Magnetic Structure Determination and Refinement

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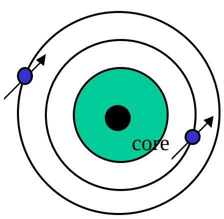
Content:

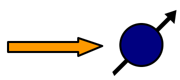
- What's and why magnetic structures
- Formalism to describe magnetic structures
- Magnetic neutron scattering
- Magnetic structure determination:
  - Indexing: ***SuperCell***
  - Symmetry Analysis: ***BasIreps***
  - Simulated Annealing: ***FullProf***
- Examples: practical sessions

Ions with intrinsic magnetic moments

Atoms/ions with unpaired electrons

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





Ni^{2+}

m = g **J** (rare earths)

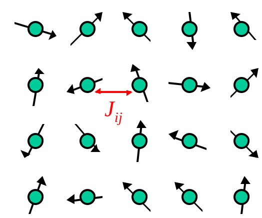
m = g **S** (transition metals)

What is a magnetic structure? (1)

Paramagnetic state:
Snapshot of magnetic moment configuration

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

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

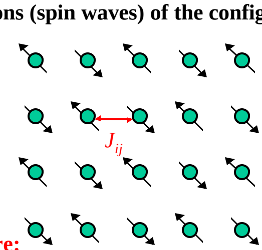


What is a magnetic structure? (2)

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

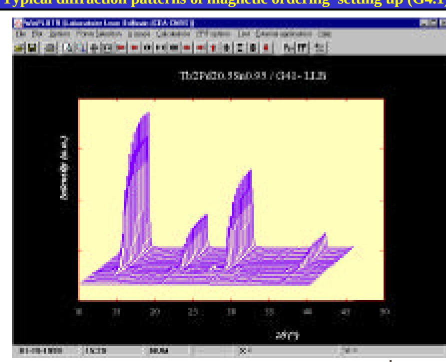
$$E_{ij} = -J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j$$

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



Magnetic structure:
Quasi-static configuration of magnetic moments

Typical diffraction patterns of magnetic ordering setting up (G4.1)



Formalism to describe magnetic structures

Magnetic structures
Magnetic moment of each atom: Fourier series

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

Necessary condition for real $\mathbf{m}_{lj} \Rightarrow \; \mathbf{S}_{-\mathbf{k}j} = \mathbf{S}_{\mathbf{k}j}^{\;*}$

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

Examples of Fourier coefficients for simple magnetic structures

Single propagation vector

k = (0,0,0) or **k**=1/2 **H**

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

REAL Fourier coefficients ≡ magnetic moments

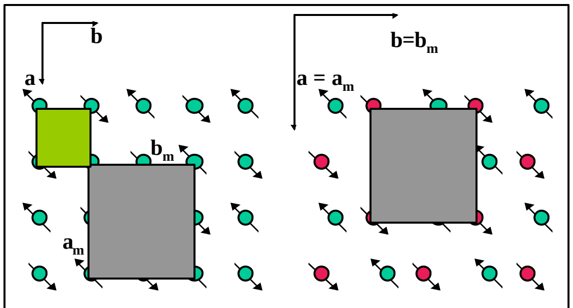
The simplest case

Single propagation vector

k = (0,0,0)

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

- The magnetic structure may be described within the crystallographic unit cell
- Magnetic symmetry similar to conventional crystallography plus time reversal operator.



k= (1/2, 1/2) **k**= (0, 0)

Fourier coefficients of sinusoidal structures

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

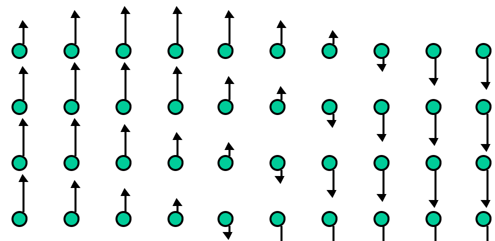
Real $\mathbf{S}_\mathbf{k}$, or imaginary component in the same direction as the real one

$$\mathbf{m}_{lj} = \mathbf{S}_{\mathbf{k}j} \; expi\{-\mathbf{k}\mathbf{R}_l\} + \mathbf{S}_{-\mathbf{k}j} \; expi\{+\mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{S}_{\mathbf{k}j} = \frac{1}{2} m_j \mathbf{u}_j \; exp\{-2p \; i f_{\mathbf{k}j}\}$$

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

Sinusoidal magnetic structure



$\mathbf{k}$= (k_x, k_y)

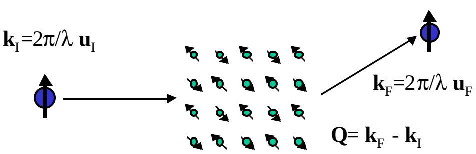
Fourier coefficients of helical structures
k interior of the Brillouin zone
Real component of $\mathbf{S_k}$ perpendicular to the imaginary component

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

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

Magnetic neutron scattering

Magnetic scattering of neutrons



Dipolar interaction ($\mathbf{m}_n$, $\mathbf{m}$): vector scattering amplitude

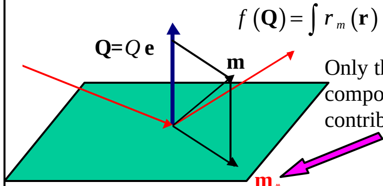
$$\mathbf{a}_M(\mathbf{Q}) = \frac{1}{2} r_e \gamma\, f(\mathbf{Q})\left\{\mathbf{m} - \frac{\mathbf{Q}\,(\mathbf{m}\,\mathbf{Q})}{Q^2}\right\}$$

Magnetic scattering of neutrons

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

p=0.2696 10^{-12} cm

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



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

Magnetic 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:

Ü **Scattering vector**

Magnetic structures

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

The magnetic structure factor:

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

$$y_{\mathbf{k}js} = \Phi_{\mathbf{k}j} + f_{\mathbf{k}js}$$

$\Phi_{\mathbf{k}j}$ is a phase factor which is not determined by symmetry.

$f_{\mathbf{k}js}$ is a phase factor determined by symmetry.

$$\mathbf{S}_{\mathbf{k}js} = M_{js}\mathbf{S}_{\mathbf{k}j}\ exp\{-2p\ i f_{\mathbf{k}js}\}$$

The matrices M_{js} and phases $f_{\mathbf{k}js}$ can be deduced from the atomic basis functions.

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

The magnetic structure factor:

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

$$\Downarrow$$

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

Magnetic structure determination

Steps for Magnetic structure determination from Neutron Powder Diffraction

Propagation vector(s) *SuperCell*	Symmetry Analysis *BasIreps*	Magnetic structure solution *FullProf* (Simulated Annealing)
Peak positions of magnetic reflections Cell parameters	*Propagation vector Space Group Atom positions*	*Integrated intensities Coefficients of the atomic components of basis functions*

The Program *SuperCell*

(distributed within ***WinPLOTR***)

Program: ***SuperCell*** (J.Rodríguez-Carvajal, LLB-December-1998)

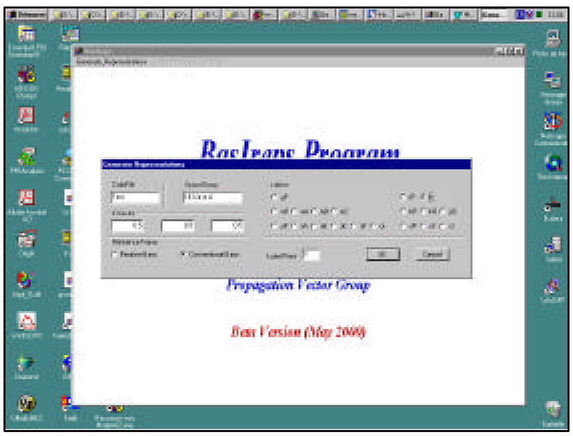
- This program can be used to index superstructure reflections from a powder diffraction pattern.
- The first approach consist in searching the best "magnetic unit cell" compatible with a set of observed SUPERSTRUCTURE lines in the powder diffraction pattern.
- If the first approach fails to give a suitable solution, the superstructure may be incommensurate and a direct search for the propagation vector and one of its harmonics have to be used.

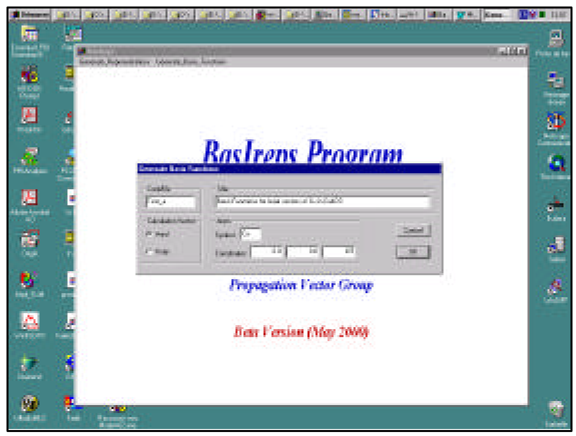
BasIreps **provides the basis functions (normal modes) of the irreducible representations of the wave-vector group $\mathbf{G_k}$**

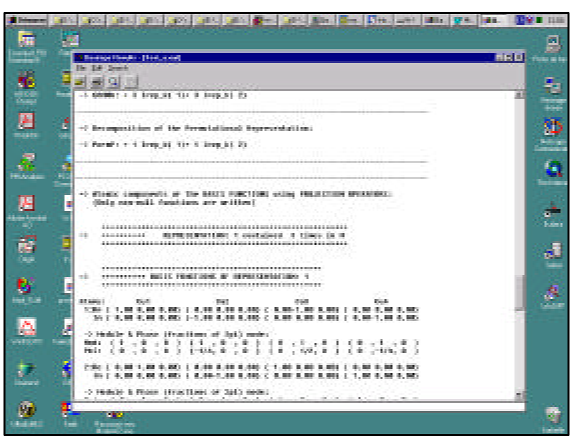
$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}js}\, exp\{-2p\, i\mathbf{k}\mathbf{R}_l\}$$

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

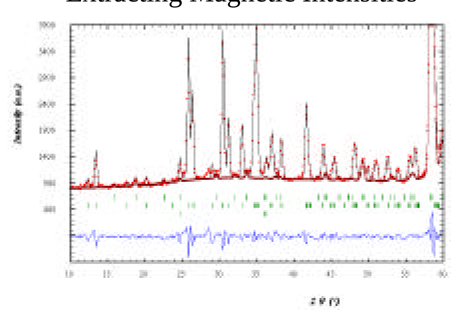
Basis Functions (constant vectors): $\mathbf{S}^{\mathbf{k}n}_{nl}\,(js)$







Extracting Magnetic Intensities



Direct space methods:

•**Look directly for coefficients of the expansion:**

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

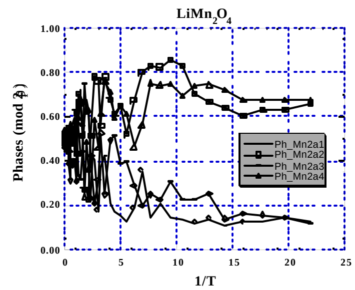
or components of S_k and phases, explaining the experimental data

•**Minimise a reliability factor with respect to the "configuration vector"**

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

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

Behavior of parameters in Simulated Annealing runs



Average step ...