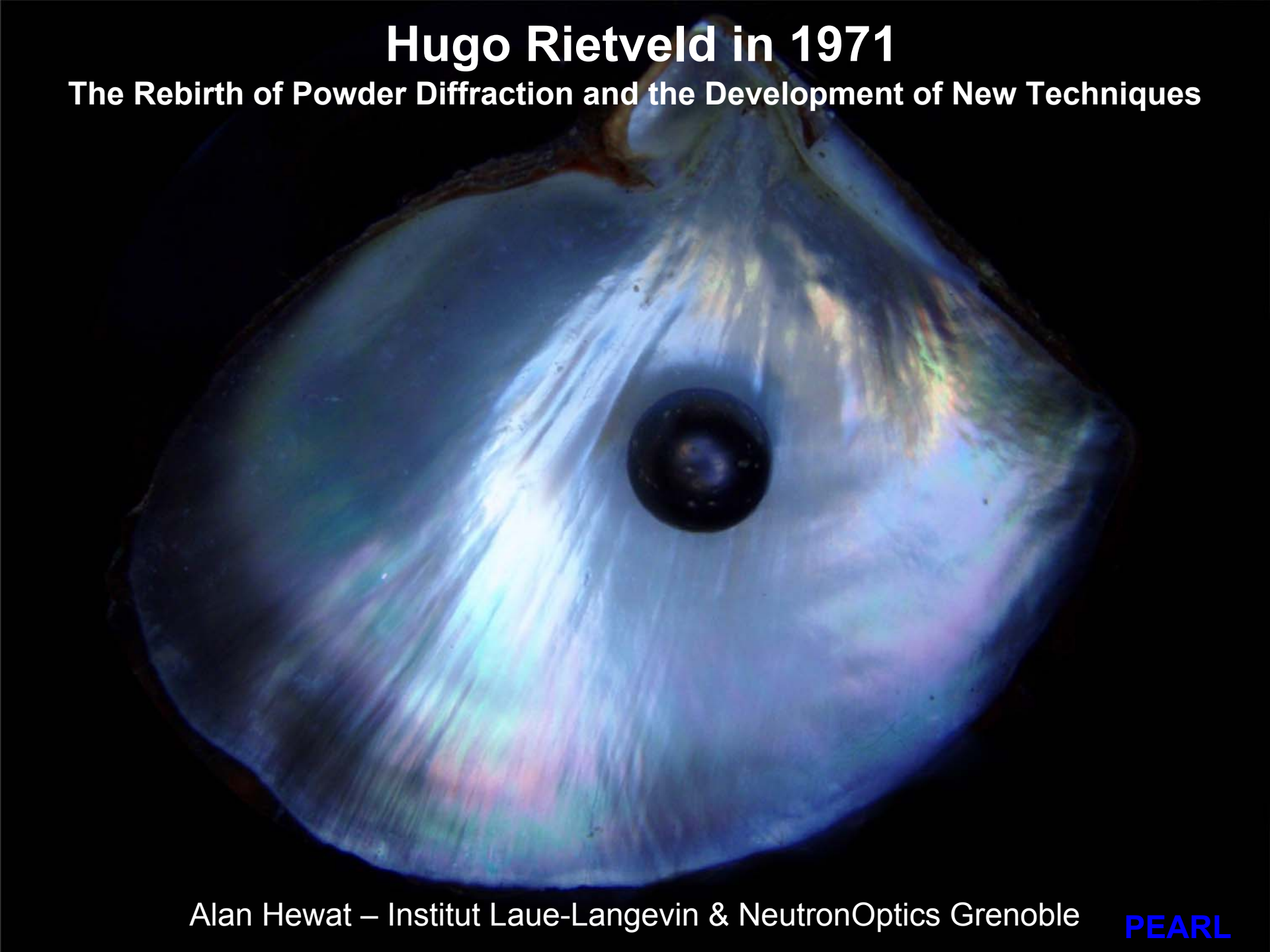
Hugo Rietveld in 1971

The Rebirth of Powder Diffraction and the Development of New Techniques



Alan Hewat – Institut Laue-Langevin & NeutronOptics Grenoble

PEARL

Figure 1. Staff and PhD students of the University of Western Australia in 1979.

HIFAR 1958
High Flux Australian Reactor

Figure 1. Staff and PhD students of the University of Western Australia in 1979.

HIFAR 1958
High Flux Australian Reactor

~3000 km

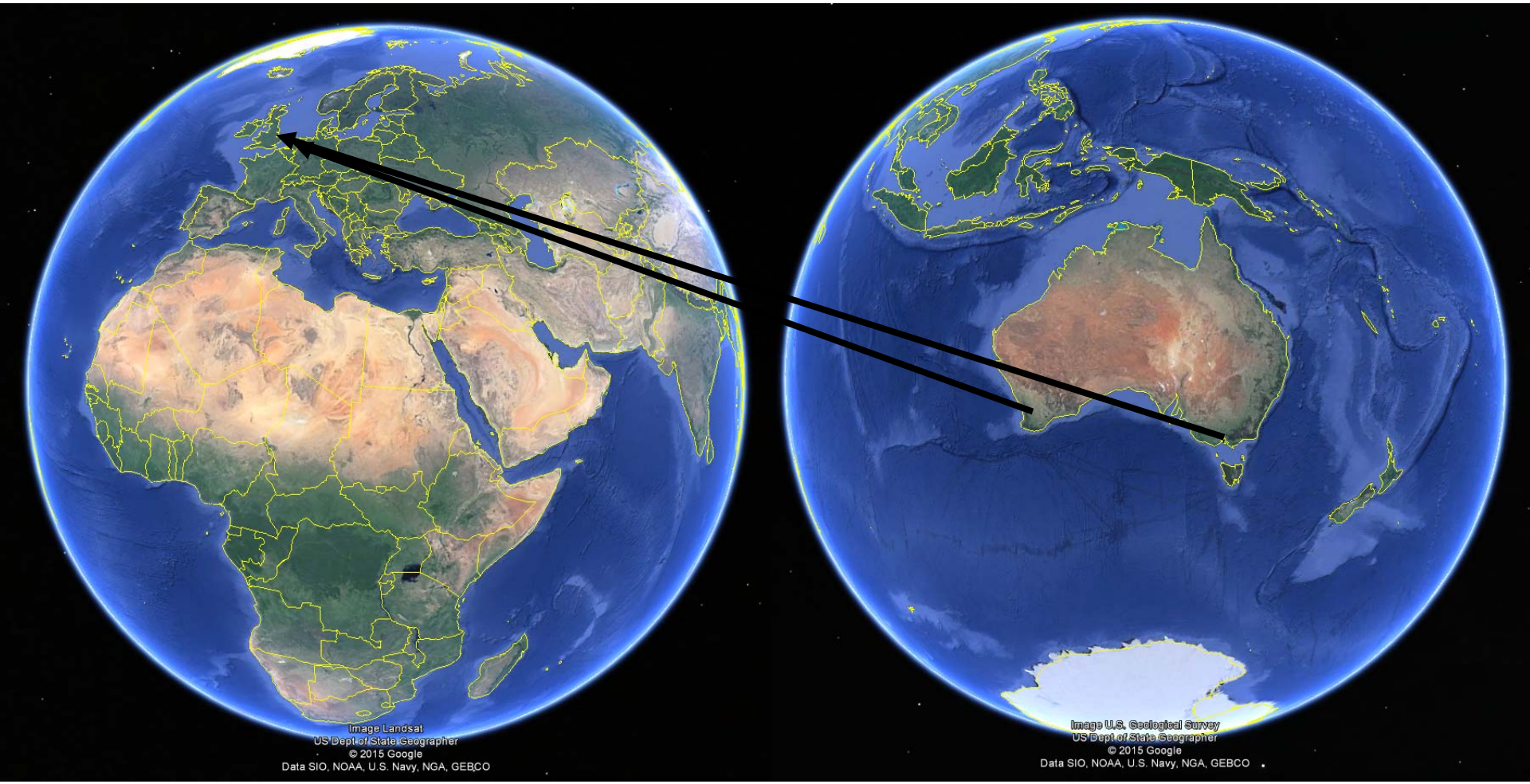
AH
1961

Figure 1. Staff and PhD students of the University of Western Australia in 1979.

~3000 km

AH
1961

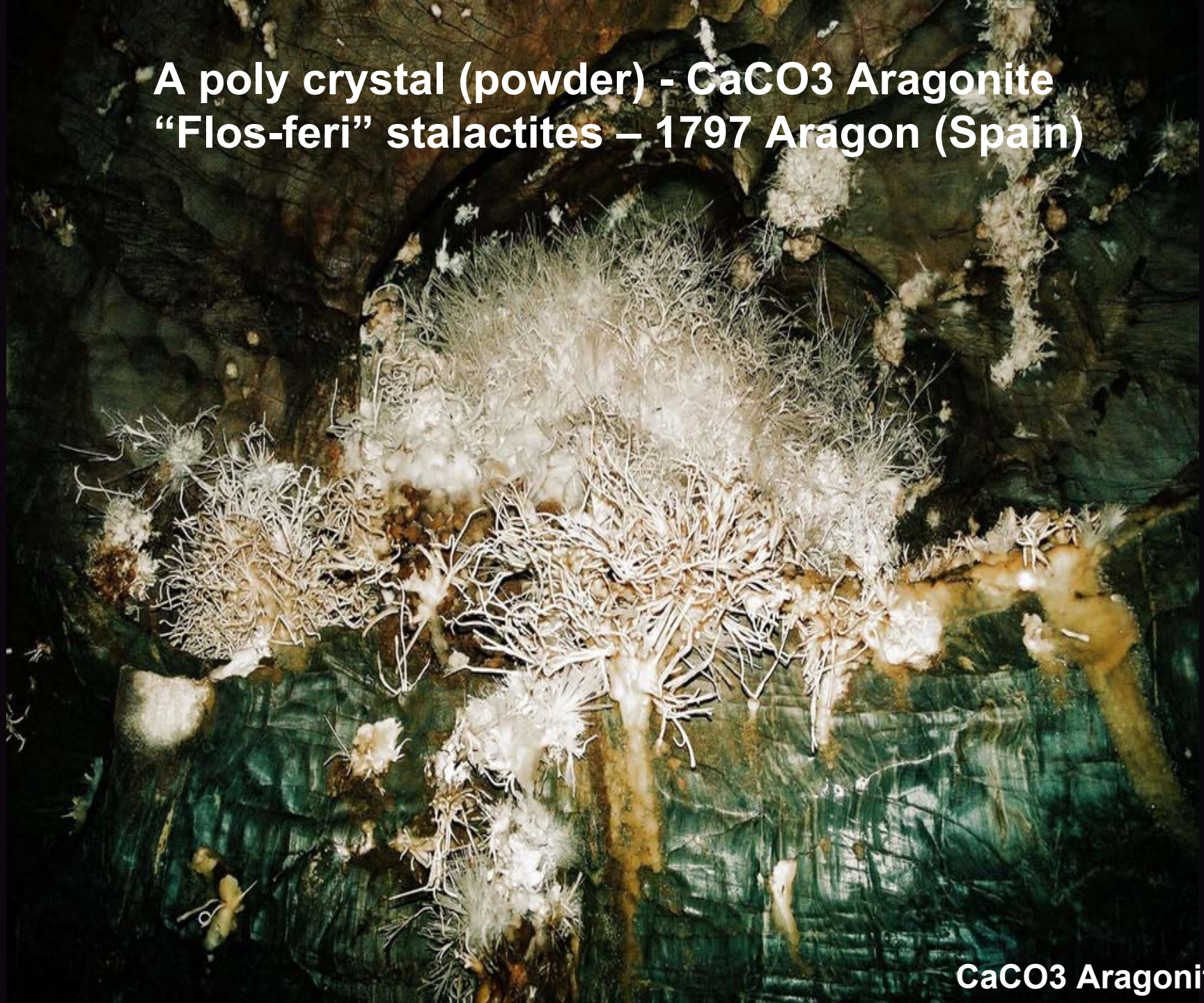
Clews C J B, Maslen E N, Rietveld H M and Sabine T M (1961) Nature 192 154
"X-Ray and Neutron Diffraction Examination of p-Diphenylbenzene (crystals)"
Rietveld H M (1963) PhD Thesis Univ. of Western Australia

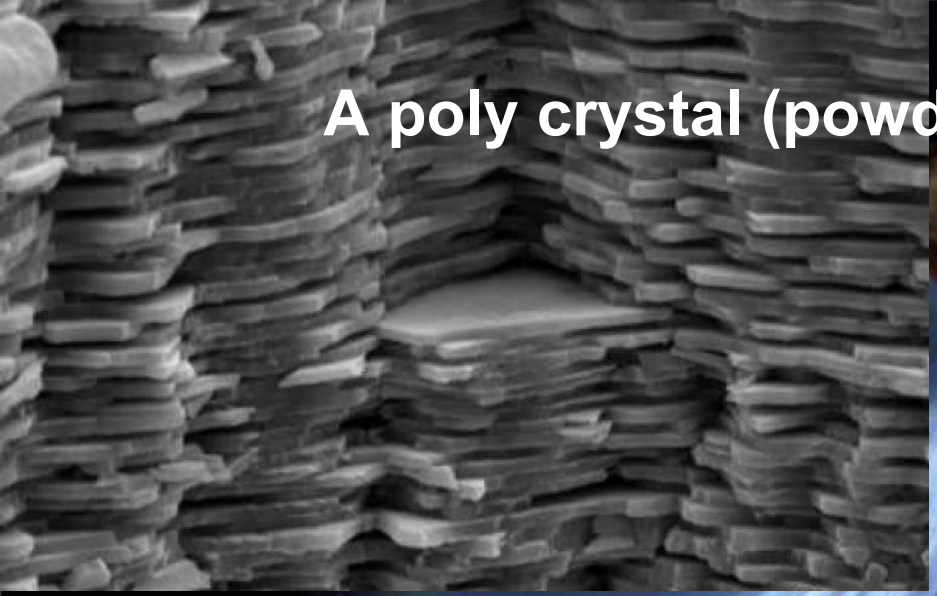


Hewat A W (1970) Solid State Communications, 8, 187
"Lattice Dynamics of ZnO and BeO (single crystals)"
Hewat, A W (1970) PhD Thesis Univ. of Melbourne, Australia

A single crystal - $CaCO_3$ Aragonite
cf $CaCO_3$ Calcite

$CaCO_3$ Aragonite


A poly crystal (powder) - CaCO3 Aragonite
“Flos-feri” stalactites – 1797 Aragon (Spain)
CaCO3 Aragonite



A poly crystal (powder) - $CaCO_3$ Aragonite
Pearl & Pearl shell

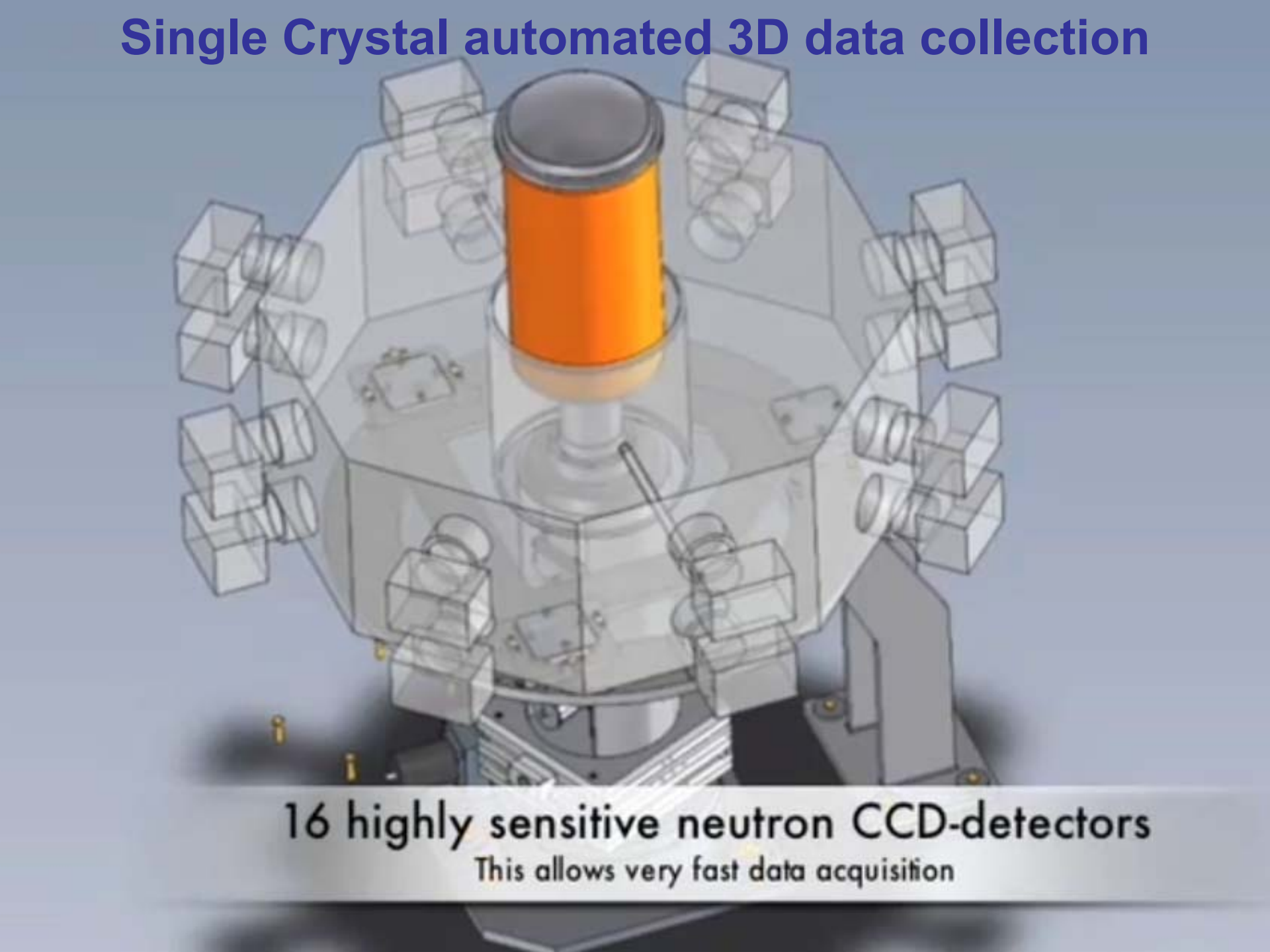
$CaCO_3$ Aragonite

X-rays or Neutrons
Reflected from facets

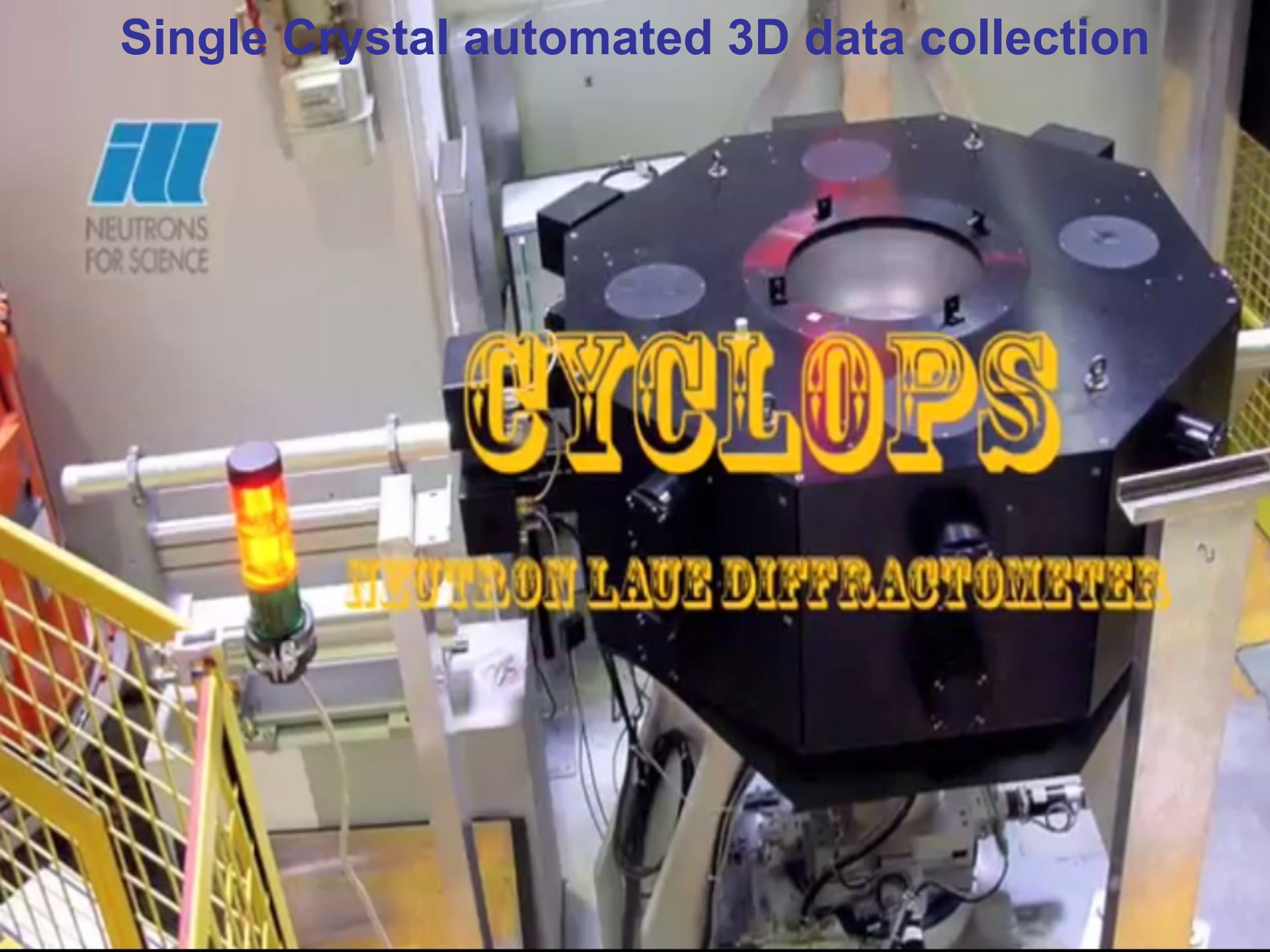
Reflected intensities
give atomic structure

Aragonite $CaCO_3$ Single Crystal

Single Crystal automated 3D data collection



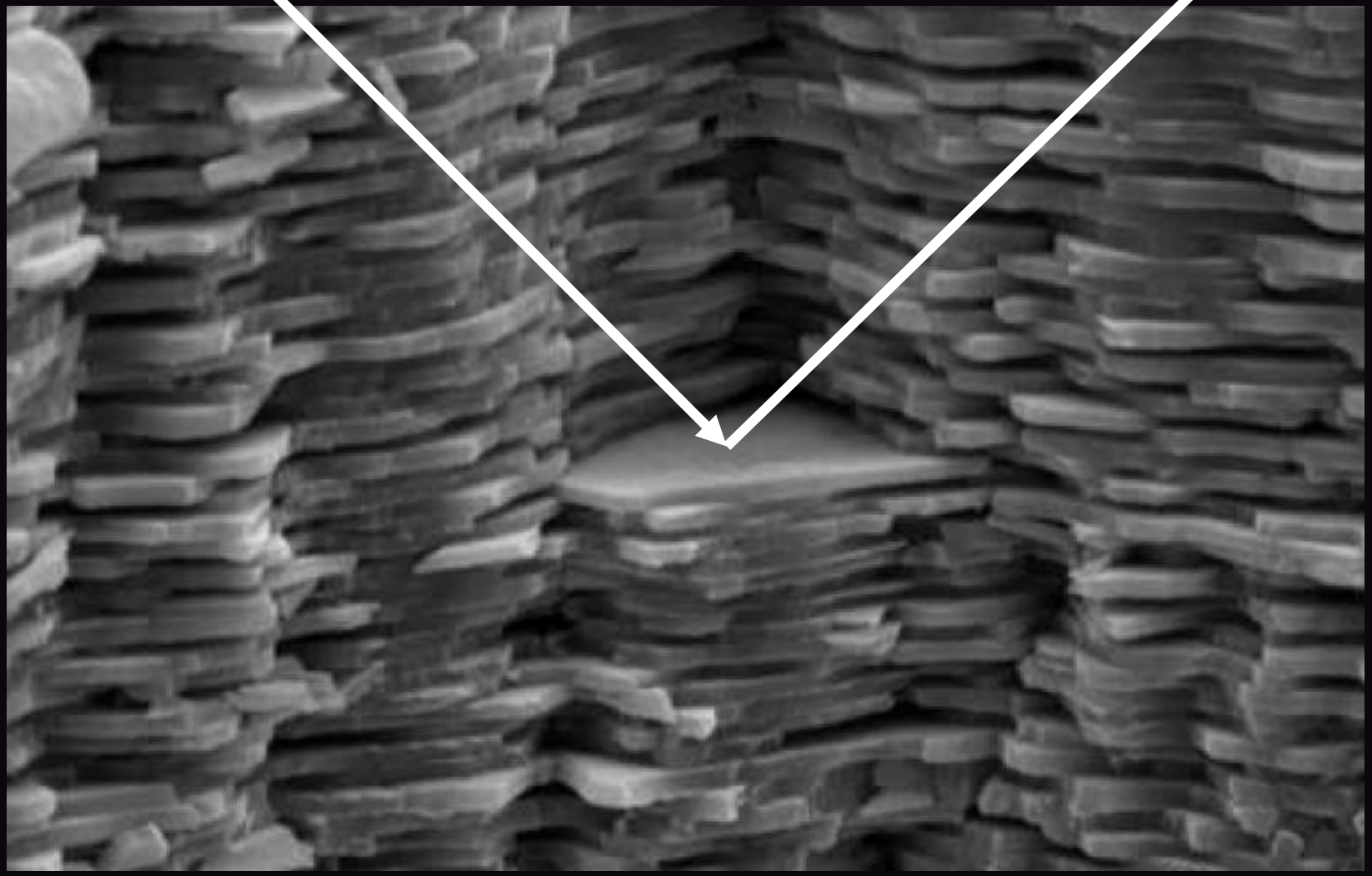
Single Crystal automated 3D data collection



Single Crystal automated 3D data collection

X-rays or Neutrons
Reflected from facets

Reflected intensities
give atomic structure



Aragonite $CaCO_3$ Poly- Crystal

Poly-crystal automated 1D data collection

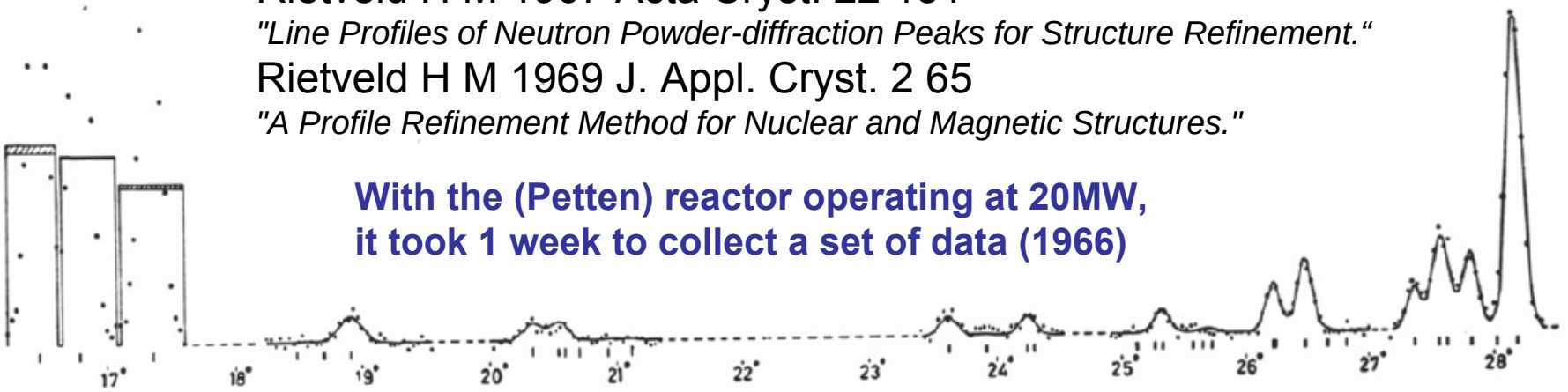
Rietveld H M 1967 Acta Cryst. 22 151

"Line Profiles of Neutron Powder-diffraction Peaks for Structure Refinement."

Rietveld H M 1969 J. Appl. Cryst. 2 65

"A Profile Refinement Method for Nuclear and Magnetic Structures."

With the (Petten) reactor operating at 20MW, it took 1 week to collect a set of data (1966)



Integrate intensities of isolated peaks

Fit overlapping peaks to crystal structure

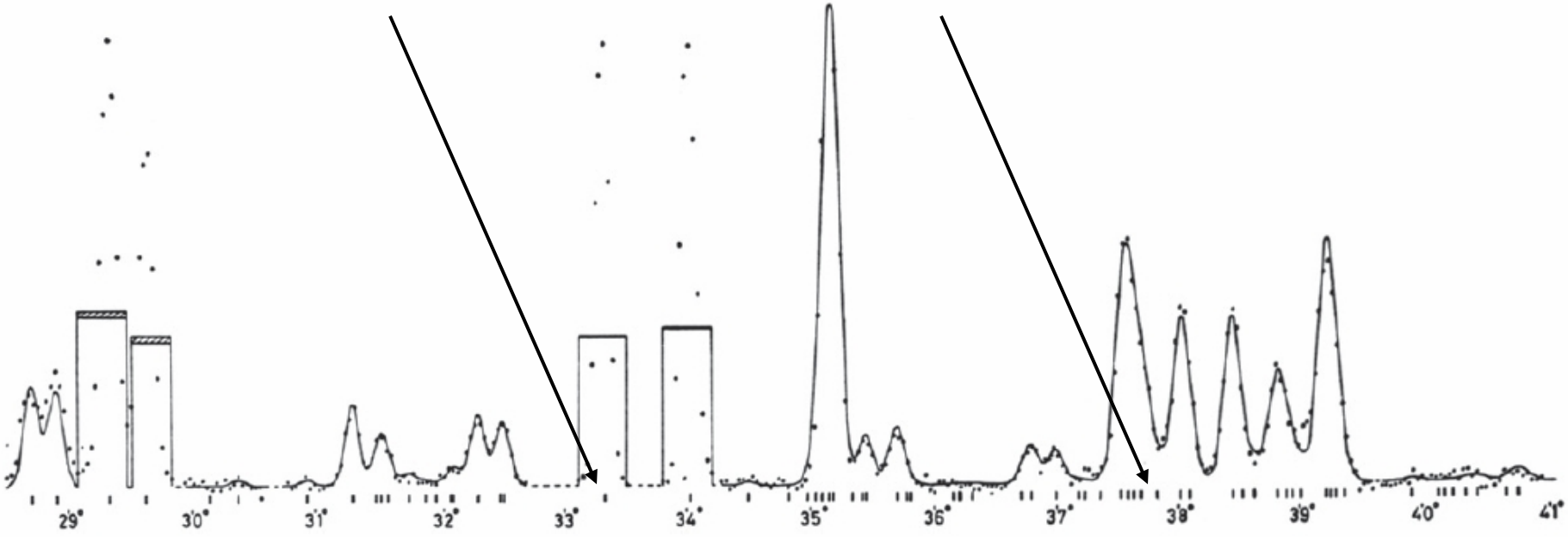


Figure 7. Neutron Powder diagram of WO(3).

The Crystal Structure of Potassium Hydrogeniodate (V), $KIO_3.HIO_3$

G. KEMPER AND AAFJE VOS

Laboratorium voor Structuurchemie, Universiteit Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands

AND

H. M. RIETVELD

Reactor Centrum Nederland, Petten (N.H.), The Netherlands

***Canadian Journal of Chemistry*, 1972, 50(8): 1134**

1972 Combination of x-ray single crystal and neutron powder data

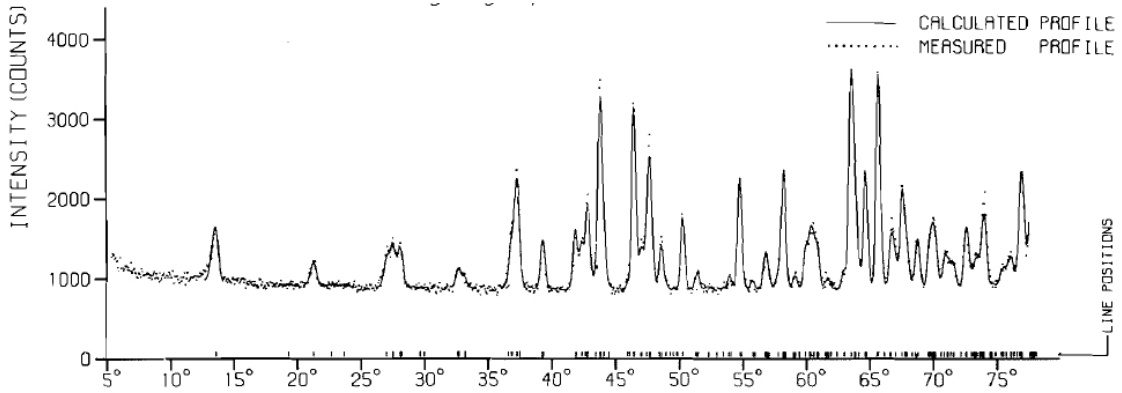
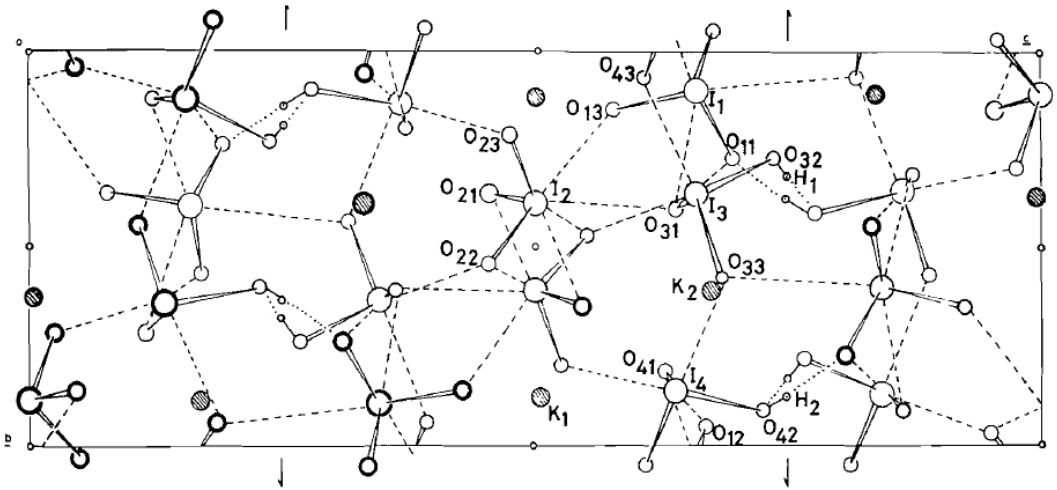


FIG. 1. Observed and calculated neutron diffraction profiles of $KIO_3.DIO_3$ at room temperature.



Structural Transitions or Why I met Hugo

Useful material properties often depend on structural instabilities >> phase transitions

Ferroelectricity - spontaneous electric polarization

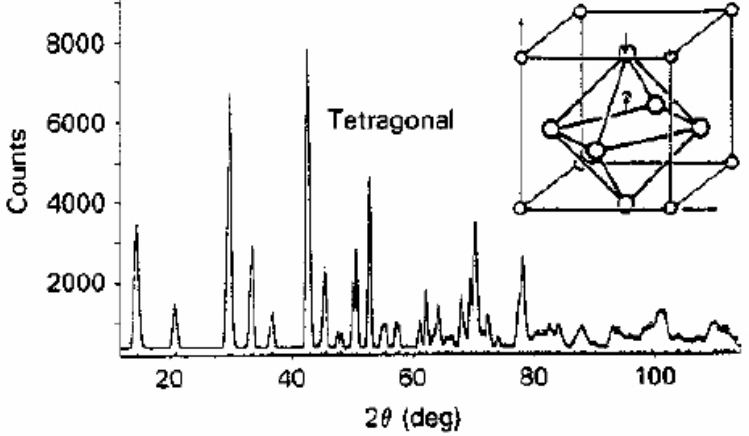
So we need to study not just "the structure"
But how the structure CHANGES (with field, temp...)

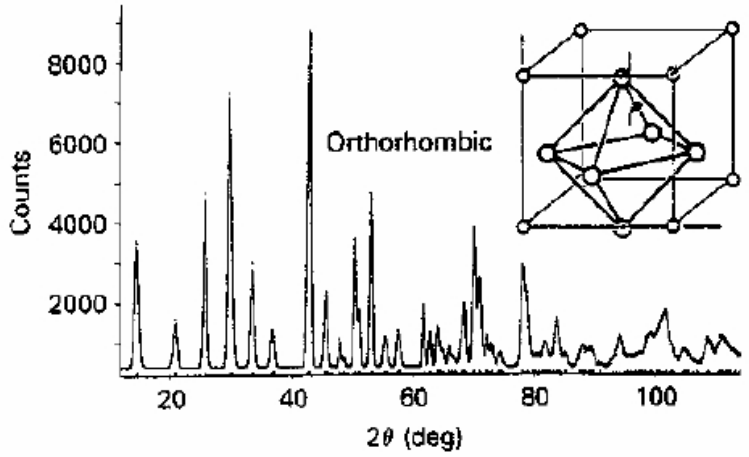
This is DIFFICULT because…
A transition usually breaks up the crystal

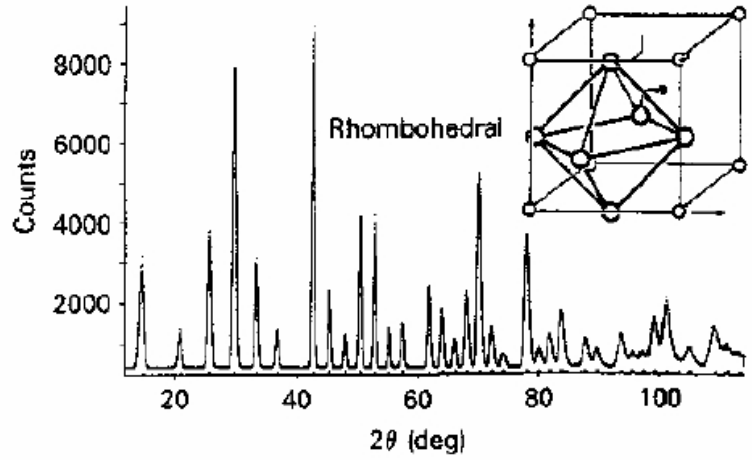
Many examples in magnetism, superconductivity…

Neutron patterns very different for different phases
How to extract information about phase transitions?

George Bacon told me of some chap in Holland…
So in 1971 I visited Hugo Rietveld in Petten.







Structural Transitions

NOT FOR PUBLICATION

AERE-R7350

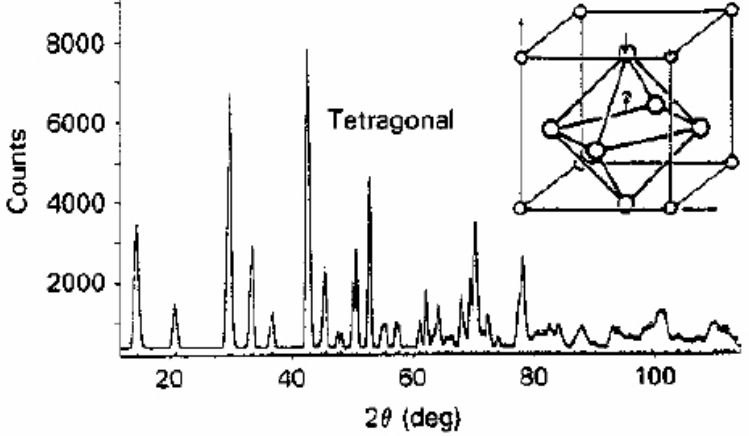
THE RIETVELD COMPUTER PROGRAM FOR THE PROFILE REFINEMENT OF NEUTRON DIFFRACTION POWDER PATTERNS MODIFIED FOR ANISOTROPIC THERMAL VIBRATIONS

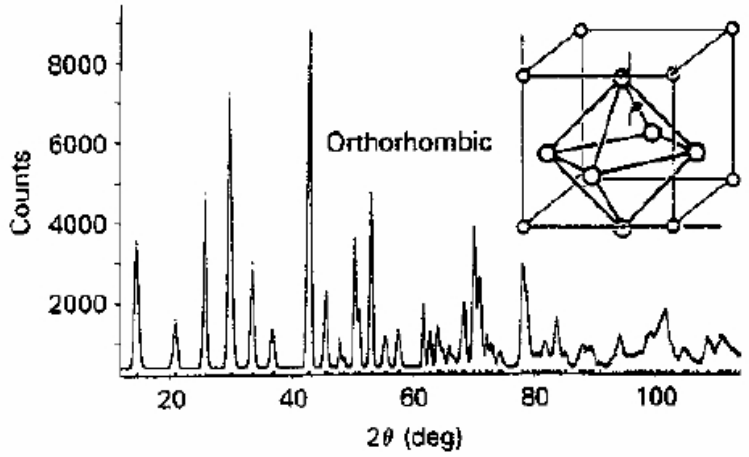
by

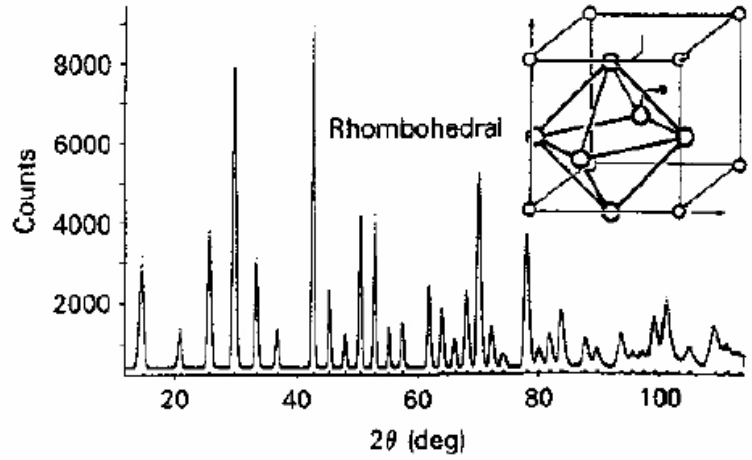
A. W. HEWAT

Materials Physics Division,
UKAEA Research Group,
Atomic Energy Research Establishment,
HARWELL

January 1973.







Cubic-tetragonal-orthorhombic-rhombohedral ferroelectric transitions in perovskite potassium niobate: neutron powder profile refinement of the structures

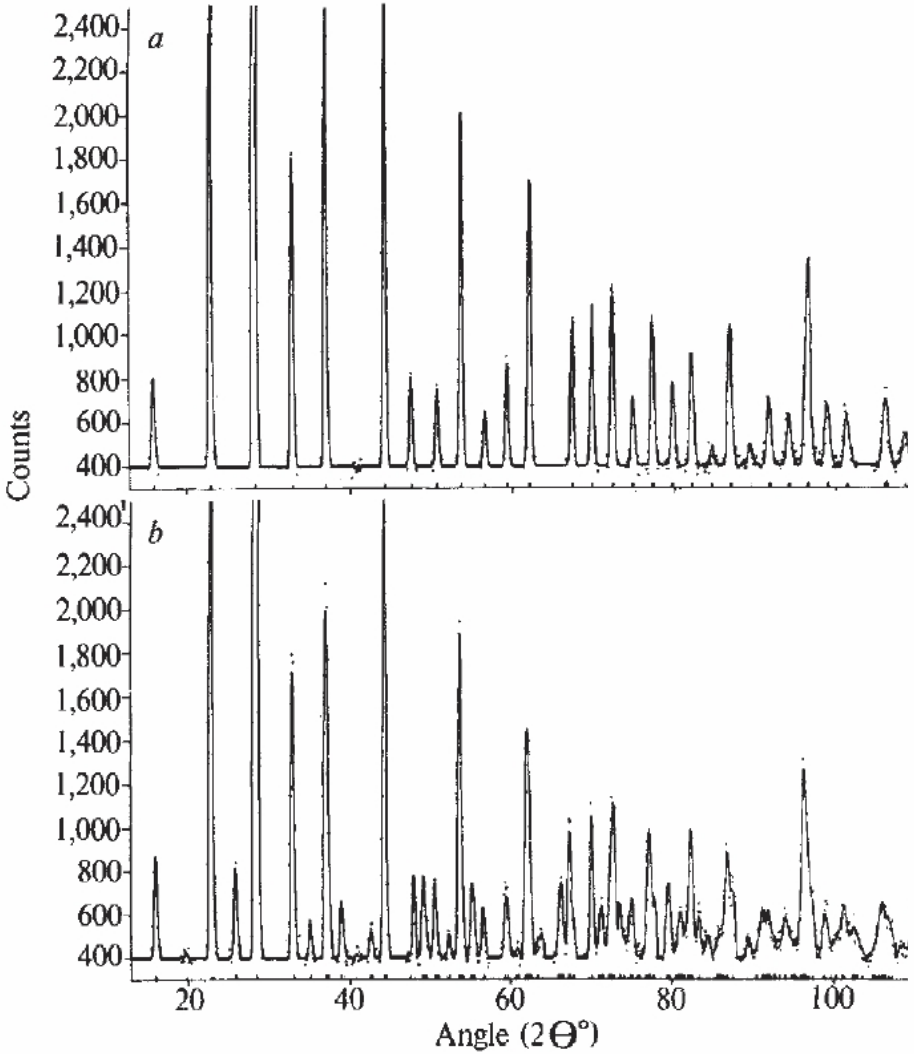
A W Hewat 1973 *J. Phys. C: Solid State Phys.* **6** 2559

Rietveld Refinement & Structural Transitions

Hewat A W 1973 Nature 246,90

"Location of Hydrogen Atoms in ADP by Neutron Powder Profile Refinement."

1973 Neutron powder data alone



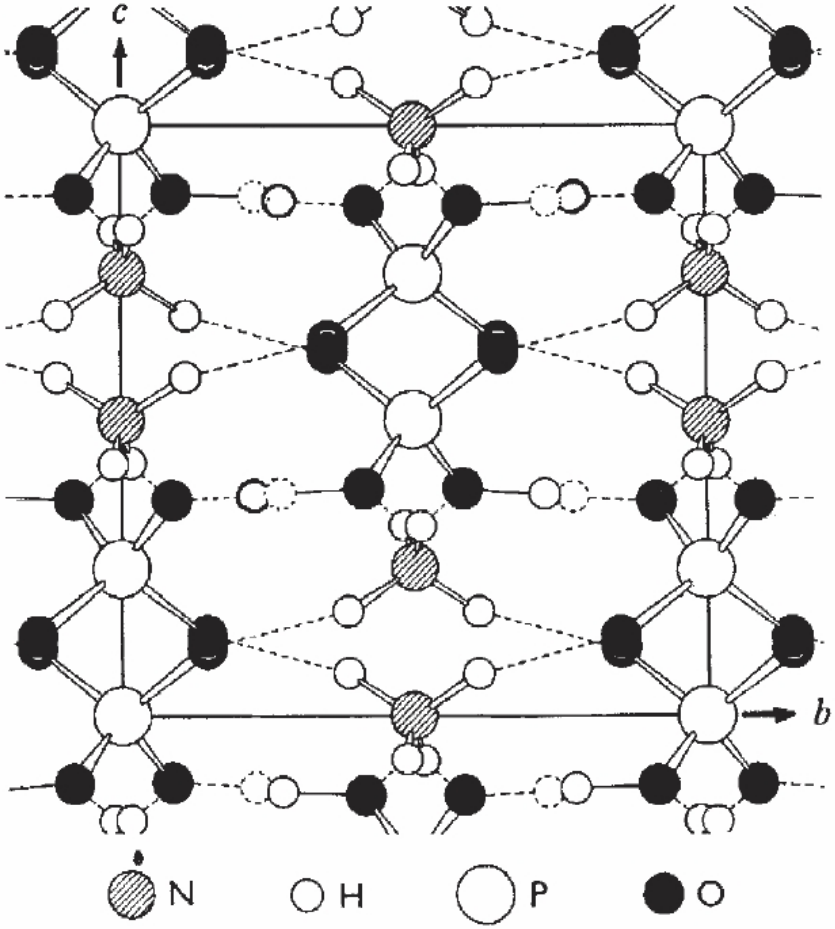


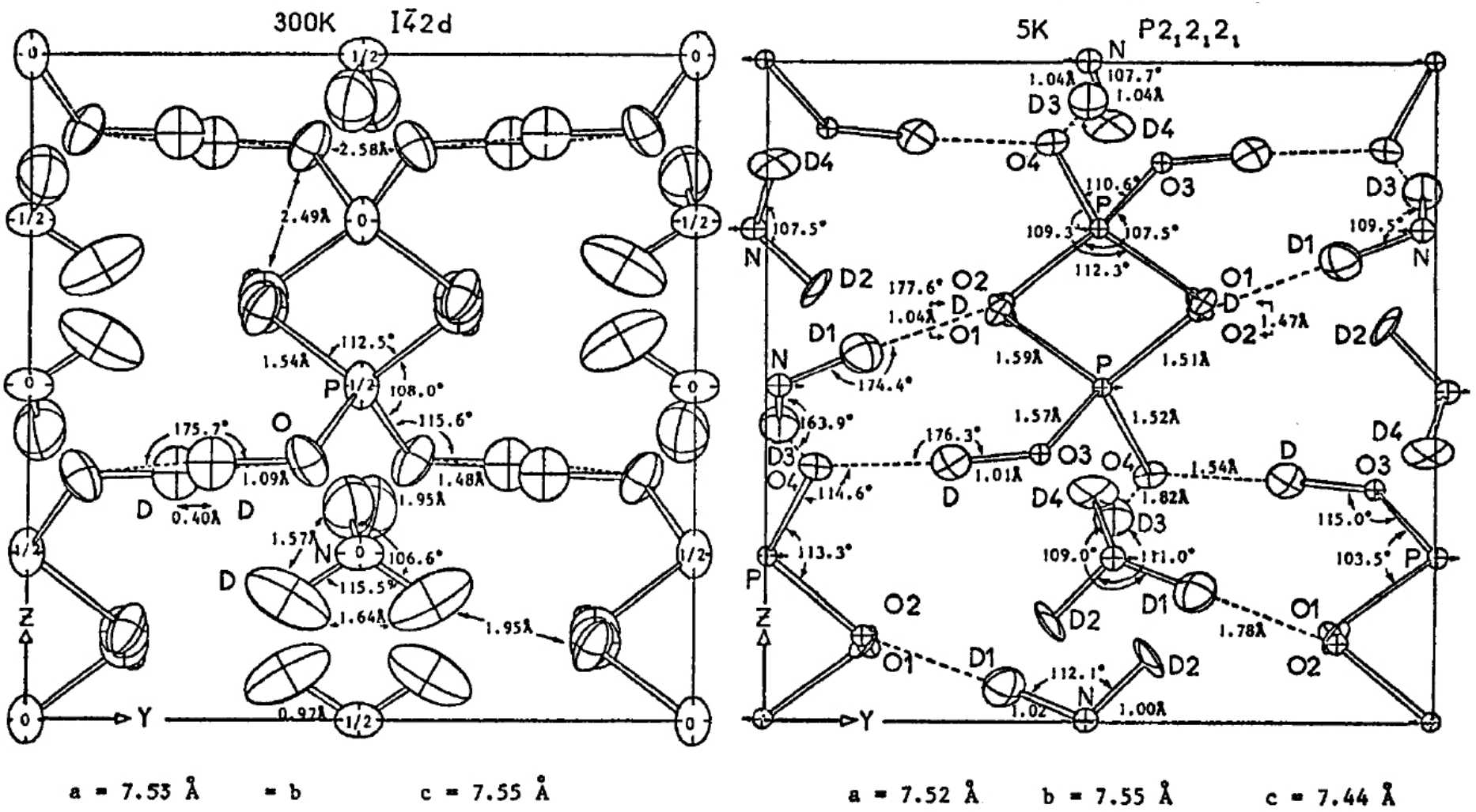
Fig. 1 The [100] projection of the $NH_4H_2PO_4$ structure showing the two positions between which the hydrogen atom linking PO_4 groups can tunnel (after Tenzer *et al.*[4]).

Rietveld Refinement & Structural Transitions

Hewat A W 1973 Nature 246,90

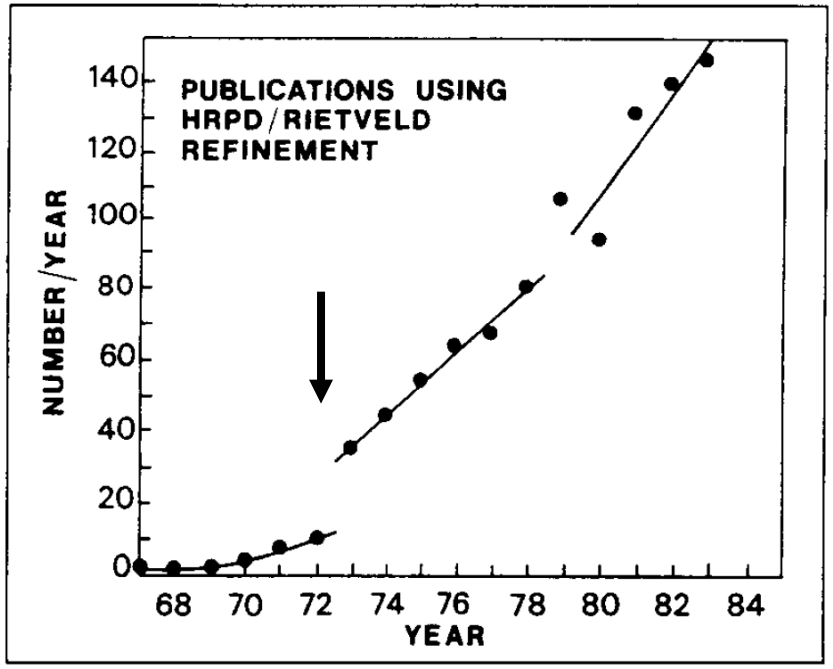
"Location of Hydrogen Atoms in ADP by Neutron Powder Profile Refinement."

1973 Neutron powder data alone



Exponential Growth of Use of the Rietveld Method

1986 A W Hewat Mat.Sci.Forum 9, 69



Number of publications using high resolution powder diffraction or Rietveld refinement showing rapid increases with the dissemination of the techniques and the construction of new diffractometers.

2014 H M Rietveld Phys. Scr. 89

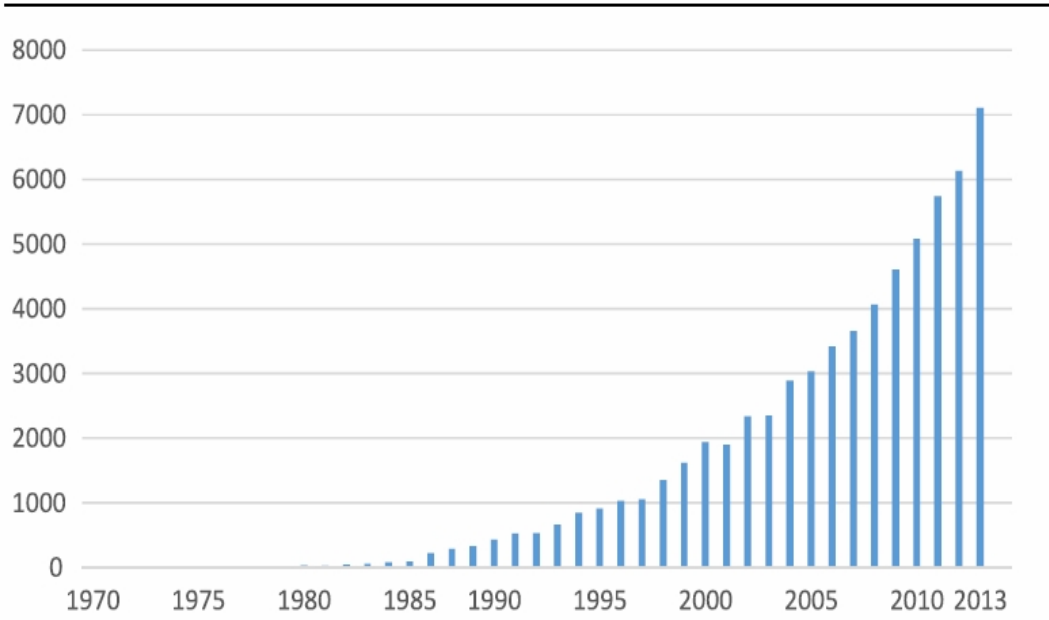


Figure 8. The number of publications per year citing the Rietveld Method according to Google Scholar.

Not just publications - Highly cited publications On New Materials

Lithium insertion into manganese spinels

MM Thackeray, **WIF David**, PG Bruce… - Materials Research …, 1983 - Elsevier
Abstract Lithium has been inserted chemically and electrochemically into Mn 3 O 4 and Li [Mn 2] O 4 at room temperature. From X-ray diffraction, it is shown that the [Mn 2] O 4 subarray of the A [B 2] X 4 spinels remains unperturbed and that the electrons **...**
Cited by 1179 ←

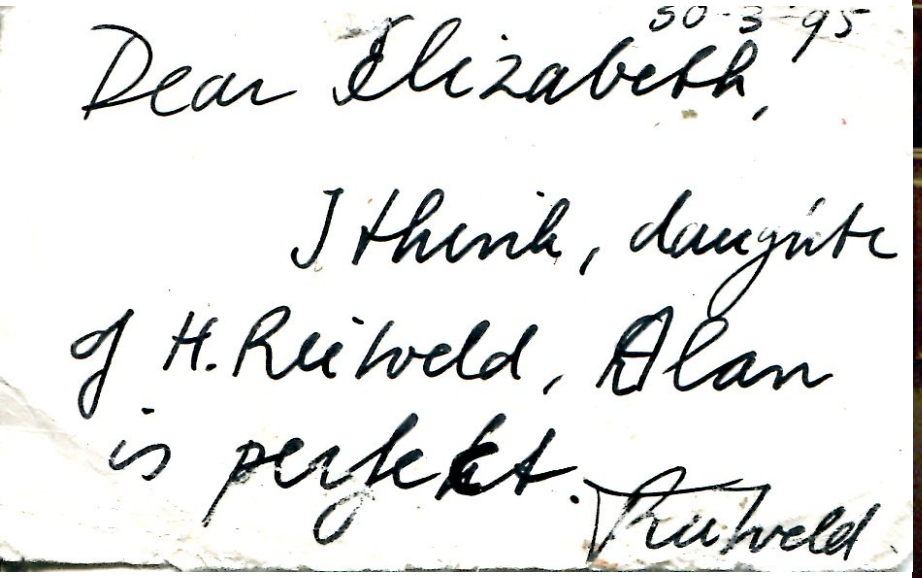
Oxygen ordering and the orthorhombic-to-tetragonal phase transition in YBa2Cu3O7−x

JD Jorgensen, MA Beno, DG Hinks, L Soderholm… - Physical Review B, 1987 - APS
Abstract In situ neutron powder diffraction measurements show that the orthorhombic-to-tetragonal phase transition in Y Ba 2 Cu 3 O 7− x, which occurs near 700 C in a pure oxygen atmosphere, is an order-disorder transition in which the disordering of oxygen atoms into **...**
Cited by 1195 ←

Structural anomalies, oxygen ordering & superconductivity in oxygen deficient Ba2YCu3Ox

RJ Cava, **AW Hewat**, EA Hewat, B Batlogg… - Physica C: …, 1990 - Elsevier
Abstract We report the characterization of series of oxygen deficient Ba 2 YCu 3 O x samples for 7≥ x≥ 6 prepared by Zr gettered annealing at 440 C. Measurements include complete crystal structure analysis at 5 K by powder neutron diffraction, electron microscopy study of **...**
Cited by 1153 ←

1995 Aminoff Prize To Hugo Rietveld



1995 Aminoff Prize To Hugo Rietveld

Not just Rietveld Refinement – Efficient Instruments

With the reactor operating at 20 MW thermal power, it took one week to collect a set of data.

H. M. RIETVELD (1966) Acta Cryst. (1966). 20, 508

The Delft reactor operates at only 2 MW thermal power - 10 weeks to collect a set of data ?

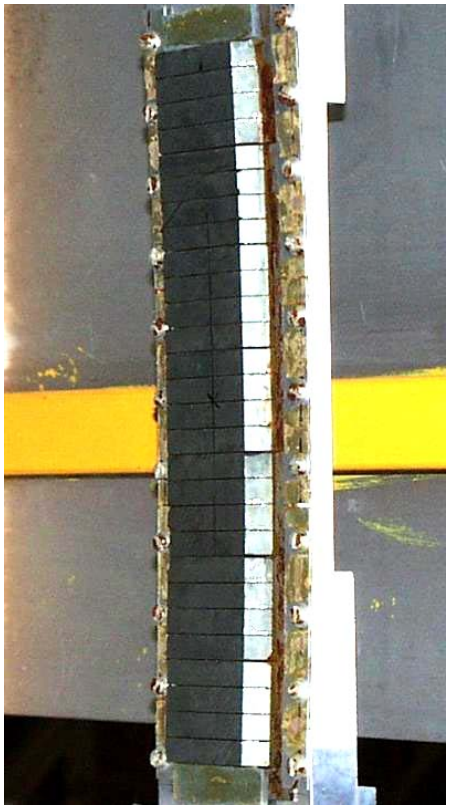
1973 D1A instrument at ILL Grenoble – 1 small detector c.f. instrument at Petten

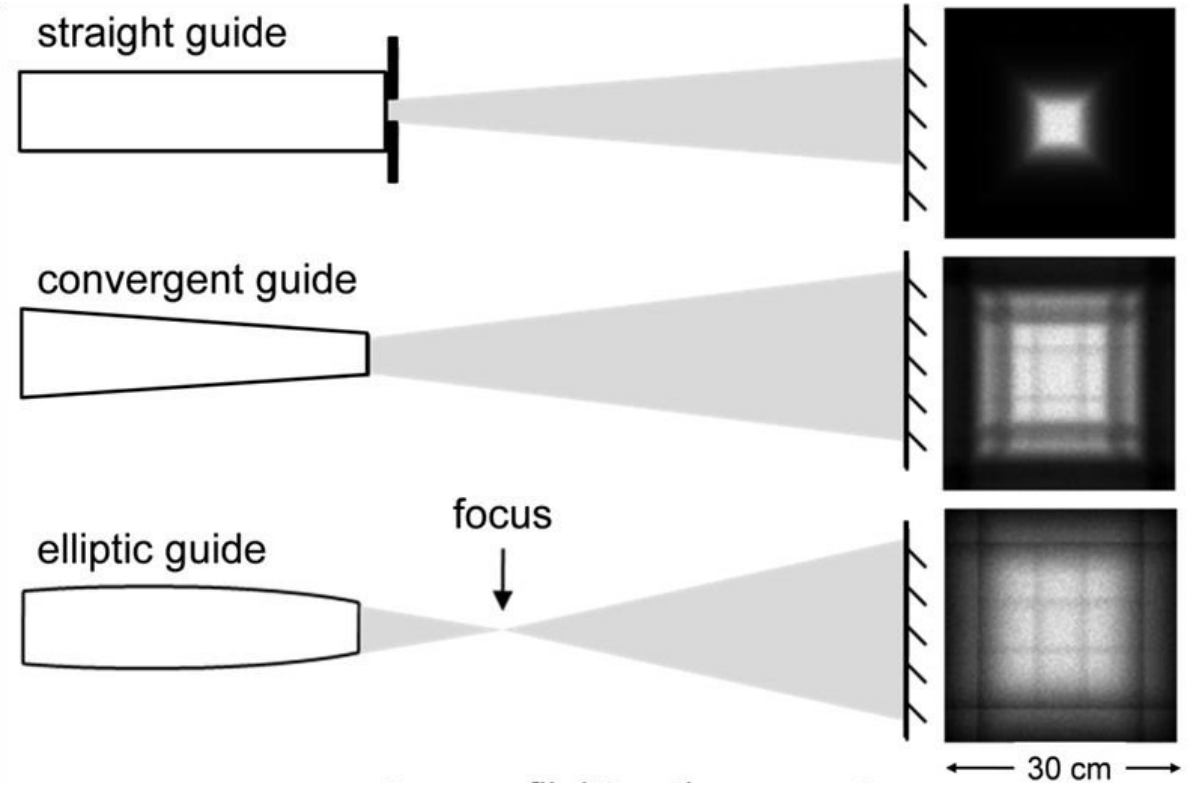
Not just Rietveld Refinement – Efficient Instruments

Efficiency for a given sample & resolution = time averaged flux on sample x detector solid angle

"Scientific opportunities with advanced facilities for neutron scattering"
Jorgensen, J.D., Cox, D.E., Hewat, A.W., Yelon, W.B. (1984)
US Shelter Island Workshop, Nuc. Inst. Methods B12, 525-561

Focussing Monochromators & Focussing Guides increase the neutron flux on the sample





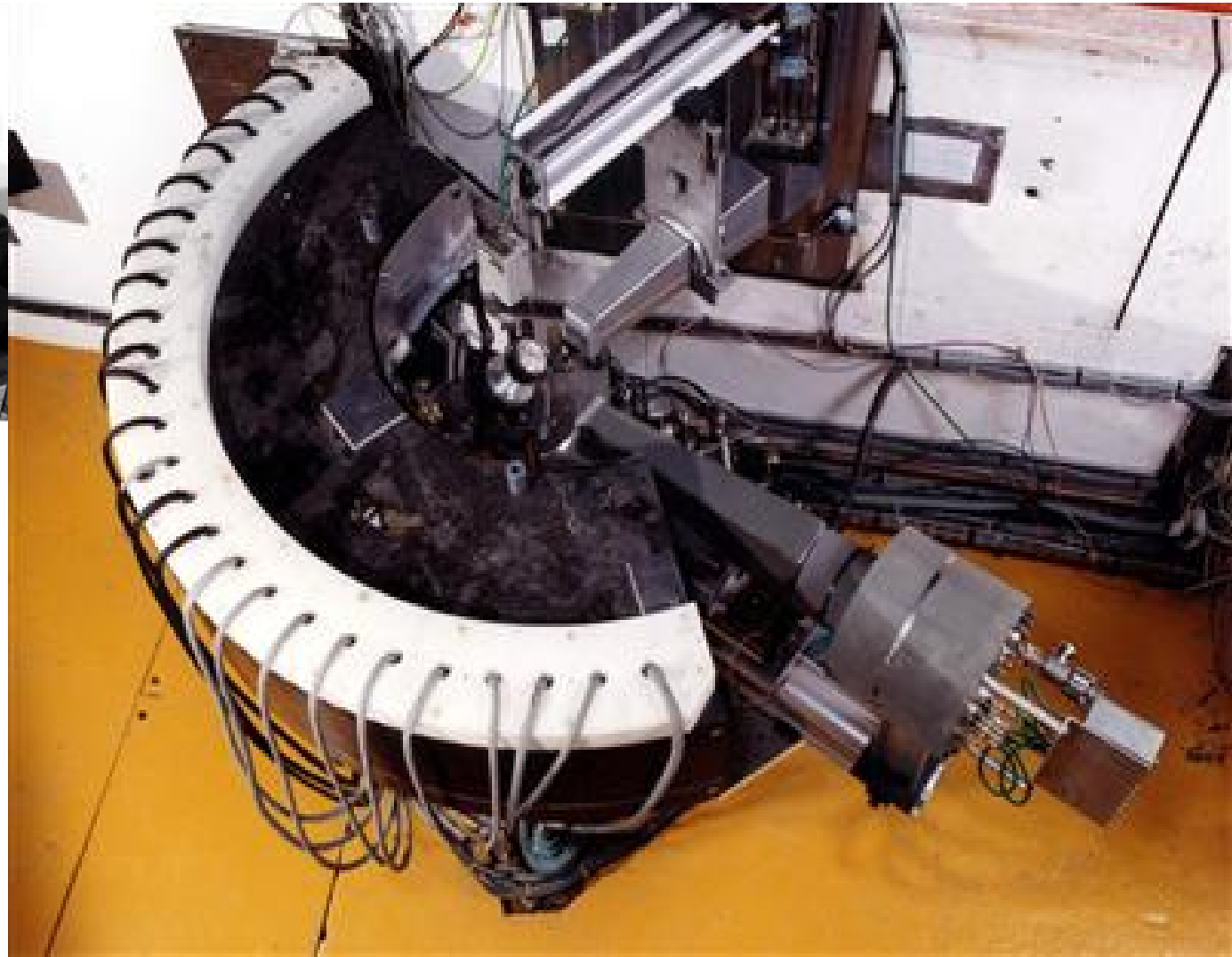
1976 Hewat D1A monochromator **2005 Nikolay Kardjilov, Peter Böni** (Helmholtz-Zentrum Berlin)

Not just Rietveld Refinement – Efficient Instruments

Large area detectors to increase the solid angle

1973 D1a at ILL

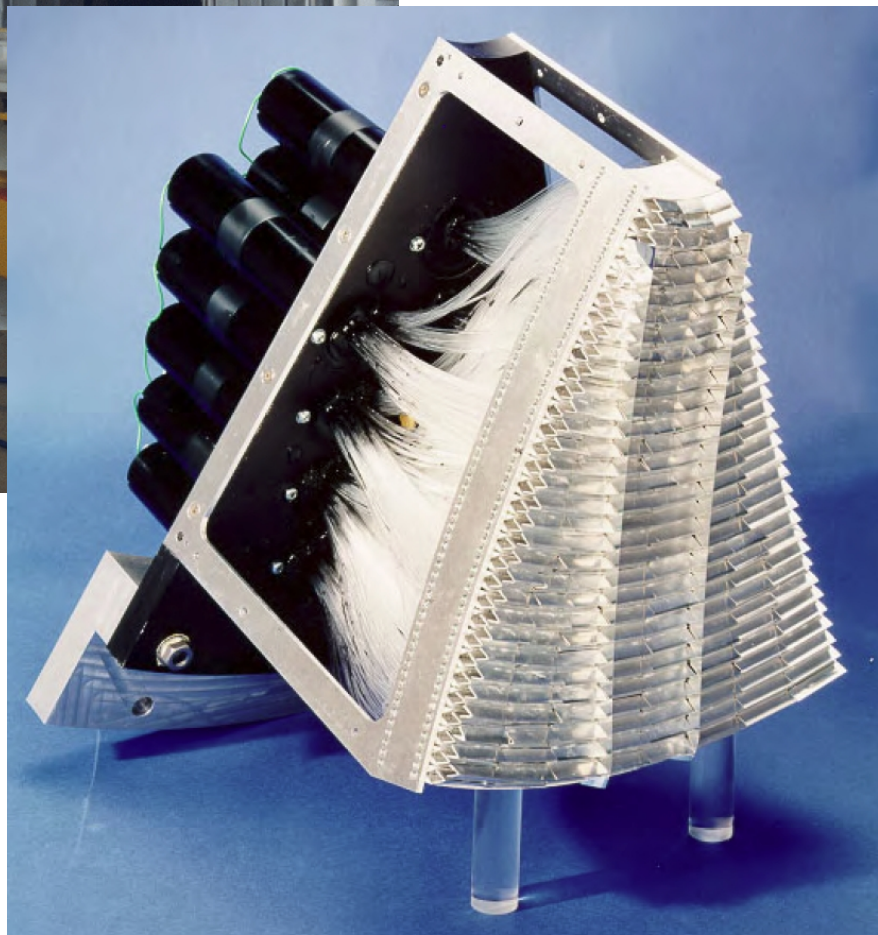
1975-1978 D1a at ILL with large 25-detector bank covering 160°



Not just Rietveld Refinement – Efficient Instruments

Large area detectors to increase the solid angle

1985 D20 He3 PSD at ILL



HRPD scintillator-PM at ISIS
(cf PEARL detector)

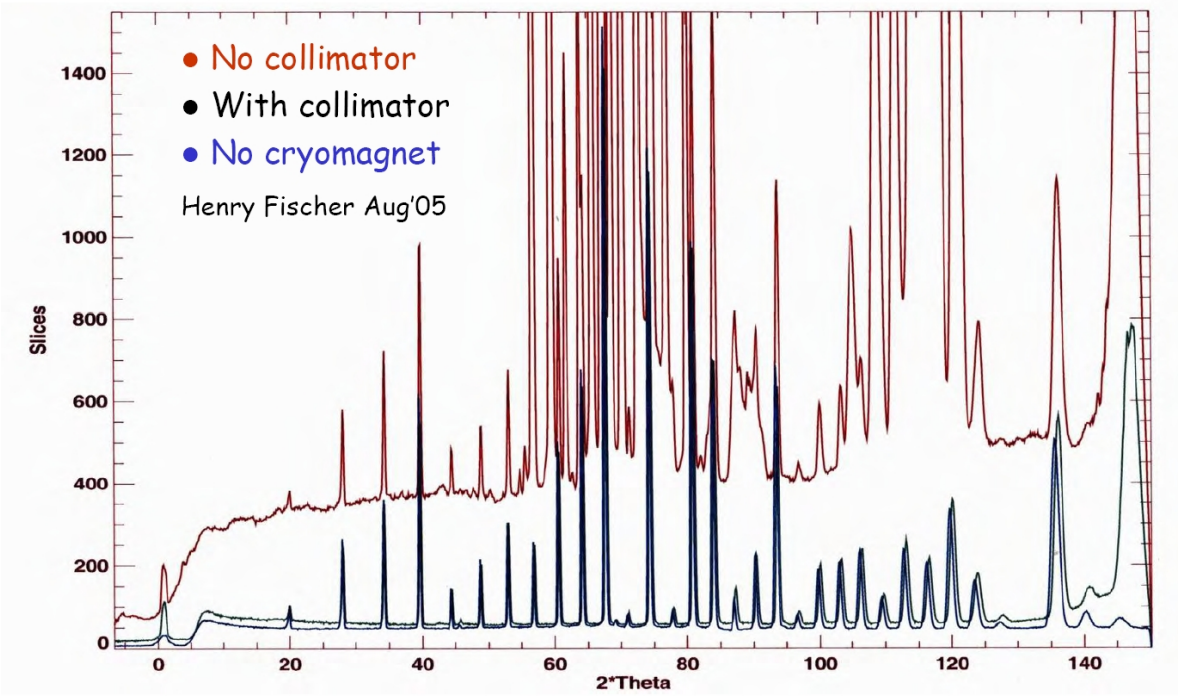
Not just Rietveld Refinement – Efficient Instruments

Radial Collimator selects scattering from only the sample, not the environment

Pressure cell in a Cryostat

ILL D20 Radial Collimator

Radial Collimator = 95% transmission, 3% background

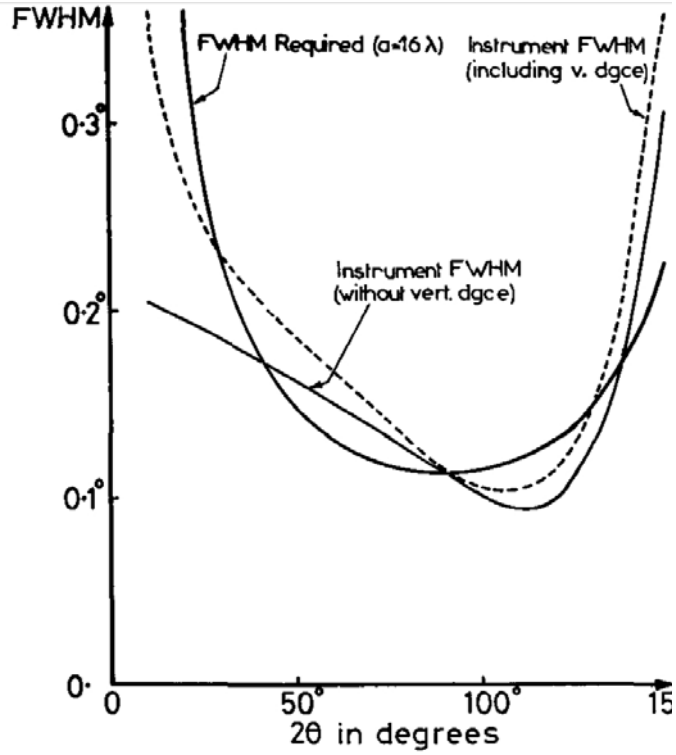


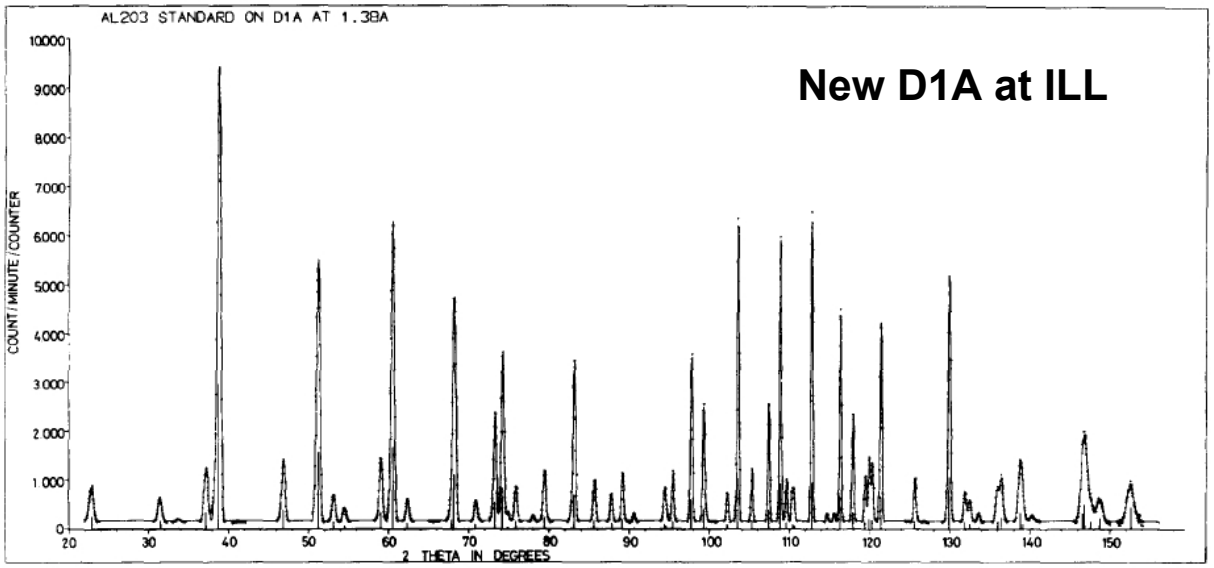
Not just Rietveld Refinement – Efficient Instruments

New instrument geometry to improve focussing at high scattering angles

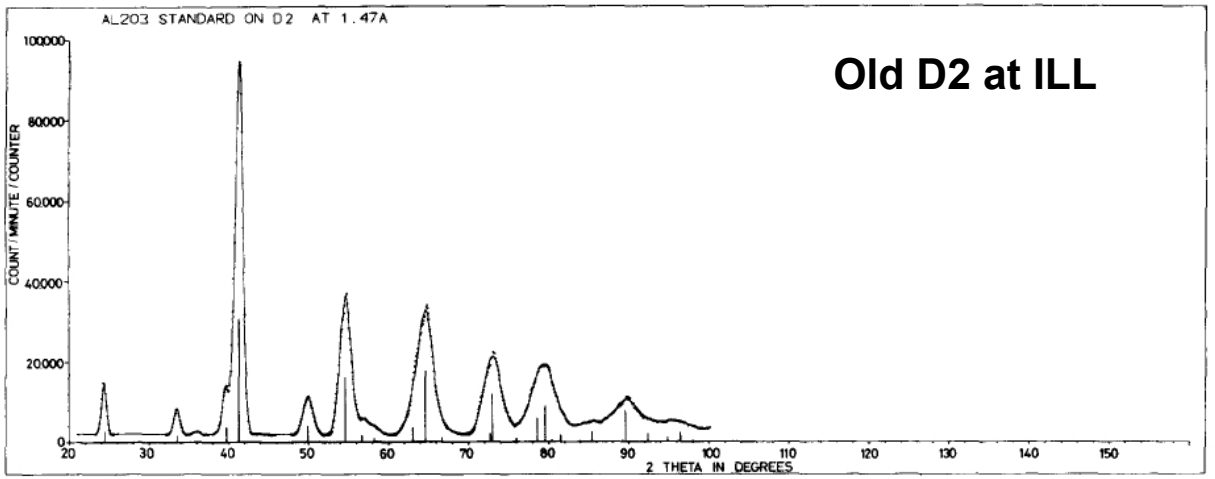
1976 A W Hewat & I Bailey
Nuc. Inst. Methods 137 463-47

High monochromator angle to focus at
High angles with highest peak density





(a)



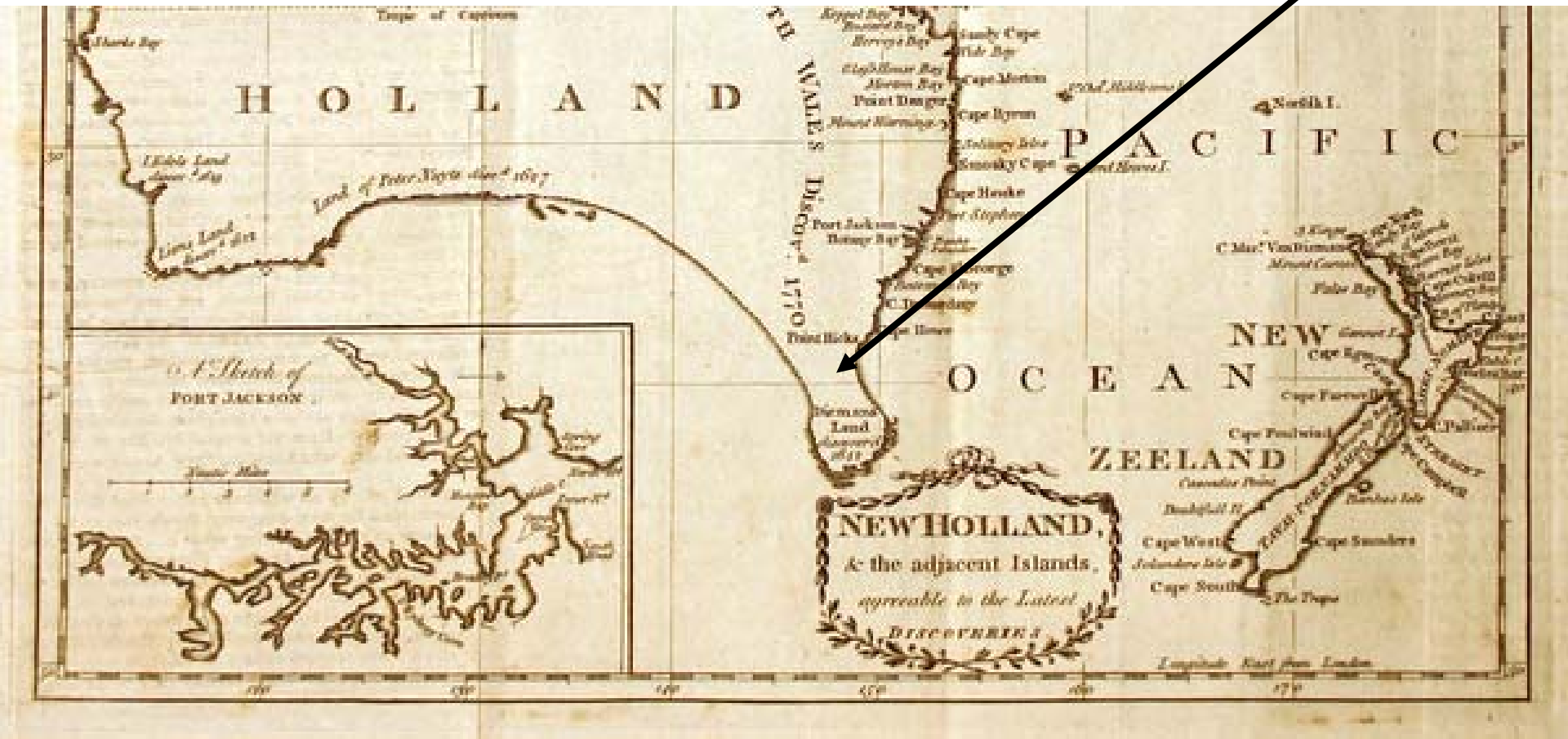
Not just Rietveld Refinement – Efficient Instruments

Instrument Optimisation – Leo Cussen 2005-2008

Better powder diffractometers–choice of beam elements and trade-offs in design
Nuclear Instruments and Methods in Physics Research A 554 (2005) 406–414

Better powder diffractometers. II—Optimal choice of U, V and W
Nuclear Instruments and Methods in Physics Research A 583 (2007) 394–406

Vertical focusing on neutron powder diffractometers—How much is useful?
Nuclear Instruments and Methods in Physics Research A 587 (2008) 363–370



Not just Rietveld Refinement – Efficient Instruments

TNW optimised instruments with large area detectors to increase the solid angle

Katia PAPPAS, Marnix WAGEMAKER, Ad van WELL, Luana CARON, Lambert van EIJCK

Large ISIS scintillator-PM detector on PEARL at Delft (backside)

Design and Detectors make PEARL competitive with instruments on more powerful reactors

Powerful neutron sources are important; good instrument design is even better