Neutron Diffractometers at HFIR and SNS (ORNL)

Stuart Calder
Oak Ridge National Laboratory, High Flux Isotope Reactor (HFIR)
First magnetic neutron diffraction performed at Oak Ridge National Laboratory (ORNL)

- Clifford G. Shull received 1994 Nobel prize in Physics.
- First direct evidence of antiferromagnetism in MnO.
- Neel model of ferrimagnetism confirmed in Fe$_3$O$_4$.
- First magnetic form-factor data obtained in Mn compounds.
- Production of polarized neutrons by Bragg reflection from ferromagnets demonstrated.
Oak Ridge National Laboratory (ORNL)

• **Neutrons:** High Flux Isotope Reactor (HFIR)
  Spallation Neutron Source (SNS)

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

- Several complimentary diffraction beamlines at ORNL.
- Science of the material will dictate choice of instrument(s).
- Second target station will add further capabilities.
Powder diffraction
HB-2A Powder diffractometer (HFIR)

- Constant wavelength diffractometer: $\lambda=2.41 \text{ Å}$ or $1.54 \text{ Å}$
- 2theta range 3 deg to 155 deg.
- Available for users since 2009.
- Focus is magnetic diffraction, balance between intensity and resolution.
- Clean background ideal for magnetism and complex sample environments.
Sample environments (HB-2A)

Low Temperature
- Conventional closed cycle refrigerators (CCR) 4 K – 700 K.
- $^4\text{He}$ crystats (1.5 K – 300 K)
- $^3\text{He}$-$^4\text{He}$ dilution (27 millikelvin)

High Magnetic fields
- 5 T standard (16 T and pulsed available on other beamlines)
- Can combine 27 mK with 5 T.

High Pressures
- HB-2A offers Clamp cells (2 GPa) and Fluid/gas cells (10 kbar)
- Dedicated beamline (SNAP) with diamond anvil cells (to 100 Gpa)

Polarized neutrons on HB-2A
- Incident polarized beam available for ferromagnetic and ferrimagnetic studies.
Neutrons confirm long predicted metal-insulator transition theory

Slater MIT mechanism demonstrated in NaOsO$_3$ on HB-2A diffractometer

- The metal-insulator transition (MIT), of both fundamental and technological interest, is one of the most dramatic manifestations of electron correlations in materials.

- Several mechanisms that produce MITs have been considered over the years, including Mott (electron localization via Coulomb repulsion), Anderson (localization via disorder), and Peierls (localization via distortion of a one-dimensional lattice).

- A mechanism proposed by Slater in 1951, in which long-range magnetic order drives the MIT, has remained elusive.

- Neutron scattering at the Neutron Powder Diffractometer and Polarized Triple-Axis Spectrometer at the High Flux Isotope Reactor, along with x-ray scattering at the Advanced Photon Source, were used to probe the 5d transition metal oxide NaOsO$_3$.

- The experiments uncovered the Slater mechanism for magnetic ordering in NaOsO$_3$ and are the first definitive demonstration of this long-predicted MIT.

S. Calder et al., PRL 108 257209 (2012)
**Cu(Mn$_{1-x}$Cu$_x$)O$_2$ : Tuning of Magnetism by chemical substitution**

- V. O. Garlea et al., PRB 83, 172407 (2011)
Spallation Neutron Source at Oak Ridge National Laboratory

The world’s most intense pulsed, accelerator-based neutron source

* Scheduled commissioning date

**LEGEND**
- Operating instrument in user program
- In commissioning or operating development beamline
- In design or construction
- Under consideration

**Nanoscience Ordered Materials Diffractometer (NOMAD)** - BL-1B
- Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
- Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
- J. Zhang, Neutron, 865-241-1393, zhanges@ornl.gov

**Wide Angular-Range Chopper Spectrometer (WARS)** - BL-18
- Atomic-level dynamics in materials science, chemistry, condensed matter sciences
- D. Allen, Neutron, 865-241-2592, allen@ornl.gov

**Fine-Resolution Fermi Chopper Spectrometer (SEQUSIA)** - BL-17
- Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
- K. Gray, Neutron, 865-241-2570, grayk@ornl.gov

- Life sciences, polymers, materials science, earth and environmental sciences
- B. Grimes, Neutron, 865-241-2679, grimes@ornl.gov

**Vibrational Spectrometer (VISION)** - BL-16B
- Vibration dynamics in molecular systems, chemistry
- D. Johnson, Neutron, 865-241-5818, johnson@ornl.gov

**Neutron Spin Echo Spectrometer (NSE)** - BL-15
- High-resolution dynamics of slow processes, polymers, biological macromolecules
- M. Iwata, Neutron, 865-241-5739, iwata@ornl.gov

**Hybrid Polarized Beam Spectrometer (HYSPEC)** - BL-14B
- Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
- R. Wirth, Neutron, 865-241-6800, wirthr@ornl.gov

**Fundamental Neutron Physics Beam Line** - BL-13
- Fundamental properties of neutrons
- D. Ogawa, Neutron, 865-241-4072, ogawad@ornl.gov

**Single-Crystal Diffraction Spectrometer (TOPAZ)** - BL-12
- Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
- C. Hoffmann, Neutron, 865-241-4072, hoffmann@ornl.gov

**Macromolecular Neutron Diffraction Spectrometer (MaNDI)** - BL-11B
- Atomic-level structures of macromolecules, drug complexes, DNA
- L. Gao, Neutron, 865-241-4072, gao@ornl.gov

**Elastic Diffuse Scattering Spectrometer (CORELLY)** - BL-9 (2014)
- Detailed studies of disorder in crystalline materials
- Y. Sato, Neutron, 865-241-4072, sato@ornl.gov

**Powder Diffractometer (POWGEN)** - BL-11A
- Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
- A. R. Heap, Neutron, 865-241-4072, heap@ornl.gov

**Magnetism Reflectometer** - BL-4A
- Chemistry, magnetism of layered systems and interfaces
- W. Seel, Neutron, 865-241-5739, seel@ornl.gov

**Cold Neutron Chopper Spectrometer (CNC)** - BL-5
- Condensed matter physics, materials science, chemistry, biology, environmental sciences
- G. Siller, Neutron, 865-241-5739, siller@ornl.gov

**Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS)** - BL-6
- Life science, polymer and colloidal systems, materials science, earth and environmental sciences
- W. Keller, Neutron, 865-241-5739, keller@ornl.gov

**Liquids Reflectometer** - BL-4B
- Interfaces in complex fluids, polymers, chemistry
- G. K. Weir, Neutron, 865-241-5739, weirg@ornl.gov

**Spallation Neutrons and Pressure Diffractometer (SNAP)** - BL-3
- Materials science, geology, earth and environmental sciences
- C. Tuk, Neutron, 865-241-5739, tukc@ornl.gov

**Backscattering Spectrometer (BASIS)** - BL-2
- Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
- E. M. M. Neutron, 865-241-5739, mries@ornl.gov
POWGEN (SNS)

- General purpose diffractometer that encompasses magnetic scattering.
- Optimized for crystal structure determination.
- Alternative design to previous spallation diffractometers → data reduced to single pattern.
- Different wavelengths (Frames) available. Magnetic Frame: $Q = 0.4 \, \text{Å}^{-1}$ to $3 \, \text{Å}^{-1}$
  Generally a wide detector angular coverage $20<2\Theta<159$
- Currently optimized for high Q, but more low angular detector coverage planned.
Neutrons Discover Unusually Strong Long Range Superexchange Interactions in Mixed Transition Metal Oxides

Scientific Achievement
Neutron powder diffraction on double perovskite Sr$_2$CoOsO$_6$ reveals a magnetic structure in which the two magnetic sublattices order independently at different temperatures via four bond superexchange pathways.

Significance and Impact
These results provide important information for designing magnetic materials with magnetic transition metals from differing rows of the periodic table, a situation where the long standing Goodenough-Kanamori rules fail to apply.

Research Details
- Os spins order at 108K via a ferromagnetic Os-O-Co-O-Os exchange pathway while Co spins order at 70K via an antiferromagnetic Co-O-Os-Co exchange pathway
- Complimentary DFT calculations find that typically dominant nearest neighbor Co-O-Os exchange is an order of magnitude weaker, resulting in decoupled sublattices

Work was performed at the ORNL Spallation Neutron Source’s POWGEN instrument.

Magnetite (Fe₃O₄)

- Sample cooled down to 10 K at a nominal 1 K/minute
- Temperature controlled for a near constant $\frac{\Delta T}{\Delta p(\text{charge})} = \text{constant counting statistics}$
- Ramping accelerates with increasing beam power & halts when it trips

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

- Temperature sliced data perfectly usable for refinement....
- Extension to parametric studies a logical step

Magnetic structure refinement of Fe₃O₄ at 295 K with a 5 K slice (nominally 5 minutes) of the ramping data
Single crystal diffraction
TOPAZ (SNS BL-12): Single crystals

**Instrument Parameter**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderator</td>
<td>decoupled poisoned super critical $H_2$</td>
</tr>
<tr>
<td>Source to sample</td>
<td>18 m</td>
</tr>
<tr>
<td>Sample to detector</td>
<td>0.395-0.460 m</td>
</tr>
<tr>
<td>Detector angular coverage</td>
<td>$13.5^\circ &lt; 2\theta &lt; 160^\circ$</td>
</tr>
<tr>
<td>Detector solid angle coverage</td>
<td>2.4 ster.</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>$\sim 3.6$ Å</td>
</tr>
<tr>
<td>Frames 1 &amp; 2 ($\lambda$ range at 60Hz)</td>
<td>0.25 - 3.85 Å; 3.9 - 7.1 Å</td>
</tr>
<tr>
<td>Sample size: Diameter, Volume</td>
<td>0.05 - 2.5 mm, &gt;0.10 mm$^3$</td>
</tr>
<tr>
<td>Unit cell length, Resolution</td>
<td>$&lt;70$ Å, $d_{min}$ &gt; 0.4 Å</td>
</tr>
</tbody>
</table>

**Sample Environment**

- Crystal Logic Goniostat: Fixed chi at 135° with 360° rotations in omega and phi
- CryoStream 700Plus: 90 K-500 K
- Upgrade – Cryogenic Goniometer: 5 K to 295 K

**Primary Usage**

TOPAZ is a high resolution time-of-flight Laue diffractometer. It is capable of measuring a 3D volume of reciprocal space during each pulse from a small stationary single crystal using an array of state-of-the-art neutron area detectors with sub-microsecond readout time for individual neutron events.

- Chemical crystallography complementary to X-rays
- Magnetic structure
- Diffuse scattering
- Neutron event-based parametric study of nuclear and magnetic structural phase transitions

**Science Highlight**

The structure of an Fe-based electrocatalyst mimicking the [FeFe]-hydrogenase was determined from neutron diffraction. Single-crystal neutron diffraction reveals the first time a unusually strong acidic $N-H^{\delta+}$ and hydridic $Fe-H^{\delta}$ hydrogen bonding interaction resulted from the heterolytic cleavage of $H_2$, and provides insight into making more efficient electrocatalyst for the oxidation of $H_2$ in fuel cells.


JANA2006 can now read TOPAZ data and apply neutron wavelength-dependent extinction correction for TOF Laue data with direction cosines.
Four-circle diffractometer (HB-3A)

- Beam size of $6\times8\text{mm}^2 \rightarrow$ minimum crystal of $1\text{mm}^3$
- 2D detector and single-point $^3\text{He}$ detector
- Choice of incident wavelengths from vertical focusing Si monochromator: 1.0 Å, 1.54 Å and 2.54 Å
- Full $\chi$ circle goniometer.
A New Direction for Iron-Based Superconductors

Scientific Achievement
Single-crystal neutron diffraction is a powerful means of determining magnetic structures. In this study, the technique was used to show that the parent phase of superconductors in the $K_{x}Fe_{2-y}Se_{2}$ family has a novel magnetically ordered semiconducting ground state.

Significance and Impact
This research opens new avenues for comprehending the magnetism of iron-based superconductors and sets a new direction in the search for magnetic high-temperature superconductors.

Research Details
– Superconductivity was introduced by electron doping, which suppresses the stripe AF order, leading to a magnetic phase diagram similar to those of cuprates and iron pnictides.
– Neutron diffraction was used to study the structure, magnetic order, and stoichiometry of single crystals of $K_{x}Fe_{2-y}Se_{2}$ compounds.


Work was performed at the HFIR Four-Circle Diffractometer.
Spin Reorientation in TlFe$_{1.6}$Se$_2$ with Complete Vacancy Ordering

Ordered vacancies tune the magnetic order.

- Detailed characterization of single crystal TlFe$_{1.6}$Se$_2$ with complete chemical and vacancy order reveals a previously unobserved spin reorientation with spins lying in the ab plane for T < 100 K.
- A strong interaction between the ordered and disordered regions must prevent this ground state from occurring in the partially disordered crystals at low temperatures.
- Single-crystal neutron diffraction was used at the HB-3A four-circle diffractometer, High Flux Isotope Reactor, ORNL, to determine these magnetic structures as a function of temperature.

Powder and/or single crystal diffraction
WAND

- **Vertical focusing hot-pressed Ge monochromator** – \( \lambda = 1.48 \text{ Å} \) (113) or \( \lambda = 0.94 \text{ Å} \) (115) without significant higher order contamination.

- **Medium-Resolution High intensity powder diffractometer** – allows fast measurements for parametric studies.

- **Continuous detector 1D position sensitive detectors**. 624 anodes with 0.2 degree separation.

- **Single crystal measurements**: the good signal to noise ratio allows the detection of weak signals from superstructure, low dimensional magnetic order.
Spallation Neutron Source at Oak Ridge National Laboratory

The world’s most intense pulsed, accelerator-based neutron source

**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
Jie Du, Neutron: 931.21.3189, ndrew@ornl.gov

**Wide Angular-Range Chopper Spectrometer (ARCS) - BL-18**
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
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**Fine-Resolution Fermi Chopper Spectrometer (SEQOIA) - BL-17**
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
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**Ultra-Small-Angle Neutron Scattering Instrument (USANS) - BL-1A (2014)**
Life sciences, polymers, materials science, earth and environmental sciences
M. Herney, Neutrons: 865.241.3226, herneym@ornl.gov

**Vibrational Spectrometer (VISION) - BL-16B**
Vibrational dynamics in molecular systems, chemistry
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**Neutron Spin Echo Spectrometer (NSE) - BL-15**
High-resolution dynamics of slow processes, polymers, biological macromolecules
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**Hybrid Polarized Beam Spectrometer (HYSPEC) - BL-14B**
Atomic-level dynamics in single crystals, magnetism, condensed matter sciences
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**Fundamental Neutron Physics Beam Line - BL-13**
Fundamental properties of neutrons
Geoffrey Greene: 931.241.5304, greenejg@ornl.gov

**Single-Crystal Diffraclometer (TOPAZ) - BL-12**
Atomic-level structures in chemistry, biology, earth sciences, materials science, condensed matter physics
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**Macromolecular Neutron Diffractometer (MaNDi) - BL-11B**
Atomic-level structures of membrane proteins, drug complexes, DNA
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**Powder Diffraclometer (POWGEN) - BL-11A**
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Ashley Kuo: 931.241.3226, kuoa@ornl.gov

**Magnetism Reflectometer - BL-4A**
Chemistry, magnetism of layered systems and interfaces
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**Liquids Reflectometer - BL-4B**
Interfaces in complex fluids, polymers, chemistry
Zaini Antono: 931.241.2853, antonoz@ornl.gov

**Cold Neutron Chopper Spectrometer (CNCI) - BL-5**
Condensed matter physics, materials science, chemistry, biology, environmental science
Georgi Efremov: 931.241.3226, efremovg@ornl.gov

**Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) - BL-6**
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
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**Elastic Diffuse Scattering Spectrometer (CORELLI) - BL-9 (2014)**
Detailed studies of disorder in crystalline materials
Fang Ye: 931.241.3226, yeafc@ornl.gov

**Versatile Neutron Imaging Instrument at SNS (VENUS) - BL-10**
Energy-selective imaging in materials science, engineering, materials processing, environmental sciences and biology
Hensel Bilbao: 931.241.3226, bilbaoh@ornl.gov

**Powder Diffractometer (POWGEN) - BL-11A**
Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
Ashley Kuo: 931.241.3226, kuoa@ornl.gov

**Spallation Neutrons and Pressure Diffractometer (SNAP) - BL-3**
Materials science, geology, earth and environmental sciences
Chris Tulk: 931.241.3226, tulkac@ornl.gov
SNAP

- Dedicated pressure beamline.
- Source to sample distance 15 m.
- Optimized for powders, crystals possible.
- Accessible Q as low as 0.78 Å⁻¹.
- Pressure 0-25 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 Mn₃O₄” PRB 87 014417 (2013)
Scientific Achievement

In-Situ neutron scattering measurements of a single crystal under pressure reveal the magnetic structure resulting from the Antiferromagnetic Long Range Ordering in SrCu$_2$(BO$_3$)$_2$, a Shastry-Sutherland lattice model material. The Shastry-Sutherland model has played an influential role in developing the modern condensed matter physics field because it is sufficiently simple to be exactly soluble, but sufficiently rich to capture interesting physics.

Significance and Impact

The ability to measure data from single crystalline sample under high pressure (up to 100 KBar) enables researchers to reconcile the exploration of pressure as tuning parameter in quantum systems despite their characteristic weak magnetic signal.

Research Details

– A previously cut and aligned single crystal of SrCu$_2$(BO$_3$)$_2$ was loaded in a pressure cell able to cool the cell to 90K
– The precise alignment of the crystal and placement of the instrument detectors allowed the monitoring of the location where magnetic scattering is expected
– The highly localized scattering characteristic of single crystal diffraction allows the measurement of small reflections. Such experiments are inaccessible to standard powder diffraction.

Research performed at the SNAP Instrument at the Spallation Neutron Source, Oak Ridge National Laboratory
Applying for beamtime at ORNL

• Two proposal calls per year (Spring/Fall)
• Next call and details: http://neutrons.ornl.gov/users/proposals.shtml
• SNS and HFIR in same proposal call.
• Contact instrument scientists to improve chances of beamtime!

POWGEN Mail In Program

• Proposals accepted continuously (not limited to general call).
• Temperatures between 10 K and 300 K.
• Maximum of 8 hours.
• http://neutrons.ornl.gov/powgen/mail-in-pgm.html