

Single-Crystal Neutron Diffraction: Present and Future Applications

Christina Hoffmann

SNS

Nancy Ross

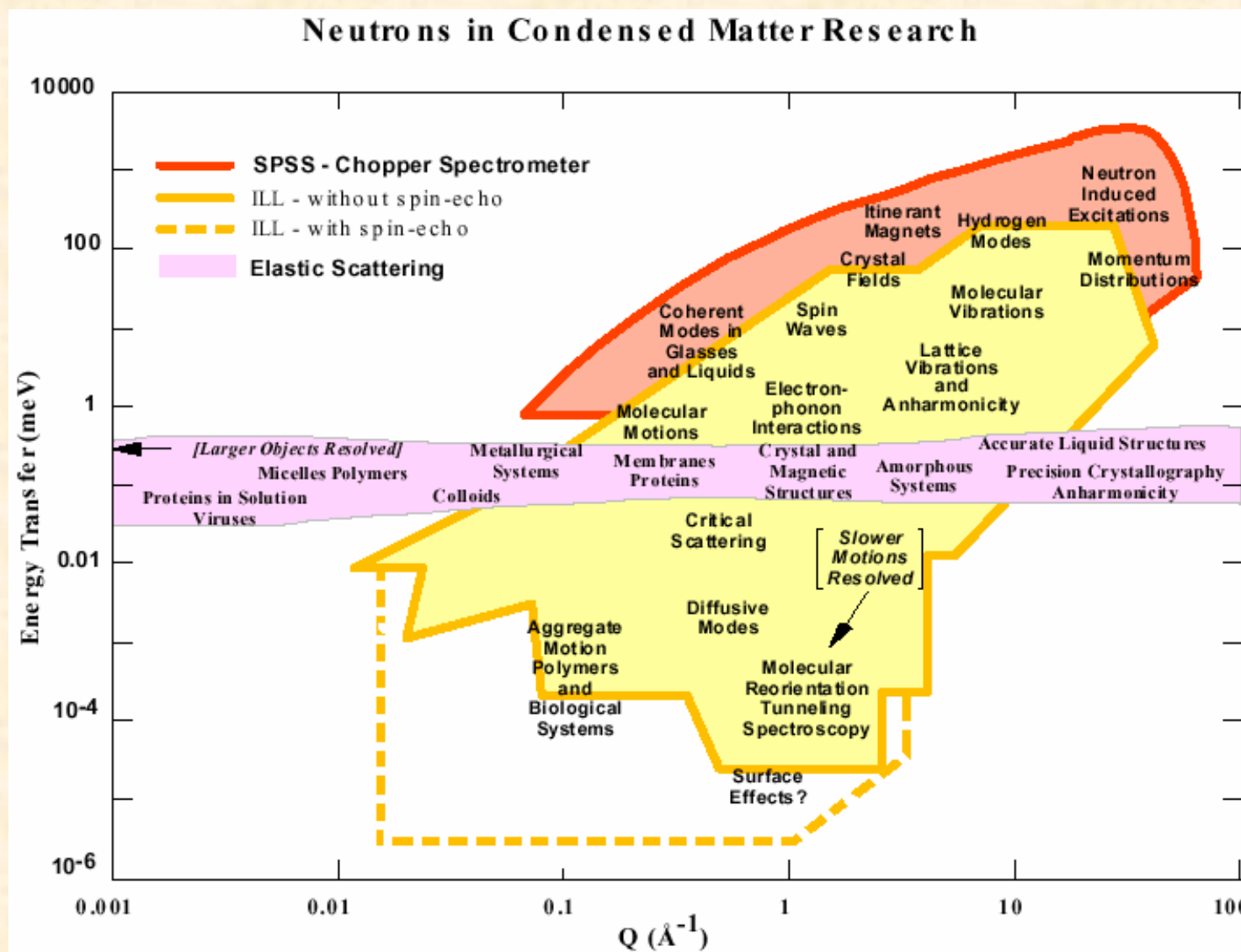
Virginia Tech



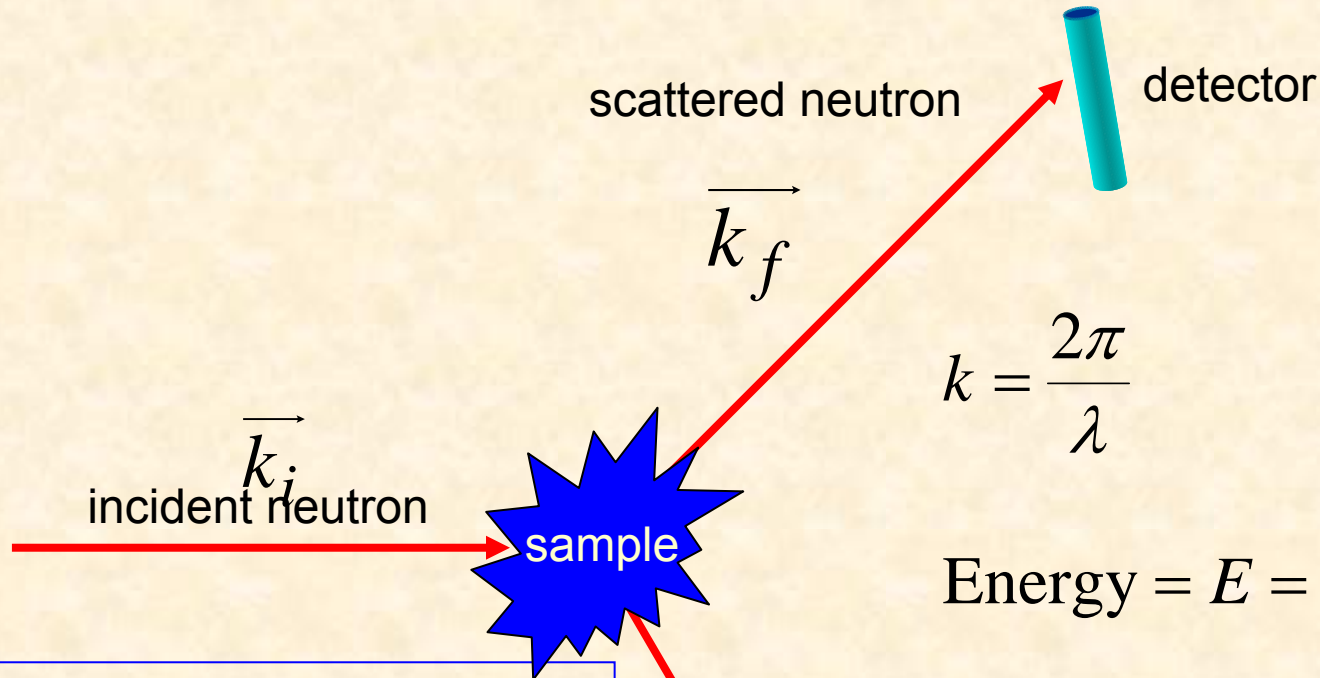
MSA Short Course, Neutron Scattering in Earth Sciences, 12/7-12/8/06



Why Neutron Scattering?



A Basic SND Instrument



$$k = \frac{2\pi}{\lambda}$$

$$\text{Energy} = E = \frac{(\hbar k)^2}{2m_n}$$

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$

$$\text{Energy Transfer} = \hbar\omega = E_i - E_f$$

Measure scattered neutrons as a function of Q and $\omega \rightarrow S(Q, \omega)$.

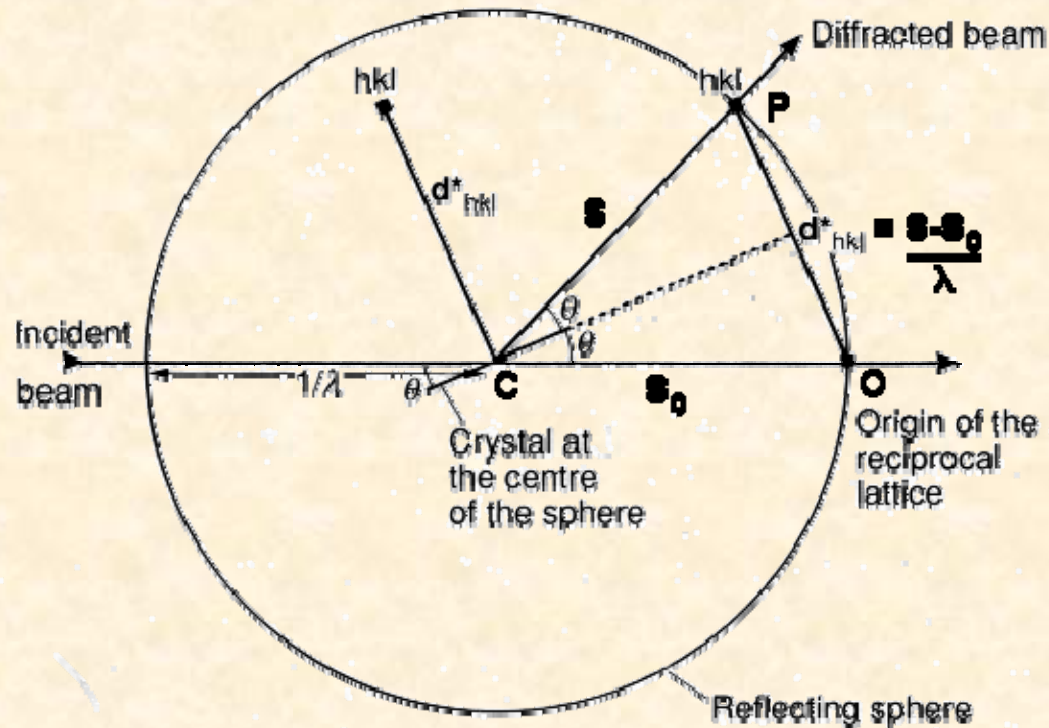
$\omega = 0 \rightarrow$ elastic

$\omega \neq 0 \rightarrow$ inelastic

ω near 0 \rightarrow quasielastic

Ewald Construction

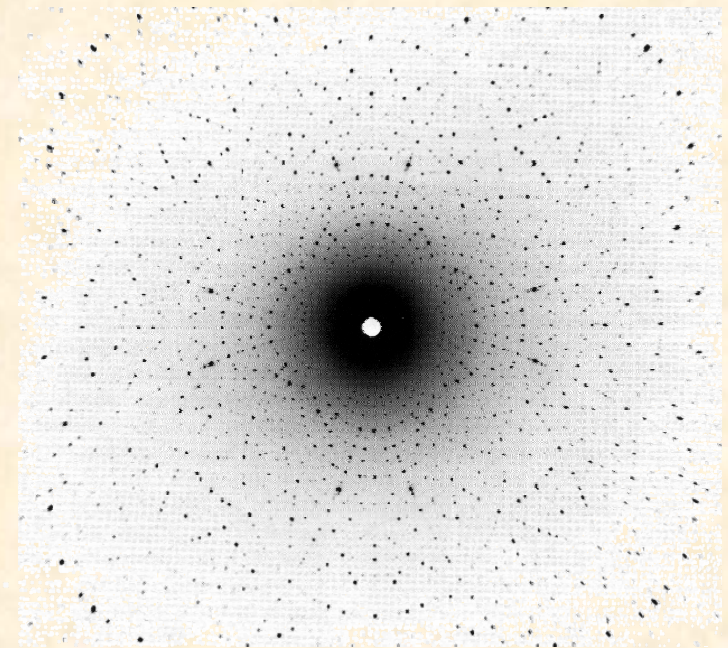
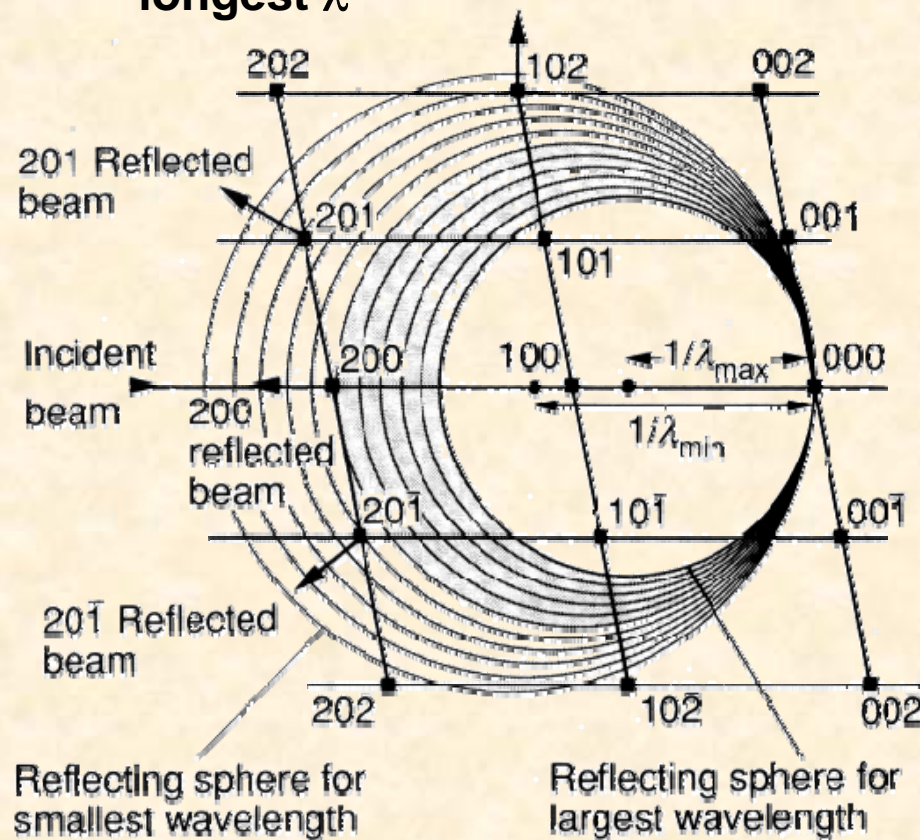
The origin of direct and reciprocal space are separated by placing the crystal at the center of a sphere of radius $1/\lambda$. The origin of reciprocal space is placed on the surface of the sphere where S_0 (the incident beam) exits the sphere.



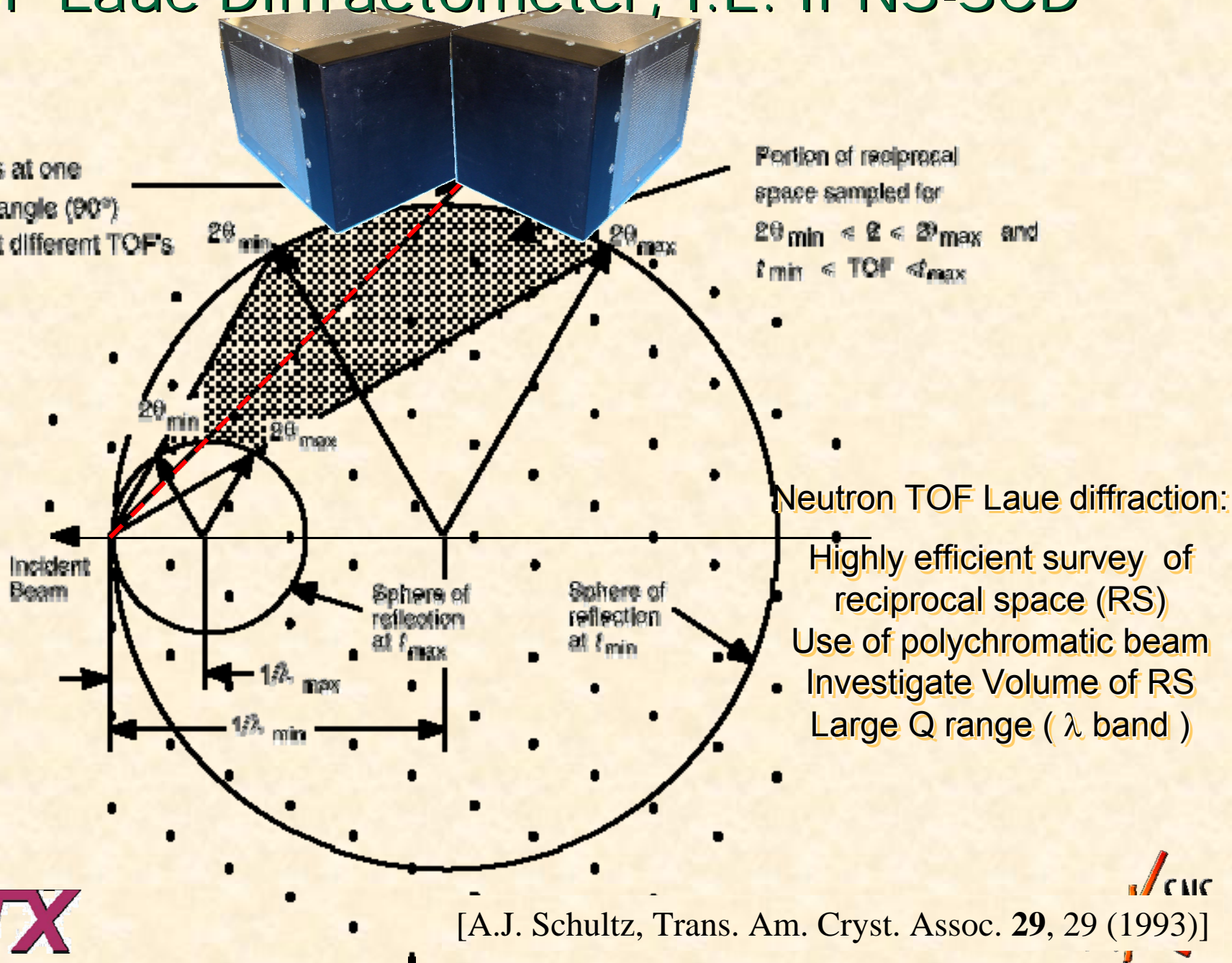
Laue Geometry

The Laue technique for collecting large amounts of data quickly.

Polychromatic radiation modifies the Ewald construction
Multiple Ewald spheres, enscribe the shortest λ and the longest λ



TOF Laue Diffractometer, I.E. IPNS-SCD



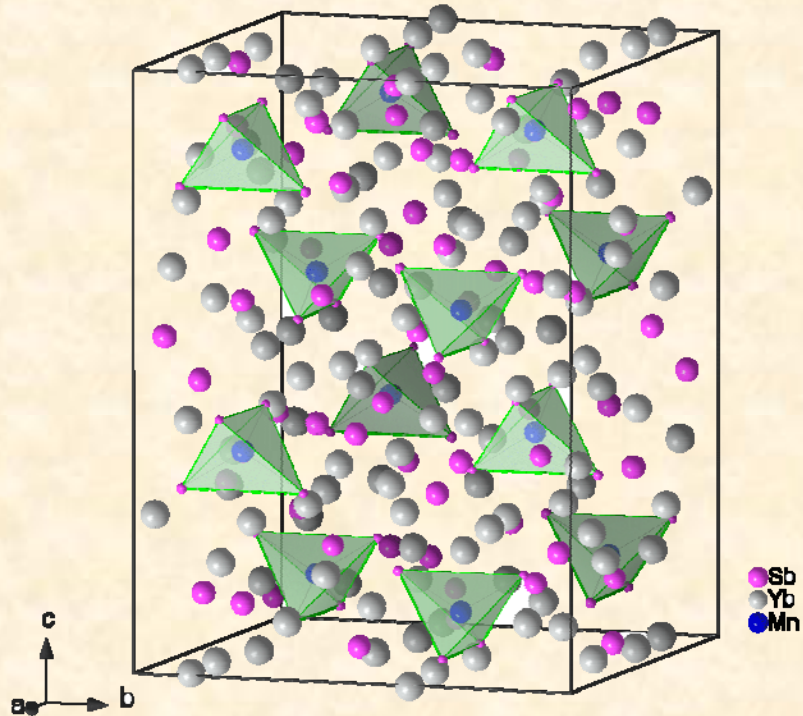
A TOF Laue SND Measurement

- **Mount a sample** → sample sizes are $> 1\text{mm}^3$
- **Load sample**
 - Sample environment: vacuum, cooling, heating, pressure, magnetic field, electric field
- **Start measurement**
 - Data collection time according to sample properties
Scattering power, composition, crystal quality, crystal size
- **Data collection**
- **Data reduction:**
 - Peak search
 - UB matrix
 - Peak integration
 - Corrections for instrument specific parameters
 - detector efficiency, neutron spectrum, intrinsic background, sample environment
 - Corrections for sample specific parameters
 - Absorption and empirical extinction
 - ...
 - Produce output file for conventional data analysis package
 - GSAS, ShelX, JANA, FulProf, ...

Let's do an Experiment at
IPNS-SCD..

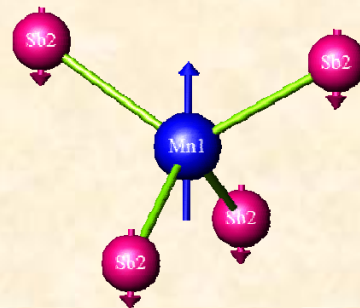
This Experiment was done this Year in March..

A Structure to Investigate



Yb14MnSb11

- Tetragonal with space group $I41/acd$
 - 1 Mn atom
 - 4 inequivalent Sb atoms
 - Sb (2) involved in Mn-Sb tetrahedra
- Ferromagnet regarded as a rare example of an underscreened Kondo lattice. ($T_C = 53$ K)
- It is proposed a Mn^{2+} ($d5$) configuration with the moment compensated by the anti-aligned spin of an Sb 5p hole.



V.O. Garlea[HFIR], G.L. Jones[HAMILTON], B. Collett[HAMILTON], W.C. Chen[NIST], T.R. Gentile[NIST], P.M.B. Piccoli[IPNS], M.E. Miller[IPNS], A.J. Schultz[IPNS], H.Y. Yan[IUCF], X. Tong[IUCF], M. Snow[IUCF], B.C. Sales[HFIR], S.E. Nagler[HFIR], W.T. Lee[SNS], C. Hoffmann[SNS]

Mounting the Single Crystal Sample..

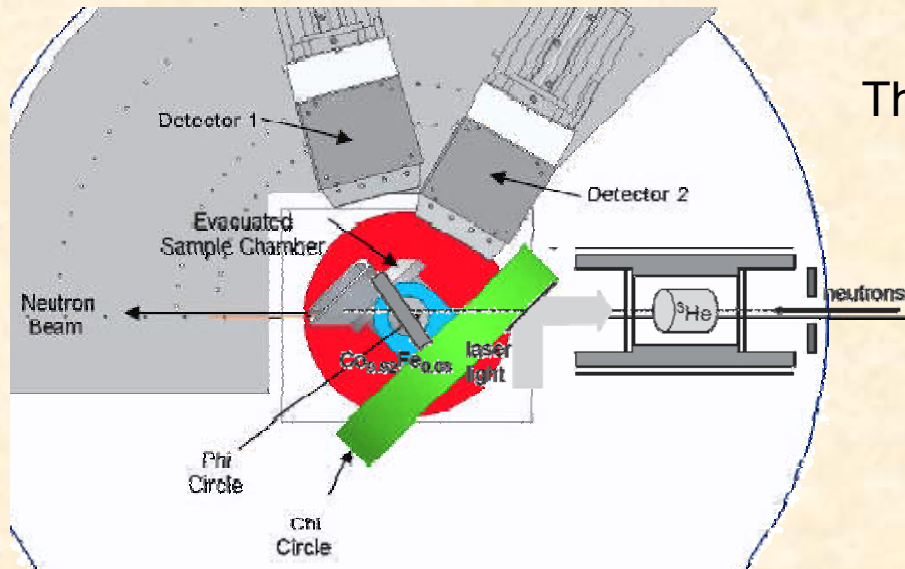


- Mount the single crystal on a sample pin for cryogenic, vacuum, or heating experiments to refine the nuclear atomic or molecular structure
- Mount the sample between permanent magnets to refine nuclear + magnetic structure
- Special mounting schemes for pressure, gas flow, larger magnetic fields,..



Sample wrapped with Al-foil between SmCo magnets

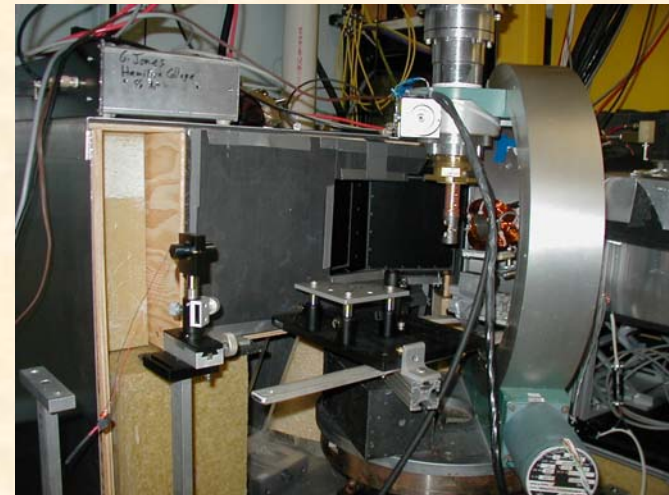
The IPNS - SCD Instrument:



The



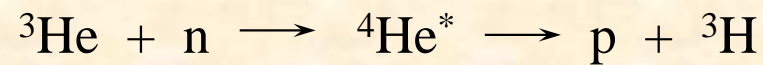
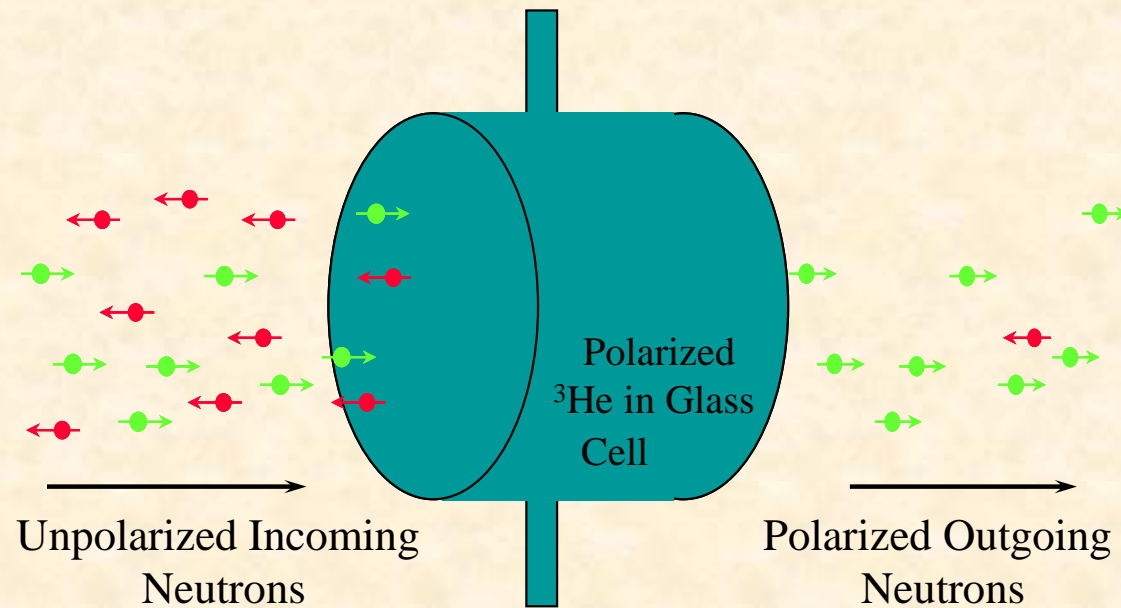
- **Tof Laue single crystal diffractometer (SCD)**
- **White beam (0.5 – 10 Å)**
- **Two energy sensitive area detectors, centered at 75° and 123°**
- **Cryogenic sample environment with 4 K displax**



VTX

SNS
SPALLATION NEUTRON SOURCE

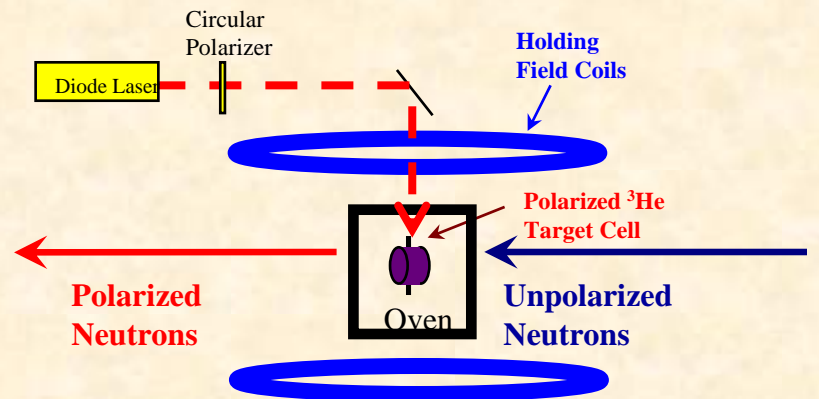
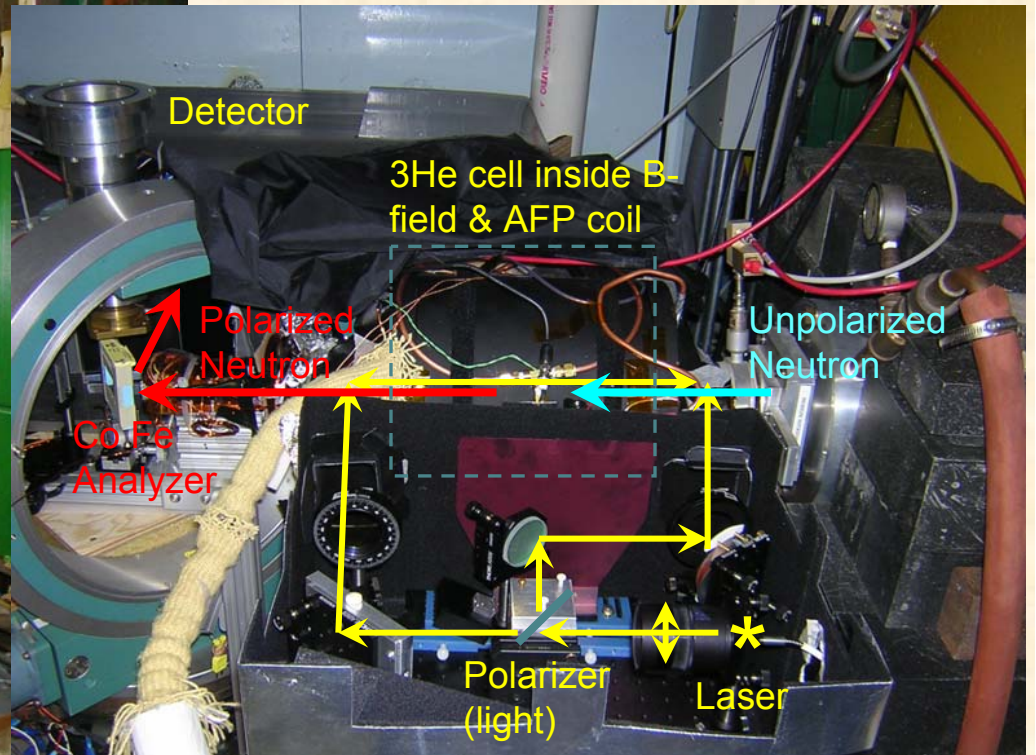
Spin Dependent Neutron Absorption in Polarized ^3He



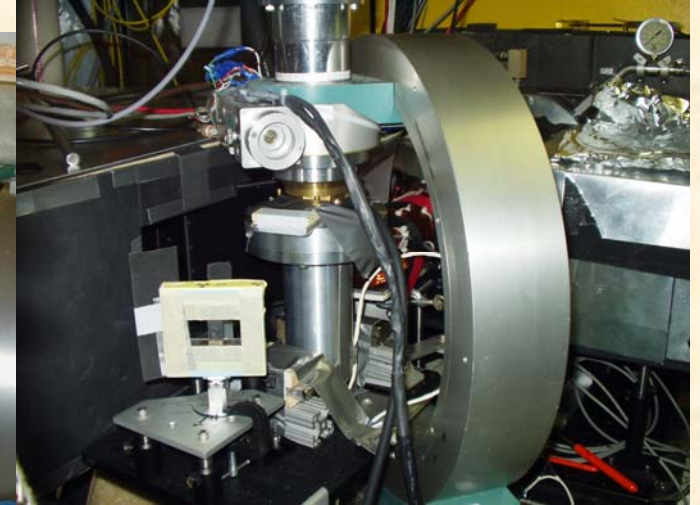
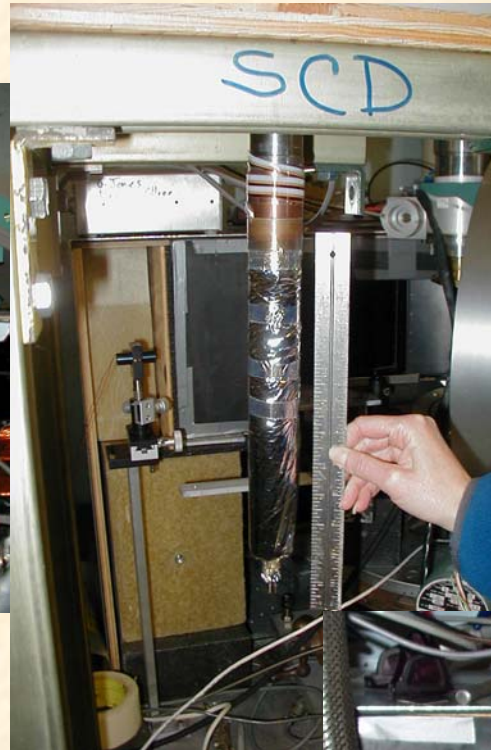
2006 Experiment at SCD, IPNS, Polarization Setup

Special now but Standard in the Future

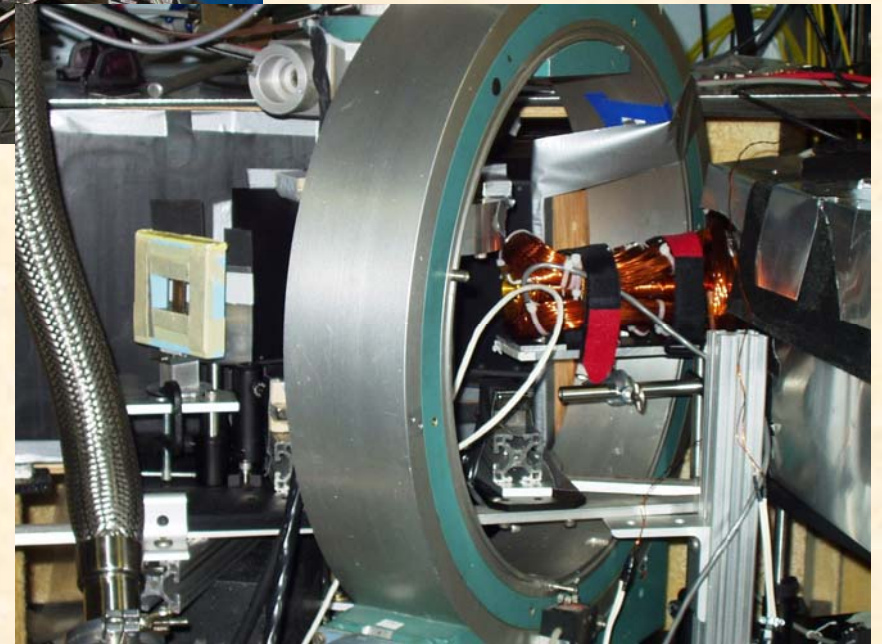
The Incident Neutron Beam is Polarized by Installing a ^3He Neutron Spin Filter on the SCD Beam Path



Mounting the Sample on the Instrument..

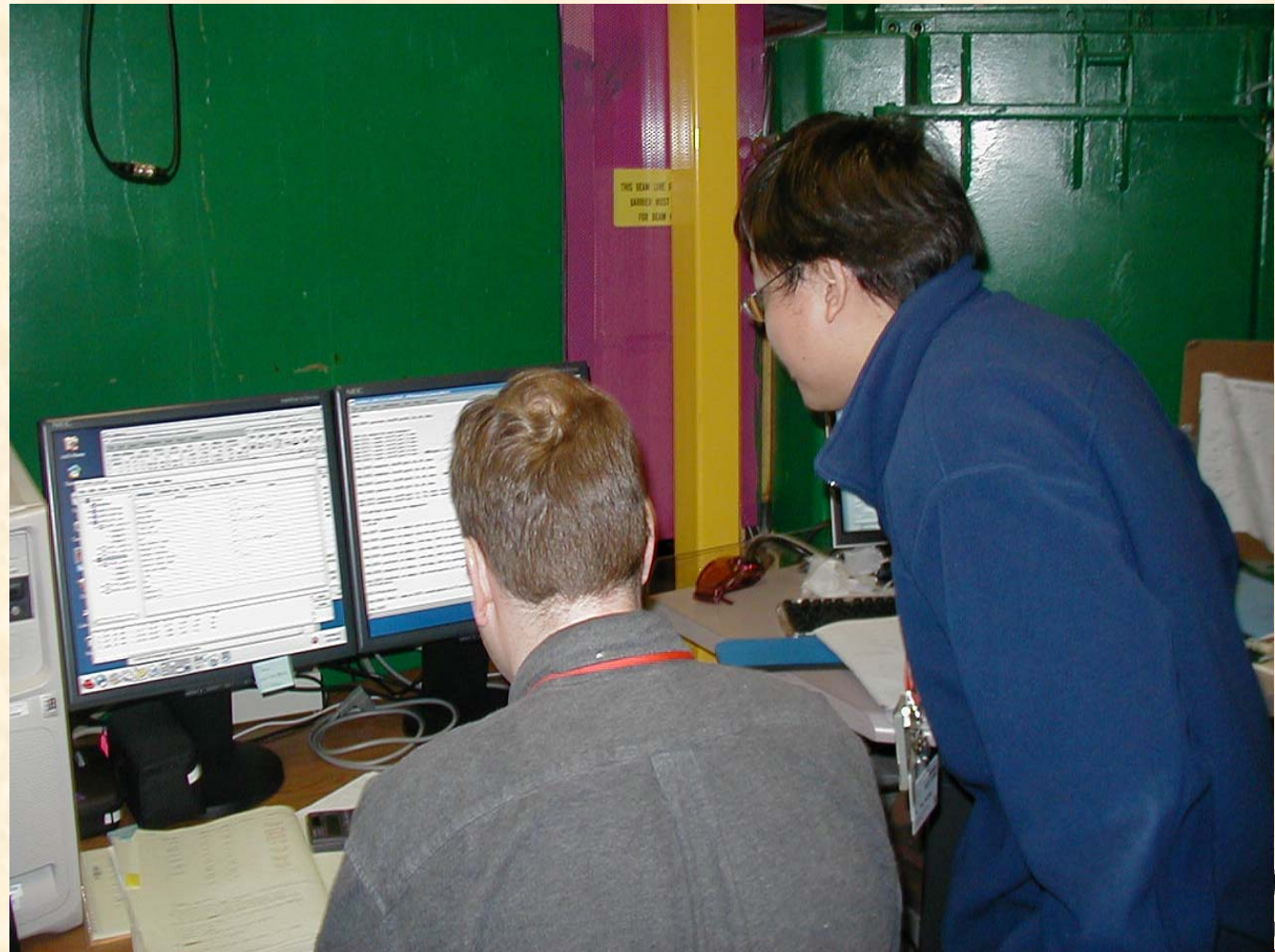


- **The sample with the magnet is mounted on the displacer**



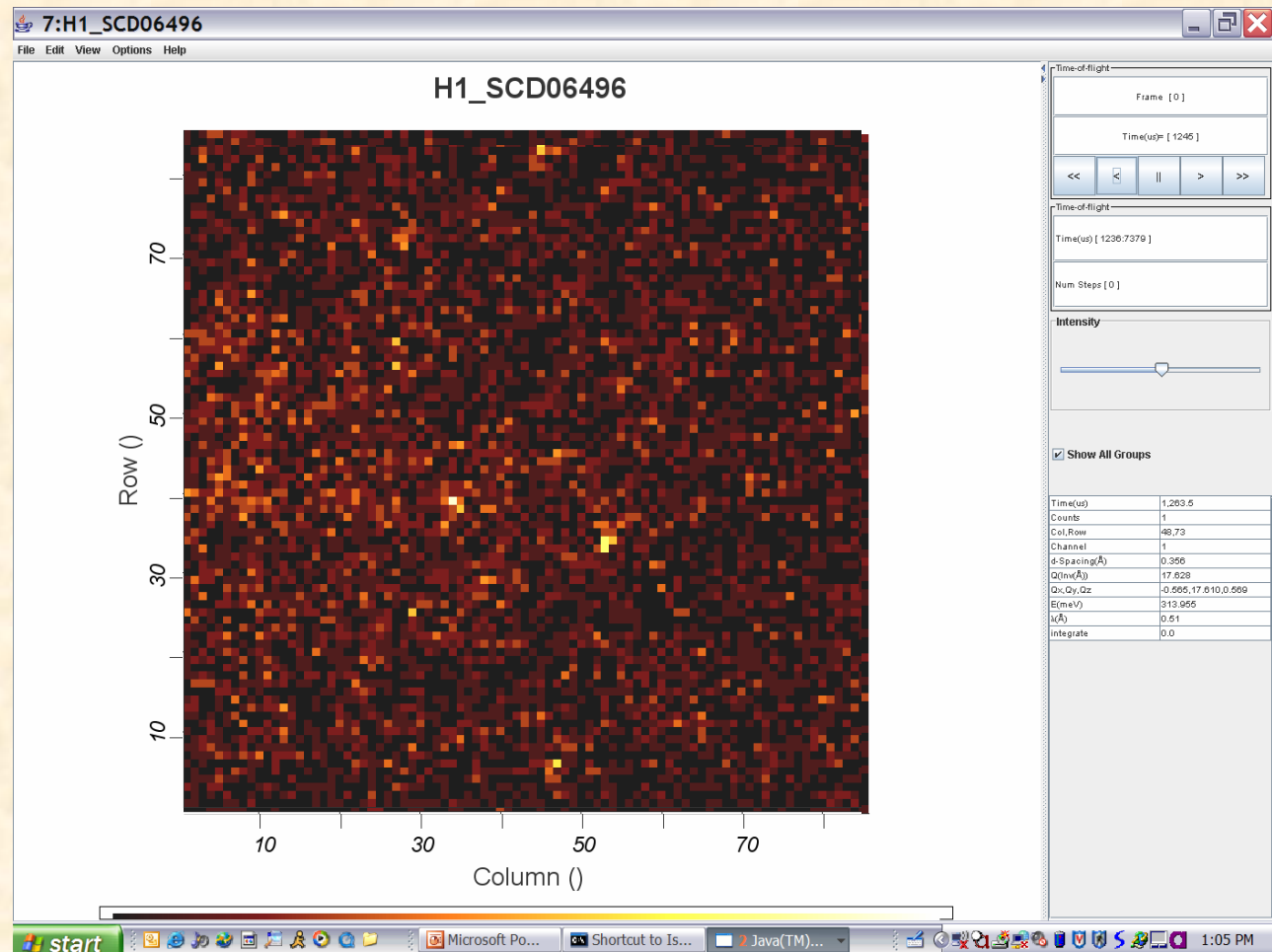
Start a Data Collection

- Use local software to set measurement time and number of crystal settings according to symmetry.



Start a Data Collection

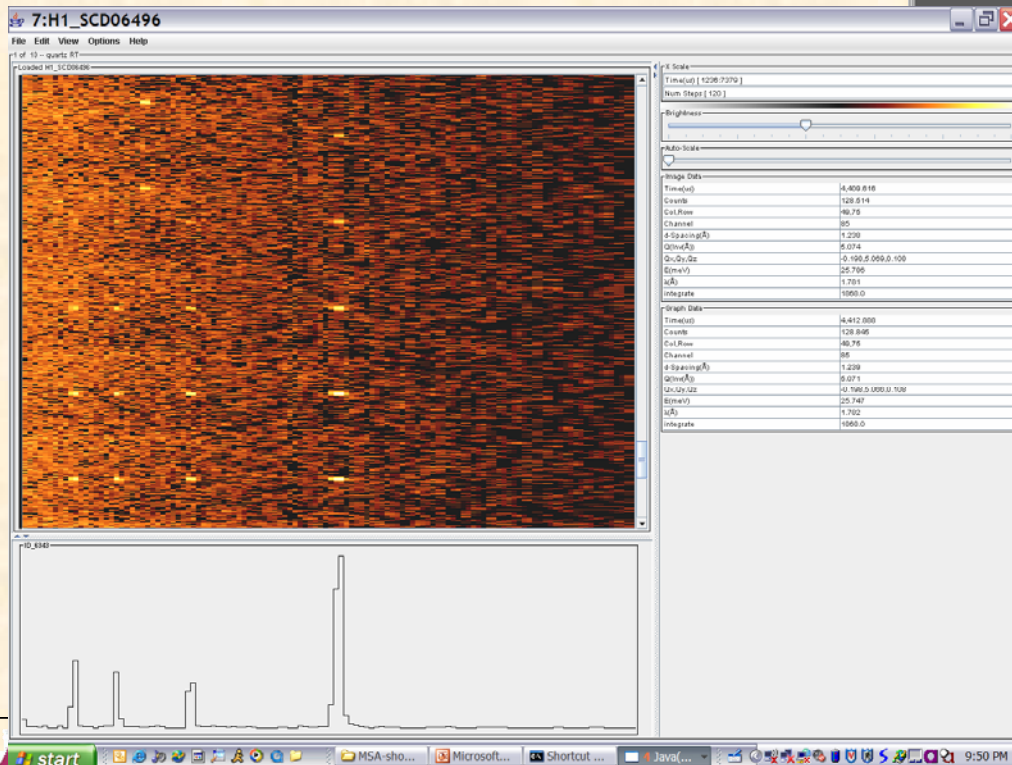
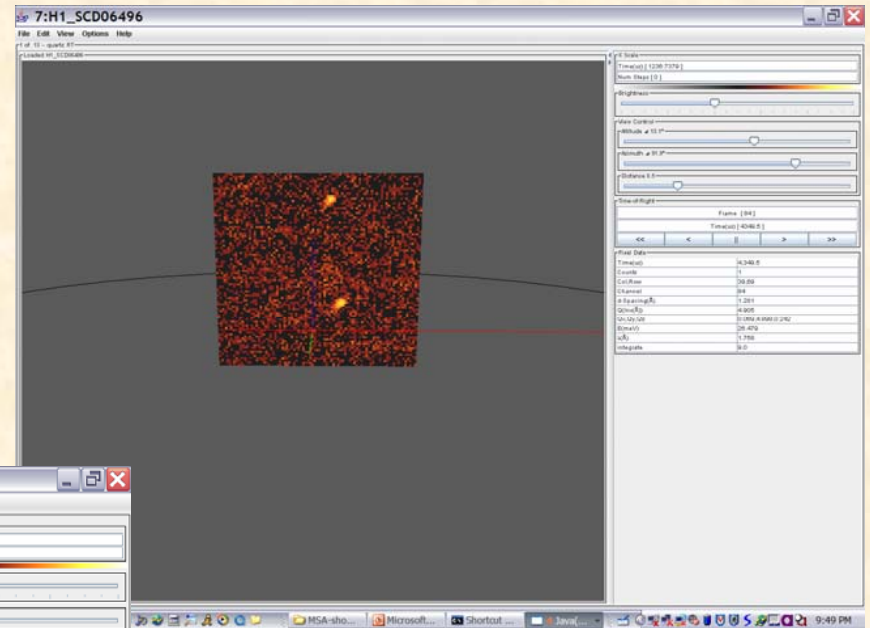
- First reflections on the detector



Detector Representation of Data

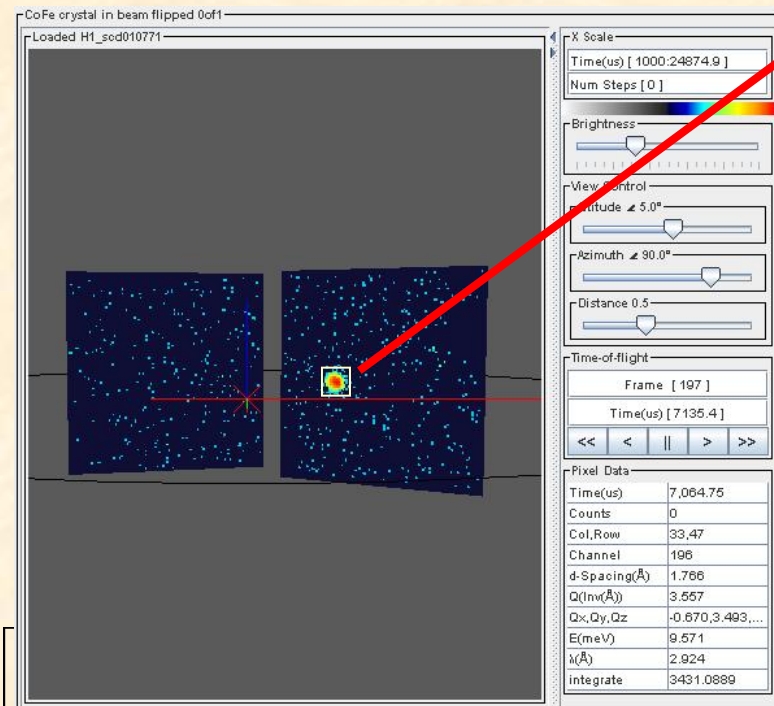
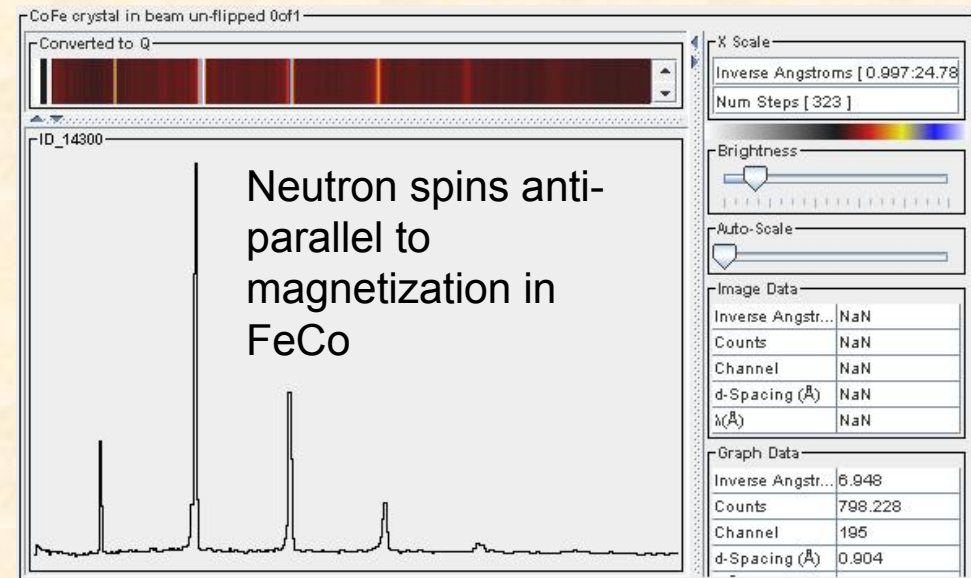
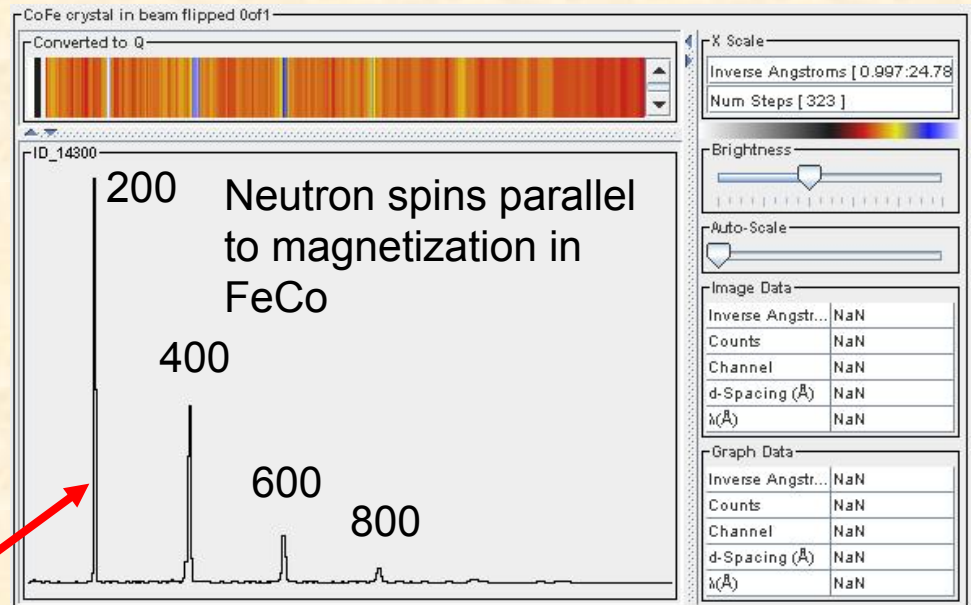
Position of reflections →

Wavelength of reflections ↙



Polarization of the Neutrons

The ratio of the (2 0 0) reflection between spin flips is 0.5:7.3 which results in $[(7.3-0.5)/(7.3+0.5)] = 0.87$, corresponding to the Neutron polarization P_n .



Peak Search, UB Matrix

- Using ISAW at IPNS
- Available on the [IPNS web site](http://www.pns.anl.gov) to download
- Mailing list available

<http://www.pns.anl.gov>

The screenshot displays the ISAW 1.8.0 Gamma5 software interface. The main window shows a project directory tree on the left and a data table on the right. Overlaid on this are six instances of the 'Initial SCD Peaks Wizard' dialog boxes, each representing a different form in the wizard sequence (Form 1 to Form 6). The bottom-most instance, Form 6: JIndex, is the most detailed, showing sections for 'CONSTANT PARAMETERS' (Peaks File), 'USER SPECIFIED PARAMETERS' (Matrix file, Restrict Runs, Delta h, Delta k, Delta l, Update peaks file?, Append to log file?), and 'RESULTS' (Index.J log file). A status window at the bottom left of the wizard stack displays the message: 'FORM ERROR: Parameter SCD Calibration File is invalid.' The Windows taskbar at the bottom shows the start button, system tray icons, and the time 8:23 AM.

VTX



Integration, Corrections, Data Reduction

ISAW 1.8.0 alpha5

File Edit View Operations Macros Wizards Help

Attributes DataSet Log Session Log System Props Scripts

Attribute	Value
DataSet Tag.Title	9:H1_SCD06496
File	C:\Program Files\ISAW\SampleRuns\SCD06496.RUN

Session

- Modified
- SCD06496.RUN
 - 8:M1_SCD06496
 - 9:H1_SCD06496

Daily SCD Peaks Wizard

File View Project Directory Help

Form 4: IntegrateMultiRunsForm

CONSTANT PARAMETERS

Raw Data Path: C:\Program Files\ISAW\SampleRuns/ Browse

Peaks File Output Path: C:\Program Files\ISAW\SampleRuns/ Browse

Experiment name:

SCD Calibration File: C:\Program Files\ISAW\SampleRuns Browse

SCD Calibration File Line to Use: -1

USER SPECIFIED PARAMETERS

Run Numbers:

Centering Type: primitive

Time-Slice Range: -1.3

Amount to Increase Slice Size By: 1

Minimum d-spacing: 0.0

Append to File?

Integrate 1 peak method: MaxToSigl

Box Delta x (col) Range: -2.2

Box Delta y (row) Range: -2.2

RESULTS

Integrated Peaks File: Browse

Reset IntegrateMultiRunsForm Progress Do

Reset All Wizard Progress: 0 of 4 Forms done Do All

First Form Back One Forward One Last Form

Status

Executing...

FORM ERROR: Parameter SCD Calibration File is invalid.

Executing...

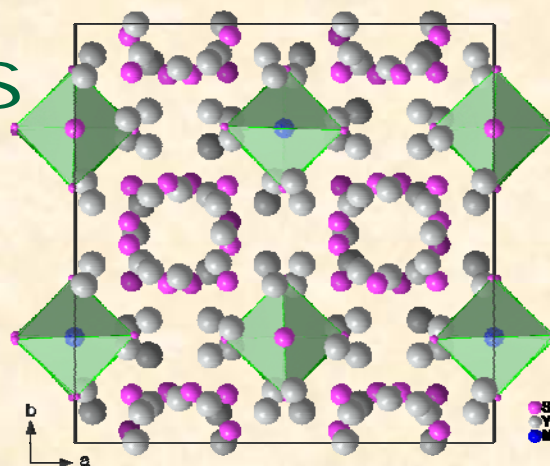
FORM ERROR: Parameter SCD Calibration File is invalid.

Save Clear



Data Analysis & Results

- Data at 70 K for a GSAS refinement of the nuclear structure confirms previously solved structure
- Unpolarized neutron beam
- Above phase transition



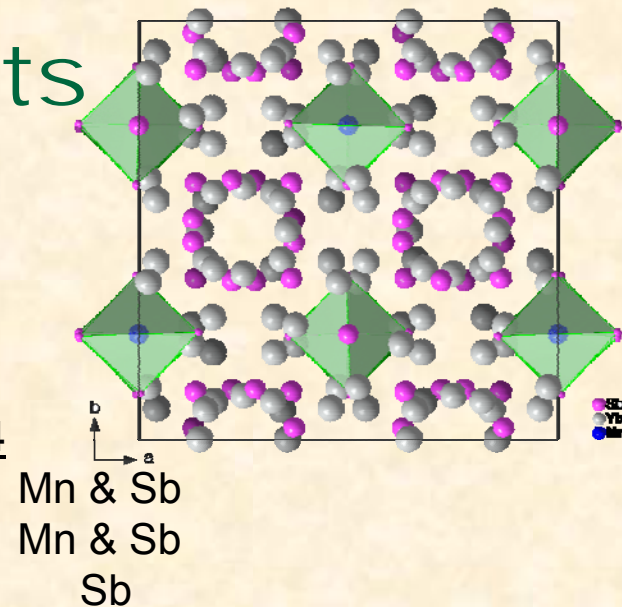
Data Analysis & Results

Reflection Selection rules :

$$\text{Mn (8a): } 2h + l = 4n$$

$$\text{Sb (32g): } h + k + l = 2n$$

h	k	l	l^+	l^-	$\lambda(\text{\AA})$	$Q(\text{\AA}^{-1})$	l^+/l^-	$(2h+l)/4$
6	0	0	293.3	222.6	5.18	2.26	1.317	3
8	0	0	1315.8	920.7	2.43	3.02	1.429	4
6	1	-1	223.8	306.8	4.67	2.31	0.729	2.75

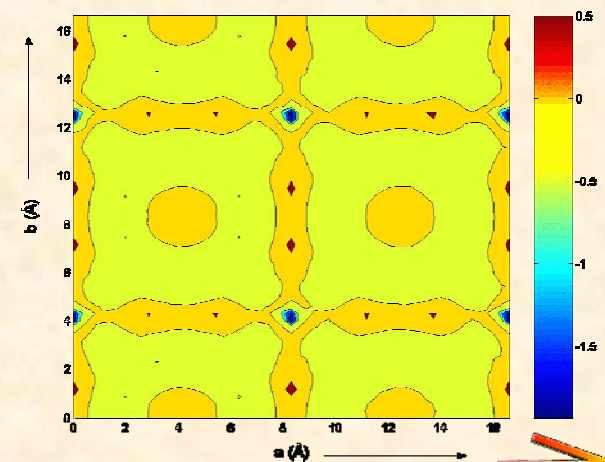


Polarized neutron diffraction data (47 reflections)


→ MaxEnt reconstructions of spin density distribution

→ maximum entropy magnetization density reconstruction reveals the presence of a magnetic moment on the Sb site with opposite sign with respect to the Mn moment

Projection of the spin density in Yb₁₄MnSb₁₁ along the c-axis.



Data Presentation and Publication..



Polarized neutron diffraction study of the ferromagnetic semiconductor $\text{Yb}_{14}\text{MnSb}_{11}$

V. O. Garlea¹, G. L. Jones², B. Collett², W. C. Chen^{3,5}, T. R. Gentile³, P. M. B. Piccoli⁴, M. E. Miller⁴, A. J. Schultz⁴,
H. Y. Yan⁵, X. Tong⁵, M. Snow⁵, B. C. Sales¹, S. E. Nagler¹, W. T. Lee¹, C. Hoffmann¹

¹Oak Ridge National Laboratory, Oak Ridge, TN, ²Hamilton College, Clinton, NY, ³NIST Center for Neutron Research, Gaithersburg, MD
⁴Intense Pulsed Neutron Source, Argonne, IL, ⁵IUCF, Indiana University, Bloomington, IN

INDIANA UNIVERSITY

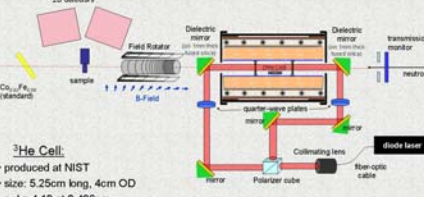
NIST
Hamilton

Polarized neutron diffraction provides the spatial distributions of magnetization as well as the direction of the magnetization vector on an atomic scale in a wide range of materials of fundamental and technological importance. Recent advances in the development of ^3He spin filters have made it possible to polarize neutrons efficiently at neutron spallation sources.

We report the results of a test experiment carried out using a polarized ^3He filter installed at the Single-Crystal Diffractometer (SCD) instrument at the Intense Pulsed Neutron Source (IPNS). The goal of the experiment was to determine the distribution of the spin density in the MnSb_4 tetrahedra of the Zintl semiconductor $\text{Yb}_{14}\text{MnSb}_{11}$.

Experimental Details

- compact system to continuously polarize a ^3He spin filter by spin-exchange optical pumping
- ^3He Spin Filter polarizes broad energy range of neutrons with minimal effect on beam divergence
- NMR coils are used to quickly flip the ^3He polarization with 0.01% loss




^3He Cell:

- produced at NIST
- size: 5.25cm long, 4cm OD
- $n=1 = 4.19$ at 0.496nm
- 2.2 bar of ^3He , 60 mbar of N_2 , drop of Rb

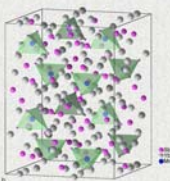
Parameters:

- size: length ~ 31 cm, O.D. ~ 28 cm
- beam size = 9mm
- T_p = approx. 88%
- 2 double paned fused silica windows ~ 4mm total
- 2 dielectric mirrors on fused silica ~ 2mm total
- Cell windows ~ 3mm total

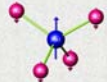


$\text{Yb}_{14}\text{MnSb}_{11}$

- Tetragonal with space group $I4_1/acd$
- 1 Mn atom
- 4 inequivalent Sb atoms
- Sb (2) involved in Mn-Sb tetrahedra
- Ferromagnet regarded as a rare example of an underscreened Kondo lattice. ($T_c = 53 \text{ K}$)



- It is proposed a Mn^{2+} (d^5) configuration with the moment compensated by the anti-aligned spin of an Sb 5p hole.




- neutron scattering on $\text{Yb}_{14}\text{MnSb}_{11}$ single crystals grown by Sn flux technique
- custom made permanent magnet arrangement to apply a magnetic field of approximately 0.4 T at low temperatures of 6 K at the sample position

Neutron diffraction results

ISAW program: data visualization and integrating peaks

- Neutron diffraction measurements at $T = 70 \text{ K}$, above the transition temperature, confirmed the nuclear structure of $\text{Yb}_{14}\text{MnSb}_{11}$



selection rules:

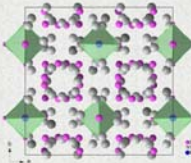
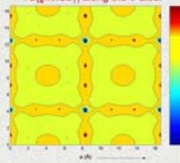
Mn (8a): $2h + l = 4n$

Sb (32g): $h + k + l = 2n$

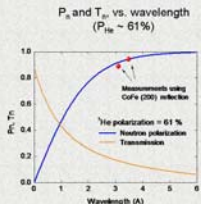
Selected reflections:

h	k	l	I	I/A	Q(A ⁻¹)	I/I ₀	(2h+k)/4	Mn & Sb	
6	0	0	293.3	222.6	5.18	2.26	1.317	3	Mn & Sb
8	0	0	1315.8	920.7	2.43	3.02	1.429	4	Mn & Sb
6	1	-1	223.8	306.8	4.67	2.31	0.729	2.75	Sb

Polarized neutron diffraction data (47 reflections)
→ MaxEnt reconstructions of spin density distribution

→ maximum entropy magnetization density reconstruction reveals the presence of a magnetic moment on the Sb site with opposite sign with respect to the Mn moment



$P_{\text{He}}(\lambda) = T_p e^{-n\sigma_p \lambda}$

$T_p = T_0 \cosh(P_{\text{He}} n \sigma_p \lambda)$

$P_{\text{He}} = \tanh(P_{\text{He}} n \sigma_p \lambda) = 1 - \frac{T_0^2}{T_p^2}$

T_p = transmission l = cell length
 P_{He} = neutron polarization λ = neutron wavelength
 P_{He} = ^3He polarization n = number density of ^3He

- The achieved 61% ^3He polarization corresponds to $P_{\text{He}} = 94\%$ at $\lambda = 3.47 \text{ \AA}$, confirmed by measuring the ratio between spin-flips of the (200) reflection of the CoFe crystal standard.

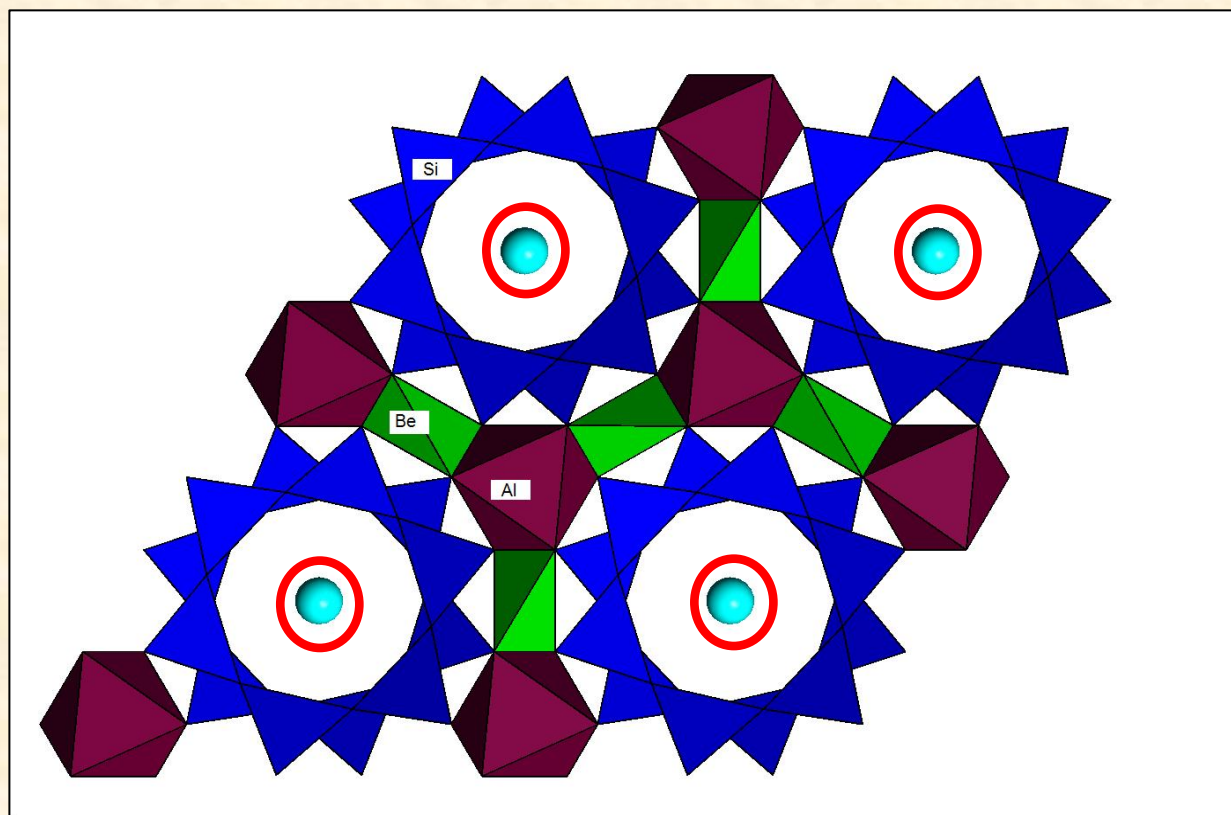
II. Applications of Single Crystal Neutron Diffraction in Earth Sciences

- **Water in minerals**
- **Cation site partitioning**
- **Atomic displacement parameter analysis**
- **Magnetic structures**
- **Charge density distributions**
- **Quantitative diffuse scattering**

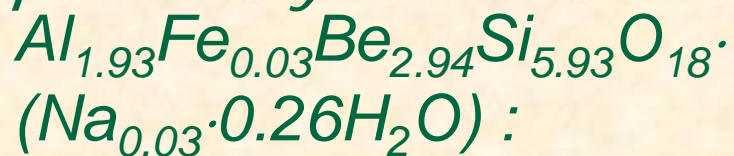
Water in Hydrous Minerals



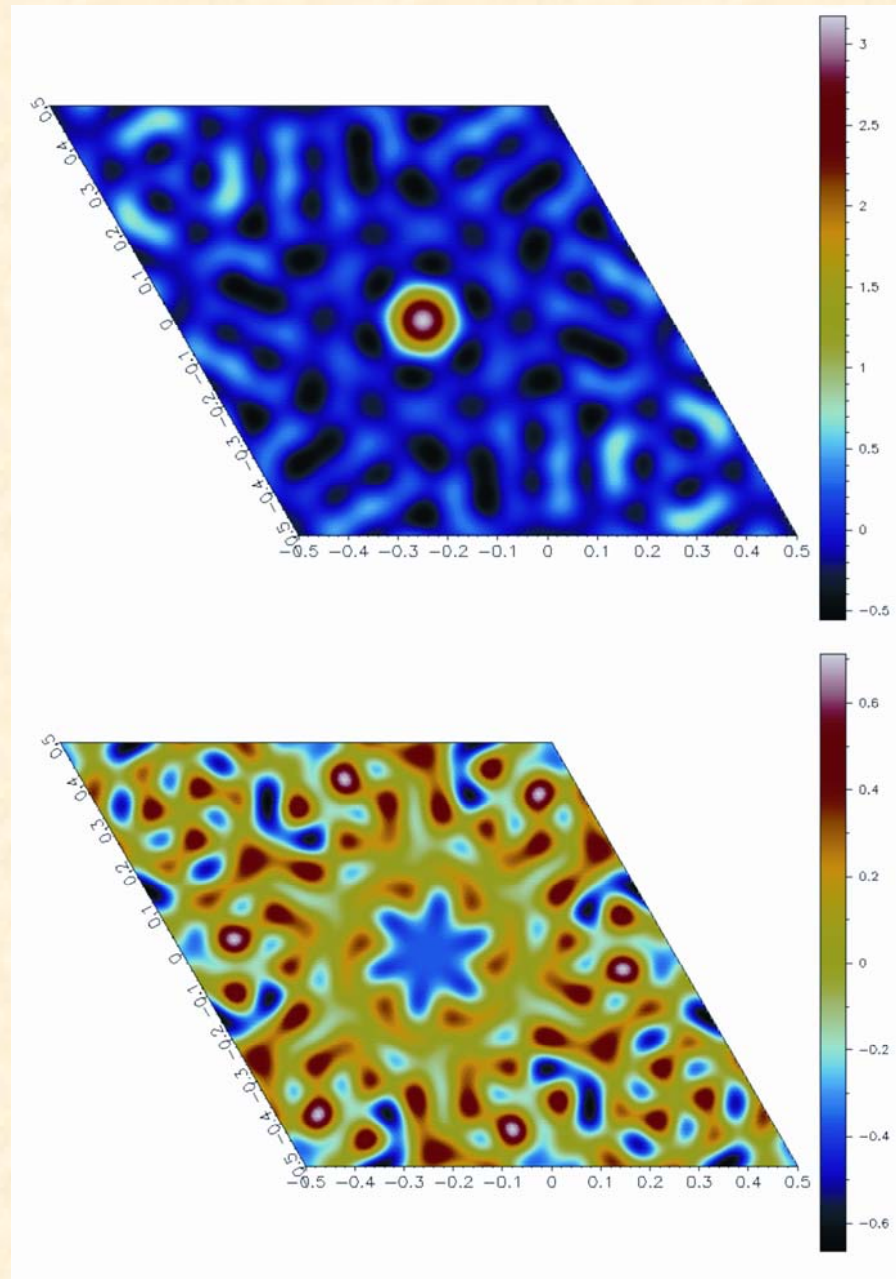
- **Beryl** $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$
- **Space Group:** *P6/mcc*.



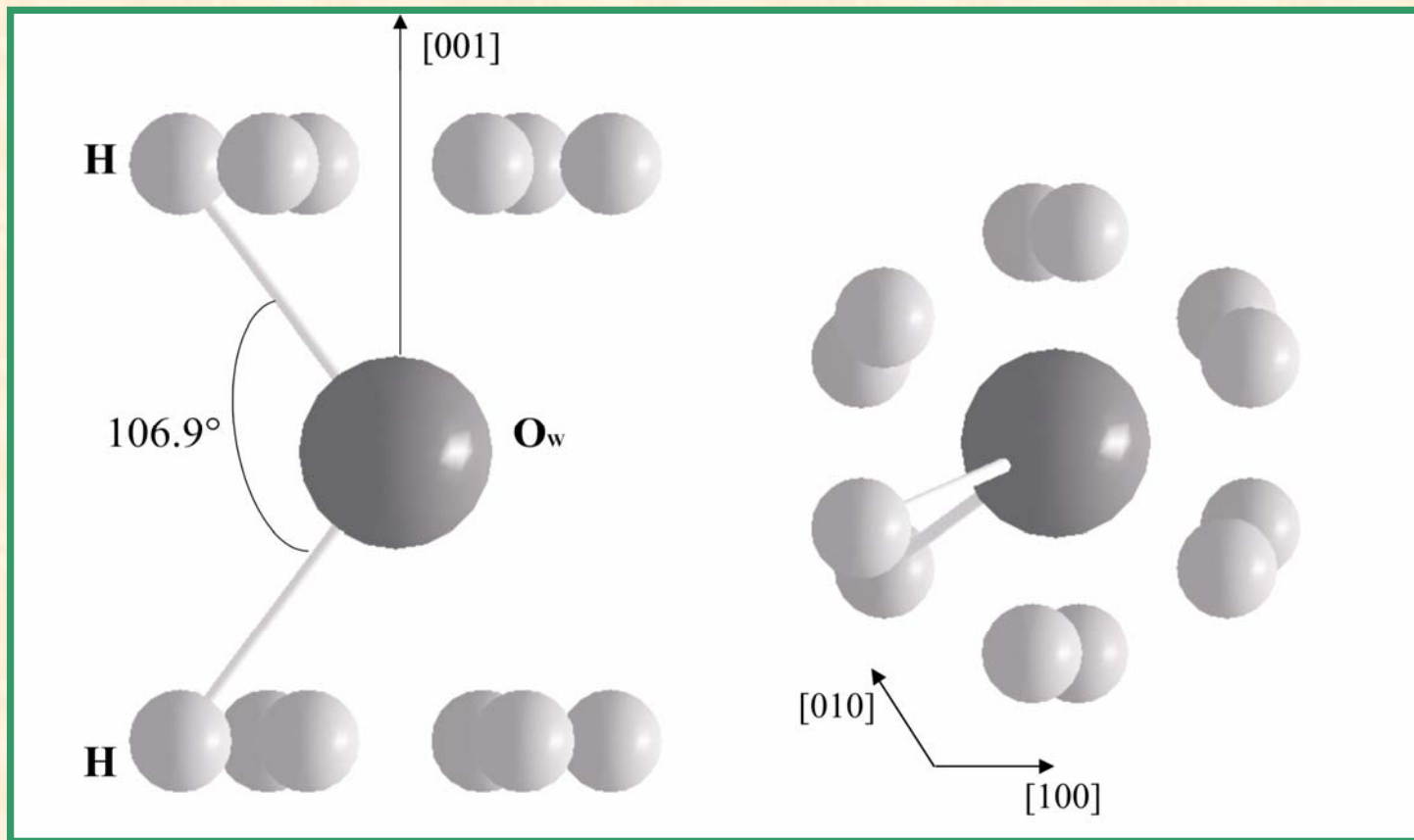
*Gatta et al. (2006)
determined topological
configuration of the
channel content in alkali-
poor beryl*



- Crystal size: 1.1 x 1.3 x 2.0 mm³
- SV28 beam-line at the DIDO reactor
Forschungszentrum Juelich, Germany



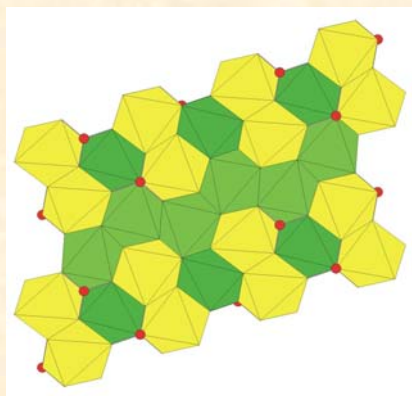
Topological configuration of water molecules into the channel of the alkali-poor beryl, viewed down [100] (left) and down [001] (right):



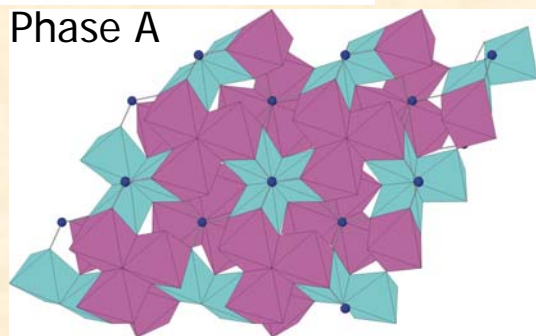
(Gatta et al. 2006)

Dense Hydrous Magnesium Silicates (DHMS)

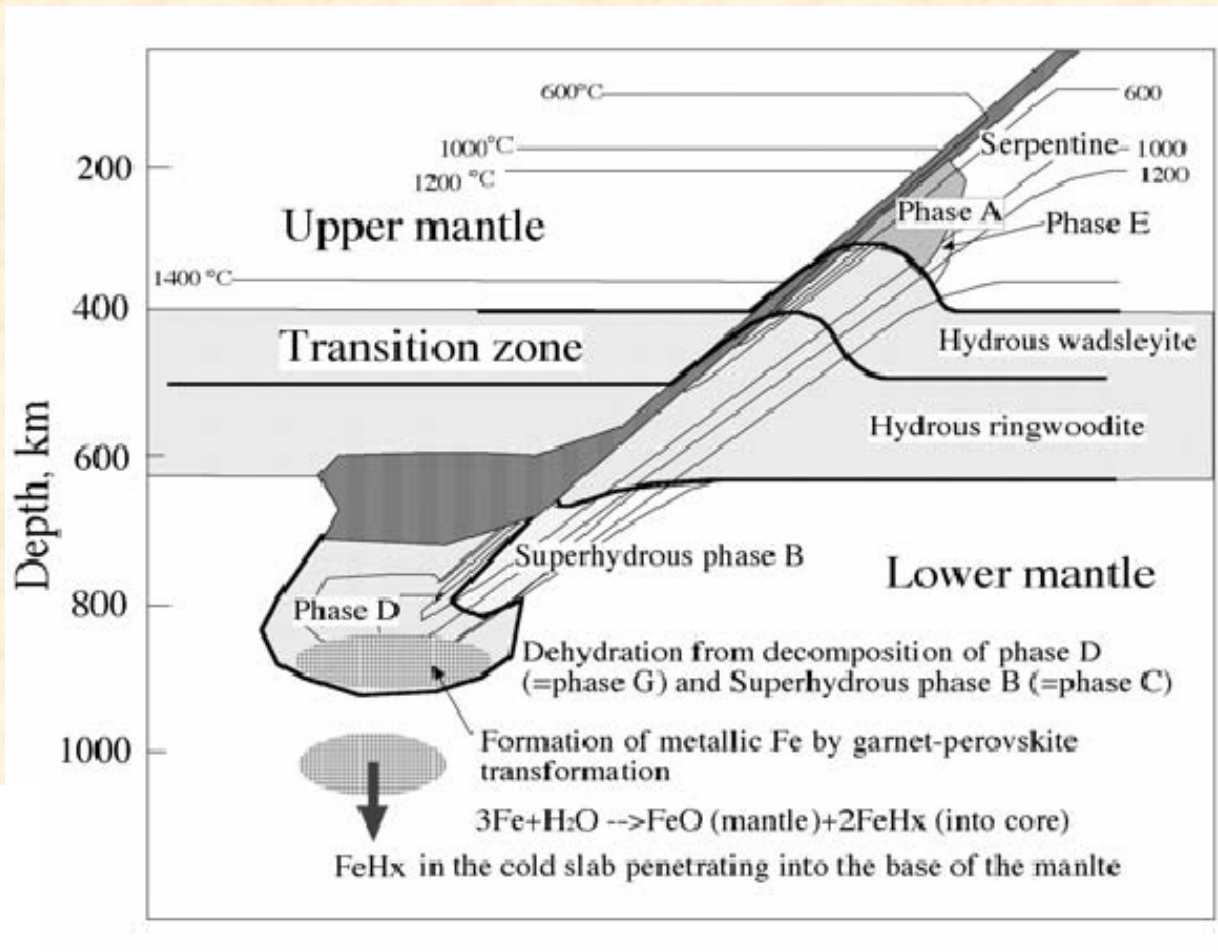
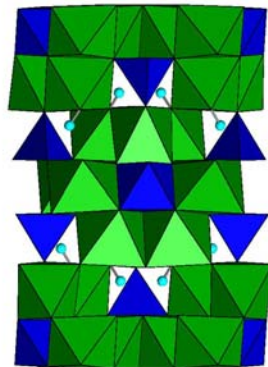
OH-chondrodite



Phase A



Phase B

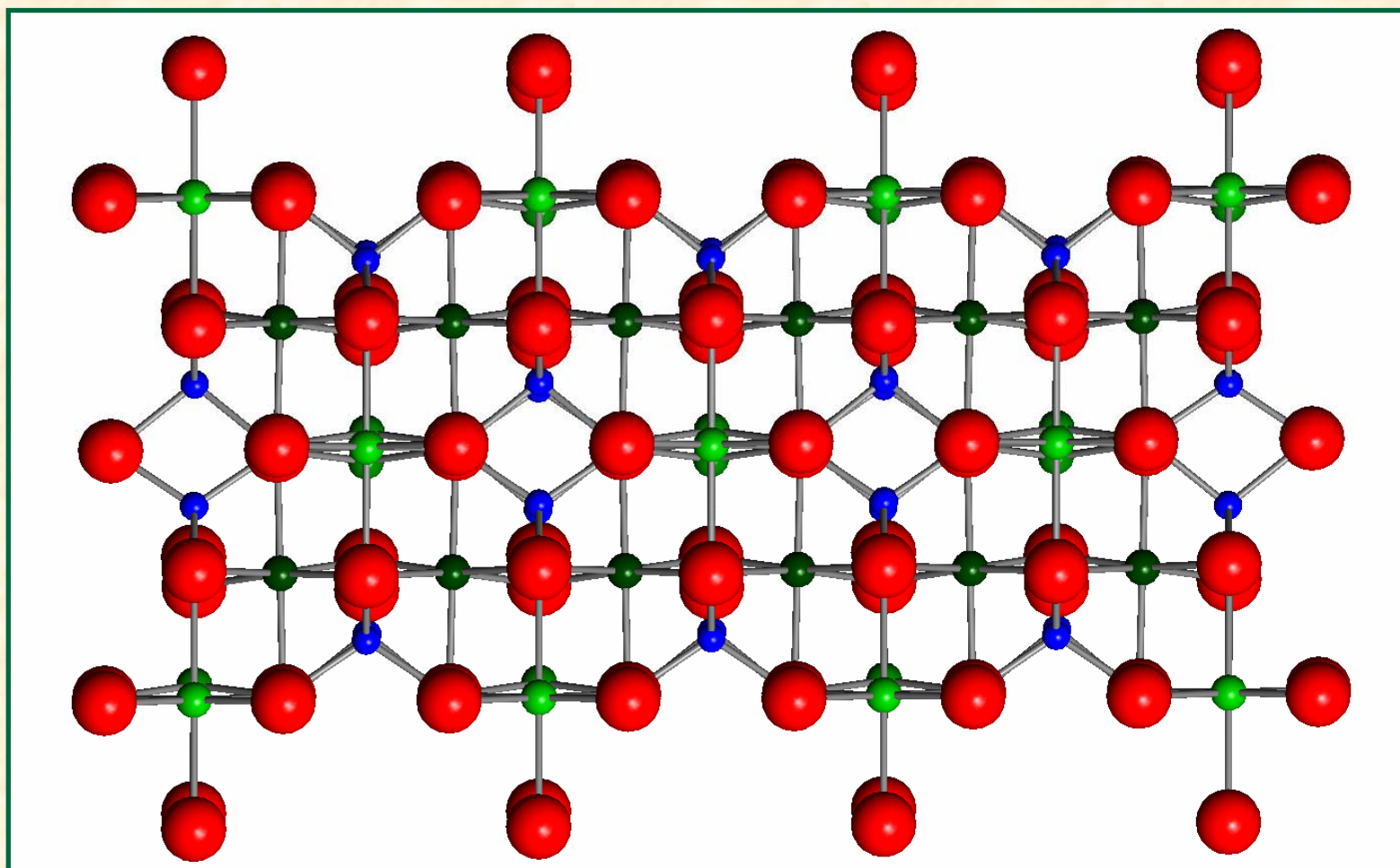


(from E. Ohtani)



Wadsleyite ($\beta\text{-Mg}_2\text{SiO}_4$)

Stable in the Earth's transition zone (400 km depth)



Size of high P - T phases and neutron fluxes are merging . . .

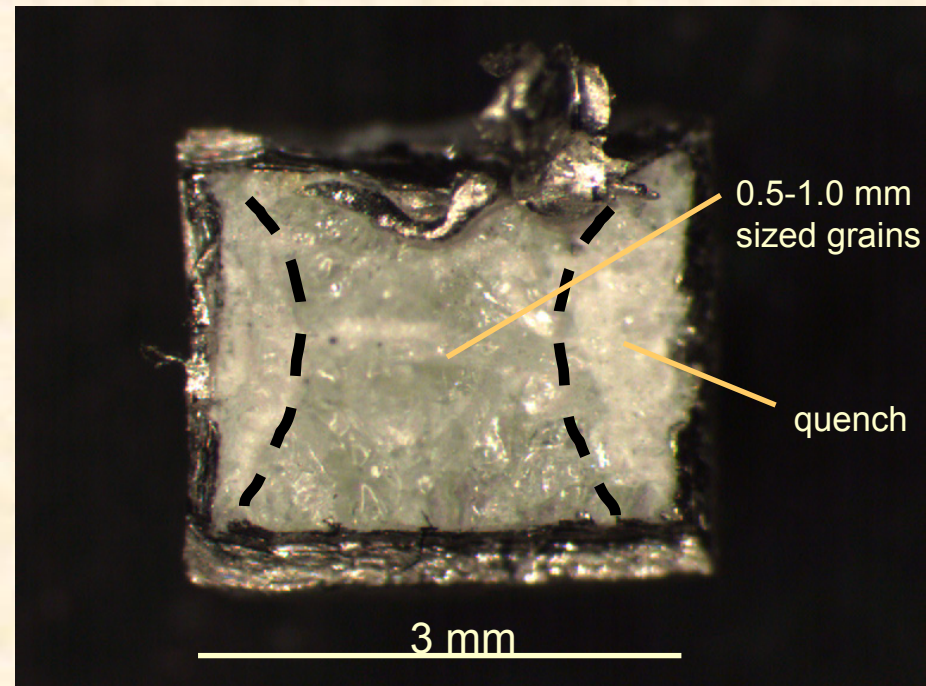


5000-ton large-volume press in Bayreuth

VTX



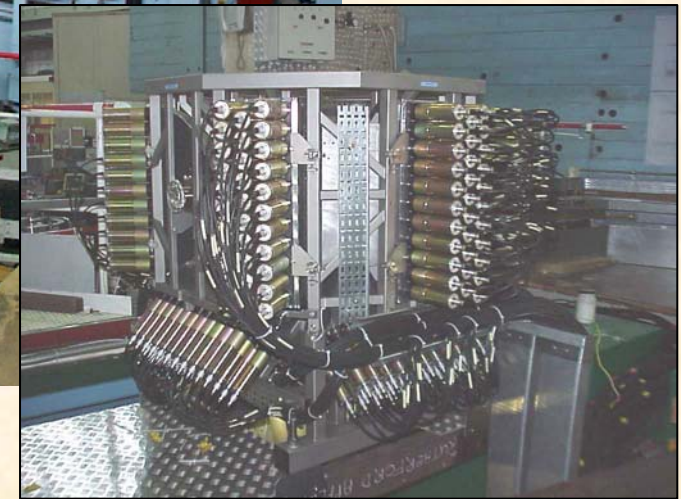
Steve Jacobsen (Geophysical Laboratory)
Daniel Frost (Bayerisches Geoinstitut)
Joseph Smyth (University of Colorado)



e.g. hydrous wadsleyite:
(containing ~1 wt% H₂O)



Hydrous wadsleyite: Single crystal ND



SXD instrument at ISIS

VTX

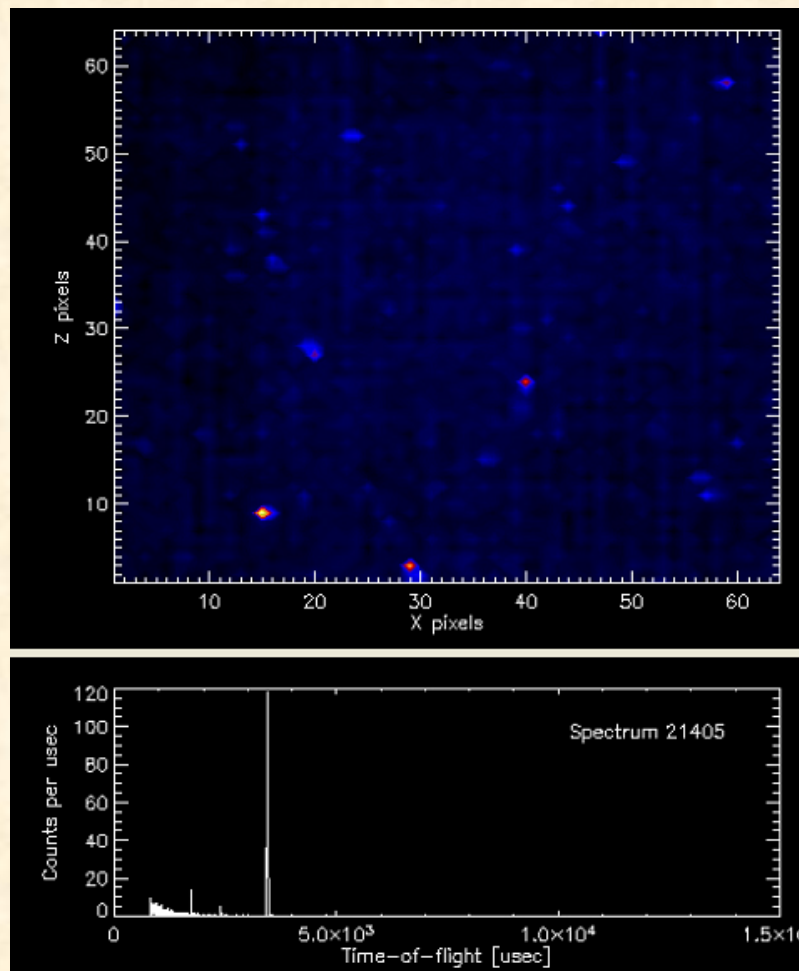
M. Gutmann

11-bank scintillating ZnS detector
ISIS
SPALLATION NEUTRON SOURCE

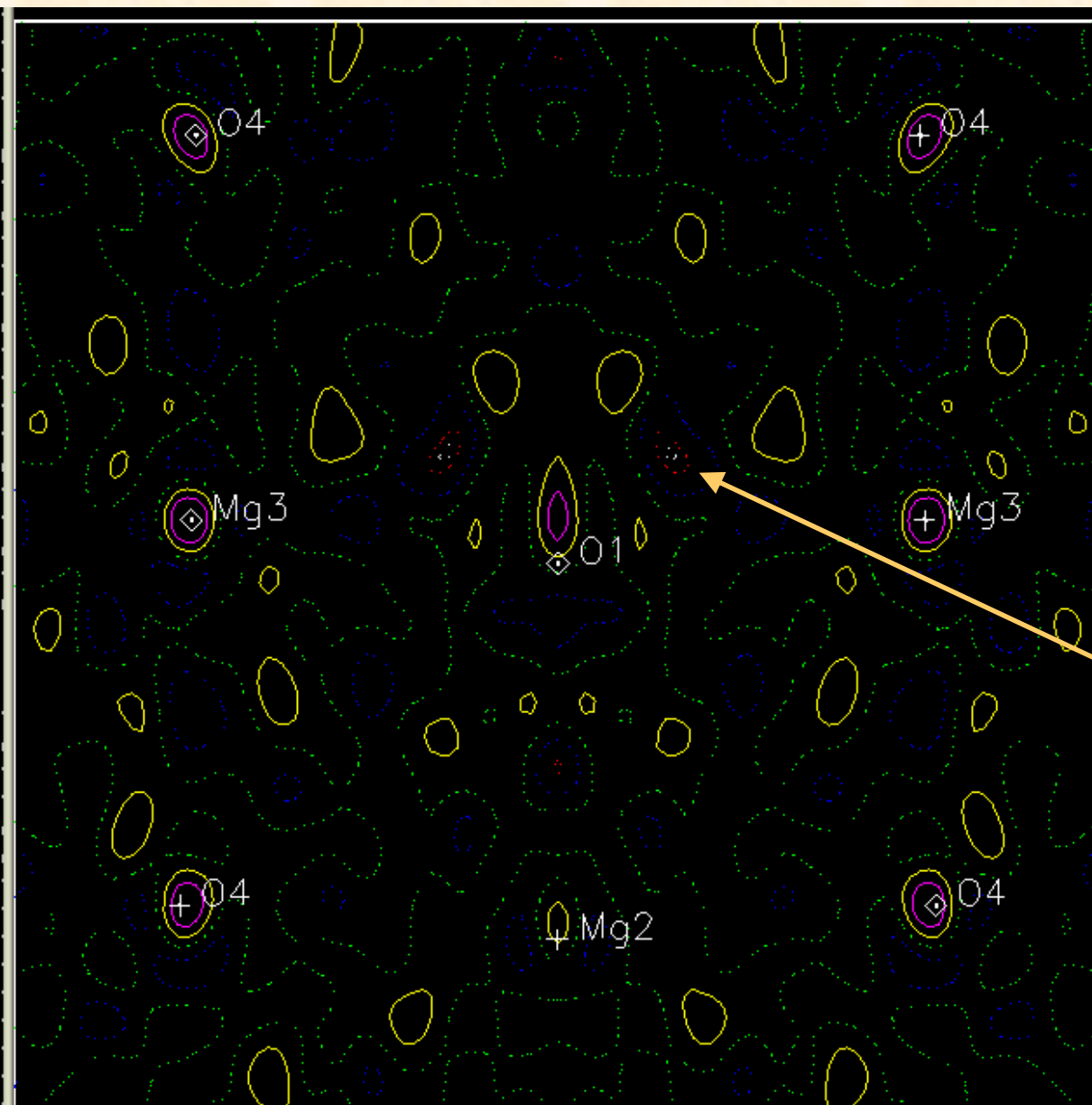
Mounting a wadsleyite crystal onto the SXD goniometer at ISIS



Screenshot: SXD2001/Matthias Gutmann



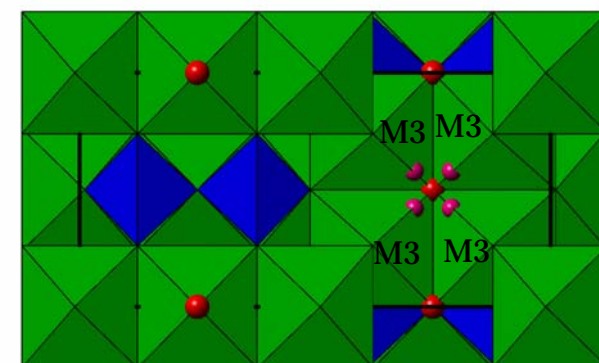
Neutron diffraction from single-crystal wadsleyite
Crystal volume is $\sim 0.25 \text{ mm}^3$



Center of reference
 0.500 0.750 0.720
 Height above center
 0.000 Å
 Map size 6.000 Å
 Orientation matrix
 U V UXV
 0.1237 0.0000 -0.1237
 -0.0614 0.0000 -0.0614
 0.0000 0.1208 0.0000
 Contours are drawn at
 -0.22 -0.20 -0.10
 0.00 0.10 0.20
 Times 1.

There is about 10%
 M3 vacancy

H14: 0.42 0.79 0.79



$d(\text{O}-\text{H})=0.9\text{Å}$

wadsleyite combined data 17222 17223 17224 DELF
 from C:/data/ISIS_Neutron_Data/new_Apr 05 20:12:04 2005

VIA

Atomic Displacement Parameters

“ ADPs are still regarded by many scientists as unreliable, since in many of the earliest structure determinations, ADPs often became repositories for much of the error in the structure refinement....”

(Sales et al. 1999)

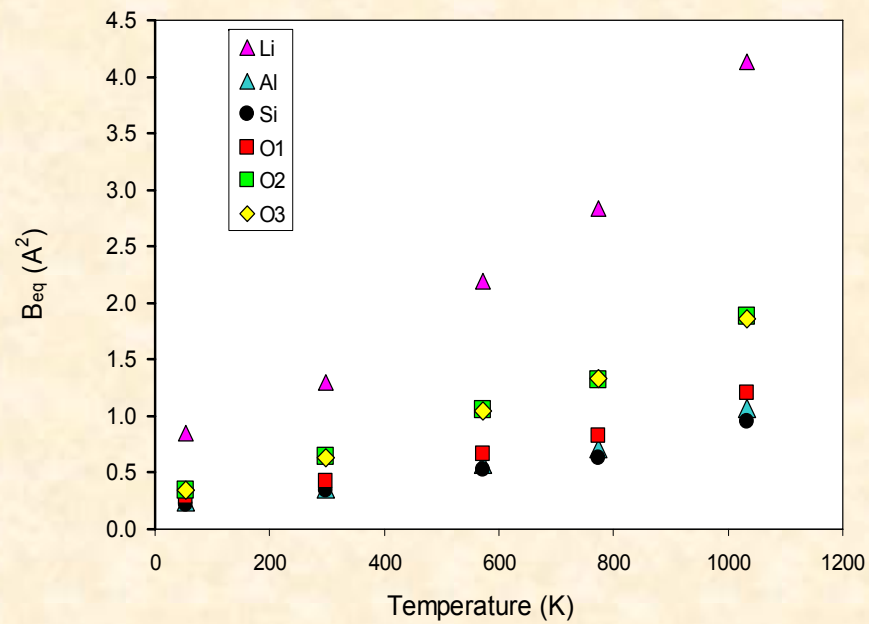
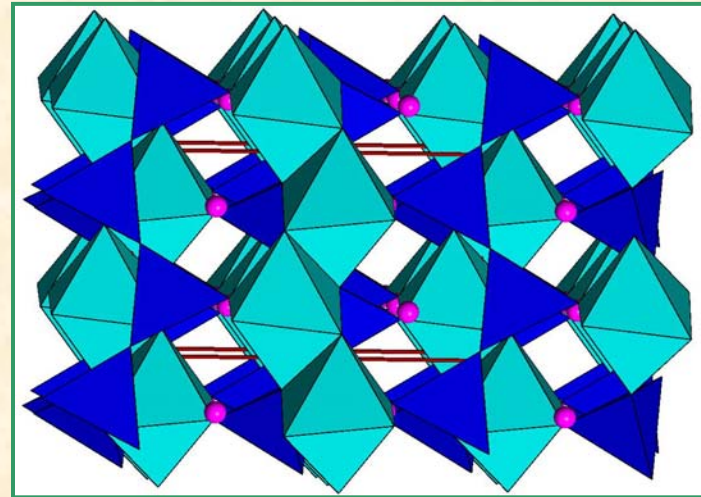
Why neutrons?

- X-ray diffraction yields information on the time- and volume-averaged electron- charge distribution in the crystal.
- Neutron diffraction instead yields information on the position of the atomic nuclei and their thermal motion and is therefore the preferred primary technique to measure reliable adp's.



Spodumene, $\text{LiAlSi}_2\text{O}_6$

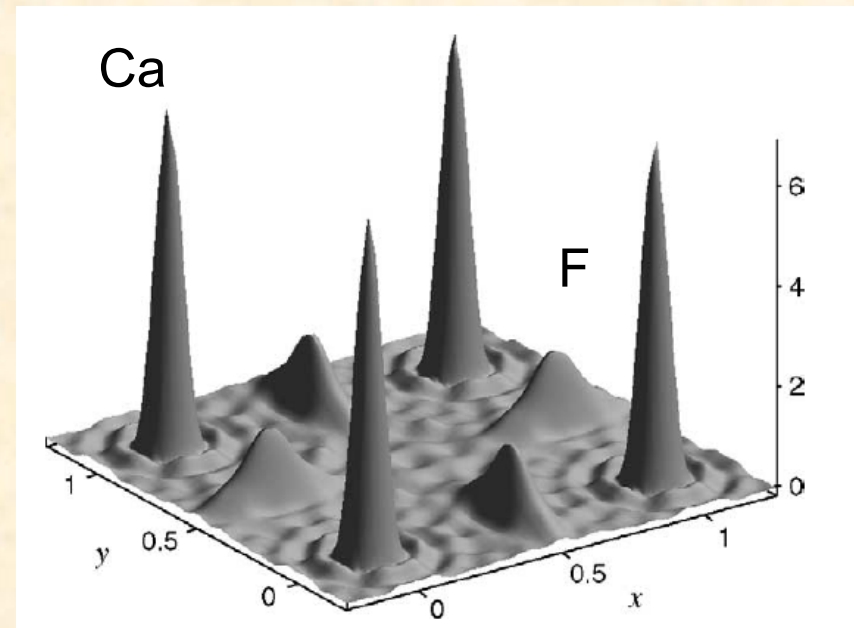
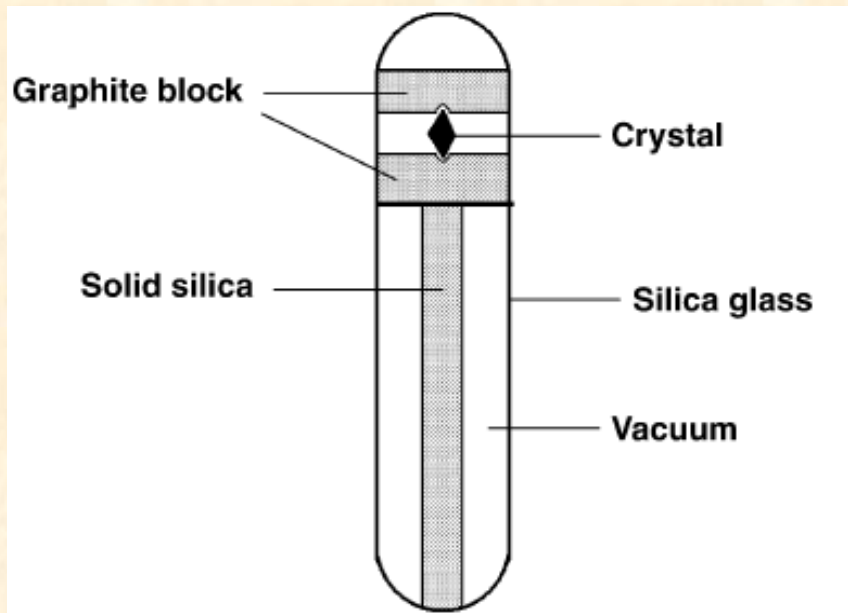
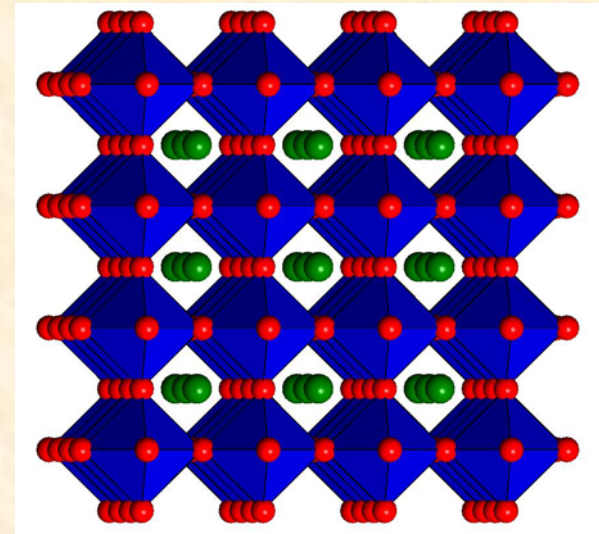
- ADP (B_{eq}) for Li in spodumene larger than that at $M2$ in other pyroxenes.
- The presence of significant zero-point motion is in agreement (diopside, albite, anorthite, pyrope)

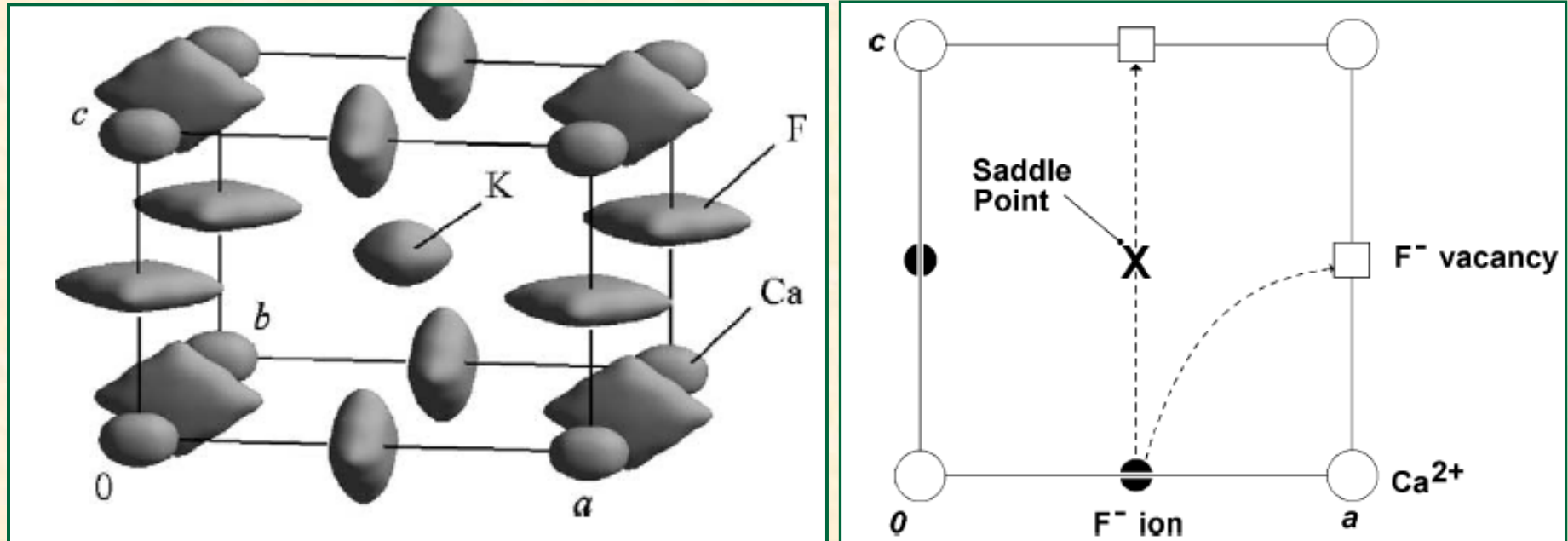


Tribaudino et al. (2003)

Anion Disorder in KCaF_3

- fast ion conductor at high T
- High-T SND, D9 at ILL



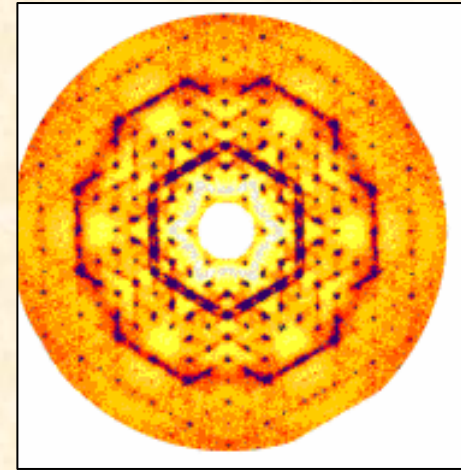
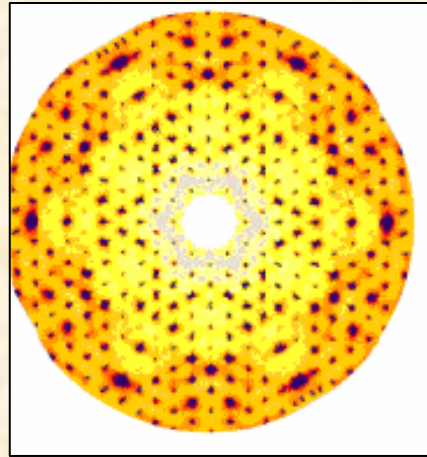


- The F⁻ ions show a large degree of anisotropy in their vibrational envelopes and appear to vibrate towards a saddle point, at the centre of a cube face, between two neighboring K⁺ ions.
- Vacancy migration mechanism involves the F ion jumping to a next nearest neighbor site in the (100) plane

Other applications of ADPs

- *Sales et al. (1999) showed for large classes of clathrate-like compounds, the room temperature ADP data reported as part of crystal structure determinations can be used to estimate the Debye temperature, velocity of sound, mean free path of phonons, lattice thermal conductivity, heat capacity, and the Einstein frequency of the rattler.*

Diffuse Scattering

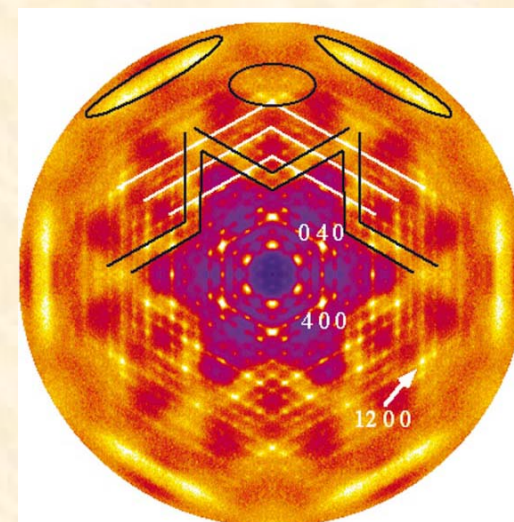
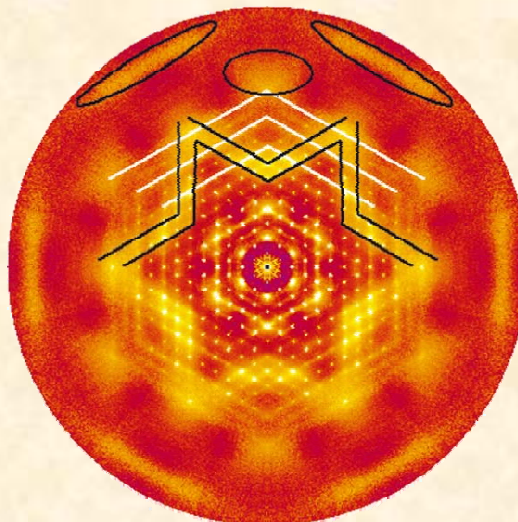
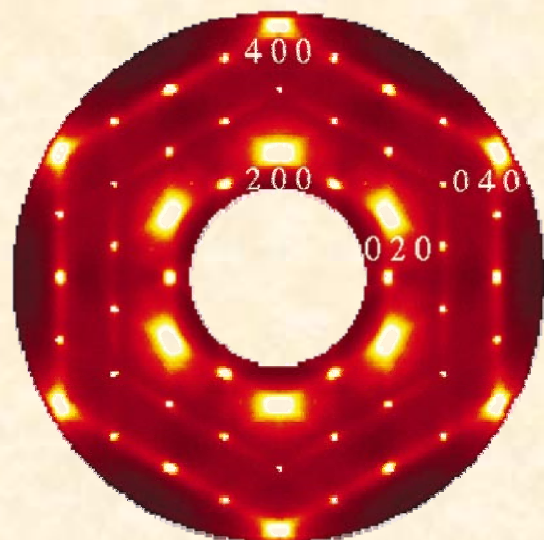
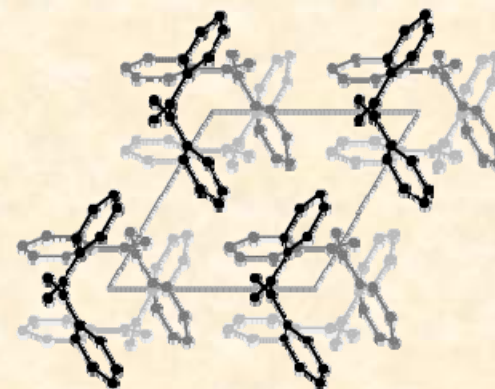
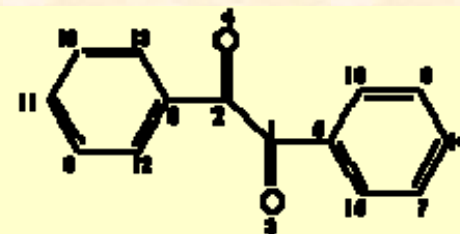


M.G. Tucker, D.A. Keen & M.T. Dove (2000-2001)

- Deviations from average structure
 - e.g. disordered materials
 - thermally induced disorder
 - disorder resulting from defect impurities
 - structure of short range magnetically ordered systems
- Incommensurate structures

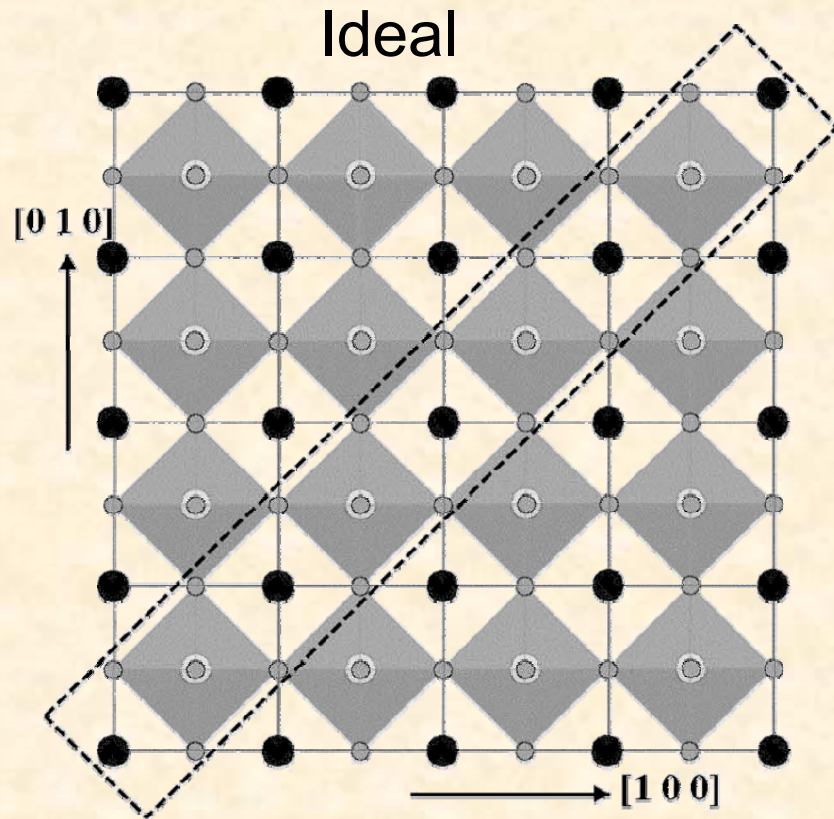
Benzil

- Welberry et al. (2003) TOF Laue on $C_{14}D_{10}O_2$
- Phonon and diffuse scattering modes overlap but can be deconvoluted using high Q data from SND

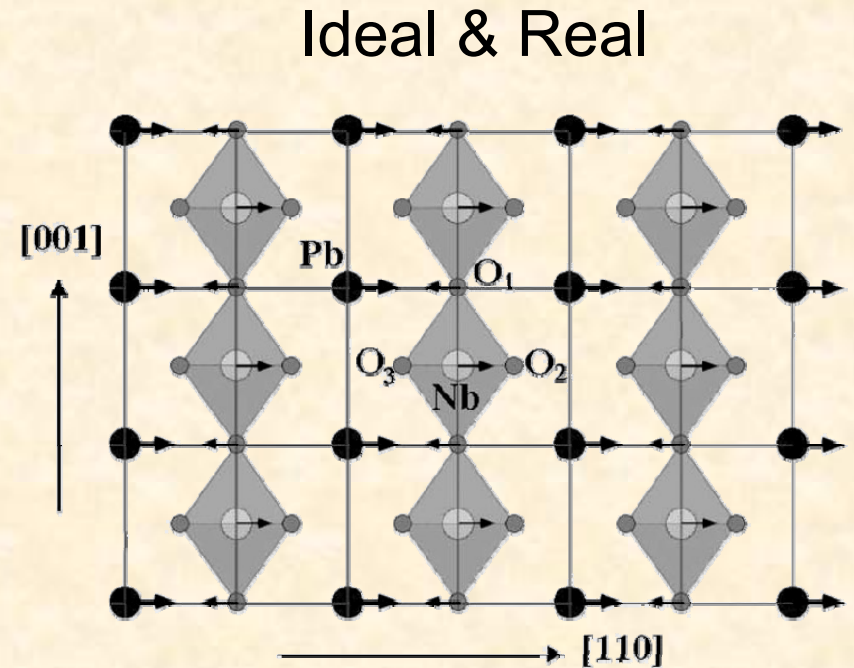


Welberry et al., J. Appl. Cryst., 2003

Overall Structure Interpretation of PZN



Conventional data
analysis & refinement



Monte Carlo data
analysis & refinement

*To correctly describe the real structural features
modulated structure analysis of diffuse scattering*

Relaxor Ferroelectric $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3 \Rightarrow \text{PZN}$

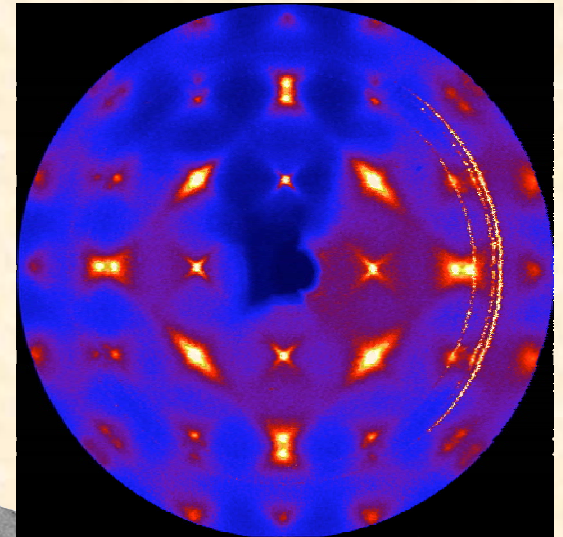
X-Ray



Neutron



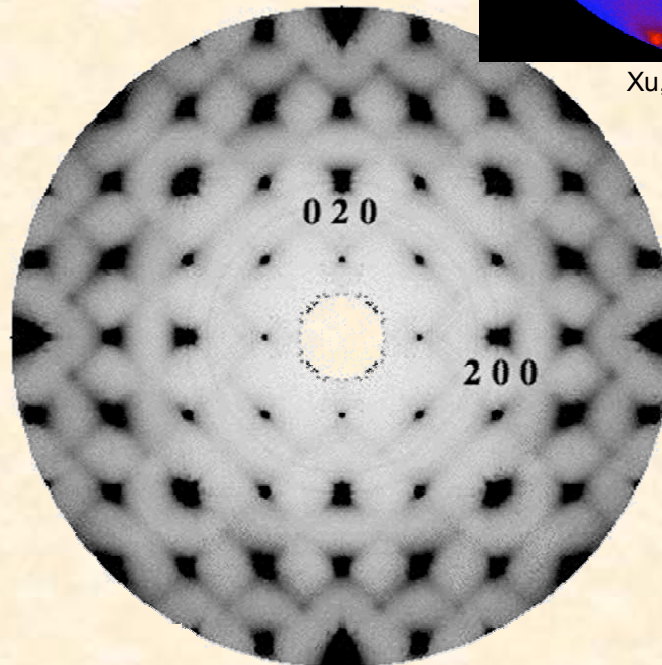
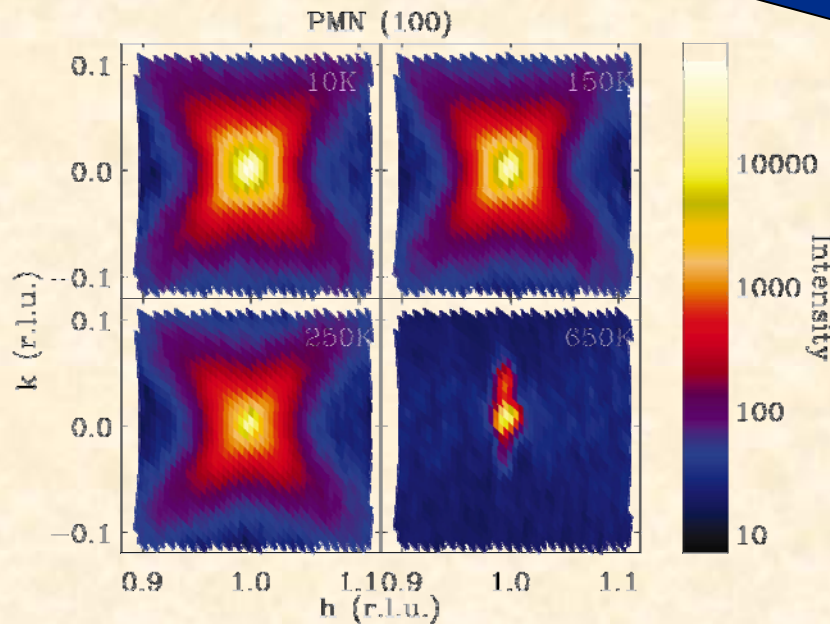
PZN-8PT T=200 K



Xu, Zhong, Shirane, Phys. Rev., B 70, 174109 (2004)

XU, SHIRANE, COBLEY, AND GEHRING

PHYSICAL REVIEW B 69, 054112 (2004)

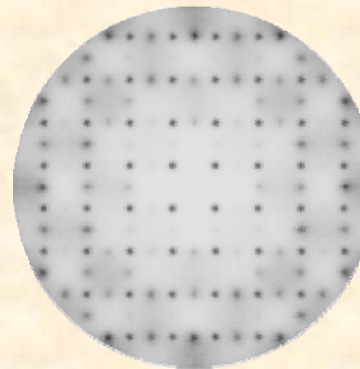
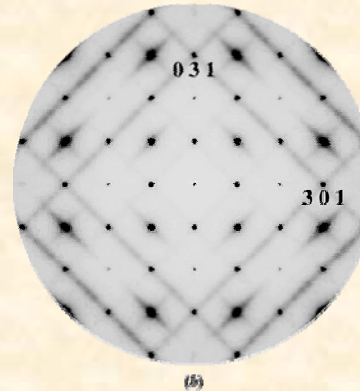
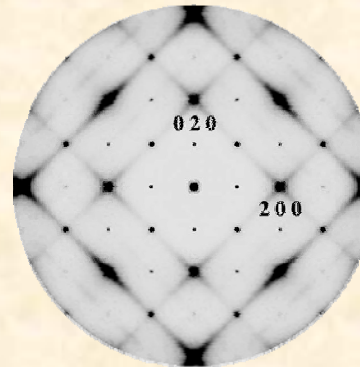
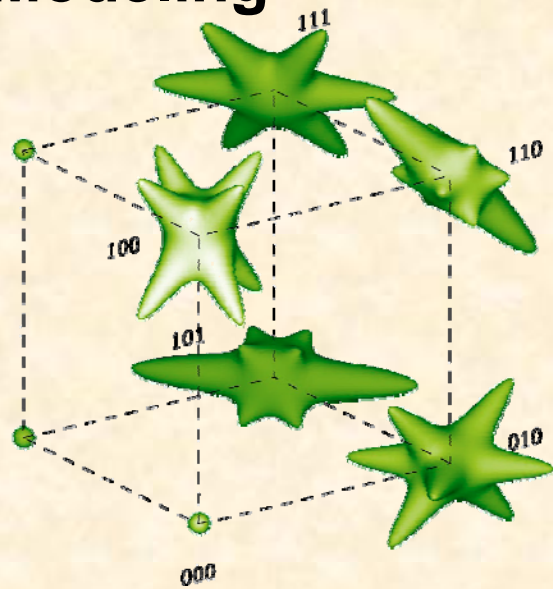


Welberry *et al.*, J. Appl. Cryst., 38, 639 (2005)



Analysis Results - Global and Local Pattern

- MC Simulation
- Modeling



⇒ Deriving the modeling results spanned several years

⇒ Disordered part of structure influences properties

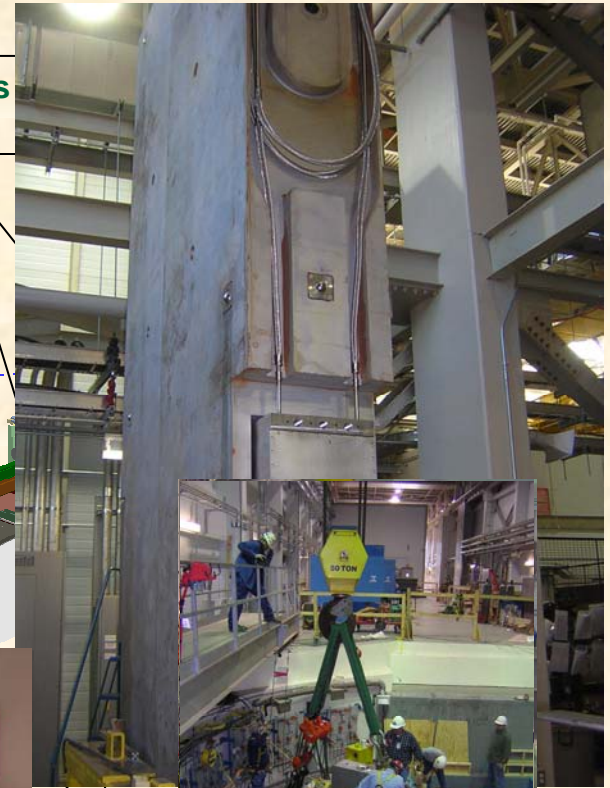
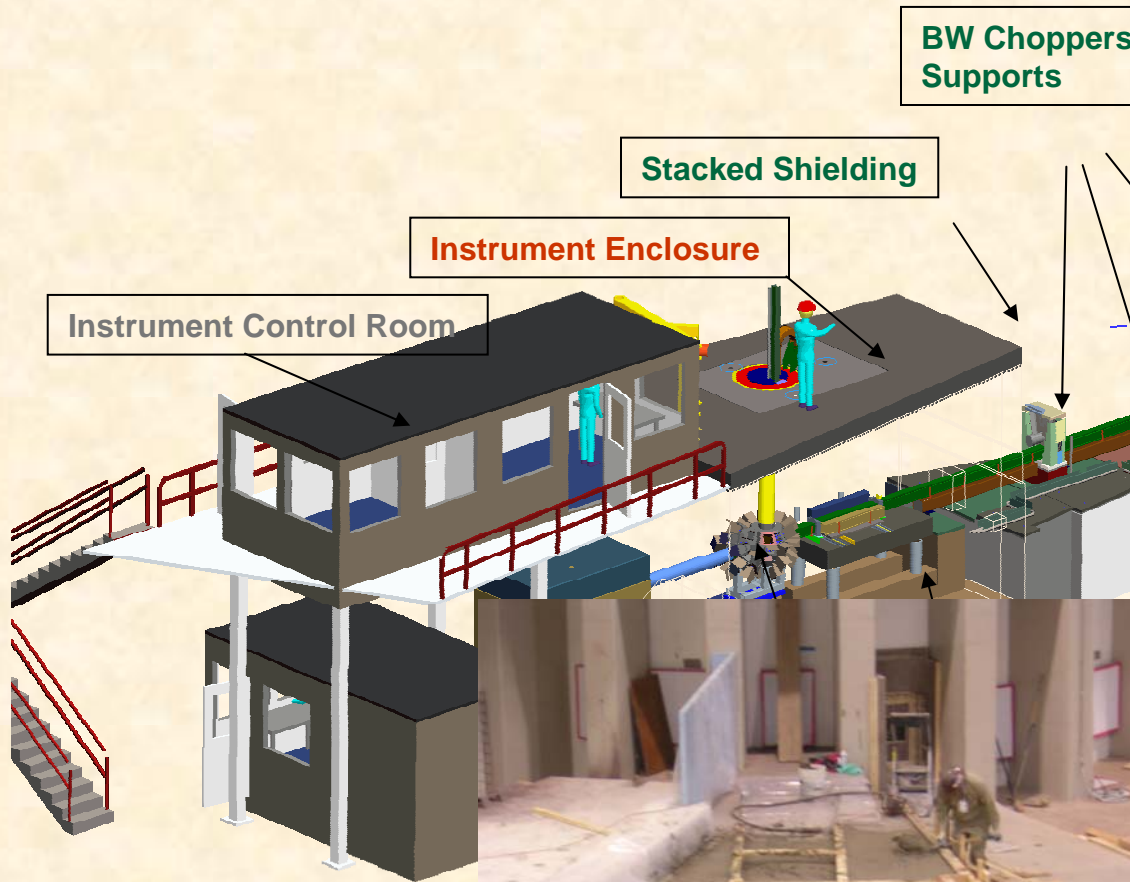
New Horizons

- Faster structures ($\ll 1$ day)
- More complex structures
- Smaller crystals ($\ll 1$ mm³)
- More parametric (T, P, H, E, \dots) studies
- More quantitative diffuse scattering

Moving forward



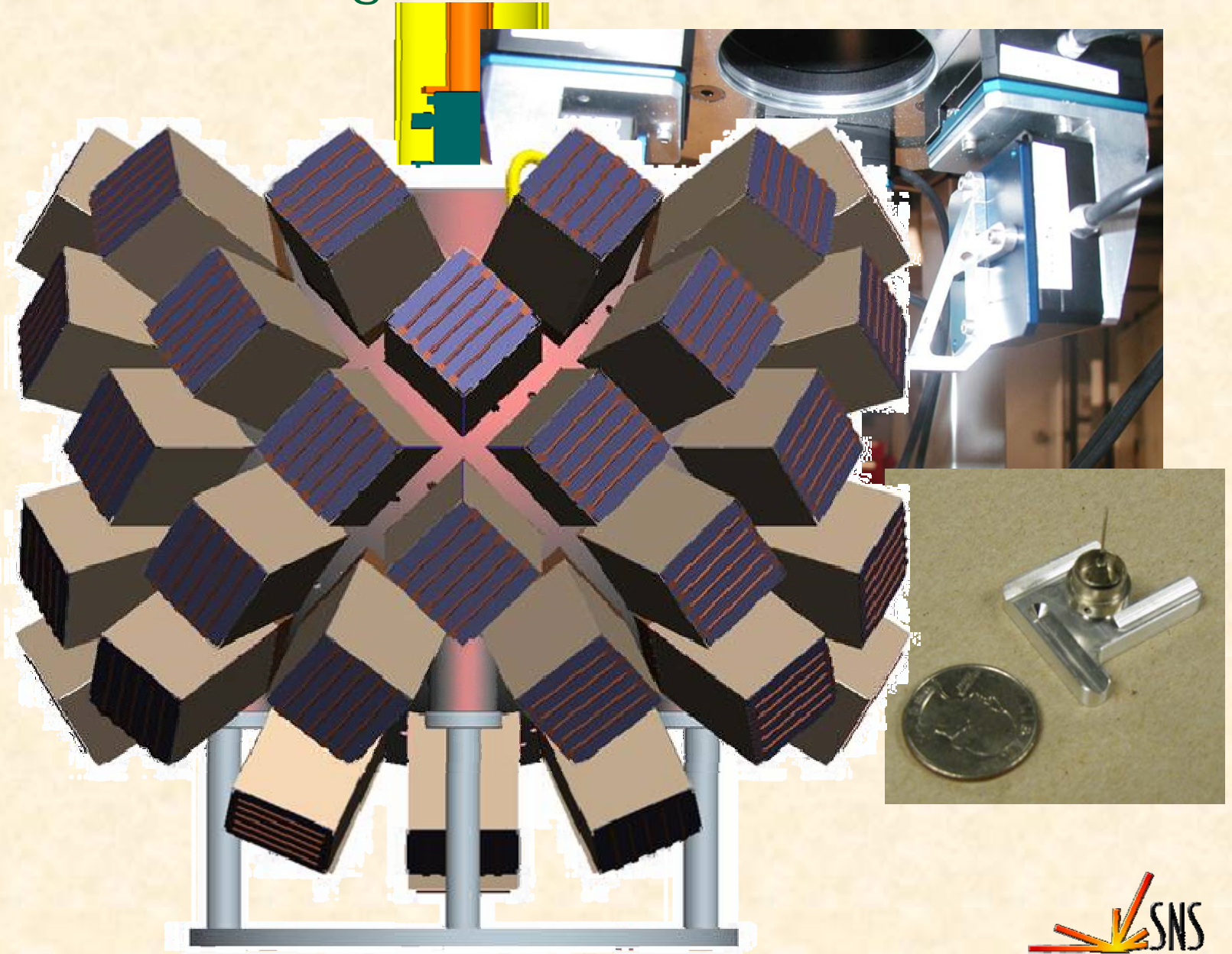
The Single Crystal TOPAZ Beamline at SNS



Shielding
de



Sample Positioning, Environment, Detectors



You can teach robots anything....

Acknowledgements

•TOPAZ-SCD Instrument Support

- IDT and Executive team: Bob Bau, Art Schultz, Tom Koetzle, Thomas Proffen, Bryan Chakoumakos, Heinz Nakotte, Bo Iversen
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- Alexandru Stoica, Hal Lee, Xun-Li Wang

• Micro Focusing KB- Mirror (Spearheaded by SNAP team)

- Group of Gene Ice, Cam Hubbard, Chris Tulk

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• Management, Project Support, QA, etc.

• Project Funding

