X-Ray and Neutron Diffraction Instruments

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CPDW18

Overview

Survey – Analytical Techniques by Radiation Type

Properties of the Neutron

Neutron Production

Neutron Detection and Instrumentation

Differences between X-Ray Diffraction and Neutron Diffraction

Selected Applications of Neutron Diffraction – Chemical Crystallography

Survey of Analytical Techniques by Radiation Type

MRI

Ultrasound

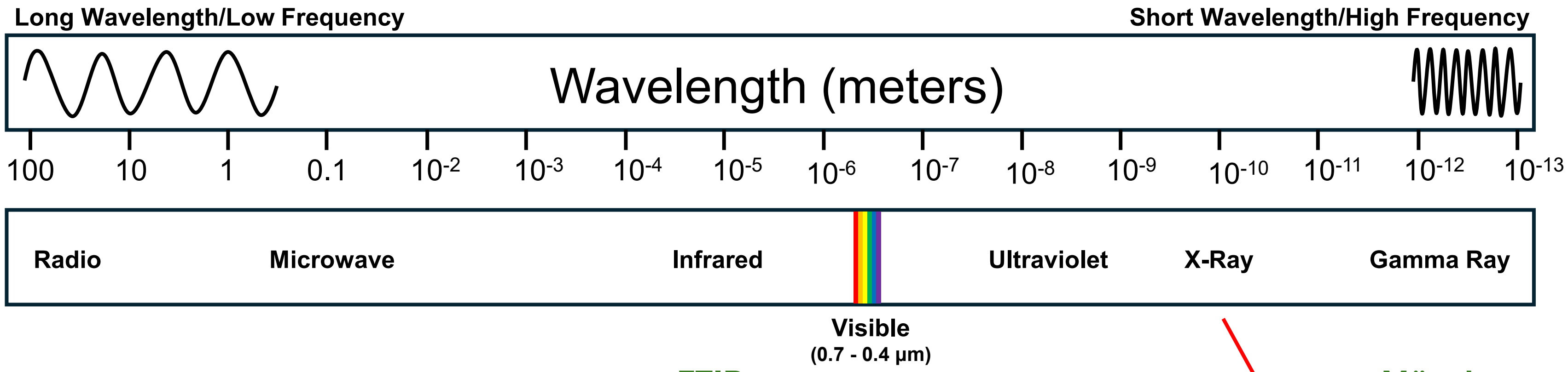
Imaging

Pathology

Medical X-Rays

Nuclear imaging

PET



NMR

Rotational spectroscopy

FTIR

Raman

UV-VIS (HPLC)

Optical Microscopy

Laser Diffraction

Circular Dichroism

Atomic Absorption

MFI/HIAC…

Mössbauer spectroscopy

Diffraction (XRD)

Fluorescence Spectroscopy (XRF)

Absorption Spectroscopy (XAFS/XANES)

Microscopy/Imaging

Computed Tomography (CT)

Resonant Scattering

The wavelength of light is matched to the purpose of the study. Many of these techniques can be utilized in a user laboratory.

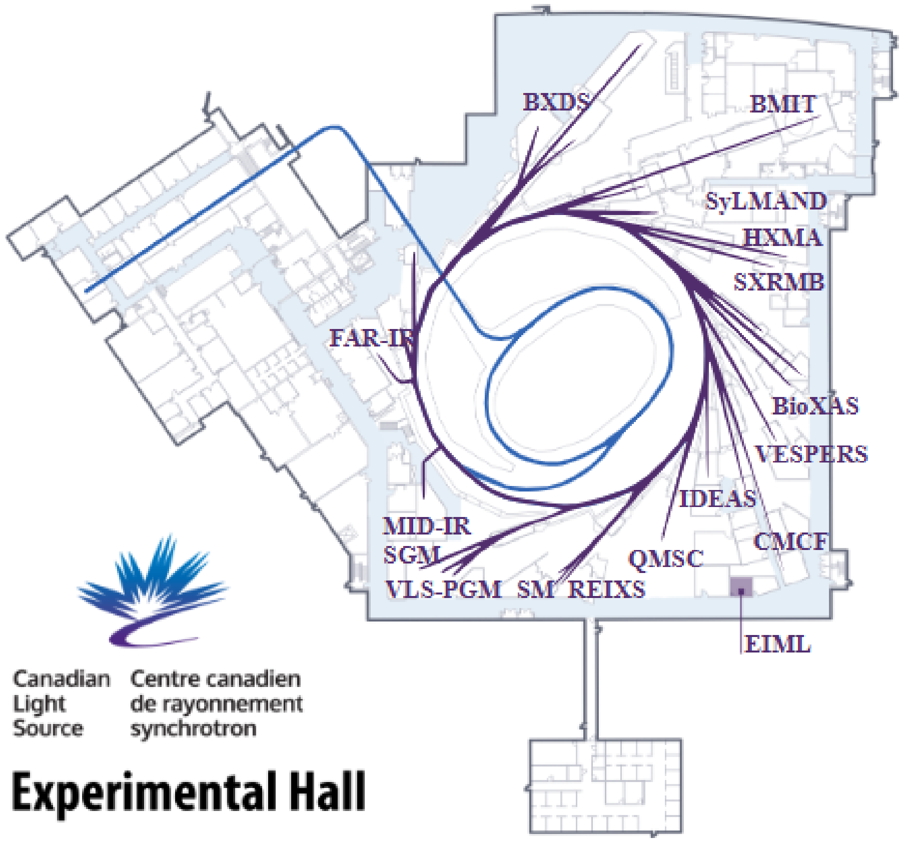
Why X-Rays for diffraction?

X-Radiation is ~1 Å in wavelength (~10^{-10} m) – this is the order of a chemical bond length – good for probing structure at the molecular level.

Beamlines at the Canadian Light Source

BioXAS-Imaging
BioXAS-Spectroscopy
BMIT | Biomedical Imaging and Therapy Facility
BXDS | Brockhouse Diffraction Sector
CLS@APS | Canadian Access to the Advanced Photon Source
CMCF | Canadian Macromolecular Crystallography Facility
EIML | Electron Imaging & Microanalysis Lab
Far-IR | Far Infrared Spectroscopy
HXMA | Hard X-ray Micro-Analysis Beamline
IDEAS | Industry, Development, Education, Applications, Students Beamline
Mid-IR | Mid Infrared Spectromicroscopy
QMSC | Quantum Materials Spectroscopy Centre
REIXS | Resonant Elastic and Inelastic X-ray Scattering
SGM | Spherical Grating Monochromator Beamline
SM | Soft X-ray Spectromicroscopy
SXRMB | Soft X-ray Microcharacterization Beamline
SyLMAND | Synchrotron Laboratory for Micro And Nano Devices
VESPERS | Very Sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron
VLS-PGM | Variable Line Spacing Plane Grating Monochromator Beamline

Beamline Map



Synchrotron advantages over lab sources:
- Smaller sample sizes
- Increased beam intensity, highly oriented beams
- Access to multiple wavelengths

So – we have lab sources and synchrotrons for the study of condensed matter. Why use neutron scattering?

Properties of the Neutron

Gentle ➢ *have energies comparable to elementary excitations in condensed matter*

Neutral ➢ *carry no electric charge, not dominated by electromagnetic interactions*

Sensitive ➢ *have irregular scattering cross sections, providing contrast & sensitivity to light atoms (e.g. H, C) and adjacent elements in the periodic table (e.g., N, O)*

Penetrative ➢ *scatter by nuclear forces, interacting directly with atomic nuclei in the bulk*

Magnetic ➢ *have an intrinsic magnetic moment, interacting with magnetic electrons*

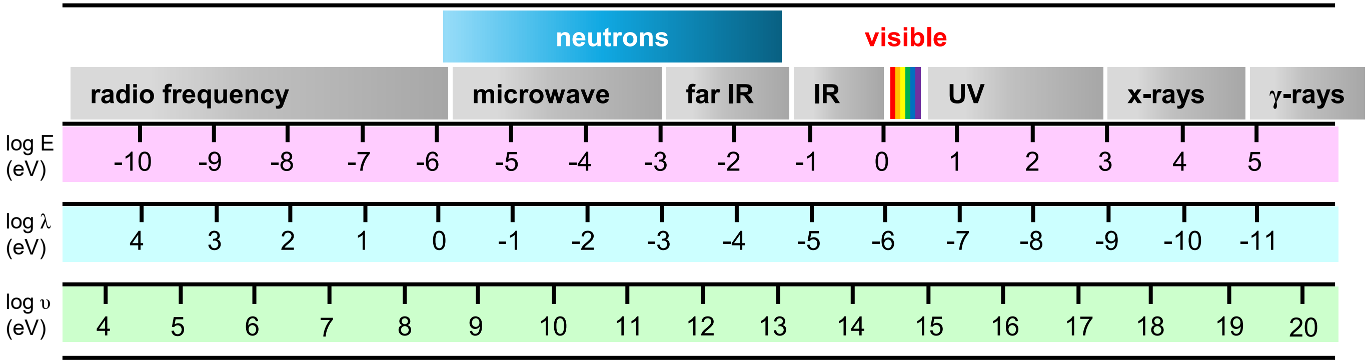
Precise ➢ *have sharp spatial & energetic resolution to recognize structural and dynamic features*

Democratic ➢ *survey ~10^{23} atoms, yielding accurate many-body effects*

The Neutron Can be a Particle or a Wave Compared to the Electromagnetic Spectrum

Material research concerns only the Slow Neutrons

Ultra Cold	Very Cold	Cold	Thermal	Epithermal	
		0.5-5	5-50	50-1000	(meV)
		13-4	4-1.3	1.3-0.3	(Å)

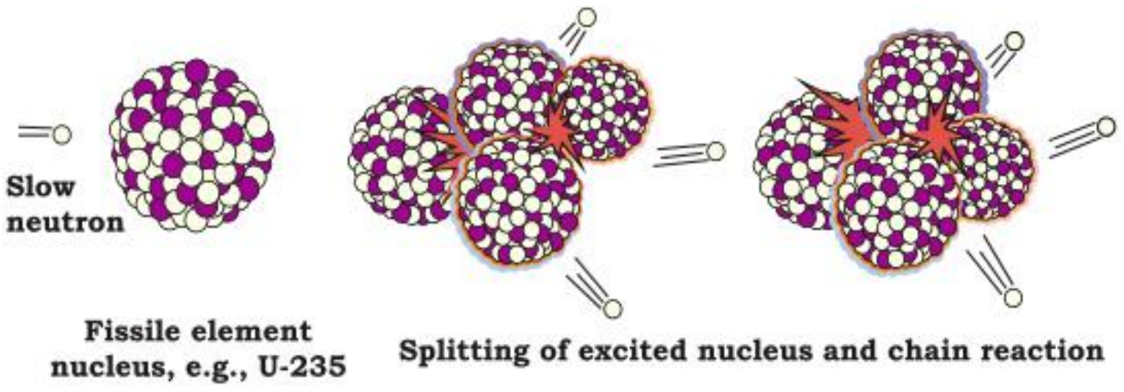


- Zero charge
- Mass m = 1.0087 a.m.u.
- Spin ½
- Magnetic moment μ_n = -1.9
- Wave nature of the neutron:
  - $E = h^2/(2m\lambda^2) = k_B T = ½mv^2$
  - $\lambda = h/(mv) = (h/m)\cdot(t/L)$

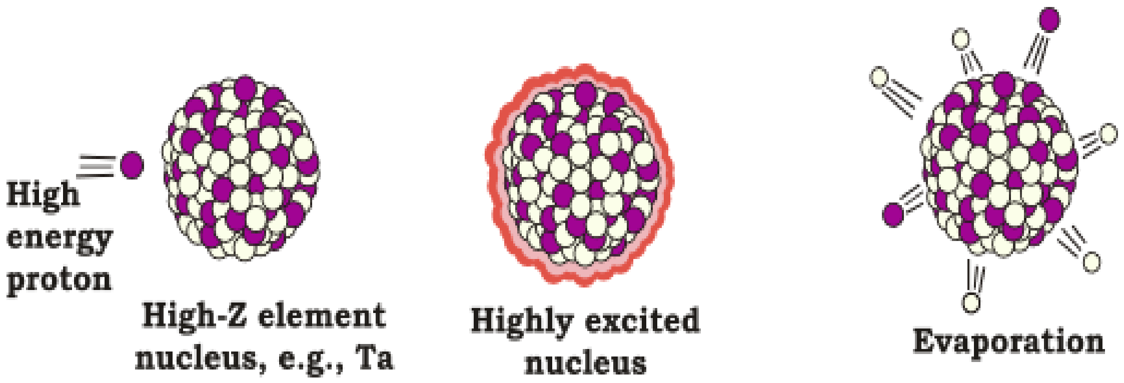
- For T = 300 K:
  - E = 25 meV = ~200 cm^{-1}
  - v = 2200 m/sec
  - λ = 1.8 Å
- For λ = 1.0 Å:
  - E = 81 meV
    - = ~650 cm^{-1}
    - = ~2 kcal/mol
    - (For 1 Å X-ray, E = 12 keV)
  - v = ~4000 m/sec = 4 m/msec

Neutron Production and Neutron Sources

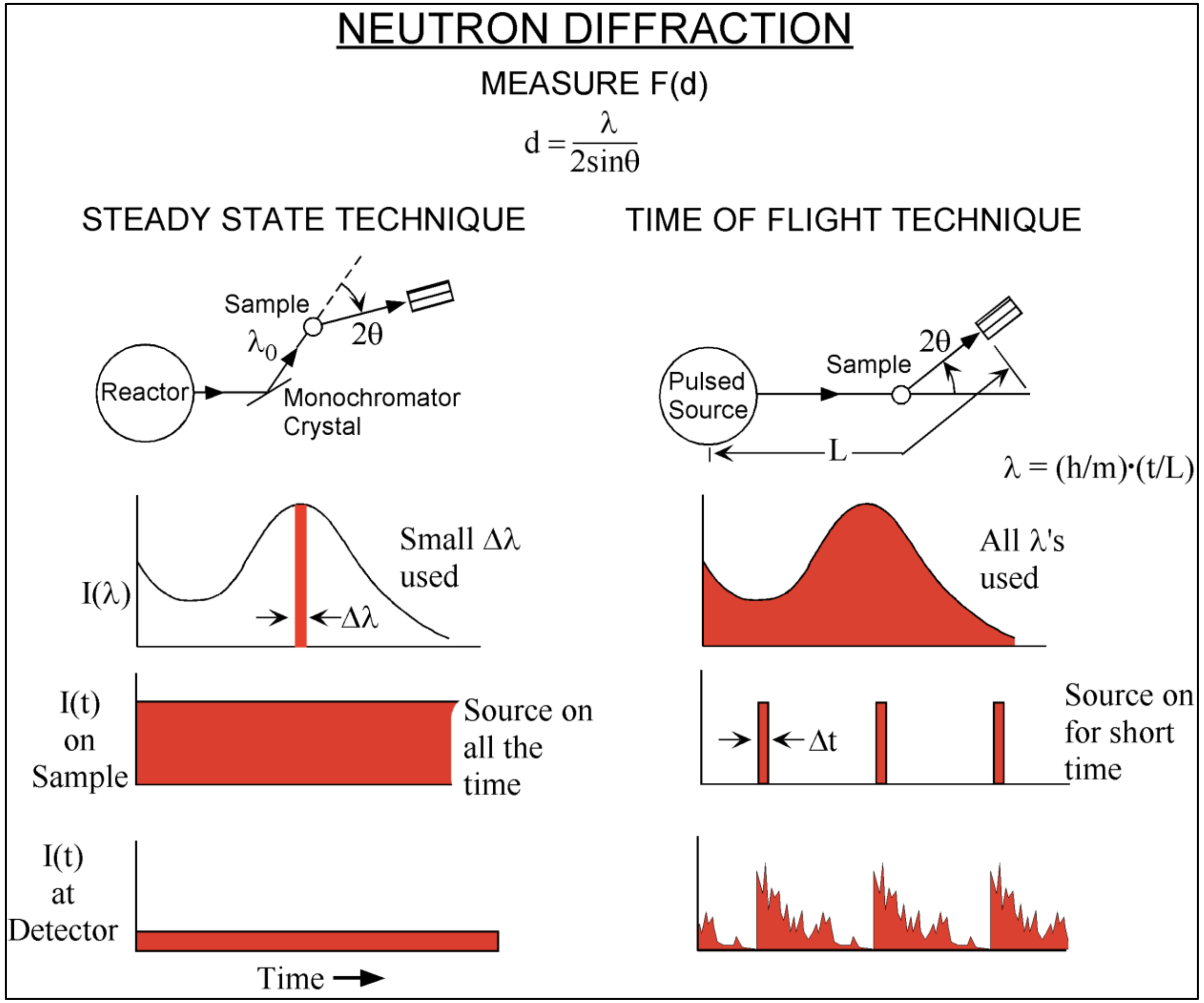
Fission – employed by reactor sources



Spallation – employed by pulsed sources



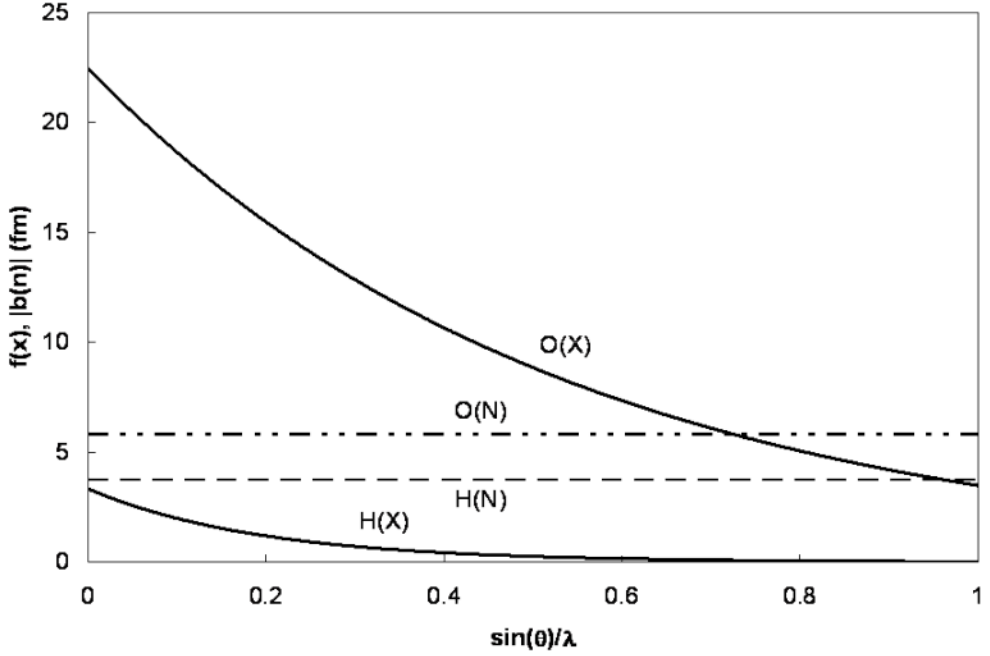
Top-down View



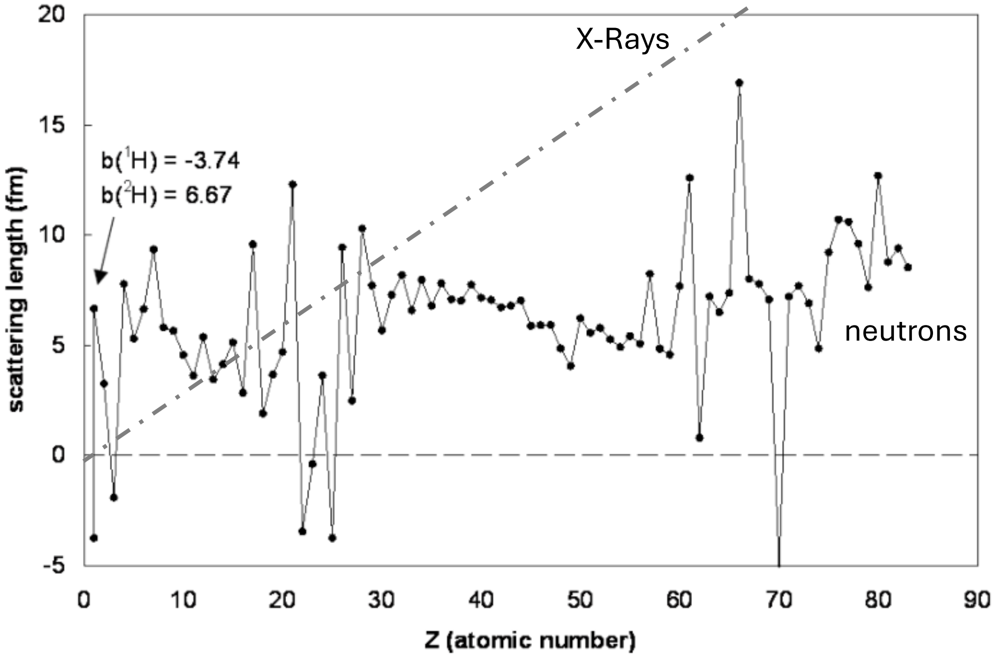
To slow the neutrons down for instrumental analysis, the incident beam is passed through a moderator with a high hydrogen content such as liquid hydrogen or methane

Differences between X-Ray and Neutron Scattering

Scattering factor falloff for X-rays vs. neutrons



Neutron scattering length as a function of atomic number



- X-Ray scattering lengths increase linearly with increasing atomic number (dependent on electron density)
- Neutron scattering lengths are irregular with respect to atomic number and can have a negative scattering length
- Neutron scattering may distinguish between elements of similar atomic number and/or between isotopes (dependent on elemental cross sections for scattering)
- Neutron scattering is complementary to X-Ray scattering

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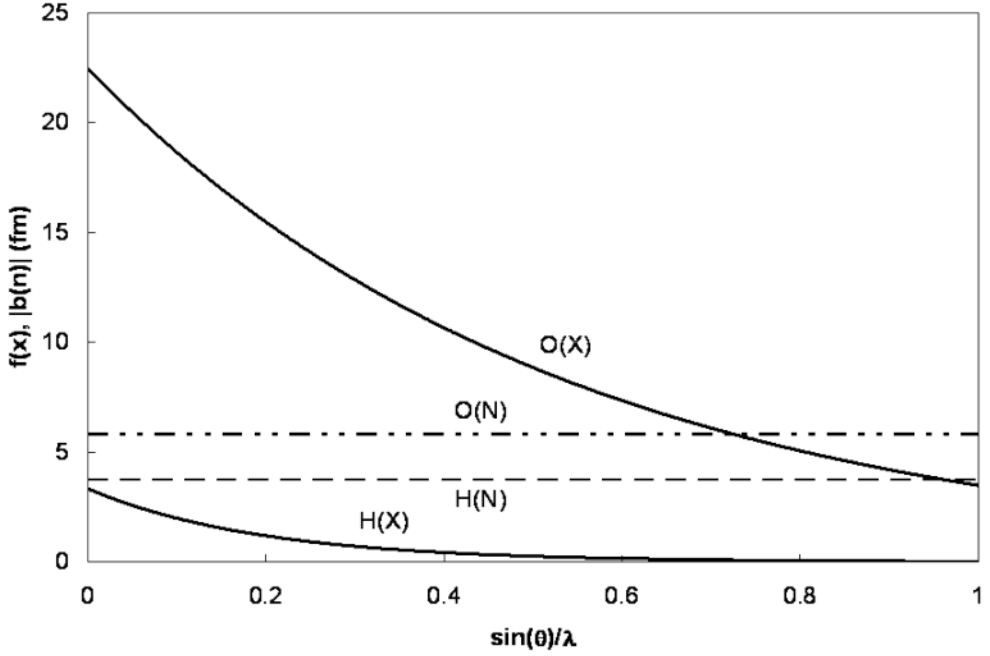
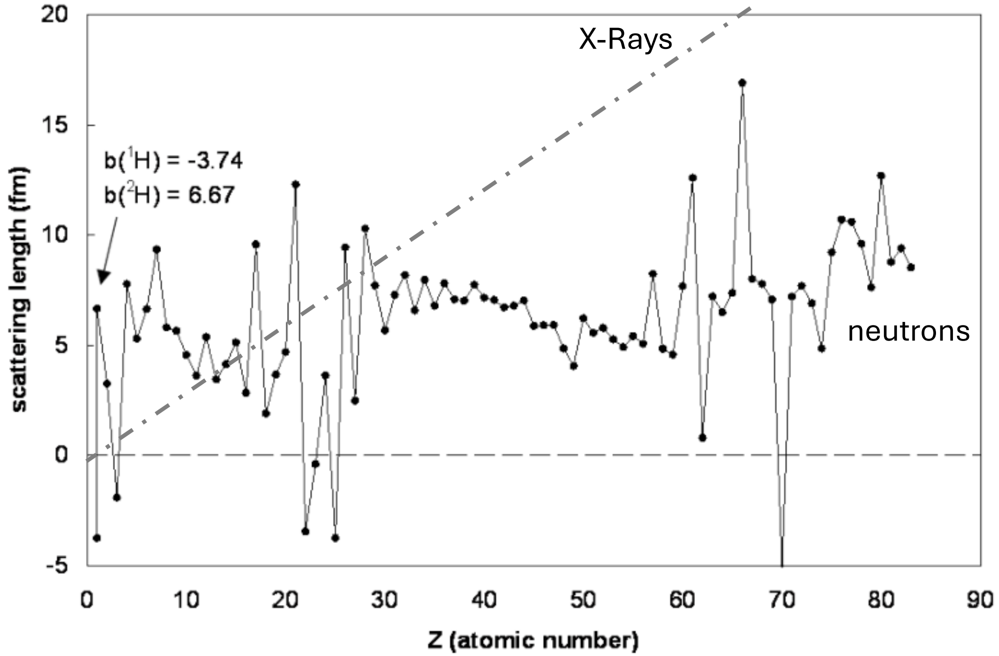


Neutron scattering length as a function of atomic number



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X-Ray Powder Patterns

- Higher resolution
- Intensity fall-off at small d-spacings
- Better at resolving small lattice distortions

Neutron Powder Patterns

- Lower resolution
- Higher intensity at small d-spacings
- Better atomic positions/thermal parameters

Neutron Scattering Cross Sections

Coherent scattering: scattered waves from all nuclei have definite relative phases and constructively interfere with each other.

Incoherent scattering: scattered waves from different nuclei have random/indeterminate relative phases and cannot constructively interfere with each other – results as high background.

Neutron scattering lengths and cross sections

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
^{1}H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
^{2}H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
^{3}H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

Neutron scattering lengths and cross sections

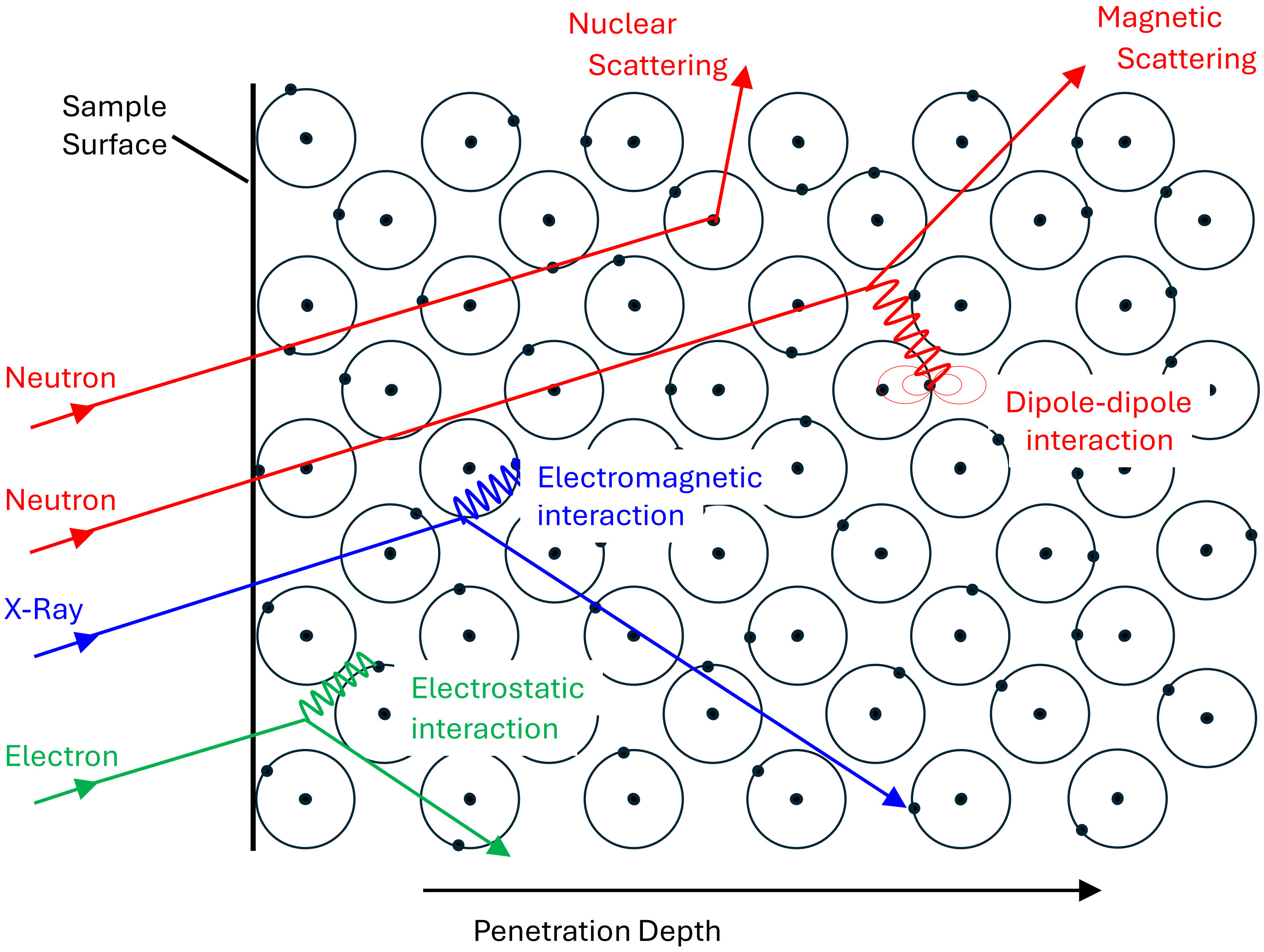
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
B	---	5.30-0.213*i*	---	3.54	1.7	5.24	767.(8.)
^{10}B	20	-0.1-1.066*i*	-4.7+1.231*i*	0.144	3	3.1	3835.(9.)
^{11}B	80	6.65	-1.3	5.56	0.21	5.77	0.0055

A large cross section for absorption may cause issues with the data collection due to absorption of the neutron . Neutron scattering is sensitive to specific isotopes for each element.

Isotopic labeling can leverage the differences in cross sections between isotopes of the same element:

- Contrast matching: ^{1}H and ^{2}H are out of phase with each other; selective deuteration can provide information regarding different portions of a structure. Especially useful in small angle neutron scattering or protein crystallography.
- Isotopic labeling to improve data quality (swap for ^{11}B over natural abundance B to reduce the absorption effect, swap ^{1}H for ^{2}H to improve high background effects, etc.).

Interactions with Matter



Neutrons are Neutral, Penetrative, Magnetic

- produce data free of the influence of electronic effects
- determine magnetic structure
- well suited to analyze samples in special sample environments (cryostats, furnaces, *in-situ* experiments, magnetic fields, etc.)

Attenuation (decrease in intensity) for the incident beam into an aluminum sample (example):

1% per mm for low-energy neutrons

99% per mm for X-Rays

Reconstructed from Pynn, R. Neutron Scattering – A Primer. *Los Alamos Science*, **1990**, *19*, 1-31.

Neutron Detection

- Cannot directly detect a slow neutron because of its charge neutrality
- Need to use nuclear reactions to "convert" neutrons into charged particles

<u>Example Reactions for Neutron Detection</u>

Position Sensitive/Multiwire Detectors

- $n + {}^{3}He \rightarrow {}^{3}H + {}^{1}H + 0.764$ MeV
  - Example: ^{3}He gas-filled tubes or MultiWire Proportional Chamber

Anger Cameras

Wavelength Shifting Fiber

- $n + {}^{6}Li \rightarrow {}^{4}He + {}^{3}H + 4.79$ MeV
  - Example: ^{6}Li embedded scintillator glass
  - Example: ZnS:Ag/^{6}LiF scintillator detector

- $n + {}^{10}B \rightarrow {}^{7}Li^{*} + {}^{4}He \rightarrow {}^{7}Li + {}^{4}He + 0.48\ MeV\ \gamma + 2.3$ MeV (93%)
  $\rightarrow {}^{7}Li + {}^{4}He + 2.8$ MeV (7%)

Image Plates

- $n + {}^{155}Gd \rightarrow Gd^{*} \rightarrow \gamma$-ray spectrum $\rightarrow$ conversion electron spectrum
- $n + {}^{157}Gd \rightarrow Gd^{*} \rightarrow \gamma$-ray spectrum $\rightarrow$ conversion electron spectrum
  - Example: BaFBr:Eu^{2+} mixed with Gd_2O_3

Neutron Scattering Instrumentation and Applications

Elastic Scattering

No change in the energy of the incident neutron (the direction of the scattered vector changes but the amplitude does not change).

Elastic scattering measures stationary atomic positions and molecular structure.

Neutron Diffraction
- Powder, Single Crystal
- Stress/Strain
- Disordered Materials (PDF)
- *Measurements for atomic structure*

Small Angle Scattering (SANS, USANS)
- Measurements for large-scale objects (~1-1000 nm)
- Particle shapes and inter-particle correlations
- *Microstructure (proteins, micelles, polymers, porous media)*

Neutron Reflectometry
- Thin film analyses
- Chemical or structural interfaces

Inelastic Scattering

The exchange of energy and momentum between the incident neutron and the sample changes both the direction and the amplitude of the scattered vector.

Inelastic scattering measures atomic motions.

Neutron Spectroscopy (Triple-Axis Spectrometer)
- Lattice vibrational energy
- Atomic motions in liquids/glasses
- Translational/rotational diffusion
- Rotational tunneling
- Transitions between crystal fields
- Magnetic excitations

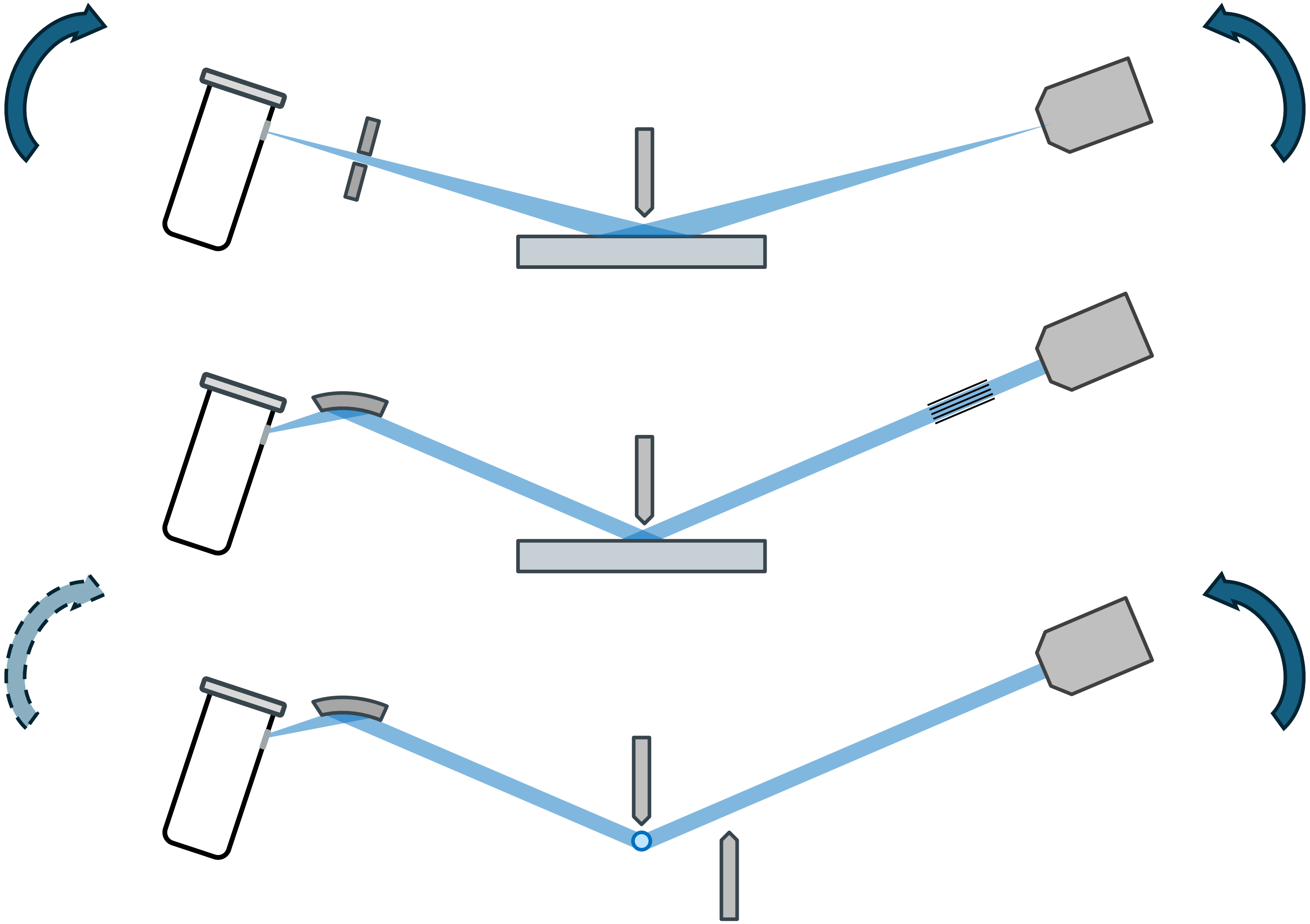
Conventional X-Ray Powder Diffraction Experiments – Laboratory Source

Bragg-Brentano
- Large beam footprint
- Best resolution
- Best intensity

Parallel Beam
- No displacement error
- Grazing incidence diffraction

Microdiffraction
- Small spot size
- 1D/2D data collection

Capillary
- Contained sample
- Reduced preferred orientation

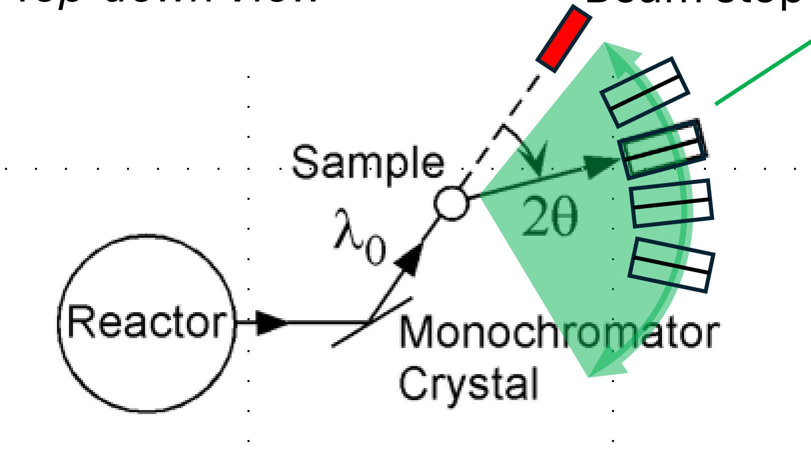


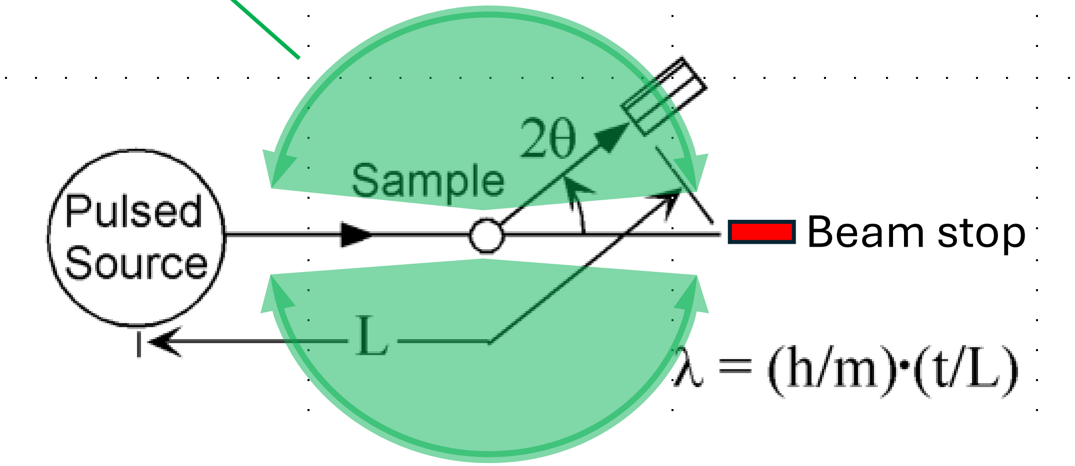
Incident angle can be fixed or variable; detector typically in motion

Neutron Powder Diffraction

Banks of stationary detectors covers a large 2ϴ range. Oftentimes - neither the source nor the detectors are moving during the neutron powder diffraction experiment.

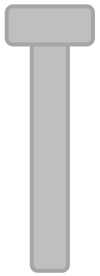
Top-down View





- Neutrons for condensed matter research are first slowed down to thermal energies by passing through a moderator (liquid H_2 or CH_4, water, etc.)
- Incident flight path components include shutter, monitor, collimators, applicable filters or polarizers, flight tube, choppers or other optics as dictated by the experiment
- Scattered neutrons are detected using a suitable detector
- Instruments are highly shielded to minimize background and user exposure to radiation

- Sample holder for general powder diffraction experiments is typically a metal canister such as vanadium or aluminum (relatively transparent to neutrons); various volumes are possible
- Similar to a capillary but easier to load
- Sample environment is typically fixed without rotation
- Special environments can be accommodated (cold, hot, magnetic fields, etc.)



Neutrons are Sensitive: Al/Si site refinement of $Ba_8Al_{14}Si_{31}$

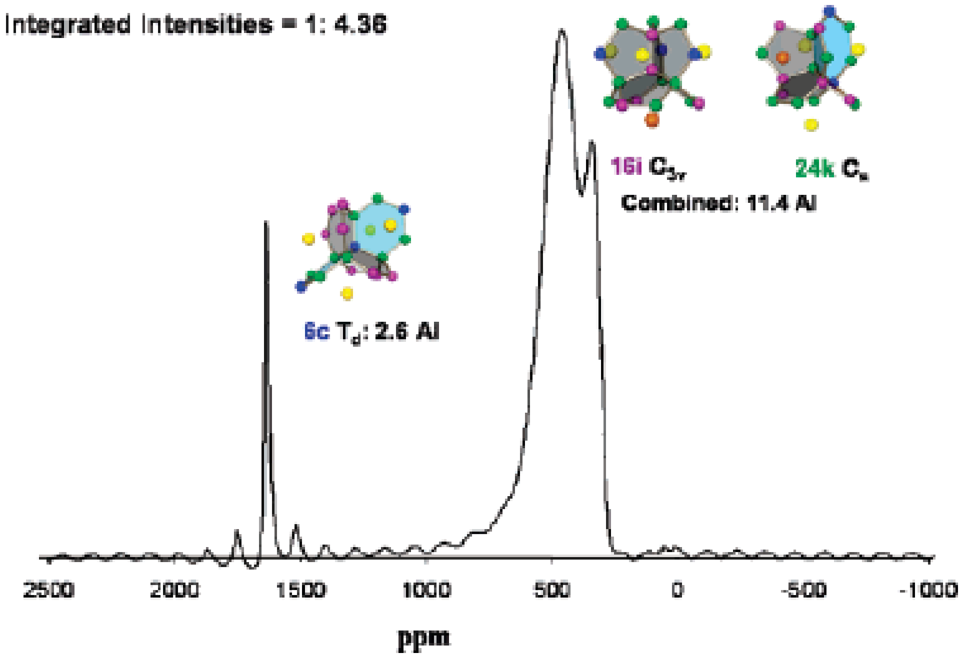
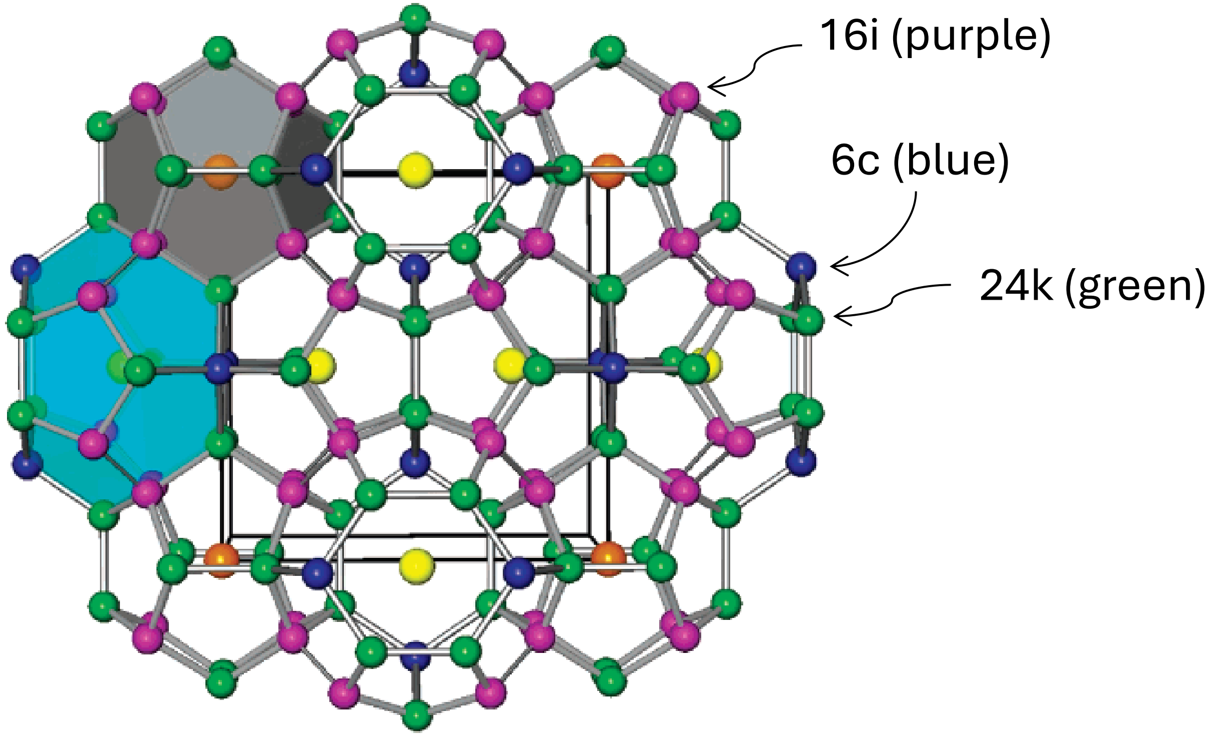


Figure 2. ^{27}Al MAS NMR for $Ba_8Al_{14}Si_{31}$. Figures represent the local site symmetry of the framework sites. The 6c sites are blue; the 16i sites are purple, and the 24k sites are green. The 2a sites are orange, and the 6d sites are yellow.



Characterization of $Ba_8Al_{14}Si_{31}$

Table 3. Refined Occupancies for Si and Calculated Al/Si Occupancies Assuming a Total Occupancy of 0.965 for Each Framework Site

atom	site	refined Si occupancy	f^a	Al occupancy^b	Si occupancy^b	total Al	total Si
M1	6c	0.876(13)	0.363	0.547	0.438	3.28	2.62
M2	16i	0.921(9)	0.382	0.270	0.704	4.32	11.26
M3	24k	0.921(9)	0.382	0.270	0.704	6.48	16.89
All		0.915(8)	0.380	0.306	0.669	14.08	30.77

^{a} Product of the refined Si occupancy times the Si scattering length (b_{Si} = 0.41491). ^{b} Obtained from $f = 0.965[xb_{Al} + (1 - x)b_{Si}]$, where $0.965x$ ie Al occupancy and $0.965(1 - x)$ is the Si occupancy.

Neutron Scattering Lengths

b_{Al} = 0.3449 x 10^{-12} cm
b_{Si} = 0.41491 x 10^{-12} cm

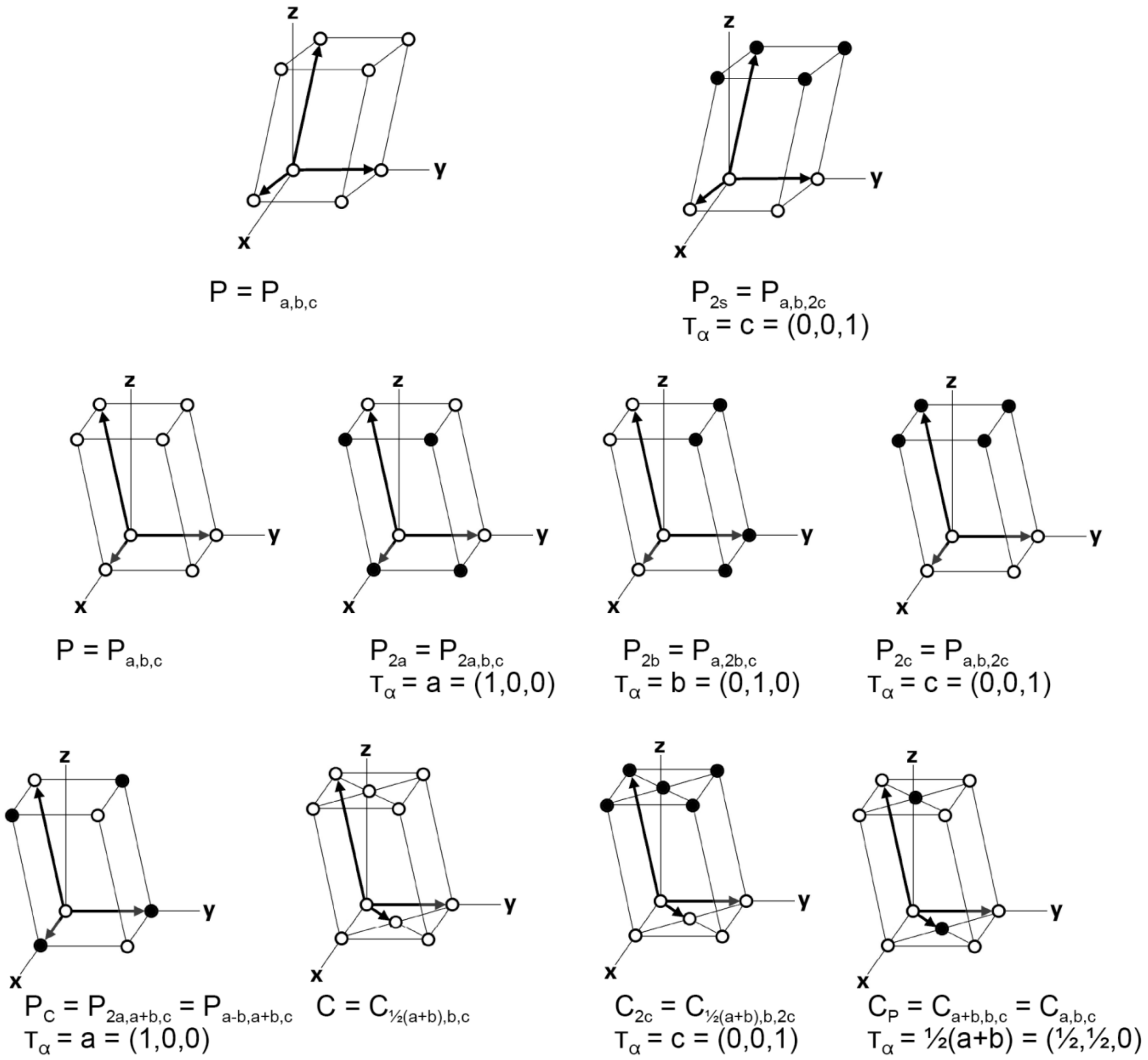
Condron *et al.*, *Inorg. Chem.*, **2006**, *45*, 9381.

Neutrons are Magnetic: Determine Magnetic Structure

Magnetic scattering may or may not coincide with ordinary nuclear Bragg scattering.

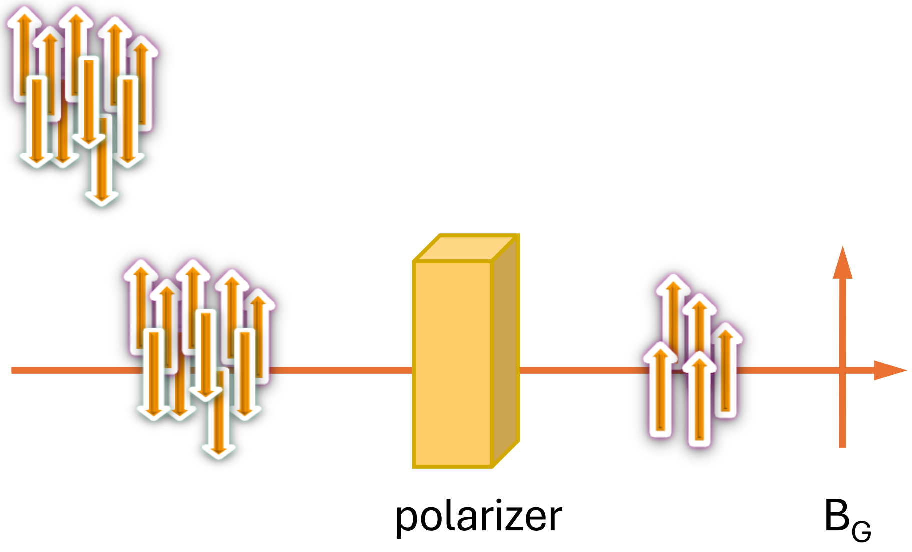
The magnetic component is proportional to the sine of the angle between the diffraction vector and the spin and is therefore dependent on the direction and spatial distribution of magnetization.

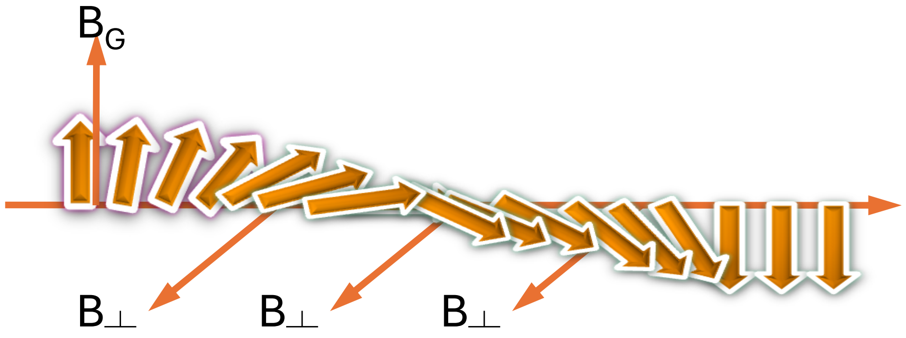
122 magnetic point groups
1651 magnetic space groups



Neutrons are Magnetic: Polarized Neutron Diffraction

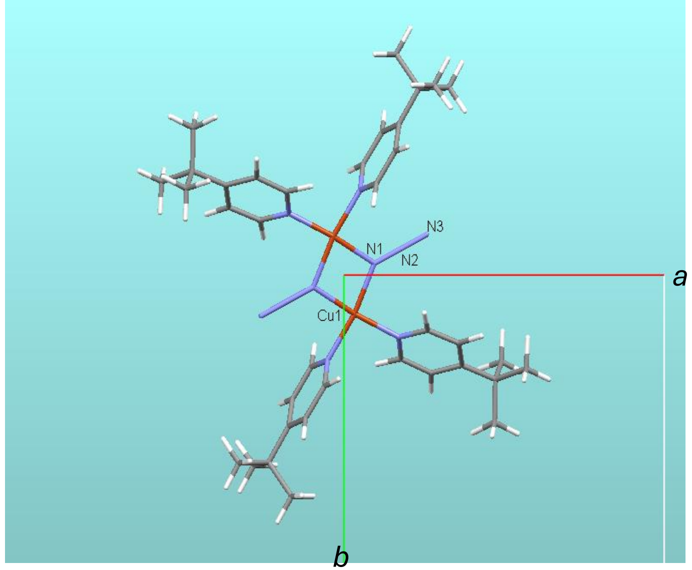
- In an unpolarized beam neutron arrive at the sample in random spin orientations
- With the use of polarizing devices such as Heusler crystals, magnetized mirrors (CoFe) and transmission through ^3He spin filters, only neutrons of one spin orientation will reach the sample
- Spin flippers may be employed to change the orientation of the neutron beam from *up* to *down* by rotating the direction of the magnetic field





- Due to the geometry of the instrument and the direction of the magnetic field, the sample can only be mounted in limited orientations (perpendicular to the scattering plane) and can only be rotated by a few degrees
- Only those reflections with nuclear Bragg intensities $|F_N| > 10^{-12}$ cm are collected in the polarized experiment to avoid multiple scattering, which can affect the weakest reflections
- With a subsequent limited data set (~200-300 reflections) the spin density may only be modeled for a limited number of atoms

Neutrons are Magnetic: Spin density determination from polarized neutron diffraction



a = 12.716(13), b = 13.441(13), c = 13.094(13) Å
β= 99.282(1)°; $P2_1/c$
crystal mounted with c aligned with the magnetic field for polarized data collection at 1.6 K

For centrosymmetic crystals, flipping ratios are related to the nuclea and magnetic structure factors:

$$R(\vec{\mathbf{K}}) = \frac{F_N^{\,2} + 2q^2 F_N F_M + q^2 F_M^{\,2}}{F_N^{\,2} - 2q^2 F_N F_M + q^2 F_M^{\,2}}$$

Magnetic structure factors, determined from the F_M/F_N ratio, are the Fourier components of the magnetization spin density.

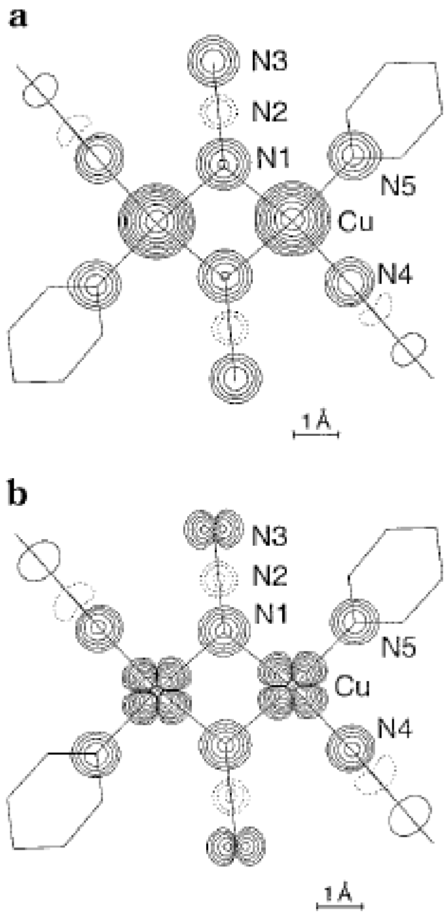
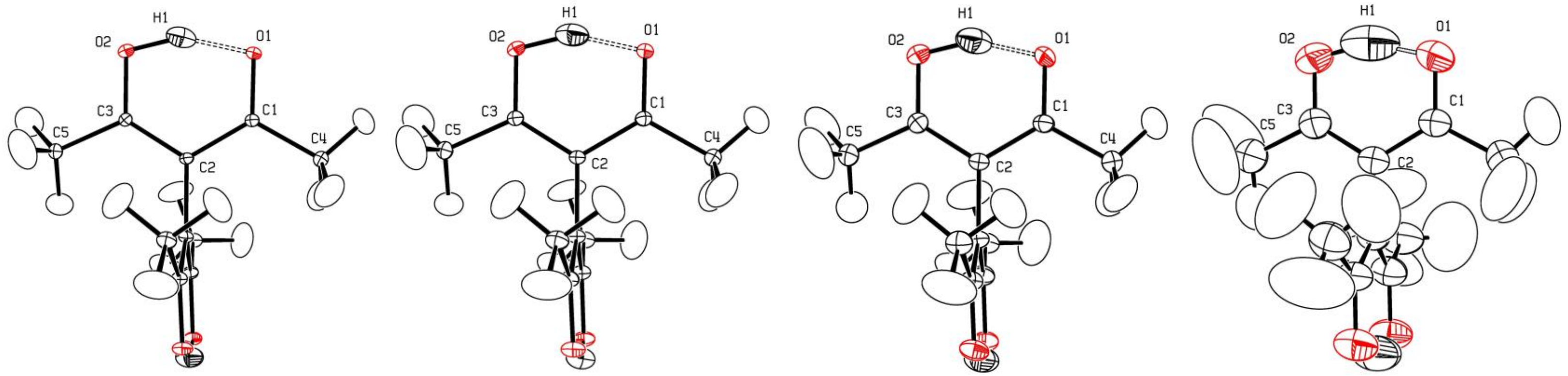


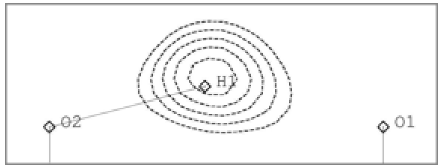
Figure 4. Spin density projection along a direction perpendicular to the Cu−N1−Cu′ plane obtained by multipole refinement: (a) for the spherical model (A) and (b) for the constrained model (B)

Aebersold et al. *J. Am. Chem. Soc.* **1998**, *120*, 5238-5245.

Neutrons are Sensitive: Location of Hydrogen Atomic Positions



40 K 70 K 110 K 298 K

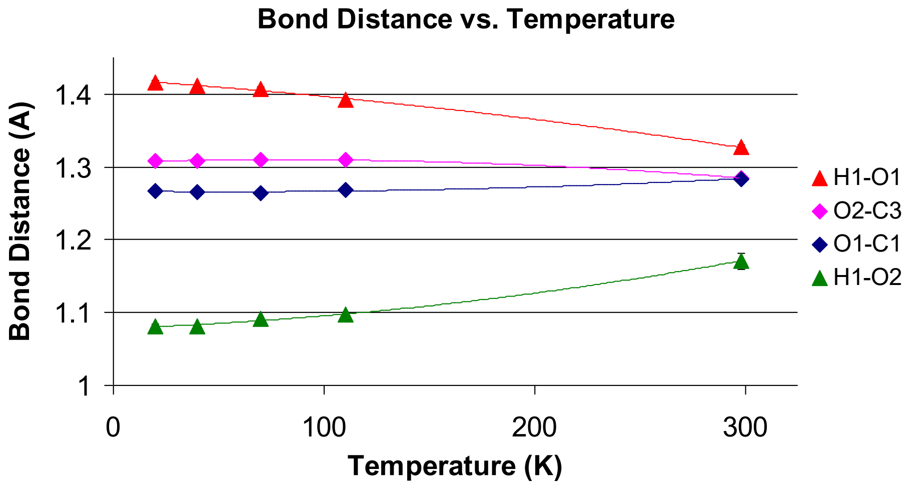


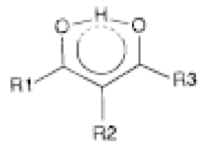
At 298 K, the difference Fourier map shows a large single minimum when H1 is omitted from the refinement.

The convergence of the C-O bond lengths to identical values at 298 K illustrates the dynamic equilibrium between the keto- and enol tautomers of this compound and is consistent with a resonance assisted hydrogen bond.

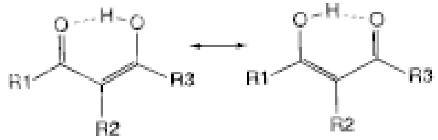
Also consistent with this bonding model are the changes in the C2-C1 and C2-C3 distances from a localized model at 20 K (C2-C1 = 1.434(1) Å, C2-C3 = 1.391(1) Å) to a more delocalized model at room temperature (C2-C1 = 1.418(3) Å, C2-C3 = 1.403(3) Å).

Although the H1 proton migrates towards the center as temperature increases, it does not result in a symmetric hydrogen bond.





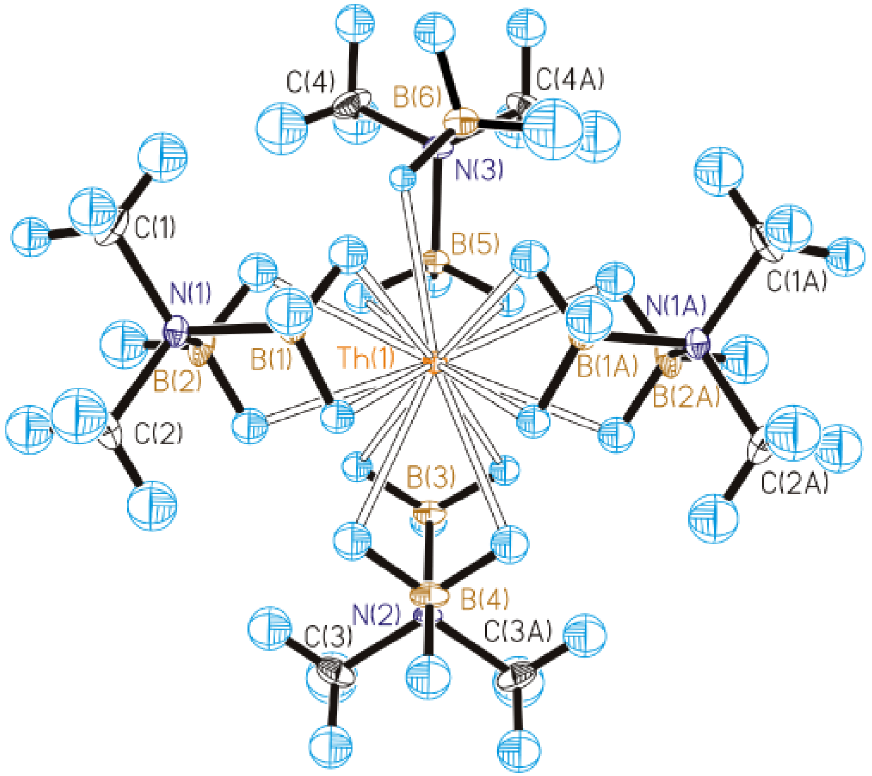
Resonance assisted hydrogen bonding model



Disordered keto-enol tautomers

J. Phys. Chem. A **2008**, *112*, 6667–6677

Neutrons are Sensitive: Location of Hydrogen Atomic Positions



[Th($H_3BNMe_2BH_3$)$_4$] , neutron data at 193 K

Space group *Pnma*

Mirror plane at (*x, ¼, z*)

15 coordinate; r_{ionic} = 0.96, $r_{covalent}$ = 2.06

Angew. Chem. Int. Ed. **2010**, *49*, 3379 –3381

Challenges: Boron atoms have high cross-section for neutron absorption and hydrogen atoms have a high cross-section for incoherent scattering; leads to non-optimal neutron scattering data quality. For X-Ray diffraction, location of light H atoms in a structure containing the heavy Th atom is extremely difficult.

Solution: used X-Ray data for the location and refinement of the heavier atoms and neutron data for the refinement of the hydrogen atoms. X-Ray and neutron data were acquired at the same temperature to match thermal anisotropic displacement parameters.

- Joint X-ray and neutron refinement
- All hydrogen atoms successfully located in neutron Fourier maps and refined exclusively with neutron data
- Soft restraints added to make all B-H_t equal, all B-H_b equal, all C-H equal

- Monomeric; boron atoms arranged about Th in a distorted D_{2d} arrangement
- Th···B(1-5) = 2.882(3) - 2.949(3) Å
- Th···B(6) = 3.193(5) Å (disordered)
- Th-H = 2.37(2) to 2.539(18) Å

  Shorter than for Th hydride complexes and comparable to B-H-Th complexes

First structurally characterized 15-coordinate complex

DFT calculations suggest this would be 16-coordinate in the gas phase, but the aminodiboranate ligands break this symmetry.

Summary

X-ray and Neutron Scattering are complementary techniques – the X-Ray experiment precedes the Neutron experiment

Neutron Advantages

- find light atoms in the presence of heavy atoms
- distinguish between isotopes of the same element and between atoms of similar atomic number
- determine magnetic structure
- produce data free of the influence of electronic effects
- penetrative nature of neutrons allows for bulk material study and experiments in special environments

Neutron Disadvantages

- neutron sources are relatively weak (this is getting better!)
- some elements strongly absorb neutrons (B, Gd, Cd)
- Unable to access all energy and/or momentum transfers

Like synchrotron beamlines, neutron scattering facilities are user facilities and are located worldwide

- wide variety of instruments for elastic and inelastic scattering techniques
- magnetic scattering
- imaging

Resources: Pynn, R. Neutron Scattering – A Primer. Los Alamos Science, 1990, 19, 1-31.
(may be sourced online at https://neutrons.ornl.gov/sites/default/files/intro_to_neutron_scattering.pdf)