Group theory of magnetic structures
-An Introduction to Representational Analysis in Crystalline Solids

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Group theory (and magnetism)

- **Frameworks**
  - Allow methods for simplifying **analysis** of a problem in systems possessing some degree of symmetry.
    - **Symmetry works with Landau theory (more later)**
  - What is allowed vs. what is not allowed
    - And what might be allowed **iff (iff = if and only if) …**
    - Neumann's principle (relating symmetry to physical properties)
      - If a crystal is invariant with respect to certain symmetry elements, any of its physical properties must also be invariant with respect to the same symmetry elements
      - Keyword: Invariance of the physical properties under application of symmetry operators.
    - Couplings $\int \phi_1^* \hat{O} \phi_0 \, d\tau = \left\langle \phi_1 | \hat{O} | \phi_0 \right\rangle$

Group theory (and magnetism)

- History has given us several formalisms
  - Space groups (black and white, 'magnetic', coloured, spin space groups, superspace groups)
  - Representation theory
    - **Often interpreted as 'the method of Bertaut'**
    - **Broader group theory framework (including representations and corepresentations)**
- FAQ - Which is best?
  - An echo of the past:
    - 'A comparison of these two papers - the one by E. S. Fedorov [1891] and the other by A. Schoenflies [1888] -clearly shows two principally different approaches by the two scientists : for Schoenflies it is just an interesting case of representation in the theory of groups, in particular infinite groups, which were being developed at that time; for Fedorov it is a means of studying real systems of configurations, the underlying feature of a crystal.'

https://www.iucr.org/publ/50yearsofxraydiffraction/full-text/fedorov
Translated by: A. Werner, Bell Telephone Laboratories, Inc., N.Y.

Overview of course
Part 1- Magnetic structures (by all the speakers)

- **Using the symmetry language**
  - Listen to the historical background and their frameworks
  - Be open to different views (**e.g. 'time reversal' :-**) - build your perspective
  - We will show you the rules - what magnetic structures are
  - Symmetry operations define a group. Their properties are defined/ underpinned by representation theory.
  - **'Symmetry' is an unspecific term. Think of a hierarchical structure with differences being about particular foci.**
  - **Start thinking about the unseen, why your refined structure is just be part of what is happening**

➡ Goal : learning to translate your problem into the different languages.

My part of the course - today
Part 2a- Recap of group theory and representations

- **The basics**
  - Why do we need to invoke symmetry?
  - Recap of some group theory, multiplication table …
- **Moving from point groups to crystalline (commensurate) solids**
  - Rotation-translation operations
  - Introduction of translational periodicity
  - Representations and irreducible representations
  - More complex irreducible representations

➡ **Goal : starting to think about the different types of symmetry and how those of a can be broken down in to separate contributions**

My part of the course
Part 2b- Building a magnetic structure

- **From irreducible representations (IRs) to basis vectors**
  - The propagation vector, the Brillouin zone
  - From the space group G_0 to the little group of the propagation vector G_k
  - Magnetic representation
    - Permutation representation
    - Axial and polar vectors, representations
  - Basis vectors : a general basis vector space

➡ **Goal : Explore the basis vector description of magnetic structures**

My part of the course
Part 3 - Refining magnetic structures

- **Philosophies and pathways**
  - Continuous phase transitions
  - Opening the door - zeroth order approximations
    - Isotropy / stabilizer groups
  - Energy scales - a hand-waving approach
  - Couplings - food for thought
    - ***"A single IR"***
  - Symmetry and phase transitions
- **My 'building-up' principle**

➡ **Goal : Using necessity - Ockham's razor - and care for the unknown**

My part of the course - workshops
Part 4- Hands on calculations and data refinement

- **Later parts of the course are focused on introducing SARAh and using it with FullProf and GSAS (NOT GSAS-2).**
  - Go through several examples of commensurate and incommensurate structures
  - (GSAS-2, is not ready for representational analysis yet… Sorry, Bob!)

Let's kick off :

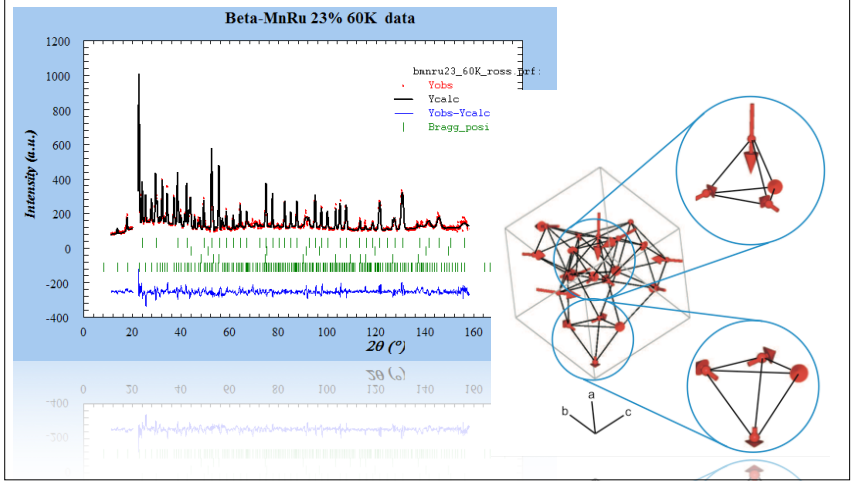
Q. Why should an experimentalist use symmetry?

Why should an experimentalist use symmetry?

- Look at your Hamiltonian, ***H,*** and then think of the more likely magnetic structure
  - Don't have ***H*** ? Then have many possibilities …
- Information is destroyed in many ways
  - The magnetic form factor: J(**Q**)
  - The magnetic structure factor: $\boldsymbol{F}_{M\perp}(\mathbf{Q})$
  - Powder averaging (S, k - domains)
  - Domain averaging (powder, single crystal)

→ **Under-defined problem**

Complex incommensurate magnetic ordering in B-$Mn_{1-x}Ru_x$ (x=0.12) - don't expect an east answer!



Phase transitions in solids

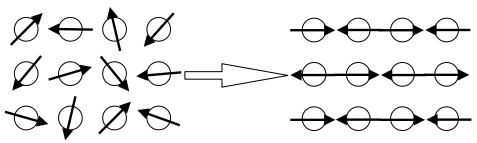
- Phase transitions typically involve **symmetry breaking**
  - going to a phase with lower symmetry
- Transition are classified as either 1st order (discontinuous) or 2nd order (continuous)
- 2nd order transitions follow Landau theory
- A simple example:

  Paramagnetic → Antiferromagnetic

High symmetry phase

↓

Lower symmetry phase



Symmetry operations are lost, e.g. rotational-translations, translational symmetry, and 'time-reversal', the symmetry under reversal of the electric current

Groups - putting symmetry operations together → point groups and space groups

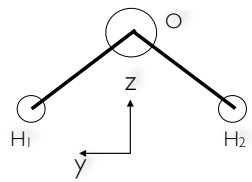
G_0

- a set of elements A,B,C…
- the product of 2 elements is a member of the group AB∈G
- the product is associative A(BC)=(AB)C
- there exists a unique identity (E)
- every element has a unique inverse

  $AA^{-1}=A^{-1}A=E$
- We will note the order of a group *h*

  (The order of a group is simply the number of elements in a group)

Applying operations in sequence – the multiplication table

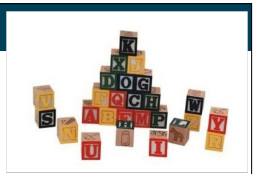


C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
E	E	$C_2(z)$	σ_{xz}	σ_{yz}
$C_2(z)$	$C_2(z)$	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	$C_2(z)$
σ_{yz}	σ_{yz}	σ_{xz}	$C_2(z)$	E

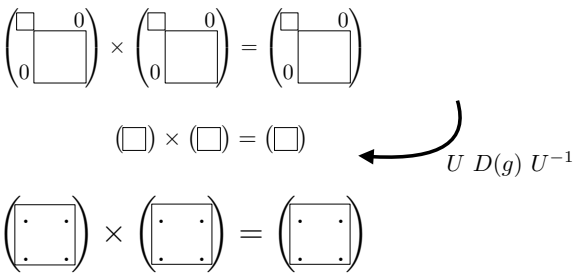
- 4 different operations
- Combine operations, e.g. look at the atoms H1 and H2, the p_x orbital on O

$$\sigma(xz) \times C_2(z) = \sigma(yz)$$

Irreducible representations



- In matrix terms:
  - A representation is reducible if there is a similarity transformation (change of basis) that sends all the matrices *d*(*g*) to the same block-diagonal form
  - All other representatives can be written in terms of these IRs
- A finite group has a limited number of these IRs

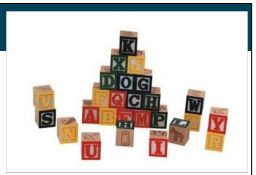


IRs- point groups and space groups

Irreducible representations

- *"a set of matrices, each corresponding to a single operation of the group, that can be combined amongst themselves in a manner parallel to the group elements"*
- Irreducible- these are building blocks of symmetries
- In point groups irreducible representations are order 1 (A,B), 2 (E), 3 (T), e.g. T_{2g}, E_g
- In space groups the rotational-translational operations lead to IRs of order up to 6
  - **Marked increase in the complexity of possible structures**

IRs and the Great Orthogonality Theorem



- If D is a reducible representation.
- The number of times that a representation *i* appears in a decomposition of D is

$$n_i = \frac{1}{h}\sum_{g\in G}\chi_i(g)^*\chi(g)$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
D	3	0	1

$$nA_1 = 1/6(1\times 3 + 2\times[1\times 0] + 3\times[1\times 1]) = 1$$
$$nA_2 = 1/6(1\times 3 + 2\times[1\times 0] + 3\times[-1\times 1]) = 0$$
$$nE = 1/6(2\times 3 + 2\times[-1\times 0] + 3\times[0\times 1]) = 1$$

Irreducible Representations of Space Groups

Table 1
Irreducible representations of R3c–C_{3v}^6, $k = 0$ and R3m–C_{3v}^5, $k = 0$ and $k = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$

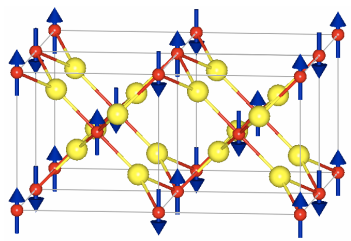
Symmetry operations	1	3	3^2	c or m	$c3$ or $m3$	$c3^2$ or $m3^2$
Representations						
Γ_1 A_1 τ_1	1	1	1	1	1	1
Γ_2 A_2 τ_2	1	1	1	−1	−1	−1
Γ_3 E τ_3	$\begin{pmatrix}1 & \cdot\\ \cdot & 1\end{pmatrix}$	$\begin{pmatrix}\epsilon & \cdot\\ \cdot & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & \cdot\\ \cdot & \epsilon\end{pmatrix}$	$\begin{pmatrix}\cdot & 1\\ 1 & \cdot\end{pmatrix}$	$\begin{pmatrix}\cdot & \epsilon^*\\ \epsilon & \cdot\end{pmatrix}$	$\begin{pmatrix}\cdot & \epsilon\\ \epsilon^* & \cdot\end{pmatrix}$
Magnetic moment transformations						
example 1	S_{1x}	S_{1z}	S_{1y}	$-S_{2y}$	$-S_{2x}$	$-S_{2z}$
example 2	S_{1x}	S_{3z}	S_{2y}	$-S_{2y}$	$-S_{2y}$	$-S_{3z}$
	S_{1y}	S_{3x}	S_{2z}	$-S_{2x}$	$-S_{1z}$	$-S_{3y}$
	S_{1z}	S_{3y}	S_{2x}	$-S_{2z}$	$-S_{1y}$	$-S_{3x}$

Group theory of magnetic structures

Part 2b: Building a magnetic structure- from irreducible representations to basis vectors

A crystalline material: a starting point for some symmetries
A framework that needs different symmetries

1. Translational symmetry
   - Propagation vector, k
2. Space group
   - parent symmetry
   - compatibility with k
3. Atom position
4. Magnetic moment
5. The Hamiltonian



Rephrasing symmetries

0. Magnetic structures as Fourier sums
1. Space group (before the ordering), G_0
2. The ordering wave vector, ***k***
3. The symmetry that is compatible with ***k***, the little group $G_{\boldsymbol{k}}$
4. The symmetries of $G_{\boldsymbol{k}}$, the irreducible representations
5. The symmetry of a magnetic moment in a crystal structure, i.e. the position (permutation representation) and the moment itself (axial vector)
6. The symmetry of, and **within**, basis vector spaces, isotropy groups
7. The symmetry of any single-ion effects (consequences of spin-orbit)
8. Symmetry of the Hamiltonian, symmetry of G_0

Definition of magnetic structures, phonons, electronic orbitals

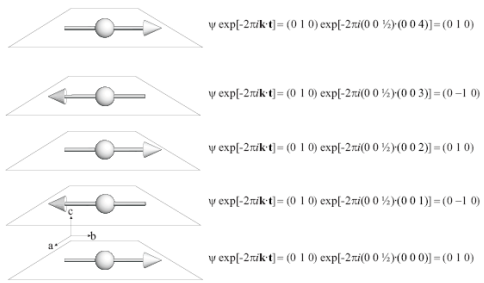
- A linear combination of plane waves (basis vectors, Fourier components)
- Bloch waves - Eigenfunctions of a periodic Hamiltonian can be constructed from Fourier components

$$\vec{\psi}^{\vec{k}}_{j,\nu} \equiv \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

$$\vec{m}_j \equiv \sum_{\nu;\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

- Once the moments in the primitive unit cell are defined, the ***k*** vector defines every other spin in the structure

The propagation of magnetic structures through the crystal- with a single k-vector



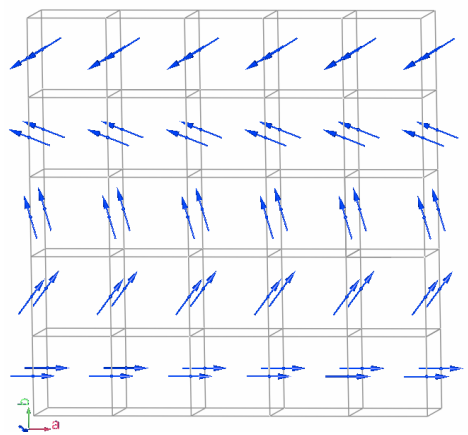
$$\vec{m}_j = \sum_{\nu,\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

- The wavevector ***k*** (the propagation vector) of the magnetic structure works with the basis vectors to create a simple definition of the structure
  - Once the moment orientations in the **zeroth (nuclear) cell are known**, those of **all other moments** related by primitive lattice translations in the cell can be calculated from $\boldsymbol{t}_{ij}$ (the translation vector relating the two moments)

The formalism of the propagation vector, k

$$\vec{m}_j = \sum_{\nu,\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

- Example - single moment in the asymmetric unit (the primitive unit cell)
- Once ***k*** is defined, total degrees of freedom = 3
  - **Don't need to increase unit cell or change of lattice basis**



k-vector reduces space group symmetry : $G_0 \rightarrow G_k$

Constructing $G_{\boldsymbol{k}}$ (the space group of the propagation vector)

- Need only consider the rotational part (*h*) of symmetry operation (*g*):

$$g = \{h|\vec{\tau}\}$$

- a subset of space group G_0 elements A,B,C… that leave the k-vector invariant $G_k \in G_0$

i.e. $\vec{k}' = \vec{k}h \pm \vec{\tau}$ ← Reciprocal lattice vector

- i.e. defines those that are compatible with the translational symmetry of ***k***

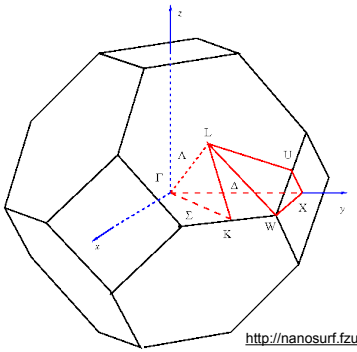
$$G_{\vec{k}} \subseteq G_0$$

Space group G_0, k-vector, G_k

#227	k=(0 0 0) (Γ)	48 elements
	k=(0.5 0 0) (K)	8
	k=(0.5 0.5 0.5) (L)	12

- Different points, lines, planes correspond to different symmetries. They will have different $G_{\boldsymbol{k}}$.

The Brillouin zone and different G_k, e.g. FCC



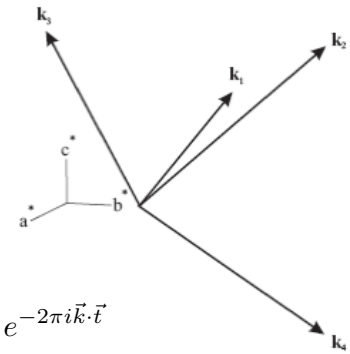
$$\vec{k}' = \vec{k}h \pm \vec{\tau}$$

http://nanosurf.fzu.cz/wiki/doku.php?id=band_structure

- The symmetry types of the different points in reciprocal space
- Different points, lines and planes have different compatible symmetry operations; different G_k
- (Care with axis system)
- Several notations exist, Kovalev, Miller and Love, etc

The star of the propagation vector
e.g. k=(0.5 0.5 0.5) in space group Fd-3m,

$$\mathbf{k}_1 = \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right) \mathbf{k}_2 = \left(\frac{\bar{1}}{2},\frac{1}{2},\frac{1}{2}\right) \mathbf{k}_3 = \left(\frac{1}{2},\frac{\bar{1}}{2},\frac{1}{2}\right) \mathbf{k}_4 = \left(\frac{1}{2},\frac{1}{2},\frac{\bar{1}}{2}\right)$$



$$m_j^{\vec{k}} = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}} \; \psi_\nu^{\vec{k}} \; e^{-2\pi i \vec{k}\cdot\vec{t}}$$

← some or all of these arms may be involved

Back to the space group G_0

- **G_0 is the space group of the crystal structure** a set of elements A,B,C…
  - Group structure of symmetry operations
    - the product of 2 elements is a member of the group A∈BG
    - the product is associative A(BC)=(AB)C
    - there exists a unique identity (E)
    - every element has a unique inverse
    - $AA^{-1}=A^{-1}A=E$
  - Groups have irreducible representations
    - **G_k is also a space group …**

Irreducible Representations of Space Groups

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			S_{1y}	S_{3x}	S_{2z}	$-S_{2x}$	$-S_{1z}$	$-S_{3y}$
			S_{1z}	S_{3y}	S_{2x}	$-S_{2z}$	$-S_{1y}$	$-S_{3x}$

- Constructed IRs from the little space group G_k
- Character tables are not enough
- Source is important- calculated or tabulated

Summary - Irreducible representations (IRs)

- Define the basic symmetry types for a group of symmetry operations
  - Other symmetries can be built from combination of IRs

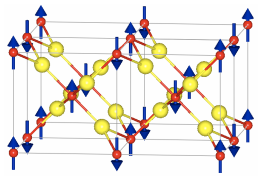
$$\Gamma = \sum_{\nu} n_\nu \Gamma_\nu$$

- In molecules, point groups have IRs up to order 3
  - A (1x1 matrices), E (2x2 matrices), T (3x3 matrices)
- In solids, space groups lead to IRs up to order 6

$$\Gamma^{(1)}, \Gamma^{(2)}, ..., \Gamma^{(6)}$$

Projection of basis vectors : from IRs to BVs

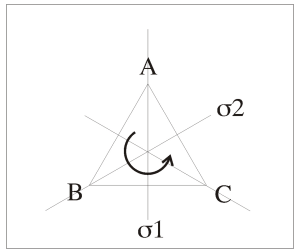
- **What are we trying to do?**
  - Find out what types of structure are possible for moments at atomic positions
- **How?**
  1. Permutation representation
     - How the atoms are interchanged under the symmetry operations of G_k
  2. Axial vector representation
     - How the magnetic moments are rotated under the symmetry operations of G_k



- **Decompose symmetries using IRs of G_k**

The permutation representation Γ_{perm}

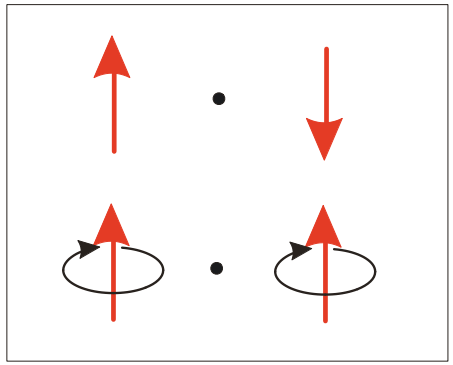
- Recap- a crystal structure is invariant under the symmetry operations of its point/space group. However, equivalent positions can be interchanged, permuted



$A \to A$	$A \to C$	$A \to B$
$\sigma 1: B \to C$	$\sigma 2: B \to B$	$3^+: B \to C$
$C \to B$	$C \to A$	$C \to A$
$\chi(\sigma 1) = 1$	$\chi(\sigma 2) = 1$	$\chi(3^+) = 0$

- Γ_{perm} describes how all the atoms are permuted

Symmetry of magnetic moments and displacement vectors under improper rotations



Polar

Axial

Polar vectors are reversed by inversion operation, axial vectors are not.

Symmetry of magnetic moments and displacement vectors under improper rotations

Polar

$$R(I)\vec{M} = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} = \begin{pmatrix} -m_x \\ -m_y \\ -m_z \end{pmatrix}$$

Axial

$$R(I)\vec{M} = det(h) \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix} = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}$$

$$det(I) = -1$$

Polar vectors are reversed by inversion operation, axial vectors are not. Mathematically, we can deal with this by multiplying by the determinant

Putting it all together- the magnetic (displacement) representation

- The permutation representation and the axial vector representation are independent

$$\Gamma_{mag} = \Gamma_{permutation} \times \Gamma_{axial}$$

- The magnetic representation can be decomposed into IRs of G_k

$$\Gamma_{mag} = \sum_{\nu} n_\nu \Gamma_\nu$$

- The number of times IR Γ_ν appears is given by

$$n_\nu = \frac{1}{n(G_{\vec{k}})} \sum_{g \in G_{\vec{k}}} \chi_{\Gamma_{mag}}(g) \chi_{\Gamma_\nu}(g)^*$$

Putting it all together- the magnetic (displacement) representation

- The number of times IR Γ_ν appears is given by

$$n_\nu = \frac{1}{n(G_{\vec{k}})} \sum_{g \in G_{\vec{k}}} \chi_{\Gamma_{mag}}(g) \chi_{\Gamma_\nu}(g)^*$$

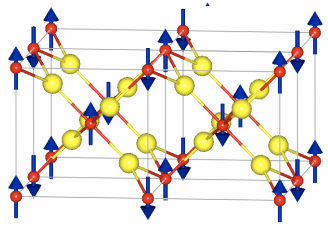
- This depends on the atomic site and may look like

$$\Gamma_{mag,2a} = 1\Gamma_1^{(1)} \oplus 1\Gamma_2^{(1)} \oplus 0\Gamma_3^{(2)}$$

or

$$\Gamma_{mag,6c} = 2\Gamma_1^{(1)} \oplus 0\Gamma_2^{(1)} \oplus 2\Gamma_3^{(2)}$$

Basis functions



- Symmetry adapted functions that have the same symmetry as the IR- 'associated', non-unique

$$\boldsymbol{\psi}_\nu^{i\lambda} = \sum_{g \in G_{\mathbf{k}}} d_\nu^\lambda(g)^* \delta_{i,gi} \; \mathrm{e}^{-2\pi i \mathbf{k}\cdot(\mathbf{r}_{gi} - \mathbf{r}_i)} det(h) R^h \boldsymbol{\phi}_\beta$$

and a series of test functions, e.g.

$$\vec{\phi}_1 = (1\ 0\ 0),\ \vec{\phi}_2 = (0\ 1\ 0), \vec{\phi}_3 = (0\ 0\ 1)$$

Basis vectors

- Define a degree of freedom
  - Follows the symmetry of the associated IR
  - Can be used to classify symmetry
- **Does not decrease number of degrees of freedom**
  - i.e. 3 moment degrees of freedom per atom
  - *n* atoms will have 3*n* basis vectors
  - Simplicity from dealing with the categories separately
- **Define symmetry as a linear combination, refine in terms of mixing (weighting) coefficients**

$$\vec{m} = \sum_i C_i \vec{\psi}_i \qquad m_j^{\vec{k}} = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}} \; \psi_\nu^{\vec{k}} \; e^{-2\pi i \vec{k}\cdot\vec{t}}$$

Working with basis vectors

Making magnetic structures with basis vectors

- Expanding the exponential
  - The eigenfunctions of an electrons with a periodic Hamiltonian are Bloch waves.

    with the form: $$\vec{m}_j = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}}\ \vec{\psi}_{i,\nu}^{\vec{k}}\ e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$
  - Magnetic structures are eigenfunctions of the spin-dependent electronic Hamiltonian and have the same form
  - If we expand the exponential, we see that it is made up of a **Re**al cosine part and an **Im**aginary sine part

$$\vec{m}_j = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}}\ \vec{\Psi}_{i,\nu}^{\vec{k}} \left[\cos(-2\pi\vec{k}\cdot\vec{t}) + i\ \sin(-2\pi\vec{k}\cdot\vec{t})\right]$$

- This formalism very general and we will see that it can describe simple and exotic structures, such as sinusoidal and helical structures

(*Note SARAh, works with atoms in the zeroth unit cell)

Basis vectors and k-vectors - a simple example

- Simple structures ~~and 'sine' structures~~
  - The translational properties of a magnetic structure may be described by

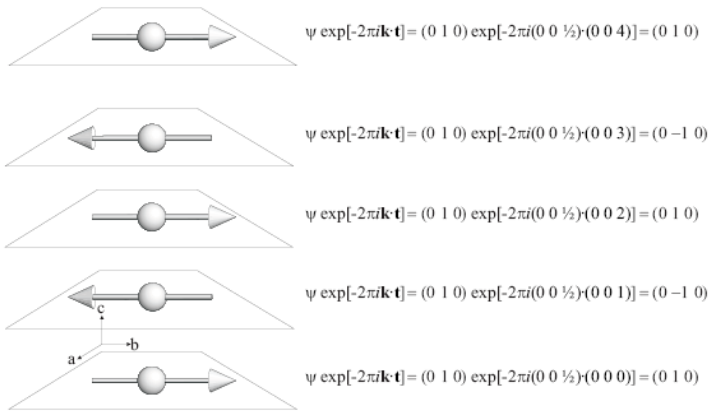
$$m_j = \sum_{\nu,k} C_\nu^k\ \psi_{i,\nu}^k\ e^{-2\pi i k\cdot t_{ij}}$$

  - Working with only one basis vector, ignoring the coefficient for simplicity and expanding the exponential, this becomes

$$\vec{m}_j = \vec{\psi}_{i,\nu}^{\vec{k}} \left[\cos(-2\pi\vec{k}\cdot\vec{t}_{ij}) + i\ \sin(-2\pi\vec{k}\cdot\vec{t}_{ij})\right]$$

  - If $\vec{\psi}$ is real and the propagation vector is such that the sine part is zero, we are left with a **simple cosine curve** with the moments of the same amplitude.

A simple antiferromagnetic (~~sine~~) structure



Moving to incommensurate magnetic structures

What do we do differently for incommensurate structures?

Basis vectors and k-vectors

- Ψ is <u>real</u> and ***k*** is such that the sine component is non-zero
  - Leads to $\boldsymbol{m}_j$ being complex, so need to make it real
  - The moment vector for an atom in the *n*th cell related to that in the zeroth cell by translation $\boldsymbol{t}_{ij}$ is given by

$$m_j = C_\nu^k \; \psi_{i,\nu}^k \; e^{-2\pi i k \cdot t_{ij}} + C_\nu^k \; \psi_{i,\nu}^{-k} \; e^{-2\pi i (-k) \cdot t_{ij}}$$

$$m_j = C_\nu^k \; \psi_{i,\nu}^k \; e^{-2\pi i k \cdot t_{ij}} + C_\nu^k \; (\psi_{i,\nu}^k)^* \; e^{-2\pi i (-k) \cdot t_{ij}}$$

  - As

$$\psi_{i,\nu}^{-k} = \psi_{i,\nu}^{k,*}$$

  - Substitution and expansion of the exponential leads to

$$\vec{m}_j = 2Re(\vec{\psi}_{i,\nu}^{\vec{k}}) \left[\cos(-2\pi \vec{k} \cdot \vec{t}_{ij})\right] + 2Im(\vec{\psi}_{i,\nu}^{\vec{k}}) \left[\sin(-2\pi \vec{k} \cdot \vec{t}_{ij})\right]$$

  - Where the second term is zero as Ψ is real → Amplitude modulated sine structure (spin density wave)

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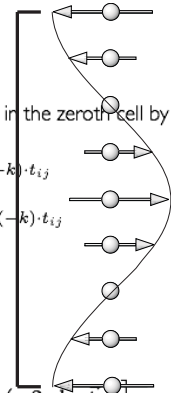

h) sine or cosine

Basis vectors and k-vectors

- Ψ is <u>complex</u> and ***k*** is incommensurate
  - Leads to ***m*** being complex, so need to make real moments
  - The atomic vector for an atom in the nth cell related to that in the zeroth cell by translation t is given by

$$m_j = C_\nu^k \; \psi_{i,\nu}^k \; e^{-2\pi i k \cdot t_{ij}} + C_\nu^k \; (\psi_{i,\nu}^k)^* \; e^{-2\pi i (-k) \cdot t_{ij}}$$

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  - Where the second term is non-zero.
  - If the real and imaginary parts are not parallel → circular or elliptical helix

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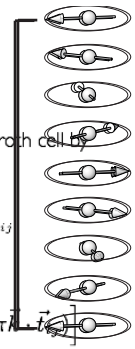


i) elliptical helix

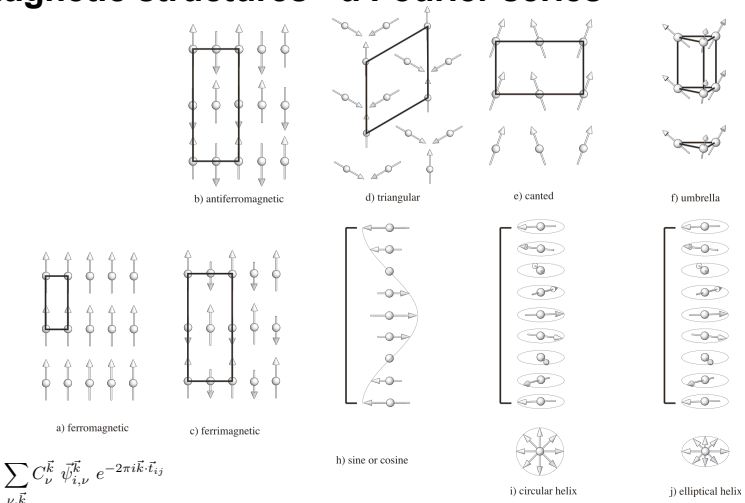
(*Note SARAh, works with atoms in the zeroth unit cell)

Building structures : basis vectors and k-vectors

- A sine structure helix
  - ***k*** incommensurate
    - Ψ has is real, in a plane that contains (longitudinal) or does not contain (transverse) ***k***
- A circular helix
  - ***k*** incommensurate
    - Ψ has is complex, and has non-collinear real and imaginary components (equal magnitude) in a plane that does not contain ***k***
- A conical structure
  - ***k*** incommensurate
    - Ψ has is complex, and has non-collinear real and imaginary components (equal magnitude) in a plane that does not contain ***k***
  - ***k***=(000)
    - Ψ is ferromagnetic and is perpendicular to the helix
- A cycloid
  - ***k*** incommensurate
    - Ψ has is complex, and has non-collinear real and imaginary components (equal magnitude) in a plane that contains ***k***

Which could happen? Think about entropy and phase transitions

Magnetic structures - a Fourier series



$$\vec{m}_j = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}} \; \vec{\psi}_{i,\nu}^{\vec{k}} \; e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

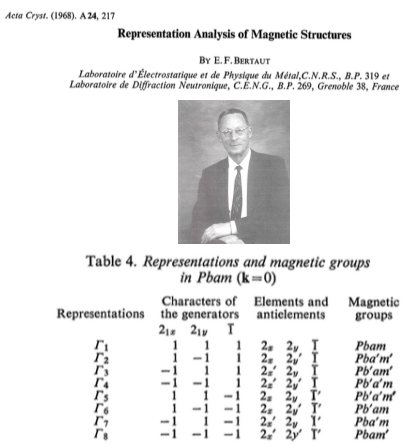
Magnetic Representational Analysis with SARAh and SARAh-Refine

Andrew S. Wills
UCL Chemistry

Group theory (and magnetism)

- Frameworks and method for simplifying analysis of a problem in systems possessing some degree of symmetry.
  - **Works with Landau theory (more later)**
- What is allowed vs. what is not allowed
  - And what might be allowed **iff…**
    - **The 'iff' opens up the questions**
  - Couplings $\int \phi_1^* \hat{O} \phi_0 \; d\tau = \left\langle \phi_1 | \hat{O} | \phi_0 \right\rangle$
- History
  - Space groups (black and white, 'magnetic', coloured, spin space groups, superspace groups)
  - Representation theory
  - ***'The method of Bertaut'***
  - Broader framework (representations and corepresentations)

"Representation analysis of magnetic structures" - the method of Bertaut



Acta Cryst. (1968). A24, 217

Representation Analysis of Magnetic Structures

By E. F. Bertaut

Laboratoire d'Électrostatique et de Physique du Métal, C.N.R.S., B.P. 319 et Laboratoire de Diffraction Neutronique, C.E.N.G., B.P. 269, Grenoble 38, France

Table 4. *Representations and magnetic groups in Pbam* (k = 0)

Representations	Characters of the generators 2_{1x}	2_{1y}	$\bar{1}$	Elements and antielements			Magnetic groups
Γ_1	1	1	1	2_x	2_y	$\bar{1}$	*Pbam*
Γ_2	1	−1	1	2_x	$2_y'$	$\bar{1}$	*Pba'm'*
Γ_3	−1	1	1	$2_x'$	2_y	$\bar{1}$	*Pb'am'*
Γ_4	−1	−1	1	$2_x'$	$2_y'$	$\bar{1}$	*Pb'a'm*
Γ_5	1	1	−1	2_x	2_y	$\bar{1}'$	*Pb'a'm'*
Γ_6	1	−1	−1	2_x	$2_y'$	$\bar{1}'$	*Pb'am*
Γ_7	−1	1	−1	$2_x'$	2_y	$\bar{1}'$	*Pba'm*
Γ_8	−1	−1	−1	$2_x'$	$2_y'$	$\bar{1}'$	*Pbam'*

- **E.F. Bertaut**, Acta. Cryst. A24, 217 (1968)
  - Applied k-vector **(focus)**
  - Showed magnetic space groups could be constructed from character tables of the irreducible representations (of $\mathbf{G_k}$)
  - Used projection method to generate basis functions
  - Fourier series

$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i\vec{k}\cdot\vec{t}_{ij}}$$

$$\vec{m}_j = \sum_{\nu,\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i\vec{k}\cdot\vec{t}_{ij}}$$

Bertaut's method

- **Fundamental propôsition**
  - The eigenfunctions of an electrons with a periodic Hamiltonian are Bloch waves with the form:

$$\vec{m}_j = \sum_{\nu,\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\psi}^{\vec{k}}_{i,\nu}\ e^{-2\pi i\vec{k}\cdot\vec{t}_{ij}}$$

  - Magnetic structures are eigenfunctions of the spin-dependent electronic Hamiltonian and have the same form
  - If we expand the exponential, we see that it is made up of a **Re**al cosine part and an **Im**aginary sine part

$$\vec{m}_j = \sum_{\nu,\vec{k}} C^{\vec{k}}_{\nu}\ \vec{\Psi}^{\vec{k}}_{i,\nu}\left[\cos(-2\pi\vec{k}\cdot\vec{t}) + i\ \sin(-2\pi\vec{k}\cdot\vec{t})\right]$$

➡***This formalism is very general and elegantly describes simple and exotic structures, such as sinusoidal and helical structures. You can read a structure from its basis vectors and the k vector***

Basis vectors and k-vectors

- Ψ is complex and ***k*** is incommensurate
  - Leads to ***m*** being complex, so need to make real moments
  - The atomic vector for an atom in the nth cell related to that in the zeroth cell by translation t is given by

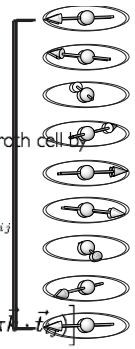
$$m_j = C^k_{\nu}\ \psi^k_{i,\nu}\ e^{-2\pi i k\cdot t_{ij}} + C^k_{\nu}\ (\psi^k_{i,\nu})^*\ e^{-2\pi i(-k)\cdot t_{ij}}$$

  - Substitution and expansion of the exponential leads to

$$\vec{m}_j = 2Re(\vec{\psi}^{\vec{k}}_{i,\nu})\left[\cos(-2\pi\vec{k}\cdot\vec{t}_{ij})\right] + 2Im(\vec{\psi}^{\vec{k}}_{i,\nu})\left[\sin(-2\pi\vec{k}\cdot\vec{t}_{ij})\right]$$

  - Where the second term is non-zero.
  - If the real and imaginary parts are not parallel → circular or elliptical helix

➡***Requires non parallel BVs***



i) circular helix ii) elliptical helix

(*Note SARAh, works with atoms in the zeroth unit cell)

When working with BVs, there is real and there is real...

$$\vec{m} = \sum_i C_i\vec{\psi}_i$$

- A purely imaginary basis vector is as real as a purely real one…

$$\vec{\psi}_1 = (1,0,0)\,;\vec{\psi}_2 = (i,0,0)$$
$$\vec{\psi}_2 = -i.\vec{\psi}_1$$

  - They are equivalent

- The linear combination of basis vectors can involve complex numbers (phase relationships)

$$\vec{\psi}_1 + \vec{\psi}_1^* = 2Re(\vec{\psi}_1)$$
$$(-i\times\vec{\psi}_1) + (i\times\vec{\psi}_1^*) = 2Im(\vec{\psi}_1)$$

Look at interactive Pdf

"Representation analysis" the method of Bertaut

$$G_0 \xrightarrow{\vec{k}} G_{\vec{k}}$$

Table 1
Irreducible representations of R3c–C_{3v}^6, $k = 0$ and R3m–C_{3v}^5, $k = 0$ and $k = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$

Symmetry operations			1	3	3^2	c or m	$c3$ or $m3$	$c3^2$ or $m3^2$
Representations								
Γ_1	A_1	τ_1	1	1	1	1	1	1
Γ_2	A_2	τ_2	1	1	1	−1	−1	−1
Γ_3	E	τ_3	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	$\begin{pmatrix} \varepsilon & \\ & \varepsilon^* \end{pmatrix}$	$\begin{pmatrix} \varepsilon^* & \\ & \varepsilon \end{pmatrix}$	$\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}$	$\begin{pmatrix} & \varepsilon^* \\ \varepsilon & \end{pmatrix}$	$\begin{pmatrix} & \varepsilon \\ \varepsilon^* & \end{pmatrix}$

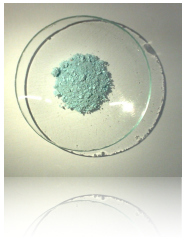
"A set of matrices, each corresponding to a single operation in a group, that can be combined amongst themselves in a manner parallel to the group elements."
(Cotton, Chemical applications of group theory)

```
BASIS VECTOR COMPONENTS FOR EACH SITE OBTAINED BY CLASSICAL PROJECTION:
(NOTE THAT THESE ARE WITH RESPECT TO SPACE GROUP AXES)

IR  # 1, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 1)
ATOM  1:  (     0     0     6)  +  1(     0     0     0)     0)
ATOM  2:  (     0     0    -6)  +  1(     0     0     0)     0)
******


IR  # 3, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 2)
ATOM  1:  (     0     0     6)  +  1(     0     0     0)     0)
ATOM  2:  (     0     0     6)  +  1(     0     0     0)     0)
******

IR  # 5, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 3)
ATOM  1:  (     3     0     0)  +  1(-1.732-3.464     0)     0)
ATOM  2:  (     0     0     0)  +  1(     0     0     0)     0)

IR  # 5, BASIS VECTOR: #   2 (ABSOLUTE NUMBER:# 4)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)     0)
ATOM  2:  (    -3    -3     0)  +  1(-1.732 1.732     0)     0)

IR  # 5, BASIS VECTOR: #   3 (ABSOLUTE NUMBER:# 5)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)     0)
ATOM  2:  (    -3    -3     0)  +  1( 1.732-1.732     0)     0)

IR  # 5, BASIS VECTOR: #   4 (ABSOLUTE NUMBER:# 6)
ATOM  1:  (     3     0     0)  +  1( 1.732 3.464     0)     0)
ATOM  2:  (     0     0     0)  +  1(     0     0     0)     0)
```

Projection of vibrational modes (basis vectors) associated with the Irreducible Representations (IRs)

All symmetry does is classify degrees of freedom

- 'Rules' have to come from somewhere else
- **Landau theory** is historically the most important framework
- It is **THE** reference
  - Many of its rules were originally designed for prediction
    - But your ***H*** may appear to break them (a bit, a lot or completely). The transition may not be as simple as you think



- Given that warning, let's have a look…

J. Manuel Perez-Mato RAMS 5

Landau theory - second-order phase transitions

- The minimum in free energy defines the equilibrium state

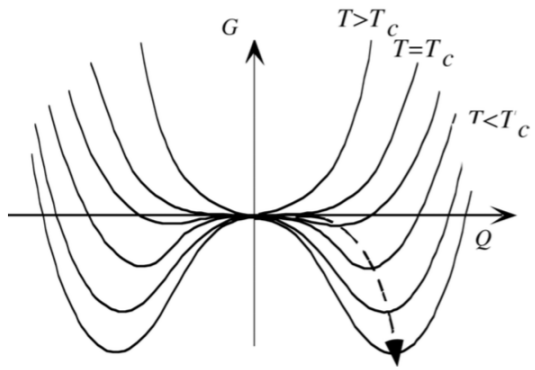
$$\left(\frac{\partial G}{\partial Q}\right)_{Q_0} = 0, \left(\frac{\partial^2 G}{\partial Q^2}\right)_{Q_0} > 0$$

- Free energy varies **continuously** as a function of temperature
  - Symmetry change is not continuous
- Assume that the free energy can be expanded as a function of an **order parameter** with temperature-dependent coefficients
  - Order parameter could be polarisation, strain, mixing coefficients
  - The minima also change as a function of temperature

$$G = G_0 + \frac{1}{2}rQ^2 + dQ^3 + uQ^4$$

Landau (1937), Landau and Lifshitz (1950):

Landau theory



For $T > T_c$, $r(T) > 0$

For $T < T_c$, $r(T) < 0$

- The condition $G(-\mathbf{Q}) = G(\mathbf{Q})$ requires that the power series only has even powers of $\mathbf{Q}$
- We will truncate the power series as soon as practically possible
- "Representation analysis" of free-energy invariants, groups, subgroups

$$G = G_0 + \frac{1}{2}rQ^2 + dQ^3 + uQ^4$$

Landau theory

- The symmetry group of the magnetic structure should a subgroup of the space group before the transition
- **A transition should involve a single IR, that of the G_0**
  - When there are more than one arms to the star, the symmetry operations are divided amongst the arms (cosets)
  - Bringing together these symmetry-related operations recovers those of G_0
  - So, the rotationally related IRs of G{k} come together, they define a collection of matrices that involve all the operations of G_0.
    - It is this IR that Landau says guides the transition, it could couple IRs within the little group G_k or those for different k-vectors
  - **Bertaut broke away from this G_0 -based description to focus on G_k. A single IR of G_k is a good starting point, but there may be coupling from IRs with isotropy groups with the same MSG/MPG or when viewed from G_0**

Landau (1937), Landau and Lifshitz (1950):

Landau theory

- Rewrite the free energy in terms of **polynomial of degree n** that is invariant under G_0 using the order parameter, so

$$G = G_0 + \frac{1}{2} r Q^2 + d Q^3 + u Q^4$$

becomes

$$G = \sum_n P_n \{\vec{\eta}_\lambda\}$$

e.g. where

$$\vec{\eta} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

or

$$\vec{\eta} = \begin{pmatrix} C_1 \\ 0 \end{pmatrix}$$

etc, are valid **order parameters**

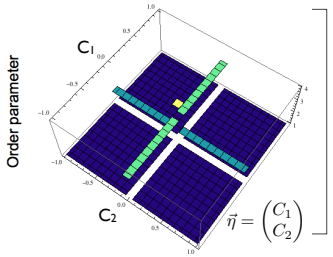
$$m_j = \sum_{\nu,k} C_\nu^k \; \psi_{i,\nu}^k \; e^{-2\pi i k \cdot t_{ij}}$$

Landau (1937), Landau and Lifshitz (1950):

Order parameter and basis vector combinations

$$m_j^{\vec{k}} = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}} \; \psi_\nu^{\vec{k}} \; e^{-2\pi i \vec{k} \cdot \vec{t}}$$

- Let's rephrase - symmetry groups based on the **mixing coefficients** can be defined according to which symmetry operations have IR matrices that leave a vector in IR space invariant, i.e. $d(h)\vec{\eta} = \vec{\eta}$



- During the transition, symmetry breaks. The symmetry group changes from G to a subgroup H.
- H could be the group of the IR, or a subgroup of it

$$G \to H$$

MSGs, MPGs and couplings between IRs

- For a given η, for a given IR of G_k we can list the symmetry operations that leave it invariant or reverse it. These form the MPGs or the MSGs of the relevant basis vector combination

$$\vec{\eta} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

- **In the language of Landau {η} are order parameters. More generally**, let's call them **'stationary vectors'**. They define high symmetry basis vector combinations within an IR's symmetry space (cf position vectors and special positions in Bz)
- The set of important {η} defines a unique collection of **MPGs or MSGs** within an IR
- **If two representations contain the some of the same image matrices, then the same MPGs and MSGs can occur in the different IRs. (The same symmetry group may span IRs), even if the degrees of freedom are orthogonal!**
- If this happens, coupling can occur between them. One IR may drive the transition (primary) and another may be induced by it through coupling. This is a secondary order parameter. They are not expected to have the same temperature dependence, but will have the same critical temperature

$$\int \phi_1^* \hat{O} \phi_0 \; d\tau = \left\langle \phi_1 | \hat{O} | \phi_0 \right\rangle$$

Landau (1937), Landau and Lifshitz (1950):

Looking back at some of the complexity - IR Dimension

- **Remember IRs can be of dimension 1 to 6.**
  - **IRs of order 1 :**
    - Matrix representatives all have the elements 1 and -1
    - If the translations match, can be used directly to construct magnetic space groups (take primed and unprimed operations)
  - **IRs of order 2+ :**
    - Matrices are irreducible, i.e. cannot be reduced further
    - Their general symmetry space does not correspond to a single magnetic space group
    - The high symmetry structures are possible within them
    - Think of projection as superposition of components of waves with different phases (be they real or complex) from the IR components belonging to the different symmetry operations g in **G_k (forms a space group). Use to define a group $G_{\{k,-k\}}$, and then make magnetic space groups, but also <u>magnetic point groups</u>.**

Table 1
Irreducible representations of R3c–C_{3v}^4, $k = 0$ and R3m–C_{3v}^5, $k = 0$ and $k = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$

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A newer refinement strategy combining ideas

Table 1
Irreducible representations of R3c–C_{3v}^4, $k = 0$ and R3m–C_{3v}^5, $k = 0$ and $k = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$

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Γ_3	E	τ_3	$\begin{pmatrix}1 & \\ & 1\end{pmatrix}$	$\begin{pmatrix}\epsilon & \\ & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & \\ & \epsilon\end{pmatrix}$	$\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}$	$\begin{pmatrix} & \epsilon^* \\ \epsilon & \end{pmatrix}$	$\begin{pmatrix} & \epsilon \\ \epsilon^* & \end{pmatrix}$

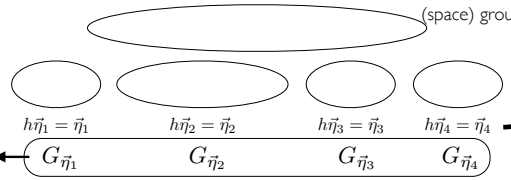
```
BASIS VECTOR COMPONENTS FOR EACH SITE OBTAINED BY CLASSICAL PROJECTION:
(NOTE THAT THESE ARE WITH RESPECT TO SPACE GROUP AXES)

IR  # 1, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 1)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)
ATOM  2:  (     0     0    -6)  +  1(     0     0     0)
******

IR  # 3, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 2)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)
ATOM  2:  (     0     0     6)  +  1(     0     0     0)
******

IR  # 5, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 3)
ATOM  1:  (     3     0     0)  +  1(-1.732-3.464     0)
ATOM  2:  (     0     0     0)  +  1(     0     0     0)

IR  # 5, BASIS VECTOR: #   2 (ABSOLUTE NUMBER:# 4)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)
ATOM  2:  (    -3    -3     0)  +  1(-1.732 1.732     0)

IR  # 5, BASIS VECTOR: #   3 (ABSOLUTE NUMBER:# 5)
ATOM  1:  (     0     0     0)  +  1(     0     0     0)
ATOM  2:  (    -3    -3     0)  +  1( 1.732-1.732     0)

IR  # 5, BASIS VECTOR: #   4 (ABSOLUTE NUMBER:# 6)
ATOM  1:  (     3     0     0)  +  1( 1.732 3.464     0)
ATOM  2:  (     0     0     0)  +  1(     0     0     0)
```

Projection of basis vectors

Refine with mixing coefficients following symmetry types, high symmetry linear combinations

Characterise resulting structure with magnetic point (space) groups defined by **η**.

Basis vector symmetry spaces: kernels and epikernels



$h\vec{\eta}_1 = \vec{\eta}_1$ $\quad h\vec{\eta}_2 = \vec{\eta}_2$ $\quad h\vec{\eta}_3 = \vec{\eta}_3$ $\quad h\vec{\eta}_4 = \vec{\eta}_4$

$\vec{\eta} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$

Magnetic point groups $G_{\{k,-k\}}$, space group

$G_{\vec{\eta}_1}$ $\quad G_{\vec{\eta}_2}$ $\quad G_{\vec{\eta}_3}$ $\quad G_{\vec{\eta}_4}$

Landau Theory- When it appears not to work it might still be useful :-)

- Irreducible representations role is to classify symmetry types
- The observation of several IRs involved in a magnetic transition (structure) gives you information about the energy drives
- The difference between weakly and strongly first order

$$\hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4$$

Refining magnetic structures with SARAh and SARAh-Refine - ideas

- **Philosophies and pathways**
  - **Basis vectors give allowed directions of spins**
  - **Commensurate, incommensurate k - no difference in process**
  - **Work within G_k and begin from "a single IR"**
    - **Definition of IR within Bertaut's theory is within G_k. In Landau theory it begins in G_0. G_0 can be constructed from G_k**
  - **Refine using basis vectors and mixing coefficients. *Use isotropy/ stabilizer groups/ epikernals and magnetic point groups***
  - **FullGroups, multi k - coming soon**
  - Continuous phase transitions ? Landau
  - Couplings - food for thought
    - ***Let the data tell you what "a single IR" means***
- **My 'building-up' principle**

➡ *Goal : Using necessity - Ockham's razor - and take care of the unknown*

Things to keep in mind

- **k-vectors in centred cells need to be handled with care, e.g. k=(100) in BCC**
  - When in doubt, convert to primitive and transform to centred setting
  - Helpful information, e.g. ferromagnetism required **k**=000
- **Representational analysis calculations do not get rid of degrees-of-freedom**
  - Symmetry is about classifying the 3n components (n = num atoms in prim cell)
  - Deal with only a few variables at a time. More models, each with fewer variables
  - Stationary vectors/ epikernels mean even fewer at a time (only a couple may be active)
- **Basis vectors can involve complex numbers**
  - Enjoy what this can make as a structure
  - The space that they define shows you what is possible within your unknown Hamiltonian. Think of the physics you are looking for
- **Relate your analysis to other information**
  - Don't use diffraction in isolation

Things to keep in mind

- **If you need to couple IRs**
  - Do it ***consciously*** - think about it (does this make sense? How does it work with Landau theory? What can cause it? Look at the various rules)
- **Are there things that you cannot see?**
  - e.g. multi k structures. Very cool and we know little about them (because we rarely think about them)
- **Building up magnetic structures**
  - The Fourier sum can build any magnetic structure. Just keep adding what you need.

$$m_j^{\vec{k}} = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}}\ \psi_\nu^{\vec{k}}\ e^{-2\pi i \vec{k}\cdot\vec{t}}$$

Add what you need, when you need it … - Building-up the magnetic structure

- **Ockham's razor**
  - **pluralitas non est ponenda sine necessitate**

    ("*plurality should not be posited without necessity*")

    ("*Don't use variables unless you need to*")

  - Work out what the necessity is
    - Think about why!
    - There lies the fun…
    - There lies the physics

Refining magnetic structures with SARAh and SARAh-Refine - practicalities

SARA*h*- what it does

- SARAh = **S**imulated **A**nnealing and **R**epresentational **A**nalysis
  - Perform symmetry analysis of possible magnetic structures using Representational (and Corepresentational Theory)
    - Information for analysing data and understanding phase transitions
  - Clip-on front-end to facilitate reverse Monte Carlo refinement of structures in GSAS using basis vectors and mixing coefficients
    - Symmetry-free simulated annealing is not normally enough
    - Simulated annealing is not normally required
  - Clip-on front-end for FullProf and TOPAS using basis vectors and mixing coefficients

SARAh- How it does it

- **GSAS implementation (k vector *X*)**
  - The start of direct basis vector refinements (refine C_i) for magnetic structures
  - **SARAh controls all aspects of symmetry and the moment orientations**, the rest is normal GSAS
  - P1 phase in GSAS (avoid red/ black, allow complex symmetries). Full magnetic cell
  - Lock down non-magnetic variables
  - Set GSAS for 2-3 LS cycles (i.e. converge), normal user control
  - SARAh edits .exp file to insert all atom positions
  - User selects symmetry type (representation, basis vectors)
  - SARAh matches atoms being refined, replaces moments, launches GENLES
  - **RMC**/Simulated Annealing refinement - **χ^2 maps against C_i**
  - **Clone refinements to explore uniqueness of the refined solution**

SARAh- How it does it

- **Fullprof implementation (k vector✓)**
  - External front end to **prepare and edit the pcr file**, write fst file
  - Not command line, simplest user choices. Buttons, scroll bars, etc
    - Help user as much as possible***
    - Simplicity***
  - Unique k-search engine
  - Main technical difficulties are with:
    - Format in FullProf, its ongoing development !! Complex basis vectors but real or imaginary mixing coefficients…
    - Definition of the magnetic structure- Fullprof over-defines the structure, better to generate each moment 1 time

SARAh- How it does it

- **TOPAS implementation (k vector ✗)**
  - External front end to **prepare and edit the ins file**,
  - Not command line, simplest user choices. Buttons, scroll bars, etc
    - Help user as much as possible***
    - Simplicity***
  - Main technical difficulties are with:
    - No - vector. Commensurate structures only.
    - Format may need fixes - I don't have TOPAS 5, 6 or 7 ;-)

SARAh -

- Where to begin?
  - *SARAh A1 : Magnetic structure determination with SARAh - Introductions and FullProf*
  - *SARAh A2 : Magnetic structure determination with SARAh - Introductions and FullProf*
  - *SARAh B : Magnetic structure determination with SARAh - Introductions and GSAS*

And answering 3 questions …

20+ years on, time for a refresh? Web version (Google : fermat + sarah)