Determination of Magnetic Structures Magnetic Structure Factors

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Outline:

1. Magnetic Structures and neutron scattering
2. Representation Analysis and Magnetic Structures
3. Magnetic Structure determination. Magnetic Structure Factors

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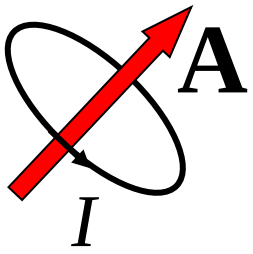
Magnetic dipoles

Magnetic dipole moment in classical electromagnetism



$$\boldsymbol{\mu} = I\mathbf{A}$$

In terms of orbital angular momentum for an electron

$$\boldsymbol{\mu}_L = -\left(\frac{e}{2m_e}\right)\mathbf{L}$$

$$\boldsymbol{\mu}_S = -\left(\frac{e}{m_e}\right)\mathbf{S}$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Dirac postulated in 1928 that the electron should have an *intrinsic* angular momentum: the "spin"

$$\boldsymbol{\mu}_J = -g\left(\frac{e}{2m_e}\right)\mathbf{J}$$

Magnetic moment

Angular momenta are measured in units of $\hbar = \frac{h}{2\pi}$

$$\boldsymbol{\mu} = -g\mu_B \mathbf{J} \qquad with \qquad \mu_B = \frac{e\hbar}{2m_e}$$ Bohr Magneton

The gyromagnetic ratio is defined as the ratio of the magnetic dipole moment to the total angular momentum

$$\gamma = -g\left(\frac{e}{2m_e}\right) \rightarrow -g\mu_B = \gamma\hbar$$

So we have: $\boldsymbol{\mu} = -g\mu_B \mathbf{J} = \gamma\hbar\mathbf{J}$

Magnetic properties of the neutron

According to quantum mechanics the classical angular momentum is replaced by an operator **σ**

$$\boldsymbol{\mu} = \gamma\hbar\boldsymbol{\sigma}$$

The neutrons have a spin-only angular momentum operator with eigenvalues $\pm\frac{1}{2}\hbar$. The components of the operator **σ** for a spin-½ particle are the Pauli spin matrices:

$$\sigma_x = \frac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \frac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \frac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Magnetic properties of the neutron

Gyromagnetic ratios of common spin-1/2 particles

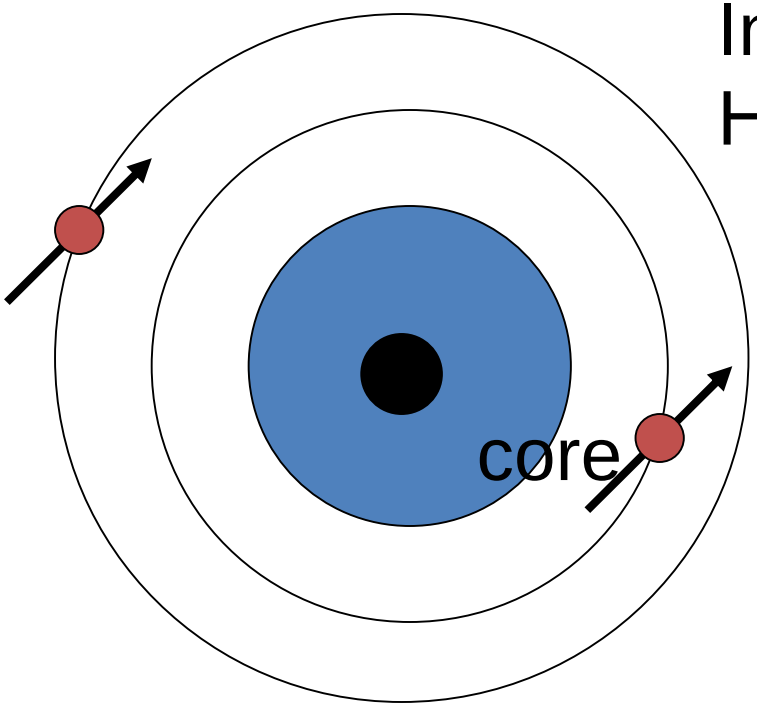
Electron: 1.76×10^5 MHz/T
Proton: 267 MHz/T
Neutron: 183 MHz/T

The neutron moment is around 960 times smaller that the electron moment.

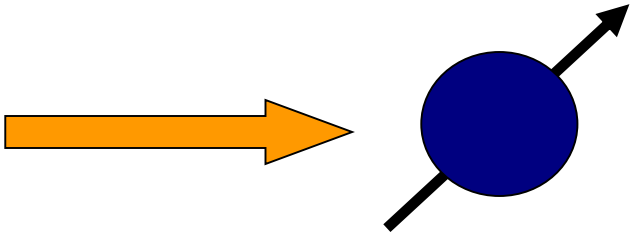
Nuclear magnetons: $\mu_N = \frac{e\hbar}{2m_p}$ proton $\mu_p = 2.793\mu_N$ neutron $\mu_n = 1.913\mu_N$

For neutrons: $\boldsymbol{\mu}_n = -\gamma_n \mu_N \boldsymbol{\sigma}$ *with* $\gamma_n = 1.913$

Atoms/ions with unpaired electrons



Intra-atomic electron correlation
Hund's rule: maximum S/J



$\mathbf{m} = - g_J \mu_B \mathbf{J}$ (rare earths)

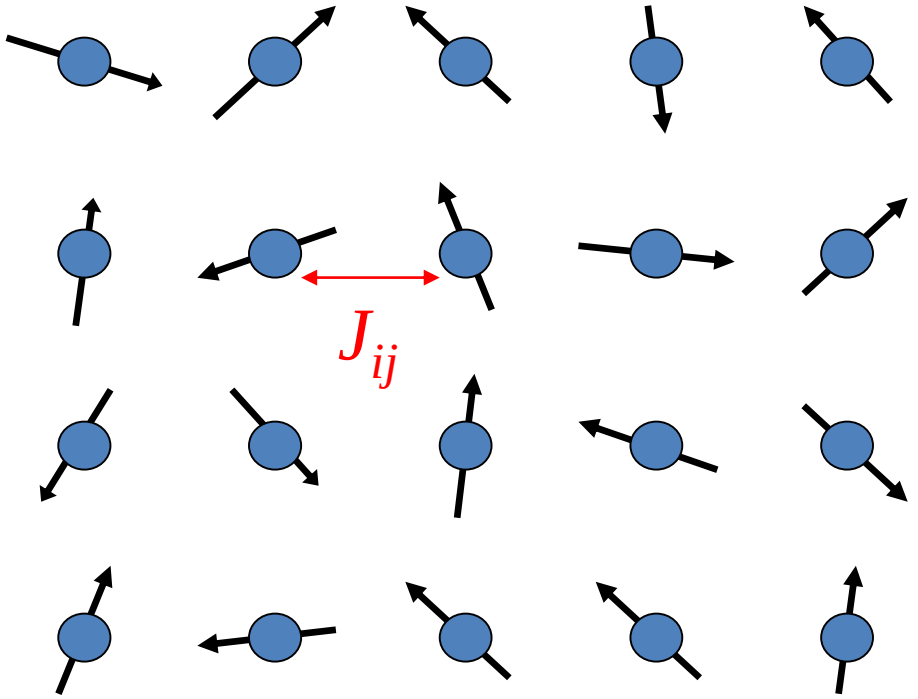
Ni^{2+} $\mathbf{m} = - g_S \mu_B \mathbf{S}$ (transition metals)

What is a magnetic structure?

Paramagnetic state:
Snapshot of magnetic moment configuration

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

$$\langle \mathbf{S}_i \rangle = 0$$

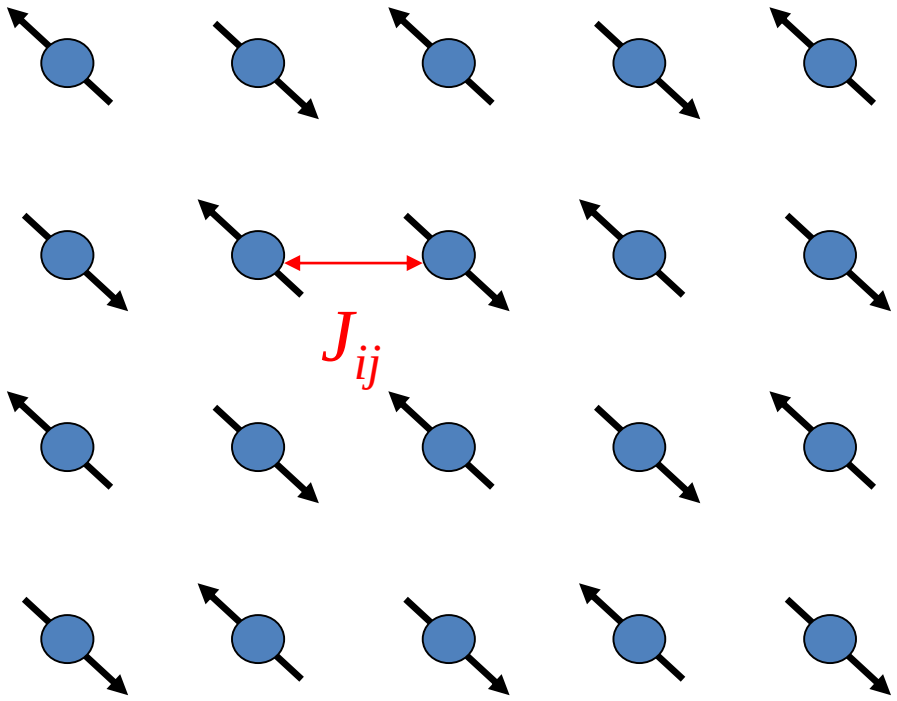


What is a magnetic structure?

Ordered state: Anti-ferromagnetic
Small fluctuations (spin waves) of the static configuration

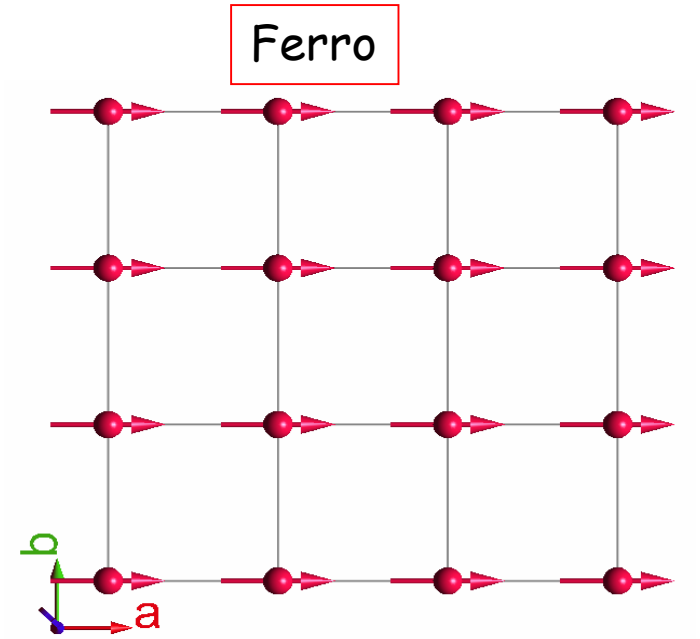
$$E_{ij} = -J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j$$

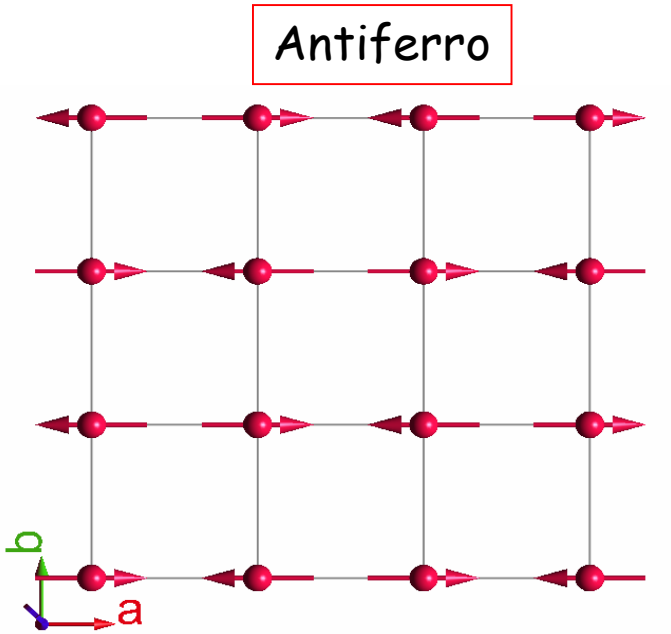
$$\langle \mathbf{S}_i \rangle \neq 0$$



Magnetic structure:
Quasi-static configuration of magnetic moments

Types of magnetic structures





Very often magnetic structures are complex due to :

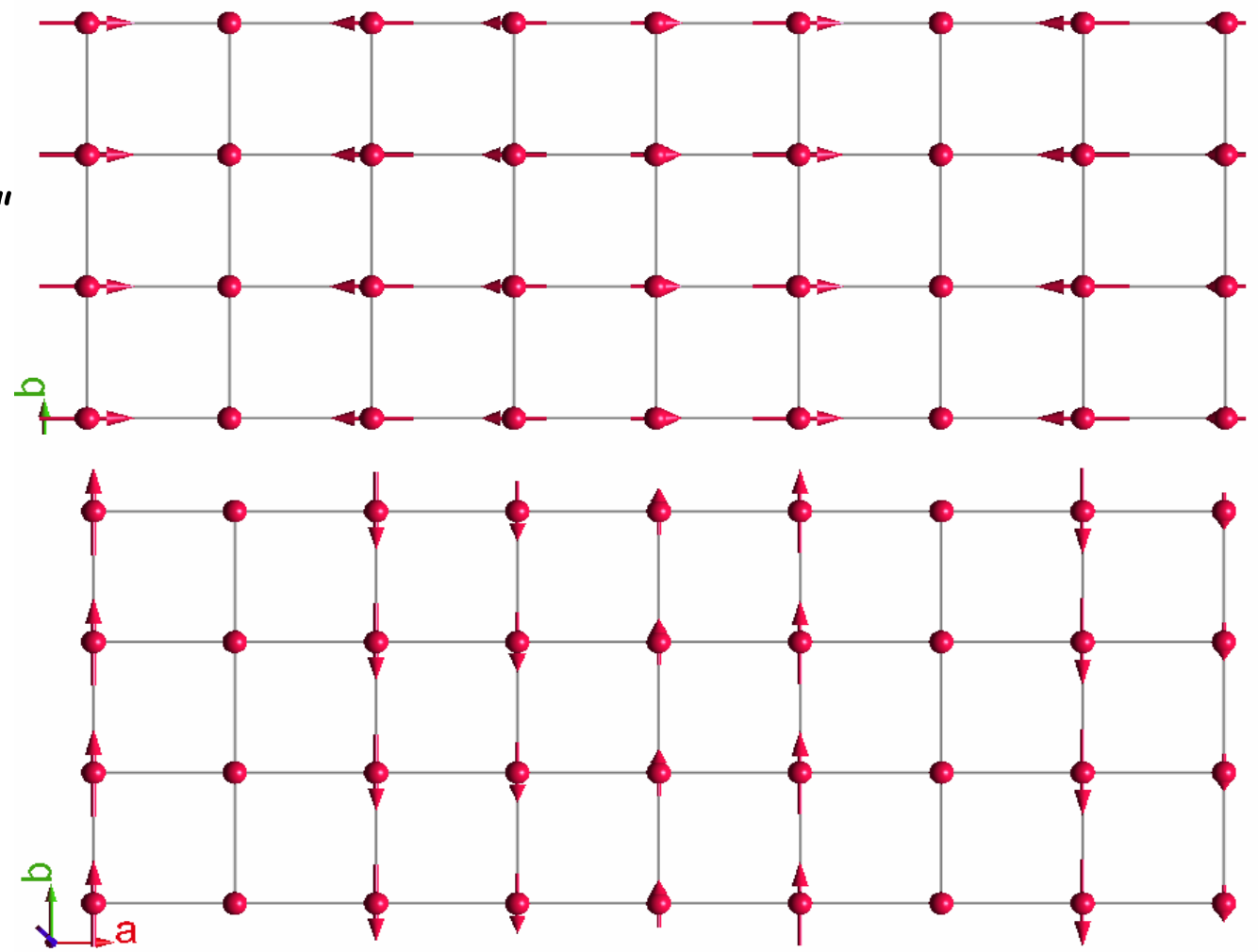
- competing exchange interactions (i.e. RKKY)
- geometrical frustration
- competition between exchange and single ion anisotropy
- . . . . . .

Types of magnetic structures

Amplitude-modulated or Spin-Density Waves

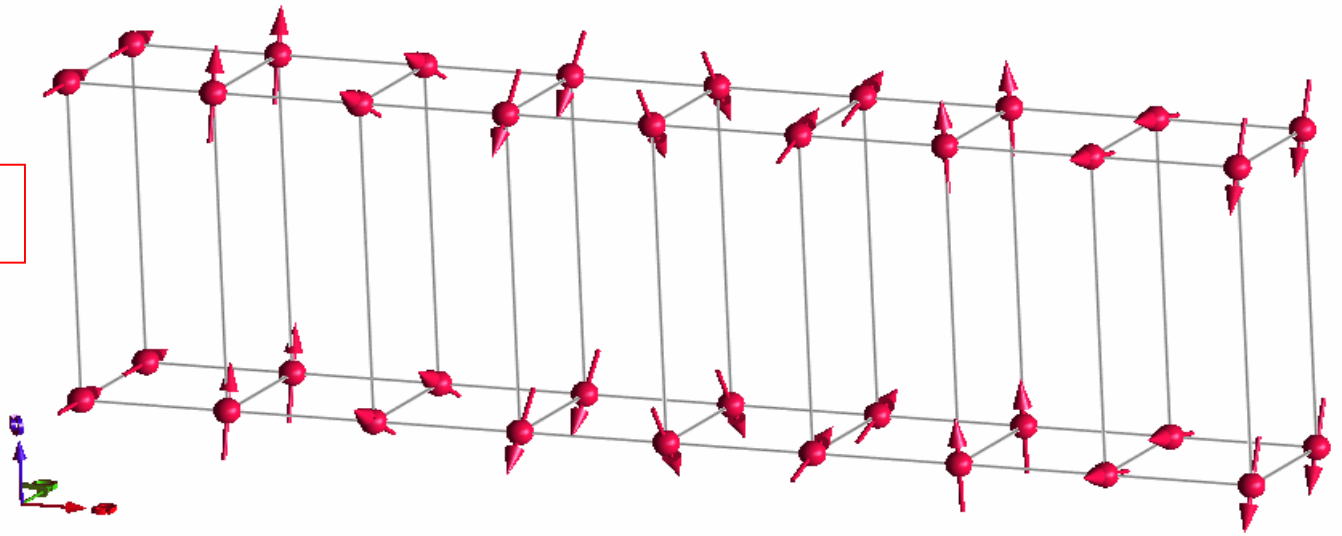
"Longitudinal"

"Transverse"

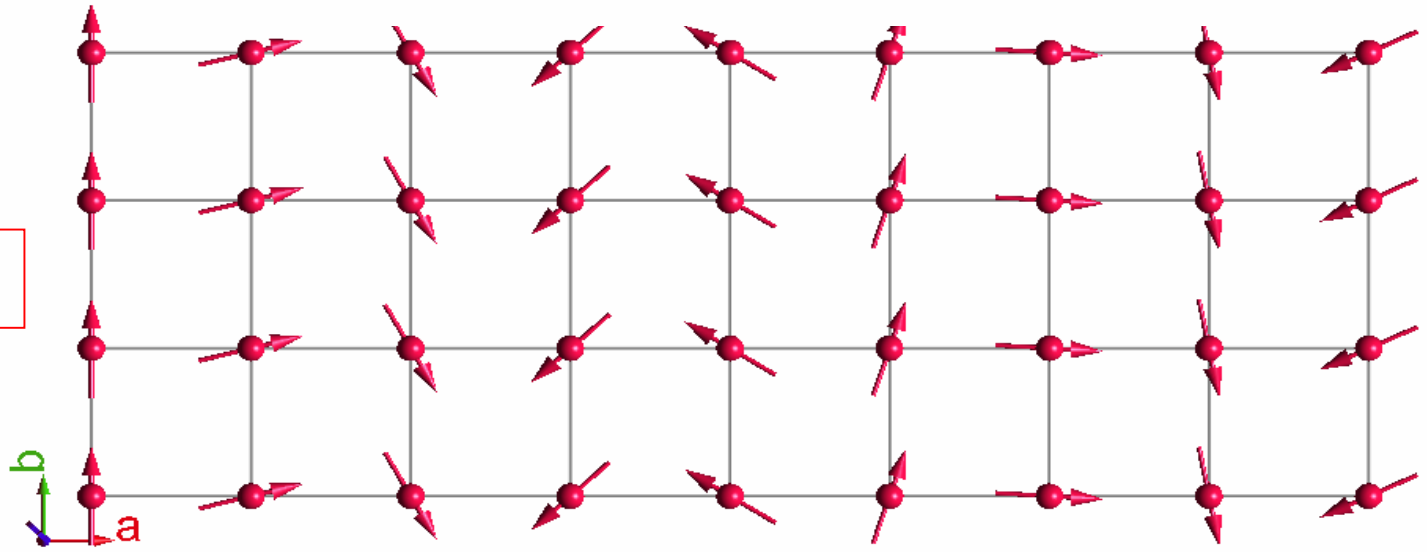


Types of magnetic structures

Spiral

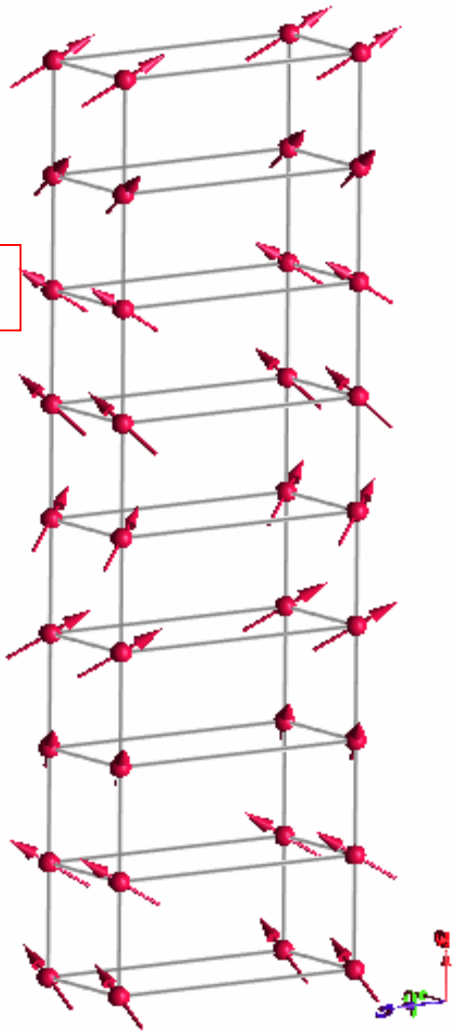


Cycloid



Types of magnetic structures

Conical



The (magnetic) structure of crystalline solids possess always a series of geometrical transformations that leave invariant the atomic (spin) arrangement.

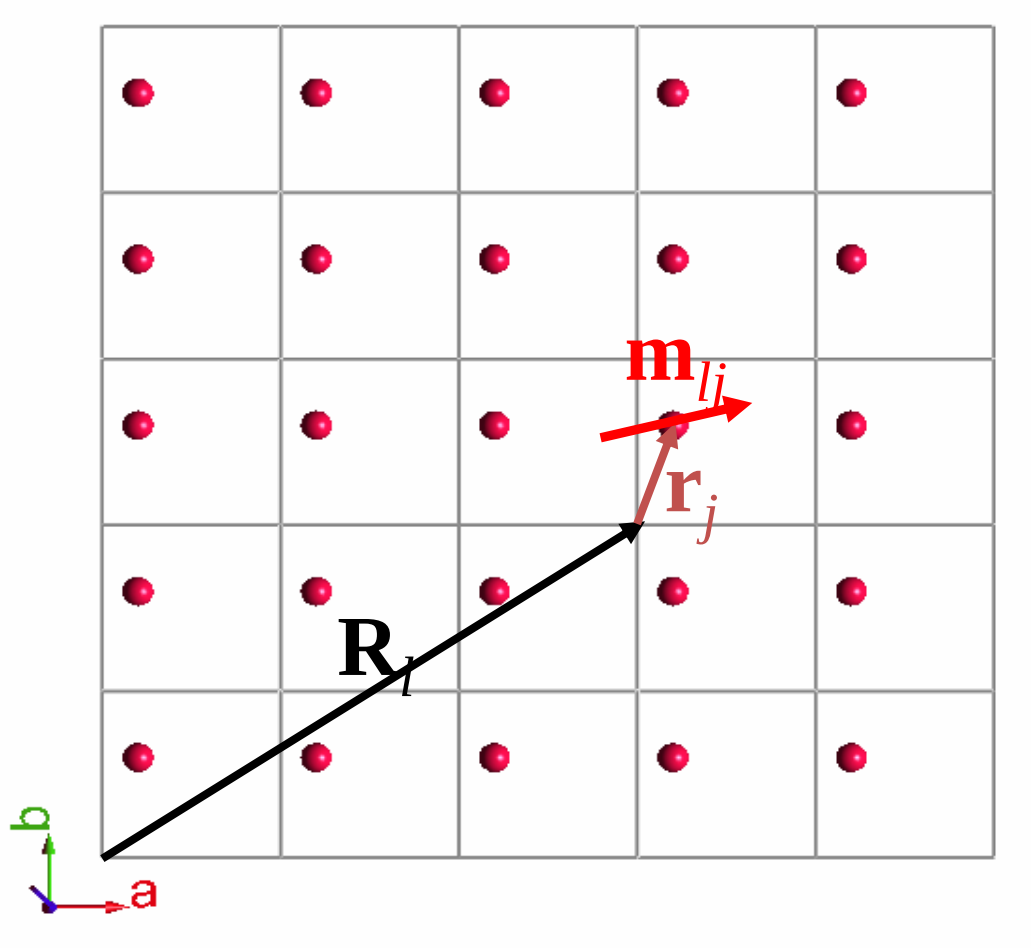
These transformations constitute a **symmetry group** in the mathematical sense: point groups, space groups, Shubnikov groups, superspace groups, …
The Shubnikov groups describe commensurate magnetic structures

Description of magnetic structures: k-formalism

The position of atom *j* in unit-cell *l* is given by:

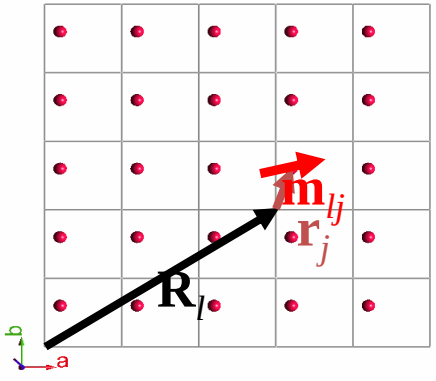
$$\mathbf{R}_{lj}=\mathbf{R}_l+\mathbf{r}_j$$

where $\mathbf{R}_l$ is a pure lattice translation



Formalism of propagation vectors

Whatever kind of magnetic structure in a crystal can be described mathematically by using a Fourier series



$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c} + x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

Necessary condition for real $\mathbf{m}_{lj}$

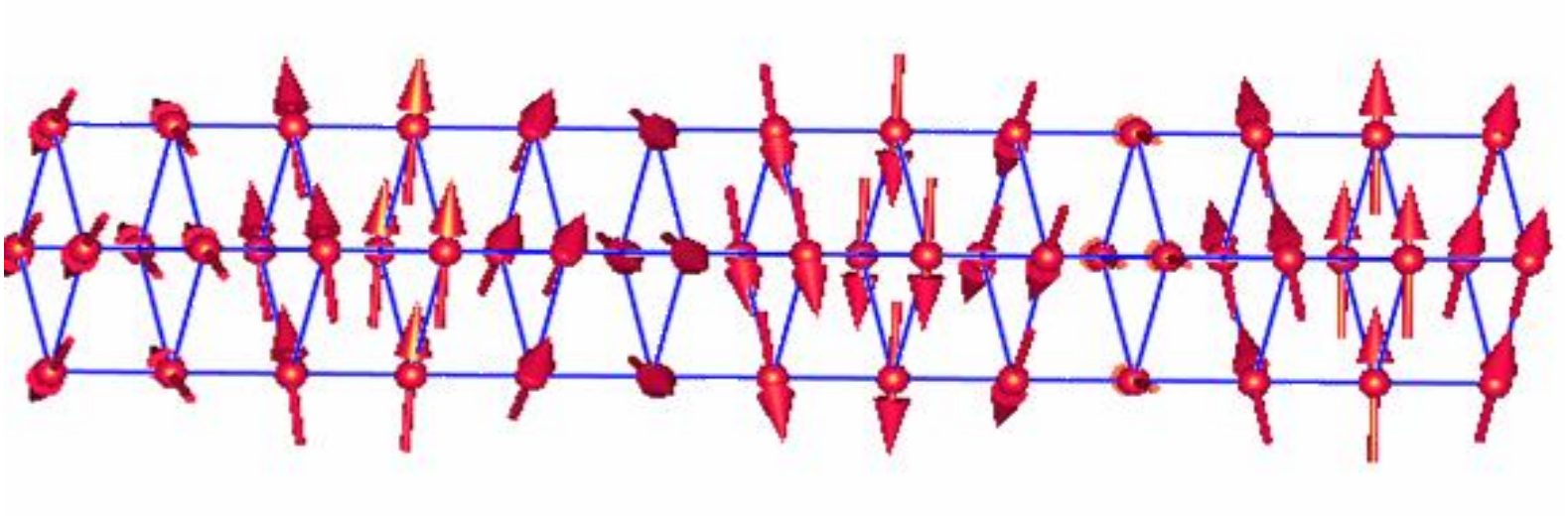
$$\mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^{*}$$

Formalism of propagation vectors

A magnetic structure is fully described by:

i) Wave-vector(s) or propagation vector(s) $\{\mathbf{k}\}$.

ii) Fourier components $\mathbf{S}_{\mathbf{k}j}$ for each magnetic atom j and wave-vector $\mathbf{k}$, $\mathbf{S}_{\mathbf{k}j}$ is a complex vector (6 components) !!!



Formalism of k-vectors: a general formula

$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}js}\ exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

l : index of a direct lattice point (origin of an arbitrary unit cell)
j : index for a Wyckoff site (orbit)
s: index of a sublattice of the j site

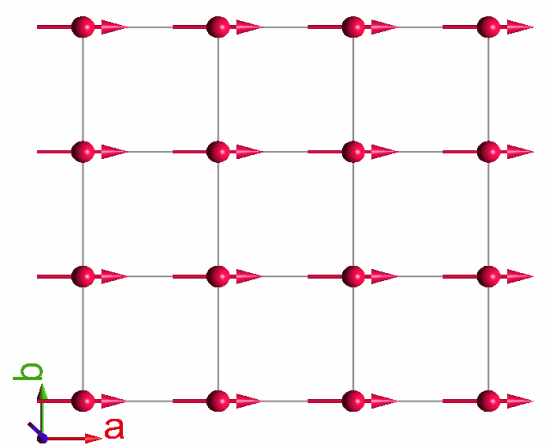
Necessary condition for real moments $\mathbf{m}_{ljs} \Rightarrow \mathbf{S}_{-\mathbf{k}js} = \mathbf{S}_{\mathbf{k}js}^{*}$

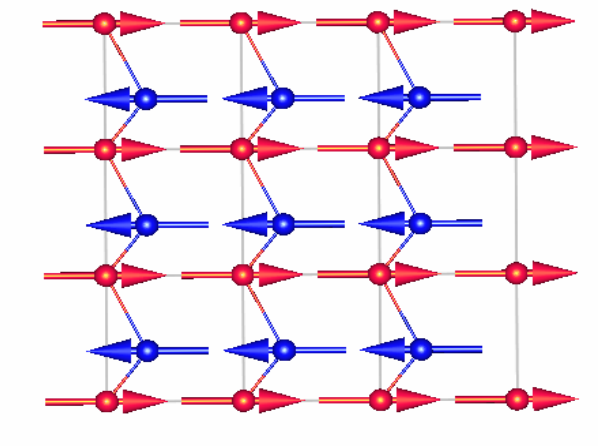
General expression of the Fourier coefficients (complex vectors) for an arbitrary site (drop of js indices) when $\mathbf{k}$ and $-\mathbf{k}$ are not equivalent:

$$\mathbf{S}_{\mathbf{k}} = \frac{1}{2}(\mathbf{R}_{\mathbf{k}} + i\mathbf{I}_{\mathbf{k}})\exp\{-2\pi i\phi_{\mathbf{k}}\}$$

Only six parameters are independent. The writing above is convenient when relations between the vectors $\mathbf{R}$ and $\mathbf{I}$ are established (e.g. when $|\mathbf{R}|=|\mathbf{I}|$, or $\mathbf{R} \cdot \mathbf{I} = 0$)

Single propagation vector: k=(0,0,0)



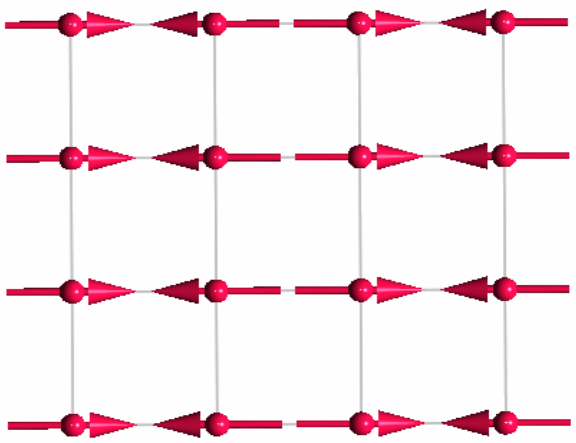


The propagation vector **k**=(0,0,0) is at the centre of the Brillouin Zone.

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j}\, exp\{-2\pi i \mathbf{k}\mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}$$

- The magnetic structure may be described within the crystallographic unit cell
- Magnetic symmetry: conventional crystallography plus spin reversal operator: crystallographic magnetic groups

Single propagation vector: k=1/2H



The propagation vector is a special point of the Brillouin Zone surface and **k**= ½ **H**, where **H** is a reciprocal lattice vector.

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \exp\{-2\pi i\, \mathbf{k}\, \mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j} \exp\{-\pi i\, \mathbf{H}\, \mathbf{R}_l\}$$

$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} \left(-1\right)^{n(l)}$$

REAL Fourier coefficients ≡ magnetic moments

The magnetic symmetry may also be described using crystallographic magnetic space groups

Fourier coefficients of sinusoidal structures

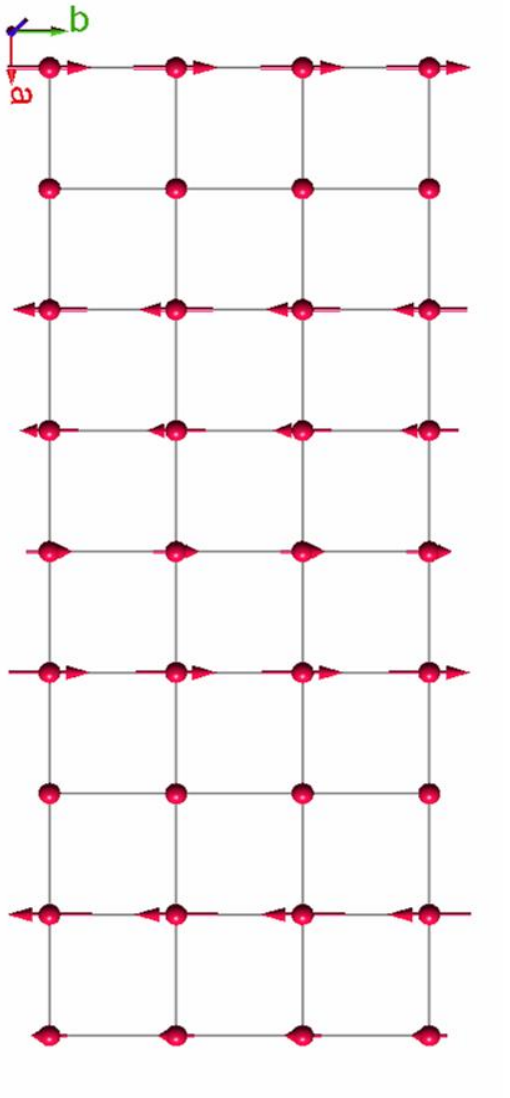
- **k** interior of the Brillouin zone (IBZ) (pair **k**, -**k**)

- Real $\mathbf{S_k}$, or imaginary component in the same direction as the real one

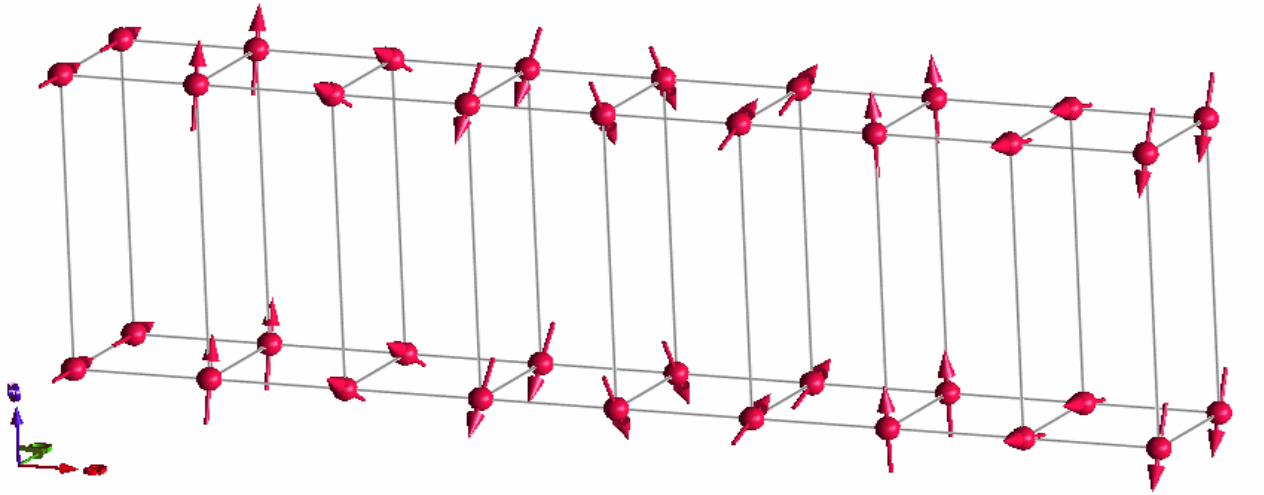
$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{kj}} \exp(-2\pi i \mathbf{k}\mathbf{R}_l) + \mathbf{S}_{\mathbf{-kj}} \exp(2\pi i \mathbf{k}\mathbf{R}_l)$$

$$\mathbf{S}_{\mathbf{kj}} = \frac{1}{2} m_j \mathbf{u}_j exp(-2\pi i \phi_{\mathbf{kj}})$$

$$\mathbf{m}_{lj} = m_j \mathbf{u}_j \cos 2\pi(\mathbf{k}\mathbf{R}_l + \phi_{\mathbf{kj}})$$



Fourier coefficients of helical structures

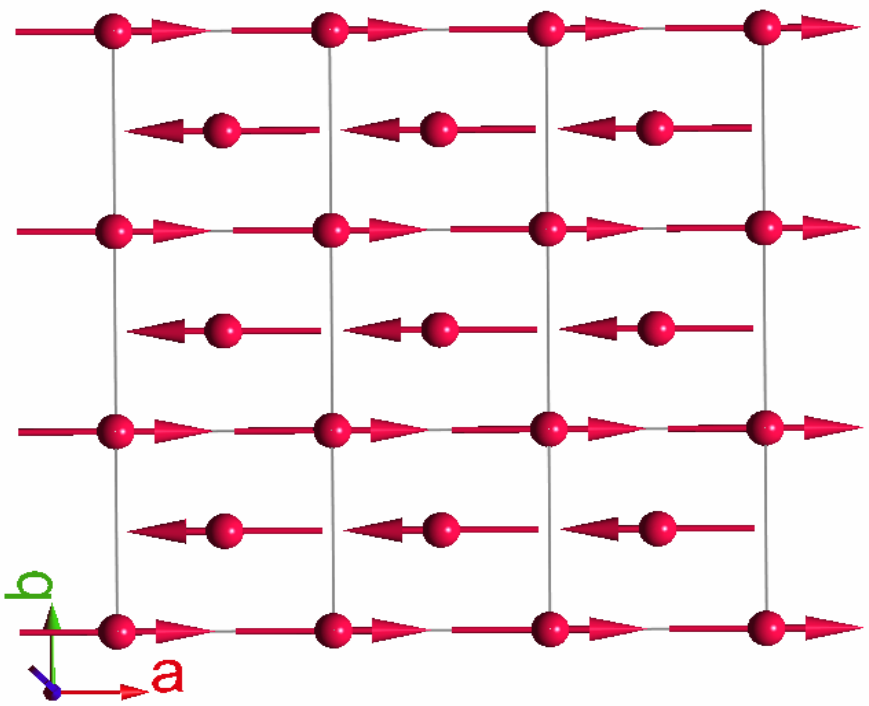


- **k** interior of the Brillouin zone
- Real component of $\mathbf{S_k}$ perpendicular to the imaginary component

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2}[m_{uj}\mathbf{u}_j + im_{vj}\mathbf{v}_j]exp(-2\pi i\phi_{\mathbf{k}j})$$

$$\mathbf{m}_{lj} = m_{uj}\mathbf{u}_j \cos 2\pi(\mathbf{kR}_l + \phi_{\mathbf{k}j}) + m_{vj}\mathbf{v}_j \sin 2\pi(\mathbf{kR}_l + \phi_{\mathbf{k}j})$$

Note on centred cells



$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{kj}} \; exp\{-2\pi\, i\mathbf{k}\mathbf{R}_l\}$$

The **k** vectors are referred to the reciprocal basis of the conventional direct cell and for centred cells may have values > 1/2

k=(1,0,0) or (0,1,0) ?

$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c} + x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

The translation vectors have fractional components when using centred cells. The index *j* runs on the atoms contained in a PRIMITIVE cell

How to play with magnetic structures and the k-vector formalism

$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}js} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

The program **FullProf Studio** performs the above sum and represents graphically the magnetic structure.
This program can help to learn about this formalism because the user can write manually the Fourier coefficients and see what is the corresponding magnetic structure immediately.

Web site: http://www.ill.eu/sites/fullprof

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Magnetic scattering: Fermi's golden rule

Differential neutron cross-section:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{s\lambda\to s'\lambda'} = \frac{k'}{k}\left(\frac{m_n}{2\pi\hbar^2}\right)^2 \left|\left\langle \mathbf{k}'s'\lambda'\left|V_m\right|\mathbf{k}s\lambda\right\rangle\right|^2 \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

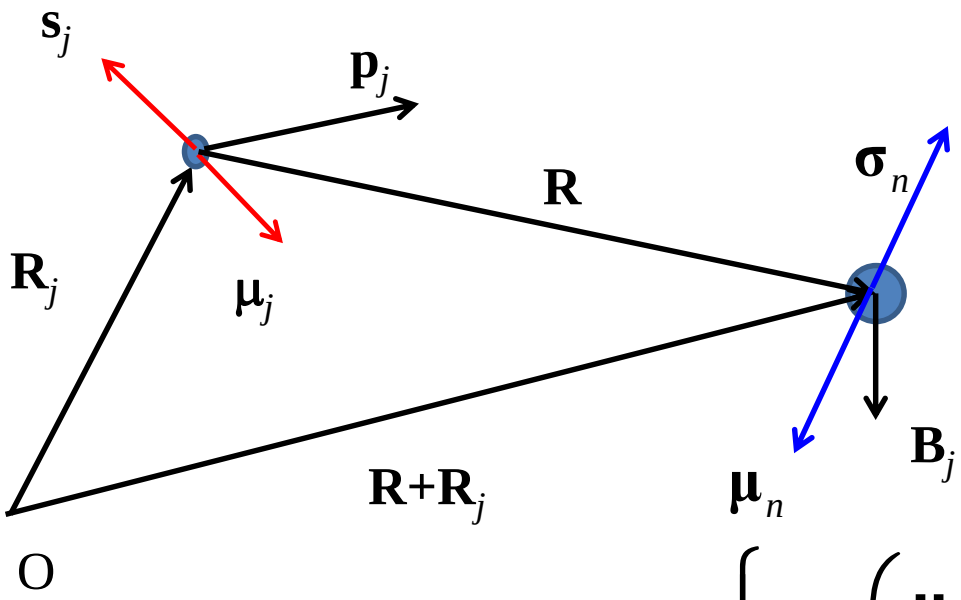
This expression describes all processes in which:

- The state of the scatterer changes from λ to λ'
- The wave vector of the neutron changes from **k** to **k**' where **k**' lies within the solid angle $d\Omega$
- The spin state of the neutron changes from s to s'

$V_m = \boldsymbol{\mu}_n.\mathbf{B}$ is the potential felt by the neutron due to the magnetic field created by moving electrons. It has an orbital an spin part.

Magnetic scattering: magnetic fields

Magnetic field due to spin and orbital moments of an electron:



Magnetic vector potential of a dipolar field due to electron spin moment

$$\mathbf{B}_j = \mathbf{B}_{jS} + \mathbf{B}_{jL} = \frac{\mu_0}{4\pi}\left\{\nabla \times \left(\frac{\boldsymbol{\mu}_j \times \hat{\mathbf{R}}}{R^2}\right) - \frac{2\mu_B}{\hbar}\frac{\mathbf{p}_j \times \hat{\mathbf{R}}}{R^2}\right\}$$

Biot-Savart law for a single electron with linear momentum **p**

Magnetic scattering: magnetic fields

Evaluating the spatial part of the transition matrix element for electron *j*:

$$\langle \mathbf{k}' | V_m^j | \mathbf{k} \rangle \propto \exp(i\mathbf{Q}\mathbf{R}_j) \left\{ \hat{\mathbf{Q}} \times (\mathbf{s}_j \times \hat{\mathbf{Q}}) + \frac{i}{\hbar Q} (\mathbf{p}_j \times \hat{\mathbf{Q}}) \right\}$$

Where $\hbar\mathbf{Q} = \hbar(\mathbf{k} - \mathbf{k}')$ is the momentum transfer

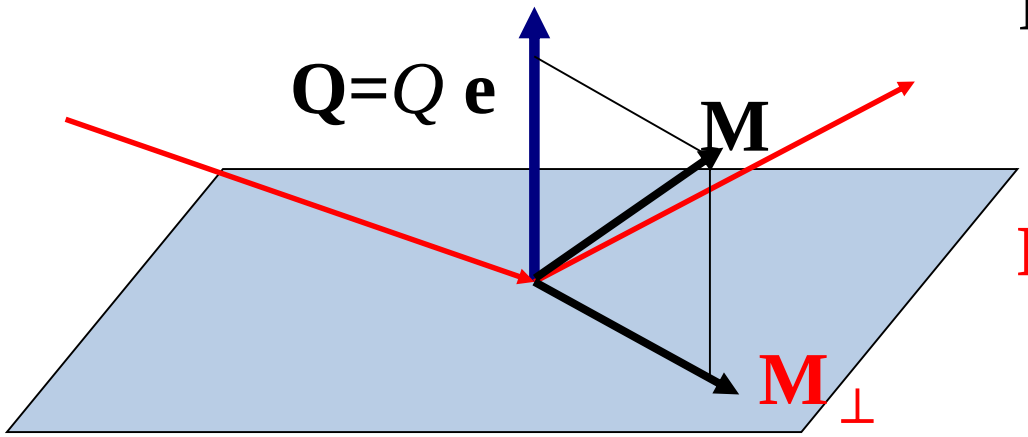
Summing for all unpaired electrons we obtain:

$$\sum_j \langle \mathbf{k}' | V_m^j | \mathbf{k} \rangle \propto \hat{\mathbf{Q}} \times (\mathbf{M}(\mathbf{Q}) \times \hat{\mathbf{Q}}) = \mathbf{M}(\mathbf{Q}) - (\mathbf{M}(\mathbf{Q}).\hat{\mathbf{Q}}).\hat{\mathbf{Q}} = \mathbf{M}_\perp(\mathbf{Q})$$

$\mathbf{M}_\perp(\mathbf{Q})$ is the perpendicular component of the Fourier transform of the magnetisation in the scattering object to the scattering vector. It includes the orbital and spin contributions.

Magnetic scattering

$\mathbf{M}_\perp(\mathbf{Q})$ is the perpendicular component of the Fourier transform of the magnetisation in the sample to the scattering vector.



Magnetic structure factor

$$\mathbf{M}(\mathbf{Q}) = \int \mathbf{M}(\mathbf{r}) \exp\left(i\mathbf{Q}\cdot\mathbf{r}\right) d^3\mathbf{r}$$

Magnetic interaction vector

$$\mathbf{M}_\perp = \mathbf{e}\times\mathbf{M}\times\mathbf{e} = \mathbf{M} - \mathbf{e}\,(\mathbf{e}\cdot\mathbf{M})$$

Elastic scattering:

$$\left(\frac{d\sigma}{d\Omega}\right) = (\gamma r_0)^2 \mathbf{M}_\perp^* \mathbf{M}_\perp$$

Neutrons only see the components of the magnetisation that are perpendicular to the scattering vector

Scattering by a collection of magnetic atoms

We will consider in the following only elastic scattering.
We suppose the magnetic matter made of atoms with unpaired electrons that remain close to the nuclei.

Vector position of electron *e*: $\mathbf{R}_e = \mathbf{R}_{lj} + \mathbf{r}_{je}$

The Fourier transform of the magnetization can be written in discrete form as

$$\mathbf{M}(\mathbf{Q}) = \sum_e \mathbf{s}_e \exp(i\mathbf{Q}\cdot\mathbf{R}_e) = \sum_{lj} \exp(i\mathbf{Q}\cdot\mathbf{R}_{lj}) \sum_{e_j} \exp(i\mathbf{Q}\cdot\mathbf{r}_{je})\mathbf{s}_{je}$$

$$\mathbf{F}_j(\mathbf{Q}) = \sum_e \mathbf{s}_{je} \exp(i\mathbf{Q}\cdot r_{je}) = \int \boldsymbol{\rho}_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r}$$

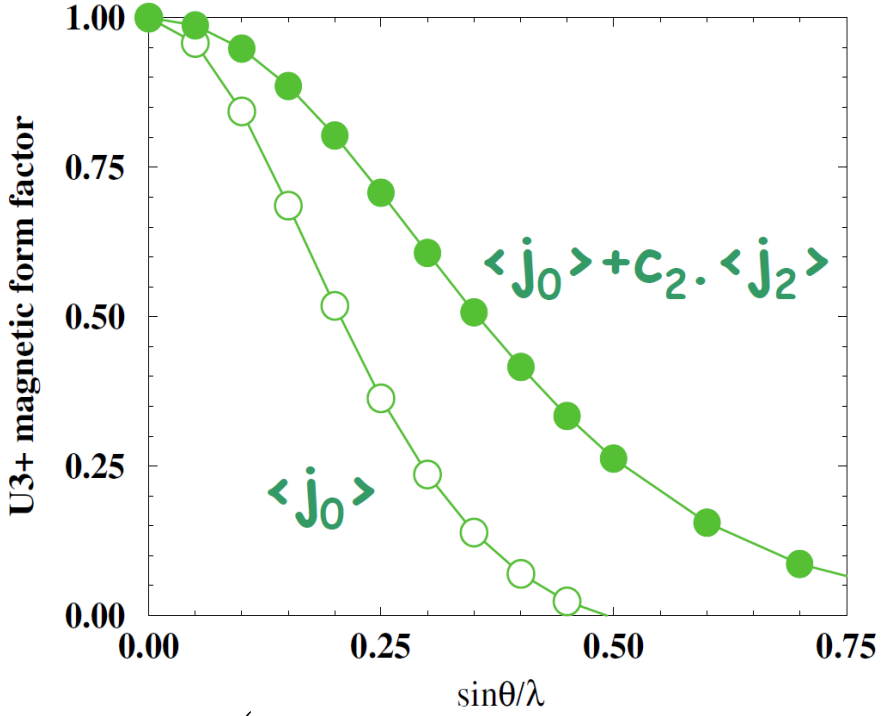
$$\mathbf{F}_j(\mathbf{Q}) = \mathbf{m}_j \int \rho_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r} = \mathbf{m}_j f_j(Q)$$

$$\mathbf{M}(\mathbf{Q}) = \sum_{lj} \mathbf{m}_{lj} f_{lj}(Q) \exp(i\mathbf{Q}\cdot\mathbf{R}_{lj})$$

Scattering by a collection of magnetic atoms

$$\mathbf{F}_j(\mathbf{Q}) = \sum_e \mathbf{s}_{je} \exp(i\mathbf{Q}\cdot r_{je}) = \int \boldsymbol{\rho}_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r}$$

$$\mathbf{F}_j(\mathbf{Q}) = \mathbf{m}_j \int \rho_j(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d^3\mathbf{r} = \mathbf{m}_j f_j(Q)$$



If we use the common variable s=sinθ/λ, then the expression of the form factor is the following:

$$f(s) = \sum_{l=0,2,4,6} W_l \left\langle j_l(s) \right\rangle$$

$$\left\langle j_l(s) \right\rangle = \int_0^\infty U^2(r) j_l(4\pi sr) 4\pi r^2 dr$$

$$\left\langle j_l(s) \right\rangle = s^2 \left(A_l \exp\{-a_l s^2\} + B_l \exp\{-b_l s^2\} + C_l \exp\{-c_l s^2\} + D_l \right) \qquad for \quad l = 2,4,6$$

$$\left\langle j_0(s) \right\rangle = A_0 \exp\{-a_0 s^2\} + B_0 \exp\{-b_0 s^2\} + C_0 \exp\{-c_0 s^2\} + D_0$$

Elastic Magnetic Scattering by a crystal (1)

The Fourier transform of the magnetization of atomic discrete objects can be written in terms of atomic magnetic moments and a form factor for taking into account the spread of the density around the atoms

$$\mathbf{M}(\mathbf{Q}) = \sum_{lj} \mathbf{m}_{lj} f_{lj}(Q) \exp(i\mathbf{Q}\cdot\mathbf{R}_{lj})$$

For a crystal with a commensurate magnetic structure the content of all unit cell is identical, so the expression above becomes factorised as:

$$\mathbf{M}(\mathbf{Q}) = \sum_{j} \mathbf{m}_{j} f_{j}(Q) \exp(i\mathbf{Q}\cdot\mathbf{r}_{j}) \sum_{l} \exp(i\mathbf{Q}\cdot\mathbf{R}_{l}) \propto \sum_{j} \mathbf{m}_{j} f_{j}(Q) \exp(2\pi i\mathbf{H}\cdot\mathbf{r}_{j})$$

The lattice sum is only different from zero when $\mathbf{Q}=2\pi\mathbf{H}$, where $\mathbf{H}$ is a reciprocal lattice vector of the magnetic lattice. The vector M is then proportional to the magnetic structure factor of the magnetic cell

Elastic Magnetic Scattering by a crystal (2)

For a general magnetic structure that can be described as a Fourier series:

$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{M}(\mathbf{h}) = \sum_{lj}\sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \exp(-2\pi i \mathbf{k}\mathbf{R}_l) f_{lj}(h) \exp(2\pi i \mathbf{h}\cdot\mathbf{R}_{lj})$$

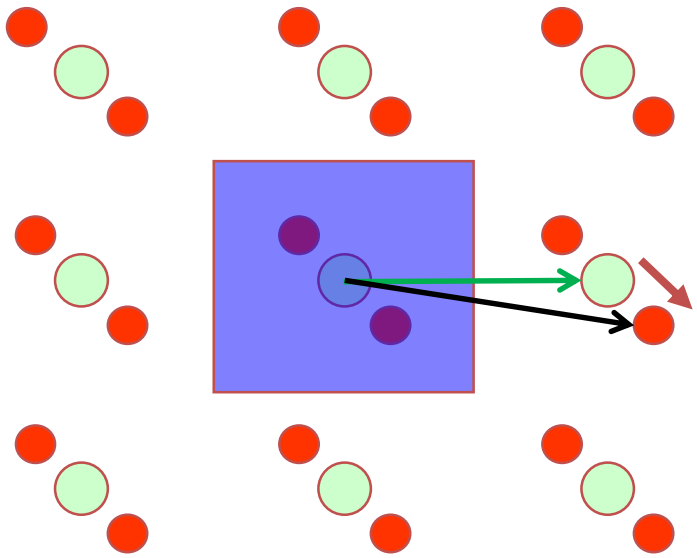
$$\mathbf{M}(\mathbf{h}) = \sum_{j} f_j(h) \exp(2\pi i \mathbf{h}\cdot\mathbf{r}_j) \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \sum_{l} \exp(2\pi i (\mathbf{h}-\mathbf{k})\cdot\mathbf{R}_l)$$

$$\mathbf{M}(\mathbf{h}) \propto \sum_{j} \mathbf{S}_{\mathbf{k}j} \, f_j(Q) \exp(2\pi i (\mathbf{H}+\mathbf{k})\cdot\mathbf{r}_j)$$

The lattice sum is only different from zero when **h-k** is a reciprocal lattice vector **H** of the crystallographic lattice. The vector **M** is then proportional to the magnetic structure factor of the unit cell that now contains the Fourier coefficients $\mathbf{S}_{\mathbf{k}j}$ instead of the magnetic moments $\mathbf{m}_j$.

Diff. Patterns of magnetic structures

Portion of reciprocal space



Magnetic reflections

Nuclear reflections

h = H+k

Magnetic reflections: indexed by a set of propagation vectors {**k**}

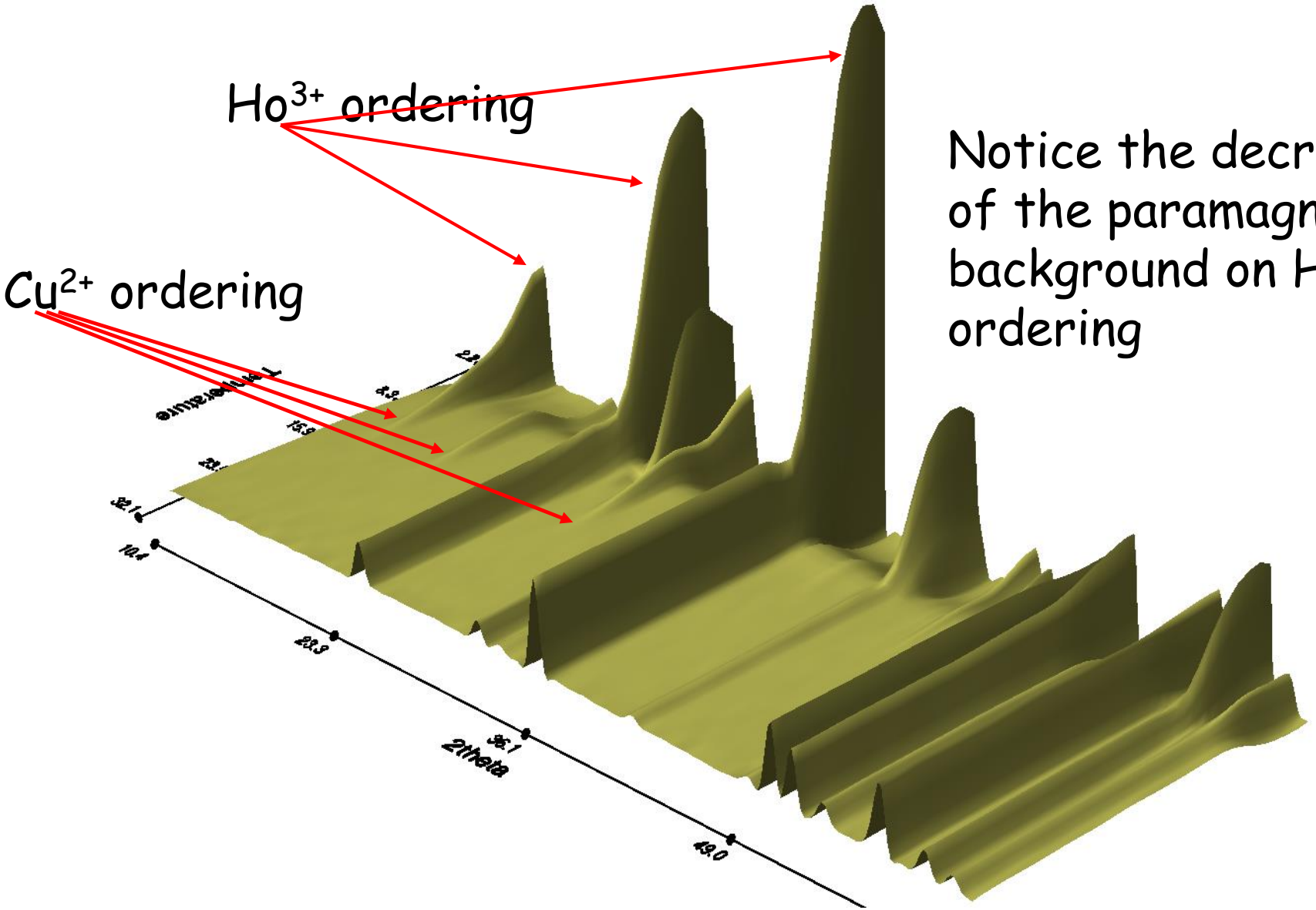
h is the scattering vector indexing a magnetic reflection

H is a reciprocal vector of the crystallographic structure

k is one of the propagation vectors of the magnetic structure

(**k** is reduced to the Brillouin zone)

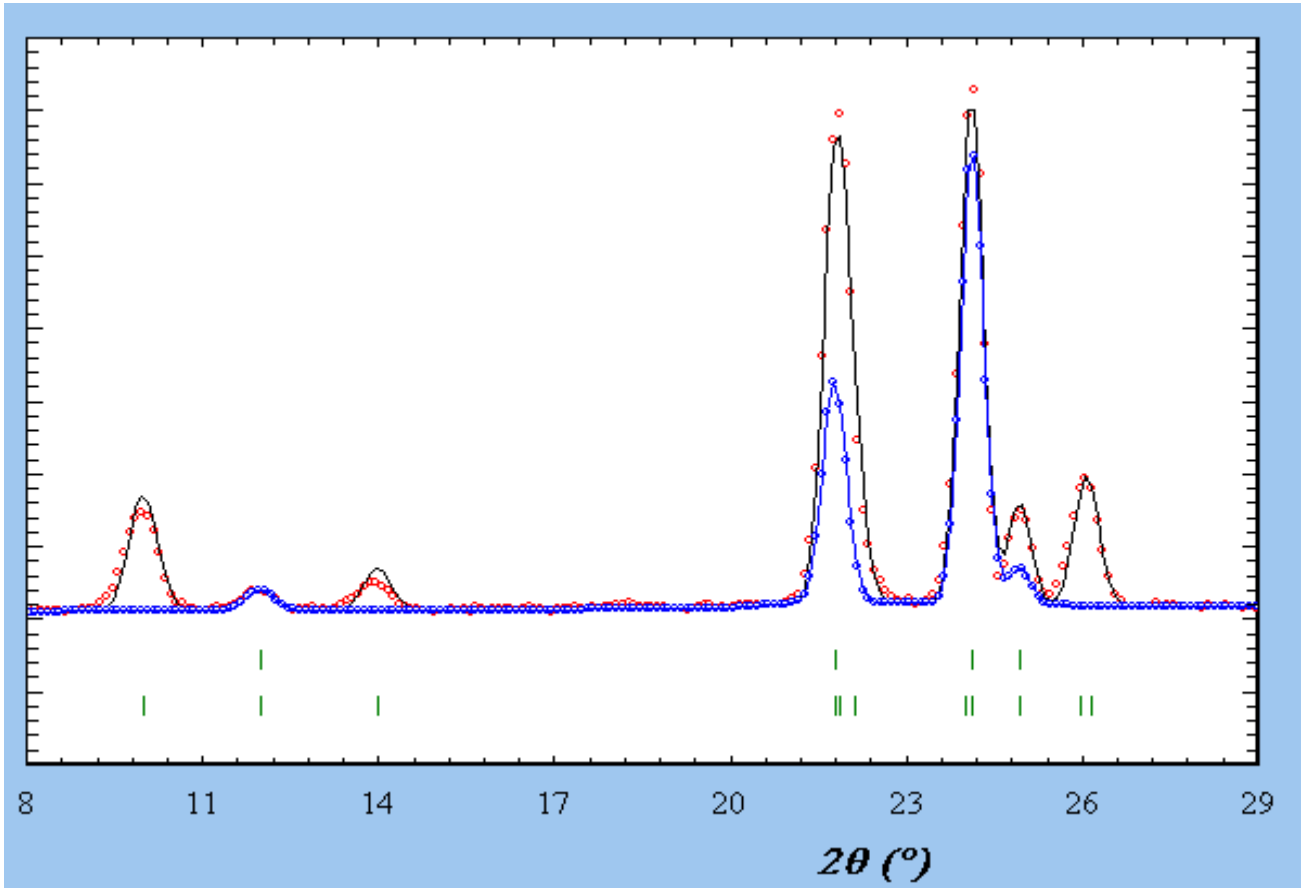
Diffraction patterns of magnetic structures



Diffraction patterns of magnetic structures

Magnetic structure of $DyMn_6Ge_6$

Conical structure with two propagation vectors



Nuclear contribution in blue

Elastic Magnetic Scattering by a crystal (3)

From now the we will call **M**(**h**) the magnetic structure factor

$$\mathbf{M}(\mathbf{h}) = \sum_j \mathbf{S}_{\mathbf{kj}} f_j(Q) \exp(2\pi i(\mathbf{H}+\mathbf{k})\cdot\mathbf{r}_j)$$

And its perpendicular component to **h**, $\mathbf{M}_\perp(\mathbf{h})$, is the magnetic interaction vector of the crystallographic unit cell. The elastic cross section (intensity of a Bragg reflection) is then:

$$\left(\frac{d\sigma}{d\Omega}\right) = (\gamma r_0)^2 \mathbf{M}_\perp^* \mathbf{M}_\perp$$

Where $\mathbf{M}_\perp(\mathbf{h})$ is calculated for a finite number of magnetic atoms inside the crystallographic unit cell. Notice that the magnetic moments do not appear directly in the expression of **M**(**h**).

Outline:

1. Magnetic Structures and neutron scattering
2. **Representation Analysis and Magnetic Structures**
3. Magnetic Structure determination. Magnetic Structure Factors

Group representations (representation analysis)

Magnetic Structure Description and Determination

Bertaut is the principal developer of the representation analysis applied to magnetic structures

Representation analysis of magnetic structures

E.F. Bertaut, Acta Cryst. (1968). A24, 217-231

Magnetic Structure Description and Determination

After the first experiments in magnetic neutron diffraction done at Oak Ridge demonstrating the occurrence of antiferromagnetism, **Bertaut** went to the USA in 1951/1953 and worked with **Corliss** and **Hasting** at the Brookhaven National Laboratory. From 1958 to 1976 **Bertaut** was the head of the laboratory called "Diffraction Neutronique" at the CENG in Grenoble.

After the first **International Conference on Neutron Scattering** (Grenoble, 1963) **Bertaut** and **Néel** pushed the French authorities to construct a nuclear reactor in Grenoble that became the highest flux reactor for studying condensed matter physics and chemistry: The **Institute Laue-Langevin**.

Bertaut became the leader of the Grenoble School on magnetic structure determination.

Magnetic Structure Description and Determination

Yurii Alexandrovich Izyumov (1933-2010) and collaborators, mainly V.E. Naish and R.P. Ozerov.

They published a series of 5 articles in Journal of Magnetism and Magnetic Materials on representation analysis and magnetic structure description and determination, giving explicit and general formulae for deducing the basis functions of irreps.

Symmetry Analysis in Neutron Diffraction Studies of Magnetic Structures, JMMM 1979-1980

Summary of Group representation theory

A representation of a group is a set of matrices satisfying the same operation rules as the group elements

$$\Gamma = \{\Gamma(g) \,|\, g \in G\}, \quad \Gamma(g_1 g_2) = \Gamma(g_1)\Gamma(g_2)$$

Under the ordinary matrix product the given set constitutes an isomorphic group (preserves the multiplication table).

A similarity transformation applied to all matrices provides an equivalent representation (the matrix U is generally unitary: $U^{-1}=U^{\dagger}$).

$$\Gamma(g) = U\,\Gamma(g)\,U^{-1}\{with\ g \in G\}$$

A particular group has an infinite number of representations of arbitrary dimensions. The most important representations are called "Irreducible Representations" (Irreps). An arbitrary representation may be reduced to "block-diagonal form" by an appropriate similarity transformation. Those representations that cannot be reduced are the Irreps.

Summary of Group representation theory

Given the representation $\Gamma=\{\Gamma(e), \Gamma(a), \Gamma(b)\ldots\}$ of the group $\boldsymbol{G}=\{e, a, b,\ldots\}$, if we are able to find a similarity transformation U converting all matrices to the same block-diagonal form, we obtain an equivalent representation that can be decomposed as follows:

$$\Gamma(g)=U\,\Gamma(g)\,U^{-1} \quad \{with\ g\in G\} \Rightarrow \quad \Gamma=U\,\Gamma\,U^{-1}$$

$$\Gamma(g)=\begin{pmatrix} A_{11} & A_{12} & 0 & 0 & 0 & 0 & 0 \\ A_{21} & A_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & B_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & B_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{11} & C_{12} & C_{13} \\ 0 & 0 & 0 & 0 & C_{21} & C_{22} & C_{23} \\ 0 & 0 & 0 & 0 & C_{31} & C_{32} & C_{33} \end{pmatrix} = A(g)\oplus 2B(g)\oplus C(g)$$

Irreducible representations

$\Gamma^1=\{A(e), A(a), A(b),\ldots\}$

$\Gamma^2=\{B(e), B(a), B(b),\ldots\}$

$\Gamma^3=\{C(e), C(a), C(b),\ldots\}$

In general: $$\Gamma=\sum_{\oplus\nu} n_\nu\Gamma^\nu = n_1\Gamma^1\oplus n_2\Gamma^2\ldots\oplus n_m\Gamma^m$$

Master formulae of group representation theory

We shall note the different irreducible representations with the index ν and a symbol Γ that may be used also for matrices. The dimension of the representation Γ_ν is l_ν. The characters of a representation (traces of the matrices) will be represented as $\chi^\nu(g)$

The great orthogonality theorem:

$$\sum_{g\in G}\Gamma^{\nu}_{ij}(g)\Gamma^{*\mu}_{lm}(g)=\frac{n(G)}{l_\nu}\,\delta_{il}\,\delta_{jm}\,\delta_{\mu\nu}$$

Particularized for the characters:

$$\sum_{g\in G}\chi^{\nu}(g)\chi^{*\mu}(g)=n(G)\,\delta_{\mu\nu}$$

Decomposition of a representation in Irreps:

$$\Gamma=\sum_{\oplus\nu}n_\nu\Gamma_\nu,\qquad n_\nu=\frac{1}{n(G)}\sum_{g\in G}\chi(g)\chi^{*\nu}(g)$$

Basis functions of a representation

The elements of the symmetry groups act on position vectors. For each particular problem we can select a set of physically relevant variables φ_i $\{i = 1, 2, \ldots p\}$ spanning a working functional space **W**. These functions constitute a basis of the **W** space.

The action of the operator associated to a symmetry operator when applied to a function of position vectors is defined by the expression:

$$O(g)\varphi(\mathbf{r}) = \varphi(g^{-1}\mathbf{r}) \equiv \varphi'(\mathbf{r})$$

When using the functions φ_i (**r**), the action of the operator $O(g)$ gives rise to a linear combination, defining a representation of the group G:

$$O(g)\varphi_j(\mathbf{r}) = \varphi'(\mathbf{r}) = \sum_i \Gamma_{ij}(g)\varphi_i(\mathbf{r})$$

Basis functions of irreducible representations

If we take another basis ψ related to the initial one by a unitary transformation we may get the matrices of the Γ representation in block-diagonal form.

$$\psi_j(\mathbf{r}) = \sum_i U_{ij}(g)\varphi_i(\mathbf{r})$$

The system of p ψ-functions splits in subsystems defining irreducible subspaces of the working space **W**. If we take one of these subspaces (labelled ν), the action of the operator $O(g)$ on the basis functions is:

$$O(g)\psi_j(\mathbf{r}) = \sum_{i=1}^{l_\nu} \Gamma^\nu_{ij}(g)\psi_i(\mathbf{r})$$

Here the functions are restricted to those of the subspace ν

Basis functions of Irreps: Projection operators

Projection operators

There is a way for obtaining the basis functions of the Irreps for the particular physical problem by applying the following projection operator formula:

$$\psi_i^{\nu} = P^{\nu}\varphi = \frac{1}{n(G)} \sum_{g \in G} \Gamma^{*\nu}_{i[j]}(g)\, O(g)\, \varphi \qquad (i = 1, \ldots l_{\nu})$$

The result of the above operation is zero or a basis function of the corresponding Irrep. The index [j] is fixed, taking different values provide new basis functions or zero.

Representations of the translation group (1)

Representations of the translation group

The translation group is Abelian so the Irreps are all *one-dimensional*.
Considering the properties of the translation operators and the Born-Von Karman periodic boundary conditions the representation matrix (a single number equal to its character) is given by the expression:

$$O(\mathbf{t}) = O(l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3) = O(\mathbf{a}_1)^{l_1} O(\mathbf{a}_2)^{l_2} O(\mathbf{a}_3)^{l_3}$$

$$O(\mathbf{a}_j)^{N_j+1} = O(\mathbf{a}_j)$$

$$O(\mathbf{t}) \rightarrow \exp\left\{2\pi i\left(\frac{p_1 l_1}{N_1} + \frac{p_2 l_2}{N_2} + \frac{p_3 l_3}{N_3}\right)\right\}, \qquad 0 \leq p_i \in Z \leq N_i - 1$$

There are $N = N_1 \times N_2 \times N_3$ representations labelled by the reciprocal space vector:

$$\mathbf{k} = \left(\frac{p_1}{N_1}, \frac{p_2}{N_2}, \frac{p_3}{N_3}\right) = \frac{p_1}{N_1}\mathbf{b}_1 + \frac{p_2}{N_2}\mathbf{b}_2 + \frac{p_3}{N_3}\mathbf{b}_3$$

Representations of the translation group (2)

The matrix of the representation **k** corresponding to the translation **t** is then:

$$\Gamma^{\mathbf{k}}(\mathbf{t}) = \exp\left\{2\pi i\left(\frac{p_1 l_1}{N_1} + \frac{p_2 l_2}{N_2} + \frac{p_3 l_3}{N_3}\right)\right\} = \exp\{2\pi i\,\mathbf{k}\,\mathbf{t}\}$$

Where the **k** vectors in reciprocal space are restricted to the first Brillouin Zone. It is clear that adding a reciprocal lattice vector **H** to **k**, does not change the matrix, so the vectors **k**'=**H**+**k** and **k** are equivalent.

The basis functions of the group of translations must satisfy the equation:

$$O(\mathbf{t})\psi^{\mathbf{k}}(\mathbf{r}) = \Gamma^{\mathbf{k}}(\mathbf{t})\psi^{\mathbf{k}}(\mathbf{r}) = \exp\{2\pi i\,\mathbf{k}\,\mathbf{t}\}\psi^{\mathbf{k}}(\mathbf{r})$$

The most general form for the functions $\psi^{\mathbf{k}}(\mathbf{r})$ are the Bloch functions:

$$\psi^{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp\{-2\pi i\,\mathbf{k}\mathbf{r}\},\ with\ u_{\mathbf{k}}(\mathbf{r}\pm\mathbf{t}) = u_{\mathbf{k}}(\mathbf{r})$$

This is easily verified by applying the rules or the action of operators on functions

$$O(\mathbf{t})\psi^{\mathbf{k}}(\mathbf{r}) = \psi^{\mathbf{k}}(\mathbf{r}-\mathbf{t}) = u_{\mathbf{k}}(\mathbf{r}-\mathbf{t})\exp\{-2\pi i\,\mathbf{k}(\mathbf{r}-\mathbf{t})\} =$$

$$= \exp\{2\pi i\,\mathbf{k}\mathbf{t}\}\,u_{\mathbf{k}}(\mathbf{r})\exp\{-2\pi i\,\mathbf{k}\,\mathbf{r}\} = \exp\{2\pi i\,\mathbf{k}\mathbf{t}\}\psi^{\mathbf{k}}(\mathbf{r})$$

k-vectors: Brillouin zones

The k-vector Types of Group 10 [*P*2/*m*]

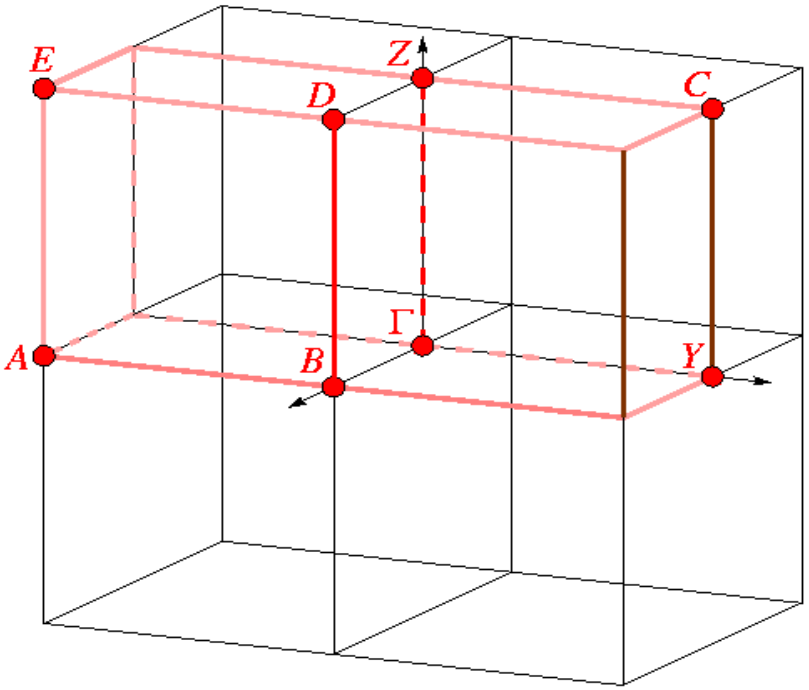
Brillouin zone

(Diagram for arithmetic crystal class 2/mP)

P112/m (P2/m)-C_{2h}^1 (10), P11$2_1$/m (P2_1/m)-C_{2h}^2 (11), P112/a (P2/c)-C_{2h}^4 (13), P11$2_1$/a (P2_1/c)-C_{2h}^5 (14)

Reciprocal-space group (P112/m)*, No. 10

The table with the k vectors.



k-vectors: Brillouin zones

The k-vector Types of Group 71 [*Immm*]

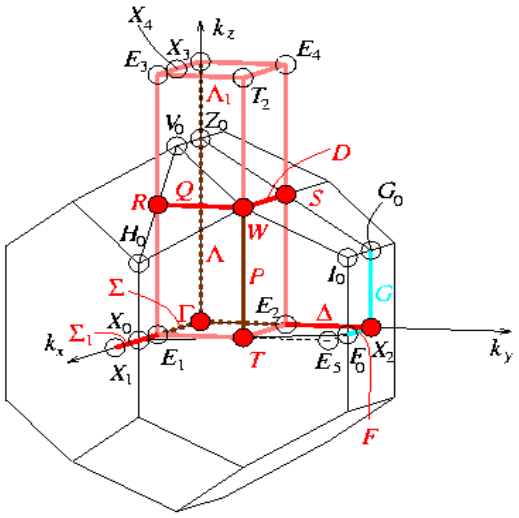
Brillouin zone

(Diagram for arithmetic crystal class mmmI)

(b>a>c or b>c>a) Immm-D_{2h}^{25} (71) to Imma-D_{2h}^{28} (74)

Reciprocal-space group (Fmmm)*, No.69 : $b^*<a^*<c^*$ or $b^*<c^*<a^*$

The table with the k vectors.



The k-vector Types of Group 71 [*Immm*]

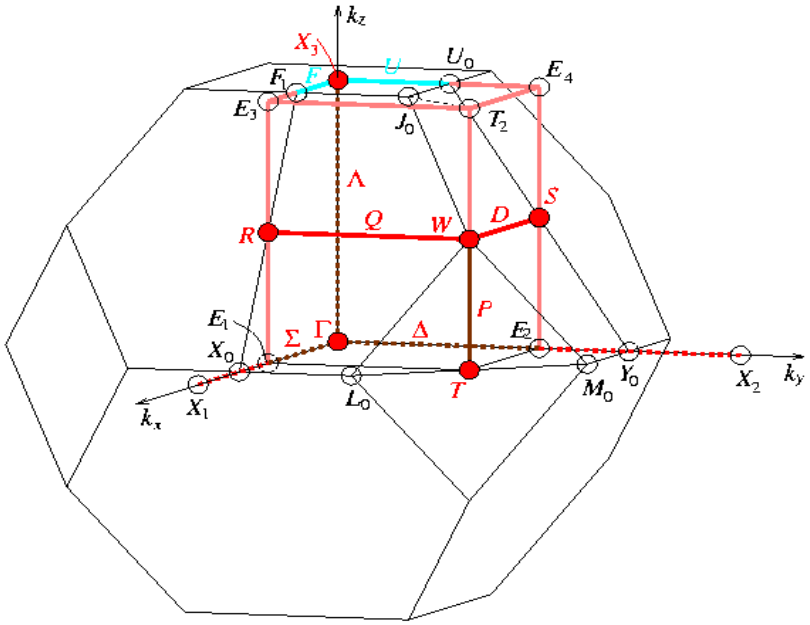
Brillouin zone

(Diagram for arithmetic crystal class mmmI)

(c>b>a or c>a>b) Immm-D_{2h}^{25} (71) to Imma-D_{2h}^{28} (74)

Reciprocal-space group (Fmmm)*, No.69 : $c^*<b^*<a^*$ or $c^*<a^*<b^*$

The table with the k vectors.



Representations of space groups: basis functions

For constructing the representations of the space groups it is important to start with the basis functions. Let us see how the Bloch functions behave under the action of a general element of the space group $g=\{h|\mathbf{t}_h\}$

$$O(g)\psi^{\mathbf{k}}(\mathbf{r}) = \{h \mid \mathbf{t}_h\}\psi^{\mathbf{k}}(\mathbf{r}) = \psi'(\mathbf{r})$$

To determine the form of the functions $\psi'(\mathbf{r})$ one can see that they should also be Bloch functions with a different **k**-label

$$\begin{aligned} O(\mathbf{t})\psi'(\mathbf{r}) &= \{1 \mid \mathbf{t}\}\psi'(\mathbf{r}) = \{1 \mid \mathbf{t}\}\{h \mid \mathbf{t}_h\}\psi^{\mathbf{k}}(\mathbf{r}) = \{h \mid \mathbf{t}_h\}\{1 \mid h^{-1}\mathbf{t}\}\psi^{\mathbf{k}}(\mathbf{r}) = \\ &= \{h \mid \mathbf{t}_h\}\exp\{2\pi i\,\mathbf{k}\,h^{-1}\mathbf{t}\}\psi^{\mathbf{k}}(\mathbf{r}) = \exp\{2\pi i\,\mathbf{k}\,h^{-1}\mathbf{t}\}\{h \mid \mathbf{t}_h\}\psi^{\mathbf{k}}(\mathbf{r}) = \\ &= \exp\{2\pi i\, h\mathbf{k}\,\mathbf{t}\}\psi'(\mathbf{r}) \end{aligned}$$

So that: $O(g)\psi^{\mathbf{k}}(\mathbf{r}) = \{h \mid \mathbf{t}_h\}\psi^{\mathbf{k}}(\mathbf{r}) = \psi^{h\mathbf{k}}(\mathbf{r})$

The Bloch functions also serve as basis functions but the representations are no longer one-dimensional because the Bloch functions whose wave vectors are related by the rotational part of $g \in \mathbf{G}$ belong to a same subspace.

The star of the vector k: little group

The set of non-equivalent **k** vectors obtained by applying the rotational part of the symmetry operators of the space group constitute the so called "star of **k**"

$$\{\mathbf{k}\} = \{\mathbf{k}_1, h_1\mathbf{k}_1, h_2\mathbf{k}_1, h_3\mathbf{k}_1, \ldots\} = \{\mathbf{k}_1, \mathbf{k}_2, \ldots \mathbf{k}_{l_k}\}$$

The $\mathbf{k}_i$ vectors are called the arms of the star. The number l_k is less or equal to the order of the point group $n(\mathbf{G}_0)$

The set of elements $g \in \mathbf{G}$ leaving the **k** vector invariant, or equal to an equivalent vector, form the group $\mathbf{G_k}$. Called the group of the wave vector (or propagation vector group) or the "little group". It is always a subgroup of **G**. The whole space/point group (little co-group) can be decomposed in cosets of the propagation vector group:

$$\mathbf{G} = \mathbf{G_k} + g_2\mathbf{G_k} + \ldots = \sum_{L=1}^{l_k} g_L\mathbf{G_k} \qquad \mathbf{k}_L = g_L\mathbf{k}$$

$$\mathbf{G}_0 = \mathbf{G}_{0\mathbf{k}} + h_2\mathbf{G}_{0\mathbf{k}} + \ldots = \sum_{L=1}^{l_k} h_L\mathbf{G}_{0\mathbf{k}} \qquad \mathbf{k}_L = h_L\mathbf{k}$$

The representations of G_k and G

We need to know the Irreps of $\mathbf{G_k}$ $\Gamma^{\mathbf{k}\nu}$ only for the coset representatives (with respect to the translation group) of $\mathbf{G_k}$

$$\mathbf{G_k} = 1\mathbf{T} + g_2\mathbf{T} + g_3\mathbf{T} + \ldots + g_n\mathbf{T}$$

For a general element of $G_\mathbf{k}$ we have:

$$\Gamma^{\mathbf{k}\nu}(g) = \Gamma^{\mathbf{k}\nu}(\{h\,|\,\mathbf{t}_h + \mathbf{t}\}) = \Gamma^{\mathbf{k}\nu}(\{1\,|\,\mathbf{t}\}\{h\,|\,\mathbf{t}_h\}) = \Gamma^{\mathbf{k}\nu}(\{1\,|\,\mathbf{t}\})\ \Gamma^{\mathbf{k}\nu}(\{h\,|\,\mathbf{t}_h\})$$

$$\Gamma^{\mathbf{k}\nu}(\{h\,|\,\mathbf{t}_h + \mathbf{t}\}) = e^{2\pi i \mathbf{k}\,\mathbf{t}}\ \Gamma^{\mathbf{k}\nu}(\{h\,|\,\mathbf{t}_h\})$$

The matrices $\Gamma^{\mathbf{k}\nu}$ can be easily calculated from the projective (or *loaded*) representations that are tabulated in the Kovalev book

$$\Gamma^{\mathbf{k}\nu}(g) = \Gamma^{\mathbf{k}\nu}(\{h\,|\,\mathbf{t}_h\}) = \Gamma^{\nu}_{proj}(h)\, e^{2\pi i \mathbf{k}\,\mathbf{t}_h}$$

Alternatively they can be calculated using special algorithms (Zak's method)

The representations of G_k and G

Let us note the irreducible representations of $\mathbf{G_k}$ as $\Gamma^{\mathbf{k}\nu}$ of dimensionality l_ν .
The basis functions should be of the form: $\psi_i^{\mathbf{k}\nu}(\mathbf{r}) = u_{\mathbf{k}i}{}^{\nu}(\mathbf{r}) \exp(-2\pi i \mathbf{kr})$ $(i=1,\ldots l_\nu)$

Under the action of the elements of $\mathbf{G_k}$ the functions transform into each other with the same **k**-vector.

Using the elements of **G** not belonging to $\mathbf{G_k}$ one generates other sets of basis functions: $\psi_i^{\mathbf{k}_1\nu}(\mathbf{r})$; $\psi_i^{\mathbf{k}_2\nu}(\mathbf{r})$; … $\psi_i^{\mathbf{k}l_k\nu}(\mathbf{r})$ that constitute the basis functions of the representations of the total space group.

These representations are labelled by the star of the **k** vector as: $\Gamma^{\{\mathbf{k}\}\nu}$ and are of dimensionality $l_\nu \times l_k$. Each irreducible "small representation" induces an irreducible representation of the total space group. The *induction formula* is:

$$\Gamma^{\{\mathbf{k}\}\nu}_{Li,Mj}(g) = \Gamma^{\mathbf{k}\nu}_{ij}(g_L^{-1} g\, g_M)\,\delta_{g_L^{-1} g\, g_M \in \mathbf{G_k}}$$

The last symbol is 1 if the subscript condition is true, otherwise is zero

Outline:

1. Magnetic Structures and neutron scattering
2. Representation Analysis and Magnetic Structures
3. **Magnetic Structure Determination. Magnetic Structure Factors**

Magnetic Bragg Scattering

Intensity (non-polarised neutrons)

$$I_{\mathbf{h}} = N_{\mathbf{h}} N_{\mathbf{h}}^{*} + \mathbf{M}_{\perp \mathbf{h}} \cdot \mathbf{M}_{\perp \mathbf{h}}^{*}$$

Magnetic interaction vector

$$\mathbf{M}_{\perp \mathbf{h}} = \mathbf{e} \times \mathbf{M}(\mathbf{h}) \times \mathbf{e} = \mathbf{M}(\mathbf{h}) - \mathbf{e}\,(\mathbf{e} \cdot \mathbf{M}(\mathbf{h}))$$

$$\mathbf{h} = \mathbf{H} + \mathbf{k} \quad \Leftarrow \text{Scattering vector} \qquad \mathbf{e} = \frac{\mathbf{h}}{h}$$

Magnetic structure factor: Shubnikov groups

The use of Shubnikov groups implies the use of the **magnetic unit cell** for indexing the Bragg reflections

$$\mathbf{M}_{\perp} = \mathbf{e}\times\mathbf{M}\times\mathbf{e} = \mathbf{M} - \mathbf{e}\,(\mathbf{e}\cdot\mathbf{M}) \qquad I \propto \mathbf{M}_{\perp}^{*}\mathbf{M}_{\perp}$$

Magnetic structure factor: $\mathbf{M}(\mathbf{H}) = p\sum_{m=1}^{N_{mag}} \mathbf{m}_m f_m(H) \exp(2\pi i \mathbf{H}\cdot\mathbf{r}_m)$

n independent magnetic sites labelled with the index j

The index s labels the representative symmetry operators of the Shubnikov group: $\mathbf{m}_{js} = \det(h_s)\,\delta_s\, h_s\, \mathbf{m}_j$ is the magnetic moment of the atom sited at the sublattice s of site j.

$$\mathbf{M}(\mathbf{H}) = p\sum_{j=1}^{n} O_j f_j(H) T_j \sum_{s} \det(h_s)\,\delta_s\, h_s\, \mathbf{m}_j exp\{2\pi i[(\mathbf{H}\{h|\mathbf{t}\}_s \mathbf{r}_j]\}$$

The maximum number of parameters n_p is, in general, equal to $3n$ magnetic moment components. Special positions make $n_p < 3n$.

Magnetic Structure Factor: k-vectors

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{s} \mathbf{S}_{\mathbf{k}js}\, exp\{2\pi i[(\mathbf{H}+\mathbf{k})\{S|\mathbf{t}\}_s \mathbf{r}_j]\}$$

j : index running for all magnetic atom sites in the magnetic asymmetric unit ($j = 1,\ldots n$)

s : index running for all atoms of the orbit corresponding to the magnetic site j (s=1,… p_j). Total number of atoms: N = Σ p_j

$\{S|\mathbf{t}\}_s$ Symmetry operators of the propagation vector group or a subgroup

If no symmetry constraints are applied to S_k, the maximum number of parameters for a general incommensurate structure is 6N (In practice 6N-1, because a global phase factor is irrelevant)

Group Theory and representation analysis

According to the Landau theory of phase transitions, **it is expected that the configuration of the magnetic moments can be described in terms of the basis functions of the Irreps of the propagation vector group** $\mathbf{G_k}$. The Irreps of $\mathbf{G_k}$ are tabulated or can be calculated independently of the problem

But, knowing the classical Hamiltonian of the spin system, the ground state (magnetic structure at T= 0 K) should minimize the energy

$$H = \sum_{jl\alpha,im\beta} J^{\alpha\beta}_{jl,im} S_{jl\alpha} S_{im\beta} + \ldots O(S^n)$$

The symmetry of the Hamiltonian may be higher than the space group symmetry (e.g. isotropic exchange interactions)

Group Theory and representation analysis

A reducible representation of the propagation vector group can be constructed by selecting the atoms of a Wyckoff position and applying the symmetry operators to both positions and axial vectors. This gives rise to the so called Magnetic Representation of dimension: $3n_a$ (being n_a the number of atoms in the primitive cell)

This representation can be decomposed in Irreps and the number of times a particular Irreps, Γ^{ν}, is included can be easily calculated

$$\Gamma_{Mag} = \Gamma_{Perm} \otimes \Gamma_{Axial} = \sum_{\oplus \nu} n_{\nu} \, \Gamma^{\nu}$$

The basis functions, for each Irrep and each sublattice of a Wyckoff site, can be calculated by using the projection operator formula. The basis functions are constant vectors of the form (1,0,0), (0.5, 1,0) … with components referred to the crystallographic unitary frame: {**a**/a, **b**/b, **c**/c} attached to each sublattice.

The working space for symmetry analysis of magnetic structures: magnetic representation

One can generate a reducible representation of $\mathbf{G_k}$ by considering the complex working space spanned by all the components of $\mathbf{S}_{\mathbf{k}js}$.
Each vector has three complex components.

As the atoms belonging to different sites do not mix under symmetry operators, we can treat separately the different sites. The index j is then fixed and the index s varies from 1 to p_j. Being p_j the number of sublattices generated by the site j.

Case α=y and s

The working complex space for site j has dimension $n_j=3\times p_j$ is then spanned by unit vectors $\{\boldsymbol{\varepsilon}^{\mathbf{k}j}{}_{\alpha s}\}$($\alpha$ = 1, 2, 3 –*or* x, y, z and $s = 1\ldots p_j$,) represented as column vectors (with a single index n) with zeroes everywhere except for $n=\alpha+3(s-1)$. The n_j vectors refers to the zero-cell.

$$\boldsymbol{\varepsilon}^{\mathbf{k}j}_{ys} = \begin{pmatrix} 0 & x,1 \\ 0 & y,1 \\ \vdots & \vdots \\ 0 & z,s-1 \\ 0 & x,s \\ 1 & y,s \\ 0 & z,s \\ \vdots & \vdots \\ \vdots & \vdots \\ \vdots & \vdots \\ 0 & y,p_j \\ 0 & z,p_j \end{pmatrix}$$

The working space for symmetry analysis of magnetic structures: magnetic representation

One can extend the basis vectors to the whole crystal by using the Bloch propagation then forming column vectors of $n_j \times N$ dimensions:

$$\boldsymbol{\varphi}^{\mathbf{k}j}_{\alpha s} = \sum_{\oplus l} \boldsymbol{\varepsilon}^{\mathbf{k}j}_{\alpha s} \exp(-2\pi i \mathbf{k}\mathbf{R}_l)$$

If one applies the symmetry operators of $\mathbf{G_k}$ to the vectors $\{\boldsymbol{\varepsilon}^{\mathbf{k}j}{}_{\alpha s}\}$, taking into account that they are axial vectors, we obtain another vector (after correcting for the Bloch phase factor if the operator moves the atom outside the reference zero-cell) of the same basis. The matrices $\Gamma^{\mathbf{k}j}{}_{\alpha s,\beta q}(g)$ of dimension $n_j \times n_j = 3p_j \times 3p_j$ corresponding to the different operators constitute what is called the "Magnetic Representation" for the site j and propagation vector $\mathbf{k}$.

The magnetic representation

The vectors $\{\boldsymbol{\varepsilon}^{j}{}_{\alpha s}\}$ are formed by direct sums (juxtaposition) of normal 3D vectors $\mathbf{u}^{j}{}_{\alpha s}$. Applying a symmetry operator to the vector position and the unit spin associated to the atom *js* along the α-axis, changes the index *js* to *jq* and reorient the spin according to the nature of the operator $g=\{h|\mathbf{t}_h\}$ for axial vectors.

$$g\mathbf{r}_s^j = h\mathbf{r}_s^j + \mathbf{t}_h = \mathbf{r}_q^j + \mathbf{a}_{gs}^j; \quad gs \rightarrow (q, \mathbf{a}_{gs}^j)$$

$$(g\mathbf{u}_{\alpha s}^j)_\beta = \det(h)\sum_n h_{\beta n}(\mathbf{u}_{\alpha s}^j)_n = \det(h)\sum_n h_{\beta n}\delta_{n,\alpha} = \det(h)h_{\beta\alpha}$$

$$O(g)\boldsymbol{\varepsilon}_{\alpha s}^{\mathbf{kj}} = \sum_{\beta q}\Gamma_{\beta q,\alpha s}^{\mathbf{kj}}(g)\,\boldsymbol{\varepsilon}_{\beta q}^{\mathbf{kj}} = \sum_{\beta q} e^{2\pi i\mathbf{k}\mathbf{a}_{gs}^j}\det(h)h_{\beta\alpha}\delta_{s,gq}^j\boldsymbol{\varepsilon}_{\beta q}^{\mathbf{kj}}$$

Matrices of the magnetic representation

$$\Gamma_{Mag} \rightarrow \Gamma_{\beta q,\alpha s}^{\mathbf{kj}}(g) = e^{2\pi i\mathbf{k}\mathbf{a}_{gs}^j}\det(h)h_{\beta\alpha}\delta_{q,gs}^j$$

The magnetic representation as direct product of permutation and axial representations

An inspection to the explicit expression for the magnetic representation for the propagation vector **k**, the Wyckoff position *j*, with sublattices indexed by (*s*, *q*), shows that it may be considered as the direct product of the permutation representation, of dimension $p_j \times p_j$ and explicit matrices:

$$\Gamma_{Perm} \rightarrow P_{qs}^{\mathbf{kj}}(g) = e^{2\pi i \mathbf{k}\mathbf{a}_{gs}^{j}} \delta_{q,gs}^{j}$$

Permutation representation

by the axial (or in general "vector") representation, of dimension 3, constituted by the rotational part of the $\mathbf{G}_{\mathbf{k}}$ operators multiplied by -1 when the operator $g=\{h|\mathbf{t}_h\}$ corresponds to an improper rotation.

$$\Gamma_{Axial} \rightarrow V_{\beta\alpha}(g) = \det(h) h_{\beta\alpha}$$

Axial representation

$$\Gamma_{Mag} \rightarrow \Gamma_{\beta q,\alpha s}^{\mathbf{kj}}(g) = e^{2\pi i \mathbf{k}\mathbf{a}_{gs}^{j}} \det(h) h_{\beta\alpha} \delta_{q,gs}^{j}$$

Magnetic representation

Basis functions of the Irreps of G_k

The magnetic representation, hereafter called Γ_M irrespective of the indices, can be decomposed in irreducible representations of $\mathbf{G_k}$.

We can calculate a priori the number of possible basis functions of the Irreps of $\mathbf{G_k}$ describing the possible magnetic structures. This number is equal to the number of times the representation Γ^ν is contained in Γ_M times the dimension of Γ^ν. The projection operators provide the explicit expression of the basis vectors of the Irreps of $\mathbf{G_k}$

$$\boldsymbol{\psi}_\lambda^{\mathbf{k}\nu}(j) = \frac{1}{n(\mathbf{G_{0k}})} \sum_{g \in \mathbf{G_{0k}}} \Gamma^{*\nu}_{\lambda[\mu]}(g)\, O(g)\, \boldsymbol{\varepsilon}_{\alpha s}^{\mathbf{k}j} \qquad (\lambda = 1, \ldots l_\nu)$$

$$\boldsymbol{\psi}_\lambda^{\mathbf{k}\nu}(j) = \frac{1}{n(\mathbf{G_{0k}})} \sum_{g \in \mathbf{G_{0k}}} \Gamma^{*\nu}_{\lambda[\mu]}(g) \sum_{\beta q} \exp(2\pi i\, \mathbf{k}\, \mathbf{a}_{gs}^{j}) \det(h) h_{\beta\alpha} \delta^{j}_{s,gq} \boldsymbol{\varepsilon}^{\mathbf{k}j}_{\beta q}$$

Basis functions of the Irreps of G_k

It is convenient to use, instead of the basis vectors for the whole set of magnetic atoms in the primitive cell, the so called *atomic components* of the basis vectors, which are normal 3D constant vectors attached to individual atoms:

$$\boldsymbol{\psi}_{\lambda}^{\mathbf{k}\nu}(j) = \sum_{\oplus, s=1,\ldots p_j} \mathbf{S}_{\lambda}^{\mathbf{k}\nu}(js)$$

The explicit expression for the atomic components of the basis functions is:

$$\mathbf{S}_{\lambda}^{\mathbf{k}\nu}(js) \propto \sum_{g \in \mathbf{G_{0k}}} \Gamma_{\lambda[\mu]}^{*\nu}(g)\, \mathrm{e}^{2\pi i \mathbf{k}\mathbf{a}_{gs}^{j}}\, \det(h)\delta_{s,g[q]}^{j} \begin{pmatrix} h_{1\alpha} \\ h_{2\alpha} \\ h_{3\alpha} \end{pmatrix}$$

Fundamental hypothesis of Symmetry Analysis

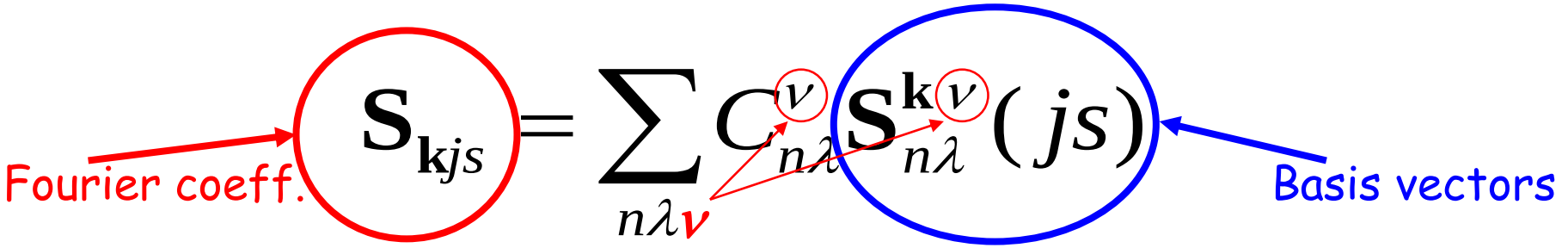
The fundamental hypothesis of the Symmetry Analysis of magnetic structures is that the Fourier coefficients of a magnetic structure are linear combinations of the basis functions of the irreducible representation of the propagation vector group $\mathbf{G_k}$

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_{n\lambda} C^{\nu}_{n\lambda} \sum_{s} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js) exp\{2\pi i\, \mathbf{h}_s \mathbf{r}_j\}$$

Magnetic structure factor in terms of basis vectors of irreducible representations and refinable coefficients C_i

Fourier coefficients and basis functions of the irreps



The coefficients $C^{\nu}_{n\lambda}$ are the free parameters of the magnetic structure. Called "mixing coefficients" by Izyumov

Indices:

k : reference to the propagation vector

ν : reference to the irreducible representation Γ^{ν}

n : index running from 1 up to $n_{\nu} \Rightarrow \quad \Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu}\, \Gamma^{\nu}$

λ : index running from 1 up to $\dim(\Gamma^{\nu})$

Going beyond G_k: more symmetric magnetic structures using the representations of the whole space Group

Up to now we have considered only the Irreps of the little group. In some cases we can add more constraints considering the representations of the whole space group. This is a way of connecting split orbits (*j* and *j*') due, for instance to the fact that the operator transforming **k** into –**k** is lost in $\mathbf{G_k}$.

$$\mathbf{G} = \mathbf{G_k} + g_2\mathbf{G_k} + \ldots g_{l_k}\mathbf{G_k} = \sum_{L=1}^{l_k} g_L\mathbf{G_k} = \sum_{L=1}^{l_k}\{h_L \mid \mathbf{t}_{h_L}\}\mathbf{G_k} \qquad \mathbf{k}_L = h_L\mathbf{k}$$

Star of $\mathbf{k}$: $\{\mathbf{k}\}=\{\mathbf{k},\ h_2\mathbf{k},\ h_3\mathbf{k},\ \ldots\ h_{l_k}\mathbf{k}\}=\{\mathbf{k}_1,\ \mathbf{k}_2,\ \mathbf{k}_3,\ \ldots\ \mathbf{k}_{l_k}\}$

The little groups $\mathbf{G_{kL}}$ are conjugate groups to $\mathbf{G_k}$

$$\mathbf{G}_{\mathbf{k}_L} = g_L\mathbf{G_k}g_L^{-1} \qquad g_L\mathbf{r}_s^j = h_L\mathbf{r}_s^j + \mathbf{t}_{h_L} = \mathbf{r}_q^{j'} + \mathbf{a}_{g_L s}^j$$

$$\mathbf{\Gamma}^{\mathbf{k}_L\nu}(g) = \mathbf{\Gamma}^{\mathbf{k}\nu}(g_L g g_L^{-1}) \qquad \mathbf{\Psi}_\lambda^{\mathbf{k}_L\nu} = O(g_L)\mathbf{\Psi}_\lambda^{\mathbf{k}\nu} \qquad (\lambda = 1,\ldots l_\nu)$$

Going beyond G_k: more symmetric magnetic structures using the representations of the whole space Group

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

Applying the formulae we have for applying the operators to the basis vectors we obtain for the atomic components the following relations:

$$g_L \mathbf{r}^j_s = h_L \mathbf{r}^j_s + \mathbf{t}_{h_L} = \mathbf{r}^{j'}_q + \mathbf{a}^j_{g_L s}$$

$$\mathbf{S}^{\mathbf{k}_L \nu}_{\lambda}(j'q) = \mathrm{e}^{2\pi i \mathbf{k}_L \mathbf{a}^j_{g_L s}} \det(R) R(h_L)\, \mathbf{S}^{\mathbf{k}\,\nu}_{\lambda}(js)$$

If we consider that our magnetic structure can be described by a representation of the whole space group the Fourier coefficients of atoms that are not connected by a symmetry operator of $\mathbf{G_k}$ are related by:

$$\mathbf{S}_{\mathbf{k}_L j'q} = \mathrm{e}^{2\pi i \mathbf{k}_L \mathbf{a}^j_{g_L s}} \det(R_L) R_L \mathbf{S}_{\mathbf{k}js}$$

Usefulness of the Symmetry Analysis

The maximum number of free coefficients to describe the magnetic structure is proportional to the number *m* of independent basis vectors

if we consider real coefficients when $\mathbf{k} = ½\ \mathbf{H}$

$$n_f = m \times \dim(\Gamma^\nu)$$

if we consider complex coefficients when $\mathbf{k} \in$ IBZ

$$n_f = 2m \times \dim(\Gamma^\nu) - 1$$

The analysis is successful when one of the following conditions apply:

$$n_f = 2m \times \dim(\Gamma^\nu) - 1 < 6p_j \text{ (for } \mathbf{k} \text{ non equivalent to } -\mathbf{k})$$
$$n_f = m \times \dim(\Gamma^\nu) < 3p_j \text{ (for } \mathbf{k} \text{ equivalent to } -\mathbf{k})$$

Where p_j is the number of sublattices (atoms) of site *j*. The effective number of free parameters is lower in general as soon as one uses the relation between basis vectors of different arms of the star {**k**} or select special direction in representation space for $\dim(\Gamma^\nu) > 1$.

Different ways of treating magnetic structures in FullProf

Different ways of treating magnetic structures in FullProf

(1) Standard Fourier (all kind of structures) coefficients refinement with $\mathbf{S}_\mathbf{k}$ described with components along {**a**/a, **b**/b, **c**/c} (**`Jbt = 1,10`**), or in spherical coordinates with respect to a Cartesian frame attached to the unit cell (**`Jbt = -1, -10`**).

(2) Time reversal operators, presently only for **k**=(0,0,0) (**`Jbt = 10 + Magnetic symmetry`** keyword after the symbol of the SPG)

(3) Shubnikov Groups in BNS formulation (**`Jbt = 10 + Isy=2`**). Whatever magnetic space group in any setting. The PCR file may be generated from a mCIF file.

(4) Real space description of uni-axial conical structures (**`Jbt = 5`**)

(5) Real space description of multi-axial helical structures with elliptic envelope (**`Jbt = -1, -10 + (More=1 & Hel = 2)`**)

(6) Refinement of $C^{\nu}_{n\lambda}$ coefficients in the expression: $\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}\left(js\right)$

`Jbt = 1 and Isy=-2`

Magnetic structures in FullProf

(1) Standard Fourier coefficients (`Jbt = +/-1, +/-10`)

The Fourier component **k** of the magnetic moment of atom $j1$, that transforms to the atom js when the symmetry operator $g_s=\{S|t\}_s$ of $G_{\mathbf{k}}$ is applied ($\mathbf{r}^j{}_s=g_s\mathbf{r}^j{}_1=S_s\mathbf{r}^j{}_1+\mathbf{t}_s$), is transformed as:

$$\mathbf{S}_{\mathbf{k}js} = M_{js}\mathbf{S}_{\mathbf{k}j1}exp\{-2\pi i\phi_{\mathbf{k}js}\}$$

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j f_j(\mathbf{h}) T_j \sum_s \mathbf{S}_{\mathbf{k}js} exp\ \{2\pi i[(\mathbf{H}+\mathbf{k})\{S|\mathbf{t}\}_s \mathbf{r}_j - \Phi_{\mathbf{k}j}]\}$$

The matrices M_{js} and phases $\phi_{\mathbf{k}js}$ can be deduced from the relations between the Fourier coefficients and atomic basis functions. The matrices M_{js} correspond, in the case of commensurate magnetic structures, to the rotational parts of the magnetic Shubnikov group acting on magnetic moments.

Magnetic structures in FullProf

(1) Standard Fourier coefficients

```
Ho2BaNiO5
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   2   0   0 0.0 0.0 1.0   1  -1  -1   0    0          0.000    1   5    0
I -1                          <-- Space group symbol for hkl generation
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM  x,y,z
MSYM  u,v,w, 0.0
SYMM  -x,y,-z
MSYM  u,v,w, 0.0
SYMM  -x,-y,-z
MSYM  u,v,w, 0.0
SYMM   x,-y, z
MSYM  u,v,w, 0.0
!
!Atom Typ  Mag Vek     X       Y       Z       Biso    Occ      Rx       Ry       Rz
!     Ix      Iy      Iz     beta11  beta22  beta33   MagPh
Ho   JHO3  1  0  0.50000 0.00000 0.20245 0.00000 0.50000   0.131    0.000    8.995
                    0.00    0.00   81.00    0.00    0.00  191.00     0.00  181.00
. . . . . . . . . . . . . .
!     a          b          c         alpha      beta       gamma
   3.756032   5.734157  11.277159  90.000000  89.925171  90.000000
. . . . . . . . . . . . . . . . . .
! Propagation vectors:
   0.5000000   0.0000000   0.5000000          Propagation Vector  1
    0.000000    0.000000    0.000000
```

The symbol of the space group is used for the generation of the parent reflections. In this case half reciprocal lattice is generated

Magnetic structure factor: Shubnikov groups

The use of Shubnikov groups implies the use of the **magnetic unit cell** for indexing the Bragg reflections, the concept of propagation vector is absent in this approach

$$\mathbf{M}_{\perp} = \mathbf{e}\times\mathbf{M}\times\mathbf{e} = \mathbf{M} - \mathbf{e}\,(\mathbf{e}\cdot\mathbf{M}) \qquad I \propto \mathbf{M}_{\perp}^{*}\mathbf{M}_{\perp}$$

Magnetic structure factor:

n independent magnetic sites labelled with the index *j*

The index *s* labels the representative symmetry operators of the Shubnikov group: $\mathbf{m}_{js} = \det(h_s)\,\delta_s\, h_s\, \mathbf{m}_j$ is the magnetic moment of the atom sited at the sublattice *s* of site *j*.

$$\mathbf{M}(\mathbf{H}) = p\sum_{j=1}^{n} O_j\, f_j\,(H)\, T_j \sum_{s} \det(h_s)\,\delta_s\, h_s\, \mathbf{m}_j exp\{2\pi i[(\mathbf{H}\{h|\mathbf{t}\}_s \mathbf{r}_j]\}$$

Magnetic structures in FullProf

(2) **Time reversal operators**, presently only for **k**=(0,0,0) (**`Jbt = 10`**
+
`Magnetic symmetry` keyword after the symbol of the space group)

```
Name:CuCr2O4
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   3   0   0 0.0 0.0 1.0  10   0   0   1   0        611.770   0   7   0
!
F d d d                 Magnetic symmetry below
! Time Reversal Operations on Crystal Space Group
  1 -1  1 -1  1
!Atom   Typ     Mag Vek       X          Y          Z        Biso       Occ     N_type
     Spc/
!        Rx         Ry         Rz         Ix         Iy         Iz       MagPh   / Line
     below:Codes
!       beta11    beta22    beta33    beta12    beta13    beta23   / Line below:Codes
Cu      MCU2       1  0    0.12500    0.12500    0.12500    0.04112    0.12500     1     0
                              0.00       0.00       0.00     141.00       0.00
      0.00000   -0.74340    0.00000    0.00000    0.00000    0.00000    0.00000 <-MagPar
         0.00     191.00       0.00       0.00       0.00       0.00       0.00
  . . . . .
```

Magnetic structures in FullProf

(3) Shubnikov Groups in BNS formulation (`Jbt = 10 + Isy=2`).

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
  18   0   0 0.0 0.0 1.0  10   0   2   0    0       1992.773   0   7   0
!
C_ac  number:"9.41"      <--Magnetic Space group symbol (BNS symbol & number)
! Nsym   Cen  N_Clat N_Ant
     2     0     1     2
! Centring vectors
   0.00000   0.50000   0.50000
! Anti-Centring vectors
   0.00000   0.00000   0.50000
   0.00000   0.50000   0.00000
! Symmetry operators
  1 x,y,z,+1
  2 x+1/2,-y+1/4,z,+1
!
!Atom   Typ     Mag Vek      X          Y          Z        Biso       Occ     N_type!
Rx        Ry         Rz         Ix         Iy         Iz       MagPh
!      beta11    beta22    beta33    beta12    beta13    beta23
Dy_1   JDY3       1  0     0.62500  -0.04238    0.12500  0.44667    1.00000     1     0   #
                              0.00      0.00       0.00     0.00       0.00
     5.10000   2.00000   1.00000   0.00000   0.00000  0.00000    0.00000 <-MagPar
               0.00      0.00      0.00      0.00
Fe_1   MFE2       1  0     0.62500   0.86347  -0.00391  0.74386    1.00000     1     0   #
                              0.00      0.00       0.00     0.00       0.00
     1.00000   3.00000   1.00000   0.00000   0.00000  0.00000    0.00000 <-MagPar
               0.00      0.00      0.00      0.00
```

Magnetic structures in FullProf

(5) Real space description of multi-axial helical structures with elliptic envelope (`Jbt = -1,-10 + More=1 & Hel = 2`)

Same as **(1)**, but the Fourier component **k** of the magnetic moment of atom *j*1, is explicitly represented as:

$$\mathbf{S}_{\mathbf{k}j1} = \frac{1}{2}[m_{uj}\mathbf{u}_j + im_{vj}\mathbf{v}_j]exp(-2\pi i\phi_{\mathbf{k}j})$$

With $\mathbf{u}_j$, $\mathbf{v}_j$ orthogonal unit vectors forming with $\mathbf{w}_j = \mathbf{u}_j \times \mathbf{v}_j$ a direct Cartesian frame.

Refineable parameters: m_{uj}, m_{vj}, $\phi_{\mathbf{k}j}$
plus the Euler angles of the Cartesian frame $\{\mathbf{u}, \mathbf{v}, \mathbf{w}\}_j$

Magnetic structures in FullProf

(5) Real space description of multi-axial helical structures with elliptic envelope (`Jbt = -1,-10 + More=1 & Hel = 2`)

```
Jbt=-1
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   3   0   0 0.0 0.0 1.0  -1   4  -1   0   0          0.000  -1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift
   3   0   2   0   0   0  1.0000  1.0000  0.0000  0.0000    1       0       0
!
P -1                        <--Space group symbol
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM   x, y, z
MSYM   u, v, w, 0.00
.....

!Atom Typ  Mag Vek     X       Y       Z       Biso    Occ      Mr       Mi      Chi
!   Phi    Theta  unused  beta11  beta22  beta33   MagPh
Fe   MFE3  1  0  0.12340 0.02210 0.25000 0.00000 0.50000   3.450    3.450   0.000
                    0.00    0.00    0.00    0.00    0.00    0.00     0.00    0.00
  15.000  25.000   0.000   0.000   0.000   0.000 0.00000
   0.00     .00    0.00    0.00    0.00    0.00    0.00
.....
```

Magnetic structures in FullProf

(5) Real space description of multi-axial helical structures with elliptic envelope (`Jbt = -1,-10 + More=1 & Hel = 2`)

```
Jbt=-10
....
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   3   0   0 0.0 0.0 1.0 -10   4  -1   0   0        492.121  -1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift
   3  -1   2   0   0   0  1.0000  1.0000  0.0000  0.0000    1       0       0
!
P -1                      <--Space group symbol
!Nsym Cen Laue MagMat
   4   1   1   1
!
SYMM   x, y, z
MSYM   u, v, w, 0.00
...
!Atom Typ     Mag Vek       X          Y          Z        Biso       Occ     N_type
!      Mr        Mi         Chi        Phi      Theta    unused       MagPh
!    beta11   beta22    beta33    beta12    beta13    beta23   / Line below:Codes
Fe    MFE3       1  0    0.12340   0.02210   0.25000   0.00000   0.50000     1     0
                          0.00       0.00      0.00      0.00      0.00
   4.46000   4.46000    0.00000  10.00000  25.00169   0.00000   0.12110 <-MagPar
      0.00      0.00       0.00      0.00       .00      0.00      0.00
....
```

Magnetic structures in FullProf

(6) Coefficients of basis functions refinement:

A magnetic phase has **`Jbt = 1 and Isy=-2`**

$$\mathbf{M}(\mathbf{h}) = p\sum_{j=1}^{n} O_j\, f_j(\mathbf{h})\, T_j \sum_{n\lambda} C_{n\lambda}^{\nu} \sum_{s} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)\, exp\left\{2\pi i\left[\mathbf{h}_s\mathbf{r}_j - \Phi_{\mathbf{k}j}\right]\right\}$$

The basis functions of the Irreps (in numerical form) are introduced together with explicit symmetry operators of the crystal structure. The refined variables are directly the coefficients C1, C2, C3, ….

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)$$

$$C_{n\lambda}^{\nu}$$

Magnetic structures in FullProf

(6) Coefficients of basis functions refinement:

```
Ho2BaNiO5     (Irep 3 from BasIreps)
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   2   0   0 0.0 0.0 1.0   1  -1  -2   0   0          0.000     1   5    0
I -1                        <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
     2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM x,y,z
BASR   1  0  0    0  0  1
BASI   0  0  0    0  0  0
SYMM  -x,y,-z
BASR   1  0  0    0  0  1
BASI   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
Ho    JHO3  1  0  0.50000 0.00000 0.20250 0.00000 1.00000    0.127    8.993    0.000
                     0.00     0.00    81.00     0.00     0.00    71.00   181.00     0.00
. . . . . . . . . . . . . . . . . . .
!     a          b          c         alpha       beta        gamma
   3.754163   5.729964  11.269387  90.000000  90.000000  90.000000
. . . . . . . . . . . . . . . . . . .
! Propagation vectors:
   0.5000000   0.0000000   0.5000000          Propagation Vector  1
```

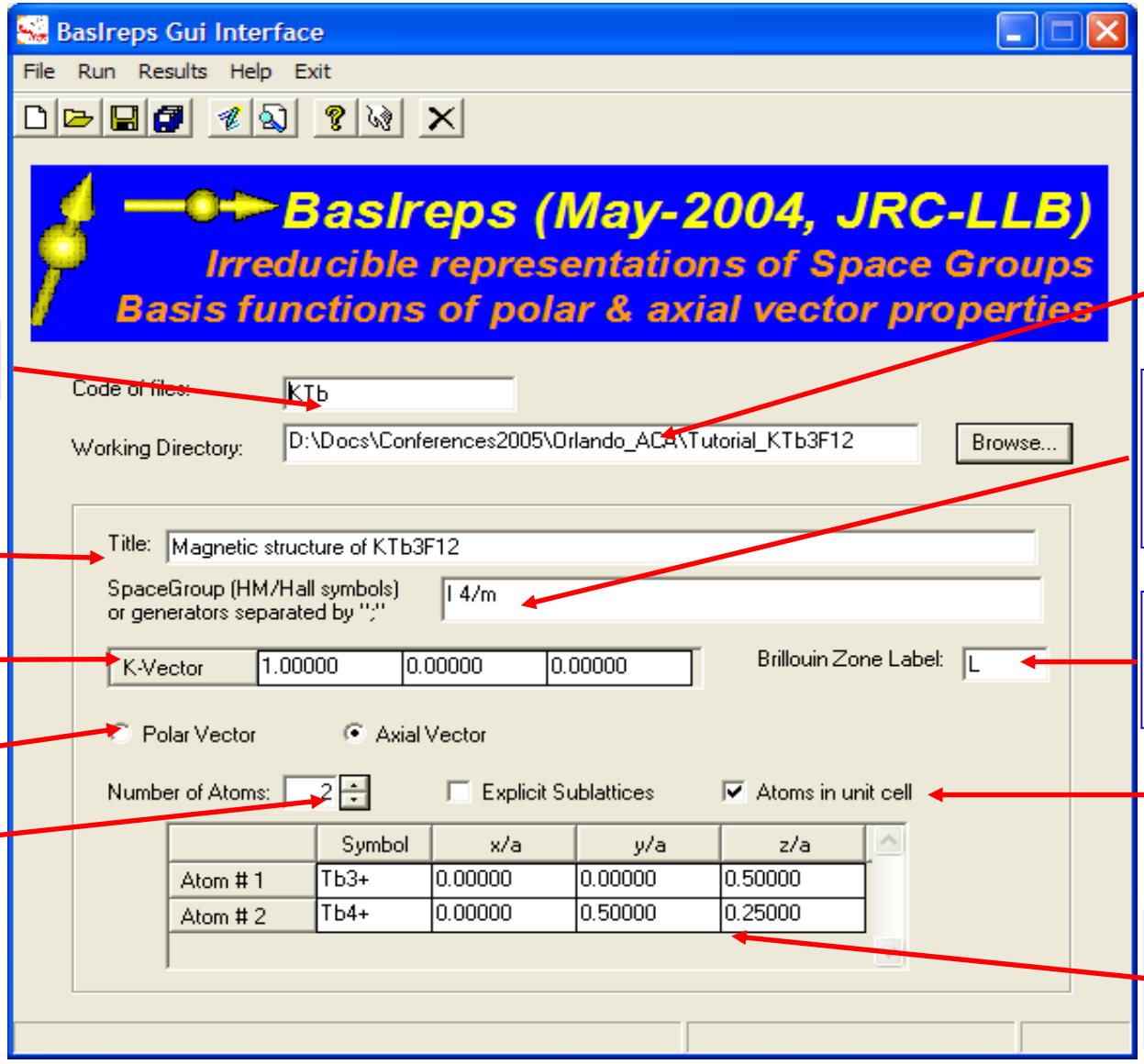
Programs for symmetry analysis

The irreducible representations of space groups can be obtained consulting tables or using computer programs for calculating them.

The basis functions of the irreducible representations depend on the particular problem to be treated and they have to be calculated by using projection operator formula. A series of programs allow these kind of calculations to be done. Doing that by hand may be quite tedious and prone to errors.

Concerning magnetic structures three programs are of current use: **BasIreps** (J. Rodríguez-Carvajal), **SARAh** (Andrew Wills) and **MODY** (Wiesława Sikora). One can use also **BCS** (Perez-Mato et al.) or **ISODISTORT** (B.Campbell and H. Stokes)

GUI for BasIreps



Code of files

Working directory

Title

SG symbol or generators

k-vector

Brillouin Zone label

Axial/polar

Atoms in Unit Cell

Number of atoms

Atoms positions

Output of BasIreps

BasIreps **provides the basis functions (normal modes) of the irreducible representations of the wave-vector group $\mathbf{G_k}$**

$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}js} exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

Output of *BasIreps* $\Rightarrow$ Basis Functions (constant vectors)

$$\mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

Output of BasIreps

KEDIT - [D:\Docs\Conferences2003\RSEFQ-Madrid\Lamno3.bsr]

File Edit Actions Options Window Help

norm

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


  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
 => Basis functions of Representation IRrep( 1) of dimension  1 contained 3 times in GAMMA
  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

SYMM  x,y,z   -x+1,-y,z+1/2   x-1/2,-y+1/2,-z   -x+1/2,y+1/2,-z+1/2
Atoms:      Mn_1              Mn_2              Mn_3              Mn_4
 1:Re (    1    0    0) (   -1    0    0) (    1    0    0) (   -1    0    0)
 2:Re (    0    1    0) (    0   -1    0) (    0   -1    0) (    0    1    0)
 3:Re (    0    0    1) (    0    0    1) (    0    0   -1) (    0    0   -1)


----- LINEAR COMBINATIONS of Basis Functions: coefficients u,v,w,p,q ....
      General expressions of the Fourier coefficients Sk(i) i=1,2,...nat

      Fourier coefficient for SYMM x,y,z                 Atom: Mn_1 | 0.5000  0.0000  0.0000
                              Sk( 1): ( u, v, w )

      Fourier coefficient for SYMM -x+1,-y,z+1/2         Atom: Mn_2  0.5000  0.0000  0.5000
                              Sk( 2): (-u,-v, w )

      Fourier coefficient for SYMM x-1/2,-y+1/2,-z       Atom: Mn_3  0.0000  0.5000  0.0000
                              Sk( 3): ( u,-v,-w )

      Fourier coefficient for SYMM -x+1/2,y+1/2,-z+1/2   Atom: Mn_4  0.0000  0.5000  0.5000
                              Sk( 4): (-u, v,-w )

  ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

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Output of BasIreps

KEDIT - [D:\Docs\Conferences2003\RSEFQ-Madrid\Lamno3.fp]

File Edit Actions Options Window Help

norm

```
=====>

                    X        Y        Z            for site:  1
 -> Mn_1     :    0.5000   0.0000   0.0000   : (x,y,z)
 -> Mn_2     :    0.5000   0.0000   0.5000   : (-x,-y,z+1/2) + ( 1   , 0   , 0   )
 -> Mn_3     :    0.0000   0.5000   0.0000   : (x+1/2,-y+1/2,-z) + (-1   , 0   , 0   )
 -> Mn_4     :    0.0000   0.5000   0.5000   : (-x+1/2,y+1/2,-z+1/2) + ( 0   , 0   , 0   )

 => Basis functions of Representation IRrep( 1) of dimension  1 contained 3 times in GAMMA
    Representation number     :  1 for Site:  1
    Number of basis functions:  3

 ----- Block-of-lines for PCR start just below this line
P -1                        <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
     4     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
SYMM x,y,z
BASR   1  0  0   0  1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+1,-y,z+1/2
BASR  -1  0  0   0 -1  0   0  0  1
BASI   0  0  0   0  0  0   0  0  0
SYMM x-1/2,-y+1/2,-z
BASR   1  0  0   0 -1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
SYMM -x+1/2,y+1/2,-z+1/2
BASR  -1  0  0   0  1  0   0  0 -1
BASI   0  0  0   0  0  0   0  0  0
```

Format for ***FullProf***

k=(0,0,0), ν=1, n=1,2,3
λ=1, j=1, s=1,2,3,4

$$\mathbf{S}_{n\lambda}^{\mathbf{k}\,\nu}(js)$$

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Steps for magnetic structure determination using powder diffraction

Step	Input
Propagation vector(s) *k_Search*	*Peak positions of* ⇐ *magnetic reflections* *Cell parameters*
Symmetry Analysis *BasIreps, MODY,* *SARAh, BCS, Isotropy*	*Propagation vector* ⇐ *Space Group* *Atom positions*
Magnetic structure solution (Sim. Ann.) *FullProf*	*Integrated intensities* ⇐ *Atomic components of basis functions or Shubnikov group symmetry operators*

Magnetic Structure Refinement using powder diffraction

NEUTRONS FOR SCIENCE

Input

Magnetic structure Refinement
FullProf

⇐ *Complete structural model should be provided*

Different runs of SAnn jobs may give you an idea of the degeneracy of solutions for your particular problem.

In many cases the number of free parameters is too much high to be refined by LSQ: try to reduce the number of parameters or make soft constraints.

Use spherical components of Fourier coefficients in order to have better control of the amplitude of the magnetic moment

The End!