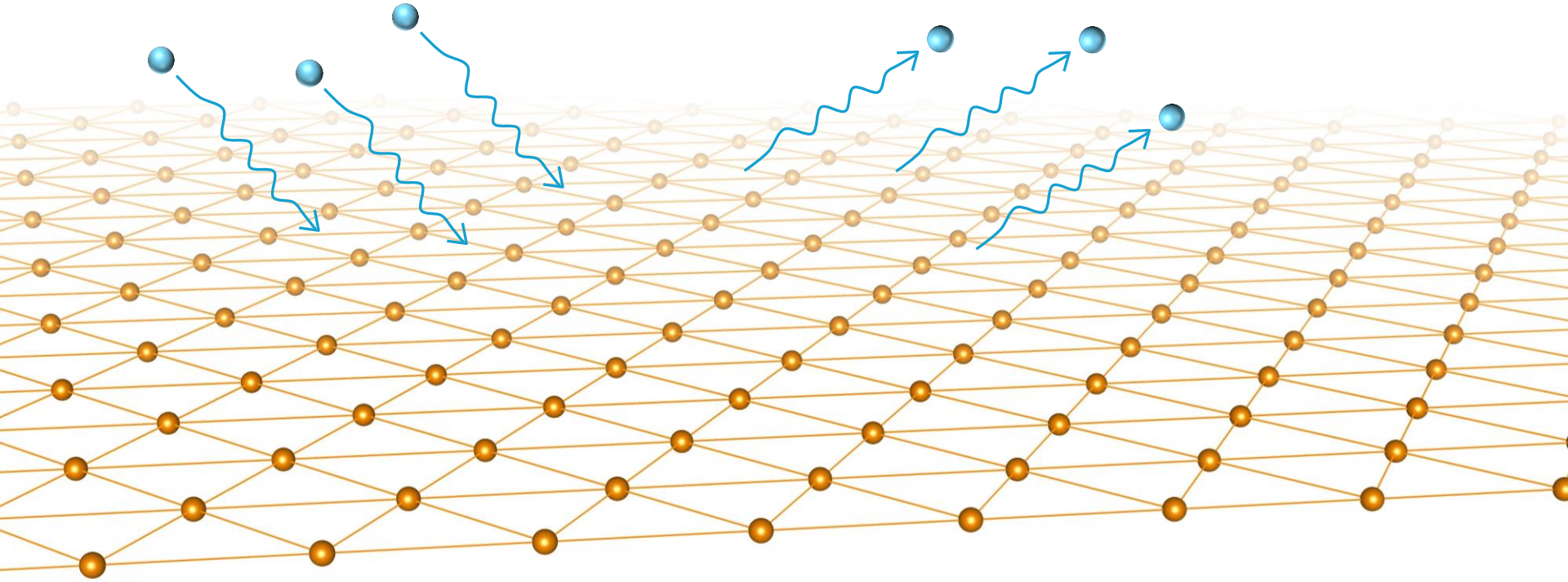

NEUTRON SCATTERING TECHNIQUES FOR STUDIES OF MAGNETIC SYSTEMS

Matej Pregelj
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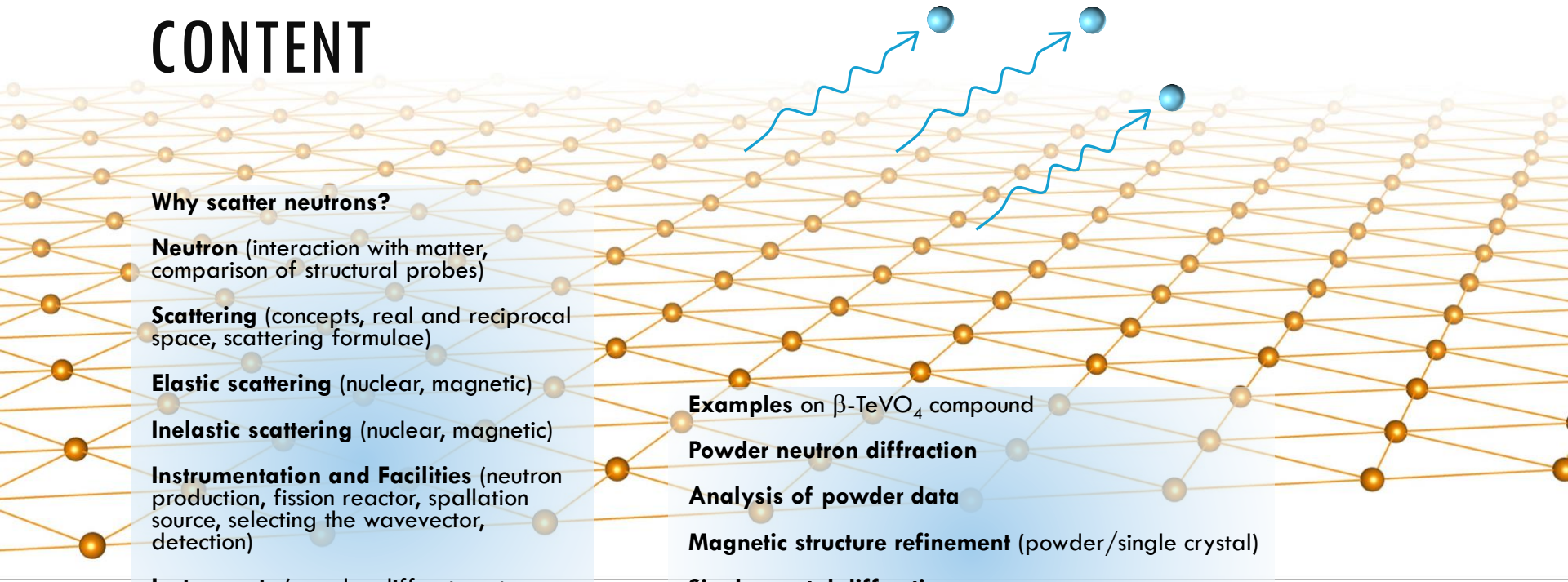
1000 Ljubljana, Slovenia

CONTENT



Why scatter neutrons?

Neutron (interaction with matter, comparison of structural probes)

Scattering (concepts, real and reciprocal space, scattering formulae)

Elastic scattering (nuclear, magnetic)

Inelastic scattering (nuclear, magnetic)

Instrumentation and Facilities (neutron production, fission reactor, spallation source, selecting the wavevector, detection)

Instruments (powder diffractometer, four-circle diffractometer, triple axis spectrometer, Time of flight spectrometer)

Analysis (Fullprof)

Examples on β-$TeVO_4$ compound

Powder neutron diffraction

Analysis of powder data

Magnetic structure refinement (powder/single crystal)

Single-crystal diffraction

Inelastic neutron scattering (powder, single crystal)

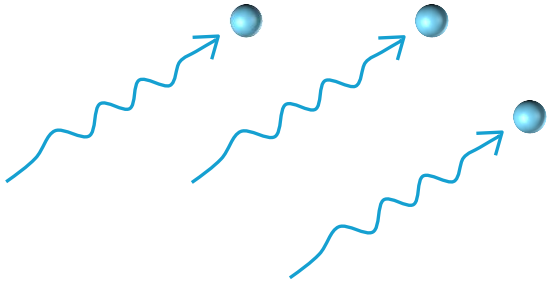
Using triple axis spectrometer

WHY SCATTER NEUTRONS?

- To determine the positions and motions of atoms in condensed matter

  1994 Nobel prize awarded to Shull and Brockhouse

  (see http://www.nobel.se/physics/educational/poster/1994/neutrons.html)

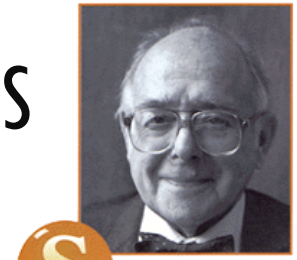


- Neutron advantages
  - Wavelength comparable with interatomic spacings
  - Kinetic energy comparable with that of atoms in a solid
  - Weak interaction with matter makes relatively easy interpretation of the scattering data
  - Deep penetration –> bulk properties are measured (all sample at once)
  - Isotopic sensitivity allows contrast variation
  - **Neutron magnetic moment couples to magnetic field (B) –> neutron "sees" unpaired electron spins**

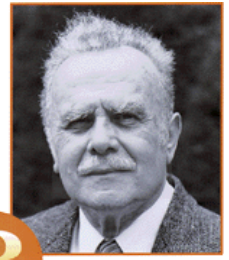
- Neutron disadvantages
  - Neutron sources are weak –> low signals, need for large samples etc.
  - Some elements (e.g. Cd, B, Gd) absorb strongly – become active during the experiment
  - Kinematic restrictions (can't access all energy & momentum transfers)

THE 1994 NOBEL PRIZE IN PHYSICS

Clifford G. Shull & Bertram N. Brockhouse

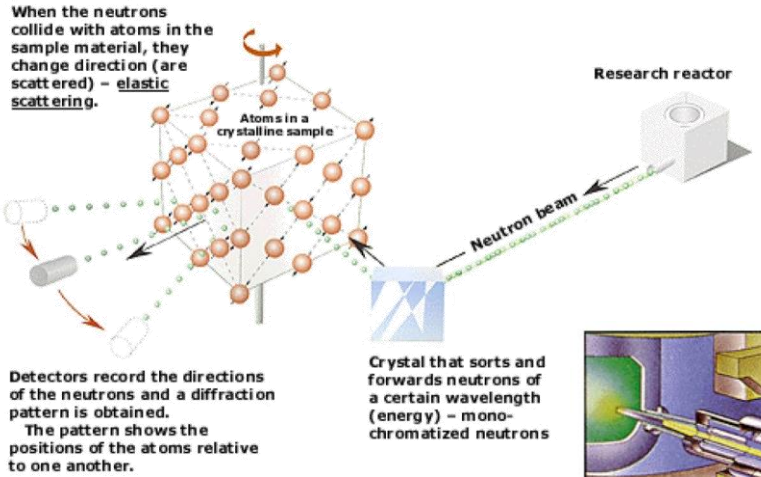


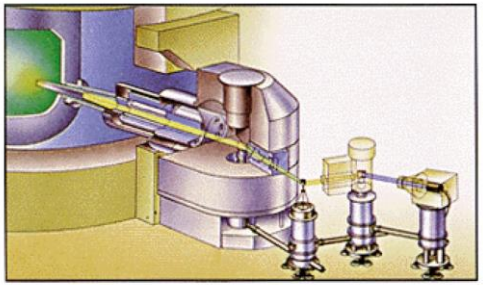
Clifford G. Shull, MIT, Cambridge, Massachusetts, USA, receives one half of the 1994 Nobel Prize in Physics for development of the neutron diffraction technique.



Betram N. Brockhouse, McMaster University, Hamilton, Ontario, Canada, receives one half of the 1994 Nobel Prize in Physics for the development of neutron spectroscopy.

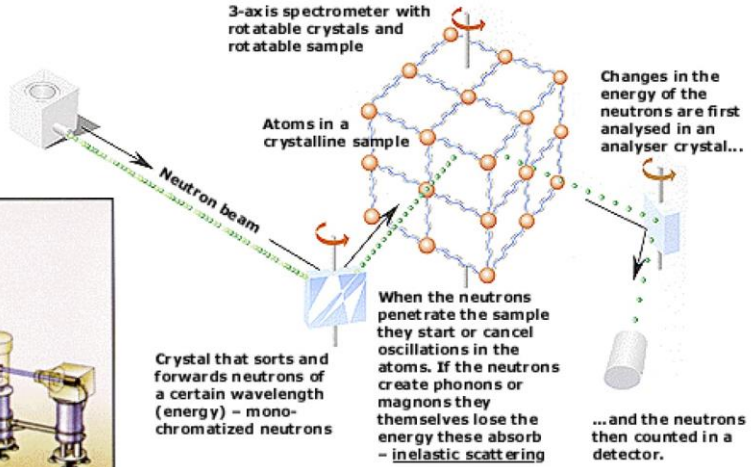
Neutrons show where atoms are…





3-axis spectrometer

… and what atoms do.



NEUTRON

- Composition: 1 up and 2 down quarks
- Massive: $m_n = 1.675 \times 10^{-27}$ kg – almost equal to proton
- No electric charge
- Spin: $S = 1/2$
- Magnetic moment: $\mu_n = -0.966 \times 10^{-26}$ J/T $= -1.042 \times 10^{-3}\ \mu_B$ (Bohr magneton)
  $= -1.913\ \mu_N$ (nuclear magneton)
- Kinetic energy (E), velocity (v), wave vector (k), wave length (λ), temperature (T) relations:

$$E = m_n v^2/2 = k_B T = (hk/2\pi)^2/2m_n \quad k = 2\pi/\lambda = m_n v/(h/2\pi) \qquad \lambda = h/m_n v \text{ (de Broglie wavelength)}$$

	E (meV)	T (K)	λ (nm)	v (m/s)	k (nm^{-1})
Cold	0.1 – 10	1 – 120	0.3 – 3	140 – 1000	2.2 – 22
Thermal	5 – 100	60 – 1000	0.1 – 0.4	1000 – 4000	15 – 70
Hot	100 – 500	1000 – 6000	0.04 – 0.1	4000 – 10000	70 – 155

INTERACTION WITH MATTER

Two types of interaction:

- with atomic nuclei: nuclear force – residual strong interaction
- with magnetic field: electromagnetic force – magnetic dipolar interaction

Sensitive to atomic position as well as magnetic moment

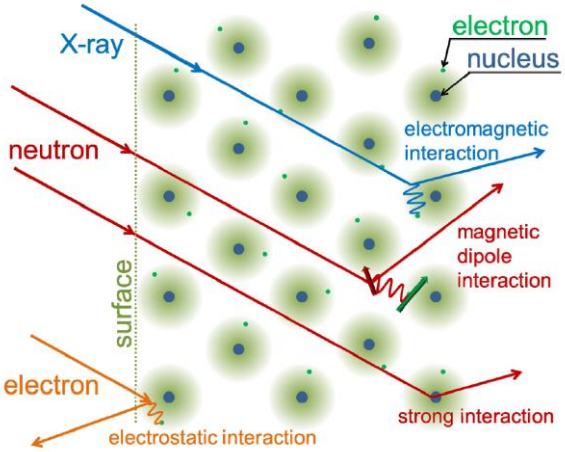
Nuclear force range ~1 fm ≪ *neutron wavelength* leading to "point like" nuclear scattering

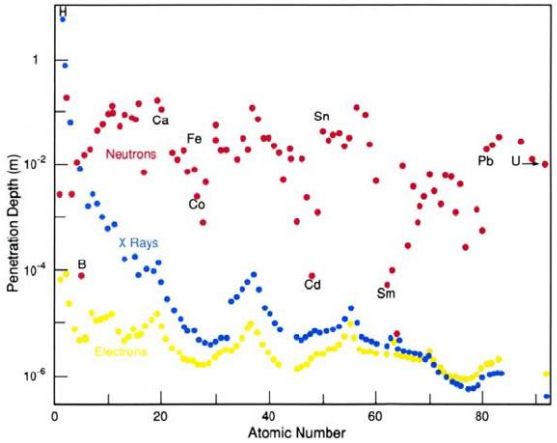
Magnetic interaction extends further leading to finite magnetic structure factor

Penetrate 1cm to 1 m deep into the matter

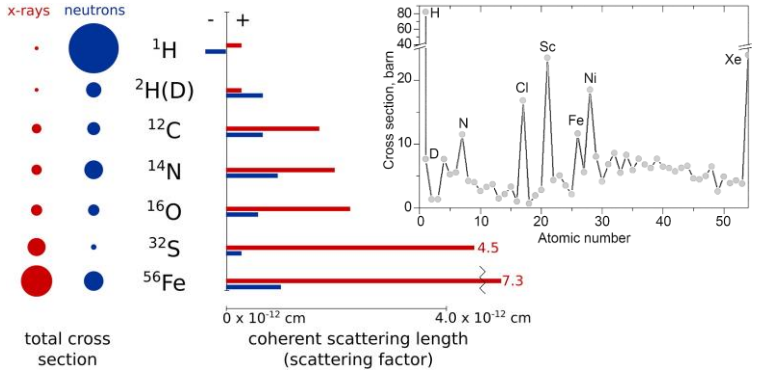
- Good for scattering experiments
- Require thick shielding

When neutrons are absorbed γ-rays are emitted – massive shielding is required





INTERACTION WITH MATTER



Scattering cross sections are different then for x-rays

Two contributions:

- coherent scattering – depends on scattering vector
- Incoherent scattering – uniform in all directions

Several nuclei scatter very weakly, while several have very strong/dominant incoherent scattering

- Al is used for windows and sample containers
- V is used for sample containers and sensor calibration
- Difference between ^{1}H and ^{2}H in can be used for contrast
- Hydrogen samples are often deuterated (^{1}H –> ^{2}H)
- ^{3}He is used for detectors
- Heavy elements have high absorption and can get very active during experiments

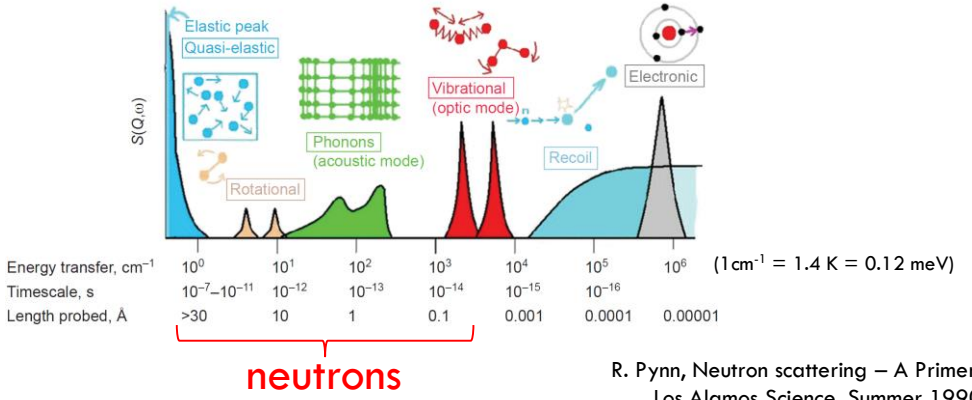
Nucleus	Cross section (1 barn = 10^{-24} cm^2)			
	Coherent	Incoherent	Total	Absorption
^{1}H	1.8	80.2	82.0	0.3
^{2}H	5.6	2.1	7.7	0
^{3}He	4.4	1.6	6.0	5333
^{4}He	1.3	0	1.3	0
C	5.6	0	5.6	0
N	11.0	0.5	11.5	1.9
O	4.2	0	4.2	0.0
Al	1.5	0.01	1.5	0.2
S	1.0	0	1.0	0.5
V	0.02	5.1	5.1	5.1
Fe	11.5	0.4	11.9	2.6
Co	0.8	4.8	5.6	37.2
Cu	7.5	0.5	8.0	3.8

https://www.nist.gov/ncnr/neutron-scattering-lengths-list

COMPARISON OF STRUCTURAL PROBES

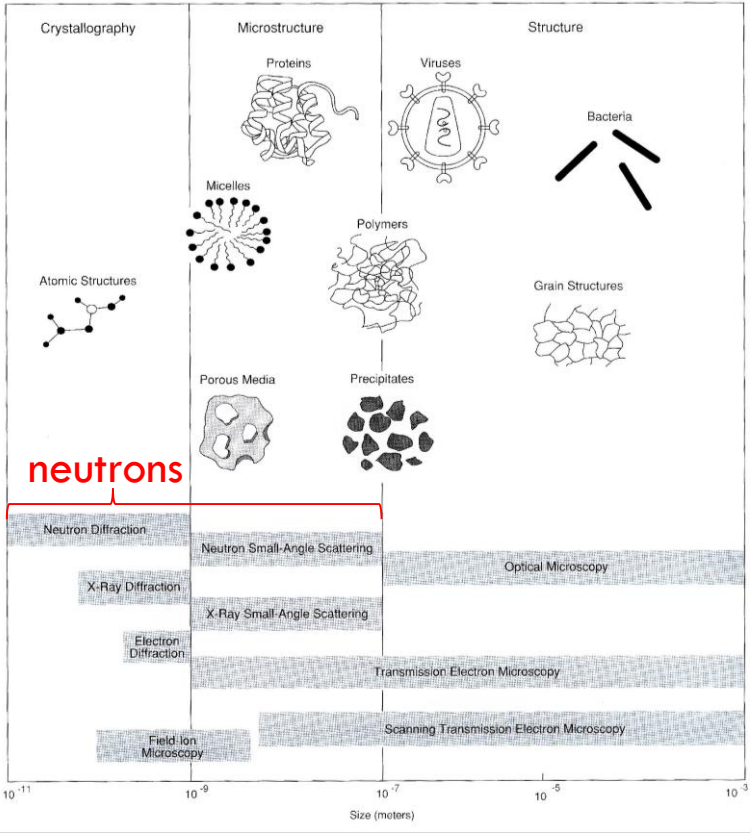
For optical/transmission techniques higher resolution is always related with more localized information of the structure

Scattering techniques provide statistically averaged information on the structure – not a real-space picture of particle positions

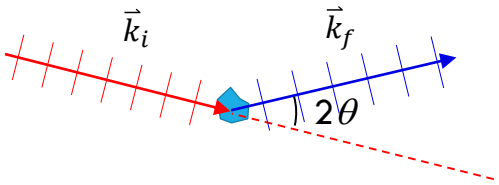


(1cm^{-1} = 1.4 K = 0.12 meV)

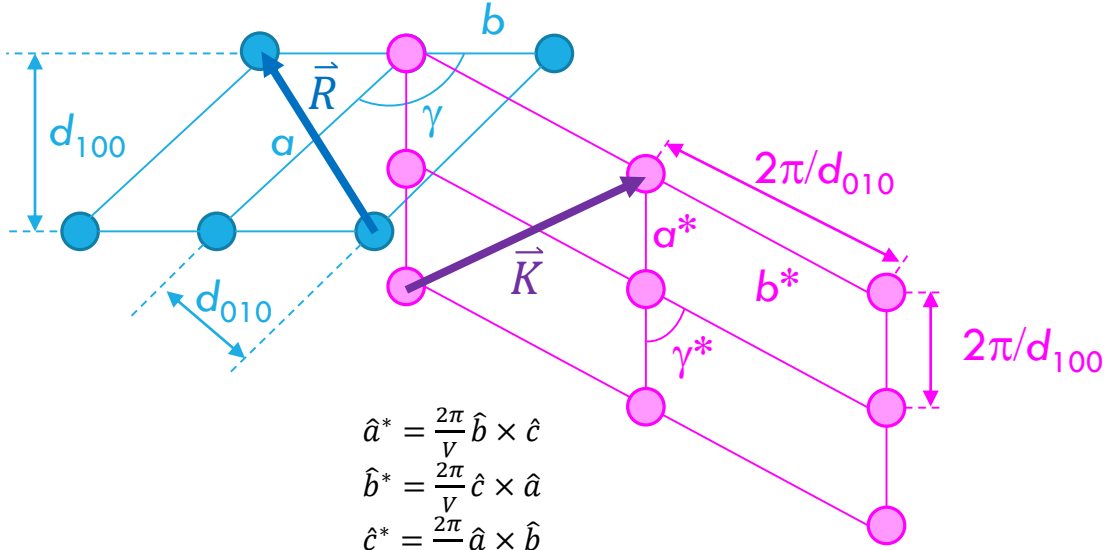
R. Pynn, Neutron scattering – A Primer, Los Alamos Science, Summer 1990



SCATTERING



Real space and Reciprocal space: $e^{i\vec{K}\cdot\vec{R}} = 1$



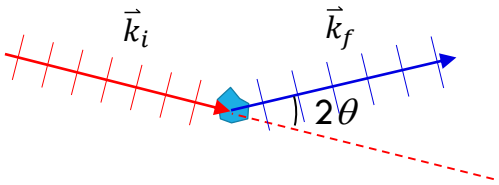
$$\hat{a}^* = \frac{2\pi}{V}\hat{b}\times\hat{c}$$
$$\hat{b}^* = \frac{2\pi}{V}\hat{c}\times\hat{a}$$
$$\hat{c}^* = \frac{2\pi}{V}\hat{a}\times\hat{b}$$

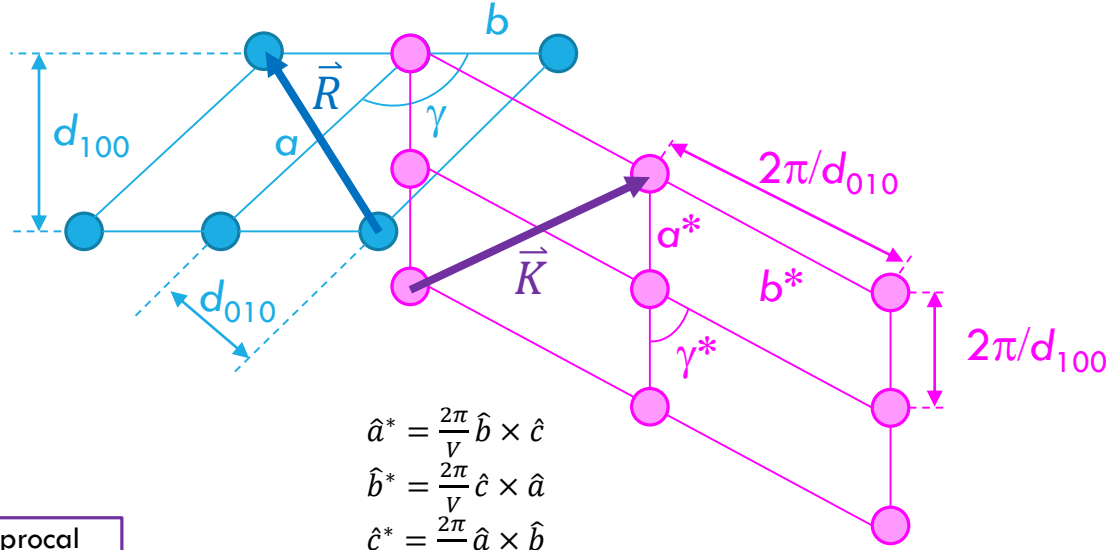
$$e^{i\vec{K}\cdot\vec{R}} = 1 \Rightarrow \hat{a}^*\cdot\hat{a} = \hat{b}^*\cdot\hat{b} = \hat{c}^*\cdot\hat{c} = 2\pi$$
$$\hat{a}^*\cdot\hat{b} = \ldots = 0$$

$\vec{K} = 2\pi\left(\frac{h}{a},\frac{k}{b},\frac{l}{c}\right)$ - reciprocal lattice vector

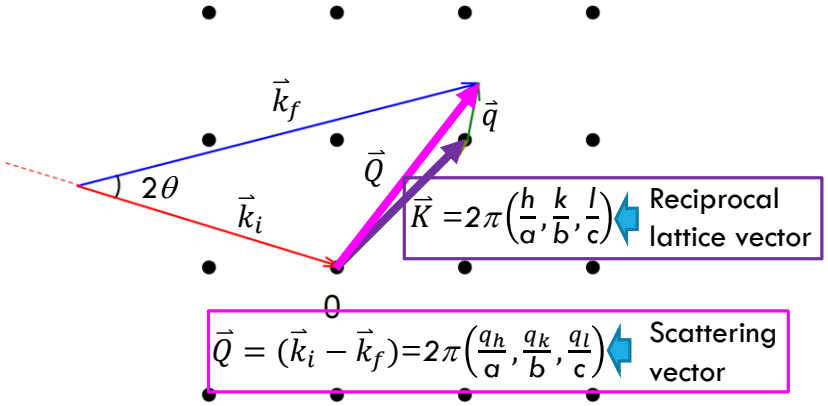
SCATTERING

Real space and Reciprocal space: $e^{i\vec{K}\cdot\vec{R}} = 1$





Reciprocal space



$\vec{K} = 2\pi\left(\frac{h}{a}, \frac{k}{b}, \frac{l}{c}\right)$ ⟸ Reciprocal lattice vector

$\vec{Q} = (\vec{k}_i - \vec{k}_f) = 2\pi\left(\frac{q_h}{a}, \frac{q_k}{b}, \frac{q_l}{c}\right)$ ⟸ Scattering vector

$k = 2\pi/\lambda$ –> larger λ better resolution

$$\hat{a}^* = \frac{2\pi}{V}\hat{b} \times \hat{c}$$
$$\hat{b}^* = \frac{2\pi}{V}\hat{c} \times \hat{a}$$
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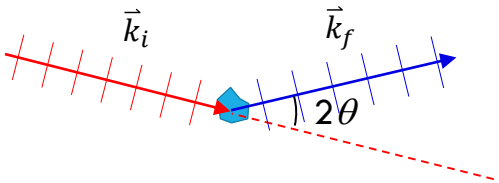
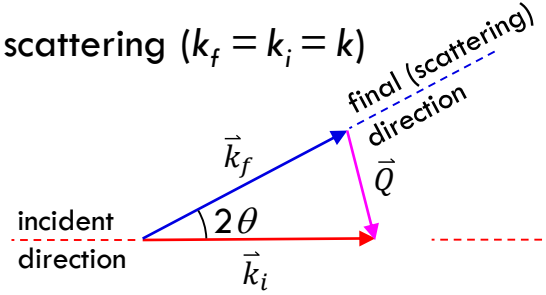
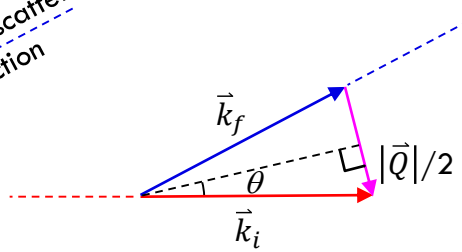
SCATTERING



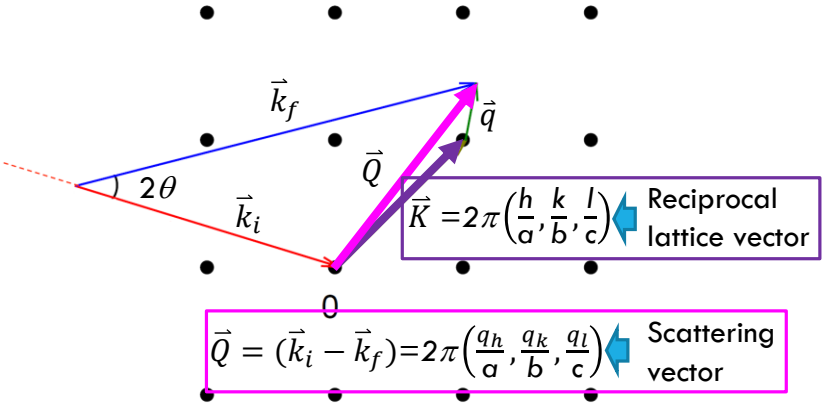
- Elastic scattering ($k_f = k_i = k$)





$$\sin\theta = \frac{Q/2}{k}$$

Reciprocal space



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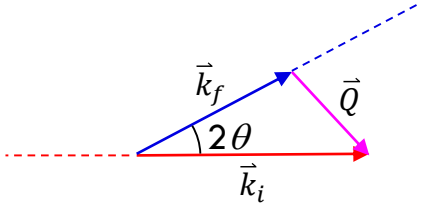
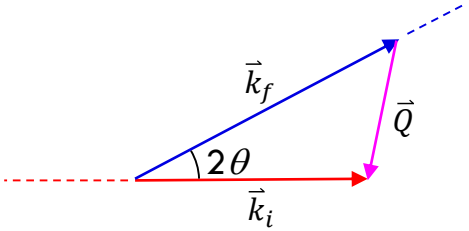
- Inelastic scattering ($k_f \neq k_i$)



Neutron losses energy ($k_f < k_i$)

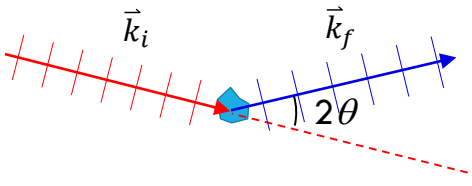


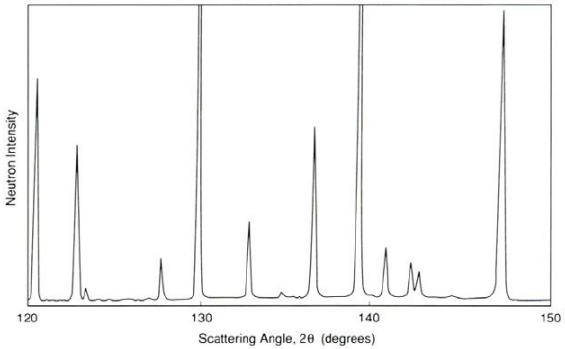
Neutron gains energy ($k_f > k_i$)

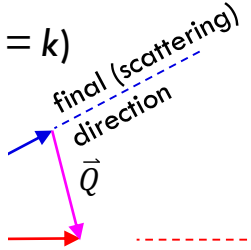
$$E = \hbar\omega = E_i - E_f = \frac{\hbar}{2m}\left(k_i^2 - k_f^2\right); \quad Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta$$

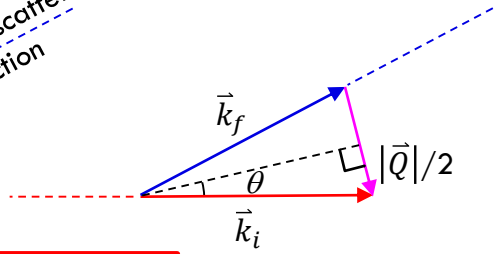
SCATTERING

- Elastic scattering ($k_f = k_i = k$)









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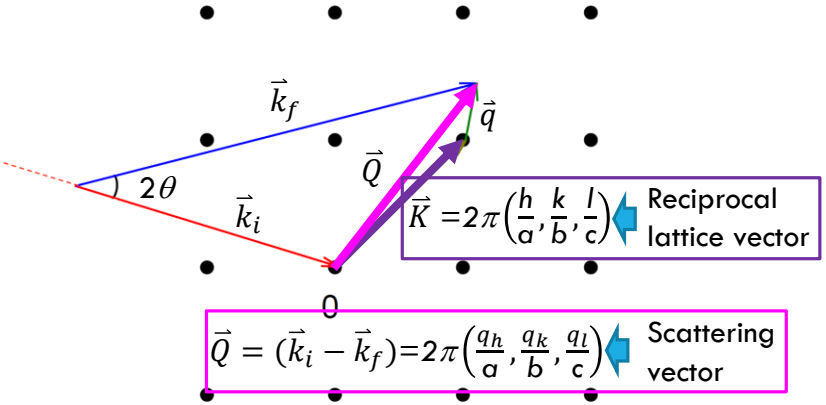
Reciprocal space



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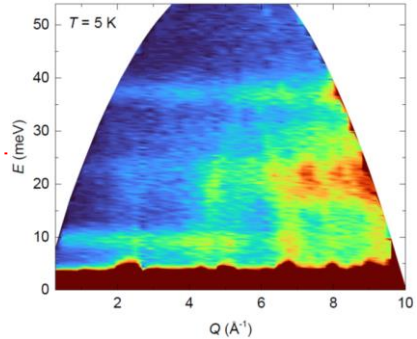

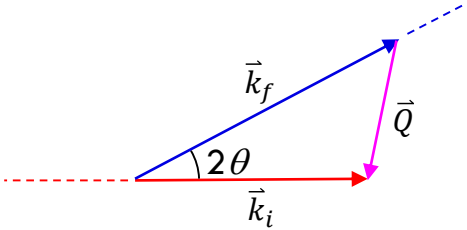

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SCATTERING FORMULAE

Basic quantity: ***differential cross section*** $\frac{d\sigma}{d\Omega} = \frac{\text{numbers of neutrons scattered per second into } d\Omega}{(\text{number of incident neutrons per area unit per second})\cdot d\Omega}$

- Incident neutron flux: Φ = number of incident neutrons per area unit per second
- Cross section: σ = total number of neutrons scattered per second/Φ
- Dimensions: $\left[\frac{d\sigma}{d\Omega}\right] = \frac{1}{[\Delta\Omega]\,[t]\,[\Phi]}$ = area ([ ] - dimensions)

Calculation of $\frac{d\sigma}{d\Omega}$ through Fermi's Golden Rule: $\frac{d\sigma}{d\Omega} = \frac{W}{\Phi}$

Transition rate: $W = \frac{2\pi}{\hbar}\left|\langle \vec{k}_f | V | \vec{k}_i \rangle\right|^2 \rho_f(E)$

matrix element (contains physics); interaction; density of final states

- $|k_i\rangle = \frac{1}{\sqrt{L^3}} e^{i\vec{k}_i\cdot\vec{r}}$
- $|k_f\rangle = \frac{1}{\sqrt{L^3}} e^{i\vec{k}_f\cdot\vec{r}}$

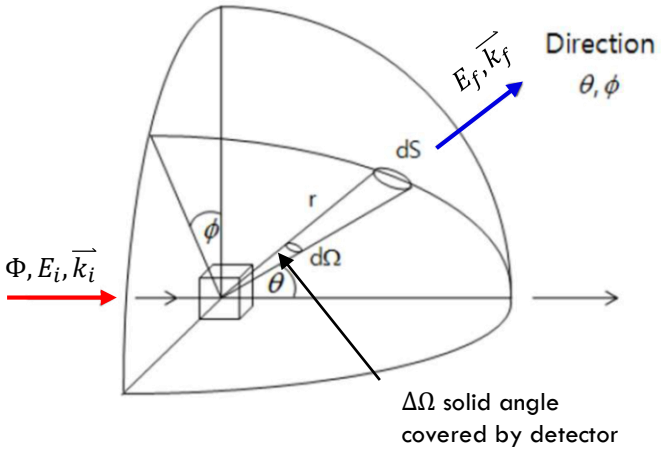
plane waves, normalized to sample size L (Born approximation)

- $\rho_f(E) = \left(\frac{L}{2\pi}\right)^3 \frac{d\vec{k}_f}{dE} = \left(\frac{L}{2\pi}\right)^3 k_f^2 \frac{dk_f}{dE} d\Omega = \left(\frac{L}{2\pi}\right)^3 \frac{m_n k_f}{\hbar^2} d\Omega$

density of states in *k*-space; $d\vec{k}_f = k_f^2\, dk_f\, d\Omega$; $\frac{dE}{dk_f} = \frac{\hbar^2 k_f}{m_n}$

Incident neutron flux: $\Phi = \frac{\text{velocity}}{L^3} = \frac{\hbar^2 k_i}{m_n L^3}$

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_i}\left(\frac{m_n L^3}{2\pi\hbar^2}\right)^2 \left|\langle \vec{k}_f | V | \vec{k}_i \rangle\right|^2$$

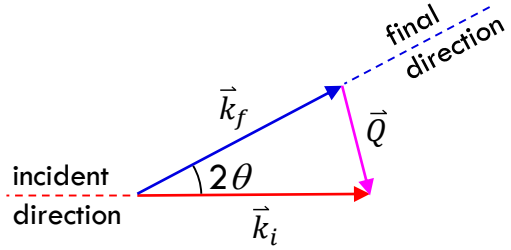


ELASTIC NUCLEAR SCATTERING

For elastic scattering: $k_i = k_f$

$$\frac{d\sigma}{d\Omega} = \frac{W}{\Phi} = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\int V e^{i(\vec{k}_i - \vec{k}_f)\cdot\vec{r}}\, d\vec{r}\right|^2 = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\int V e^{i\vec{Q}\cdot\vec{r}}\, d\vec{r}\right|^2$$

"Born approximation": taking scattered wave function as a plane wave



For short-range (nuclear) force, approximate "**point-like**" potential:

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b\,\delta(\vec{r} - \vec{R});$$

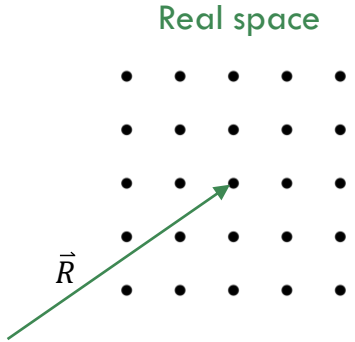
- Position of the nucleus: $\vec{R}$
- Scattering length b depends on the details of the nuclear structure and varies greatly (table in previous slide)

For **single nucleus:** $\frac{d\sigma}{d\Omega} = |b|^2$ –> Total cross section: $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi b^2$

Lattice of nuclei:

$$V(\vec{r}) = \frac{2\pi\hbar^2}{m_n} \sum_{\vec{R}} b_{\vec{R}}\,\delta(\vec{r} - \vec{R}); \quad b_{\vec{R}}: \text{scattering length of nucleus at site } \vec{R}$$

$$\frac{d\sigma}{d\Omega} = \left|\int \sum_{\vec{R}} b_{\vec{R}}\,\delta(\vec{r} - \vec{R})\, e^{i\vec{Q}\cdot\vec{r}} d\vec{r}\right|^2 = \left|\sum_{\vec{R}} b_{\vec{R}} e^{i\vec{Q}\cdot\vec{R}}\right|^2 \leftarrow \text{function of } \vec{Q}$$



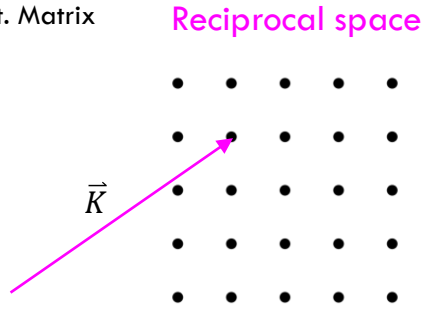
ELASTIC NUCLEAR SCATTERING

For most $\vec{Q}$, matrix elements are very small because phase factors from different nuclei cancel out. Matrix element is large only when $\vec{Q} = \vec{K}$, where $\vec{K}$ is "*reciprocal lattice vector*" defined as $e^{i\vec{K}\cdot\vec{R}} = 1$.

The constructive interference leads to a huge enhancement, i.e., "Brag peak"

Using $\left|\sum_{\vec{R}} e^{i\vec{Q}\cdot\vec{R}}\right|^2 = N\frac{(2\pi)^3}{v_0}\sum_{\vec{K}}\delta(\vec{Q}-\vec{K})$

- Total number of unit cells: N
- Volume of unit cell: v_0



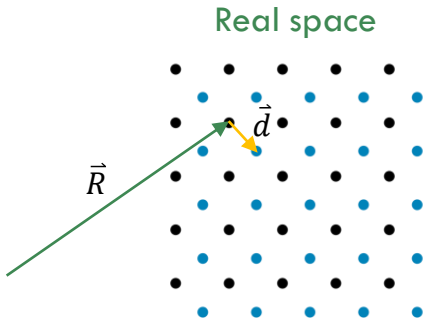
For all nuclei being identical:

$$\frac{d\sigma}{d\Omega} = b^2\frac{N(2\pi)^3}{v_0}\sum_{\vec{K}}\delta(\vec{Q}-\vec{K})$$

Nuclear Bragg diffraction for unit cell with several atoms with *basis vectors* $\vec{d}$

$$\frac{d\sigma}{d\Omega} = \frac{N(2\pi)^3}{v_0}\sum_{\vec{K}}\delta(\vec{Q}-\vec{K})\left|F_N(\vec{K})\right|^2,$$

where $F_N(\vec{K}) = \sum_{\vec{d}} e^{i\vec{Q}\cdot\vec{d}} b_{\vec{d}}$ is the "nuclear structure factor".



ELASTIC NUCLEAR SCATTERING

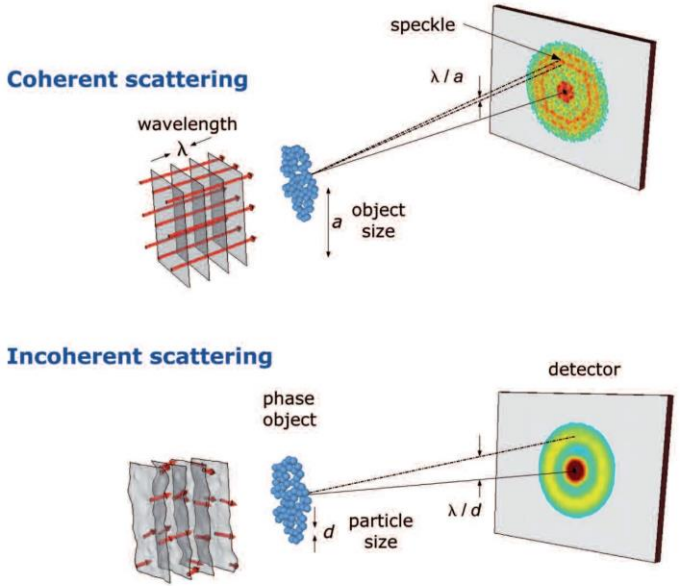
Two contributions

$$\frac{d\sigma}{d\Omega} = \underbrace{N\frac{(2\pi)^3}{v_0}\langle b\rangle^2 \sum_{\vec{K}} \delta\left(\vec{Q}-\vec{K}\right)}_{\text{“coherent” scattering}} + \underbrace{N[\langle b^2\rangle - \langle b\rangle^2]}_{\text{“incoherent” scattering}}$$

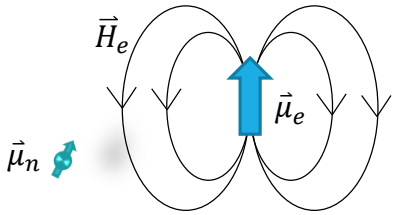
Coherent scattering carries information about the crystal structure and depends on $\vec{Q}$.

Incoherent scattering carries information about the grain sizes and is for large grains (even for most powders) almost uniform across the Q space.

Both contributions strongly differ between different nuclei – see table at the beginning of the presentation.



ELASTIC MAGNETIC SCATTERING



From the Fermi's Golden Rule, similar as in nuclear neutron scattering

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\langle \vec{k}_f m_f | H_m | \vec{k}_i m_i \rangle\right|^2 \text{ with } H_m = -\vec{\mu}_n \cdot \vec{H}_e$$

- Neutron spin state: $|m\rangle = |\pm 1\rangle$
- Electron magnetic field: $\vec{H}_e$

Vector potential of dipole field (classical electromagnetism)

$$\vec{A}_e = \frac{\mu_0}{4\pi}\frac{\vec{\mu}_e \times \vec{r}}{|\vec{r}^3|} = \frac{\mu_0}{4\pi}\vec{\mu}_e \times \vec{\nabla}\frac{1}{|\vec{r}|}\,; \quad \vec{H}_e = \vec{\nabla} \times \vec{A}_e = \frac{\mu_0}{4\pi}\vec{\nabla} \times \left(\vec{\mu}_e \times \vec{\nabla}\frac{1}{|\vec{r}|}\right)$$

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 (2\gamma\mu_N\mu_B)^2 \left|\left\langle \vec{k}_f m_f \left| \vec{\sigma}_n \cdot \vec{\nabla} \times \left(\vec{s}_e \times \vec{\nabla}\frac{1}{|\vec{r}|}\right)\right| \vec{k}_i m_i \right\rangle\right|^2$$

- Collecting all prefactors: $\left(\frac{m_n}{2\pi\hbar^2}\right)^2 (2\gamma\mu_N\mu_B)^2 \left(\frac{\mu_0}{4\pi}\right)^2 (4\pi)^2 = (\gamma r_0)^2$
- Classical electron radius: $r_0 = 2.8 \times 10^{-15}\text{m}$

Finally we obtain: $\frac{d\sigma}{d\Omega} = (\gamma r_0)^2 \left|\langle m_f | \vec{\sigma} \cdot \vec{s}_{e\perp} | m_i \rangle\right|^2$

neutron beam polarization

Using the relation:

$$\int \frac{d\vec{p}}{|\vec{p}|^2} e^{i\vec{p}\cdot\vec{r}} = 2\pi \int_0^\infty d|\vec{p}| \int_{-1}^1 e^{i|\vec{p}||\vec{r}|\cos\Theta} d(\cos\Theta)$$
$$= 2\pi \int_0^\infty d|\vec{p}| \frac{\sin|\vec{p}||\vec{r}|}{|\vec{p}||\vec{r}|} = \frac{2\pi^2}{|\vec{r}|}$$

The vector product can be rewritten as:

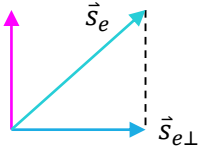
$$\vec{\nabla} \times \left(\vec{s}_e \times \vec{\nabla}\frac{1}{|\vec{r}|}\right) = \frac{1}{2\pi^2}\int \frac{d\vec{p}}{|\vec{p}|^2} \vec{\nabla} \times \left(\vec{s}_e \times \vec{\nabla}\right) e^{i\vec{p}\cdot\vec{r}}$$
$$= \frac{1}{2\pi^2}\int \vec{p} \times (\vec{s}_e \times \vec{p}) e^{i\vec{p}\cdot\vec{r}} d\vec{p}$$

And finally:

$$\left\langle \vec{k}_f \left| \vec{\nabla} \times \left(\vec{s}_e \times \vec{\nabla}\frac{1}{|\vec{r}|}\right)\right| \vec{k}_i \right\rangle = \frac{1}{2\pi^2}\int d\vec{r}\, e^{-i\vec{Q}\cdot\vec{r}} \int d\vec{p}\, \vec{p} \times (\vec{s}_e \times \vec{p}) e^{i\vec{p}\cdot\vec{r}}$$
$$= 4\pi \underbrace{\vec{Q} \times \left(\vec{s}_e \times \vec{Q}\right)}_{\equiv\, \vec{s}_{e\perp}}$$

When the relation:

$$\frac{1}{(2\pi)^2}\int d\vec{r}\, e^{-i(\vec{p}-\vec{Q})\cdot\vec{r}} = \delta\left(\vec{p} - \vec{Q}\right) \text{ is used.}$$



$\vec{s}_{e\perp}$ is magnetic component perpendicular to $\vec{Q}$!

ELASTIC MAGNETIC SCATTERING

For **unpolarized** neutrons we have to average across all neutron spin states $|m\rangle$. For convenience we choose neutron quantization axis $\hat{z} \parallel \vec{s}_{e\perp}$:

$$\langle m_f|\vec{\sigma}\cdot\vec{s}_{e\perp}|m_i\rangle = s_{e\perp}\langle m_f|\sigma_z|m_i\rangle = \begin{cases} s_{e\perp} \text{ if } m_f = m_i \\ 0 \text{ otherwise} \end{cases}$$

The cross section *for a* **single electron** at rest for an unpolarized neutron beam is:

$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2|s_{e\perp}|^2$; with $\vec{s}_{e\perp}$ the projection of the electron spin perpendicular to $\vec{Q}$

Generalization for **an atom**:

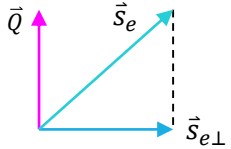
$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2|\hat{\eta}_\perp|^2\left|f(\vec{Q})\right|^2 = (\gamma r_0)^2\left[1-\left(\hat{\eta}\cdot\hat{Q}\right)^2\right]\left|f(\vec{Q})\right|^2;$$

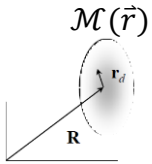
- **Magnetic form factor:** $f(\vec{Q}) = \frac{1}{2\mu_B}\int \mathcal{M}(\vec{r})e^{i\vec{Q}\cdot\vec{r}}$
- Magnetic dipole moment density due to unpaired electrons in the atom: $\vec{\mathcal{M}}(\vec{r}) = \mathcal{M}(\vec{r})\hat{\eta}$

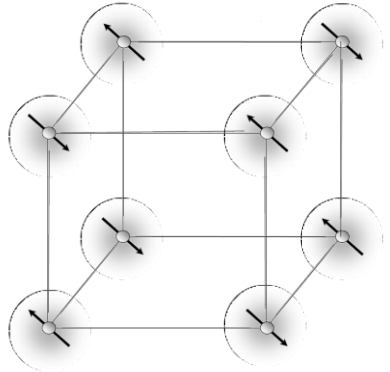
Generalization for **collinear magnets** (ordered):

$$\frac{d\sigma}{d\Omega} = (\gamma r_0)^2\left[1-\left(\hat{\eta}\cdot\hat{Q}\right)^2\right]N\frac{(2\pi)^3}{v_0}\sum_{\vec{K}_M}\delta\left(\vec{Q}-\vec{K}_M\right)\left|F_M\left(\vec{K}_M\right)\right|^2$$

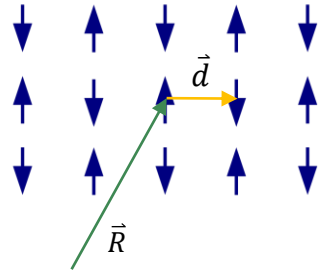
- Magnetic reciprocal lattice vector: $\vec{K}_M$
- Magnetic structure factor: $F_M(\vec{Q}) = \sum_{\vec{d}}(\pm)e^{i\vec{Q}\cdot\vec{d}}f_{\vec{d}}(\vec{Q})$, sign $\pm$ depend on orientation in respect to $\hat{\eta}$ at $\vec{d}$.





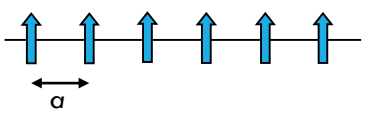


Real space



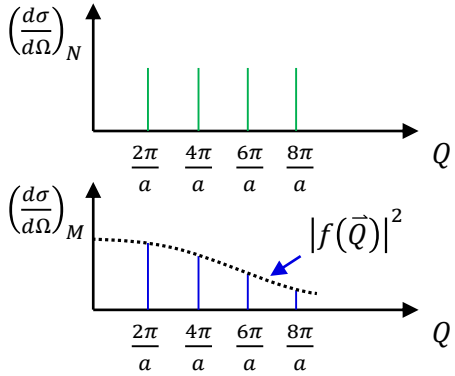
ELASTIC MAGNETIC SCATTERING

One-dimensional ferromagnet

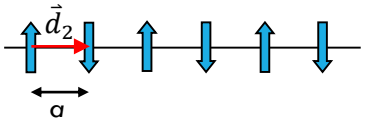


Nuclear mad magnetic unit cells are identical

$\vec{K}_M = \vec{K}_M = \frac{2\pi}{a} n$; where n is integer



One-dimensional antiferromagnet

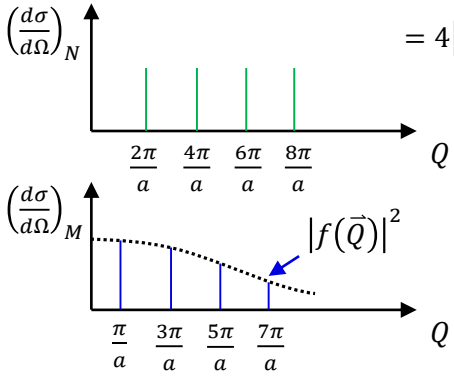


Basis: $\vec{d}_1 = 0, \vec{d}_2 = \hat{a}$,
Mag. structure factor: $f_{\vec{d}_2}(\vec{Q}) = -f_{\vec{d}_1}(\vec{Q})$

Magnetic unit cell is twice as large as nuclear unit cell

$\vec{K}_M = \frac{\pi}{a} n \neq \vec{K}_N = \frac{2\pi}{a} n \rightarrow |F_M|^2 = \left|\sum_{\vec{d}} e^{i\vec{Q}\cdot\vec{d}} f_{\vec{d}}(\vec{Q})\right|^2 = |f(\vec{Q})|^2 \left|+1 - e^{iQa}\right|^2$

$= 4|f(\vec{Q})|^2 \left(\sin\frac{Qa}{2}\right)^2 = \begin{cases} 4|f(\vec{Q})|^2 & \text{for } n \text{ odd} \\ 0 & \text{for } n \text{ even} \end{cases}$



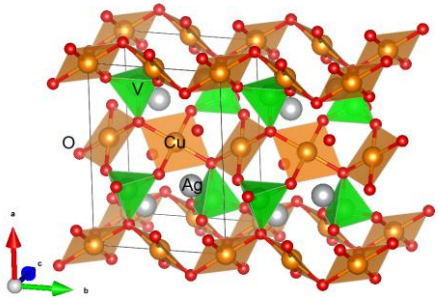
SCATTERING SUMMARY

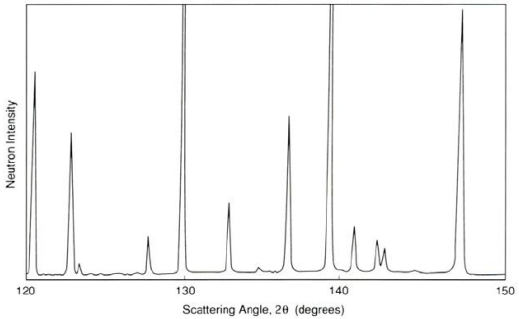
Nuclear scattering:

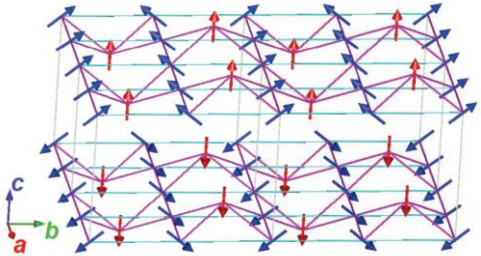
- Unit cell – position of reflections
- Position of the atoms in the unit cell – peak intensities
- Types of atoms – peak intensities

Magnetic scattering:

- Magnetic unit cell/modulation – peak position
- Type of magnetic order – peak position
- Orientation of magnetic moments – peak intensities
- Size of magnetic moments – peak intensities







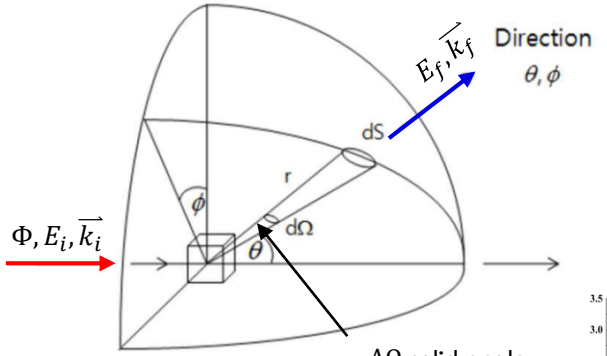
INELASTIC SCATTERING

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\text{numbers of neutrons scattered per second into } d\Omega \text{ \& } dE}{\Phi d\Omega dE}$$

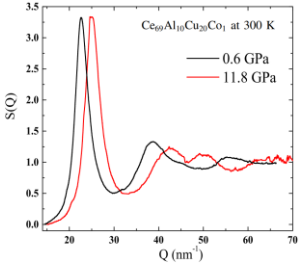
Conservation of energy

$$\frac{d^2\sigma(\vec{Q},E)}{d\Omega dE} = \frac{k_f}{k_i}\left|\langle \vec{k}_f m_f | V | \vec{k}_i m_i \rangle\right|^2 \delta(E_i - E_f + E)$$

Matrix element - contains physics



$\Delta\Omega$ solid angle covered by detector



Nuclear scattering

$$\frac{d^2\sigma}{d\Omega dE} = N\frac{k_f}{k_i}b^2 S(\vec{Q},\omega), \qquad \omega = E/\hbar$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty}\sum_{j,j'} e^{-i\omega t}\left\langle e^{i\vec{Q}\cdot\vec{r}_j(0)} e^{i\vec{Q}\cdot\vec{r}_{j'}(t)}\right\rangle dt$$

Magnetic scattering

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{g_n r_0}{2}\right)^2 f^2(\vec{Q}) e^{-2W(\vec{Q},T)}\frac{k_f}{k_i}\sum_{\alpha\beta}\left(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta\right)S^{\alpha\beta}(\vec{Q},\omega)$$

$$S^{\alpha\beta}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\sum_{j,j'} e^{i\vec{Q}\cdot(\vec{r}_j - \vec{r}_{j'})} e^{-i\omega t}\left\langle S^{\alpha}_{j'}(0) S^{\beta}_{j'}(t)\right\rangle dt$$

b – scattering length
N – number of atoms
S – scattering function, which is Fourier transforms of time dependent pair correlations functions of either atomic or spin component
f – magnetic form factor (Bessel functions, decays with Q)
There is no form factor for nuclear scattering, as the nucleus can be considered as a point compared to the neutron wavelength!
W – Debye-Waller factor accounts for attenuation of coherent neutron scattering due to thermal motion of atoms
$g_n = 1.913$
$r_0 = 2.8 \times 10^{-15}$ m is the classical electron radius

INELASTIC SCATTERING

Expressions for $S(\vec{Q},\omega)$ can be worked out for a number of cases e.g.:

- Excitation or absorption of one quantum of lattice vibrational energy (phonon)
- Various models for atomic motions in liquids and glasses
- Various models of atomic & molecular translational & rotational diffusion
- Rotational tunnelling of molecules
- Single particle motions at high momentum transfers
- Transitions between crystal field levels
- Magnons and other magnetic excitations such as spinons

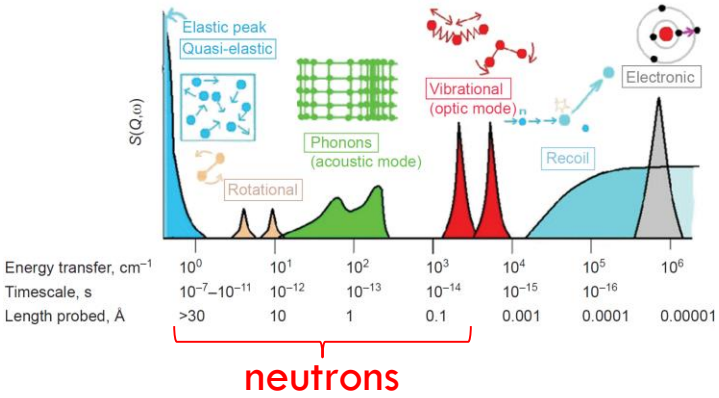
Inelastic neutron scattering reveals details of the shapes of interaction potentials in materials

Nuclear scattering function

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar N}\int_{-\infty}^{\infty}\sum_{j,j'} e^{-i\omega t}\,\langle e^{i\vec{Q}\cdot\vec{r}_j(0)} e^{i\vec{Q}\cdot\vec{r}_{j'}(t)}\rangle\, dt$$

Magnetic scattering function

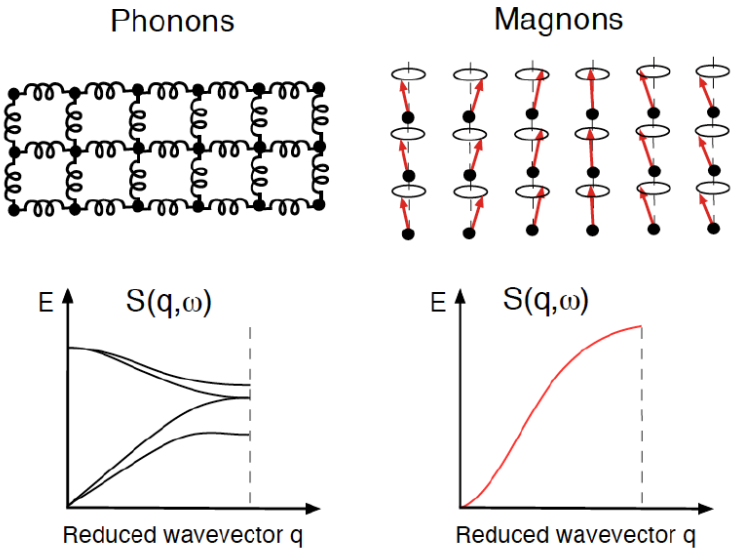
$$S^{\alpha\beta}(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\sum_{j,j'} e^{i\vec{Q}\cdot(\vec{r}_j-\vec{r}_{j'})} e^{-i\omega t}\,\langle S^{\alpha}_{j'}(0) S^{\beta}_{j'}(t)\rangle\, dt$$



INELASTIC SCATTERING

Lattice waves => collective acoustic and optic lattice vibrations – **Phonons**

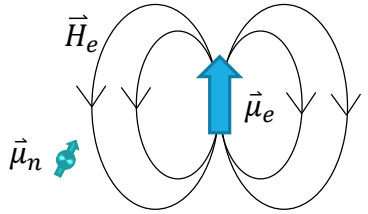
Spin-waves => collective magnetic excitations associated to the in-phase precession of the spin moments – **Magnons**



Phonons and magnons are quasi-particles (excitations) associated to the lattice and spin excitations

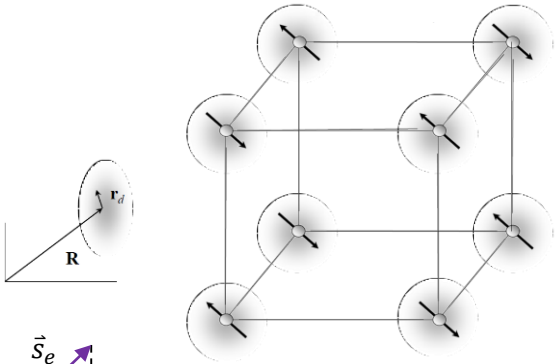
- They are characterized by a frequency ω and a wavevector $\vec{q}$
- Dispersion relationship between energy $\hbar\omega$ and momentum $\hbar\vec{q}$

MAGNETIC SCATTERING SUMMARY



The magnetic moment of the neutron interacts with *B* fields caused, for example, by unpaired electron spins in a material

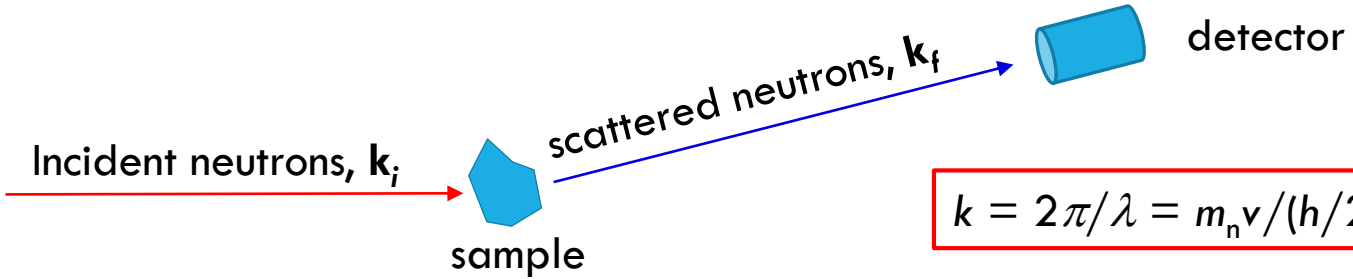
- Nuclear and magnetic scattering have similar magnitudes
- Both spin and orbital angular momentum of electrons contribute to *B*
- Magnetic scattering involves a form factor – FT of electron spatial distribution
  - Electrons are distributed in space over distances comparable to neutron wavelength
  - Elastic magnetic scattering of neutrons can be used to probe electron distributions
- Magnetic scattering depends *only* on component of *B* perpendicular to Q
- For neutrons spin polarized along a direction *z* (defined by applied H field):
  - Correlations involving B_z do not cause neutron spin flip
  - Correlations involving B_x or B_y cause neutron spin flip
- Coherent & incoherent nuclear scattering also affects spin polarized neutrons



INSTRUMENTATION AND FACILITIES

What are basic requirements to perform neutron scattering?

- A source of neutrons
- A method to choose the wavevector of the incident neutrons k_i
- A sample
- A method to determine the wavevector of the scattered neutrons k_f (not needed for elastic scattering)
- A neutron detector



NEUTRON PRODUCTION

Fission reactor:

- Chain reaction: neutron + ^{235}U –> Fission products + 2.4 neutrons (average)
- Very intense source (~10^{12} n/s per megawatt in research reactors)

Spallation source:

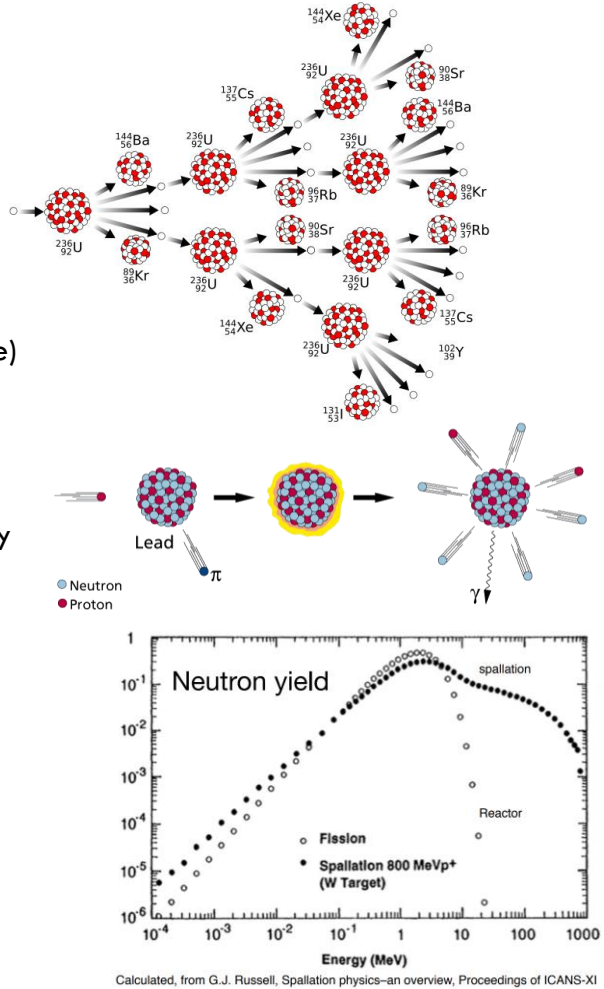
- No chain reaction – pulsed or continuous operation.
- Protons, accelerated by particle accelerator, strike a target made of heavy elements (e.g. mercury), where excited nuclei emit neutrons

Moderators:

- Neutrons have very high energies (~1 MeV) so they must be slowed down
  - Liquide graphite for hot neutrons
  - Water or heavy water for thermal neutrons
  - Liquid deuterium for cold neutrons

Neutron guides:

- From the source neutrons are guided to instruments by evacuated tubes
- These may be coated from the inside by supermirror multilayers



NEUTRON FACILITIES

Large scale facilities

- Instruments are arranged around the neutron source
- Complex operation requires support from a local contact
- A variety of sample environments (cryostats, magnets, …)
- One needs to apply for neutron beam time

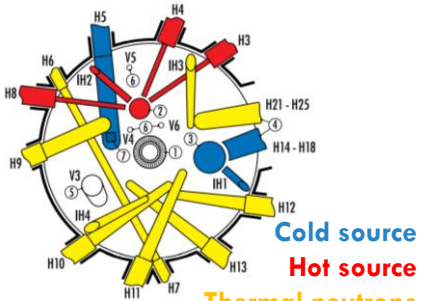
PSI, Villigen, Switzerland

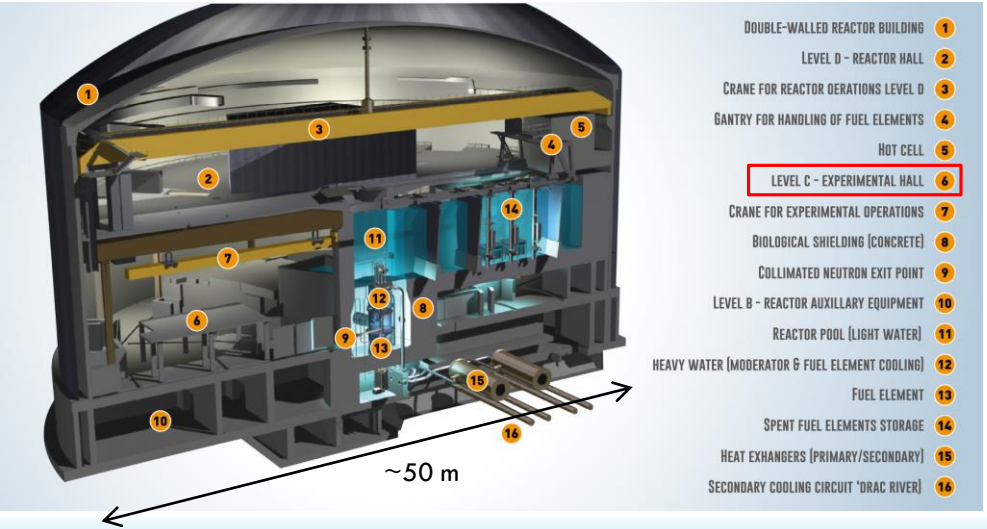
ILL, Grenoble, France

FISSION REACTOR

Example: Institute Laue Langevin (ILL), Grenoble, France

- Leading neutron research facility in the world
- Most intense flux in the moderator region 10^{15} $s^{-1}cm^{-2}$, thermal power of 58.3 MW

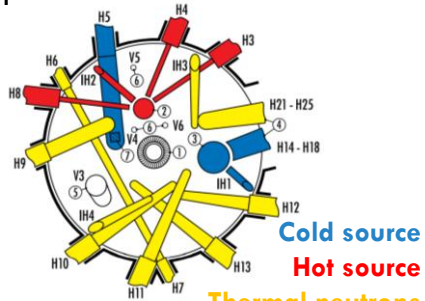




FISSION REACTOR

Example: Institute Laue Langevin (ILL), Grenoble, France

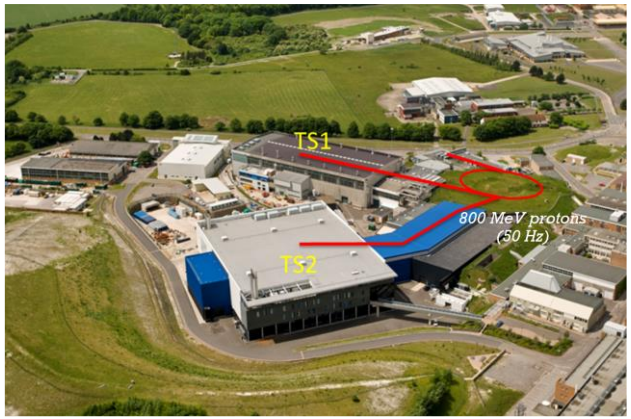
- Leading neutron research facility in the world
- Most intense flux in the moderator region 10^{15} $s^{-1}cm^{-2}$, thermal power of 58.3 MW
- About 40 instruments
- Two calls for proposals, one in spring and one in autumn



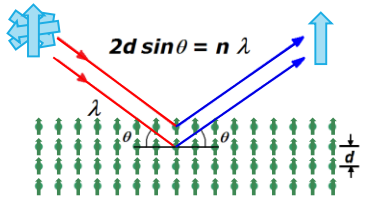
SPALLATION SOURCE

Example: ISIS, Rutherford Appleton Laboratory, UK

- Pulsed neutron spallation source
- Two targets
- Targets made of Tungsten is being replaced every 2 to 5 years
- 800 MeV protons at 50 Hz
- Short pulses of ~0.5 μs
- cca 25 instruments

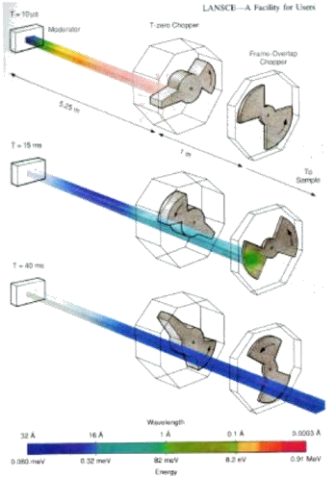


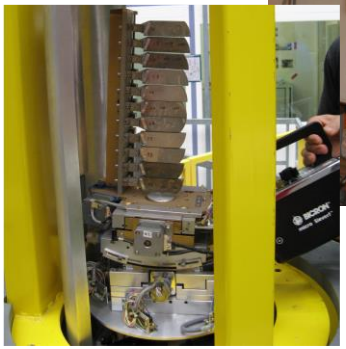
SELECTING THE WAVEVECTOR



Monochromators

- Bragg reflection of a single crystal
- Ferromagnetic crystal – polarized neutrons
- Neutron energy determined by physical limitations



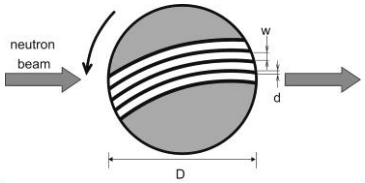


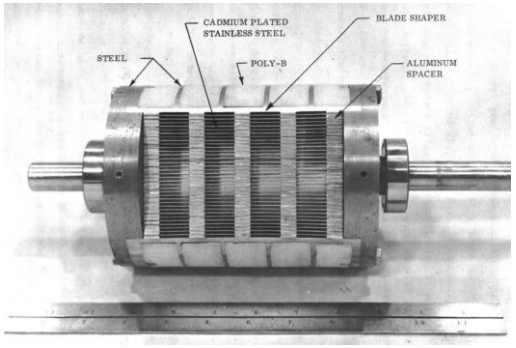
Disc choppers

- Disc with a hole
- Typically two one after another
- Very versatile, yet limited by rotation speed
- Better for lower energy neutrons

Fermi choppers

- Drum with a whole
- Sheets of absorbing material
- Curved – optimized for specific energy ranges
- Rotate up to 600 Hz
- Also for higher energy neutrons 15 meV to 2 eV

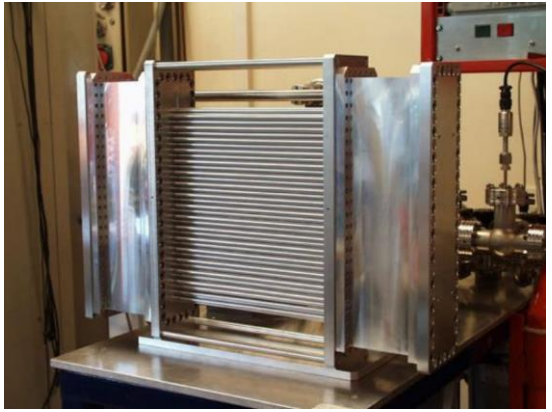




DETECTION

- $^3He + n \rightarrow {}^3H + p + 0.764$ MeV
- Ionization caused by triton and proton is collected on an electrode
- 70% of neutrons are absorbed when the product of:

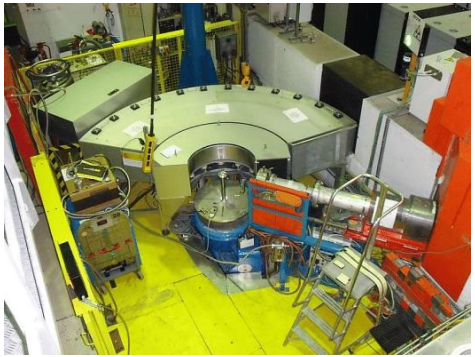
  gas pressure x thickness x neutron wavelength = 16 atm x cm x Å
- Modern detectors are often "position sensitive" – charge division is used to determine where the ionization cloud reached the cathode
- Most detectors need bulky shielding as they are also sensitive to γ-rays



The first MultiTube (in operation at LLB, France)

The IN5 Large area Multitube at ILL, France
12 modules of 32 tubes (+ 1 spare)
Distance sample – detector = 4 m
Each tube is 2.54 cm diameter, 3 m long
Volume of ^3He = 600 litres * Pressure (4.5 bar) = 2700 litres

HOW IS NEUTRON SCATTERING MEASURED?



Large penetration depth

- Large samples
- Massive detectors, shielding, …
- Slow movements of instruments

Powder

- Large samples – several grams
- Typically collect broad spectrum - fast
- Measure overlapping contributions from all phases

Single crystal

- Much larger samples compared to x-ray, SQUID, specific heat, …
- Detection of single reflections – slow
- Phase specific – by choosing which reflections are being measured

Time-of-Flight – pulsed source

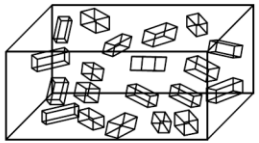
Monochromator – continuous source

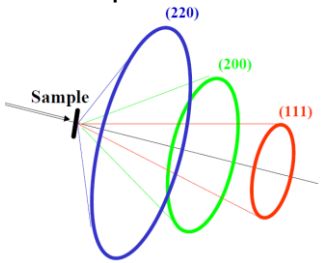
POWDER DIFFRACTOMETER

Powder = Many tiny crystals

- 1 cm^3 of 10 μm crystallites = 10^9 particles,
- 1 cm^3 of 1 μm crystallites = 10^{12} particles

All orientations of crystallites possible

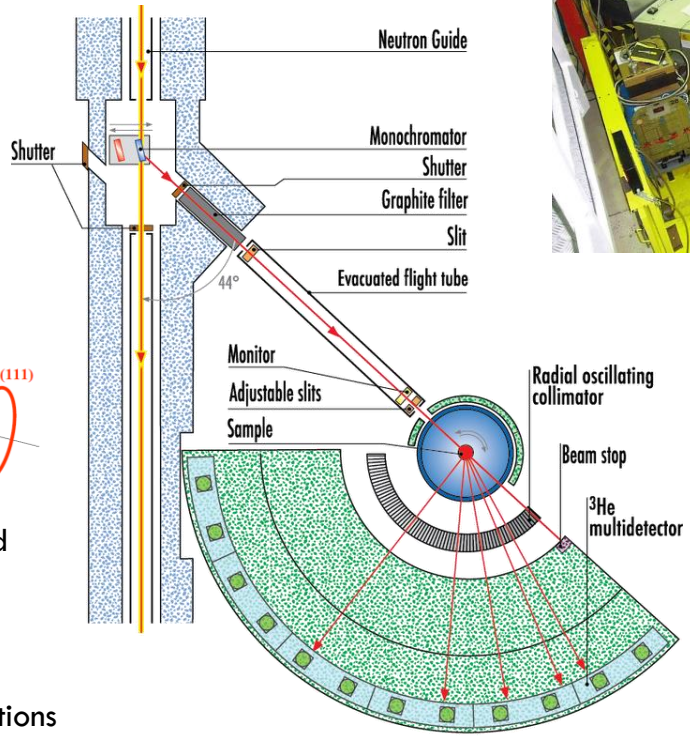


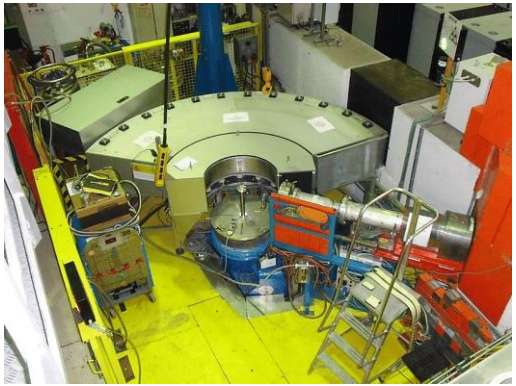


Single-crystal reciprocal lattice is smeared into spherical shells

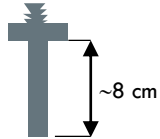
Typically data at all angles are collected simultaneously

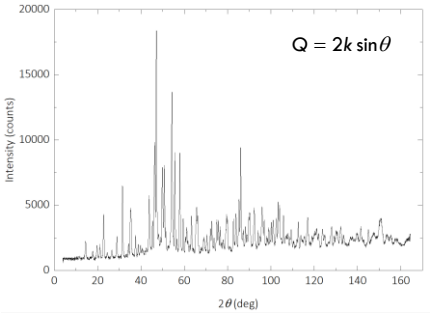
If several phases are present, all contributions sum up



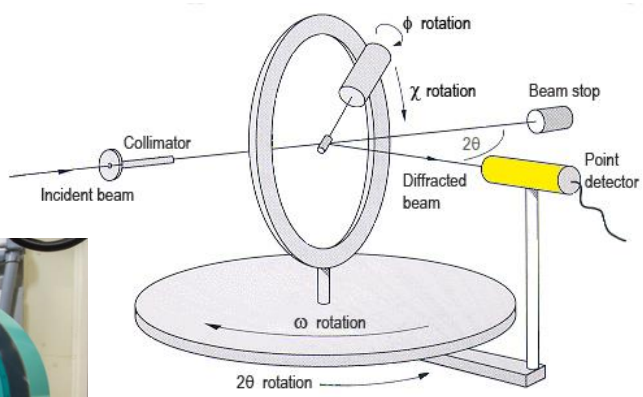


Sample container: Al, V





FOUR-CIRCLE DIFFRACTOMETER



Single crystal measurements

Four rotations are possible:

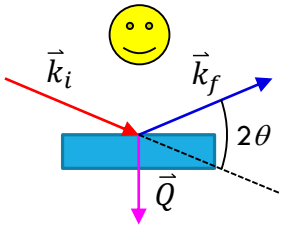
- 2θ – position of the detector in respect to incident beam
- ω – rotation of the crystal within the scattering plane
- ϕ - rotation of the crystal around the pin
- χ – rotation of the sample out of scattering plane

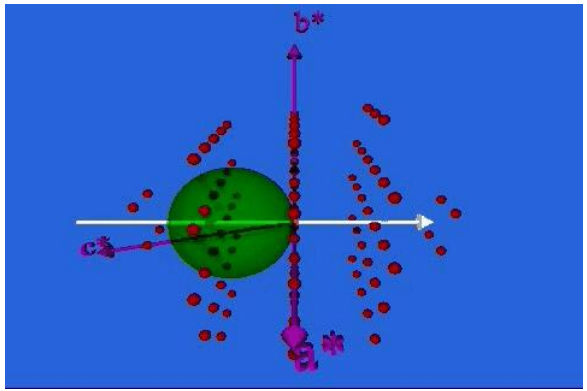
Sample glued or fixed by Al wires to an Al pin

At least crystal unit cell has to be known

Single crystal has to be aligned precisely to Bragg reflection – to start: 2θ is set for the strong reflection and then the corresponding direction is aligned by eye to bisect the incident and scattered beam, i.e., to point along Q vector

U-matrix connects the reciprocal space with ϕ, χ, and ω angles





TRIPLE AXIS SPECTROMETER

For single-crystals

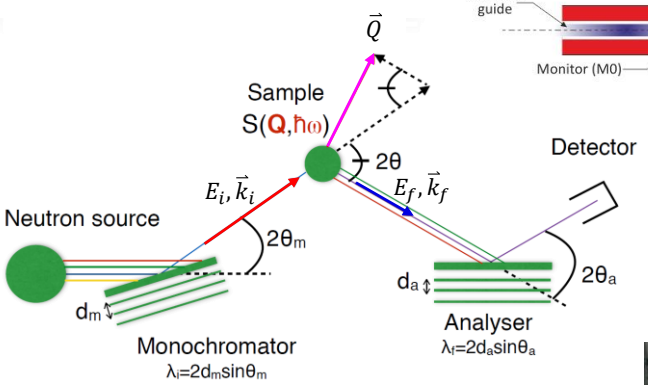
Explore energy transfer, i.e., dispersion relations

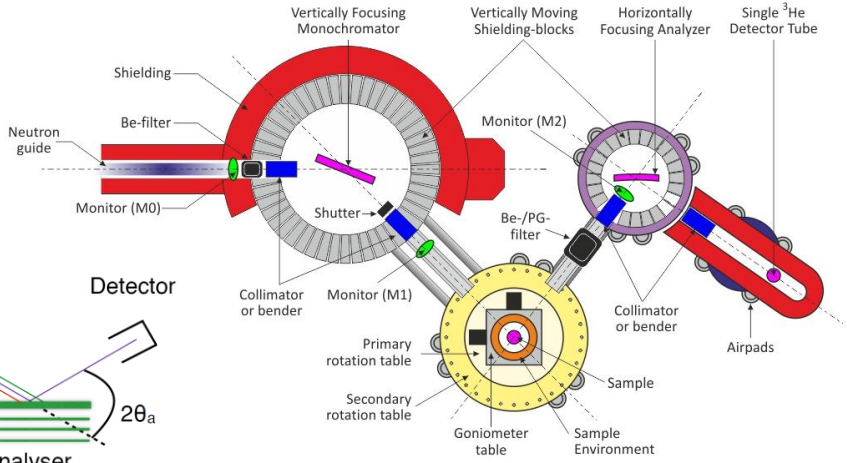
$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right)$$

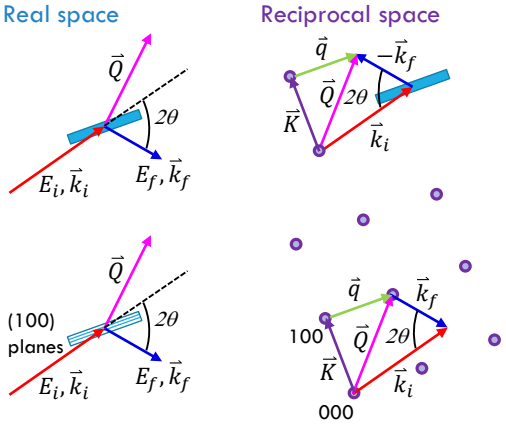
$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta$$

It allows measurement of the scattering function at any point in energy and momentum space physically accessible by the spectrometer

Typical limitation is the scattering plane







TIME OF FLIGHT SPECTROMETER

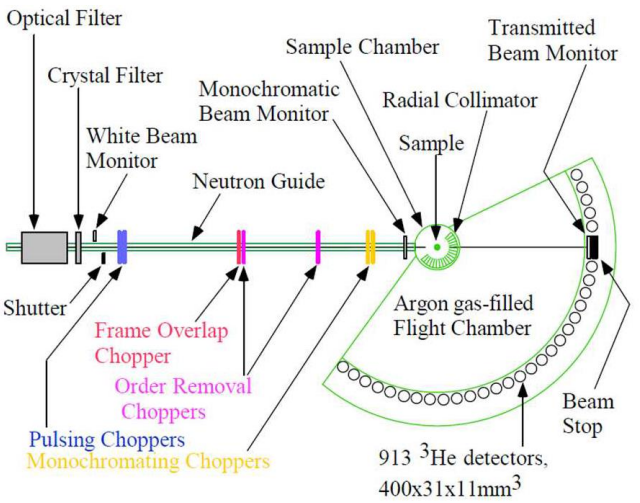
The time of flight spectrometer determines neutron energy by measuring its time of flight from one point to another.

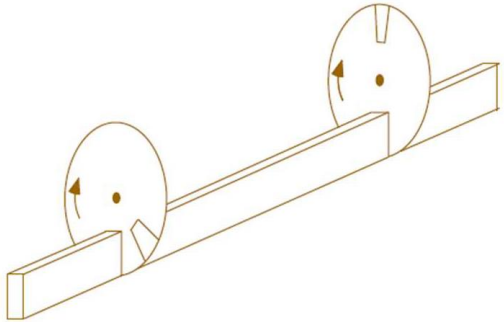
The beams are monochromated using several choppers rotating at different frequencies allowing only neutrons at certain velocity can pass through.

Since we know the distance between the sample and detectors and can measure the time for neutron to fly from the sample to the detector, we then can calculate the energy of scattered neutrons.

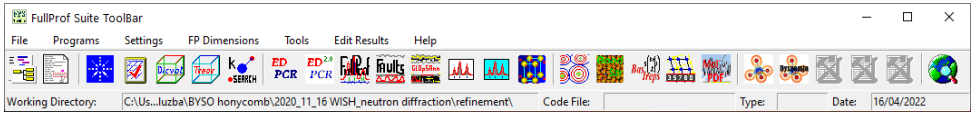
The direction of momentum can be figured out from the detector angle.

Time-of-flight method is powerful in that it can map out the huge Q-E space at a time.



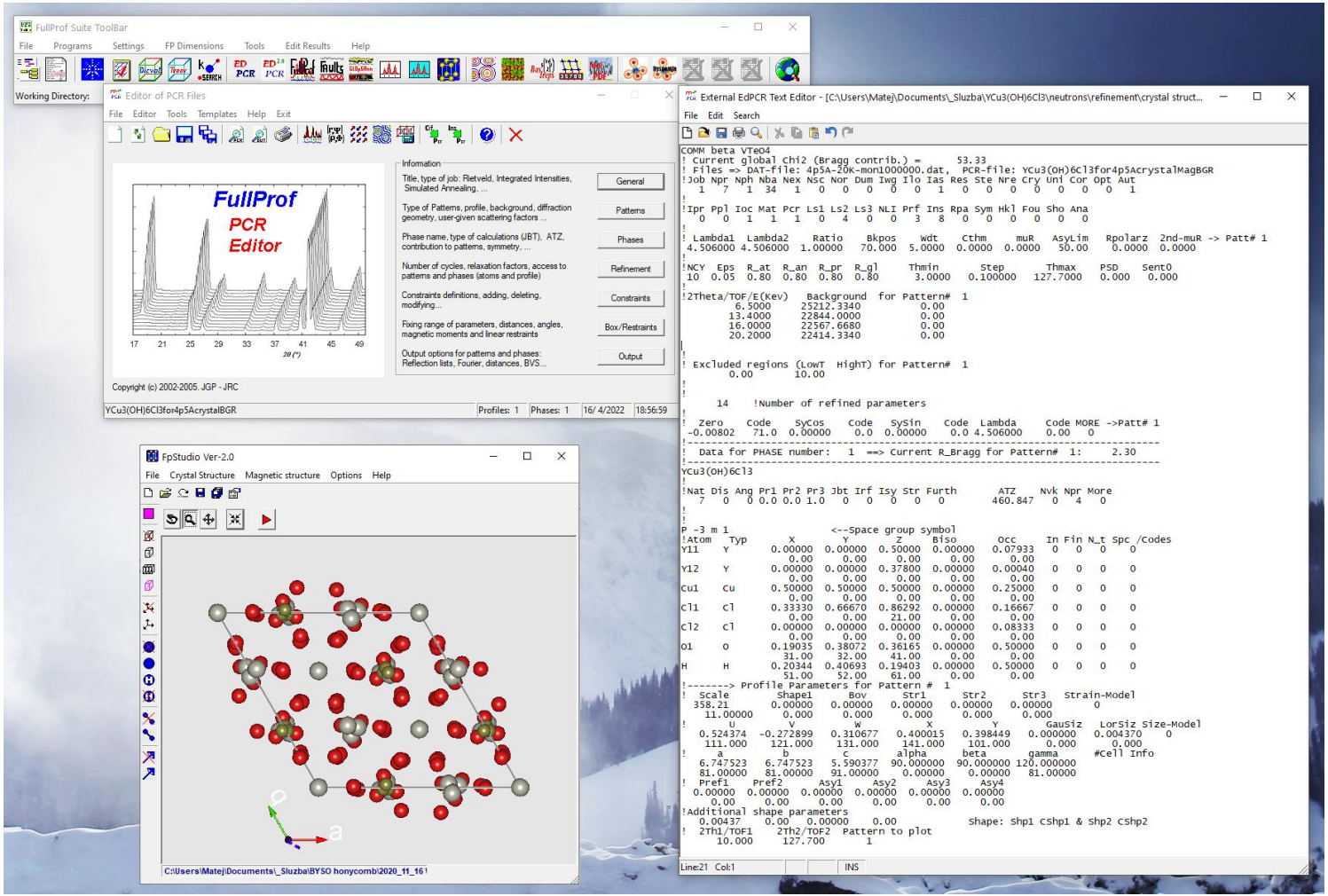


ANALYSIS - FULLPROF



Probably most widely used open source suite for analysis of diffraction data by Juan Rodríguez-Carvajal, Institut Laue-Langevin, Grenoble, France (http://www.ill.eu/sites/fullprof/)

- **WinPLOTR**: Programs for visualising powder diffraction patterns from a large number of instruments (almost each instrument has a unique file structure). Fitting independent peaks (CW and TOF)
- **FullProf**: Crystal and magnetic structure refinement, powder/single crystals, polarised neutrons, constant wavelength, TOF, energy dispersive, multiple patterns, simulated annealing for solving crystal and magnetic structures (integrated and profile intensities).
- **EdPCR**: Editor of the FullProf input control file
- **SuperCell/K_Search**: Program for searching propagation vectors
- **BasIREPS**: Program for calculating basis functions of irreducible representations of space groups. Useful for determining magnetic structures .
- **Fp_Studio**: Program for visualising crystal and magnetic structures
- And more: Fourier/GFourier and Bond_Str/GBond_Str. Fourier and distance/angle calculations; Check_Group: Program for getting the space group (powders and single crystals) Datared/GDatared: Program for single crystal data reduction; Mol_tpcr: console utility for creating Rigid body groups


FullProf Suite ToolBar
File Programs Settings FP Dimensions Tools Edit Results Help
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Information
Title, type of job: Rietveld, Integrated Intensities, Simulated Annealing, ...
General
Type of Patterns, profile, background, diffraction geometry, user-given scattering factors ...
Patterns
Phase name, type of calculations (JBT), ATZ, contribution to patterns, symmetry, ...
Phases
Number of cycles, relaxation factors, access to patterns and phases (atoms and profile)
Refinement
Constraints definitions, adding, deleting, modifying...
Constraints
Fixing range of parameters, distances, angles, magnetic moments and linear restraints
Box/Restraints
Output options for patterns and phases: Reflection lists, Fourier, distances, BVS...
Output
Copyright (c) 2002-2005, JGP - JRC
YCu3(OH)6Cl3for4p5AcrystalBGR
Profiles: 1
Phases: 1
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External EdPCR Text Editor - [C:\Users\Matej\Documents_Sluzba\YCu3(OH)6Cl3\neutrons\refinement\crystal struct...
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COMM beta YTeO4
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!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
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!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
0 0 1 1 1 0 4 0 0 3 8 0 0 0 0 0 0
! Lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz 2nd-muR -> Patt# 1
4.506000 4.506000 1.00000 70.000 5.0000 0.0000 0.0000 50.00 0.0000 0.0000
!NCY Eps R_at R_an R_pr R_gl Thmin Step Thmax PSD Sent0
10 0.05 0.80 0.80 0.80 0.80 3.0000 0.100000 127.7000 0.000 0.000
!2Theta/TOF/E(Kev) Background for Pattern# 1
6.5000 25212.3340 0.00
13.4000 22844.0000 0.00
16.0000 22567.6680 0.00
20.2000 22414.3340 0.00
! Excluded regions (LowT HighT) for Pattern# 1
0.00 10.00
14 !Number of refined parameters
! Zero Code SyCos Code SySin Code Lambda Code MORE ->Patt# 1
-0.00802 71.0 0.00000 0.0 0.00000 0.0 4.506000 0.00 0
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 2.30
YCu3(OH)6Cl3
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
7 0 0 0.0 0.0 1.0 0 0 0 0 0 460.847 0 4 0
P -3 m 1 <--Space group symbol
!Atom Typ X Y Z Biso Occ In Fin N_t Spc /Codes
Y11 Y 0.00000 0.00000 0.50000 0.00000 0.07933 0 0 0 0
0.00 0.00 0.00 0.00 0.00
Y12 Y 0.00000 0.00000 0.37800 0.00000 0.00040 0 0 0 0
0.00 0.00 0.00 0.00 0.00
Cu1 Cu 0.50000 0.50000 0.50000 0.00000 0.25000 0 0 0 0
0.00 0.00 0.00 0.00 0.00
Cl1 Cl 0.33330 0.66670 0.86292 0.00000 0.16667 0 0 0 0
0.00 0.00 21.00 0.00 0.00
Cl2 Cl 0.00000 0.00000 0.00000 0.00000 0.08333 0 0 0 0
0.00 0.00 0.00 0.00 0.00
O1 O 0.19035 0.38072 0.36165 0.00000 0.50000 0 0 0 0
31.00 32.00 41.00 0.00 0.00
H H 0.20344 0.40693 0.19403 0.00000 0.50000 0 0 0 0
51.00 52.00 61.00 0.00 0.00
!-------> Profile Parameters for Pattern # 1
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
358.21 0.00000 0.00000 0.00000 0.00000 0.00000 0
11.00000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
0.524374 -0.272899 0.310677 0.400015 0.398449 0.000000 0.004370 0
111.000 121.000 131.000 141.000 101.000 0.000 0.000
! a b c alpha beta gamma #Cell Info
6.747523 6.747523 5.590377 90.000000 90.000000 120.000000
81.00000 81.00000 91.00000 0.00000 0.00000 81.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00
!Additional shape parameters
0.00437 0.00 0.00000 0.00 Shape: Shp1 CShp1 & Shp2 CShp2
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
10.000 127.700 1
Line:21 Col:1
INS
FpStudio Ver-2.0
File Crystal Structure Magnetic structure Options Help
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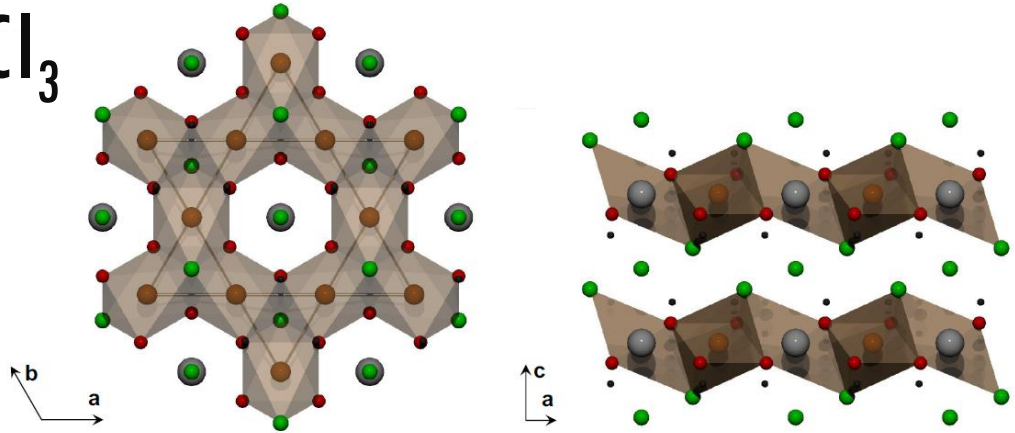
EXAMPLE: $YCu_3(OH)_6Cl_3$



Starting point

- Crystal structure
- Basic magnetic properties (Cu^{2+} $S = ½$)
- Magnetic ordering at 15 K

Our approach to determine the magnetic order

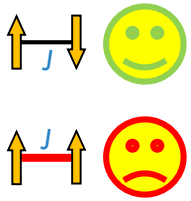
- Experiment: Powder neutron diffraction to see if long-range magnetic order develops
- Analysis: Indexation of magnetic reflections, attempt to refine the magnetic structure

A. ZORKO *et al.* PHYSICAL REVIEW B **99**, 214441 (2019)
A. ZORKO *et al.* PHYSICAL REVIEW B **100**, 144420 (2019)
T. ARH *et al.* PHYSICAL REVIEW LETTERS **125**, 027203 (2020)

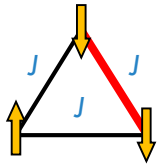
KAGOME LATTICE IN $YCu_3(OH)_6Cl_3$

Kagome lattice Cu^{2+} $S = ½$

Antiferromagnetic interaction

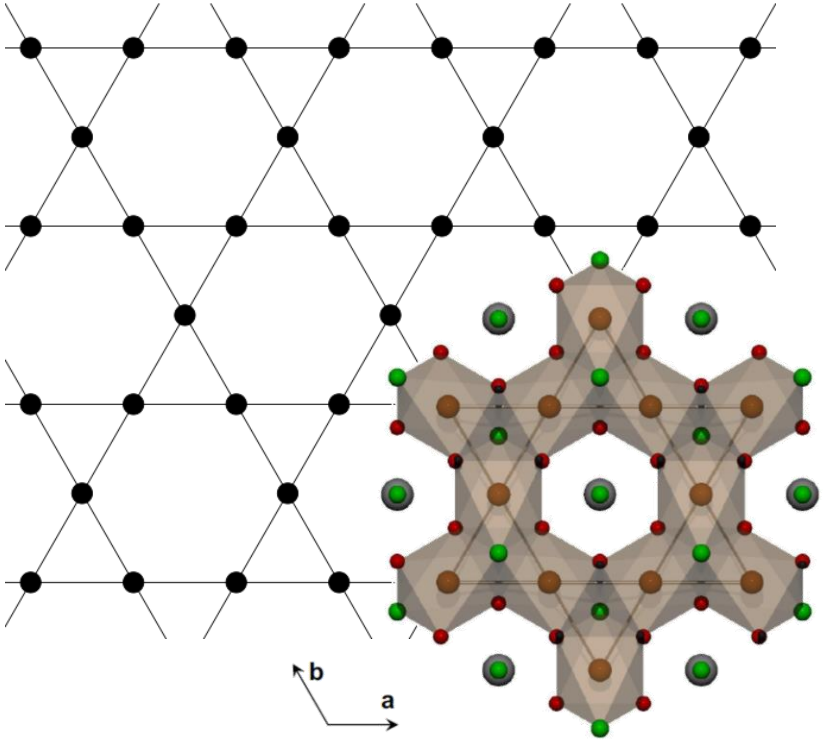


Geometric frustration



Without anisotropies spin-liquid ground state is expected

Anisotropies may stabilize magnetic order

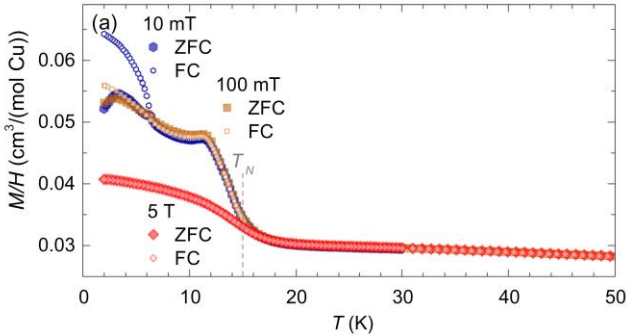


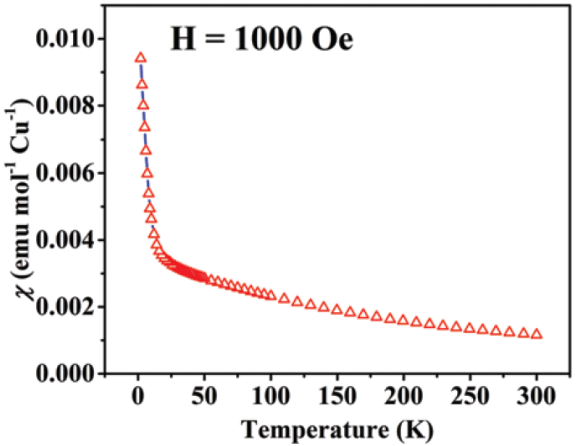
MAGNETIC SUSCEPTILIBTY

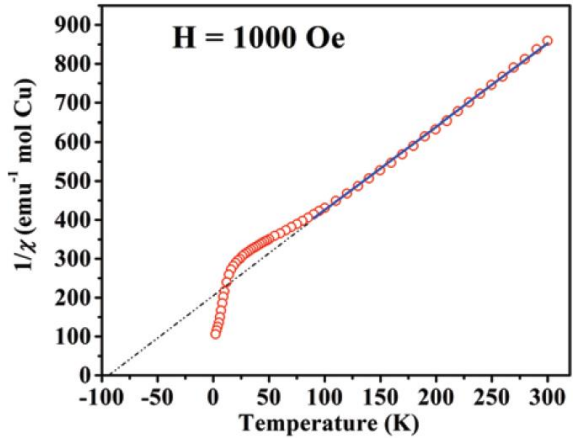
High-temperature imply Curie Weiss temperature $\theta_{CW} = -99$ K strong interactions

Magnetic order develops at $T_N = 15$ K

Strong frustration $T_N/\theta_{CW} = 0.15$





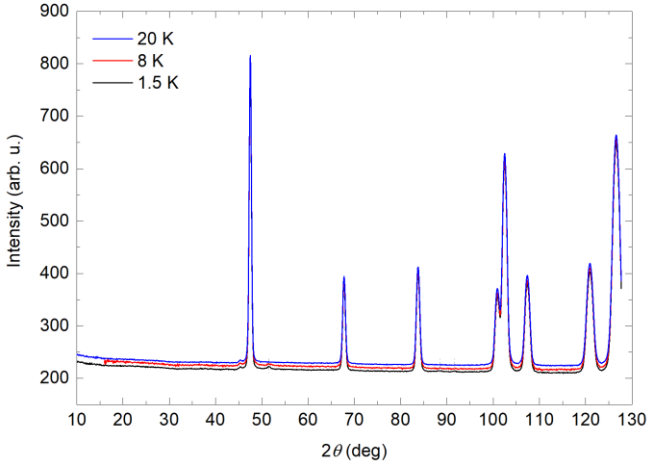


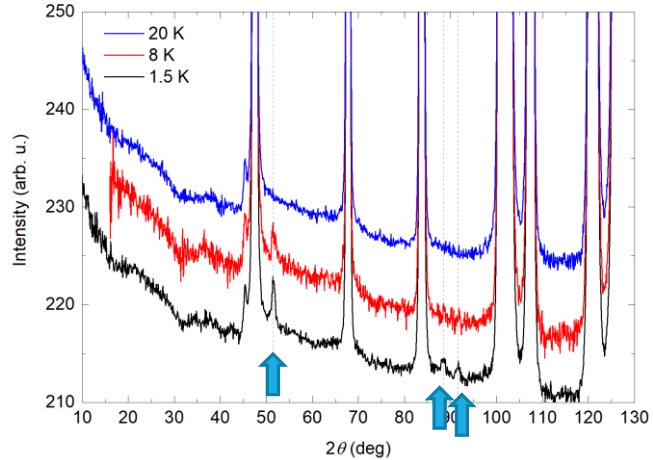
POWDER DIFFRACTION

We performed powder diffraction at several temperatures above and below T_N

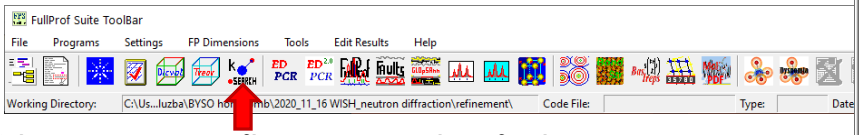
At 8 and 1.5 K additional reflections emerge

A clear sign of magnetic order





K VECTOR SEARCH



When magnetic reflections are identified, one can start thinking about the magnetic order.

Begin with identification of magnetic ordering (wave) vector (K vector) using *K-search*.

Input:

- Space group
- Lattice parameters
- Neutron wavelength and tolerance
- Incommensurability/Commensurability
- K range
- Precision

Output:

- List of 10 best solutions
- Calculated and observed angles for the best solution

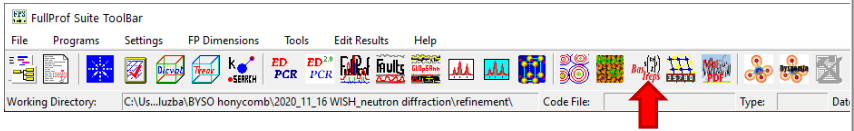
INPUT

```
TITLE YCu3(OH)6Cl3
SPGR  P -3 m 1
CELL   6.747752   6.747752   5.595633  90.000000  90.000000 120.000000
SHORT-OUTPUT
K_INCOMMENSURATE
CWTOL        4.506000    0.800
K_RANGE    0.33  0.34    -0.33  -0.34    0.0  1.0
K_DIV         100          100          100
! peak_position  peak_intensity  peak_background
2THETA_LIST    3
       51.56047     1402.85718      904.21821
       88.47054     1050.92730      915.74973
       91.56037     1060.22460      915.25976
```

OUTPUT

```
=> List of the best 10 solutions for  3 satellites

     Kx          Ky          Kz          R-factor
  0.000000    0.000000    0.500000       0.045223
  0.330700   -0.330000    0.030000       0.368579
  0.330600   -0.330000    0.030000       0.368635
  0.330500   -0.330000    0.030000       0.368699
  0.330400   -0.330000    0.030000       0.368755
  0.330300   -0.330000    0.030000       0.368829
  0.330200   -0.330000    0.030000       0.368900
  0.330100   -0.330000    0.030000       0.368966
  0.330000   -0.330000    0.030000       0.369022
  0.330800   -0.330000    0.030000       0.373744

=> A probable solution is the special kvector ks =(  0.0000  0.0000  0.5000)
=> The corresponding R-factor is:       0.0452


=> List of satellites (hkl)+(Kx,Ky,Kz) for the best solution:

         Kx= 0.0000    Ky= 0.0000    Kz= 0.5000

  H  K  L   n     D*(cal)     D*(obs)     2Th(cal)    2Th(obs)  2Th(obs-cal)
  ------------------------------------------------------------------------
  1  0  1   1      0.1930      0.1930     51.5627     51.5605      -0.0023
  2 -1  1   1      0.3096      0.3096     88.4478     88.4705       0.0227
  1  0 -1   1      0.3180      0.3181     91.5359     91.5604       0.0245

=>  Best R-factor:  0.0452 %  for propagation vector:
                              k  = (  0.0000  0.0000  0.5000)

              Total CPU-Time
```

REPRESENTATION ANALYSIS



If positions of the observed magnetic reflections match the calculated ones, i.e., *if the derived magnetic wave vector is correct, one can try to refine magnetic structure.*

Starting point is **representation analysis** – the crystal-structure space group and magnetic wave vector impose symmetry restrictions for possible magnetic structures (in case of second-order magnetic transition) – using *BasIreps*.

One can derive magnetic group (little group) and its possible irreducible representations (IRR), on of which should in principle describe the emergent magnetic order.

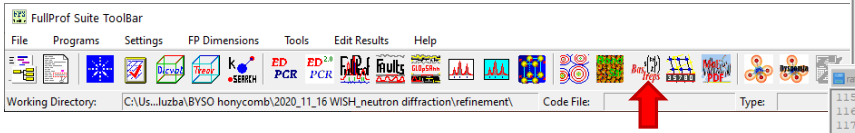
INPUT

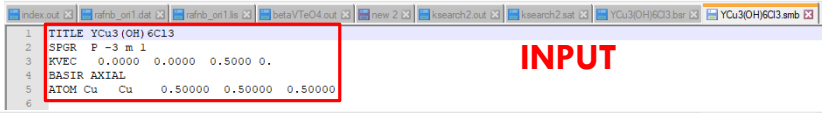
```
TITLE YCu3(OH)6Cl3
SPGR  P -3 m 1
KVEC   0.0000   0.0000   0.5000 0.
BASIR AXIAL
ATOM Cu   Cu    0.50000   0.50000   0.50000
```

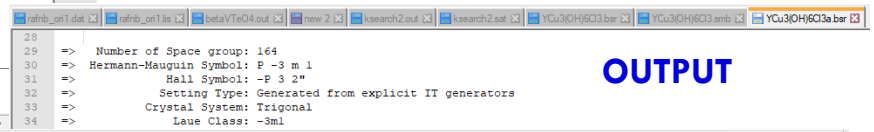
OUTPUT

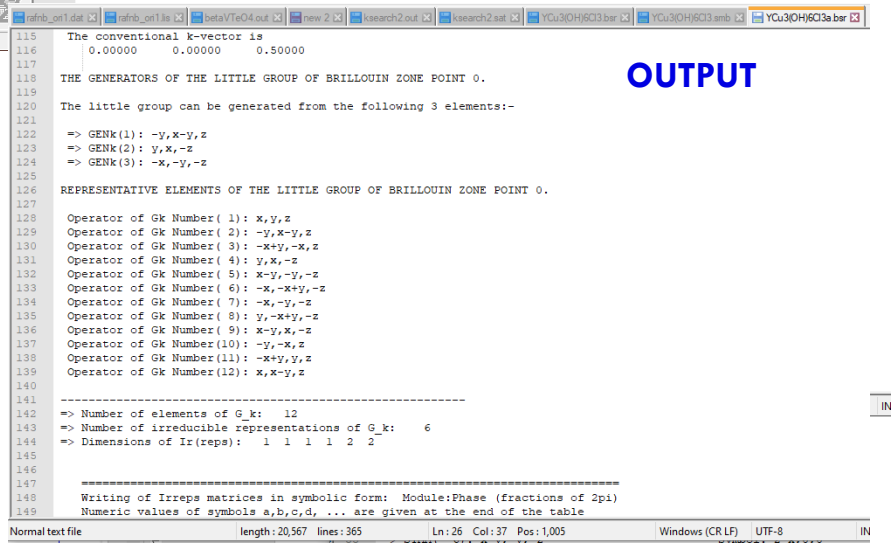
```
=>  Number of Space group: 164
=>  Hermann-Mauguin Symbol: P -3 m 1
=>            Hall Symbol: -P 3 2"
=>           Setting Type: Generated from explicit IT generators
=>         Crystal System: Trigonal
=>             Laue Class: -3ml
=>            Point Group: -3m
=>        Bravais Lattice: P
=>         Lattice Symbol: hP
=>  Reduced Number of S.O.:   6
=>    General multiplicity:  12
=>          Centrosymmetry: Centric (-1 at origin)
=>  Generators (exc. -1&L):   2
=>         Asymmetric unit:  0.000 <= x <=  0.667
                             0.000 <= y <=  0.333
                             0.000 <= z <=  1.000
=> Centring vectors:  0

=> List of all Symmetry Operators and Symmetry Symbols

=> SYMM(  1): x,y,z                              Symbol: 1
=> SYMM(  2): -y,x-y,z                           Symbol: 3+ 0,0,z
=> SYMM(  3): y,x,-z                             Symbol: 2 x,x,0
=> SYMM(  4): -x+y,-x,z                          Symbol: 3- 0,0,z
=> SYMM(  5): -x,-x+y,-z                         Symbol: 2 0,y,0
=> SYMM(  6): x-y,-y,-z                          Symbol: 2 x,0,0
=> SYMM(  7): -x,-y,-z                           Symbol: -1 0,0,0
=> SYMM(  8): y,-x+y,-z                          Symbol: -3+ 0,0,z; 0,0,0
=> SYMM(  9): -y,-x,z                            Symbol: m x,-x,z
=> SYMM( 10): x-y,x,-z                           Symbol: -3- 0,0,z; 0,0,0
=> SYMM( 11): x,x-y,z                            Symbol: m 2x,x,2z
=> SYMM( 12): -x+y,y,z                           Symbol: m x,2x,z
```

REPRESENTATION ANALYSIS









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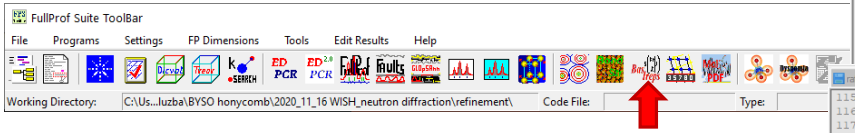

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KVEC   0.0000  0.0000  0.5000 0.
BASIR AXIAL
ATOM Cu   Cu    0.50000  0.50000  0.50000
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OUTPUT

```
=>   Number of Space group: 164
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=>            Hall Symbol: -P 3 2"
=>           Setting Type: Generated from explicit IT generators
=>         Crystal System: Trigonal
=>             Laue Class: -3ml
```
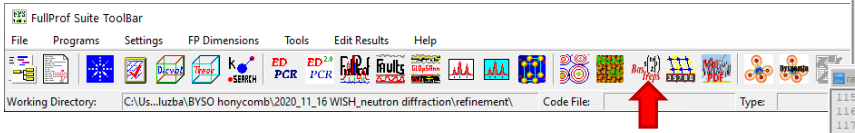

OUTPUT

```
 The conventional k-vector is
    0.00000     0.00000     0.50000

THE GENERATORS OF THE LITTLE GROUP OF BRILLOUIN ZONE POINT 0.

The little group can be generated from the following 3 elements:-
```

OUTPUT

```
 ===============

=> No. of sites:    1

=> Calculation for axial vectors

=> List of atoms within a primitive unit cell:
                X       Y       Z           for site:  1
-> Cu_1    :   0.5000  0.5000  0.5000  : (x,y,z)
-> Cu_2    :  -0.5000  0.0000  0.5000  : (-y,x-y,z)
-> Cu_3    :   0.0000 -0.5000  0.5000  : (-x+y,-x,z)

 ==========================
 CALCULATIONS FOR SITE : 1
 ==========================

=> Decomposition of the Magnetic/Mechanic representation:

-> GAMMA(Magnetic):   2 Irep_k( 2) + 1 Irep_k( 4) + 3 Irep_k( 5)

=> Atomic components of the BASIS FUNCTIONS using PROJECTION OPERATORS:
                Calculation for SITE number:  1
            (Only non-null functions are written)
```

REPRESENTATION ANALYSIS



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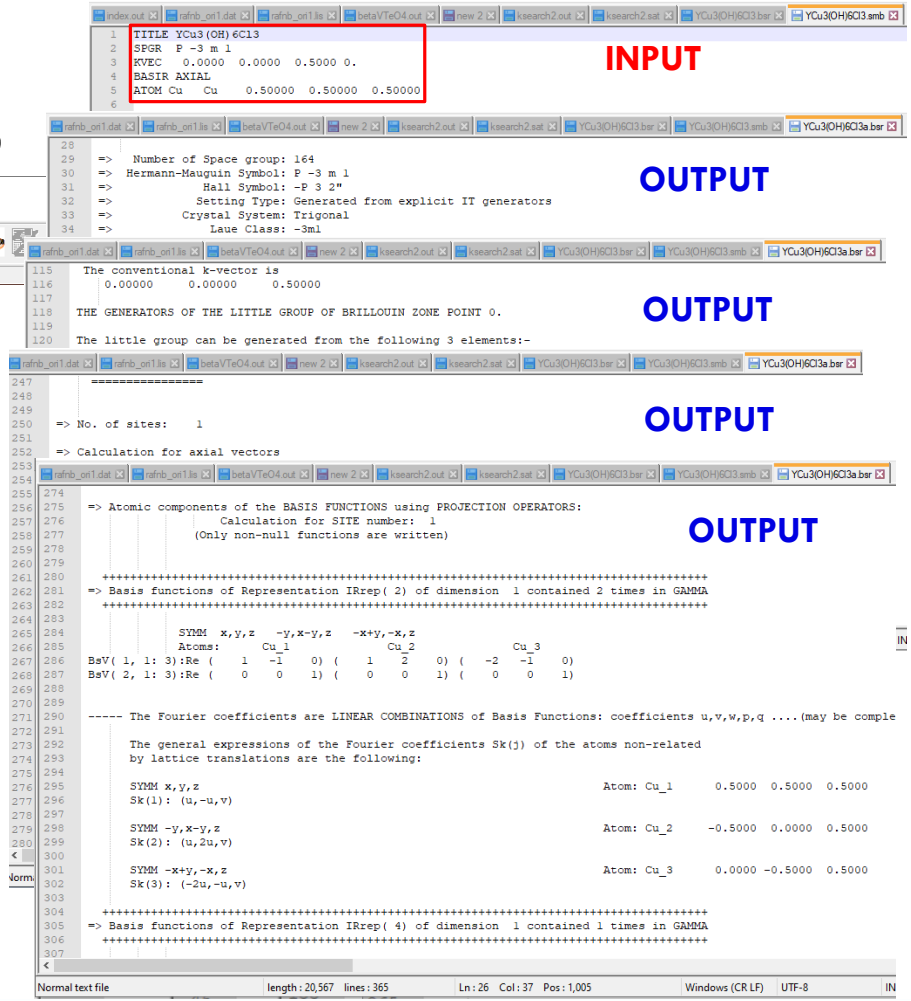


REPRESENTATION ANALYSIS

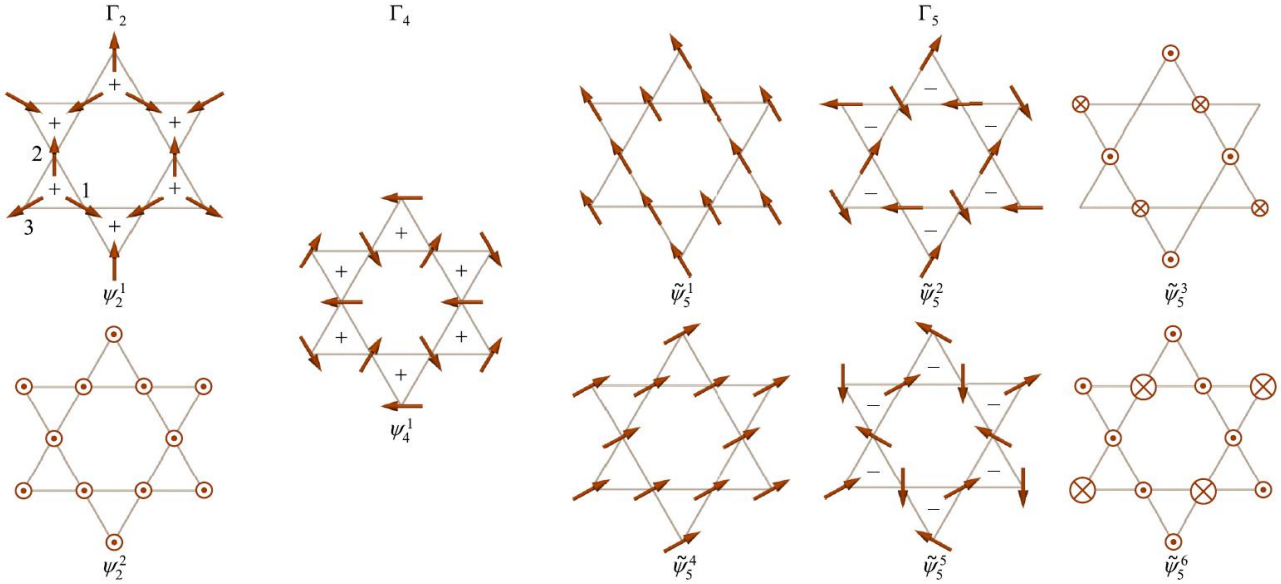
For (0 0 0.5) vector and magnetic (Cu^{2+}) site at (0.5, 0.5, 0.5) three irreducible representations (IRR) of space group P-3m1are possible

Γ_2 and Γ_4 are one dimensional, while Γ_5 is two dimensional, each can have more basis vectors, which describes the relation of the magnetic components on different sites

irrep	Basis vector	Atom 1			Atom 2			Atom 3		
		m_a	m_b	m_c	m_a	m_b	m_c	m_a	m_b	m_c
Γ_2	ψ_2^1	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	0	$\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	0	$-\frac{2}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	0
	ψ_2^2	0	0	1	0	0	1	0	0	1
Γ_4	ψ_4^1	1	1	0	−1	0	0	0	−1	0
Γ_5	ψ_5^1	1	0	0	0	$-\frac{1}{2}-i\frac{\sqrt{3}}{2}$	0	$\frac{1}{2}-i\frac{\sqrt{3}}{2}$	$\frac{1}{2}-i\frac{\sqrt{3}}{2}$	0
	ψ_5^2	0	1	0	$\frac{1}{2}+i\frac{\sqrt{3}}{2}$	$\frac{1}{2}+i\frac{\sqrt{3}}{2}$	0	$-\frac{1}{2}+i\frac{\sqrt{3}}{2}$	0	0
	ψ_5^3	0	0	1	0	0	$-\frac{1}{2}-i\frac{\sqrt{3}}{2}$	0	0	$-\frac{1}{2}+i\frac{\sqrt{3}}{2}$
	ψ_5^4	0	−1	0	$-\frac{1}{2}+i\frac{\sqrt{3}}{2}$	$-\frac{1}{2}+i\frac{\sqrt{3}}{2}$	0	$\frac{1}{2}+i\frac{\sqrt{3}}{2}$	0	0
	ψ_5^5	−1	0	0	0	$\frac{1}{2}-i\frac{\sqrt{3}}{2}$	0	$-\frac{1}{2}-i\frac{\sqrt{3}}{2}$	$-\frac{1}{2}-i\frac{\sqrt{3}}{2}$	0
	ψ_5^6	0	0	1	0	0	$-\frac{1}{2}+i\frac{\sqrt{3}}{2}$	0	0	$-\frac{1}{2}-i\frac{\sqrt{3}}{2}$

REPRESENTATION ANALYSIS

One ends up with 9 different basis vectors (2 for Γ_2, 1 for Γ_4, and 6 for Γ_5)



Real basis for Γ_5:

$$\tilde{\psi}_5^1 = iA\psi_5^1 + B_{++}\psi_5^2 + B_{-+}\psi_5^4 + iA\psi_5^5,$$

$$\tilde{\psi}_5^2 = B_{--}\psi_5^1 - iA\psi_5^2 - iA\psi_5^4 + B_{+-}\psi_5^5,$$

$$\tilde{\psi}_5^3 = C_+\psi_5^3 + C_-\psi_5^6,$$

$$\tilde{\psi}_5^4 = A\psi_5^1 + iB_{--}\psi_5^2 + iB_{-+}\psi_5^4 - A\psi_5^5,$$

$$\tilde{\psi}_5^5 = iB_{++}\psi_5^1 - A\psi_5^2 + A\psi_5^4 + iB_{+-}\psi_5^5,$$

$$\tilde{\psi}_5^6 = D_+\psi_5^3 + D_-\psi_5^6,$$

where $A = 1/\sqrt{3}$, $B_{\pm\pm} = (\pm 1 \pm i/\sqrt{3})/2$,

$C_\pm = (-\sqrt{3} \pm i)/4$, and $D_\pm = (1 \pm i/\sqrt{3})/\sqrt{8}$,

MAGNETIC STRUCTURE REFINEMENT

The output from the Baslreps, can be used as an input for FullProf

Magnetic structure should correspond to a single irreducible representation (IRR), yet it can be a combination of several basis vector corresponding to the same IRR

If the transition is of a first-order type this is not the case – everything is allowed

Show Fullprof

INPUT

```
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:  57.9951
!-------------------------------------------------------------------------------
MCu
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1  -1  -2   0   0        11.910  -1   4   0
!
!
P -1                    <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
    3     1     1     -1     6
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0  0  0  0
!
SYMM x,y,z
BASR   0  1  0    0  0 -1  -1  0  0   2  1  0  -1 -2   0   0  0  1
BASI   0  0  0    0  0  0   0  0  0   0  0  0   0  0   0   0  0  0
SYMM -y,x-y,z
BASR   0  1  0    0  0  1   1  1  0   2  1  0  -1  1   0   0  0  1
BASI   0  0  0    0  0  0   0  0  0   0  0  0   0  0   0   0  0  0
SYMM -x+y,-x,z
BASR   0  1  0    0  0  0   0 -1  0   2  1  0   2  1   0   0  0 -2
BASI   0  0  0    0  0  0   0  0  0   0  0  0   0  0   0   0  0  0
!
!Atom   Typ  Mag Vek    X       Y       Z       Biso     Occ      C1       C2       C3
!      C4      C5      C6       C7       C8       C9       MagPh
Cu1    MCU2  1   0  0.50000 0.50000 0.50000 0.00000  1.00000    0.000    0.000    0.326
                                0.00     0.00     0.00     0.00     0.00     0.00     0.00    11.00
       0.000    0.000    0.000    0.000    0.000    0.000    0.000    0.00000
       0.00     0.00     0.00     0.00     0.00     0.00     0.00
!-------> Profile Parameters for Pattern #  1
!  Scale          Shape1       Bov        Str1       Str2       Str3    Strain-Model
  358.65        0.00000    0.00000    0.00000    0.00000    0.00000        0
    0.00000       0.000      0.000      0.000      0.000      0.000
!      U          V          W          X          Y        GauSiz   LorSiz Size-Model
   0.657111  -0.438899   0.368451   0.361234   0.357385   0.000000   0.004370    0
     0.000      0.000      0.000      0.000      0.000      0.000      0.000
!      a          b          c        alpha       beta       gamma      #Cell Info
   6.747336   6.747336   5.590014  90.000000  90.000000 120.000000
   0.00000    0.00000    0.00000    0.00000    0.00000    0.00000
!  Pref1    Pref2      Asy1       Asy2       Asy3       Asy4
  0.00000  0.00000  0.00000  0.00000  0.00000  0.00000
     0.00     0.00     0.00     0.00     0.00     0.00
!Additional shape parameters
   0.00437    0.00   0.00000    0.00            Shape: Shp1 CShp1 & Shp2 CShp2
! Propagation vectors:
   0.0000000   0.0000000   0.5000000          Propagation Vector  1
   0.000000    0.000000    0.000000
!  2Th1/TOF1    2Th2/TOF2  Pattern to plot
     10.000      127.700        1
```

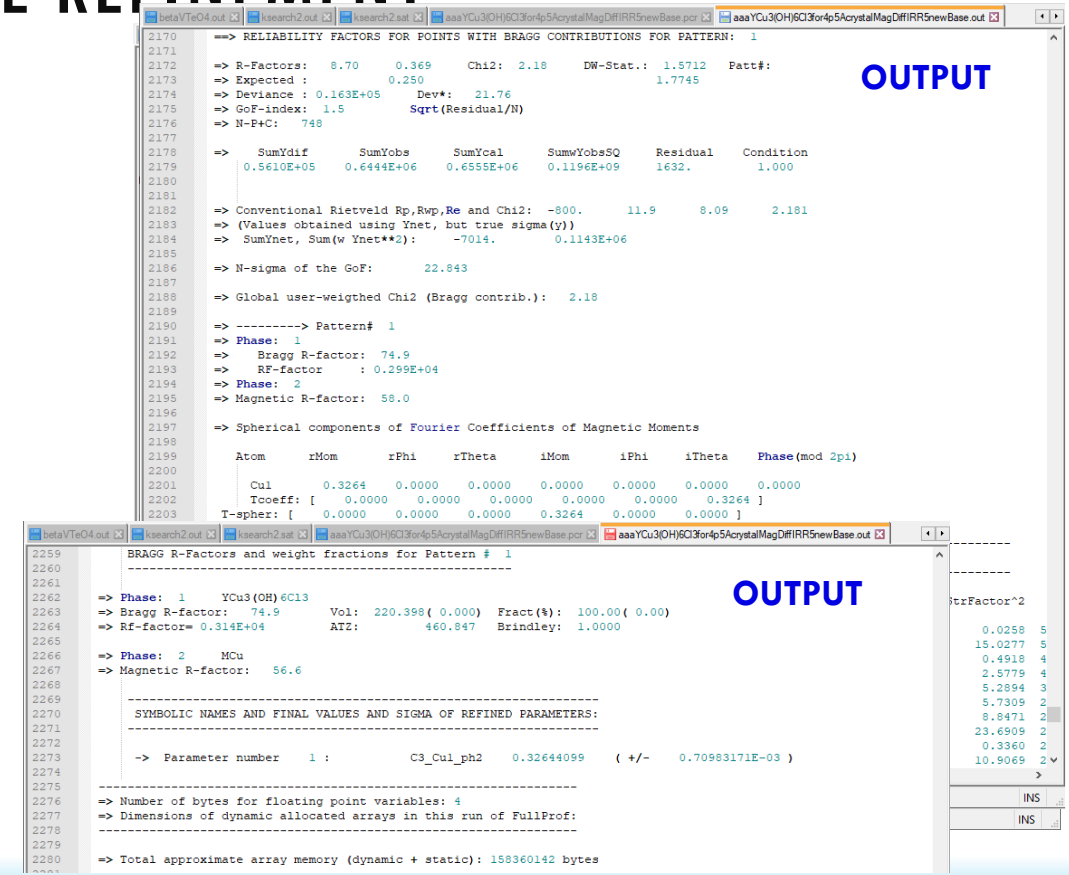
MAGNETIC STRUCTURE REFINEMENT

The output from the Baslreps, can be used as an input for FullProf

Magnetic structure should correspond to a single irreducible representation (IRR), yet it can be a combination of several basis vector corresponding to the same IRR

If the transition is of a first-order type this is not the case – everything is allowed

Show Fullprof



REFINEMENT RESULTS

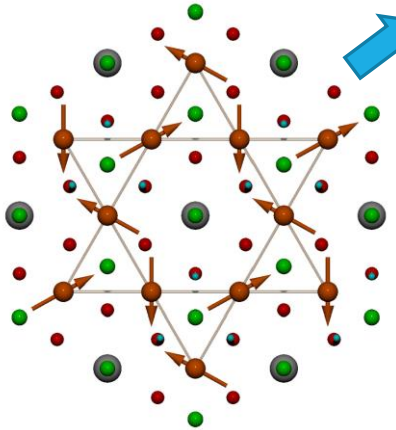
Refinement is typically performed separately for each IRR

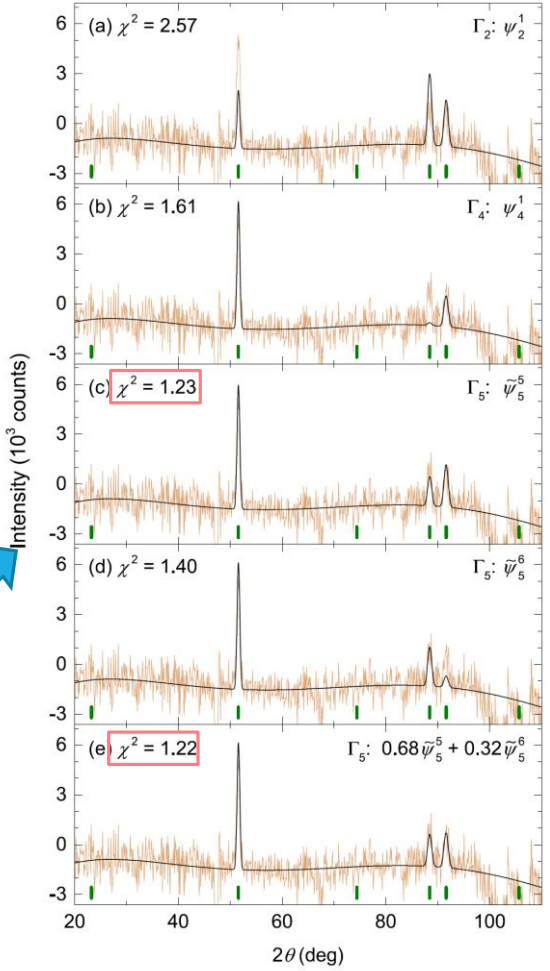
Then the results are compared

First criteria is the quality of the refinement –> χ^2

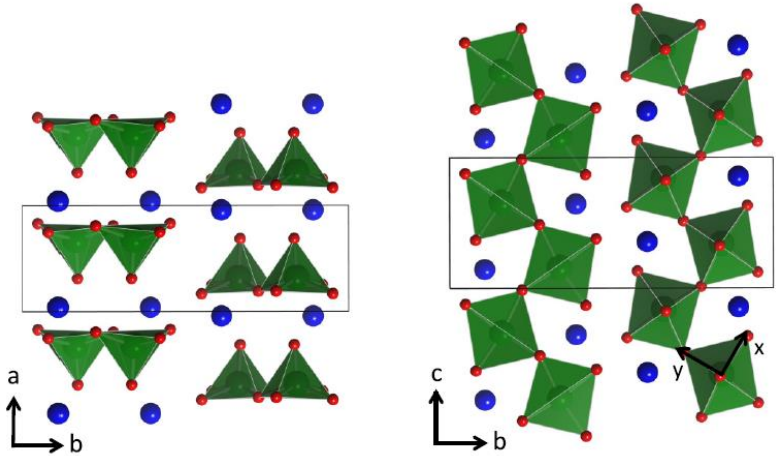
Second is the physical relevance

Considering antieferromagnetic interaction an potential strength of anisotropies we found that the more likely solution corresponds to the ψ_5^5 basis vector





EXAMPLE: β-$TeVO_4$



Starting point

- Crystal structure
- Basic magnetic properties (V^{4+} $S = ½$)
- Magnetic ordering at 4.6 K

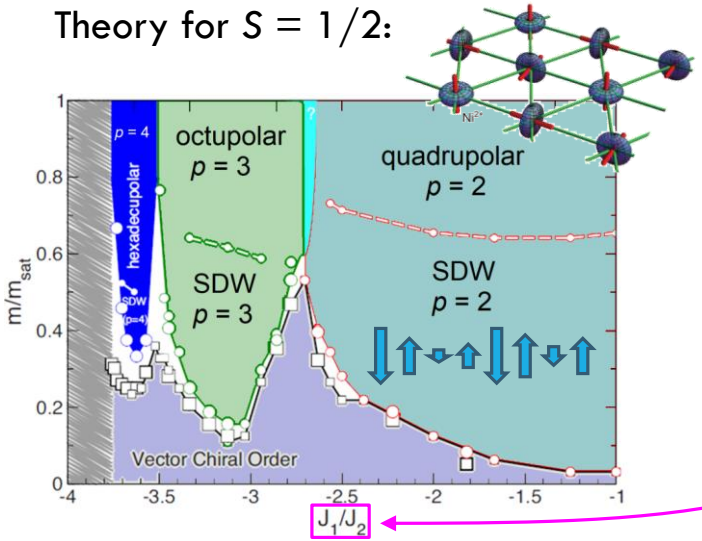
Our approach to determine the magnetic order

- Experiment: Powder neutron diffraction to see if long-range magnetic order develops
- Analysis: Indexation of magnetic reflections, attempt to refine the magnetic structure – *inconclusive*
- Experiment: Single crystal diffraction to resolve magnetic wave vector and collect magnetic reflections
- Analysis: Refinement of magnetic structure – *inconclusive*
- Experiment: Polarized neutron scattering – resolv between colinear and spiral
- Experiment: Single-crystal inelastic neutron scattering on tripe axis spectrometer
- Analysis: Modelling of spin-wave excitations

M. Pregelj *et al.* Nat. Commun. 6, 7255 2015
M. Pregelj *et al.* Phys. Rev B 94, 081114(R), 2016
M. Pregelj *et al.* Phys. Rev B 98, 094405, 2018
M. Pregelj *et al.* Phys. Rev B 100, 094433, 2019
M. Pregelj *et al.* npj Quantum Materials 22, 1, 2019
M. Pregelj *et al.* Phys. Rev B 102, 081104(R), 2020
M. Pregelj *et al.* Phys. Rev B 105, 035145, 2022

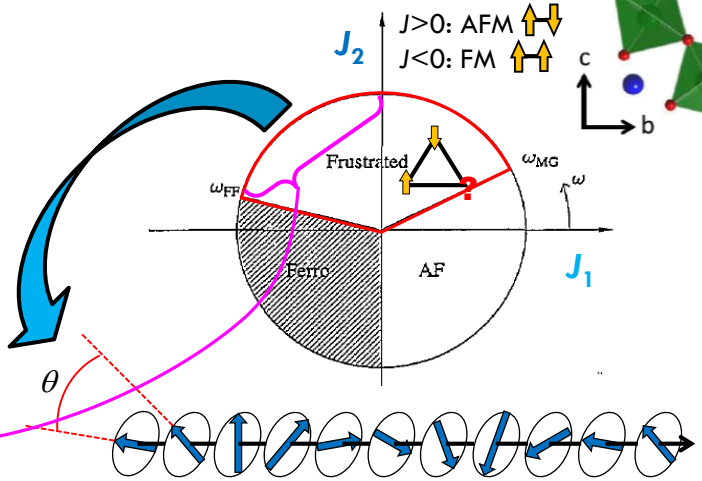
ZIGZAG $S = ½$ CHAIN

Theory for $S = 1/2$:



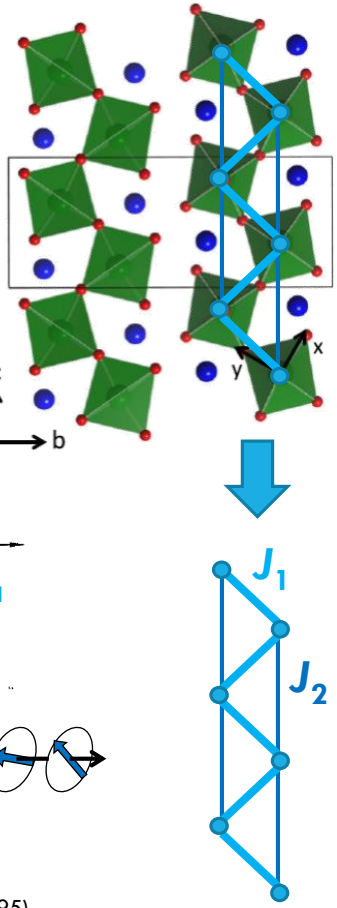
J. Sudan *et al.*, *Phys. Rev.* B **80,** 140402(R) (2009).

Theory for classical spin:



$\theta = \arccos(-J_1/4J_2)$

R. Bursill *et al.*, *J. Phys.: Condens. Mater* **7,** 8605 (1995)



β-$TeVO_4$ – MAGNETIC SUSCEPTIBLY

Initial modeling: a simple spin chain model with AFM interactions J = 21.4 K.

Significantly smaller Curie-Weiss temperature θ = 1.6-4.4 K.

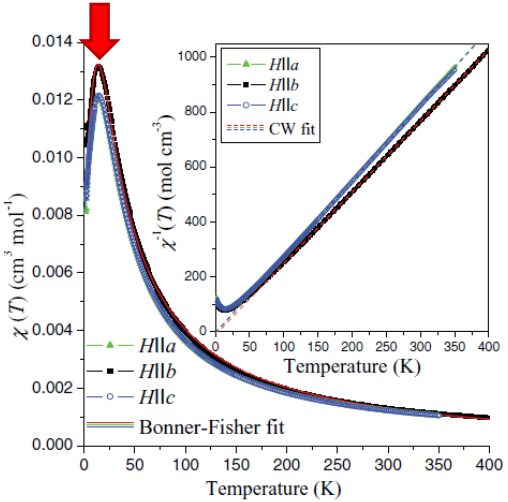
Interactions of different signs?

At low temperatures several magnetic transitions exist:

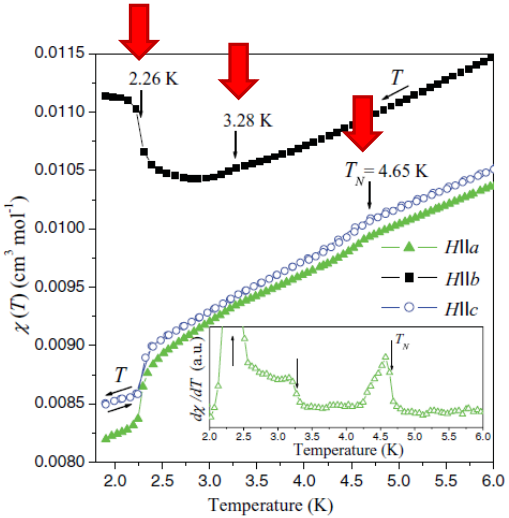
T_{N1} = 4.65 K, T_{N2} = 3.28 K, T_{N3} = 2.26 K

This indicates the existence of several energetically almost equivalent magnetic states.

Magnetic frustration!



Field direction	Curie-Weiss temp θ (K)	g-value for the V^{4+} ion
$H\|\|b$	+4.418	2.027
$H\|\|a$ ($H\perp b$)	+1.598	1.962
$H\|\|c$ ($H\perp b$)	+1.658	1.965



Savina et al. PRB **84**, 104447 (2011).

POWDER NEUTRON DIFFRACTION

At 4.4 K new reflections occur.

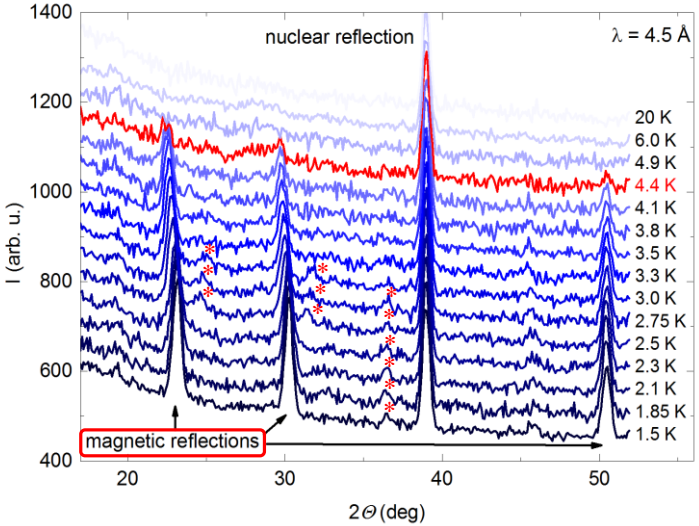
At 3.0 K potential very weak reflections appear

Some of these seem to disappear below 2.3 K

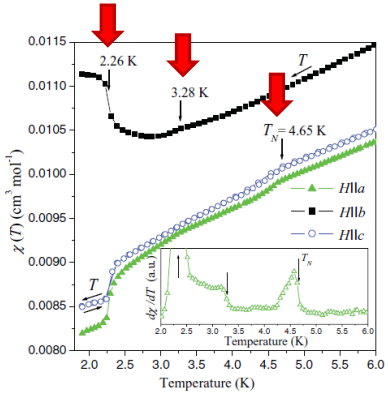
These temperatures are in line with anomalies in susceptibility:
T_{N1} = 4.65 K, T_{N2} = 3.28 K, T_{N3} = 2.26 K

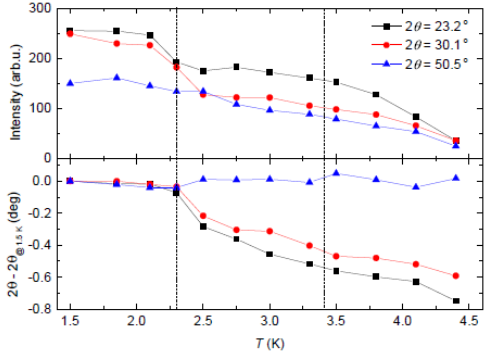
The position of the stronger three reflections changes continuously with temperature – implying incommensurate magnetic order.

Below 2.3 K the intensity and position of the reflections appears to saturate.

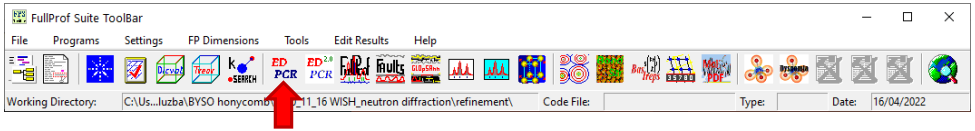


T_{N1}





CRYSTAL STRUCTURE REFINEMENT



Refinement of **crystal structure** above the transition (at 20 K) to check the quality of the sample (potential impurities, crystallinity, …).

Based on known crystal structure, we adjust the *.pcr file:

Starting from working file, we insert new space group, lattice parameters, new atoms and positions. **see FullProf manual**

INPUT

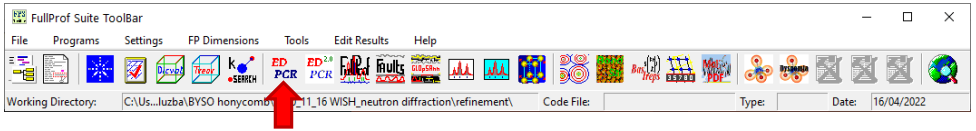
External EdPCR Text Editor - [C:\Users\Matej\Documents_Sluzba\PSI_projects\beta-TeVO4\neutrons\2012_06_06 DMC\refine...

File Edit Search

```
COMM beta VTeO4
! Current global Chi2 (Bragg contrib.) =      236.5
! Files => DAT-file: 6p0K-4p5A.dat,  PCR-file: betaVTeO4-4p5A
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   7   2   0   1   0   0   0   0   0   1   0   0   0   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   1   0   1   1   1   0   4   0   0   3   8   1   1   0   1   0   1
!
! Lambda1  Lambda2    Ratio     Bkpos     Wdt     Cthm      muR    AsyLim    Rpolarz  2nd-muR -> Patt# 1
 4.500000 4.500000  1.00000   70.000  5.0000  0.0000  0.0000   50.00    0.0000  0.0000
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax     PSD    SentO
 20  0.05  0.80  0.80  0.80  0.80     10.0000    0.100000   129.7000   0.000   0.000
!
! Excluded regions (LowT  HighT) for Pattern#  1
        0.00          17.00
!
!
      12    !Number of refined parameters
!
!  Zero     Code    SyCos    Code    SySin    Code  Lambda     Code MORE ->Patt# 1
 -0.02468   21.0  0.00000     0.0  0.00000     0.0 4.500000    0.00   0
!   Background coefficients/codes  for Pattern#  1  (Polynomial of 6th degree)
     458.019        14.933        125.069       -248.039       12.041        82.796
      51.00          61.00         71.00         81.00         91.00         101.00
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:    11.53
VTeO4
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth         ATZ     Nvk Npr More
   6   0   0 0.0 0.0 1.0   0   0   0   0   0        970.156   0   4   0
!
P 1 21/c 1                 <--Space group symbol
!Atom   Typ         X           Y           Z          Biso       Occ      In Fin N_t Spc /Codes
Te1    Te      0.05223   0.39141   0.63805   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
V1     V       0.70422   0.17572   0.64156   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
O1     O       0.30019   0.16548   0.66704   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
O2     O       0.82715   0.04847   0.86045   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
O3     O       0.80175   0.22442   0.98076   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
O4     O       0.74794   0.07960   0.35864   0.00000   1.00000   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale        Shape1        Bov        Str1        Str2        Str3   Strain-Model
  103.34       0.00000     0.00000     0.00000     0.00000     0.00000      0
    11.00000     0.000       0.000       0.000       0.000       0.000
!     U           V           W           X           Y        GausiZ   LorSiz Size-Mode
   0.310000  -0.120000   0.180000   0.438600   0.390400   0.000000   0.004370    0
      0.000       0.000       0.000       0.000       0.000       0.000       0.000
!     a           b           c        alpha       beta       gamma      #Cell Info
   4.333238  13.473461   5.435995  90.000000  91.643265  90.000000
  111.00000  121.00000  41.00000     0.00000  31.00000     0.00000
!  Pref1      Pref2      Asy1       Asy2       Asy3       Asy4
  0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
     0.00      0.00      0.00      0.00      0.00      0.00
!Additional shape parameters
   0.00437     0.00   0.00000     0.00              Shape: Shp1 cShp1 & Shp2 cShp2
!-------------------------------------------------------------------------------
!  Data for PHASE number:   2  ==> Current R_Bragg for Pattern#  1:     0.00
!-------------------------------------------------------------------------------
Al
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth         ATZ     Nvk Npr More
   1   0   0 0.0 0.0 2.0   0   0   0   0   0        312.300   0   4   0
!
F M -3 M                   <--Space group symbol
!Atom   Typ         X           Y           Z          Biso       Occ      In Fin N_t Spc /Codes
Al1    Al       0.00000   0.00000   0.00000   0.00000   0.02083   0   0   0   0
                 0.00      0.00      0.00      0.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale        Shape1        Bov        Str1        Str2        Str3   Strain-Model
  500.69       0.00000     0.00000     0.00000     0.00000     0.00000      0
     0.00000     0.000       0.000       0.000       0.000       0.000
!     U           V           W           X           Y        GausiZ   LorSiz Size-Mode
   0.310000  -0.120000   0.180000   0.438600   0.390400   0.000000   0.004370    0
      0.000       0.000       0.000       0.000       0.000       0.000       0.000
!     a           b           c        alpha       beta       gamma      #Cell Info
   4.049750   4.049750   4.049750  90.000000  90.000000  90.000000
     0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
!  Pref1      Pref2      Asy1       Asy2       Asy3       Asy4
  0.00000   0.00000   0.00000   0.00000   0.00000   0.00000
     0.00      0.00      0.00      0.00      0.00      0.00
!Additional shape parameters
   0.00437     0.00   0.00000     0.00              Shape: Shp1 cShp1 & Shp2 cShp2
!  2Th1/TOF1    2Th2/TOF2  Pattern # 1
     17.000      121.600       1
```

Line:1 Col:1 NUM INS

CRYSTAL STRUCTURE REFINEMENT



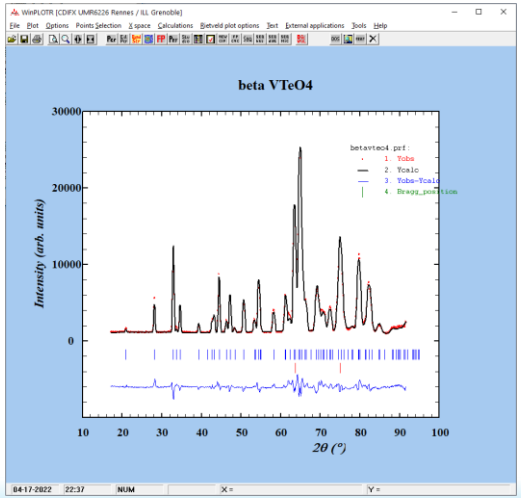
Refinement of **crystal structure** above the transition (at 20 K) to check the quality of the sample (potential impurities, crystallinity, …).

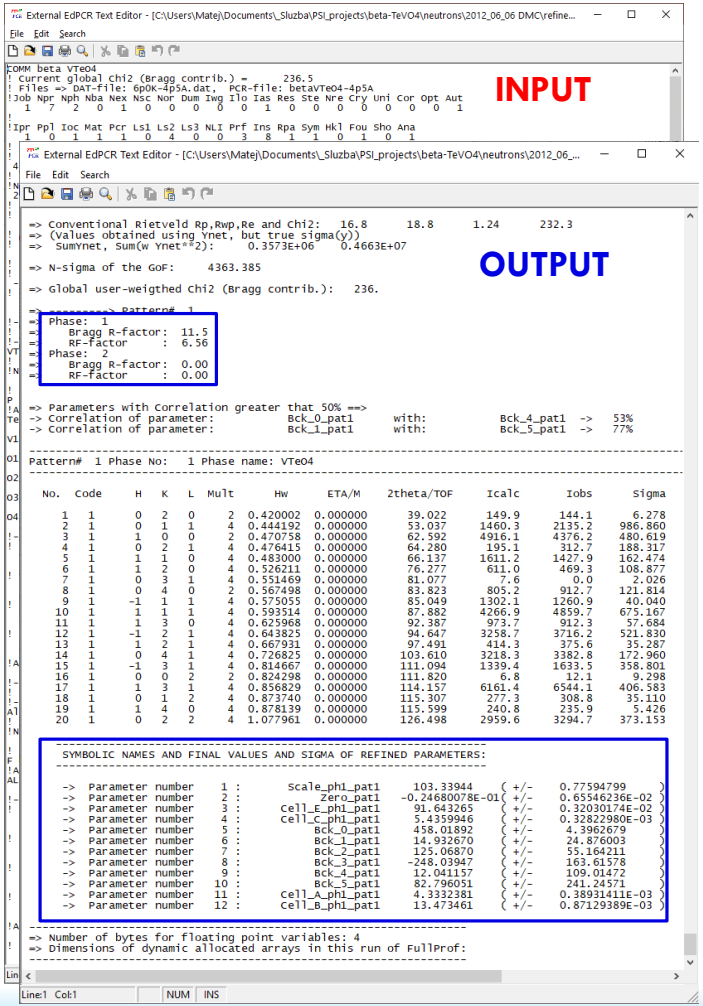
Based on known crystal structure, we adjust the *.pcr file:

Starting from working file, we insert new space group, lattice parameters, new atoms and positions. **see FullProf manual**

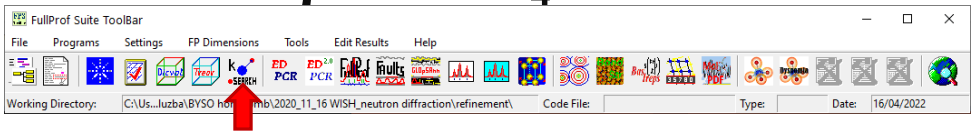
In the refinement we free the parameters slowly – first unit cell, then background, then strong scattering atoms (be careful with vanadium), …

The refinement output can be seen in the *. out file, while for visulaisation WinPLOTER is used.





K SEARCH β-$TeVO_4$



C:\Users\Matej\Documents_Sluzba\PSI_projects\beta-TeVO4\neutrons\2012_06_06 DMC\refinement\k-search.sat - Notepad++

```
TITLE beta-TeVO4
SPGR  P 21/c
CELL   4.353033  13.548018   5.462657  90.000000  91.697357  90.000000
SHORT-OUTPUT
K_INCOMMENSURATE
CWTOL         2.465764     0.300
K_RANGE     0.0  1.0     0.0  1.0     0.0  1.0
K_DIV          100          100          100
! peak_position  peak_intensity  peak_backgrouna
2THETA_LIST     5
       12.58047     1042.85718      784.21821
       16.40054      960.92730      735.74973
       24.51537      715.22460      682.25976
       26.86618      834.75980      683.83283
       28.56618      784.75980      683.83283
```

INPUT

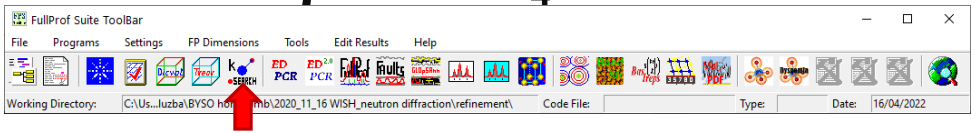
C:\Users\Matej\Documents_Sluzba\PSI_projects\beta-TeVO4\neutrons\2012_06_06 DMC\refinement\k-search.kup - Notepad++

```
=> List of the best 10 solutions for  5 satellites

     Kx          Ky          Kz          R-factor
 0.380000    1.000000    0.080000    1.481212
 0.380000    0.000000    0.080000    1.481212
 0.380000    1.000000    0.890000    1.547473
 0.380000    0.000000    0.890000    1.547480
 0.380000    0.010000    0.080000    1.797936
 0.380000    0.990000    0.080000    1.797943
 0.380000    0.990000    0.890000    1.909574
 0.380000    0.010000    0.890000    1.909576
 0.180000    0.250000    0.410000    2.068398
 0.380000    0.020000    0.080000    2.449845

=> List of satellites (hkl)+(Kx,Ky,Kz) for the best solution:

          Kx= 0.3800    Ky= 1.0000    Kz= 0.0800

 H  K  L   n     D*(cal)     D*(obs)    2Th(cal)    2Th(obs)  2Th(obs-cal)
 ------------------------------------------------------------------------
 0  1  0   1      0.0890      0.0889     12.5964     12.5805      -0.0160
 0  2  0   1      0.1156      0.1157     16.3890     16.4005       0.0115
 0 -1  0   1      0.1724      0.1722     24.5387     24.5154      -0.0233
 0  1  1   1      0.1875      0.1884     26.7268     26.8662       0.1394
 0  2  1   1      0.2015      0.2001     28.7652     28.5662      -0.1991

=>  Best R-factor:  1.4812 %  for propagation vector:
                                 k  = (  0.3800  1.0000  0.0800)

                    Total CPU-Time

               CPU-seconds:            0.34
               CPU-minutes:            0.01
               CPU-hours  :            0.00
```

OUTPUT

Very similar quality

K SEARCH β-$TeVO_4$



C:\Users\Matej\Documents_Sluzba\PSI_projects\beta-TeVO4\neutrons\2012_06_06 DMC\refinement\k-search.sat - Notepad++

File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ?

new 3 | new 1 | BEBO_sim-new-data-dia-X8Y1_states.res | BEBO_sim-new-data-dia-D2Y2_states.res | k-search.sat | k-search.kup

```
TITLE beta-TeVO4
SPGR  P 21/c
CELL   4.353033  13.548018   5.462657  90.000000  91.697357  90.000000
SHORT-OUTPUT
K_INCOMMENSURATE
CWTOL          2.465764     0.300
K_RANGE     0.0  1.0     0.0  1.0     0.0  1.0
K_DIV           100          100          100
! peak_position  peak_intensity  peak_backgrouna
2THETA_LIST     5
        12.58047     1042.85718      784.21821
        16.40054      960.92730      735.74973
        24.51537      715.22460      682.25976
        26.86618      834.75980      683.83283
        28.56618      784.75980      683.83283
```

INPUT

C:\Users\Matej\Documents_Sluzba\PSI_projects\beta-TeVO4\neutrons\2012_06_06 DMC\refinement\k-search.kup - Notepad++

File Edit Search View Encoding Language Settings Tools Macro Run Plugins Window ?

new 3 | new 1 | BEBO_sim-new-data-dia-X8Y1_states.res | BEBO_sim-new-data-dia-D2Y2_states.res | k-search.sat | k-search.kup

```
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     Kx          Ky          Kz          R-factor
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 0.380000    0.000000    0.080000    1.481212
 0.380000    1.000000    0.890000    1.547473
 0.380000    0.000000    0.890000    1.547480
 0.380000    0.010000    0.080000    1.797936
 0.380000    0.990000    0.080000    1.797943
 0.380000    0.990000    0.890000    1.909574
 0.380000    0.010000    0.890000    1.909576
 0.180000    0.250000    0.410000    2.068398
 0.380000    0.020000    0.080000    2.449845

=> List of satellites (hkl)+(Kx,Ky,Kz) for the best solution:

        Kx= 0.3800    Ky= 1.0000    Kz= 0.0800

 H  K  L   n      D*(cal)      D*(obs)     2Th(cal)     2Th(obs)  2Th(obs-cal)
 ------------------------------------------------------------------------------
 0  1  0   1       0.0890       0.0889      12.5964      12.5805      -0.0160
 0  2  0   1       0.1156       0.1157      16.3890      16.4005       0.0115
 0 -1  0   1       0.1724       0.1722      24.5387      24.5154      -0.0233
 0  1  1   1       0.1875       0.1884      26.7268      26.8662       0.1394
 0  2  1   1       0.2015       0.2001      28.7652      28.5662      -0.1991

=>  Best R-factor:  1.4812 %  for propagation vector:
                                  k  = (  0.3800  1.0000  0.0800)

                    Total CPU-Time

                CPU-seconds:            0.34
                CPU-minutes:            0.01
                CPU-hours  :            0.00
```
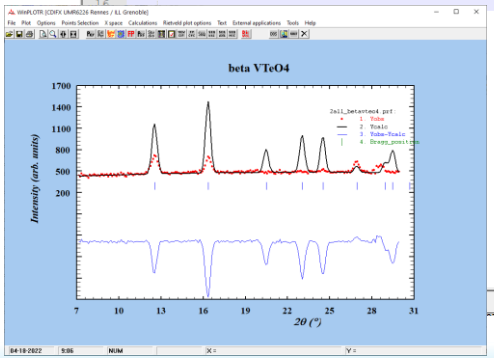
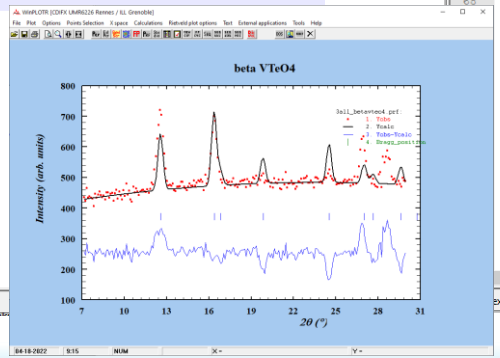
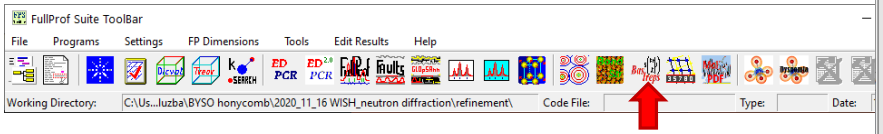

OUTPUT

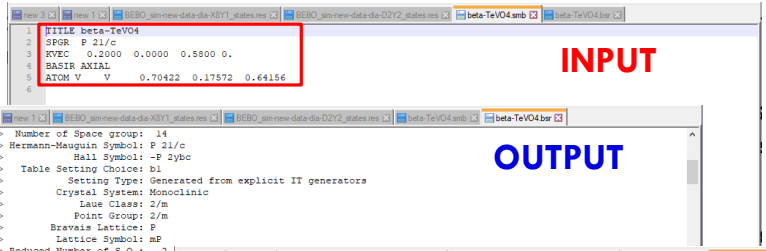
Very similar quality

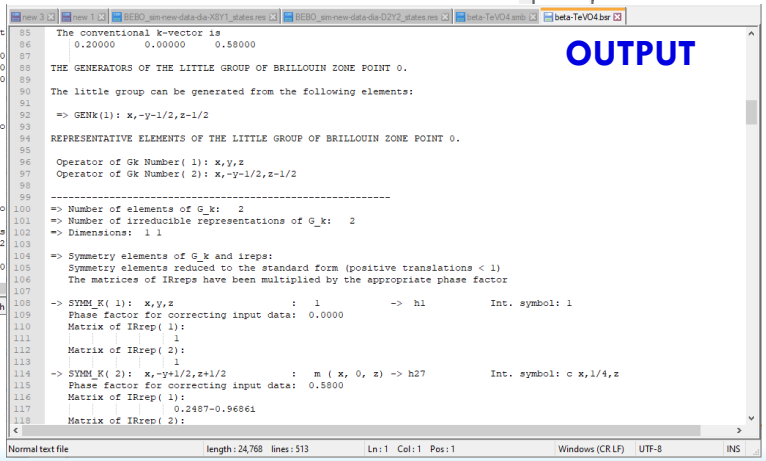


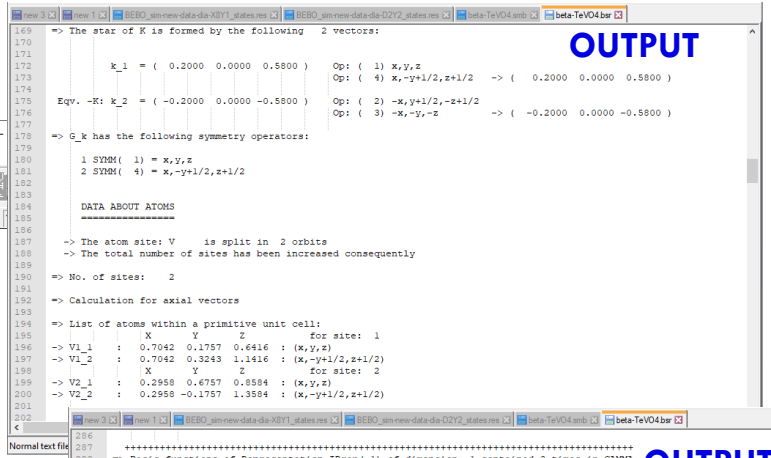


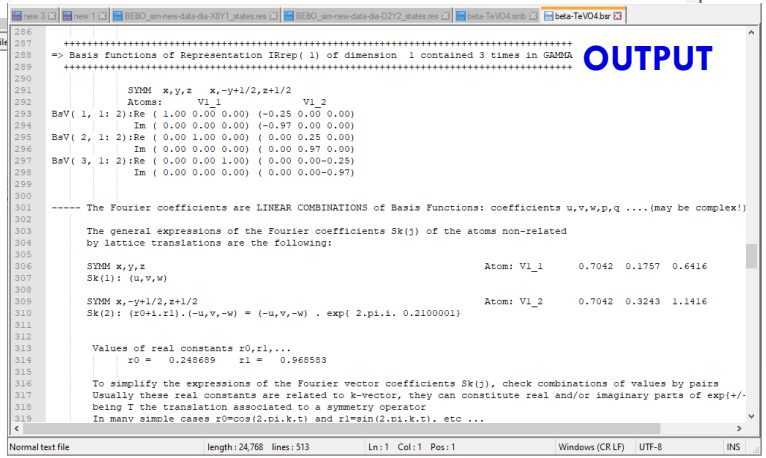
REPRESENTATION ANALYSIS











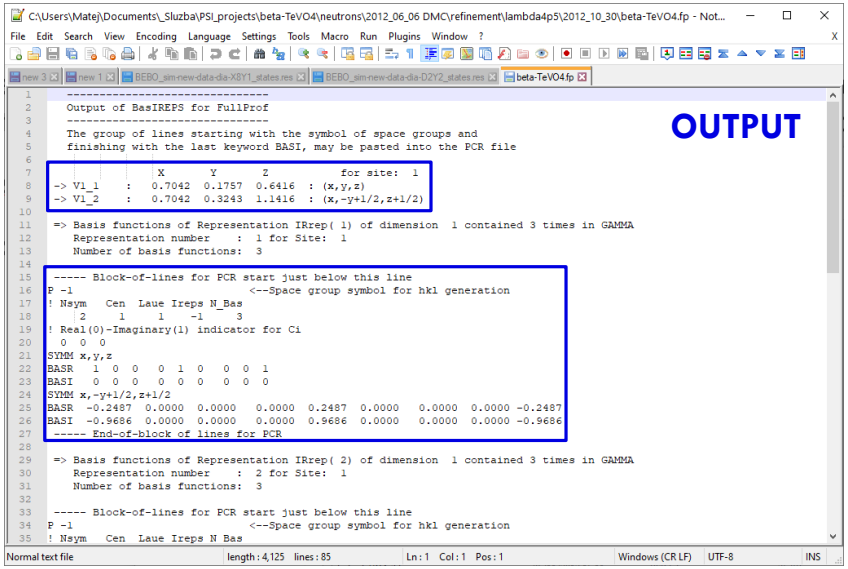
MAGNETIC STRUCTURE REFINEMENT – POWDER

Irreducible representations determine possible magnetic moment components and determine how are these related between different magnetic atoms – output of *BasIreps*

Each representation demands a separate *FullProf* treatment, i.e., a separate *.pcr file.

BasIreps provides a symmetry related part for the *.pcr file for the magnetic structure refinement with the *FullProf*.

Powder refinement inconclusive

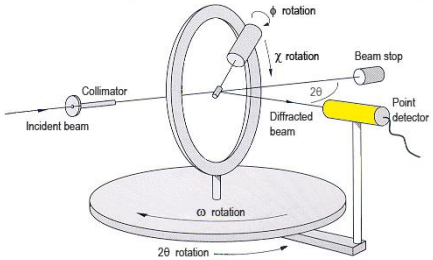


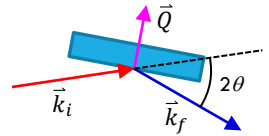
SINGLE-CRYSTAL DIFFRACTION

Single crystal has to be aligned precisely to Bragg reflection

- 1. step: 2θ is set for the strongest (h 0 0), (0 k 0) or (0 0 l)
- 2. step: this crystal axis is by eye aligned to bisect the incident and scattered beam, i.e., pointing along Q vector
- 3. step: crystal is rotated until the detector detect intensity
- 4. step: centre and proceed to next reflection
- …
- (n -1). step: index the reflections – based on the angles calculate possible (h, k, l)
- n. step: after collecting several reflections along all three crystal axes, one can refine the U-matrix, connecting the reciprocal space with ϕ, χ, and ω angles

Having the U matrix, a large number of reflections can be scanned, which can then be used for the refinement.






```
 1  TeVO4
 2  4.379 13.5211 5.4633  90.00  91.72 90.0 2.317 5.5
 3  30.622     95.8   181.126 0. 0.7
 4  32.15   79.705   178.16 0. 0.7
 5  36.27   68.02   174.6 0. 0.7
 6  0
 7
```

```
27      17   -1.   -2.    0.      -0.24
28      18   -1.    2.    0.      -0.24
29      19    1.   -2.    0.      -0.24
30      20    1.    2.    0.      -0.24
31     THIS CAN BE THE ANGLE BETWEEN HKL1 AND HKL2
32
33        HKL1          HKL2       CALC.ANGLE    OBS-CALC
34   -1.  0.  0.   -1. -1.  0.       17.94        -1.06
35   -1.  0.  0.   -1.  1.  0.       17.94        -1.06
36    1.  0.  0.    1. -1.  0.       17.94        -1.06
37    1.  0.  0.    1.  1.  0.       17.94        -1.06
38     THIS CAN BE THE ANGLE BETWEEN HKL1 AND HKL2
39
40        HKL1          HKL2       CALC.ANGLE    OBS-CALC
41   -1.  0.  0.   -1. -2.  0.       32.92        -2.24
42   -1.  0.  0.   -1.  2.  0.       32.92        -2.24
43    1.  0.  0.    1. -2.  0.       32.92        -2.24
44    1.  0.  0.    1.  2.  0.       32.92        -2.24
45     THIS CAN BE THE ANGLE BETWEEN HKL1 AND HKL2
46
47        HKL1          HKL2       CALC.ANGLE    OBS-CALC
48   -1. -1.  0.   -1. -2.  0.       14.98        -1.11
49   -1.  1.  0.   -1.  2.  0.       14.98        -1.11
50    1. -1.  0.    1. -2.  0.       14.98        -1.11
51    1.  1.  0.    1.  2.  0.       14.98        -1.11
52
53     FOLLOWING COMBINATIONS OF HKL WILL EXPLAIN THE DATA. NOTE THAT THERE MIGHT BE SEVERAL SYMMETRY RELATED SETS.
54   REFLECTION NUMS          HKLS
55
56     -1  0  0   -1 -1  0   -1 -2  0
57     -1  0  0   -1  1  0   -1  2  0
58      1  0  0    1 -1  0    1 -2  0
59      1  0  0    1  1  0    1  2  0
60
```

spice file — length : 2,267 lines : 60

INPUT

```
 1  HKL: 0 4 0, TeVO4 ORI3 in_10mm_12mm out_nothing
 2  2 1 0 0 45 3 4 1 .5 0
 3  0 2.317
 4  0 .0 0 .0 0 .0
 5  0 4.379 0 13.5211 0 5.4633 0 90 0 91.72 0 90
 6      0.0000     4.0000     0.0000    40.090    12.098     0.209
 7      0.0000     2.0000     1.0000    31.647    58.999     0.628
 8      0.0000     1.0000     1.0000    26.445    73.347     0.997
 9      0.0000     2.0000     2.0000    54.460    87.429     1.690
10      0.0000     5.0000     2.0000    74.162    74.028     1.707
11      0.0000     3.0000     3.0000    86.937   103.647     2.297
12      0.0000     8.0000     1.0000    91.750    55.294     0.980
13
14  -1
15
```

OUTPUT

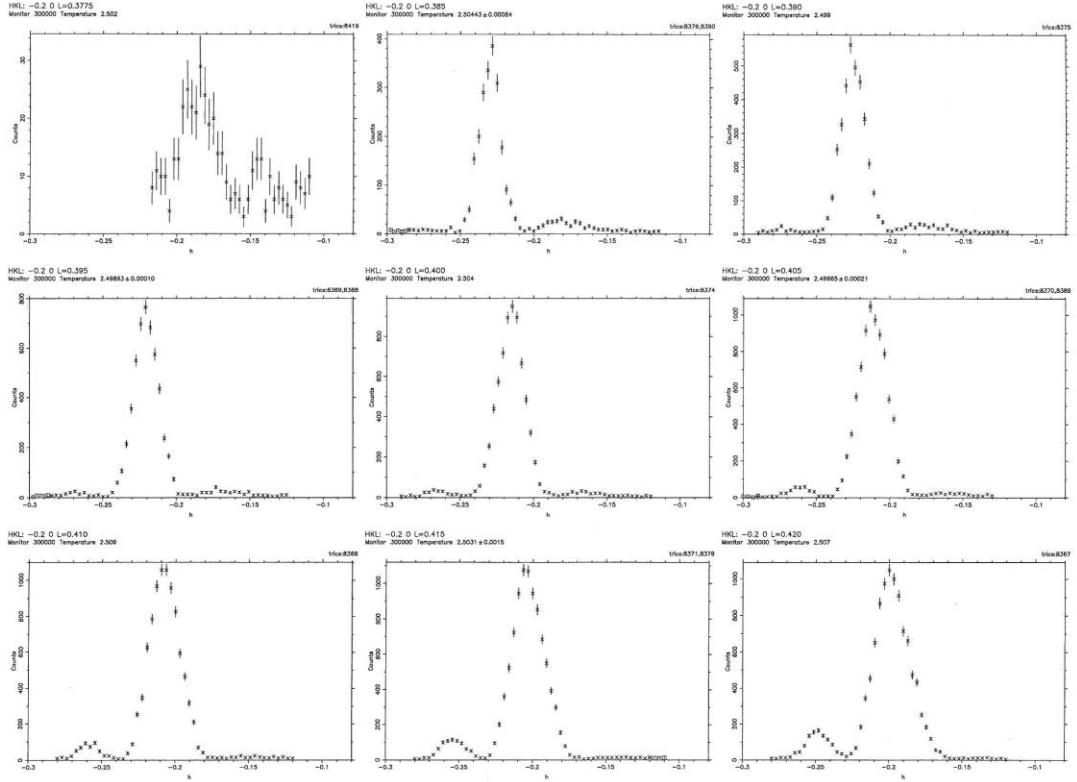
```
121
122  0RESULTS AT THE END OF THE LAST CYCLE (no :   3)
123  ------------------------------------------------------------------------------
124       H    K    L          GAMMA                    OMEGA                    NU
125                      obs      cal      diff      obs      cal      diff      obs      cal      diff  Wa
126  ------------------------------------------------------------------------------
127     0.0  4.0  0.0   40.090   40.086    0.004    12.098   12.214   -0.116    0.209    0.126    0.083
128     0.0  2.0  1.0   31.647   31.642    0.005    58.999   59.063   -0.064    0.628    0.824   -0.196
129     0.0  1.0  1.0   26.445   26.441    0.004    73.347   73.406   -0.059    0.997    0.793    0.204
130     0.0  2.0  2.0   54.460   54.448    0.012    87.429   87.419    0.010    1.690    1.585    0.105
131     0.0  5.0  2.0   74.162   74.157    0.005    74.028   73.979    0.049    1.707    1.680    0.027
132     0.0  3.0  3.0   86.937   86.687    0.250   103.647  103.544    0.103    2.297    2.378   -0.081
133     0.0  8.0  1.0   91.750   91.702    0.048    55.294   55.216    0.078    0.980    1.013   -0.033
134
135   Mean abs(dev.) (no *false* ref.):          0.0471                    0.0685                    0.1043
136  ------------------------------------------------------------------------------
137  0PARAMETER      VALUE   (ST.DEV.)      CORRELATIONS
138       1 =   1.915E-02(  9.535E-02)    1.00  0.01  0.56
139       2 =  -2.040E-02(  4.102E-02)    0.01  1.00  0.02
140       3 =   6.278E-02(  5.687E-02)    0.56  0.02  1.00
141  ------------------------------------------------------------------------------
142  0FINAL ORIENTATION [UB] MATRIX
143      -0.0007665     0.0732688     0.0249128
144
145      -0.0001918    -0.0100739     0.1813289
146
147       0.2284642     0.0002374     0.0057323
```

SINGLE-CRYSTAL DIFFRACTION

A list of reflections can be generated either by FullProf or by some other program.

After measurements a batch fit can be applied to the collected data.

The results need to be inspected if there are some anomalies – split reflections, misalignment, …



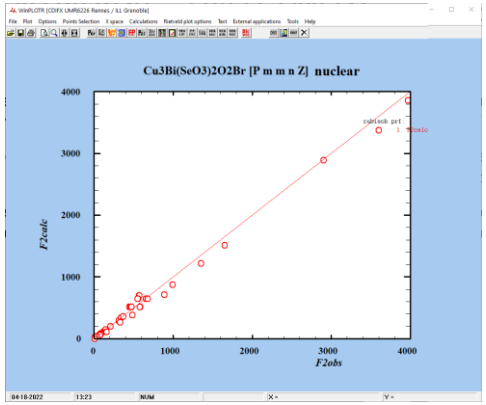
STRUCTURE REFINEMENT – SINGLE CRYSTAL

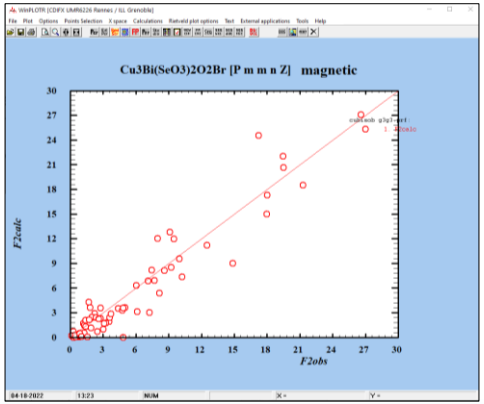
Similar to powder, accept that instead of profile matching the input for the program is now a list of integrated intensities.

The intensities must be determined from "ω scans" – rotation of the sample perpendicular to the scattering plane at fixed 2θ.

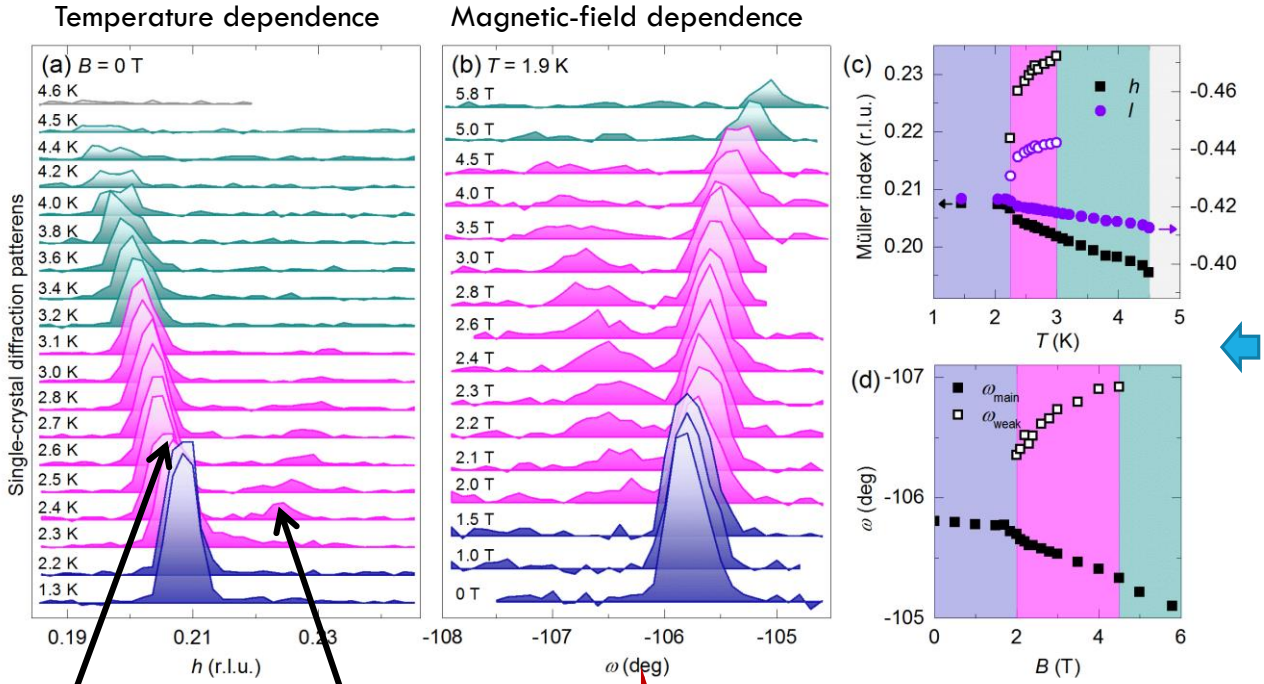
The integrated intensities must be corrected for the Lorentz factor, i.e., multiplied by $\sin(2\theta)$, due to angular range during which the reflection is reflecting into detector.

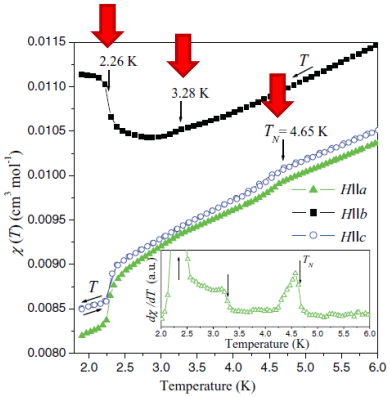
Show FullProf sample



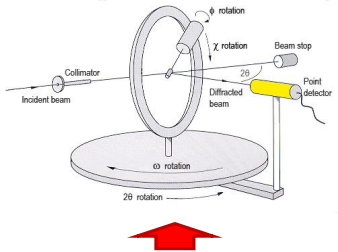


SINGLE-CRYSTAL DIFFRACTION - β-$TeVO_4$





At TriCS and TASP instruments, at PSI, Switzerland

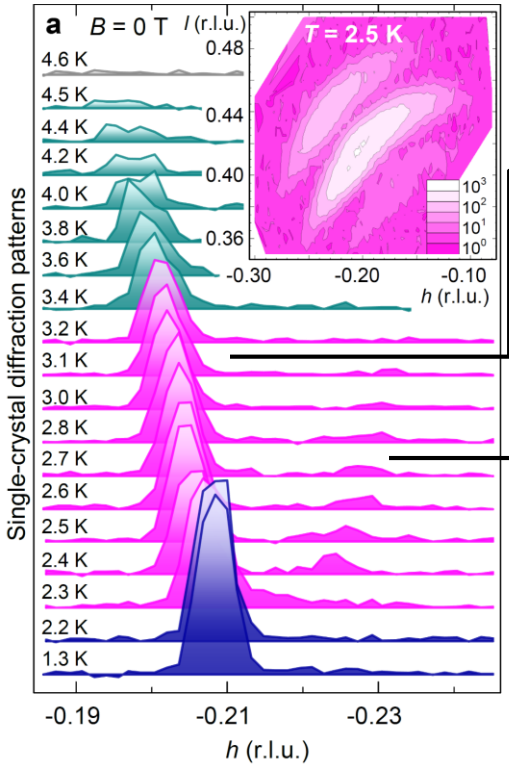


k = (*h*, 0, *l*)

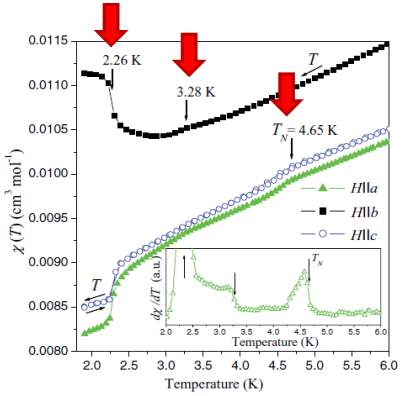
k+Δ**k** = (*h*+Δ*h*, 0, *l*+Δ*l*)

Scan along special reciprocal direction demands rotation of several motors simultaneously!

MAGNETIC ORDERS AT ZERO FIELD

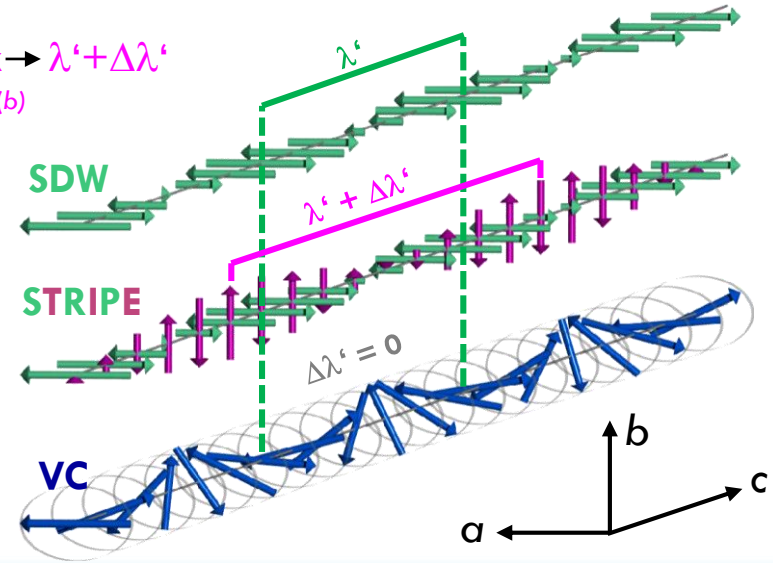


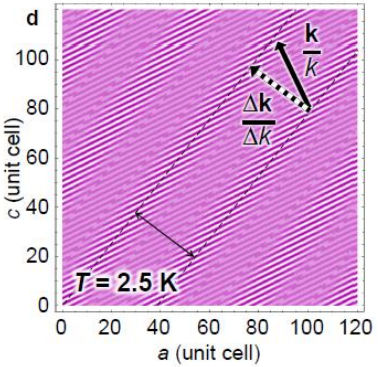
Modulation along the chain matches the classical pitch angle for $J_1/J_2 = -1.25$.



k → λ‘
SDW(ac)

k+Δ**k** → λ‘+Δλ‘
SDW(b)





M. Pregelj *et al.* Nature Communications 2015

POWDER INELASTIC SCATTERING – β-$TeVO_4$

To obtain an overview of excitations one typically begins with measurements on powder samples

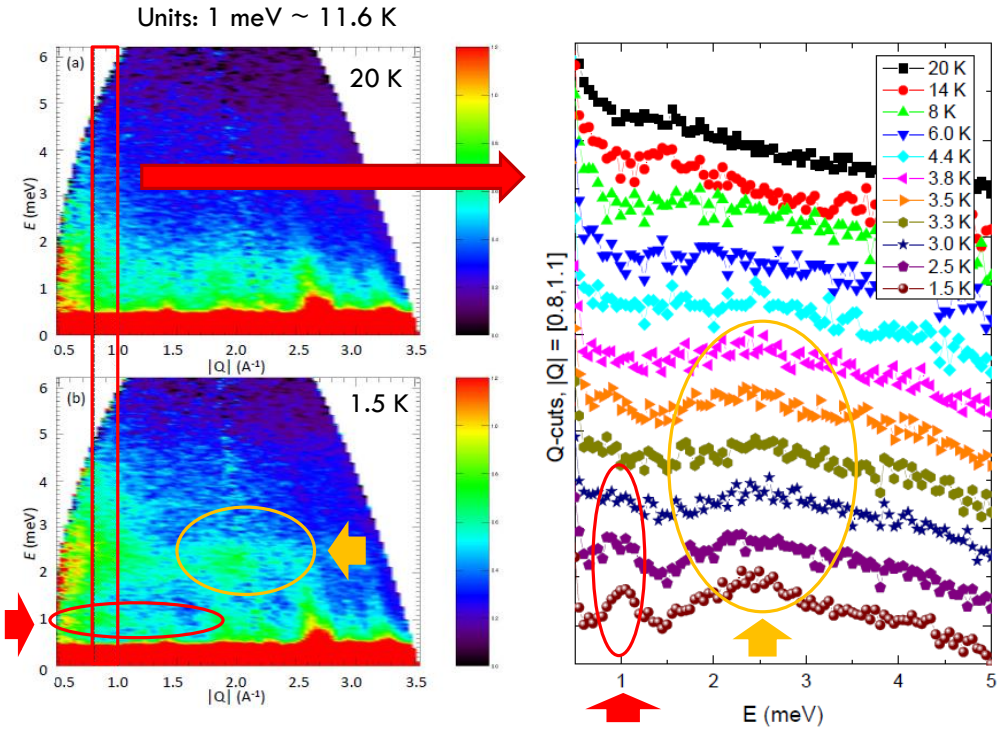
The energy range is chosen based on the knowledge of the main exchange interaction

Similar to diffraction one typically measure Energy-Q map above and below the magnetic transition

Magnetic excitations are rather weak hence they are typically measured at lowest temperatures

The excitations may persist significantly above the ordering temperature

Powder data are rarely sufficient for precise determination of the spin Hamiltonian –> for this, single crystal measurements are preferable.



SINGLE-CRYSTAL INELASTIC SCATTERING – β-$TeVO_4$

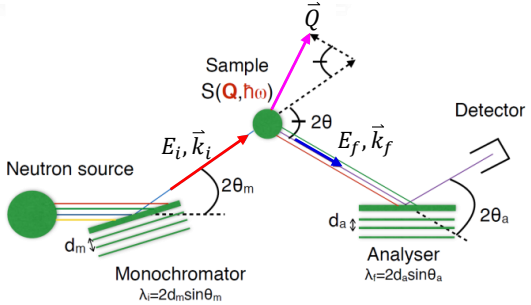
Single crystals measurements are typically performed on Triple Axis Spectrometer

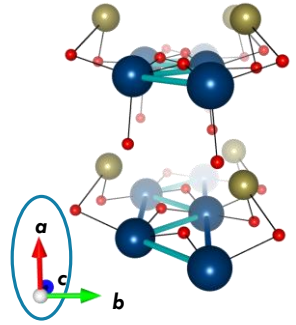
Due to weak signal often several crystals need to be aligned before the experiment (larger crystals are often unavailable)

For mounting one should as little material as possible (preferably Al) and avoid glues, which typically contain hydrogen (strong incoherent scatterer)

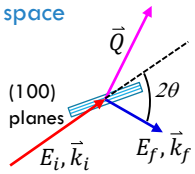
All the crystals should be as close as possible

The resolution is dictated by the precision of the alignment (~1-3 deg)



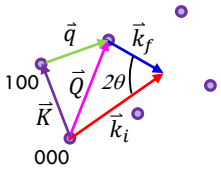


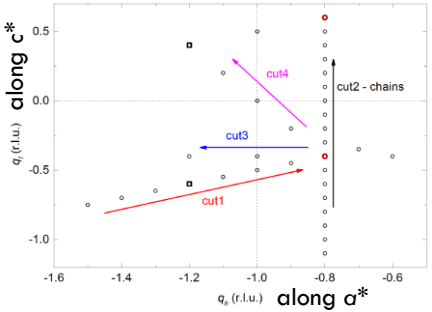
Real space



a and c are in the scattering plane

Reciprocal space





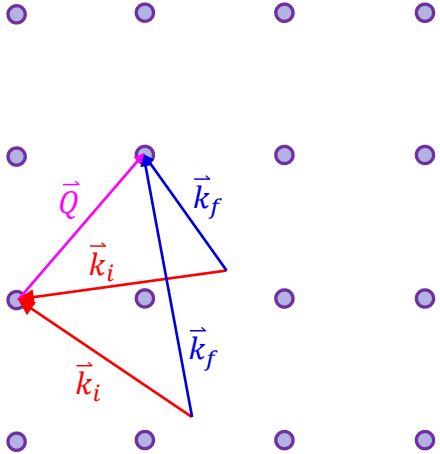
TRIPLE AXIS SPECTROMETER

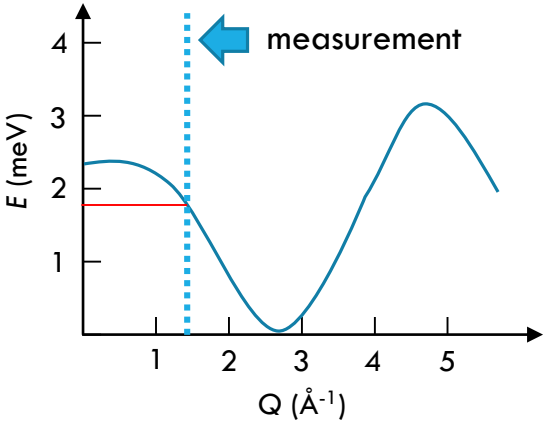
Constant Q measurements

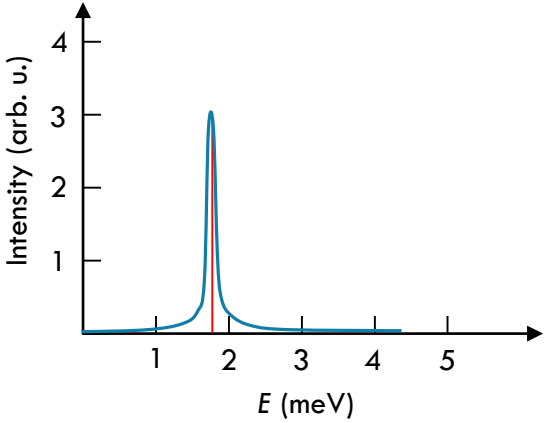
$\vec{Q}$ is kept constant, while changing $\vec{k}_i$ and $\vec{k}_f$, i.e., while changing the energy transport $E = \hbar\omega$

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right)$$

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$



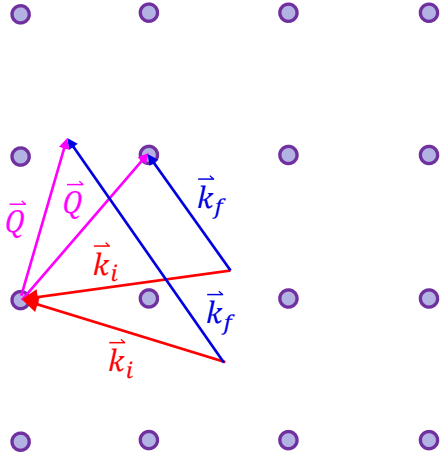




TRIPLE AXIS SPECTROMETER

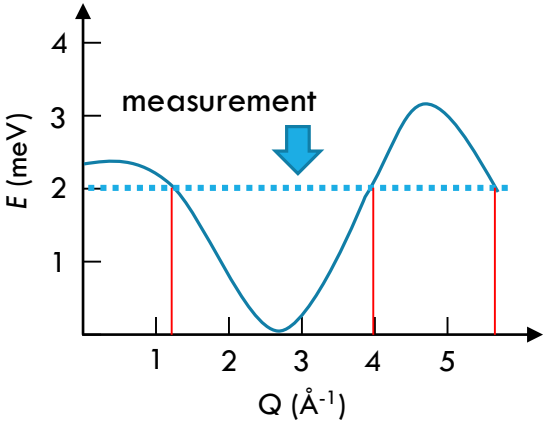
Constant *E* measurements

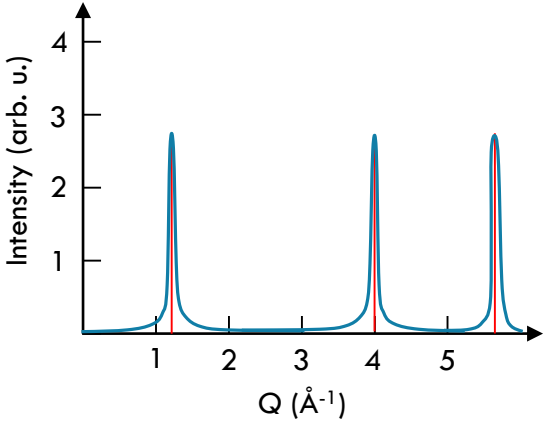
$\vec{Q}$ is being changed while keeping $E = \hbar\omega$



$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right)$$

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$



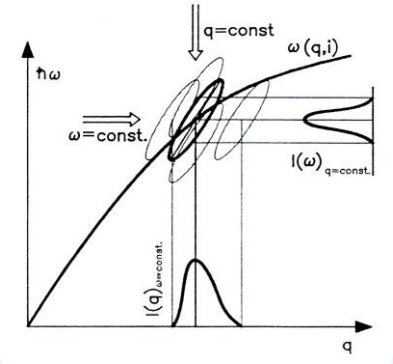


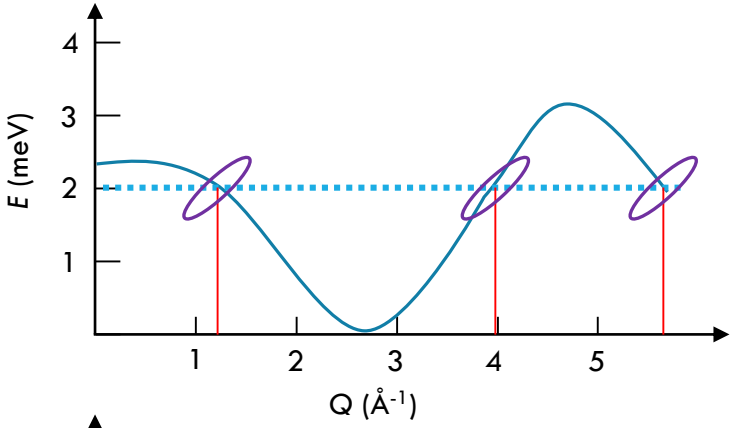
TRIPLE AXIS SPECTROMETER

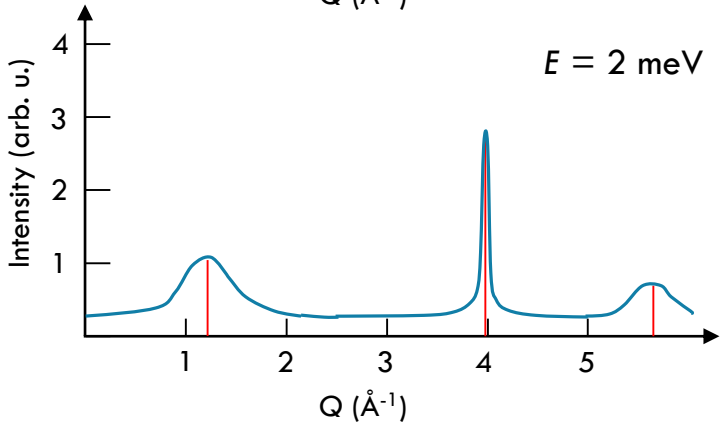
Due to experimental limitations **Q** and ***E***, i.e., ω, are defined only to a certain level of precision

Reducing these uncertainties leads to a **better resolution BUT** it also leads to **lower counts**

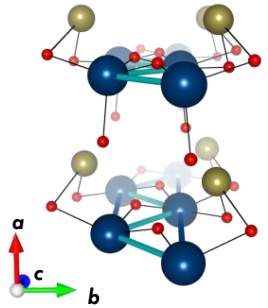
Resolution ellipsoid: resolution volume, with distinct orientations in $(\vec{Q}, E)$ space



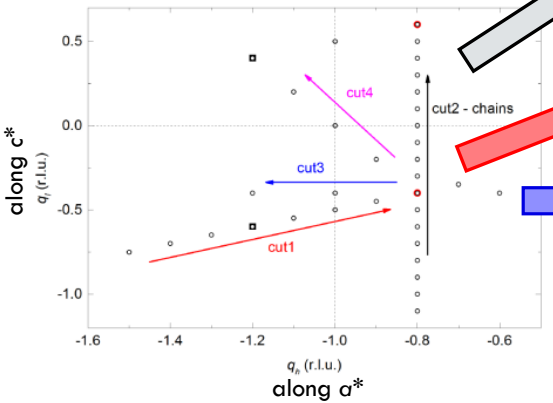


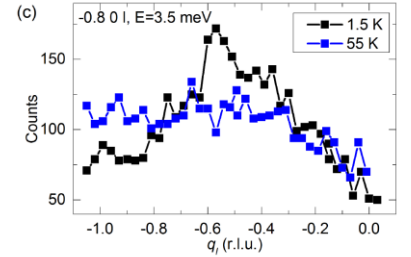


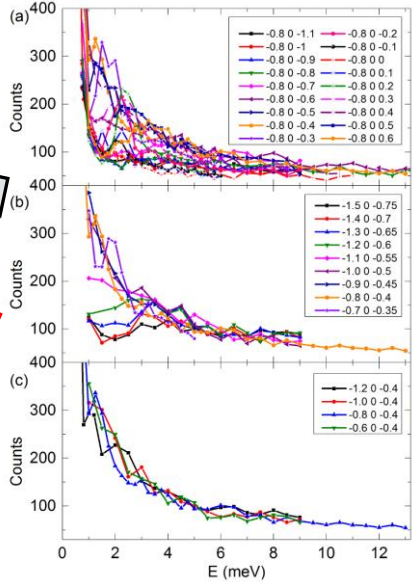
β-$TeVO_4$ RESULTS



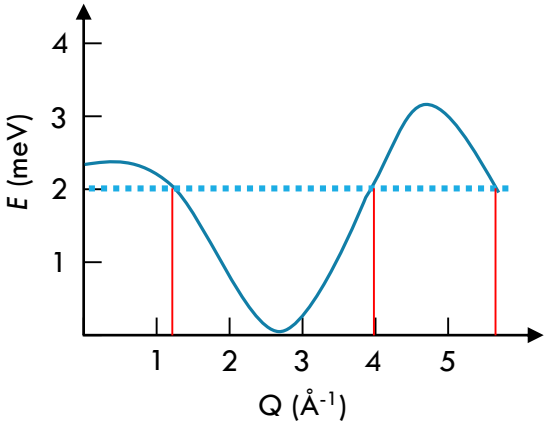
$J \sim 20$ K ~ 2 meV

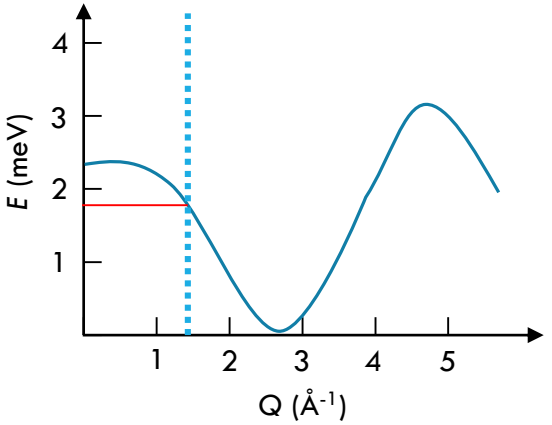




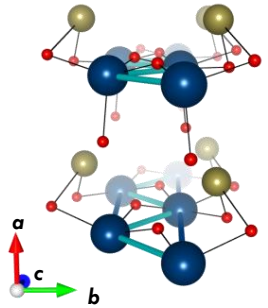


(1 meV = 11.6 K)

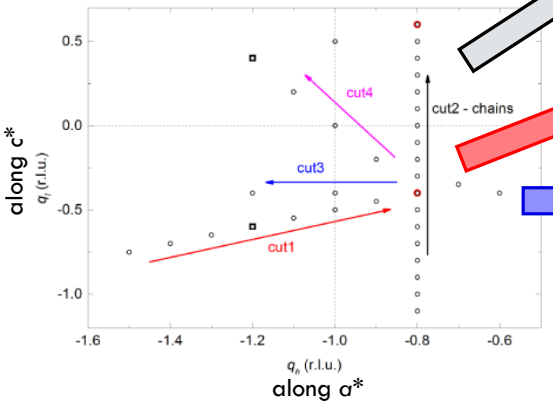


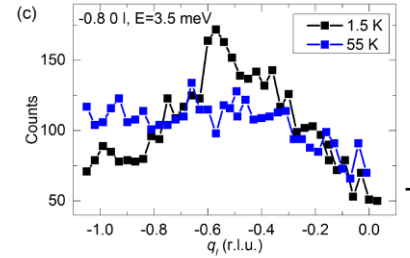


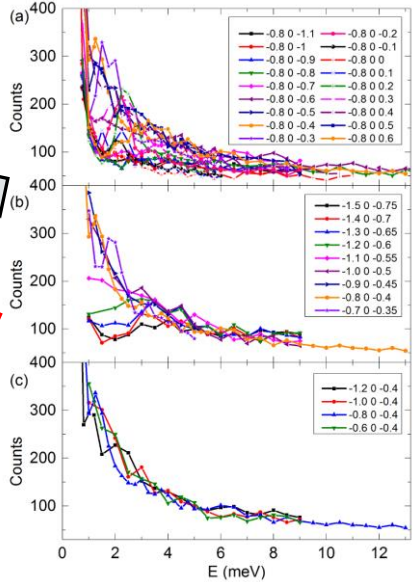
β-$TeVO_4$ RESULTS



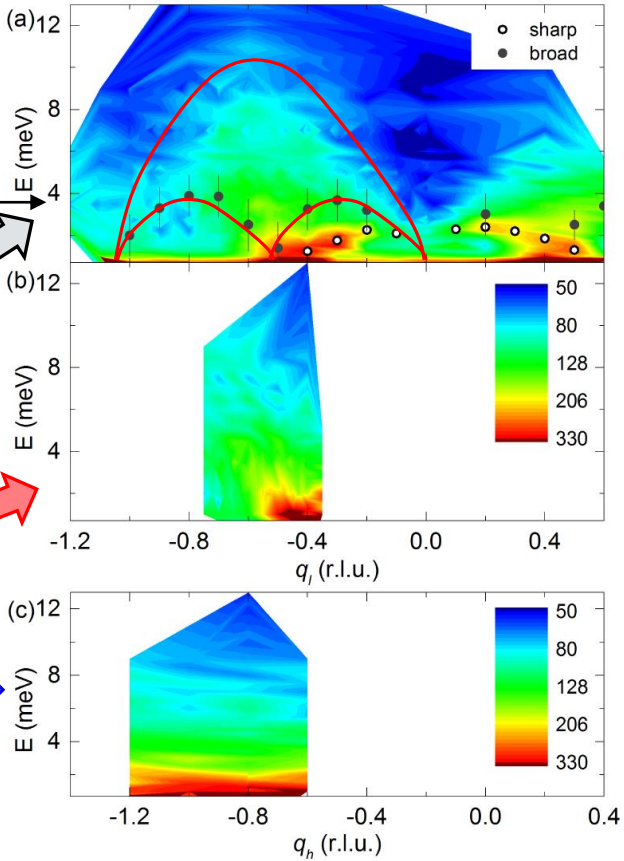
$J \sim 20$ K ~ 2 meV





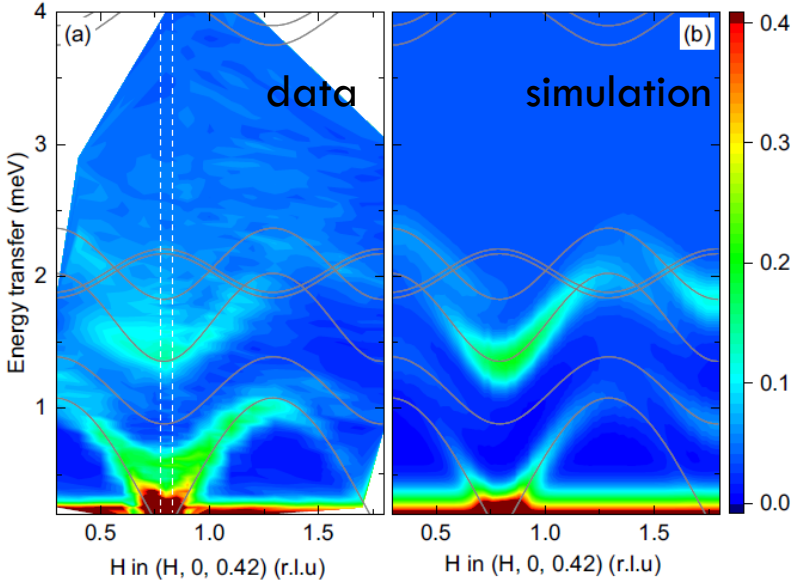


(1 meV = 11.6 K)

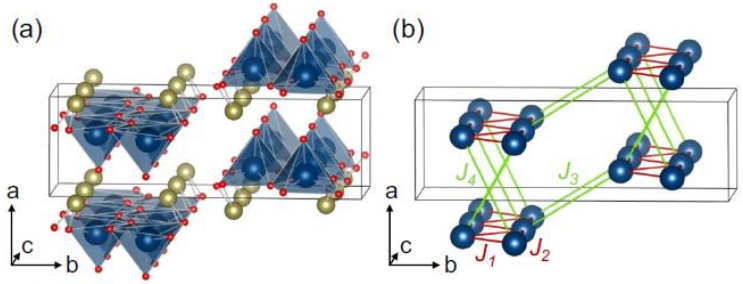


ANALYSIS – β-$TeVO_4$

Inelastic neutron scattering at 1.7 K and 0 T.



SpinW - https://spinw.org

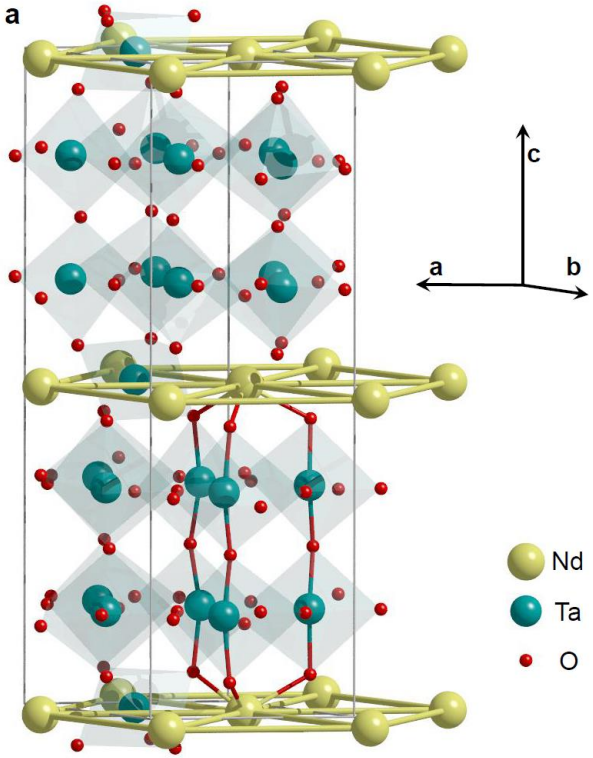


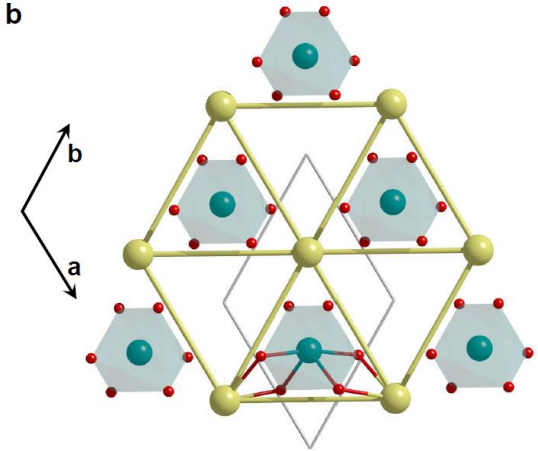
$$H = J_1 \sum_{n,j} \left(\mathbf{S}_{n,j} \cdot \mathbf{S}_{n,j+1} + \delta_1^b S_{n,j}^b S_{n,j+1}^b + \delta_1^c S_{n,j}^c S_{n,j+1}^c\right)$$
$$+ J_2 \sum_{n,j} \left(\mathbf{S}_{n,j} \cdot \mathbf{S}_{n,j+2} + \delta_2^b S_{n,j}^b S_{n,j+2}^b + \delta_2^c S_{n,j}^c S_{n,j+2}^c\right)$$
$$+ J_3 \sum_{\langle n,m\rangle,j} \mathbf{S}_{n,j} \cdot \mathbf{S}_{m,j-1} + J_4 \sum_{\langle n,m'\rangle,j} \mathbf{S}_{n,j} \cdot \mathbf{S}_{m',j+1}, \quad (1)$$

$\mathbf{k}_{IC} = (-0.208, 0, 0.419)$ and magnetic moments lying in the ac plane. The corresponding parameters are $J_1 = -38$ K, $J_2 = 38$ K, $J_3 = 3$ K, $J_4 = -1.9$ K, $\delta_1^b = 0.106$, $\delta_2^b = -0.126$, $\delta_1^c = 0.01$, and $\delta_2^c = 0.01$. uncertainty of ~5% for J_i (i = 1-4), ~20% for δ_i^b (i = 1,2), and ~50% for δ_i^c (i = 1,2).

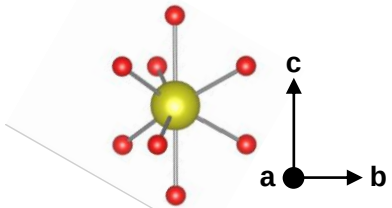
M. Pregelj et al. PRB **98,** 094405 (2018)

TRINAGULAR ANTIFERROMAGNET $NdTa_7O_{19}$

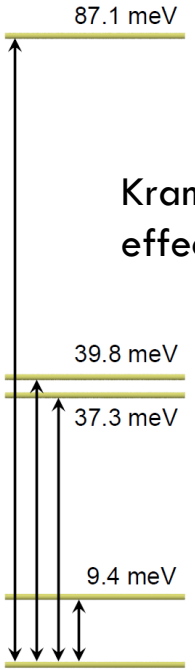




Rare earth: Nd^{3+} ($^4I_{9/2}$)



Crystal electric field levels:



Kramers doublet
effective $S = 1/2$

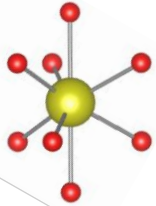
BULK MAGNETIC PROPERTIES

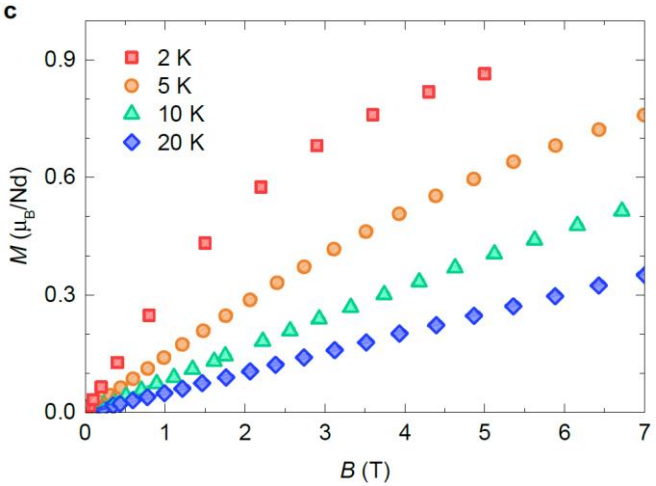
Nd^{3+} f-electrons: highly localized orbitals.

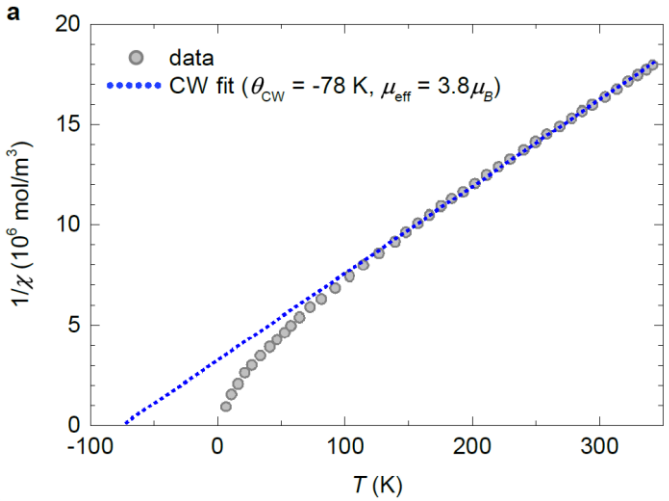
Interactions of several Kelvins are expected.

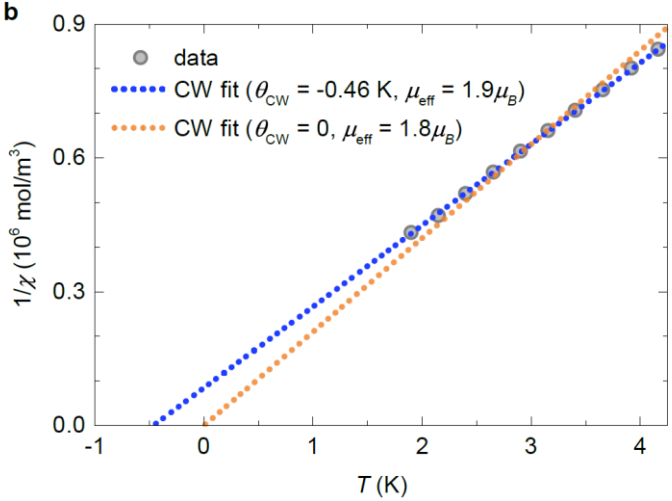
No magnetic order down to 2 K.

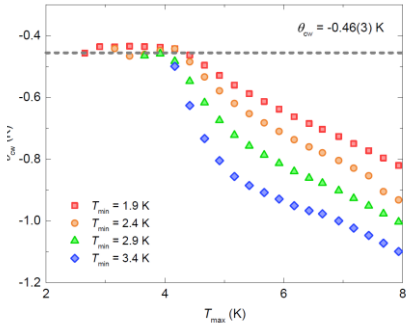
Magnetizem at higher temperatures is defined by crystal-electric-field (CEF) levels.





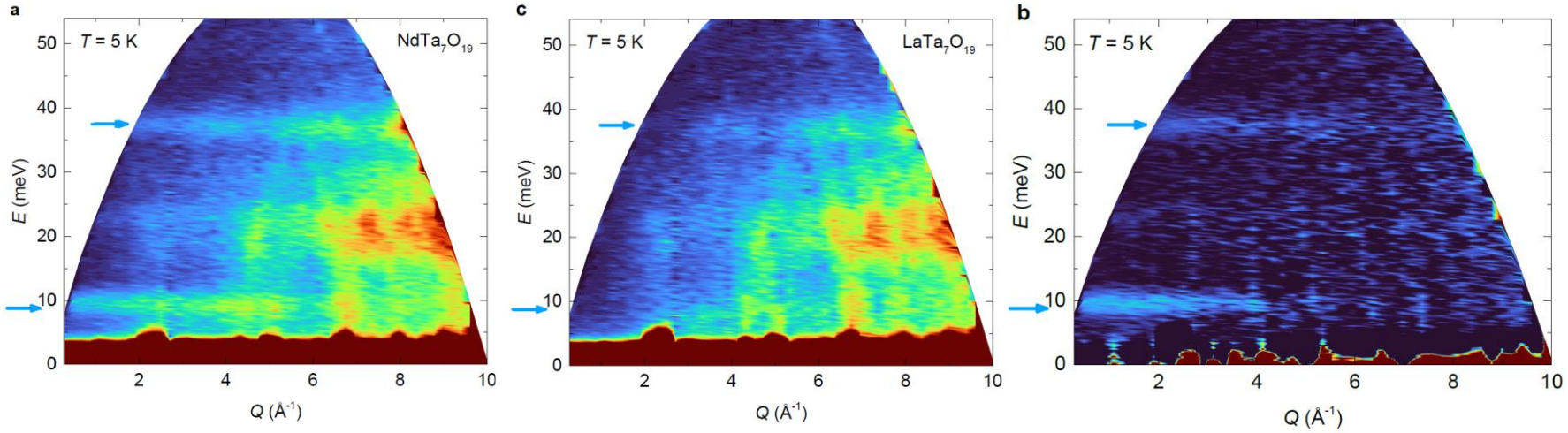






INELASTIC NEUTRON SCATTERING (INS)

Time-of-flight method at MARI instrument at ISIS source, UK.

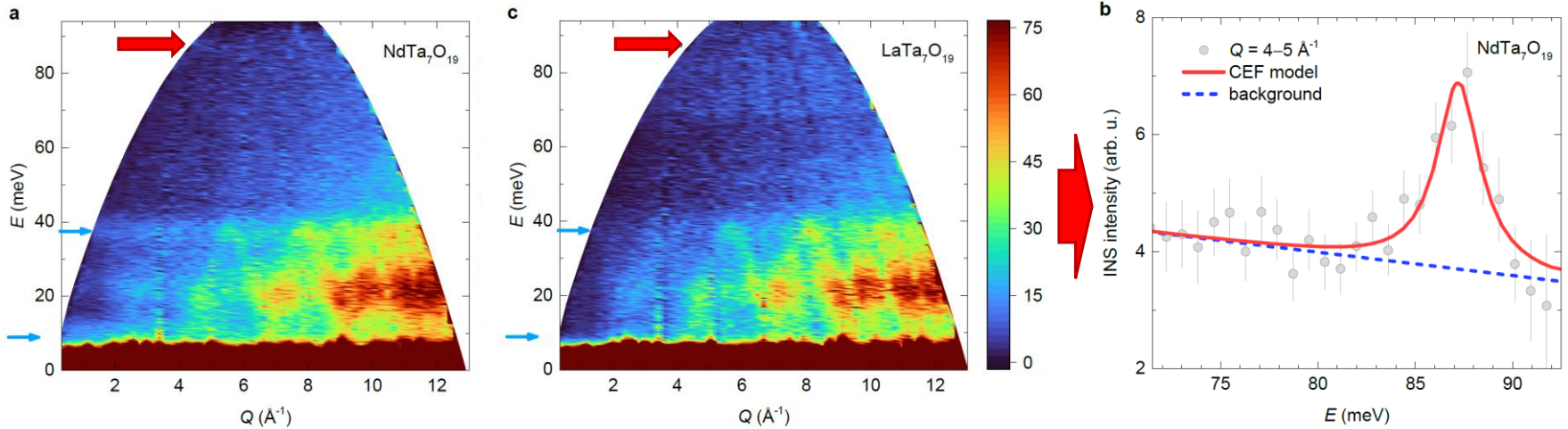


Measurements on magnetic ($NdTa_7O_{19}$) and non-magnetic ($LaTa_7O_{19}$) powders at 5 K.

Difference between the two yields magnetic signal – two flat levels.

No dispersion – single-ion property. Intensity goes down with Q – magnetic signature.

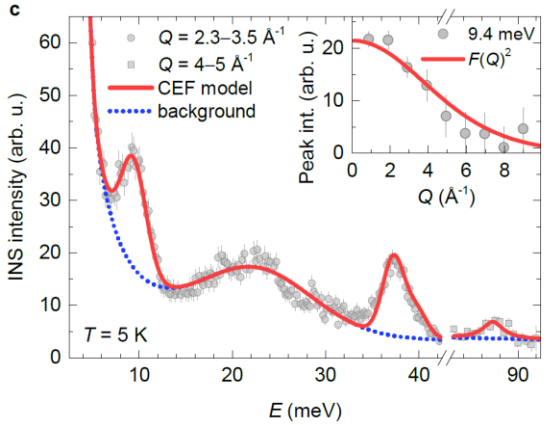
INELASTIC NEUTRON SCATTERING (INS)

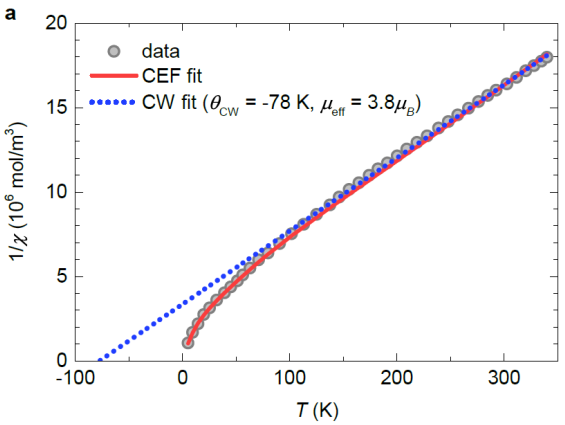


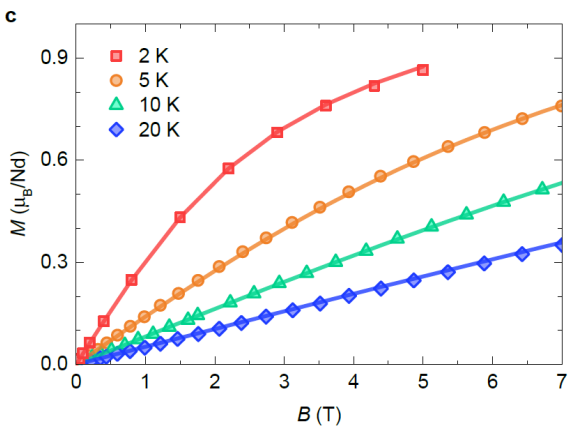
Same measurements performed with higher incident-neutron energies.

Additional flat level at higher-energies.

CRYSTAL ELECTRIC FIELD REFINEMENT







Combined refinement of INS, susceptibility and magnetization results. Program PHI (https://www.nfchilton.com/phi.html) and/or Mantid.

A single solution for CEF levels – energy levels and magnetic states.

Magnetic ground state is of Ising type – magnetic moment perpendicular to the plane (along the c axis) is dominant.

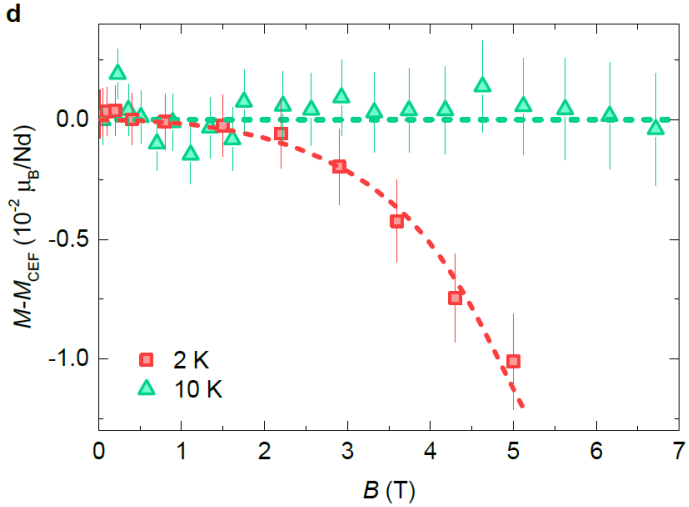
$$g \text{ factors } g_z = 2.78 \text{ and } g_{xy} = 1.22$$

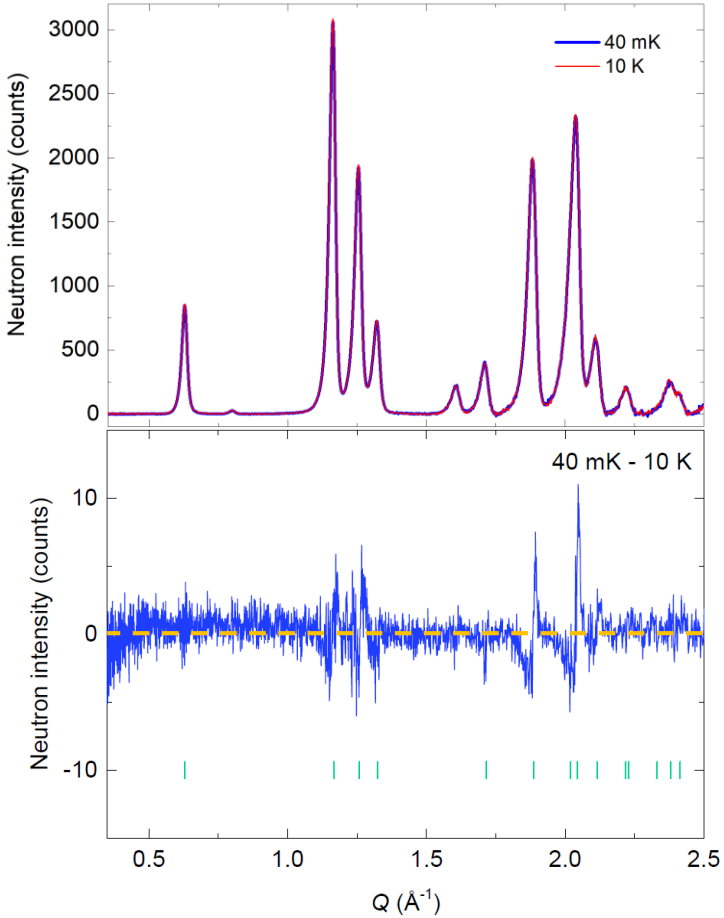
$\lvert \pm m_J \rangle$	$\pm\omega_0$	$\pm\omega_1$	$\pm\omega_2$	$\pm\omega_3$	$\pm\omega_4$
$\lvert \pm 9/2 \rangle$	0	± 0.590	0	± 0.807	0
$\lvert \pm 7/2 \rangle$	0	0	± 0.425	0	0
$\lvert \pm 5/2 \rangle$	0.933	0	-0.017	0	∓ 0.358
$\lvert \pm 3/2 \rangle$	0	0.021	0	-0.015	0
$\lvert \pm 1/2 \rangle$	0	0	-0.515	0	0
$\lvert \mp 1/2 \rangle$	∓ 0.244	0	∓ 0.574	0	-0.588
$\lvert \mp 3/2 \rangle$	0	± 0.807	0	∓ 0.590	0
$\lvert \mp 5/2 \rangle$	0	0	± 0.015	0	0
$\lvert \mp 7/2 \rangle$	0.263	0	-0.474	0	± 0.725
$\lvert \mp 9/2 \rangle$	0	0	0	0	0
E(meV)	0	9.4	37.3	39.8	87.1

GROUND STATE

CEF model does not account for complete M(H) at lowest temperature of 2 K

Comparison of neutron diffraction (WISH at ISIS) at 40 mK an 10 K imply potential presence of diffuse magnetic scattering.



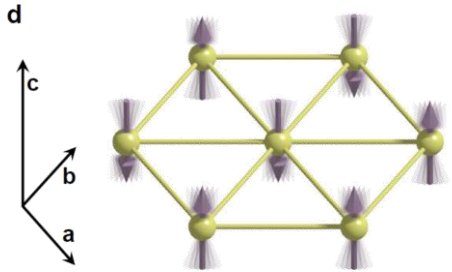


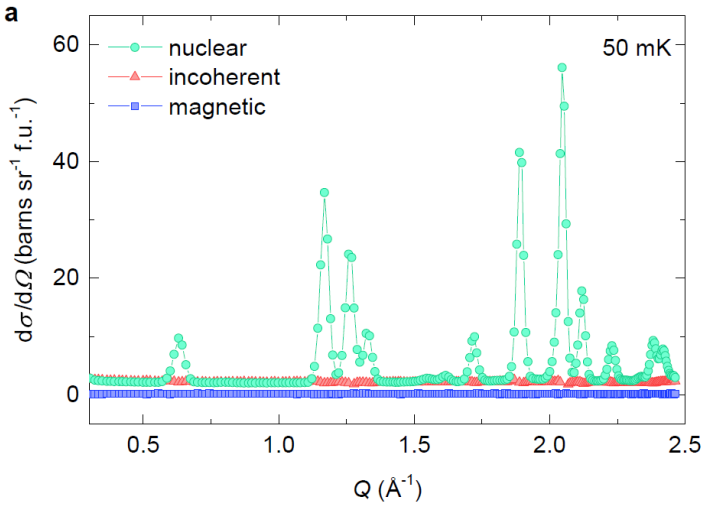
POLARIZED NEUTRON SCATTERING

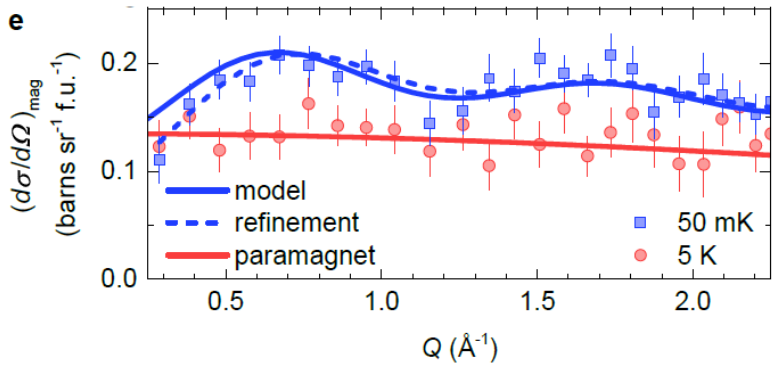
At D7 instrument at ILL, France.

Directly distinguish magnetic and non-magnetic contribution – no need for subtraction.

Reveal magnetic nearest-neighbour Ising correlations at 50 mK.

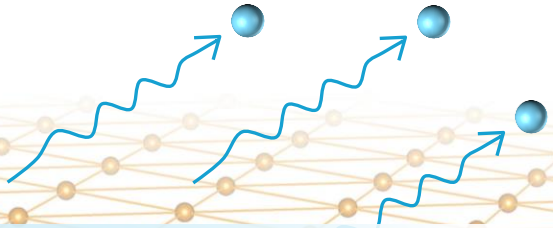






T. Arh *et al.* Nat. Matter. 21, 416, 2022

SUMMARY



Basic neutron advantages:

- Wavelength and kinetic energy comparable with interatomic spacings and excitations in solids
- Weak interaction with matter - convenient for scattering, simple interpretation
- Neutron magnetic moment couples to magnetic field - neutron “sees” magnetism

Magnetic scattering by unpaired electron spins

- Both spin and orbital angular momentum of electrons contribute
- Magnetic interactions are long range and non-central - neutrons can be used to probe electron distributions
- Nuclear and magnetic scattering have similar magnitudes
- Magnetic scattering depends only on component of B perpendicular to Q
- Polarized neutrons are sensitive to a particular magnetization direction

Inelastic neutron scattering reveals details of the shapes of interaction potentials in materials

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