NEUTRONS FOR SCIENCE

Introduction to Magnetic Structures Symmetry, magnetic structure determination

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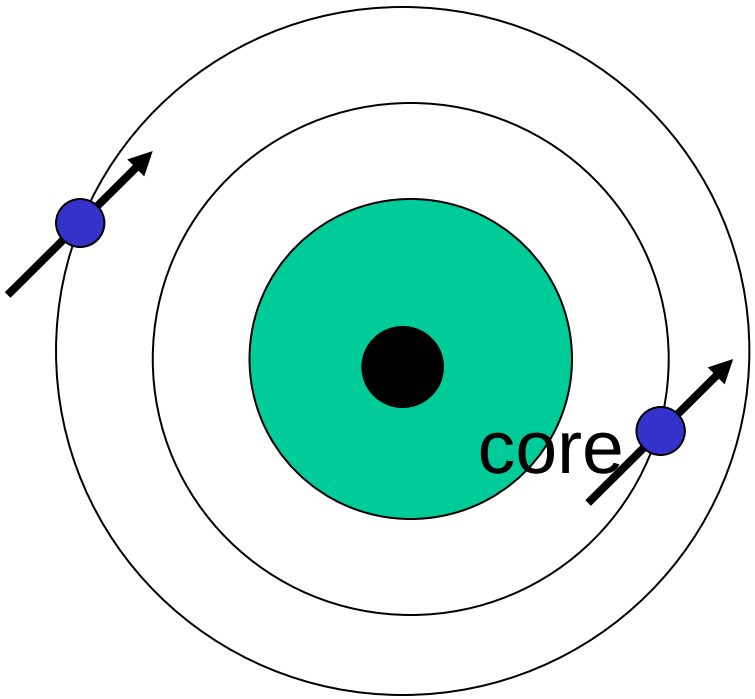
Outline

➔ Description of magnetic structures. Fourier formalism and group representation analysis.

➔ Magnetic structure factor. Determination of magnetic structures using powder diffraction

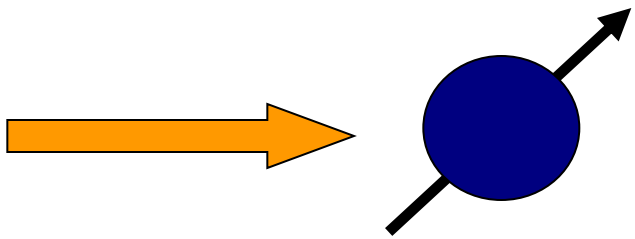
Ions with intrinsic magnetic moments

Atoms/ions with unpaired electrons



Ni^{2+}

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



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

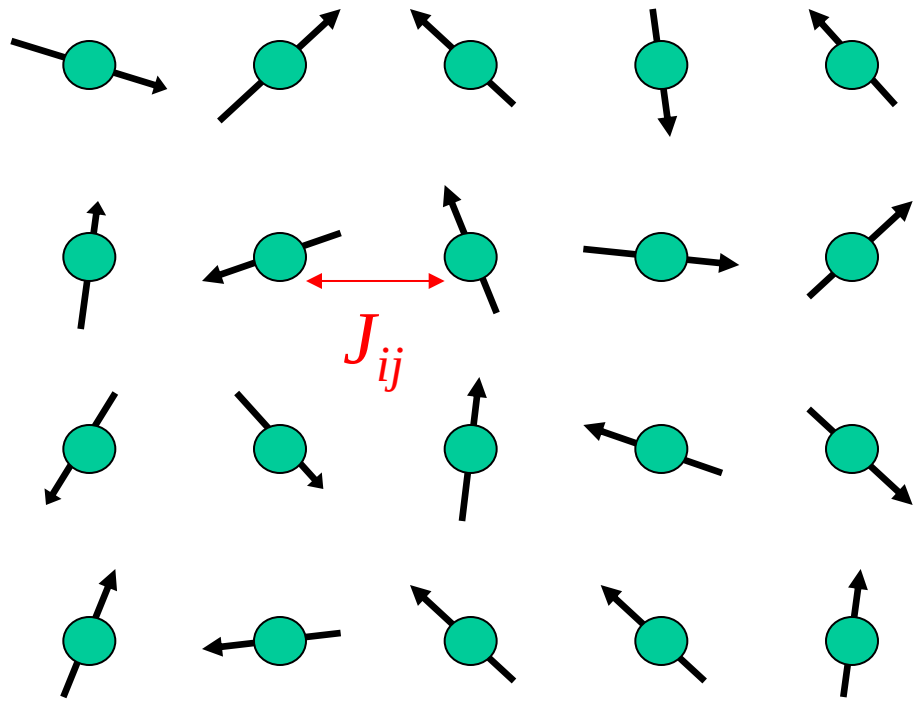
$\mathbf{m} = g_S\,\mathbf{S}$ (transition metals)

What is a magnetic structure?

Paramagnetic state:
Snapshot of magnetic moment configuration

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

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

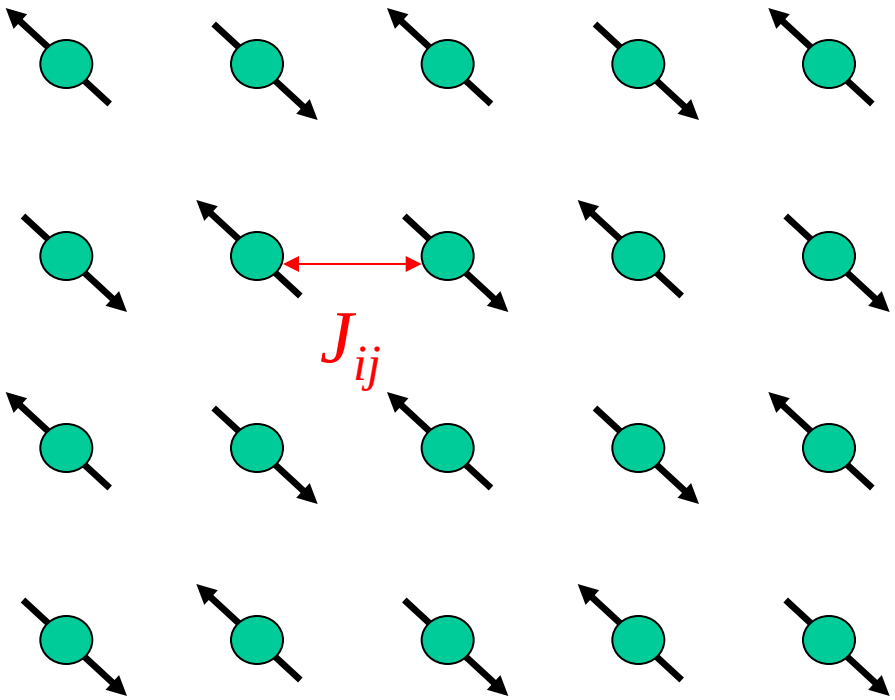


What is a magnetic structure?

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

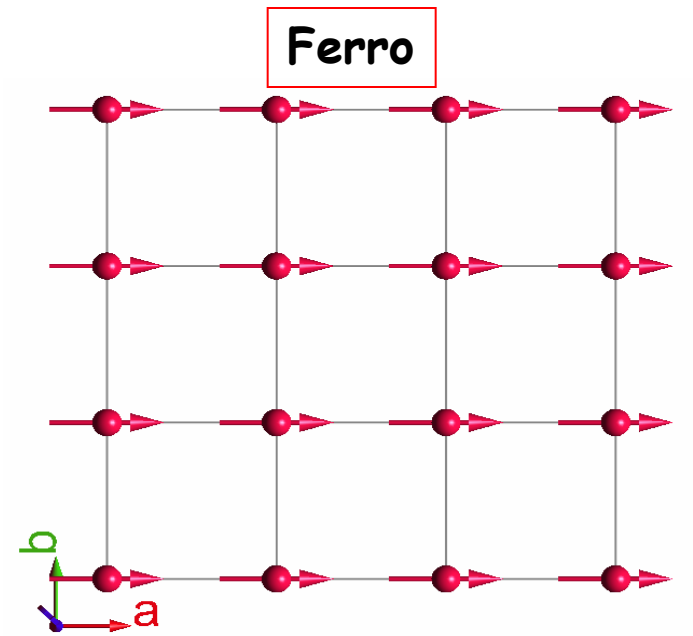
$$E_{ij} = -J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j$$

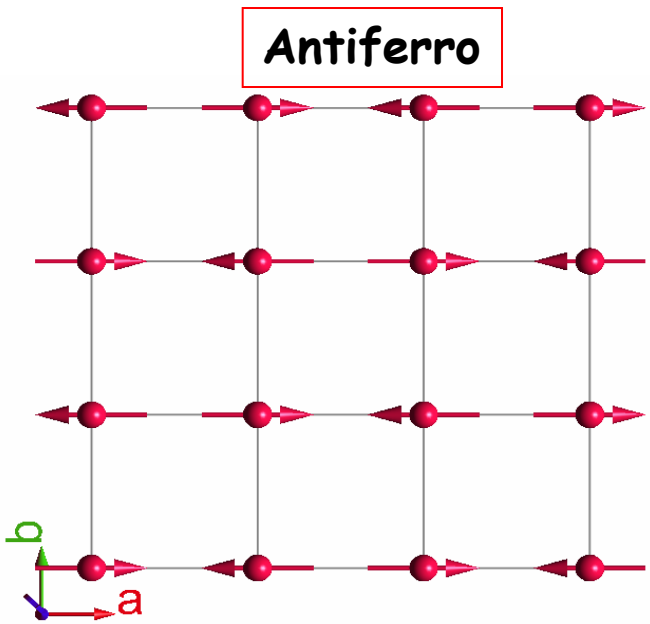
$$\langle \mathbf{S}_i \rangle \neq 0$$



Magnetic structure:
Quasi-static configuration of magnetic moments

Types of magnetic structures





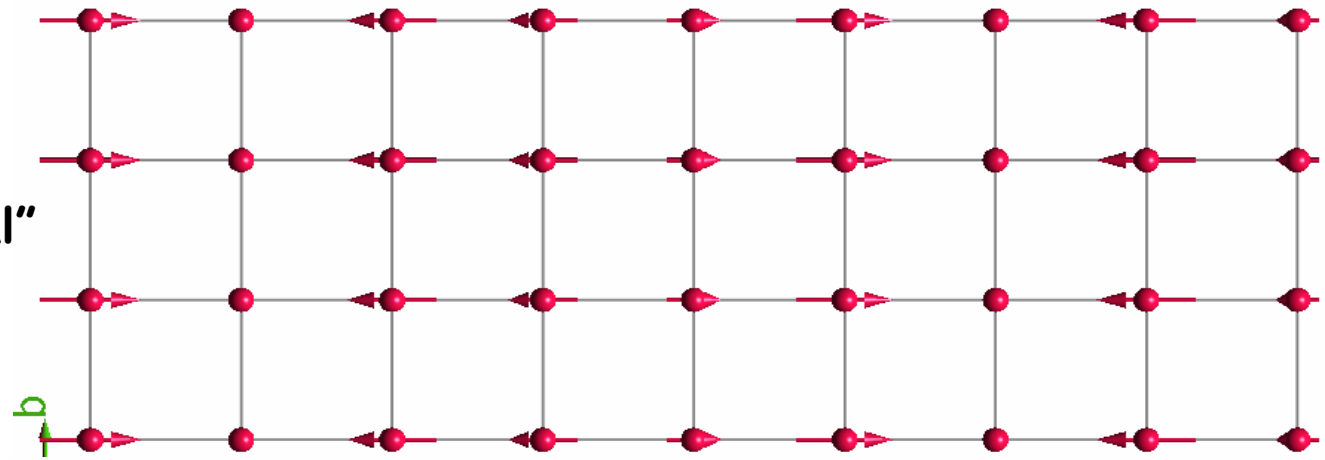
Very often magnetic structures are complex due to :

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

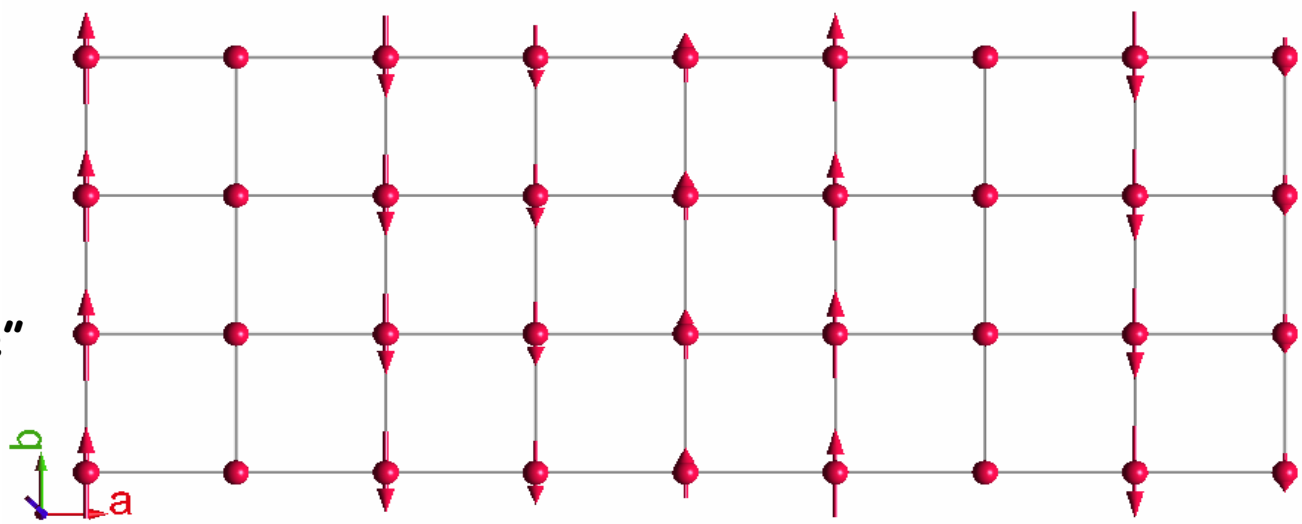
Types of magnetic structures

Amplitude-modulated or Spin-Density Waves

"Longitudinal"

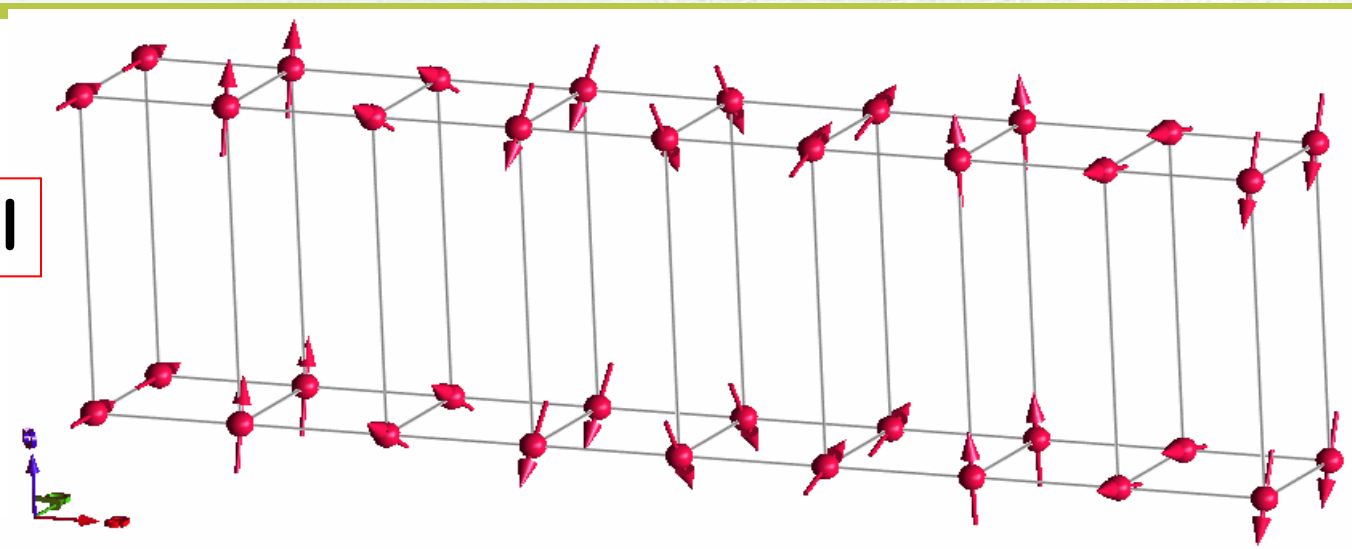


"Transverse"

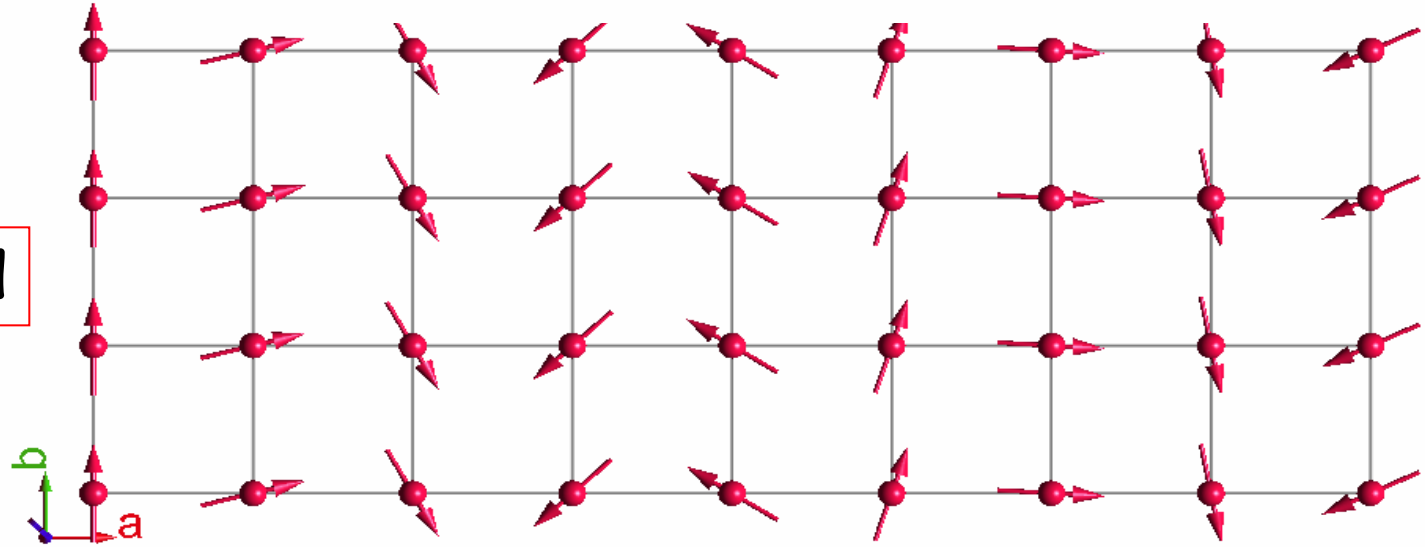


Types of magnetic structures

Spiral

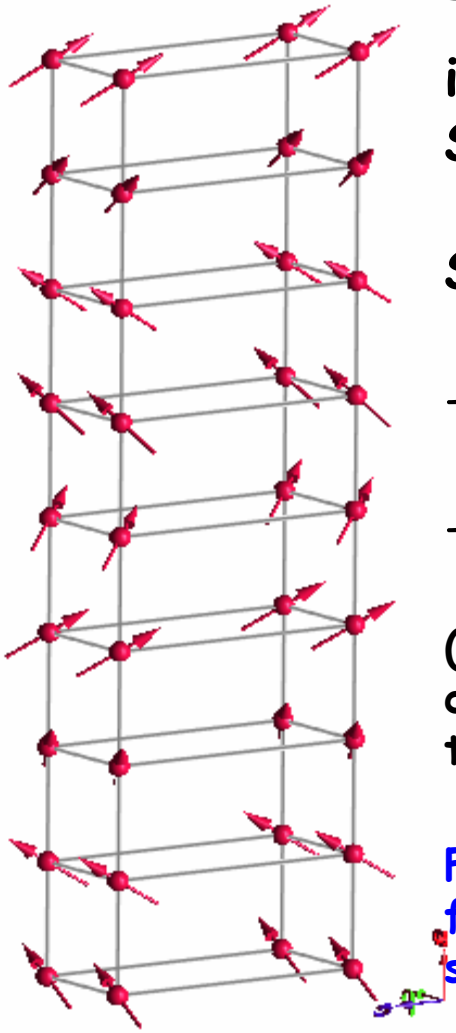


Cycloid



Types of magnetic structures

Conical



The equivalent to crystallographic space groups in magnetic crystallography are the so called Shubnikov groups or Magnetic Space Groups

Shubnikov groups are limited to:

- Commensurate magnetic structures

- Real representations of dimension 1

(for higher dimensional representations it may exist different Shubnikov groups of a different symmetry family than that of the crystallographic group)

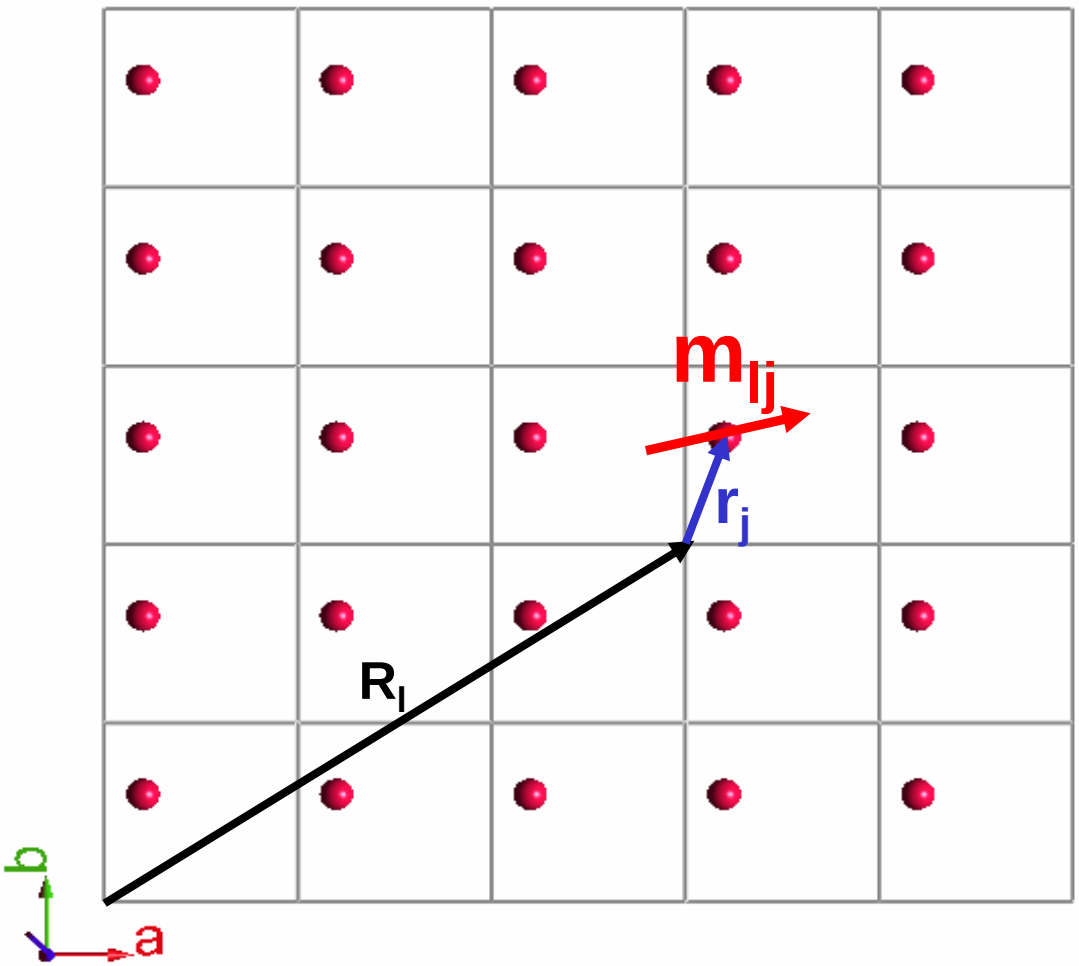
For incommensurate magnetic structures superspace formalism is also an option. Conventional descriptions of superspace in magnetism is still lacking.

Formalism of propagation vectors

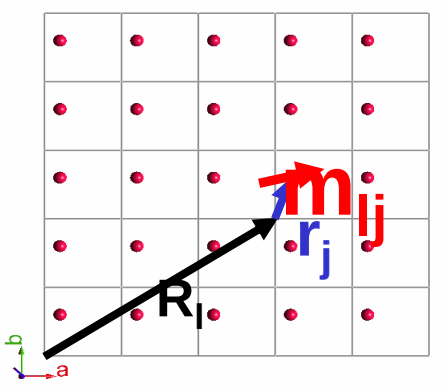
Position of atom *j* in unit-cell *l* is given by:

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

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



Formalism of propagation vectors



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

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

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

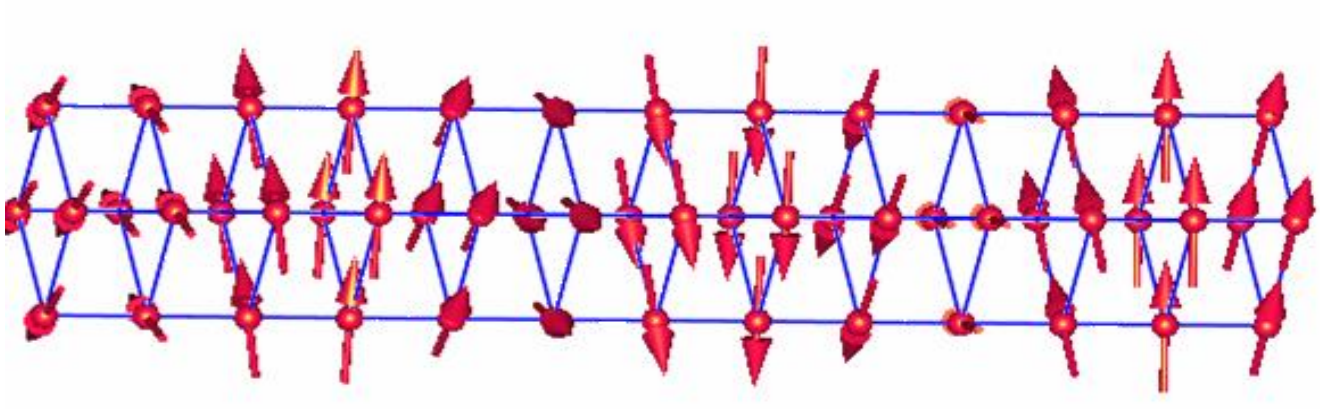
$$\boxed{\mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^{\ *}}$$

Formalism of propagation vectors

A magnetic structure is fully described by:

- Wave-vector(s) or propagation vector(s) {**k**}.

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



Formalism of propagation vectors: a more 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

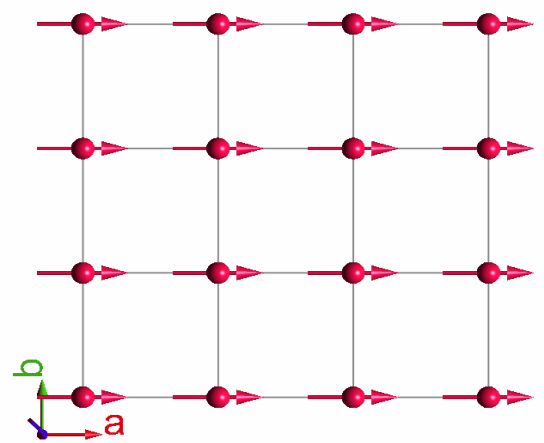
Necessary condition for real moments $\mathbf{m}_{ljs} \Rightarrow \mathbf{S}_{-\mathbf{k}js} = \mathbf{S}_{\mathbf{k}js}^{*}$

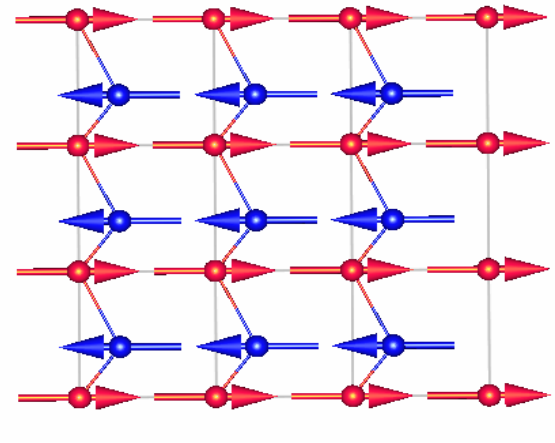
General expression of the Fourier coefficients (complex vectors) for an arbitrary site (drop of js indices) when $\mathbf{k}$ and $-\mathbf{k}$ are not equivalent:

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

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 $\mathbf{R}\,.\,\mathbf{I}=0$)

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

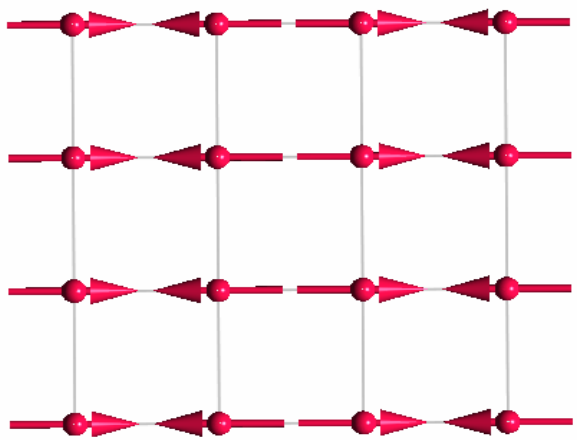




$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j}\, exp\left\{-2\pi i \mathbf{k}\mathbf{R}_l\right\} = \mathbf{S}_{\mathbf{k}j}$$

- 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=1/2 H



$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j}\, exp\left\{-2\pi i\, \mathbf{k}\, \mathbf{R}_l\right\} = \mathbf{S}_{\mathbf{k}j}\left(-1\right)^{n(l)}$$

REAL Fourier coefficients ≡ magnetic moments
The magnetic symmetry may also be described using crystallographic magnetic space groups

Fourier coefficients of sinusoidal structures

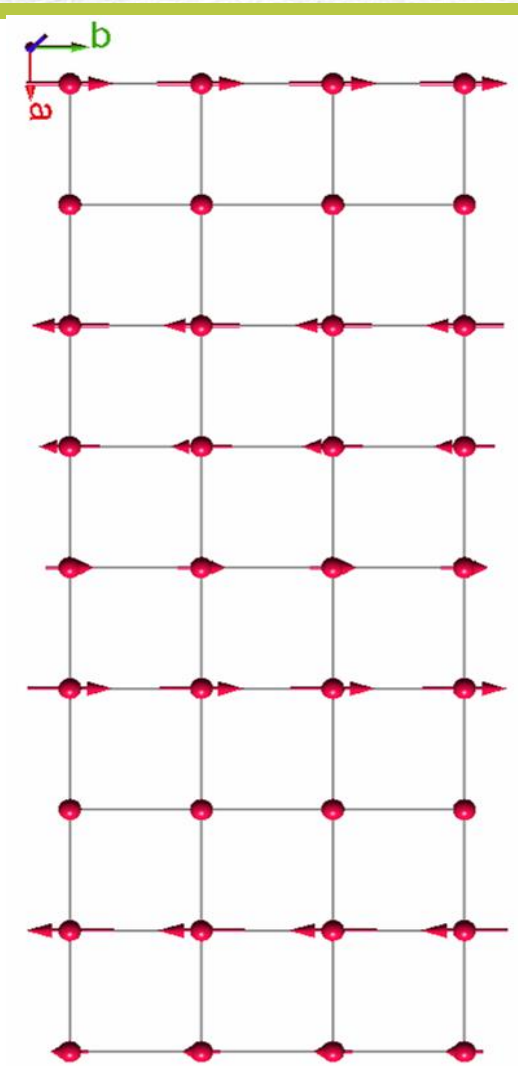
- **k** interior of the Brillouin zone (pair **k**, -**k**)

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

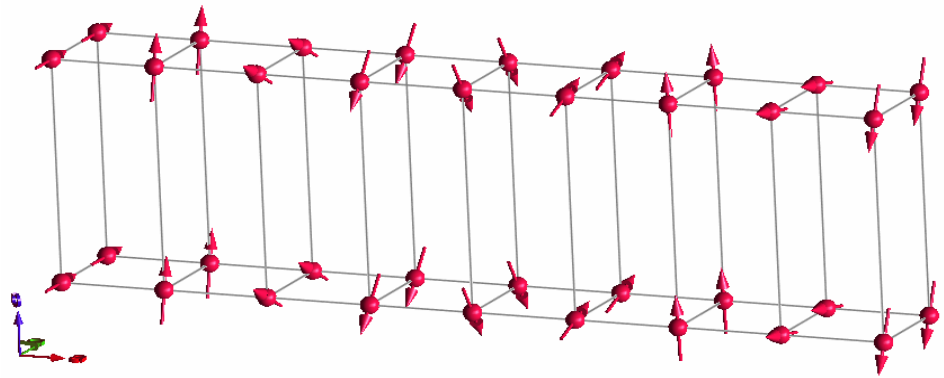
$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} \; exp(-2\pi i \mathbf{k}\mathbf{R}_l) + \mathbf{S}_{-\mathbf{k}j} \; exp(2\pi i \mathbf{k}\mathbf{R}_l)$$

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

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



Fourier coefficients of helical structures

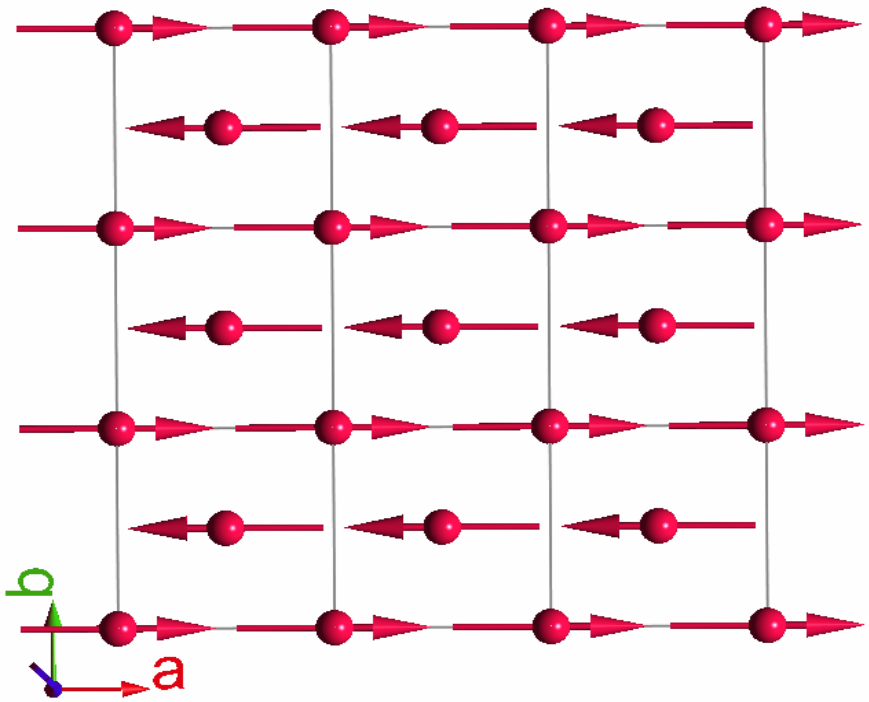


- **k** interior of the Brillouin zone
- Real component of $\mathbf{S}_\mathbf{k}$ perpendicular to the imaginary component

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

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

Centred cells!



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

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

Magnetic structures

Magnetic moment of each atom: Fourier series

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

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/

Introduction to Group representation theory

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

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

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.

Group theory: Irreducible representations

Given the representation $\Gamma=\{D(E),D(A),D(B)\ldots\}$ of the group $G=\{E,A,B,\ldots\}$, 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:

$$D'(g)=U\,D(g)\,U^{-1}\left\{with\ g\in G\right\}\Rightarrow\Gamma'=U\,\Gamma\,U^{-1}$$

$$D'(A)=U^{-1}D(A)U=\begin{pmatrix} D'_1(A) & & & 0 \\ & D'_2(A) & & \\ & & D'_3(A) & \\ 0 & & & D'_4(A) \end{pmatrix}$$

$$D'(B)=U^{-1}D(B)U=\begin{pmatrix} D'_1(B) & & & 0 \\ & D'_2(B) & & \\ & & D'_3(B) & \\ 0 & & & D'_4(B) \end{pmatrix}$$

Irreducible representations

$\Gamma_1=\{D'_1(A),D'_1(B),\ldots\}$

$\Gamma_2=\{D'_2(A),D'_2(B),\ldots\}$

$$\Gamma'=U\,\Gamma\,U^{-1}=\Gamma_1\oplus\Gamma_2\oplus\Gamma_3\ldots$$

$$\Gamma'=\sum_{\oplus\nu}n_\nu\Gamma_\nu$$

Formulas of the 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:

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

Basic 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 $(\mathbf{r})$, the action of the operator $O(g)$ gives rise to a linear combination, defining a representation of the group G:

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

Basic functions of irreducible representation

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.

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

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:

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

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:

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

$$(i = 1, \ldots l_{\nu})$$

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:

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

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

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

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 translations 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:

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

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

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

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

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

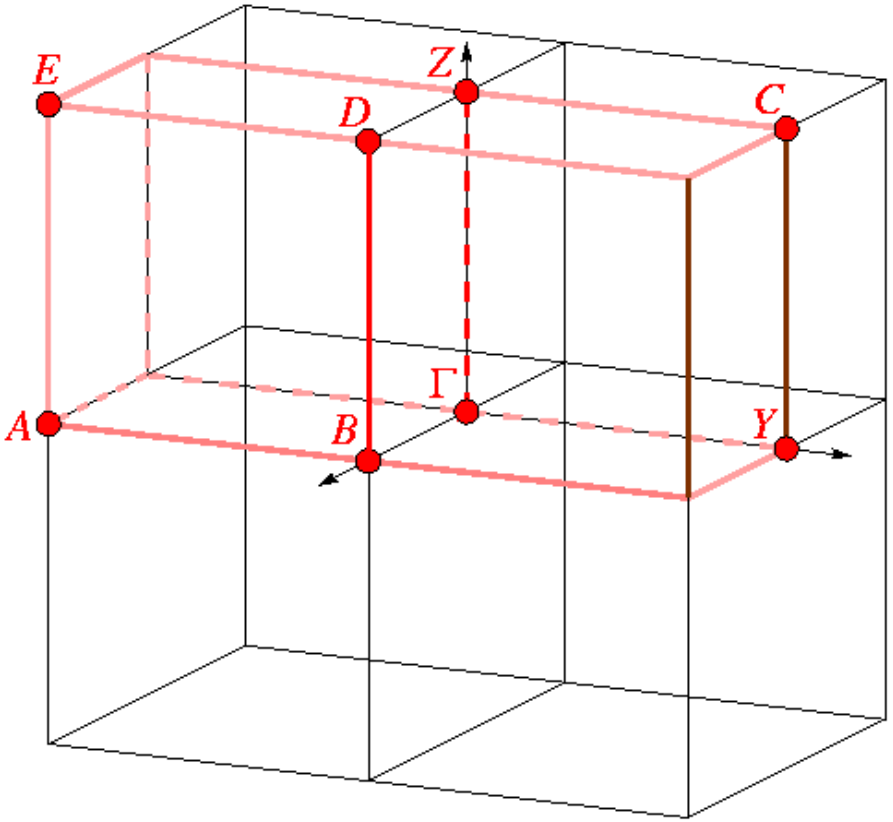
Brillouin zone

(Diagram for arithmetic crystal class 2/mP)

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

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

The table with the k vectors.



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

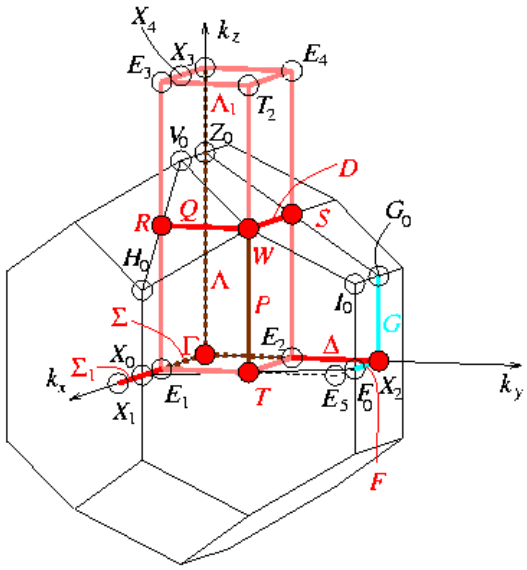
Brillouin zone

(Diagram for arithmetic crystal class mmml)

(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*]

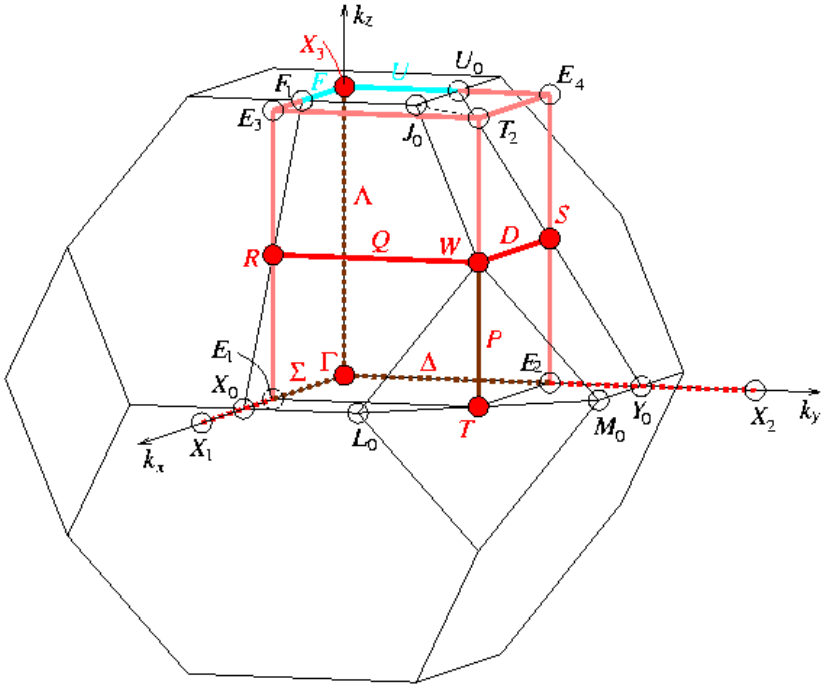
Brillouin zone

(Diagram for arithmetic crystal class mmml)

(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.



The k-vector Types of Group 69 [*Fmmm*]

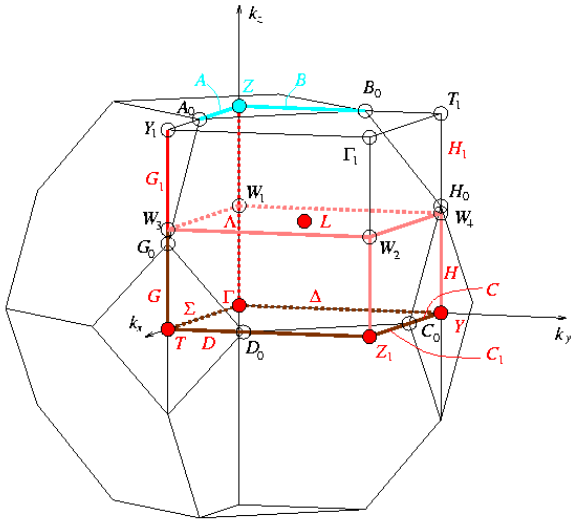
Brillouin zone

(Diagram for arithmetic crystal class mmmF)

($a^{-2}<b^{-2}+c^{-2}$, $b^{-2}<c^{-2}+a^{-2}$, and $c^{-2}<a^{-2}+b^{-2}$) Fmmm-D_{2h}^{23} (69), Fddd-D_{2h}^{24} (70)

Reciprocal-space group (Immm)*, No. 71:(a*2<b*2+c*2, b*2<c*2+a*2 , and c*2<a*2+b*2)

The table with the k vectors.



The k-vector Types of Group 69 [*Fmmm*]

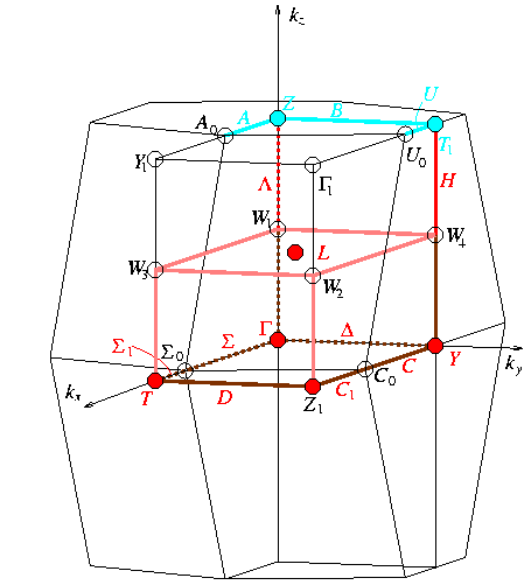
Brillouin zone

(Diagram for arithmetic crystal class mmmF)

($a^{-2}>b^{-2}+c^{-2}$) Fmmm-D_{2h}^{23} (69), Fddd-D_{2h}^{24} (70)

Reciprocal-space group (Immm)*, No.71: a*2>b*2+c*2

The table with the k vectors.



The k-vector Types of Group 69 [*Fmmm*]

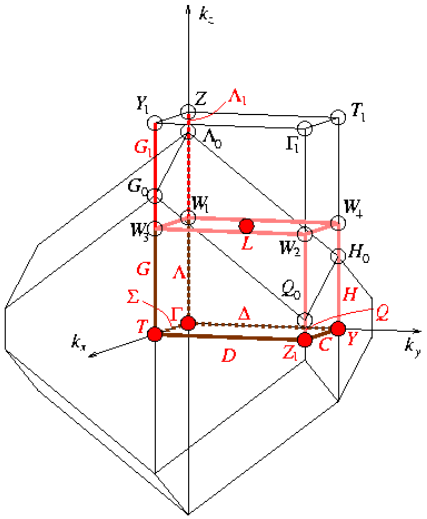
Brillouin zone

(Diagram for arithmetic crystal class mmmF)

($c^{-2}>a^{-2}+b^{-2}$) Fmmm-D_{2h}^{23} (69), Fddd-D_{2h}^{24} (70)

Reciprocal space group (Immm)*, No.71: c*2>a*2+b*2

The table with the k vectors.



The star of the vector k and the 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 "start 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 $n(G_0)$

The set of elements $g \in G$ leaving the **k** vector invariant, or equal to an equivalent vector, form the group $G_{\mathbf{k}}$. 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 can be decomposed in cosets of the propagation vector group:

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

$$G_0 = G_{0\mathbf{k}} + h_2 G_{0\mathbf{k}} + \ldots = \sum_{L=1}^{l_k} h_L G_{0\mathbf{k}} \qquad \mathbf{k}_L = h_L \mathbf{k}$$

The representations of $G_{\mathbf{k}}$ and G

Let us note the irreducible representations of $G_{\mathbf{k}}$ 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 $G_{\mathbf{k}}$ the functions transform into each other with the same **k**-vector.

Using the elements of G not belonging to $G_{\mathbf{k}}$ one generates other sets of basis functions: $\psi_i^{\mathbf{k}_1\nu}(\mathbf{r})$; $\psi_i^{\mathbf{k}_2\nu}(\mathbf{r})$; … $\psi_i^{\mathbf{k}_L\nu}(\mathbf{r})$ 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:

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

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

The representations of $G_{\mathbf{k}}$ and G

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

$$G_{\mathbf{k}} = 1\mathrm{T} + g_2\mathrm{T} + g_3\mathrm{T} + \ldots + g_n\mathrm{T}$$

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)

Group theory: 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** $G_{\mathbf{k}}$ (subgroup of the SG formed by those elements that leave $\mathbf{k}$ invariant). The Irreps of $G_{\mathbf{k}}$ 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: 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 (spins). 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.

Relation of Fourier coefficients and basis functions of Irreps

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

Fourier coeff.

Basis vectors

The coefficients $C_{n\lambda}^{\nu}$ are the free parameters of the magnetic structure (order parameters of the phase transition in the Landau theory)

Indices:

$\mathbf{k}$: 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 $\dim(\Gamma_{\nu})$

Outline

➔ Description of magnetic structures. Fourier formalism and group representation analysis.

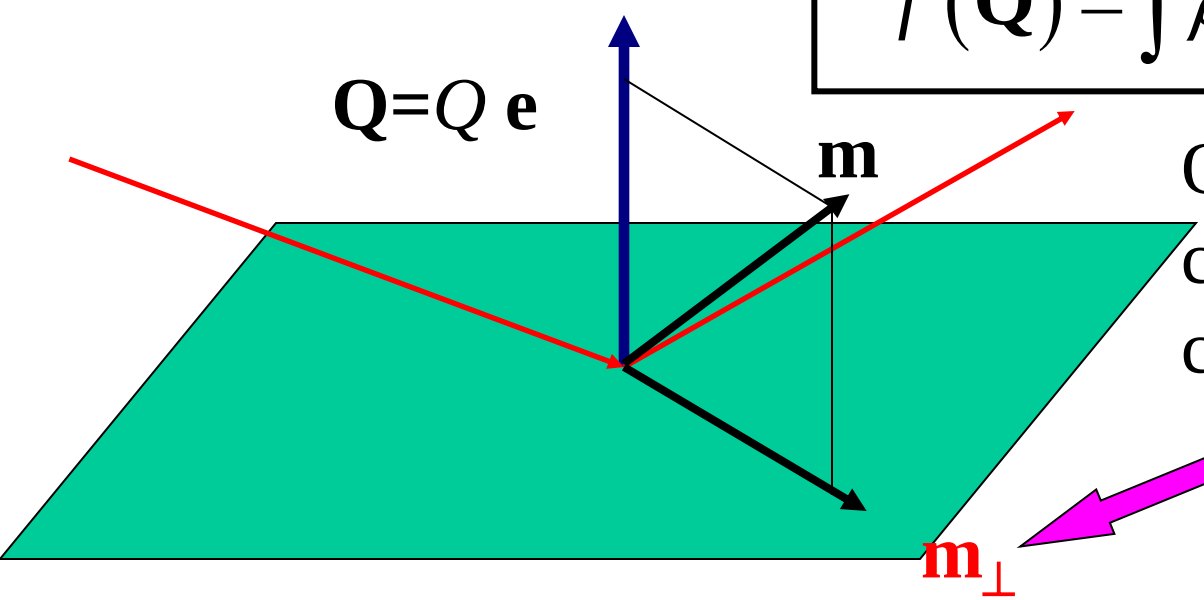
➔ **Magnetic scattering. Magnetic structure factor. Determination of magnetic structures using powder diffraction**

Magnetic neutron scattering

$$\mathbf{a}_M(\mathbf{Q}) = \frac{1}{2} r_e \gamma f(\mathbf{Q}) \left\{ \mathbf{m} - \frac{\mathbf{Q}\,(\mathbf{m}\,\mathbf{Q})}{Q^2} \right\} = p\, f(\mathbf{Q})\, \mathbf{m}_\perp$$

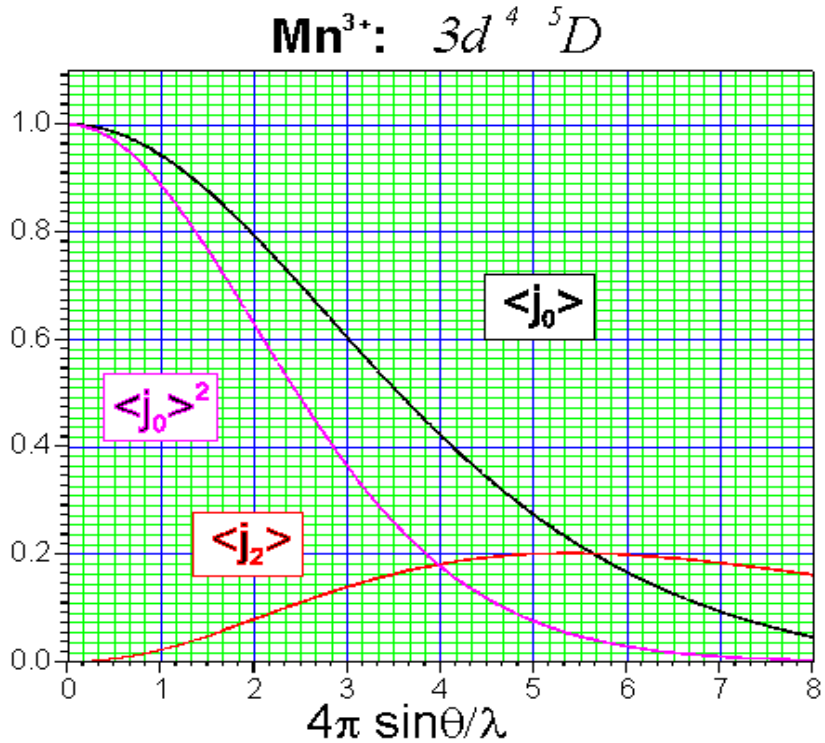
p=0.2696 10^{-12} cm

$$f(\mathbf{Q}) = \int \rho_m(\mathbf{r}) \exp(i\,\mathbf{Q}\,\mathbf{r})\, d^3\mathbf{r}$$



Only the perpendicular component of **m** to **Q**=2π**h** contributes to scattering

Magnetic form factor



In the dipolar approximation:

$$f(Q) = \langle j_0(Q) \rangle + (1 - \frac{2}{g}) \langle j_2(Q) \rangle$$

International Tables of Crystallography, Volume C,
ed. by AJC Wilson, Kluwer Ac. Pub., 1998, p. 513

Magnetic Bragg scattering

Intensity (non-polarised neutrons)

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

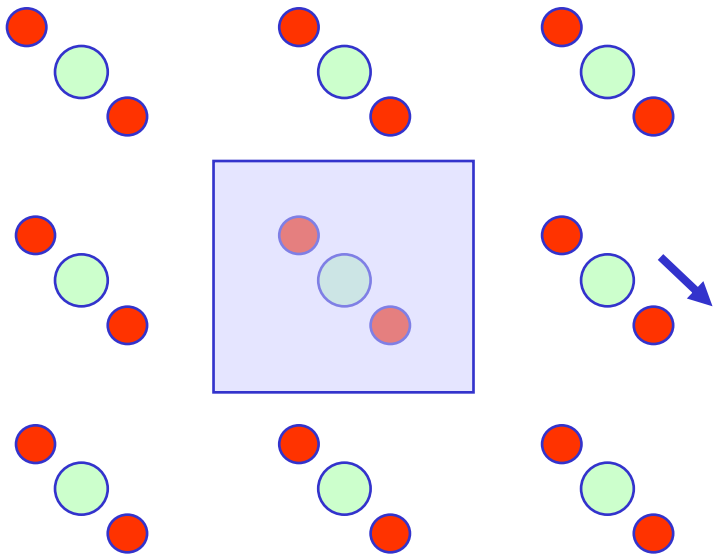
Magnetic interaction vector

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

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

Diffraction pattern of incommensurate magnetic structures

Portion of reciprocal space



Magnetic reflections

Nuclear reflections

h = H+k

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

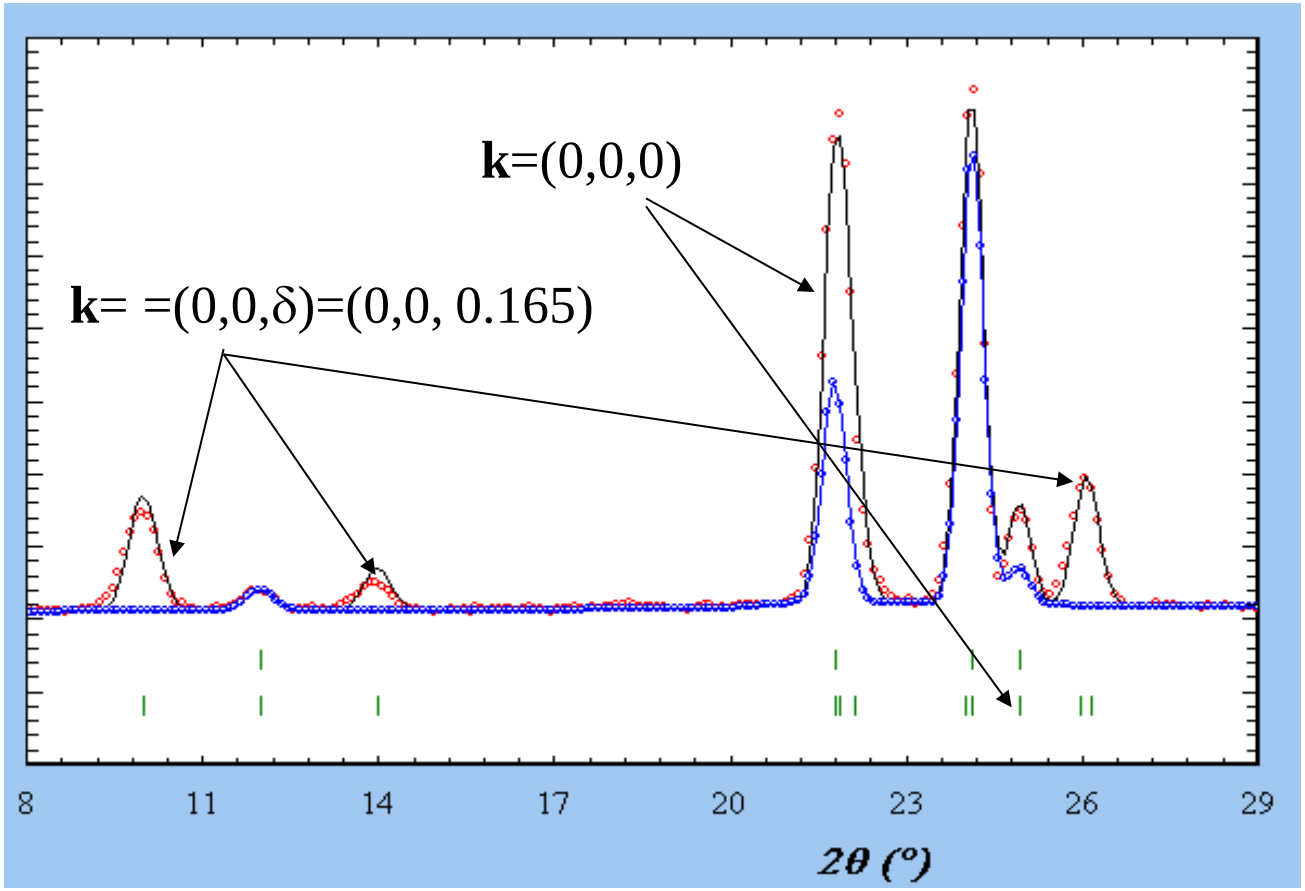
H is a reciprocal vector of the crystallographic structure

k is one of the propagation vectors of the magnetic structure

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

Magnetic structure of $DyMn_6Ge_6$

Conical structure with two propagation vectors



Nuclear contribution in blue

Magnetic Powder Diffraction

$$y_{ci} = \sum_{\{\mathbf{h}\}} I_{\mathbf{h}} \Omega(T_i - T_{\mathbf{h}}) + b_i$$

$$I_{\mathbf{h}} = S(jLO)_{\mathbf{h}} \, \mathbf{M}_{\perp\mathbf{h}} \cdot \mathbf{M}^*_{\perp\mathbf{h}}$$

Magnetic Interaction Vector: $\mathbf{M}_{\perp\mathbf{h}}$

Magnetic Structure Factor : $\mathbf{M}(\mathbf{h})$

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

$\mathbf{h} = \mathbf{H} + \mathbf{k}$ $\Leftarrow$ **Scattering vector** $\quad \mathbf{e} = \dfrac{\mathbf{h}}{h}$

The magnetic structure factor

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

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

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

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

Maximum number of parameters for a general incommensurate structure: 6N

Group Theory: Symmetry Analysis

Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group $G_{\mathbf{k}}$

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

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

The different ways of treating magnetic structures in *FullProf*

(1) Standard Fourier (all kind of structures) coefficients refinement with $\mathbf{S_k}$ 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) Real space description of uni-axial conical structures (**`Jbt = 5`**)

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

(5) Refinement of $C^{\nu}_{n\lambda}$ coefficients in the expression: $\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$
`Jbt = 1 and Isy=-2`

The different ways of treating 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
 . . . . .
```

The different ways of treating magnetic structures in *FullProf*

Standard Fourier coefficients refinement:
A magnetic phase has **`Jbt = +/-1, +/-10`**

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

The magnetic symmetry is introduced together with explicit symmetry operators of the crystal structure. The refined variables are directly the components of the $\mathbf{S}_{\mathbf{k}js}$ vectors. Not all components of $\mathbf{S}_{\mathbf{k}js}$ are free (reason of the phase factors) and a relation exist between $\mathbf{S}_{\mathbf{k}j1}$ and $\mathbf{S}_{\mathbf{k}js}$

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

Standard Fourier components refinement

```
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

The different ways of treating magnetic structures in *FullProf*

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.

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

The refined variables are directly the coefficients C1, C2, C3, ….

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

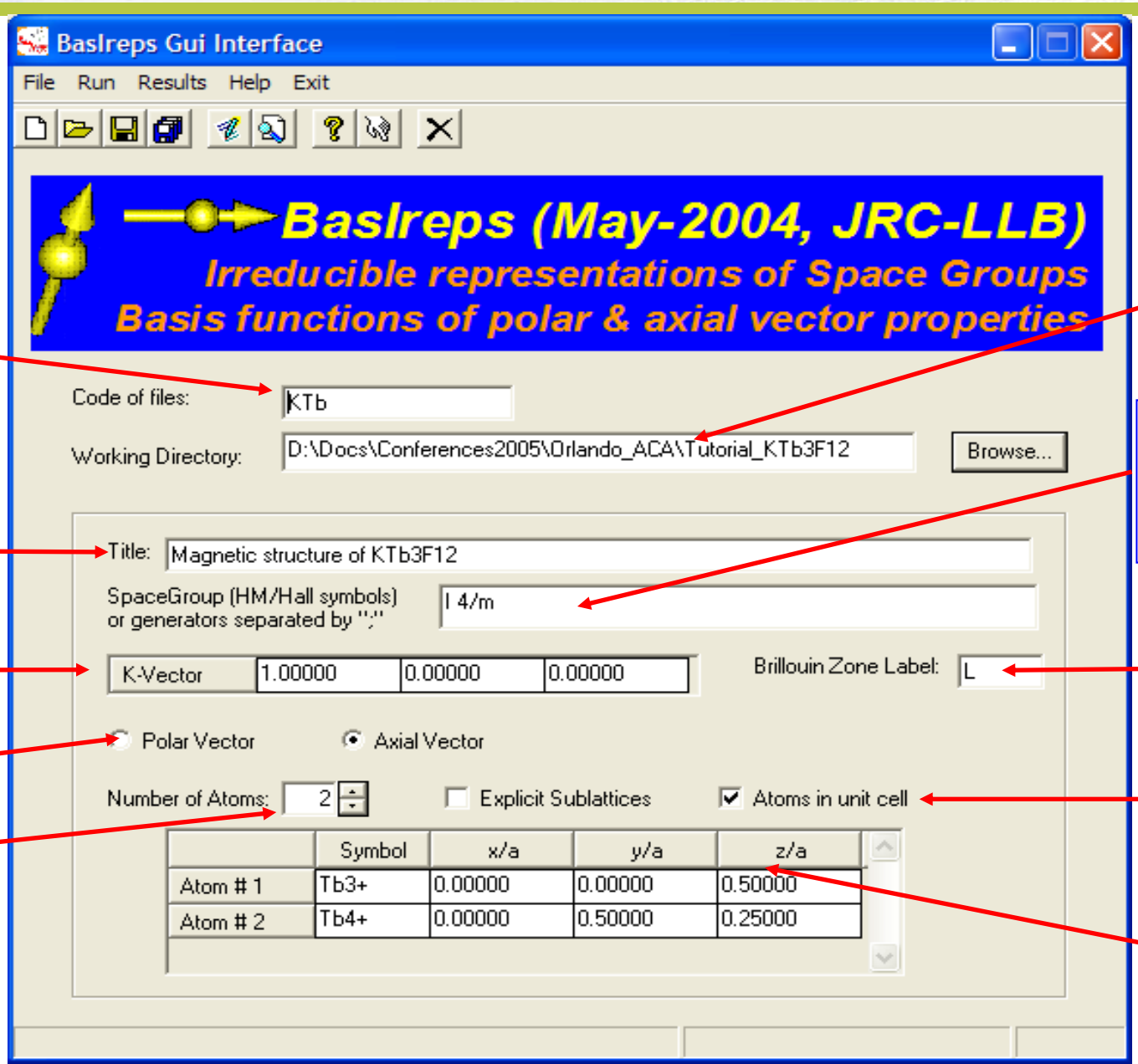
Basis functions coefficients refinement

```
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
```

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*	⇐ *Propagation vector* *Space Group* *Atom positions*
Magnetic structure solution (Sim. Ann.) *FullProf*	⇐ *Integrated intensities* *Atomic components of basis functions*

GUI for *BasIreps*



Code of files

Working directory

Space group symbol or generators

Title

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)**

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

Example of BasIreps output

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

File Edit Actions Options Window Help

```
====>
 => 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 )

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

Line=437 | Col=69 | Alt=3,3;3 | Size=526 | Files=3 | Windows=3 | OVR | R/W | 12:59 AM

Example of BasIreps output

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

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

Line=6 Col=1 Alt=0,0:0 Size=107 Files=2 Windows=2 OVR R/W 12:48 AM

Magnetic structure determination in complex systems
Simulating Annealing (SAnn)

What is Simulated Annealing?

Simulated Annealing:

The SA method is a general purpose optimisation technique for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

Minimize a cost function, energy E(ω), with respect to the configuration vector ω.

Origin: Monte Carlo methods for simulating properties of liquids (Metropolis algorithm)

Algorithm trying to mimic the process of annealing a sample to obtain a good crystalline state (ground state):

A temperature schedule (starting high temperature + cooling rate) is needed.

Procedure to generate new configurations (Markov chains) and a Boltzmann probability to explore the phase space (importance sampling)

Simulated Annealing

The SA method applied to structural problems:

- J. Pannetier, J. Bassas-Alsina, J. Rodríguez-Carvajal and V. Caignaert, *Nature* **346**, 343-345 (1990)

- J.M. Newsam, M.W. Deem and C.M. Freeman, Accuracy in Powder Diffraction II. NIST Special Publ. No. **846**, 80-91 (1992)

- J. Rodríguez-Carvajal, Physica B **192**, 55-69 (1993) (program MAGSAN)

Simulated Annealing for magnetic structures

Look directly for coefficients of the expansion:

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

or components of $\mathbf{S}_{\mathbf{k}}$ and phases, explaining the experimental data

•Minimize a reliability factor with respect to the "configuration vector"

$$\boldsymbol{\omega} = \left| C_1, C_2, C_3, C_4, C_5, \ldots C_m \right\rangle$$

$$R_m(\boldsymbol{\omega}) = c \sum_{r=1}^{N} \left| G_{obs}^2(\mathbf{h}_r) - G_{calc}^2(\mathbf{h}_r, \boldsymbol{\omega}) \right|$$

The Simulated Annealing Algorithm

begin

Initialise (set to zero useful quantities, do preliminary calculations)

$\tau = 1$

do

do

Perturb the system:

$\omega_{old} \rightarrow \omega_{new}$, $\Delta = E(\omega_{new}) - E(\omega_{old})$

if $\Delta \leq 0$ **then accept**, **else**

if $\exp(-\Delta/T_\tau) >$ **random[0,1] then accept**

if accept then **Update** (**replace** ω_{old} **by** ω_{new})

until equilibrium is approached closely enough (Ncyc)

$T_{\tau+1} = f(T_\tau)$ **(decrease temperature, usually** $T_{\tau+1} = q\, T_\tau$, $q \approx 0.9$**)**

$\tau = \tau + 1$

until stop criterion is true (maximum τ, **convergence, low % accepted...)**

end

Simulated Annealing run of *FullProf*

FullProf.2k_Multi_Pattern

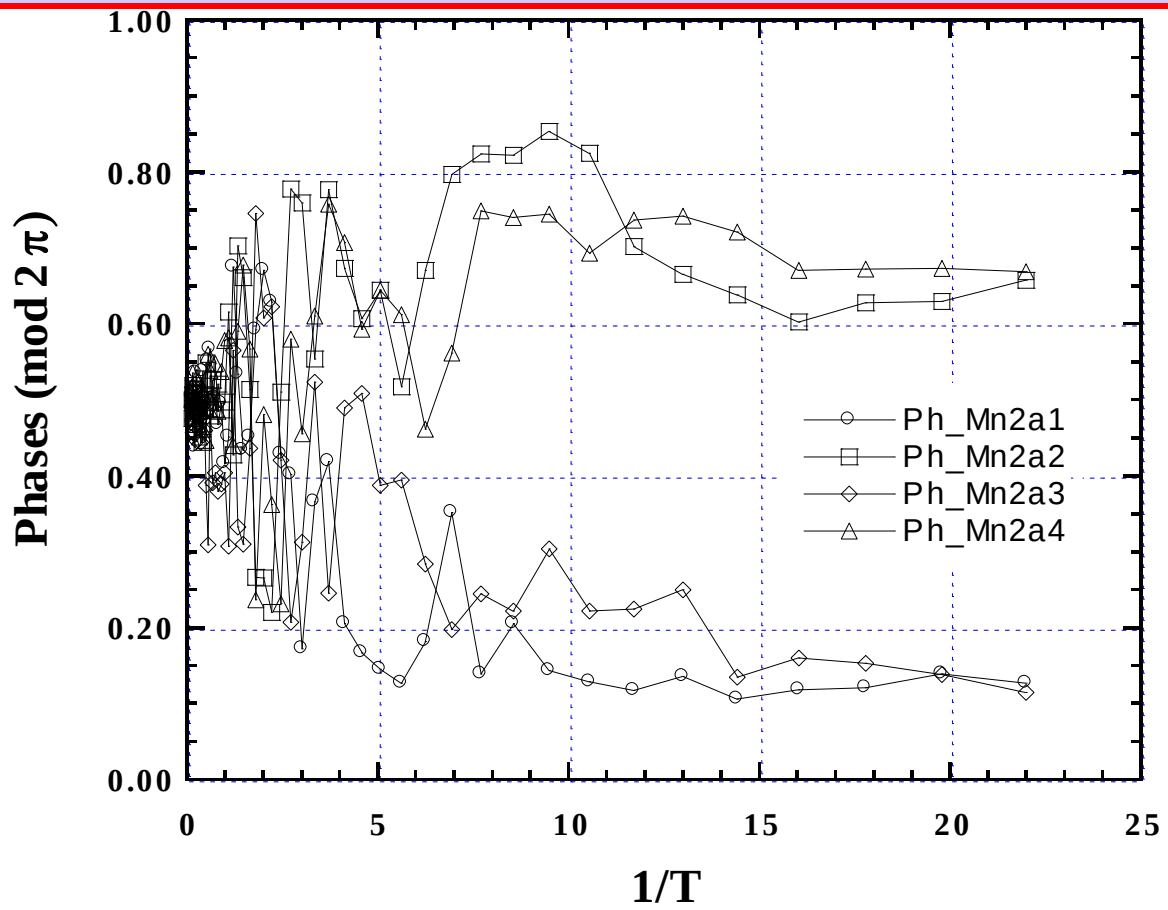
```
=>   ***************************************************************
=>   ** PROGRAM FullProf.2k (Version 2.40 - May2003-LLB JRC) **
=>   ***************************************************************
=>                    M U L T I -- P A T T E R N
=>        Rietveld, Profile Matching & Integrated Intensity
=>            Refinement of X-ray and/or Neutron Data
=>               (Multi_Pattern: Windows-version)


=> START Date:10/07/2003  Time => 07:24:51.793
=> Reading control file *.PCR ...
=> End of preliminary calculations !

=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****

=> Initial configuration cost:     40.49
=> Initial configuration state vector:
=>   Rmom_Mn1 RPhi_Mn1 RPhi_Mn1 RPhi_Mn2 RPhi_Mn2
=>          1        2        3        4        5
=>     2.3146 156.3578 152.2612 319.1841  73.4829
=> NT:  1 Temp: 10.00 (%Acc): 51.40  <Step>:288.8000  <R-factor>: 53.6836
=> NT:  2 Temp:  9.00 (%Acc): 47.00  <Step>:288.6956  <R-factor>: 50.6513
=> NT:  3 Temp:  8.10 (%Acc): 45.60  <Step>:288.3760  <R-factor>: 45.8823
=> NT:  4 Temp:  7.29 (%Acc): 39.20  <Step>:288.3134  <R-factor>: 43.0660
```

Simulated Annealing run of *FullProf*

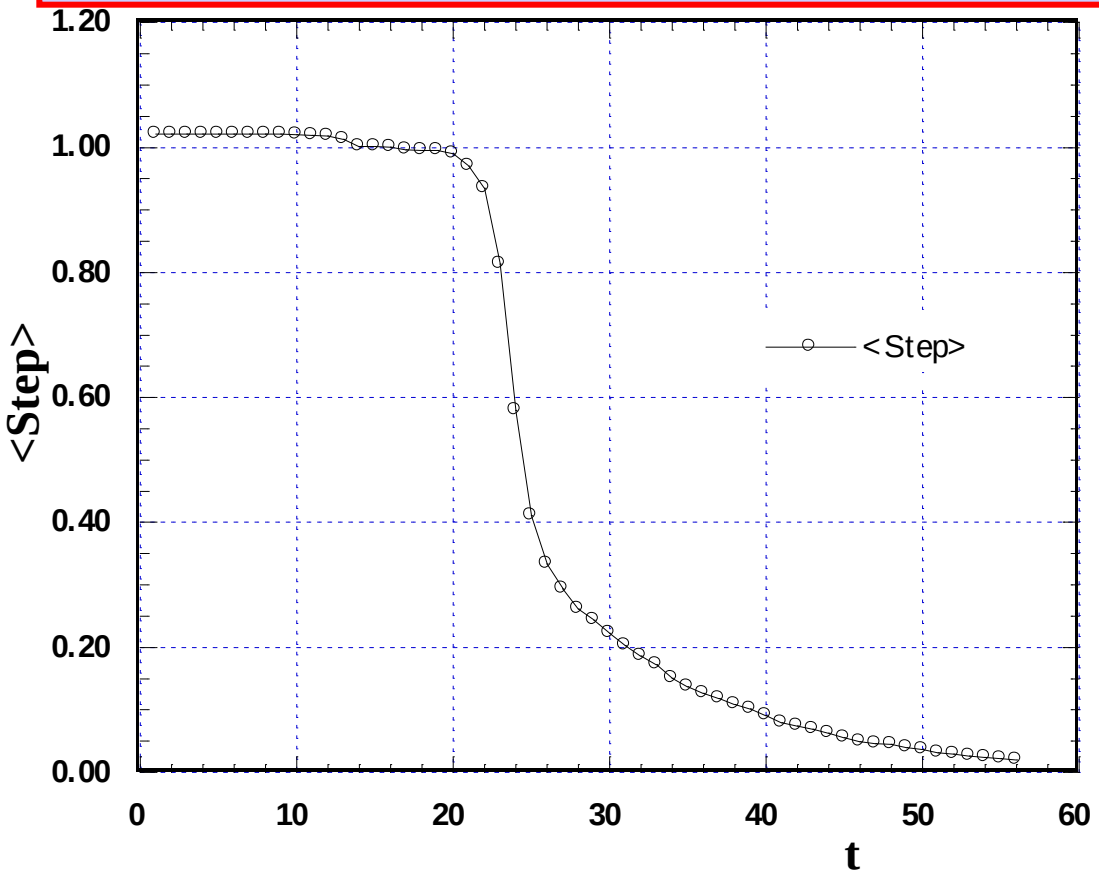
FullProf.2k_Multi_Pattern

```
=> NT: 69 Temp:  0.01 (%Acc): 42.40  <Step>:  0.2036  <R-factor>: 13.3120
=> NT: 70 Temp:  0.01 (%Acc): 40.60  <Step>:  0.1972  <R-factor>: 13.3079
=> NT: 71 Temp:  0.01 (%Acc): 41.60  <Step>:  0.1710  <R-factor>: 13.3025
=> NT: 72 Temp:  0.01 (%Acc): 46.60  <Step>:  0.1551  <R-factor>: 13.2982
=> NT: 73 Temp:  0.01 (%Acc): 35.80  <Step>:  0.1404  <R-factor>: 13.2960

=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:       1
=> -> Configuration parameters (   150 reflections):

=> Sol#: 1 RF2=  13.282 ::
=>   Rmom_Mn1 RPhi_Mn1 RPhi_Mn1 RPhi_Mn2 RPhi_Mn2
=>          1        2        3        4        5
=>     2.9250  53.2323 324.9417 217.1961 144.8587


=>              CPU Time:    48.610 seconds
=>                            0.810 minutes

=> END   Date:10/07/2003  Time => 07:25:40.413

=> Data Files :
=>             - simann
=> PCR  File  : simann-t
```

Behavior of parameters in Simulated Annealing runs



Average step … Corana algorithm



Refinement of magnetic structures using neutron powder diffraction

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