Representation Theory in Magnetic Structure Analysis

-An introduction

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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 thus to simplify, clarify and reveal…)

Group theory (Representation Theory)

- **Symmetry is a framework and method**
  - Simplifies 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 (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.

Difficulties

- **Symmetries in solids are subtle**
  - A few hours to learn (!); a lot longer to master
  - They have to be
    - Look at what their job is!
  - Takes time to learn what electronic structures are possible and what they involve:

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

- But, the language of representations is one that we are used to from other contexts

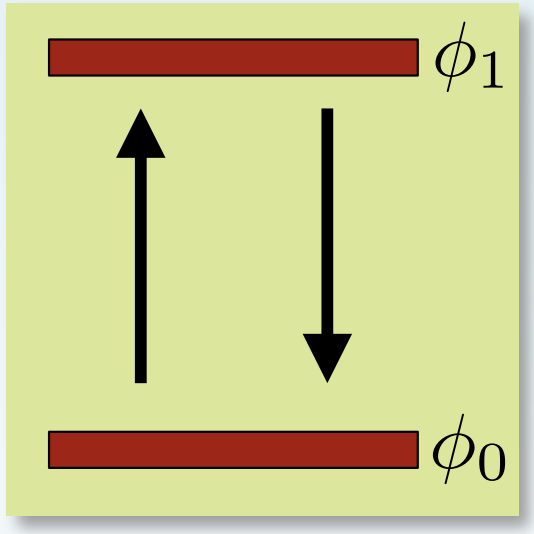
We have already seen that there is never enough information…

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

→ Under-defined problem
→ Hidden (unconsidered) possibilities

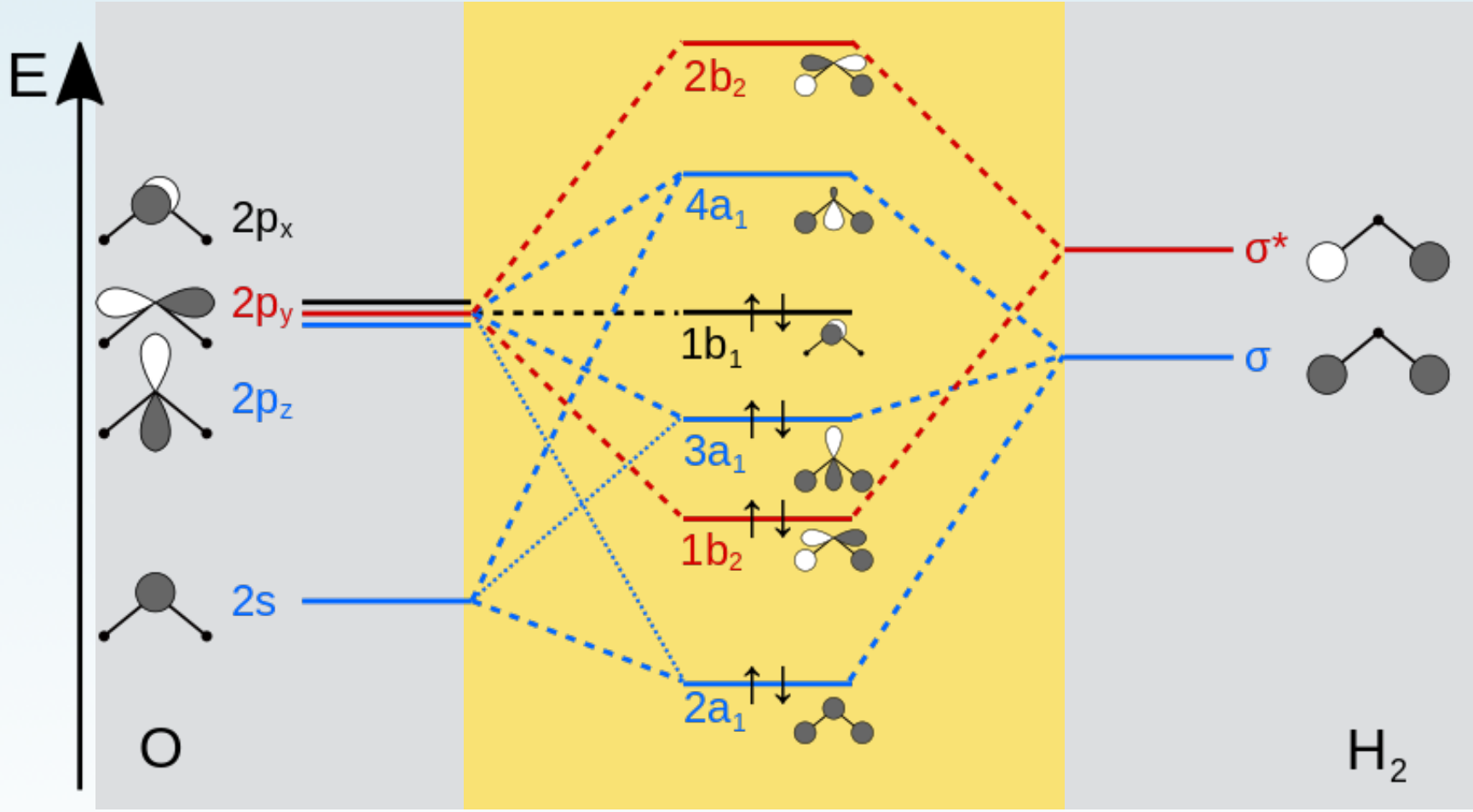
Spectroscopic transitions - working with eigenfunctions

- ground state, ϕ_0
- excited state, ϕ_1
- transition operator, $\hat{O}$
- transition integral $\int \phi_1^* \hat{O} \phi_0 \, d\tau = \left\langle \phi_1 | \hat{O} | \phi_0 \right\rangle$



- if ϕ_1 and $\hat{O}\phi_0$ have different symmetries, the integral is zero (use $\hat{O} = \hat{\mu}$ for IR, $\hat{O} = \hat{\alpha}$ for Raman, etc)

Molecular orbitals - interactions between AOs with same symmetry



Orbitals of central atom

Molecular orbitals are linear combinations of atomic orbitals

$$\Psi = \sum_i C_i \phi_i$$

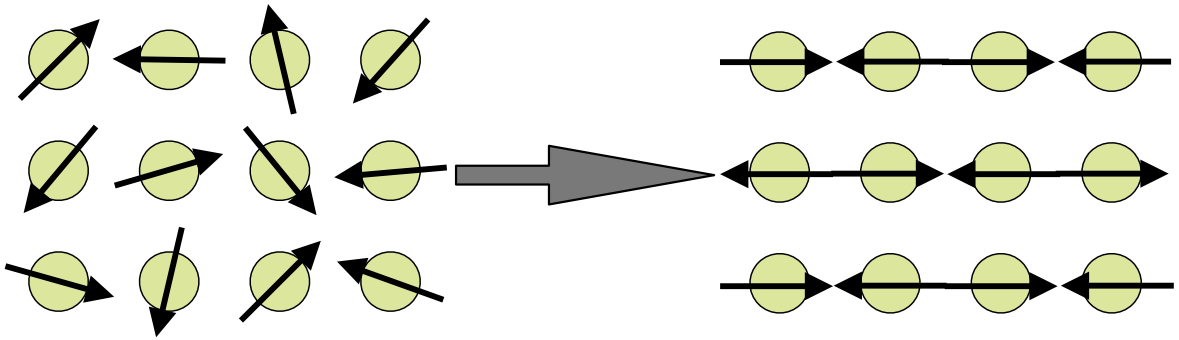
SALCs of H atoms

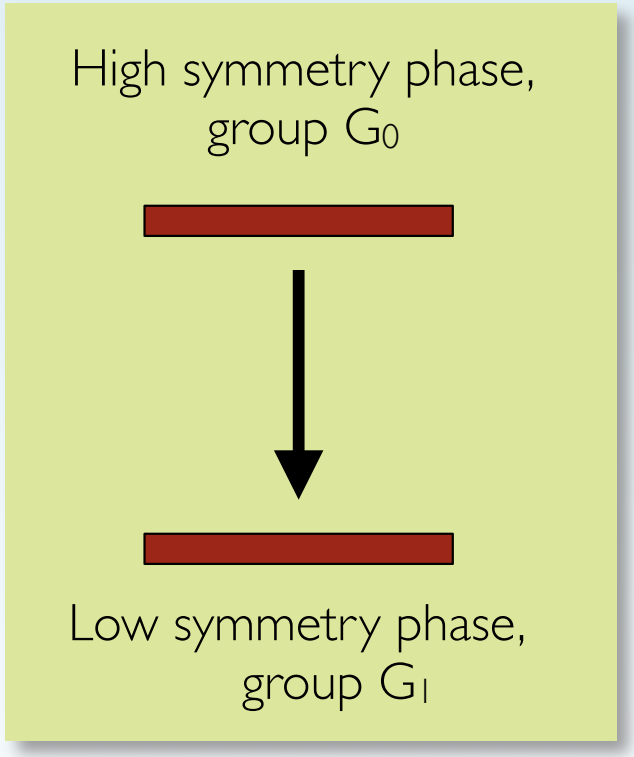
https://en.wikipedia.org/wiki/Molecular_orbital_diagram

Phase transitions in solids

- Phase transitions often involve going between phases with different symmetry
- Transition are classified as either 1st order (inhomogeneous) or 2nd order (homogeneous/ continuous)
- 2nd order transitions follow Landau theory
- A simple example:

  Paramagnetic → Antiferromagnetic





Symmetry operations are lost, e.g. "time-reversal", the symmetry under reversal of the electric current

Starting place - 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).

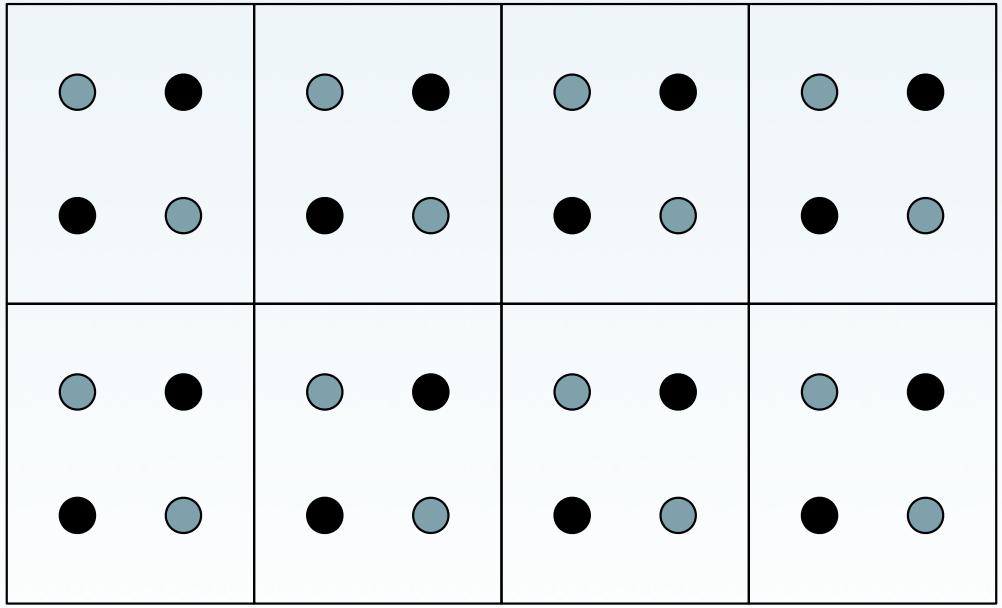
Rotation + translation	Screw axis	N_j
Reflection + translation	Glide plane	$a,\ b,\ c,\ n,\ d$

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

And …
there is 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

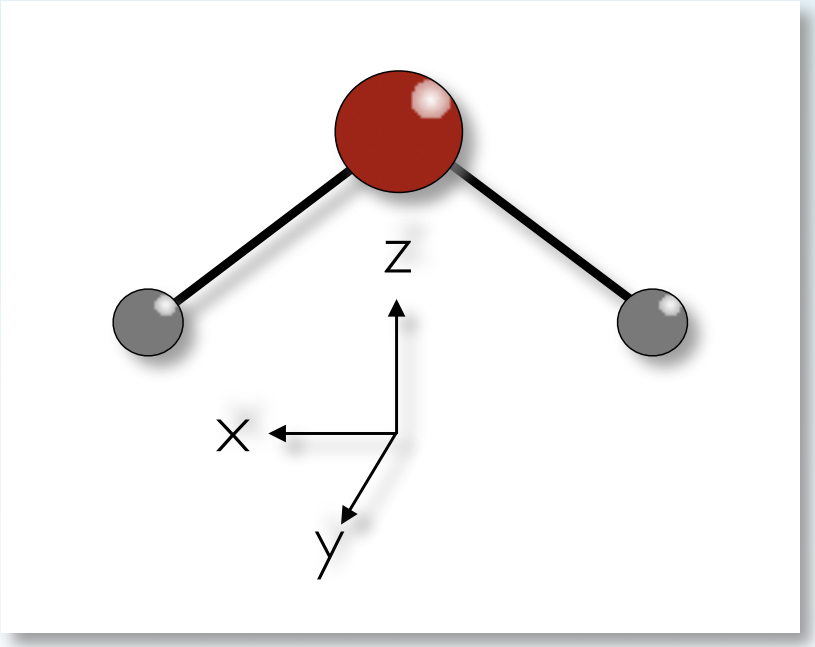
G_0

- 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

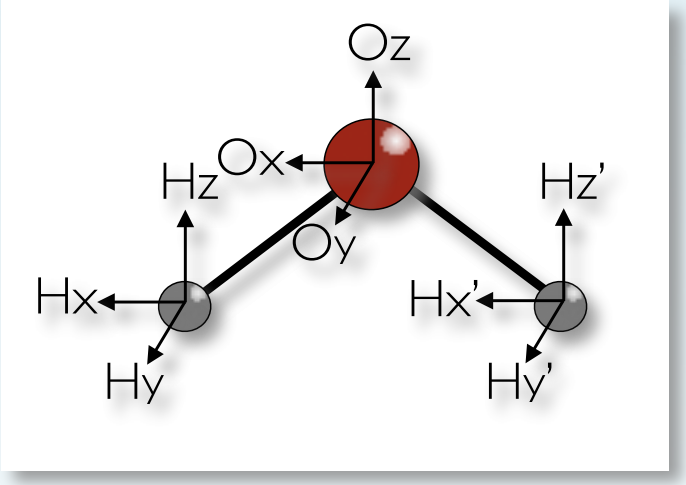


C_{2v}	E	$C_2(z)$	σ_{xz}	σ_{yz}
E	E	$C_2(z)$	σ_{xz}	σ_{yz}
$C_2(z)$	$C_2(z)$	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	$C_2(z)$
σ_{yz}	σ_{yz}	σ_{xz}	$C_2(z)$	E

- 4 different operations

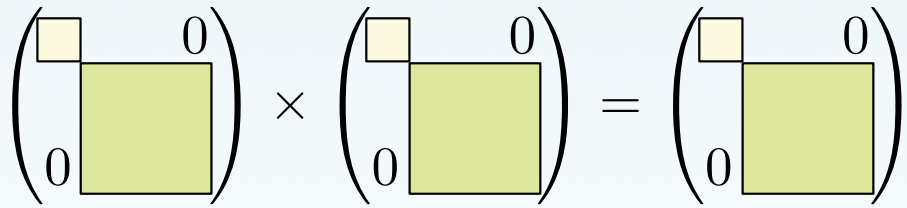
  C_{2v} E $C_2(z)$ σ_{xz} σ_{yz}

Block-diagonal matrices - Simplifying matrix representatives



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

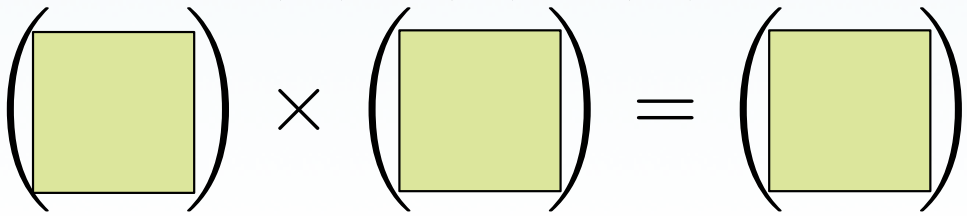
$$\begin{pmatrix} 1&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0\\ 0&0&0&1&0&0&0&0\\ 0&0&0&0&-1&0&0&0\\ 0&0&0&0&0&1&0&0\\ 0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&1 \end{pmatrix} \begin{pmatrix} 0&0&0&-1&0&0&0&0\\ 0&0&0&0&-1&0&0&0\\ 0&0&0&0&0&1&0&0\\ -1&0&0&0&0&0&0&0\\ 0&-1&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0\\ 0&0&0&0&0&0&-1&0\\ 0&0&0&0&0&0&0&-1\\ 0&0&0&0&0&0&0&1 \end{pmatrix} = \left(\begin{array}{ccc|ccc|ccc} 0&0&0&-1&0&0&0&0&0\\ 0&0&0&0&1&0&0&0&0\\ 0&0&0&0&0&1&0&0&0\\ \hline -1&0&0&0&0&0&0&0&0\\ 0&1&0&0&0&0&0&0&0\\ 0&0&1&0&0&0&0&0&0\\ \hline 0&0&0&0&0&0&-1&0&0\\ 0&0&0&0&0&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{array}\right)$$



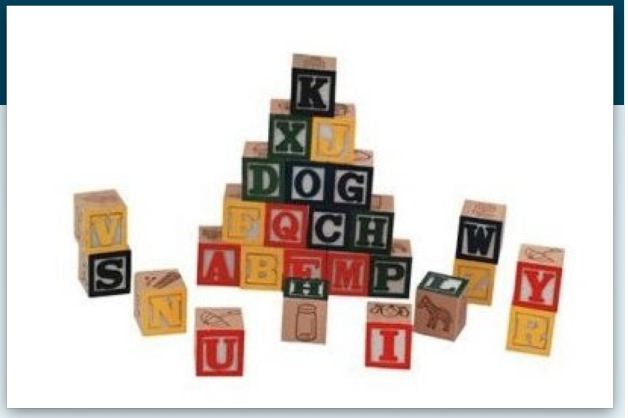
$$U\ D(g)\ U^{-1}$$

- Change to block structure. Blocks are multiplied separately

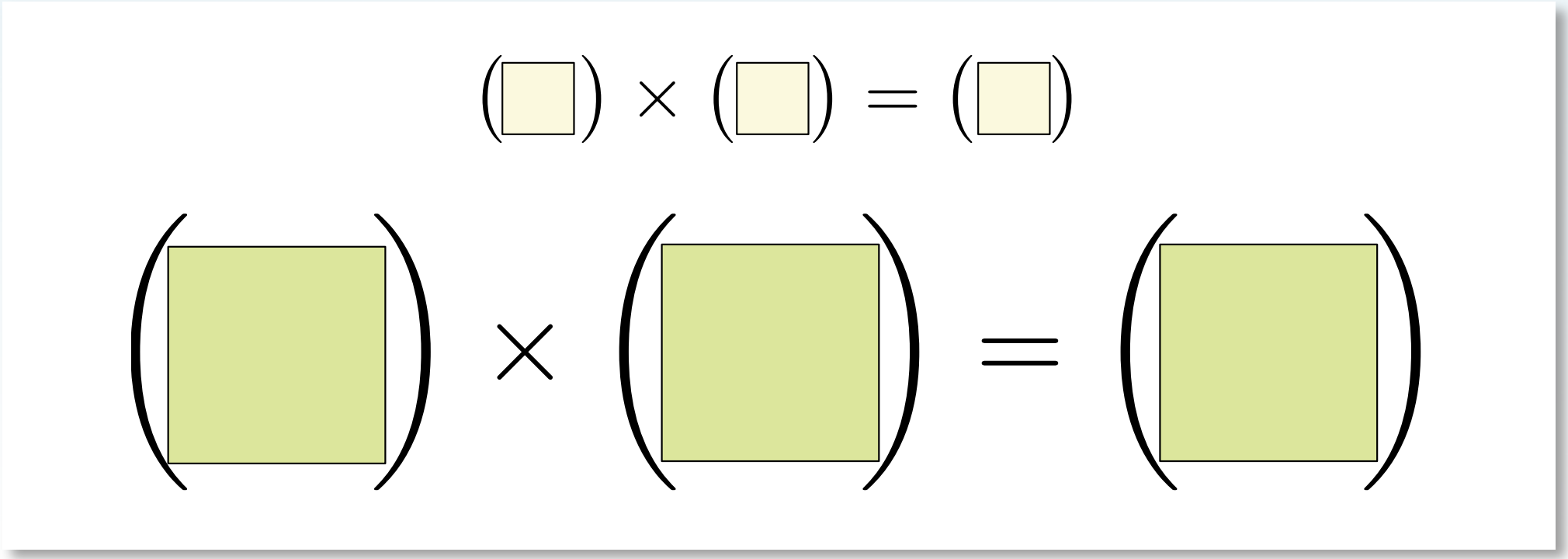
$$(\square) \times (\square) = (\square)$$



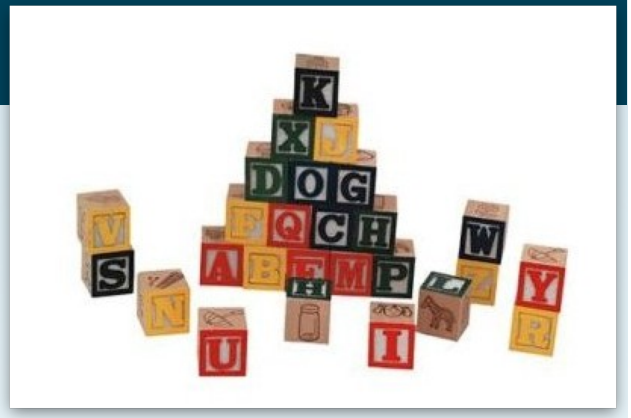
Irreducible representations



- 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 and the Great Orthogonality Theorem



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

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

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

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

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
  - "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)

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"
- 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

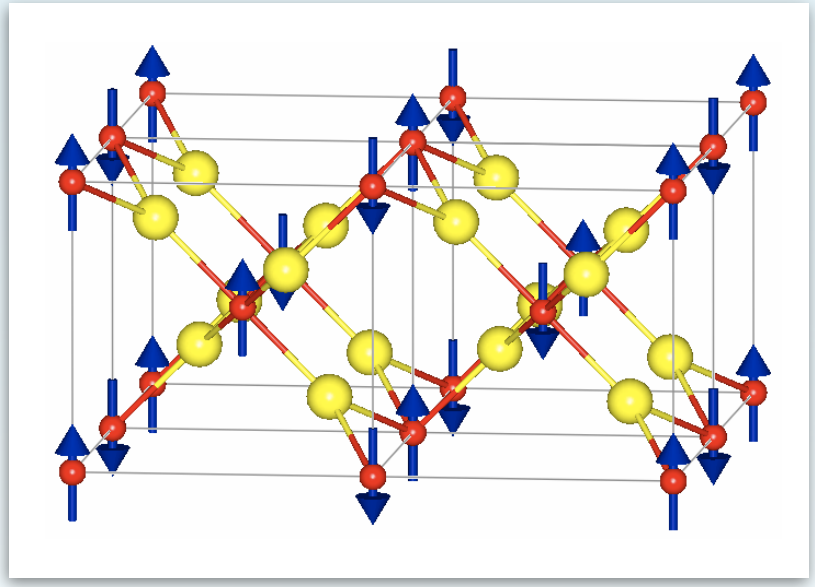
➡ Irreducible and fundamental - building blocks of symmetries

Irreducible Representations of Space Groups

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

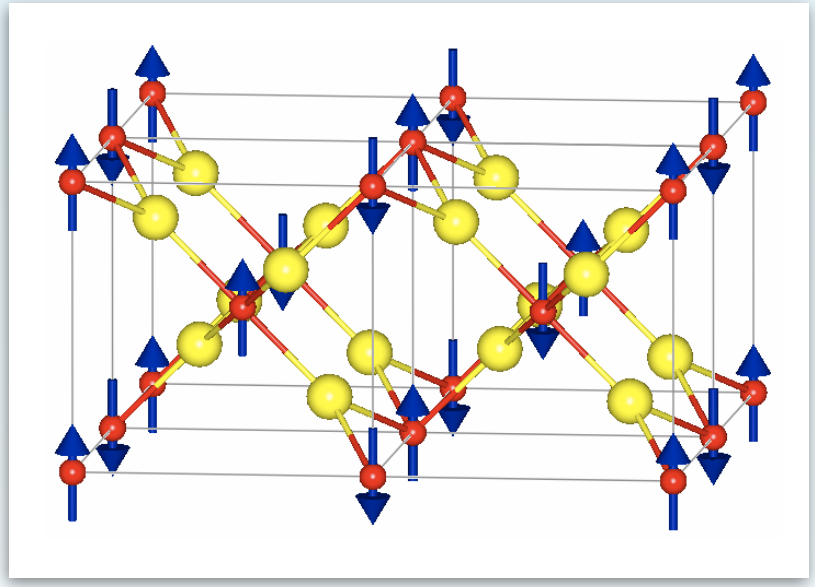
Symmetry operations			1	3	3^2	c or m	$c3$ or $m3$	$c3^2$ or $m3^2$
Representations								
Γ_1	A_1	τ_1	1	1	1	1	1	1
Γ_2	A_2	τ_2	1	1	1	−1	−1	−1
Γ_3	E	τ_3	$\begin{pmatrix} 1 & . \\ . & 1 \end{pmatrix}$	$\begin{pmatrix} \epsilon & . \\ . & \epsilon^* \end{pmatrix}$	$\begin{pmatrix} \epsilon^* & . \\ . &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

Material symmetries



0. Magnetic structures as Fourier sums
1. Space group (before the ordering), G_0
2. The ordering wave vector, $\boldsymbol{k}$
3. The symmetry that is compatible with $\boldsymbol{k}$, 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
7. Symmetry of the Hamiltonian

Material 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_k**
4. **The symmetries of G_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
7. Symmetry of the Hamiltonian

The propagation vector

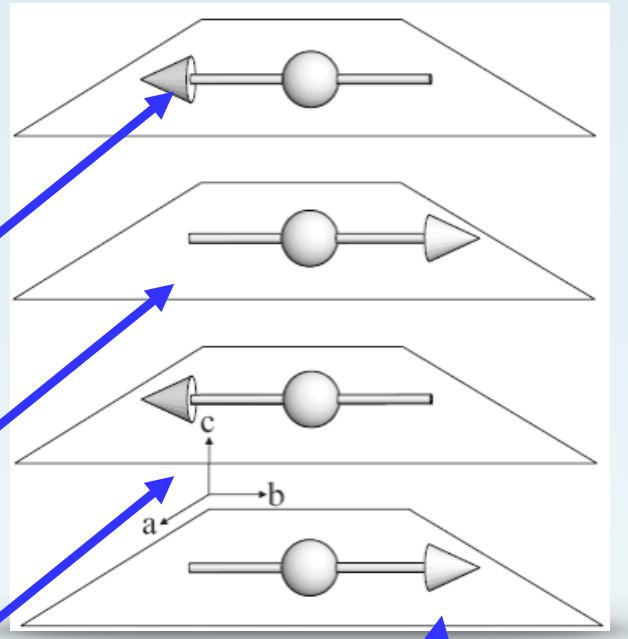
$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\, e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}} \quad \text{with} \quad \vec{\psi}^{\vec{k}}_{i,\nu} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 3 \end{pmatrix}\right] = -\vec{\psi}^{\vec{k}}_{i,\nu}$$

$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 2 \end{pmatrix}\right] = \vec{\psi}^{\vec{k}}_{i,\nu}$$

$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}\right] = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-\pi i\right] = -\vec{\psi}^{\vec{k}}_{i,\nu}$$

$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-2\pi i \begin{pmatrix} 0 \\ 0 \\ 0.5 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}\right] = \vec{\psi}^{\vec{k}}_{i,\nu}\, \exp\left[-2\pi i 0\right] = \vec{\psi}^{\vec{k}}_{i,\nu}$$



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

Constructing 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 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***

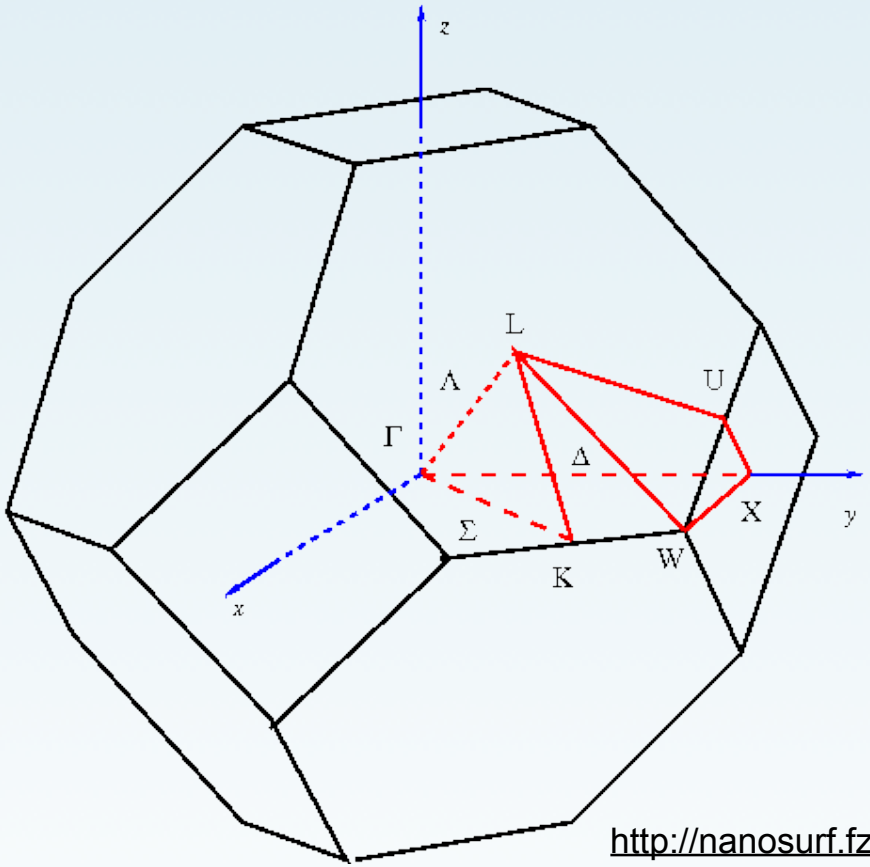
$$G_{\vec{k}} \subseteq G_0$$

Space group: G_0.
Space group of 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_k.

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



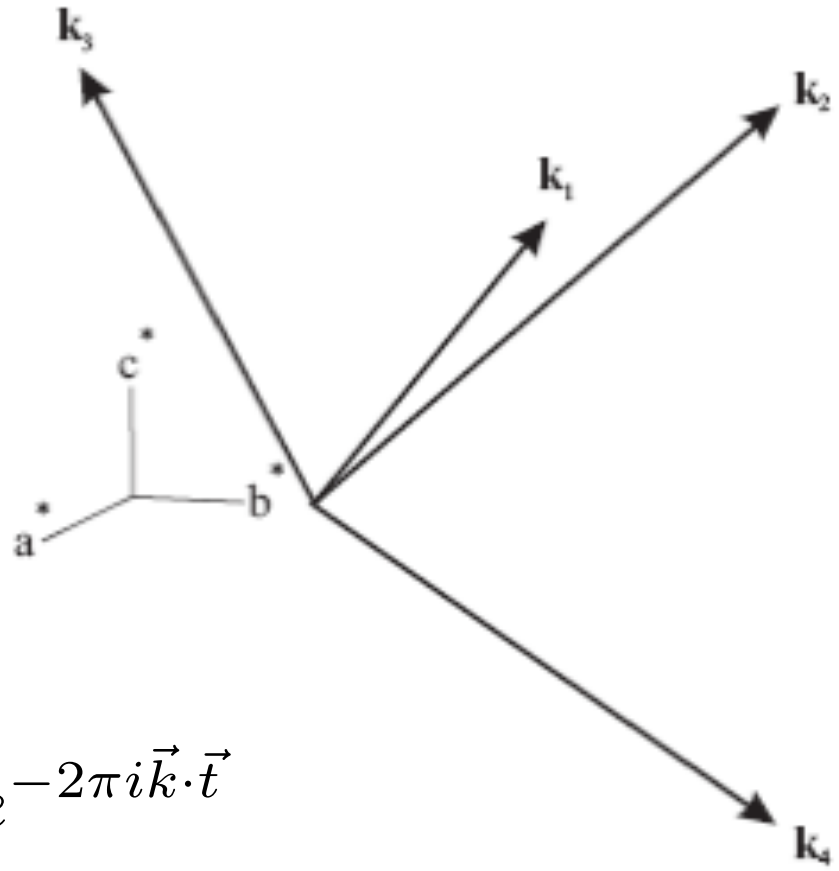
$$\vec{k}' = \vec{k}h \pm \vec{\tau}$$

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,

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



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

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 $A \in BG$
    - 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

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

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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 of lecture
Part 1- Recap of group theory and representations

- 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
  - Representations and irreducible representations (up to 6x6 matrices)

➡*Goal : starting to think about complex symmetry*

Next - Projection - making symmetry adapted functions

Projection of basis vectors : from IRs to BVs

–What are we trying to do?

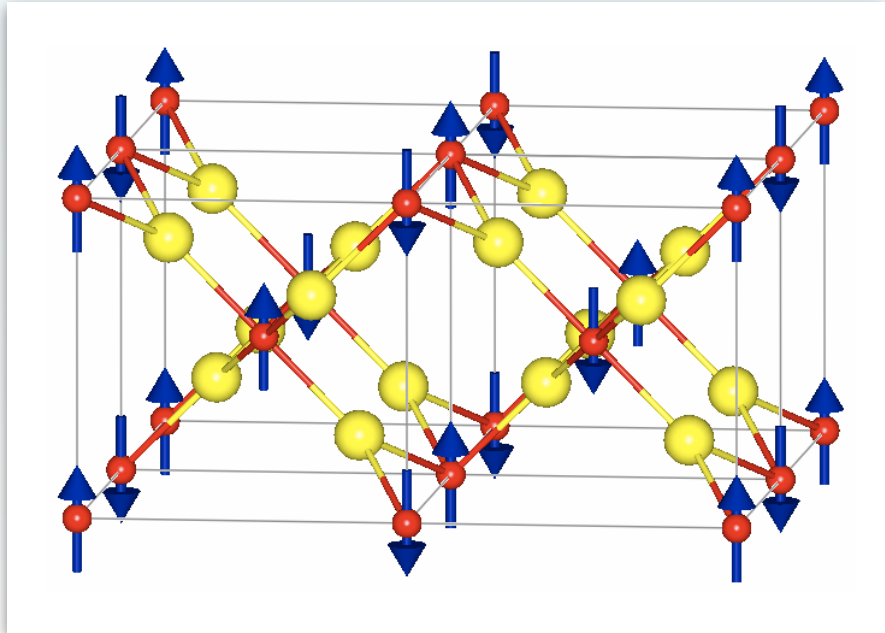
- Find out what types of structure are possible for moments at atomic positions

–How?

–Look at these symmetries in turn

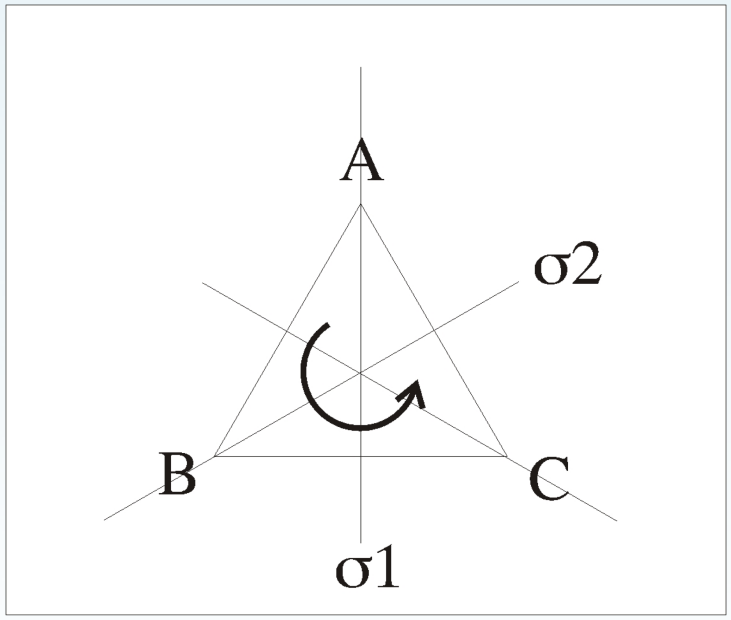
- Permutation representation
  - –How the atoms are interchanged under the symmetry operations of G_k
- Axial vector representation
  - –How the magnetic moments
  - –are rotated under the
  - –symmetry operations of G_k

–Decompose symmetries using IRs



The permutation representation Γ_{perm}

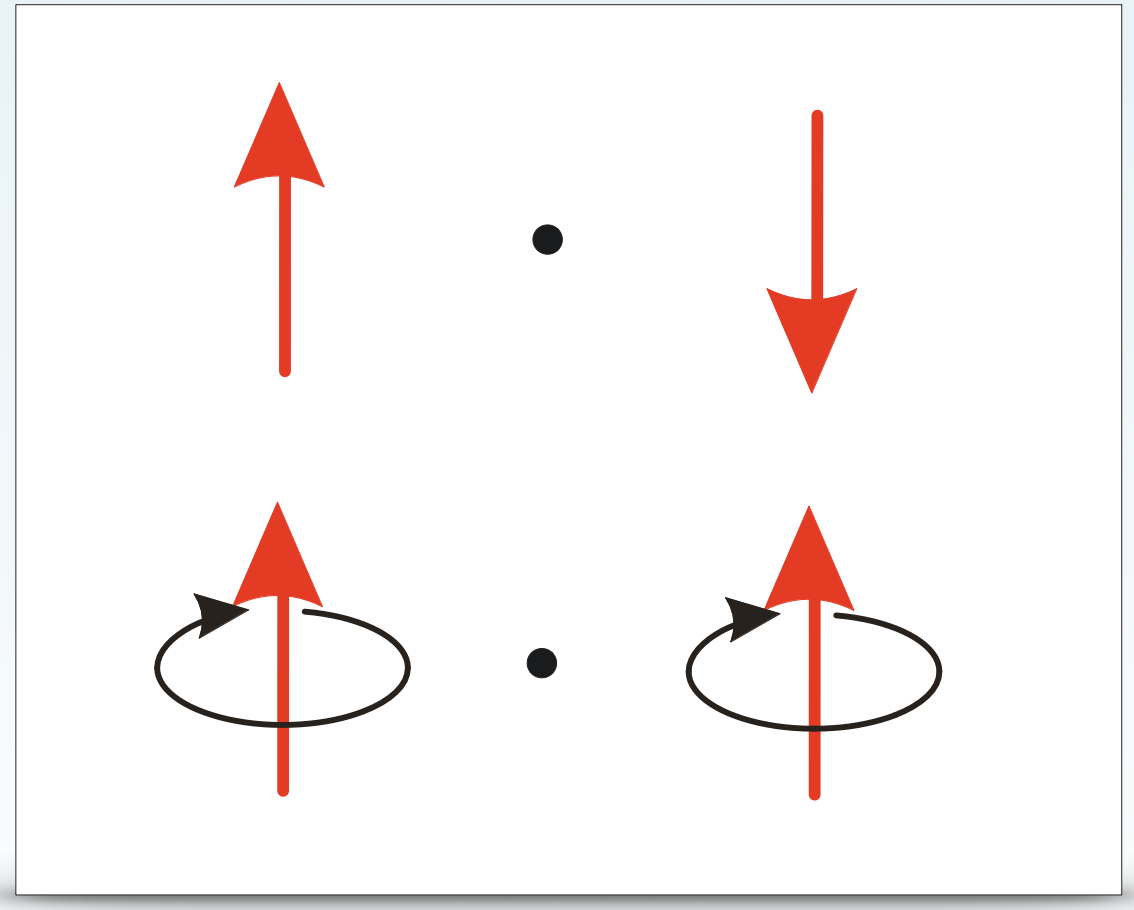
- Recap- a crystal structure is invariant under the symmetry operations of its point/space group. However, equivalent positions can be interchanged, permuted



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

- 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

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

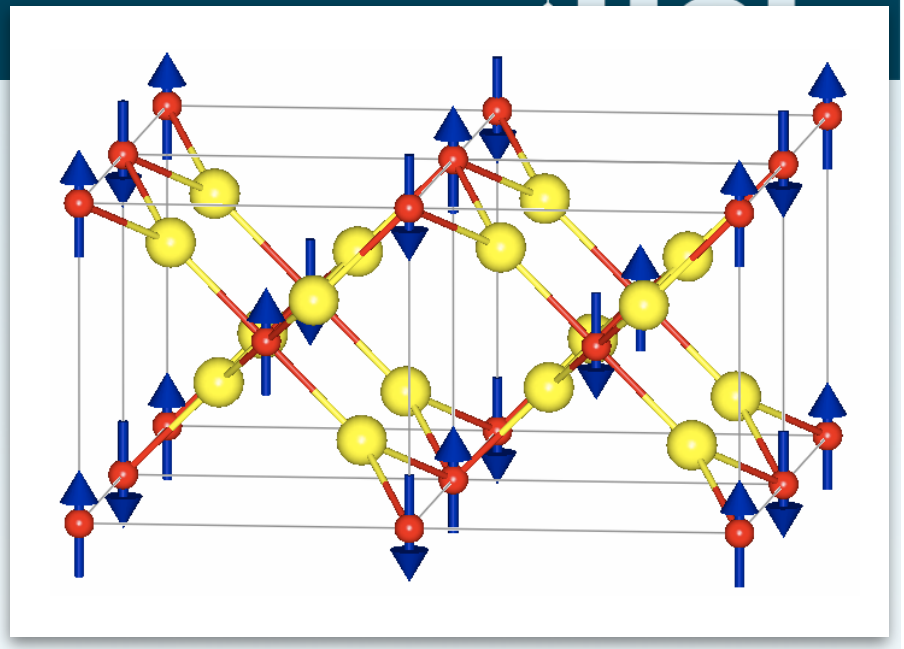
- This depends on the atomic site and may look like

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

or

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

Basis functions



- Symmetry adapted functions with the same symmetry as the IR- 'associated'. Not unique. Made by projection

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

and a series of test functions, e.g.

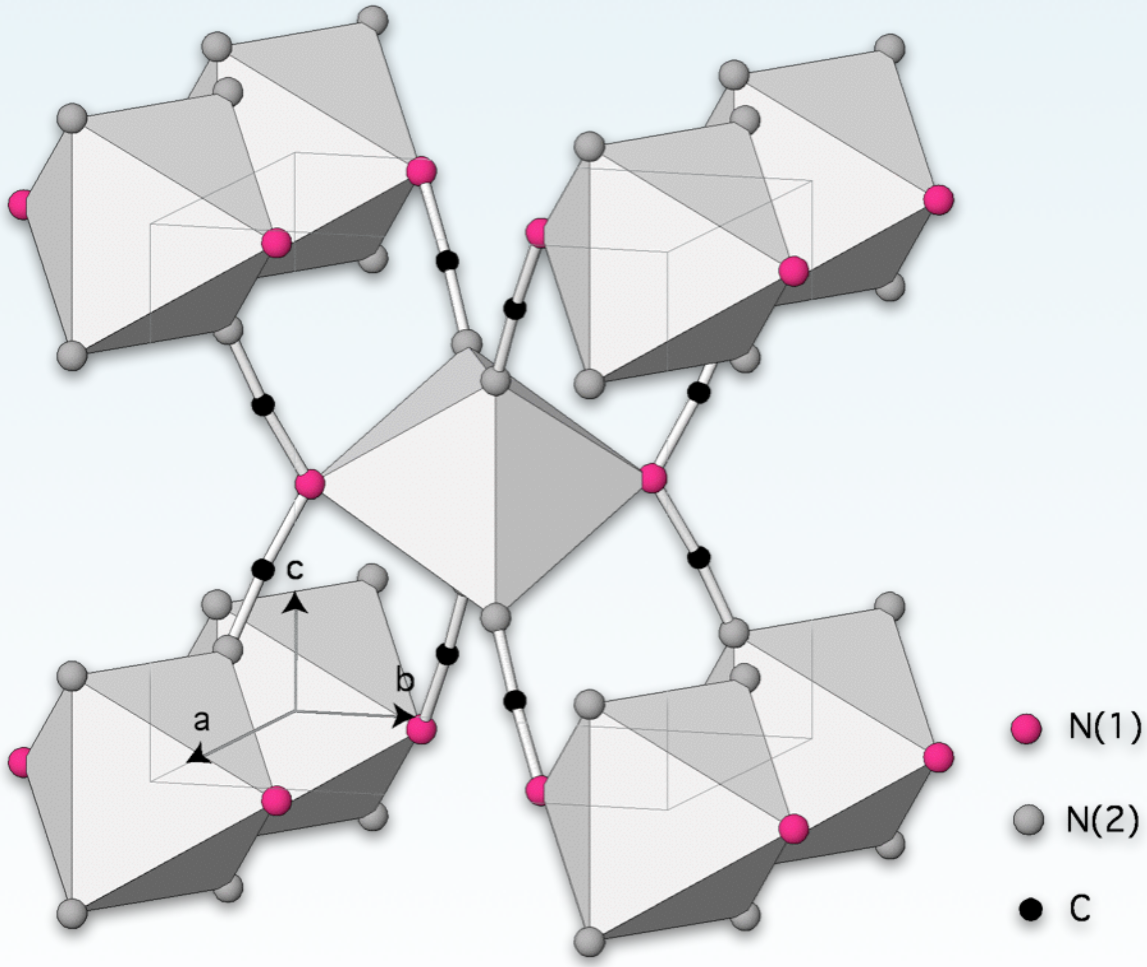
$$\vec{\phi}_1 = (1\ 0\ 0),\ \vec{\phi}_2 = (0\ 1\ 0), \vec{\phi}_3 = (0\ 0\ 1)$$

An example of using *basis functions and exploring basis vector spaces

---

*basis vectors
-symmetry types that are adapted to the problem…

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



Pnnm

A. Lappas et al, Phys. Rev. B 67, 144406 (2003)
A.S. Wills and A. Lappas, J. Phys. Chem. Solids 65, 65 (2004)

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

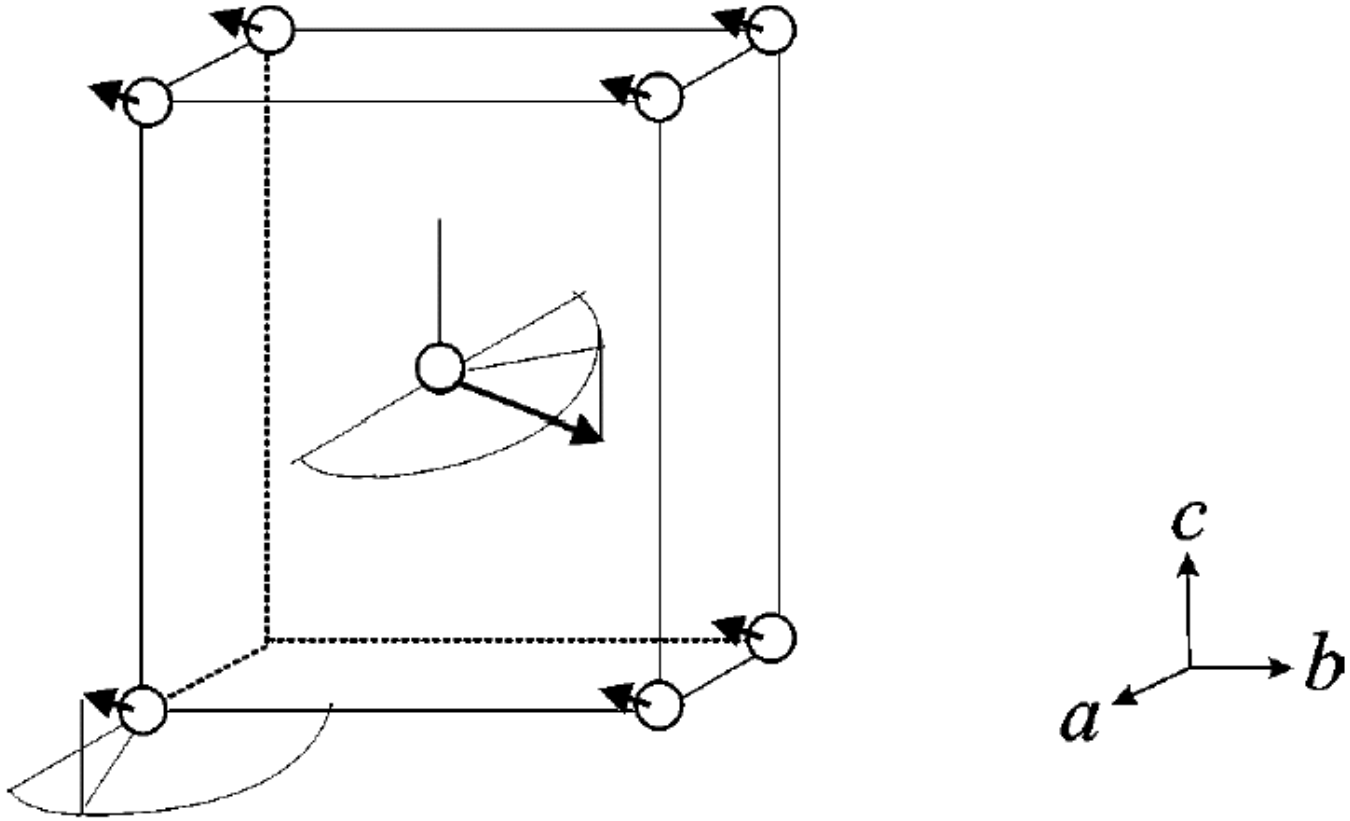


FIG. 11. Configuration of the Mn^{2+} magnetic moments in the unit cell. The corner and center arrows have same lengths, but they appear of different lengths due to the perspective view.

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

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

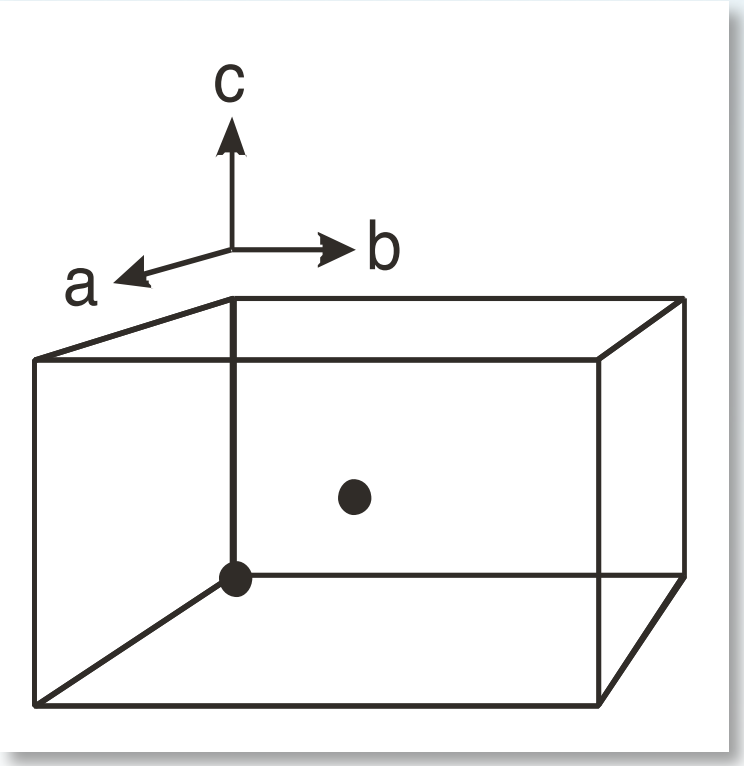
IR	BV	Basis vector components					
		m_{1a}	m_{1b}	m_{1c}	m_{2a}	m_{2b}	m_{2c}
Γ_1	ψ_1	0	0	1	0	0	-1
Γ_3	ψ_2	1	0	0	1	0	0
	ψ_3	0	1	0	0	-1	0
Γ_5	ψ_4	1	0	0	-1	0	0
	ψ_5	0	1	0	0	1	0
Γ_7	ψ_6	0	0	1	0	0	1

Space group Pnnm, k=(000), m1=(0 0 0) and m2=(.5 .5 .5)

$Mn[N(CN)_2]_2$ and $Fe[N(CN)_2]_2$

– Linear combinations and 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

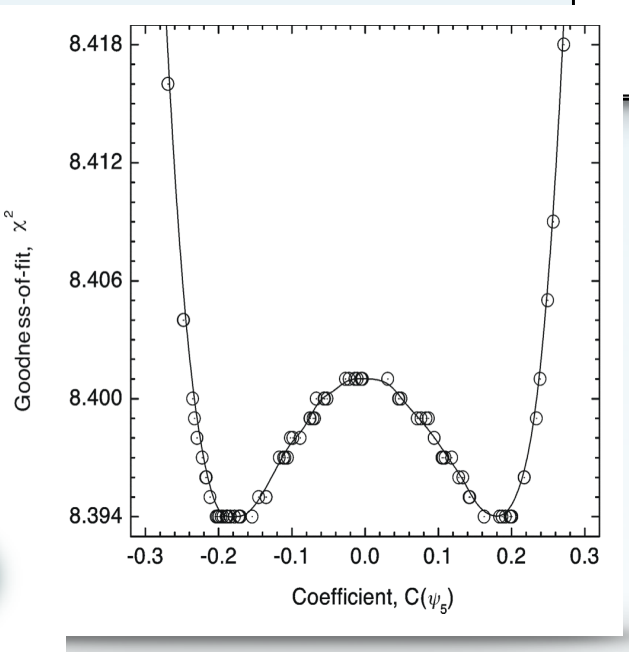


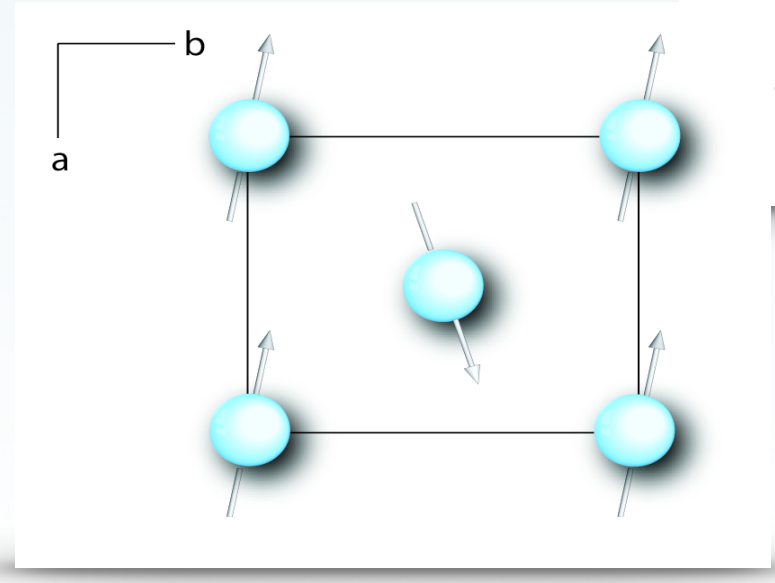
- $\vec{\Psi} = c_1\vec{\psi}_1$
- $\vec{\Psi} = c_2\vec{\psi}_2 + c_3\vec{\psi}_3$
- $\vec{\Psi} = c_4\vec{\psi}_4 + c_5\vec{\psi}_5$
- $\vec{\Psi} = c_6\vec{\psi}_6$

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

$Mn[N(CN)_2]_2$ 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
	ψ_6	0	0	1	0	0	1





For D-M interaction to exist, the antiferromagnetic and ferromagnetic components must have the same symmetry : Γ_3 and Γ_5

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

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

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 be sophisticated, e.g. for basis vectors related by complex conjugation

$$\vec{\psi}_1 + \vec{\psi}_1^* = 2Re(\vec{\psi}_1)$$

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

Putting it all together

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

C_{3v}	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

"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)

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	$\begin{pmatrix} 1 & \cdot \\ \cdot & 1 \end{pmatrix}$	$\begin{pmatrix} \epsilon & \cdot \\ \cdot & \epsilon^* \end{pmatrix}$	$\begin{pmatrix} \epsilon^* & \cdot \\ \cdot & \epsilon \end{pmatrix}$	$\begin{pmatrix} \cdot & 1 \\ 1 & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \epsilon^* \\ \epsilon & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \epsilon \\ \epsilon^* & \cdot \end{pmatrix}$

```
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)  +  i(     0     0     0)
ATOM  2:    (     0     0    -6)  +  i(     0     0     0)
*******

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

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

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

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

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

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

Summary of lecture
Part 2- To atomic moments

- From irreducible representations 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
  - Permutation representation
  - Axial and polar vectors, representations
  - Magnetic representation
  - Basis vectors

➡ *Goal : introduce the language for understanding magnetic structures*

Landau Theory

- **Continuous transitions (2nd order) have rules**
  - often - only one IR becoming critical
  - no third order invariants

- **Structure with mixed IRs are possible**
  - Sequential transitions
  - 1st order transition
  - Higher order contributions in Landau theory, e.g 4th order coupling terms
  - …

Some results of Landau theory

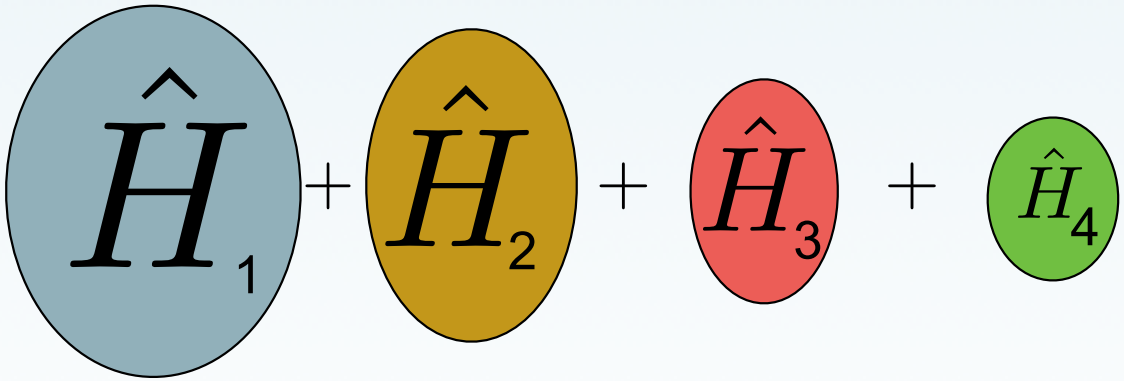
- 3rd order parameters
  - Stop the transition being second order
- The 'law' of ordering according to a single IR becoming critical
  - **A 'law' or a starting point?**
- Can a magnetic structure involve more than one IR?
  - Yes
    - If it does not introduce 3rd order invariants
    - If there is a coupling term. Remember transition integrals?

$$\int \phi_1^* \hat{O} \phi_0 \, d\tau$$

  - e.g. , the coupling could involve a secondary order parameter (mixing coefficients another IR)
    - Still have only a single T_c,
    - Does not drive the symmetry breaking
      - Would not break all the symmetry elements that the primary order parameter does
      - Causing the critical parameter to be larger
    - Have a smaller amplitude than the primary order parameter
    - The coupling creates polynomials in the free energy (typically we work with order 4)

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



Couplings and time reversal

- **Not all couplings come from Landau theory**
  - Antiunitary symmetry, e.g. complex conjugation in quantum mechanics $\psi^* \psi$
  - Corepresentation theory (Wigner)
    - There are 3 types of co-irreducible representations: a, b, c
      - a, are simple
      - b, built from 2 equivalent IRs
      - c ,built from 2 inequivalent IRs, i.e. combine IRs
  - Spins are quantum …

OK, I have data where do I go from here?

- **Do we know the k vector**
  - We hope
  - Do we know that there is more than one? Maybe…
- **Carry out representational analysis calculations for each separately**
- **Do we know which IR is primary?**
  - No, so cycle through IRs until you find it
  - At this point freely explore coefficients
- **Refine moment orientations**
  - Refine mixing coefficient combinations
  - Add basis vectors within IR if they improve fit
- **Add secondary IR if the fit is improved**
  - Search through mixing coefficient combinations
- **Add another k vector if there are peaks that do not line up**
  - » Repeat as needed

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
- **Representational analysis calculations do not get rid of degrees-of-freedom**
  - Symmetry is about classifying them
  - Deal with only a few variables at a time. More models, each with fewer variables
  - Order parameter directions mean even fewer at a time (only a couple may be active)
- **Basis vectors can be complex**
  - 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
- **Consider the information that is lost**
  - e.g. by powder or domain averaging

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?)
- **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)
- **Multiple phase transitions and 1st order transitions**
  - Typically high temperature one is 2nd order; the low temp one is 1st order (often involving another IR coming in)
  - 1st order does not follow Landau theory, but might (mostly). A sliding scale
  - Treat the 'single IR law' as a reference. Look for where it is broken and think about what this means!
- **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")
  - Work out what the necessity is
    - Think about why!
    - There lies the fun…
    - There lies the physics

➡ Use with symmetry to help define the question '**why**'

Summary of lecture
Part 3 - Phase transitions

- Introduction to Landau theory
  - Continuous phase transitions
  - Opening the door - a zeroth order approximation
  - Energy scales - a hand waving approach
  - Couplings - food for thought
  - Symmetry and phase transitons
- My 'building-up' principle

➡ *Goal : Using necessity - Ockham's razor. Necessity is a clear observation that allows you to ask why it is needed, e.g. single-k, multi-k, single IR, mixed IRs, which BVs*