



# Materials Research at CCLRC European Labs.

Alan Hewat, ILL Grenoble



## Grenoble France

ILL-Grenoble in Europe  
showing member countries



- | World's most intense neutron source
- | ~300 staff
- | ~1250 visiting scientists each year
- | ~500 scientific papers each year
- | physics, chemistry, biology, materials

ILL member countries are shown in green



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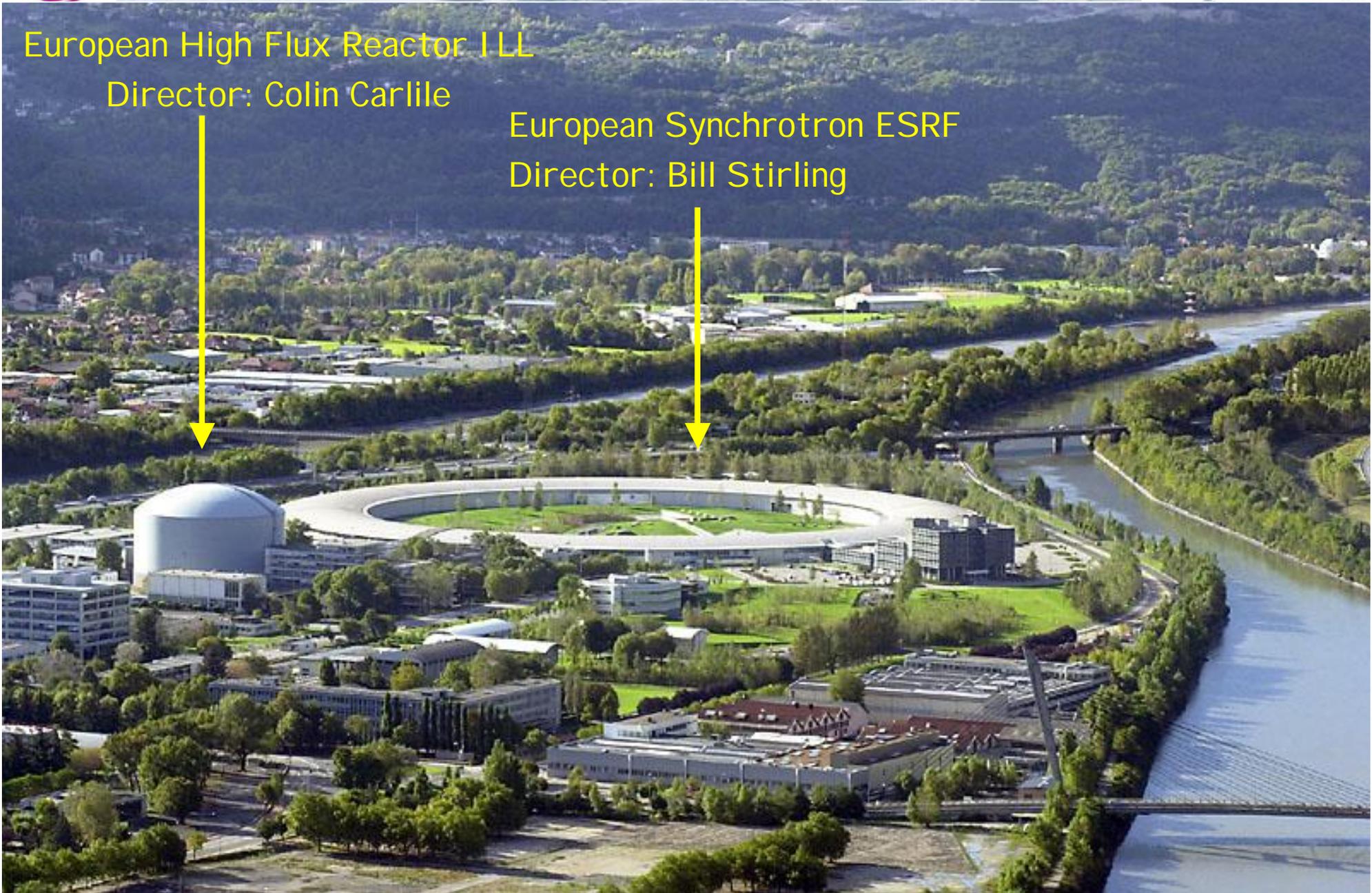
European High Flux Reactor ILL

Director: Colin Carlile



European Synchrotron ESRF

Director: Bill Stirling



# An Interesting Environment – On a Good Day



# An Interesting Environment – On a Bad Day





# Neutrons compared to X-Rays/Synchrotrons



## Why International ?

- | Publicising UK Science (“Rayonnement” of the country).
- | Meeting people with other ideas (“canteen” effect ).
- | Cost effective (cost/instrument day is actually lower).



# Neutrons compared to X-Rays/Synchrotrons



## Why Neutrons ?

- | Neutrons are electrically neutral & more penetrating than X-rays.
- | Light atoms scatter neutrons as strongly as heavy atoms.
- | Neutrons are tiny magnets, & can determine magnetic structures.



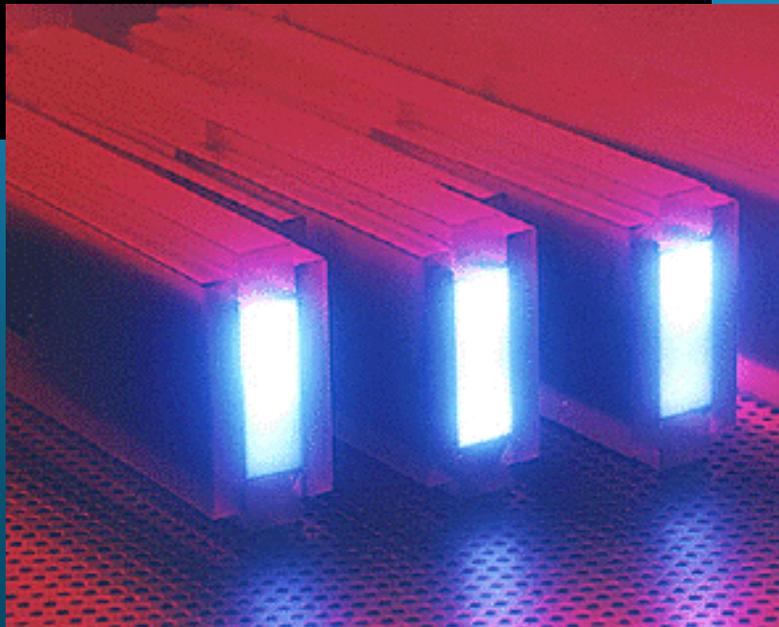
# Neutrons - Neutral Particles & also Waves



Neutrons can be transmitted like light in an optic fibre

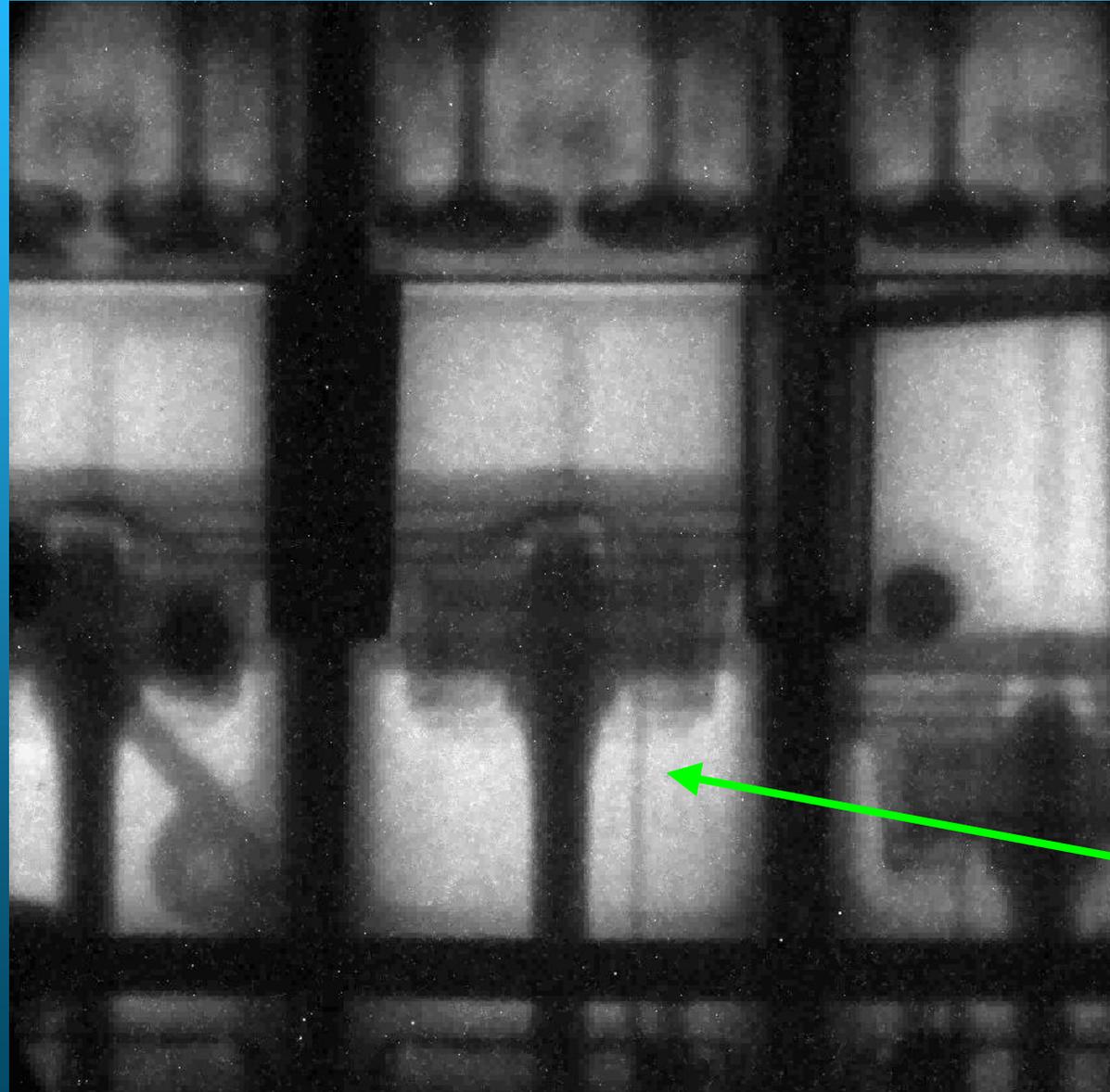


- “Neutron guide tubes” bring the neutrons to the experiment





Neutrons are more penetrating than X-rays  
And see light atoms - hydrocarbons



Neutron radiograph  
of a real BMW engine  
Time 0.5 milliseconds

Cooling oil splash

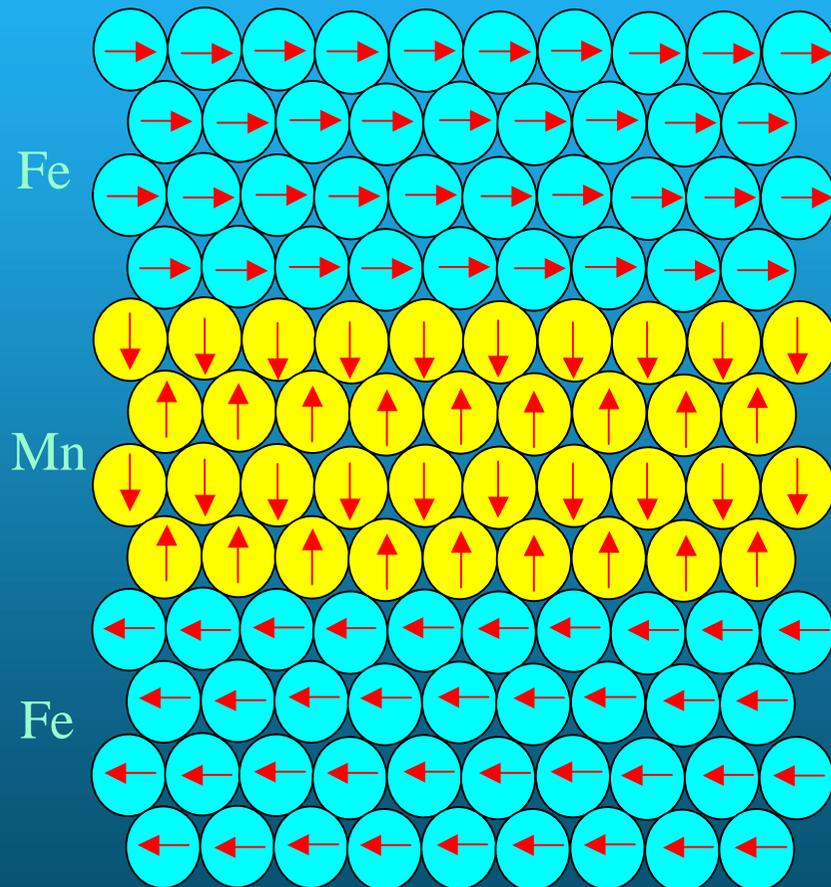
A. Hillenbach (Munich & ILL)



# Neutrons can study magnetic materials



## Magnetic multilayers



- | Molecular Beam Epitaxy MBE allows us to build up layers on an atomic scale – Nano-structures
- | Neutrons are tiny magnets, so can be used to probe magnetic interactions between layers – neutron reflectometry
- | Devices made from magnetic multilayers include “spin valves” used for computer disks and non-volatile memory

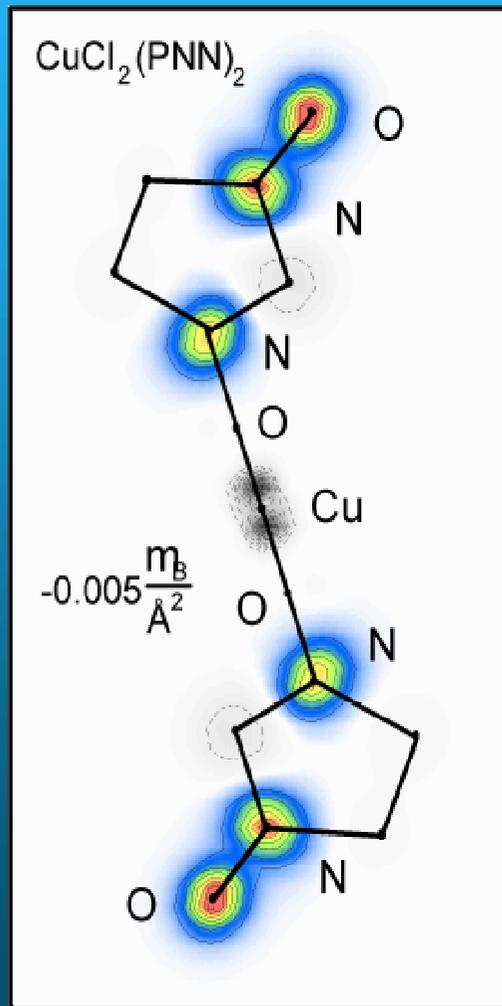
J. Goff, S. Lee, R. Ward, M. Wells, G. McIntyre (Liverpool & ILL)



# Neutrons can study magnetic materials



## 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

E. LeLievre-Berna et al. ILL (D3 originally developed by P.J.Brown & B.Forsyth)



# Neutrons are Expensive - Need Every Neutron



## Neutron Image Plate Detectors - a neutron camera

All of the scattered neutron peaks are recorded simultaneously

Neutron  
Shutter

Crystal

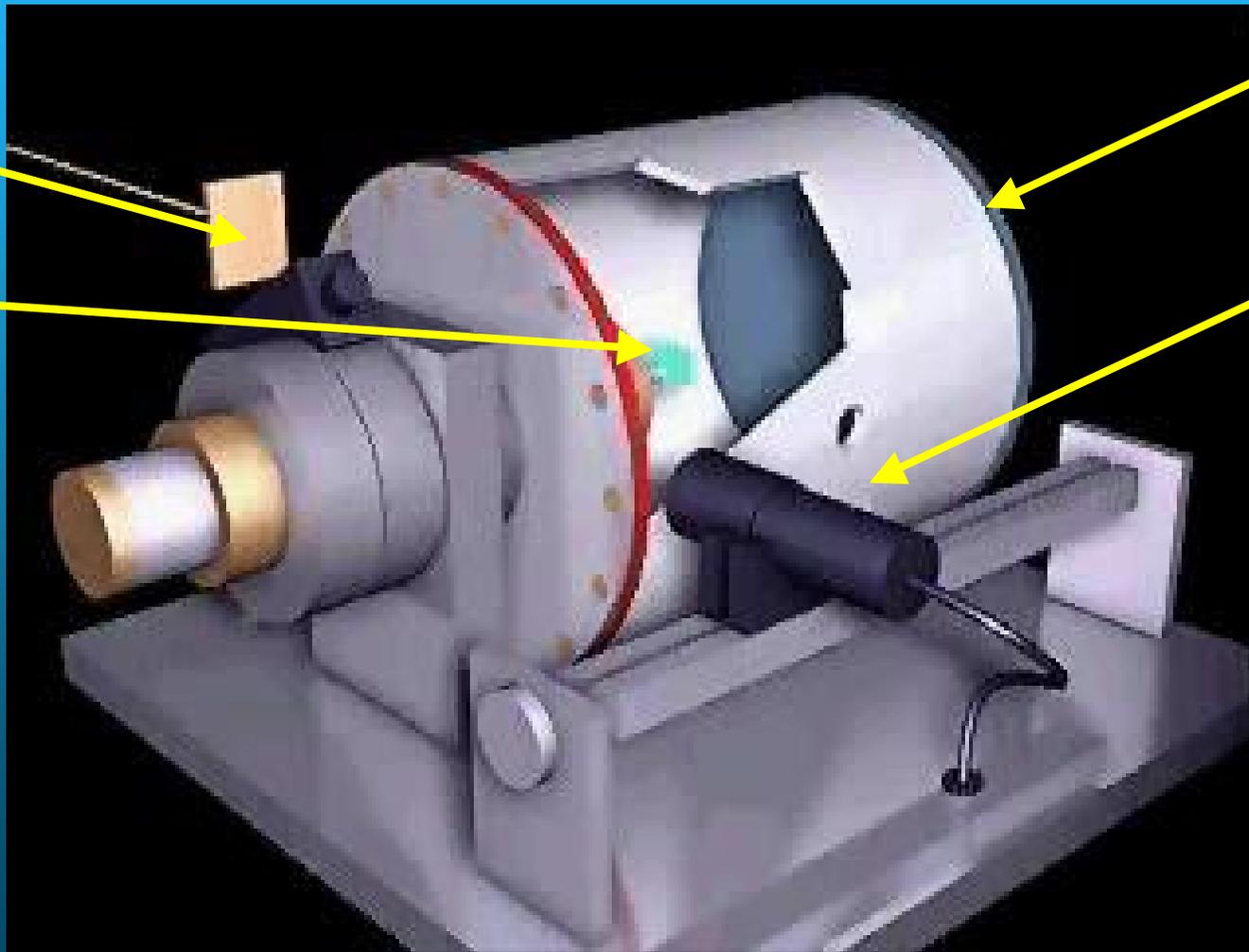


Image Plate

Read-out  
Laser

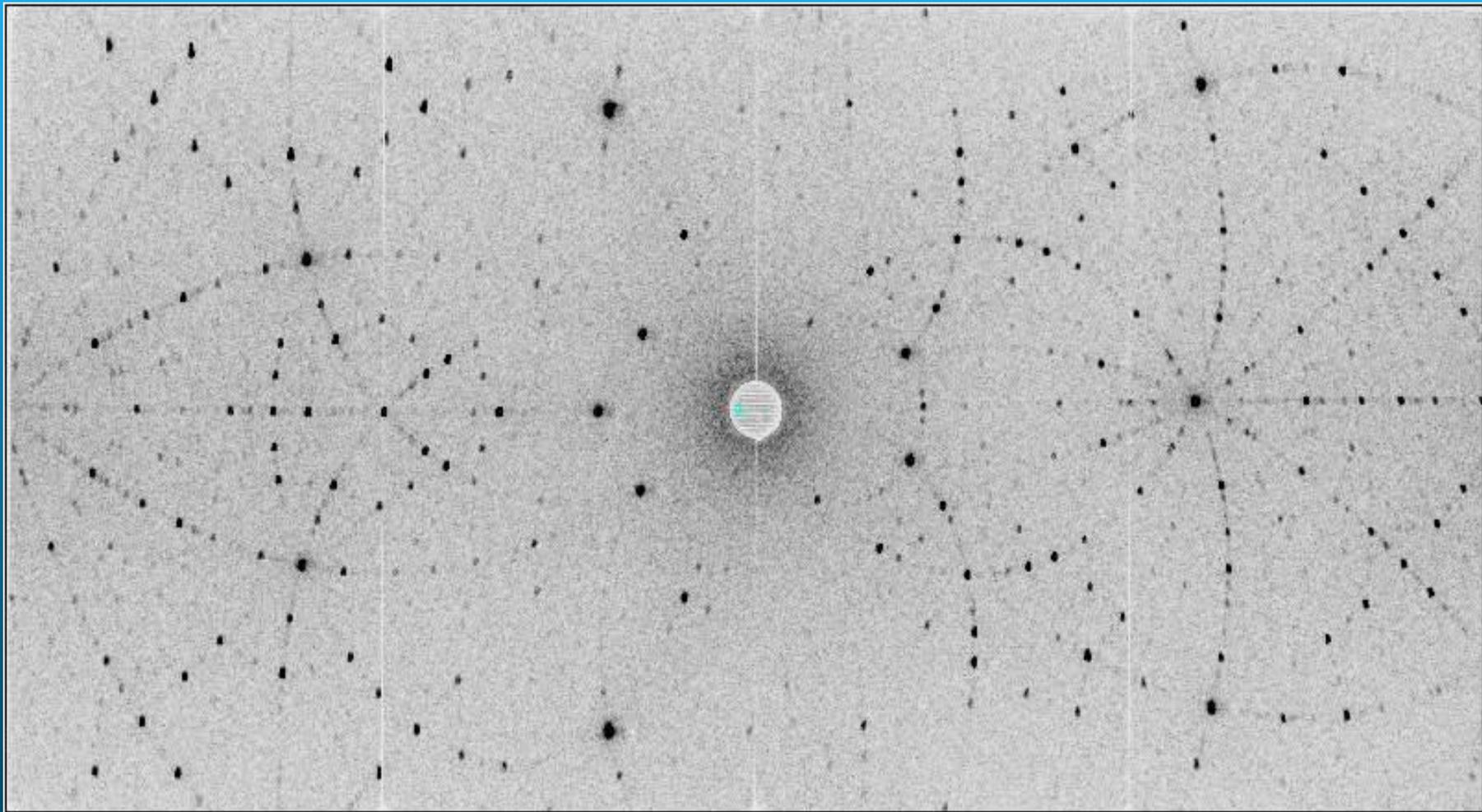
C.Wilkinson  
M.Lehmann  
D.Myles  
F.Cipriani  
G.McIntyre  
(EMBL & ILL)



Neutrons are Expensive – Need Every Neutron



Neutron Image Plate & 5-fold symmetry of a quasi-crystal  
All of the scattered neutron peaks are recorded simultaneously





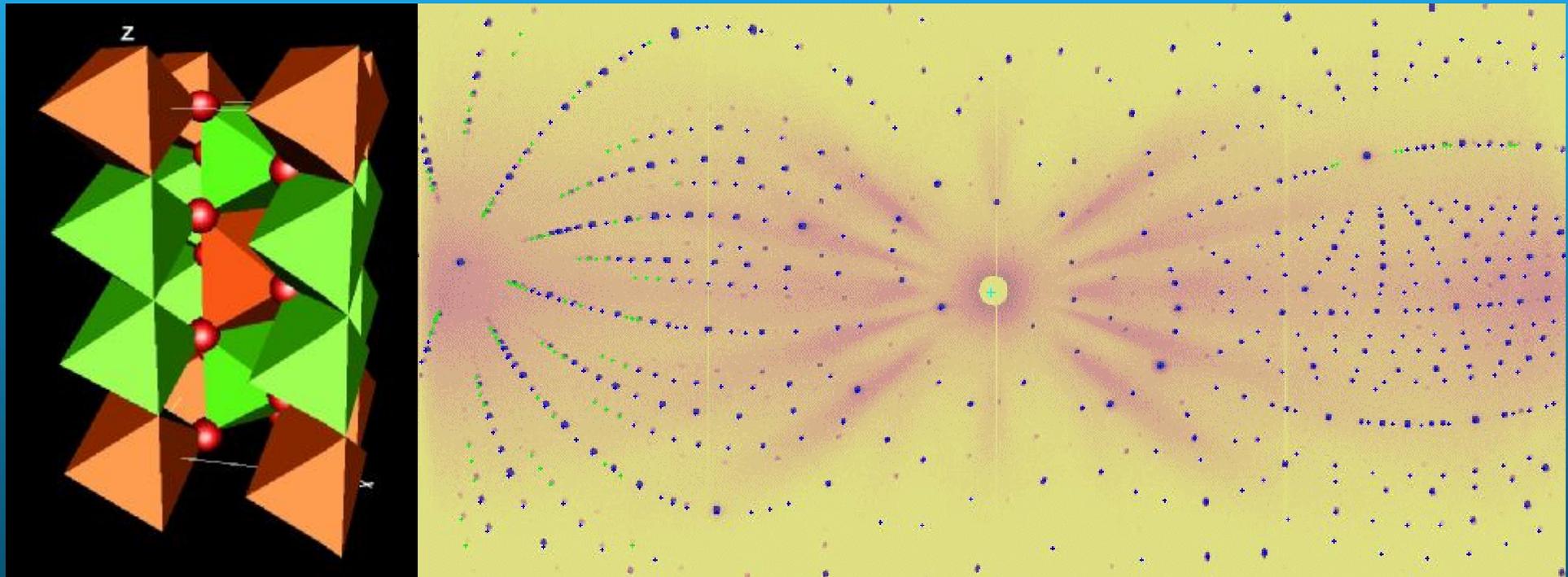
# Neutron Detectors and Magnetic Materials



## Magnetic order in Tapiolite $\text{FeTa}_2\text{O}_6$

VIVALDI image plate detector photos at 10K and 2K

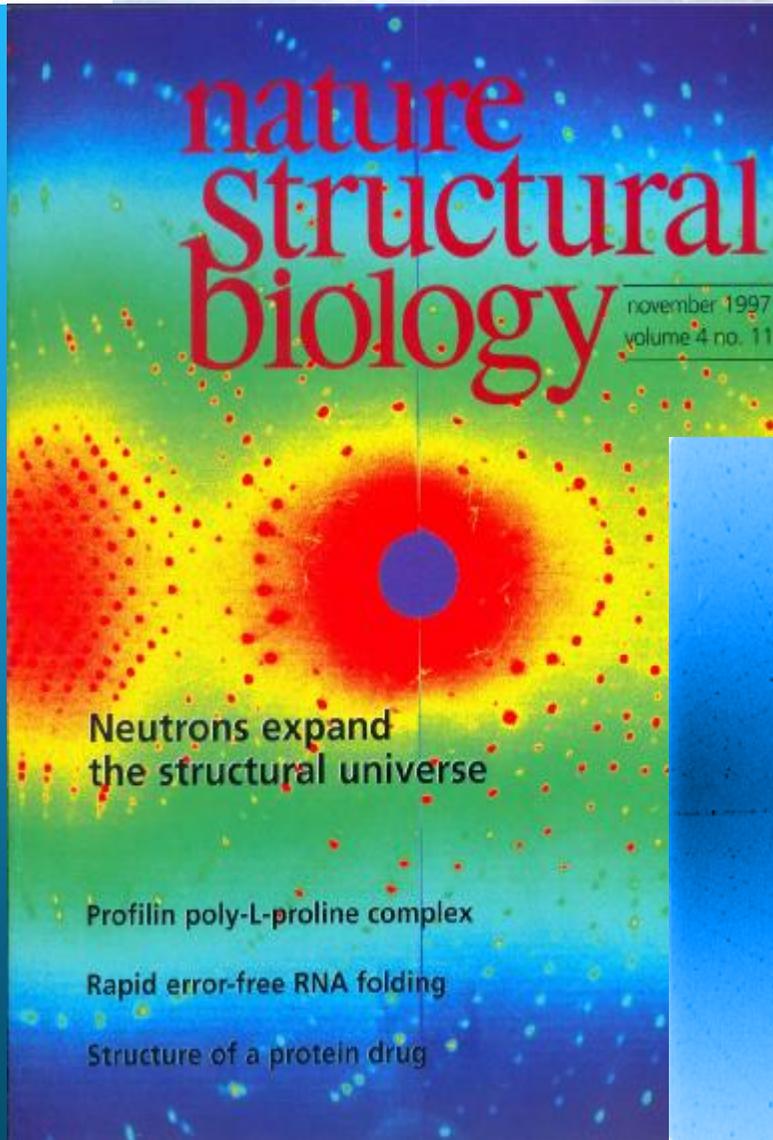
Tiny 100 micron crystals, 1000's of spots in a few hours



G.McIntyre, C.Wilkinson, D.McPaul et al. (ILL & Warwick)



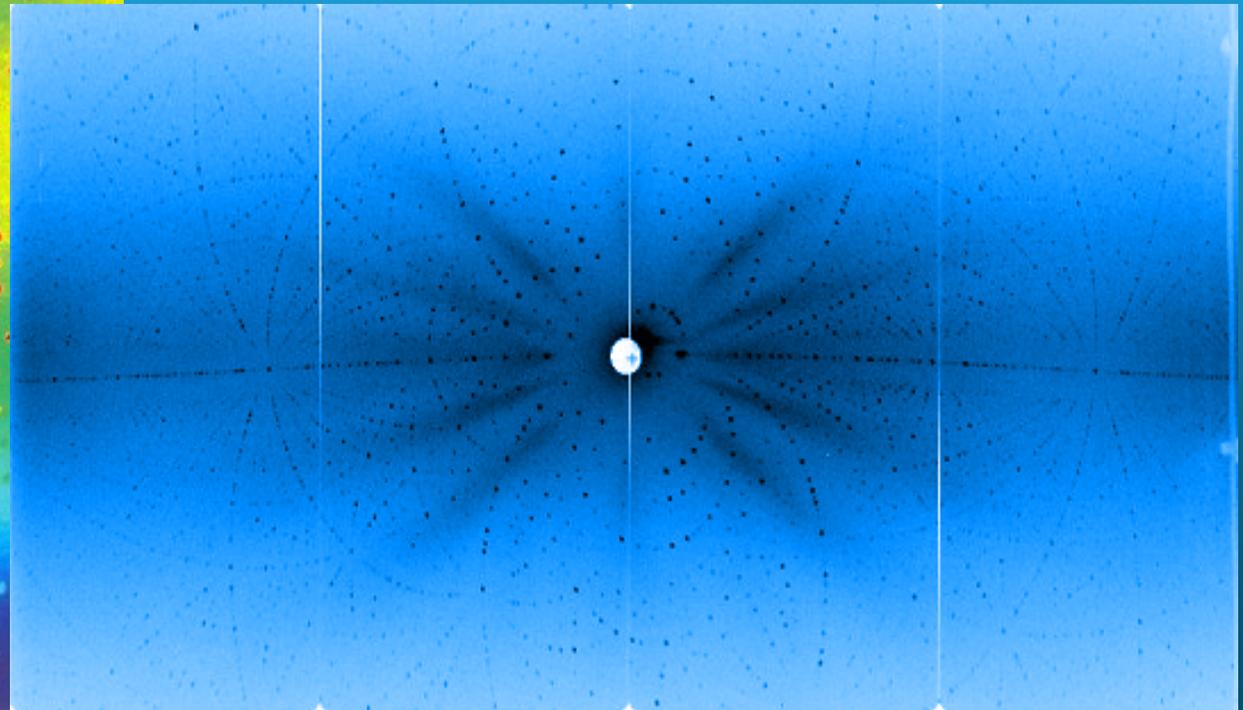
# Neutrons and Life - hydrocarbons



## Neutron image plate detector

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

C.Wilkinson et al. (ILL & King's College)



Vitamin B12 - 10,000 reflections in 8 hours from 1 mm<sup>3</sup> crystal



# Neutrons are Expensive – Need Every Neutron



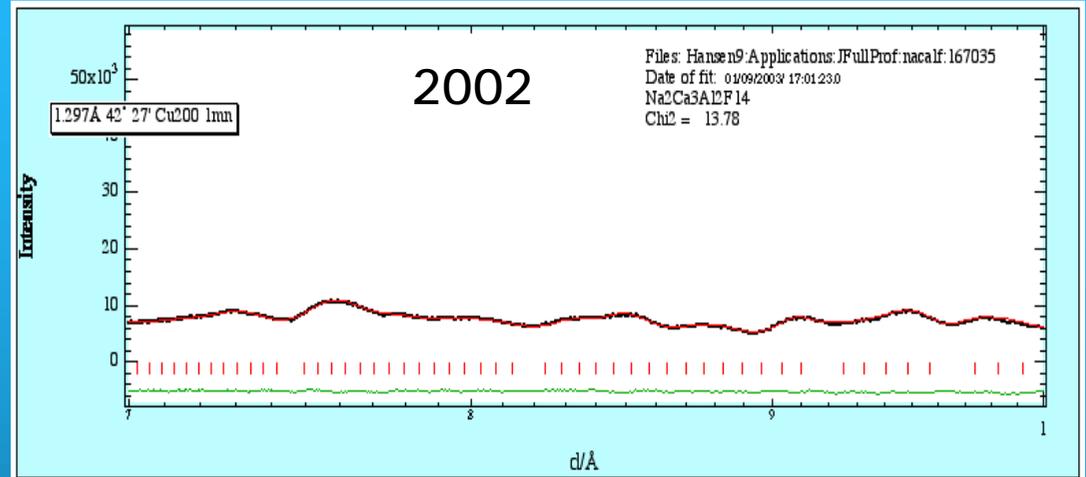
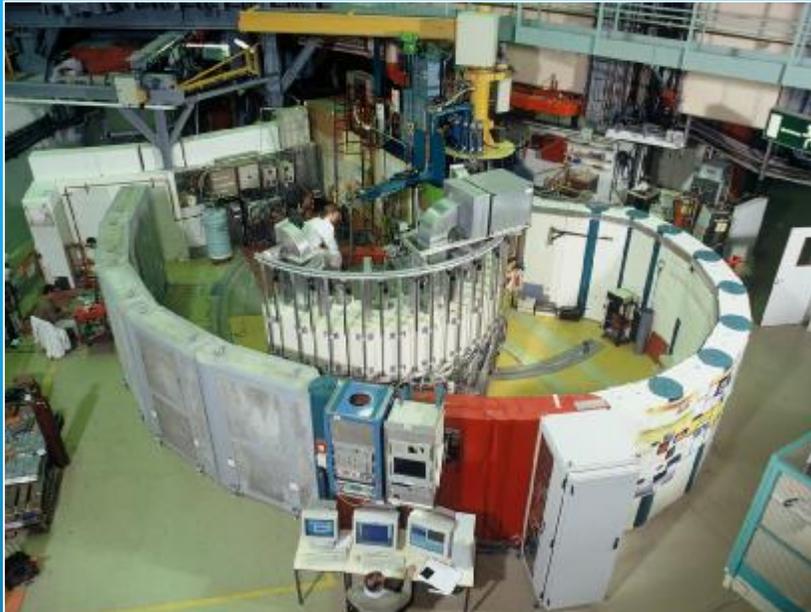
Neutron intensities are low, so large detectors are needed  
Construction of a microstrip position-sensitive detector (printed circuit)



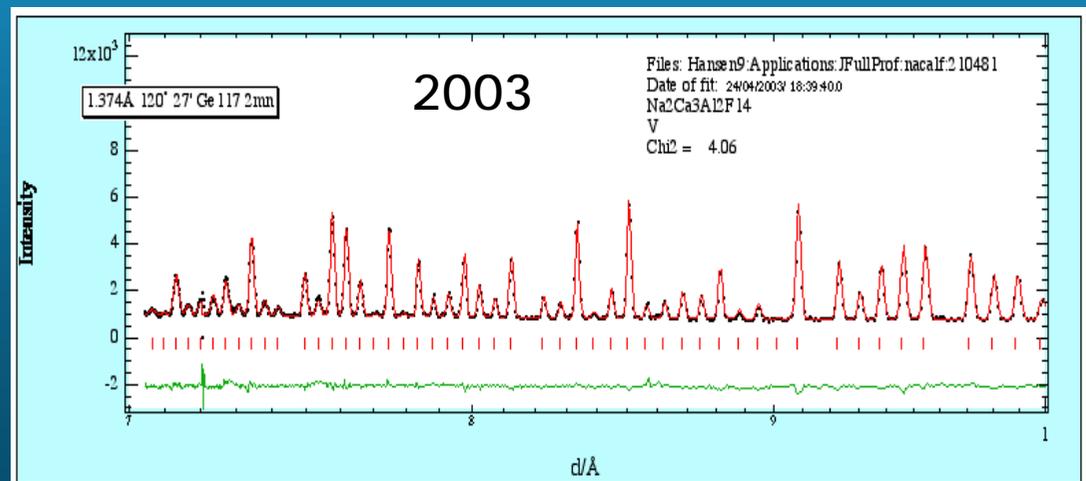
A.Oed,  
P.Convert,  
T. Hansen,  
et al...  
(ILL)



# A Continuing Fight to Improve Performance



Before and After (data in 2 min.)



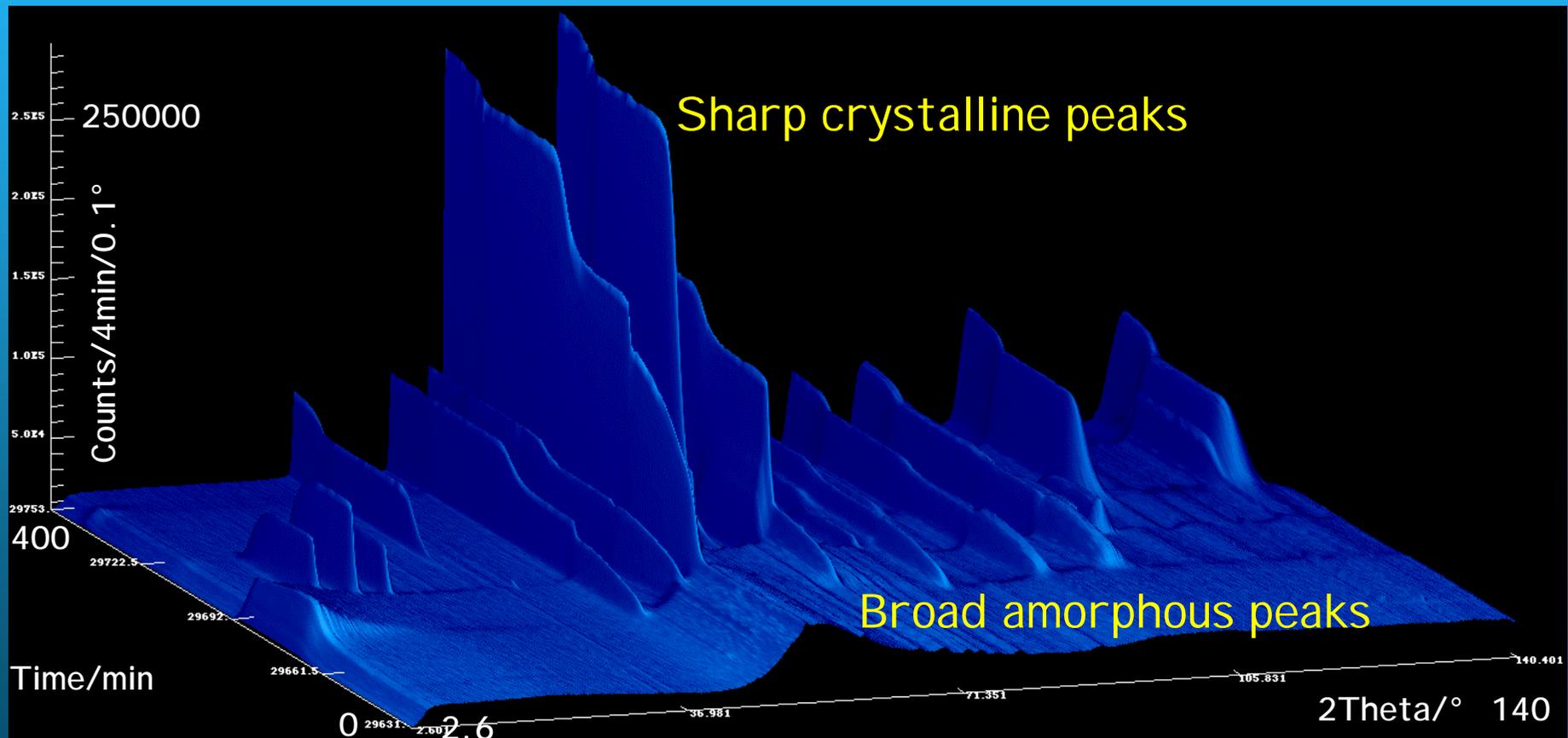
Higher D20 resolution since 2003



# Applications of large fast detectors



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



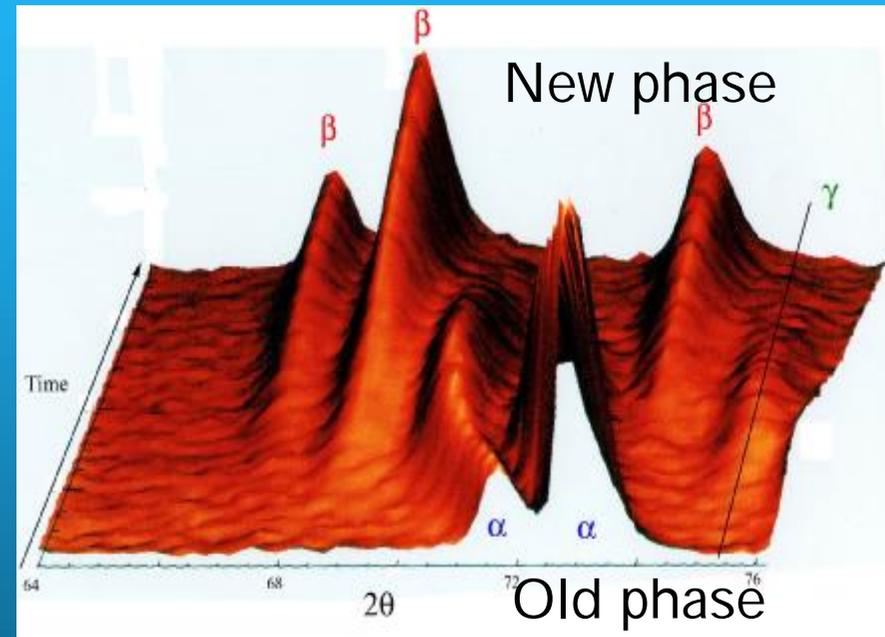
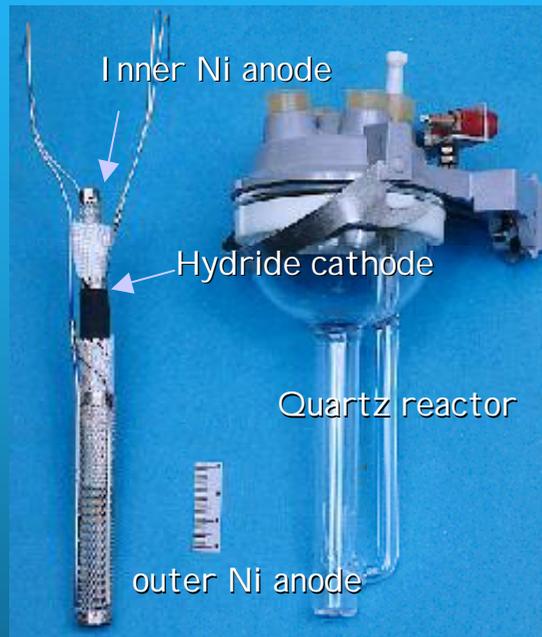
Complete diffraction pattern in minutes or seconds, scanning through temperature  
R. Cywinski, S. Kilcoyne (St Andrews)



# Applications of large fast detectors



## 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

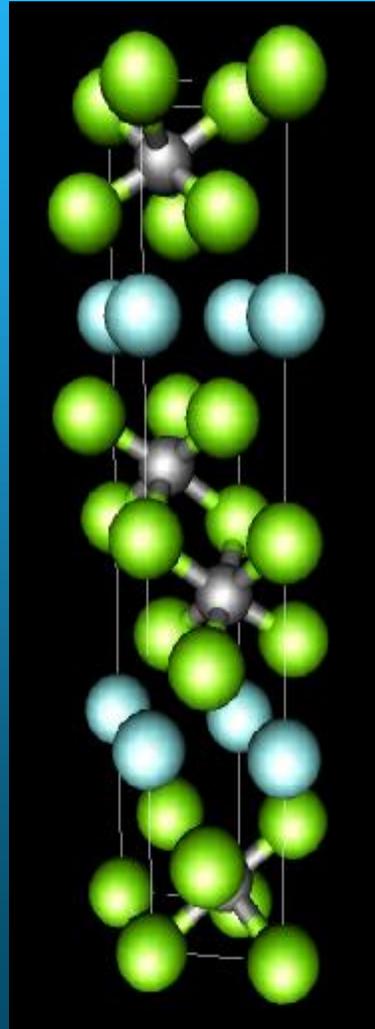
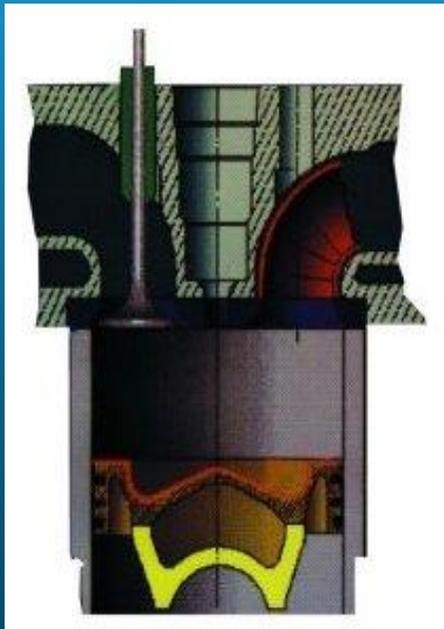
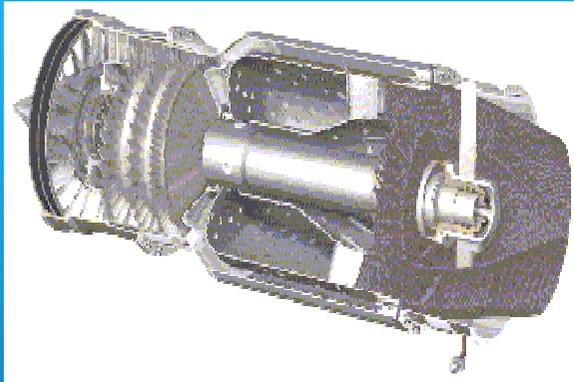
Y. Chabre, M. Latroche, M.R. Palacin,  
O. Isnard, G. Rousse (CNRS, CIC-Spain + ILL)



# Applications of large fast detectors



## 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 was used to study Self-propagating High-temperature Synthesis - SHS

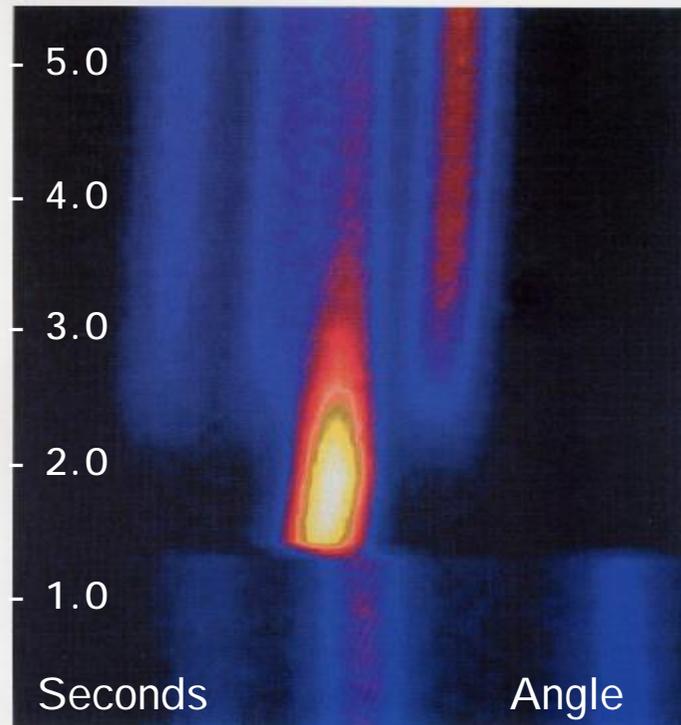
**D.Riley, E.Kisi, T.Hansen, A.Hewat**



# Applications of large fast detectors



## New ceramics to replace metals in engineering components



**Journal**  
of the American Ceramic Society  
Incorporating Advanced Ceramic Materials and Communications  
Volume 85 Number 10 October 2002

- | 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 300 ms intervals – **A World Record**
- | Knowledge of the SHS process allows us to prepare a pure  $\text{Ti}_3\text{SiC}_2$  product

**D.Riley, E.Kisi, T.Hansen, A.Hewat**

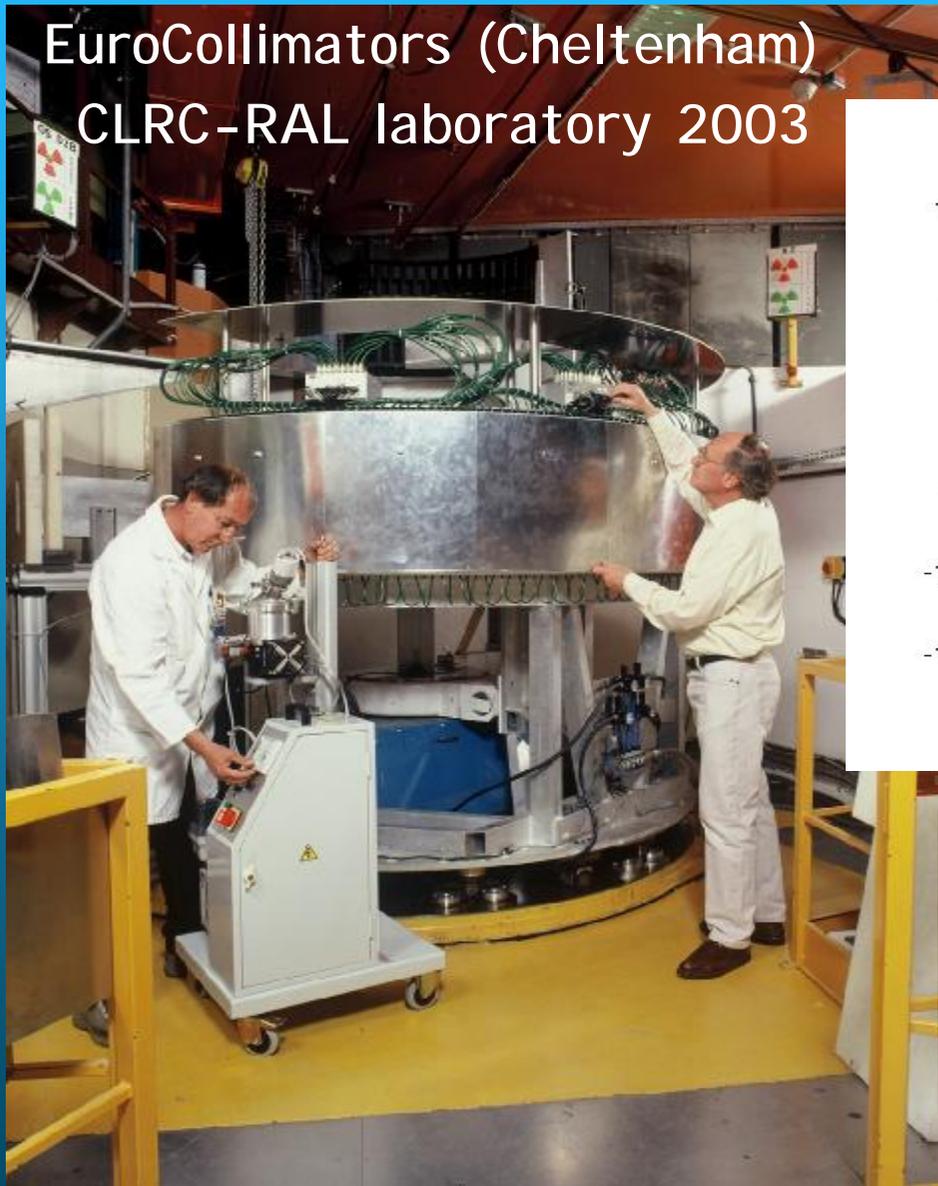


EPSRC

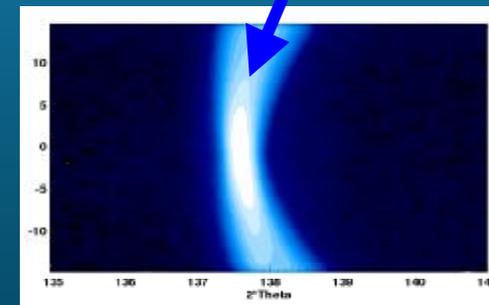
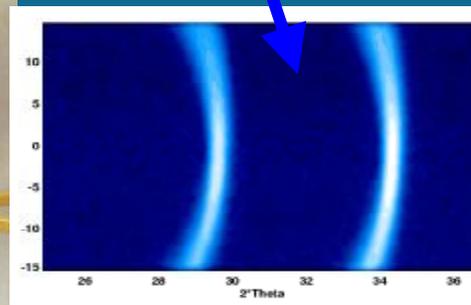
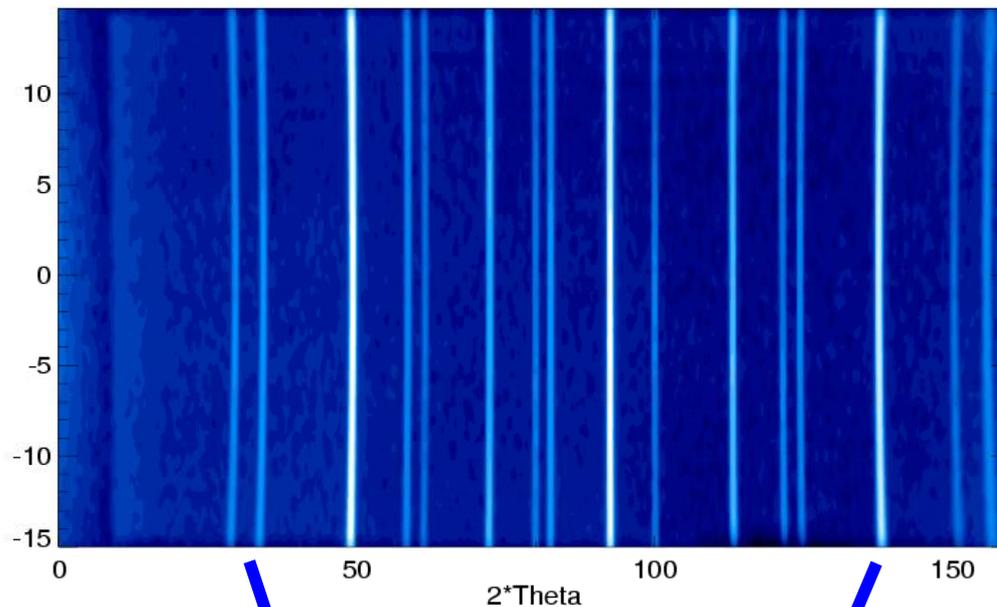
# Need Every Neutron



EuroCollimators (Cheltenham)  
CLRC-RAL laboratory 2003



UK-EPSRC project Super-D2B



E.Suard, C.Ritter, A.Hewat, P.Attfield... (Edin.)

Alan Hewat, CCLRC-IOP Materials Awareness Workshop, London 10 March 2004



EPSRC

# Applications of D2B

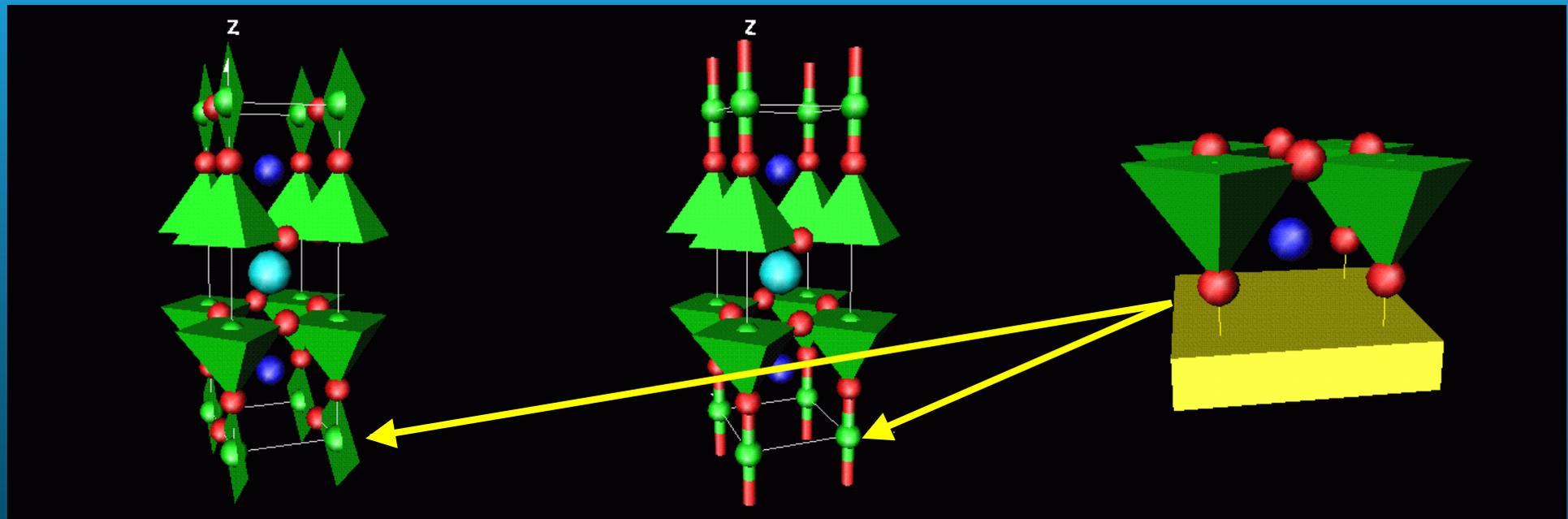


## The importance of oxygen for high- $T_c$ superconductors

Neutrons are sensitive to oxygen – “charge reservoir” concept

Very precise measurement of oxidation state of metal ions

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



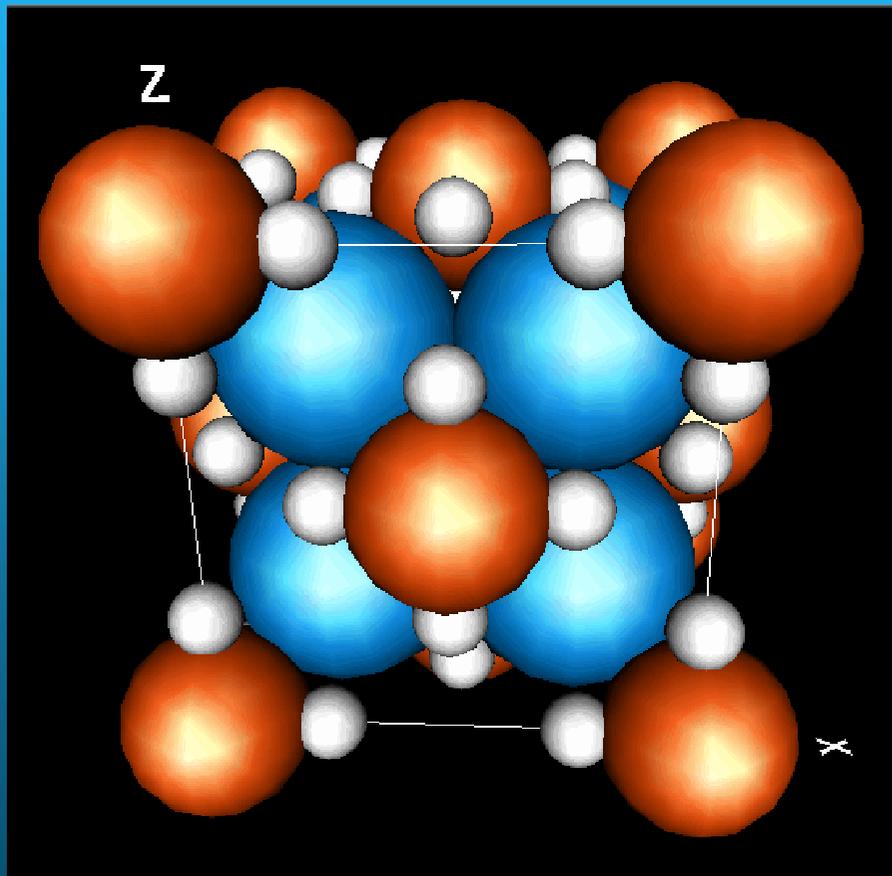
R. Cava, A. Hewat, E. Hewat, M. Marezio et al.



# Neutrons and the Energy Economy



## Potential Hydrogen storage materials



- | We need a material to store hydrogen
- |  $\text{Mg}_2\text{FeH}_6$  (left) stores twice as much hydrogen as the same volume of 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 metal atoms

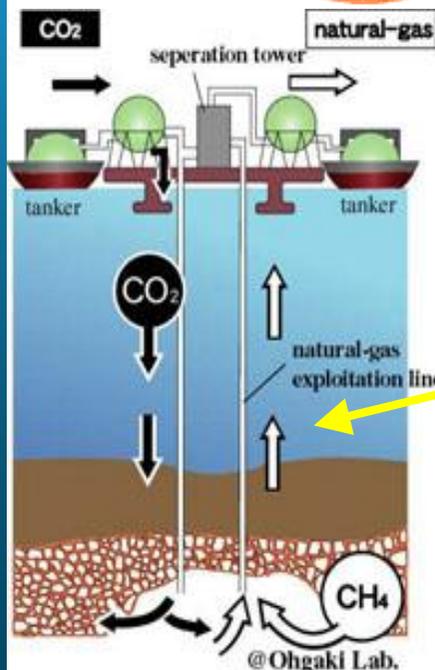
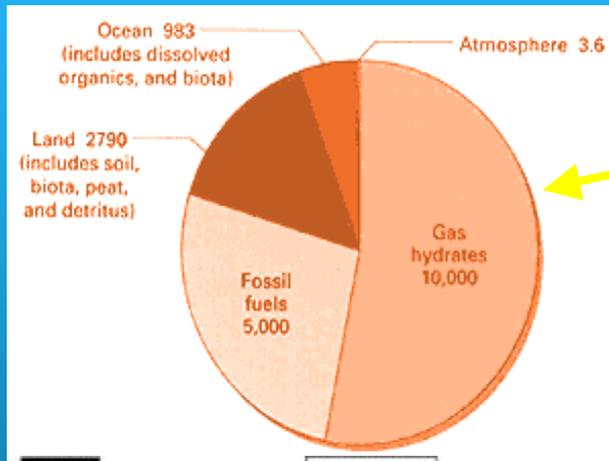
K. Yvon (Geneva)



# Neutrons and the Energy Economy



## 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 CO<sub>2</sub> in the deep ocean

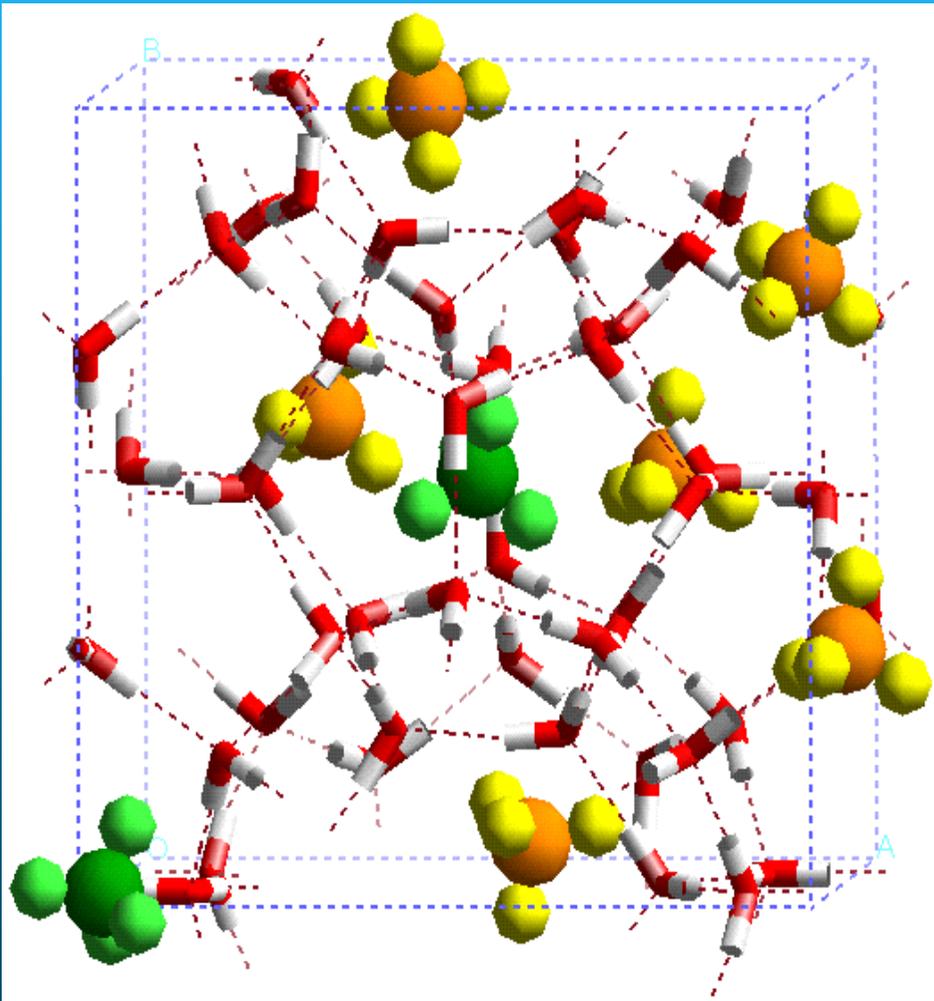
Neutrons are needed to learn more about these strange “clathrates”



# Neutrons and the Energy Economy



## 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 obtained, to help with seismic searches for clathrates

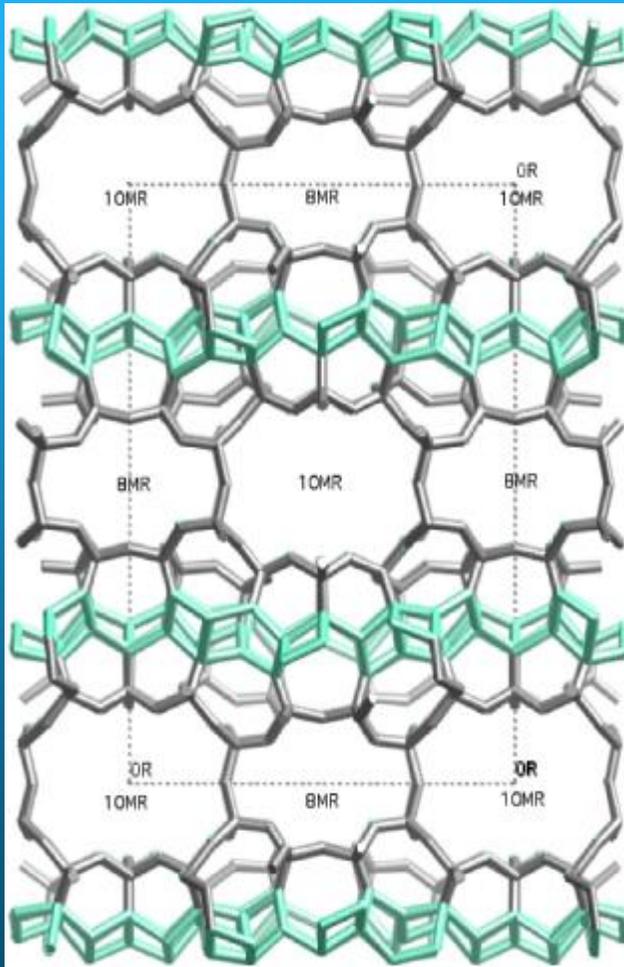
B.Chazallon, A.Klaproth, D.Staykova, W.Kuhs (Göttingen), John Finney (UC London)



# Neutrons and the Environment



## 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)



EPSRC finances very large 2D-Detector for D19

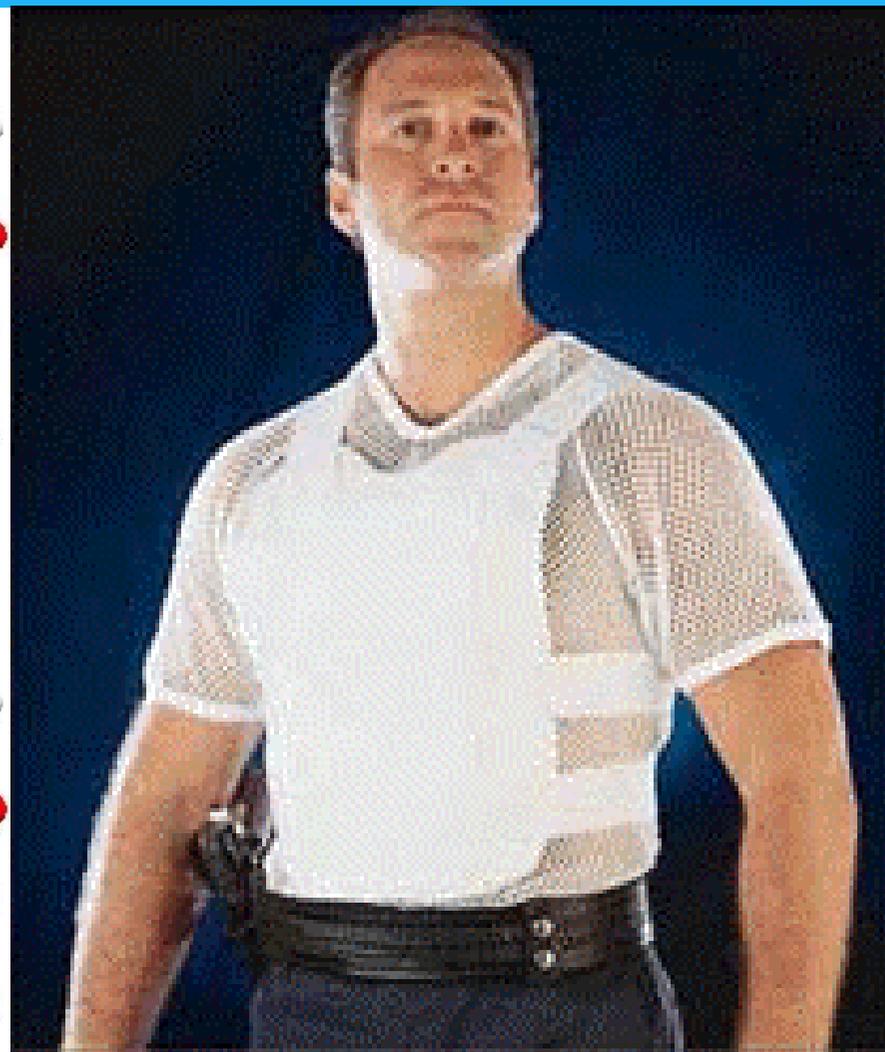
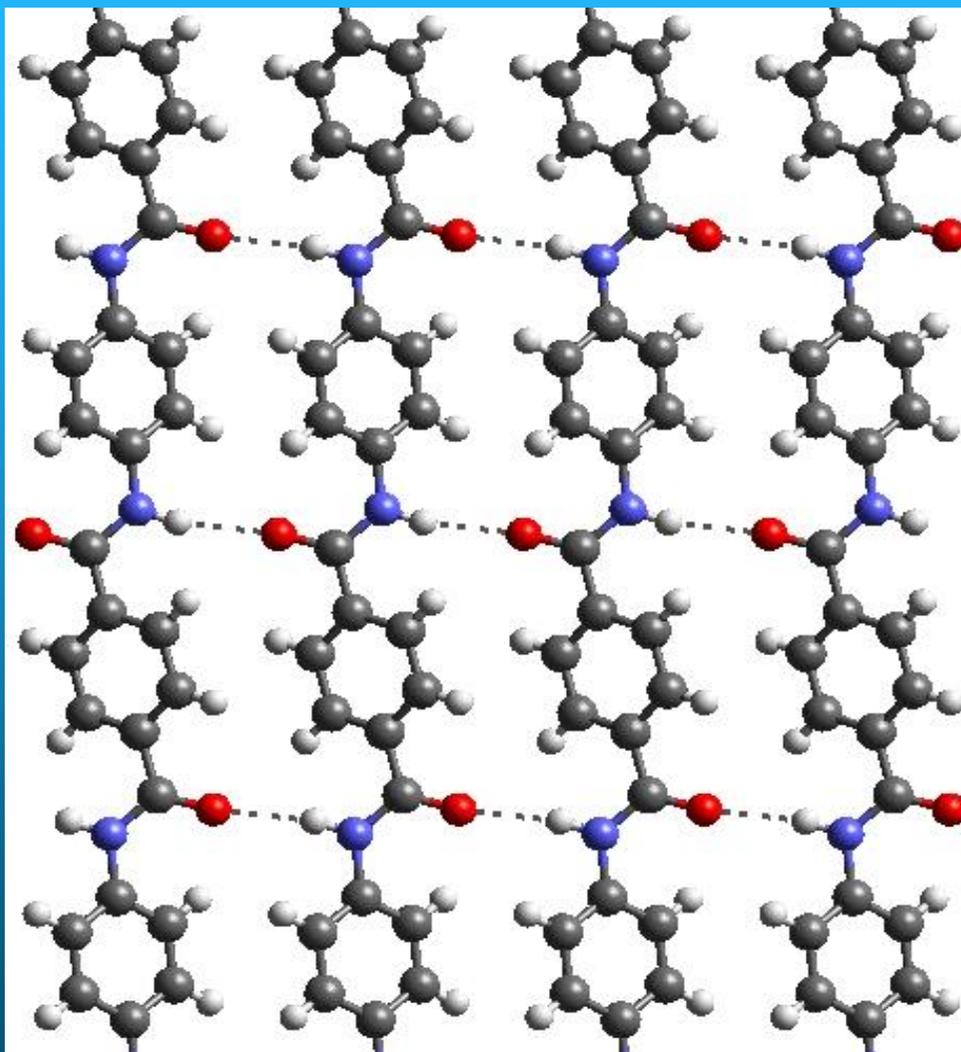


...with Judith Howard

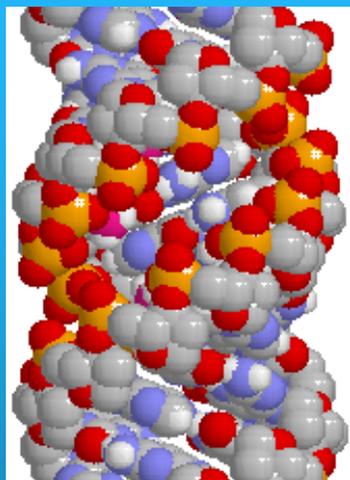


...and Jason Green, EPSRC

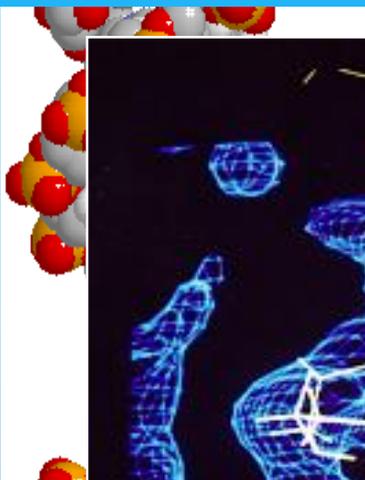
T. Forsyth, S. Mason (Keel & ILL)



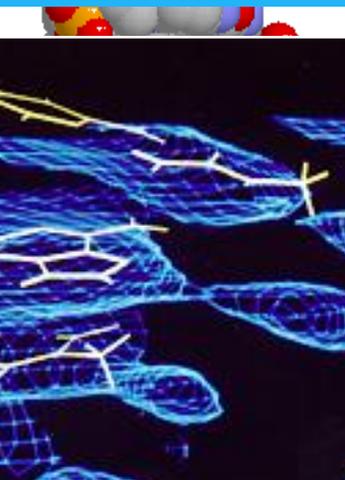
Polymer KEVLAR crystallises in hydrogen bonded sheets



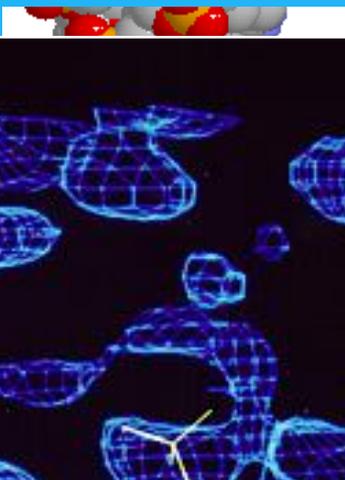
A-DNA  
RH  
11 bp/turn  
pitch=28.2Å



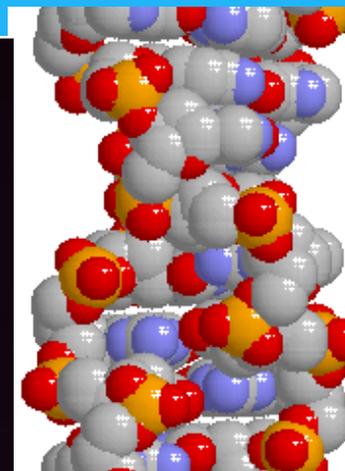
B-DNA  
RH  
10 bp/turn  
pitch=34.4Å



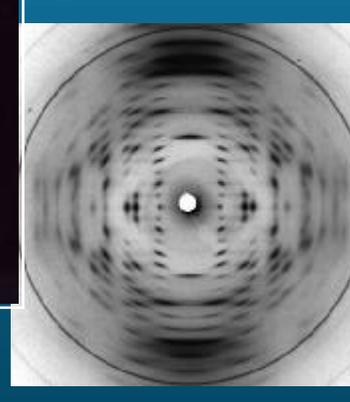
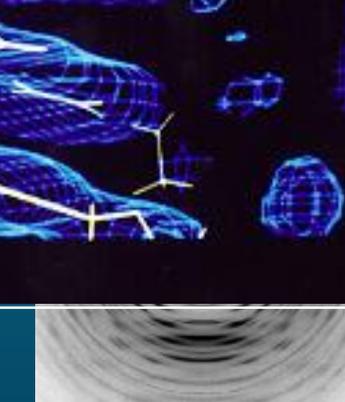
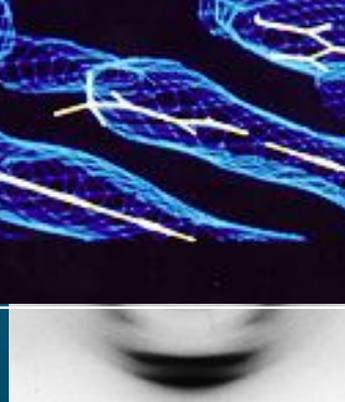
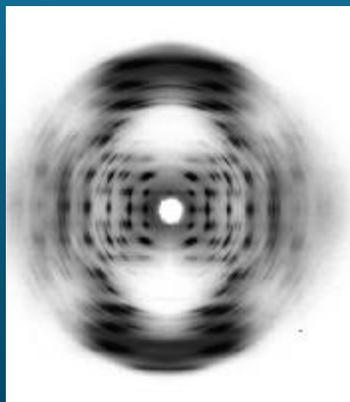
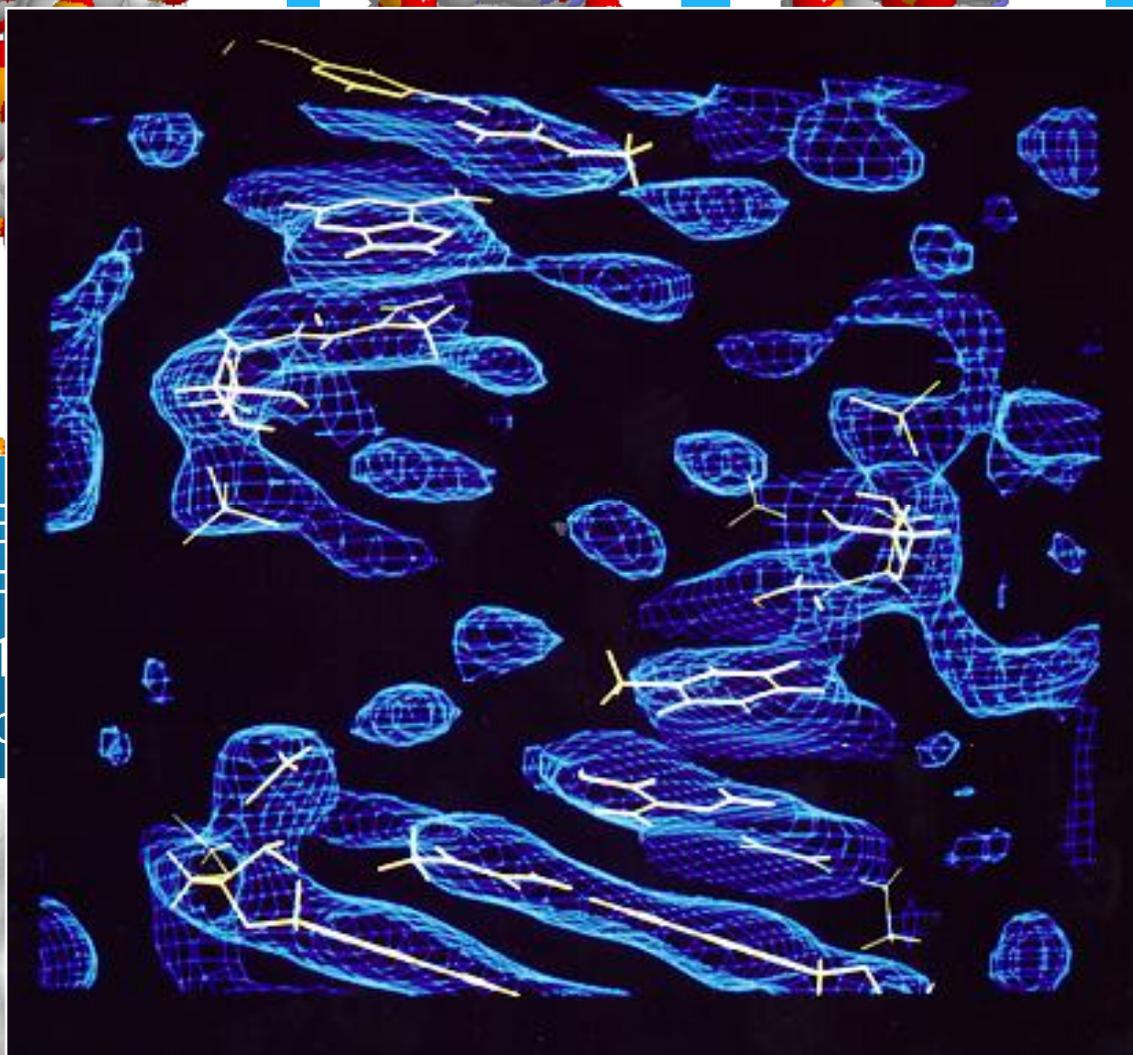
C-DNA  
LH  
9 bp/turn  
pitch=29.7Å



D-DNA  
LH  
8 bp/turn  
pitch=28.2Å

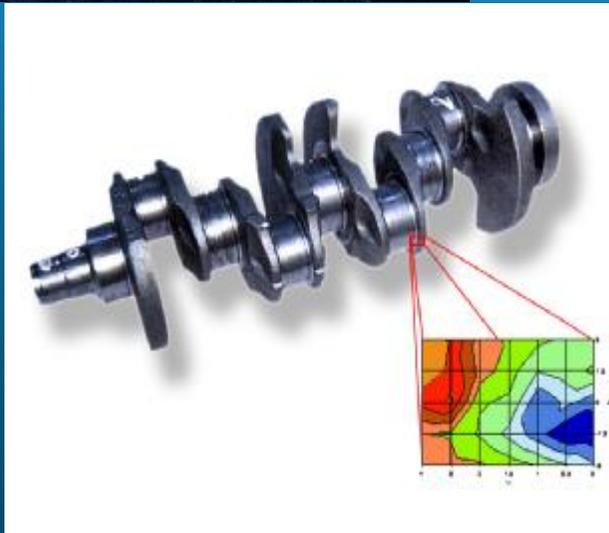


Z-DNA  
LH  
12 bp/turn  
pitch=43Å





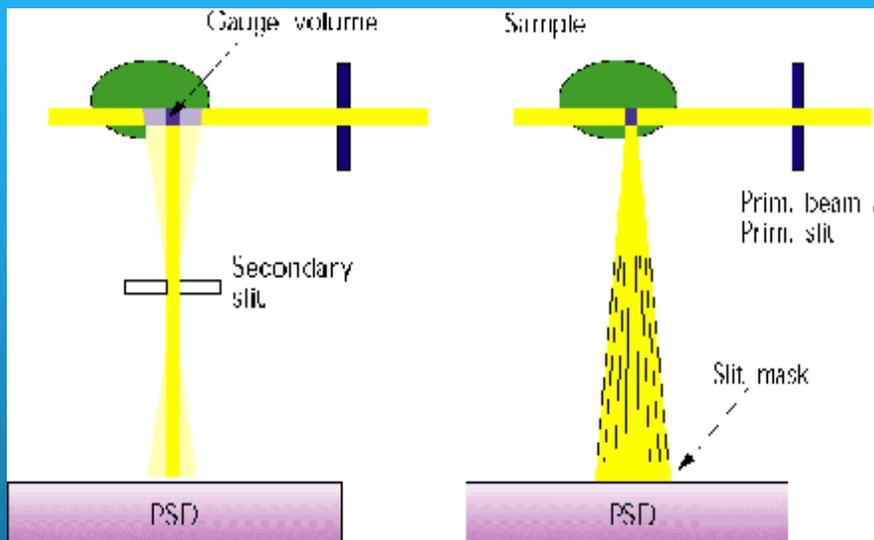
## Measuring stresses deep inside engineering components



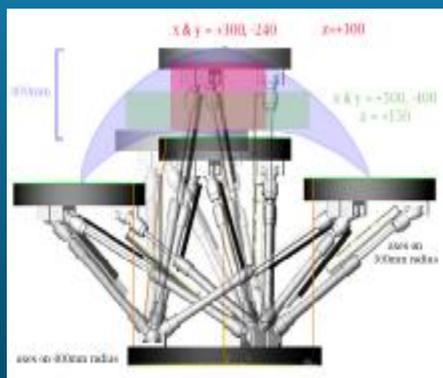
- | Tensile stress can produce cracks
- | Compressive stress toughens materials
- | Neutrons can penetrate deep inside materials (~10cm) and measure stress by changes in atom spacings
- | The compressive stress (blue) deep inside a VW crankshaft
- | Design of stronger, lighter engines



## Measuring stresses deep inside engineering components



- | The neutron beam is collimated to a  $1\text{mm}^3$  "gauge volume" of measurement
- | The scattered peak is measured on a position-sensitive detector (PSD)
- | Small shifts in peak positions map the strain as the sample is scanned



- | Very large engineering components (1 tonne) can be scanned using a "hexapod" platform (similar to the platform of an aircraft flight simulator)

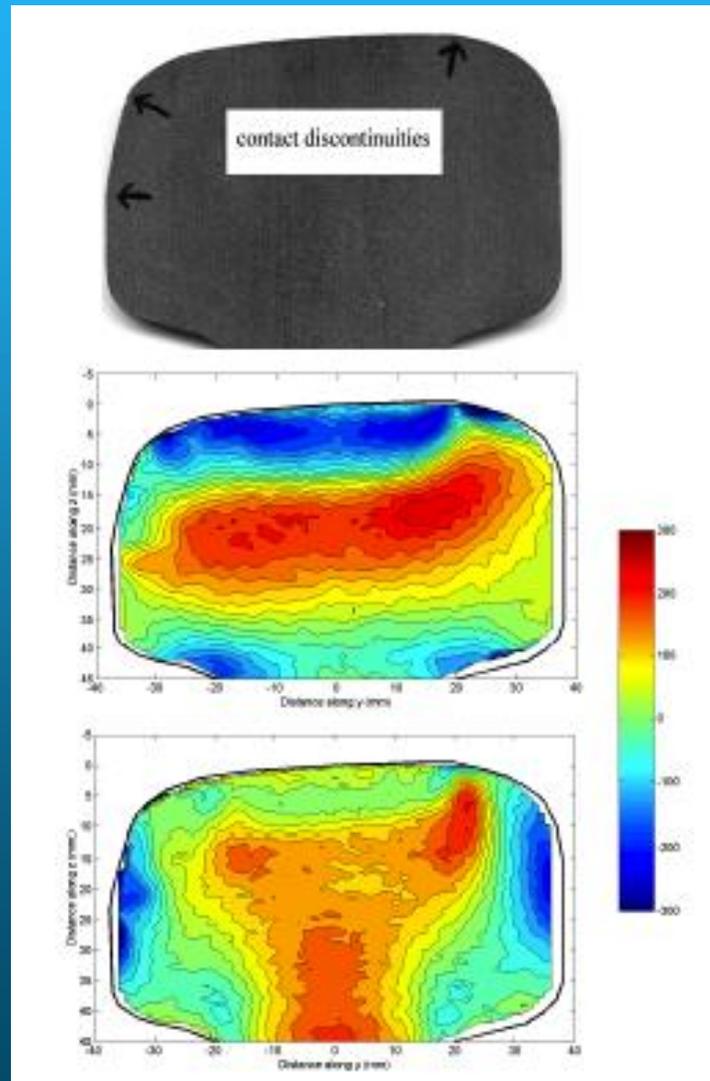


Giovanna, ILL Hexapod Model & British Rail





Map internal stress deep inside engineering components





# The Future ? While Waiting for ESS



A U.S. Department of Energy multilaboratory project

## Spallation Neutron Source



Institute of Materials Structure Science  
High Energy Accelerator Research Organization

Neutron Science Laboratory (KE)

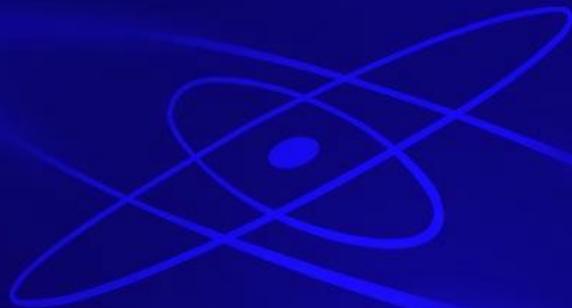


高エネルギー加速器研究機構物質構造科学研究所

## 中性子科学研究施設

Ansto

Replacement Research Reactor



FRM-II Munich  
Started 2 March





Can we compete with the USA & Japan ?



**D**iffractometer for  
**R**apid  
**A**cquisition over  
**U**ltra  
**L**arge  
**A**reas



Can we compete with the USA & Japan ?



## Comparison of future US Neutron Sources

Shelter Island Workshop, N.Y.

Nuclear Instruments and Methods in Physics Research B12 (1985) 525-561

Efficiency for a given resolution = time averaged flux on sample  
\* sample volume  
\* detector solid angle

The European reactor ILL will still produce more neutrons  
- on the sample !

But we need very big detectors – success of CCLRC-ISIS



Can we compete with the USA & Japan ?



## Comparison of future US Neutron Sources

Shelter Island Workshop, N.Y.

Nuclear Instruments and Methods in Physics Research B12 (1985) 525-561

	D20	DRACULA	SNS
time averaged sample flux	$5 \times 10^7$	$\sim 10^8$	$\sim 2.5 \times 10^7$
detector solid angle	0.27 sr	1.5 sr*	3.0 sr
efficiency	1.7	18	9

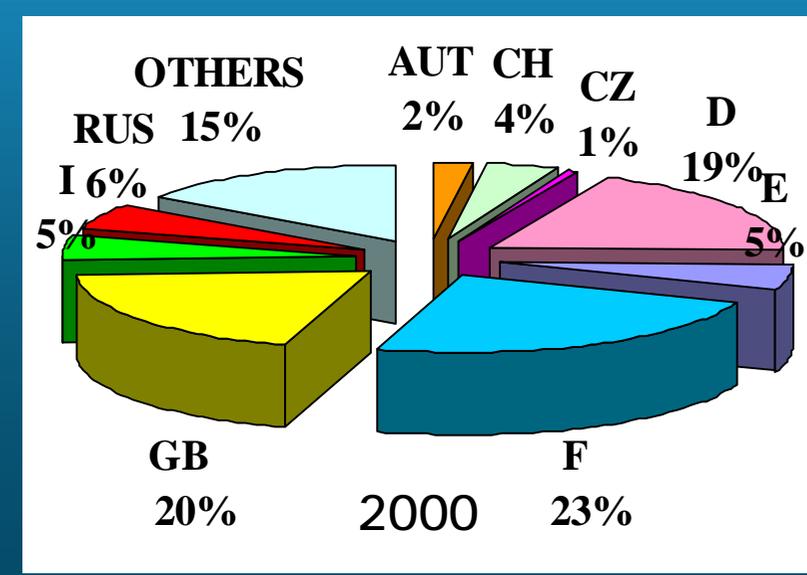
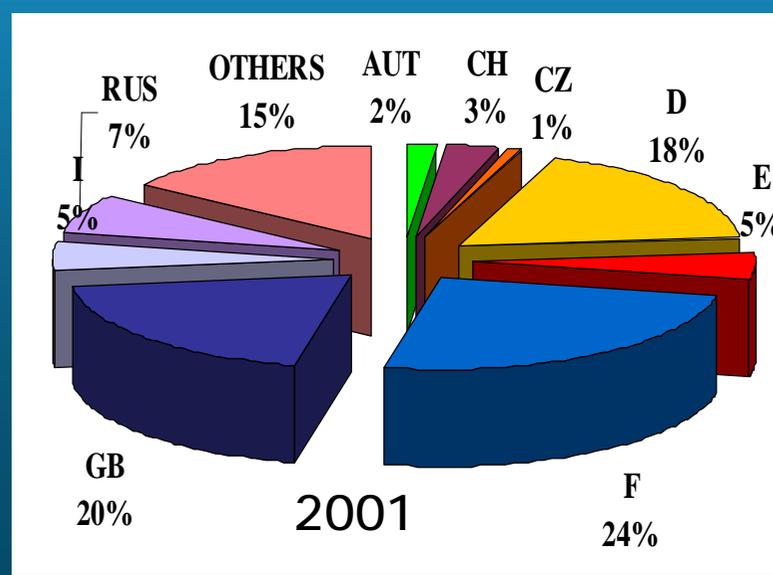
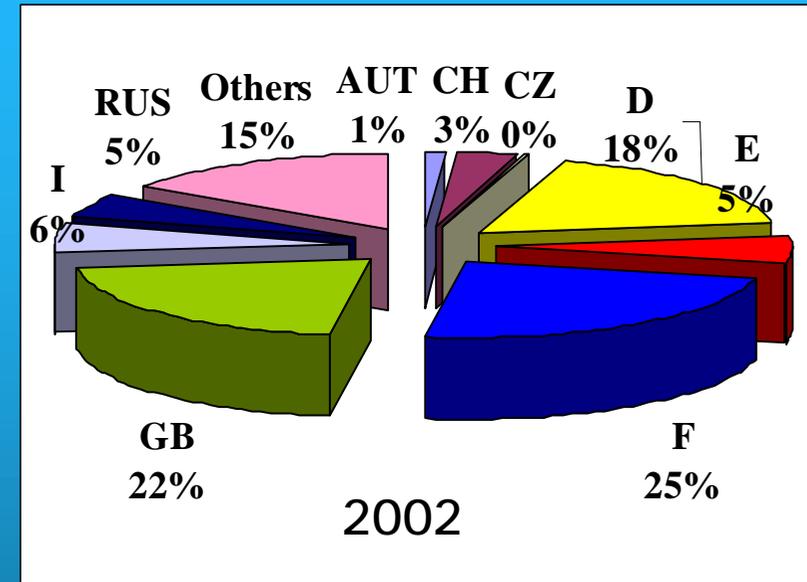
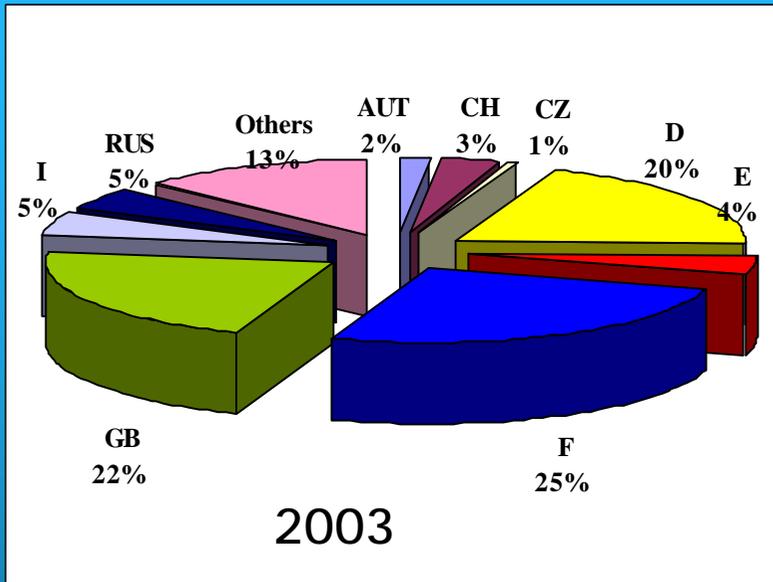
\* Based on D19 detector: R=760 mm, h=400 mm, 800 resistive wires covering  $30^\circ \times 160^\circ$

We can do twice as well as the Americans, but...  
A x5 bigger detector is needed for DRACULA  
Already developed for the EPSRC-D19 project !





# Use of ILL is shared fairly - GB=D=F





# ILL-CRGs (Collaborating Research Groups) French, German, Italian... but no UK-CRGs



D1B	powder diffractometer	CRG-A	French-Spanish
IN13	backscattering spectrometer	CRG-A	Italian
ADAM	reflectometer	CRG-B	German
BRISP	Brillouin spectrometer	CRG-B	Italian
D15	single-crystal diffractometer	CRG-B	French
D23	single-crystal diffractometer	CRG-B	French
EVA	reflectometer	CRG-B	German
IN12	three-axis spectrometer	CRG-B	German
IN22	three-axis spectrometer	CRG-B	French
S18	interferometer	CRG-C	Austrian
<b>BRITTAX</b>	<b>two-axis materials diffractometer</b>	<b>CRG-B</b>	<b>British ???</b>



# BRITTAX

## BRITish Two-AXis CRG proposal



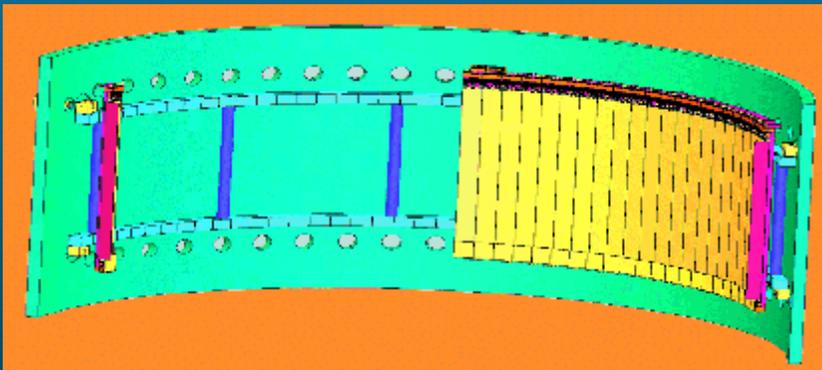
A Proposal for a UK-CRG High Flux Diffractometer on the D1A position

See: <http://icsd.ill.fr/uk-crg/>

### Consortium of 12 UK University Groups

*We propose to capitalise on the new techniques for detectors and neutron optics, developed with recent EPSRC investment in ILL projects, to provide a unique high flux CRG diffractometer in the present D1A position.*

*This new CRG diffractometer will be comparable to D20 for flux, and to D1A for resolution but will also be used like D19 for single crystals.*



	D20	GEM	BRITTAX
time averaged flux (f)	$5 \times 10^7$	$\sim 2 \times 10^6$	$\sim 10^7$
detector (sr)	0.27	4.0	1.0
efficiency (f*sr)	1.7	1	1.2

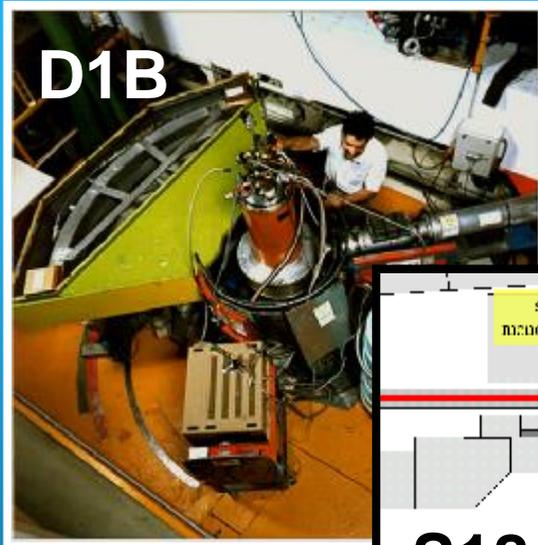
### Materials Problems to be addressed

- High Pressure Synthesised Materials
- High Pressure/Temperature Behaviour of Minerals
- Novel Ferromagnetic and Intermediate Valence
- Small Samples of Mixed Metal Oxides
- Transition Metal Oxides, Fluorides and Sulphides
- Structural Studies of Relaxor Ferroelectrics
- Magnetism and Polarised Neutron Diffraction
- Functional Organic Materials
- Molecular Compounds with Pharmaceutical & Photo-Optical Applications.
- Small Single Crystals & Weakly Diffracting Samples

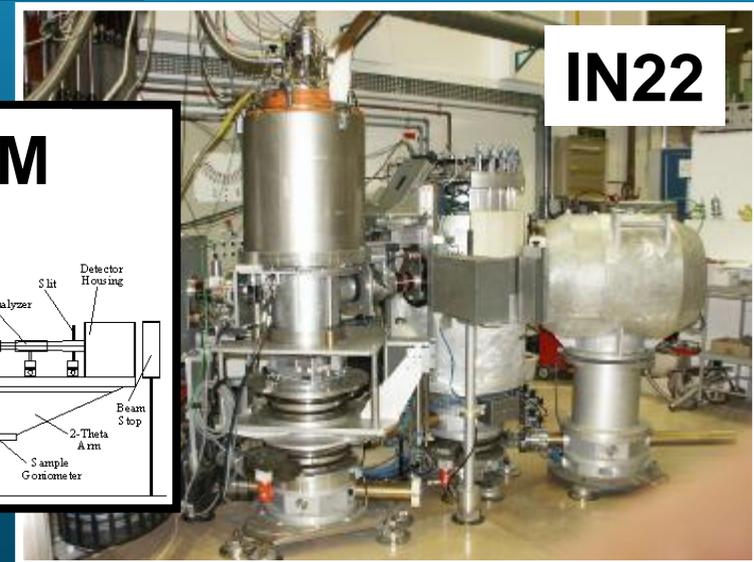
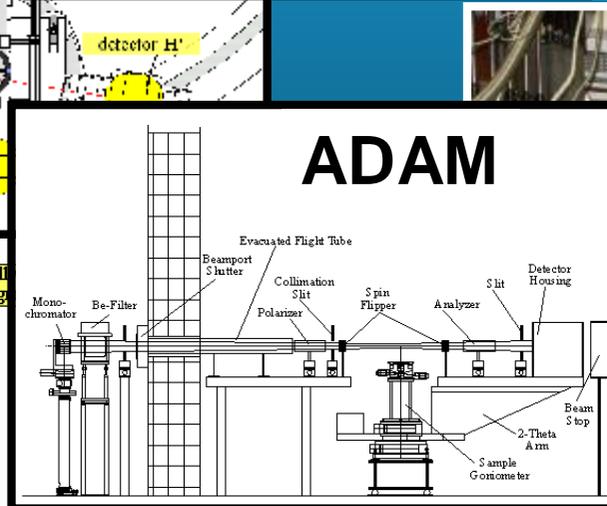
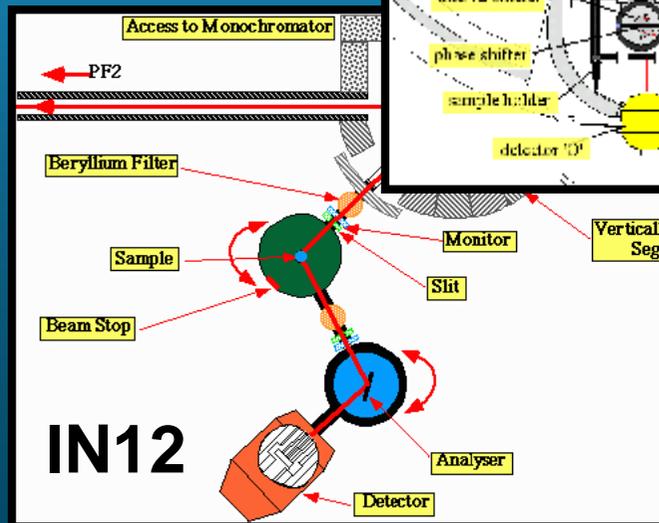
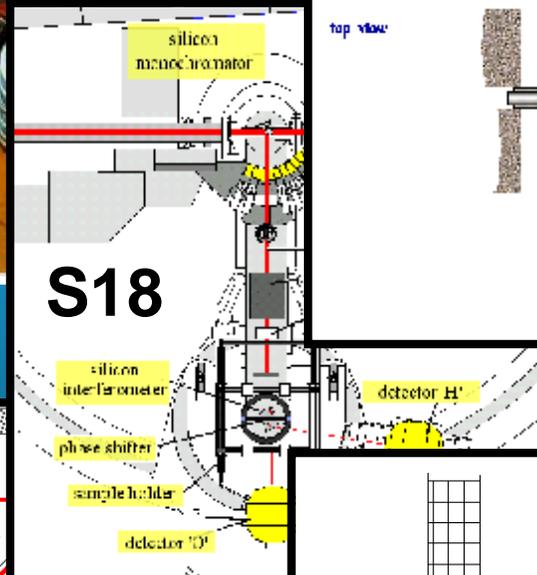
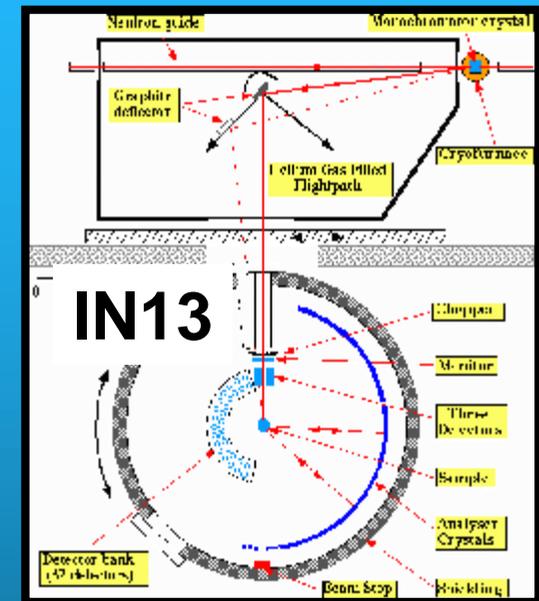
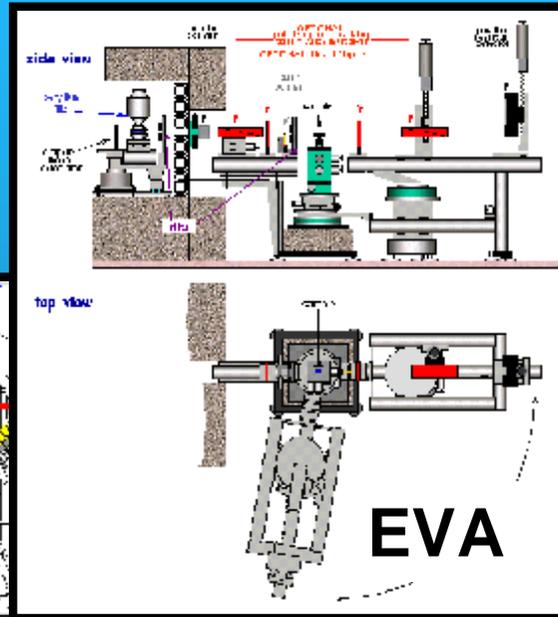




# ILL-CRGs (Collaborating Research Groups) French, German, Italian... but no UK-CRGs



**D1B**



**IN22**



ILL-CRGs (Collaborating Research Groups)  
French, German, Italian... but no UK-CRGs



Large new Italian CRG at ILL (BRI SP)





# Materials Research at CCLRC European Labs.

Alan Hewat, ILL Grenoble



## Grenoble France

- | World's most intense neutron source
- | ~300 staff
- | ~1250 visiting scientists each year
- | ~500 scientific papers each year
- | physics, chemistry, biology, materials



ILL member countries are shown in green



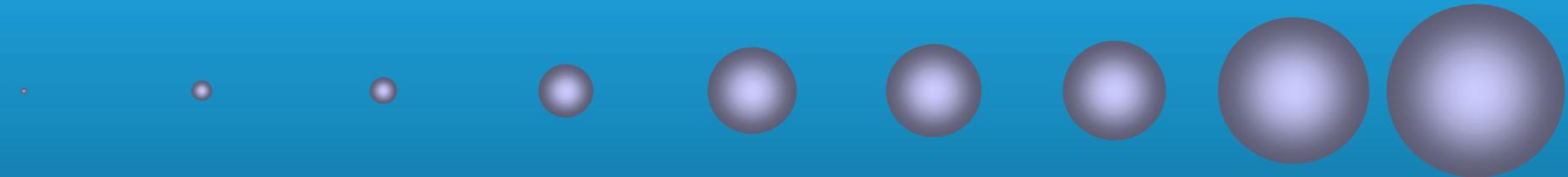
# Neutrons see light atoms - eg hydrocarbons



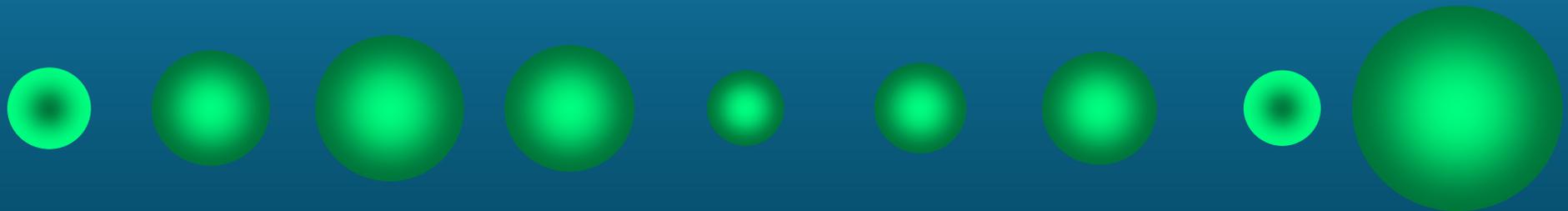
X-ray

Scattering proportional to Z

H	B	C	O	Al	Si	P	Ti	Fe
1	3	4	8	13	14	15	22	26

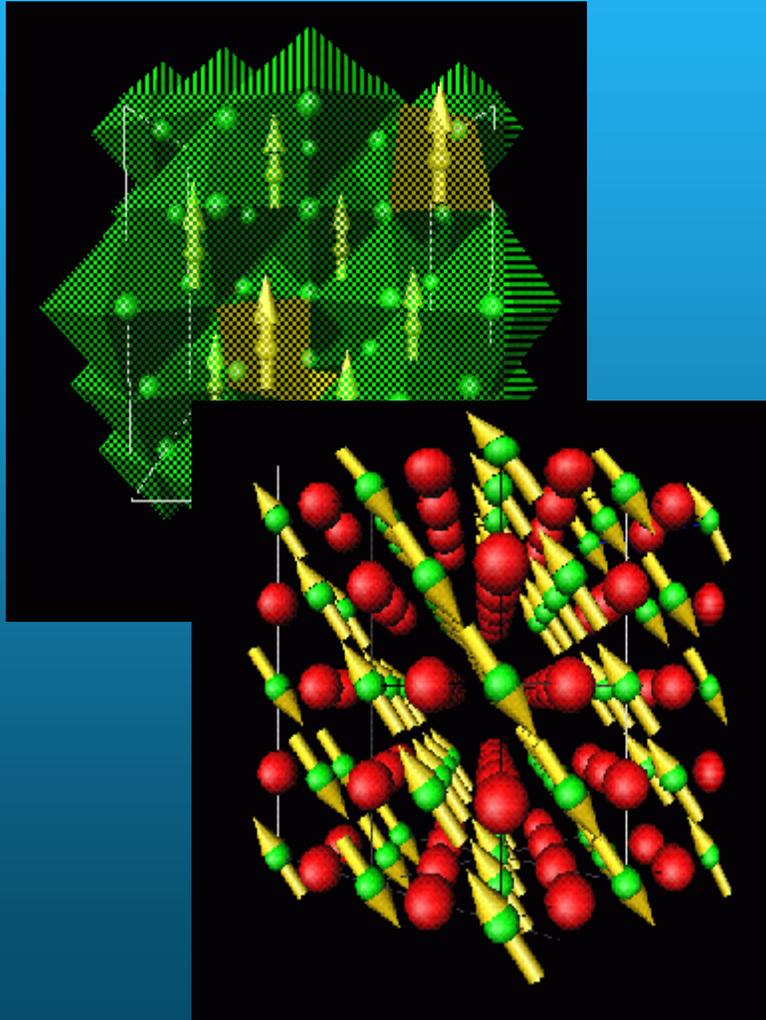


-3.74	5.30	6.65	5.80	3.45	4.15	5.13	-3.44	9.45
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# Neutrons can study magnetic materials



- | 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  $\text{MnO}$



EPSRC

## Applications of D2B



### Potential Applications of HiTc superconductors

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





# Neutrons and the Energy Economy



## Potential 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

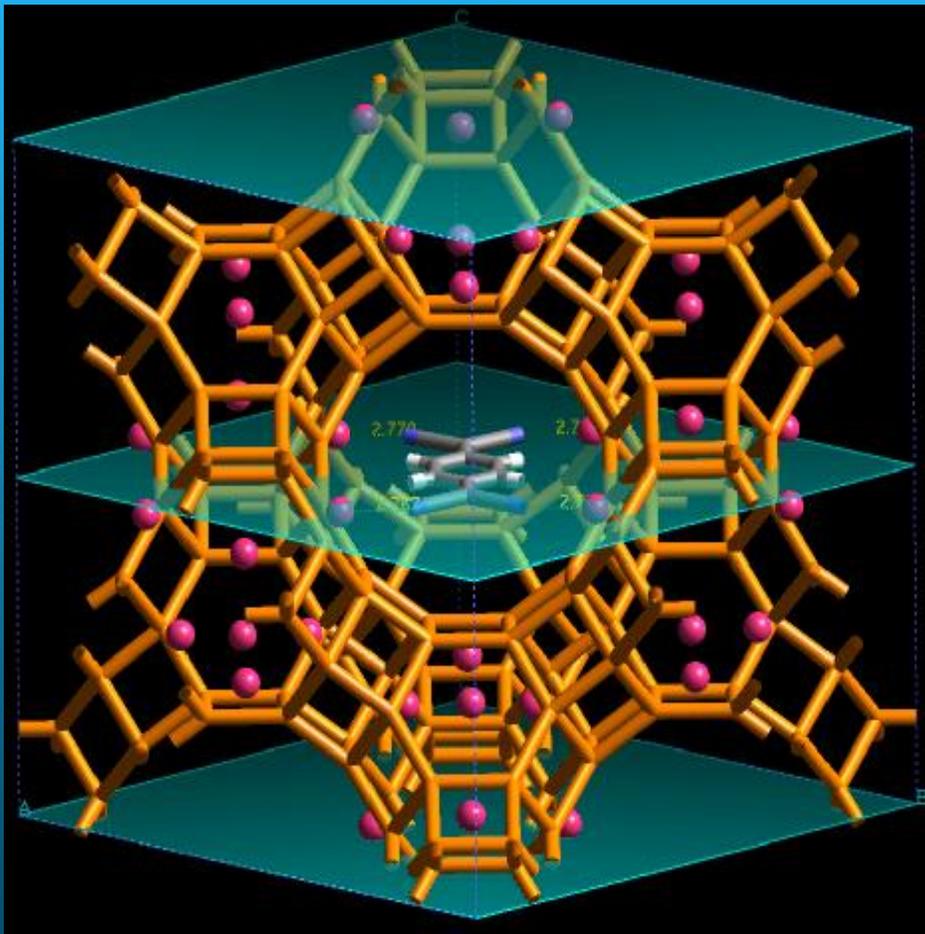
K. Yvon (Geneva)



# Neutrons and the Energy Economy

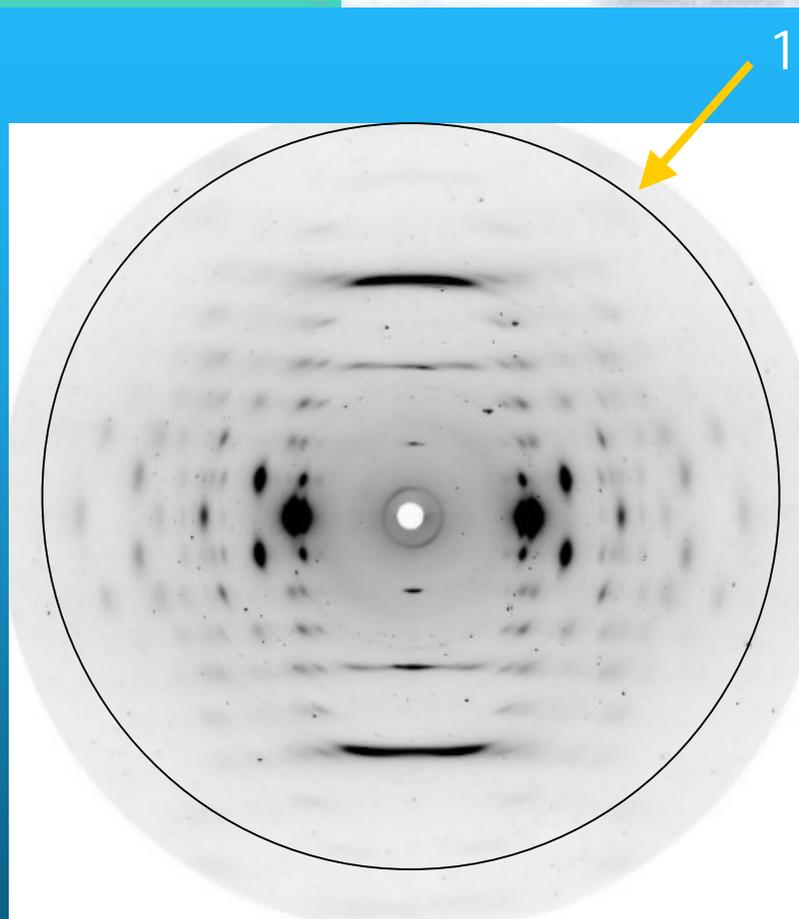


## New zeolites to catalyse petro-chemical reactions

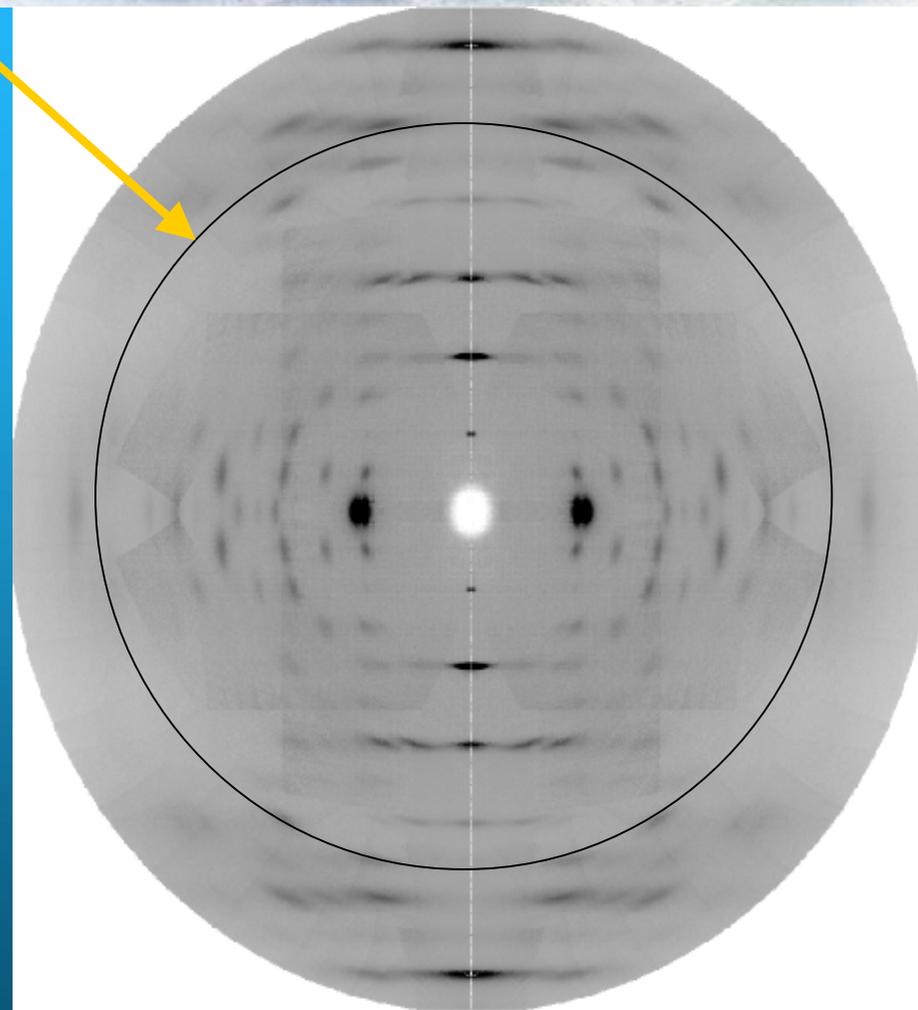


- | Zeolites are very important in industry as catalysts for petro-chemicals etc
- | Neutrons are used to understand how light hydrocarbon molecules interact
- | Neutrons can also distinguish between silicon and aluminium in the framework
- | A small organic molecule trapped inside the pore of NaY-zeolite.

C. Baehtz, H. Fuess (Darmstadt)



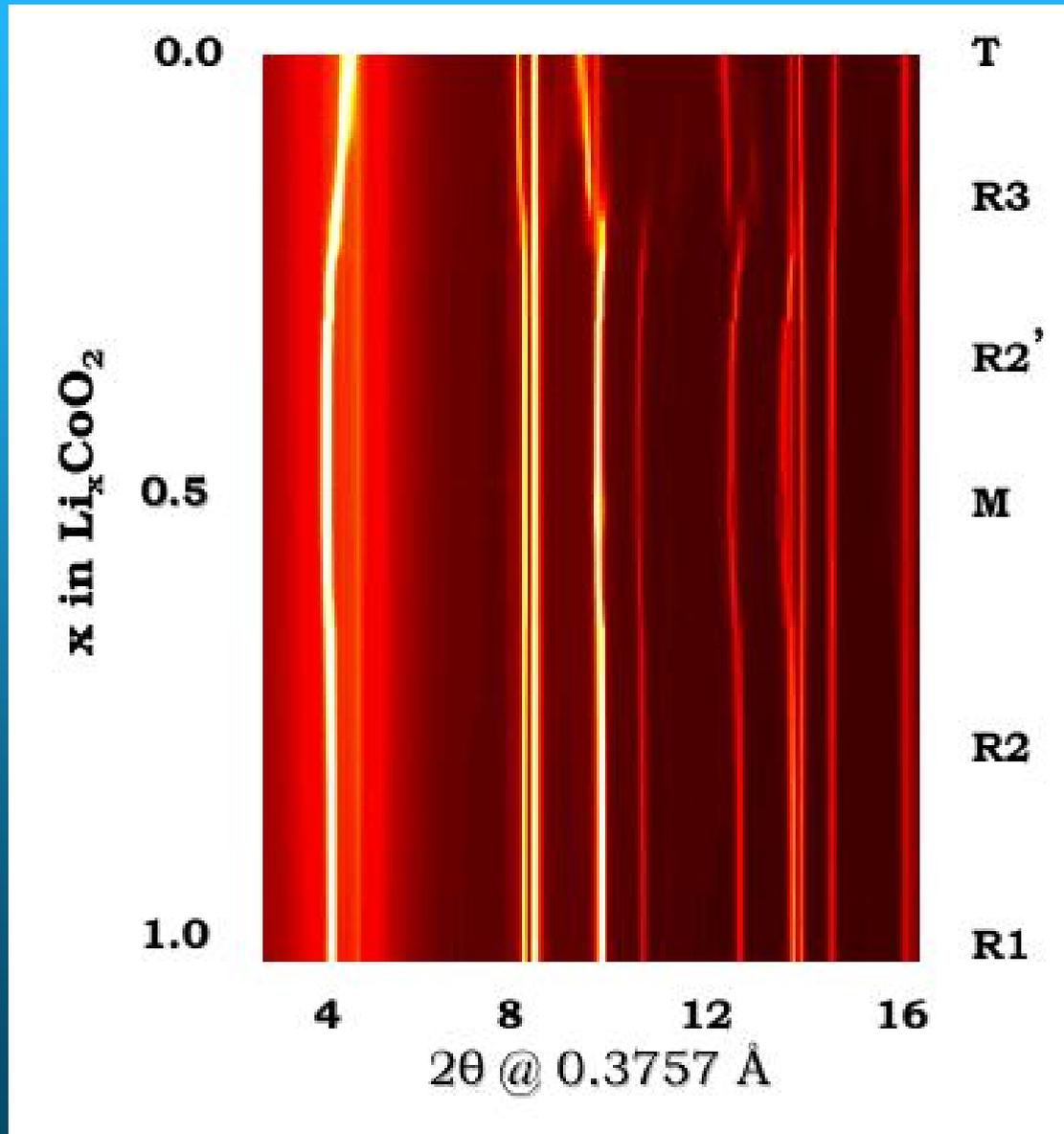
Kevla, x-ray data from APS  
 $\lambda=0.8\text{\AA}$



Kevla, neutron data from ILL  
 $\lambda=1.31\text{\AA}$



# Applications of large fast detectors



ESRF X-ray diffraction  
from a  $\text{Li}_x\text{CoO}_2$  battery

The letters to the right  
show different phases as  
a function of Li-content  $x$



# Applications of large fast detectors



## Self-Propagating Synthesis - ESRF Synchrotron Radiation

