



| The European Synchrotron

Part III

Examples of Applications

Vera Cuartero (Sakura Pascarelli)

European Synchrotron Radiation Facility, Grenoble, France

Examples of applications

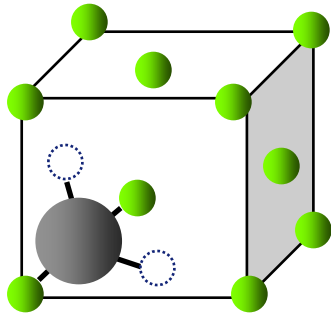
- Major historical EXAFS breakthroughs
- Selection of recent results at the ESRF

Major historical EXAFS breakthroughs

- **Atomic scale structure in solid solutions**
- **Lattice distortions around impurities in dilute alloys**
- **Structure of amorphous materials**

Solid solutions: Vegard's law and the Virtual Crystal Approximation

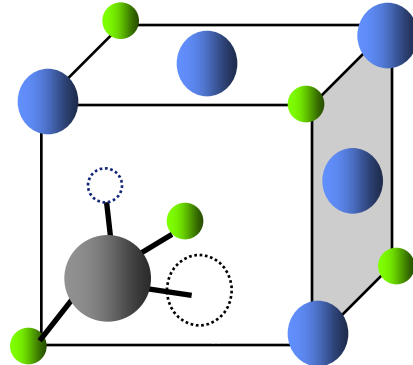
AC



a_{AC}

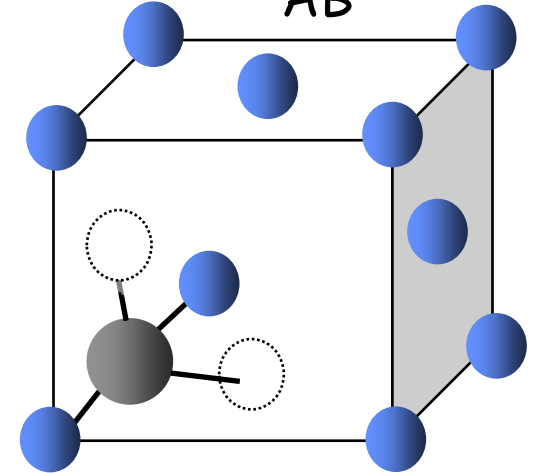
$$R_{AC}^0 = \frac{\sqrt{3}}{4} a_{AC}$$

$AB_x C_{1-x}$



$a(x)$

AB



a_{AB}

$$R_{AB}^0 = \frac{\sqrt{3}}{4} a_{AB}$$

VCA assumes that all atoms occupy average lattice positions defined by X-ray lattice constants (disorder 1st principle calculations)

VCA: $R_{AB}(x) = R_{AC}(x) = \frac{\sqrt{3}}{4} a(x)$

Vegard's Law: $a(x) \approx a_{AC} + (a_{AB} - a_{AC})x$

Atomic scale structure in solid solutions

VOLUME 49, NUMBER 19

PHYSICAL REVIEW LETTERS

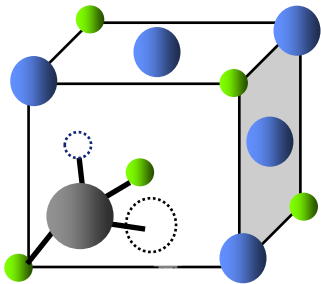
8 NOVEMBER 1982

Atomic-Scale Structure of Random Solid Solutions: Extended X-Ray-Absorption Fine-Structure Study of $\text{Ga}_{1-x}\text{In}_x\text{As}$

J. C. Mikkelsen, Jr., and J. B. Boyce

Xerox Palo Alto Research Centers, Palo Alto, California 94304

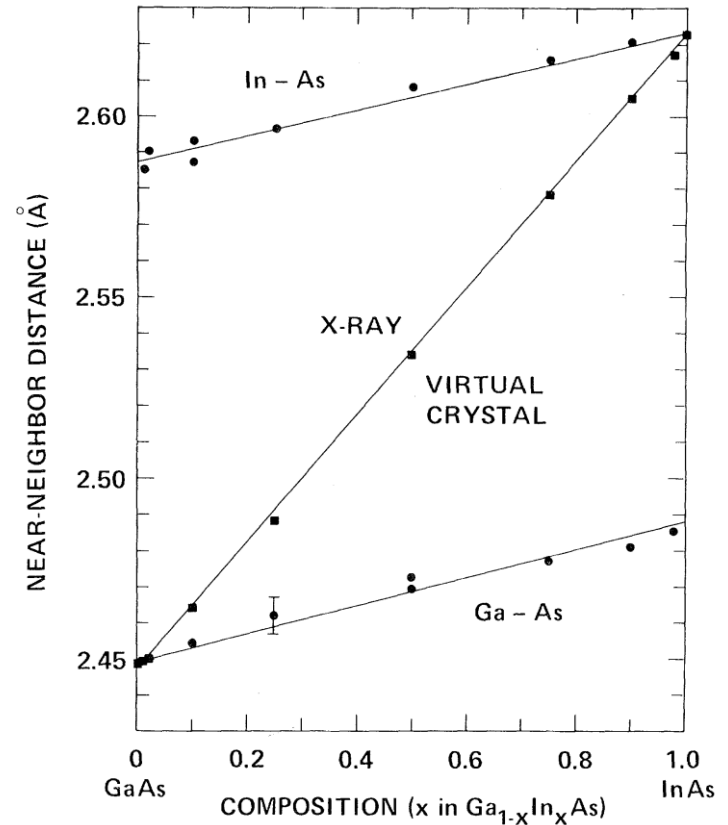
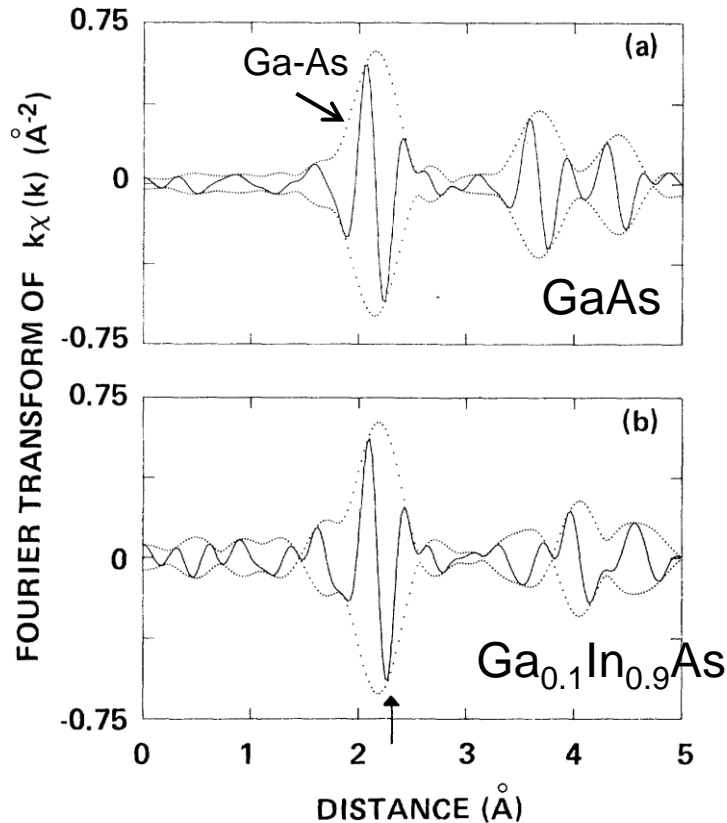
(Received 23 August 1982)



- Calculations of the properties of solid solutions have often relied on simple approximations (i.e. VCA)
- Atomic scale structure not well understood: XRD averages structure over distances that are large on the scale of a lattice constant.

- With the use of the VCA, properties of alloys may be calculated whether or not the alloys's lattice constant varies linearly with composition between those of the end members (follows Vegard's law)

Atomic scale structure in solid solutions



- GaAs and InAs bonds change only by 0.04 \AA in whole x range !!
- Contradicts underlying assumptions of VCA
- Important distortions within unit cell accommodated by bond angle distortions

Lattice distortions around impurities in dilute alloys

PHYSICAL REVIEW B

VOLUME 44, NUMBER 18

1 NOVEMBER 1991-II

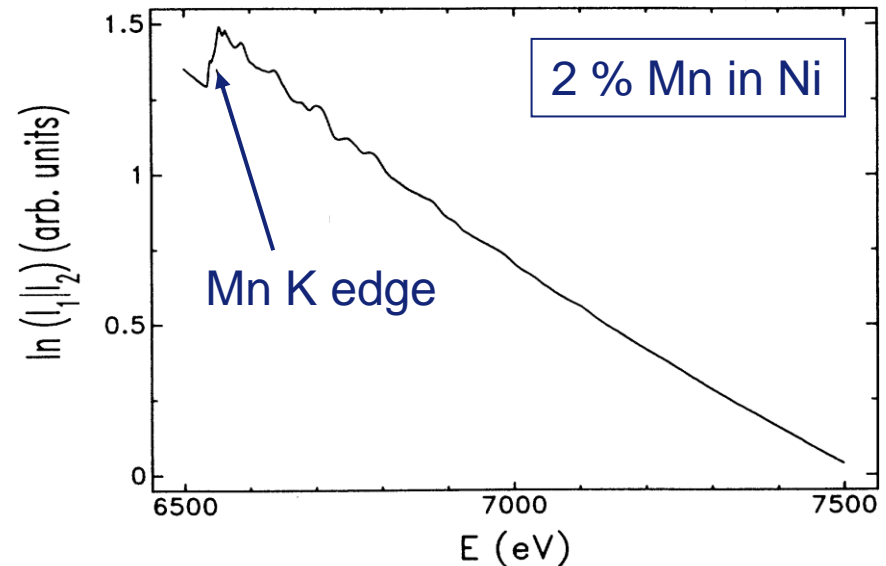
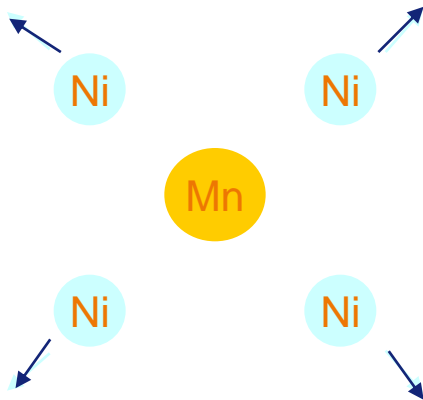
Lattice distortion of solute atoms in metals studied by x-ray-absorption fine structure

U. Scheuer and B. Lengeler

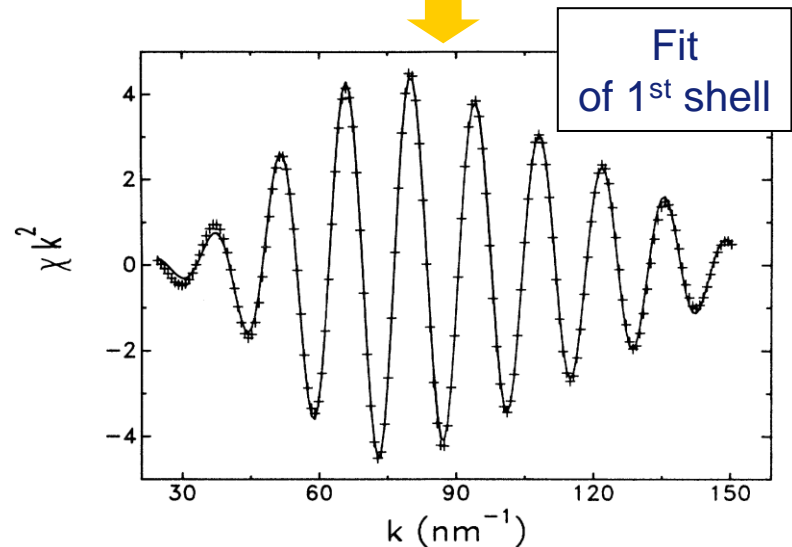
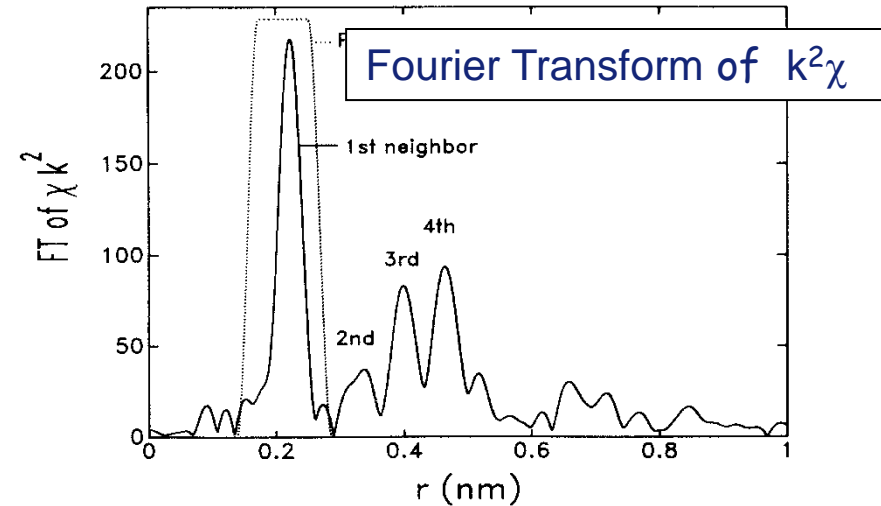
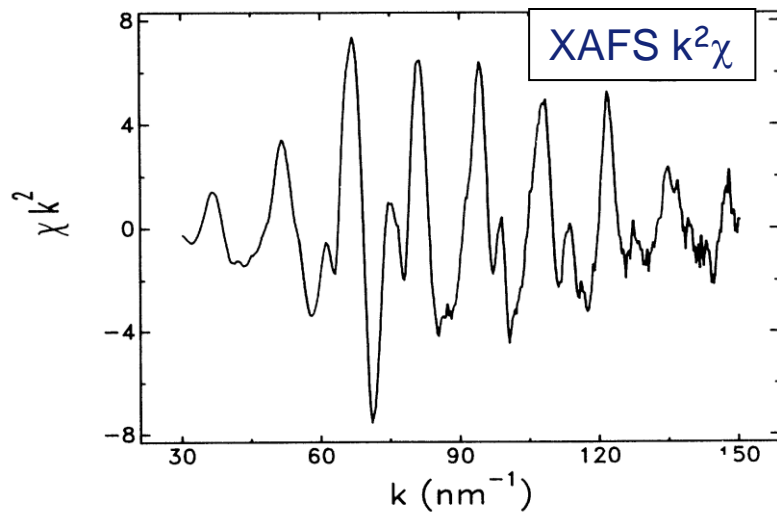
Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany

(Received 14 February 1991)

- systematic study of substitutional impurities in fcc and bcc metals
- important shifts in first shell bond length detected



Lattice distortions around impurities in dilute alloys

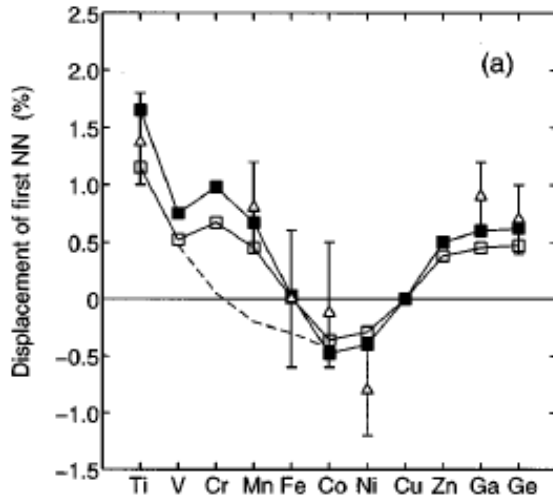


Mn shifts 12 Ni nearest neighbors outwards by:

$$0.023 \pm 0.004 \text{ \AA}$$

(1 % of distance)

Comparison to band structure calculations



□ ■ Band structure calculations
 △ XAS

N. Papanikolaou et al., Phys. Rev. B **55**, 4157 (1997)

➔ *ab initio* study of structural changes around point defects in transition metals within the framework of the KKR Green function method.

Displacements δ has two contributions:

1. **Valence difference** between impurity and host

- change of charge density in impurity cell
- parabolic dependence $\delta(Z)$

2. **Magnetoelastic contribution** Cr, Mn, Fe in Cu → majority and minority bands are split

- large magnetic moment
- low DOS at Fermi level
- low binding energy
- increased interatomic distance

Structure of amorphous materials

VOLUME 35, NUMBER 9

PHYSICAL REVIEW LETTERS

1 SEPTEMBER 1975

New Method to Measure Structural Disorder: Application to GeO₂ Glass*

D. E. Sayers and E. A. Stern

Physics Department, University of Washington, Seattle, Washington 98195

and

F. W. Lytle

Boeing Company, Seattle, Washington 98124

(Received 24 March 1975)

From X-ray scattering experiments on glasses:

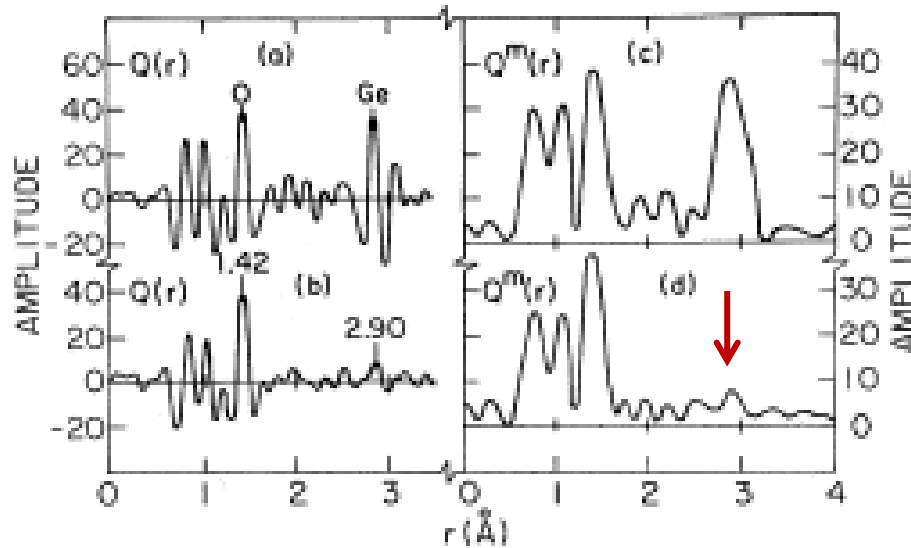
Random network model:

GeO₂ tetrahedra connected by bridging Oxygen with deviations about bond angles such that long range periodicity destroyed

Microcrystalline model:

GeO₂ composed of 15-20 Å crystallites – too small to give rise to sharp diffraction peaks

EXAMPLES OF APPLICATIONS



crystalline-GeO₂

glass-GeO₂

	r_1	$\Delta\sigma_1$	N_1	r_2	$\Delta\sigma_2$	$\theta_{\text{Ge-Ge}}$ (deg)
Glass	1.74	0.00 ± 0.018	4.0 ± 0.08	3.15	0.077 ± 0.014	130 ± 6.5
Crystalline (hexagonal)	1.74	...	4	3.15	...	130

EXAFS determines:

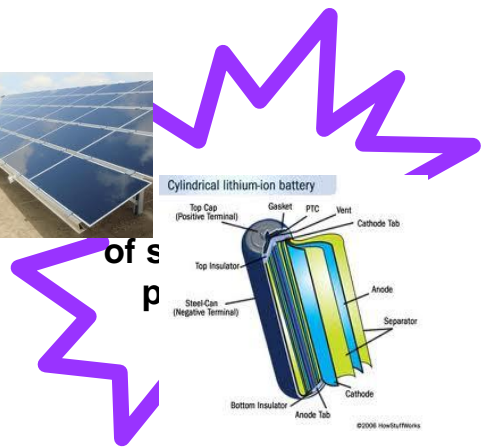
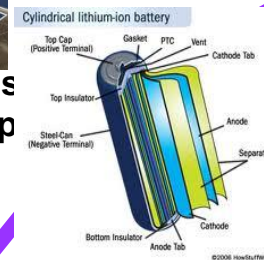
- identical 1st shell coordination number (to within 2%)
- increased disorder on Ge-Ge shell
- microcrystalline model definitively ruled out

WHAT CAN XAS BE MEASURED ON?

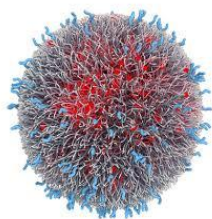
... just about almost anything and with most elements of the periodic table



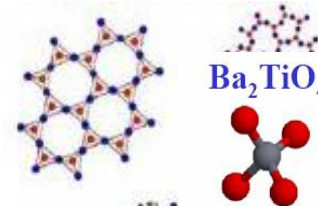
Art: Cultural Heritage



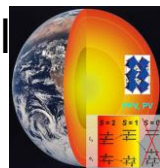
Biology



Material Science



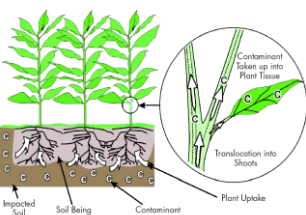
Environmental Science
Geology



Chemistry
Catalysis



Local probe!
Physics

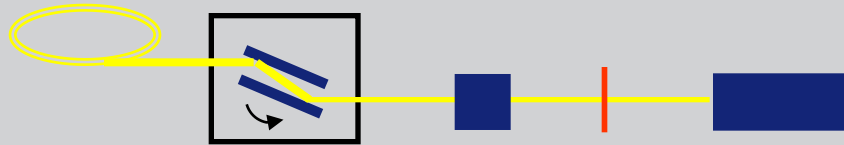


Selection of recent results at the ESRF

- **XAFS beamlines at the ESRF**
- **BM23: General Purpose EXAFS**
 - Chemistry of Xe at extreme conditions
 - As sequestration by organic sulphur in peat
 - Ligand discrimination in biological complexes
- **ID24: Energy Dispersive XAS**
 - Mechanism and kinetics of Pt sintering and redispersion
 - Melting of Fe at the Mbar: first XAS results
 - Single shot EXAFS on dynamically compressed Fe

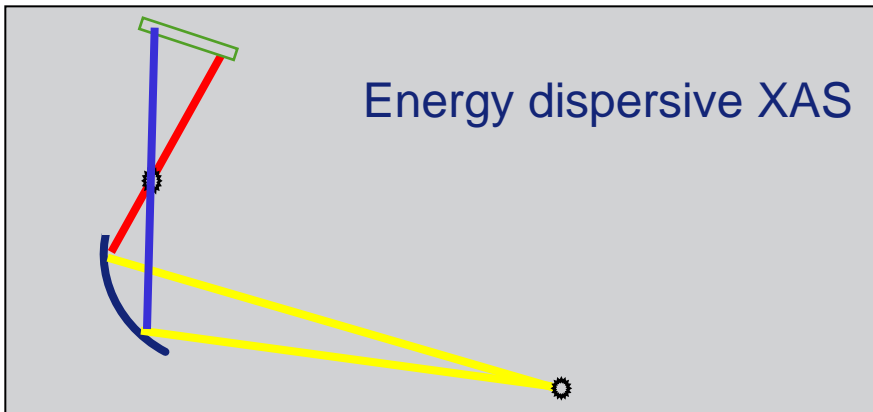
XAFS beamlines at the ESRF

Energy scanning XAS

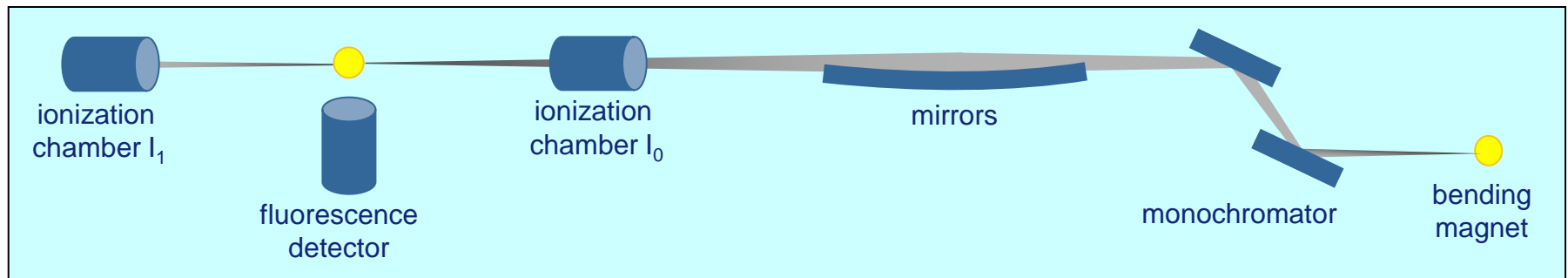


- ID12, ID26, ID32, ID20, etc ..
- BM23
- CRGs :
BM01, BM08, BM20, BM26, BM30

Energy dispersive XAS



- ID24

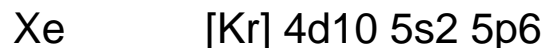


➤ An instrument to cover needs in area of conventional XAS

- large energy range 4.5 – 75 KeV
- excellent S/N ratio over a large k-range
- versatility
- high automation level
- 3 μm x 3 μm spot

Main Applications: Materials Science, Chemistry, Catalysis, Geochemistry, Environment, Condensed Matter Physics

Understand abundance of Xe in atmospheres of giant planets
 Deficiency in Earth and Mars atmospheres

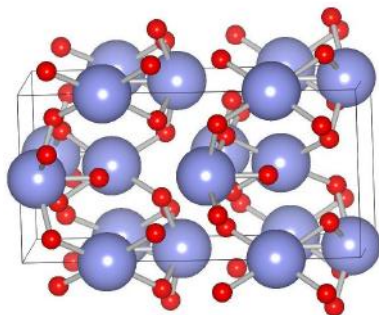


- “Heavy rare gases reluctant to form bonds”
- Xe oxides not stable at ambient P, T
- **Xe-O interactions at HP**



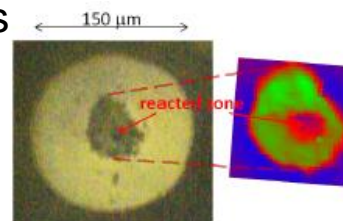
Stability of xenon oxides at high pressures

- None of the predicted phases observed
- XRD alone unable to determine oxide structure

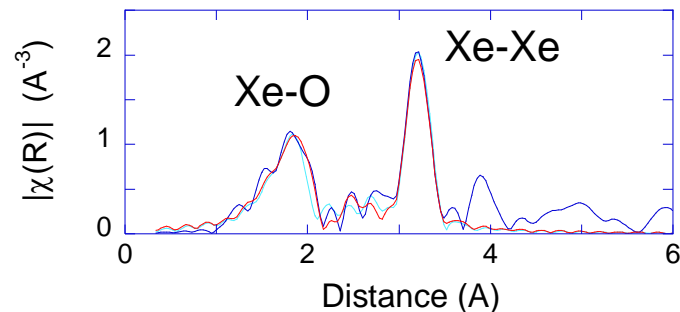
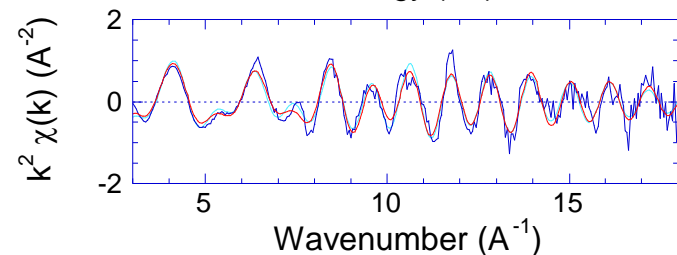
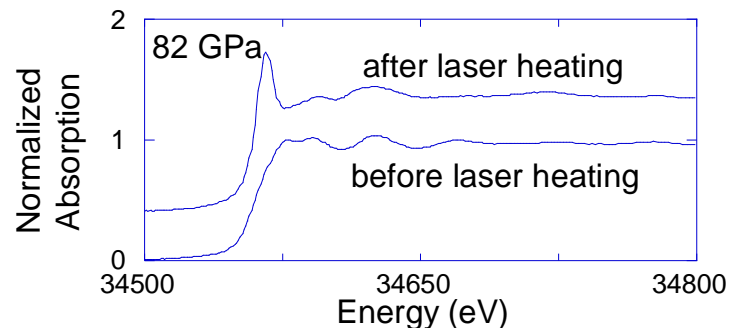


Xe₂O₅
 P4/ncc space group

Dewaele (submitted)



BM23



BM23

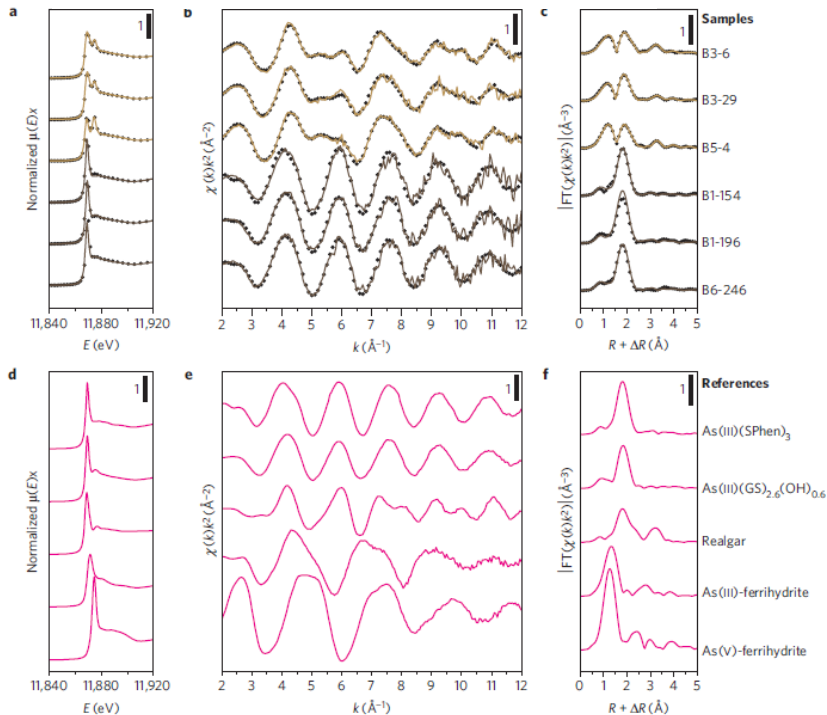
Wetlands cover more than 6% of the global ice-free land area

Play major role in storage, transformation, mobilization of trace elements

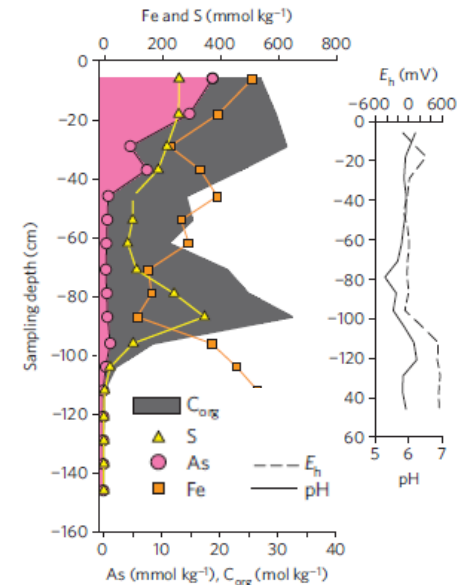
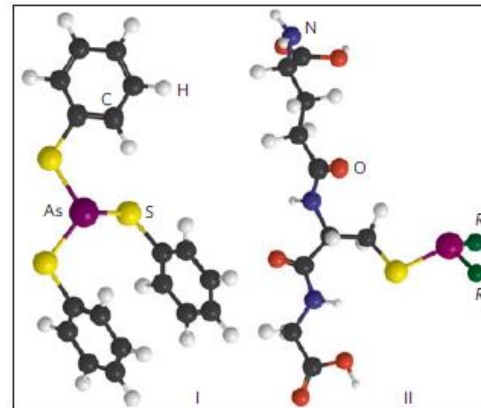
Sorption of As to peat thought to suppress As mobility, but binding mechanisms unknown

Does natural organic matter serve as geochemical trap for As ?

As K- EXAFS (3-1000 ppm)



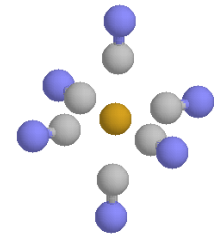
Trap: covalent bonds between As³⁺ and organic S groups



1. Spectroscopic evidence for As binding to peat
2. Identified dominating binding mechanism
3. Quantified extent of As binding to peat

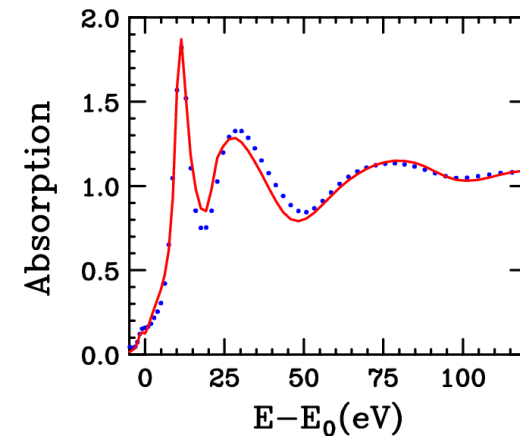
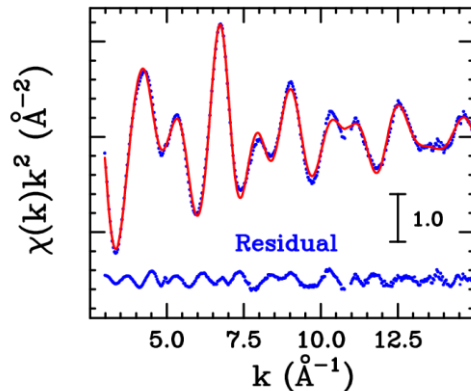
Full quantitative multiple scattering analysis of XAS: Application to $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$

- Example of application of MXAN -



- Fitting procedures now possible also in XANES region
- Higher sensitivity to geometry and chemical nature of scattering atoms
- For biological systems, EXAFS not very sensitive to number and chemical nature of ligands

➤ Combined quantitative multiple scattering analysis of EXAFS and XANES



K. Hayakawa et al., J. Am. Chem. Soc. 126, 15618 (2004)

$K_3Fe(CN)_6$ in water solution

- Quantitative analysis using CN, CO and NO as ligands

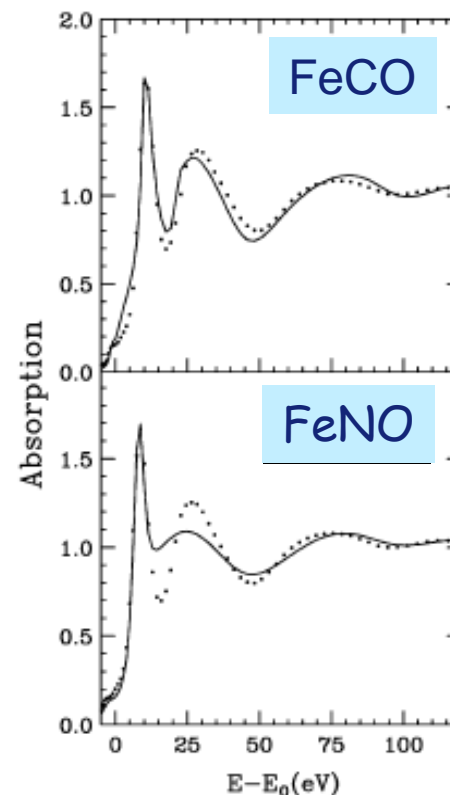
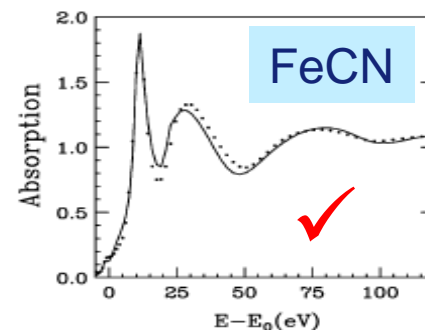
EXAFS: cannot discriminate (residuals within 3%)

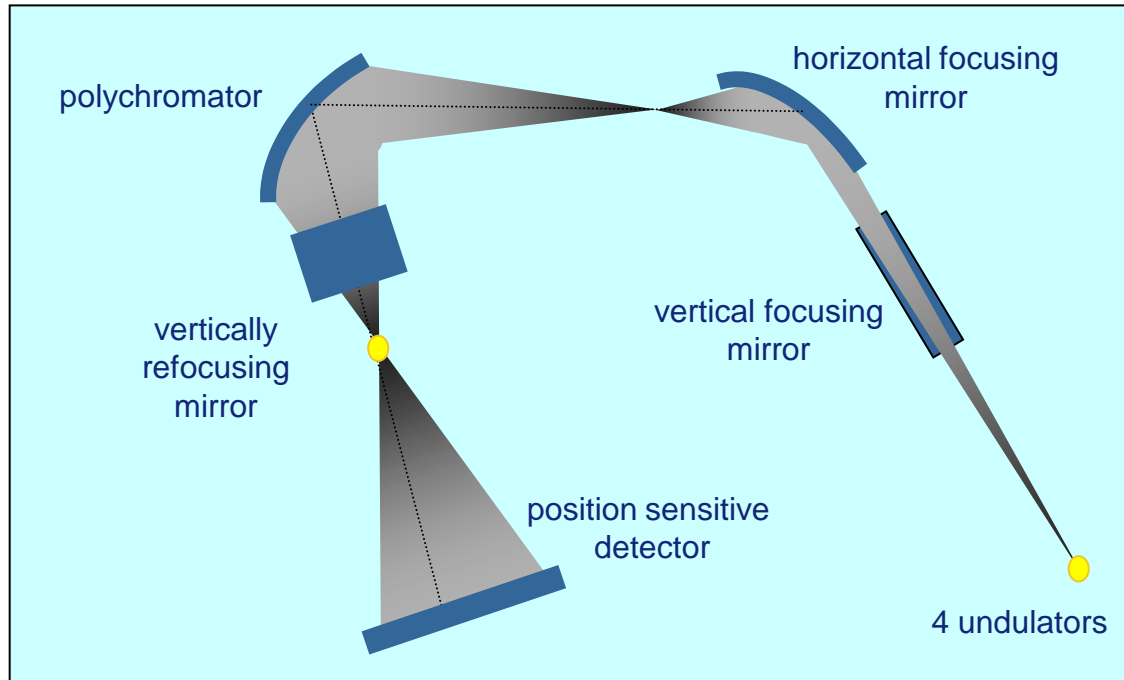
XANES: can discriminate CN, CO or NO

Table 2. Structural Parameters for Fe^{3+} Complexes Obtained from the MXAN Data Analysis

	CN	CO	NO
R_{Fe-L_1} (Å)	1.93(1)	1.94(1)	1.92(1)
$R_{L_1-L_2}$ (Å)	1.15(1)	1.11(1)	1.16(1)
$\theta_{Fe-L_1-L_2}$ (deg)	180(1.3)	180 ^a	180 ^a
R_{tq}	20.8	28.8	50.0

- First quantitative demonstration of the ability of XANES in ligand discrimination for both first and second shell coordinating atoms.





An unprecedented investment into high brilliance EDXAS

➤ Provide the users' community a unique instrument

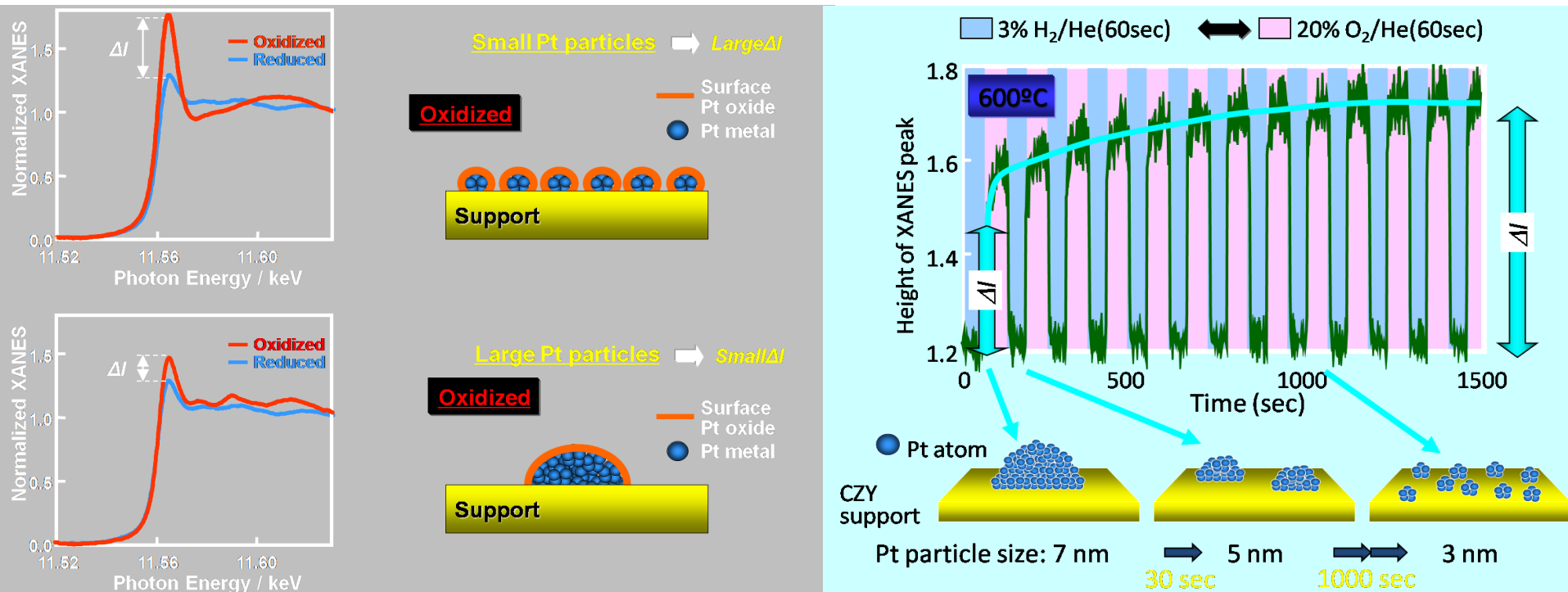
- small focal spot \sim few μm
- high flux ($\sim 10^{14}$ ph/s)
- fast acquisition (100 ps)

Main Applications: Earth and Planetary Science, Solid State Physics, Chemistry, Catalysis, Magnetism, Materials Science

ID24

5 years of research and development with Toyota

Design of completely new sample environment to comply with Toyota's needs



Establish mechanism and kinetics of Pt sintering and redispersion

Nagai Angew. Chemie 2008

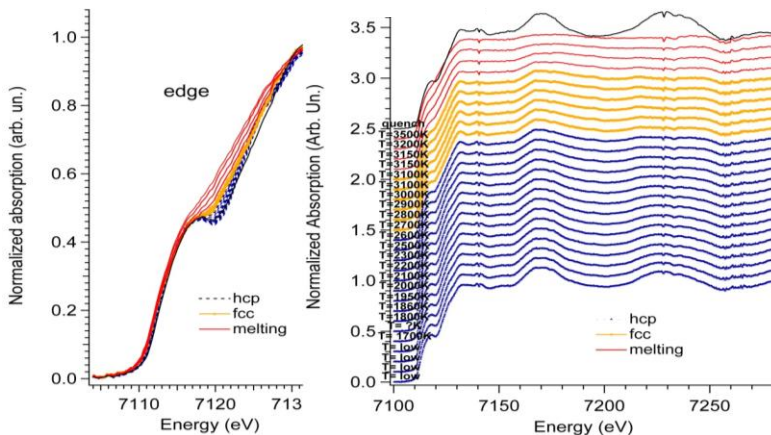
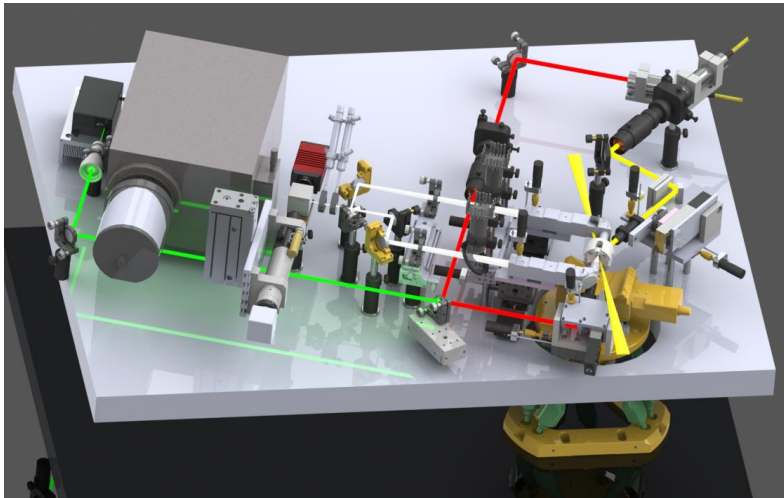
MELTING OF FE AT THE MEGABAR: FIRST XAS RESULTS

Temperature at the inner core boundary expected to be close to melting point of Fe at 330 GPa.

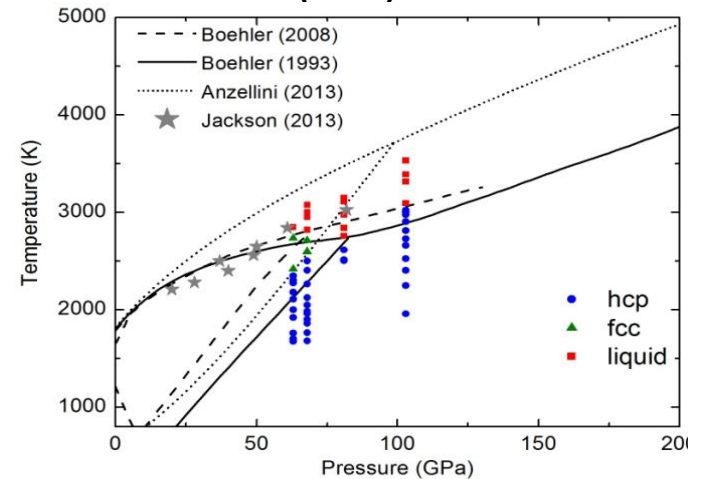
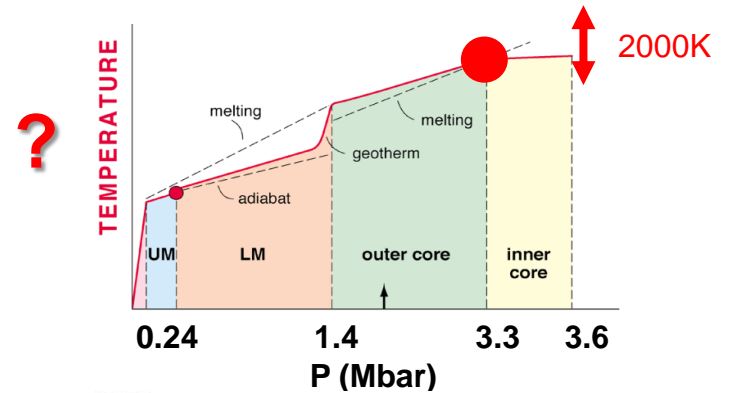
Large controversy on melting temperature of Fe at these extreme pressures

ID24

(Boehler, Nature 1993; Anzellini, Science 2013)



Anzellini (in preparation)



Aquilanti, Boehler et al., PNAS (2015)

SINGLE SHOT EXAFS ON DYNAMICALLY COMPRESSED FE

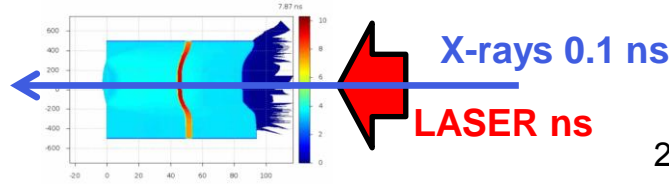
ID24



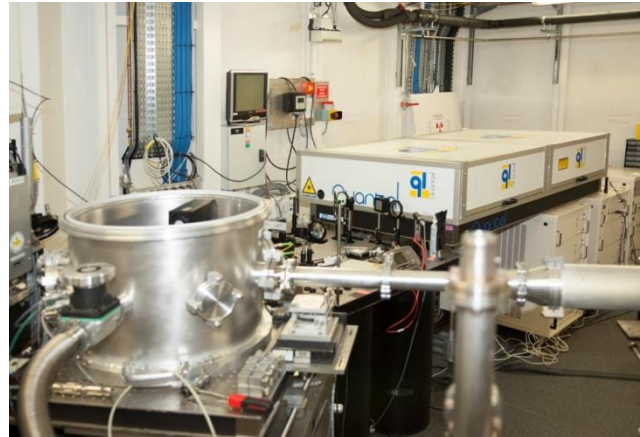
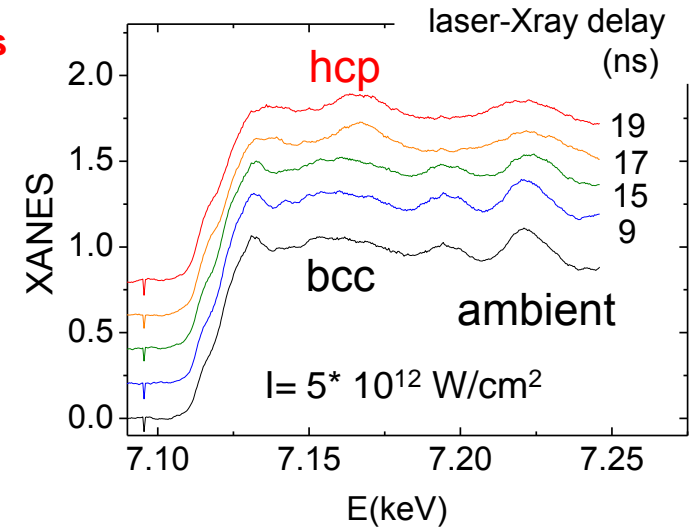
Institute of Shock Physics



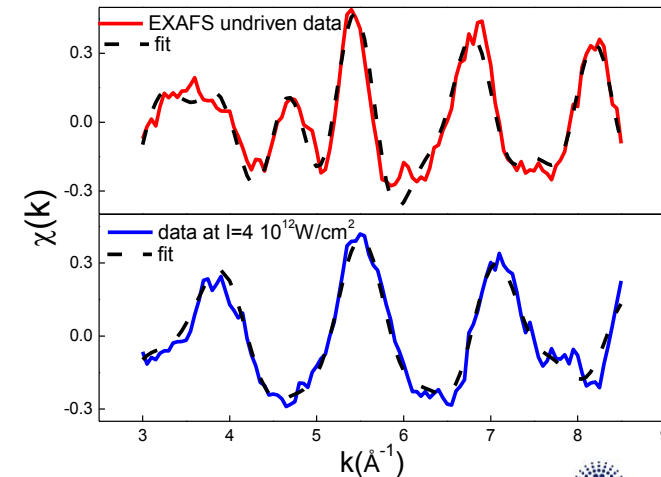
Science & Technology Facilities Council



Single bunch XANES

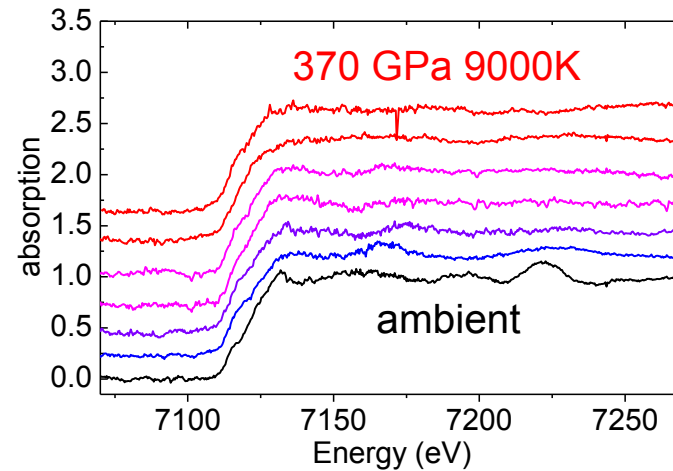


Single bunch EXAFS

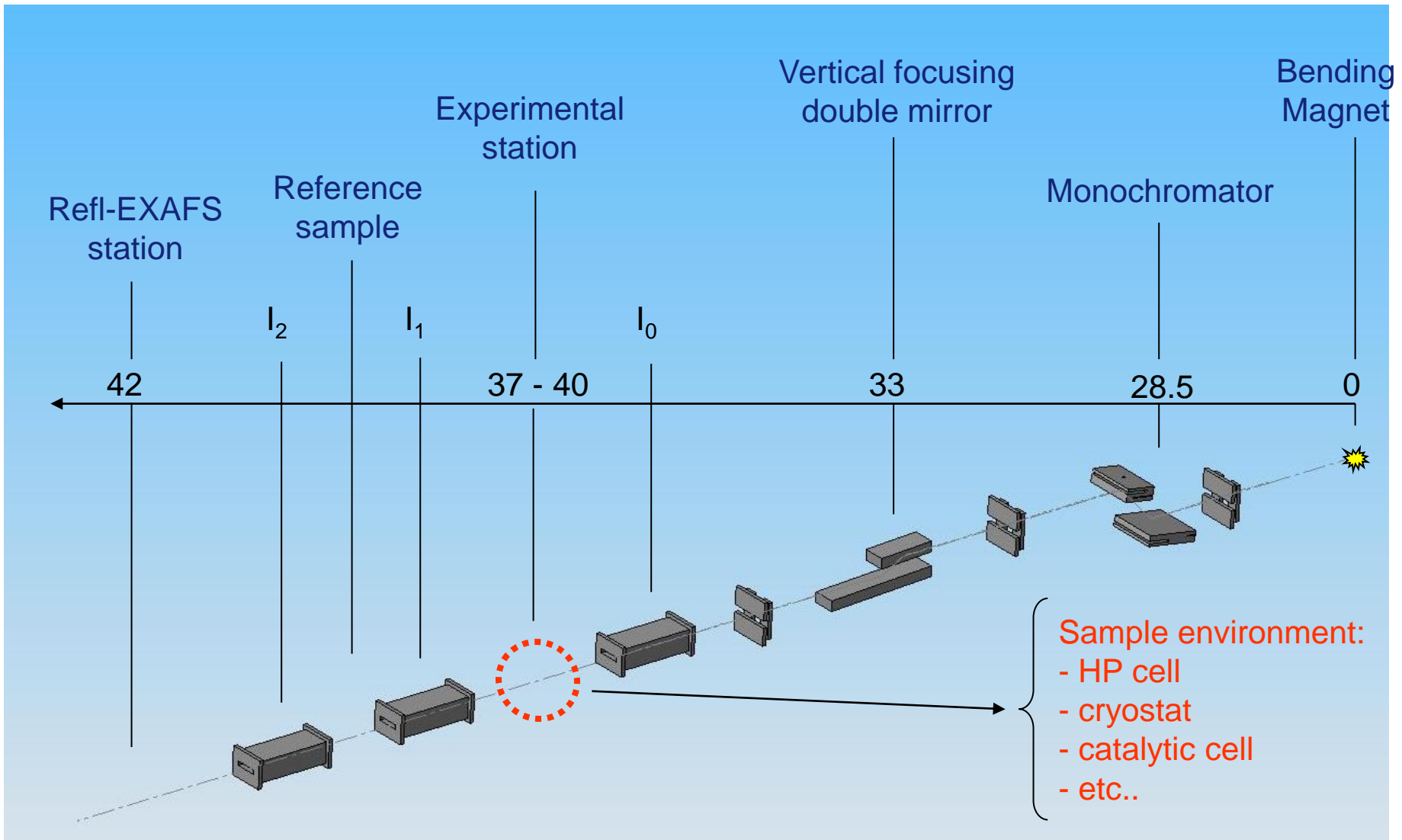


- 10 ns pulse
- energy: 30 J
- focus: 90 – 400 μm
- P ~ 4 Mbar T ~ 1.0 eV

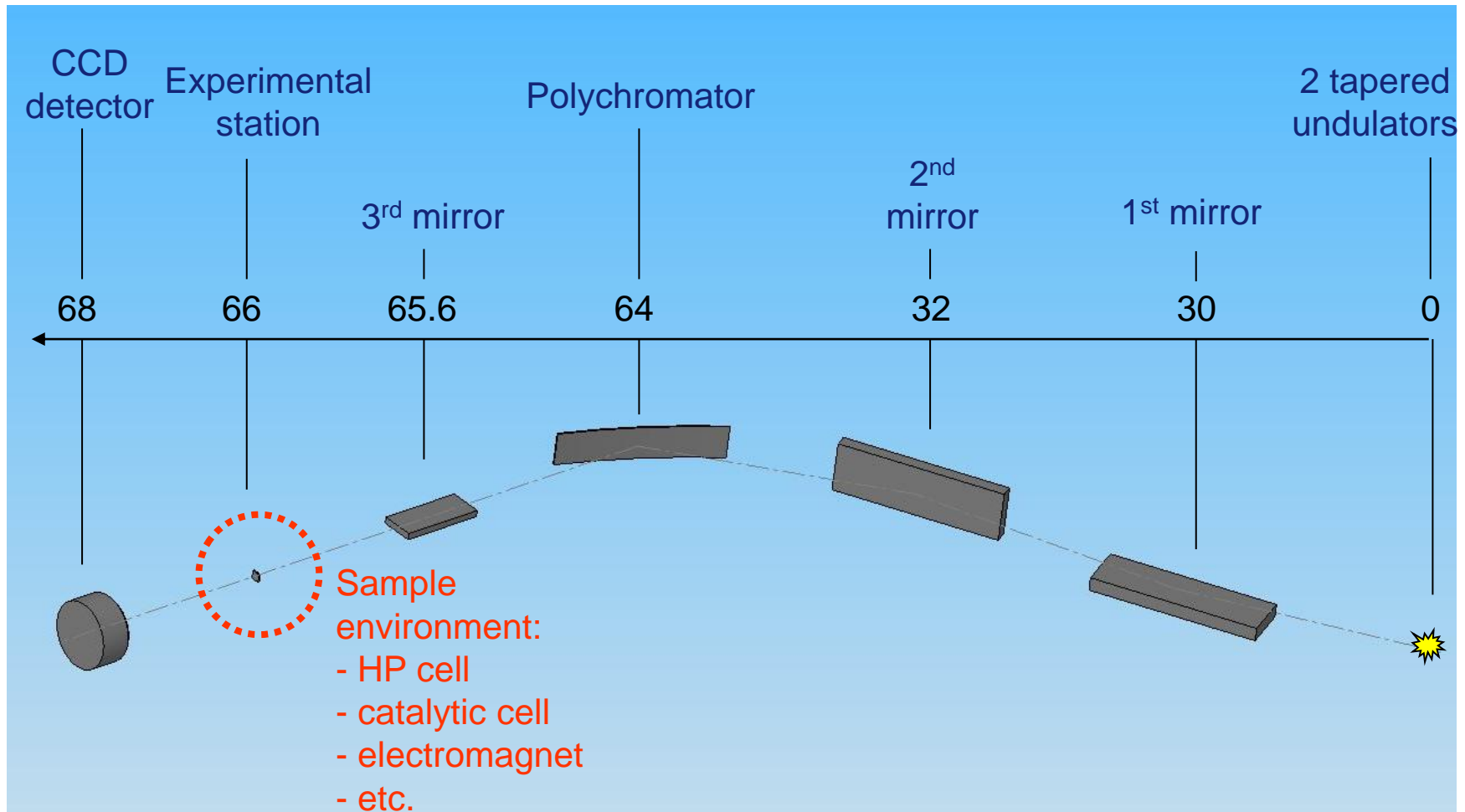
I(W/cm ²)	P(GPa)	T(K)
1 10 ¹³	160	2800
2 10 ¹³	270	7000
3 10 ¹³	320	8000
5 10 ¹³	370	10000



BM23 @ ESRF



ID24 @ ESRF



More information: web links

International XAFS Society: <http://ixs.iit.edu/>

Tutorials and other Training Material: <http://xafs.org/Tutorials>

→ <http://gbxafs.iit.edu/training/tutorials.html>

Software Resources EXAFS:

<http://xafs.org/Software>

<http://leonardo.phys.washington.edu/feff>

<http://gnxas.unicam.it/>

More information: Books and Review Articles

Fundamentals of XAFS

Introduction to XAFS: A Practical Guide to X-ray Absorption Fine Structure Spectroscopy,
G. Bunker, Cambridge University Press, 2012

X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, in
Chemical Analysis 92, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988

FEFF

Theoretical approaches to x-ray absorption fine structure
J. Rehr et al., Rev. Mod. Phys. 72, 621 - 654 (2000)

GNXAS

X-ray absorption spectroscopy and n-body distribution functions in condensed matter (I): theory of the GNXAS data-analysis method
A. Filipponi, A. Di Cicco and C. R. Natoli, Phys. Rev. B 52, 15122 (1995)

MXAN

Geometrical fitting of experimental XANES spectra by a full multiple-scattering procedure
M. Benfatto and S. Della Longa J. Synchr. Rad. 8, 1087 (2001)