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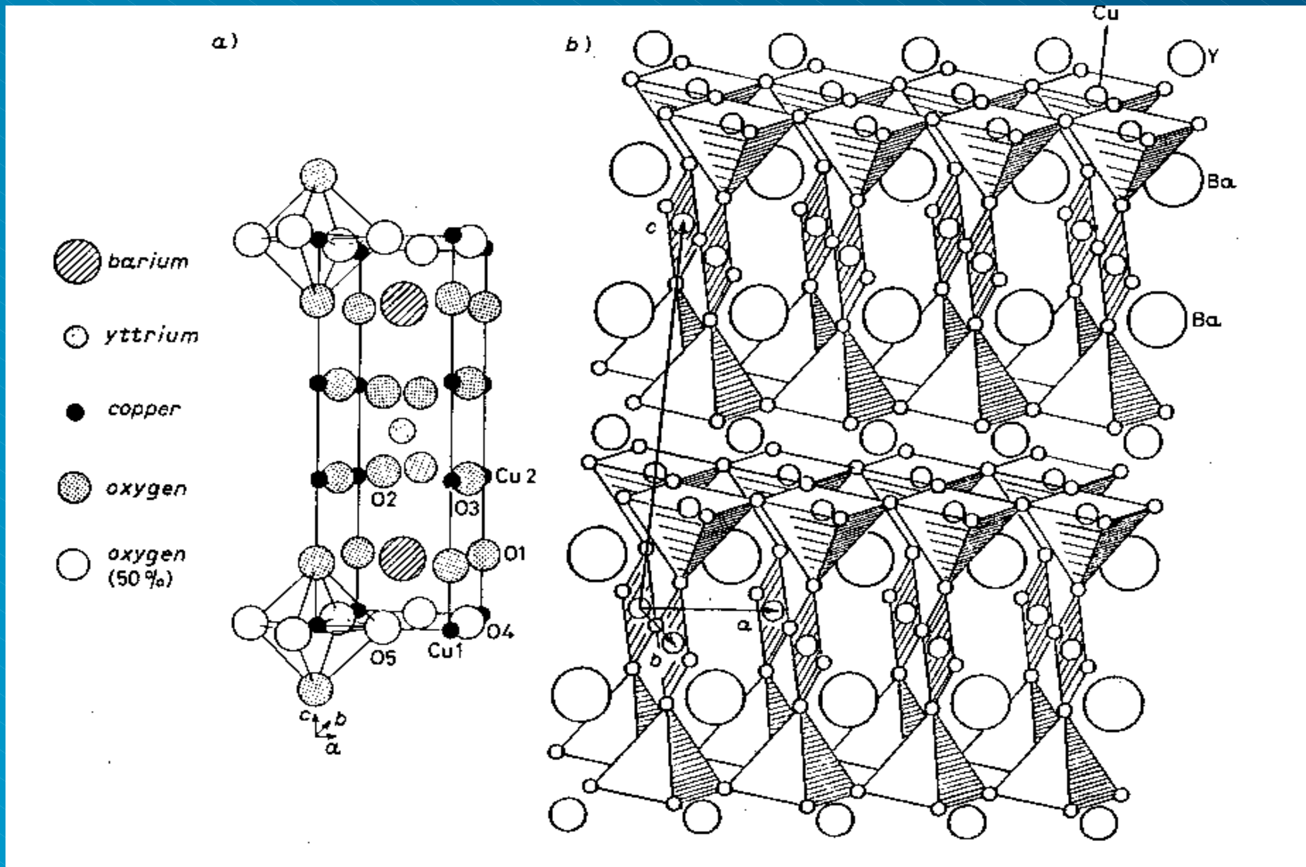
Neutron Powder Diffraction and Novel Materials

8th Zuoz Summer School on Neutron Scattering, 5-11 August 2000

Why Use Neutron Powder Diffraction ?



$YBa_2Cu_3O_7$ drawing from Capponi et al. Europhys Lett **3** 1301 (1987)

- **Structure of the 90K high Tc superconductor**
  - **Left - by X-rays (Bell labs & others)**
  - **Right - by Neutrons (many neutron labs)**
- **The neutron picture gave a very different idea of the structure - important in the search for similar materials.**

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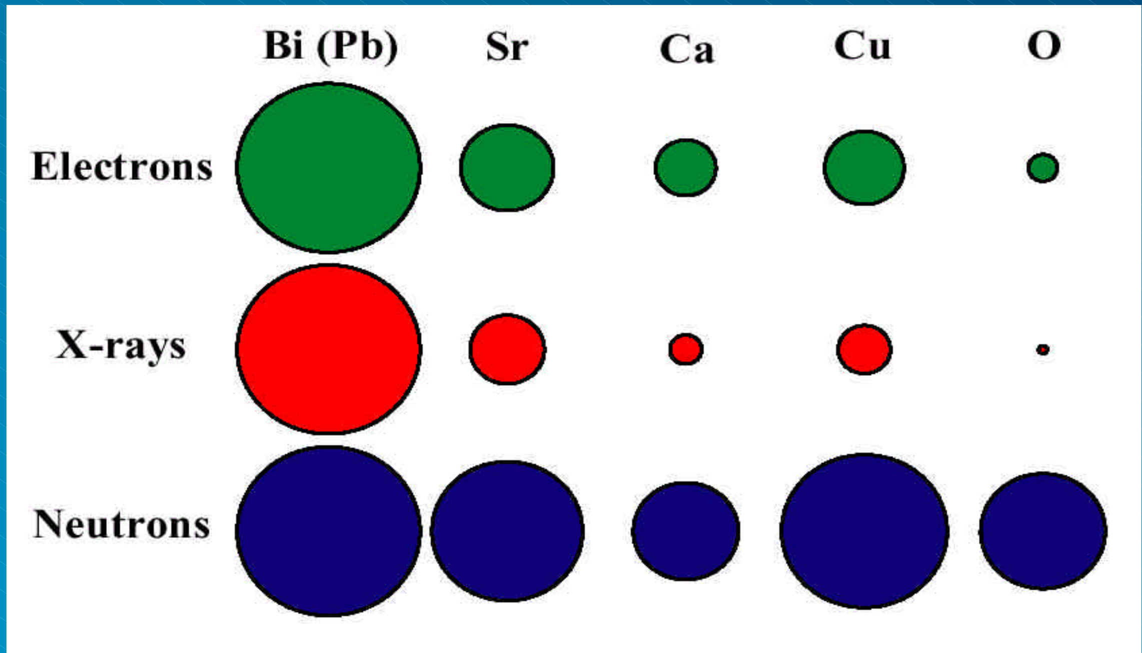
Why Neutrons ?

- **Relative Scattering Powers of the Elements**



- **Neutrons scatter strongly from light elements**

(Because neutron scattering is a nuclear interaction)

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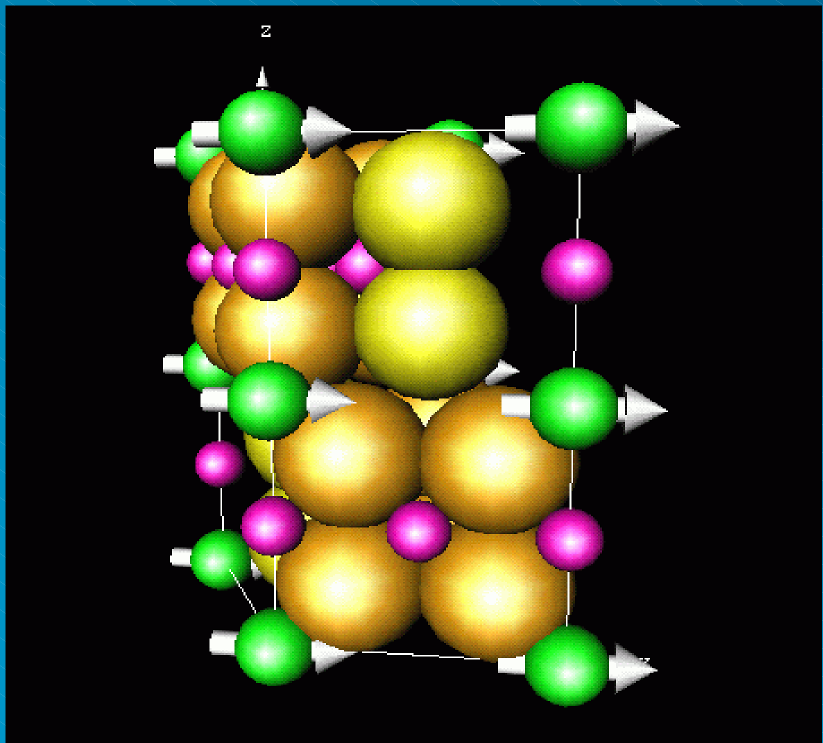
Why Neutrons ?

- **Neutrons are unique for Magnetic Structures**



- **H.M. Rietveld**

Structure of Magnetic Materials

$MnTa_4S_8$ - the famous example given in the original Rietveld manual

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Why Powders ?

- …Well, if you don't have a single crystal…
- For many new, interesting materials, single crystals are not available
    - Zeolites, Superconductors, GMR materials...
- And many other materials are not really single crystals
    - At least not at 0 K, the most important temperature

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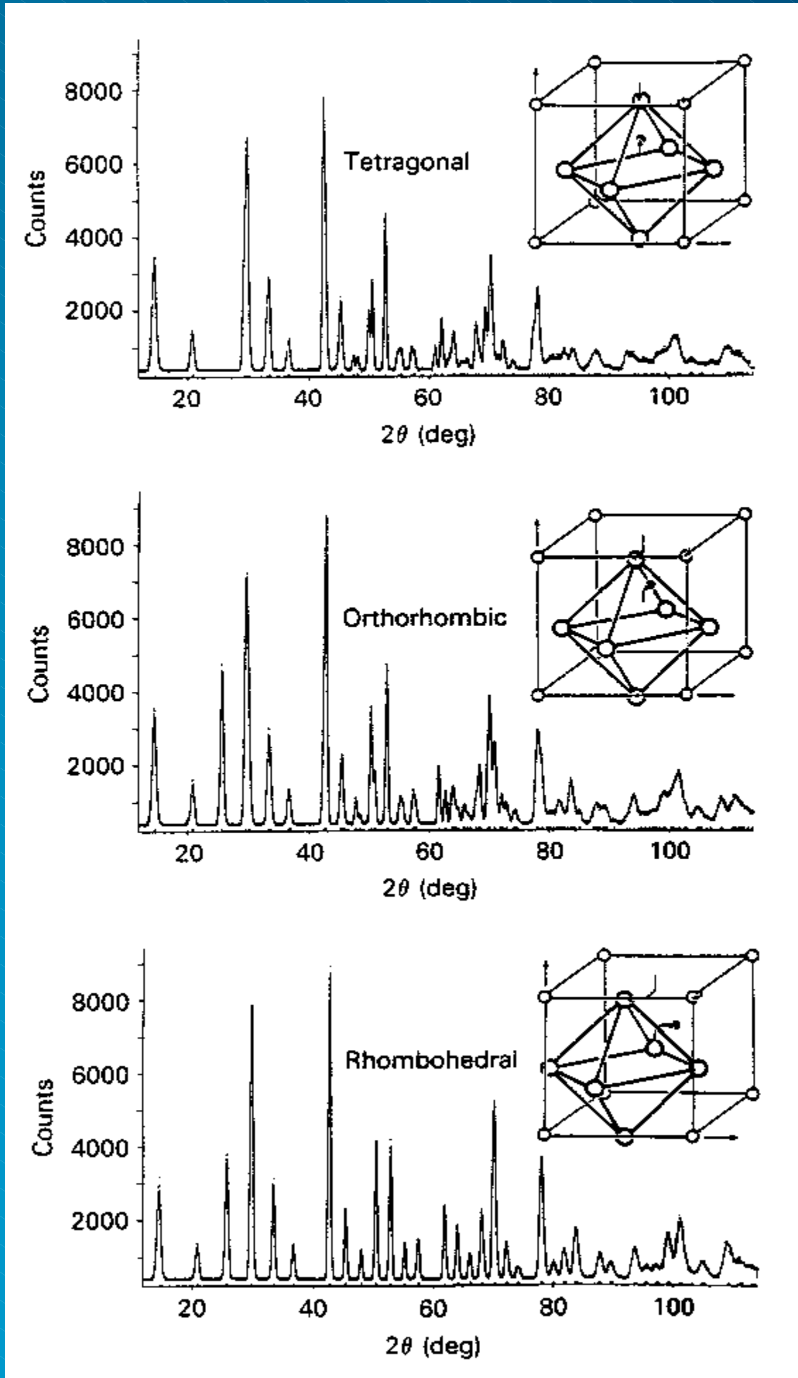
Why Powders ?



- Destructive Phase T/Ns
  - Classical Perovskite transitions
    Small displacements of light atoms
  - Subtle changes in the powder ‘profile’
    - interest of “Profile Refinement”
- And <u>no single crystals</u>

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Why Rietveld Refinement ?

- Strongly overlapping reflections
  - Previously, integrated intensities were obtained for groups of overlapping reflections.

- Key to success of RR
  - inclusion of all the information
  - refinement of physically meaningful parameters (reduction of correlation between parameters)

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Why not X-ray Powder Diffraction ?

(Question from Bruno Dorner)

- Magnetic structures... not possible with x-ray powders
- X-rays best (synchrotrons) for **SOLVING** structures
  - Easier to find the heavy atoms first
  - All atoms are 'equal' for neutrons
- Neutrons are best for **REFINING** structures
  - Few systematic errors (average over big samples etc...)
  - Easier sample environment (low temperatures etc...)
- Interest of very precise structure measurements
  - Precise bond lengths
  - Study charge ordering, metal-insulator transitions...

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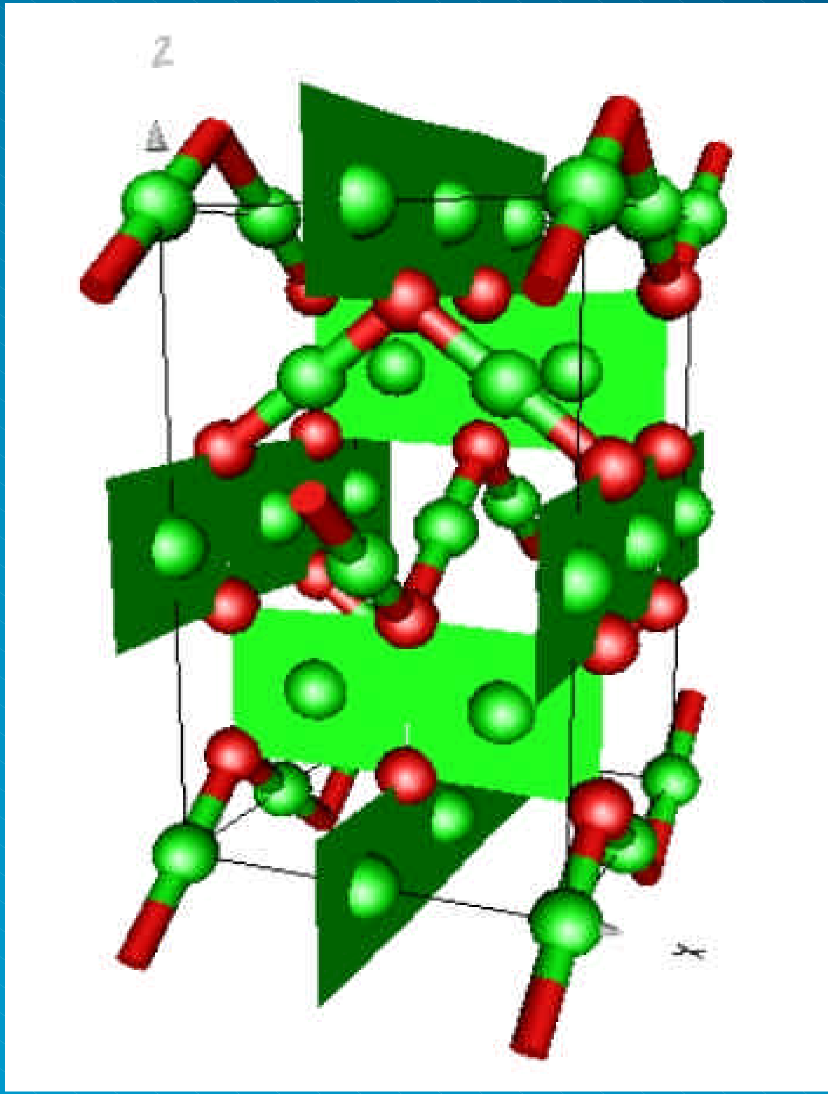
Valence Sum Calculations

What is the valence of Cu in Cu_4O_3 ? (Exercise)

O'Keeffe, M. Bovin, J. Am. Miner **63** 180 (1978)



- Average Cu valence = 2*3/4 = 1.5
  - Just from the formula Cu_4O_3
- 2 types of Cu
  - Cu^+ at (0,0,0) with 2 oxygens
  - Cu^{++} at $(0,0,{}^1/_2)$ with 4 oxygens
- Valence Sum $V=\Sigma_i[\exp(Ro-Ri)/B]$
  - Ri = Cu-Oi bond lengths
  - Ro= 1.610 for Cu^+ to O^{2-}
  - B = 0.370
- Calculate Ri bond lengths & hence V

  Hints:
  - All bonds approx equal
  - Each bond contributes ~ 0.5

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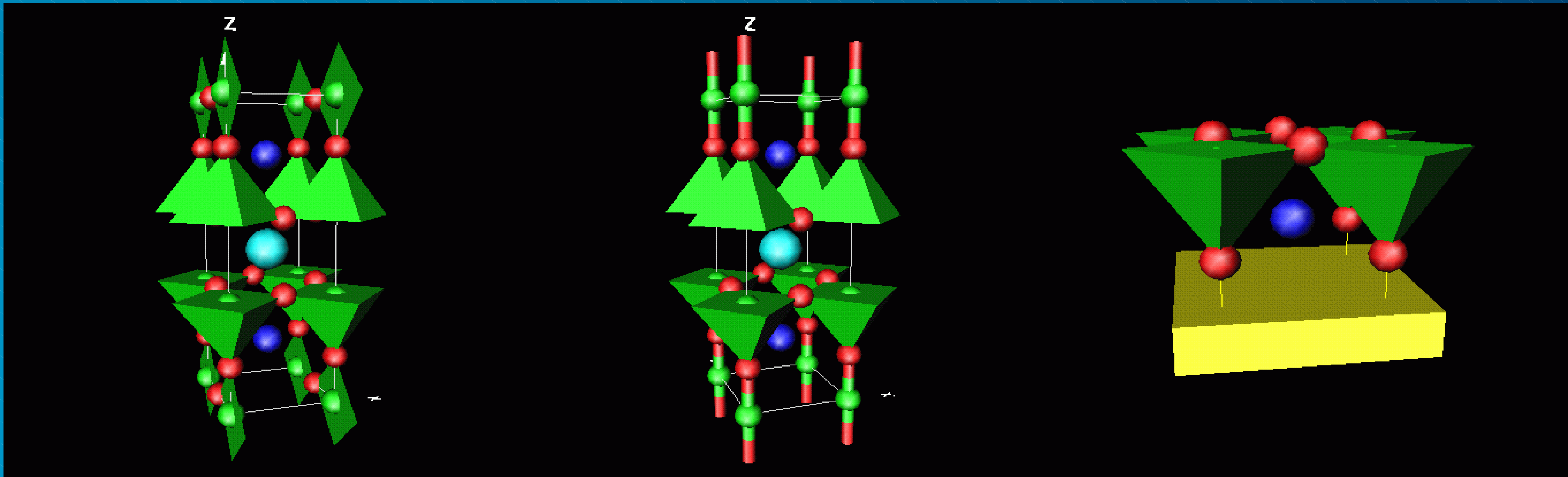
Valence Sums & "Charge Transfer"

Most cited neutron papers - "charge reservoir" concept in oxide superconductors

- **Superc. $YBa_2Cu_3O_7$**
- **Non-superc. $YBa_2Cu_3O_6$**
- **Charge Reservoir**



- Cava, R. J. et al. (1990). Physica C. **165:** 419 (Bell labs/CNRS/ILL)
- Jorgensen, .D. et al. (1990) Phys. Rev. B41, 1863 (Argonne)

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Valence Sums & "Charge Transfer"

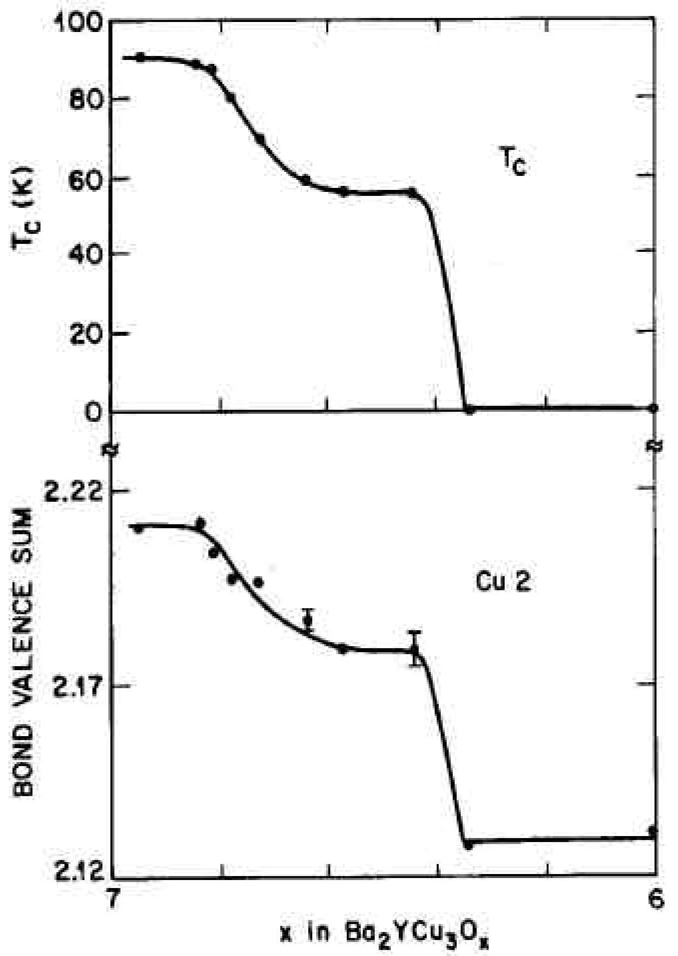

Fig. 16. Comparison of T_c and bond valence sum around the plane copper as a function of oxygen stoichiometry.

- Relation between bond lengths, charge transfer and superconducting Tc
- The "Charge Reservoir" concept encouraged many chemists to successfully search for similar materials with different charge reservoir layers

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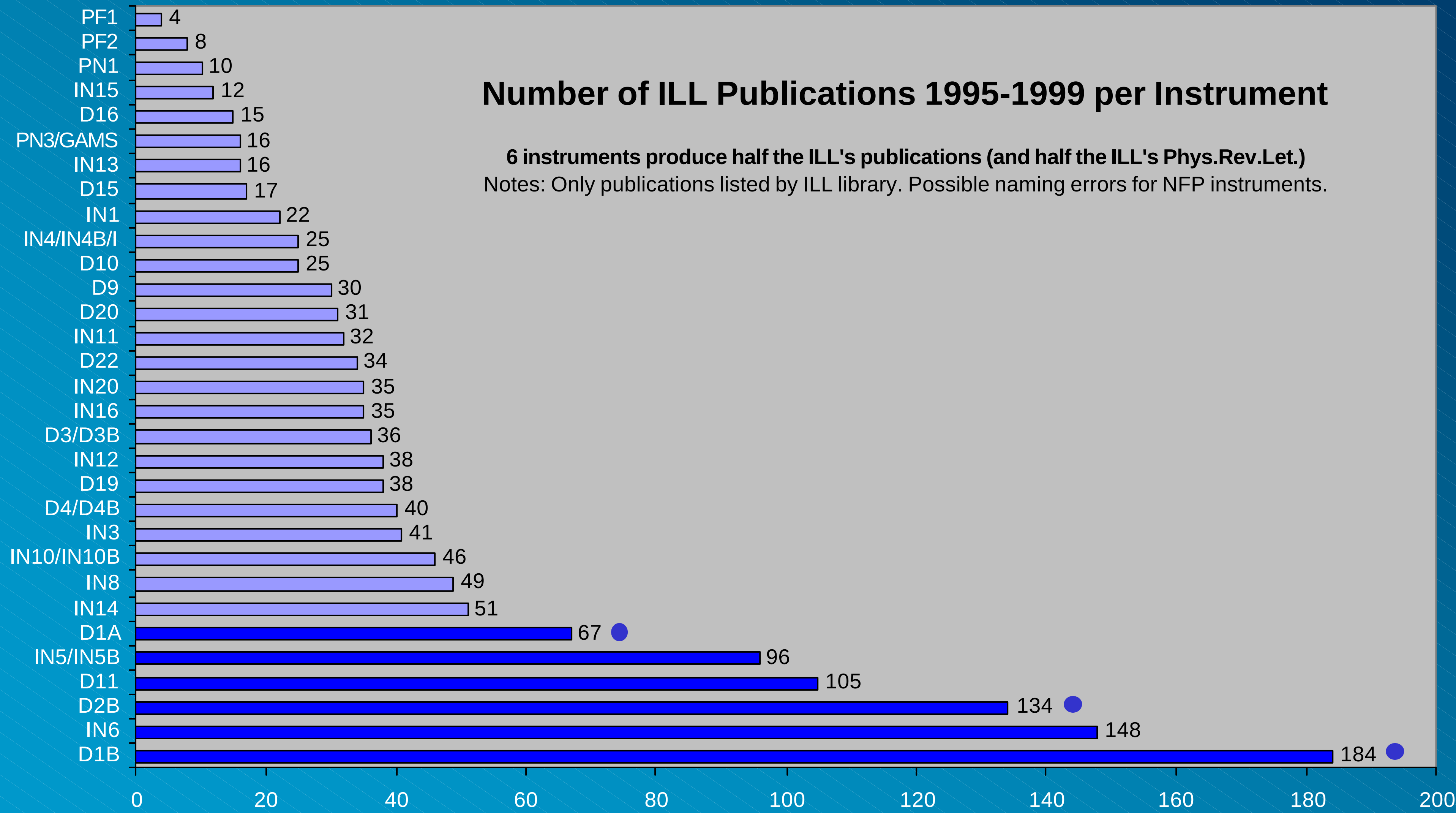
Popularity of Neutron Powder Diffraction



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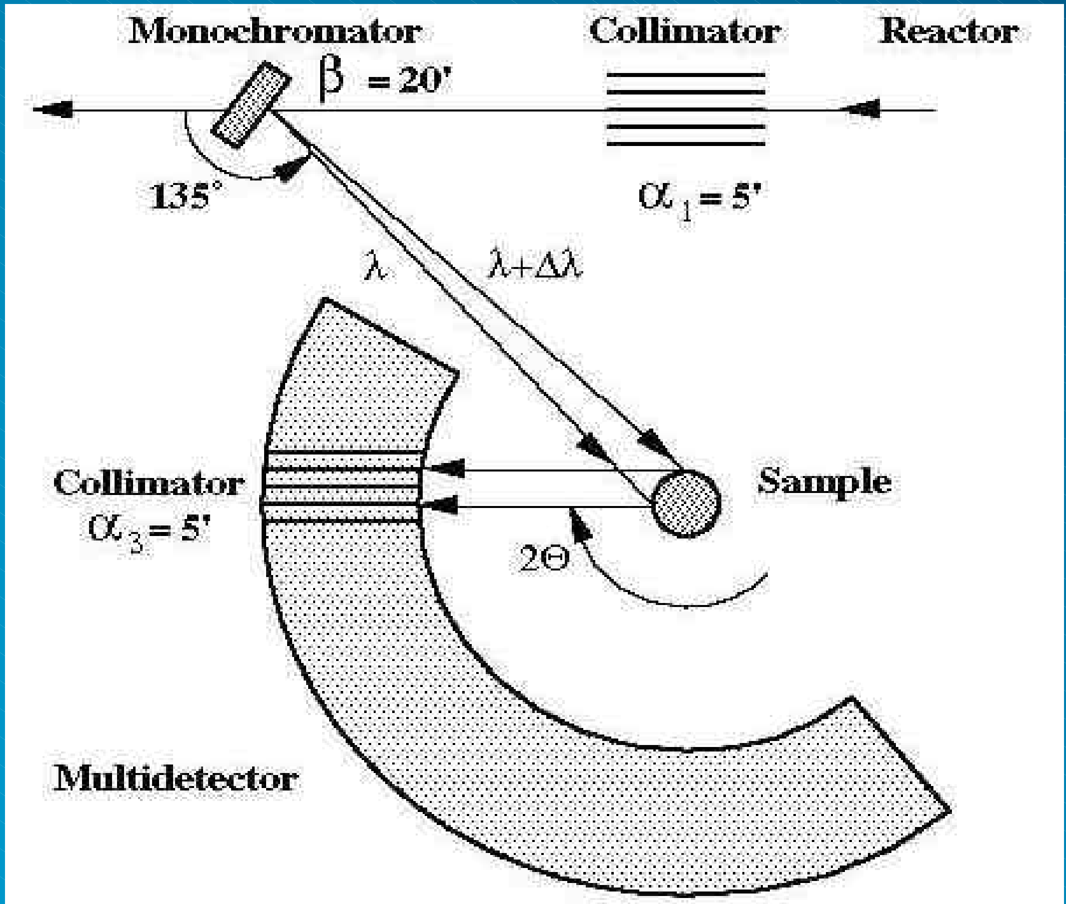
Powder Diffractometers are Simple



- A continuous neutron source
- Incident collimation
- A Monochromator
- The Sample & environment
- Scattering collimation
- A Detector

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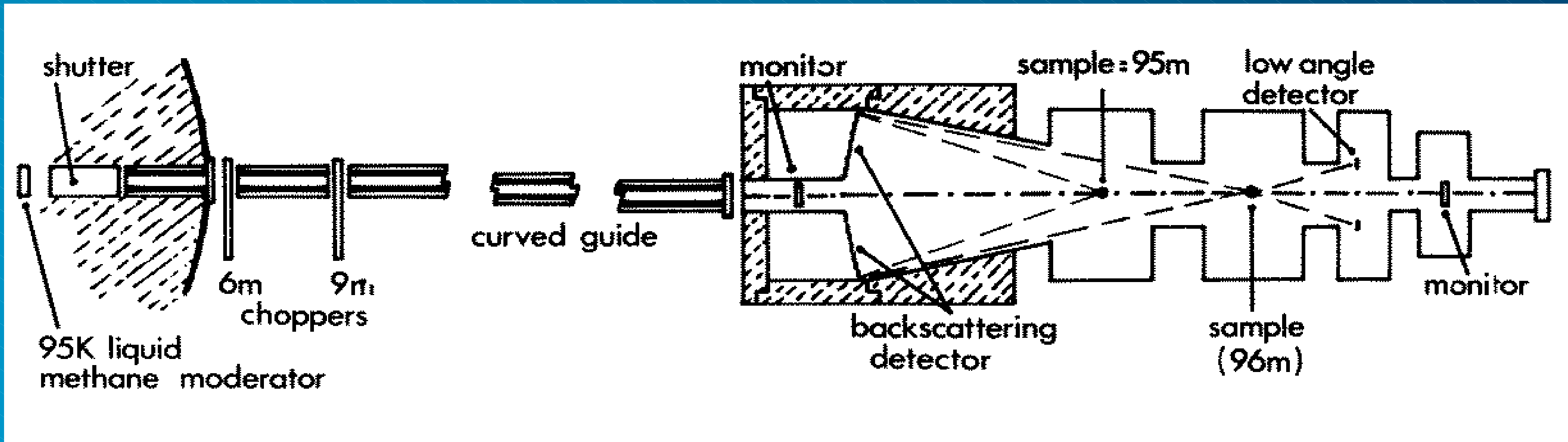
Alternative TOF techniques

- Time-of-flight diffractometers (E.Steichele, Munich)
  - J. Jorgensen, Argonne (SEPD, GPPD)
  - B. Fender & A. Hewat, Rutherford Lab.



- HRPD ISIS (High Resolution Powder Diffractometer)
  W. David et al.

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Early Days at ILL Grenoble (1972)

- First ILL Powder Diffractometers D1A,D2
  - Single detector
  - Small soller collimator
  - Shared monochromator
- -High Resolution, BUT
  -Very Low Intensity

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Early Days at ILL Grenoble (1974)

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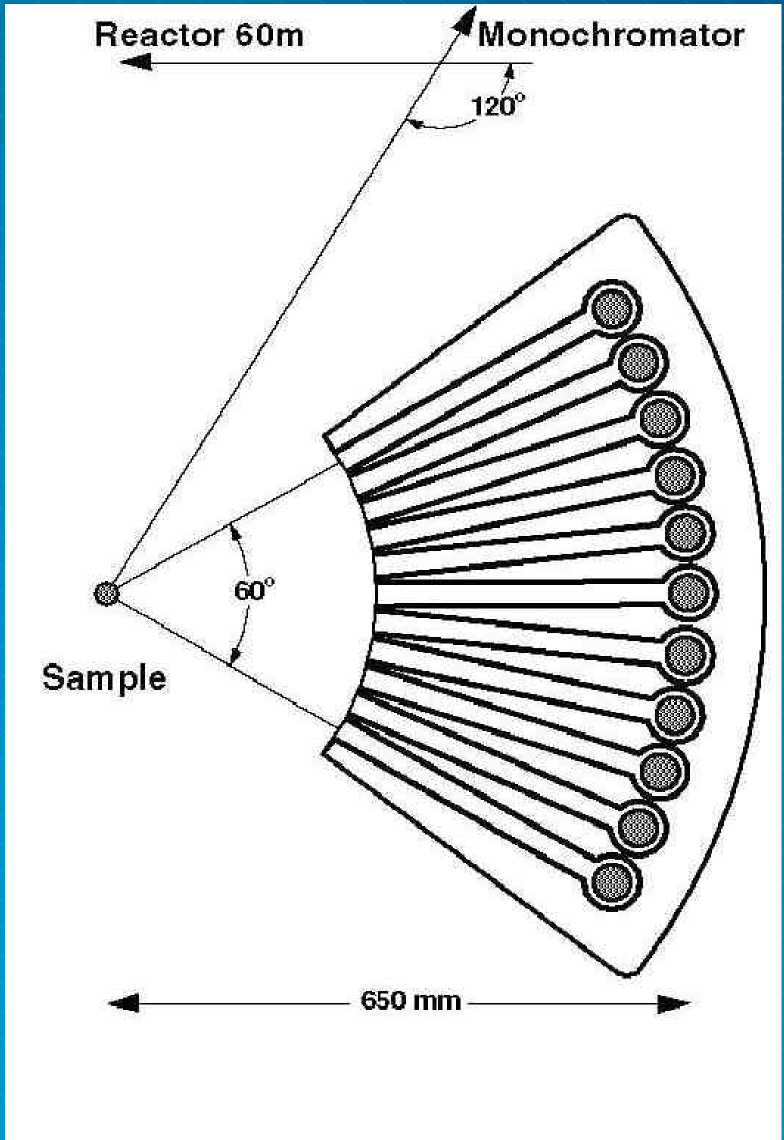

- Orders of Magnitude Improvement - D1A
  - Multiple detectors
  - Large efficient collimators
  - Focussing Monochromator

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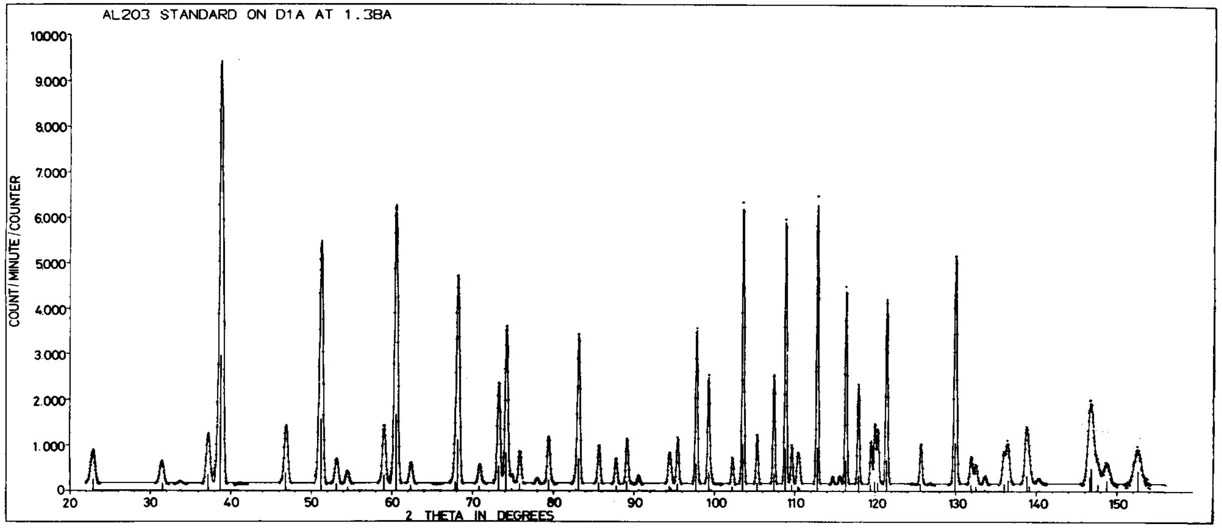
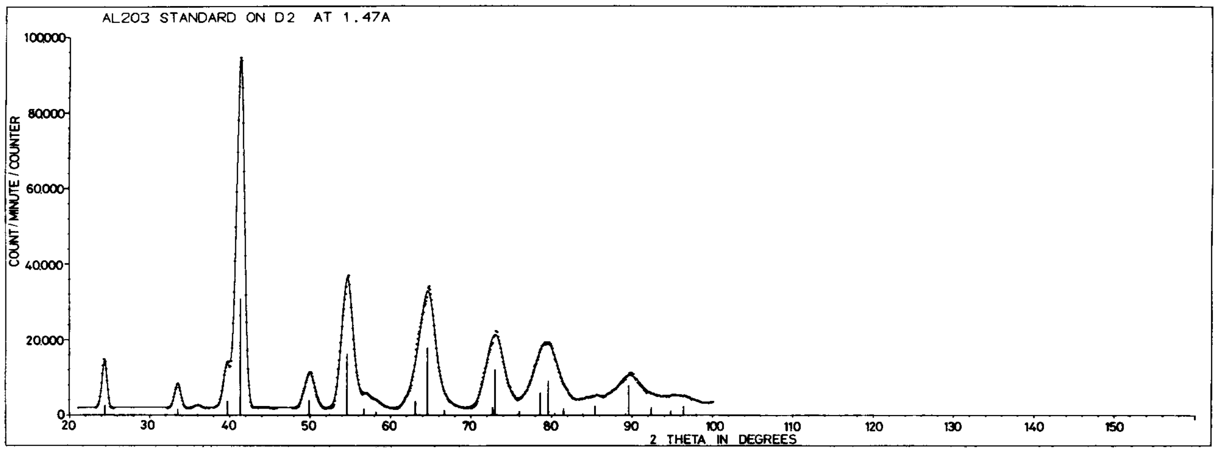
Comparison of D1A with D2 (1974)



(a)



(b)

- The same Al2O3 sample on D1A (top) and the old D2 at ILL.

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Early Days at ILL Grenoble (1973)

- New types of PSD's
  - Position Sensitive Detector used for the first time
  - Very Fast machine (Faster than X-rays)
  - Moderate Resolution
- In-situ Chemistry with RR (Convert, Riekel …)

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The Second Generation (80's)

- High Resolution with Very Large Detector banks (D2B, ILL)

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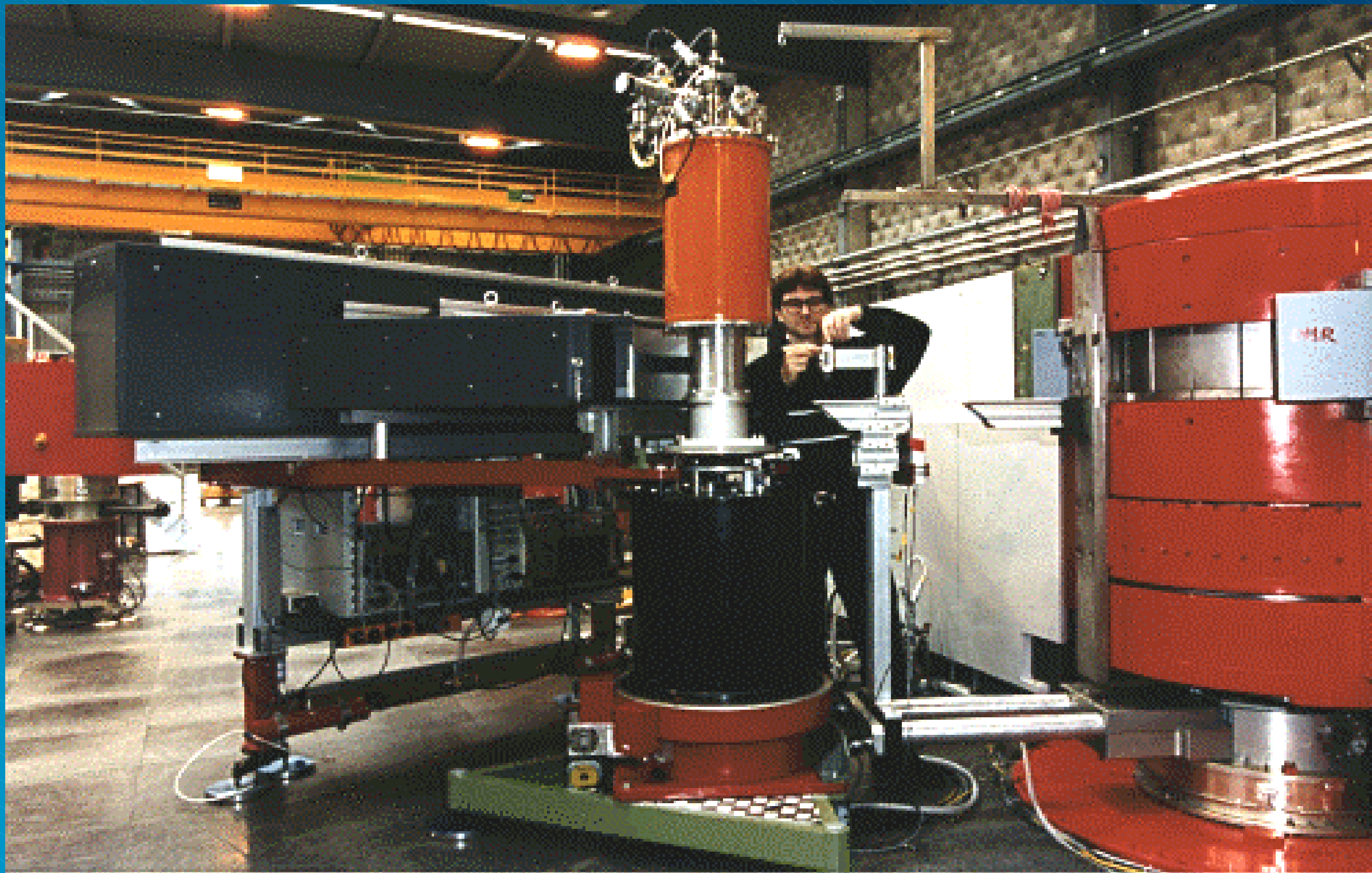
The Second Generation (80’s)



- DMC high efficiency PSD powder diffractometer PSI (Zurich)
  P. Fischer et al.

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An Inexpensive but Effective PSD

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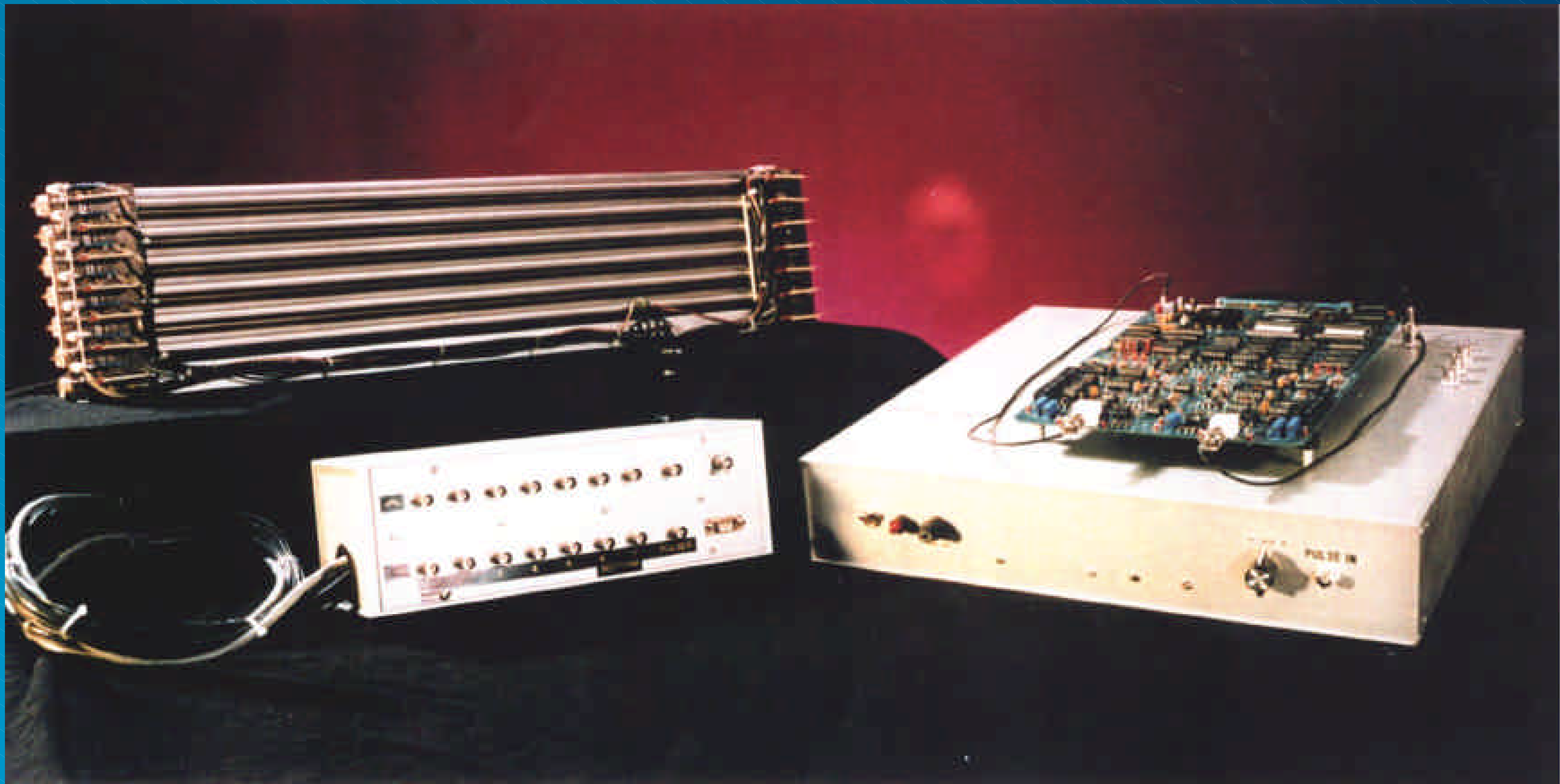

The liner wire PSD powder diffractometer at Kjeller, Norway.

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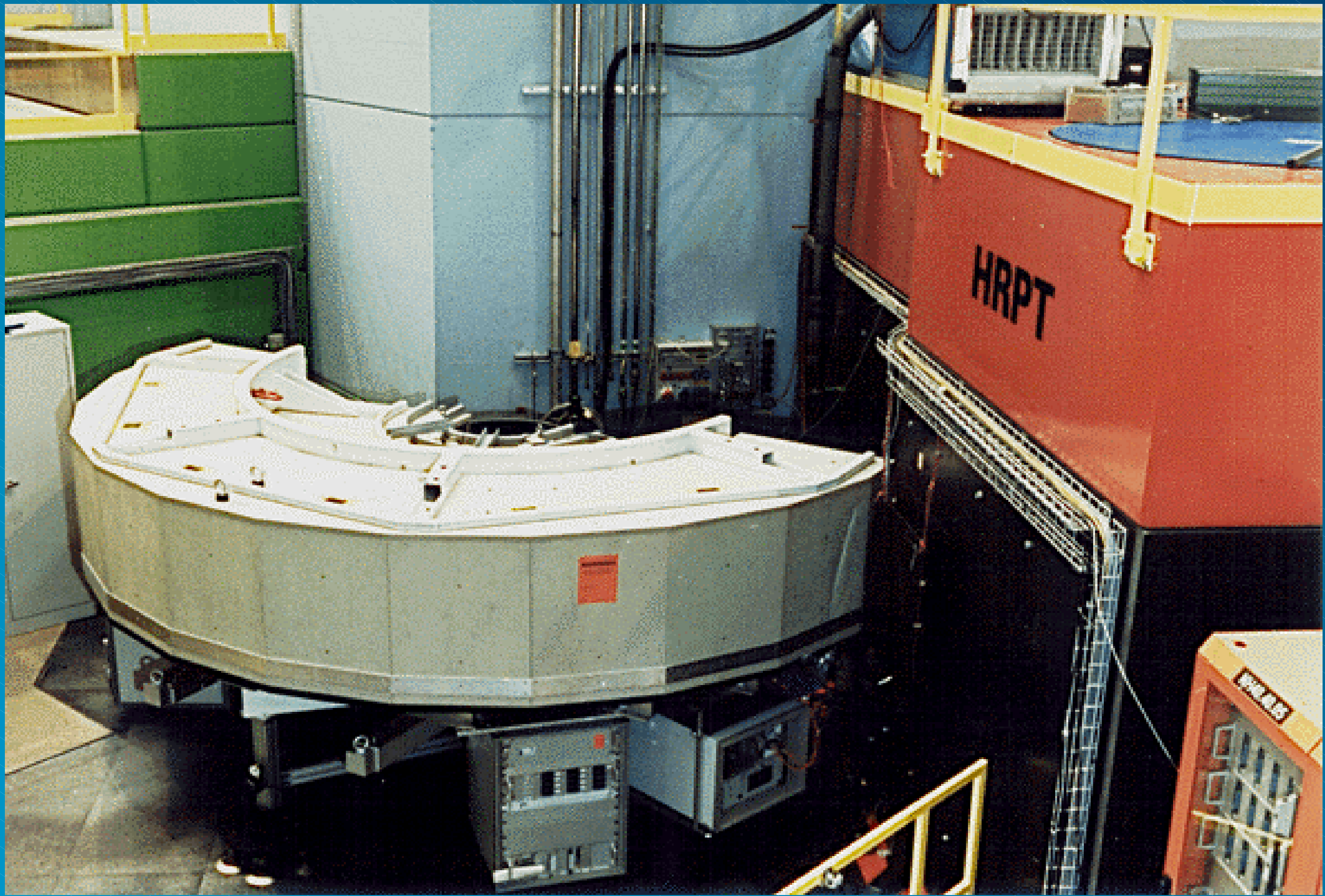
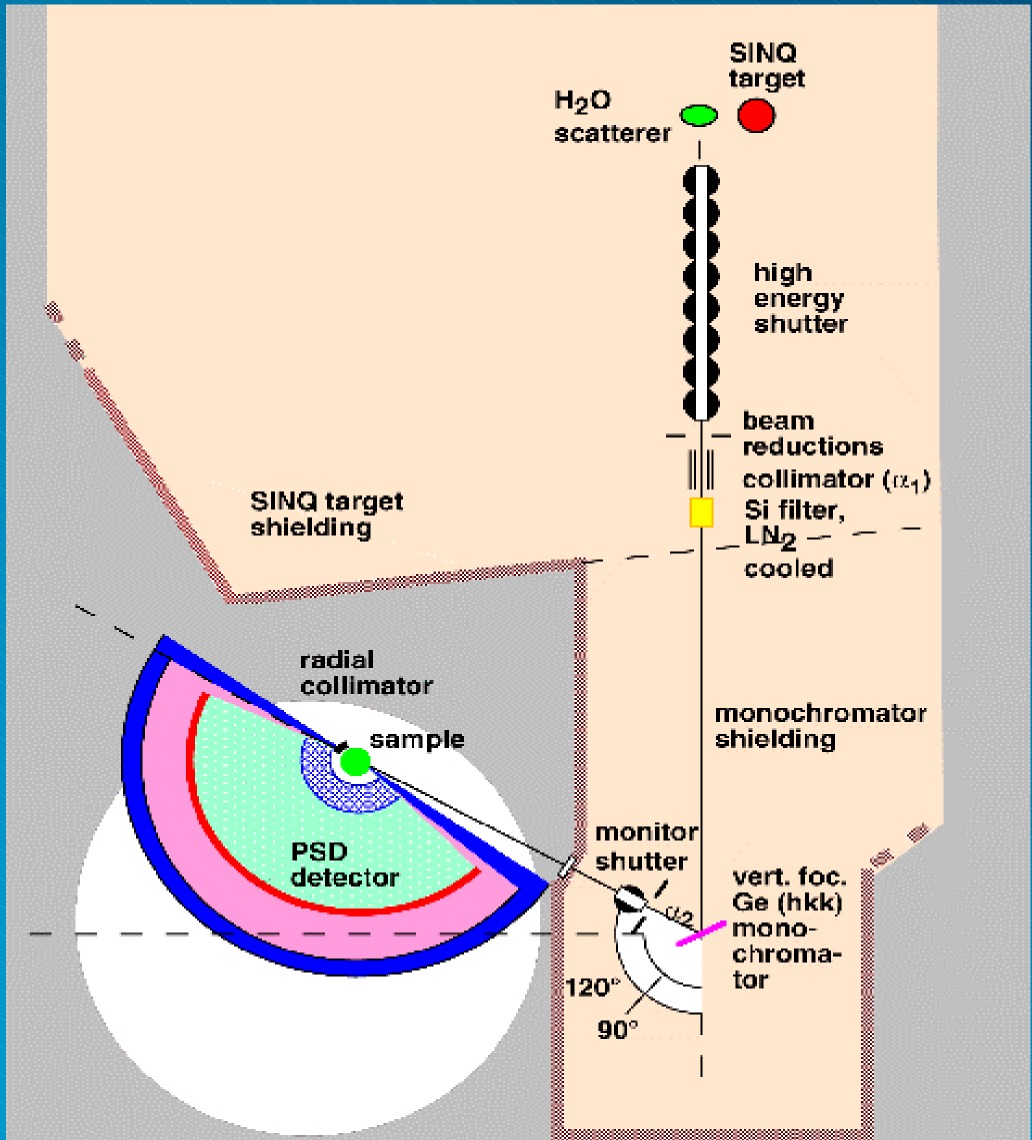
State of the Art Powder Machines



- HRPT 1600 cell PSD powder diffractometer at PSI (Zurich)
  P. Fischer et al.

State of the Art Powder Machines



- HRPT 1600 cell PSD powder diffractometer at PSI (Zurich)
  P. Fischer et al.

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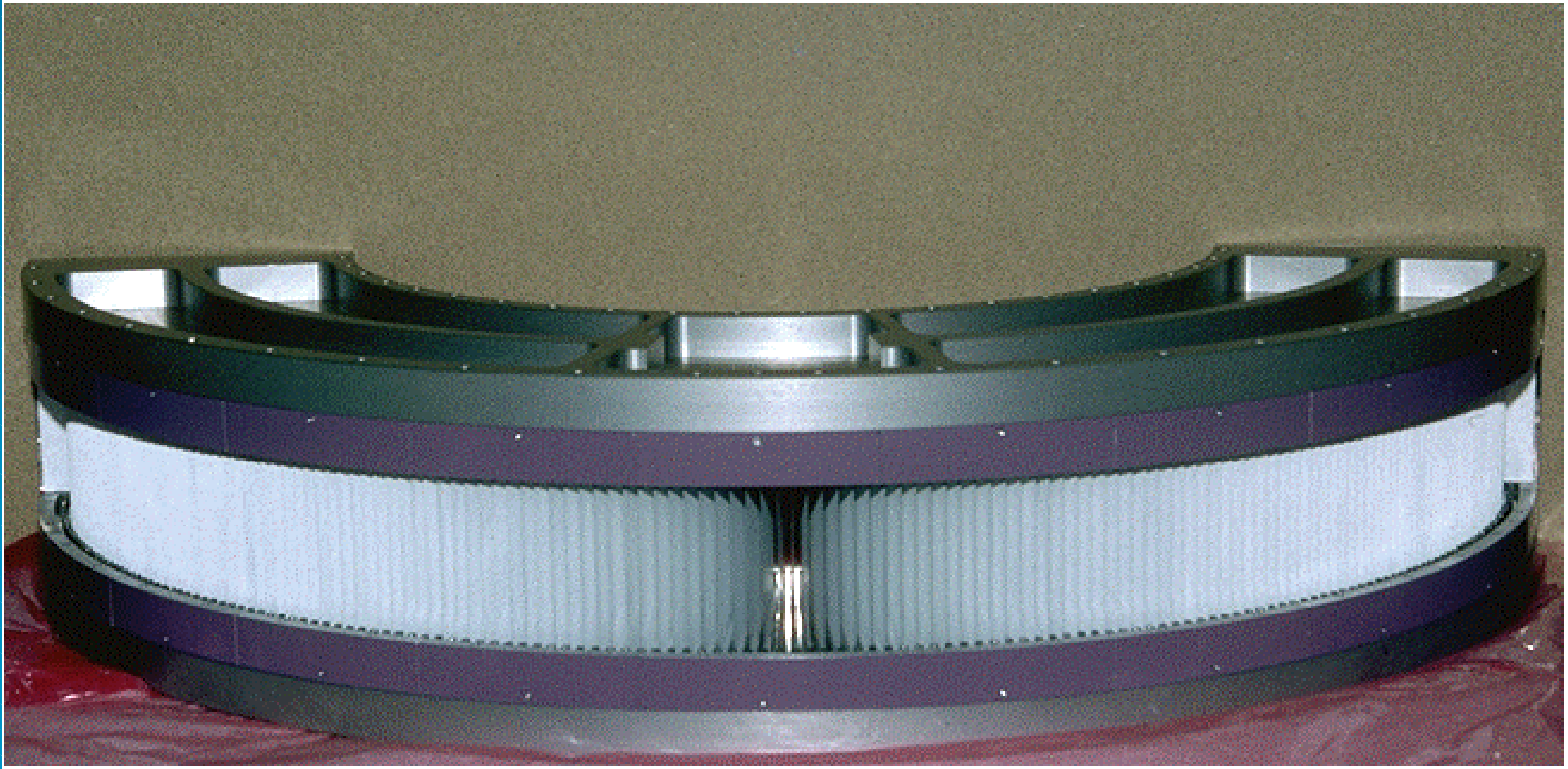
State of the Art Powder Machines

1600 wire PSD on a continuous spallation neutron source



- Radial Collimator for new HRPT diffractometer at PSI Zurich (Fast, medium-high resolution machine) Peter Fischer et al.

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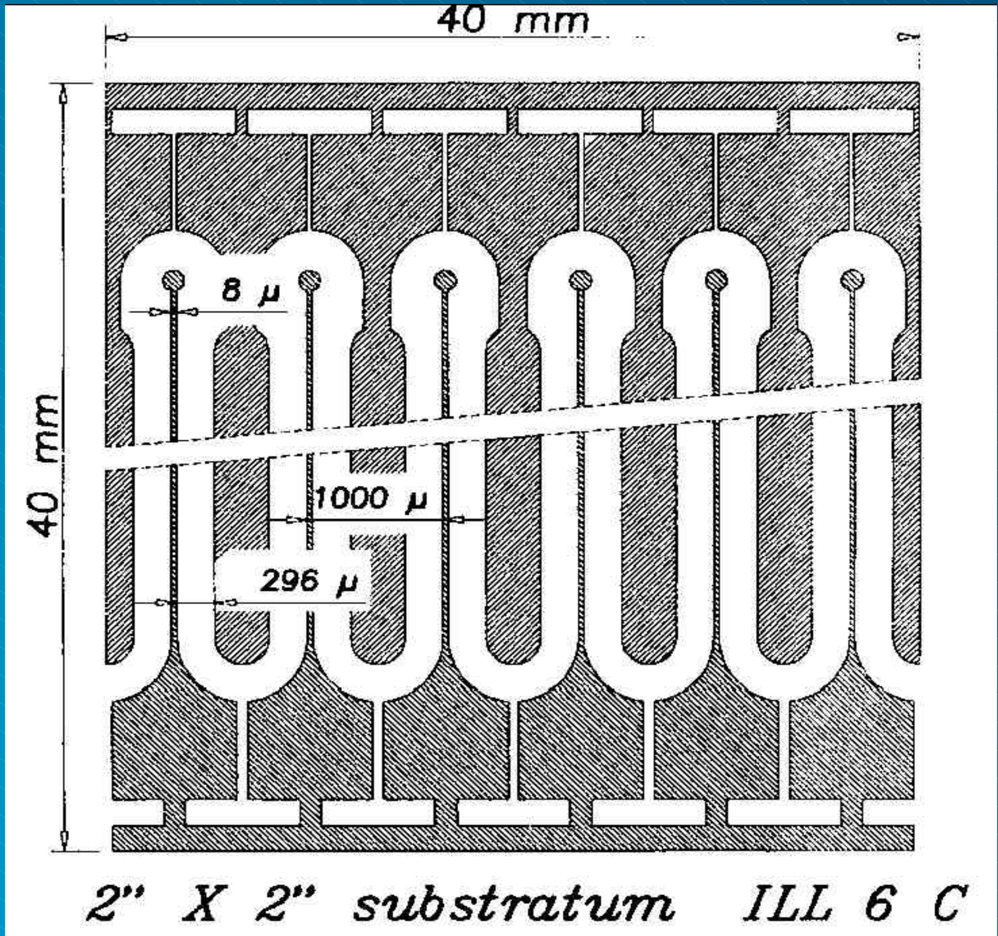
Microstrip Detectors



- The wires are replaced by a printed circuit on a glass substrate
- A high electric field is produced around the thin anodes.
- The glass substrate is electrically conducting to remove charge build-up

- PSD for 1600 element microstrip detector D20 at ILL Grenoble (Fast medium-high resolution machine) Pierre Convert et al.

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What is a Microstrip Detector ?

The printed circuit allows high resolution, mechanical stability…

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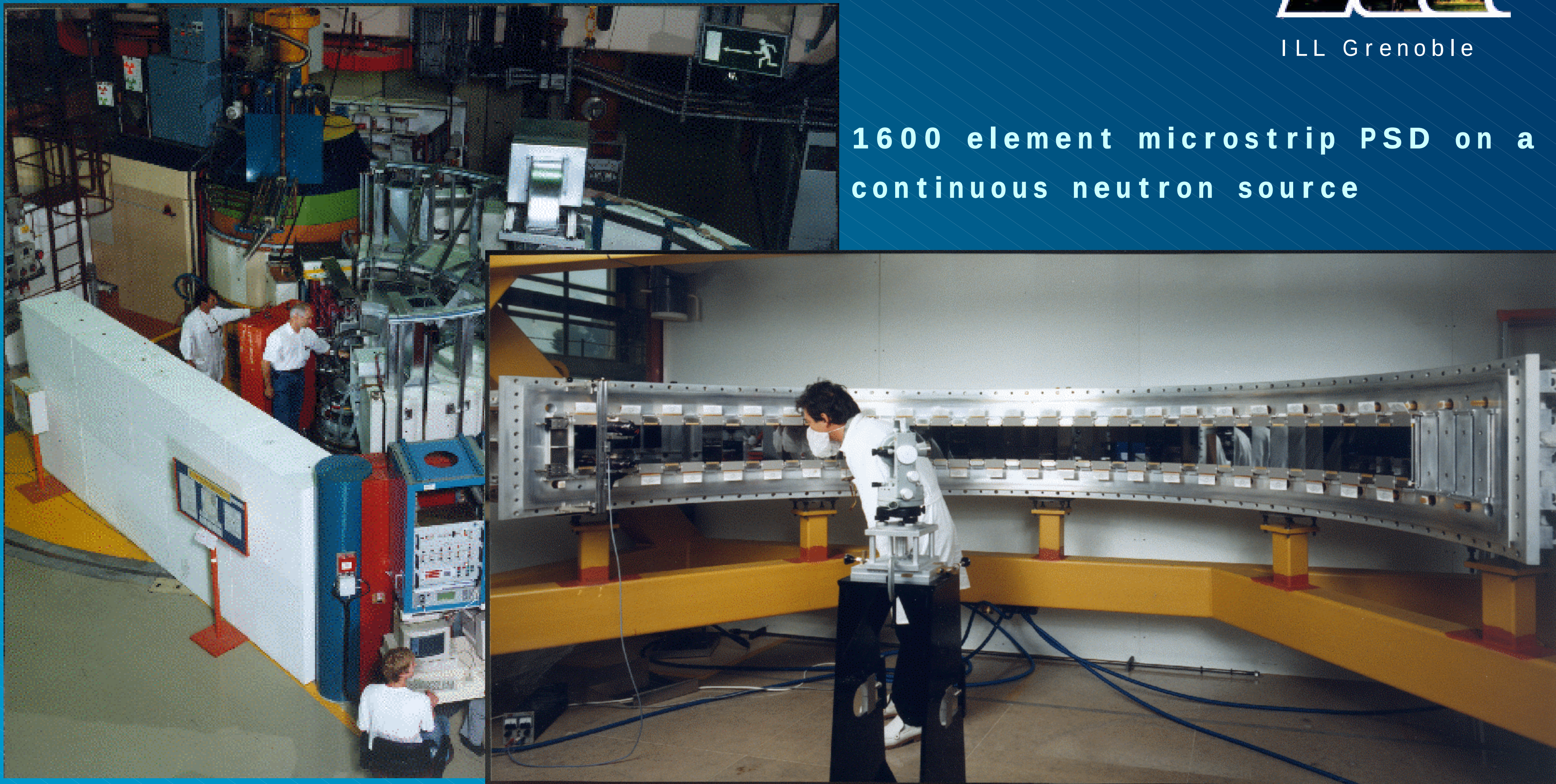
The Future - Big Detectors



1600 element microstrip PSD on a continuous neutron source

- Large 1600 element microstrip detector, D20 at ILL Grenoble (Fast medium-high resolution machine) Pierre Convert et al.

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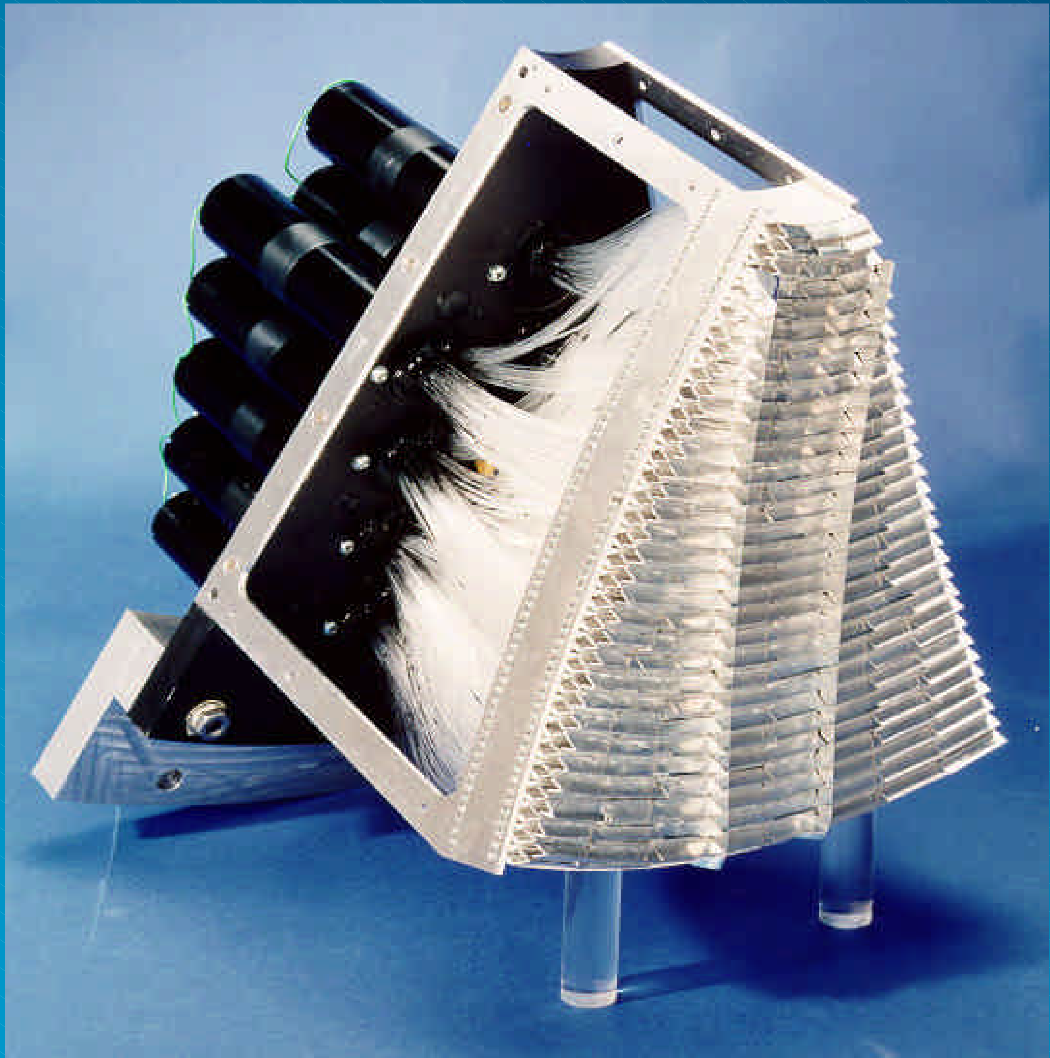
The Future - Big Detectors



- HRPD & GEM, ISIS
  - New scintillator detector element.
  - Project for new 90° (medium resolution) detector bank

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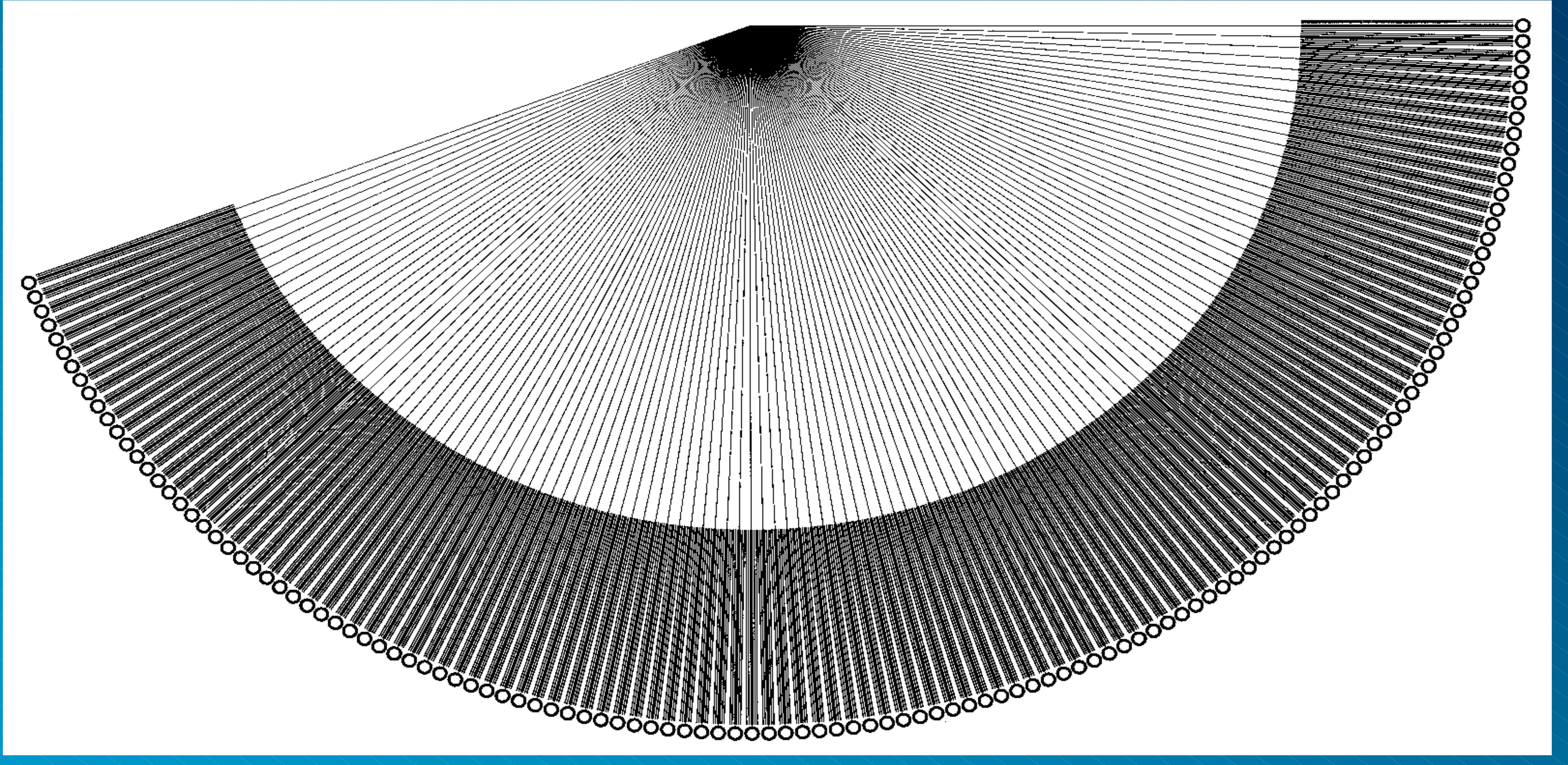
The Future - Big Detectors

Large detector array on a continuous neutron source



- Super-D2B at ILL Grenoble, very large high resolution detector

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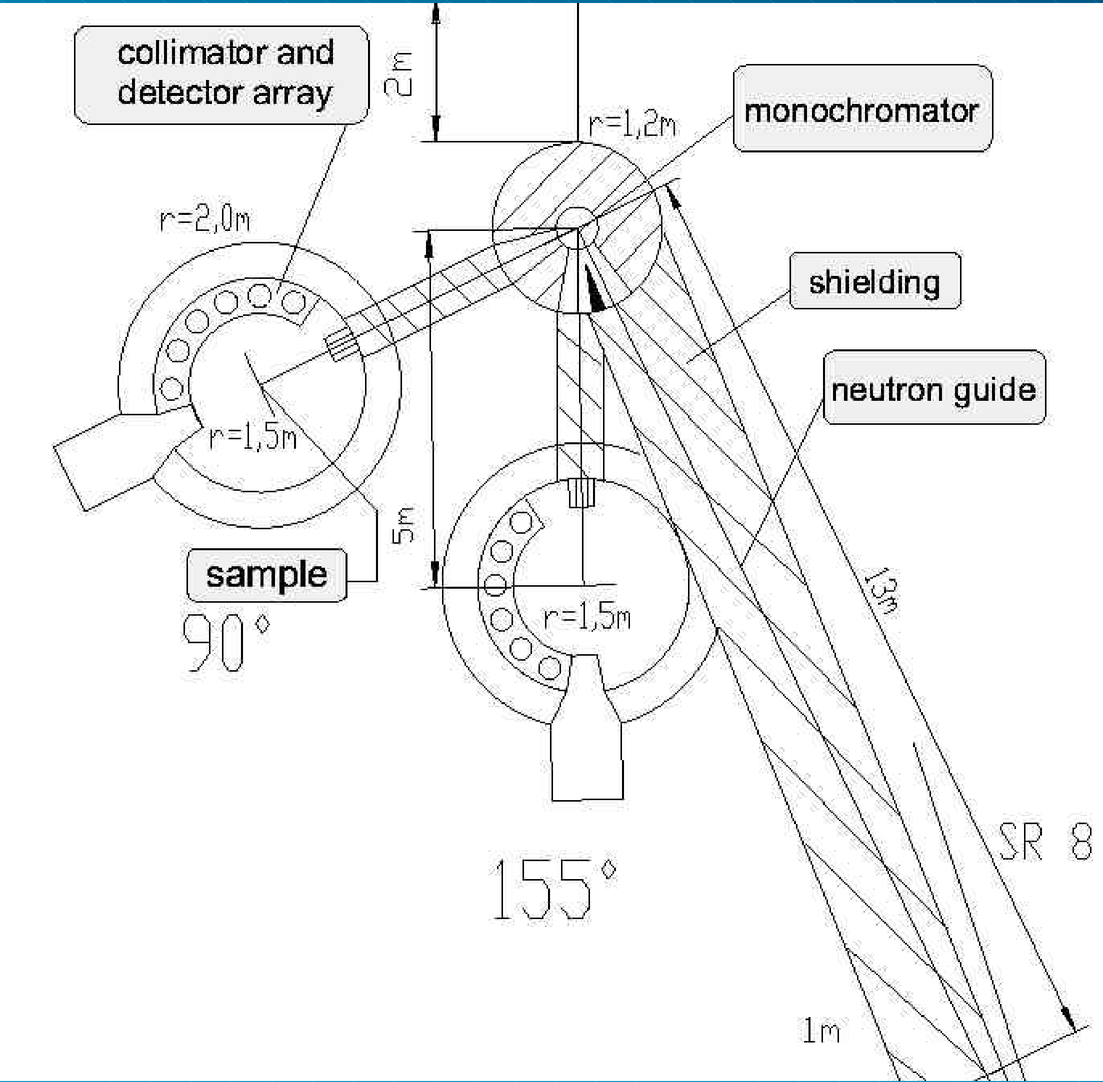
New Munich Reactor FRM-II

SPODI Structure Powder Diffractometer cf super-D2B



- Source distance 14.5m
  - Neutron supermirror guide
- Monochromator
  - Ge [551] vertical focus
  - Angle 90^0, 135^0, 155^0
  - Mosaic 20'
- 80 Mylar 10' collimators
- 80 He3 detectors
  - 300 cm high
  - Linear wire PSD
- cf ILL super-D2B project.

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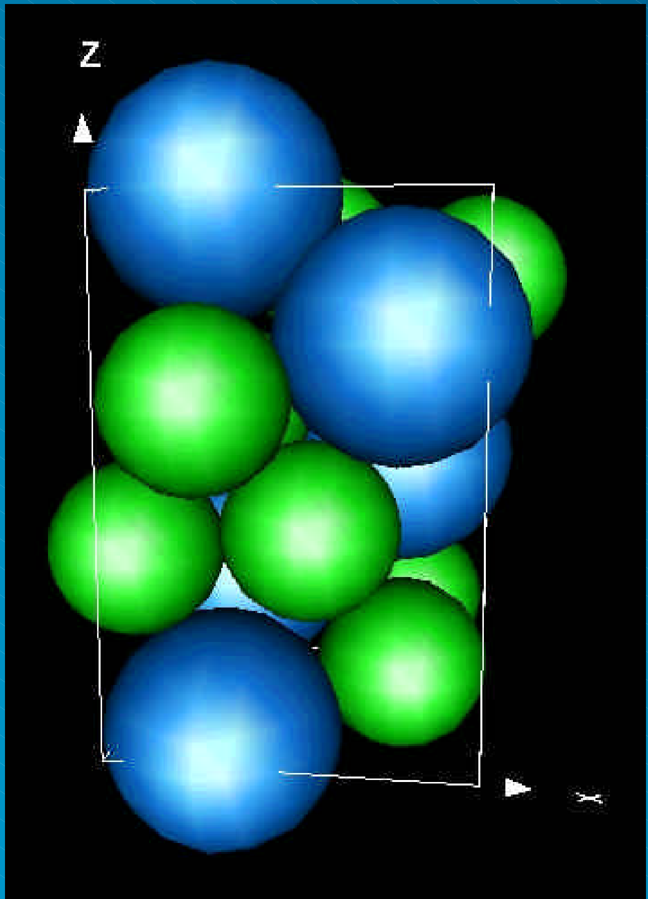
Neutron Powder Diffraction

Real Materials, not crystals - Hydrogen in Metals



- Hydrogen storage in metals
  - Location of H among heavy atoms
  - No single crystals
- Laves phases eg $LnMg_2H_7$ (La,Ce)
  - Binary alloys with large/small atoms
  - Various stackings of tetrahedral sites –can be occupied by H-atoms
  - Up to 7 Hydrogens per unit
- Can even find H in Eu on D20 !

Gingl, Yvon et al. (1997) J. Alloys Compounds **253**, 313.
Kohlmann, Gingl, Hansen, Yvon (1999) Angew. Chemie **38**, 2029. etc..

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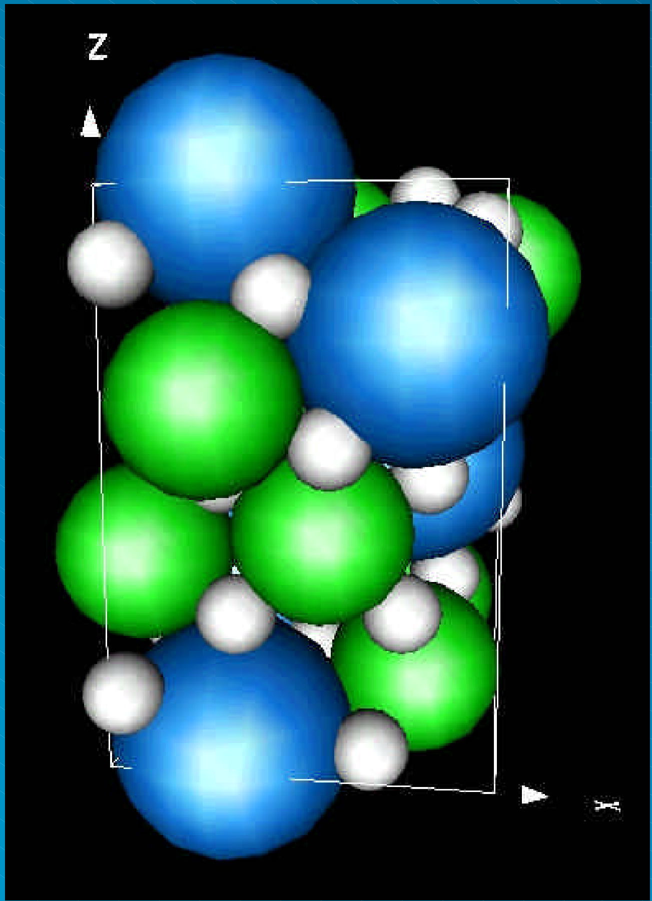
Neutron Powder Diffraction

Real Materials, not crystals - Hydrogen in Metals



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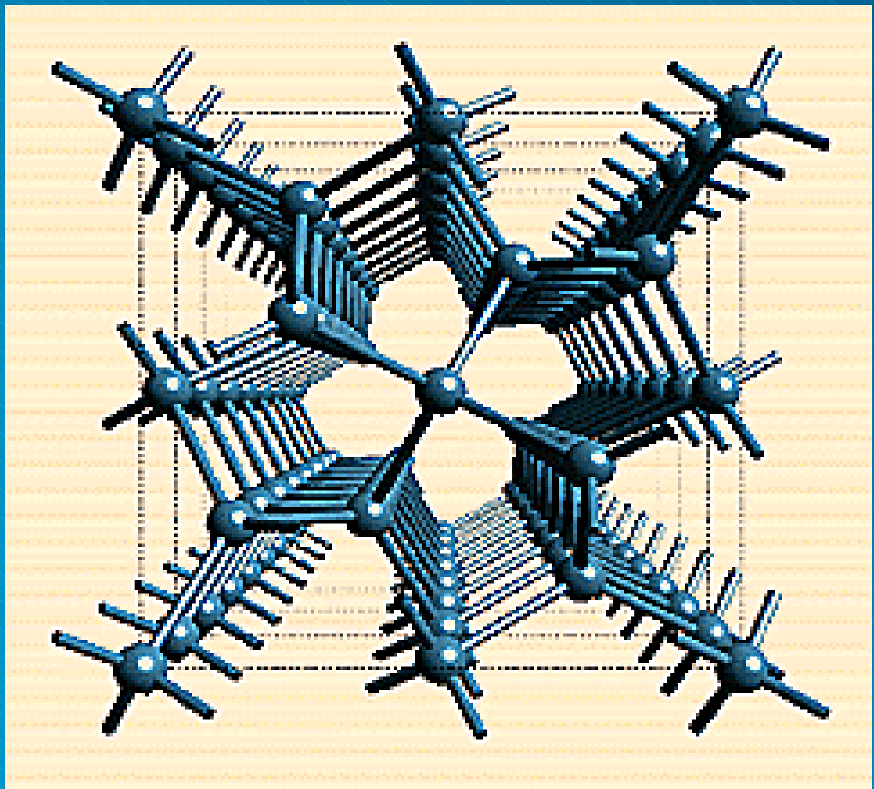
High Pressure Powder Diffraction

New phases of Ice discovered by neutron diffraction



- **Mixture of 5- and 7-membered rings of Ice XII.**
- **Delicate balance between competing ice phases - tests water potential functions in chemical & biological systems**
- **Model metastable structures**

Lobban, Finney, Kuhs (1998) Nature 391, 268.
Kuhs, Lobban, Finney (1999) Rev.High Press.Sci.& Tech. 7.

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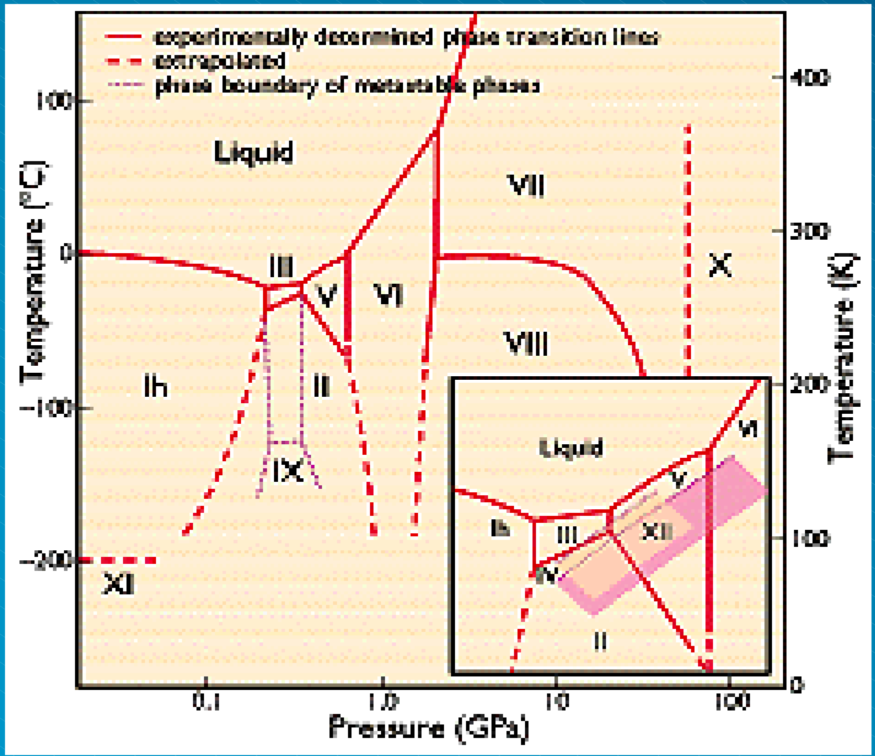
High Pressure Powder Diffraction

New phases of Ice discovered by neutron diffraction



- Ice-XII - densest form of ice without interpenetration
- Ice-IV - auto-clathrate interpenetration of H-bonds for even higher density
- Ice-He clathrate like Ice-II

Lobban, Finney, Kuhs (1998) Nature 391, 268.

Kuhs, Lobban, Finney (1999) Rev.High Press.Sci.& Tech. 7.

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Applications of large fast detectors

Real-time Phase Diagrams

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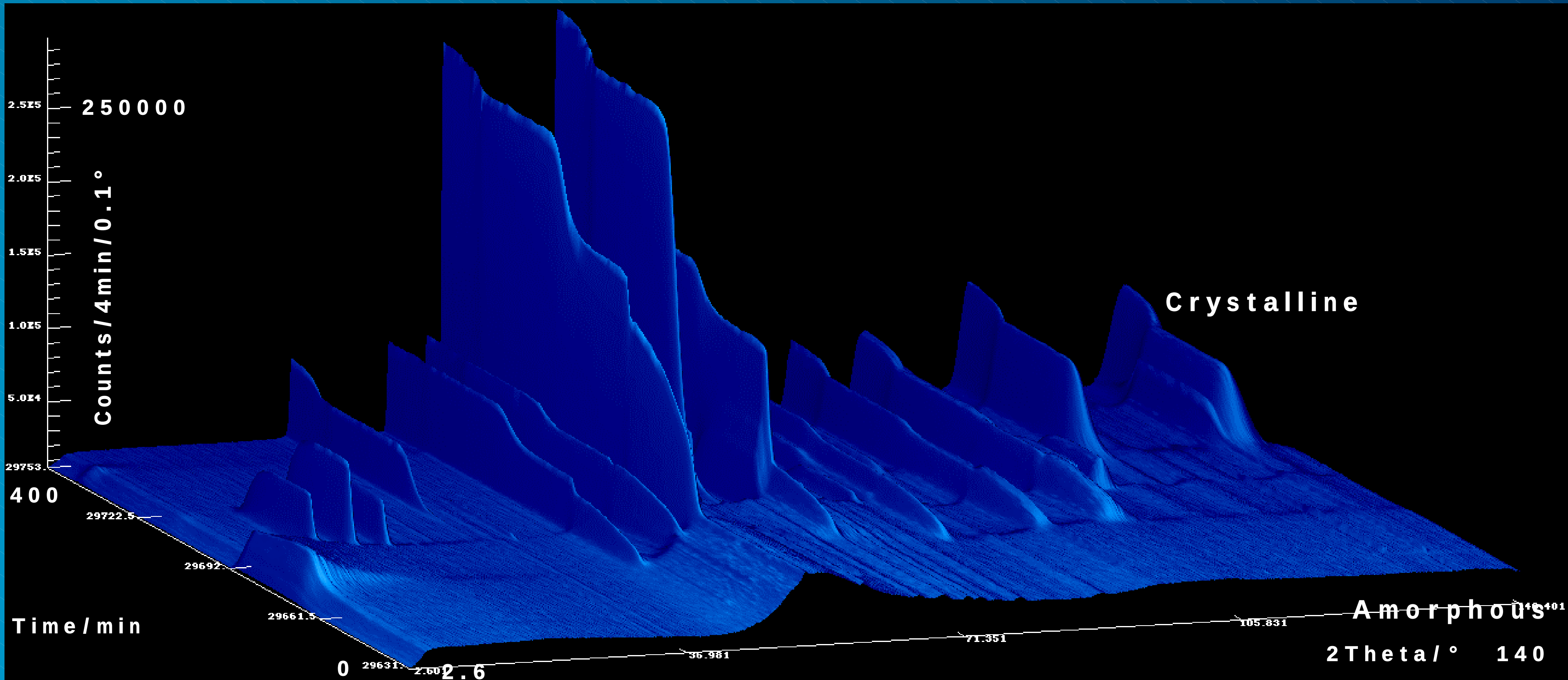
Sue Kilcoyne, Bob Cywinski et al.

Crystallisation of amorphous alloys $Y_{67}Fe_{33}$ with increasing temperature



Complete diffraction pattern in minutes or seconds, scan through temperature

Applications of large fast detectors

Pseudo-binary RMn_2 compounds: $Dy_{1-x}Y_x Mn_2$

Clemens Ritter, R. Cywinski et al on D1B

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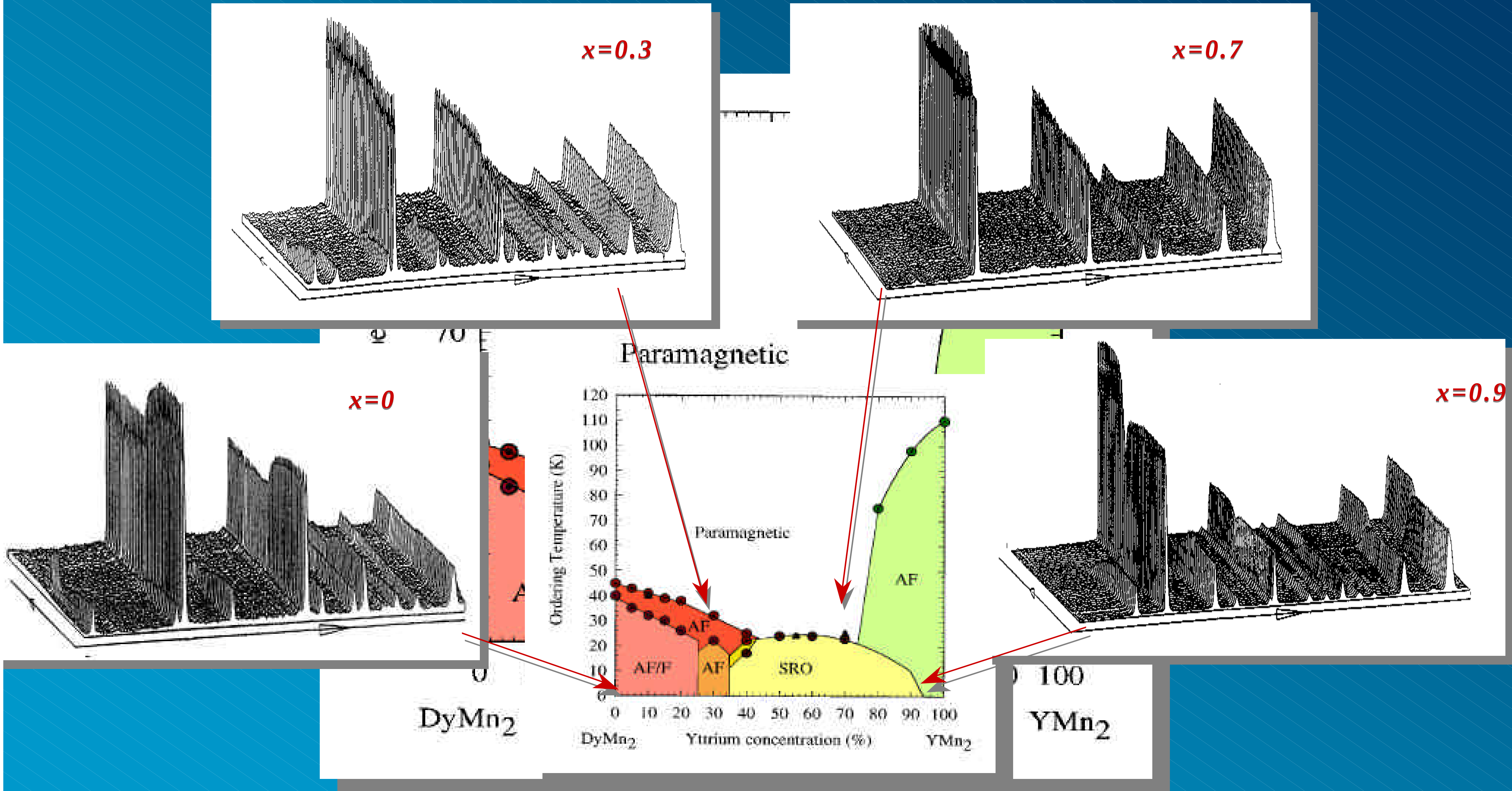

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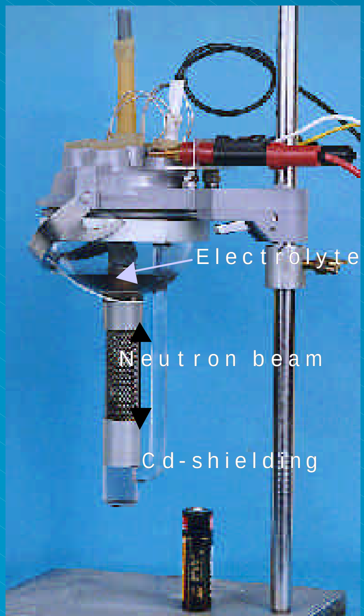
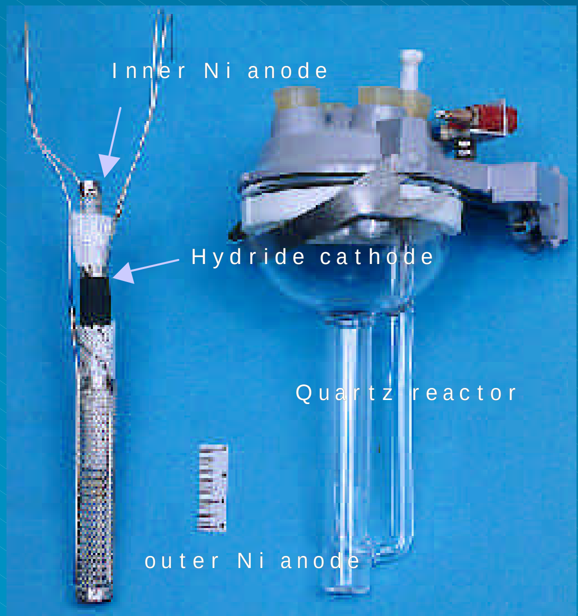
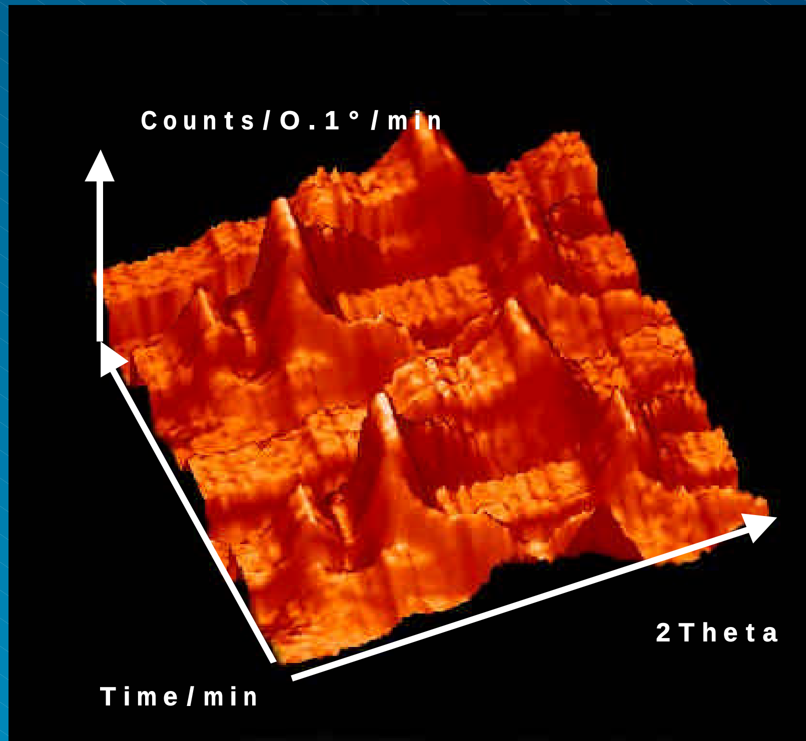
Applications of large fast detectors

Real-time electro-chemistry

- **Latroche, Chabre et al.**
  In-situ Charging and discharging of metal hydride electrodes LaNi5







Discharging

Charging

Discharging

Charging

- **Follow chemical changes with battery charge/dischage cycle**

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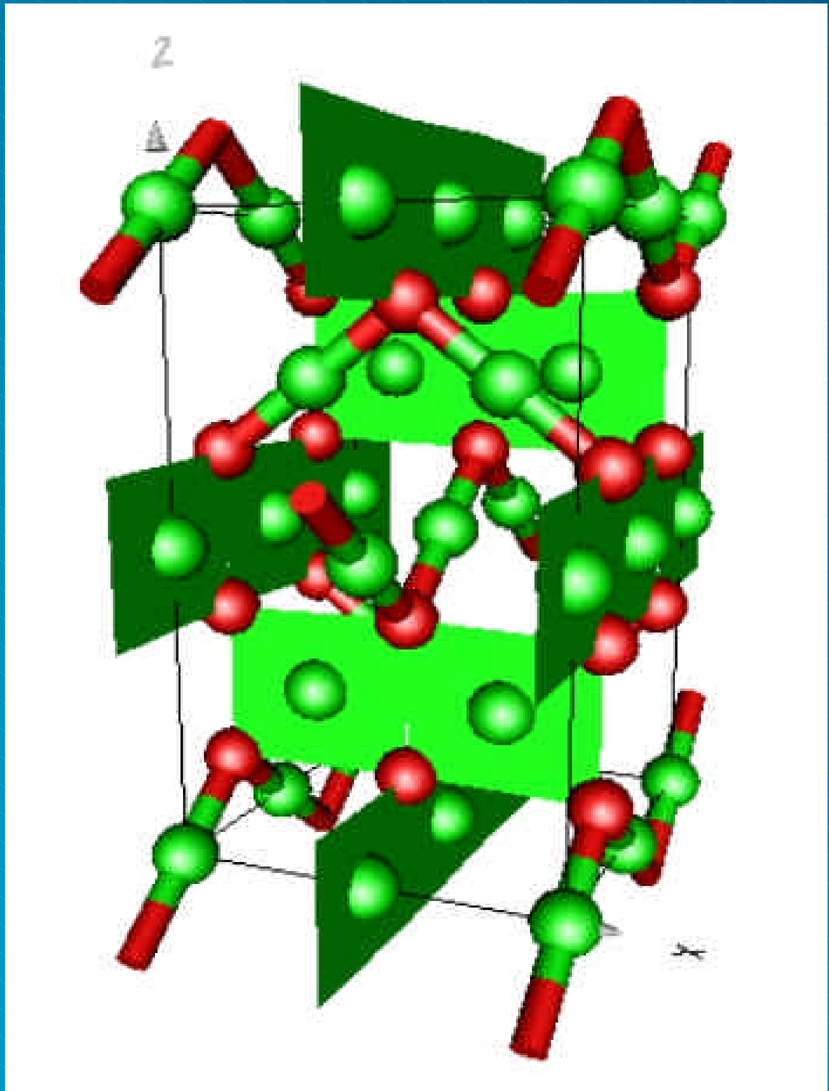
Valence Sum Calculations

What is the valence of Cu in Cu_4O_3 ?

O'Keeffe, M. Bovin, J. Am. Miner **63** 180 (1978)



- Average Cu valence = 2*3/4 = 1.5
- 2 types of Cu
  - Cu^{+} at (0,0,0) with 2 oxygens
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- Valence Sum $V=\Sigma_i[\exp(Ro-Ri)/B]$
  - Ri = Cu-Oi bond lengths
  - Ro= 1.610 for Cu^{+} to O^{2-}
  - B = 0.370
- Calculate Ri bond lengths & hence V

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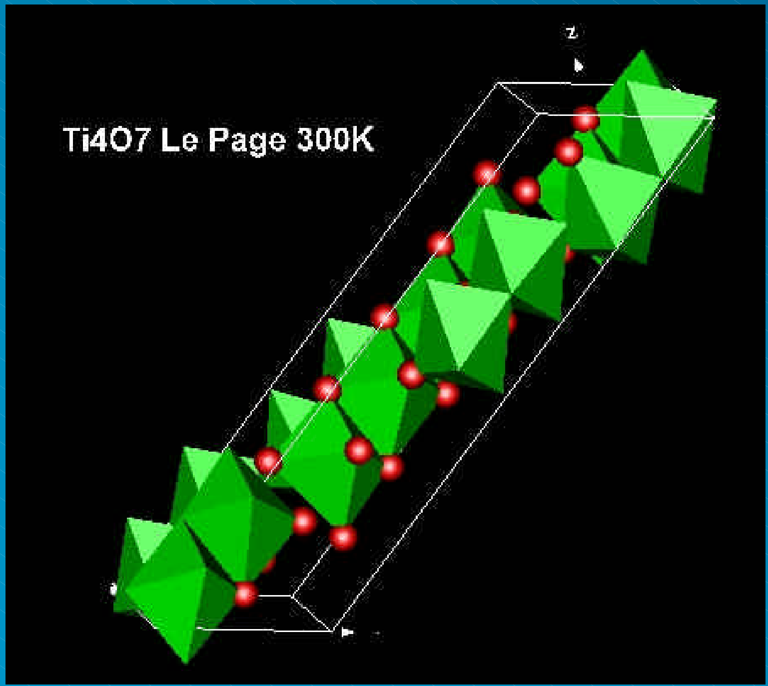
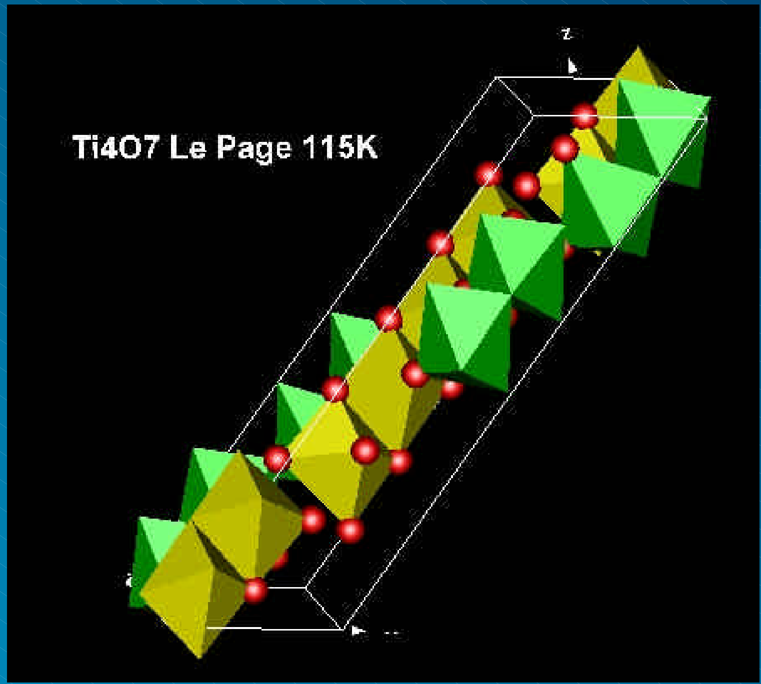
Electronic Order-Disorder

- Oxide superconductors, CMR, Vewey transition…
- Precise structural measurements vs temperature





- Example: charge ordering in Ti_4O_7 (Le Page et al.

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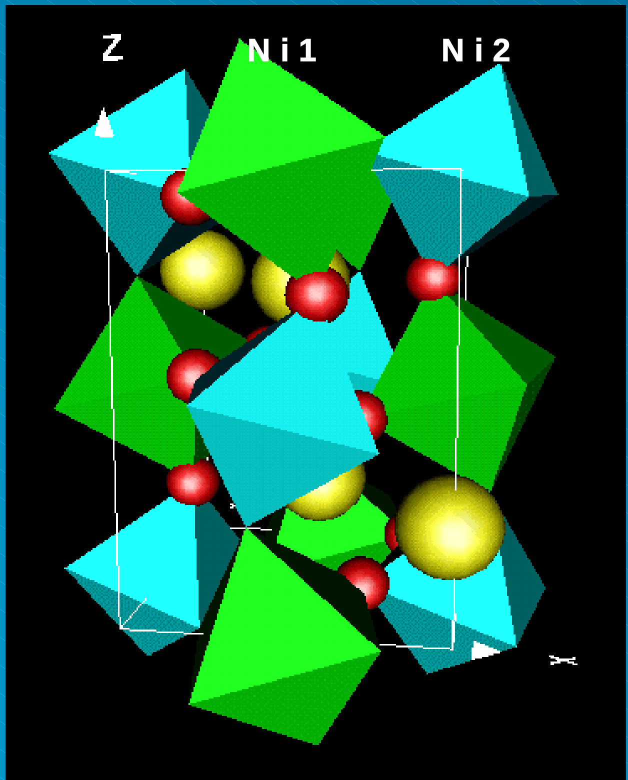
Neutron Powder Diffraction

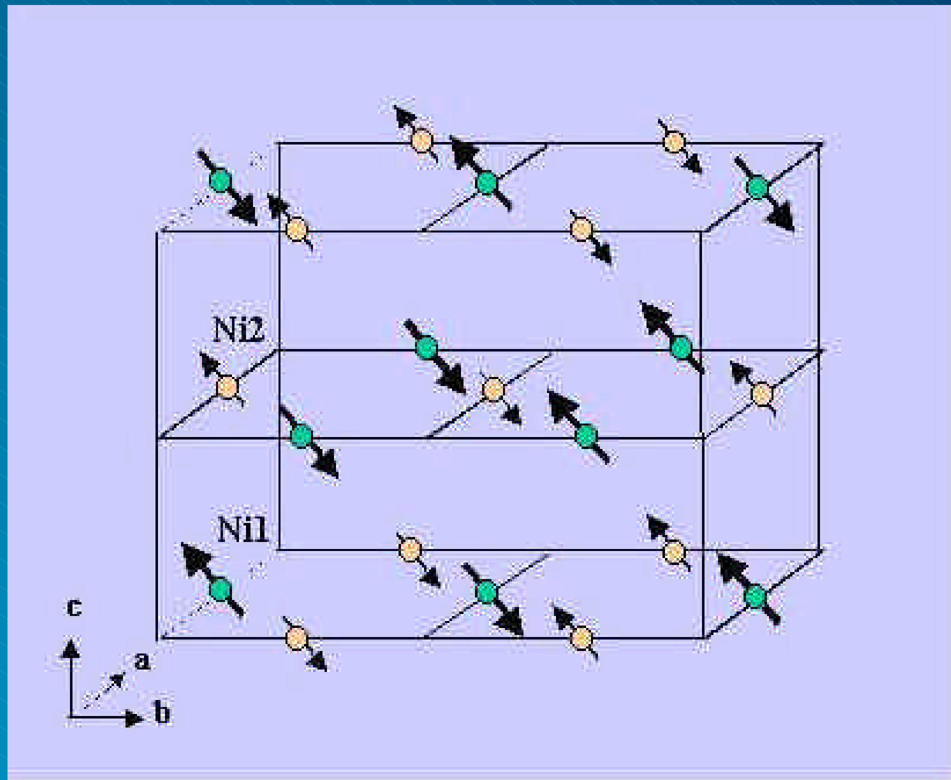
Charge Transfer in $YNiO_3$

Marie-Theresa Fernandez-Diaz et al.

Combined ESRF, D1B and D2B data - Alonso J.A. et al (1999) PRL 82, 3873

Metallic Ortho. YNiO3 -> Insulating Mono. YNiO3 T < 582K   Ni valence 3-**d**, 3+ **d**





V(Ni1) = 2.62   V(Ni2) = 3.17   M(Ni1) = -1.4 $\mathbf{m}_B$ M(Ni2) = 0.7 $\mathbf{m}_B$

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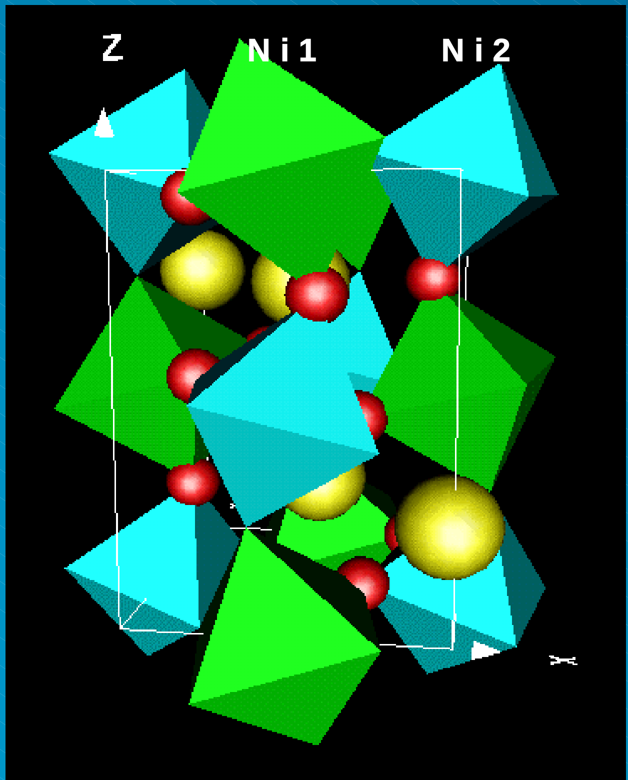

V(Ni1) = 2.62   V(Ni2) = 3.17

- Double evidence for charge transfer
  - Magnetic superstructure and different moments on Ni-sites
  - Different Ni-O distances around Ni1 and Ni2 sites mean ‘charge transfer’
- Neutrons provide both. But need:
  - High resolution to resolve symmetry
  - High flux to see superstructure

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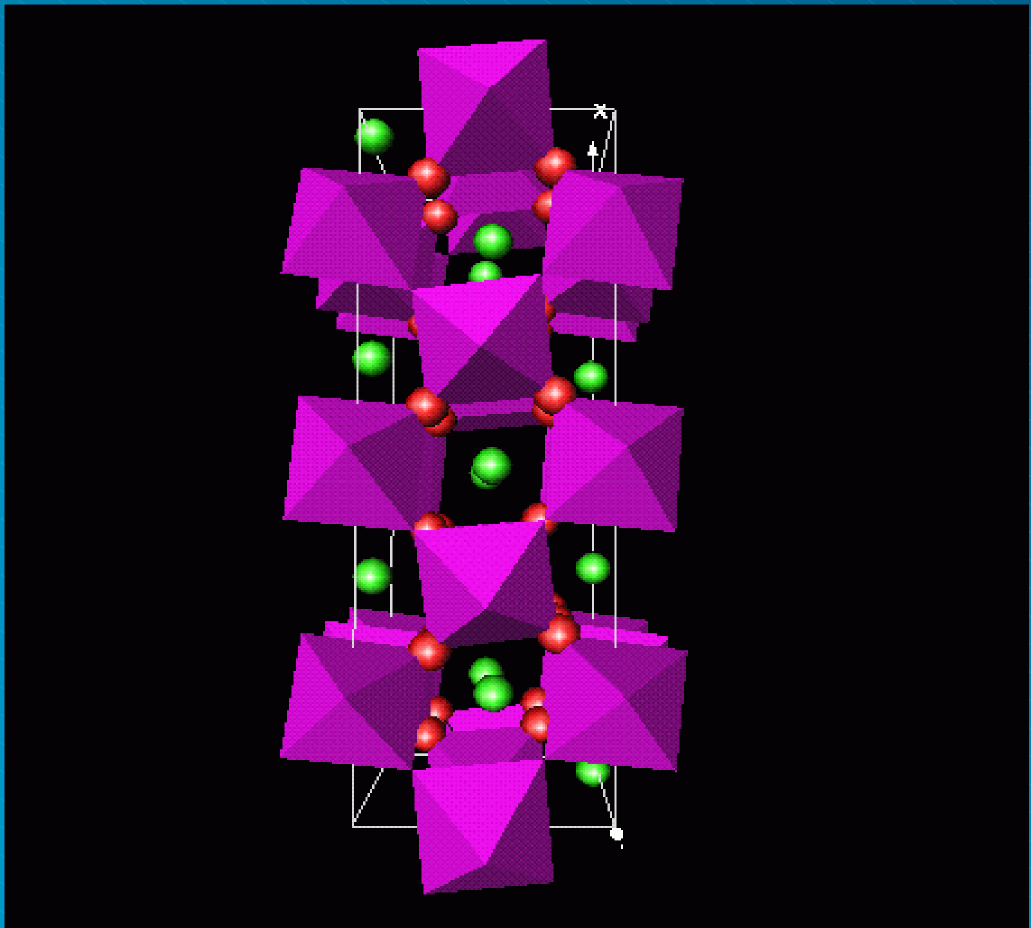
Giant Magneto-Resistive Ceramics

$La_{0.333}Ca_{0.667}MnO_3$



- Very large changes in electrical resistivity with temperature
- cf oxide superconductors
- mixed valence charge-ordering Mn^{3+}/Mn^{4+}
- GMR effect near room temperature
- applications to magnetic storage of data (new high density IBM hard disks)

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GMR Stripes and Charge Ordering

1D-ordering ? Dimensionality important for theory.

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- Remarkable electron microscope images of 1D stripe pattern in GMR $La_{0.33}Ca_{30.67}MnO_3$
- Evidence also for 1D ordering in high-Tc superconductors (Cu^{3+} stripes, spin-ladders etc)

Mori et al. Nature (1998) 392,473

Other papers in Phys. Rev. Letters

Alan Hewat

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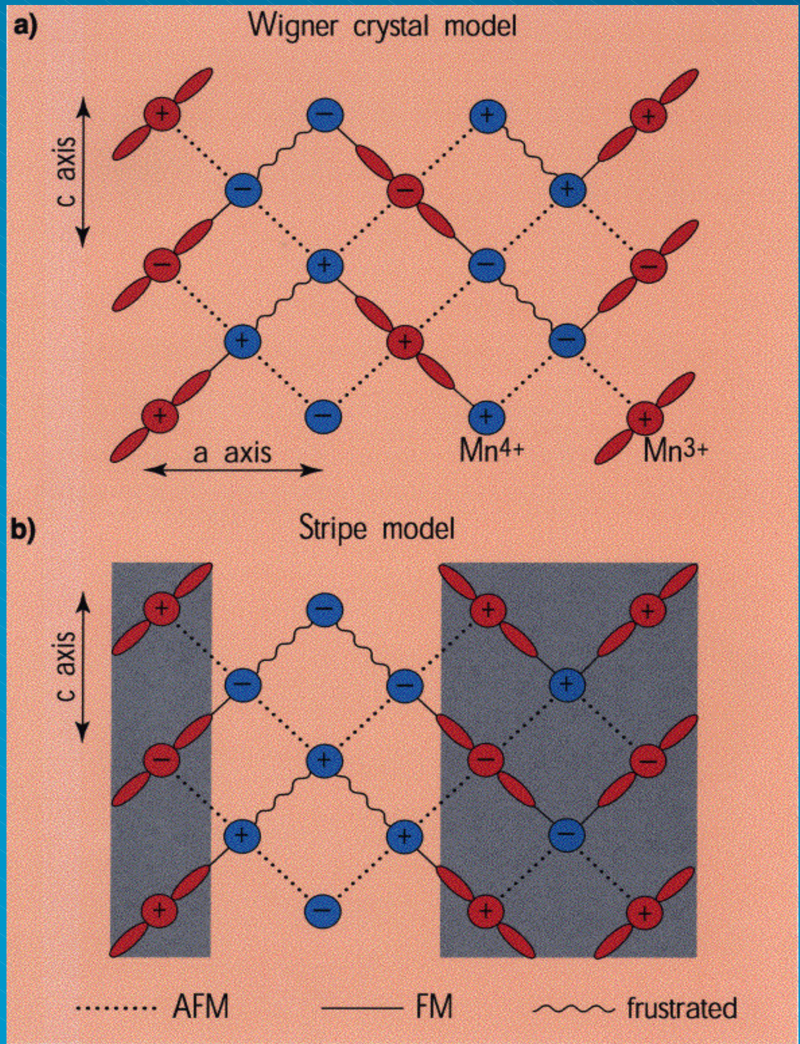
GMR Stripes and Charge Ordering

1D-ordering ? Dimensionality important for theory.



- Expect instead Mn^{3+}/Mn^{4+} to be uniformly distributed (2D Wigner crystal model of Goodenough)

- The 1D-stripe model would have very important consequences for the theory of superconductors and GMR oxides

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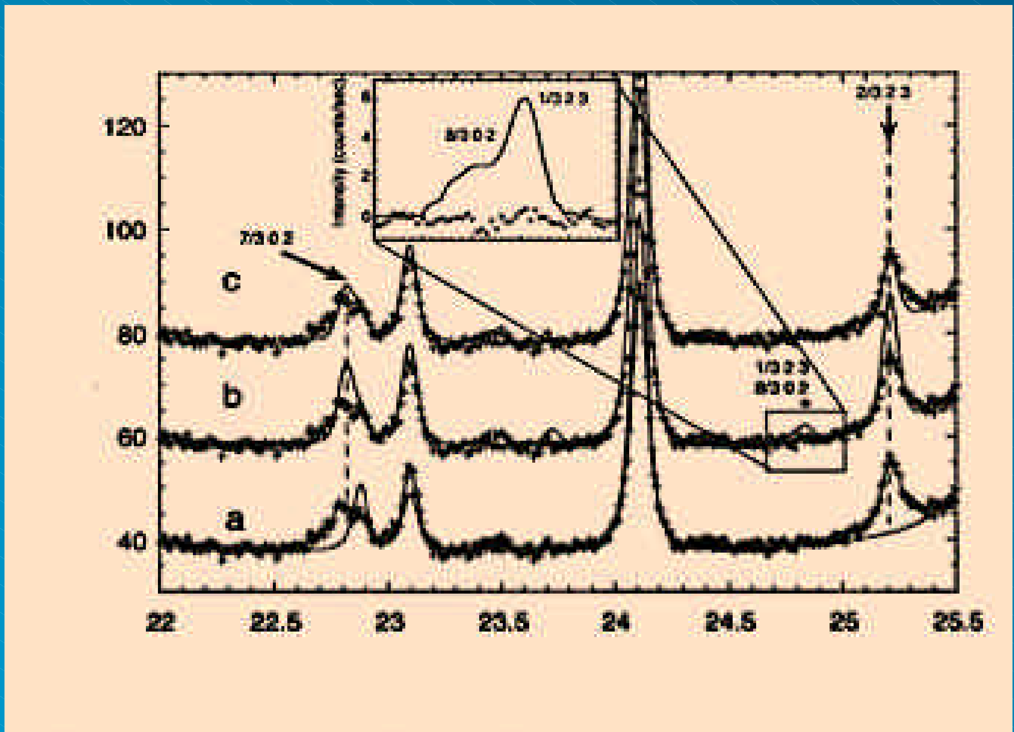
GMR Stripes and Charge Ordering

Neutron + Synchrotron Powder Diffraction



Radaelli et al. (1999) Phys. Rev B

X-ray work on X7A (BNL)

Neutron work on D2B (ILL)

- High resolution synchrotron powder data (Brookhaven) reveals true symmetry & ss
- High resolution neutron powder data (ILL Grenoble) allows refinement of real structure

  a) Average Structure

  b) Stripe Structure

  c) Wigner Crystal Structure (best fit)

- <u>The stripe structure is not supported</u>

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Neutron Powder Diffraction

- **What has been achieved ? Exciting new science ?**
  - High impact even outside the crystallographic community
  - Magnetism, Superconductors, Giant Magneto-Resistance

- **Why Neutrons ? Why not X-rays ?**
  - Neutrons+X-rays complementary
  - Solution of structures with X-rays
  - Refinement of important details with neutrons – valence sums

- **Why Powders ? Why not crystals ?**
  - Crystals should be used when available
  - Much new work started with powders - high Tc, GMR...