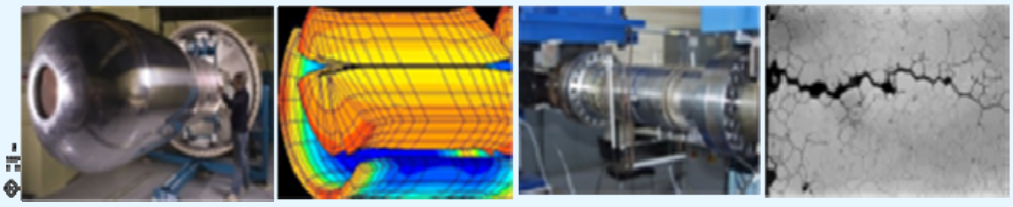
MINOS

Centre of Excellence for Nuclear Materials

Workshop

Materials Innovation for Nuclear Optimized Systems



December 5-7, 2012, CEA – INSTN Saclay, France

Jean-Luc BÉCHADE et al.

CEA (France)

New Characterizations at the MARS Beamline (SOLEIL Synchrotron Radiation)

Workshop organized by:

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Workshop Materials Innovation for Nuclear Optimized Systems
December 5-7, 2012, CEA – INSTN Saclay, France

New Characterizations at the MARS Beamline (SOLEIL Synchrotron Radiation)

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MARS (Multi-Analyses on Radioactive Samples) is the X-ray bending magnet beamline of the French synchrotron facility SOLEIL dedicated to the study of radioactive matter by means of a multi-technique equipment [1].

The MARS beamline is the fourth dedicated beamline for studying radionuclides in Europe (after the ROBL beamline at ESRF (Grenoble, France), the INE beamline at ANKA (Karlsruhe, Germany) and the microXAS beamline at SLS (Villingen, Switzerland) and aims at extending the possibilities of synchrotron based X-ray characterizations towards a wider variety of radioactive elements (α, β, γ and n emitters). Thus, its specific and innovative infrastructure has been optimized to carry out analyses on radioactive materials with global activities up to 18.5 GBq per sample [2]. Particularly, it offers unique possibilities for studying γ and neutrons emitters' samples with an activity up to 2 GBq. Nevertheless, such a possibility supposes to obtain special authorizations from French safety authorities (ASN) based on specific technical innovations to assure the confinement of samples and to reduce the dose rate during their manipulation on the beamline.

This beamline, which has been built thanks to a close partnership and support by the CEA, has been designed to provide X-rays in the energy range of 3.5 keV to 35 keV. Three main techniques are progressively proposed on MARS beamline: transmission and high-resolution powder X-ray diffraction (respectively TXRD and HRXRD), X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF) [3].

After the preliminary experiences performed in 2009-2010 on un-irradiated samples [1, 3, 4], this presentation deals with recent results obtained at the MARS beamline, thanks, (i) to very powerful and useful improvements brought to the experimental set-up of the beamline (especially High Resolution diffractometer, fig. 1) and (ii) to various materials irradiated at high doses with ions (ODS up to 200 dpa) and also Zr based alloys irradiated with neutrons in Pressurized Water Reactors up to 5 PWR cycles.

The results obtained by X ray Diffraction on secondary phases evolutions as a function of irradiation doses for both ODS and Zr based alloys will be exposed, along with the very first XAS experiences performed on ODS materials.

Finally, future prospects and main objectives concerning the evolution of the beamline for our program on irradiated materials will be discussed; for example the milestone for 2013 concerning the analysis on ODS irradiated at high doses with neutrons.

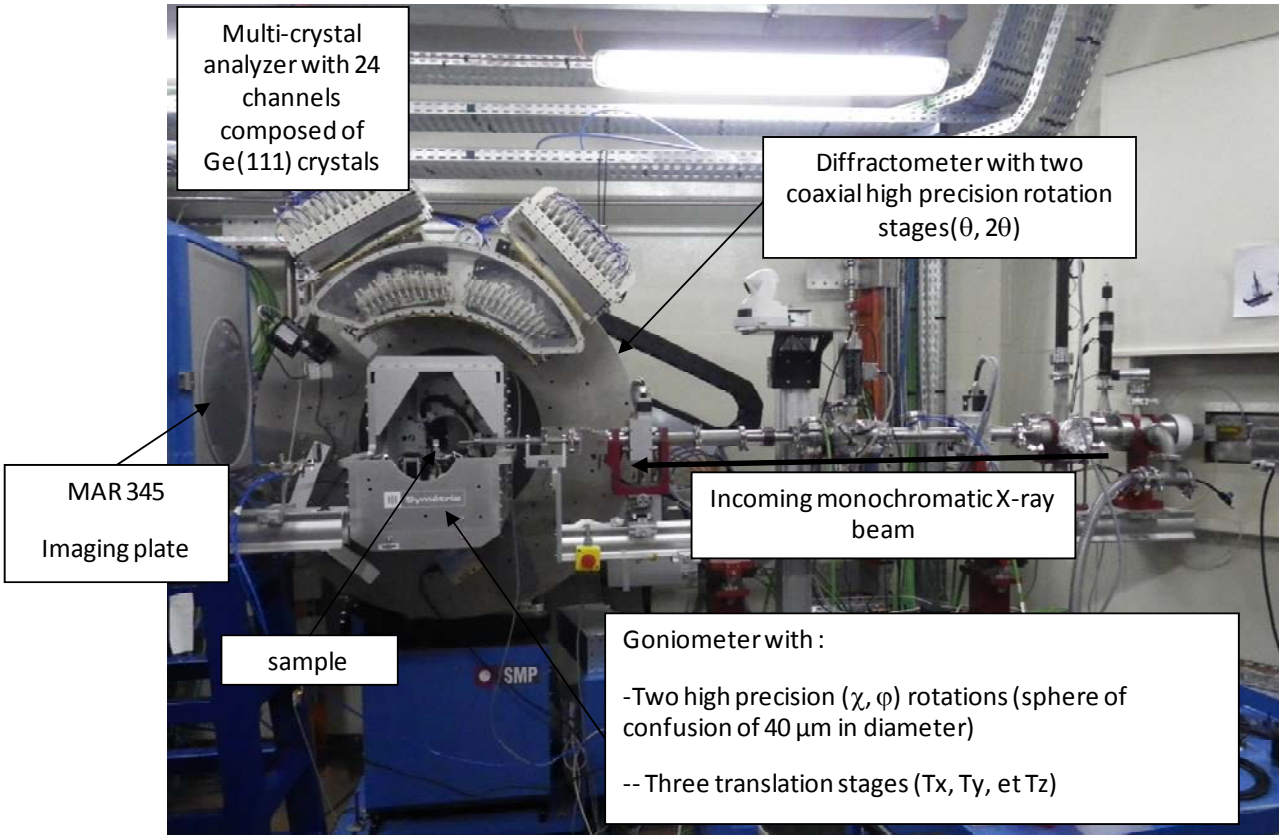

Fig. 1: High Resolution X Ray Diffractometer at the MARS beamline.

References

[1] B. Sitaud, P.L. Solari, S. Schlutig, I. Llorens, H. Hermange, Characterization, of radioactive materials using the MARS beamline at the synchrotron SOLEIL. Journal of Nuclear Materials 425 (2012) 238-243.

[2] P.L. Solari, S. Schlutig, H. Hermange and B. Sitaud. Journal of Physics: Series 190 (2009) 012042.

[3] S. Schlutig, P.L. Solari, H. Hermange, B. Sitaud, Basic Actinide Science and Materials for Nuclear Applications, 2010. Materials Research Society Symposium Proceedings, 1264, p.131-136.

[4] J.-L. Béchade, D. Menut, M.-L. Lescoat, B. Sitaud, S. Schlutig, P.L. Solari, I. Llorens, H. Hermange, Y. de Carlan, J. Ribis, L. Toualbi, Application of synchrotron radiation to analyze the precipitation in ODS materials before irradiation in Fe–9%Cr single grain of powder and consolidated Fe–18%Cr. Journal of Nuclear Materials 428 (2012) 183-191.

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New characterizations at the MARS* beamline (SOLEIL synchrotron radiation)

J.-L. Béchade[1], D. Menut[1],
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**** Multi Analyses on Radioactive Samples***

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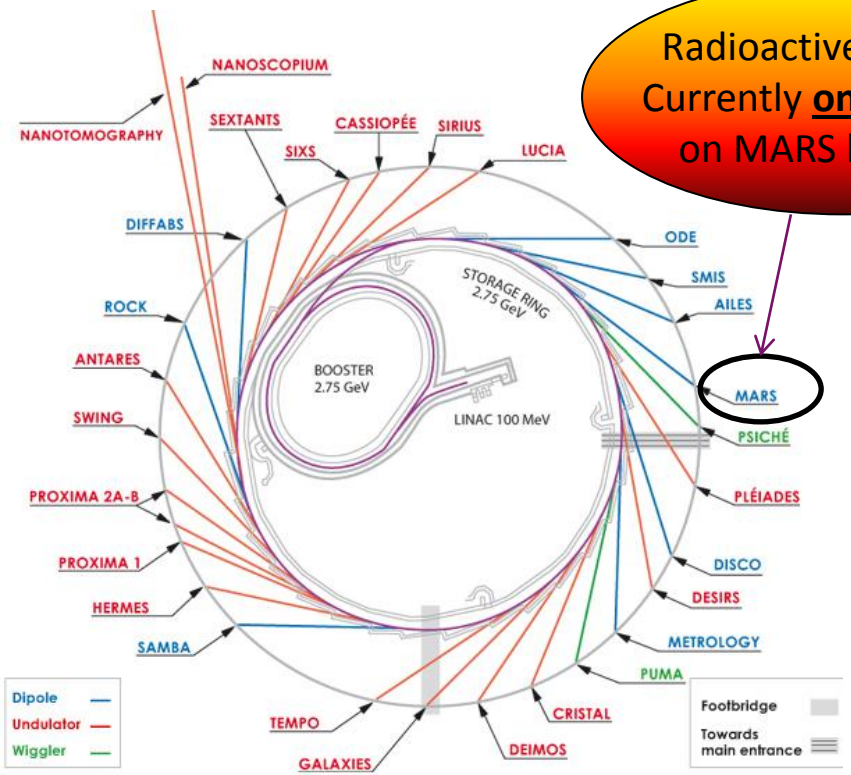
BRIEF OVERVIEW OF THE MARS BEAMLINE

National synchrotron facility, third generation source

Nominal Energy	2.75 GeV
Circumference	354 m
Emittance H	4 nm.rad
Current Intensity	400 mA (430 mA in 2012)

(1st beam in december 2008)



Radioactive samples: Currently **only** allowed on MARS beamline

29 beamlines foreseen

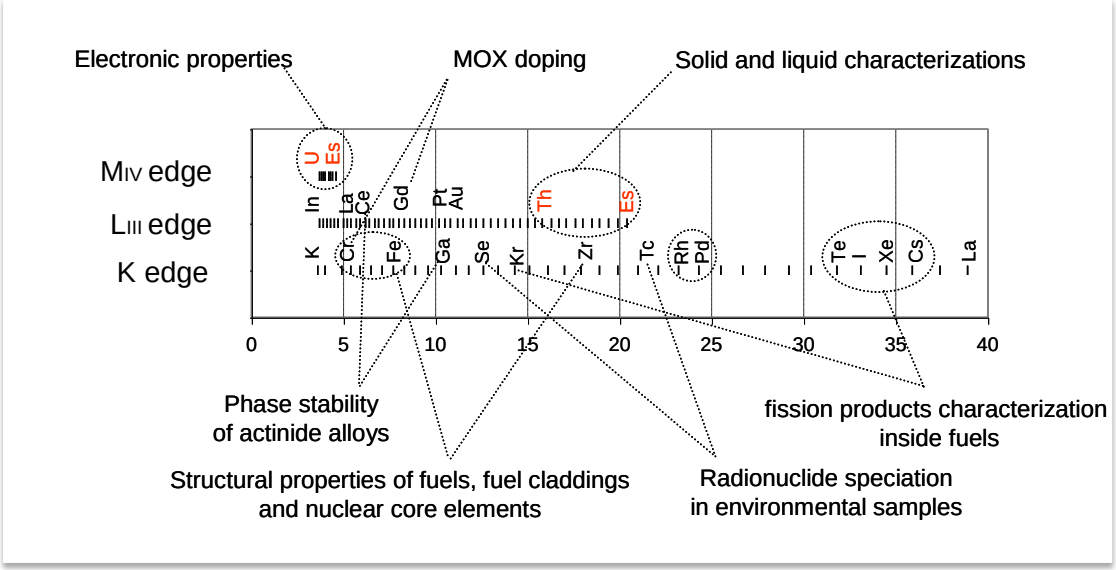
24 beamlines opened to users on 2nd semester 2012

MARS A DEDICATED X-RAY BEAMLINE FOR RADIOACTIVE MATTER

Multi-Analysis on Radioactive Sample (MARS) beamline, at synchrotron SOLEIL, is fully dedicated to advanced structural and chemical characterizations of radioactive matter (solid or liquid).

- Energy range of the X-ray beam : **3.5 to 35 keV**

A multi-technique beamline infrastructure and optics optimized for : Absorption spectroscopy, Fluorescence, Diffraction



- Sample maximum activity on MARS beamline :
  - ✓ 18.5 GBq per sample for α- and β-emitters
  - ✓ 2.0 GBq per sample for γ- and n-emitters

LAYOUT OF THE MARS BEAMLINE (SIDE VIEW)

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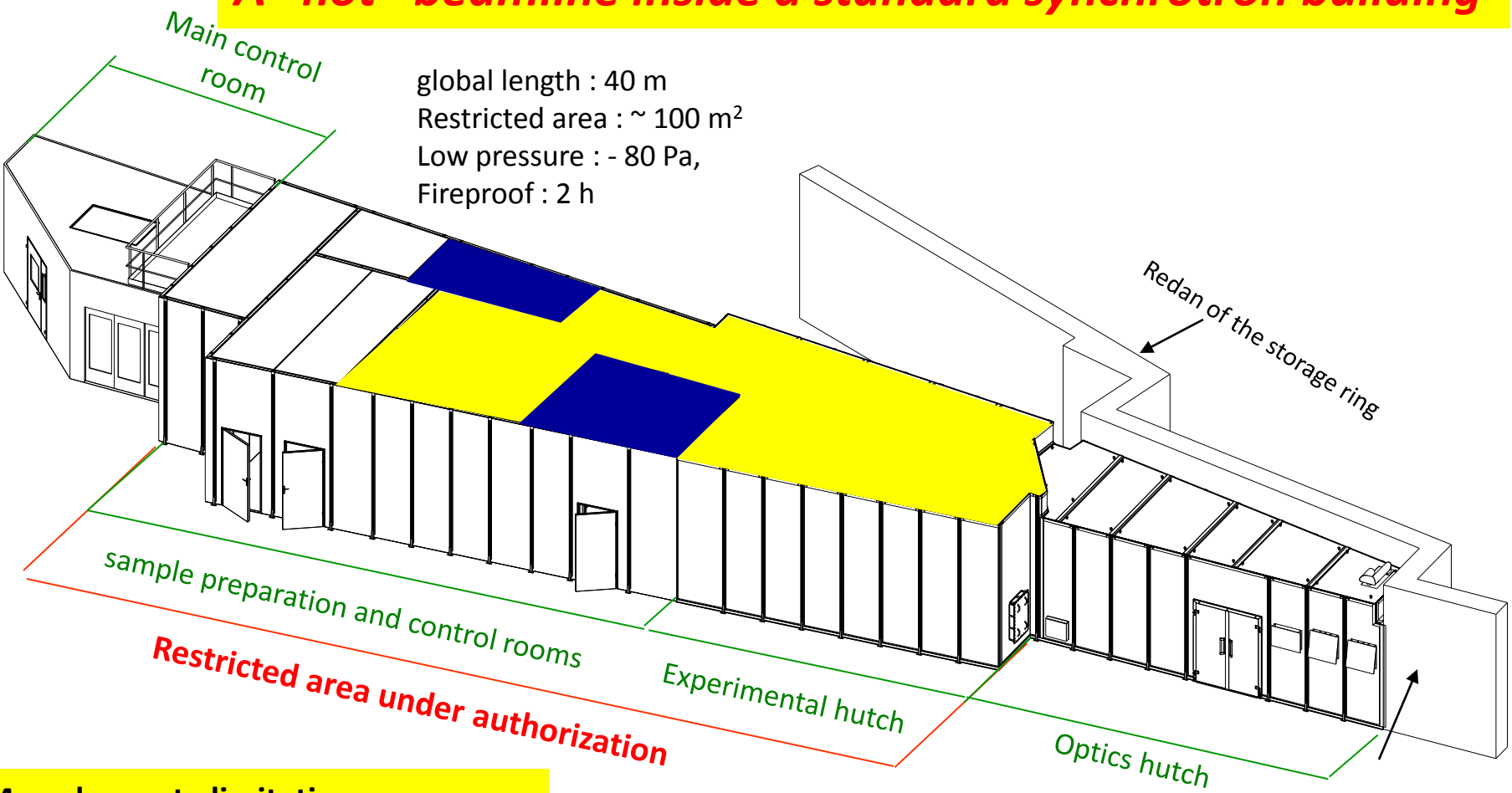
A "hot" beamline inside a standard synchrotron building



global length : 40 m
Restricted area : ~ 100 m^2
Low pressure : - 80 Pa,
Fireproof : 2 h

port D03-1
1.7 T bending magnet

Max. dose rate limitation :
inside 2 mSv/h and outside 0.5µSv/h

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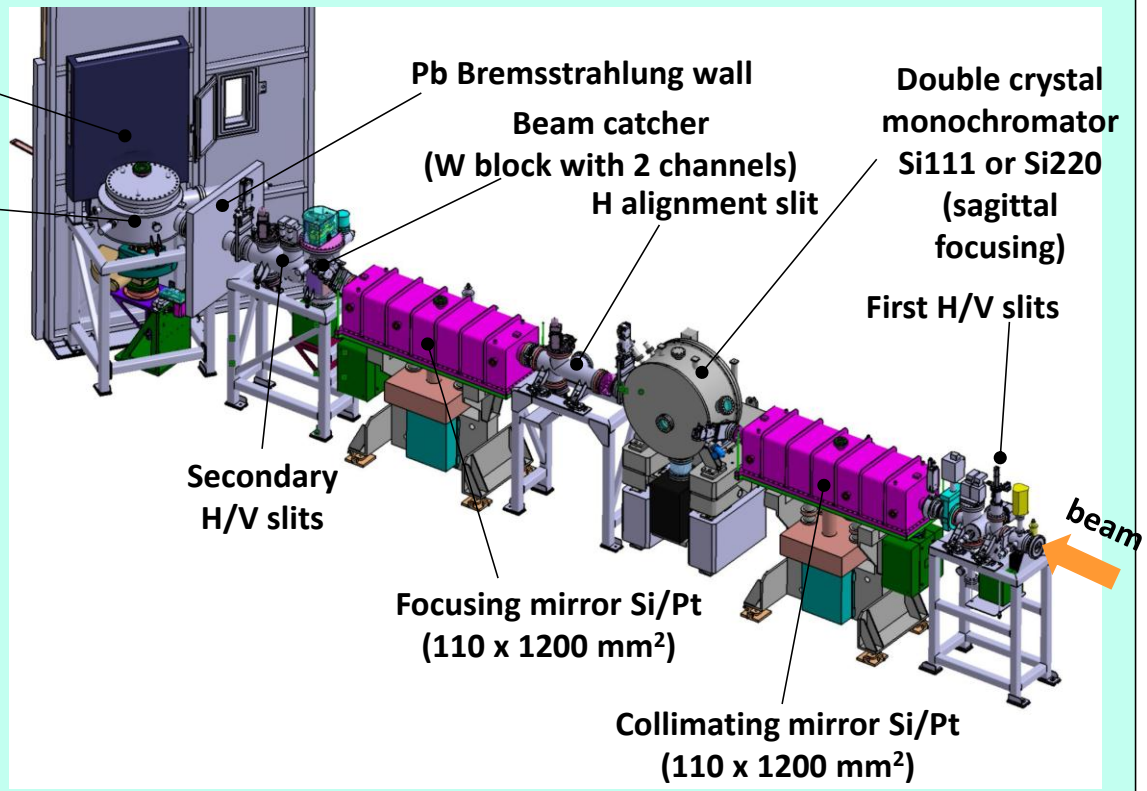
W beam shutter
Single crystal monochromator Si111 or Si311 (2013 or later)
Pb Bremsstrahlung wall
Beam catcher (W block with 2 channels)
H alignment slit
Double crystal monochromator Si111 or Si220 (sagittal focusing)
First H/V slits
Secondary H/V slits
beam
Focusing mirror Si/Pt (110 x 1200 mm²)
Collimating mirror Si/Pt (110 x 1200 mm²)

Two experimental stations are being used alternatively on the monochromatic branch

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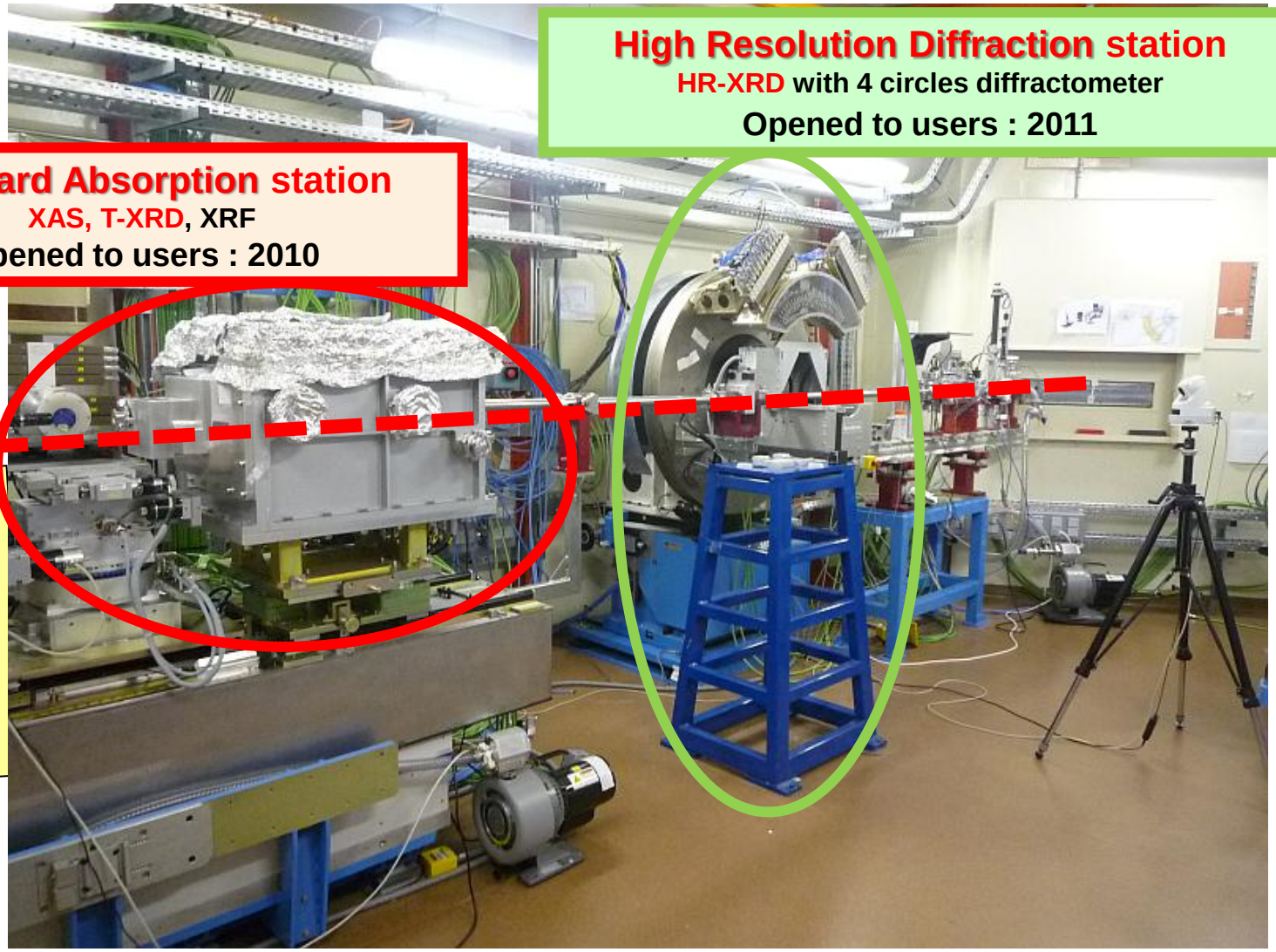

High Resolution Diffraction station
HR-XRD with 4 circles diffractometer
Opened to users : 2011

Standard Absorption station
XAS, T-XRD, XRF
Opened to users : 2010

Monochromatic branch:
Standard spot size (HxV) ~ 300 x 200 µm²
Flux 5x10¹¹ ph/s at 17 keV
with Si(220) and I = 400mA

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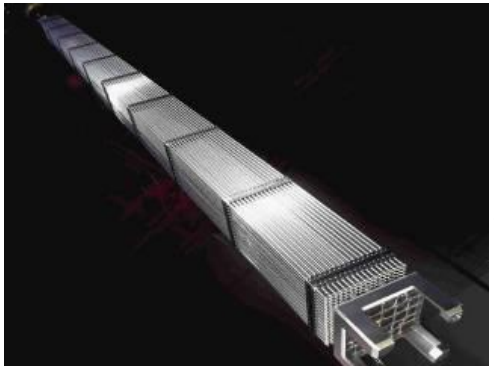
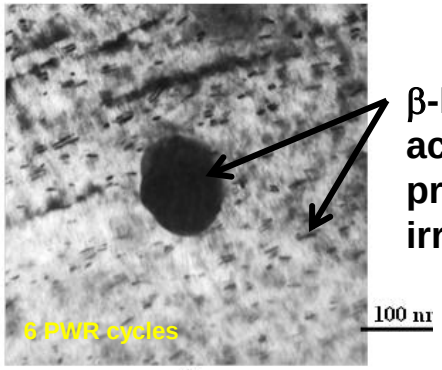
Fuel cladding materials studied at the Nuclear Energy Division:

Zr based alloys for Gen2&3 reactors (PWR)



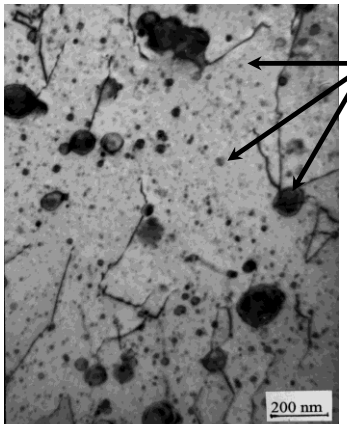
M5™: Zr-1%Nb corrosion behaviour largely improved thanks to Nb addition



β-Nb: natives + accelarated precipitation under irradiation

ODS steels for Gen4 reactors (SFR)

Ferritic/martensitic steel: to reduce swelling, reinforced with nanometric oxide to reduce thermal creep



oxides

Same goal for both studies: secondary phases (less than 0.5% vol. fraction) evolutions under irradiation

1 - Zr BASED ALLOYS IRRADIATED IN PWR CONDITIONS: 0, 1, 2 AND 5 PWR CYCLES (up to 11.10^{25} n/m² @ 330°C)

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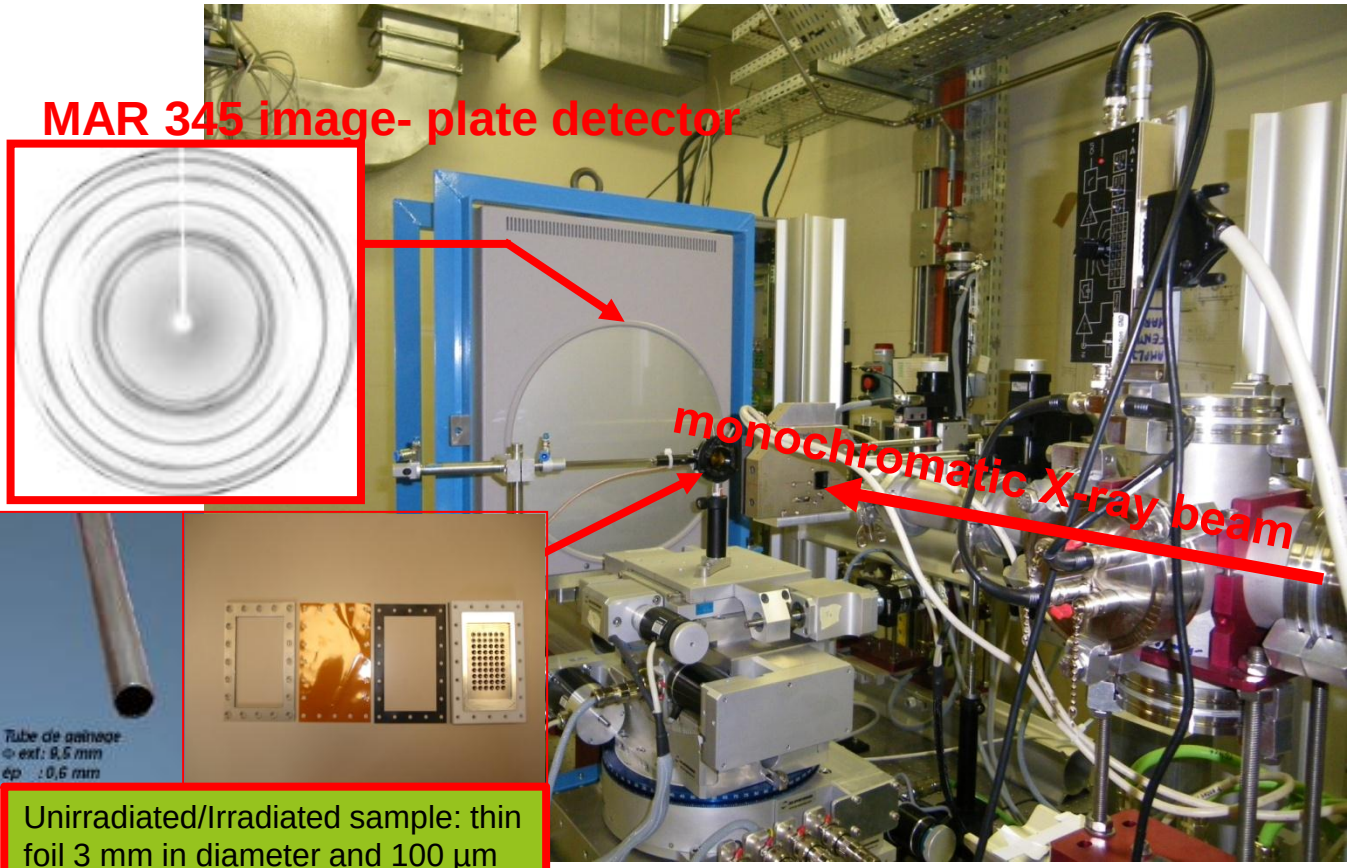
XAS station used: Transmission X-Ray Diffraction



Unirradiated/Irradiated sample: thin foil 3 mm in diameter and 100 µm thickness machined from the tube

XRD analysis in transmission mode

Using a 2-dimensions image-plate detector

Sample positionned on an 8-axis motorized stage

- ✓ X-ray beam energy : 17.038 keV
- ✓ Beam size (H x V) : 100 x 100 µm²
- ✓ Exposure time : about 240 s

RESULTS (1/2)

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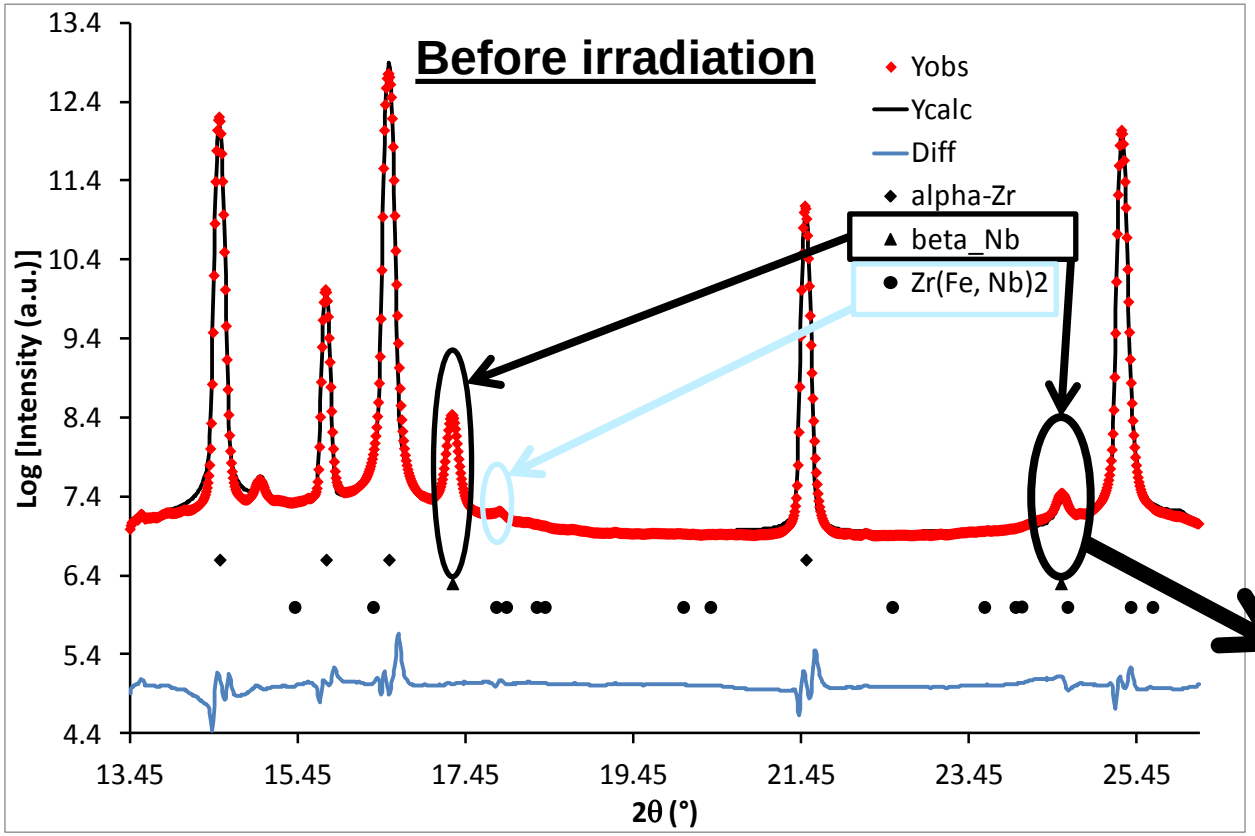
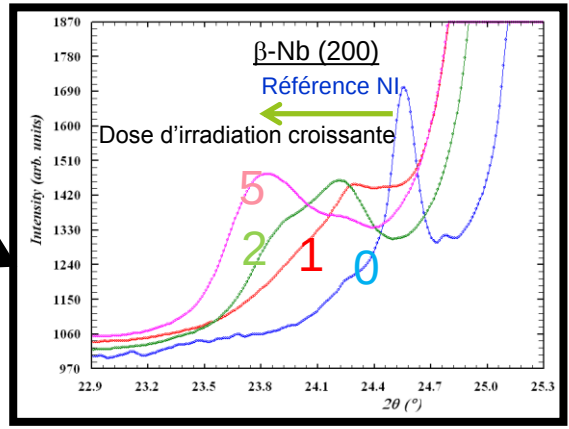


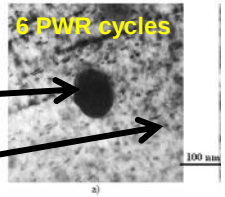
With increasing irradiation doses



- *Paper accepted at ASTM 2013 ,17th International Symposium on "Zirconium in the Nuclear Industry", February 03-07, 2013, Taj Krishna, Hyderabad, India*

The β-Nb diffraction peak after irradiation is the convolution of 2 contributions :

- Native β-Nb precipitates
- Radiation-enhanced β-Nb particles



RESULTS (2/2)

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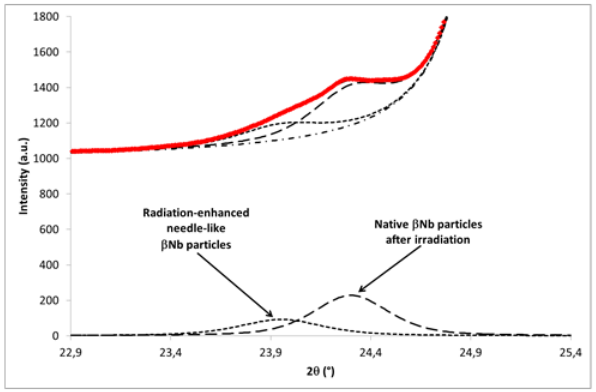
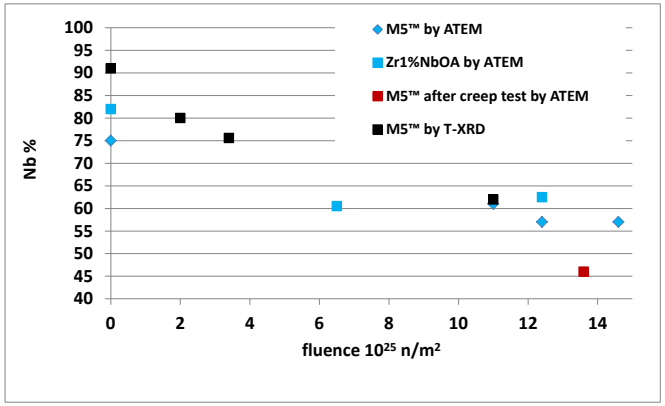
➢ Analyses of the **initial β-Nb precipitates** vs irradiation dose

Consistent with TEM analyses *(S. Doriot, M. Griffith, V. Shishov, ASTM 1996)* but with higher statistic and better accuracy



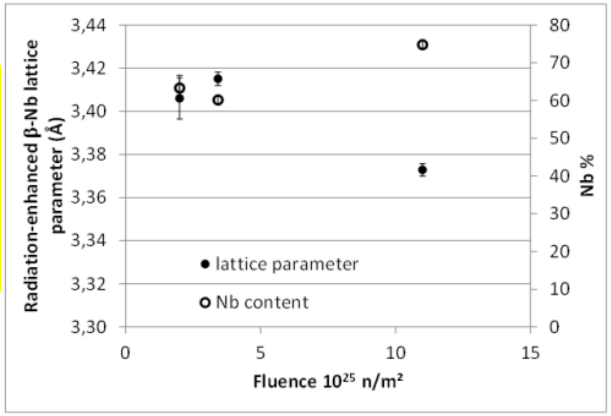
Example of deconvolution: 2 PWR cycles



Nb content in the native precipitates

➢ Analyses of the **radiation-enhanced β-Nb particles** vs irradiation dose

Data not accessible by TEM: nanometric particles (less than 0.5 vol. fraction) can be analyzed using XRD at MARS beamline



- *Journal of Nuclear Materials submitted in octobre 2012, conf. Size and Strain VI 2011*
- *Paper accepted at ASTM 2013 ,17th International Symposium on "Zirconium in the Nuclear Industry", February 03-07, 2013, Taj Krishna, Hyderabad, India*

HIGH RESOLUTION POWDER DIFFRACTION STATION (HR-XRD)

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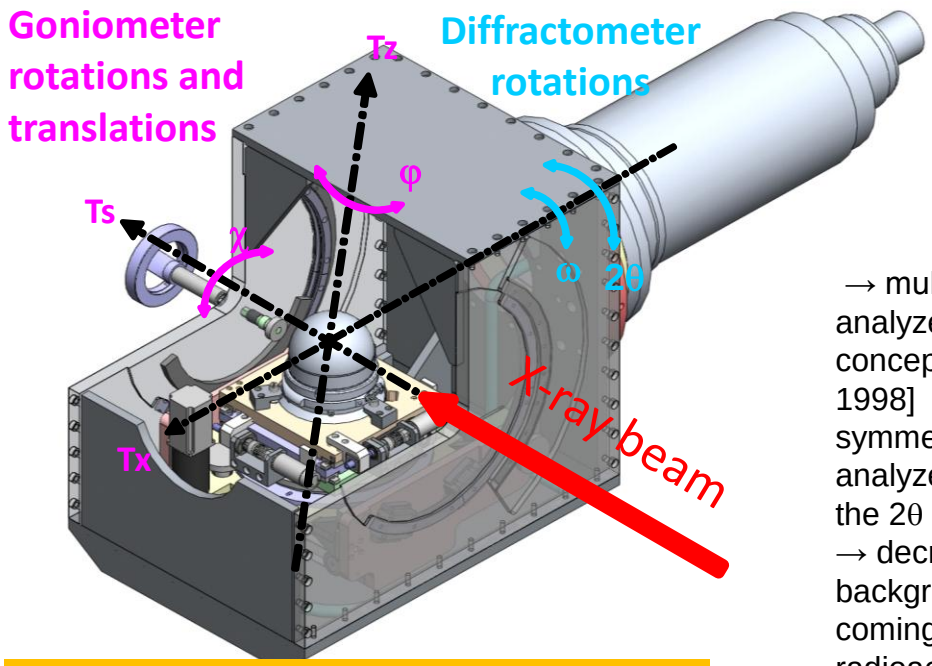
Scientific applications of HR-XRD can broadly classified as **:**

- solving and refining of **complex crystal structures,**
- measurements of **residual stress, textures,**
- microstructure characterizations from **analysis of peak shapes,….**



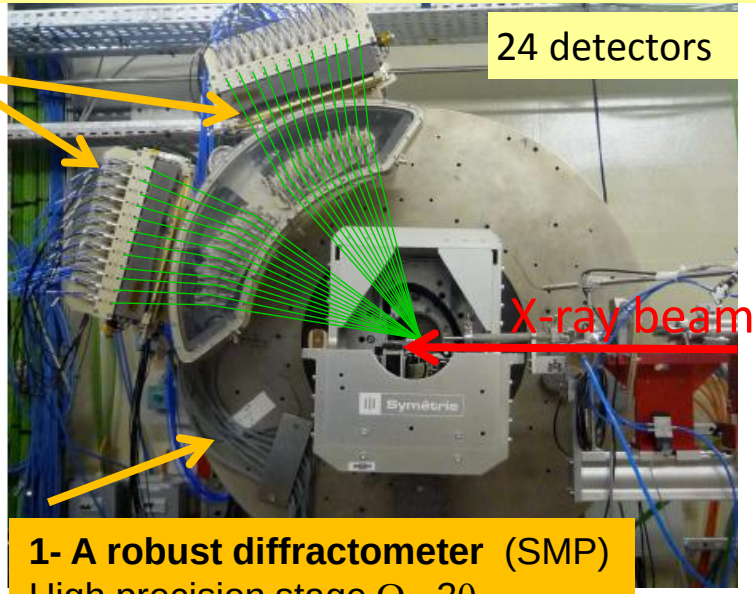
2 - A goniometer (CEA/DEN, Symétrie)

With high precision, weight capacity of 5 Kg, a sphere of confusion of *40 µm* between 3 rotation axes, Ω, χ and φ

3 - A detection system (CEA/DEN, COMAT)

24 crystals analyzer Ge(111 crystals)

→ multi-crystal analyzer stage concept [Hodeau 1998] : 2 systems of symmetrical 12 analyzers mounted on the 2θ arms (67.4°)
→ decrease the background radiation coming from high radioactive samples



1- A robust diffractometer (SMP)
High precision stage Ω, 2θ

TYPICAL HIGH RESOLUTION DIFFRACTION PATTERN: APPLICATION TO GROWTH UNDER IRRADIATION FOR Zr ALLOYS

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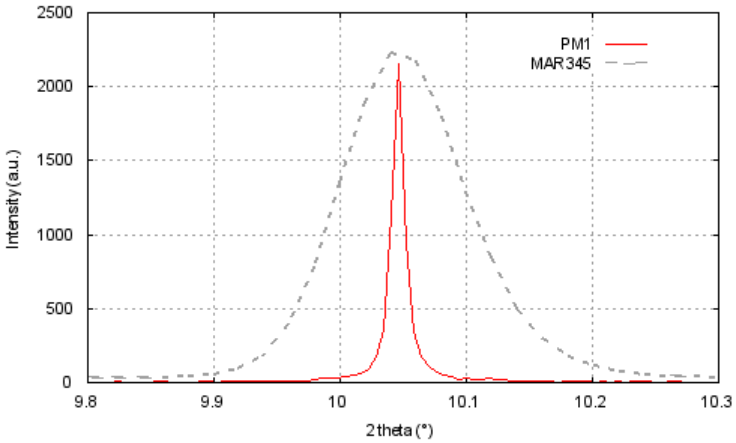
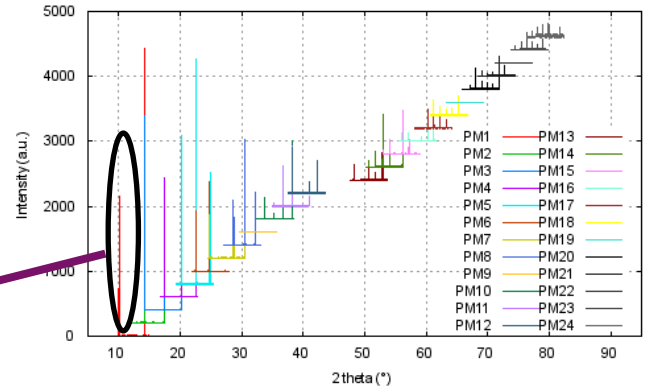
Comparison between the diffraction peak from the (100) reflection of the **standard NIST LaB6 powder** recorded at 17.038 keV with the PM1 detector of the **multi-crystal analyzer and with a MAR345 detector**





A constant intensity shift for each PM above the PM1 is introduced here only for the easy visualization of each individual signal.

=> Typically the **FWHM linewidth is reduced by a factor of 10** with the use of the multi-analyser (FWHM are below 0.01°) compared to the **MAR345** result.

Application to irradiation defects in Zr based alloys

<c> loops density, directly linked to radiation induced growth of Zr alloys

Broadening of diffraction peaks (~micro-deformation) => work in progress

2 - ODS FERRITIC/MARTENSITIC STEELS FOR SFR

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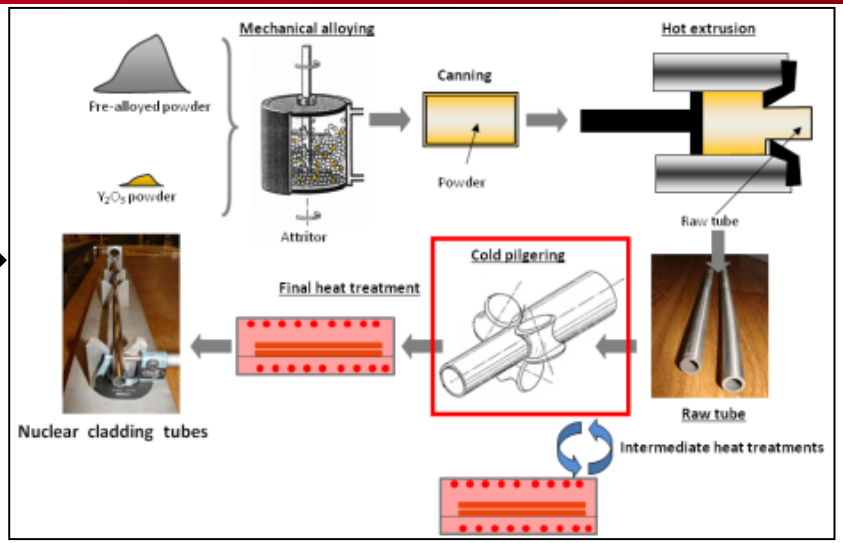
ODS alloys studied

Fe-9Cr-0.1C-1W + 10 wt% Y_2O_3
as modelling alloy at powder state

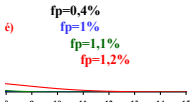
Fe-18Cr-1W-0.4Ti + 0.56 wt% Y_2O_3
as consolidated samples

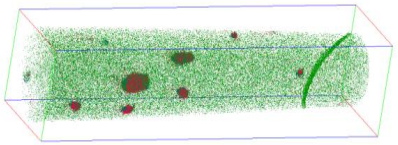
CEA fabrication/ODS Project
Y De Carlan ,J. Nucl. Mater. 386–388 (2009) 430–432.



Characterization of the nano-oxide dispersion

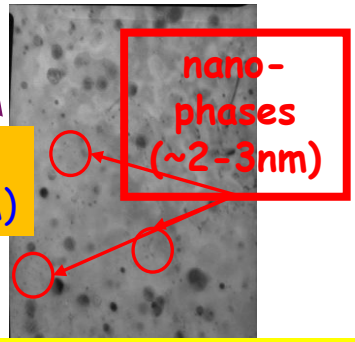
SANS





TAP

TEM (EDS and EFTEM)



What about the crystallographic structure, local environment during the process and before/after irradiation ?

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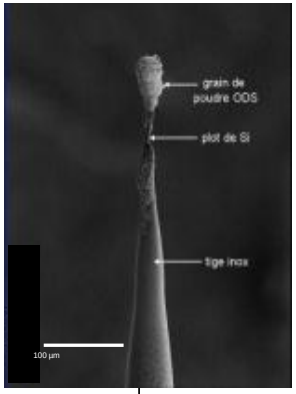
RESULTS: XRD ANALYSES AT DIFFERENT SCALES AND STEPS IN THE FABRICATION PROCESS (before irradiation)

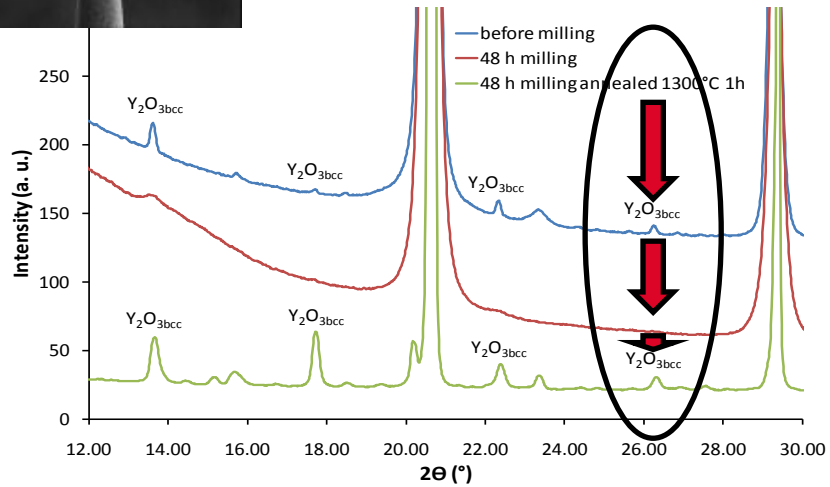
XAS station used: Transmission X-Ray Diffraction



A single grain of powder mounted on an iron based tip and glued with silver lacquer

Fe-9Cr-0.1C-1W + 10 wt% Y_2O_3 model alloy

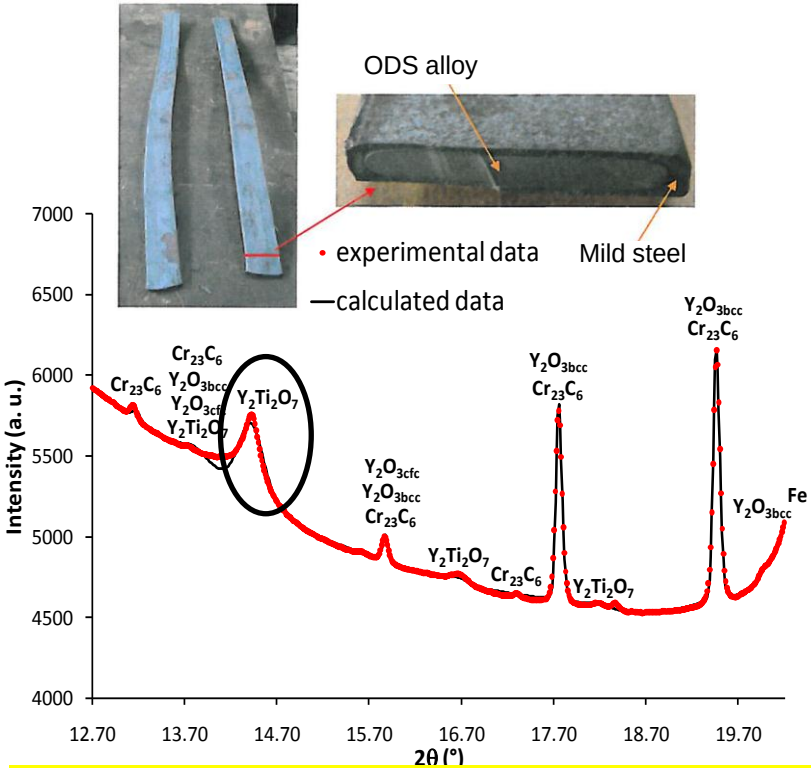
Global TXRD diffractogram obtained for a single grain of powder during the process



Precipitation happens during the consolidation process with thermal annealing => Y_2O_{3bcc} cristallite sizing ~20 nm
(L Toualbi et al. JNM 2012)

Consolidated thick rectangular bar annealed at 1300°C 1h

Fe-18Cr-1W-0.4Ti + 0.56 wt% Y_2O_3

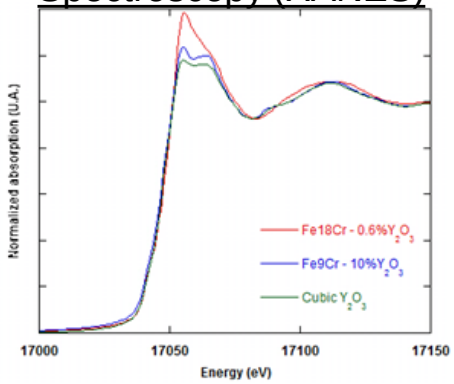


Nano structured $Y_2Ti_2O_7$ pyrochlore type phase can be analyzed using XRD at MARS beamlline, cristallite sizing ~15 nm (*ML Lescoat et al. JNM 2012*)

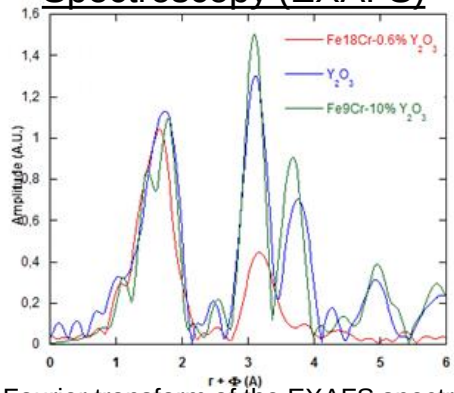
RECENT ANALYSES: X RAY ABSORPTION SPECTROSCOPY (XAS)

- For previous materials: in fluorescence mode at the Y K_α-edge (E ~17.038 keV) in a He flow cryostat running at ~10 K

X-ray Absorption Near Edge Spectroscopy (XANES)



Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS)



Fourier transform of the EXAFS spectra

9%Cr ODS alloy is very similar to the one from Y_2O_3-bcc reference, 18%Cr ODS alloy: coexistence of structures other than Y_2O_3-bcc, $Y_2Ti_2O_7$ nano-structured

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- EXAFS spectra at 20°C on Fe-K edge (7.112 keV)

Fe18Cr1W0.8Ti+0.3MgO model alloy, **after ion-irradiations** (Jannus Saclay) at 500°C *(ML Lescoat, 2012).*

⇒ 50 to 215 dpa : quantitative analysis of the local atomic configuration as a function of irradiation dose

work in progress

CONCLUSIONS AND PERSPECTIVES

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CEA/DEN sponsoring the MARS beamline since the begining => **first analyses** for samples with activities < exemption limit (**weakly activated materials**) at room temperature using approved sample holders.

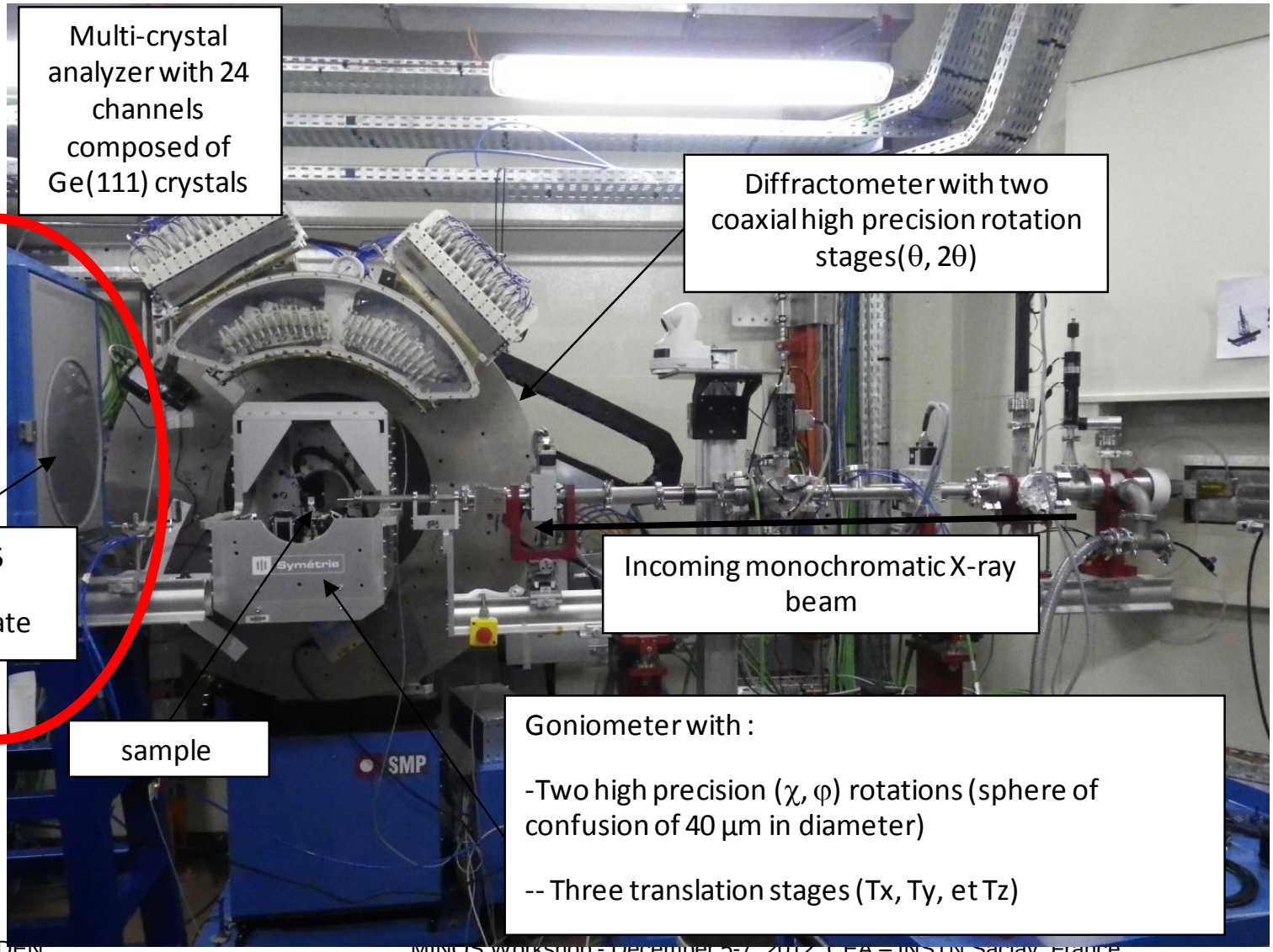
- Original results concerning secondary phases evolution under **neutron irradiation (Zr based alloys, M5™ from 1 to 5 PWR cycles)**

Beamline is operational using a standard focused beam (300x200µm²) **HR-XRD station** and collimated beam (50x50µm²) **XAS station.**

- HR-XRD station is in operation (irradiation defects have be quantified in Zr based alloy) ; adding off axis imaging plate geometry (excellent sensitivity) .★
- XAS station : Analyses using micro focused beam with KB optics (10x10 µm²) are available => local analyses and small quantity of material can be studied (ODS powder grain, Zr metal/oxide interfaces,…).
- XAS station : XANES and EXAFS from 10K to RT, before/after irradiation (demonstration from charged particles-Jannus-irradiated ODS steels => D. Menut PhD 2012-2015).

Future:

Beamline should be opened for samples with activities **above the exemption level** and for low and high temperature conditions after authorizations from the French Safety Authority (ASN), **September 2013**.★


Multi-crystal analyzer with 24 channels composed of Ge(111) crystals
Diffractometer with two coaxial high precision rotation stages(θ, 2θ)
MAR 345
Imaging plate
Incoming monochromatic X-ray beam
sample
Goniometer with :
-Two high precision (χ, φ) rotations (sphere of confusion of 40 µm in diameter)
-- Three translation stages (Tx, Ty, et Tz)

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