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
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

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

- What was Achieved?
  - Interesting new science?

- Why Neutrons?
  - Why not X-rays?

- Why Powders?
  - Why not crystals?

- Why Rietveld?
  - Why not F-extraction?
Why Neutrons?

- **Relative Scattering Powers of the Elements**

![Diagram showing scattering powers of different elements with electrons, X-rays, and neutrons.]

- Neutrons scatter strongly from light elements
  (Because neutron scattering is a nuclear interaction)
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)
30 Years of Rietveld Refinement
Neutron Powder Diffraction

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 $M_3\text{UO}_6$
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First Applications of Rietveld Refinement

- H.M. Rietveld

Structure of Heavy Metal salts

The Structure of Some Alkaline-Earth Metal Uranates
30 Years of Rietveld Refinement
Neutron Powder Diffraction

Heavy metal oxides are still with us - Superconductors, GMR

- 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.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ drawing from Capponi et al 1987
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$_4$S$_8$ - the famous example given in the original Rietveld manual
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
Why Powders?

- Rietveld Refinement at Harwell, UK (1972)
  - Already 3 years after Rietveld’s paper!

  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
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
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)
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
Numbers of Studies using RR

- 3804 Structures with Neutron RR

(According to the Inorganic Crystal Structure Database http://barns.ill.fr)
Numbers of Studies using RR

- 3804 Structures with Neutron RR
- 3146 Structures with X-ray RR
### Numbers of Studies using RR

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

![Screen shot of ILL database](image)
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
Refinement of Rietveld?

(Semantic question of Ray Young & Terry Sabine)

1995 - Aminoff Prize presented to Hugo Rietveld by King Carl Gustaf of Sweden
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
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.
Comparison of D1A with old D2 at ILL

- The same Al2O3 sample on D1A (top) and the old D2 at ILL.
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 …)
Early Days at ILL Grenoble (70's)

- Real-Time Chemistry on D1B at ILL (Riekel, Pannetier)
The Second Generation (80's)

- High Resolution with Very Large Detector banks (D2B, ILL)
Comparison of D2B with old D1A

- Al2O3 standard IUCr intercomparison sample

*Note the splitting of Al2O3 peaks
The Second Generation (80's)

- 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.
The Second Generation (80's)

- GPPD Argonne (General Purpose Powder Diffractometer)
  J. Jorgensen et al.
HRPD “Outstation” at ISIS
ILL “Outstation” at ESRF?
The Second Generation (80’s)

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

- HRPD ISIS
- New scintillator detector element.
- Project for new 90° (medium resolution) detector bank
The Future - Big Detectors

• GEM ISIS

Element of an array of detectors for a very fast medium resolution machine
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.
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.
The Future - Big Detectors

Large detector array on a continuous neutron source

- Super-D2B at ILL Grenoble, very large high resolution detector
RR & most cited Neutron Papers

RR has had the biggest impact of any neutron technique

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

  Structure of the single-phase high-temperature superconductor Y Ba_2 Cu_3 O_7-delta

  Structure of the 100 K Superconductor Ba_2 Y Cu_3 O_7 between (5-300)K by Neutron Powder Diffraction

  Oxygen ordering in the crystal structure of the 93-K superconductor Y Ba_2 Cu_3 O_7 using powder neutron diffraction at 298 and 79.5 K

  Structure and crystal chemistry of the high Tc superconductor Y Ba_2 Cu_3 O_7-x

  Crystallographic description of phases in the Y-Ba-Cu-O superconductor.

  A Revised Structural Model for the Ba-Y-Cu-O Superconductor

  Structure of the high-temperature superconductor Ba_2 Y Cu_3 O_7 by X-ray and neutron powder diffraction.
RR & most cited Neutron Papers

RR has had the biggest impact of any neutron technique

Most cited contribution - “charge reservoir” concept in oxide superconductors

- Superc. $\text{YBa}_2\text{Cu}_3\text{O}_7$
- Non-superc. $\text{YBa}_2\text{Cu}_3\text{O}_6$
- Charge Reservoir

Cava, R. J. et al. (1990). Physica C. 165: 419 (Bell labs/CNRS/ILL)

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

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.

High Pressure Powder Diffraction

Paris-Edinburgh pressure cell for neutron diffraction

- Compact high pressure cell which allows pressures ~50 kbar and eventually ~200 kbar.

- X-ray and especially synchrotron pressure cells can go much higher, but neutrons needed for many interesting model systems containing hydrogen or 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)
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 phases with increasing temperature

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

- Follow chemical changes with battery charge/discharge cycle
- Microsymposium Sunday 8th 10:00 (Advanced Batteries & Fuel Cells)
Giant Magneto-Resistive Ceramics

$\text{La}_{0.333}\text{Ca}_{0.667}\text{MnO}_3$

- Radaelli, Cox, Capogna, Cheong, Marezio (1998)
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)
Stripes and Charge Ordering

1D-ordering? Dimensionality important for theory.

- Remarkable electron microscope images of 1D stripe pattern in GMR $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$

- Evidence also for 1D ordering in high-Tc superconductors ($\text{Cu}^{3+}$ stripes, spin-ladders etc)

Other papers in Phys. Rev. Letters
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
Stripes in GMR oxides?

Magnetic+Oxide+T/N - Neutron powder diffraction

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

- Magnetic structure of $\text{La}_{0.33}\text{Ca}_{30.67}\text{MnO}_3$
  - consistent with the Wigner model, symmetry difficult to reconcile with a stripe model

Fernandez-Diaz et al. (1999)
Neutron work on D1B+D2B (ILL)
Stripes in GMR oxides?

Neutron + Synchrotron Powder Diffraction

- 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

X-ray work on X7A (BNL)
Neutron work on D2B (ILL)
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.