



*The Abdus Salam*  
**International Centre for Theoretical Physics**



**2332-3**

**School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications**

*19 - 30 March 2012*

**Time resolved and high pressure science**

S. Pascarelli  
*ESRF (France)*

## XAS, XANES, EXAFS, and XMCD

- X-ray Absorption
- X-ray Absorption Fine Structure
- Simple Theoretical Description
- XANES
- Major historical EXAFS breakthroughs
- Examples of applications at ELETTRA
- Introduction to XMCD

yesterday

today

## Energy Dispersive XAS

- X-ray Absorption Spectrometers
- EDXAS
  - Basic principles, historical evolution
  - Examples of applications at ESRF
  - Future opportunities for studies of matter at extremes
- Probing laser induced extreme states of matter

synchrotron  
source

monochromator

$I_0$

$I_F$

$I$

sample

XAS measures the energy dependence of the x-ray absorption coefficient  $\mu(E)$  at and above the absorption edge of a selected element.

$\mu(E)$  can be measured two ways:

### Transmission:

The absorption is measured directly by measuring what is transmitted through the sample:

$$I = I_0 e^{-\mu(E)t}$$

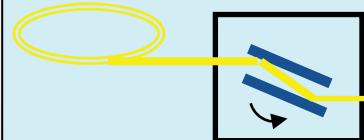
$$\mu(E) t = - \ln(I/I_0)$$

### Fluorescence:

The re-filling the deep core hole is detected. Typically the fluorescent x-ray is measured.

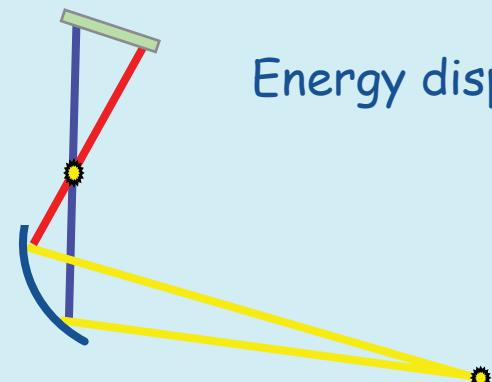
$$\mu(E) \sim I_F / I_0$$

## Energy scanning XAS



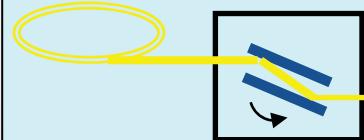
- ID12, ID26, ID32, ID22, etc ..
- BM23
- CRGs (BM08, BM20, BM30 etc..)

## Energy dispersive XAS



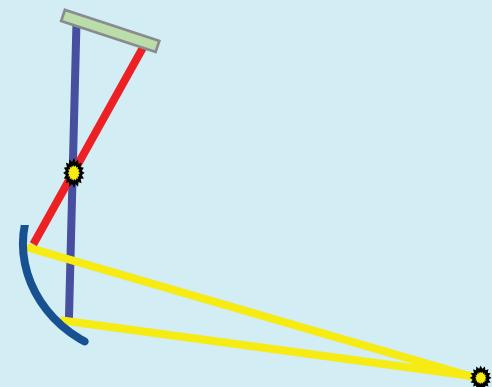
- ID24

## BM23

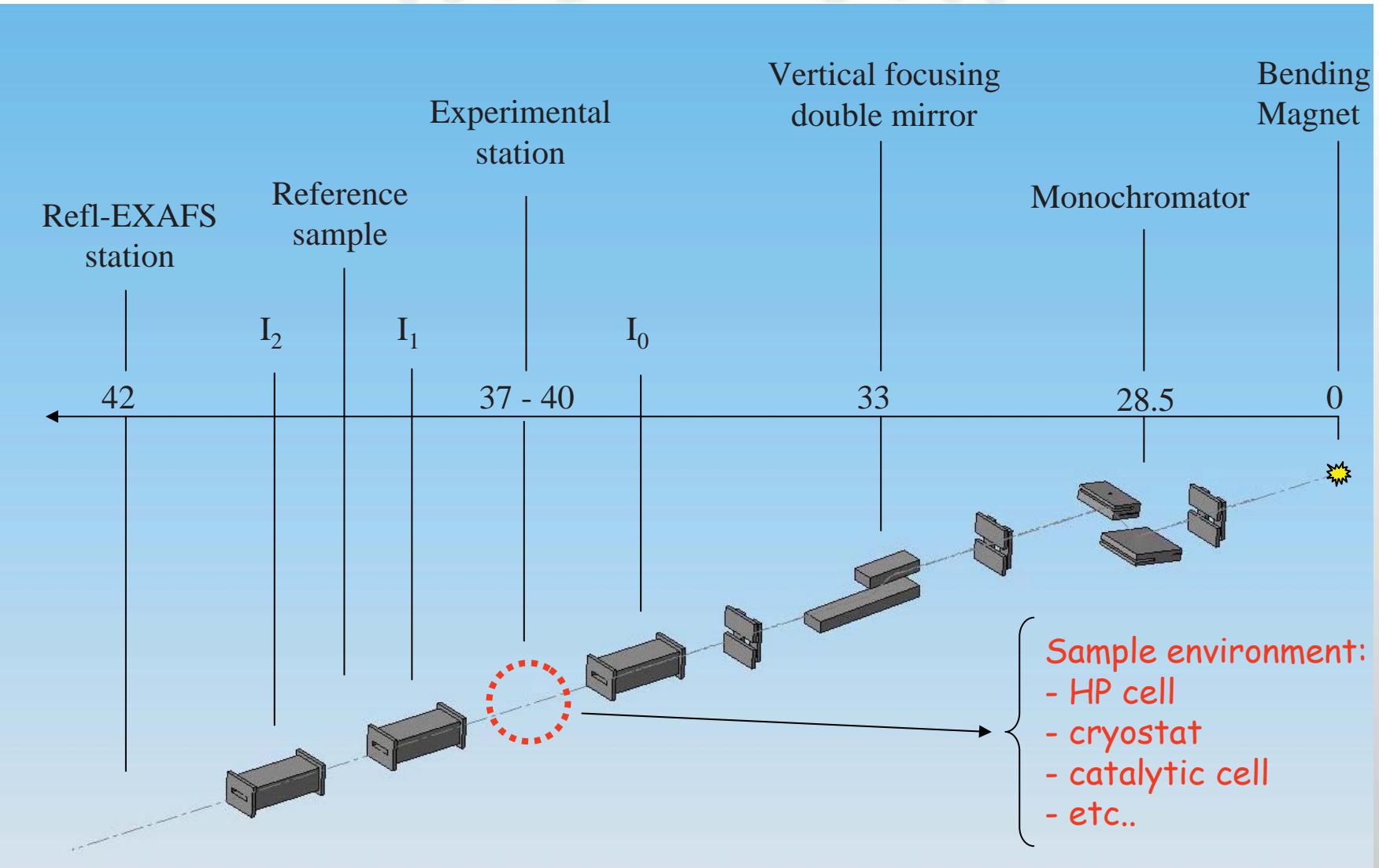


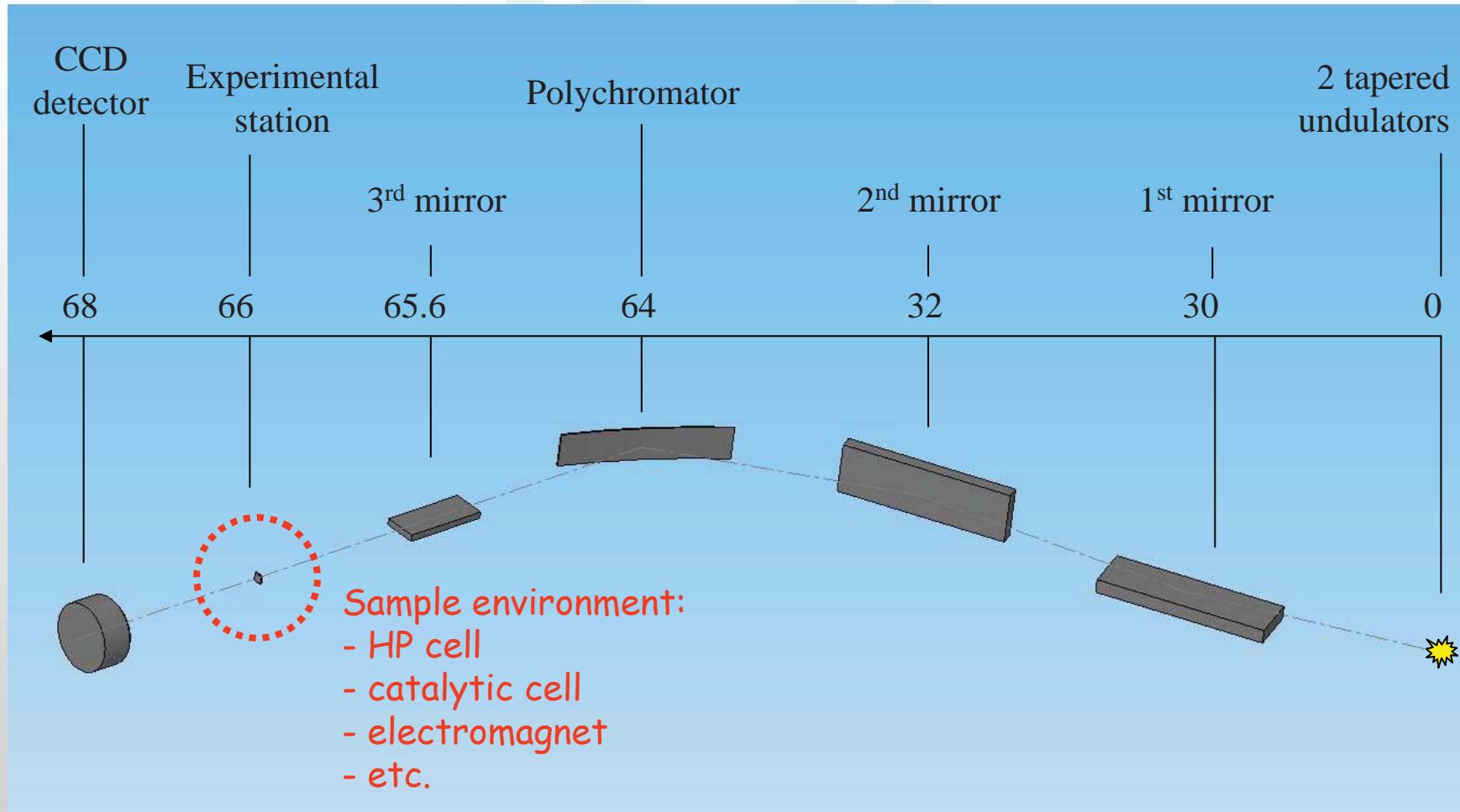
- excellent S/N ratio over a large k-range
- large energy range 4.5 - 75 KeV
- versatility
- high automation level

## ID24



- small focal spot ( $\sim 5 \times 5 \mu\text{m}^2$ )
- fast parallel acquisition ( $\sim 1 \text{ msec}$ )
- high flux ( $\sim 10^{13} \text{ ph/s/0.1\%BW}$ )





# Combining time resolved and extreme conditions XAS

## 1. Technical Challenges

### Source

- high brilliance
- energy tunability

### Optics

- small focal spot ( $\mu\text{m} \rightarrow \text{nm}$ ) - stability
- energy range (50-1000 eV) - stability

### Detection

- fast acquisition (ms  $\rightarrow$  ps)
- synchronization

## 2. Acquisition schemes

### Pump-probe

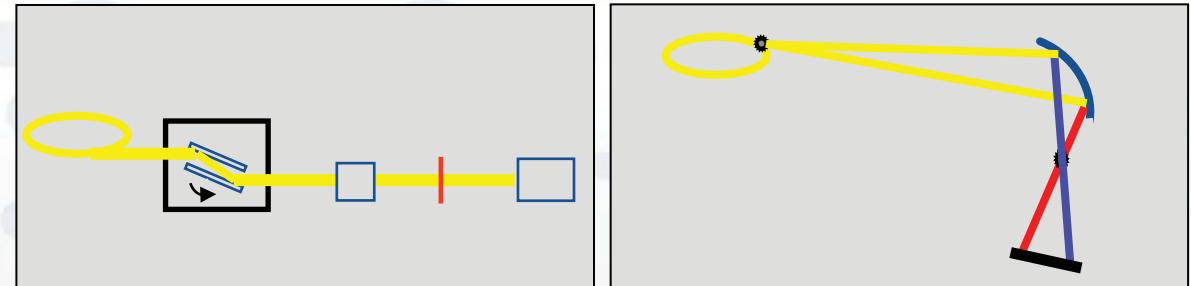
- reversible processes
- sample translation/cycle, ....

### Single-shot

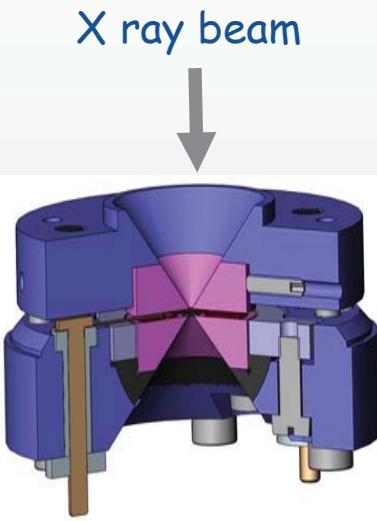
- non-reversible processes
- destruction of sample environment
- limited pump repeatability

## 3. Energy scanning vs energy dispersive spectroscopy

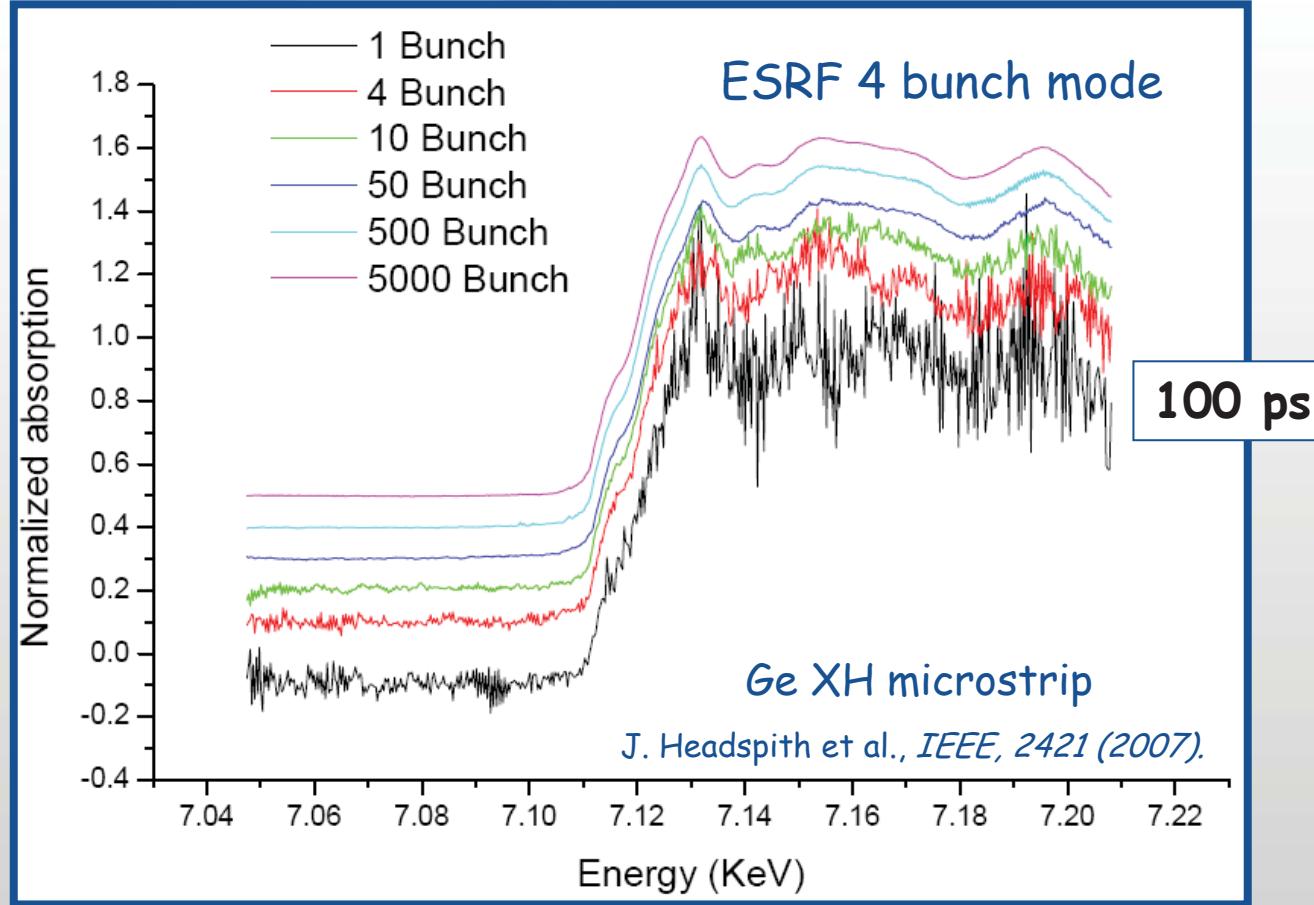
# Energy scanning vs energy dispersive spectrometer



	Energy Scanning	Energy Dispersive
stability	mechanical movement	no movement of optics during acquisition
speed	energy points acquired sequentially	all energy points acquired simultaneously
optical scheme	simple	less simple
detection de-excitation channels (XRF, XES, RIXS)	straightforward	flux-energy resolution tradeoff
demands on sample microstruct	low	high
focal spot min	50-100 nm	2-3 $\mu$ m
pump-probe	ps/energy point	ps/full spectrum
single shot	50 - 100 ms/spectrum	1 $\mu$ s/spectrum at 3 <sup>rd</sup> gen

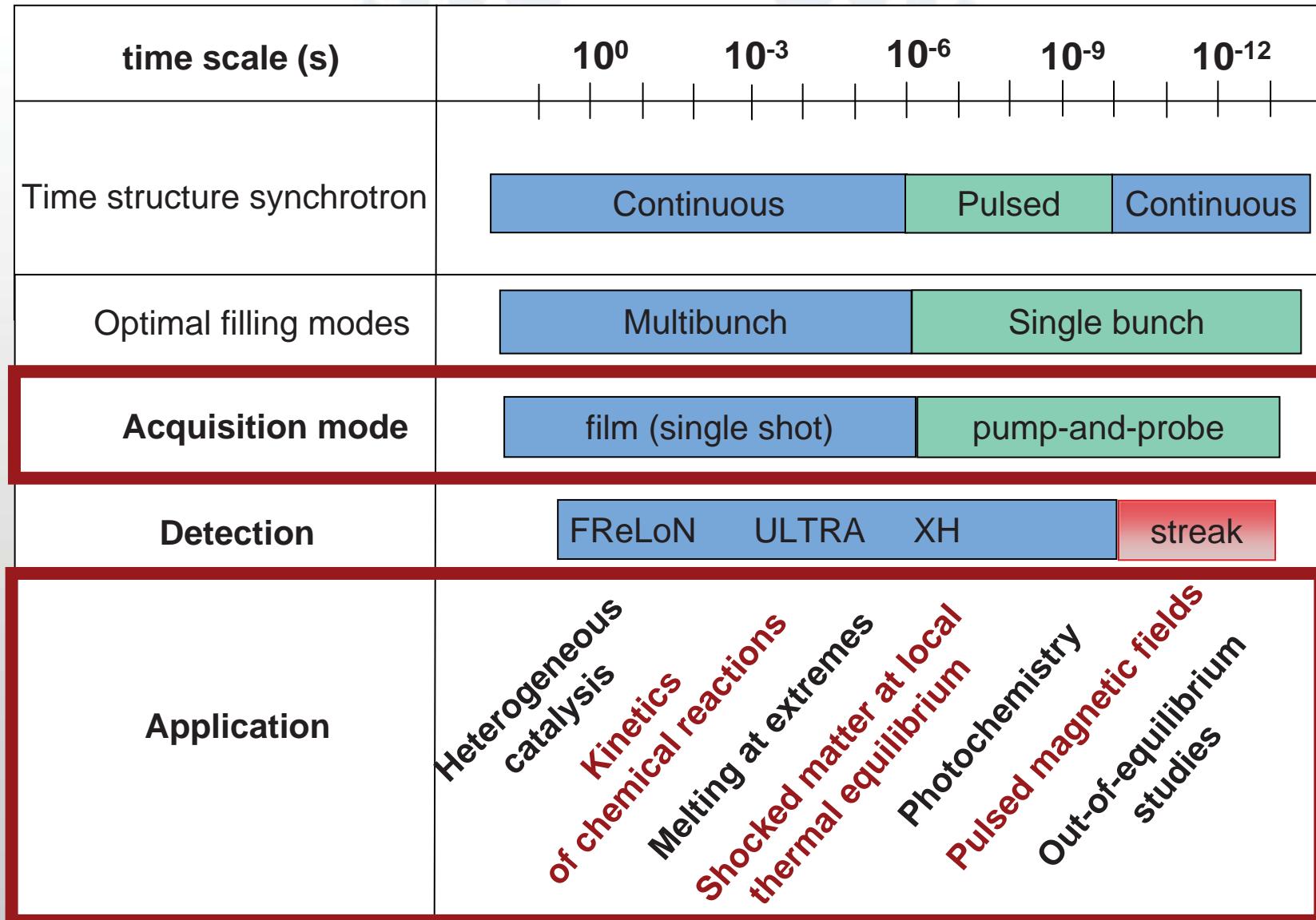


Fe foil



Edge shifts and XANES features clearly detectable with 50 bunches  
( $3 \mu\text{s}$  in Uniform mode)

# Exploiting time resolution: present and future



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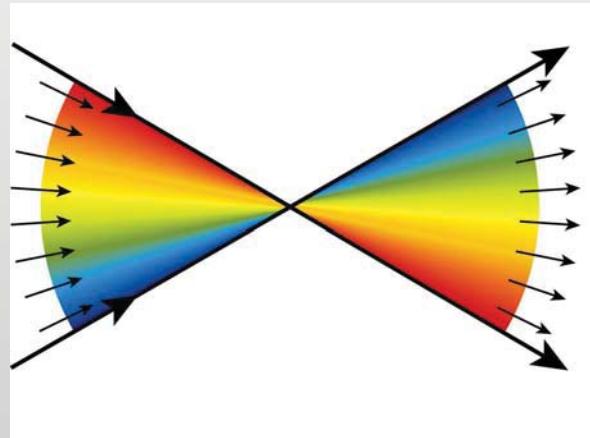
# First idea of energy dispersive concept

1978

In 1978, a small workshop was held in Osaka on an EXAFS spectrometer to be constructed at the Photon Factory which started construction at that time.

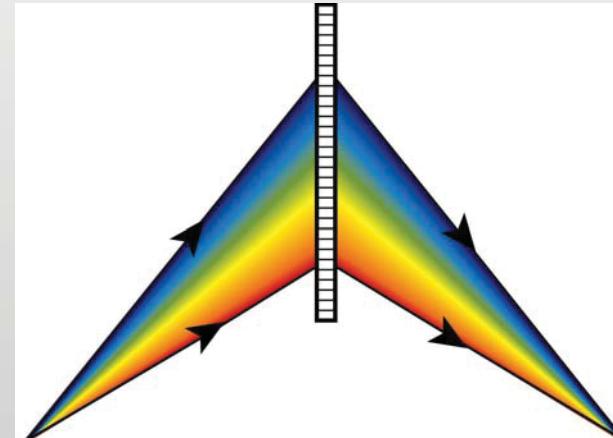
A professor of Tohoku university commented about the necessity of a quick EXAFS spectrometer for time-resolved study of reacting objects.

Immediately in the conference room



No mechanical movement during  
the measurement

On the train back to Tokyo



Focalization by a Laue-case  
single crystal

Taken from Prof. Matsushita's talk at 2009 Workshop @ ESRF

# EDXAS on synchrotron beamline at Stanford

1981

JAPANESE JOURNAL OF APPLIED PHYSICS  
VOL. 20, No. 11, NOVEMBER, 1981 pp. 2223–2228

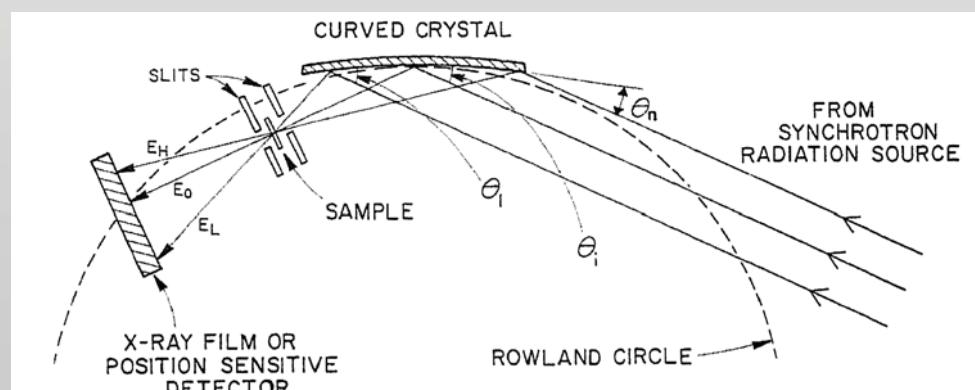
## A Fast X-Ray Absorption Spectrometer for Use with Synchrotron Radiation

Tadashi MATSUSHITA\* and R. Paul PHIZACKERLEY

Stanford Synchrotron Radiation Laboratory, Stanford University,  
SLAC, P.O. Box 4349, Bin 69, Stanford, California 94305, USA

(Received July 6, 1981; accepted for publication August 22, 1981)

A quasi-parallel and polychromatic beam of synchrotron radiation is focused and dispersed by a curved crystal, so that the energy of each ray of the focused beam varies as a function of convergence angle through the focus. The specimen is placed at the focus. By measuring the X-ray intensity distribution across the beam behind the focus, in the presence and absence of the specimen, the absorption spectra of Cu and Ni metal foils were obtained. Using an X-ray film as the detector, a spectrum from a Cu foil was obtained in 0.1 seconds when the SPEAR storage ring at Stanford was operated at 3.1 GeV and 80 mA. The energy resolution is approximately 2.0 eV and the energy range of the spectrum is approximately 1 keV.



1982

December, 1982] © 1982 The Chemical Society of Japan

Bull. Chem. Soc. Jpn., 55, 3911—3914 (1982)

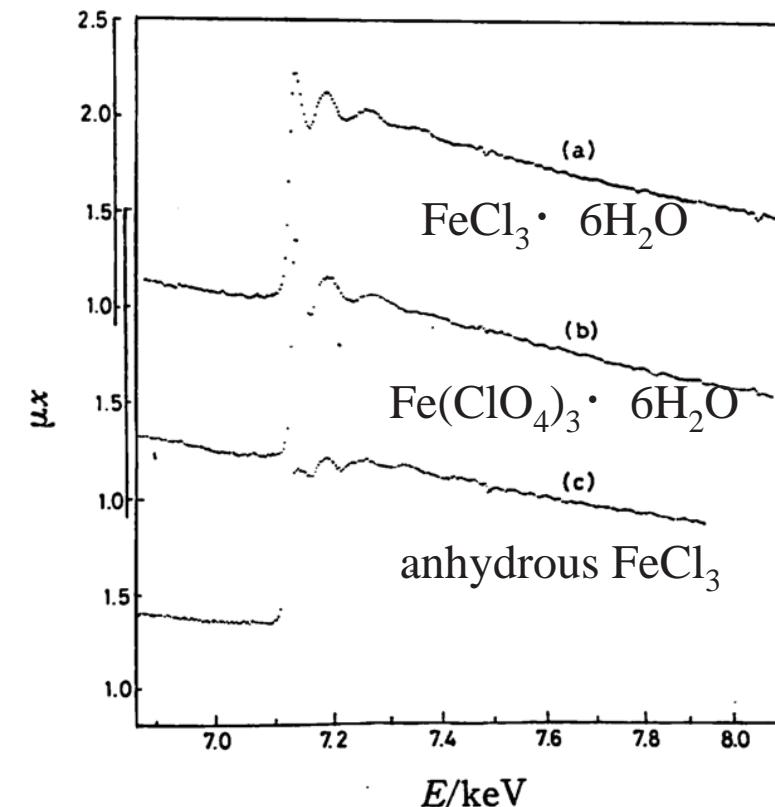
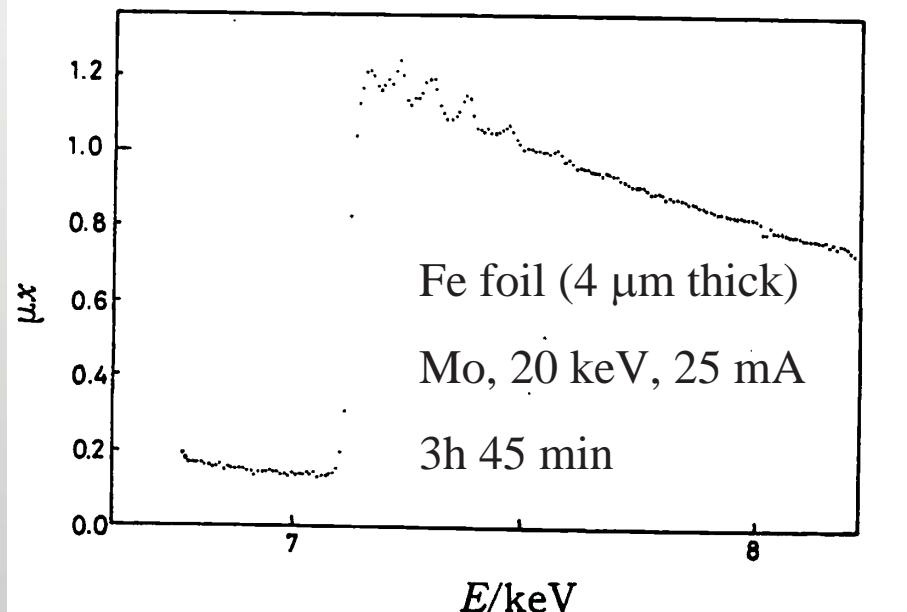
## EXAFS Spectroscopy of Some Iron(III) Compounds by Use of Dispersive-type In-laboratory X-Ray Spectrometer

Masaharu NOMURA, Kiyotaka ASAKURA, Ukyo KAMINAGA,<sup>†</sup> Tadashi MATSUSHITA,<sup>†</sup>  
Kazutake KOHRA,<sup>†</sup> and Haruo KURODA\*

Department of Chemistry and Research Center for Spectrochemistry, Faculty of Science,  
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

\*Photon Factory, National Laboratory for High Energy Physics, Oho-Machi, Tsukuba, Ibaraki 305

(Received June 28, 1982)



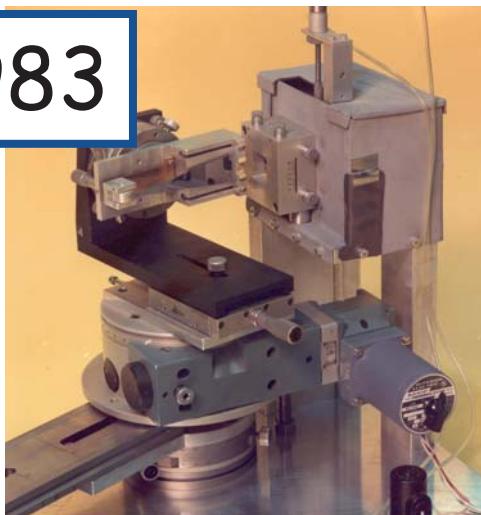
# EDXAS around the world



# Pioneer EDXAS beamlines (1980s)

BL	Source	Synch. facility	Location
BL-4A	BM	PF	Tsukuba, Japan
D11	BM	Lure	Orsay, France
7.4	BM	SRS	Daresbury, UK

1983



R. P. Phizackerly, Z. U. Rek, G. B. Stephenson, S. D. Conradson, K. O. Hodgson,  
T. Matsushita and H. Oyanagi  
*J. Appl. Cryst.* **16**, 220 (1983)

JOURNAL DE PHYSIQUE  
Colloque C8, supplément au n° 12, Tome 47, décembre 1986

#### LINEAR DETECTOR FOR TIME-RESOLVED EXAFS IN DISPERSIVE MODE

H. OYANAGI, T. MATSUSHITA\*, U. KAMINAGA\*\* and H. HASHIMOTO\*\*\*

*Electrotechnical Laboratory, Sakuramura, Niiharigun,  
Ibaraki 305, Japan*

*\*National Laboratory for High Energy Physics, Ohomachi,  
Ibaraki 305, Japan*

*\*\*Rigaku Corporation, Matsubaracho, Akishima, Tokyo 196, Japan*

*\*\*\*Toray Research Center Inc., Sonoyama, Ohtsu, Shiga 520, Japan*

JAPANESE JOURNAL OF APPLIED PHYSICS  
VOL. 25, No. 7, JULY, 1986, pp. L523-L525

#### Twenty-Five Millisecond Resolution Time-Resolved X-Ray Absorption Spectroscopy in Dispersive Mode

Tadashi MATSUSHITA, Hiroyuki OYANAGI,† Satoshi SAIGO,††  
Ukyo KAMINAGA,††† Hideki HASHIMOTO,\* Hitoshi KIHARA,††  
Noboru YOSHIDA\*\* and Masatoshi FUJIMOTO\*\*

*Photon Factory, National Laboratory for High Energy Physics,  
Oho-machi, Tsukuba-gun, Ibaraki 305*

*†Electrotechnical Laboratory, Umezono, Sakura-mura, Niihari-gun, Ibaraki 305*

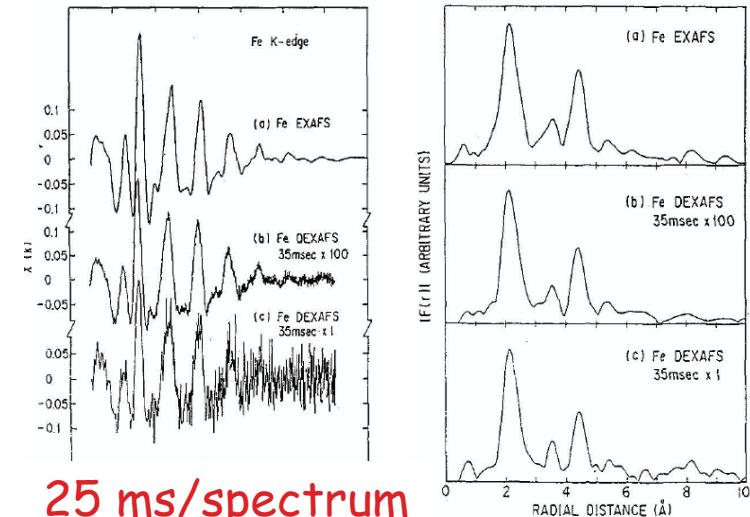
*††Department of Physics, Jichi Medical School, Minamikawachi-machi,  
Kawachi-gun, Tochigi 329-04*

*†††Rigaku Corporation, Matsubara-cho, Akishima, Tokyo 196*

*\*Toray Research Center Inc., Sonoyama, Ohtsu, Shiga 520*

*\*\*Department of Chemistry, Faculty of Science, Hokkaido University,  
Kitajyoh, Kita-ku, Sapporo, Hokkaido 062*

(Received May 22, 1986; accepted for publication June 21, 1986)



# Pioneering work at BL-4A, D11 and 7.4

The Journal of  
**Physical Chemistry**

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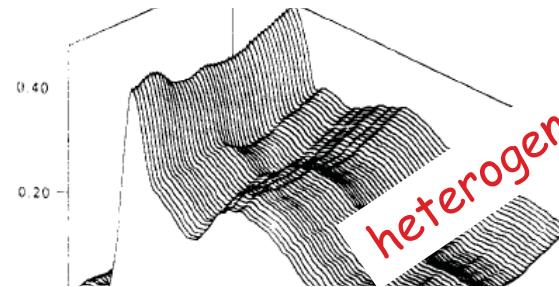
## In Situ Studies of the Dehydration of Zeolitic Catalysts by Time-Resolved Energy-Dispersive X-ray Absorption Spectroscopy

J. W. Couves, J. M. Thomas,\* C. R. A. Catlow,\*

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London WIX 4BS, U.K.

G. N. Greaves,\* G. Baker, and A. J. Dent

SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K. (Received: May 1



VOLUME 63, NUMBER 4

PHYSICAL REVIEW LETTERS

24

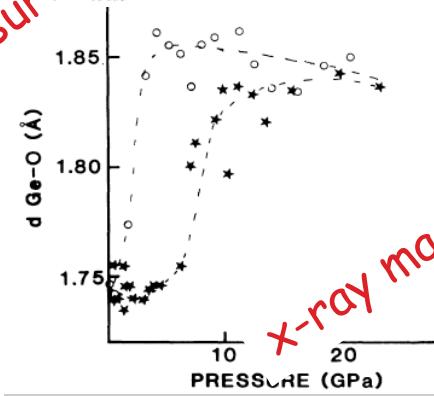
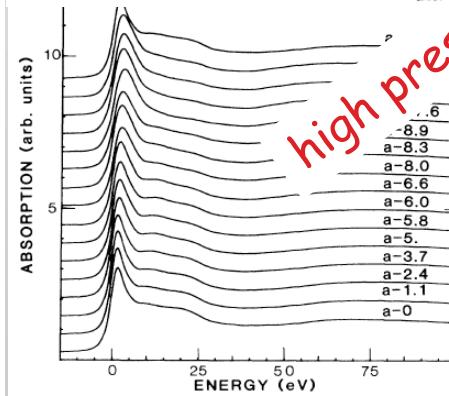
## Pressure-Induced Coordination Changes in Crystalline and Vitreous $\text{GeO}_2$

J. P. Itie,<sup>(1)</sup> A. Polian,<sup>(1)</sup> G. Calas,<sup>(2)</sup> J. Petiau,<sup>(2)</sup> A. Fontaine,<sup>(3)</sup> and H. Tolentino<sup>(3)</sup>

<sup>(1)</sup>Laboratoire de Physique des Milieux Condensés, Université de Paris 6, 75252 Paris, France

<sup>(2)</sup>Laboratoire de Minéralogie-Cristallographie, Universités de Paris 6 et 7 et Centre National de la Recherche Scientifique, 75252 Paris, France

<sup>(3)</sup>Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Commissariat à l'Energie Atomique, Ministère de l'Education Nationale, Centre National de la Recherche Scientifique, Université de Paris-Sud, 91403 Orsay CEDEX 9893



JOURNAL DE PHYSIQUE

Colloque C8, supplément au n° 12, Tome 47, décembre 1986

## STOPPED-FLOW X-RAY ABSORPTION SPECTROSCOPY IN DISPERSIVE MODE

S. SAIGO, H. OYANAGI\*, T. MATSUSHITA\*\*, H. HASHIMOTO\*\*\*, N. YOSHIDA\*, M. FUJIMOTO\* and T. NAGAMURA\*\*

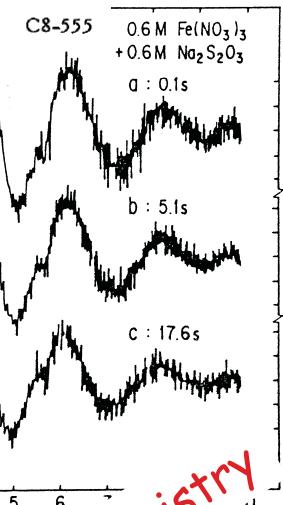
Department of Physics, Jichi-Medical School, Minamimikawachi-gun, Tochigi 329-04, Japan

\*Electrotechnical Laboratory, Umezono, Sakura-mura, Ibaraki 305, Japan

\*\*Photon Factory, National Laboratory for High Energy Physics, Oho-machi, Tsukuba-gun, Ibaraki 305, Japan

\*\*\*Toray Research Center, Sonoyama, Ohno-machi, Saitama 330, Japan

•Department of Chemistry II, Faculty of Science, Hokkaido University, Sapporo 060, Japan



NUMBER 5

PHYSICAL REVIEW JOURNAL

4 AUGUST 1986

## Dispersive X-Ray Spectroscopy for Time-Resolved Observation of Electrochemical Inclusion of Metallic Clusters within Conducting Polymer

G. Tourillon, E. Dartige, A. Fontaine, and A. Jucha

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Centre National d'Orsay, France (Received 27 June 1985)

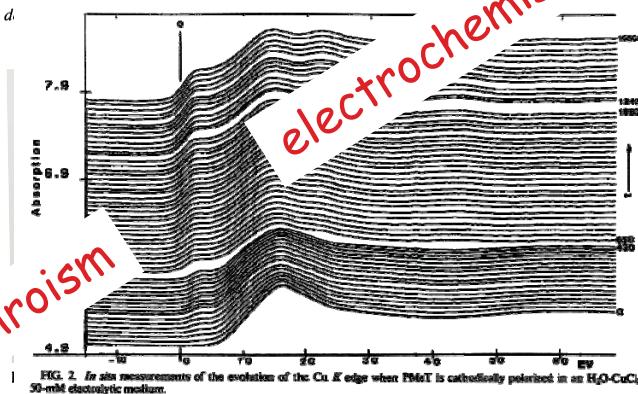


FIG. 2. *In situ* measurements of the evolution of the Cu K edge when PMET is cathodically polarized in an  $\text{H}_2\text{O}-\text{CuCl}_2$  50-mM electrolytic medium.

Europhys. Lett., 13 (5), pp. 131-137 (1990).

## Magnetic Properties of $\text{REFe}_2$ (RE: Ce, Gd, Lu) Compounds Studied by Magnetic X-Ray Dichroism.

F. BAUDELLET<sup>(\*)</sup>, C. BROUARD<sup>(\*\*)</sup>, E. DARTIGE<sup>(\*)</sup>, A. FONTAINE<sup>(\*)</sup>, J. P. KAPPFER<sup>(\*\*\*)</sup> and G. REILL<sup>(\*\*)</sup>

<sup>(\*)</sup>LURE, LP CNRS 008, Université de Paris-Sud - 91405 Orsay, France

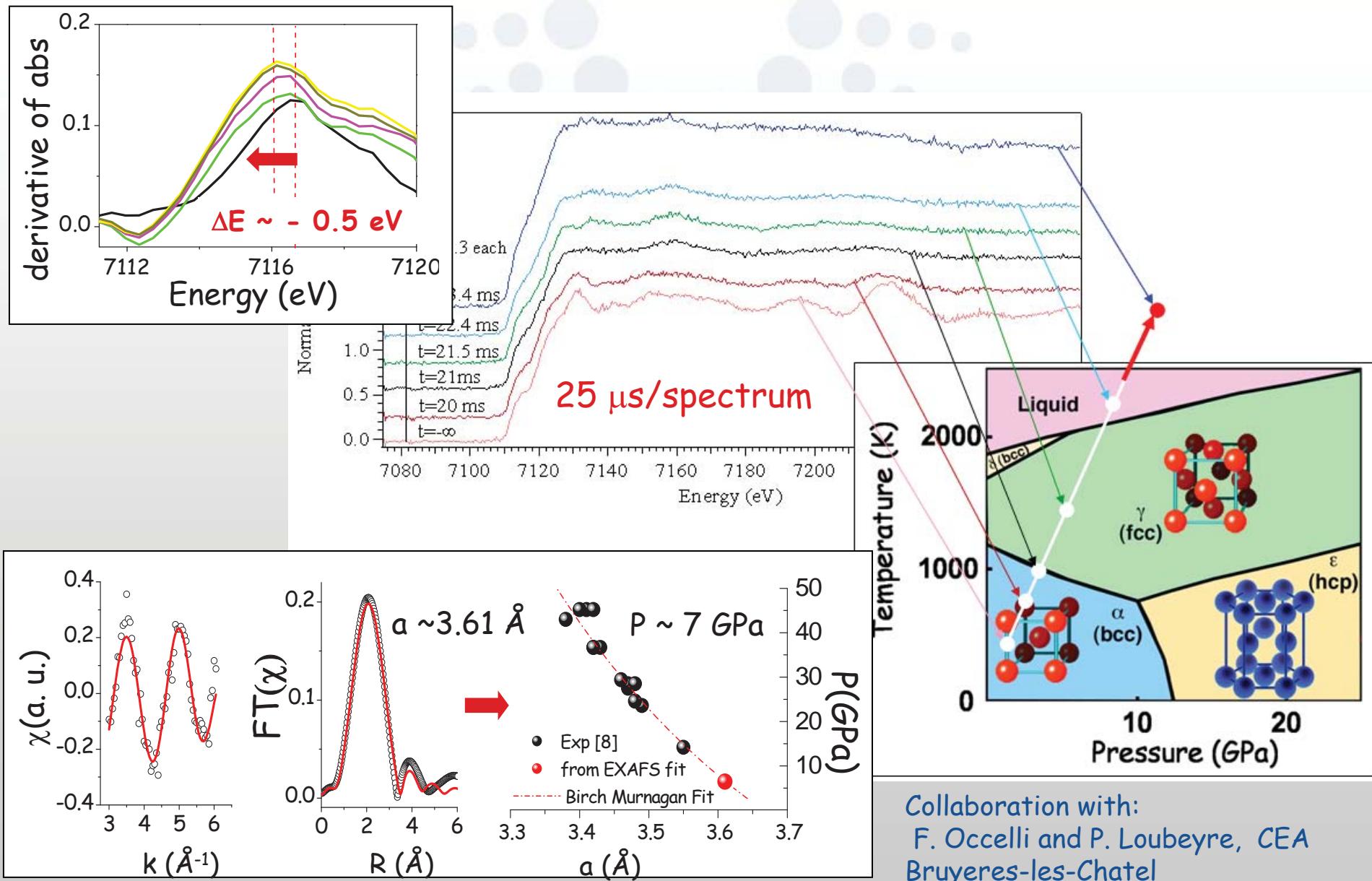
<sup>(\*\*)</sup>Laboratoire de Physique des Solides, UA CNRS 155, Université de Paris-Sud, 91405 Orsay, France

<sup>(\*\*\*)</sup>IPCM, GEMME, UM CNRS 58046, Université Louis Pasteur 67070 Strasbourg, France

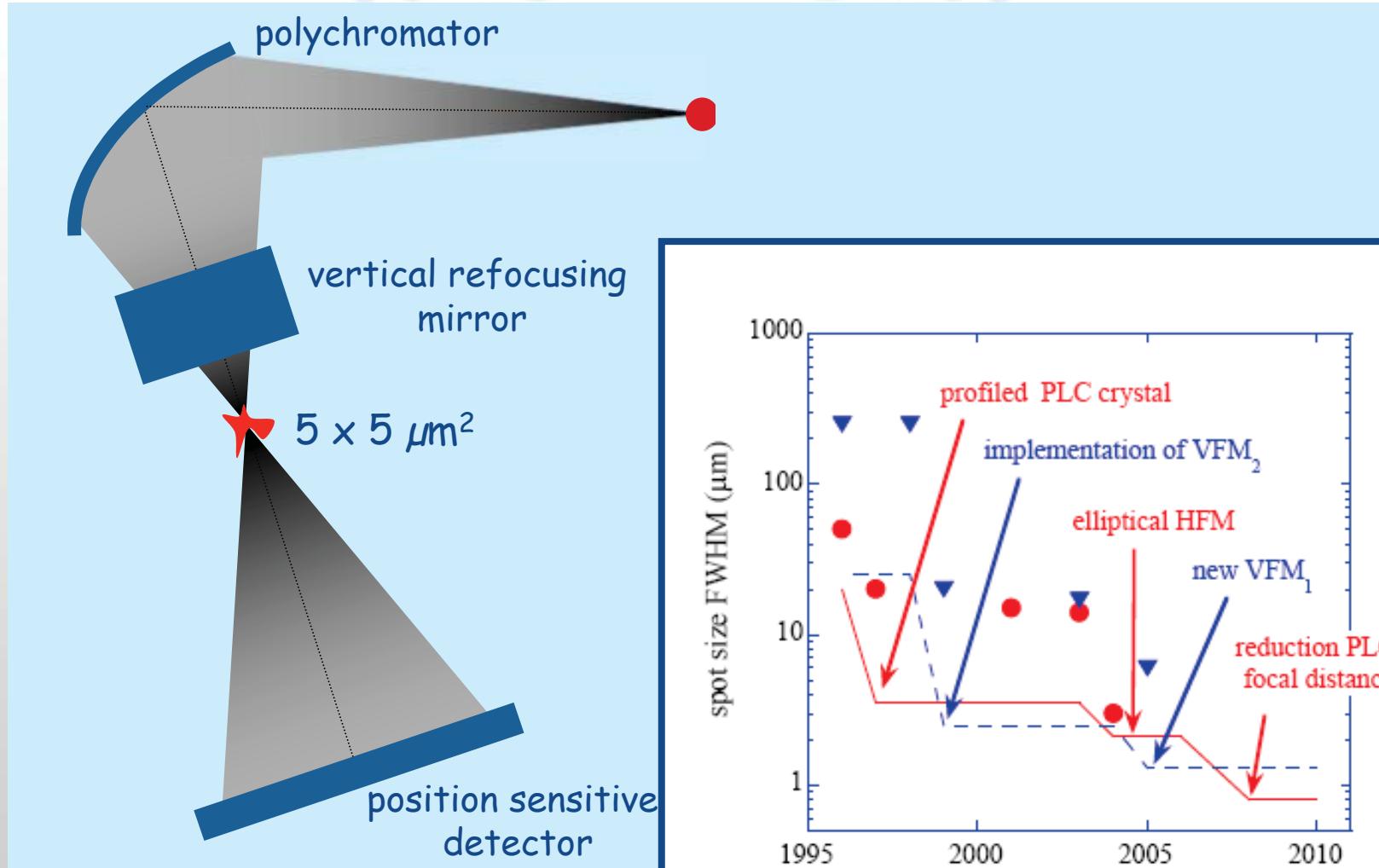
# EDXAS around the world



# Advances in detection: $\mu$ -sec resolved XANES



Collaboration with:  
F. Occelli and P. Loubeyre, CEA  
Bruyeres-les-Chatel

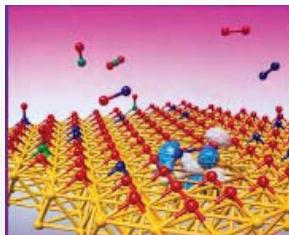


Hagelstein J. Phys. IV France 1997

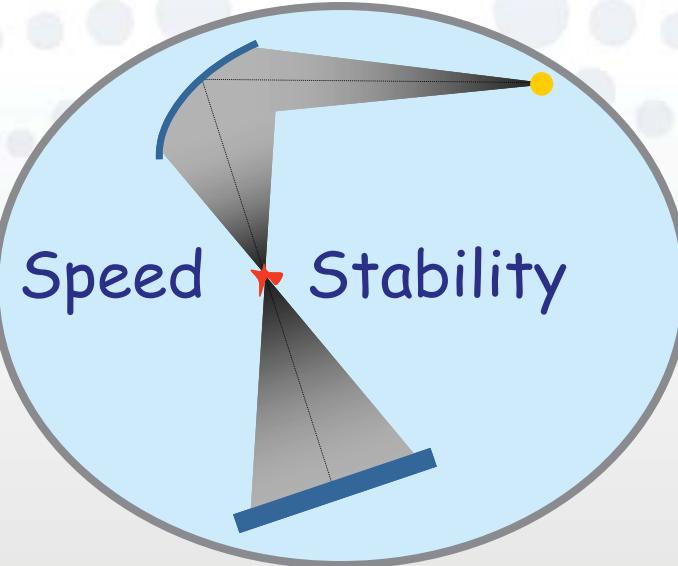
Pascarelli J. Synchrotron Rad. 2006

# Main areas of applications

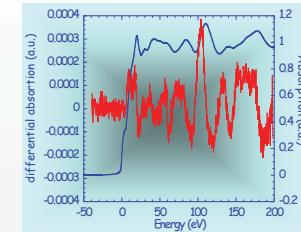
## Time resolved XAS



Full energy spectrum  
acquired simultaneously



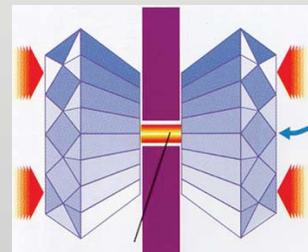
## Differential XAS



Monitor subtle changes in  
XAS exploiting X-ray  
polarization

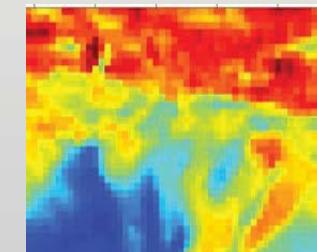
## Micro XAS

### Extreme conditions



Structural studies on tiny  
samples in extreme environments

### 2D mapping



Full XAS spectrum in each pixel  
(fluorescence or transmission)

Review paper: Pascarelli PCCP 2010

## XAS, XANES, EXAFS, and XMCD

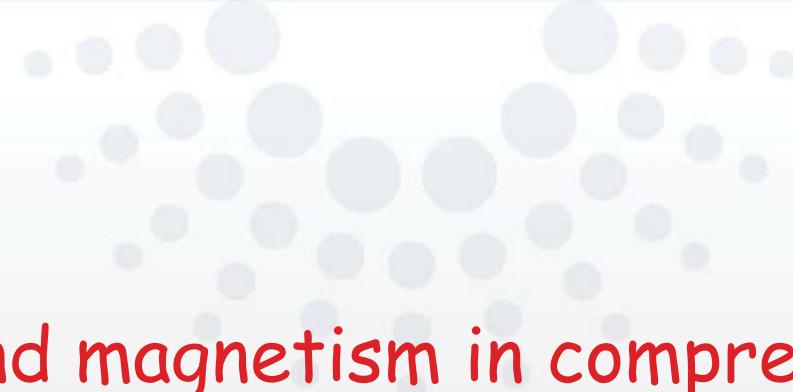
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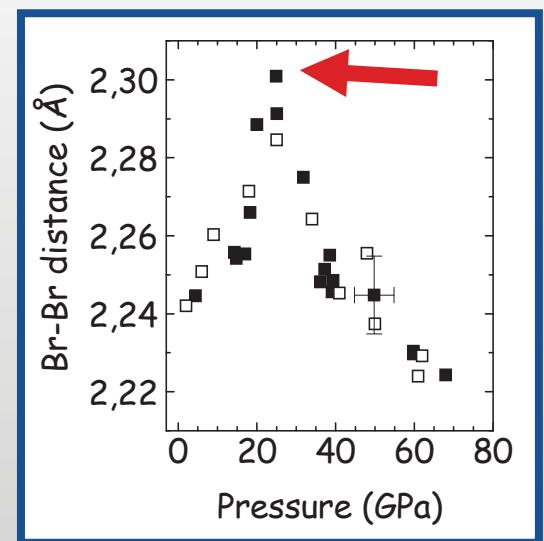
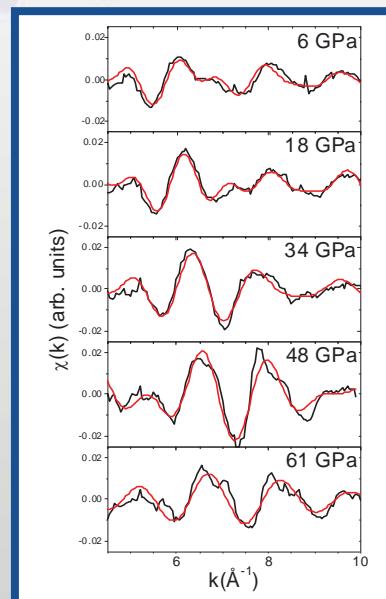
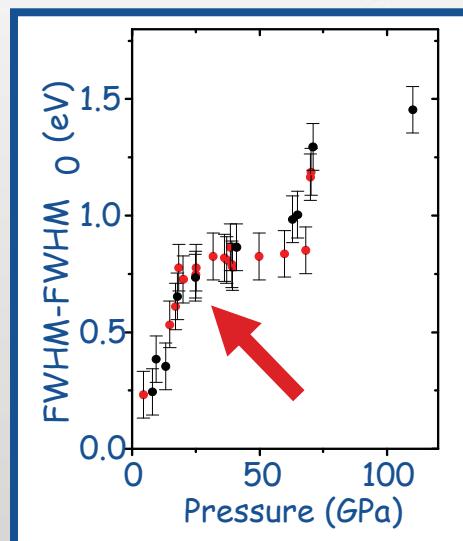
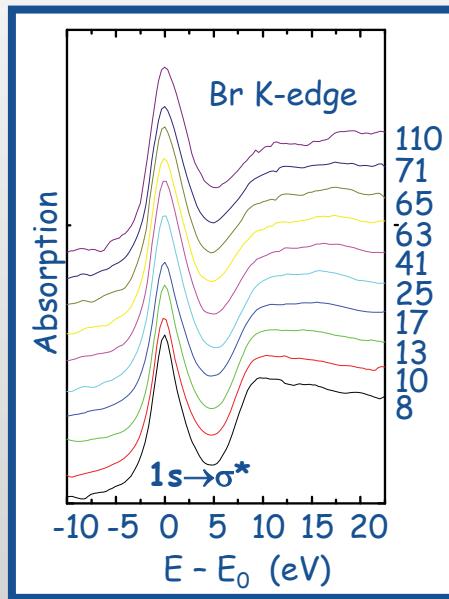
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- Structure and magnetism in compressed matter
- Geochemistry
- Element selective magnetism at pulsed 30T fields

# Metallization and dissociation of diatomic molecules

- Heavier halogens ( $\text{Br}_2$ ,  $\text{I}_2$ ), constitute model systems for the study of simple molecular solids under high pressure
- Metallization and dissociation:  $\text{Br}_2 \sim 60 \text{ GPa}$  and  $115 \text{ GPa}$  [84 GPa IP]
- XRD : Molecular phase stable up to 80 GPa - intramolecular distance rigid



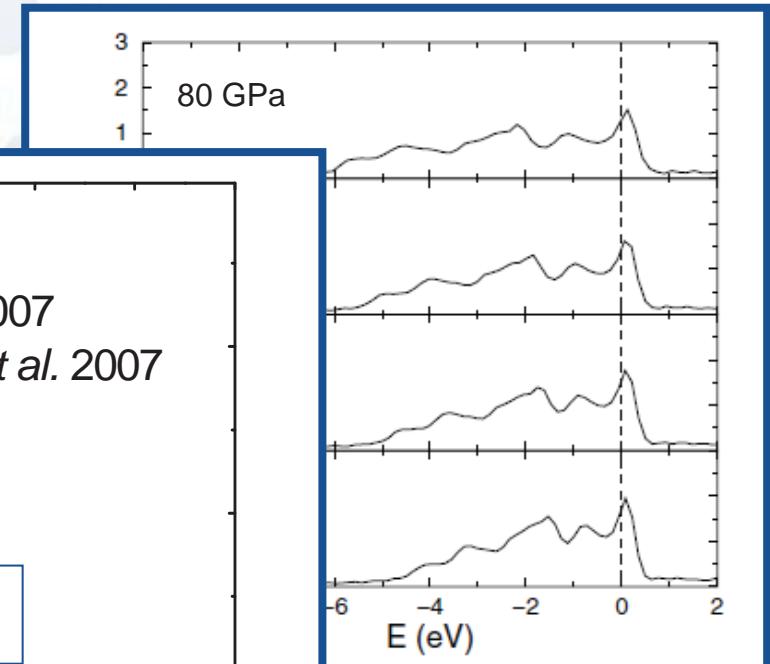
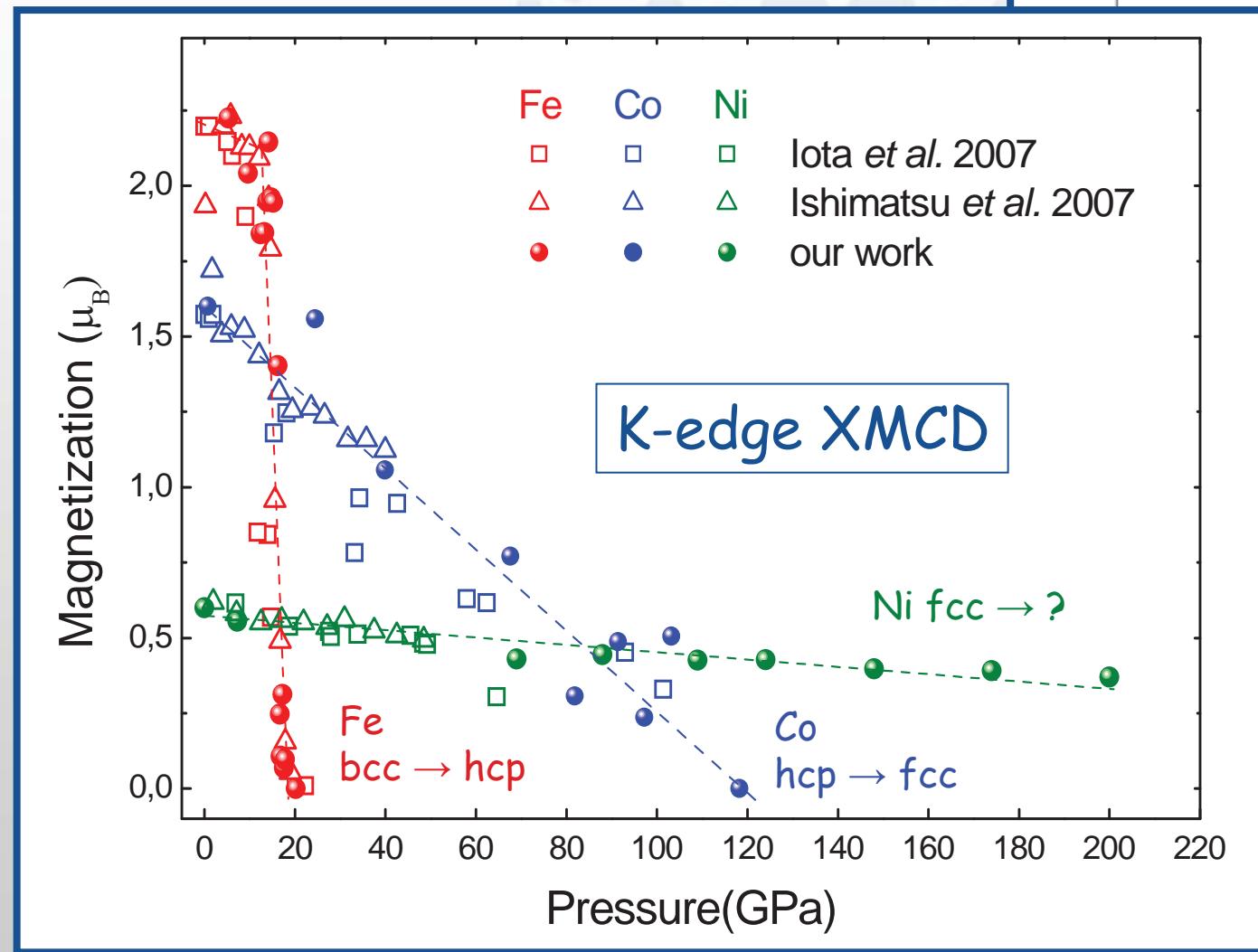
New phase transition at 25 GPa with a loss of molecular character

A. San Miguel et al., Eur. Phys. J. B (2000)

A. San Miguel et al., PRL 99 015501 (2007)

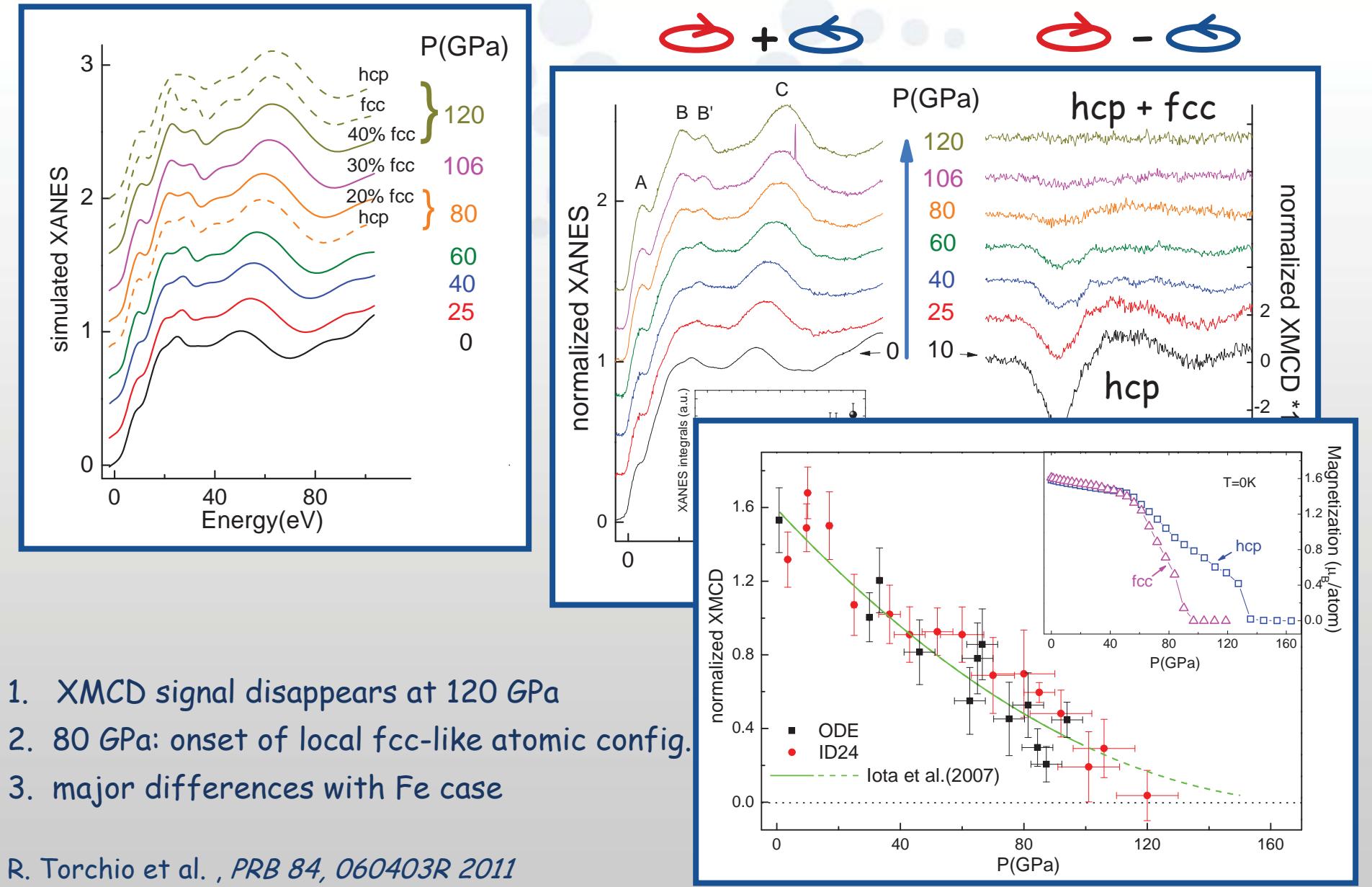
# Collapse of ferromagnetism in 3d metals

In the 3d metals, application of pressure leads to the loss of ferromagnetism



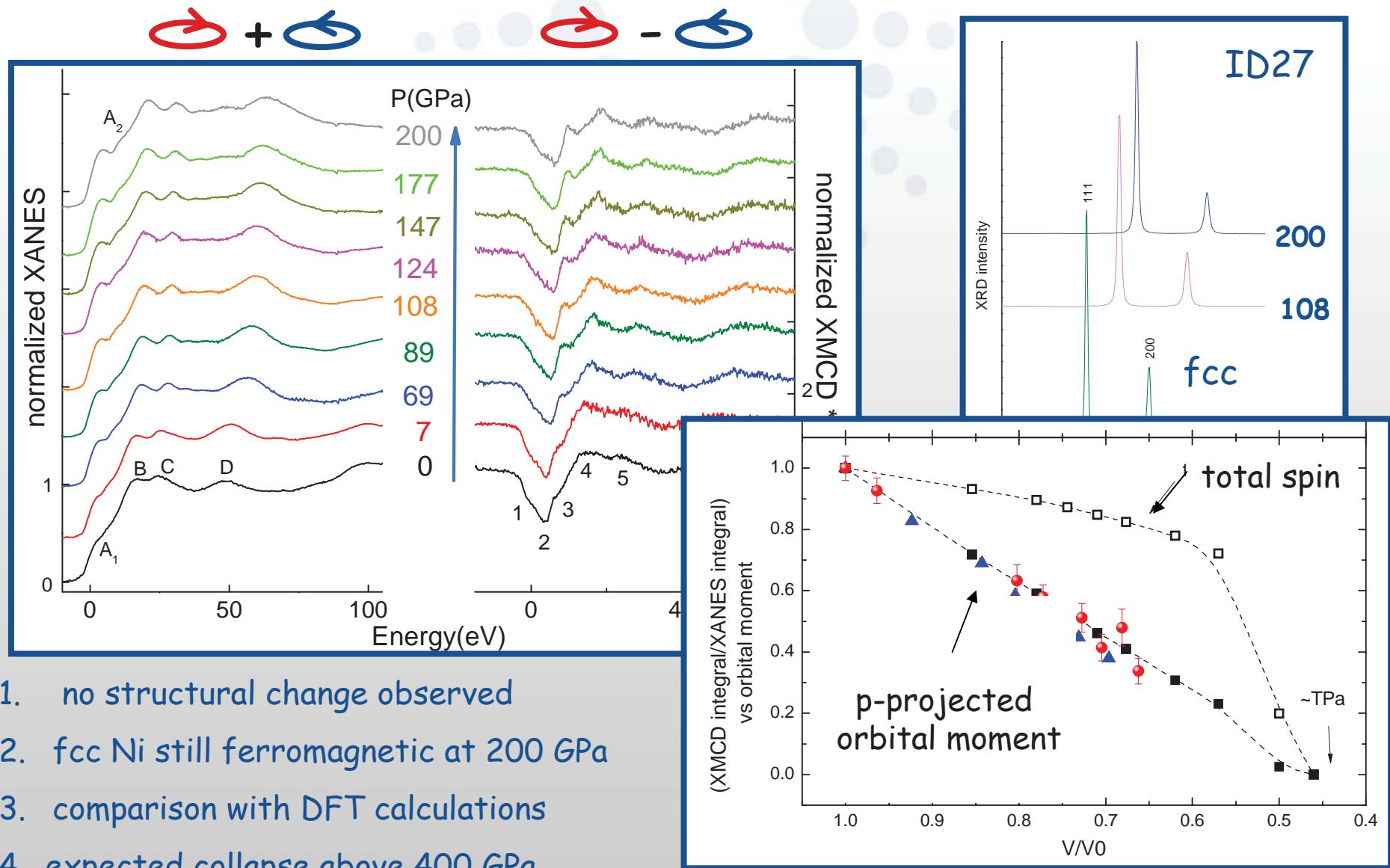
itinerant-electron  
ferromagnetism  
 $\times \text{DOS} (E_F) > 1$   
Stoner (1939)

# Collapse of ferromagnetism in Co



R. Torchio et al. , PRB 84, 060403R 2011

# Resistant ferromagnetism in Ni

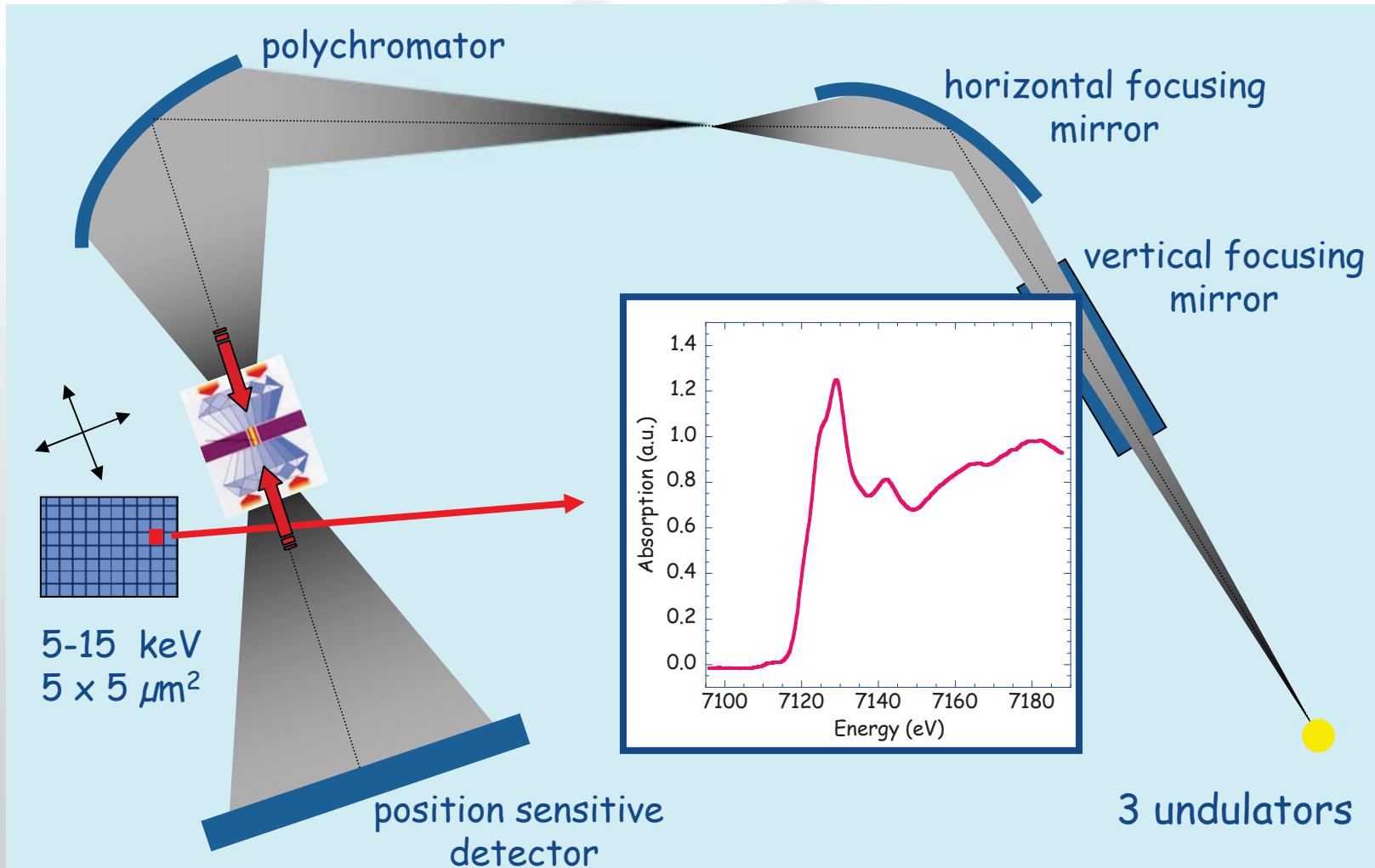


1. no structural change observed
2. fcc Ni still ferromagnetic at 200 GPa
3. comparison with DFT calculations
4. expected collapse above 400 GPa

R. Torchio et al., PRL 107, 237202 2011



- Structure and magnetism in compressed matter
- Geochemistry
- Element selective magnetism at pulsed 30T fields



S. Pascarelli et al. *J. of Synchrotron Rad.* 13, 351 (2006)

# Redox and speciation mapping in the DAC

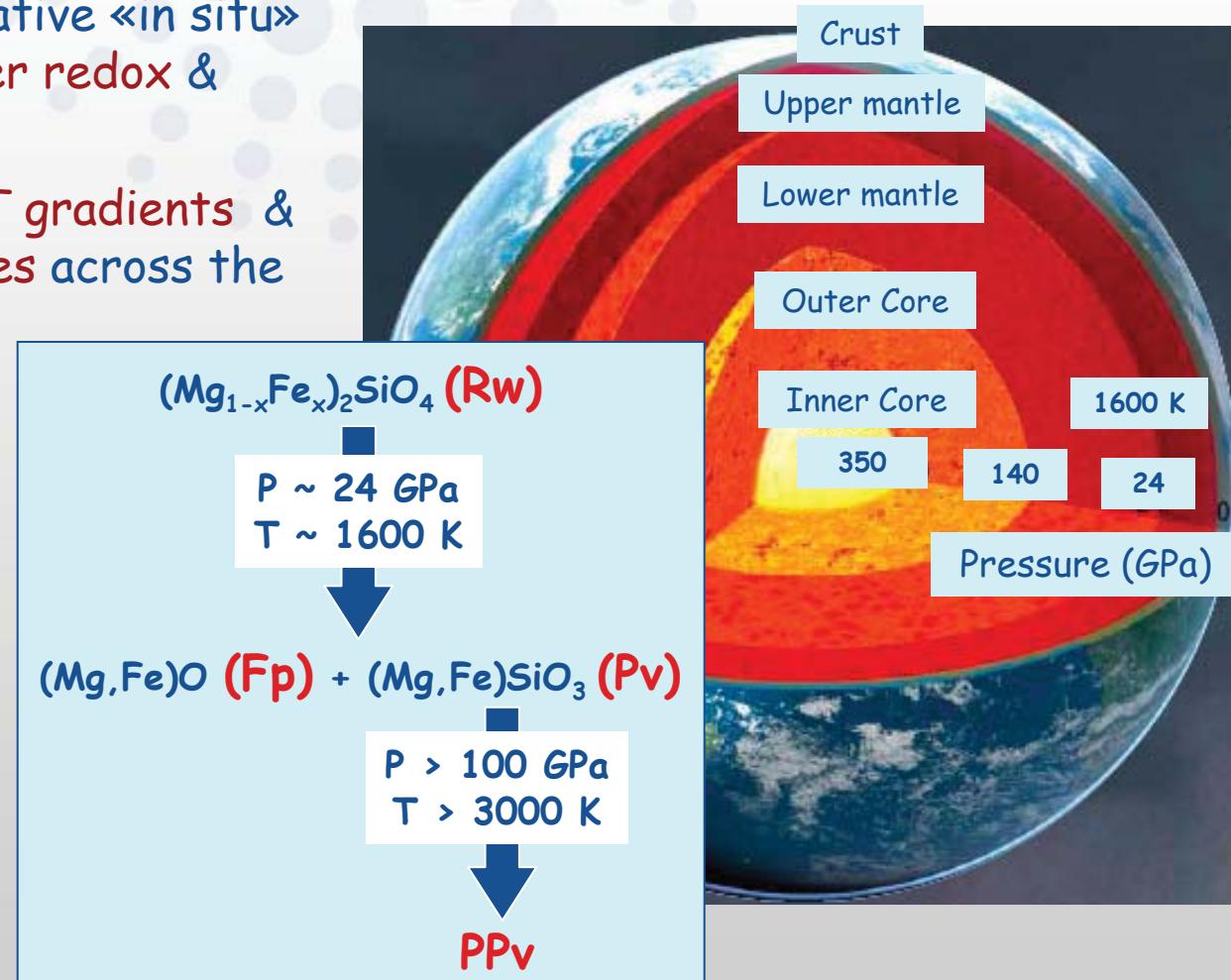
**lack of in situ experiments under relevant P and T conditions**

- opens the way to quantitative «in situ» observations of absorber redox & speciation
- allows to quantify P and T gradients & absorber inhomogeneities across the laser heated spot

Effect of spin crossover  
on Fe partitioning ?

How much Fe in PPv ?

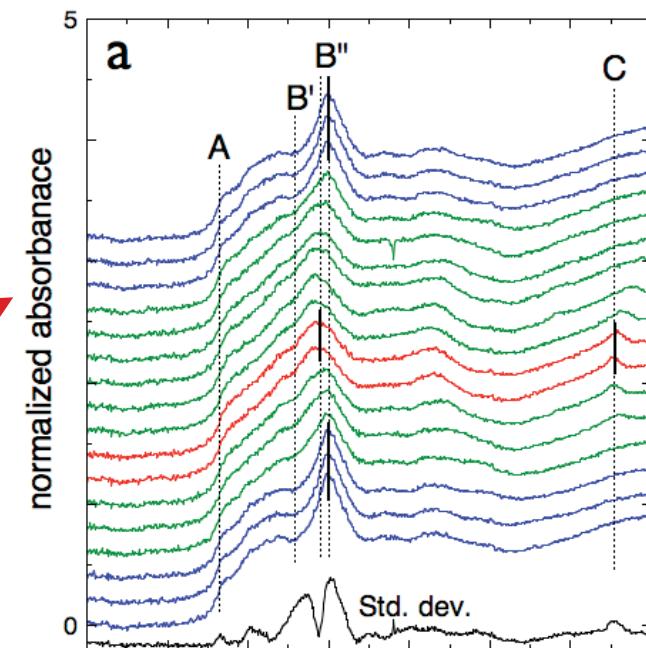
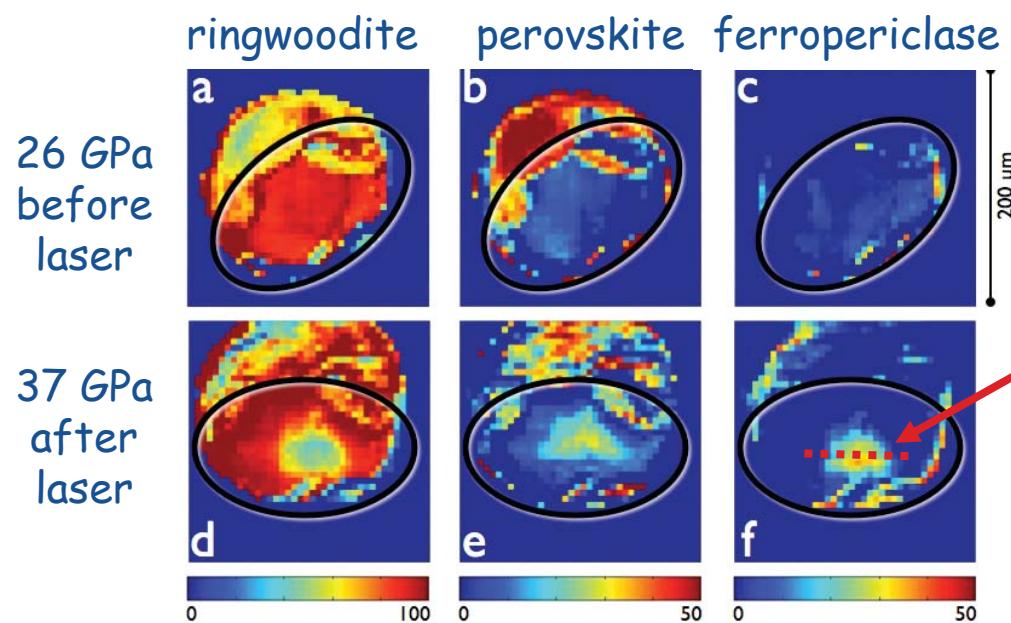
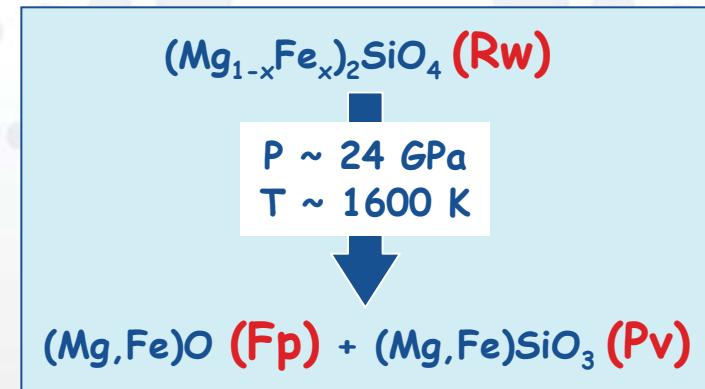
Valence of Fe in PPv ?



M. Muñoz et al *High Pressure Research* 28, 665 (2008)

G. Aquilanti et al., *J. Synchr. Rad.* 16, 376 (2009)

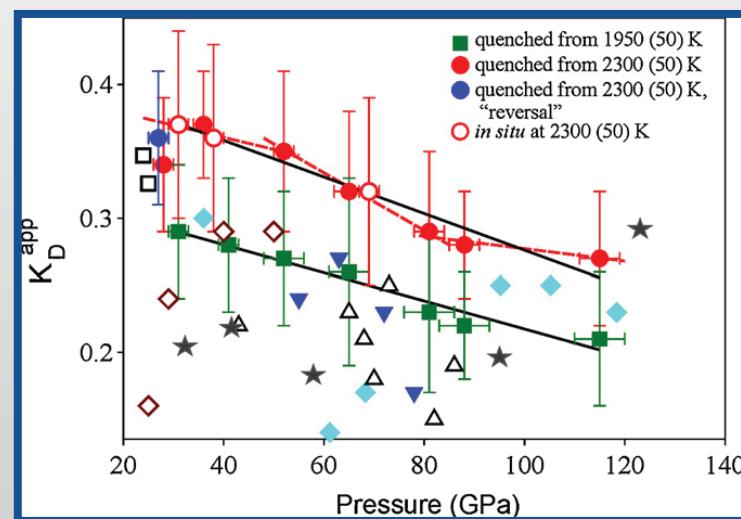
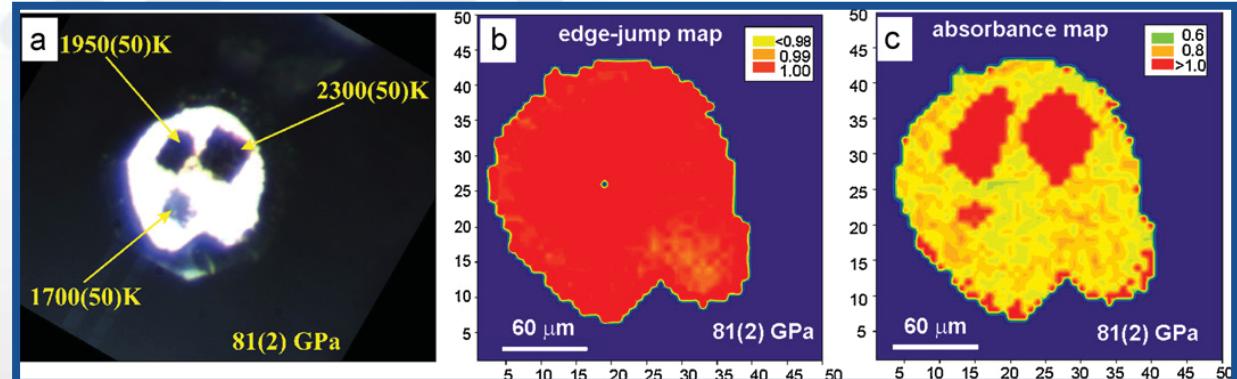
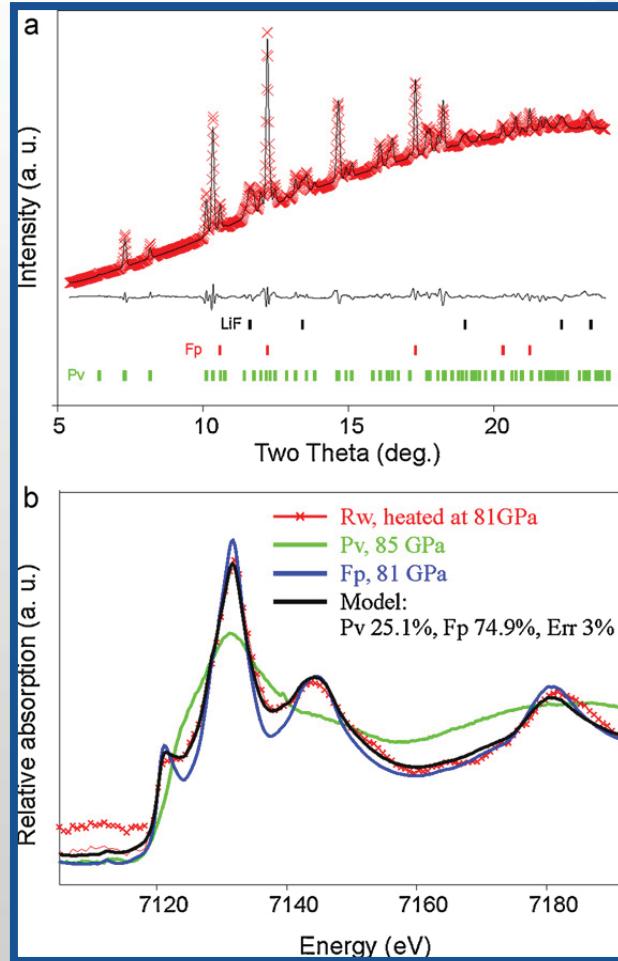
# Structural decomposition of $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$ ringwoodite



M. Muñoz et al *High Pressure Research* 28, 665 (2008)

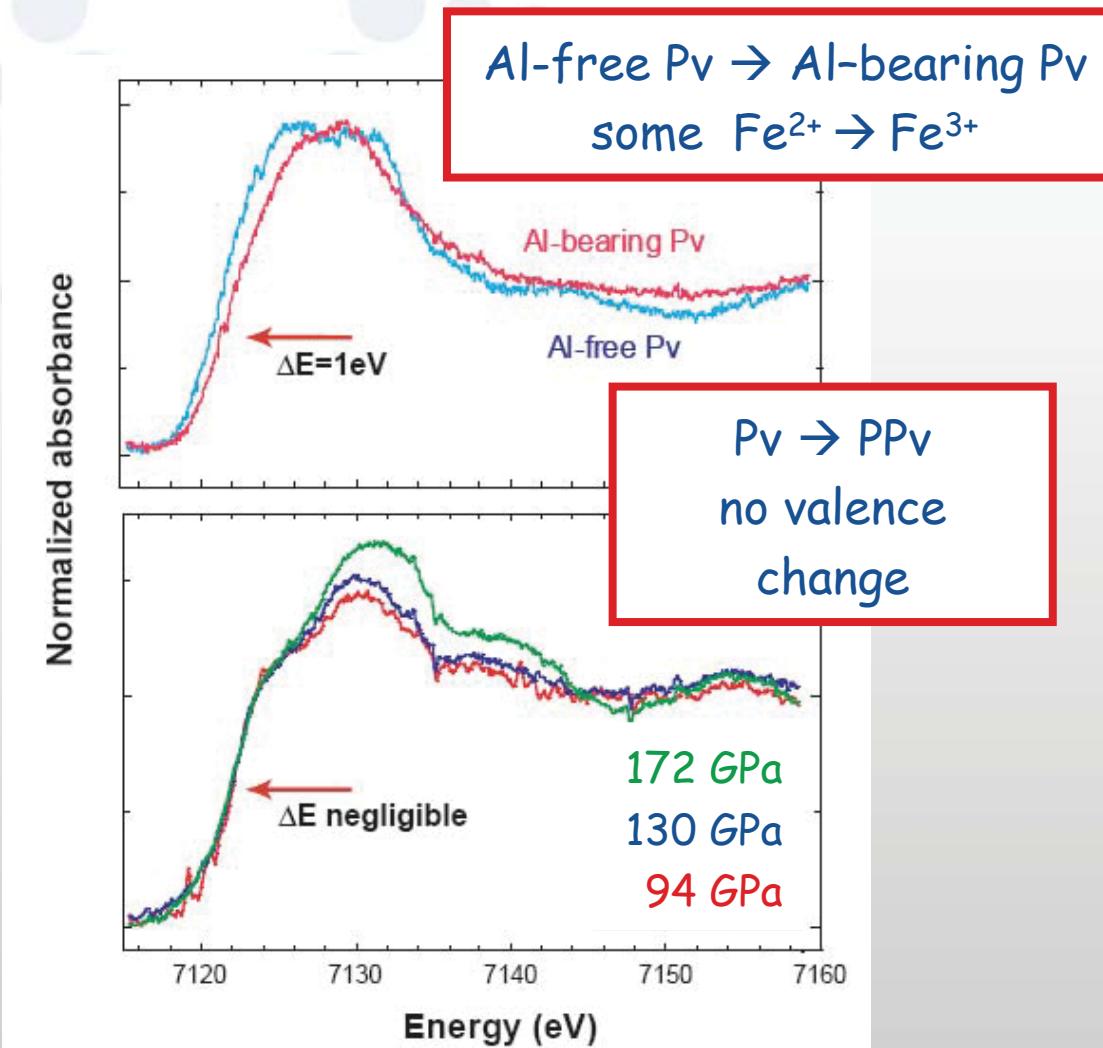
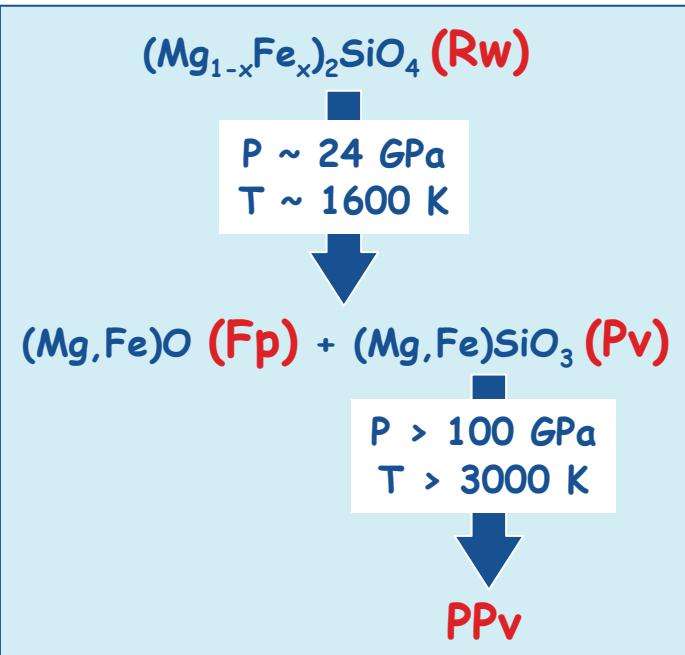
# Partitioning of Fe between Pv and Fp

O. Narygina et al., *Physics of the Earth and Planetary Interiors* 185, 107, (2011)



1. T promotes Fe partitioning in Pv, P acts oppositely
2. no major effect of spin crossover on Fe partitioning
3. no appreciable chemical dishomogeneity in lower mantle

# Valence of Fe in $(\text{Mg},\text{Fe})\text{SiO}_3$ postperovskite phase



D. Andrault et al., EPSL 293, 90-96 (2010)

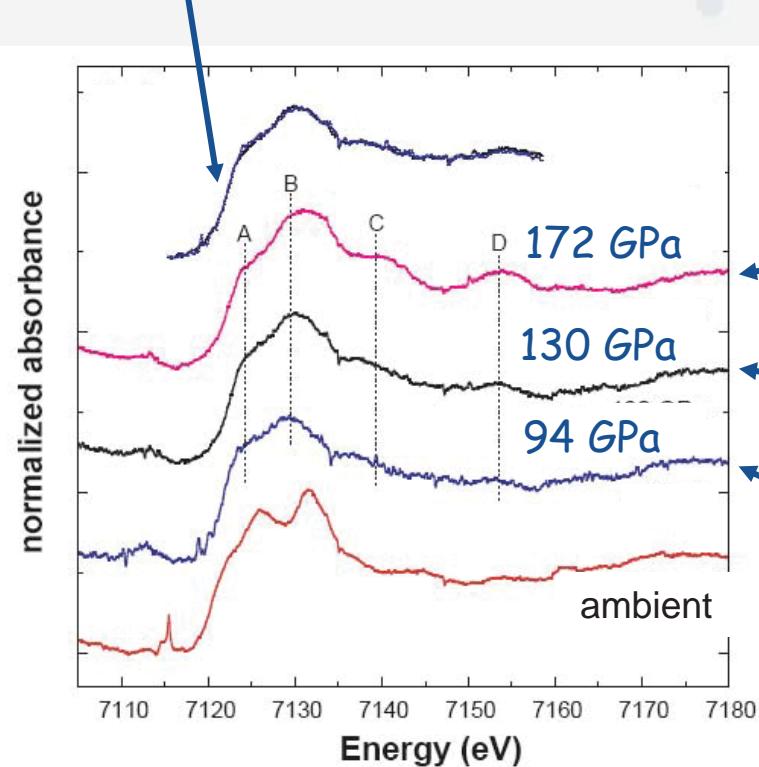
# Partitioning of Fe between perovskite and postperovskite phase



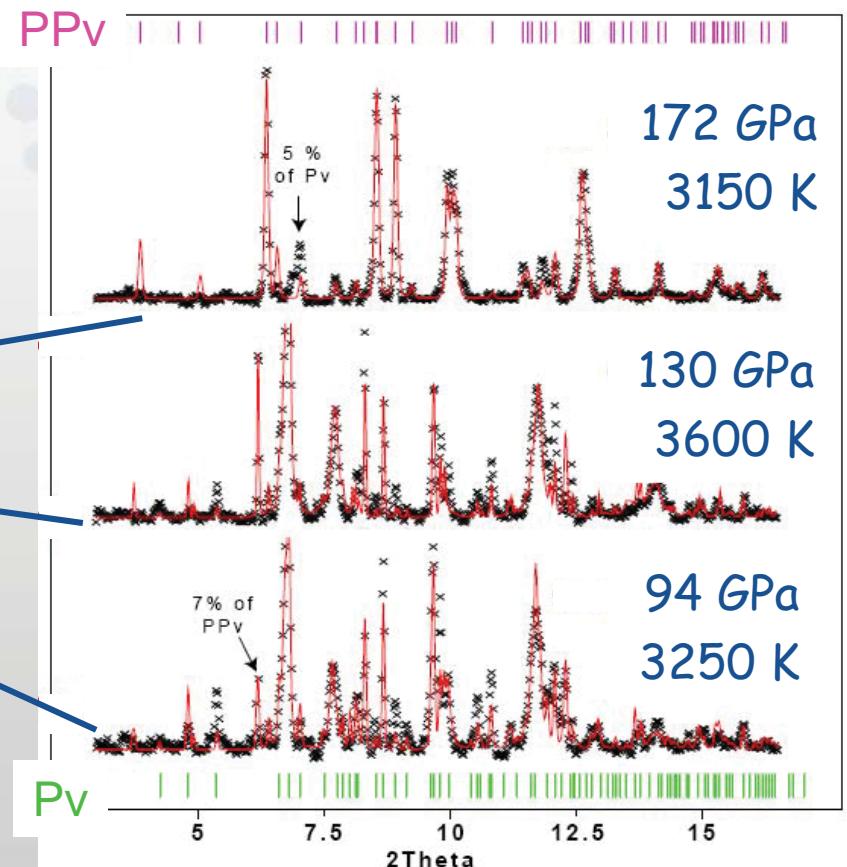
D. Andrault et al., EPSL 293, 90 (2010)

## Fe K-edge XANES (ID24)

$$[130 \text{ GPa}] = 85\% [94 \text{ GPa}] + 15\% [172 \text{ GPa}]$$



## X-ray Diffraction (ID27)



The PPv phase appears largely depleted in Fe compared to Pv  $\rightarrow K_{\text{Fe}}^{\text{Pv/PPv}} = 4.2 \pm 0.5$



- Structure and magnetism in compressed matter
- Geochemistry
- Element selective magnetism at pulsed 30T fields

# Ferrimagnetic materials: high fields

- spinel ferrites  $PQ_2X_4$ :  $Fe_3O_4$ ,  $MgFe_2O_4$ ,  $MnO_3$  ...
- rare earth iron garnets  $P_3Q_2R_3O_{12}$ :  $Y_3Fe_5O_{12}$ ,  $Er_3Fe_5O_{12}$ ,  $Yb_3Fe_5O_{12}$
- double perovskites  $A_2BB'O_6$ :  $Ca_2FeReO_6$ ,  $Sr_2FeMoO_6$  ...
- intermetallics R-T:  $ErCo_2$ ,  $GdNi_2$ ,  $Ho_2Fe_{17}$ ...
- hexagonal magnetoplumbites  $PO \cdot 6Fe_2O_3$ :  $BaFe_{12}O_{19}$  ...
- ...

high fields are required to break  
ferrimagnetic correlations

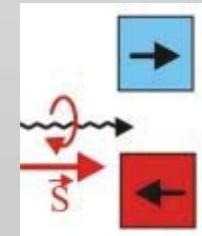


Louis Néel

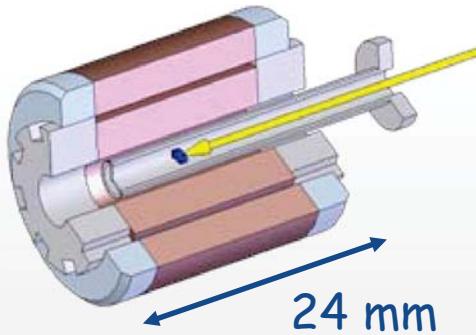
$$H_R = H_0 + \lambda_{RR}M_R - \lambda M_{Fe}$$
$$H_{Fe} = H_0 - \lambda M_R + \lambda_{FeFe}M_{Fe}$$

X-ray Magnetic Circular Dichroism  
allows to address sublattices independently

$$XMCD = \frac{\mu^L - \mu^R}{\mu^L + \mu^R}$$

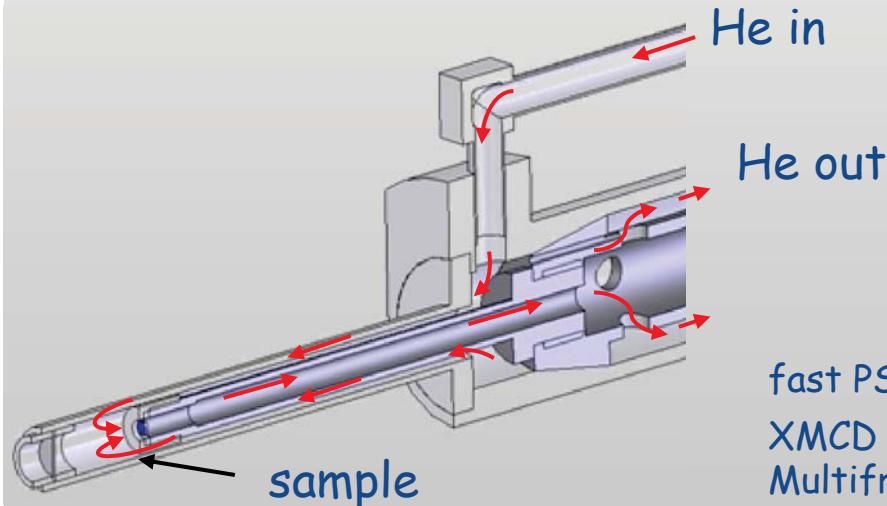


# Pulsed high magnetic fields at ID24

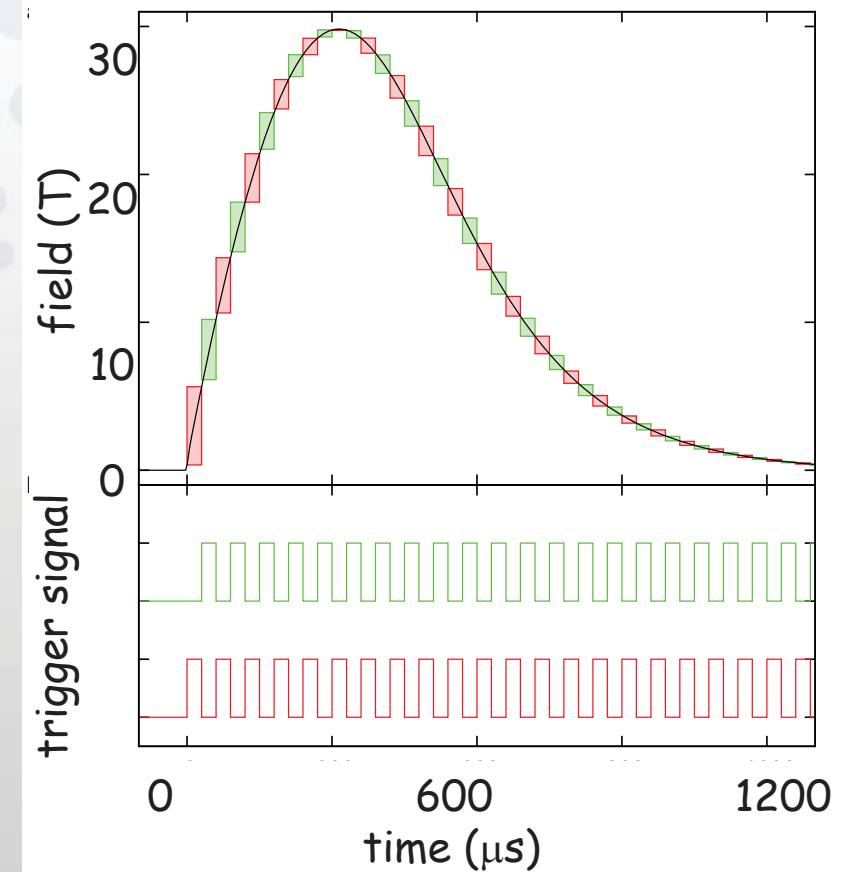


- compact size
- high repetition rate, 30 T every 12 seconds
- independent sample cryostat 5 K - 300 K

P. van der Linden, et al. *Rev. Sci. Inst.* **79**, 075104 (2008)



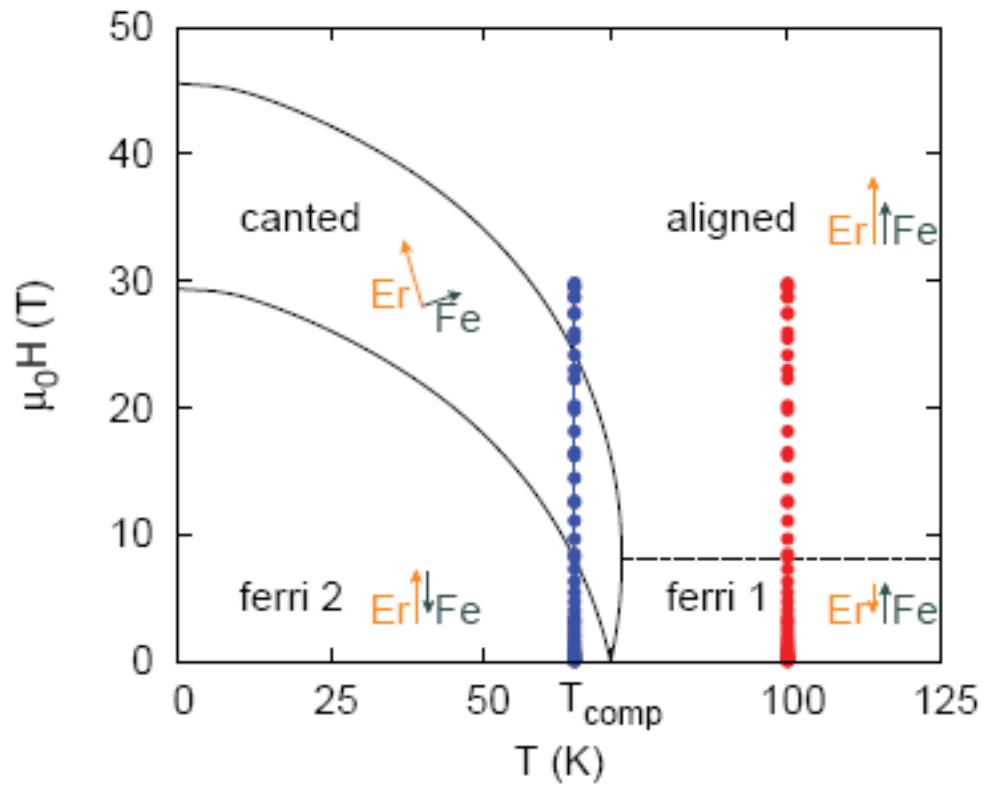
field pulse and acquisition windows



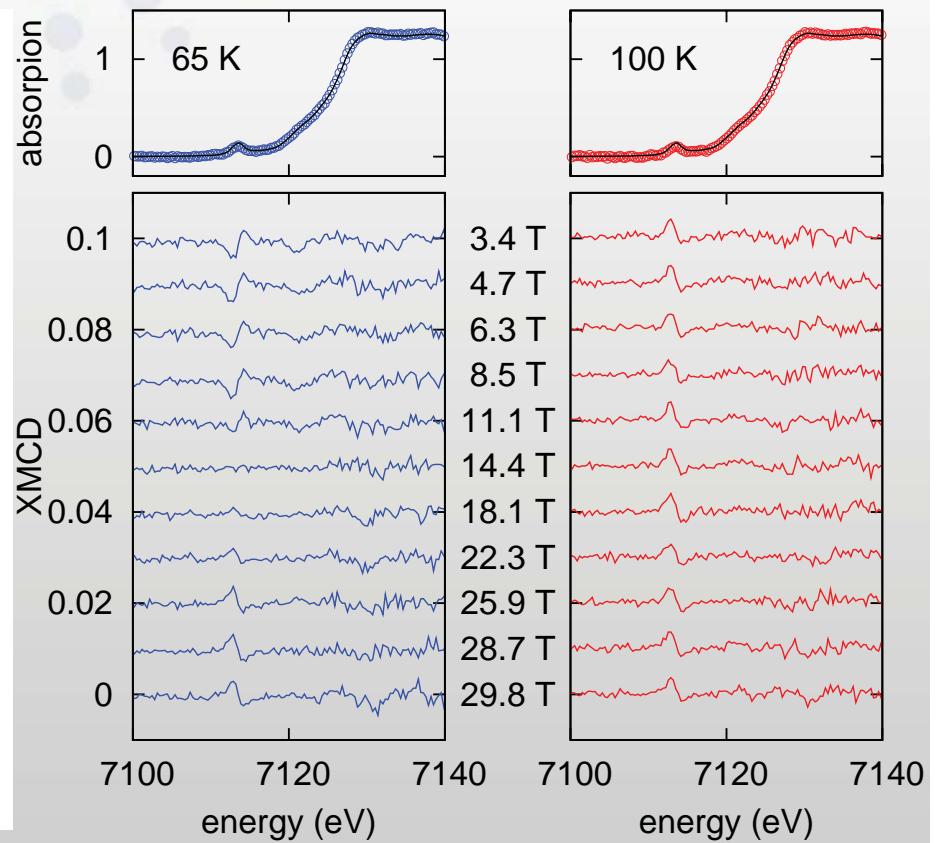
fast PSD "Ultra System": Headspith et al proc. of NSS-MIC2007  
XMCD in pulsed fields: O. Mathon et al. *JSR* **14**, 409 (2007)  
Multiframe detection: C. Strohm et al. accepted in *JSR* (2011)

# Fe K-edge XMCD in $\text{Er}_3\text{Fe}_5\text{O}_{12}$

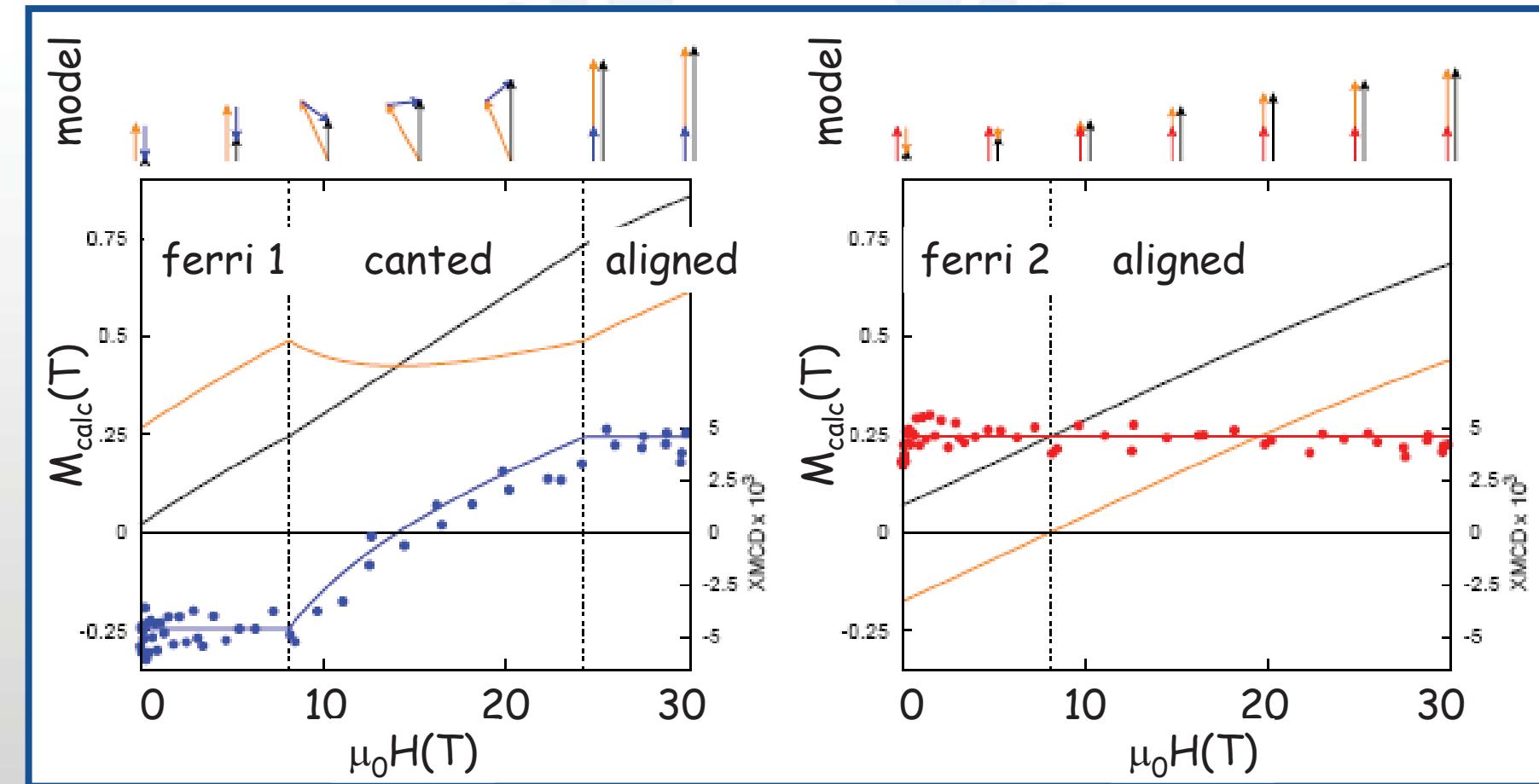
phase diagram (field along 100)



Fe K edge XMCD spectra



# Fe sublattice magnetization in $\text{Er}_3\text{Fe}_5\text{O}_{12}$



- XMCD amplitude - direct probe of Fe-sublattice magnetization
- direct observation of spin reorientation in canted phase

C. Strohm et al. *in preparation*

## XAS, XANES, EXAFS, and XMCD

- X-ray Absorption
- X-ray Absorption Fine Structure
- Simple Theoretical Description
- XANES
- Major historical EXAFS breakthroughs
- Examples of applications at ELETTRA
- Introduction to XMCD

yesterday

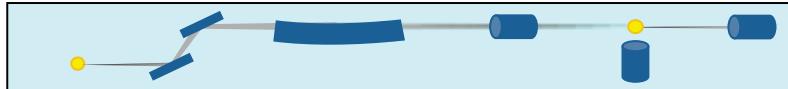
today

## Energy Dispersive XAS

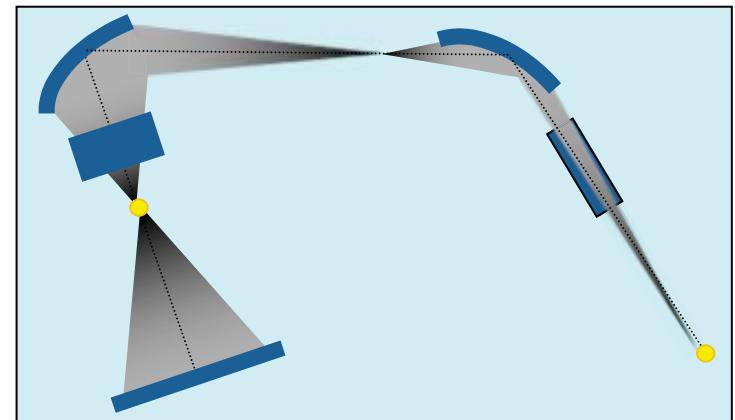
- X-ray Absorption Spectrometers
- EDXAS
  - Basic principles, historical evolution
  - Examples of applications at ESRF
  - Future opportunities for studies of matter at extremes
- Probing laser induced extreme states of matter

# UPBL11: Time Resolved and Extreme Conditions XAS

- Transfer of EXAFS bl BM29 to BM23



- Re-design of EDXAS bl ID24



- Stability → re-design of optics and experimental stations
- Focal spot → double branch (3 vs 100  $\mu\text{m}$ ) on time-shared basis
- Detection → new generation of micro-strip detectors ( $\mu\text{s}$ )

Opening dates for public:

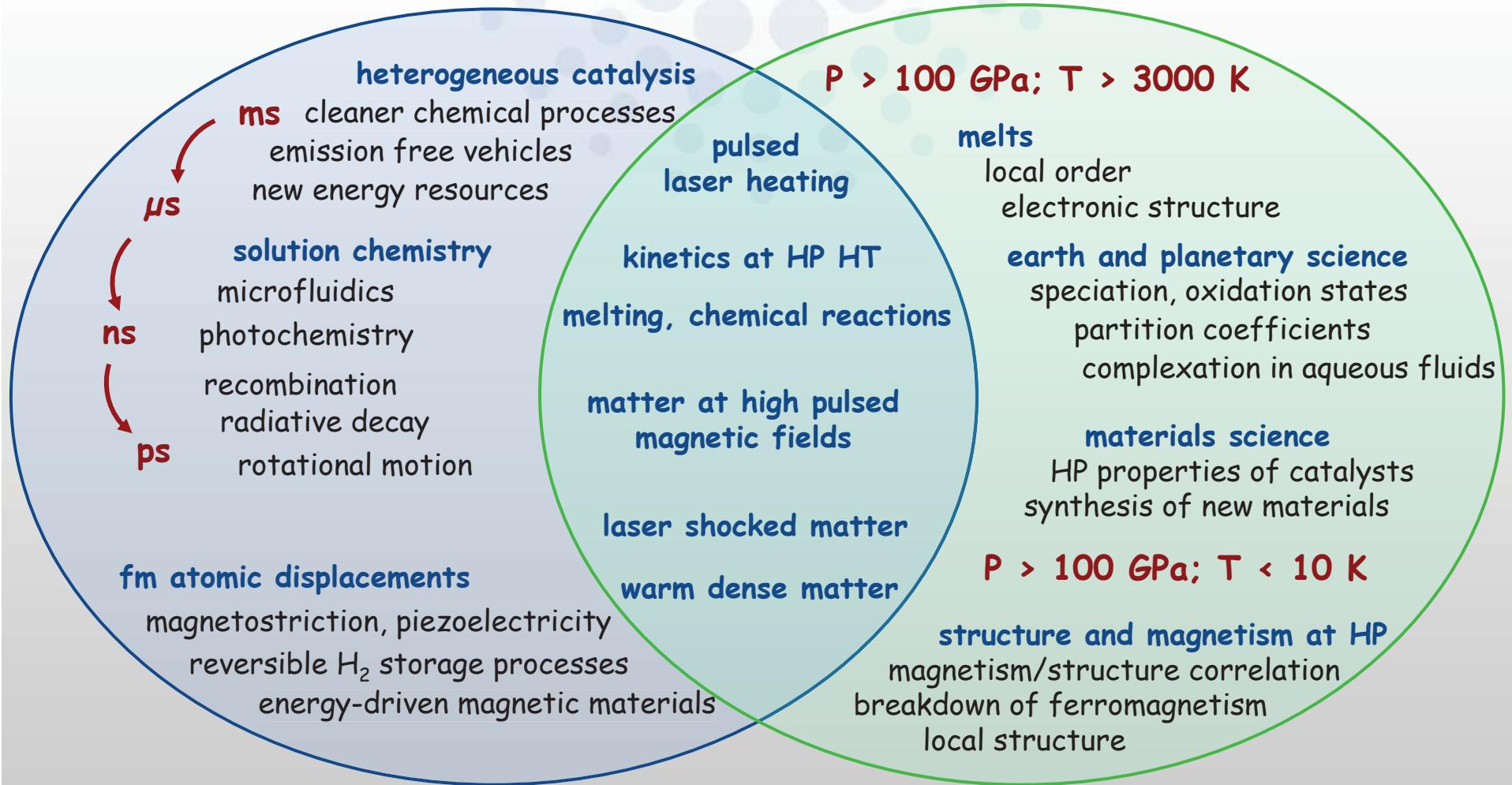
BM23:

March 2011

ID24:

May 2012

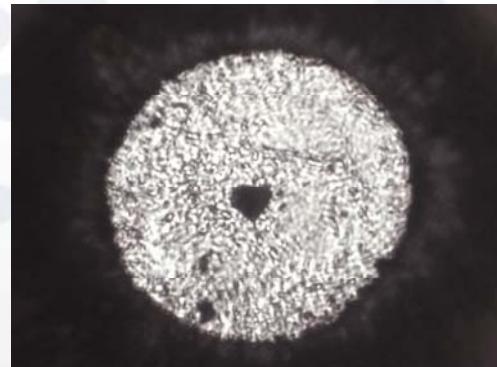
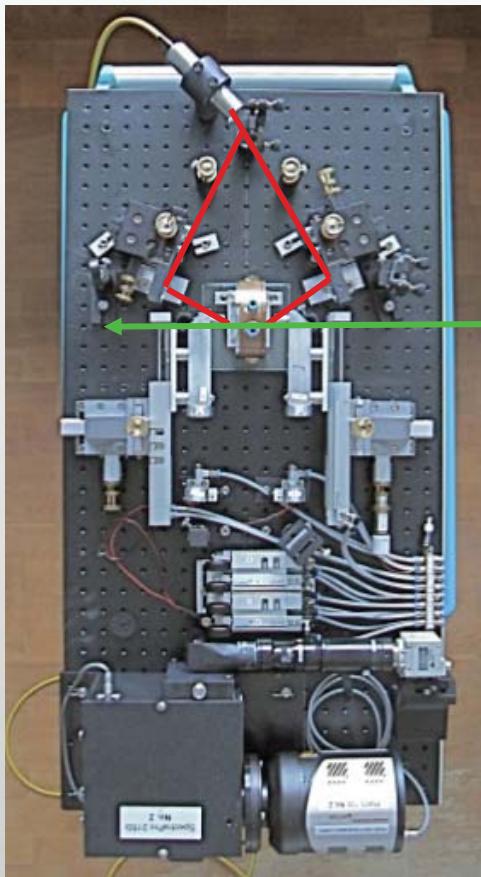
## time resolved



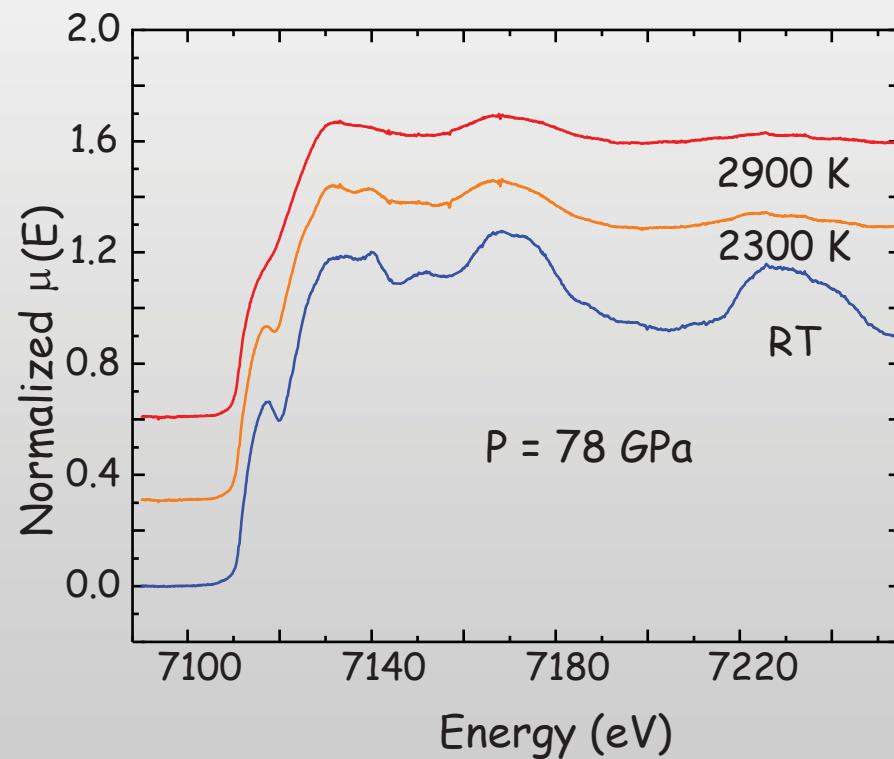
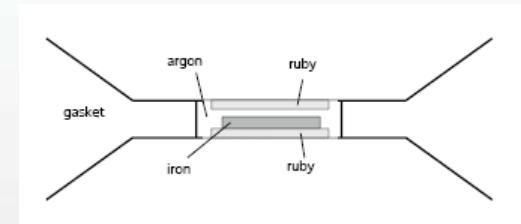
## extreme conditions

# Melting of Fe in the DAC

Fiber pumped near infrared laser ( $P=110$  W,  $\lambda=1070$  nm)



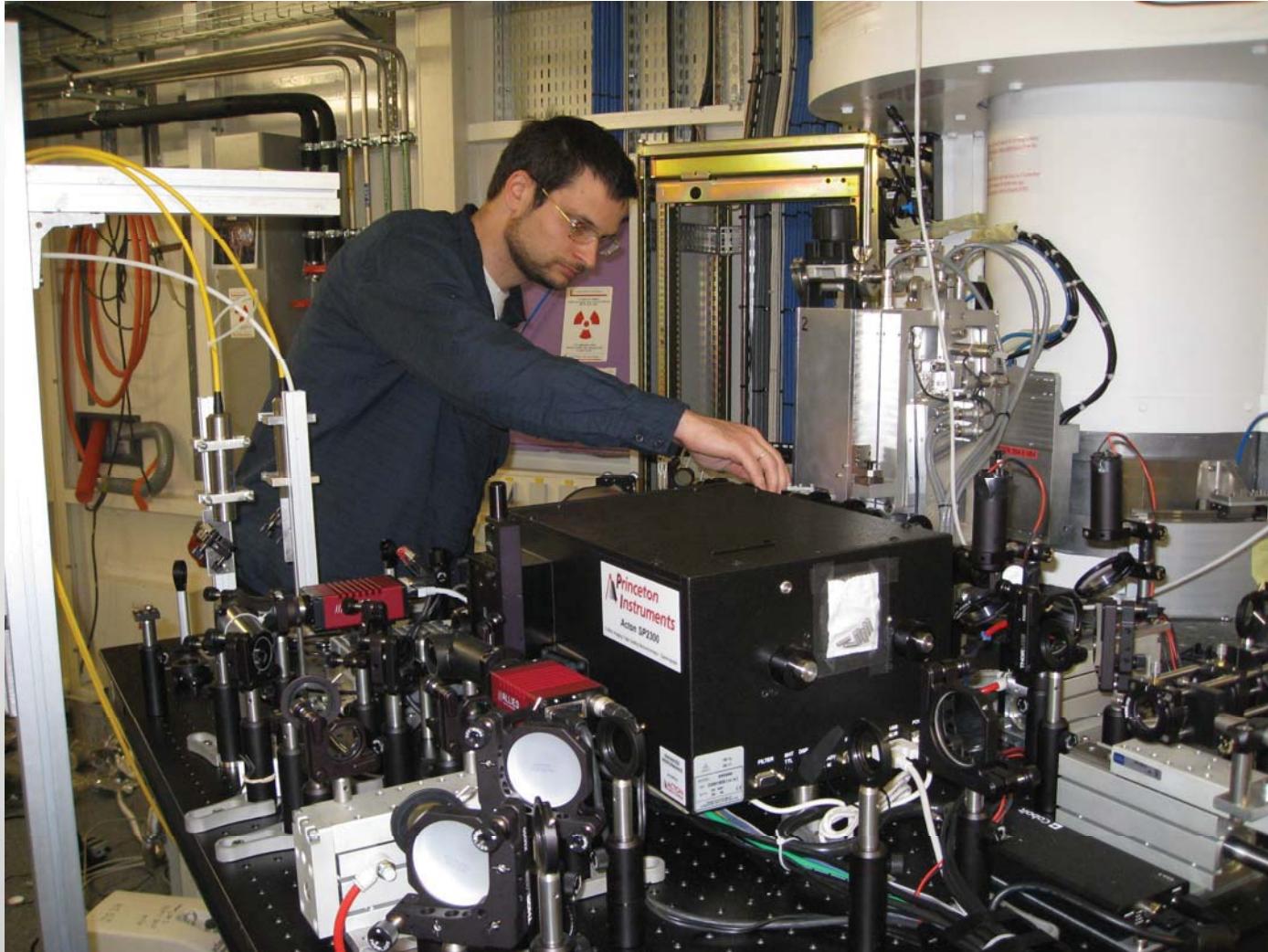
- spherical shape
- size commensurate with laser beam ( $< 30 \mu\text{m}$ )



R. Boehler et al., Rev. Sci. Instr. 80, 045103 (2009)

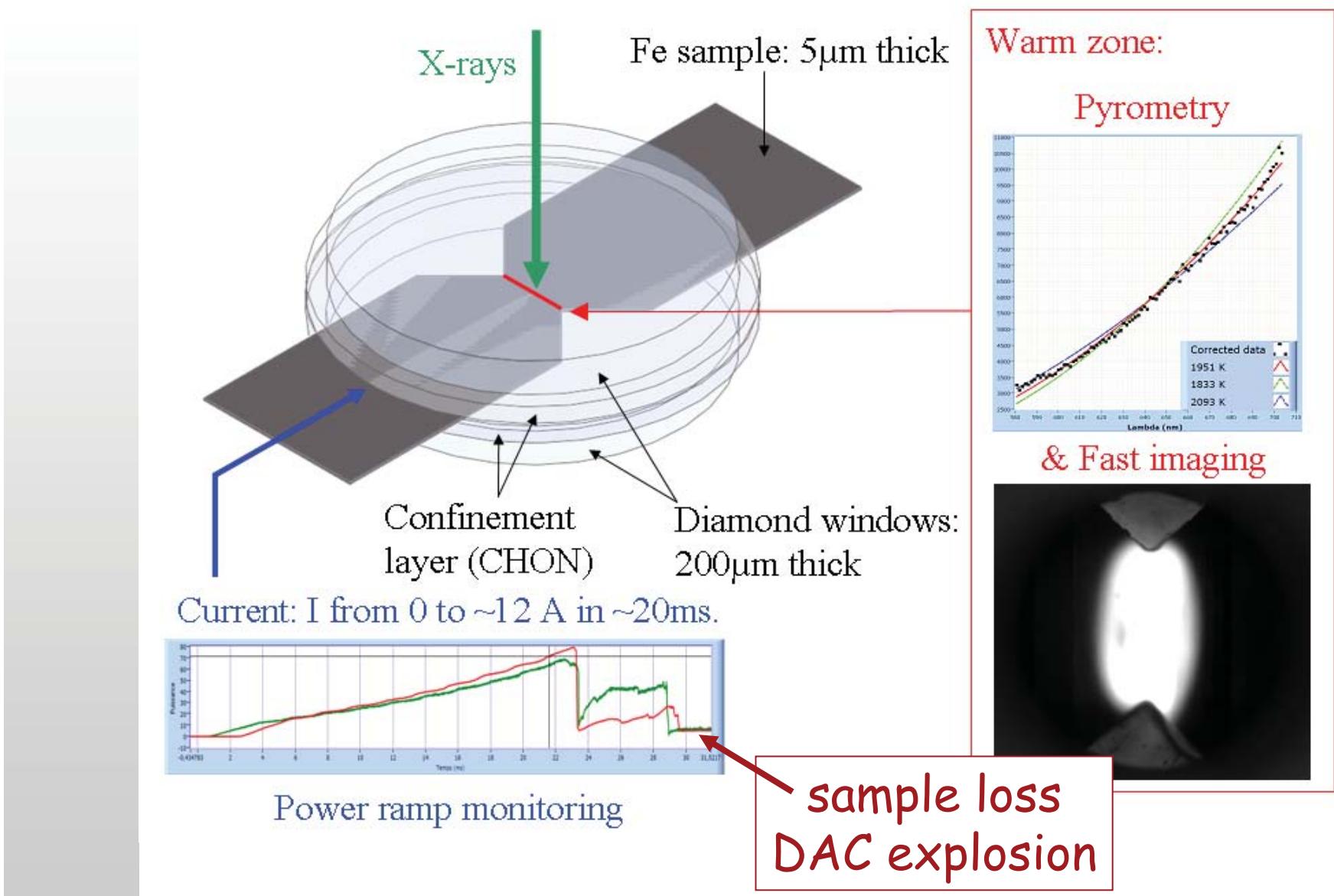
# UPBL11 : commissioning of laser heating facility

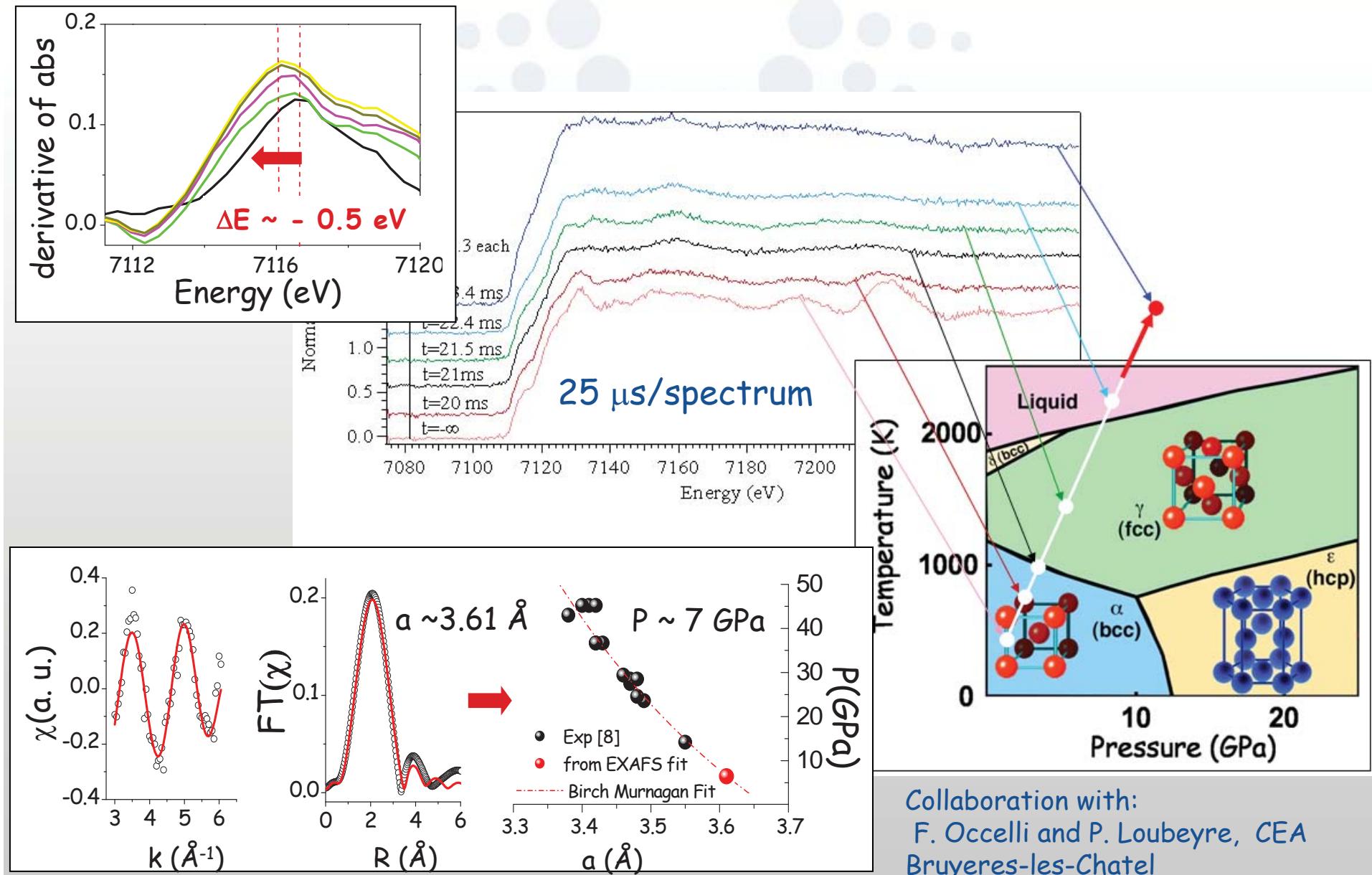
Innokenty Kantor



HP/HT laser setup installed on EDXAS-S for commissioning (Nov 2011)

# Electric discharge through a conducting sample: first attempts to probe warm dense Fe





Collaboration with:  
 F. Occelli and P. Loubeyre, CEA  
 Bruyeres-les-Chatel