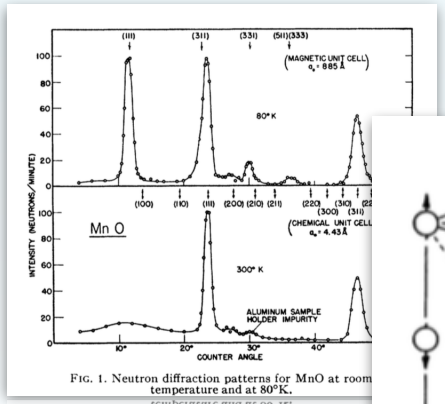
Refining magnetic structures using representational theory and *SARAh* - learning from simplicity and *Serendipity*

Andrew S. Wills

UCL Chemistry

Associate Dean for Research

Mathematical and Physical Sciences



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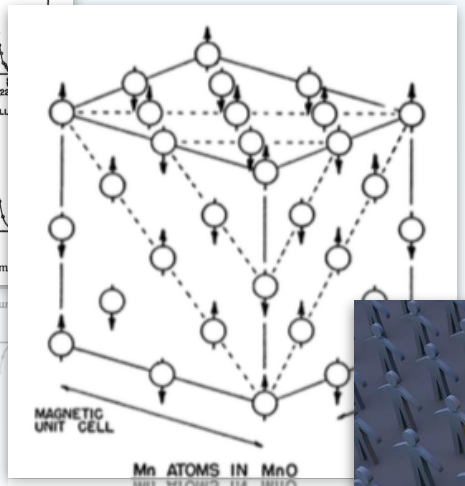
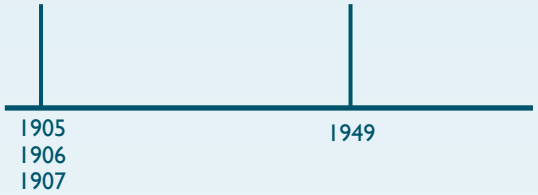


Diamagnetism, Paramagnetism, Ferromagnetism



MAGNÉTISME ET THÉORIE DES ÉLECTRONS;

PAR M. P. LANGEVIN.

$$\chi = \frac{n\mu_0\mu_B^2}{k_b T}$$

$$\chi = \frac{C}{T}$$

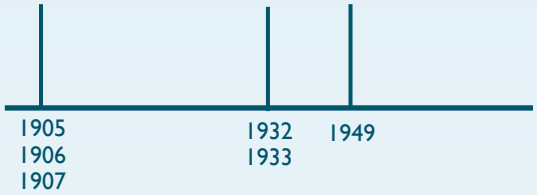
PHYSIQUE. — *La variation du ferromagnétisme avec la température.* Note (²) de M. PIERRE WEISS, présentée par M. J. Violle.

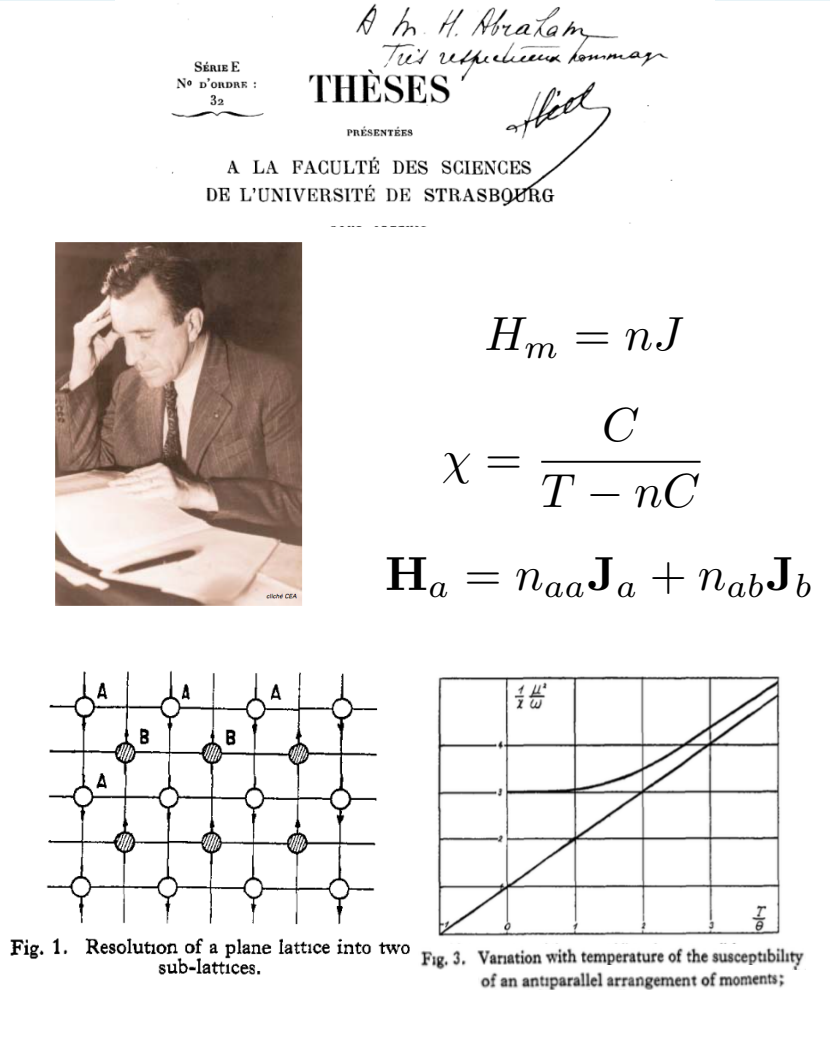
$$H_m = nJ$$

$$\chi = \frac{C}{T - nC}$$

- **P. Langevin**, Ann. de Chim. et de Phys. 5, 70 (1905)
  - Electronic theory of diamagnetism
  - Kinetic theory of paramagnetism, explaining Curie law
- **P. Weiss**, C. R. Ac. Sc. 143 1137 (1906); J. Phys. 6, 666 (1907)
  - **'Molecular field' (uniform)**
  - Spontaneous magnetisation
  - Ferromagnets
  - Curie-Weiss law

Negative molecular field





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N° D'ORDRE :
32

THÈSES

PRÉSENTÉES

A LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ DE STRASBOURG

$$H_m = nJ$$

$$\chi = \frac{C}{T - nC}$$

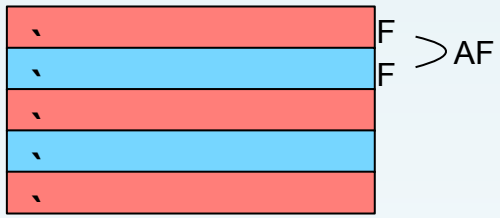
$$\mathbf{H}_a = n_{aa}\mathbf{J}_a + n_{ab}\mathbf{J}_b$$

Fig. 1. Resolution of a plane lattice into two sub-lattices.

Fig. 3. Variation with temperature of the susceptibility of an antiparallel arrangement of moments;

- **L. Neel**, Ann. de Phys. 17, 5 (1932). C .R. Acad. Sci. Paris, 203, 304 (1936)
  - Negative local molecular field
    - ➡ Antiparallel arrangement of sublattices
    - ➡ Transition temperature T_N
  - Magneto-crystalline coupling
    - Moments have preferred directions
  - Imperfect antiferromagnetism

Negative molecular field



- **L.D. Landau**, Phys. Z. Sowjet 4, 675 (1933).
  - Layered material
  - Positive interactions within layer, negative between

$$F = \frac{1}{2}(a - A)\,l^2 + \frac{1}{4}b\,l^4 + \frac{1}{2}\alpha(l_x^2 + l_y^2) + \frac{1}{2}(a + A)\,m^2 + \frac{1}{2}\alpha(m_z^2 + m_y^2) + \frac{1}{2}b\,m^2\,l^2 + b(\boldsymbol{m}\cdot\boldsymbol{l})^2 + \frac{1}{4}b\,m^4 - (\boldsymbol{H}\cdot\boldsymbol{m}).$$

Landau objected to Neel's model - it wasn't an eigenstate and would be destroyed by spin fluctuations. Also, he probably didn't like unconstrained mean field models that looked like back on an envelope calculations…

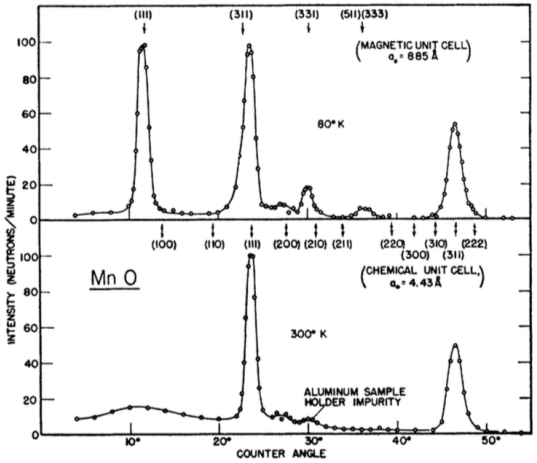
Antiferromagnetic order

1949
1951

PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee



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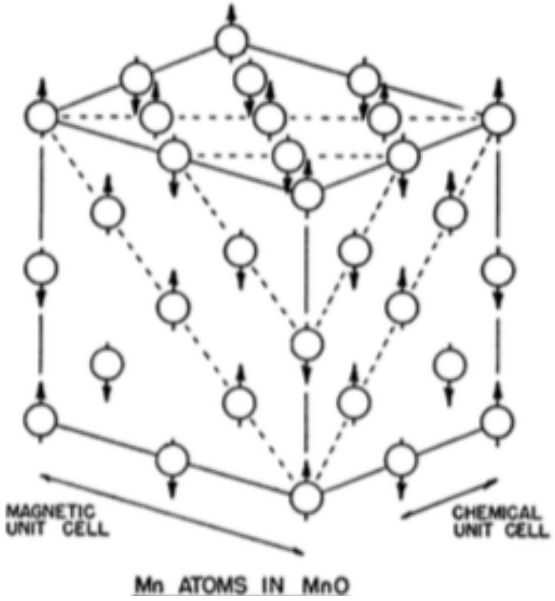
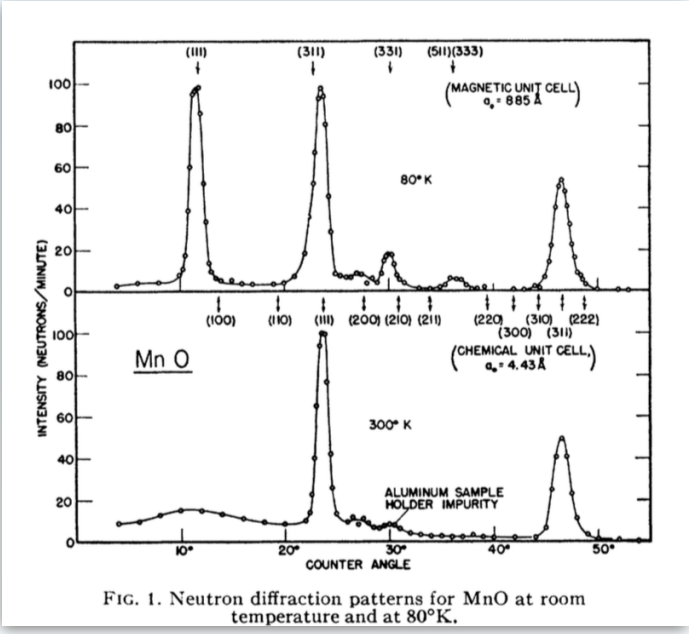


- Neel, was asked why he had persisted with his theory of antiferromagnetism in the light of Lev Landau's prediction that only ferromagnetism was possible in nature, Néel thanked heaven he was not that smart or '**Sancta Simplicitas**'.

Magnetic structure determination and analysis - *Software*



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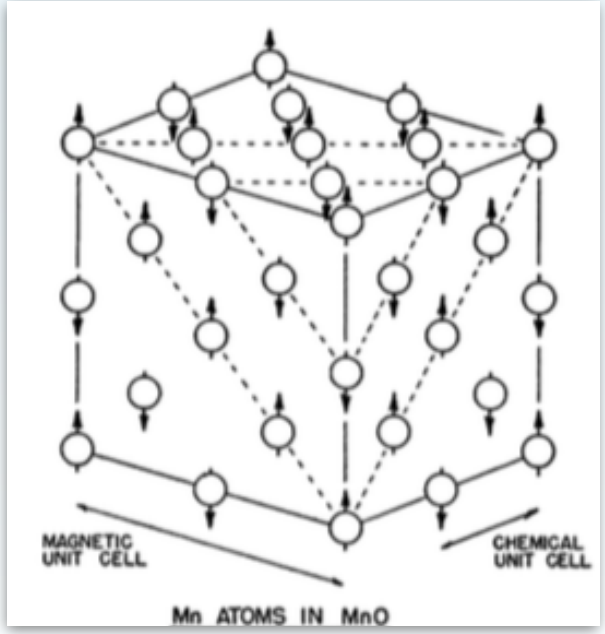
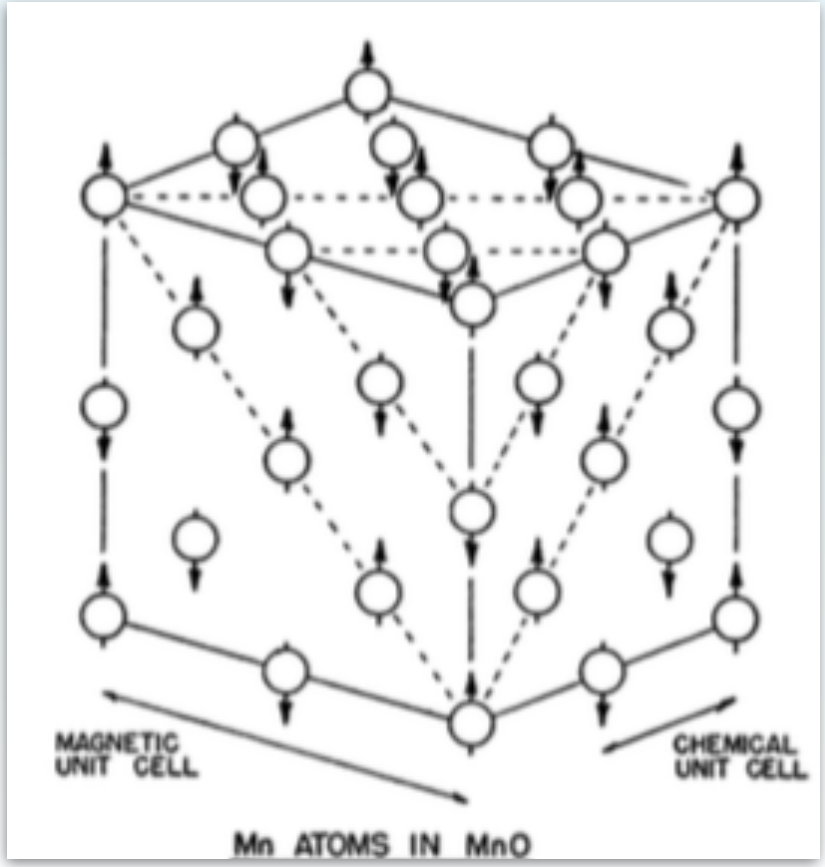


Foundations - pillars



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- 1981 Jaric; 1984 Stokes and Hatch Isotropy subgroups
- 2001 Sikora - Quadrupoles

Foundations - pillars

There is a lot of history. It can create confusion and inconsistencies…

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Refining magnetic structures and symmetry analysis Start with 'what are they?'

- 'Original' SARAh - Representational Analysis (1999)
  - **History** - refinements using manually defined magnetic space groups (GSAS, FullProf) or one of several structure definitions (FullProf), e.g. helical structure. Quite specialist. Lots of mistakes, particularly over what a k-vector is..
  - **Performed calculations of representational analysis** (Bertaut's method) using the tables of Kovalev to give irreducible representations (IRs) and basis vectors (BVs)
  - **SARAh-Refine** was a front-end (meta-program) that took the BVs from SARA*h*, substituted related moments into the **GSAS** exp file, ran GENLES, read the results and carried out **simulated annealing** (**reverse-Monte Carlo**). Moved refinement from moment components to basis vectors and mixing coefficients - **direct basis vector refinement**

$$\{m_a, m_b, m_c\} \rightarrow \vec{m}_j = \sum_{\nu,k} C_\nu^k \ \vec{\psi}_{i,\nu}^k \ e^{-2\pi i k \cdot t_{ij}}$$

  - SARA*h* = **S**imulated **A**nnealing and **R**epresentational **A**nalysis (works for commensurate and single-k incommensurate structures)
  - FullProf then introduced mixing coefficient refinement and **SARAh-Refine** was extended to work with **Fullprof** and **TOPAS** by making template for the magnetic phases and editing the refinement files.

Refining magnetic structures, symmetry analysis of magnetic structures

- **web SARAh** (2018)
  - Move from Windows-based codes to web code with calculations carried out in **Wolfram Mathematica.** Functionality independent of operating system, users do not need licences.
  - Performs the same calculations as original SARAh - Representational Analysis (following Bertaut's method) to give Irreducible Representations (IRs) and basis vectors (BVs)
  - Extended to include (amongst other things)
    - **Stationary vectors** (analogous to 'isotropy groups', of Javic and the Isotropy suite) but using the **Black+White point groups** rather than magnetic space groups
      - These define high-symmetry structures within the space of an IR
      - Treat commensurate and incommensurate structures as the same
    - **Exchange Multiplets** (Izyumov) to connect IRs with isotropic spin and exchange symmetry
- **webSARA*h* Refine** (2022)
  - Works with FullProf. Makes magnetic phases, edits .pcr file directly for easy selection and refinement of BVs (using B+W stationary groups and exchange multiplets)

SARAh- Refine Flow chart

space group
k vector
atom positions

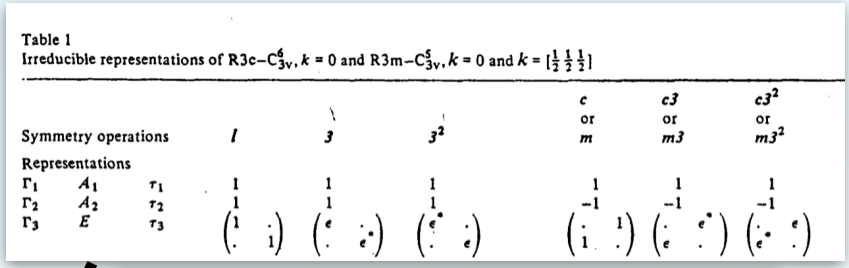


Table 1
Irreducible representations of R3c–C_{3v}^6, k = 0 and R3m–C_{3v}^5, k = 0 and k = [$\frac{1}{2}\frac{1}{2}\frac{1}{2}$]

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

Projection of basis vectors

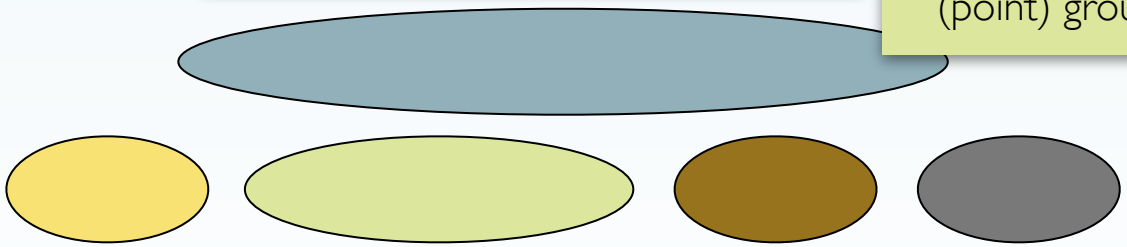
```
BASIS VECTOR COMPONENTS FOR EACH SITE OBTAINED BY CLASSICAL PROJECTION:
(NOTE THAT THESE ARE WITH RESPECT TO SPACE GROUP AXES)

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)
```

exchange multiplets

Refine with mixing coefficients following symmetry types.

Characterise resulting structure with magnetic space (point) groups defined by **η**.

Basis vector symmetry spaces



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

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

Black and white point groups

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

Symmetry analysis and refining magnetic structures
Now move to 'why this one?'

- **Current developments** - moving beyond the mechanics of describing magnetic structures and helping create understanding of the physical reasons for a magnetic structure to form. See this as key to control or properties and intelligent design)
  - Introduce **anti-unitary symmetry** (Wigner) which brings in complex conjugation and time-reversal in a complete way
  - Calculations of **invariant polynomials** to enable better understanding of energy drives for a given magnetic structure, also to reduce confusion over Landau theory…
  - **Quadrupoles - tensor analysis** and useful for **orbital ordering**
  - '**Serapsis**' - another view of the relationships between representation theory, and magnetic space groups and spin groups
  - *Making coherent use of the various theories to maximise the information that we have and use when we analyse magnetic structures - a philosophy and an educational-piece*

Broadening the foundations SARAh

History can make confusions and be daunting…

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Broadening the foundations SARAh

Try to make an easier path…

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Add what you need, when you need it …
- My building-up principle for magnetic structures

Ockham's razor

- pluralitas non est ponenda sine necessitate
  - ("plurality should not be posited without necessity")
  - ("don't use variables unless you need to")
  - ("don't make your refinement any harder than you need to")

Theories help you work out what the necessity is

- Think about why!
- There lies the fun…
- There lies the physics

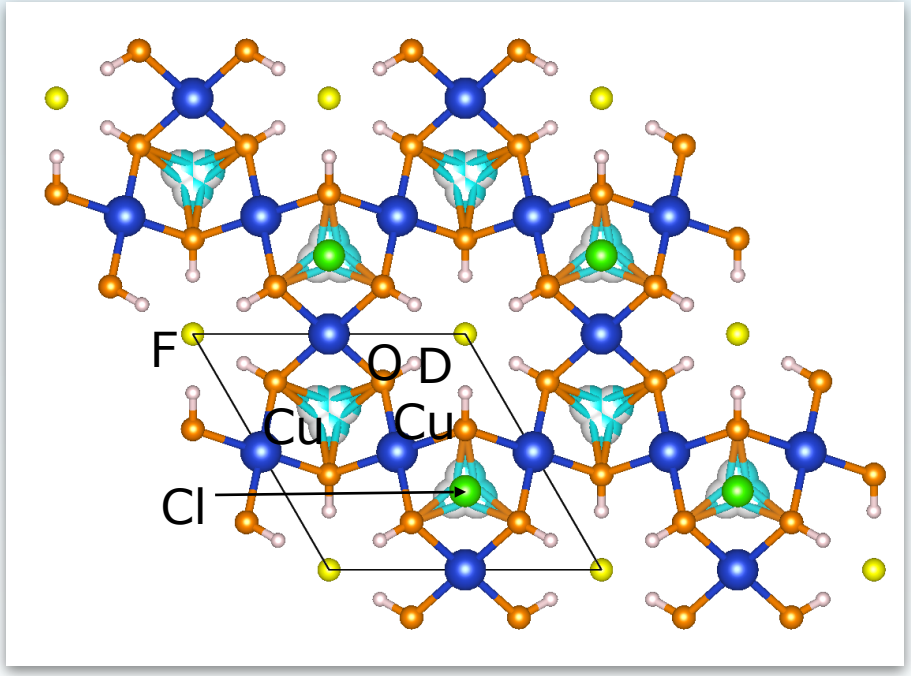
Symmetry analysis and refining magnetic structures

Epilogue

- Landau was not entirely wrong in his view that antiferromagnetic states were unstable with respect to quantum fluctuations. This notion was continued by the nobel prize winning physics Phil Anderson in 1973. He was exploring how Neel order could be destabilised by quantum fluctuations. This was a route to a new type of magnetic ground state called the **Resonating Valence Bond (RVB)** state, that was defined by fluctuations and topology rather than static order and local symmetry.
- Anderson proposed that the RVB could be favoured by frustration and would underlie the transition to high temperature superconductivity in the cuprates.
- Landau's ideas would later point to an entirely new direction in condensed matter science and a new class of electronic state called **quantum spin liquids** and started the search for example materials. Most notably studies of **S=1/2 kagome antiferromagnets …**

S = ½ kagome antiferromagnets

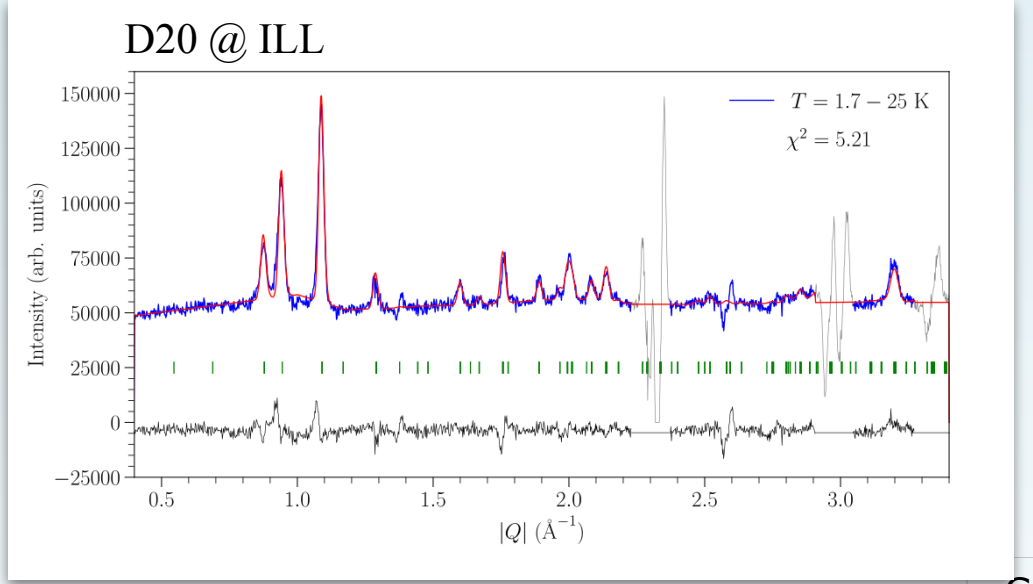
Madeleine Georgopoulou (UCL, ILL) and Björn Fåk (ILL)



Claringbullite: $Cu_4(OD)_6FCl$

- AA stacking of kagome planes
- P63/mmc at high temperature
- Pnma at low temperature
- **μSR**: antisite disorder is an order of magnitude lower than in herbertsmithite
- Magnetic order T<17 K
- Goal - use exchange interactions to understand the Hamiltonian of the Zn-doped material, $ZnCu_3(OD)_6FCl$ which we believe to be an candidate quantum spin liquid

$Cu_4(OD)_6FCl$: Magnetic structure from neutron diffraction and exchange model



- Magnetic space group: *Pn'm'a*
- **k** = **0**, Irrep Γ_7 (Kovalev's notation)
- 3 Cu sites with different sized ordered moments. **Complex canting!**

Cu site	Claringbullite Γ_7		
	Moment size (μ_B)	AFM out-of-plane canting	FM in-plane canting
Cu1	0.3	0	0
Cu2	0.4	18	0
Cu3	0.5	0	17

M. Georgopoulou, *et al.*, Phys. Rev. B 107, 024416 (2023).
K. Tustain, *et al.*, Chem. Mater. 33, 9638 (2021).

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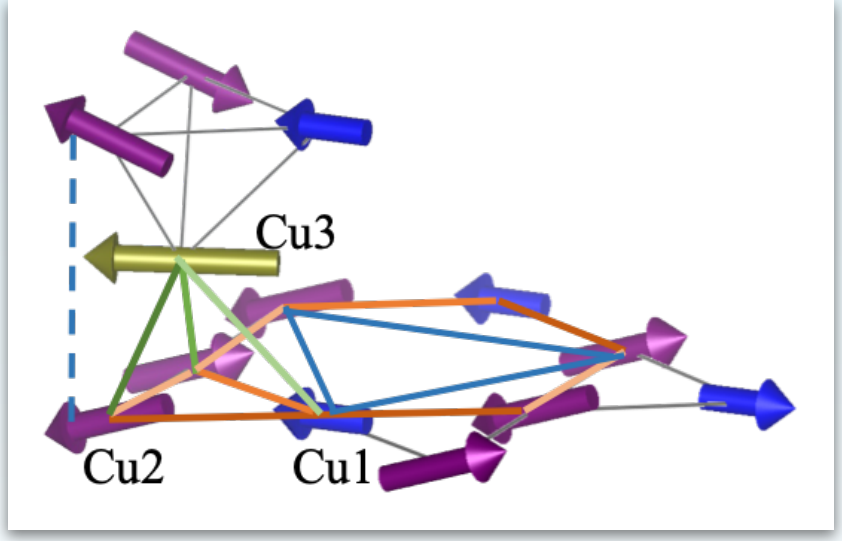

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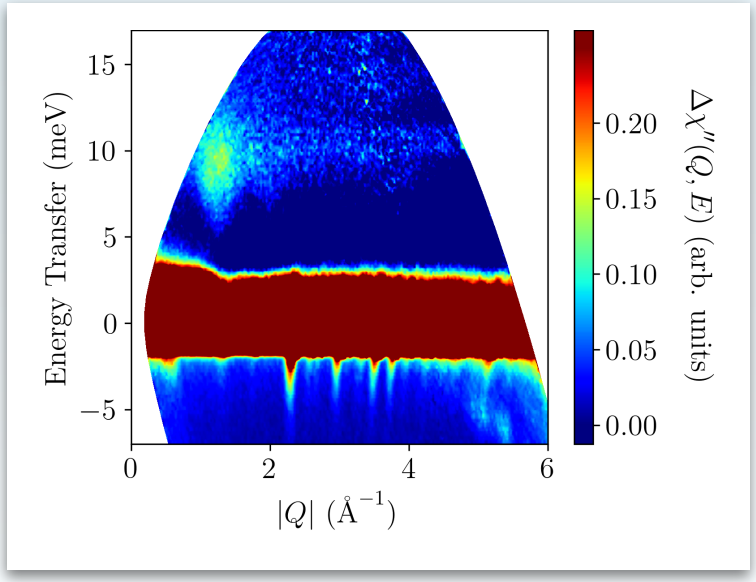
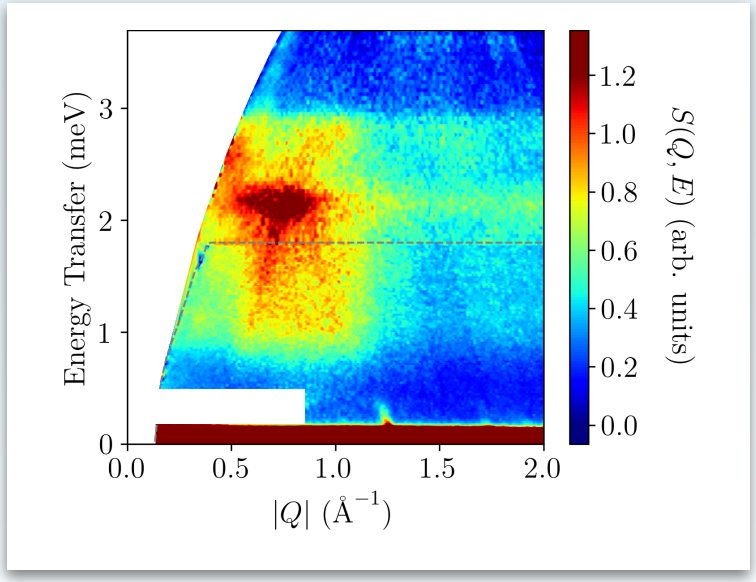
$Cu_4(OD)_6FCl$: Spin waves using data from PANTHER and IN5 @ ILL

T=1.8 - 100 K
E_i = 19.2 meV
Q=1.25 Å^{-1} , Bandwidth = 8.3 meV,



T=1.6 K, E_i = 3.55 & 5.11 meV
Q=0.73 Å^{-1} , Bandwidth = 2.77 meV,
Zero-energy gap = 0.45 meV.

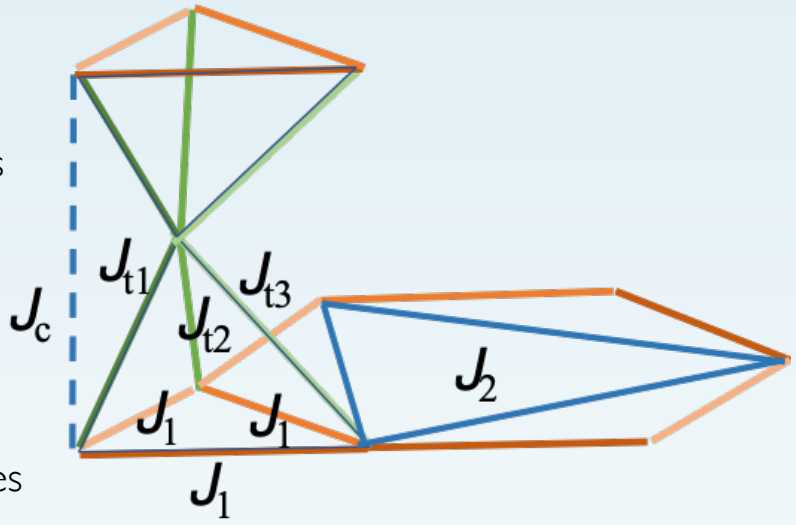


- Two magnetic responses gapped from each other
- Gapless excitations

M. Georgopoulou, B. Fåk, D. Boldrin and A.S. Wills, (2021). doi:10.5291/ILL-DATA.INTER-516
M. Georgopoulou, B. Fåk, D. Boldrin, J. Ollivier and A.S. Wills, (2021). doi:10.5291/ILL-DATA.INTER-519

$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW Results

- Starting point: DFT and tenth-order high-temperature series expansion[1]
  - 4 exchanges: did not stabilise the experimental magnetic structure (no go in SpinW)
- Claringbullite, this work
  - "**Serendipity**": new protocol for determining exchanges that stabilise observed magnetic structure[2]
  - Antiferromagnetic kagome + interplanar exchanges
  - Ferromagnetic 'tripod' exchanges
  - DM = 10% J_{ij}
  - θ_W = -95 K (exp. = -136 K)



Signs agree with Cu-O(D)-Cu superexchange angles.

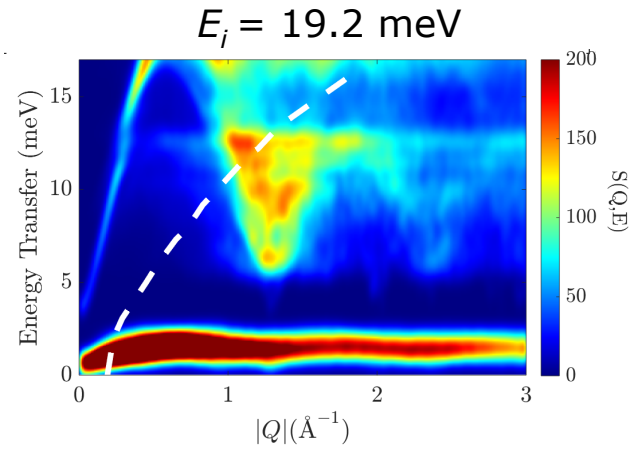
J_i	Value (meV)
J_1	14
J_{t1}	-6.5
J_{t2}	-3.5
J_{t3}	-6
J_c	4
J_2	0.2

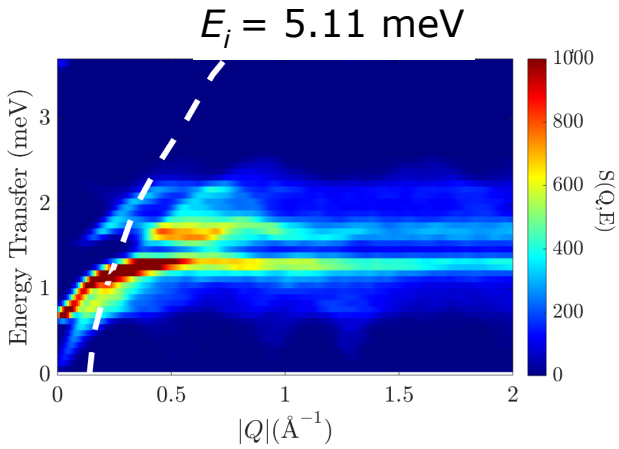
[1] H. O. Jeschke, *et al.*, Phys. Rev. B 92, 094417 (2015).
[2] A. S. Wills, Serendipity, *unpublished*.

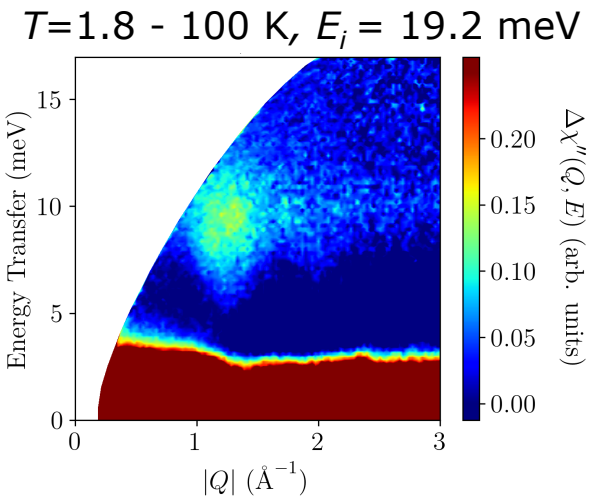
$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW

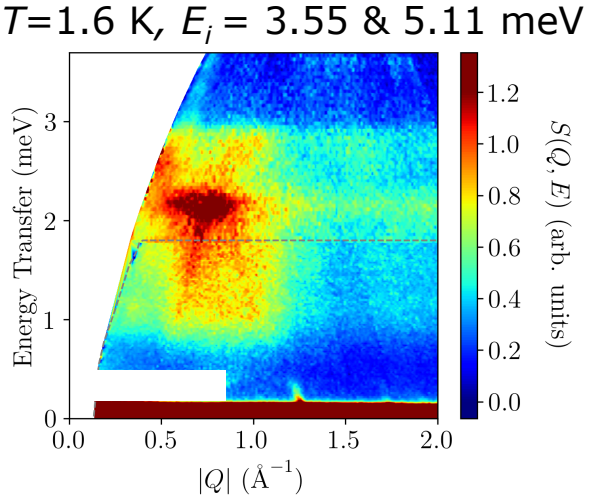
Model versus experiment

- 2 magnetic responses with appropriate gap sizes.
- 10 meV excitation: good agreement in Q and bandwidth.
- 2 meV excitation: two excitation bands but less good agreement.
- (not necessarily the end, but a very good start)







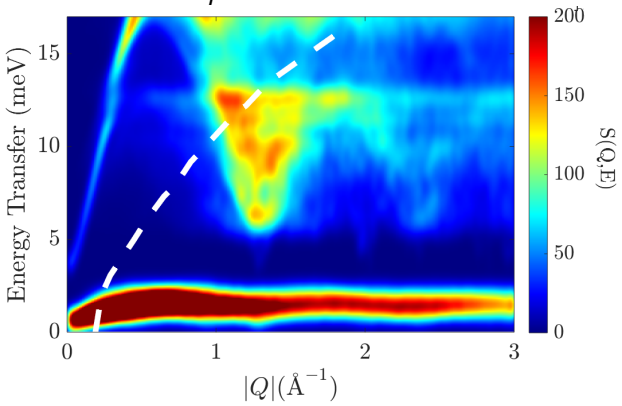


M. Georgopoulou, *et al.*, Phys. Rev. B 107, 024416 (2023).

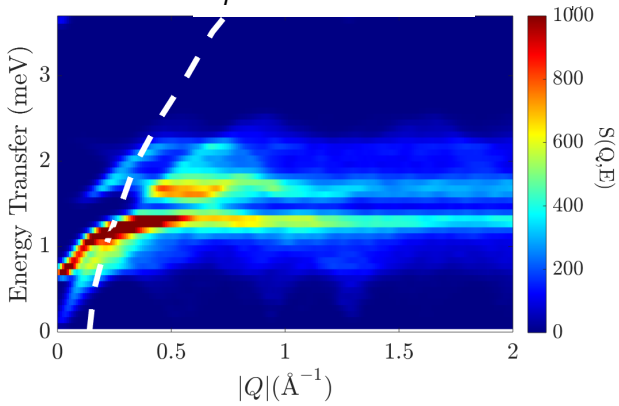
$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW

J_i	Value (meV)
J_1	14
J_{t1}	-6.5
J_{t2}	-3.5
J_{t3}	-6
J_c	4
J_2	0.2

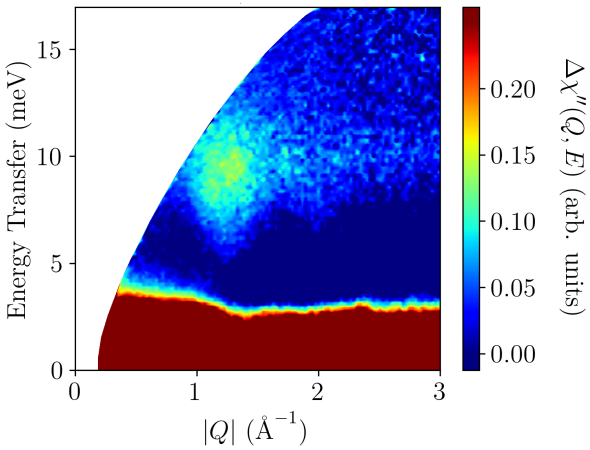
E_i = 19.2 meV



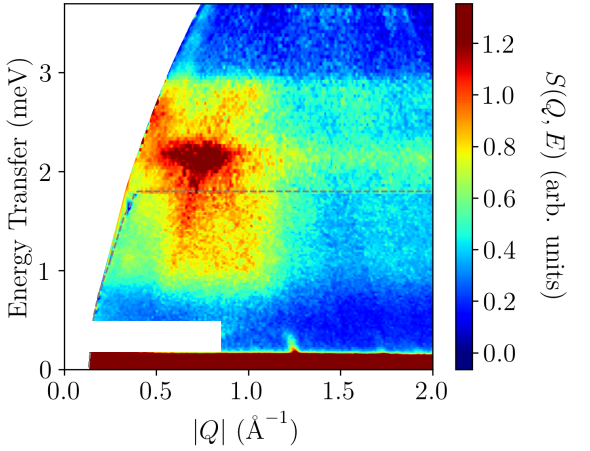
E_i = 5.11 meV



T=1.8 - 100 K, E_i = 19.2 meV



T=1.6 K, E_i = 3.55 & 5.11 meV



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$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW Analysis technique?

- The 4 exchange parameters from literature did not give a stable magnetic structure in SpinW and could not be used to model the spin wave spectra
- Need something that can handle 8 exchange interactions
- What to do?
  - Use eigenvectors?
  - Use Monte Carlo?

Early ideas - Villain, Lyons and Kaplan,

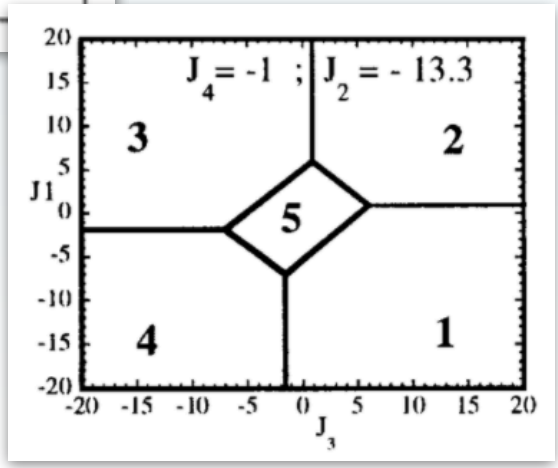
1. Diagonalise the Fourier matrix of exchange interactions - eigenvectors describe the spin configuration of the ordered state
   - The problem is that this gives a global phase
   - Not much information for non-collinear structures where the the angles between the moments are not simple

$$\xi_{ij}(\mathbf{k}) = -\sum_{p} J_{ij}(\mathbf{R}_p) e^{-2\pi i \mathbf{k}\mathbf{R}_p}$$

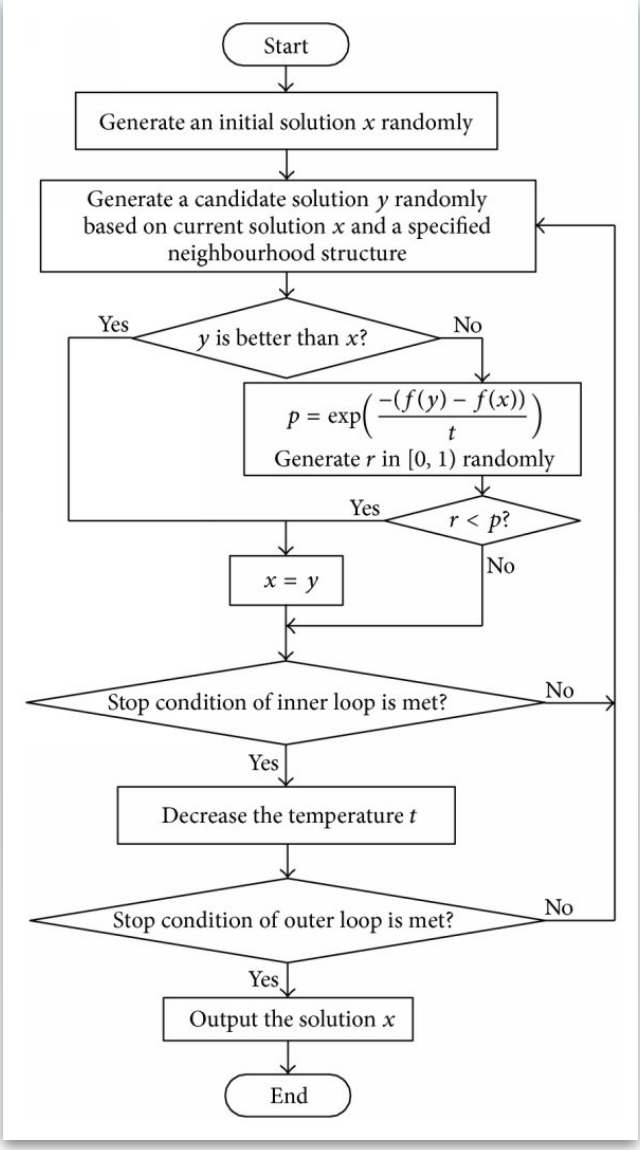
	Sign sequences of collinear magnetic moments							
Structure	M_{M1}	M_{M2}	M_{M3}	M_{M4}	M_{Fe1}	M_{Fe2}	M_{Fe3}	M_{Fe4}
1 : k=(0,0,0)	+	-	+	-	-	+	-	+
2 : k=(0,0,0)	+	+	+	+	+	+	+	+
3 : k=(0,0,0)	+	-	+	-	+	-	+	-
4 : k=(0,0,0)	+	+	+	+	-	-	-	-
5 :	Case of disordered or incommensurate structures							

- Tends to be used to make high-level phase diagrams
- This cannot be used algebraically for complex matrices as the eigenvectors will involve complex roots. Use grid search.

This technique isn't heavily used to understand the orderings of magnetic structures



Early ideas - Monte Carlo



1. Follow Bertaut - set up an exchange matrix. Include Dzyaloshinski and Moriya vectors
2. Go beyond Bertaut 's theory and use the exchange matrix to perform symmetry analysis of the related isotropic exchange Hamiltonian
3. Monte Carlo- conventional thought may be to
    1. Make a large unit cell/set boundary conditions
    2. Take a set of exchange values (vector in the space of exchange interactions)
    3. determine stable magnetic structure by MC protocol - make changes to spin structure,
    4. Repeat to validate solution
4. Problem - **computationally very expensive**. I started from needing to go beyond the literature models, and **the next step looked like an 8 exchange values. Taking 10 trial values for each exchange energy gives >10^8 sets of SA runs.** With 1 hour per run this direction of study effectively fails… Need another way…

$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW Analysis technique?

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- What to do?
  - Use eigenvectors? Not enough 'angular resolution'
  - Use Monte Carlo? Too expensive/slow for this problem
- Something more creative? … Literally focusing on the problem - **what stabilises the experimental structure**…

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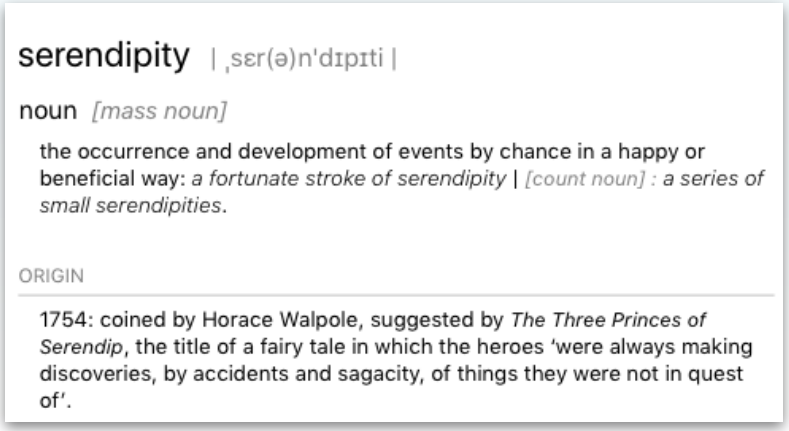

Serendipity and finding stability values

1. Follow Bertaut's macroscopic theory - set up an exchange matrix. Include Dzyaloshinski - Moriya vectors
2. Follow Weiss. Make random exchange values → 10^6 'energy vectors' that follow Weiss temperature'
3. Test eigenvectors of energy vectors against experimental magnetic structure (Bertaut, Kaplan, and Luttinger-Tizsa)
4. Calculate mean field at each site and trim energy vectors with large deviation of moments from mean field direction.
5. Make pool of 10^5 comparison magnetic structures. Calculate their energies
6. Substitute each trial energy vector into energies of the magnetic structure pool, find lowest energy structure
7. Take energy vectors those that stabilise experimental and close magnetic structures (don't forget those that stabilise other structures - could help analysis with AI)
8. 6 dimensional energy phase is hard to draw. Use cluster analysis on selected energy vectors to define regions in exchange space. Define cluster centres

   → Run time 6-8 hours (old laptop) with 6 exchange parameters
9. Test energy vectors of cluster centres with SpinW

A. S. Wills, Serendipity, *unpublished*.

Serendipity and finding stability values

experimental structure energy:
$-1.51326\ J_1 + 1.51326\ J_{10} + 1.00595\ J_{11} - 0.647744\ J_{12} + 0.647744\ J_{13} + 1.71456\ J_{14} + 1.00595\ J_{15} + 1.51326\ J_{16} - 0.647744\ J_{17} + 0.647744\ J_{18} + 0.647744\ J_{19} + 1.51326\ J_2 + 1.09154\ J_{20} - 0.647744\ J_{21} - 1.00595\ J_3 - 0.647744\ J_4 + 1.09154\ J_5 + 0.647744\ J_6 - 0.42864\ J_7 - 0.215296\ J_8 - 0.42864\ J_9 - 0.211584\ D_b - 1.49846\ D_c$

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Foundations of *Serendipity*
Some background theories

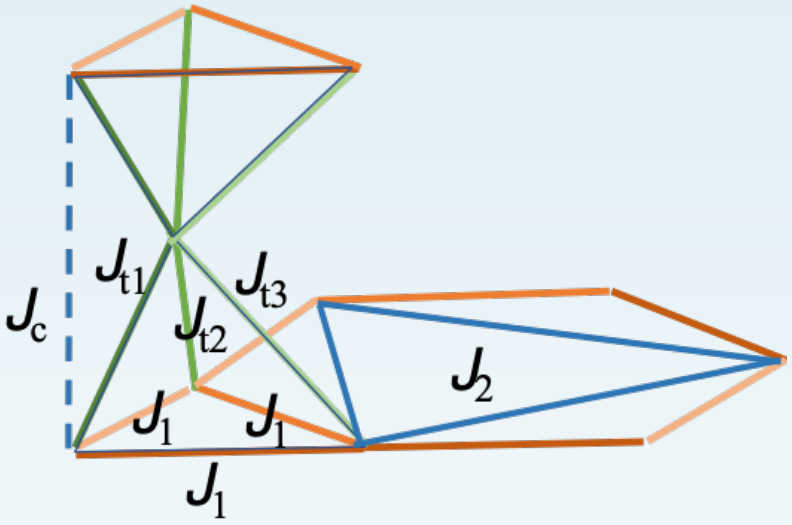
- 1906 Weiss
- 1937 Landau, Dzyaloshinski - Phase transitions
- 1936 Wigner - Antiunitary symmetry
- 1946 Luttinger-Tisza - minimum energy spin arrangement. 1958, Dzyaloshinski, 1960 Moriya,
- 1959, 60s Vilain and Kaplan eigenvectors and positive eigenvalues - minimum energy spin arrangement
- 1962 Bertaut - Exchange interactions and Hamiltonians
- 1968 Bertaut - Representation theory
- 1979 Izyumov - Exchange multiplets
- 1981 Jaric; 1984 Stokes and Hatch Isotropy subgroups
- Serapsis is likely to be helpful with possible tie in with Landau theory

A. S. Wills, Serendipity, *unpublished*.

$Cu_4(OD)_6FCl$: Modelling spin waves in SpinW

- Starting point: DFT and tenth-order high-temperature series expansion[1]
  - 4 exchanges: did not stabilise the experimental magnetic structure (no go in SpinW)
- Claringbullite, this work
  - "**Serendipity**": new Monte-Carlo based refinement protocol for determining exchanges that stabilise observed magnetic structure[2]
  - Antiferromagnetic kagome + interplanar exchanges
  - Ferromagnetic 'tripod' exchanges
  - DM = 10% J_{ij}
  - θ_W = -95 K (exp. = -136 K)

Need more test systems!



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Symmetry analysis, refining magnetic structures, stability conditions, spin wave analysis

- **My current developments** - moving beyond the mechanics of describing magnetic structures and focussing on creating understanding of the physical reasons for a magnetic structure to form
- A personal view
  - Software needs to be based on physical principles (AI development now moves towards physics-encoded AI)
  - History often makes inconsistencies and confusion
  - **webSARAh**, **webSARAh-Refine** have a development track to make a clear path through historical theories and refine the analysis technique of direct basis vector refinement.
  - **Serendipity** is a new way to study magnetic stabilities (and help spin wave studies!). It was built for Claringbullite (a rather hard problem). I am very happy to discuss ideas and learn more from people that actually understand spin waves
  - **SERAPSIS** is (I hope) going to connect symmetry ideas and make clarity