High Resolution Powder Diffraction with Synchrotron X-Rays and Neutrons

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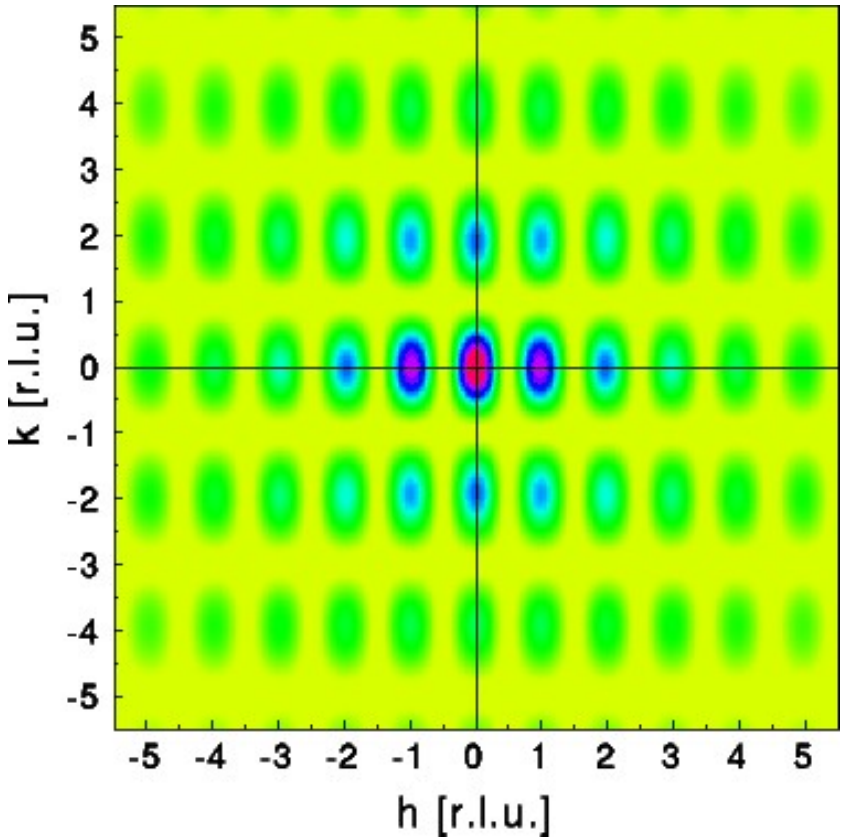
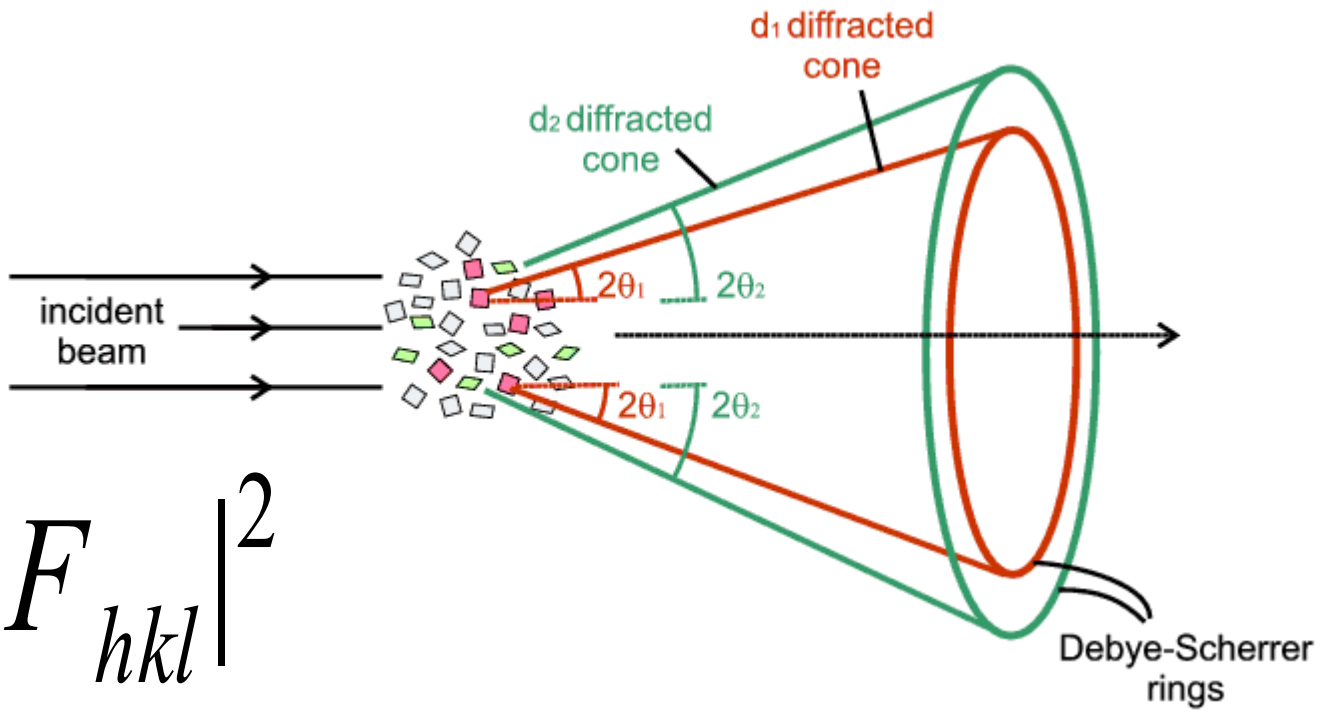
Single Crystal Crystallography

$$I(hkl) \propto |F(hkl)|^2 = \left| \sum b_j e^{i2\pi \left(hx_j + ky_j + lz_j \right)} \right|^2$$

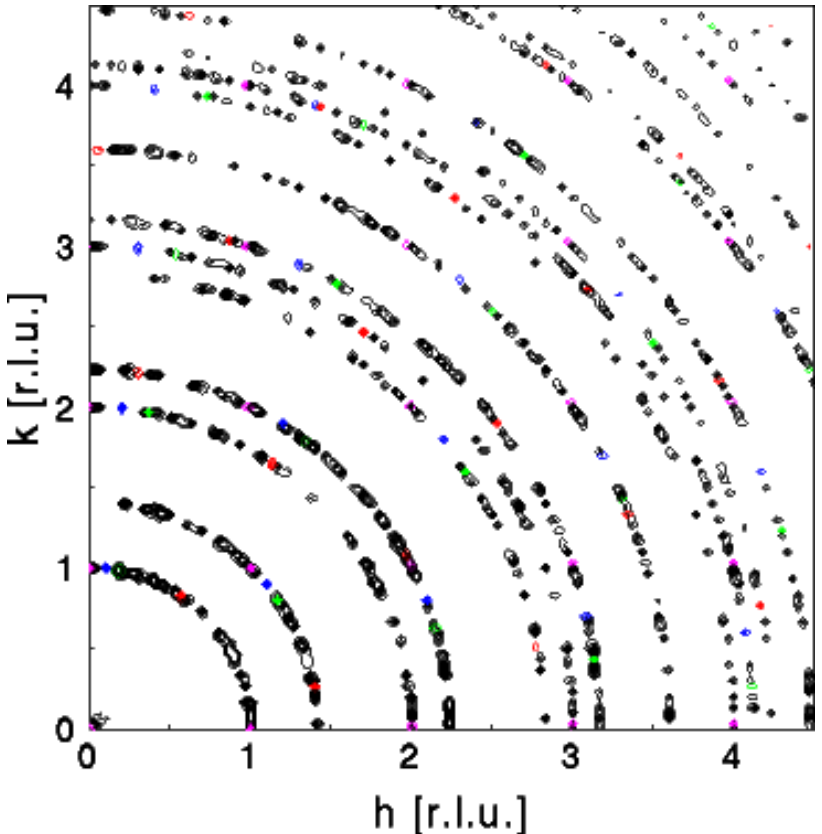


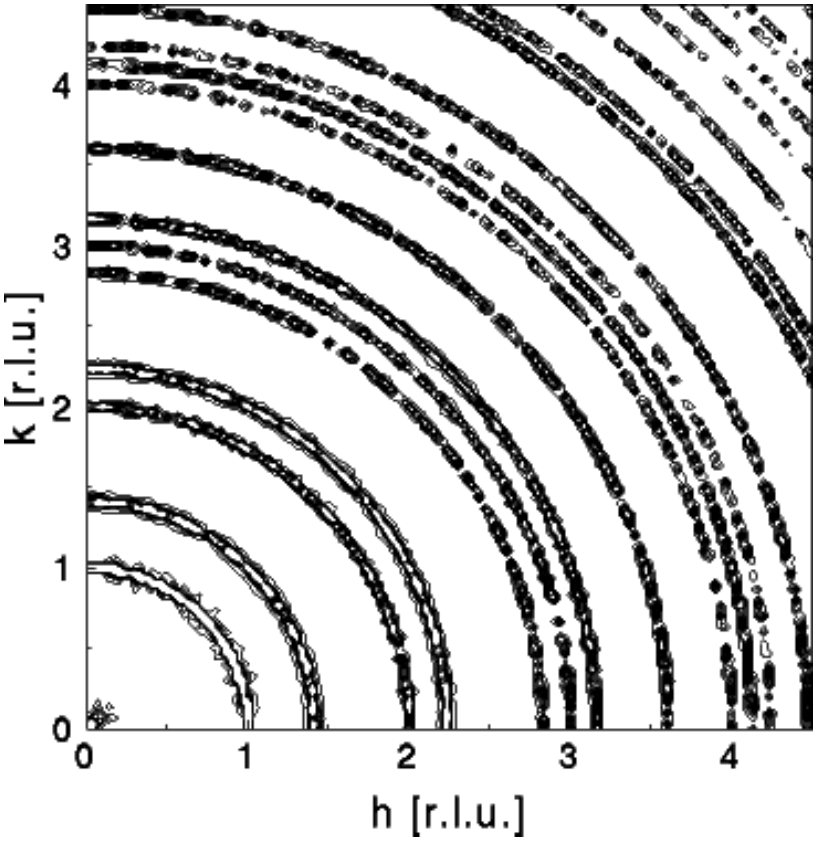
- Intensities I(hkl) determined with accuracy (vectors **G** well spaced in the 3D reciprocal space).
- Structure is solved through well established crystallographic methods (direct methods for small structures).

Powder Diffraction



$$I_{hkl} = cmL|F_{hkl}|^2$$





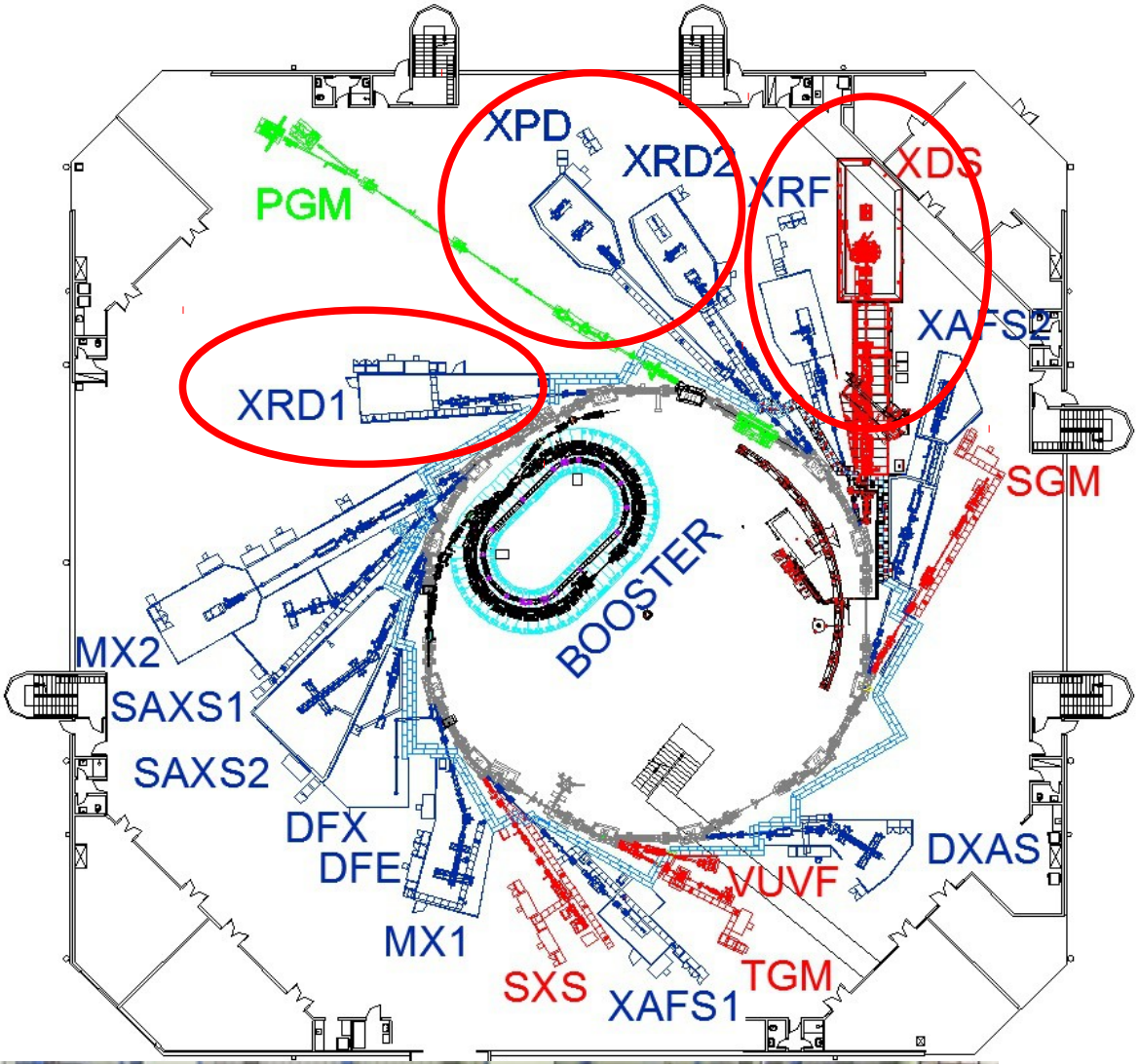
Why using the powder method ?

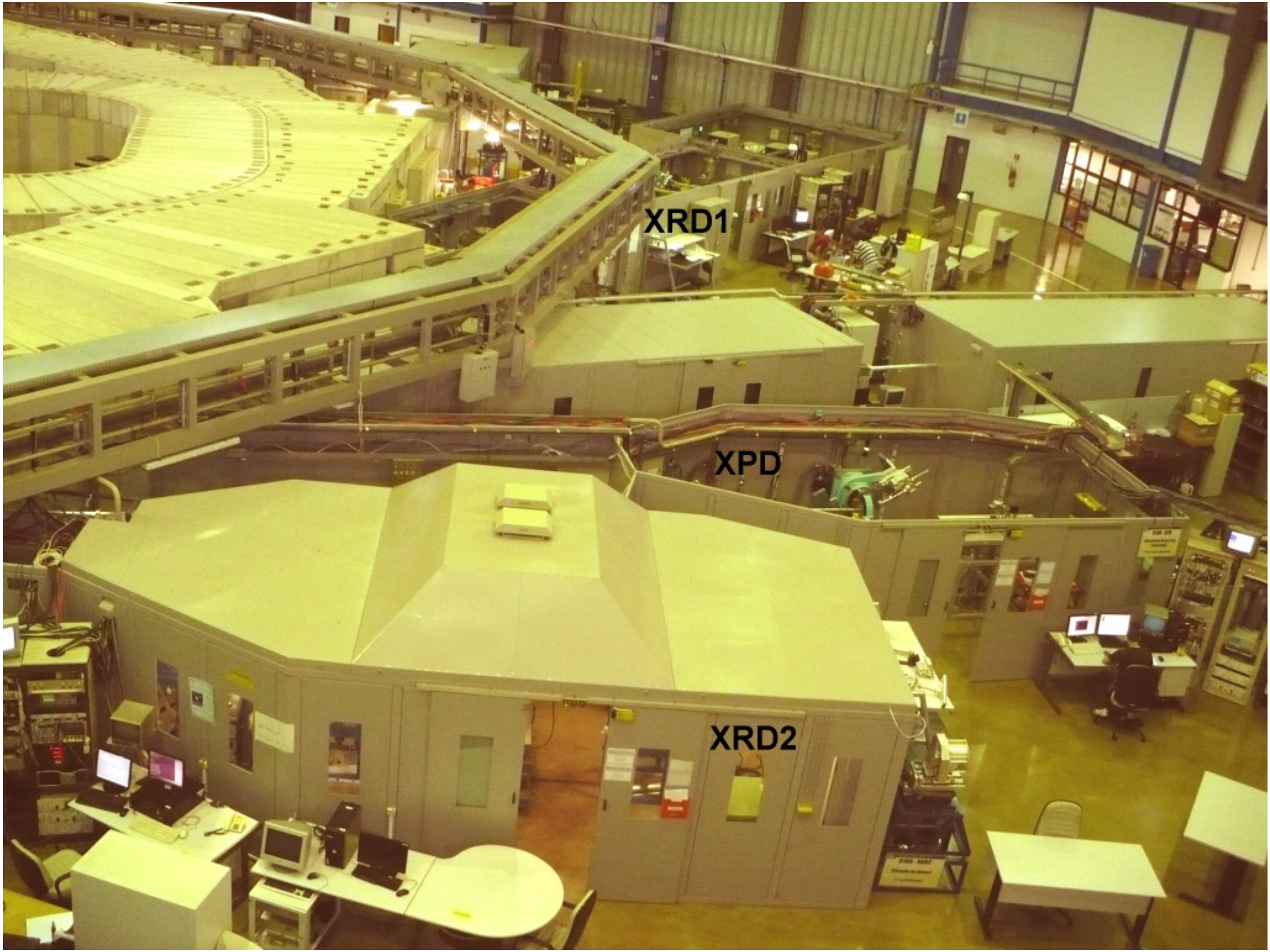
- The greatest majority of new materials are firstly sinthesized in powders; single crystals are typically grown several years after the initial discovery.
  - Superconducting cuprates, manganites, etc...
  - Many 'single crystals' show twinning.
  - Precise lattice parameters → subtle structural transitions.
  - Thermal environment may be more conveniently controlled.

PART I
PD with synchroton x-rays

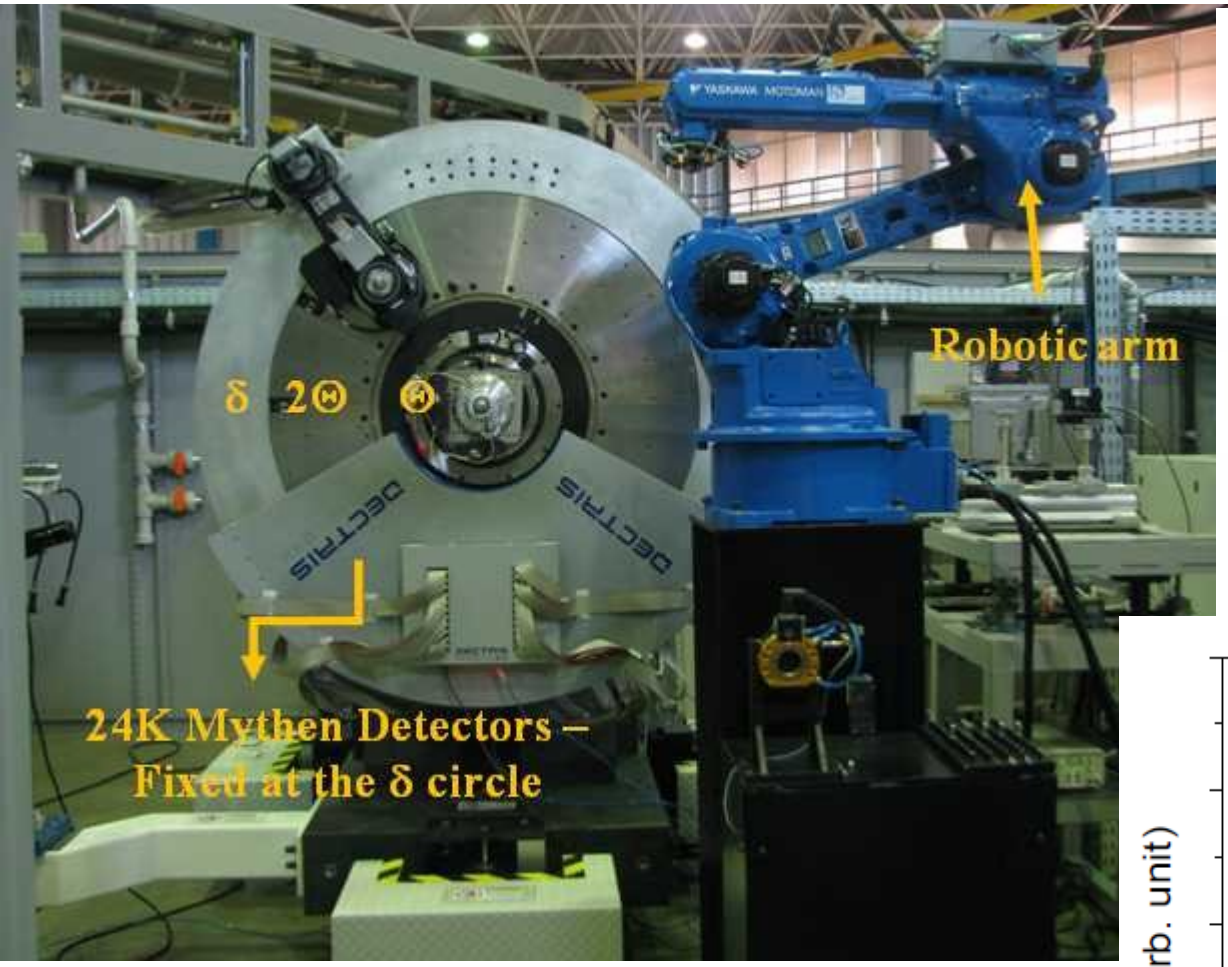
LNLS
1.37 GeV
4 straight sections:

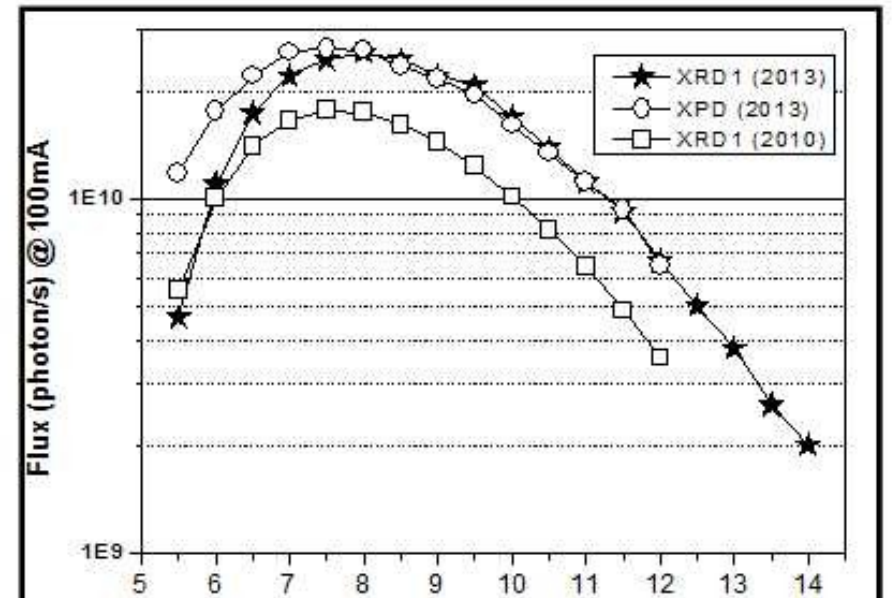
1 regular Wiggler for PX – MX2 beamline
1 undulator for soft x-rays - PGM beamline
Superconducting Wiggler – XDS beamline

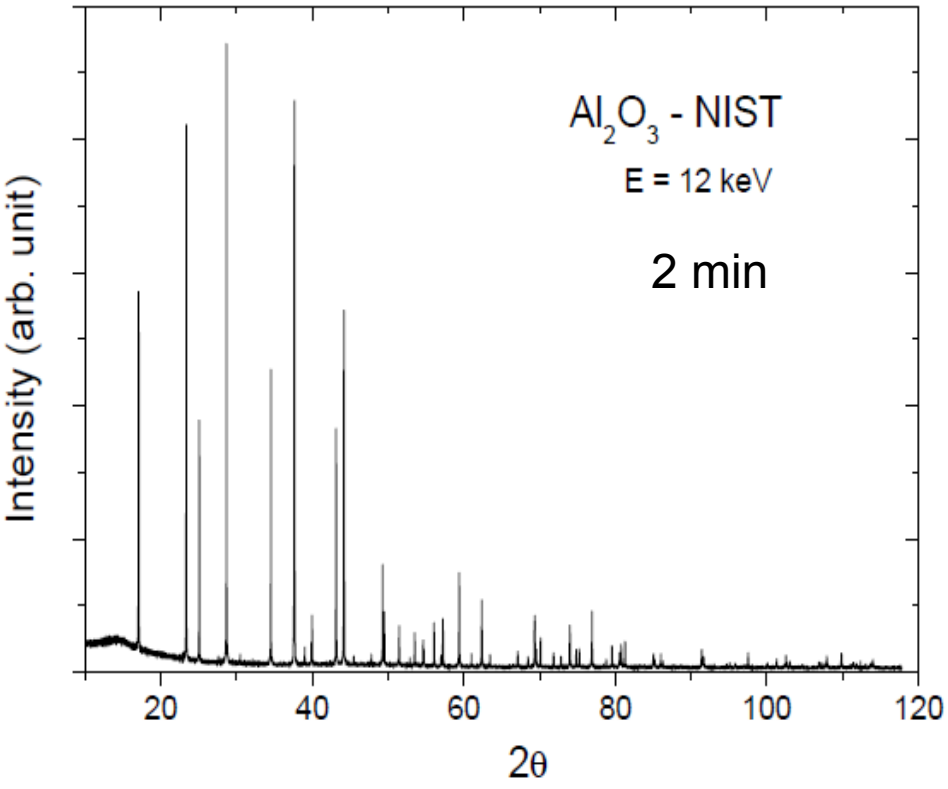



XRD1
XPD
XRD2

Beamlines: XRD-1







Heavy-duty powder diffractometer – excellent for fast automatized powder diffraction measurements in cyllindrical (Debye-Scherrer) geometry

XPD beamline

- Huber 4+2 circle diffractometer
- Coupling with furnaces (300-1273K), criostats (1.7-400K), pressure cell, etc.
- Allows for low-background high-resolution (Ge analyser) or high-intensity (Mythen 1K) powder diffraction measurements.

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X-ray powder diffraction beamline at D10B of LNLS: application to the Ba_2FeReO_6 double perovskite

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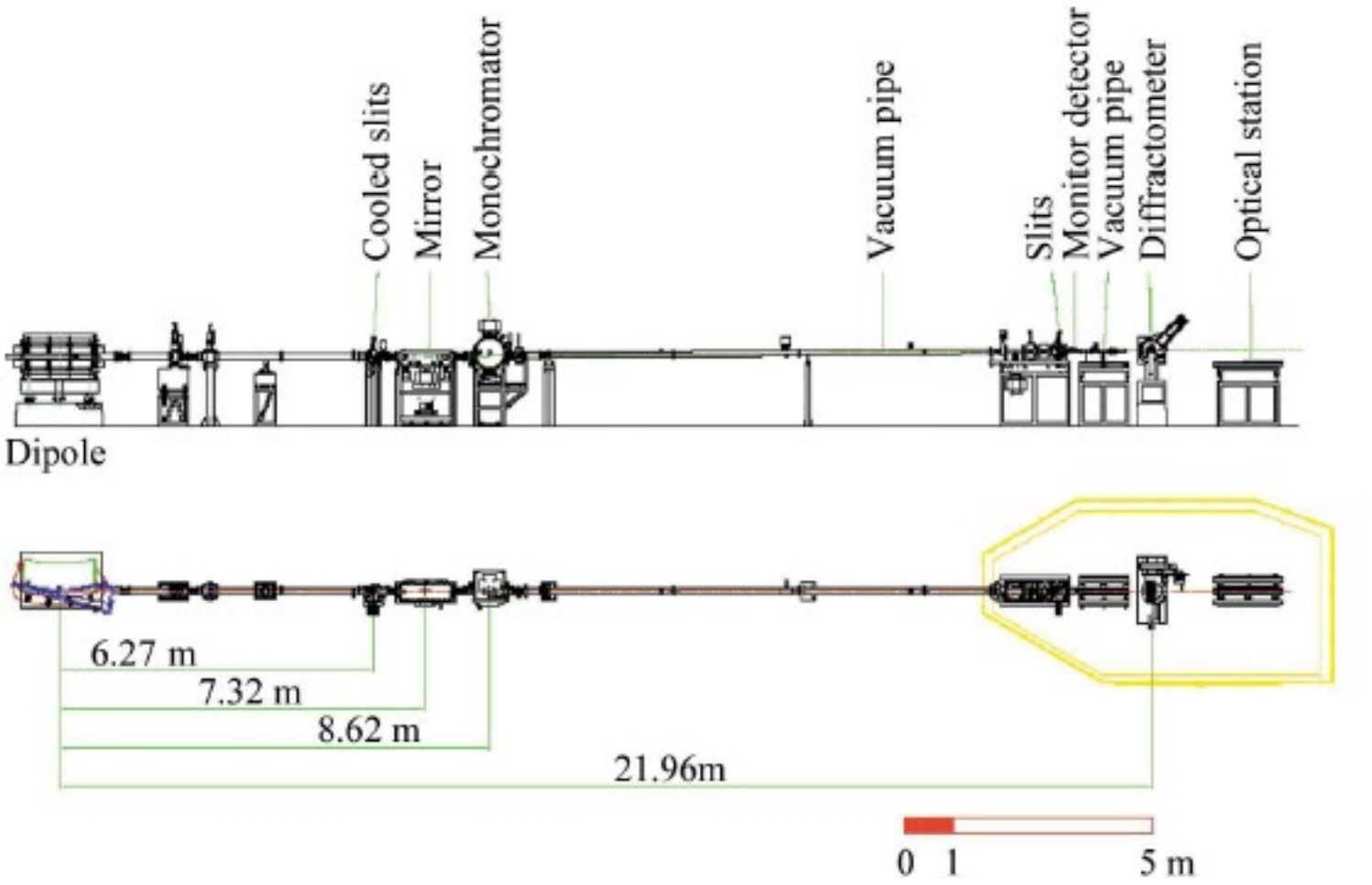


A case example (XPD beamline): $BiMn_2O_5$ multiferroic

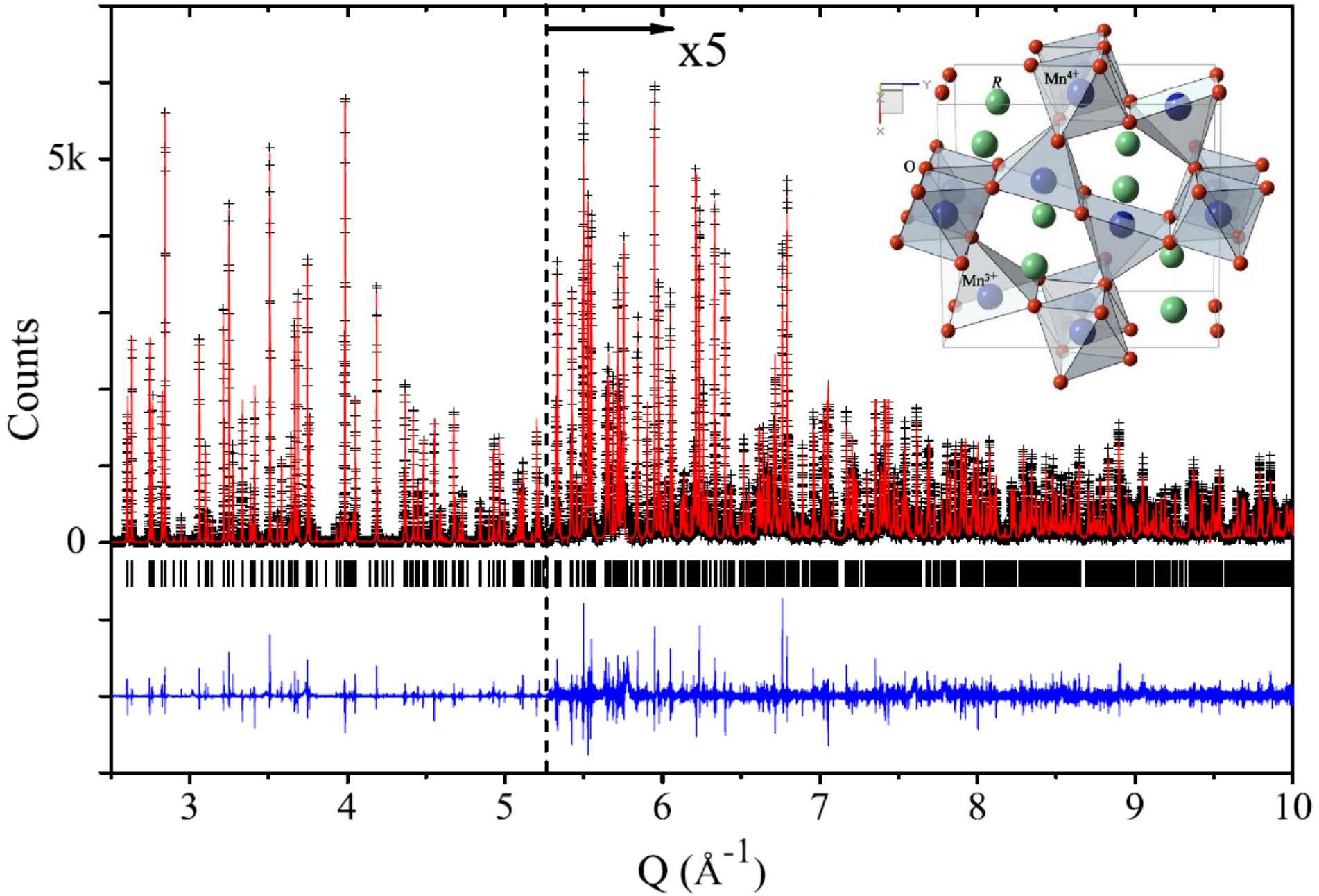
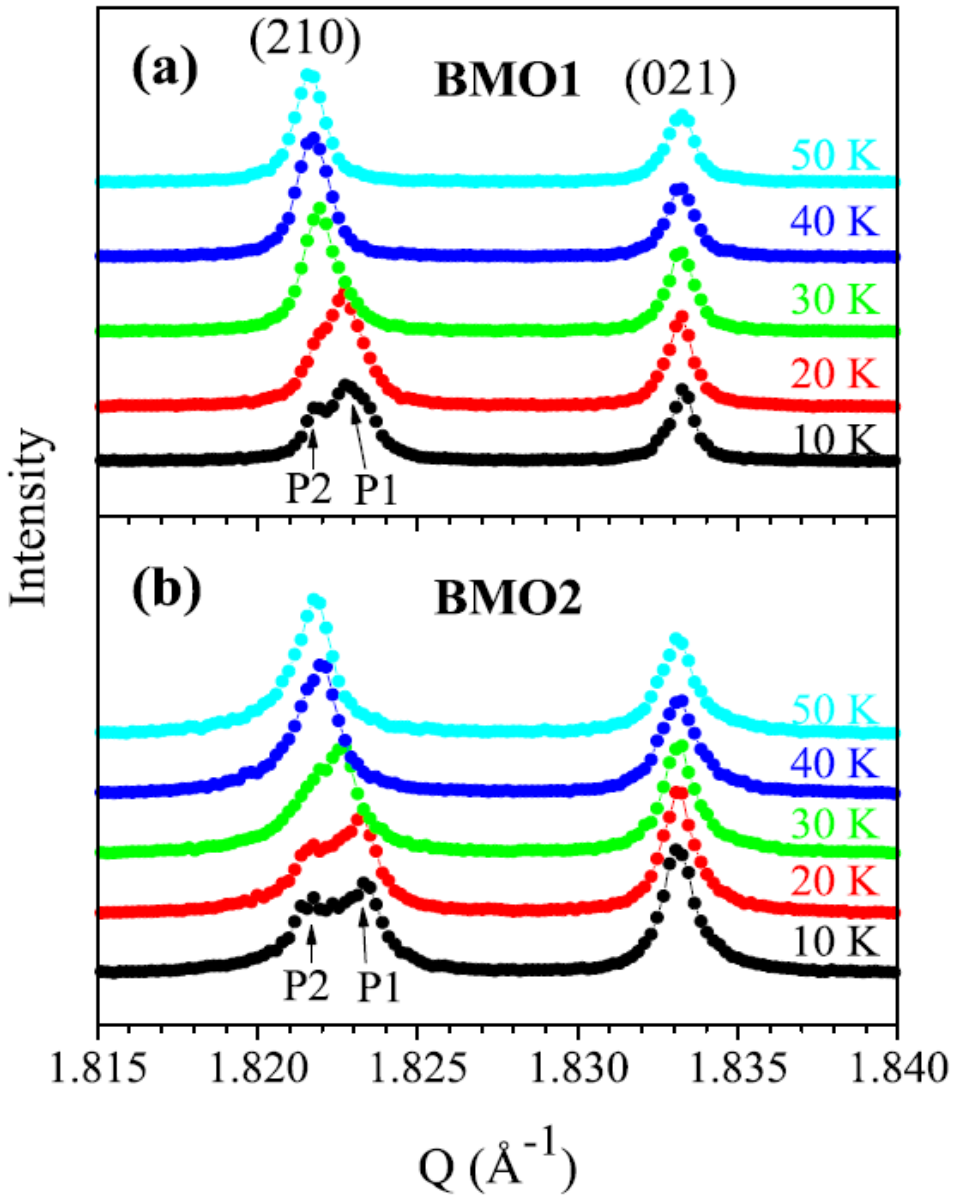
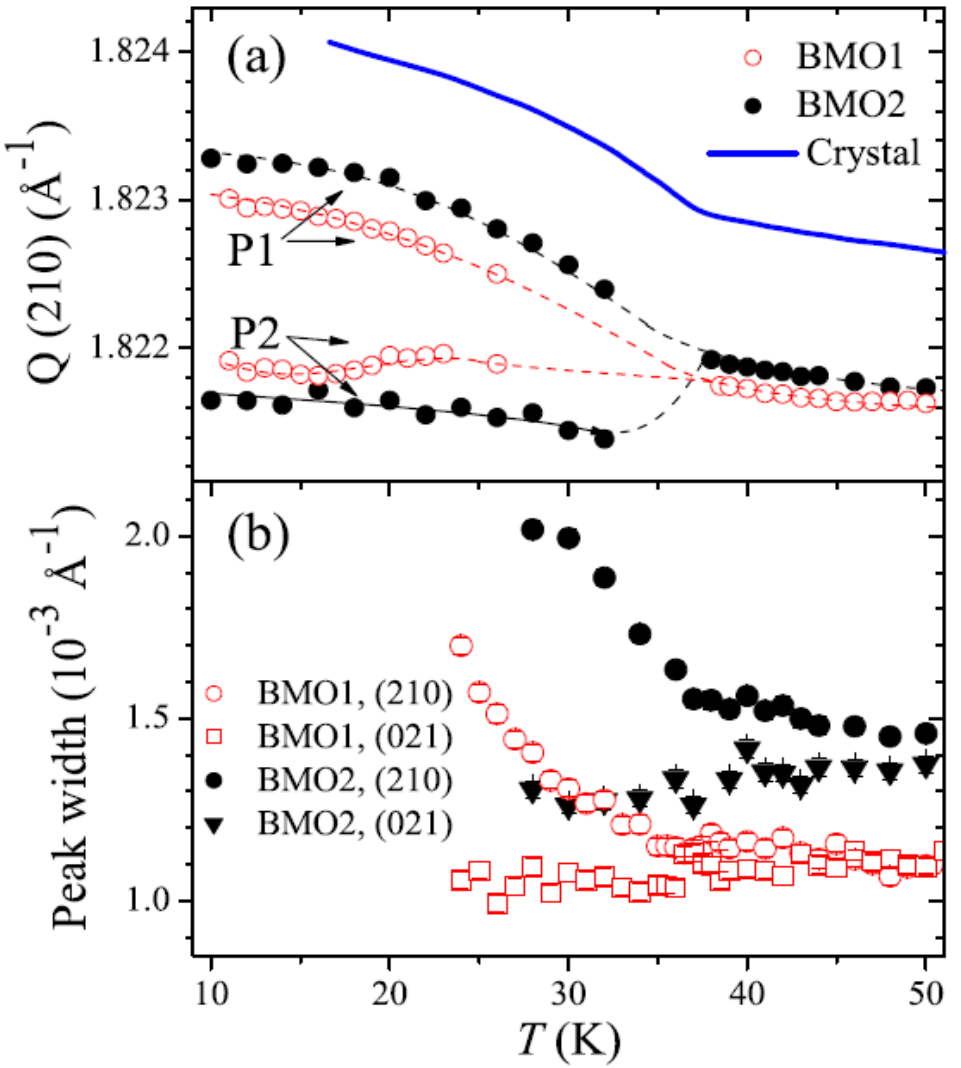


TABLE I. Refined lattice and atomic parameters of sample BMO2 at 100 K. Errors in parentheses are statistical only, and represent one standard deviation.

$T=100$ K		*Pbam*	$a=7.54116(1)$ Å	$b=8.52994(1)$ Å	$c=5.75437(1)$ Å	
Atom	Site	x	y	z	U_{iso} (Å^2)	Frac
Bi	4*g*	0.15896(4)	0.16556(4)	0	0.00588(6)	0.938(4)
Mn1	4*f*	1/2	0	0.2596(2)	0.0021(2)	1
Mn2	4 h	0.40755(15)	0.35091(14)	1/2	0.0029(2)	1
O1	4*e*	0	0	0.2876(10)	0.0048(5)	1
O2	4*g*	0.1567(8)	0.4453(6)	0	0.0048(5)	1
O3	4 h	0.1437(7)	0.4243(6)	1/2	0.0048(5)	1
O4	8*i*	0.3866(5)	0.2018(4)	0.2525(7)	0.0048(5)	1
$R_p=13.6\%$			$R_{wp}=25.3\%$			$\chi^2=1.86$


(a)
(210)
BMO1
(021)
50 K
40 K
30 K
20 K
10 K
P2
P1
(b)
BMO2
50 K
40 K
30 K
20 K
10 K
P2
P1
Intensity
1.815
1.820
1.825
1.830
1.835
1.840
Q (Å-1)


(a)
BMO1
BMO2
Crystal
P1
P2
1.824
1.823
1.822
Q (210) (Å-1)
(b)
BMO1, (210)
BMO1, (021)
BMO2, (210)
BMO2, (021)
2.0
1.5
1.0
Peak width (10-3 Å-1)
10
20
30
40
50
T (K)

PHYSICAL REVIEW B 77, 134101 (2008)

Magnetoelastic and thermal effects in the $BiMn_2O_5$ lattice: A high-resolution x-ray diffraction study

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High-resolution synchrotron x-ray diffraction measurements were performed on single crystalline and powder samples of $BiMn_2O_5$. A linear temperature dependence of the unit cell volume was found between $T_N = 38$ and 100 K, suggesting that a low-energy lattice excitation may be responsible for the lattice expansion in this temperature range. Between $T^* \sim 65$ K and T_N, all lattice parameters showed incipient magnetoelastic effects, due to short-range spin correlations. An anisotropic strain along the **a** direction was also observed below T^*. Below T_N, a relatively large contraction of the a parameter following the square of the average sublattice magnetization of Mn was found, indicating that a second-order spin Hamiltonian accounts for the magnetic interactions along this direction. On the other hand, the more complex behaviors found for b and c suggest additional magnetic transitions below T_N and perhaps higher-order terms in the spin Hamiltonian. Polycrystalline samples grown by distinct routes and with nearly homogeneous crystal structure above T_N presented structural phase coexistence below T_N, indicating a close competition amongst distinct magnetostructural states in this compound.

DOI: 10.1103/PhysRevB.77.134101 PACS number(s): 75.30.Kz, 77.80.Bh, 61.05.cp, 61.50.Ks

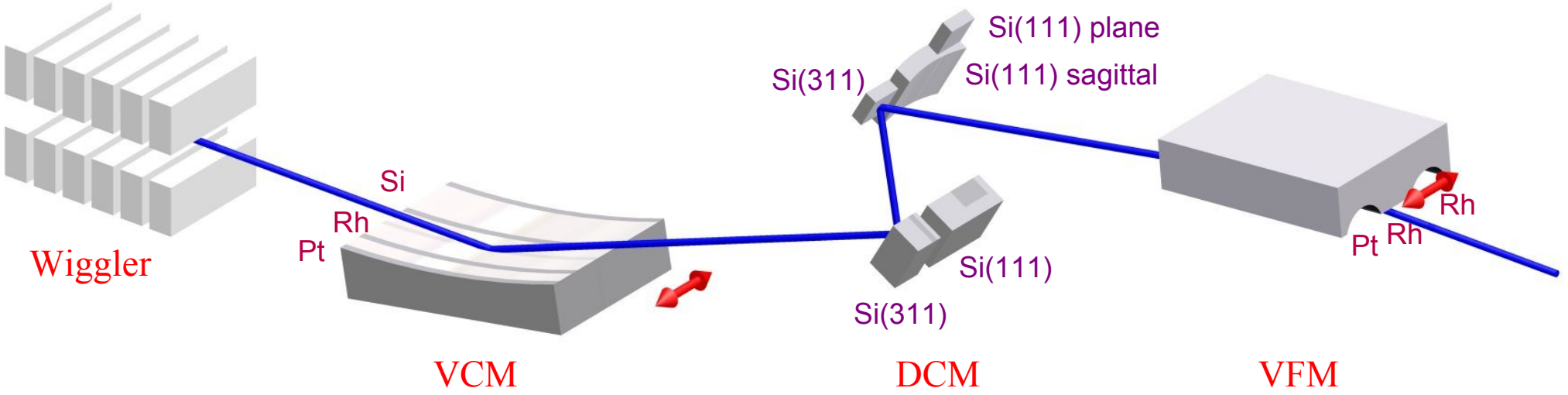
The need for a higher energy and more intense beamline

- Typical flux for bending magnet beamlines @ 8keV: 5 x 10^{10} ph/s/250 mA. Energy did not exceed ~12 keV.

- Meanwhile, a third generation, ~3 GeV machine, was being prepared (SIRIUS).

- The Materials Science users of LNLS-1 needed a high-flux hard x-ray beamline to attack previously unaccessible problems, meet a more challenging scientific agenda, and get ready for the new machine.

XDS beamline - Optical Layout



- Vertically collimating mirror (VCM):
  - Water cooled
  - Three stripes, Si (5-10 keV), Rh (9-20 keV), Pt (14-30 keV).

- Double Crystal Monochromator (DCM):
  - First crystals: LN2-refrigerated Si(111) [5-20 keV) and Si(311) [14-30 keV]
  - Second crystals: Plane Si(111), plane Si(311), sagittal Si(111)

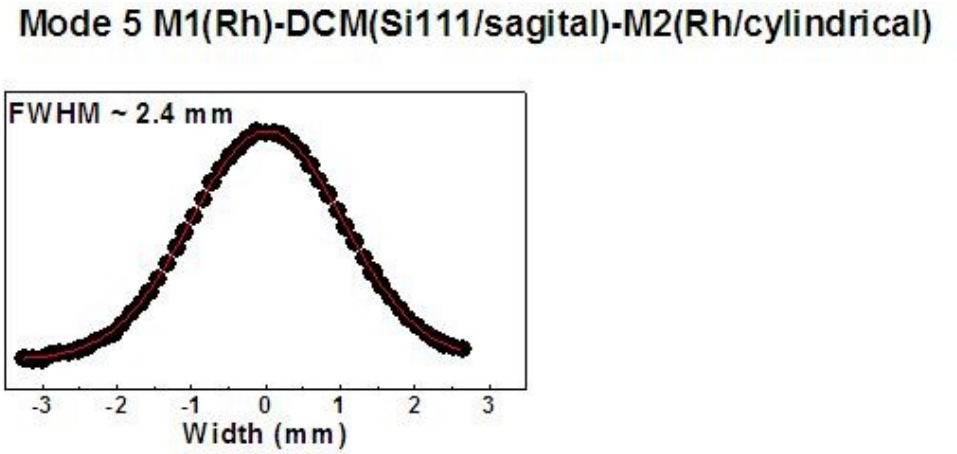
- Focusing Mirror (VFM)
  - Three stripes: Rh toroidal, Pt toroidal, Rh cylindrical (for use with sagittal DCM)

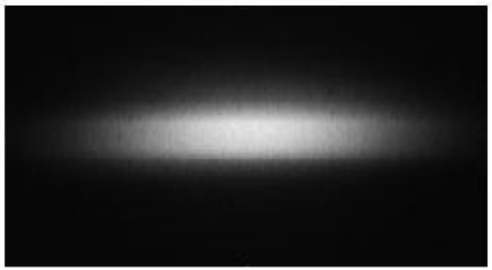
Beam shape at focal point (sagittal monochromator)

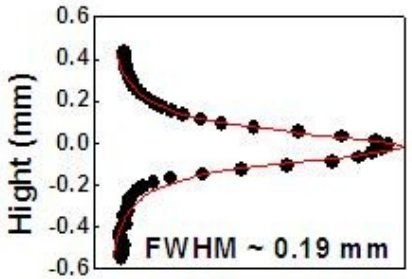
E = 11 keV

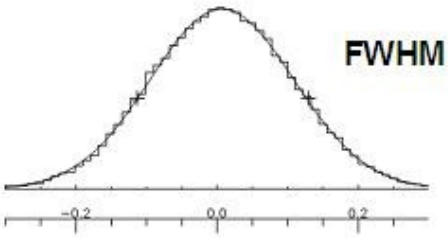
Observed

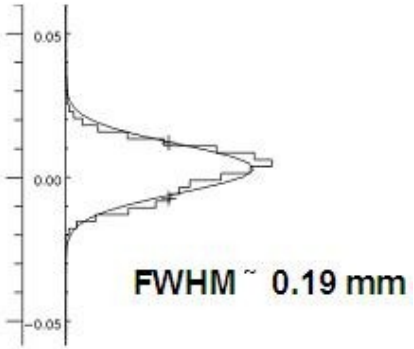
Simulated (ray-tracing)



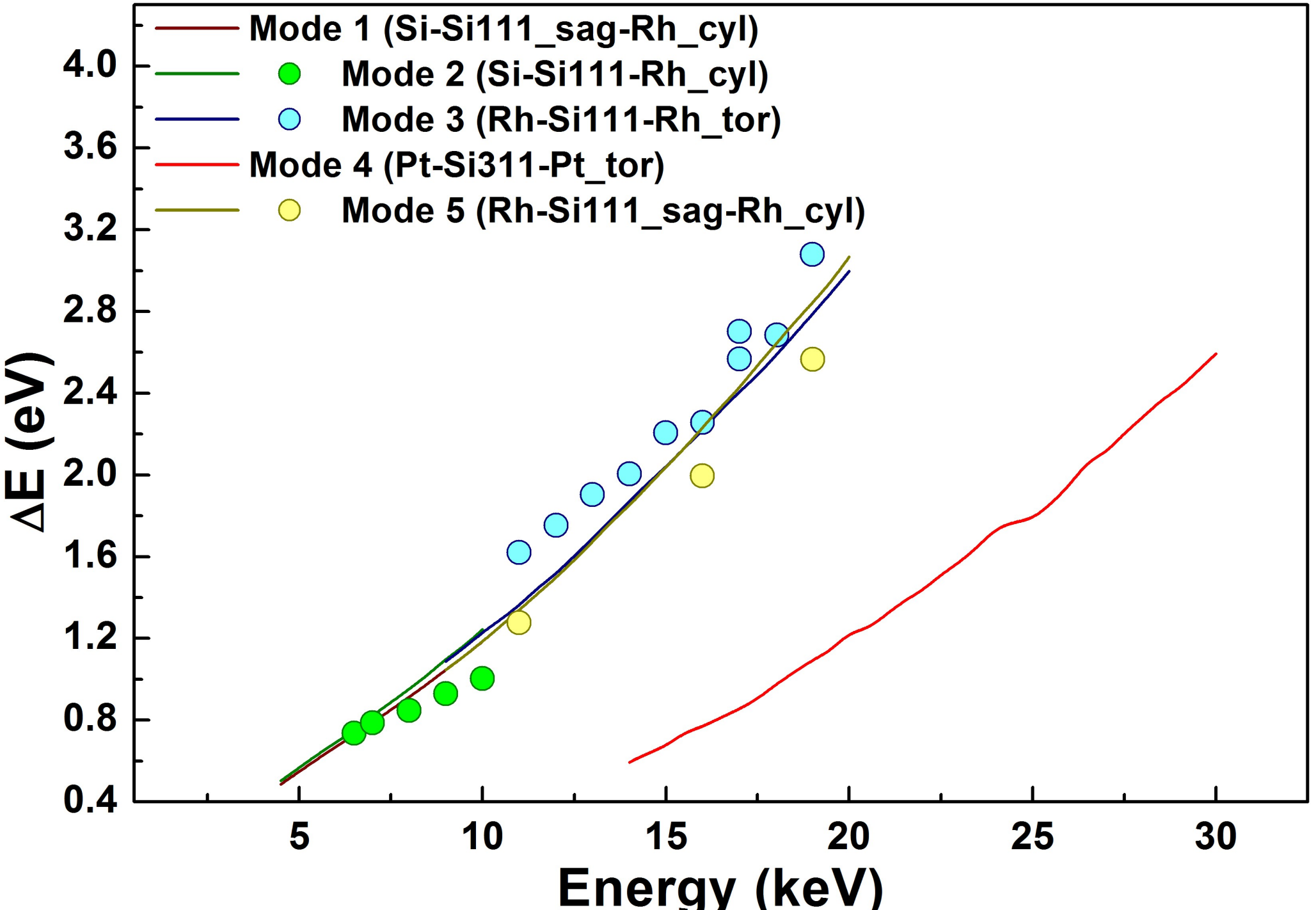




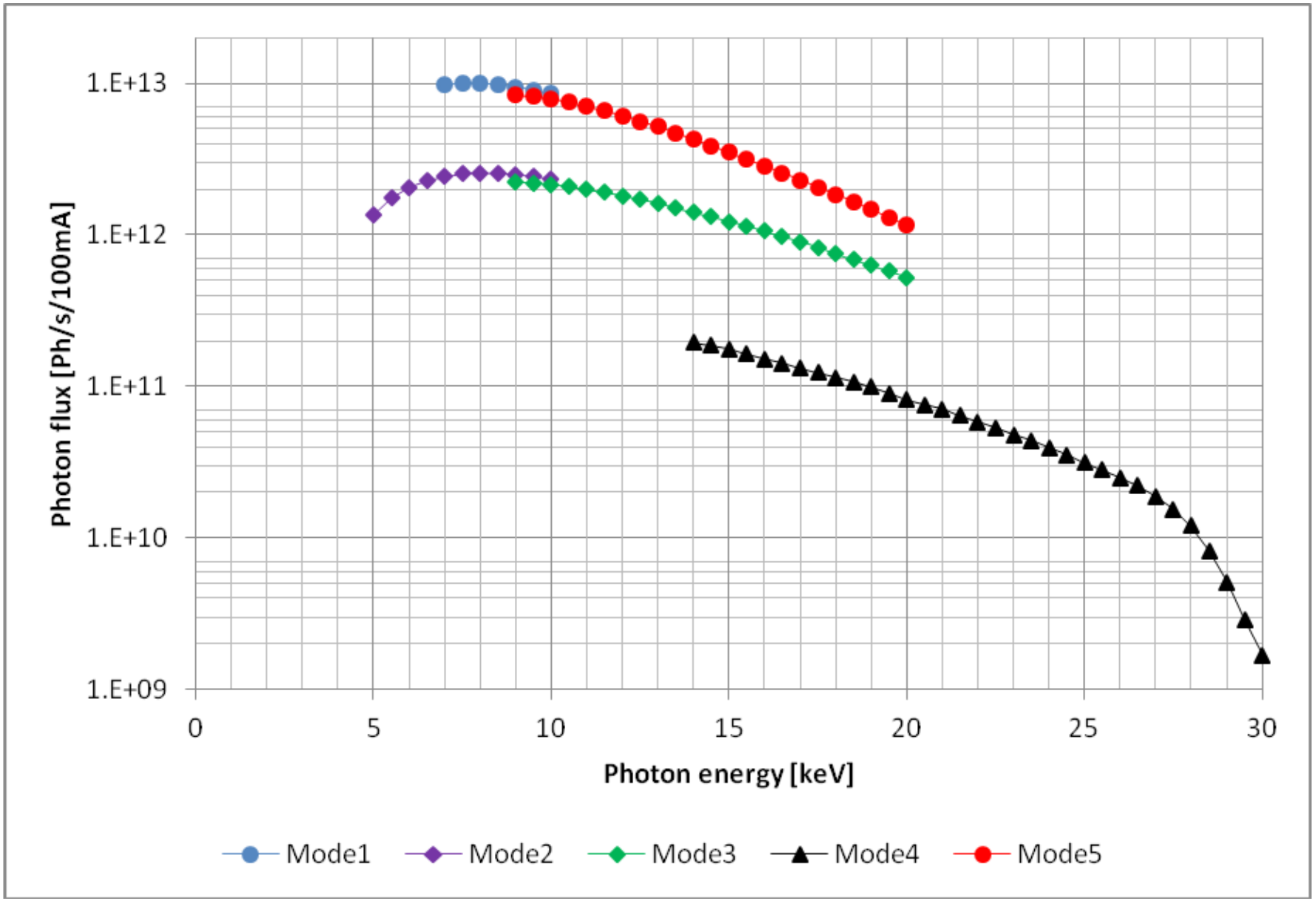




Energy resolution



Calculated Flux @ 3.8 T



Some New perspectives for Science at LNLS with the XDS beamline

- "High" Energy Photons → up to 30 keV
  - X-ray diffraction under high pressure (DAC cells)
  - X-ray diffraction under high magnetic fields (6 tesla)
  - New absorption edges for XAS / EXAFS (4^{th} row of periodic table)
  - Pair distribution function (PDF) analysis
  - X-ray diffraction up to high Q → more reliable crystal structures

- High Intensity → up to ~10^{13} ph/s
  - XAS/EXAFS of highly diluted elements (ppm)
  - Resonant / magnetic x-ray diffraction
  - Inelastic x-ray scattering (X-ray Raman / RIXS)
  - High resolution x-ray emission spectroscopy

beamlines

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XDS: a flexible beamline for X-ray diffraction and spectroscopy at the Brazilian synchrotron

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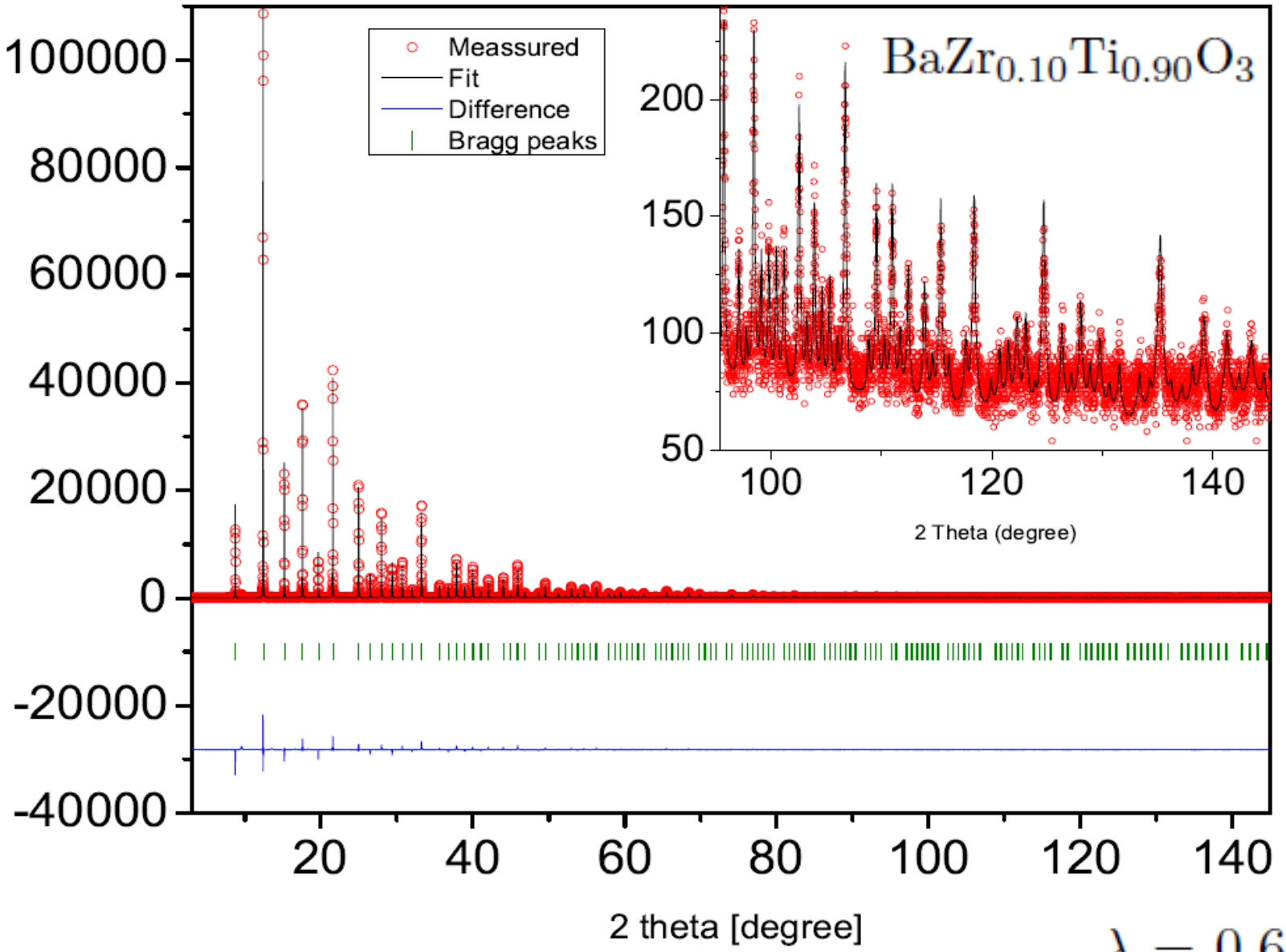
Preliminary PDF Studies on the $Ca_{1-x}Ba_xTi_{1-y}Zr_yO_3$ ferroelectric/relaxor system (Martín Saleta)



$\lambda = 0.6204$ Å

Part II – High resolution Neutron Powder diffraction

Neutron facts

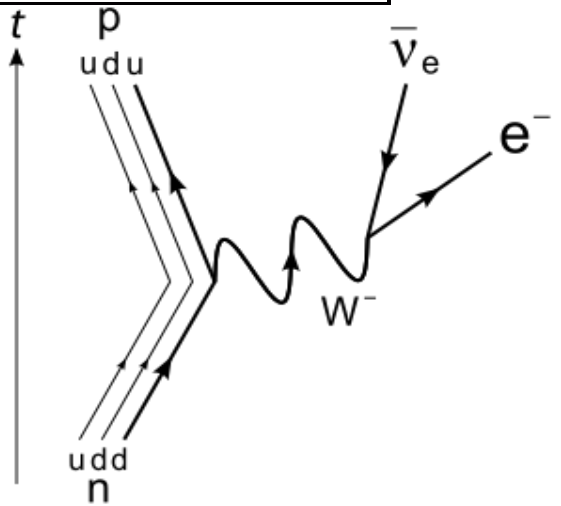
Properties of the neutron

Mass (m)	1.68×10^{-27} kg
Charge	0
Spin	1/2
Magnetic moment (μ_n)	−1.913 nuclear magneton
Wavelength (λ)	h/mv
Wavevector (k)	magnitude $2\pi/\lambda$
Momentum (p)	$\hbar k$
Energy (E)	$1/2\ mv^2 = \frac{h^2}{2m\lambda^2}$

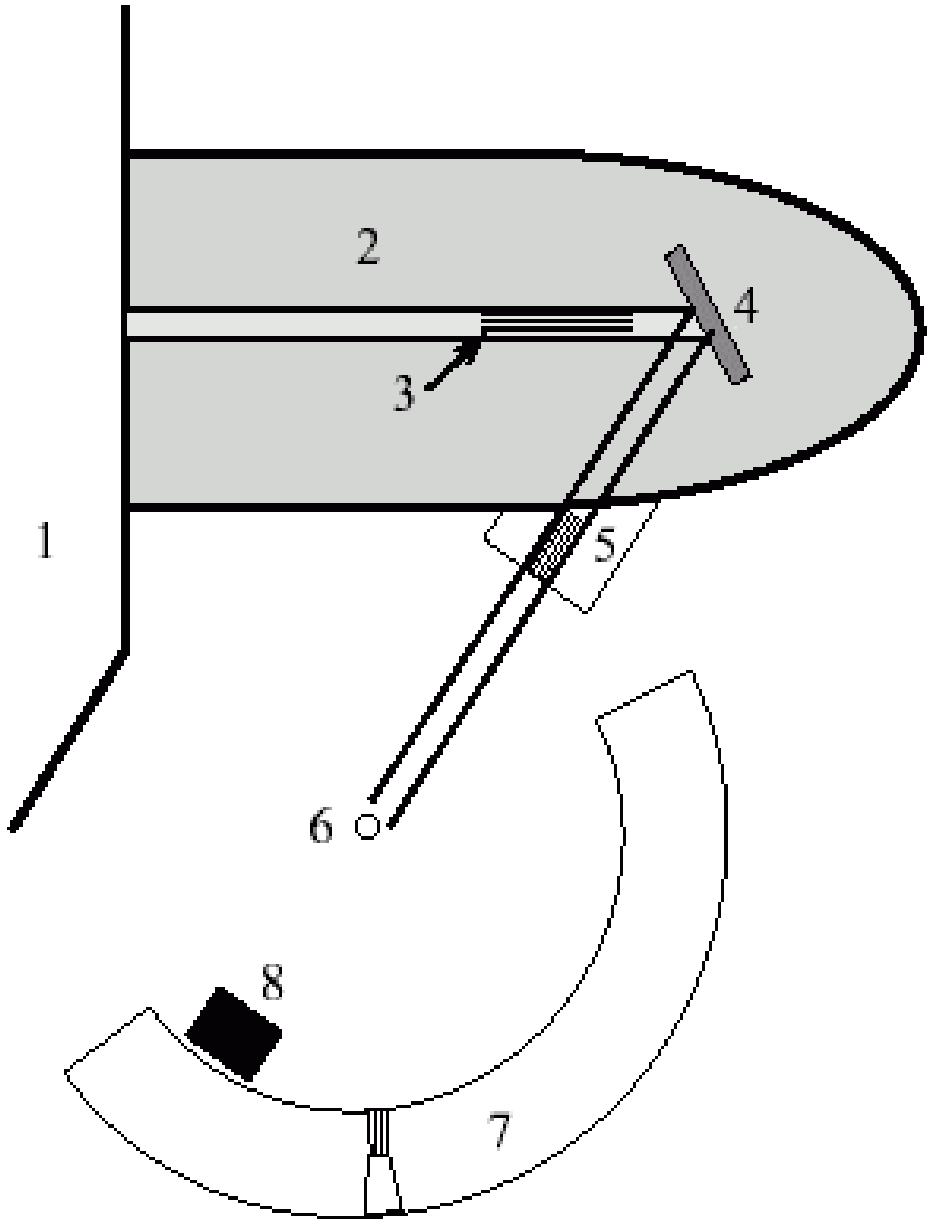
Free neutrons are unstable against b-decay
– no neutrons as cosmic rays !

$(n^0 \rightarrow p^+ + e^- + \bar{\nu}_e)$

mean lifetime: 881.5±1.5 s

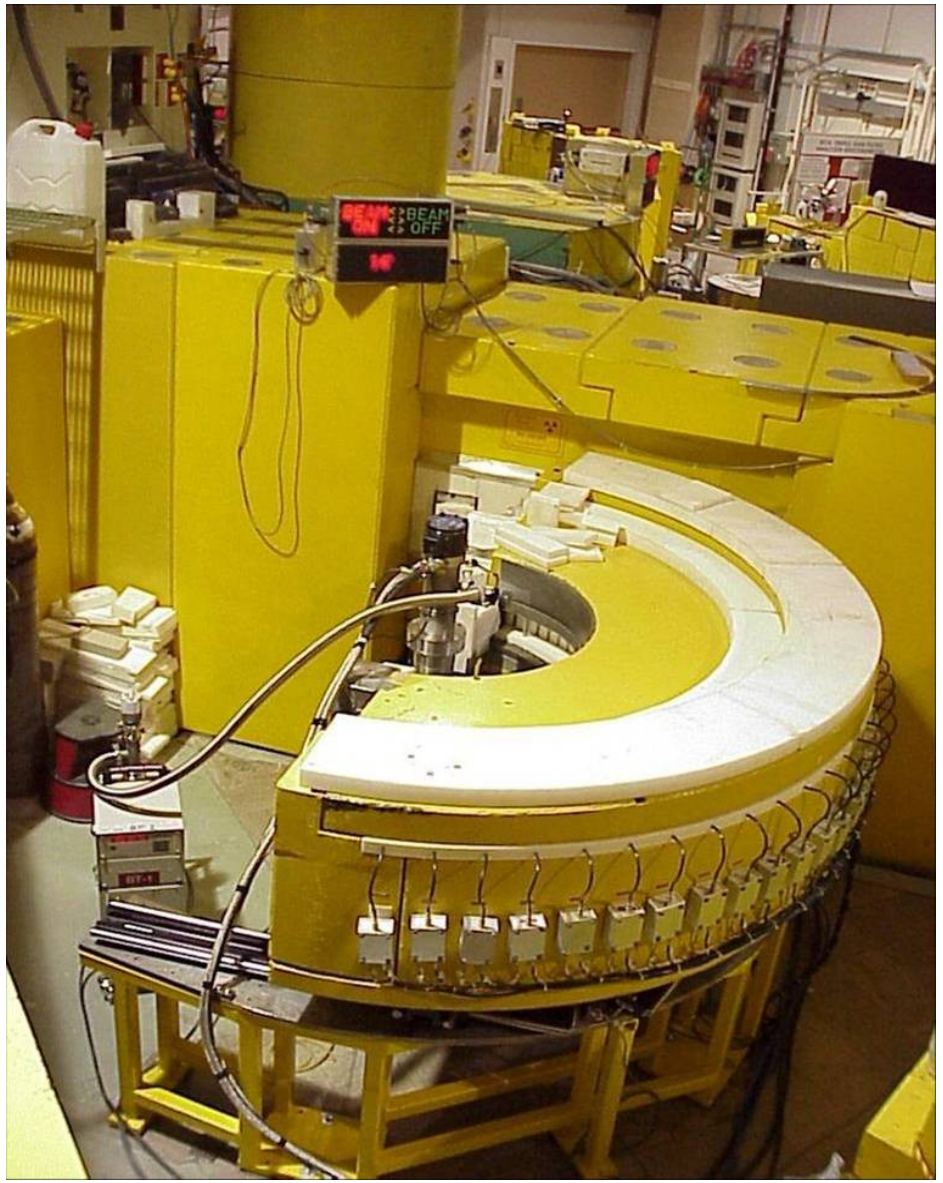


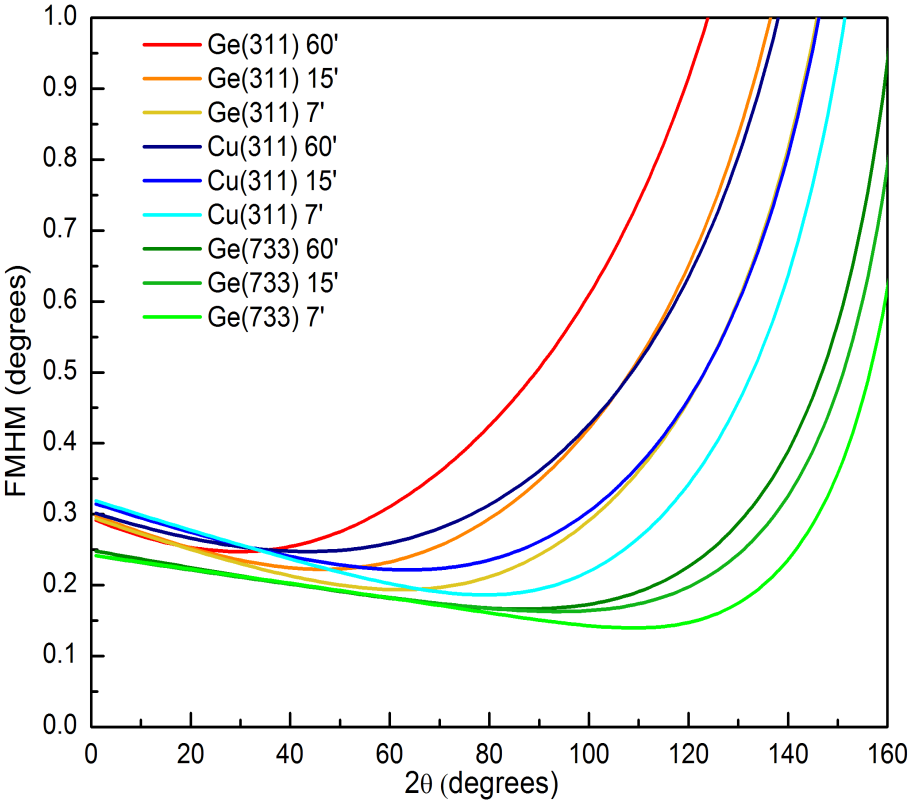
Basic geometry of a NPD experiment - CW



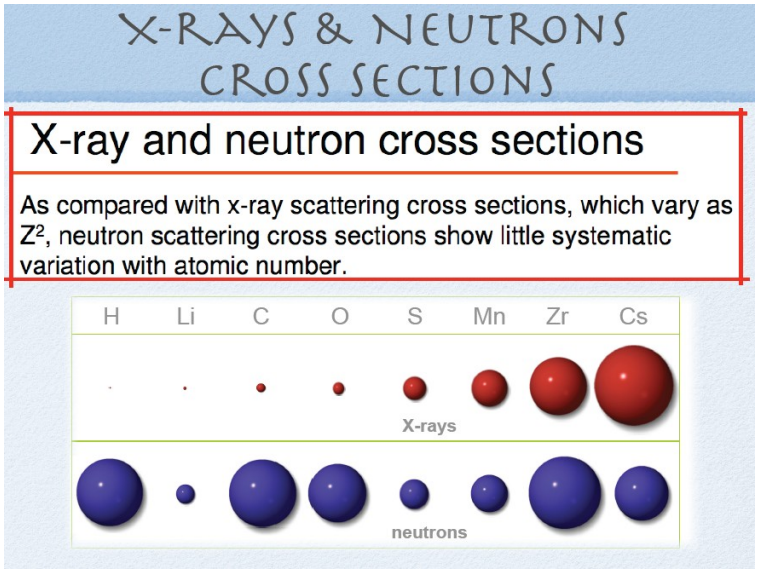
1. Reator face
2. Shielding
3. Primary collimation
4. Monochromator
5. Secundary collimation
6. Sample
7. Terciary collimation, detector
8. Beam stop

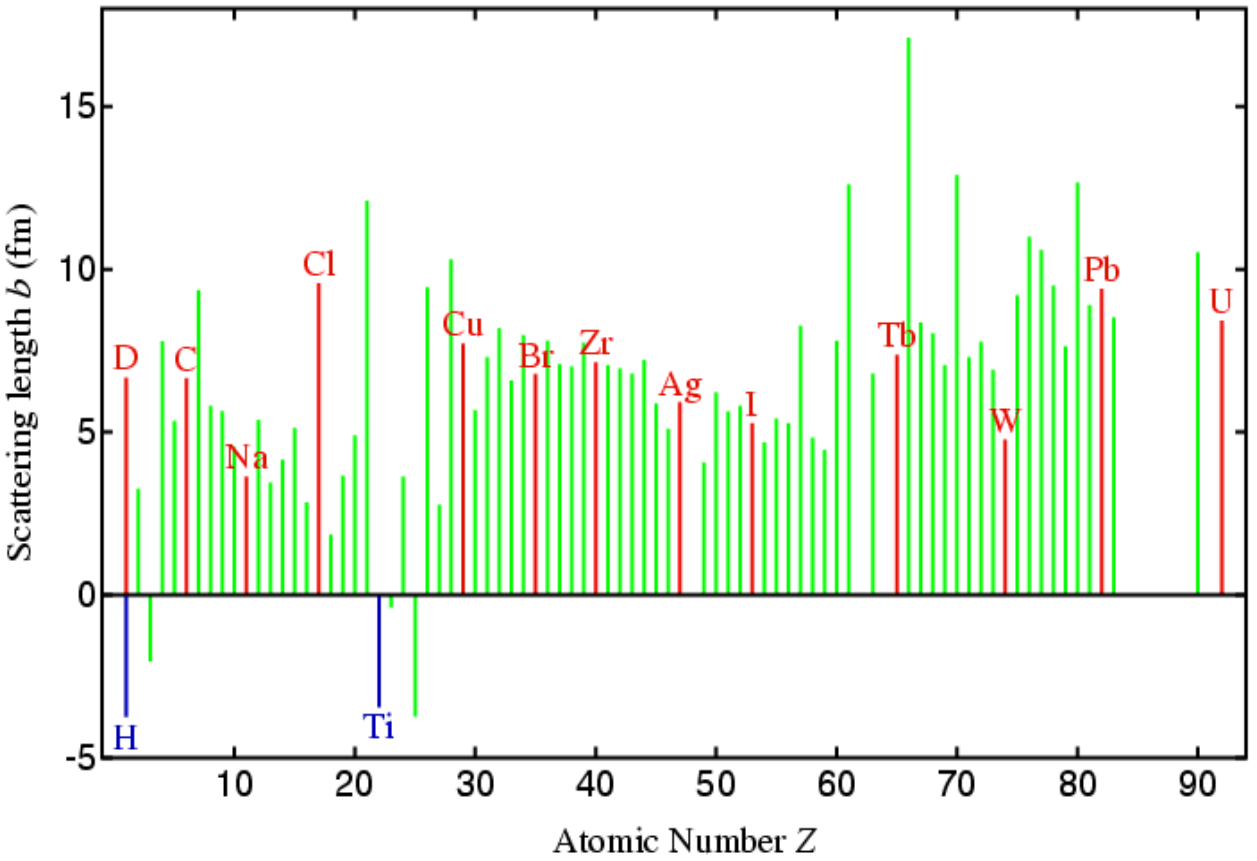
Example: BT1 Beamline, NCNR, NIST, Gaitherburg, Maryland, USA





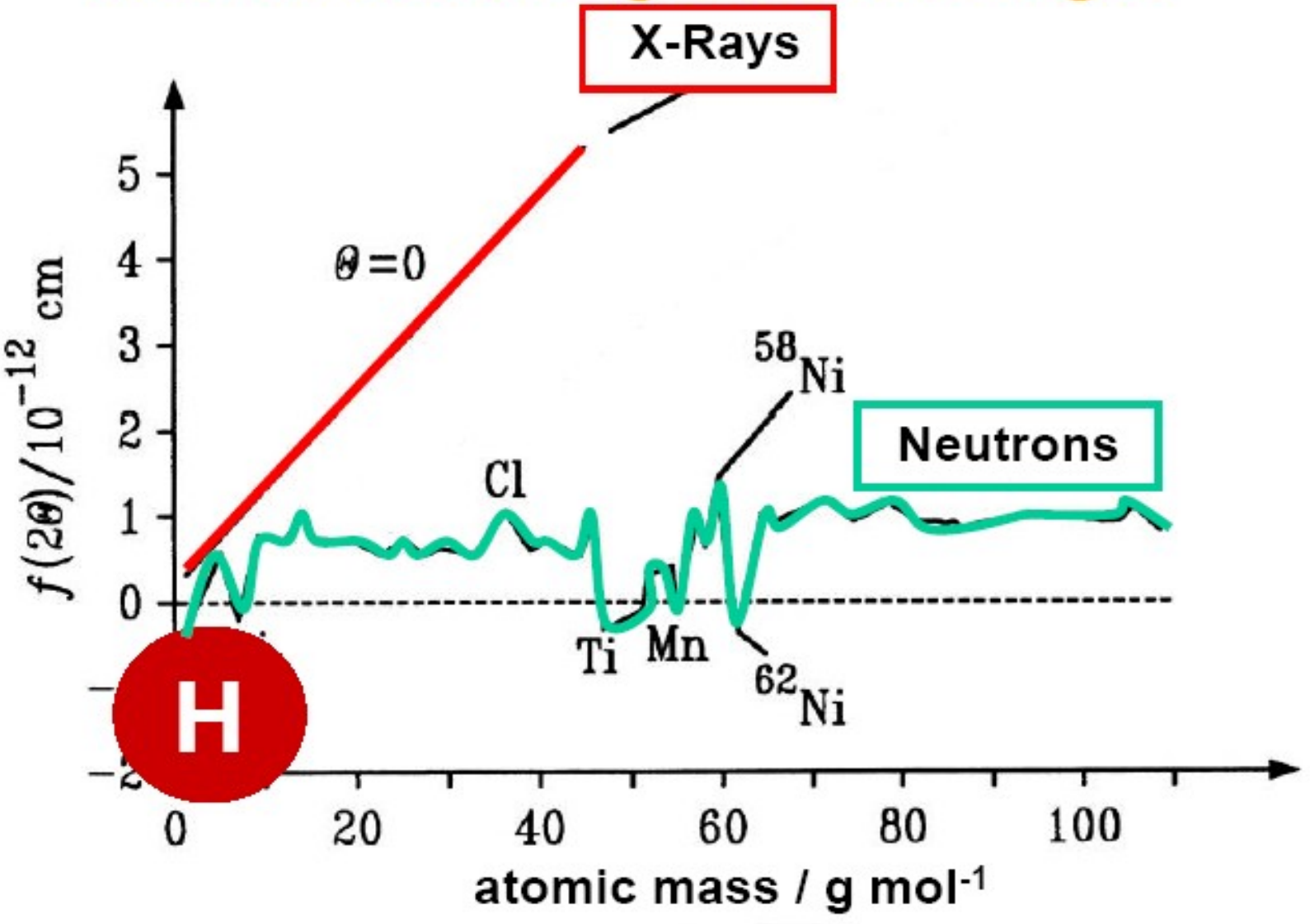
Why neutron powder diffraction (I) – scattering factors





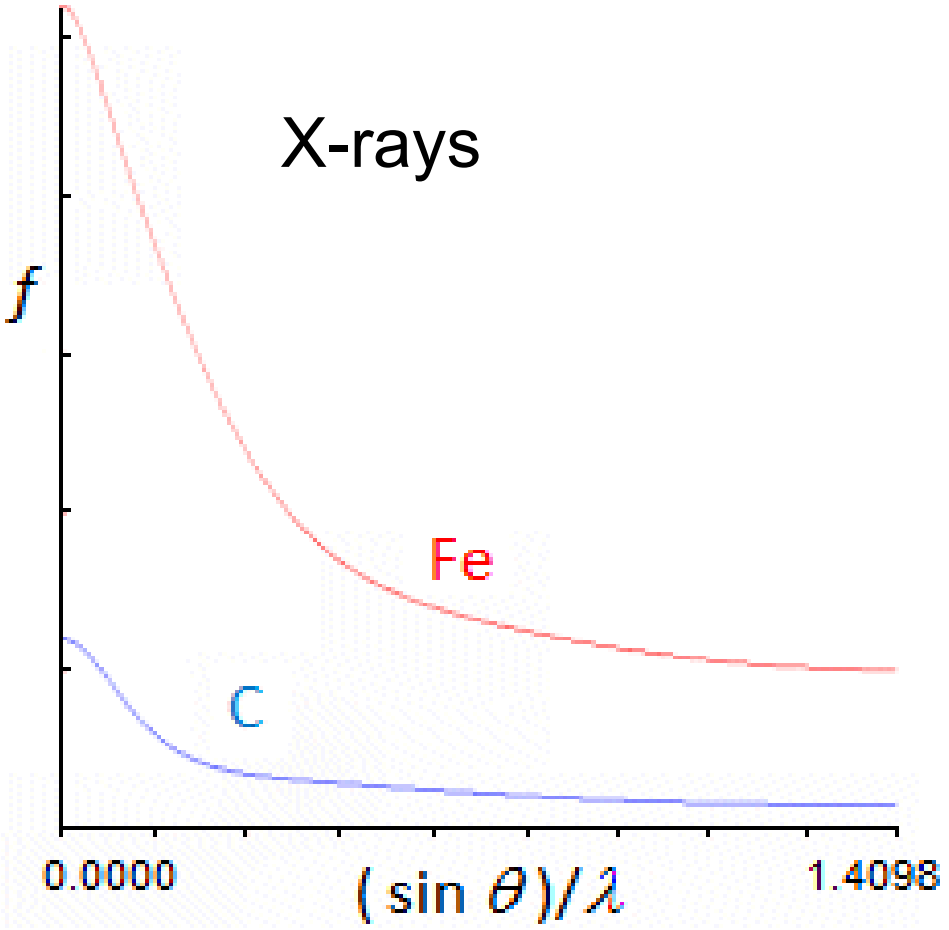
Neutron scattering occurs through nuclear interactions → no systematic atomic number dependence

Atomic Scattering factors / length



R.Winter, F. Noll: Methoden der biophysikalischen Chemie, Teubner (1998)

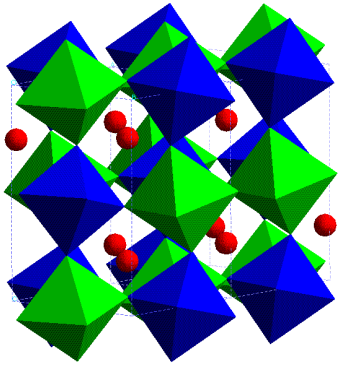
Why neutron powder diffraction (II) – no form factor

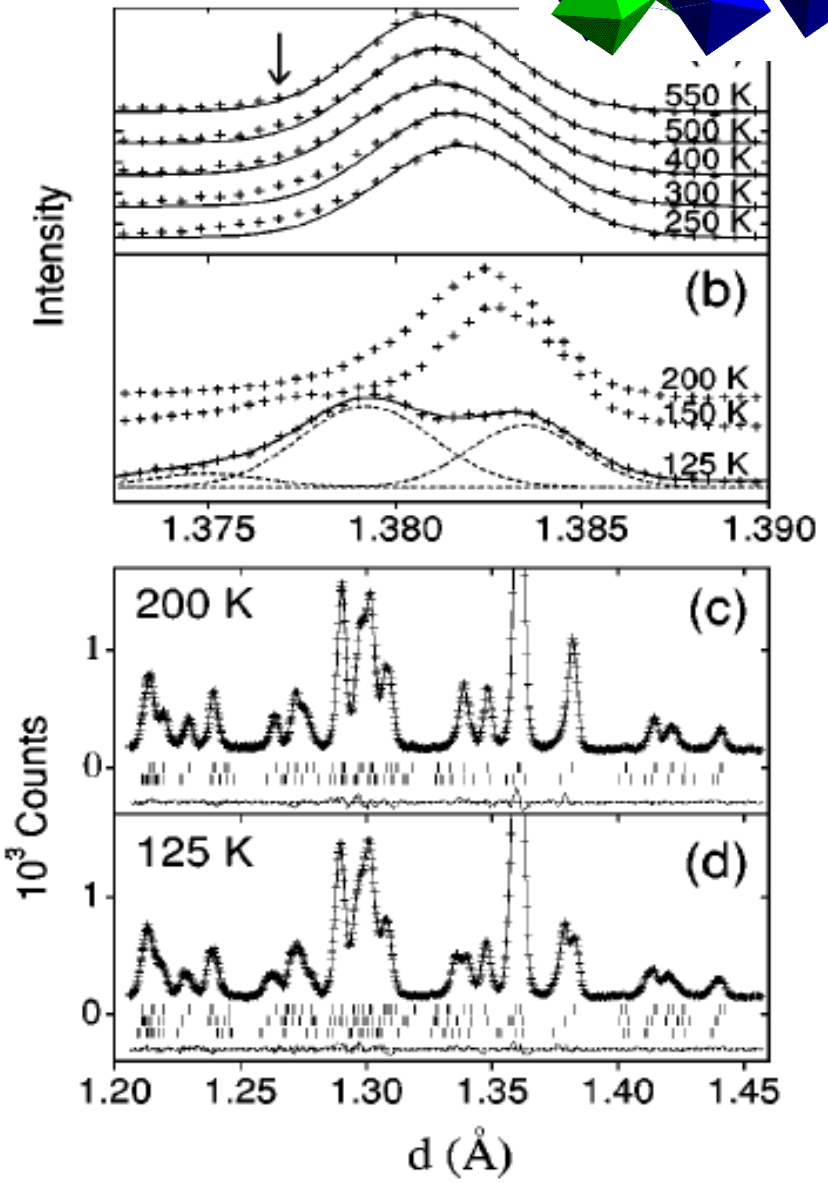


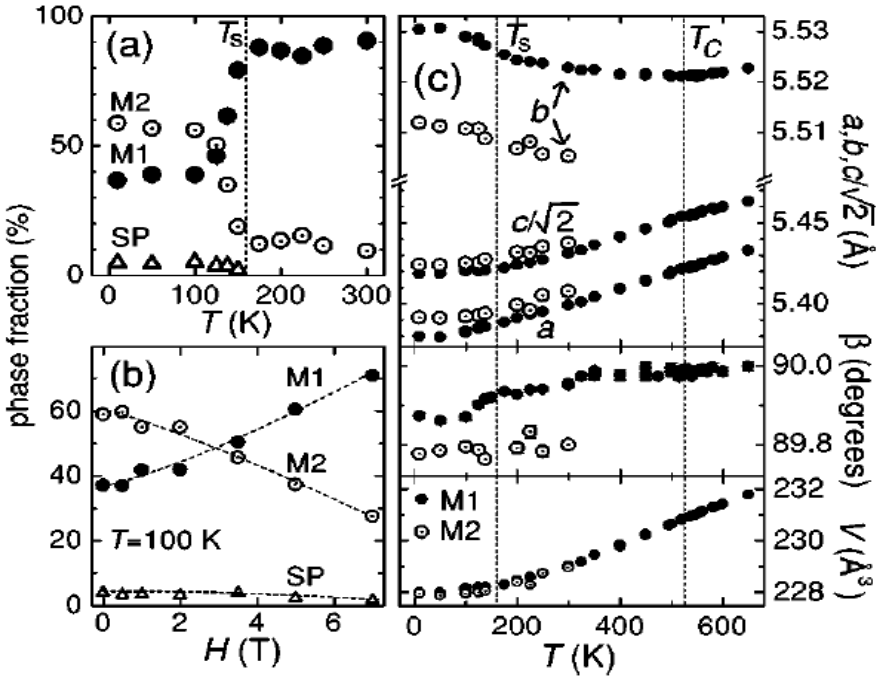
Other possible reasons for neutron powder diffraction

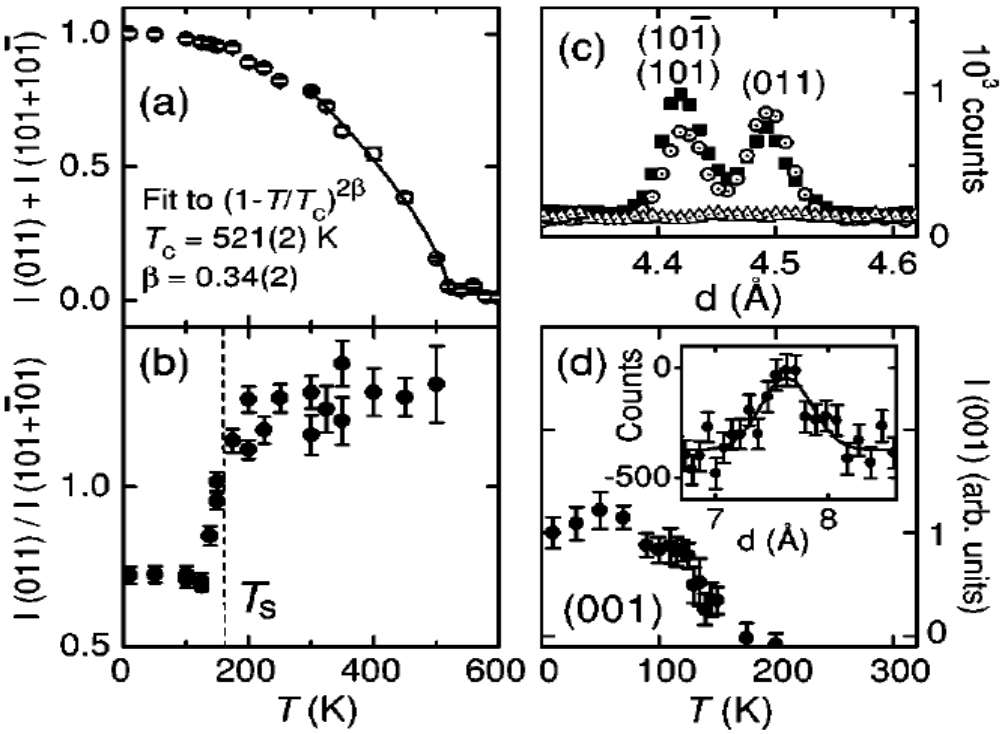
- Magnetic structure determination / refinement (see tomorrow talk)
- Large sample volume is probed
- Allows for good powder averaging (large number of grains in Bragg condition)
- Preferred orientation effects minimized

Ca_2FeReO_6

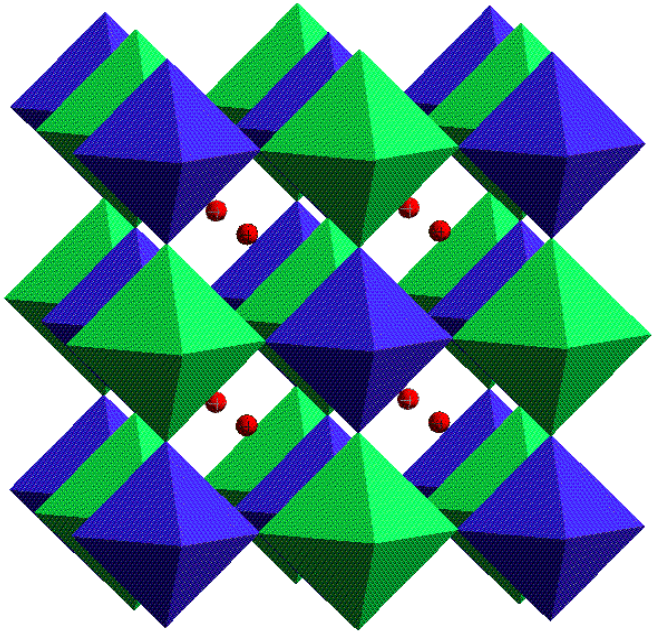




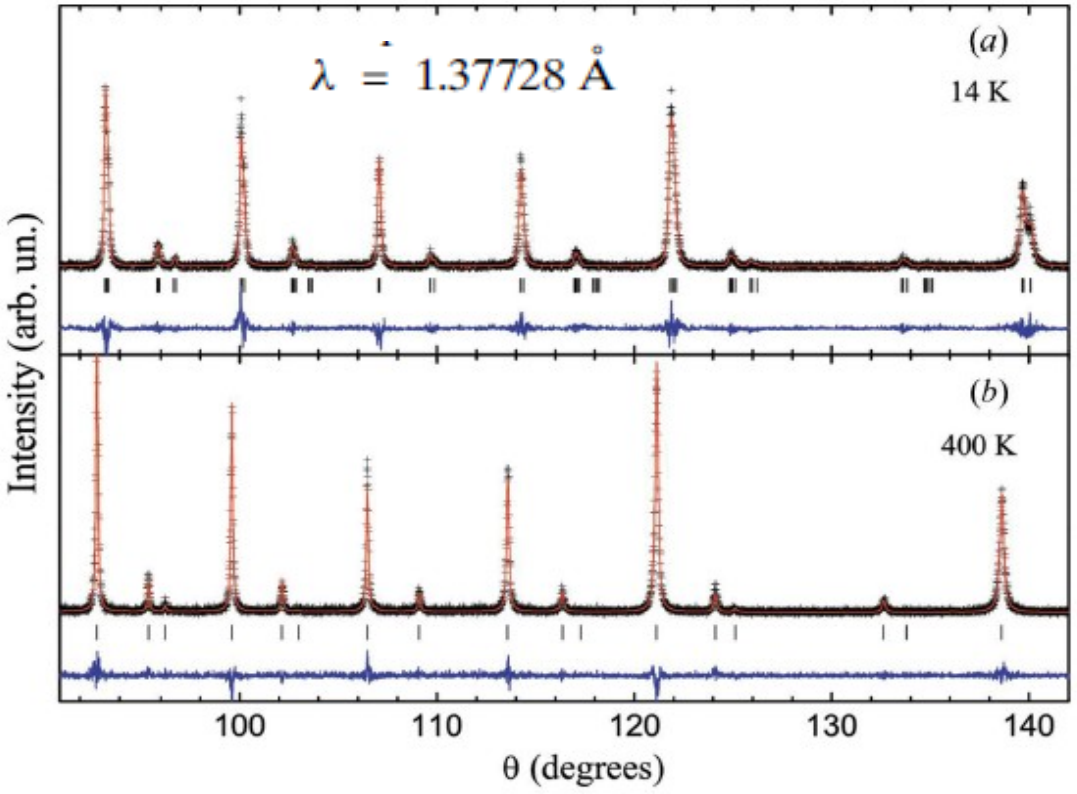




E. Granado *et al.*, PRB **66**, 064409 (2002)



Combining neutrons and synchrotron x-rays: Ba_2FeReO_6



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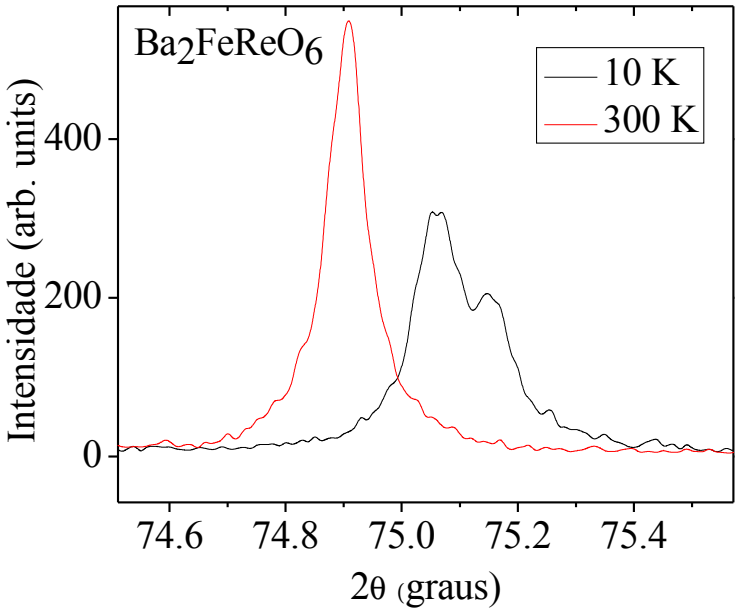
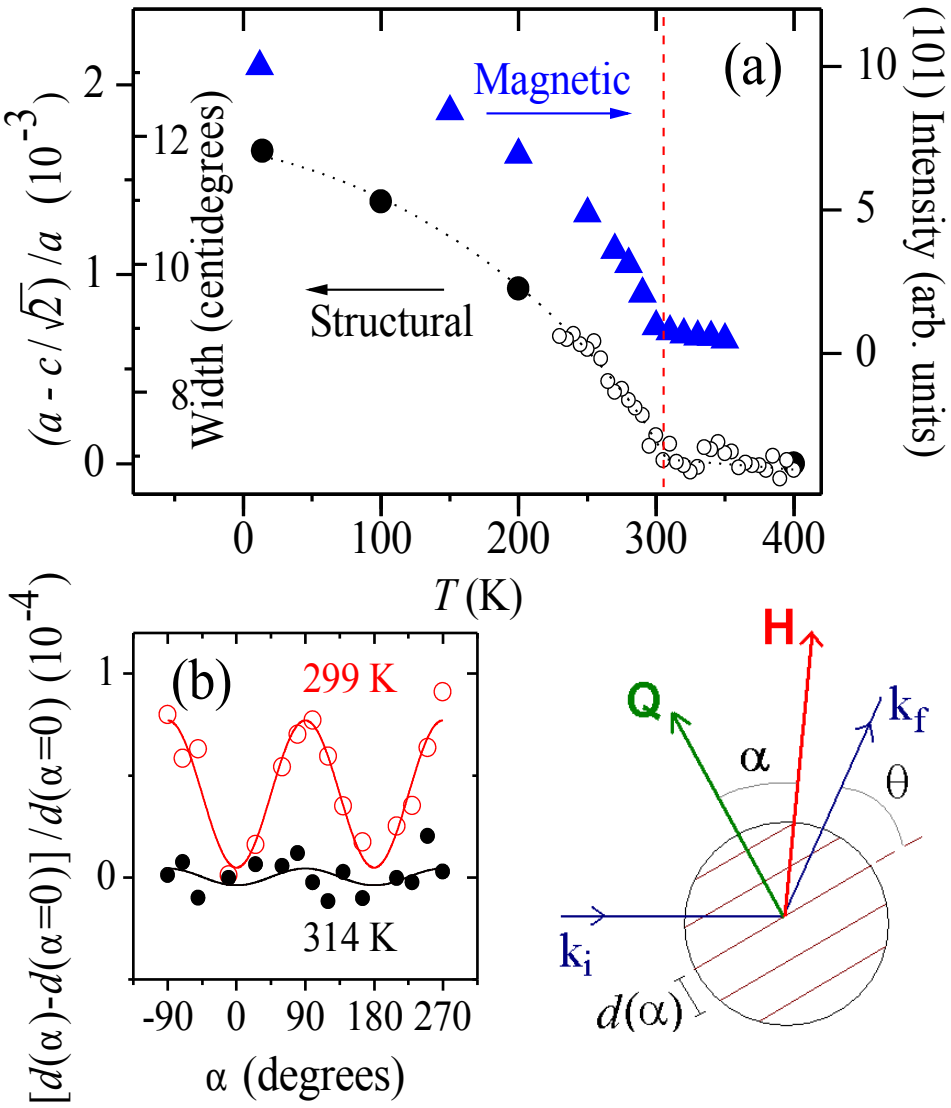
Temperature	14 K	400 K
Space group	*I*4/*mmm* (#139)	*Pm*$\bar{3}$*m* (#225)
a (Å)	5.68278 (2)	8.063328 (13)
c (Å)	8.02337 (5)	–
Fe	2a (0, 0, 0)	4a (0, 0, 0)
Re	2b (0, 0, 1/2)	4b (1/2, 1/2, 1/2)
B_{iso} (Fe, Re) (Å^2)	0.66 (2)	0.79 (2)
Ba	4d (1/2, 0, 1/4)	8c (1/4, 1/4, 1/4)
B_{iso} (Ba) (Å^2)	0.26 (2)	0.57 (2)
O1	8h (*x*, *x*, 0)	24e (*x*, 0, 0)
x	0.2569 (13)	0.2608 (9)
O2	4e (0, 0, *z*)	–
z	0.255 (2)	–
B_{iso} (O1,O2) (Å^2)	0.1 (1)	0.7 (1)
d(Fe–O1) (Å)	2.065 (11)	2.103 (8)
d(Fe–O2) (Å)	2.044 (17)	–
d(Re–O1) (Å)	1.953 (11)	1.929 (8)
d(Re–O2) (Å)	1.968 (17)	–
R_{pb}	15.1%	13.0%
R_{wpb}	37.5%	28.8%
χ^2	1.89	1.68

Ba_2FeReO_6

The high-resolution of XPD beamline was essencial to pin down the lattice symmetry reduction associated with the Fe/Re spin ordering at 305 K, caused by a strong magnetoelastic coupling.



$\lambda = 1.37728$ Å



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Incipient Orbital Order in Half-Metallic Ba_2FeReO_6

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Largely unquenched Re $5d$ orbital magnetic moments in half-metallic Ba_2FeReO_6 drive a symmetry lowering transition from a cubic paramagnet to a compressed tetragonal ($c/a < 1$) ferrimagnet below $T_C \sim 305$ K, with a giant linear magnetoelastic constant and the spins lying spontaneously along the unique tetragonal axis. The large orbital magnetization and degree of structural deformation indicate proximity to a metal-insulator transition. These results point to an incipient orbitally ordered state in the metallic ferrimagnetic phase.

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Summary

- High-resolution x-ray Powder diffraction experiments in solids under a variety of conditions can be performed at the XPD and XDS beamlines of LNLS.

- Observation of very slight structural distortions ($\delta a/a \sim 10^{-3}$) can only be seen with synchrotron XPD.

- Reliable structure factor determination of a larger number of reflections is obtained under high-resolution setup → more reliable extraction of atomic and Debye-Waller parameters.

- High-resolution Neutron Powder Diffraction is the desired technique if:
  - (i) A magnetic structure/ordered moments is being probed
  - (ii) Position of light atoms (e.g., hydrogen) is important
  - (iii) Preferred orientation / powder averaging is an issue in synchrotron x-ray experiments

Thank you !