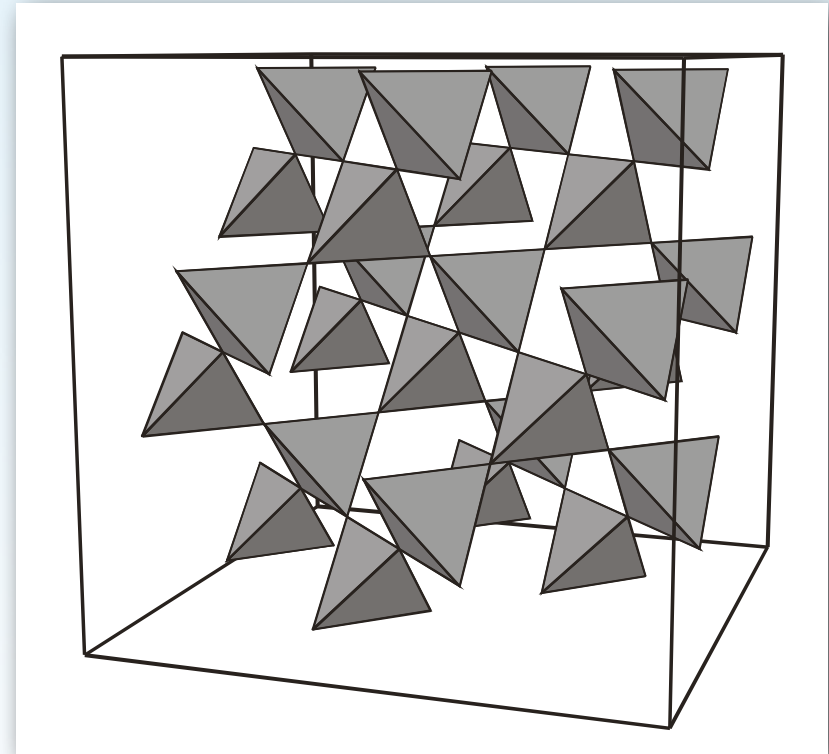


Now for some examples

Example 1) $\text{Er}_2\text{Ti}_2\text{O}_7$ introduction

- Pyrochlore with frustrated AFM interactions
 - Er^{3+} ($4I_{15/2}$), XY anisotropy
 - $\theta_{\text{CW}} = -22\text{K}$
 - 1 ordering transition
 - Second order
 - $T = 1.173\text{K}$
 - Néel order
 - $k = 000$
 - Extensive quantum fluctuations stabilise particular ground state



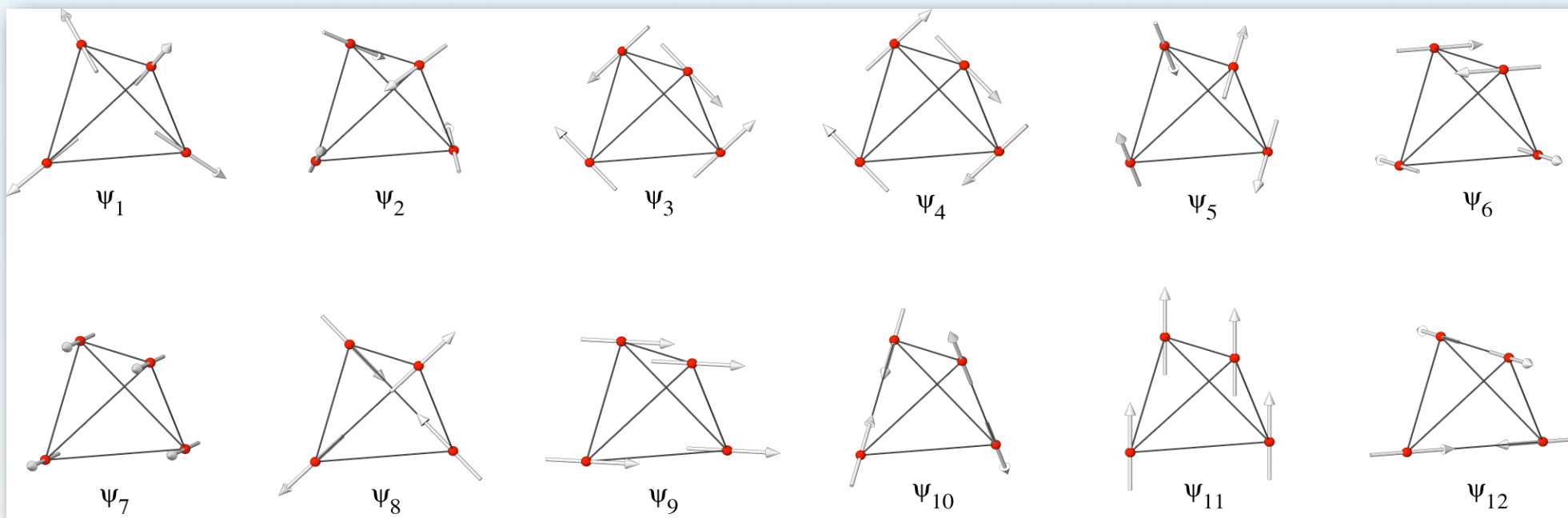
Er₂Ti₂O₇ : k=0

Γ_3 FeF₃ structure

Γ_5 an XY structure

Ground states of AF Td Γ_7

Ground states for dipolar pyrochlore model

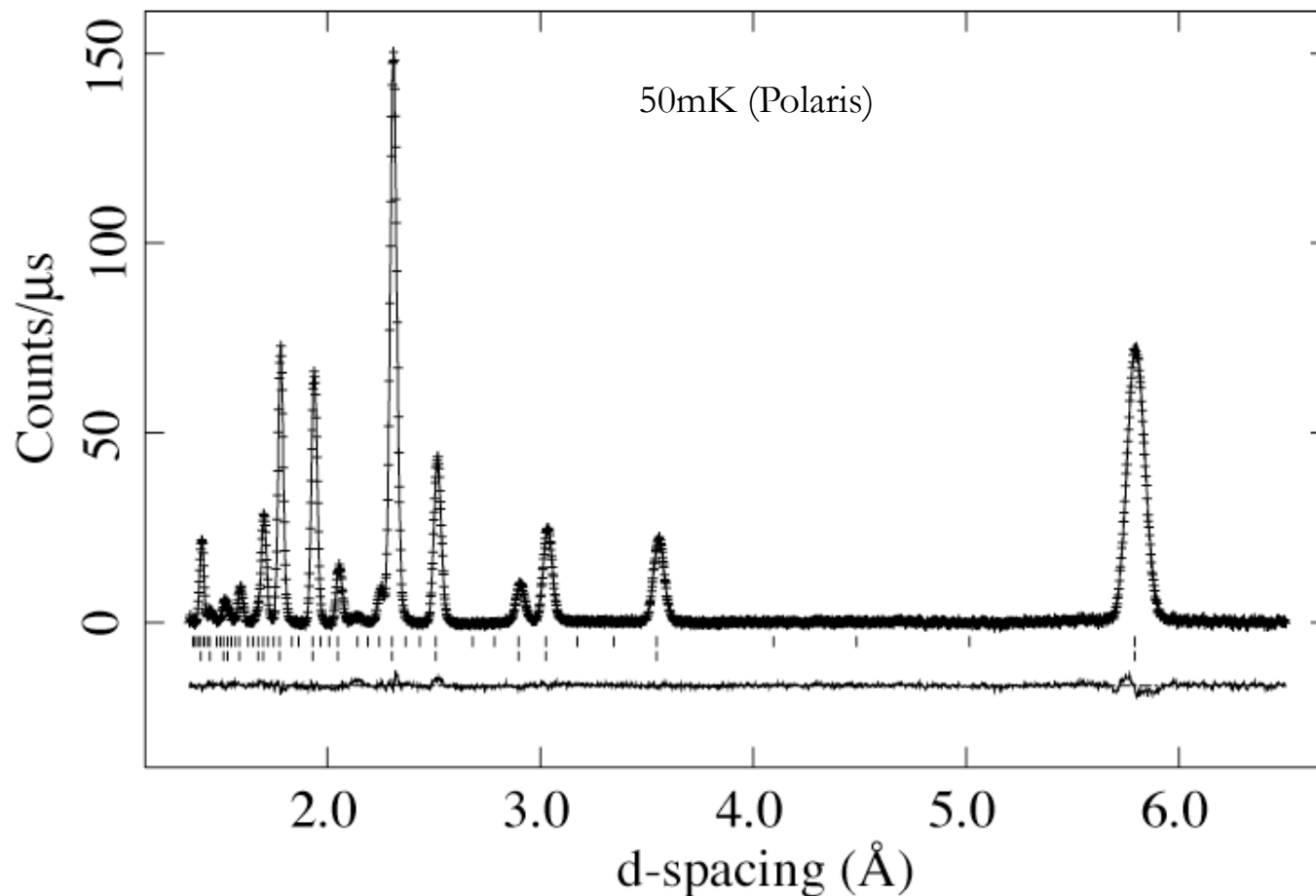
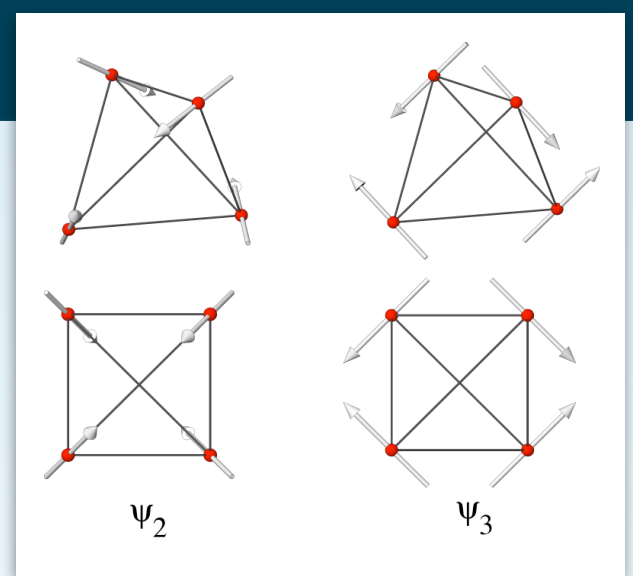


Γ_9

Spin ice, Soft spin ices

Er₂Ti₂O₇ : Powder diffraction

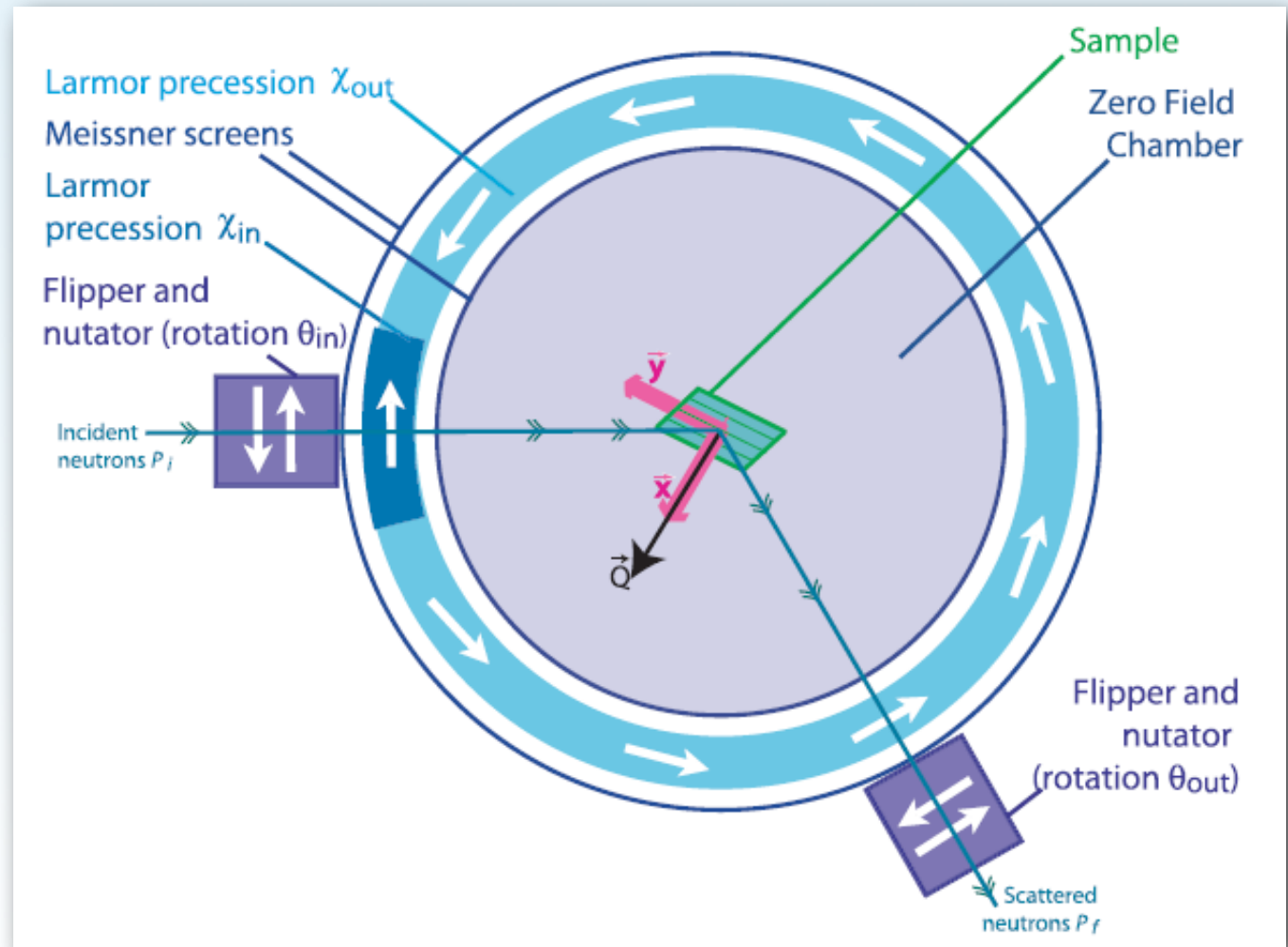
k=000



- Simulations show Ψ_2 to be weakly stabilised by thermal fluctuations
- Ψ_2/Ψ_3 ratio changes as function of T ?
- Powder diffraction cannot tell !

Spherical Neutron Polarimetry-Access transverse components of the polarisation

- CRYOPAD
 - CRYOgenic
 - Polarisation
 - Analysis
 - Device
- Zero magnetic field chamber
- Neutron spin vector
 1. Defined
 2. Rotated by the sample magnetism
 3. Project out components



Er₂Ti₂O₇- Spherical Neutron Polarimetry

- Analysis based on Blume- Maleev equations

$$\begin{aligned}
 \vec{P}_f \sigma &= (\vec{P}_i N N^*) + (-i(\vec{M}_\perp^* \times \vec{M}_\perp)) \\
 &+ (-\vec{P}_i(\vec{M}_\perp \cdot \vec{M}_\perp^*) + (\vec{M}_\perp(\vec{P}_i \cdot \vec{M}_\perp^*) + \vec{M}_\perp^*(\vec{P}_i \cdot \vec{M}_\perp)) \\
 &+ (N\vec{M}_\perp^* + N^*\vec{M}_\perp - i(N\vec{M}_\perp^* - N^*\vec{M}_\perp) \times \vec{P}_i)
 \end{aligned}$$

$$\begin{aligned}
 \sigma &= (N N^*) + (i\vec{P}_i \cdot (\vec{M}_\perp^* \times \vec{M}_\perp)) \\
 &+ (\vec{M}_\perp \cdot \vec{M}_\perp^*) + (\vec{P}_i \cdot (\vec{M}_\perp N^* + \vec{M}_\perp^* N))
 \end{aligned}$$

Er₂Ti₂O₇- Spherical Neutron Polarimetry

$$\mathcal{P} = \begin{pmatrix} (N^2 - \mathbf{M}_\perp^2)/I_x & J_{nz}/I_x & J_{ny}/I_x \\ -J_{nz}/I_y & (N^2 - \mathbf{M}_\perp^2 + R_{yy})/I_y & R_{yz}/I_y \\ -J_{ny}/I_z & R_{zy}/I_z & (N^2 - \mathbf{M}_\perp^2 + R_{zz})/I_z \end{pmatrix}$$

$$\mathbf{P}'' = \begin{pmatrix} -J_{yz}/I \\ R_{ny}/I \\ R_{nz}/I \end{pmatrix} \quad \begin{aligned} I_x &= \mathbf{M}_\perp^2 + N^2 + P_x J_{yz} \\ I_y &= \mathbf{M}_\perp^2 + N^2 + P_y R_{ny} \\ I_z &= \mathbf{M}_\perp^2 + N^2 + P_z R_{nz} \\ I &= \mathbf{M}_\perp^2 + N^2 + P_x J_{yz} + P_y R_{ny} + P_z R_{nz} \end{aligned}$$

$$N^2 = N(\mathbf{k})N^*(\mathbf{k})$$

$$R_{ij} = 2\Re(\mathbf{M}_{\perp i}(\mathbf{k})\mathbf{M}_{\perp j}^*(\mathbf{k}))$$

$$J_{ij} = 2\Im(\mathbf{M}_{\perp i}(\mathbf{k})\mathbf{M}_{\perp j}^*(\mathbf{k}))$$

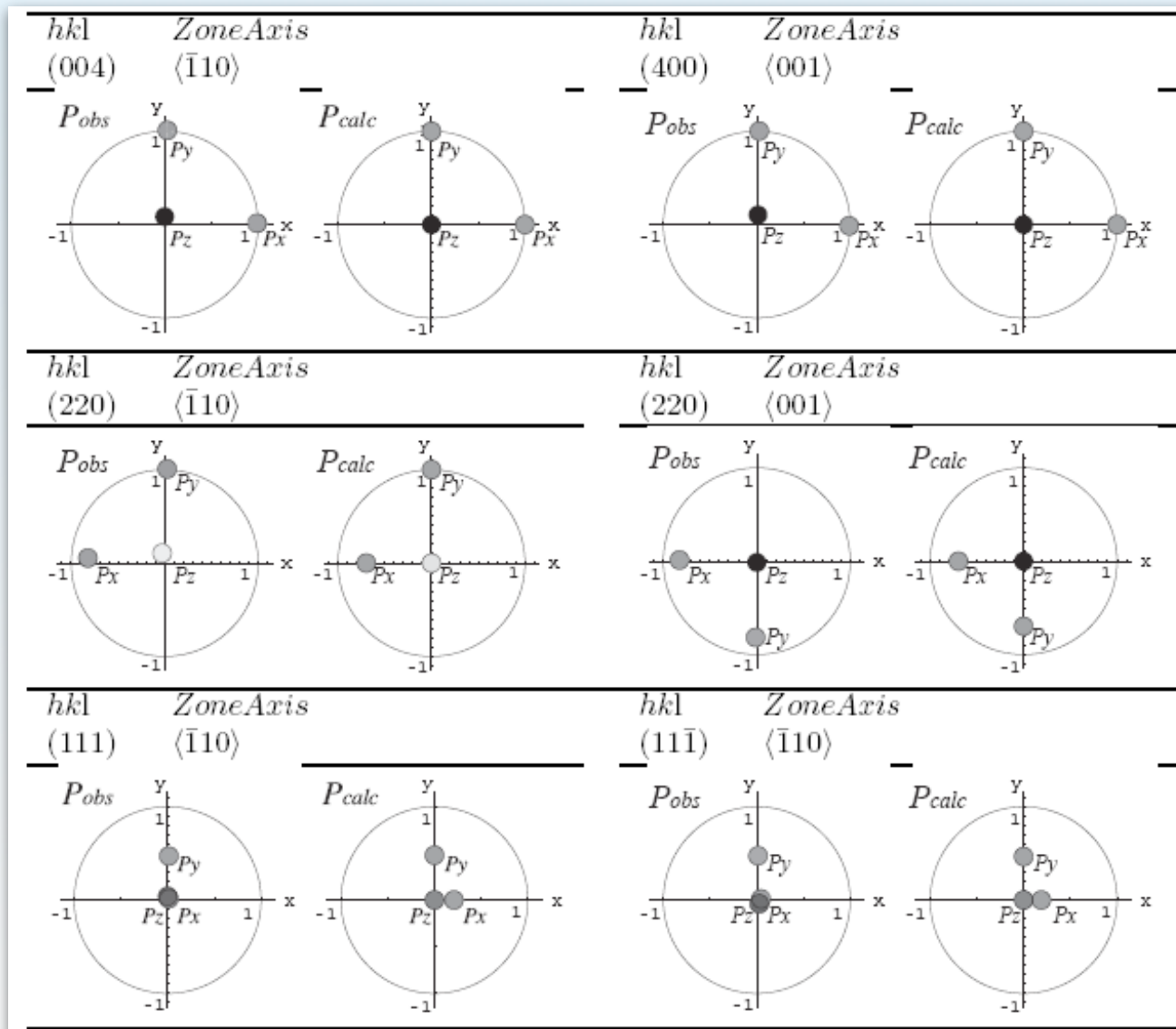
$$\mathbf{M}_\perp^2 = \mathbf{M}_\perp(\mathbf{k}) \cdot \mathbf{M}_\perp^*(\mathbf{k})$$

$$R_{ni} = 2\Re(N(\mathbf{k})\mathbf{M}_{\perp i}^*(\mathbf{k}))$$

$$J_{ni} = 2\Im(N(\mathbf{k})\mathbf{M}_{\perp i}^*(\mathbf{k}))$$

Note that when written in this simplified way \mathcal{P} isn't strictly a tensor because the denominators may depend on the input polarisation direction

Er₂Ti₂O₇ - Spherical Neutron Polarimetry

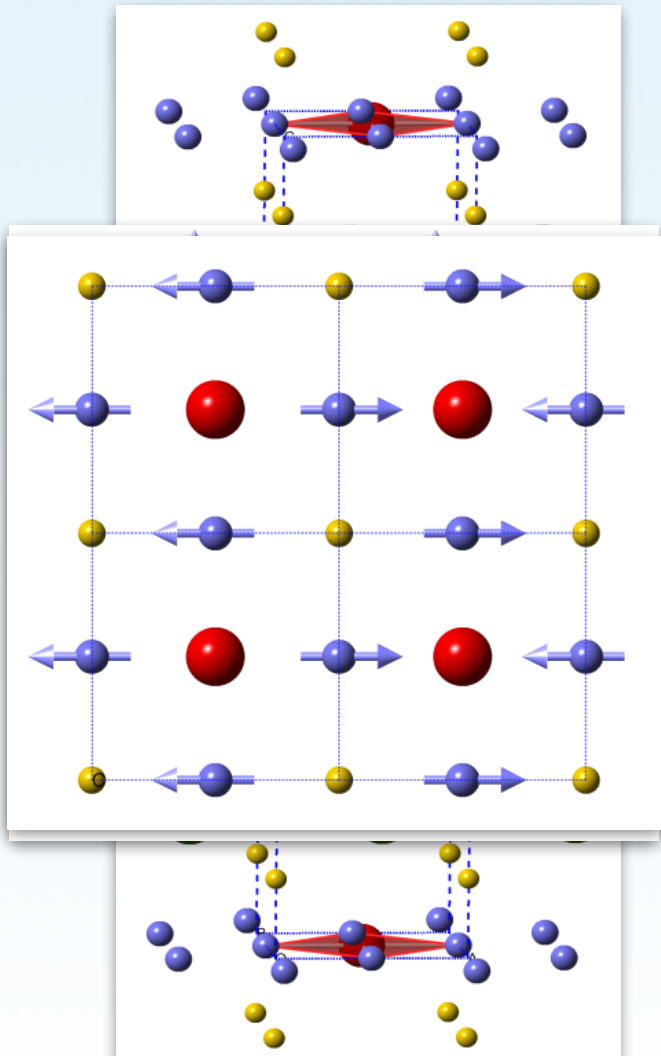


- Γ_5 with 3 + 3'
- RMC refinement
- 3 minima (+ time reversed)
- $\mu_{Er^{3+}} = 3.25\mu_B$
- $\mu_{Er^{3+}(Free\ ion)} = 9.59\mu_B$

$\text{Er}_2\text{Ti}_2\text{O}_7$: $\mathbf{k}=\mathbf{000}$

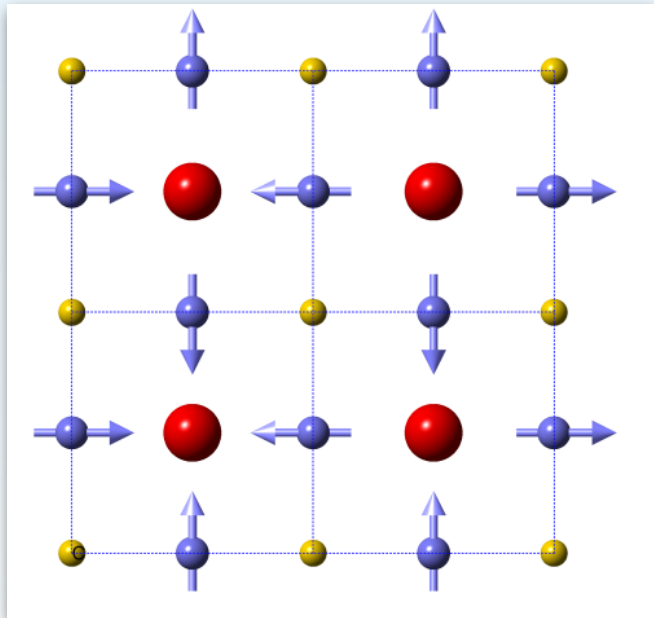
- Neutron powder diffraction data fit Γ_5 (ψ_2, ψ_3)
 - SNP indicates ψ_2 with 3+3' S-domains (MPG 4'/mmm')
 - NOT the dipolar ground state. Why does it happen?
 - ψ_2 is stabilised sixth order terms that create a thermal order-by-disorder selection
 - Remember that IRs are eigenfunctions of the exchange Hamiltonian
- » **Take care not to second guess**

La₂O₂Fe₂OSe₂ - MSG and RA analysis



- Related to the iron-based superconductors, but has magnetic order
- Want to understand drives and the competition between magnetic order and superconductivity
- Antiferromagnetic order below ~ 90 K
- Can be solved using a magnetic space group with a smaller C-centred monoclinic unit cell : C_a2/m (12.64)
- $\mathbf{k}_1=(\frac{1}{2}, 0 \frac{1}{2})$ or $\mathbf{k}_2=(0 \frac{1}{2} \frac{1}{2})$ with respect to the crystallographic space group $I4/mmm$
 - In 1-k structure, 2 orbits. Need : Γ_2 ($m||a$) on Fe1 and Γ_3 ($m||a$) on the Fe2 site. Collinear
 - In 2 k structure, just Γ_3 from Fe2 and **think about why it is 2-k**

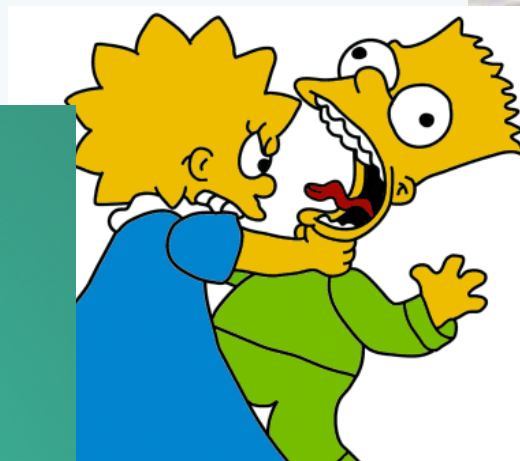
La₂O₂Fe₂OSe₂ - MSG and RA analysis



- Related to the iron-based superconductors, but has magnetic order
- Want to understand drives and the competition between magnetic order and superconductivity
- Antiferromagnetic order below ~ 90 K
- Can be solved using a magnetic space group C_2/m
- $\mathbf{k}_1 = (\frac{1}{2}, 0, \frac{1}{2})$ and $\mathbf{k}_2 = (0, \frac{1}{2}, \frac{1}{2})$ with respect to the crystallographic space group $I4/mmm$
 - 2 k structure, just Γ_3 from Fe₂ and **think about why it is 2-k**
 - **Not obvious. Both components have the same energy. Not possible to make 2-k structure with 2nd order terms, $S_1 \cdot S_2$ or $S_1 \times S_2$**
 - **Ising anisotropy with higher order anisotropic exchange terms**

Magnetic structures- very final thoughts

- Subtle physical properties will come from a subtle electronic properties and subtle couplings. Expect a subtle magnetic structure
- The wolf in sheep clothing



An introduction to SARAh and SARAh Refine

Andrew S. Wills

University College London

SARAh- what it does

- SARAh = **S**imulated **A**nnealing and **R**epresentational **A**nalysis
 - Perform symmetry analysis of possible magnetic structures using Representational (and Corepresentational Theory)
 - Information for analysing data and understanding phase transitions
 - Clip-on front-end to facilitate reverse Monte Carlo refinement of structures in GSAS using basis vectors and mixing coefficients
 - Symmetry-free simulated annealing is not normally enough
 - Clip-on front-end for FullProf using basis vectors and mixing coefficients

SARAh- Why it does what it does

- History (back in the 90s...)
 - Magnetic structures are largely misunderstood
 - K-vector often unknown
- Few people knew how to do representational theory.
 - Only a handful of examples in the literature
- Irreducible representation sources-
 - Books
 - Karep
 - Kovalev (little understood)
- Basis functions
 - calculated by hand
 - CS
 - Mody
 - » Generally there was much confusion!

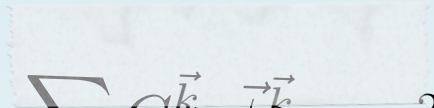
SARAh- Why it does what it does

- Refining a magnetic structure from NPD
 - GSAS uses Red/Black symmetry (restricted, difficult, leads to confusion- 'magnetic unit cell'), used only by the few ...
 - FullProf had many different ways of defining structures
 - e.g. rotation matrices, separate definition for helices
 - Complicated, so users built libraries of pcrs

SARAh- Why it does what it does

- Make the refinement more physical :
 - **Use a symmetry framework**
 - » **Restrict models to being physically reasonable**
 - » **Create link between magnetic structures and the underlying physics**

- Enable researchers to refine directly in terms of symmetry output
 - Use mixing coefficients as refinement variables
 - Use basis vectors and k-vectors to define symmetry relationships
 - » **Create a general refinement system**
 - *Do not reinvent the wheel (i.e. let users use GSAS, FullProf)*
 - » **SARAh as a suite of programs**
 - Symmetry calculations
 - Refinement assistant
 - *Help* unspecialised users as much as possible
 - k -search with FullProf
 - » **Generate better understanding, better analyses**



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

SARAh- How it does it

- **GSAS implementation**

- External front end, reverse Monte-Carlo refinement
 - GSAS magnetic symmetry definitions are limited (!), no k vector
 - External control of moment orientations
 - External use of a k-vector (need to put in a P1 magnetic cell)
- Not command line, simplest user choices. Buttons, scroll bars, etc

SARAh- How it does it

- **GSAS typical setup**

- SARAh controls all aspects of symmetry and the moment orientations, the rest is normal GSAS
- PI phase in GSAS (avoid red/ black, allow complex symmetries). Full magnetic cell
- Lock down non-magnetic variables
- Set GSAS for 2-3 LS cycles (i.e. converge), normal user control
- SARAh edits .exp file to insert all atom positions
- User selects symmetry type (representation, basis vectors)
- SARAh matches atoms being refined, replaces moments, launches GENLES
- RMC/Simulated Annealing refinement

SARAh- How it does it

- **Fullprof implementation**

- External front end to prepare and edit the pcr file, write fst file
- Not command line, simplest user choices. Buttons, scroll bars, etc
- Unique k-search engine
- Main technical difficulties are with:
 - Complex basis vectors but real or imaginary mixing coefficients...

SARAh- How it does it

- **Fullprof setup**

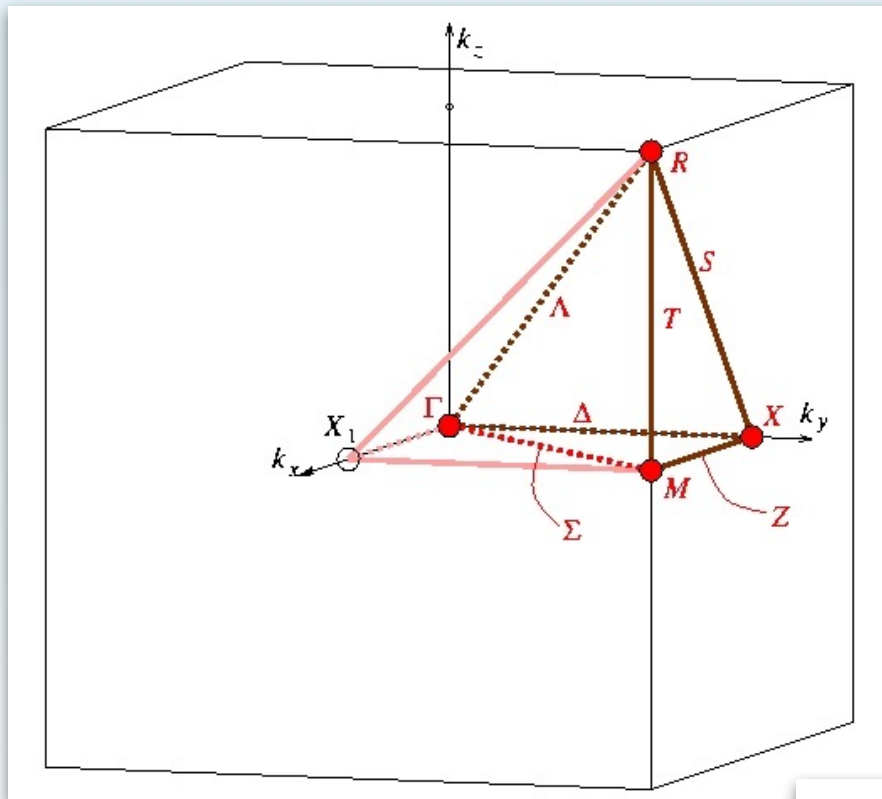
- SARAh generates magnetic phase
- User selects symmetry type (representation, basis vectors)
- SARAh generates the description of the magnetic structure (each moment is generated one time only)
- User can selectively edit the magnetic phase with basis vectors of choice
- User refines with FullProf normally
- SARAh reads in *.pcr and generates *.fst for visualisation
- Direct space RMC k-search

SARAh- under the hood

- **Mathematics**

- VB implementation of KAREP (E.R. Hovestreydt, M.I. Aroyo and H. Wondratschek, J. Appl. Cryst. 25, 544, 1992)
- Kovalev's tables (O.V. Kovalev, "Representations of the Crystallographic Space Groups" Edition 2, Gordon and Breach Science Publishers, Switzerland, 1993)
 - Conversion of all settings to IT standard, not Kovalev's
 - Verified IRs, transparent usage (as possible)

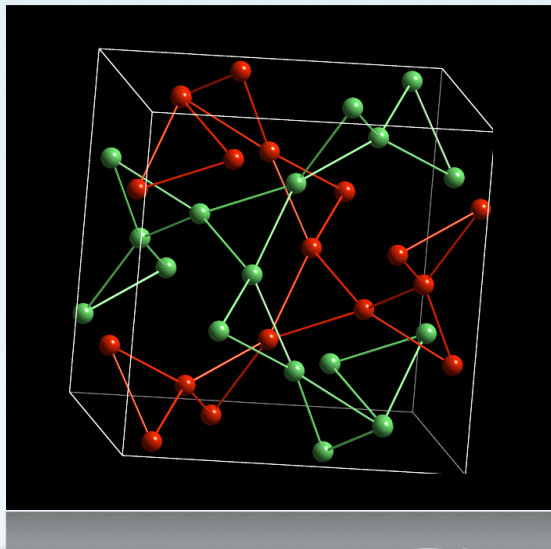
Indexing complex magnetic ordering with SARAh



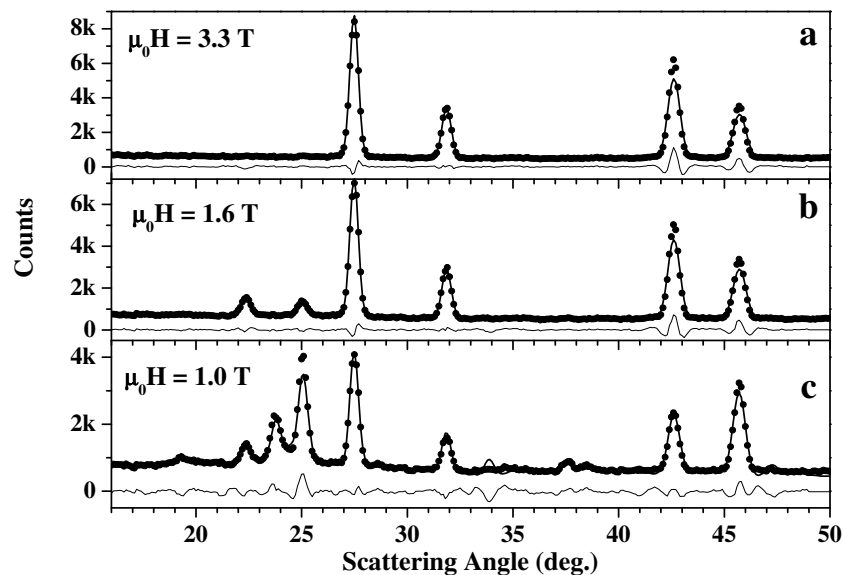
- Combine direct and reciprocal space
 - Aim to be physically meaningful
 - Put moments at atomic positions
 - RMC/least squares refine the moment orientations (20 cycles, no symmetry constraint other than the k-vector)
 - Explore randomly the points, lines and planes of symmetry
 - Gives only a *few* possible k-vectors

| Point [16] | Point [17] | Coordinates | Point [16] | Point [17] | Coordinates |
|------------|------------|-------------------------------|-------------|------------|---|
| k_1 | A | $u, v, 0$ | k_8h_5 | Δ | $0, 0, u$ |
| k_2h_5 | B | $u, v, \frac{1}{2}$ | k_9 | Λ | u, u, u |
| k_3 | C | u, u, v | $k_{10}h_5$ | X | $0, 0, \frac{1}{2}$ |
| k_4 | Σ | $u, u, 0$ | k_{11} | M | $\frac{1}{2}, \frac{1}{2}, 0$ |
| k_5h_5 | S | $u, u, \frac{1}{2}$ | k_{12} | Γ | $0, 0, 0$ |
| k_6h_9 | Z | $\frac{1}{2}, 0, u$ | k_{13} | R | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ |
| k_7 | T | $\frac{1}{2}, \frac{1}{2}, u$ | | | |

Example: GGG, complex magnetic ordering



- Highly frustrated lattice with the garnet structure
- 24 magnetic Gd ions per unit cell, divided into two interpenetrating sublattices
- Difference neutron powder diffraction profiles for in an applied field of (a) 3.3 T, (b) 1.6 T and (c) 1.0 T at $T = 80$ mK
- Peaks cannot be indexed on commensurate magnetic cell
- Neutron powder diffraction data
 - Conventional wisdom: take the positions of the observed reflections, compare with positions predicted by trial-and-error/random search
 - Too many possibilities, not a prayer...



| Field, T | $k_1 = (000)$ | $k_2 = (001)$ | $k_3 = (0, 0, 0.724)$ |
|----------|---------------|---------------|-----------------------|
| 1.0 | • | • | • |
| 1.6 | • | • | — |
| 3.3 | • | — | — |

Acknowledgements

- EU Marie-Curie Program
- Royal Society
- CEA Grenoble, DRFMC

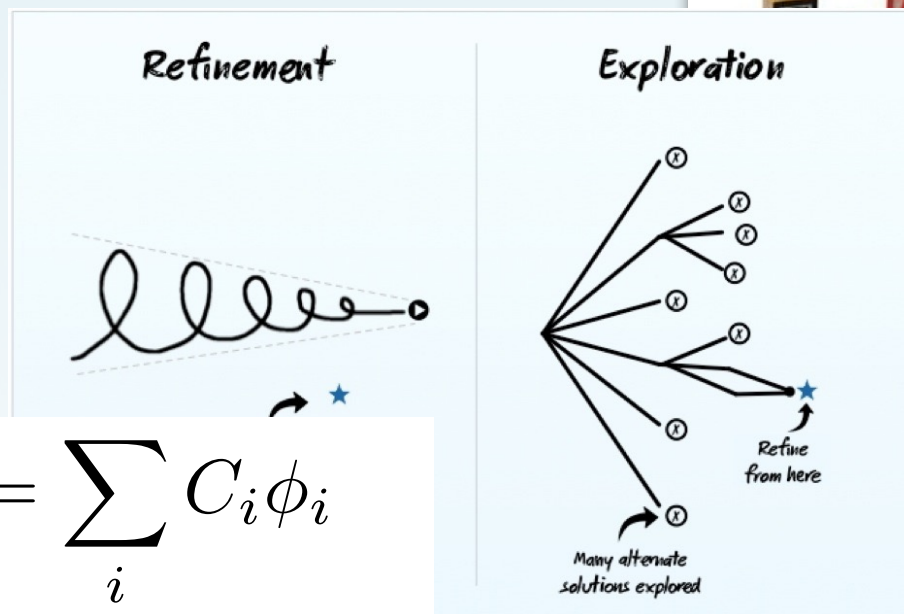
SARAh -

- Let's start with 3 questions ...

Examples

- Calculations and refinements
 - AgFe (GSAS, FP)
- Calculations to think a bit about BVs
 - NiO, R-3m, $k = 0\ 0\ 1.5$, Ni @ 0 0 0
- Then some audience examples
 - SG189, $k = 0.355\ 0\ 0$, Mn@0.5967 0 0.5

SARAh - SARAh Refine



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

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

$$\hat{H}_1 + \hat{H}_2 + \hat{H}_3 + \hat{H}_4$$

It starts with 3 questions...