

# Neutron Diffraction and Comparison with X-ray and Electron Diffraction

Graham King

Brockhouse Instrument Scientist

Canadian Light Source

October 30<sup>th</sup>, 2020



Canadian  
Light  
Source    Centre canadien  
de rayonnement  
synchrotron

THE BRIGHTEST LIGHT IN CANADA | [lightsource.ca](https://lightsource.ca)

# The Big Picture

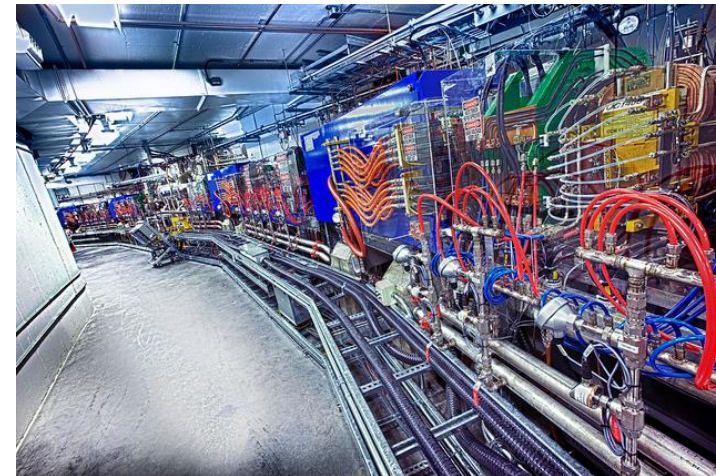
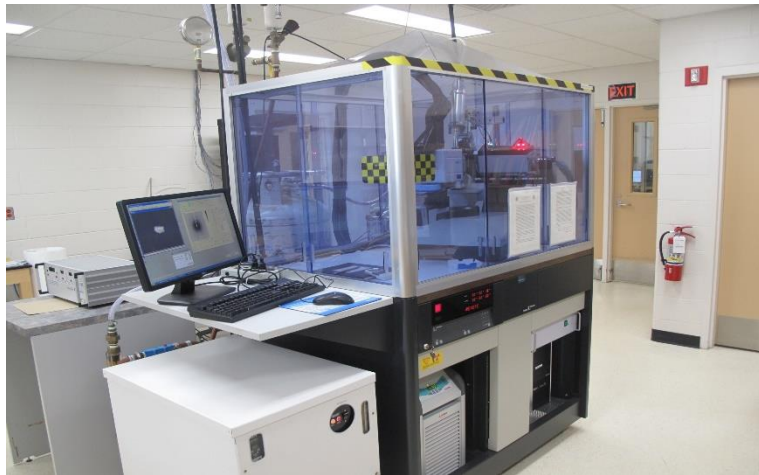
- Radiation which scatters off atoms leads to interference patterns (diffraction) which can be used to probe how the atoms are arranged in a material.
- There are three types of radiation which are used for this purpose: Photons (X-rays), neutrons, and electrons.
- These methods have different sensitivities, advantages/disadvantages, and much different instrumentation.
- The best method depends on the specific problem. The methods are complementary and often two or all three methods are needed to gain a complete structural understanding.

# X-ray Diffraction

X-ray wavelength  $\sim$  spacing between atoms.

The X-ray interaction with matter is **Moderate**.

X-ray diffraction is by far the most common method used as X-rays can be produced relatively cheaply with high flux.

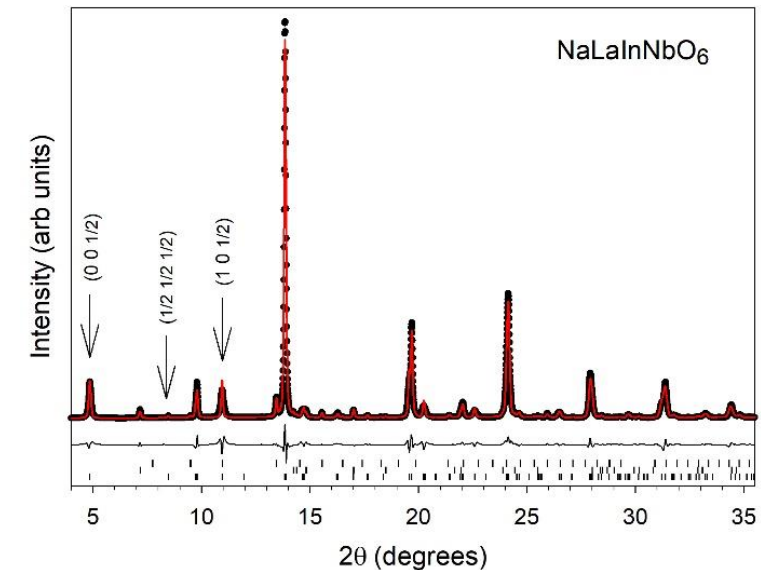


X-ray tubes consist of an anode material which is bombarded by electrons to give off X-rays at a characteristic wavelength. Cu and Mo are the most common anodes.

Synchrotrons and free electron lasers can produce extremely bright X-ray beams.

# Mechanism and (Dis)Advantages of X-ray Diffraction

- X-rays scatter off the electrons, hence they tell you about the electron density.
- As electrons density is diffuse X-ray scattering has a form factor (the intensity falls off at large Q from destructive interference within an atom).
- They interact strongly enough that small samples can be used, but weakly enough that multiple diffraction usually isn't a problem.
- X-rays can be easily produced by laboratory machines.
- Extremely bright X-ray sources at user facilities allow sub-second data acquisition, enabling time resolved studies.
- Light elements can be difficult to locate in the presence of heavy elements.



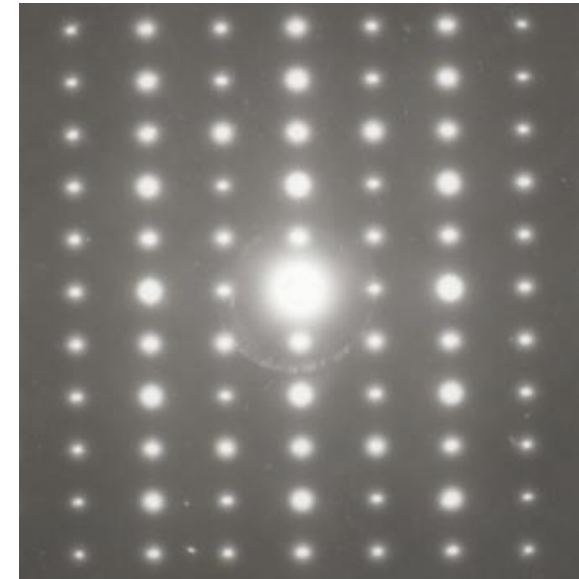
# Basics of Electron Diffraction

The interaction of electrons with matter is **Strong**. Electrons interact through the Coulomb force and are affected by both the electrons and protons in the nucleus. The strong scattering is both the advantage and disadvantage of electron diffraction.

Usually performed on individual crystals. Single crystal diffraction patterns from powder sized crystals! Can be very useful for indexing.

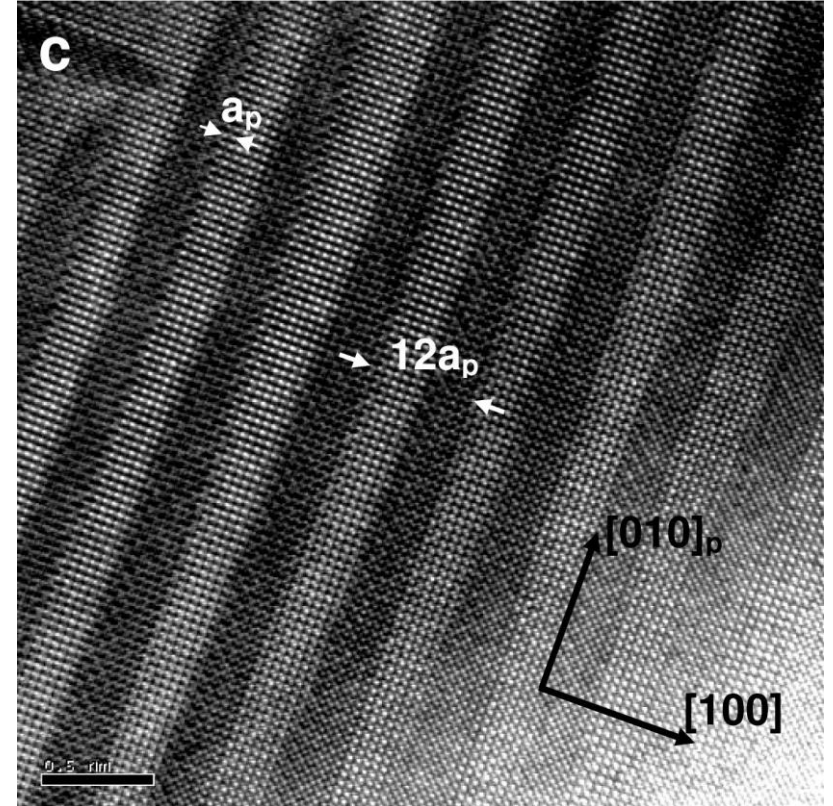
Very weak peaks can be clearly seen in electron diffraction.

However, multiple diffraction is common so the structure usually cannot be solved from the intensities like with single crystal X-ray diffraction.



# Information Obtained from Electron Diffraction

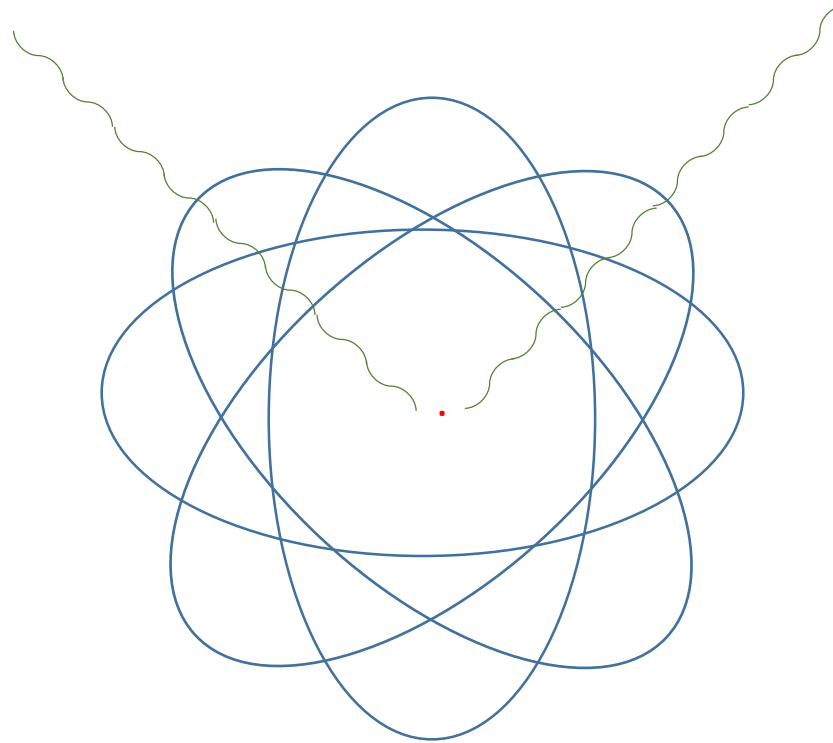
- Done in conjunction with Transmission Electron Microscopy as they use the same instrument.
- Very useful for space group determination.
- EELS (Electron Energy Loss Spectroscopy) for elemental mapping.
- Very subtle superstructures can be clearly observed that are undetected by other types of diffraction (figure left).
- It is not a bulk technique, only a few crystallites will be studied, need to be representative.
- Often the first step in the solution of a complex structure.



# Mechanism of Neutron Diffraction

## Basic Neutron Facts:

- No electric charge
- Have significant mass but also wave properties
- Have a magnetic moment
- Unstable outside of the nucleus, lifetime of ~15 minutes



Neutrons interact with the nuclei of atoms through the strong nuclear force, instead of the electron cloud.\* As this force is very short range and nuclei are tiny compared to the atoms neutron scattering is **Weak**.

\* Except in the case of magnetic scattering from unpaired electrons. This is covered later.



# Types of Neutron Interactions with Matter

## Scattering

### Coherent Elastic

The kind that gives rise to diffraction.

### Incoherent Elastic

Does not contain structural information.

### Coherent Inelastic

Gives information on atom dynamics.

### Incoherent Inelastic

Measures self-correlation.

## Absorption

Neutron is absorbed into the nucleus, changing the isotope.

Coherent means the phase of the wave is preserved after scattering.

Elastic means that no energy is transferred, the scattered wave has the same energy as the incident one.



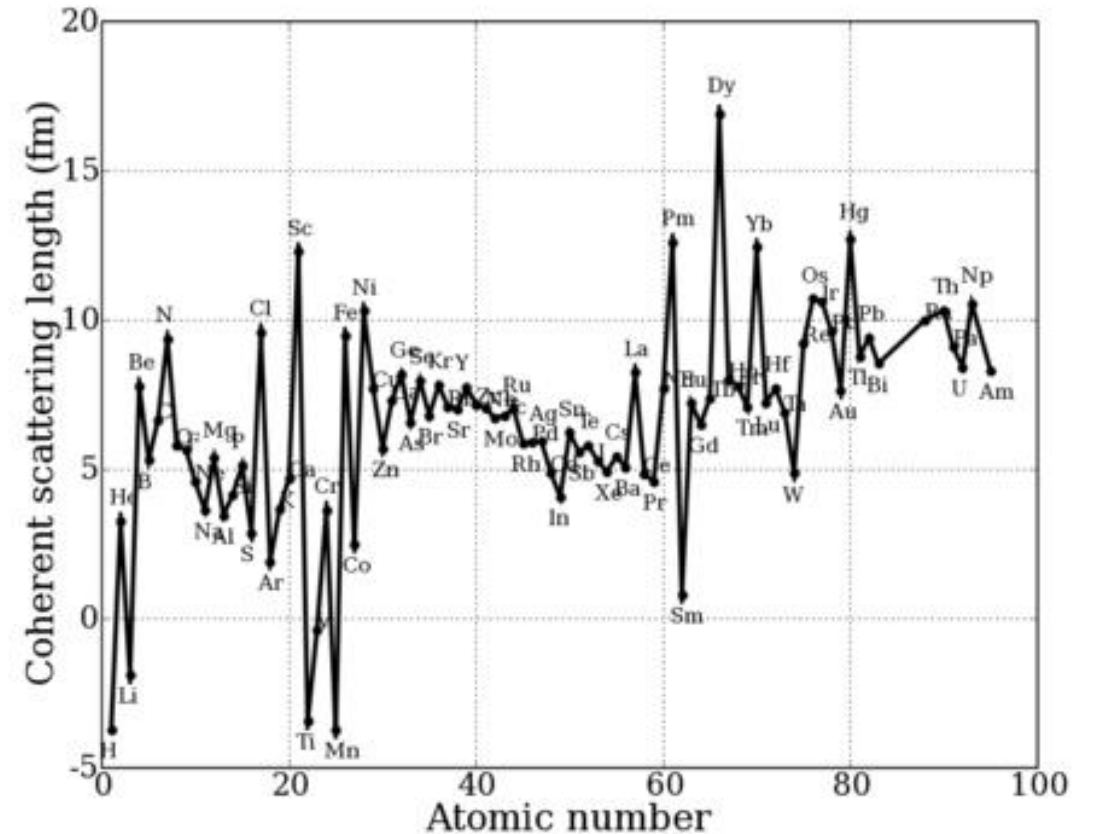


# Neutron Scattering of Elements

Measured as a cross section ( $\sigma$ ) with units of barns (1 barn =  $10^{-24}$  cm<sup>2</sup>). The scattering length,  $b$ , is more commonly used and is related as  $\sigma=4\pi b^2$ .

Scattering length does not have any periodic trend, it varies randomly across the periodic table.

As the neutron interacts with the nucleus, each isotope has different scattering and absorption characteristics. Values given are for the weighted average of all naturally occurring isotopes unless otherwise specified.

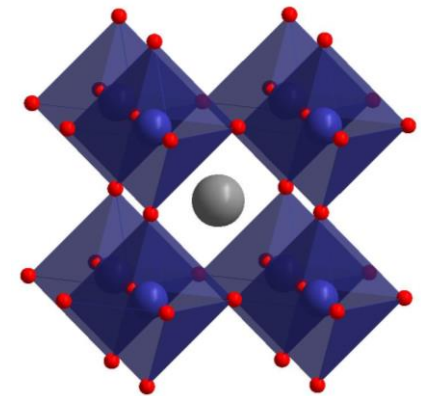
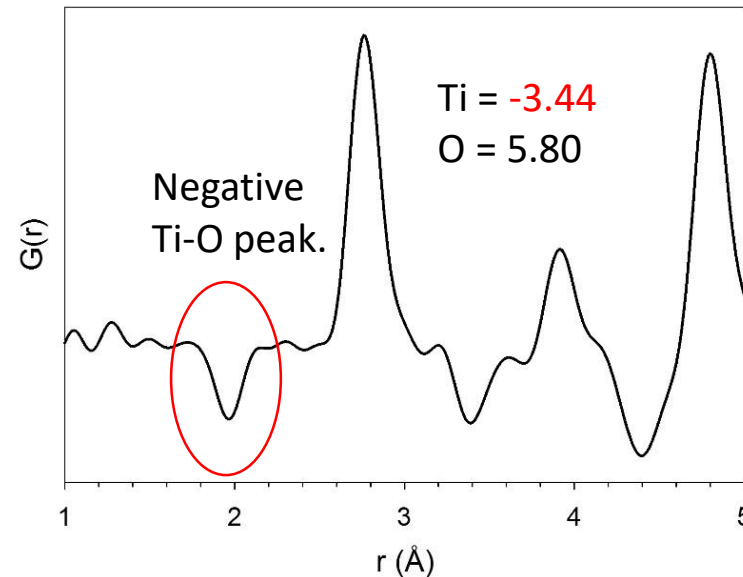


# Negative Scattering Length

When X-rays scatter there is always a phase shift. When neutrons scatter there is usually a phase shift, but for some elements there is not. This makes these waves have opposite phase (negative scattering length).

|             |            |
|-------------|------------|
| Mn<br>-3.73 | Fe<br>9.45 |
|-------------|------------|

This can lead to very strong contrast between some elements.



Pair distribution function and crystal structure of SrTiO<sub>3</sub>.

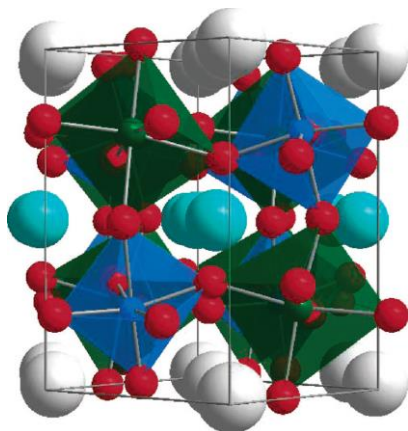
Can lead to negative peaks in a PDF.

# Main Advantages of Neutron Scattering Contrast

O  
5.80

W  
4.86

Locating light atoms in the presence of heavy atoms.

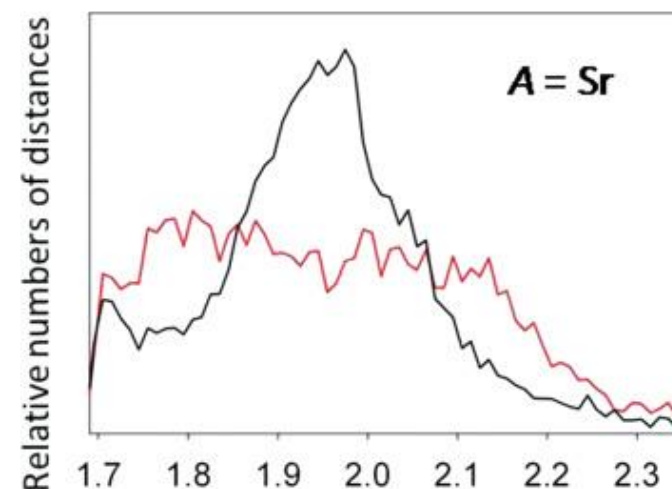


Neutrons were used to determine the tilting of the oxygen octahedra in NaLaMnWO<sub>6</sub> (left). Neutron PDF is able to separate out the local Mn-O and Ru-O bond lengths in AMn<sub>0.5</sub>Ru<sub>0.5</sub>O<sub>3</sub> (right).

Co  
2.49

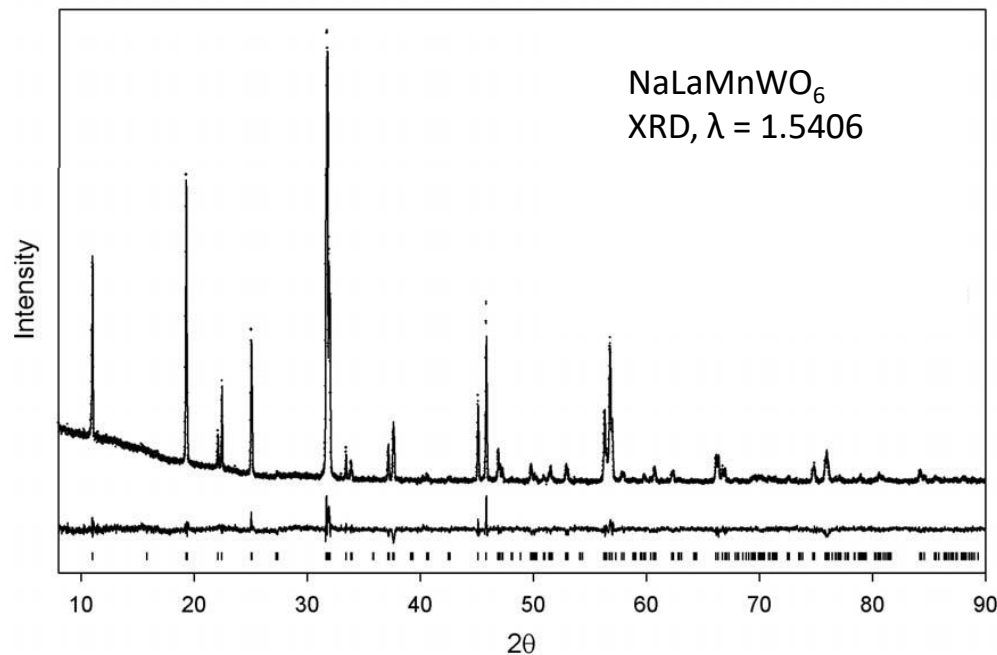
Ni  
10.3

Differentiating atoms with similar X-ray scattering.

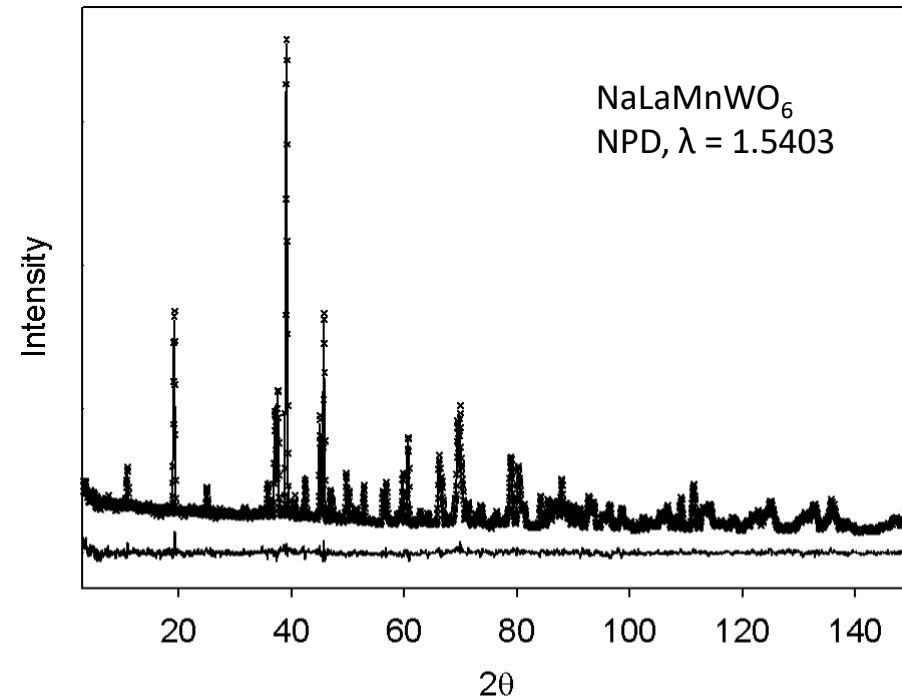


# No Form Factor

X-rays have a form factor due to destructive interference between electrons of the same atom. As the nucleus of an atom is very small compared to the distance between atoms neutrons have no form factor.



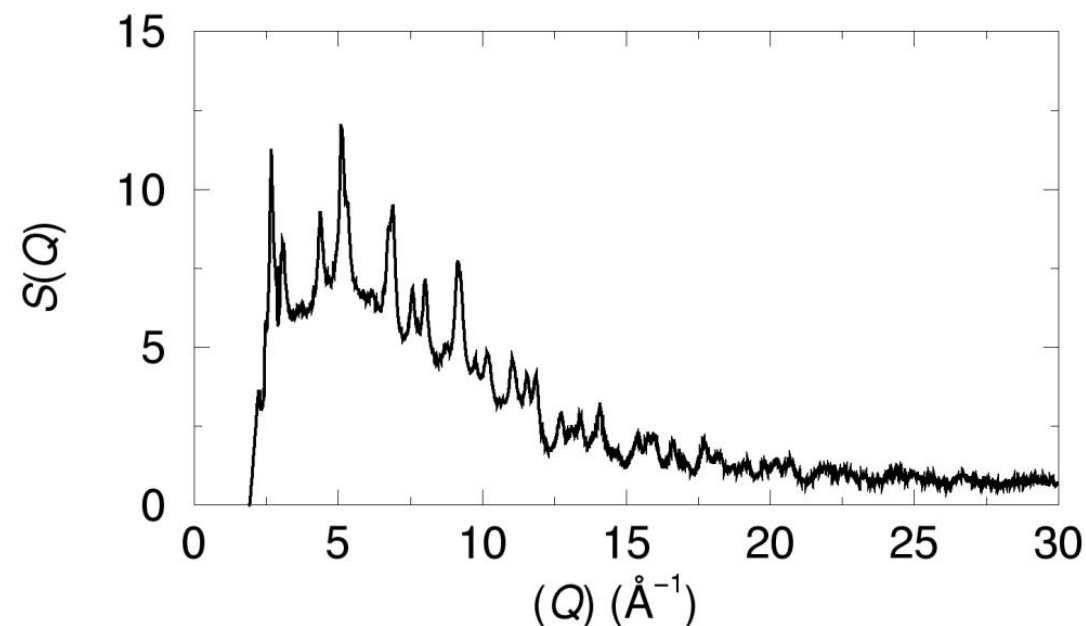
X-ray diffraction patterns fall off at high angle due to thermal motion and the form factor.



Neutron patterns have stronger intensity at high Q. Better for determining thermal parameters.

# Incoherent Scattering

- Occurs as a result of having different isotopes of an atom randomly distributed on a nucleus having multiple nuclear spin states.
- Contains no structural information.
- Adds background to diffraction patterns.
- Needs to be removed for PDF, no analytical way to do this but some ways to estimate and subtract.



# Absorption

Varies by many orders of magnitude between elements as well as among isotopes.  
No trends based on periodic table, as with other neutron properties there is no pattern.

## Some Elements with Large Neutron Absorptions (cross sections in barn):

- Gd (49,700), largest of all elements by far. 7 naturally occurring isotopes, absorption is huge for 2, large for 1, moderate for 1 and small for 3. Isotopic substitution is therefore possible but expensive.
- Sm (5,922)
- Eu (4,530)
- Cd (2,520), sometimes used in shielding
- Dy (994)
- B (767), boron compounds often used as shielding, absorption is due to  $^{10}\text{B}$  ( $\sigma = 3,835$ ; abundance 20%), pure  $^{11}\text{B}$  can be used ( $\sigma = 0.006$ ).
- Ir (425)
- Hg (372), can be used a liquid shutter
- In (194); Rh (145); Er (159)



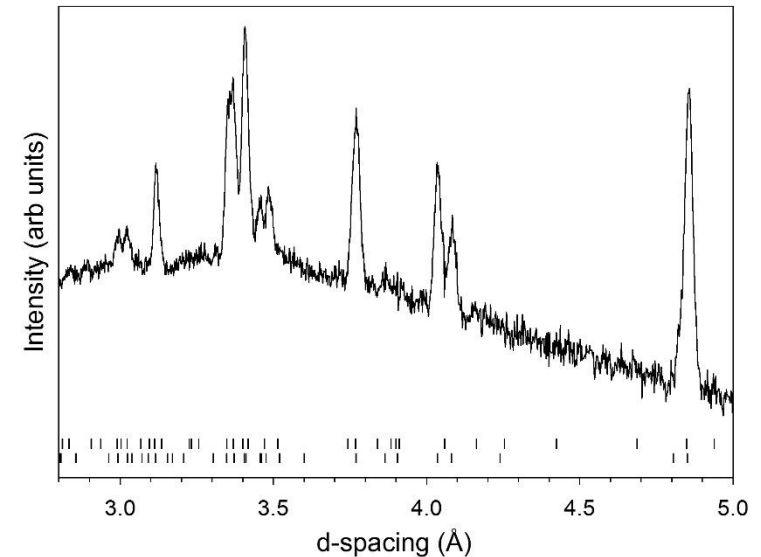
# Some Notes about Hydrogen

## Both good and bad for neutrons:

- Negative  $b$  of -3.74 fm means it can be easily detected in the presence of heavy elements.
- Large incoherent  $\sigma$  (82 barn) gives rise to large backgrounds.
- Deuterium ( $^2\text{H}$ ) has a  $b$  of 6.67 fm and incoherent  $\sigma$  of only 2.1 barn, samples are often deuterated to reduce incoherent noise.

Bond lengths involving H are longer when determined by neutrons than X-rays, as the center of electron density cannot be approximated as being at the nucleus.

Side note: In small angle scattering and reflectometry of soft matter involving two component with similar scattering density, one component can be deuterated while the other isn't to increase contrast.



Scattering from a sample containing hydrogen.

# Some Notes about Lithium

- Li positions are difficult to detect using X-ray diffraction, especially when heavier elements are present.
- The neutron  $b$  of Li (-1.90) has a small magnitude but the scattering is still closer in magnitude to most heavier metals than with X-rays. The negative sign also helps provide contrast.
- Li has a moderate absorption cross section of 70.5 barn.
- So neither X-rays nor neutrons are great for finding Li, although neutrons are usually better. Many neutron proposals are for studying Li ion conductors.
- The absorption of Li is mainly due to the  $^6\text{Li}$  isotope, which has a an absorption of 940 barn and a natural abundance of 7.5%. Pure  $^7\text{Li}$  can be used to reduce absorption.



# Some Notes about Oxygen

Neutrons are great for studying oxygen. It has a medium sized  $b$  of 5.803 and negligible incoherent  $\sigma$  and absorption. Many proposals are for accurately locating O positions in compounds with heavy metals.

|           |           |           |
|-----------|-----------|-----------|
| N<br>9.45 | O<br>5.80 | F<br>5.65 |
|-----------|-----------|-----------|

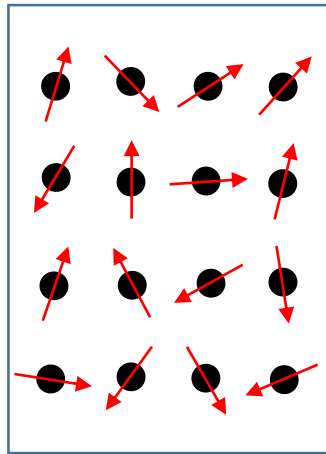
Neutrons are also great for finding N and F positions. In oxynitrides neutrons can easily differentiate between the O and N. For oxyfluorides neither X-rays nor neutrons can tell O and F apart with much accuracy, indirect assignments based on bond lengths are the only way.

# Magnetic Scattering

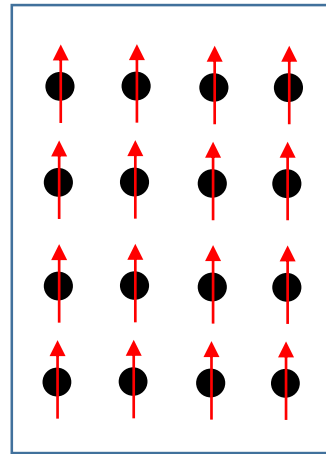
- Neutrons are spin  $\frac{1}{2}$  particles with a magnetic moment.
- While neutrons do not interact with the electrons through the Coulomb force, they do interact with unpaired electrons through the magnetic force.
- Magnetic scattering happens to be of a similar magnitude to nuclear scattering.
- As the unpaired electrons are in the outer shells, they are very diffuse. Therefore, magnetic scattering does have a form factor and peaks from magnetism fall off very rapidly with  $Q$ .
- Magnetic structure determination is a major use of neutron diffraction.

# What is a Magnetic Structure

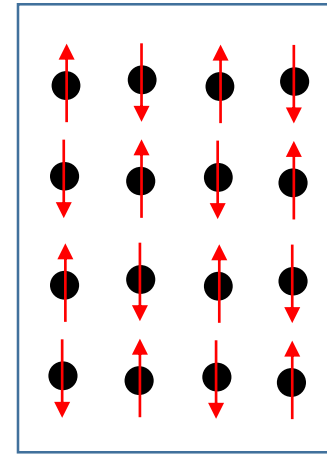
The magnetic moments of the unpaired electrons can crystallographically order.



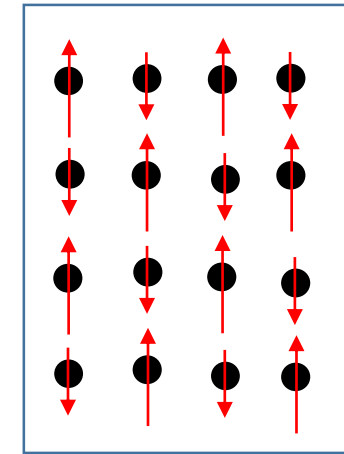
**Paramagnetic**  
Above a certain temperature the spins randomly fluctuate, no net moment without a field.



**Ferromagnetic**  
Spins all aligned in the same direction, strong net moment.

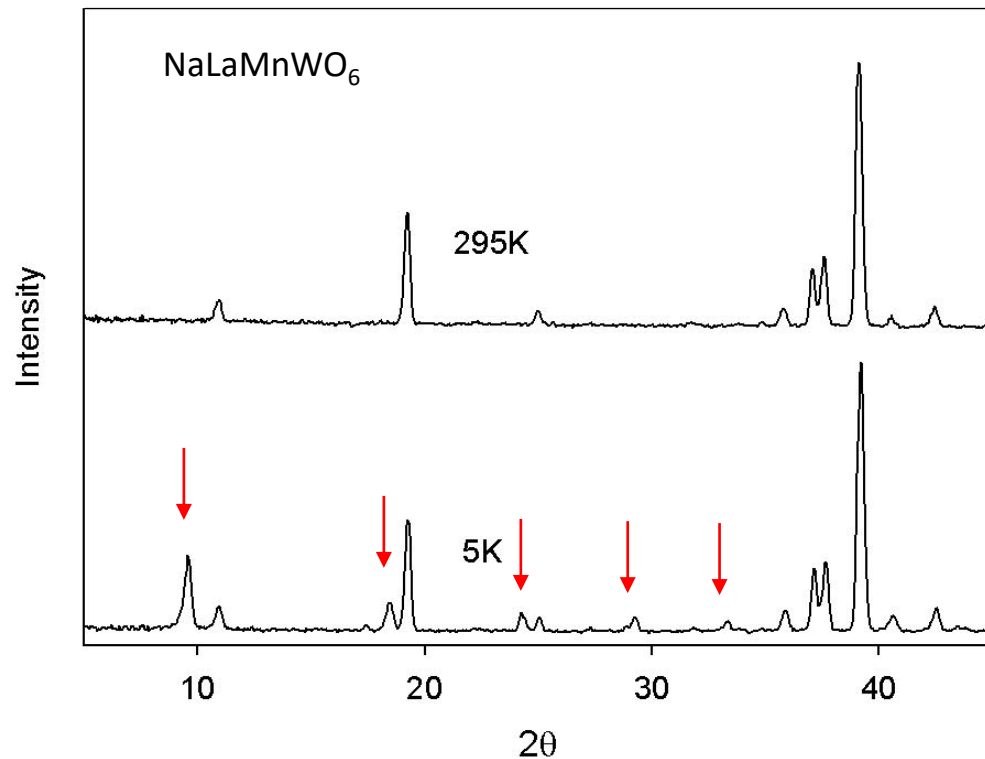


**Antiferromagnetic**  
Spins all aligned in the opposite direction, no net moment.



**Ferrimagnetic**  
Unequal spins aligned oppositely, net moment.

# Magnetic Structure Determination



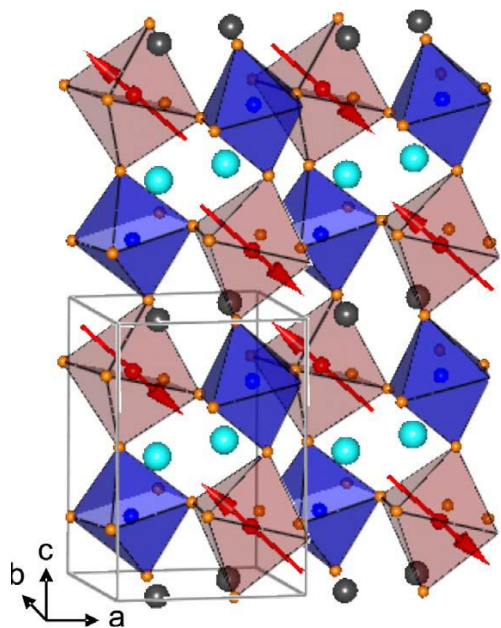
Collect diffraction patterns above and below the magnetic ordering temperature.

- Index relative to the nuclear unit cell using a propagation vector.
- This pattern is indexed with  $k = \frac{1}{2} 0 \frac{1}{2}$
- In other words, the magnetic unit cell is  $2 \times 1 \times 2$  the size of the nuclear unit cell.
- Propagation vectors can be incommensurate.
- Rietveld refinements used to solve magnetic structure.

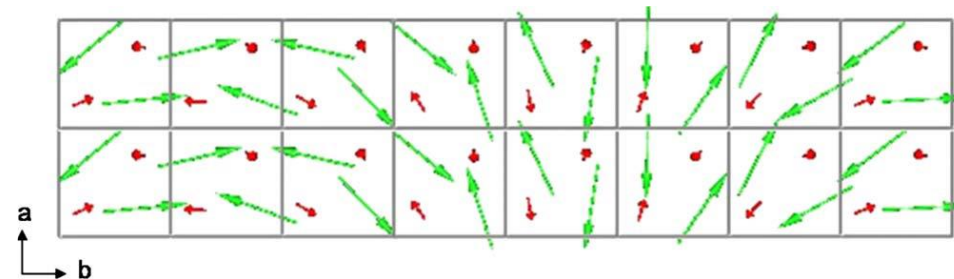
# Types of Magnetic Structures

Many types of magnetic structures are possible:

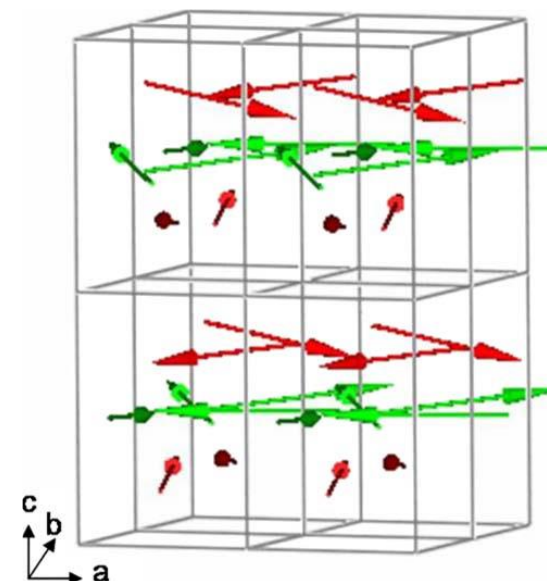
- Commensurate and incommensurate
- Collinear, non-collinear, spiral, conical



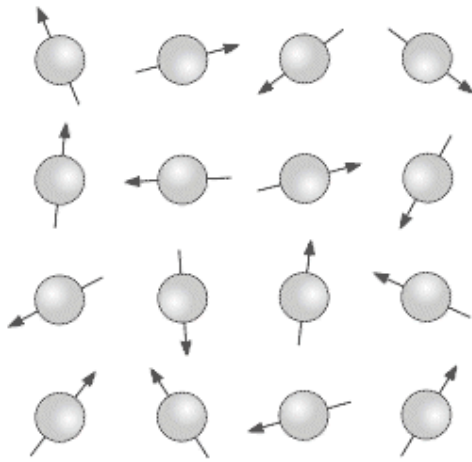
The AFM  $k = \frac{1}{2} 0 \frac{1}{2}$  commensurate and collinear structure of NaLaMnWO<sub>6</sub>. Red arrows are the moments on Mn<sup>2+</sup>.



The AFM structure of NaTbMnWO<sub>6</sub>, showing an incommensurate spiral. Red arrows are Mn<sup>2+</sup> moments and green arrows are Tb<sup>3+</sup> moments.



# Short Range Magnetic Order



Magnetic pair distribution function is an emerging technique to study short range correlations in spin glasses, spin liquids, and other exotic phases.

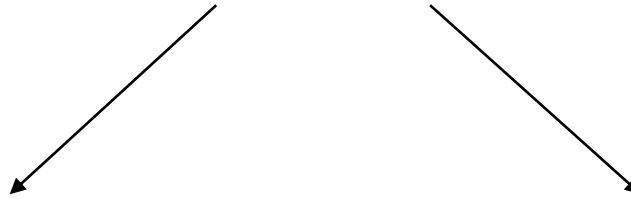
Magnetic PDF is obtained by subtracting the nuclear PDF from a sample to get the contribution from diffuse magnetic scattering.

It's important to keep in mind that even if you are not interested in magnetism but you have unpaired electrons, magnetic scattering will be present and a source of error.



# Overview of Neutron Sources

## Two Main Types



### Reactor:

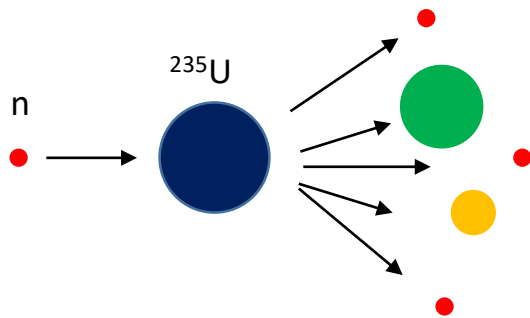
- Based on fission of radioactive elements (U), similar to a nuclear power plant.
- Usually used for monochromatic beams.

### Spallation:

- Uses proton beams to blast apart heavy elements.
- Usually used for pulsed beams (time-of-flight).



# Reactor Sources



- Neutrons are produced by controlled fission of enriched uranium fuel.
- When a U atoms decays several neutrons are released. Some of these trigger new nuclear decays while other escape down flight tubes to be used for experiments.
- Similar to a nuclear power plant but the goal is neutron production instead of heat production.
- Beryllium reflectors used inside.
- Reactors produce a **steady supply of neutrons**.





# Reactor Powder Diffractometers

- Generally similar to synchrotron beamlines.
- A large single crystal monochromator is used to select a single wavelength.
- The diffraction pattern is then collected as a function of angle.
- Often many detectors are used in an array to speed data collection as the flux is much smaller than for X-rays.



The BT-1 diffractometer at the NIST NCNR. It has 32 detectors that only need to rotate 5 degrees.



# Spallation Sources

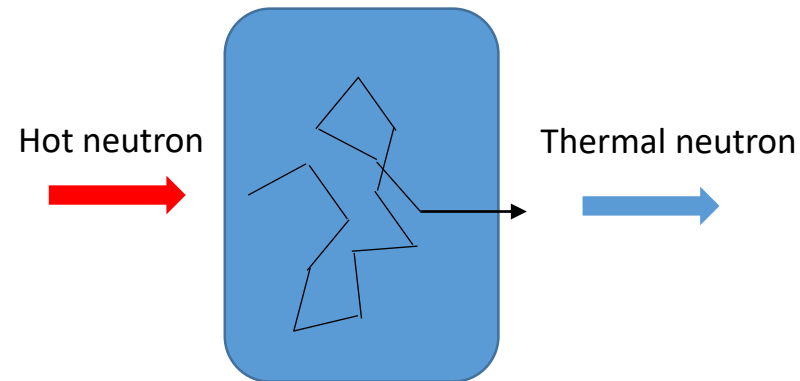
- Spallation is a process by which a heavy nucleus is blasted into pieces after being hit by another particle.
- Spallation neutron sources use pulsed proton beams.
- The protons are created by stripping the electrons off hydrogen, accelerating them to near the speed of light in a linear accelerator, then smashing them into a target.
- The target is often W but could be other heavy metals. Hg is used in some newer facilities for easier cooling.
- The heavy nucleus breaks into two smaller nuclei and also releases many free neutrons.
- This creates pulses of neutrons, usually at rates of 10's of hertz.\*
- All new facilities being built are spallation.



The linear accelerator at LANSCE,  
Los Alamos National Lab.

# Moderators

Neutrons produced by fission or spallation are very high energy (MeV). To be useful for diffraction they need to be slowed down (meV).



- This is done by having the neutrons collide with nuclei to give up their energy.
- **The temperature of the moderator determines the spectrum of neutron energies exiting.**
- For diffraction room temperature neutrons have the right wavelength range.
- Materials with lots of H are usually used. Often just water, sometime liquid methane or liquid H<sub>2</sub>.
- Some neutrons don't fully thermally equilibrate. These epithermal neutrons are important for the high Q-range of spallation source.

# Time-of-Flight (TOF) Diffraction

In TOF the angle is fixed and the wavelength is varied.

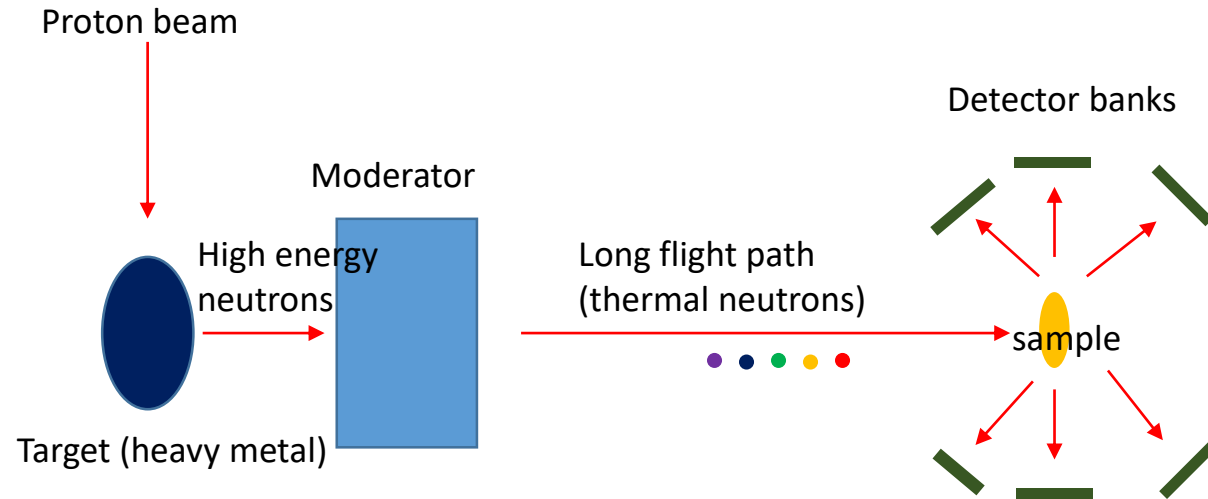
$$\longrightarrow \lambda = 2d\sin(\theta) \longleftarrow$$

Normally the wavelength is fixed and the angle is varied to get d.

- As neutrons are particles with mass, their speed varies with their energy/wavelength.
- At a spallation source, pulses of neutrons with a spectrum of wavelengths are produced. The time it takes them to reach the detector is recorded. Diffraction occurs when they have the right wavelength to satisfy Bragg's law.
- A plot of diffraction intensity vs. time is recorded, which can be converted into d-spacing.
- Detectors are placed at fixed angles. Several different angles can be used. These different detector banks each record their own diffraction pattern. Depending on the angle the patterns have different d-spacing coverage and resolution.
- While TOF is normally done at spallation sources, it can be done at a reactor source by placing a chopper in the beam to create pulses.



# Time-of-Flight Instruments



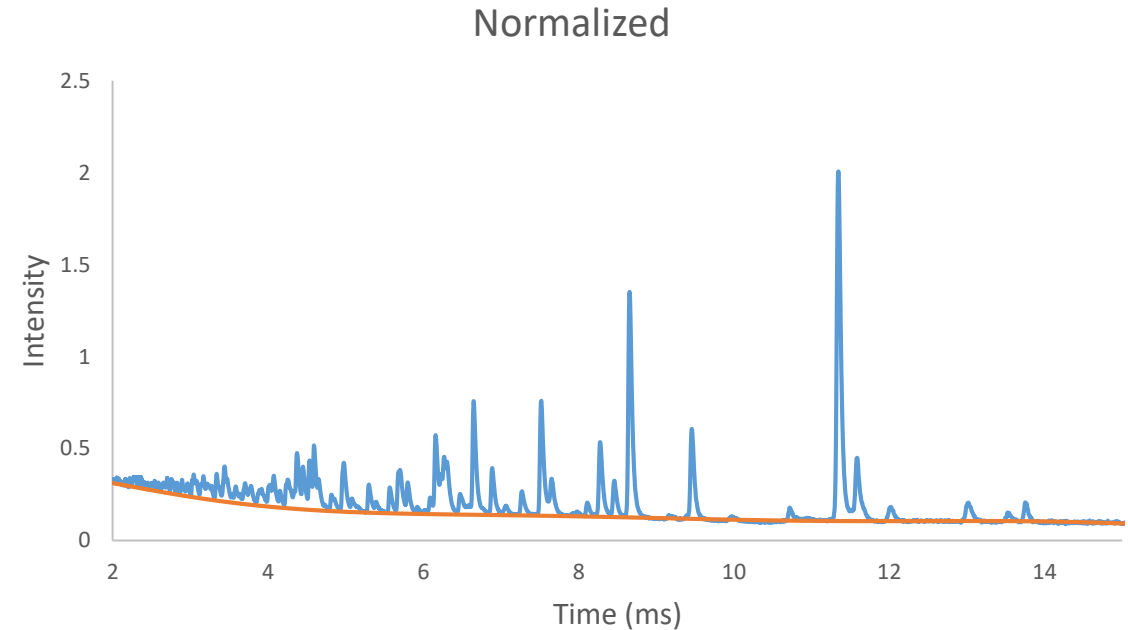
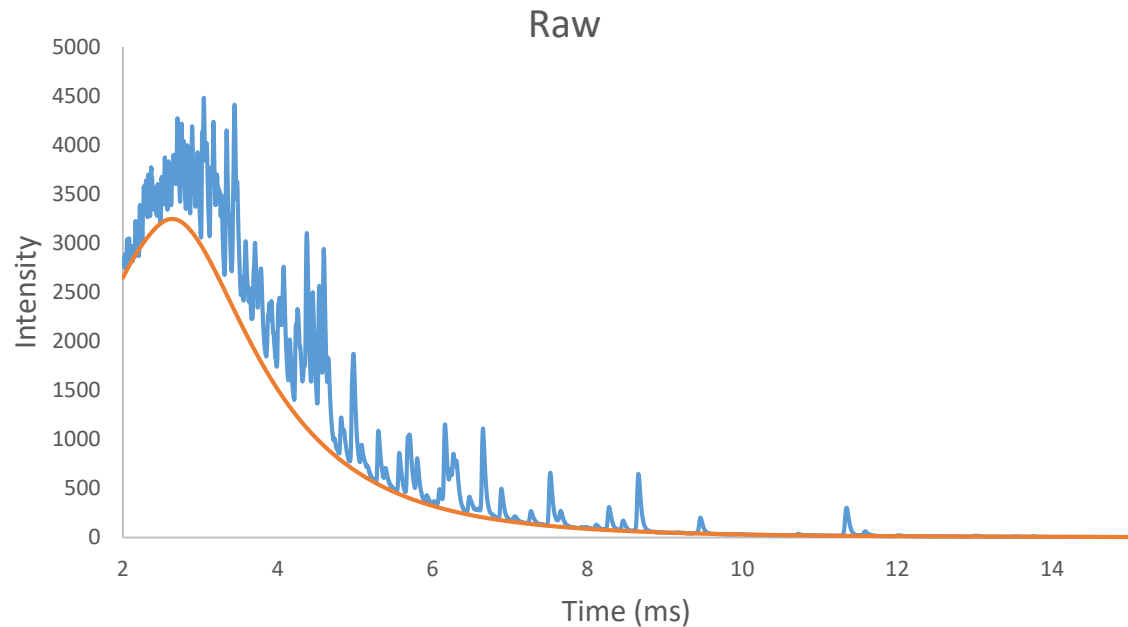
A few other notes:

- Beamlines sometimes have chopper that is closed at  $t_0$  to protect detectors from gamma rays and fast neutrons.
- A trigger measures the  $t_0$  when the proton pulse arrives.
- A “get lost tube” at the end absorbs the un-scattered beam.

## Intensity vs. Resolution

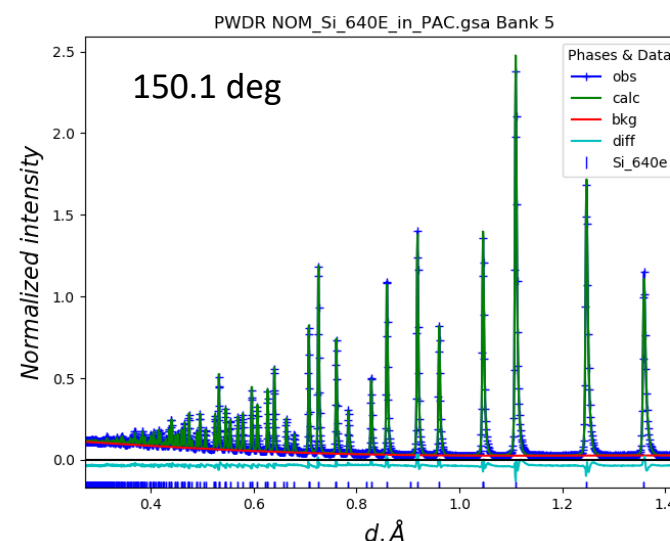
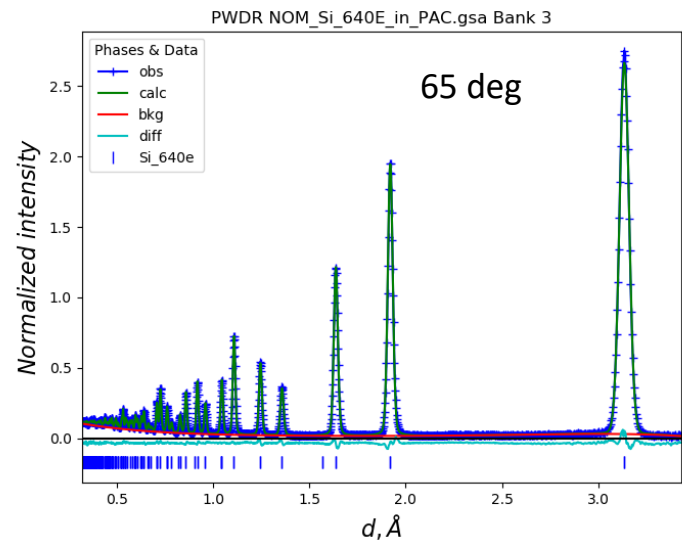
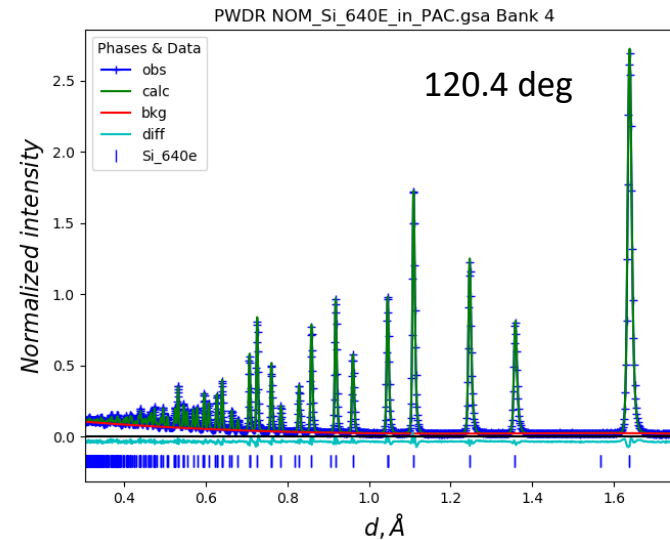
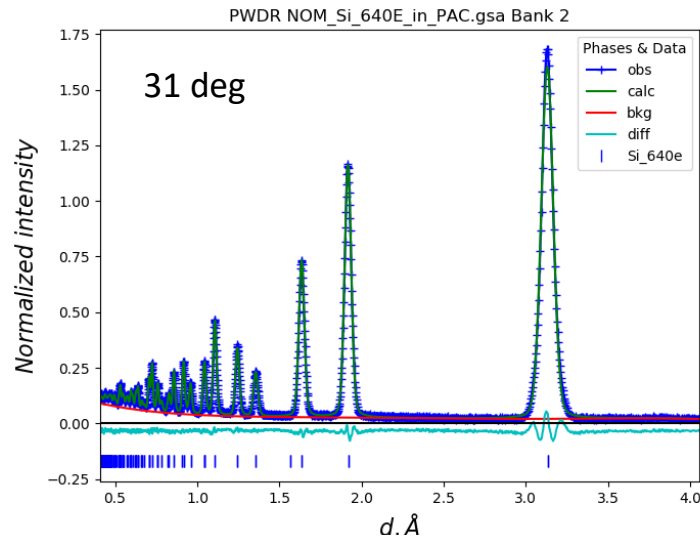
- Is determined by the flight path length.
- The longer the path the more time the neutrons have to sort themselves by energy, so the better the resolution.
- The intensity falls off as  $1/r^2$ , so the closer the better the flux.
- It is important to keep in mind that as neutrons have no charge, they cannot be steered by magnetic fields. They also cannot be easily focused by lenses.
- Neutron guide materials based on refraction do exist to help keep flux on long beamlines, but these are mostly used for longer wavelength neutrons.

# Time-of-Flight Data



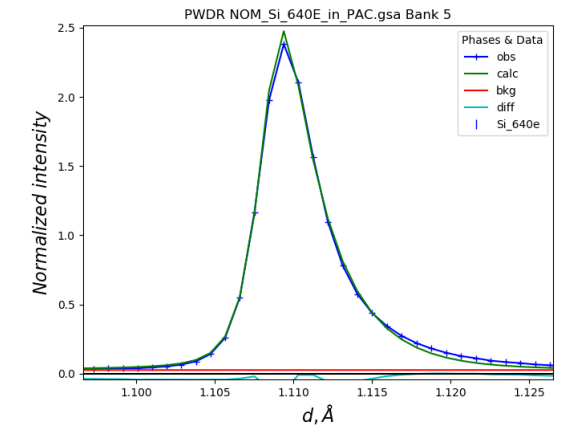
The distribution of energies in a neutron pulse is not uniform. Patterns usually divided by incident flux. Keep in mind that the high d-spacing region of each bank has lower counting statistics than the small d-spacing region. Incident flux is determined by measuring vanadium, which has a small coherent  $b$  of  $-0.38$  fm but a moderate incoherent  $\sigma$  of 5.08 barn.

# Detector Banks in TOF



Low angle banks cover a large range of high d-spacing with low resolution.

High angle banks cover small range of low d-spacing with high resolution.



TOF peaks have an odd and complex shape.



# Practical Aspects of Conducting a Neutron Experiment

Neutrons are very penetrating: **Everything is bigger with neutrons.**

- Neutron beams cannot be focused and must be large (mm scale). Sample sizes of a few grams are often preferred, a few hundred mg can be used. Much more sample is needed than for X-rays.
- Samples are often contained in a V can, as V has very weak coherent scattering.
- Collection times are usually several minutes to several hours, much longer than for X-rays.
- Many samples will become radioactive. You can't get them back right away. If some elements, such as Co, are present you will never get them back.





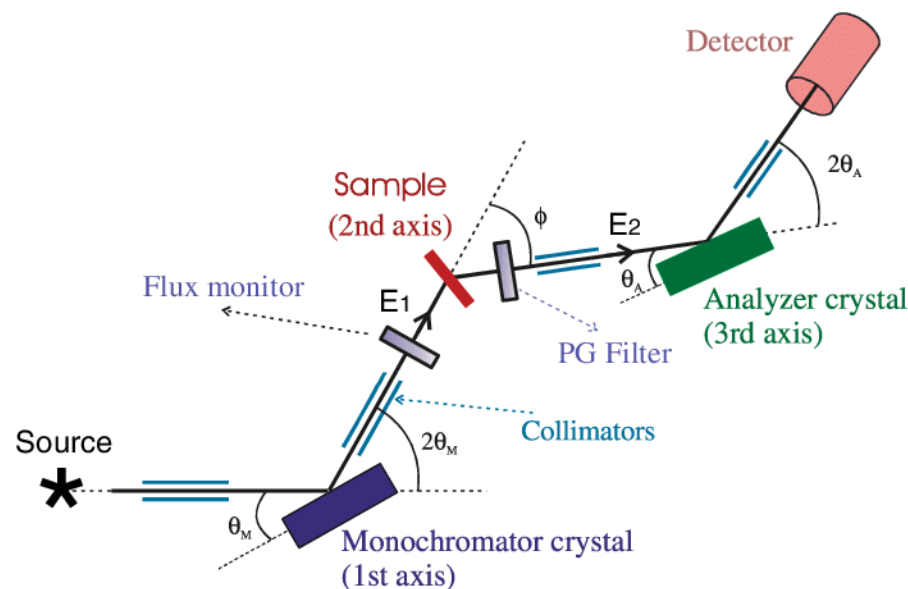
# Inelastic Neutron Scattering

Neutrons are great as they can probe the structure AND dynamics of matter. They can tell you where the atoms are and what they are doing.

Thermal neutron energies are comparable to lattice vibrations. Phonons are typically a few tenths of a percent to a few percent of the neutron energy. X-rays are much higher energy and require much greater energy resolution for inelastic experiments. Phonons, magnons, and other excitations can be measured.

$$S(Q, \omega)$$

The dynamic structure factor can be measured and contains all the information about the system. This is a sort of master function of condensed matter physics.



## Triple Axis Spectrometer

Uses monochromatic radiation, then a second analyzer crystal to determine energy transfer. Slow measurement but gives much information.

# Neutron User Facilities

## USA

NIST NCNR: reactor source

Oak Ridge has 2 neutrons sources:

HFIR is a high flux reactor

SNS is a high power spallation



SNS at Oak Ridge

## Europe

ISIS spallation source in England

ILL reactor source in France

European Spallation Source (ESS): under construction, will be the most powerful source, user program begins in 2023.

## Japan

J-PARC spallation source

Note: This list is not comprehensive. These were selected as they are probably the most relevant to Canadian researchers.

# Take Home Messages

- Neutrons interact weakly with matter and are very penetrating. Neutron flux is also much lower than at X-ray sources.
- Neutrons scattering varies randomly with Z.
- Neutrons can often locate light atoms in the presence of heavy ones.
- Neutrons can often distinguish neighboring elements.
- Neutrons can be used to solve magnetic structures.