Neutron diffraction patterns measured with a high-resolution powder diffractometer installed on a low-flux reactor

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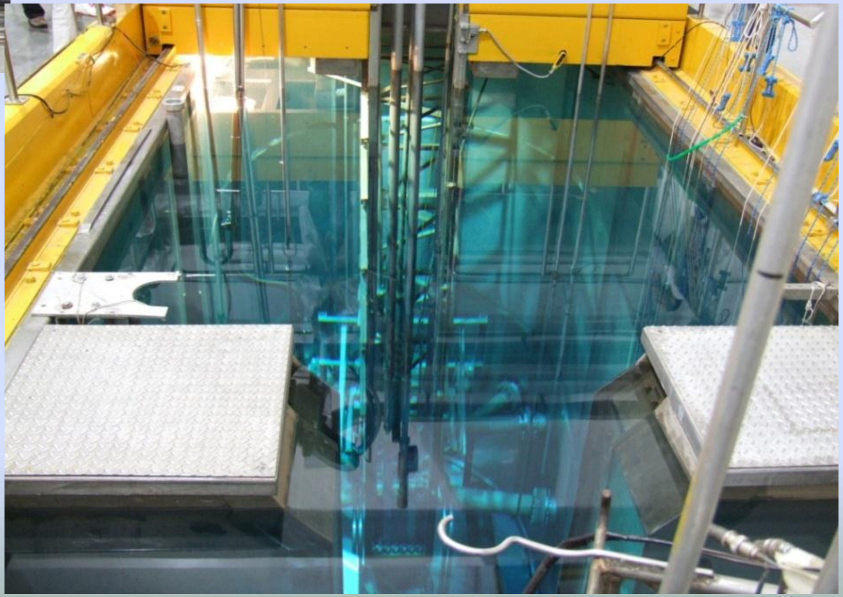
CRPq's main program

- *Nuclear and condensed matter physics*
- *Neutron activation analysis*
- *Nuclear metrology*
- *Applied nuclear physics*
- *Graduate and postgraduate teaching*
- *Reactor operators training*

IEA-R1 Reactor

- *Swimming pool type, light water moderated with 23 graphite and 9 beryllium reflectors, designed to operate at 5 MW*
- *Current power: 4.5 MW*
- *Neutron in core flux: 7,0 x 10^{13}n/cm^2.s*
- *Suitable for the use in: basic and applied research, production of medical radioisotopes, industry and natural sciences applications.*



The old IPEN-CNEN/SP neutron multipurpose diffractometer

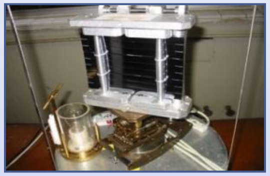
- a single BF_3 detector
- a single wavelength (λ =1.137 Å)
- a point-to-point scanning data measurement

The new IPEN-CNEN/SP neutron powder diffractometer

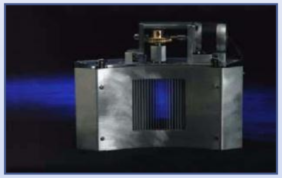
- a Position Sensitive Detector (PSD) array formed by 11 linear proportional ^{3}He detectors, scanning a $2\theta = 20°$ interval
- 400 intensity points measured in a single 2θ step all at once ($\Delta 2\theta = 0.05°$)
- 4 different λs: 1.111, 1.399, 1.667, 2.191 Å

Aurora – High Resolution Powder Diffractometer*

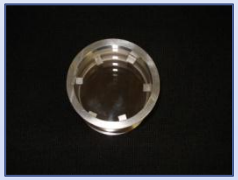
Neutron monochromator (inside the main shield)



Rotating-Oscillating Collimator (ROC)



Sapphire filter (inserted into the in-pile collimator)

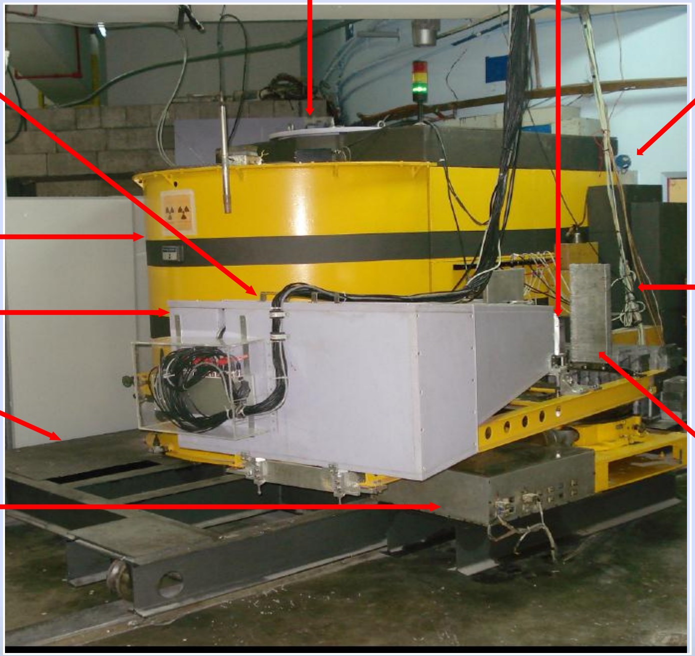


Position Sensitive Detector (PSD) (inside the PSD shield)

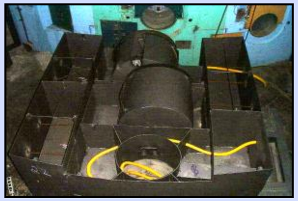
Main neutron shield

PSD neutron shield

Movable platform



Beam shutter (inside the main shield)



Extra shield

2θ-ω drive mechanism

*Parente, C. B. R., Mazzocchi, V. L., Mestnik-Filho, J., Mascarenhas, Y. P., Berliner, R. Nucl. Instr. and Meth. in Phys. Res. A 622 (2010) 678-684.

Electronics associated to the HRPD "Aurora"

Beam shutter control

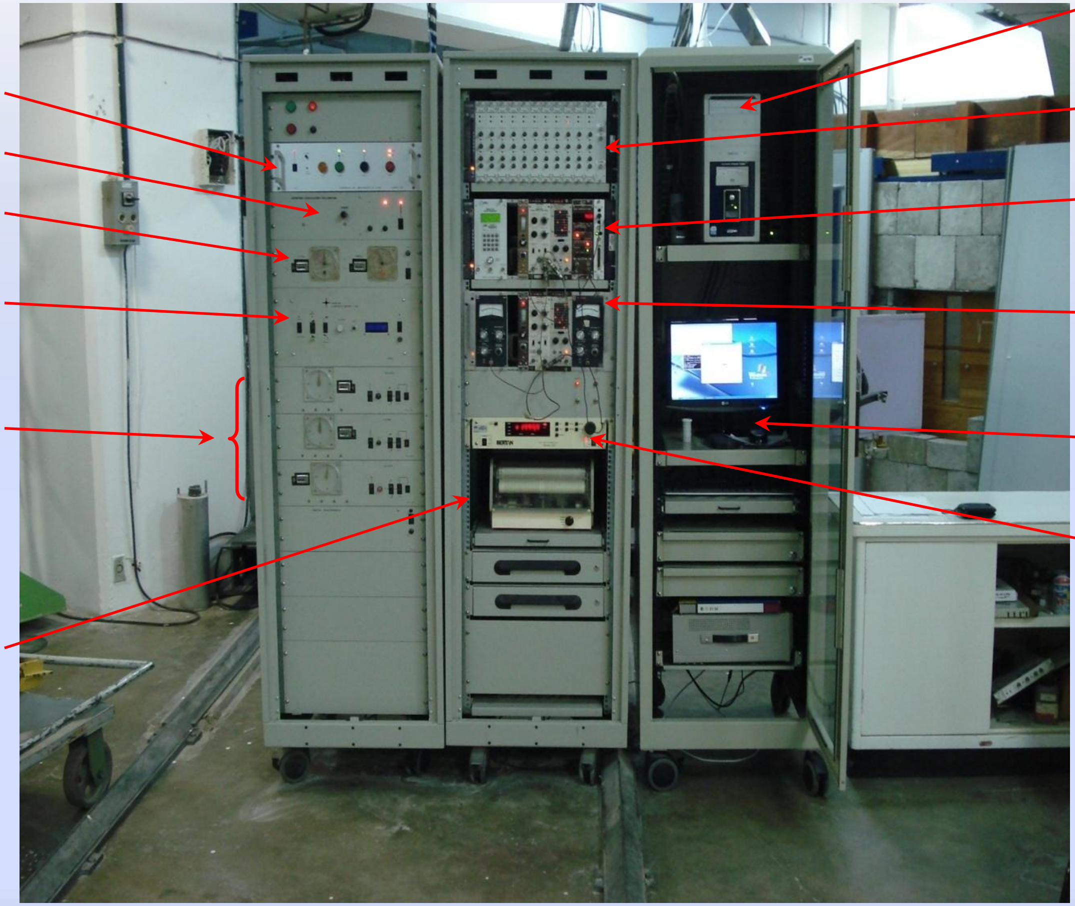
ROC control

2θ/ω angle indicators

2θ stepper motor driver

Monochromator control modules (rocking, tilting and translation)

Two-pen recorder (neutron monitor + ambient BG)



Control and data acquisition PC

PEMs

Pulser + neutron monitor electronics

Ambient BG electronics

PC monitor and keyboard

PSD HV source

(HRPD = High Resolution Powder Diffractometer)

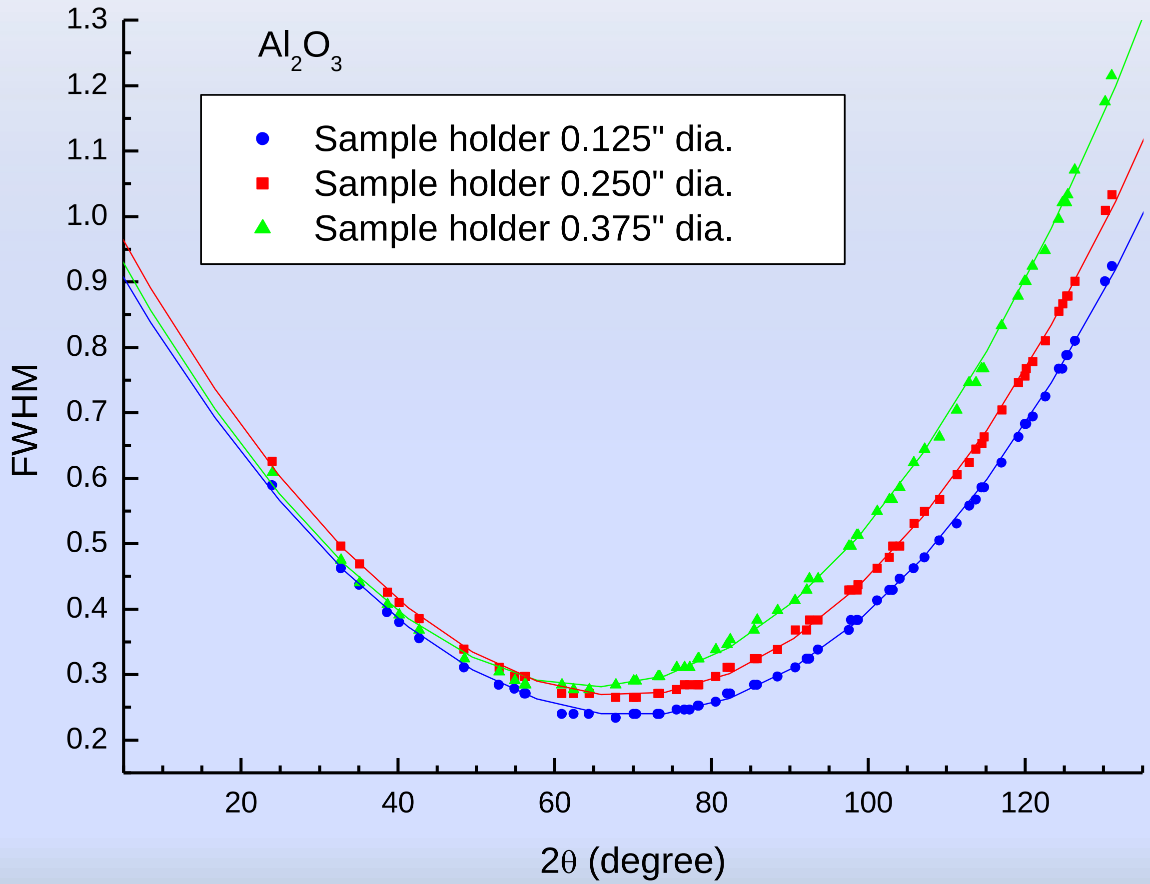
PSD + focusing Si bent monochromator

in comparison to the old diffractometer

- powder patterns with higher resolution
- rate of data collection higher by an average factor of 600 (per intensity point)
- more λs available, more different materials can be studied

Great interest of the scientific and technological communities for crystallographic studies in new materials.

Resolution curves for the HRPD "Aurora"



⇒ *Fitting of an experimental powder diffraction pattern by the profile of a theoretical pattern, calculated according to a structure model assumed for the material under analysis.*

⇒ *Deviation between experimental and theoretical patterns is minimized by the least-squares method.*

⇒ *Analysis of multiphase patterns obtained with x-rays or neutrons:*
- *refinement of the structural parameters of the phases;*
- *quantitative phase analysis;*
- *microstructural phase analysis (surface roughness effects, microabsorption and mean grain size).*

Definition of the numerical criteria of fit

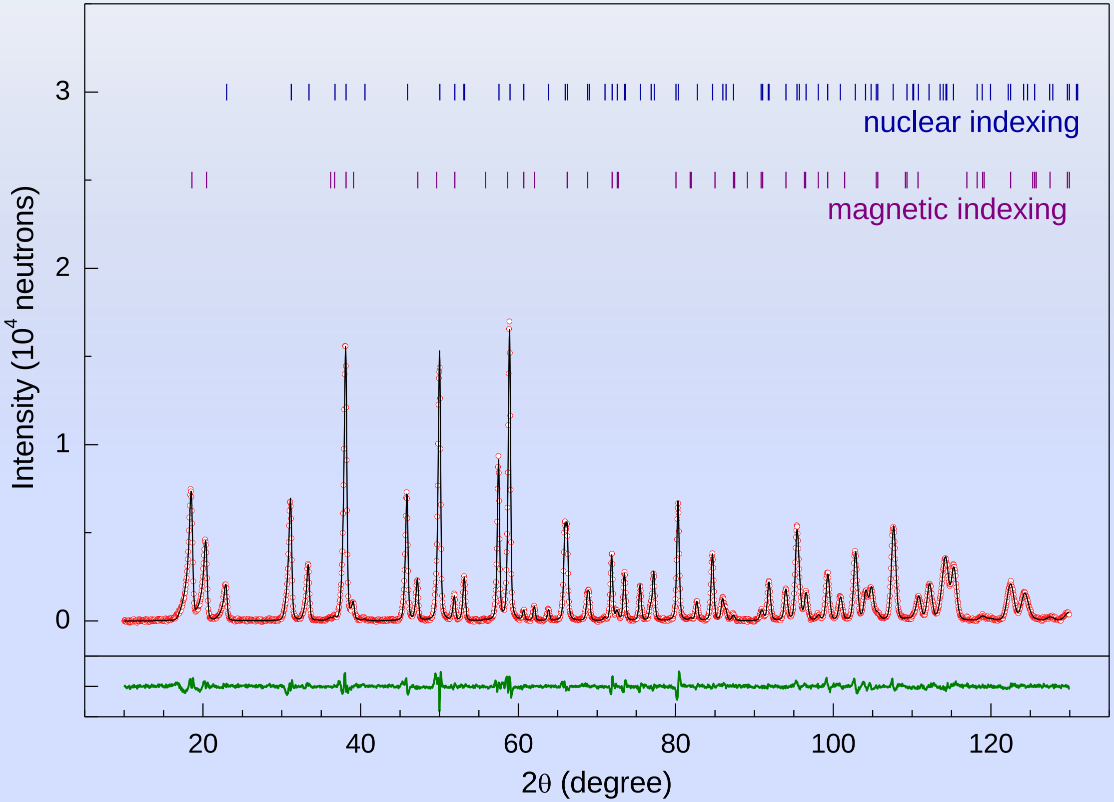
R_P = R-pattern: $$R_p = 100\left\{\frac{\Sigma\left|y_i(obs) - y_i(calc)\right|}{\Sigma y_i(obs)}\right\}$$

R_{WP} = R-weighted pattern: $$R_{wp} = 100\sqrt{\frac{\Sigma w_i[y_i(obs) - y_i(calc)]^2}{\Sigma w_i y_i^{2}(obs)}}$$ ***, with*** $w_i = 1/y_i(obs)$

R_e = R-expected: $$R_e = 100\sqrt{\frac{(N-P)}{\Sigma w_i y_i^2(obs)}}$$

Goodness-of-fit: $S = \dfrac{R_{wp}}{R_e}$ ***or*** $\chi^2 = S^2$

Rietveld profile fit for Fe_2O_3



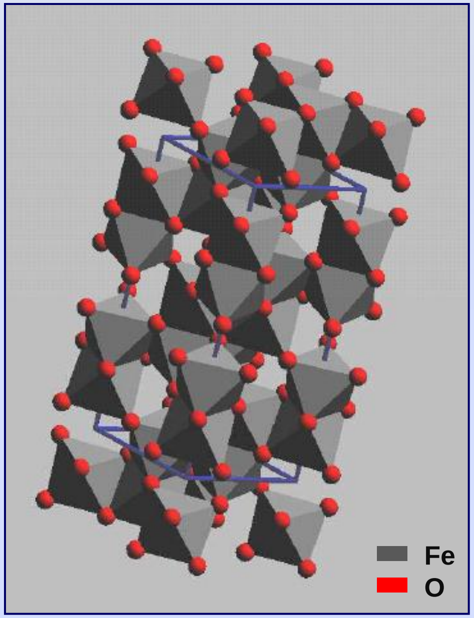
⇒ ***Time of measurement = 48 h***
⇒ ***Reactor power = 4.0 MW***

Numerical criteria of fit: - R_P = 0.047
- R_{WP} = 0.060
- Reduced χ^2 = 3.4

Crystalline structure:

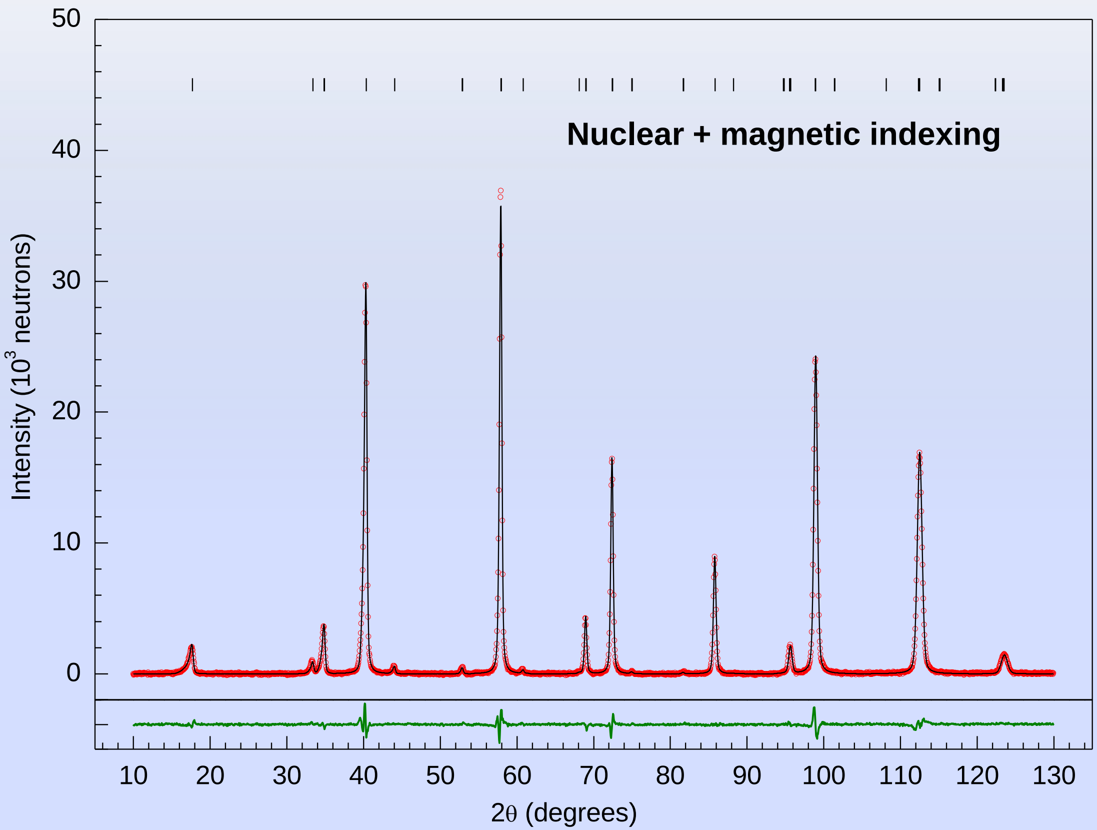
Space Group ⇒ $R\bar{3}c$ (trigonal)

Atomic positions ⇒ Fe (4c) and O (6e)



Magnetic structure:

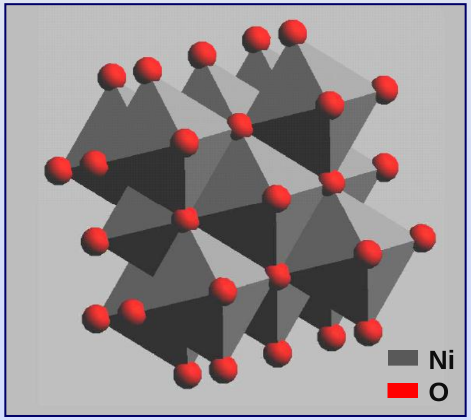
Antiferromagnetic - $\mu(Fe) = 4.9\ \mu_B$



Crystalline structure:

Space Group ⇒ Fm3m (cubic)

Atomic positions ⇒ Ni (4a) and O (4b)



Magnetic structure:

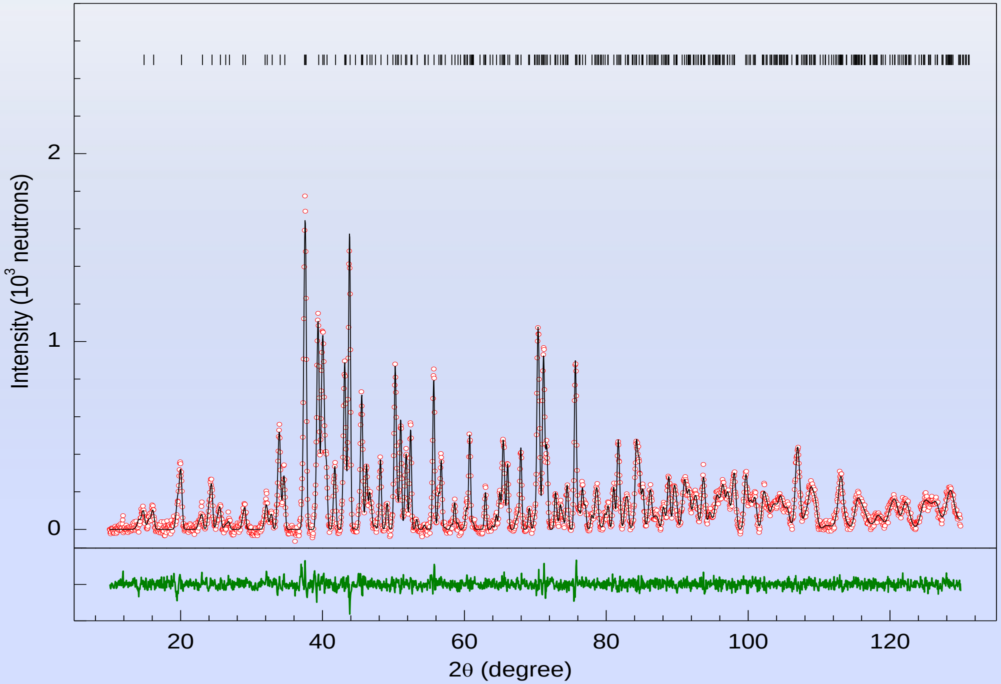
Antiferromagnetic - $\mu(Ni^{2+}) = 2\ \mu_B$

⇒ Time of measurement = 48 h
⇒ Reactor power = 4.0 MW

Numerical criteria of fit: - $R_P = 0.041$
- $R_{WP} = 0.051$
- Reduced $\chi^2 = 2.9$

Rietveld profile fit for BaY_2F_8:Nd

Work in cooperation with 'Laboratório de Crescimento de Cristais do IPEN-CNEN/SP'



Crystalline structure:

Space Group ⇒ C2/m (monoclinic)

Atomic positions ⇒ Ba (2a); Y,Nd(4h) and F(8j)

Numerical criteria of fit: - R_P = 0.040

- R_{WP} = 0.051

- Reduced χ^2 = 1.2

⇒ Time of measurement = 24 h

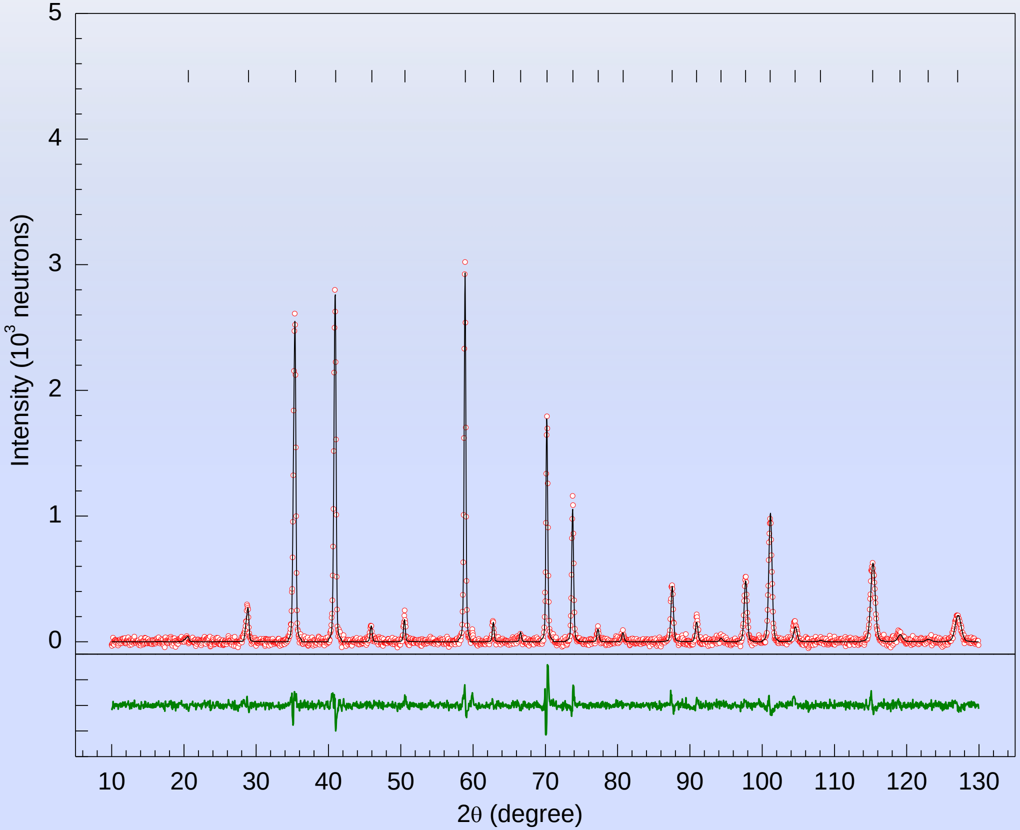
⇒ Reactor power = 2.0 MW

** f for (senθ)/λ = 0.5 Å^{-1}*

		Neutrons			X Rays		
Element	Z	μ (cm^{-1})	b (10^{-12} cm)	b^2 (10^{-24} cm^2)	μ (cm^{-1})	f * (10^{-12} cm)	f^2 (10^{-24} cm^2)
F	9	-----	0.565	0.3192	-----	0.75	0.5625
Y	39	0.031	0.775	0.6006	596	5.4	29.16
Ba	56	0.01	0.507	0.2570	1155	8.3	68.89
Nd	60	0.76	0.769	0.5914	2580	9.0	81.0

Rietveld profile fit for $Pb_{0.6}Ba_{0.4}Zr_{0.65}Ti_{0.35}O_3$ (PBZT40)

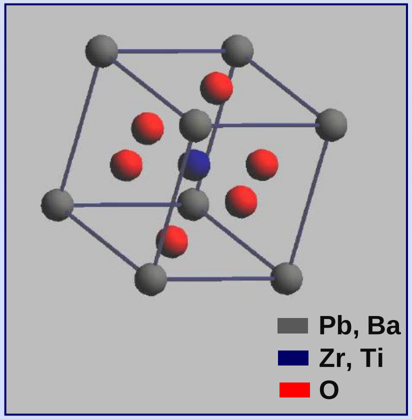
Work in cooperation with 'Laboratório de Cristalografia do IFUSP- São Carlos'



Crystalline structure:

Space Group ⇒ Pm3m (cubic)

Atomic positions ⇒ Pb,Ba (2a); Zr,Ti(4h) and O(8j)

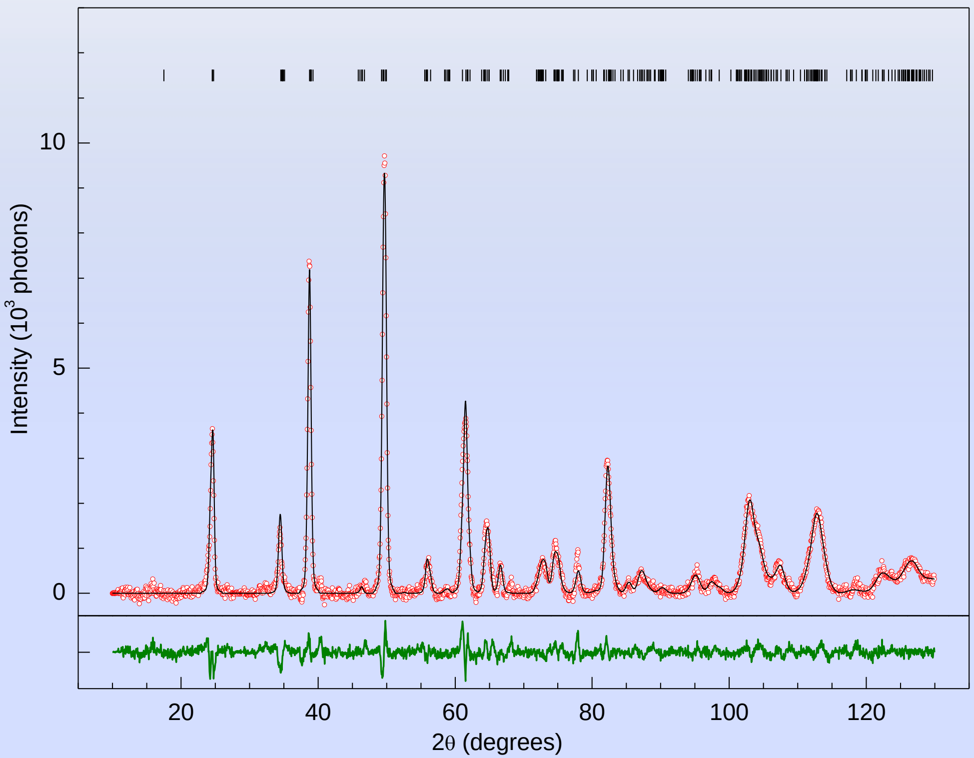


⇒ Time of measurement = 30 h
⇒ Reactor power = 2.0 MW

Numerical criteria of fit:
- $R_P = 0.048$
- $R_{WP} = 0.063$
- Reduced $\chi^2 = 1.4$

Rietveld profile fit for ReO_2

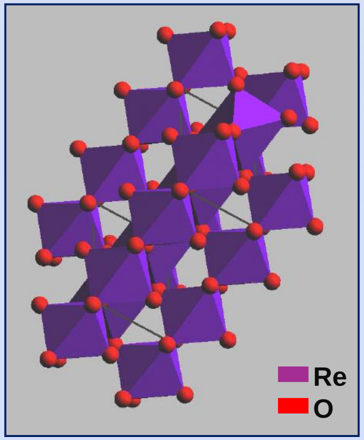
Work in cooperation with 'Departamento de Física Aplicada da UFES'



Crystalline structure:

Space Group ⇒ $P2_1/c$ (monoclinic)

Atomic positions ⇒ Re (4e); O(4e)



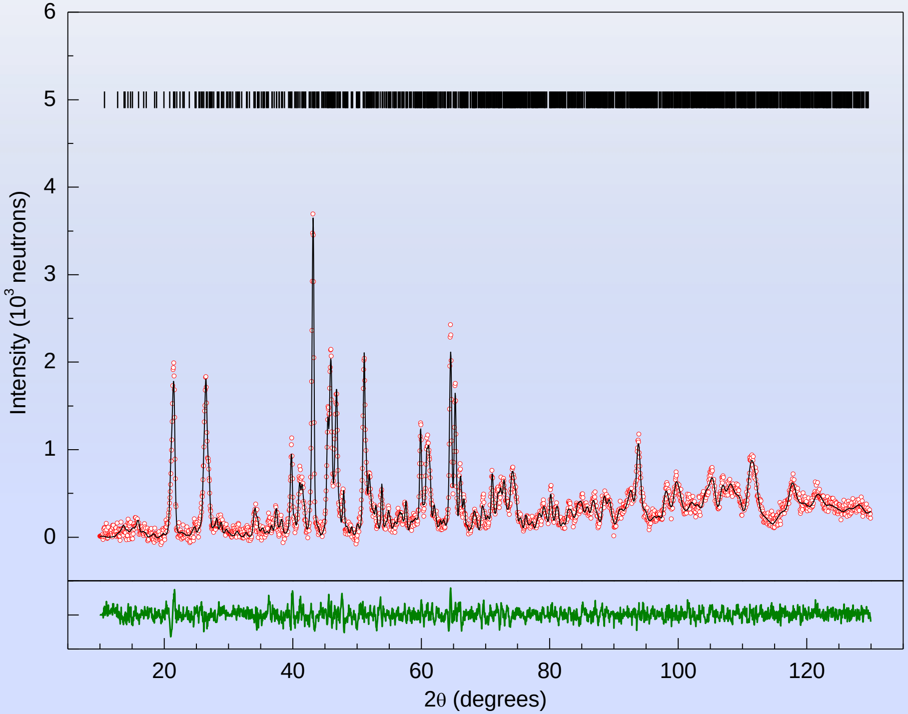
⇒ Time of measurement = 54 h

⇒ Reactor power = 3.5 MW

Numerical criteria of fit:
- $R_P = 0.019$
- $R_{WP} = 0.025$
- Reduced $\chi^2 = 2.7$

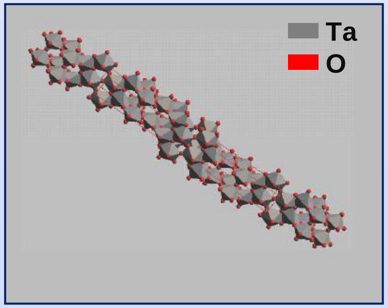
Rietveld profile fit for Ta_2O_5

Work in cooperation with 'Laboratório de Crescimento de Cristais do IFUSP - São Carlos'



Crystalline structure:

Space Group ⇒ Pmm2 (orthorrombic)



Numerical criteria of fit:
- $R_P = 0.021$
- $R_{WP} = 0.027$
- Reduced $\chi^2 = 1.9$

⇒ Time of measurement = 57 h

⇒ Reactor power = 3.5 MW

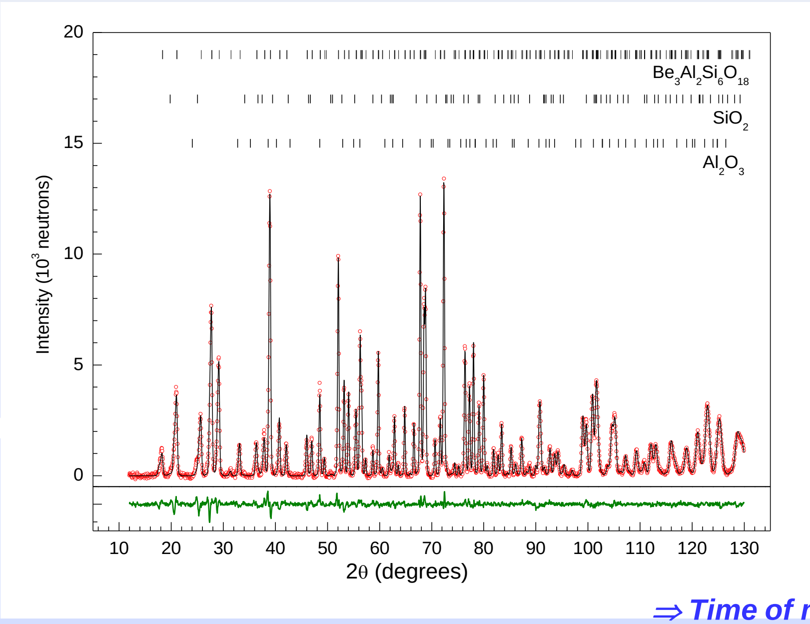
* f for $(\mathrm{sen}\theta)/\lambda = 0.5$ Å^{-1}

		Neutrons			X Rays		
Element	Z	μ (cm^{-1})	b (10^{-12} cm)	b^2 (10^{-24} cm^2)	μ (cm^{-1})	f * (10^{-12} cm)	f^2 (10^{-24} cm^2)
O	8	-----	0.580	0.3364	-----	0.62	0.3844
Ta	73	0.7	0.692	0.4789	2750	11.3	127.69

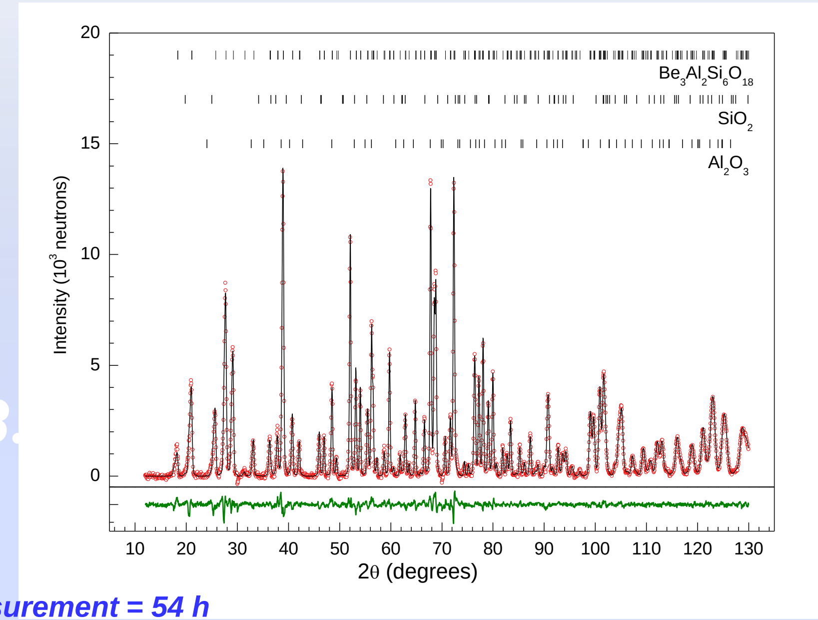
Rietveld profile fit for $Be_3Al_2Si_6O_{18}$

Work in cooperation with 'Instituto de Física da USP – São Paulo'

⇒ $Be_3Al_{1.89}Fe_{0.11}Na_{0.25}Si_6O_{18}$ (beryl)



⇒ $Be_3Al_{1.83}Fe_{0.17}Na_{0.03}Si_6O_{18}$ (aquamarine)

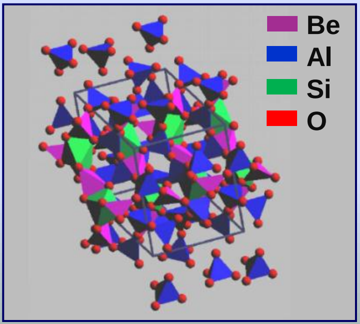


⇒ Time of measurement = 54 h

⇒ Reactor power = 3.5 MW

Wt. % ($Be_3Al_{1.89}Fe_{0.11}Na_{0.25}Si_6O_{18}$) = 96.94
Wt. % (SiO_2) = 2.70
Wt. % (Al_2O_3) = 0.36

<u>Numerical criteria of fit</u>: - R_P = 0.022
- R_{WP} = 0.032
- Reduced χ^2 = 4.0



Wt. % ($Be_3Al_{1.83}Fe_{0.17}Na_{0.03}Si_6O_{18}$) = 97.87
Wt. % (SiO_2) = 1.75
Wt. % (Al_2O_3) = 0.38

<u>Numerical criteria of fit</u>: - R_P = 0.024
- R_{WP} = 0.034
- Reduced χ^2 = 4.7

At present:
-Rietveld quantitative phase analysis of powder patterns measured at room temperature

In the near future:
- Measurements at high and low temperatures
- Measurements at high pressure (room temperature)
- Residual stress measurements

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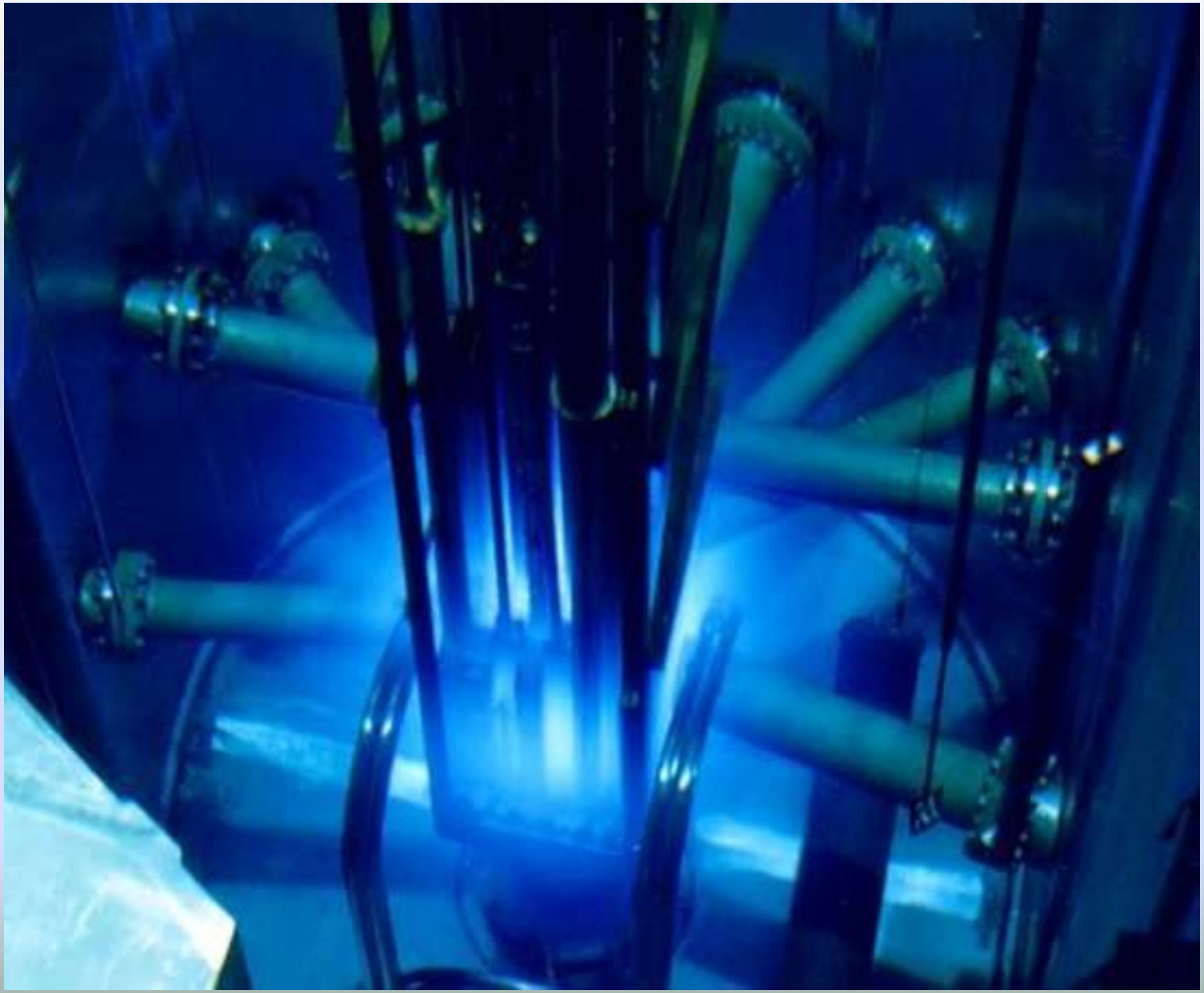
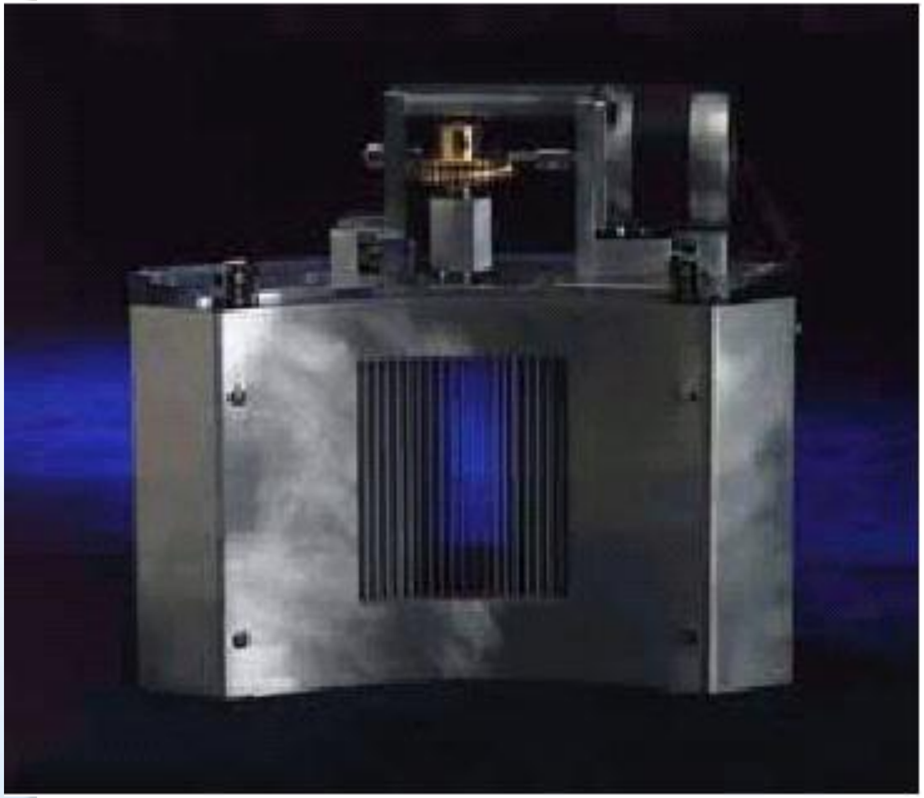
- Dr. Luiz Carlos de Campos (lccampos@pucsp.br)
Pontifícia Universidade Católica de São Paulo (PUCSP), São Paulo, SP, Brazil.

IEA-R1 reactor core



The Rotating-Oscillating Collimator (ROC)*

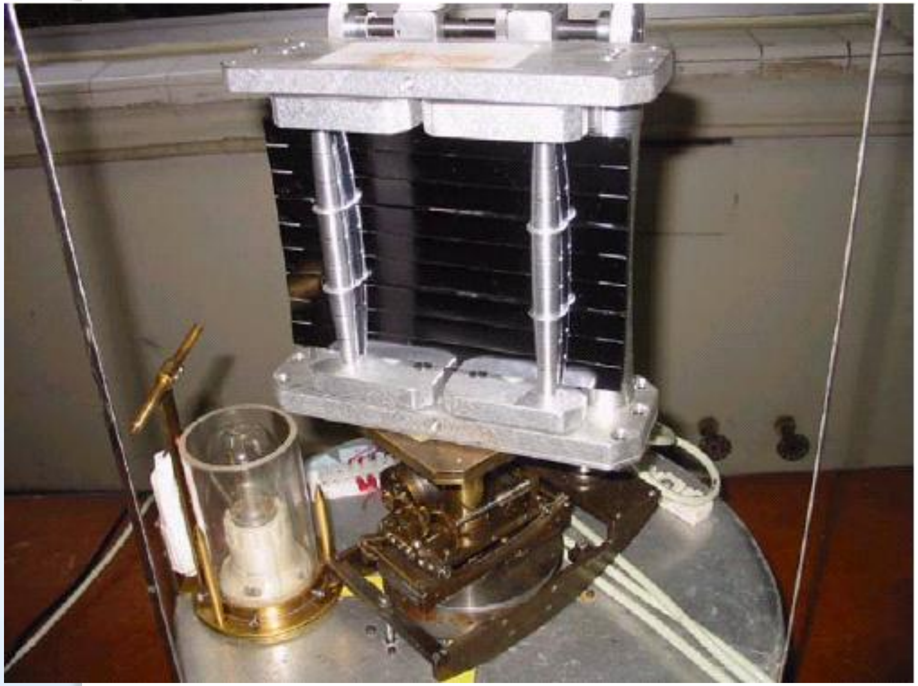


Placed at the entrance to the PSD shield in order to:

- eliminate parasitic scattering from furnaces or cryorefrigerators (only reducing the scattered intensity by *ca.* 10%);
- make the PSD less sensitive to ambient background.

* **Built by *Instrumentation Associates*, 2 Davis Drive, P.O. Box 13169, Research Triangle Park, N.C. 27709-3169, USA (rberliner@InstrumentationAssociates.com)**

The focusing Si bent monochromator*



Close-up of the focusing Si bent monochromator, goniometer and luminaire

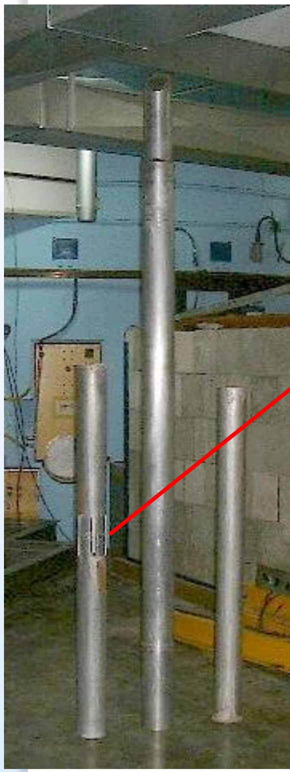
At a take-off angle of 84° the following reflections/wavelengths can be attained:

533 / 1.111 Å
511 / 1.399 Å
331 / 1.667 Å
311 / 2.191 Å
(nominal values)

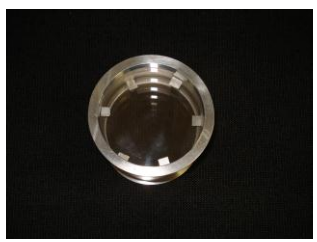
*** Built by *Instrumentation Associates*, 2 Davis Drive, P.O. Box 13169, Research Triangle Park, N.C. 27709-3169, USA (rberliner@InstrumentationAssociates.com)**

The sapphire filter

A sapphire filter has been installed in the neutron powder diffractometer “Aurora”. The filter reduces the background (BG) of the diffraction patterns by cutting fast and epithermal neutrons ($\lambda \leq 1.0$ Å) off the polychromatic beam. It has been inserted into the in-pile collimator.



A “cage” in the middle of the collimator accommodates the sapphire filter.

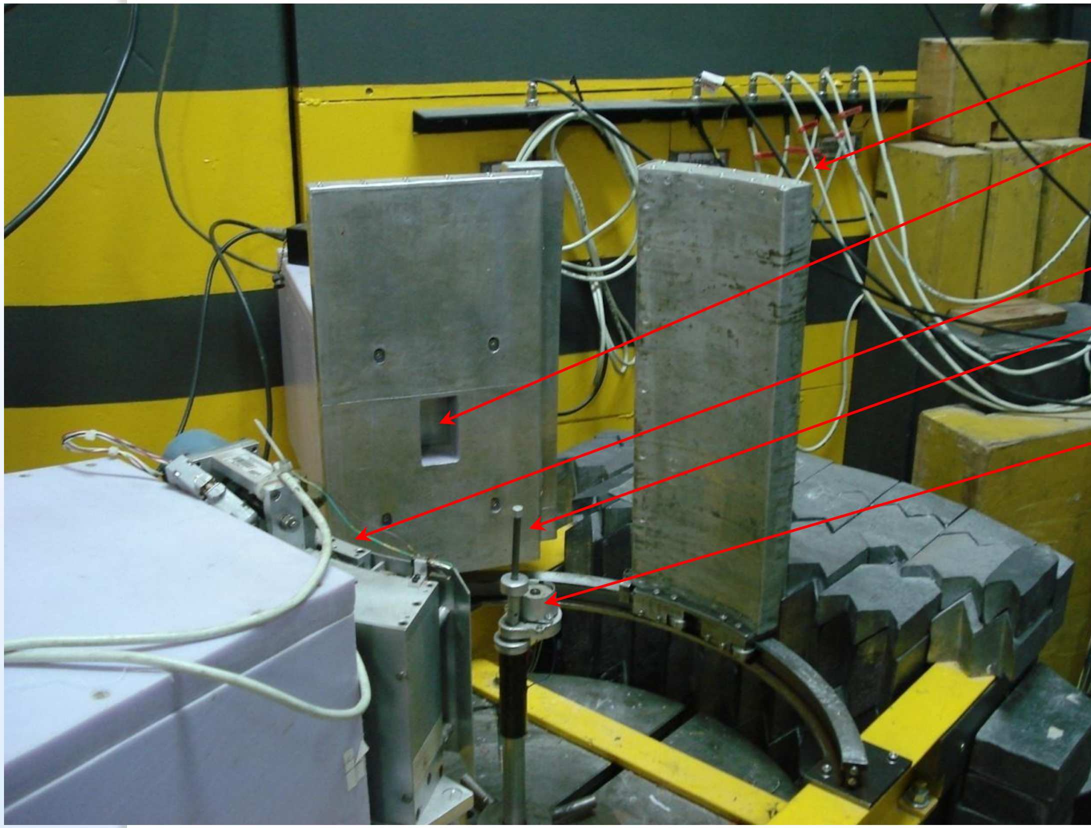


The filter is formed by 3 sapphire windows* encased in an aluminum cylinder. Characteristics of windows:

- orientation C plane
- 100 mm dia. x 25.4 mm thick
- polished both faces
- chamfered both faces

*Single crystals of good optical quality grown by *Crystan Ltd., UK* (sales@crystran.co.uk).

A sample holder immersed in the monochromatic neutron beam



Extra shield

Neutron beam monitor (fission chamber)

ROC

*Vanadium cylindrical sample holder**

Sample rocking device

** Vanadium sample holders currently used (0.15 mm wall thickness):*
- 3.17 and 6.35 mm diameter (~67 mm height)
- 9.52 mm diameter (~50 mm height)