30 Years of Rietveld Refinement

I.U.Cr. Microsyposium, 10:00 Monday 5th August 1999

- **H.M.Rietveld**
  The Rietveld Method
- **A.W.Hewat**
  Neutron Powder Diffraction
- **F.Izumi**
  Applications to Inorganic materials
- **D.Louer**
  Laboratory X-rays
- **A.Fitch**
  Synchrotron Radiation

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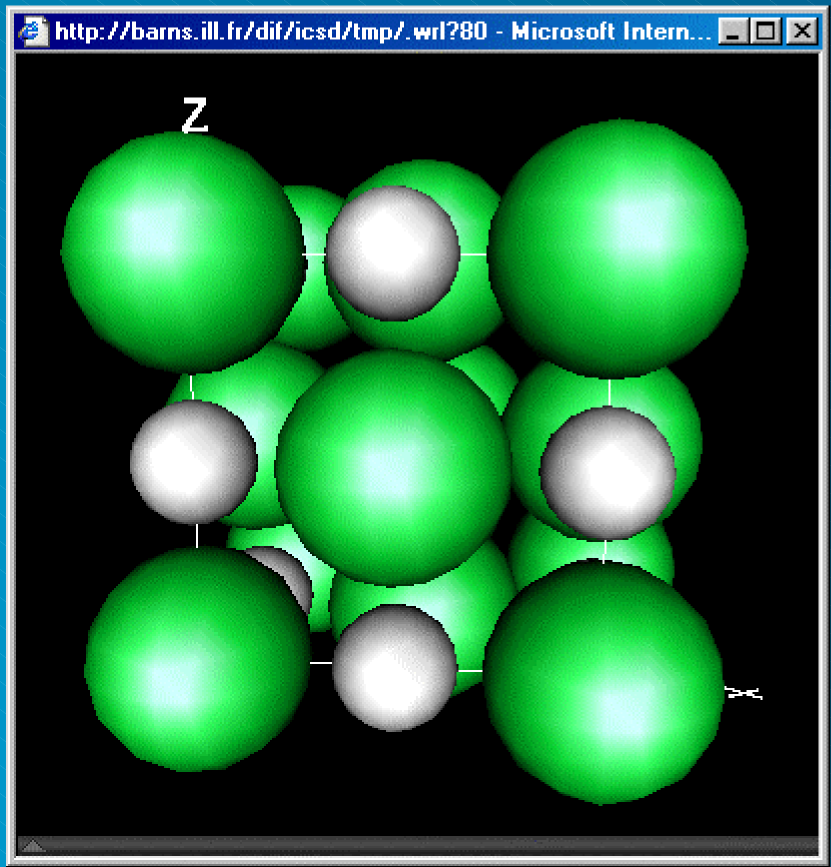
30 Years of Rietveld Refinement
Neutron Powder Diffraction

But more than 50 years of Neutron Powder Diffraction



- **1948 - First Neutron Crystallography - with Powders !!**

  Shull,CG. Wollan,EO. Morton,GA. Davidson,WL (1948) Phys.Rev. 73 842
  Neutron Diffraction Studies of NaH and NaD

- **1952 - First Neutron Single Crystal Work**

30 Years of Rietveld Refinement Neutron Powder Diffraction

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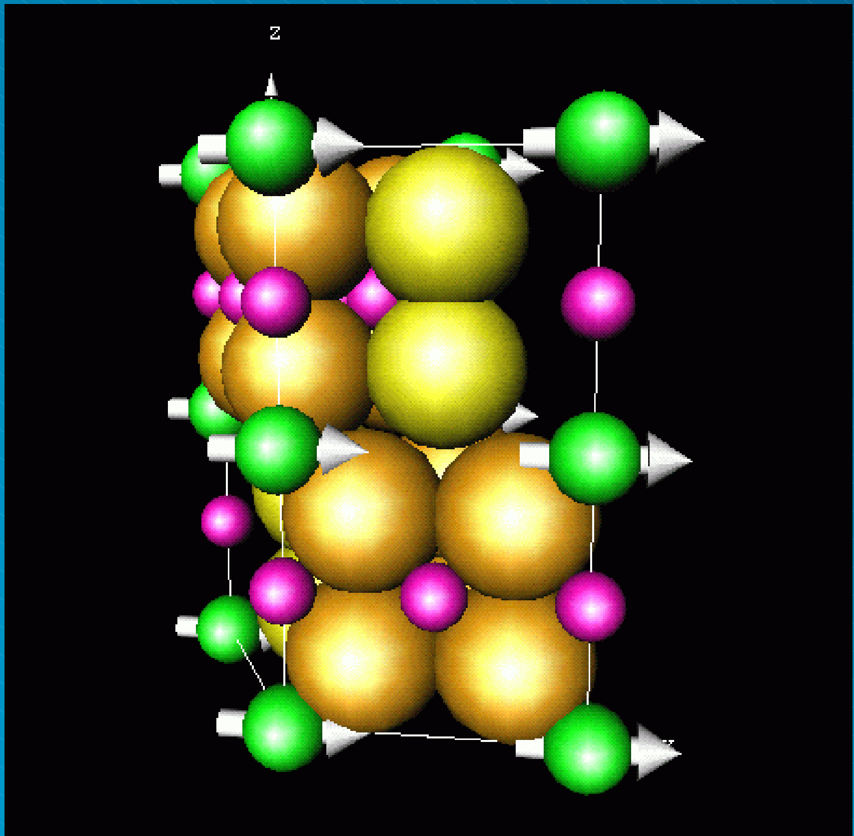
1967-69 H.M. Rietveld - “Neutron Profile Refinement”



$MnTa_4S_8$ H.M. Rietveld (1969) RCN -104

- **What was Achieved ?**
  - **Exciting new science ?**
- **Why Neutrons ?**
  - **Why not X-rays ?**
- **Why Powders ?**
  - **Why not crystals ?**
- **Why Rietveld ?**
  - **Why not F-extraction ?**

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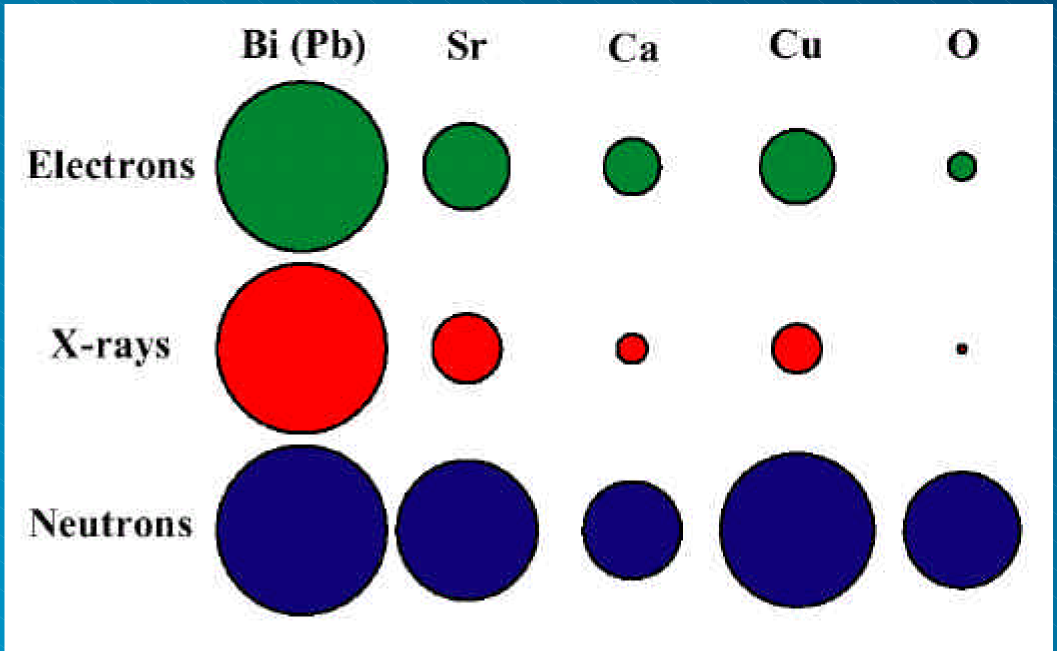
Why Neutrons ?

- **Relative Scattering Powers of the Elements**



- **Neutrons scatter strongly from light elements**

  (Because neutron scattering is a nuclear interaction)

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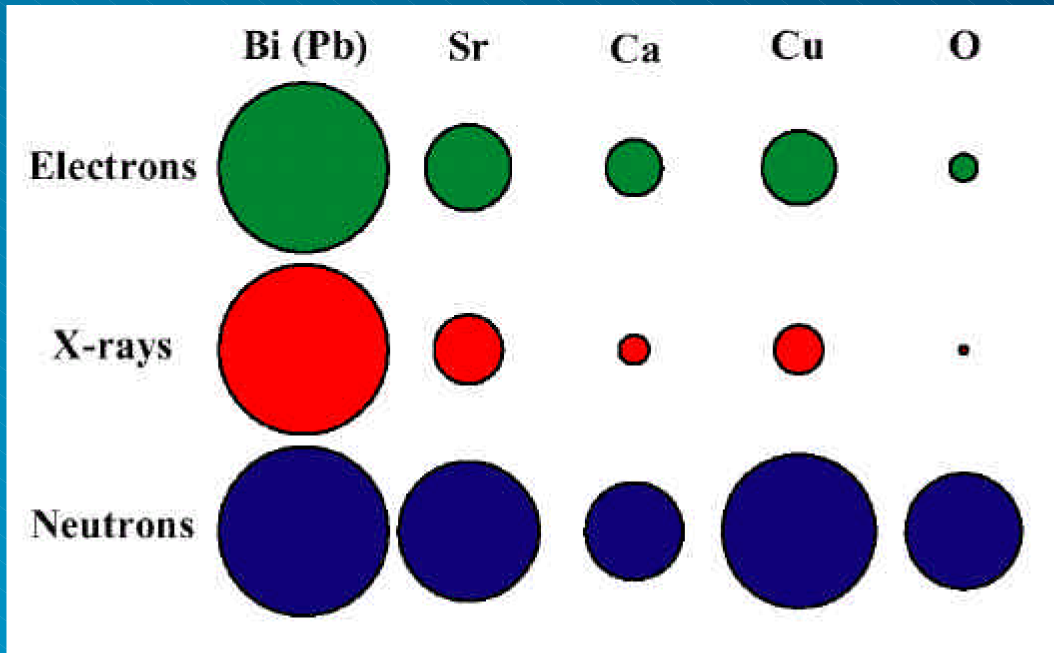
Why Neutrons ?

- **Relative Scattering Powers of the Elements**



- **This was indeed why Rietveld invented RR**

(At a Nuclear Lab. he worked on heavy metal oxides)

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30 Years of Rietveld Refinement
Neutron Powder Diffraction

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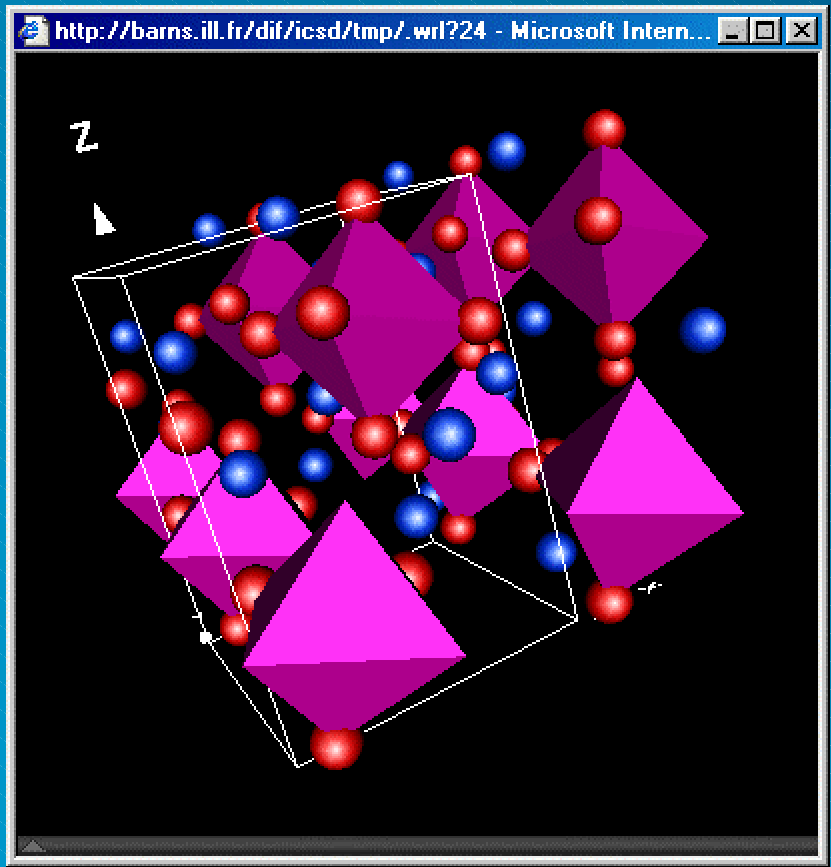
First Applications of Rietveld Refinement



- **H.M. Rietveld**

  Structure of Heavy Metal salts

  - Rietveld,HM. (1966) Acta Cryst. **20** 508. **The Crystal Structure of some Alkaline Earth Metal Uranates of the Type M_3UO_6**

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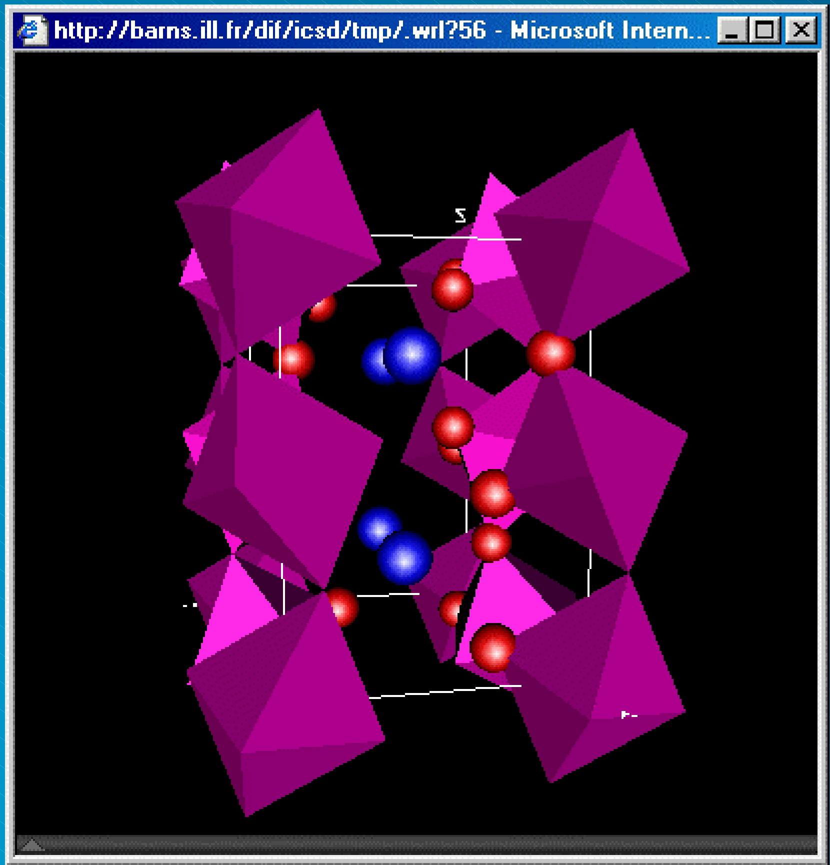
30 Years of Rietveld Refinement Neutron Powder Diffraction

First Applications of Rietveld Refinement



- **H.M. Rietveld**

  Structure of Heavy Metal salts

  - Loopstra,BO. Rietveld,HM. (1969) Acta Cryst.,B**25** 787.
    The Structure of Some Alkaline-Earth Metal Uranates

30 Years of Rietveld Refinement Neutron Powder Diffraction

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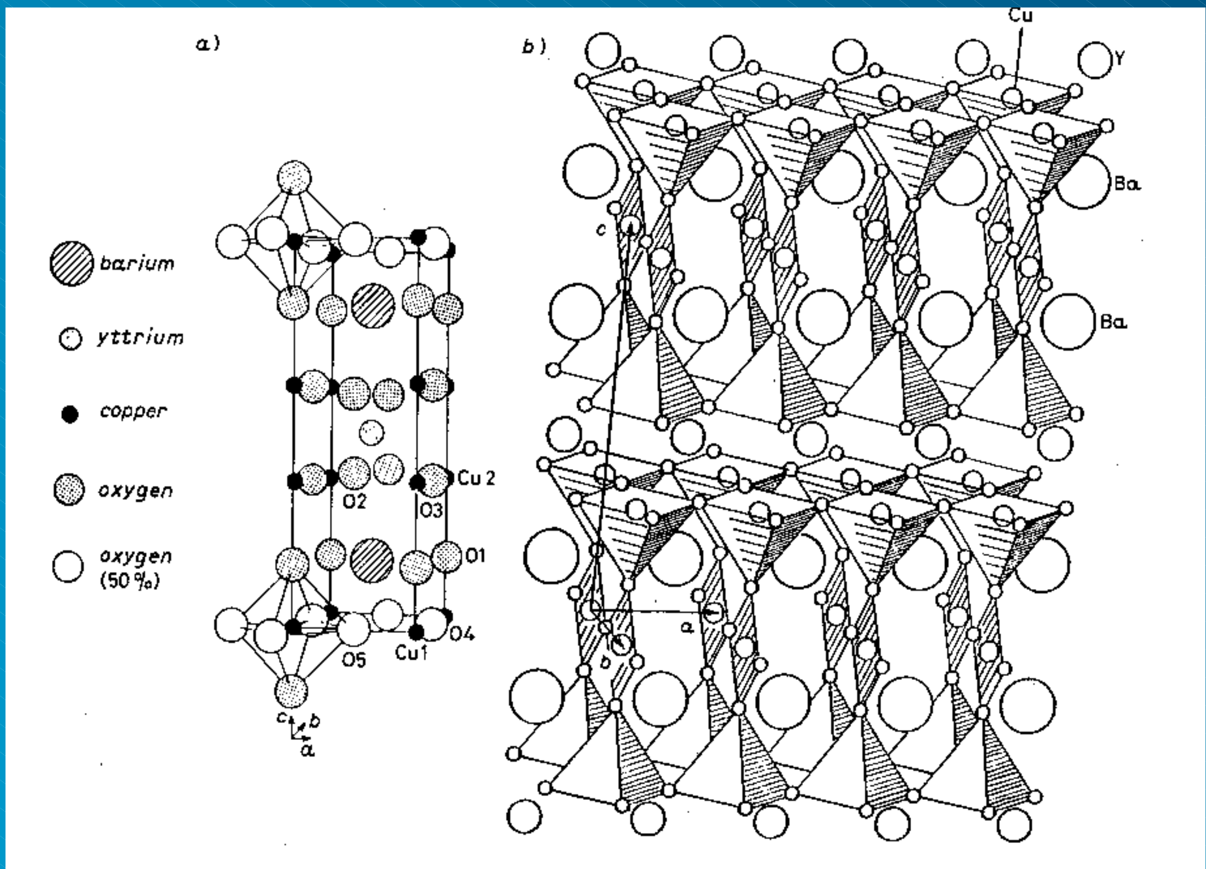
Heavy metal oxides are still with us - Superconductors, GMR



$YBa_2Cu_3O_7$ drawing from Capponi et al 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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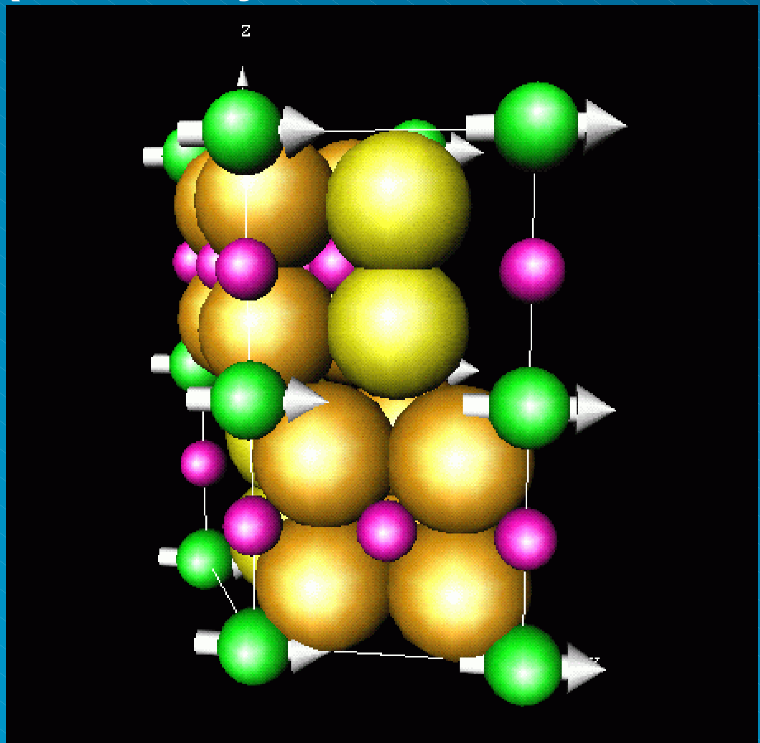
Why Neutrons ?

- **Neutrons are unique for Magnetic Structures**

(Even if Synchrotron Radiation can be used for some things)



- **H.M. Rietveld**

  Structure of Magnetic Materials

- **Report RCN -104**

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

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Why Powders ?

- …Well, if you don’t have a single crystal…
  - If you do have a single crystal, then use it !
- 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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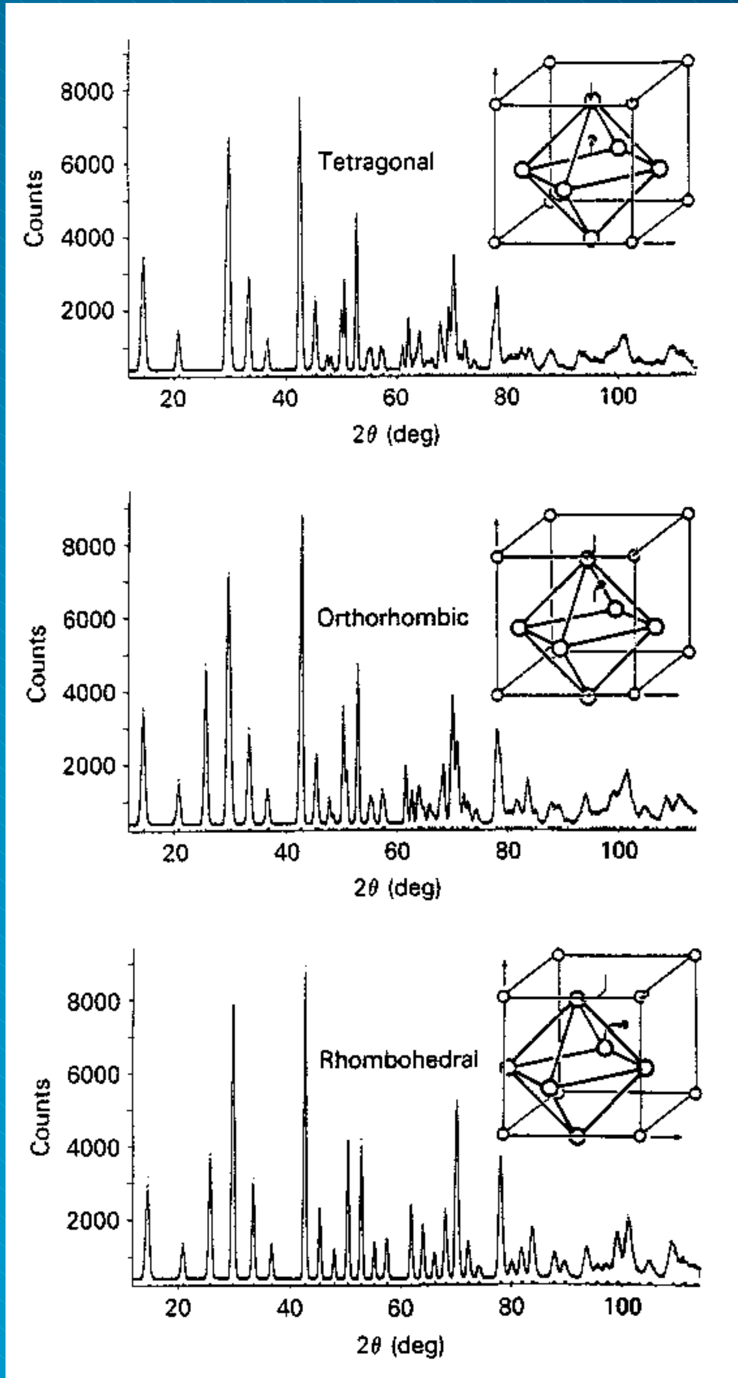
Why Powders ?

- **Rietveld Refinement at Harwell, UK (1972)**
  - **Already 3 years after Rietveld's paper !**
  - **Work for B.T.M Willis and W. Cochran on soft vibrational modes in perovskite ferro-electrics.**

    These materials break up with the ferro-electric transition - difficult to obtain precise structure - small displacements of light atoms.
  - **Visit to Hugo Rietveld in Petten & he provided his program - the basis of all of the others - GSAS (Bob von Dreele then at Oxford) FullProf via the original Wiles and Young program...etc**



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Why Powders ?

- **Destructive Phase T/Ns**
  - **Classical Perovskite structure transitions**
    Small displacements of light (oxygen) atoms
  - **Subtle changes in the powder 'profile' - interest of "Profile Refinement"**
- **Then, no single crystals**
- **Microsymposium Wed 11 10:00**
  - **P.Attfield, E.Suard et al**

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Why Rietveld Refinement ?

- Strongly overlapping reflections
  - Previously at Harwell, integrated intensities were obtained for groups of overlapping reflections.
  - (Controversy about validity of Rietveld Refinement)

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

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Spread of Rietveld Refinement

- Harwell was the first “User Laboratory”
  - Users came from many Universities, and this meant that new techniques spread very quickly
  - Proximity of chemists at Oxford - Cheetham et al.
- 1967-1972 only a handful of RR papers
- 1972-1977 an explosion of the use of RR
- 1987 impact of high Tc superconductors
- 1997 Giant Magneto-Resistive materials

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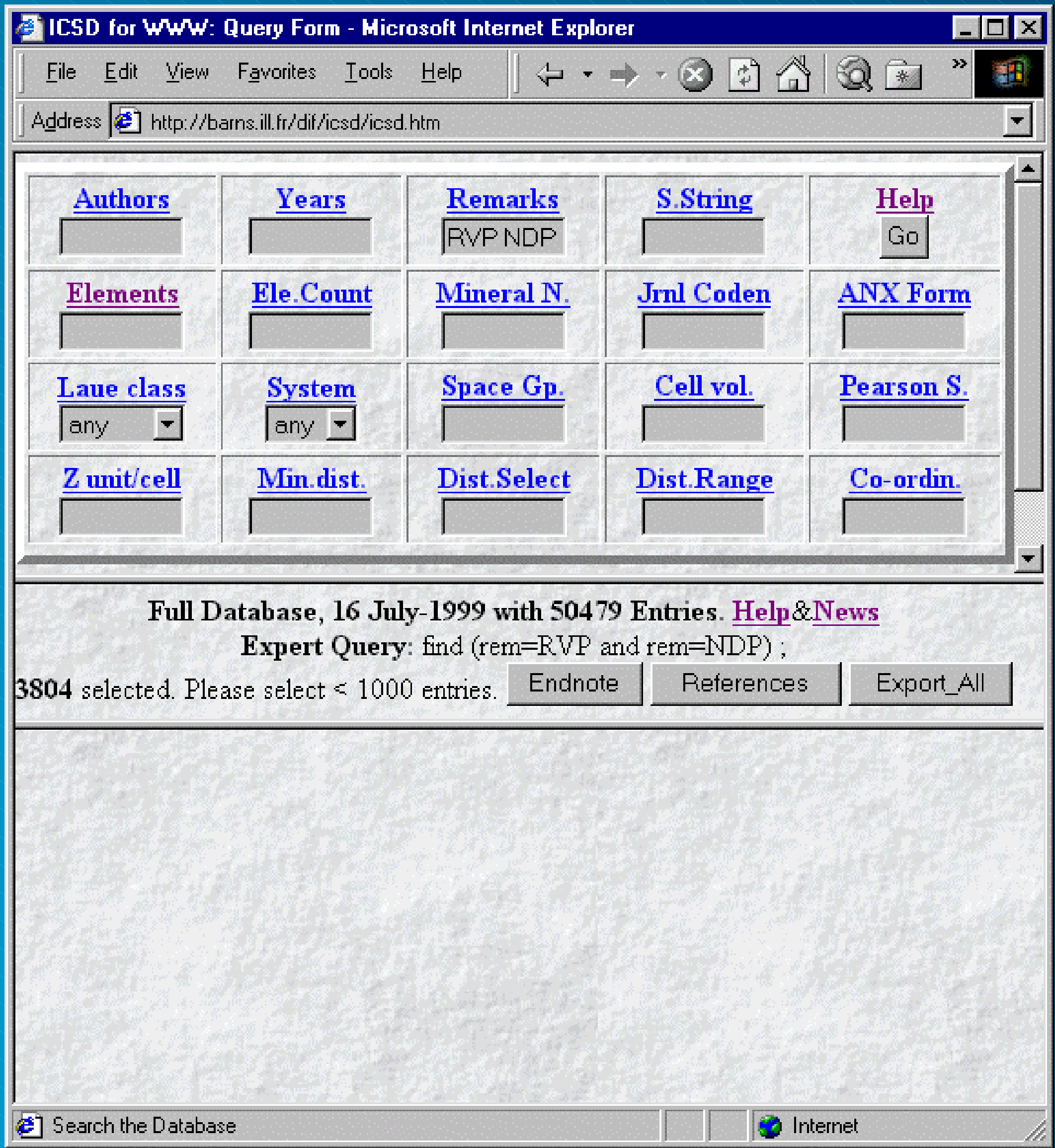
Numbers of Studies using RR



- **3804 Structures with Neutron RR**

(According to the Inorganic Crystal Structure Database http://barns.ill.fr)

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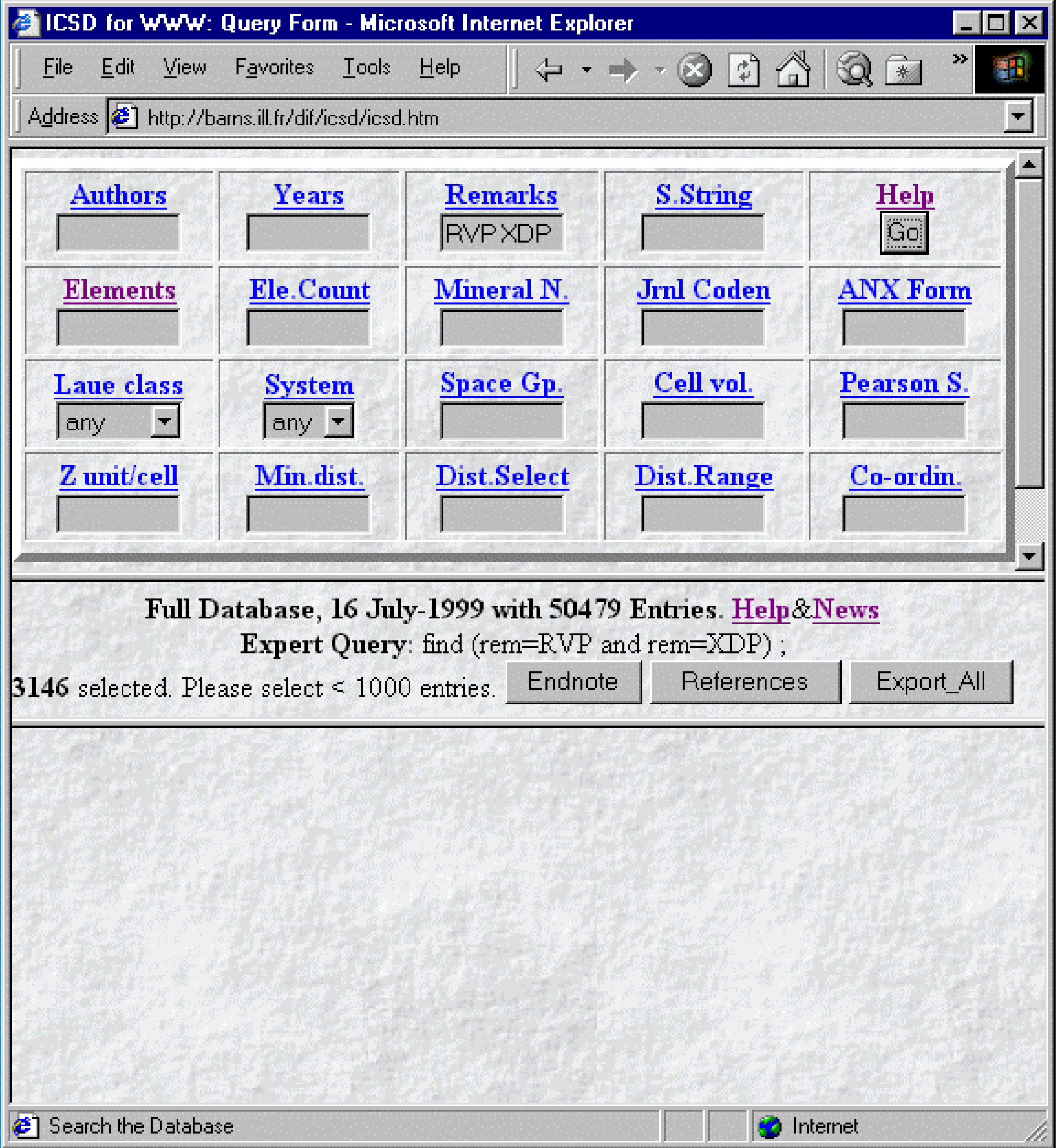
Numbers of Studies using RR



- **3804 Structures with Neutron RR**
- **3146 Structures with X-ray RR**

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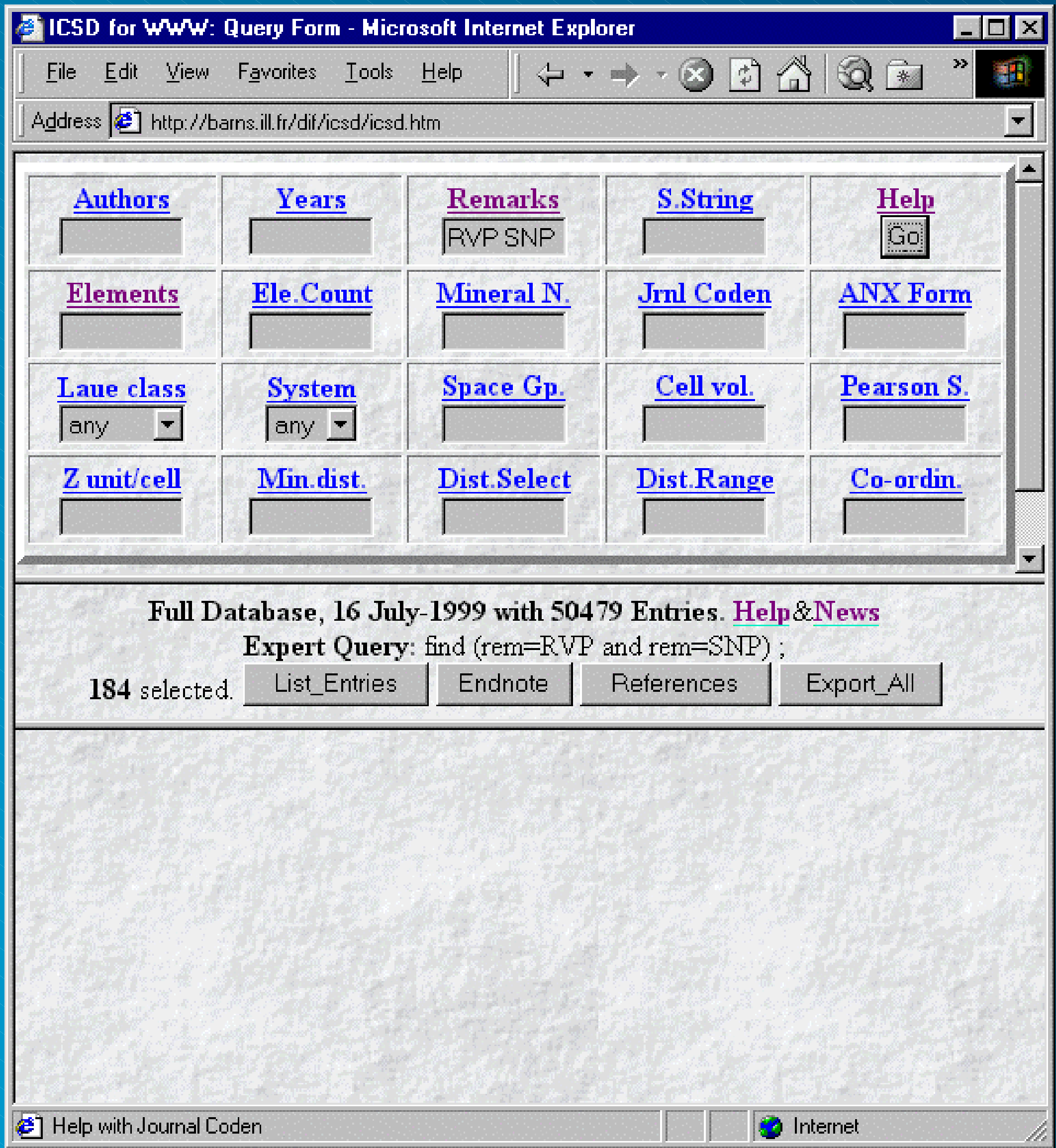
Numbers of Studies using RR



- **3804 Structures with Neutron RR**
- **3146 Structures with X-ray RR**
- **184 Structures with Synchrotrons**

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Numbers of Rietveld Refinements
Total in ICSD = 7089

(This includes refinements at multiple temperatures)

- Total numbers
  - 3804 Neutron RR
  - 3146 X-ray RR
  - 184 Synchrotron RR
- Total numbers in last 5 years (1994-1998)
  - 1874 Neutron RR
  - 2007 X-ray RR
  - 143 Synchrotron RR
- More than HALF in the last 5 years - and almost all Synchrotron Rietveld Refinements

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Refinement of Rietveld ?

(Semantic question of Ray Young & Terry Sabine)

1995 - Aminoff Prize presented to Hugo Rietveld by King Carl Gustaf of Sweden

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Early Days at ILL Grenoble (1972)

(Less refined)

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

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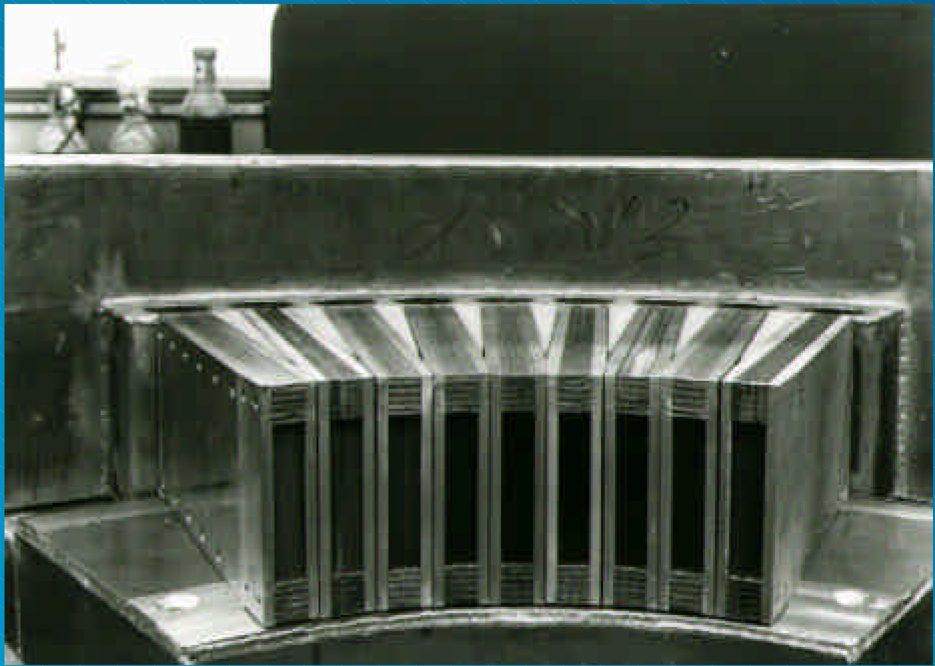
Early Days at ILL Grenoble (1974)



- **Orders of Magnitude Improvement - D1A**
  - **Multiple detectors**
  - **Large efficient collimators**
  - **Focussing Monochromator**
- **Exponential growth in the application of RR.**

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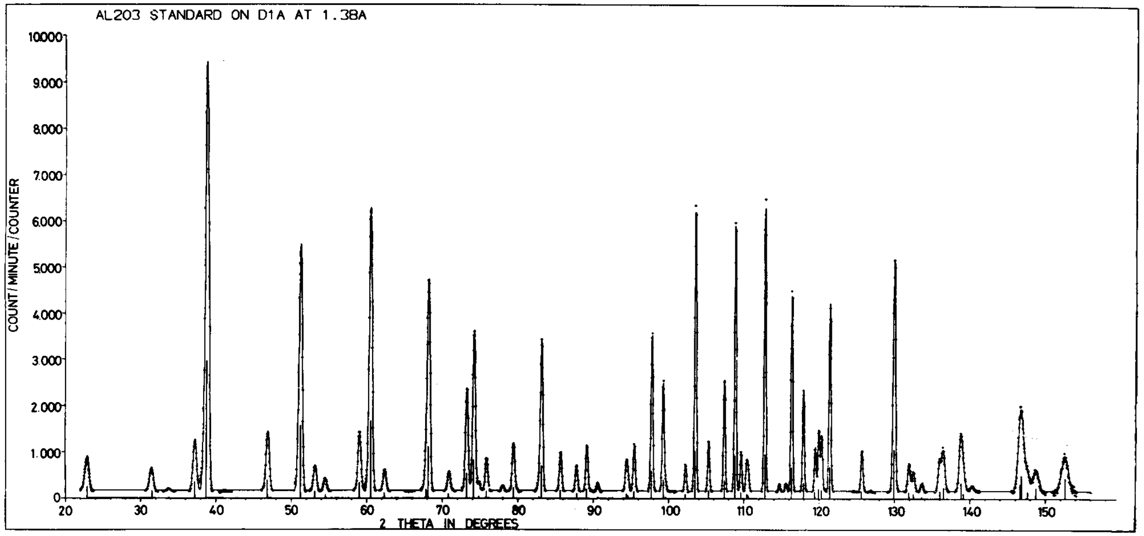
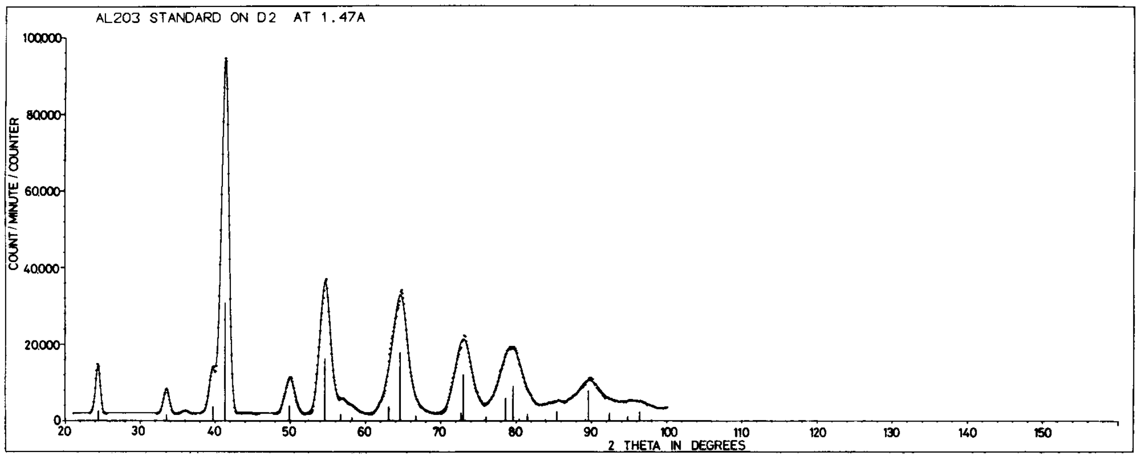
Comparison of D1A with old D2 at ILL



(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)

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- 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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Early Days at ILL Grenoble (70's)

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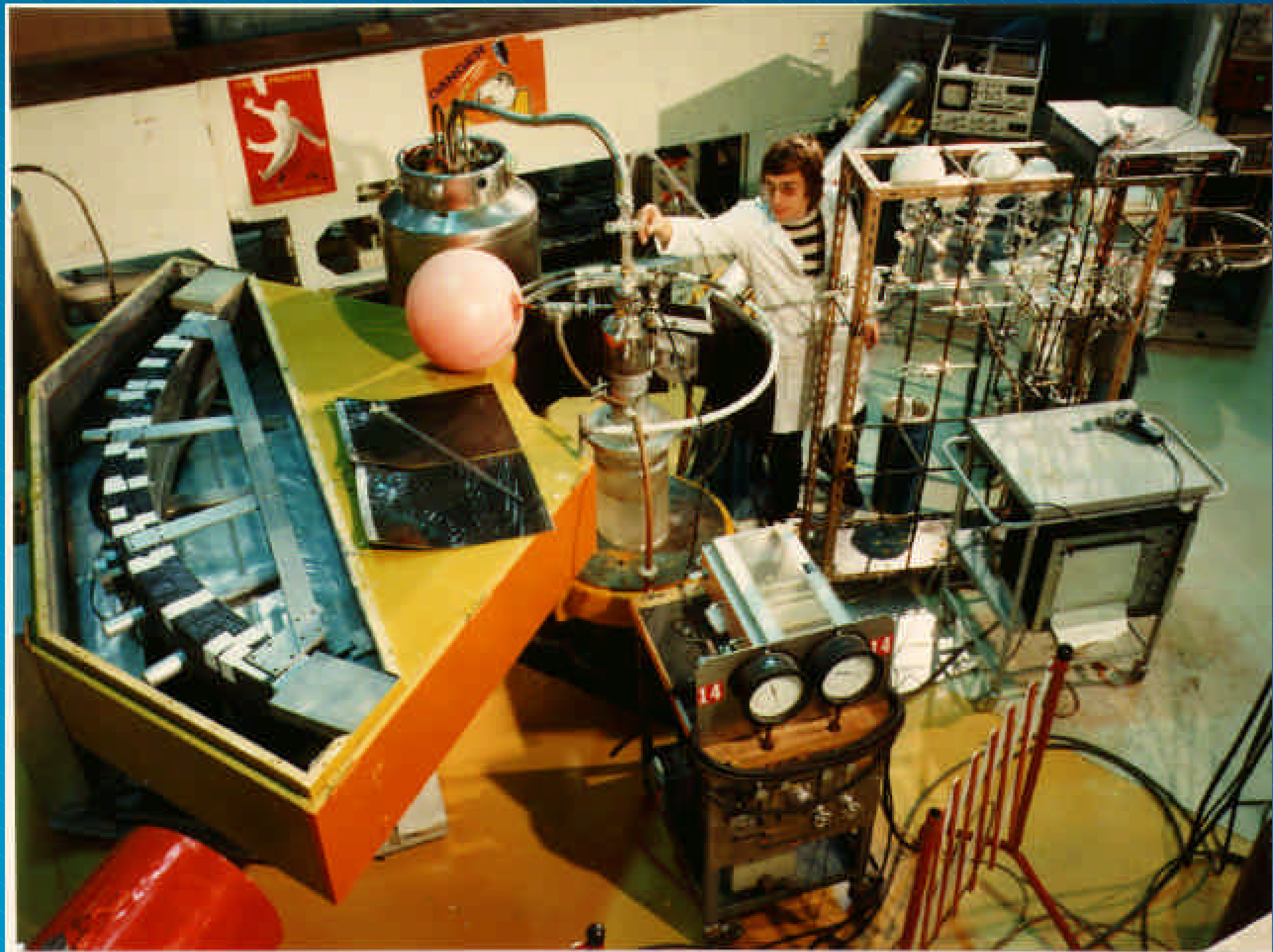

Christian Riekel doing chemistry in-situ on D1B

- **Real-Time Chemistry on D1B at ILL (Riekel, Pannetier)**

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The Second Generation (80's)

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

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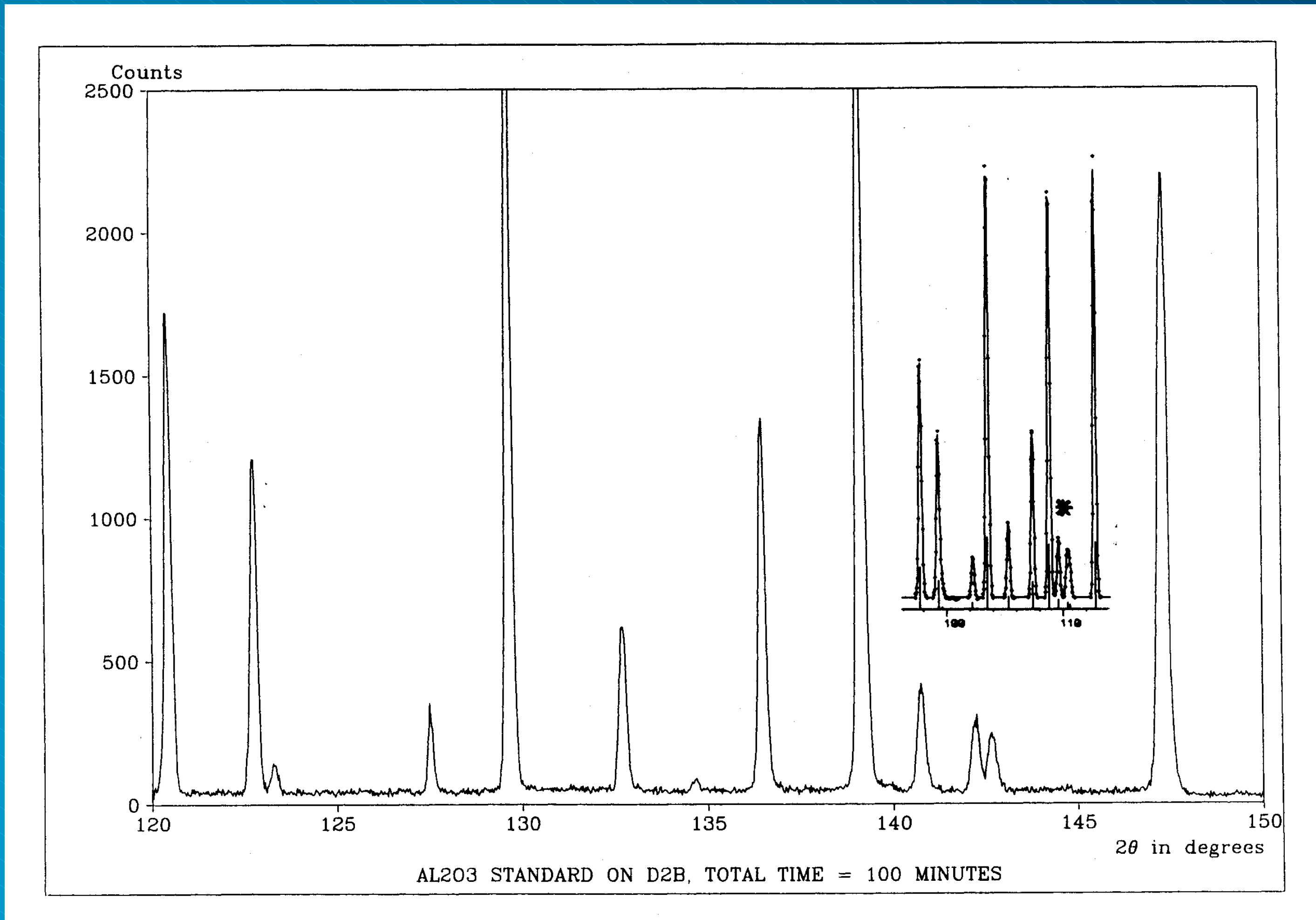
Comparison of D2B with old D1A

- Al2O3 standard IUCr intercomparison sample



- *Note the splitting of Al2O3 peaks

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The Second Generation (80's)

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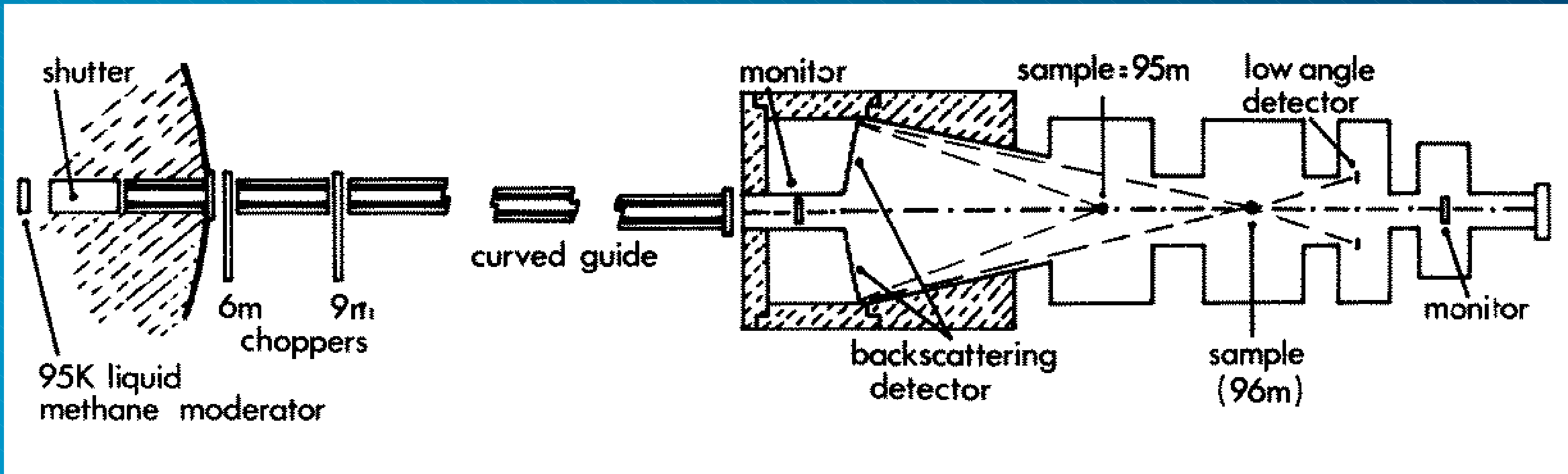
- **New Time-of-flight diffractometers (E.Steichele, Munich)**
  - **J. Jorgensen, Argonne (SEPD, GPPD)**
  - **B. Fender et al., Rutherford; W. David et al. ISIS (HRPD)**



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

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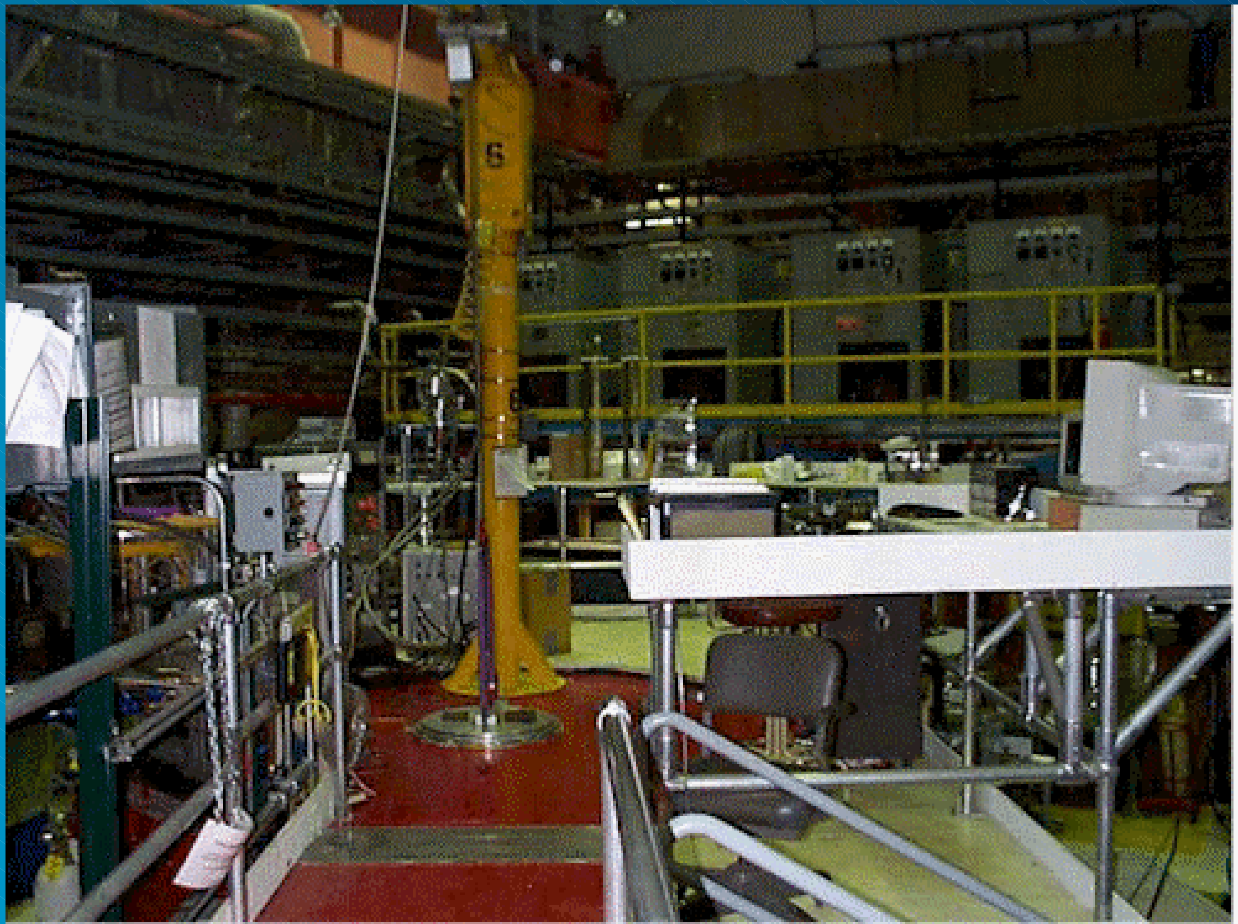
The Second Generation (80's)



- **GPPD Argonne (General Purpose Powder Diffractometer)
  J. Jorgensen et al.**

HRPD "Outstation" at ISIS

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ILL “Outstation” at ESRF ?

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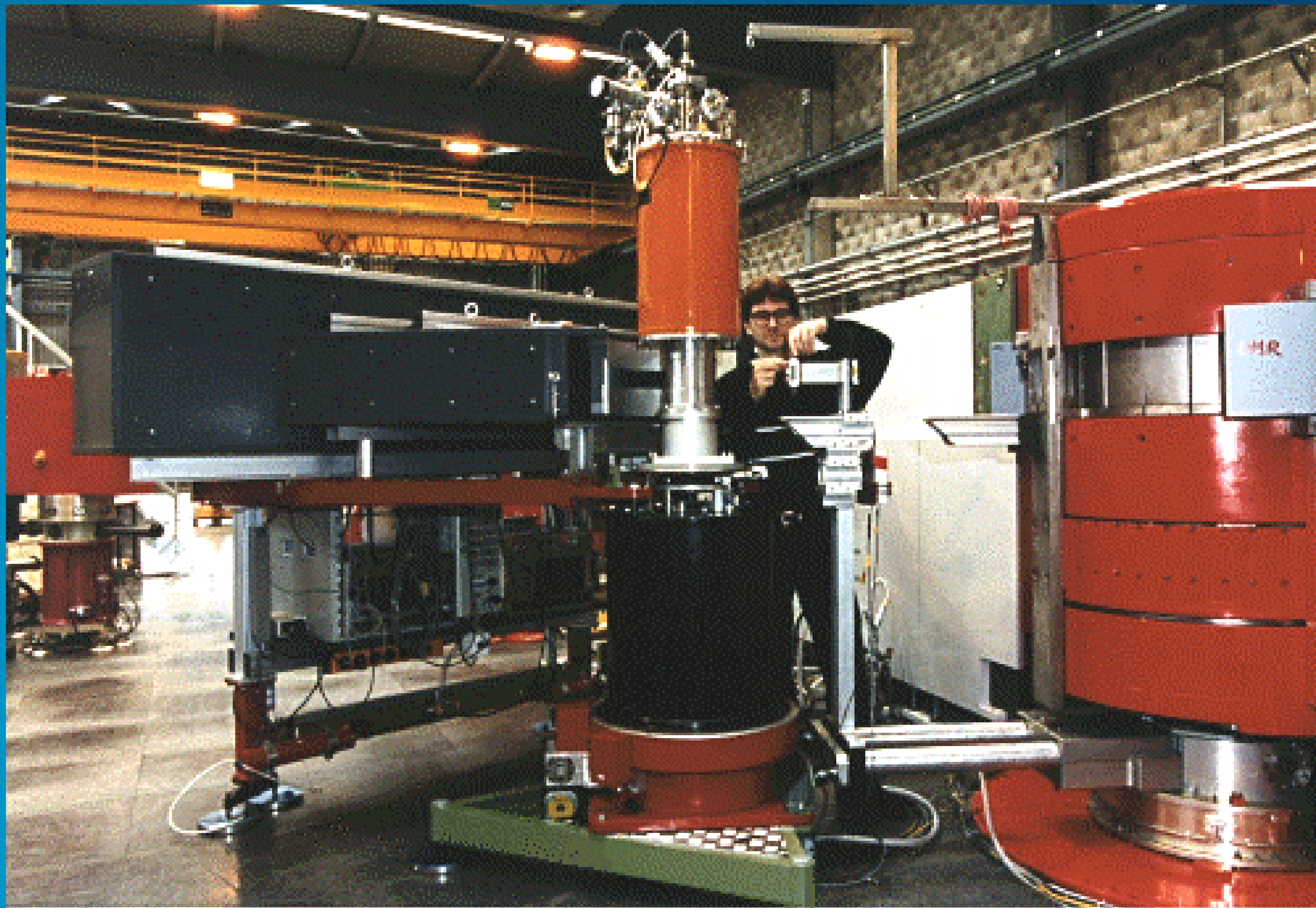
The Second Generation (80's)



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

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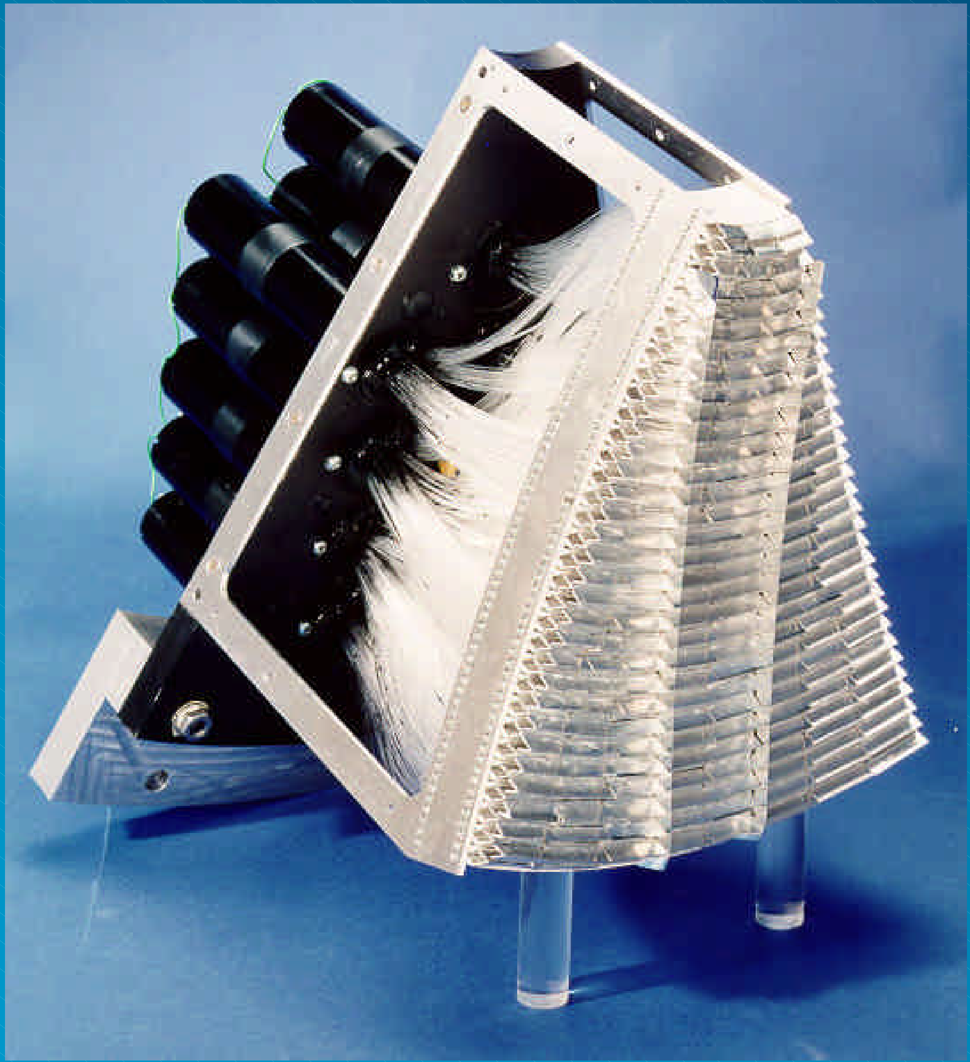
The Future - Big Detectors



- **HRPD ISIS**
  - **New scintillator detector element.**
  - **Project for new 90º (medium resolution) detector bank**

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The Future - Big Detectors

- **GEM ISIS**

  Element of an array of detectors for a very fast medium resolution machine

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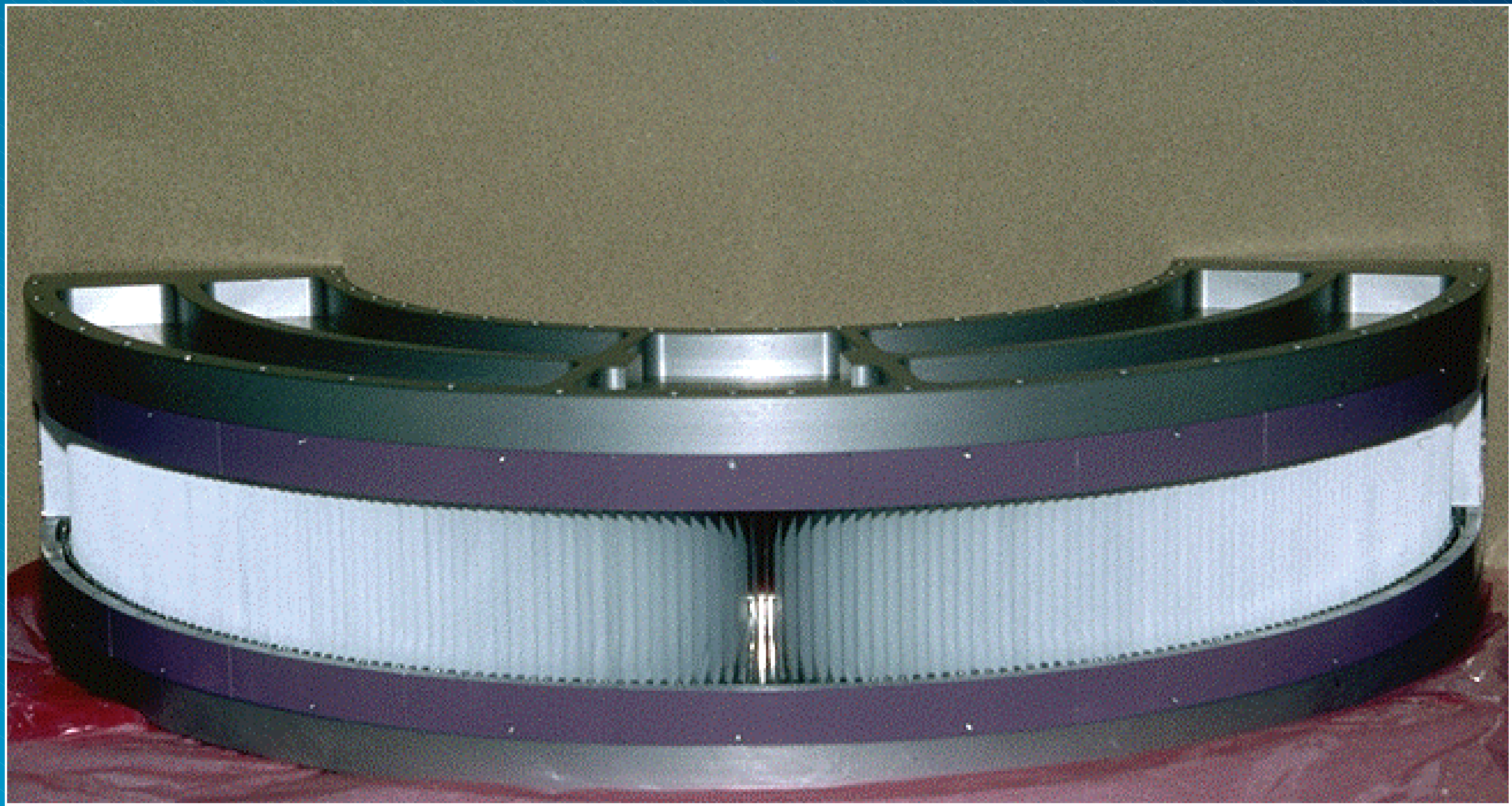
The Future - Big Detectors

1600 wire PSD on a continuous neutron source



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

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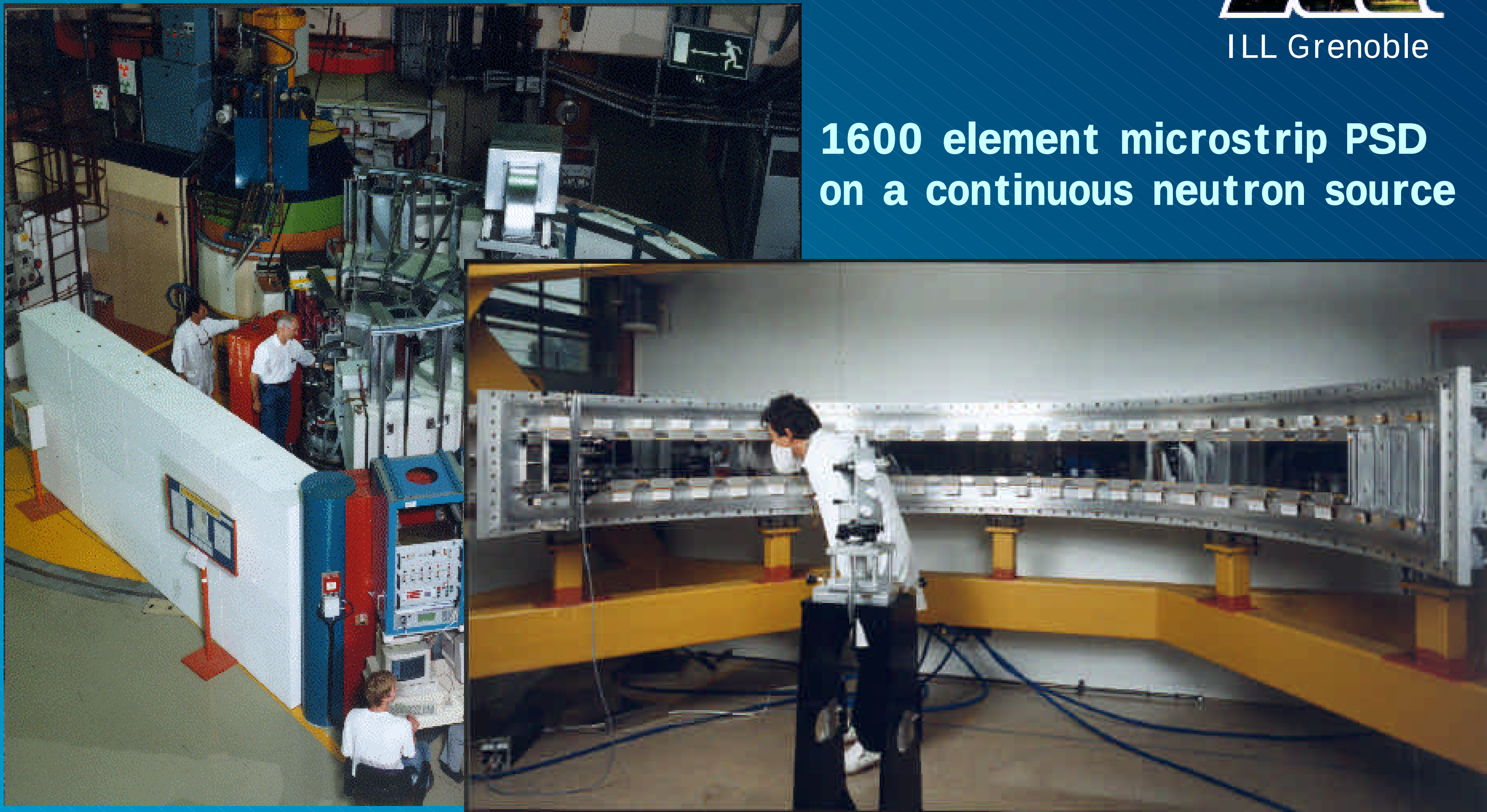
The Future - Big Detectors



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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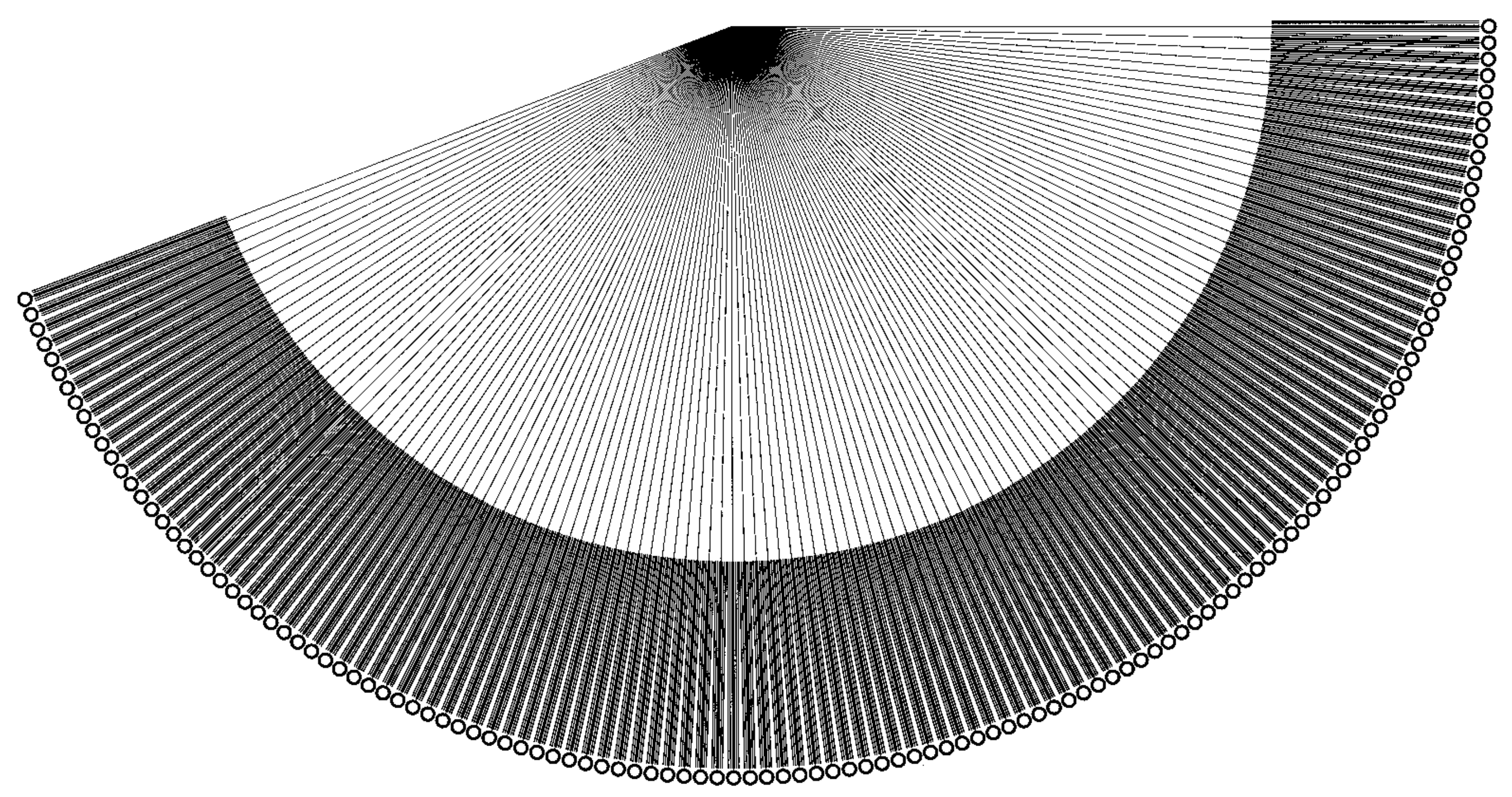
The Future - Big Detectors

Large detector array on a continuous neutron source



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

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RR & most cited Neutron Papers

RR has had the biggest impact of any neutron technique

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Magnetism, Phase T/Ns, Ionic conductors, Zeolites, and especially High-Tc superconductors

- Beno,MA. Soderholm,L. Capone,DWII. Hinks,DG. Jorgensen,JD. Grace,JD. Schuller,IK. Segre,CU. Zhang,K. (1987) Appl.Phys.Lett. **51** 57-59
  Structure of the single-phase high-temperature superconductor Y Ba2 Cu3 O7-delta
- Capponi,JJ. Chaillout,C. Hewat,AW. Lejay,P. Marezio,M. Nguyen,N. Raveau,B. Soubeyroux,JL. Tholence,JL. Tournier,R. (1987) Europhysics Letters **3** 1301-1307
  Structure of the 100 K Superconductor Ba2 Y Cu3 O7 between (5-300)K by Neutron Powder Diffraction
- Greedan,JE. O'Reilly,AH. Stager,CV. (1987) Phys.Rev.B,Condens.Mat. **35** 8770-8773
  Oxygen ordering in the crystal structure of the 93-K superconductor Y Ba2 Cu3 O7 using powder neutron diffraction at 298 and 79.5 K
- David,WIF. Harrison,WTA. Gunn,JMF. Moze,O. Soper,AK. Day,P. Jorgensen,JD. Hinks,DG. Beno,MA. Soderholm,L. Capone,DW. Schuller,IK. Segre,CU. Zhang,K. Grace,JD. (1987) Nature (London) **327** 310-312
  Structure and crystal chemistry of the high Tc superconductor Y Ba2 Cu3 O7-x
- Hazen,RM. Finger,LW. Angel,RJ. Prewitt,CT. Ross,NL. Mao,HK. Hadidiacos,CG. Hor,PH. Meng,RL. Chu,CW. (1987) Phys.Rev.B,Condens.Mat. **35** 7238-7241
  Crystallographic description of phases in the Y-Ba-Cu-O superconductor.
- Izumi,F. Asano,H. Ishigaki,T. (1987) Japanese Journal of Applied Physics, Part 2 **26** L617-L618
  A Revised Structural Model for the Ba-Y-Cu-O Superconductor
- Francois,M. Walker,E. Jorda,JL. Yvon,K. Fischer,P. (1987) Solid State Commun. **63** 1149-1153
  Structure of the high-temperature superconductor Ba2 Y Cu3 O7 by X-ray and neutron powder diffraction.

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RR & most cited Neutron Papers

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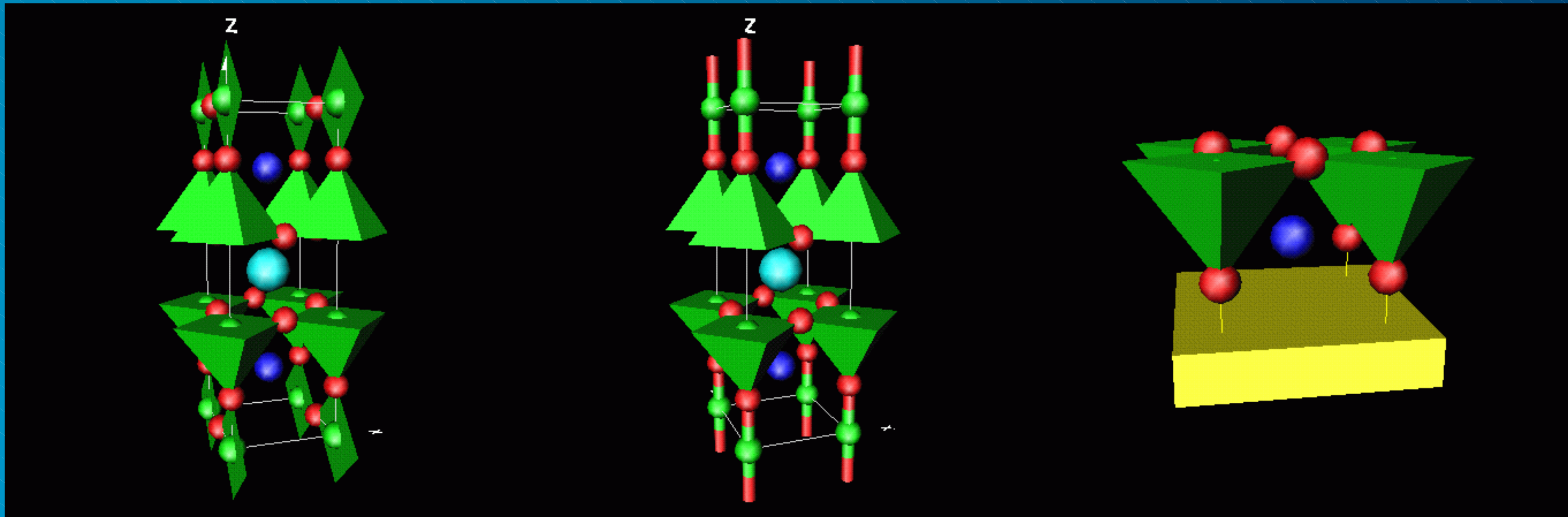
RR has had the biggest impact of any neutron technique

Most cited contribution - "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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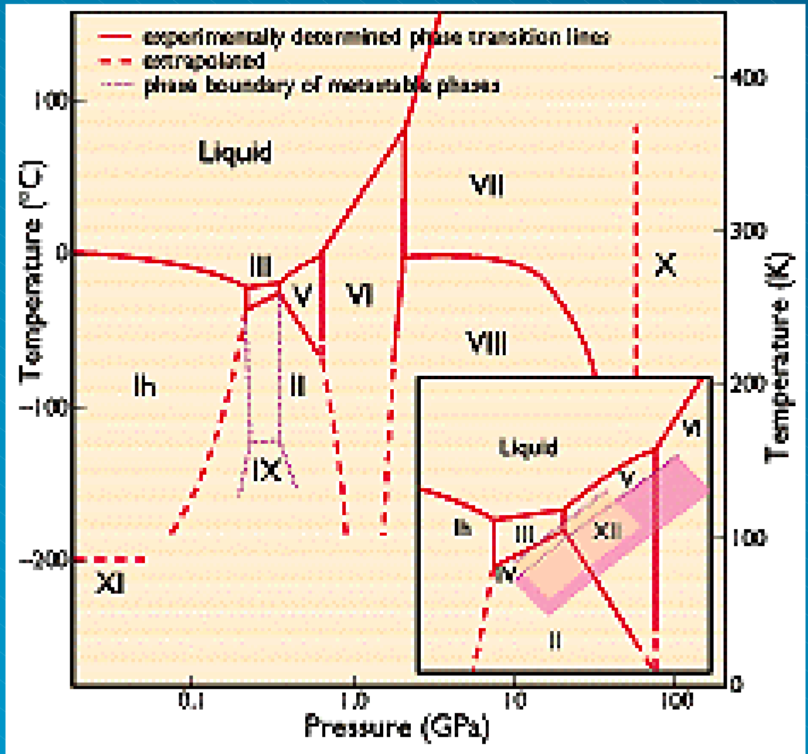
High Pressure Powder Diffraction

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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High Pressure Powder Diffraction

New phases of Ice discovered by neutron diffraction

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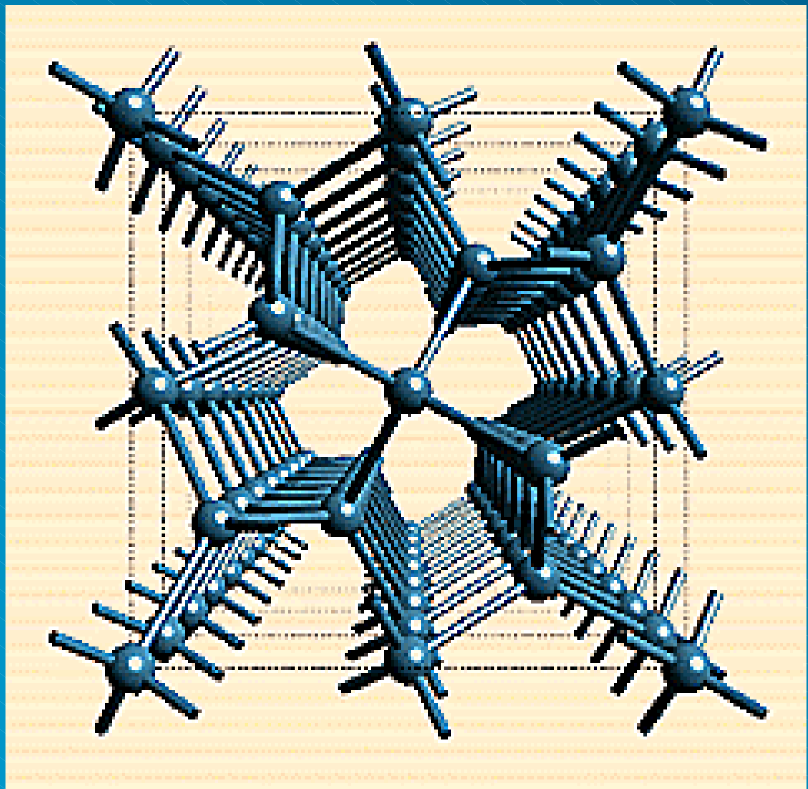

- **Mixture of 5- and 7-membered rings of Ice XII.**
- **Delicate balance between compting ice phases tests water potential functions in chemicl & biological systems**
- **Model metastable structures**

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

Paris-Edinburgh pressure cell for neutron diffraction

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- Compact high pressure cell which allows pressures ~50 kbar and eventuallly ~200 kbar.
- X-ray and especially synchrotron pressure cells can go much higher, but neutrons needed for many interesting model systems containing hydrogen r light atoms - ice, ammonium salts etc
- Microsyposium Sunday 8th 10:00,Monday 9th 14:45
  - High Pressure Structure & Phase T/Ns (S.Hull, J.Parise et al)
  - High Pressure Data Acquisition & Analysis (powder)

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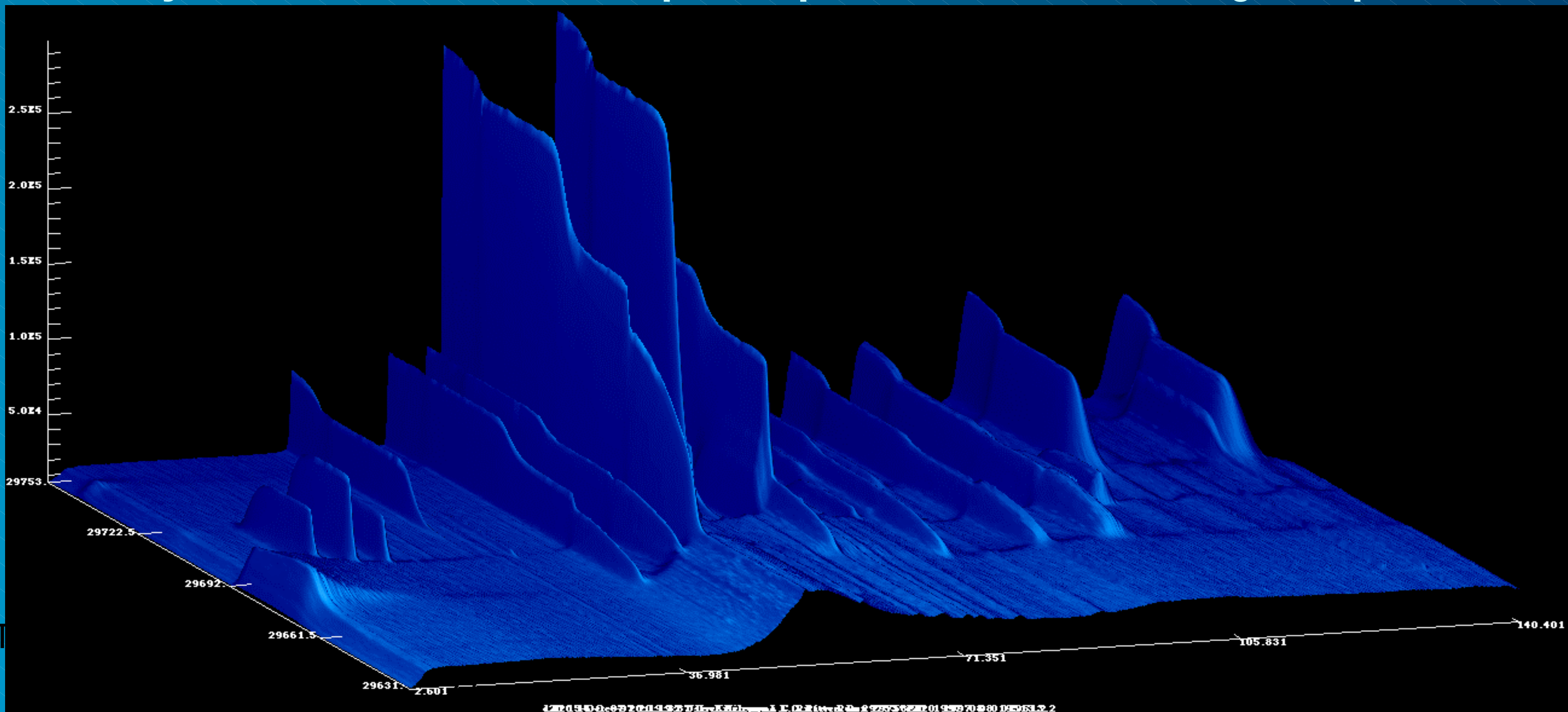
Applications of large fast detectors

Real-time Phase Diagrams (eg D20, future GEM)

- Kilcoyne et al.: (see lecture by Thomas Hansen, Saturday am)
  Crystallisation from amorphous pases with increasing temperature



- Complete diffraction pattern in seconds, scan through temperature
- Microsymposium Saturday 7th 10:00 “In Situ studies using Powders”

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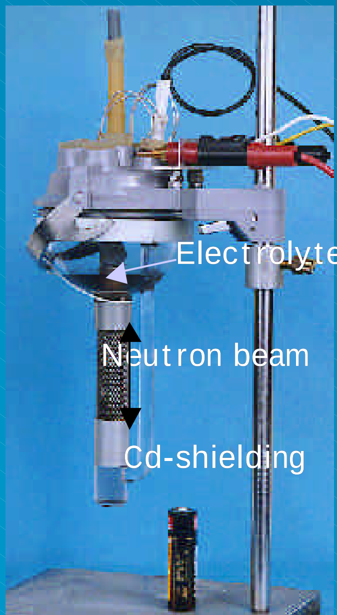
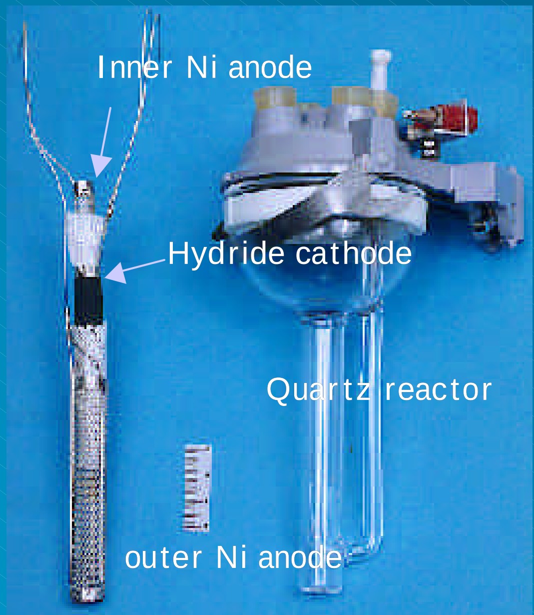
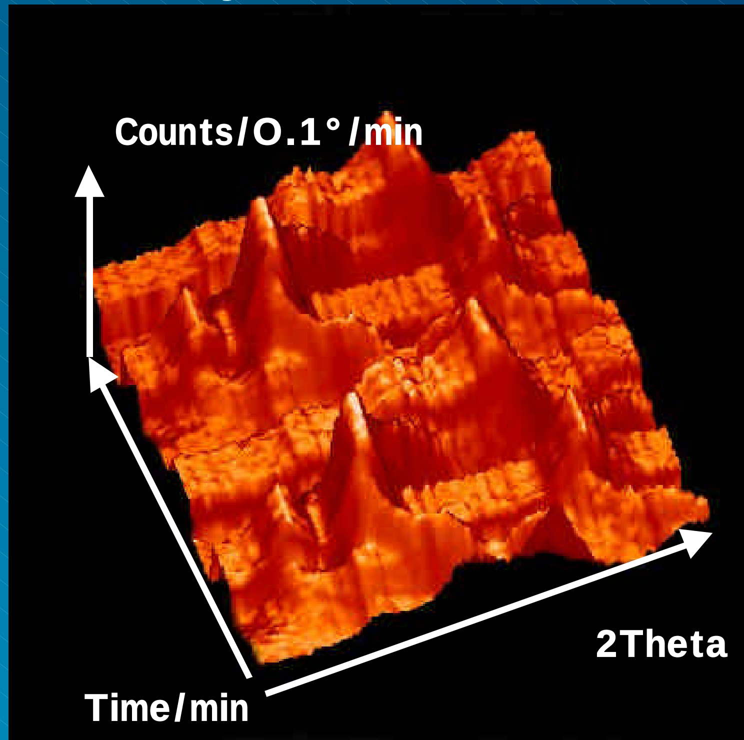
Applications of large fast detectors

Real-time electro-chemistry

- **Latronche, Chabre et al.: (lecture by Thomas Hansen, Saturday am)**
  In-situ Charging and discharging of metal hydride electrodes LaNi5







Discharging

Charging

Discharging

Charging

- **Follow chemical changes with battery charge/dischage cycle**
- **Microsymposium Sunday 8th 10:00 (Advanced Batteries & Fuel Cells)**

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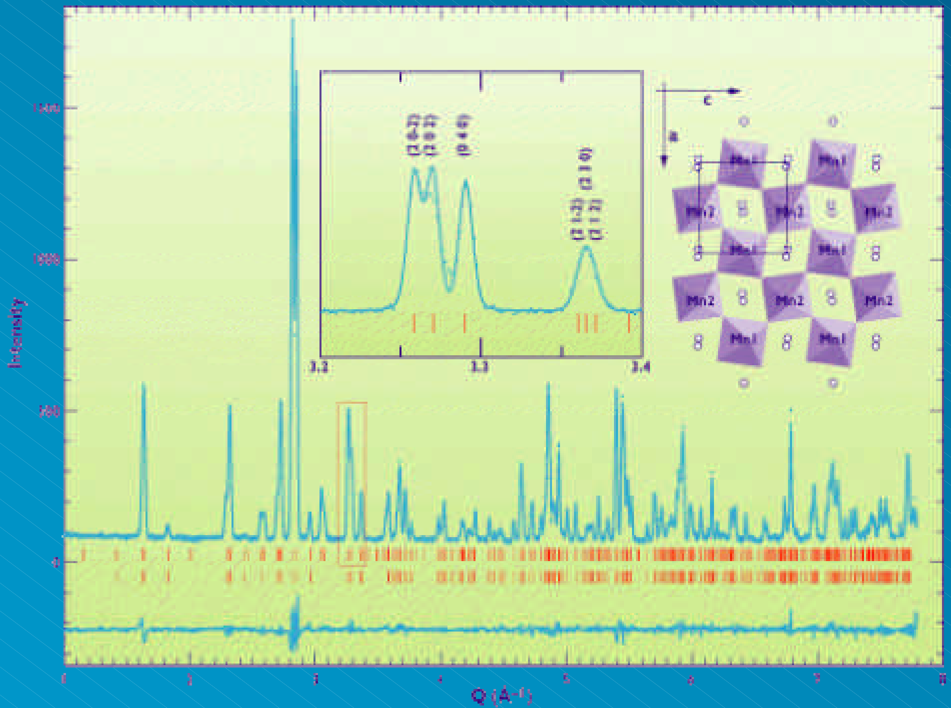
Giant Magneto-Resistive Ceramics $La_{0.333}Ca_{0.667}MnO_3$



- Caignaert, Suard, Maignan, Simon, Raveau (1996) J.Mag.Mag.Mat.153,L260
- Radaelli, Cox, Capogna, Cheong, Marezio (1998)
- Fernandez-Diaz, Martinez, Alonso, Herrero (1999) Phys.Rev.B59,1277

Giant Magneto-Resistive Ceramics $La_{0.333}Ca_{0.667}MnO_3$

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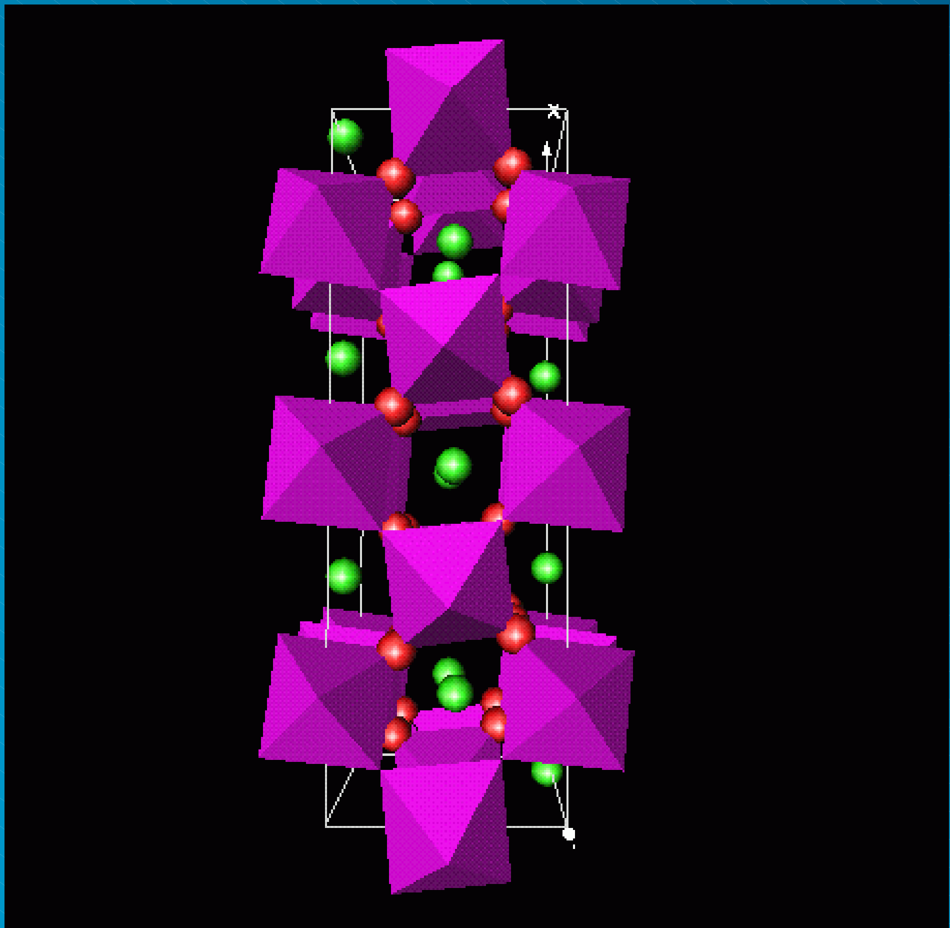

- Very large changes in electrical resistivity with temperature
- cf oxide superconductors
- mixed valence charge-ordering Mn^{3+}/Mn^{4+}
- GMR effect near room temperature
- applications to magnetic storage of data (new high density IBM hard disks)

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Stripes and Charge Ordering

1D-ordering ? Dimensionality important for theory.

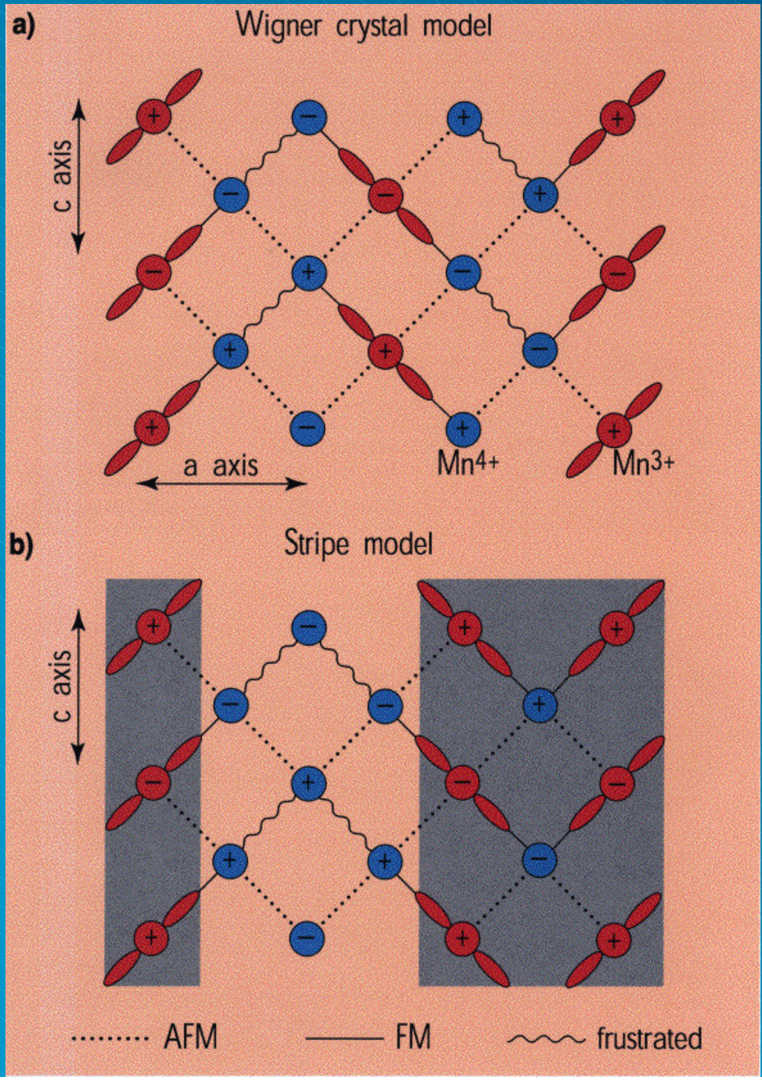
Mori et al. Nature (1998) 392,473
Other papers in Phys. Rev. Letters

- **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)**

Alan Hewat
ILL Grenoble

Stripes and Charge Ordering

1D-ordering ? Dimensionality important for theory.



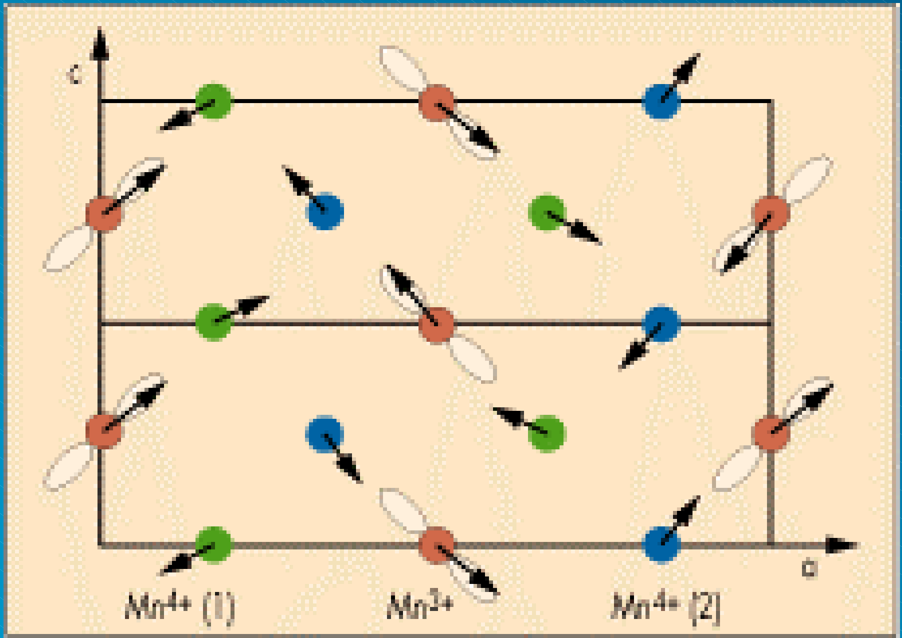
- **Expect instead Mn^{3+}/Mn^{4+} to be uniformly distributed (2D Wigner crystal model of Goodenough)**
- **The 1D-stripe model would have very important consequences for the theory of superconductors and GMR oxides**

Alan Hewat

ILL Grenoble

Stripes in GMR oxides ?

Magnetic+Oxide+T/N - Neutron powder diffraction



Fernandez-Diaz et al. (1999)
Phys. Rev B59, 1277.
Neutron work on D1B+D2B
(ILL)

- **A classical problem for RR of neutron powder data**
  - **magnetic structure**
  - **details of oxygen structure**
  - **destructive phase transition**

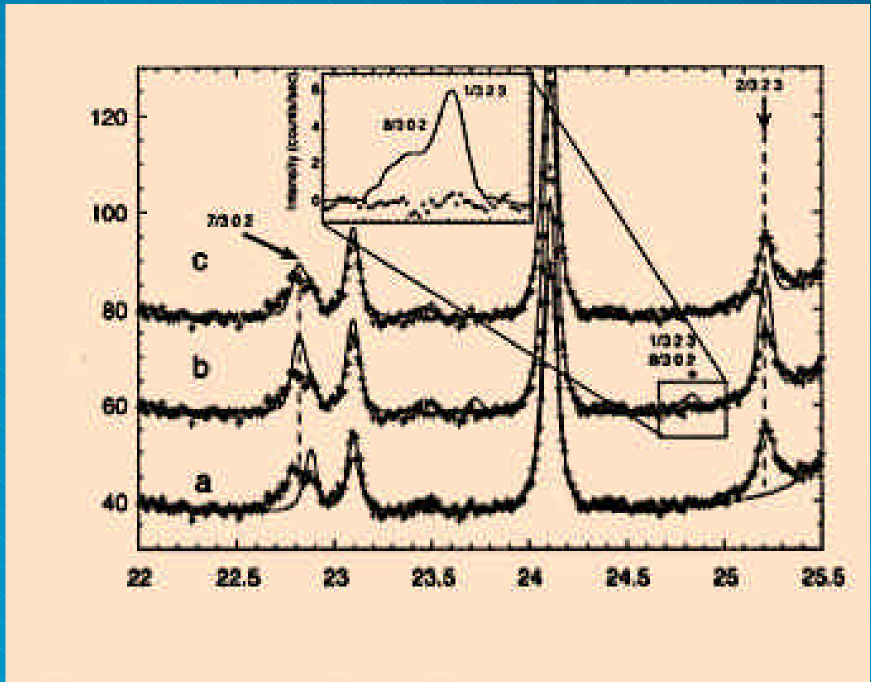
- **Magnetic structure of $La_{0.33}Ca_{30.67}MnO_3$**
  - **consistent with the Wigner model, symmetry difficult to reconcile with a stripe model**

Alan Hewat

ILL Grenoble

Stripes in GMR oxides ?

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 and superstructure**
- **High resolution neutron powder data (ILL Grenoble) allows refinement of the real structure**
- **The stripe structure is not supported**
  - **P. Radaelli,**
  - **J.Rodriguez, D.Argyriou et al**
  - **Thursday 12th**

Alan Hewat
ILL Grenoble

30 Years of Rietveld Refinement Neutron Powder Diffraction

- What was Achieved ? Exciting new science ?
  - High impact even outside the crystallographic community
  - Magnetism, Superconductors, Giant Magneto-Resistance
  - Keynote Lecture Friday 6th D. Cox
- Why Neutrons ? Why not X-rays ?
  - Neutrons+X-rays complementary
  - Solution of structures with X-rays (C. Baerlocher Thur 12th)
  - Refinement of important details with neutrons
- Why Powders ? Why not crystals ?
  - Crystals are use when available
  - Much new work started with powders - high Tc, GMR...
- Why Rietveld ?
  - Friday 6th “Challenging Rietveld” B. von Dreele et al.