

Challenges for energy dispersive
X-ray absorption spectroscopy
at the ESRF:
microsecond time resolution
and megabar pressures

Thesis realised at the ESRF (ID24)

Strong experimental character

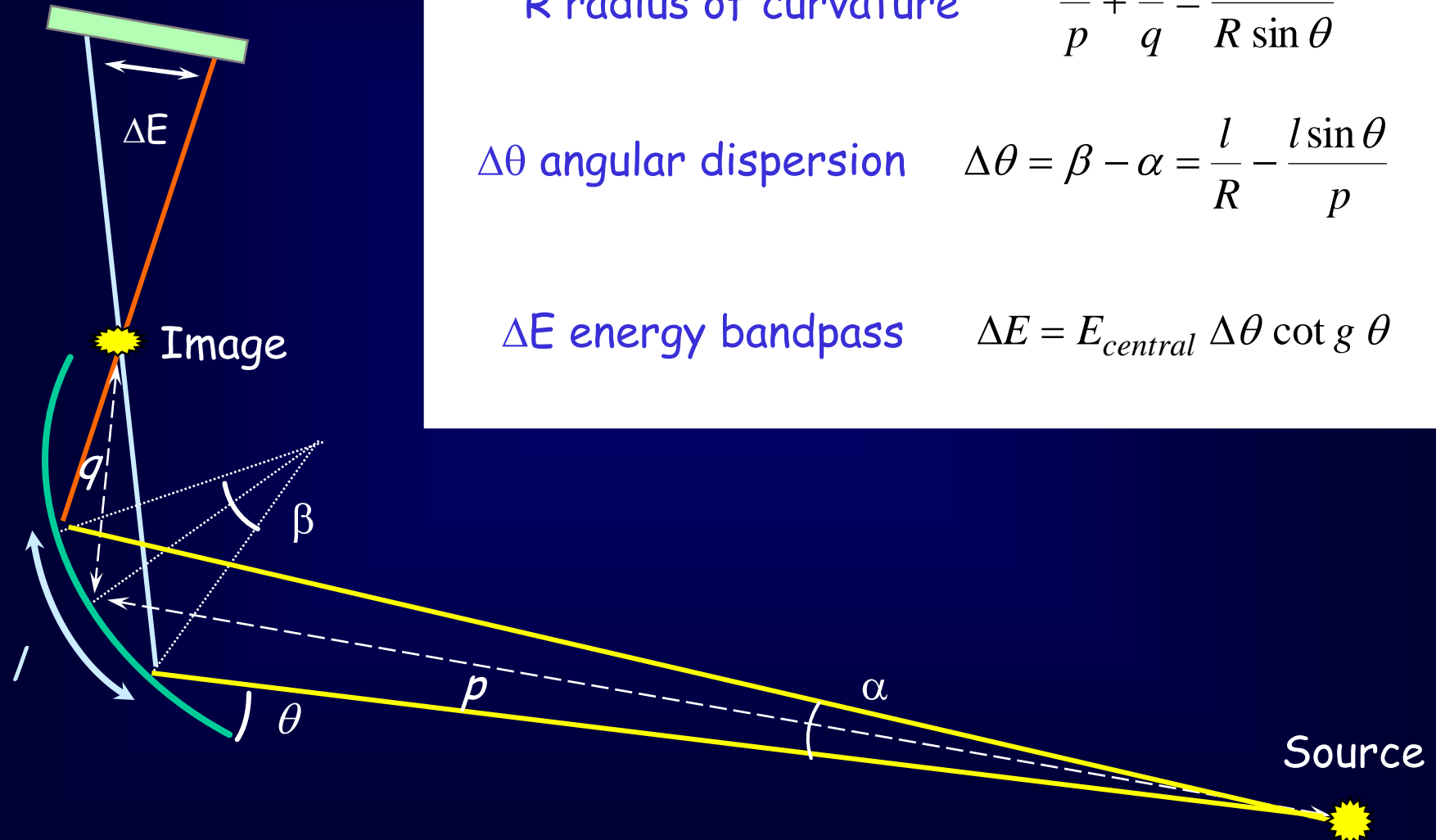
Underlying theme:

exploitation of the capabilities of
an X-ray absorption spectrometer
in dispersive geometry
on a third generation synchrotron source

- Description of the energy dispersive optics
 - Beamline ID24
 - Possible applications
- Organization of the manuscript
- Study of InAs under pressure
 - Introduction
 - XRD experiment and results
 - XAS experiment and results

Energy dispersive optics

Position sensitive detector



R radius of curvature

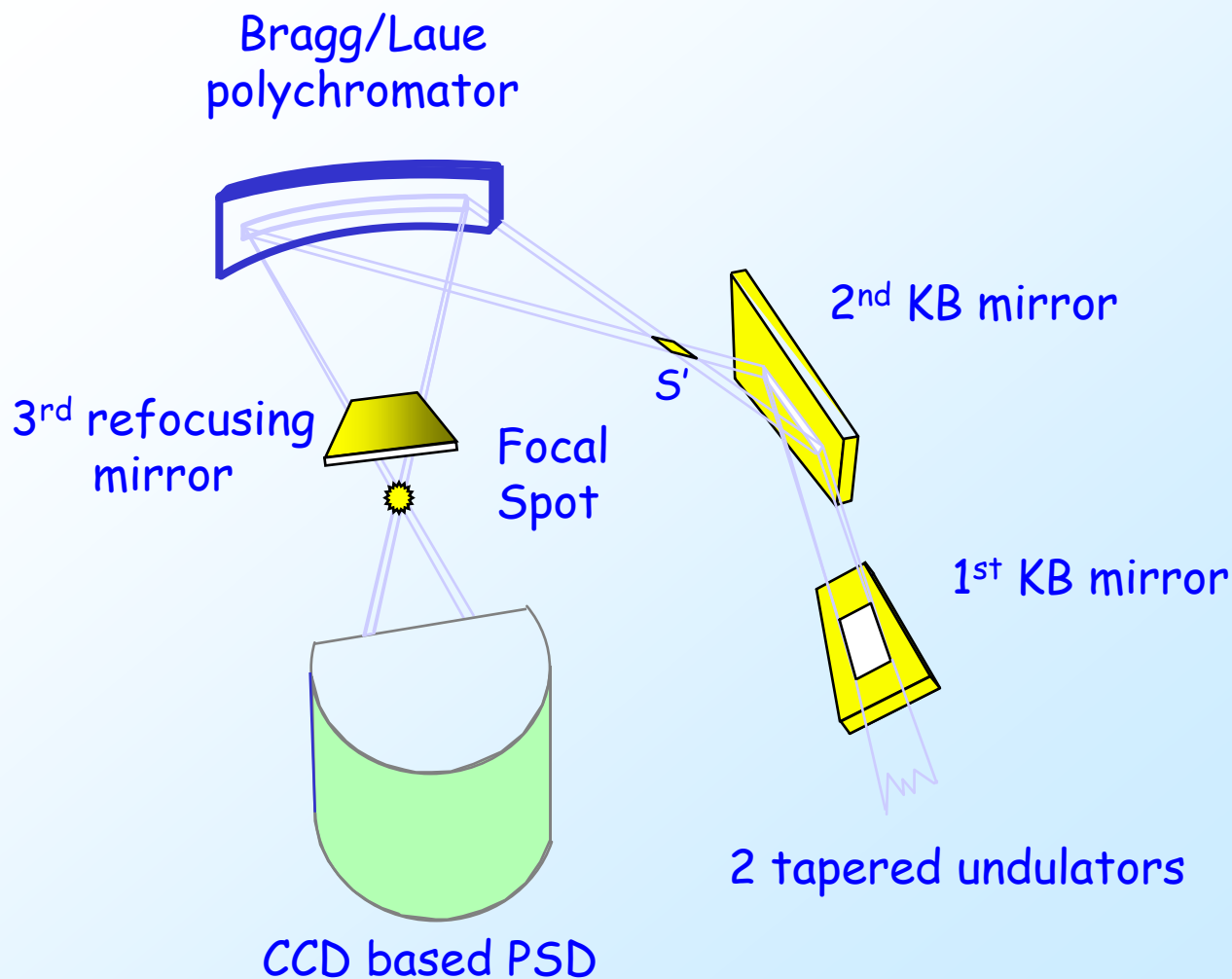
$$\frac{1}{p} + \frac{1}{q} = \frac{2}{R \sin \theta}$$

$\Delta\theta$ angular dispersion

$$\Delta\theta = \beta - \alpha = \frac{l}{R} - \frac{l \sin \theta}{p}$$

ΔE energy bandpass

$$\Delta E = E_{\text{central}} \Delta\theta \cot \theta$$



Source: 2 undulators

Dim. of the beam at the source:
400(H) μm \times 10(V) μm

5-27 keV

KB mirrors at fixed angle 3 mrad

3rd mirror for vertical focusing

Typical flux:
 10^{12} ph/sec in the whole energy bandwidth

dispersive geometry

no movement of optics during acquisition

- energy scale stability

- focal spot position stability

small spot size

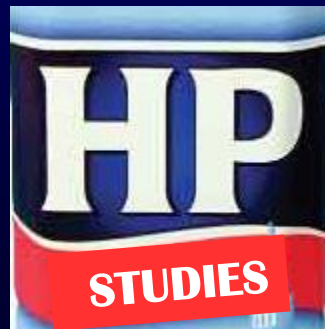
- small samples can be measured

- sensitivity to sample inhomogeneities

parallel data acquisition

- possibility of fast acquisitions

- sensitivity to beam instability (I_0 and I_1 not measured simultaneously)



TR studies

TIME-RESOLVED STUDIES

- Overview of TR studies using XAS
 - Studies whose goal is the determination of the structure of matter in its metastable excited state
- Characteristics of BL ID24 for TR studies
 - Detection system
 - Different acquisition systems
 - Synchronization methods
- $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$
 - Previous works
 - TR experiment
 - Effect of X-rays on the sample

HIGH-PRESSURE STUDIES

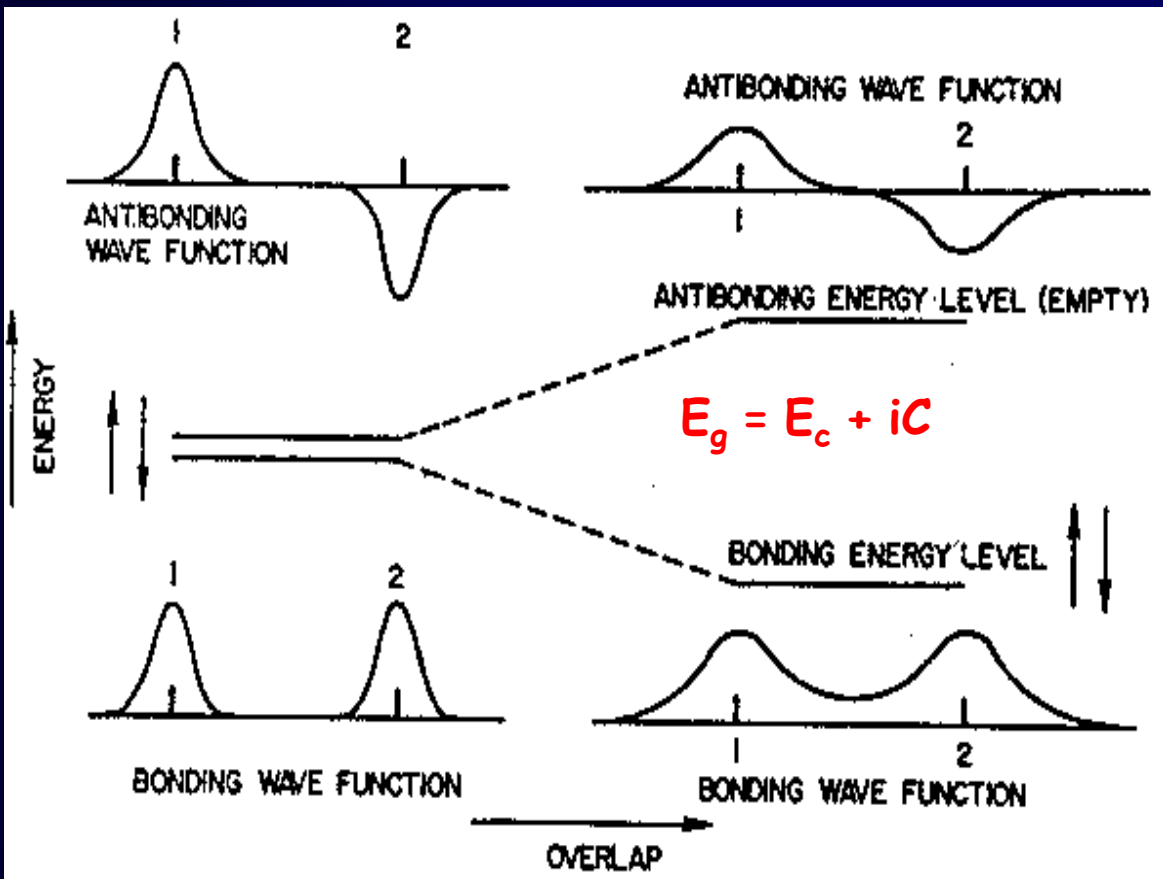
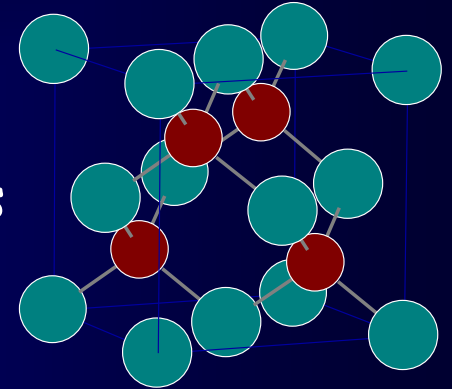
- Introduction on HP studies
 - Effect of pressure on matter
 - HP experimental methods: P generation, gasketing, P measuring..
- XAS and HP
 - Survey of XAS studies at HP
 - HP XAS stations worldwide
 - Requirements for HP XAS studies using DACs
- Technical developments on ID24
 - Local feedback
 - Third focusing mirror
 - New opportunities: low energies
 - combined XAS and XRD
 - combined HP/HT
- Study of InAs at HP/HT

Absence of the high pressure CsCl
phase in
III-V semiconductors

$A(N)B(8-N)$ compounds
(III-V semiconductors)

Covalent bonds - sp^3 hybridized orbitals

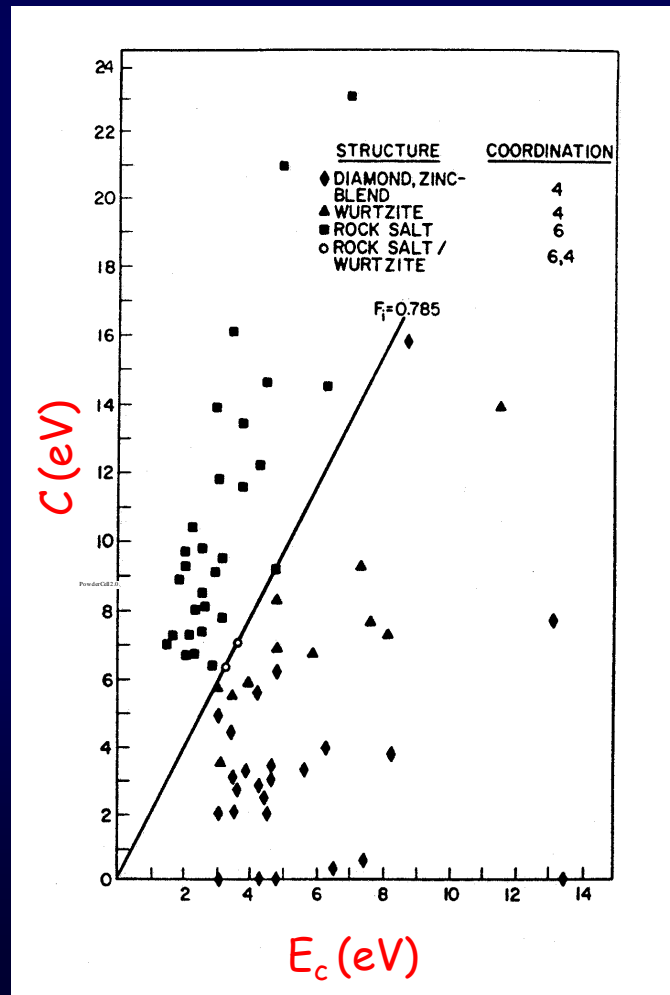
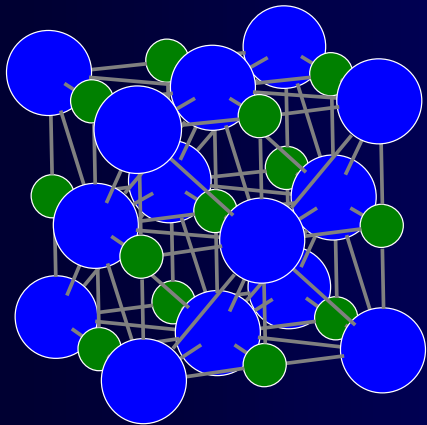
4-fold coordinated structures



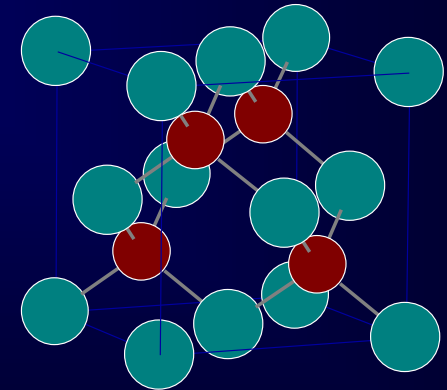
Importance of the ionic character of the bond

Ionicity largely determines the ambient pressure crystallization behaviour (4-fold or 6-fold) (Phillips 73)

NaCl

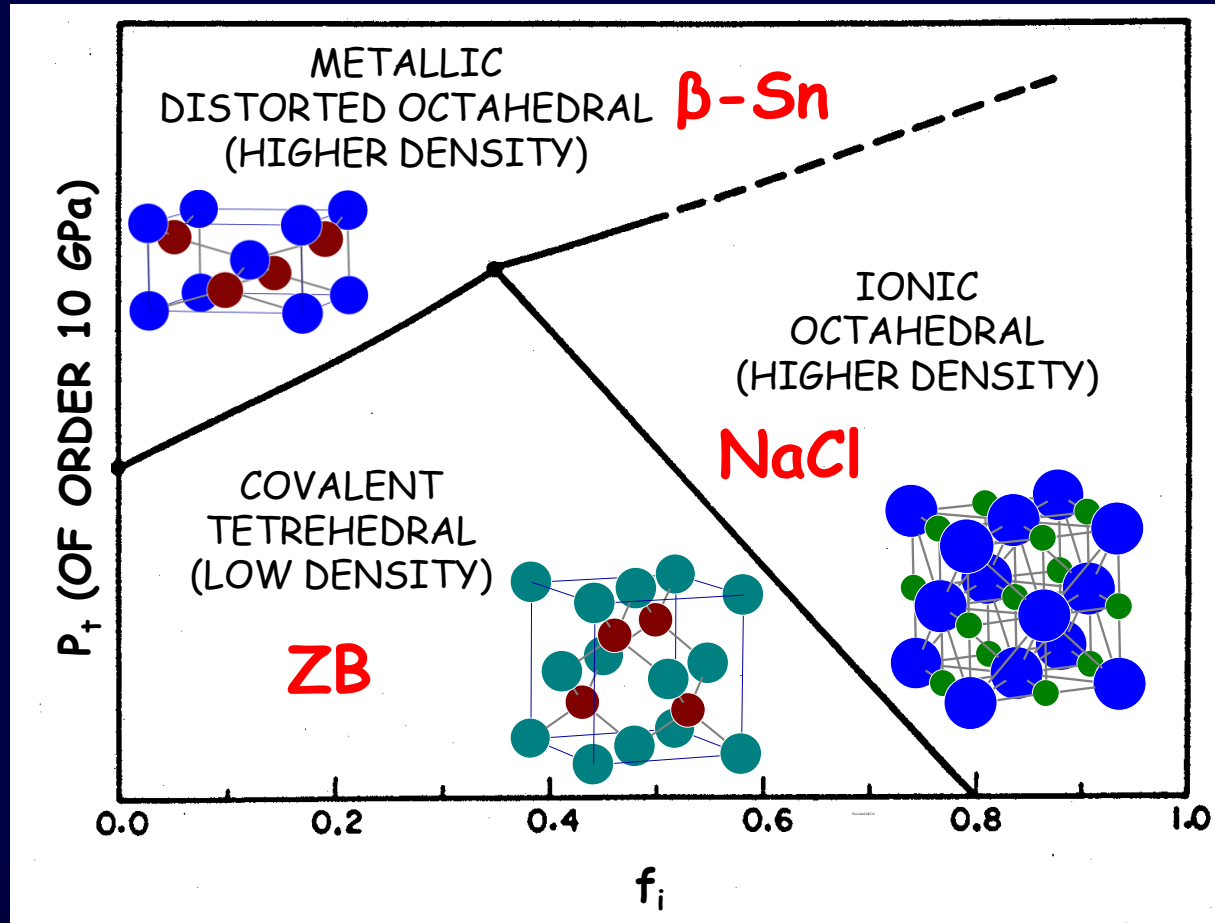


ZB

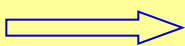


Behaviour under compression

Pressure transforms the low density 4-fold coordinated structures in higher density ones with higher coordination numbers



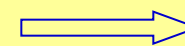
ZB



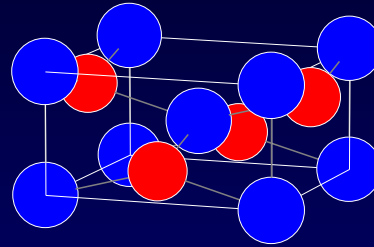
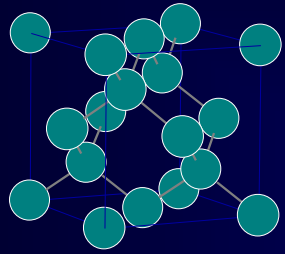
NaCl



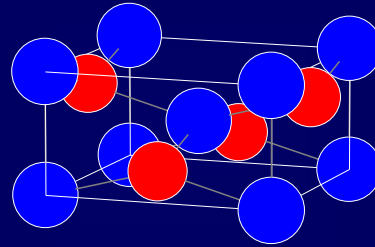
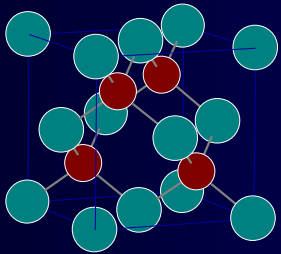
β -Sn



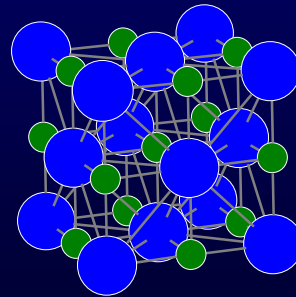
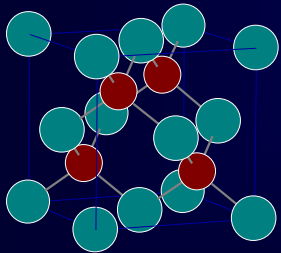
CsCl



Si, Ge

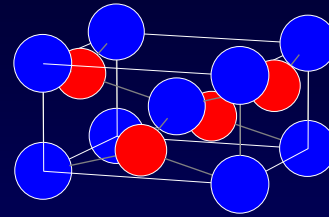
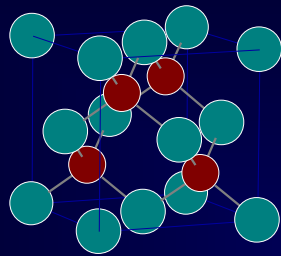


AlSb, GaSb, InSb

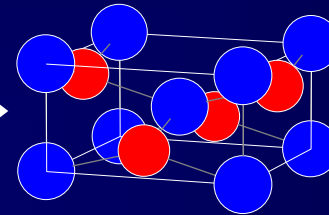
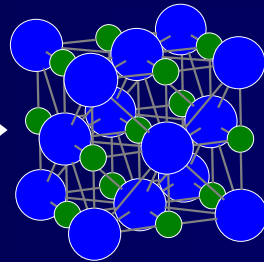
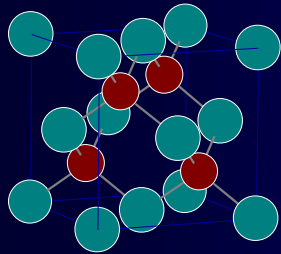


InAs, InP

70s and 80s' works



GaP



InAs, InP,
II-VI

Theoretical studies

First calculations based on total energy approach

ZB



NaCl



β -Sn



CsCl

Recent (experimental) studies

Technical developments: ADXRD

Image plate technique

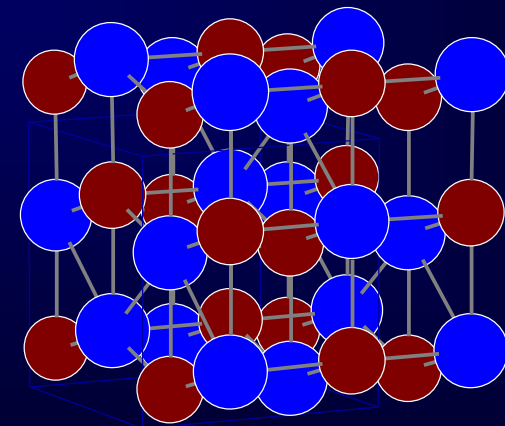
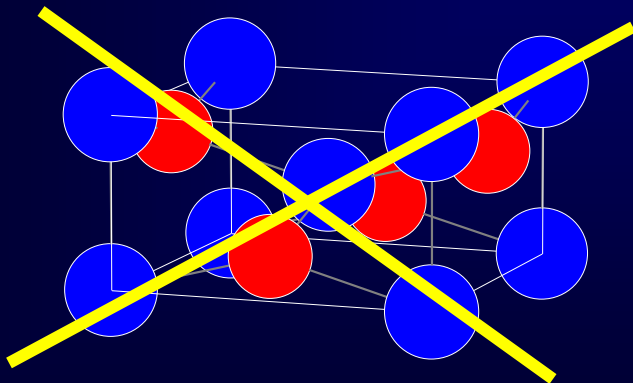
Review of structural systematics of III-V II-VI semiconductors

"True" structures

more complex

larger unit cells

lower symmetry



Phonon dynamics inclusion in the theory

Low pressure range (Ozoliņš and Zunger PRL (1999))

Systematic absence of

- NaCl for more covalent compounds

GaAs, InSb, GaSb, GaP, AlAs

- β -Sn for more ionic compounds

InP, InAs

High pressure range (Kim, Ozoliņš and Zunger PRB (1999))

- phonon instabilities prevent formation of CsCl for:

GaP, GaAs, InP, InAs

- possible candidate replacing CsCl:

InBi ($P4/nmm$), AuCd ($Pmma$)

These calculations confirmed recent experiments

Experimental searches for the proposed crystal structures are called for

Behaviour of InAs under compression

- InAs has lowest predicted transition pressure to CsCl (AuCd, InBi)

Theory (Mujica and Needs, *PRB*, **55** (1997))



Experiment (Nelmes et al., *J. Phys. Chem. Solids*, **56** (1995))



No XAS measurements have been done so far at HP

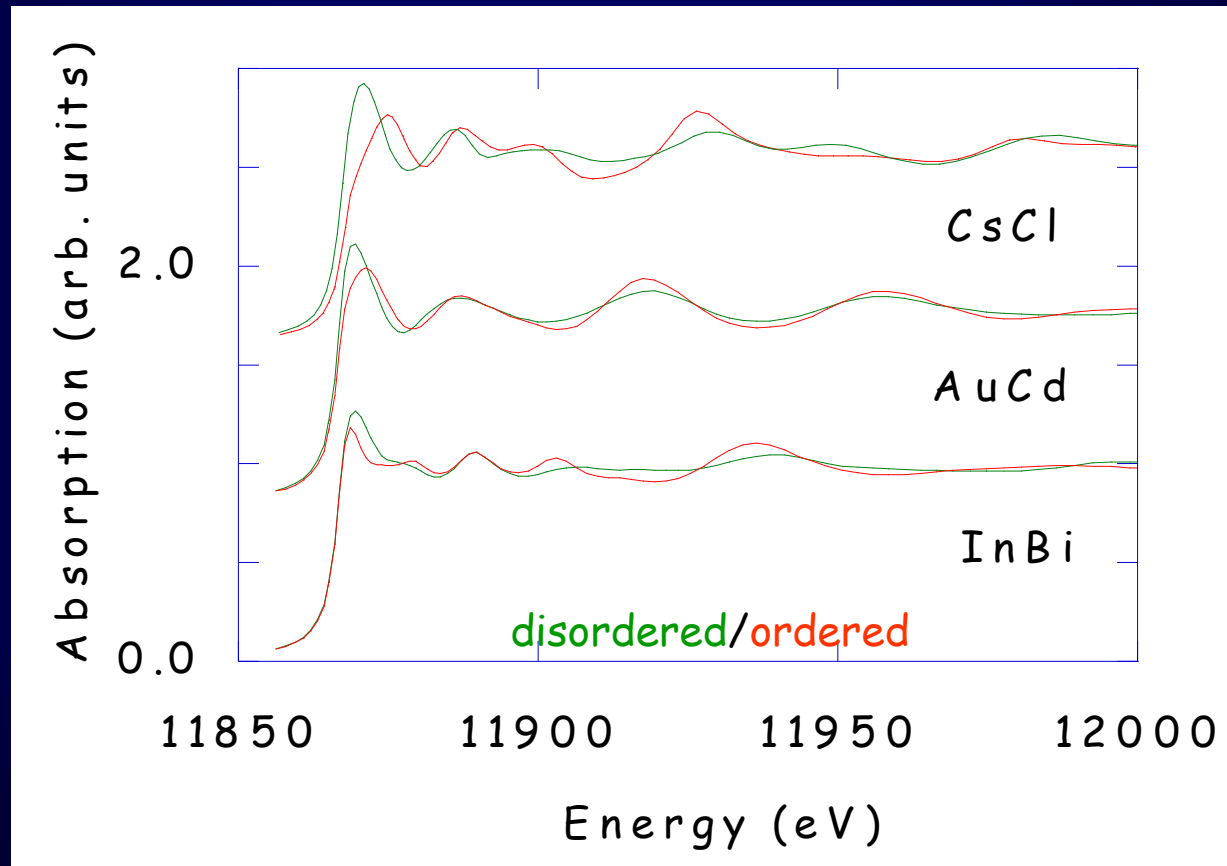
Aim of this study

In the unexplored pressure range

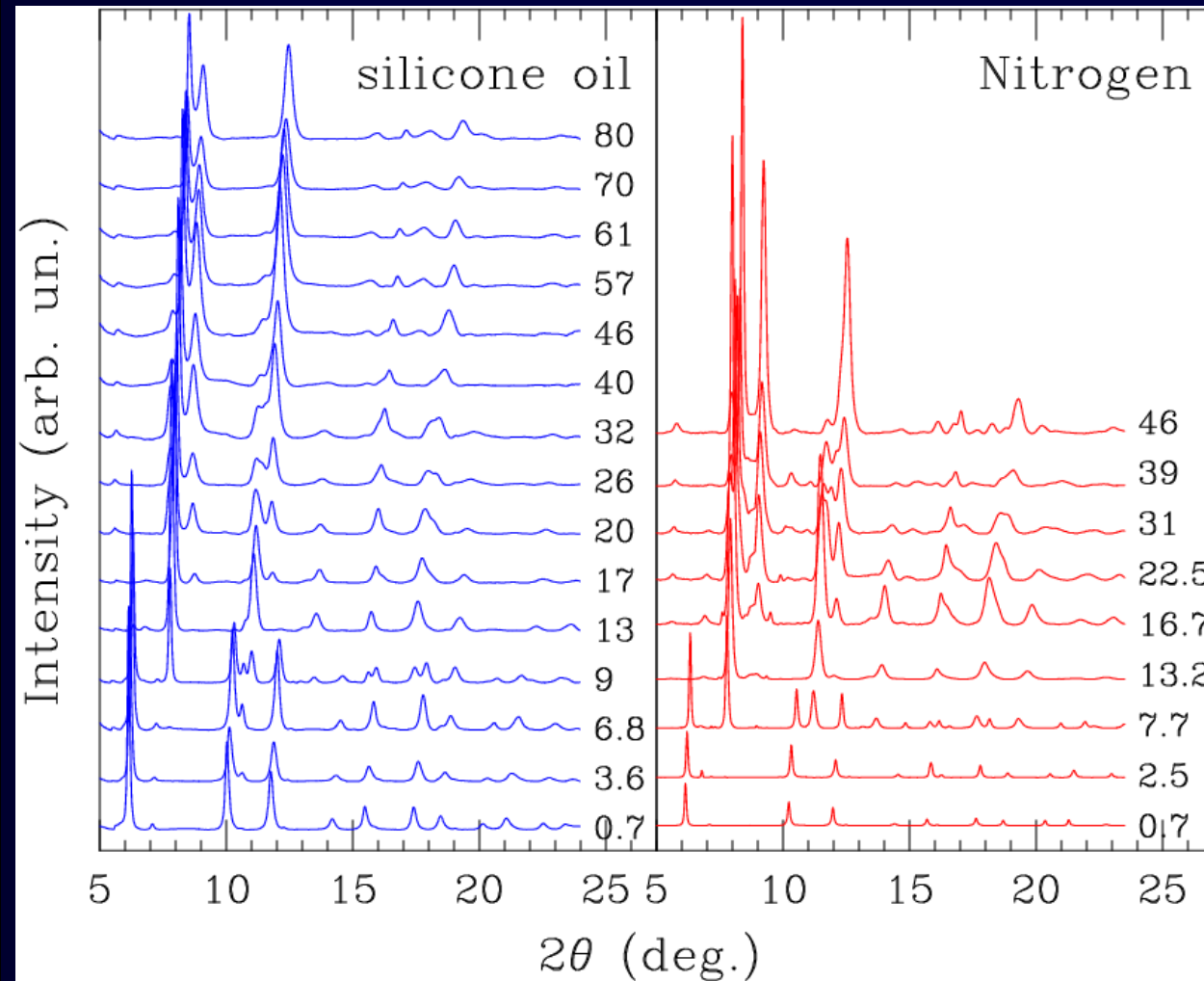
- verify the non existence/existence of CsCl
- verify the existence/non existence of alternative structures:
InBi ($P4/nmm$), AuCd ($Pmma$)

In the whole pressure range

- address properly the question of chemical ordering

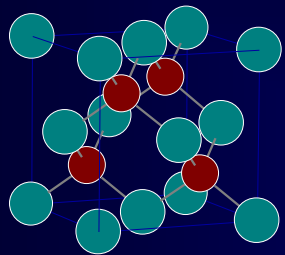


X-ray diffraction experiment

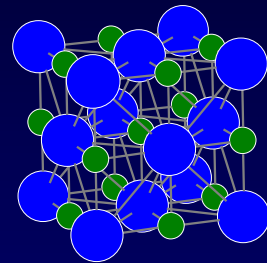


- ID30
- $\lambda = 0.3738 \text{ \AA}$
- Si(111) polychromator
- focal spot: $15 \mu\text{m} \times 15 \mu\text{m}$
- Chervin-type DAC
- bevel-edged Drukker diamonds
- $150 \mu\text{m}$ culet
- PTM Silicone oil and N_2
- ruby fluorescence method
- $P_{\text{max}} = 80(15) \text{ GPa}$

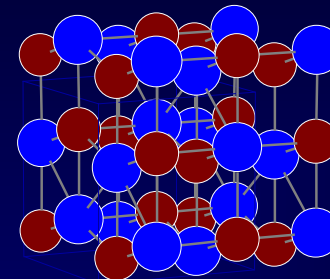
Determination of the structural sequence (preserved for the two PTM)



F4-3m (Zincblende)



Fm3m (NaCl)

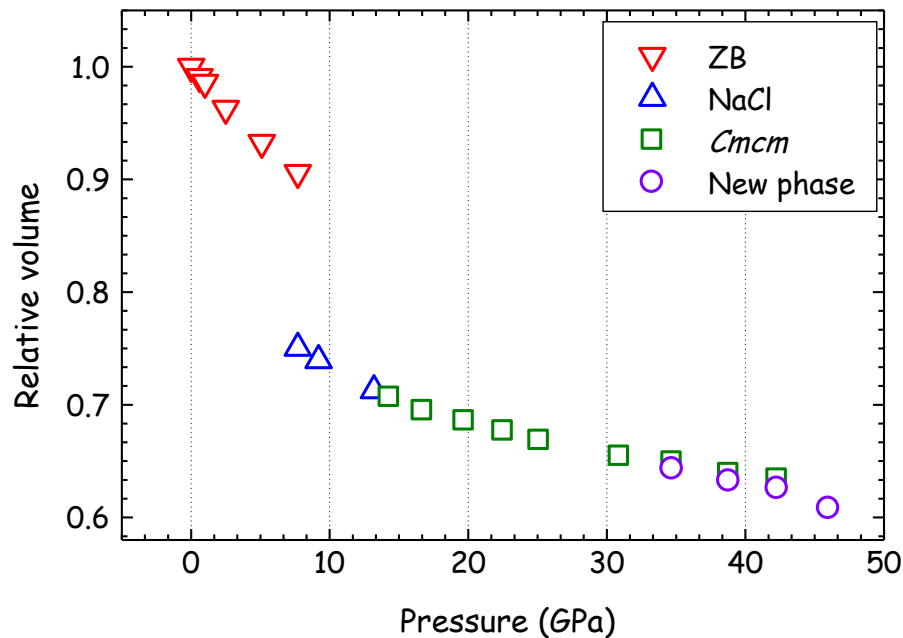


Cmcm



New phase

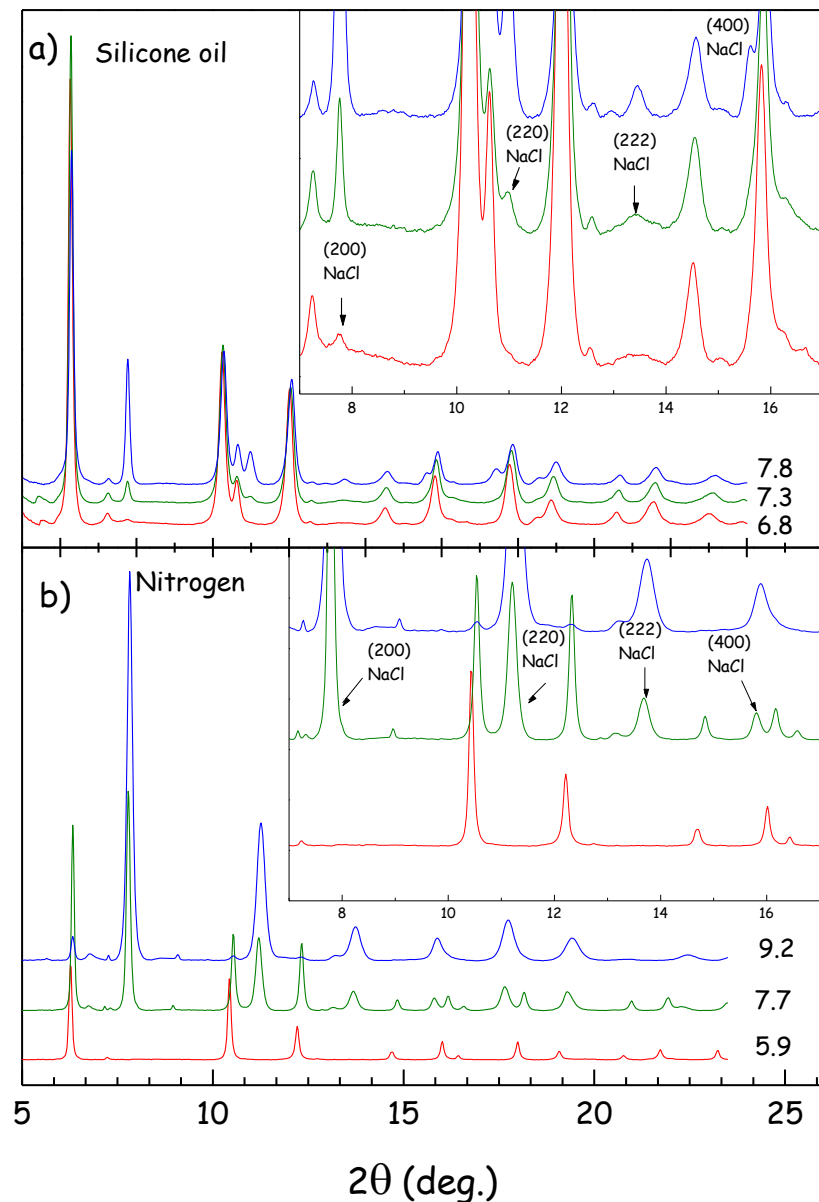
?



$\Delta V/V \sim -18\%$
ZB to NaCl

$\Delta V/V \sim 0\%$
Other transitions

Zincblende to NaCl transition



This transition strongly depends on the PTM

Silicone oil

(200) NaCl at 6.8 GPa

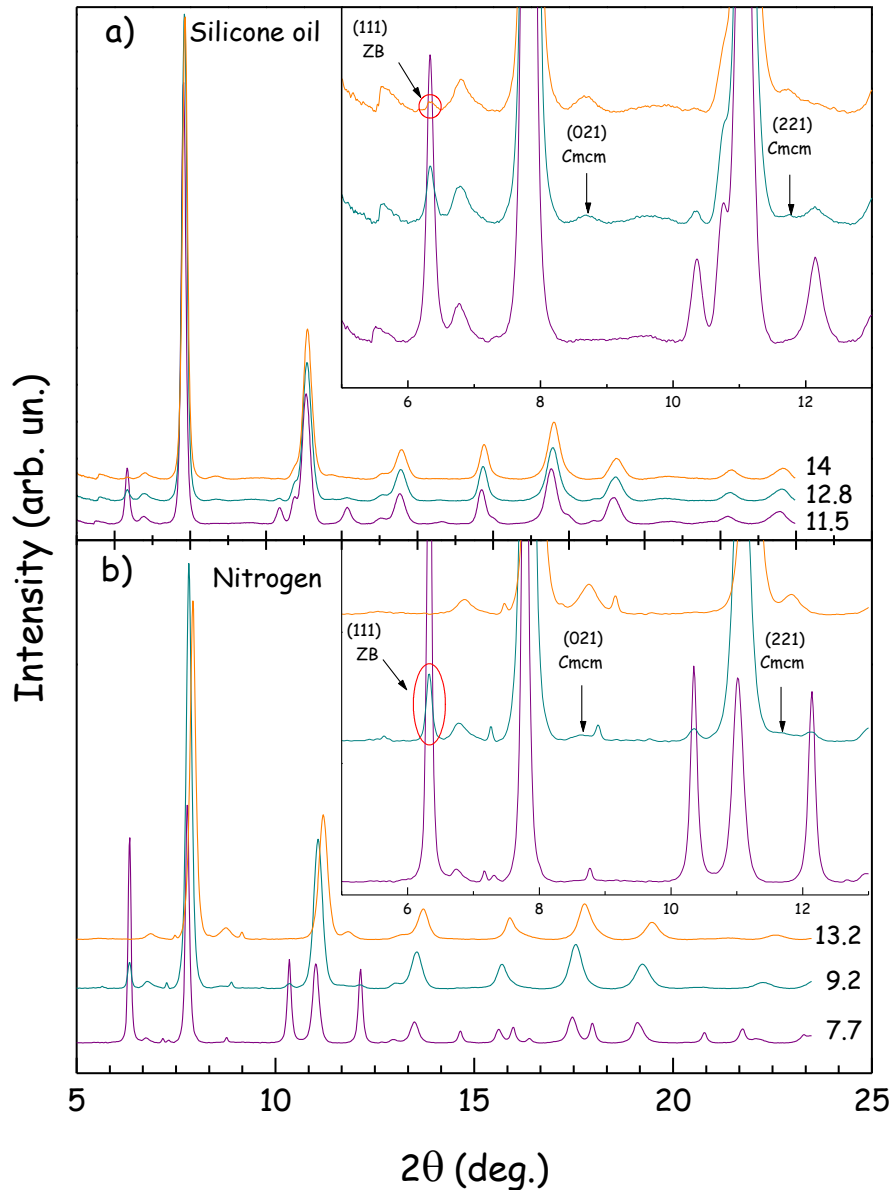
(220), (222) NaCl at 7.3 GPa

(400) NaCl at 7.8 GPa

Nitrogen

50:50 ZB:NaCl at 7.7 GPa

Does a pure NaCl phase exists?



Silicone oil

(021) Cmc_m at 12.8 GPa

(221) Cmc_m at 14 GPa

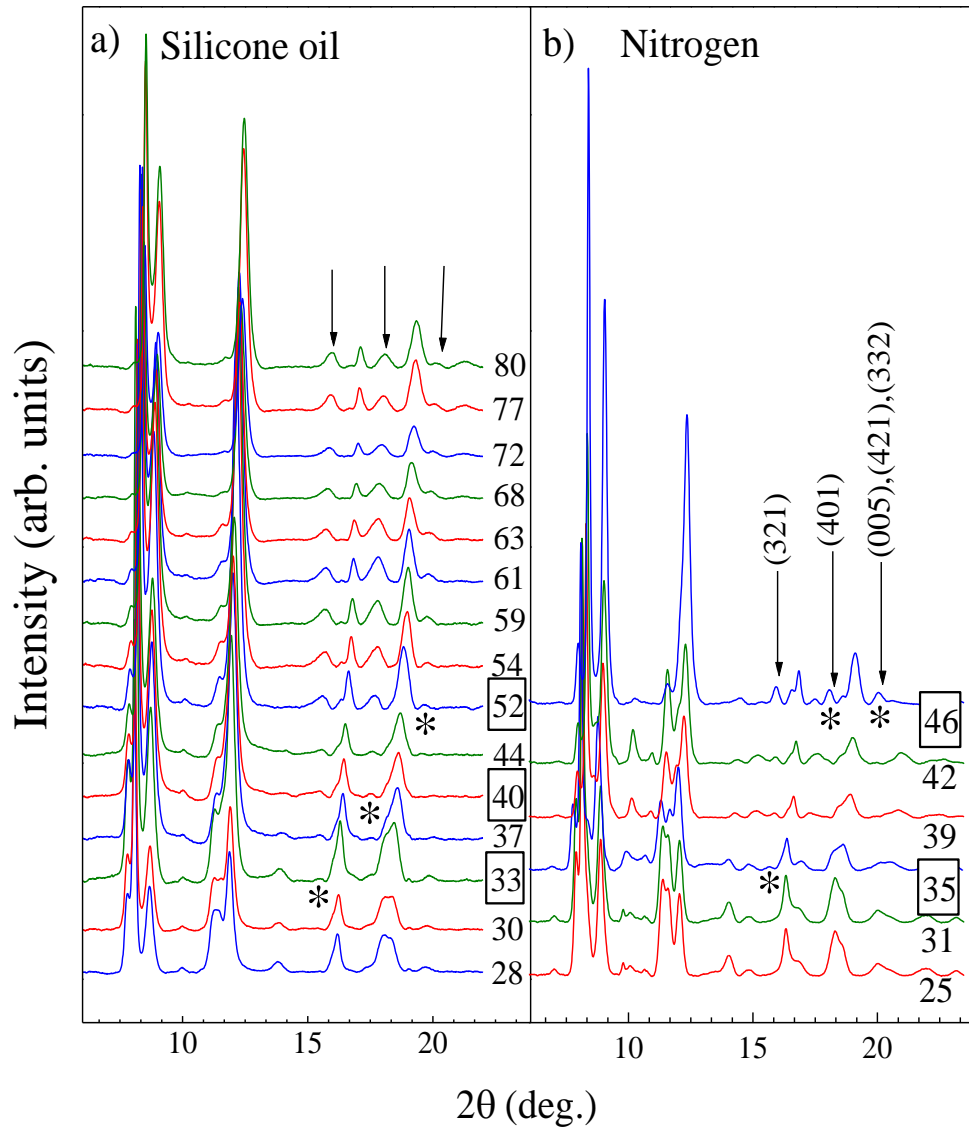
(111) ZB at 14 GPa

Nitrogen

(111) ZB; (021), (221) Cmc_m at 12.8 GPa

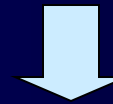
NaCl reflections

Cmcm to "New phase of lower symmetry" transition



- New Bragg reflections (16, 17.5, 20 deg.)
- They are forbidden by the centering condition of *Cmcm*

Trends in the previous *Cmcm* peaks are continued in the new phase



The new phase is a SUBGROUP of *Cmcm*

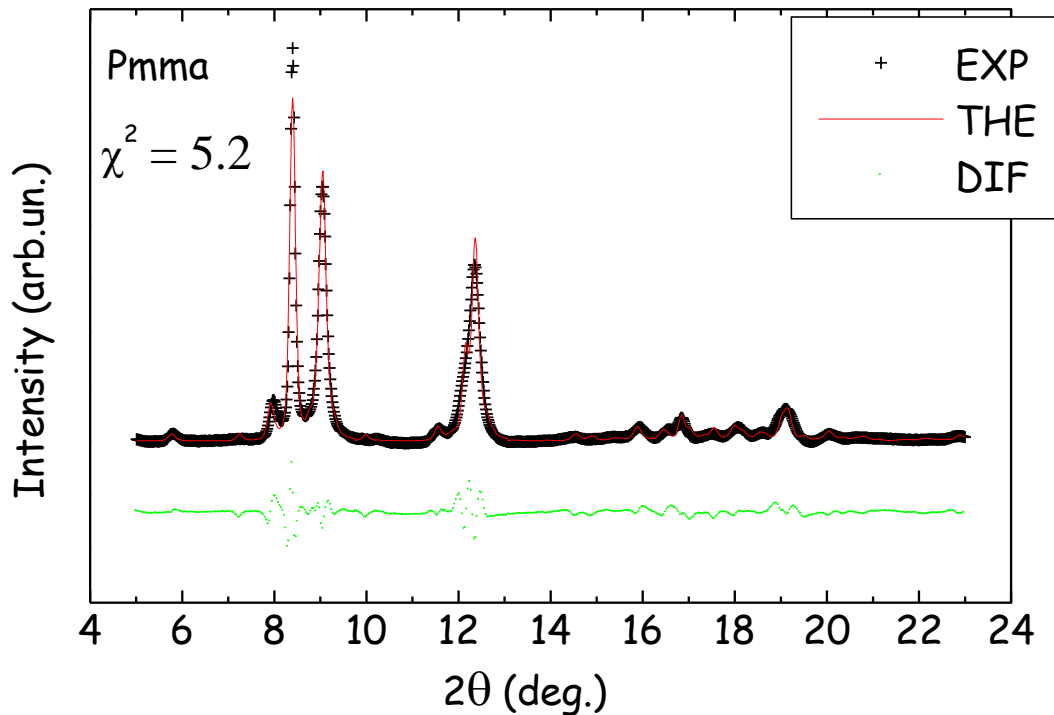
Lost of C-centering of *Cmcm*



Lower symmetry subgroup of *Cmcm*

The new phase has a $Pm\bar{m}a$ symmetry !

The HP phase has been indexed with the most likely phases obtainable by distortion of $Cmcm$ (belonging to subgroups of $Cmcm$).



$P = 46 \text{ GPa}$

$a = 4.8931(18)$

$b = 5.1069(4)$

$c = 5.4117(9)$

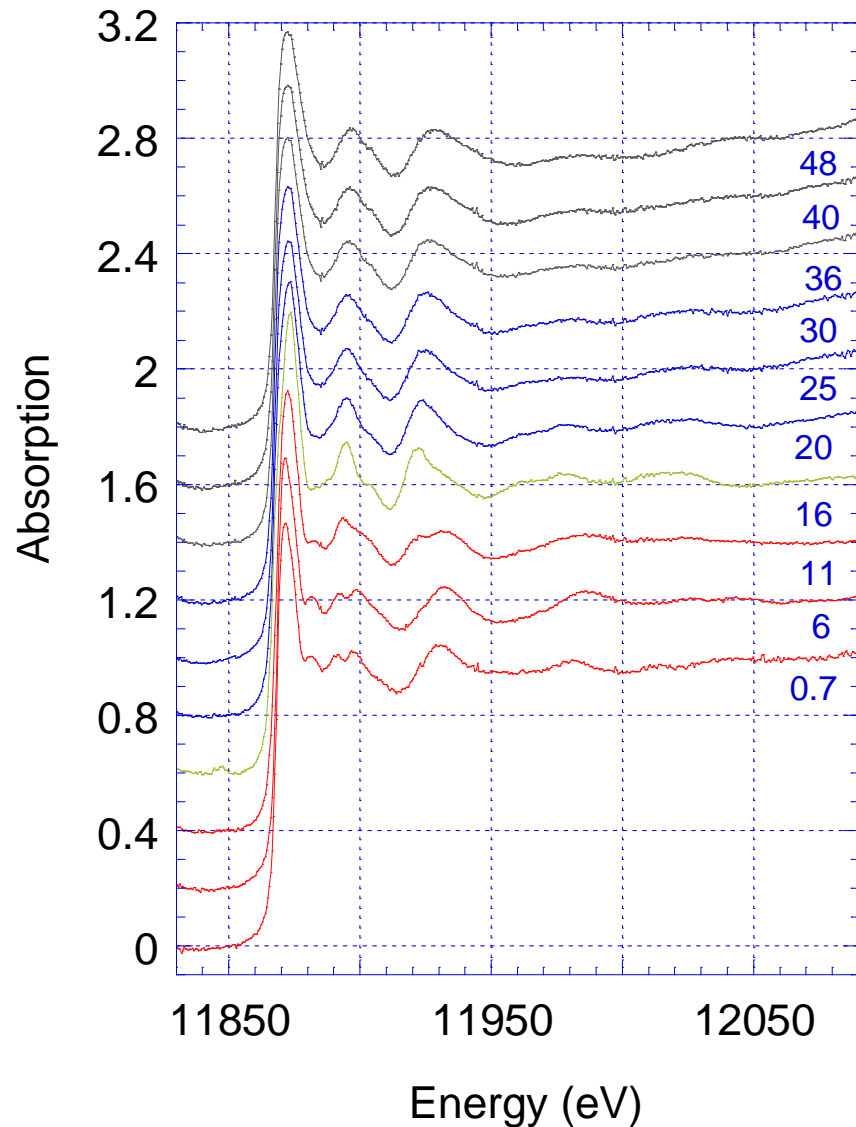
In $[2e: 3/4, 0, 0.3735(20)]$

As $[2e: 3/4, 0, 0.8776(25)]$

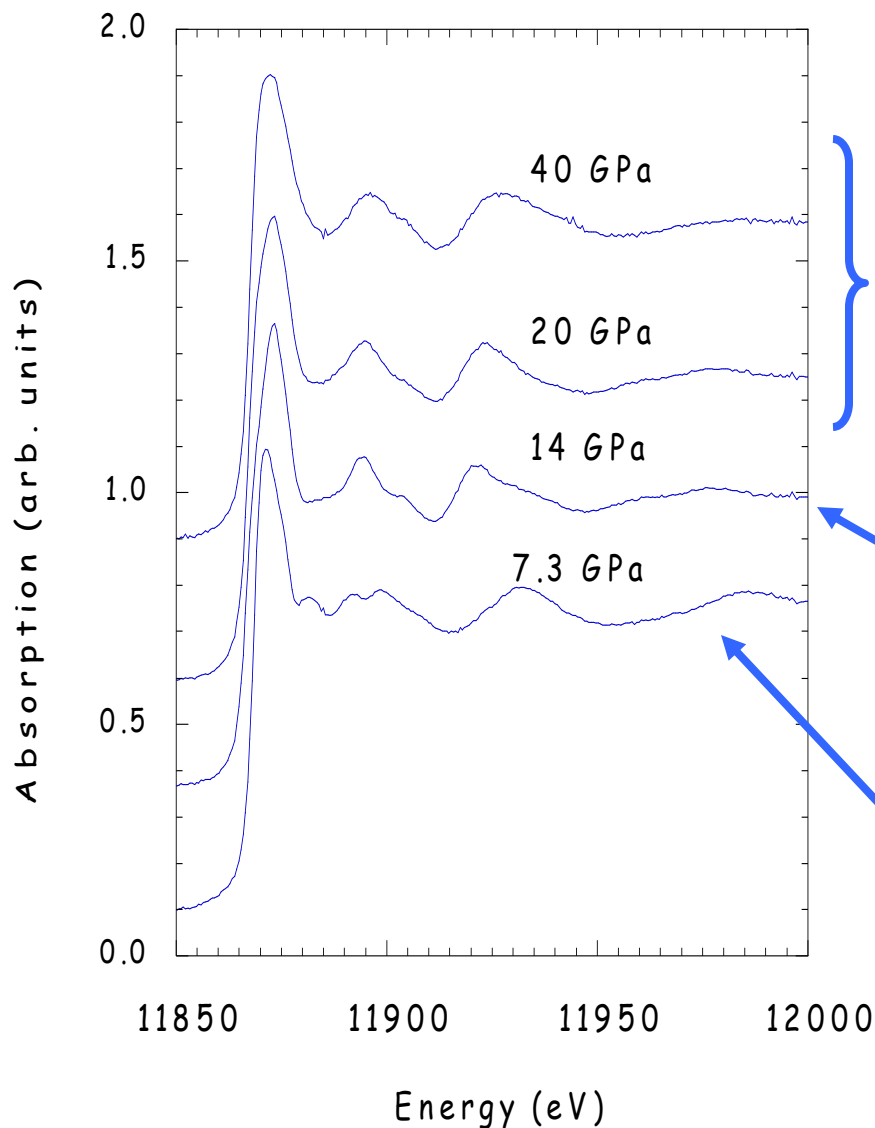
In $[2f: 1/4, 1/2, 0.1065(28)]$

As $[2f: 1/4, 1/2, 0.5570(21)]$

X-ray absorption experiment



- ID24
- As K-edge ($E=11867$ eV)
- Powdered InAs sample
- Chervin-type DAC
- standard Drukker diamonds
- 320 μm culet
- Sample thickness: 35 μm
diameter: 150 μm
- PTM Silicone oil
- fluorescence ruby method
- Si(111) Bragg polychromator
- focal spot: 30 μm \times 30 μm
- $P_{\text{max}} = 50(7)$ GPa

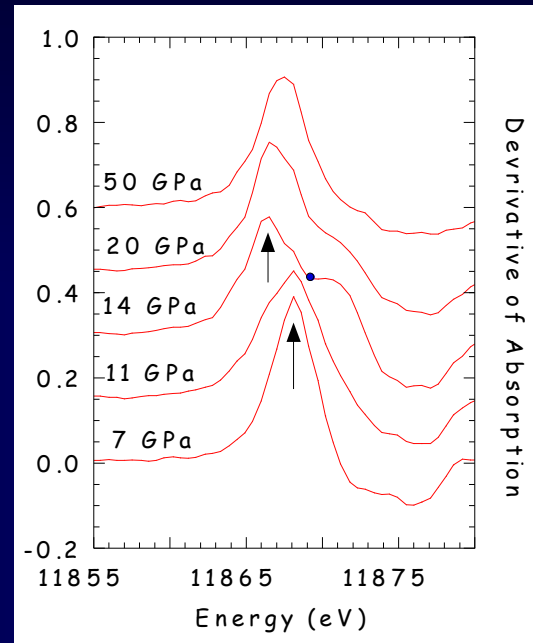
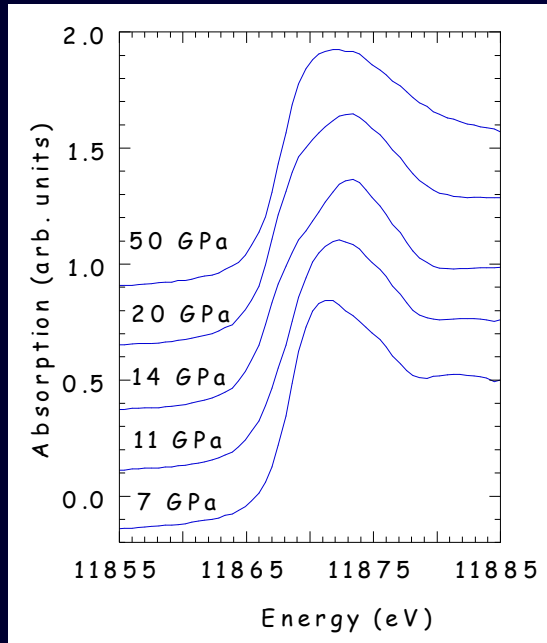


- Gradual loss of the high-energy shoulder on the first oscillation at 11.9 keV
- Decrease of the main frequency
- Overall broadening of the features

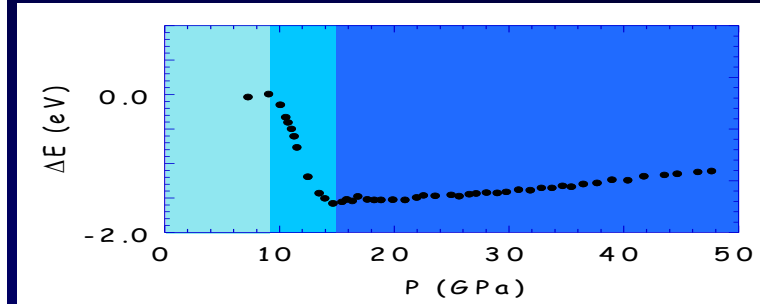
NaCl phase
(6-fold coordinated)

ZB phase
(4-fold coordinated)

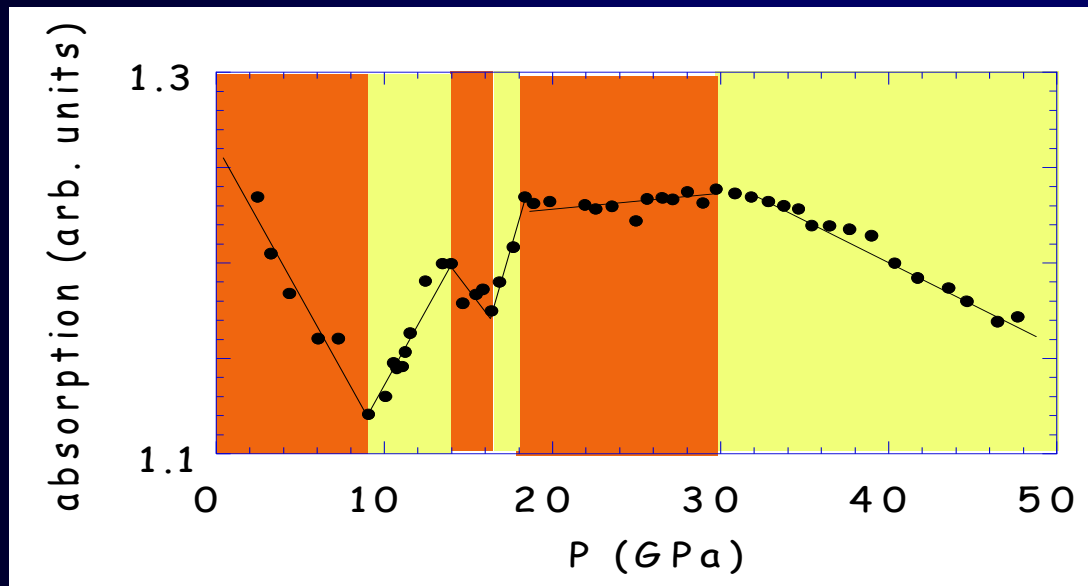
Edge region and derivative



Shift of the absorption edge ($\Delta E \sim -1.6$ eV)



It starts at 9 GPa and it is max at 14 GPa



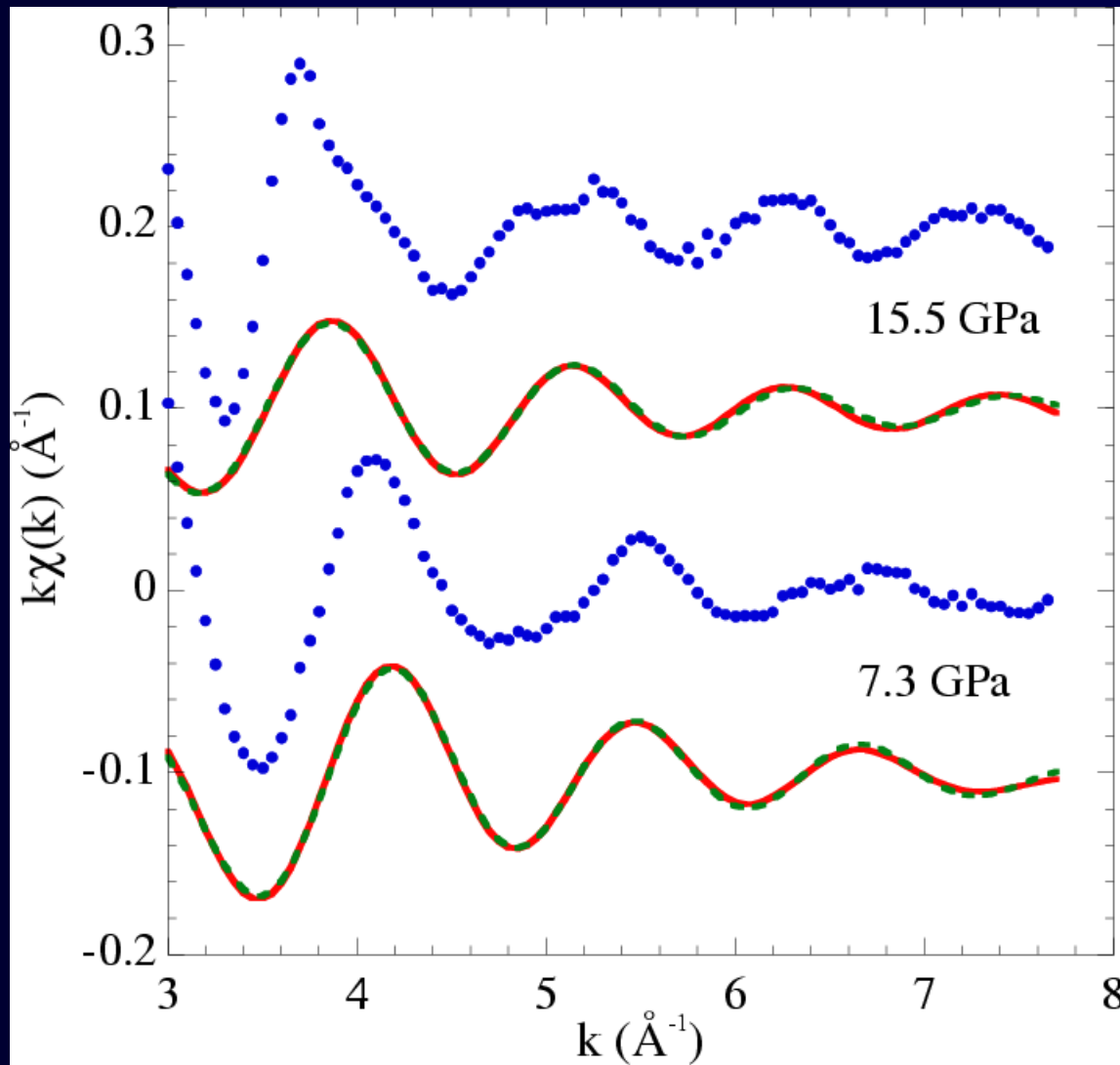
ZB (semiconductor)



NaCl (metal)

ZB to NaCl transition

The local structure around As changes dramatically at this phase transition



6 In atoms

$$R_{As-In} = 2.7 \text{ \AA}$$

4 In atoms

$$R_{As-In} = 2.5 \text{ \AA}$$

In the unexplored pressure range

- verify the non existence/existence of CsCl
- verify the existence/non existence of alternative structures:
InBi ($P4/nmm$), AuCd ($Pmma$)

In the whole pressure range

- address properly the question of chemical ordering

Chemical ordering

Ordered structure

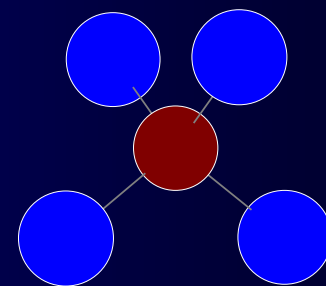
Different atomic species occupy different atomic position with an average occupancy of 1

Disordered structure

Different atomic species occupy the same atomic position with a fractional occupancy

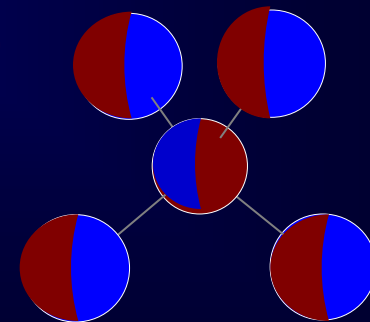
Chemically ORDERED InAs in ZB structure (space group F4-3m)

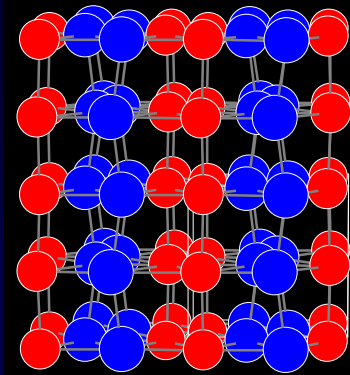
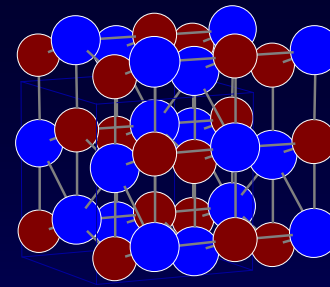
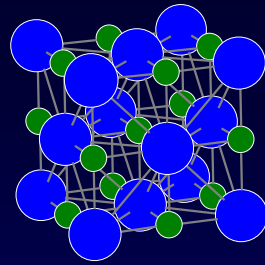
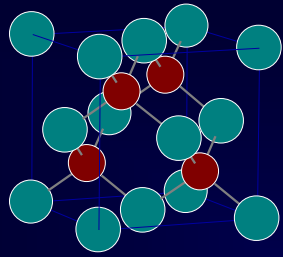
	Wyck	x	y	z	occup
In	4a	0	0	0	1
As	4c	1/4	1/4	1/4	1



Chemically DISORDERED InAs in ZB structure (space group Fd3m)

	Wyck	x	y	z	occup
In	4a	0	0	0	0.5
In	4c	1/4	1/4	1/4	0.5
As	4a	0	0	0	0.5
As	4c	1/4	1/4	1/4	0.5





F4-3m (Zincblende)



Fm3m (NaCl)



Cmcm



Pm3m

What is the short-range chemical ordering of the HP phases?

Rietveld refinement is not particularly sensitive to the level of site occupancies by each of the In or As

However

XAS can identify the degree of *sr-co* in the new phases, since it probes selectively the local environment of the photoabsorber and is sensitive to the nature of the surrounding neighbours

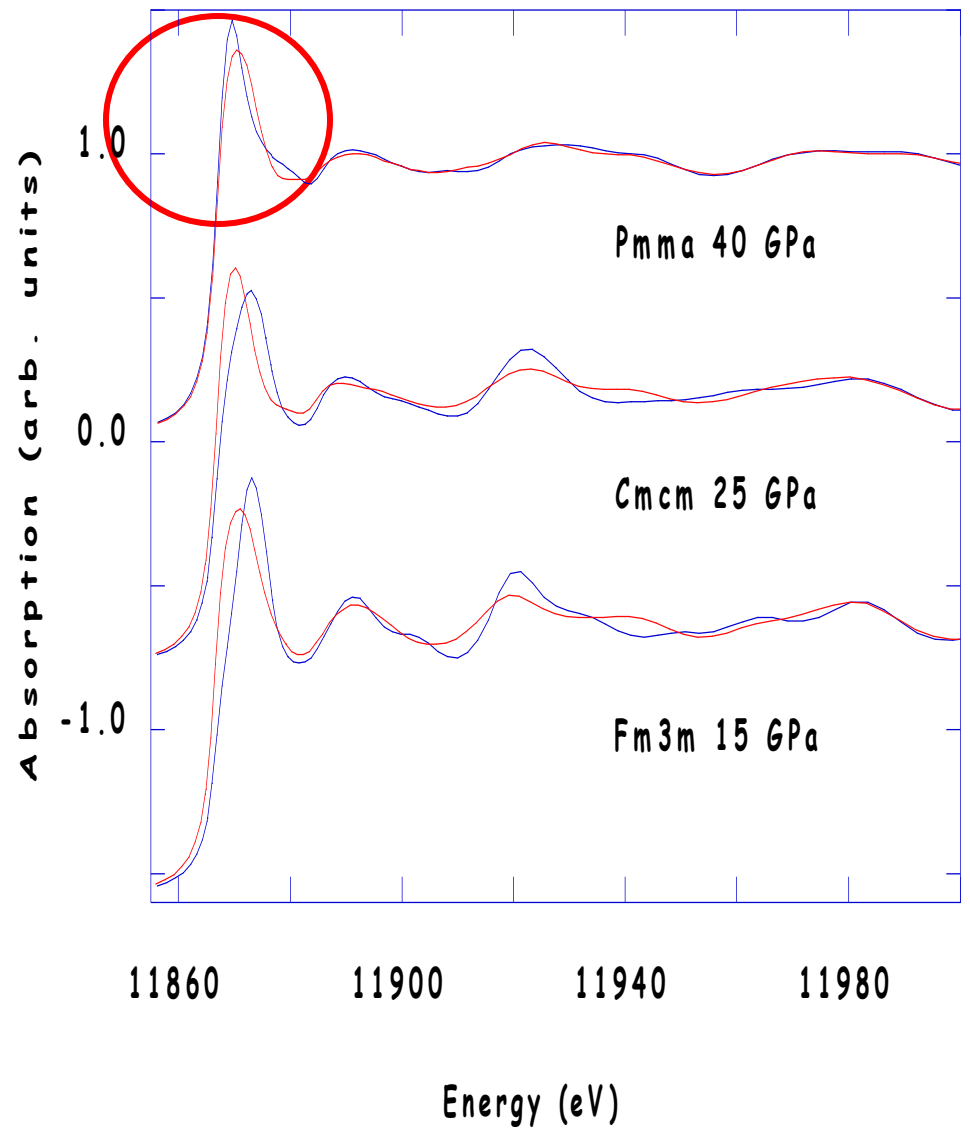
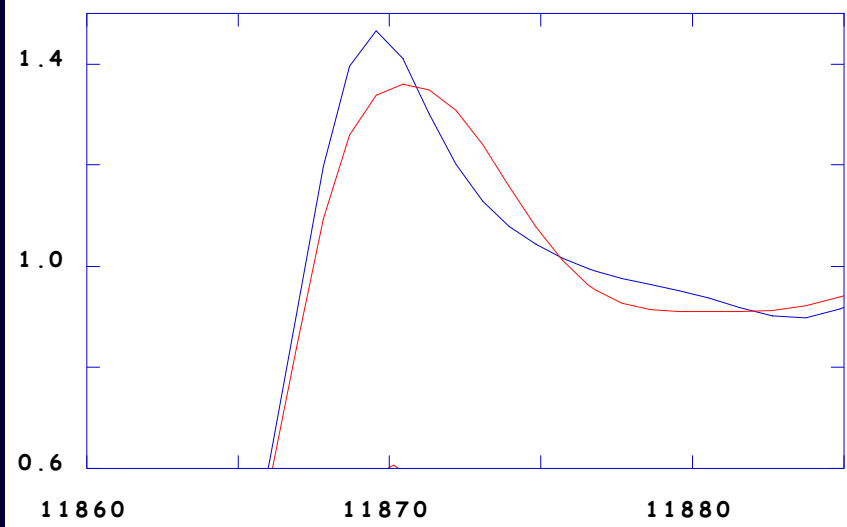
- Cluster from the structural parameters obtained from XRD data

- Full multiple scattering XANES calculations (using FEFF8) carried out on chemically ordered and disordered clusters

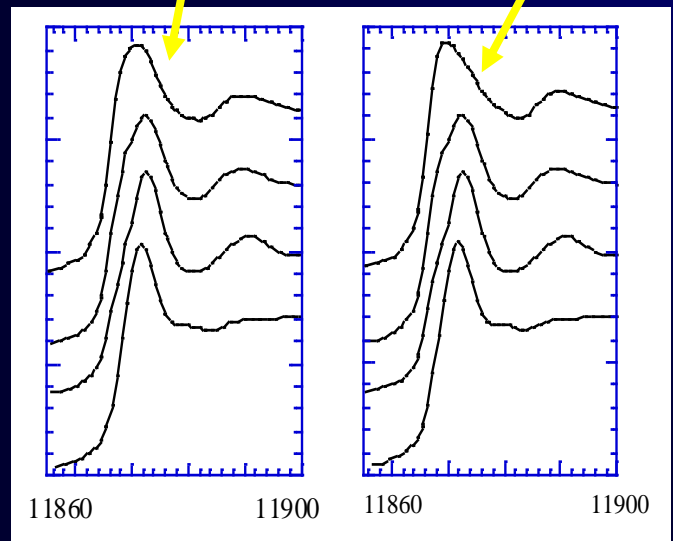
co clusters: each coordination shell determined by the group symmetry and by the internal site occupation of each atom

cd clusters: obtained by randomly mixing the chemical composition of each coordination shell in the ordered cluster

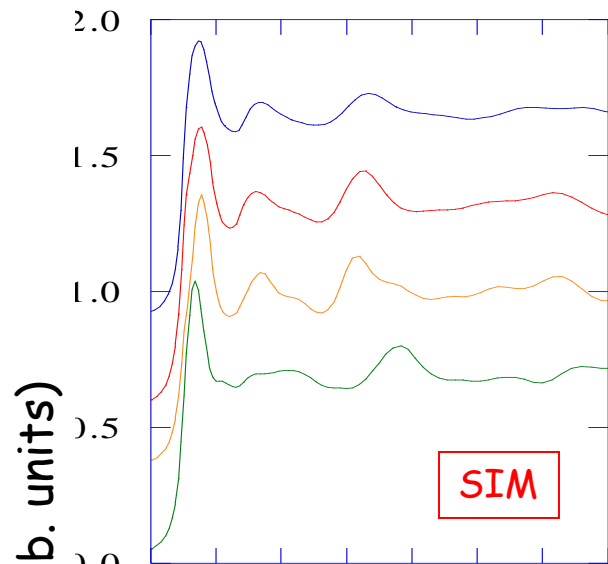
- Comparison of the calculations with our data



sr-co Cmcm/sr-cd Pmma
 sr-co Cmcm/sr-co Pmma



Comparison with the data

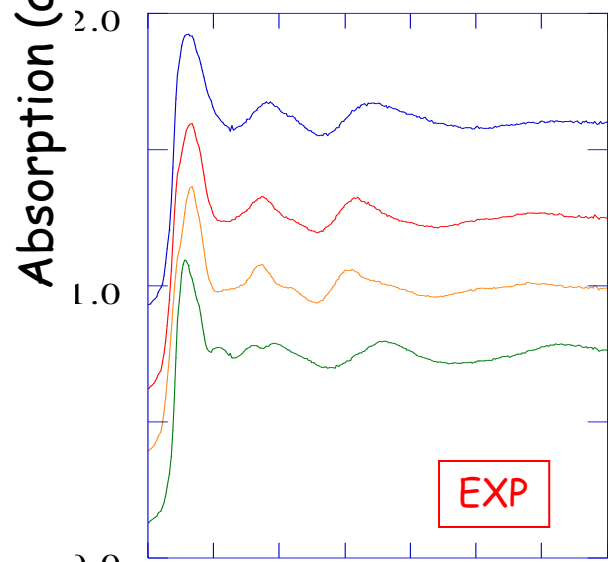


sr-co Cmc m + sr-cd Pmma

sr-co Cmc m

sr-co Fm3m (NaCl)

F4-3m (ZB)

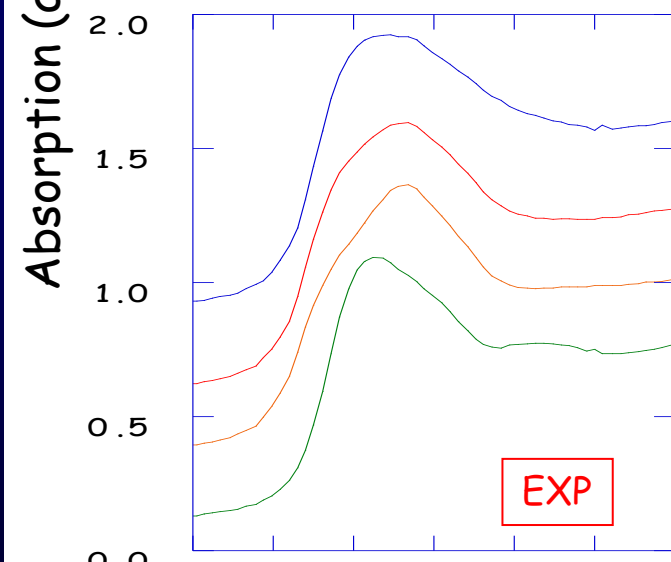
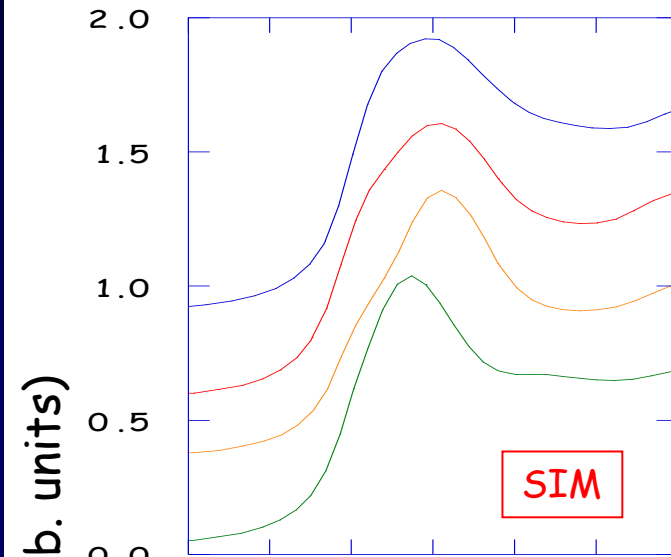


48 GPa

19 GPa

14 GPa

7.3 GPa



11860

11880

Energy(eV)

Energy(eV)

We performed combined XRD and XAS measurements on InAs up to 80(15) GPa and 50(7) GPa

- The high pressure phase is not CsCl. This result is in agreement with recent theories based on phonon dynamics calculations according to which the CsCl phase, even though statically stable, is dynamically unstable
- We find that the HP phase has a Pmma symmetry. Our structure is different with respect to that (AuCd-like) found by the same theories, but it shares the same symmetry (Pmma).

- AuCd: Au atoms occupy only the $2e$ positions $\pm(3/4, 0, z_1)$
Cd atoms occupy only the $2f$ positions $\pm(1/4, 1/2, z_2)$
- Our refinement of InAs gives atomic positions at
 $(3/4, 0, z_1), (3/4, 0, z_2), (1/4, 1/2, z_3), (1/4, 1/2, z_4)$

This difference arises from the starting point:

- Our Pmma derives from the observed Cmcm
- The calculated Pmma derives from a distortion of a cubic CsCl

- XAS also gives information about the degree of chemical ordering of all the HP phases:

All the phases below P_mm_a are short range chemically ordered

The HP data (above 30 GPa) cannot be described by a pure C_mc_m local environment, be it ordered or disordered, but it requires a contribution of a chemically disordered P_mm_a environments

CONCLUSIONS

We experimentally examined a theoretical prediction concerning the phase stability of ZB semiconductors

We proved that the combination of XRD and XAS is essential to fully describe the new phases

In particular InAs transforms to a short-range chemically disordered Pmma phase, that persists, at least, up to 46 GPa

A structure with *Pmma* symmetry has recently been shown to be a direct consequence of a phonon instability of *CsCl*

Although we cannot exclude at higher pressures the presence of a *Pmma*-distorted *CsCl*-like structure, this finding suggests the the *CsCl* phase is likely not to occur as a HP phase in InAs,

and could have important implications for a large class of semiconductors that are all expected to transform to *CsCl* at HP

Acknowledgements

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Olivier Mathon

Technical staff of ID24

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