Magnetic Representational Analysis with SARAh and SARAh-Refine

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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)
    - ***We don't know the Hamiltonian !***
  - Useful to introduce a grand **simplifying structure** (makes rules, classes of behaviour, and thus to simplify, clarify and reveal…)
    - ***The difference between ingredients and menus…***

Why use symmetry?

- Electronic structures are complex
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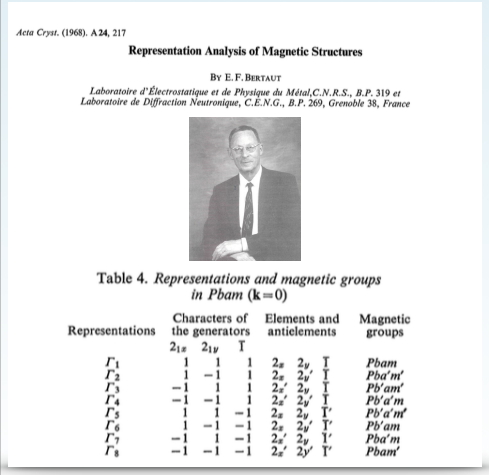
Group theory (and magnetism)

- 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'*

1949
1951
1953

1968

- **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 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 ze translation t is given by

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

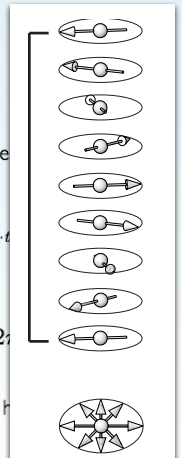
  - Substitution and expansion of the exponential leads to

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

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

➡***Requires non parallel BVs***

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



j) elliptical helix

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

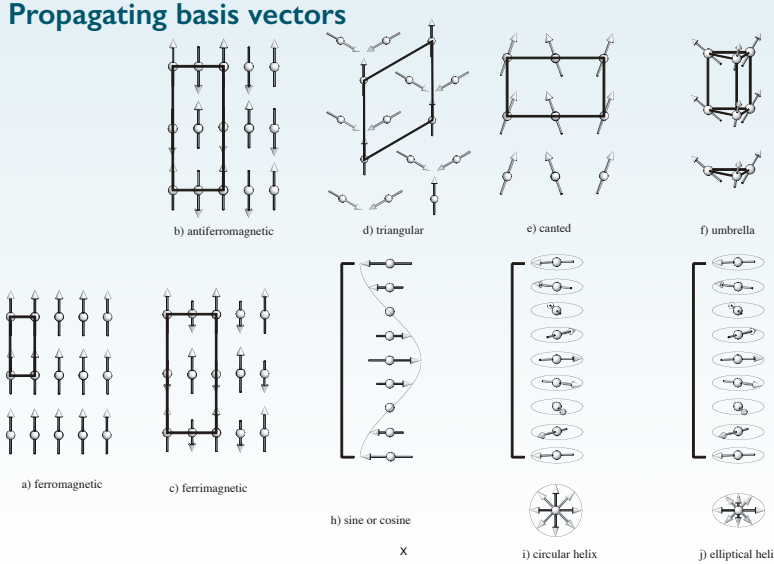
- The linear combination of basis vectors can involve complex numbers (phase relationships)

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

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

Look at interactive Pdf

Propagating basis vectors



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

"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)

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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)
ATOM  2:  (     0     0    -6)  +  1(     0     0     0)
******

IR  # 3, BASIS VECTOR: #   1 (ABSOLUTE NUMBER:# 2)
ATOM  1:  (     0     0     6)  +  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 vibrational modes (basis vectors) associated with the Irreducible Representations (IRs)

Magnetic structures - built from 2 length scales

1. **basis vectors**
   - Build up symmetry within primitive unit cell, G_0

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

2. **k-vector**
   - Propagate (a component of) the magnetic structure through the crystal to moments related by lattice translation, i.e. a primitive lattice vector
   - Define translational periodicity and corresponding orientation dependence

Which moments are related by symmetry?

CONTINUED No. 227 $F\,d\,\bar{3}\,m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(0,\frac{1}{2},\frac{1}{2})$; $t(\frac{1}{2},0,\frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			Reflection conditions
			$(0,0,0)+$	$(0,\frac{1}{2},\frac{1}{2})+$	$(\frac{1}{2},0,\frac{1}{2})+$	$(\frac{1}{2},\frac{1}{2},0)+$	General: h,k,l permutable
192	i	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(3) $\bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$	hkl : $h+k=2n$ and $h+l,k+l=2n$
			(5) z,x,y	(6) $z+\bullet,\bar{x}+\bullet,y+\bullet$	(7) $\bar{z}+\bullet,\bar{x}+\bullet,y+\bullet$	(8) $\bar{z}+\bullet,x+\bullet,\bar{y}+\bullet$	$0kl$: $k+l=4n$ and $k,l=2n$
			(9) y,z,x	(10) $\bar{y}+\bullet,z+\bullet,\bar{x}+\bullet$	(11) $y+\bullet,\bar{z}+\bullet,\bar{x}+\bullet$	(12) $\bar{y}+\bullet,\bar{z}+\bullet,x+\bullet$	hhl : $h+l=2n$
			(13) $y+\bullet,x+\bullet,\bar{z}+\bullet$	(14) $\bar{y}+\bullet,\bar{x}+\bullet,\bar{z}+\bullet$	(15) $y+\bullet,\bar{x}+\bullet,z+\bullet$	(16) $\bar{y}+\bullet,x+\bullet,z+\bullet$	$h00$: $h=4n$
			(17) $x+\frac{1}{4},z+\frac{1}{4},\bar{y}+\frac{1}{4}$	(18) $\bar{x}+\frac{1}{4},z+\frac{1}{4},y+\frac{1}{4}$	(19) $\bar{x}+\frac{1}{4},\bar{z}+\frac{1}{4},\bar{y}+\frac{1}{4}$	(20) $x+\frac{1}{4},\bar{z}+\frac{1}{4},y+\frac{1}{4}$	
			(21) $z+\frac{1}{4},y+\frac{1}{4},\bar{x}+\frac{1}{4}$	(22) $z+\frac{1}{4},\bar{y}+\frac{1}{4},x+\frac{1}{4}$	(23) $\bar{z}+\frac{1}{4},y+\frac{1}{4},x+\frac{1}{4}$	(24) $\bar{z}+\frac{1}{4},\bar{y}+\frac{1}{4},\bar{x}+\frac{1}{4}$	
			(25) $\bar{x},\bar{z},\bar{y}$	(26) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}+\bullet$	(27) $x+\frac{1}{2},\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(28) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	
			(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z}+\bullet,x+\bullet,y+\bullet$	(31) $z+\bullet,x+\bullet,\bar{y}+\bullet$	(32) $z+\bullet,\bar{x}+\bullet,y+\bullet$	
			(33) $\bar{y},\bar{z},\bar{x}$	(34) $y+\bullet,\bar{z}+\bullet,x+\bullet$	(35) $\bar{y}+\bullet,z+\bullet,x+\bullet$	(36) $y+\bullet,z+\bullet,\bar{x}+\bullet$	
			(37) $\bar{y}+\frac{1}{4},\bar{x}+\frac{1}{4},\bar{z}+\frac{1}{4}$	(38) y,x,z	(39) $\bar{y}+\frac{1}{4},x+\frac{1}{4},z+\frac{1}{4}$	(40) $y+\frac{1}{4},\bar{x}+\frac{1}{4},z+\frac{1}{4}$	
			(41) $\bar{x}+\frac{1}{4},\bar{z}+\frac{1}{4},y+\frac{1}{4}$	(42) $x+\frac{1}{4},\bar{z}+\frac{1}{4},\bar{y}+\frac{1}{4}$	(43) x,z,y	(44) $\bar{x}+\frac{1}{4},z+\frac{1}{4},\bar{y}+\frac{1}{4}$	
			(45) $\bar{z}+\frac{1}{4},\bar{y}+\frac{1}{4},x+\frac{1}{4}$	(46) $\bar{z}+\frac{1}{4},y+\frac{1}{4},\bar{x}+\frac{1}{4}$	(47) $z+\frac{1}{4},\bar{y}+\frac{1}{4},\bar{x}+\frac{1}{4}$	(48) z,y,x	
							Special: as above, plus
96	h	$..2$	$0,x,\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},z+\bullet$	$\frac{1}{2},y+\frac{1}{2},y+\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2}$	no extra conditions
			$\bar{x},0,y$	$\bar{x}+\bullet,z+\bullet,\bar{x}+\bullet$	$y+\frac{1}{2},x+\frac{1}{2},y+\frac{1}{2}$	$y+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2}$	
			$y,\bar{x},0$	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	$y+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$	$\bar{x}+\bullet,y+\frac{1}{2},z+\frac{1}{2}$	
			$0,\bar{x},y$	$\frac{1}{2},y+\frac{1}{2},y+\frac{1}{2}$	$\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2}$	$\frac{1}{2},y+\frac{1}{2},\bar{x}+\frac{1}{2}$	
			$y,0,\bar{x}$	$y+\bullet,z+\bullet,\bar{x}+\bullet$	$\bar{x}+\bullet,\bar{x}+\bullet,\bar{y}+\bullet$	$\bar{x}+\bullet,\bar{x}+\bullet,y+\bullet$	
			$\bar{y},y,0$	$y+\bullet,y+\bullet,\bullet$	$\bar{y}+\bullet,\bar{y}+\bullet,\bullet$	$y+\bullet,\bar{y}+\bullet,\bullet$	
96	g	$..m$	x,x,z	$\bar{x}+\bullet,\bar{x}+\bullet,z+\bullet$	$\bar{x}+\bullet,x+\bullet,\bar{z}+\bullet$	$x+\bullet,\bar{x}+\bullet,\bar{z}+\bullet$	no extra conditions
			z,x,x	$z+\bullet,\bar{x}+\bullet,\bar{x}+\bullet$	$\bar{z}+\bullet,\bar{x}+\bullet,x+\bullet$	$\bar{z}+\bullet,x+\bullet,\bar{x}+\bullet$	
			x,z,x	$\bar{x}+\frac{1}{2},z+\frac{1}{2},\bar{x}+\frac{1}{2}$	$x+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{x}+\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},x+\frac{1}{2}$	
			$x+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	$\bar{x},\bar{x},\bar{z}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	
			$x+\frac{1}{2},z+\frac{1}{2},\bar{x}+\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},x+\frac{1}{2}$	$\bar{x},\bar{z},\bar{x}$	$x+\frac{1}{2},\bar{z}+\frac{1}{2},x+\frac{1}{2}$	
			$z+\frac{1}{2},x+\frac{1}{2},\bar{x}+\frac{1}{2}$	$z+\frac{1}{2},\bar{x}+\frac{1}{2},x+\frac{1}{2}$	$\bar{z}+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$	$\bar{z},\bar{x},\bar{z}$	
48	f	$2..mm$	$x,\frac{1}{4},\frac{1}{4}$	$\bar{x}+\frac{1}{2},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},x,\frac{1}{4}$	$\frac{1}{4},\bar{x}+\frac{1}{2},\frac{1}{4}$	hkl : $h=2n+1$ or $h+k,l=4n$
			$\frac{1}{4},x+\frac{1}{2},\frac{1}{4}$	$\frac{1}{4},\bar{x},\frac{1}{4}$	$x+\frac{1}{2},\frac{1}{4},\frac{1}{4}$	$\bar{x}+\frac{1}{2},\frac{1}{4},x+\frac{1}{2}$	
32	e	$.3m$	x,x,x	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},x+\frac{1}{2}$			no extra conditions
			$\bar{x}+\frac{1}{2},x+\frac{1}{2},\bar{x}+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2}$			
			$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2}$	$\bar{x},\bar{x},\bar{x}$			
			$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},x+\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$			
16	d	$\bar{3}..m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	hkl : $h=2n+1$ or $h+k,l=4n+2$ or $h,k,l=4n$
16	c	$.\bar{3}..m$	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	
8	b	$\bar{4}.3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$			hkl : $h=2n+1$ or $h+k,l=4n$
8	a	$\bar{4}.3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$			

Symmetry of special projections

Along [001] $p4mm$
$\mathbf{a} = \frac{1}{2}(\mathbf{a}-\mathbf{b})$ $\mathbf{b} = \frac{1}{2}(\mathbf{a}+\mathbf{b})$
Origin at $\frac{1}{4},\frac{1}{4},z$

Along [111] $p6mm$
$\mathbf{a} = \frac{1}{3}(2\mathbf{a}-\mathbf{b}-\mathbf{c})$ $\mathbf{b} = \frac{1}{3}(-\mathbf{a}+2\mathbf{b}-\mathbf{c})$
Origin at x,x,x

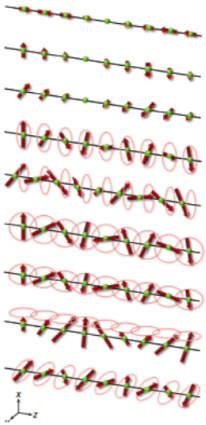
Along [110] $c2mm$
$\mathbf{a} = \frac{1}{2}(-\mathbf{a}+\mathbf{b})$ $\mathbf{b} = \mathbf{c}$
Origin at $x,x,0$

576 Variables (done badly) Down to 144…

48 or 12?

Atomic moments in a crystalline environment

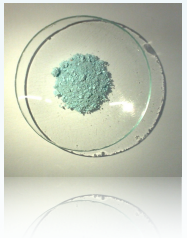
Point group symmetry of spin chains



	Point group		
	No lattice	Cubic lattice	Hexagonal lattice
Collinear longitudinal	∞/mm1′	4/mmm1′	6/mmm1′
Collinear transversal	mmm1′	mmm1′	mmm1′
Collinear transversal oblique	12/m11′	12/m11′	12/m11′
Proper screw	∞21′	4221′	6221′
Conical screw	∞2′	42′2′	62′2′
Cycloid	2mm1′	2mm1′	2mm1′
Elliptical cycloid	2mm1′	2mm1′	2mm1′
Transverse cone	2′mm′	2′mm′	2′mm′
Elliptical oblique cycloid	1m11′	1m11′	1m11′

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…

Landau theory - second-order phase transitions

- The minimum in free energy defines the equilibrium state

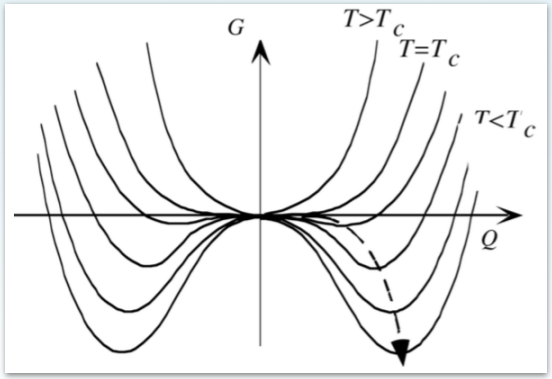
$$\left(\frac{\partial G}{\partial Q}\right)_{Q_0} = 0, \left(\frac{\partial^2 G}{\partial Q^2}\right)_{Q_0} > 0$$

- 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



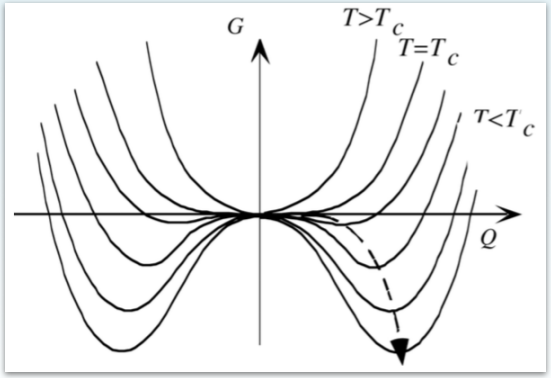
For $T > T_c$, $r(T) > 0$

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



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

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

Assuming r is linear in $T \rightarrow$ Use $r(T - T_c)$,

where T_c is the critical temperature

$$G = G_0 + \frac{1}{2} r(T - T_c) Q^2 + u Q^4$$

and take the other coefficients as temperature independent.

X

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 - some specifics for us

- The reference structure is the space group **G_0** before the magnetic order
- The Hamiltonian needs to be invariant under **G_0**
- The resulting **symmetry group** of the structure is a subgroup of **G_0**. Symmetry group means that we are considering **real moments** or **real energy terms** under symmetry operations
- **Order parameters** characterise the transition : its strength (modulus) and the symmetry that remains in the phase **after the ordering**
- The mixing coefficients are the refined parameters of a magnetic structure
  - **They are also valid order parameters for Landau theory**

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

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

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

X

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):

Landau theory

- **In IR space** we can describe the action of the symmetry operations on the order parameter, e.g.

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

- This is done by considering the action of the IR matrix of a given symmetry operation g, define this as

$$g\vec{\eta} = D_\nu(g)\vec{\eta}$$

- Simplify things by looking at the unique matrices of an IR, these form the image of the IR.
- Look at which operates leave η invariant and which change it to symmetry related vectors **(compare this with making the star of k)**
- Use this set of {η} to calculate the polynomial of invariants, as F must be invariant under these operations. The result has to be consistent (invariant) under all these operations simultaneously, e.g.

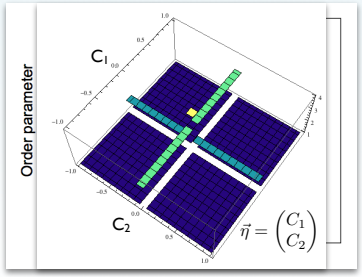
$$F = r(\eta_1^2 + \eta_2^2 + \eta_3^2) + v\eta_1\eta_2\eta_3 + u_1(\eta_1^4 + \eta_2^4 + \eta_3^4) + u_2(\eta_1^2\eta_2^2 + \eta_1^2\eta_3^2 + \eta_2^2\eta_3^2)$$

X

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 magnetic point groups.**

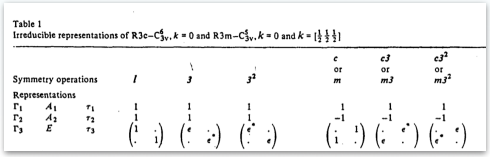


Table 1
Irreducible representations of R3c–C_{3v}^6, $k = 0$ and R3m–C_{3v}^5, $k = 0$ and $k = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]$

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

A newer refinement strategy combining ideas

Table 1
Irreducible representations of R3c–C^6_{3v}, k = 0 and R3m–C^5_{3v}, 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	$\begin{pmatrix}1 & \\ & 1\end{pmatrix}$	$\begin{pmatrix}\epsilon & \\ & \epsilon^*\end{pmatrix}$	$\begin{pmatrix}\epsilon^* & \\ & \epsilon\end{pmatrix}$	$\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}$	$\begin{pmatrix} & \epsilon^* \\ \epsilon & \end{pmatrix}$	$\begin{pmatrix} & \epsilon \\ \epsilon^* & \end{pmatrix}$

```
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)
ATOM  2:  (     0     0    -6)  +  1(     0     0     0)
******

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

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

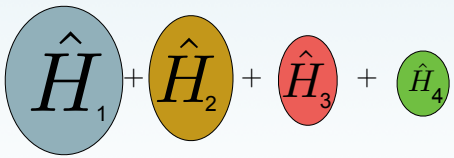
$\vec{\eta} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$

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

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

How can magnetic structures be described

- Work with $\boldsymbol{m}_{\|a}$, $\boldsymbol{m}_{\|b}$, $\boldsymbol{m}_{\|c}$ (the components parallel to the crystal axes)
  - Form real moments from **ψ** and **ψ***(can involve combining basis vectors from same IR or IRs related by complex conjugation)
  - Basis vectors are symmetry adapted functions - they are symmetry adapted to the system **you** are dealing with, and will allow complex symmetries. **Isotropy groups are contained within representation theory**
  - Choice to work with the simple repetition of a unit cell (magnetic space group - MSG, superspace group), or a propagation vector and the original unit cell
  - **The description of a magnetic structure use a MSG is not always the same as using a single IR of G_k.**
    - **Coupling and/or high symmetry structures are possible**
      - ➡ **Equivalent descriptions can be constructed**
  - Which is best ? Beauty is in the eye of the beholder.
    - The elegance description of a structure depends on what you want and your preferred point of reference. Couplings are treated differently and need care

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