Does Structure Matter ?

Alan Hewat, Diffraction Group, ILL.

ILL Grenoble

Alan Hewat

Is it necessary to know the details of crystal and magnetic structures, and if so, why do we need diffractometers on a high flux reactor ?

Does Structure Matter ?

Alan Hewat, Diffraction Group, ILL.

With special reference to the Millennium Plan

But I won't talk about

- Neutron Strain Scanner (SC lecture by Philip Withers)
- ^{3}He Neutron Spin Filter (SC lecture by Werner Heil)

Both important Millennium Diffraction Projects

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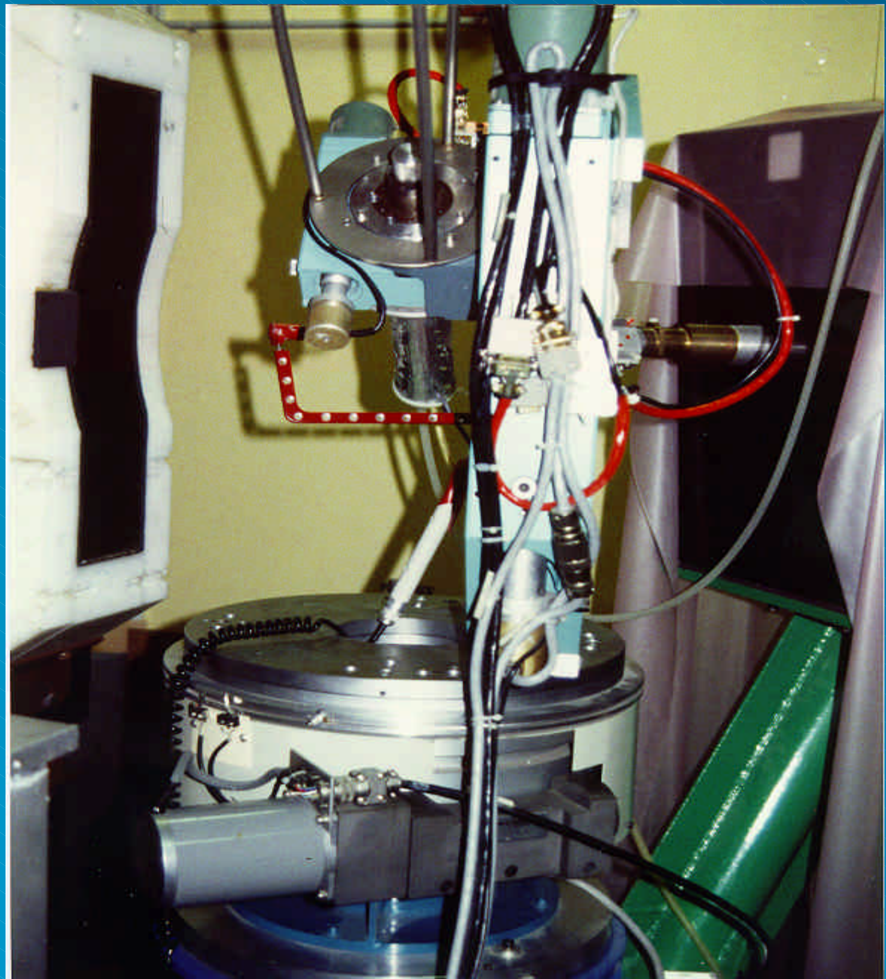
Life without Crystals on D19
Water in DNA Fibres & Sheets

Trevor Forsyth, Paul Langan, Sax Mason

Alan Hewat



- **Bound water is essential for the structural stability of DNA**
- **5 conformations of hydrated DNA**
- **Specific patterns of hydration may contribute to the recognition of these sequences by proteins**
- **But we must study (non-crystalline) hydrated material (fibres, sheets)**
- **Diffuse diffraction patterns from D19 used to locate water**

Hydration cell on D19 with Large ‘banana’ 2D PSD to left, neutron source to right

Life without Crystals on D19
Water in B-DNA sheets

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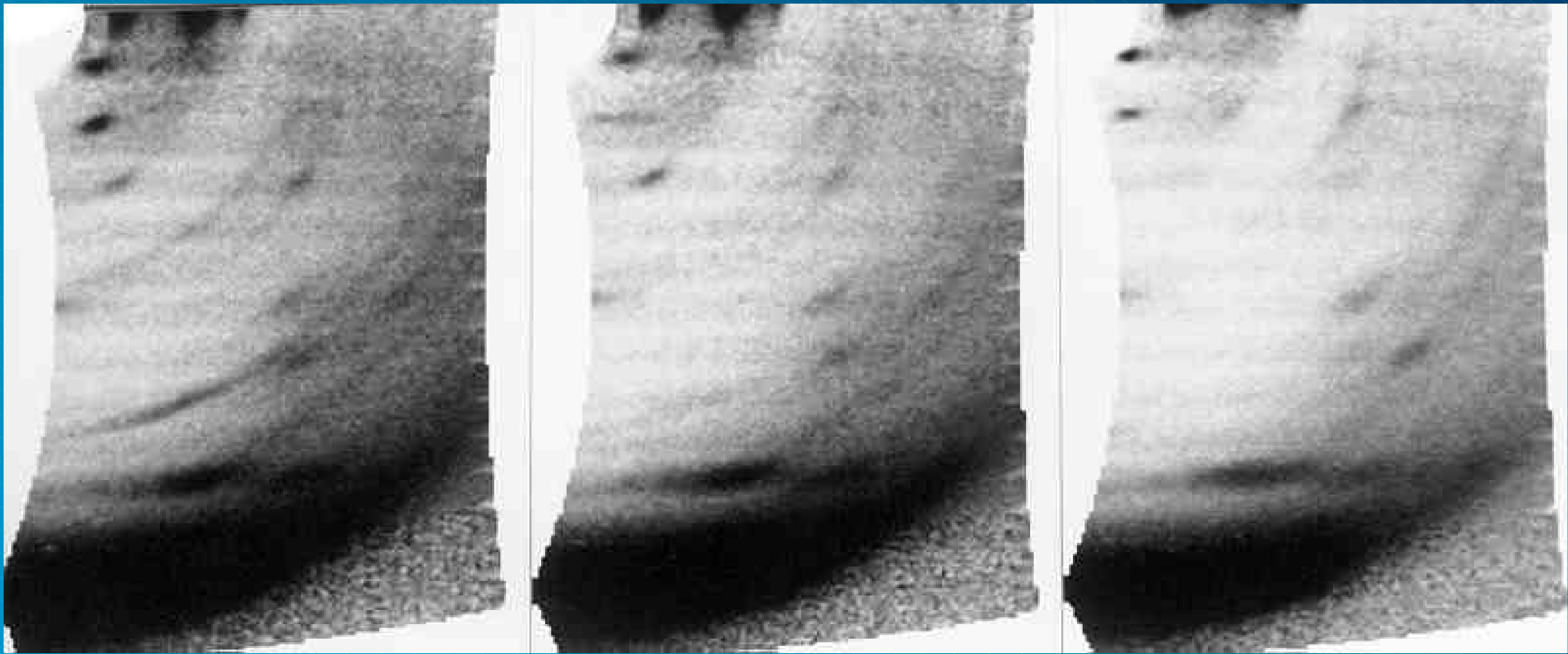

Diffuse 3D diffraction patterns from D2O in stacked sheets of B-DNA on D19
Note data collected in horizontal stripes due to the limitations of the PSD detector

Life without Crystals on D19
Water in A-DNA Fibres

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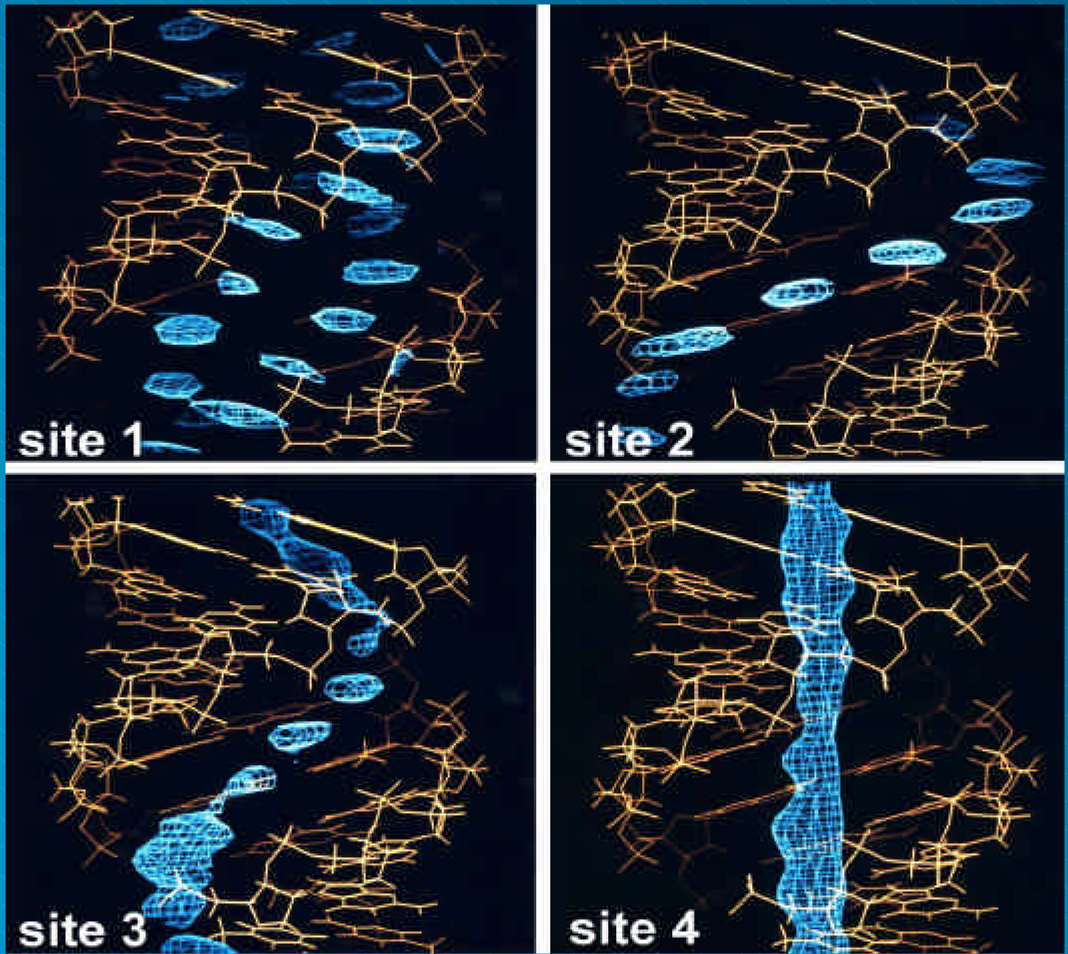

- **B-DNA sheets, but A-DNA fibres**
- **100 individual DNA fibres in D_2O**
- **Diffuse fibre diffraction patterns from D19 used to locate water**
- **4 distinct water sites located along double helix backbone**

1) Bridging phosphate groups
2) Center of opening of major groove
3) Deep inside the major groove
4) Disordered string along helix axis

Shotton *et al*, (1998) *Biophys. Chem.*, **69**, 8; Pope *et al*, (1998) *Physica* ***B*241**, 1156.

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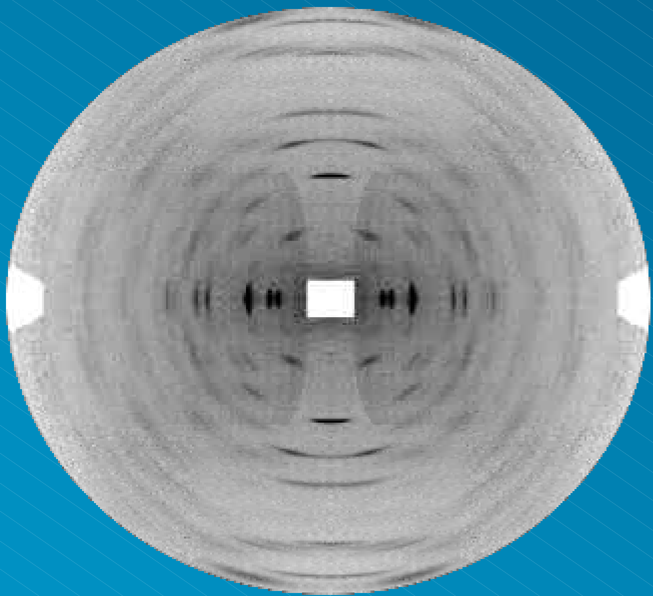
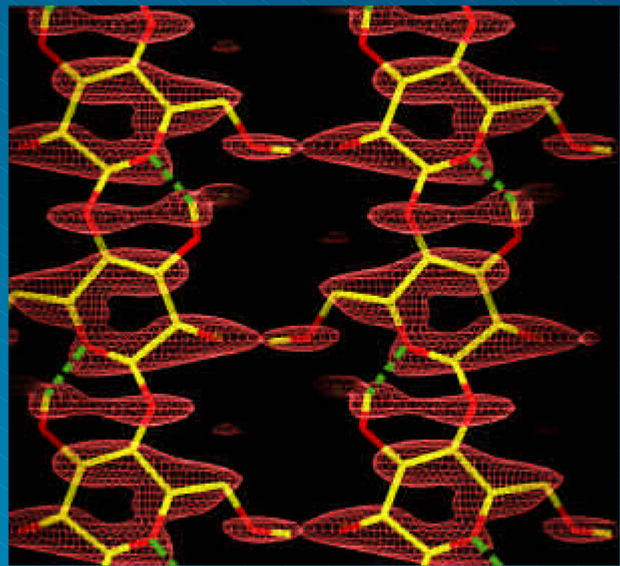
Life without Crystals on D19
Hydrogen bonding in Cellulose

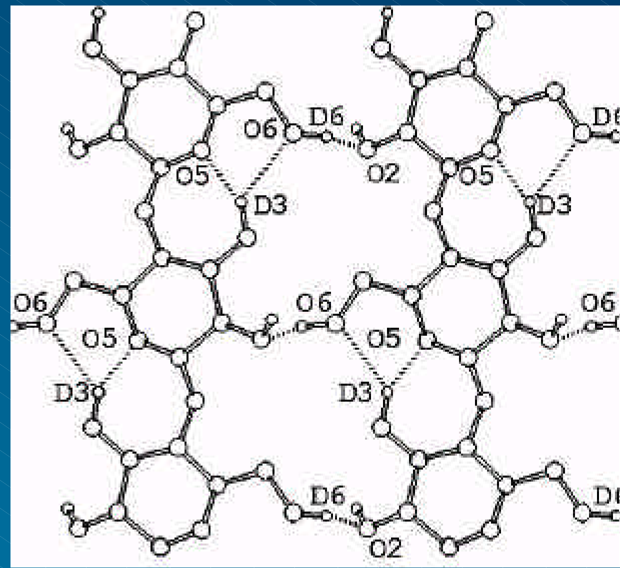
Alan Hewat



D19 data



Density Map



Hydrogen Bond Network

Nishiyama, Okano, Langan, Chanzy, *Int.J.Biol.Macr*; Langan, Nishiyama, Chanzy, *J.Am.Chem.Soc.*

- **Neutron diffraction essential complement to NMR, X-rays, electron micro.**
- **Cellulose extracted from cell walls of algae – 7mm stack of cellulose sheets**
- **100's of diffraction spots obtained with neutrons, much better than X-rays**
- **Contrast between H- and D-samples allowed determination of H-bonds**

Life without Crystals on D19

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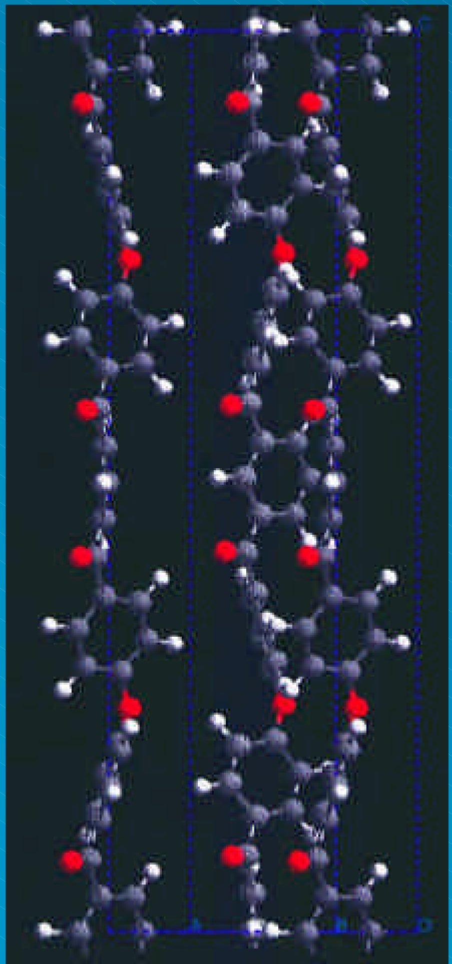
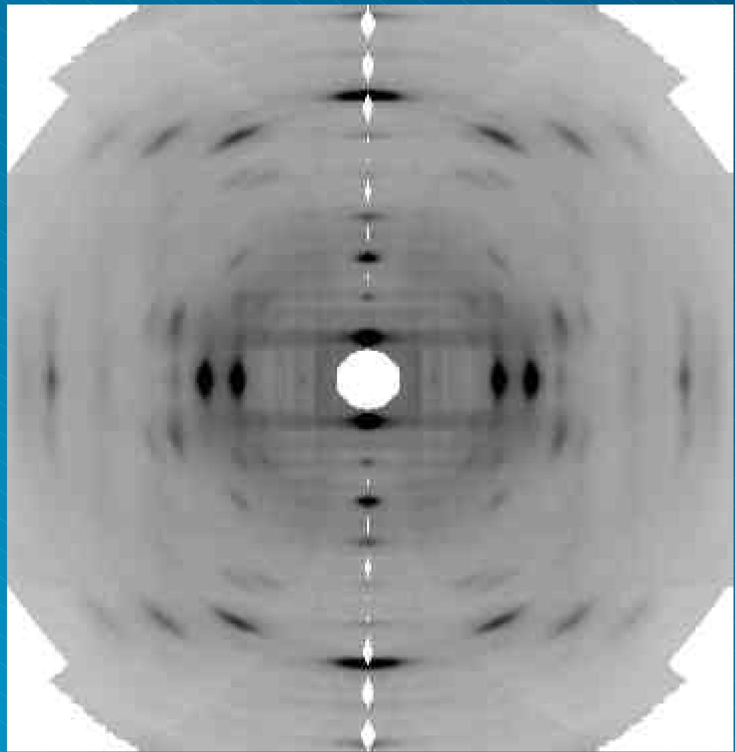
KEELE UNIVERSITY Physics Department

Industrial polymers

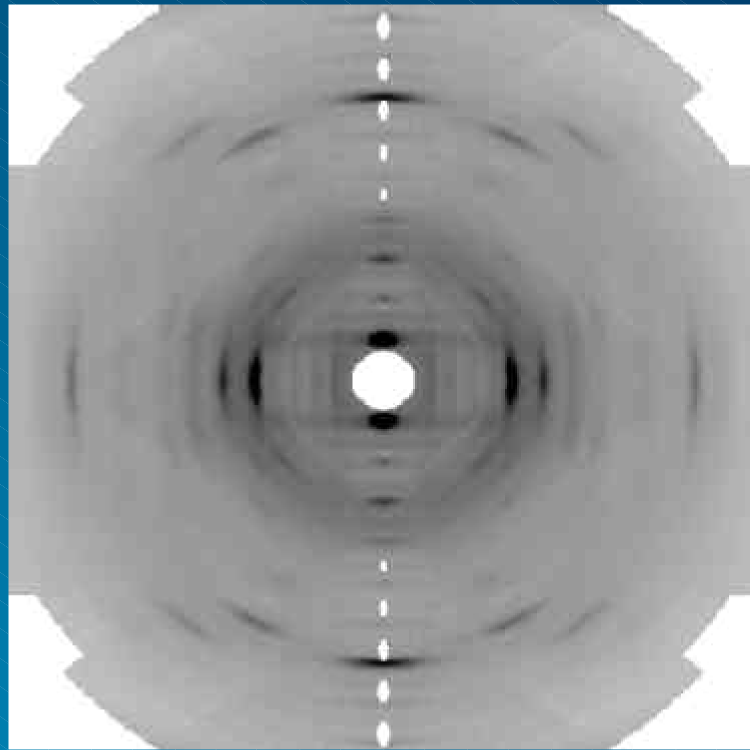
poly (aryl ether ketone ketone)

DU PONT





Hydrogenated polymer



Deuterated analogue

Life without Crystals on D19
Detector Limitations

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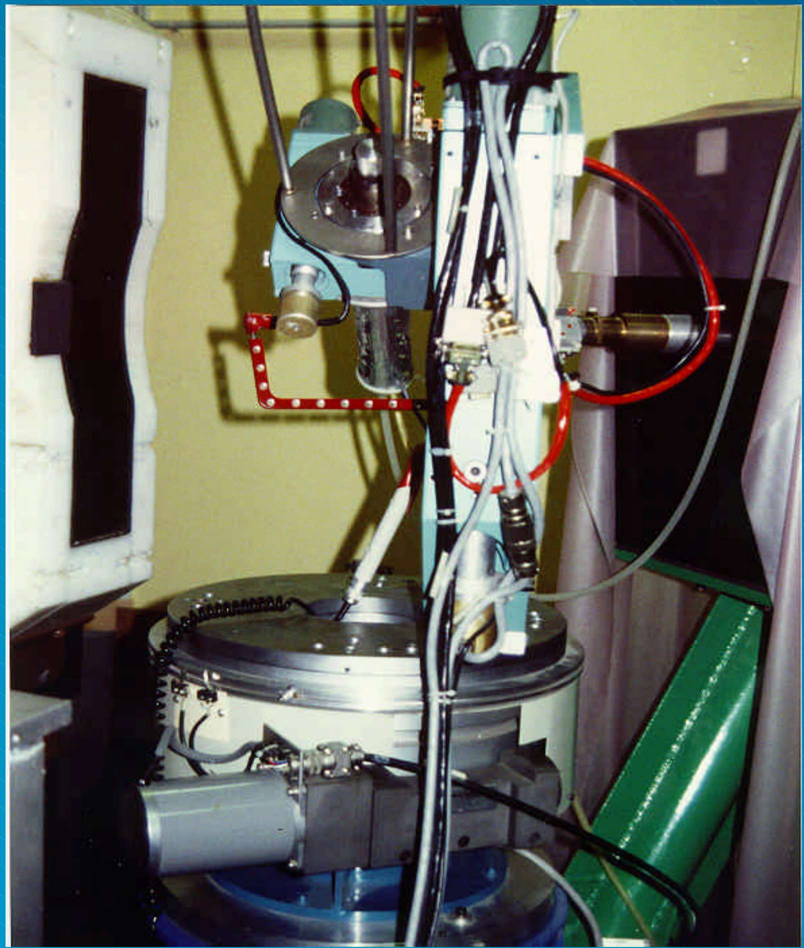

4^{o}x64^{o} 2D “banana” PSD detector

Need ~20 scans to obtain 1 pattern

Life without Crystals on D19
Proposal for a x20 PSD Detector

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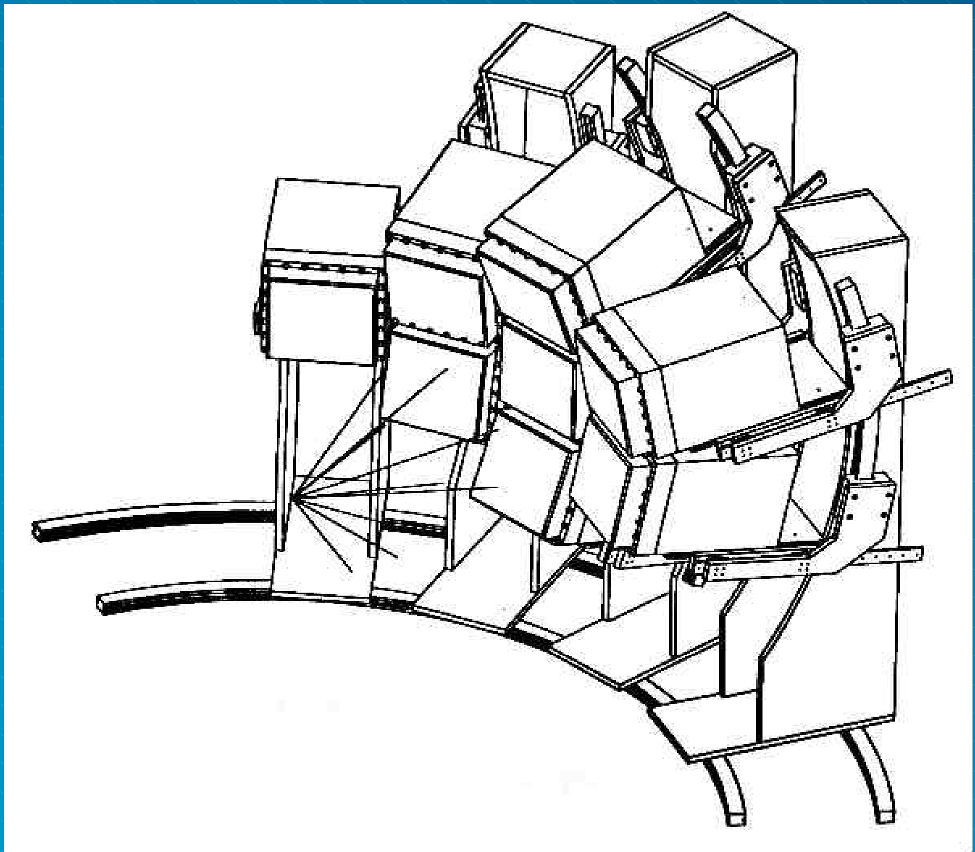

- 15 year old D19 detector covers only thin 2D strip
- Replace with array of high resolution 2D modules
- Increase efficiency x20
- In-situ hydration studies, larger molecule structures.

Proposed array of 2D wire or microstrip detectors for D19 (cf PSI project)

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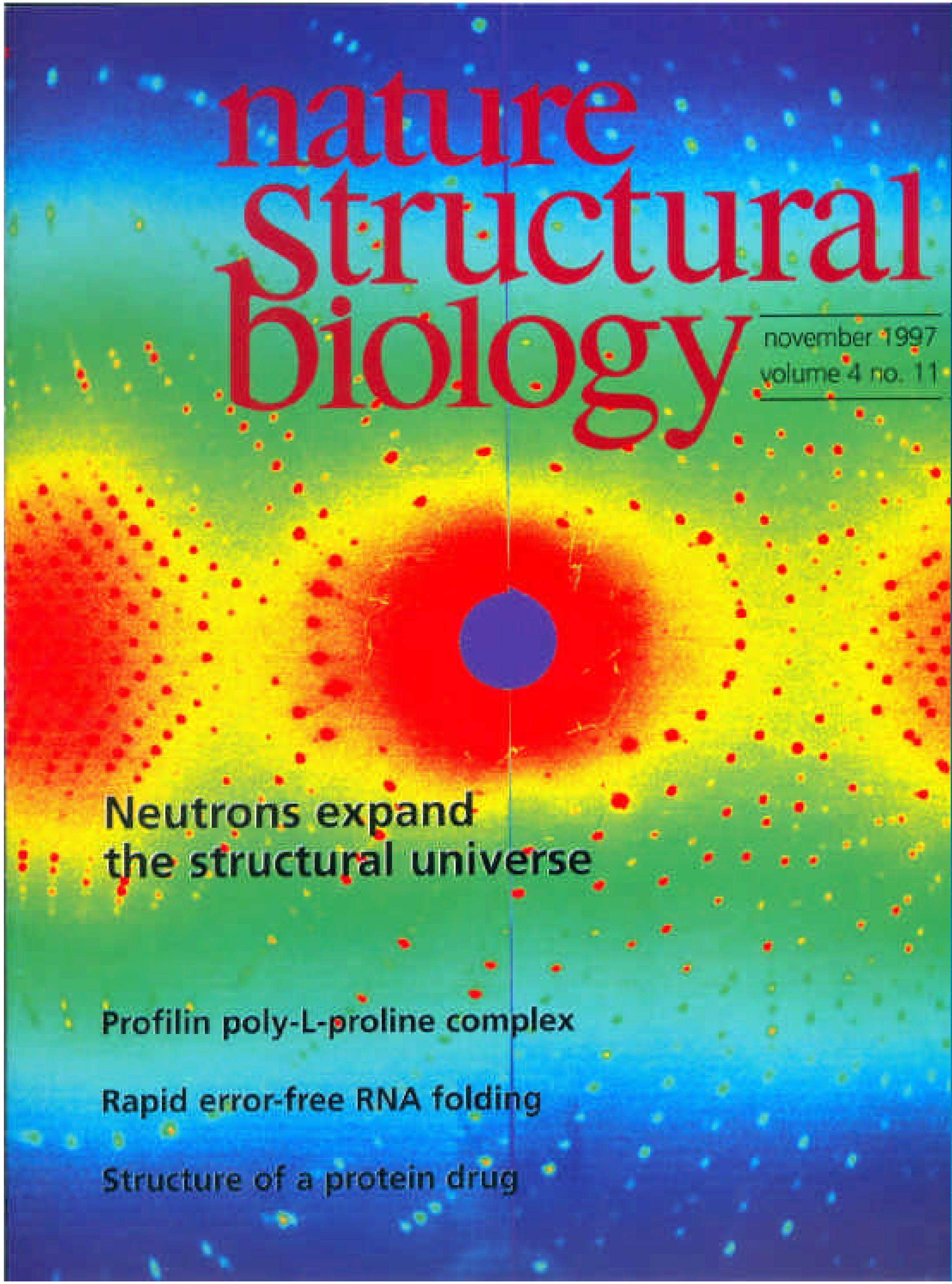
Why can't we do it with X-rays ?

- Yes, water structure and hydrogen bonding is important, BUT
- Hydrogen atoms can be located with X-rays, especially with Synchrotron Radiation
- But only if we have very good crystals that diffract to high resolution (1.2Å)
- Only a few % of organic crystals diffract to 1.2Å !!!
- But half diffract to ~1.8Å, sufficient for neutron studies



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Neutron Image Plates & Microstrip Detectors

Do we need both ?

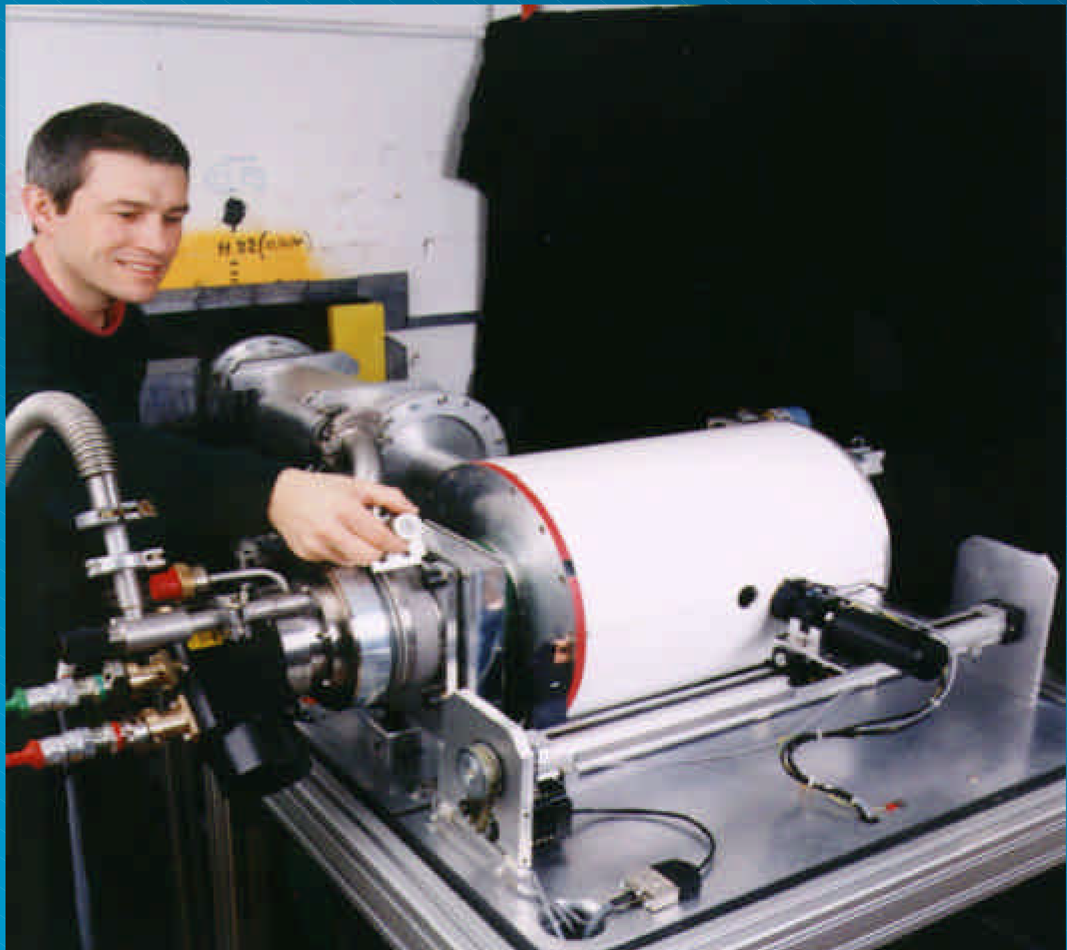
ILL Science Council 22 Oct 1999

ILL Grenoble

T-LADI Neutron Image Plate for physics and chemistry

Dean Myles, Clive Wilkinson, Garry McIntyre

Alan Hewat



- Thermal neutron guide
- Band of neutron energies
- View reciprocal space
- In-situ laser readout
- Unique survey of P/T
- Phase T/Ns, superstruct.

Dean Myles with LADI and cryo-refrigerator on thermal guide H22

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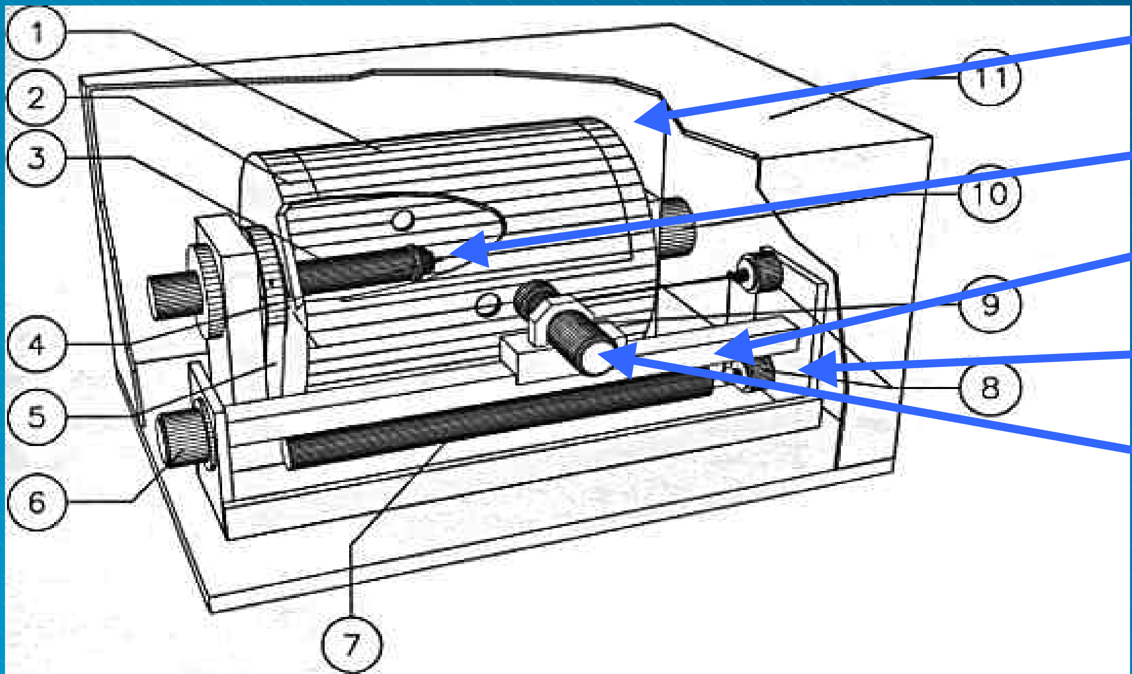
T-LADI Neutron Image Plate for physics and chemistry

Alan Hewat



1. Image plate on rotating drum

3. Sample holder

7. He-Ne laser

8. Focussing mirrors

9. Reader head, photomultiplier

Phonograph readout time 4 min.
4000x2000 pixels of 200 mm

Original cold-LADI for biological structures (ILL/EMBL collaboration)

F. Cipriani, F. Castagna, C. Wilkinson, P. Oleinek & M.S. Lehmann (1996) Neutron Res. **4**,79-85.

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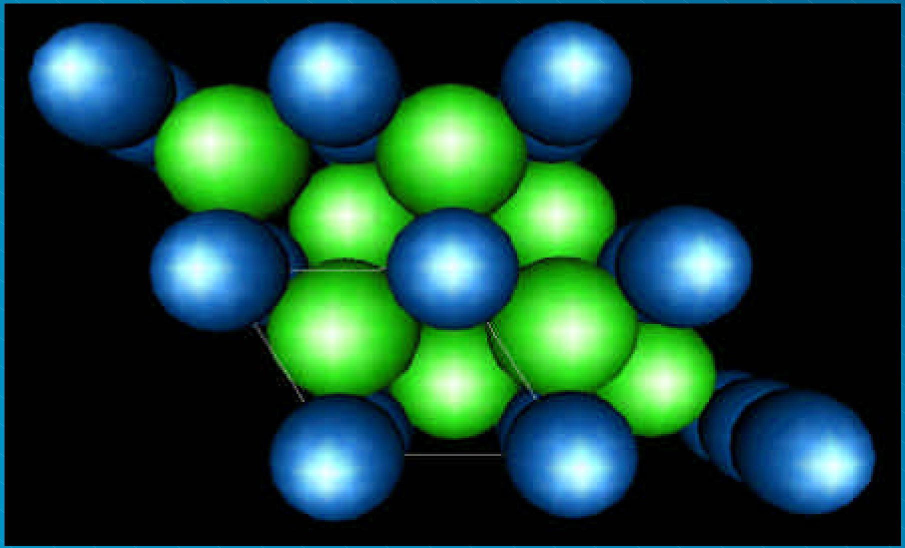
T-LADI Neutron Image Plate Superstructure in $La_2Co_{1.7}$



- Hexagonal $La_2Co_{1.7}$
  - HCP packing of La (green)
  - Co (blue) in hexagonal holes
  - But Co too large for holes
  - Incommensurate 1D chains of Co along the c-axis
  - Interesting magnetic structure

Schweizer et al (1971); Gignoux et al (1985); Ballou et al (1986)

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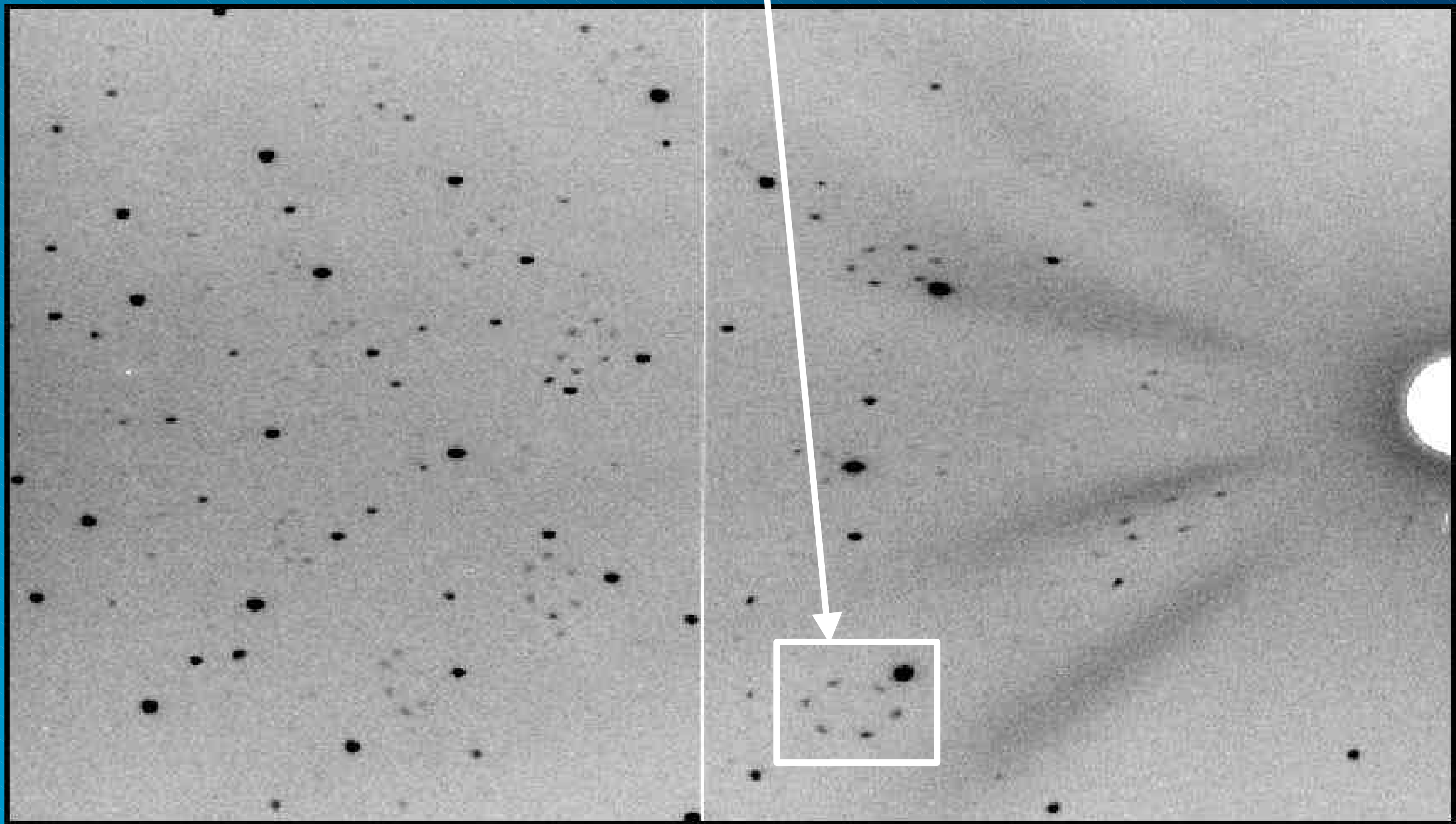
T-LADI Neutron Image Plate
Superstructure in $La_2Co_{1.7}$

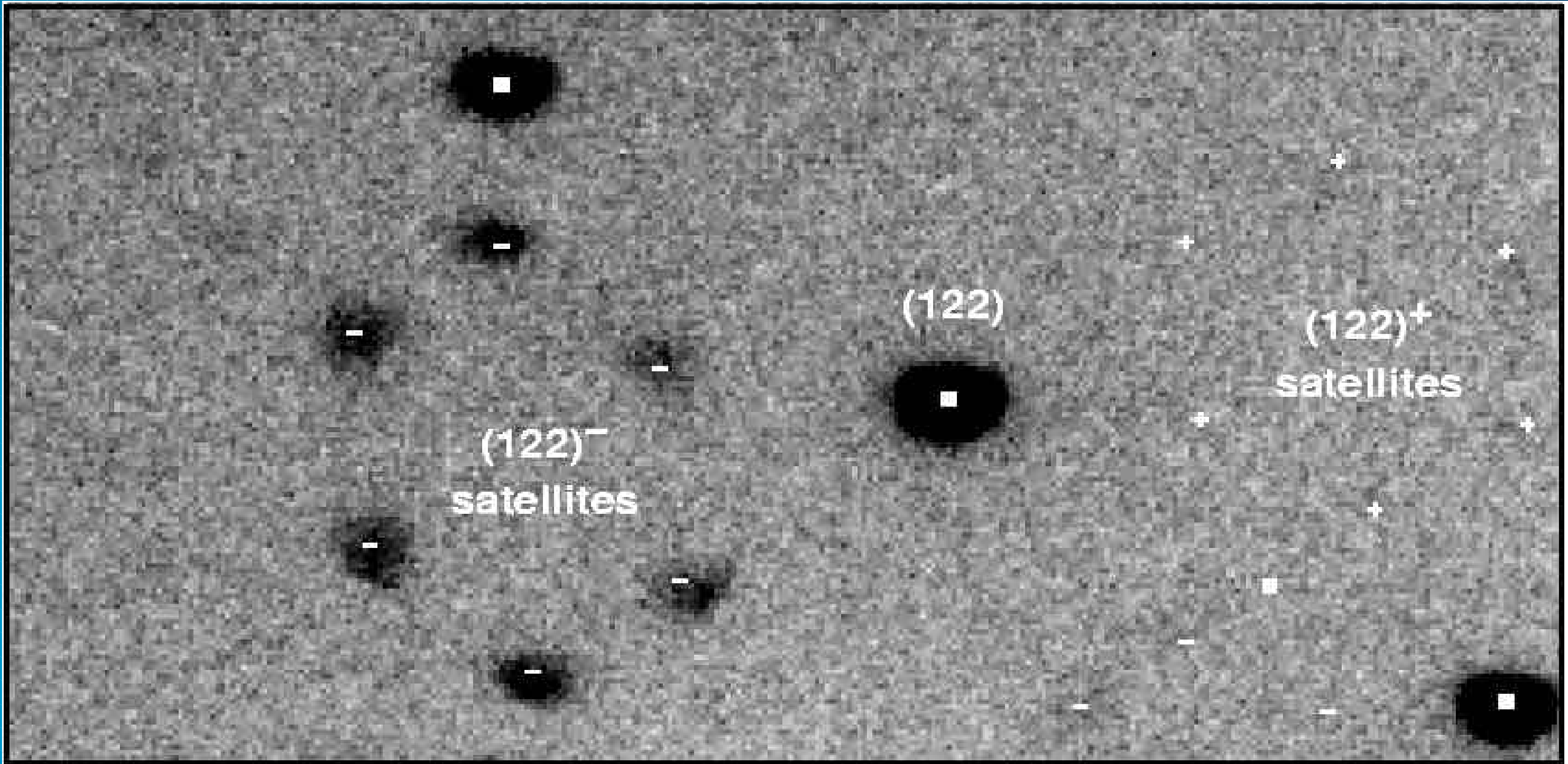


$La_2Co_{1.7}$ on T-LADI showing incommensurable superstructure

T-LADI Neutron Image Plate
Superstructure in $La_2Co_{1.7}$

Alan Hewat

- 6-domain ring of $(122)^-$ superstructure



$La_2Co_{1.7}$ on T-LADI showing incommensurable superstructure

T-LADI Neutron Image Plate Superstructure in $La_2Co_{1.7}$

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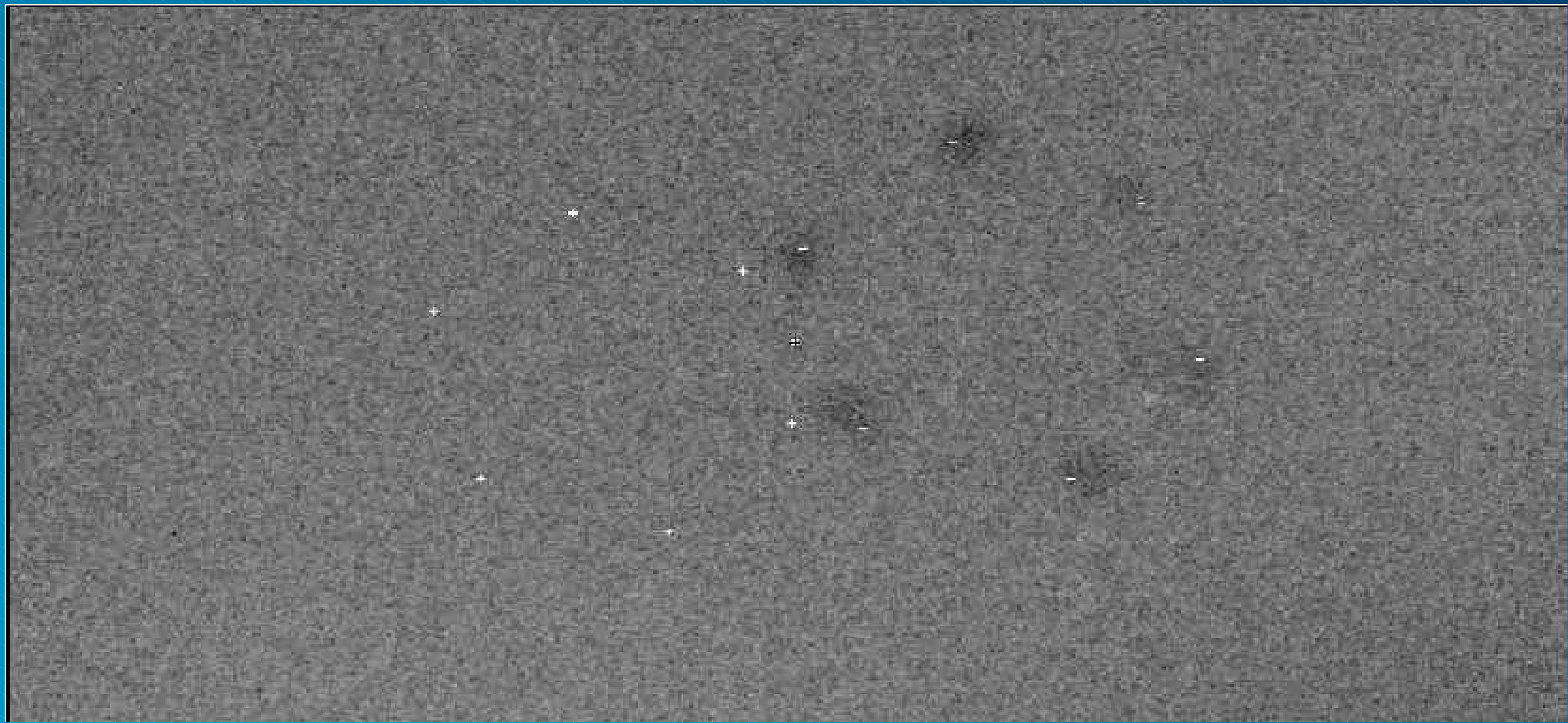
- **Corresponding 6-domain magnetic superstructure**



$La_2Co_{1.7}$ on T-LADI showing incommensurable superstructure

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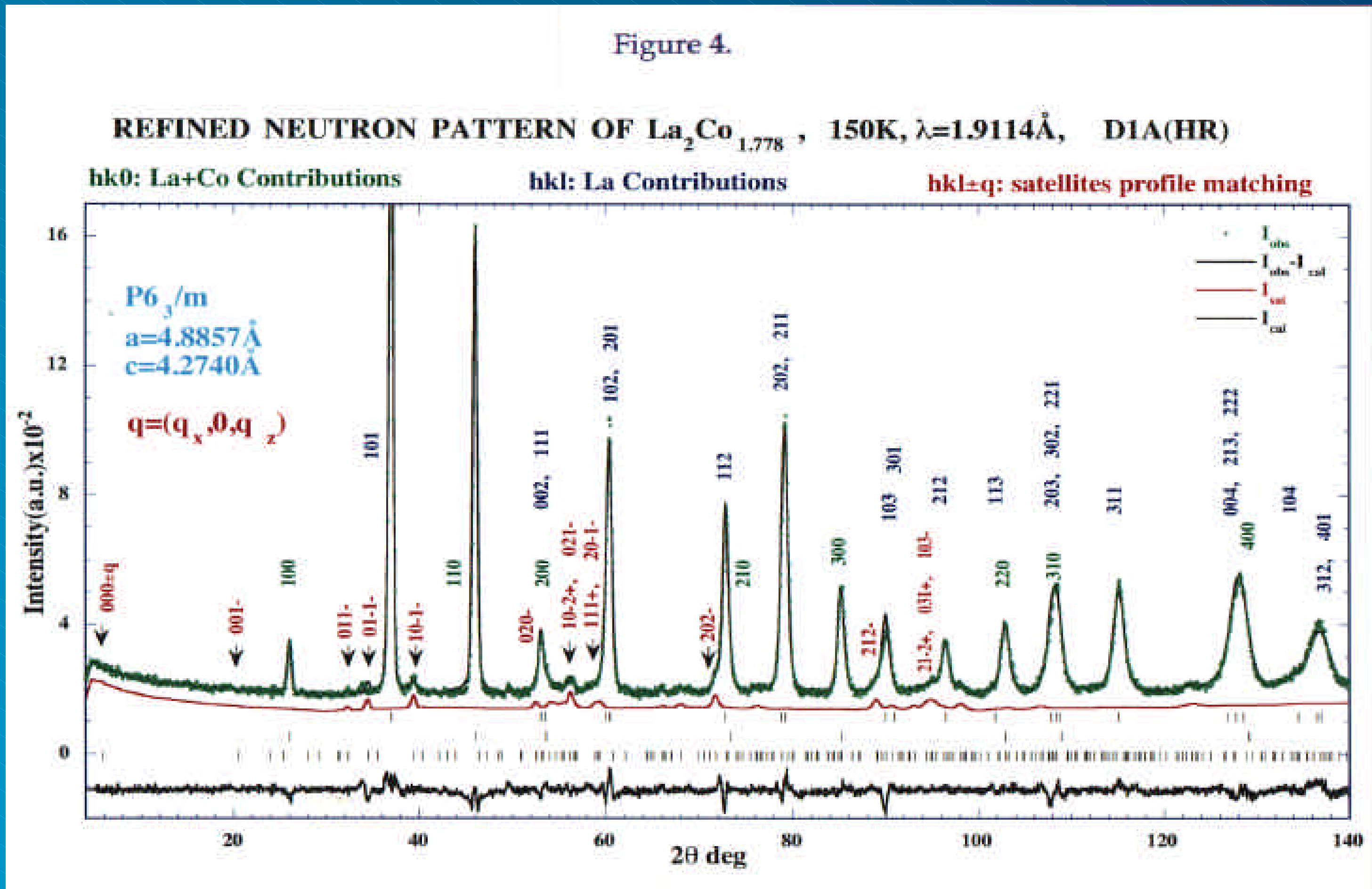
T-LADI and D1A Powder Diffraction Superstructure in $La_2Co_{1.7}$



$La_2Co_{1.7}$ on D1A showing fit to superstructure

T-LADI and D1A Powder Diffraction Superstructure in $La_2Co_{1.7}$

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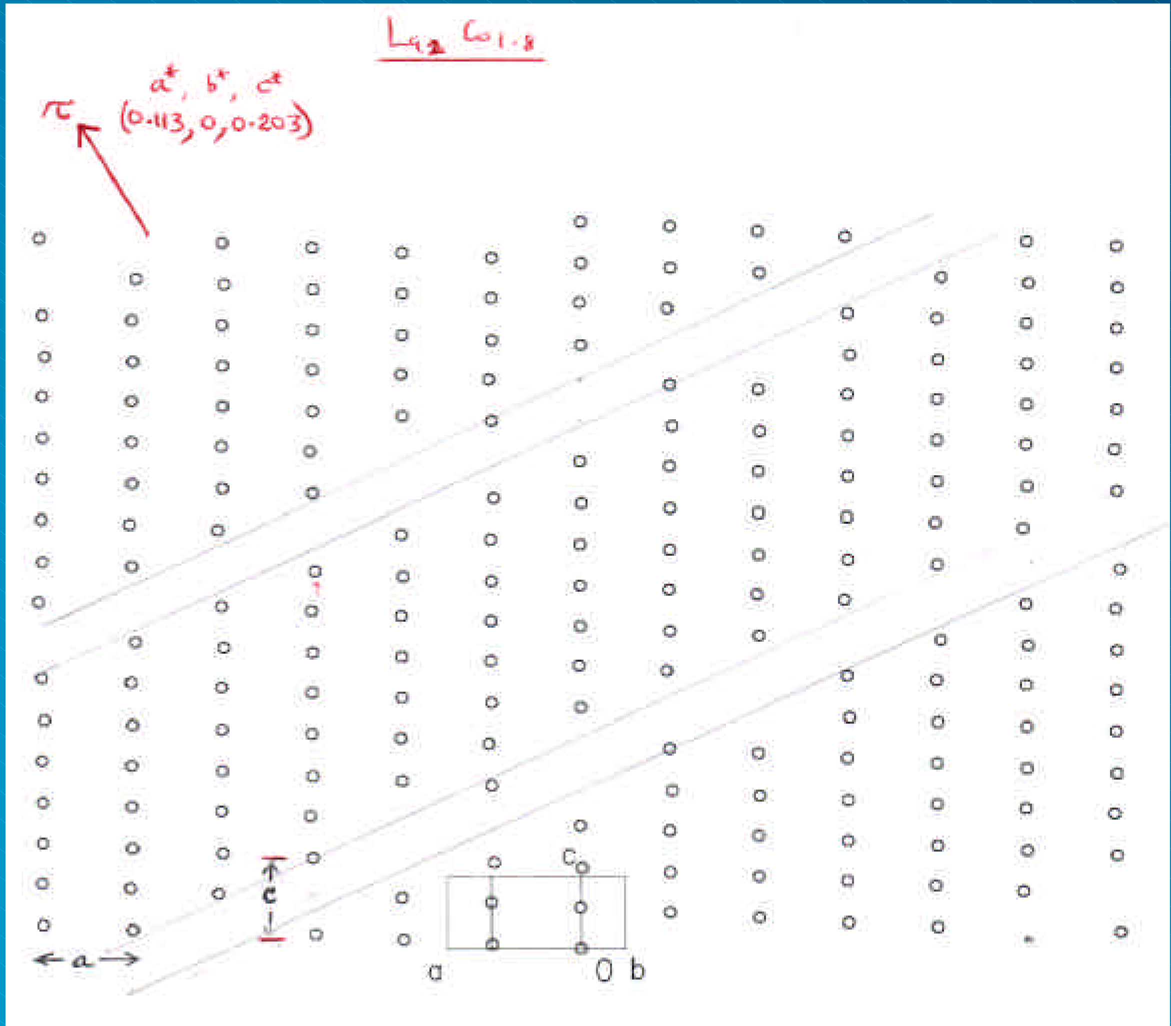

Incommensurable superstructure (Co vacancies)

- Co-packing along c crowded for La_2Co_2
- Co-displacements and Co-vacancies to relieve crowding
- Incommensurable or block superstructure
- $La_2Co_{1.7}$ stoichiometry
- Incommensurable mag. superstructure

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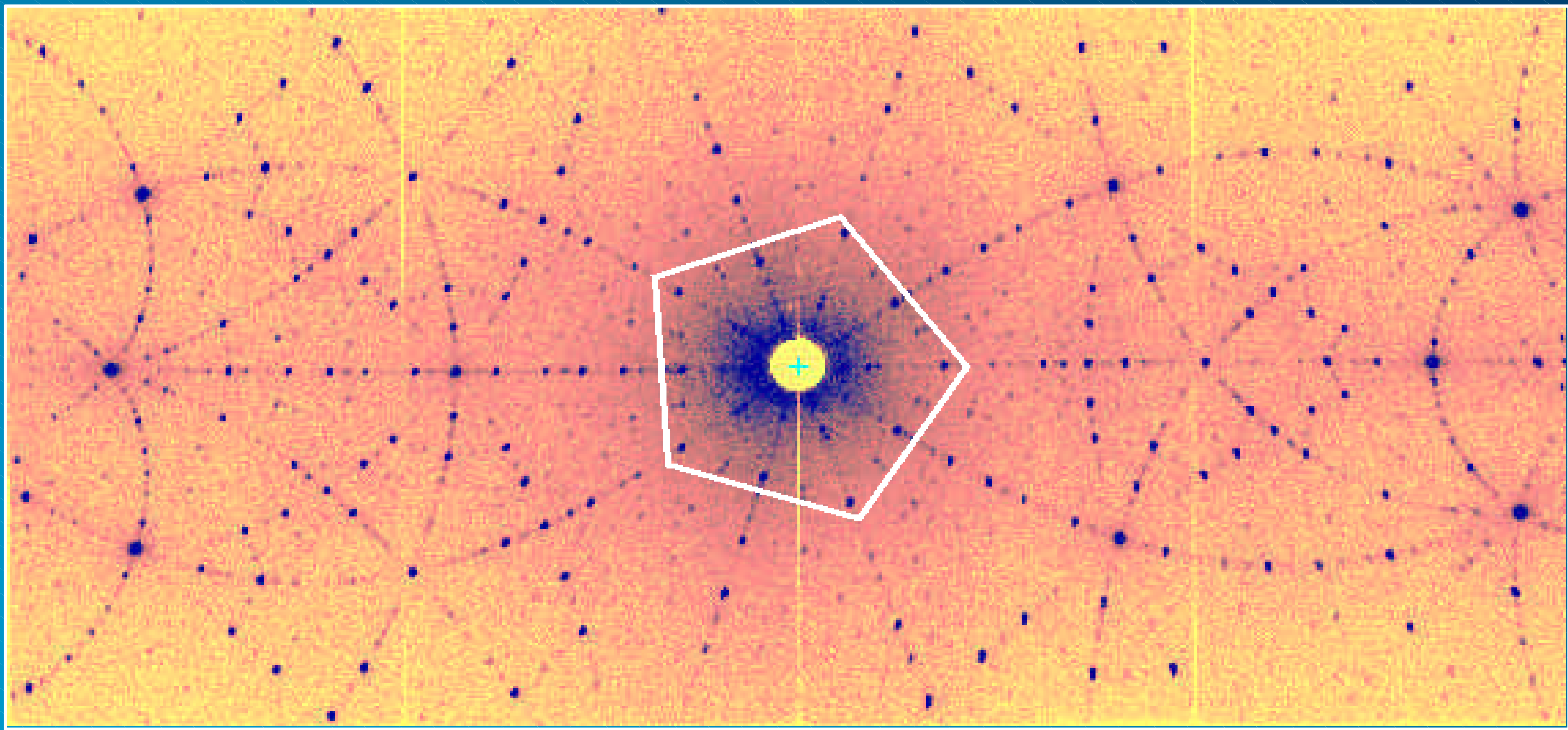
T-LADI Neutron Image Plate
5-fold symmetry of quasi-crystal

Alan Hewat

5-fold symmetry axis in ZnMgY quasi-crystal - De Boissieu et al. (1999)



T-LADI neutron image plate photo courtesy of G. McIntyre, Oct 1999

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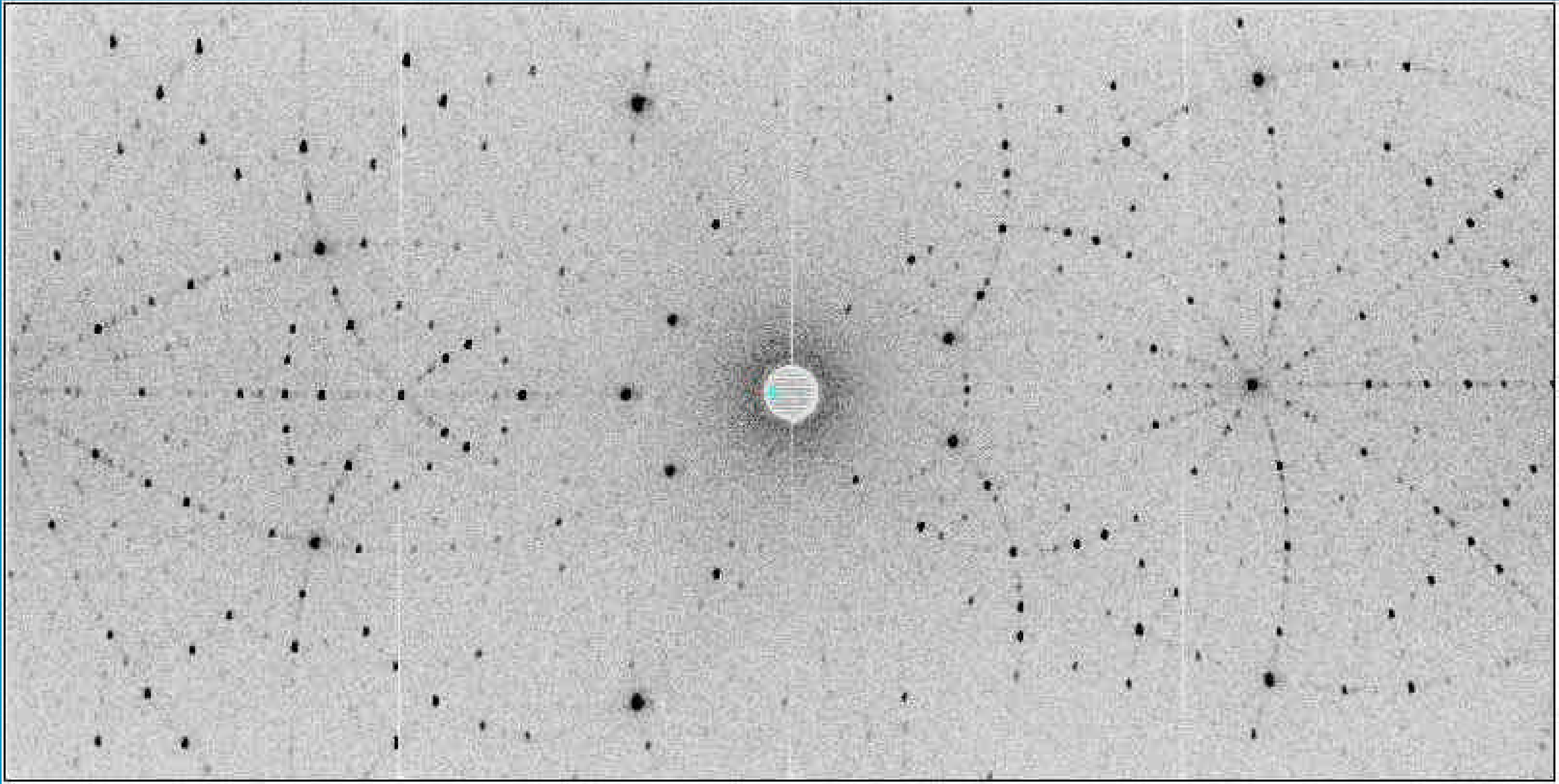
T-LADI Neutron Image Plate
5-fold symmetry of quasi-crystal

Rocking the ZnMgY quasi-crystal (Dynamics) – McIntyre, Cowan (1999)



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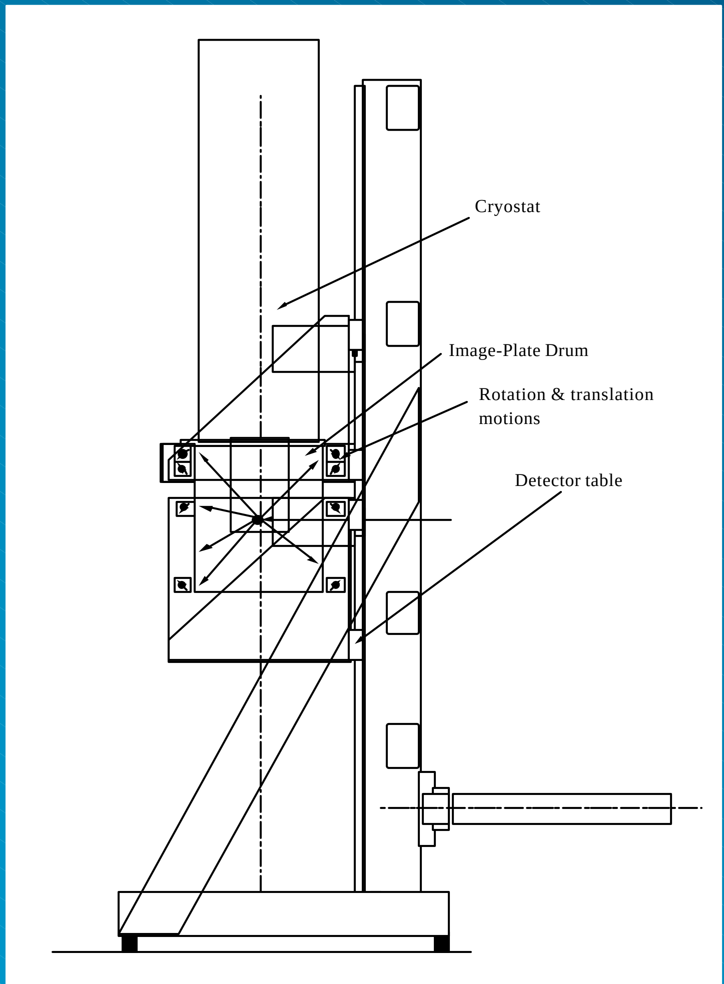
T-LADI Neutron Image Plate
Why Image-plates + Microstrips ?

Alan Hewat



Disadvantages of Image-plates

- Photographic technique
- Accumulate background
- Background from all l (wide Dl)
- H-background

For X-rays, photographic techniques are now replaced by electronic PSD's

New T-LADI (ILL/EMBL collaboration) uses thermal neutrons, more efficient interior read-out optics, vertical geometry allowing use of cryostats, furnaces, magnets, pressure cells

"LADI II – Preliminary Specifications. R4" F. Cipriani, Oct.4 1998

Physics & Chemistry without Crystals
Neutron Powder Diffraction – D1b

Bachir Ouladdiaf et al.

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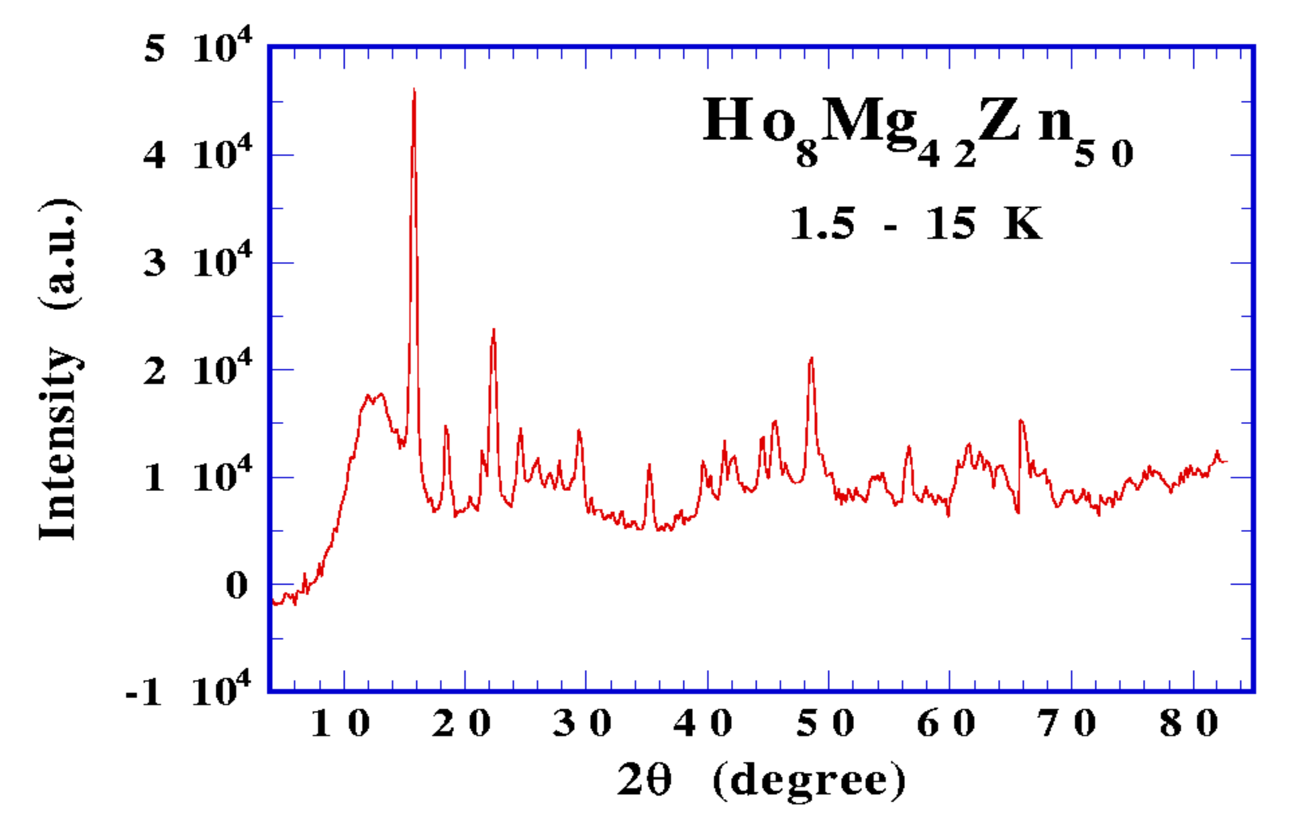
Alan Hewat

1st Magnetic Order in Quasicrystals – Charrier et al. (1997) PRL 78, 4637



- Quasi-crystals usually obtained by quenching (no single crystals)
- Usually Al (few RE QCs)
- Narrow magnetic peaks in difference pattern
  - Long range magnet order
- Broad magnetic peaks
  - Short range correlations
- Both features go at >20K

1.5K-15K magnetic difference pattern

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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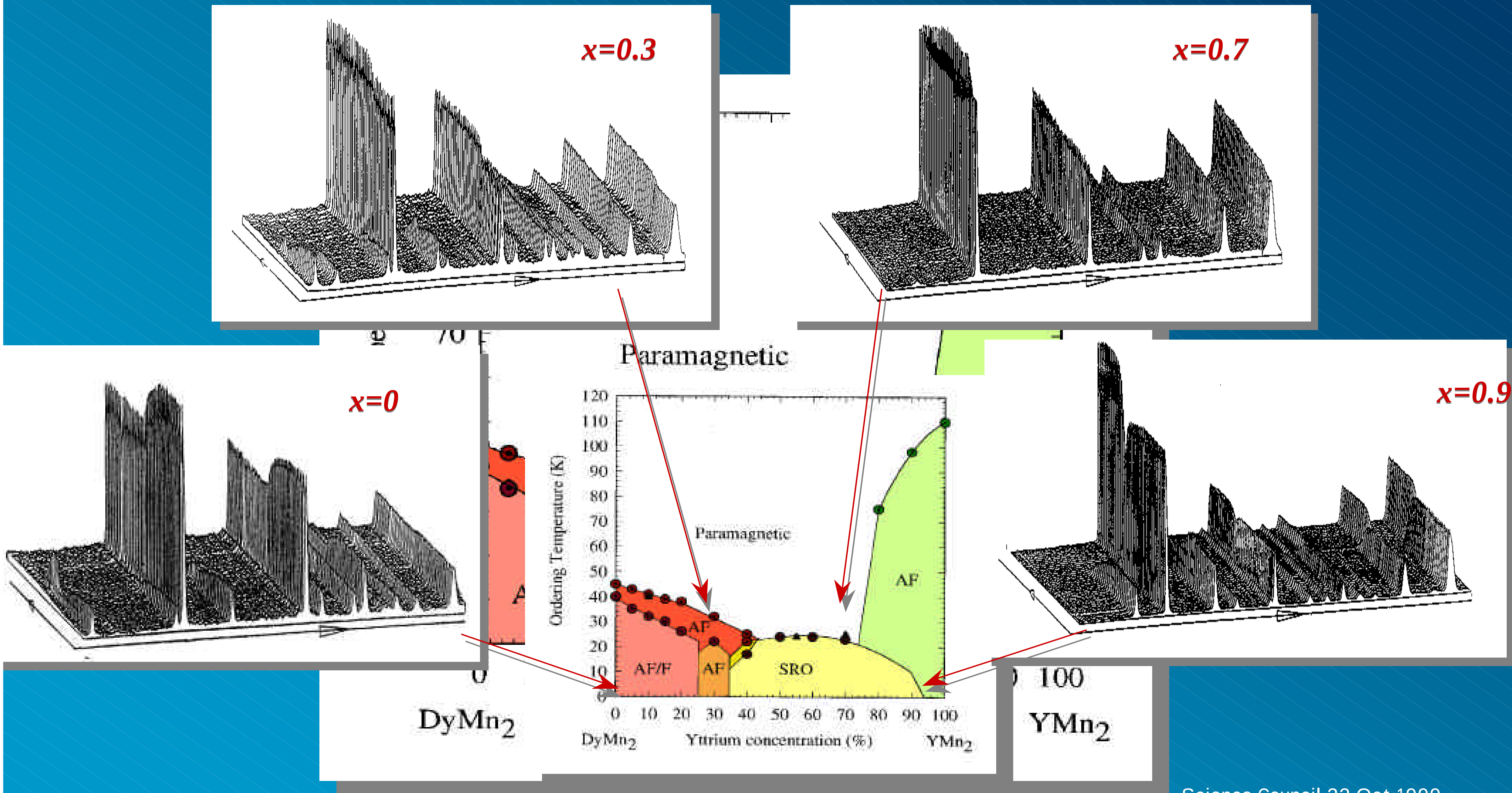


Applications of large fast detectors
Real-time Phase Diagrams (D20, GEM)

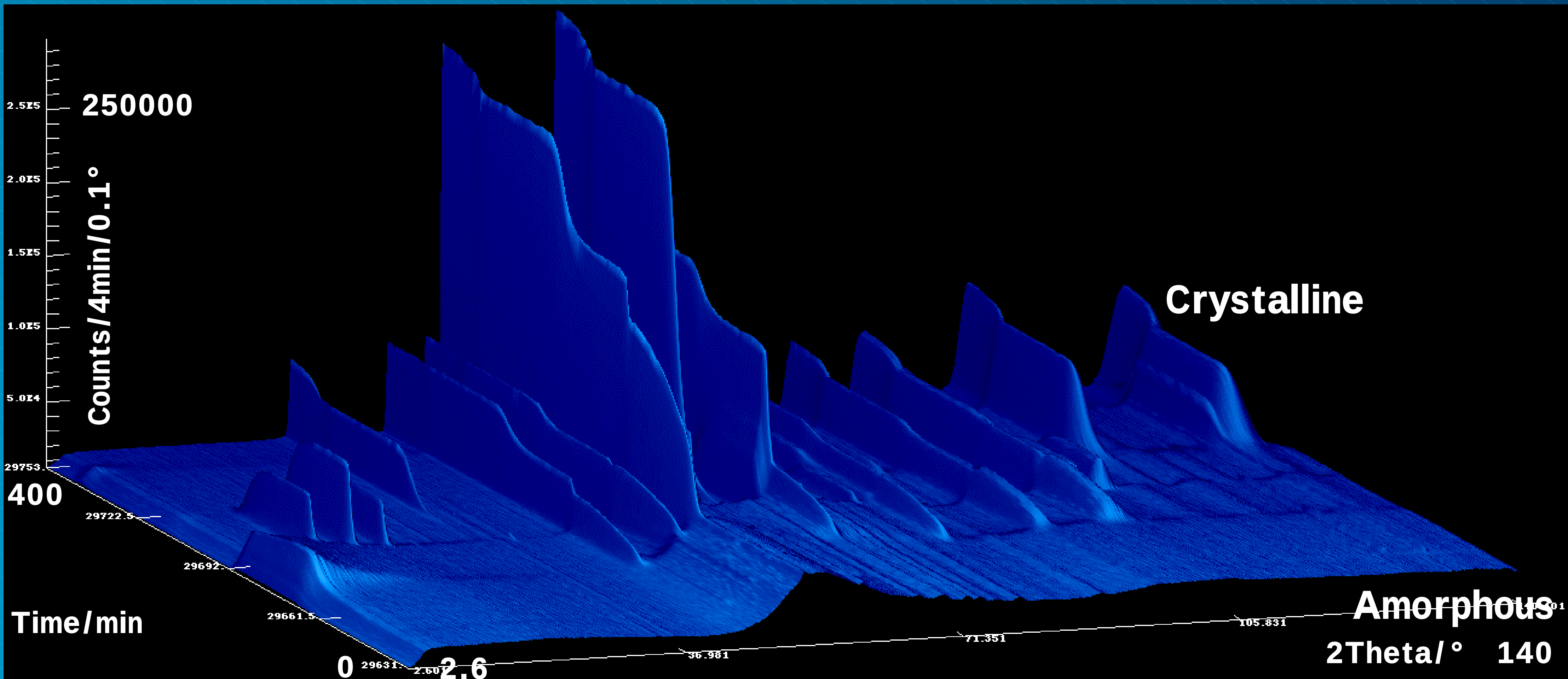
Pierre Convert, Thomas Hansen

ILL Grenoble

Alan Hewat

Kilcoyne et al.

Crystallisation from amorphous phases with increasing temperature



Complete diffraction pattern in seconds, scan through temperature

Applications of large fast detectors

Real-time electro-chemistry

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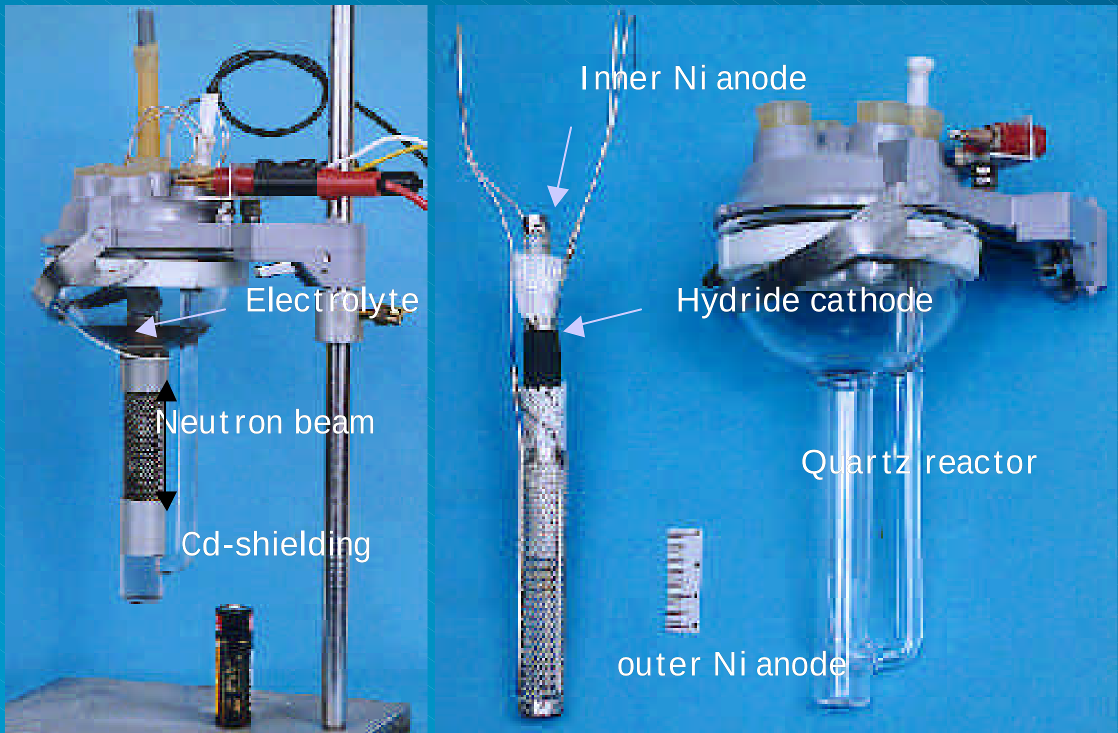
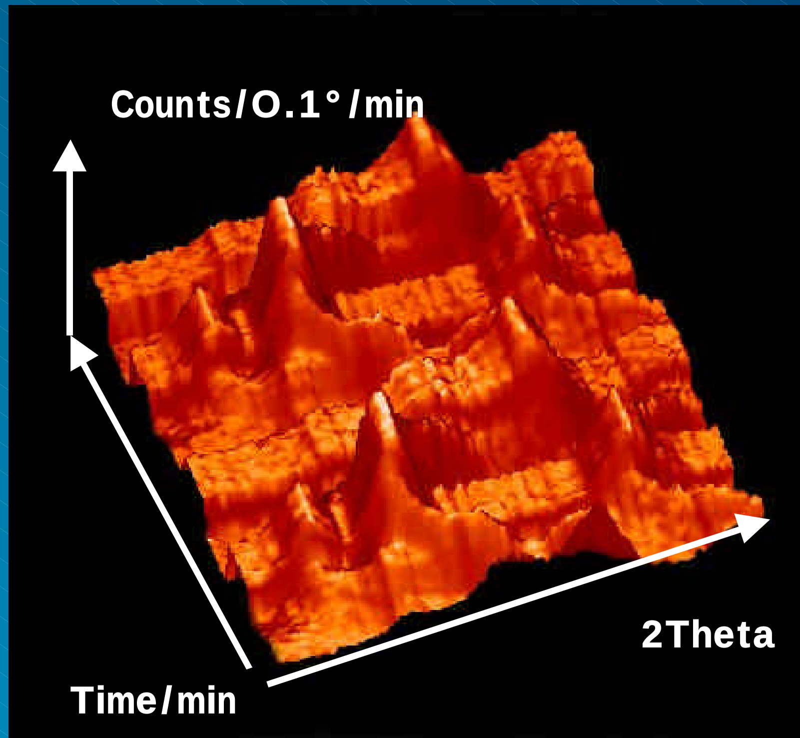
- **Latronche, Chabre et al.: (lecture by Thomas Hansen, IUCr Glasgow)**
  In-situ Charging and discharging of metal hydride electrodes LaNi5





Discharging

Charging

Discharging

Charging

- Follow chemical changes with battery charge/discharge cycle

Applications of large fast detectors

Real-time electro-chemistry

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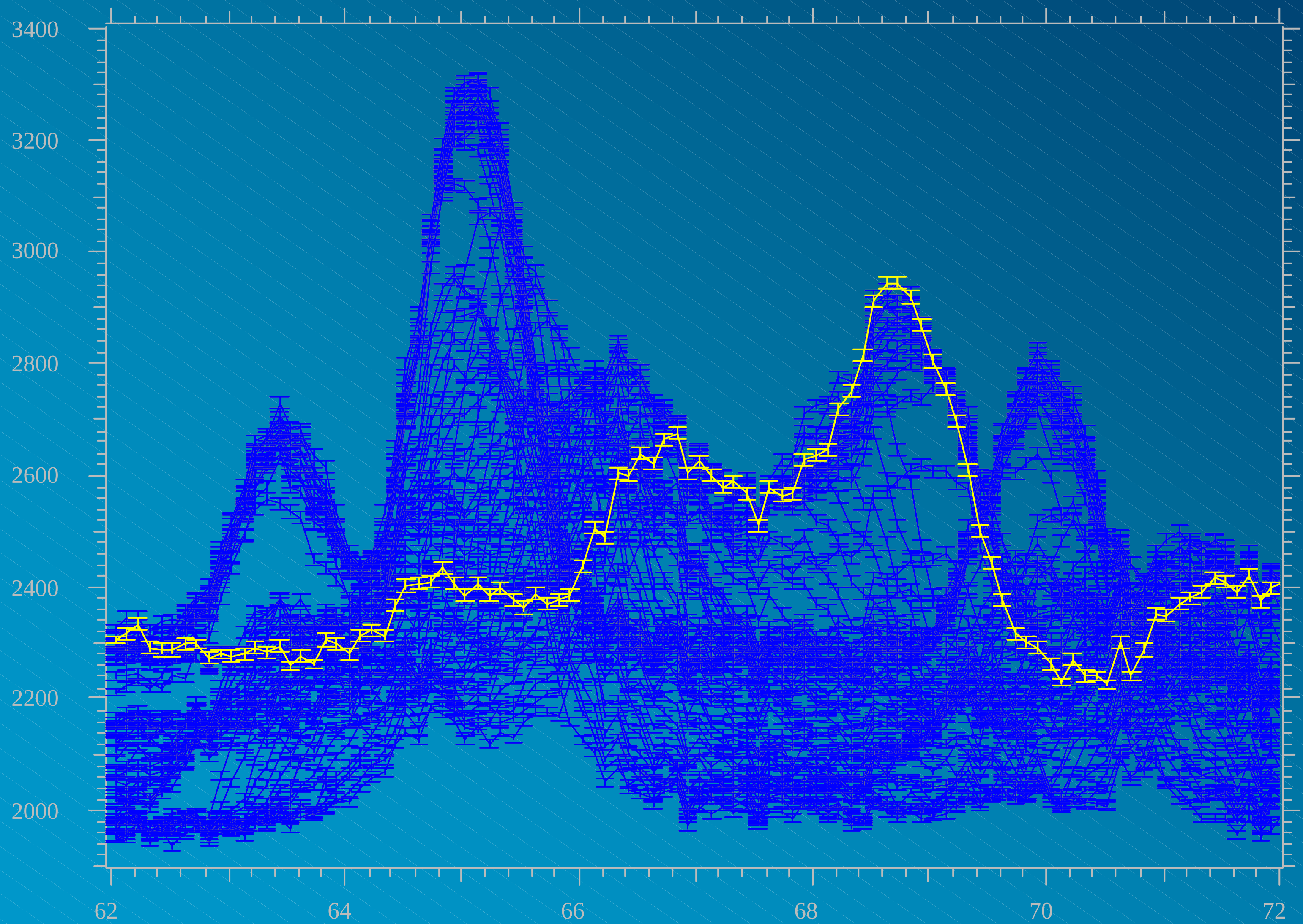

Applications of large fast detectors
Real-world samples

Alan Hewat

- Neutrons much more penetrating than X-rays
  - Can use “real-world samples”
  - Eg a real battery
- NB Very short λ X-rays from Synchrotron sources are also very penetrating, BUT
  - Impose very low angle scattering

Neutron Powder Diffraction

Real Materials, not crystals - Hydrogen in Metals

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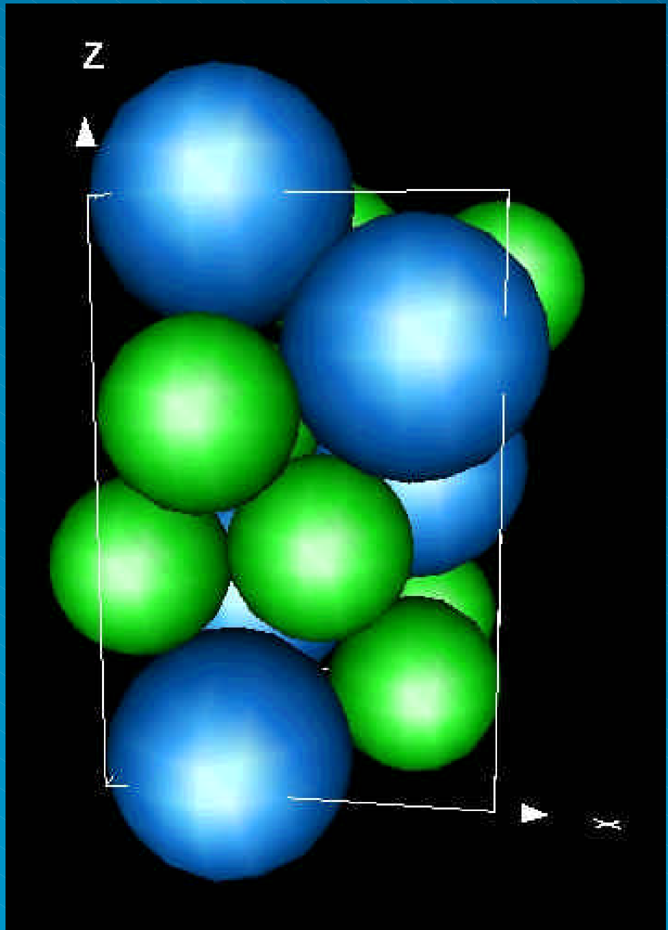

- **Hydrogen storage in metals**
  - **Location of H among heavy atoms**
  - **No single crystals**

- **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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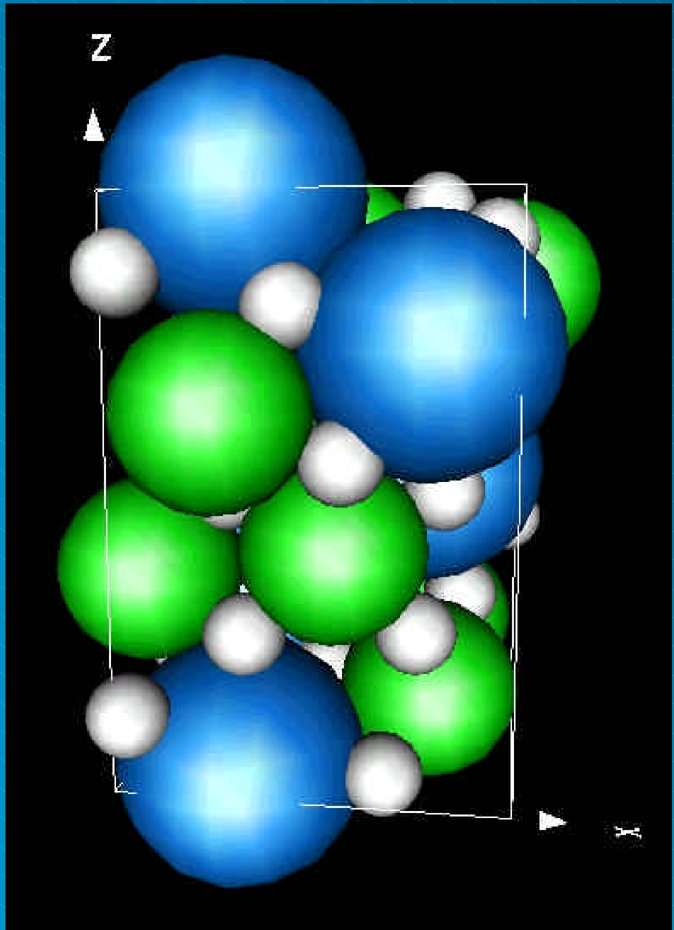
Neutron Powder Diffraction

Real Materials, not crystals - Hydrogen in Metals



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Gingl, Yvon et al. (1997) J. Alloys Compounds **253**, 313.
Kohlmann, Gingl, Hansen, Yvon (1999) Angew. Chemie **38**, 2029. etc..

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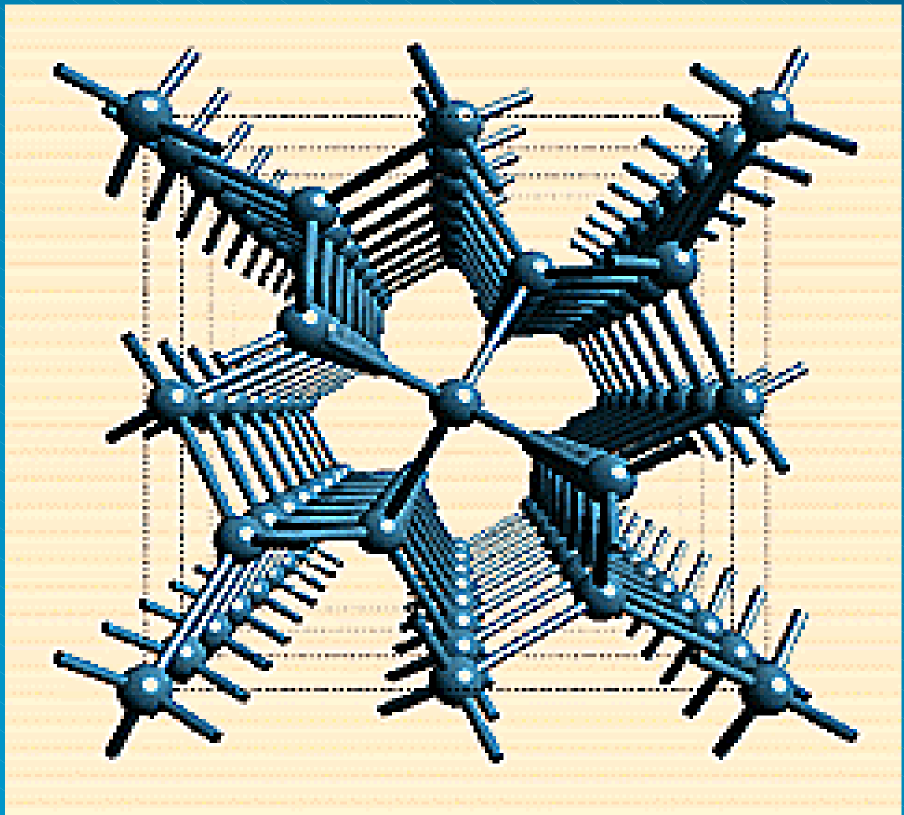
High Pressure Powder Diffraction

Werner Kuhs, John Finney

New phases of Ice discovered by neutron diffraction

Alan Hewat



- **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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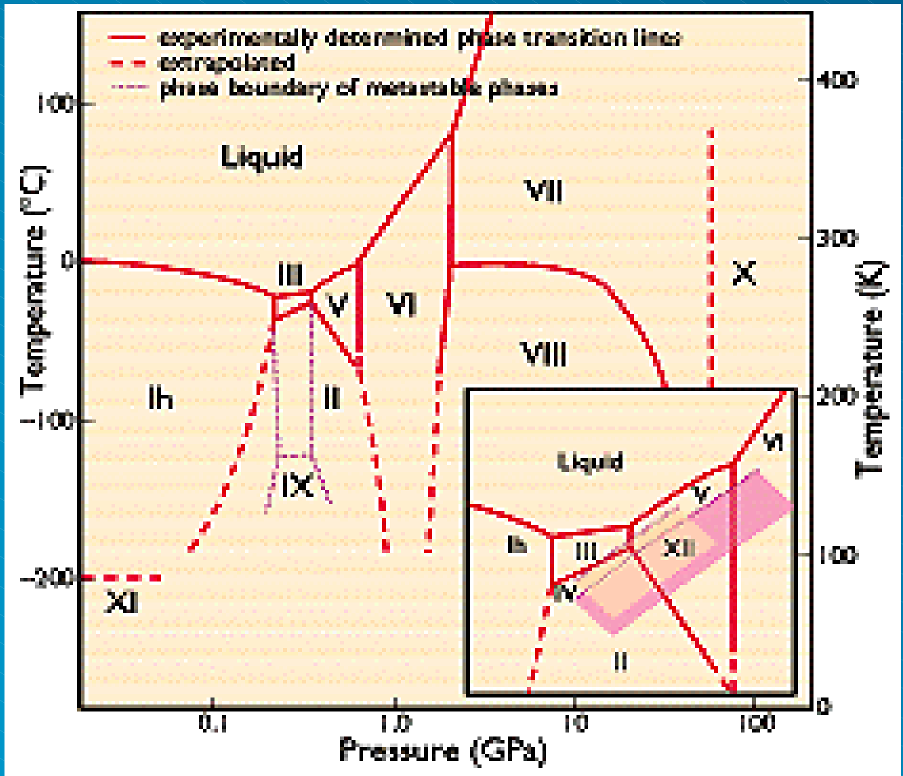
High Pressure Powder Diffraction

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**

Lobban, Finney, Kuhs (1998) Nature 391, 268.
Kuhs, Lobban, Finney (1999) Rev.High Press.Sci.& Tech. 7.

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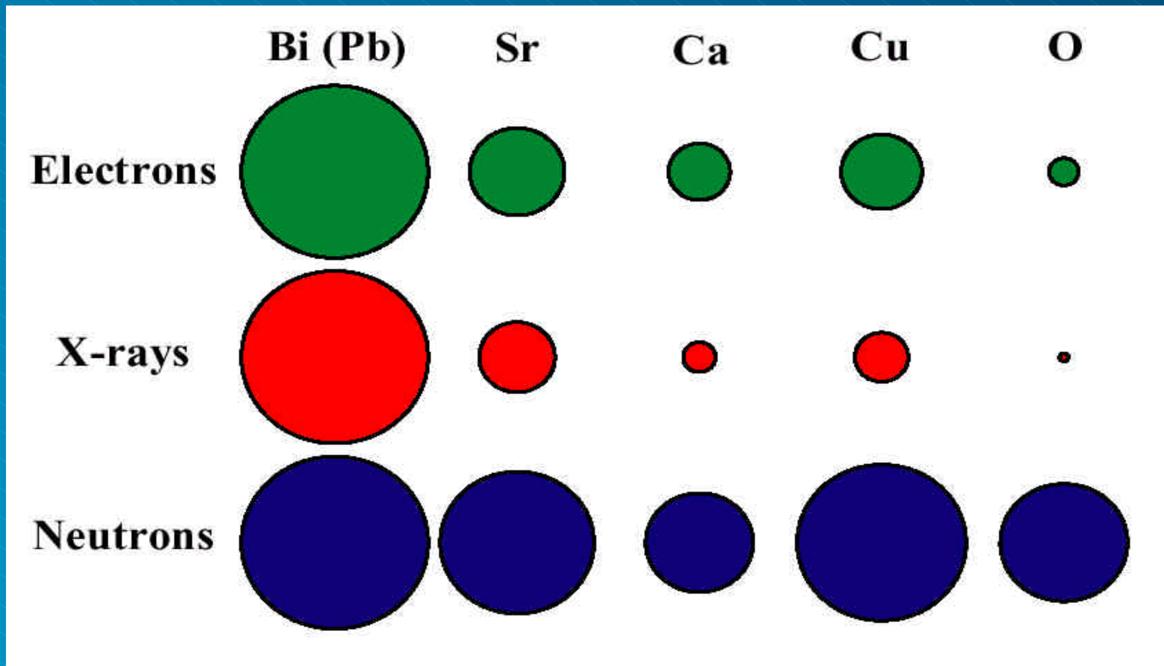
Why Neutrons ?

- Strong Magnetic Scattering of Neutrons
- Relative Scattering Powers of the Elements



- Neutrons scatter strongly from light elements
- Neutrons scatter strongly at high angles (resolve)

Neutron Powder Diffraction
Charge Transfer in $YNiO_3$

Marie-Theresa Fernandez-Diaz et al.

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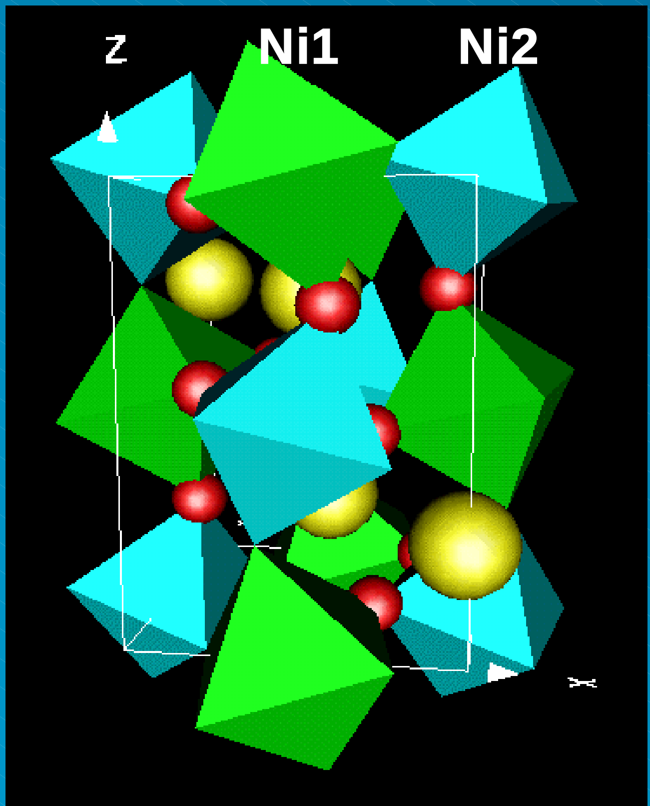
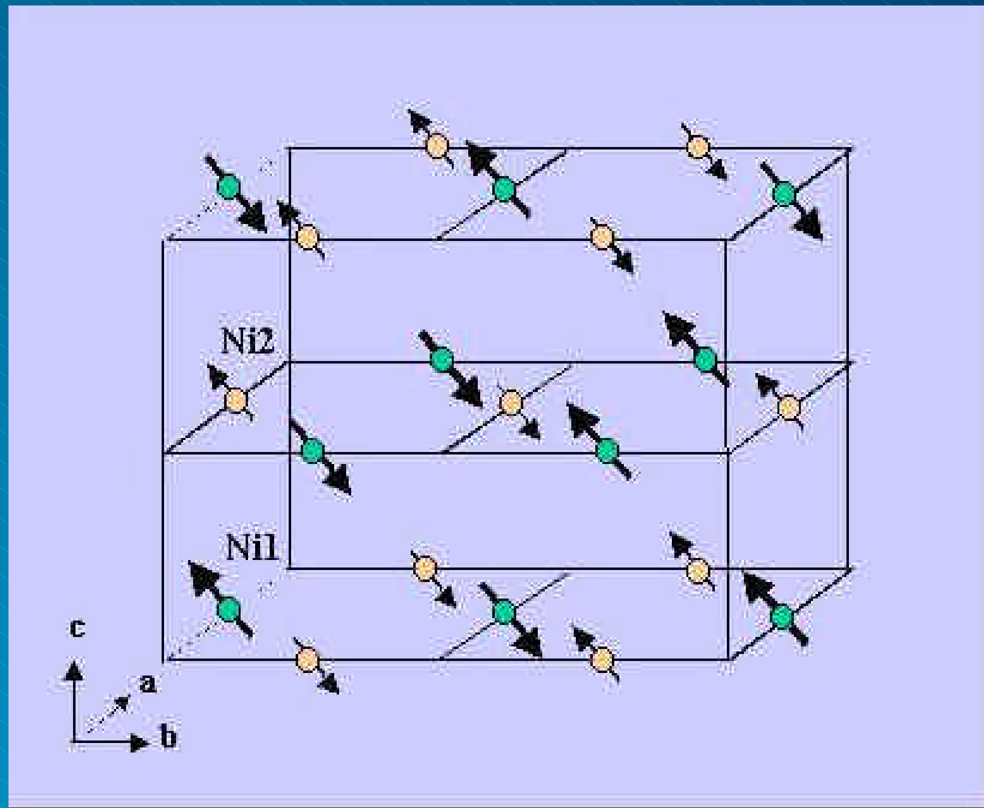
Alan Hewat

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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Neutron Powder Diffraction
Charge Transfer in $YNiO_3$

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

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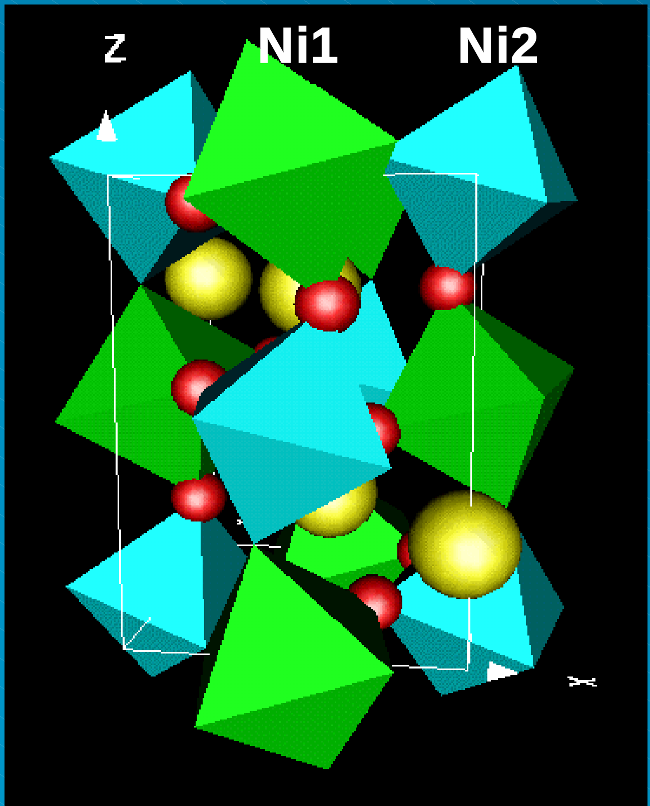

V(Ni1) = 2.62   V(Ni2) = 3.17

- 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

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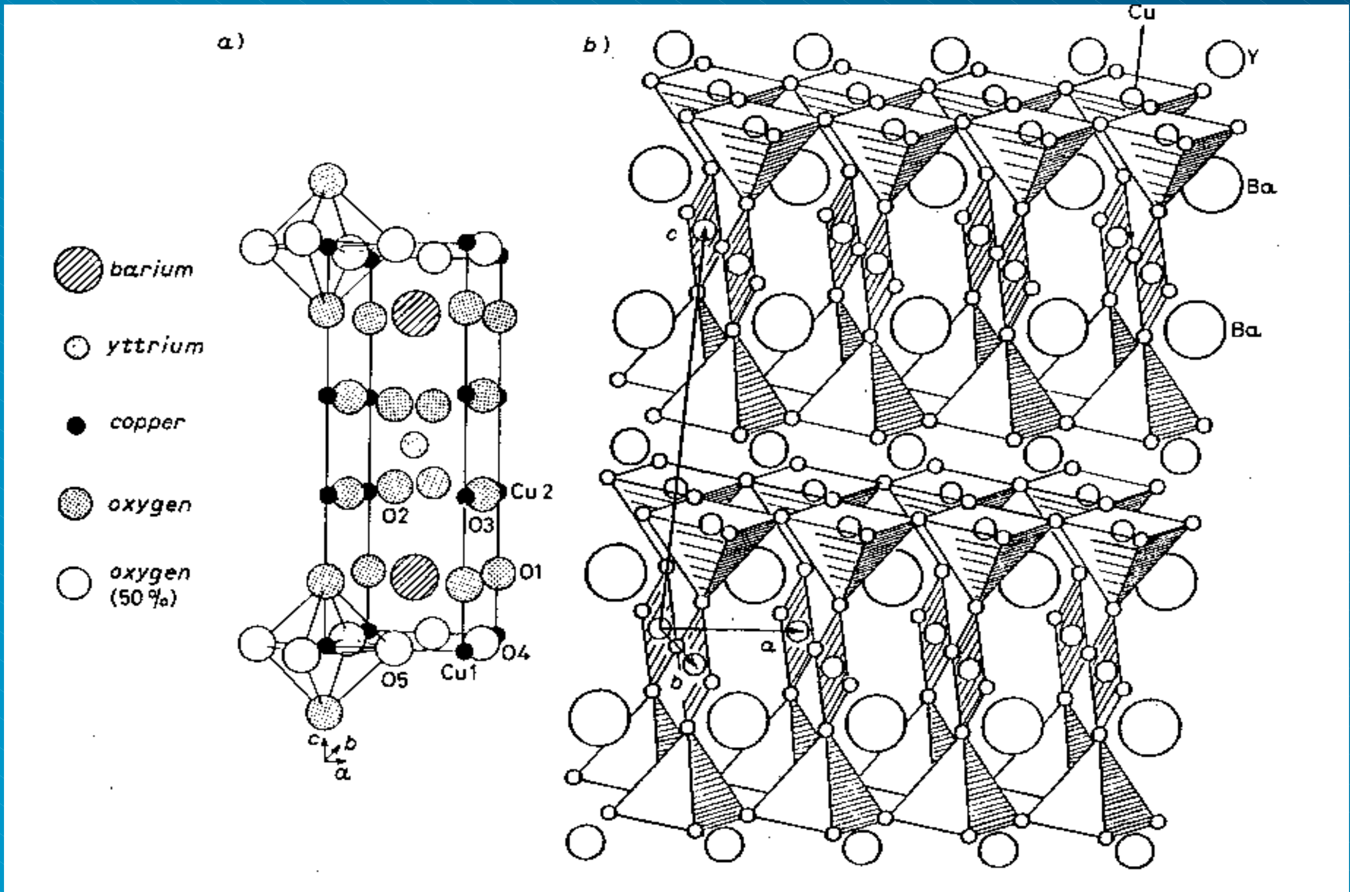
Physics & Chemistry without Crystals
Neutron Powder Diffraction

Alan Hewat

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.

$YBa_2Cu_3O_7$ drawing from Capponi et al 1987 (2nd most cited ILL paper)

Neutron Powder Diffraction
Essential technique for new materials

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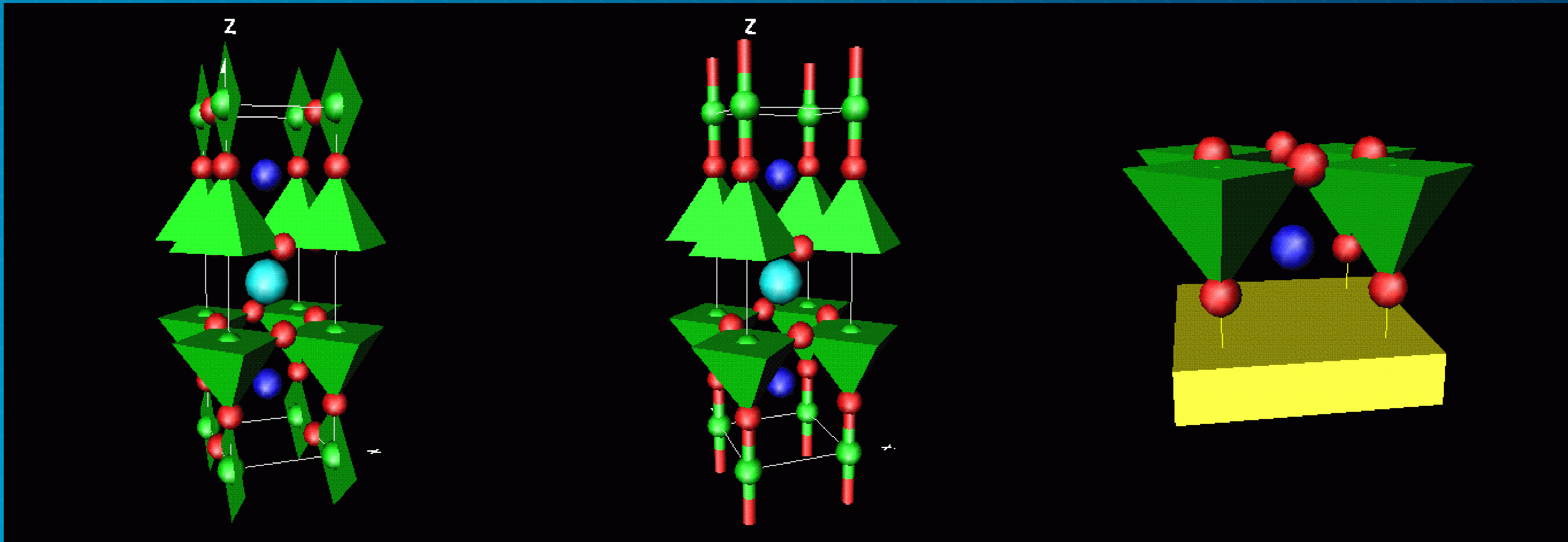
Alan Hewat

Most cited ILL paper - "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, J.D. et al. (1990) Phys.Rev. **B41**,1863 (Argonne)

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Neutron Powder Diffraction
Essential technique for new materials

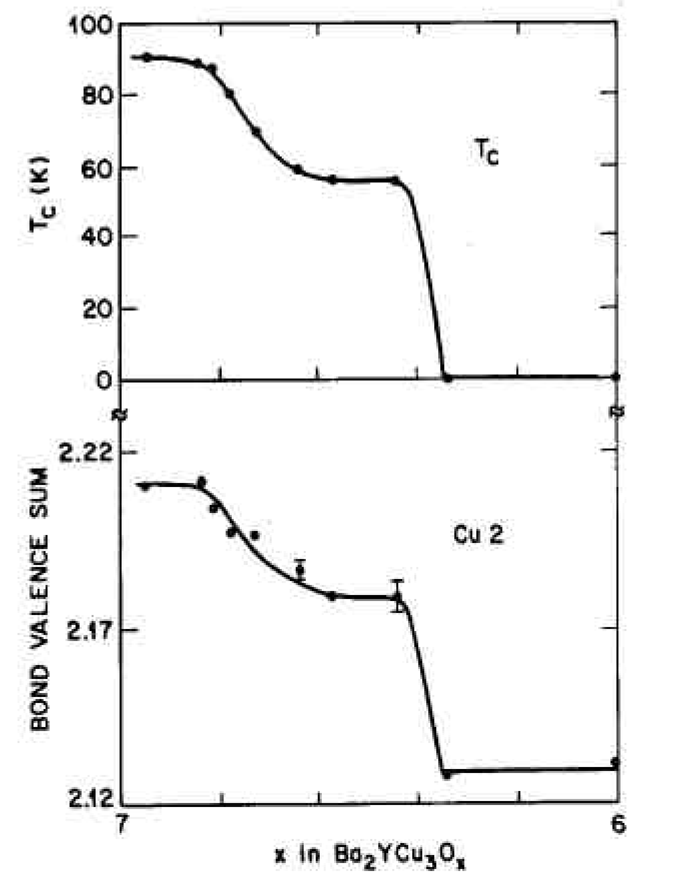


Fig. 16. Comparison of T_c and bond valence sum around the plane copper as a function of oxygen stoichiometry.

- With oxidation of the “charge reservoir”, copper in the superconducting layer was <u>also oxidized</u>.
- This was shown by precise measurement of changes in the Cu-O bond lengths
- Of course this doesn’t “explain” high-Tc
- But the “Charge Reservoir” concept encouraged many chemists to successfully search for similar materials with different charge reservoir layers

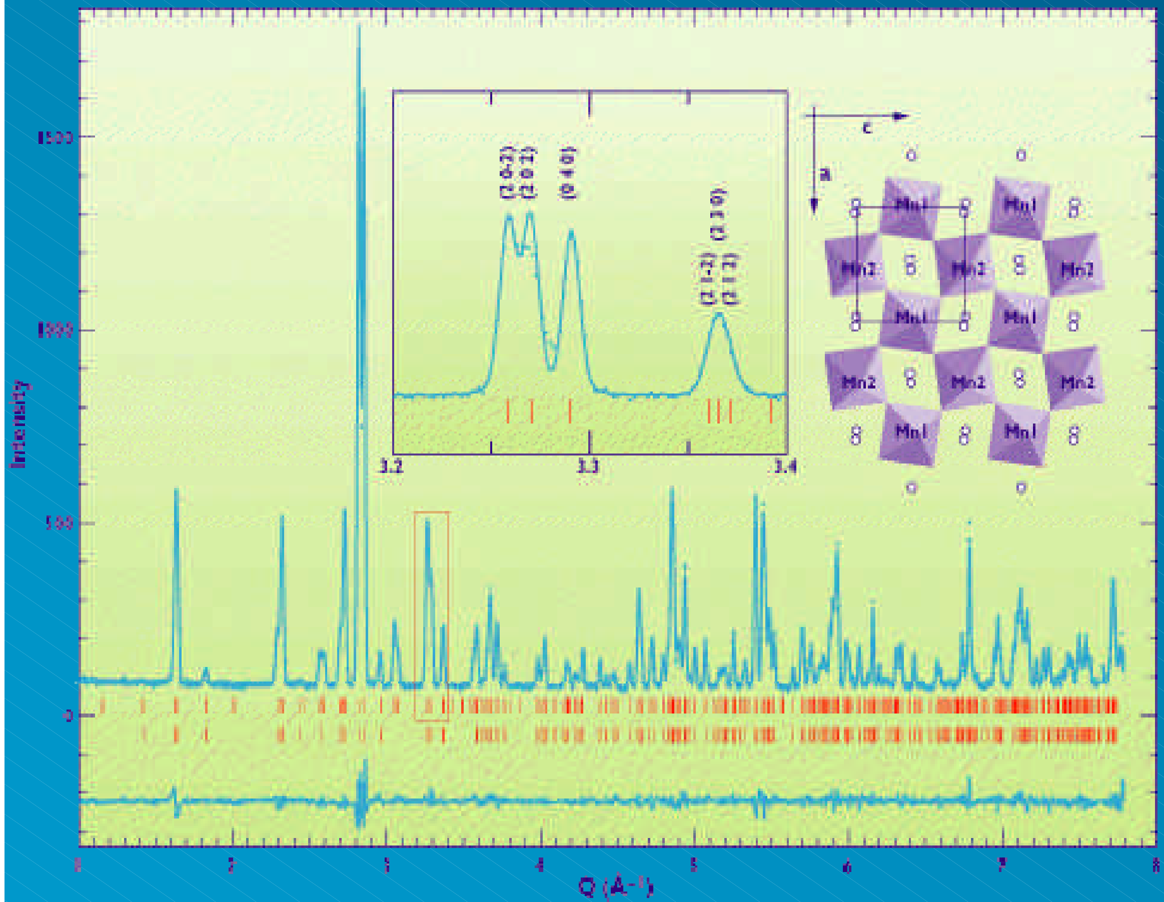
Giant Magneto-Resistive Ceramics $La_{0.333}Ca_{0.667}MnO_3$ on D2B

ILL Grenoble

Emmanuel Suard, Marie-Theresa Fernandez-Diaz, Paolo Radaelli

Alan Hewat

Another high profile example of neutron powders and new materials



(courtesy of Emmanuel Suard)

- Caignaert, Suard, Maignan, Simon,Raveau (1996) J.Mag.Mag.Mat.153,L260
- De Teresa, Ibarra, Algarabel, Ritter, Marquina, Blasco, Garcia, del Moral, Arnold (1997) Nature 386,256
- Radaelli, Cox, Capogna, Cheong, Marezio (1999) Phys.Rev.B59, 14440
- Fernandez-Diaz, Martinez, Alonso, Herrero (1999) Phys.Rev.B59,1277

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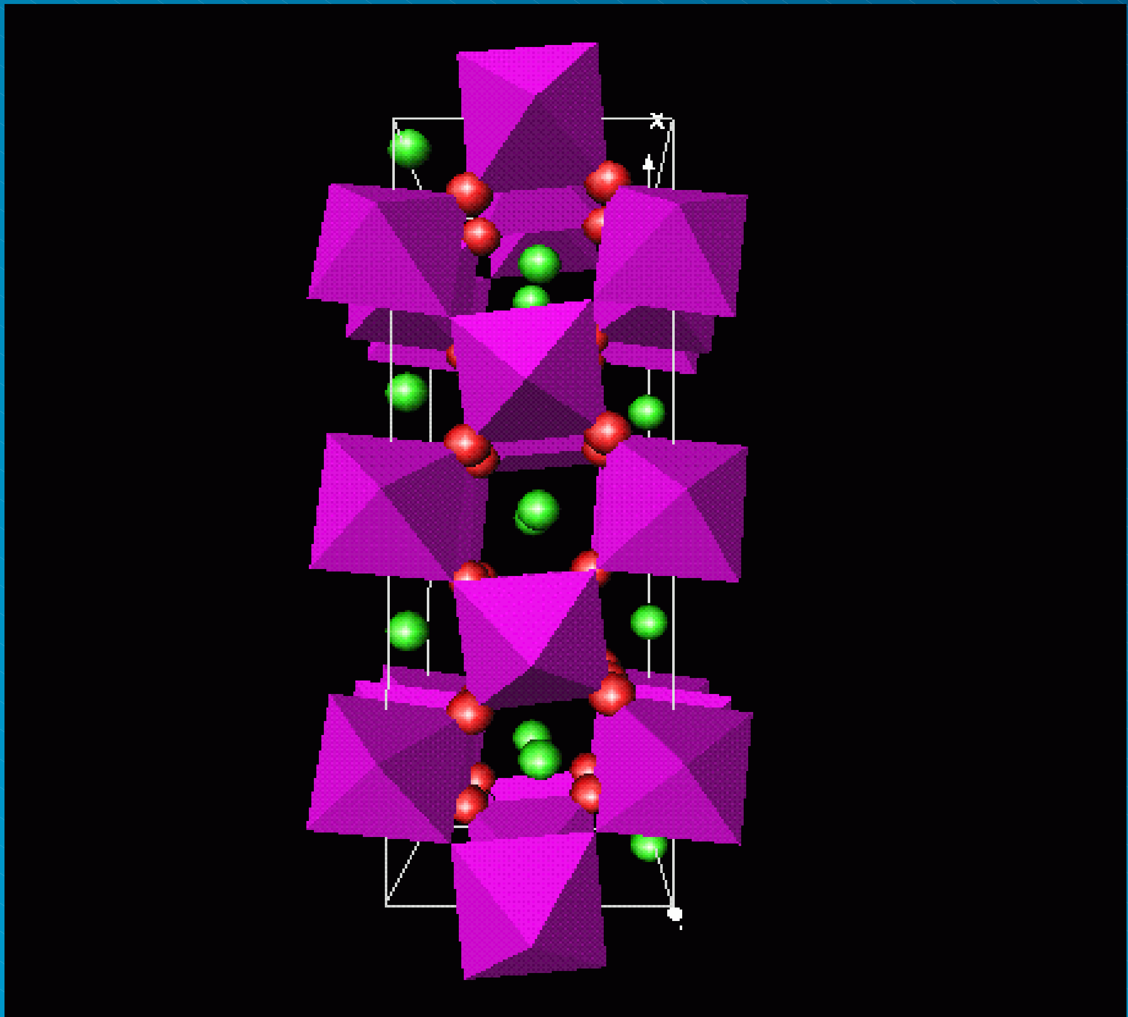
Giant Magneto-Resistive Ceramics
$La_{0.333}Ca_{0.667}MnO_3$ on D2B

Alan Hewat



- 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)

GMR Stripes and Charge Ordering

1D-ordering ? Dimensionality important for theory.

Alan Hewat

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)**

GMR Stripes and Charge Ordering

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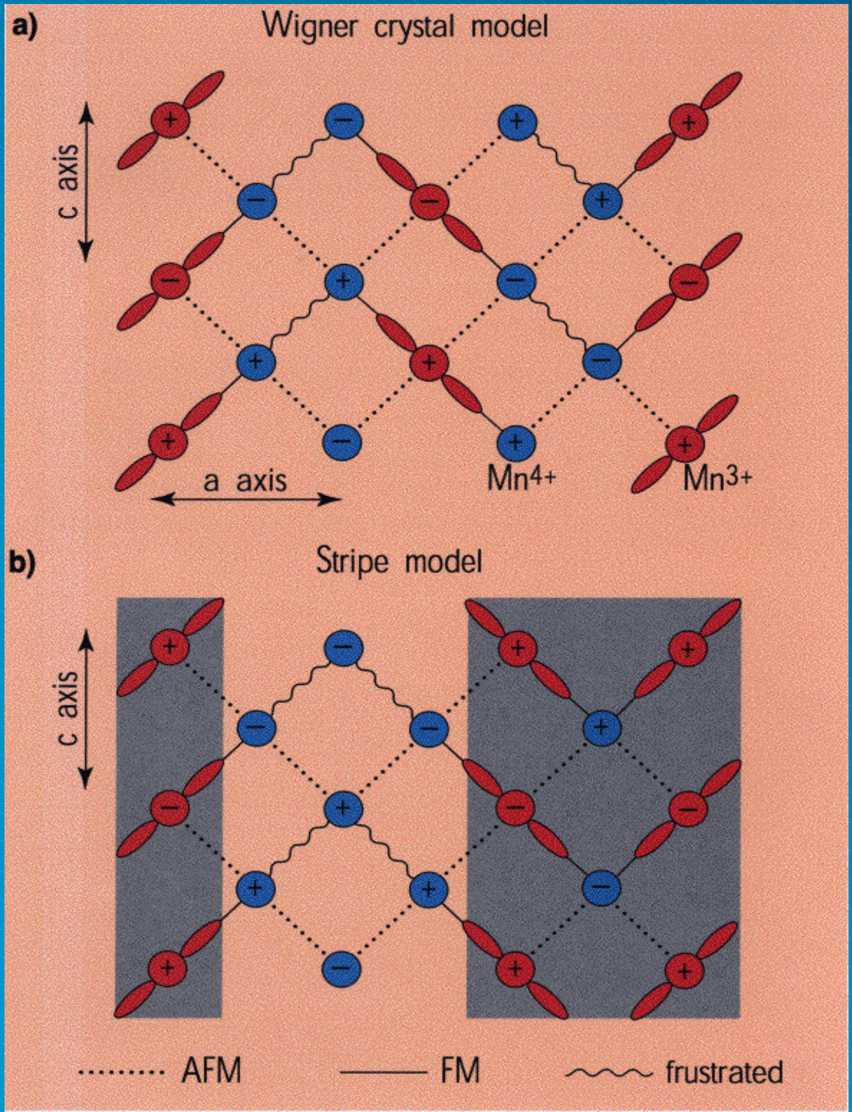
1D-ordering ? Dimensionality important for theory.



- **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**

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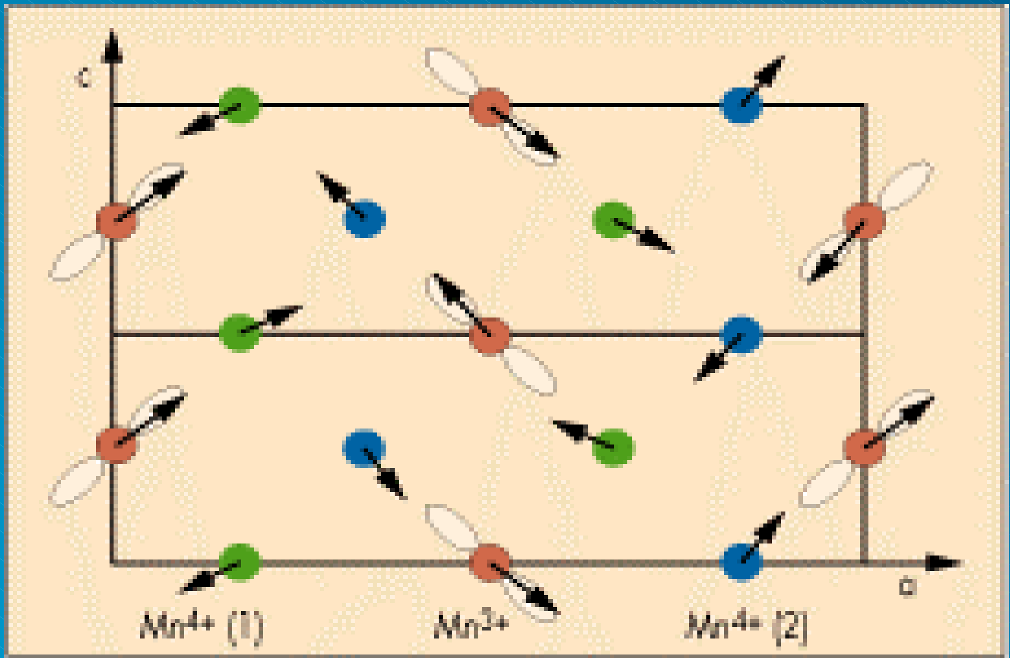
GMR Stripes and Charge Ordering

Magnetic+Oxide+T/N - Neutron powder diffraction



Fernandez-Diaz et al. (1999)
Phys. Rev B59, 1277.
Neutron work on D1B+D2B (ILL)

- **A classical problem for RR of neutron powder data**
  - **magnetic structure**
  - **details of oxygen structure**
  - **destructive phase transition**
- **Magnetic structure of $La_{0.33}Ca_{30.67}MnO_3$**
  - **consistent with the Wigner model, symmetry difficult to reconcile with a stripe model**

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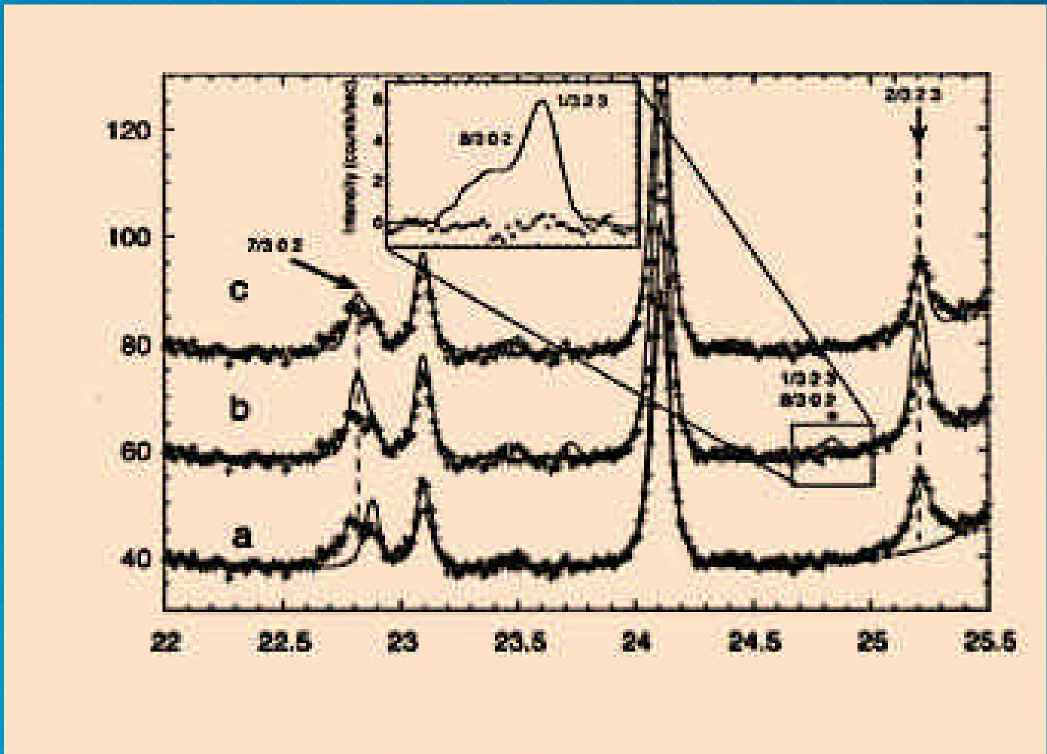
GMR Stripes and Charge Ordering

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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GMR Stripes and Charge Ordering

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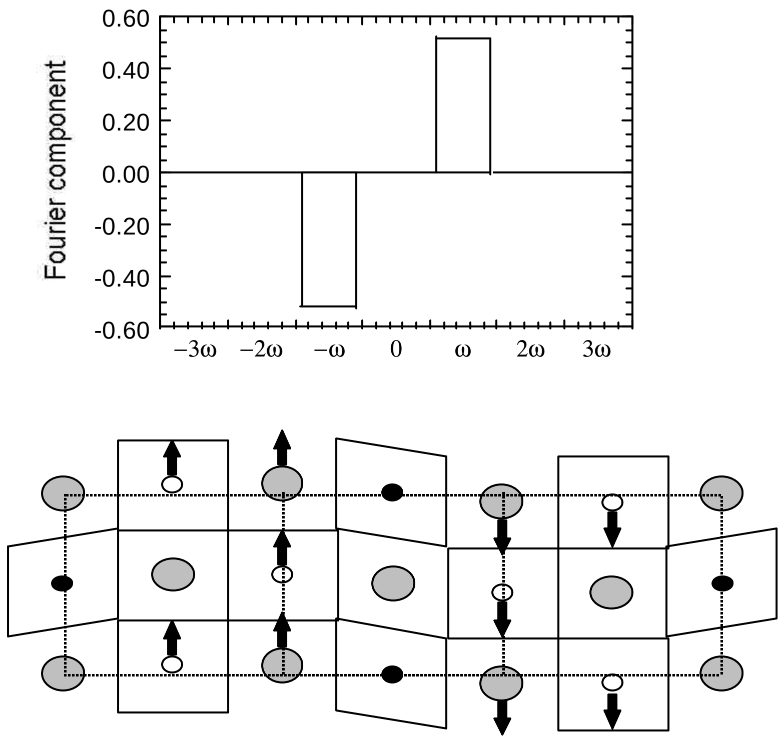
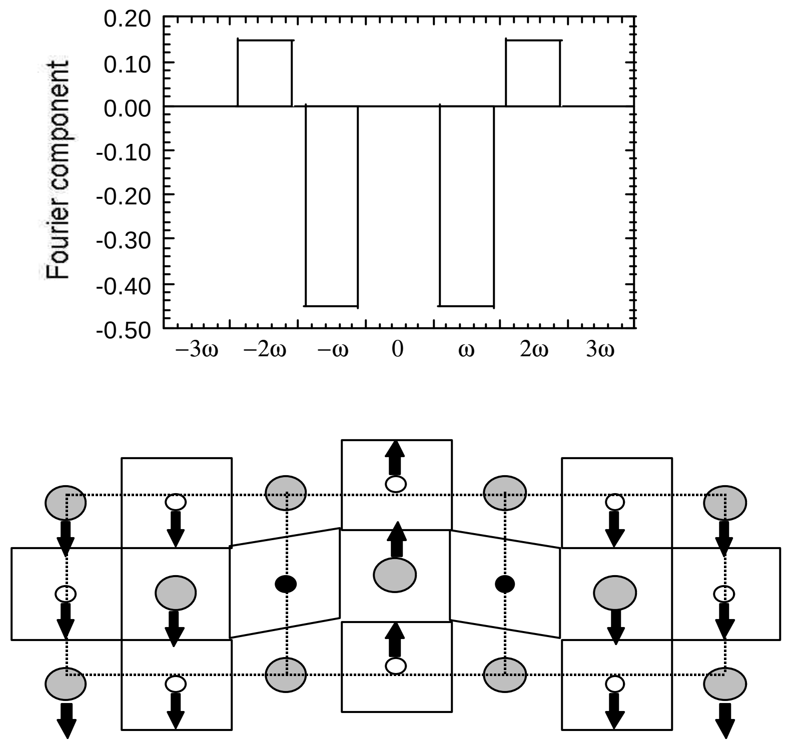
“Wigner crystal” model



“Stripe” model



GMR Stripes and Charge Ordering

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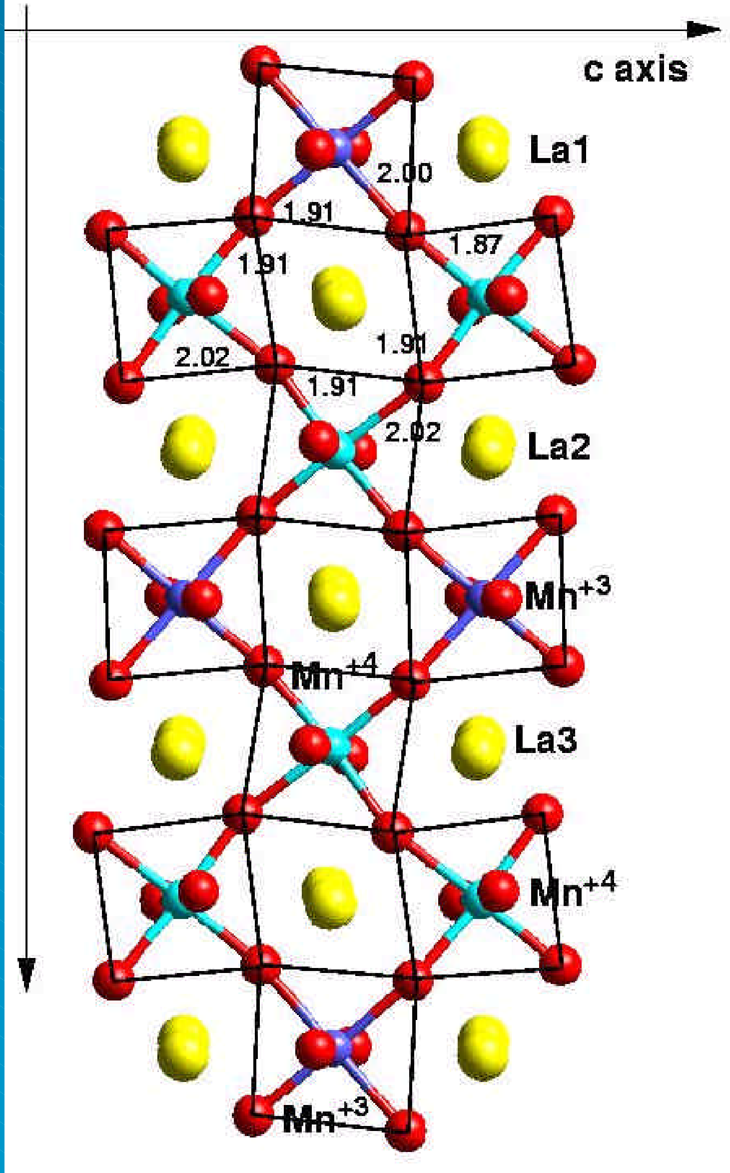
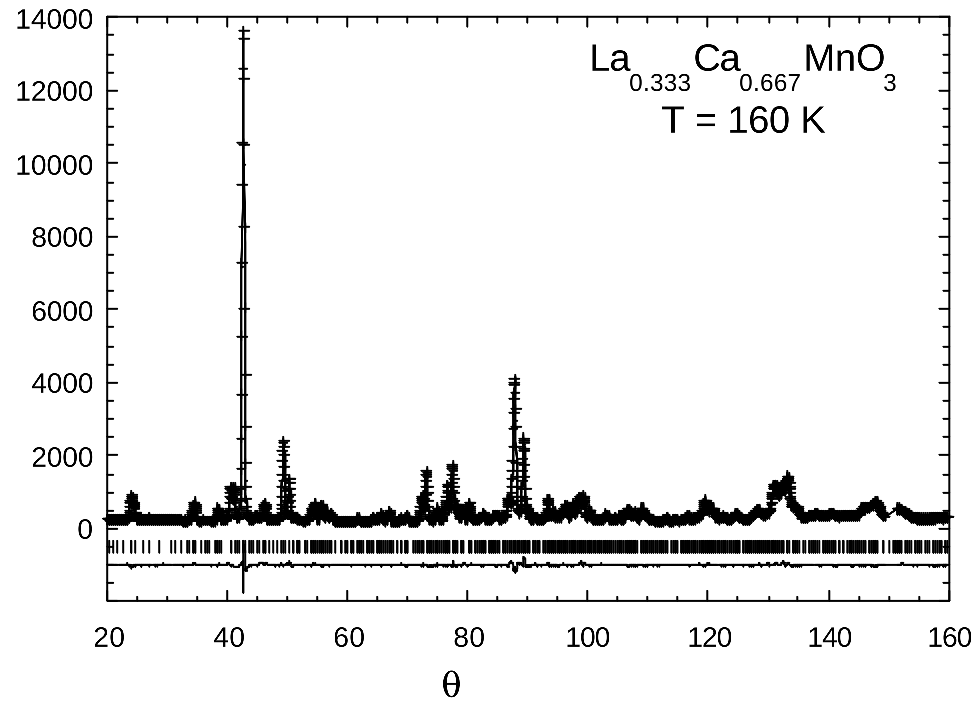




Refined Neutron Powder Pattern (D2B)

Early Days at ILL Grenoble (1972)

First ILL Powder Diffractometer D1a

Alan Hewat

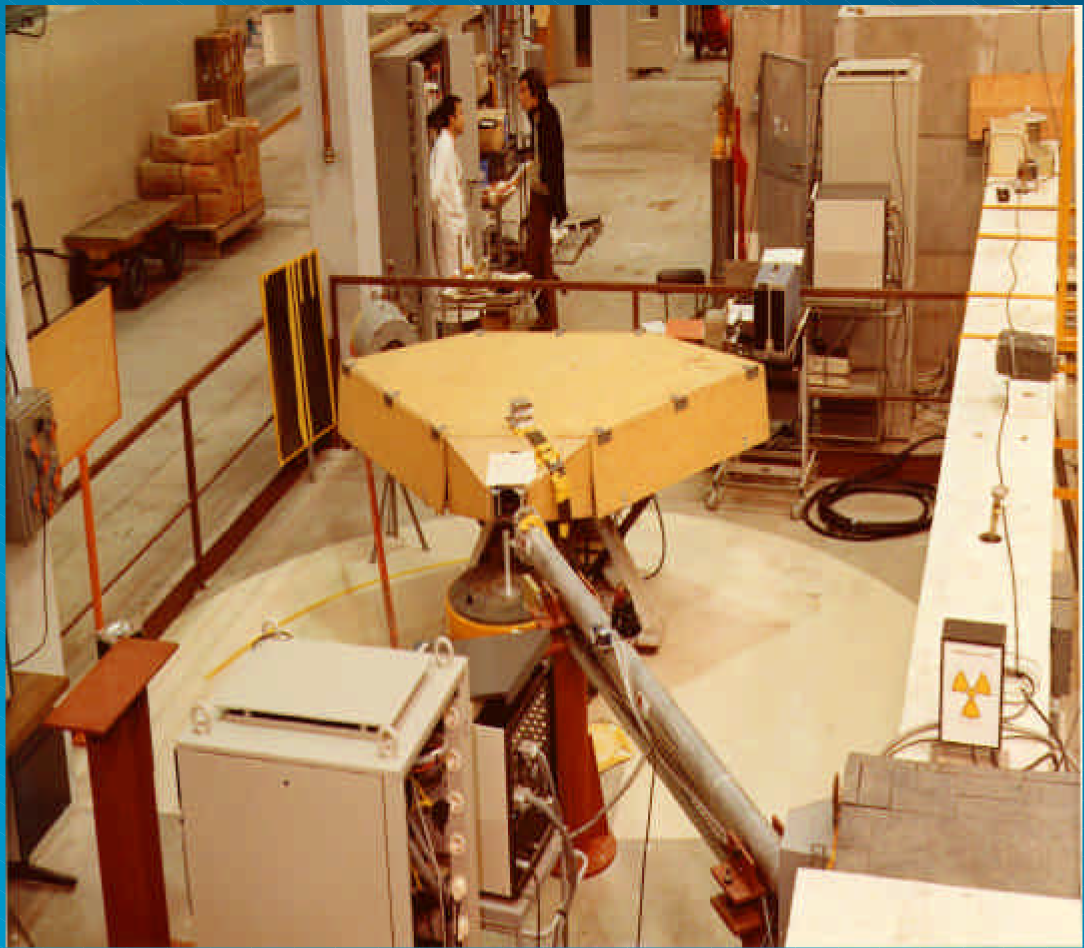
- Small soller collimator
- Single detector
- Shared monochromator
- -High Resolution, BUT
  -Very Low Intensity

ILL Grenoble

Alan Hewat

Early Days at ILL Grenoble (1973)

First PSD (Position Sensitive Detector) D1b



- Very Fast machine (Faster than X-rays)
- Rather Low Resolution
- Limited d-spacing range

Second Generation Machines (1984)

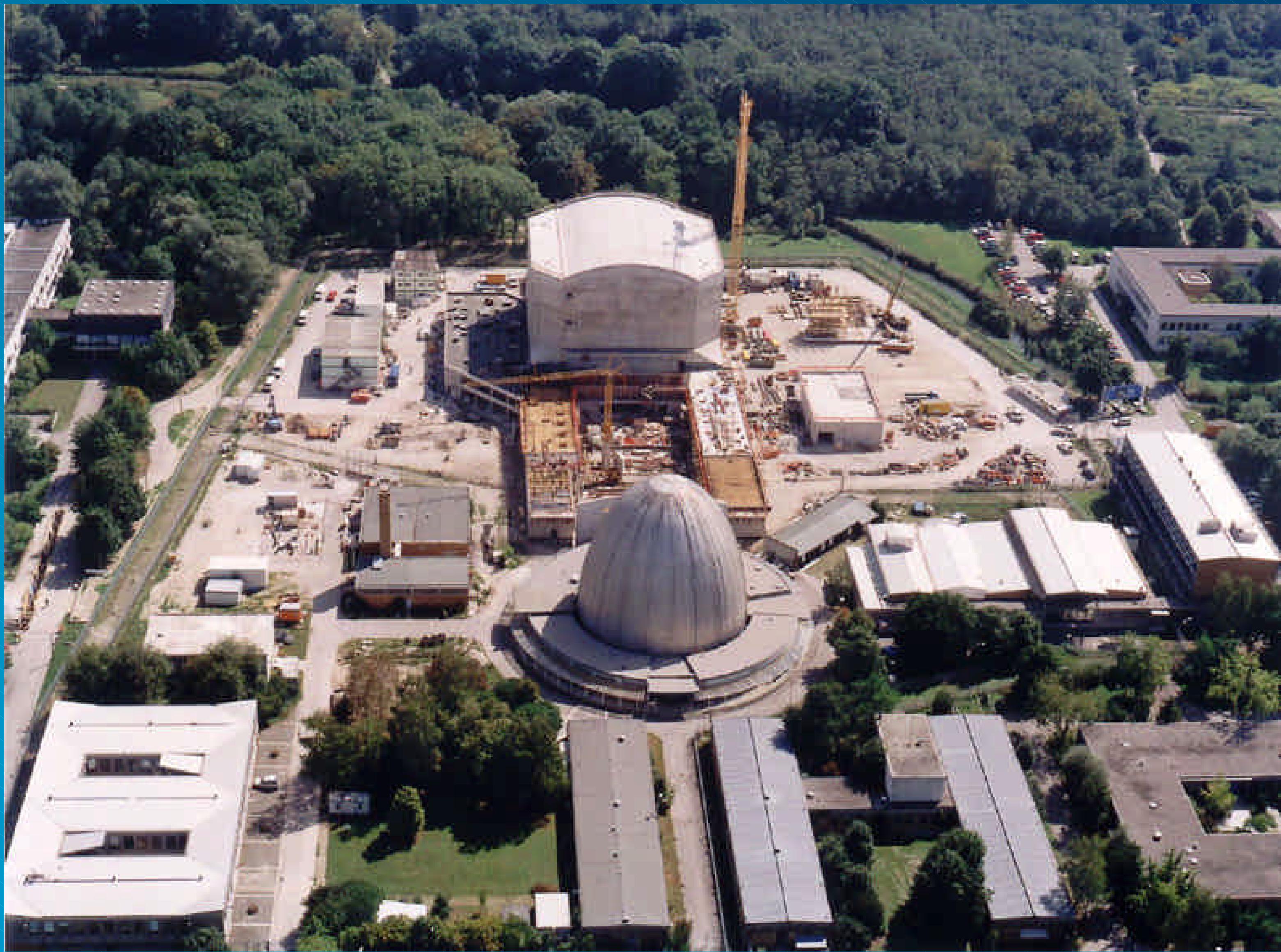
High Resolution with Very Large Detector bank (D2B)

Alan Hewat

- 64 High Resolution Plastic Foil Collimators
- Large Composite Focussing Monochromator
- High Resolution
- Good Intensity

New Munich Reactor FRM-II

September 1999



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New Munich Reactor FRM-II
Planned Instruments

ILL Grenoble

Alan Hewat

- **Diffractometers**
  - STRESS-SPEC Material Science Diffractometer (W. Reimers) (cf D1A)
  - SPODI High Resolution Powder Diffract. (H. Boysen,H. Fueß, R. Gilles) (cf D2B)
  - Single Crystal Diffractometer with hot neutrons (G. Heger et al) (cf D9)
  - RESI Single Crystal Diffractometer with thermal neutrons (F. Frey) (cf D10)
- **Small Angle Scattering, Reflectometry**
  - Small-Angle Scattering Diffraktometer SANS (B. Ewen et al) (cf D22)
  - REFSANS - Reflectometry and SAS (E. Sackmann et al) (cf D17)
  - Instrument for long wave length neutrons (J. Felber, W. Gläser) (cf D16?)
- **3-Axis**
  - PANDA 3-Axis cold neutrons with polarisation analysis (M. Loewenhaupt et al)
  - PUMA Double focussing 3-Axis with thermal neutrons (G. Eckold et al).

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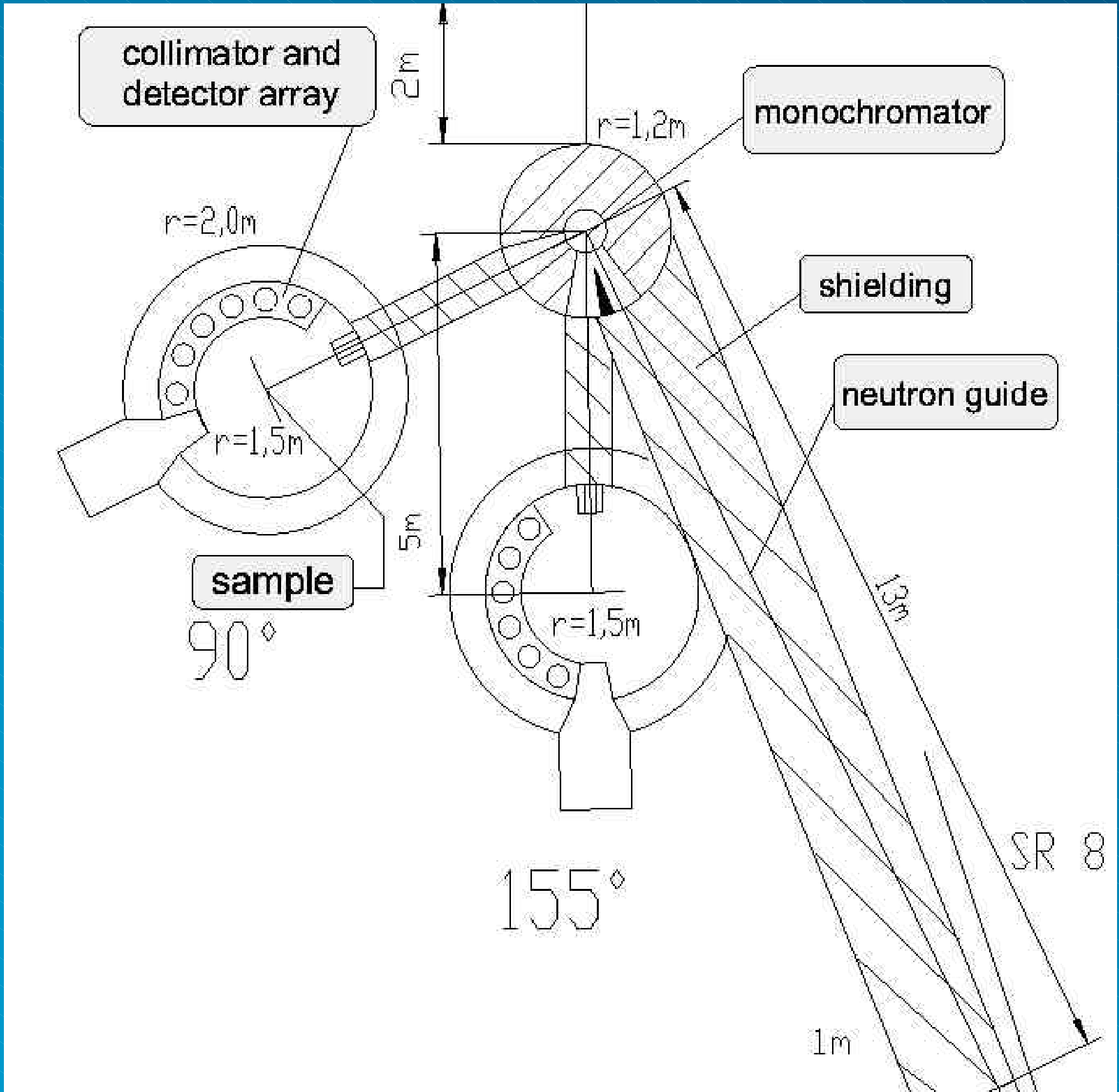
New Munich Reactor FRM-II

SPODI Structure Powder Diffractometer cf super-D2B

Alan Hewat



- **Source distance 14.5m**
  - **Neutron supermirror guide**
- **Monochromator**
  - **Ge [551] vertical focus**
  - **Angle 90^0, 135^0, 155^0**
  - **Mosaic 20'**
- **80 Mylar 10' collimators**
- **80 He3 detectors**
  - **300 cm high**
  - **Linear wire PSD**
- **cf ILL super-D2B project**

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New Munich Reactor FRM-II

Planned Instruments

- **Spectrometers**
  - RESEDA neutron-resonance-spin-echo (NRSE) (R. Gähler et al)
  - High resolution time-of-flight with cold neutrons (W. Petry, et al)
  - Crystal-time-of-flight spectrometer (W. Press et al)
  - BSM Back scattering spectrometer (D. Richter et al)
- **Nuclear and Fundamental Physics**
  - Instrument for fundamental physics with cold neutrons (H. Abele, D. Dubbers)
  - Ultra cold neutron source (option) (S. Paul, D. Dubbers)
  - MAFF Fision fragment accelerator (option) (D. Habs, M. Groß)
  - Physics with fast neutrons (W. Waschkowski)
  - Positron source (W. Triftshäuser et al)
- **Medical applications (neutron therapy)** (M. Molls)

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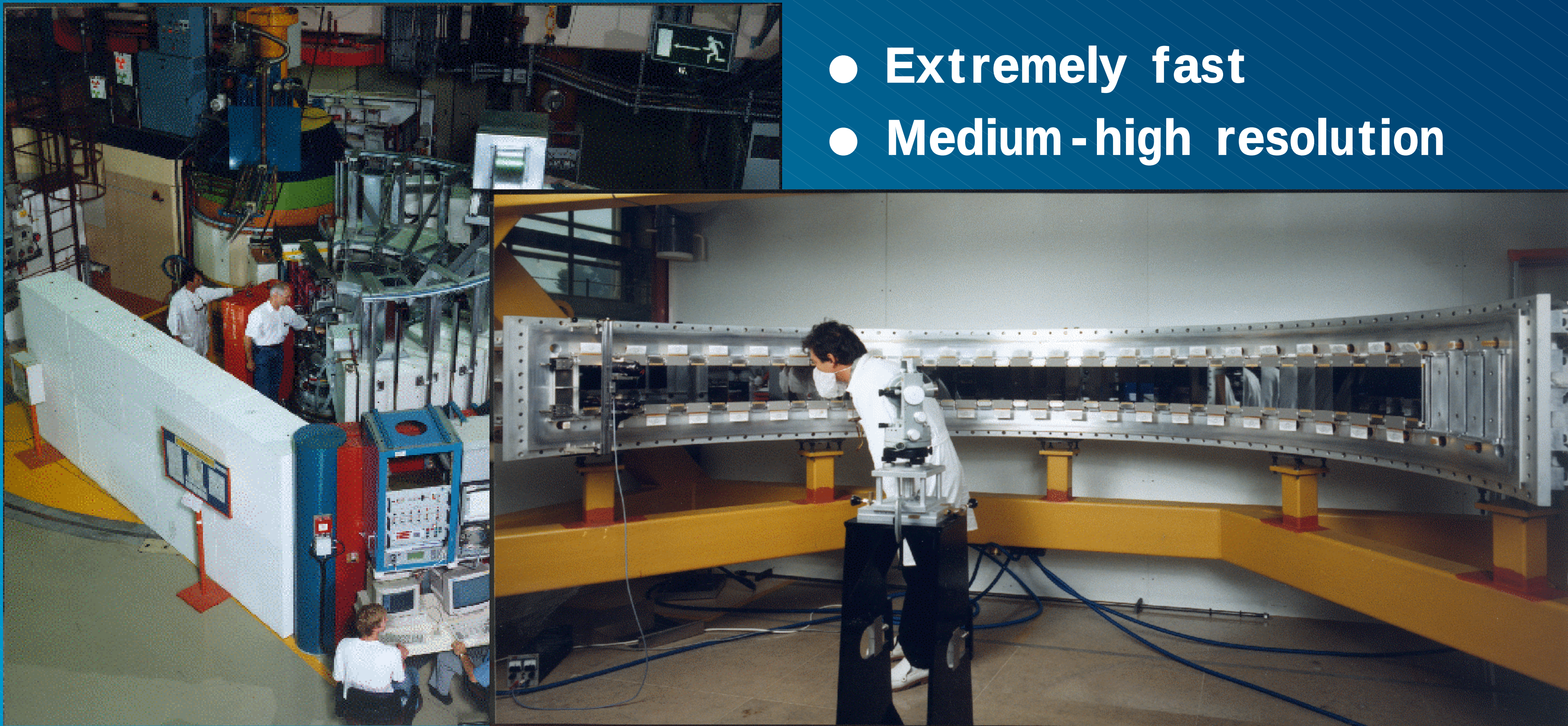
The Future - Big Detectors D20

1st 1600 Element Microstrip Position Sensitive Detector

Alan Hewat



- Extremely fast
- Medium-high resolution

- Proposed by the ILL Science Council in the early 1980's

The Future-Big Detectors super-D2B

Large pseudo-2D PSD (array of linear-wire detectors)

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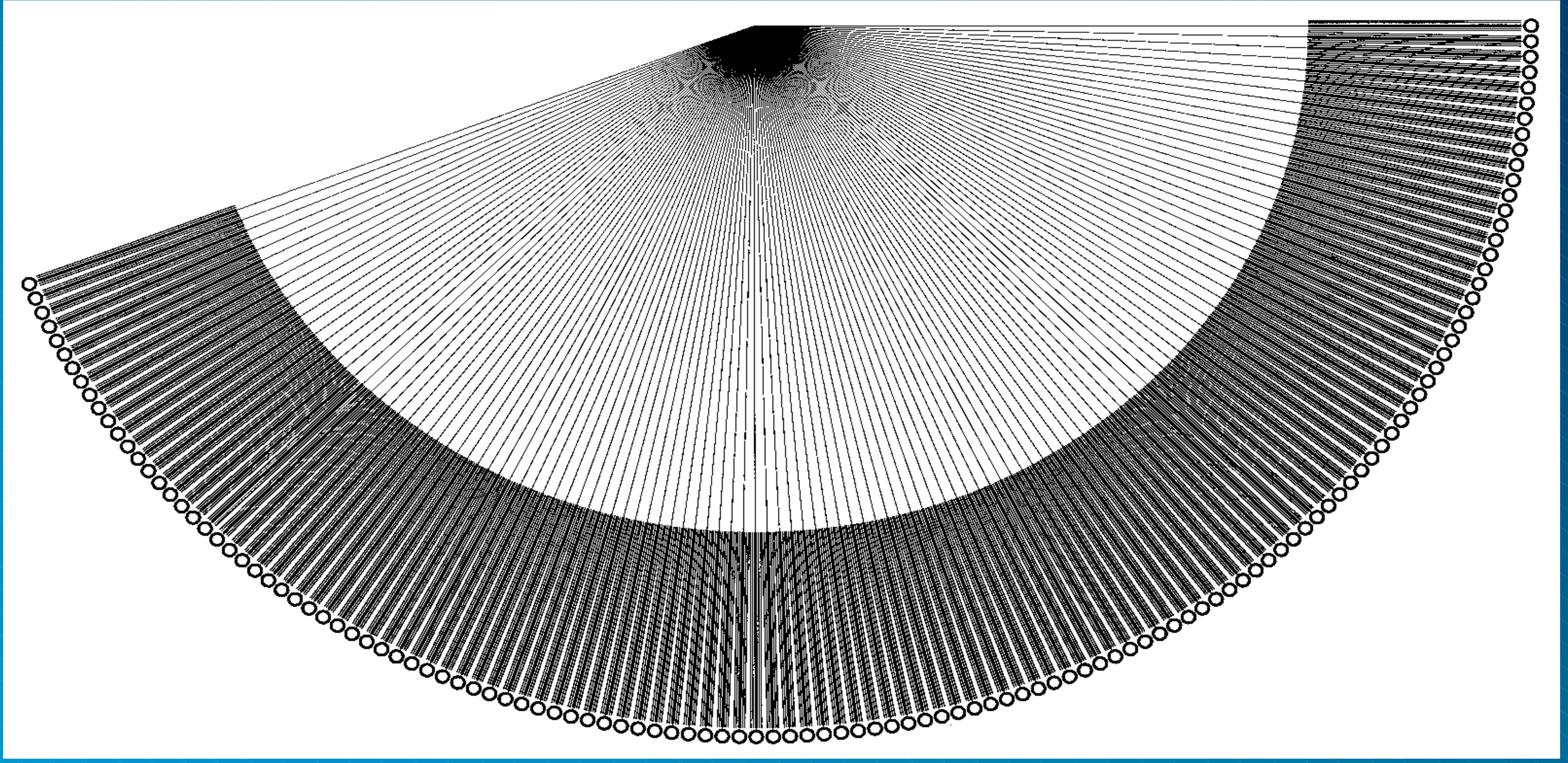

- 2D detector allows both high efficiency & high resolution

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Bigger Detectors - The Future ?

- "Will Higher Flux = more 2nd Rate Science ?" (theoretician)
- "How do we Measure Second Rate Science ?" (experiment.)
  - Number of proposals ?
    - D2B has most proposals: 68/529 in current round
  - Number of publications ?
    - D1B has most publications: ~60/400 per year
  - Number of citations ?
    - ILL powder machines have most: 10 of the top 44 experimental pubs.
- Theoretician's Test of 1st Rate Science – The instrument is *routinely* turning away PRL/Nature/Science quality work
  - Number of PRL's
    - ILL power machines have most PRL's: 10/76 from 1996

ILL Grenoble

Does Structure Matter ?

Alan Hewat, Diffraction Group, ILL.

Alan Hewat

Is it necessary to know the details of crystal and magnetic structures, and if so, why do we need diffractometers on a high flux reactor ?