Symmetry and magnetic structures -An introduction to the application of Representational Analysis to *Crystalline Solids*

Part 1 – From space groups to irreducible representations

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Why use symmetry?

- Electronic structures are complex
- We rarely have as much information about them as we would like
  - Experimentalists typically deal with under-defined problems (there are too many possible solutions)
  - Useful to introduce a grand simplifying structure (makes rules, classes of behaviour, and simplifies...)

Symmetry theory (Representation Theory)

- Method for simplifying analysis of a problem in systems possessing some degree of symmetry.
- What is allowed *vs*. what is not allowed
  - And what might be allowed iff…
  - Neumann's principle (the principle of symmetry)
    - 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.

Difficulties

- Symmetries in solids are subtle
  - They have to be
    - Look at what their job is!
  - Takes time to learn what electronic structures are possible and what they involve:

$$\vec{m} = C_1\vec{\psi}_1 + C_2\vec{\psi}_2 + \ldots$$

- But, this language is one that we are used to from other contexts

Overview of entire course
Part 1- Introductions

- Why do we need to invoke symmetry?
- Taking representation theory from point groups to crystalline solids
  - Translational periodicity
  - Increases complexity of the irreducible representations
  - Rotation-translation operations
  - The propagation vector, the k-vector
- Symmetries and changing language
  - The little group of the propagation vector G_k
  - Permutation representation
  - Axial and polar vectors, representations
  - Magnetic representation
- Landau theory
  - Opening the door - a zeroth-order approximation
- -> Gives the language for understanding magnetic structures

Overview of entire course
Part 2- Magnetic structures

- What they are, how best to describe them
  - Putting the ideas together
  - Show some examples

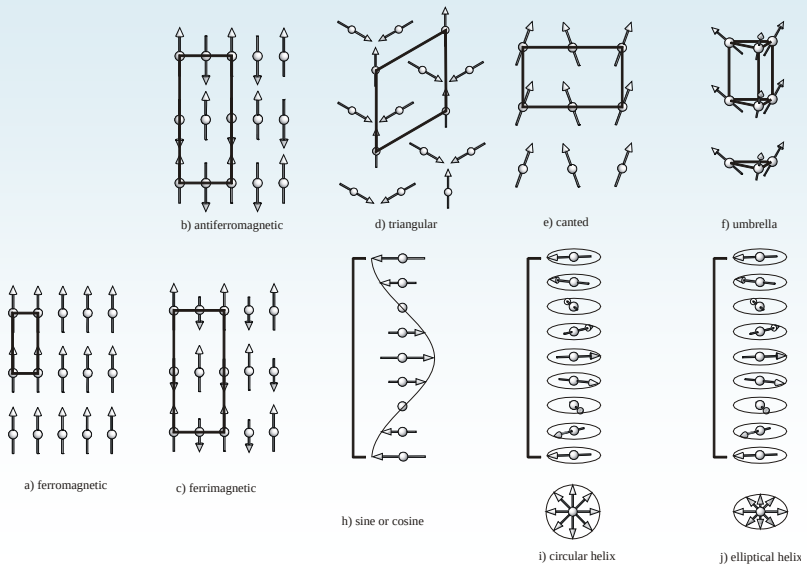
Overview of entire course
Part 3- Hands-on refinements of data

- Course is focused on FullProf
  - (But I may show you some things with GSAS)
  - Will cover using FullProf for searching for k-vectors, several examples of commensurate and incommensurate structures

Why should an experimentalist use symmetry?

- Magnetic structures are complex
- Information is destroyed in many ways
- The form factor: $J(\mathbf{Q})$
- $\boldsymbol{F}_M^{\perp}(\boldsymbol{Q})$
- Powder averaging
- Domain averaging (powder, single crystal)

Magnetic structures



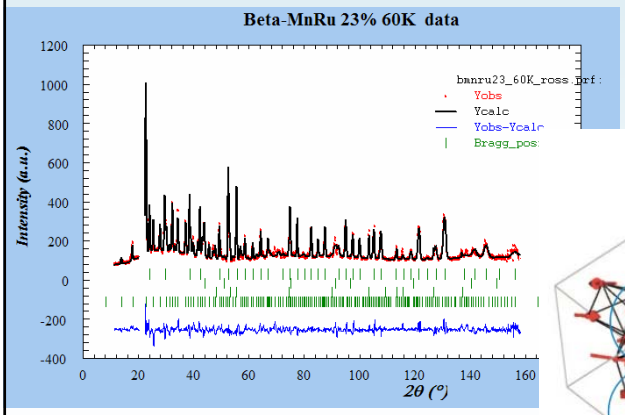
Why should an experimentalist use symmetry?

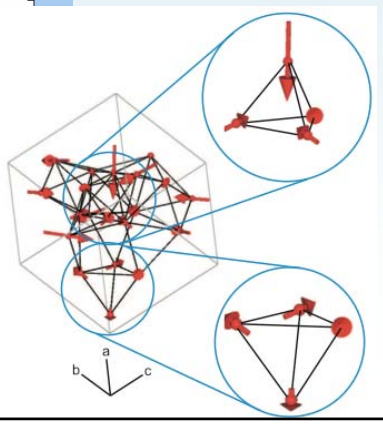
- Magnetic structures are complex
- Information is destroyed in many ways
- The form factor: $J(\mathbf{Q})$
- $\boldsymbol{F}_M\perp(\boldsymbol{Q})$
- Powder averaging
- Domain averaging (powder, single crystal)

- Luckily, we know the detailed Hamiltonian…

→ Under-defined problem

Complex incommensurate magnetic ordering in B-$Mn_{1-x}Ru_x$ (x=0.12)

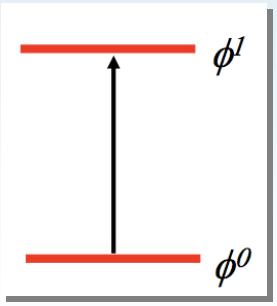




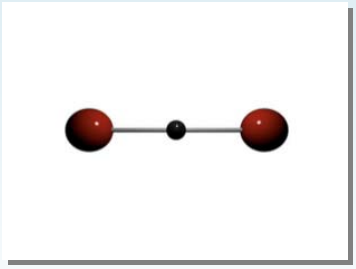
Symmetry theory – representation theory

Used in spectroscopy

- Use to predict vibration spectroscopic transitions that can be observed
- Ground state characterized by ϕ^0
- Excited state characterized by ϕ^1
- Transition operator characterised by O
- Transition integral $T = \int \phi^0 \, O \, \phi^1$
- The integrand must be invariant under application of all symmetry operations



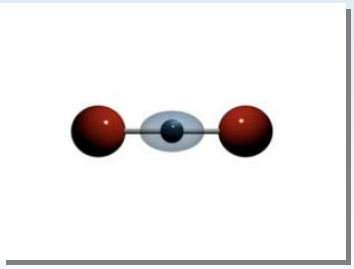
IR, Raman active modes in CO_2



IR active, change in dipole moment

$$T = \int \phi^0 \mu \phi^1$$

dipole moment operator



Raman active, change in polarizability

$$T = \int \phi^0 \alpha \phi^1$$

polarisability operator

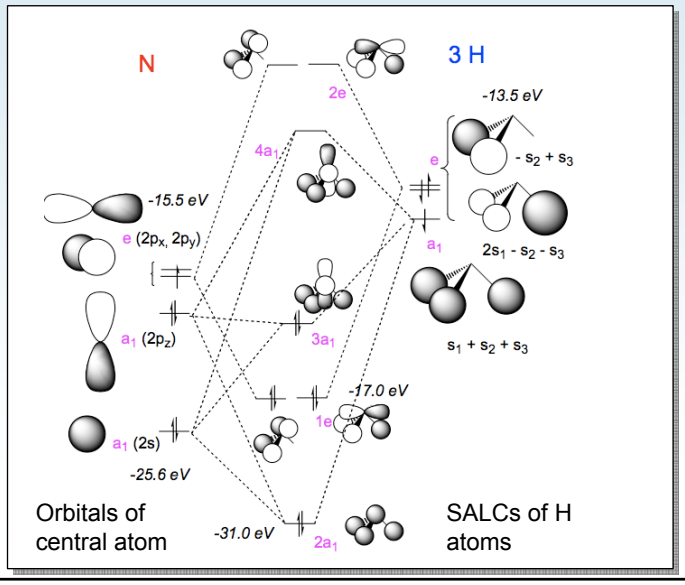
Used in molecular orbital theory - LCAO

- Molecular orbitals are linear combinations of atomic orbitals

$$\Psi = \sum_i c_i \phi_i$$

- If the molecule has symmetry, group theory predicts which atomic orbitals can contribute to each molecular orbital
- -> Symmetry adapted LCAOs

MO-LCAO

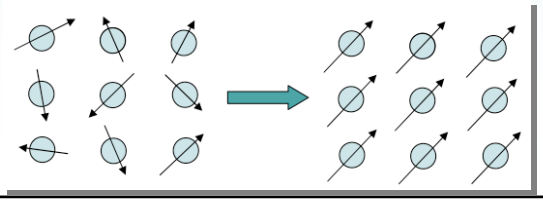


Phase transitions in solids

- Phase transitions often take place between phases of different symmetry
- 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 -> Ferromagnetic transition

High symmetry phase, Group G_0

Low symmetry phase, Group G_1



“Time-reversal” is lost. Symmetry under reversal of the electric current

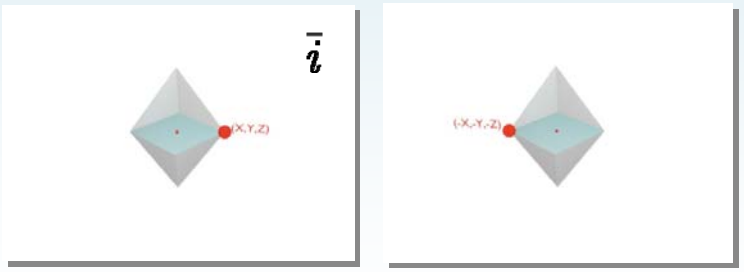
Symmetry in molecules - what do these look like ?

Symmetry operation	Symmetry element	Symbol
Identity (do nothing)		E
Rotation by $360°/n$ (a ‘proper’ rotation)	n-fold axis	C_n
Reflection	mirror plane	σ_v, σ_h or σ_d
Inversion	Centre of Inversion	i
Rotation by $360°/n$ followed by inversion (an ‘improper’ rotation)	n-fold axis + a centre of inversion	S_n

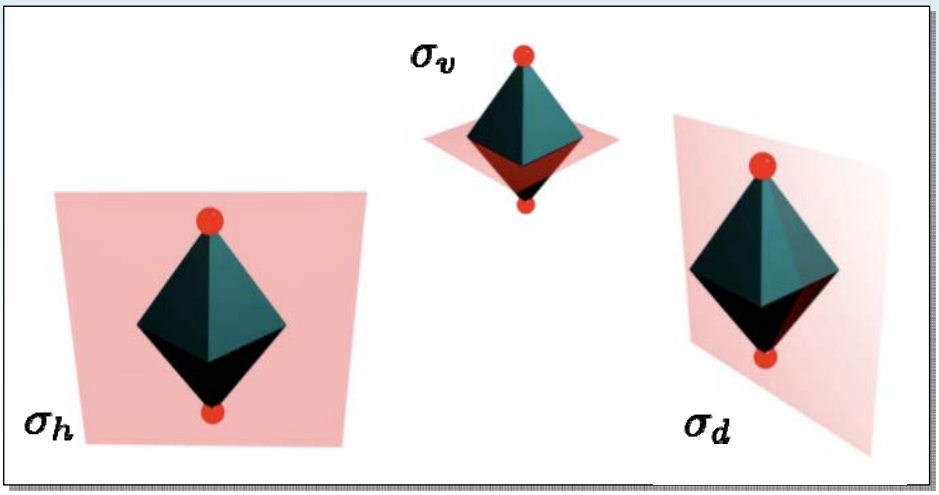
TABLE I. Symmetry operations in point groups (isolated molecules).

Inversion point

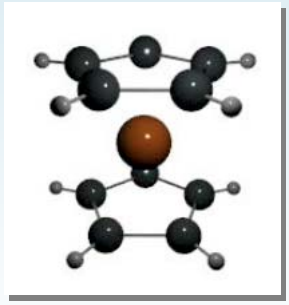
- Change coordinates of a point (*x*,*y*,*z*) to (-*x*,-*y*,-*z*)



Mirror planes

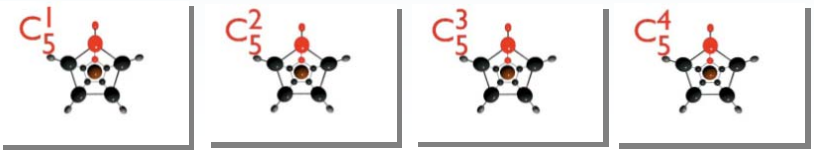


Proper rotations



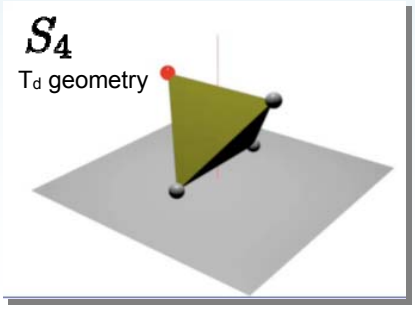
$Fe(C_5H_5)_2$
5-fold axis

C_n^k Signifies rotation of $2\pi k/n$



Improper rotations

- Combination of 2 operations
  1. Rotation C_n around an axis
  2. Inversion operation



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Symmetry operations – extension from molecules to crystals

- Crystals have translational symmetry

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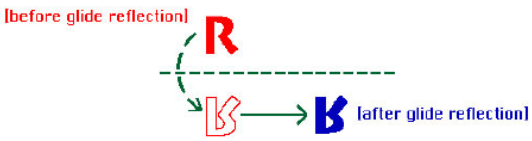
In crystalline solids there are 2 extra kinds of rotational and translational symmetry operation



A glide plane is a reflection and a translation

A screw-axis involves a rotation followed by a translation along the axis of rotation.

Symmetry operation	Symmetry element	Symbol
Rotation + translation	Screw axis	N_j
Reflection + translation	Glide plane	$a,\ b,\ c,\ n,\ d$

TABLE II. Additional symmetry operations present in extended solids (crystals).

Symmetry operations in solids

Symmetry operation	Symmetry element	Symbol
Identity (do nothing)		E
Rotation by $360°/n$ (a 'proper' rotation)	n-fold axis	C_n
Reflection	mirror plane	σ_v, σ_h or σ_d
Inversion	Centre of Inversion	i
Rotation by $360°/n$ followed by inversion (an 'improper' rotation)	n-fold axis + a centre of inversion	S_n

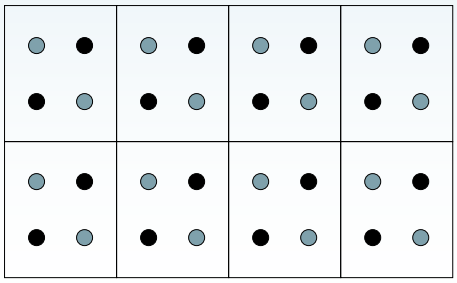
TABLE I. Symmetry operations in point groups (isolated molecules).

Rotation + translation	Screw axis	N_j
Reflection + translation	Glide plane	a, b, c, n, d

TABLE II. Additional symmetry operations present in extended solids (crystals).

And …
there is a very special translational symmetry

- The unit cell
- (Perhaps one of the most misunderstood symmetries as things often go wrong when there are moments involved)



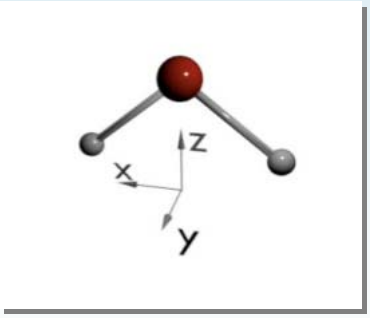
Groups - putting these operations together - point groups and space groups

G_0

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

  $AA^{-1}=A^{-1}A=E$
- (The order of a group is simply the number of elements in a group)
  - We will note the order of a group *h*.

Applying operations in sequence – the Multiplication table

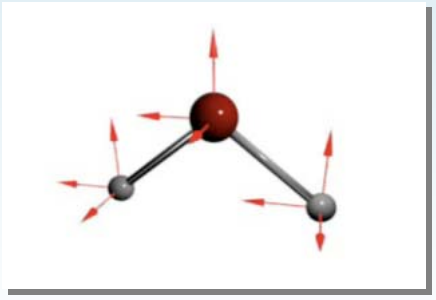


- 4 different operations

	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

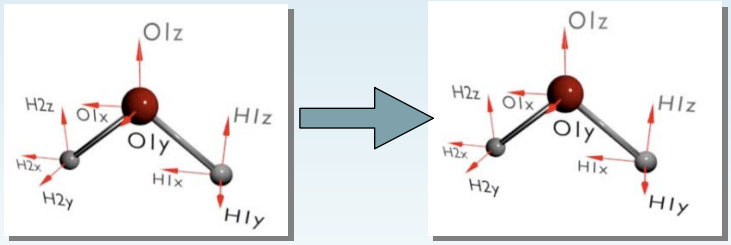
$$E,\ \sigma(xz),\ \sigma(yz),\ C_2(z)$$

Example of applying symmetry operations - H_2O modes



- A symmetry operation produces a linear transformation in the vector space, e.g. E

H_2O (E)



$$\begin{pmatrix} H1x' \\ H1y' \\ H1z' \\ H2x' \\ H2y' \\ H2z' \\ O1x' \\ O1y' \\ O1z' \end{pmatrix} = \begin{pmatrix} 1&0&0&0&0&0&0&0&0 \\ 0&1&0&0&0&0&0&0&0 \\ 0&0&1&0&0&0&0&0&0 \\ 0&0&0&1&0&0&0&0&0 \\ 0&0&0&0&1&0&0&0&0 \\ 0&0&0&0&0&1&0&0&0 \\ 0&0&0&0&0&0&1&0&0 \\ 0&0&0&0&0&0&0&1&0 \\ 0&0&0&0&0&0&0&0&1 \end{pmatrix} \begin{pmatrix} H1x \\ H1y \\ H1z \\ H2x \\ H2y \\ H2z \\ O1x \\ O1y \\ O1z \end{pmatrix}$$

$$\chi(E) = 9$$

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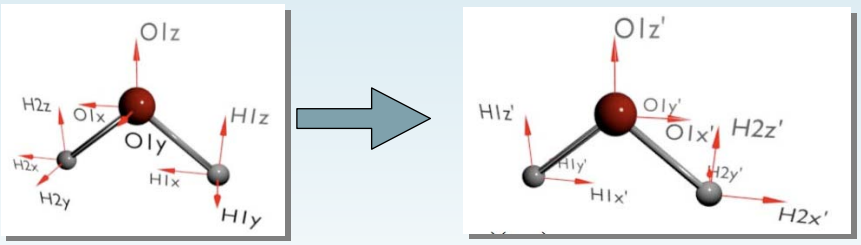
H_2O (C_2)



$$\begin{pmatrix} H1x' \\ H1y' \\ H1z' \\ H2x' \\ H2y' \\ H2z' \\ O1x' \\ O1y' \\ O1z' \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} H1x \\ H1y \\ H1z \\ H2x \\ H2y \\ H2z \\ O1x \\ O1y \\ O1z \end{pmatrix}$$

$$\chi(C_2) = -1$$

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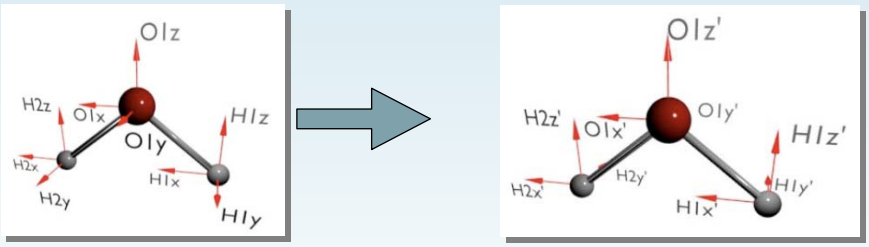
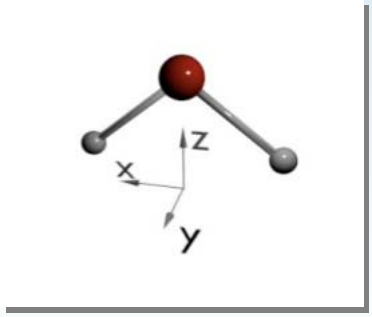
H_2O (σ_{xz})



$$\begin{pmatrix} H1x' \\ H1y' \\ H1z' \\ H2x' \\ H2y' \\ H2z' \\ O1x' \\ O1y' \\ O1z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} H1x \\ H1y \\ H1z \\ H2x \\ H2y \\ H2z \\ O1x \\ O1y \\ O1z \end{pmatrix}$$

$$\chi(\sigma_{xz}) = 3$$

Applying operations in sequence – the Multiplication table



- 4 different operations

	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

$$E,\ \sigma(xz),\ \sigma(yz),\ C_2(z)$$

Matrix representatives and matrix multiplications

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

$$\left(\begin{array}{cccccccc|cccccccc}
1&0&0&0&0&0&0&0&0&0&0&-1&0&0&0&0\\
0&-1&0&0&0&0&0&0&0&0&0&0&-1&0&0&0\\
0&0&1&0&0&0&0&0&0&0&0&0&0&1&0&0\\
0&0&0&1&0&0&0&0&-1&0&0&0&0&0&0&0\\
0&0&0&0&-1&0&0&0&0&-1&0&0&0&0&0&0\\
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0&0&0&0&0&0&1&0&0&0&0&0&0&0&-1&0\\
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\end{array}\right)
\left(\begin{array}{cccccccc|cccccccc}
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-1&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
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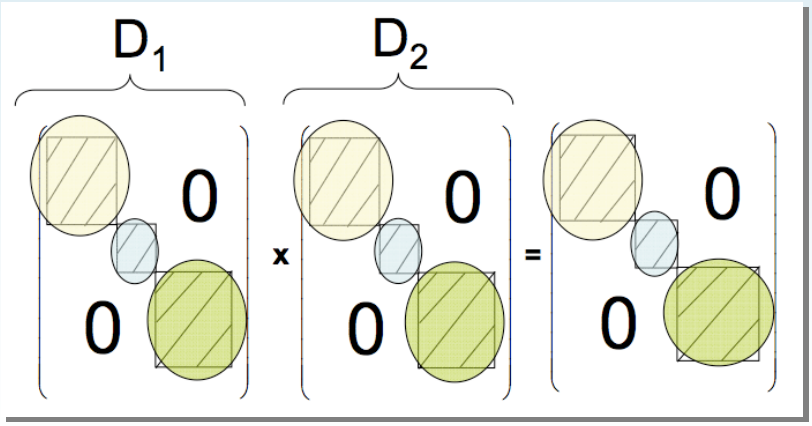
\end{array}\right)$$

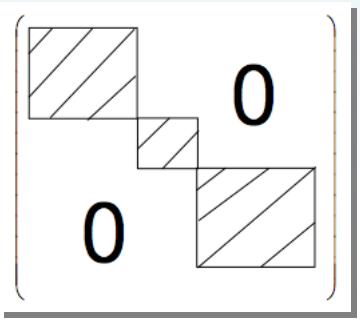
Block-diagonal matrices - Simplifying multiplication of matrix representatives



- Corresponding blocks are multiplied separately

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



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Irreducible representations and character tables

- In a finite group, there is a limited number of IRs
- IRs are described in character tables:
  - A table that list the symmetry operations horizontally, IRs labels vertically and corresponding characters

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

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Great Orthogonality theorem

- For two given IRs D_i and D_j, of dimension l_i and l_j respectively

$$\sum_{g\in G} D^i_{\alpha\beta}(g) D^j_{\alpha'\beta'}(g)^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij}\delta_{\alpha\alpha'}\delta_{\beta\beta'}$$

$$\sum_{g\in G} \left(\chi^i(g)\right)^2 = h$$

$$\sum_{g\in G} \chi^i(g)\chi^j(g)^* = 0$$

Consequences of the GOT

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

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

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

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

What irreducible representations are about…

Groups- and their irreducible representations

Irreducible representations

- a set of matrix representatives that have a homomorphism with the automorphism group of the object
  - automorphism= this is the symmetry of the object, a way of mapping an object to itself that preserves its structure
  - homomorphism=mapping between 2 algebraic structures, the algebraic structure of the group is preserved
- 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

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"*
  - (Cotton, Chemical Application of Group Theory)
- 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

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

Projection

- Projecting a vector of the vector space into the space of the IR gives the symmetry adapted basis vectors/modes

$$\hat{P}_{\lambda}^{\mu} = \sum_{g \in G} D_{\lambda\mu}(g)^* \hat{g}$$

- More about this later…

Pause!

Symmetry and magnetic structures -An introduction to the application of Representational Analysis to *Crystalline Solids*

Part 2 – From irreducible representations to their basis vectors –combining different types of symmetry

Andrew S. Wills

UCL Chemistry

Recap - Symmetry is a fundamental parameter in our understanding of physical phenomena

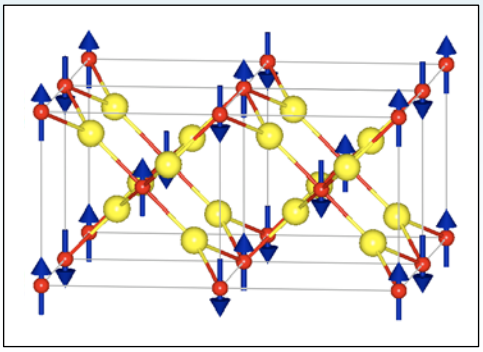
- Understanding symmetry enables a better description and analysis of electronic properties
- Symmetry formalisms (frameworks)
  - Point groups and individual molecules
    - Simple relationships between symmetry operations
  - Expand this homomorphism
    - Representations of symmetry types
    - These representations define fundamental symmetry types (irreducible representations). Other symmetries can be built by adding these together.

What language to use?

- Representations
  - Basic symmetry description in chemistry and physics
  - (Include antiunitary - time reversal - symmetry = corepresentational theory)
  - Provide the most complete/ general description of symmetry in crystalline solids
  - Used to describe the symmetries of
    - Electronic structures
    - Phonons
    - Magnetic structures
    - ***A common language to describe couplings***

A focus on some symmetries

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



The formalism of the propagation vector, ***k*** ***Translational symmetry***

- Eigenfunctions of a periodic Hamiltonian have the form of Bloch waves:

$$\vec{m}_{il} = \vec{\psi}_{i0} \exp\left(-2i\pi\vec{k}\cdot\vec{T}_{il-i0}\right)$$

- In general the moment of atom *i* in the *l*th unit cell is given by a Fourier sum:

$$\vec{m}_{il} = \sum_{k,j} \vec{\psi}_{i0}^{j,k} \exp\left(-2i\pi\vec{k}\cdot\vec{T}_{il-i0}\right)$$

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

Definition of magnetic structures, phonons, atomic displacements, electronic orbitals

- A linear combination of plane waves (basis vectors, Fourier components, Bloch waves)

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

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

The propagation vector

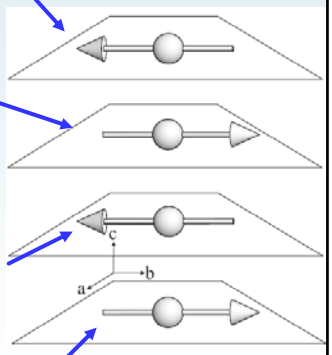
$$\vec{V}_j = \vec{V}_i \exp\left(-2\pi i \vec{k} \cdot \vec{t}\right)$$

$$\vec{V}_j = \vec{V}_i \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}\right] = \vec{V}_i \exp[-3\pi i] = -\vec{V}_i$$

$$\vec{V}_j = \vec{V}_i \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 2 \end{pmatrix}\right] = \vec{V}_i \exp[-2\pi i] = \vec{V}_i$$

$$\vec{V}_j = \vec{V}_i \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\right] = \vec{V}_i \exp[-\pi i] = -\vec{V}_i$$

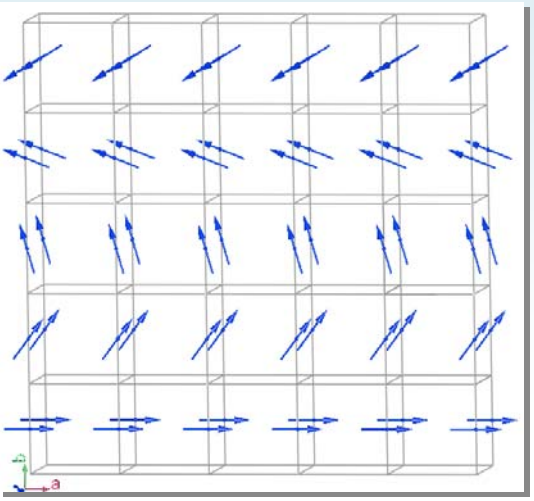
$$\vec{V}_j = \vec{V}_i \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}\right] = \vec{V}_i \exp[-2\pi i 0] = \vec{V}_i$$



The formalism of the propagation vector, ***k***

$$\vec{m}_{il} = \sum_{k,j} \vec{\psi}_{i0}^{j,k} \exp\left(-2i\pi \vec{k} \cdot \vec{T}_{il-i0}\right)$$

- 1 moment in the asymmetric unit (the primitive unit cell)
- Once ***k*** is defined, total degrees of freedom = 3



Space group G_0, k-vector and G_k

G_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 elements A,B,C… that leave the k-vector invariant $G_k \in G_0$

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

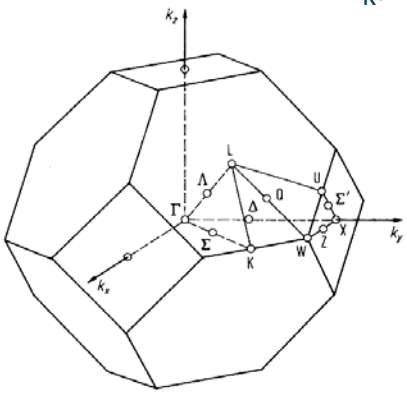
- i.e. defines those that are compatible with the translational symmetry of *k*

$$G_k \subseteq G_0$$

Different types of k vector

- Go around reciprocal space for a crystal structure and see how G_k changes
  - Example: G_0=*P*222 *(#16)* with *E*, C_{2x}, C_{2y}, C_{2z}
    - For ***k***=(0,0,0.5) G_k=*E*, C_{2x}, C_{2y}, C_{2z}
    - For ***k***=(0,0,0.51) G_k=*E*, C_{2z}
    - For ***k***=(0,0,0) G_k= *E*, C_{2x}, C_{2y}, C_{2z}
- The different types of k vector form the points, lines and planes in the Brillouin zone

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

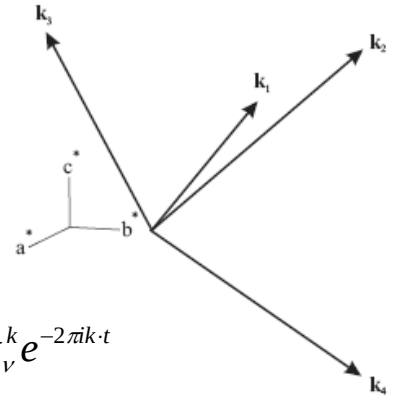


$$\vec{k}' = \vec{k}h + \vec{\tau}$$

- 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 Fd3m,

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



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

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 $A \in BG$
    - the product is associative A(BC)=(AB)C
    - there exists a unique identity (E)
    - every element has a unique inverse
    - $AA^{-1}=A^{-1}A=E$
  - Group has irreducible representations
    - G_k is also a space group

Irreducible Representations of Space Group G_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	$\begin{pmatrix} 1 & \cdot \\ \cdot & 1 \end{pmatrix}$	$\begin{pmatrix} \epsilon & \cdot \\ \cdot & \epsilon^* \end{pmatrix}$	$\begin{pmatrix} \epsilon^* & \cdot \\ \cdot & \epsilon \end{pmatrix}$	$\begin{pmatrix} \cdot & 1 \\ 1 & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \epsilon^* \\ \epsilon & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \epsilon \\ \epsilon^* & \cdot \end{pmatrix}$
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}	$-S_{2z}$	$-S_{1y}$	$-S_{3x}$

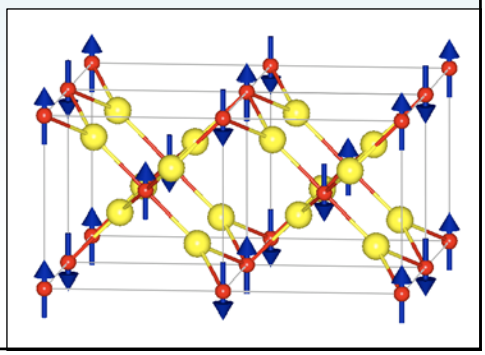
- Constructed from the little space group G_k
- Character tables are not enough
- Source is important- calculated or tabulated

Summary - Irreducible representations (IRs)

- Define the basic symmetry types for a group of symmetry operations
  - All 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
  - $\Gamma^{(1)}, \Gamma^{(2)}, \ldots, \Gamma^{(6)}$

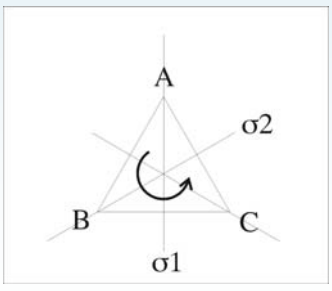
Projection of basis vectors

- What are we trying to do?
  - Find out what types of structure are possible for moments at atomic positions
- How?
- Look at these symmetries in turn
  - Permutation representation
    - How the atoms are interchanged under the symmetry operations of G_k
  - Axial vector representation
    - How the magnetic moments
    - are rotated under the
    - symmetry operations of G_k



The permutation representation Γ_{perm}

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



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

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

Permutation representation Γ_{perm}

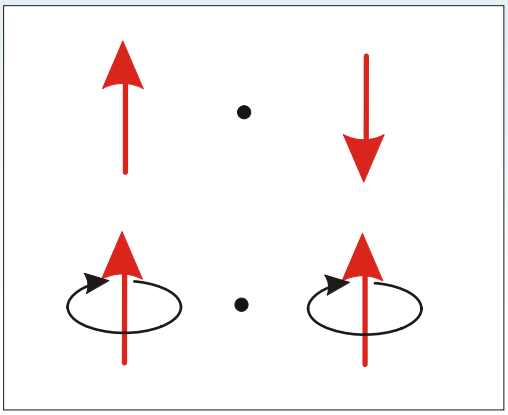
$$\Gamma^{E}_{perm}(P) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} \qquad \Gamma^{C_{2z}}_{perm}(P) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

The character of the permutation representation for a symmetry operation, $\chi_{perm}(g)$ is simply the number of position labels that are unchanged under its action, *e.g.* in this case

$$\chi_{perm}(C_{2z}) = 1$$

$$\chi_{perm}(E) = 3$$

Symmetry of magnetic moments and displacement vectors under inversion



Polar

Axial

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

Symmetry of magnetic moments and displacement vectors under improper rotations

Polar

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

Axial

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

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

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

- And so are their characters

$$\chi_{magnetic} = \chi_{permutation} \times \chi_{axial}$$

Putting it all together- the magnetic (displacement) representation

- The magnetic representation can be decomposed into IRs of G_k

$$\Gamma_{magnetic} = \sum_{\nu} n\Gamma_{\nu}$$

- The number of times IR Γ_ν appears is given by

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

Putting it all together- decomposing the magnetic (displacement) representation

- The number of times IR Γ_ν appears is given by $n_{\nu} = \frac{1}{n(G_k)} \sum_{g \in G_k} \chi_{\Gamma_{mag}}(g) \chi_{\Gamma_{\nu}}^{*}$

- This depends on the atomic site and may look like $\Gamma_{mag,2a} = 1\Gamma_1 + 0\Gamma_2 + 2\Gamma_3$

Basis functions

- Symmetry adapted functions that have the same symmetry at the IR- 'associated', non-unique
- Calculated using the projection operator

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

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

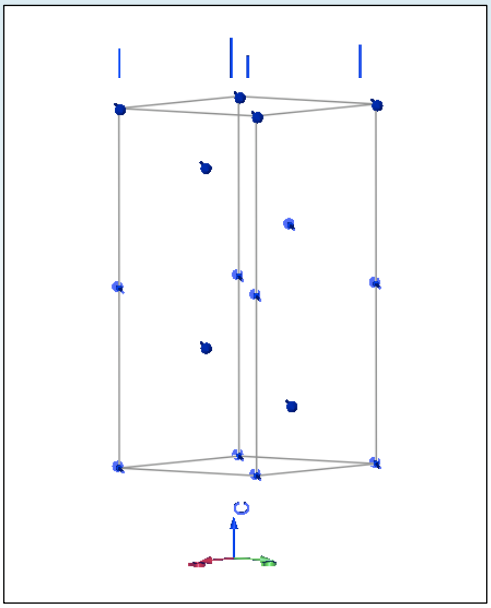
Basis vectors

- R3c
- $\boldsymbol{k}_{\text{primitive}}$=(1/2, 1/2, 1/2); $\boldsymbol{k}_{\text{hexagonal}}$=(0,0,3/2)
- Moment @ (0, 0, 0)

$\Gamma_{Mag} = 1\Gamma_1^{(1)} + 1\Gamma_2^{(1)} + 2\Gamma_3^{(2)}$.
The atoms are defined according to
1: (0, 0, 0), 2: (0, 0, .5)

IR	BV	Atom	BV components		
			$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$
Γ_1	1	1	0	0	0
		2	0	0	-1
	2	1	0	0	1
		2	0	0	0
Γ_2	3	1	1	0	0
		2	-1	0	0
	4	1	-1	-1	0
		2	-1	-1	0
Γ_3	5	1	1	-1	0
		2	1	-1	0
	6	1	-1	-2	0
		2	1	2	0

Basis vectors



ψ_1
ψ_2
ψ_3
ψ_4
ψ_5
ψ_6

Basis vectors

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

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

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…

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

  - They are equivalent
- A linear combination of basis vectors has the same symmetry

$$\psi_1 + \psi_1^* = 2Re(\psi_1)$$
$$(-i \times \psi_1) + (i \times \psi_1^*) = 2Im(\psi_1)$$

Projection of the basis vectors

- These have the symmetry of the IR that they are projected from

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

  - Non-unique
  - Visualisation of the degrees of freedom of the magnetic structure
  - Classification of their symmetry by IR
  - Structures are built from a linear combination of basis vectors

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

Projection of the basis vectors

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

- $\psi_n^{i\lambda}$ is the basis vector projected from the λth row of the nth irreducible representation
- $g \in G_k$ means that the sum is over the symmetry elements that are in the space group G_k
- $D_\nu^{\lambda *}(g)$ is the complex conjugate of the element of the matrix representative that is being examined: it is the λth row of the matrix representative of the νth irreducible representation, for symmetry operation g

Filter 4- Phase transition theory

- Landau Theory of a continuous transition
  - The rule of a single (co)representation becoming critical
  - ***<u>This is an assumption</u>***
    - In more complex Hamiltonians this rule may be relaxed
      - Specific representations mix, perhaps to form corepresentations, perhaps corepresentations will mix
    - Perhaps the transition is 1st order
      - Weakly 1st order (structure follows Landau theory with minor change)
      - Strongly first order (all bets are off!)

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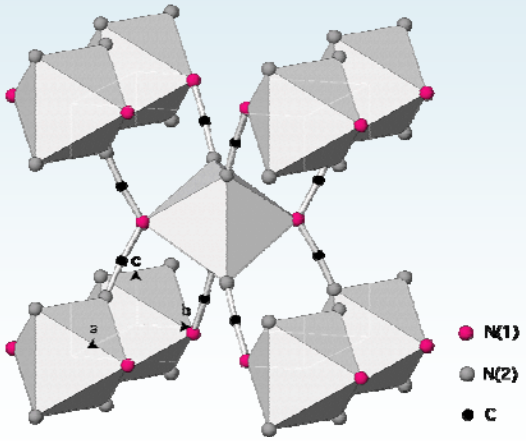
An example of <u>using</u> basis functions
-symmetry types that are <u>adapted</u> to the problem…

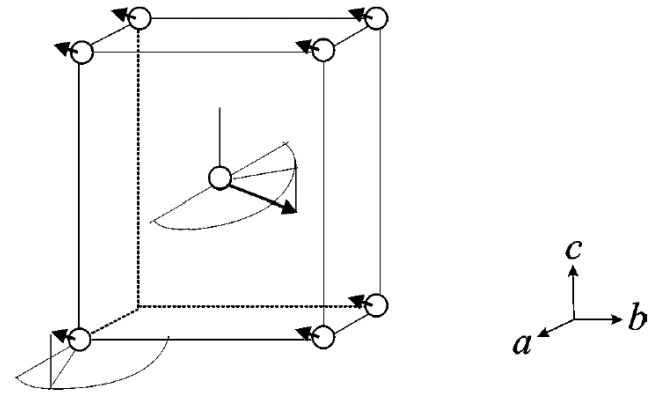
UCL

The Dzyaloshinsky-Moriya effect in
$Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ - canted ferromagnets



Pnnm

The Dzyaloshinsky-Moriya effect in $Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ - canted ferromagnets



C.R Kmety et al, Phys. Rev. B 62, 5576 (2000)

FIG. 11. Configuration of the Mn^{2+} magnetic moments in the unit cell. The corner and center arrows have same lengths, but they appear of different lengths due to the perspective view.

$Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ – possible magnetic structures

IR	BV	Basis vector components					
		m_{1a}	m_{1b}	m_{1c}	m_{2a}	m_{2b}	m_{2c}
Γ_1	ψ_1	0	0	1	0	0	-1
Γ_3	ψ_2	1	0	0	1	0	0
	ψ_3	0	1	0	0	-1	0
Γ_5	ψ_4	1	0	0	-1	0	0
	ψ_5	0	1	0	0	1	0
Γ_7	ψ_6	0	0	1	0	0	1

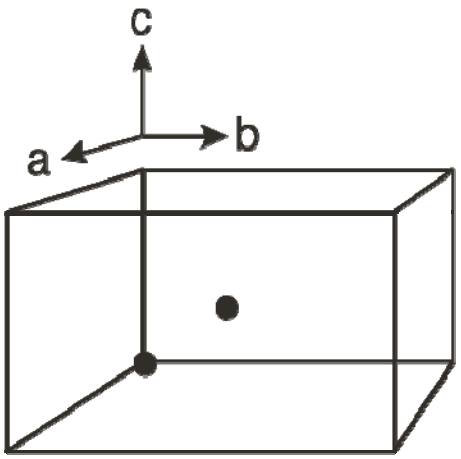
Space group P_{nnm}, k=(000), m_1=(0 0 0) and m_2=(.5 .5 .5)

$Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ – Linear combinations and possible magnetic

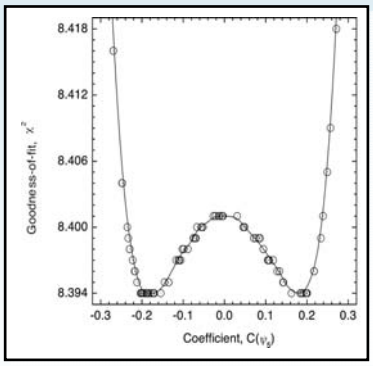
IR	BV	Basis vector components					
		m_{1a}	m_{1b}	m_{1c}	m_{2a}	m_{2b}	m_{2c}
Γ_1	ψ_1	0	0	1	0	0	-1
Γ_3	ψ_2	1	0	0	1	0	0
	ψ_3	0	1	0	0	-1	0
Γ_5	ψ_4	1	0	0	-1	0	0
	ψ_5	0	1	0	0	1	0
Γ_7	ψ_6	0	0	1	0	0	1

$$\vec{\Psi} = c_1\vec{\psi}_1$$
$$\vec{\Psi} = c_2\vec{\psi}_2 + c_3\vec{\psi}_3$$
$$\vec{\Psi} = c_4\vec{\psi}_4 + c_5\vec{\psi}_5$$
$$\vec{\Psi} = c_6\vec{\psi}_6$$

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

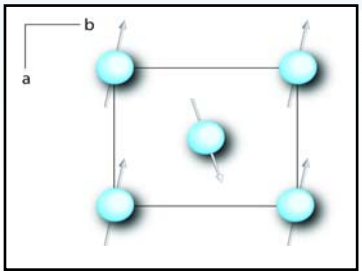


$Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$ – possible magnetic structures



For D-M interaction to exist, the antiferromagnetic and ferromagnetic state must have the same symmetry, i.e. Γ_3 or Γ_5

IR	BV	Basis vector components					
		m_{1a}	m_{1b}	m_{1c}	m_{2a}	m_{2b}	m_{2c}
Γ_1	ψ_1	0	0	1	0	0	-1
Γ_3	ψ_2	1	0	0	1	0	0
	ψ_3	0	1	0	0	-1	0
Γ_5	ψ_4	1	0	0	-1	0	0
	ψ_5	0	1	0	0	1	0
Γ_7	ψ_6	0	0	1	0	0	1



Landau Theory

- Continuous transitions (2nd order) involve
  - only ‘one IR’ becoming critical
  - no third order invariants
- Structure with mixed IRs
  - Sequential transitions
  - 1st order transition
  - Higher order contributions in Landau theory
  - Or a phase separated sample…

Landau Theory- When it doesn’t work it might still be useful :-)

- Irreducible representations ***still*** 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