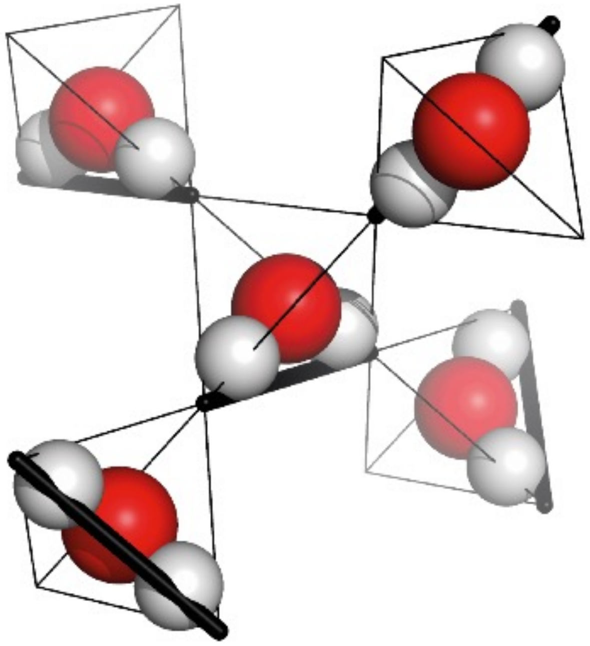
Refinement of magnetic diffuse scattering data

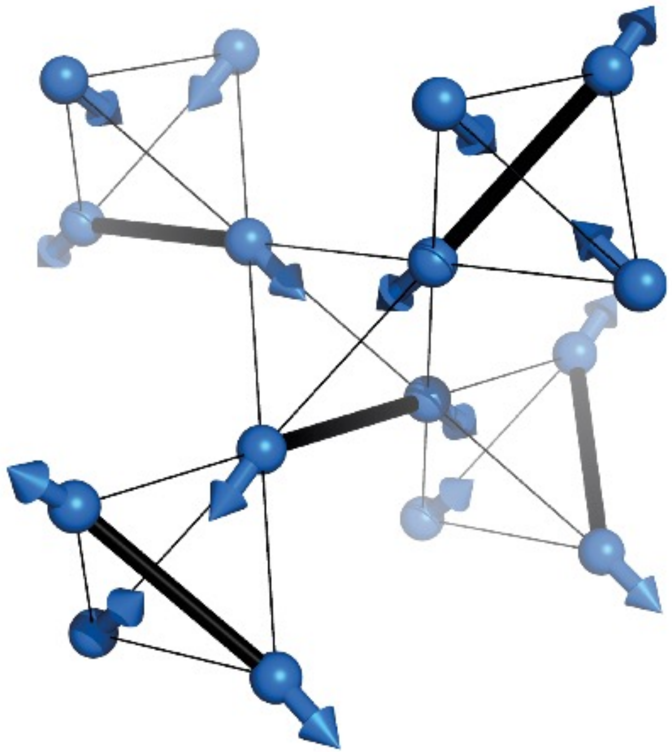
Joe Paddison

What does diffuse scattering measure?

- Correlated disorder, e.g. ice rules



Water ice

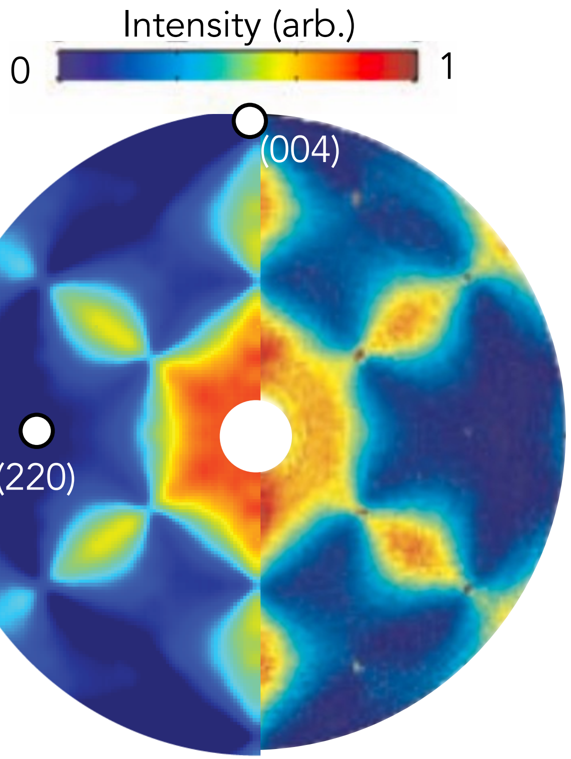


Spin ice

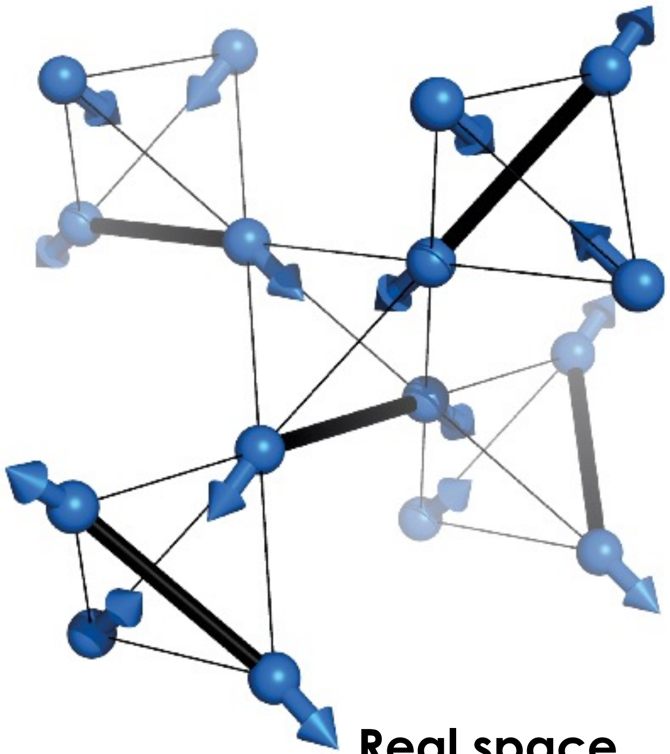
Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935)
Bramwell & Harris, *PRL* **79**, 2554 (1997)
Images: Keen & Goodwin, *Nature* **521**, 303 (2015)

What does diffuse neutron scattering measure?

- Neutron has magnetic moment → correlated **magnetic** disorder



Reciprocal space

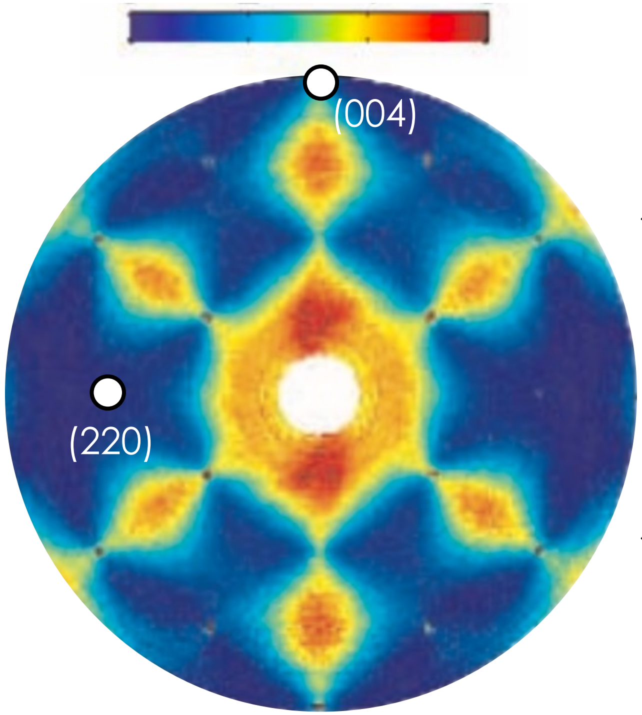


Real space

Bramwell & Harris, *PRL* **79**, 2554 (1997)
Left data: Fennell et al., *Science* **326**, 415 (2009)

Diffuse scattering analysis – an overview

Data

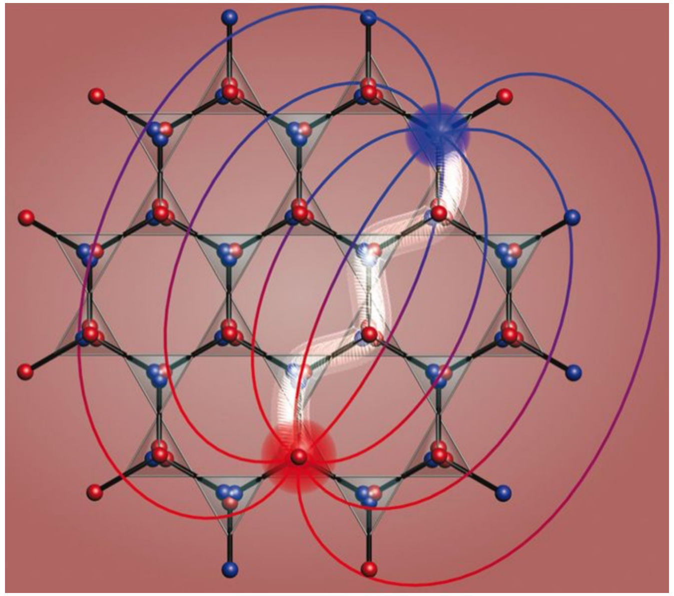


Reciprocal space

structure refinement

interaction modelling

Model



Real space

Left data: Fennell *et al.*, *Science* **326**, 415 (2009)
Right image: Castelnovo, Moessner & Sondhi, *Nature* **451**, 42 (2008)

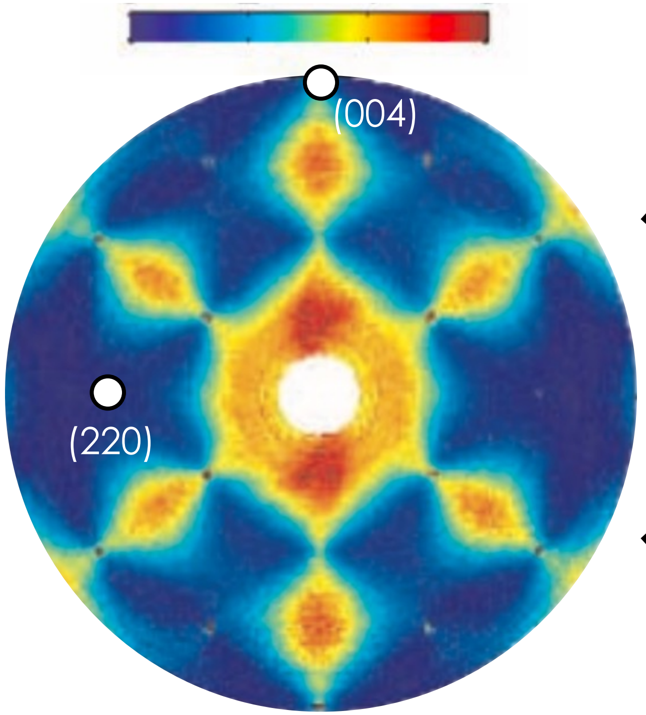
Diffuse scattering analysis – an overview

Data

small-box analysis
(magnetic PDF)

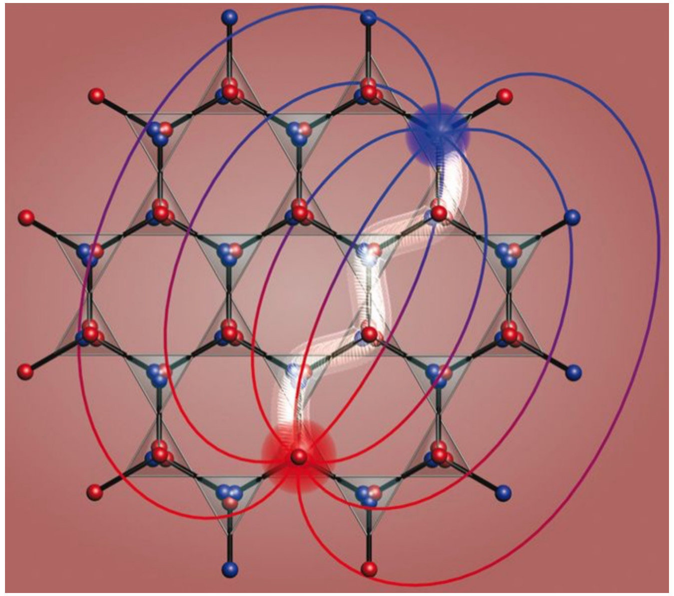
big-box analysis
(reverse Monte Carlo)

Model



structure refinement

interaction modelling



Reciprocal space

Real space

Left data: Fennell *et al.*, *Science* **326**, 415 (2009)
Right image: Castelnovo, Moessner & Sondhi, *Nature* **451**, 42 (2008)

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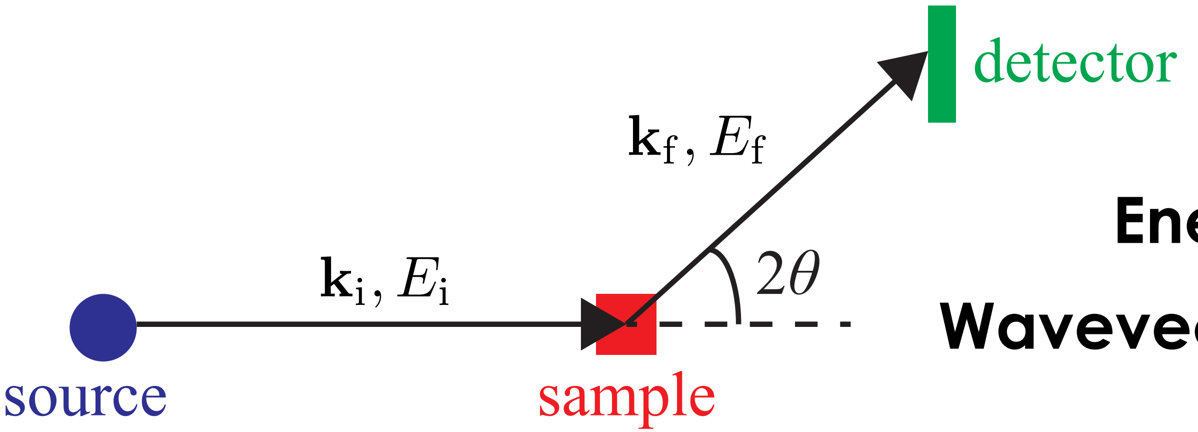
Plan for today

- Overview
- **Experiment & Theory**
- Magnetic structure refinement: *Spinvert*
- Magnetic interaction modelling: *Spinteract*

Neutron scattering



Energy transfer $E = E_\mathrm{i} - E_\mathrm{f}$

Wavevector transfer $\mathbf{Q} = \mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{f}$

- Consider scattering intensity integrated over energy transfer

$$I(\mathbf{Q}) = \int_{-\infty}^{\infty} I(\mathbf{Q}, E)\,\mathrm{d}E$$

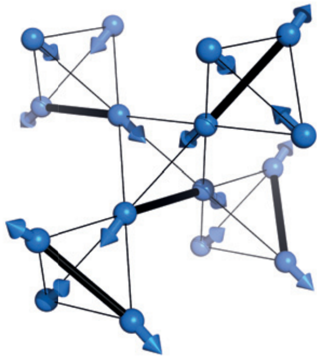
- This measures instantaneous correlations
- **Quasistatic approximation:** $\int \mathrm{d}E \approx \int \mathrm{d}E_\mathrm{f}$ if $E << E_\mathrm{i}$

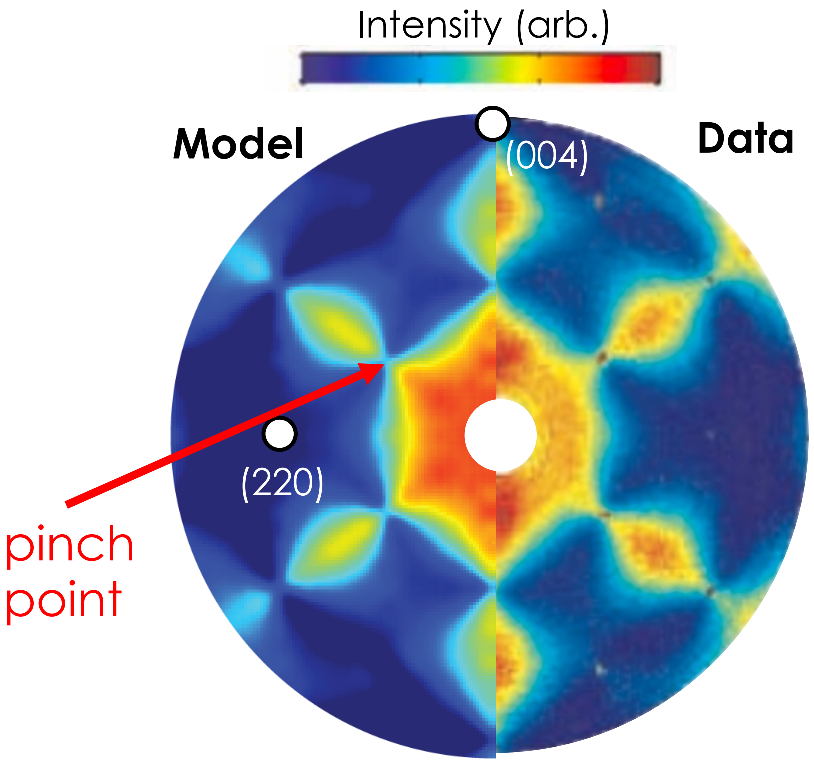
diffraction (E_f not analyzed)

$$Q = |\mathbf{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

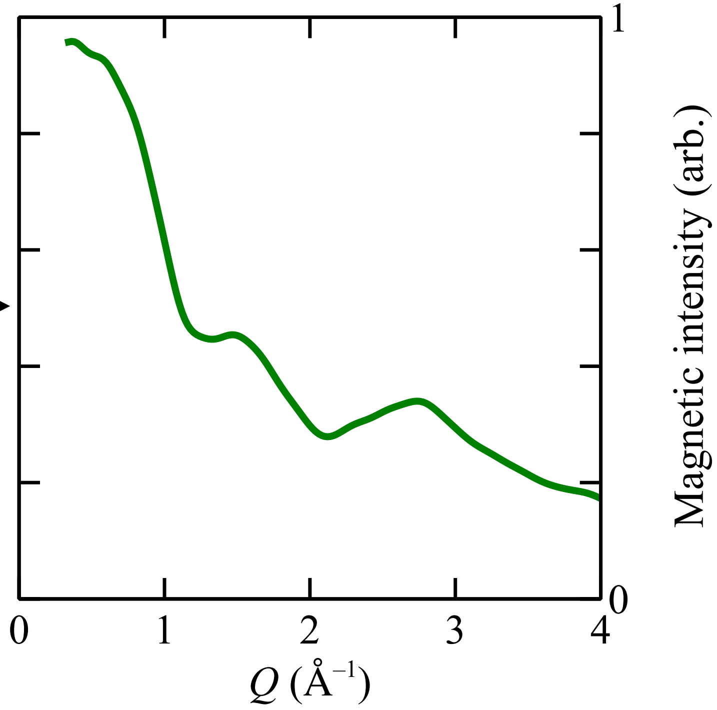
Single crystals vs polycrystals (powders)

- e.g. spin ice, $Ho_2Ti_2O_7$





spherical average



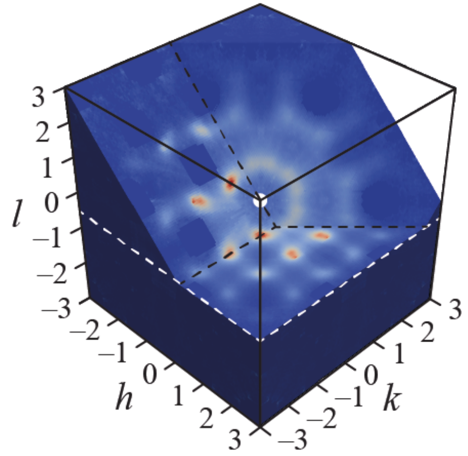
Single crystal

Powder

Left data: Fennell et al., *Science* **326**, 415 (2009)

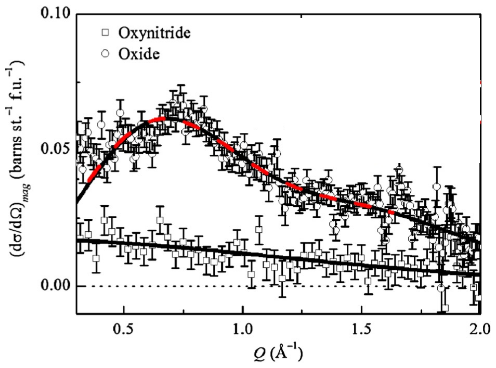
Experiment design

- Measure wide range of **Q** (for crystals)
  - e.g. Corelli @ ORNL, SXD @ ISIS…



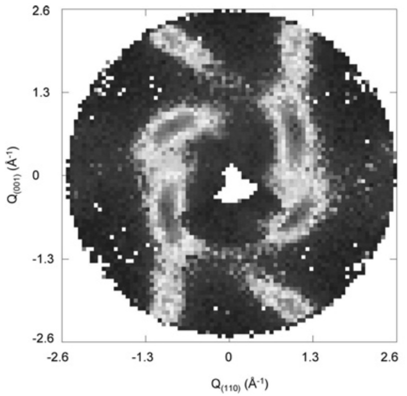
MnO
SXD @ ISIS

- Measure and subtract background
  - Or polarisation to isolate magnetic signal



D7 @ ILL
$\mu_{\mathrm{eff}} = 0.11\mu_{\mathrm{B}}$

- Ensure quasistatic approximation is valid
  - Choose $E_{\mathrm{i}} > |\theta_{\mathrm{CW}}|$ (interaction strength)



MnO
$|\theta_{\mathrm{CW}}| = 500$ K
$E_{\mathrm{i}} = 40$ K

Top data: Paddison et al., *PRB* **97**, 014429 (2018); **Centre data**: Clark et al., *PRL* **113**, 117201 (2014); **Lower data**: courtesy J. R. Stewart

Nuclear intensity

Single crystal

$$\langle b^2\rangle + \frac{1}{N}\sum_{i,j\neq i}\langle b_i b_j\rangle \exp\left[\mathrm{i}\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_i)\right]$$

Powder

$$\langle b^2\rangle + \frac{1}{N}\sum_{i,j\neq i}\langle b_i b_j\rangle \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

Debye formula
r_{ij} = radial distance
b_i = coherent scattering length

Magnetic intensity

Single crystal

$$C[gf(Q)]^2\left\{\frac{2}{3}S(S+1)+\frac{1}{N}\sum_{i,j\neq i}\langle \mathbf{S}_i^{\perp}\cdot\mathbf{S}_j^{\perp}\rangle \exp\left[\mathrm{i}\mathbf{Q}\cdot(\mathbf{r}_j-\mathbf{r}_i)\right]\right\}$$

$$C=\left(\frac{\mu_0}{4\pi}\frac{\gamma_{\mathrm{n}}e^2}{2m_e}\right)^2 = 0.07265\,\mathrm{barn}$$

$$\mathbf{S}^{\perp}=\mathbf{S}-\mathbf{QS}\cdot\mathbf{Q}/Q^2$$

$f(Q)$ = magnetic form factor

Powder

$$C[gf(Q)]^2\left\{\frac{2}{3}S(S+1) + \frac{1}{N}\sum_{i,j\neq i}A_{ij}\left[\frac{\sin Qr_{ij}}{Qr_{ij}}+B_{ij}\left(\frac{\sin Qr_{ij}}{(Qr_{ij})^3}-\frac{\cos Qr_{ij}}{(Qr_{ij})^2}\right)\right]\right\}$$

$$A_{ij}=\mathbf{S}_i\cdot\mathbf{S}_j-(\mathbf{S}_i\cdot\hat{\mathbf{r}}_{ij})(\mathbf{S}_j\cdot\hat{\mathbf{r}}_{ij})$$

$$B_{ij}=3(\mathbf{S}_i\cdot\hat{\mathbf{r}}_{ij})(\mathbf{S}_j\cdot\hat{\mathbf{r}}_{ij})-\mathbf{S}_i\cdot\mathbf{S}_j$$

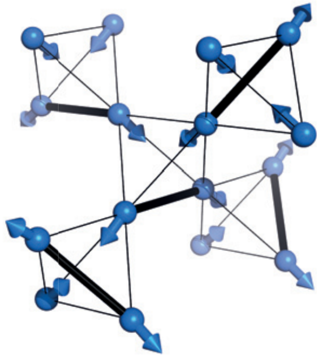
Debye, *Ann. Phys.* (Berlin) **351**, 809 (1915)
Blech & Averbach, *Physics* **1**, 31 (1964)

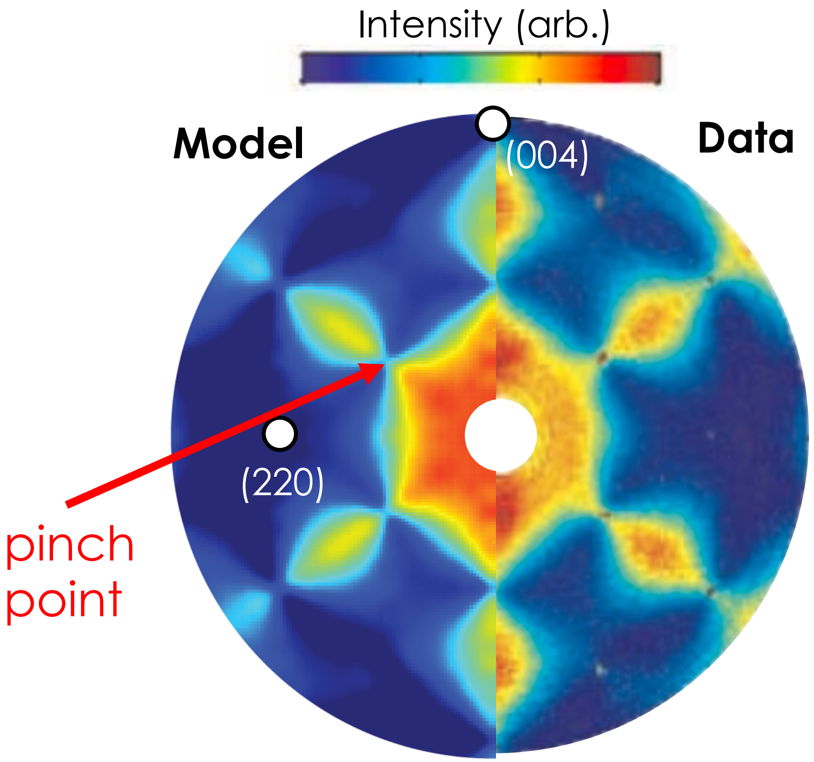
Plan for today

- Overview
- Experiment & Theory
- **Magnetic structure refinement: *Spinvert***
- Magnetic interaction modelling: *Spinteract*

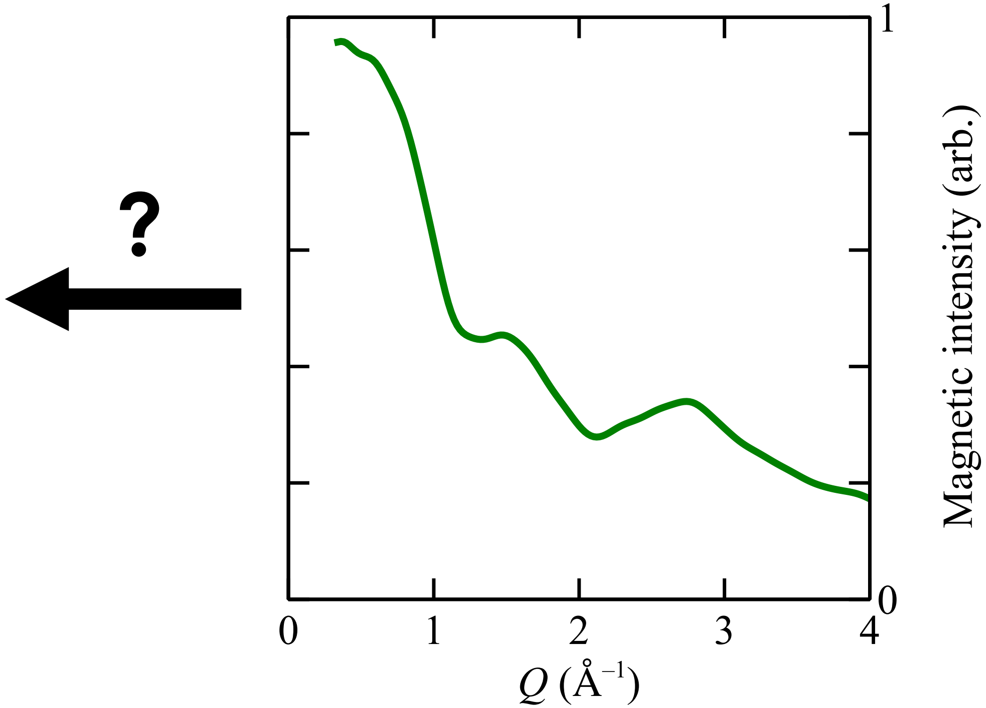
Can we recover ice rules by fitting to diffuse scattering?

- e.g. spin ice, $Ho_2Ti_2O_7$





Single crystal



Powder

Left data: Fennell et al., *Science* **326**, 415 (2009)

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Reverse Monte Carlo method

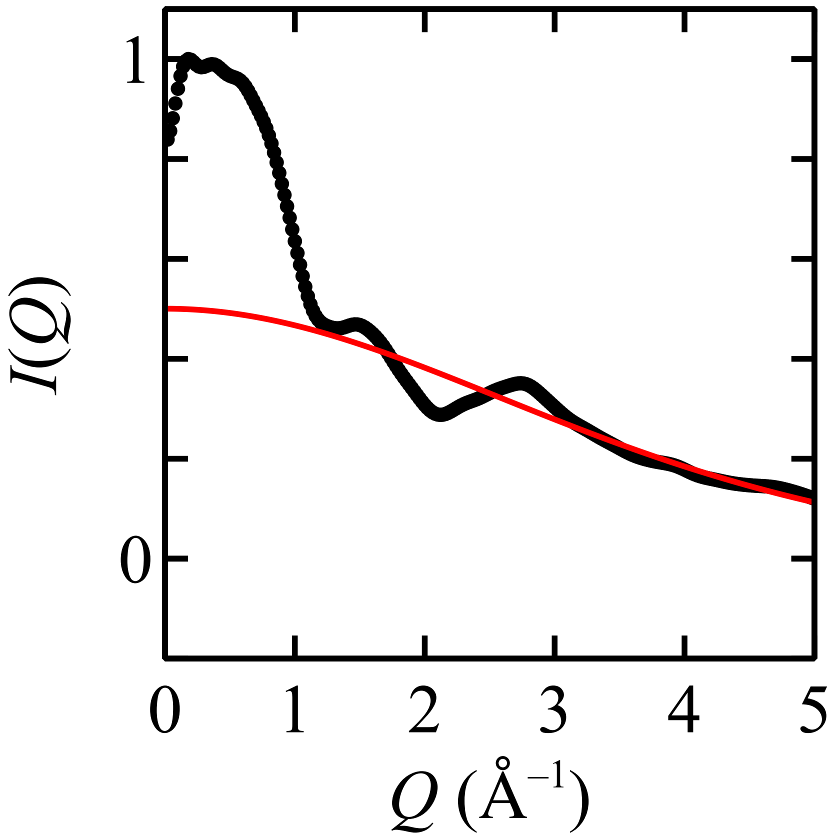
1. **Create** ~10^3 spins with random orientations and fixed positions
2. **Flip** a randomly-chosen spin
3. **Calculate** change in goodness-of-fit to data
4. **Accept** flip if fit improved; otherwise accept flip with some probability

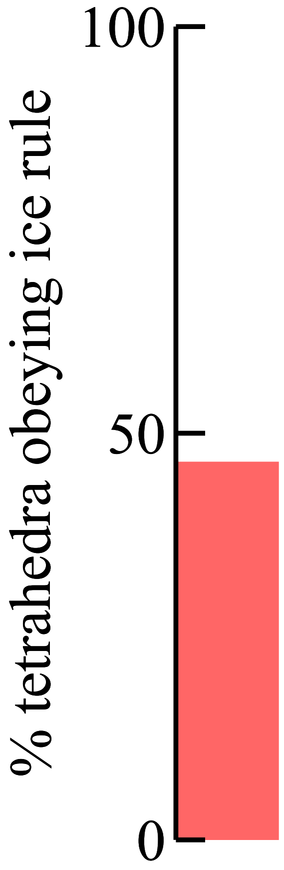
$$I_{\mathrm{m}}(Q) = C[gf(Q)]^2 \left\{ \frac{2}{3}S(S+1) + \frac{1}{N}\sum_{i,j\neq i} A_{ij}\left[\frac{\sin Qr_{ij}}{Qr_{ij}} + B_{ij}\left(\frac{\sin Qr_{ij}}{(Qr_{ij})^3} - \frac{\cos Qr_{ij}}{(Qr_{ij})^2}\right)\right]\right\}$$

McGreevy, *JPCM* **13**, R877 (2001)
Tucker *et al.*, *JPCM* **19**, 335218 (2007)

RMC: Proof of principle

- e.g. fit to virtual "data" for spin ice





Paddison & Goodwin, *PRL* **108**, 017204 (2012)

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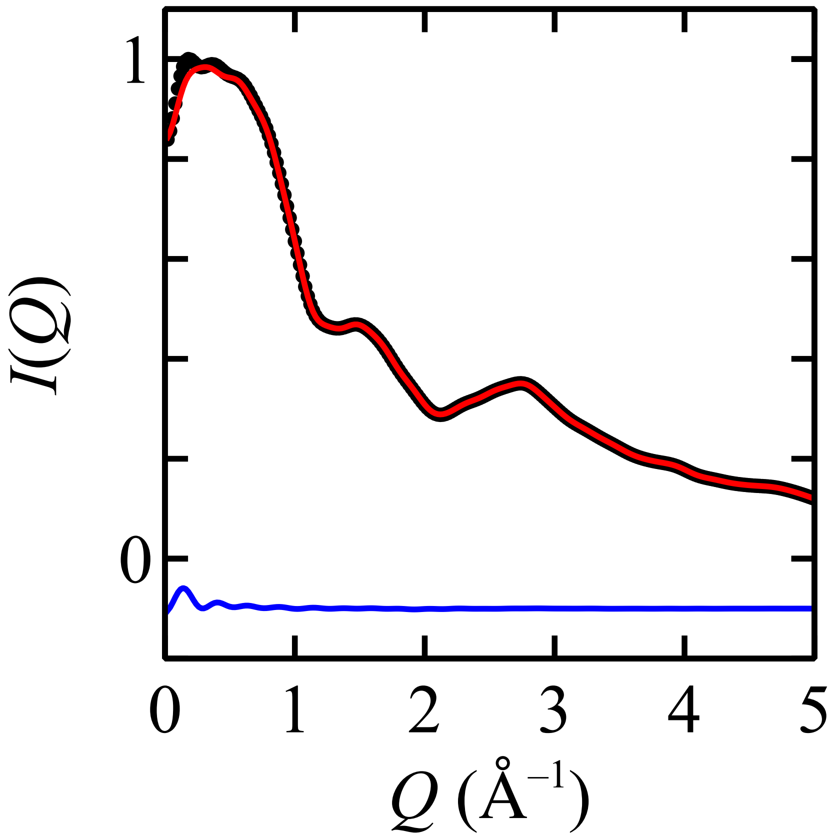
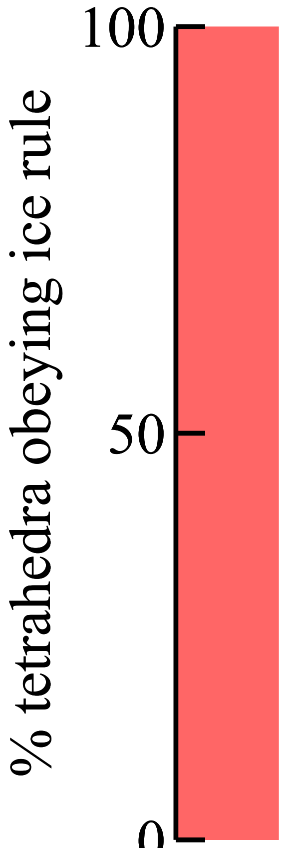
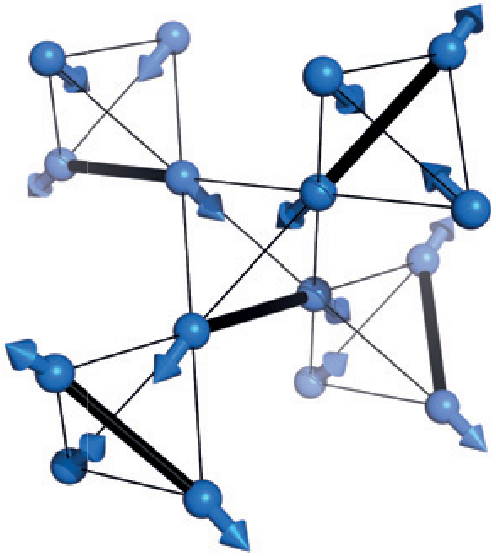
RMC: Proof of principle

- e.g. fit to virtual "data" for spin ice

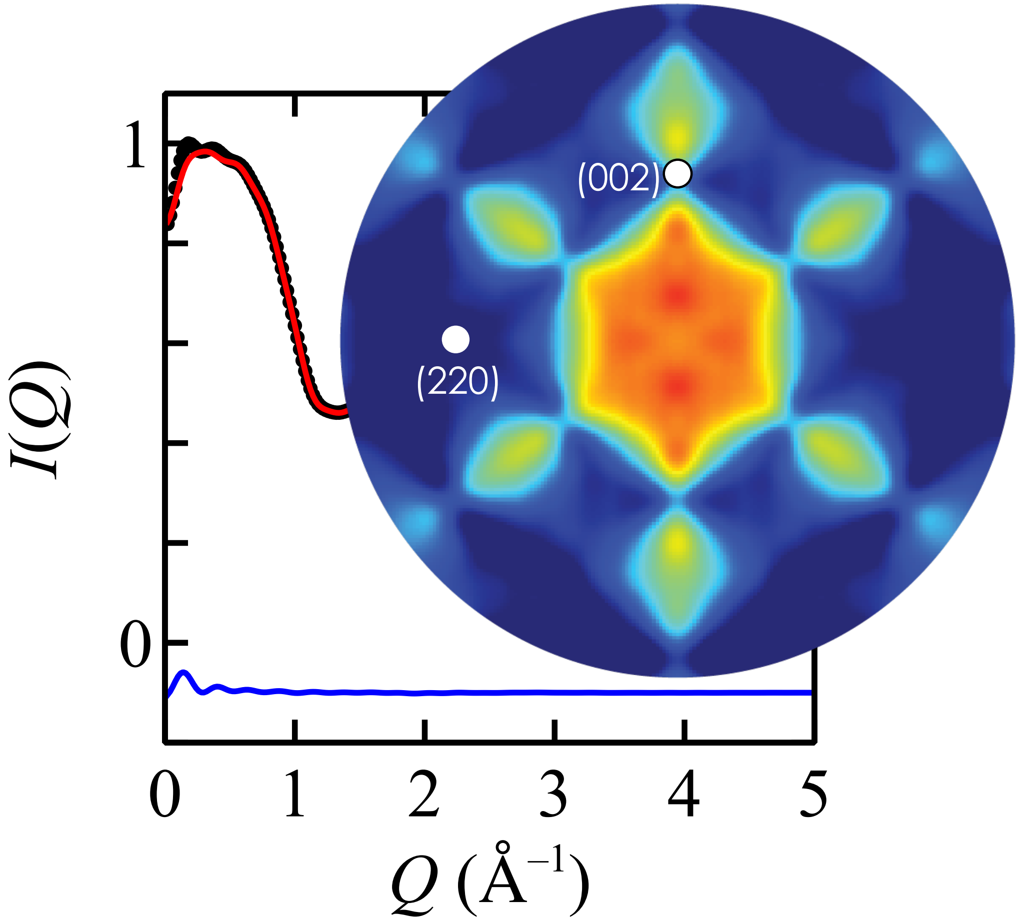


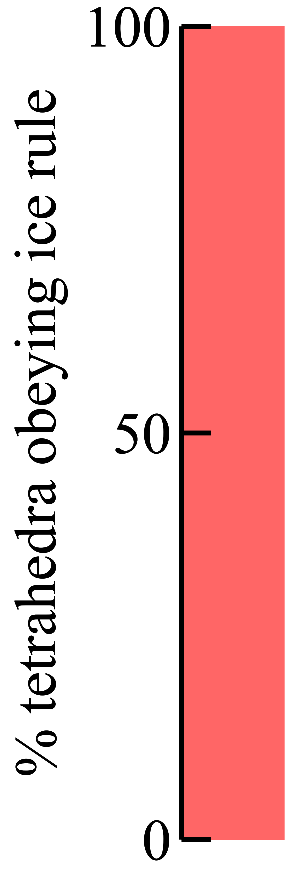


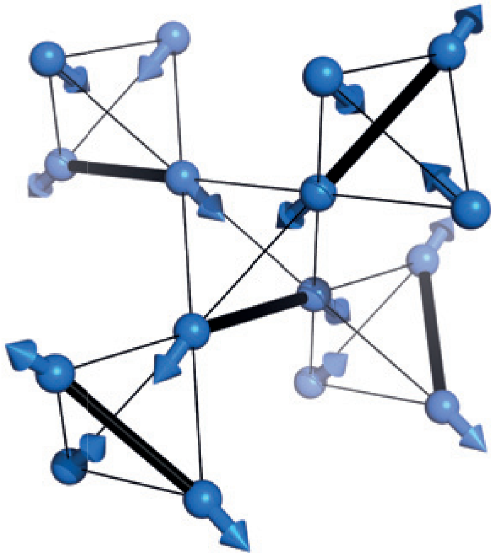


Paddison & Goodwin, *PRL* **108**, 017204 (2012)

RMC: Proof of principle







Paddison & Goodwin, *PRL* **108**, 017204 (2012)

Spinvert program

Andrew Goodwin
University of Oxford

Ross Stewart
ISIS Neutron Source

IOP PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **25** (2013) 454220 (15pp) — doi:10.1088/0953-8984/25/45/454220

SPINVERT: a program for refinement of paramagnetic diffuse scattering data

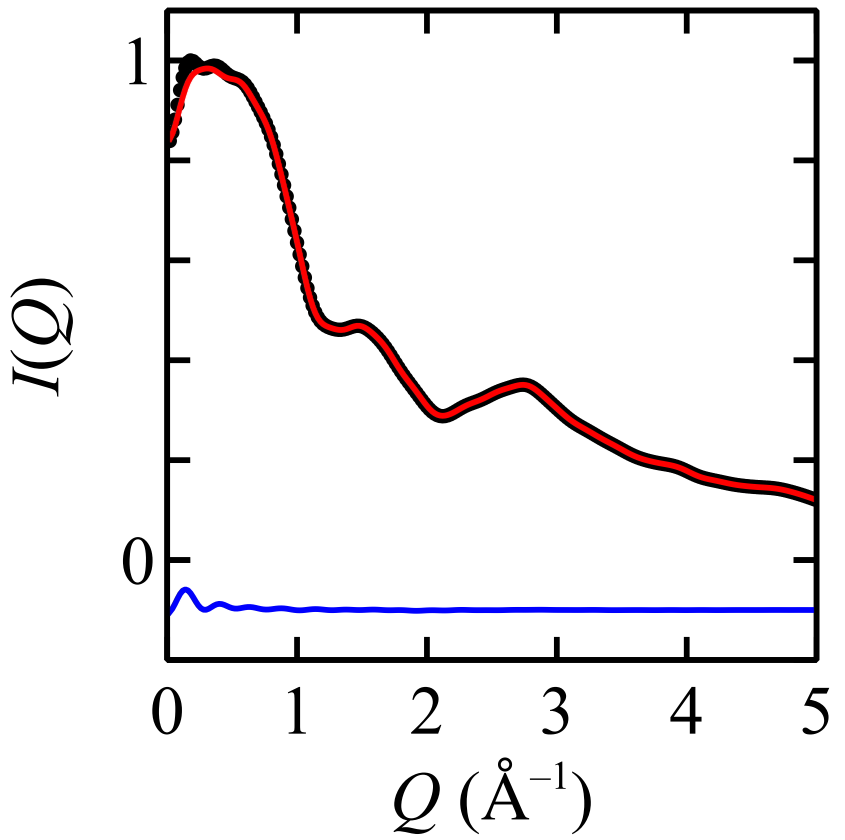
Joseph A M Paddison[1,2], J Ross Stewart[2] and Andrew L Goodwin[1]

- Refine “big box” model to magnetic diffuse scattering data
- Structure refinement method – no spin Hamiltonian used
- **Download:** joepaddison.com/software

Paddison, Stewart & Goodwin, *J. Phys.: Condens. Matter* **25**, 454220 (2013)

Spinvert program

joe.paddison.com/software



spinice_config.txt — Edited

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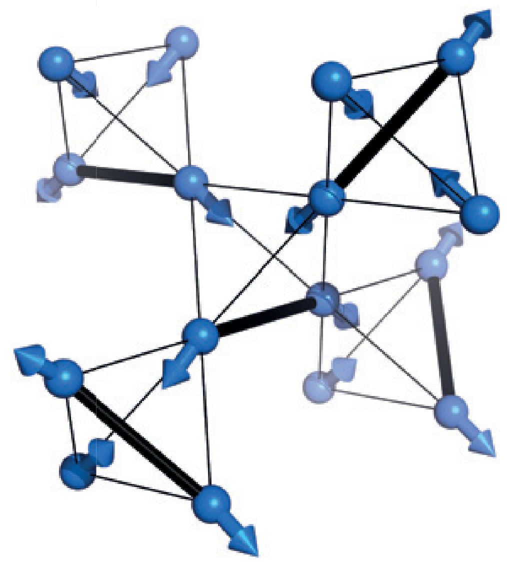
TITLE spinice

CELL 10.100 10.100 10.100 90 90 90
SITE 0.5000 0.5000 0.5000
SITE 0.5000 0.0000 0.0000
SITE 0.0000 0.0000 0.5000
SITE 0.0000 0.5000 0.0000
SITE 0.5000 0.7500 0.7500
SITE 0.5000 0.2500 0.2500
SITE 0.0000 0.2500 0.7500
SITE 0.0000 0.7500 0.2500
SITE 0.7500 0.5000 0.7500
SITE 0.7500 0.0000 0.2500
SITE 0.2500 0.0000 0.7500
SITE 0.2500 0.5000 0.2500
SITE 0.7500 0.2500 0.0000
SITE 0.7500 0.7500 0.5000
SITE 0.2500 0.7500 0.0000
SITE 0.2500 0.2500 0.5000

SPIN_DIMENSION 1
ANISOTROPY 1 1 1
ANISOTROPY 1 1 1
ANISOTROPY 1 1 1
ANISOTROPY 1 1 1
ANISOTROPY 1 -1 -1
ANISOTROPY 1 -1 -1
ANISOTROPY 1 -1 -1
ANISOTROPY 1 -1 -1
ANISOTROPY -1 1 -1
ANISOTROPY -1 1 -1
ANISOTROPY -1 1 -1
ANISOTROPY -1 1 -1
ANISOTROPY -1 -1 1
ANISOTROPY -1 -1 1
ANISOTROPY -1 -1 1
ANISOTROPY -1 -1 1

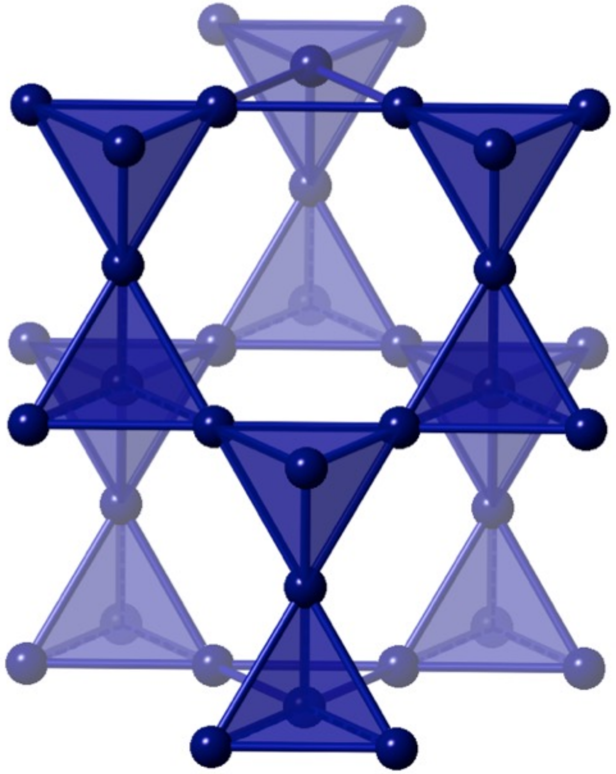
FORM_FACTOR_J0 0.0566 18.3176 0.3365 7.6880 0.6317 2.9427 -0.0248
MOVES 100
BOX 6 6 6
SCALE refine
WEIGHT 1.0
```



Paddison, Stewart & Goodwin, *J. Phys.: Condens. Matter* **25**, 454220 (2013)

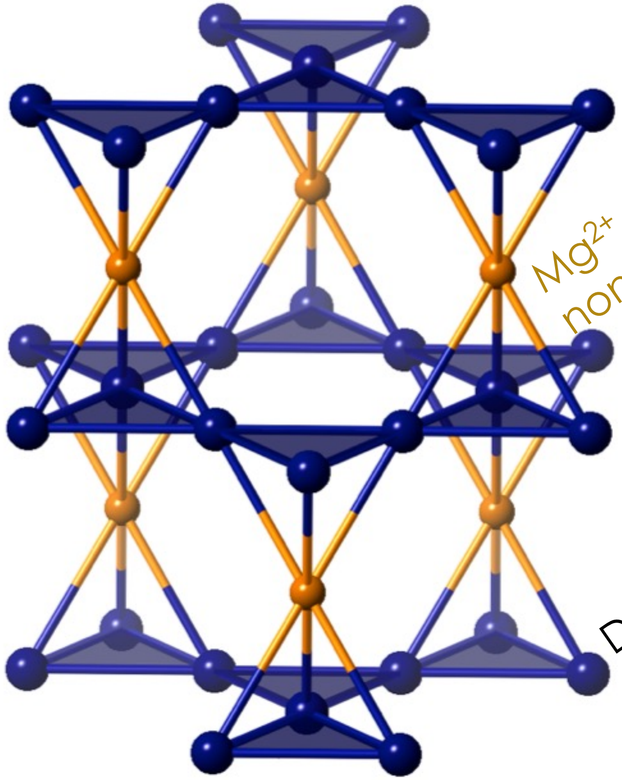
Spinvert example 1: Kagome $Dy_3Mg_2Sb_3O_{14}$

Pyrochlore $Dy_2Ti_2O_7$



Space group *Fd*–3*m*

Kagome $Dy_3Mg_2Sb_3O_{14}$



Space group *R*–3*m*

Siân Dutton
Cambridge

Martin Mourigal
Georgia Tech

Paromita Mukherjee
Cambridge

Xiaojian Bai
Georgia Tech

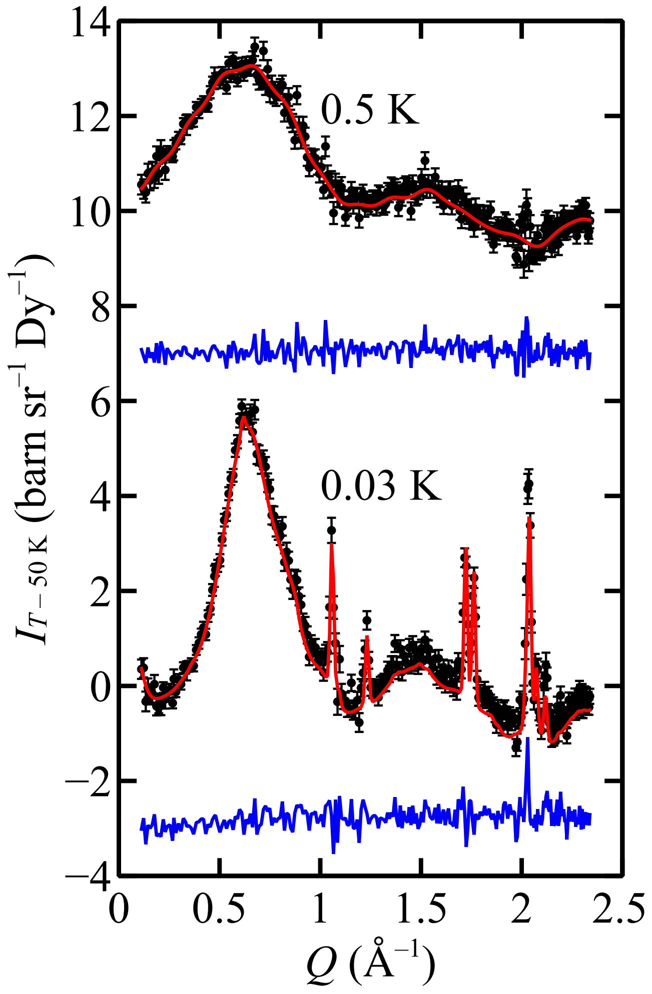
Sanders *et al.*, *J. Mater. Chem. C* **4**, 541–550 (2016)

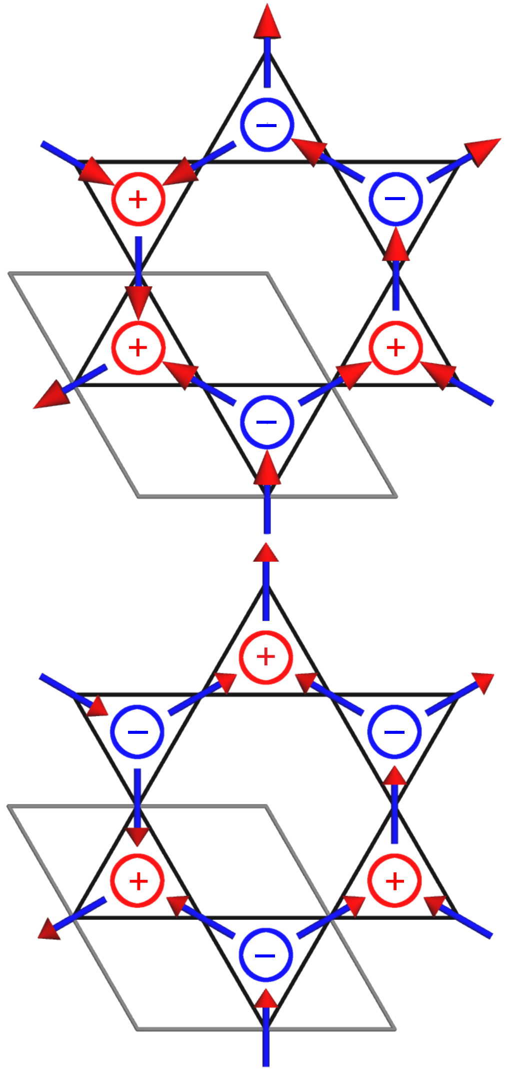
Spinvert example 1: Kagome $Dy_3Mg_2Sb_3O_{14}$

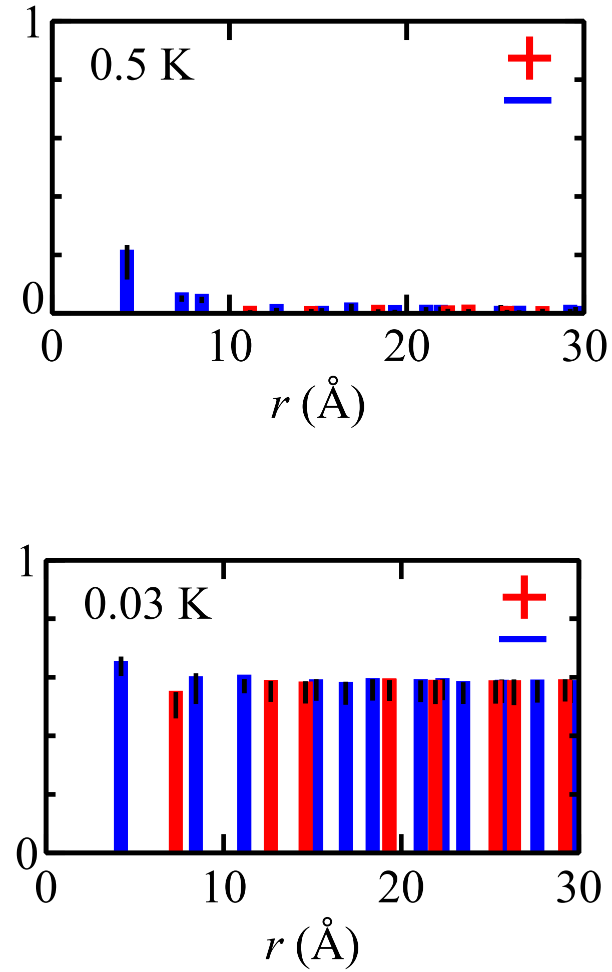
Diffuse scattering

Local magnetic structure

"Emergent charge" correlations



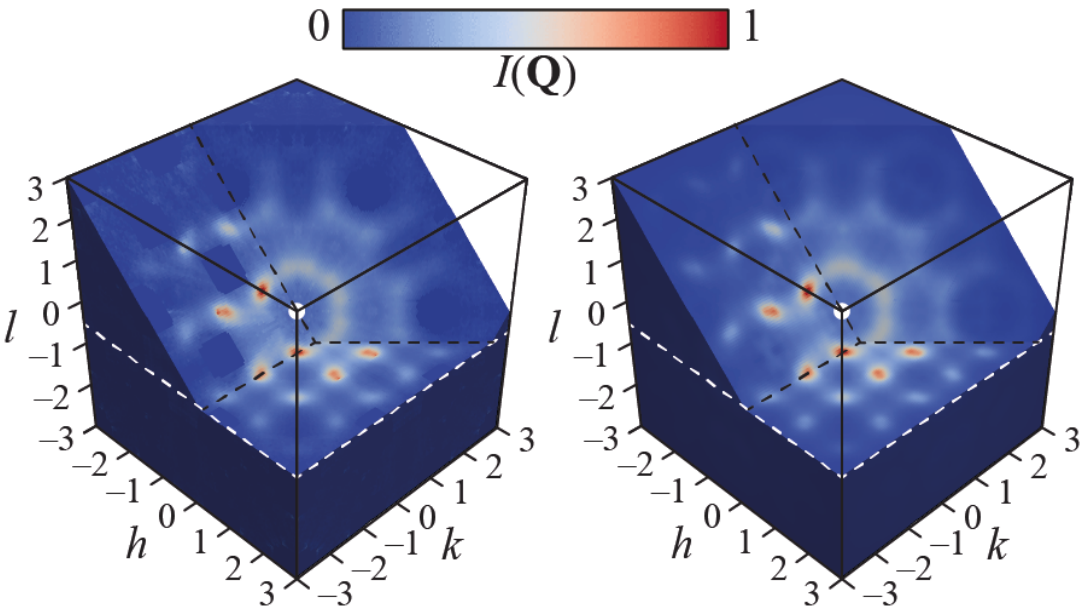




Paddison *et al.*, *Nature Commun.* **7**, 13842 (2016)

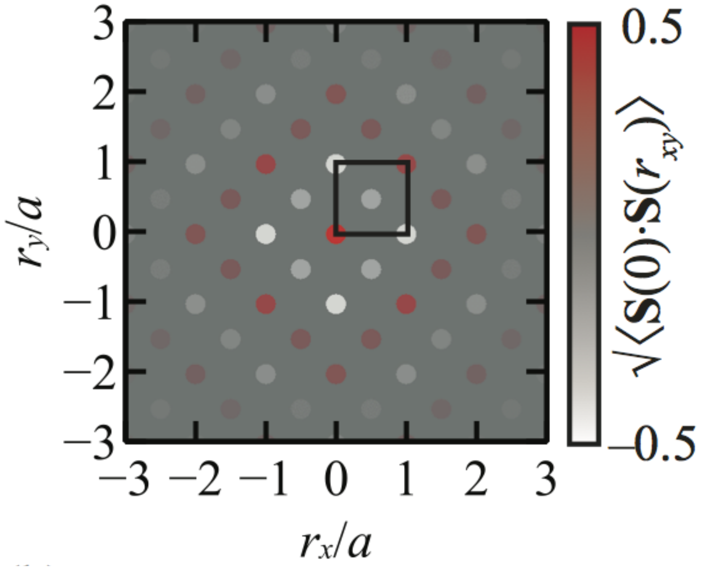
Spinvert example 2: Manganese oxide, MnO

- Single-crystal magnetic reverse Monte Carlo



Data **RMC fit**

Paramagnetic MnO, 160 K (SXD, ISIS)



Spin-spin correlation function
~ 3D magnetic PDF

Paddison, Gutmann, Stewart *et al.*, *PRB* **97**, 014429 (2018)

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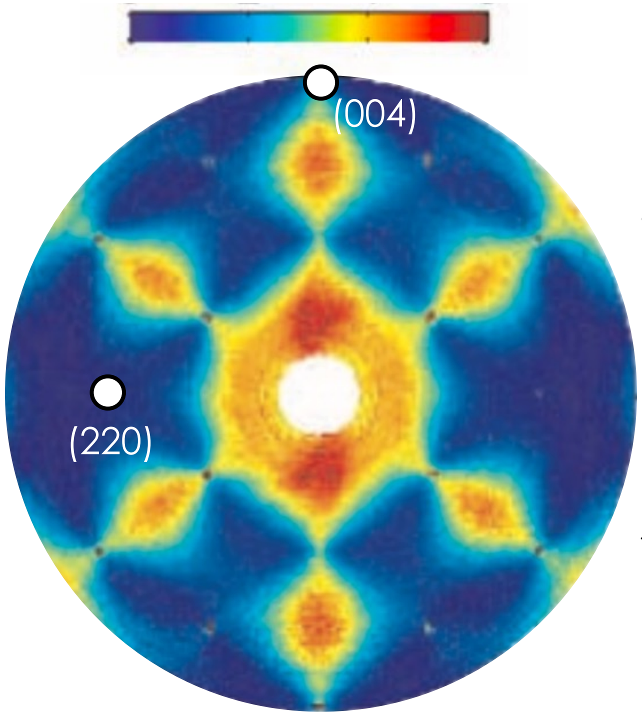
- Magnetic structure refinement: *Spinvert*
- **Magnetic interaction modelling: *Spinteract***

Diffuse scattering analysis – an overview

Data

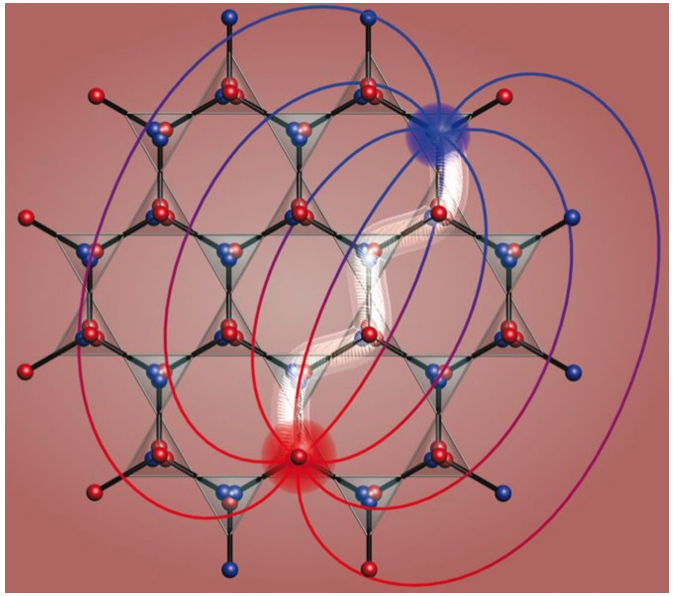


Reciprocal space

structure refinement

interaction modelling

Model**



Real space

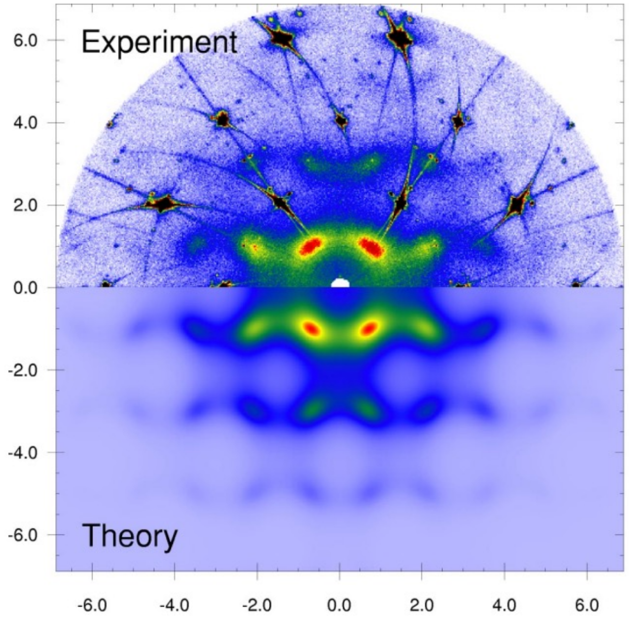
Left data: Fennell *et al.*, *Science* **326**, 415 (2009)
Right image: Castelnovo, Moessner & Sondhi, *Nature* **451**, 42 (2008)

Magnetic interaction modelling has a long history

- e.g. paramagnetic MnO; $$H = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

Single-crystal data

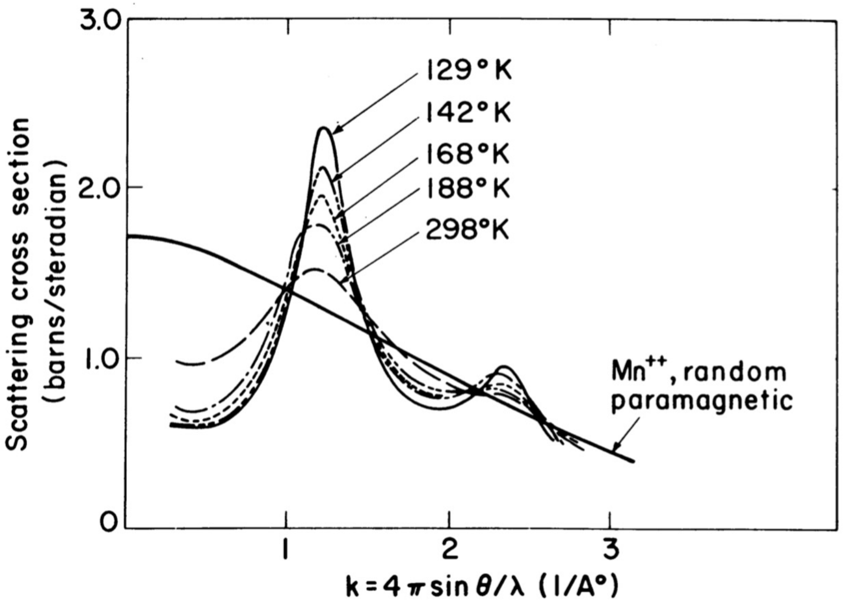
Fitted $\boldsymbol{J_1}$ **= 3.3 K,** $\boldsymbol{J_2}$ **= 4.6 K**



Hohlwein *et al.*, *PRB* **68**, 140408(R) (2003)

Powder data

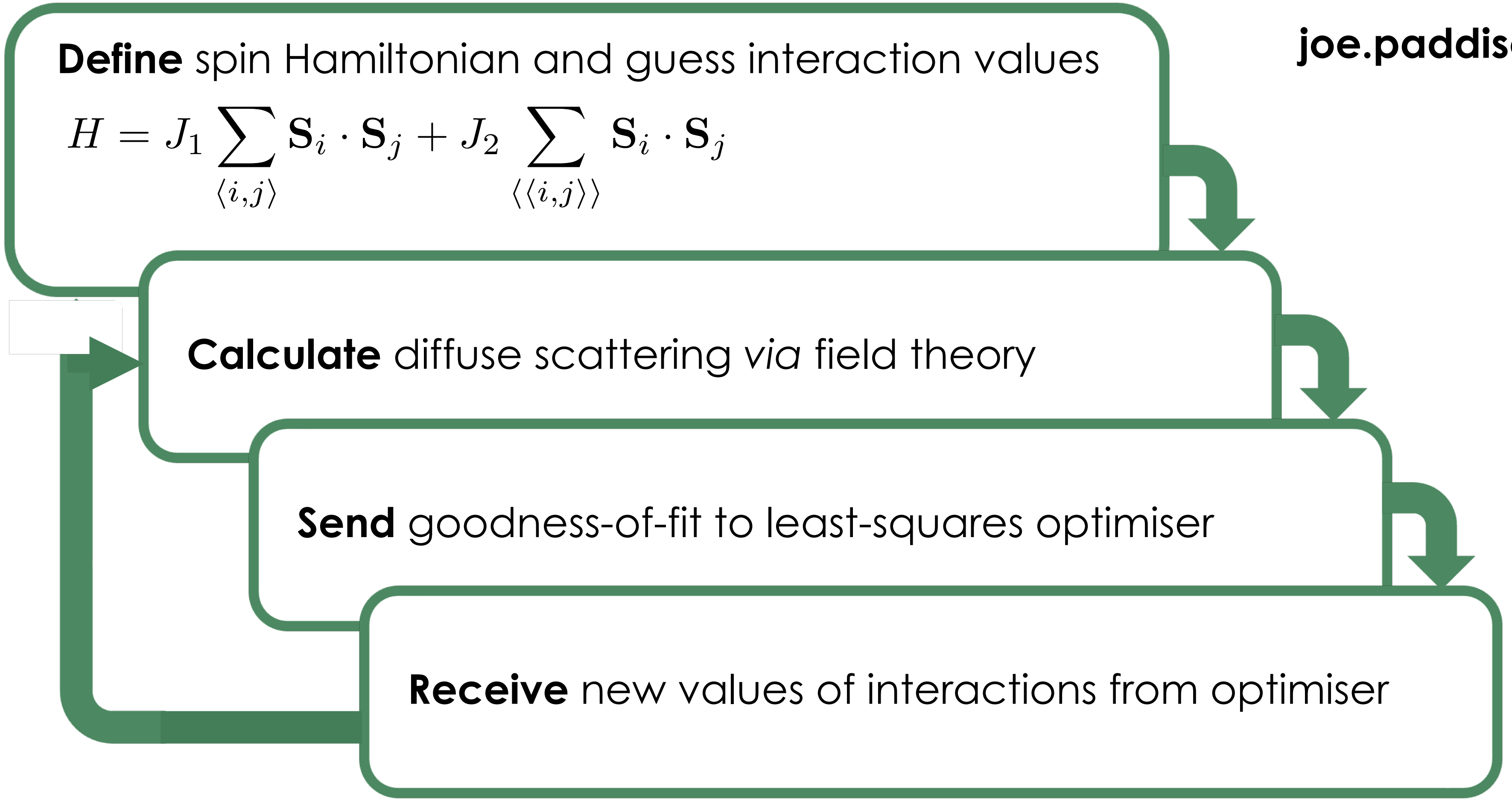
Fitted $\boldsymbol{J_2}$ **= 4.65 K**



Blech & Averbach, *Physics* **1**, 31 (1964)

Spinteract program

joe.paddison.com/software



$$I(\mathbf{Q}) \propto \frac{[f(Q)]^2 \chi_0 T}{1 - \chi_0 [J(\mathbf{Q}) - \lambda]}$$

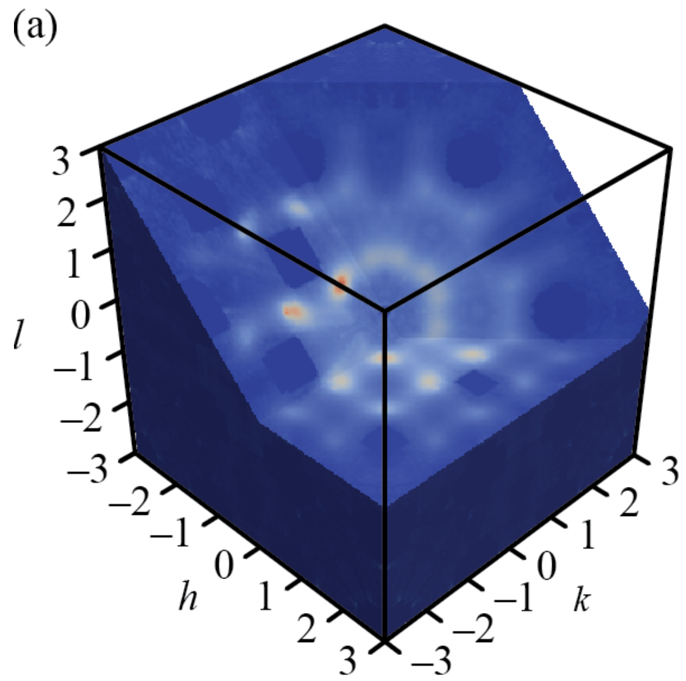
$$J(\mathbf{Q}) = \sum_j J_{ij} \exp(i\mathbf{Q} \cdot \mathbf{R}_j)$$

Paddison, arXiv:2210.09016 (2022)
Brout & Thomas, *Physics Physique Fizika* **3**, 317 (1967)
James & Roos, *Comp. Phys. Commun.* **10**, 343 (1975)

Spinteract example 1: MnO

- Same data as previously shown (SXD @ ISIS)

Data
T = 160 K



MnO_config.txt — Edited

```
TITLE MnO

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PATTERSON_GROUP Fm-3m

SITE 0.0 0.0 0.0

SPIN_DIMENSION 3
SPIN_LENGTH_SQUARED 8.75
FORM_FACTOR_J0 0.4220 17.6840 0.5948 6.0050 0.0043 -0.6090 -0.0219

XTAL_SCALE refine
XTAL_FLAT_BACKGROUND refine
XTAL_TEMPERATURE 160.0

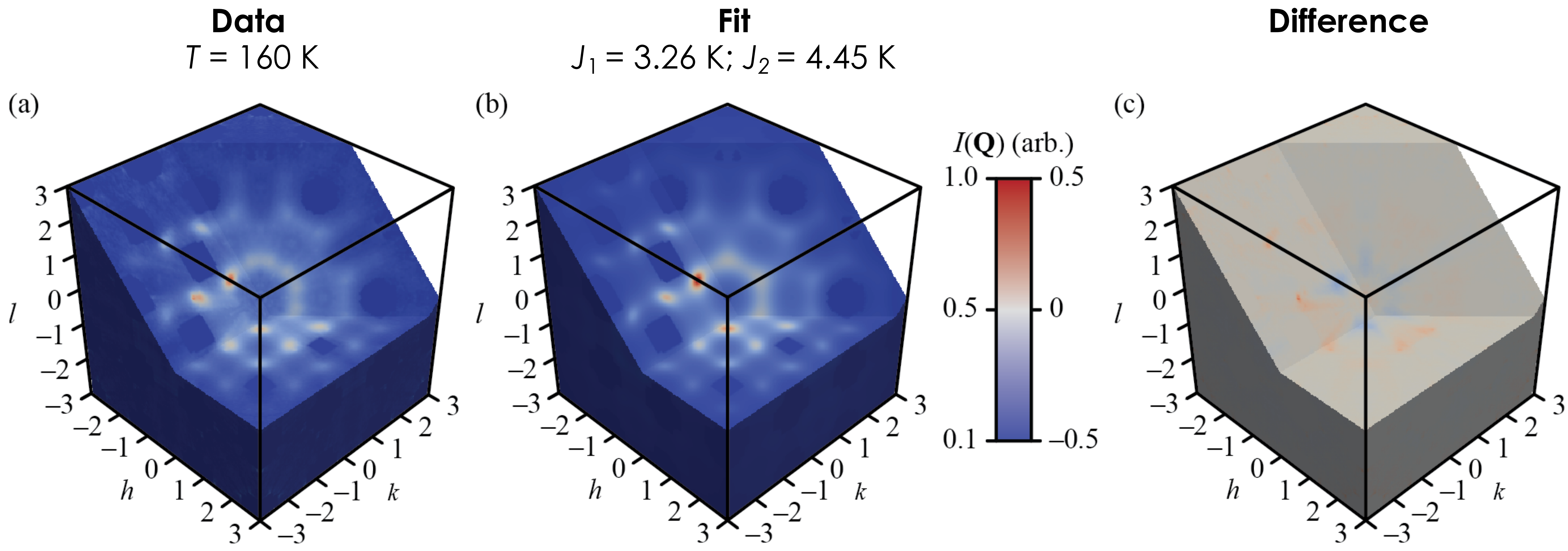
BZ_POINTS 32 32 32

ORIGIN -3.0 -3.0 -3.0
X_AXIS 6.0 0.0 0.0 151
Y_AXIS 0.0 6.0 0.0 151
Z_AXIS 0.0 0.0 6.0 151
```

Paddison, arXiv:2210.09016 (2022)
Data: Paddison, Gutmann, Stewart *et al.*, *PRB* **97**, 014429 (2018)

Spinteract example 1: MnO

- Same data as previously shown (SXD @ ISIS)

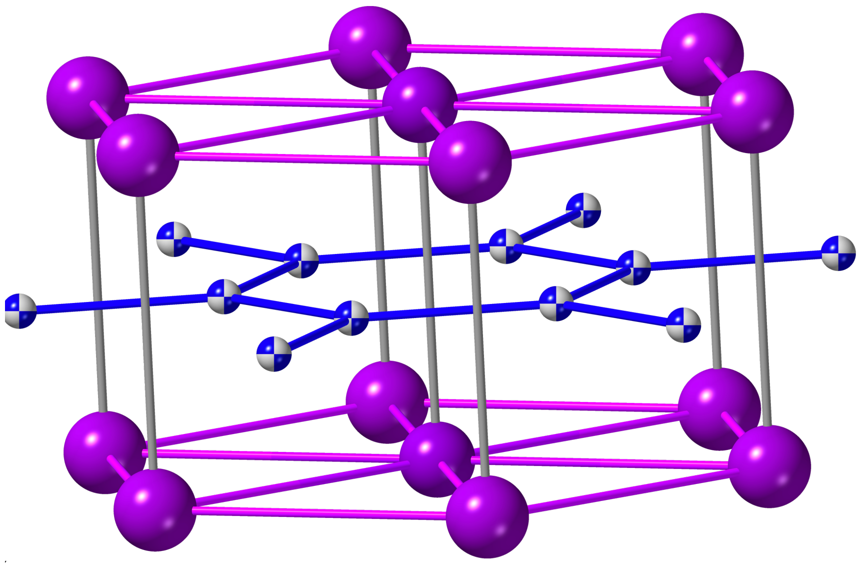


Paddison, arXiv:2210.09016 (2022)
Data: Paddison, Gutmann, Stewart *et al.*, *PRB* **97**, 014429 (2018)

Spinteract example 2: Skyrmion crystal Gd_2PdSi_3

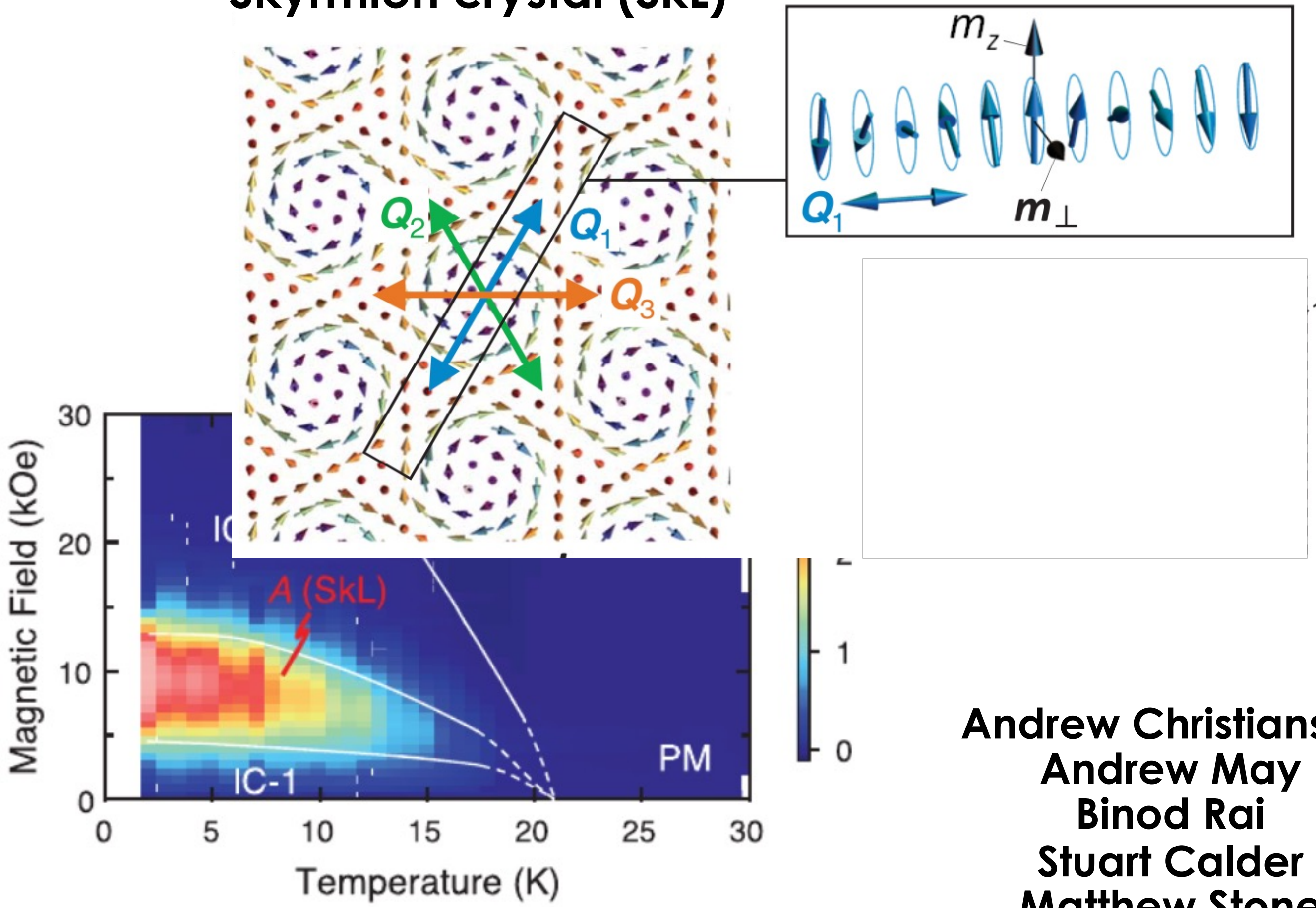
- **Below T_N**: "Giant" topological Hall effect in applied field

Gd^{3+} ($S = 7/2$
$\theta_W \sim 30$ K)



Space group *P6/mmm*
a = 4.069 Å, c = 4.088 Å

Skyrmion crystal (SkL)



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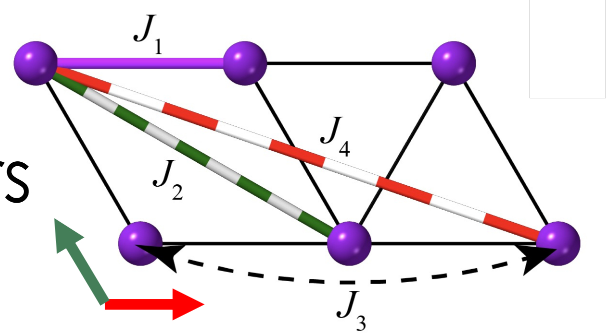
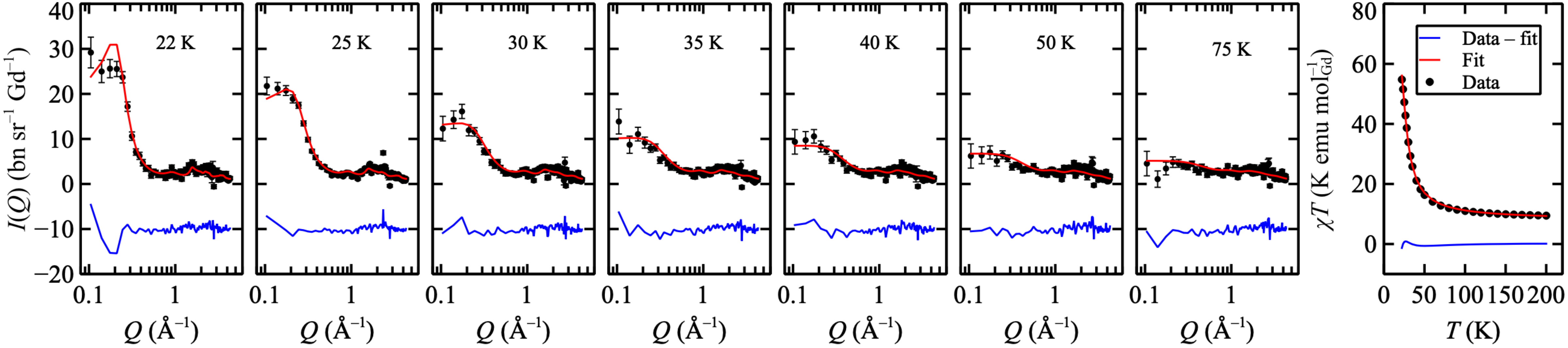
Right image: Kurumaji *et al.*, *Science* **365**, 914 (2019)
Saha *et al.*, *Phys. Rev. B* **60**, 12162 (1999)

Spinteract example 2: Gd_2PdSi_3

- **Above T_N:** Good fit with 5 interaction parameters
  - J_c is inter-layer coupling





J_c (K)	J_1 (K)	J_2 (K)	J_3 (K)	J_4 (K)
1.97(46)	0.31(9)	0.19(15)	0.27(18)	−0.21(5)

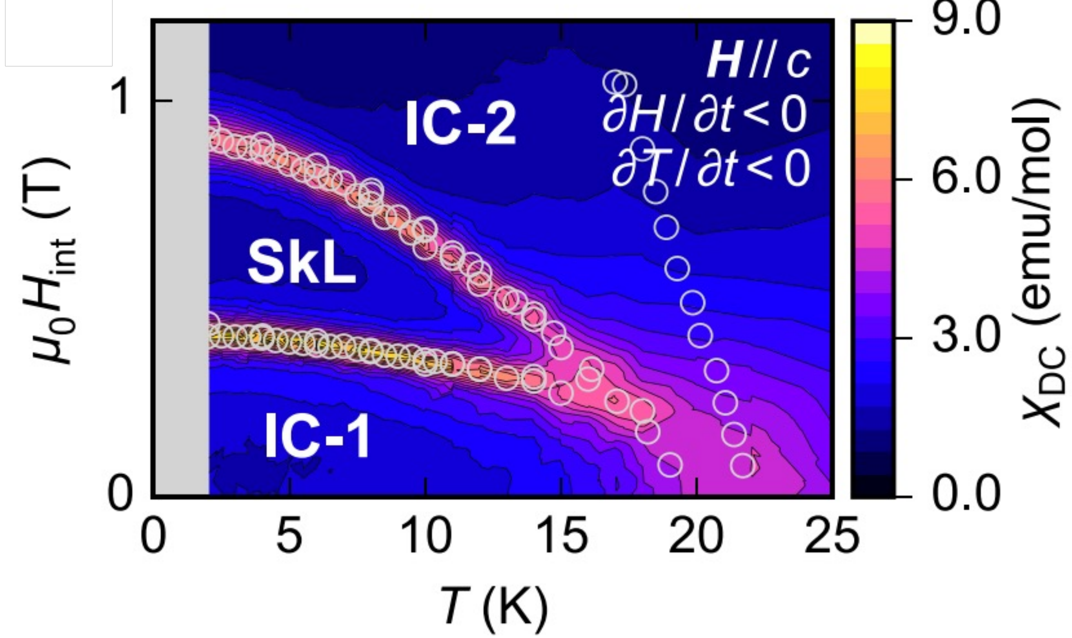
Ferromagnetic values are +ve
Uncertainties 3σ

Paddison *et al.*, *PRL* **129**, 137202 (2022)

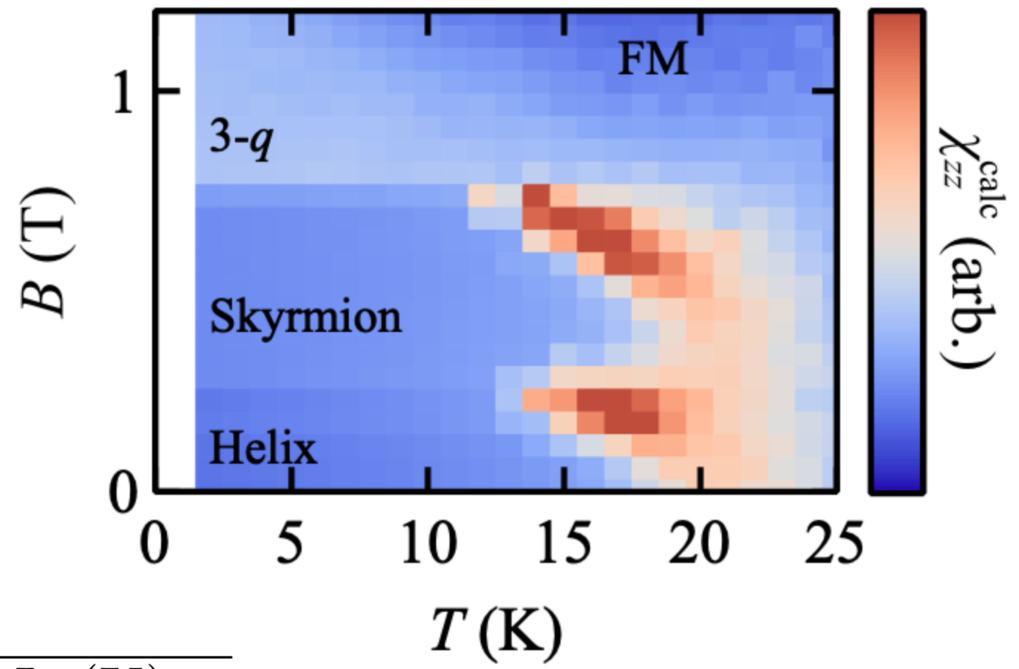
Spinteract example 2: Gd_2PdSi_3

$$H=-\frac{1}{2}\sum_{i,j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+g\mu_\mathrm{B}B\sum_i S_i^z+D\sum_{i>j}\frac{\mathbf{S}_i\cdot\mathbf{S}_j-3\left(\mathbf{S}_i\cdot\hat{\mathbf{r}}_{ij}\right)\left(\mathbf{S}_j\cdot\hat{\mathbf{r}}_{ij}\right)}{\left(r_{ij}/r_1\right)^3}$$

Data: Hirschberger *et al.*, *PRB* **101**, 220401(R) (2020)



Calculation: Classical Monte Carlo



J_c (K)	J_1 (K)	J_2 (K)	J_3 (K)	J_4 (K)
1.97(46)	0.31(9)	0.19(15)	0.27(18)	−0.21(5)

Utesov, *arXiv* 2109.13682 (2021)
Paddison *et al.*, *PRL* **129**, 137202 (2022)

Spinteract example 3: $KYbSe_2$

- Triangular lattice of Yb^{3+} with effective spin-½

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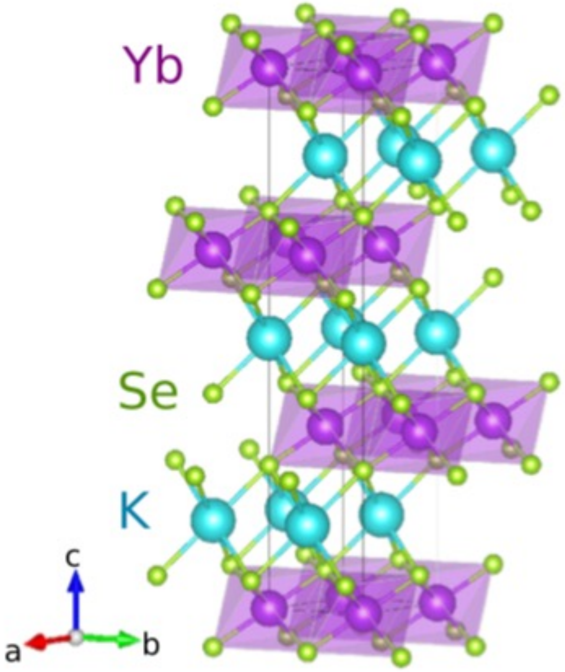
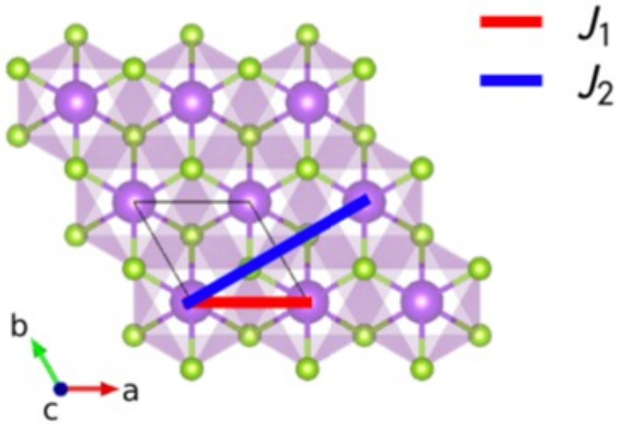
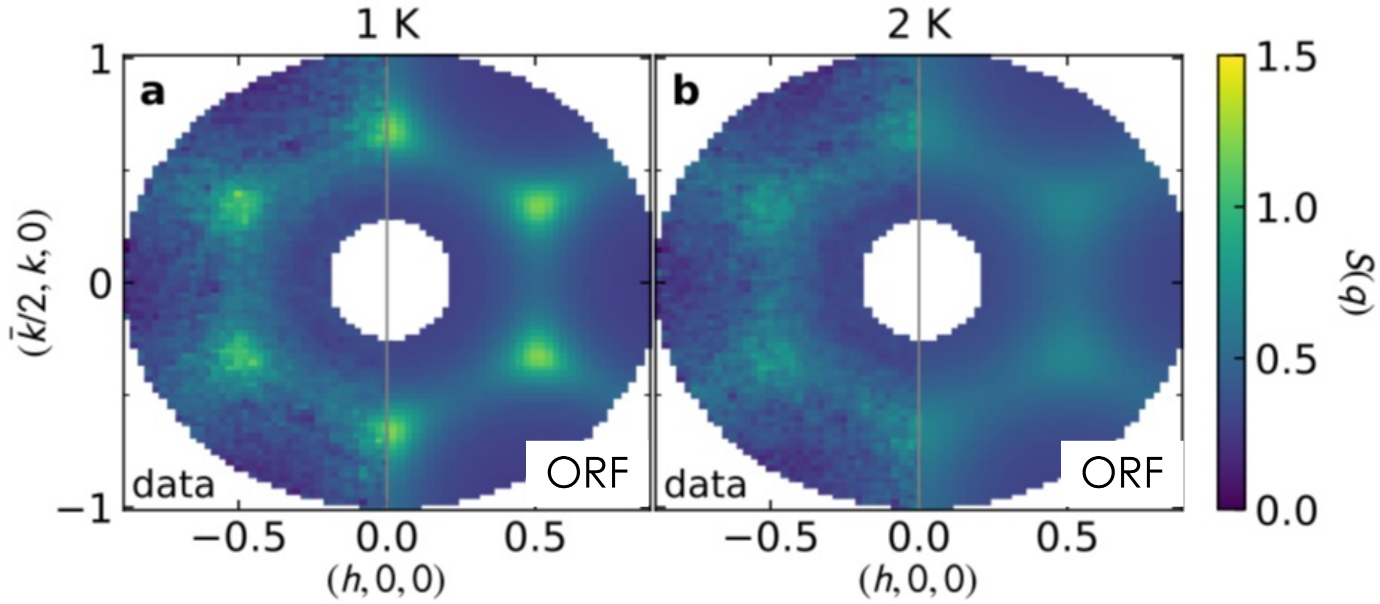


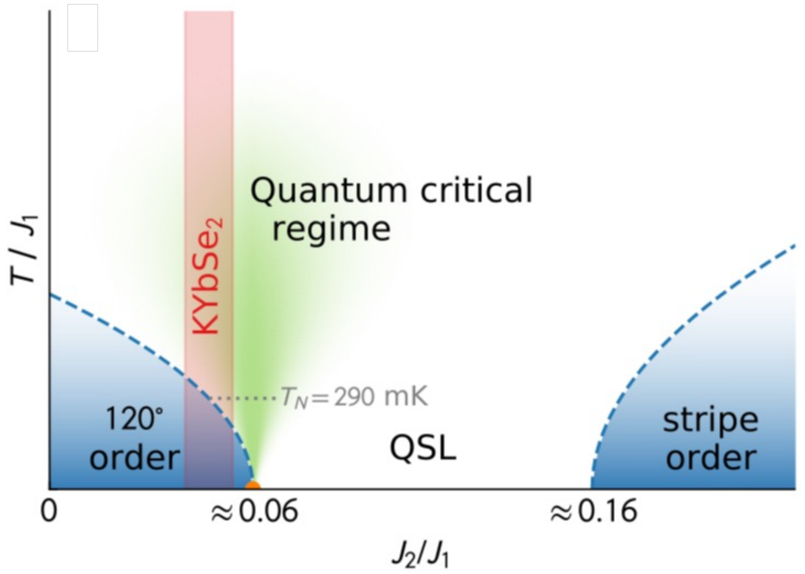


Scheie, Ghioldi, Xing, Paddison *et al.*, *arXiv* 2109.11527 (2021)
Scheie *et al.*, *arXiv* 2207.14785 (2022)

Spinteract example 3: $KYbSe_2$

- Fits show <3% deviation from Heisenberg model





Theoretical technique	J_1 (meV)	J_2/J_1
Onsager reaction field	*NA*	0.047 ± 0.007
Nonlinear spin waves	0.456 ± 0.013	0.043 ± 0.010
Heat capacity	0.429 ± 0.010	0.037 ± 0.013
Weighted mean:	0.438 ± 0.008	0.044 ± 0.005

Scheie, Ghioldi, Xing, Paddison *et al.*, *arXiv* 2109.11527 (2021)
Scheie *et al.*, *arXiv* 2207.14785 (2022)

Conclusions

- Magnetic diffuse scattering is a rich source of information
  - **Spin correlations (mPDF)**: Reverse Monte Carlo (Spinvert, RMCProfile, RMCDiscord)
  - **Magnetic interactions:** Spinteract
- Powder data often more informative than we might expect!
- I'll distribute tutorial files at the tutorial sessions

joepaddison.com/software

Thanks for listening!

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