Neutron Diffraction

CENSC, Budapest 7-11 April 2003

Alan Hewat, ILL Grenoble, FRANCE

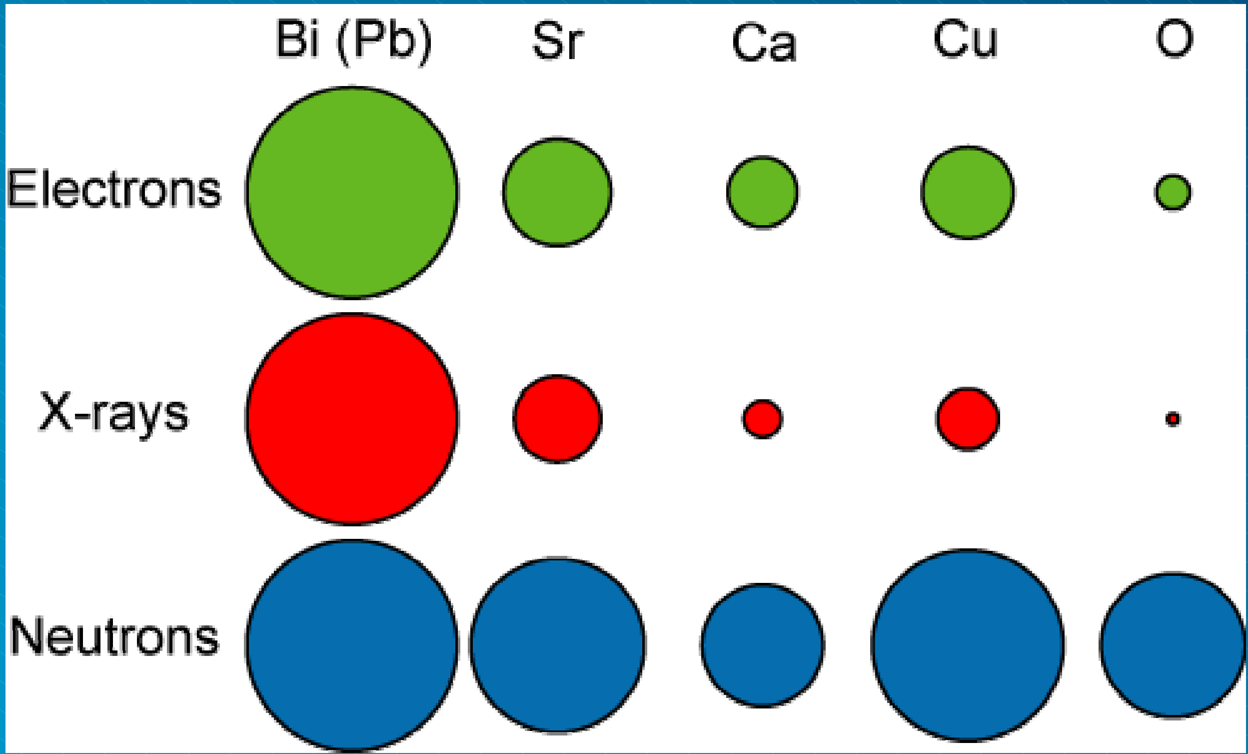
Why Neutrons ?

- Neutrons act like both particles and waves
- Neutrons are electrically neutral & more penetrating than X-rays.
- Neutrons interact with nuclei & locate atoms more precisely.
- Light atoms scatter neutrons as strongly as heavy atoms.
- Neutrons are tiny magnets, & can determine magnetic structures.
- Neutrons can study atom dynamics & the forces between atoms.

Neutron Diffraction

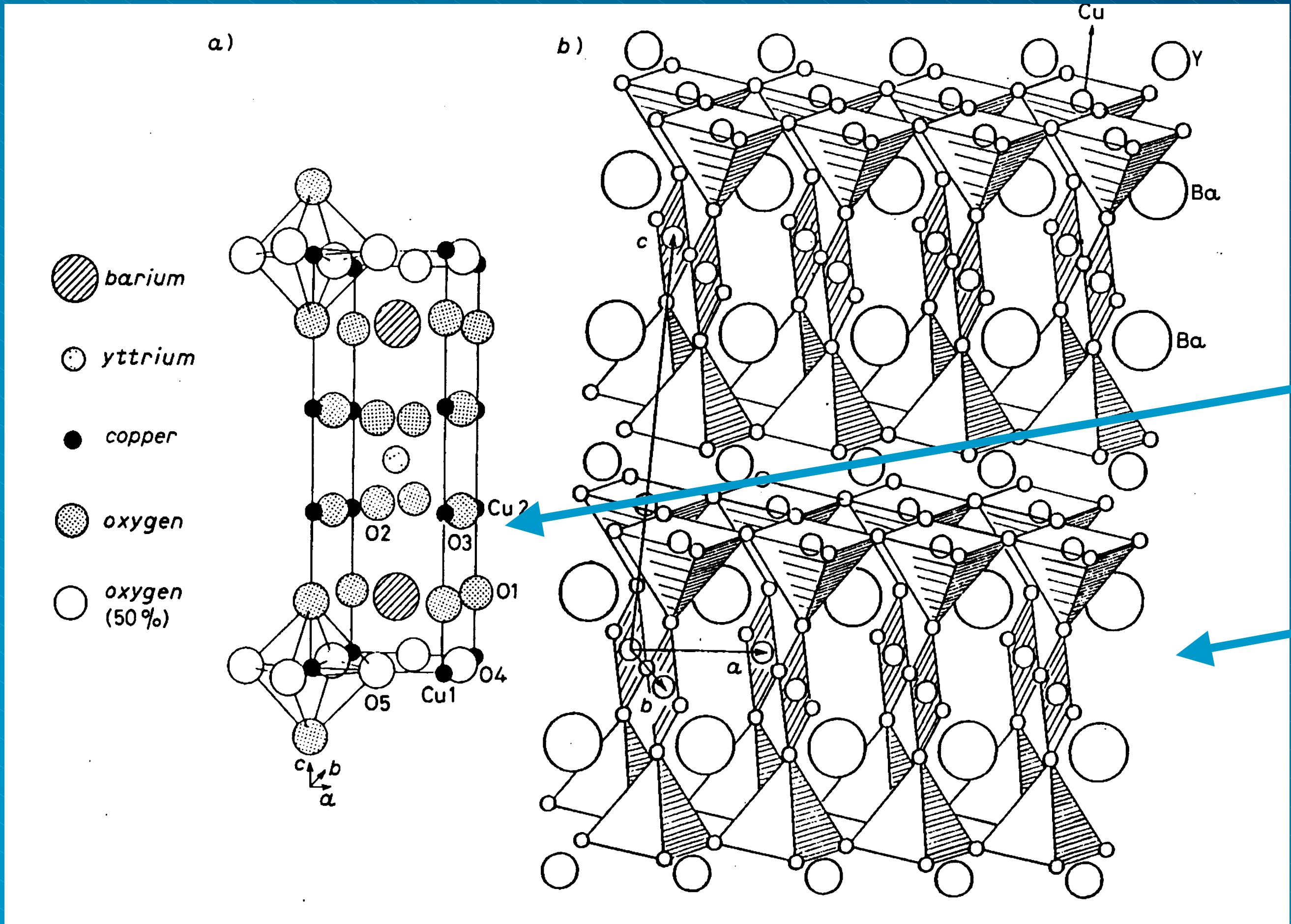
Neutrons scatter strongly from light atoms

- Neutron scattering is of similar magnitude for all atoms
- X-ray scattering is proportional to the number of electrons
- Electron scattering depends on the electrical potential



Neutron Diffraction

Neutrons scatter strongly from light atoms



The 90K high Tc Superconductor $Y_1Ba_2Cu_3O_7$

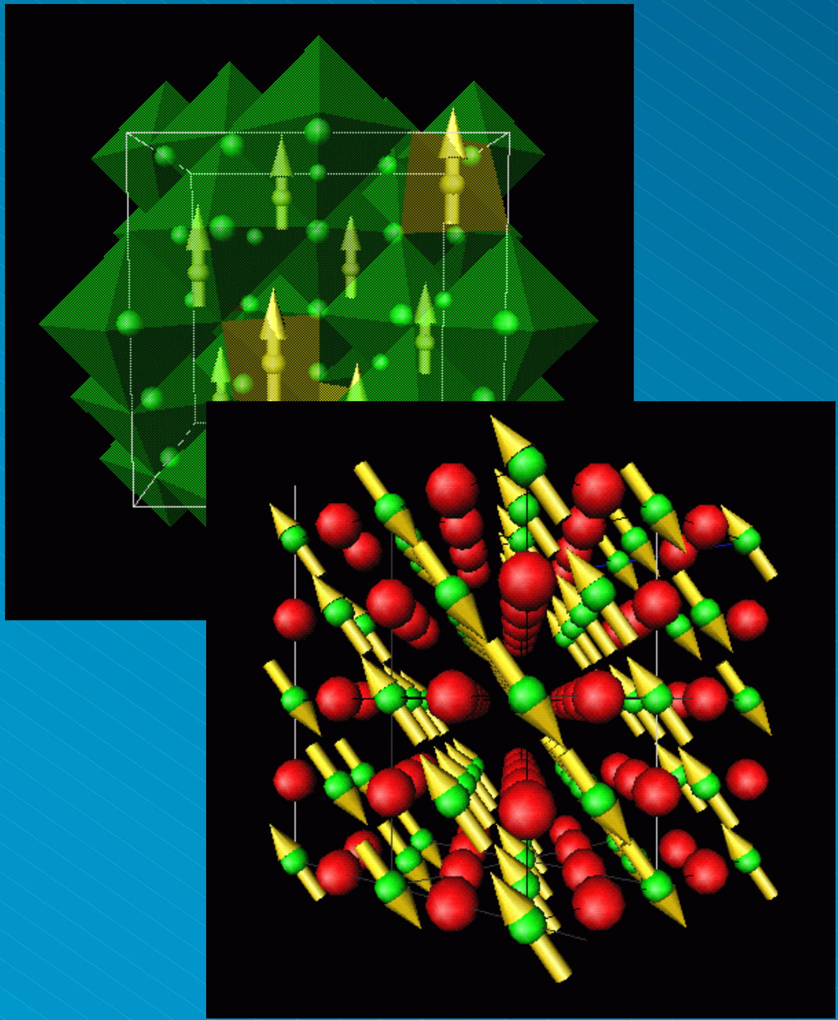
- Left -by X-rays (Bell labs. & others)
- Right -by Neutrons (ILL & others)

Neutrons gave new insight, important in searching for similar materials.

M. Marezio, J-J. Capponi, A. Hewat...(CNRS & ILL)

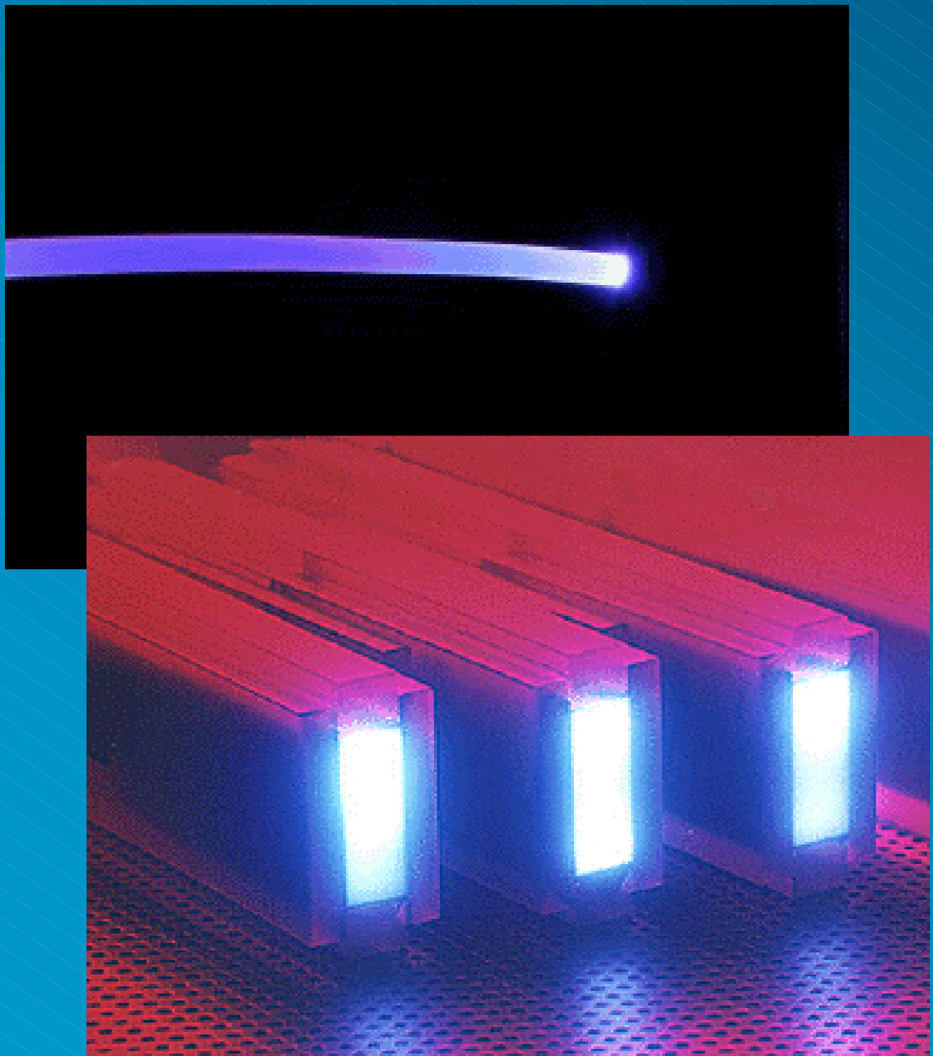
Neutron Diffraction

Neutrons scatter strongly from magnetic atoms



- Neutrons act like tiny magnets
- Interact with atomic magnetic moments
- Neutrons determine magnetic structures
- Ferromagnetic magnetite Fe_3O_4 (top)
- Antiferromagnetic manganese oxide MnO

Neutrons can be transmitted like light in an optic fibre

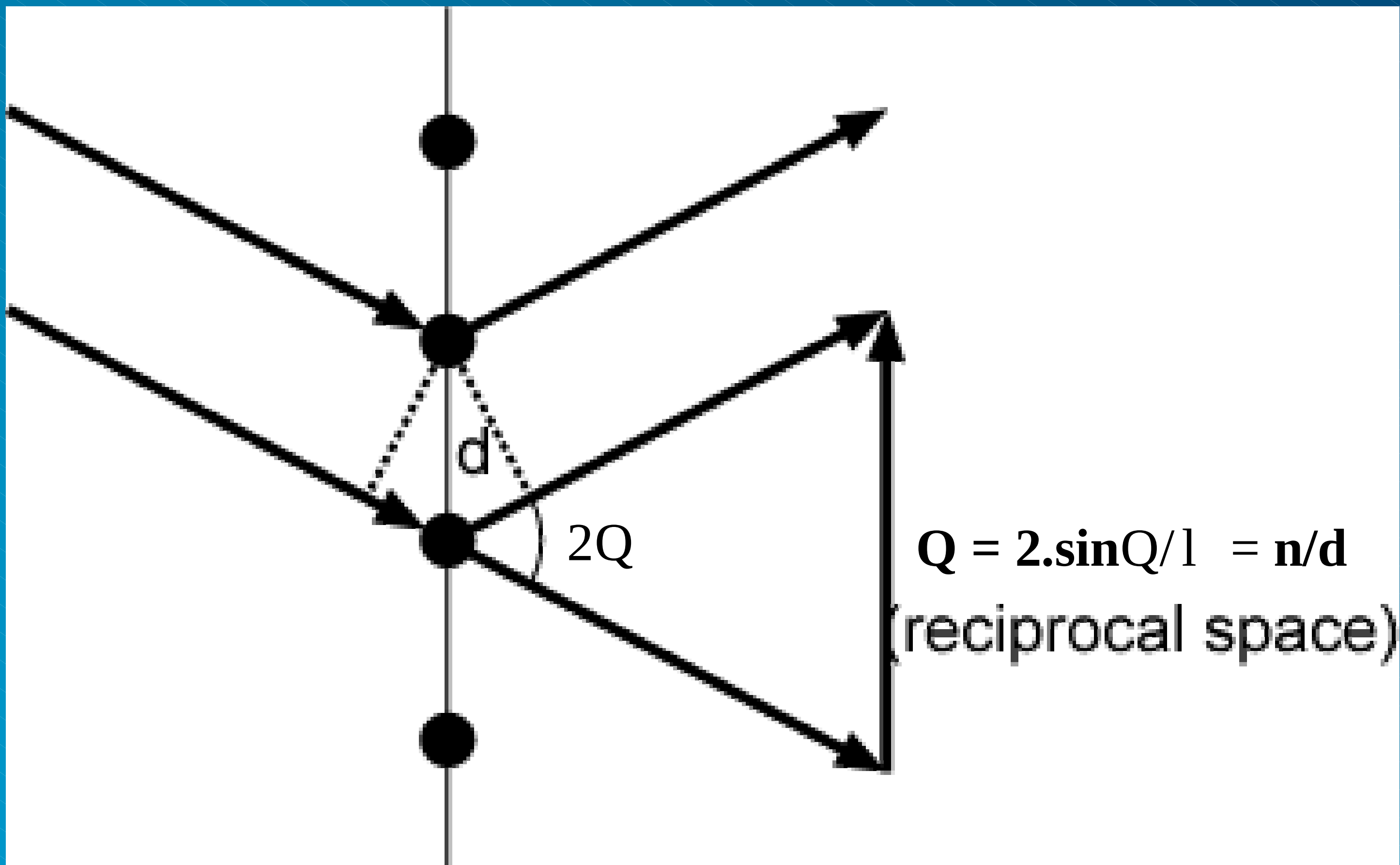


- "Neutron guide tubes" bring the neutrons to the experiment
- The transmitted intensity (solid angle) depends on the neutron wavelength
- Only neutrons are transmitted (low background).

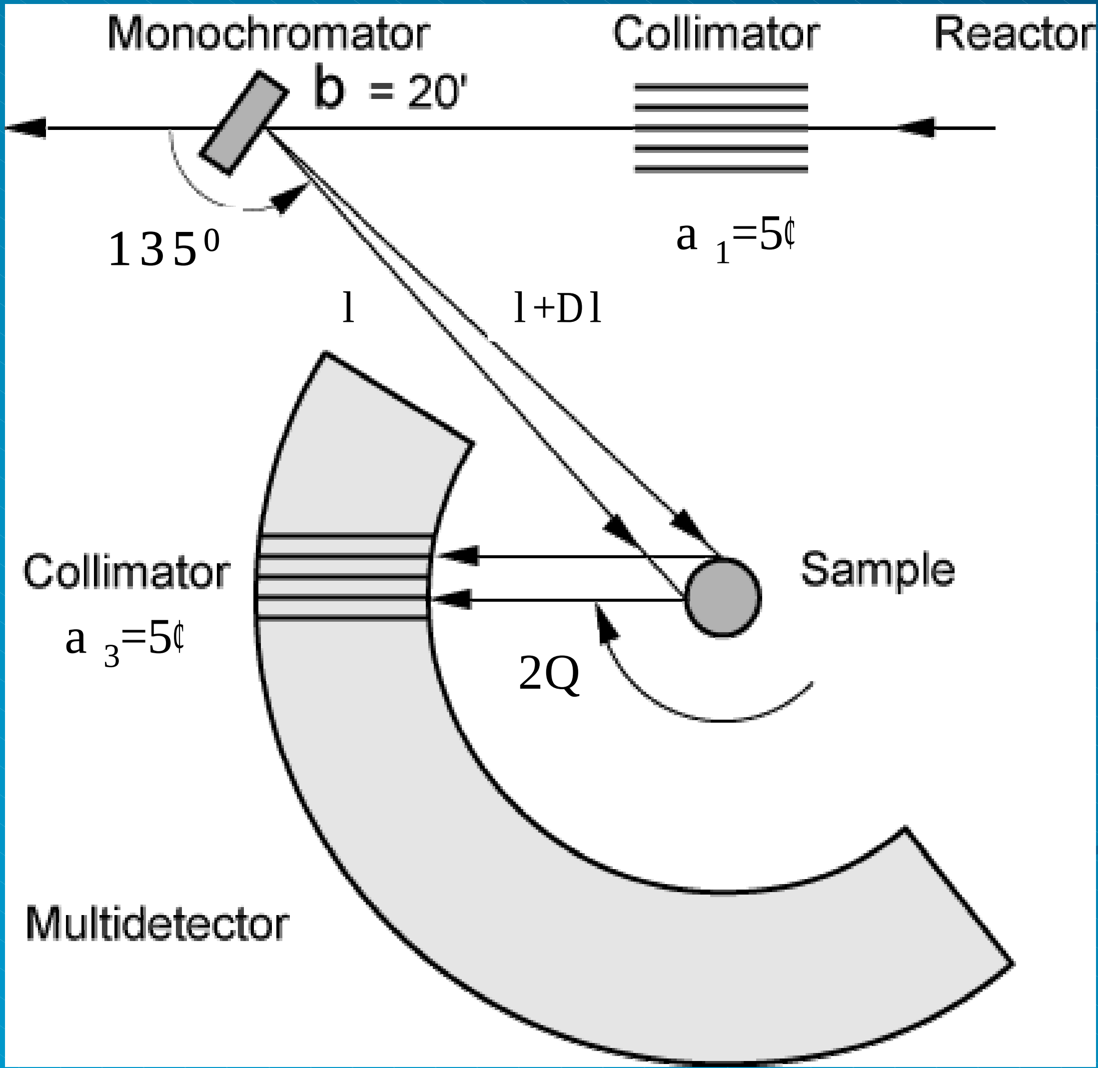
Neutron Diffraction

Neutrons scatter like waves from atomic planes

- The neutron wavelength is similar to the atomic spacing
- Scattered neutrons determine the atomic structure of materials



Neutron Diffraction



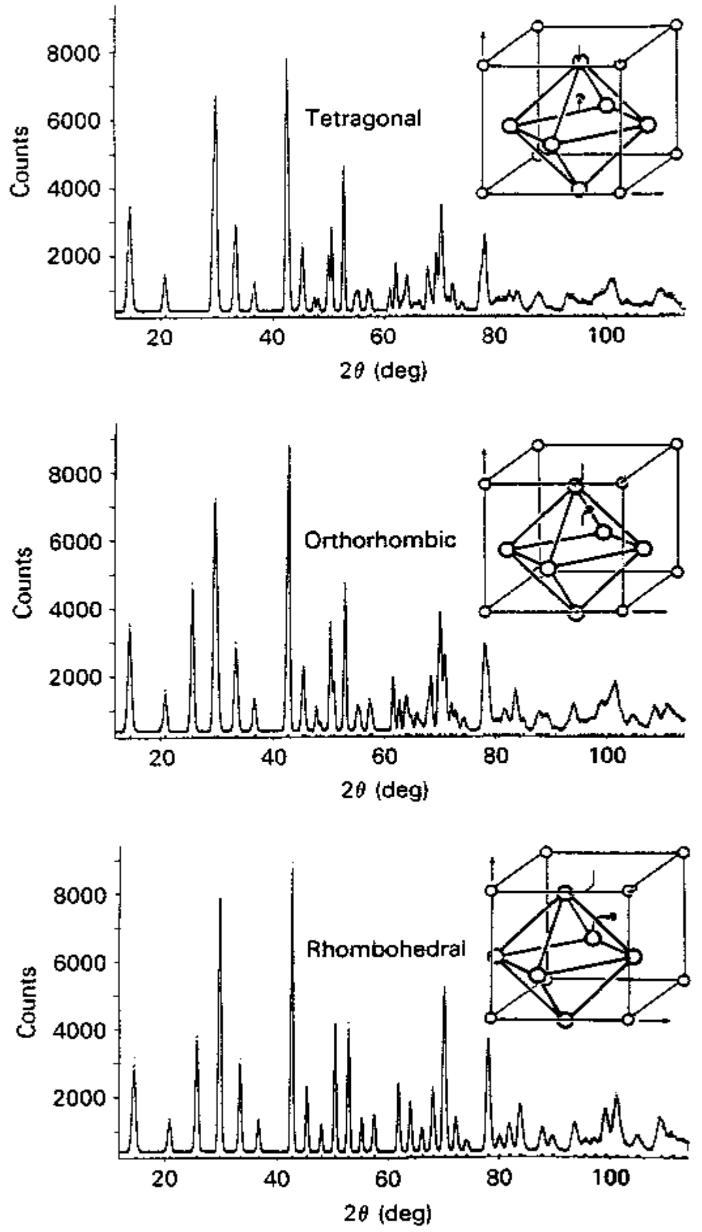
Neutron diffractometers are simple

- A “white” beam of neutrons from the reactor is collimated
- A large focussing monochromator selects particular wavelengths
- This small band of wavelengths is scattered by the sample
- A large multi-detector collects the neutrons scattered at all angles

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

Neutron Diffraction



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

Why Rietveld Refinement ?

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

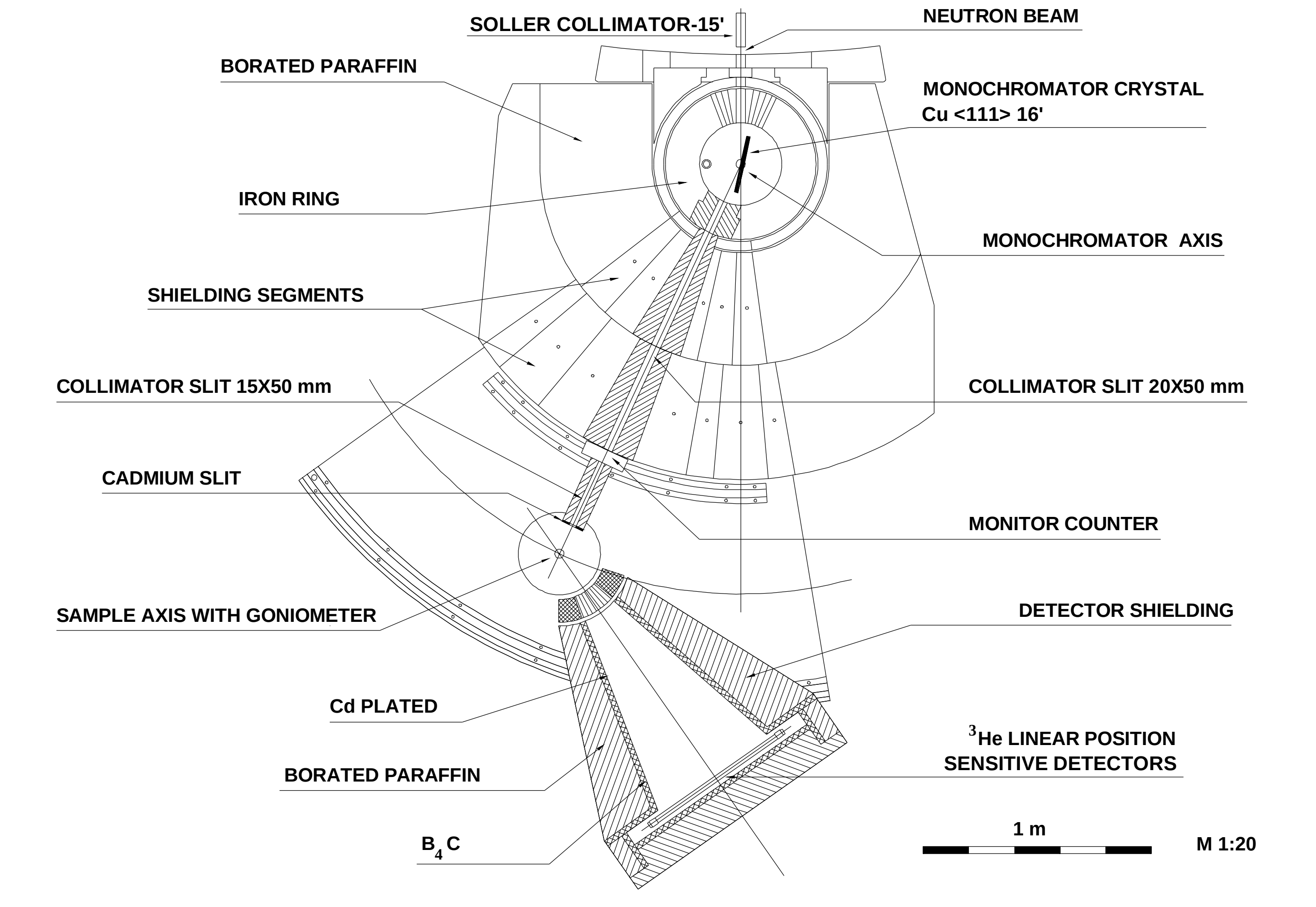
- Key to success of RR
  - inclusion of all the information
  - refinement of physically meaningful parameters (reduction of correlation between parameters)

Why not X-ray Powder Diffraction ?

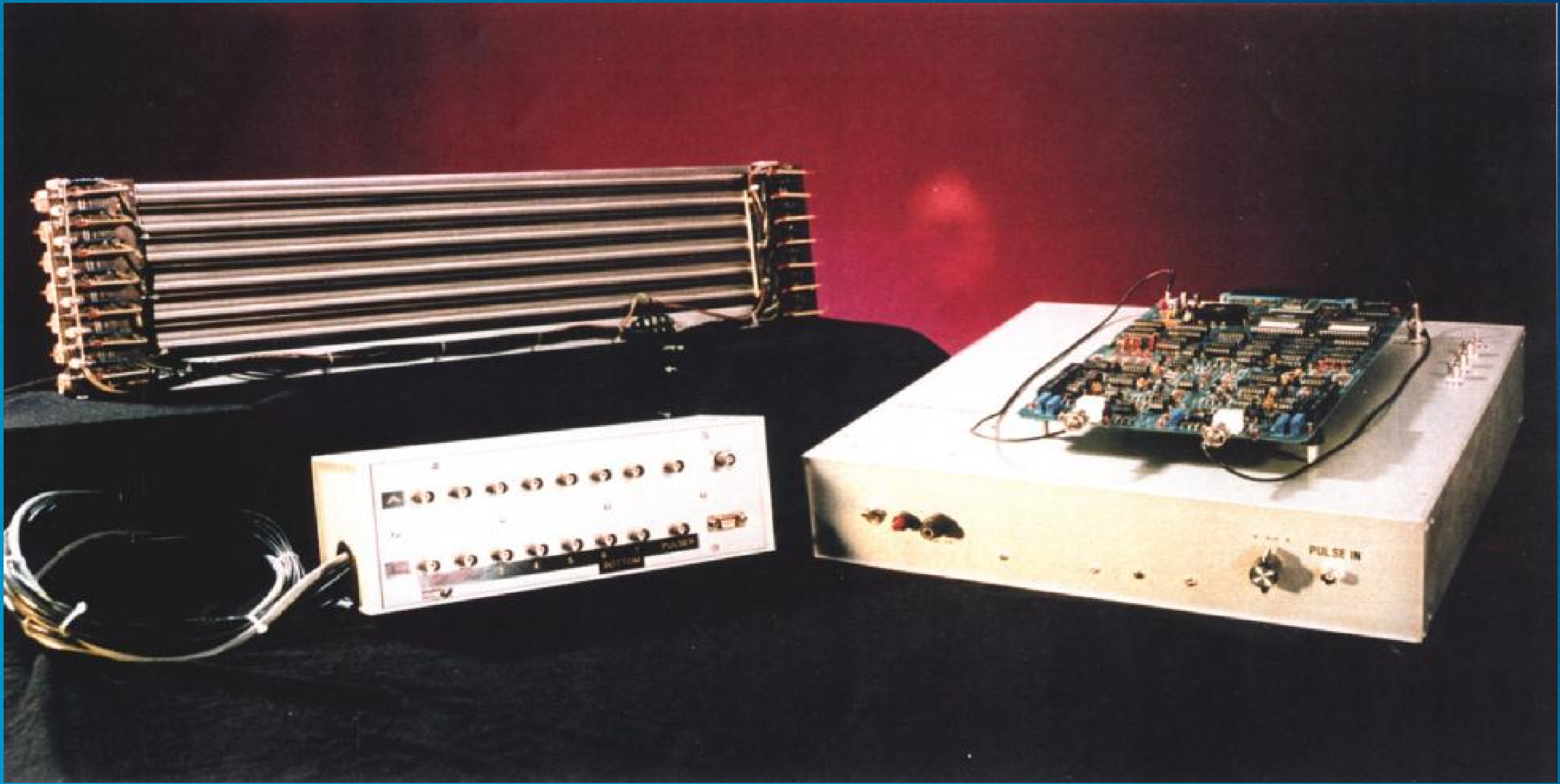
- Magnetic structures… not possible with x-ray powders
- X-rays best for SOLVING structures
  - Easier to find the heavy atoms first
  - All atoms are 'equal' for neutrons
- Neutrons are best for REFINING structures
  - Few systematic errors (average over big samples etc…)
  - Easier sample environment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

Neutron Diffraction

PSD - Neutron diffractometer at Budapest (Erzsébet Sváb)



An inexpensive but effective Position Sensitive Detector



The linear wire PSD powder diffractometer

Neutron Diffraction

PSD - Neutron diffractometer at Budapest (Erzsébet Sváb)

Take-off monochromator angle	**$-5° < 2Q_M < 45°$**	
Monochromator and mosaicity	**Cu(111), 16'**	**Cu(220), 20'**
Monochromatic wavelength	**1.0689 Å**	**0.663 Å**
Resolution, Dd/d	**$1.2 \cdot 10^{-2}$**	**$2.4 \cdot 10^{-2}$**
Flux at the sample position	**10^6 n/(cm^{2}s)**	**10^5 n/(cm^{2}s)**
Beam size at the specimen	**15 mm×50 mm**	
Scattering angle, 2q	**5° < 2Q < 110°**	
Scattering vector interval, Q	**0.6-9.2 Å^{-1}**	**0.8-15.8 Å^{-1}**
Monitor counter and efficiency	**fission chamber, $1.2 \cdot 10^{-4}$**	
Detector system	**3 linear position sensitive ^{3}He detectors the detector spans 25° scattering angle**	

Neutron Diffraction

PSD - Neutron diffractometer at Budapest (Erzsébet Sváb)

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Atomic structure study of crystalline materials

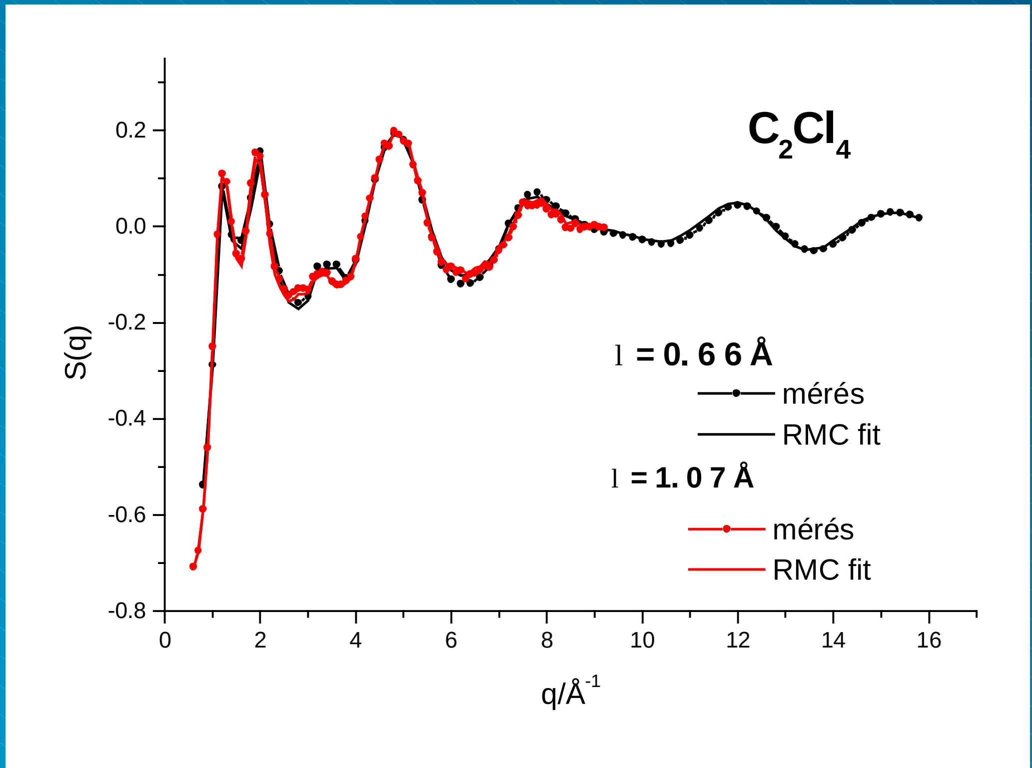
- Hydrated Zr(1%)Nb fuel cladding tube material;
- Nano-sized hexaferrite, magnetite, maghemite used for permanent magnets, microwave devices and recording media
- Yttrium-aluminium-borates (YAB) used in laser engineering.
- For data evaluation full profile *Rietveld method* is used.

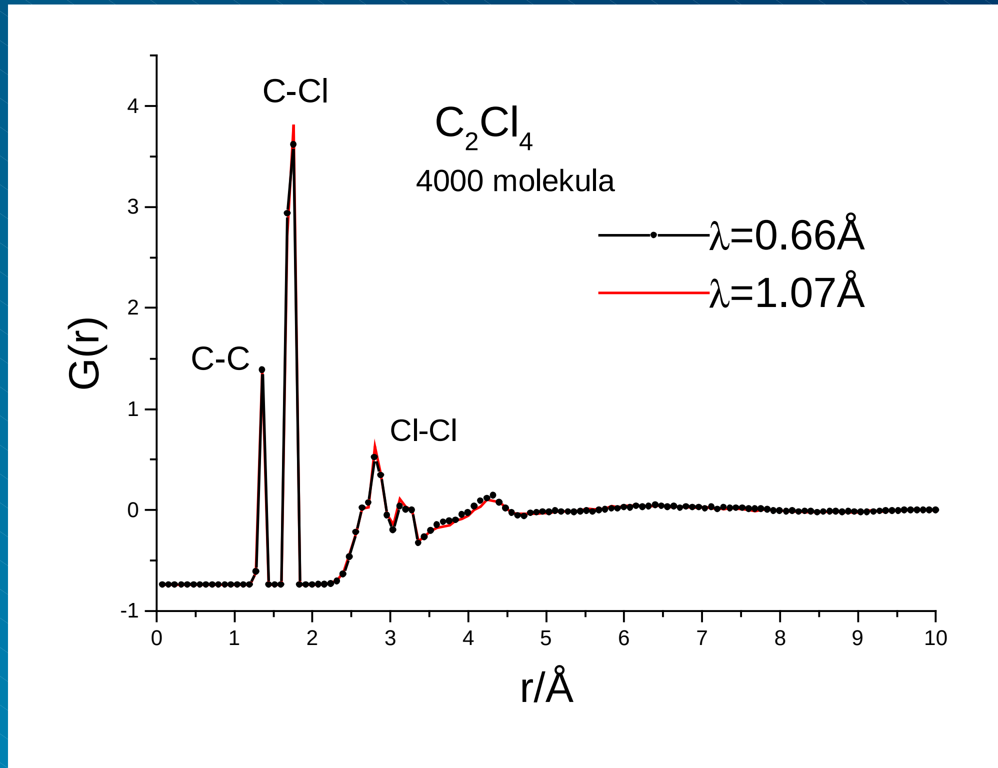
Short range order in molecular liquids and amorphous materials

- Amorphous S, P, Se and phase transitions in dependence of temperature;
- Amorphous two component alloys (Be-Zr, Ni-B).
- For data evaluation, *reverse Monte Carlo* (RMC) simulation technique
- Partial structure factors and atomic pair correlation functions

Neutron Diffraction

PSD - Neutron diffractometer at Budapest (Erzsébet Sváb)





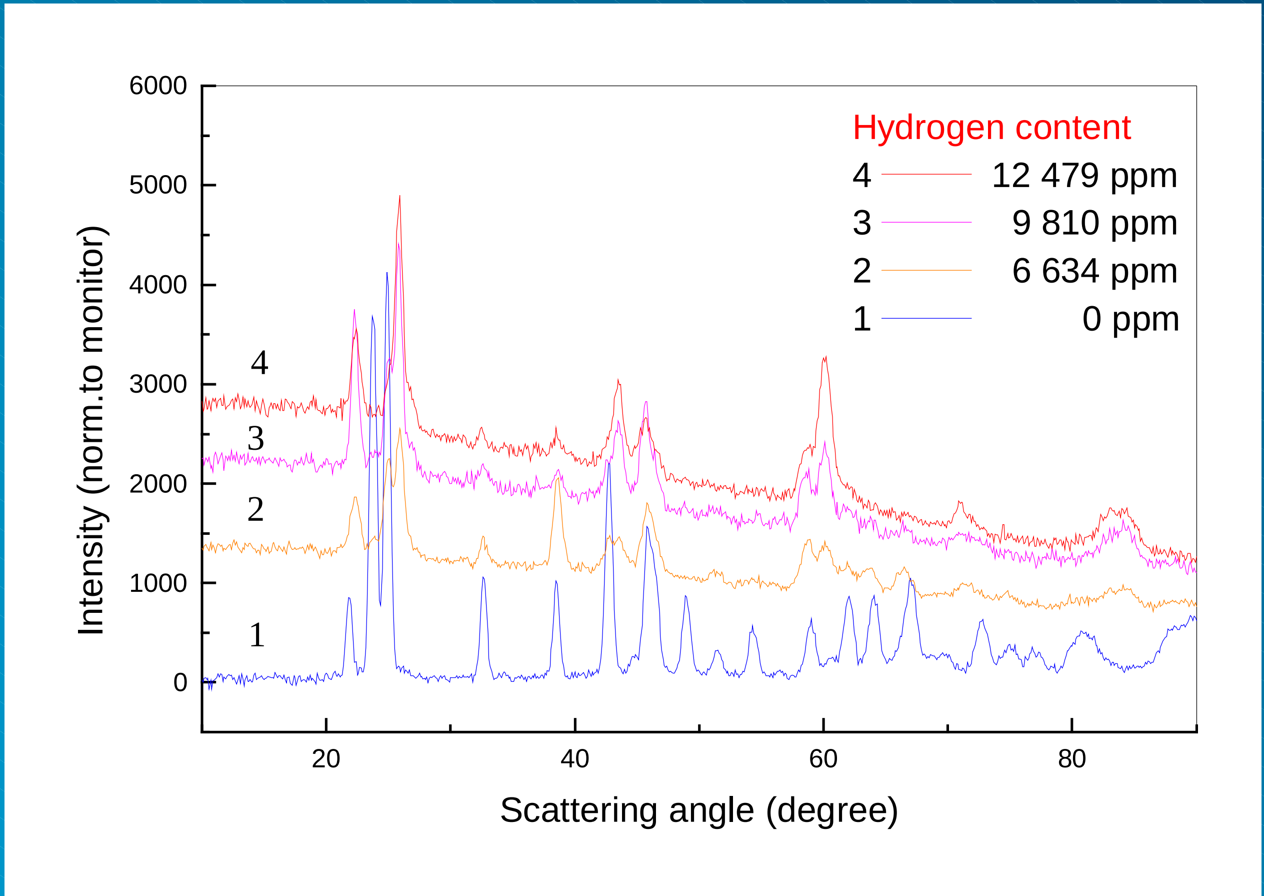
Structure factors S(q) for C_2Cl_4

Pair correlation function G(r)

P. Jóvári, Gy. Mészáros, L. Pusztai, L. Sváb,
Neutron diffraction studies on liquid CCl_4 and C_2Cl_4
Physica B276-278, 491-492 (2000)

Neutron Diffraction

PSD - Neutron diffractometer at Budapest (Erzsébet Sváb)



Zr(1%)Nb cladding tubes increasing hydrogen content

E. Sváb, Gy. Mészáros, Z. Somogyvári, M. Balaskó, F. Kőrösi

Neutron Imaging of Zr-1%Nb Fuel Cladding Material Containing Hydrogen

Applied Radiation and Isotopes (2001)

Neutron Diffraction

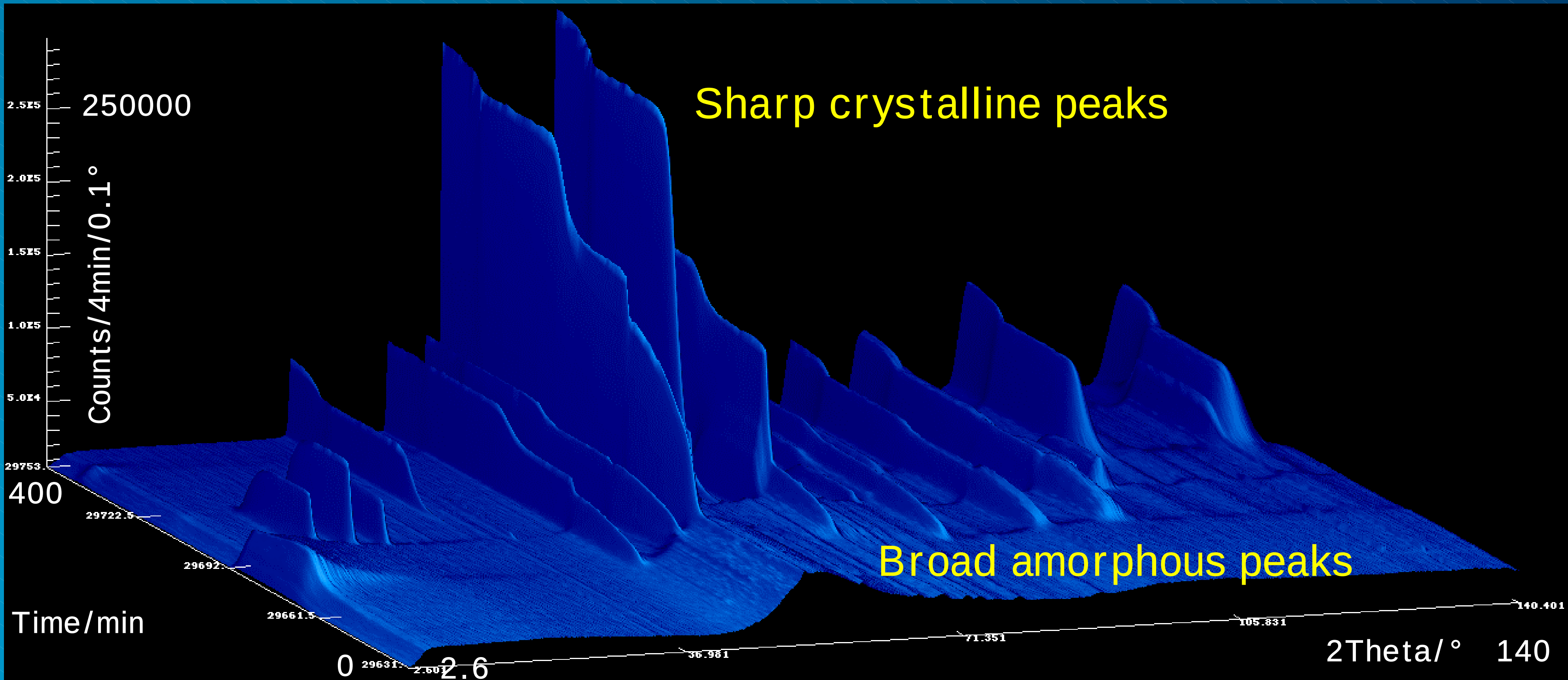
Neutron intensities are low, so large detectors are needed

Construction of a microstrip position-sensitive detector at ILL (printed circuit)

Neutron Diffraction

Applications of large fast detectors

Real-time Reactions - Crystallisation of amorphous alloy $Y_{67}Fe_{33}$

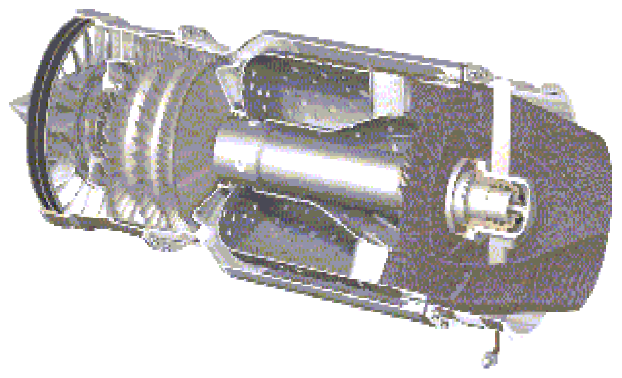


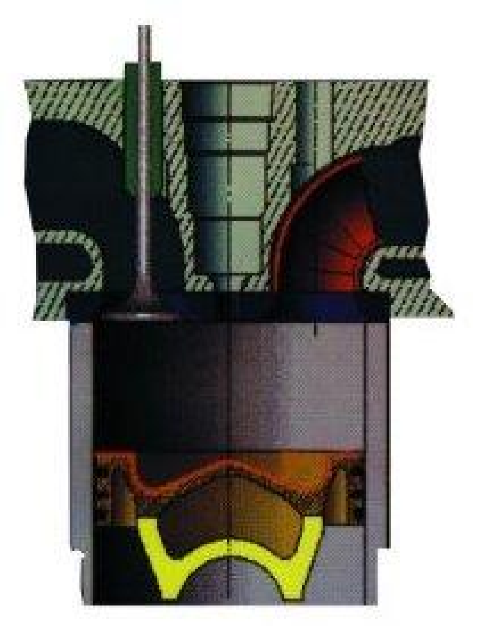
Complete diffraction pattern in minutes or seconds, scanning through temperature

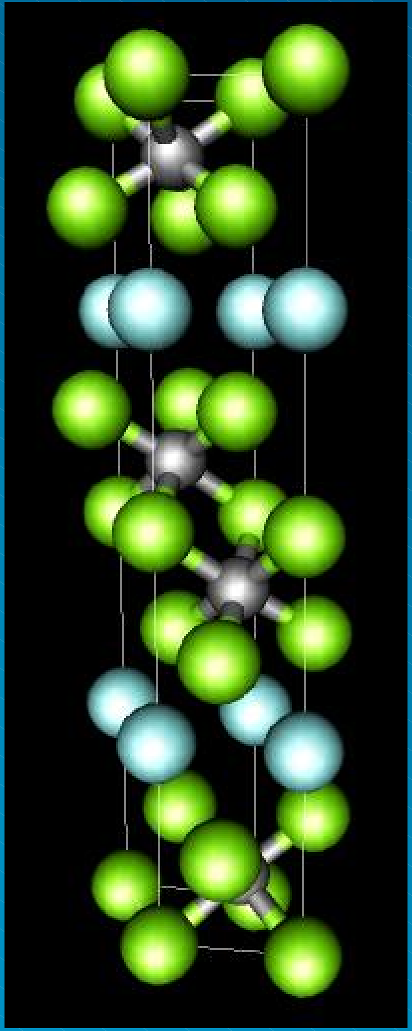
R. Cywinski, S. Kilcoyne (St Andrews)

Neutron Diffraction

New ceramics to replace metals in engineering components





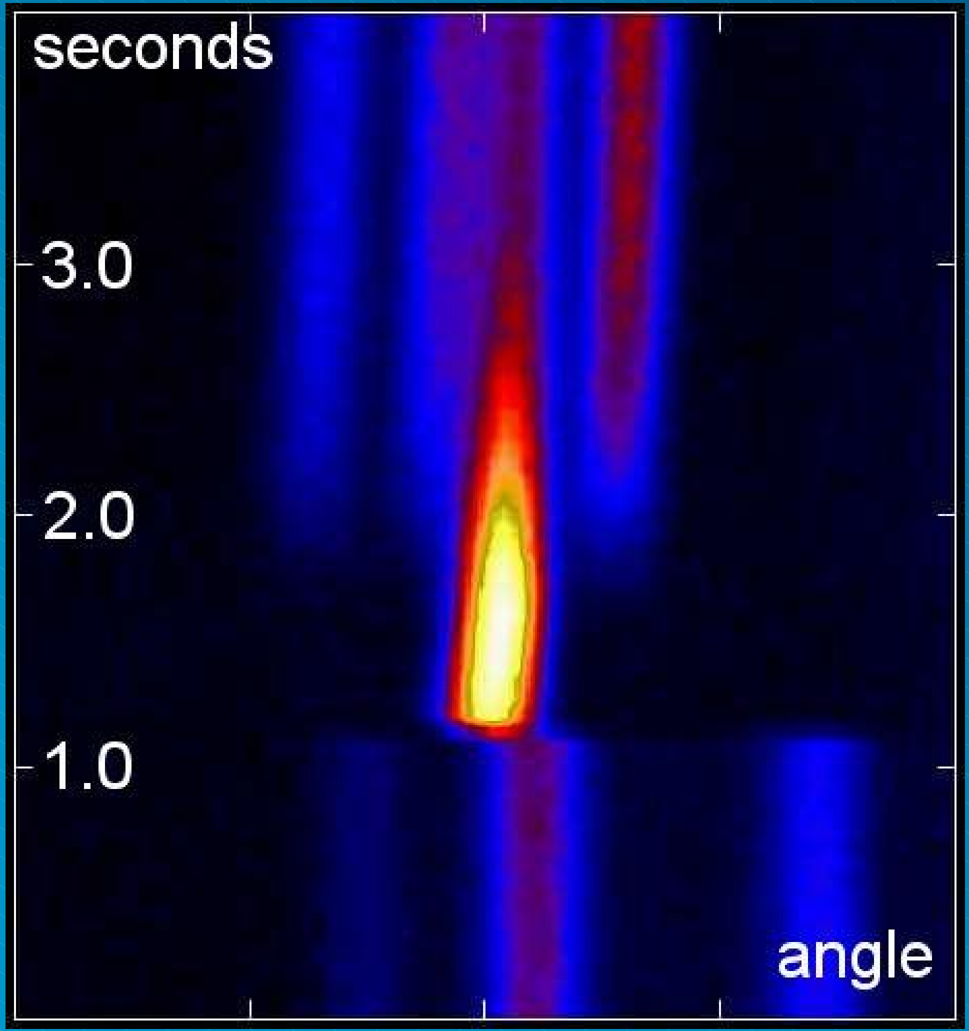


- Titanium silicon carbide Ti_3SiC_2 conducts heat and electricity
- It is tough, easily machinable
- Potential engineering applications as a light replacement for metals
- BUT, difficult to prepare pure
- Neutron diffraction has been used to study high temperature self propagating synthesis – SHS

D. Riley, E. Kisi (Newcastle, Aust.)

Neutron Diffraction

New ceramics to replace metals in engineering components

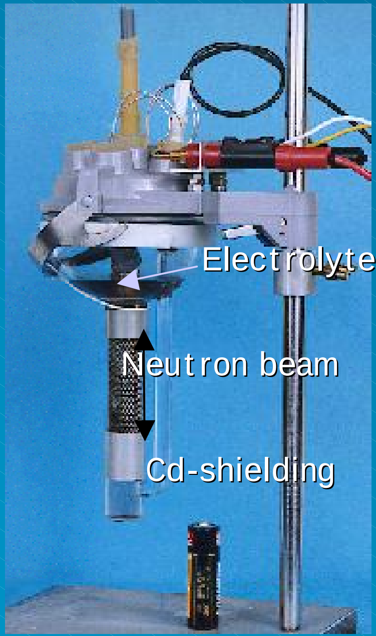


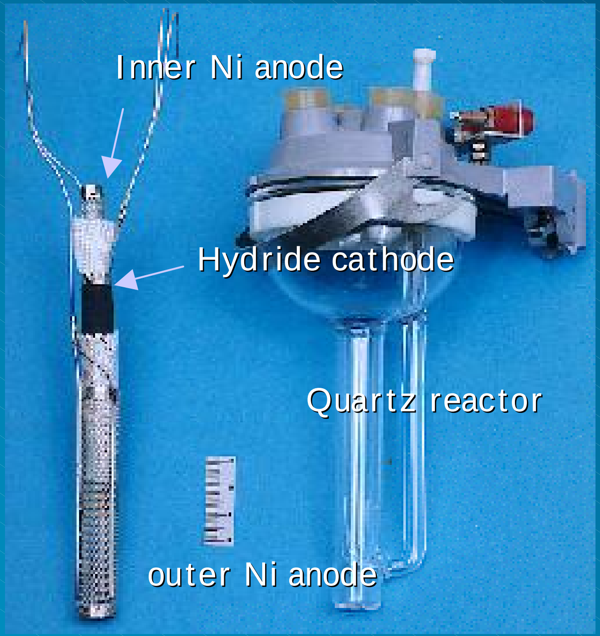
- The explosive SHS reaction was studied in real time with neutrons
- The reaction is exothermic, & heats the sample to 2200^0C in <1 sec
- The complete diffraction pattern (left) is collected at 500 ms intervals
- Knowledge of the SHS process allows us to prepare a pure Ti_3SiC_2 product

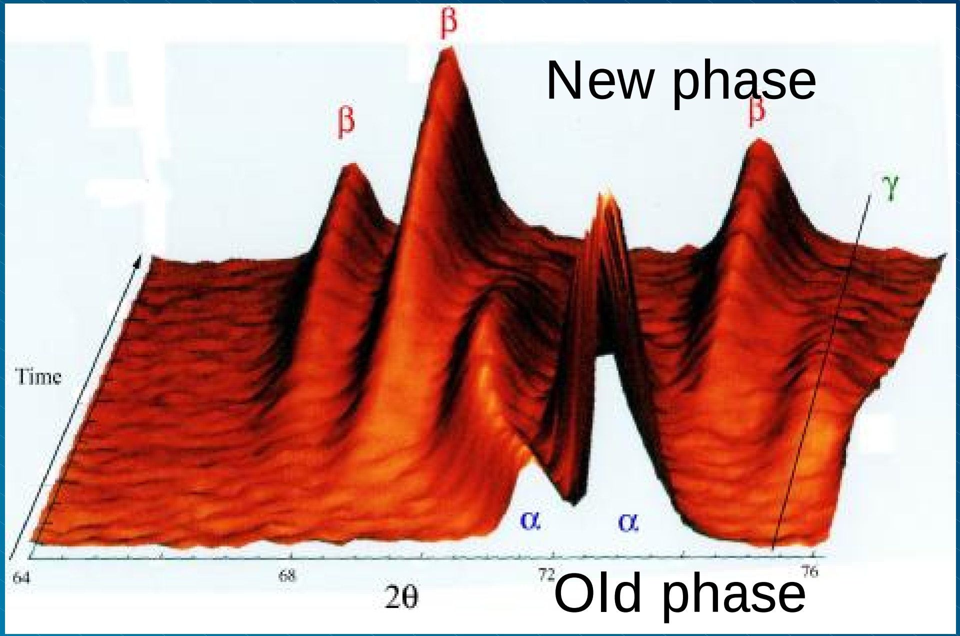
D. Riley, E. Kisi (Newcastle, Aust.)

Neutron Diffraction

Electrochemistry of batteries & real-time neutron scattering



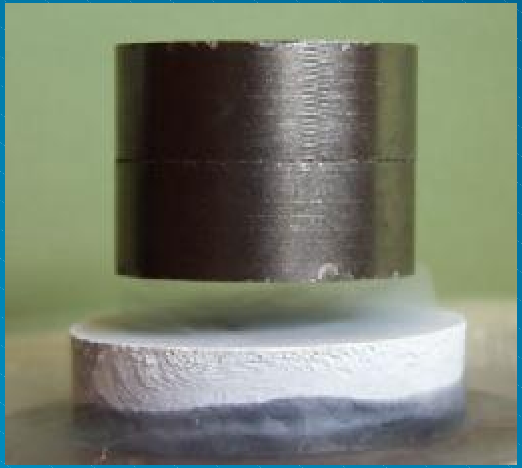




- Neutrons penetrate deep inside batteries during charge-discharge cycle
- Chemical changes due to charge-discharge can be followed in real time
- The hope is to make better batteries

Y. Chabre, M. Latroche, M.R. Palacin,
O. Isnard, G. Rousse (CNRS, CIC-Spain + ILL)

Neutron Diffraction



High temperature superconductors

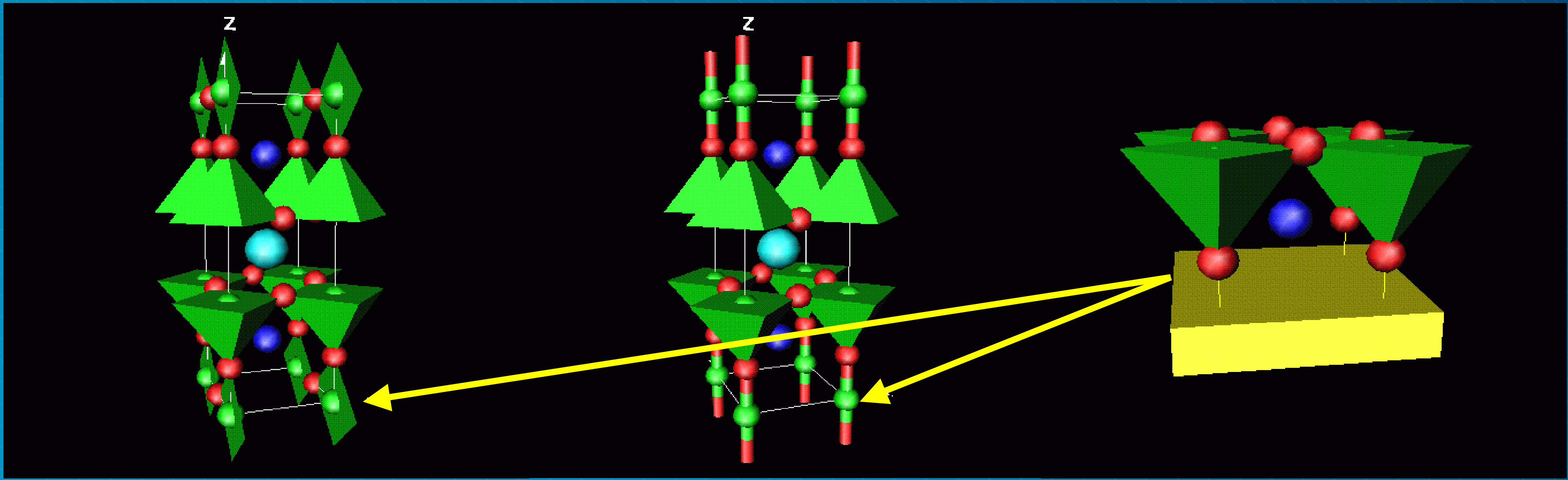
- New magnets for medical scanners & research
- Sensitive magnetometers for mapping
- Fast connections in computer microchips
- Linear motors for high speed maglev trains

Neutron Diffraction

The importance of oxygen for high-Tc superconductors

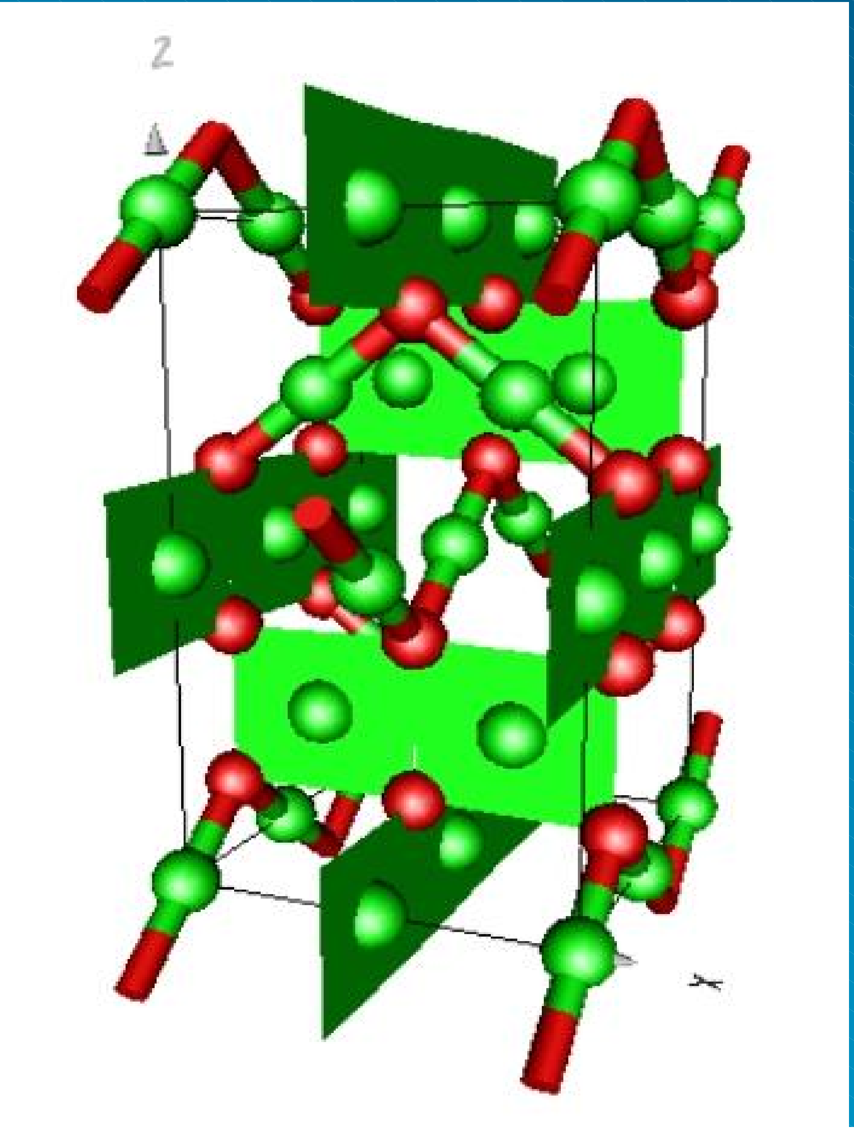
Neutrons are sensitive to oxygen – “charge reservoir” concept

Superconducting $YBa_2Cu_3O_7$ Non-supercond. $YBa_2Cu_3O_6$ Charge reservoir layer



R. Cava, A. Hewat, E. Hewat, M. Marezio (Bell labs & ILL)

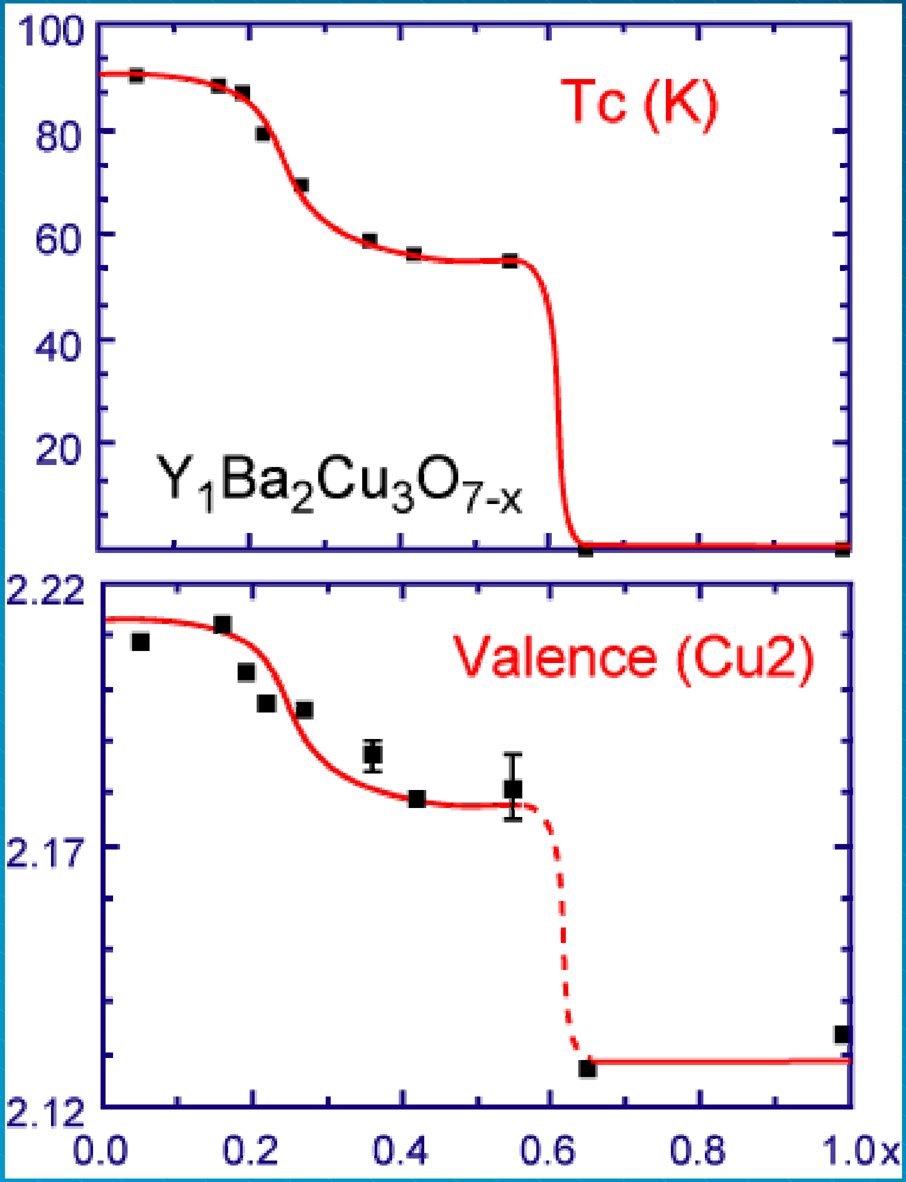
What is the valence of Cu in Cu_4O_3 ?



- 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 $V=\Sigma_i[\exp(Ro-Ri)/B]$
- Calculate Ri bond lengths & hence V

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

Neutron Diffraction



High-Tc superconductors

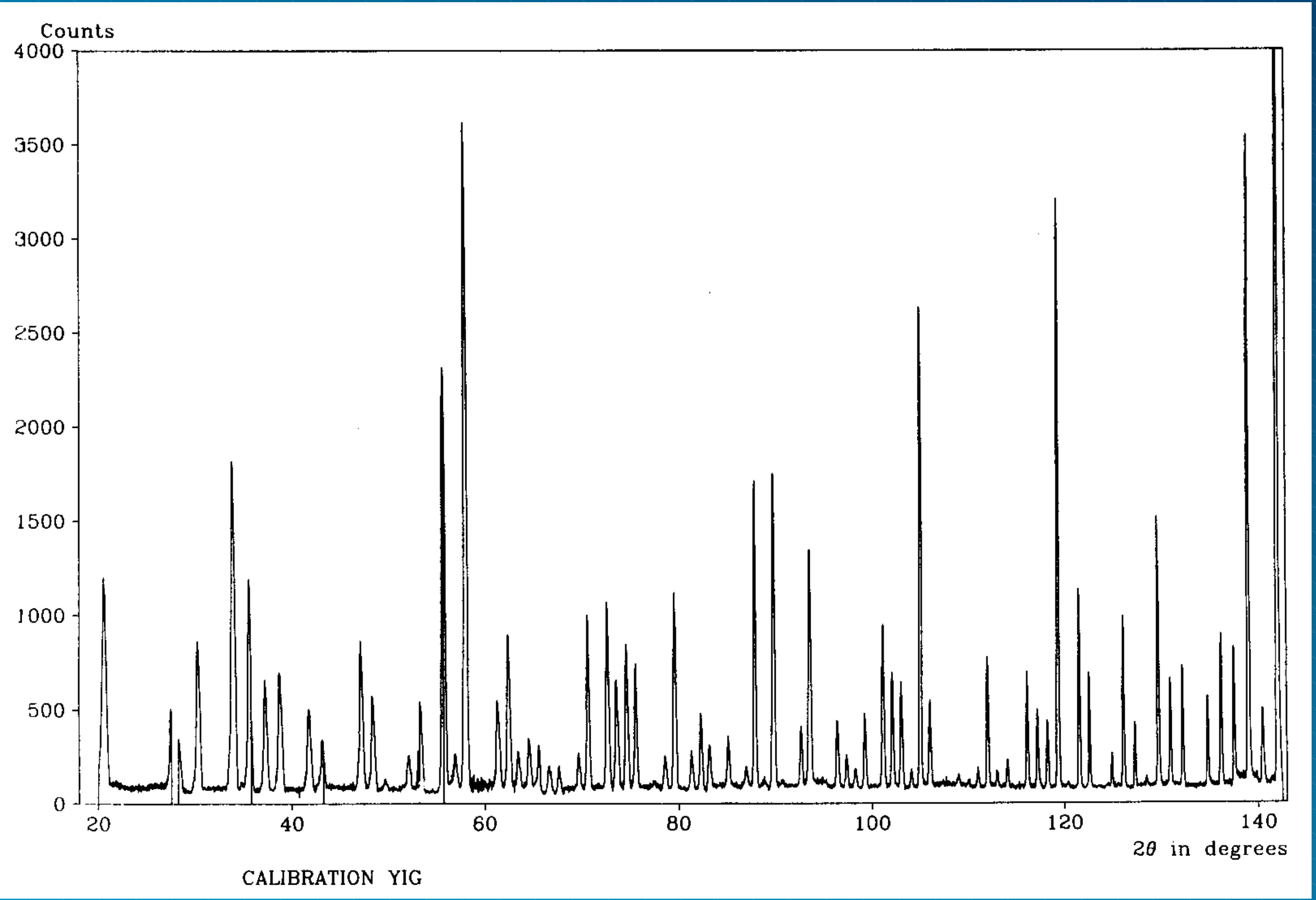
- Charge reservoir concept
- Tc depends on oxidation
- Imagine new charge reservoirs
- Discovery of new materials

R. Cava, A. Hewat, E. Hewat, M. Marezio

Neutron Diffraction

High resolution neutron diffractometers – D2B at ILL

Strong peaks at high angles give high precision structures of materials

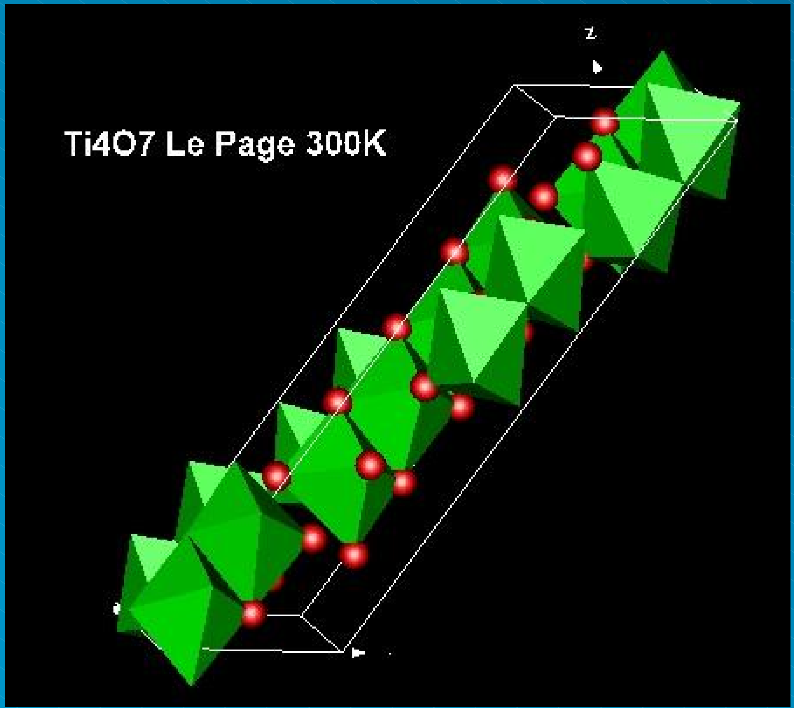


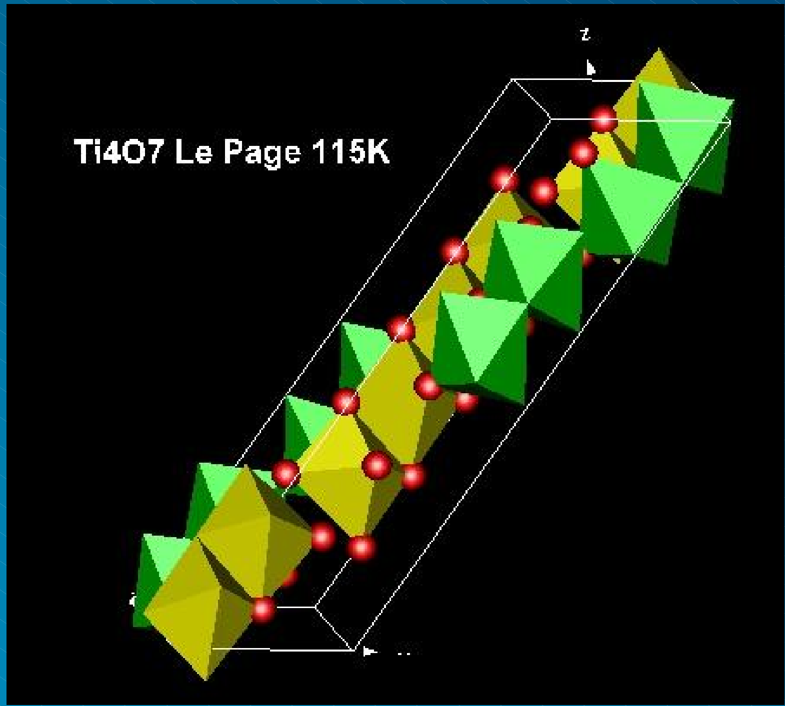
Super-D2B high resolution 2D linear wire detector

- 128 individual collimators & detectors
- Increase detector height to 300mm
- Use linear wire detectors to correct for curvature of the diffraction cones

Electronic Order-Disorder

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



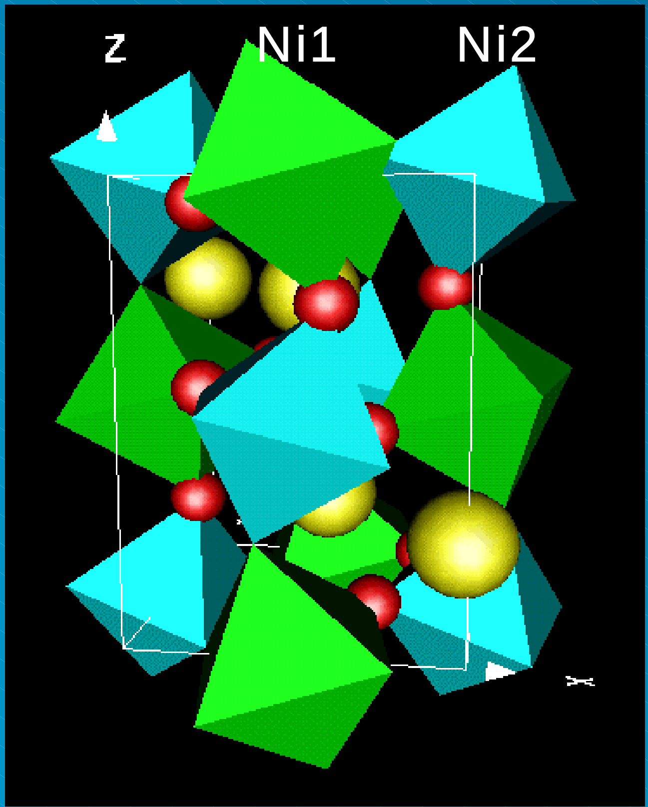


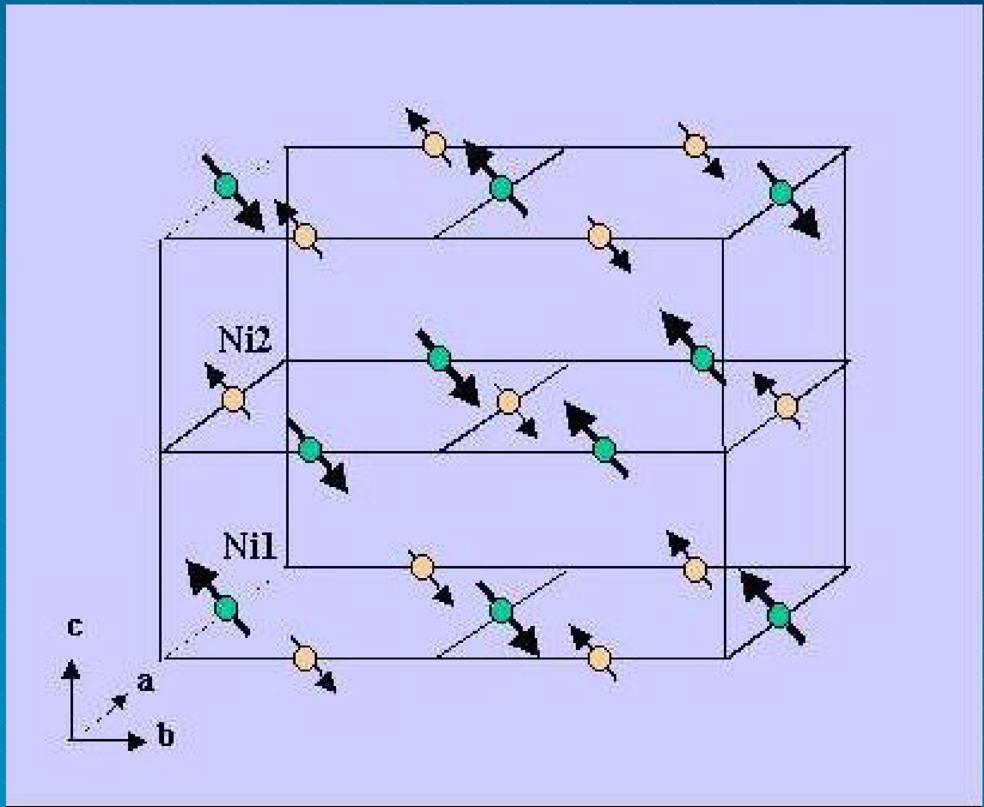
- Example: charge ordering in Ti_4O_7 (Le Page et al.

Charge Transfer in $YNiO_3$

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 m_B M(Ni2) = 0.7 m_B

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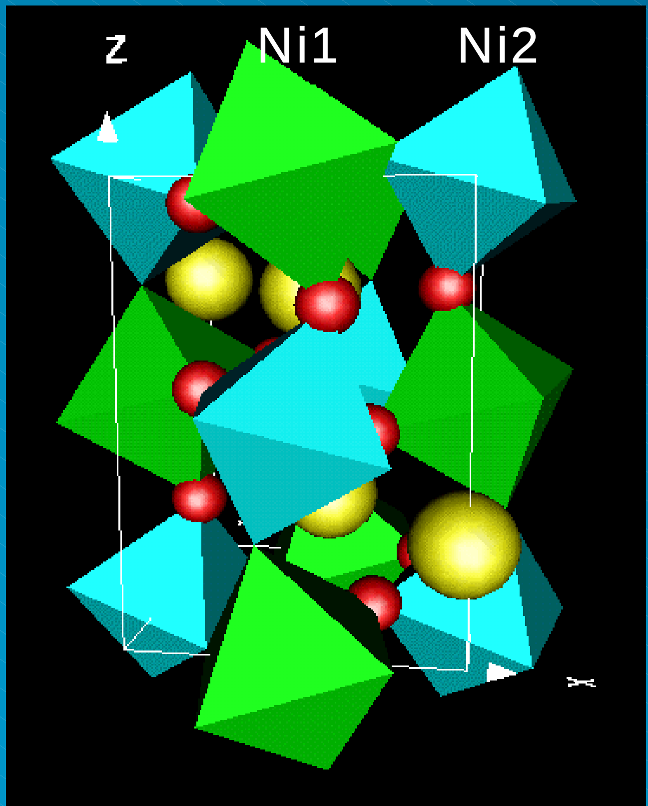


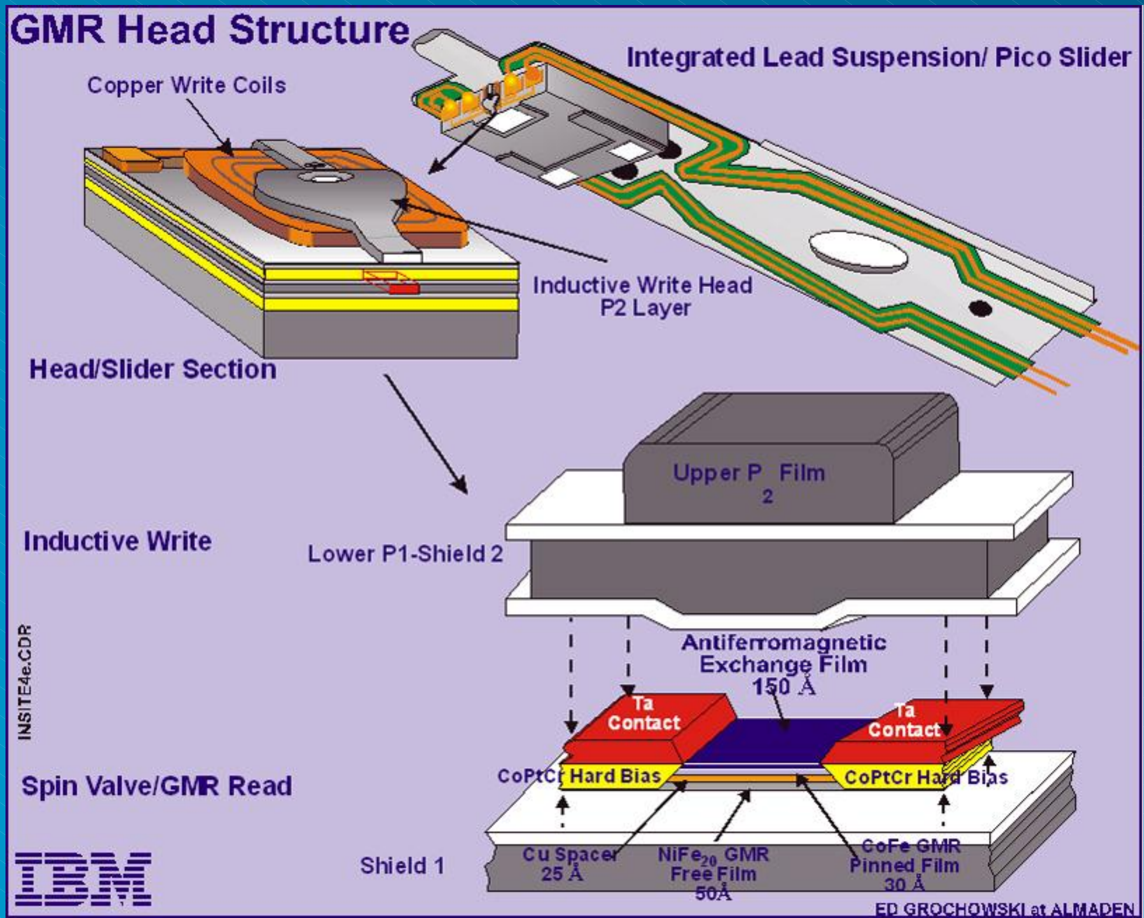
V(Ni1) = 2.62   V(Ni2) = 3.17

- 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

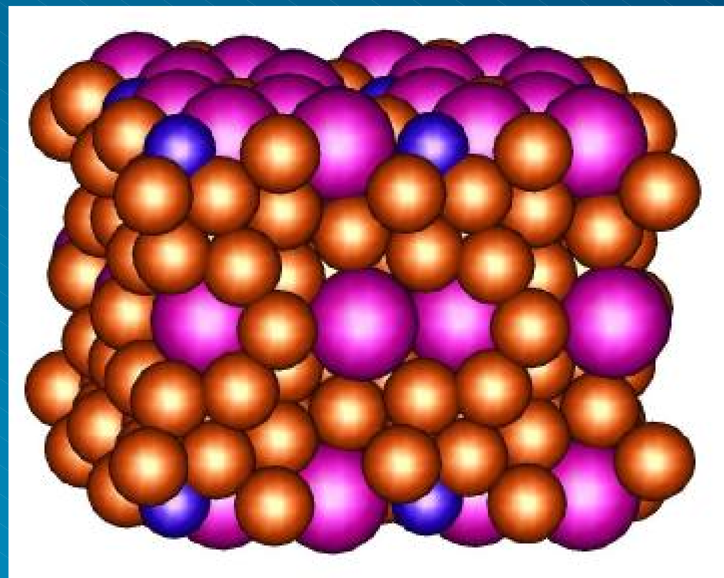
Neutron Diffraction

Charge & magnetic order - Giant Magneto-Resistance (GMR)

- Neutrons are important for the study of magnetic structure
- New magnetic materials for electric motors, information storage etc...

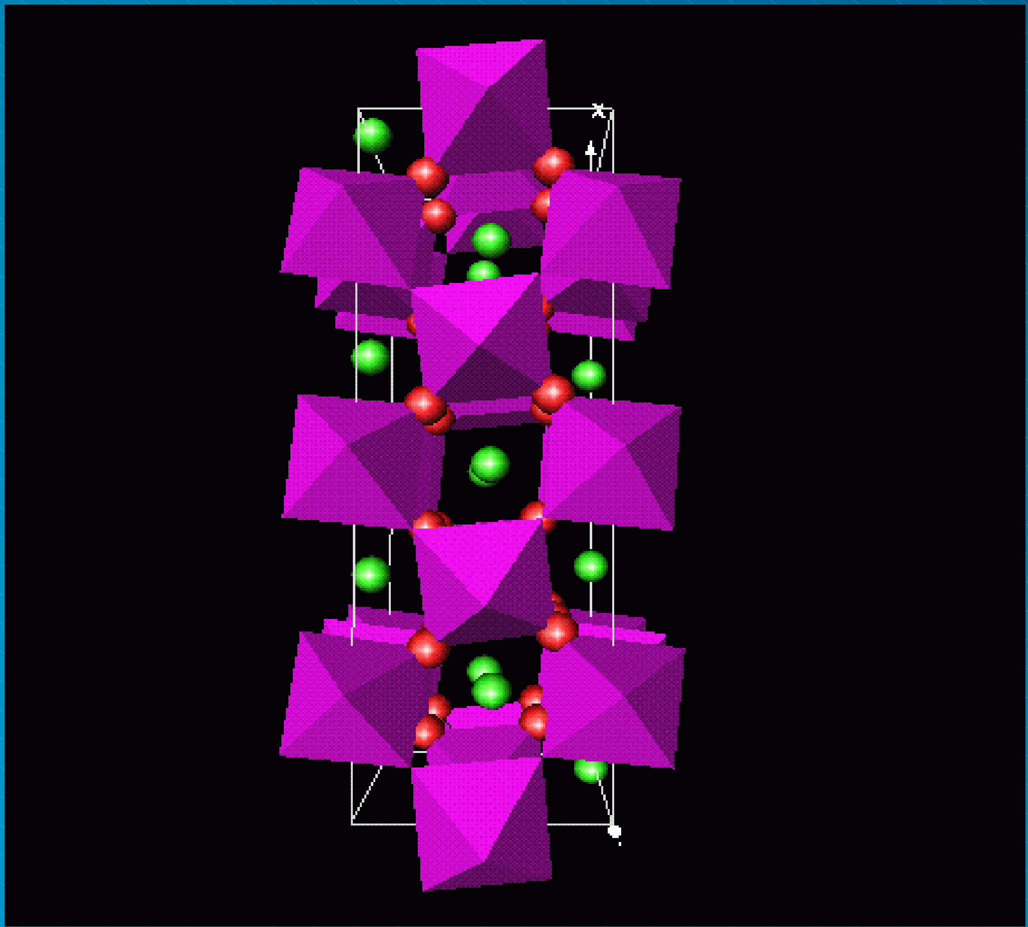


- Left – GMR computer disk
- Below – NdFeB Hard magnet



Neutron Diffraction

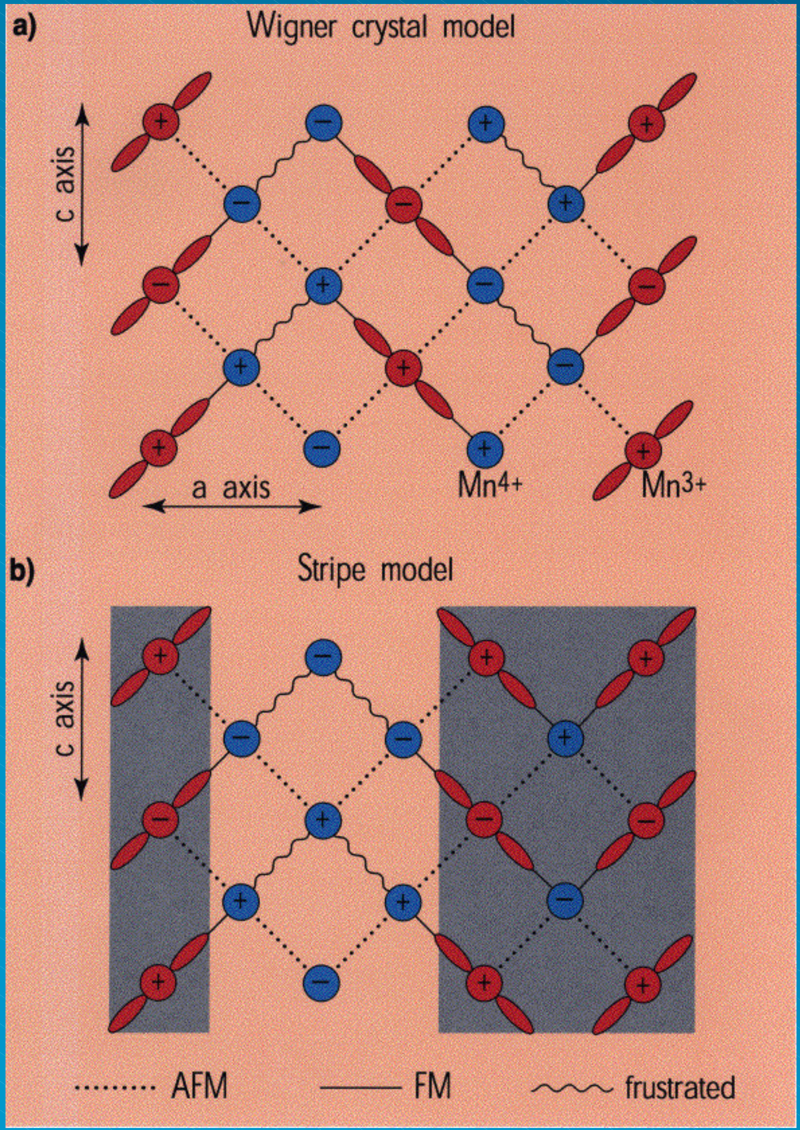
New CMR materials (Colossal MagnetoResistive) $(La,Ca)MnO_3$



- Very large changes in electrical resistivity with temperature
- Mixed valence charge-ordering Mn^{3+}/Mn^{4+}
- CMR effect near room temperature

P. Radaelli, E. Suard,
M-T. Fernandez-Diaz,
J. Rodriguez, C. Ritter,
B. Ouladdiaf, R.Przenioslo
(ILL)

Neutron & Synchrotron radiation to obtain charge order

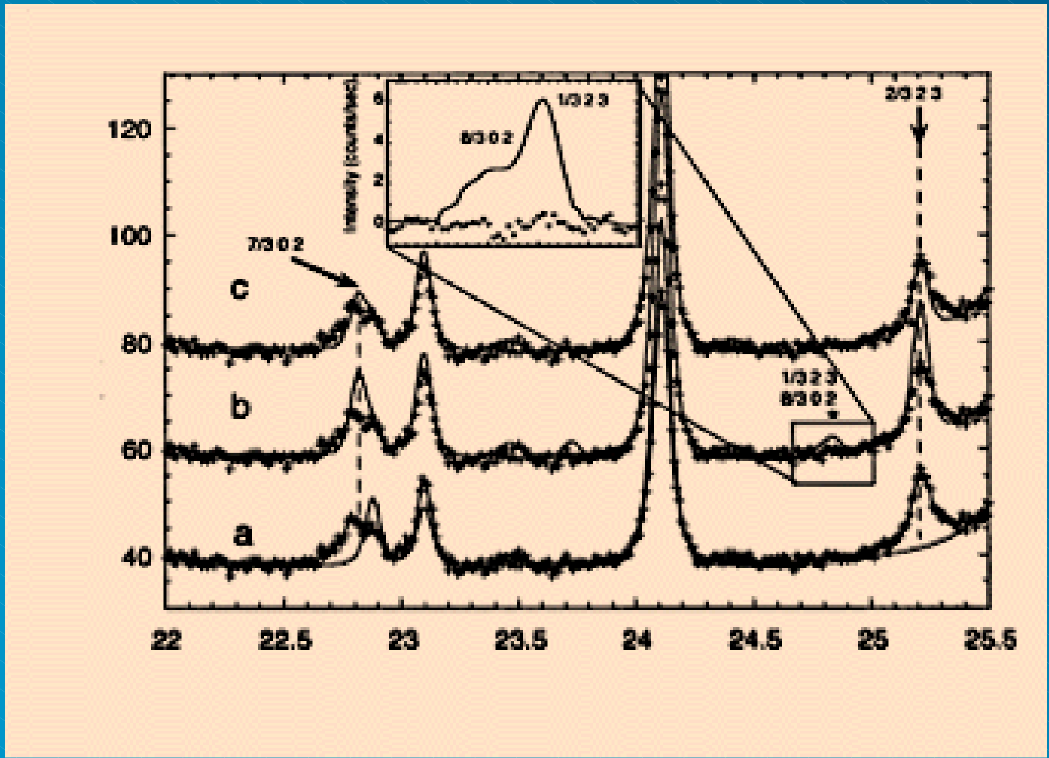


Important to decide between 2 models

a) Mn3+/Mn4+ uniformly distributed (2D Wigner model of Goodenough)

b) 1D-stripe model – this would have very important consequences for the theory of CMR materials

GMR Stripes and Charge Ordering



Radaelli et al. (1999) Phys. Rev B
X-ray work on X7A (BNL)
Neutron work on D2B (ILL)

Neutron + Synchrotron Diffraction

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

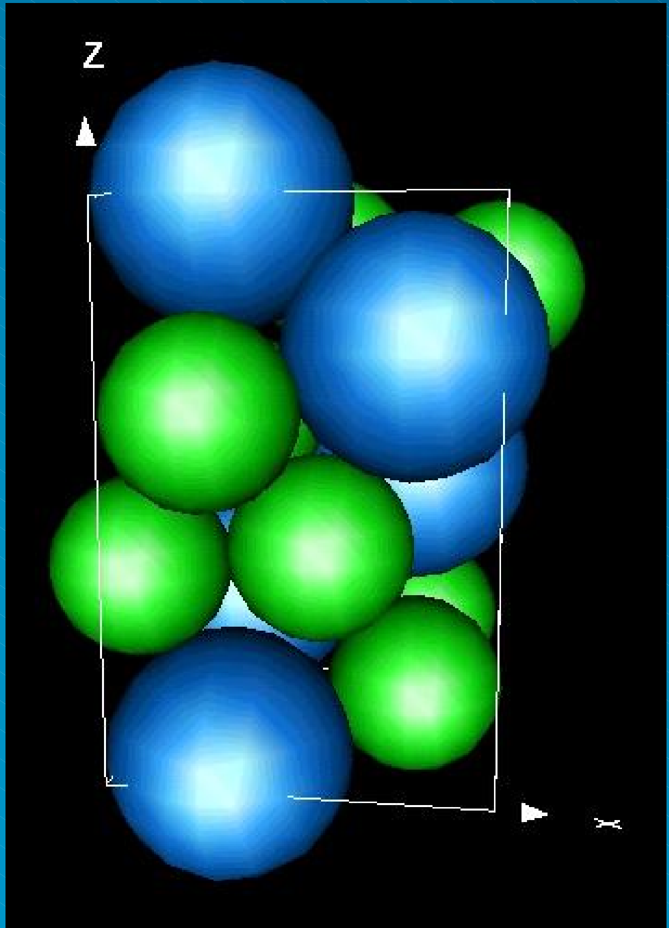
a) Average Structure
b) Stripe Structure
c) Wigner Crystal Structure (best)

Hydrogen storage materials

- Hydrogen is the ideal fuel
- It can be obtained from water
- It is light & doesn't pollute !
- But - explosive & difficult to store
- A new material to store hydrogen ?
- A Swiss hydrogen fueled bus. Solar electricity is used to obtain hydrogen

K. Yvon (Geneva)

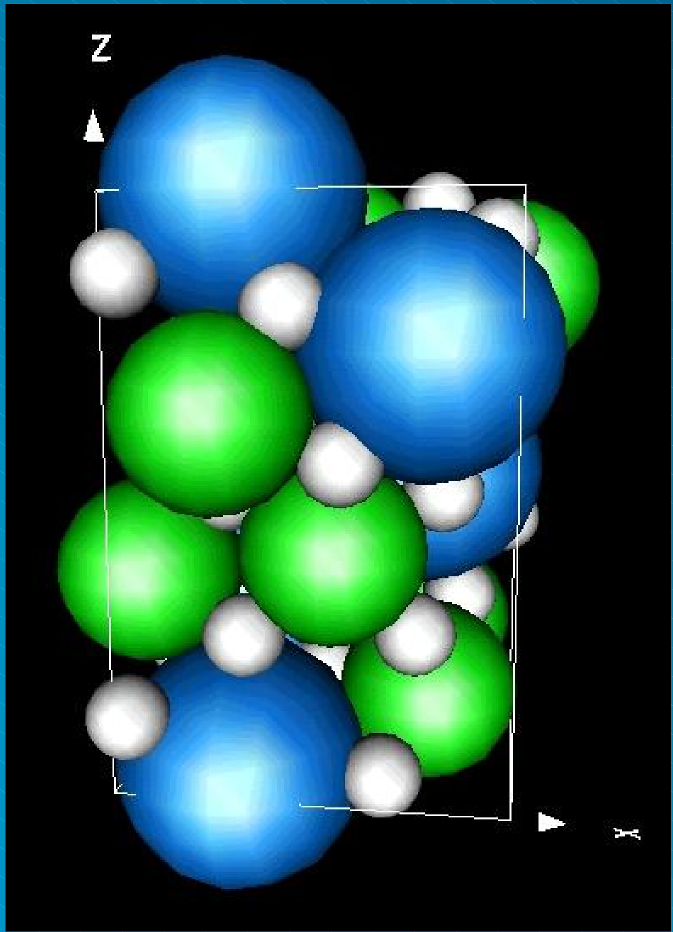
Real Materials, not crystals - Hydrogen in Metals



- 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..

Real Materials, not crystals - Hydrogen in Metals



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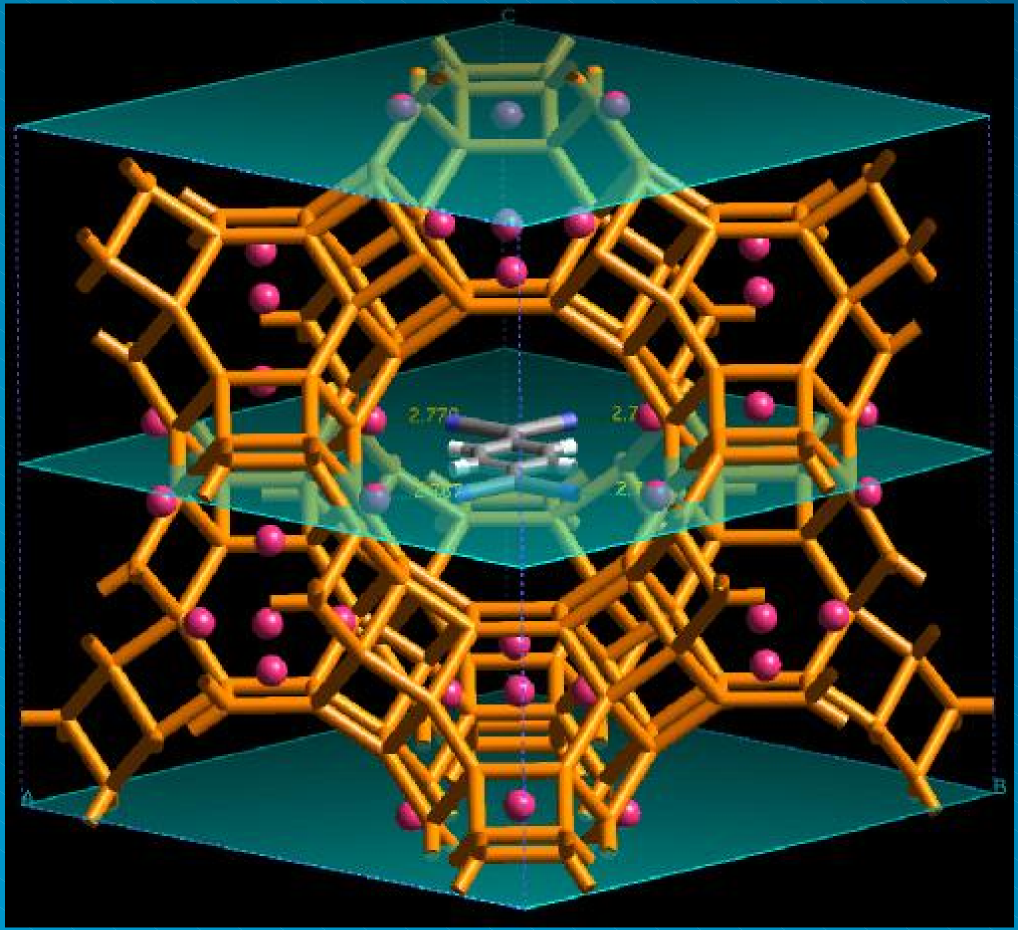
Neutron Diffraction

New zeolites to catalyse petro-chemical reactions

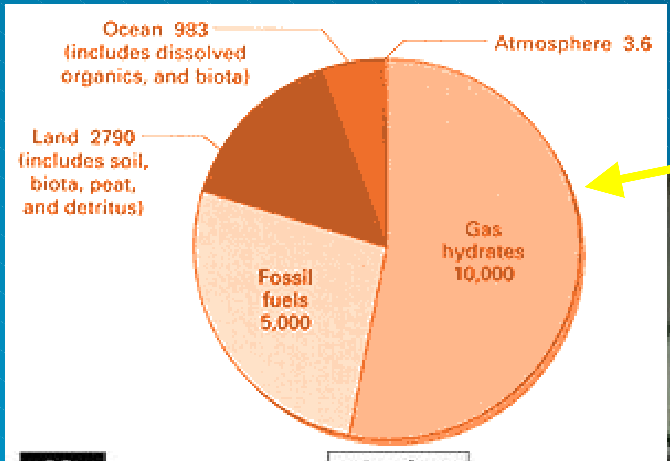


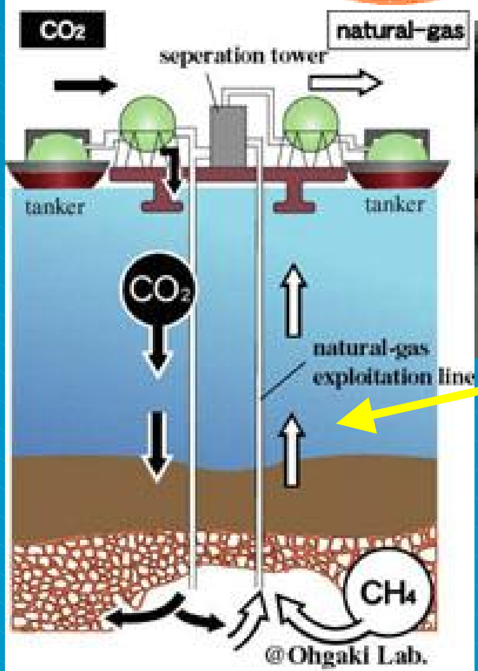
- Zeolites are very important in industry as catalysts for petro-chemicals etc
- Neutrons are used to understand how light hydrocarbon molecules interact
- Neutrons can also distinguish between silicon and aluminium in the framework
- A small organic molecule trapped inside the pore of NaY-zeolite.

C. Baehtz, H. Fuess (Darmstadt)

Neutron Diffraction

Clathrates, new gas hydrate fuel from the ocean

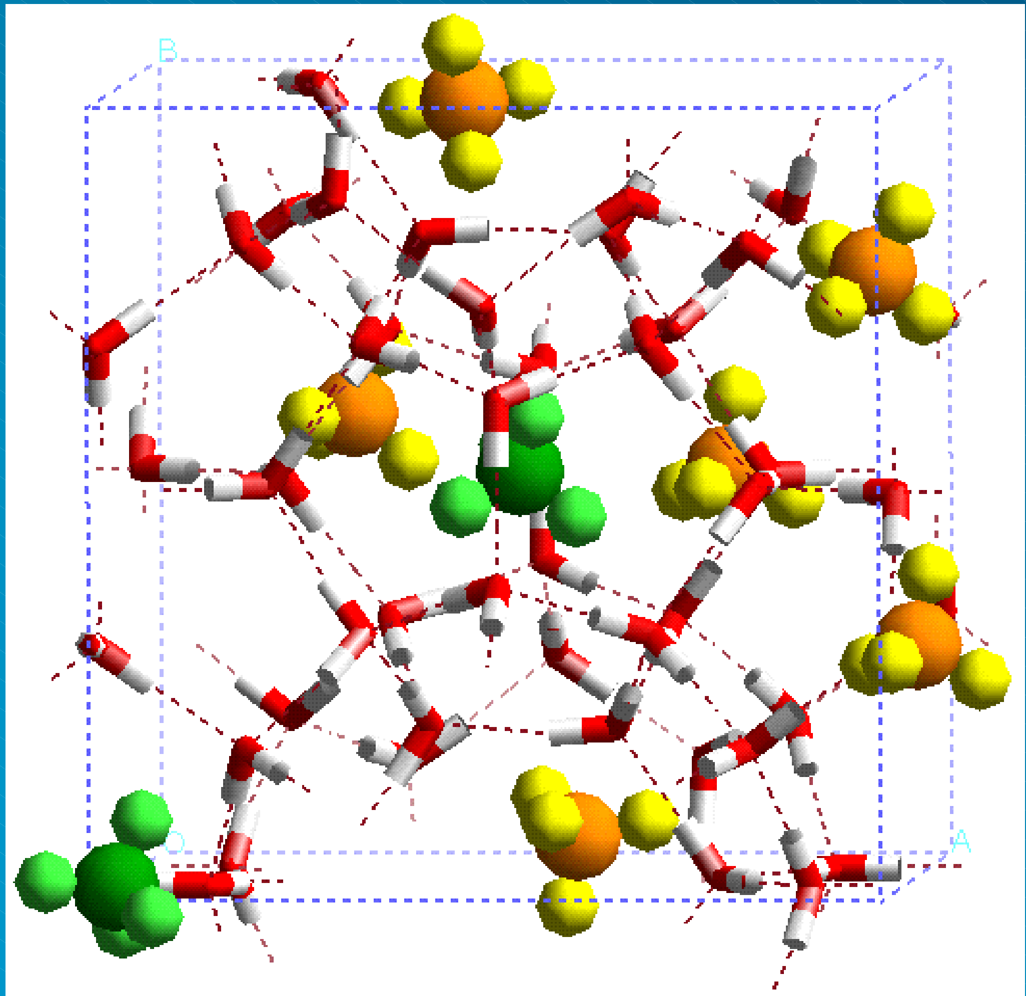




- Most hydrocarbons are locked in water cages at the bottom of the oceans
- These gas hydrates can be used as fuel
- A closed fuel cycle – extraction of methane and storage of CO2 in the deep ocean
- Neutrons are needed to learn more about these strange "clathrates"

Neutron Diffraction

Clathrates, new gas hydrate fuel from the ocean

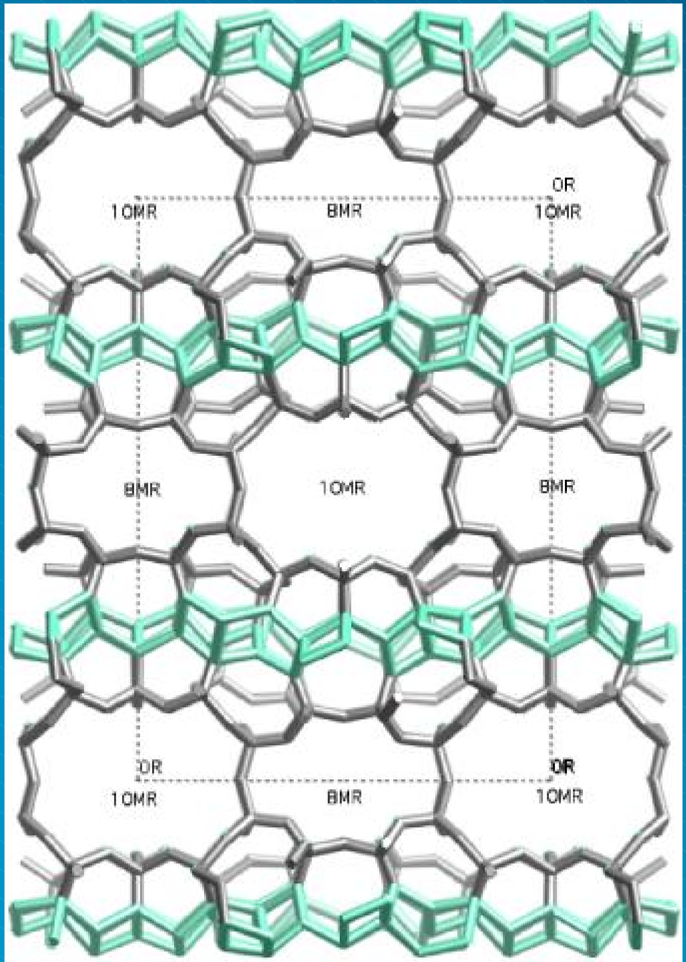


- Clathrates consist of molecular cages that can trap methane (spheres)
- Neutrons are important – they scatter strongly from the light methane atoms
- Compressibility was studied, to help with seismic searches for clathrates

B.Chazallon, A.Klaproth, D.Staykova, W.Kuhs (Göttingen)

Neutron Diffraction

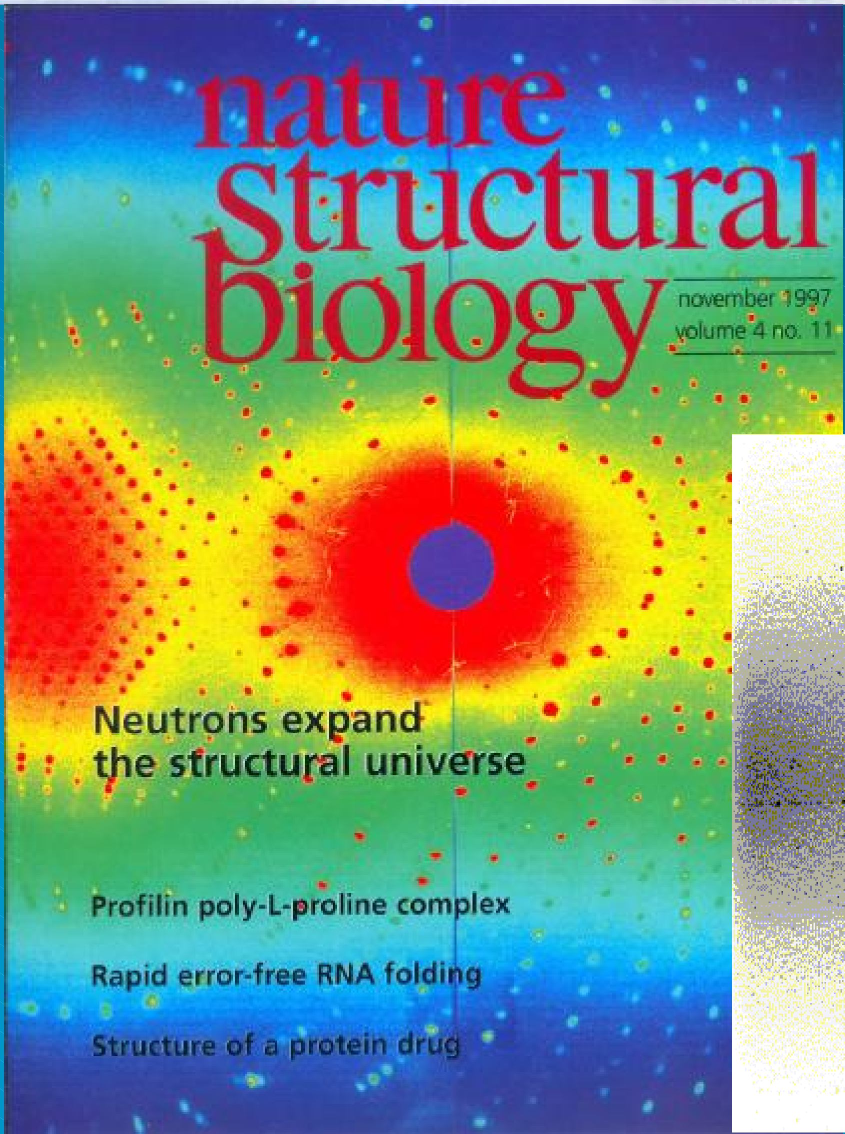
Molecular sieves and ion exchangers



- Ion exchangers can remove toxic metals from the environment
- New types of zeolite ion-exchangers are needed to trap specific elements
- Neutrons and synchrotron radiation are used to understand ion exchange
- RUB29, a new lithium zeolite for cleaning up radioactive caesium

J.B.Parise, S-H.Park, A.Tripathi, T.Nenoff, M.Nymann (SUNY & SANDIA)

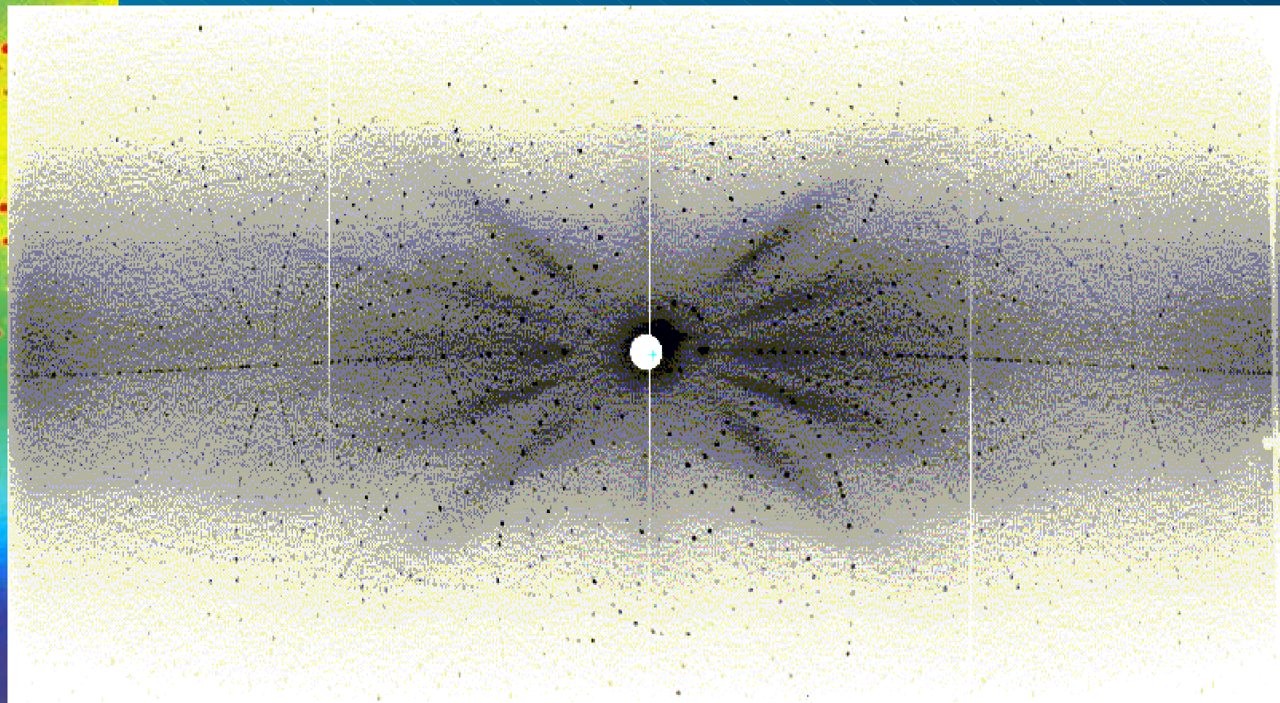
Neutron Diffraction



Neutron image plate detector

Large molecules and even proteins
can be studied – the role of water

N.Niimura, C.Wilkinson, M.Lehmann, F.Cipriani



Vitamin B12 – 10,000 reflections in 8 hours from 1 mm^3 crystal

Neutron Image Plate Detectors – like photographic film

All of the scattered neutron peaks are recorded simultaneously

Neutron Shutter

Crystal

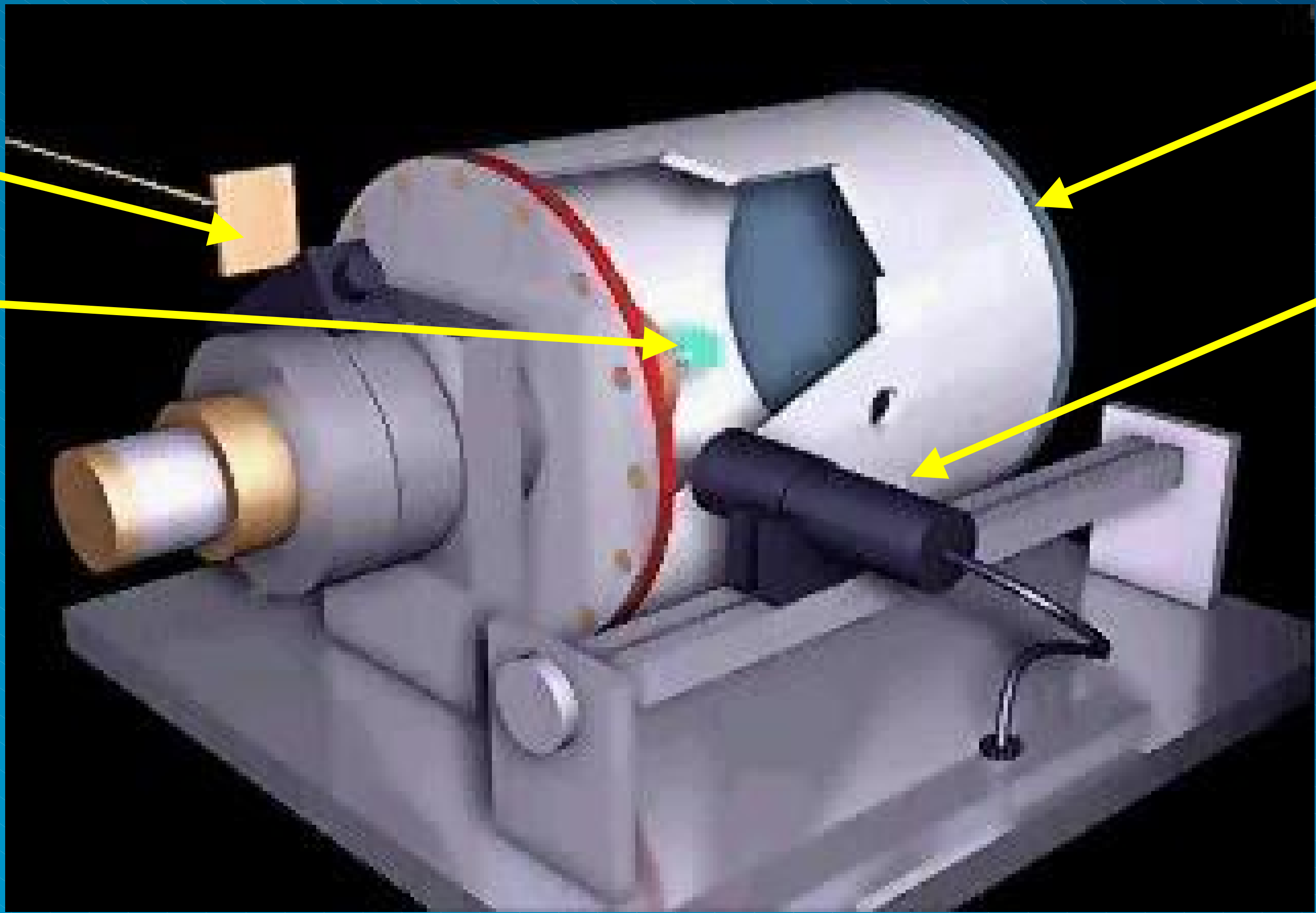


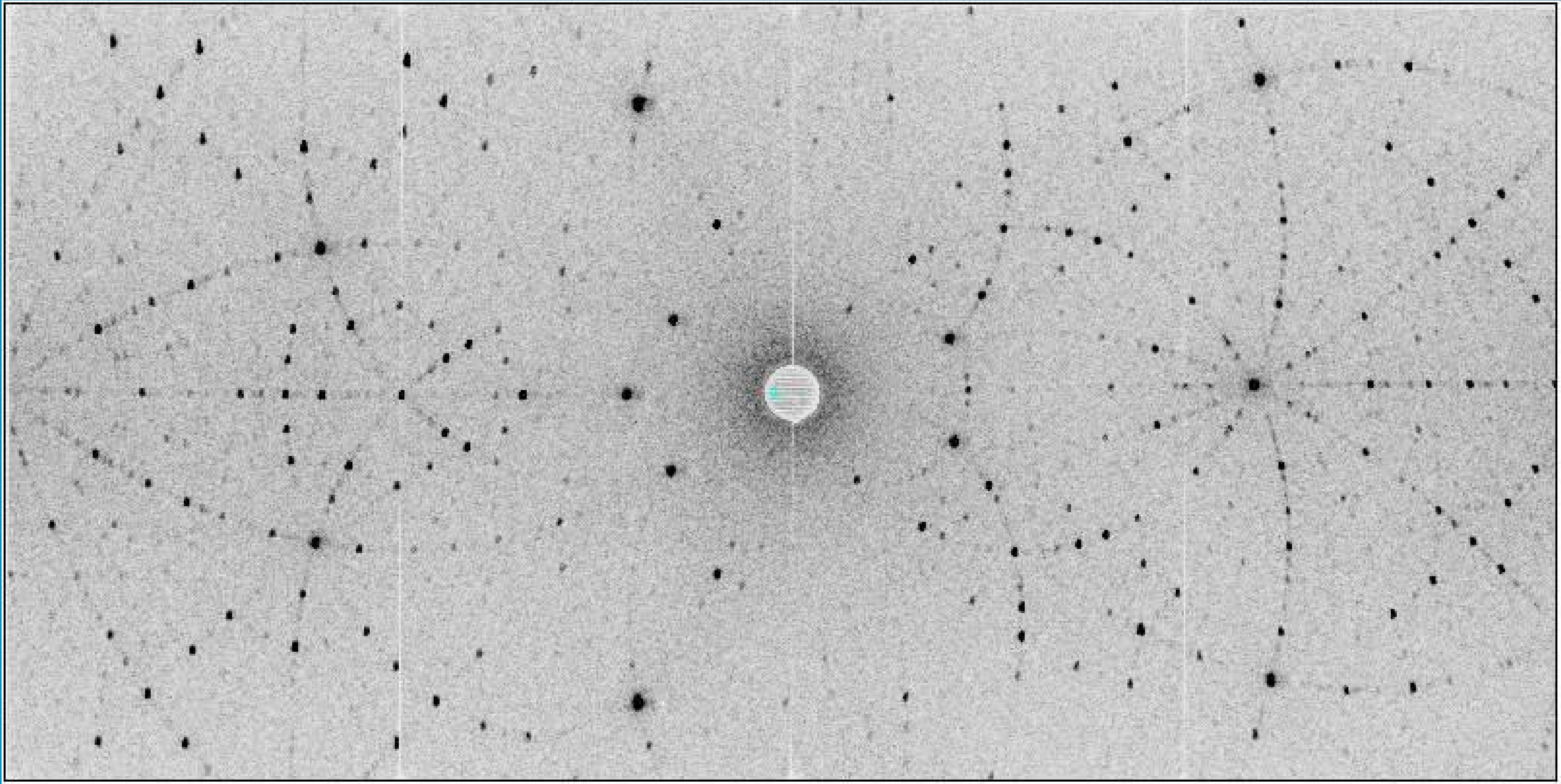
Image Plate

Read-out Laser

C.Wilkinson
M.Lehmann
D.Myles
F.Cipriani
G.McIntyre
(EMBL & ILL)

Neutron Image Plate & 5-fold symmetry of a quasi-crystal

All of the scattered neutron peaks are recorded simultaneously



Neutron Diffraction

- What has been achieved ? Exciting new science ?
  - High impact even outside the crystallographic community
  - Superconductors, Magnetism, Giant Magneto-Resistance, In-situ Chemistry, Electrochemistry, Clathrates, Zeolites…
- Why Neutrons ? Why not Xrays ?
  - Neutrons + Xrays complementary
  - Solution of structures with Xrays
  - Refinement of important details with neutrons – valence sums
- Why Powders ? Why not crystals ?
  - Crystals should be used when available (Image Plate & lrge PSD’s)
  - Much new work started with powders - high Tc, GMR…