Neutron Experiments to Determine Magnetic Structures

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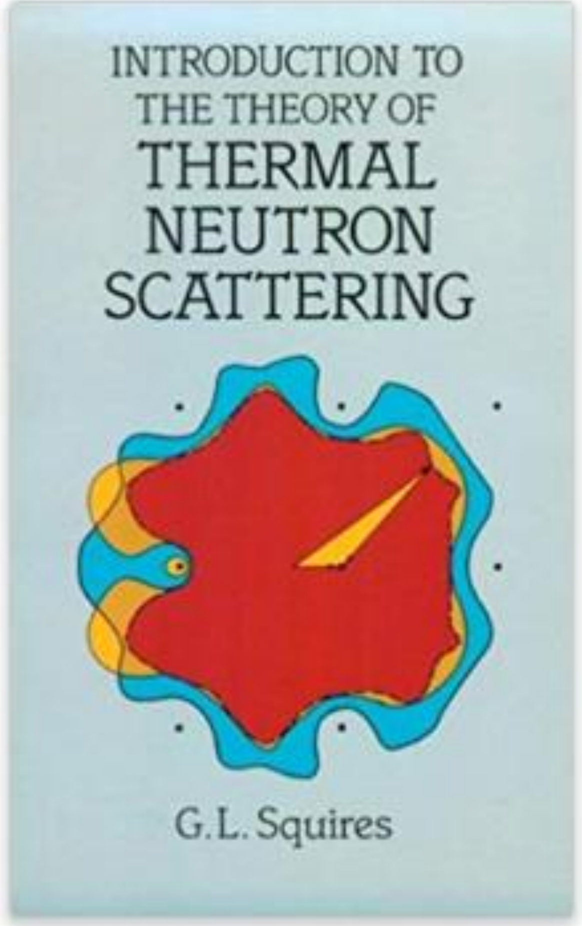
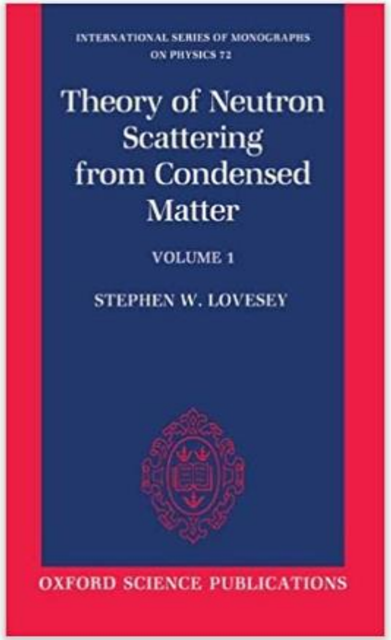
ORNL is managed by UT-Battelle, LLC for the US Department of Energy

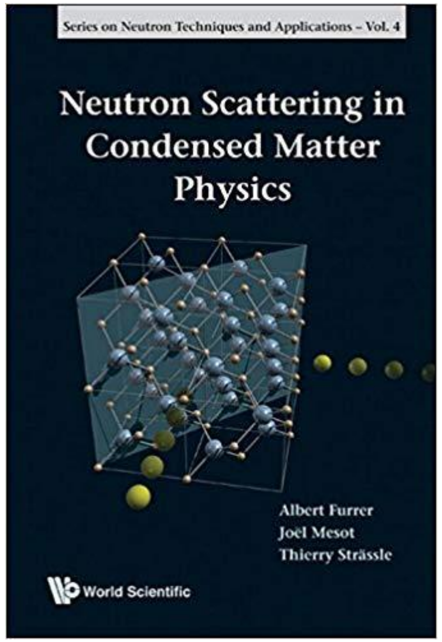
Overview

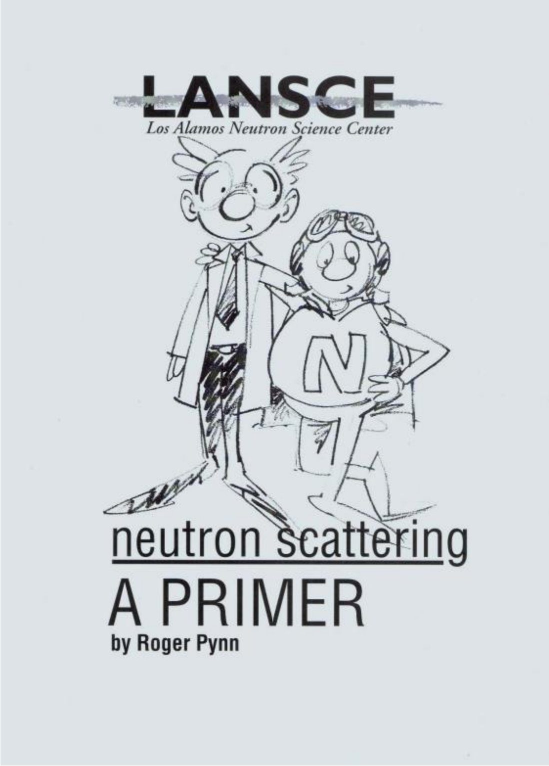
- Why use neutrons?
- Neutron sources: A (very) brief history
- Theoretical concepts of neutron scattering (recap)
- Practical aspects of neutron scattering and refinements
- Where to perform experiments: Diffraction instruments at ORNL

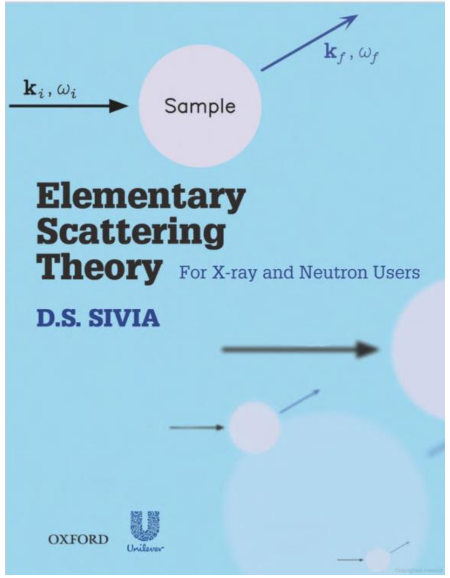
Lots of references

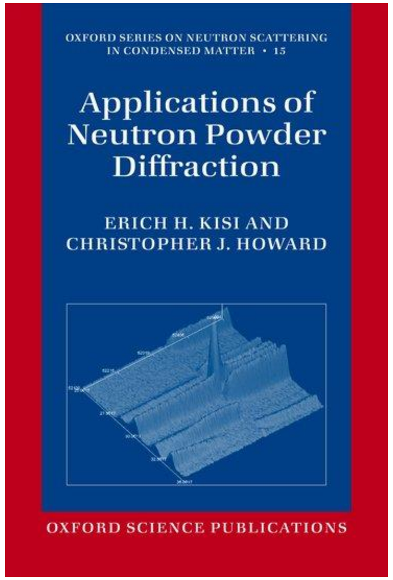


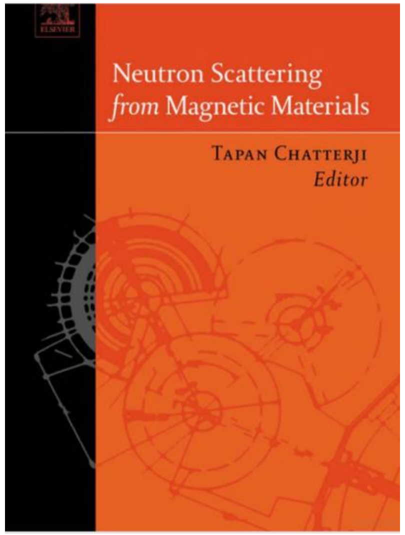










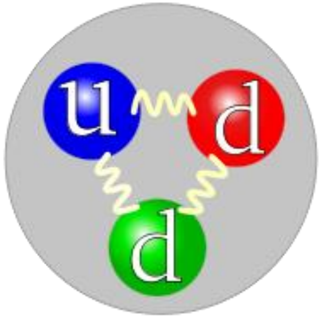


How to get microscopic structural information

- 3 main choices → Diffraction has strong advantages

Examples	Advantages	Disadvantages
Microscopy Optical, TEM, Field ion	Direct	Local information only
Scanning Probes AFM, STM, SEM	Direct	Local information only Surfaces only
Diffraction Probes Electron X-ray Neutron	Quantitative data on correlations and distribution of structural features Probes entire sample Neutrons → gives absolute values	Requires fitting

Why neutrons?



- **Wavelength**: Comparable to atomic distances (1- 5 Å)
  - Strong nuclear interaction with nuclei
- **No charge**: Can travel through thick samples (cm) and equipment
- **Neutron spin** (μ_N): dipole interaction with unpaired electrons → **μ**= -(**L** + 2**S**)μ_B
  - e.g. $3d^5$ Fe^{3+} L=0 and S=5/2 → 5μ_B
  - observed scattering of a similar magnitude to nuclear scattering (often smaller, sometimes larger)

- Magnetism can be investigated at a microscopic scale with a high precision
  - Magnetic structure
  - Quantitative moment size

  → The best probe for magnetic structure determination

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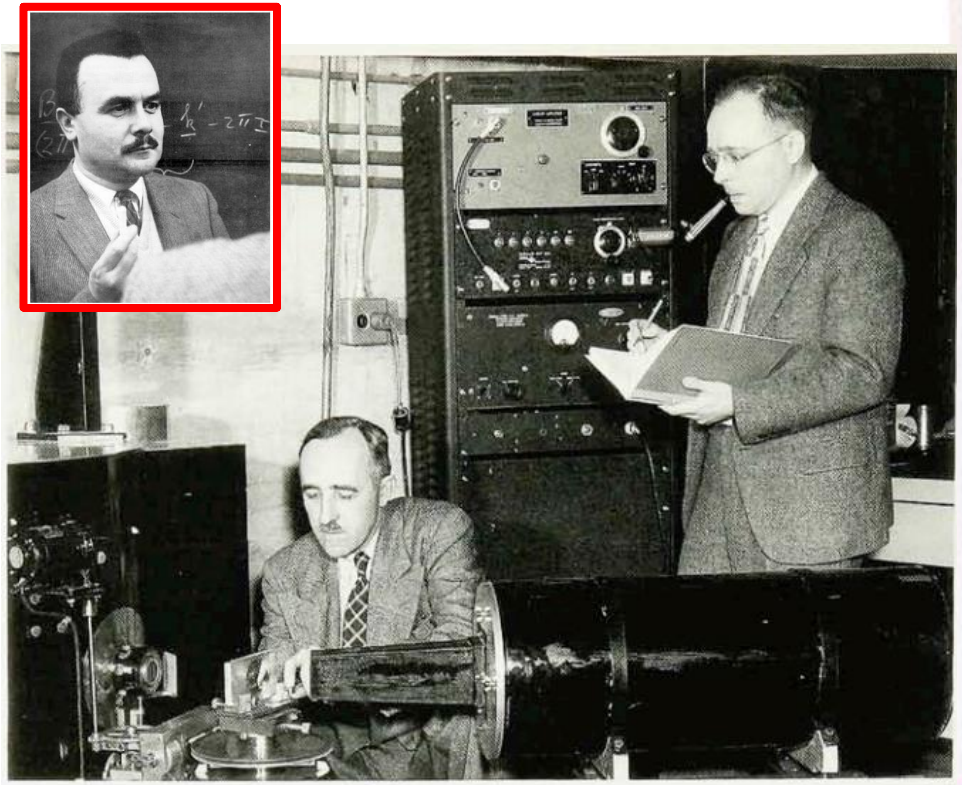
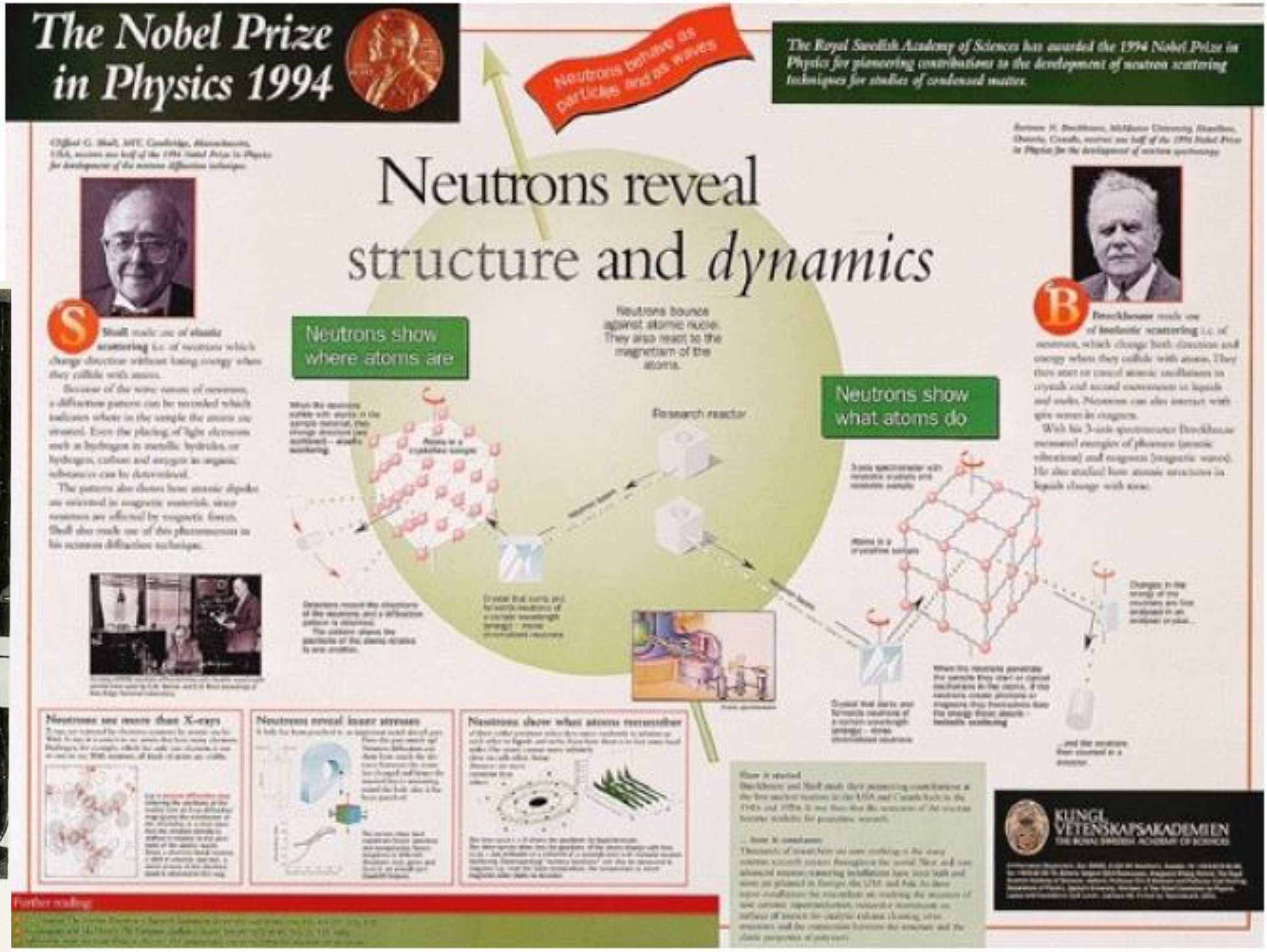
Neutron Scattering

Bertram Brockhouse and Clifford Shull - 1994 Nobel Laurate in Physics

"If the neutron did not exist, it would need to be invented"

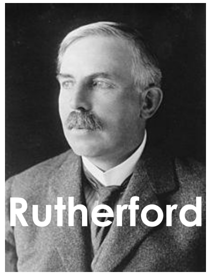


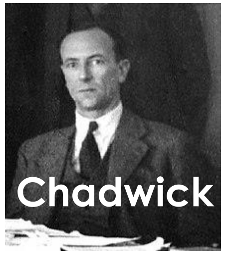
Clifford G. Shull (right) and Ernest O. Wollan shown around 1950 with a spectrometer they used for neutron scattering studies at Oak Ridge.



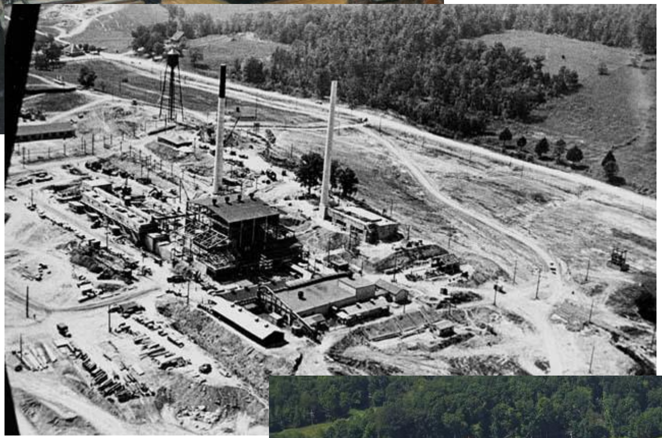
How to get neutrons: A (very) brief history

- 1920: Rutherford predicted neutron
- 1932: Neutron discovered by James Chadwick





1942: First reactor, Chicago-Pile 1 (CP-1)



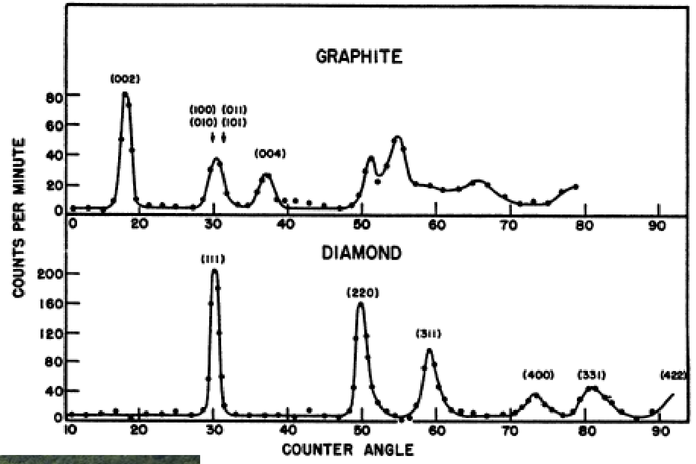
First neutron scattering 1943-1963 ORNL Graphite reactor

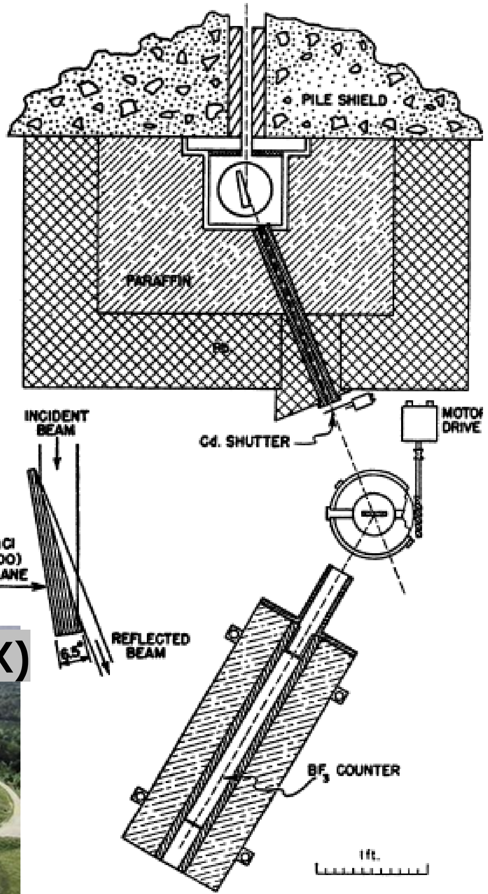
PHYSICAL REVIEW VOLUME 73, NUMBER 8 APRIL 15, 1948

The Diffraction of Neutrons by Crystalline Powders

E. O. WOLLAN AND C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received January 5, 1948)



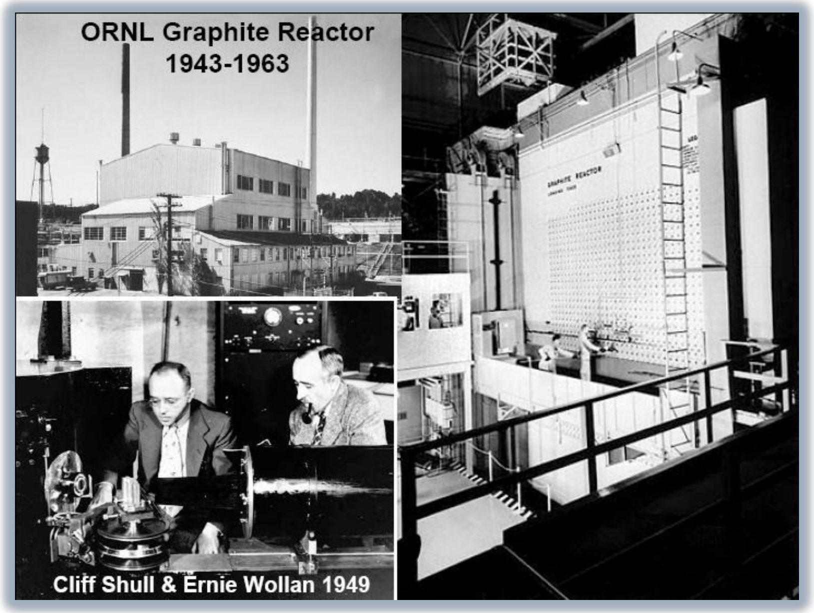


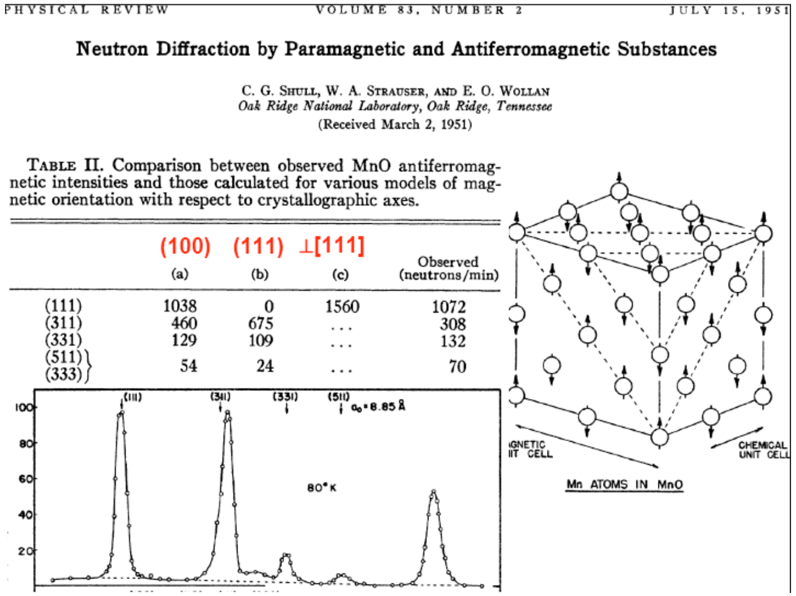
1965-present: HFIR

SNS: FTS (2006) and STS (202X)

First determination of magnetic structure performed at ORNL

- Clifford G. Shull received 1994 Nobel prize in Physics.





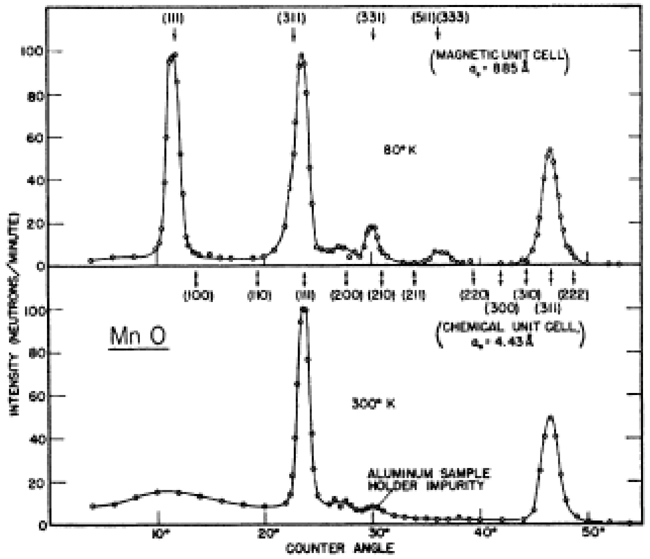
PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. Shull, W. A. Strauser, and E. O. Wollan
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)

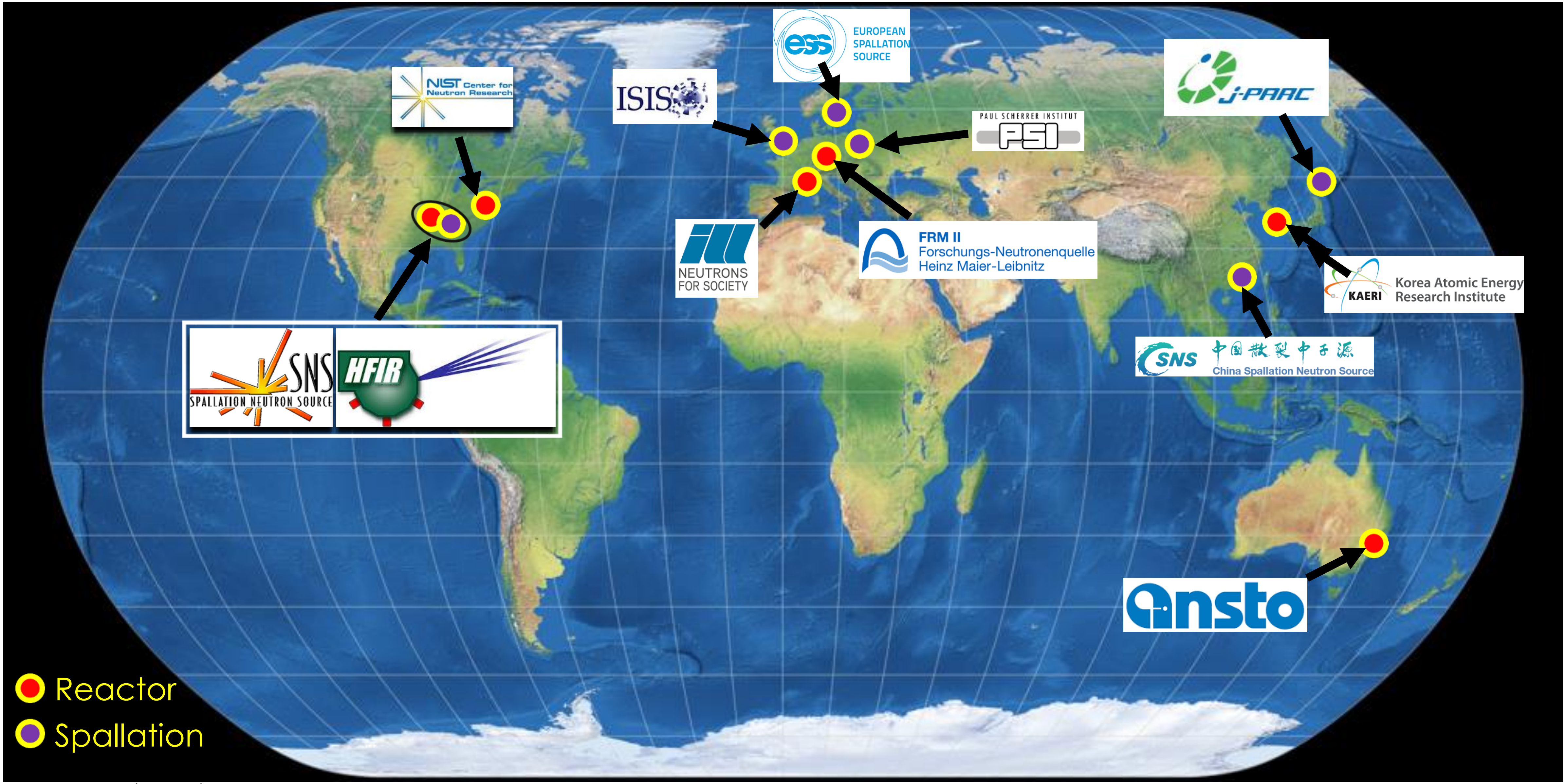
Table II. Comparison between observed MnO antiferromagnetic intensities and those calculated for various models of magnetic orientation with respect to crystallographic axes.

	(100) (a)	(111) (b)	⊥[111] (c)	Observed (neutrons/min)
(111)	1038	0	1560	1072
(311)	460	675	...	308
(331)	129	109	...	132
(511) (333)	54	24	...	70

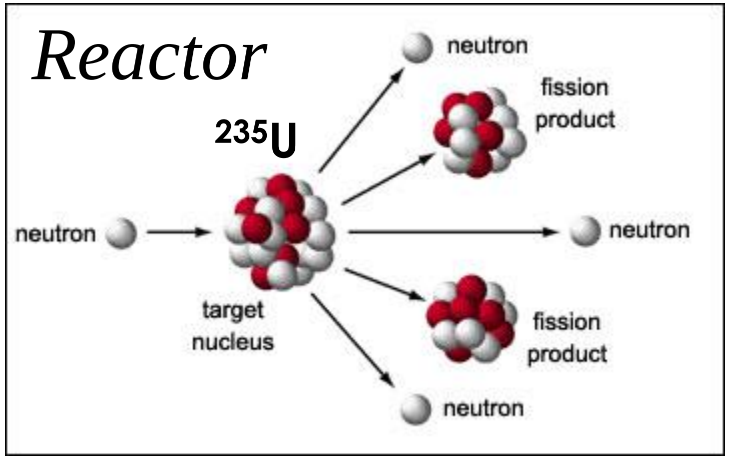


- First direct evidence of antiferromagnetism in MnO.
- Neel model of ferrimagnetism confirmed in Fe_3O_4.
- First magnetic form-factor data obtained in Mn compounds.
- Production of polarized neutrons by Bragg reflection from ferromagnets demonstrated.

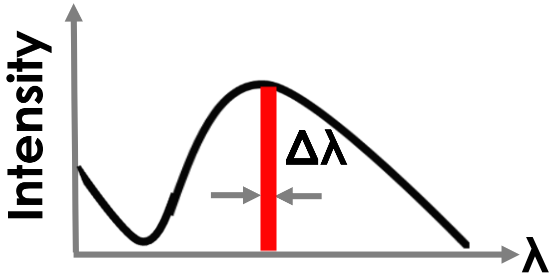
Neutron Sources around the world

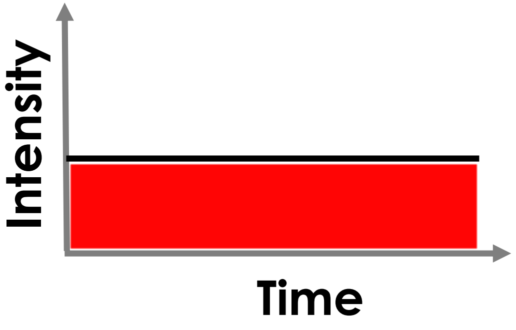


Neutron scattering: Reactor and Spallation source

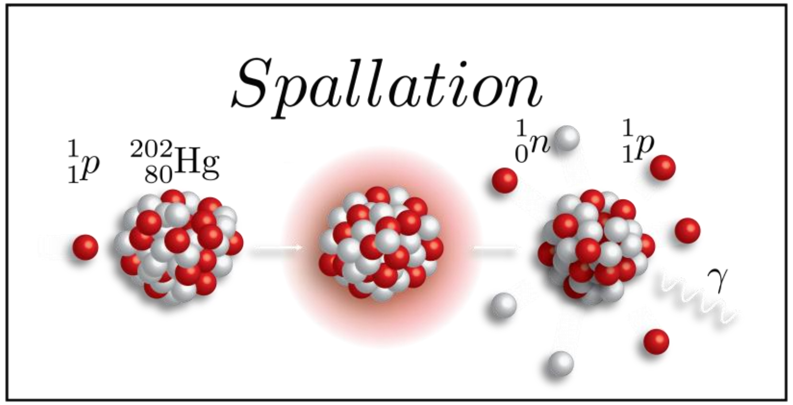


Fast neutrons are slowed by collisions in moderator (C, H_2O, D_2O) to produce thermal neutrons

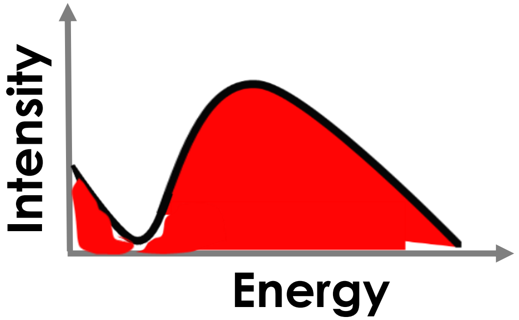




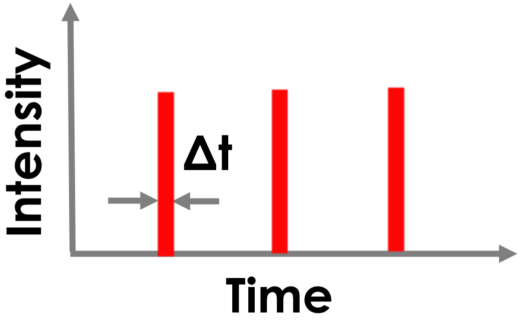
Small Δλ used, but source on all the time



A pulse of protons impacts on a target (Ta, Hg) to produce a shower of fast neutrons. These are slowed down in a moderator (H, CH_4)



Each pulse of neutrons contains a broad spectrum of energy (λ)



Pulse of neutrons ~30 times per second

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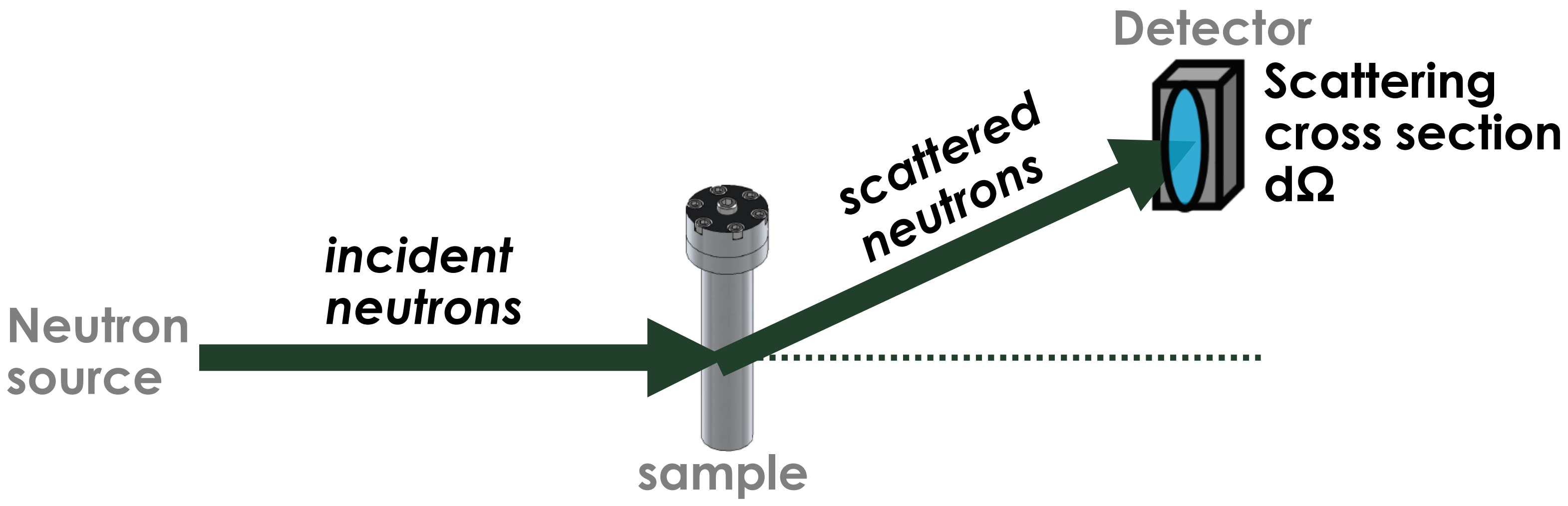
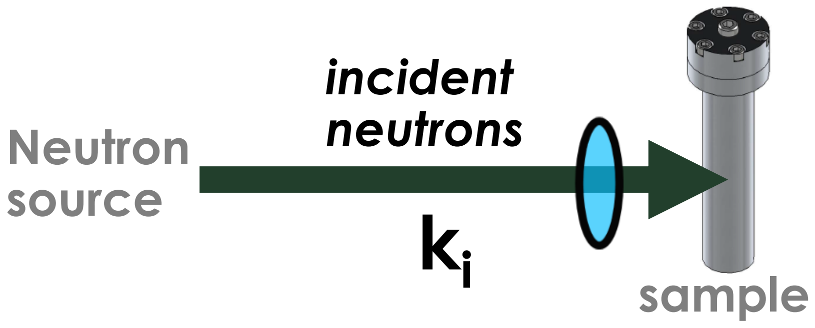
Neutron Scattering



- Neutron source produces an incident beam of neutrons that scatters from a nucleus or unpaired electron [*sample*] into a defined cross-section dΩ [*detector*].

Neutron Scattering Cross section



The scattering cross section can be measured in absolute units.

Flux: $$\Phi = \frac{\text{Rate of neutrons through area}}{\text{area}}$$ 10^6-10^9 n/cm^2/s

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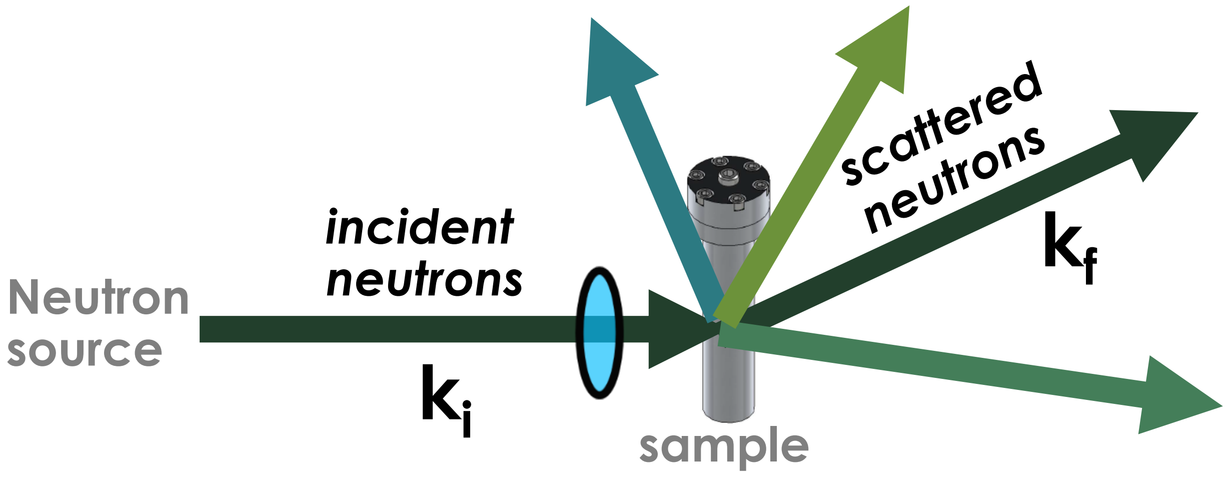

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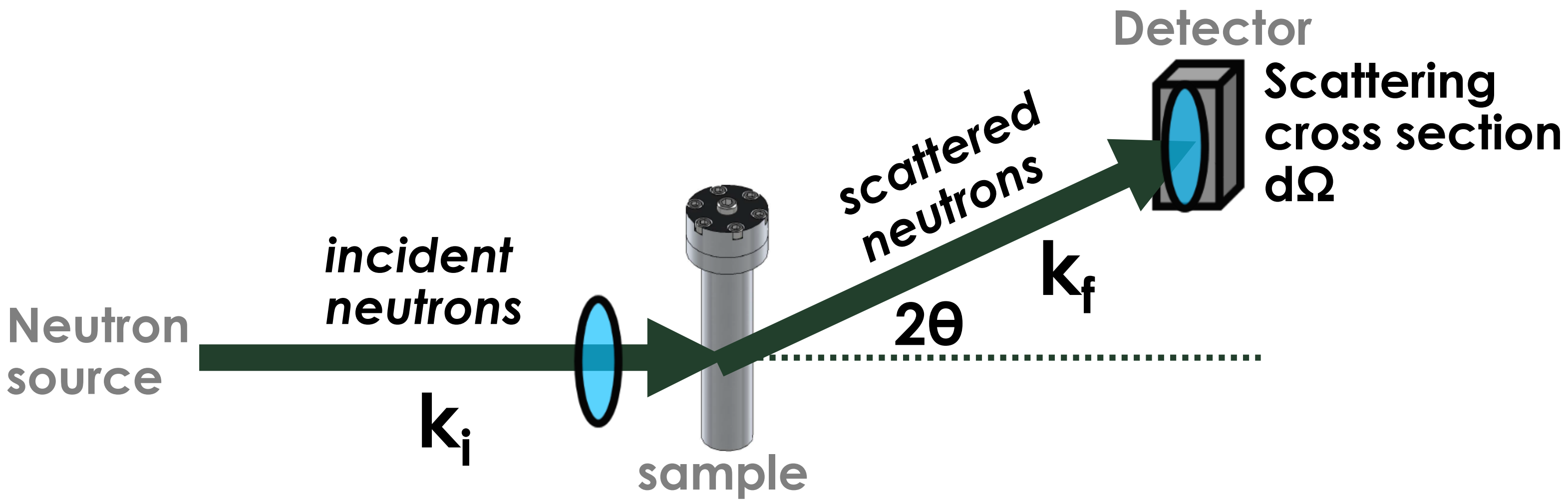
Rate of scattering: [Cross section]	$\sigma = \dfrac{\text{Rate of neutrons scattered}}{\Phi}$	Atom → 1 barn =10^{-24} cm^2. Effective surface area of nucleus

Neutron Scattering Cross section



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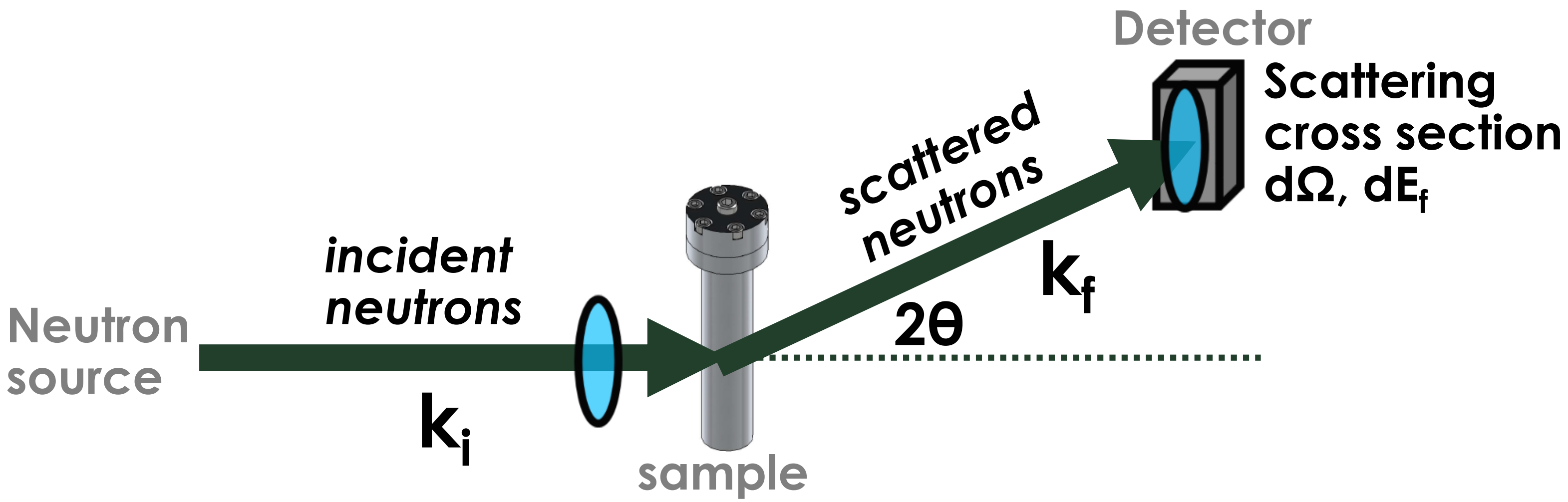
Rate of scattering into a specific solid angle: [Differential cross section]	$\frac{d\sigma}{d\Omega} = \frac{\text{Rate of neutrons scattered into } d\Omega}{\Phi \times d\Omega}$	Units of barn/steradian.

Neutron Scattering Cross section



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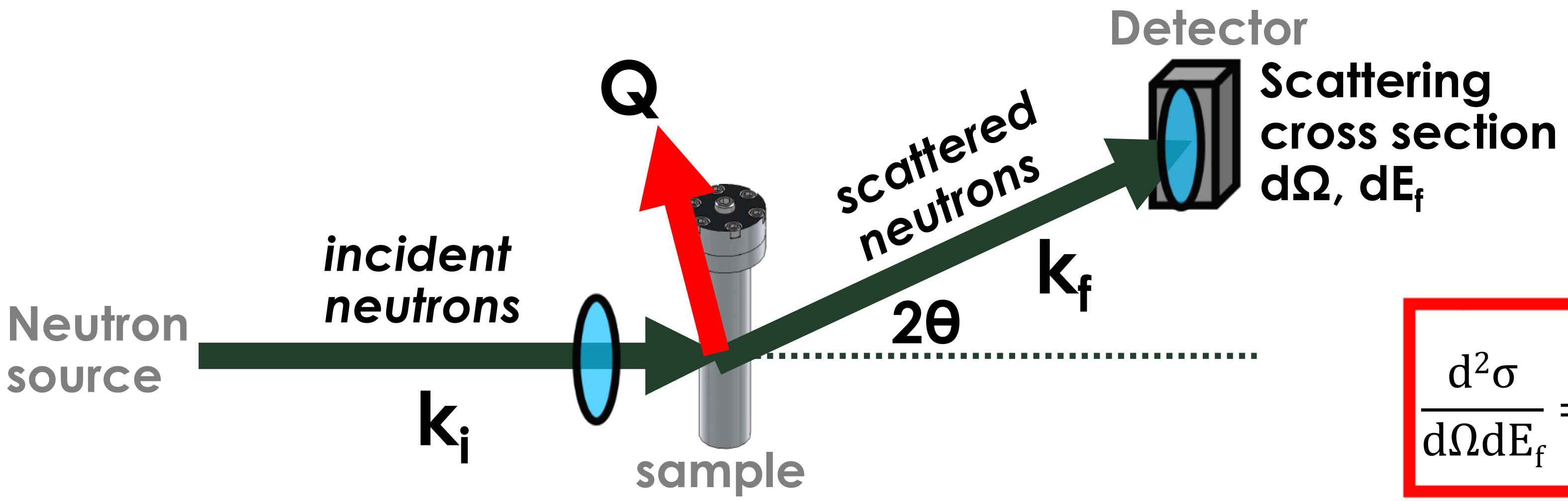
Rate of scattering into angle within energy range: [Partial differential cross section]	$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\text{Rate of neutrons into } d\Omega \text{ and dEf}}{\Phi \times d\Omega \times dE_f}$	Units of barn/steradian/meV

Neutron Scattering Cross section



The scattering cross section can be measured in absolute units.

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} S(\mathbf{Q}, \omega) \xrightarrow{\text{Diffraction}} \frac{d\sigma}{d\Omega} = S(\mathbf{Q})$$

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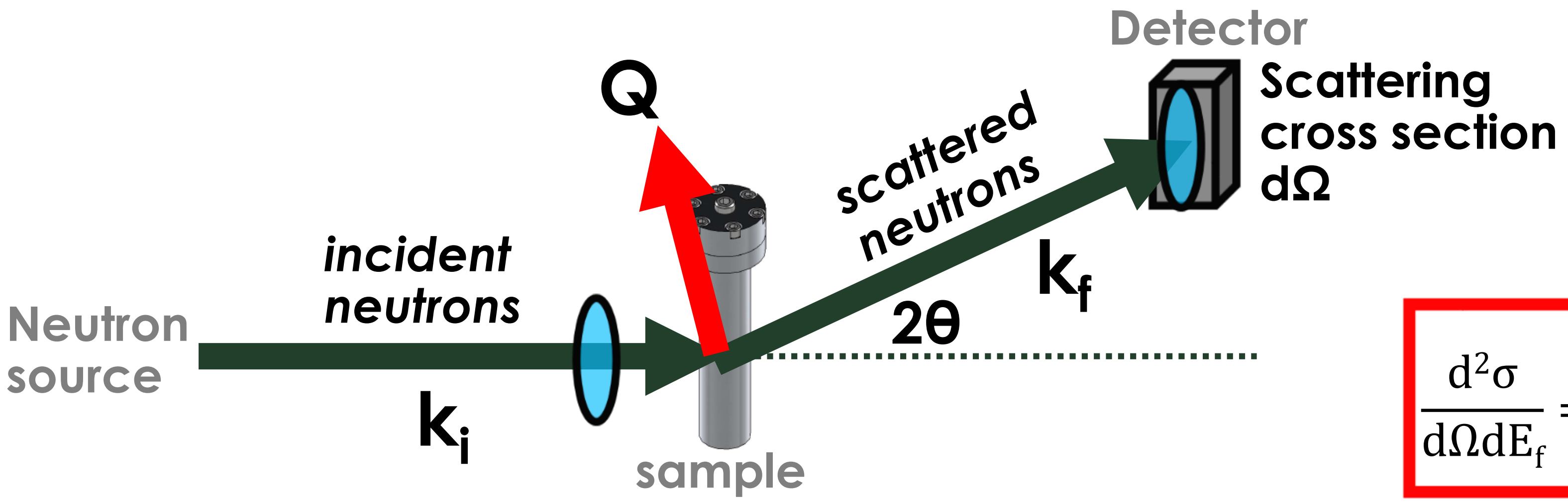
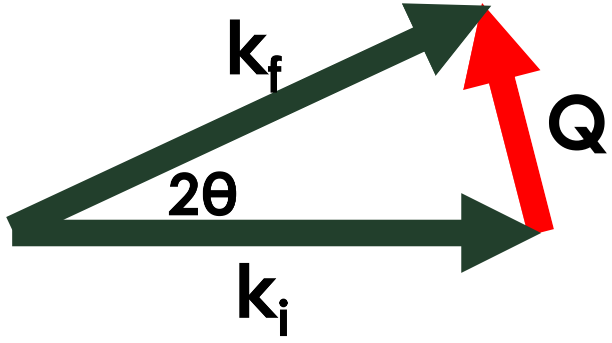
Neutron Scattering



$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} S(\mathbf{Q}, \omega) \xrightarrow{\text{Diffraction}} \frac{d\sigma}{d\Omega} = S(\mathbf{Q})$$

Scattering triangle:



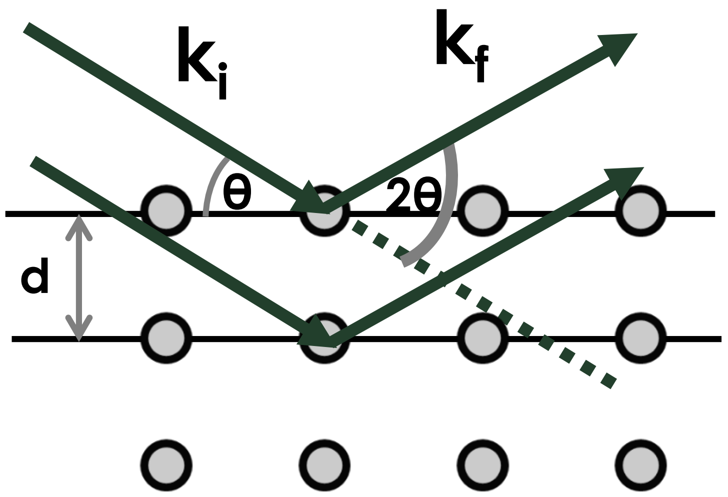
Momentum transfer: $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

Elastic scattering: $|\mathbf{k}_i| = |\mathbf{k}_f|$

Neutron diffraction: Bragg scattering

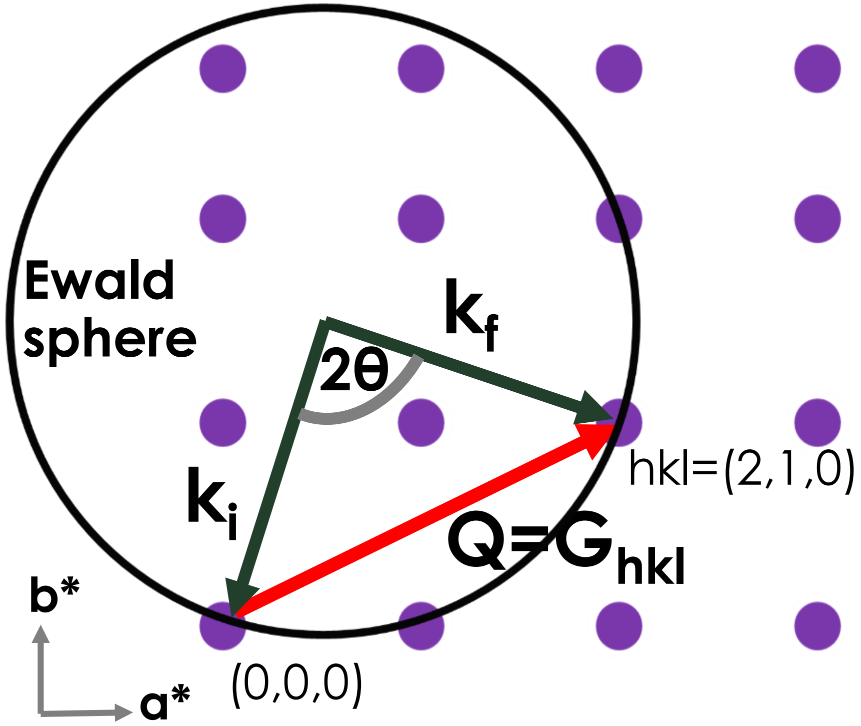
Diffraction from a crystal



Bragg peaks when: λ=2dsinθ

Braggs Law

Diffraction in reciprocal space



Bragg peaks when: $Q=G_{hkl}$

Scattering by a potential V(r): Born approximation

- Neutron scattering can be treated as scattering from a central potential (nuclear or magnetic).
- This interaction potential with neutron and matter is weak.
  - Disregard multiple scattering
- This allows the use of the Born approximation.

→ **Neutron cross-section can be completely known and modelled**

→ **Work in reciprocal space**

Born approximation

- Wavefunction of scattering by a central potential:

$$\Psi(\mathrm{r}) = e^{i\mathbf{k}.\mathbf{r}} + \left[-\frac{1}{4\pi} \int d\mathbf{r}'\, e^{i\mathbf{k}.\mathbf{r}'} V(\mathbf{r}') \Psi(\mathbf{r}') \right] \frac{e^{i\mathbf{k}.\mathbf{r}}}{r}$$

- Expand integral (Born series):

$$-\frac{1}{4\pi} \int d\boldsymbol{r}'\, e^{i\mathbf{k_f}.\mathbf{r}'} V(\boldsymbol{r}')\Psi(\mathrm{r}') \approx -\frac{1}{4\pi} \int d\boldsymbol{r}'\, e^{i\mathbf{k_f}.\mathbf{r}'} V(\boldsymbol{r}')\Psi(\mathrm{r}') e^{i\mathbf{k}.\mathbf{r}} + \left(\frac{1}{4\pi}\right)^2 \int d\boldsymbol{r} d\boldsymbol{r}' \frac{e^{i\mathbf{k}.\mathbf{r}'}}{|\boldsymbol{r}-\boldsymbol{r}'|} V(\mathbf{r}) V(\mathbf{r}') + \ldots$$

- Take first term (Born approximation):

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{Born}} = \left| \frac{1}{4\pi} \int d\mathbf{r}\, e^{-i\mathbf{Q}.\mathbf{r}'} V(\mathbf{r}) \right|^2$$

where $Q = k_f - k_i$

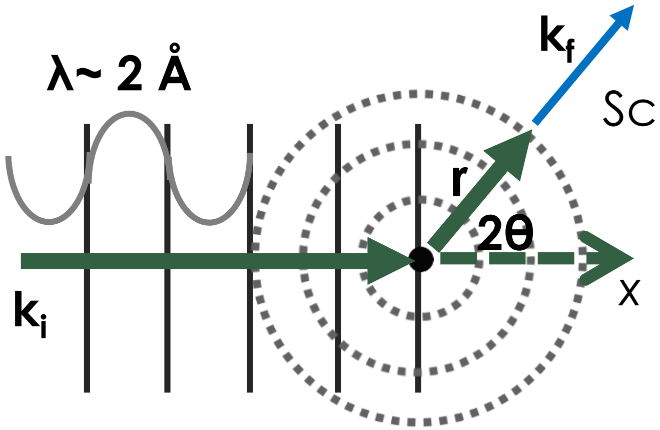
- Cross section is proportional to the Fourier transform of the potential energy, V(**r**).

Scattering potential: Scattering from a single fixed nucleus

Incident plane wave

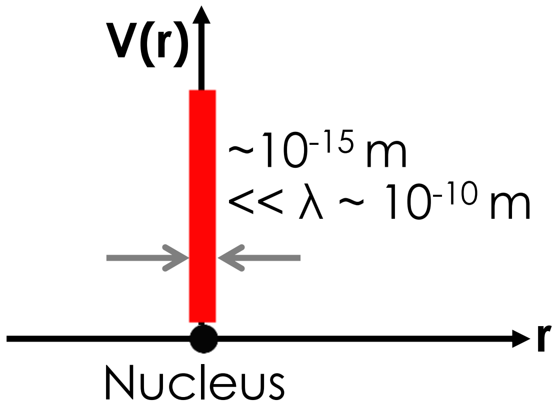
$\Psi_i \propto \exp(ik.x)$

$[k=2\pi/\lambda]$



Scattered circular wave

$\Psi_f \propto (-b/r)\exp(ik.r)$



Nuclear interaction potential:

$$V_{\text{Nuclear}}(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b\delta(\mathbf{r})$$

- Very short range (~10^{-15} m)
- Isotropic scattering
  Diffraction theory: If waves of any kind scatter from an object of a size << λ then the scattered waves are spherically symmetric (S-wave scattering).
- Scattering is elastic → nucleus is fixed
- Details of the potential (V(r)) are unimportant.
  V(r) can be described by a scalar parameter b that depends only on the nucleus and isotope [Fermi Pseudopotential]
  b = scattering amplitude / length (~10^{-12} cm)

Scattering potential: Nuclear neutron diffraction

- Nuclear interaction potential:

$$V_{\mathrm{Nuclear}}(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b\delta(\mathbf{r})$$

- Diffraction intensity: $S(\mathbf{Q}) = |\sum_j b_j \exp(i\mathbf{Q}.\mathbf{r}_j)|^2$ (sum over all nuclei in sample)

- Rigid crystal:

$$S(\mathbf{Q}) = N\frac{(2\pi)^3}{V_0}\sum_{hkl}|F_{hkl}(\mathbf{Q})|^2\delta(\mathbf{Q}-\mathbf{G}_{hkl})$$

(sum over all reciprocal lattice vectors **G** (h,k,l))

Number of unit cells in crystal

Volume of unit cell

Scattering only when **Q**=**G**, i.e. at allowed (H,K,L) positions

Structure factor

$$F_{hkl}(\mathbf{Q}) = \sum_j b_j \exp(i\mathbf{G}.\mathbf{r}_j)\exp(-W_d)$$

(sum over nuclei in unit cell)

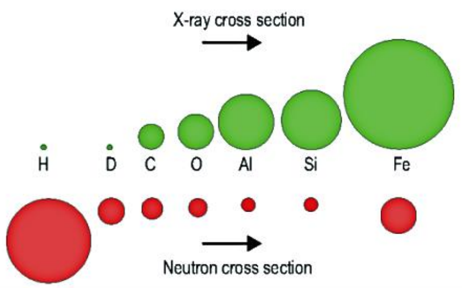
W_d → Debye-Waller factor for atomic thermal motion

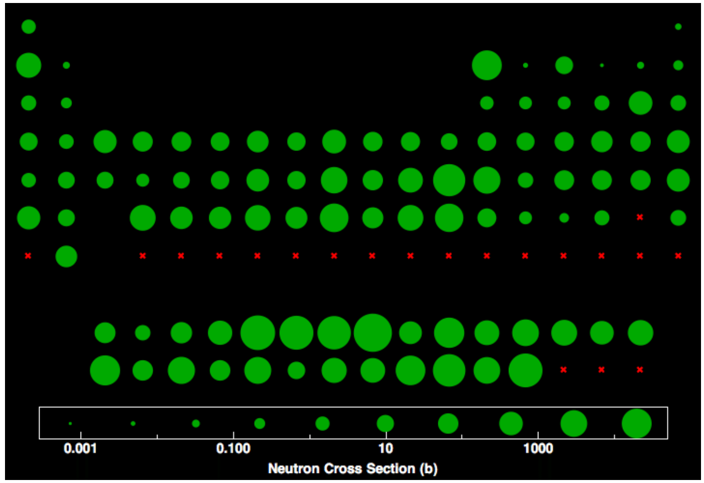
Scattering length (b)

Structure factor (nuclear)

$$F_{hkl}(\mathbf{Q}) = \sum_j b_j \exp(i\mathbf{G}.\mathbf{r}_j)\exp(-W_d)$$

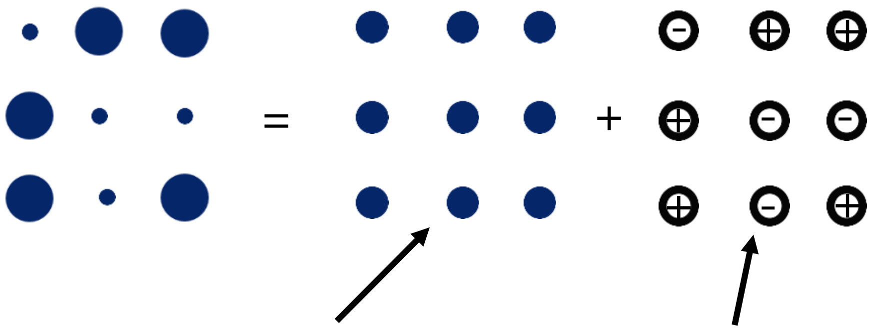
- Measured scattering depends on b, the scattering length
- b varies randomly with Z and isotope
  - offers advantages over x-rays
  - But need to check for absorption
- Coherent and incoherent nuclear scattering
- b varies with isotope and with nuclear spin orientation
- Consider a sample with two isotopes → b_1 ● and b_2 ●





Values of b_{coh} and σ_{inc} tabulated:
https://www.ncnr.nist.gov/resources/n-lengths/

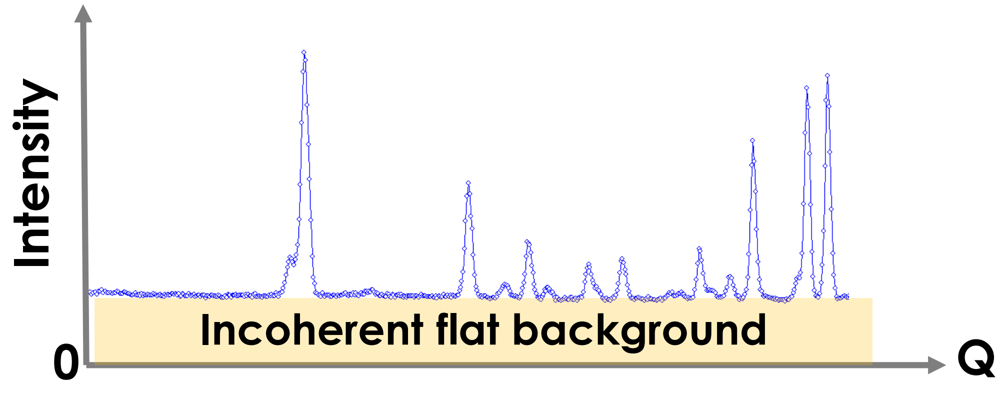
Random b1,b2



Mean b_{coh} Coherent scattering ($b \rightarrow b_{coh}$)

Deviation from mean σ_{inc} Incoherent scattering

$$S_{inc}(\mathbf{Q}) = \sum_j \frac{(\sigma_{inc})_j}{4\pi}$$



Scattering potential: Magnetic scattering

- <u>Magnetic interaction potential:</u> $V_{\text{Magnetic}(\mathbf{r})} = -\boldsymbol{\mu}_{\text{n}}.\,\mathbf{B}(\mathbf{r})$

Magnetic scattering is due to interaction of the neutron spin $\boldsymbol{\mu}_n$ *with the magnetic field of an unpaired electron,* ***B*(*r*)**.

- **B**(**r**) depends on electron spin and orbital currents
- Potential depends on direction of neutron spin → vector interaction
- Neutrons are only sensitive to the component of the magnetic moment perpendicular to **Q**
- Anisotropic scattering, unlike nuclear scattering.
- Depends on orientation of neutron spin → polarization analysis can be powerful
- Depends on electronic states → magnetic form factor is important

Scattering potential: Magnetic scattering

- Magnetic scattering is due to the interaction of the neutron spin with the magnetic field of an unpaired electron

- Interaction described by a potential:

$$-\boldsymbol{\mu}\cdot\mathbf{H} = -\gamma\mu_N \boldsymbol{\sigma}\cdot\mathbf{H}$$

Gyromagnetic ratio: $\gamma=-1.91$

Nuclear magneton:- $\mu_N=(m_e\ \mu_B) / m_n$

Pauli spin operator: $\boldsymbol{\sigma}$

- Magnetic scattering length proportional to the electron radius $e^2/m_e c^2$:

$$r_0 = -\gamma e^2 / m_e c^2 = -0.54\times10^{-12}\ \text{cm}$$

Magnetic and nuclear scattering lengths are comparable

Magnetic diffraction intensity

$$S_M(\mathbf{Q}) = C\sum_{G_M} |F_M(\mathbf{G})|^2 \delta(\mathbf{Q} - \mathbf{G}_M)$$

(sum over all magnetic reciprocal lattice vectors $\mathbf{G_M}$)

Scattering only when $\mathbf{Q}=\mathbf{G}_M$, i.e. at allowed (H,K,L) positions

Magnetic Structure factor:

$$F_M(\mathbf{G}) = \sum_j f_j(\boldsymbol{Q})\mathbf{m}_{\perp j} \exp{(i\mathbf{G}.\mathbf{r}_j)}$$

(sum over magnetically ordered nuclei in unit cell)

Form factor

Moment (perpendicular to Q)

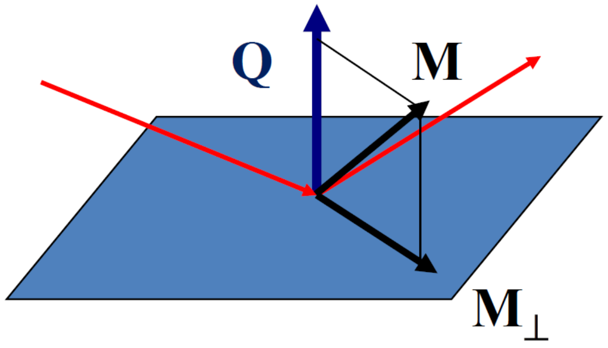
H,K,L in reciprocal space

Neutrons Only Measure Moments Perpendicular to Q

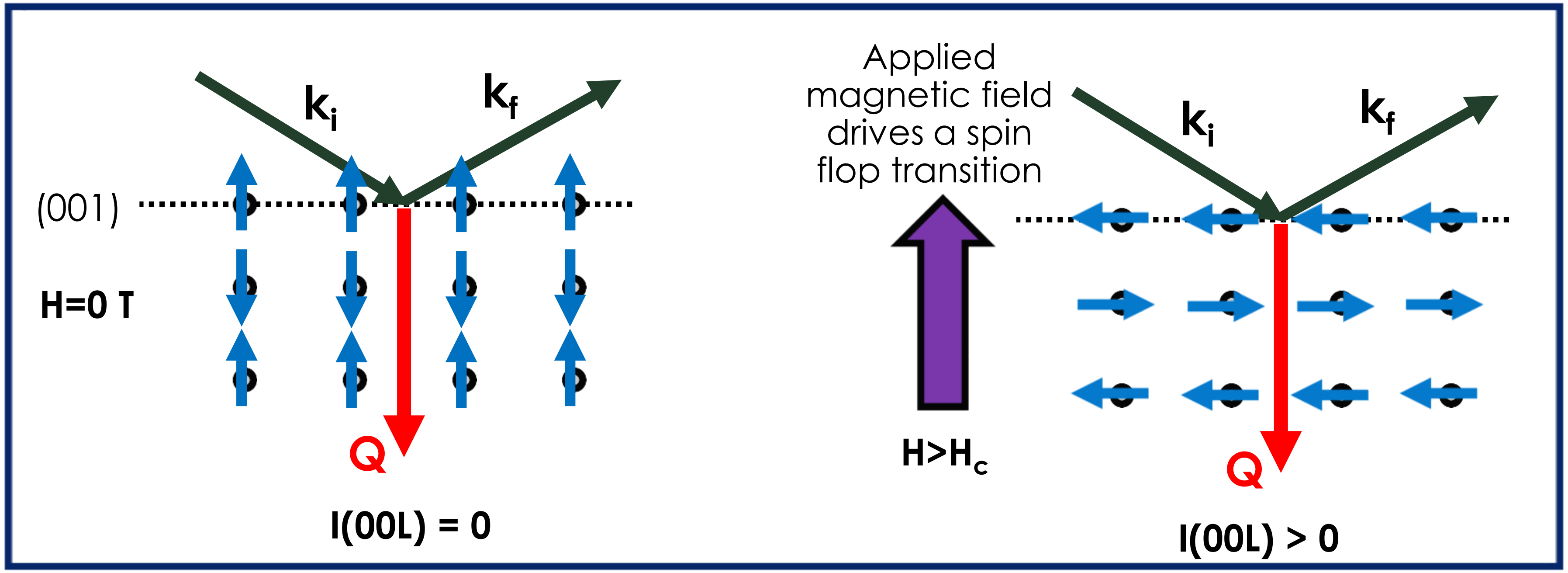
- Scattering depends on Fourier transform of $V_{magnetic}(\mathbf{r}) = -\boldsymbol{\mu}_n . \mathbf{B}(\mathbf{r})$
- From Maxwell's equation: $\nabla . \mathbf{B}(\mathbf{r}) = 0$

  Fourier transform → $i\mathbf{Q}.\mathbf{B}(\mathbf{Q}) = 0$

  → B(**Q**) is perpendicular to **Q** to be non-zero $M_{\perp}(\mathbf{Q}) = \mathbf{Q} \times (M \times \mathbf{Q})$



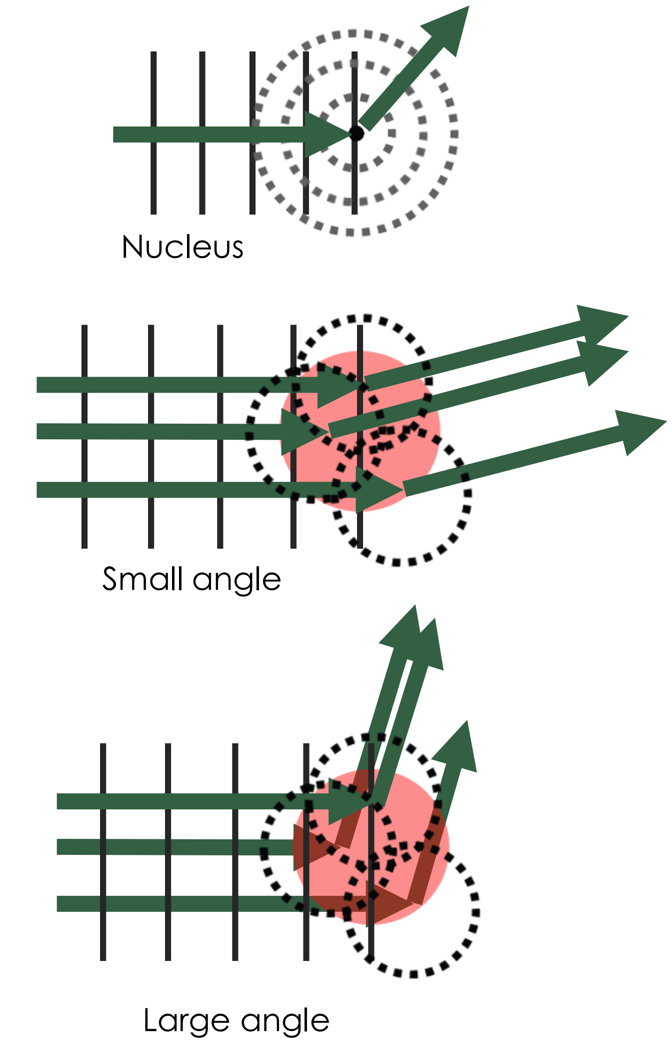
In experiments this can be a useful constraint:



Magnetic form factor

$$V_{magnetic}(\mathbf{r}) = -\boldsymbol{\mu}_n.\mathbf{B}(\mathbf{r})$$

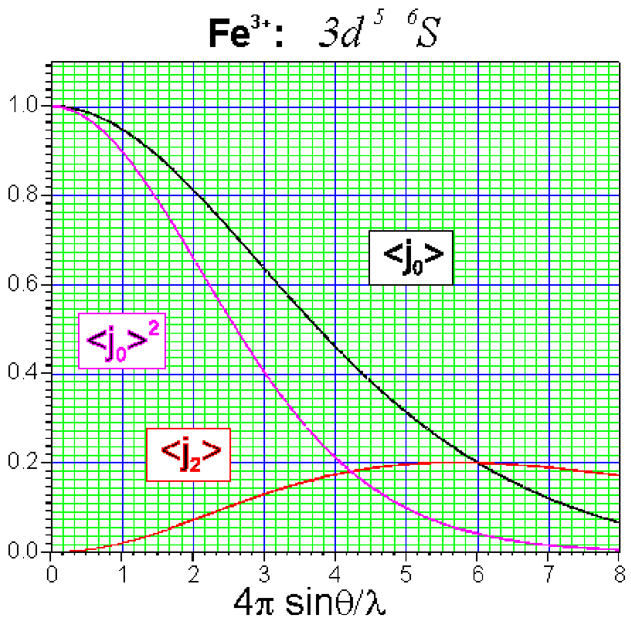
- Nuclear scattering of neutron is from a point charge → no form factor
- X-ray scattering is from charge cloud → form factor
- Magnetic scattering of neutron: **B**(**r**) depends on the electron spin and orbital motion → form factor
- Scattering decreases with increasing Q due to intra-atomic interference.
- Analytical expressions are tabulated in P.J. Brown International Tables of Crystallography, Vol. C, section 4.4.5. for j_1 (spin only),j_2 (orbital),j_3 (orbital),etc



$f(Q)=c_1\langle j_0(Q)\rangle + c_2\langle j_2(Q)\rangle + c_3\langle j_4(Q)\rangle + \ldots$

$f(0) = 1$

- Form factor depends on valance of ion.
- In general intensity drop-off more pronounced for higher Z



Neutron measurements: Nuclear and Magnetic scattering

- The scattered intensity S(**Q**) is given by:
- $S(\mathbf{Q}) = |F_N(\mathbf{Q})|^2 + P.(F_{M\perp}(\mathbf{Q})F_N^*(\mathbf{Q}) + F_{M\perp}^*(\mathbf{Q})F_N(\mathbf{Q})) + |F_{M\perp}(\mathbf{Q})|^2$
- Unpolarized measurements → no interference terms between nuclear and magnetic scattering
- $S(\mathbf{Q}) = |F_N(\mathbf{Q})|^2 + |F_{M\perp}(\mathbf{Q})|^2$
- The scattered intensity is simply the two components added together.

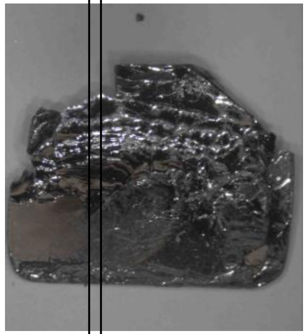
  - **In refinements this means the nuclear and magnetic phases can be refined separately. (always case for Representational analysis)**
  - **Measure at low Q to maximize scattered magnetic intensity.**
  - **Make use of the constraint that neutrons only measure perpendicular component.**

Overview

- Why use neutrons?
- Neutron sources: A (very) brief history
- Theoretical concepts of neutron scattering
- **Practical aspects of neutron scattering and refinements**
- Where to perform experiments: Diffraction instruments at ORNL and around the world?

Powder or Single crystal ?

Powder: Advantages	Powder: Disadvantages	Single crystal: Advantages	Single crystal: Disadvantages
• Often easier synthesis • See everything • Propagation vector • If powders work then saved a lot of effort. • Measurement more routine.	• Information is averaged and lost. • Hard to uniquely assign propagation vector. • No domain info • Field measurements hard to interpret quantitatively	• Propagation vector unambiguously determined. • Low background so can see smaller moments • Directional dependence of field (or strain, etc) • Domain information • Smaller mass (~mg)	• Synthesis can be hard • Data correction: absorption, extinction, etc • Need to search large reciprocal space (or have large detectors) • Sample alignment considerations.



Things to considers for an experiment

- Magnetic scattering is often weak and only observable at low Q due to magnetic form factor. Preparation is key to a successful experiment.
- Characterization in the lab is crucial (XRD, Magnetization, Heat capacity, etc)
  → know your sample and where to look with neutrons
- Powders
  – Typically the more mass the better → experiment and data analysis greatly improved.
  – Use of Al can reduces background compared to V.
    → Extra peaks, but for magnetic structure determination usually not an issue.
- Single crystal
  – Small masses often feasible (< mg), check with instrument teams.
  – Know crystal quality before experiment (alignment/mosaic/domains/twinning/etc)

Basics of fitting diffraction data

Measured peaks have position (Q or HKL), intensity and width

- **Peak positions:** determined by size and shape of unit cell
- **Peak intensities:** determined by the atomic number and position of the various atoms in the unit cell
- **Peak widths:** determined by instrument parameters as well as temperature, crystal size/quality, strain,

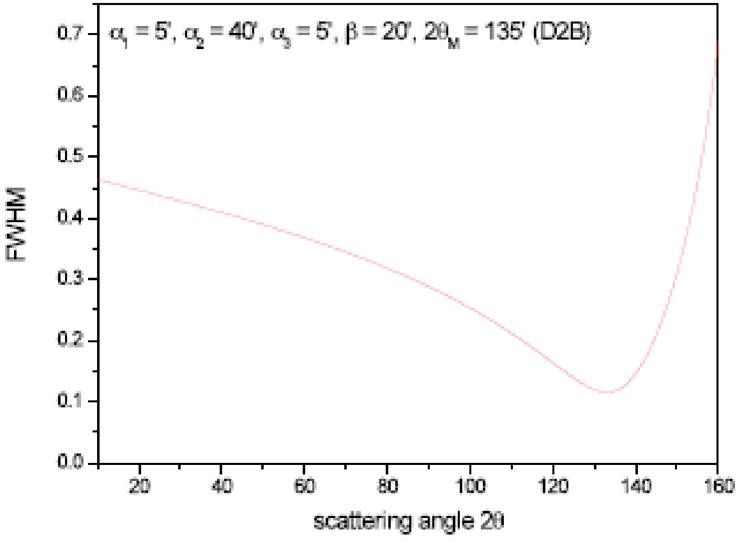
- Single crystal → integrated intensity of each peak is extracted. So in refinement only need to consider a few parameters (extinction, absorption)
- Powder → Overlapping peaks means modelling whole pattern. [Rietveld Refinement]

Fitting your data: Rietveld refinement (powder)

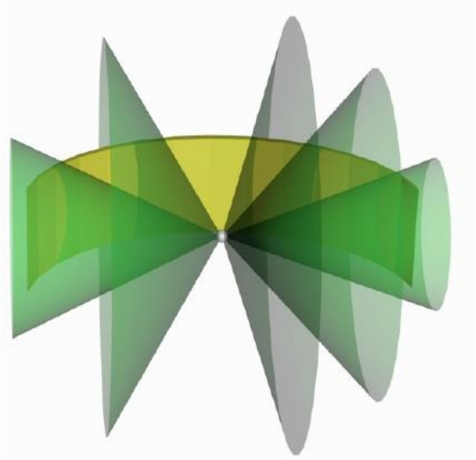
- Hugo Rietveld: "*The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often-detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram.*"
- If pattern can be modelled, the fit between observed data and model can be optimized.
- In powder, unlike single crystal, need to model experiment dependent parameters
  - Background
  - Peak broadening (sample/instrument)
  - Lattice constant
  - Absorption and sample shape
  - Preferred orientation
- Refinement → need a good starting model
- Neutron data usually required for determining occupancy.

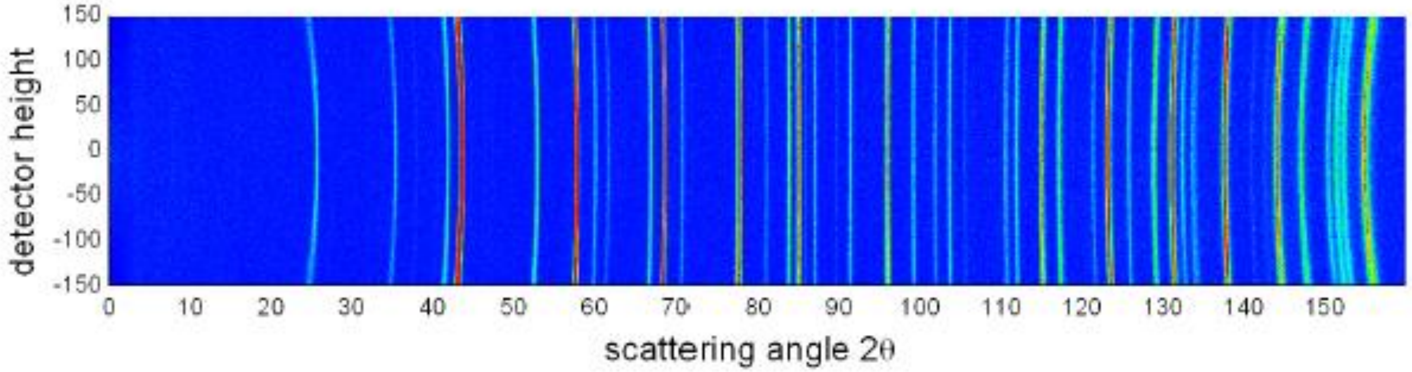
Hugo Rietveld in the Petten Reactor (~1987)

Peak shape varies with scattering angle



- Cagliotta formula: $\text{FWHM}^2 = U \tan^2\theta + V \tan\theta + W$
- *U, V, W* parameters are a function of instrument collimation and monochromator   G. Caglioti et al., Nucl. Instr. 3, 223-228 (1958)
- Does not take into account guides or focusing of monochromator.
- Spallation sources need extra terms to model resolution from pulse shape.
- Debye-Scherrer cone scattering causes asymmetric peak shapes at low/high angle in I(Q) 1d plots.





If converted to 1d → asymmetric at low 2θ, symmetric at 2θ=90°

Overview

- Why use neutrons?
- Neutron sources: A (very) brief history
- Theoretical concepts of neutron scattering
- Practical aspects of neutron scattering: performing a successful experiment
- **Where to perform experiments: Diffraction instruments at ORNL**

Oak Ridge National Laboratory (ORNL)

- **Neutrons produced from a reactor core.**
- **Highest flux reactor based source in the U.S. (80 MW)**

- **Neutrons produced from an accelerator/target.**
- **Most intense pulsed neutron beam. (60Hz, 1.4 MW)**

- **Planned Second Target Station in 202X**
- **Most intense pulsed source of cold neutrons**

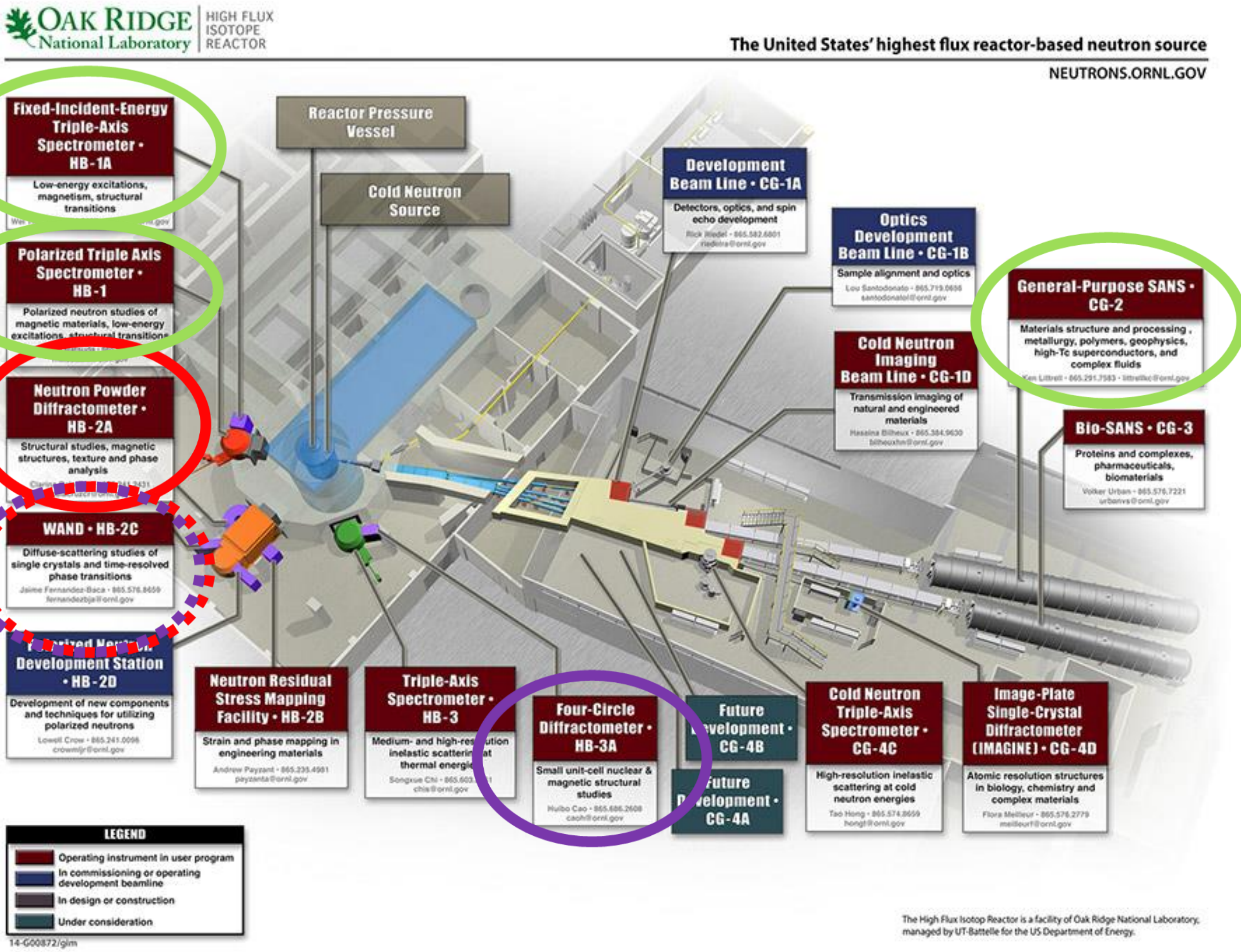
- Several complimentary diffraction beamlines at ORNL.
- Science of the material will dictate choice of instrument(s).
- Second target station will add further capabilities.

HFIR

Magnetism:

- HB-2A
- WAND^2
- HB-3A Four-Circle (DEMAND)

- Additional options:
  - HB-1A (low background)
  - GP-SANS (low Q)
  - HB-1 (polarization)

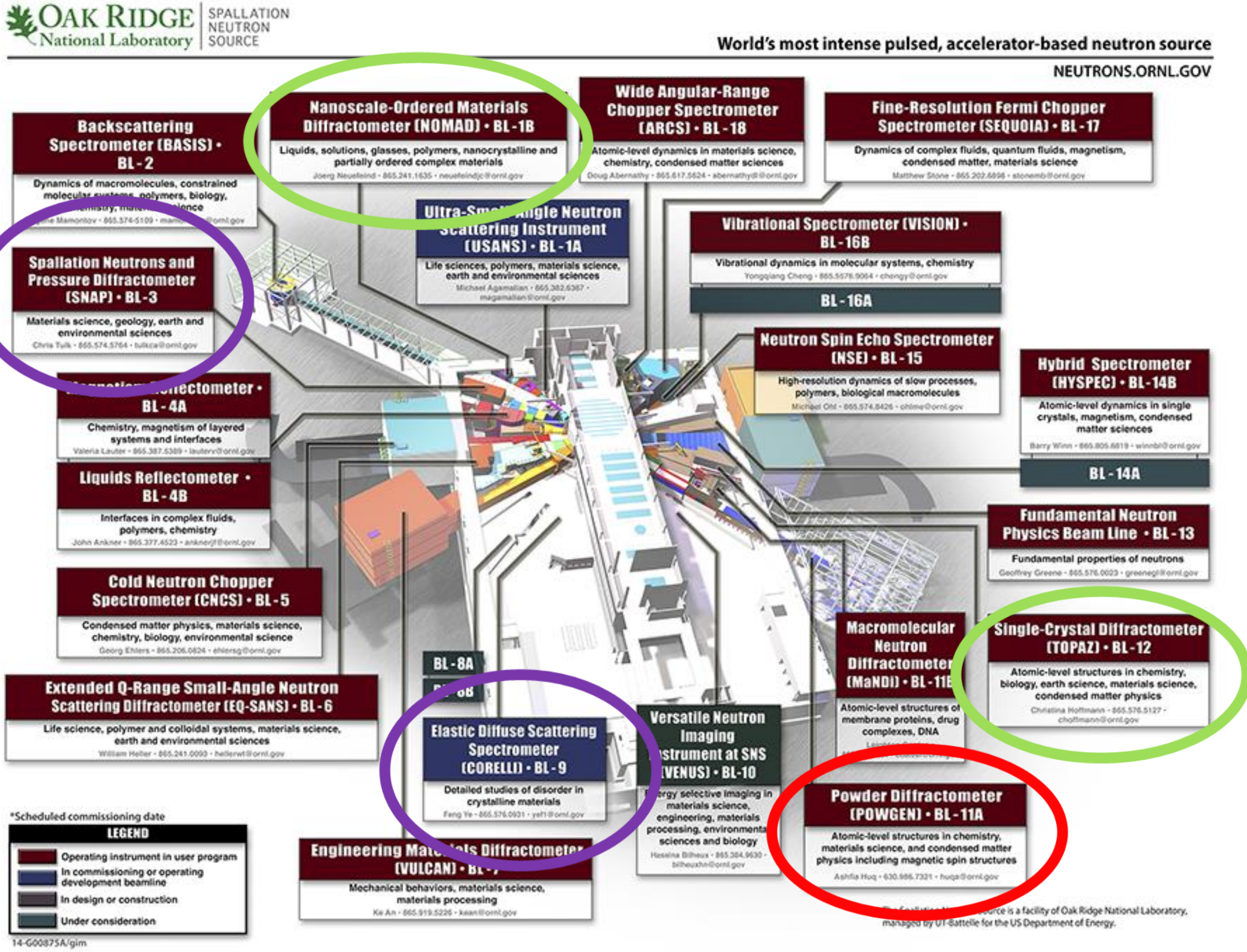


SNS

Magnetism:

- POWGEN
- CORELLI
- SNAP

- Additional options:
  - TOPAZ (large unit cells)
  - NOMAD (PDF)
  - HYSPEC (polarization)



Powder diffraction (ORNL)

- HB-2A (HFIR) → Majority of science is magnetism. Half-polarized option. Variety of sample environments.
- POWGEN (SNS) → Highest resolution for detailed crystal structure. Large Q available.
- $WAND^2$ (HFIR) → High flux, medium/low resolution

HB-2A: Instrument aims and layout

Applications	Neutron Beam	Resolution (Δd/d)	Q-range	Beam size at sample	Measurement times
Magnetic structure determination under extreme environments. Polarized capabilities.	Constant wavelength (vertically focused Ge monochromator)	$2.2e^{-3}$ (variable) Balance between high flux/resolution	0.2-5.1 $Å^{-1}$ (λ=2.41 Å) 0.35-8 $Å^{-1}$ (λ=1.54 Å)	60 x 30 mm Typical can sizes are 6-15 mm diameter and 50 mm height.	Variable. Refinable data in minutes. Magnetic structure in 0.5 - 8 hours. Typically need gram sized sample for magnetic structures.

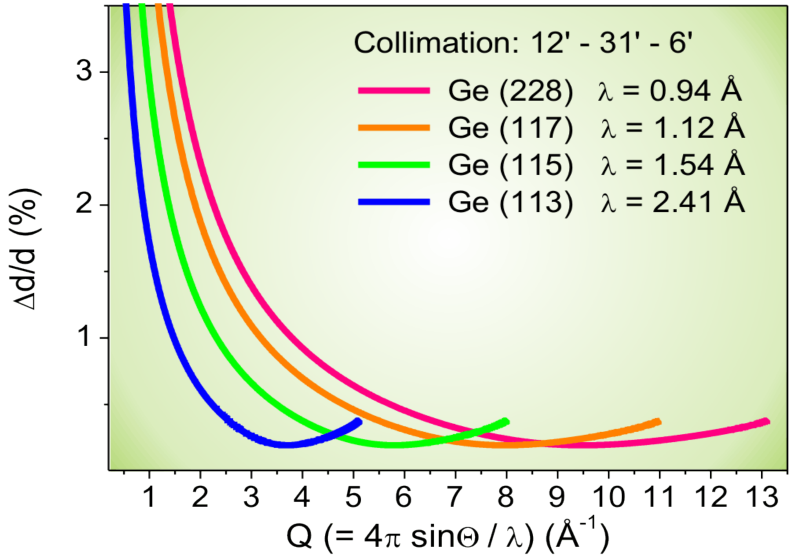
Flexible open design to allow for variety of complex and easily changeable sample environments.

Temperature: 30mK – 1700K
Magnetic field: 8T
Pressure: 2 GPa (BeCu clamp cell)
6kbar (Al helium gas pressure cell)

HB2A instrument

Ge(hkl)	λ (Å)	d_{max}(Å)	4πsinθ/λ	Flux (n/cm²s)
(113)	2.41	27.6	0.2-5.1	5 x 10^6
(115)	1.54	17.6	0.35-7.9	1 x 10^7

Resolution:

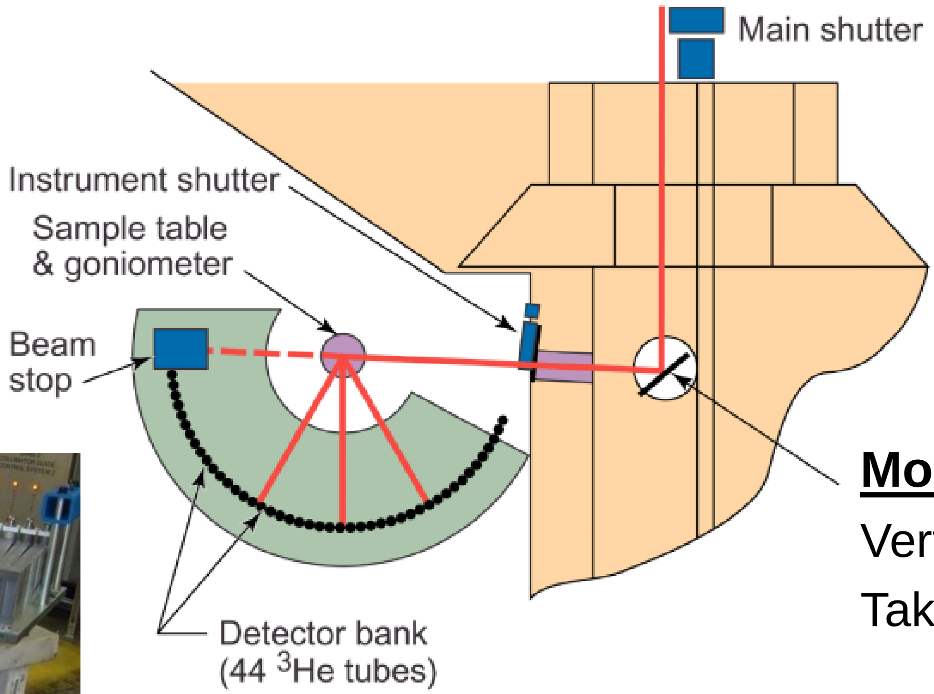


Detector bank:

44 ^{3}He tubes (11 cm x 3 cm)

spaced at ~ 2.7º intervals

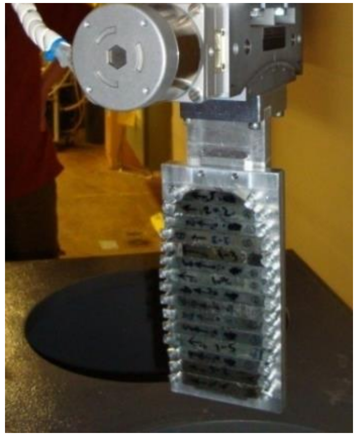
Scattering range (2θ): 2-155º



Monochromator:

Vertically focused: 15 Ge [HHL]

Take-off angle: 90°



Collimation:

pre-monochromator (α1): 12' or open (35') [Fixed]

pre-sample (α2): 6', 16', **21'**, 31', **open**

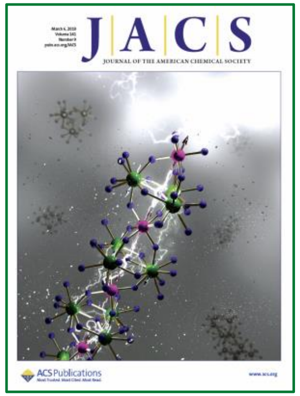
pre-detector (α3) (x 44): 12' [Fixed]

Beam size:

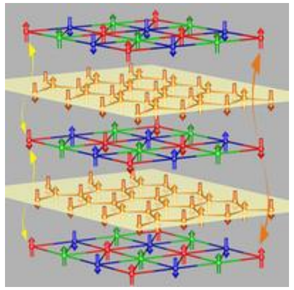
2 x 1 inches

HB2A: What science is possible?

✓ **Temperature dependence of crystal and magnetic structures (0.03 K<T < 700 K)**



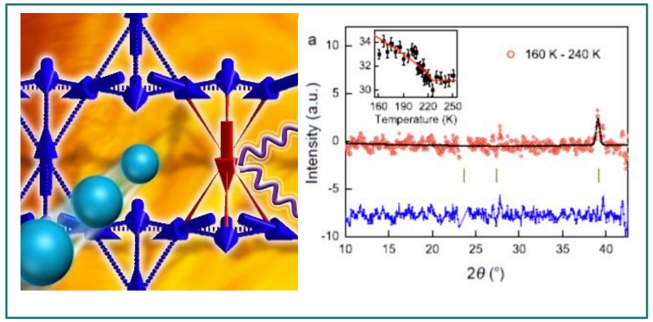
3-Sample changer available for measurements from 1.5 to 300 K. This allowed rare magnetic order of U(IV) ions to be investigated in a series of compounds.



V. O. Garlea et al., PRX 9, 011038 (2019)

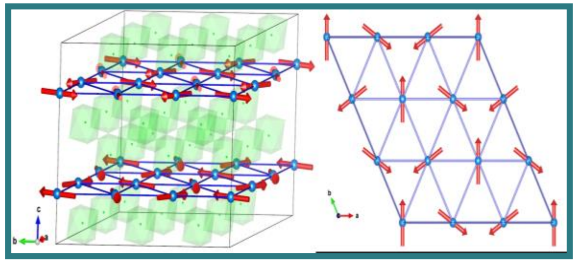
Magnetic structure and spin-orbit-driven excitation points to potential Weyl fermions

Stuart Calder (ORNL) et al.



Novel Physics in Triangular lattice antiferromagnets

Haidong Zhou (UTK) et al.



✓ **Development of High pressure cells to study magnetic materials at low T**

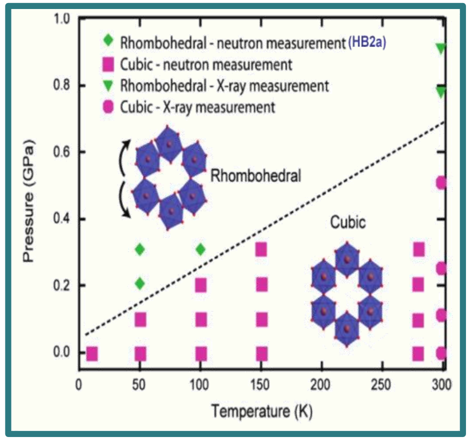
C. dela Cruz (ORNL) and Y. Uwatoko (Univ. of Tokyo)

- NiCrAl “Russian” pressure cell: 2.5 Gpa
- BeCu clamp cell: 2 GPa

✓ **Pressure studies with He gas cells up to 6 kbar**

Negative Thermal Expansion (NTE) in Cubic ScF_3

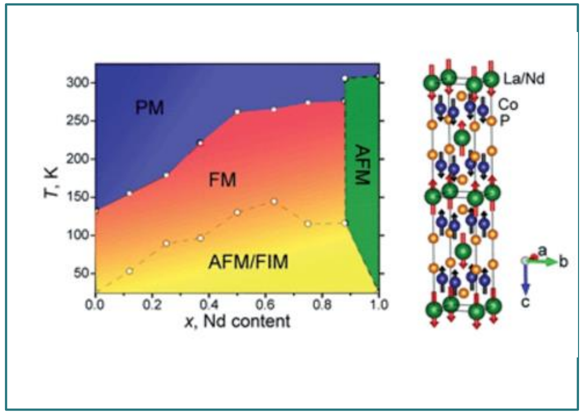
B. Greve and A. Wilkinson (Georgia Tech)



✓ **Magnetic field induced phenomena, up to 6 Tesla**

Magnetic pole reversal in $La_{1-x}Pr_xCo_2P_2$

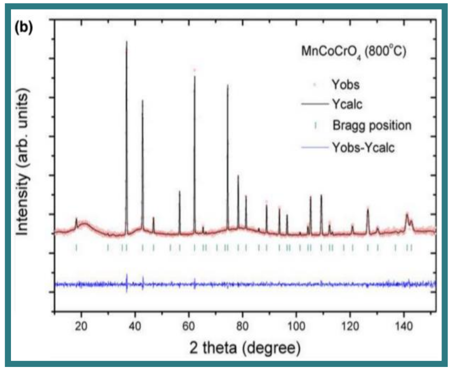
M. Shatruk (FSU) et al.



✓ **High-temperature studies, up to 1200 C**

Probing the Long term stability of Solid Oxide Fuel Cells

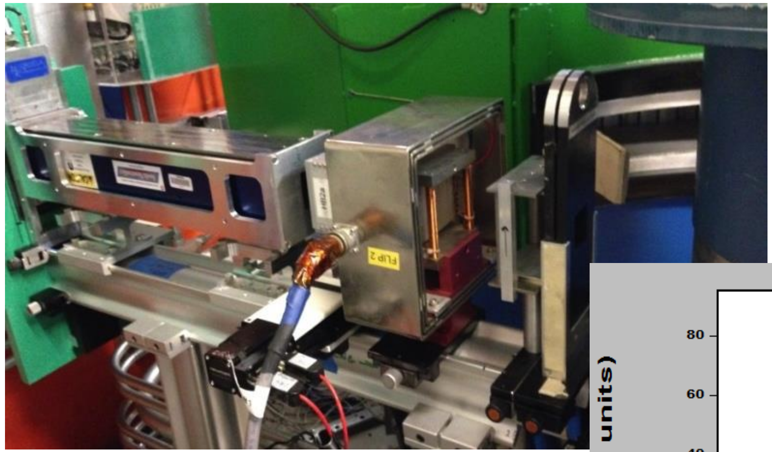
Y. Liu and J.W. Fergus (Auburn University)



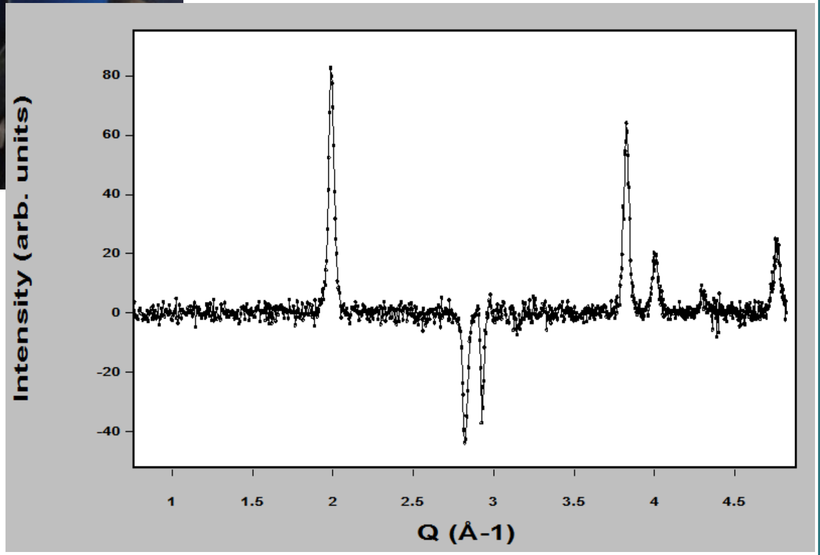
Recent developments

Polarized neutron diffraction at HB2A

➔ V-cavity polarizer commissioned.
➔ **Measurements of weak ferro- and ferri-magnets. <0.01 μ_B**
➔ Almost perfect transmission of 50% and flipping ratio of 14.
➔ The difference scattering from neutron beam polarized parallel and antiparallel to the applied magnetic field gives an **improvement of nearly one order of magnitude in moment sensitivity.**



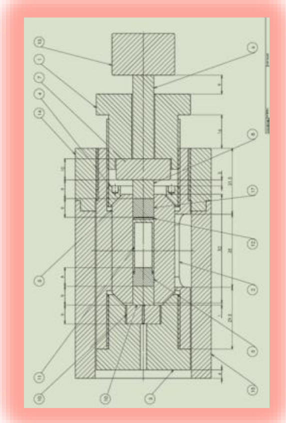
Flipping difference (I+ - I-) obtained on CrO_2 powder



Design and development of a High Pressure Cell optimized for magnetic structure determination

- Collaboration with the Uwatoko group , ISSP, Univ. of Tokyo.
- Optimized for low-Q scattering
- Designed for pelletized samples to be pressurized up to **2 Gpa**
- Compatible with low temperature liquid Helium cryostats to reach base temperatures of 1.5K

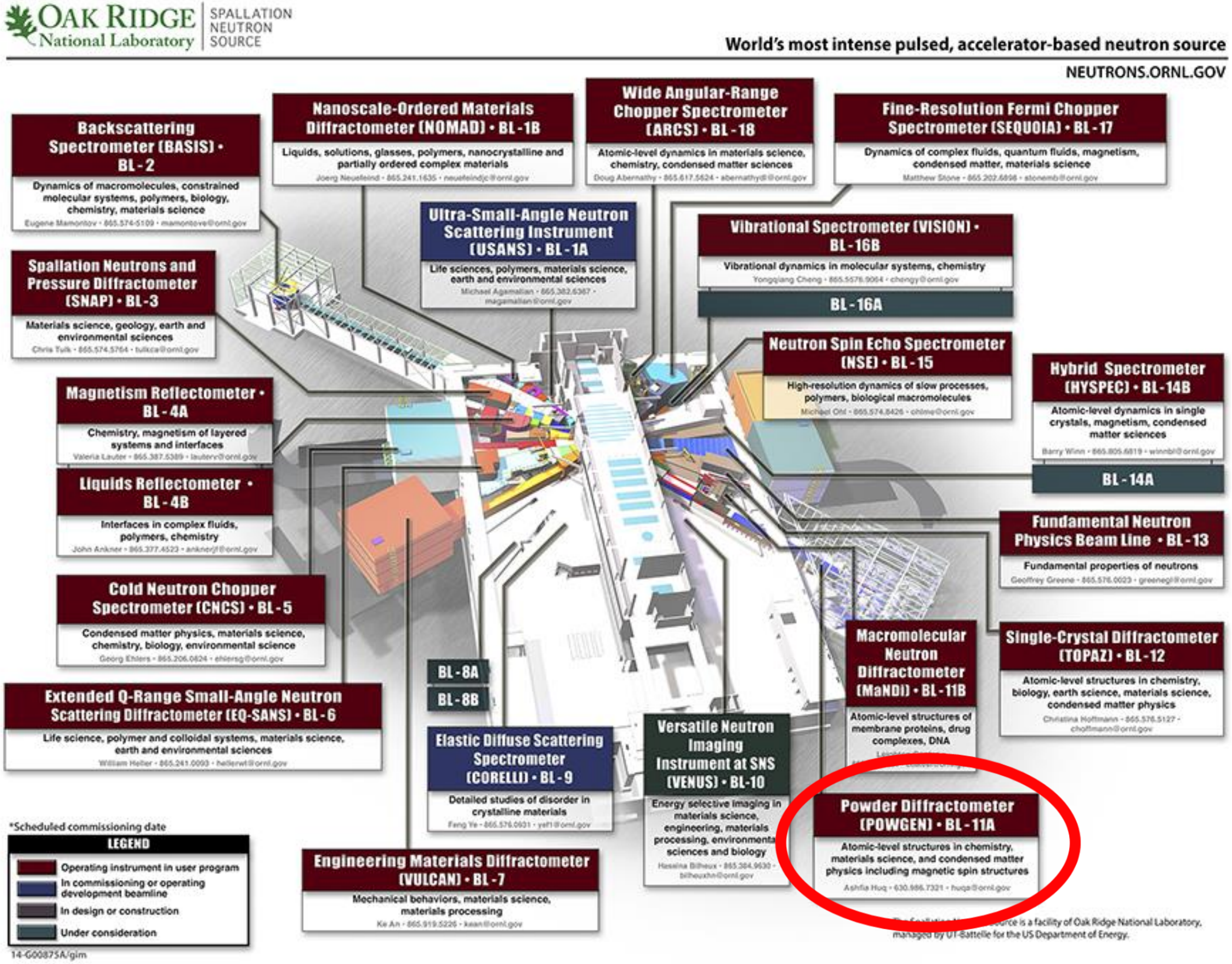
NiCrAl "Russian" pressure cell: 2.5 GPa
Multigram sample in BeCu clamp cell: 1.5 GPa
***In-situ* Al-He gas cell: 6 kbar**



The University of Tokyo
The Institute for Solid State Physics

SNS

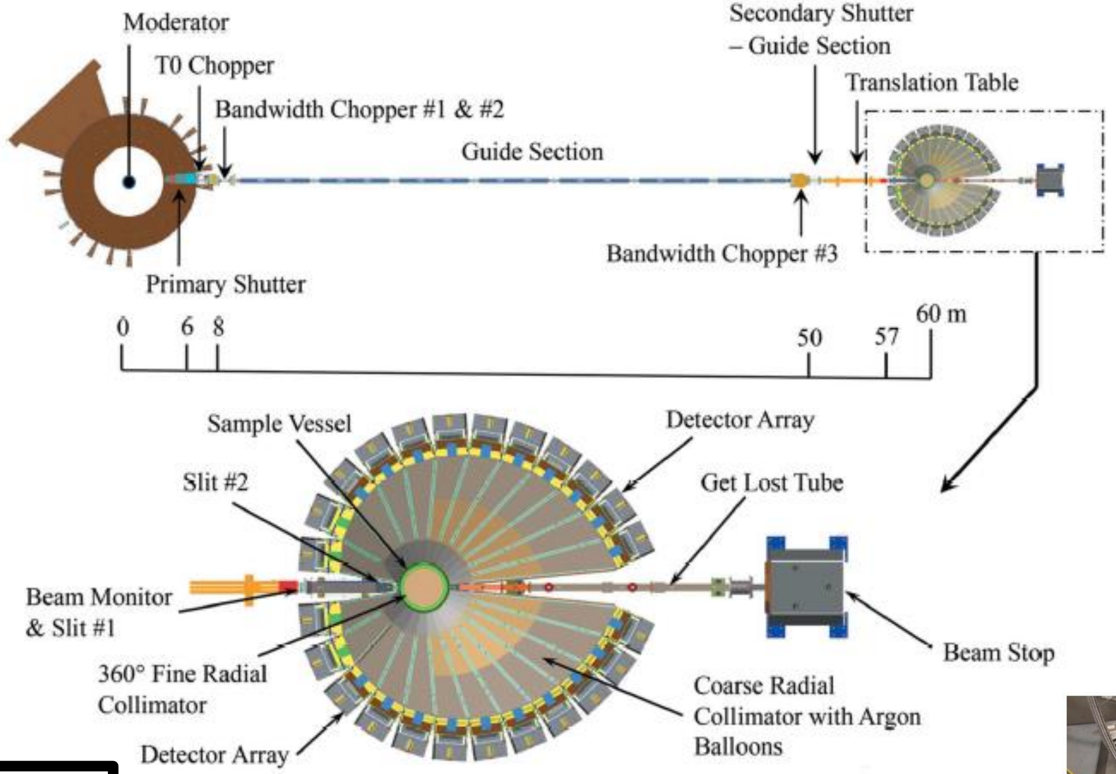
- POWGEN

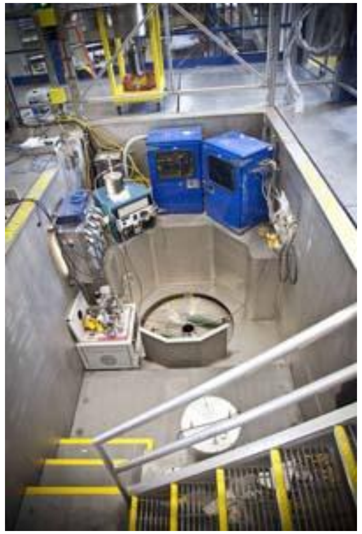


OAK RIDGE National Laboratory
SPALLATION NEUTRON SOURCE
World's most intense pulsed, accelerator-based neutron source
NEUTRONS.ORNL.GOV
Backscattering Spectrometer (BASIS) • BL-2
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
Nanoscale-Ordered Materials Diffractometer (NOMAD) • BL-1B
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Wide Angular-Range Chopper Spectrometer (ARCS) • BL-18
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) • BL-17
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Ultra-Small-Angle Neutron Scattering Instrument (USANS) • BL-1A
Life sciences, polymers, materials science, earth and environmental sciences
Vibrational Spectrometer (VISION) • BL-16B
Vibrational dynamics in molecular systems, chemistry
BL-16A
Spallation Neutrons and Pressure Diffractometer (SNAP) • BL-3
Materials science, geology, earth and environmental sciences
Neutron Spin Echo Spectrometer (NSE) • BL-15
High-resolution dynamics of slow processes, polymers, biological macromolecules
Hybrid Spectrometer (HYSPEC) • BL-14B
Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
BL-14A
Magnetism Reflectometer • BL-4A
Chemistry, magnetism of layered systems and interfaces
Liquids Reflectometer • BL-4B
Interfaces in complex fluids, polymers, chemistry
Fundamental Neutron Physics Beam Line • BL-13
Fundamental properties of neutrons
Cold Neutron Chopper Spectrometer (CNCS) • BL-5
Condensed matter physics, materials science, chemistry, biology, environmental science
Macromolecular Neutron Diffractometer (MaNDi) • BL-11B
Atomic-level structures of membrane proteins, drug complexes, DNA
Single-Crystal Diffractometer (TOPAZ) • BL-12
Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
BL-8A
BL-8B
Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) • BL-6
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
Elastic Diffuse Scattering Spectrometer (CORELLI) • BL-9
Detailed studies of disorder in crystalline materials
Versatile Neutron Imaging Instrument at SNS (VENUS) • BL-10
Energy selective imaging in materials science, engineering, materials processing, environmental sciences and biology
Powder Diffractometer (POWGEN) • BL-11A
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Engineering Materials Diffractometer (VULCAN) • BL-7
Mechanical behaviors, materials science, materials processing
*Scheduled commissioning date
LEGEND
Operating instrument in user program
In commissioning or operating development beamline
In design or construction
Under consideration
14-G00875A/gim

POWGEN (SNS)

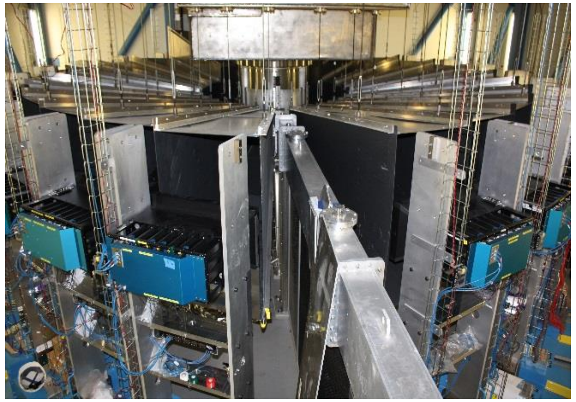
- General purpose diffractometer that encompasses magnetic scattering.
- Alternative design to previous spallation diffractometers
  → data reduced to single pattern.
- Recently upgraded detector layout.
- Different wavelengths (Frames) available.

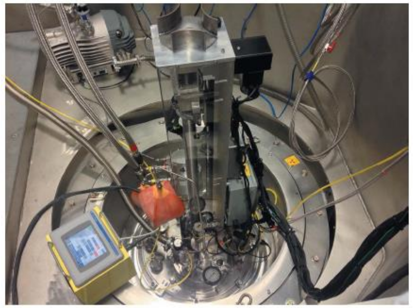




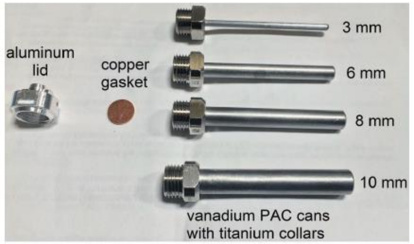
Standard settings for data collection at POWGEN for which the instrument is calibrated.

Frequency	λ_{center} (Å)	λ_{min} (Å)	λ_{max} (Å)	d_{min} (Å)	d_{max} (Å)	Q_{min} (Å^{-1})	Q_{max} (Å^{-1})
60	0.800	0.267	1.333	0.13	8.2	0.766	46.9
60	1.500	0.967	2.033	0.485	14.0	0.449	12.9
60	2.665	2.132	3.198	1.070	22.2	0.283	5.9
60	4.797	4.264	5.330	2.140	33.0	0.190	2.9





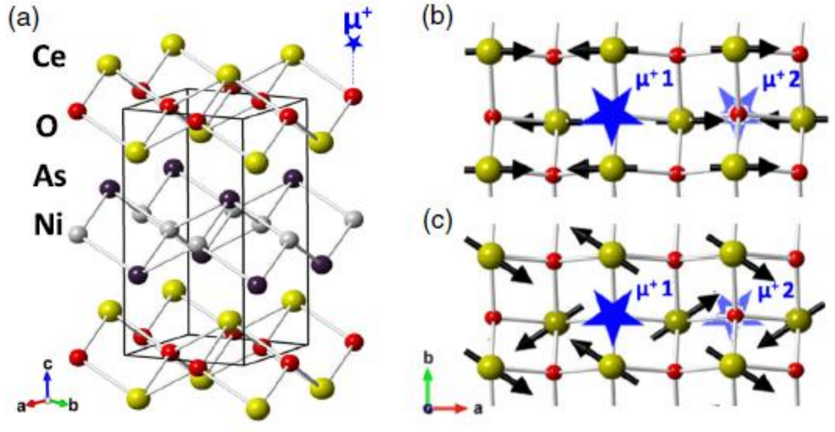
(a)



Recent detector upgrade: https://doi.org/10.1107/S160057671901121X

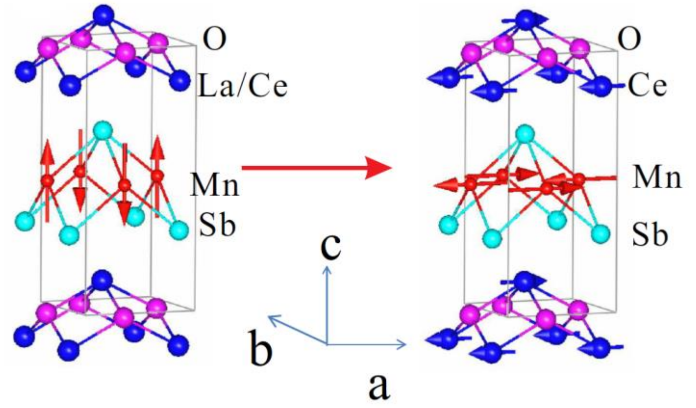
Science: magnetism plus structure

- **Large Q range for doing simultaneous structural and magnetic refinements:**
- magnetic structure, magnetoelastic coupling, etc.



(a) Crystallographic structure of CeNiAsO, (b) incommensurate spin density waves for $T_{N2} < T < T_{N1}$, and (c). coplanar commensurate order for $T < T_{N2}$.

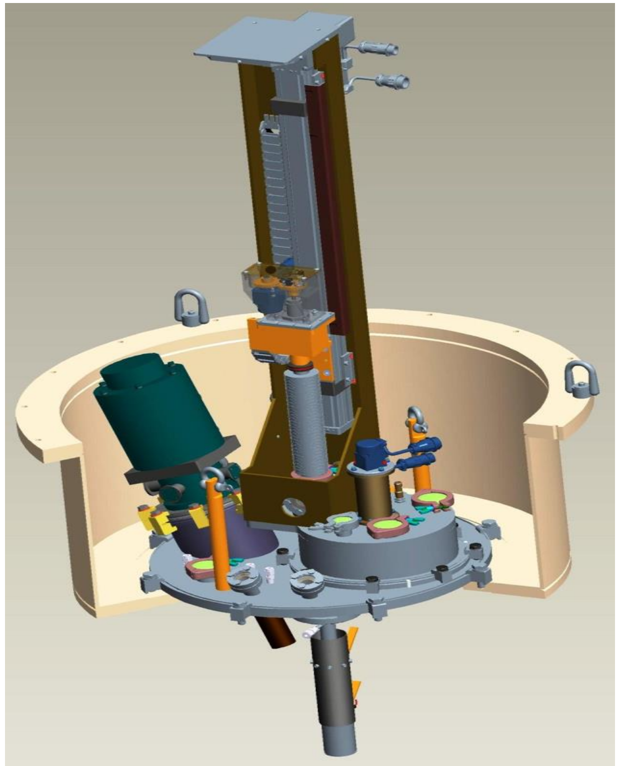
Wu et al., Physical Review Letters, 122, 197203 (2019)



Mn spin-reorientation in CeMnSbO

Zhang et al., Physical Review B, 93, 094413 (2016)

POWGEN Mail-in program

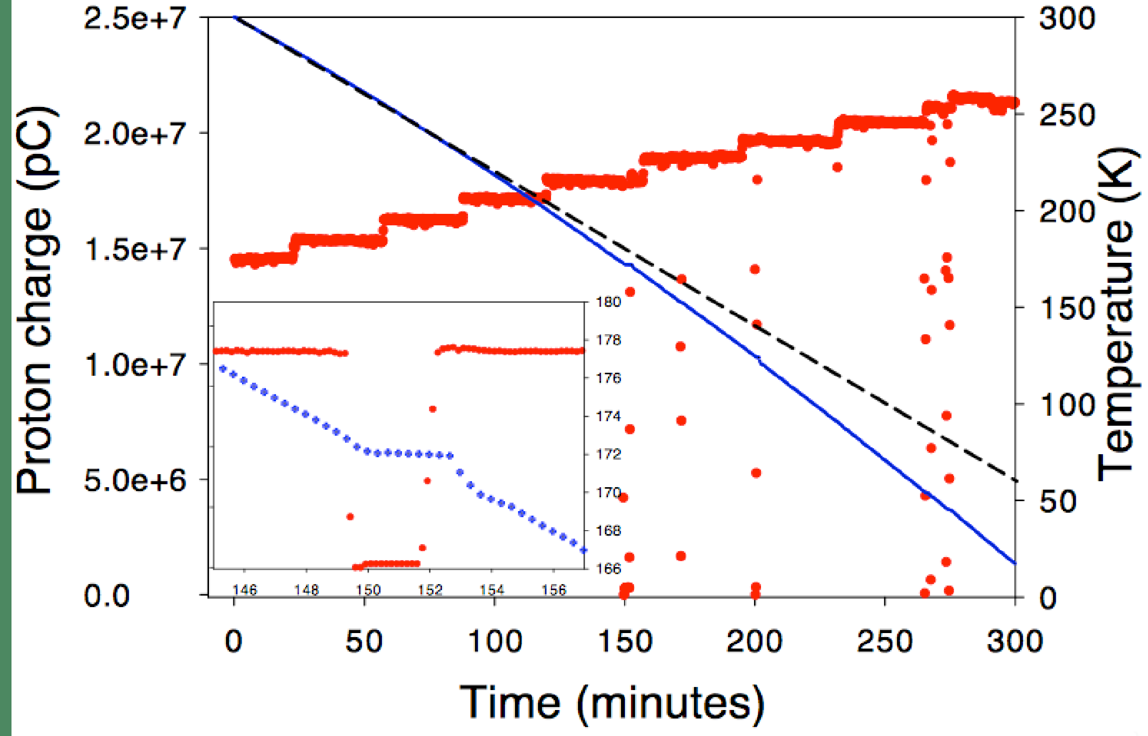


24-sample PAC changer available for measurements from 10 to 300 K:
mail-in / rapid access proposals

https://neutrons.ornl.gov/powgen/mail-in

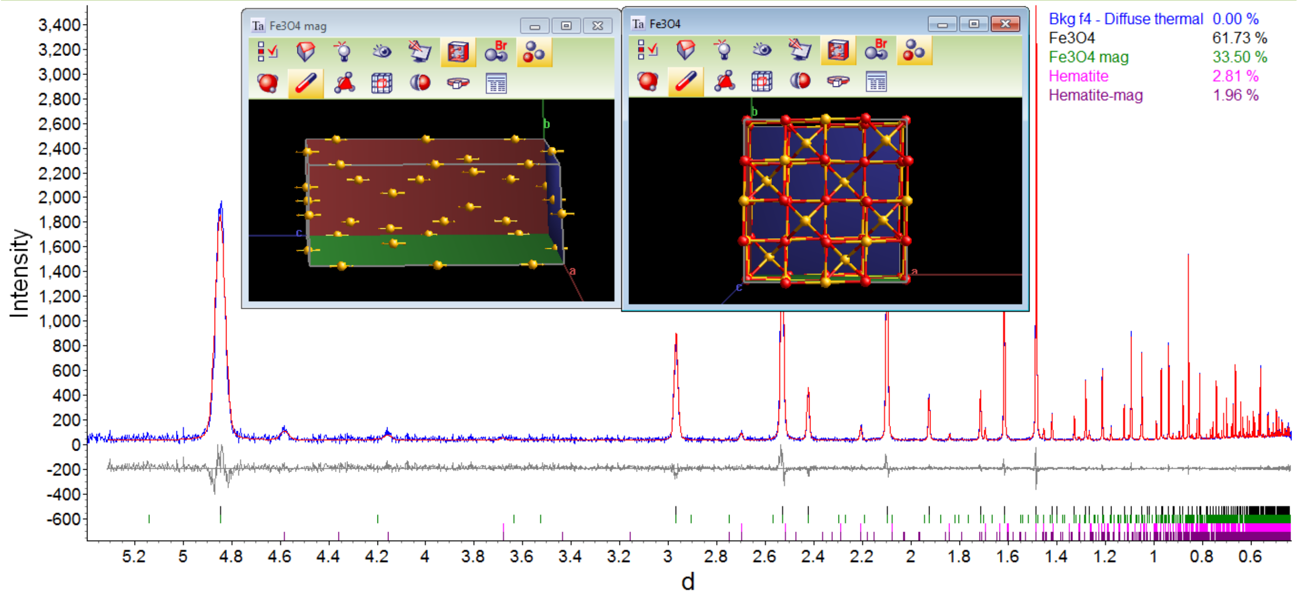
Magnetite (Fe3O4)

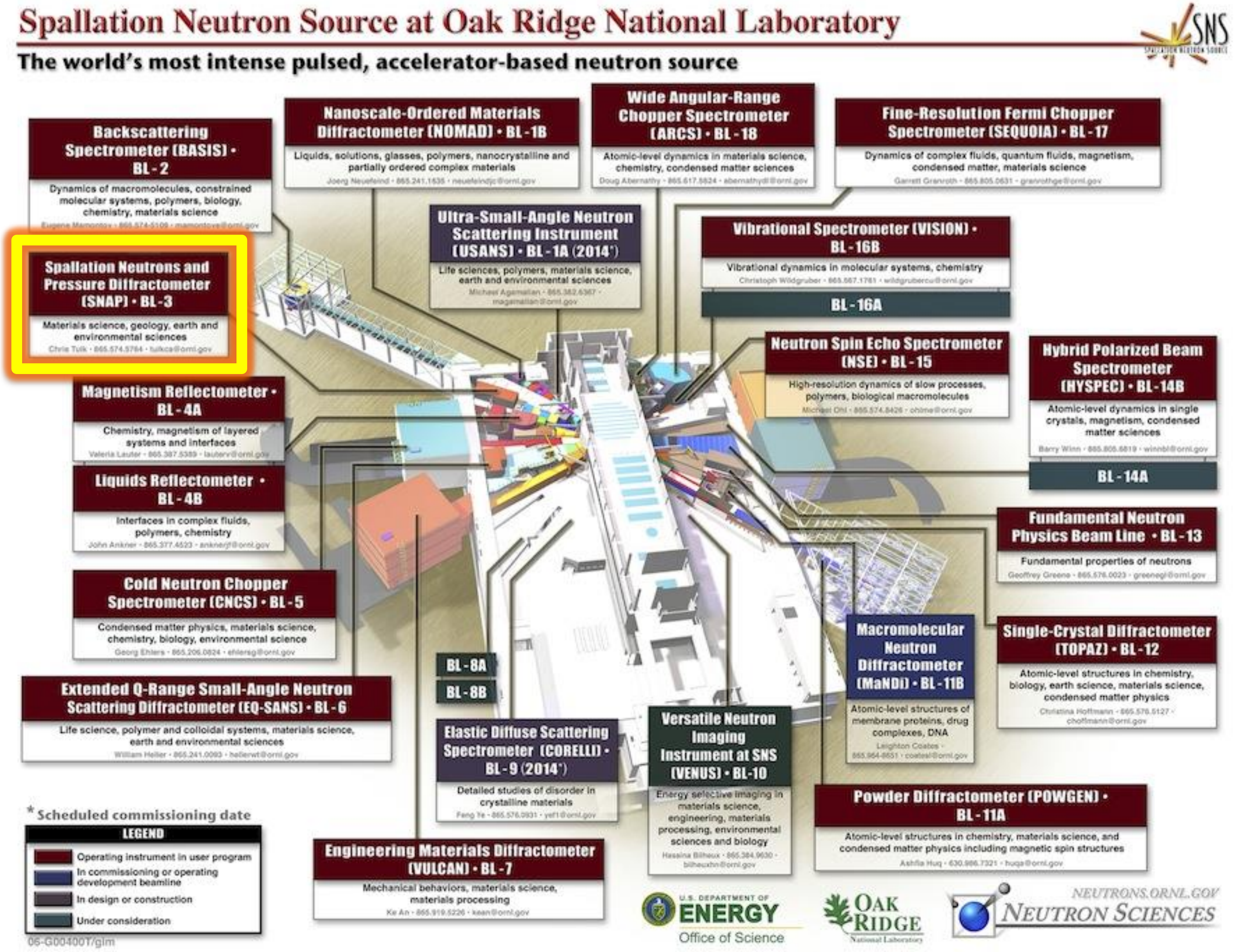
- Sample cooled down to 10 K at a nominal 1 K/minute
- Temperature controlled for a near constant DT/D(pcharge) = constant counting statistics
- Ramping accelerates with increasing beam power & halts when it trips



Plot of proton charge and controller set-point during data collection on Fe3O4.

Magnetic structure refinement taken from a slice of temperature ramping data at 295 K

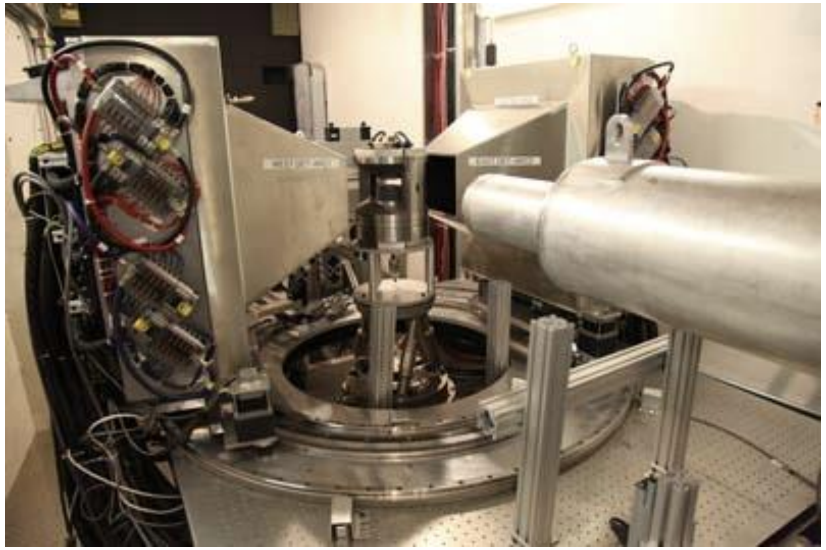


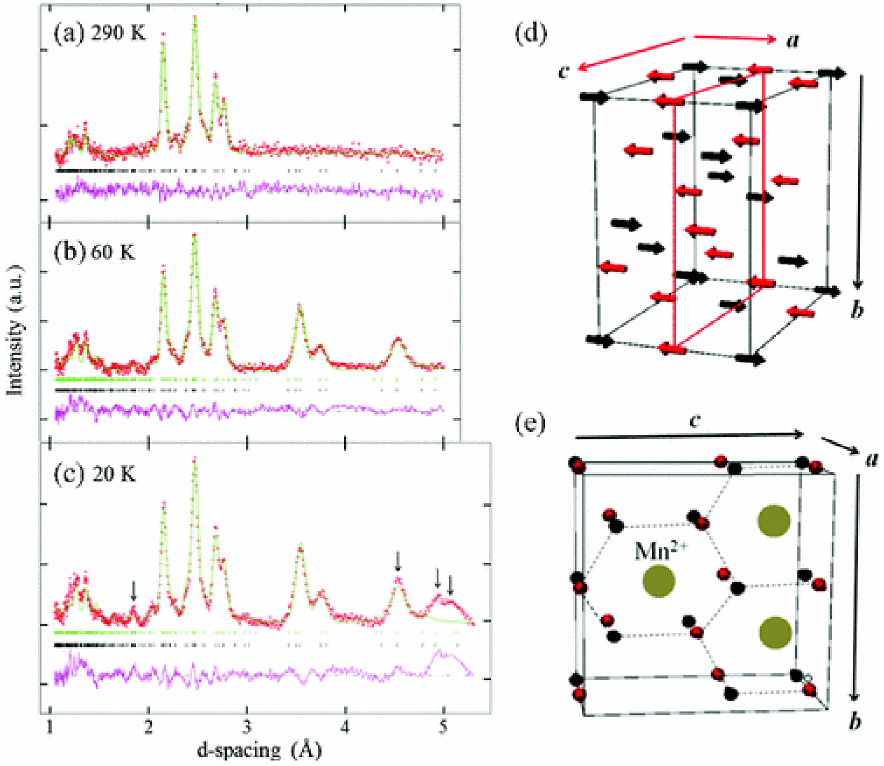


OAK RIDGE National Laboratory

SNAP (SNS)

- Dedicated pressure beamline.
- Powders and single crystals possible.
- Accessible Q as low as 0.78 $Å^{-1}$.
- Pressure 0-80 GPa at room temperature.
- 0-10 GPa between 85 and 300 K.
  Furnace also available.



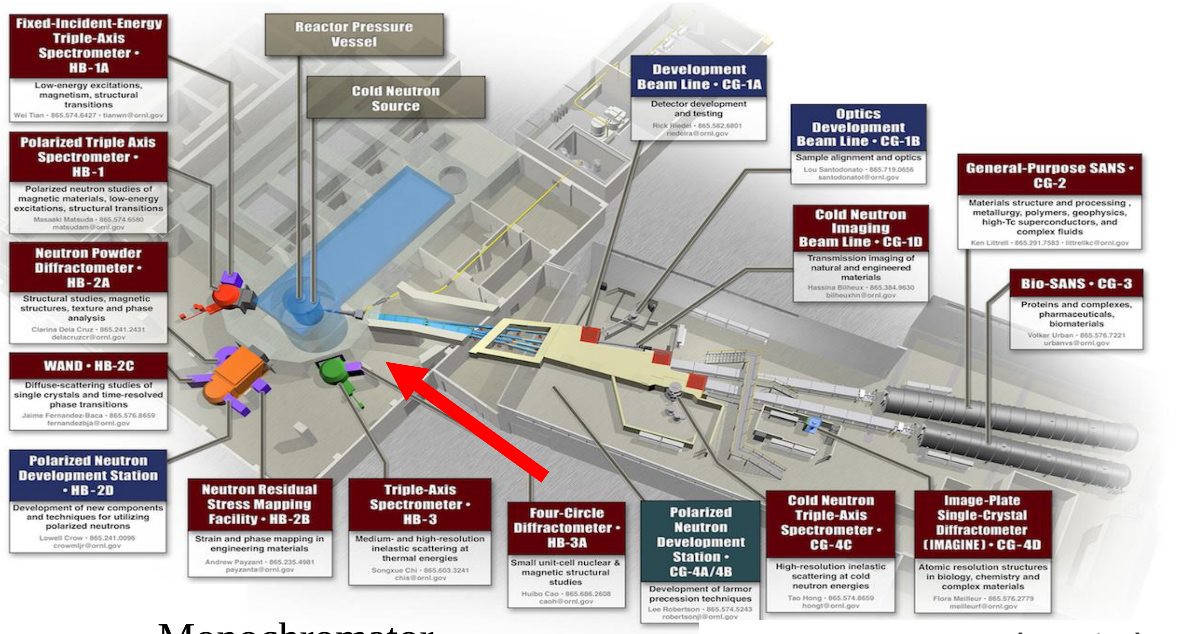


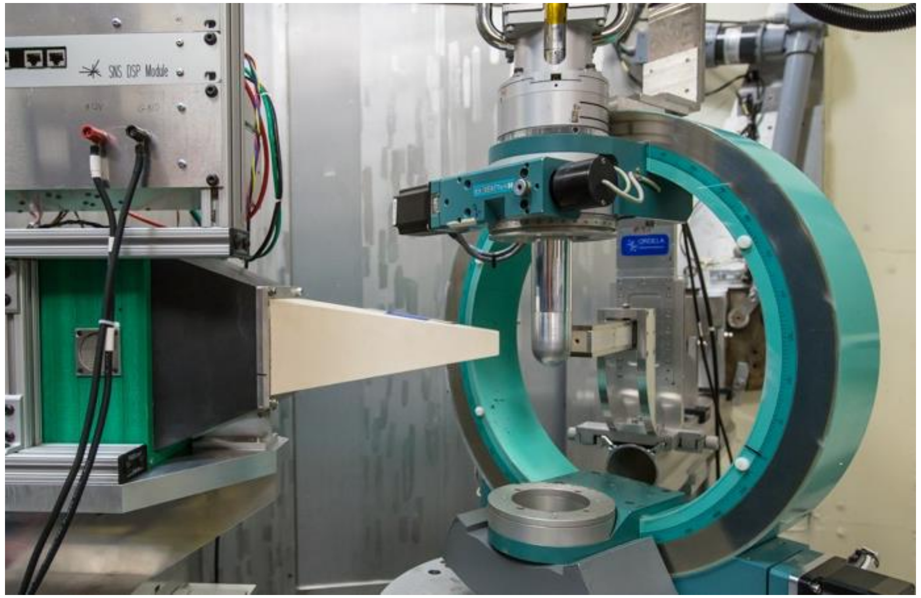
S. Hirai, et al. "Giant atomic displacement at a magnetic phase transition in metastable Mn_3O_4" PRB 87 014417 (2013)

Single crystal diffraction (ORNL)

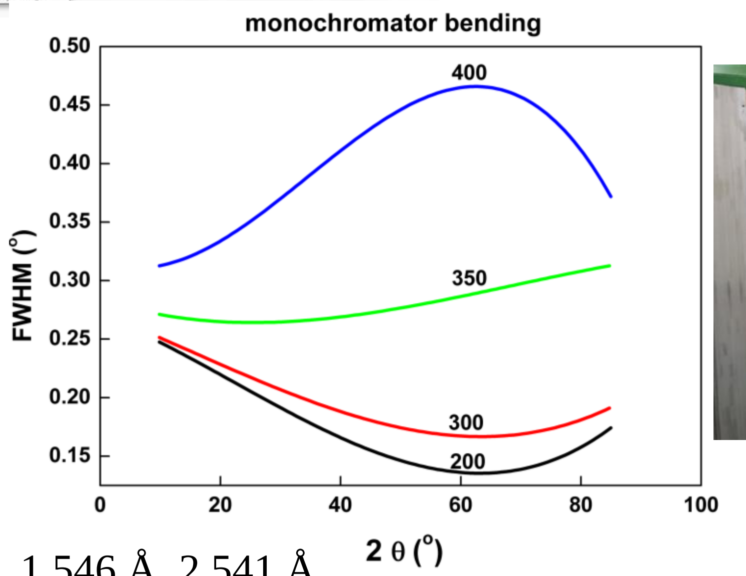
- HB-3A (DEMAND) → magnetic structure determination → new detector for larger Q coverage and use with extreme sample environments
- Corelli → Diffuse and large access to full reciprocal space.
- WAND^2 → Diffuse and standard diffraction. Very fast!

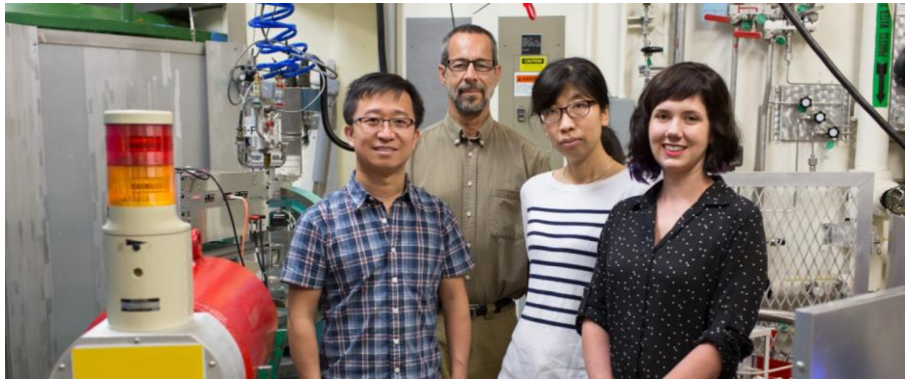
Current capabilities at DEMAND





Monochromator

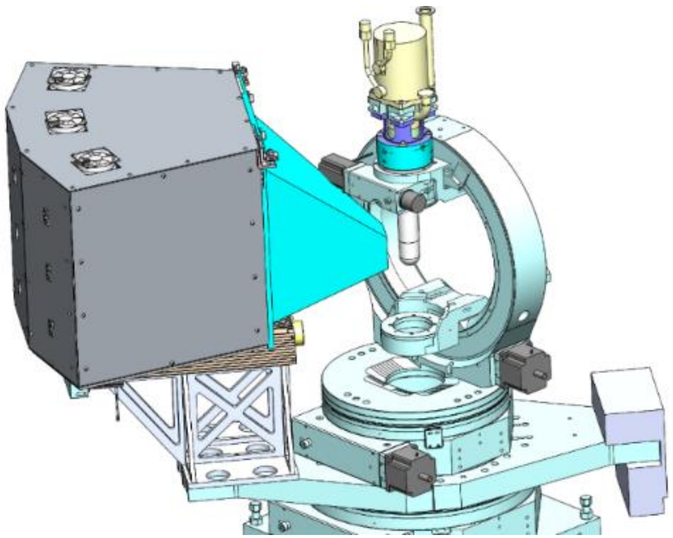




Magnetism use 80% beam time

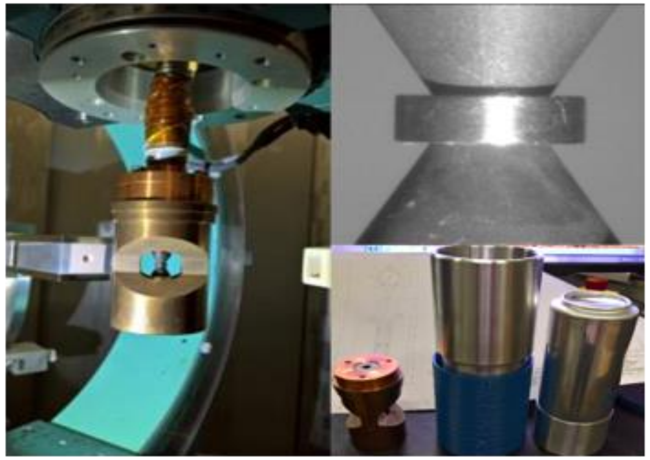
Wavelengths: 1.005 Å, 1.546 Å, 2.541 Å

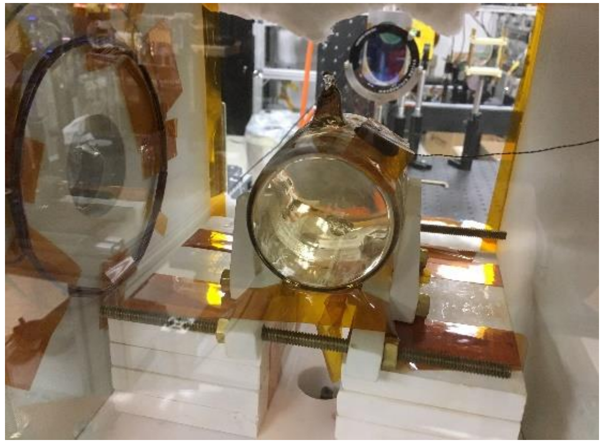
DEMAND – extreme sample environment and polarized neutron diffraction

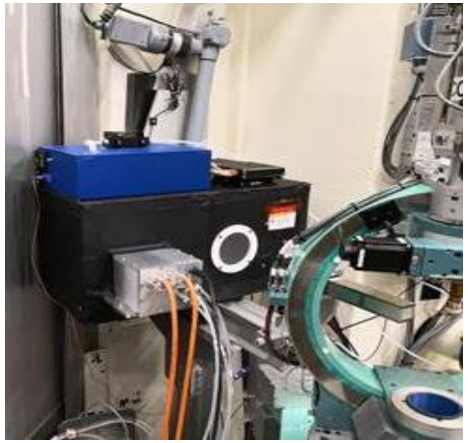


T = 50 mK -800 K
H = 0- 5 T
P = 0 - 10 GPa
E =0 - 1100 Volts

Unpolarized/polarized neutron diffraction



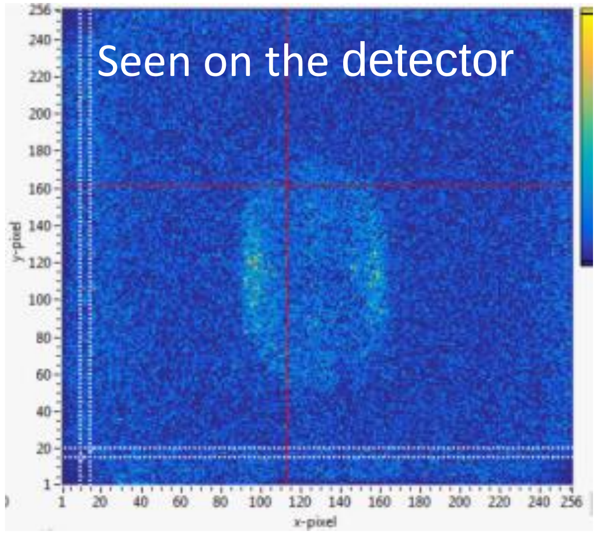


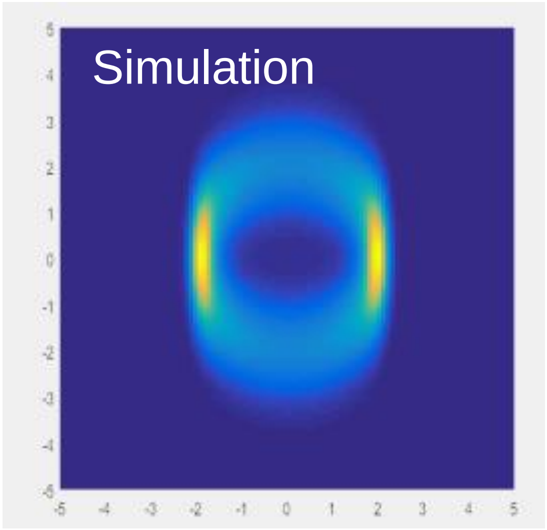


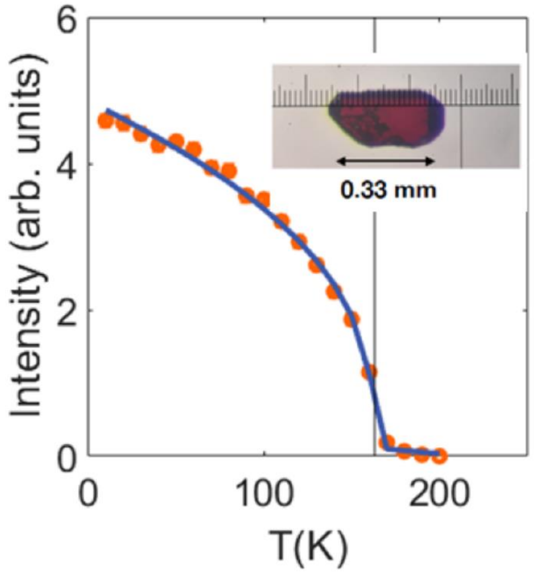
OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

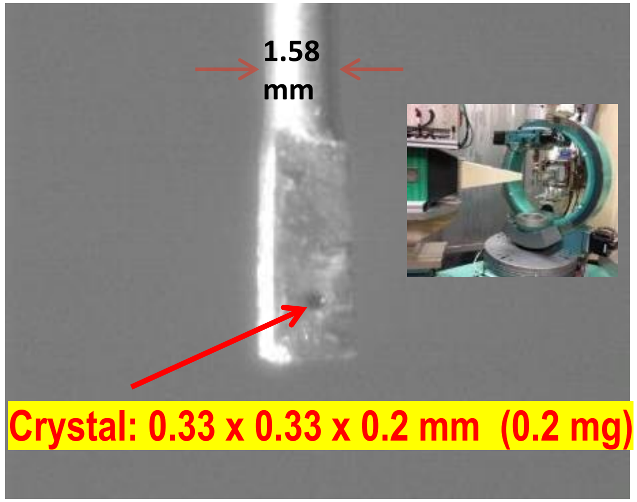
Cao H.B., Chakoumakos B.C., Andrews K.M., Wu Y., Riedel R.A., Hodges J.P., Zhou W., Gregory R., Haberl B., Molaison J.J., Lynn G.W., "DEMAND, a Dimensional Extreme Magnetic Neutron Diffractometer at the High Flux Isotope Reactor", *Crystals*, **9**, 1, 5 (2019).

Capabilities at DEMAND - high flux

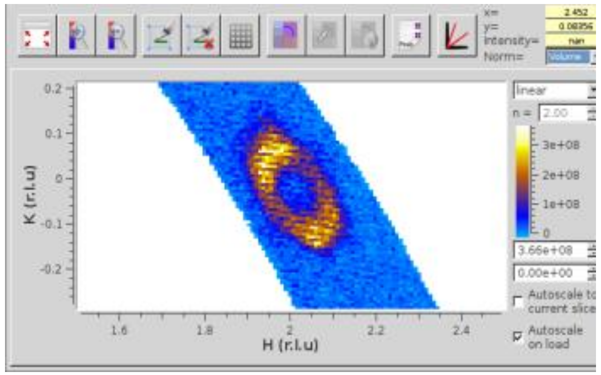


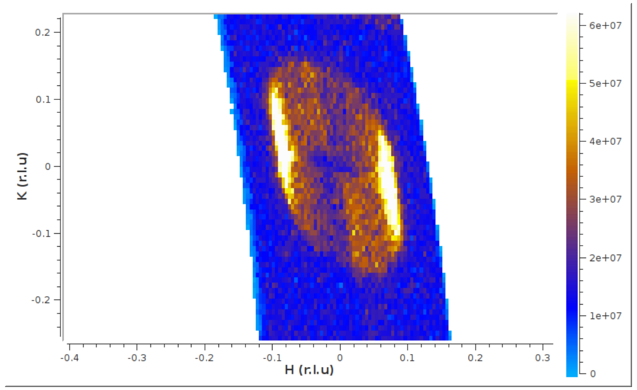






The circular distribution of k-vectors definitively confirms Fe_3PO_7 to have a "partially ordered" antiferromagnetic (AFM) helical state. One candidate for such a state is a short-range ordered AFM Skyrmion phase.



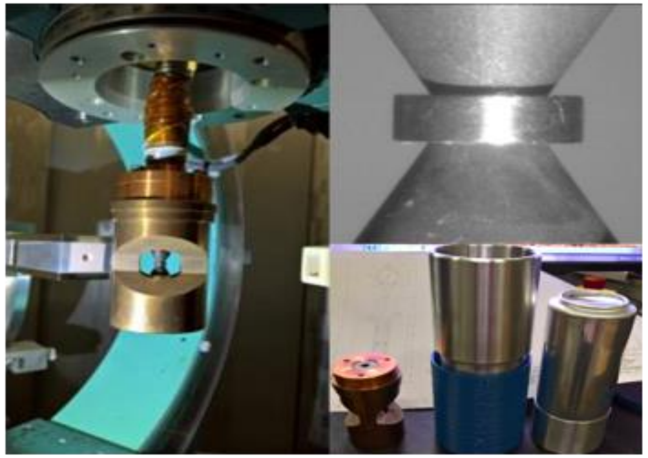


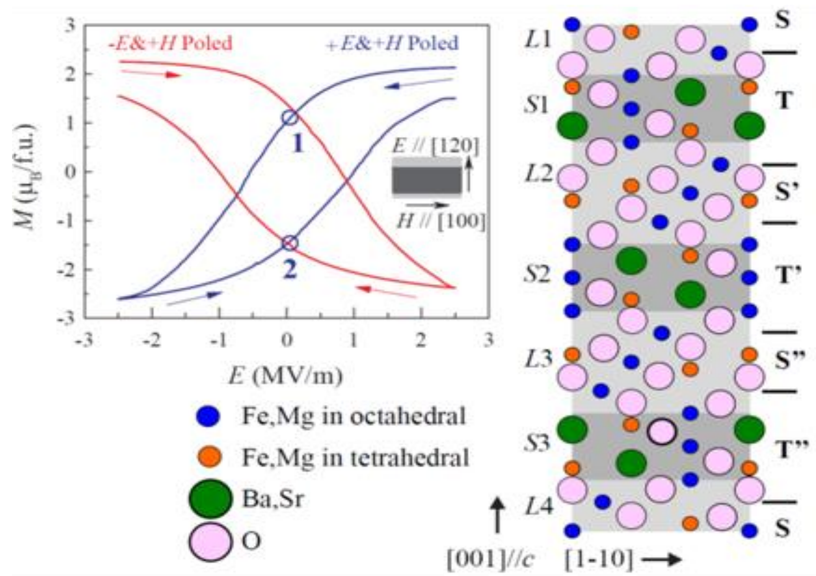
Kathryn Ross, Colin Sarkis, James Nielson (Colorado State University)
Huibo Cao (ORNL)

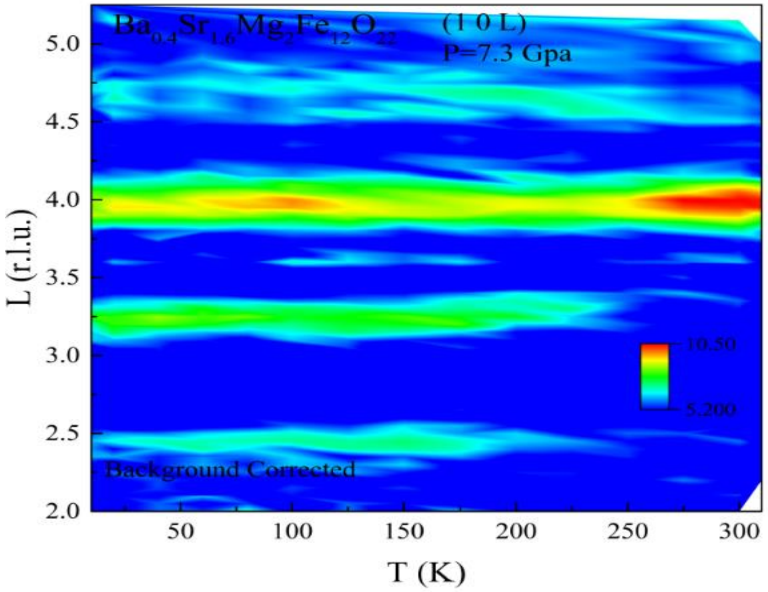
Sliced in HK-plane with MantidPlot

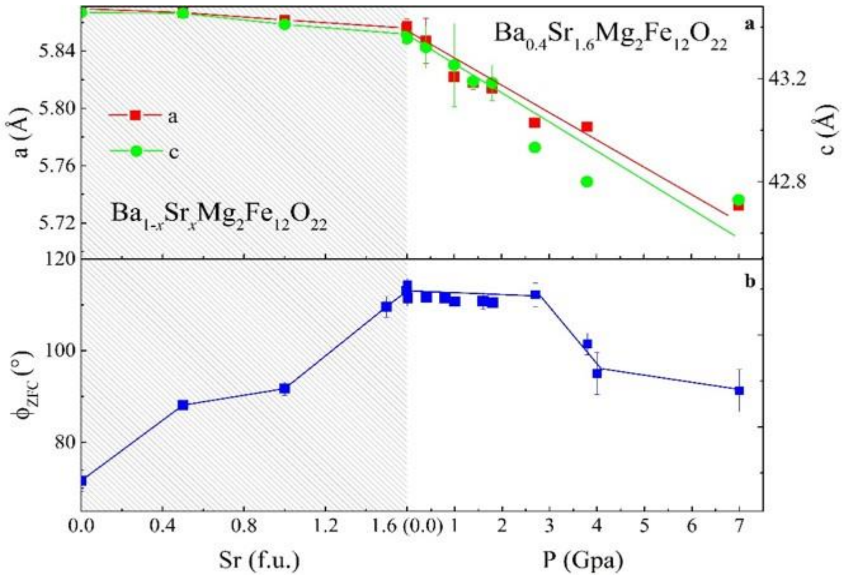
Capabilities at DEMAND - high pressure

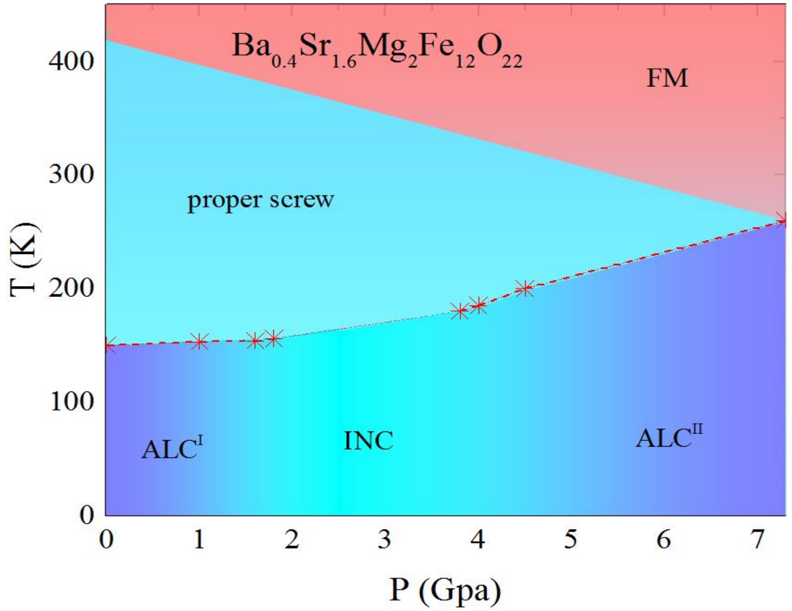
Hydrostatic pressure to 7.4 Gpa
~0.1 mm^3 crystal





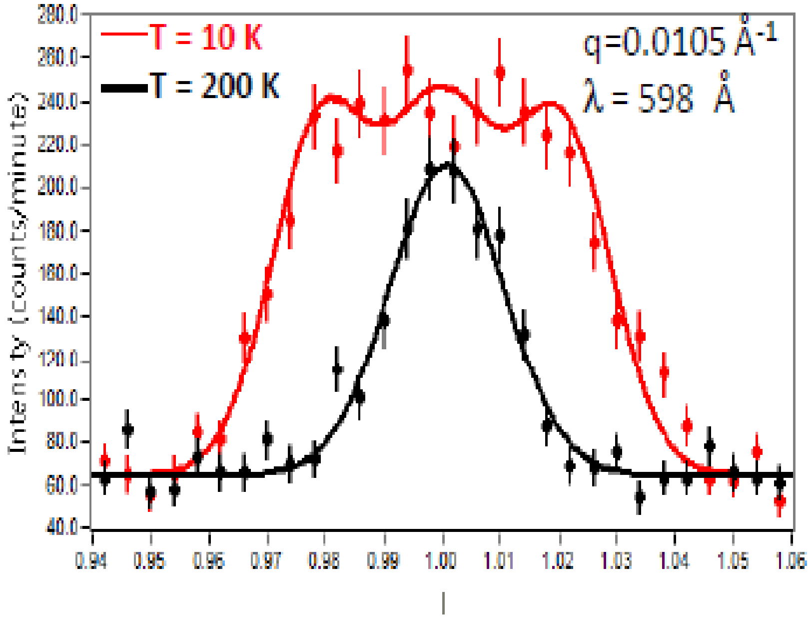


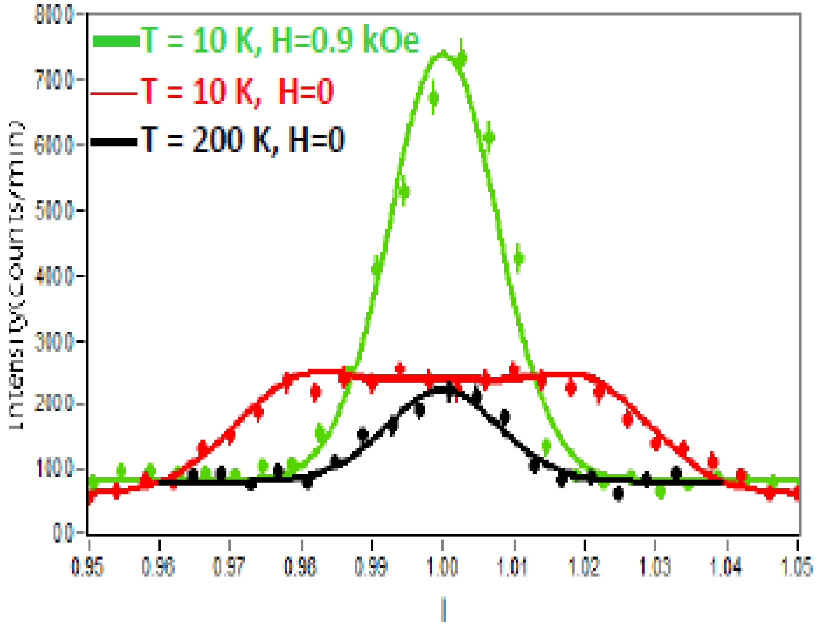


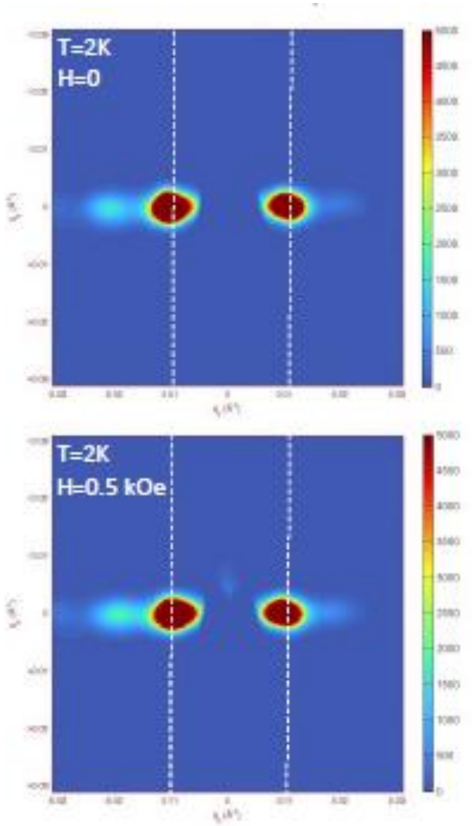


Zhai K., Wu Y., Shen S., Tian W., Cao H.B., Chai Y.S., Chakoumakos B.C., Shang D., Yan L., Wang F., Sun Y., *Nature Communications*, **8,** 519 (2017).

Capabilities at DEMAND - high q-resolution

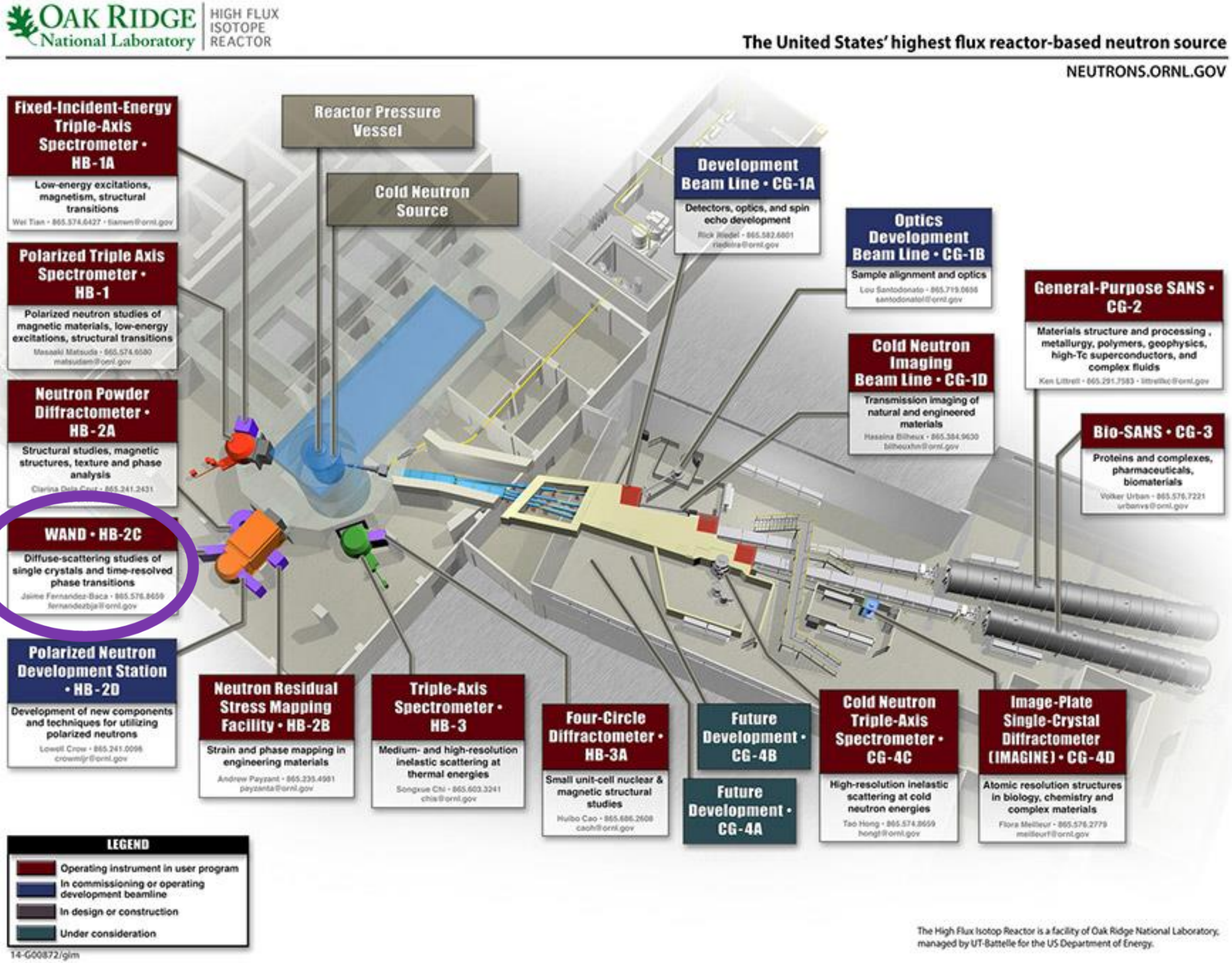






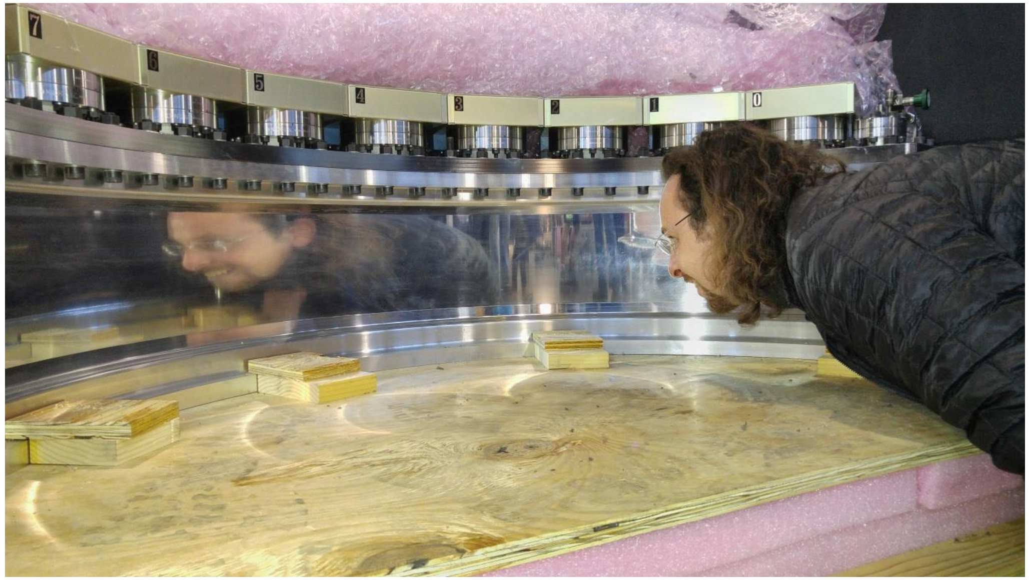
DEMAND =============Cold neutron================➔ SANS

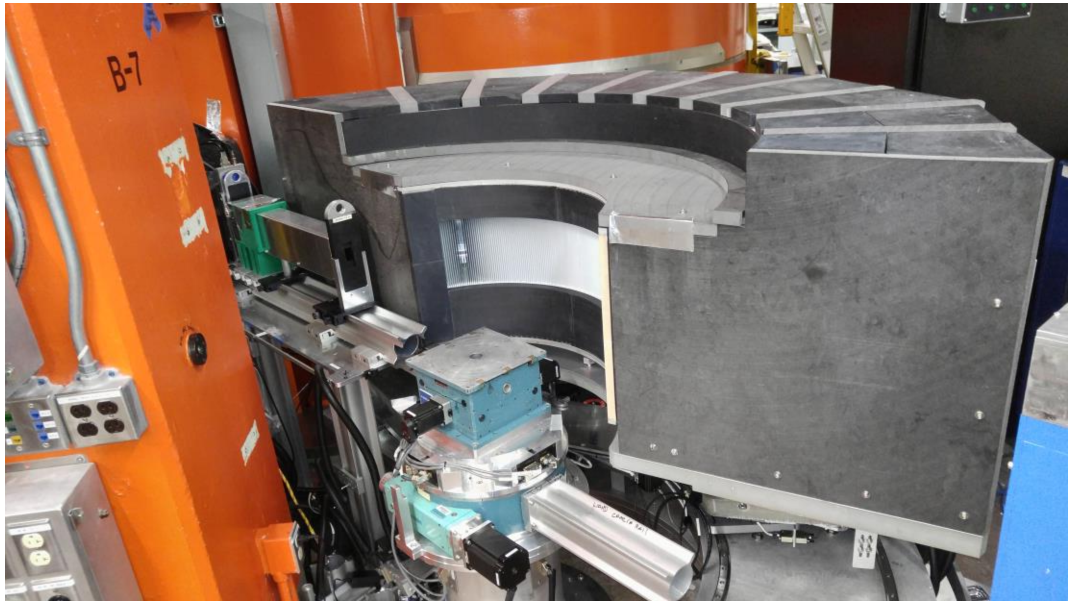
HFIR


OAK RIDGE National Laboratory
HIGH FLUX ISOTOPE REACTOR
The United States' highest flux reactor-based neutron source
NEUTRONS.ORNL.GOV
Fixed-Incident-Energy Triple-Axis Spectrometer • HB-1A
Low-energy excitations, magnetism, structural transitions
Polarized Triple Axis Spectrometer • HB-1
Polarized neutron studies of magnetic materials, low-energy excitations, structural transitions
Neutron Powder Diffractometer • HB-2A
Structural studies, magnetic structures, texture and phase analysis
WAND • HB-2C
Diffuse-scattering studies of single crystals and time-resolved phase transitions
Polarized Neutron Development Station • HB-2D
Development of new components and techniques for utilizing polarized neutrons
Reactor Pressure Vessel
Cold Neutron Source
Neutron Residual Stress Mapping Facility • HB-2B
Strain and phase mapping in engineering materials
Triple-Axis Spectrometer • HB-3
Medium- and high-resolution inelastic scattering at thermal energies
Four-Circle Diffractometer • HB-3A
Small unit-cell nuclear & magnetic structural studies
Future Development • CG-4B
Future Development • CG-4A
Cold Neutron Triple-Axis Spectrometer • CG-4C
High-resolution inelastic scattering at cold neutron energies
Image-Plate Single-Crystal Diffractometer (IMAGINE) • CG-4D
Atomic resolution structures in biology, chemistry and complex materials
Development Beam Line • CG-1A
Detectors, optics, and spin echo development
Optics Development Beam Line • CG-1B
Sample alignment and optics
Cold Neutron Imaging Beam Line • CG-1D
Transmission imaging of natural and engineered materials
General-Purpose SANS • CG-2
Materials structure and processing, metallurgy, polymers, geophysics, high-Tc superconductors, and complex fluids
Bio-SANS • CG-3
Proteins and complexes, pharmaceuticals, biomaterials
LEGEND
Operating instrument in user program
In commissioning or operating development beamline
In design or construction
Under consideration
The High Flux Isotop Reactor is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.
14-G00872/gim

WAND^2

- Recently upgraded detector.
- 120 degree coverage in-plane.
- Plus/minus 7.5 degree out of plane.
- High flux, medium to low resolution.
- Array of complex sample environment with easy access to install.
- 0.05 K, 1000 K, 0-8 T, Pressure



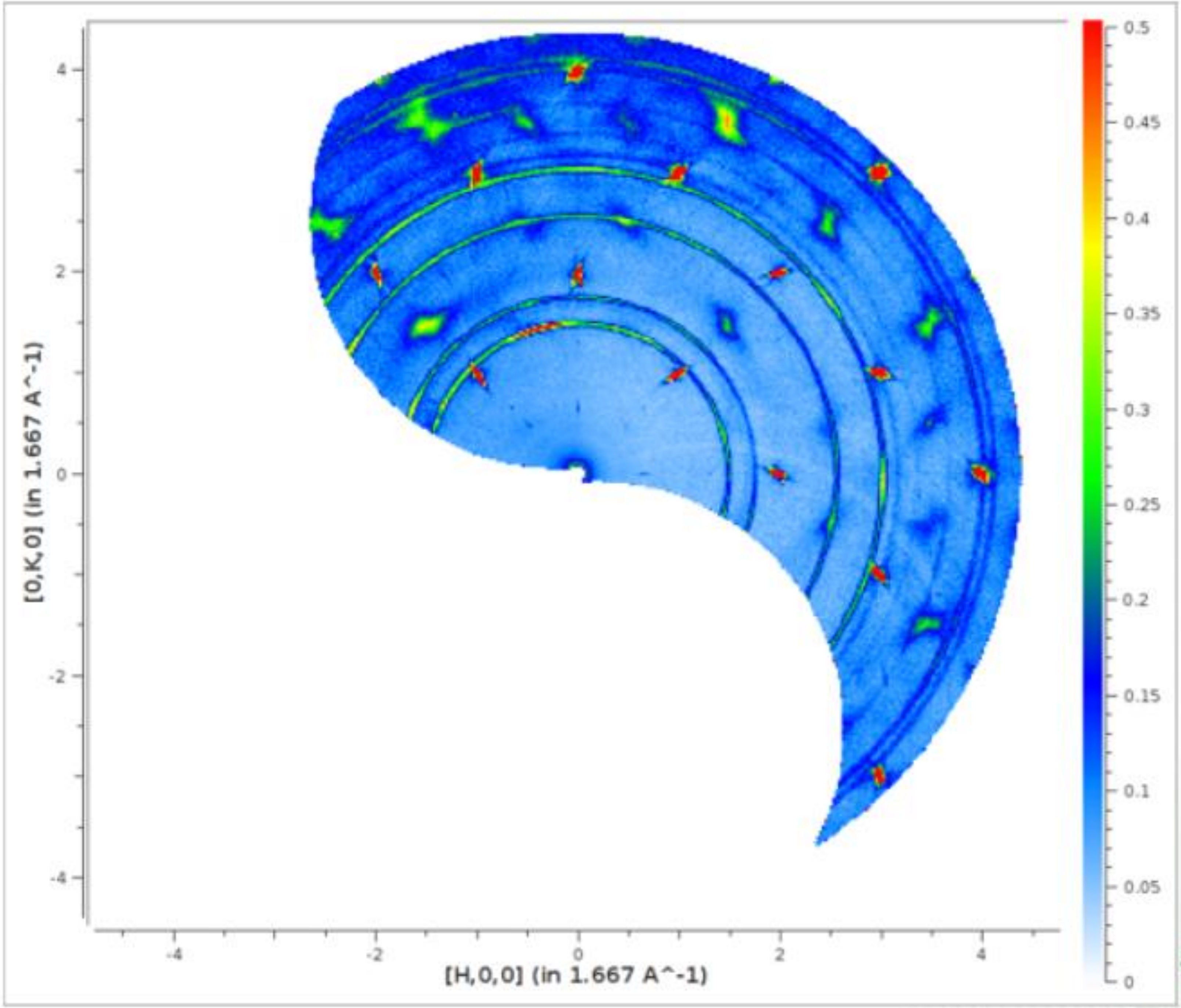


WAND² - Science

- LaSrCuO4

  Igor Zaliznyak

LSCO
T = 300 K; HK2



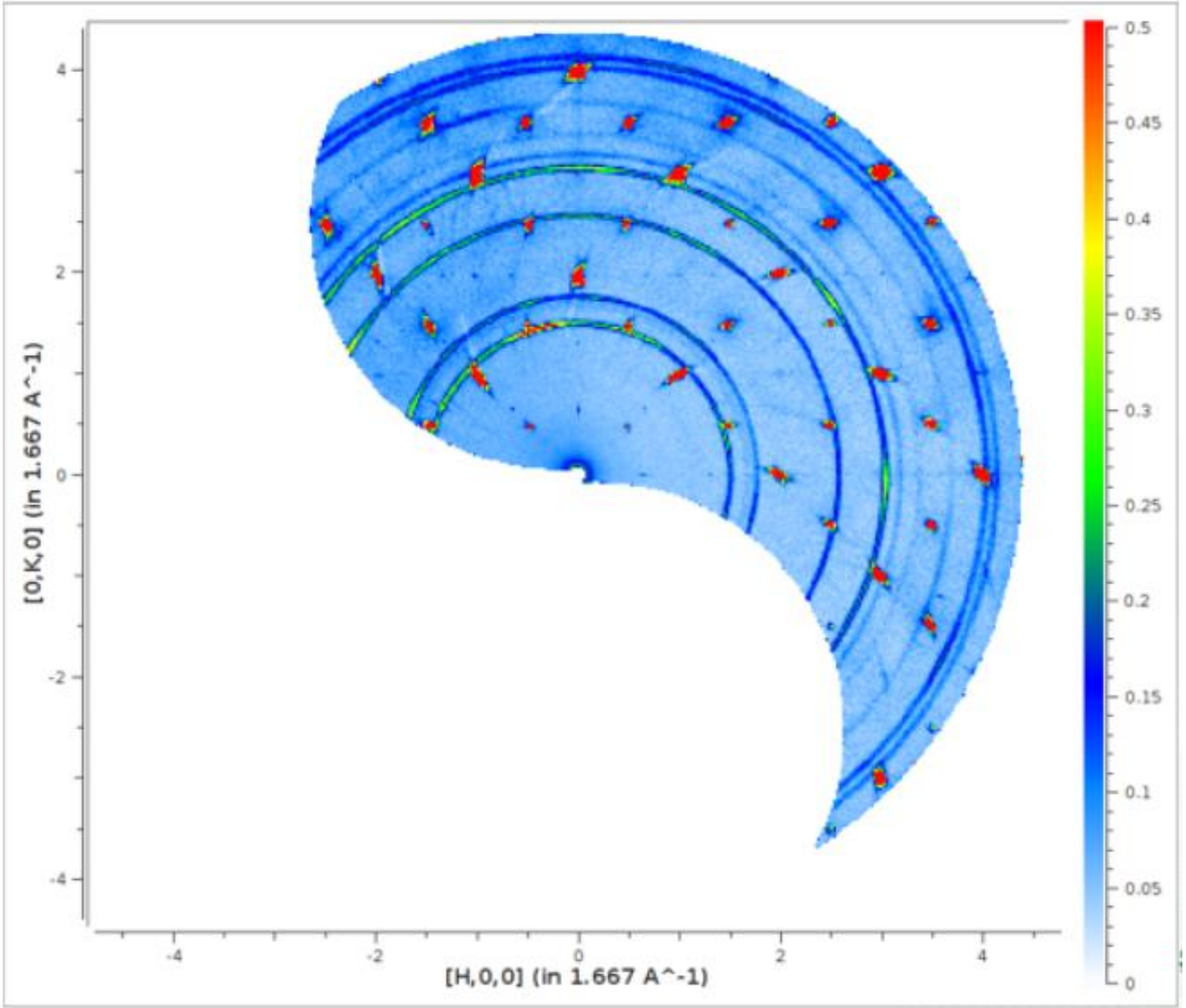
- 3D mapping of diffuse scattering

WAND^2 - Science

- LaSrCuO4

  Igor Zaliznyak

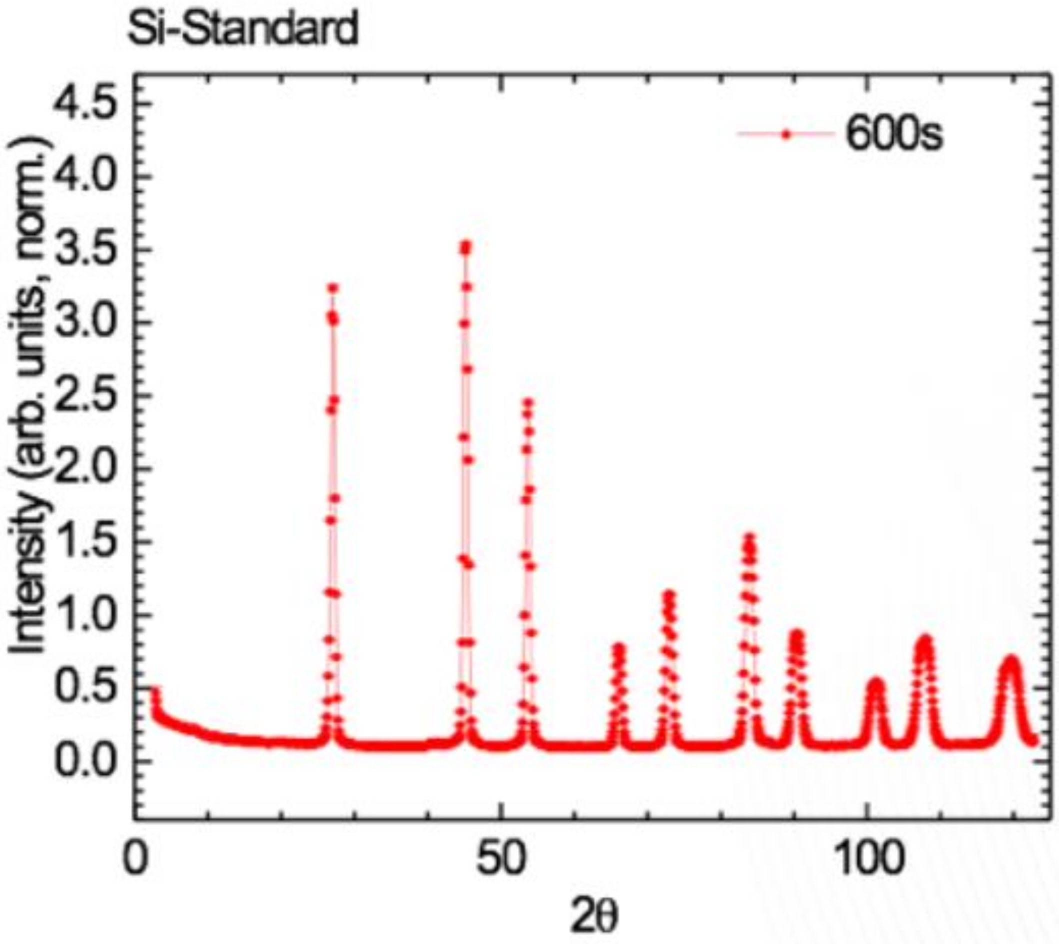
LSCO
T = 4.5 K; HK2



- 3D mapping of diffuse scattering

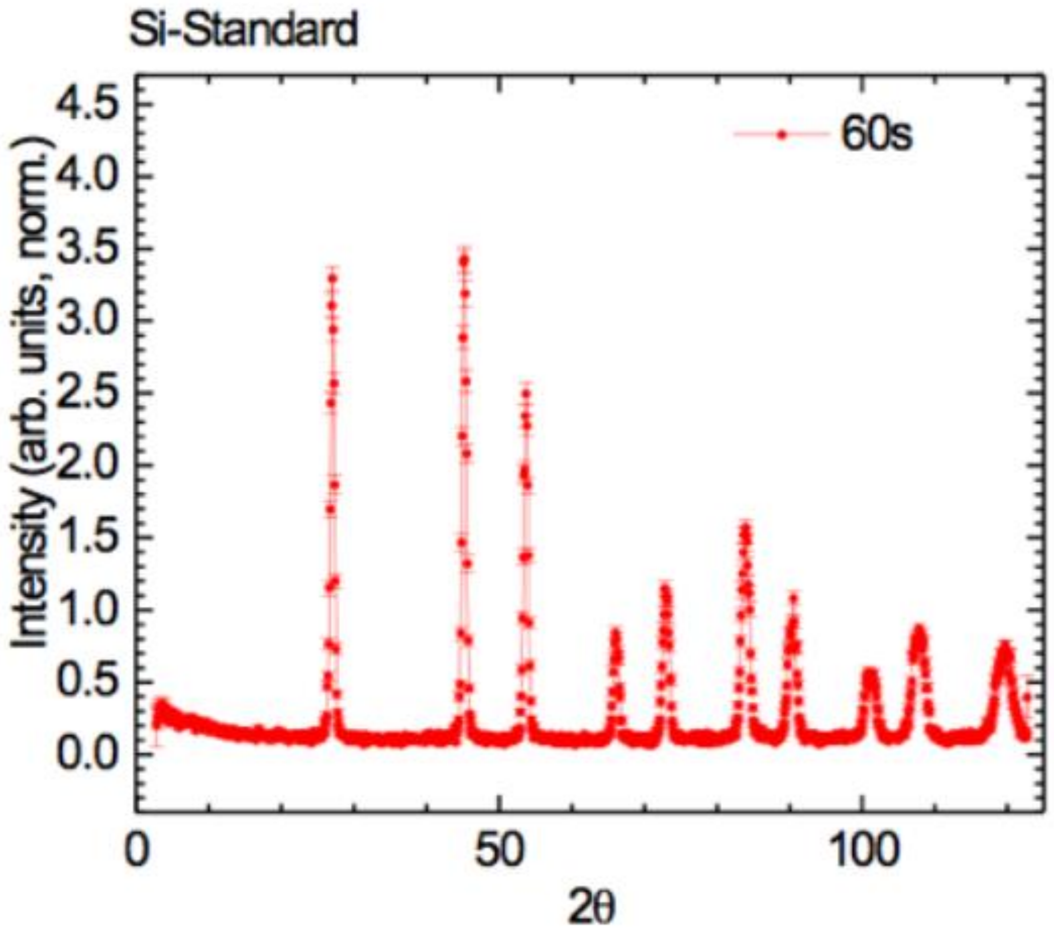
WAND^2

- Shorter data collection time → In-situ synthesis
- Pump-Probe experiments
- Stroboscopic measurement for reversible processes



WAND^2

- Shorter data collection time → In-situ synthesis
- Pump-Probe experiments
- Stroboscopic measurement for reversible processes



WAND^2

- Shorter data collection time → In-situ synthesis
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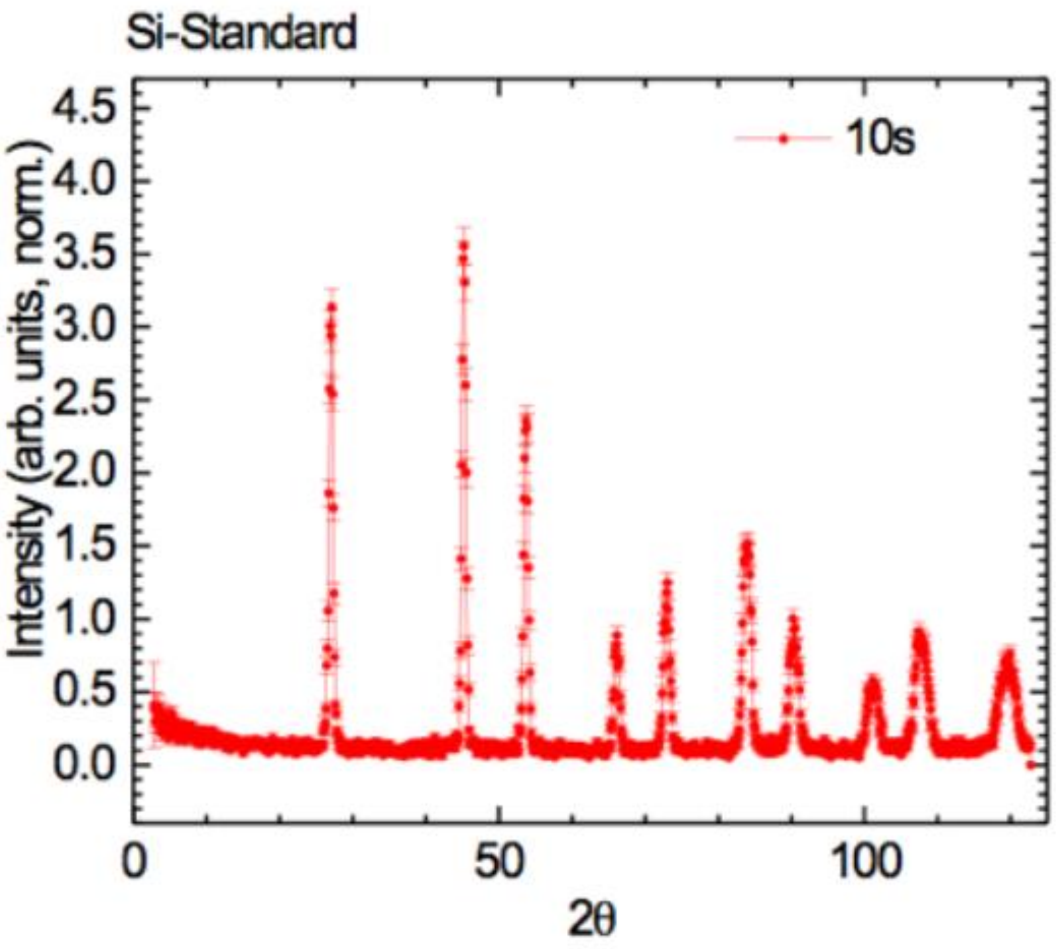
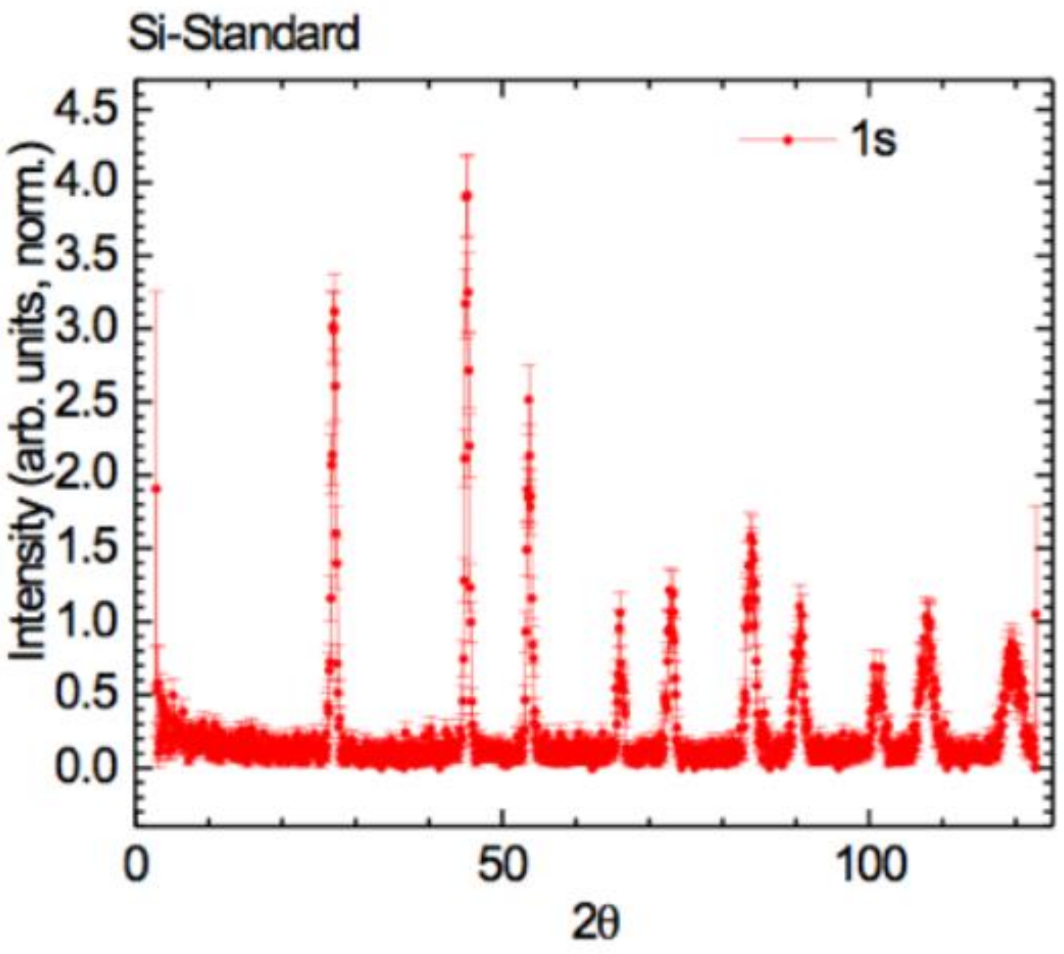


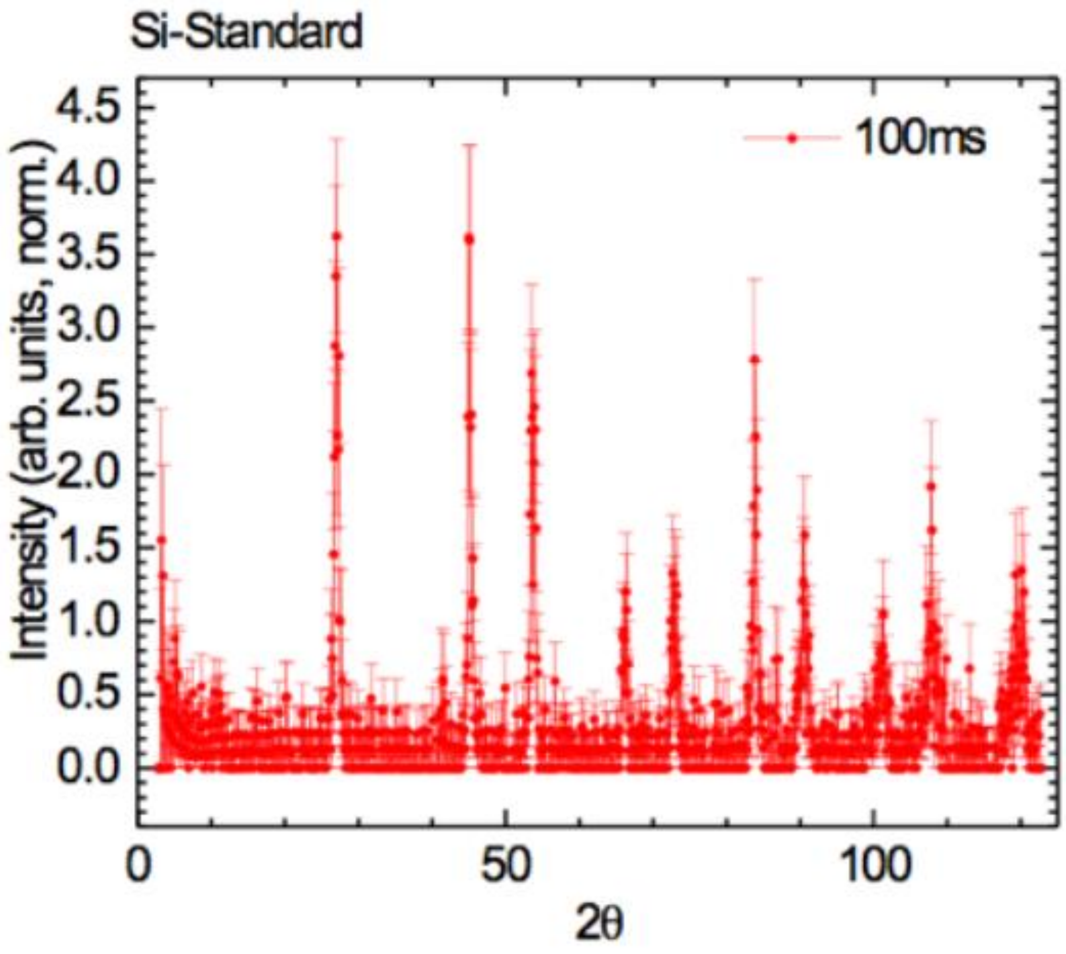
WAND^2

- Shorter data collection time → In-situ synthesis
- Pump-Probe experiments
- Stroboscopic measurement for reversible processes



WAND^2

- Shorter data collection time → In-situ synthesis
- Pump-Probe experiments
- Stroboscopic measurement for reversible processes



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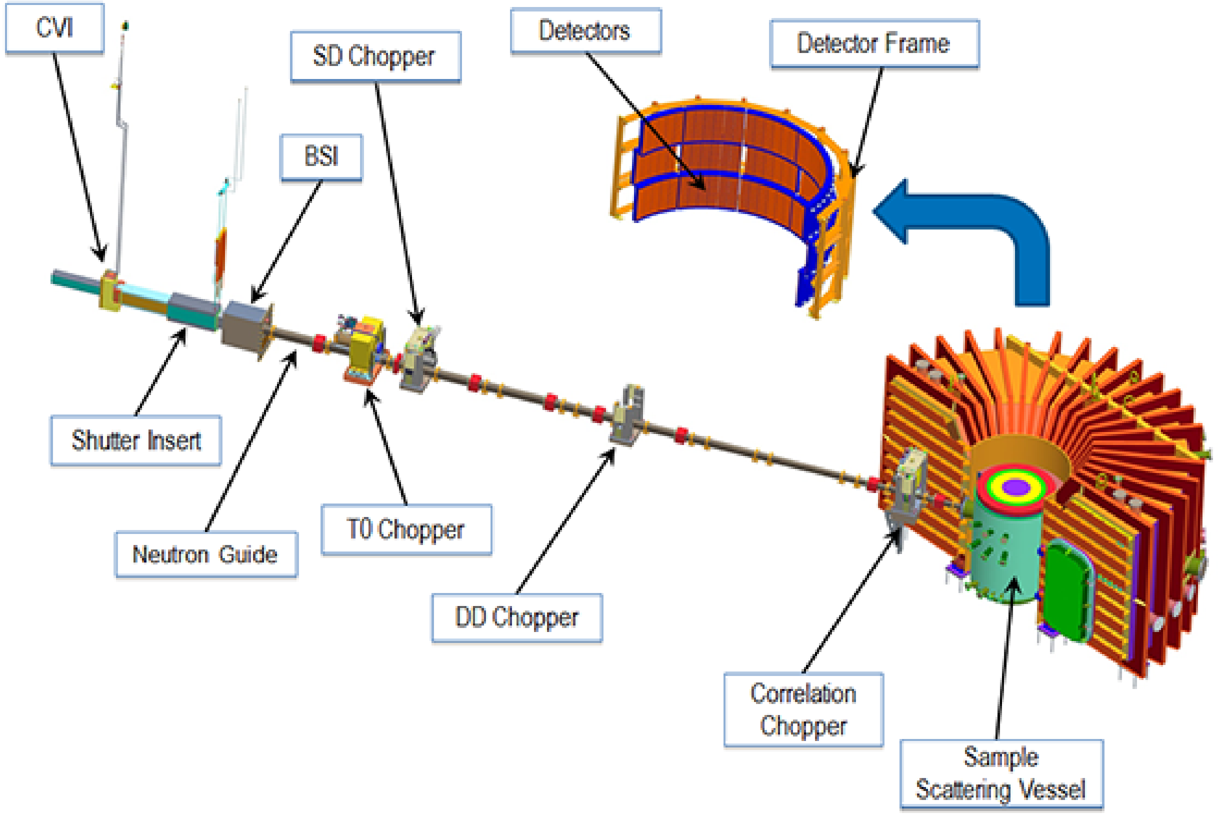
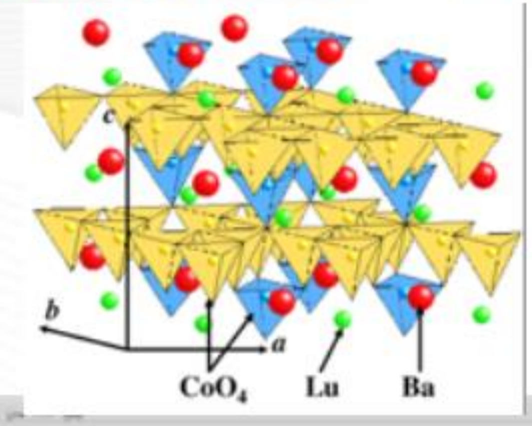
Corelli (SNS)

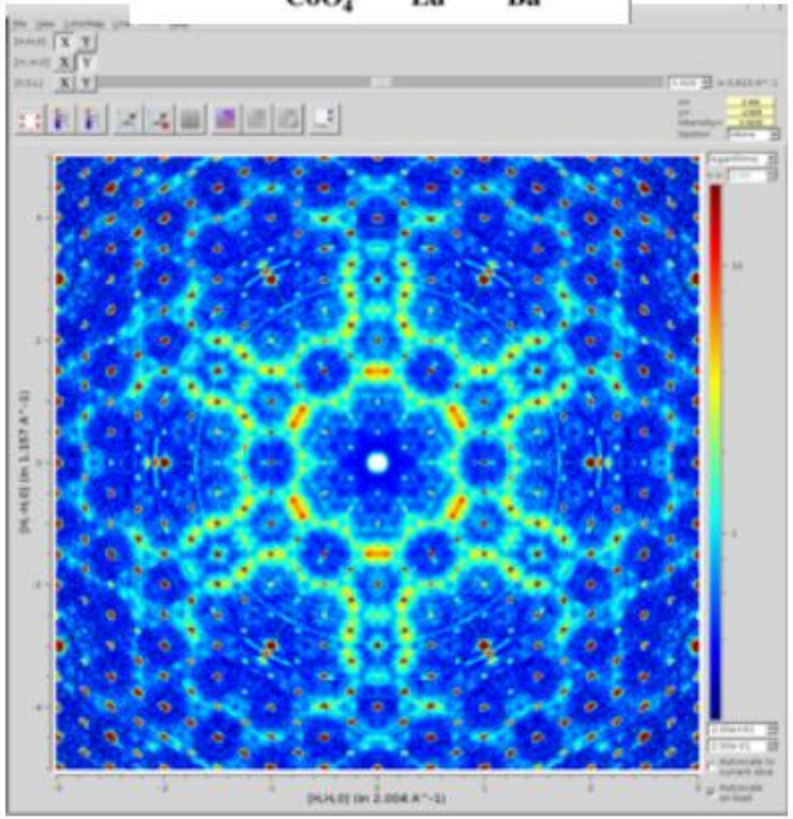


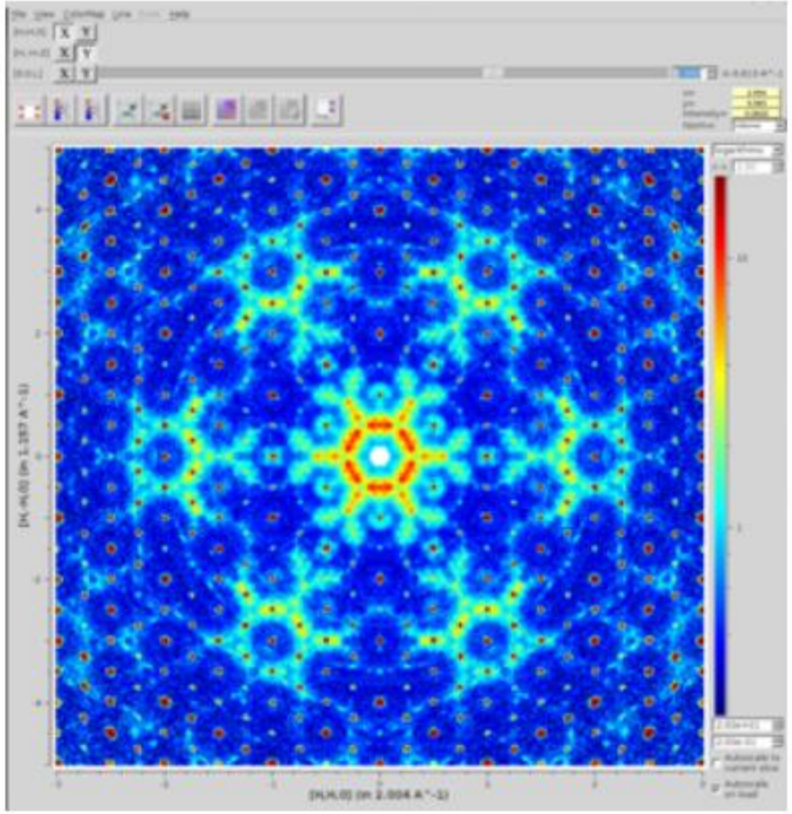
- Large detector coverage
- Most/all HKL covered for crystals
- Diffuse scattering.
- Magnets, pressure, dilution temperatures available.

CORELLI - Science



Magnetic diffuse scattering with alternating kagome/triangular lattices— $LuBaCo_4O_7$





CORELLI - Science

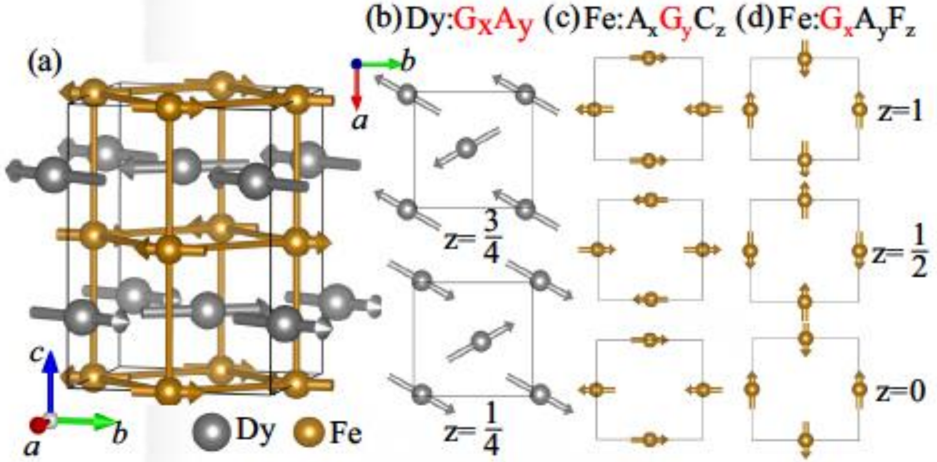
RAPID COMMUNICATIONS

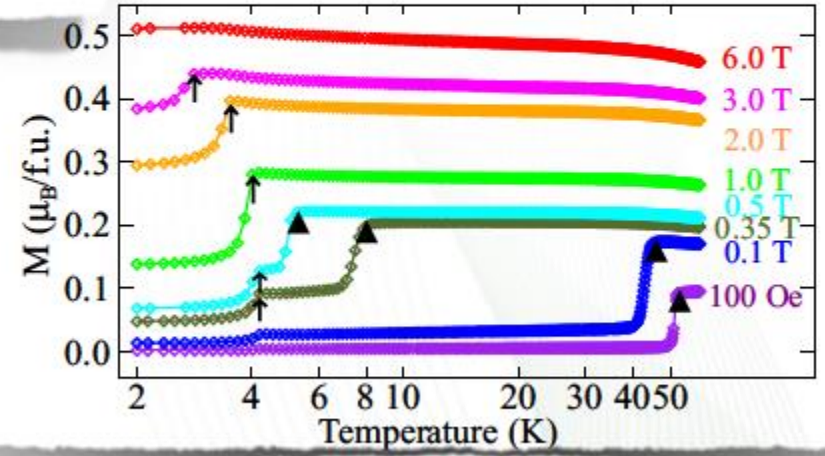
PHYSICAL REVIEW B **93**, 140403(R) (2016)

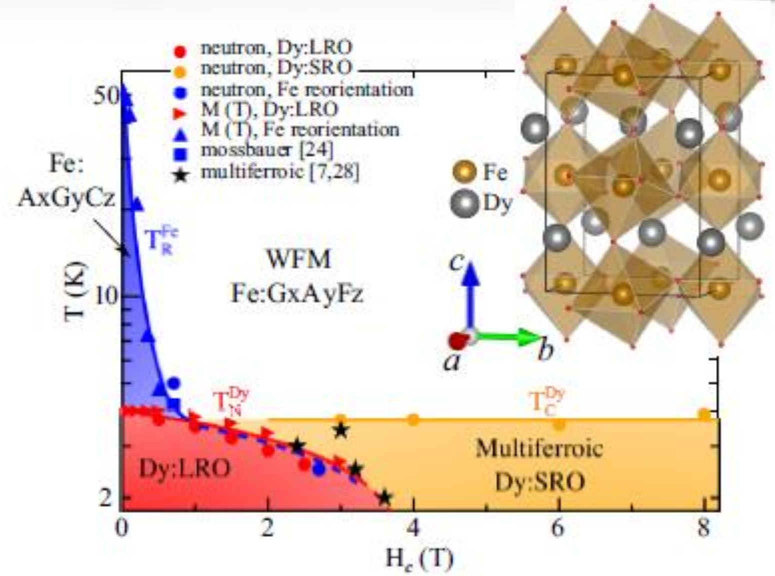
Simultaneous occurrence of multiferroism and short-range magnetic order in $DyFeO_3$

Jinchen Wang,[1,2,3] Juanjuan Liu,[1] Jieming Sheng,[1] Wei Luo,[1] Feng Ye,[2,3] Zhiying Zhao,[4,5,6] Xuefeng Sun,[4,5,6] Sergey A. Danilkin,[7] Guochu Deng,[7] and Wei Bao[1,*]

[1] *Department of Physics, Renmin University of China, Beijing 100872, China*
[2] *Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[3] *Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506, USA*
[4] *Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China*
[5] *Key Laboratory of Strongly-Coupled Quantum Matter Physics, Chinese Academy of Sciences, Hefei, Anhui 230026, People's Republic of China*
[6] *Collaborative Innovation Center of Advanced Microstructures, Nanjing, Jiangsu 210093, People's Republic of China*
[7] *Bragg Institute, ANSTO, Locked Bag 2001, Kirrawee DC NSW 2232, Australia*







Conclusion: Determining a magnetic structure with neutron scattering

- Find a good problem and grow sample (powder or crystal)
- Do lots of characterization measurements in laboratory
- Understand background/theory of sample and neutron
- Apply for beamtime (speak to instrument scientist)
- Sample and experiment preparation are crucial (speak to instrument scientist)
- Perform measurement
- Analyze crystal structure (maybe need more measurements)
- <u>Analyze magnetic structure: Starting model (magnetic symmetry) → compare to data → repeat</u>
- If lucky write up paper
- Otherwise more data → Powder → single crystal → polarization → inelastic → etc

Learn about the STS and have input on the development