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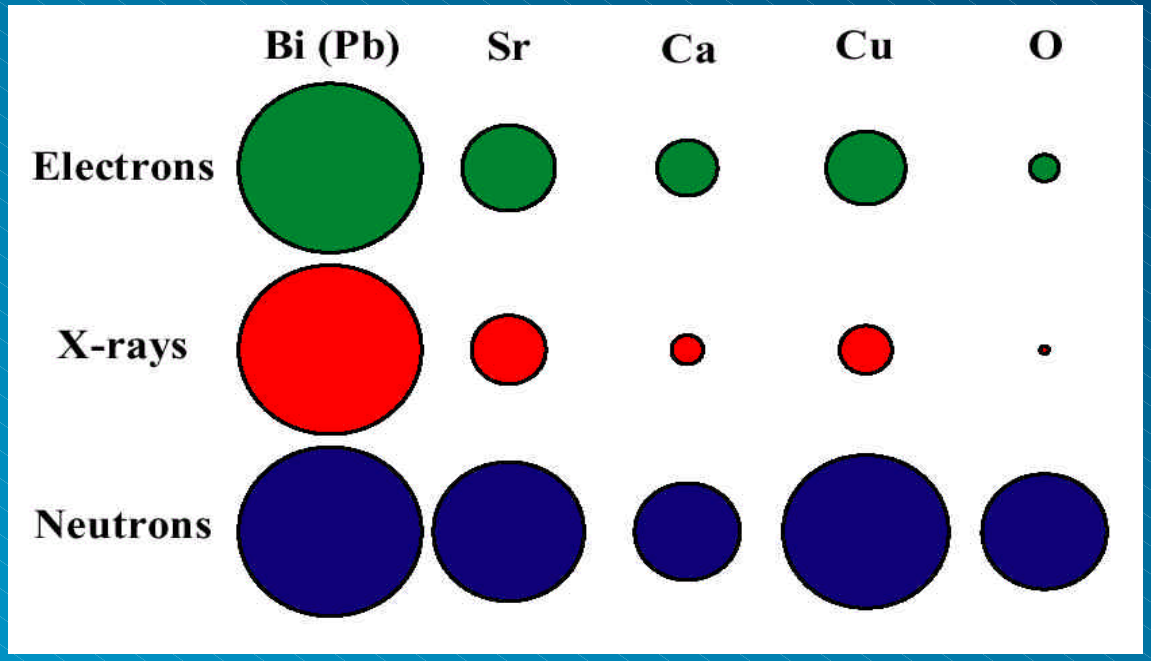
Why Neutrons ?

- **Relative Scattering Powers of the Elements**



- **Neutrons scatter strongly from light elements**

(Because neutron scattering is a nuclear interaction)

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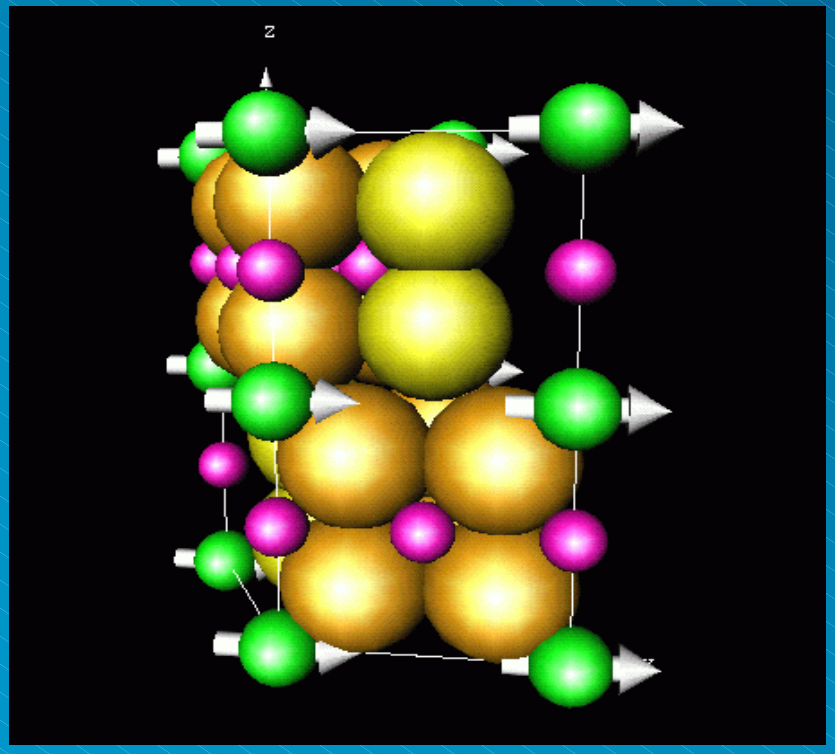
Why Neutrons ?

- **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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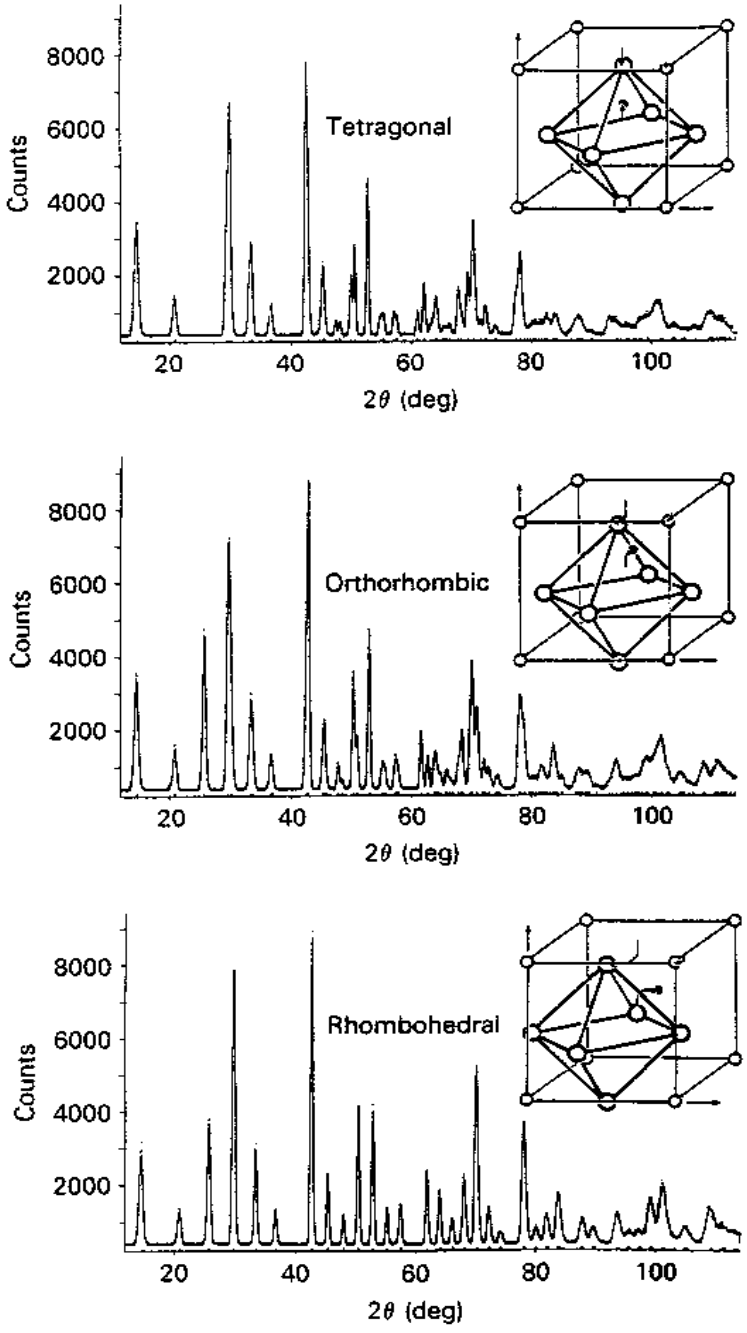
Why Powders ?



- **Destructive Phase T/Ns**
  - **Classical Perovskite transitions**
    Small displacements of light atoms
  - **Subtle changes in the powder 'profile'**
    - interest of "Profile Refinement"
- **And no single crystals**
- **Examples:**
  - $KNbO_3$
  - $NaNbO_3$

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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)

Why not X-ray Powder Diffraction ?

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- 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…

Popularity of Neutron Powder Diffraction

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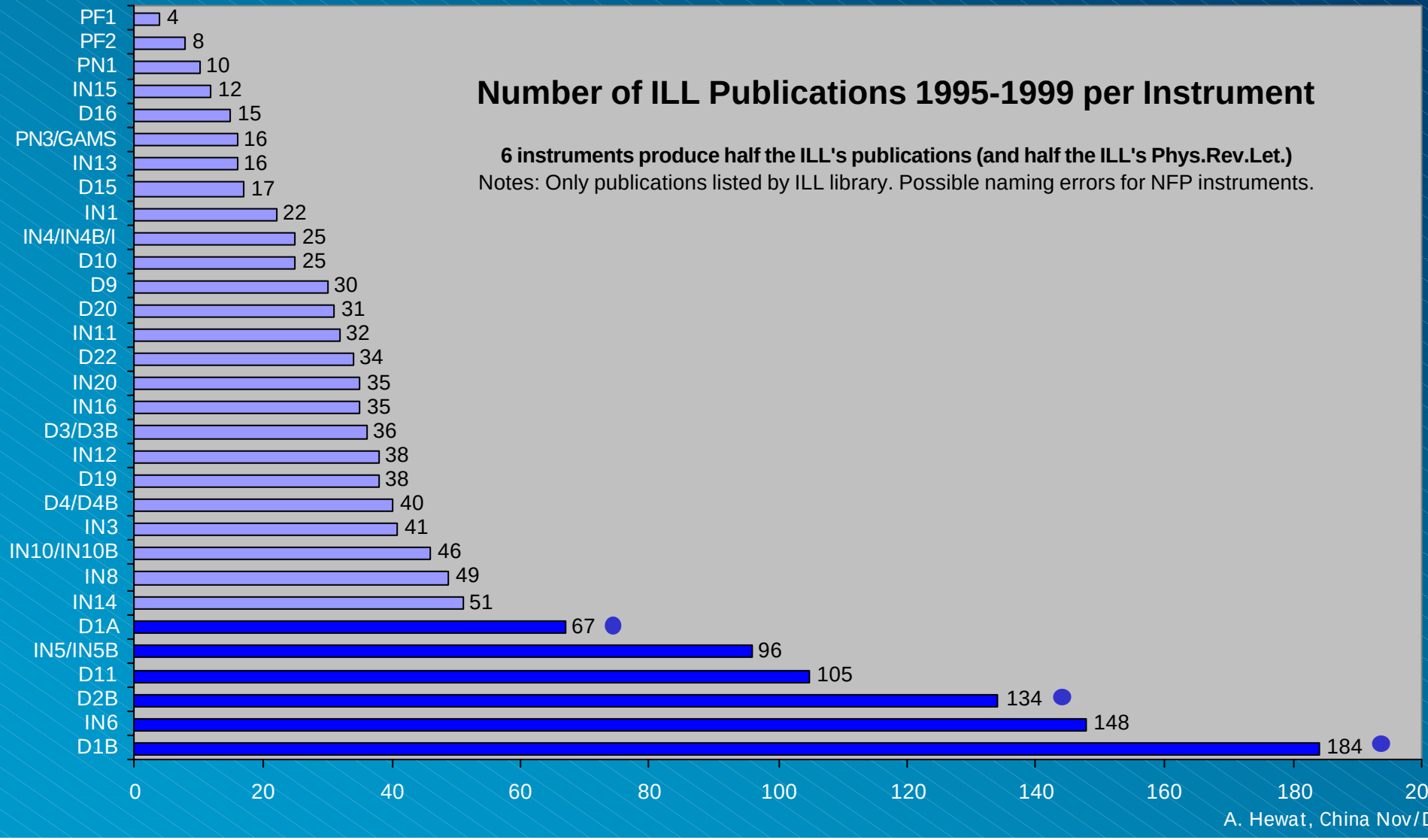

A. Hewat, China Nov/Dec 2000

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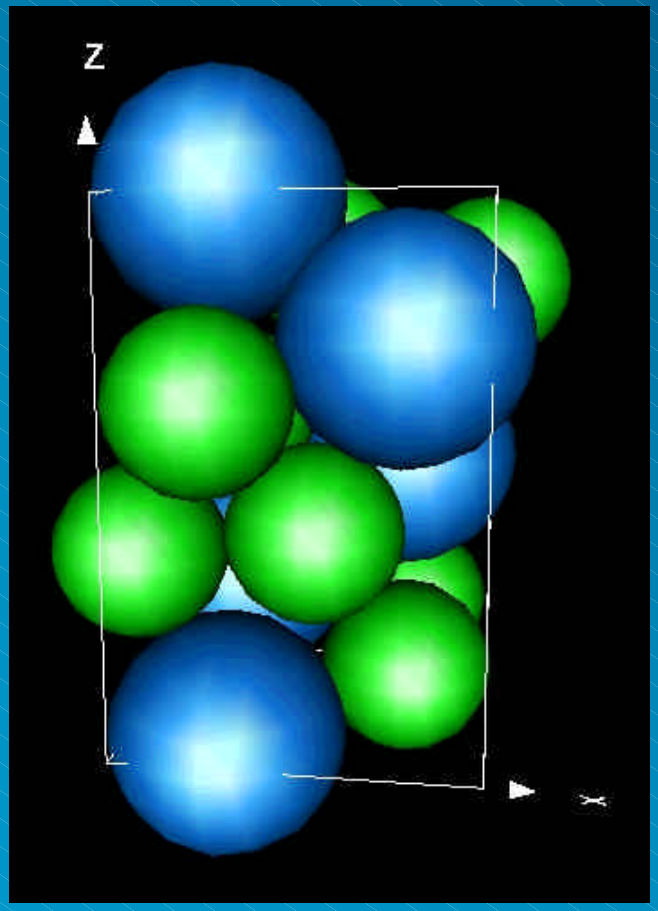
Neutron Powder Diffraction

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

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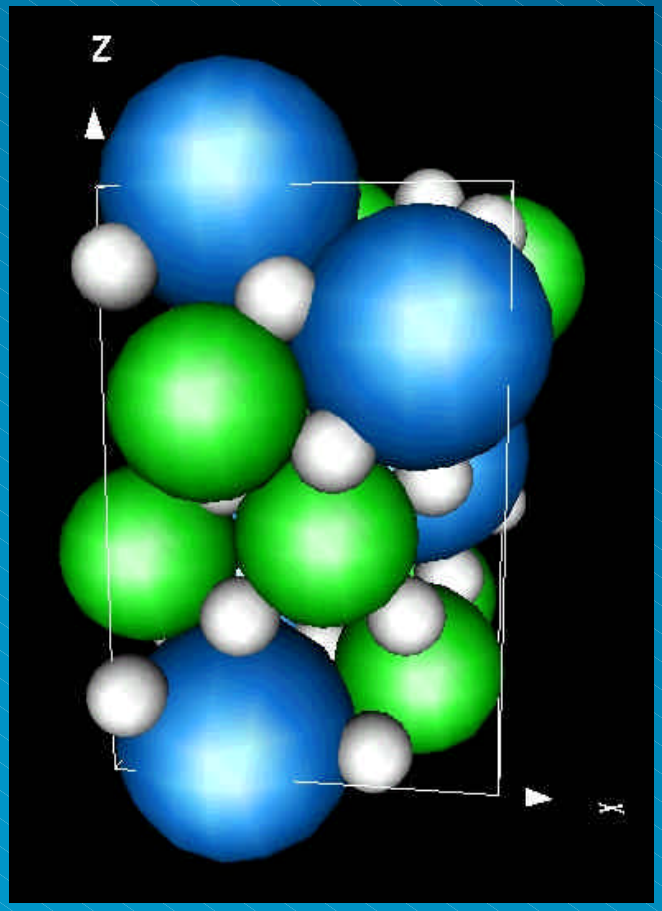

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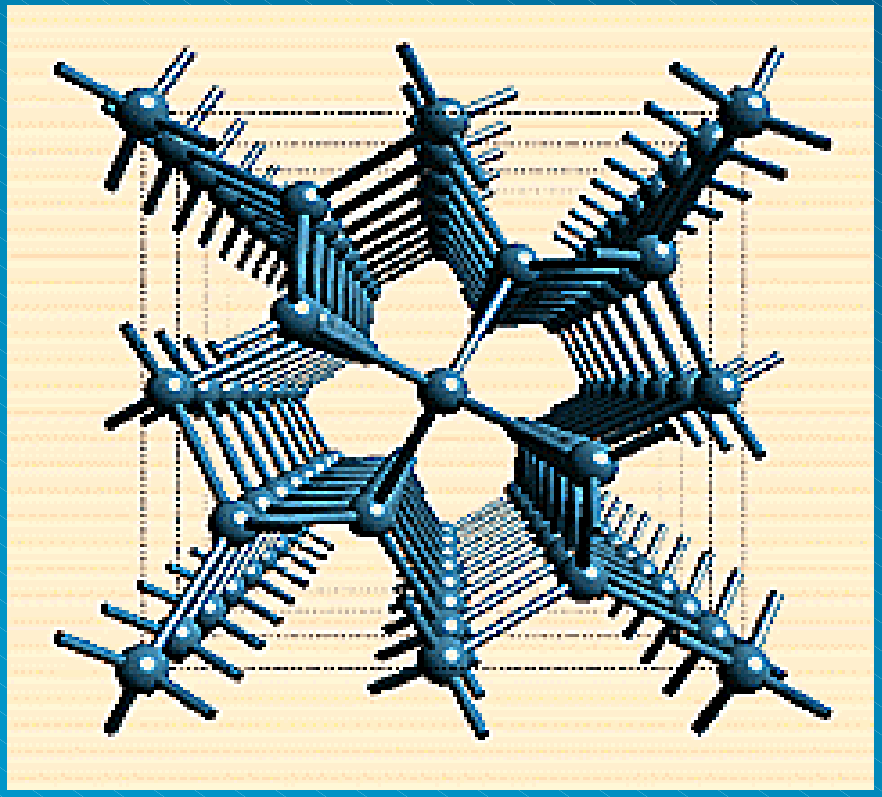
High Pressure Powder Diffraction

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

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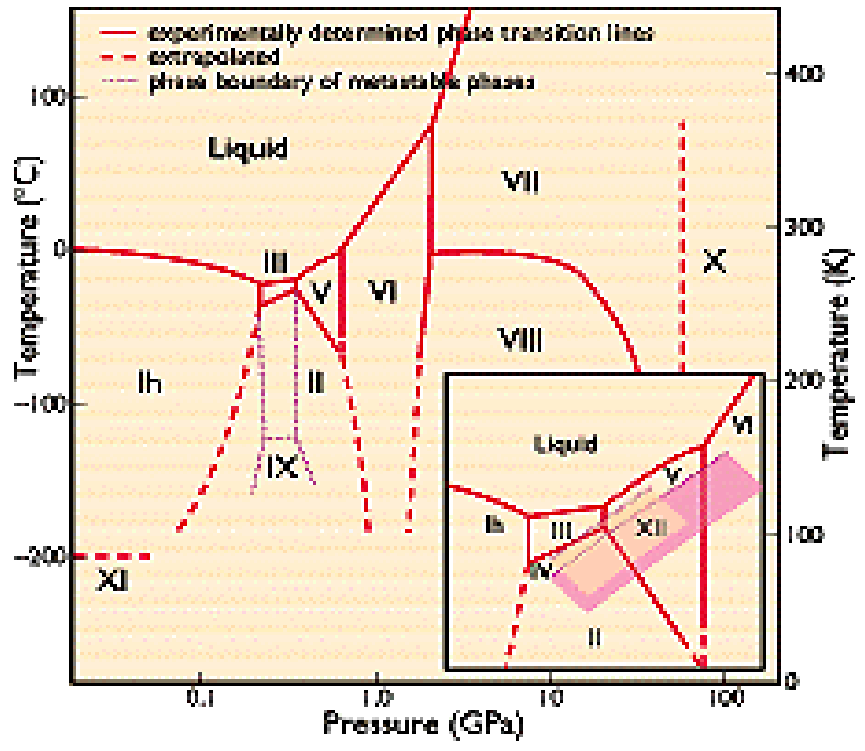

- **Ice-XII - densest form of ice without interpenetration**
- **Ice-IV - auto-clathrate interpenetration of H-bonds for even higher density**
- **Ice-He clathrate like Ice-II**

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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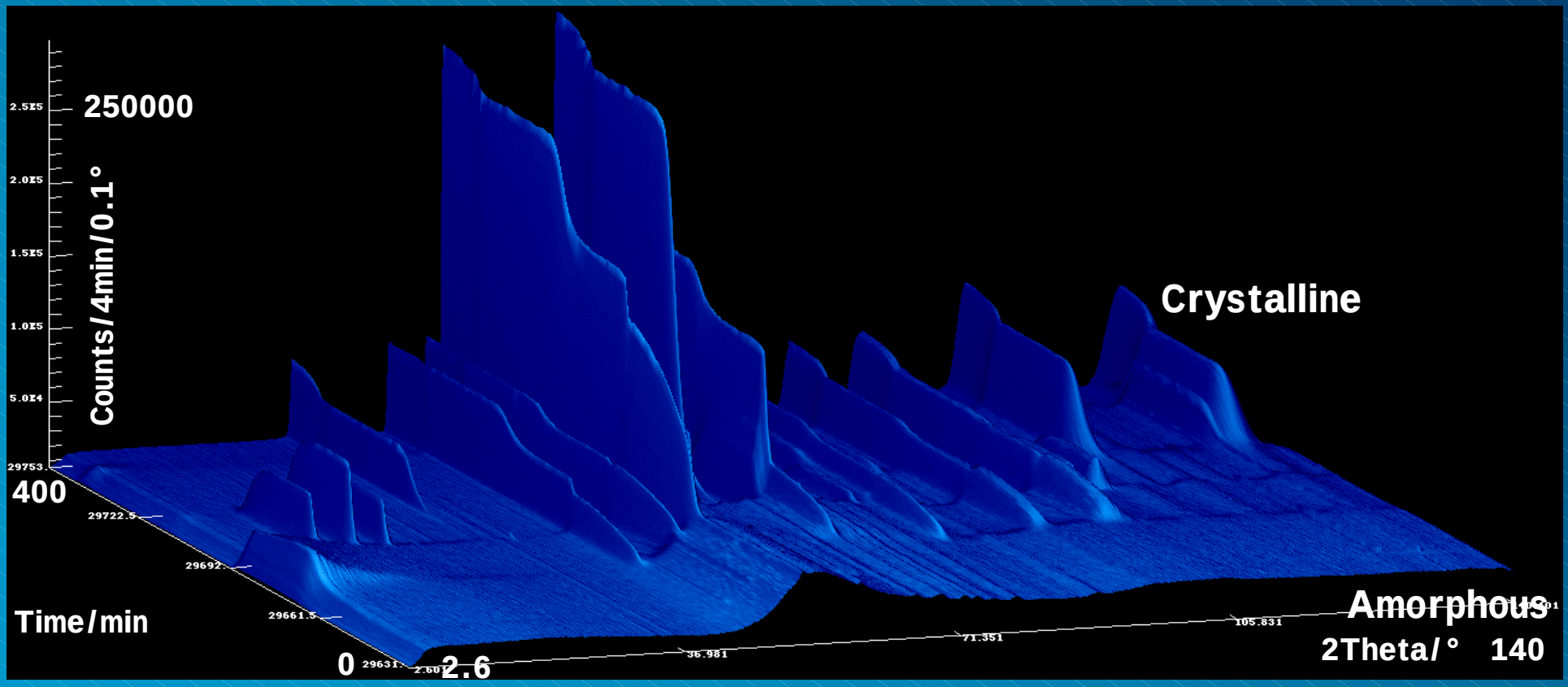
Sue Kilcoyne, Bob Cywinski et al.

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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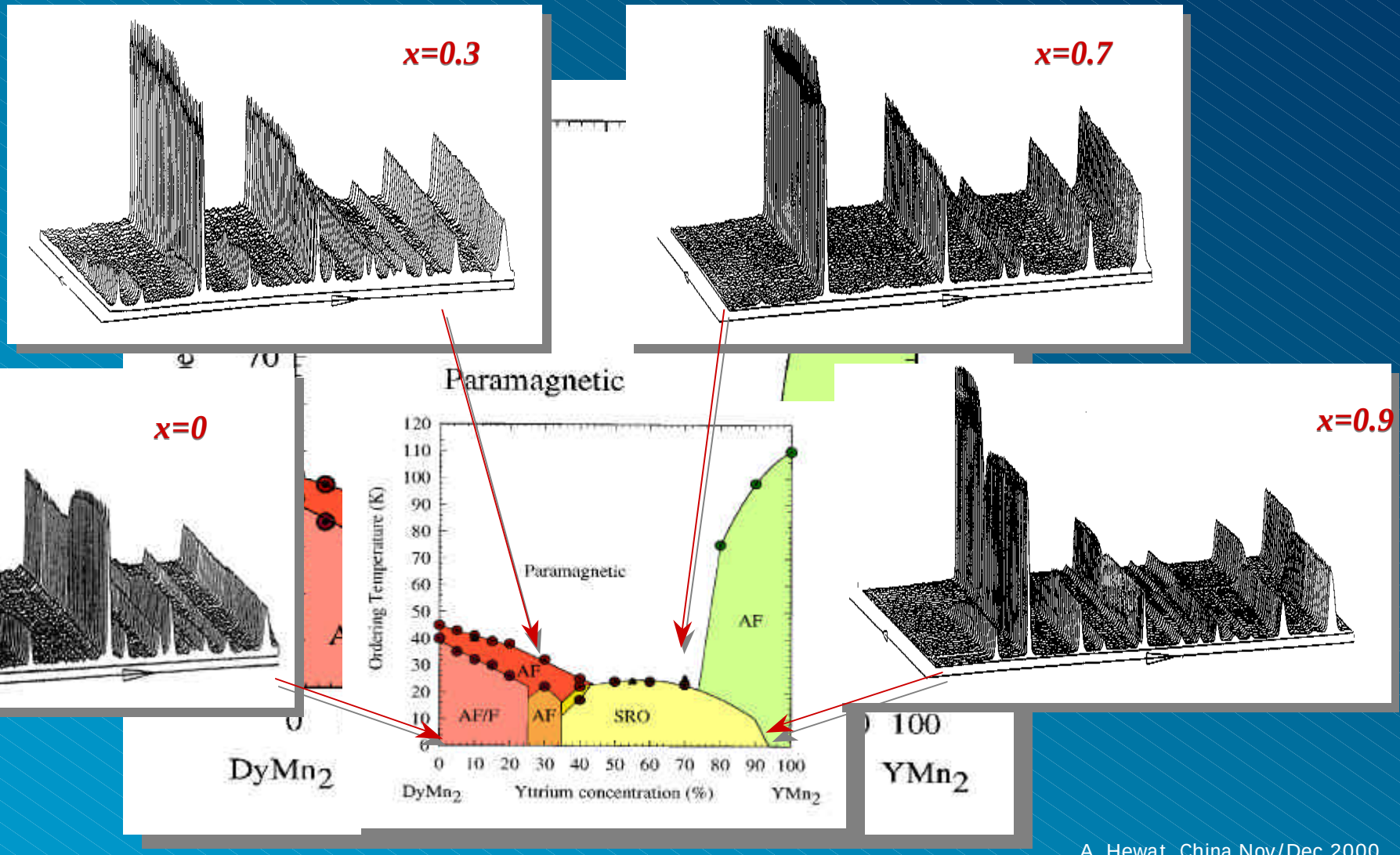

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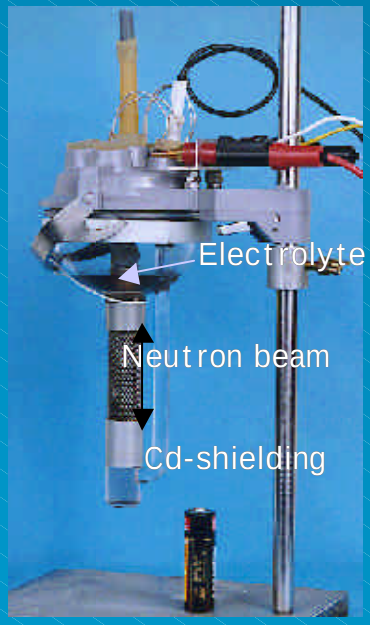
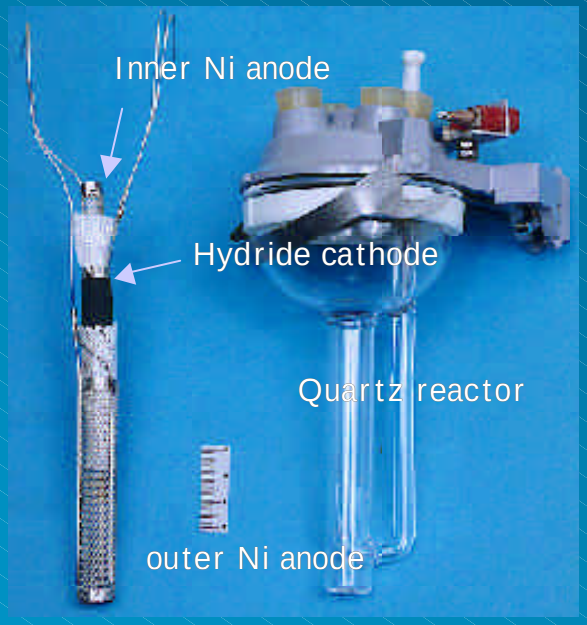
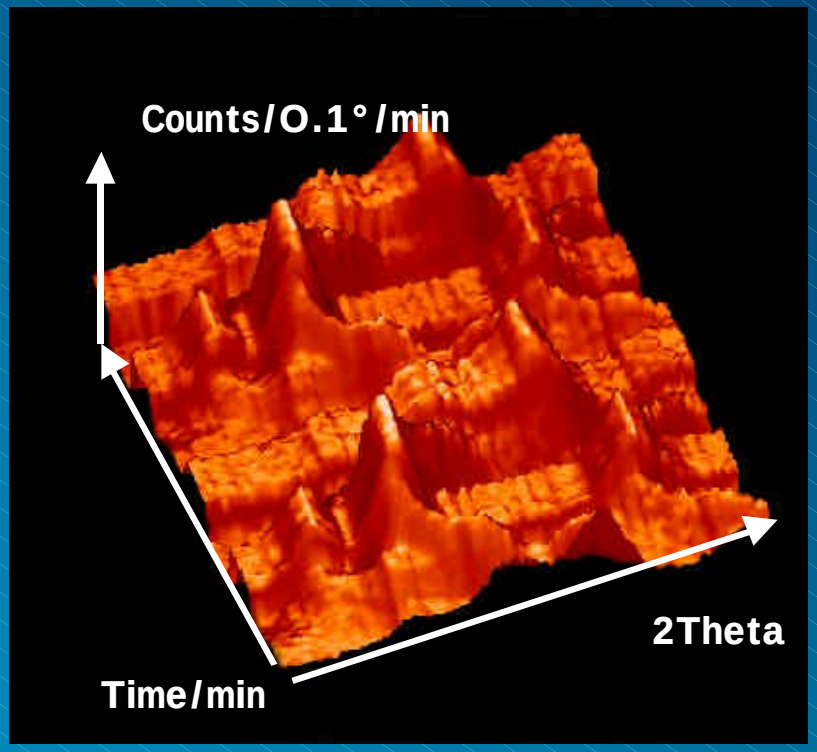
Applications of large fast detectors

Real-time electro-chemistry

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







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

Neutron Powder Diffraction and Novel Materials

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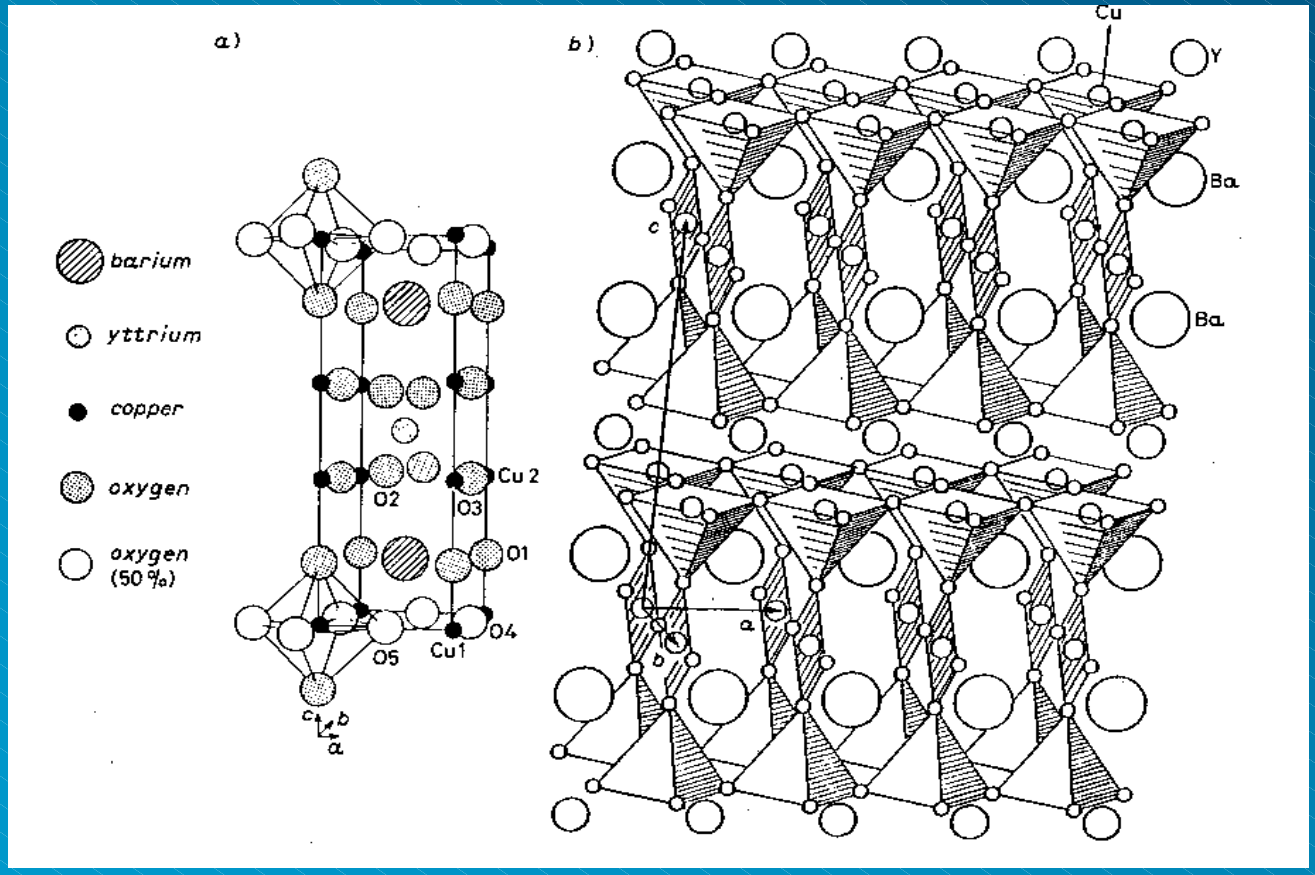
Why Use Neutron Powder Diffraction ?



- 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.

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

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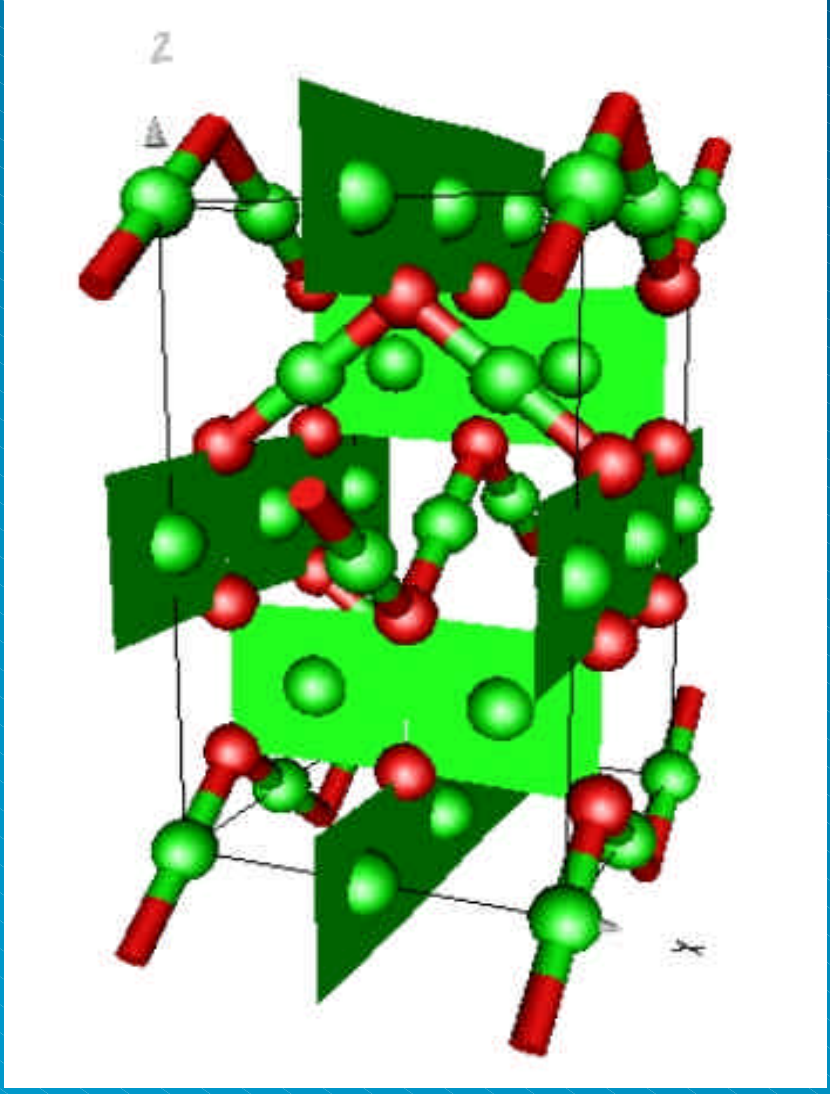
Valence Sum Calculations

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
  - 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

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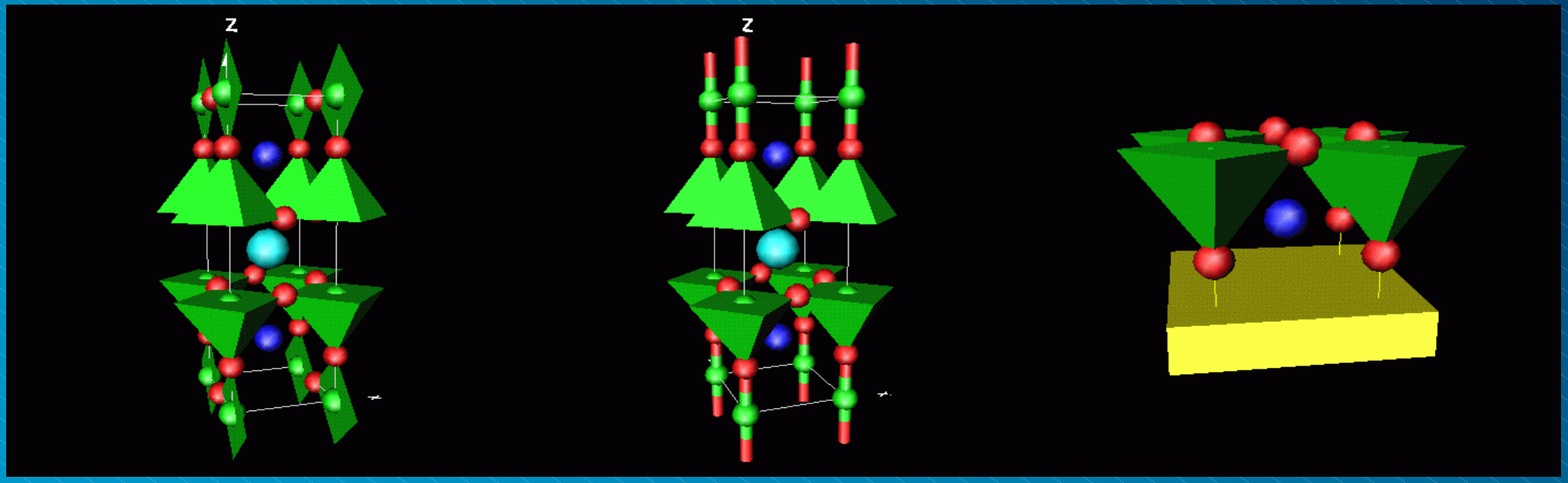
Valence Sums & “Charge Transfer”

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"

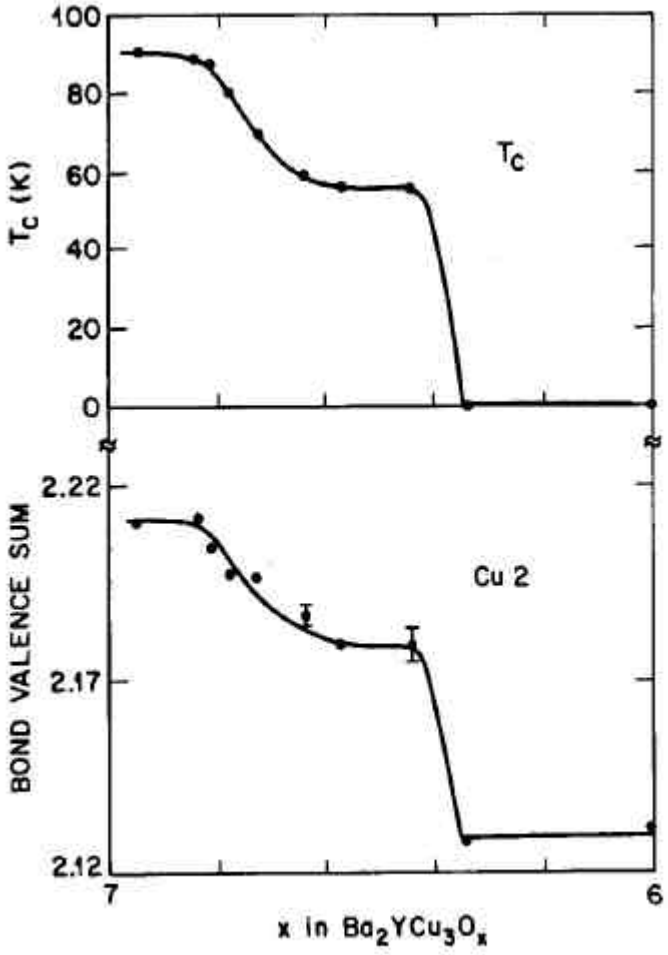

Fig. 16. Comparison of T_c and bond valence sum around the plane copper as a function of oxygen stoichiometry.

- 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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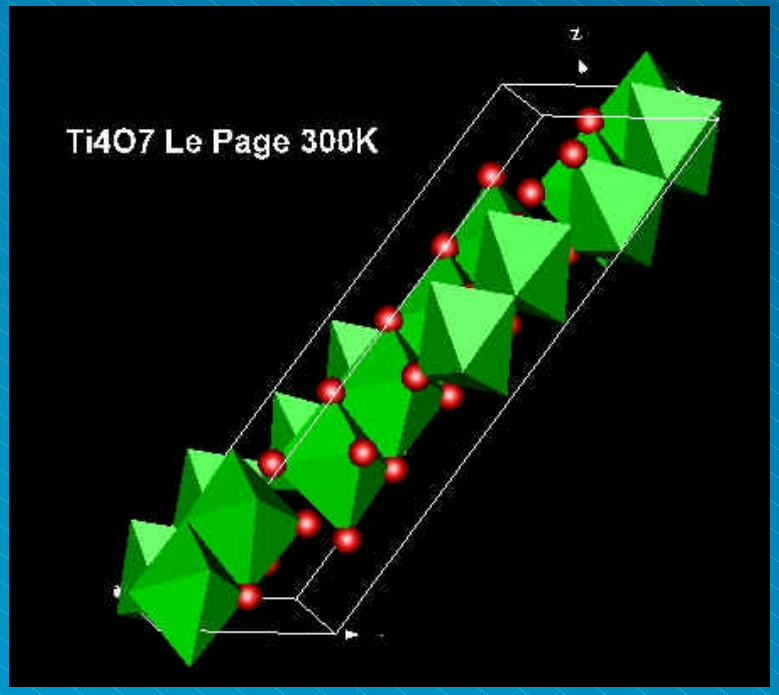
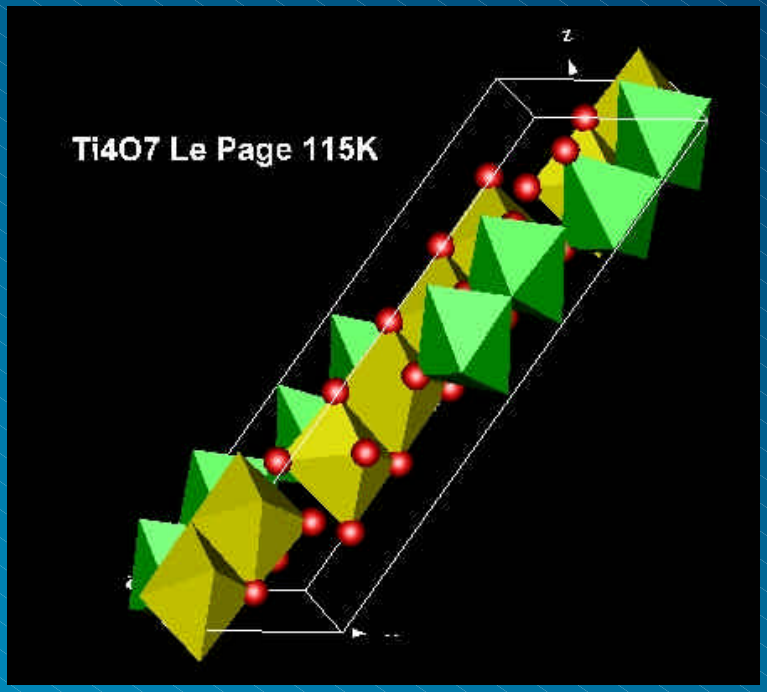
Electronic Order-Disorder

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





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

Neutron Powder Diffraction
Charge Transfer in $YNiO_3$

Marie-Theresa Fernandez-Diaz et al.

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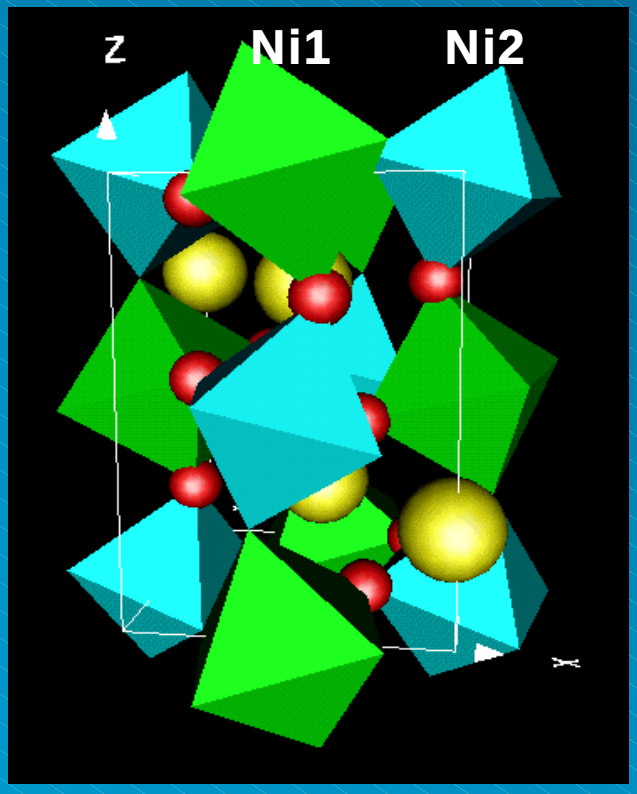
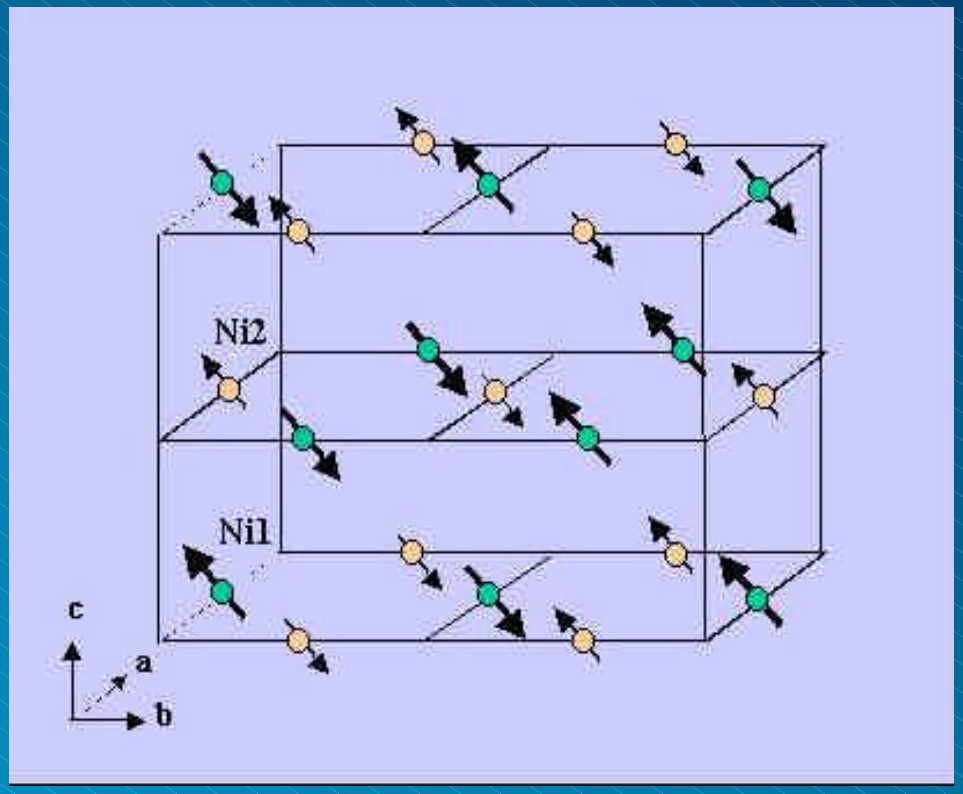
Combined ESRF, D1B and D2B data - Alonso J.A. et al (1999) PRL 82, 3873

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 μ_B M(Ni2) = 0.7 μ_B

Neutron Powder Diffraction
Charge Transfer in $YNiO_3$

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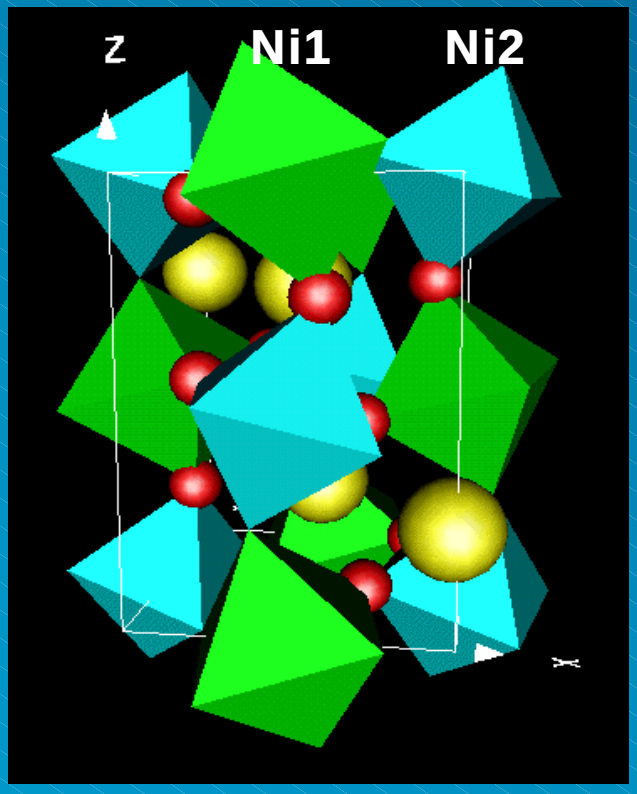

V(Ni1) = 2.62 V(Ni2) = 3.17

- 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

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

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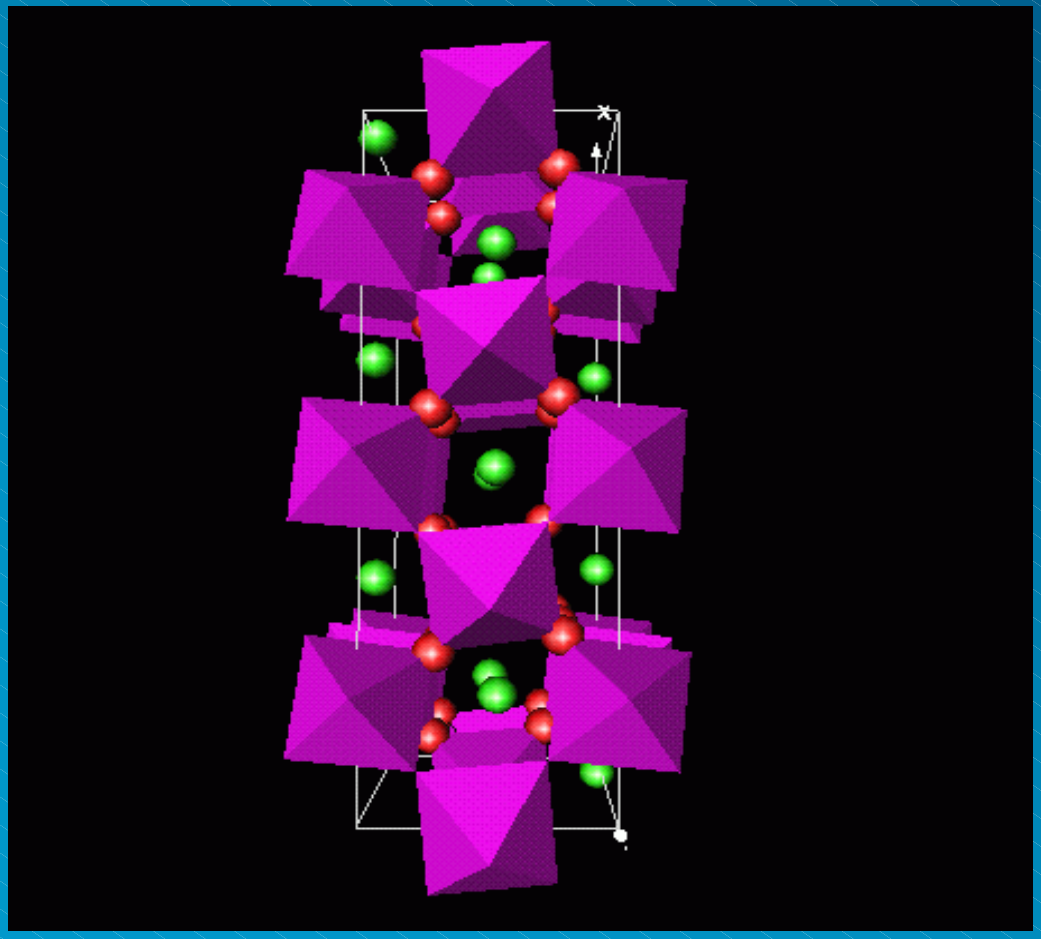

- Very large changes in electrical resistivity with temperature
- cf oxide superconductors
- mixed valence charge-ordering Mn^{3+}/Mn^{4+}
- GMR effect near room temperature
- applications to magnetic storage of data (new high density IBM hard disks)

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GMR 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)

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GMR Stripes and Charge Ordering

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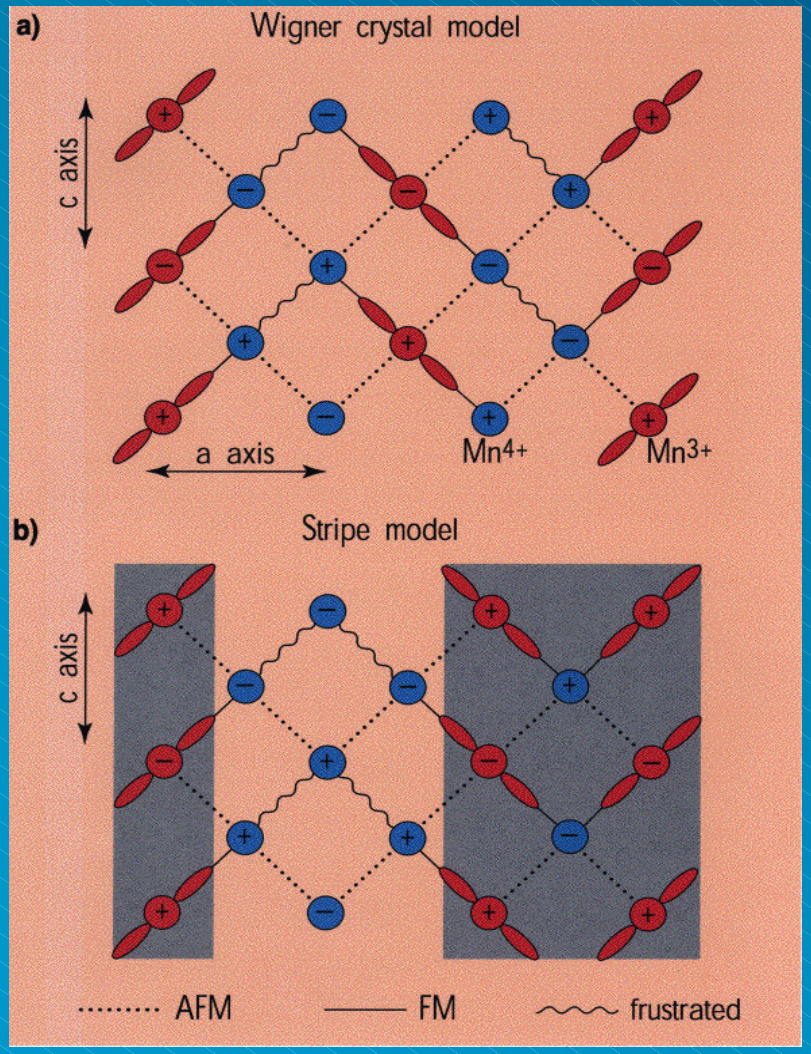

- Expect instead Mn^{3+}/Mn^{4+} to be uniformly distributed (2D Wigner crystal model of Goodenough)
- The 1D-stripe model would have very important consequences for the theory of superconductors and GMR oxides

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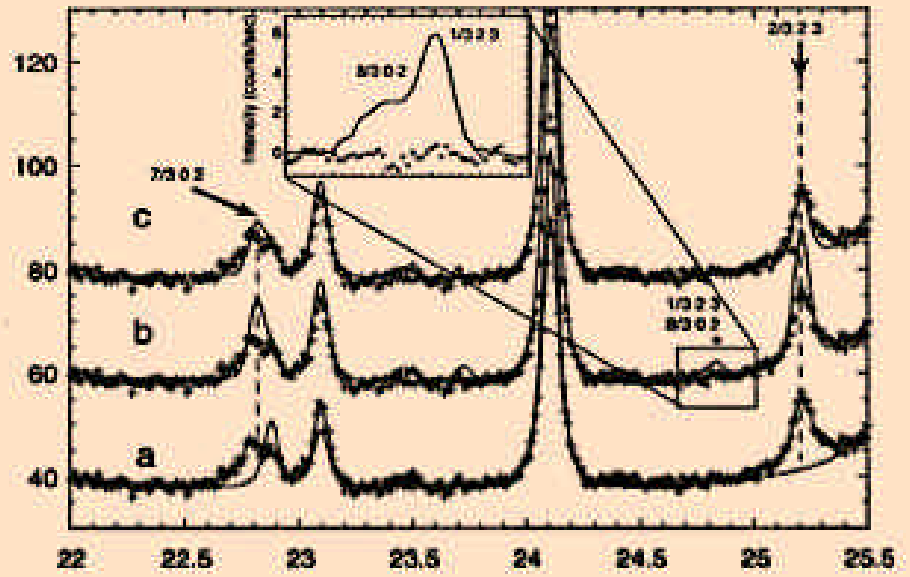
GMR Stripes and Charge Ordering

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...