Experimental aspects of magnetic structure determination and magnetic space groups

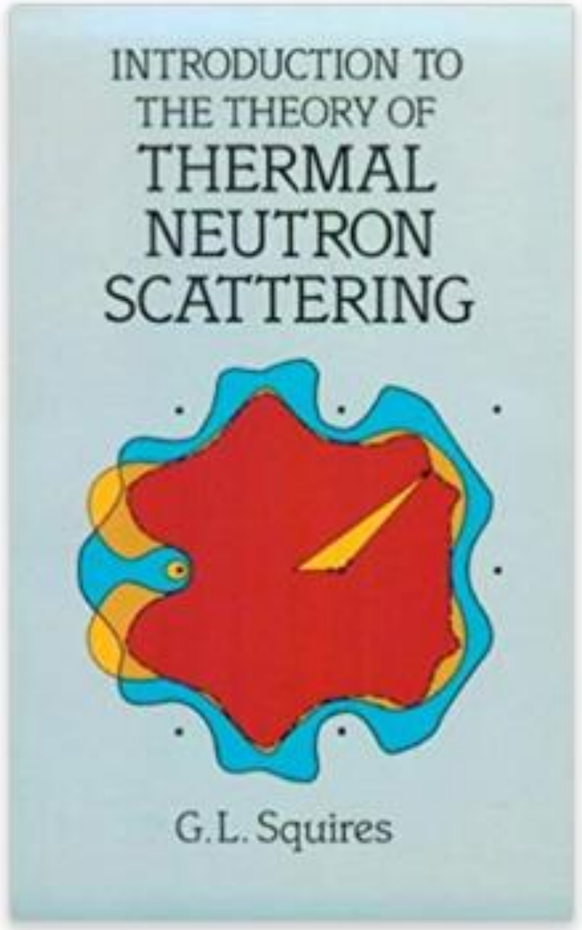
Stuart Calder
Instrument Scientist on HB-2A
Powder Diffractometer, HFIR

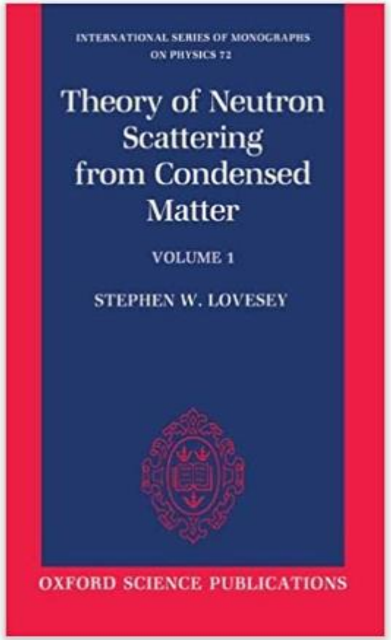
Neutron Scattering Division
Oak Ridge National Laboratory

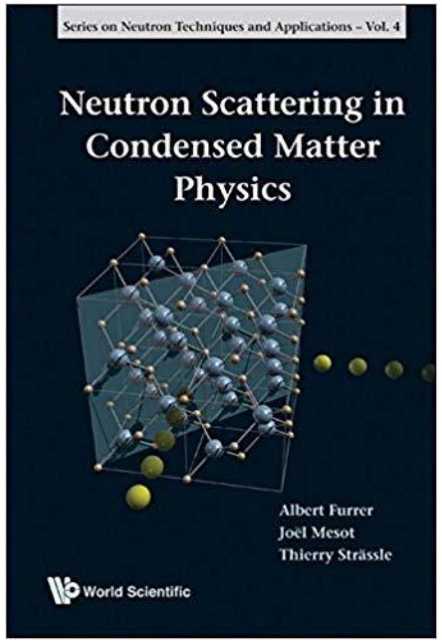
Overview

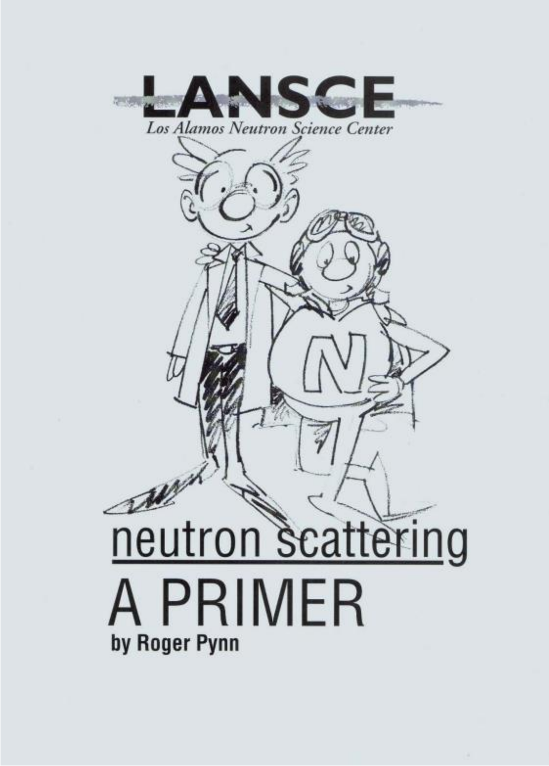
- Recap concepts for Magnetic Structures
- Magnetic Space Group approach
- Neutron Scattering to determine magnetic structures

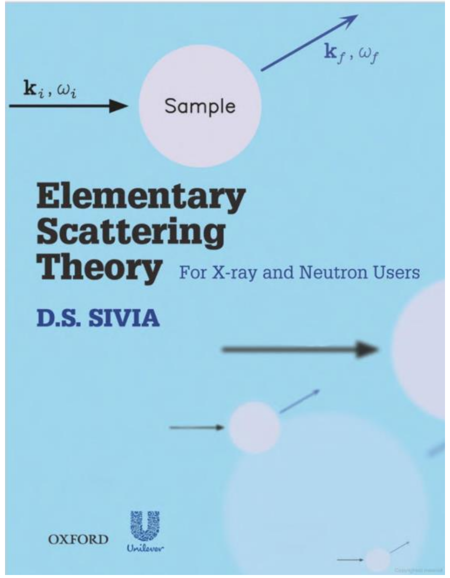
Lots of references for neutron scattering

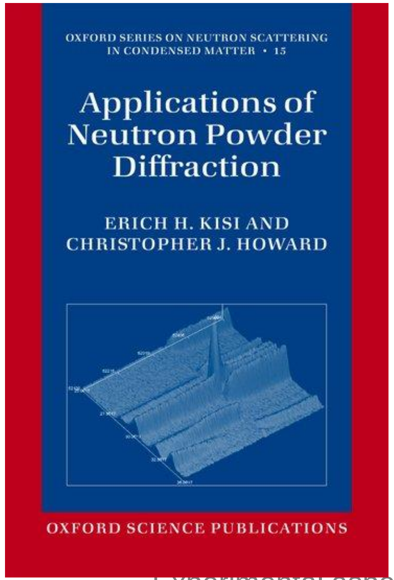


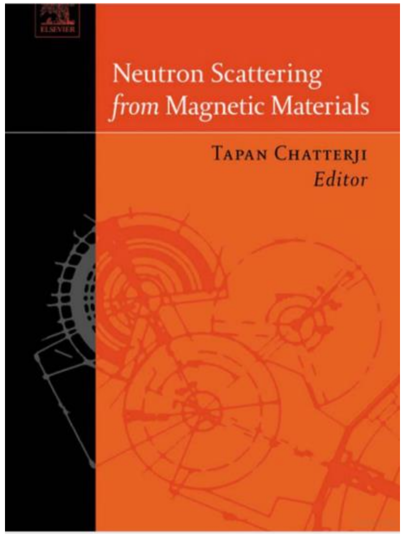












References on magnetic symmetry

- Garlea and Chakoumakos, *"Magnetic Structures" chapter in* Experimental Methods in the Physical Sciences vol. 48, p.203-290 *Academic Press, 2016*

- Juan Rodríguez-Carvajala, JacquesVillain, "Magnetic structures" https://doi.org/10.1016/j.crhy.2019.07.004

- J. Rodríguez-Carvajal and F. Bourée, "Symmetry and magnetic structures" DOI: 10.1051/epjconf/20122200010

- J M Perez-Mato, J L Ribeiro, V Petricek and M I Aroyo "Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases". doi:10.1088/0953-8984/24/16/163201

- A. Wills, "Magnetic structures and their determination using group theory" https://doi.org/10.1051/jp4:2001906

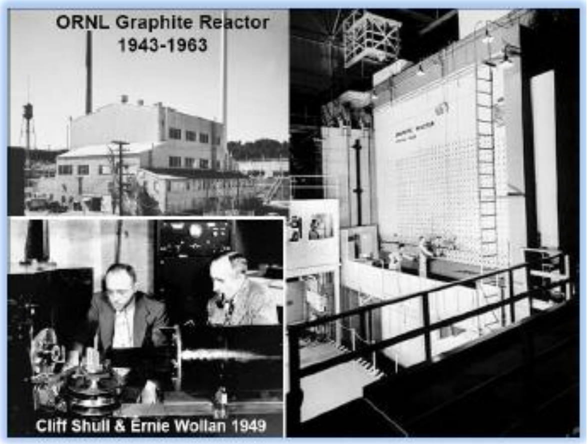
- Yurii A Izyumov, "Neutron-diffraction studies of magnetic structures of crystals" https://doi.org/10.1070/PU1980v023n07ABEH005115

- J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo, "Symmetry-Based Computational Tools for Magnetic Crystallography" 10.1146/annurev-matsci-070214-021008

Neutron Scattering and Magnetism

- ~500 BC: Ferromagnetism documented
- 1932 Neel proposes antiferromagnetism
- 1943: First neutron experiments at ORNL
- 1951: Antiferromagnetism measured in MnO and Ferrimagnetism in Fe_3O_4 at ORNL by Shull and Wollan.
- 1950-60: Shubnikov and Bertaut develop methods for magnetic structure description.

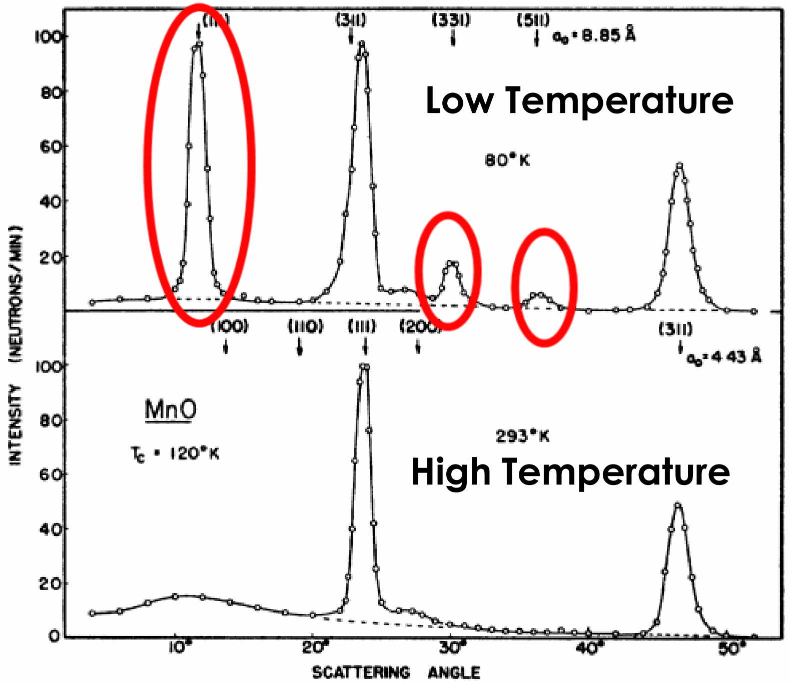
Sinan, ~200 BC

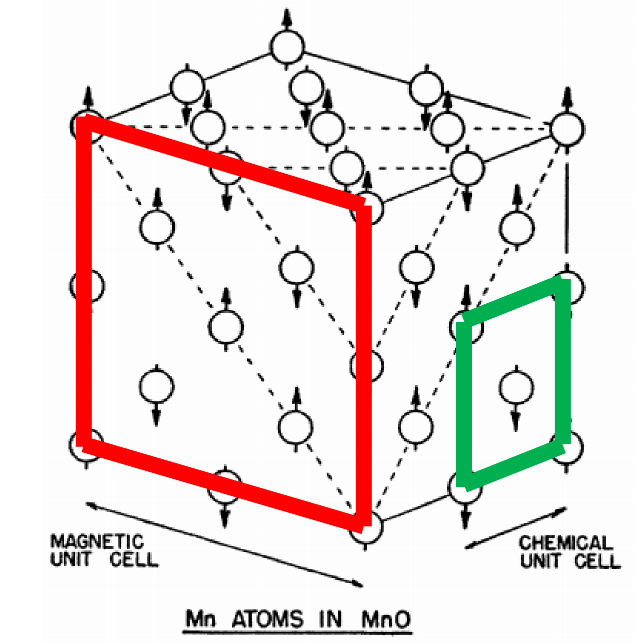


PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)

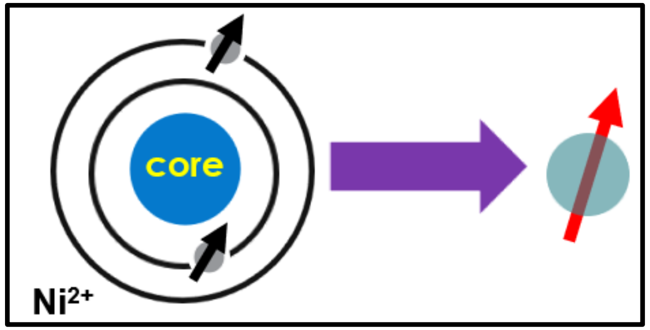




<u>Neutron scattering remains the best tool for determining magnetic structures</u>

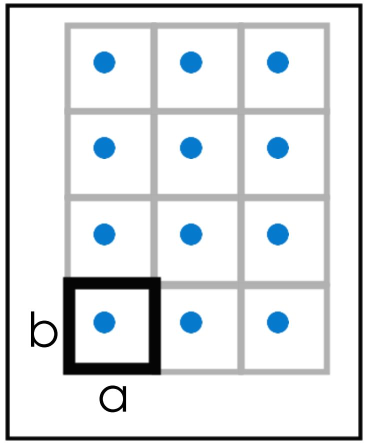
OAK RIDGE National Laboratory | HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

Magnetic order: Magnetic moment and interactions



m=g_J**J** (rare earths)
m=g_s**S** (transition metals)
Ni^{2+} has a localized magnetic moment of $2\mu_B$

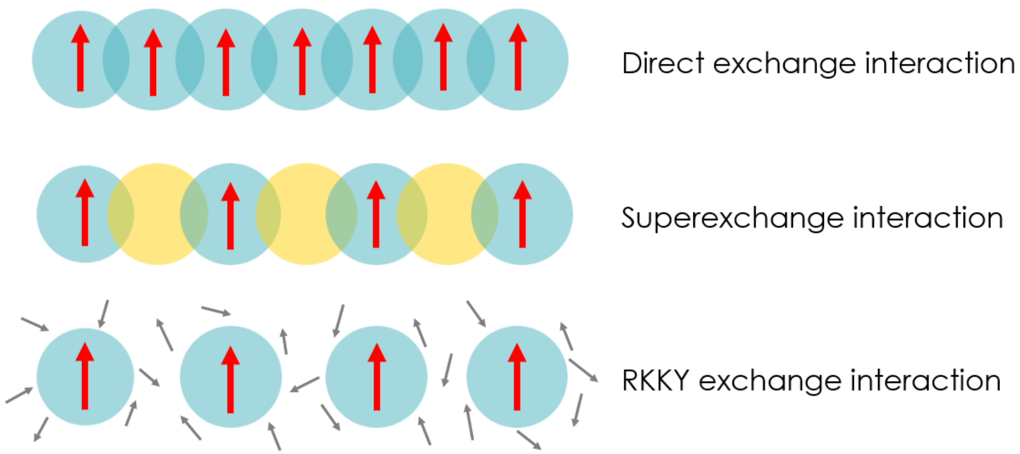
+

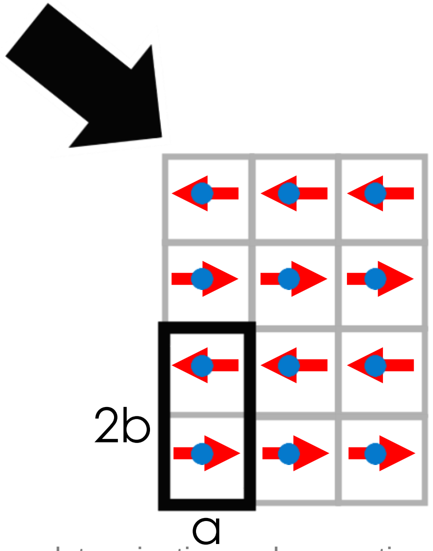


+

$$\mathcal{H}_{ex} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$

- Described by Hamiltonian with exchange parameter *J*





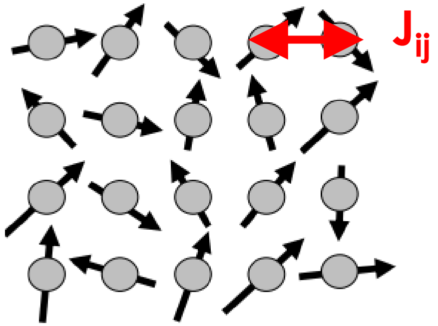
Moment + Crystal + Interaction = Magnetic Structure

Magnetic structure: Ordered spins in a crystalline lattice

Paramagnetism

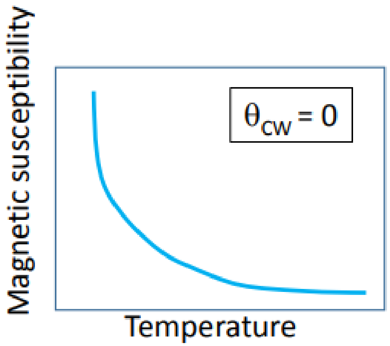
High temperature, $J < k_B T$

$E_{ij} = -J_{ij}\mathbf{S}_i.\mathbf{S}_j$



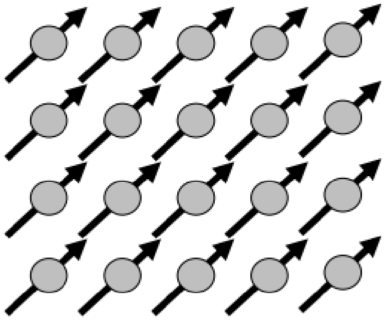
Paramagnetic state (no order)

Curie-Weiss: $\chi = C/(T-\theta_{CW})$

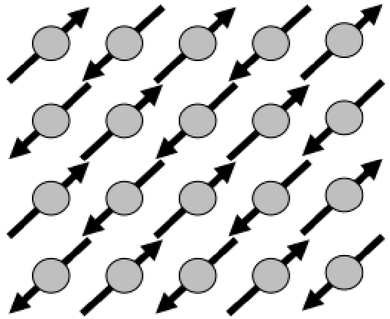


Long range magnetic order

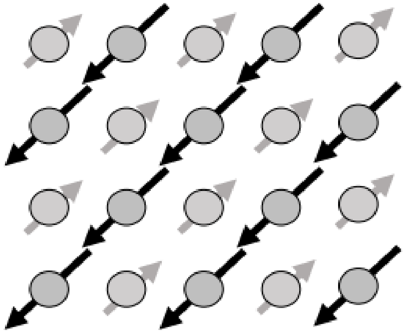
Low temperature, $J > k_B T$



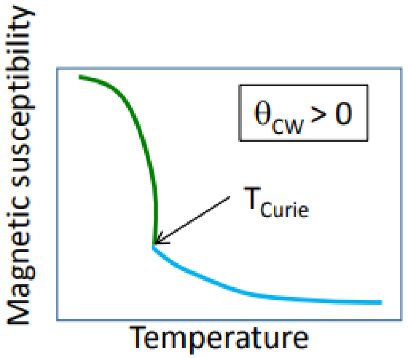
Ferromagnetic order

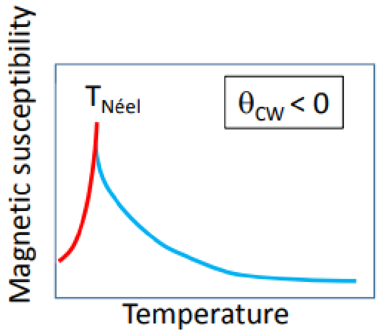


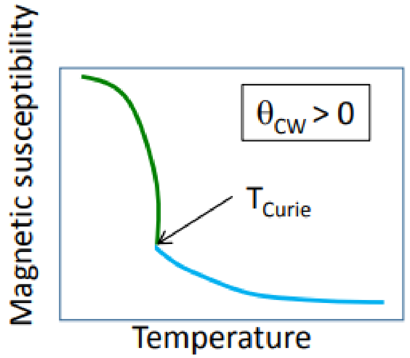
Antiferromagnetic order



Ferrimagnetic order



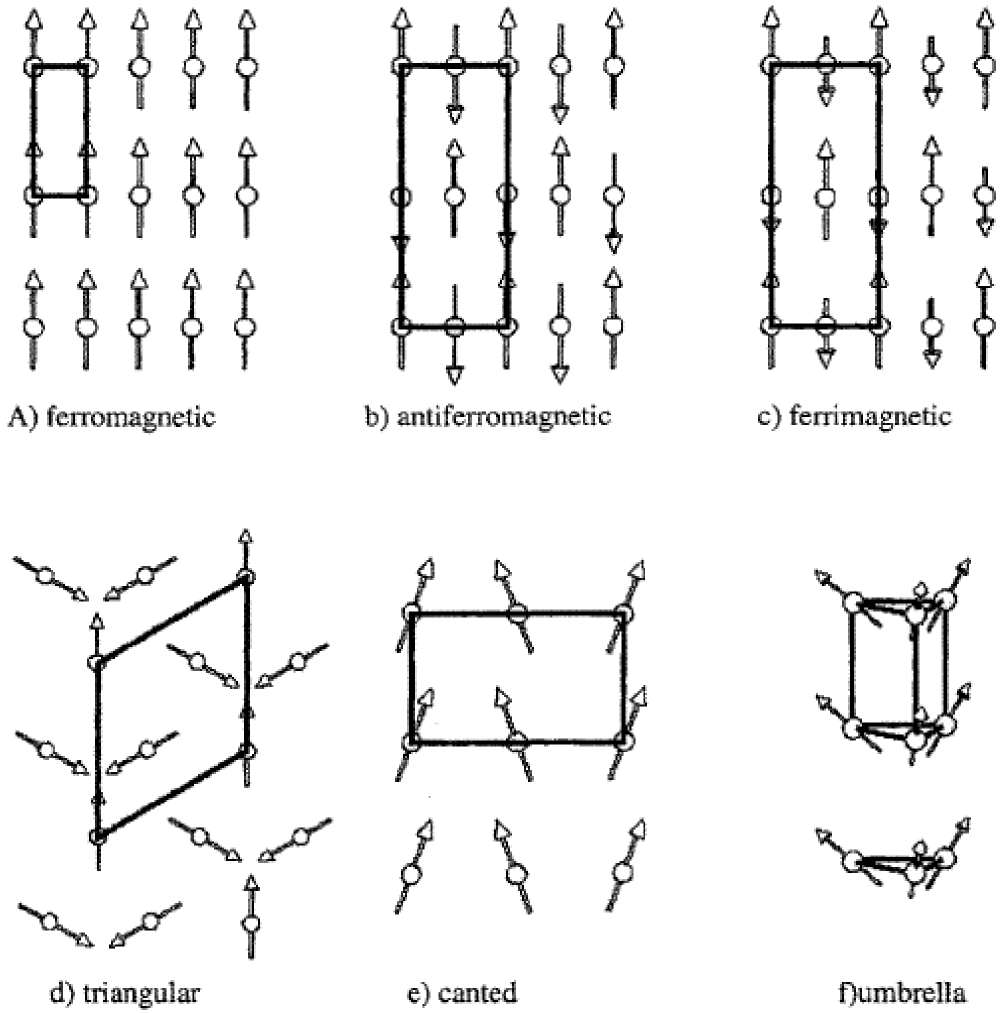




- Time-reversal is a valid symmetry operator for paramagnetic phase, but is broken in the ordered phase

Magnetic structures

- Lots of types (and mixtures of these types).

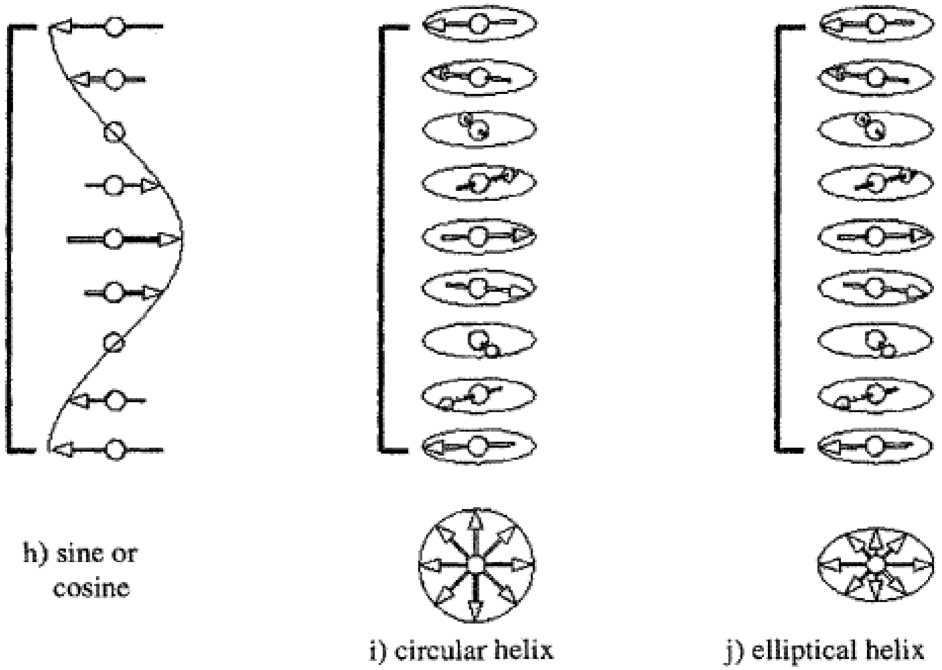


J. Phys. IV France **11** (2001) Pr9-133

Magnetic structures and their determination using group theory

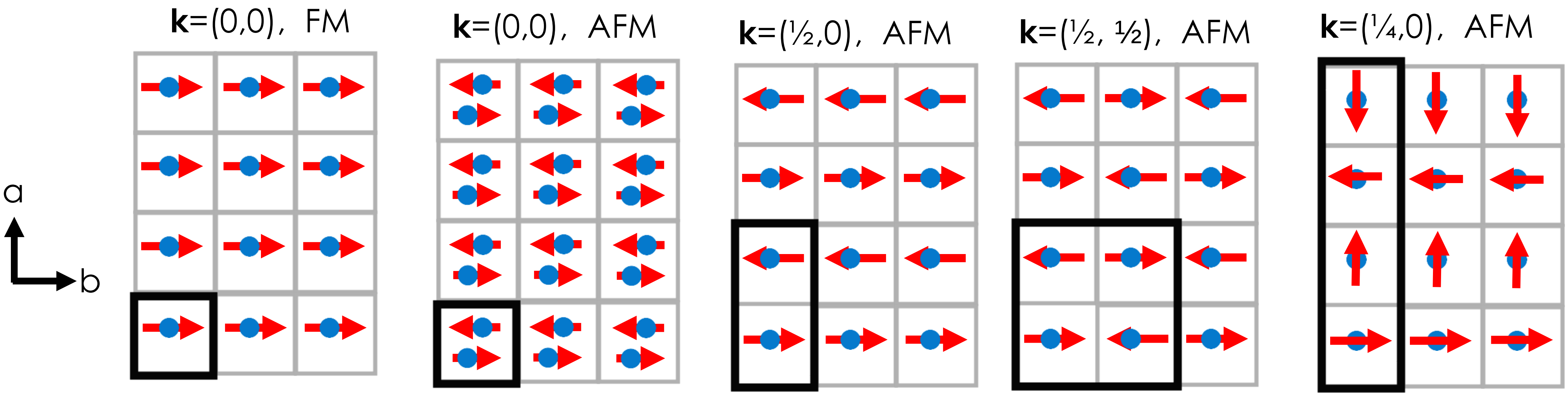
A. Wills

Institut Laue-Langevin, BP. 156x, 38042 Grenoble cedex, France



Magnetic propagation vector: **k**-vector

- k-vector describes the relation between the nuclear and magnetic unit cells



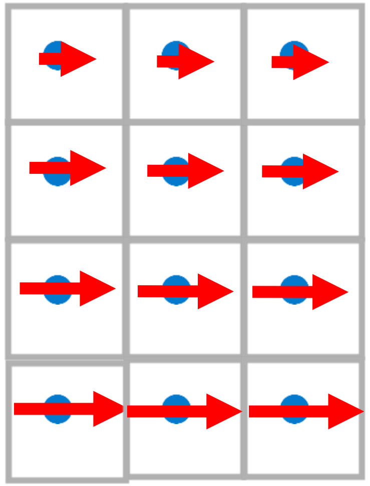
Crystal unit cell

Magnetic unit cell

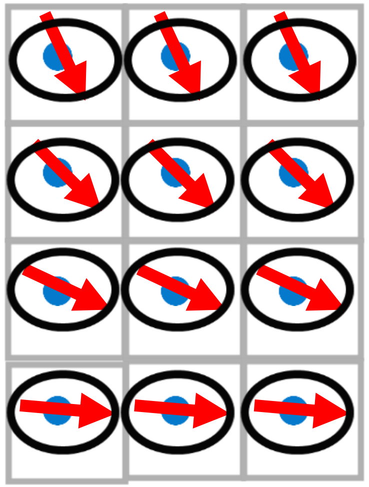
Atom

Spin

Incommensurate spin density wave structure with $\mathbf{k}_1=(\delta,0)$



Incommensurate Helical structure with $\mathbf{k}_1=(\delta,0)$



General magnetic structure description with k-vectors

- **Can state only the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.**
- All magnetic ordering is periodic, this can be expressed in the Fourier series:

k-vector

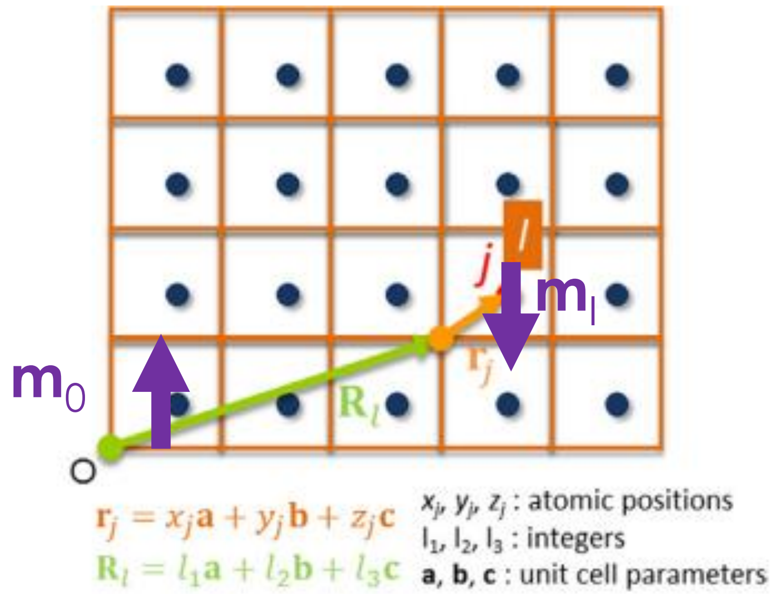
spin at the atomic site *j* in some unit cell that is related to the 0th cell (G_0) by a translation **R**.

$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\ \mathbf{S}_j^{k}\ e^{-2\pi i \mathbf{k}.R}$$

$\mathbf{S}_j$ (Basis vector): spin in the 0th cell.

Lattice translation to unit cell

Correlation of the spin m_j on atom j within unit cell l to m_0 in the 0th unit cell translated by R



What are the ways to describe magnetic structures?

- Magnetic structures can get complicated.
- Often dealing with limited data.

- **Want a systematic way to simplify, determine and describe magnetic structures**
  → Use symmetry

> "It is only slightly overstating the case to say that physics is the study of symmetry"
>
> P. W. Anderson
>
> *Science*, New Series, Vol. 177, No. 4047 (Aug. 4, 1972), 393-396.

What are the ways to describe magnetic structures?

Two main approaches

- Both based on symmetry to help constrain your model
- End results identical
- Both methods have advantages and allow checks of magnetic structure
- **GSAS-II uses Magnetic Space Groups**

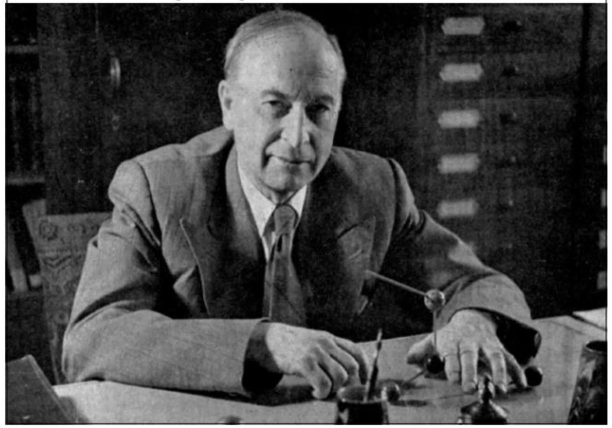
Magnetic Space Groups

- Extension of crystallographic space groups to include spin
- Describes symmetry of magnetic/non-magnetic atoms so can provide insights
- Incommensurate only recently added through supersymmetry description (not currently in GSAS-II)

Representational analysis (IRs)

- Finds basis vectors in k-vector approach
- Equally applicable to simple commensurate and complex incommensurate magnetism
- Separates magnetic/non-magnetic descriptions

Magnetic space groups (Shubnikov groups)



Alexey Vasilyevich Shubnikov 1887-1970

- Natural extension of the crystallographic space group description.
  - But only recently became widely used for magnetism.

1929: Heesch, introduces the antiidentity operation properties: u2 = 1, ut = tu for all t∈T

- **aka time reversal group = {1,1'} (Z. Krist. 71, 95)**

1945: Shubnikov re-introduces concept of bi-colour point groups

1951: Shubnikov describes and illustrates all of the bicolor point groups (→ Shubnikov groups)

1955: Belov, Neronova, Smirnova (BNS) - first complete listing of the Shubnikov groups (Sov. Phys. Crys 1, 487-488)

1957: Zamorzaev, group theoretical derivation of Shubnikov groups (Kristallografiya2, 15 (Sov. Phys. Cryst., 3, 401))

1965: Opechowski and Guccione (OG), first complete derivation and enumeration of the Shubnikov groups

2001: Litvin, corrected Opechowski-Guccione symbols (Acta Cryst. A57, 729-730)

2010: Magnetic Space Groups on computer programs (Stokes and Campbell, BYU)

Future: combine magnetic space group and representational analysis approaches for complete insights

Extend Space Group Approach to include magnetism

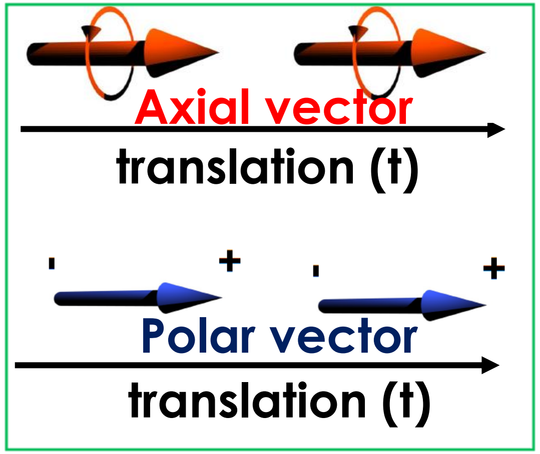
- 230 crystallographic space groups:
  - Atoms considered as simple points at a certain location, then apply symmetry operations.

- Now add magnetic moments:
  - Underlying crystal lattice unchanged, with moments at atomic positions.
  - BUT moments are not points, they are vectors … axial vectors.
  - Location and orientation need to be considered when applying symmetry operations.

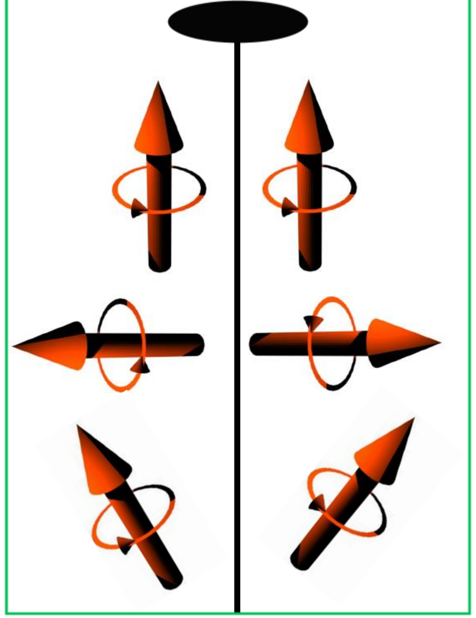
- Symmetry operations for crystal space groups not enough to describe magnetic structures.

Magnetic space groups: Spins are axial vectors

- Translation (t) and 2-fold rotation are the same for axial and polar vectors.

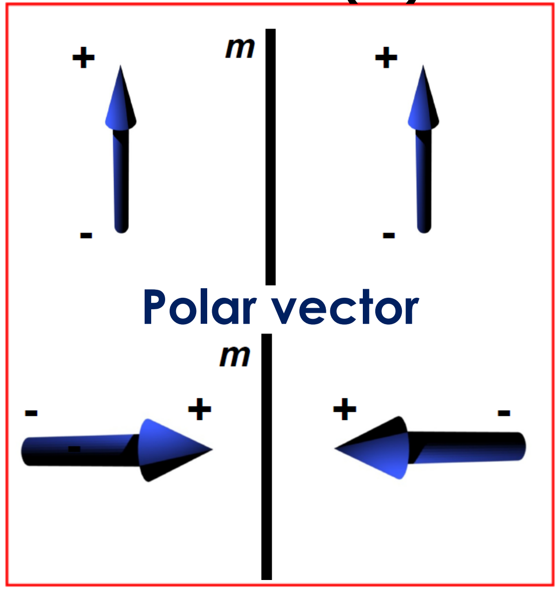


2-fold rotation

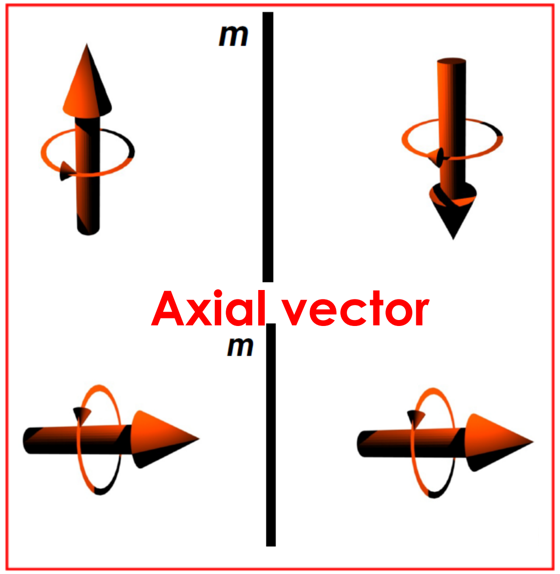


- Inversion and mirror (m) are different for axial and polar.

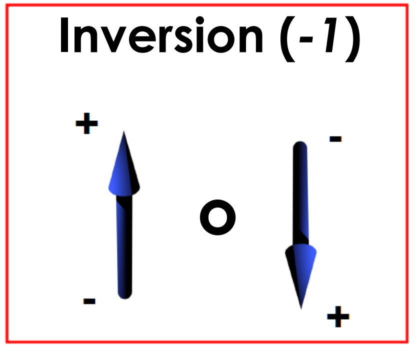
Mirror (m)



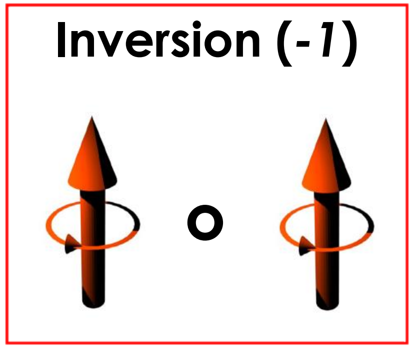
Mirror (m)



Polar vector



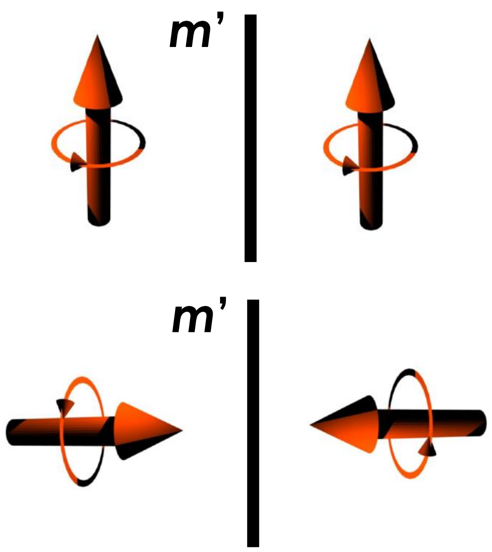
Axial vector

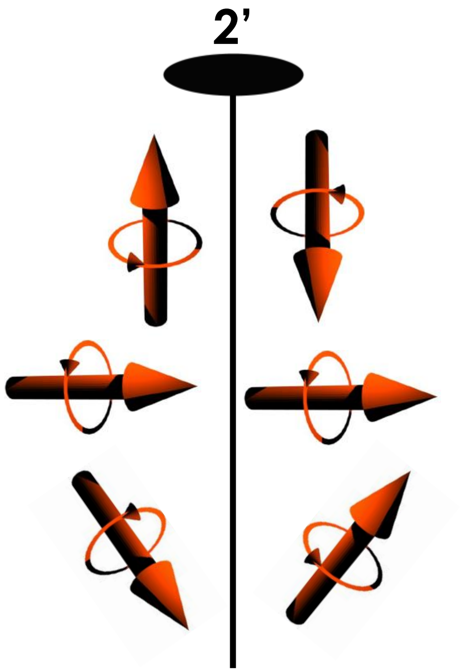


Magnetic space groups: Time-reversal

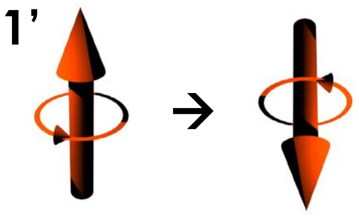
- To describe magnetic moments fully a new operator is added
  - Time reversal or prime (1’)
  - Reverses the final current loop to allow a further set of symmetry operations.
- m’ (anti-mirror) behaves like polar vector
- 2’ (anti-rotation) inverts axial vector
- **All magnetic structures can be described by a combination of primed and unprimed symmetry operators**

anti-mirror





Time reversal = spin reversal
(changes the sense of the current)



Building the magnetic space groups

- By associating the 1' spin operator with a color change (black to white or black to red) the magnetic symmetry theory was termed black-white symmetry.

- **The original 230 space groups are included as colorless groups and keep their standard labels**
  - **e.g. *Pmmm***

- **A further 230 groups are created by adding the 1' operator as an extra symmetry operation**
  - **e.g. *Pmmm'***
  - **These correspond to paramagnetic states and are termed grey (each magnetic site is both black and white = grey)**

- **The remaining 1191 magnetic space groups are created by combining the 1' operator with one or more of the symmetry operation in each of the 230 crystallographic space groups**
  - **e.g. *Pm'mm* where the mirror plane perpendicular to *a* is now an anti-mirror and the other two are unchanged.**

→ Combining all possibilities leads to 1651 magnetic space groups

Building the magnetic space groups

Example based on space group *P2/m*

Type-I	Type-II	Type-IV
Fedorov group	gray group	black/white lattice
10.42 $P2/m$	10.43 $P2/m1'$	10.48 P_b2/m
(x,y,z)	(x,y,z)	(x,y,z)
$(-x,y,-z)$	$(-x,y,-z)$	$(-x,y,-z)$
$(-x,-y,-z)$	$(-x,-y,-z)$	$(-x,-y,-z)$
$(x,-y,z)$	$(x,-y,z)$	$(x,-y,z)$
	$(x,y,z)'$	$(x,y+1/2,z)'$
	$(-x,y,-z)'$	$(-x,y+1/2,-z)'$
	$(-x,-y,-z)'$	$(-x,-y+1/2,-z)'$
	$(x,-y,z)'$	$(x,-y+1/2,z)'$

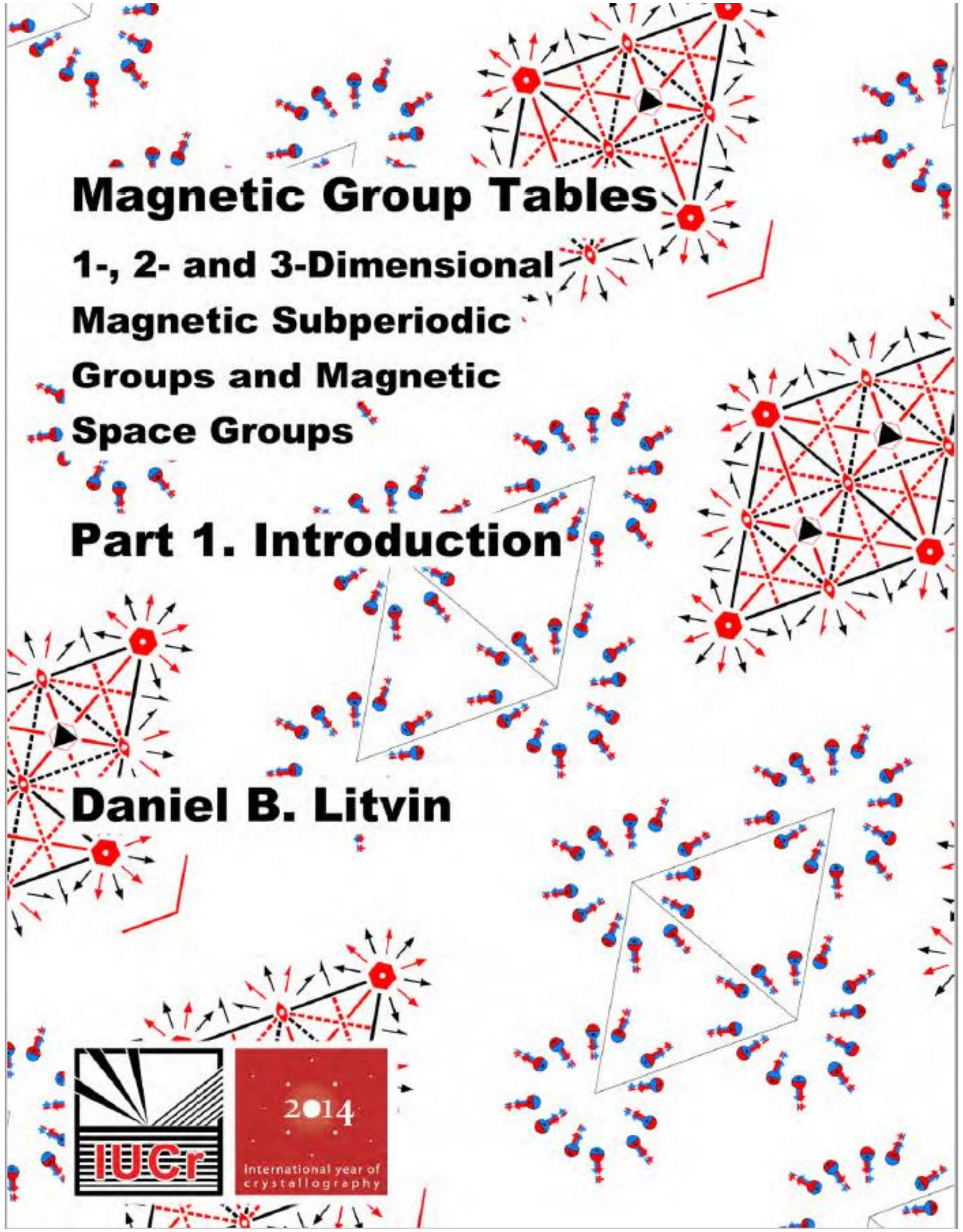
Type-III
black/white PG
10.44 $P2'/m$
(x,y,z)
$(-x,y,-z)'$
$(-x,-y,-z)'$
$(x,-y,z)$

Don't panic → All the hard work is done by **Bilbao Crystallographic Server** or **ISOTROPY** software suite

Type-I: *M=G* no primes (single color)	**230**
Type-II: *M=G+G1'* all primed and unprimed (paramagnetic or gray groups)	**230**
Type-III (3a): *M=D+(G-D)'* half are primed (black-white groups) Groups of the "first kind" D is translationgleiche *D translation is the same as G*	**674**
Type-IV (3b): *M=D+(G-D)'* half are primed (black-white groups) Groups of the "second kind" D is klassengleiche *D contains antitranslations leading to primitive magnetic cells larger than primitive crystal cells*	**517**
Total magnetic space groups	**1651**

Magnetic space groups

- Full description of all Magnetic Space groups produced.
  - Acta Cryst A57, 729-730 (2001)
  - Acta Cryst. (2008). A64, 419-424 (2008)
- Utilized in analysis tools
  - Isodistort, Bilbao (GSAS-II), Fullprof, JANA, etc



Bilbao Crystallographic Server http://www.cryst.ehu.es/

FCT/ZTF

bilbao crystallographic server

Forthcoming schools and workshops:

News:

- **MAGNDATA steadily increases**
  11/2022: The database of magnetic structures MAGNDATA reaches 2000 entries.
- **New program: Check Topological Phonons**
  11/2022: Check the topology of each gapped set of phonon bands
- **New program: ProjectiveRep PG**
  11/2022: Tables of projective representations of magnetic plane point groups
- **Space-group symmetry**
  05/2022: The monoclinic and tetragonal ITA-settings database has been

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- Space-group symmetry
- Magnetic Symmetry and Applications
- Group-Subgroup Relations of Space Groups
- Representations and Applications
- Solid State Theory Applications
- Structure Utilities
- Topological Quantum Chemistry
- Subperiodic Groups: Layer, Rod and Frieze Groups
- Structure Databases

Bilboa Crystallographic Server: Pyrochlore example

- Input space group, k-vector to obtain symmetry allowed magnetic structures.

Maximal magnetic space groups for the parent space group *Fd*-3*m* (No. 227) and the propagation vector k = (0, 0, 0)

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Space-group symmetry

Magnetic Symmetry and Applications

MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MKVEC	The k-vector types and Brillouin zones of Magnetic Space Groups
IDENTIFY MAGNETIC GROUP	Identification of a Magnetic Space Group from a set of generators in an arbitrary setting
BNS2OG	Transformation of symmetry operations between BNS and OG settings
mCIF2PCR	Transformation from mCIF to PCR format (FullProf).
MPOINT	Magnetic Point Group Tables
MAGNEXT	Extinction Rules of Magnetic Space Groups
MAXMAGN	Maximal magnetic space groups for a given space group and a propagation vector
MAGMODELIZE	Magnetic structure models for any given magnetic symmetry
STRCONVERT	Convert & Edit Structure Data (supports the CIF, mCIF, VESTA, VASP formats -- with magnetic information where available)
k-SUBGROUPSMAG	Magnetic subgroups consistent with some given propagation vector(s) or a supercell
MAGNDATA	A collection of magnetic structures with portable cif-type files
MVISUALIZE	3D Visualization of magnetic structures with Jmol
MTENSOR	Symmetry-adapted form of crystal tensors in magnetic phases
MAGNETIC REP.	Decomposition of the magnetic representation into irreps
Get_mirreps	Irreps and order parameters in a paramagnetic space group- magnetic subgroup phase transition

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
	Fd'-3'm' (#227.132) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
	Fd-3m' (#227.131) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
	Fd'-3'm (#227.130) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
	Fd-3m (#227.128) Go to a subgroup	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
	$I4_1/am'd'$ (#141.557) Go to a subgroup	$\begin{pmatrix} 0 & 0 & -1 & 1/4 \\ 1/2 & 1/2 & 0 & 1/4 \\ 1/2 & -1/2 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
6	*$I4_1'/a'm'd$* (#141.556) Go to a subgroup	$\begin{pmatrix} 0 & 0 & -1 & 1/4 \\ 1/2 & 1/2 & 0 & 1/4 \\ 1/2 & -1/2 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
7	*$I4_1'/amd'$* (#141.555) Go to a subgroup	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 1/2 & 1/2 & 0 & 1/4 \\ -1/2 & 1/2 & 0 & 1/4 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
8	*$I4_1/a'md$* (#141.553) Go to a subgroup	$\begin{pmatrix} 0 & 0 & -1 & 1/4 \\ 1/2 & 1/2 & 0 & 1/4 \\ 1/2 & -1/2 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
9	*Imm'a'* (#74.559) Go to a subgroup	$\begin{pmatrix} 1/2 & 1/2 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show
10	*Im'ma* (#74.556) Go to a subgroup	$\begin{pmatrix} 1/2 & 1/2 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	*Systematic absences* MAGNEXT *Tensor properties* MTENSOR	Show

Magnetic Structure

Selected magnetic space group: 2- *Fd-3m'* (#227.131)

Setting of the parent group

Parent space group *Fd-3m* (No. 227)

Lattice parameters: a=10.09060, b=10.09060, c=10.09060, alpha=90.0000, beta=90.0000, gamma=90.0000

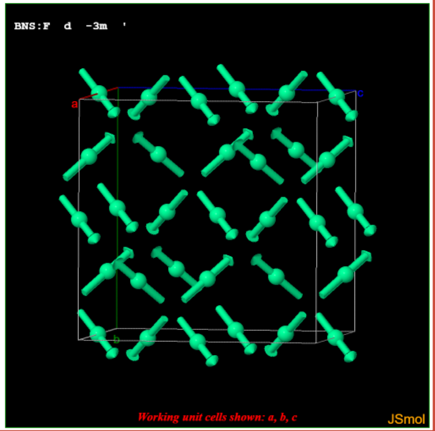
[Go to setting standard (**a**, **b**, **c** ; 0, 0, 0)]
[Go to an alternative setting]

Export data to MCIF file/Visualize | Go to a subgroup

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	Occupancy	New WP	Multiplicity	Magnetic moment	Values of M_x, M_y, M_z
1	Ho1 Ho 0.50000 0.50000 0.50000	1.	$(1/2,1/2,1/2 \mid m_x,m_x,m_x)$ $(1/4,3/4,0 \mid -m_x,-m_x,m_x)$ $(3/4,0,1/4 \mid -m_x,m_x,-m_x)$ $(0,1/4,3/4 \mid m_x,-m_x,-m_x)$ $(1/2,0,0 \mid m_x,m_x,m_x)$ $(1/4,1/4,1/2 \mid -m_x,-m_x,m_x)$ $(3/4,1/2,3/4 \mid -m_x,m_x,-m_x)$ $(0,3/4,1/4 \mid m_x,-m_x,-m_x)$ $(0,1/2,0 \mid m_x,m_x,m_x)$ $(3/4,3/4,1/2 \mid -m_x,-m_x,m_x)$ $(1/4,0,3/4 \mid -m_x,m_x,-m_x)$ $(1/2,1/4,1/4 \mid m_x,-m_x,-m_x)$ $(0,0,1/2 \mid m_x,m_x,m_x)$ $(3/4,1/4,0 \mid -m_x,-m_x,m_x)$ $(1/4,1/2,1/4 \mid -m_x,m_x,-m_x)$ $(1/2,3/4,3/4 \mid m_x,-m_x,-m_x)$	16	(M_x,M_x,M_x)	M_x = 1
2					-	-

MVISUALIZE: 3D Visualization of magnetic structures



GSAS-II pulls allowed magnetic space groups directly.

All-in, all-out magnetic structure

Bilboa Crystallographic Server (http://www.cryst.ehu.es/)

MAGNDATA → Collection of Magnetic Structures

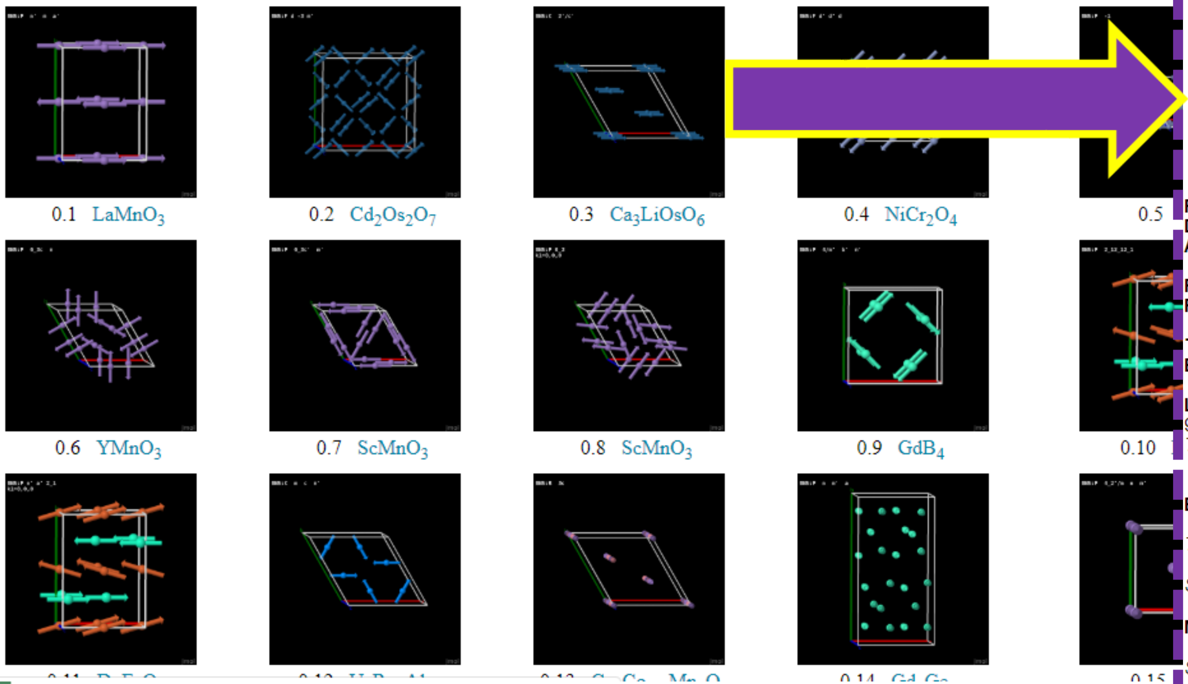
MAGNDATA: A Collection of magnetic structures with portable cif-type files

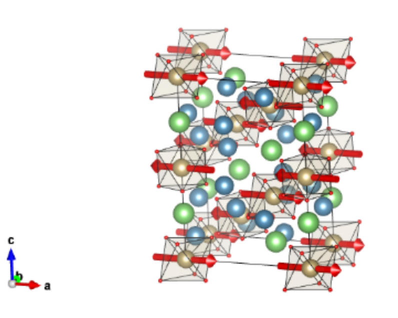
Element search (separate with space or comma): ◉ AND ○ OR Search Advanced Search & Statistics

Enter the label of the structure: Submit

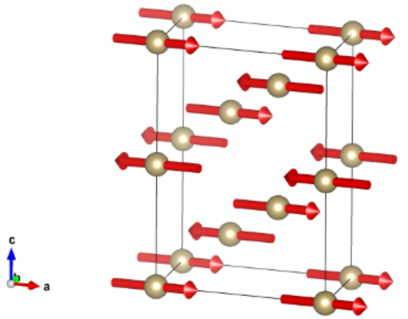
2070 structures found

Zero propagation vector





Magnetic structure with all atoms



Magnetic structure with only magnetic atoms

Reference: S. Calder, M. D. Lumsden, V. O. Garlea, J. W. Kim, Y. G. Shi, H. L. Feng, K. Yamaura, A. D. Christianson et al., *PHYSICAL REVIEW B* (2012) **86** 054403
DOI: 10.1103/PhysRevB.86.054403
Atomic positions from: same reference

Parent space group (paramagnetic phase): R-3c (#167)
Propagation vector: k1 (0, 0, 0)

Transition Temperature: 117.1 K
Experiment Temperature: 4 K

Lattice parameters of the magnetic unit cell:
9.2570 9.2570 10.7630 90.0000 90.0000 120.0000
Transformation from parent structure: (**a**,**b**,**c**;0,0,0)
[View matrix form]

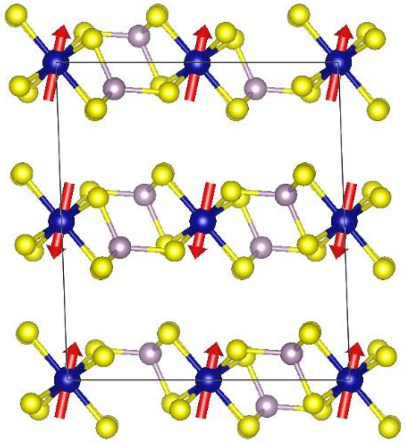
BNS Magnetic Space Group: C2'/c' (#15.89) (non-standard)
[View symmetry operations]
Transformation to a standard setting: (-**a**/3-2**b**/3-2**c**/3,-**a**,**a**/3+2**b**/3-**c**/3;0,1/2,0)
[View matrix form]
Systematic absences for this Magnetic Space Group via MAGNEXT

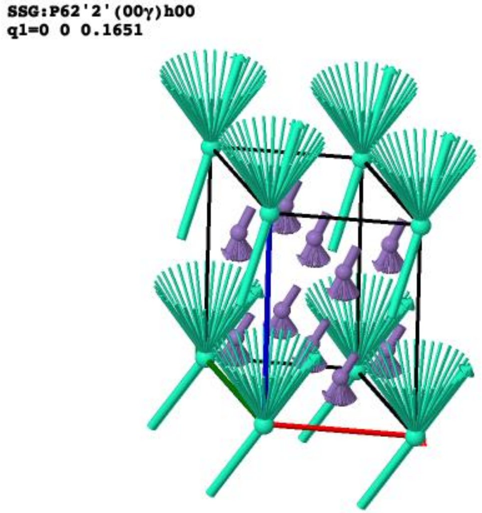
Magnetic Point Group: 2'/m' (5.5.16)
[View symmetry operations]
Symmetry-adapted form of material tensors via MTENSOR
Symmetry-adapted form of material tensors for domain-related equivalent structures via MTENSOR

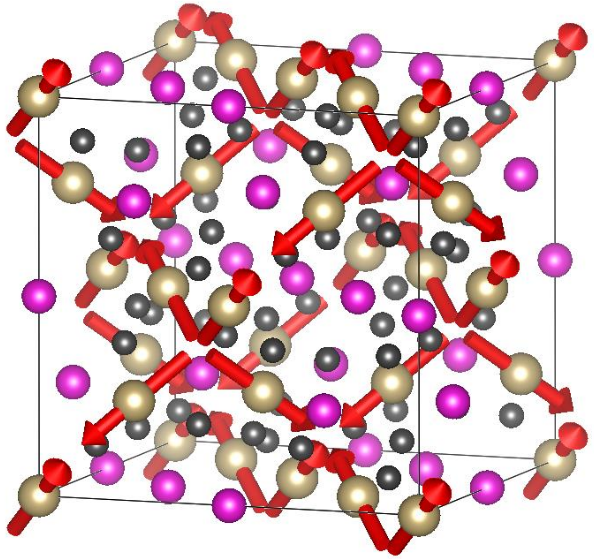
Positions and magnetic moments of symmetry independent atoms:
From now on, magnetic atoms are in boldface and colored in red. Magnetic moments are expressed in units of μB

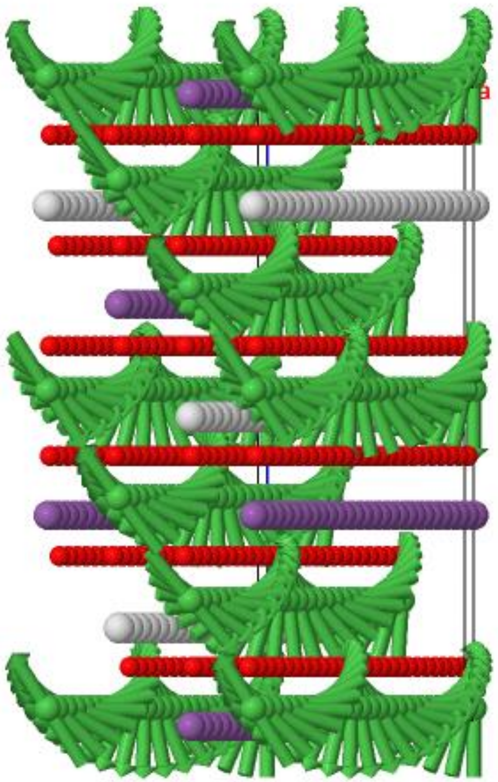
mCIF file

- Magnetic structures are now standardized.
- Output from refinement software (Fullprof, TOPAS, GSAS-II or generated from BCS, ISODISTORT).
- Read by software like cif files.
- Nice visualization with VESTA.









Magnetic Superspace groups

- Magnetic space group approach has been fully generalized to include incommensurate structures beyond the 1651 Shubnikov groups

IOP Publishing — Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **24** (2012) 163201 (20pp) doi:10.1088/0953-8984/24/16/163201

TOPICAL REVIEW

Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases

J M Perez-Mato[1], J L Ribeiro[2], V Petricek[3] and M I Aroyo[1]

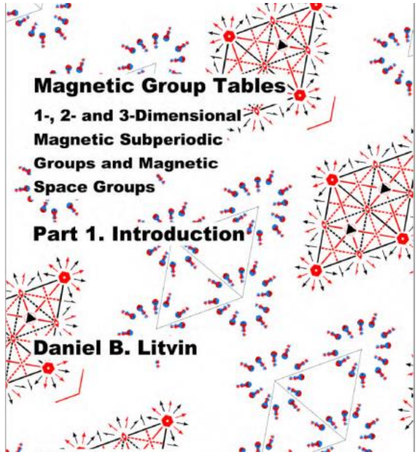
[1] Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apartado 644, E-48080 Bilbao, Spain
[2] Centro de Física da Universidade do Minho, P-4710-057 Braga, Portugal
[3] Institute of Physics, Academy of Sciences of the Czech Republic v.v.i., Na Slovance 2, CZ-18221 Praha 8, Czech Republic

E-mail: jm.perez-mato@ehu.es

Received 11 November 2011, in final form 13 February 2012
Published 26 March 2012
Online at stacks.iop.org/JPhysCM/24/163201

Abstract
Superspace symmetry has been for many years the standard approach for the analysis of non-magnetic modulated crystals because of its robust and efficient treatment of the structural constraints present in incommensurate phases. For incommensurate magnetic phases, this generalized symmetry formalism can play a similar role. In this context we review from a practical viewpoint the superspace formalism particularized to magnetic incommensurate phases. We analyse in detail the relation between the description using superspace symmetry and the representation method. Important general rules on the symmetry of magnetic incommensurate modulations with a single propagation vector are derived. The power and efficiency of the method is illustrated with various examples, including some multiferroic materials. We show that the concept of superspace symmetry provides a simple, efficient and systematic way to characterize the symmetry and rationalize the structural and physical properties of incommensurate magnetic materials. This is especially relevant when the properties of incommensurate multiferroics are investigated.

Methodology for determining magnetic structures



It is only slightly overstating the case to say that physics is the study of symmetry.

— Philip Anderson (1972)

Model:
Magnetic Space groups

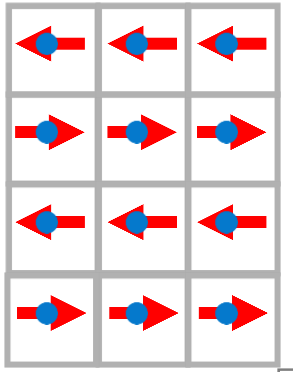
+

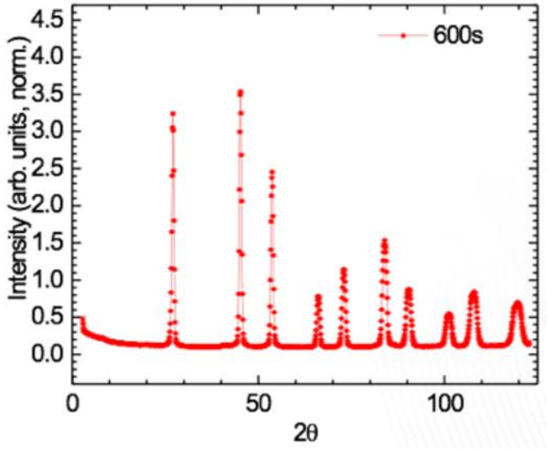
Data:
Neutron diffraction

Magnetic Refinement

GSAS-II

Magnetic structure



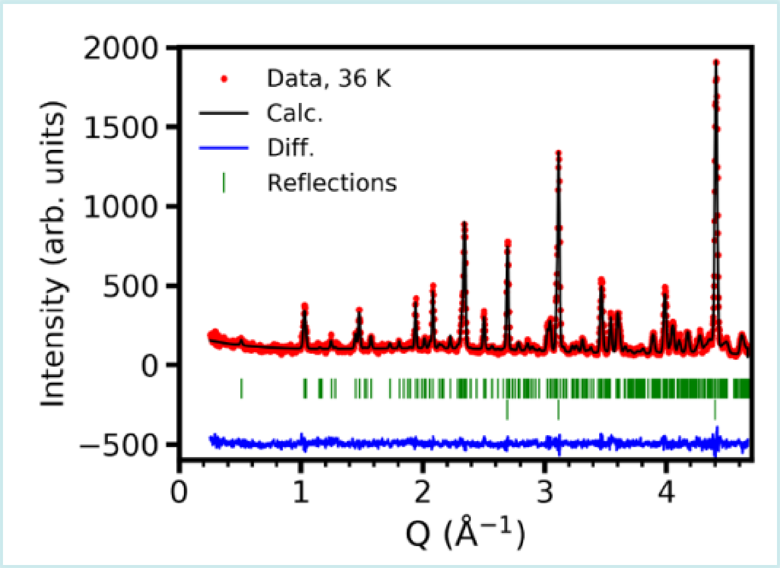


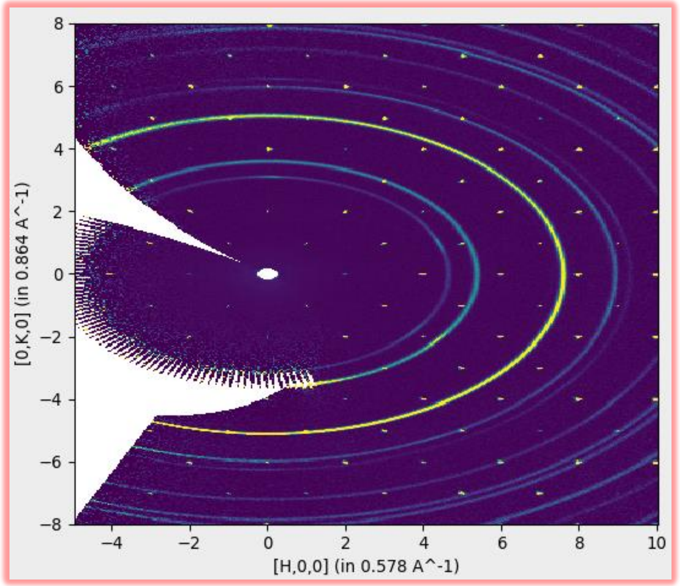
"If the neutron did not exist, it would need to be invented"

— Bertram Brockhouse

Neutron scattering

"If the neutron did not exist, it would need to be invented"
- Bertram Brockhouse





Why neutrons?

- **Wavelength**: Comparable to atomic distances (1- 5 Å)
  - Strong nuclear interaction with nuclei (nuclear scattering from a point)

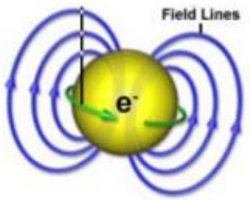
- **No charge**: Can travel through thick samples (cm) and equipment

- **Neutron spin** (μ_N): dipole interaction with unpaired electrons → $\boldsymbol{\mu} = -(\mathbf{L} + 2\mathbf{S})\mu_B$
  - Scattering from magnetic potential produced by e spin or e orbit
  - Magnetic scattering of a similar magnitude to nuclear scattering (often smaller, sometimes larger)

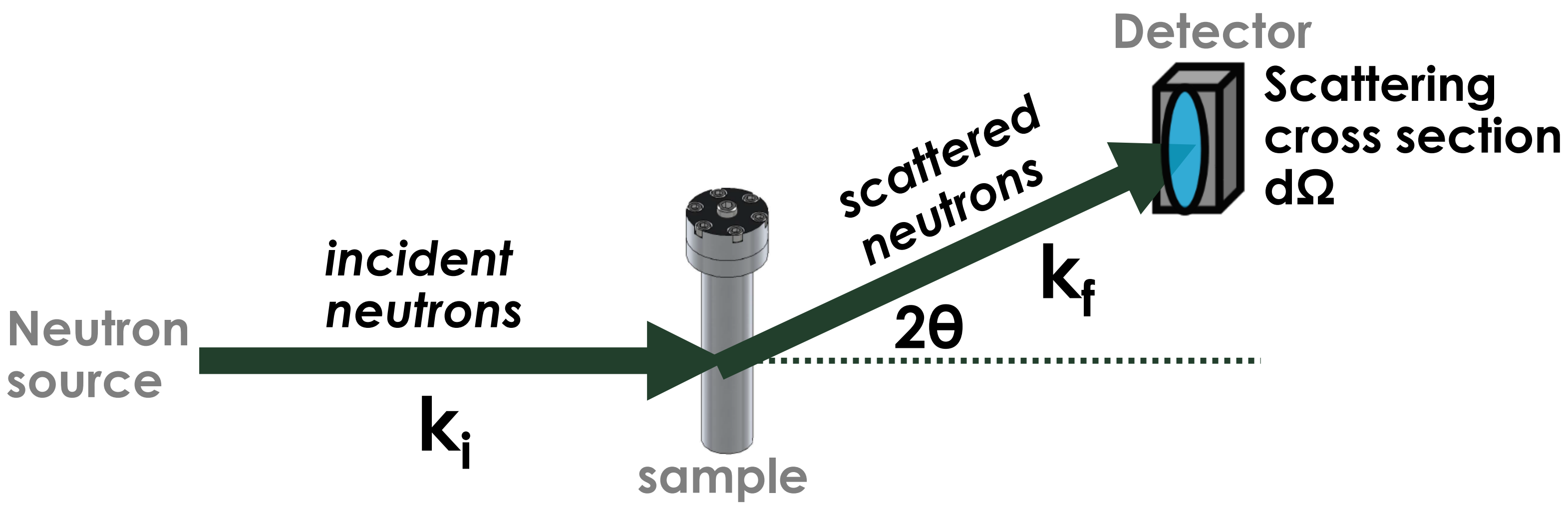
Magnetic potential (V_m) measured

$$V_m = \mu_n . B$$

Magnetic field (B) produced by unpaired electrons (spin and orbital)



Neutron Scattering Cross section for diffraction

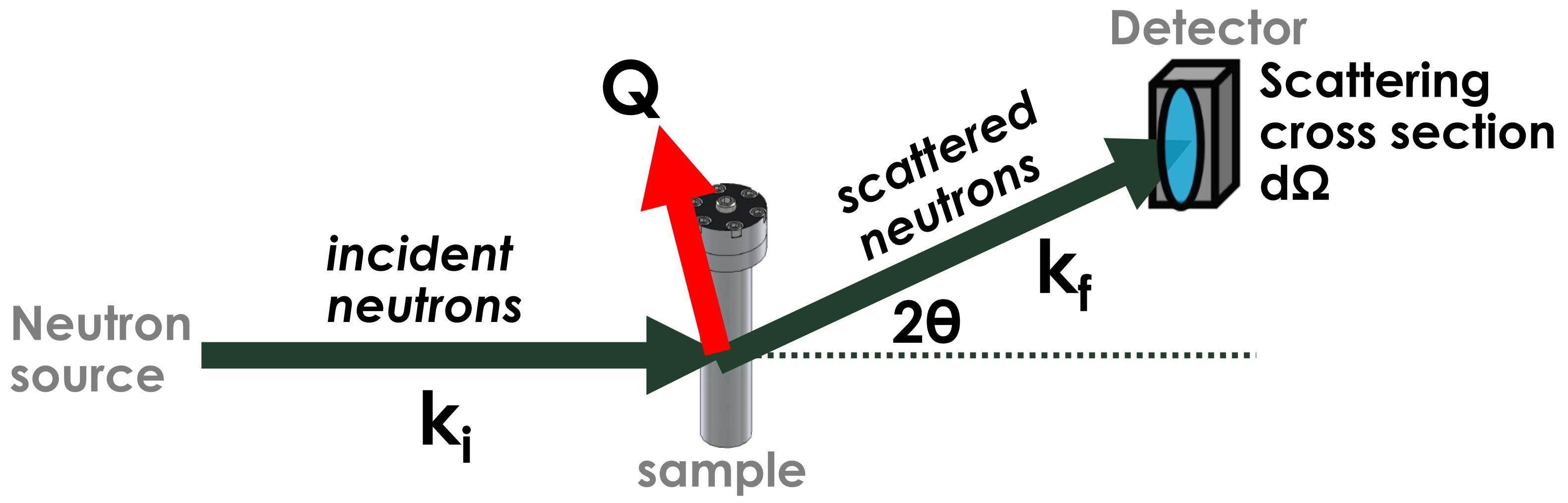


Neutron source produces an incident beam of neutrons that scatters from a nucleus or unpaired electron [*sample*] into a defined cross-section dΩ [*detector*].

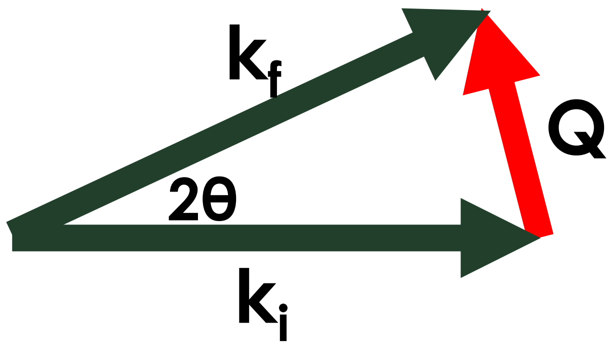
Flux:	$\Phi = \frac{\text{Rate of neutrons through area}}{\text{area}}$	10^6-10^9 n/cm²/s
Rate of scattering: [Cross section]	$\sigma = \frac{\text{Rate of neutrons scattered}}{\Phi}$	Atom → 1 barn =10^{-24} cm². Effective surface area of nucleus
Rate of scattering (dσ) into a specific solid angle (dΩ): [Differential cross section]	$\frac{d\sigma}{d\Omega} = \frac{\text{Rate of neutrons scattered into } d\Omega}{\Phi \times d\Omega}$	Units of barn/steradian.

Neutron Diffraction

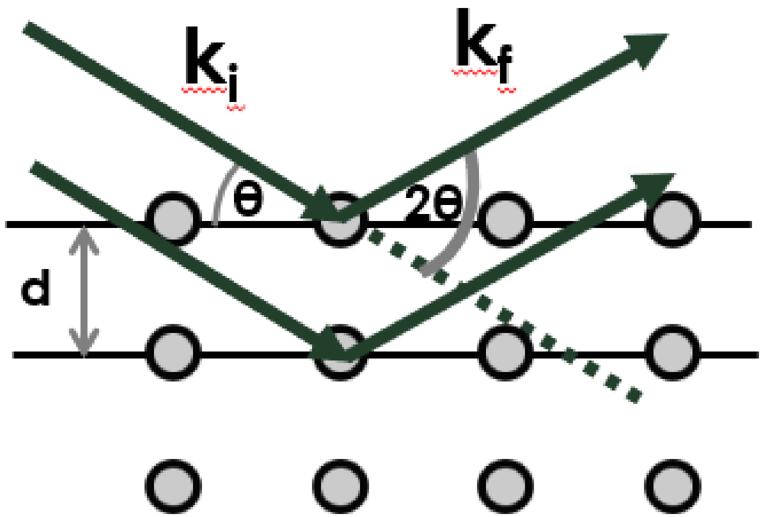
Elastic scattering: $|\mathbf{k}_i| = |\mathbf{k}_f|$



Scattering triangle:



Diffraction from a crystal



Bragg peaks when: $\lambda = 2d\sin\theta$

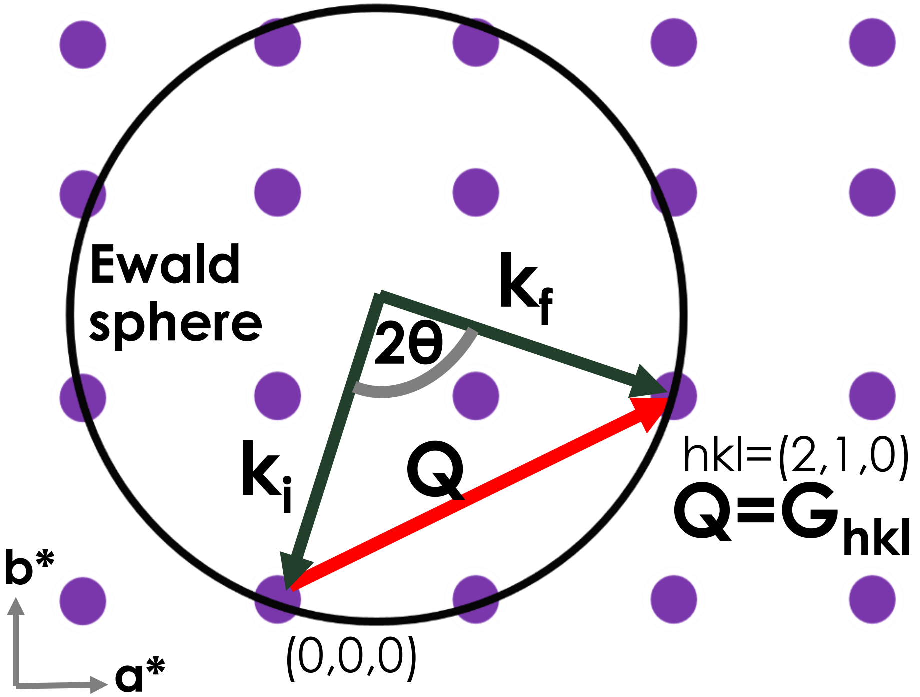
Braggs Law

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

Neutron Diffraction: Ewald sphere and reciprocal space

For a crystal, get intensity when **Q**=**G** i.e. at allowed (H,K,L) positions

Diffraction in reciprocal space



$$\frac{d\sigma}{d\Omega} = N \sum_{hkl} |F_{hkl}(\mathbf{Q})|^2 \delta(\mathbf{Q} - \mathbf{G}_{hkl})$$

Number of unit cells in crystal

Structure factor

Nuclear structure factor

$$F_{hkl}(\mathbf{Q}) = \sum_j b_j \exp(i\mathbf{G}.\mathbf{r}_j)\exp(-W_d)$$

Debye-Waller

Magnetic structure factor

$$F_M(\mathbf{G}) = \sum_j f_j(\boldsymbol{Q})\mathbf{m}_{\perp j} \exp(i\mathbf{G}.\mathbf{r}_j)$$

Form factor

Moment perp.

Neutron measurements: Nuclear and Magnetic scattering

$$\frac{d\sigma}{d\Omega}(Q) = \frac{d\sigma}{d\Omega}_{\mathrm{nuc}}(Q) + \frac{d\sigma}{d\Omega}_{\mathrm{mag}}(Q)$$

- For an unpolarized neutron measurement, there is no interference between the nuclear and magnetic scattering.
- Can be considered separately, then combined
  - This is done in experiments and analysis!
  - Magnetic Space group approach incorporates both nuclear and magnetic.

Magnetic neutron diffraction from a crystal

Form factor

Magnetic structure factor:
<u>only perpendicular component</u>

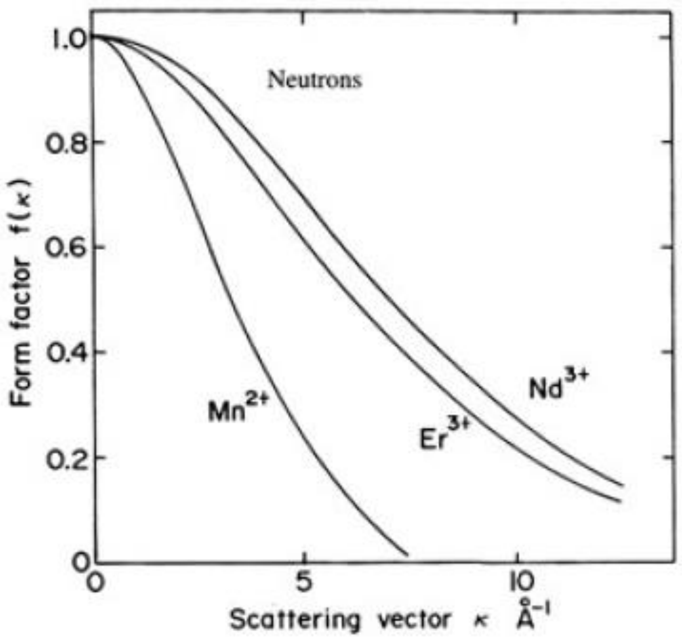
$$\frac{d\sigma}{d\Omega}_{mag} = (\gamma r_0)^2 N(\tfrac{1}{2}g\, f(Q))^2 e^{-2W} |\mathbf{F}_{\mathbf{M}\perp}(Q)|^2$$

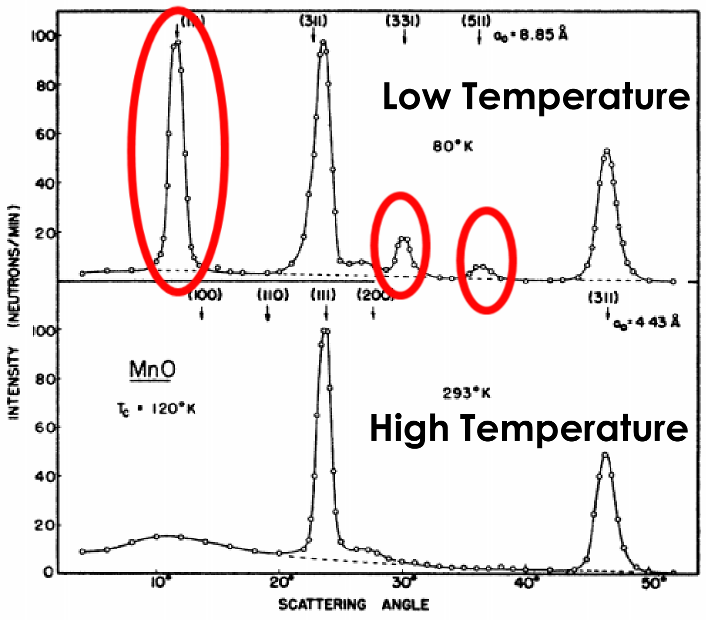
Constants

Debye-Waller factor
(thermal motion)

Magnetic form factor, f(Q)

- Magnetic scattering from extended electron cloud → form factor
- F(Q) is the Fourier transform of the spin distribution in real space: $F(Q) = \int S(r) e^{iQ.r} d^3r$





- Analytical expressions are tabulated https://www.ill.eu/sites/ccsl/ffacts/ for j_1 (spin only), j_2 (orbital), j_3 (orbital), etc

Magnetic neutron diffraction from a crystal

Form factor

Magnetic structure factor: <u>only perpendicular component</u>

$$\frac{d\sigma}{d\Omega}_{mag} = (\gamma r_0)^2 \, N \left(\tfrac{1}{2} g \, f(Q)\right)^2 e^{-2W} \, |\mathbf{F}_{\mathbf{M}\perp}(Q)|^2$$

Constants

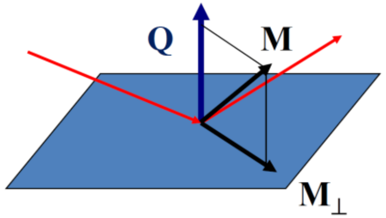
Debye-Waller factor (thermal motion)

$F_{M\perp}(Q)$: Neutrons Only Measure Moments Perpendicular to Q

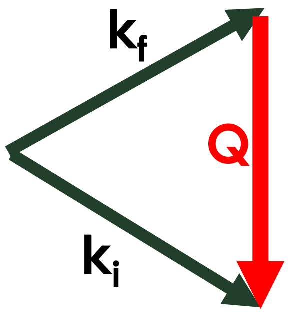
- Scattering depends on Fourier transform of $V_{magnetic}(\mathbf{r}) = -\boldsymbol{\mu}_n . \mathbf{B}(\mathbf{r})$
- From Maxwell's equation: $\nabla . \mathbf{B}(\mathbf{r}) = 0$

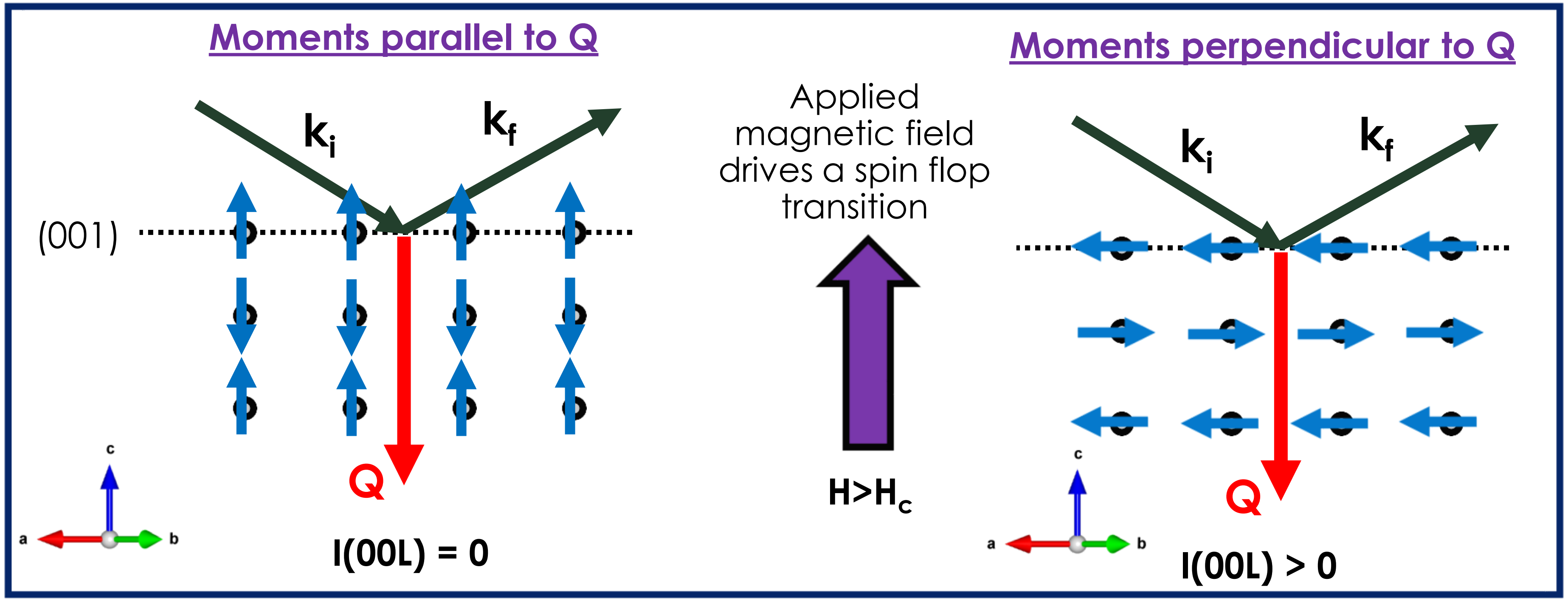
  Fourier transform → $i\mathbf{Q} . \mathbf{B}(\mathbf{Q}) = 0$

  → B(**Q**) is perpendicular to **Q** to be non-zero $M_\perp(\mathbf{Q}) = \mathbf{Q} \times (M \times \mathbf{Q})$

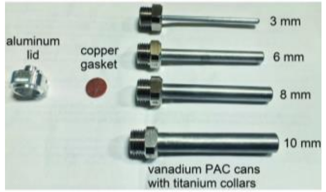


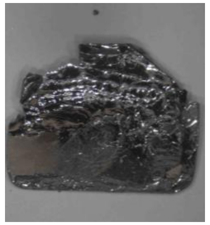
<u>In experiments this can be a useful constraint:</u>



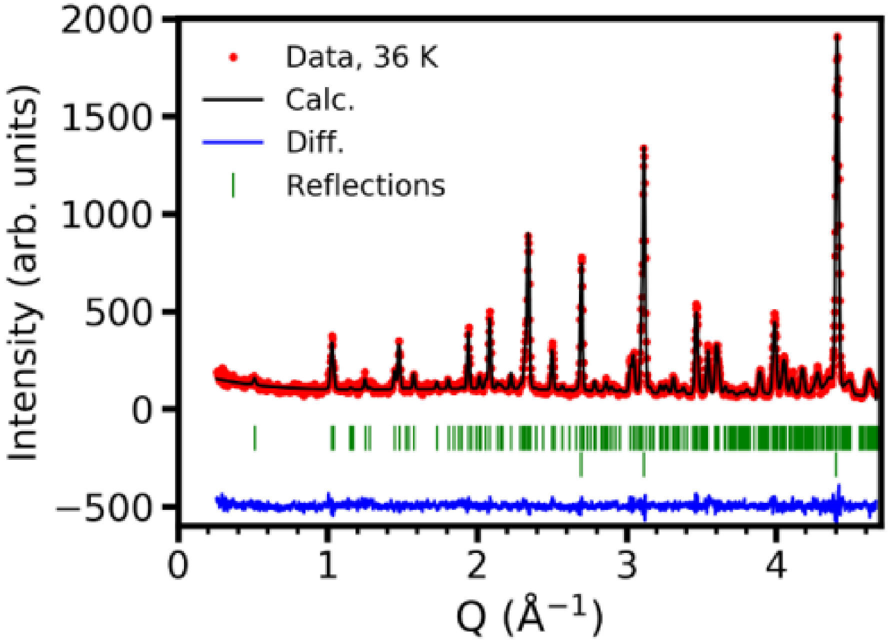


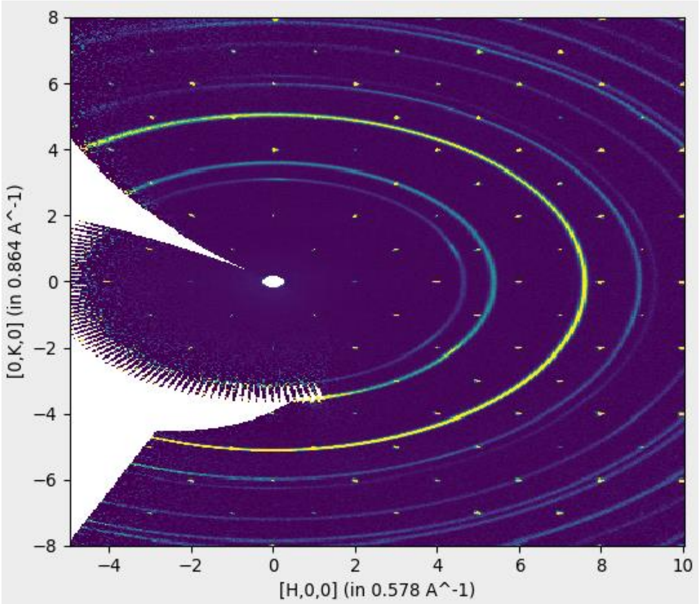
Neutron diffraction data on Powder and Single Crystals





$CrPS_4$





- See “everything”, but averaged.

- Definitive details, if accessed in experiment.

Powder or Single crystal ?

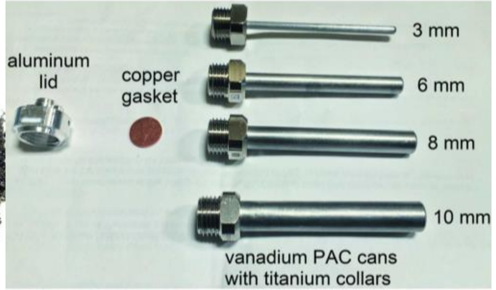
Powder

Advantages

- Often easier synthesis
- See everything
- Propagation vector
- If powders work then saved a lot of effort.
- Measurement more routine.

Disadvantages

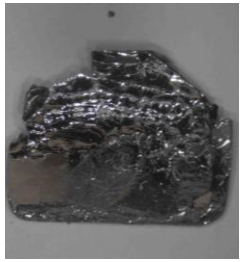
- Information is averaged and lost.
- Hard to uniquely assign some propagation vectors.
- No domain info
- Field measurements hard to interpret quantitatively



Single crystal

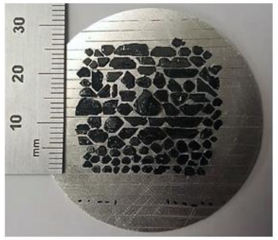
Advantages

- Propagation vector unambiguously determined.
- Low background so can see smaller moments
- Directional dependence of field (or strain, etc)
- Domain information
- Smaller mass (~mg)



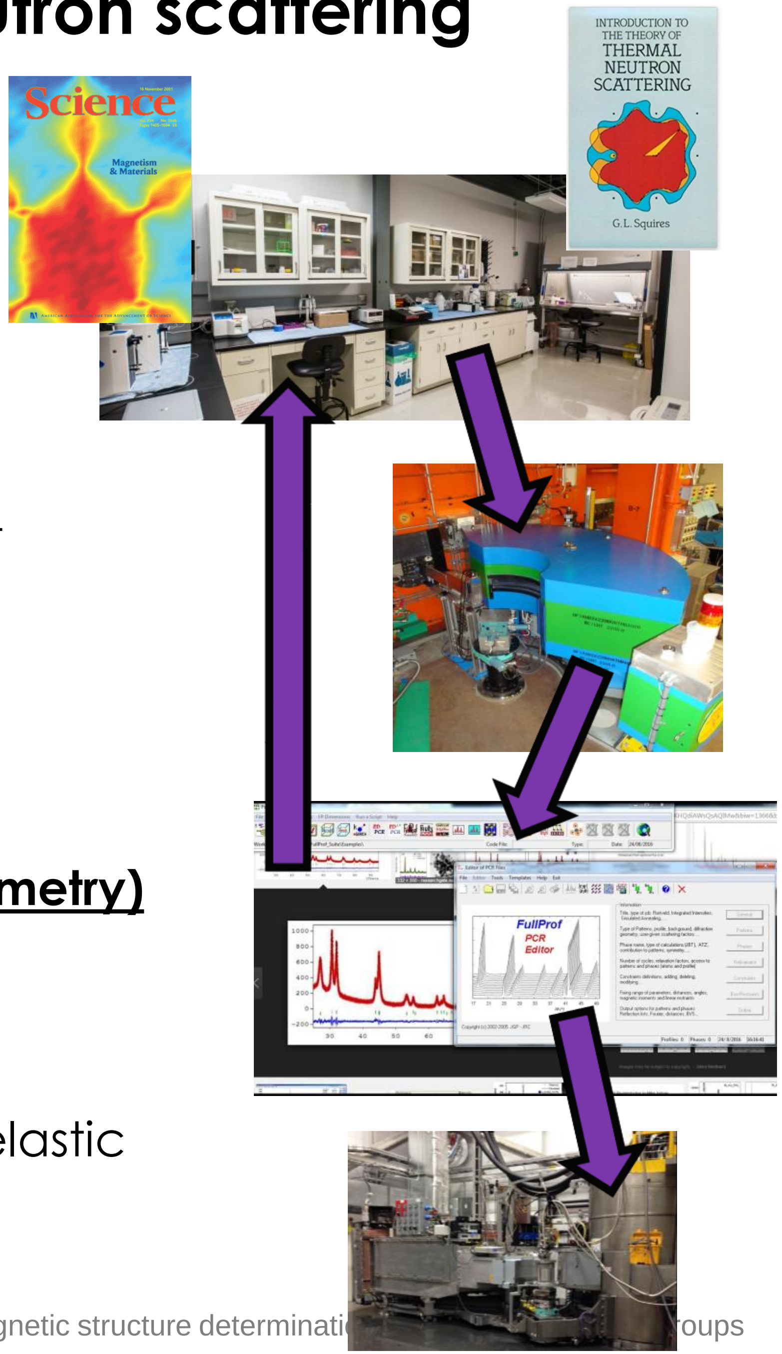
Disadvantages

- Synthesis can be hard
- Data correction: absorption, extinction, etc
- Need to search large reciprocal space (or have large detectors)
- Sample alignment considerations.



Summary: Determining a magnetic structure with neutron scattering

- Find a good problem and grow sample (powder or crystal)
- Do lots of characterization measurements in laboratory
- Understand background/theory of sample and neutron diffraction
- Apply for beamtime (speak to instrument scientist)
- Sample and experiment preparation are crucial (speak to instrument scientist)
- Perform neutron measurement
- Analyze crystal structure (maybe need more measurements)
- **Analyze magnetic structure (GSAS-II): Starting model (magnetic symmetry) → compare to data → repeat**
- If lucky write up paper
- Otherwise more data → Powder → single crystal → polarization → inelastic → etc



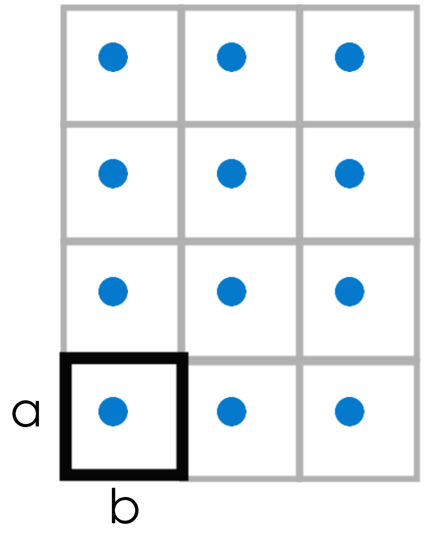
Extra slides: k-vector

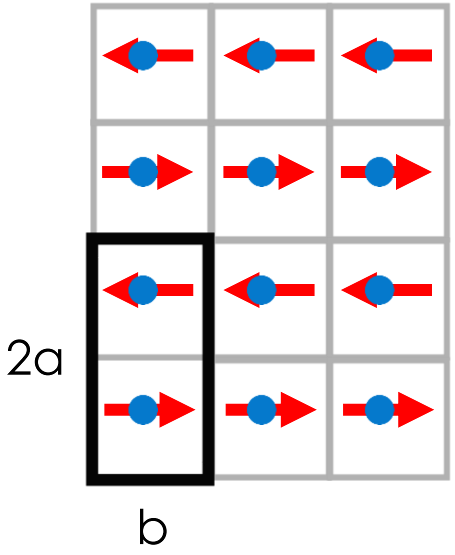
Magnetic propagation vector: **k**-vector

- **Magnetic** and **crystallographic** unit cells are not necessarily the same size.

- **k-vector** describes the relation between the nuclear and magnetic unit cells
  - Determine with neutron diffraction

- Can state just the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.



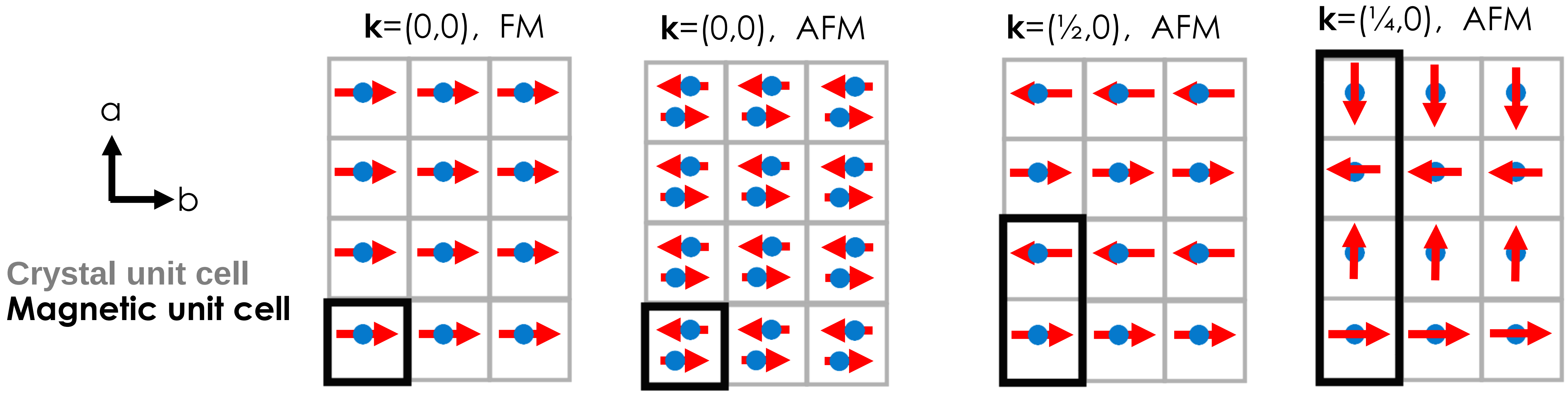


Magnetic propagation vector: **k**-vector

- Convenient to introduce a propagation vector (**k-vector**) for magnetic structures:
  Describes the relation between the crystal (nuclear) and magnetic unit cells

- **Aim: Can state just the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.**

- k-vector directly observable with neutron scattering:
  – Magnetic peaks are shifted from the positions of nuclear peaks (τ) by the **k**-vector value, i.e $Q_{mag} = \tau + k$
  – **k**-vector can be commensurate (e.g. 1/4) or incommensurate (e.g. 1/13)
  – Can have multiple k-vectors



General magnetic structure description with k-vectors

- Can state only the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.
- All magnetic ordering is periodic, this can be expressed in the Fourier series:

$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\, \mathbf{S}_j^{k}\, e^{-2\pi i \mathbf{k}.R}$$

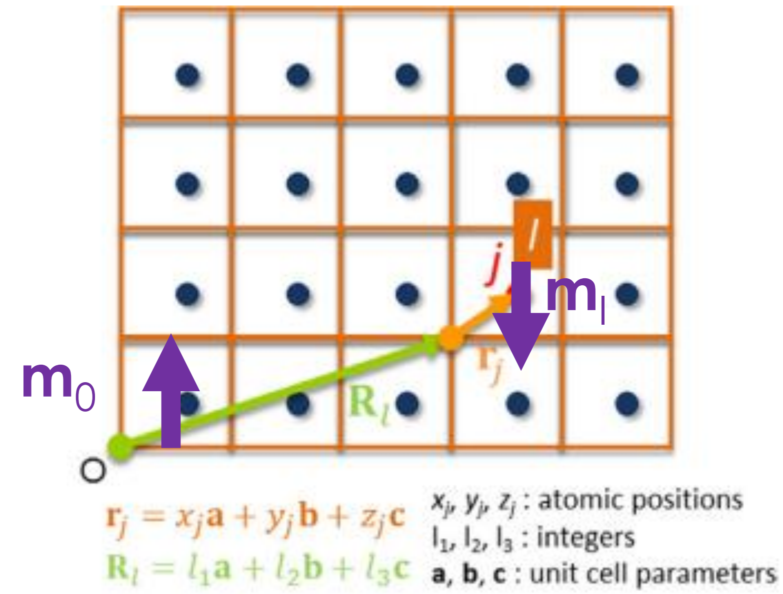
k-vector

spin at the atomic site *j* in some unit cell that is related to the 0th cell (G_0) by a translation **R**.

$\mathbf{S}_j$ (Basis vector): spin in the 0th cell.

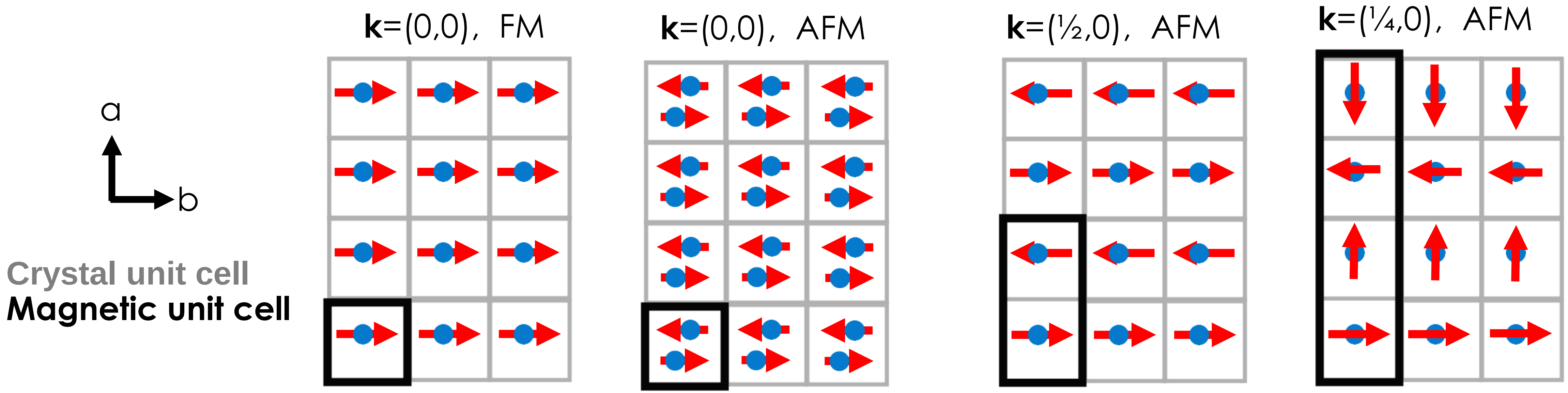
Lattice translation to unit cell

Correlation of the spin m_j on atom j within unit cell l to m_0 in the 0th unit cell translated by R



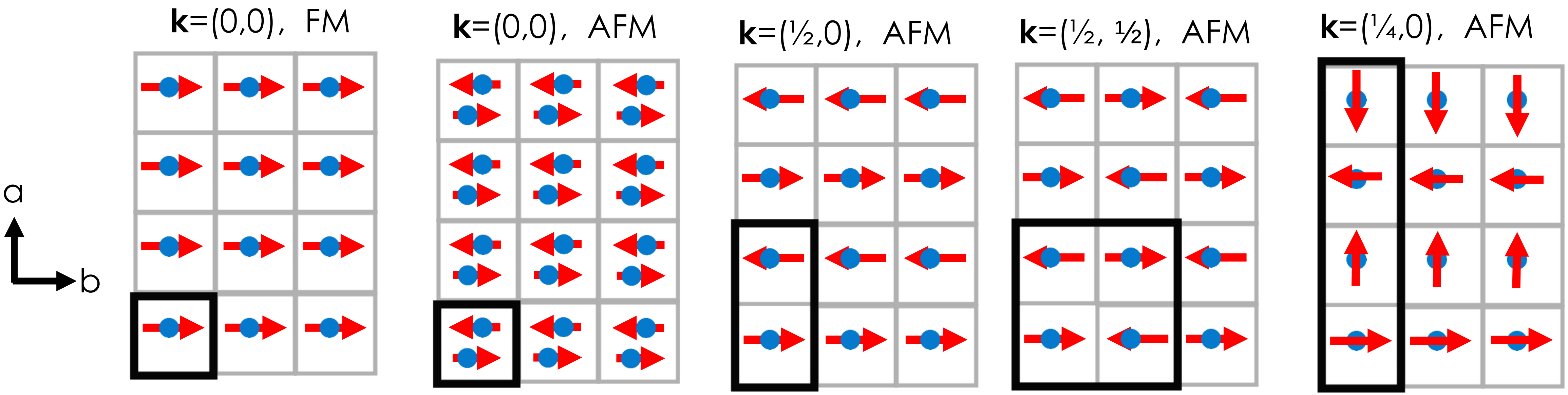
Magnetic propagation vector: **k**-vector

- Magnetic Space groups: k-vector is directly incorporated in the unit cell.
- Consider a paramagnetic crystal unit cell of **a** and **b** and a **k-vector.**
  - **If k=(0,0), then the magnetic space group unit cell is unchanged: a and b.**
  - **If k=(1/2,0), then the magnetic space group unit cell is: 2a and b.**
  - **If k=(1/4,0), then the magnetic space group unit cell is: 4a and b.**
- Need to keep track of this in refinements, cif/mCIF files, reflections and reporting of results.



Magnetic propagation vector: **k**-vector

- <u>k-vector describes the relation between the nuclear and magnetic unit cells</u>



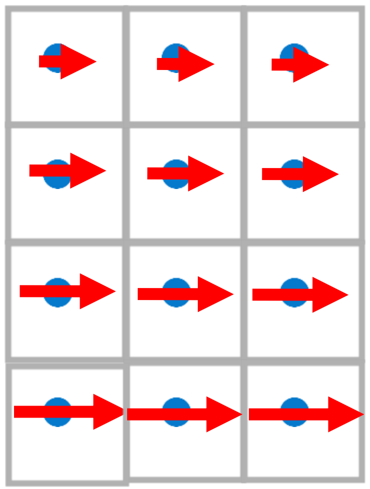
Crystal unit cell

Magnetic unit cell

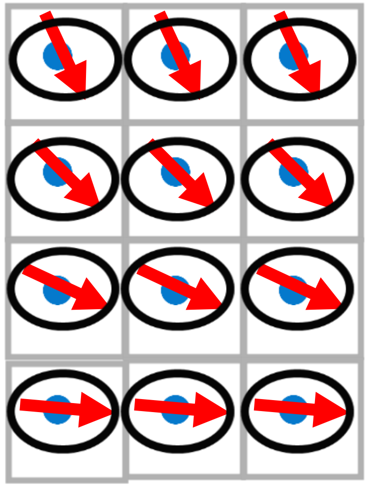
Atom

Spin

Incommensurate spin density wave structure with $\mathbf{k}_1$=(δ,0)



Incommensurate Helical structure with $\mathbf{k}_1$=(δ,0)

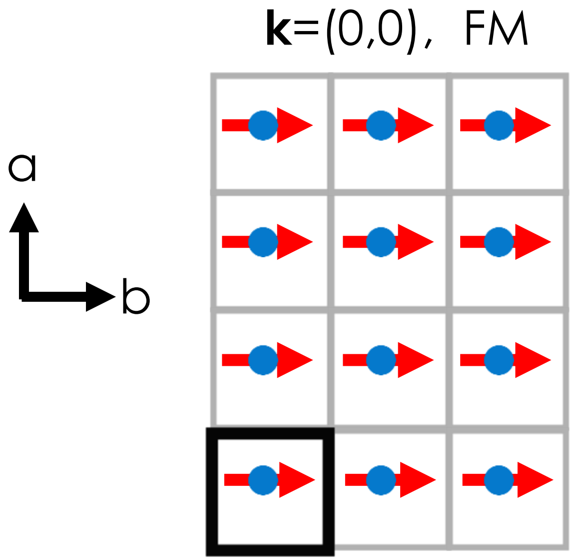


Magnetic propagation vector: **k**-vector

- **k**-vector directly observable with neutron scattering:
  - Magnetic Bragg peaks are shifted from the positions of nuclear peaks (τ) by the **k**-vector value, i.e $Q_{mag} = \tau + k$
  - **k**-vector can be commensurate (e.g. 1/4) or incommensurate (e.g. 1/13)
  - Can have multiple **k**-vectors

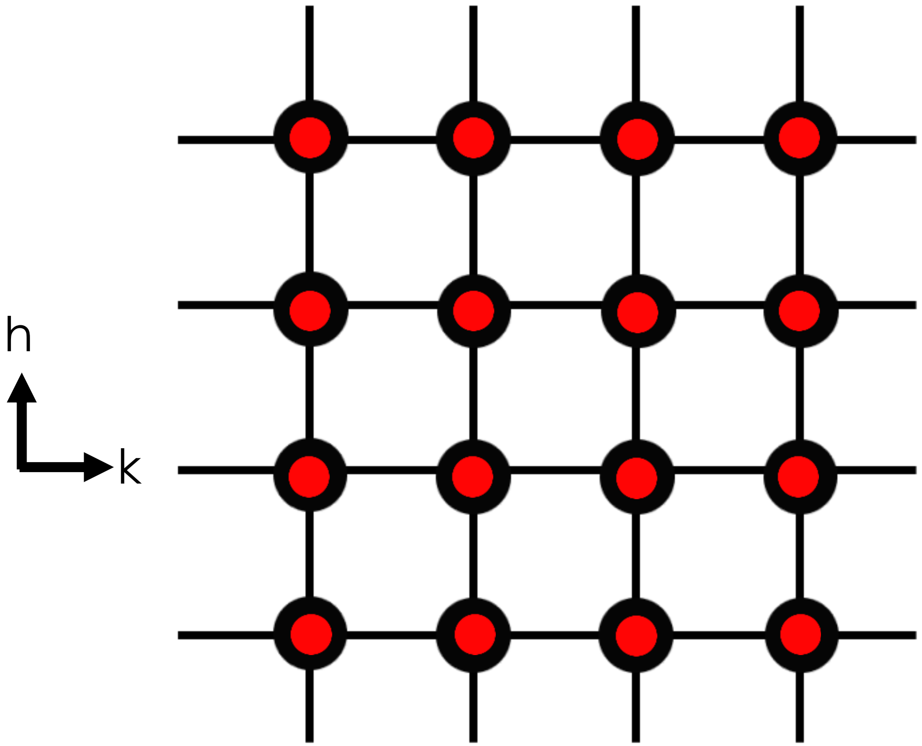
K-vector in direct and reciprocal space

Direct space



Crystal unit cell
Magnetic unit cell

Reciprocal space



Nuclear Bragg peak

Magnetic Bragg peak

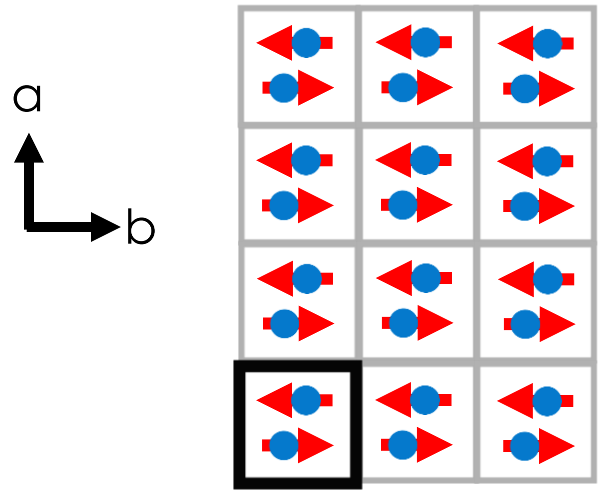
Magnetic reflections at (0,0)+k

→ (0,0), (1,0), (0,1),(1,1) etc measured with neutron scattering

K-vector in direct and reciprocal space

Direct space

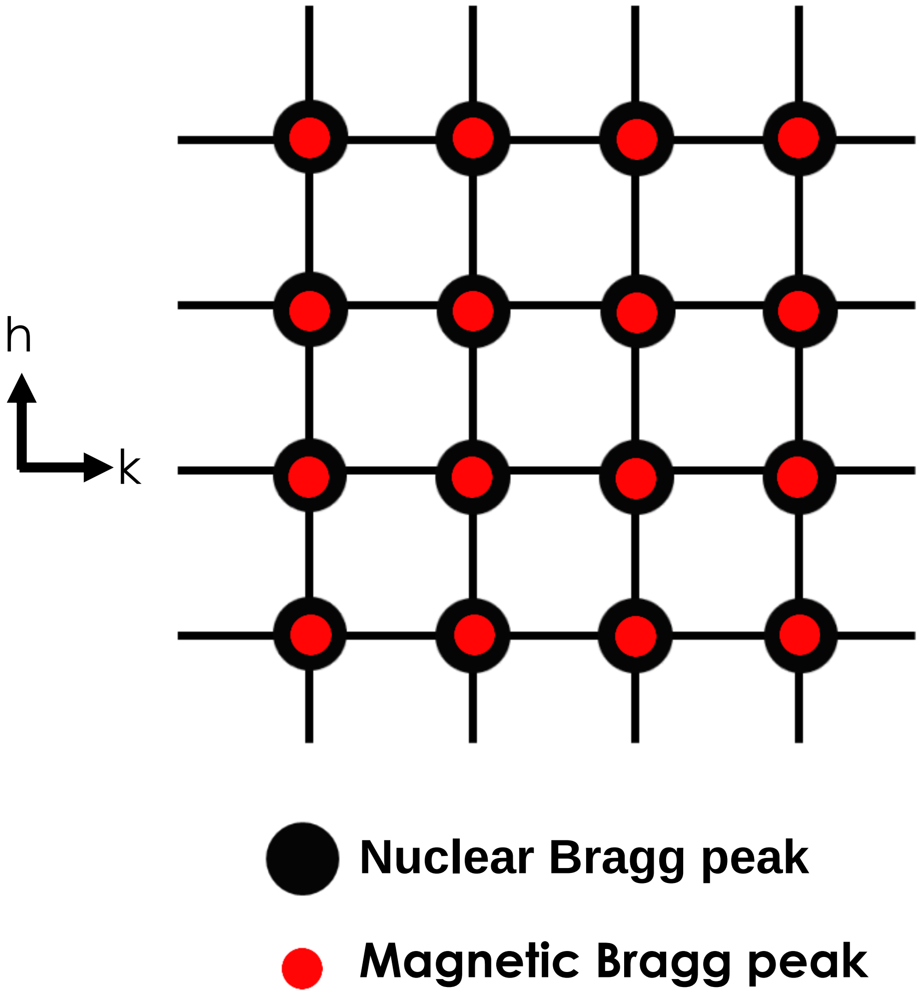
k=(0,0), AFM



Crystal unit cell

Magnetic unit cell

Reciprocal space

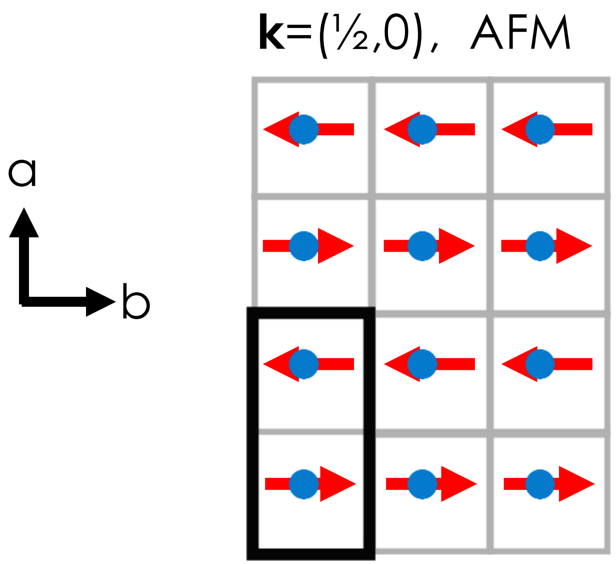


Magnetic reflections at (0,0)+k

→ (0,0), (1,0), (0,1),(1,1) etc measured with neutron scattering

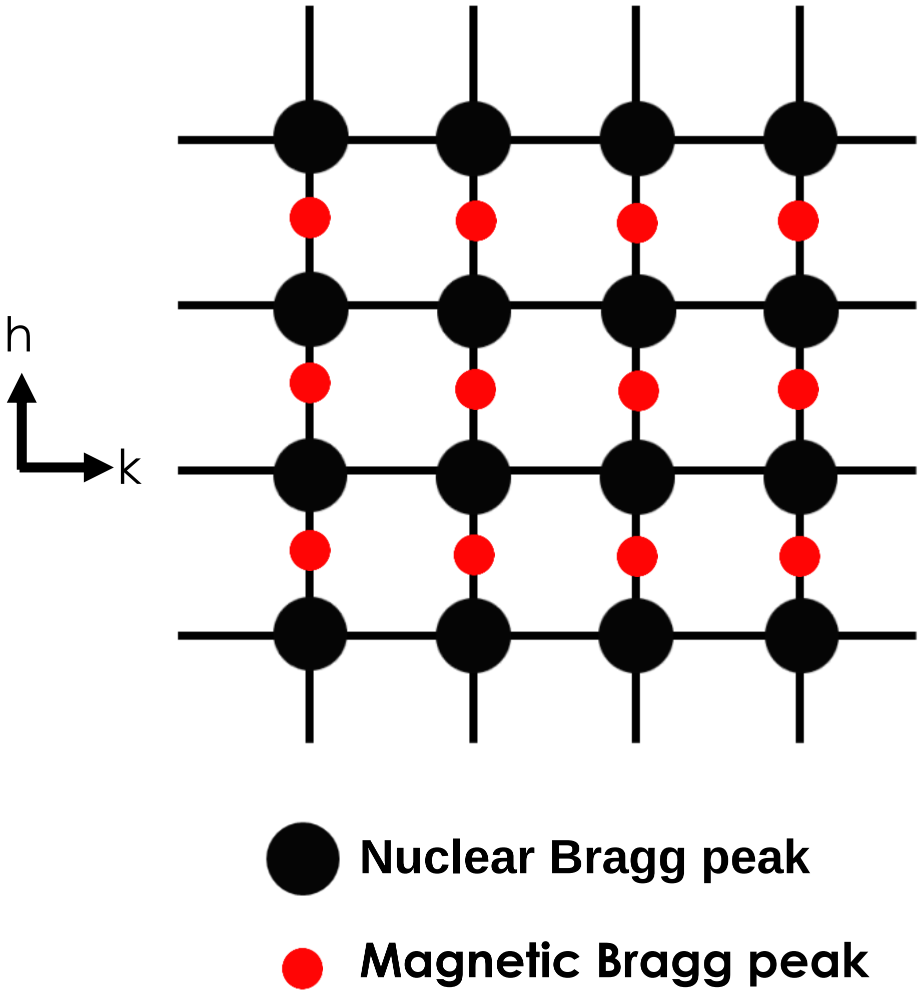
K-vector in direct and reciprocal space

Direct space



Crystal unit cell
Magnetic unit cell

Reciprocal space



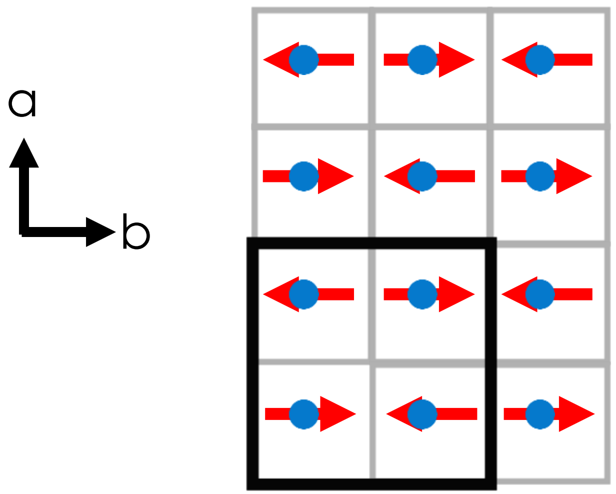
Magnetic reflections at (0,0)+k

→ (0.5,0), (1.5,0), (2.5,0), etc measured with neutron scattering

K-vector in direct and reciprocal space

Direct space

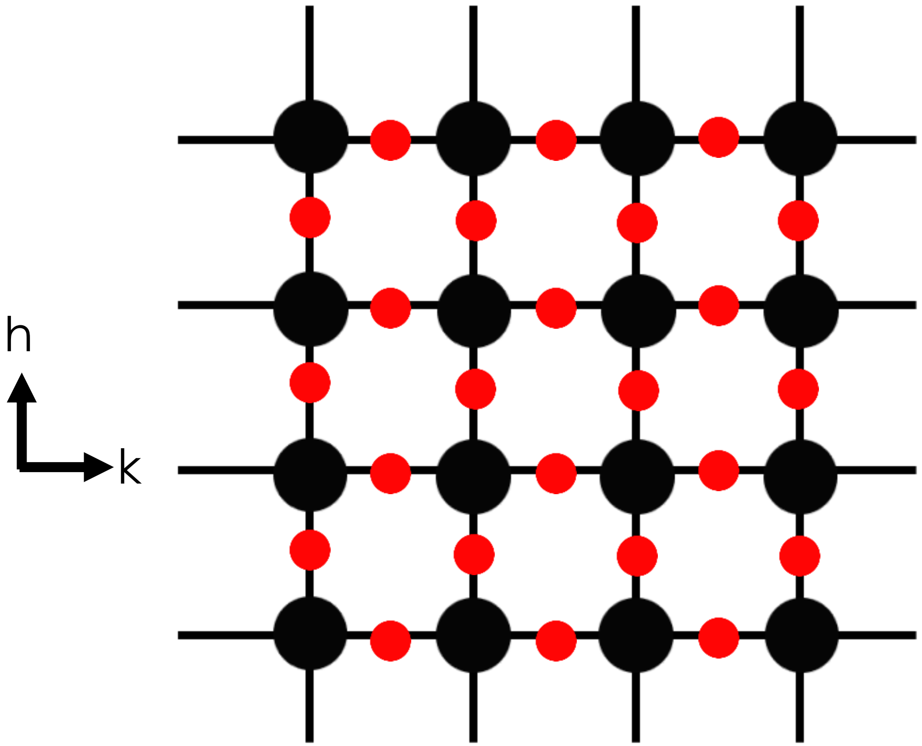
k=(½, ½), AFM



Crystal unit cell

Magnetic unit cell

Reciprocal space



Nuclear Bragg peak

Magnetic Bragg peak

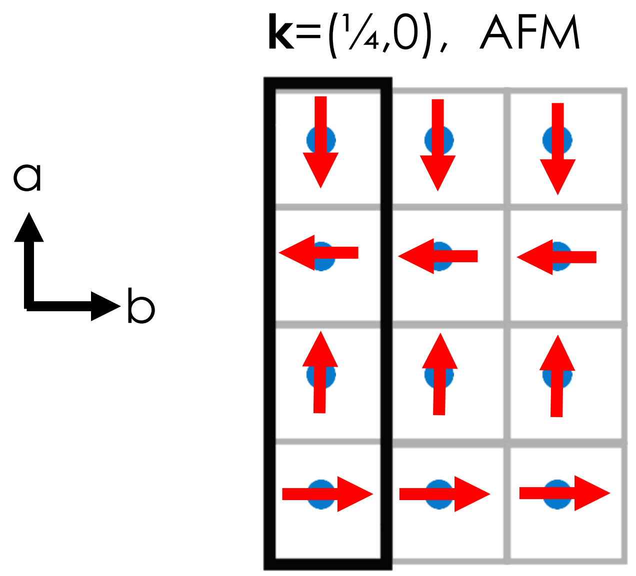
Magnetic reflections at (0,0)+k

→

(0.5,0),(0.5,0),(0.5,0.5) (1.5,0), (1.5,1.5), etc measured with neutron scattering

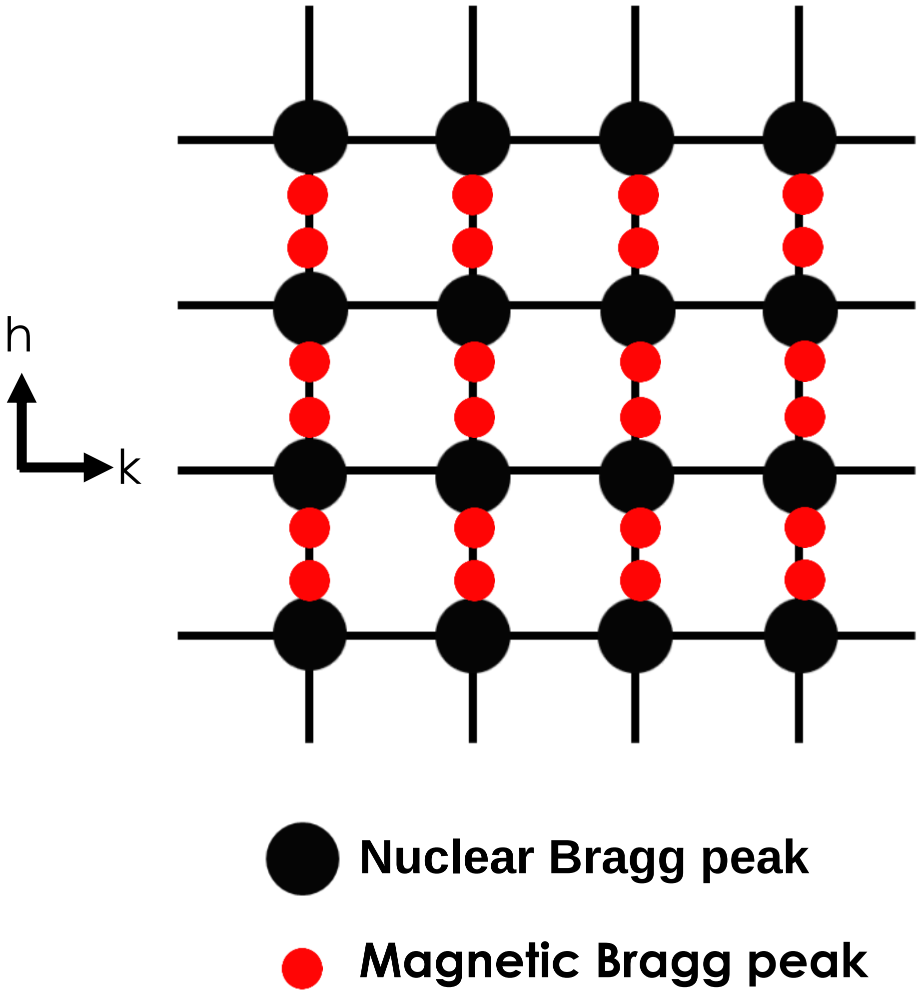
K-vector in direct and reciprocal space

Direct space



Crystal unit cell
Magnetic unit cell

Reciprocal space



Magnetic reflections at (0,0)+k

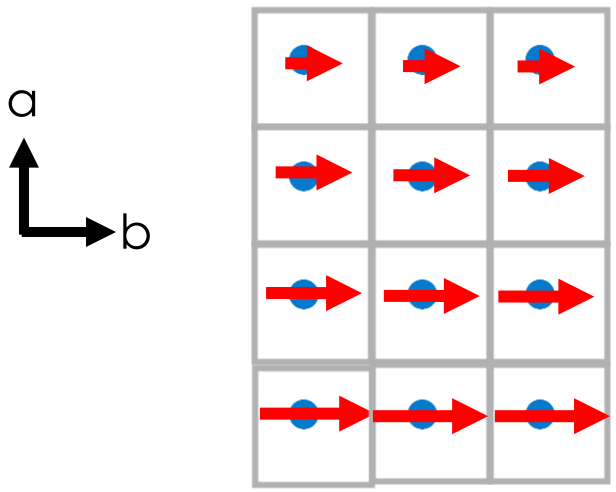
→

(0.25,0),(0.75,0),(1.25,0) (1.75,0), etc measured with neutron scattering

K-vector in direct and reciprocal space

Direct space

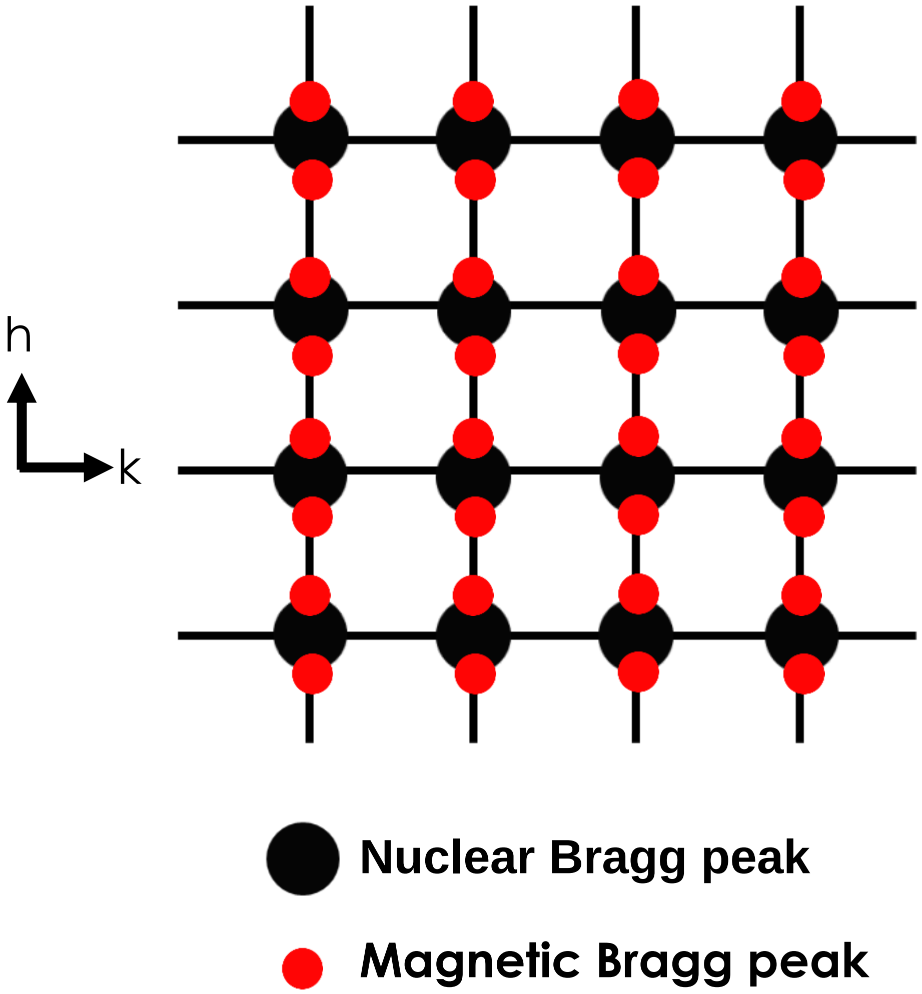
Incommensurate spin density wave structure with $\mathbf{k_1}$=(δ,0)



Crystal unit cell

Magnetic unit cell

Reciprocal space



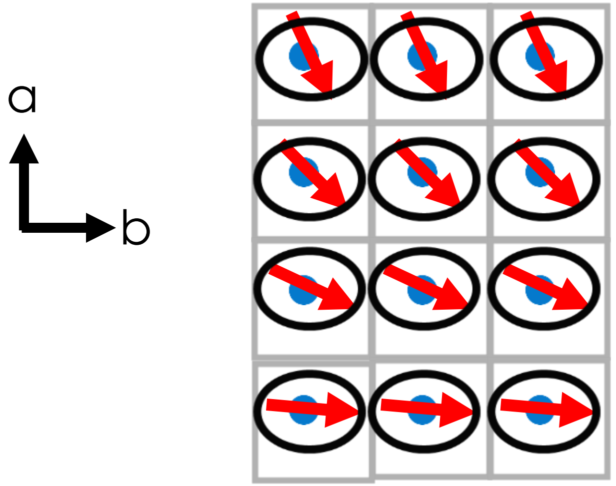
Magnetic reflections at (0,0)+k

→ (δ,0),(1-δ,0) (1+δ,0), etc measured with neutron scattering

K-vector in direct and reciprocal space

Direct space

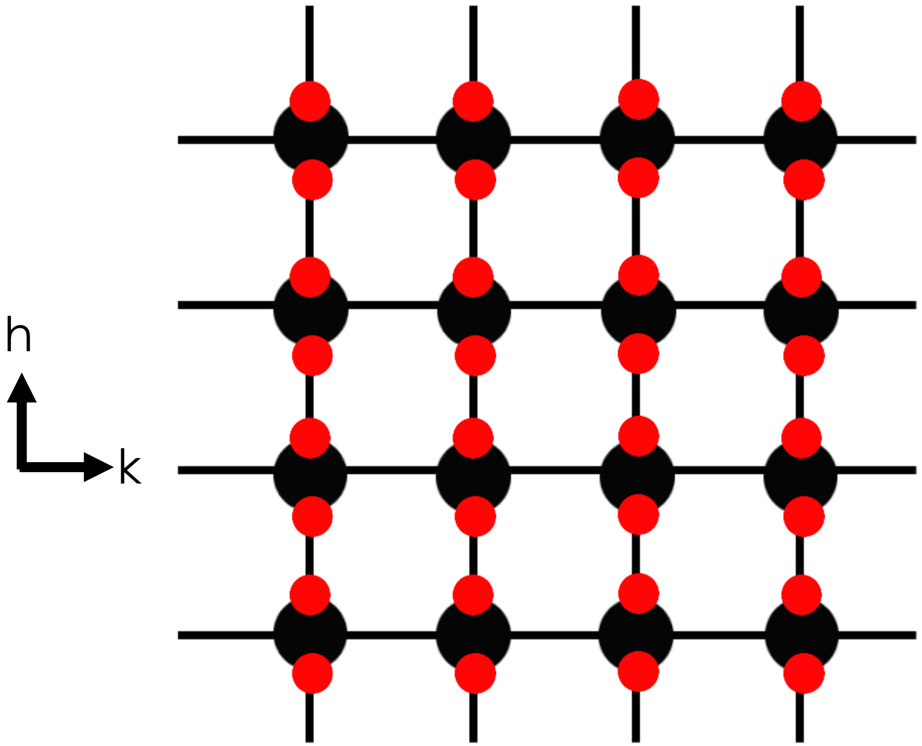
Incommensurate Helical structure with $\mathbf{k}_1$=(δ,0)



Crystal unit cell

Magnetic unit cell

Reciprocal space



Nuclear Bragg peak

Magnetic Bragg peak

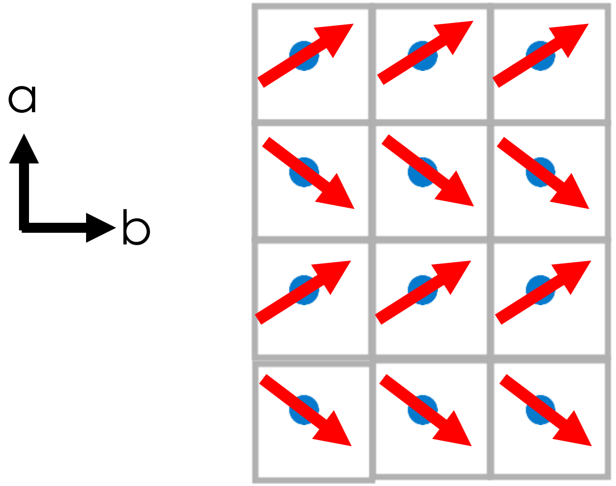
Magnetic reflections at (0,0)+k

→ (δ,0),(1-δ,0) (1+δ,0), etc measured with neutron scattering

K-vector in direct and reciprocal space

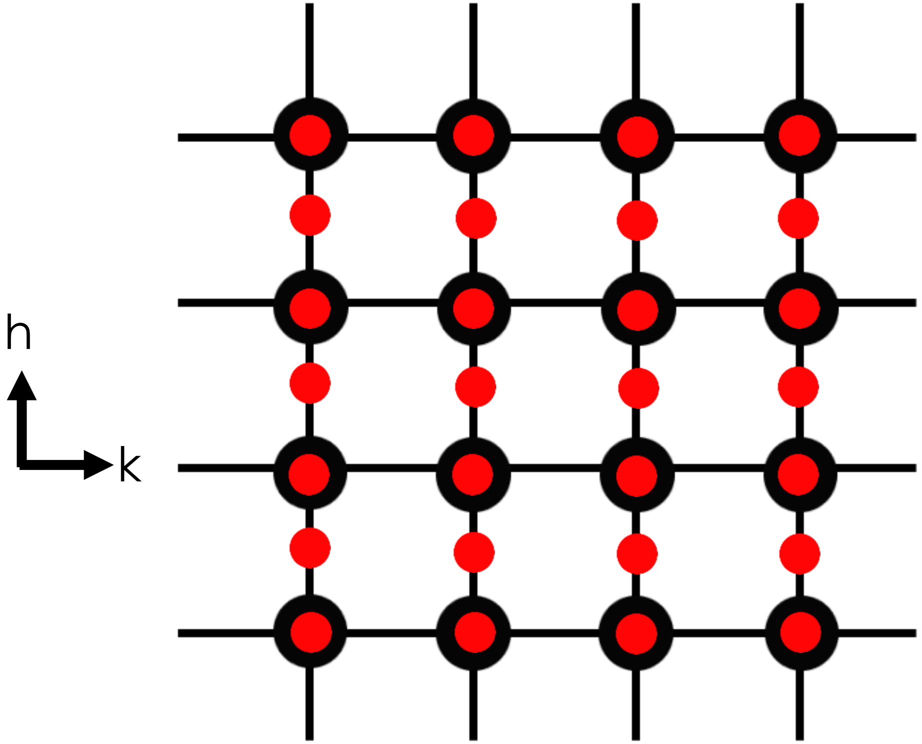
Direct space

Canted structure with
$\mathbf{k_1}$=(½,0), AFM
$\mathbf{k_2}$=(0,0), FM



Crystal unit cell
Magnetic unit cell

Reciprocal space



Nuclear Bragg peak

Magnetic Bragg peak

Magnetic reflections at (0,0)+k_1+k_2

→ (0,0),(0.5,0) (1,0), (1.5,0), etc measured with neutron scattering

Multi-k structures: the Skyrmion lattice

- Skyrmion lattice is an example of a multi-**k** incommensurate magnetic structure
- Lattice of clockwise magnetic whirlpools

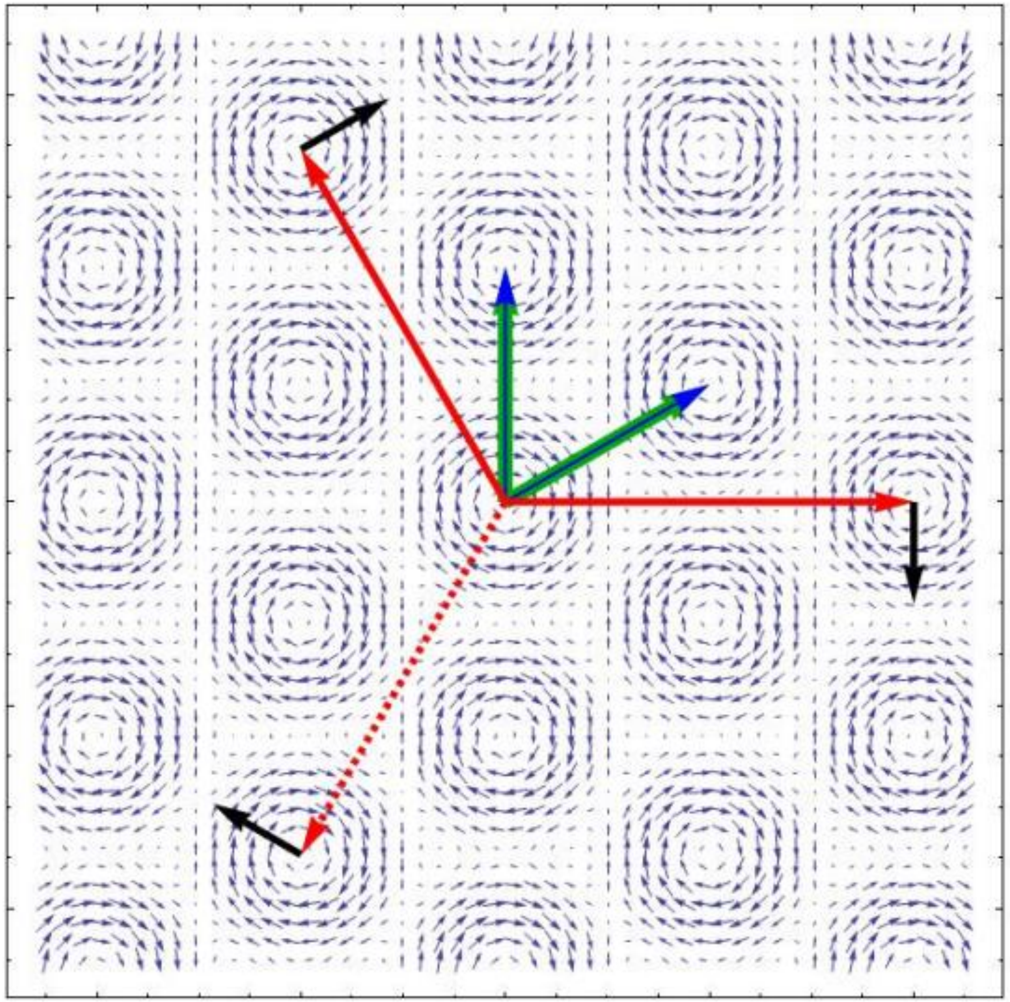
  $\mathbf{k}_1=(2\alpha,-\alpha,0)$

  $\mathbf{k}_2=(-\alpha,2\alpha,0)$

  $\mathbf{k}_3=(-\alpha,-\alpha,0)$

  Can have $\mathbf{k}_4=(000)$

- Here $\alpha=0.11$



Magnetic propagation vector: **k**-vector

Single crystal diffraction

- Magnetic reflections provide the k-vector without any analysis.
  - E.g. if you measure reflections at (0.5,0,0), then that is your propagation vector!
- Reciprocal space is large → sometimes need to know where to look or you'll miss the magnetic peaks.
  - Do powder diffraction first

Powder diffraction

- Get complete coverage of reciprocal space, but it is averaged.
- Need to index magnetic reflections → analysis tool
- Might not get unique k-vector, especially if incommensurate
  - Do single crystal to check

General magnetic structure description with k-vectors

- Can state only the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.
- All magnetic ordering is periodic, this can be expressed in the Fourier series:

k-vector

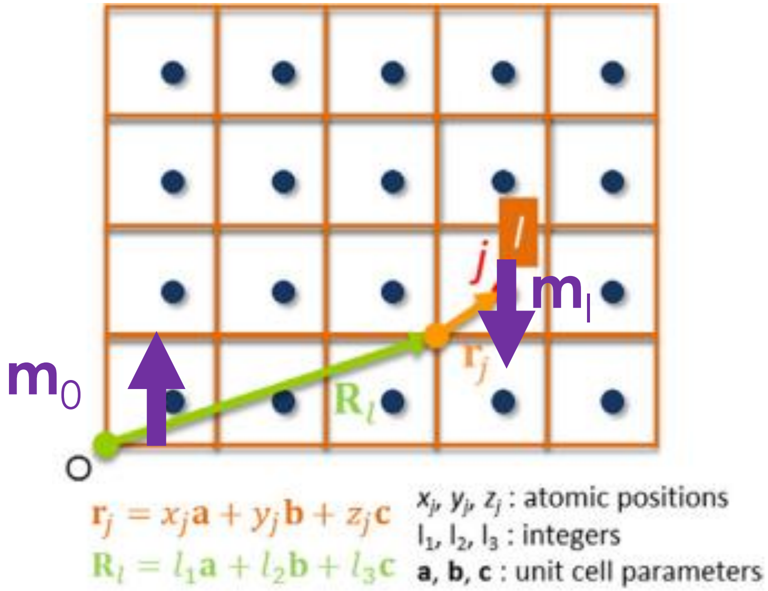
spin at the atomic site *j* in some unit cell that is related to the 0th cell (G_0) by a translation **R**.

$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\, \mathbf{S}_j^{k}\, e^{-2\pi i \mathbf{k}.R}$$

$\mathbf{S}_j$ (Basis vector): spin in the 0th cell.

Lattice translation to unit cell

Correlation of the spin m_j on atom j within unit cell l to m_0 in the 0th unit cell translated by R

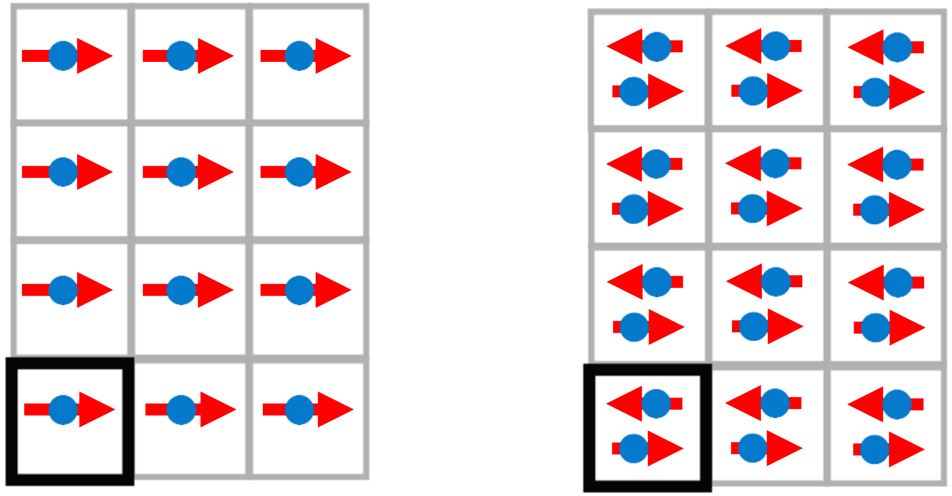


Examples of using the k-vector formulism: $\mathbf{m}_j = \mathbf{S}_j^k\, e^{-2\pi i \mathbf{k}.R}$

- <u>Simplest case of k =(0,0,0) = 0</u>
- $\mathbf{m}_{lj} = \mathbf{S}_{0j}\, e^{-2\pi i \mathbf{k}.R} = \mathbf{S}_{0j}\, e^{-2\pi i 0.R} = \mathbf{S}_{0j}\, e^{0} = \mathbf{S}_{0j} = \mathbf{m}_{0J}$
- Orientation of the magnetic moments in any cell of the crystal are identical to the 0th cell → **magnetic unit cell = crystallographic unit cell**
- K=000 could be ferromagnetic or antiferromagnetic

k=(0,0), FM

k=(0,0), AFM



Extra slides: Refining neutron data

Basics of fitting diffraction data

Measured peaks have position (Q or HKL), intensity and width

- **Peak positions:** determined by size and shape of unit cell
- **Peak intensities:** determined by the atomic number and position of the various atoms in the unit cell
- **Peak widths:** determined by instrument parameters as well as temperature, crystal size/quality, strain,

- Single crystal → integrated intensity of each peak is extracted. So in refinement only need to consider a few parameters (extinction, absorption)
- Powder → Overlapping peaks means modelling whole pattern. [Rietveld Refinement]

Fitting your data: Rietveld refinement (powder)

- Hugo Rietveld: "*The method of using the total integrated intensities of the separate groups of overlapping peaks in the least-squares refinement of structures, leads to the loss of all the information contained in the often-detailed profile of these composite peaks. By the use of these profile intensities instead of the integrated quantities in the refinement procedure, however, this difficulty is overcome and it allows the extraction of the maximum amount of information contained in the powder diagram.*"

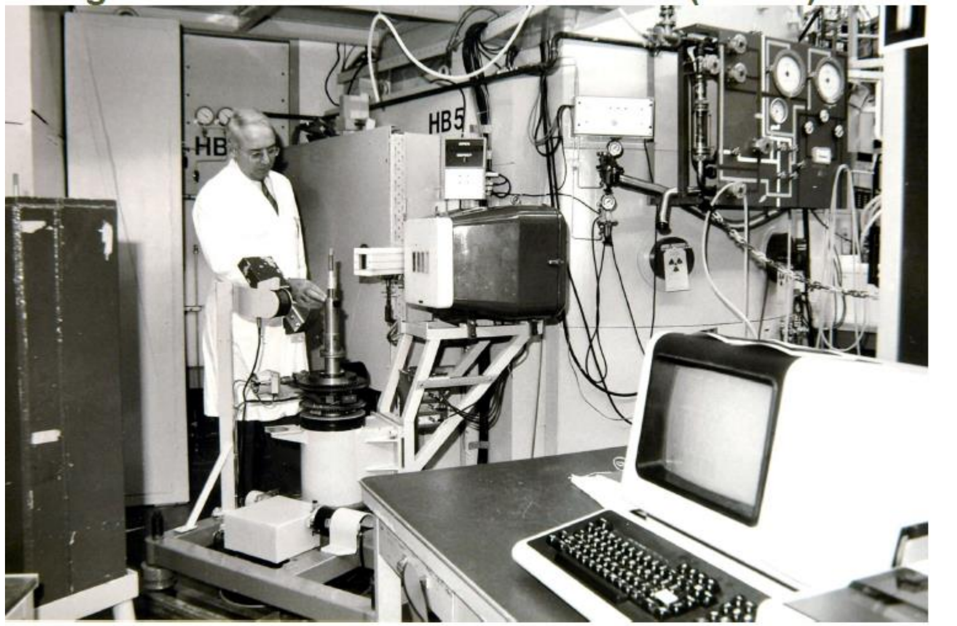
- If pattern can be modelled, the fit between observed data and model can be optimized.

- In powder, unlike single crystal, need to model experiment dependent parameters
  - Background
  - Peak broadening (sample/instrument)
  - Lattice constant
  - Absorption and sample shape
  - Preferred orientation

- Refinement → need a good starting model

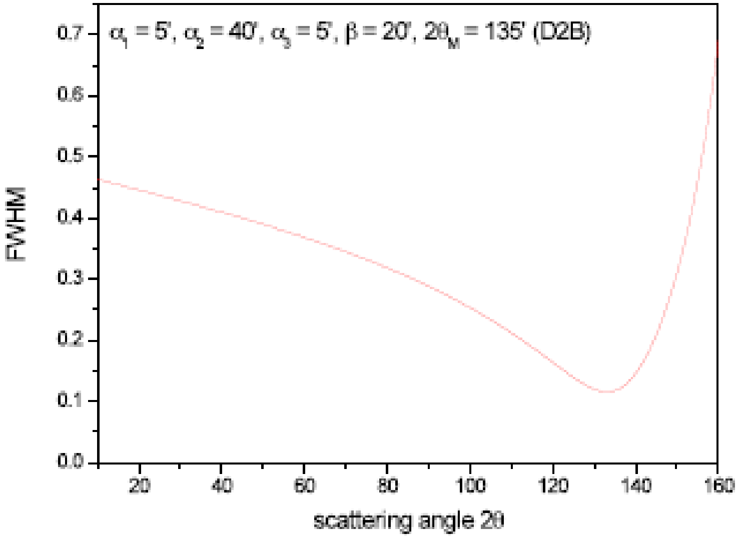
- Neutron data usually required for determining occupancy.

Hugo Rietveld in the Petten Reactor (~1987)

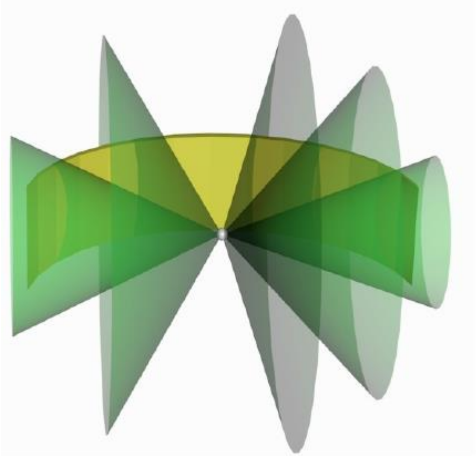


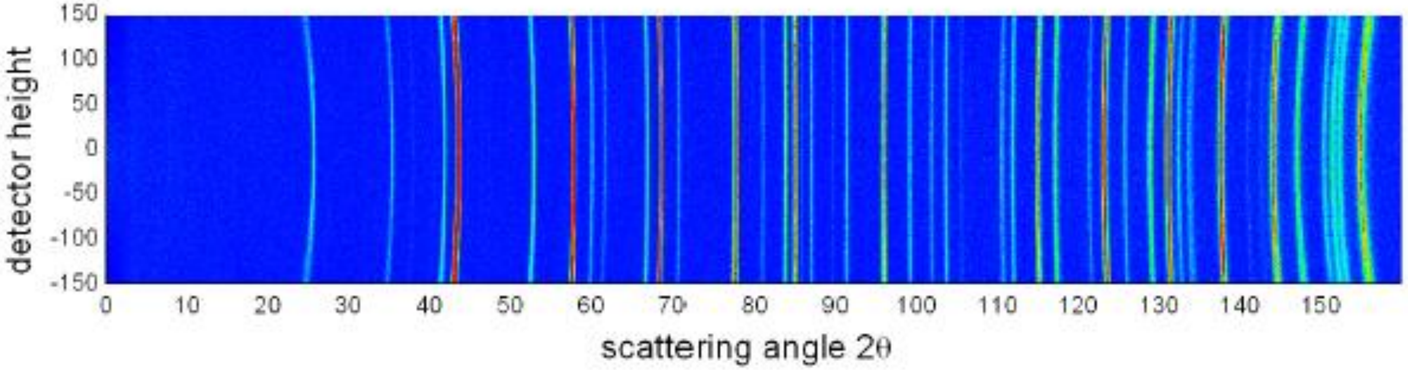
Peak shape varies with scattering angle

- Cagliotta formula: $FWHM^2 = U \tan^2\theta + V \tan\theta + W$
- *U, V, W* parameters are a function of instrument collimation and monochromator G. Caglioti et al., Nucl. Instr. 3, 223-228 (1958)
- Does not take into account guides or focusing of monochromator.
- Spallation sources need extra terms to model resolution from pulse shape.



- Debye-Scherrer cone scattering causes asymmetric peak shapes at low/high angle in I(Q) 1d plots.





If converted to 1d → asymmetric at low 2θ, symmetric at 2θ=90°