An Introduction to Magnetic Structures

-Working with the propagation vector (Crystalline Solids)

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Why use symmetry?

- **Electronic properties and structures are complex**
  - *Magnetism is the spin-dependent part*
- **Never as much information about them as we would like**
  - Experimentalists typically deal with under-defined problems (there are too many possible solutions)
  - Symmetry is useful to introduce a grand simplifying structure (makes rules - followed and broken, classes of behaviour, and thus to simplify, clarify and reveal…)

Overview of today

- **Why do we need to invoke symmetry?**
- **Taking symmetry theory from point groups to magnetic structures**
  - Translational periodicity
    - Increases complexity of the irreducible representations
    - Rotation-translation operations
    - The propagation vector, the k-vector
- **A more sophisticated language**
  - The little group of the propagation vector G_k
  - Permutation representation
  - Axial and polar vectors, representations
  - Magnetic representation
  - Basis vectors
  - Couplings - Time reversal and Landau theory
- **Symmetries and frameworks**
  - Representations and irreducible representations
  - Magnetic space groups (time reversal)

➡ *Gives the language for understanding magnetic structures, for posing questions*

Overview of today
- 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**
  - Working with necessity - *Ockham's razor*

Overview of this lecture
-Working with the propagation vector

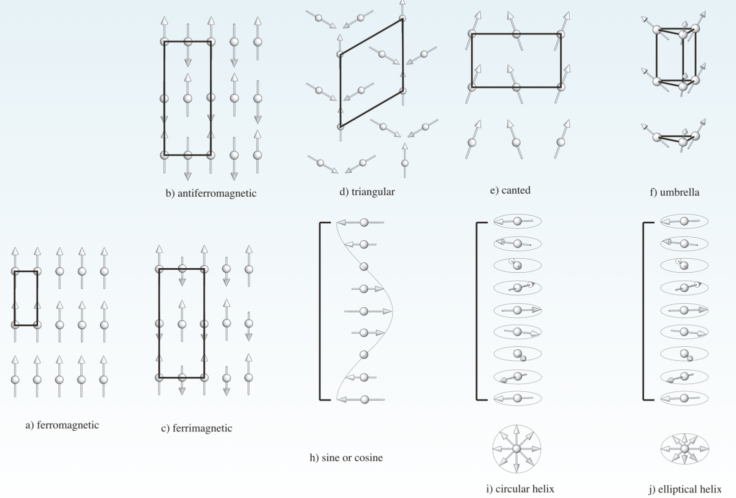
- **Using the symmetry language**
  - Away from a shaken box → Frameworks and information
  - Reveal what magnetic structures are
  - Building up descriptions to make the range of possible magnetic structures
  - Pulling together the different symmetry ideas together within representation theory

➡*Using the language to build up some structures*

Why should an experimentalist use symmetry?
-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)

Some simple magnetic structures



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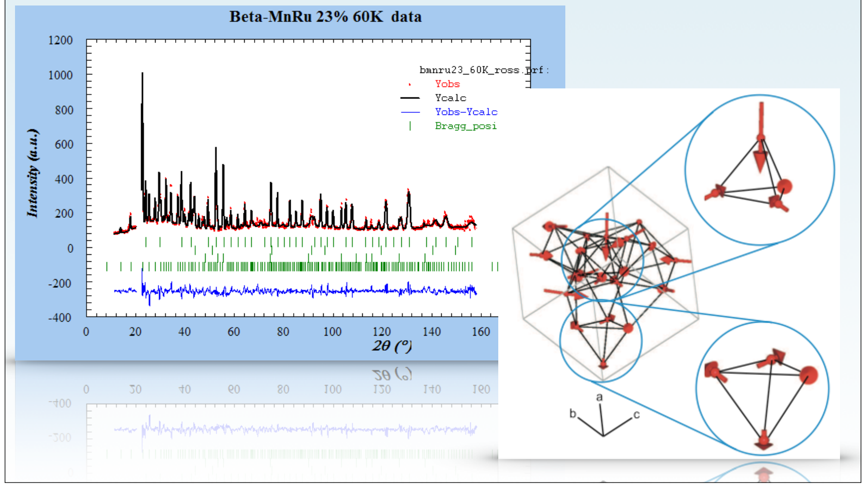
Complex incommensurate magnetic ordering in B-$Mn_{1-x}Ru_x$ (x=0.12)



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→ **Under-defined problem**
→ **Hidden (unconsidered) possibilities**

Definition of magnetic structures, phonons, electronic orbitals

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

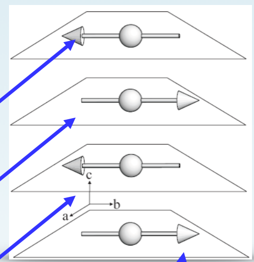
$$\vec{\psi}^{\vec{k}}_{j,\nu} \equiv \vec{\psi}^{\vec{k}}_{i,\nu}\; e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

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

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

The propagation vector

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



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

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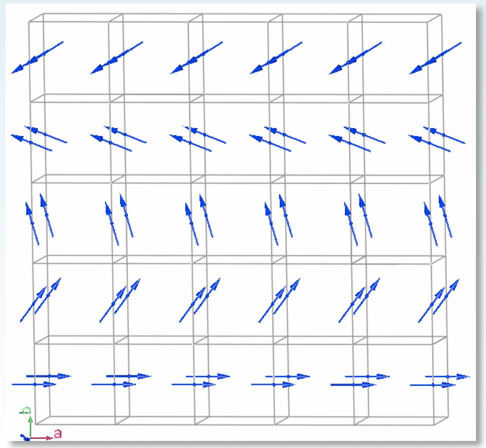
$$\vec{\psi}^{\vec{k}}_{j,\nu} = \vec{\psi}^{\vec{k}}_{i,\nu}\ \exp\left[-2\pi i \begin{pmatrix}0\\0\\0.5\end{pmatrix}\cdot\begin{pmatrix}0\\0\\0\end{pmatrix}\right] = \vec{\psi}^{\vec{k}}_{i,\nu}\ \exp\left[-2\pi i 0\right] = \vec{\psi}^{\vec{k}}_{i,\nu}$$

The formalism of the propagation vector, k

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

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



What a magnetic structure (Néel state) is

- An ordered configuration of magnetic moments with a long correlation length
  - The order has some translational symmetry (the moments in different unit cells - related by primitive lattice vectors - are related)
- The orientations of the moments are related by symmetry (what happens in detail depends on where the moments are in the system and the host crystal structure)

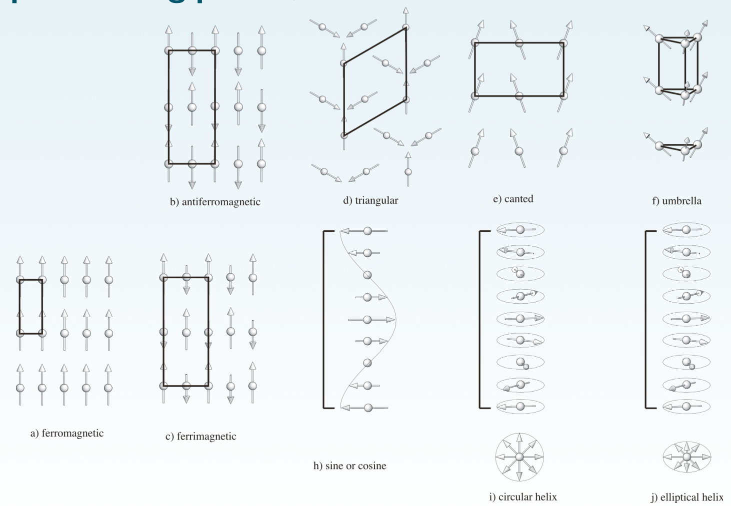
What a magnetic structure isn't

- A haphazard set of arrows (moments) in a box (crystal structure)
  - This could fail to have the translational symmetry relating moments in different unit cells (<u>careful with centred cells</u>!!!)
  - Magnetic structures are pretty well misunderstood and papers giving nonsensical structures an frequent problem…
- There are <u>rules</u>…
  - But they are open ended…

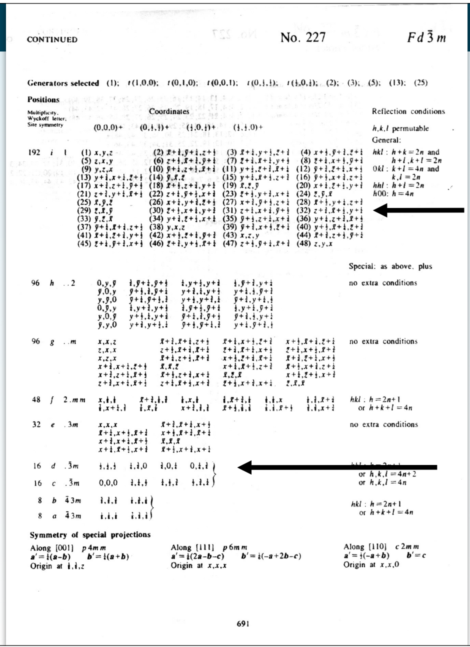
What different types of structures are possible?

- Lots:
  - Simple ferromagnetic structures (identical moments that align parallel)
  - Simple antiferromagnetic and ferrimagnetic structures (neighbouring moments align antiparallel)
  - Complex antiferromagnetic structures
    - Commensurate
    - Incommensurate (sine waves or spin density waves, helices, etc)
  - **Open ended → Mixtures**

Simple starting points, end members



Which moments are related by symmetry?



576 Variables (done badly) Down to 144…

12

Magnetic structures

- **k-vector :**
  - Propagate (a component of) the magnetic structure through the crystal
  - Define translational periodicity and orientation dependence
- **basis vectors**
  - Build up symmetry within primitive unit cell of G_0

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

How can magnetic structures be described - Simple moments and unit cells?

- People like to think in terms of $\boldsymbol{m}_{||x}$, $\boldsymbol{m}_{||y}$, $\boldsymbol{m}_{||z}$ – Don't!
- Begin with $\boldsymbol{m}_{||a}$, $\boldsymbol{m}_{||b}$, $\boldsymbol{m}_{||c}$ (the components along parallel to the crystal axes)
  - This description is intuitive
  - Best used to describe the final structure, not to refine it
  - Instead use functions that are symmetry adapted to the system you are dealing with, these will allow more complex symmetries

- People like to use unit cells (magnetic space groups)
  - This description is intuitive
  - The description of a magnetic structure within MSG framework is equivalent to using representation analysis - it has to be
  - Beauty is in the eye of the beholder.
    - Both MSGs and representation theory need to be treated with care. Couplings are treated differently, elegance of describing a structure depends on what you want and your preferred point of reference.

How can magnetic structures be described -an alternative approach

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

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

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

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

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

Basis vectors and k-vectors

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

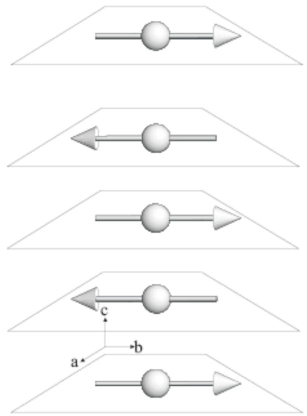
$$\vec{m}_j = \sum_{\nu,\vec{k}} C_\nu^{\vec{k}} \; \vec{\psi}_{i,\nu}^{\vec{k}} \; e^{-2\pi i \vec{k}\cdot\vec{t}_{ij}}$$

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

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

  - **If $\vec{\psi}$ is real and the propagation vector is such that the sine part is zero, e.g components 0 and 1/2**
    - ➡ **Left with a simple cosine curve with the moments of the same amplitude.**

A simple (~~cosine~~) structure



ψ exp[-2πi**k**·**t**] = (0 1 0) exp[-2πi(0 0 ½)·(0 0 4)] = (0 1 0)

ψ exp[-2πi**k**·**t**] = (0 1 0) exp[-2πi(0 0 ½)·(0 0 3)] = (0 –1 0)

ψ exp[-2πi**k**·**t**] = (0 1 0) exp[-2πi(0 0 ½)·(0 0 2)] = (0 1 0)

ψ exp[-2πi**k**·**t**] = (0 1 0) exp[-2πi(0 0 ½)·(0 0 1)] = (0 –1 0)

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Basis vectors and k-vectors

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

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

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

  - As

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

  - Substitution and expansion of the exponential leads to

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

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

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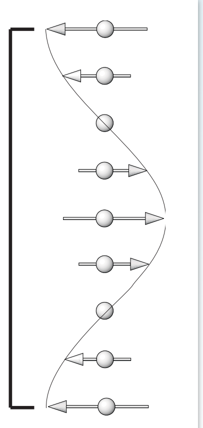

h) sine
or
cosine

Basis vectors and k-vectors

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

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

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

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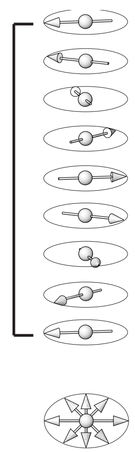


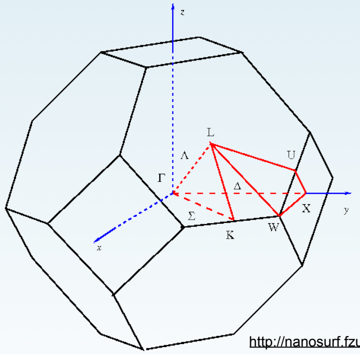
j) elliptical helix

Building structures : basis vectors and k-vectors

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

Practice making some magnetic structures

Work with the Brillouin zone and types of 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

But what about unseen complexity?

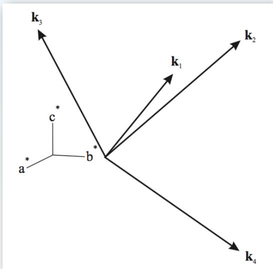
- Types of domain (characterised by the types of symmetry elements lost during the magnetic ordering)

Configurational (k) domains	(translational symmetry)
Pi domains	(time reversal)
Orientational (S) domains	(rotational symmetry)
Chiral domains	Centrosymmetry

Configurational domains (k domains)

- Arise if G_k<>G_0
  - Operating with the paramagnetic symmetry elements on ***k*** generates a set of inequivalent vectors which form the star of ***k***, e.g. $\boldsymbol{k}_1=\boldsymbol{k}_1 E$, $\boldsymbol{k}_2=\boldsymbol{k}_1 R_2$, $\boldsymbol{k}_3=\boldsymbol{k}_1 R_3$, $\boldsymbol{k}_4=\boldsymbol{k}_1 R_4$...
  - e.g. FCC lattice

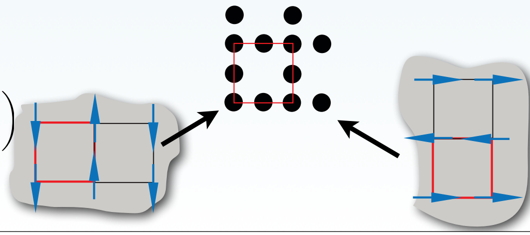
$$\vec{k}_1 = \left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$$
$$\vec{k}_2 = \left(-\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$$
$$\vec{k}_3 = \left(\frac{1}{2},-\frac{1}{2},\frac{1}{2}\right)$$
$$\vec{k}_4 = \left(\frac{1}{2},\frac{1}{2},-\frac{1}{2}\right)$$



Configurational domains (k domains)

- Each vector in the star generates a different (equivalent) configuration domain
- Each configuration domain gives a completely separate set of magnetic reflections at positions ±k from the reciprocal lattice nodes
- Each set of reflections belongs to a distinct region of the crystal, hence effectively to a single state

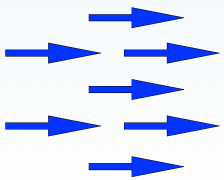
$$\vec{k}_1 = \left(\frac{1}{2},0,0\right)$$



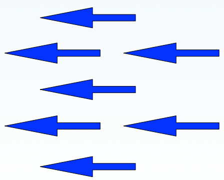
$$\vec{k}_2 = \left(0,\frac{1}{2},0\right)$$

π- domains (time reversal)

- Regions in which all the moment directions in one domain are reversed with respect to those in the other
- The two domains are related by the time inversion operator
- Ferromagnetic domains provide a simple example
- The intensity and the polarisation scattered by the two domains are identical

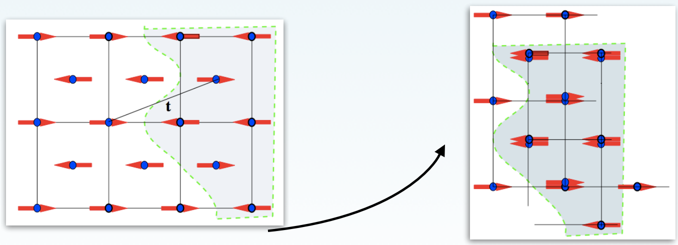


Time reversal reverses magnetic moments



Slip and translational domains

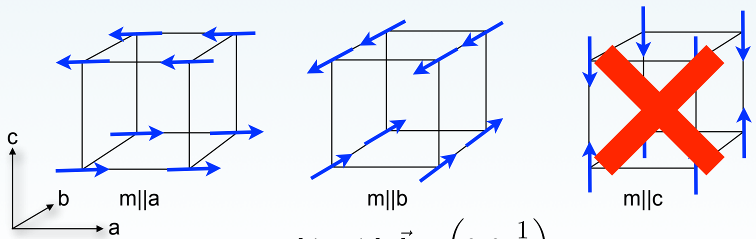
- Regions in which all the moment directions in one domain are related to another by translational symmetry
- The intensity and the polarisation scattered by the two domains are identical



Apply translation ***t***

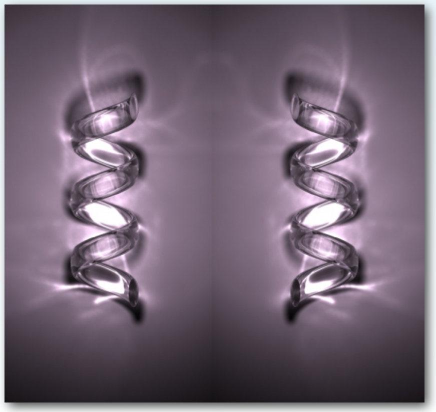
Orientational domains (S-domains)

- Occurs when the symmetry of the magnetic structure is less than that of the crystal space group
- S domains are related by the symmetry elements that are lost (***k* does not change**)
- The relationship between ***m*** and ***k*** is the same for all ***s*** domains
- Distinguish by single crystal diffraction, not powder diffraction



e.g. cubic with $\vec{k} = \left(0, 0, \frac{1}{2}\right)$

Chiral domains



- Occurs when
  - Paramagnetic space group is centrosymmetric but the magnetic structure is not
  - The magnetic moments on centrosymmetrically related sites are not parallel
  - Incommensurate structures
    - when 2***k*** is not a reciprocal lattice vector so the configurational group is acentric
    - In this case the two chirality domains correspond to +***k*** and -***k***. They both give contributions at (hkl) ± ***k***

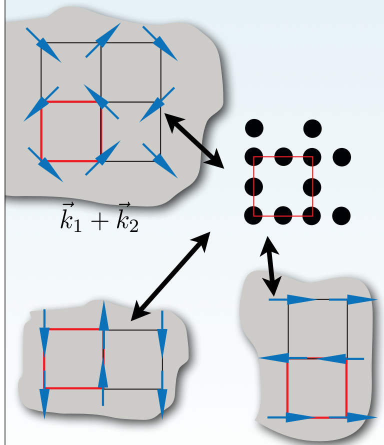
Thinking about unseen complexity

- Fourier description of magnetic structures
  - **Each single domain follows**

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

  - In the absence of unbalancing constaints (applied magnetic or electric field, pressure, etc) these will have the same energy
  - **Leads to questions**
    - are there S-domains
    - multi-k or k-domain?

k-domains vs multi k



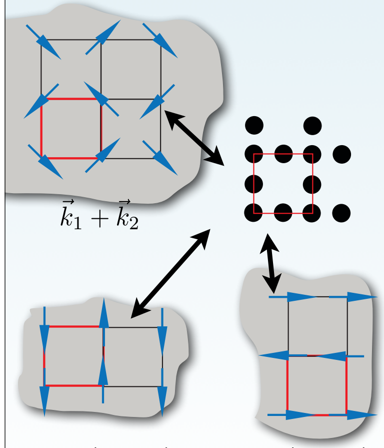
$\vec{k}_1 = \left(\frac{1}{2}, 0, 0\right)$ $\quad \vec{k}_2 = \left(0, \frac{1}{2}, 0\right)$

- Example of diffraction pattern (structure) with 2k vectors:

$$\left(\frac{1}{2}, 0, 0\right) + \left(0, \frac{1}{2}, 0\right)$$

  - Both will contribute to reflections at the same *(hkl)*
  - Cannot distinguish by simple diffraction
    - 2k structure
    - 2 k-domains

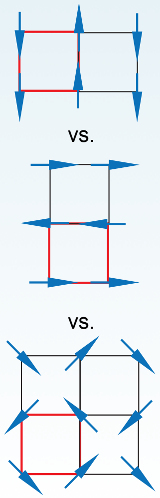
k-domains vs multi k



$\vec{k}_1 = \left(\frac{1}{2}, 0, 0\right)$ $\vec{k}_2 = \left(0, \frac{1}{2}, 0\right)$

- **External constraint, e.g.**
  - Applied magnetic field
  - Pressure
  - Leads to
    - Unbalancing domains
    - Domain repopulation
- Multi-k and k domains structures, S-domain structures will respond differently

Diffraction- Single crystal vs. powder



- Powder diffraction
  - (diffraction pattern projected onto a line)
  - Cannot even see k-domains/multi-k
  - **But you can always consider the possibilities and effects such as single-ion anisotropy…**
- Single crystal diffraction
  - Apply constraint to
    - differentiate k domains from multi-k
    - explore S-domains