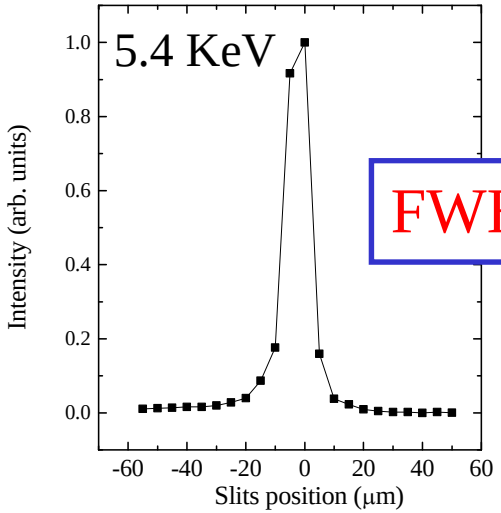


L=30 cm, t=1mm



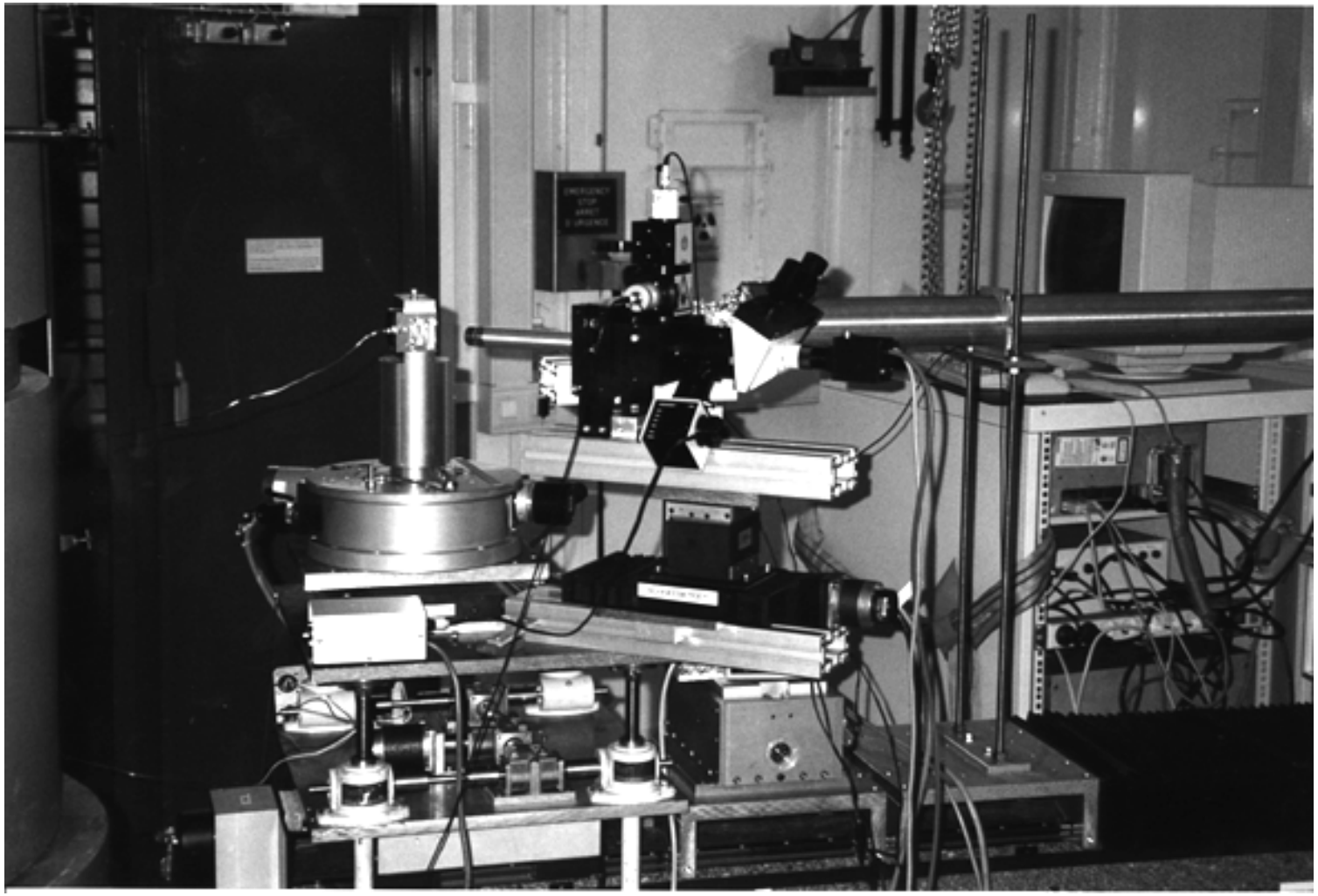
Focusing performances





FWHM = 15 μm

J. PELLICER PORRES, A. SAN MIGUEL and A. FONTAINE
Journal of Synchrotron Radiation ***5*** , *1250-1257 (1998)*



~ 1995 ~ First complete High Pressure set-up @ ID24

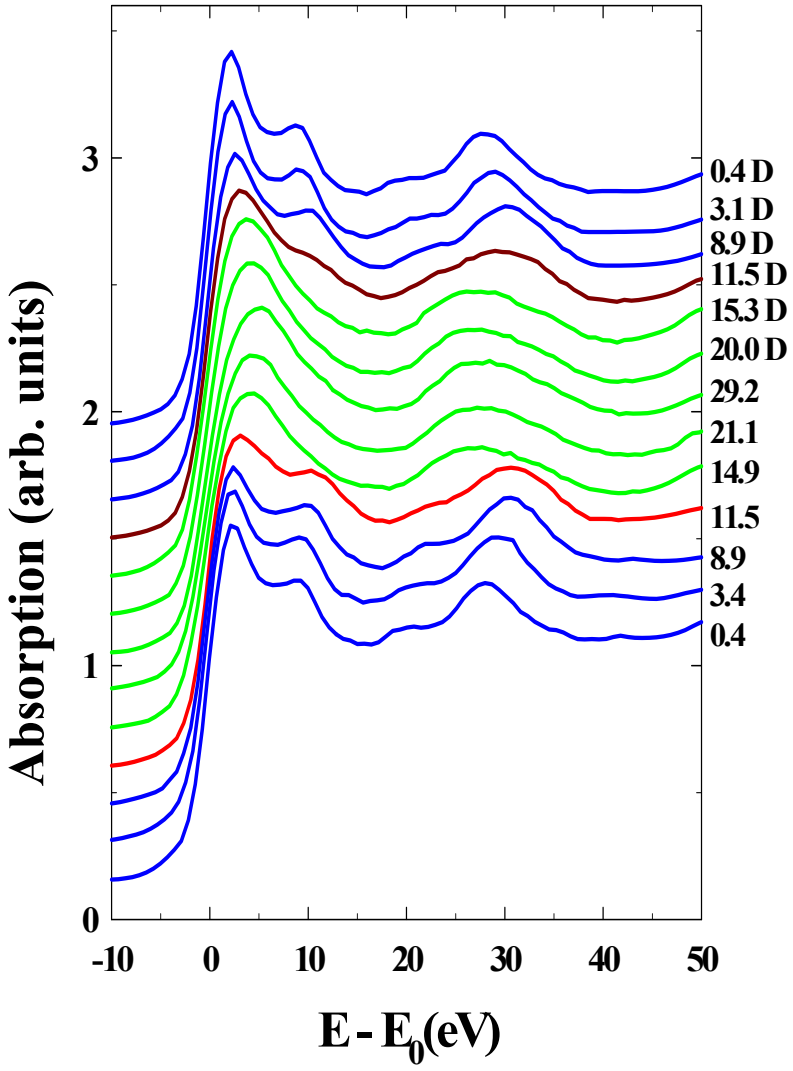
1995 : The fighters at that hard time !

Some succesful histories using HP@EDXAS

- ZnTe-II: the first high pressure crystal structure determination combining EXAFS and diffraction (LURE)
- A new phase transition in bromine (ID24)
- The compressibility of III-VI layered semiconductors (ID24)
- Exotic phase transitions in groupe-14 clathrates (ID24)

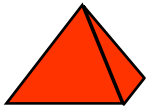
1.
ZnTe-II
the first high pressure crystal structure determination combining EXAFS and diffraction

ZnTe at the Zn K-edge under pressure

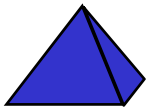


ZnTe-III : Cmcm

ZnTe-II : Cinnabar ?



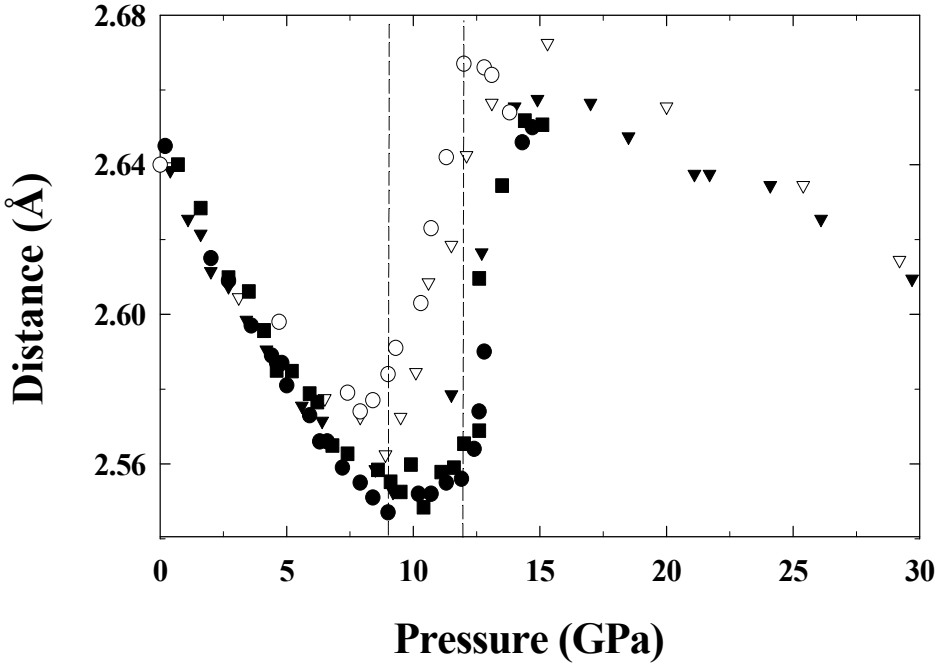
ZnTe-I: zinc blende



…at a time where X-ray Rietveld refinement in high pressure phases was not existing

Cinnabar ZnTe

DEXAFS



EDD

hkl	Computed d (Å)	Observed d (Å)	Difference
100	3.521	3.517	0.004
101	3.291	3.304	0.013
102	2.802	2.799	0.003
112	1.861	1.859	0.002
200	1.761	1.761	0.000
203	1.529	1.529	0.000
212	1.279	1.278	0.001

ZnTe at 11.7 GPa

ZnTe-II (11.7 GPa)

4-fold coordinated cinnabar (hexagonal) structure

u = v = 0.474

c/a = 2.272

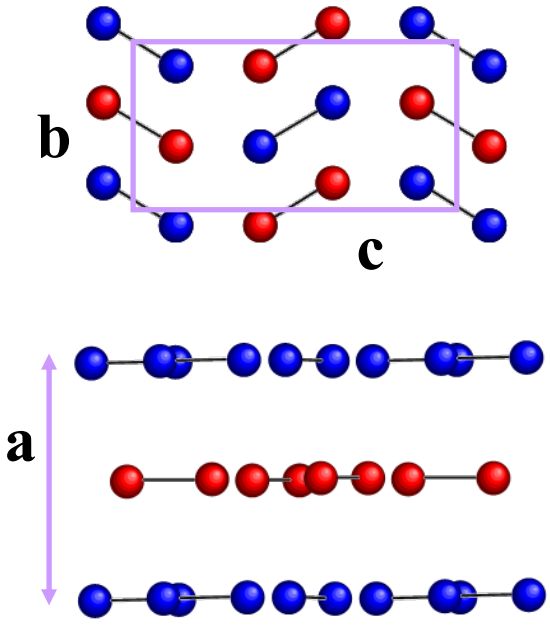
A. San Miguel, A. Polian, M. Gauthier and J.P. Itié, Phys. Rev. B, 48, 8683 (1993).

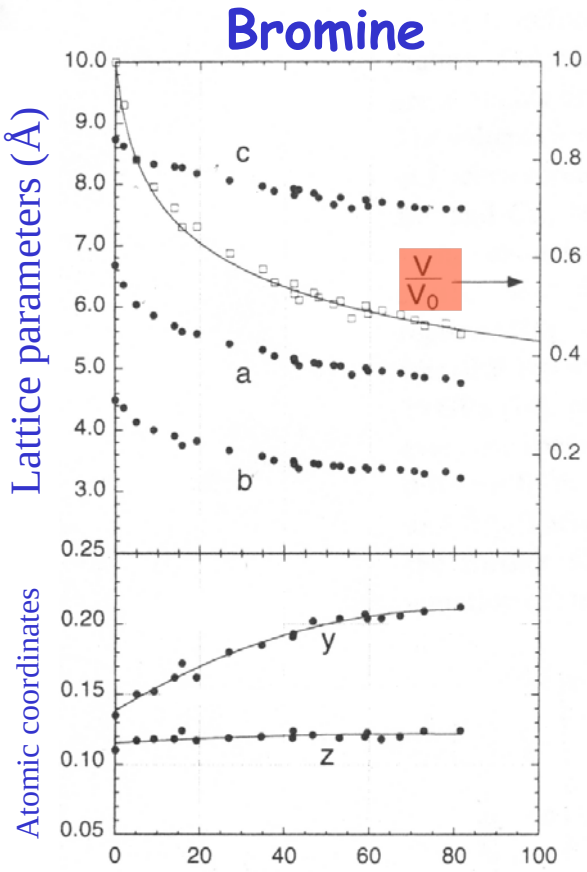
2

A new phase transition in bromine

Halogens: high pressure dissociation of molecular crystals

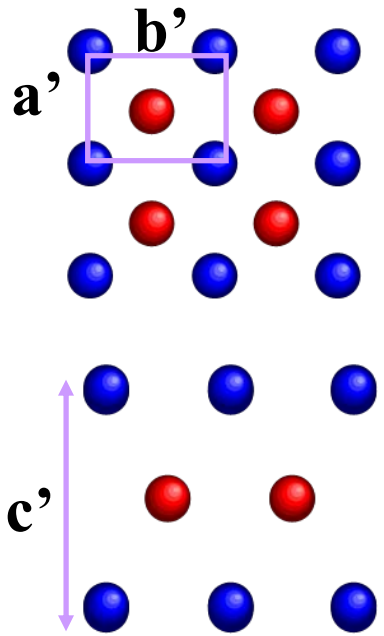
Molecular phase (orthorhombic)

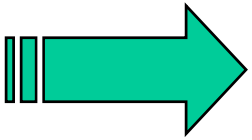




H. Fujihisa et al.
X-ray diffraction

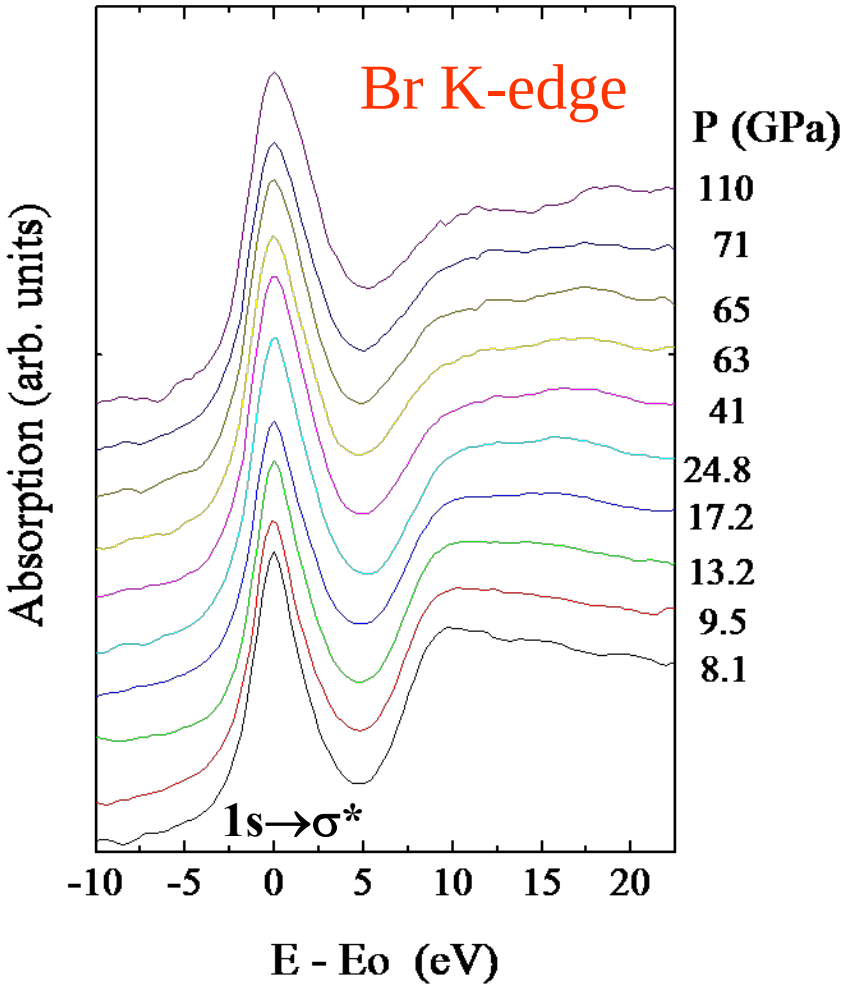
Dissociated phase

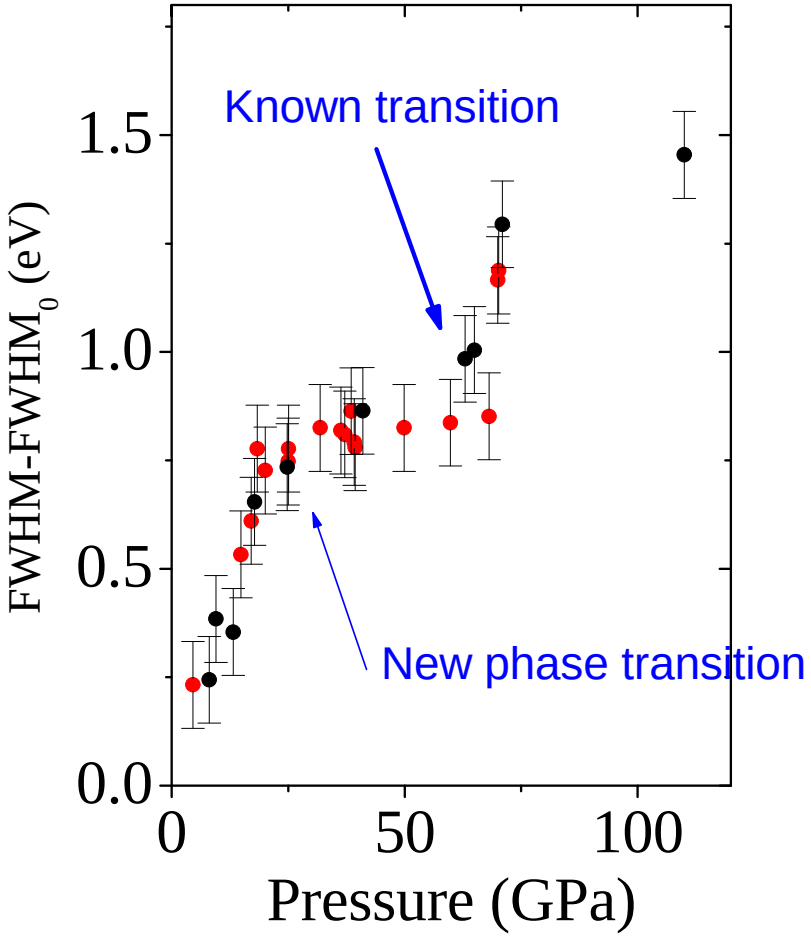




$d_{Br\text{-}Br}$ = Constant

XAS of Bromine at Megabar pressures

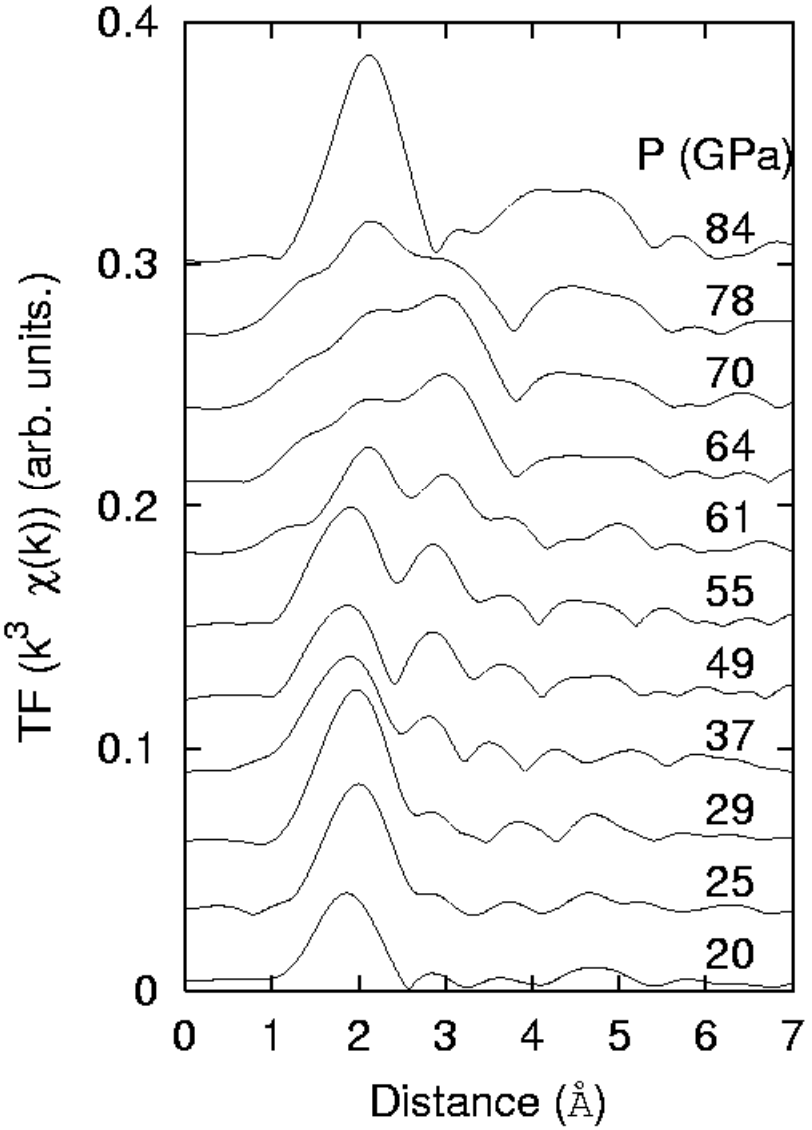


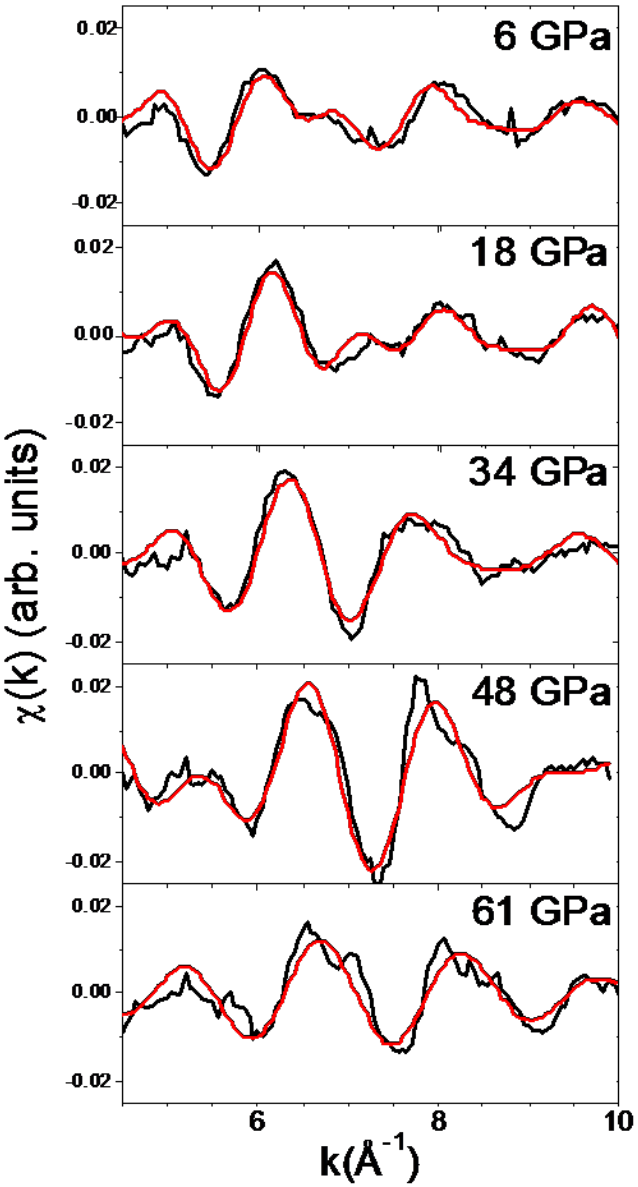


A. San-Miguel , H. Libotte, J.P. Gaspard M. Gauthier, J.P. Itie And A. Polian , Eur. Phys. J. B 17, 227-233 (2000)

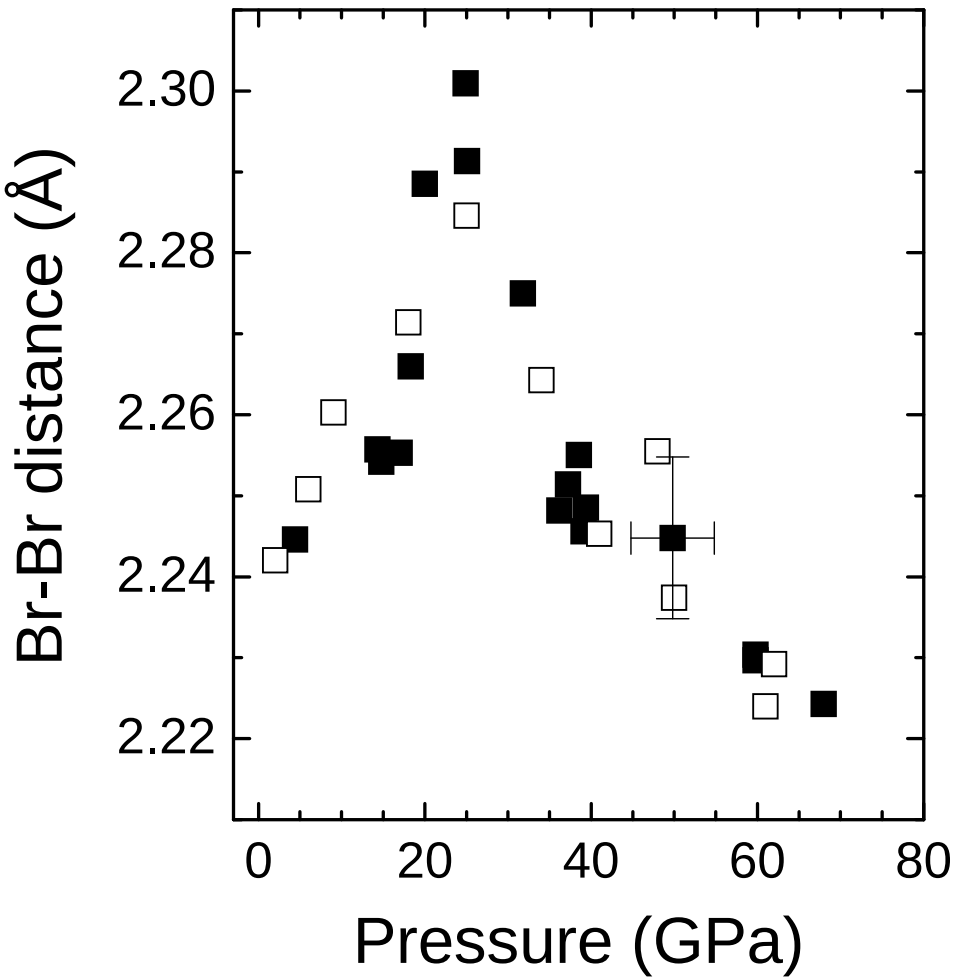
EXAFS

Bromine @ Br K-edge EXAFS





Bromine intra-molecular distance: it changes !



- *Phase transition with a loss of molecular caracter.*

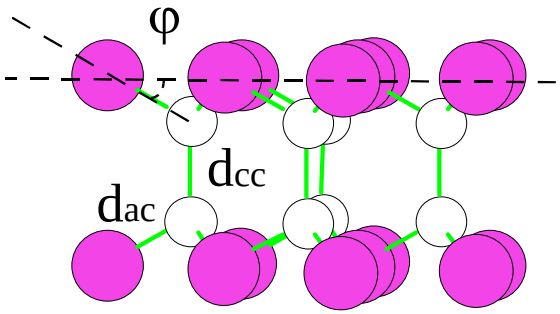
A. San Miguel, H. Libotte, J.P. Gaspard, M. Gauthier, G. Aquilanti, S. Pascarelli
Phys. Rev. Lett. **99**, 015501 (2007)

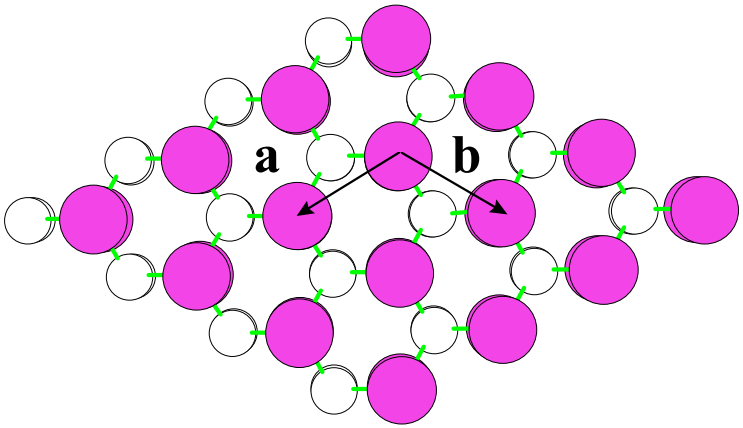
3

The compressibility of

III-VI layered semiconductors

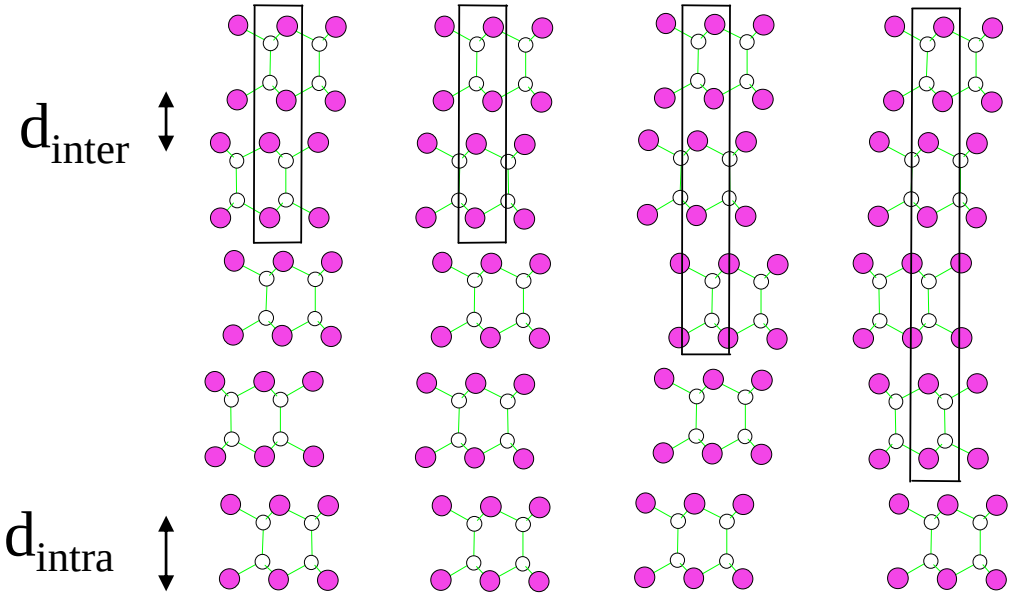
Structure of III-VI semiconductors (GaS, GaSe, InSe, GaTe)





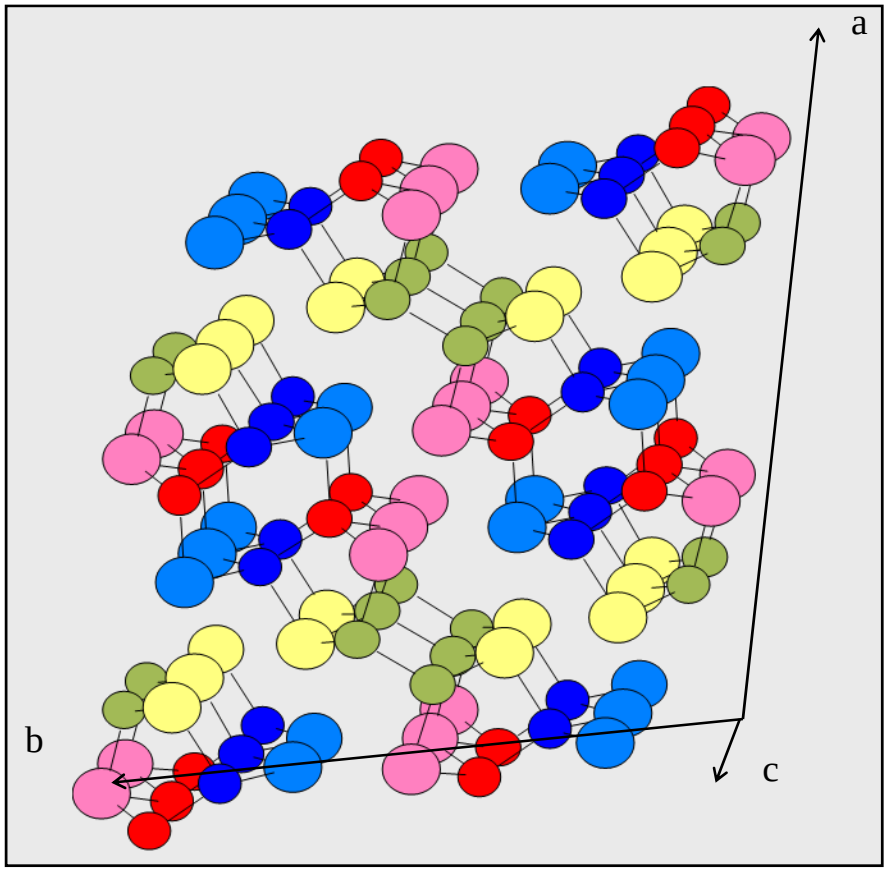
Layer structure

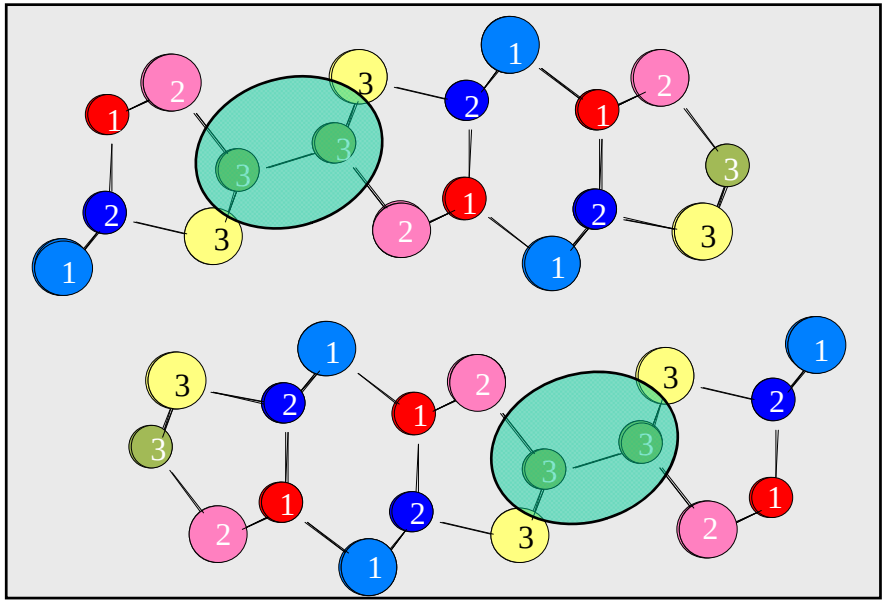
Packing configurations



(hexagonal description)

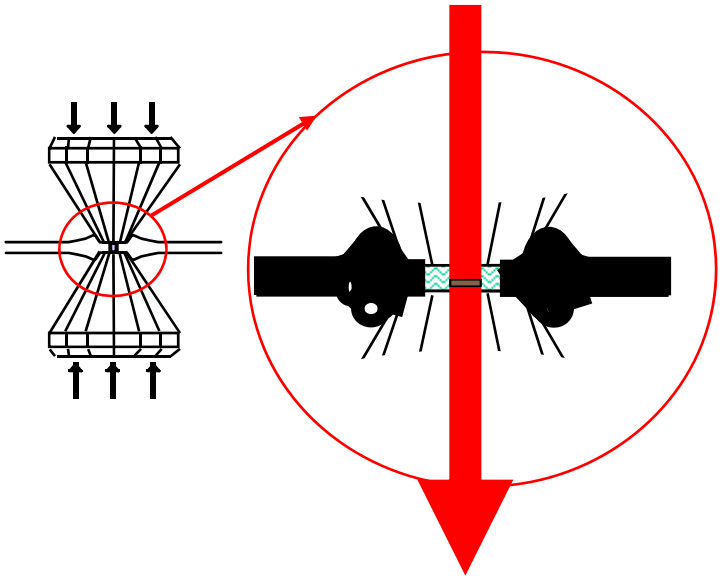
2D Semi-conductors : GaTe

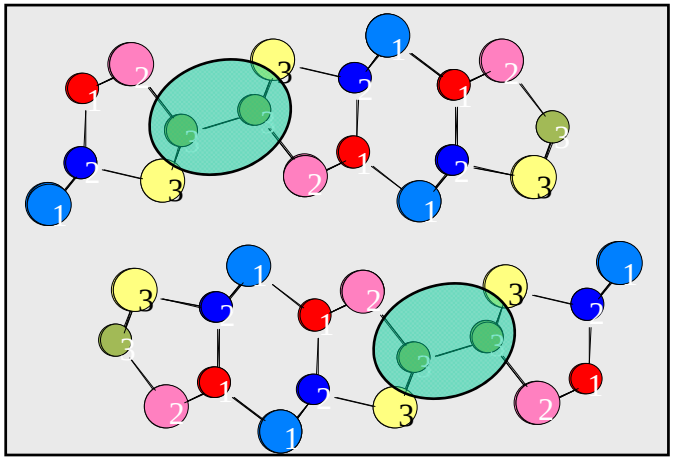




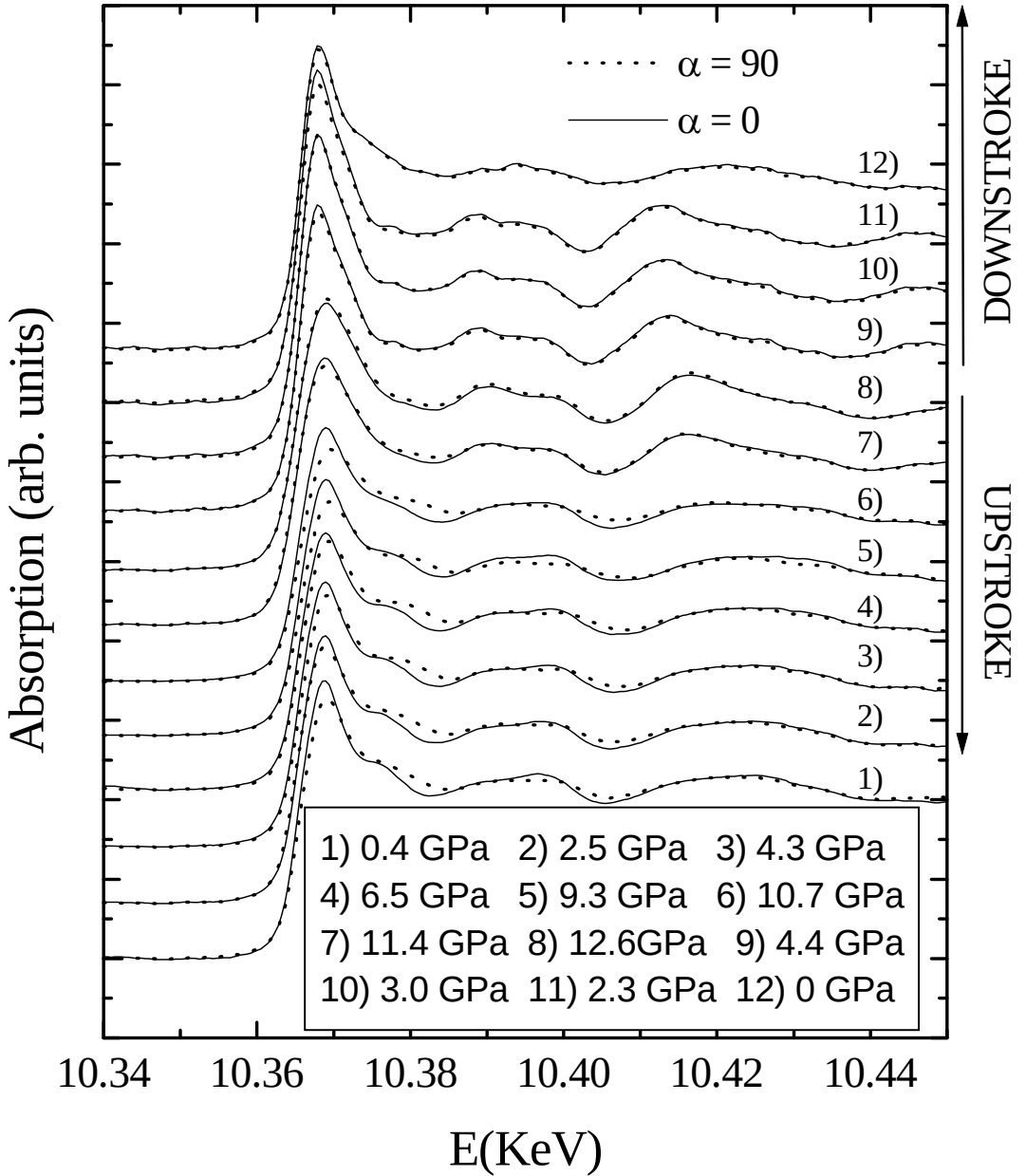
Particularity: Oriented Ga-Ga bond in the layers

XANES at the Ga k-edge of GaTe single crystal as a function of pressure (E // c and E ⊥ c)

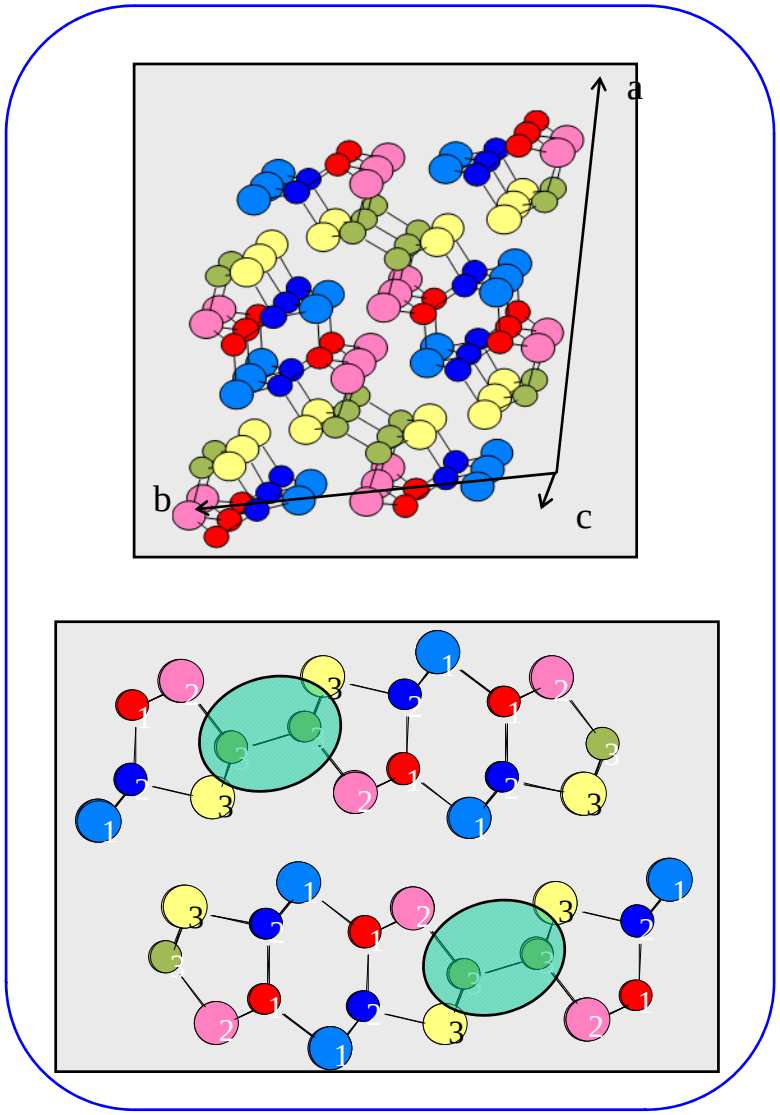


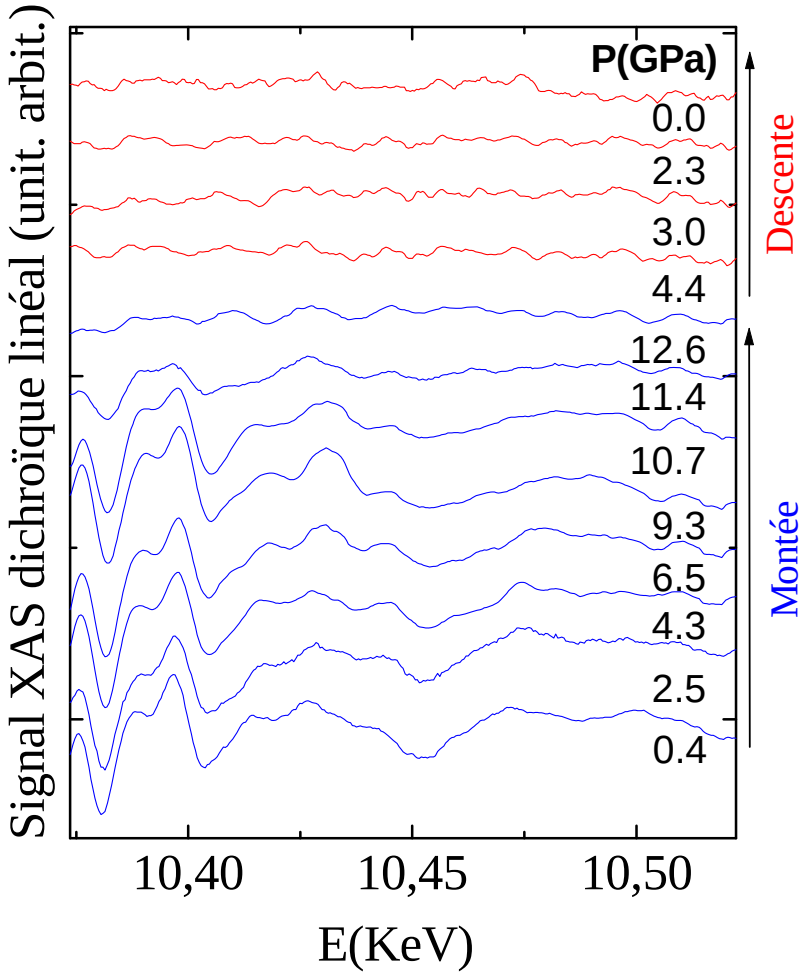


⊗ c-axis

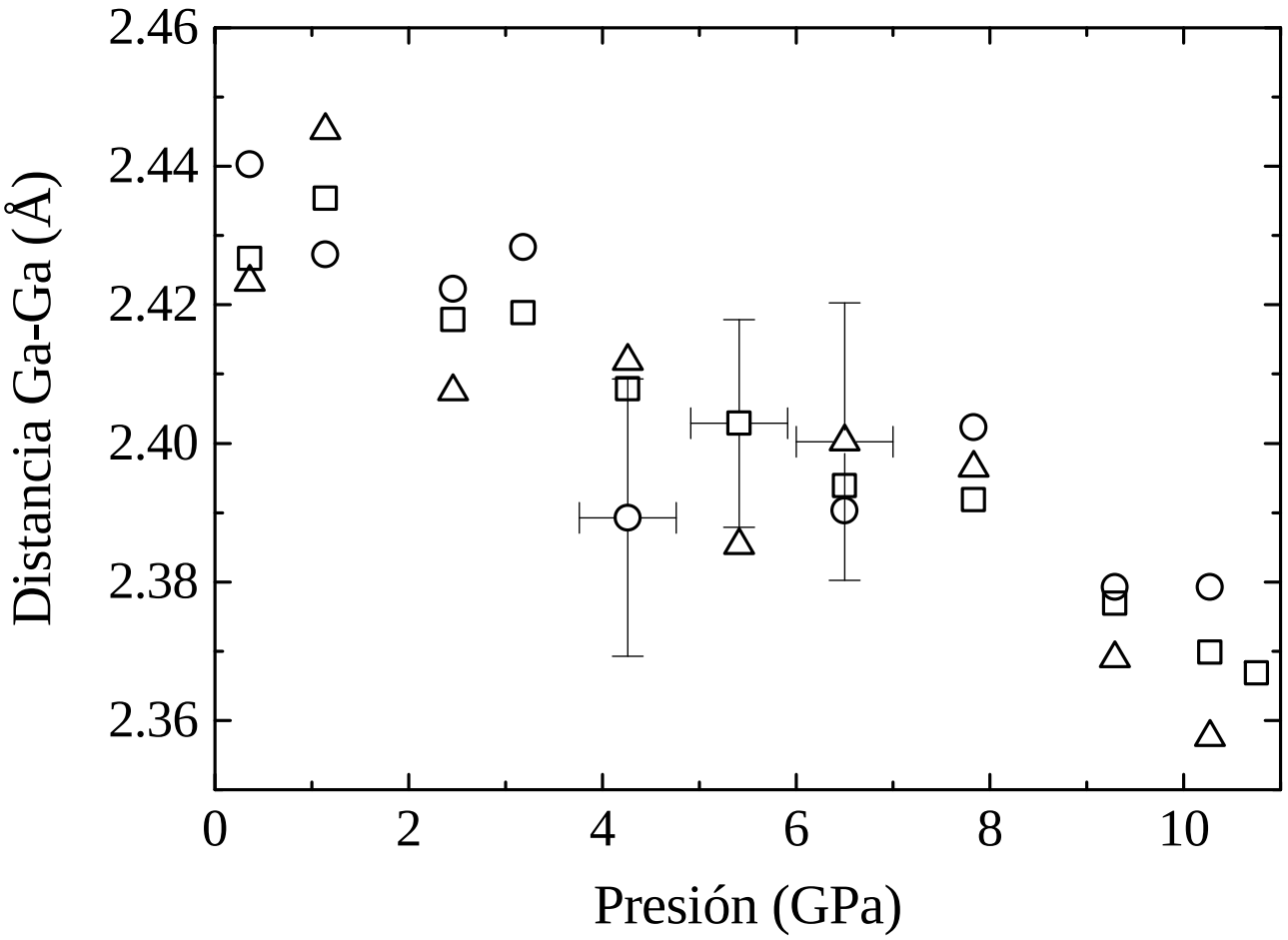


Dichroic signal at the Ga k-edge of GaTe single crystal as a function of pressure (E // c and E ⊥ c)

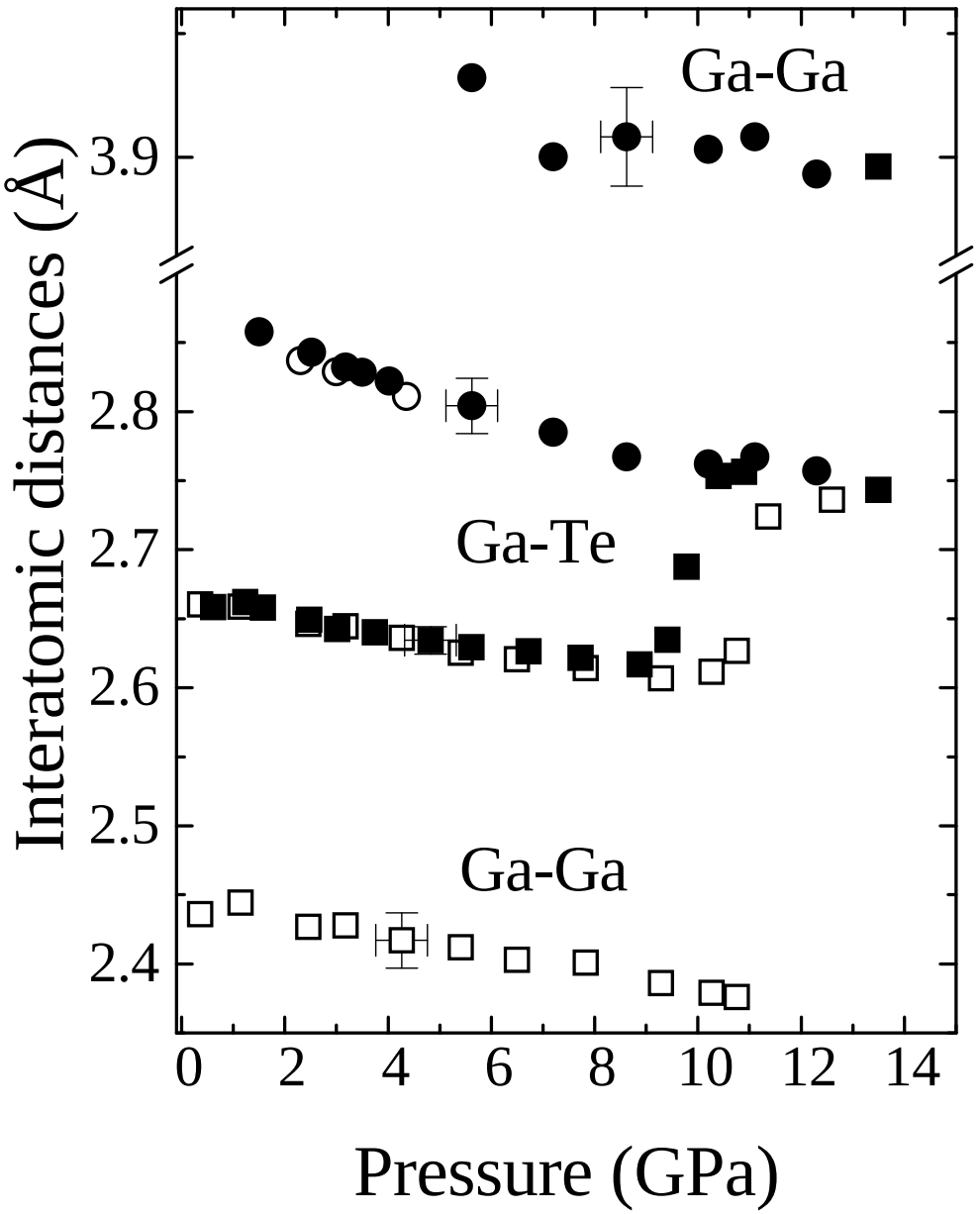




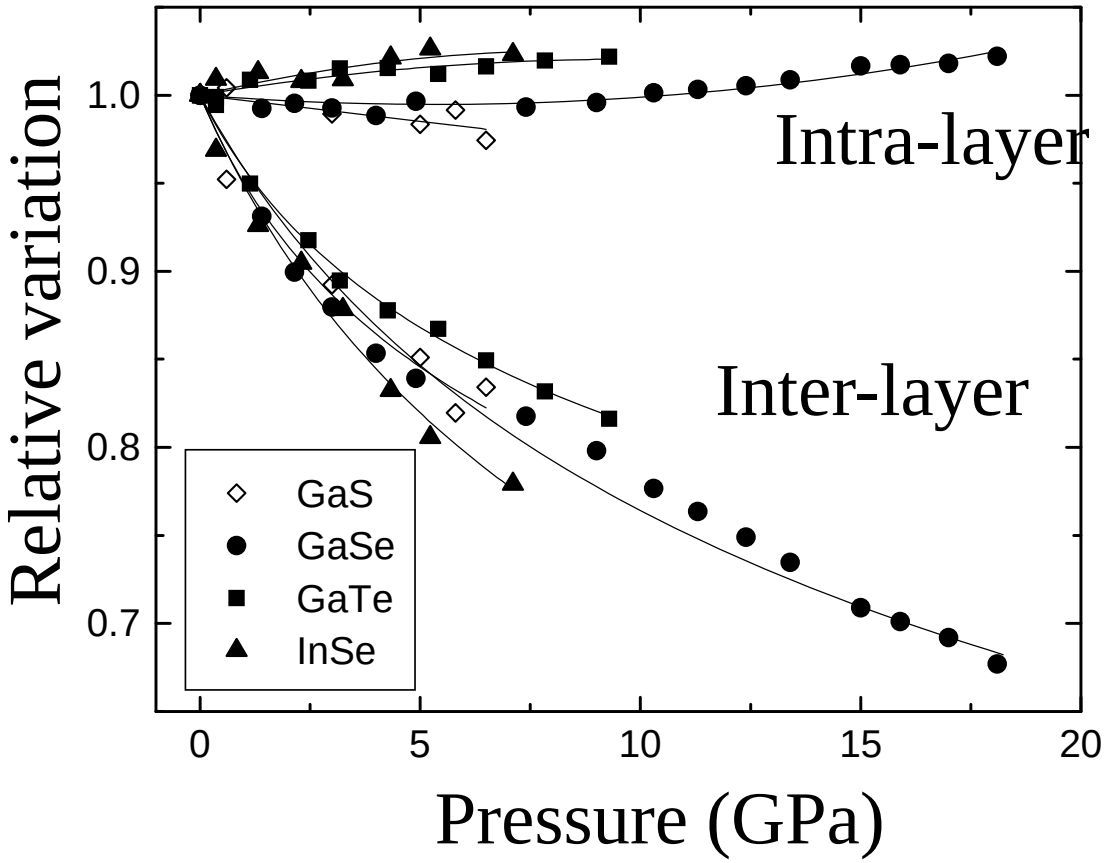
Consistency between 3 different EXAFS analysis for the Ga-Ga distance.



Result of the EXAFS analysis combining data from both polarisation



Anisotropy of the compressibitlity in III-VI semiconductors



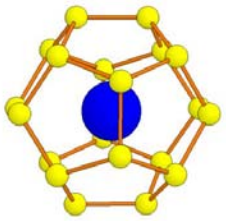
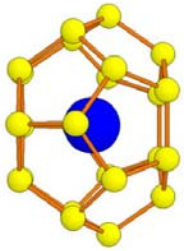
4

Exotic phase transitions in nanomaterials :

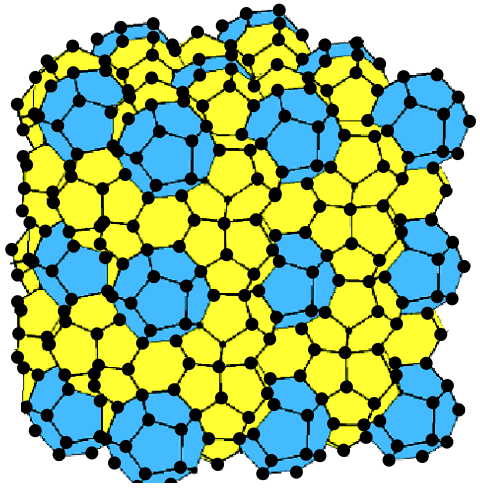
group-14 clathrates

Type-I Clathrates of C(?), Si, Ge, Sn

TYPE I
P m3n
a ~ 10.3 Å

2  **+ 6**  **=**

$M@Y_{20}$ $M@Y_{24}$



M_8Y_{46}

Group-14 clathrates

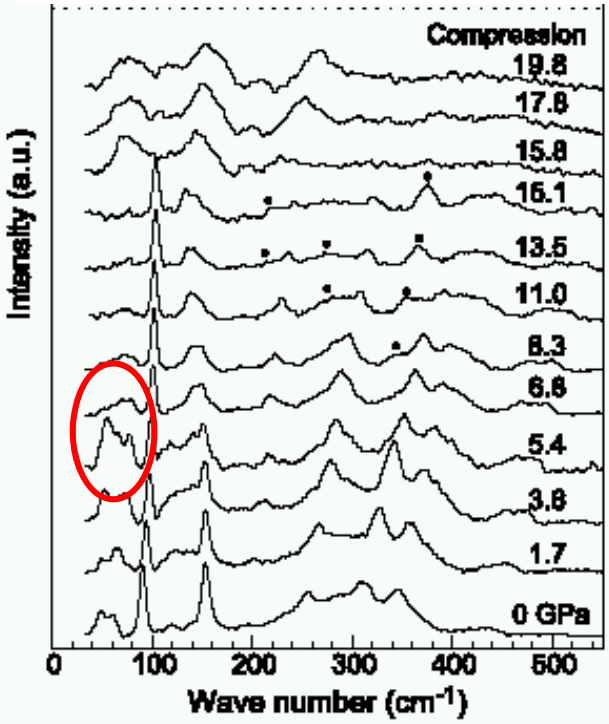
Y= C(?), Si, Ge, Sn
+Ag, Au, Ni, Cu, As, Al,…

M= Na, K, Rb, Ba, Sr, I,…

Two « exotic » isostructural phase transitions in group-14 clathrates

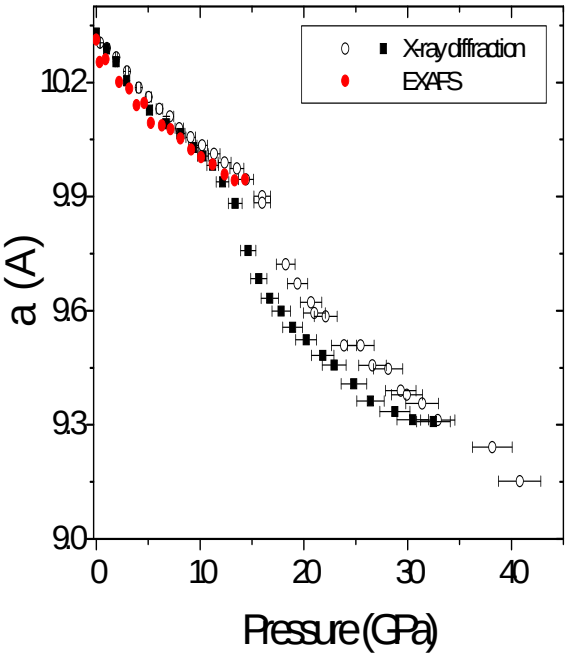
Ba_8Si_{46}

1. Loss of "guest" Raman modes



T. Kume et al. PRL **90** 155503 (2003).

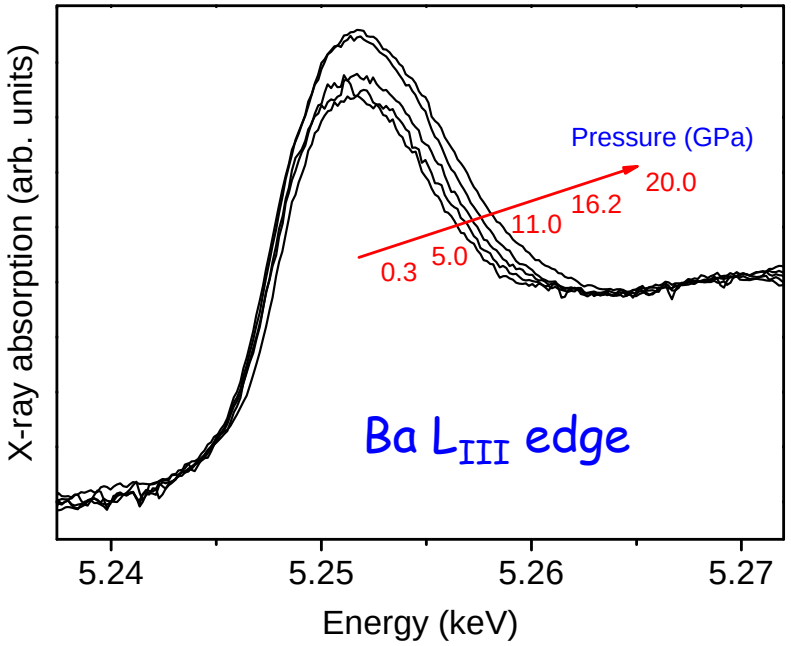
2. Homothetic volume collapse

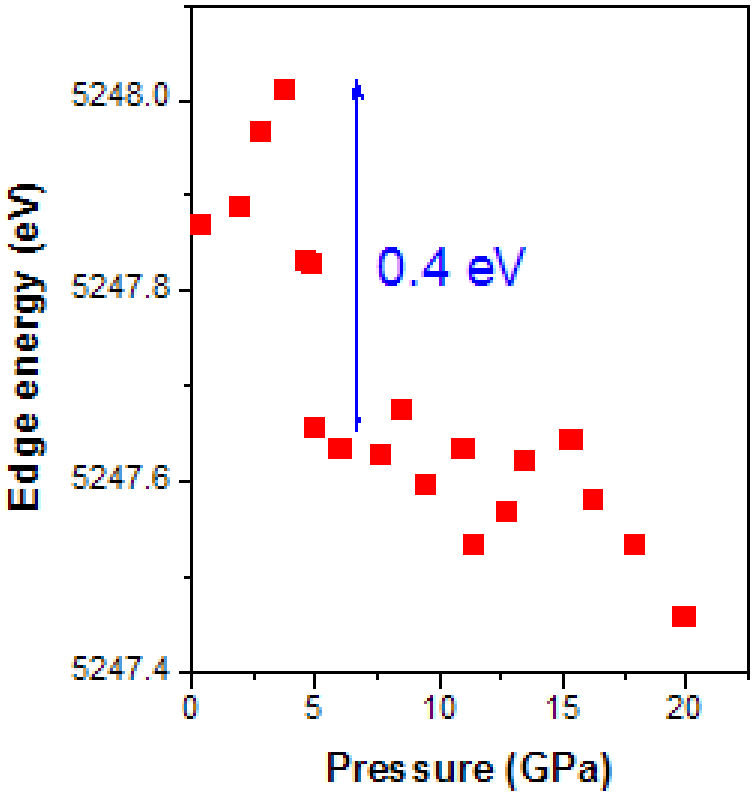


A. San Miguel et al., Phys. Rev. B. **65** (2002)

First transition in Ba_8Si_{46}

DXANES @ ID24





Experimental set-up:
4 anvils diamond cell

Change of hybridization involving Ba d-electrons

A. San Miguel, , A. Merlen, P. Toulemonde, T. Kume, S. Le Floch, A. Aouizerat, S. Pascarelli, G. Aquilanti, O. Mathon, T. Le Bihan, J.P. Itié, S. Yamanaka et al., Europhys. Lett. **69** 556 (2005)

Have a look to the framework structure: DEXAFS experiments are possible using DAC at the Ge K-edge

$Ba_8Ge_xSi_{46-x}$

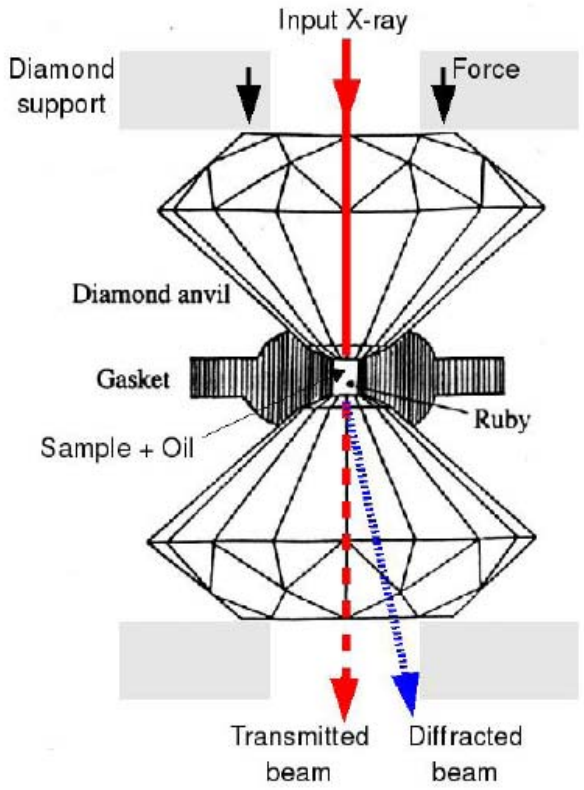


Fig. 2.1 – Schéma du type de cellule à enclumes de diamant utilisée pour les expériences à l'ESRF.

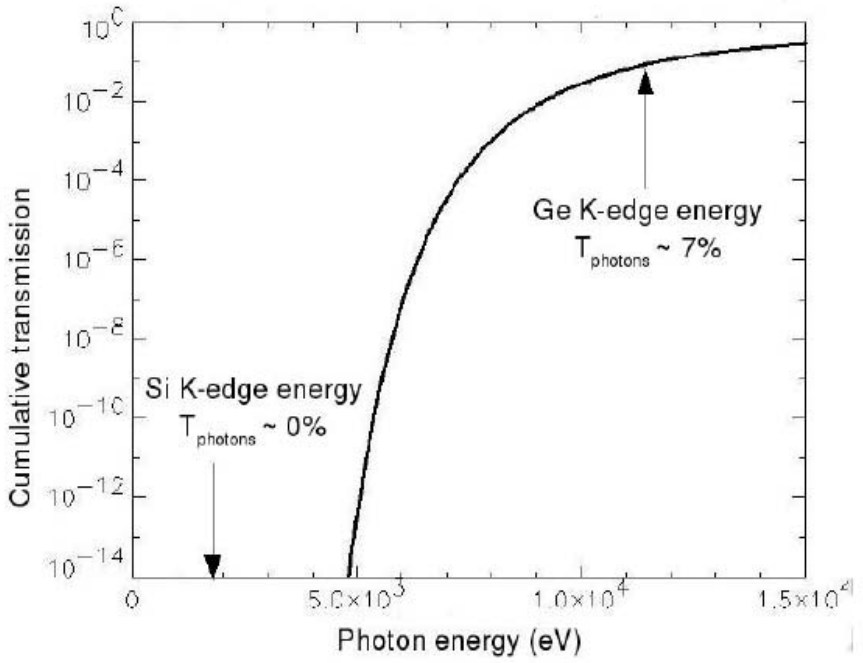
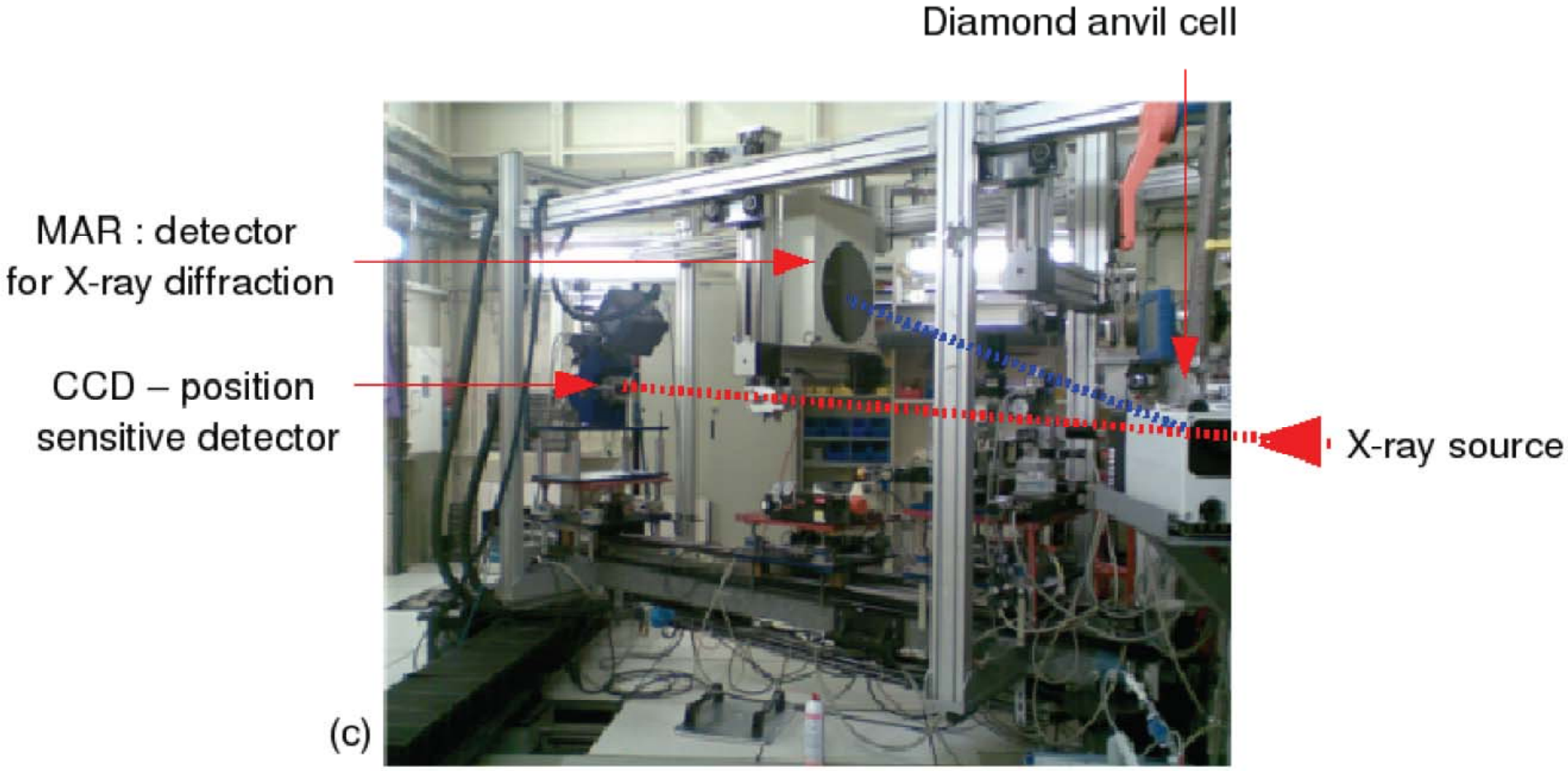
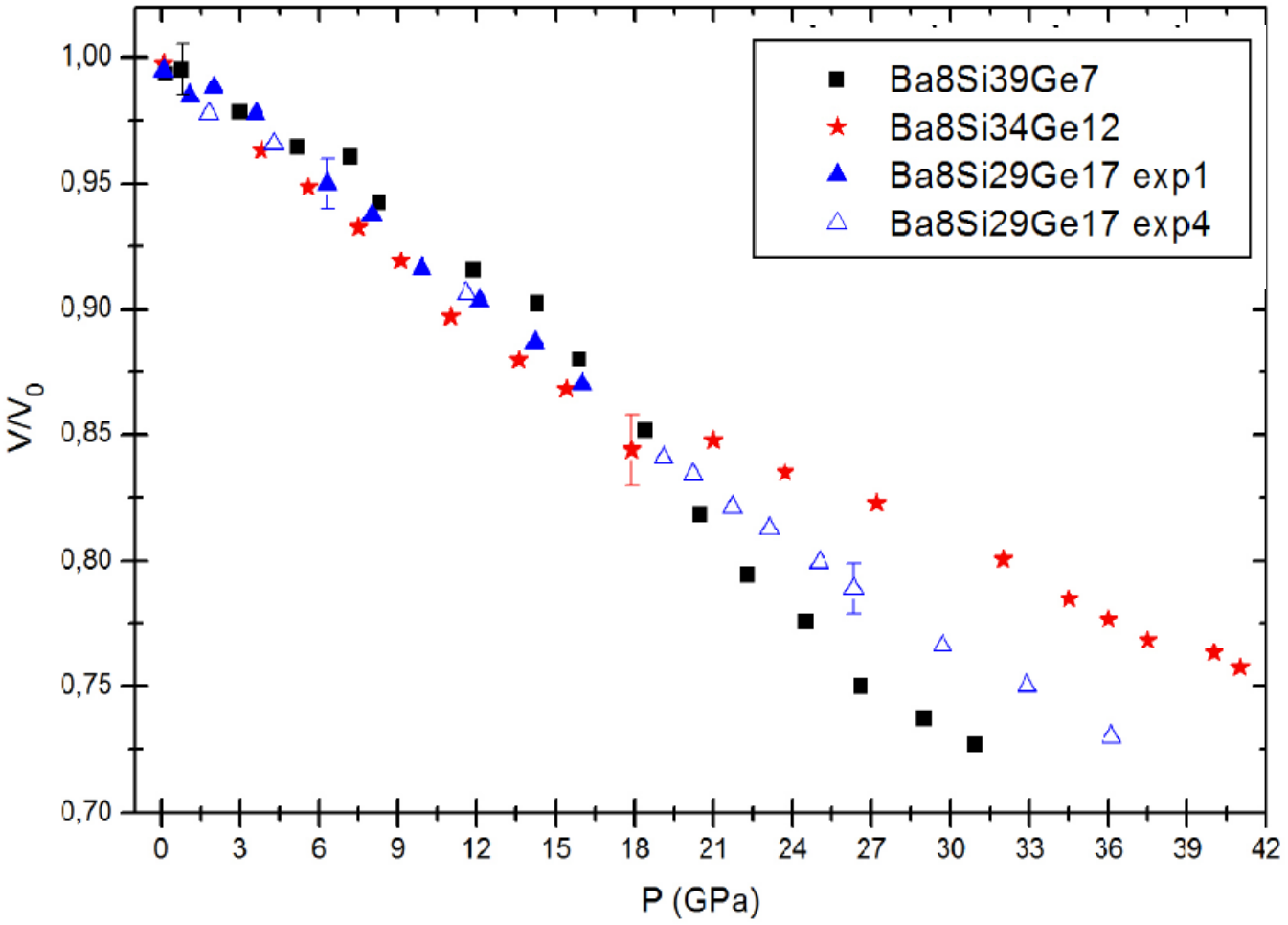


Fig. 2.2 – Taux de transmission des rayons X en fonction de leur énergie à travers 4 mm de diamant.

Combined X-ray diffraction and X-ray absorption at ID24 - ESRF



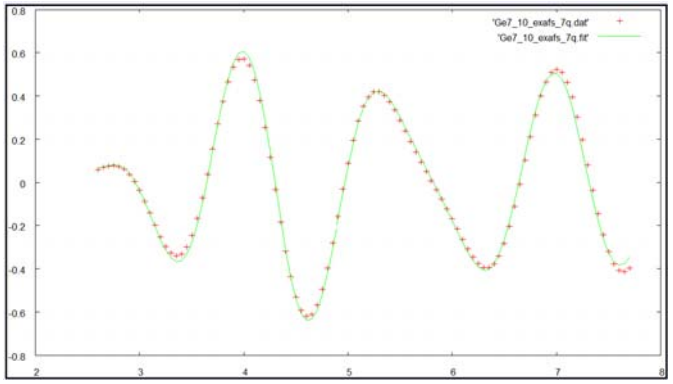
High-pressure XRD @ ID24



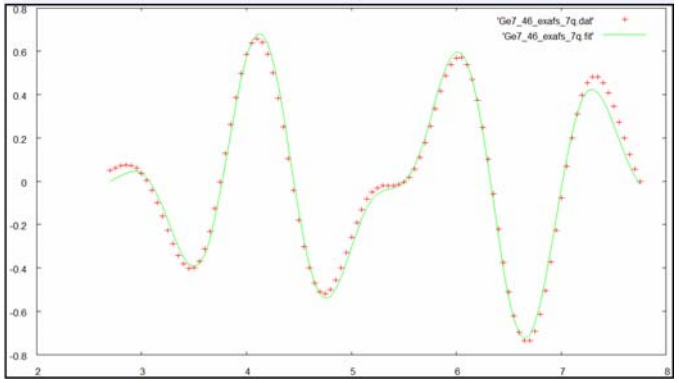
EXAFS Fit

$Ba_8Si_{39}Ge_7$

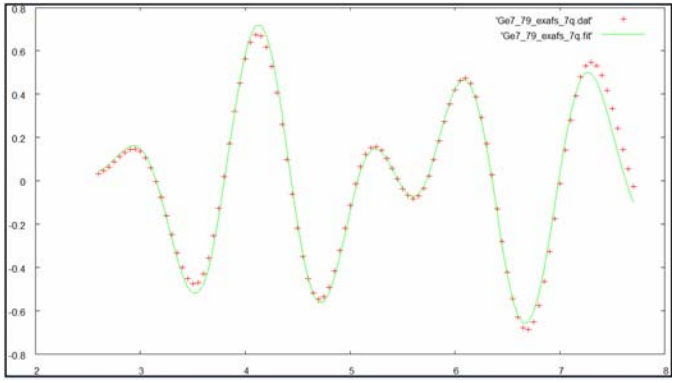
at the Ge K-edge



2 GPa



15 GPa

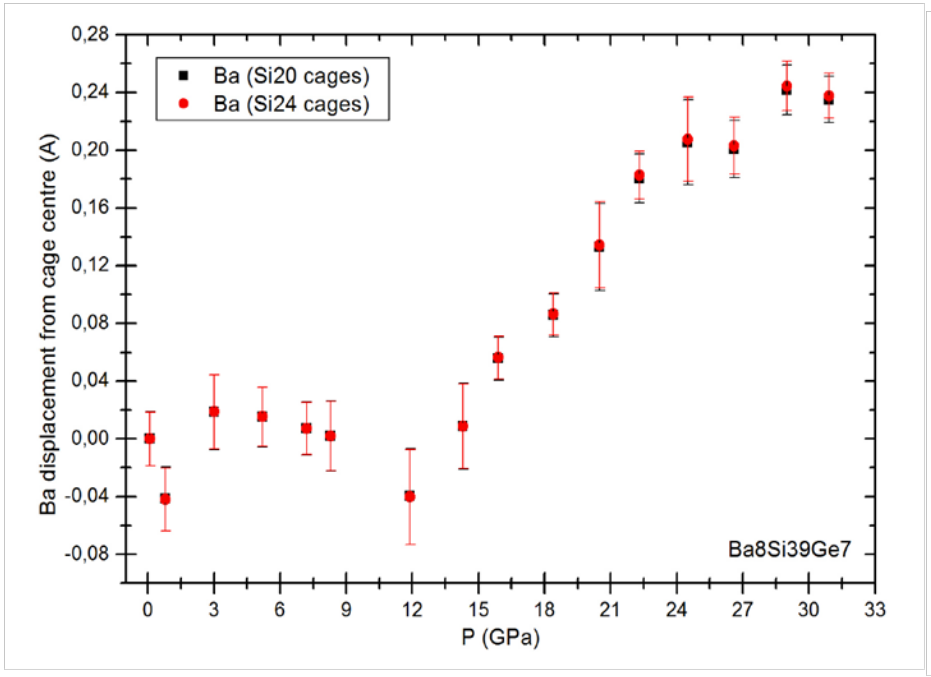


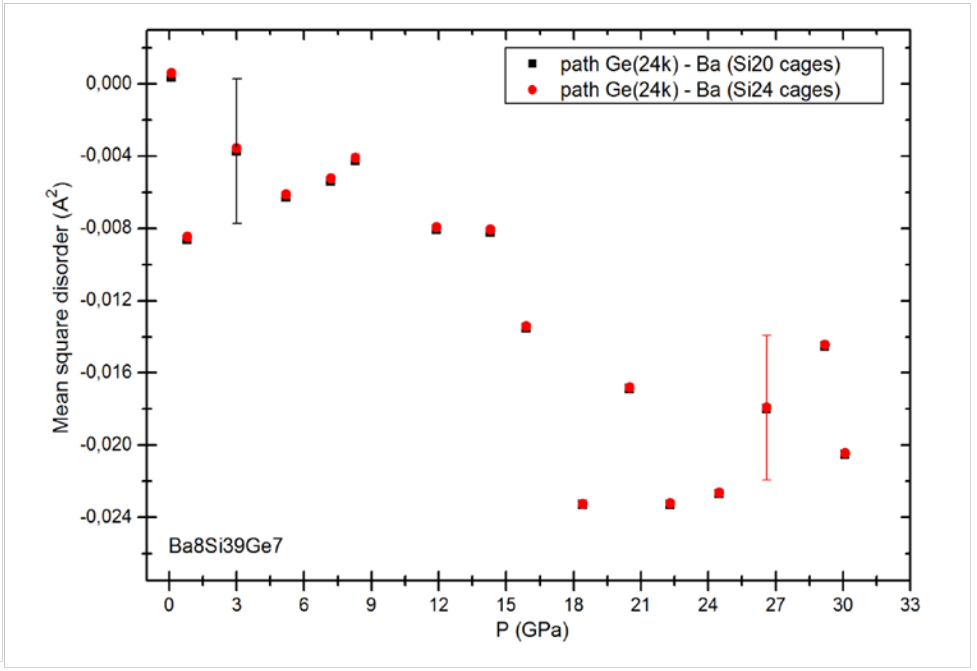
31 GPa

X-Ray Absorption results on $Ba_8Si_{39}Ge_7$

All the Ge atoms on 24k sites

1 or 2 Ge-Ge pairs and 4 or 5 Ge-Si pairs



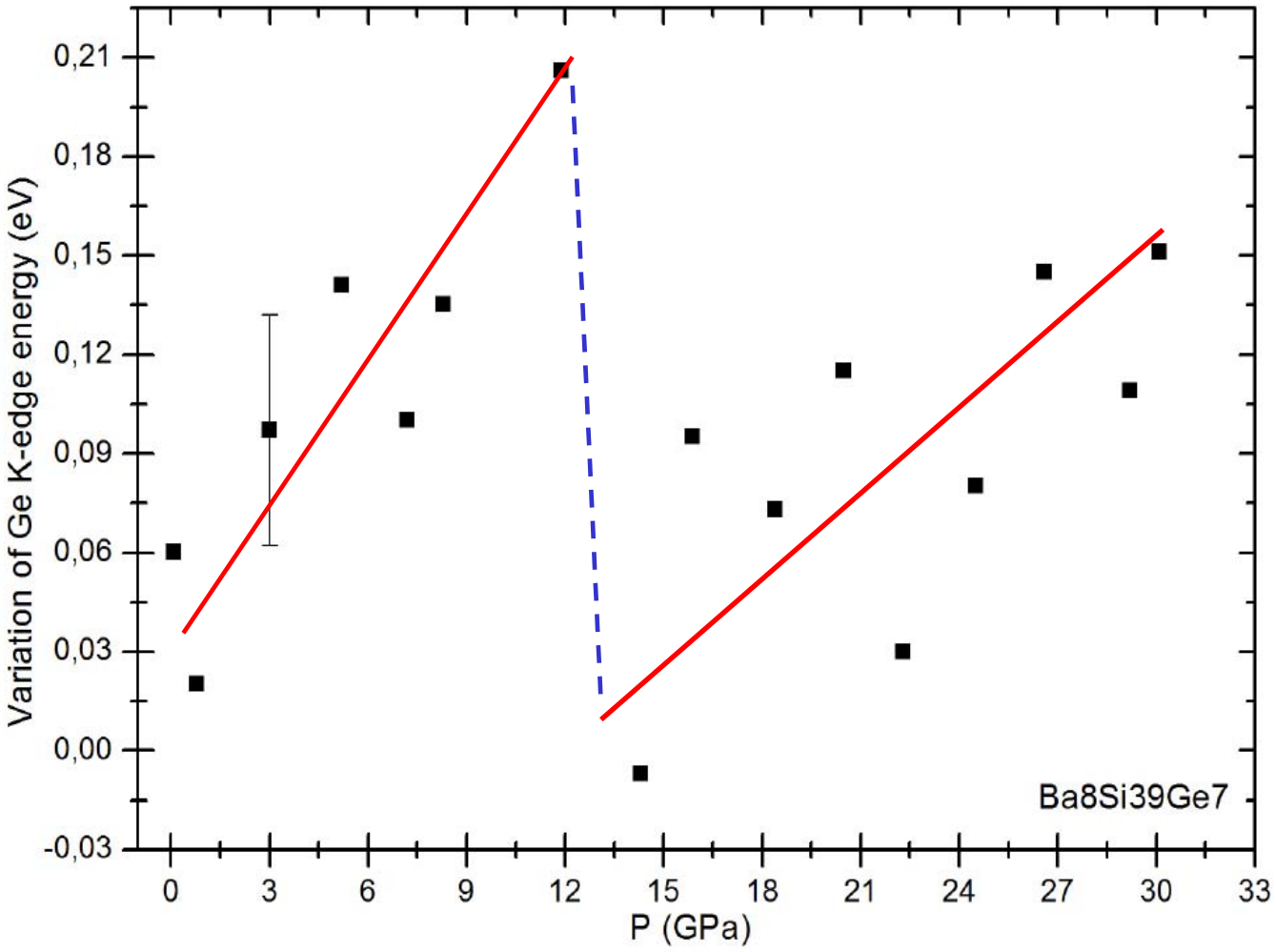


⇒ Displacement of the Ba atoms from the cages center

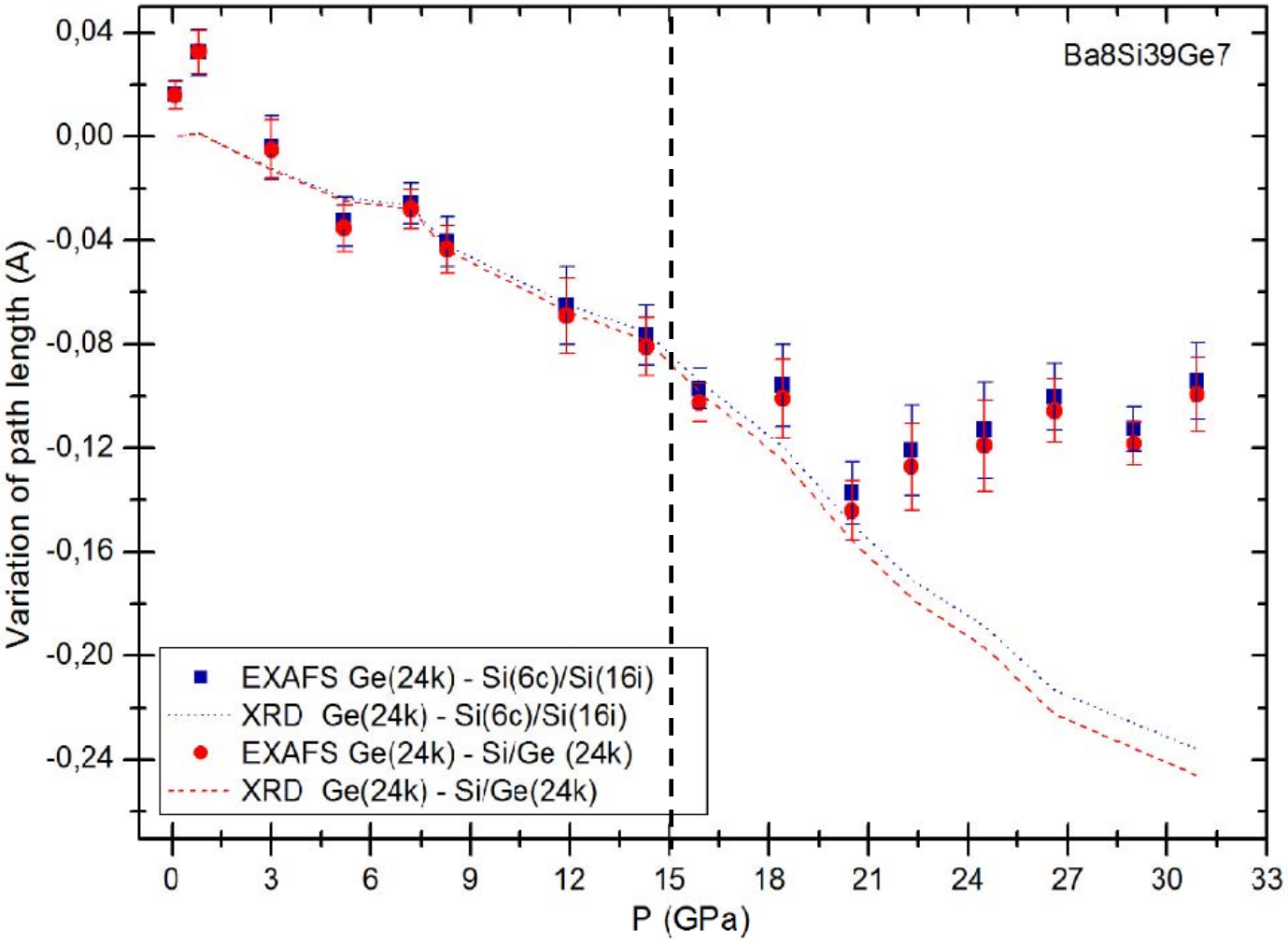
⇒ Decreasing of the mean-square disorder on the path Ge-Ba

Hybridization between Ba and Ge atoms at P ~ 15 GPa

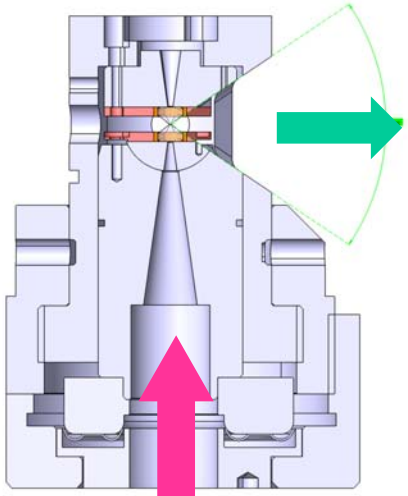
=> Change in the electronic structure of the Ge atoms

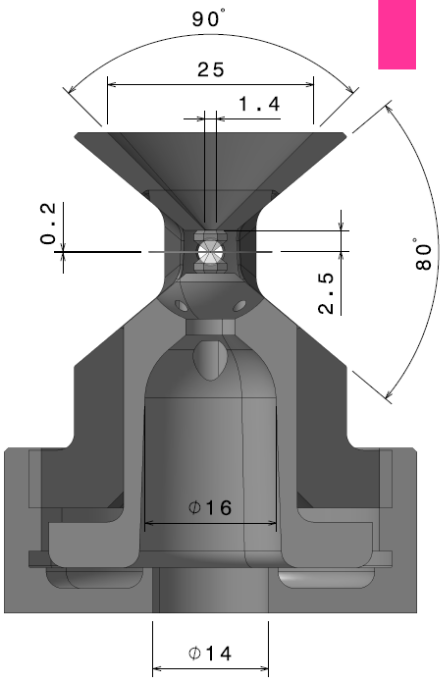


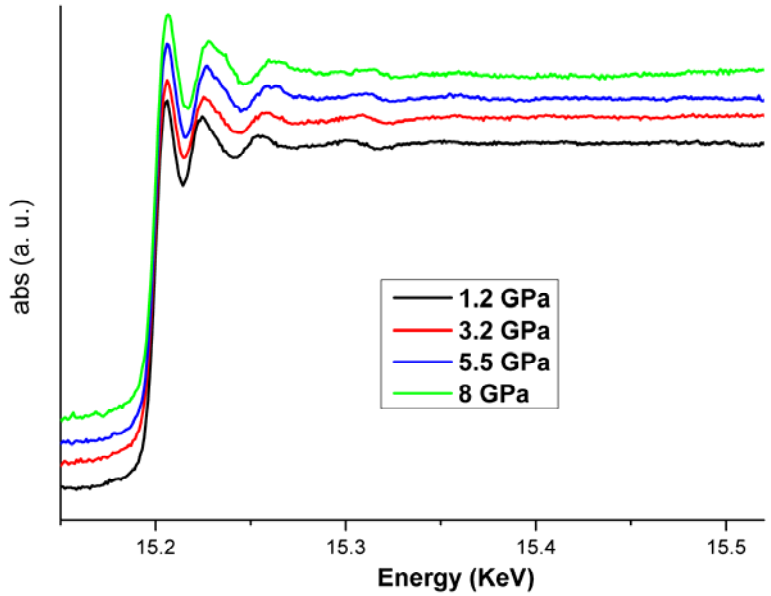
Collapse: distortion of the tetrahedra

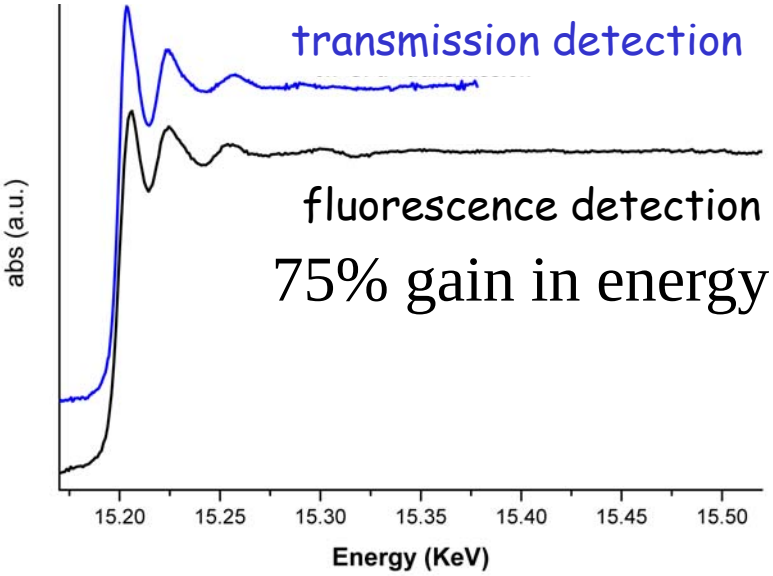


DAC with fluorescence detection at ID24









75% gain in energy

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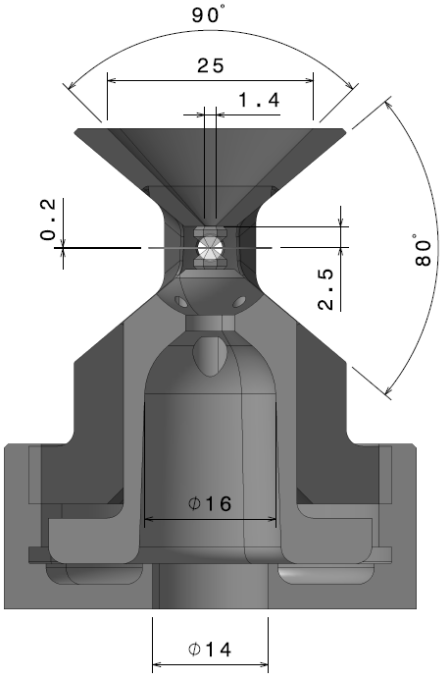
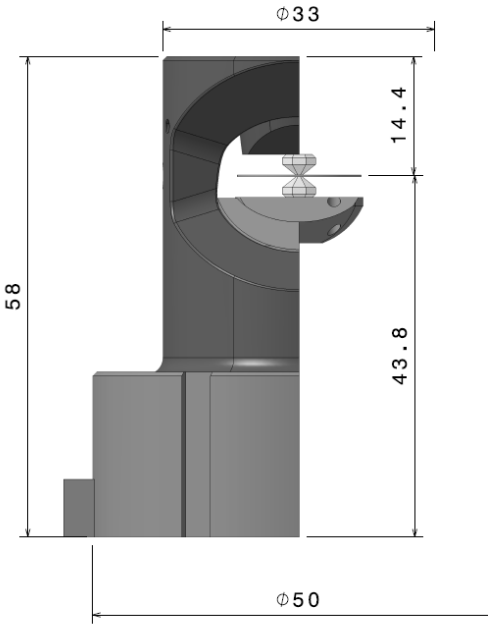
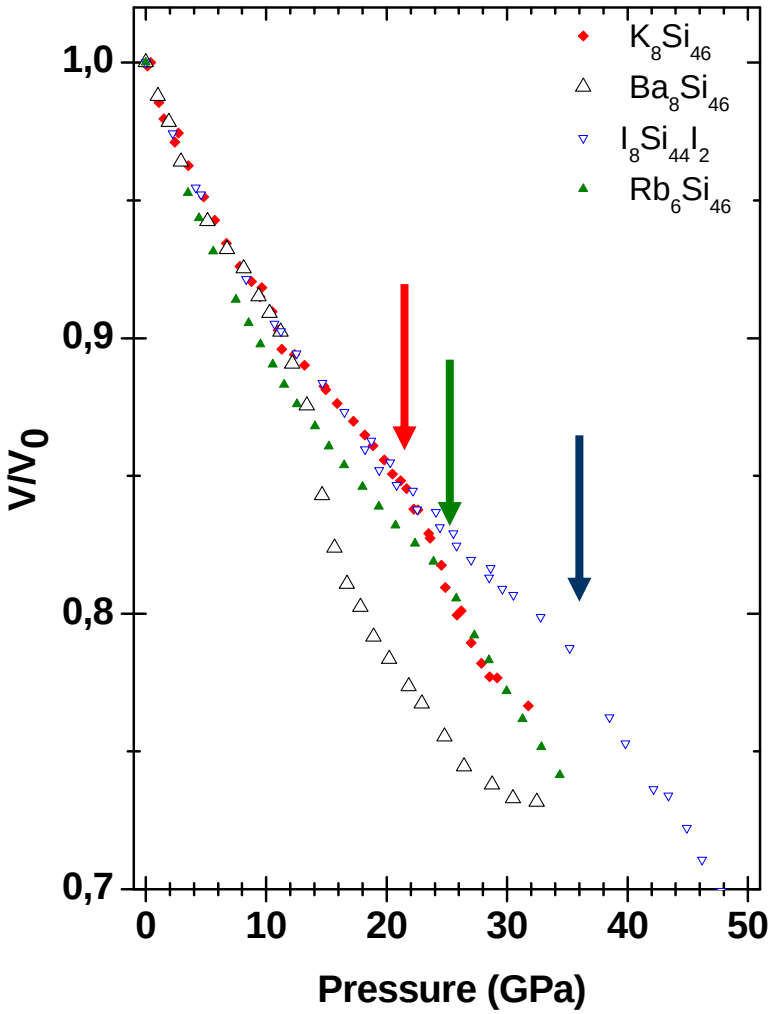
PANORAMIX DAC and Pressurization System

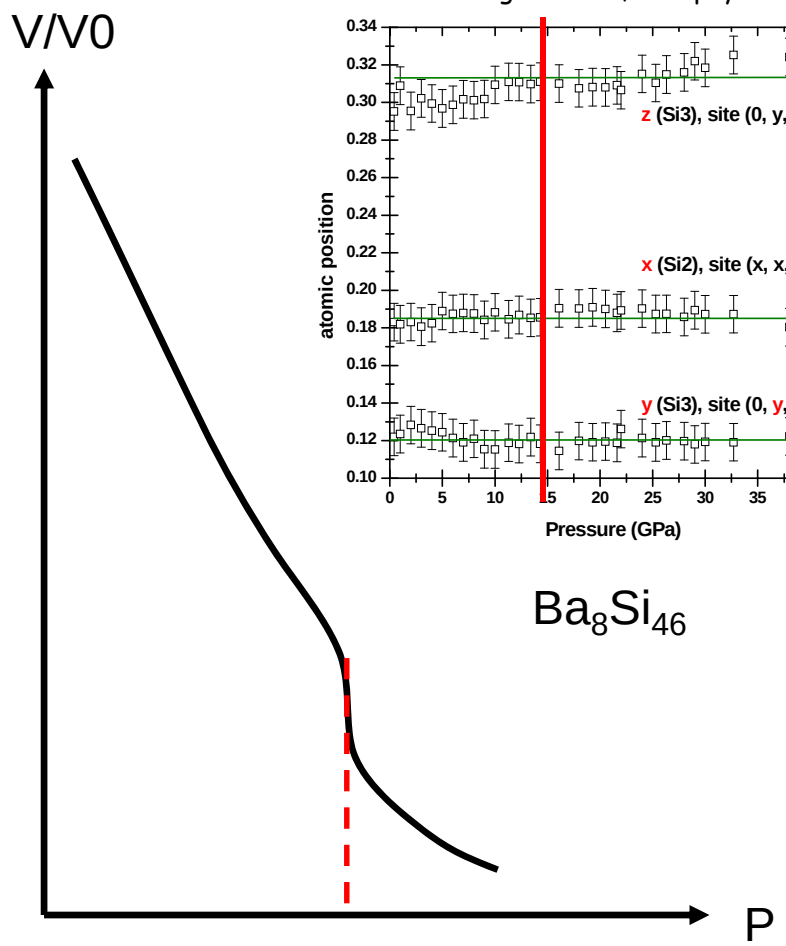




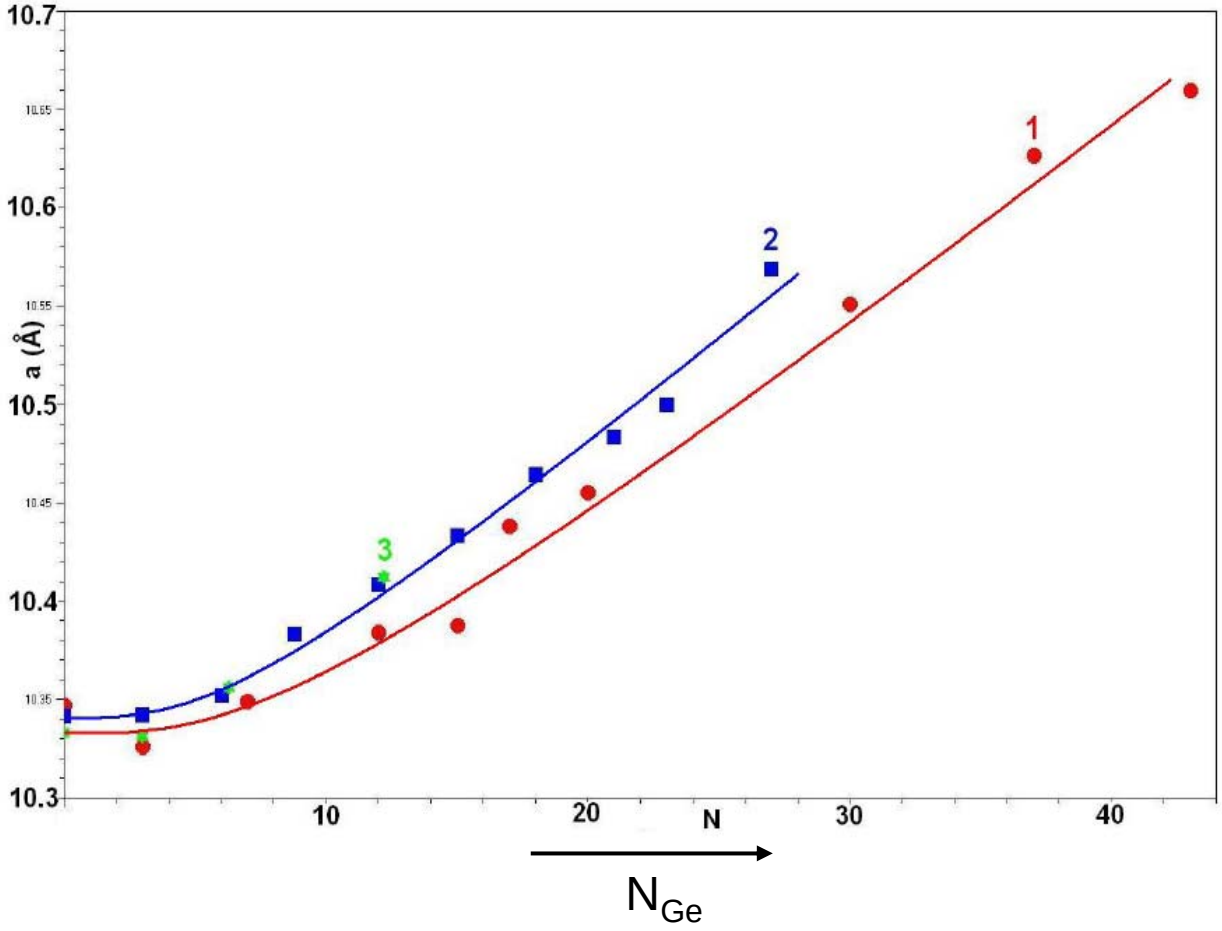
The volume collapse transition in group-14 clatrhates



A. San Miguel et al., Europhys. Lett., 69, 556

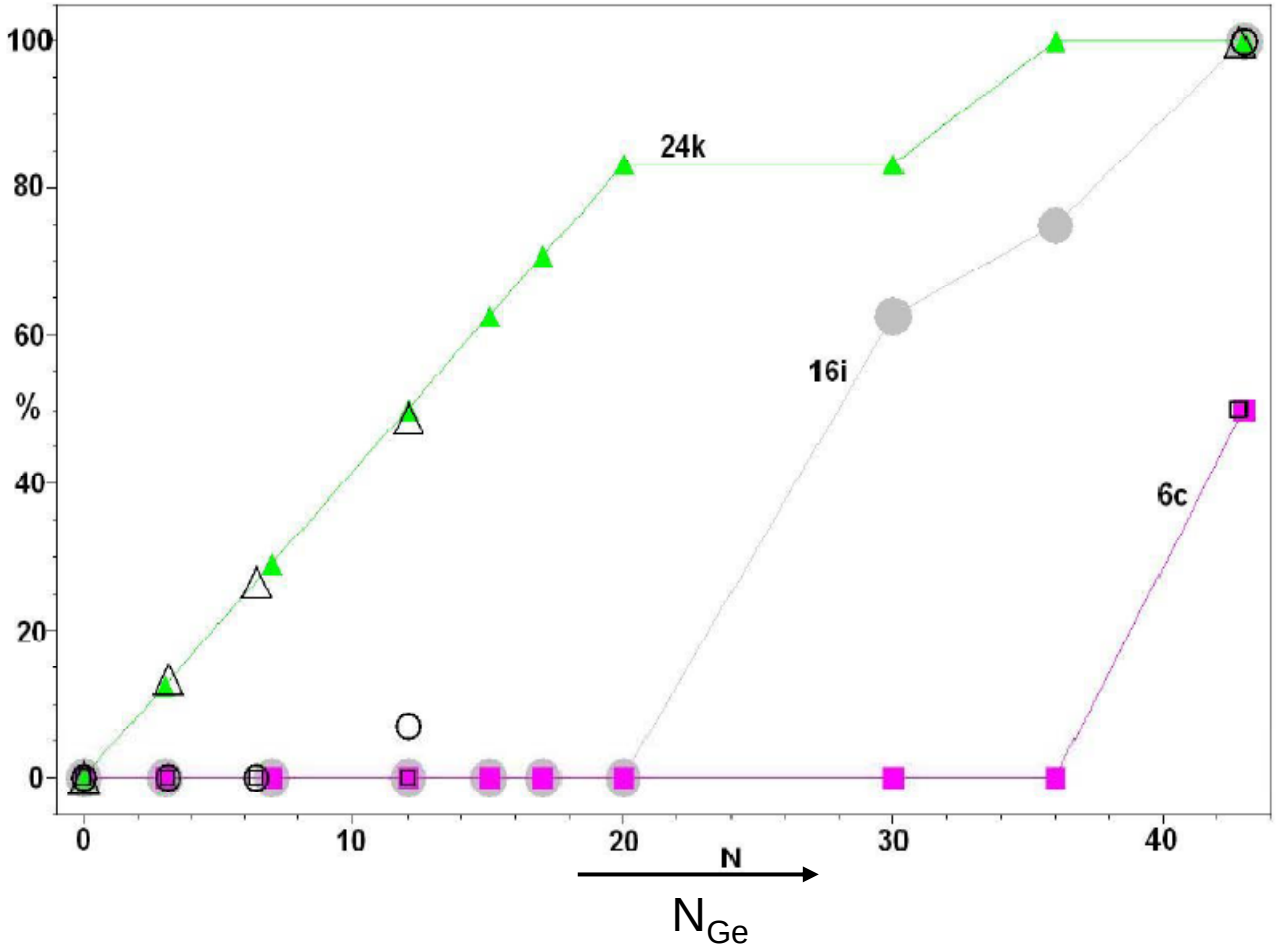


Nature of the volume collapse transition ??



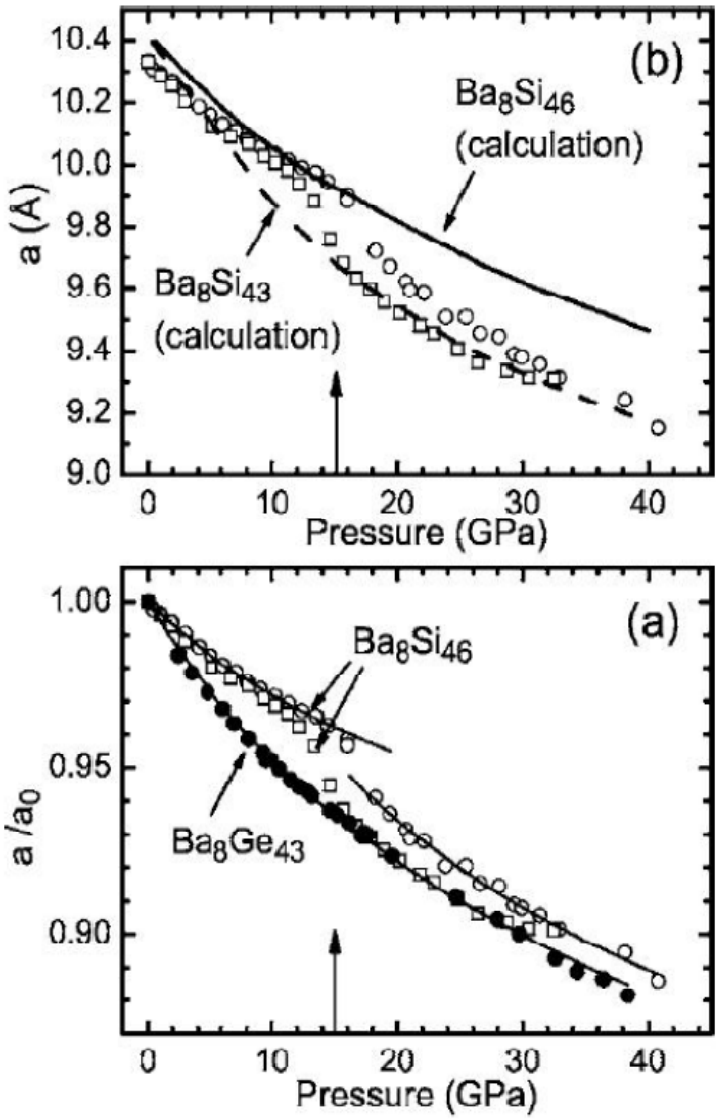
Fukuoka *et al*, J. Solid State Chemistry, **175**, 237 (2003)

Our results



Occupation of the Ge atoms in the different sites as a function of the substitution
Open symbols: Fukuoka *et al*, J. Solid State Chemistry, **175**, 237 (2003)
Solid symbols: our results

$Ba_8Ge_xSi_{46-x}$ at high pressure



No collapse in Ba_8Si_{43}

Understanding the collapse =
Understanding why it is suppressed

H. Shimizu *et al.*, J. Appl. Physics, 101, 063549 (2007)