
ESRF
The European Synchrotron

Part III

Examples of Applications

Sakura Pascarelli
European Synchrotron Radiation Facility, Grenoble, France

Examples of applications

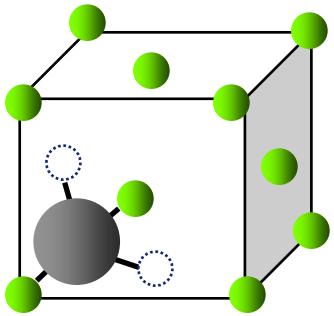
- Major historical EXAFS breakthroughs
- Selection of recent results at the ESRF

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

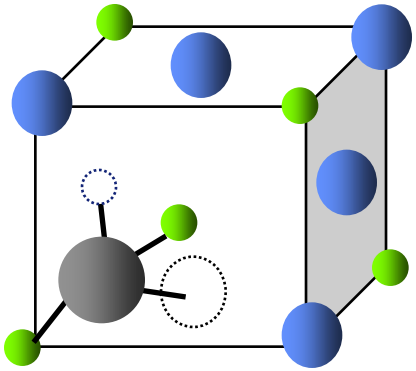
AC



a_{AC}

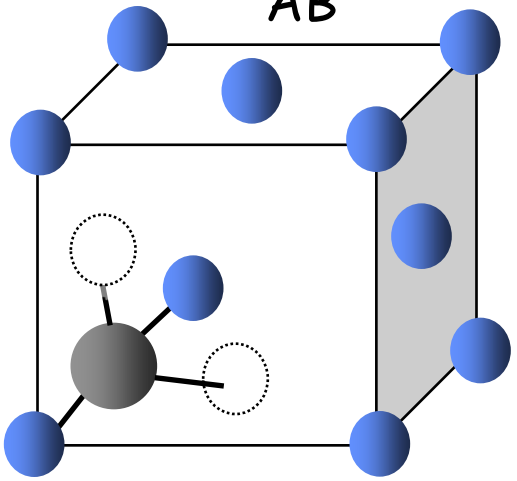
$$R^0_{AC} = \frac{\sqrt{3}}{4} a_{AC}$$

$AB_x C_{1-x}$

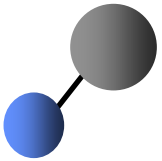


$a(x)$

AB



a_{AB}



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

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

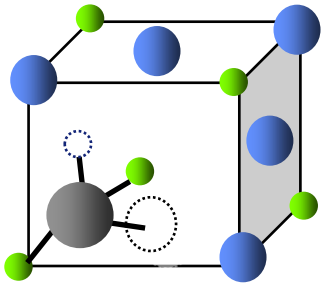
VCA: $R_{AB}(x) = R_{AC}(x) = \frac{\sqrt{3}}{4} a(x)$

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 $Ga_{1-x}In_xAs$

J. C. Mikkelsen, Jr., and J. B. Boyce
Xerox Palo Alto Research Centers, Palo Alto, California 94304
(Received 23 August 1982)

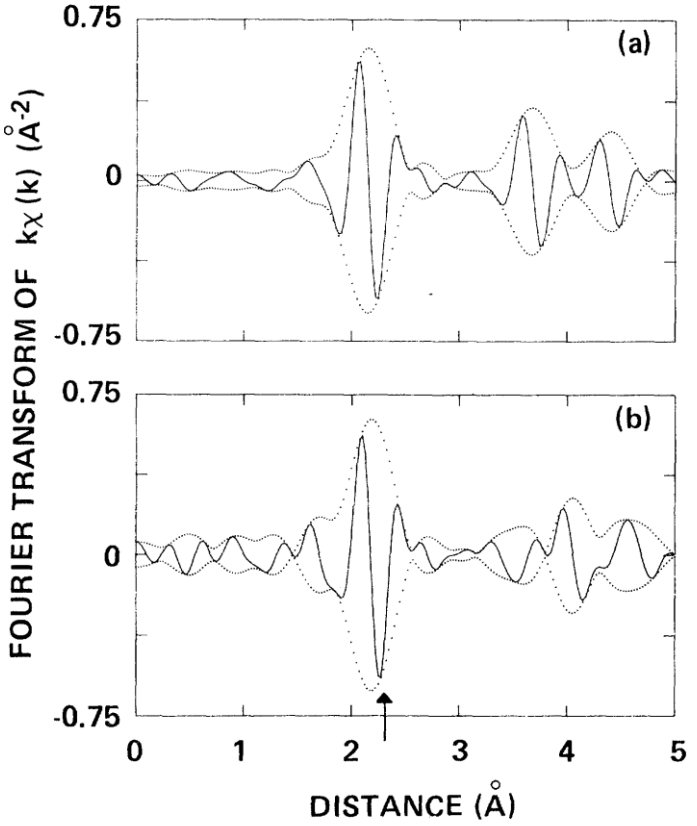


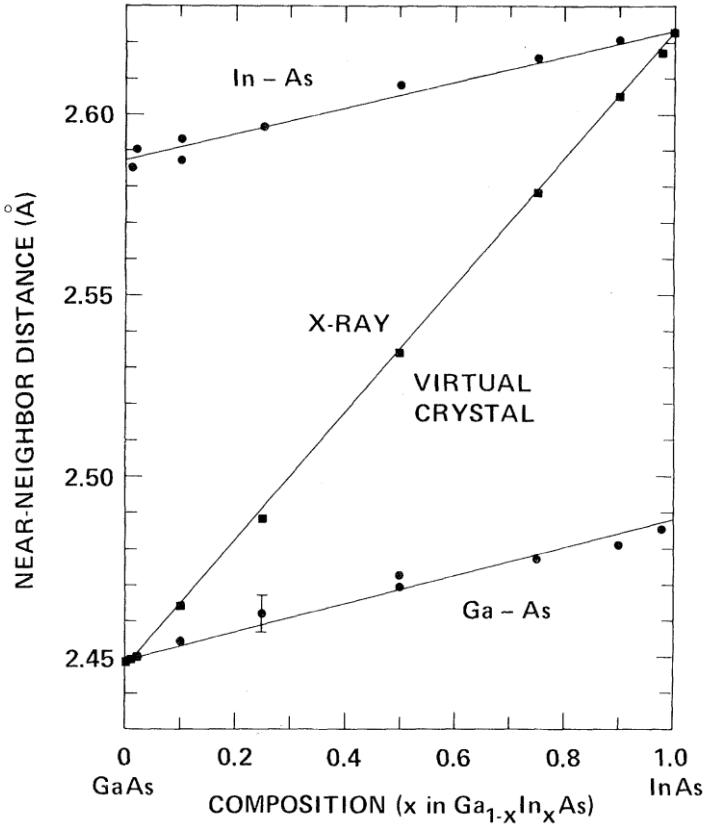
$A_xB_{1-x}C$

- Atomic scale structure not well understood: XRD averages structure over distances that are large on the scale of a lattice constant.
- Calculations of the properties of solid solutions have often relied on simple approximations (i.e. VCA)
- VCA assumes that all atoms occupy average lattice positions defined by X-ray lattice constants

- With the use of the VCA, properties of alloys may be calculated whether or not the alloys's lattice costant 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 Å in whole x range !!
- Contradicts underlying assumptions of VCA
- Important distortions within unit cell accommodated by bond angle distortions

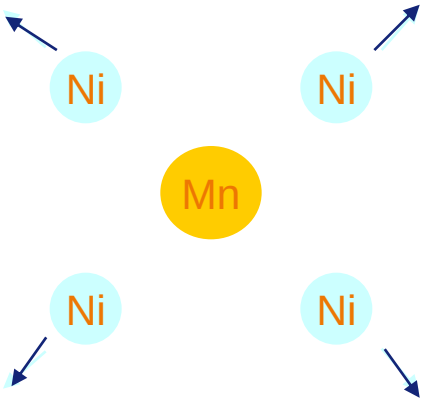
Lattice distortions around impurities in dilute alloys

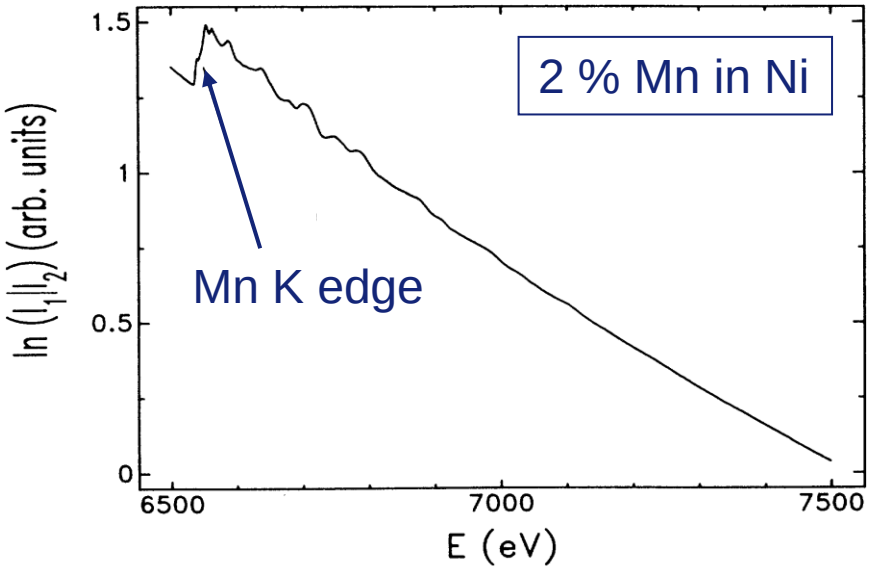
PHYSICAL REVIEW B VOLUME 44, NUMBER 18 1 NOVEMBER 1991-II

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

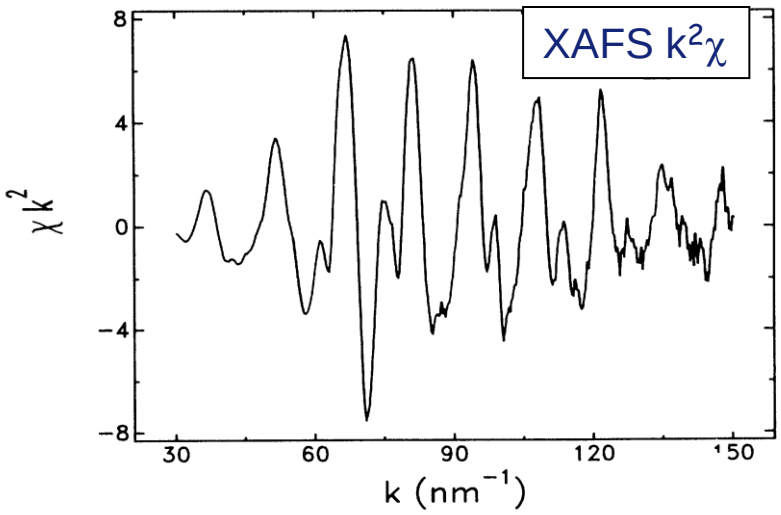
U. Scheuer and B. Lengeler
Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany
(Received 14 February 1991)

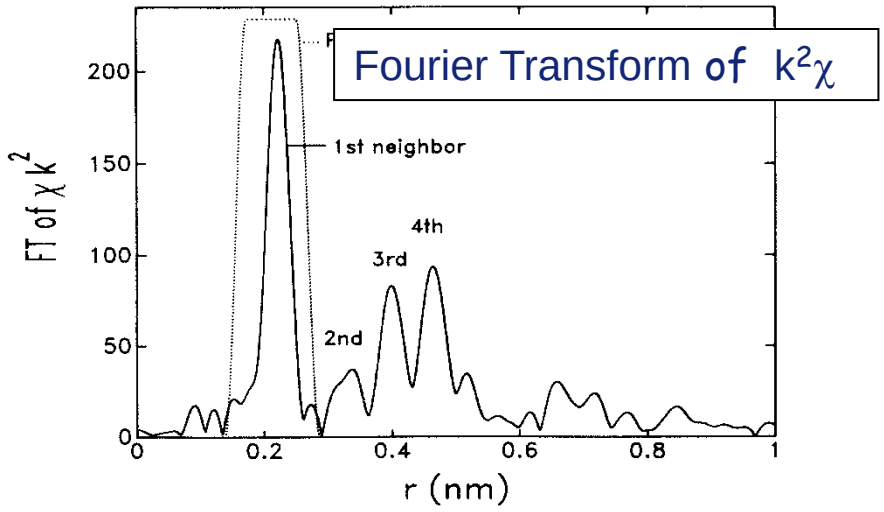
- systematic study of substitutional impurities in fcc and bcc metals
- important shifts in first shell bond length detected





Lattice distortions around impurities in dilute alloys

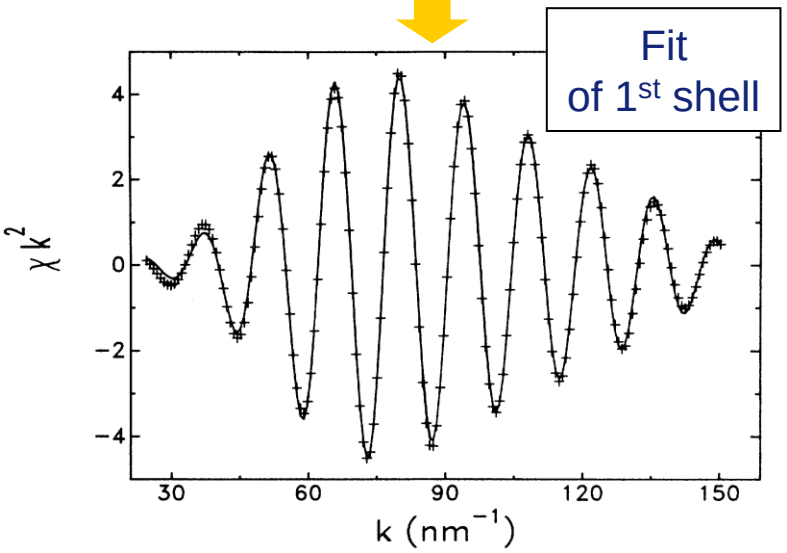




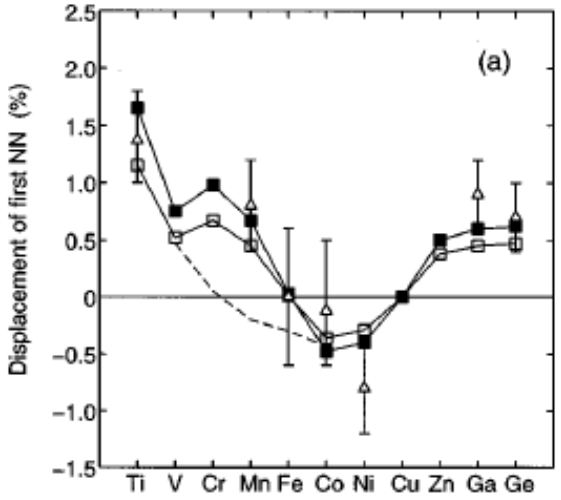
Mn shifts 12 Ni nearest neighbors outwards by:

0.023 ± 0.004 Å

(1 % of distance)



Comparison to band structure calculations



□ ■ Band structure calculations

△ XAS

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

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 GeO_2 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

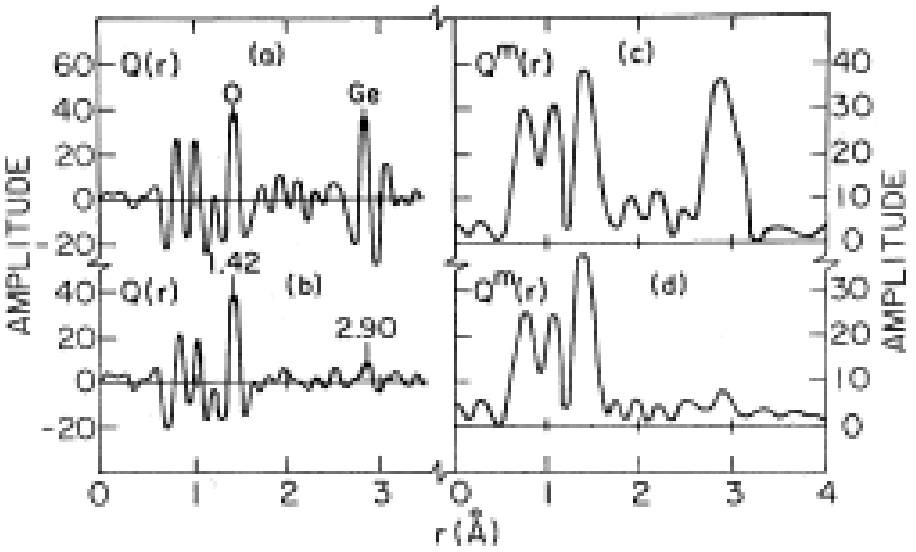
(Received 24 March 1975)

From X-ray scattering experiments on glasses:

Random network model:
GeO_2 tetrahedra connected by bridging Oxygen with deviations about bond angles such that long range periodicity destroyed

Microcrystalline model:
GeO_2 composed of 15-20 Å crystallites – too small to give rise to sharp diffraction peaks

EXAMPLES OF APPLICATIONS



c-GeO_2

g-GeO_2

	r_1	$\Delta\sigma_1$	N_1	r_2	$\Delta\sigma_2$	θ_{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

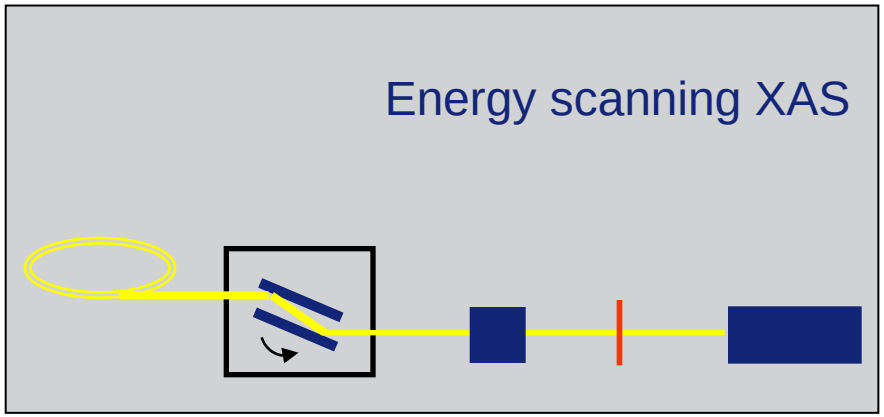
Selection of recent results at the ESRF

- **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

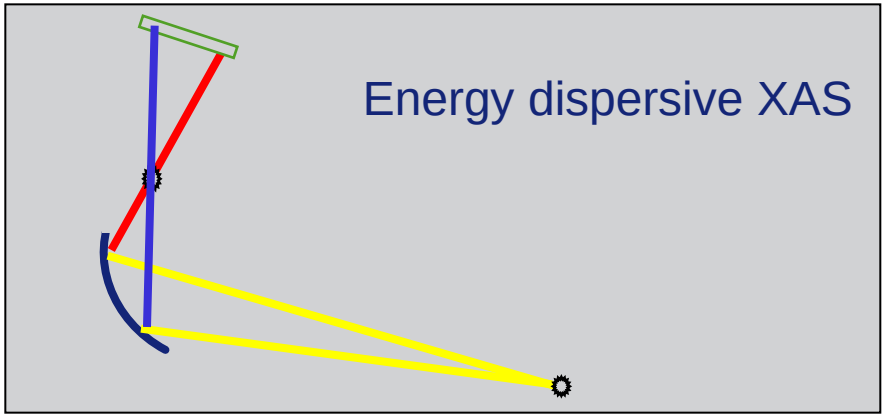
- **ID24: Energy Dispersive XAS**
  - Pd redox catalysis: structure, function, reactivity
  - Mechanism and kinetics of Pt sintering and redispersion
  - Melting of Fe at the Mbar: first XAS results
  - Single shot EXAFS on dynamically compressed Fe

XAFS beamlines at the ESRF



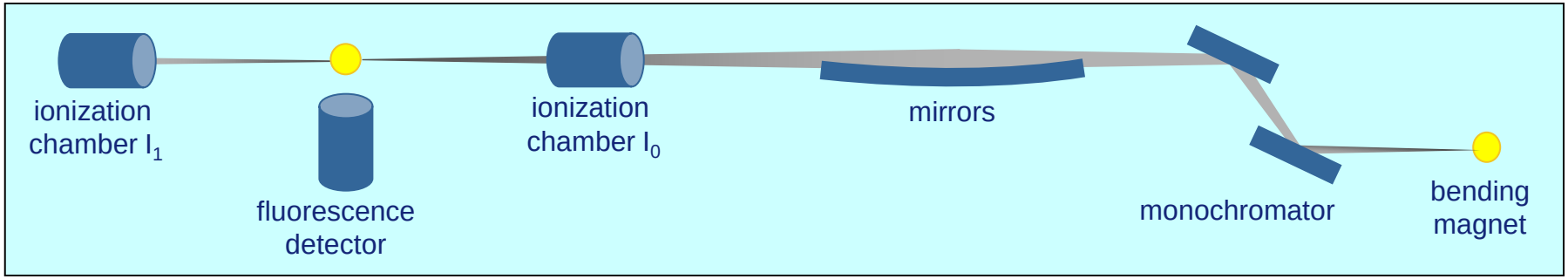
- ID12, ID26, ID32, ID22, etc ..
- BM23
- CRGs :

  BM01, BM08, BM20, BM26, BM30



- ID24

BM23: GENERAL PURPOSE EXAFS

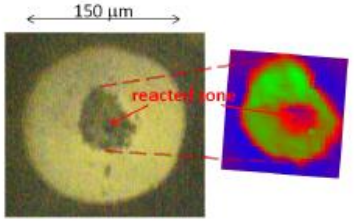


- An instrument to cover needs in area of conventional XAS
  - large energy range 4.5 – 75 KeV
  - excellent S/N ratio over a large k-range
  - versatility
  - high automation level
  - 3 μm x 3 μm spot

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

CHEMISTRY OF XENON AT EXTREME CONDITIONS

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



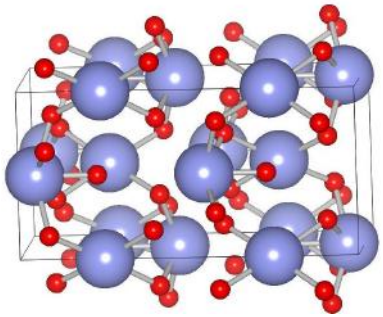
BM23

Xe [Kr] 4d10 5s2 5p6

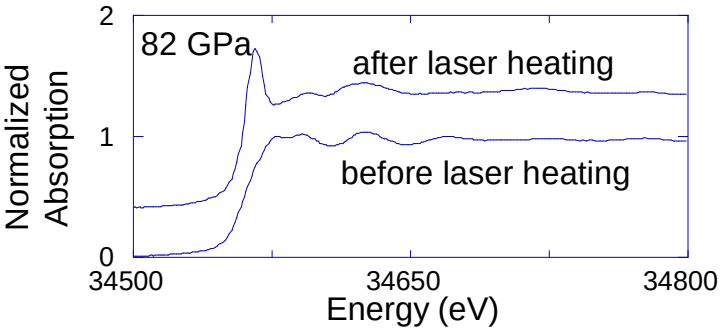
- *"Rare gases reluctant to form bonds"*
- Xe oxides not stable at ambient P, T
- Xe-O interactions at HP

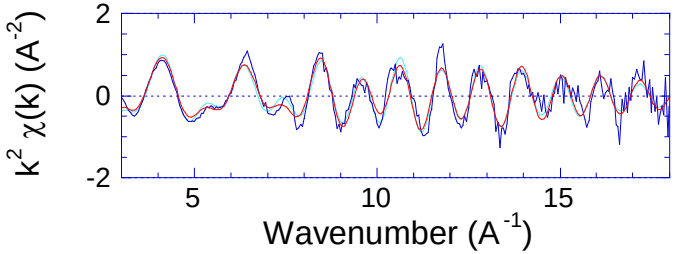
Stability of xenon oxides at high pressures

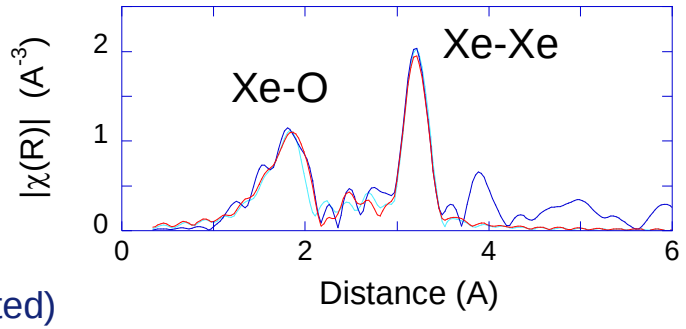
None of the predicted phases observed
XRD alone unable to determine oxide structure



Xe_2O_5
P4/ncc space group







Dewaele Nature Chemistry (accepted)

ARSENIC SEQUESTRATION BY ORGANIC SULPHUR IN PEAT

BM23

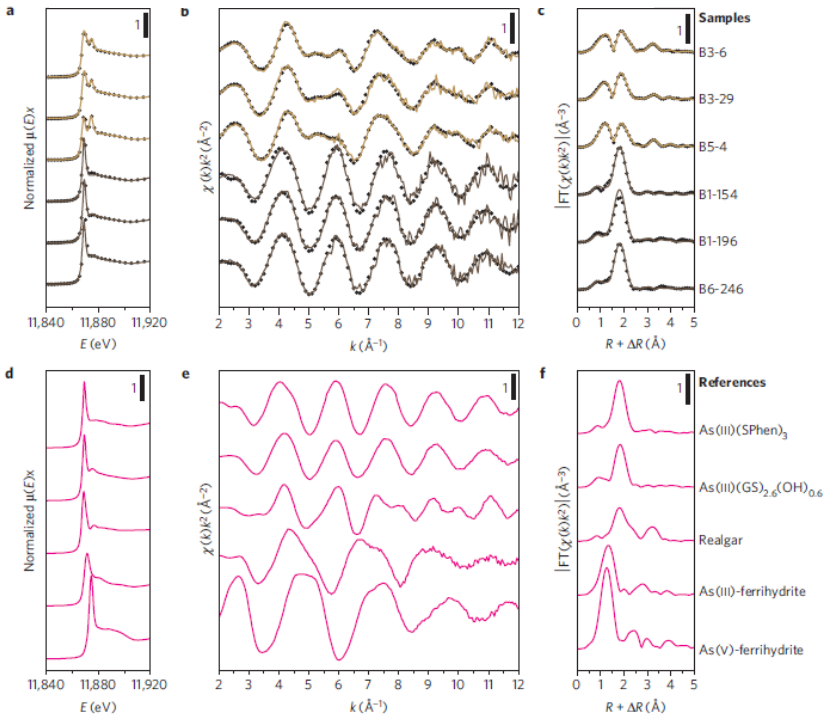
Wetlands cover more than 6% of the global ice-free land area

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

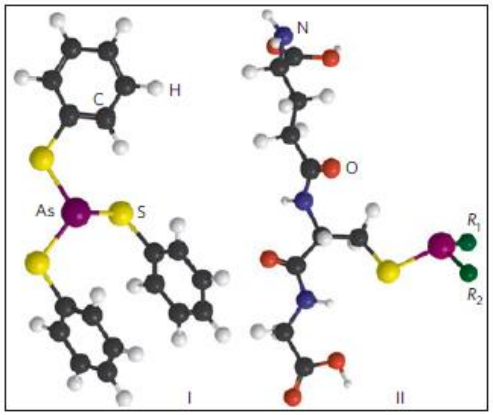
Sorption of As to peat thought to suppress As mobility, but binding mechanisms unknown

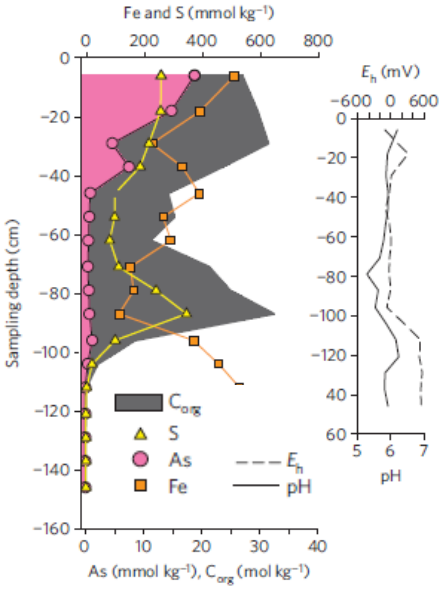
Does natural organic matter serve as geochemical trap for As ?

As K- EXAFS (3-1000 ppm)



Trap: covalent bonds between As^{+3} and organic S groups





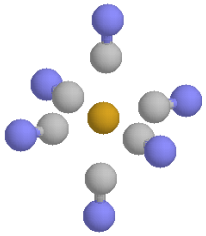
1. Spectroscopic evidence for As binding to peat
2. Identified dominating binding mechanism
3. Quantified extent of As binding to peat

Langner Nature Geoscience 2012

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

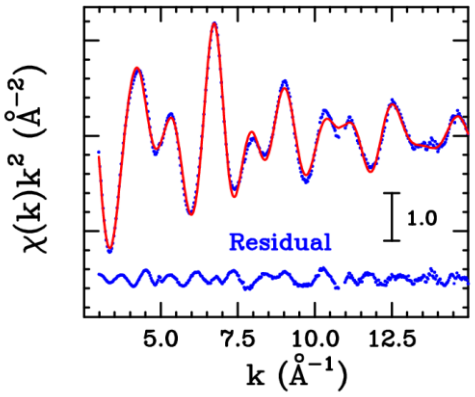
- Example of application of MXAN -

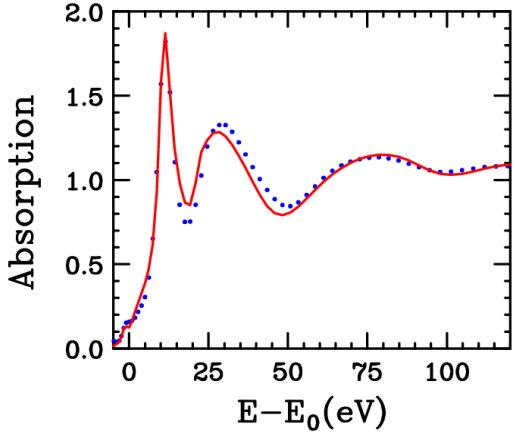
$K_3Fe(CN)_6$



- 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)

LIGAND DISCRIMINATION IN ORGANIC COMPLEXES

- Quantitative analysis using CN, CO and NO as ligands

  EXAFS: cannot discriminate (residuals within 3%)

  XANES: can discriminate CN, CO or NO

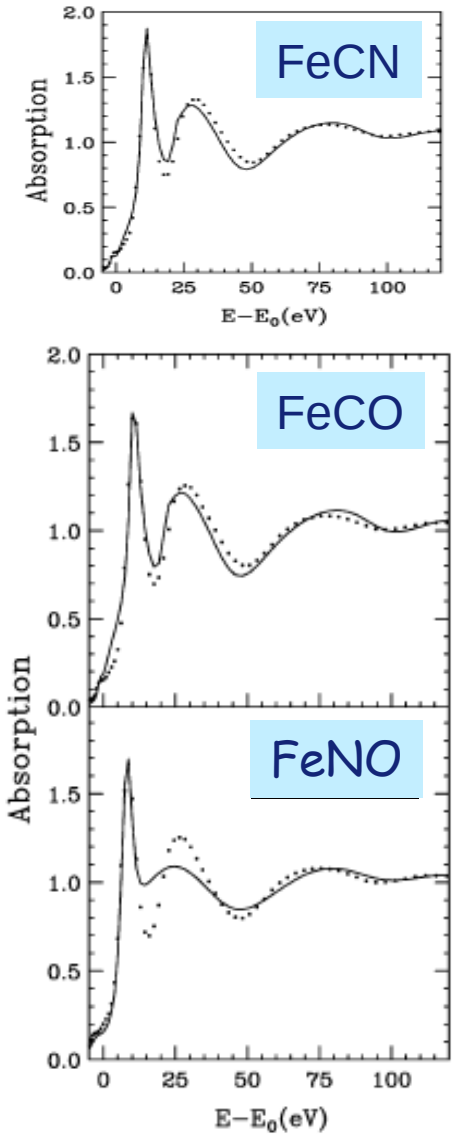
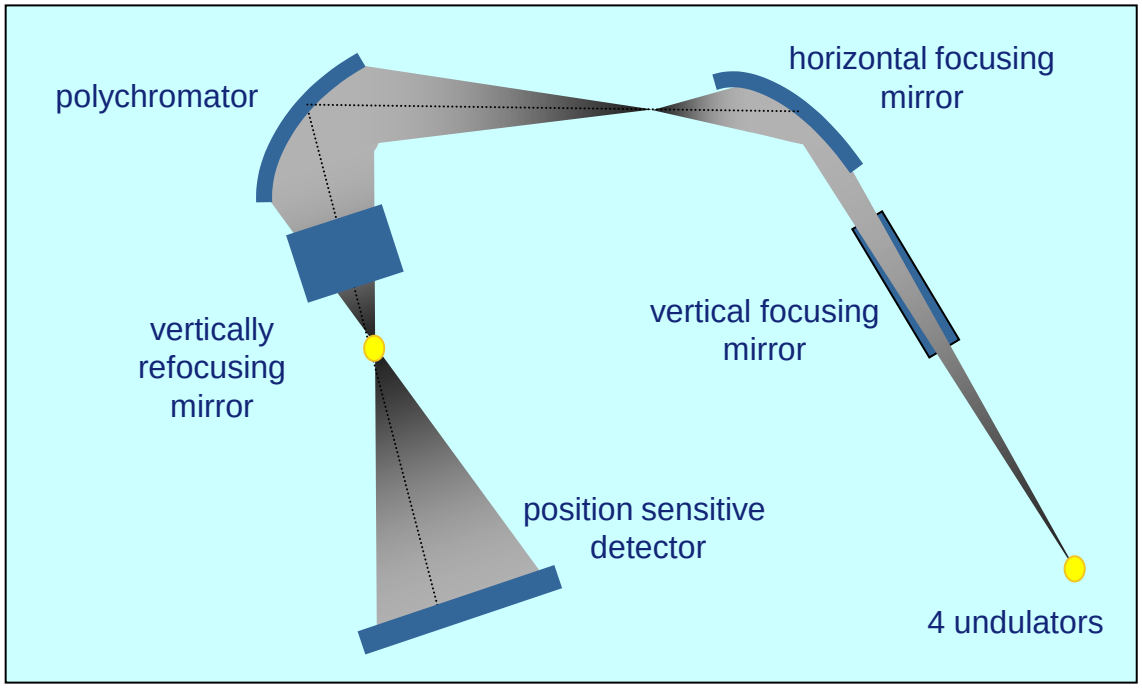


Table 2. Structural Parameters for Fe^{3+} Complexes Obtained from the MXAN Data Analysis

	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_{sq}	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.**

ID24: ENERGY DISPERSIVE XAS



An unprecedented investment into high brilliance EDXAS

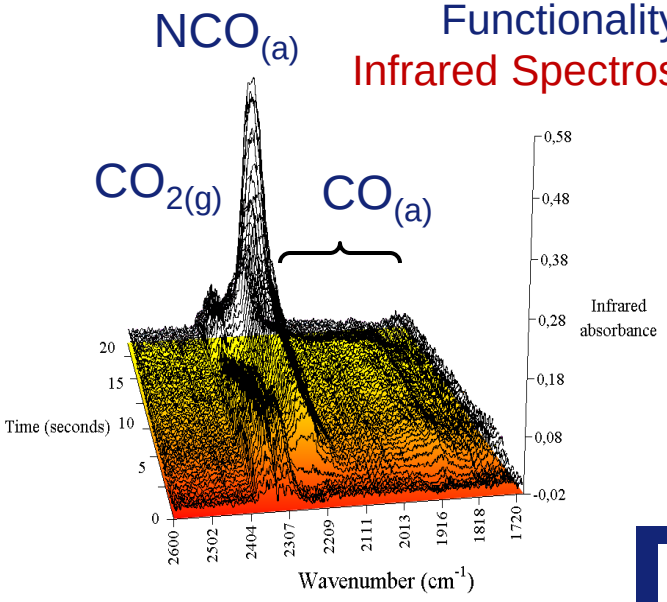
➢ Provide the users' community a unique instrument

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

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

PD REDOX CATALYSIS: STRUCTURE – FUNCTION – REACTIVITY

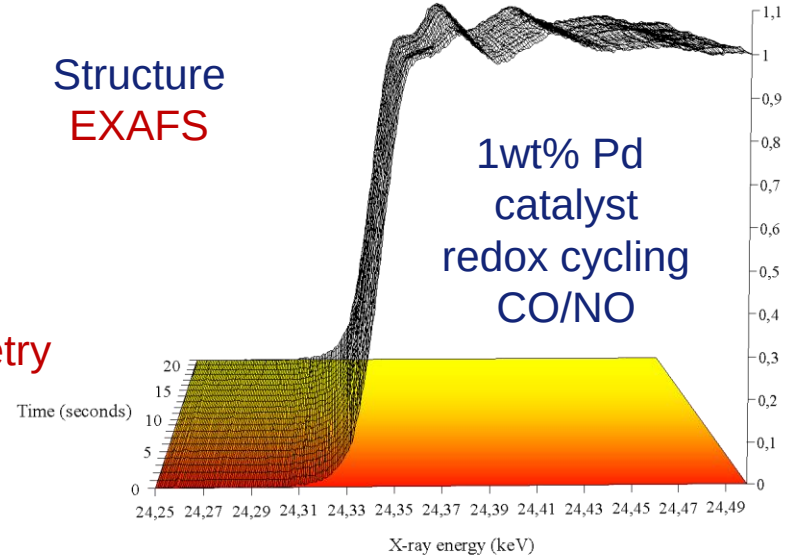
ID24

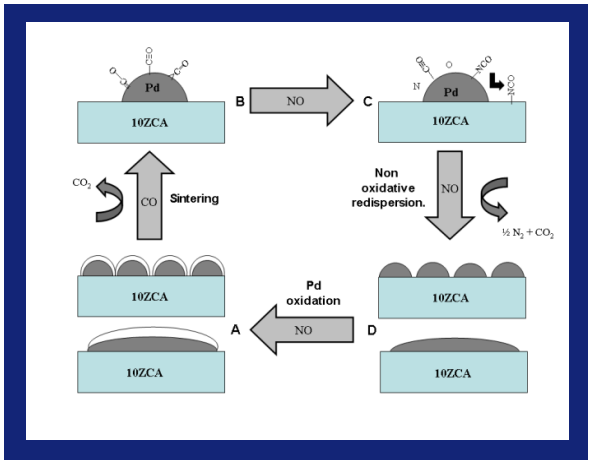


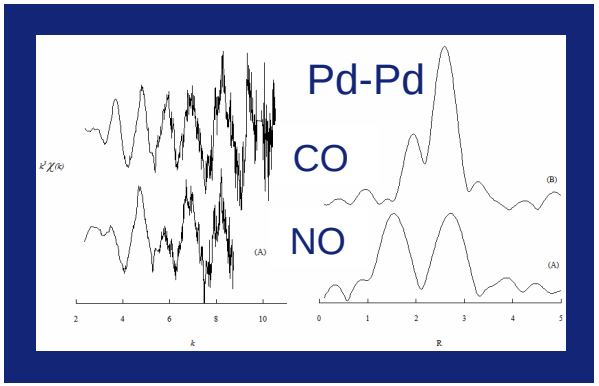
Functionality
Infrared Spectroscopy

Structure
EXAFS

Reactivity
Mass Spectrometry







- Pd particles are not passive entities
- Evidence of fast morphological change

MA Newton et al., Nature Materials (2007)

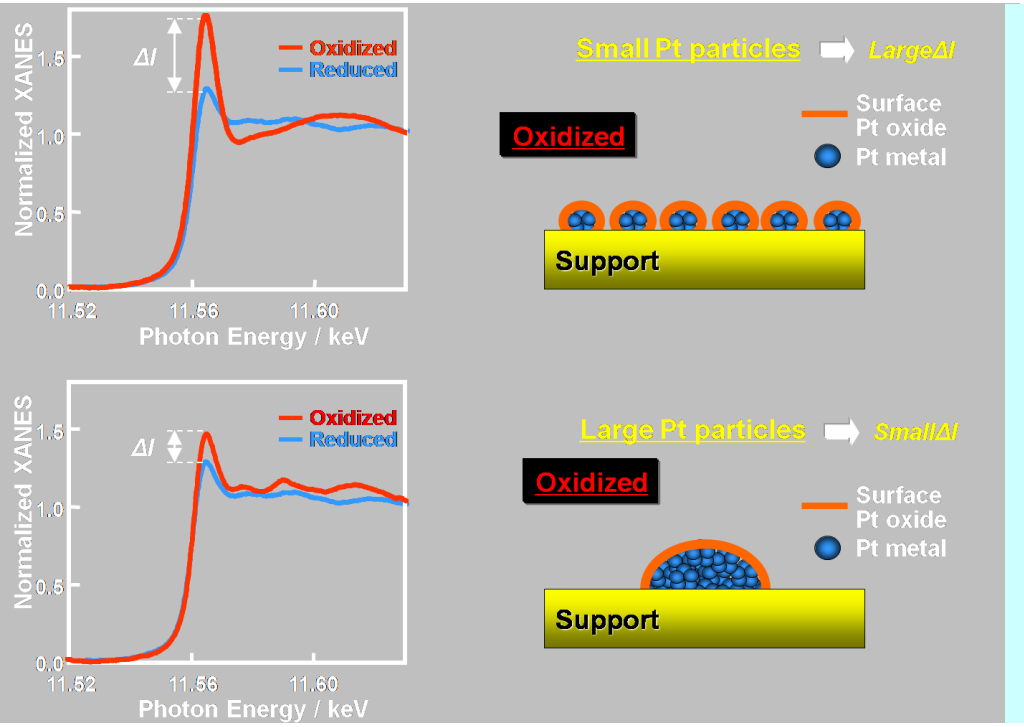
MECHANISM AND KINETICS OF PT SINTERING AND REDISPERSION

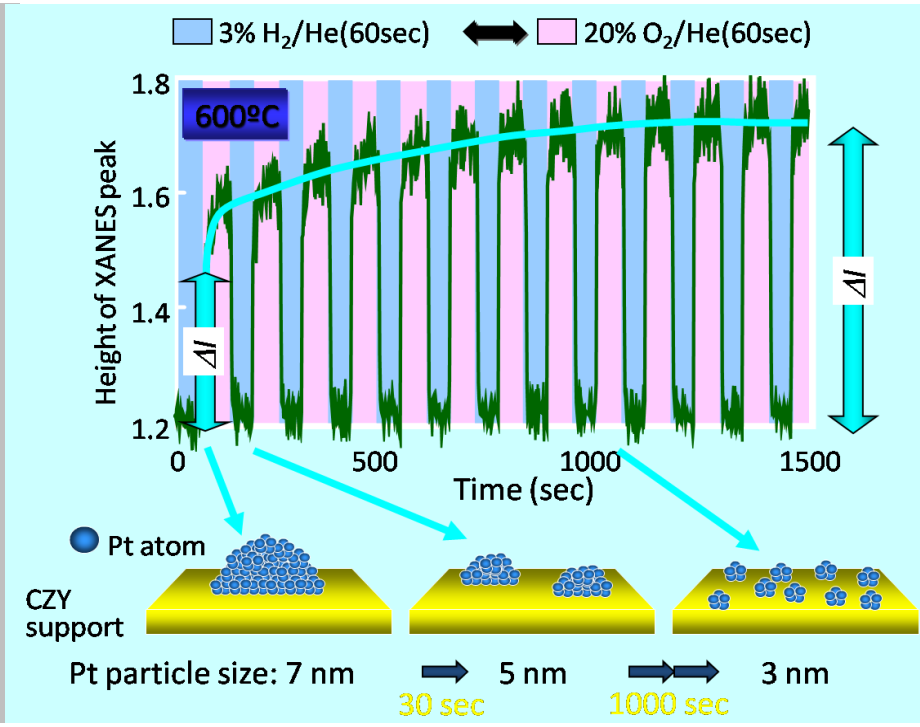
ID24

TOYOTA

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

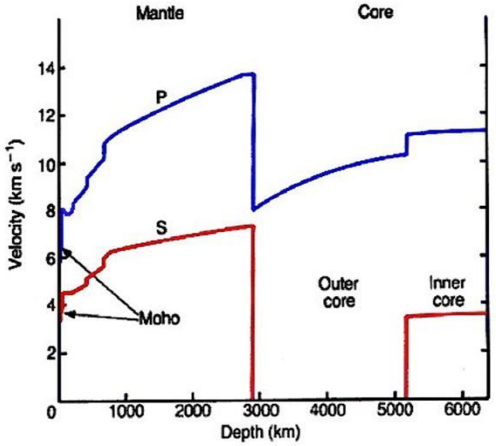
MELTING OF FE AT THE MEGABAR: FIRST XAS RESULTS

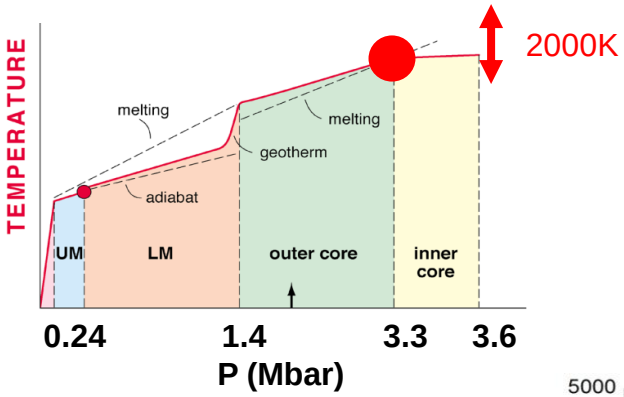
Temperature at the inner core boundary expected to be close to melting point of Fe at 330 GPa.

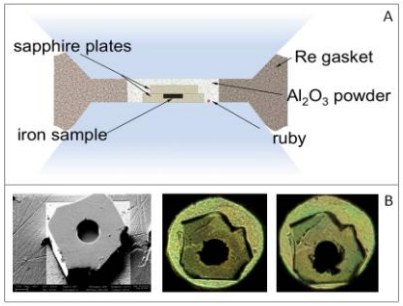
Large controversy on melting temperature of Fe at these extreme pressures

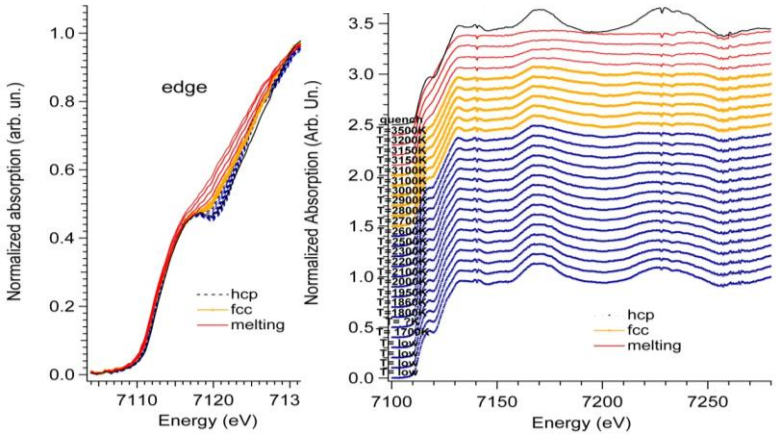
ID24

(Boehler, Nature 1993; Anzellini, Science 2013)

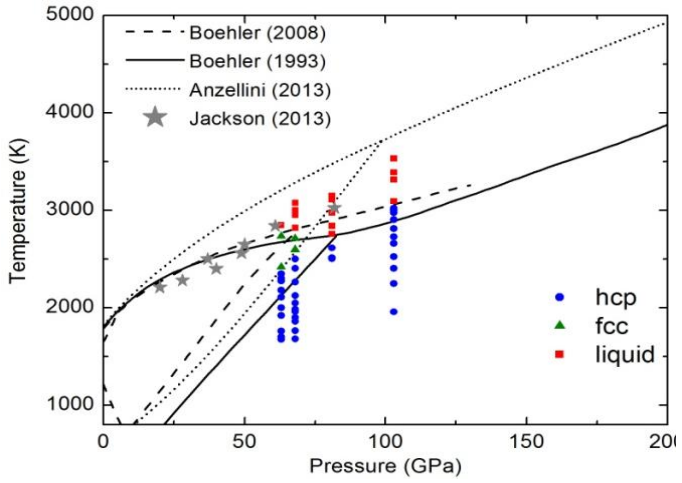








Anzellini et al., in prep.



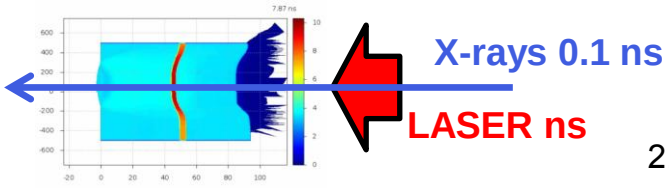
Aquilanti PNAS 2015

SINGLE SHOT EXAFS ON DYNAMICALLY COMPRESSED FE

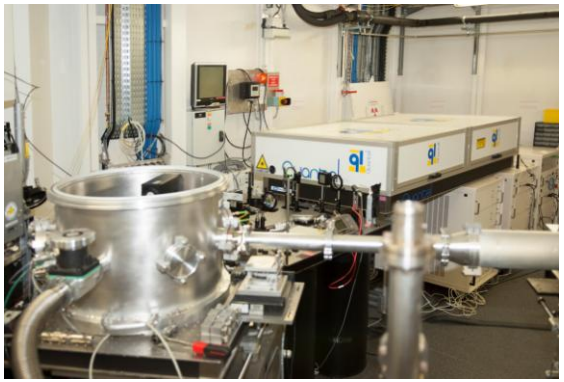
ID24

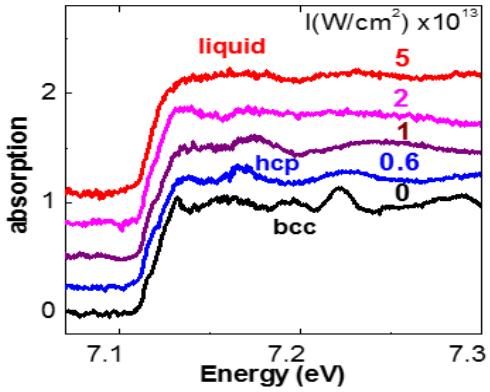
Institute of Shock Physics

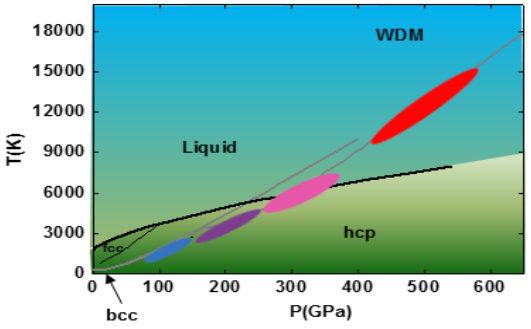
Science & Technology Facilities Council



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

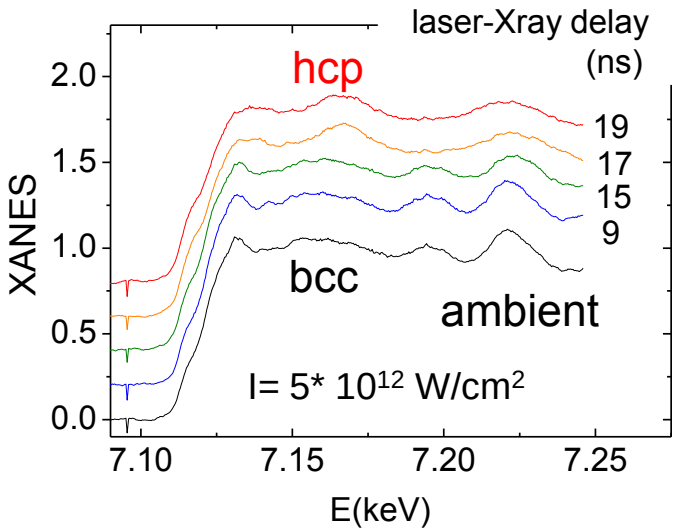




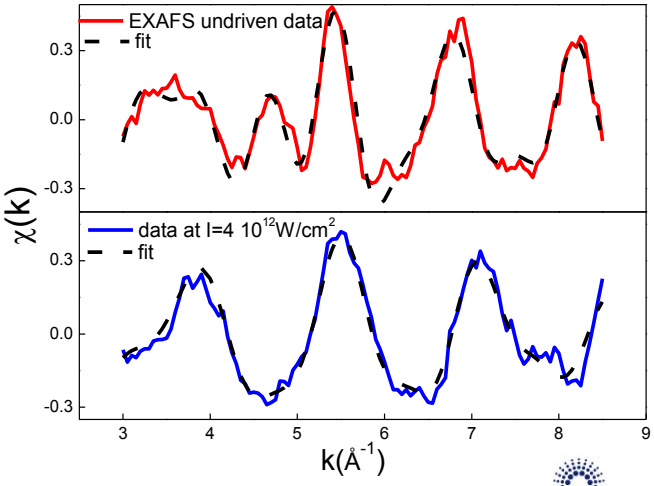


I(W/cm²)	P(GPa)	T(K)
1 10¹³	160	2800
2 10¹³	270	7000
3 10¹³	320	8000
5 10¹³	370	10000

Single bunch XANES

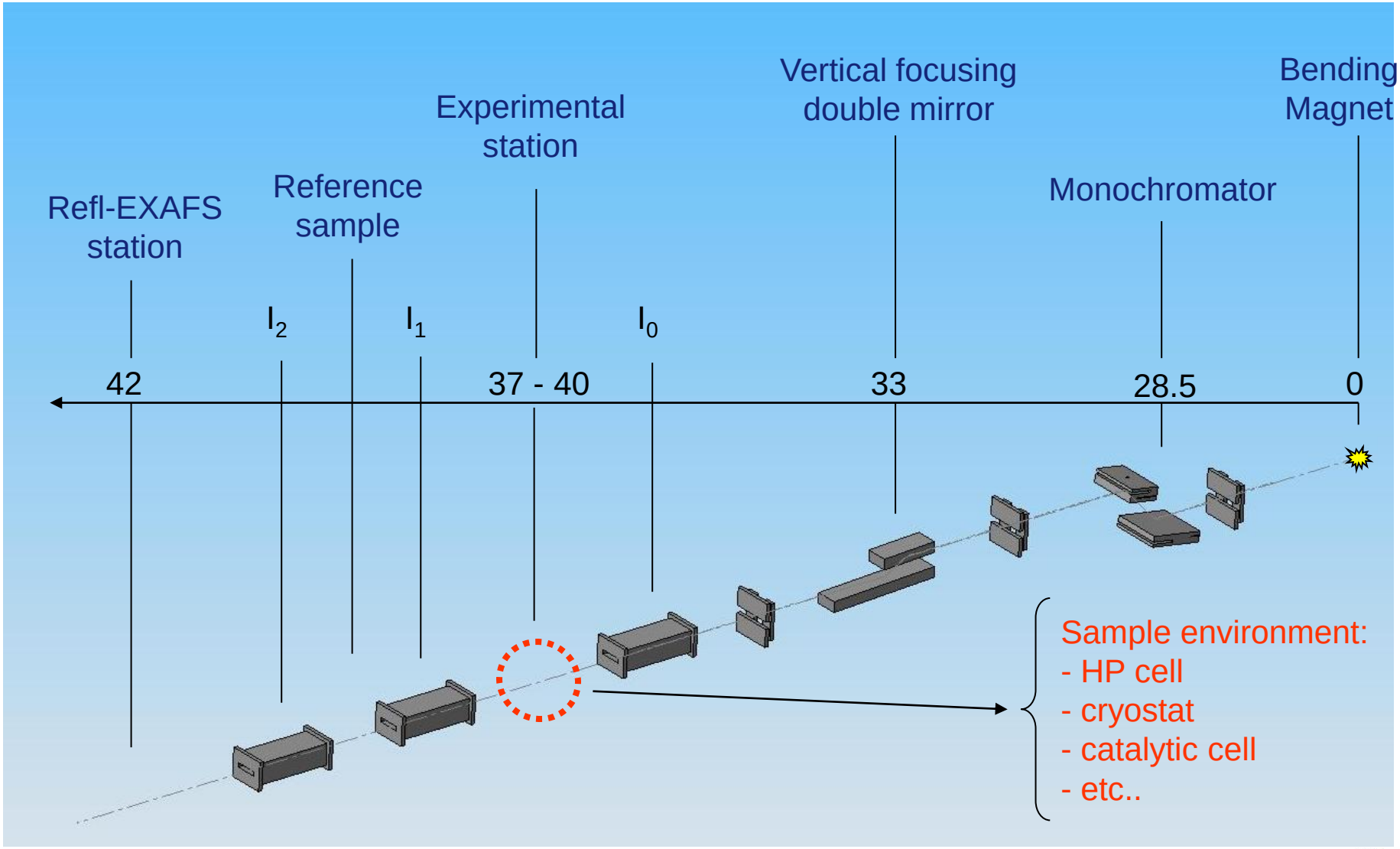


Single bunch EXAFS

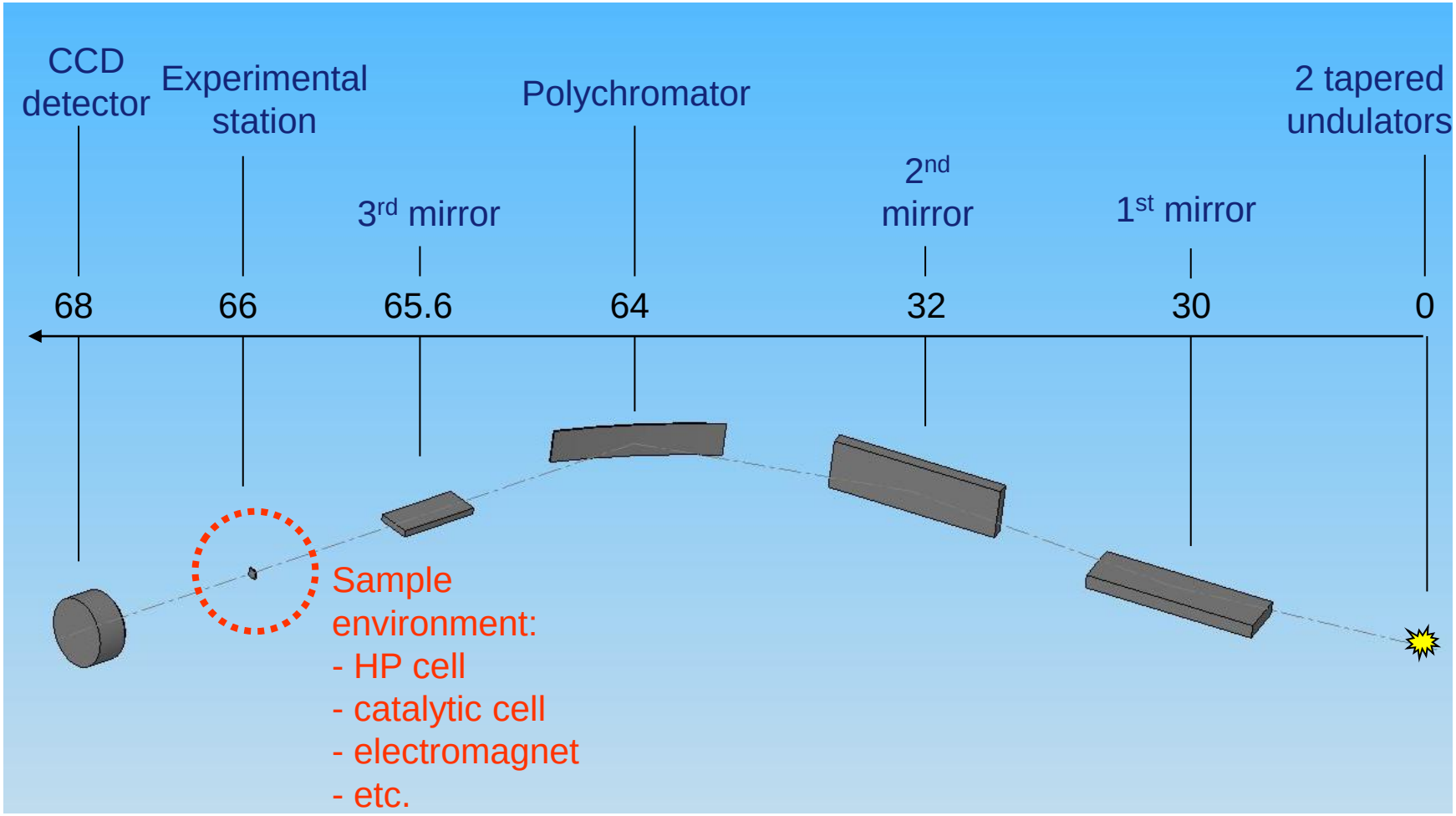


Torchio submitted.

BM23 @ ESRF


Refl-EXAFS station
Reference sample
Experimental station
Vertical focusing double mirror
Monochromator
Bending Magnet
I2
I1
I0
42
37 - 40
33
28.5
0
Sample environment:
- HP cell
- cryostat
- catalytic cell
- etc..

ID24 @ ESRF


CCD detector
Experimental station
3rd mirror
Polychromator
2nd mirror
1st mirror
2 tapered undulators
68
66
65.6
64
32
30
0
Sample environment:
- HP cell
- catalytic cell
- electromagnet
- etc.

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, D. C. Koningsberger and R. Prins, ed., John Wiley & Sons, 1988

Recent Review XAS XES*:*

X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications
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Published Online: 22 JAN 2016 09:48PM EST
DOI: 10.1002/9781118844243

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)