Magnetic structures:
Formalism of propagation vector

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1. What’s a magnetic structure?
2. How to describe magnetic structures with the formalism of propagation vector(s).
3. Plotting complex magnetic structure with FStudio.
4. Symmetry, symmetry, symmetry…
5. Strategy for solving magnetic structures, indexation, simulated annealing…

Outline

Ions with intrinsic magnetic moments
Atoms/ions with unpaired electrons
Intra-atomic electron correlation
Hund’s rule: maximum S/J

\[ m = g_s J \text{ (rare earths)} \]
\[ m = g_s S \text{ (transition metals)} \]

What is a magnetic structure?
Paramagnetic state:
Snapshot of magnetic moment configuration

\[ E_{ij} = -J_{ij} S_i \cdot S_j \]

\[ \langle S_i \rangle = 0 \]
What is a magnetic structure?

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

\[ E_{ij} = -J_{ij} S_i \cdot S_j \]

\[ \langle S_i \rangle \neq 0 \]

Magnetic structure: Quasi-static configuration of magnetic moments

Types of magnetic structures

- Ferro
- Antiferro

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

- Transverse
- Longitudinal
- Amplitude-modulated or Spin-Density Waves

Types of magnetic structures

- Spiral
- Cycloid
Types of magnetic structures

Shubnikov magnetic groups, are limited to:
- Commensurate magnetic structure.
- Real representation of dimension 1.

Formalism of prop. Vector: Basics

Position of atom \( j \) in unit-cell \( l \) is given by:
\[
R_{lj} = R_l + r_j
\]
where \( R_l \) is a pure lattice translation.

Formalism of prop. Vector: Basics

A magnetic structure is fully described by:
- Wave-vector(s) \( \{k\} \).
- Fourier components \( S_{kj} \) for each magnetic atom \( j \) and wave-vector \( k \).
  - Fourier components \( S_{kj} \) is a complex vector (6 components) !!!
  - Phase for each magnetic atom \( j \), \( \Phi_j \).

\[
\mathbf{m}_{lj} = \sum_{k} S_{kj} \exp\left\{-2\pi i \mathbf{k} \mathbf{R}_j\right\}
\]

\[
R_{lj} = \mathbf{R}_j + \mathbf{r}_j = l_i \mathbf{a} + l_o \mathbf{b} + l_c \mathbf{c} + x_i \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}
\]

Necessary condition for real \( \mathbf{m}_{lj} \)

\[
S_{-kj} = S_{kj}^*
\]
The magnetic structure may be described within the crystallographic unit cell.

- Magnetic symmetry: conventional crystallography plus time reversal operator: crystallographic magnetic groups.

Single propagation vector

\[ k = (0, 0, 0) \]

\[ m_{ij} = \sum_{k} S_{kj} \exp\left\{-2\pi i k R_{l}\right\} = S_{ij} \]

- REAL Fourier coefficients = magnetic moments
- The magnetic symmetry may also be described using crystallographic magnetic space groups.

Fourier coef. of sinusoidal structures

- \( k \) interior of the Brillouin zone (pair \( k, -k \))
- Real \( S_{k} \), or imaginary component in the same direction as the real one.

\[ m_{ij} = S_{kj} \exp(-2\pi i k R_{l}) + S_{kj} \exp(2\pi i k R_{l}) \]

\[ S_{kj} = \frac{1}{2} m_{j} u_{j} \exp(-2\pi i \phi_{kj}) \]

\[ m_{ij} = m_{j} u_{j} \cos 2\pi (k R_{l} + \phi_{kj}) \]

Fourier coefficients of helical structures

- \( k \) interior of the Brillouin zone
- Real component of \( S_{k} \) perpendicular to the imaginary component.

\[ S_{kj} = \frac{1}{2} \left[ m_{ij} u_{j} + im_{ij} v_{j} \right] \exp(-2\pi i \phi_{kj}) \]

\[ m_{ij} = m_{ij} u_{j} \cos 2\pi (k R_{l} + \phi_{kj}) + m_{ij} v_{j} \sin 2\pi (k R_{l} + \phi_{kj}) \]
Centred cells!

\[ k = (1,0,0) \text{ or } (0,1,0) \] !!!!!

Examples. Fstudio

\[
\begin{aligned}
 & \text{LATTICE P} \\
 & K 0.5 0.0 0.0 \\
 & \text{SYMM x,y,z} \\
 & \text{MSYM u,v,w,0.0} \\
 & \text{MATOM Ce1 CE 0.0 0.0 0.0} \\
 & \text{SKP 1 1 2.0 0.0 0.0 0.0 0.0 0.0 0.0} \\
\end{aligned}
\]

Type of lattice P, C, I, F......

Propagation vector(s)

List of symmetry operators with associated magnetic operator

Magnetic atom

Fourier coefficients and phase

Symmetry analysis

- Problem is underdetermined:
  - large number of parameters
    (6 Fourier coeffs.+phase per magnetic atom and per k)
  - usually few observations, especially in powder patterns.
- Magnetic form factor

Representation theory

  - What is allowed vs. what is not allowed

Keyword: Invariance of the physical properties under application of symmetry operators.
**Phase transitions in solids**

Phase transitions often take place between phases of different symmetry.

- **High symmetry phase**, Group $G_0$
  - $\Delta J = 0; \pm 1$
- **Low symmetry phase**, Group $G_1$
  - This is a "spontaneous" symmetry-breaking process.
  - Transition are classified as either 1st order (latent heat) or 2nd order (or continuous)

**A simple example:** Paramagnetic $\rightarrow$ Ferromagnetic transition

- "Time-reversal" is lost
- Symmetry under reversal of the electric current

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**Landau theory (2)**

- $\Phi$ is invariant under operations of $G$, each order of the expansion can be written given by some polynomial invariants of $c_i^n$
  
  $\Phi = \Phi_0 + \sum_n A^n(P,T) \sum_i (c_i^n)^2 + \ldots$

- In a second order phase transition, a single symmetry mode is involved.

**Landau theory**

- Ordering is characterized by a function $\rho(x)$ that changes at the transition.
- Above $T_c$, $\rho_0(x)$ is invariant under all operations of $G_0$
- Below $T_c$, $\rho_1(x)$ is invariant under all operations of $G_1$

$$ \delta \rho = \rho_1 - \rho_0 = \sum_n \sum_i c_i^n \Phi_i^n(x) $$

- Basis functions of reducible Representation of $G_0$

- At $T = T_c$, all the coefficients $c_i^n$ vanish

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**Spectroscopy**

- $T = \int \rho' \mu' \phi' \, d\phi'$
- $T = \int \rho \mu \phi \, d\phi$

**MO-LCAO**

- Spectroscopy of $\text{H atoms}$

$3\text{H}$

**SALCs** of $\text{H atoms}$
Symmetry Analysis

Fourier coefficients as linear combinations of the basis functions of the irreducible representation of the propagation vector group $G_k$

$$S_{kJ} = \sum_{n \lambda} C_{n \lambda}^{\nu} S_{n \lambda}^{\nu} (j \nu)$$

$M(h) = p \sum_{j=1}^{n} O_j f_j(h) T_j \sum_{n \lambda} C_{n \lambda}^{\nu} \sum_{z} S_{z \nu}^{n \lambda} (j \nu) \exp \left\{ \pi t \left[ h_1 r_j - \Phi_k \right] \right\}$

Symmetry Analysis

Magnetic moment is an axial (pseudo) vector.
Transformation under symmetry operation different to polar vector:

- Rotation axis
- Inversion

Representation analysis

Kovalev's book: "Irreducible representations of space group"

Software:
- MODY
- SarAh
- BasIreps
The different ways of treating magnetic structures in FullProf

Standard Fourier coefficients refinement:
A magnetic phase has $J_{bt} = +/− 1$

$$M(h) = p \sum_{j} O_{j}(h) T_{j} \sum_{S_{k_j}} \exp \left\{ 2\pi i \left[ (H+k) \cdot S_{k_j} \right] \right\}$$

The magnetic symmetry is introduced together with explicit symmetry operators of the crystal structure.
The refined variables are directly the components of the $S_{k_j}$ vectors.

The different ways of treating magnetic structures in FullProf

Coefficients of basis functions refinement:
A magnetic phase has $J_{bt} = +/− 1$ and $I_{sy} = −2$

$$M(h) = \sum_{j} O_{j}(h) T_{j} \sum_{S_{k_j}} C_{k_j} \exp \left\{ 2\pi i \left[ (H+k) \cdot S_{k_j} \cdot \Phi_{k_j} \right] \right\}$$

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 $C_{1}, C_{2}, C_{3}$...
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 consists 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.

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**Simulated Annealing (SA):**

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


The function, $E(\omega)$ to be optimised with respect to the configuration described by the vector state $\omega$ is called the "cost" function.
Simulated Annealing (SA):

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

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 chain) and a Boltzmann probability to explore the phase space (importance sampling)

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begin
  initialise (set to zero useful quantities, do preliminary calculations )
  $t = 1$
  do
    Perturb the system: $\omega_{old} \rightarrow \omega_{new}$, $\Delta = E(\omega_{new}) - E(\omega_{old})$
    if $\Delta \leq 0$ then accept, else
      if $\exp(-\Delta/T_t) > \text{random}[0,1]$ then accept
      else Update (replace $\omega_{old}$ by $\omega_{new}$)
    end
    if accept then Update
    $T_{t+1} = f(T_t)$ (decrease temperature, usually $T_{t+1} = q T_t$, $q \approx 0.9$)
    $t = t + 1$
  until equilibrium is approached closely enough (Ncyc)
  until stop criterion is true (maximum $t$, convergence, low % accepted...)
end

The Simulated Annealing Algorithm

Simulated Annealing for magnetic structures:

• Look directly for the components of $S_k$ and phases, explaining the experimental data

• Minimize a reliability factor with respect to the “configuration vector”

$\mathbf{u} = [C_1, C_2, C_3, C_4, C_5, ..., C_m]$

$R_m(\mathbf{u}) = c \sum_{i=1}^{N} \left[ G_{\text{obs}}^2 (h_i) - G_{\text{calc}}^2 (h_i, \mathbf{u}) \right]$
Simulated Annealing run of *FullProf*

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**Behavior of parameters in Simulated Annealing runs**

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**Average step ...**
**Corana algorithm**