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Neutron Diffraction: a general overview

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Outline

- Elastic scattering of neutrons from matter
- Comparison of neutron and X-ray diffraction for crystallography
- Neutron diffraction for probing magnetism
- Neutron diffraction facilities
- Larmor diffraction

Properties of neutrons

Particle-like properties:

- Mass = 1.68×10^{-27} kg (photon mass = zero)
- Charge = zero (photon charge = zero)
- Spin = ½ (photon spin = 1)
- Magnetic dipole moment = -9.66×10^{-27} JT^{-1} (photon moment zero)

$$E = \frac{1}{2} m_n v^2 = k_B T$$

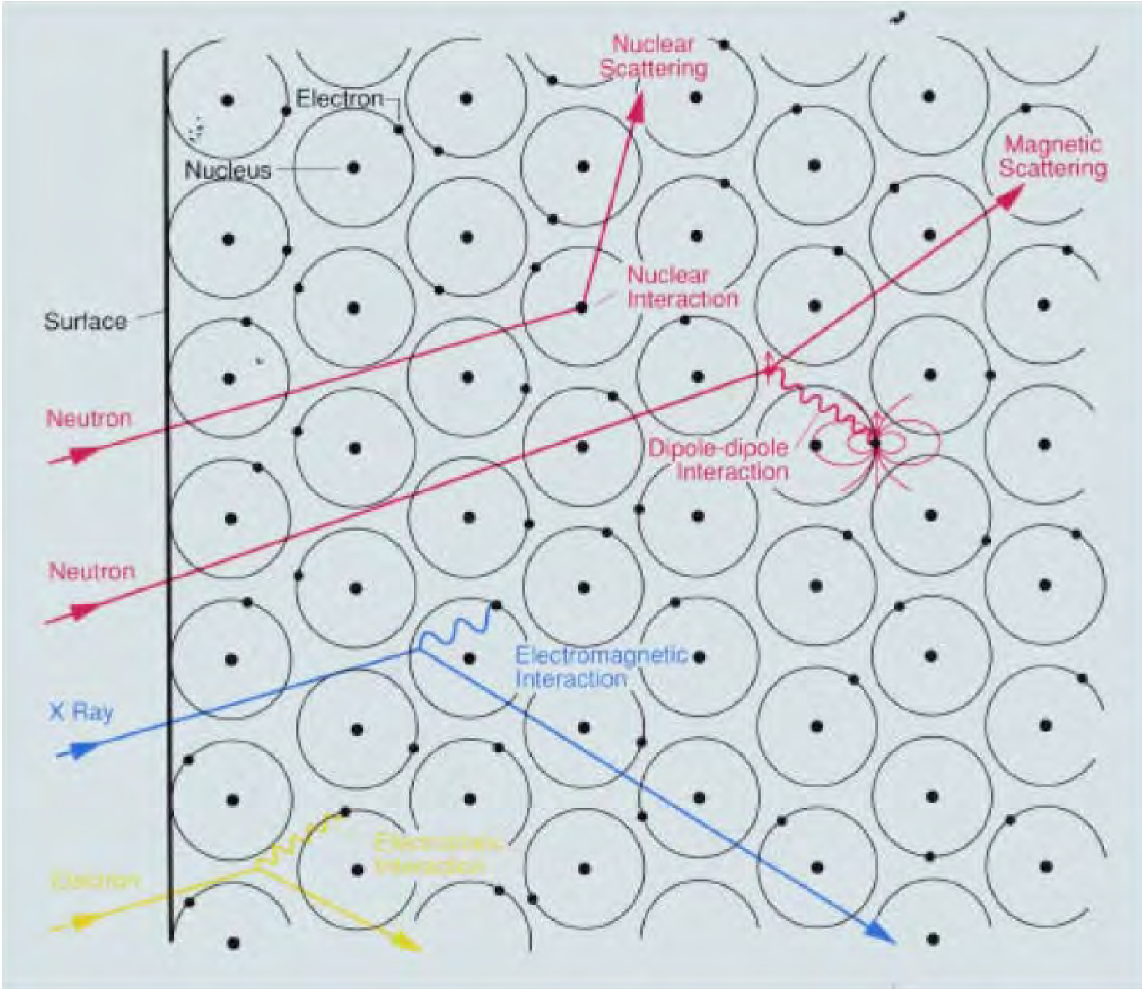
Wave-like properties:

$$\lambda = \frac{h}{m_n v}$$

Neutron type	Energy (meV)	Temperature (K)	Wavelength (Å)
"Cold"	0.1 – 10	1 – 120	4 - 30
"Thermal"	5 – 100	60 – 1000	1 – 4
"Hot"	100 – 500	1000 – 6000	0.4 – 1

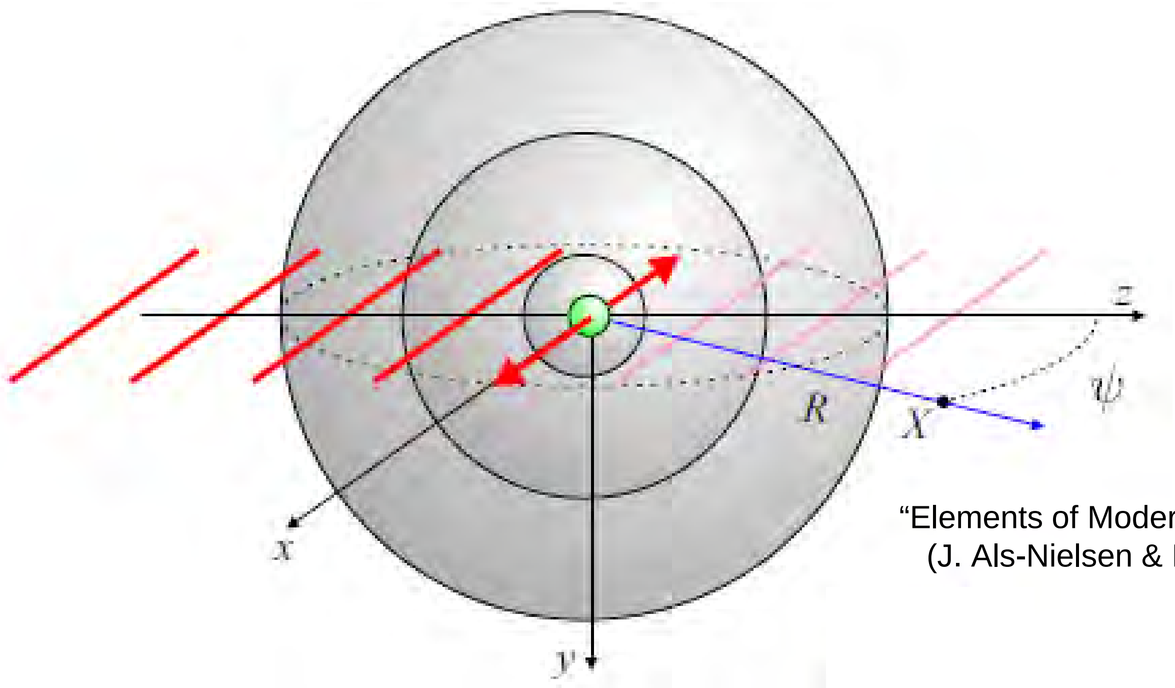
- For diffraction experiments thermal neutrons are used. Velocity is of the order of ~2000 ms^{-1} for "room temperature" neutrons (photons 3×10^8 ms^{-1}).

Interactions of neutrons and X-rays with matter



www.ncnr.nist.gov

Elastic scattering of X-rays from electrons



"Elements of Modern Xray Physics"
(J. Als-Nielsen & D. McMorrow)

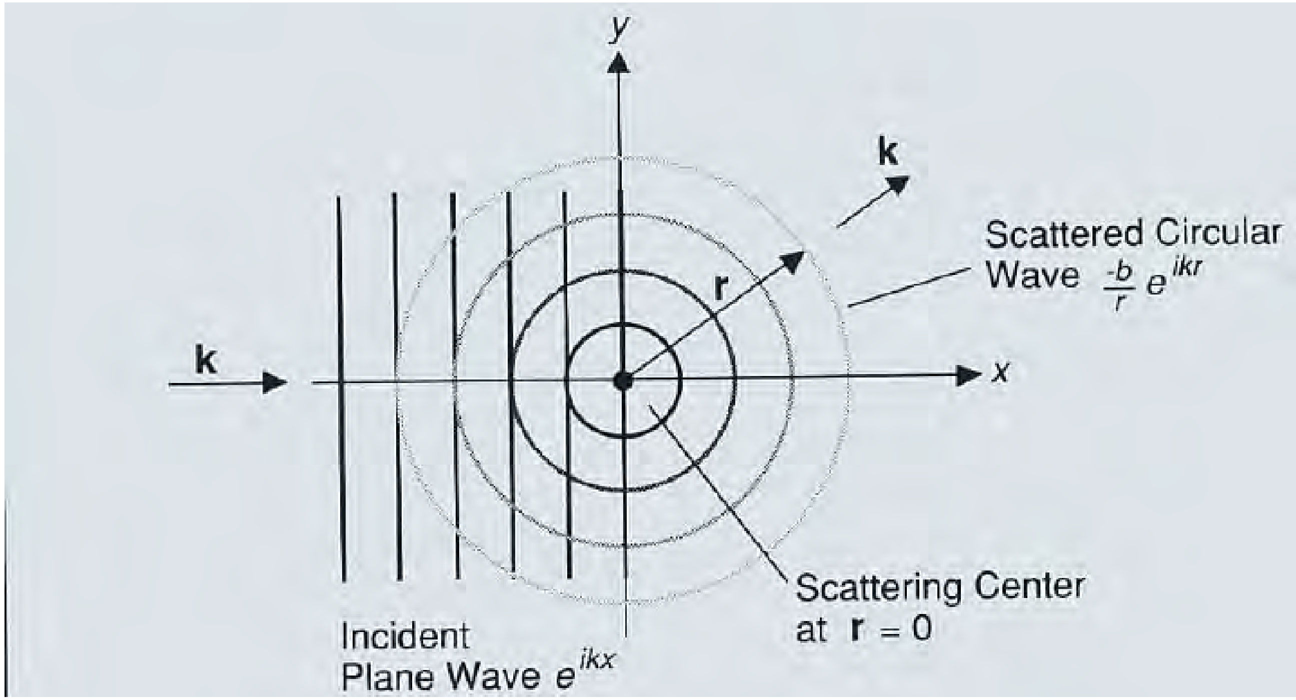
Ratio of radiated electric field magnitude to incident electric field magnitude is:

$$\frac{\mathbf{E}_{\mathbf{rad}}(R,t)}{\mathbf{E}_{\mathbf{in}}} = -\left(\frac{e^2}{4\pi\varepsilon_0 mc^2}\right)\frac{\mathrm{e}^{ikR}}{R}\cos\psi$$

Thomson scattering length $r_0 = 2.82 \times 10^{-5}$ Å
(the "ability" of an electron to scatter X-rays)

Minus sign indicates that incident and radiated fields are 180° out of phase

Elastic scattering of neutrons from nuclei



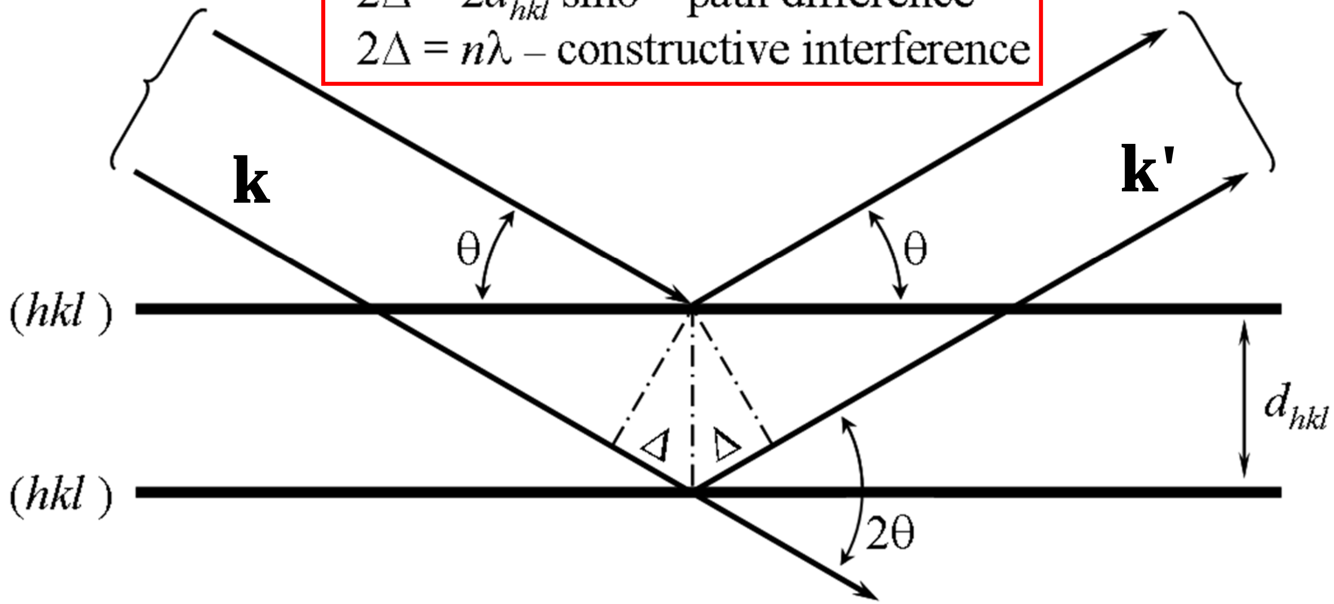
www.ncnr.nist.gov

•Neutron-nucleus interaction involves very short-range forces (on the order of 10^{-15} m). A metastable nucleus + neutron state is formed which then decays, re-emitting the neutron as a spherical wave with a phase change of 180°

•Radius of nucleus is ~10^{-17} m – much smaller than wavelength of thermal neutrons (10^{-10} m), thus can be considered "point-like"

Basics of diffraction

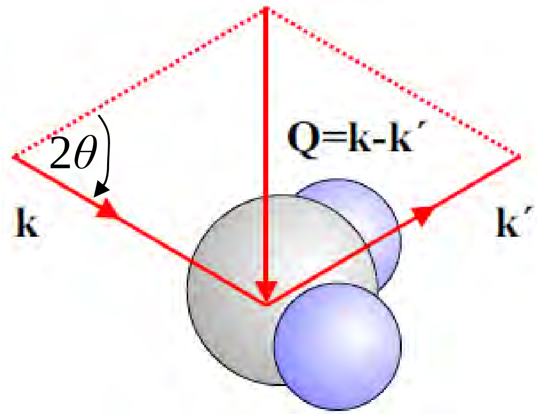
θ, 2θ – Bragg angles
$2\Delta = 2d_{hkl}\sin\theta$ – path difference
$2\Delta = n\lambda$ – constructive interference

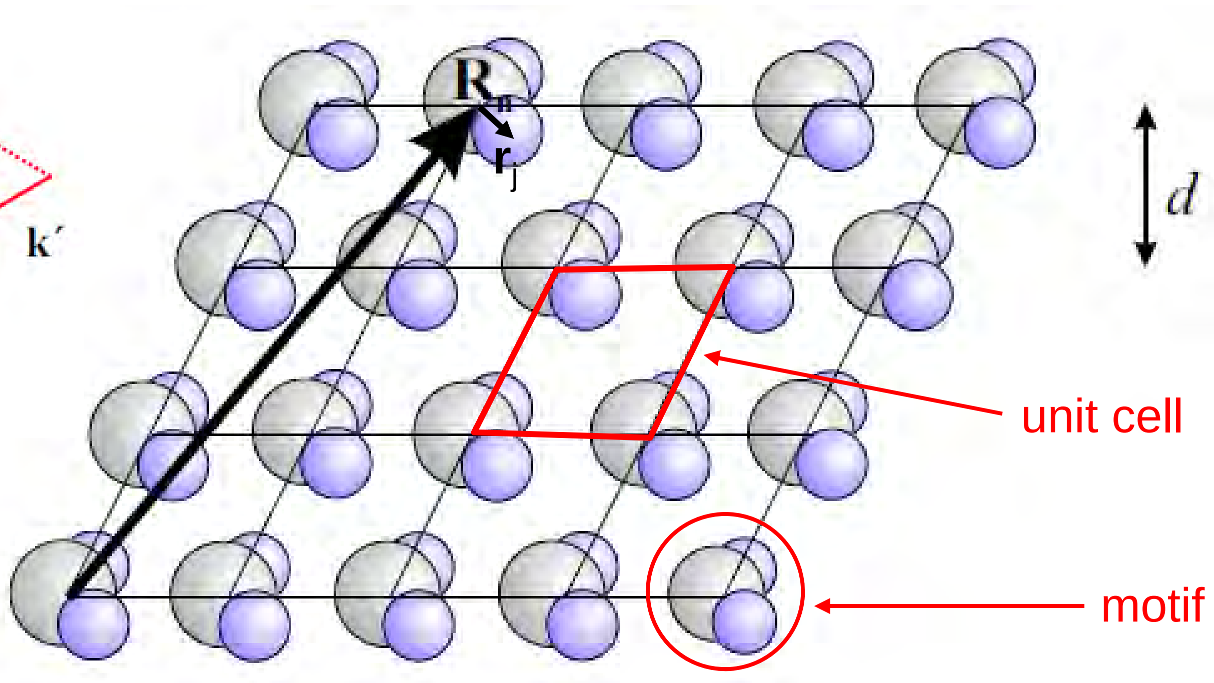


Bragg's Law:

$$n\lambda = 2d_{hkl}\,\mathbf{sin}\,\theta$$

Basics of diffraction





“Elements of Modern Xray Physics”
(J. Als-Nielsen & D. McMorrow)

Scattering amplitude for crystal:

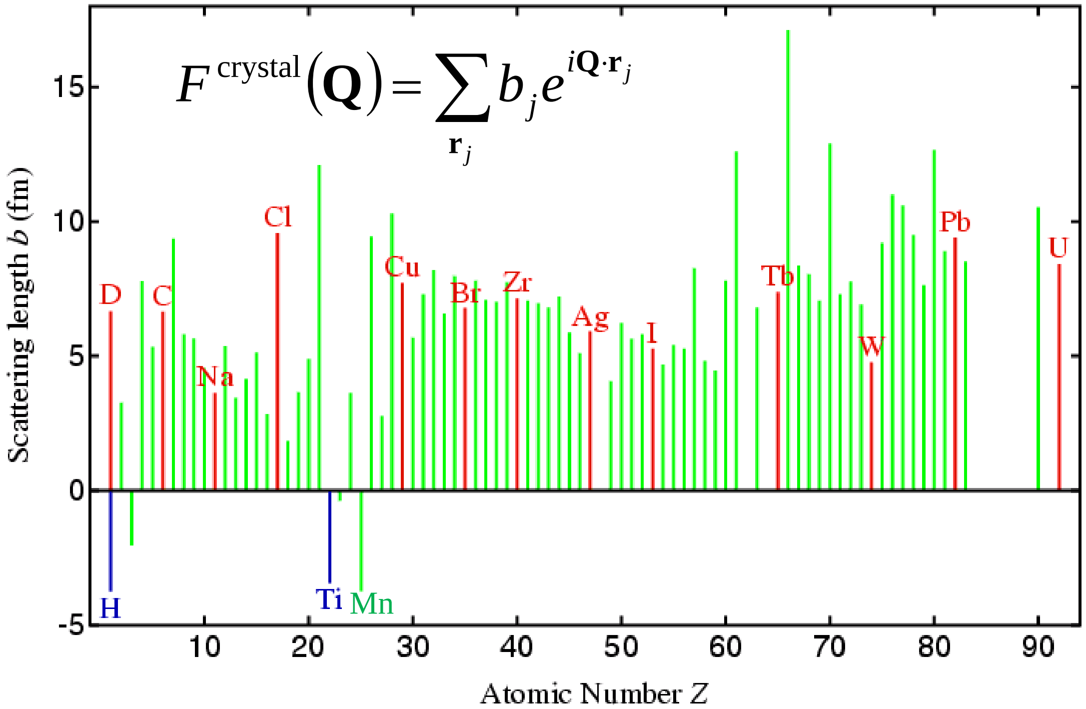
atomic form factor = number of electrons (X-rays)
nuclear scattering length (neutrons)

$$F^{\text{crystal}}(\mathbf{Q}) = \underbrace{\sum_{\mathbf{r}_j} f_j e^{i\mathbf{Q}\cdot\mathbf{r}_j}}_{\text{unit cell structure factor}} \underbrace{\sum_{\mathbf{R}_n} e^{i\mathbf{Q}\cdot\mathbf{R}_n}}_{\text{lattice sum}}$$

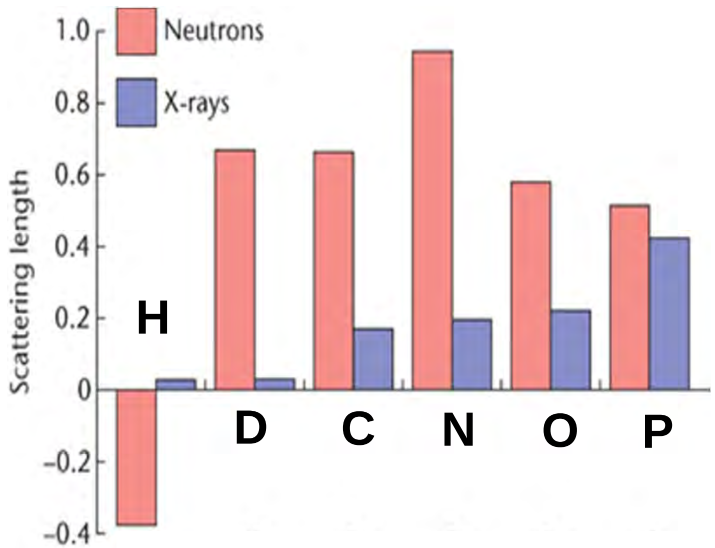
integer multiple of 2π when Bragg’s law is satisfied

unit cell structure factor **lattice sum**

Neutron v X-ray diffraction: atomic number



[http://pd.chem.ucl.ac.uk/pdnn/inst3/neutrons.htm]



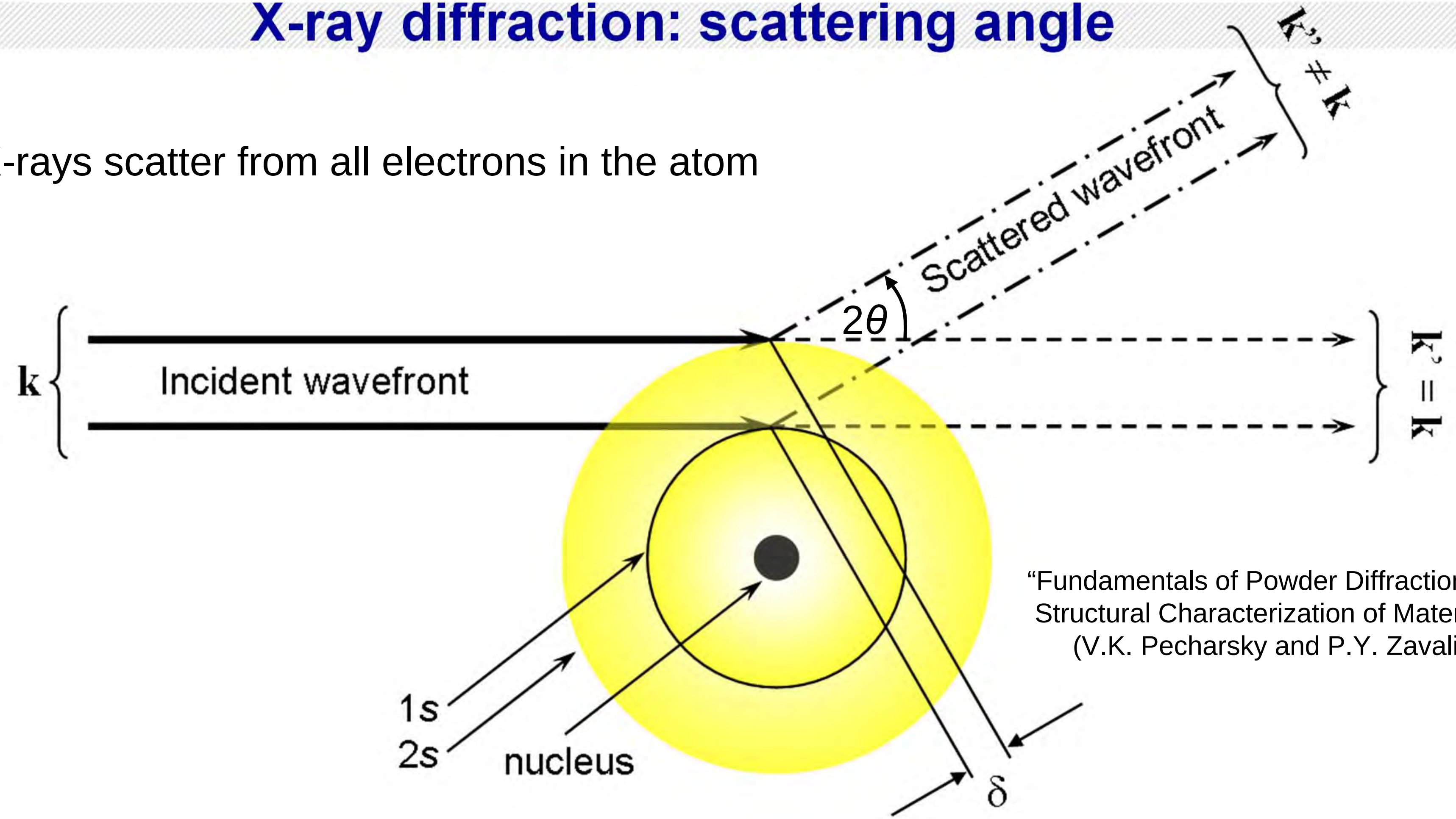
[J.P. Bradshaw, Neutron Diffraction, eLS, Wiley (2010)]

•For neutrons there is no systematic trend in scattering length with atomic number- it depends on the nucleus (isotope, nuclear spin). Scattering length is negative for some nuclei!

•Adjacent atoms in the periodic table often have very different neutron scattering lengths, allowing them to be distinguished easily.

X-ray diffraction: scattering angle

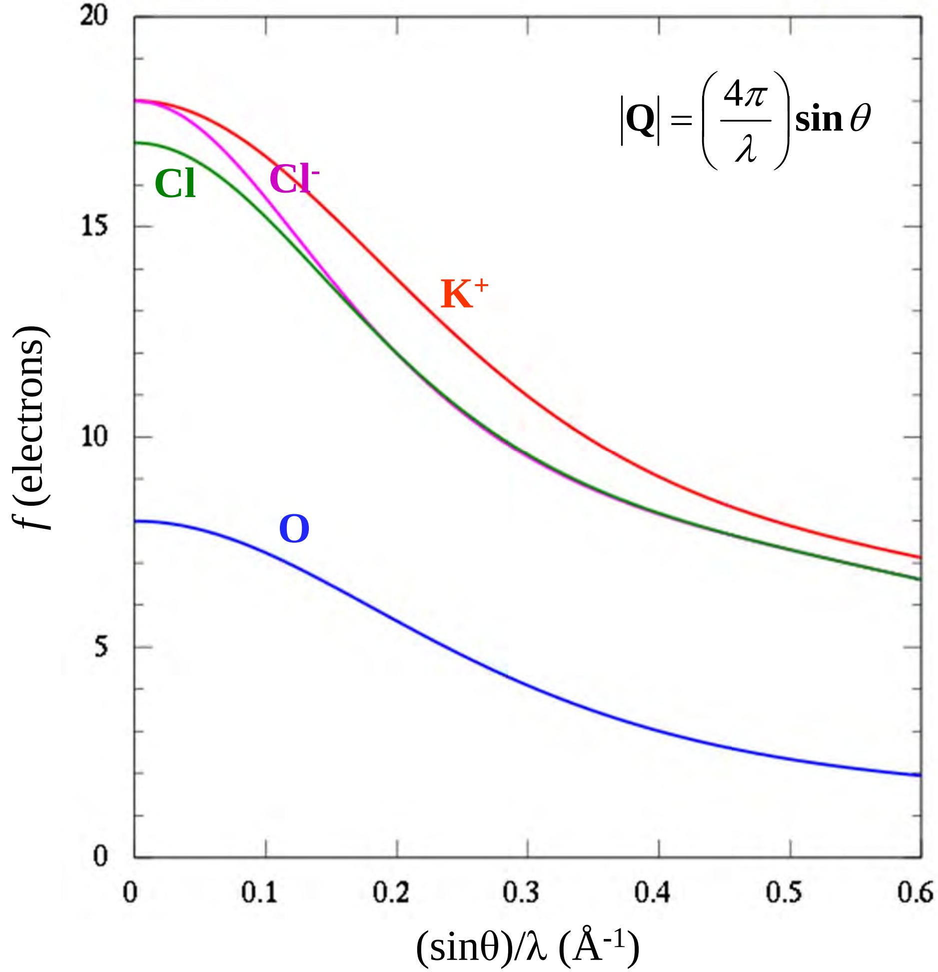
•X-rays scatter from all electrons in the atom



"Fundamentals of Powder Diffraction and Structural Characterization of Materials" (V.K. Pecharsky and P.Y. Zavalij)

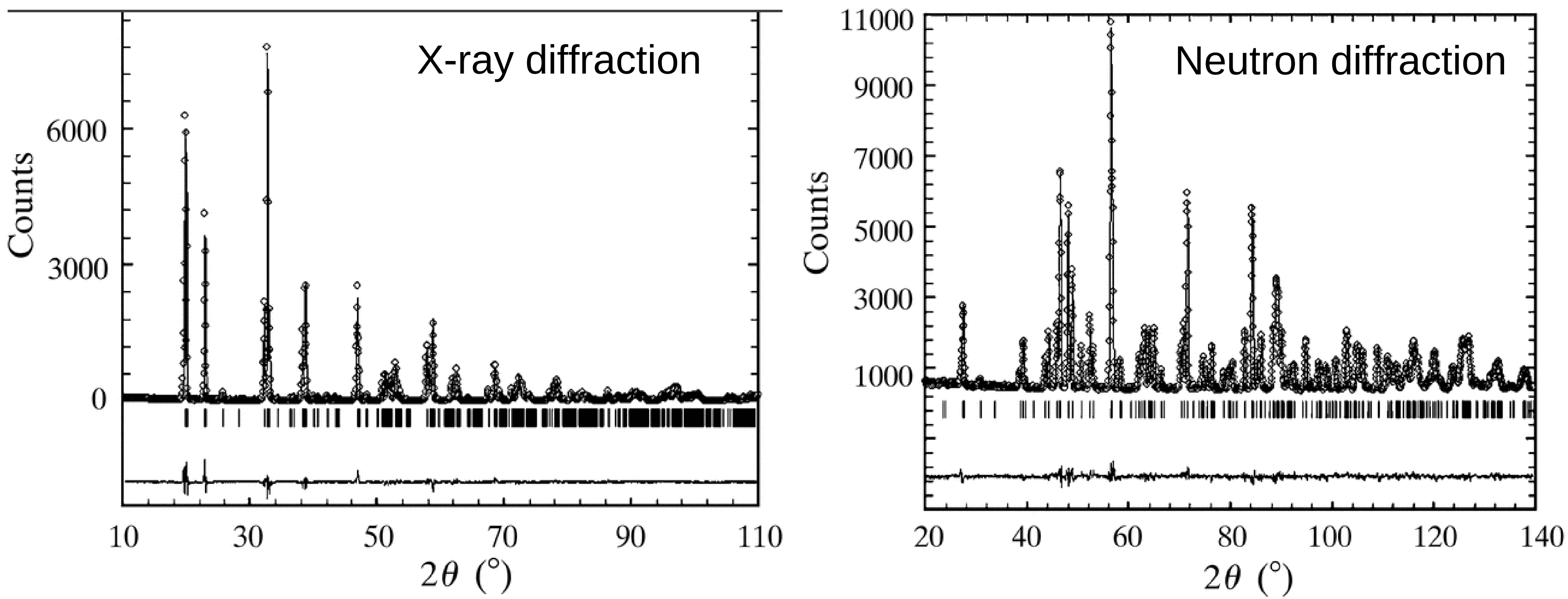
•For any scattering angle $2\theta > 0$ the electron cloud introduces a path difference δ, which leads to more destructive interference with increasing 2θ. The size of δ is significant because the size of an atom is comparable to the X-ray wavelength.

X-ray diffraction: scattering angle



- X-ray atomic form factor *f* (**Q**) depends on both *θ* and *λ*.
- Diffraction is stronger at smaller angles.

Neutron v X-ray diffraction: scattering angle

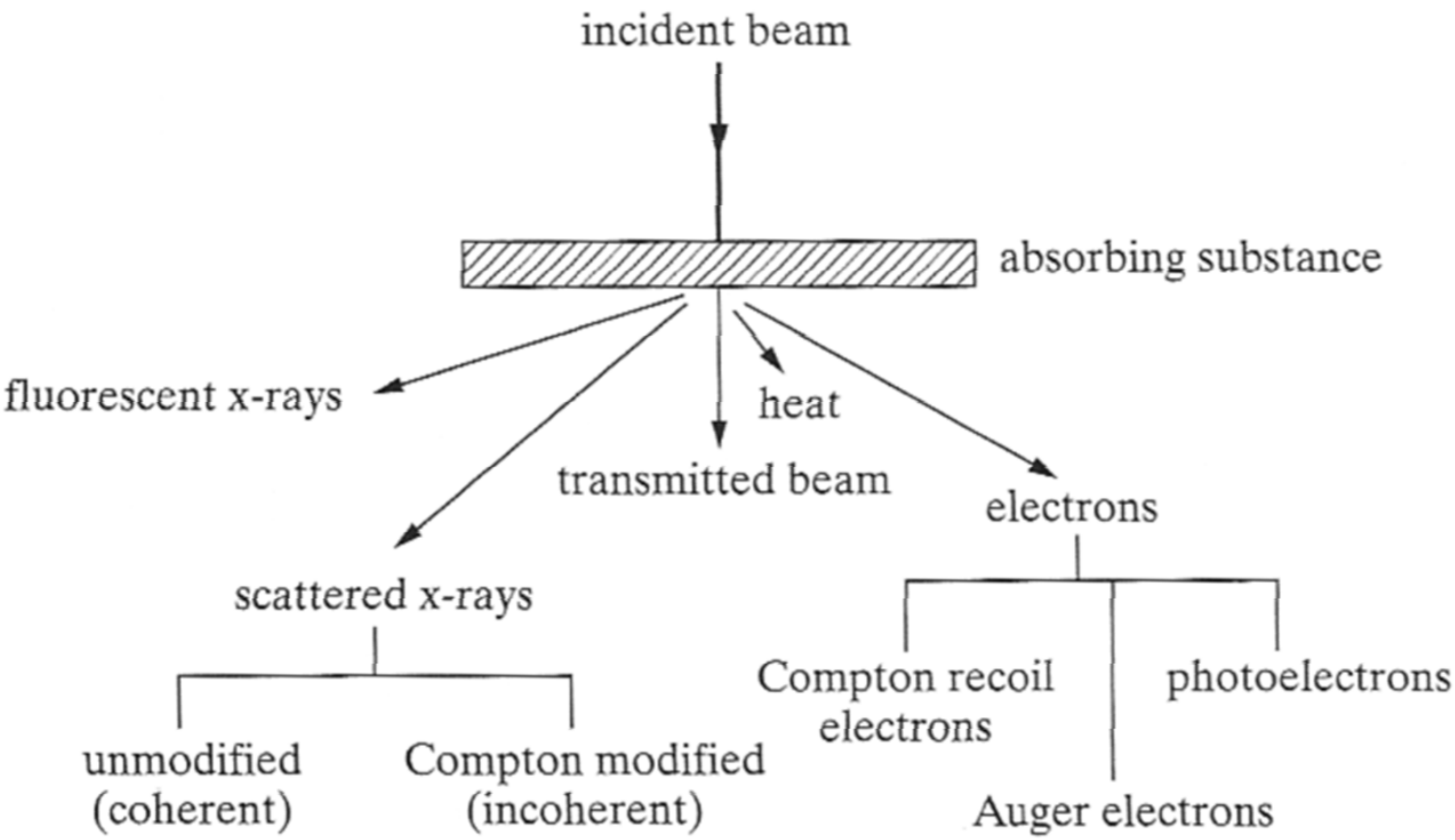


Ca_2MgWO_6 [J.H. Yang et al., Acta Crystallogr. C59, i86 (2003)]

•In neutron diffraction the fall in diffracted intensity with increasing scattering angle is much less because the nucleus is “point-like”.

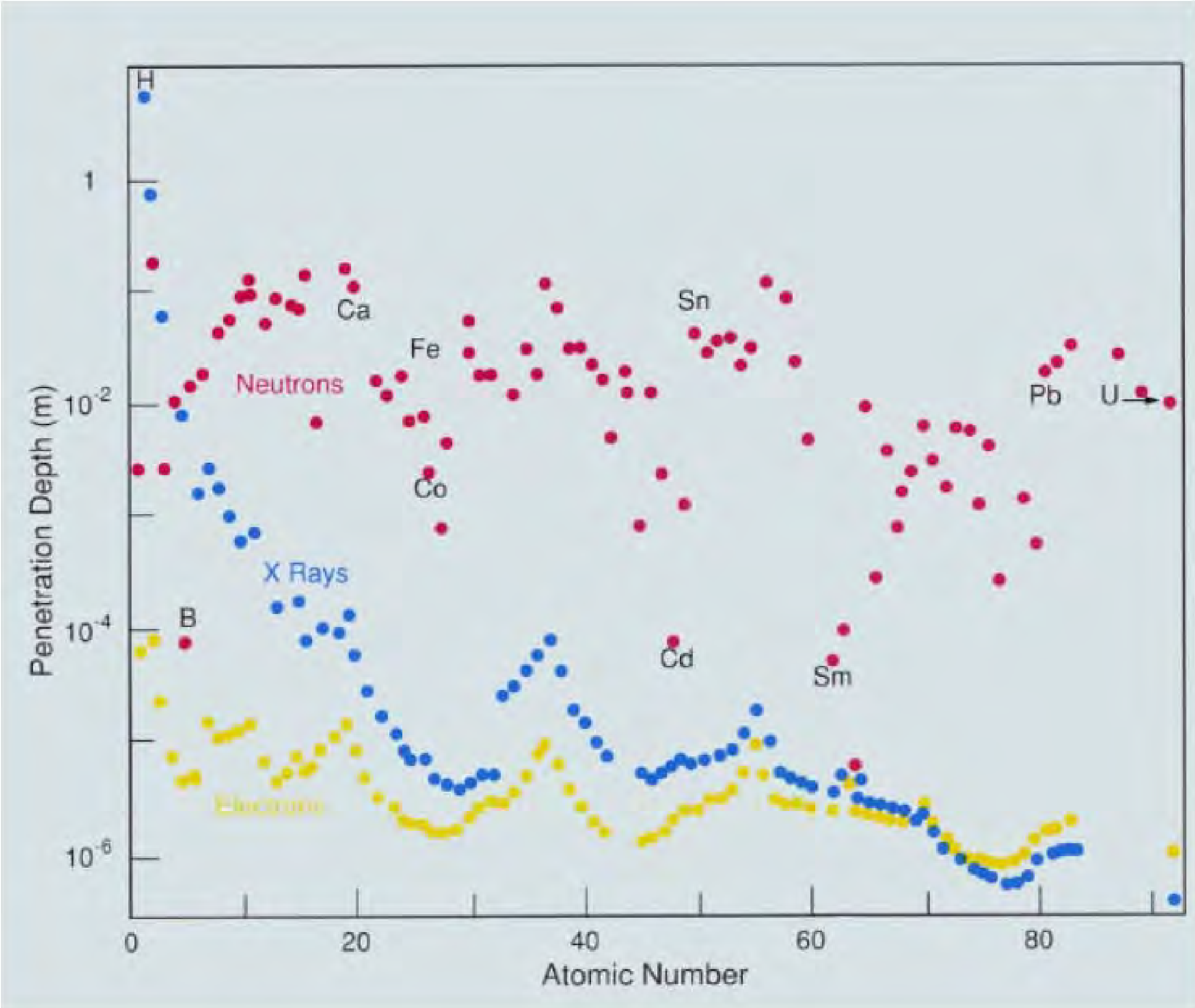
•Thermal vibrations cause a fall in diffracted intensity with 2θ in both cases.

Absorption of X-rays by matter



“Elements of X-ray Diffraction” (B.D. Cullity and S.R. Stock)

Absorption for thermal neutrons and 8keV X-rays



www.ncnr.nist.gov

- Neutrons are absorbed by nuclear processes that destroy the neutrons, emitting secondary radiation (α, β, or γ) as a result.
- For most atoms, neutrons penetrate much further into the sample than X-rays.

Sample environment for neutron diffraction

15T cryomagnet at PSI (http://lns00.psi.ch/sinqwiki)

Neutron absorption and incoherent scattering

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
Gd	---	6.5-13.82*i*	---	29.3	151.(2.)	180.(2.)	49700.(125.)
152Gd	0.2	10.(3.)	0	13.(8.)	0	13.(8.)	735.(20.)
154Gd	2.1	10.(3.)	0	13.(8.)	0	13.(8.)	85.(12.)
155Gd	14.8	6.0-17.0*i*	(+/-)5.(5.)-13.16*i*	40.8	25.(6.)	66.(6.)	61100.(400.)
156Gd	20.6	6.3	0	5	0	5	1.5(1.2)
157Gd	15.7	-1.14-71.9*i*	(+/-)5.(5.)-55.8*i*	650.(4.)	394.(7.)	1044.(8.)	259000.(700.)
158Gd	24.8	9.(2.)	0	10.(5.)	0	10.(5.)	2.2
160Gd	21.8	9.15	0	10.52	0	10.52	0.77

Isotope	conc	Coh b	Inc b
H	---	-3.7390	---
1H	99.985	-3.7406	25.274
2H	0.015	6.671	4.04
3H	(12.32 a)	4.792	-1.04

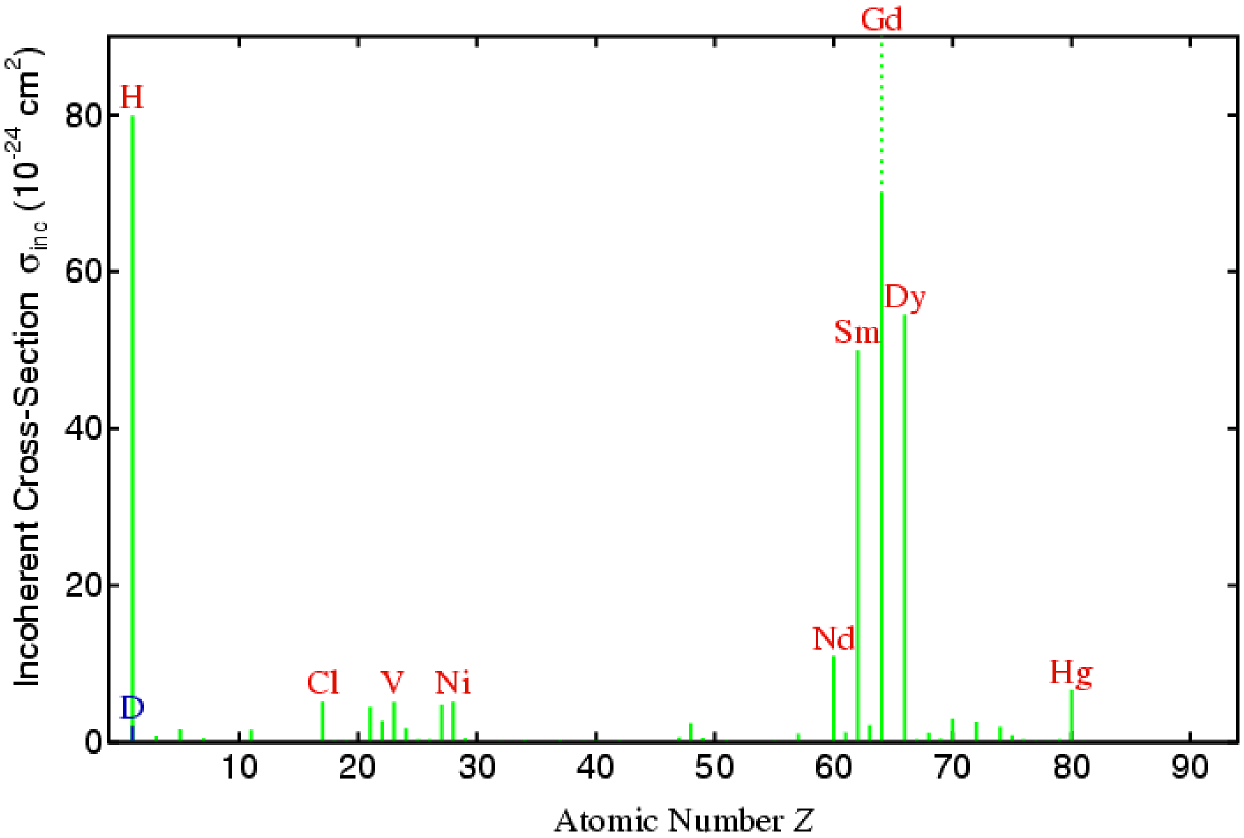
http://www.ncnr.nist.gov/resources/n-lengths/

•Scattering strength of an element is the weighted average of the scattering strengths of its isotopes with respect to their abundances.

•Isotopic substitution in samples is often used to overcome absorption and incoherent scattering problems, eg. ^{2}H (deuterium) is used instead of ^{1}H, and ^{156}Gd is used instead of “natural” Gd.

•This is often expensive and different isotopes can change the crystal structure.

Incoherent scattering of neutrons



[http://pd.chem.ucl.ac.uk/pdnn/inst3/neutrons.htm]

•Incoherent scattering component can be high for nuclei with non-zero nuclear spin, giving a high background.
•Diffraction on Gd-containing compounds is best done with X-rays.

Neutron scattering cross-sections: examples

Nuclide	σ_{coh}	σ_{inc}	Nuclide	σ_{coh}	σ_{inc}
^{1}H	1.8	80.2	V	0.02	5.0
^{2}H	5.6	2.0	Fe	11.5	0.4
C	5.6	0.0	Co	1.0	5.2
O	4.2	0.0	Cu	7.5	0.5
Al	1.5	0.0	^{36}Ar	24.9	0.0

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•V is almost transparent to neutrons and is used for sample containers and “windows” in sample environment.

•Al is also used for sample environment windows.

•^{1}H gives a very high background due to its incoherent cross-section. Samples containing H should generally be deuterated for all neutron measurements.

•Fe and Co can hardly be distinguished with X-rays, but easily with neutrons.

Neutron diffraction – magnetic structure

$$F_{hkl}^2 = F_{Nuc(hkl)}^2 + q^2 F_{Mag(hkl)}^2$$

$$q^2 = 1 - (\varepsilon \cdot \kappa)^2$$

unit vector in direction of reciprocal lattice vector for plane *hkl*

unit vector in direction of spin

Magnetic structure factor

•Nuclear and magnetic scattering intensities are additive.

Neutron diffraction – magnetic structure

$$F_{Mag(hkl)} = \sum_{1}^{N} p_n e^{2\pi i(hx_n + ky_n + lz_n)} e^{-M_n}$$

Atomic coordinates (*x*,*y*,*z*)

Thermal factor

Magnetic scattering amplitude:

$$p_n = \left(\frac{e^2\gamma}{2mc^2}\right) gSf_m$$

electron charge

neutron magnetic moment

magnetic form factor (tabulated)

electron mass

electronic spin

Landé *g* factor, usually ~2

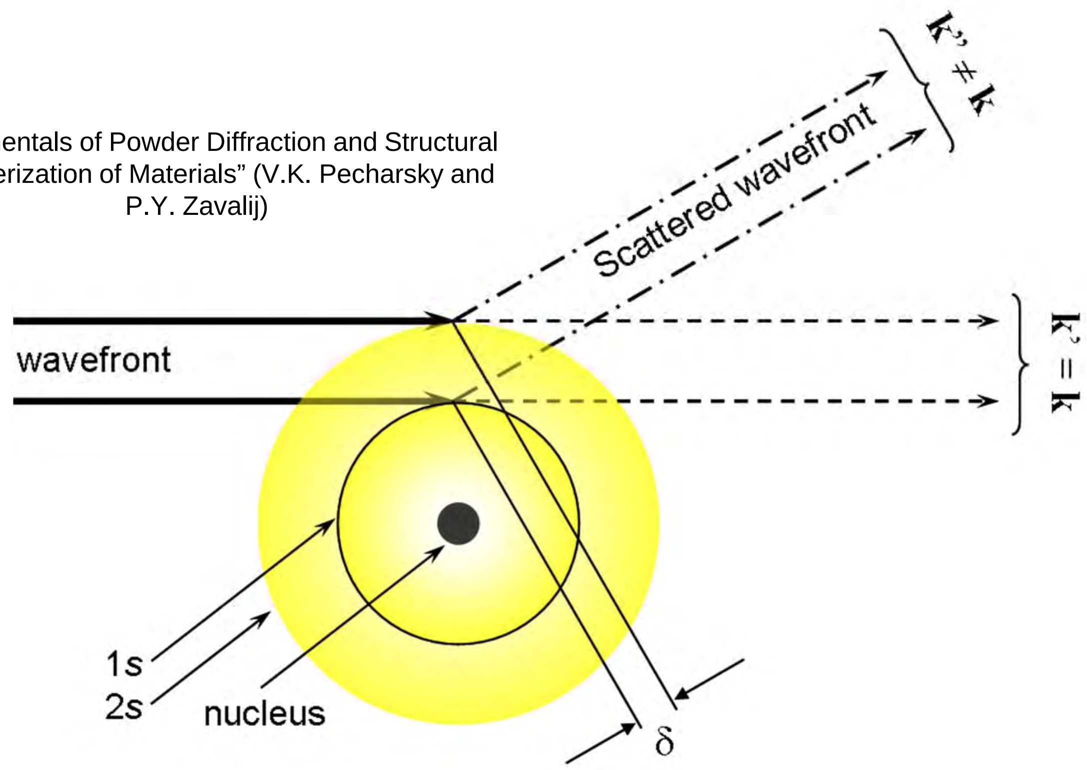
Neutron diffraction – magnetic structure

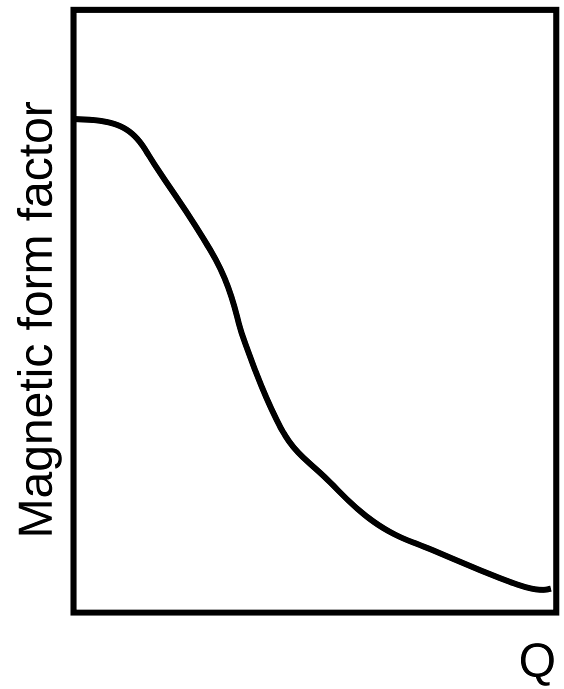
Neutron diffraction can give:

- **The positions of magnetic atoms within the unit cell**
- **The directions of their ordered magnetic moments**
- **The magnitudes of their ordered magnetic moments**

Neutron diffraction – magnetic structure

"Fundamentals of Powder Diffraction and Structural Characterization of Materials" (V.K. Pecharsky and P.Y. Zavalij)



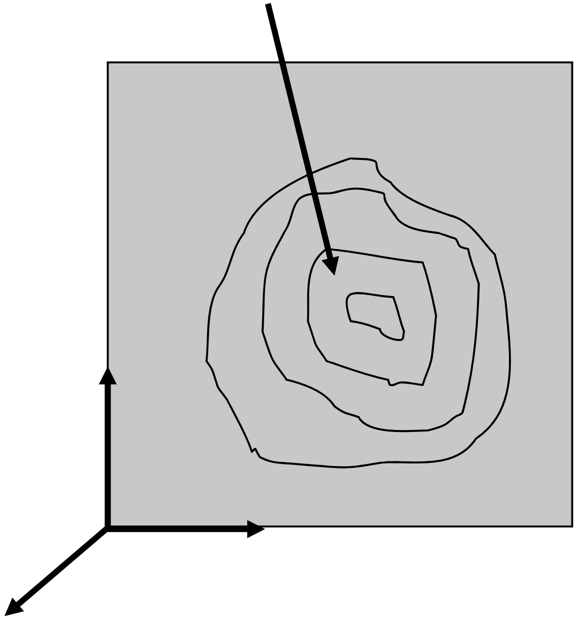


•The magnetic form factor decreases rapidly with diffraction angle (or Q) due to the size of the electron cloud (analogous to X-ray diffraction). We have to work at high d-spacing (low Q).

Introduction to magnetic symmetry

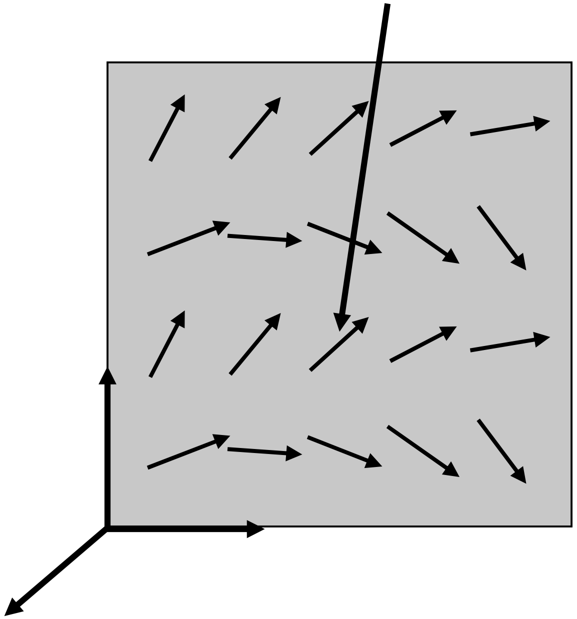
Nuclear or electronic structure:
Scalar field

electron / nuclear scattering density
(a number)



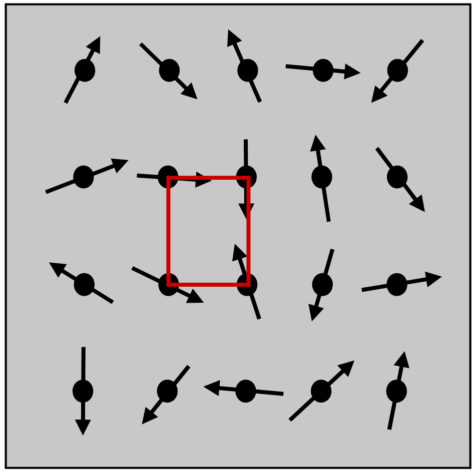
Magnetic structure:
Vector field

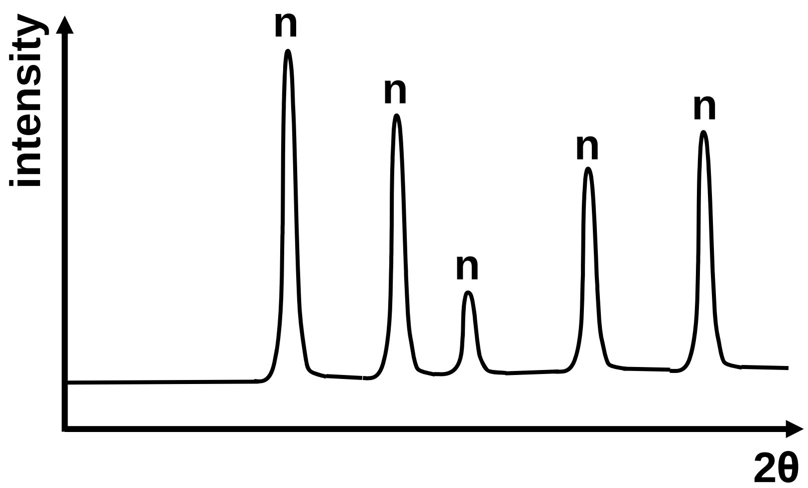
magnetic moment
(vector quantity)



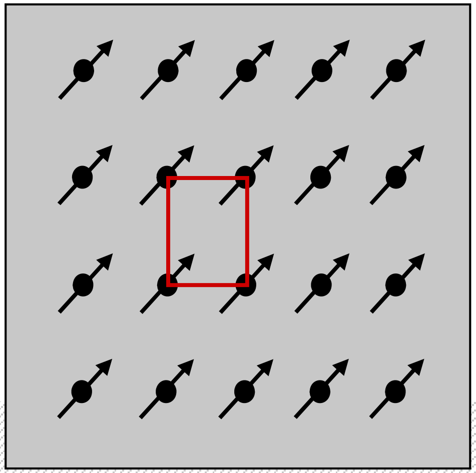
Introduction to magnetic symmetry

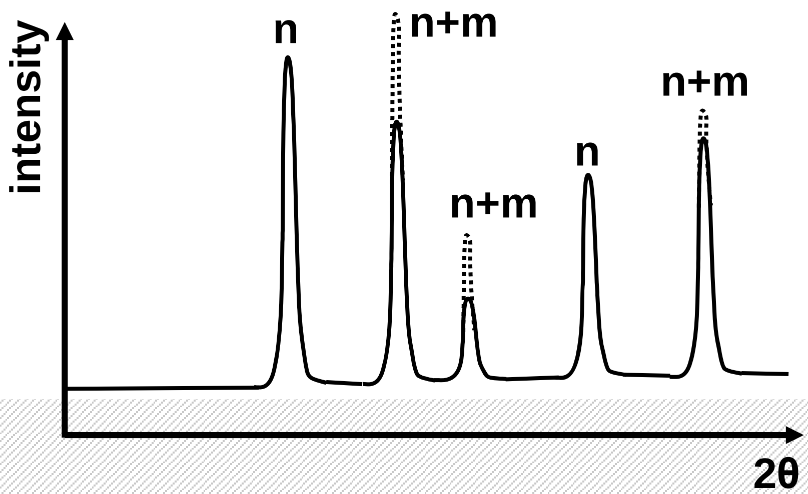
Paramagnet ($T > T_C$)





Ferromagnet ($T < T_C$)



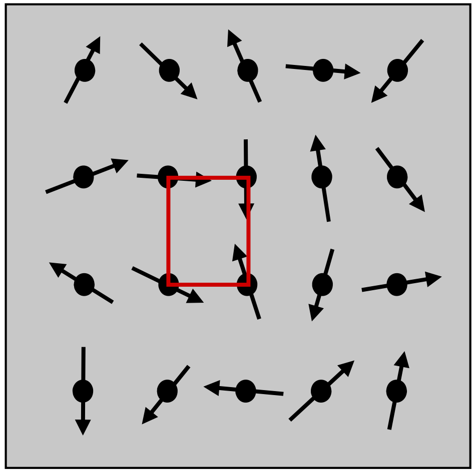


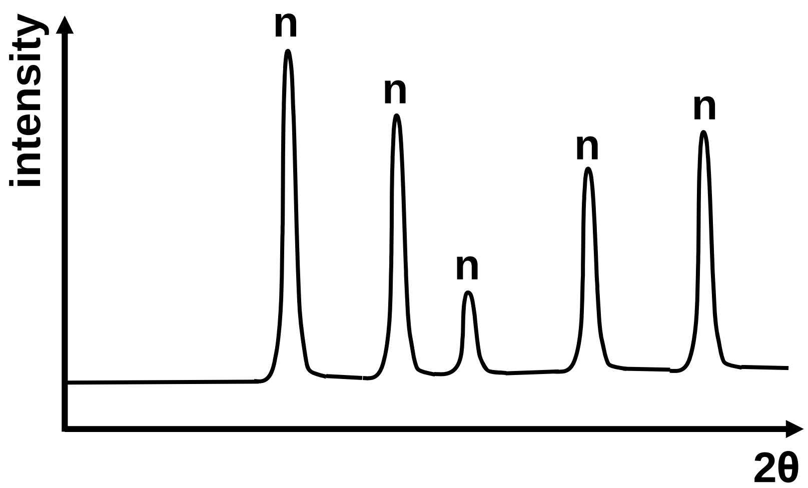
Unit cell same size

Additional intensity appears on top of existing peaks

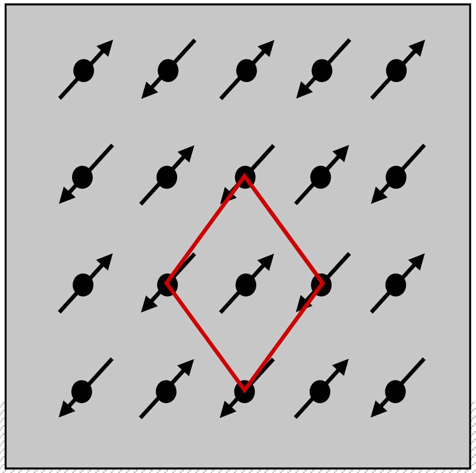
Introduction to magnetic symmetry

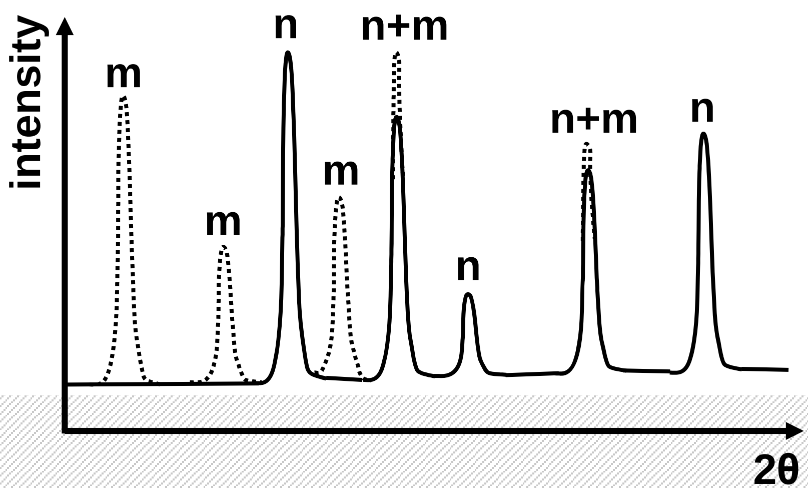
Paramagnet ($T > T_N$)





Antiferromagnet ($T < T_N$)

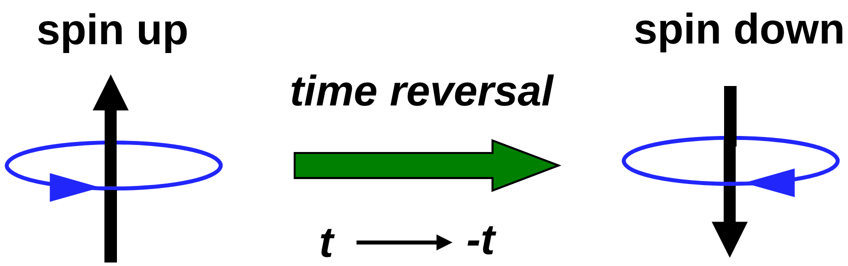




Unit cell is larger

New peaks appear

Introduction to magnetic symmetry



Ordered magnetic crystals are not symmetric to time inversion.

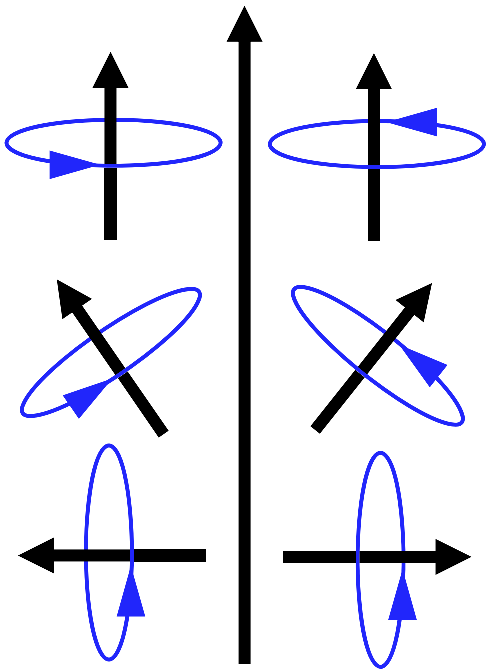
•Time reversal must be added as an extra symmetry element to fully describe magnetic structures.

•The time reversal symmetry operator is combined with an existing symmetry element and is usually represented by the ′ (prime) symbol, eg. 1′, m′, $2_1'$

Introduction to magnetic symmetry

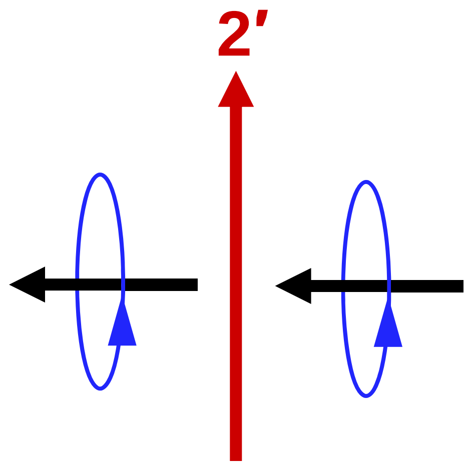
Axial vectors

2-fold rotation



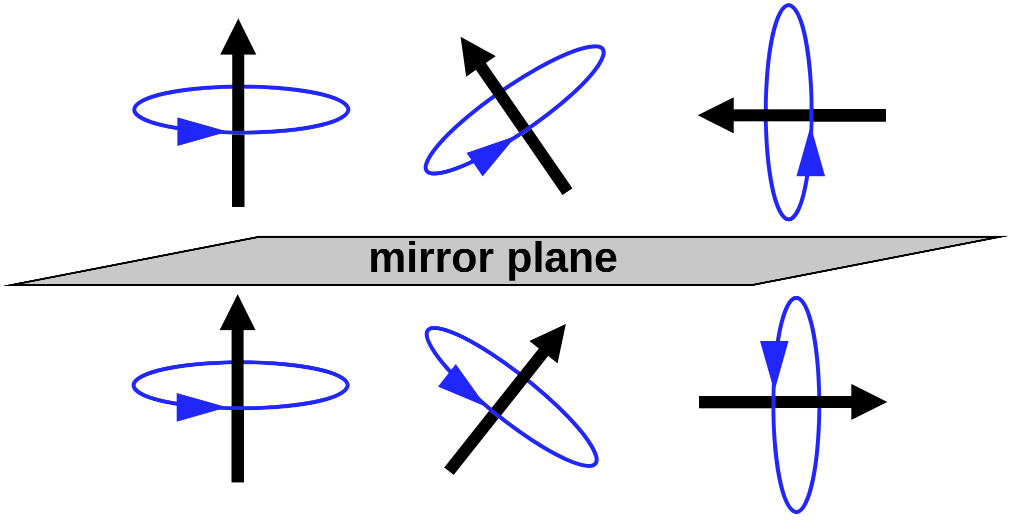
•Unprimed rotation axes (and screw axes) simply rotate the spin vector

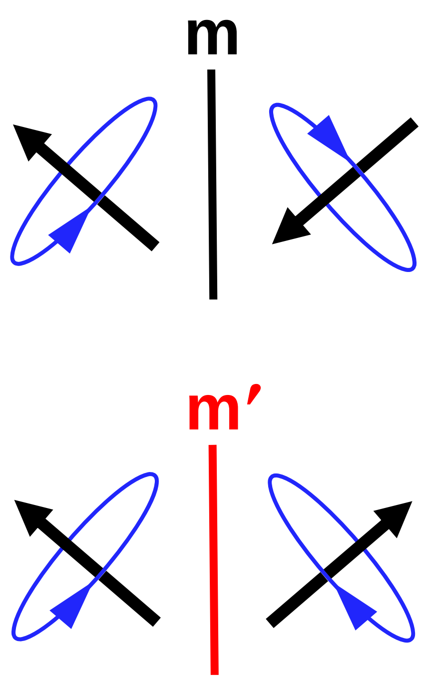
•Primed rotation axes (and screw axes) rotate and then flip the spin vector



Introduction to magnetic symmetry

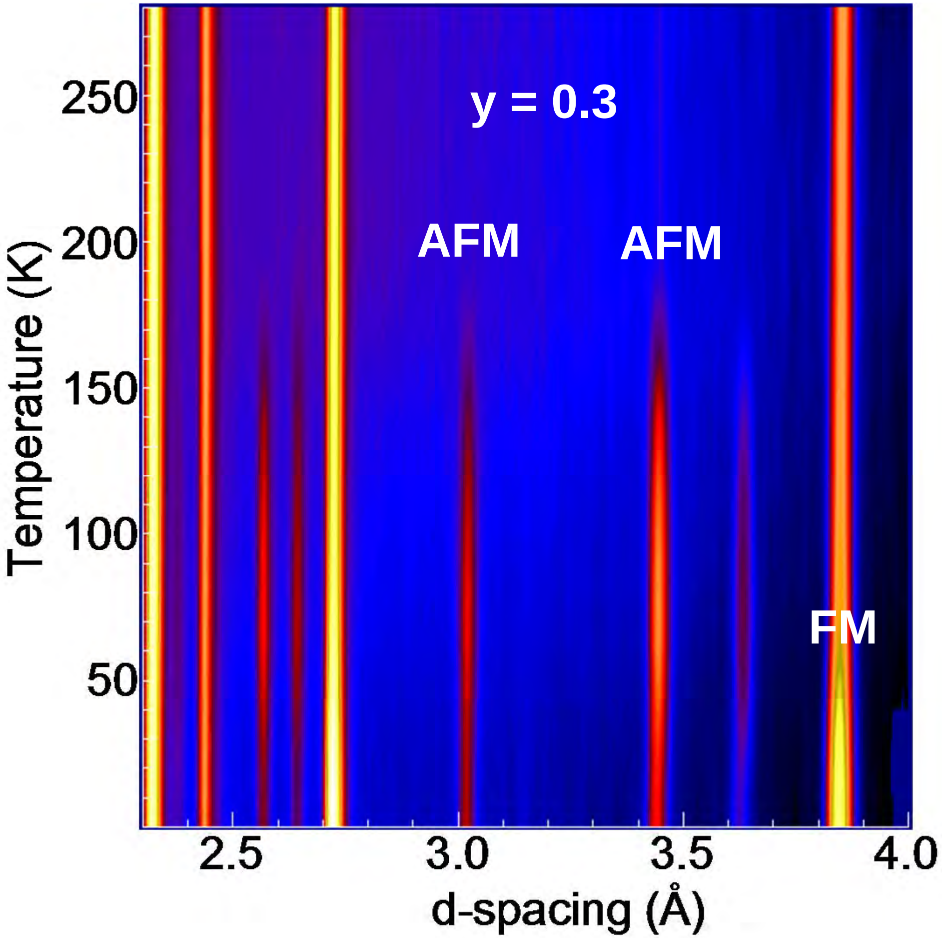
Axial vectors





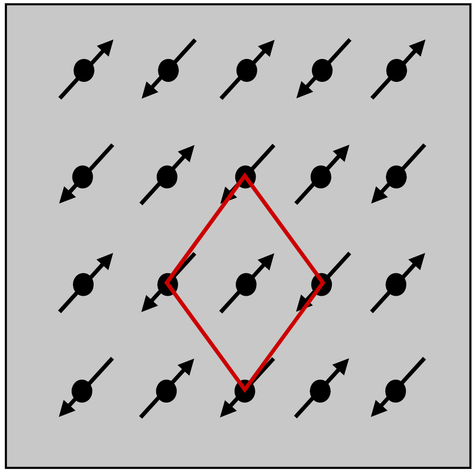
•Mirror planes (and glide planes) leave the perpendicular component of the spin vector unchanged but flip the parallel component.

Example: spin/charge ordering in a manganese oxide

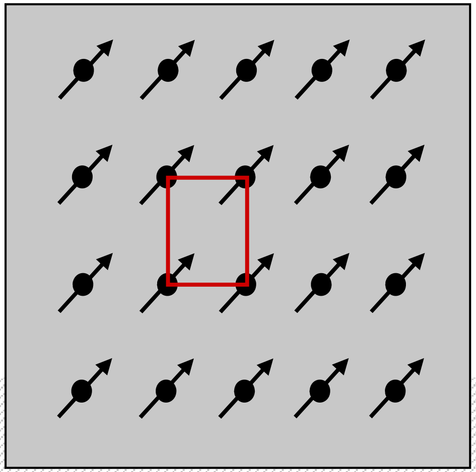


Peaks associated with magnetic ordering in $Pr_{0.65}(Ca_{1-y}Sr_y)_{0.35}MnO_3$

Antiferromagnet ($T < T_N$)

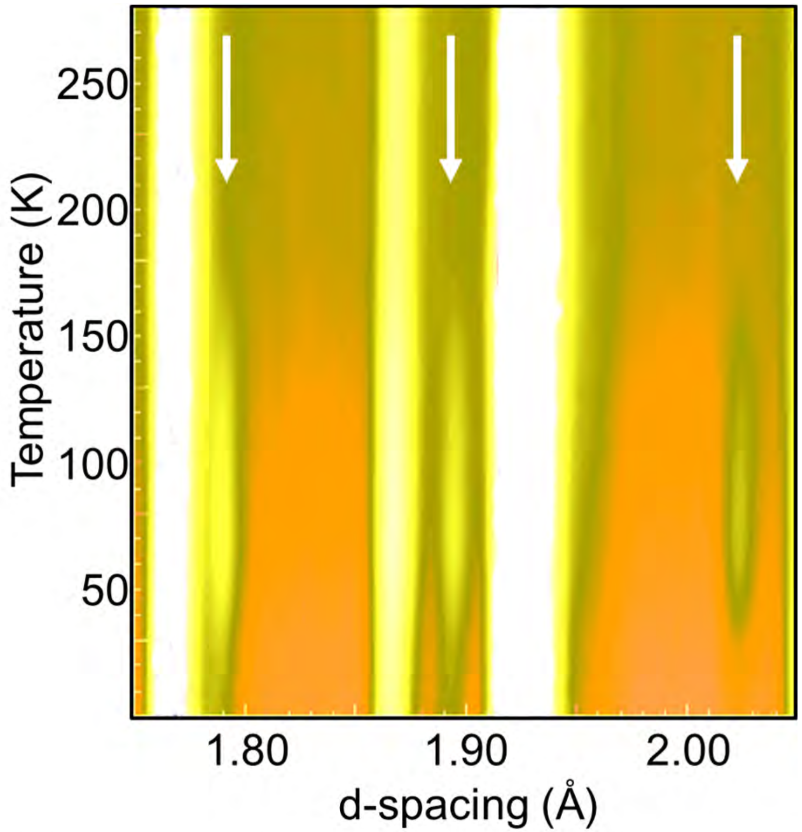


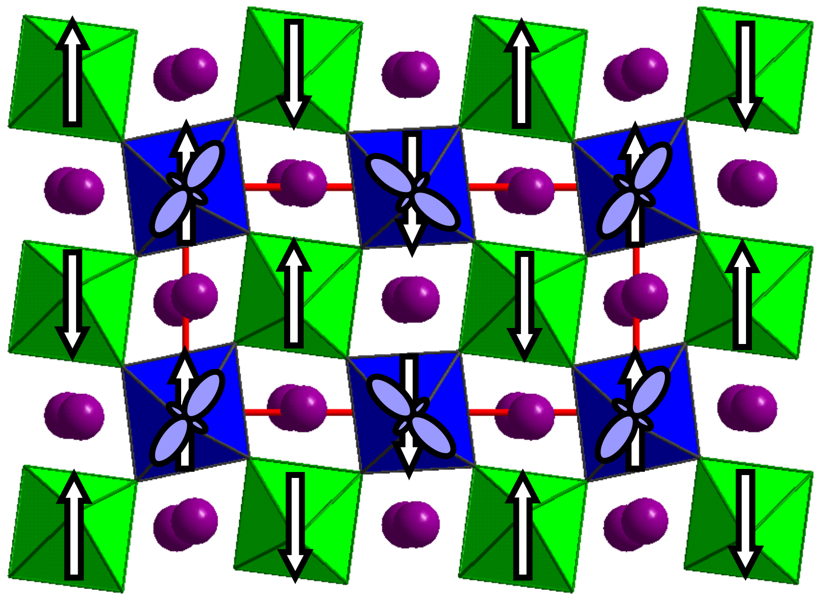
Ferromagnet ($T < T_C$)



Example: spin/charge ordering in a manganese oxide

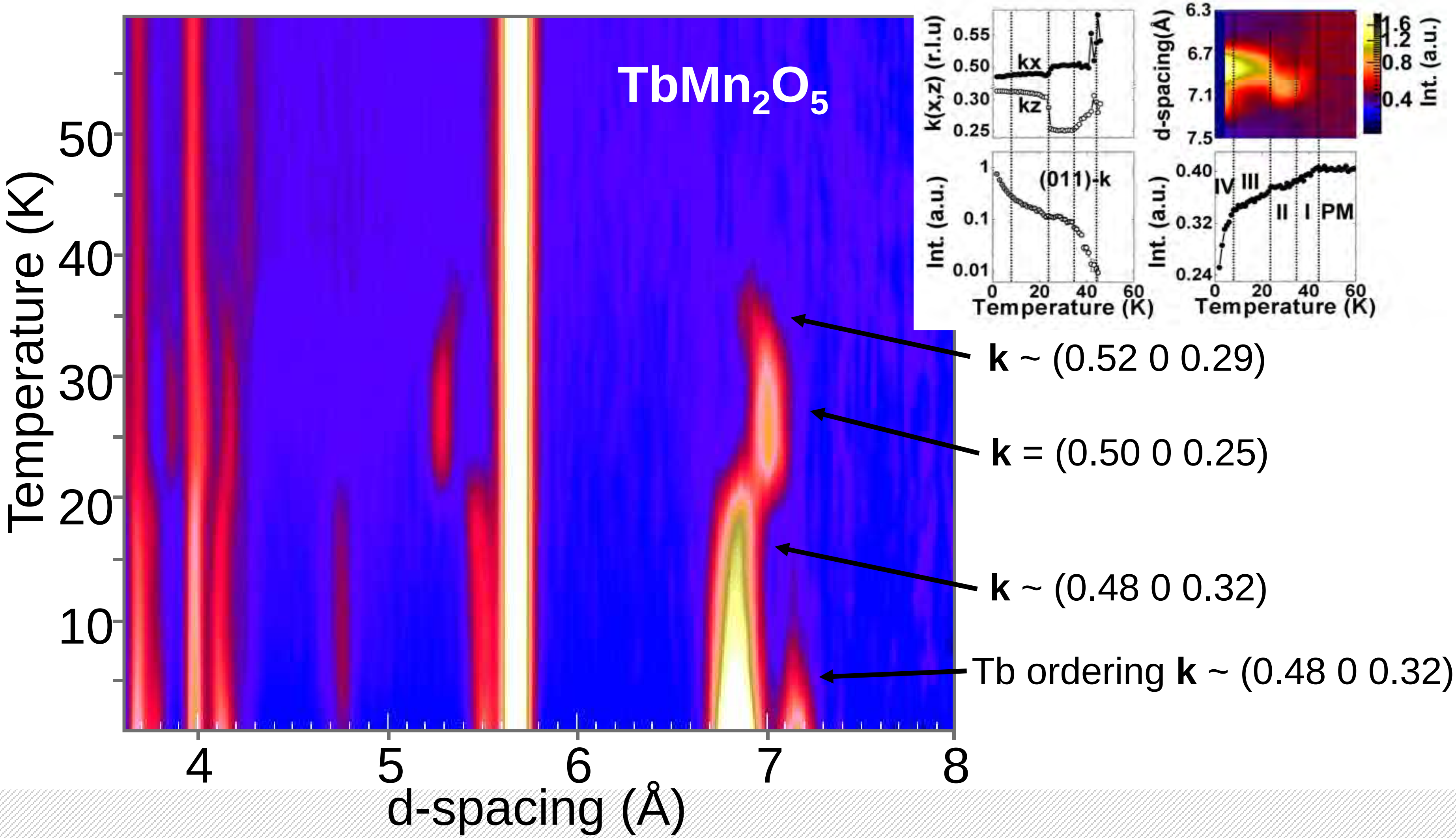
- Sensitivity of neutrons to oxygen allows Mn-O bonding pattern associated with spatial ordering of Mn^{3+} and Mn^{4+} to be determined.





Charge-ordered, orbital-ordered, spin-ordered state of $Pr_{0.65}(Ca_{0.7}Sr_{0.3})_{0.35}MnO_3$

Example: multiferroic $TbMn_2O_5$



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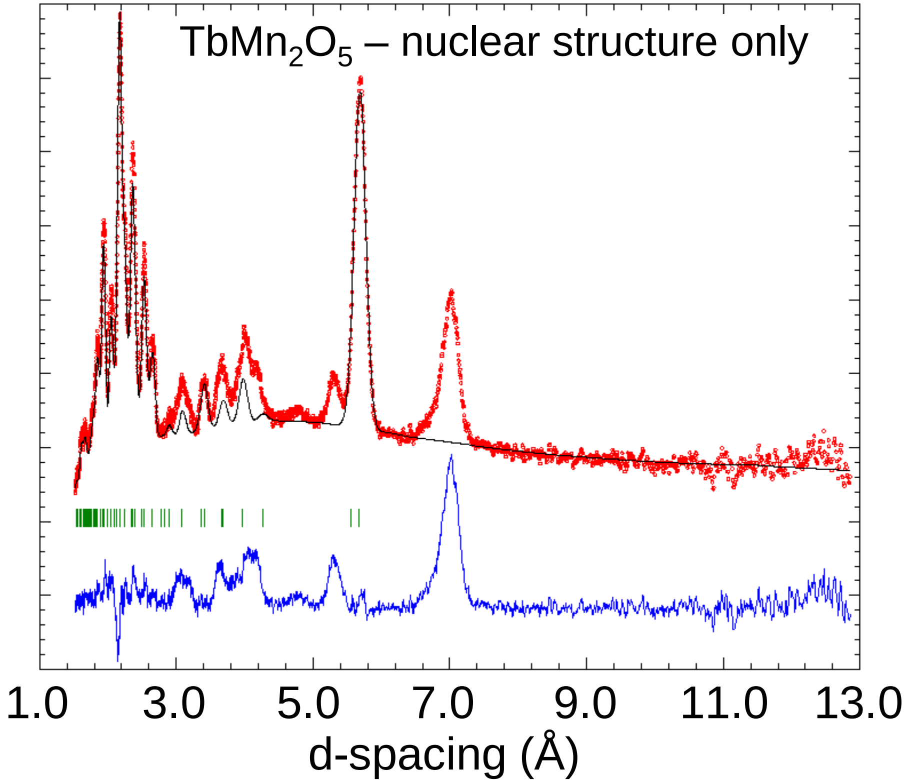
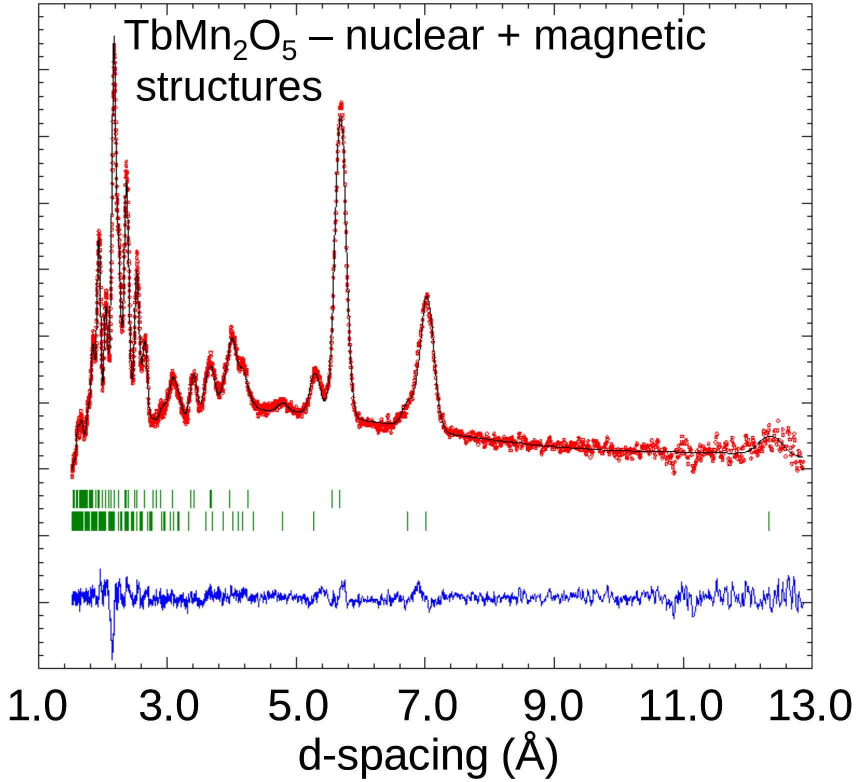
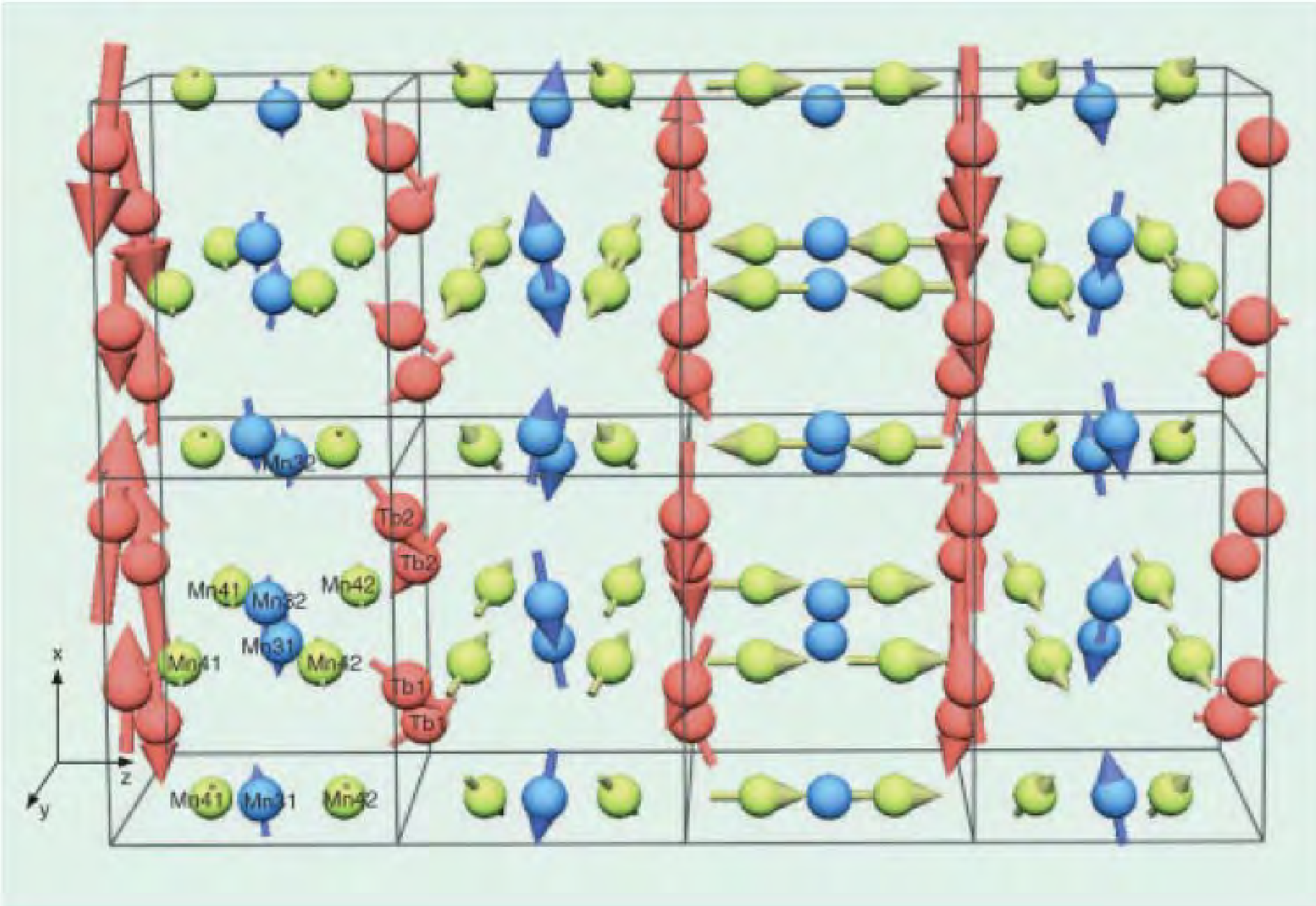




Example: multiferroic $TbMn_2O_5$

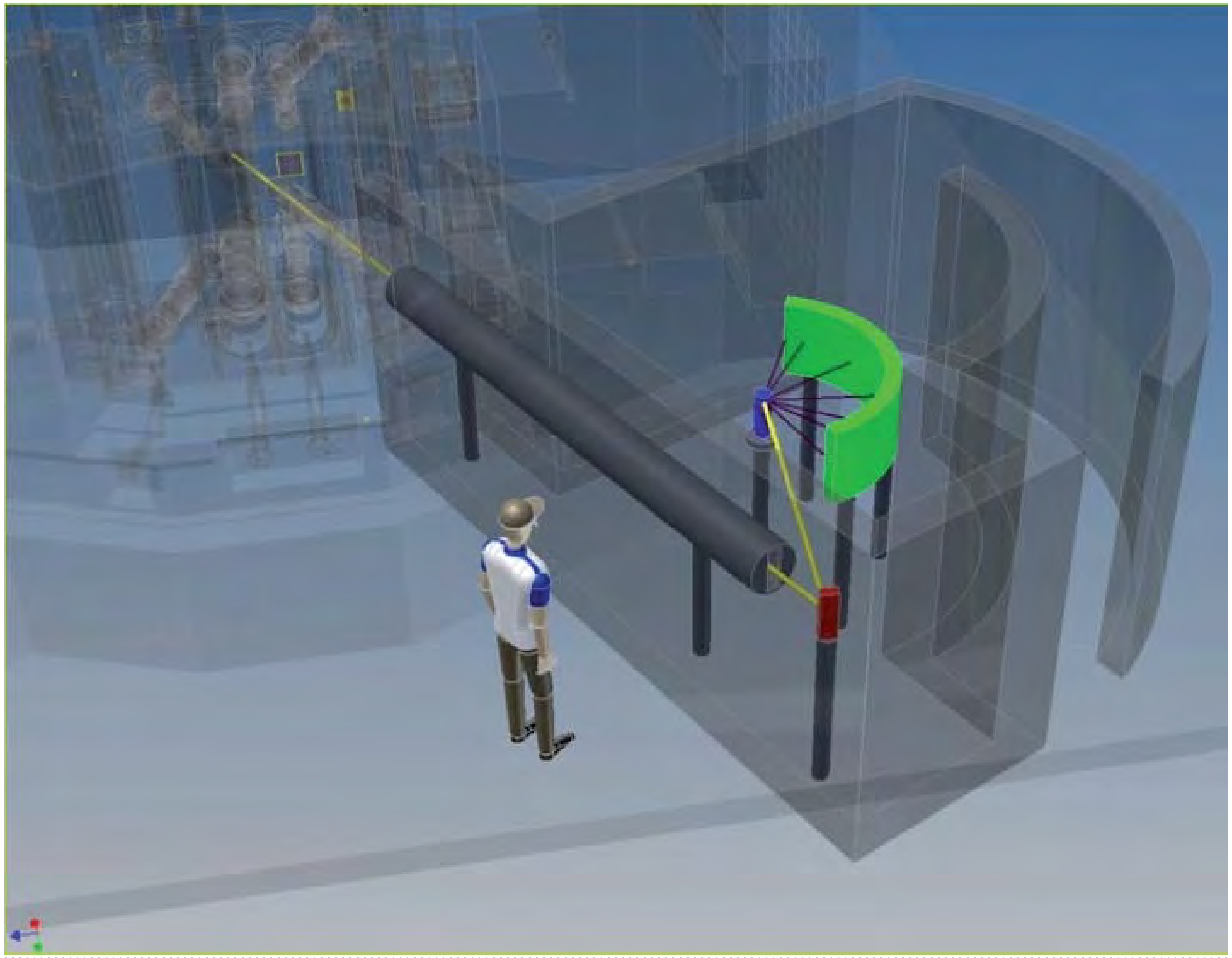


C. Wilkinson et al., Phys. Rev. B 84, 224422 (2011)

Neutron scattering facilities

www.veqter.co.uk

OYSTER at T.U. Delft

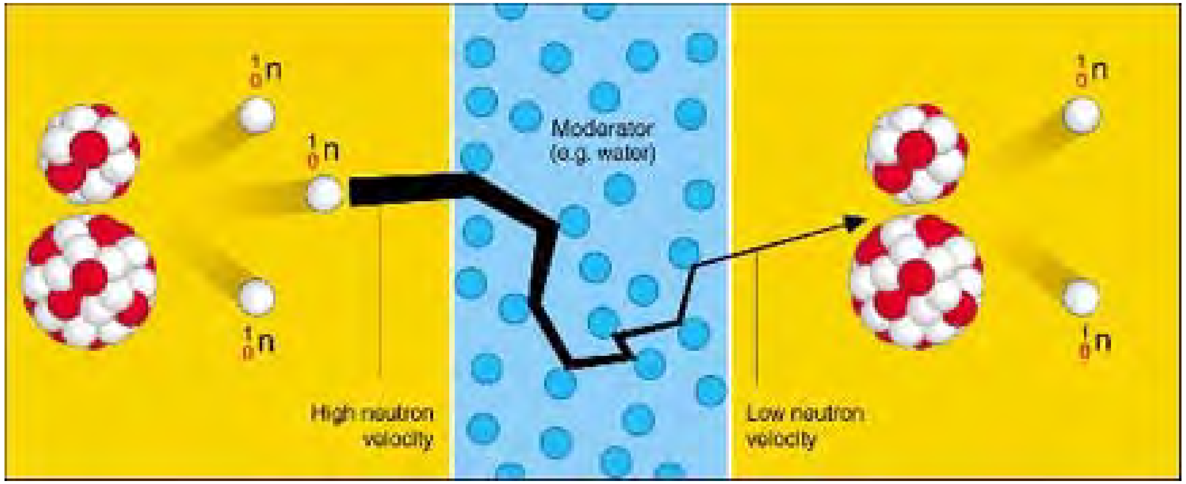


PEARL diffractometer (http://pearl.weblog.tudelft.nl/)

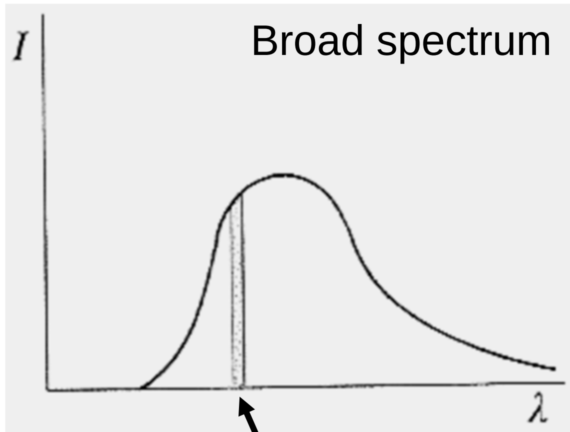
Neutron sources – nuclear reactor

•A steady supply of neutrons is produced by the ^{235}U fission chain reaction (2.5 neutrons per fission event, 1.5 are reabsorbed by the fuel).

•Neutrons are extracted from the core by neutron guide tubes and slowed down by a moderator. A particular wavelength can then be selected using a crystal monochromator.



www.euronuclear.org

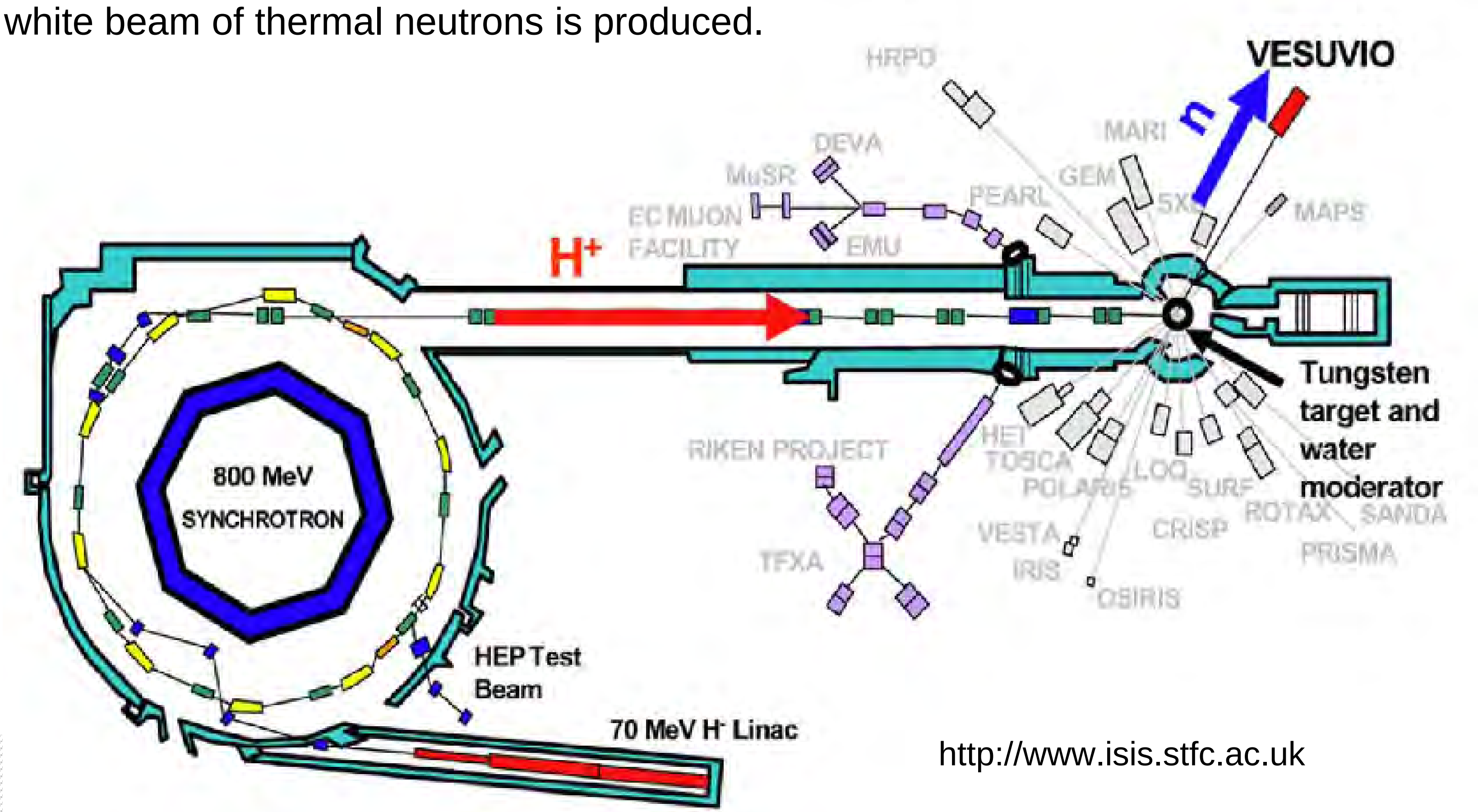


Wavelength selected by monochromator

Neutron sources – spallation (pulsed) source

•Protons are accelerated in a synchrotron ring and then collide with a heavy metal target, which emits many subatomic particles including neutrons (more than 10 per proton).

•A white beam of thermal neutrons is produced.



http://www.isis.stfc.ac.uk

Spallation sources – time-of-flight diffraction technique

arrival time of neutron at detector

$$d_{hkl} = \frac{\lambda}{2\sin\theta} = \left(\frac{h}{mv}\right)\left(\frac{1}{2\sin\theta}\right) = \frac{ht_{hkl}}{2mL\sin\theta}$$

neutron mass, velocity (momentum = $mv = h/\lambda$)

distance from source to detector ($v = L/t_{hkl}$)

•Detector is kept at fixed position (analogous to X-ray Laue technique).

•Arrival time of diffracted neutrons at detector is determined (“time-of-flight”).

•Often a large bank of many detectors covering a range of angles is used.

•Resolution in d_{hkl} can be increased by increasing distance L from the source.

Neutron v X-ray diffraction: source intensity

	Brightness *(s^{-1} m^{-2} $ster^{-1}$)*	*dE/E* *(%)*	*Divergence* *($mrad^2$)*	*Flux* *(s^{-1} m^{-2})*
Neutrons	10^{15}	2	10 x 10	10^{11}
Rotating Anode	10^{16}	3	0.5 x 10	5×10^{10}
Bending Magnet	10^{24}	0.01	0.1 x 5	5×10^{17}
Wiggler	10^{26}	0.01	0.1 x 1	10^{19}
Undulator (APS)	10^{33}	0.01	0.01 x 0.1	10^{24}

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Neutron v X-ray diffraction: source intensity

Neutron v X-ray diffraction

+ Neutrons are highly penetrating towards matter (neutral particles)- absorption is low for most elements. Allows use of heavy sample environment (cryostats, pressure cells, magnets etc.) and probes the whole sample.

+ There is often strong contrast in scattering between neighbouring elements (eg. can distinguish Mn from Fe).

+ Light elements can give strong scattering eg. ^{2}D, ^{12}C, ^{14}N, ^{16}O.

+ Strong interaction with magnetic moments- can determine magnetic structures routinely.

+ No radiation damage to samples- important for organics / biological samples.

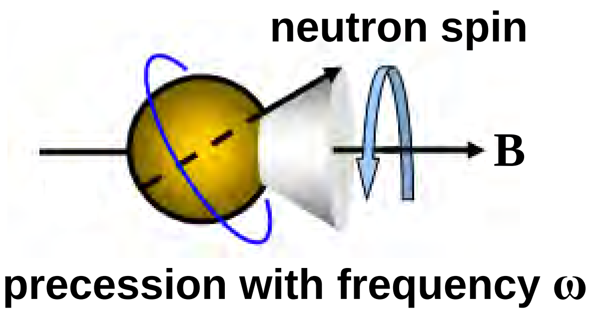
- Neutron sources are much weaker than X-ray sources – in general large samples are needed.

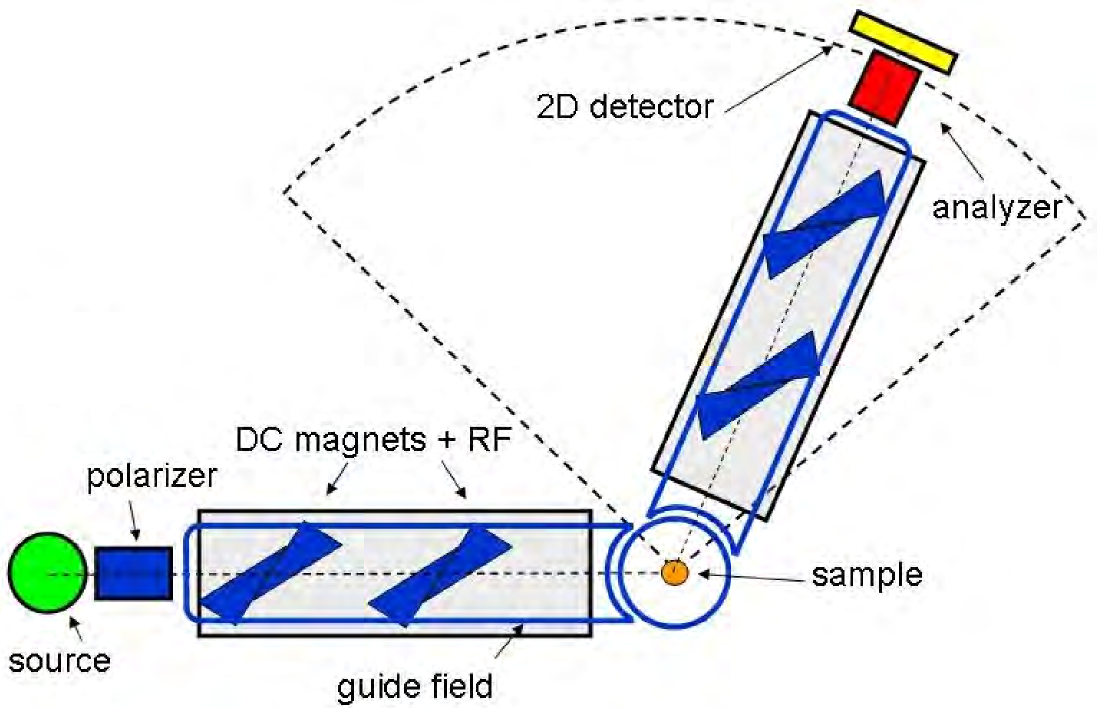
- Some nuclei strongly absorb neutrons and cannot be probed eg. ^{10}B, ^{113}Cd, ^{157}Gd.

- Some nuclei are almost transparent to neutrons and cannot easily be probed eg. ^{51}V. Some nuclei have strong incoherent scattering giving high background eg. ^{1}H.

Larmor Diffraction

- Uses the spin of the neutron.
- Allows highly accurate determination (eventually up to $\Delta d/d = 10^{-6}$) of lattice spacings.
- Also allows determination of distribution of lattice parameters in inhomogeneous / strained samples.

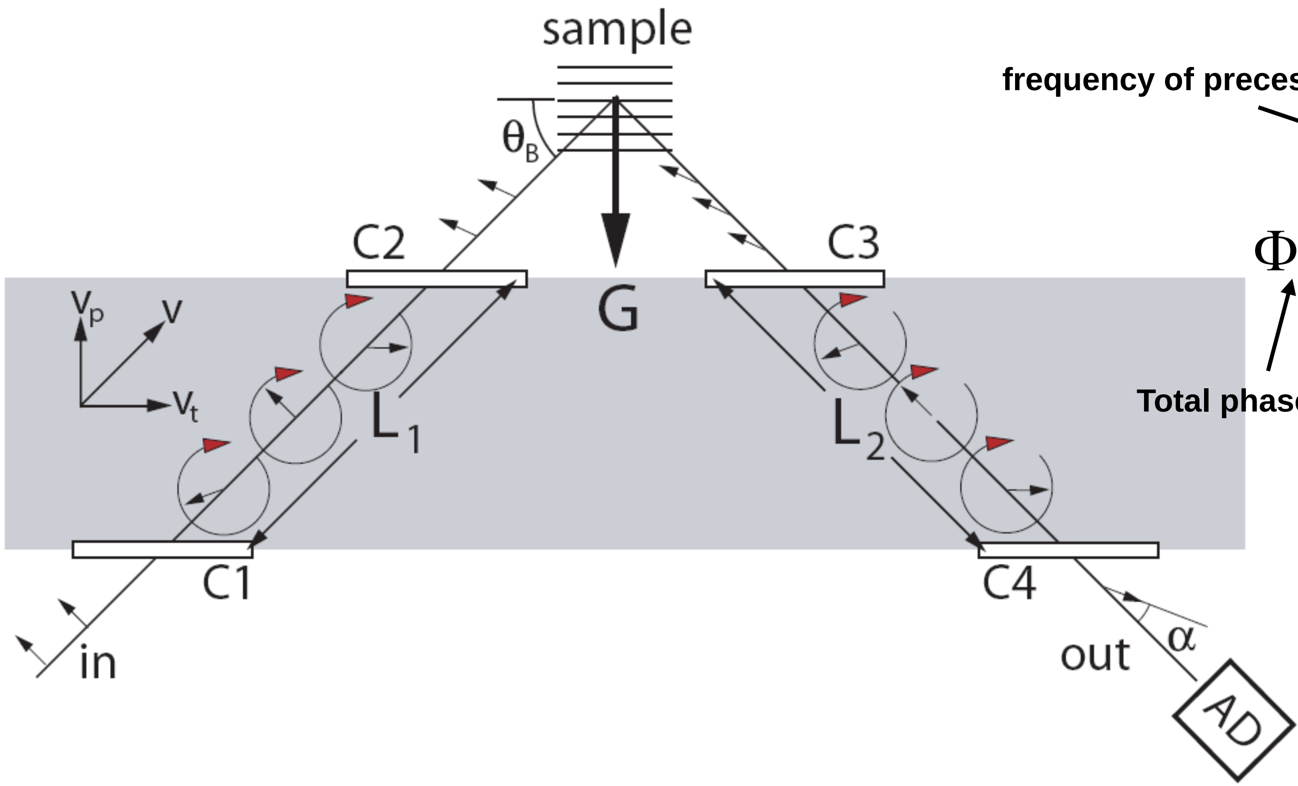




Larmor Diffraction

•The neutron spin precesses between C1 and C2, as well as between C3 and C4.

•This setup does not require a well collimated or perfectly monochromatic beam, or a perfectly aligned sample.



$$\Phi_{tot} = \left(\frac{2\omega_L L m}{\pi \hbar} \right) d$$

frequency of precession (ω_L)

$L=L_1+L_2$

Neutron mass (m)

Total phase of precession (Φ_{tot})

Lattice spacing (d)

P. G. Niklowitz et al., PRL 104, 106406 (2010)

Larmor Diffraction

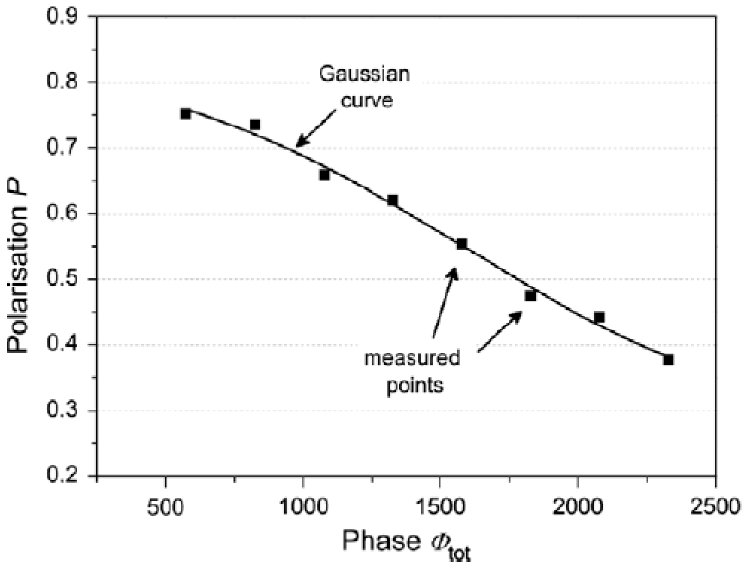
•Lattice spacing distribution can be determined by measuring beam polarisation as a function of precession frequency (~100 – 1000 kHz).

$$P(\Phi_{tot}) = P_0 \exp\left(-\frac{\Phi_{tot}^2}{16\ln 2} \varepsilon_{FW}^2 \right)$$

$$\varepsilon_{FW}^2 = \Delta G / G$$

Reciprocal lattice constant

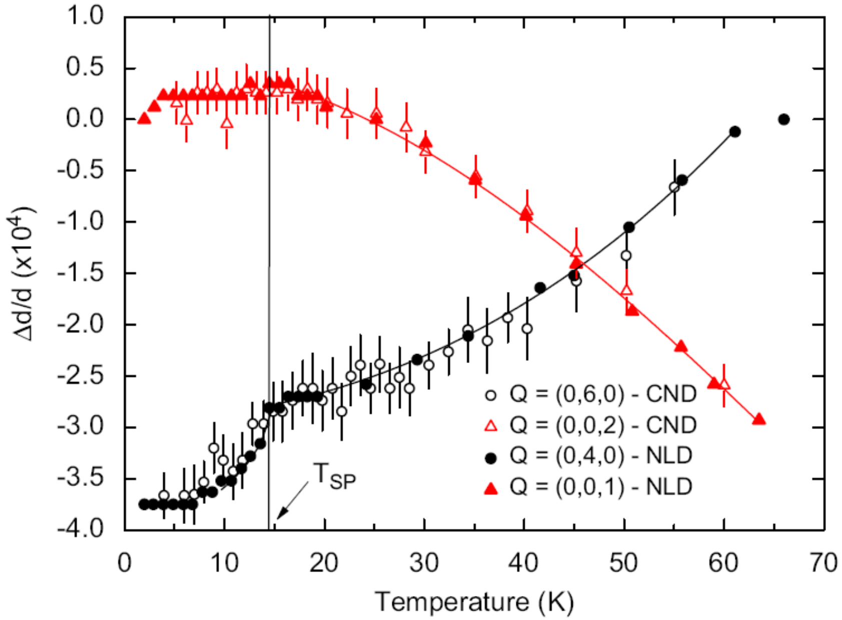
FWHM of lattice constant distribution

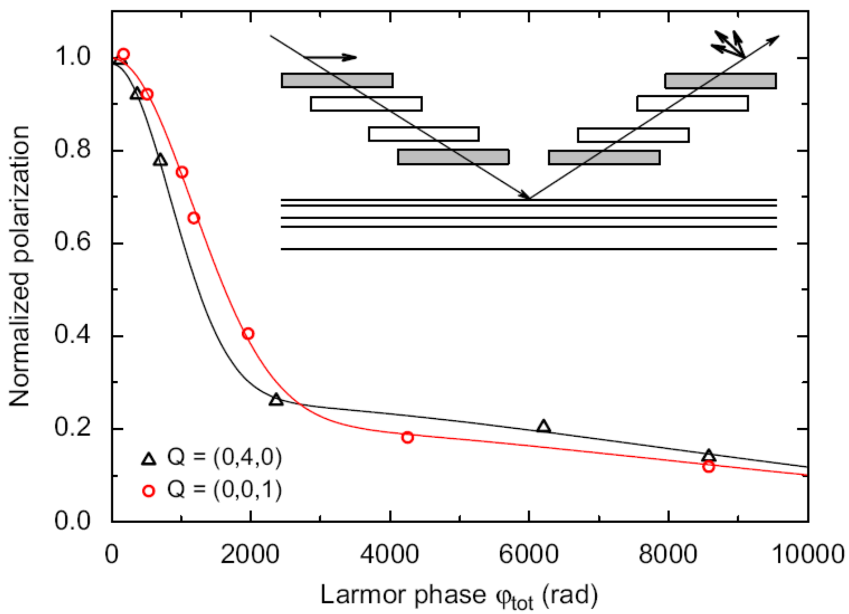


J. Repper et al., Acta Materiala 58, 3459 (2010)

Larmor Diffraction

Example: spin-Peierls transition in $CuGeO_3$. In an apparently good sample the lattice parameter distribution is much larger than the thermal expansion.





N. Martin et al., Physica B 406, 2333 (2011)

Axis	$\delta_1(10^{-3})$	w_1	$\delta_2(10^{-4})$	w_2
b	2.9(1)	0.73(2)	3.0(3)	0.26(1)
c	2.1(1)	0.79(3)	2.9(5)	0.22(3)

Larmor Diffraction

- Study subtle (magnetically induced?) structural distortions that are beyond the best resolution of "standard" X-ray / neutron diffraction
- Determine the lattice constants and distribution of lattice constants associated with domains and nanostructured materials
- Study structural changes associated with classical or quantum phase transitions
- Gain clues as to the sizes and shapes of structural domains, density of domain walls.
- Probe the above at high / low temperature, high pressure
- The time-of-flight technique at ISIS should allow powders to be measured.

Neutron diffraction: summary

- **Sensitive to light elements**
- **Bulk samples and big sample environment**
- **Distinguish neighbouring elements**
- **Sensitive to magnetic moments**

- **Neutron sources are relatively weak**
- **Some elements are strongly absorbing or give incoherent scattering**

- **Complementary to X-ray diffraction**

- **Larmor diffraction will be a more sensitive probe of structural phase transitions and sample inhomogeneity / strain**