Magnetic Symmetry: an overview of Representational Analysis and Magnetic Space groups

Stuart Calder

Neutron Scattering Division
Oak Ridge National Laboratory

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

Overview

Aim: Introduce concepts and tools to describe and determine magnetic structures

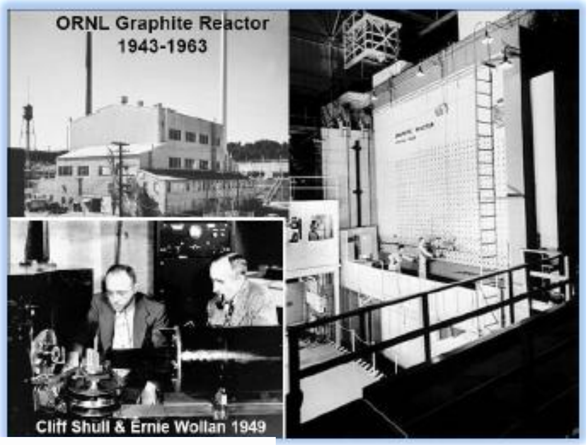
- Basic description of magnetic structures and propagation vector

- What are the ways to describe magnetic structures properly and to access the underlying physics?
  - Representational analysis
  - Magnetic space groups (Shubnikov groups)

Brief History of magnetic structures

- ~500 BC: Ferromagnetism documented in Greece, India, used in China

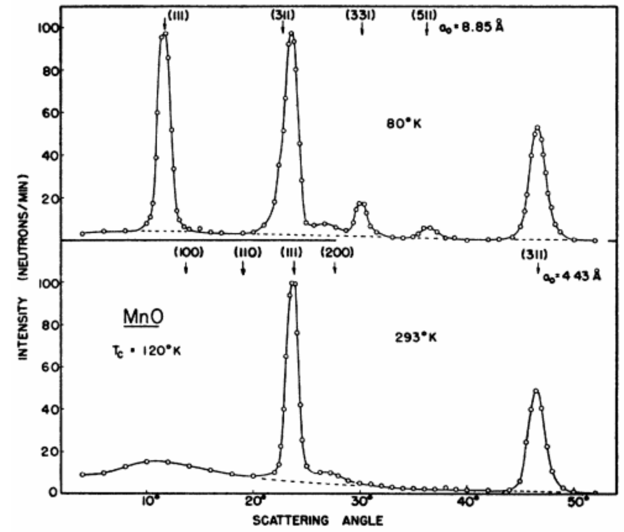
Sinan, ~200 BC



- 1932 Neel proposes antiferromagnetism

- 1943: First neutron experiments come out of WW2 Manhatten project at ORNL

- 1951: Antiferromagnetism measured in MnO and Ferrimagnetism in Fe_3O_4 at ORNL by Shull and Wollan with neutron scattering



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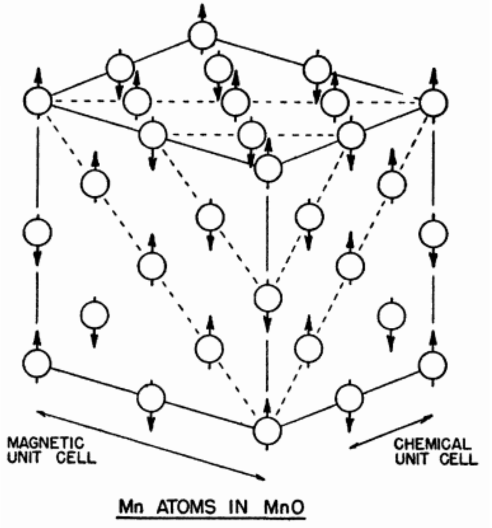
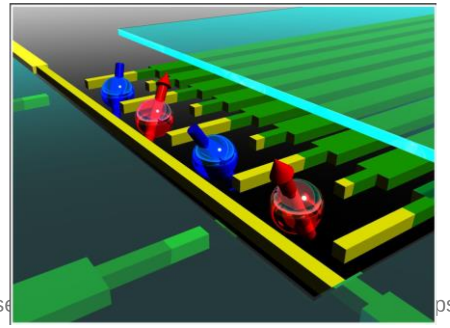
Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)



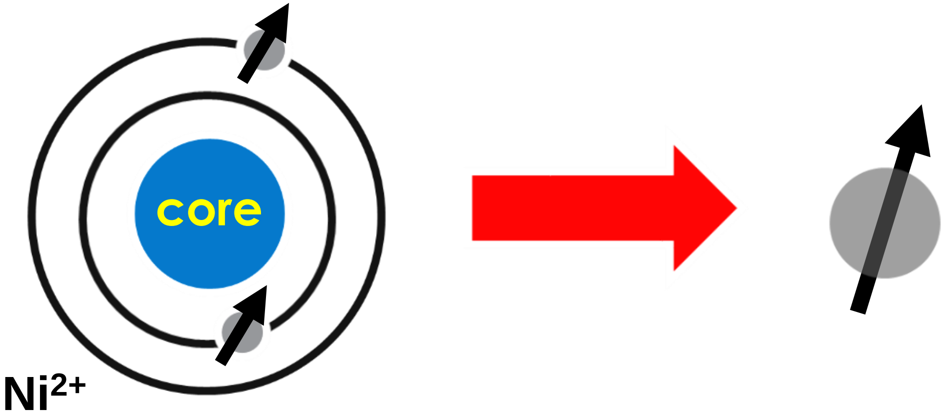
- 1950-60: Shubnikov and Bertaut develop methods for magnetic structure description

- Present/Future:
  - Powerful and accessible experimental and software tools available
  - Spintronic devices and Quantum Information Science



Intrinsic magnetic moments (spins) in ions

- Consider an ion with unpaired electrons
- Hund's rule: maximize S/J



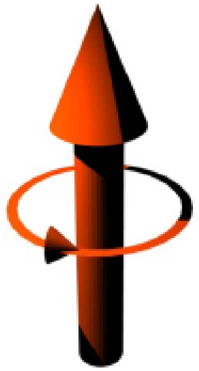
Ni^{2+}

$\mathbf{m}=g_J\mathbf{J}$ (rare earths)

$\mathbf{m}=g_s\mathbf{S}$ (transtion metals)

Ni^{2+} has a localized magnetic moment of $2\mu_B$

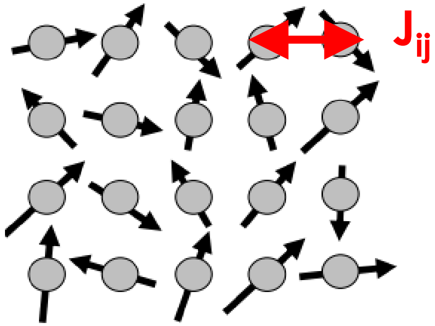
- Magnetic moment (or spin) is a classical "axial vector" (magnetic dipole) generated by an electric current.



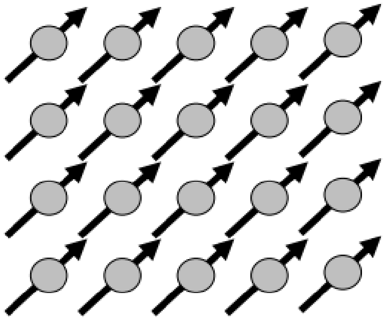
Ordered spins in a crystalline lattice

- Exchange interactions exists between ions with spin that can stabilize long range magnetic order
  - Direct, superexchange, double exchange, RKKY, dipolar

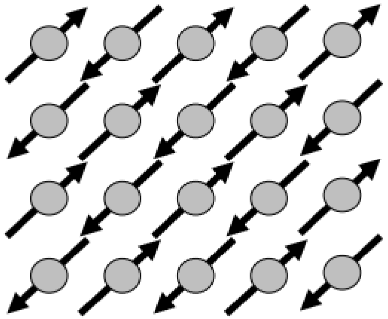
$E_{ij}=-J_{ij}\mathbf{S}_i.\mathbf{S}_j$



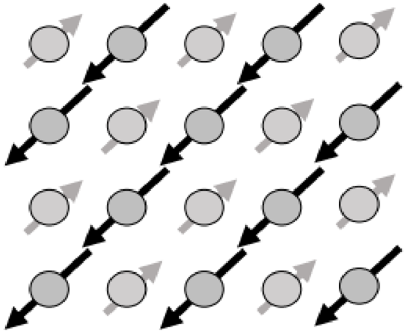
Paramagnetic state
$<\mathbf{S}_i> = 0$



Ferromagnetic state
$<\mathbf{S}_i> \neq 0$

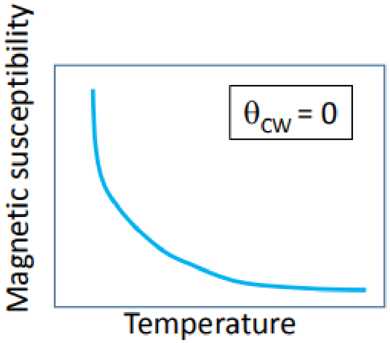


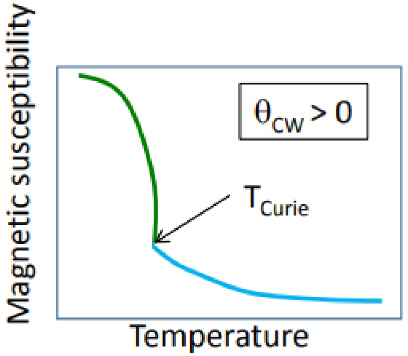
Antiferromagnetic state
$<\mathbf{S}_i> \neq 0$

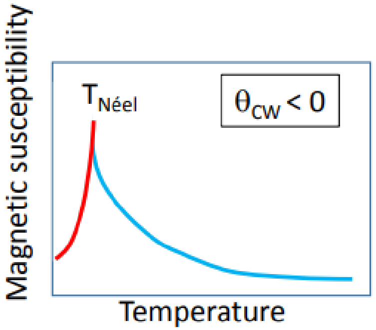


Ferrimagnetic state
$<\mathbf{S}_i> \neq 0$

Curie-Weiss:
$X= C/(T-\theta_{CW})$







Different magnetic atoms or different oxidation states for the same atom)
→ Non-zero total magnetic moment

- Time-reversal is a valid symmetry operator for paramagnetic phase, but is broken in the ordered phase

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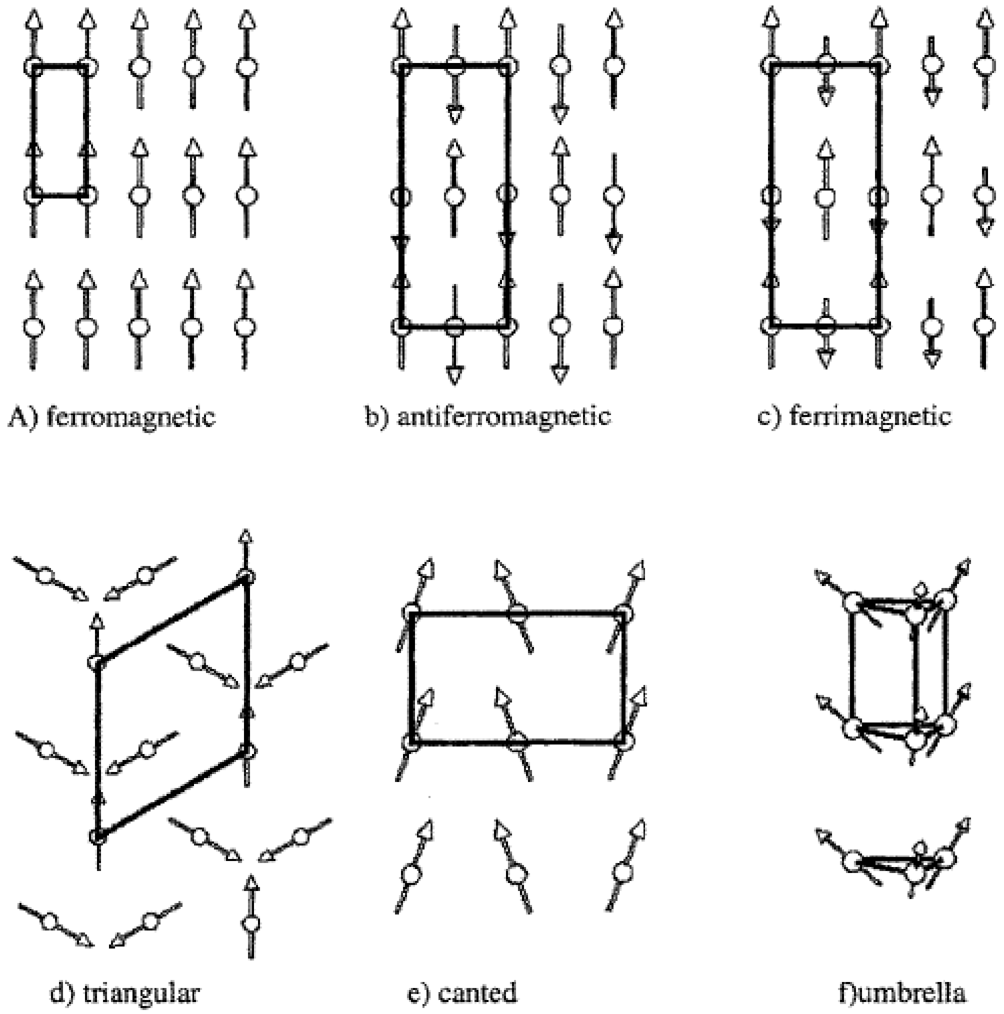
- **Basic description of magnetic structures and propagation vector**
- What are the ways to describe magnetic structures properly and to access the underlying physics?
  - Representational analysis
  - Magnetic space groups (Shubnikov groups)

Magnetic structures

- Magnetic structures can be simple or complex (frustrated, spin density wave, sine wave, canonical, helical, Skyrmion, etc).
- **What is a magnetic structure:**
  - Description of whatever magnetic atom of whatever unit cell's direction and magnitude of the magnetic moment.
  - The order has some translational symmetry (the moments in different unit cells are related in a periodic way).
  - Long correlation length
- **What is NOT a magnetic structure:**
  - An arbitrary set of arrows in a box that doesn't have any symmetry constraints
  - Problem arose from lack of standardization and software limitations (think about crystallography success)
  - Simple rules exist, complete rules now becoming accessible and mainstream

Magnetic structures

- Lots of types (and mixtures of these types).



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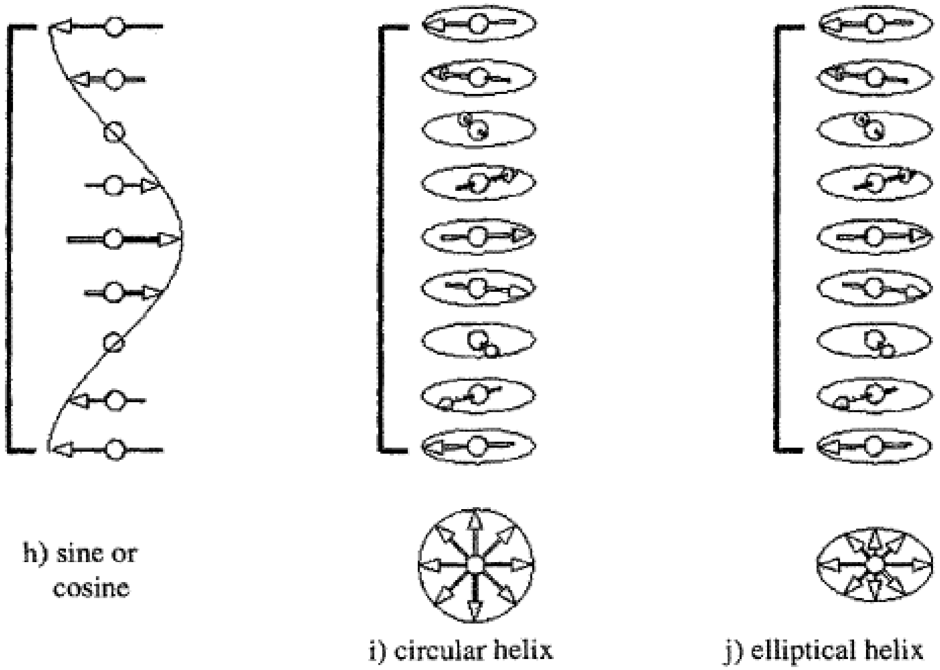
Magnetic structures and their determination using group theory

A. Wills

Institut Laue-Langevin, BP. 156x, 38042 Grenoble cedex, France



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Magnetic structures

- Lots of types (and mixtures of these types).

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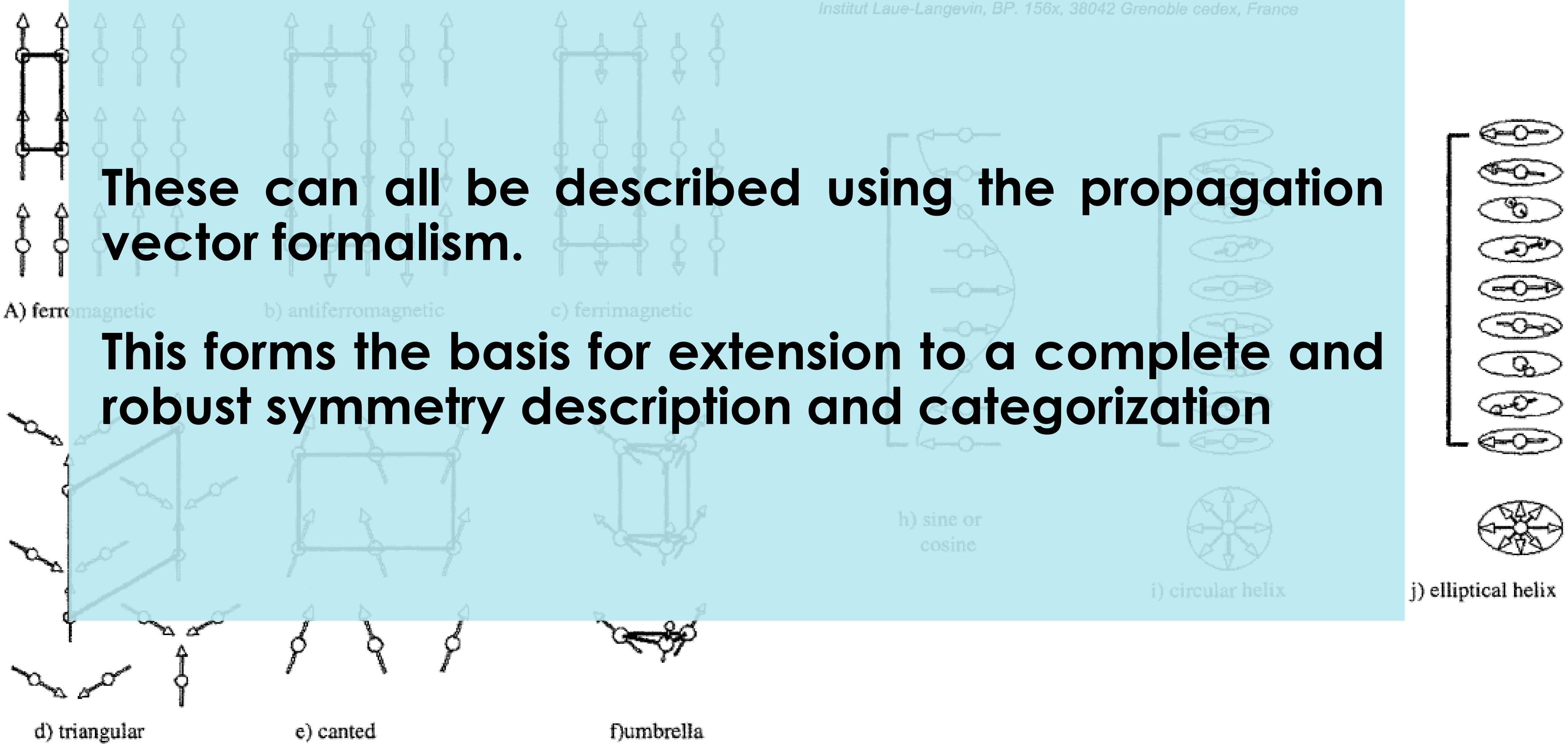
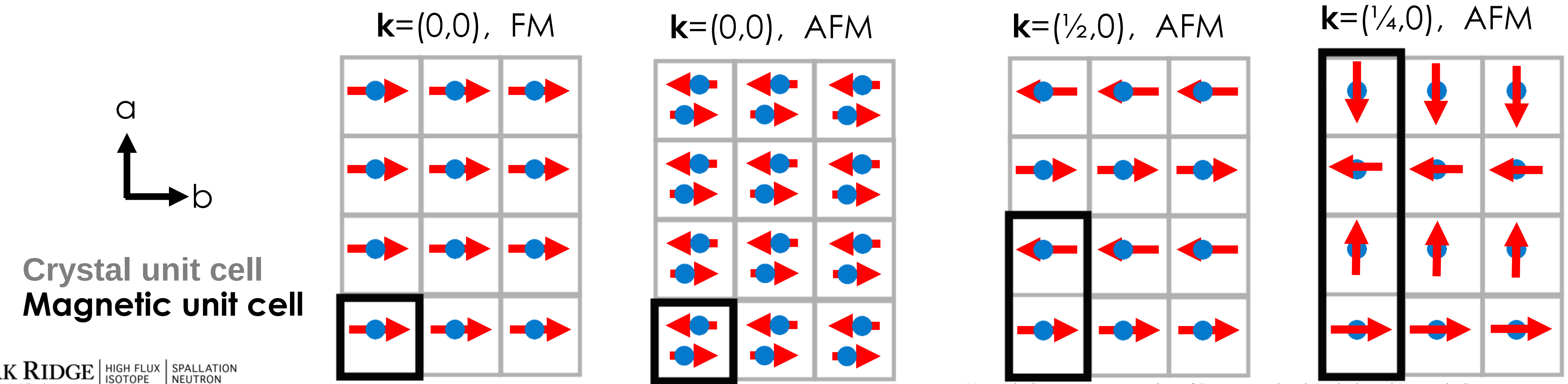


These can all be described using the propagation vector formalism.

This forms the basis for extension to a complete and robust symmetry description and categorization

Magnetic propagation vector: **k**-vector

- **Magnetic** and **crystallographic** unit cells are not necessarily the same size.
- Convenient to introduce a propagation vector (**k-vector**):
  Describes the relation between the nuclear and magnetic unit cells
- **Aim: Can state just the spins in the 0th crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.**
- k-vector directly observable with neutron scattering:
  - They are shifted from the positions of nuclear peaks (τ) by the **k**-vector value, i.e $Q_{mag} = \tau + k$
  - **k**-vector can be commensurate (e.g. 1/4) or incommensurate (e.g. 1/13)
  - Can have multiple k-vectors



General magnetic structure description with k-vectors

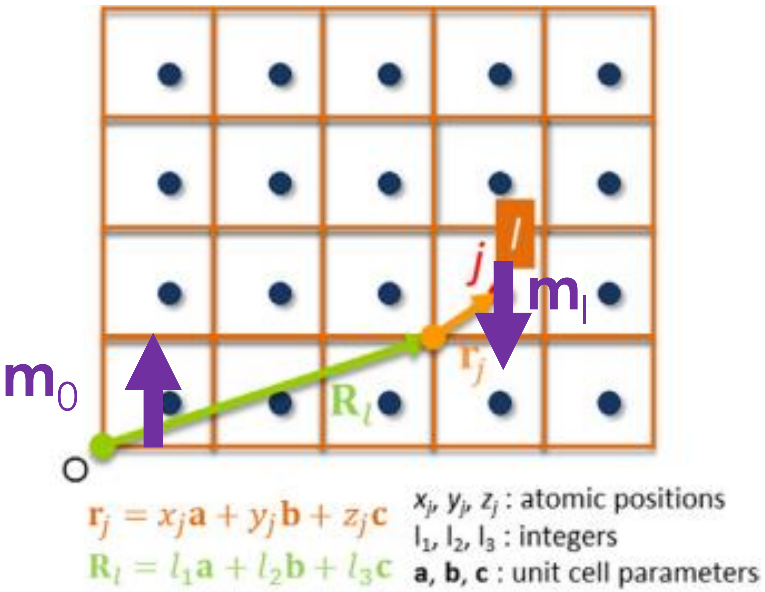
- Can state only the spins in the 0^{th} crystallographic unit cell and the k-vector describes how the spins are related in all other unit cells.
- For all magnetic ordering this can be expressed in the Fourier series:

$$\mathbf{m}_j = \Sigma_{\mathbf{k}} \mathbf{S}_j^k e^{-2\pi i \mathbf{k}.R}$$

$$\mathbf{m}_j = \Sigma_{\mathbf{k}} \mathbf{S}_j^k [\cos(-2\pi \mathbf{k}.R) + i\sin(-2\pi \mathbf{k}.R)]$$

- $\mathbf{m}_j$ is the magnetic moment at the atomic site *j* in some unit cell that is related to the 0^{th} cell (G_0) by a translation **R**.
- $\mathbf{S}_j$ (Basis vector) is the magnetic moment in the 0^{th} cell i.e. it describes the projection of the moments (aka $\mathbf{\Psi}_j$).
- **k** is the propagation vector
- For many cases the sum of several basis vectors is required $\mathbf{S}_j = \Sigma_\upsilon C_\upsilon \mathbf{S}_\upsilon$ (finding this is goal of representational analysis, see later)

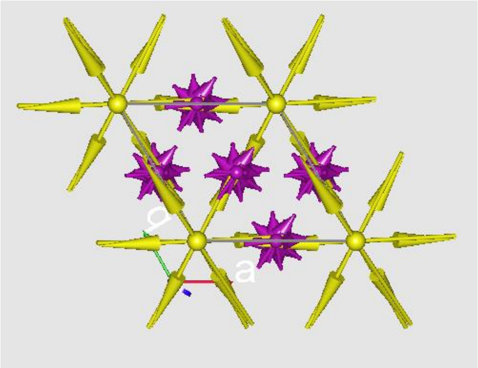
Correlation of the spin m_j on atom j within unit cell l to m_0 in the 0^{th} unit cell translated by R

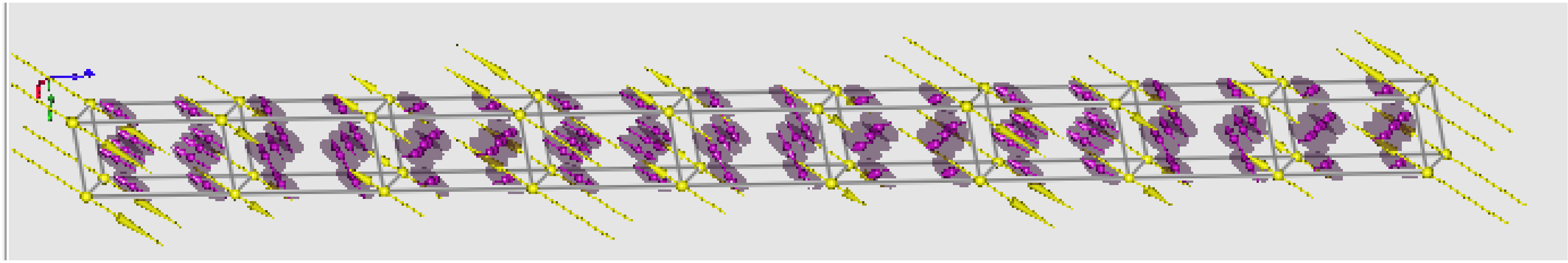


- $\mathbf{m}_j$ is real, but expression includes *i*, need the condition: $\mathbf{S}_{-kj} = \mathbf{S}_{kj}^*$

General magnetic structure description

- A magnetic structure is fully described by:
  - **k**-vector (either commensurate or incommensurate)
  - Basis vectors $\mathbf{S}_{kj}$: Fourier components for each magnetic atom j and **k**-vector ($\mathbf{S}_{kj}$ is a complex vector, 6 components)



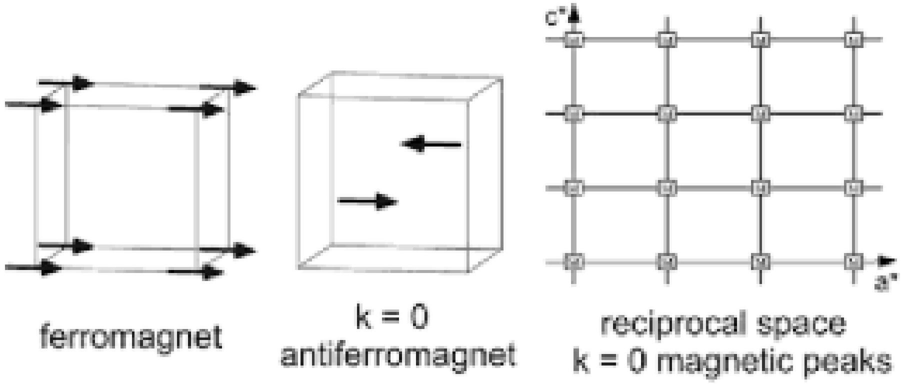


  - $DyMn_6Ge_6$: See previous Magnetic workshop tutorials for this example.

Examples of using the k-vector formulism: $\mathbf{m}_j = \mathbf{S}_j^k e^{-2\pi i \mathbf{k}.R}$

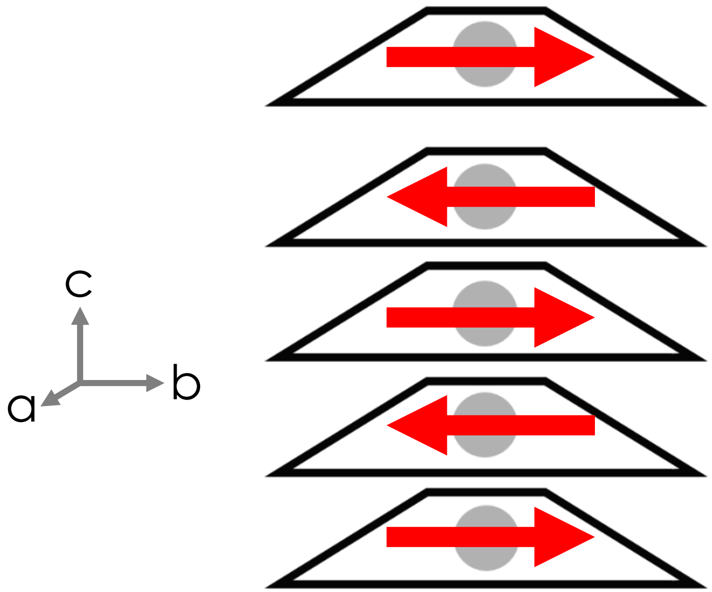
- <u>Simplest case of k =(0,0,0) = 0</u>
- $\mathbf{m}_{lj} = \mathbf{S}_{0j}\, e^{-2\pi i \mathbf{k}.R} = \mathbf{S}_{0j}\, e^{-2\pi i 0.R} = \mathbf{S}_{0j}\, e^{0} = \mathbf{S}_{0j} = \mathbf{m}_{0J}$
- Orientation of the magnetic moments in any cell of the crystal are identical to the 0^{th} cell (i.e. **magnetic unit cell = crystallographic unit cell**)

- But does NOT say what the magnetic structure is.
  - k=0 can be ferromagnetic, antiferromagnetic, ferrimagnetic, collinear or non-collinear.
  - Only for Bravais lattices (single atom per primitive cell) does it mean it is FM
  - In all other cases need the Basis vectors ($\mathbf{S}_j$) to describe magnetic structure



Examples of using the k-vector formulism: $\mathbf{m}_j = \mathbf{S}_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}}$

- Consider half a reciprocal lattice: k=00½
- Basis vector in the 0th cell is **S**=(010), i.e. spins along b
- Each plane corresponds to a lattice translation **R**=001
- This is an example of a real Basis vector → sine component is zero.



$$m_j = S_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}} = (010)\exp[-2\pi i(00½).(004)] = (010)$$

$$m_j = S_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}} = (010)\exp[-2\pi i(00½).(003)] = (0\text{-}10)$$

$$m_j = S_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}} = (010)\exp[-2\pi i(00½).(002)] = (010)$$

$$m_j = S_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}} = (010)\exp[-2\pi i(00½).(001)] = (0\text{-}10)$$

$$m_j = S_j^k \, e^{-2\pi i \mathbf{k}.\mathrm{R}} = (010)\exp[-2\pi i(00½).(000)] = (010)$$

Examples of using the k-vector formulism: $\mathbf{m}_j = \mathbf{S}_j^k e^{-2\pi i \mathbf{k}.R}$

- <u>**k** between 0 and ½ gives a non-zero sine component and **S** is real</u>
- This makes $\mathbf{m}_j$ complex, but it needs to be real

$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\, \mathbf{S}_j^k\, [\cos(-2\pi \mathbf{k}.\mathbf{R}) + i\sin(-2\pi \mathbf{k}.\mathbf{R})]$$

- Need to consider both **k** and –**k** propagation vectors
  (→ *for incommensurate need at least 2 arms of the star – see later*)

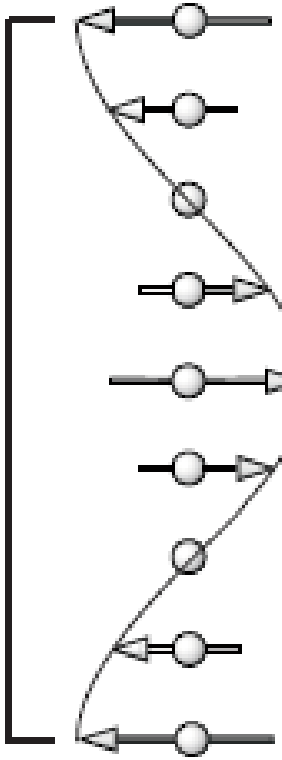
$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\, \mathbf{S}_j^k\, e^{-2\pi i \mathbf{k}.R} = \mathbf{S}_j^k\, e^{-2\pi i \mathbf{k}.R} + \mathbf{S}_j^{-k}\, e^{-2\pi i(-\mathbf{k}).R}$$

$$\mathbf{m}_j = \mathbf{S}_j^k\, e^{-2\pi i \mathbf{k}.R} + (\mathbf{S}_j^k)^*\, e^{-2\pi i(-\mathbf{k}).R} \qquad \text{since } \mathbf{S}^{-k}_j = \mathbf{S}^{k}_j{}^*$$

- Expansion of the exponentials leads to:

$$\mathbf{m}_j = 2Re\mathbf{S}_j^k\, [\cos(-2\pi \mathbf{k}.\mathbf{R})] + 2Im\mathbf{S}_j^k\, [\sin(-2\pi \mathbf{k}.\mathbf{R})]$$

- Second term is zero since **S** is real
- → Amplitude modulated sine structure (spin density wave)



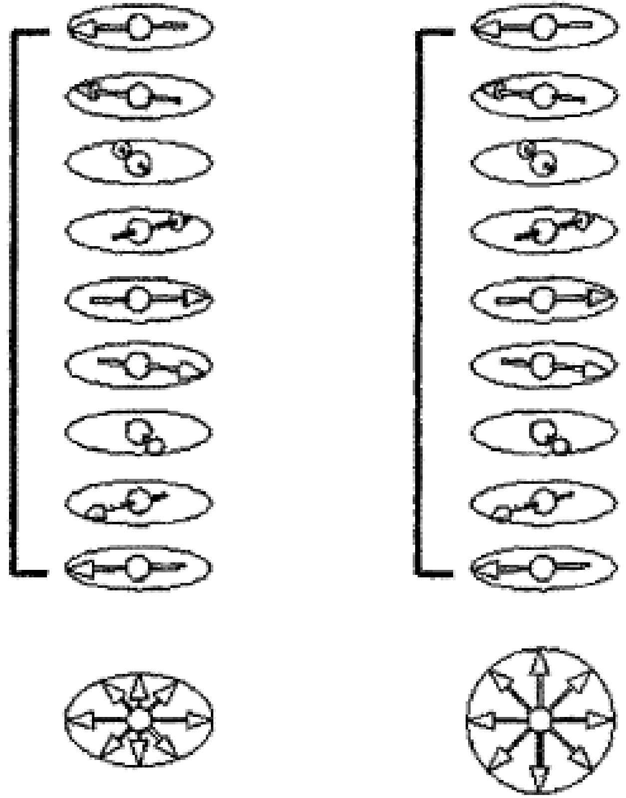
h) sine or cosine

Examples of using the k-vector formulism: $\mathbf{m}_j = \mathbf{S}_j^k e^{-2\pi i \mathbf{k}.R}$

- <u>**S** is complex and **k** is incommensurate</u>
- This makes $\mathbf{m}_j$ complex, but it needs to be real
- Again consider **k** and –**k** vectors

$$\mathbf{m}_j = 2Re(\mathbf{S}_j^k)\ [\cos(-2\pi\mathbf{k.R})] + 2Im(\mathbf{S}_j^k)\ [\sin(-2\pi\mathbf{k.R})]$$

- Now the second term is non-zero
- If $Re(\mathbf{S}) \neq Im(\mathbf{S})$ this describes an ellipse
  → elliptical helix structure
- If $Re(\mathbf{S}) = Im(\mathbf{S})$: $m_j = 2Re(\mathbf{S}_j^k)\ [\cos(-2\pi\mathbf{k.R})] + \sin(-2\pi\mathbf{k.R})]$.
  This describes a circle
  → circular helix structure



j) elliptical helix   i) circular helix

Multi-k structures: the Skyrmion lattice

- Skyrmion lattice is an example of a multi-**k** incommensurate magnetic structure
- Lattice of clockwise magnetic whirlpools

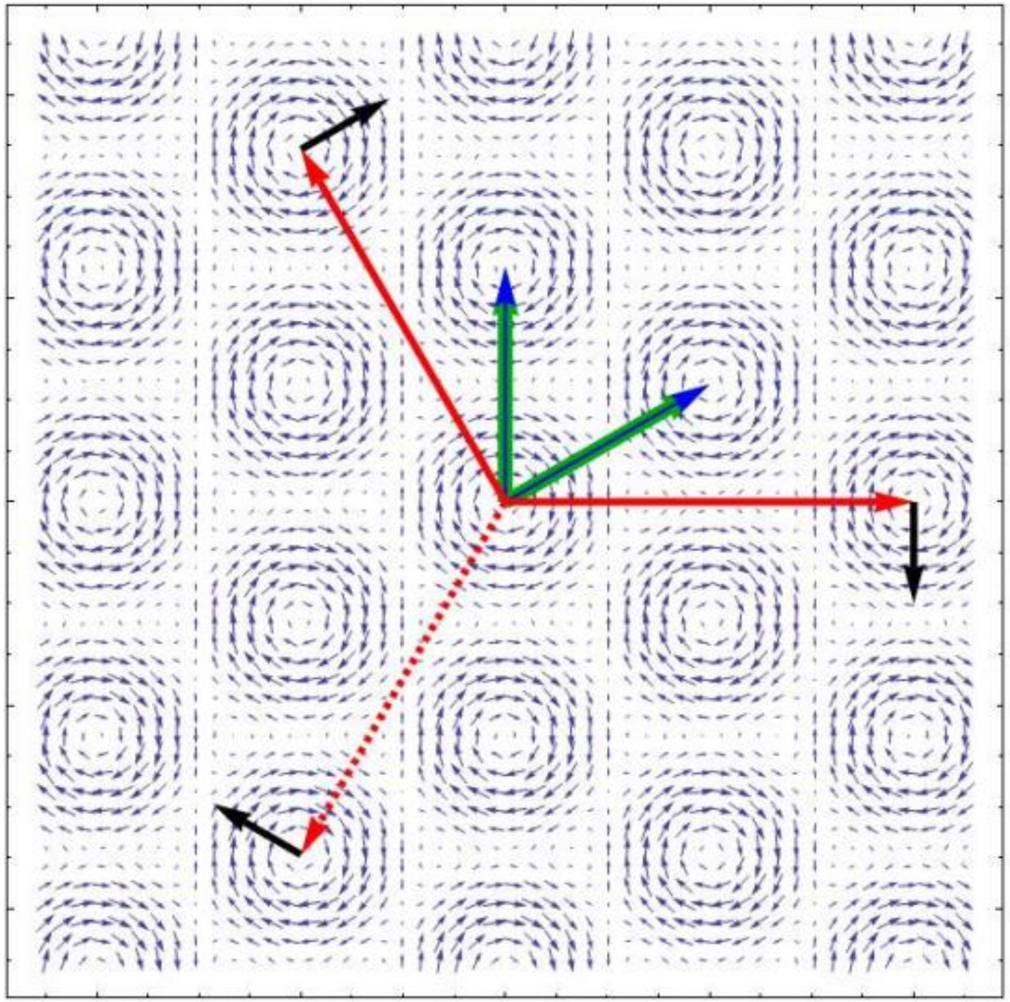
  $\mathbf{k}_1=(2\alpha,-\alpha,0)$

  $\mathbf{k}_2=(-\alpha,2\alpha,0)$

  $\mathbf{k}_3=(-\alpha,-\alpha,0)$

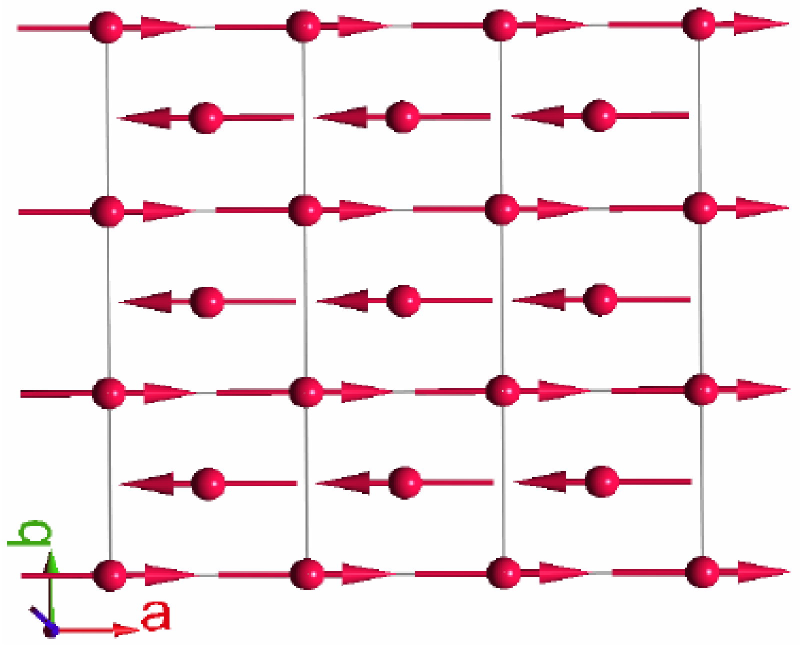
  Can have $\mathbf{k}_4=(000)$

- Here $\alpha=0.11$



k-vectors with values >1/2

- k-vectors are referred to the reciprocal basis of the conventional direct cell
- Most cases magnetic unit cell is the same or larger than the crystal unit cell
- **Centered cells → can have k>0.5 e.g. (k=010)**
- BCC is an example (conventional (cubic) unit cell contains two primitive unit cells)
- Translational vectors have fractional components
- The index j runs on the atoms contained in a primitive cell



$$\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j = l_1\mathbf{a} + l_2\mathbf{b} + l_3\mathbf{c} + x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

Star of the propagation vector

$$\mathbf{m}_j = \Sigma_{\mathbf{k}}\, \mathbf{S}_j^{k}\, e^{-2\pi i \mathbf{k}.R}$$

- Three possibilities for propagation vector in real materials:
  - Single k-vector (most common)
  - Multi-k: More than one k-vector of the **star** are involved (keep sum in expression)
  - One k-vector and its harmonics, k, k/2,… (sum over harmonics of k)

Star of the propagation vector

- Consider effects of the symmetry (*g*) of the crystal space group (G_0) on the k-vector.
  - i.e. apply a symmetry element *g* with various rotations (h) and translations (τ), i.e. g={h, τ}
- The rotation operation *h* will act on the **k**-vector: **k'**=**k***h*

  → **k**'=**k** (unchanged) or **k**'≠**k** (inequivalent propagation vector produced)
- The set of non-equivalent **k** vectors obtained by apply the rotational symmetry operations gives the "**star of k**":
- $\{\mathbf{k}\} = \{h_1\mathbf{k}_1, h_2\mathbf{k}_1, h_3\mathbf{k}_1, \ldots\} = \{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_{3,\ldots}\}$

  $\mathbf{k}_i$ vectors are called the arms of the star
- The number of arms ($l_\mathbf{k}$) of the star is equal to the number of symmetry elements of G_0 (*cosets*)
- First coset termed the "**Little group G_k**".
  - leaves **k** invariant or equal to an equivalent **k**-vector
  - G_k is always a subgroup of G_0
  - Important for Representational Analysis approach

Star of the propagation vector: Little Group (G_K)

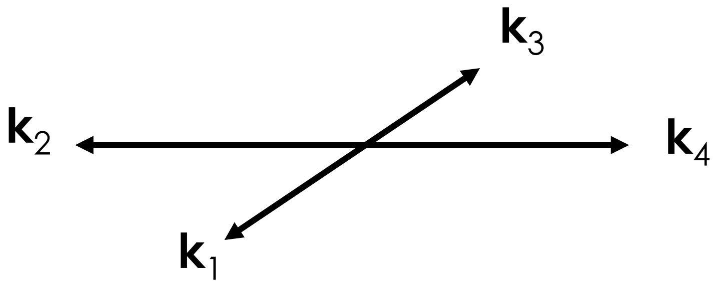
- k-vector reduces the space group symmetry from G_0 to G_k
- The number of elements of the little group G_k depend on the k-vector

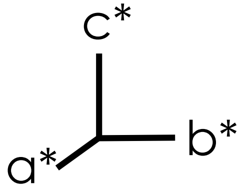
- e.g. consider space group 227:
  - If k= (0 0 0) → 48 elements in G_k
  - If k= (½ 0 0) → 8 elements in G_k
  - If k=(½ ½ ½) → 12 elements in G_k

- This is because different planes, lines and points will correspond to different symmetries and so result in different a G_k.

Star of the propagation vector

- Star of the propagation vector **k**=(x 0 0) in the tetragonal space group I4/mmm (point group D^{17}_{4h})
- The arms of the star are:
  - $\mathbf{k}_1$=(x 0 0)
  - $\mathbf{k}_2$=(0 -x 0)
  - $\mathbf{k}_3$=(-x 0 0)
  - $\mathbf{k}_4$=(*0* x 0)





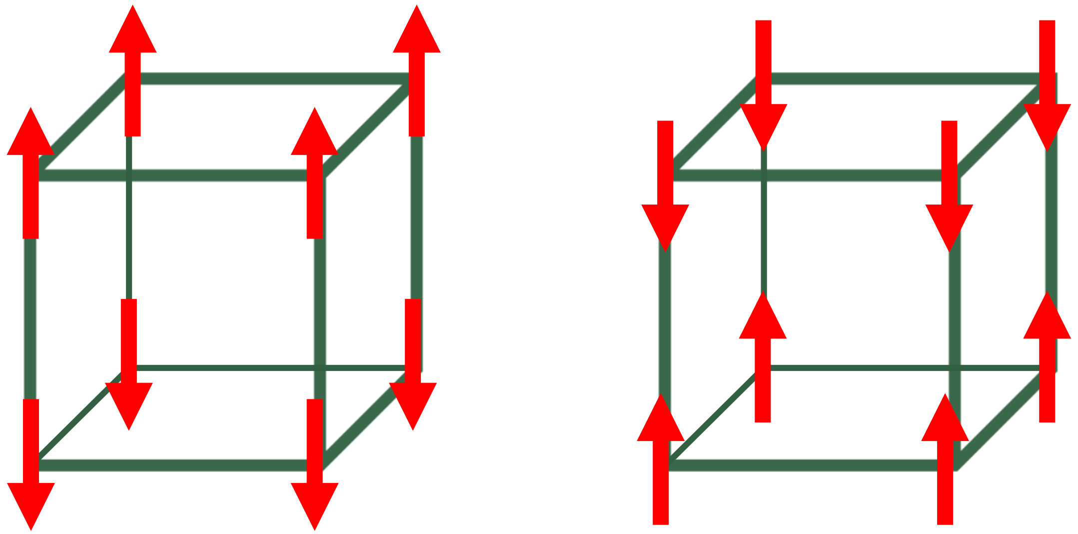
Domains

- Transition from paramagnet to ordered magnetic state lowers symmetry.
  - Can create domains
- If G_0 is paramagnetic group of order n_P and G_M is ordered magnetic space group of order n_M
  → n_P/n_M number of domains

- **4 types of domains**
  - Time-reversed domains: 180° (π) domains → loss of time-reversal symmetry
  - Orientation domains: s-domains → loss of rotation symmetry
  - Configuration domains: k-domains → loss of translational symmetry
  - Chiral domains → loss of inversion symmetry (-1)

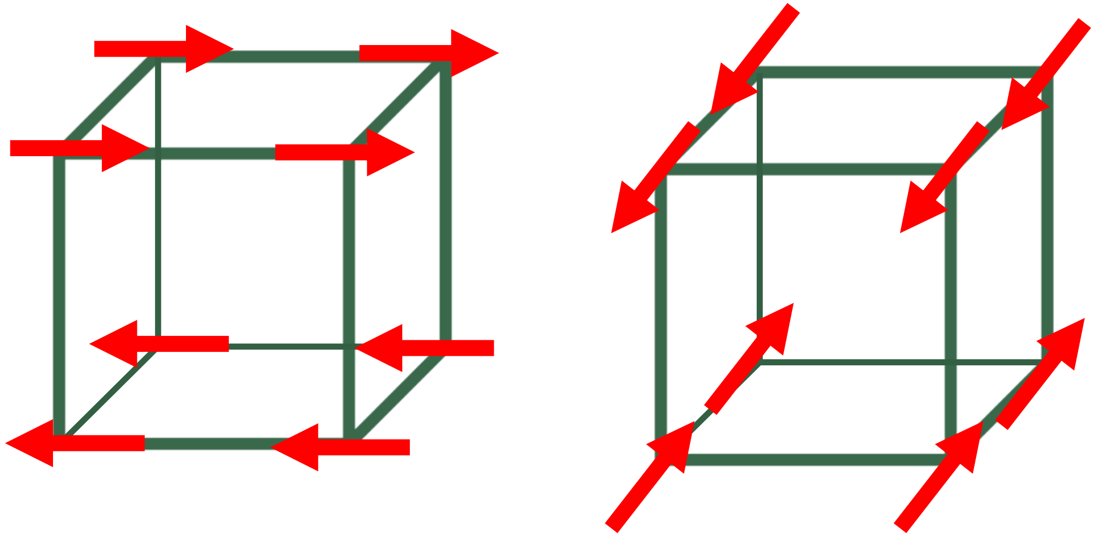
180° (π) domains → loss of time-reversal symmetry

- Moment direction reversed between domains



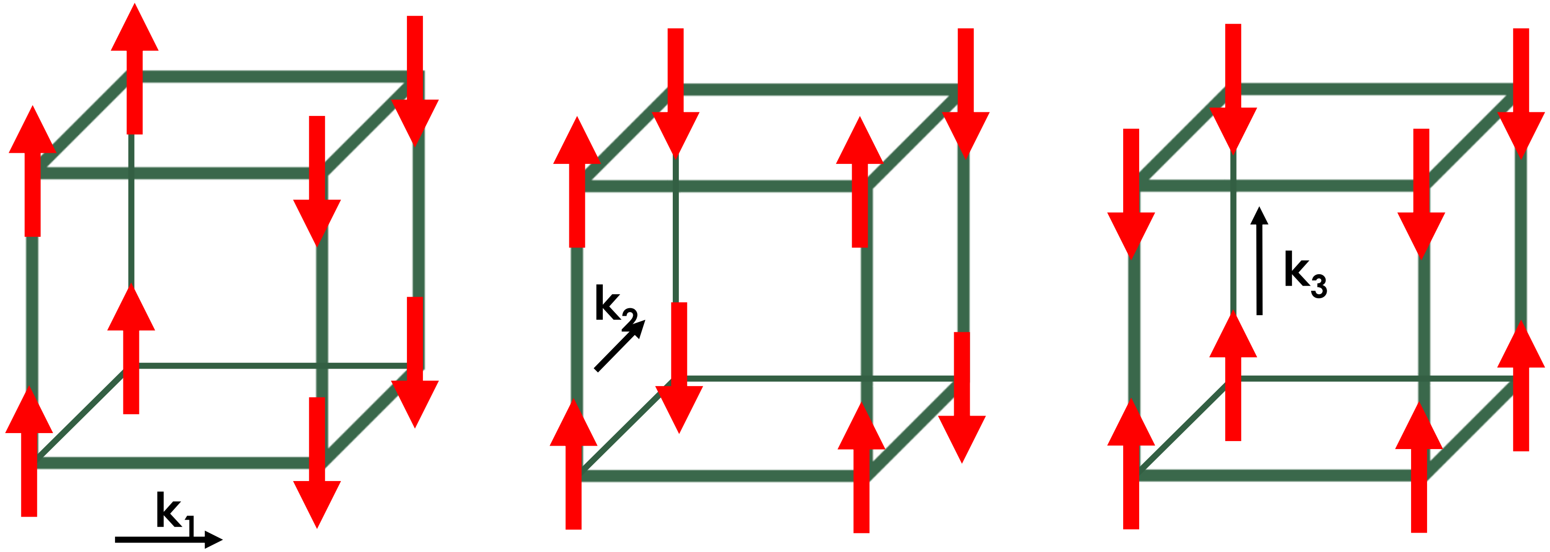
s-domains → loss of rotation symmetry

- "Orientation domains" caused by lowering of symmetry from paramagnetic to magnetic phase.
- Loss of rotational invariance.
- No loss of translational symmetry.



k-domains → loss of translational symmetry

- "Configurational domains"
- Each vector in the star generates a different (equivalent) configuration domain.
  - e.g. $\mathbf{k}_1$=(1/2,0,0), $\mathbf{k}_2$=(0,1/2,0), $\mathbf{k}_3$=(0,0,1/2)
- Each domain gives a separate set of magnetic reflections



k-domain in MnO

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A. Wills

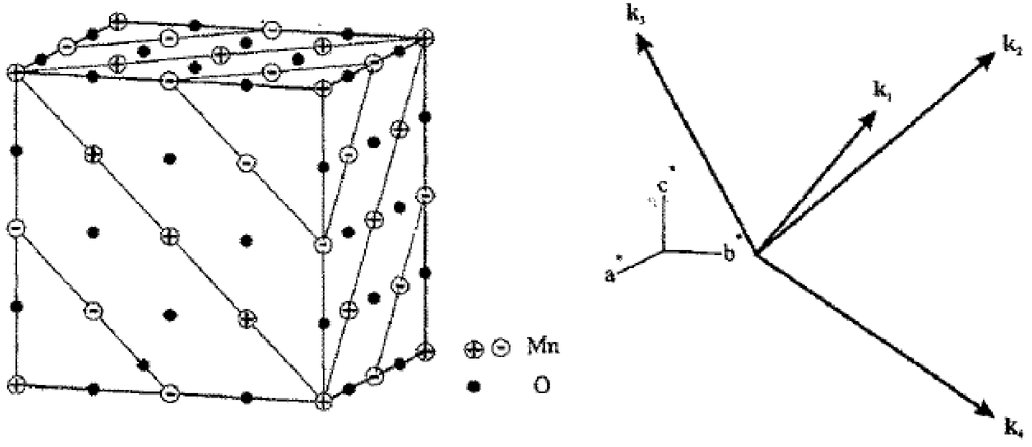
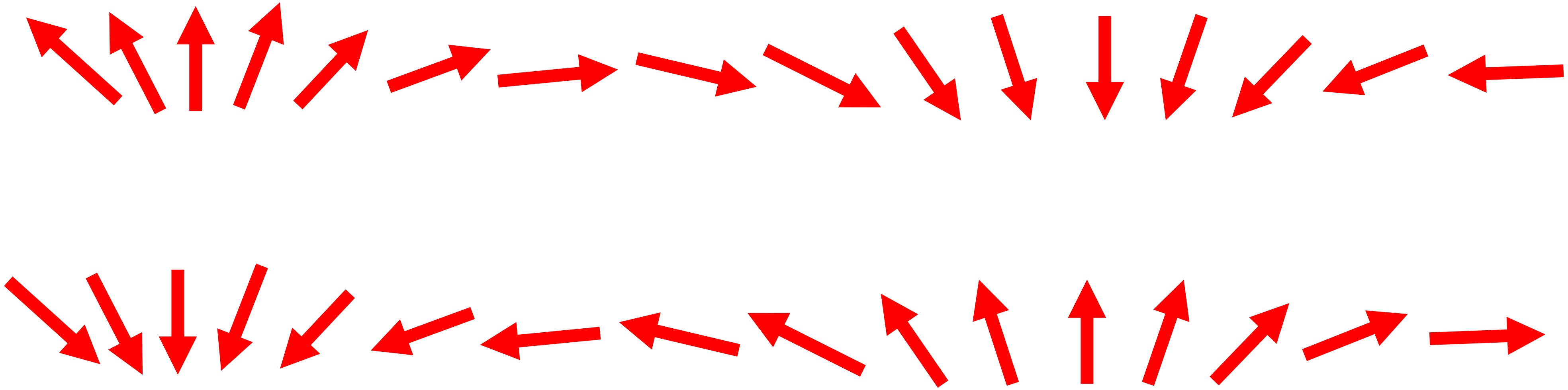


Figure 4: a) The magnetic motif of MnO made up of ferromagnetic planes of moments that are coupled antiferromagnetically. b) The star of **k** in reciprocal space is made up of the four propagation vectors related by the rotation elements of the space group G_0: $\mathbf{k}_1 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$, $\mathbf{k}_2 = \left(\frac{\bar{1}}{2}, \frac{1}{2}, \frac{1}{2}\right)$, $\mathbf{k}_3 = \left(\frac{1}{2}, \frac{\bar{1}}{2}, \frac{1}{2}\right)$ and $\mathbf{k}_4 = \left(\frac{1}{2}, \frac{1}{2}, \frac{\bar{1}}{2}\right)$. Domains are found that correspond to each of these **k**-vectors.

Chiral domains → loss of inversion symmetry

- Two domains of opposite handedness generated by loss of inversion symmetry.
- Paramagnetic space group is centrosymmetric and magnetic space group is not.



Constrain and go beyond the simple k-vector formalism

- K-vector formulism is a simple and intuition way to arrive at any magnetic structure.
- But things can get complicated fast: Lots of variables and limited information from experiment
- Want a systematic way to determine and describe magnetic structures, **i.e. a better way**

- **Symmetry analysis goes beyond trial and error analysis**
  - Neumann's principle: If a crystal is invariant under a symmetry operation, its physical properties must also be invariant under the same operation
  - Symmetry dictates what is allowed and what is forbidden/constrained → gives correct/physical magnetic structures
  - Unless there is a phase transition, what is forbidden/constrained by symmetry is "protected", i.e. it will remain forbidden unless the symmetry changes.
  - Easier
  - Software available to use

> "It is only slightly overstating the case to say that physics is the study of symmetry"
>
> P. W. Anderson
>
> *Science*, New Series, Vol. 177, No. 4047 (Aug. 4, 1972), 393-396.

Overview

Aim: Introduce concepts and tools to describe and determine magnetic structures

- Basic description of magnetic structures and propagation vector

- **What are the ways to describe magnetic structures properly and to access the underlying physics?**
  - **Representational analysis**
  - **Magnetic space groups (Shubnikov groups)**

What are the ways to describe magnetic structures?

Two main approaches

- Historically competing
- Until very recently Representational analysis "easier" to apply to experimental data
- Since 2010 magnetic space group approach standardized and now equally accessible
- Current/future: **combined approach for full insights** with lots of powerful software

Representational analysis (Irreps)

- Most general approach
- Finds basis vectors in k-vector approach
- Equally applicable to simple commensurate and complex incommensurate magnetism
- Can give direct information on Hamiltonian
- Assumes knowledge of non-magnetic crystal structure

Magnetic (Shubnikov) Space Groups

- Extension of crystallographic space groups to include spin (time-reversal)
- Maintains symmetry of magnetic/non-magnetic atoms so can provide insights
- Incommensurate only recently added through supersymmetry description

Representational analysis is, first of all, a tool for finding magnetic structures

Acta Cryst. (1968). A**24**, 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

(*Received 20 July 1967*)

In the analysis of spin structures a 'natural' point of view looks for the set of symmetry operations which leave the magnetic structure invariant and has led to the development of magnetic or Shubnikov groups. A second point of view presented here simply asks for the transformation properties of a magnetic structure under the classical symmetry operations of the 230 conventional space groups and allows one to assign irreducible representations of the actual space group to all known magnetic structures. The superiority of representation theory over symmetry invariance under Shubnikov groups is already demonstrated by the fact proven here that the only invariant magnetic structures describable by magnetic groups belong to real one-dimensional representations of the 230 space groups. Representation theory on the other hand is richer because the number of representations is infinite, *i.e.* it can deal not only with magnetic structures belonging to one-dimensional real representations, but also with those belonging to one-dimensional complex and even to two-dimensional and three-dimensional representations associated with any **k** vector in or on the first Brillouin zone.

We generate from the transformation matrices of the spins a representation Γ of the space group which is reducible. We find the basis vectors of the irreducible representations contained in Γ.

The basis vectors are linear combinations of the spins and describe the structure. The method is first applied to the $\mathbf{k}=0$ case where magnetic and chemical cells are identical and then extended to the case where magnetic and chemical cells are different ($\mathbf{k}\neq 0$) with special emphasis on **k** vectors lying on the surface of the first Brillouin zone in non-symmorphic space groups. As a specific example we consider several methods of finding the two-dimensional irreducible representations and its basis vectors associated with $\mathbf{k}=\frac{1}{2}\mathbf{b}_2=[0\frac{1}{2}0]$ in space group *Pbnm* (D_{2h}^{16}).

JOURNAL DE PHYSIQUE *Colloque C 1, supplément au n° 2-3, Tome 32, Février-Mars 1971, page* C 1 - 462

MAGNETIC STRUCTURE ANALYSIS AND GROUP THEORY

E. F. BERTAUT

C. N. R. S. and C. E. N.-G., rue des Martyrs, Grenoble

Introduction. — Representation analysis of a magnetic structure is not only *a*) labelling or classifying a structure, but consists mainly of *b*) the search for the structure before it is known and of *c*) the discussion of the interactions which might explain the final structure model. Professor Opechowski has not evaluated the merits of representation analysis for *b*) and *c*). Thus I shall answer his criticism at the end of my lecture.

matical difficulties when one is not willing to impose cyclic boundary conditions ». As far as I understand, cyclic boundary conditions are the mathematical trick to handle infinite groups (translation and space groups) on the same footing as finite groups and have led to the success of space group theory. I am not willing to abandon these achievements if there is no better theory available.

As far as usefulness is concerned I still think that C 2 gives more immediate information than C 1′. There is no difficulty in using both descriptions jointly and, as a common practice, I indicate the Shubnikov group (except P 1) in my writings.

Conclusion. — Representation analysis is, first of all, a tool for finding magnetic structures. The description of a magnetic structure by basis vectors of irreducible representations is certainly useful. Finally the construction of an effective spin hamiltonian using *all* the symmetry elements of the irreducible representation becomes possible. Of course, physicists did not wait for the theory presented here to build their hamiltonian in the helimagnetic case. But when minimizing the isotropic part of the hamiltonian, say $J_1 \cos \pi l + J_2 \cos 2\pi l$ in the case of say the dysprosium or $AuMn_2$-helix, they may have got some feeling from this lecture that their hamiltonian is invariant under the wave vector group $\mathbf{G_k}$ ($= P\,6_3\,m\,c$) with $\mathbf{k} = [0\,0\,l]$ and that the helical spin configuration may belong to a two-dimensional representation of $\mathbf{G_k}$ [10].

Thus we reach this final conclusion. When the spin arrangement belongs to an irreducible representation of order higher than one or to a complex representation, the effective spin hamiltonian has a symmetry higher than the symmetry (Shubnikov-symmetry) which leaves the magnetic structure invariant.

Representation analysis: further development by Izyumov

Neutron-diffraction studies of magnetic structures of crystals

Yu. A. Izyumov

Institute of Metal Physics of the Ural Scientific Center of the Academy of Sciences of the USSR, Sverdlovsk

Usp. Fiz. Nauk 131, 387–422 (July 1980)

The contemporary state of neutron diffraction of magnetic structures is analyzed from the standpoint of the theory of symmetry of crystals. It is shown that the varied and numerous structures determined in neutron-diffraction studies can be classified and described by the theory of representations of space groups of crystals. This approach is based on expanding the spin density of the crystal in terms of basis functions of the irreducible representations of its space group. Thus the magnetic structure can be specified by the mixing coefficients of the basis functions. Analysis of a large number of different kinds of magnetic structures shows that they arise in the overwhelming majority of cases, in accord with Landau's hypothesis, from a phase transition that follows a single irreducible representation. This means that the number of parameters that fully fix the magnetic structure of an arbitrarily complex crystal is small and equal to the dimensionality of the responsible irreducible representation. This offers great advantages in employing the symmetry approach in deciphering neutron-diffraction patterns of a crystal under study. This is because it reduces the problem of determining a large number of magnetic-moment vectors of the crystal to finding a small number of mixing coefficients. This review presents the fundamentals of such a symmetry analysis of magnetic structures and methods of determining them from neutron-diffraction data. The described method, which is closely allied to

Properties of a Group (G)

- A group contains a set of elements A,B,C… that make up the group that satisfy the requirements:
  - **Closure:** Product of two elements of a group is also a member of the group AB ∈ G
  - **Associativity:** A(BC)=(AB)C for all ABC ∈ G
  - **Identity (E):** There is an identity element (E) satisfying EA=AE=A if A ∈ G
  - **Inverse:** There must be an inverse of each element. $AA^{-1}=A^{-1}A=E$

- Order of a group (*h*) is the number of elements in the group (can be finite or infinite).

Representational analysis

- A **representation** of any group G is a mapping of the elements of G to a set of n × n matrices, Γ={(g) | g ∈ G}, which have the same group structure under matrix multiplication.
  - e.g. $\Gamma(g_1 g_2) = \Gamma(g_1)\,\Gamma(g_2)$
- The number *n* is the dimension of the abstract representation space in which the matrices are embedded and is called the dimension of the representation.
- Two matrices are equivalent if there is a similarity transformation *U* (change of basis) between them common to all matrices: $\Gamma'(g) = U\Gamma(g)U^{-1}$
- A group can have an infinite number of representations of arbitrary dimension.
- Can find an appropriate similarity transformation *U* to reduce the representation to block-diagonal form.
  - **Irreducible Representation (irreps)** are those representations that cannot be reduced further.

$$\Gamma = \sum_{\oplus\nu} n_\nu \Gamma^\nu = n_1\Gamma^1 \oplus n_2\Gamma^2 \oplus \ldots \oplus n_m\Gamma^m$$

If the dimensions of representations Γ^ν are the smallest possible, the sub-matrices for the different group elements are the irreps

Representational analysis

$$\Gamma = \sum_{\oplus\nu} n_\nu \Gamma^\nu = n_1\Gamma^1 \oplus n_2\Gamma^2 \oplus \ldots \oplus n_m\Gamma^m$$

- Consider a group **G**= {a,b,c….} that can have the representation Γ= {Γ(a), Γ(b), Γ(c),….}
- Find a similarity transformation *U* that converts all matrices to the same block-diagonal form → obtain an equivalent representation that can be decomposed: $\Gamma(g)=U\Gamma(g)U^{-1}$

$$\Gamma(g)=\begin{pmatrix} A_{11} & A_{12} & 0 & 0 & 0 & 0 & 0 \\ A_{21} & A_{22} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & B_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & B_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{11} & C_{12} & C_{13} \\ 0 & 0 & 0 & 0 & C_{21} & C_{22} & C_{23} \\ 0 & 0 & 0 & 0 & C_{31} & C_{32} & C_{33} \end{pmatrix} = A(g)+2B(g)+C(g)$$

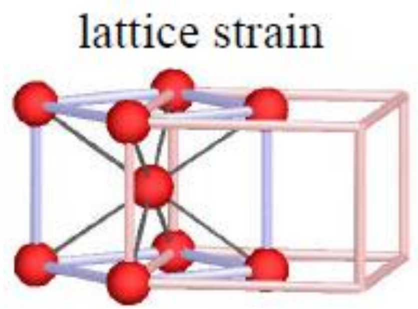
Matrices A(g),B(g) and C(g) are all representations of the group **G**.

Irreducible representations:

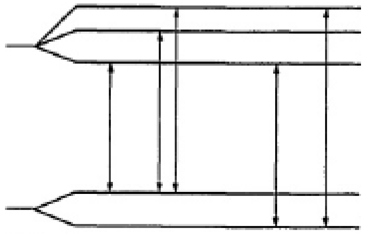
Γ^1={A(a),A(b),A(c),…}
Γ^2={B(a),B(b),B(c),…}
Γ^3={C(a),C(b),C(c),…}

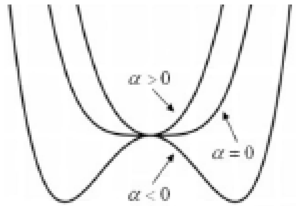
Why Representation analysis?

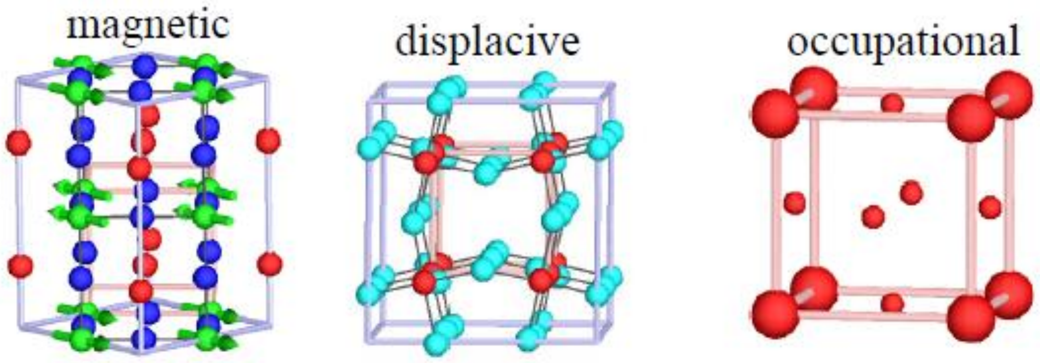
- Key point is that IRREDUCIBLE representations cannot be separated into smaller pieces.
- **Offer the building blocks to construct all possible magnetic structures.**
- A general approach to parameterize any "distortion"
  - Molecular vibrations
  - Hybridized and molecular orbitals
  - Crystal-field splitting
  - Crystal band structure



- Irreps provide a symmetry-based coordinate system (parameter set) for describing deviations from symmetry.







Why Representation analysis?

- Based on Group theory: developed to determine the coupling and orientation of $\mathbf{m}_j$
- Get several Irreps, $\mathbf{\Gamma}_{mag} = \Sigma_v n_v \mathbf{\Gamma}_v$, that describe all possible magnetic structures. Landau simplifies.
- Equally applicable to commensurate/incommensurate.
- Reduces the number of possible magnetic structures and number of parameters needed in the refinement of the structure.
  - A systematic way of finding all possible magnetic structures
  - Often complex and trivial spin orders can be determined with the same effort.
- The irreps of a system are intimately related to the eigenvectors of its Hamiltonian. Using representation theory, to define how a system changes, indirectly probes the energy terms driving a phase transition.

Using Representational analysis

- Determine k-vector, crystallographic space group (G_0) and positions of the magnetic atoms.
- Consider the little group G_K.
- Consider the effect of symmetry operations of $G_\mathbf{k}$ on the magnetic atoms, i.e., the change of the position and moment direction. The *magnetic representation* of the overall effect is given by the direct product (Γ_{mag}):

$$\Gamma_{mag} = \tilde{V} \times \Gamma_{perm}$$

$\tilde{V}$: change of roation for each atom (axial-vector representation,)

Γ_{perm}: change of position for each atom (*permutation representation*)

- Decompose the magnetic representation into the sum of irreps of $G_\mathbf{k}$.
  (i.e block diagonalize the matrix as much as possible): $\Gamma_{mag} = n_1 \Gamma_1 + n_2 \Gamma_2 + \ldots$
- For each irrep Γ_v appearing in the decomposition of Γ, find its basis vectors S_v^1, S_v^2, …
  → If it contains an *l* dimensional irrep, $\Gamma_i^{(l)}$, n_i times, there are $n_i \times l$ basis vectors.
- **The set of basis vectors for each irrep describes allowed magnetic structures.**

Basis vectors

- Consider the decomposition of the magnetic representation: $\Gamma_{mag} = 1\Gamma_1^{(1)} + 1\Gamma_2^{(2)}$

Superscript represents the order of the irreducible representation and the subscript is its index or label.

→ Γ_{mag} contains irreducible representation number 1 (which is of order 1) once, and irreducible representation number 2 (which is of order 2) once. This means that Γ_{mag} contains one basis vector associated with Γ_1 and two associated with Γ_2.

Basis vectors: Calculation of the basis vectors is done using the projection operator technique
→ take a test function and project from it the part that transforms according to each of the irreps.

Recall from earlier for magnetic structure:

$$\mathbf{m}_j = \Sigma_k \mathbf{S}_j^k e^{-2\pi i \mathbf{k}.R}$$

$$\mathbf{S}_j^{\mathbf{k}} = \Sigma_{n\lambda\nu} C_{n\lambda}^{\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(js)$$

k: propagating vector
ν: reference to irrep Γ_ν
n: index from 1 to n_ν $\Gamma_{mag} = \Sigma_\nu n_\nu \Gamma_\nu$
λ = index running from 1 to $\dim(\Gamma_\nu)$

Mixing coefficient: the free parameters that are varied to determine the magnetic structure
(they correspond to the *order parameters* in Landau theory)

Simplification of problem: Landau Theory

- **<u>Landau theory:</u> In a second order phase transition, a single symmetry mode is involved**

  → Only need one IR to describe the magnetic structure, all other irreps cancel

- For 1 atomic site can have lots of IRs. Can use this to greatly simplify analysis.

Lev. LANDAU

Nobel Prize 1962 "for his pioneering theories for condensed matter, especially liquid helium"

- Also helps with complex cases of more than one atomic site, e.g. A and B
- Assume representational analysis gives the following irreps:
  - Site A: $\Gamma_{mag} = 1\Gamma_1 + 0\Gamma_2 + 1\Gamma_3 + 1\Gamma_4$
  - Site B: $\Gamma_{mag} = 1\Gamma_1 + 1\Gamma_2 + 0\Gamma_3 + 0\Gamma_4$
- If both sites order together and this is second order
  - Magnetic structure described by only Γ_1

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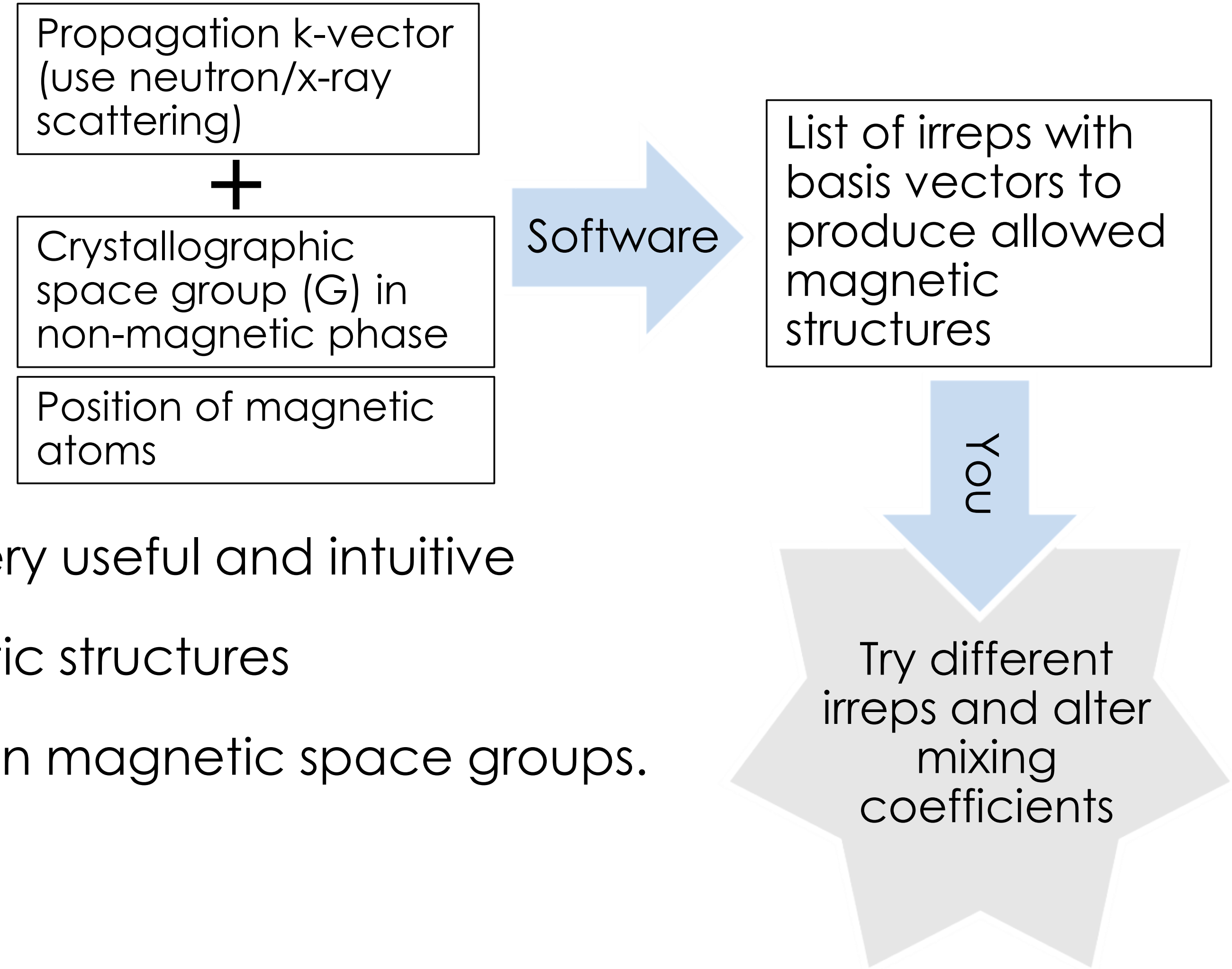
Using Representation Analysis

- Determining the basis vectors of irreps of space-groups is a **well-known but difficult** mathematical problem
- However, numerous tools are available:
  - BasIreps (included with Fullprof)
  - SARAh
  - Bilbao Crystallographic Server
  - JANA2006
  - ISOTROPY



- In practice representational analysis is very useful and intuitive
- Avoids incorrect and unphysical magnetic structures
- Perhaps conceptually more abstract than magnetic space groups.

An example of using Irreps: Pyrochlores

TABLE 3 The Basis Vectors (BV) Corresponding to the 16*d* Sites of the Pyrochlore Structure, Defined by Space Group $Fd\bar{3}m$ and Propagation Vector k = (0,0,0)

IR	BV	Atom 1 (1/2,1/2,1/2)	Atom 2 (1/2,1/4,1/4)	Atom 3 (1/4,1/2,1/4)	Atom 4 (1/4,1/4,1/2)
Γ_3	ψ_1	(1,1,1)	(1,−1,−1)	(−1,1,−1)	(−1,−1,1)
Γ_5	ψ_2	(1,−1,0)	(1,1,0)	(−1,−1,0)	(−1,1,0)
	ψ_3	(1,1,−2)	(1,−1,2)	(−1,1,2)	(−1,−1,−2)
Γ_7	ψ_4	(0,−1,1)	(0,1,−1)	(0,1,1)	(0,−1,−1)
	ψ_5	(1,0,−1)	(−1,0,−1)	(−1,0,1)	(1,0,1)
	ψ_6	(−1,1,0)	(1,1,0)	(−1,−1,0)	(1,−1,0)
Γ_9	ψ_7	(1,1,0)	(−1,1,0)	(1,−1,0)	(−1,−1,0)
	ψ_8	(0,0,1)	(0,0,1)	(0,0,1)	(0,0,1)
	ψ_9	(0,1,1)	(0,−1,−1)	(0,−1,1)	(0,1,−1)
	ψ_{10}	(1,0,0)	(1,0,0)	(1,0,0)	(1,0,0)
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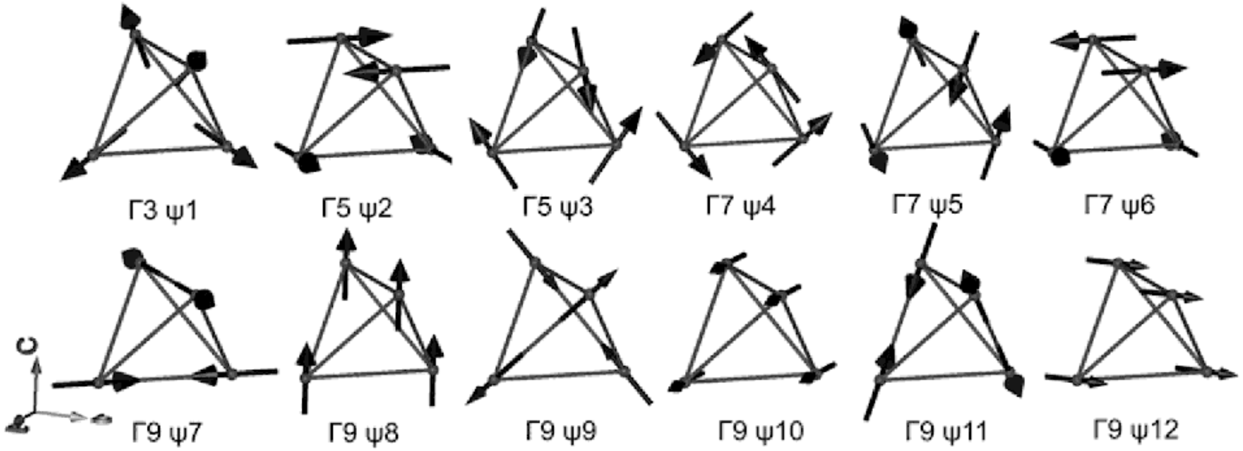
IR, irreducible representation; BV, basis vectors.

Magnetic representation of the crystallographic A^{3+} site in $A_2B_2O_7$:

$$\Gamma_{mag}(A) = 1\Gamma_3^{(1)} + 1\Gamma_5^{(2)} + 1\Gamma_7^{(3)} + 2\Gamma_9^{(6)}$$



Neutron Scattering - Magnetic and Quantum Phenomena, Chapter 4 - Magnetic Structures
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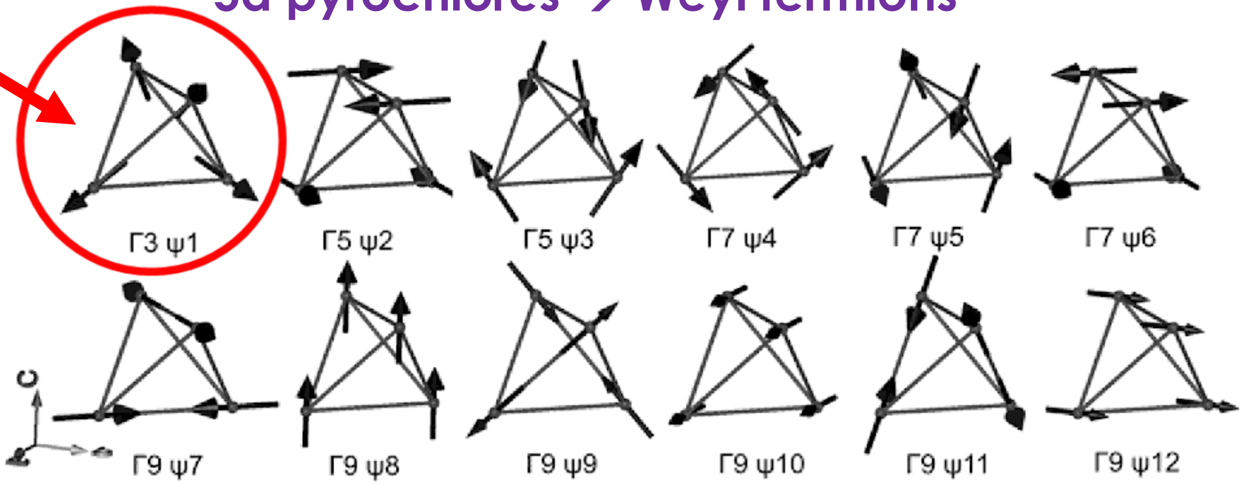
5d pyrochlores → Weyl fermions



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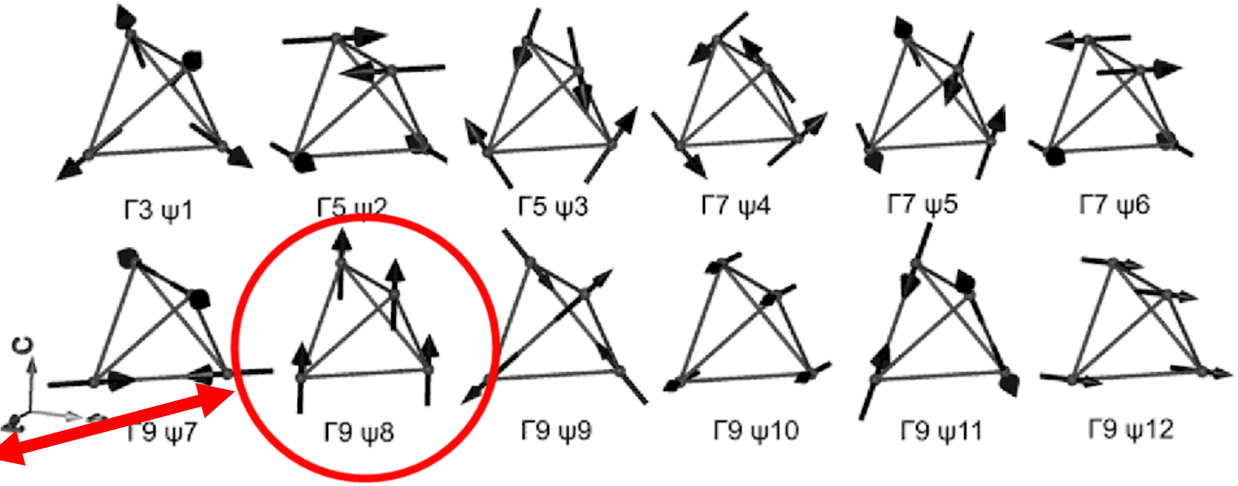

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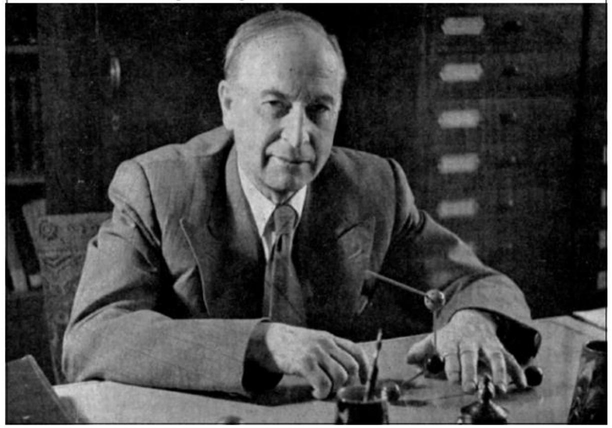
Magnetic space groups (Shubnikov groups)

Alexey Vasilyevich Shubnikov 1887-1970



- Natural extension of the crystallographic space group description.
- But only recently became accessible to the wider community.

1929: Heesch, introduces the antiidentity operation properties: u2 = 1, ut = tu for all t∈T

- **aka time reversal group = {1,1'}   (Z. Krist. 71, 95)**

1945: Shubnikov re-introduces concept of bi-colour point groups

1951: Shubnikov describes and illustrates all of the bicolor point groups (→ Shubnikov groups)

1955: Belov, Neronova, Smirnova (BNS) - first complete listing of the Shubnikov groups (Sov. Phys. Crys 1, 487-488)

1957: Zamorzaev, group theoretical derivation of Shubnikov groups (Kristallografiya2, 15 (Sov. Phys. Cryst., 3, 401))

1965: Opechowski and Guccione (OG), first complete derivation and enumeration of the Shubnikov groups

2001: Litvin, corrected Opechowski-Guccione symbols (Acta Cryst. A57, 729-730)

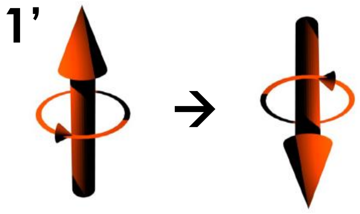
2010: Magnetic Space Groups on computer programs (Stokes and Campbell, BYU)

Future: combine magnetic space group and representational analysis approaches for complete insights

Magnetic space groups (Shubnikov groups)

- Use description from crystallography
- 230 Space groups for crystals describe **<u>positions</u>** of atoms.
- Magnetic structures → add magnetic spin to atom positions …. spins are axial vectors.
- Need spin reversal operator **1'** (aka antisymmetry, antiidentiy, or time-reversal)
  - Defines the current loop type symmetry of an axial vector
  - Can be combined with any conventional operator **h** to form a new primed operator **h'**

Time reversal = spin reversal
(changes the sense of the current)



The spin reversal operator 1' flips the magnetic moment

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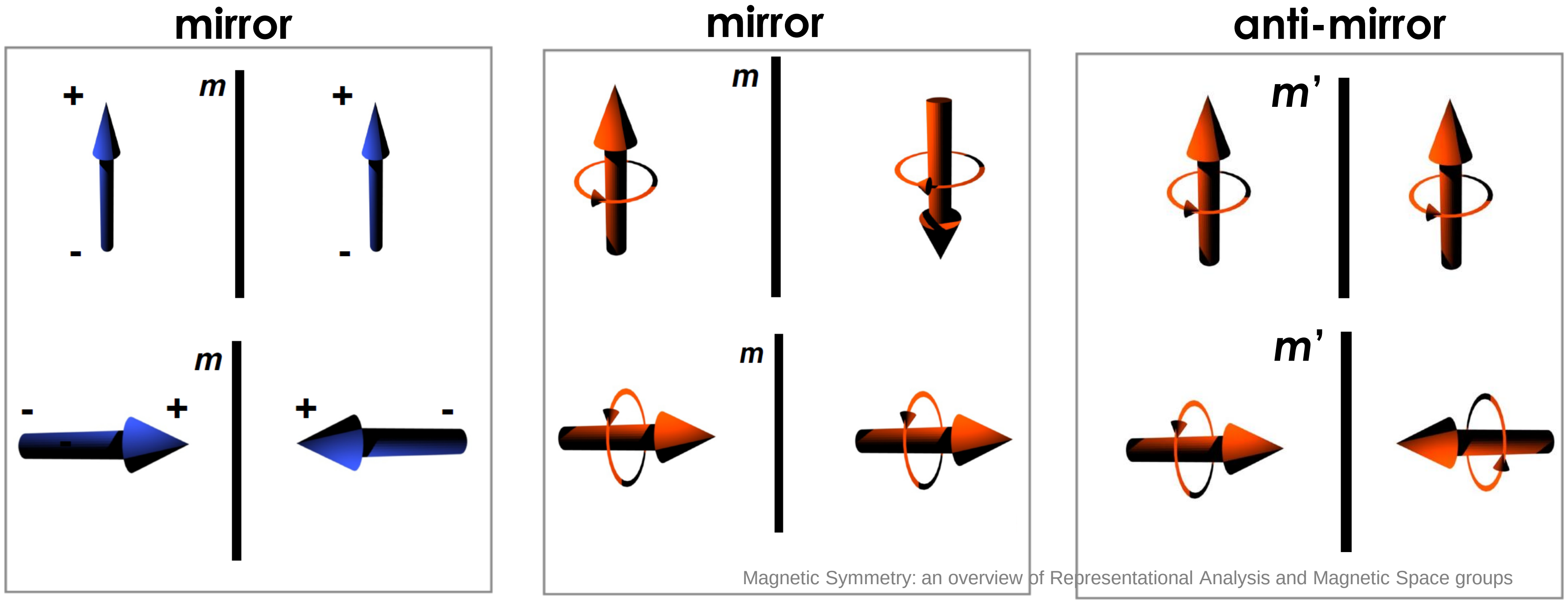
Symmetry Operations on:

- **Polar vector (e.g dipole) [Parity even, time-odd]**
- **Axial vector (magnetic spin) [Parity odd, time even]**



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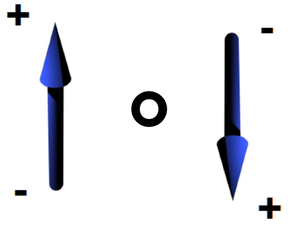
Inversion (-*1*)



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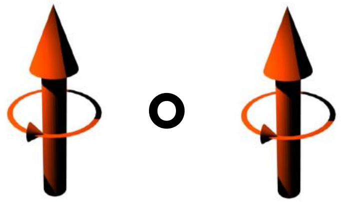

Building the magnetic space groups (Shubnikov groups)

- By associating the 1' operator with a color change (black to white or black to red) the magnetic symmetry theory was termed black-white symmetry.

- **The original 230 space groups are included as colorless groups and keep their standard labels**
  - **e.g. *Pmmm***

- **A further 230 groups are created by adding the 1' operator as an extra symmetry operation**
  - **e.g. *Pmmm'***
  - **These correspond to paramagnetic states and are termed grey (each magnetic site is both black and white = grey)**

- **The remaining 1191 magnetic space groups are created by combining the 1' operator with one or more of the symmetry operation in each of the 230 crystallographic space groups**
  - **e.g. *Pm'mm* where the mirror plane perpendicular to a is now an anti-mirror and the other two are unchanged.**

→ Combining all possibilities leads to 1651 magnetic space groups

Building the magnetic space groups

- 230 crystallographic space groups
  → add spin-reversal operator 1'
- 1651 Magnetic (Shubnikov) Space Groups

For each non-magnetic space group (*G*), we can construct multiple magnetic space groups (*M*). Some of them involve a non-magnetic subgroup (*D*) conganing half the elements of *G*

Type-I: *M=G* no primes (single color)	**230**
Type-II: *M=G+G1'* all primed and unprimed (paramagnetic or gray groups)	**230**
Type-III (3a): *M=D+(G-D)'* half are primed (black-white groups) Groups of the "first kind" D is translationgleiche *D translation is the same as G*	**674**
Type-IV (3b): *M=D+(G-D)'* half are primed (black-white groups) Groups of the "second kind" D is klassengleiche *D contains antitranslations leading to primitive magnetic cells larger than primitive crystal cells*	**517**
Total magnetic space groups	**1651**

Building the magnetic space groups

Example based on space group *P2/m*

Type-I
Fedorov group
10.42 $P2/m$
(x, y, z)
$(-x, y, -z)$
$(-x, -y, -z)$
$(x, -y, z)$

Type-III
black/white PG
10.44 $P2'/m$
(x, y, z)
$(-x, y, -z)'$
$(-x, -y, -z)'$
$(x, -y, z)$

Type-II
gray group
10.43 $P2/m1'$
(x, y, z)
$(-x, y, -z)$
$(-x, -y, -z)$
$(x, -y, z)$
$(x, y, z)'$
$(-x, y, -z)'$
$(-x, -y, -z)'$
$(x, -y, z)'$

Type-IV
black/white lattice
10.48 P_b2/m
(x, y, z)
$(-x, y, -z)$
$(-x, -y, -z)$
$(x, -y, z)$
$(x, y + 1/2, z)'$
$(-x, y + 1/2, -z)'$
$(-x, -y + 1/2, -z)'$
$(x, -y + 1/2, z)'$

Don't panic → All the hard work is done by **Bilbao Crystallographic Server** or **ISOTROPY** software suite

Type-I: *M*=*G* no primes (single color)	**230**
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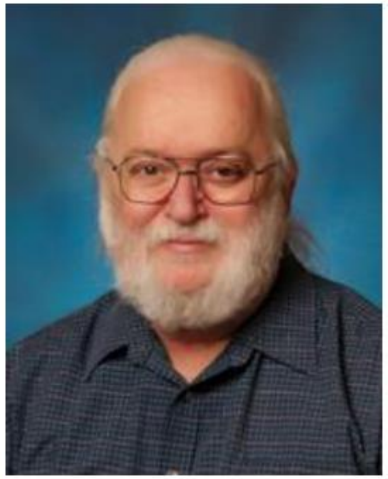
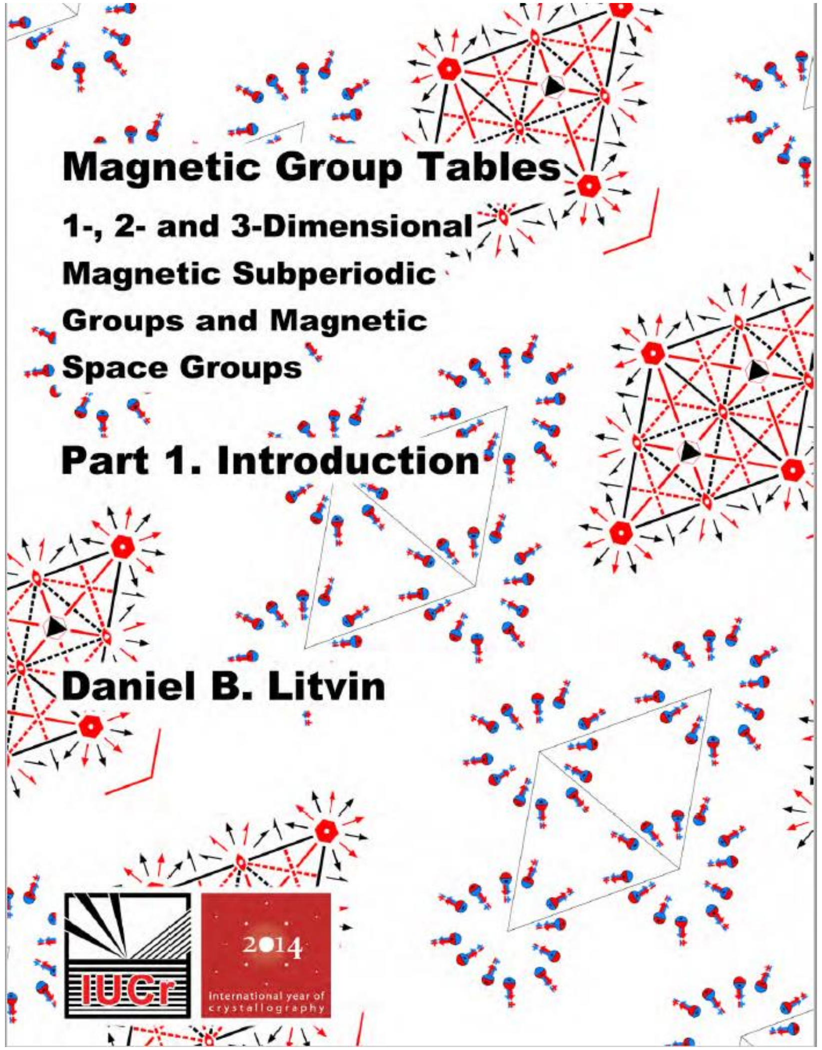
Total magnetic space groups	**1651**

Magnetic space groups

- Daniel Litvin provided a full description of all Shubnikov (Magnetic Space) groups
- Freely downloadable
  - Acta Cryst A57, 729-730 (2001)
  - Acta Cryst. (2008). A64, 419-424 (2008)

A note on magnetic space group notations

- Two notations for describing magnetic space groups in the literature:
  - **Belov-Neronova-Smirnova (BNS)**
    N. V. Belov, N. N. Neronova and T. S. Smirnova, *Kristallografiya* **2**, 315 (1957) (English translation: Sov. Phys. *Crystallogr*. **2**, 311).
  - **Opechoski-Guccione (OG)**
    W. Opechowski and R. Guccione, *Magnetic Symmetry*, in *Magnetism* (G.T. Rado and H. Shull, eds.), Vol II A, Ch. 3, 105 Academic Press, New York. (1965).
- Identical, expect for black-white magnetic space groups (type-IV).
- Recently a list of all 1651 magnetic space groups published.
  Similar form to Int. tables for crystallographic groups.
  - D. B. Litvin, *Acta Cryst*. **A64**, 419 (2008). (in OG notation)
  - H. Grimmer, *Acta Cryst*. **A65**, 145 (2009). (reinterpretation for BNS)

Magnetic Superspace groups

- Recently magnetic space group approach has now been fully generalized to include incommensurate structures beyond the 1651 Shubnikov groups

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TOPICAL REVIEW

Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases

J M Perez-Mato[1], J L Ribeiro[2], V Petricek[3] and M I Aroyo[1]

[1] Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apartado 644, E-48080 Bilbao, Spain
[2] Centro de Física da Universidade do Minho, P-4710-057 Braga, Portugal
[3] Institute of Physics, Academy of Sciences of the Czech Republic v.v.i., Na Slovance 2, CZ-18221 Praha 8, Czech Republic

E-mail: jm.perez-mato@ehu.es

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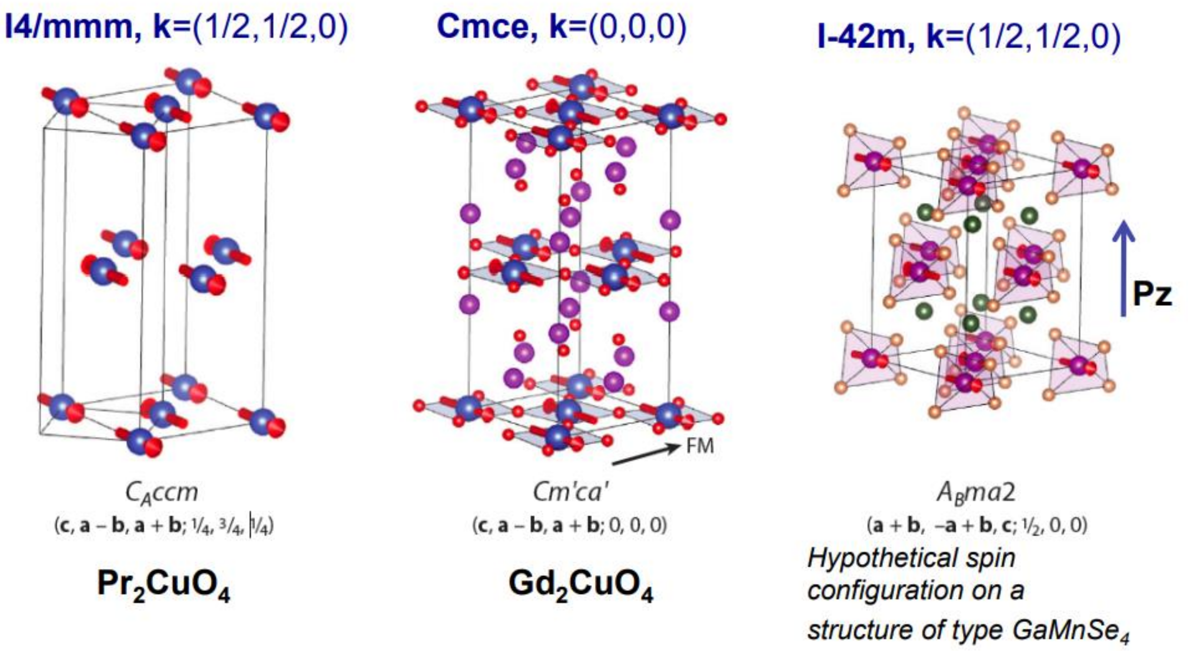
Abstract
Superspace symmetry has been for many years the standard approach for the analysis of non-magnetic modulated crystals because of its robust and efficient treatment of the structural constraints present in incommensurate phases. For incommensurate magnetic phases, this generalized symmetry formalism can play a similar role. In this context we review from a practical viewpoint the superspace formalism particularized to magnetic incommensurate phases. We analyse in detail the relation between the description using superspace symmetry and the representation method. Important general rules on the symmetry of magnetic incommensurate modulations with a single propagation vector are derived. The power and efficiency of the method is illustrated with various examples, including some multiferroic materials. We show that the concept of superspace symmetry provides a simple, efficient and systematic way to characterize the symmetry and rationalize the structural and physical properties of incommensurate magnetic materials. This is especially relevant when the properties of incommensurate multiferroics are investigated.

- Supersymmetry should soon be implemented into Fullprof

Magnetic space groups: all atoms

- The non-magnetic atoms are also often important in the physics
- Magnetic space groups contain all information on crystal and magnetic symmetry of whole structure
- The same spin arrangement can produce different magnetic space groups (and different physical properties, e.g. ferroic) depending on the symmetry of the parent

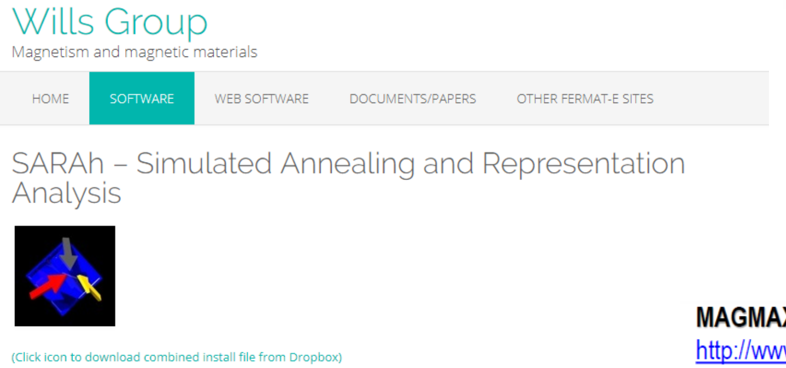


Determining magnetic structures

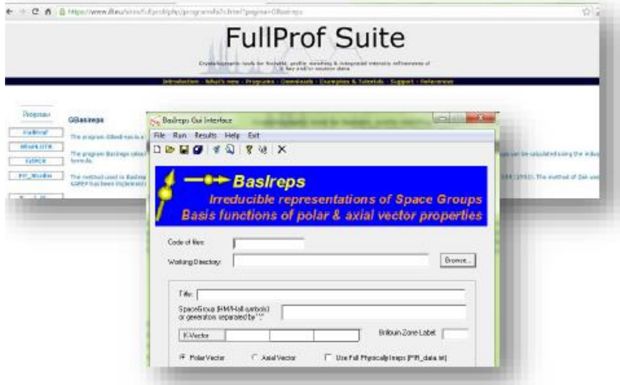
- Collect the bulk data and scattering data
- Identify the propagation vector (k-vector)
- Explore the symmetry allowed magnetic structures through Representational analysis and/or magnetic space groups
- Select the best physical meaningful models compatible with ALL data (not just neutron data)
- Refine direction and amplitude of the Fourier components (Basis vector) [Neutron diffraction]
- **Now every magnetic structure reported should (must?!) have a magnetic space group. Just like all crystal structures reported have a space group.**

Software Tools

SARAh Representational Analysis:
http://fermat.chem.ucl.ac.uk/spaces/willsgroup/software/sarah-magnetic-symmetry-calculations-magnetic-structure-analysis/

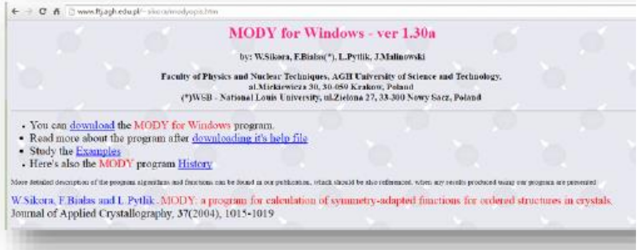


BasIreps (FullProf_Suite)
https://www.ill.eu/sites/fullprof

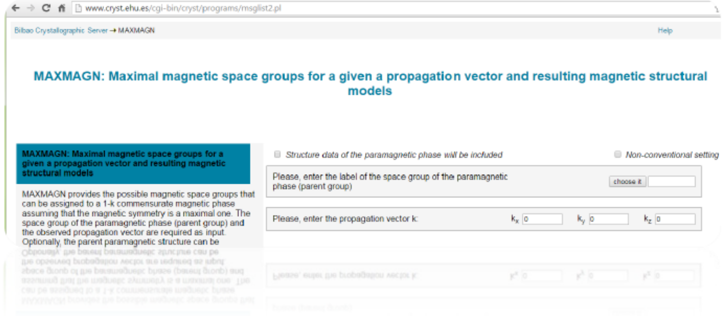


JANA: http://jana.fzu.cz/

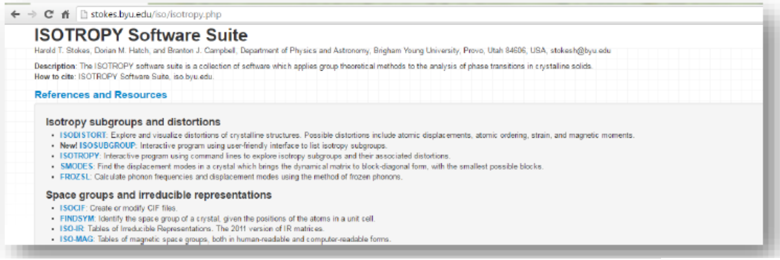
MODY
http://www.ftj.agh.edu.pl/~sikora/modyopis.htm



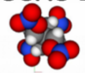
MAGMAX: Bilbao Crystallographic Server
http://www.cryst.ehu.es/cgi-bin/cryst/programs/msglist2.pl



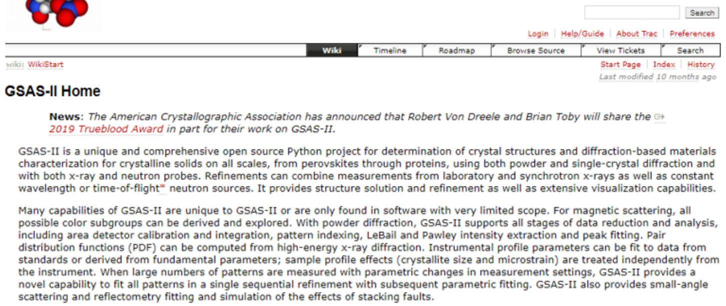
ISOTROPY Software Suite: http://stokes.byu.edu/iso/isotropy.php



GSAS-2



https://subversion.xray.aps.anl.gov/trac/pyGSAS



SpinW: https://www.psi.ch/spinw/

Some references on magnetic symmetry

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Conclusion

- Magnetic structures can be described by working through propagation vector formulism → but lack of constraints can lead to problems
- Use of symmetry is extremely powerful and helpful
- Either Representational Analysis or Magnetic Space Groups offer routes to determine the correct magnetic structure.
  – **Using both is better and gives most insights into the physics.**
- Software is now available to do both routinely.