Neutron Diffraction & the Structure of New Materials

A.W. Hewat, Institut Laue-Langevin, Grenoble FRANCE
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Mathematics, geometry, symmetry & the structure of materials

Arabesque

Moroccan star tiling

Carbon-60

Crystals & Quasicrystals
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World’s most intense neutron source
1280 visiting scientists each year
300+ scientific papers each year
physics, chemistry, biology, materials

ILL-Grenoble in Europe showing member countries

ILL member countries are shown in green
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Why Neutrons?

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

- Neutrons act like tiny magnets
- Interact with atomic magnetic moments
- Neutrons determine magnetic structures

- Ferromagnetic magnetite $\text{Fe}_3\text{O}_4$ (top)
- Antiferromagnetic manganese oxide $\text{MnO}$
Neutrons can be transmitted like light in an optic fibre

1. “Neutron guide tubes” bring the neutrons to the experiment.
2. The transmitted intensity (solid angle) depends on the neutron wavelength.
3. Only neutrons are transmitted (low background).
Neutrons scatter like waves from atomic planes

1. The neutron wavelength is similar to the atomic spacing
2. Scattered neutrons determine the atomic structure of materials

\[ q = \frac{2 \sin \theta}{l} = \frac{n}{d} \] (reciprocal space)
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
High resolution neutron diffractometers – D2B at ILL
Strong peaks at high angles give high precision structures of materials
Neutron intensities are low, so large detectors are needed.

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

Anton Oed
Bruno Guerard
Pierre Convert
Thomas Hansen
Jacques Torregrossa
Neutron intensities are low, so large detectors are needed.

Construction of a microstrip position-sensitive detector (printed circuit)
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 Image Plate Detectors - like photographic film
All of the scattered neutron peaks are recorded simultaneously

Neutron 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
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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 mm³ crystal
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
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Neutrons gave new insight, important in searching for similar materials.
M. Marezio, J-J. Capponi, A. Hewat... (CNRS & ILL)

The 90K high Tc superconductor

- Left - by X-rays
- Right - by Neutrons
The importance of oxygen for high-\(T_c\) superconductors

Neutrons are sensitive to oxygen - "charge reservoir" concept

Superconducting \(\text{YBa}_2\text{Cu}_3\text{O}_7\)  Non-supercond.\(\text{YBa}_2\text{Cu}_3\text{O}_6\) Charge reservoir layer

R. Cava, A. Hewat, E. Hewat, M. Marezio (Bell labs & ILL)
High-Tc superconductors

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

$Y_{1}Ba_{2}Cu_{3}O_{7-x}$

Valence (Cu2)

R. Cava, A. Hewat, E. Hewat, M. Marezio
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Charge & magnetic order - Giant Magneto-Resistance (GMR)

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

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

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

Stripe model excluded by the neutron and synchrotron data
Molecular Beam Epitaxy (MBE) allows us to build up layers on an atomic scale.

Neutrons are tiny magnets, so can be used to probe magnetic interactions between layers via neutron reflectometry.

Devices made from magnetic multilayers include "spin valves" used for computer disks and non-volatile memory.

J. Goff, S. Lee, R. Ward, M. Wells, G. McIntyre (Liverpool & ILL)
Molecular magnets

- Molecular magnets can be light, transparent, magneto-optic, bio-compatible etc…

- Neutrons are unique for mapping the magnetisation density on an atomic scale

- The first organic ferromagnet (left) - the magnetic density is on nitrogen & oxygen
Second-harmonic organo-metallic electro-optical materials

- Second-harmonic generators SHG double the frequency of light, changing a red laser beam to blue.
- Shorter wavelength lasers mean more information on a CD.
- SHG materials are usually inorganic, but we now have fast organic SHGs.
- Neutrons can find the light hydrogen atoms, important for understanding charge transfer.
- X-rays are used as well to determine the charge distribution (left).

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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)
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)
We need a material to store hydrogen.

Some materials, e.g., $\text{Mg}_2\text{FeH}_6$ (left), store a higher density than liquid hydrogen.

Neutrons are used to understand how hydrogen is absorbed.

Search for better storage materials.

The small white hydrogen atoms fill the holes between the large metal atoms.

K. Yvon (Geneva)
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)
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)
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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”.

Diagram showing:
- Ocean 983 (includes dissolved organic, and biota)
- Land 2790 (includes soil, biota, peat, and detritus)
- Atmosphere 3.6
- Fossil fuels 5,000
- Gas hydrates 19,000
- CO2 separation tower
- Natural gas exploitation line
- CH4 gas hydrate
- Tanker transport
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)
New ceramics to replace metals in engineering components

- Titanium silicon carbide $\text{Ti}_3\text{SiC}_2$ 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.)
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°C 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$_3$SiC$_2$ product.

D. Riley, E. Kisi (Newcastle, Aust.)
Measuring stresses deep inside engineering components

- Tensile stress can produce cracks
- Compressive stress toughens materials
- Neutrons can penetrate deep inside materials (~10cm) and measure stress by changes in atom spacings
- The compressive stress (blue) deep inside a VW crankshaft
- Design of stronger, lighter engines
Measuring stresses deep inside engineering components

1. The neutron beam is collimated to a 1mm$^3$ “gauge volume” of measurement.
2. The scattered peak is measured on a position-sensitive detector (PSD).
3. Small shifts in peak positions map the strain as the sample is scanned.
4. Very large engineering components (1 tonne) can be scanned using a “hexapod” platform (similar to the platform of an aircraft flight simulator).

T. Pirling, G. Bruno (ILL & Manchester)