Single-Crystal Neutron Diffraction: Present and Future Applications

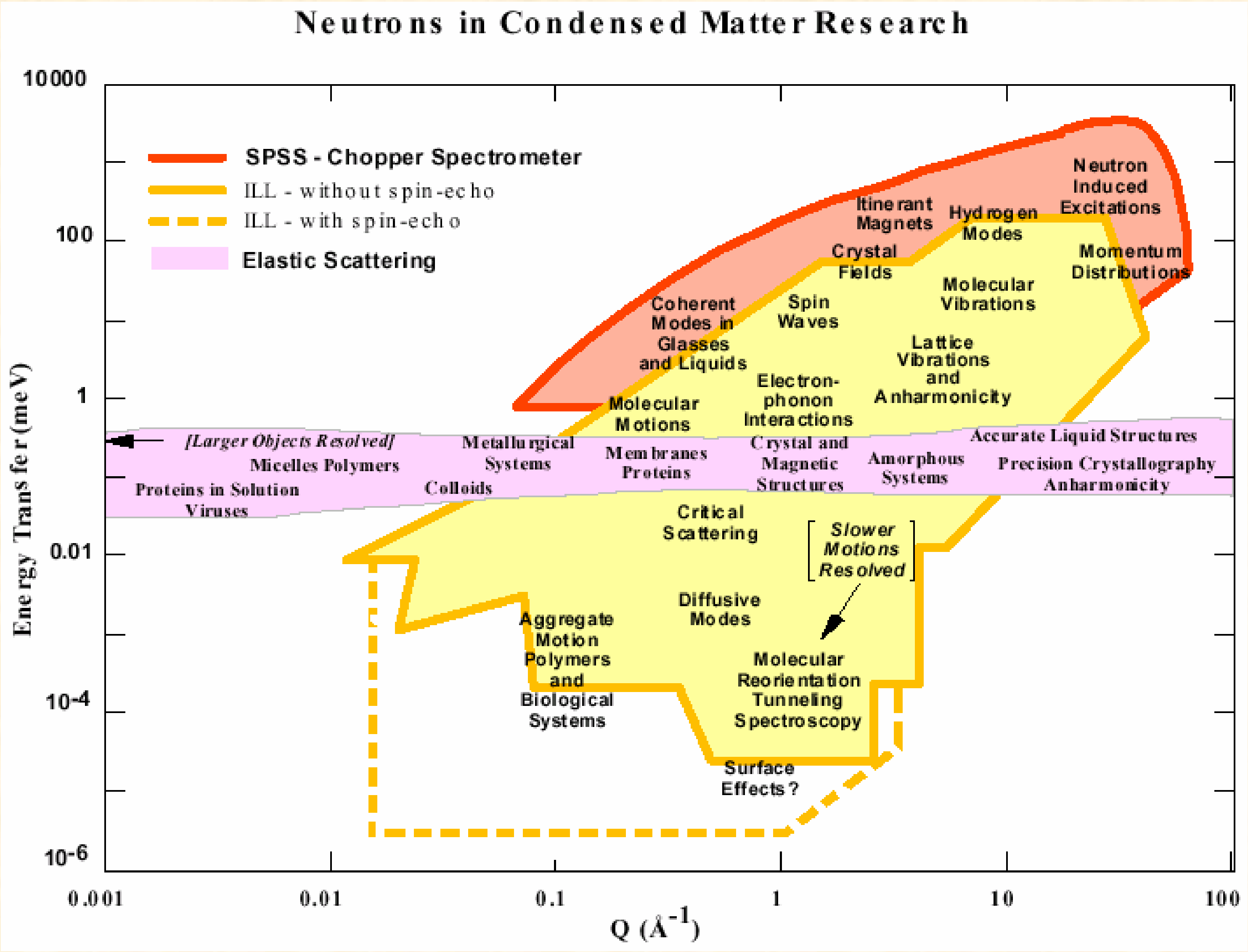
Christina Hoffmann

SNS

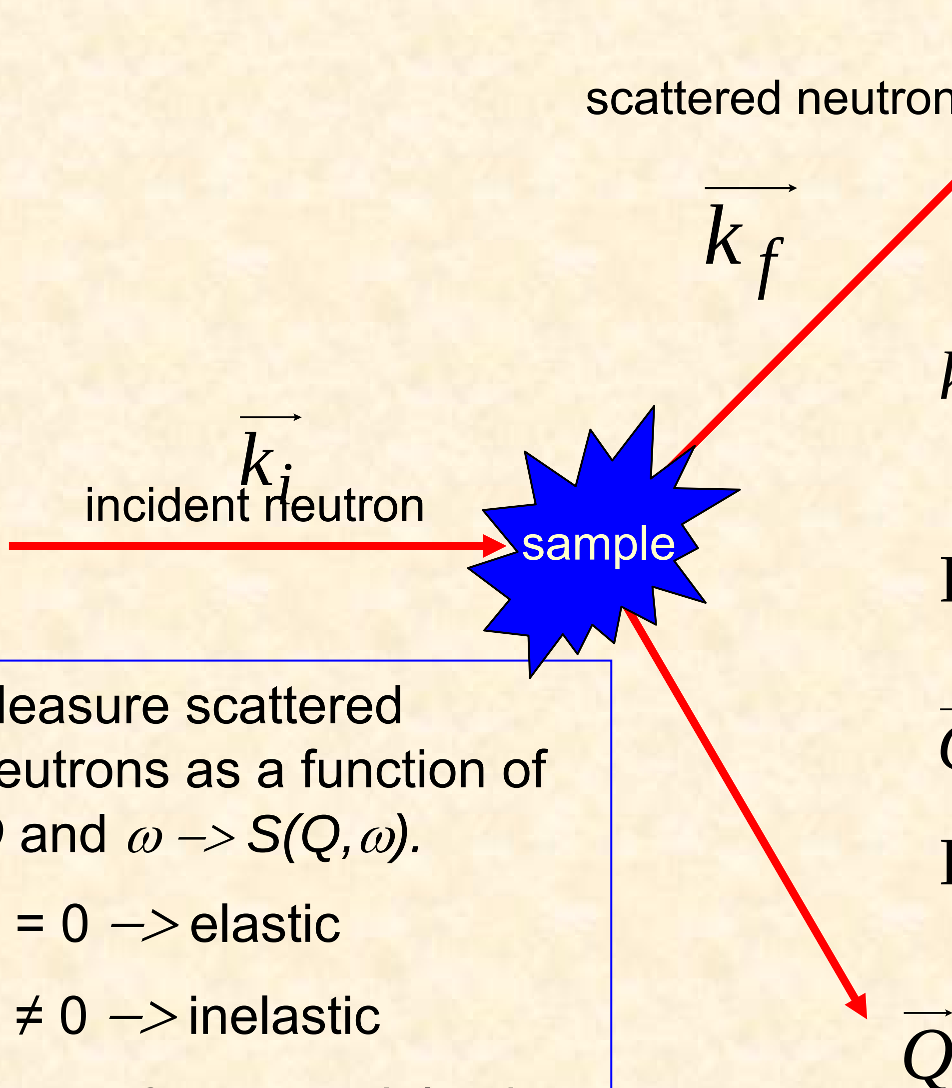
Nancy Ross

Virginia Tech

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 ω –> *S(Q,ω)*.

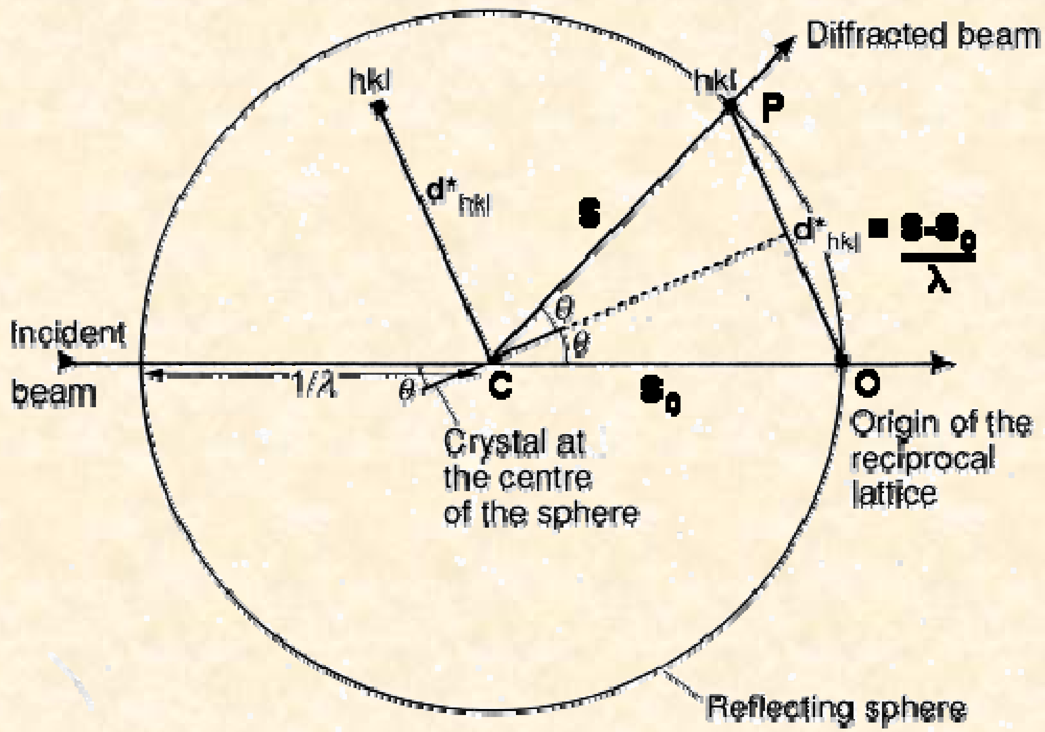
ω = 0 –> elastic

ω ≠ 0 –> inelastic

ω near 0 –> quasielastic

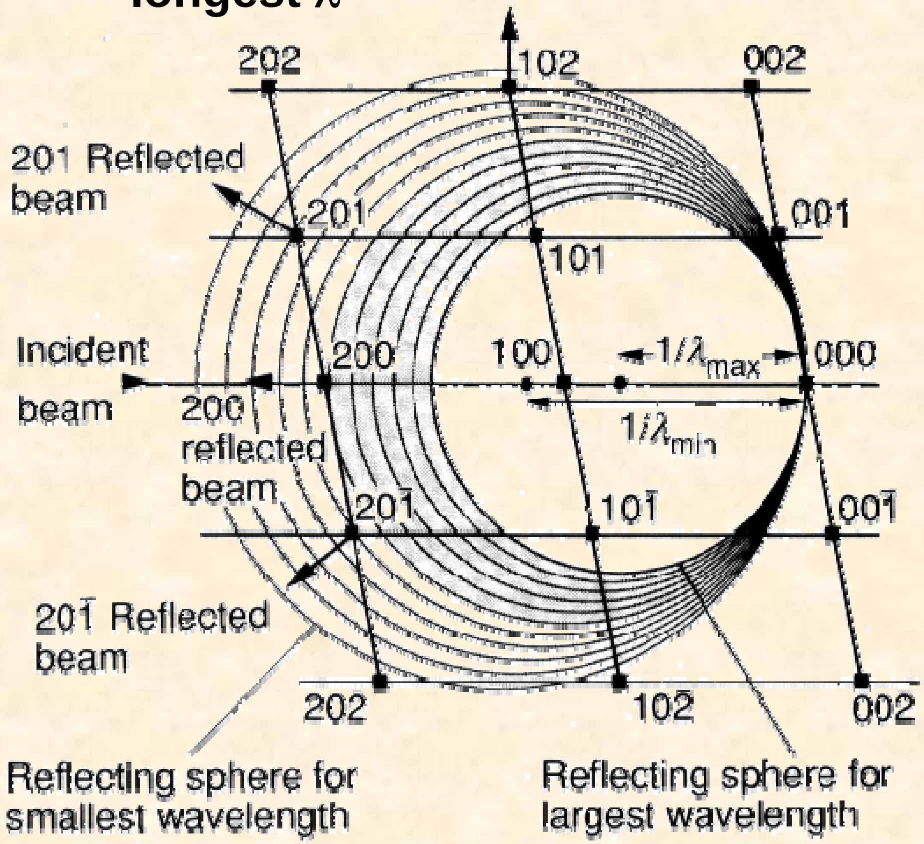
Ewald Construction

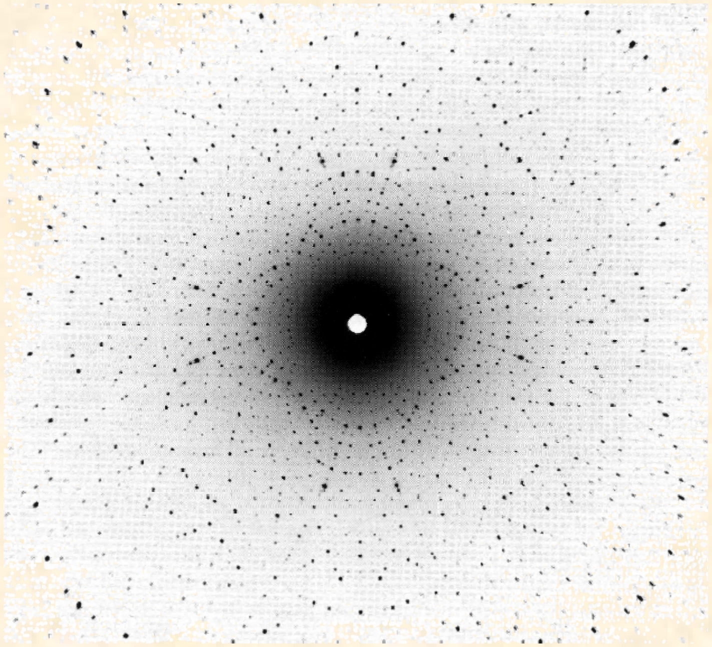
The origin of direct and reciprocal space are separated by placing the crystal at the center of a sphere of radius $1/\lambda$. The origin of reciprocal space is placed on the surface of the sphere where S_0 (the incident beam) exits the sphere.



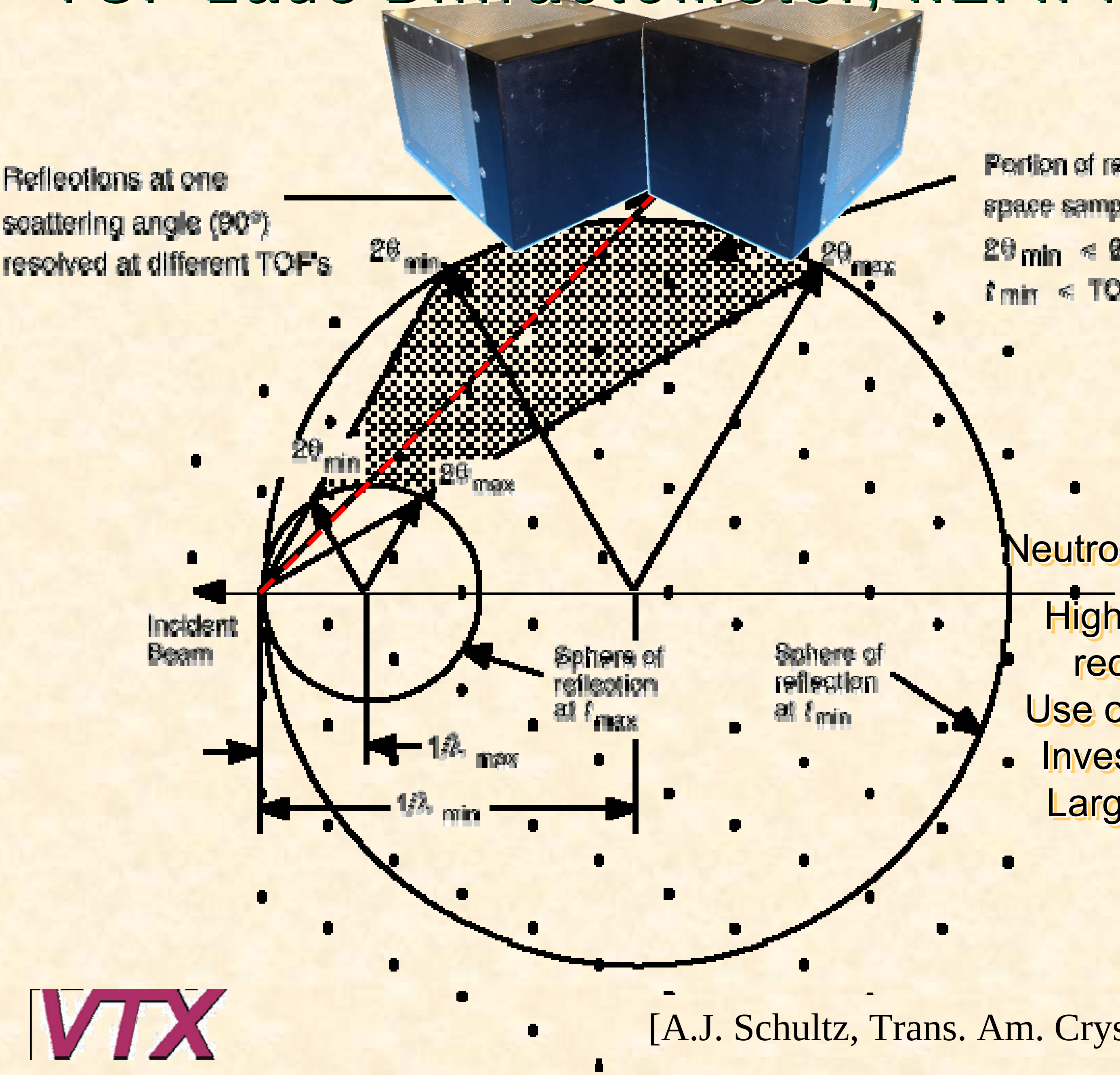
Laue Geometry

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



Neutron TOF Laue diffraction:

- Highly efficient survey of reciprocal space (RS)
- Use of polychromatic beam
- Investigate Volume of RS
- Large Q range (λ band)

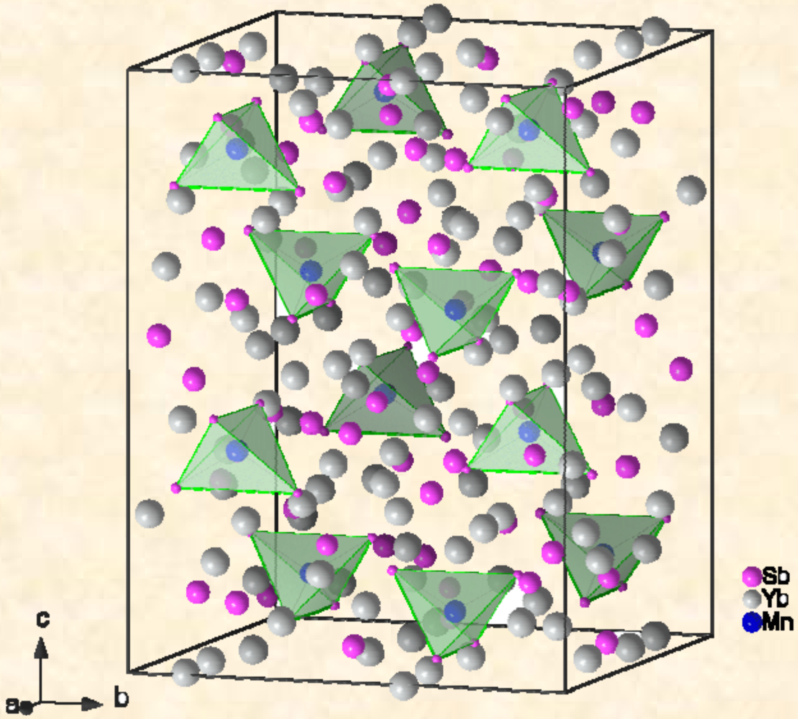
[A.J. Schultz, Trans. Am. Cryst. Assoc. **29**, 29 (1993)]

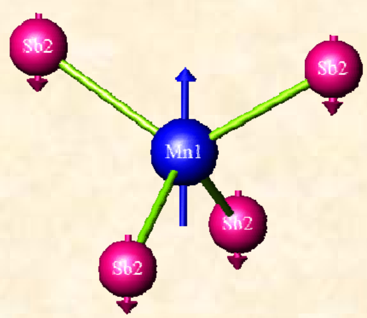
A TOF Laue SND Measurement

- **Mount a sample ➔ sample sizes are > 1mm^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-alligned 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. SchultzIPNS], 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]

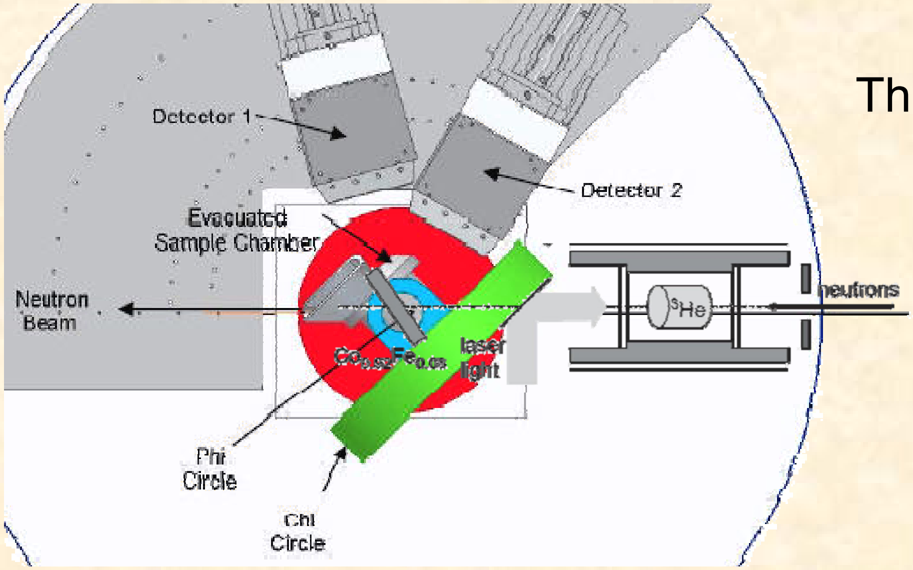
Mounting the Single Crystal Sample..

- **Mount the single crystal on a sample pin for cryogenic, vacuum, or heating experiments to refine the nuclear atomic or molecular structure**

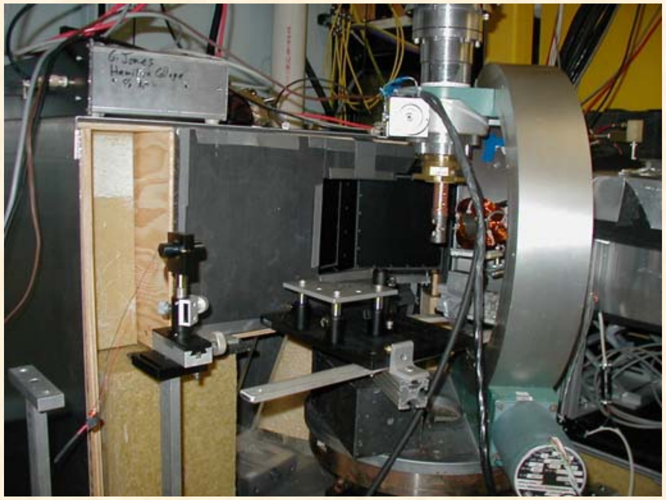
- **Mount the sample between permanent magnets to refine nuclear + magnetic structure**

- **Special mounting schemes for pressure, gas flow, larger magnetic fields,..**

The IPNS – SCD Instrument:

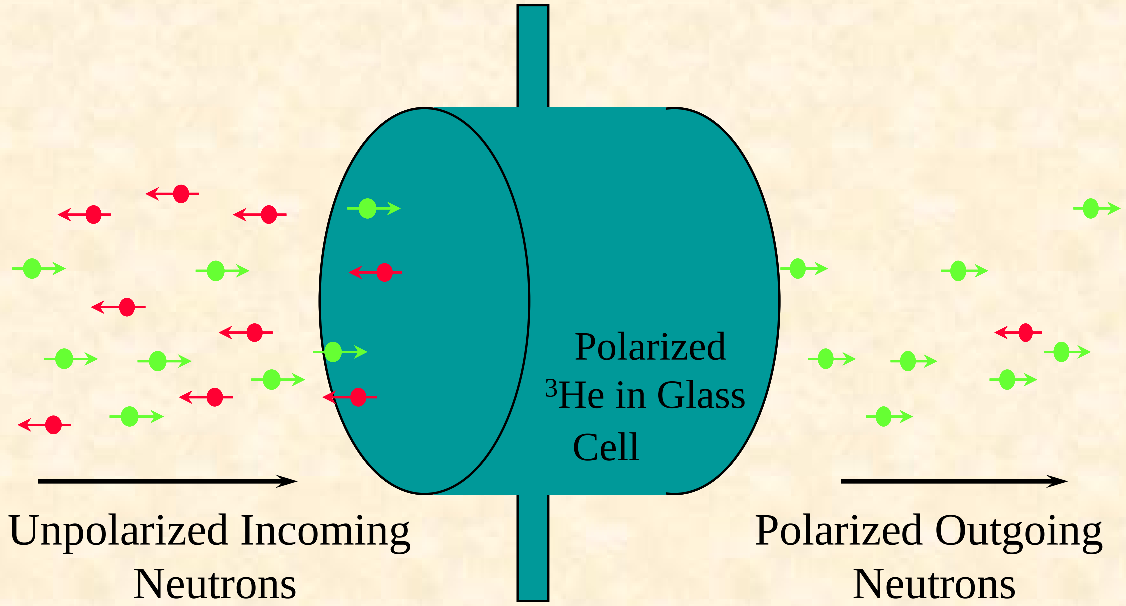


The



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

Spin Dependent Neutron Absorption in Polarized ^{3}He

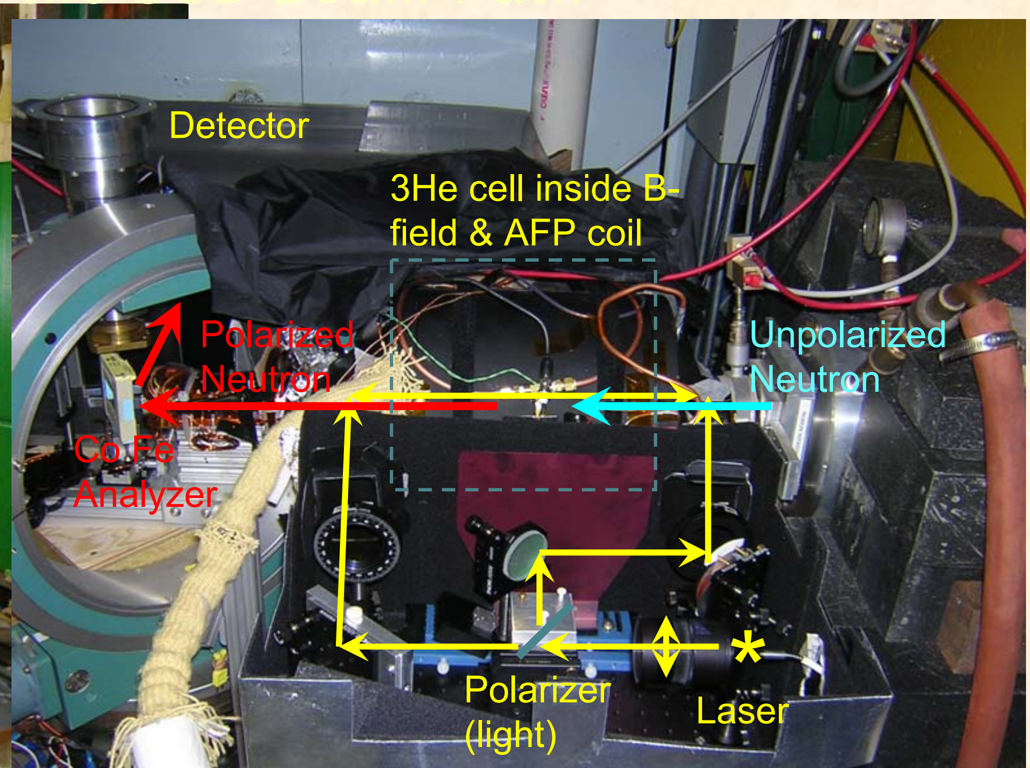


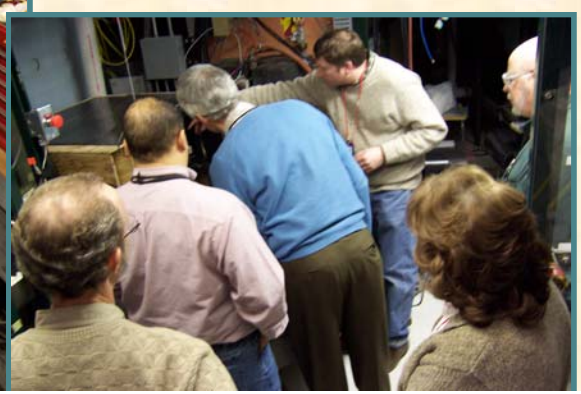
$$^3He + n \longrightarrow {}^4He^* \longrightarrow p + {}^3H$$

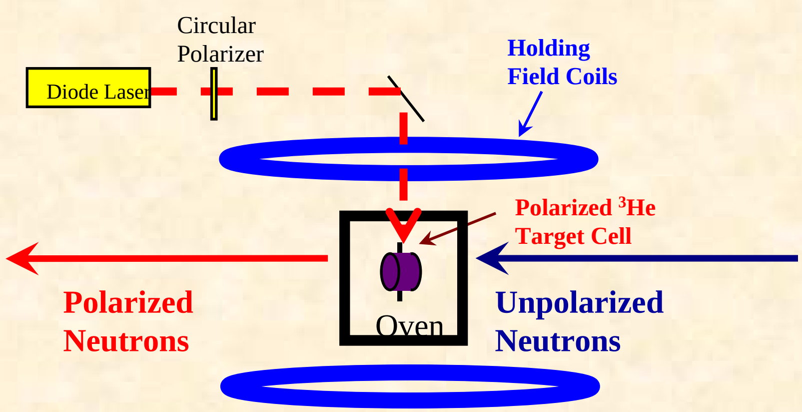
2006 Experiment at SCD, IPNS, Polarization Setup

Special now but Standard in the Future

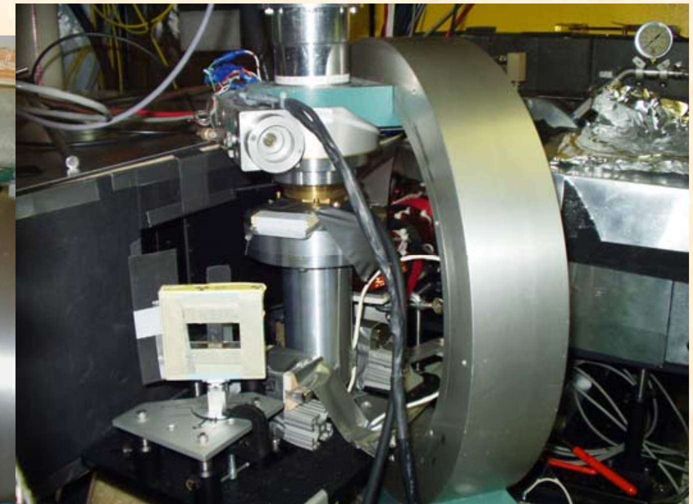
The Incident Neutron Beam is Polarized by Installing a ^{3}He Neuron Spin Filter on the SCD Beam Path

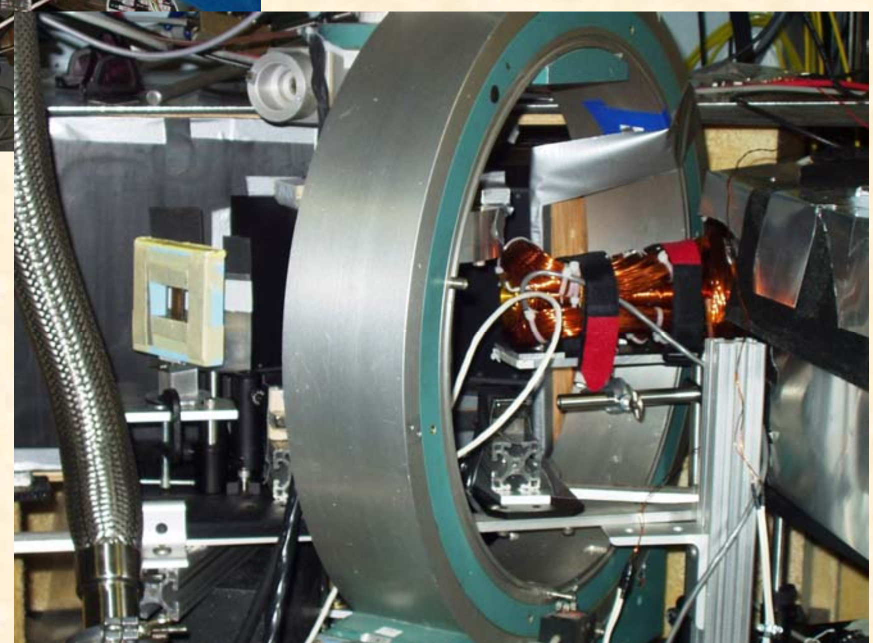






Mounting the Sample on the Instrument..

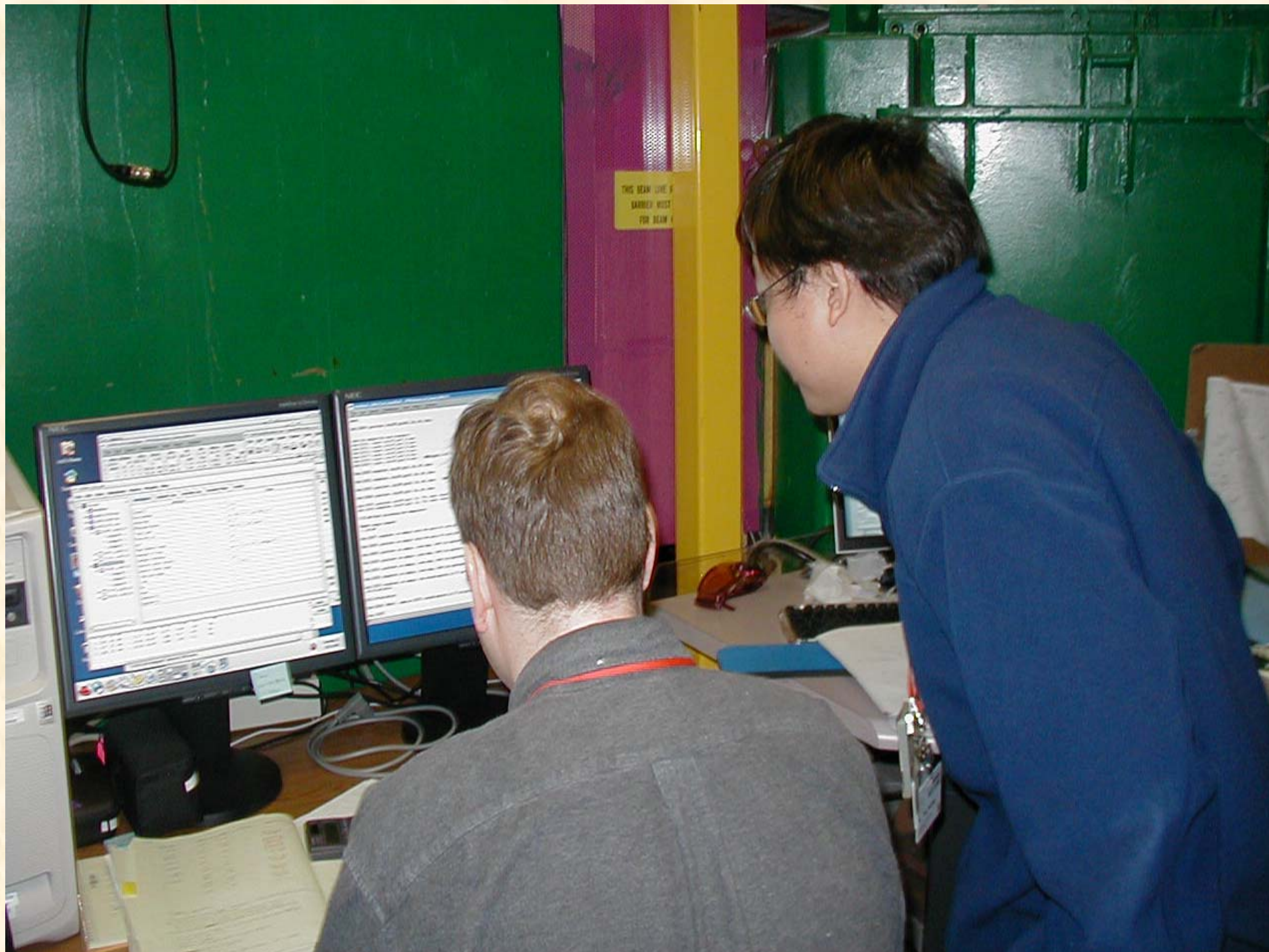




- **The sample with the magnet is mounted on the displex**

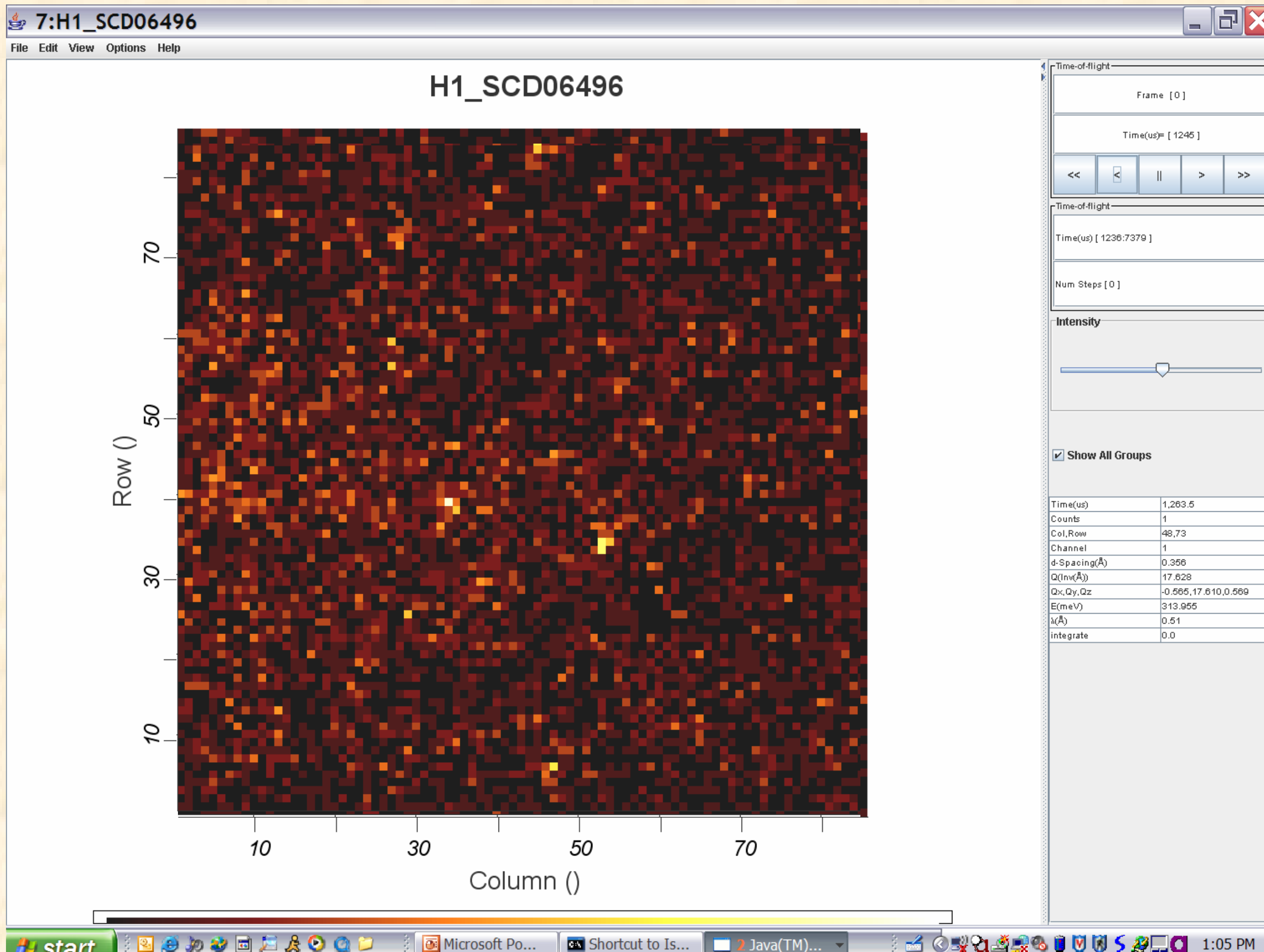
Start a Data Collection

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



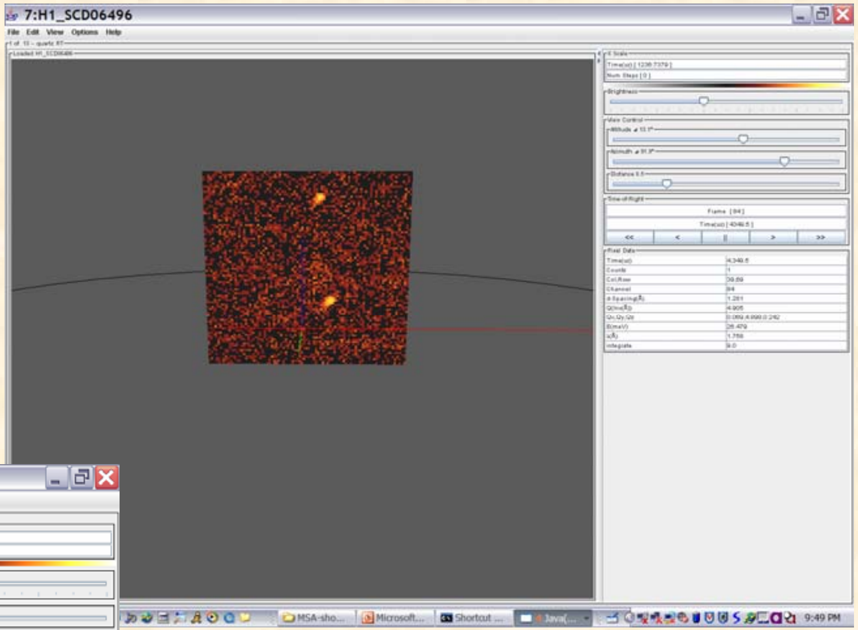
Start a Data Collection

- **First reflections on the detector**

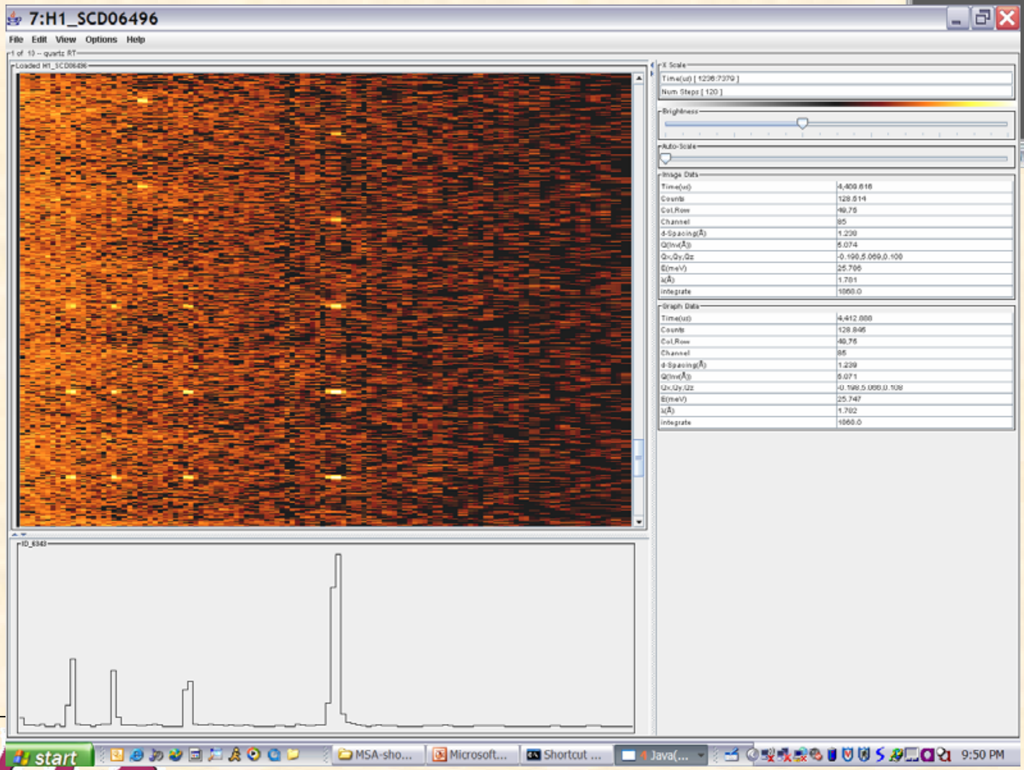


Detector Representation of Data

Position of reflections

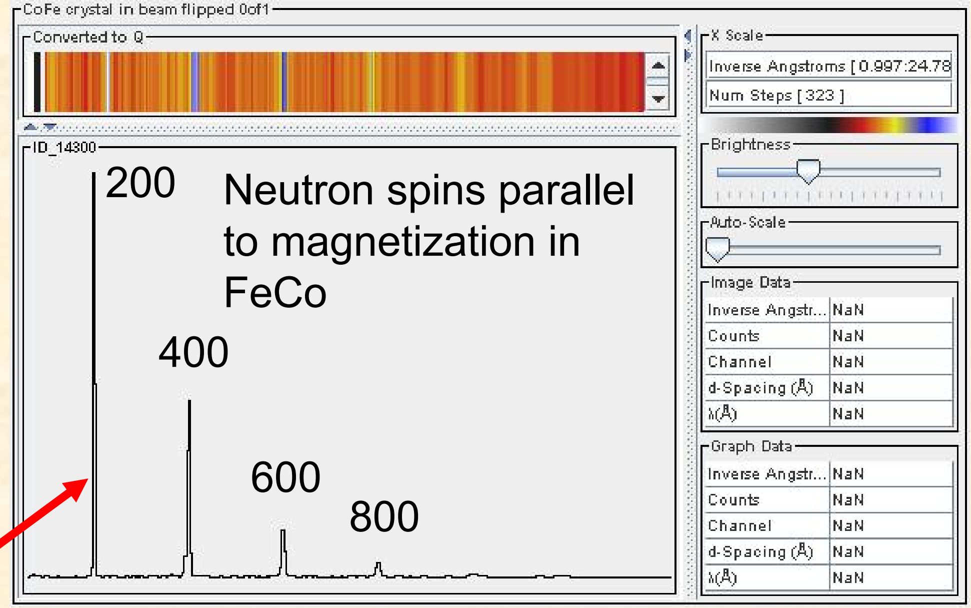


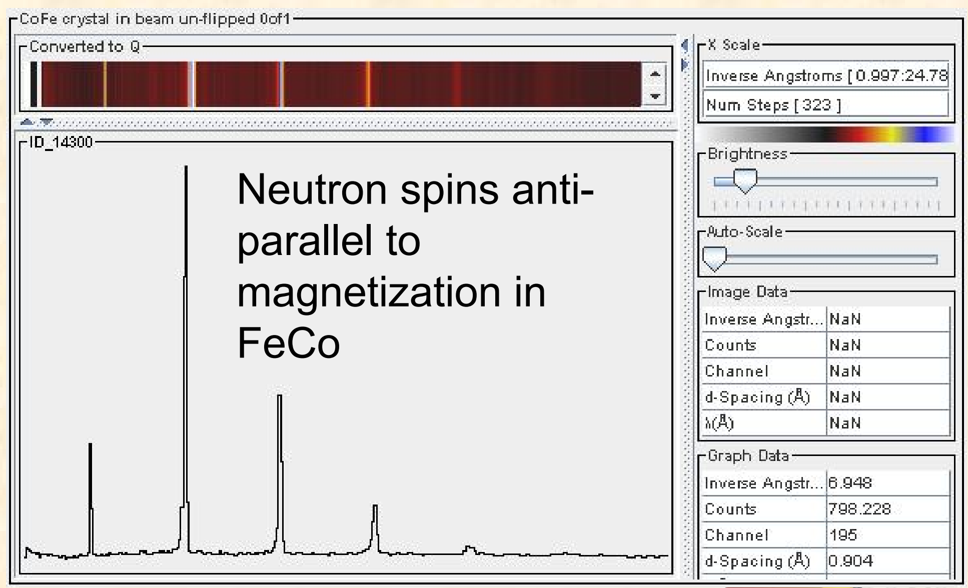
Wavelength of reflections

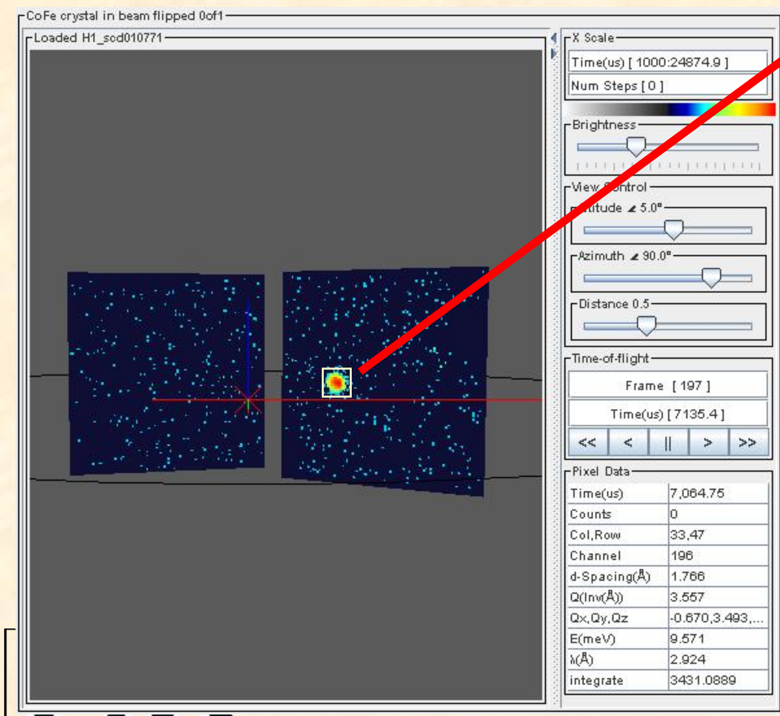


Polarization of the Neutrons

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.





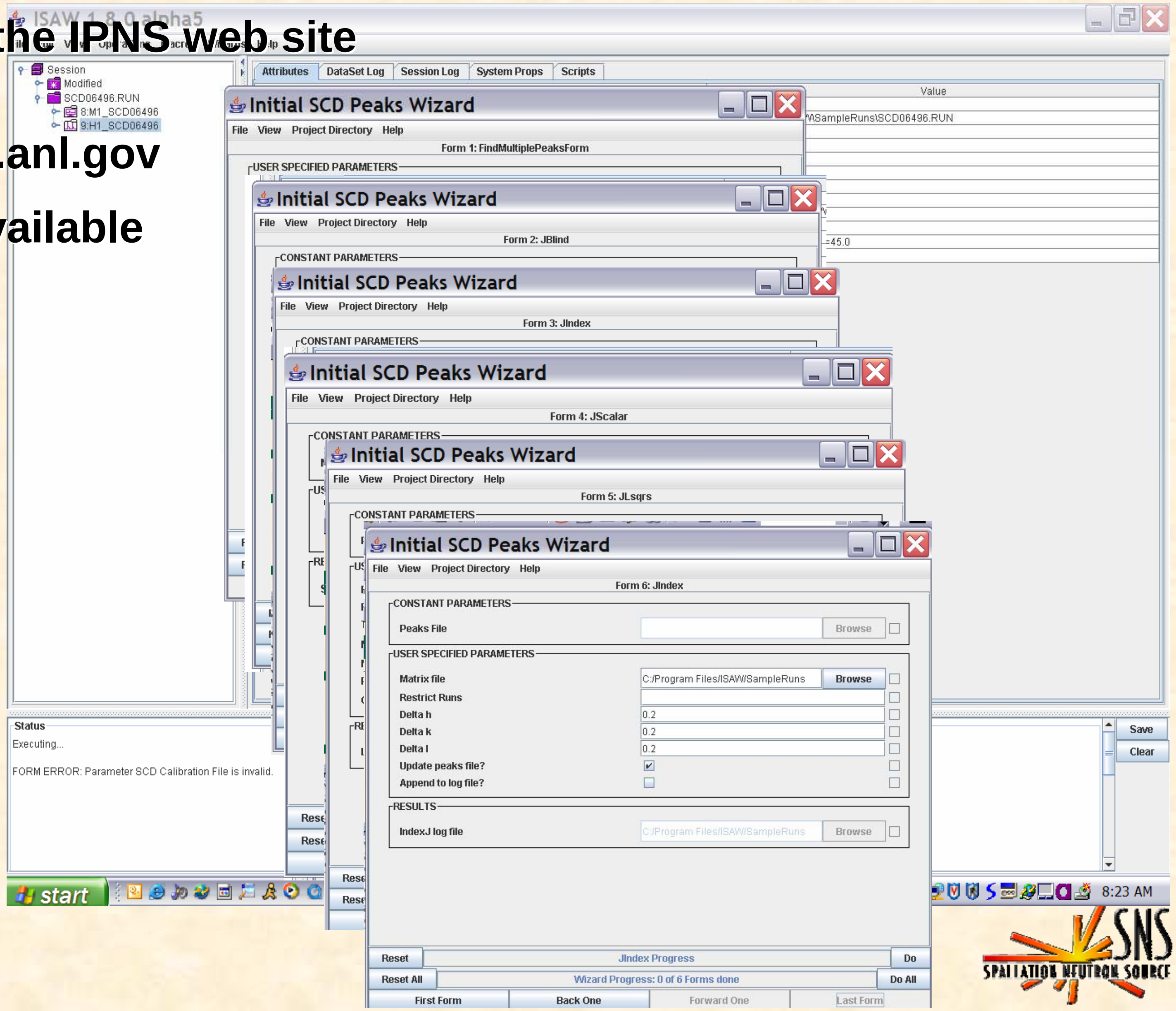


Peak Search, UB Matrix

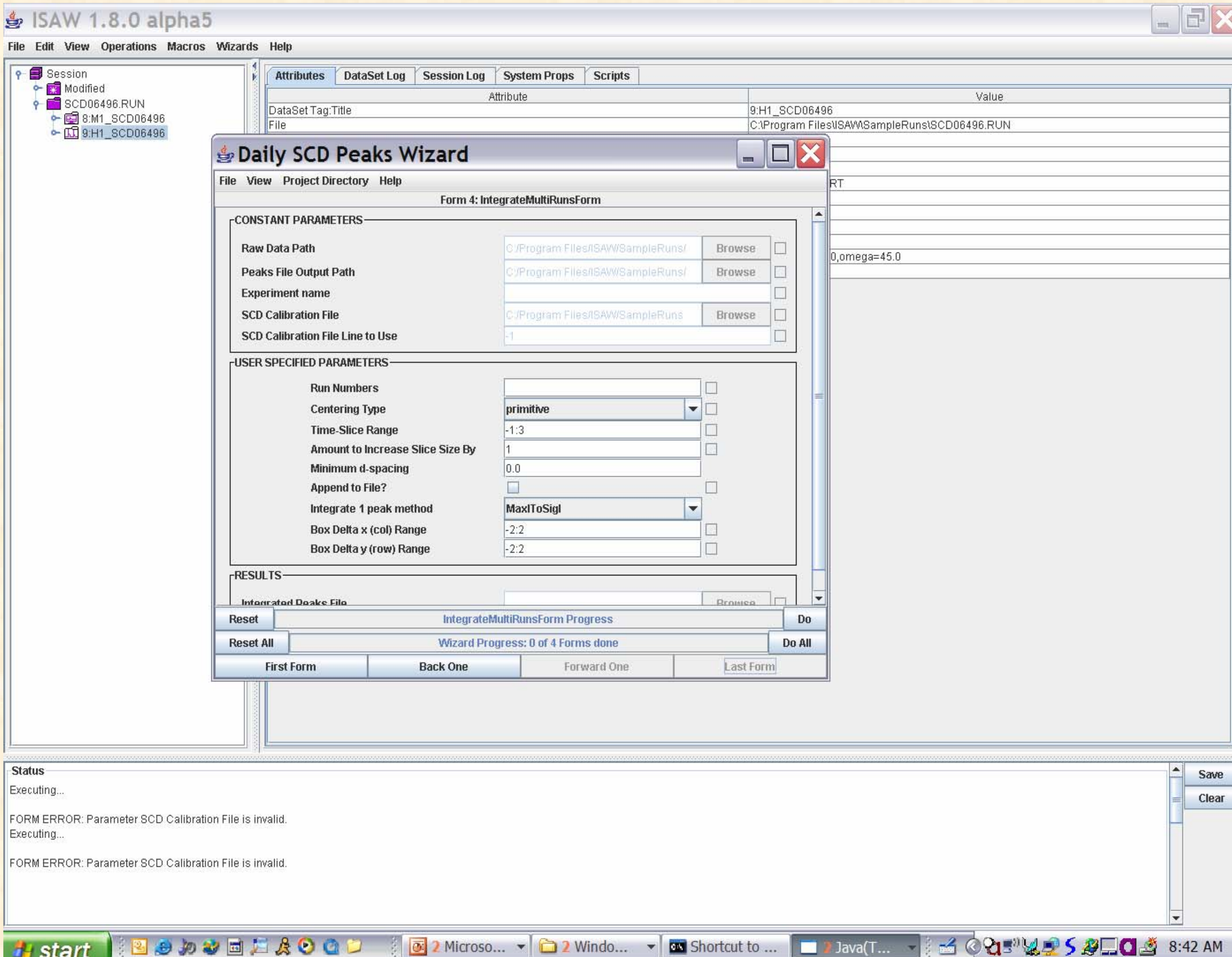
- **Using ISAW at IPNS**
- **Available on the IPNS web site to download**

http://www.pns.anl.gov

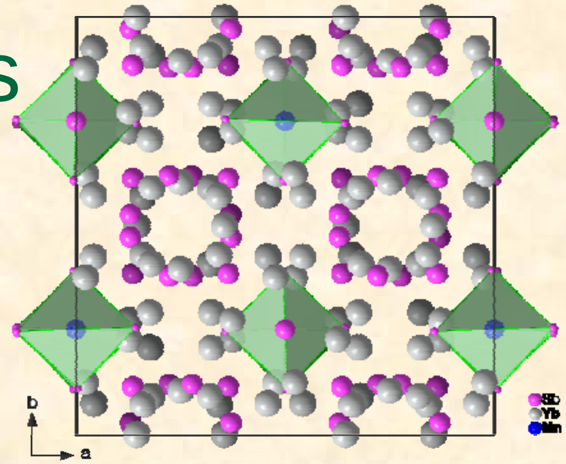
- **Mailing list available**



Integration, Corrections, Data Reduction

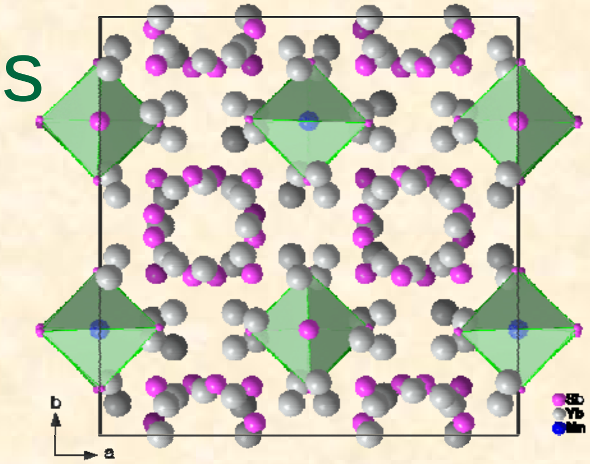


Data Analysis & Results



- 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 :

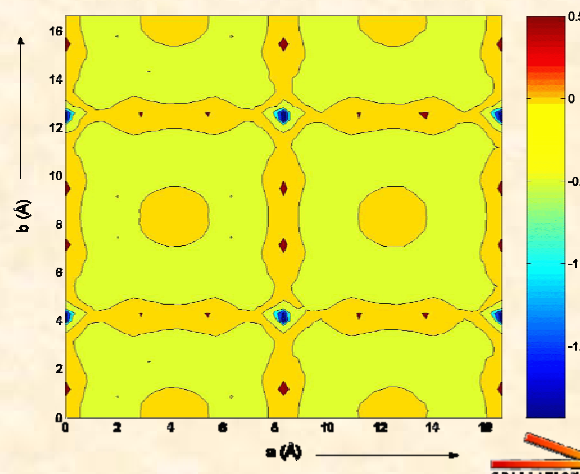
Mn (8a): 2h + l = 4n

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

h	k	l	I+	I-	λ(Å)	$Q(Å^{-1})$	I+/I-	(2h+l)/4	
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

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



→ 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

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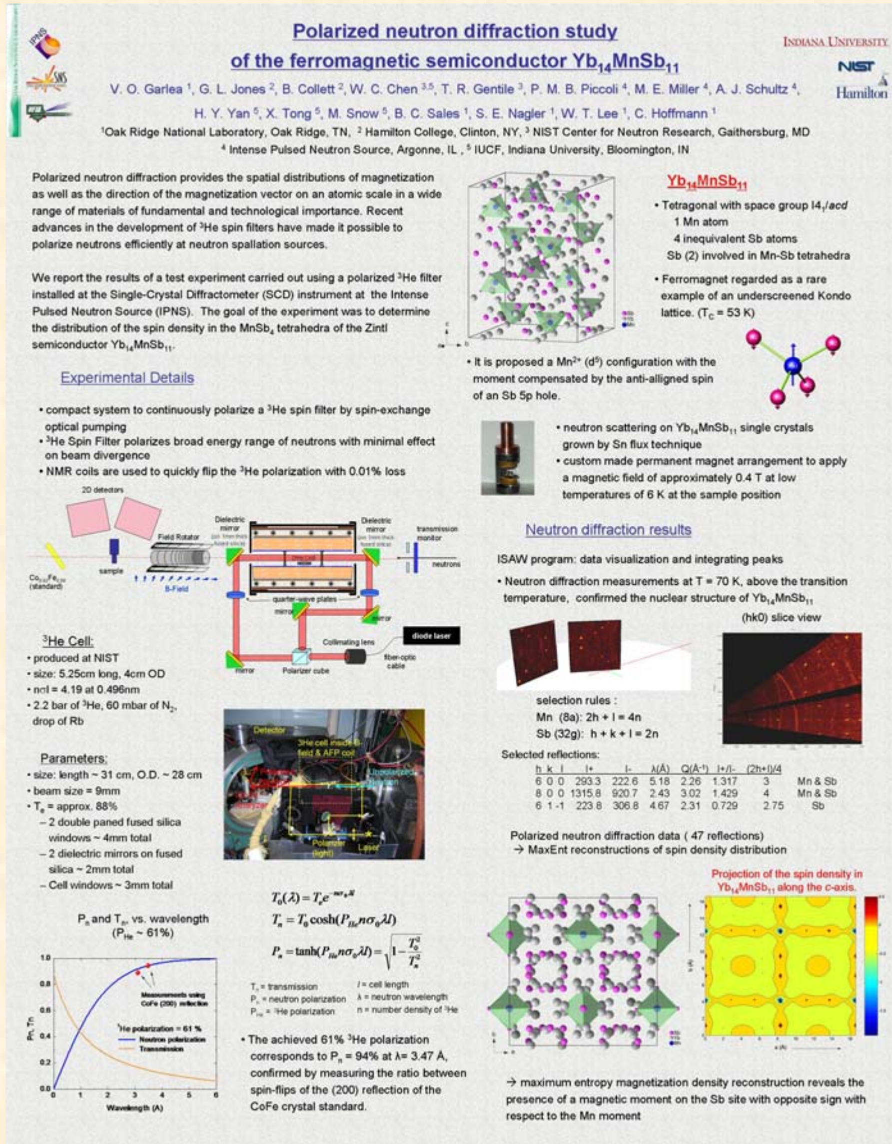
Data Presentation and Publication..



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**

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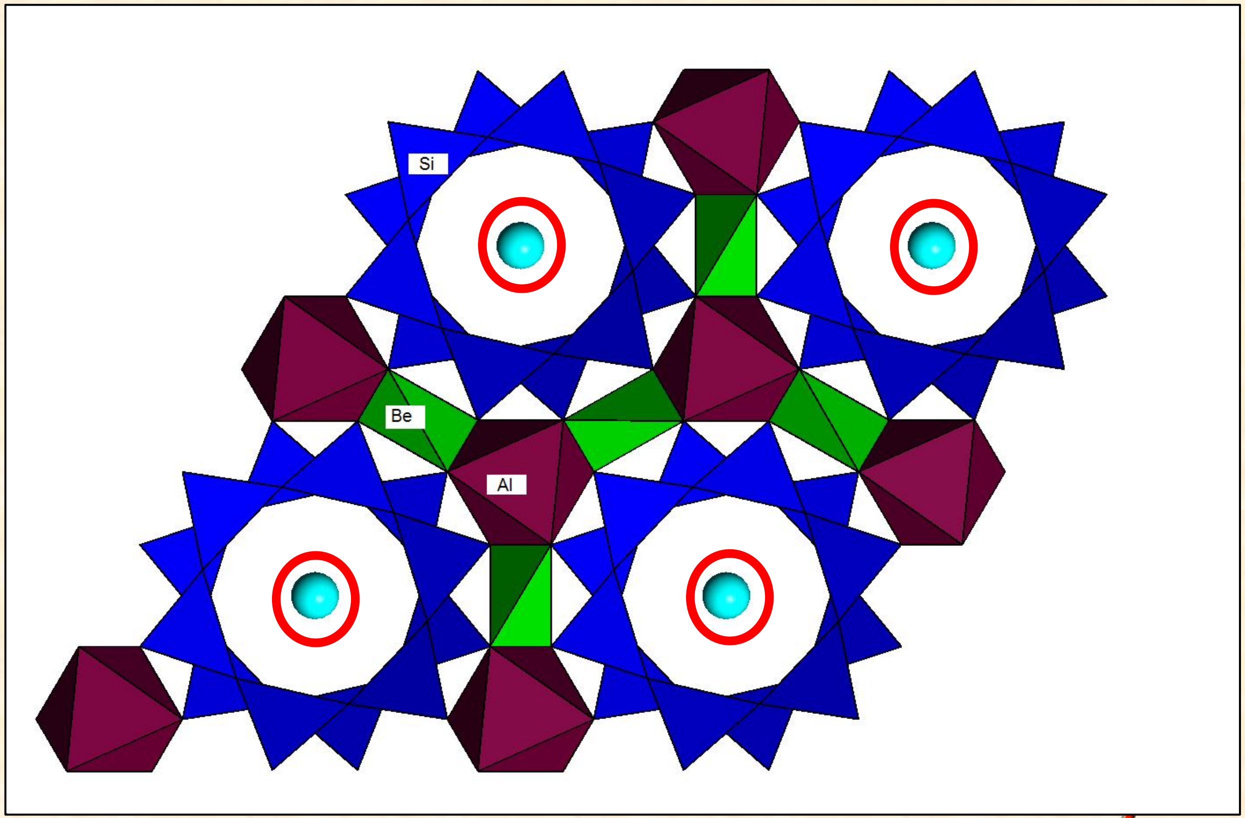
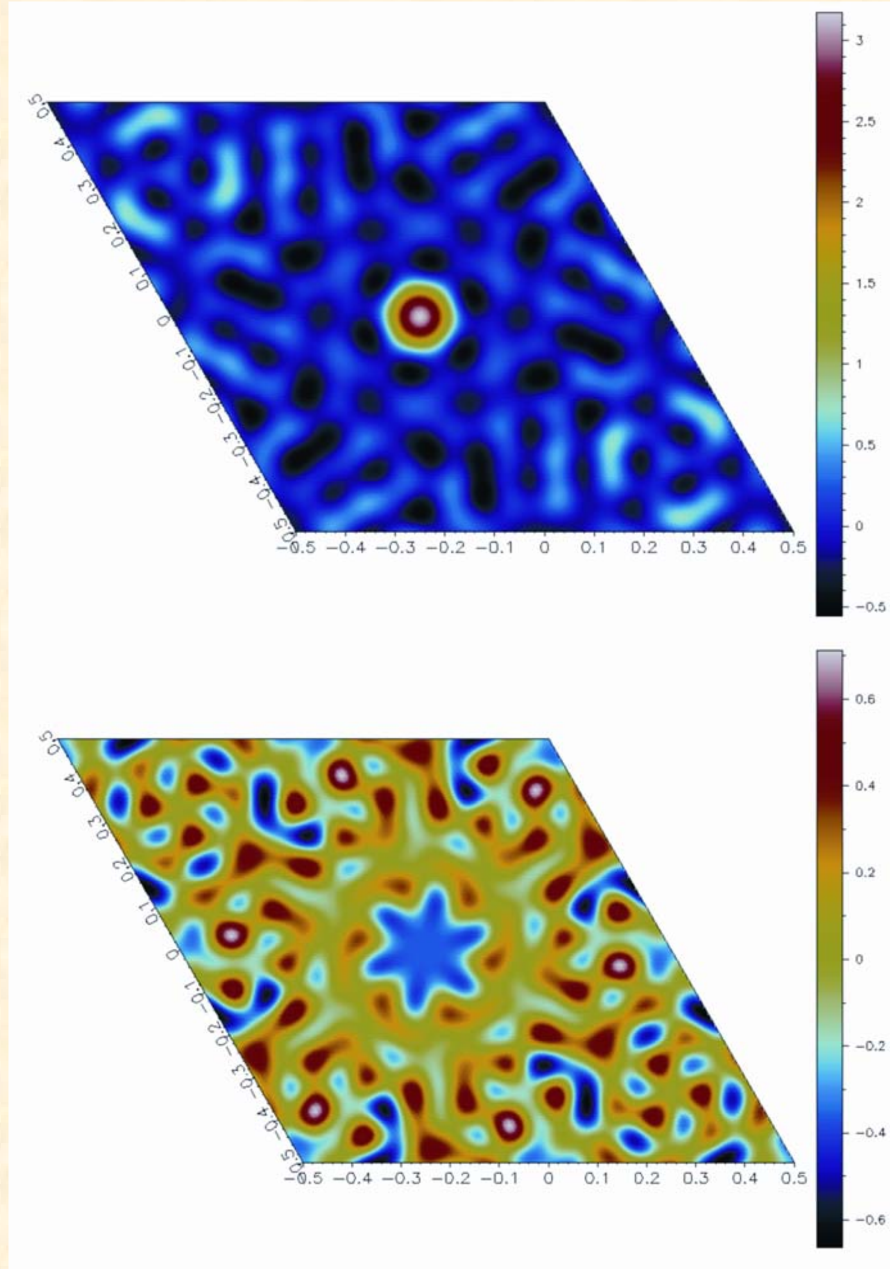
Water in Hydrous Minerals

- **Beryl $Al_2Be_3Si_6O_{18}$**
- **Space Group: *P6/mcc*.**

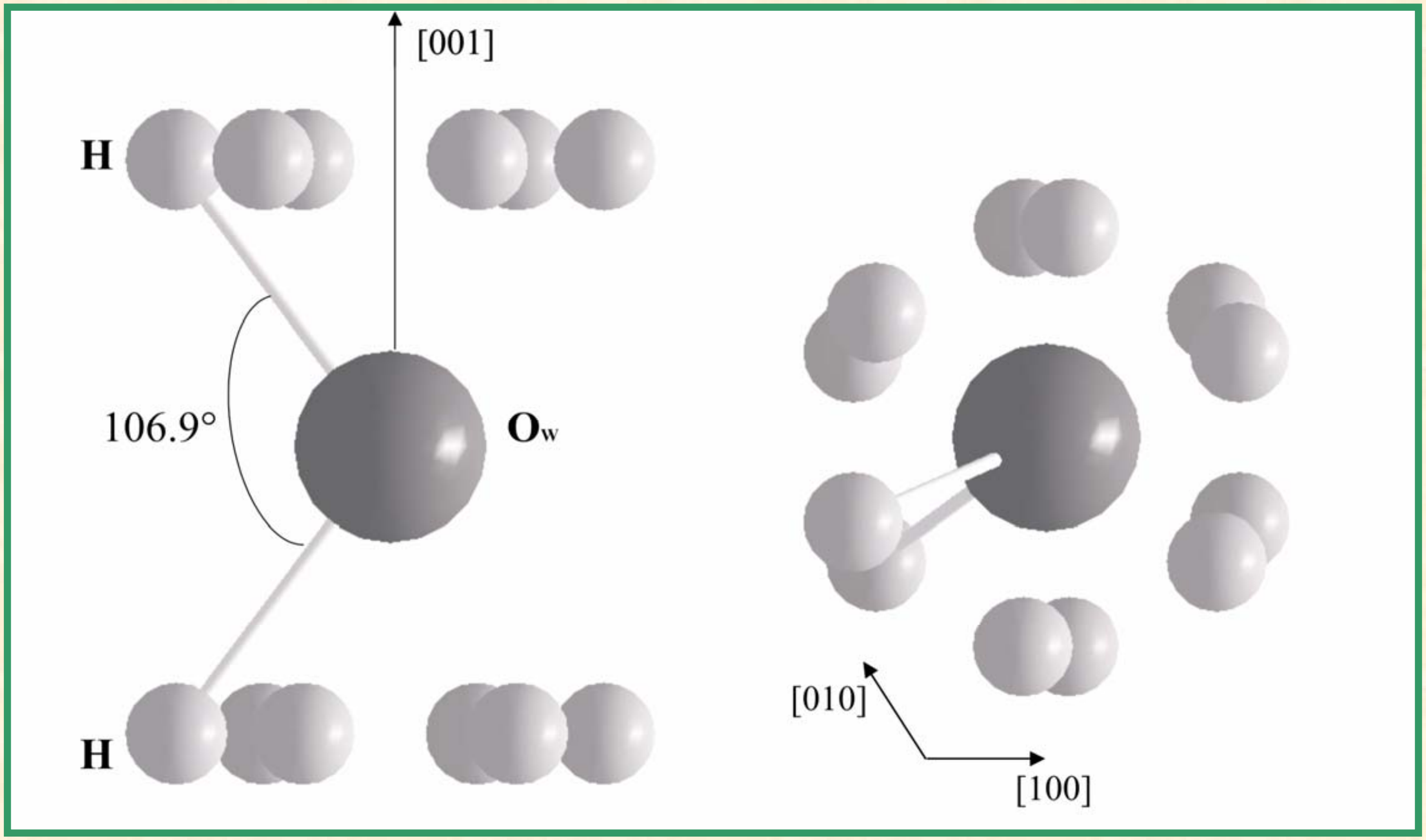


Gatta et al. (2006) determined topological configuration of the channel content in alkali-poor beryl $Al_{1.93}Fe_{0.03}Be_{2.94}Si_{5.93}O_{18} \cdot (Na_{0.03} \cdot 0.26H_2O)$:

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



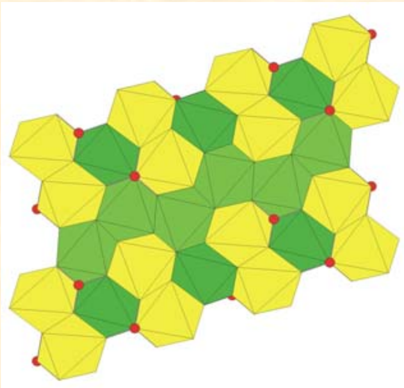
Topological configuration of water molecules into the channel of the alkali-poor beryl, viewed down [100] (left) and down [001] (right):



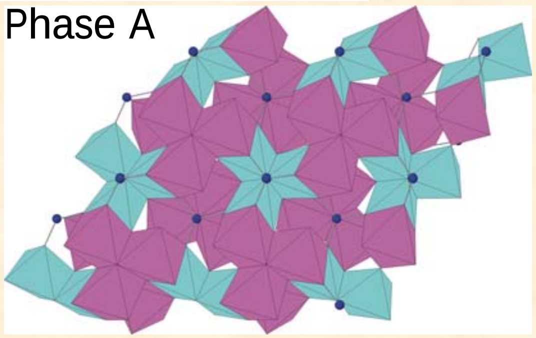
(Gatta et al. 2006)

Dense Hydrous Magnesium Silicates (DHMS)

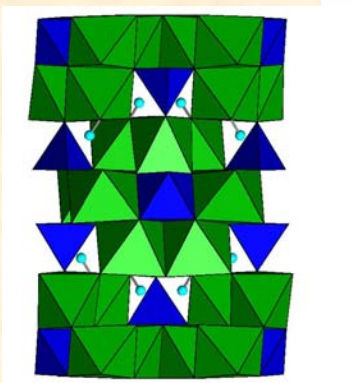
OH-chondrodite

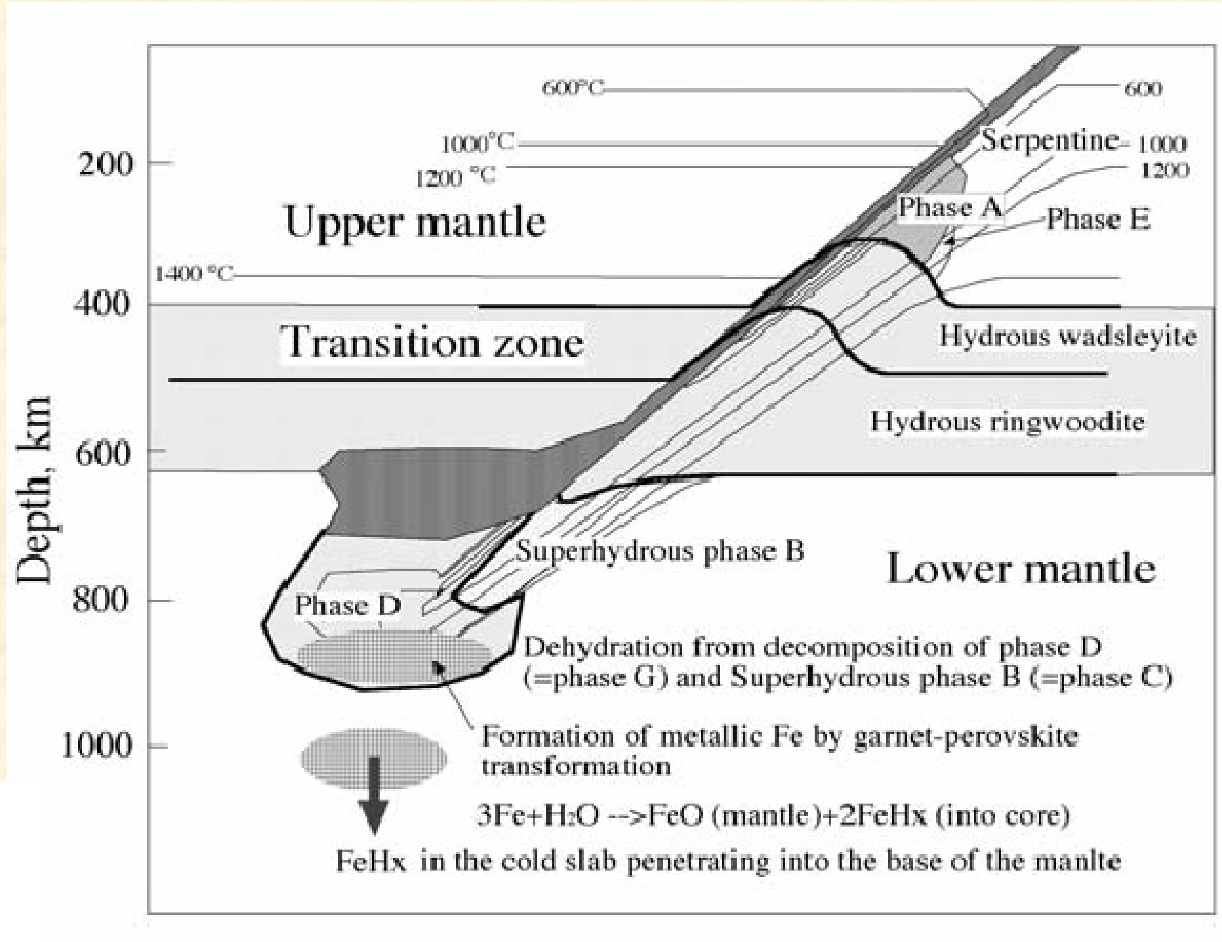


Phase A



Phase B

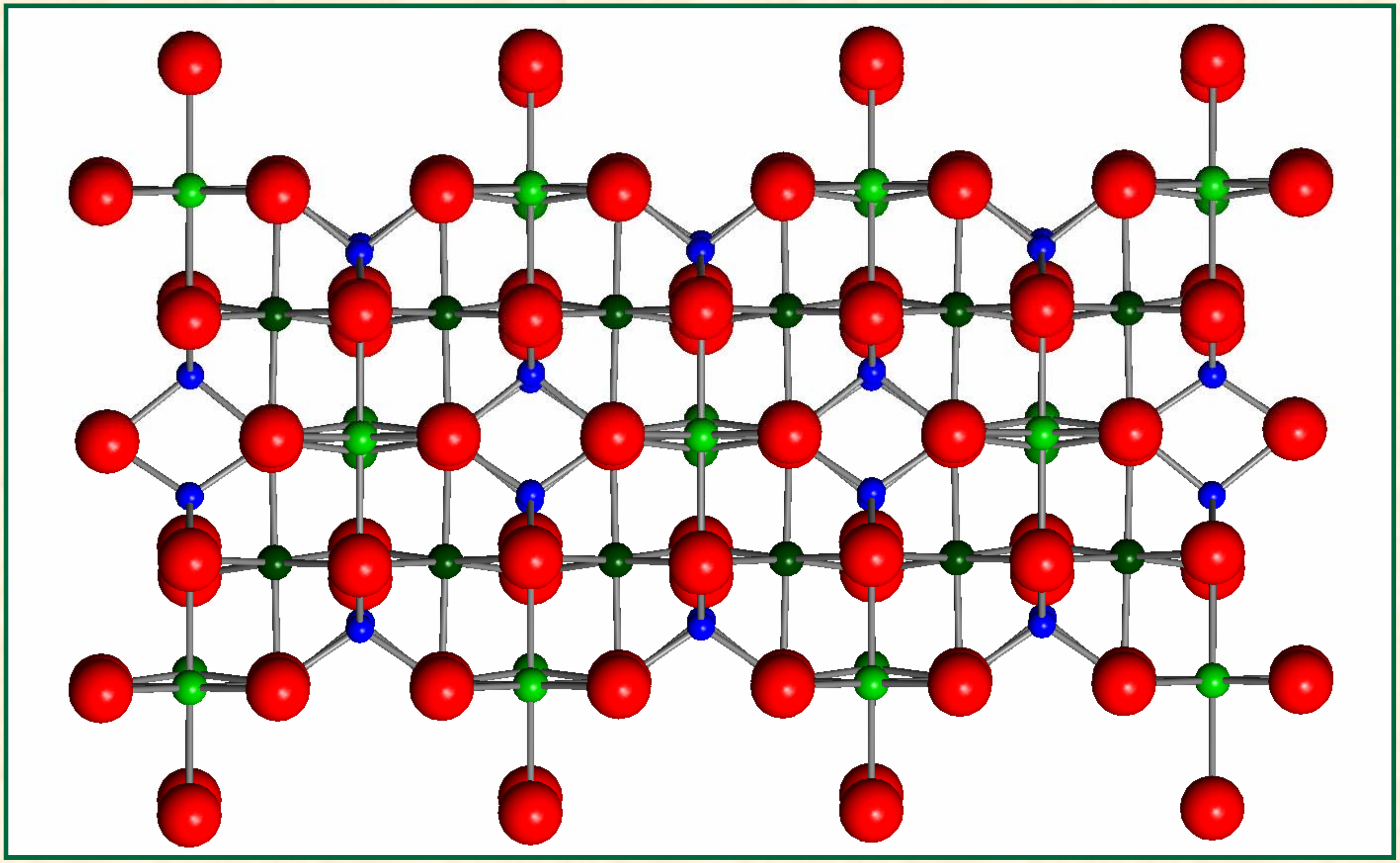




(from E. Ohtani)

Wadsleyite (β-Mg_2SiO_4)

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



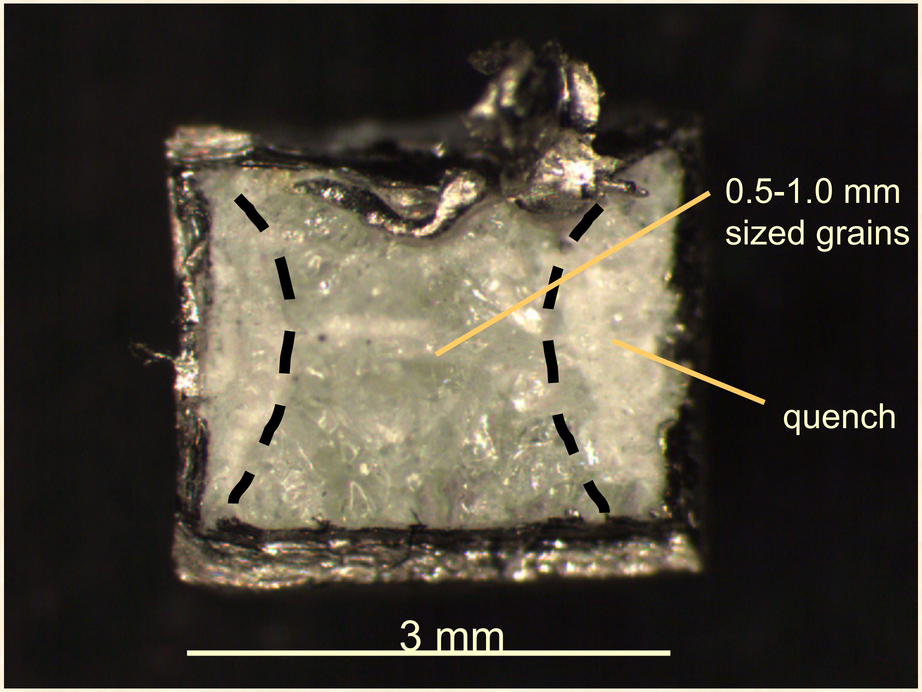
Size of high *P-T* phases
and neutron fluxes are merging . . .

5000-ton large-volume press in Bayreuth

Steve Jacobsen (Geophysical Laboratory)

Daniel Frost (Bayerisches Geoinstitut)

Joseph Smyth (University of Colorado)



e.g. hydrous wadsleyite:
(containing ~1 wt% H_2O)

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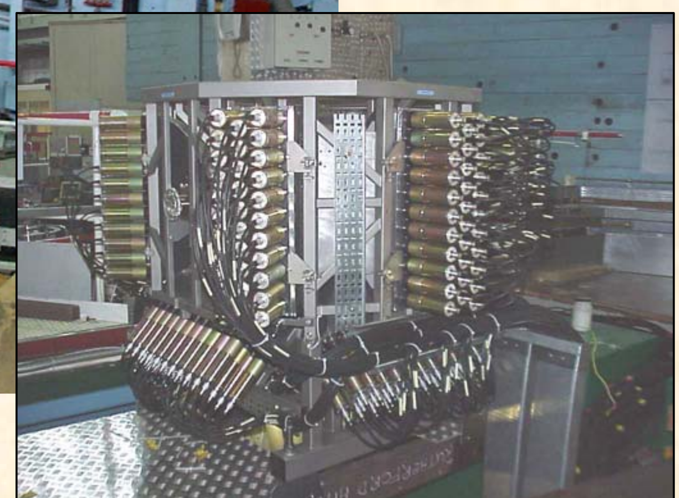
Hydrous wadsleyite: Single crystal ND



11-bank scintillating ZnS detector array

SXD instrument at ISIS

M. Gutmann

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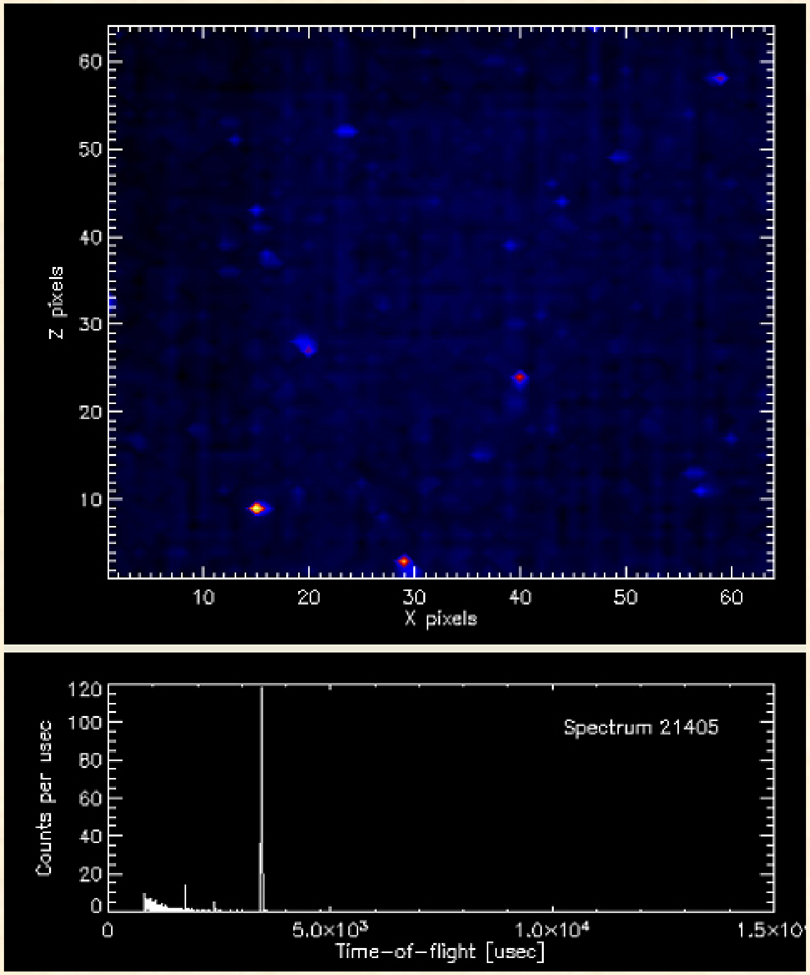
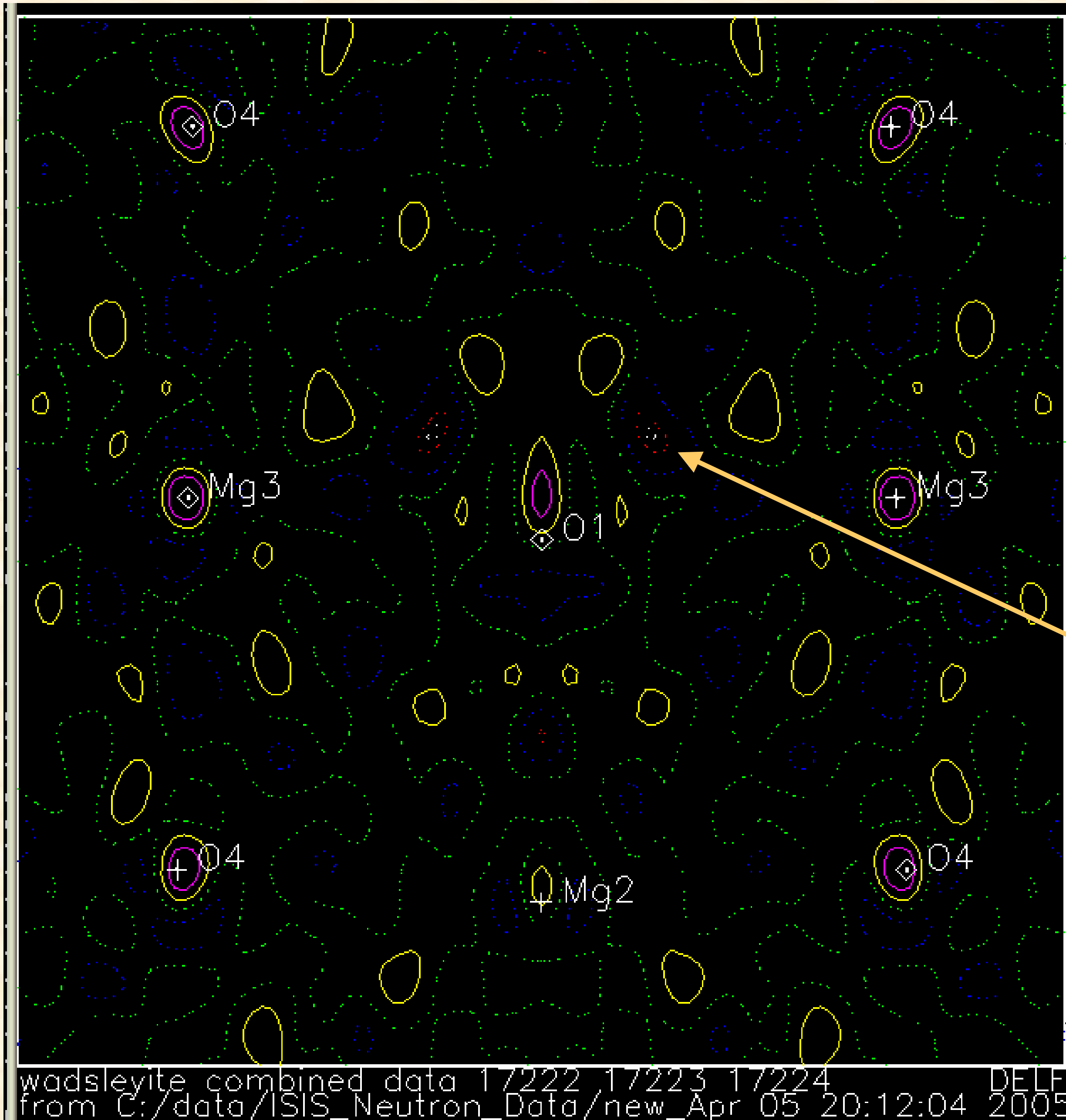
Mounting a wadsleyite crystal onto the SXD goniometer at ISIS

Screenshot: SXD2001/Matthias Gutmann

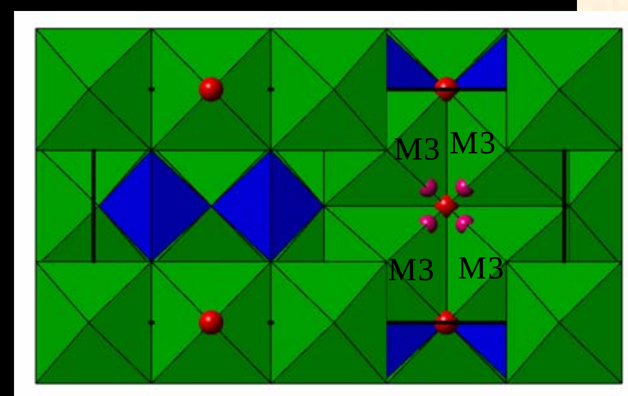


Neutron diffraction from single-crystal wadsleyite
Crystal volume is ~0.25 mm^3



There is about 10% M3 vacancy

H14: 0.42 0.79 0.79



d(O-H)=0.9Å

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?

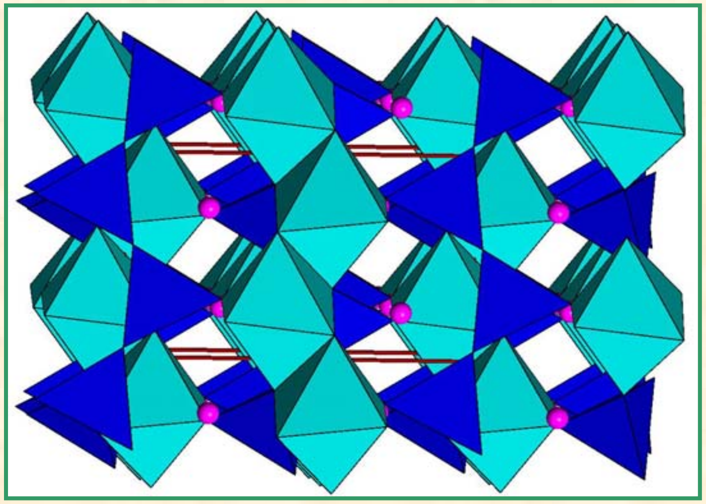
- X-ray diffraction yields information on the time- and volume-averaged electron- charge distribution in the crystal.

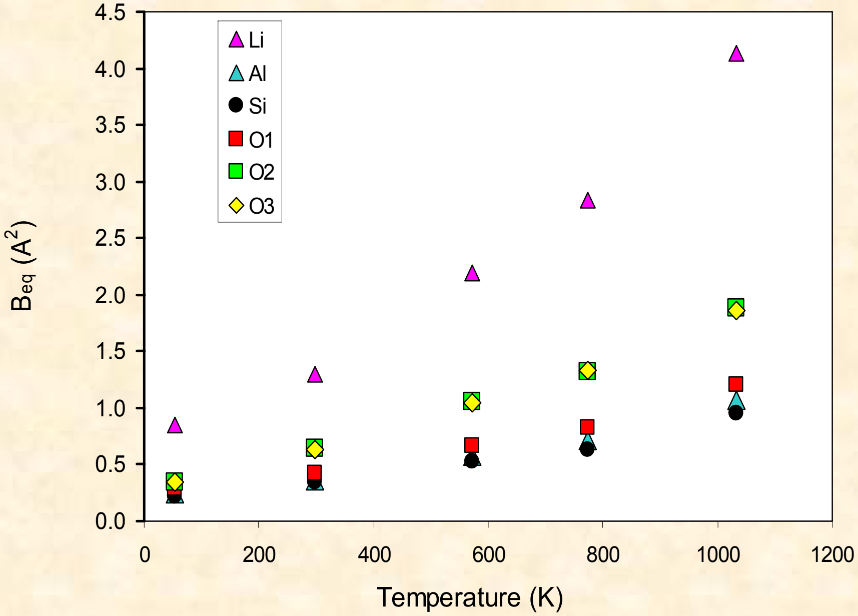
- Neutron diffraction instead yields information on the position of the atomic nuclei and their thermal motion and is therefore the preferred primary technique to measure reliable adp's.

Spodumene, $LiAlSi_2O_6$

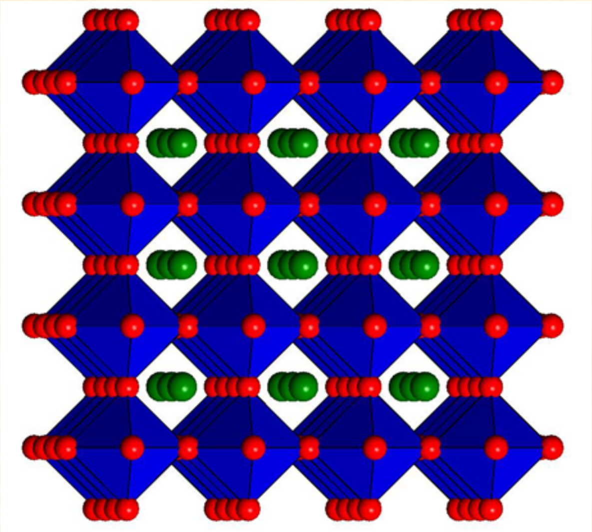
- ADP (B_{eq}) for Li in spodumene larger than that at *M*2 in other pyroxenes.
- The presence of significant zero-point motion is in agreement (diopside, albite, anorthite, pyrope)

Tribaudino et al. (2003)

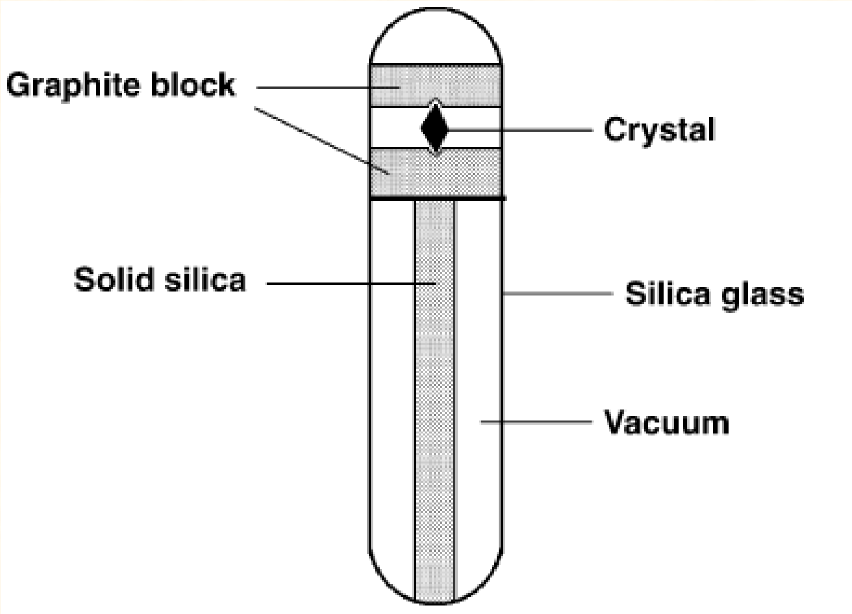


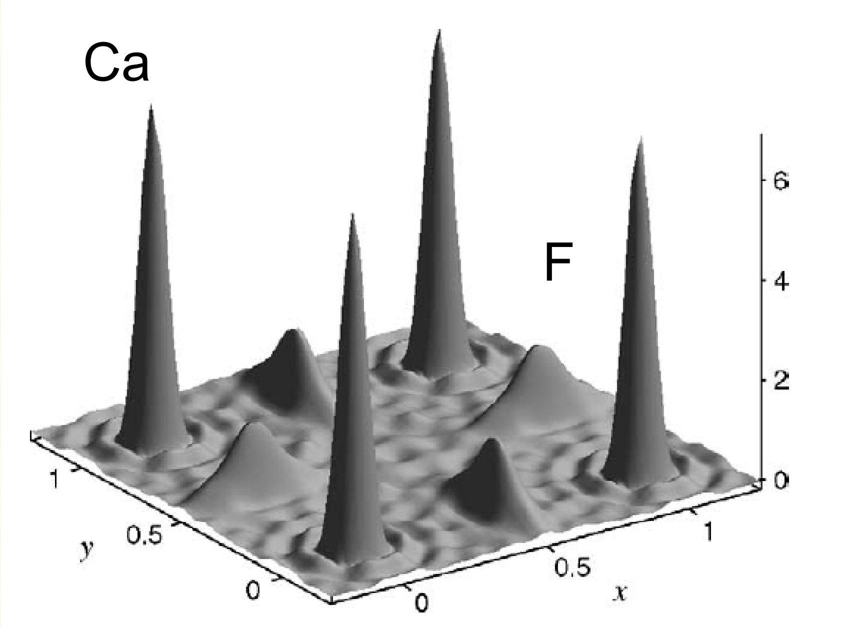


Anion Disorder in $KCaF_3$

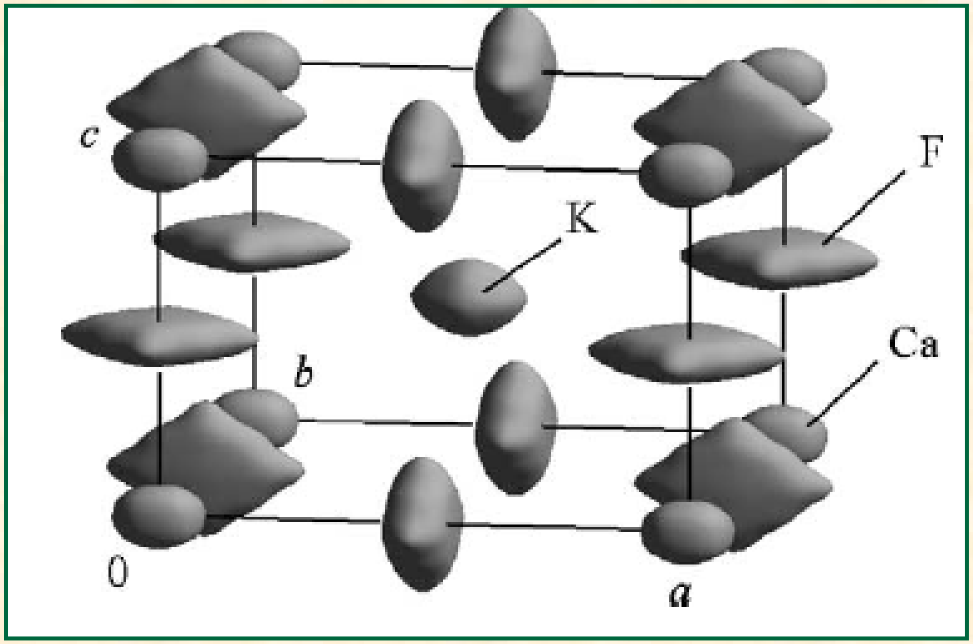


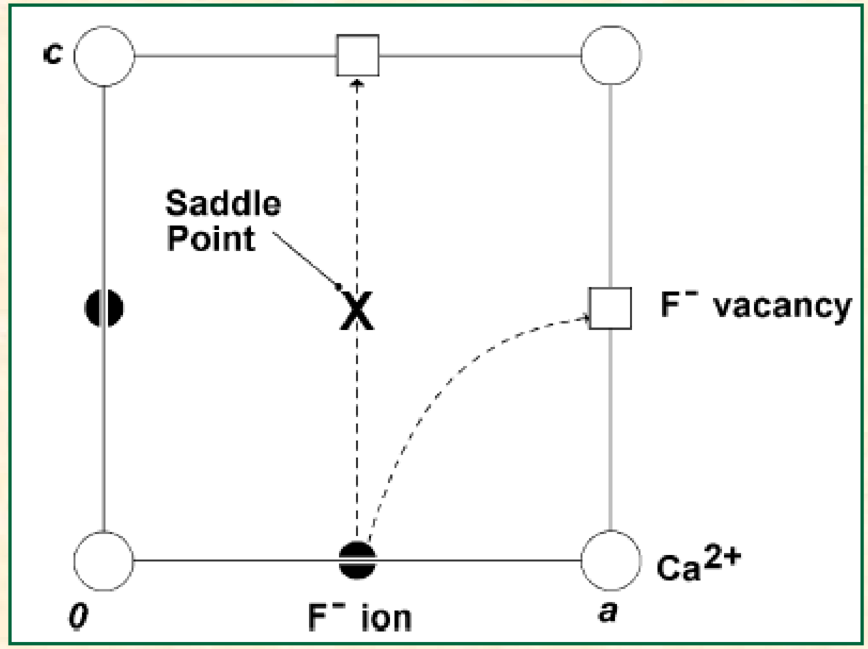
- fast ion conductor at high T
- High-T SND, D9 at ILL





Demetriou et al. 2005



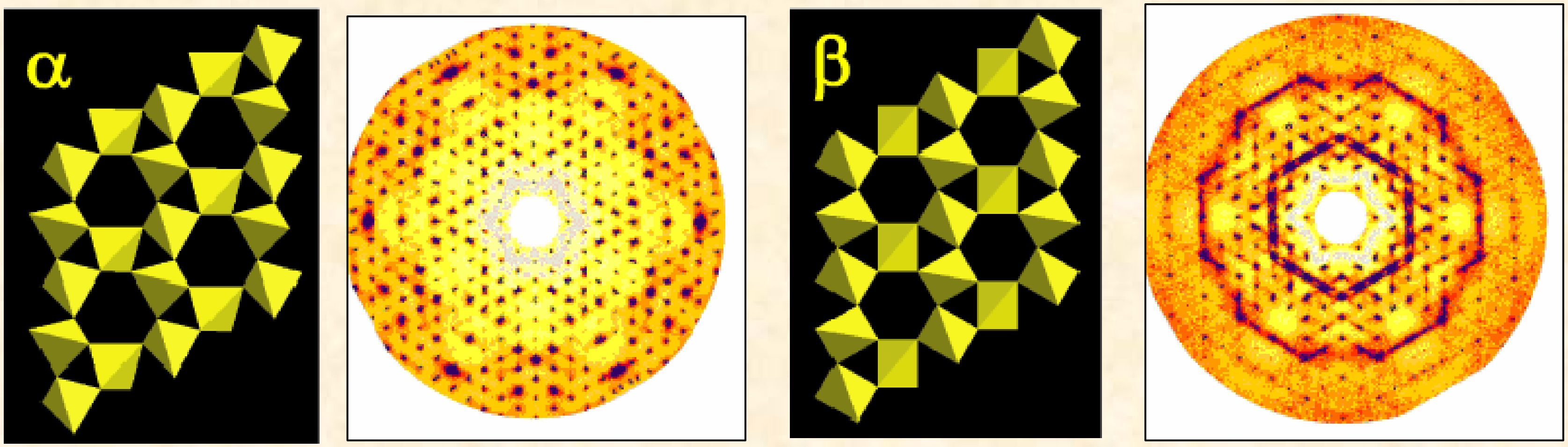


- The F- ions show a large degree of anisotropy in their vibrational envelopes and appear to vibrate towards a saddle point, at the centre of a cube face, between two neighboring K+ ions.
- Vacancy migration mechanism involves the F ion jumping to a next nearest neighbor site in the (100) plane

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

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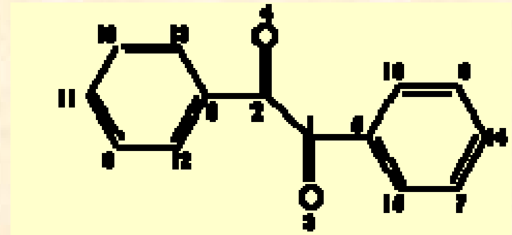
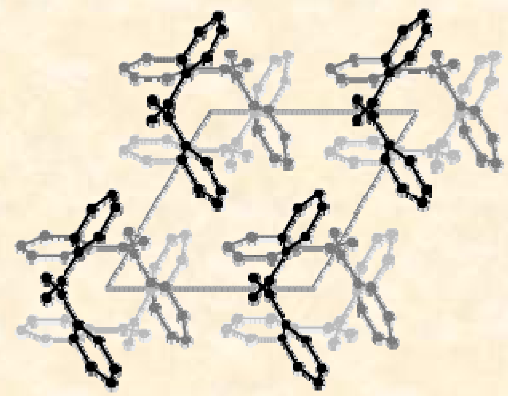
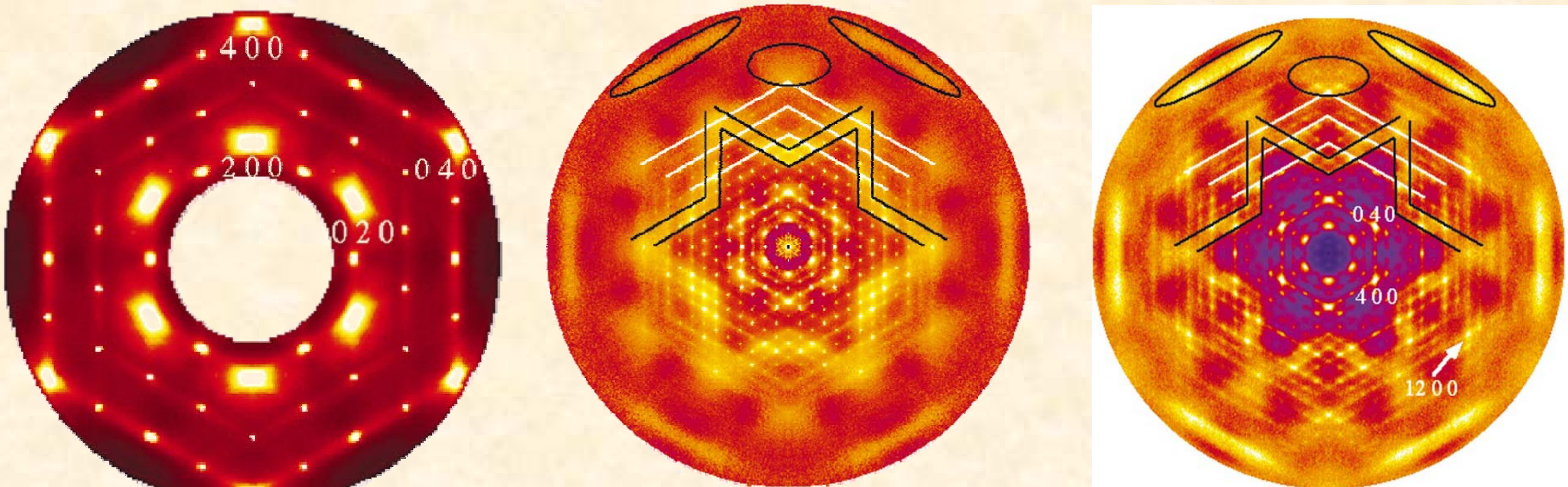
Benzil

- 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



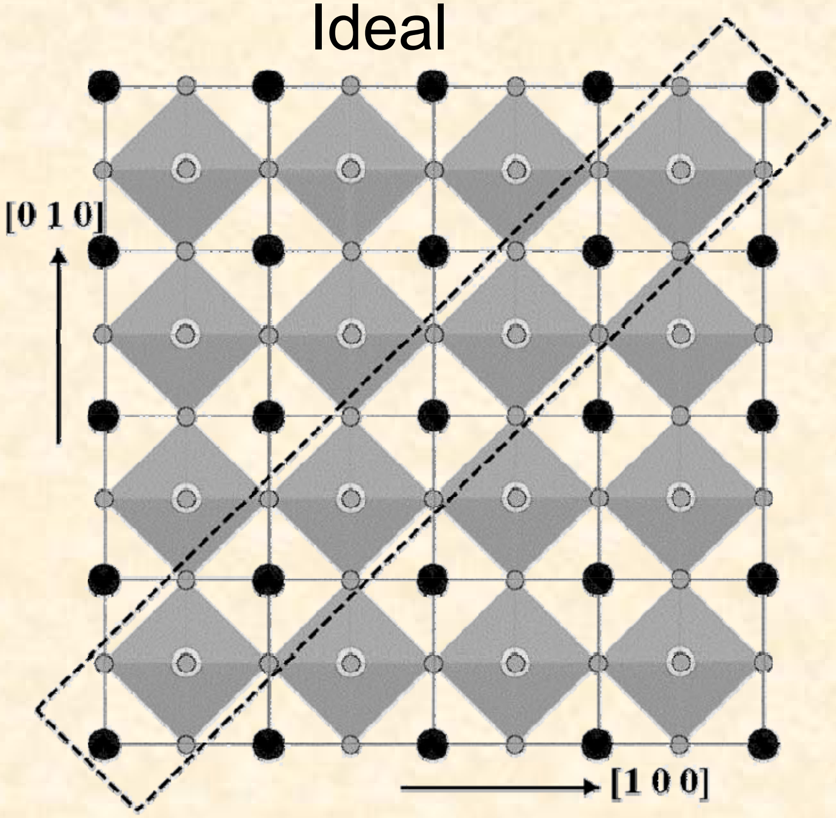




Welberry *et al*., J. Appl. Cryst., 2003

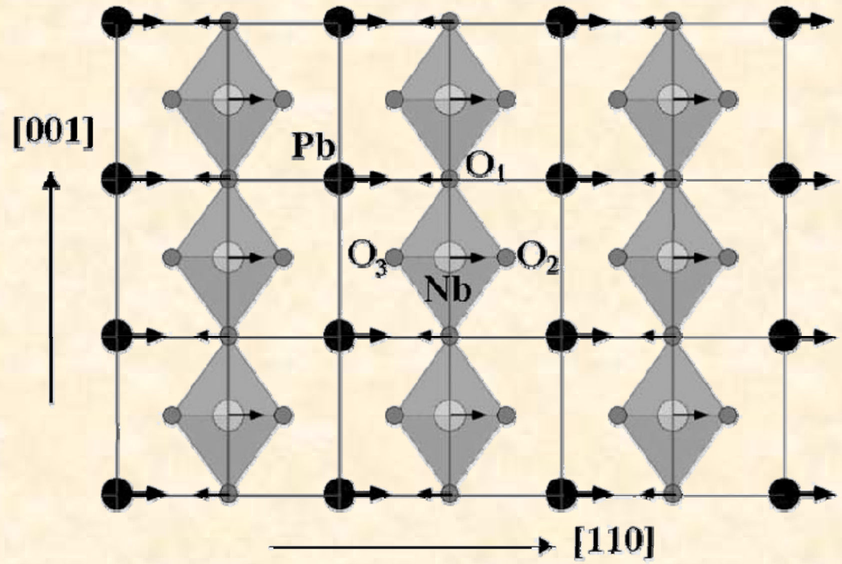
Overall Structure Interpretation of PZN

Ideal



Conventional data analysis & refinement

Ideal & Real



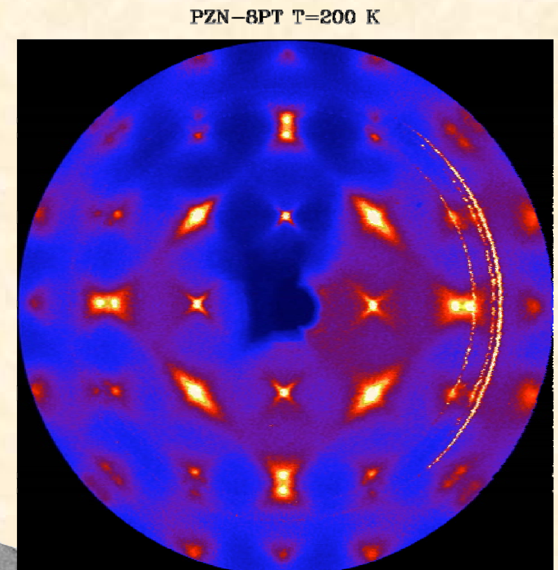
Monte Carlo data analysis & refinement

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

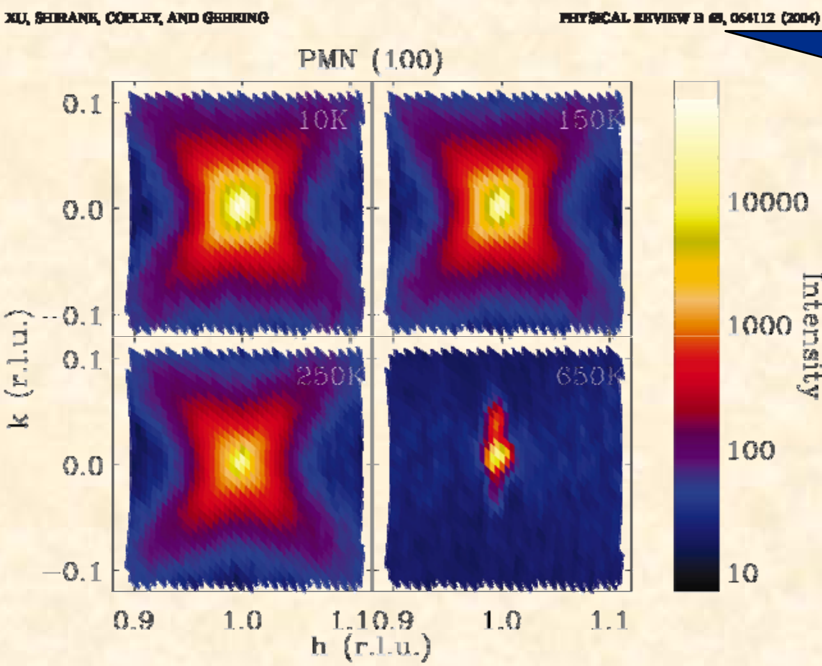
Relaxor Ferroelectric $PbZn_{1/3}Nb_{2/3}O_3$ => PZN

X-Ray

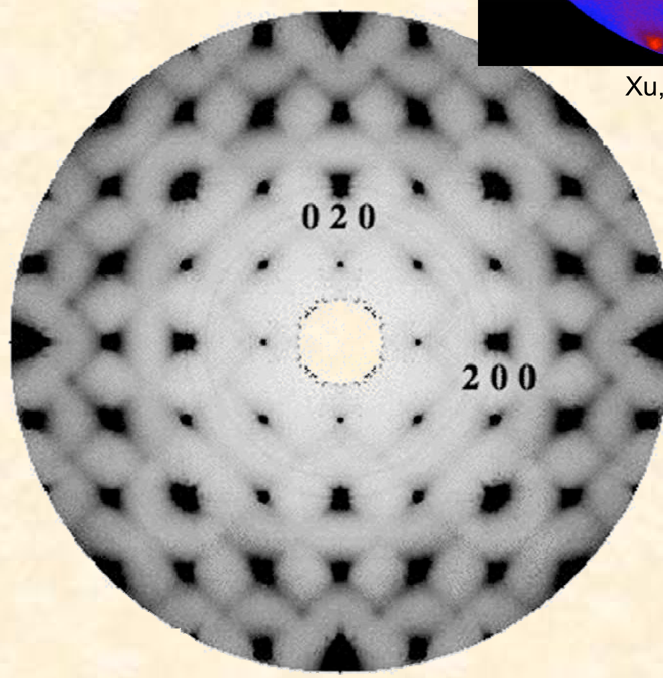
Neutron



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

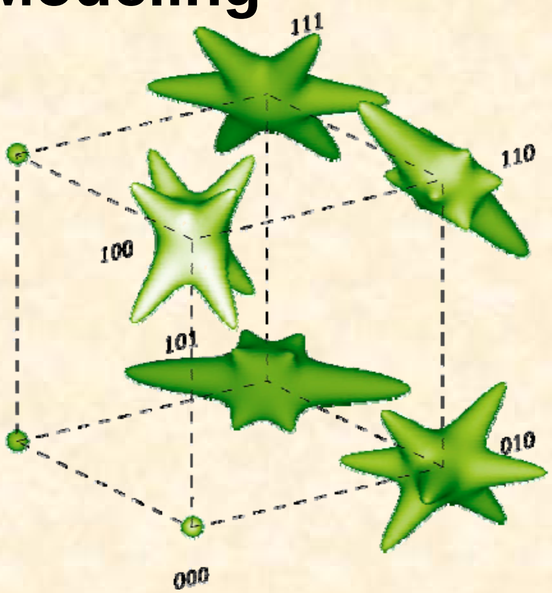


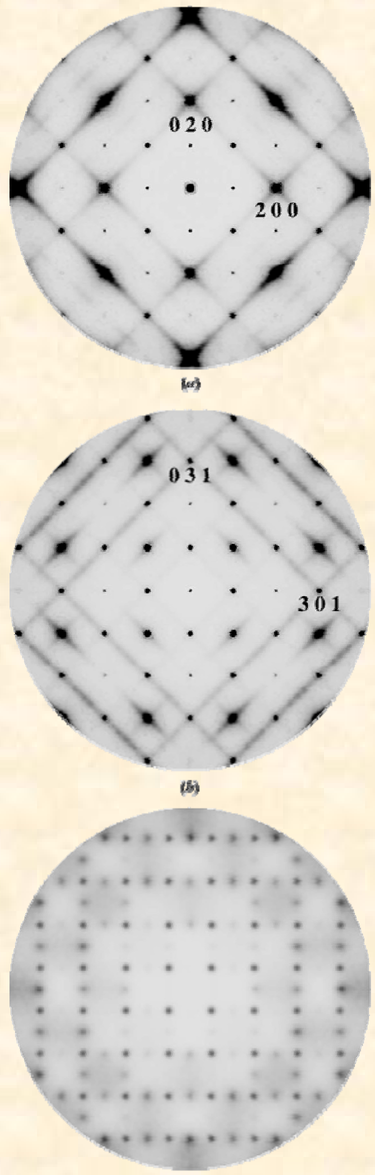
Welberry *et al*., J. Appl. Cryst., 38, 639 (2005)



Analysis Results - Global and Local Pattern

- **MC Simulation**
- **Modeling**





⇒Deriving the modeling results spanned several years

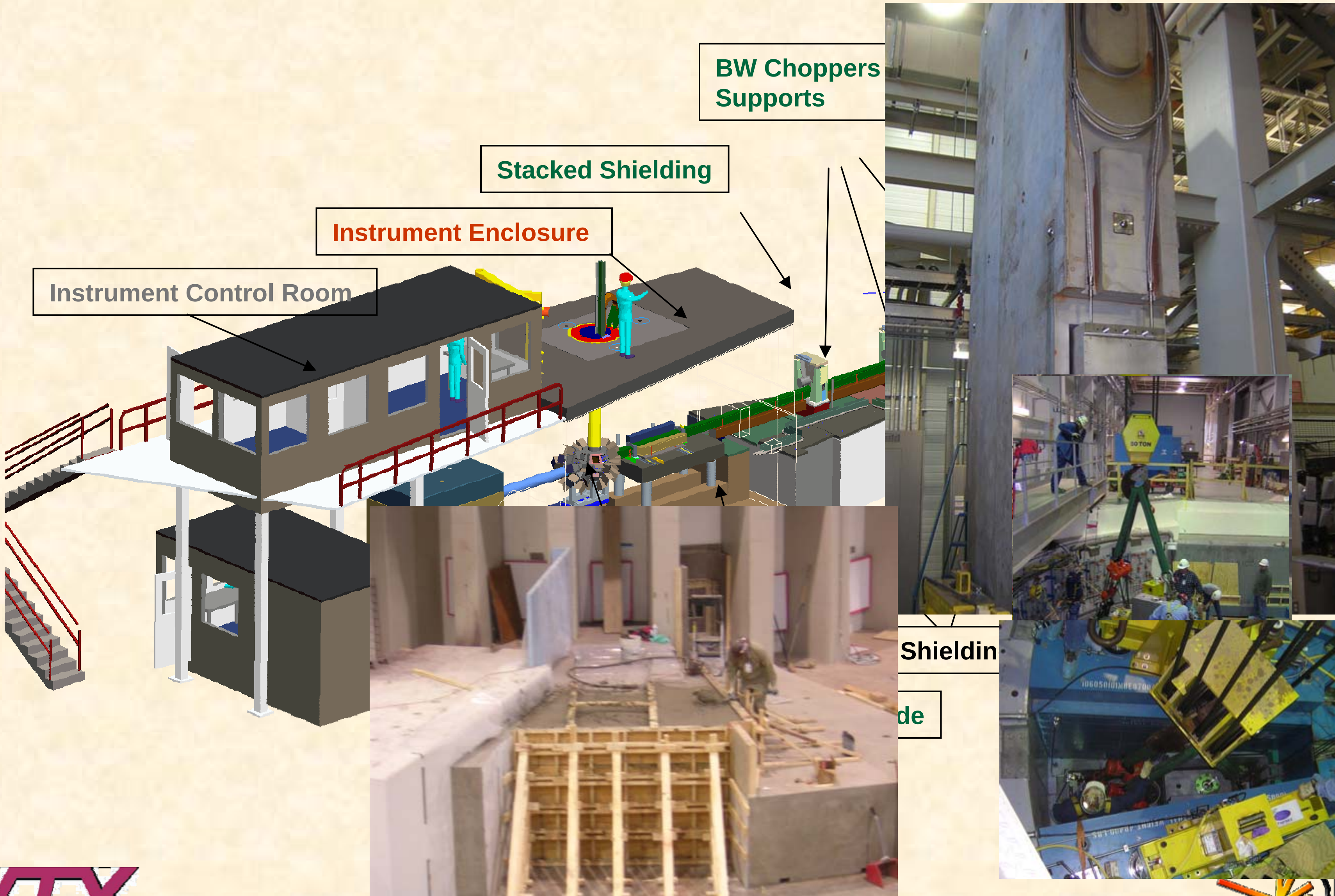
⇒Disordered part of structure influences properties

New Horizons

- Faster structures (<< 1 day)
- More complex structures
- Smaller crystals (<<1 mm3)
- More parametric (*T*,*P*,*H*,*E*,…) studies
- More quantitative diffuse scattering

Moving forward

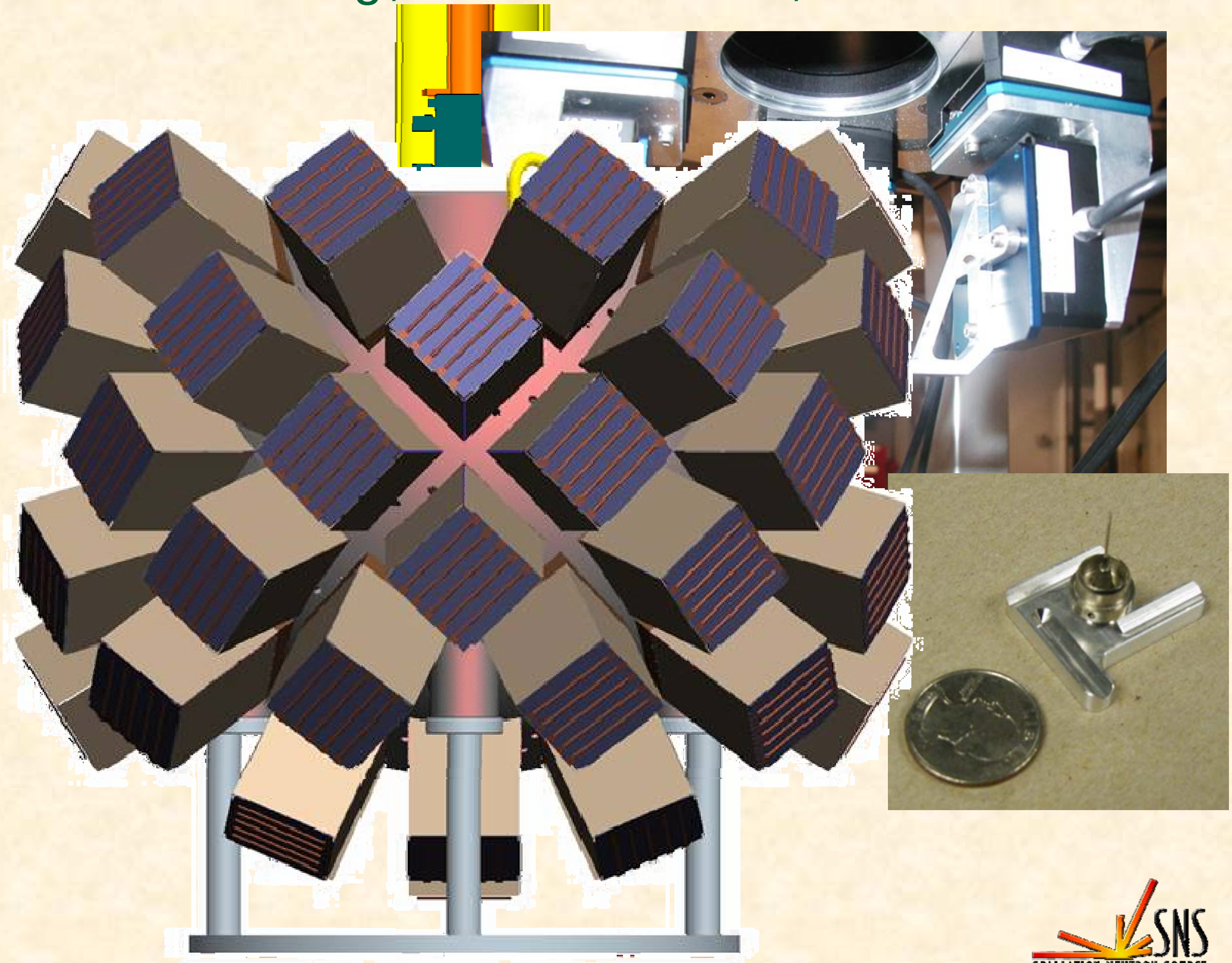
The Single Crystal TOPAZ Beamline at SNS



VTX

SNS SPALLATION NEUTRON SOURCE

Sample Positioning, Environment, Detectors



You can teach robots anything….

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