Introduction to diffuse scattering

JOE PADDISON

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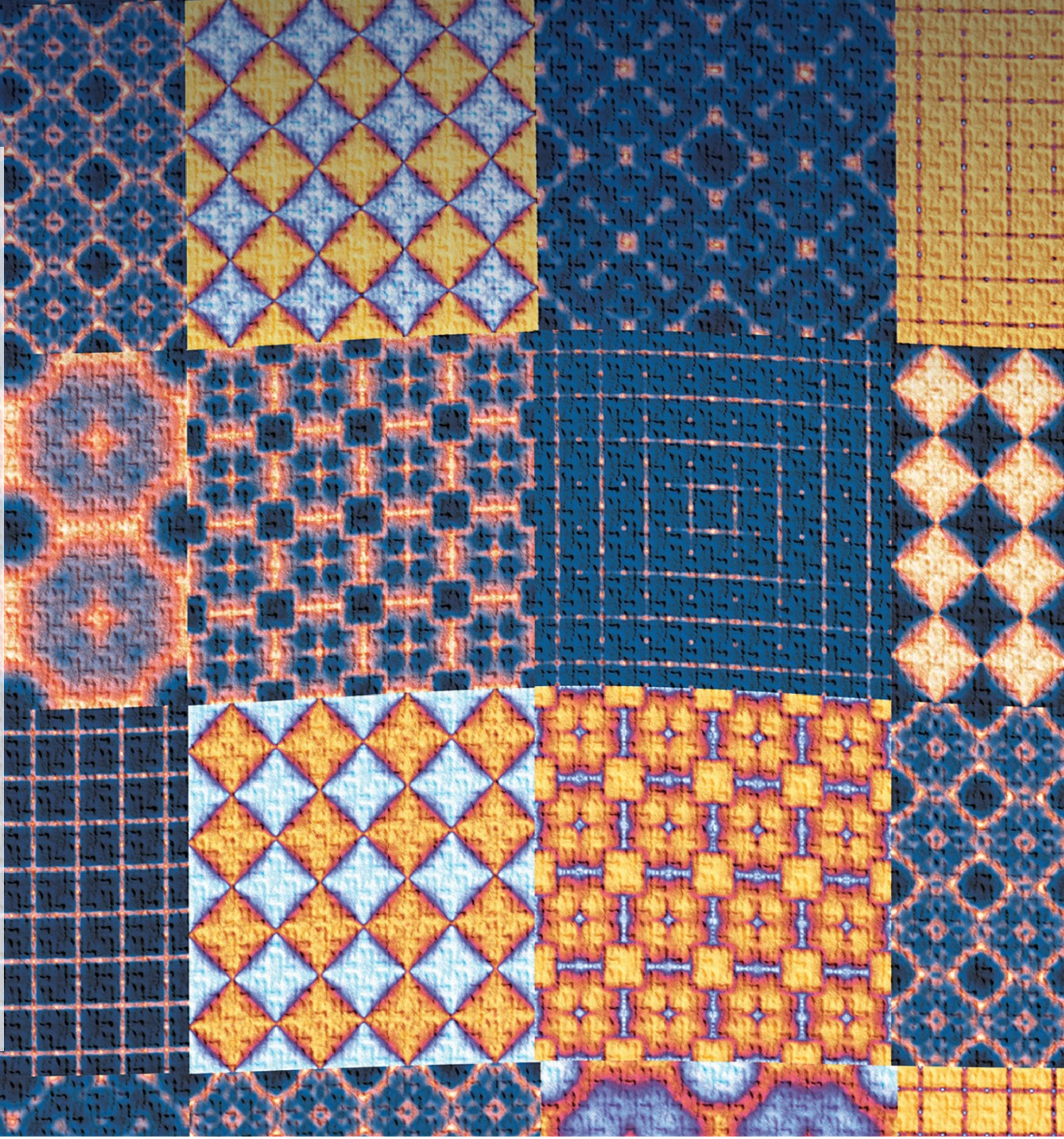


Images: Paddison & Cliffe, *ACS Central Science* **10,** 1821 (2024)

What is diffuse scattering?

- Broad features beneath and between the sharp (Bragg) peaks
- e.g. magnetic scattering from MnO

Clifford Shull

Magnetic Bragg scattering
→ *long-range magnetic order*

Magnetic diffuse scattering
→ *short-range magnetic order*

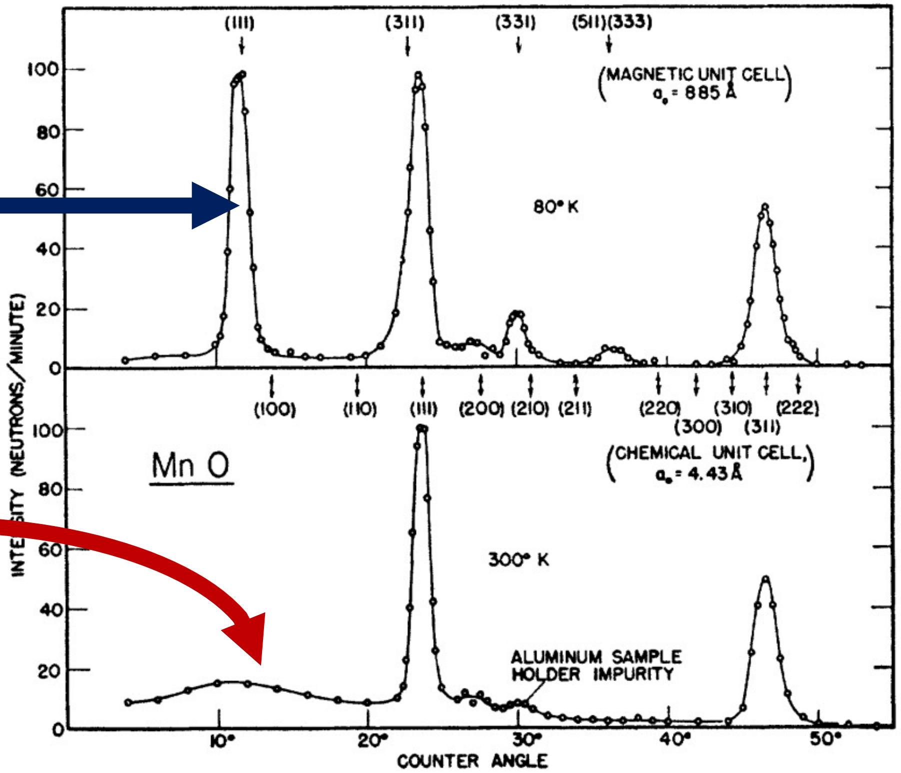


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

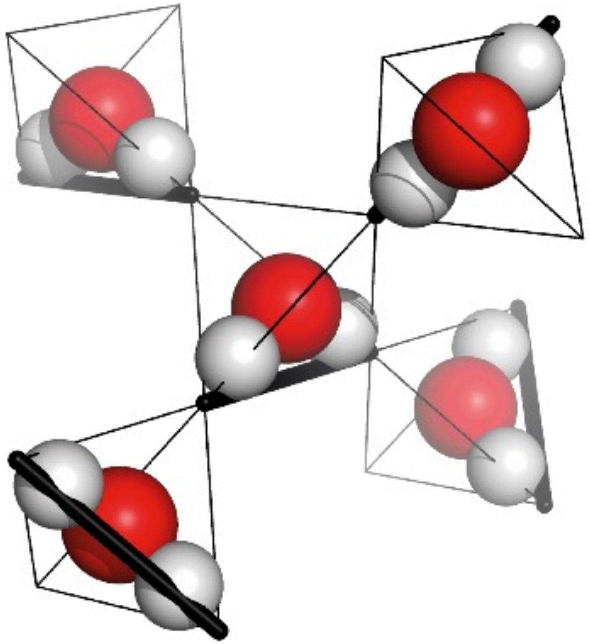
$T < T_N$

$T > T_N$

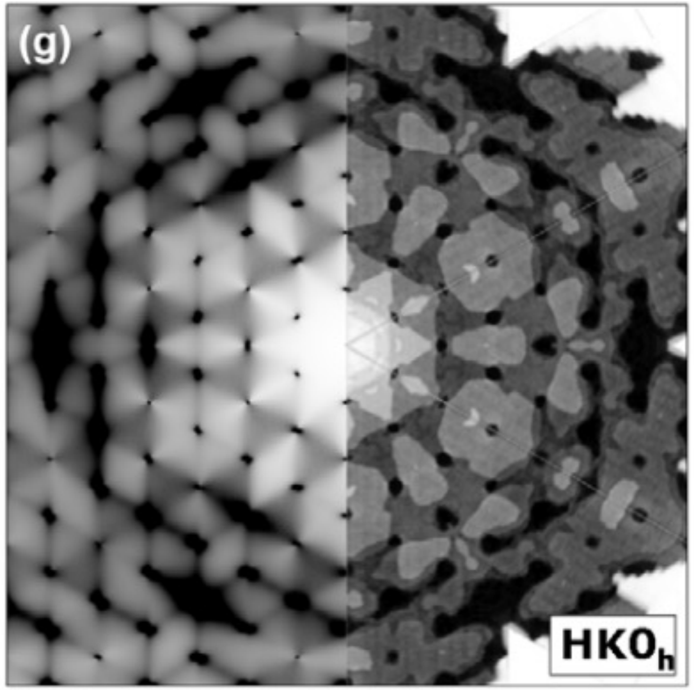
Shull and Smart, *Phys Rev* **76**, 1256 (1949)

What does diffuse scattering measure?

- Deviations from long-range order (either **chemical** or magnetic)
- Correlated disorder → structured diffuse scattering
  - e.g. "ice rules" in water ice



Water ice
*Real space, **r***

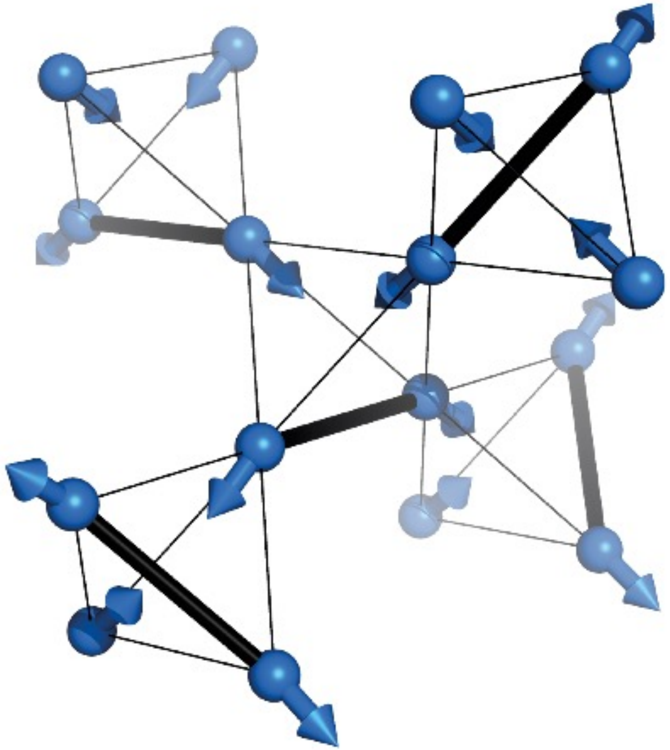


Model **Neutron data***
*Reciprocal space, **Q***

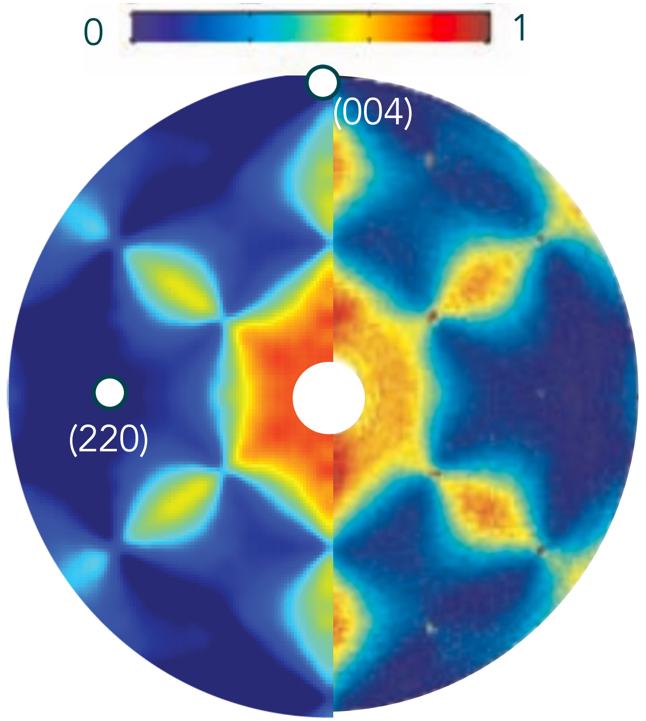
*Wehinger et al., *JPCM* **26** 265401 (2014)

What does diffuse scattering measure?

- Deviations from long-range order (either chemical or **magnetic**)
- Correlated disorder → structured diffuse scattering
  - e.g. “ice rules” in spin ice



Spin ice
*Real space, **r***



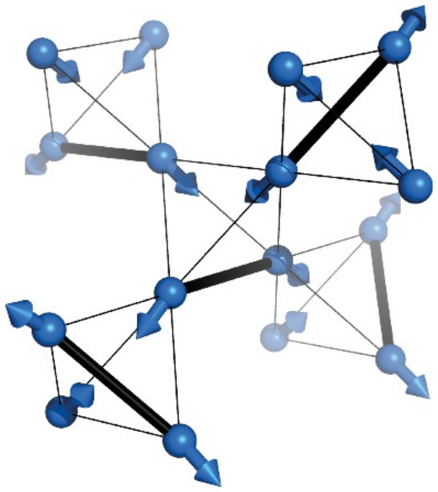
Model **Neutron data***

*Reciprocal space, **Q***

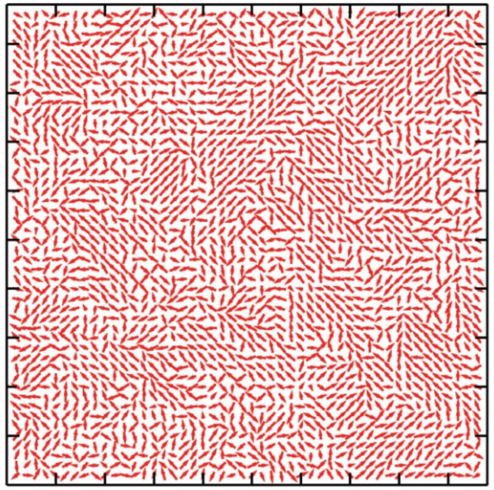
*Fennell et al., *Science* **326**, 415 (2009)

Why study diffuse scattering?

- *Functional materials*
  - Behaviour often driven by local structure distortions
  - e.g. relaxor ferroelectrics, colossal magnetoresistance manganites
- *Exotic (possibly quantum) magnetic states*
  - May not show conventional magnetic order, so best understood *via* diffuse and inelastic scattering
  - e.g. quantum spin liquids, spin ice, “hidden” order
- *Insight into interactions*
  - Magnetic diffuse scattering → magnetic Hamiltonian
  - Thermal diffuse scattering → lattice force constants



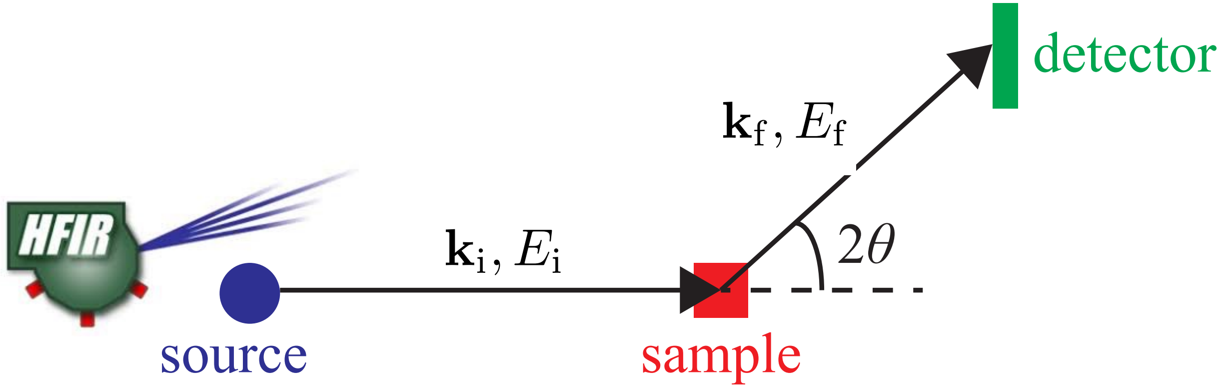
Spin orientations in spin ice



*Dipole orientations in a relaxor ferroelectric**

*Pasciak et al., *PRB* **85**, 224109 (2012)

How do we measure diffuse scattering using neutrons?



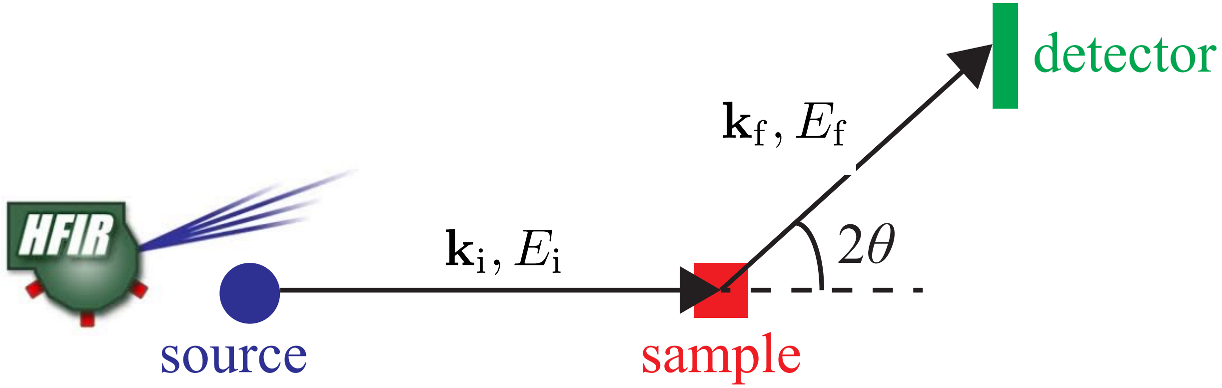
Energy transfer $E = E_\mathrm{i} - E_\mathrm{f}$

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

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

- Quantity of interest is **energy-integrated intensity** $I(\mathbf{Q}) = \int_{-\infty}^{\infty} I(\mathbf{Q}, E)\,\mathrm{d}E$
- Approximated by diffraction measurements if $E \ll E_\mathrm{f}$
- Measures **instantanenous** correlations (“snapshot picture”)

How do we measure diffuse scattering using neutrons?



Energy transfer $E = E_i - E_f$

Wavevector transfer $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$

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

- **For single crystals:** Measure large volume of **Q** (e.g. Corelli, Topaz, Mandi @ SNS)
- **For non-magnetic powders:** Maximize Q_{max} (e.g. Nomad, Powgen @ SNS)
- **For magnetic materials:** Maximize flux at small Q (e.g. Powder, Wand^2 @ HFIR)
- **For all materials:** Measure and subtract background signal
- **For all materials**: Increase sample size and counting time *vs.* Bragg diffraction

How do we calculate diffuse scattering, mathematically?

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 (Debye formula):**

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

Debye formula
r_{ij} = distance between atoms *i* and *j*
b_i = coherent scattering length

Magnetic intensity *(spin-only, single type of magnetic atom)*

- **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:**

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

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

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

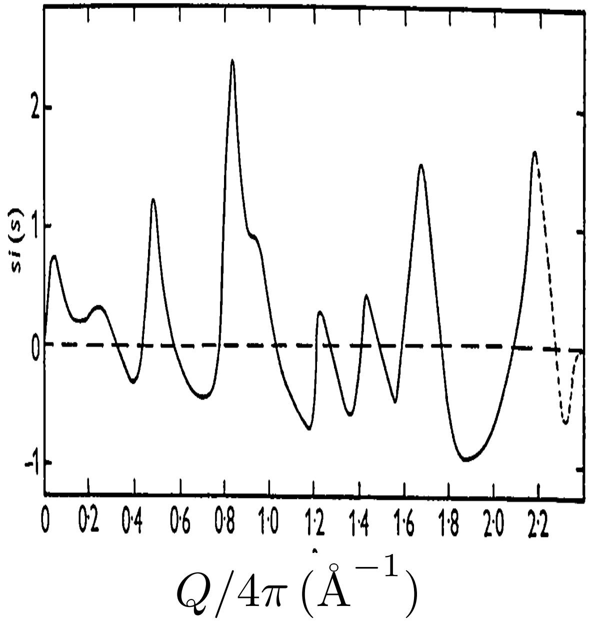
Debye, *Ann. Phys.* (Berlin) **351**, 809 (1915)
Blech & Averbach, *Physics* **1,** 31 (1964)

How can we visualize diffuse scattering data?

Rosalind Franklin

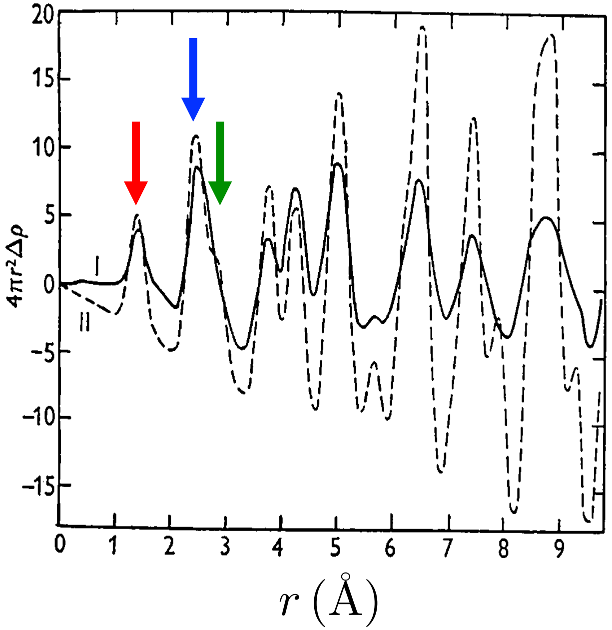
- **Non-magnetic case**: Fourier transform of powder data yields *pair-distribution function* (powder PDF) → *Kate Page's lecture*
  - Histogram of inter-atomic *distances*
  - e.g. coal

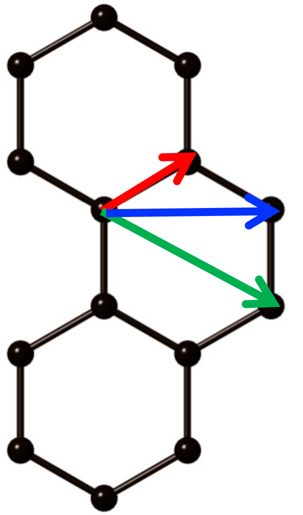
X-ray data



Fourier transform

Powder PDF

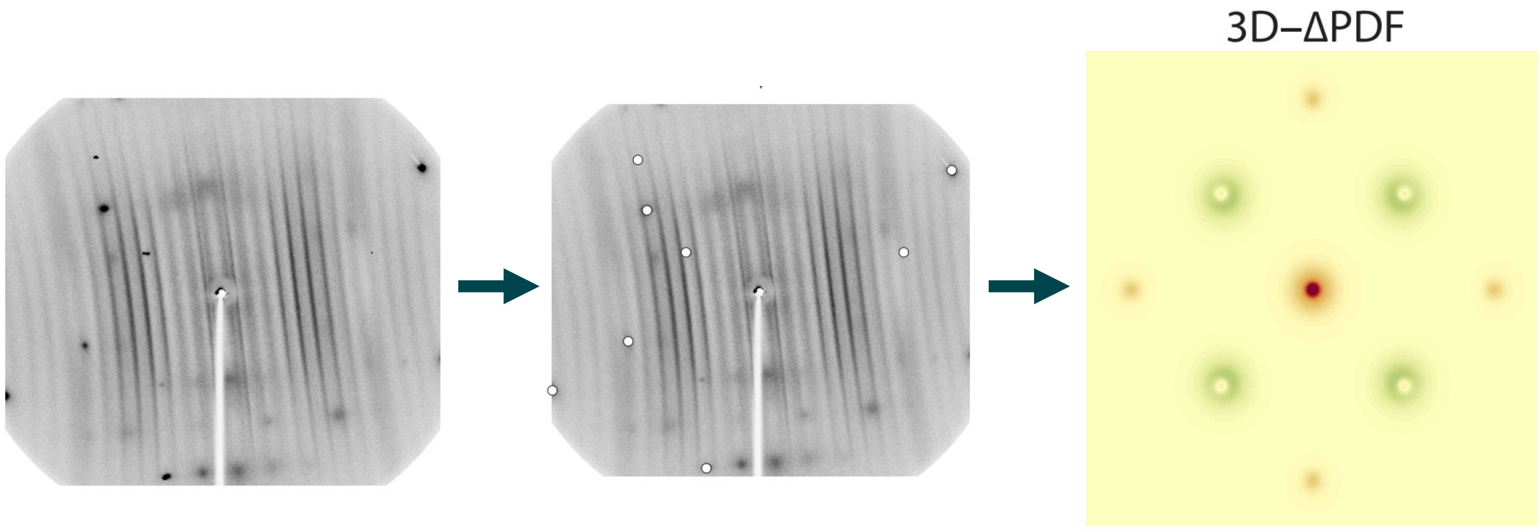




Franklin, *Acta Cryst.* **3**, 107 (1950)
Farrow & Billinge, *Acta Cryst. A* **65**, 232 (2009)

How can we visualize diffuse scattering data?

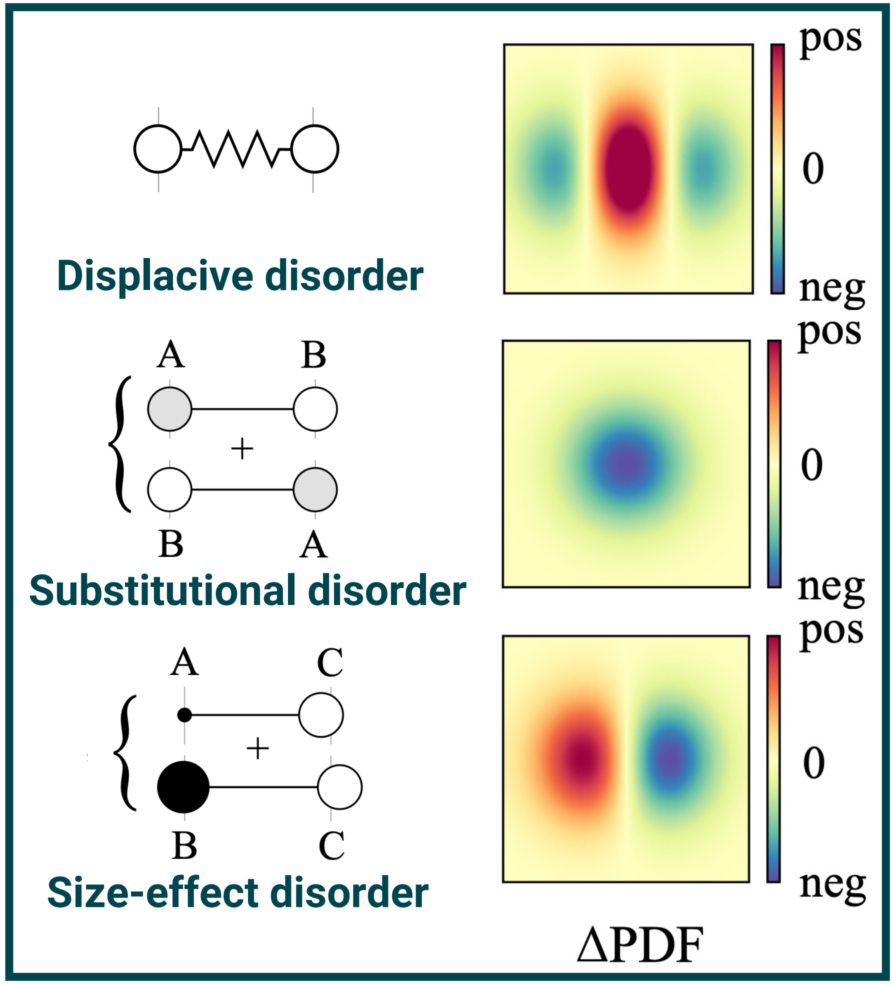
- **Non-magnetic case:** Fourier transform of single-crystal data with Bragg subtracted yields **3D-ΔPDF**
- Characteristic signals for different disorder types



Total scattering

Removed Bragg

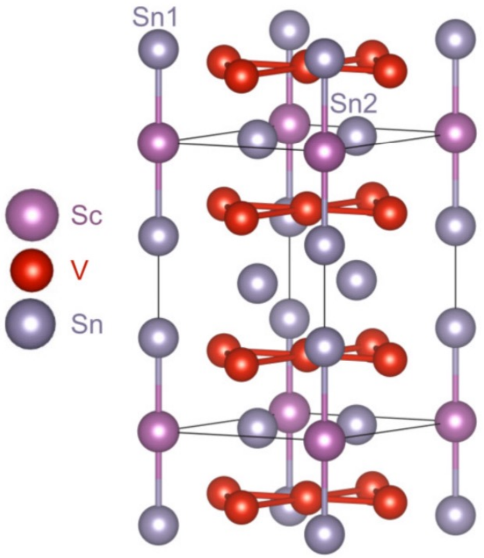
Fourier transformed



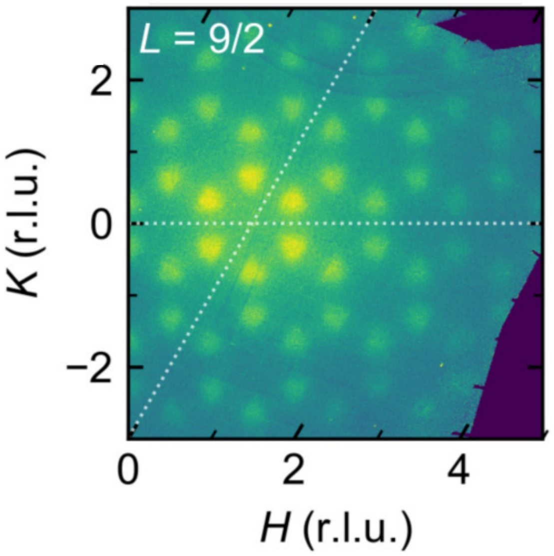
Images courtesy Arkadiy Simonov
Weber & Simonov, *Z Krist* **227**, 238 (2012)

How can we visualize diffuse scattering data?

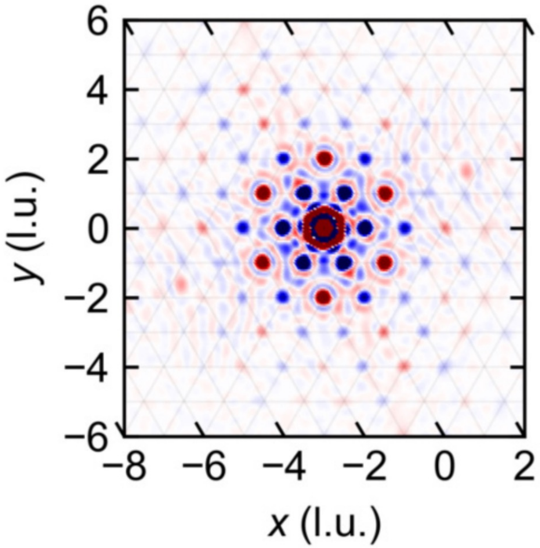
- **Non-magnetic case:** Fourier transform of single-crystal data with Bragg subtracted yields **3D-ΔPDF**
- Characteristic signals for different disorder types
  - e.g. intermetallic ScV_6Sn_6

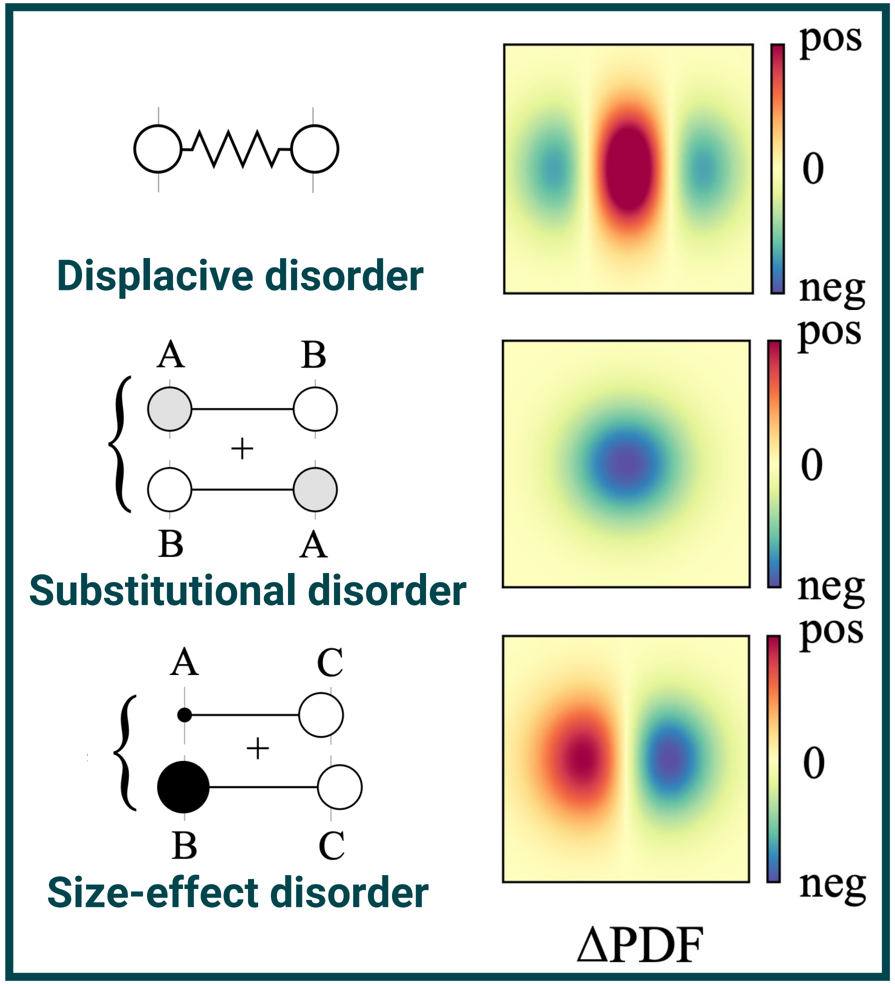


X-ray diffuse scattering



3D-ΔPDF





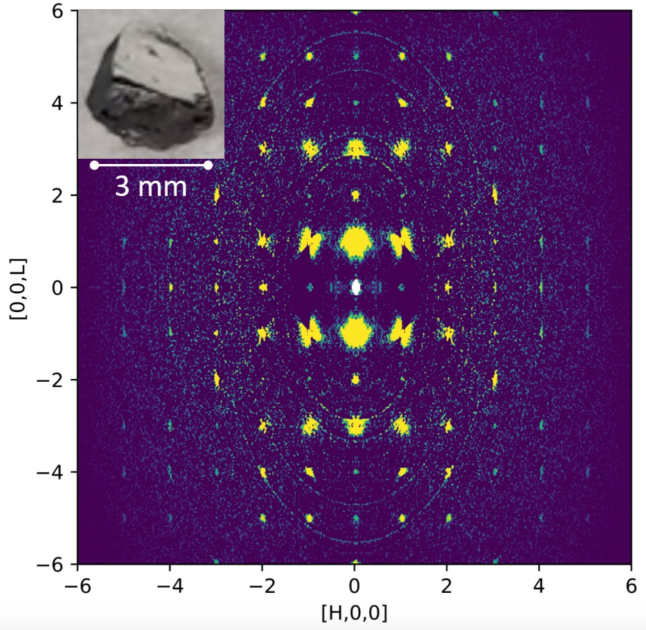
Gomez Alvarado *et al.*, *PRB* **110**, L140304 (2024)

How can we visualize diffuse scattering data?

- **Magnetic case:** Fourier transform of magnetic single-crystal data yields *3D magnetic PDF* (spin-pair correlation function)
  - Positive (negative) peaks indicate ferromagnetic (antiferromagnetic) correlations
  - e.g. magnetically-enhanced thermoelectric MnTe at $T > T_N$

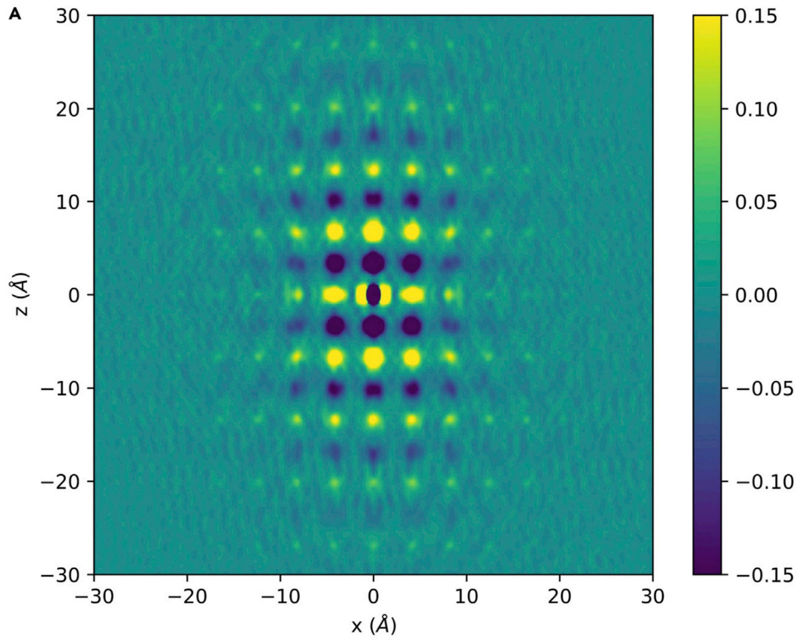
Neutron diffuse scattering

Nuclear scattering subtracted



Fourier transform

3D magnetic PDF

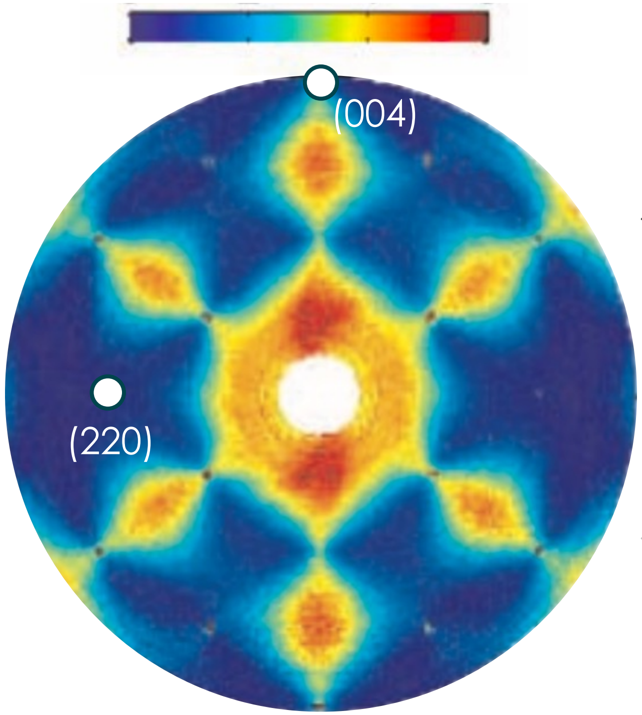


Baral *et al.*, *Matter* **5,** 1853 (2022)

diffpy.mpdf software: Frandsen *et al.*, *J Appl. Cryst.* **5**, 1377 (2022). **https://www.diffpy.org/products/mPDF.html**

How can we analyze diffuse scattering data?

Data*

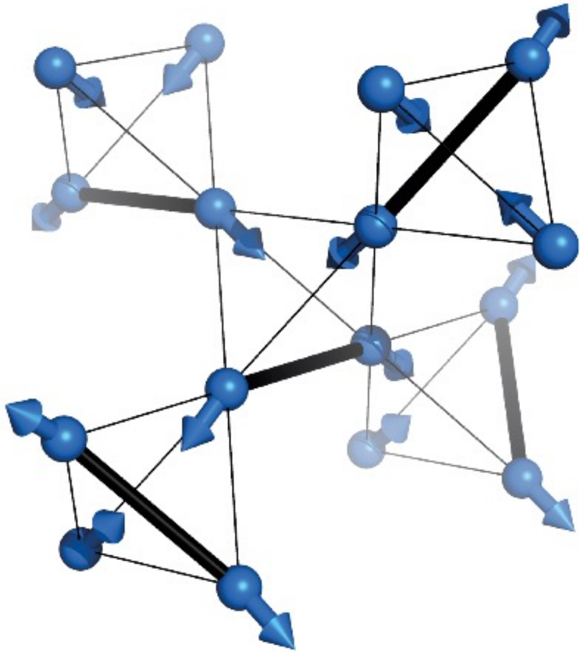


Reciprocal space

structure refinement

interaction modelling

Model**

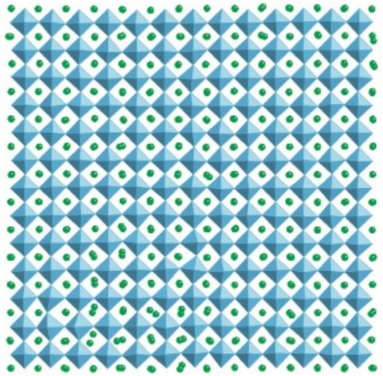


Real space

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

How can we analyze diffuse scattering data?

Big-box refinement

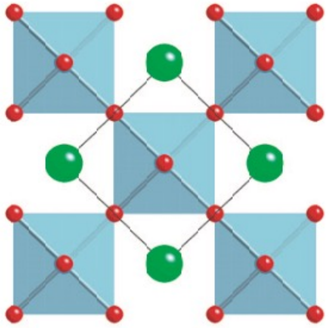


Many unit cells
Model long-range
and short-range order

e.g. reverse Monte Carlo

structure refinement

Small-box refinement

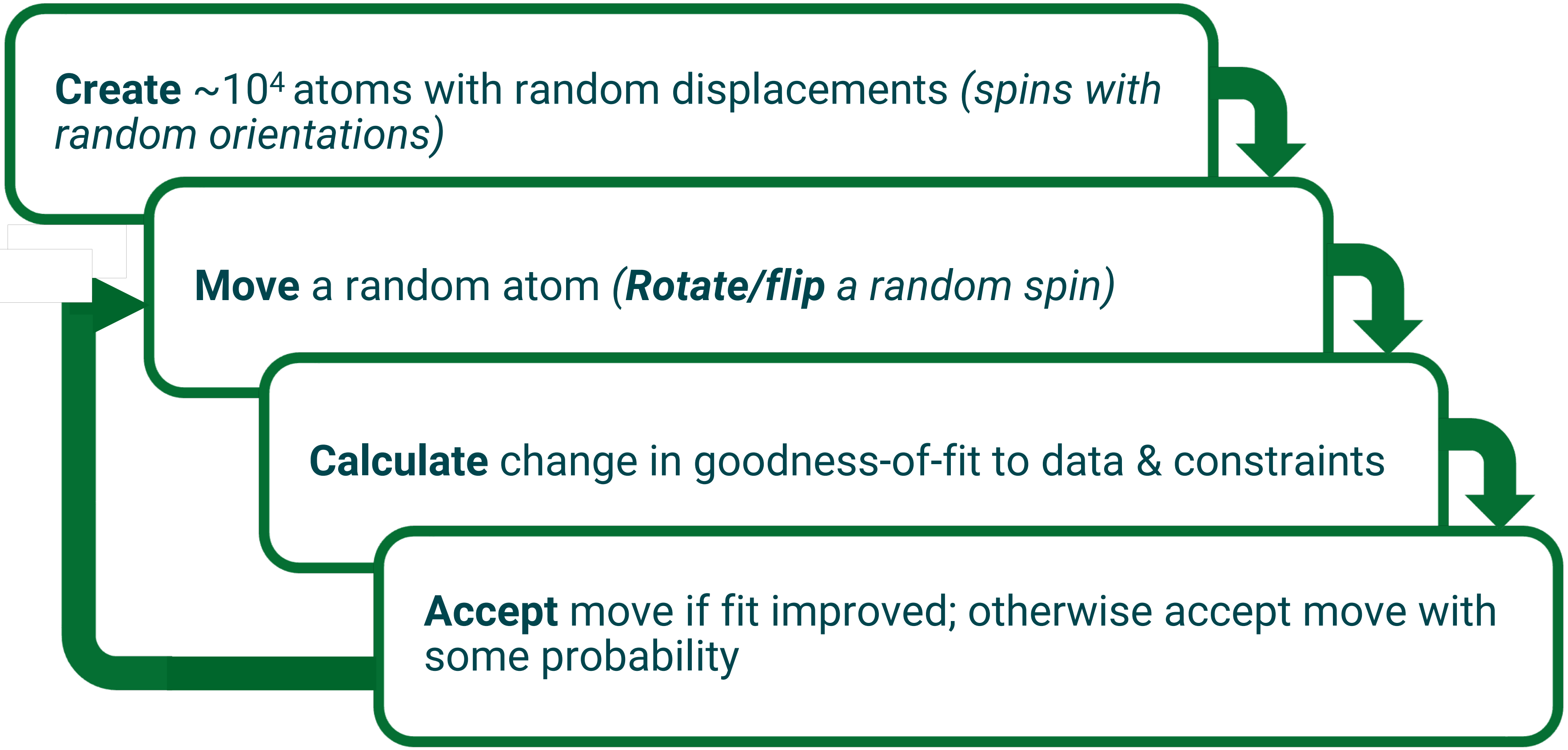


Single unit cell
Model short-range order
→ *Kate Page's lecture*

e.g. PDF analysis

Images: Hui *et al.*, *JPCM* **17**, S111 (2005)

Reverse Monte Carlo (RMC) method

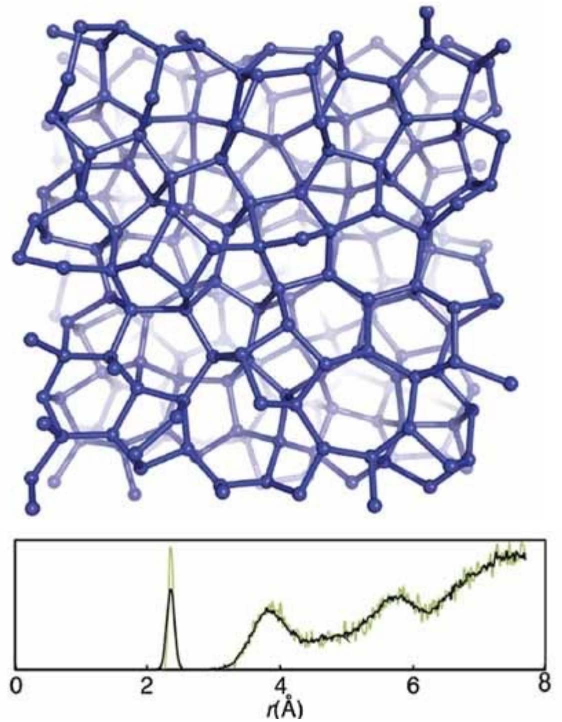


RMCProfile software: Tucker *et al.*, *JPCM* **19,** 335218 (2007)
Spinvert software: Paddison, Stewart, Goodwin *JPCM* **25,** 454220 (2013). **www.joepaddison.com/software**
RMCDiscord software: Morgan *et al.*, *J. Appl. Cryst.* **54,** 1867 (2021)

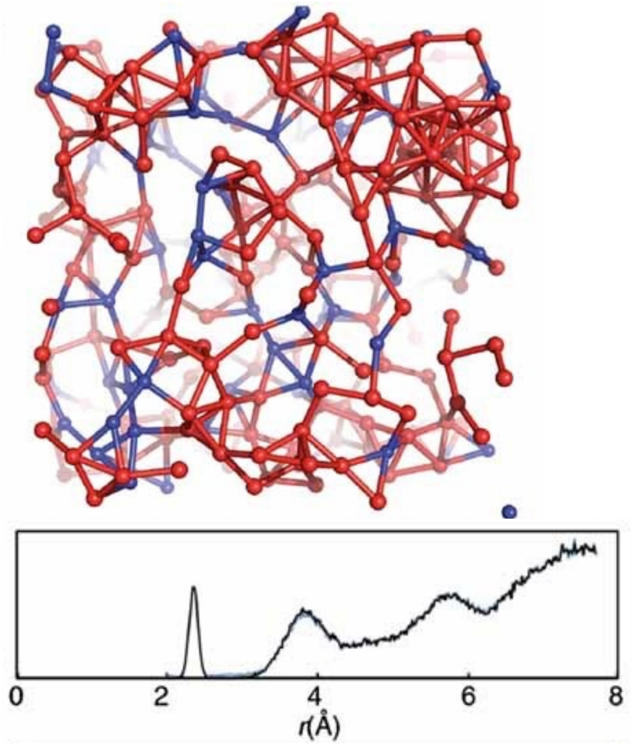
Amorphous example: a-Si

- RMC produces **most disordered** configuration consistent with data
  → constraints are often essential
- Software such as RMCProfile facilitates constrained RMC

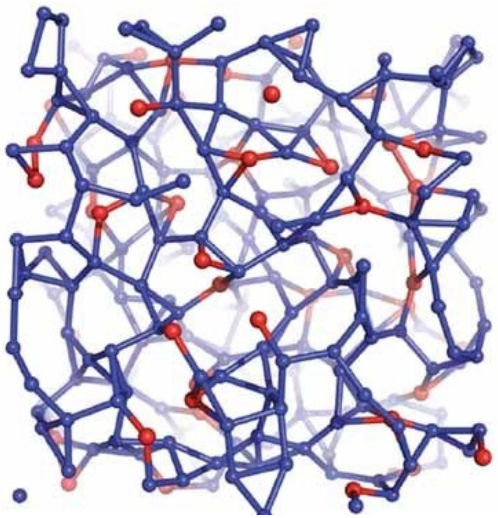
Accurate model



RMC



RMC + invariant-environment constraint



Cliffe & Goodwin, *Phys Stat Sol B* **250**, 949 (2013)
RMCProfile software: Tucker *et al.*, *JPCM* **19,** 335218 (2007)

Inorganic example: Relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$

- Local Pb displacements are correlated to form polar nano-regions
- Dense packing of nano-regions with different polarization directions

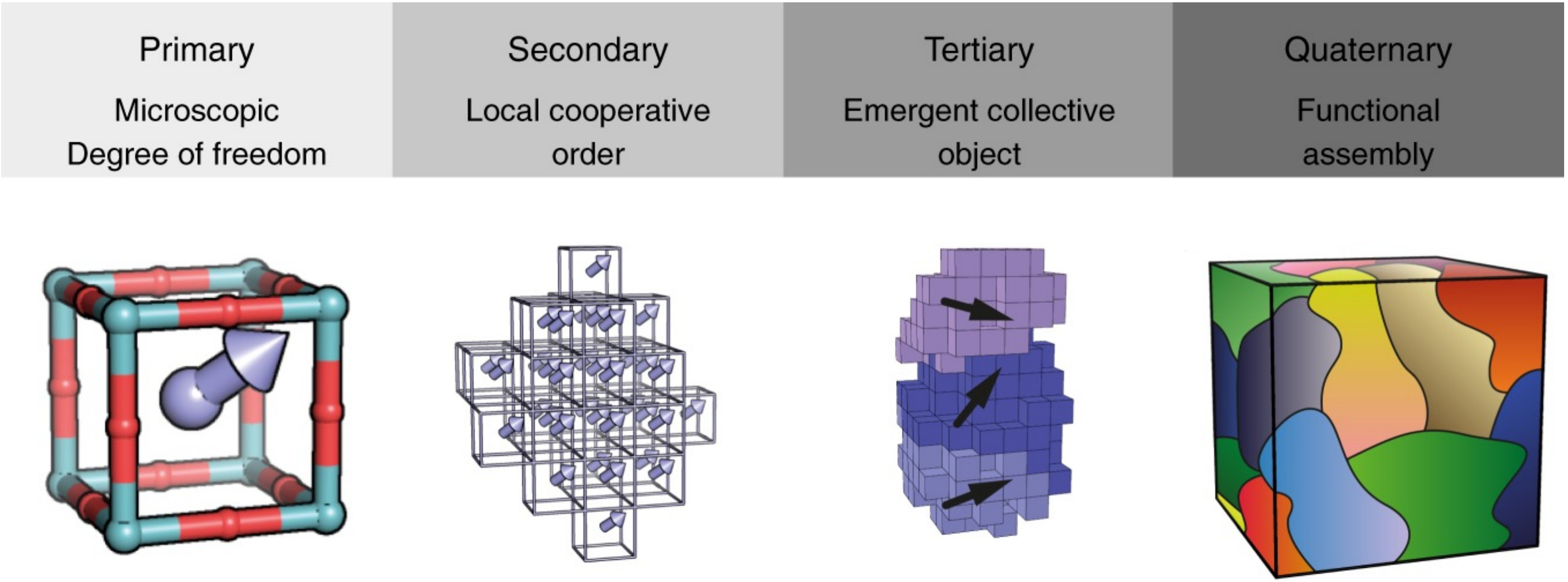
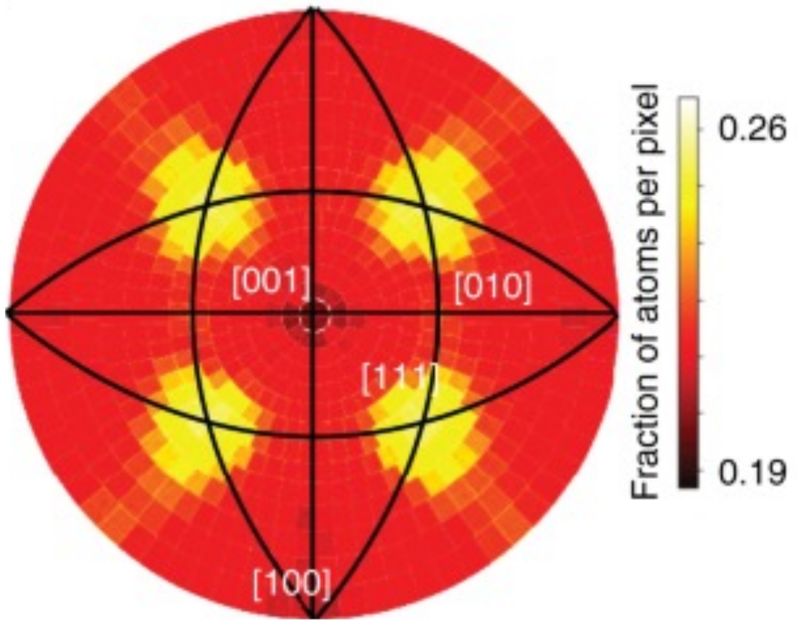
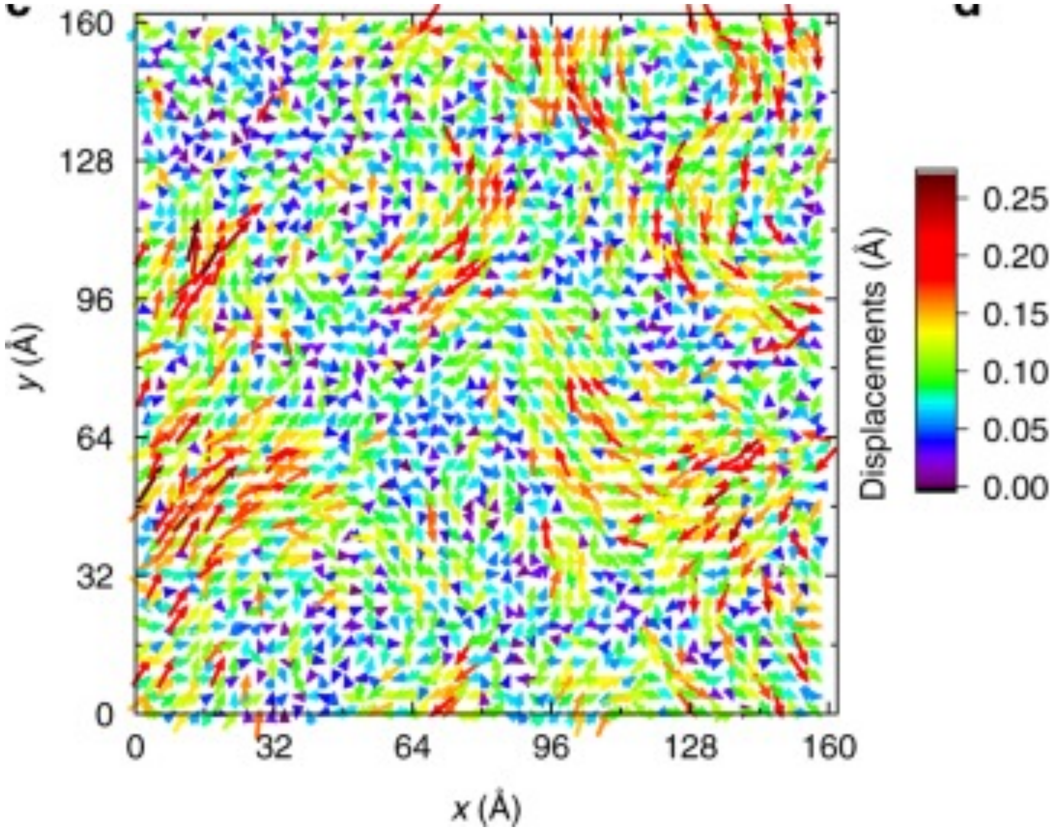


Image: Goodwin, *Nat. Commun.* **10**, 4461 (2019)

Inorganic example: Relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$

- RMC refinement to multiple data sets (neutron, X-ray, EXAFS) provides quantitative model of local structure between 1—100 Å

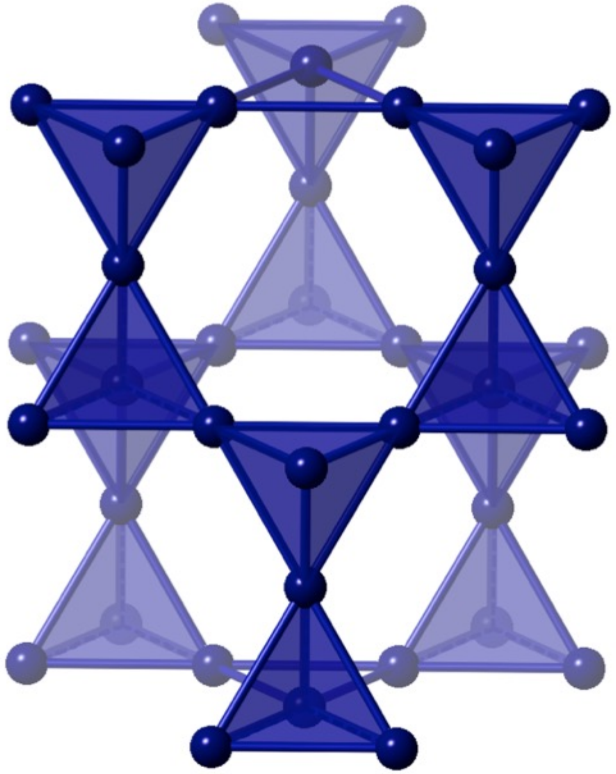




Eremenko *et al.*, *Nat. Commun.* **10,** 2978 (2019)

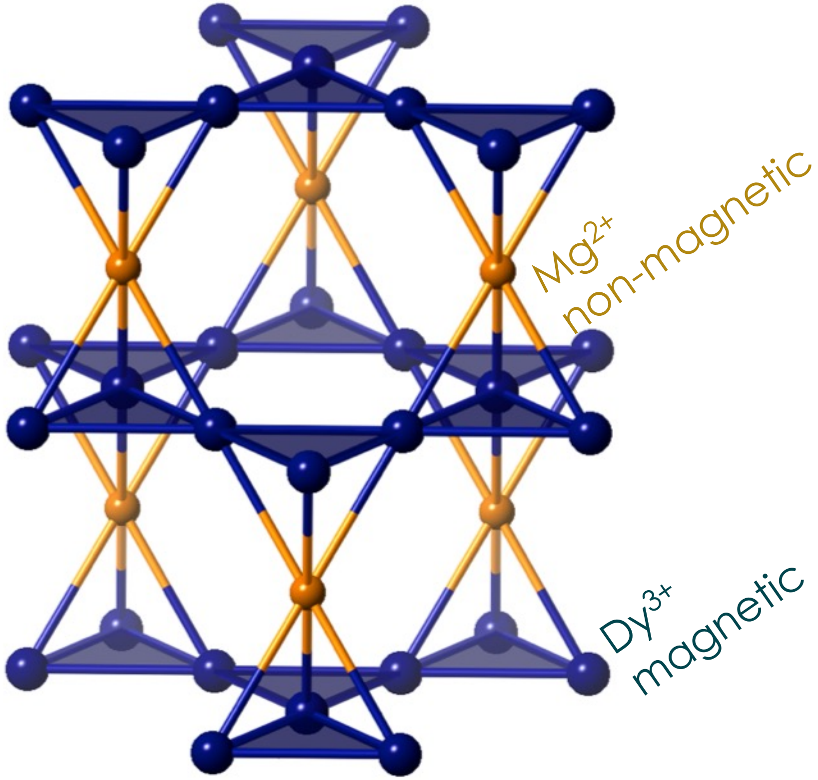
Magnetic example: Kagome ice $Dy_3Mg_2Sb_3O_{14}$

Pyrochlore $Dy_2Ti_2O_7$



Space group *Fd*–3*m*

Kagome $Dy_3Mg_2Sb_3O_{14}$

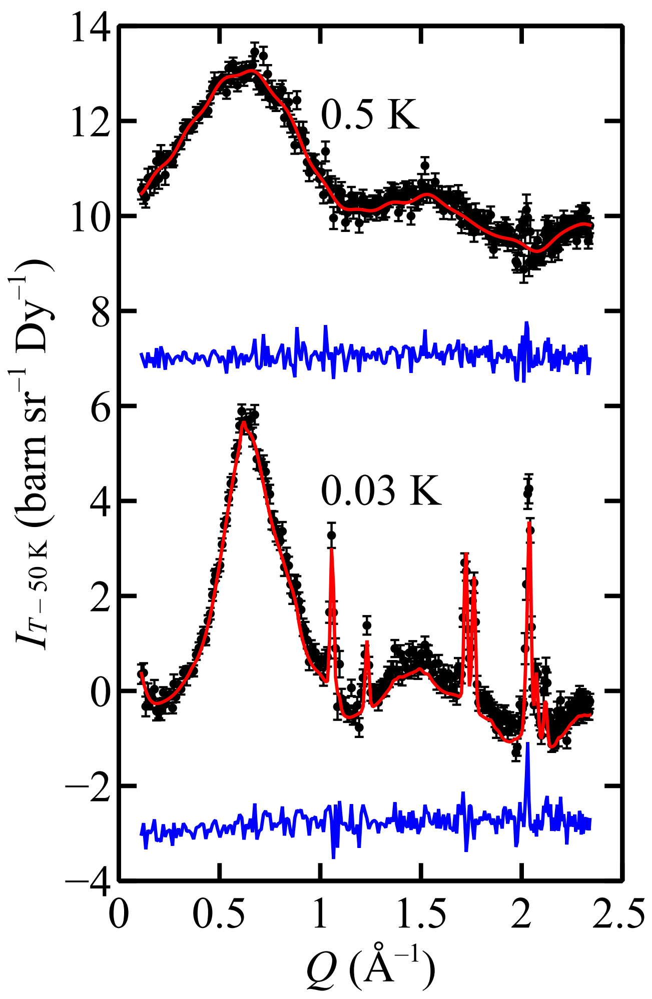


Space group *R*–3*m*

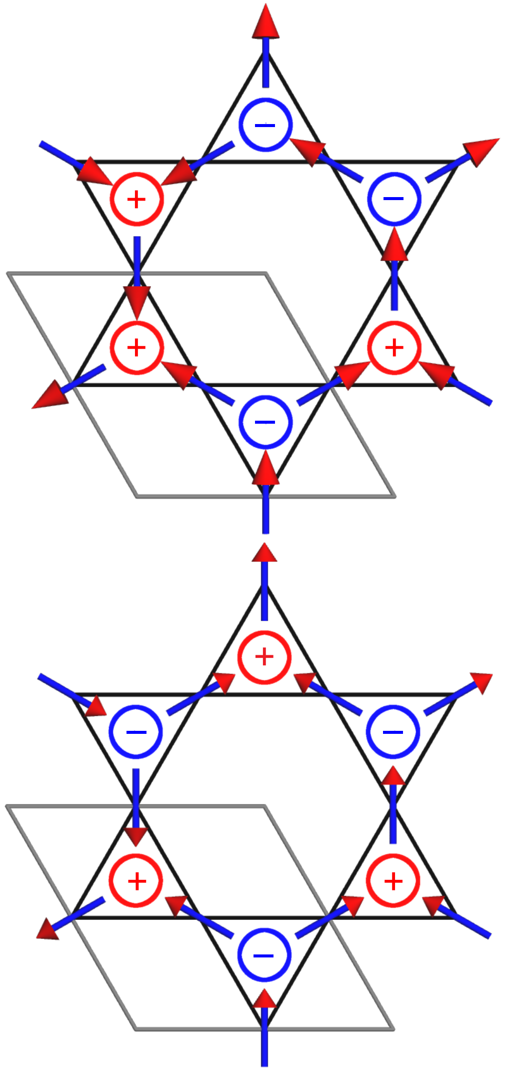
Sanders *et al.*, *J. Mater. Chem. C* **4**, 541–550 (2016)

Magnetic example: Kagome ice $Dy_3Mg_2Sb_3O_{14}$

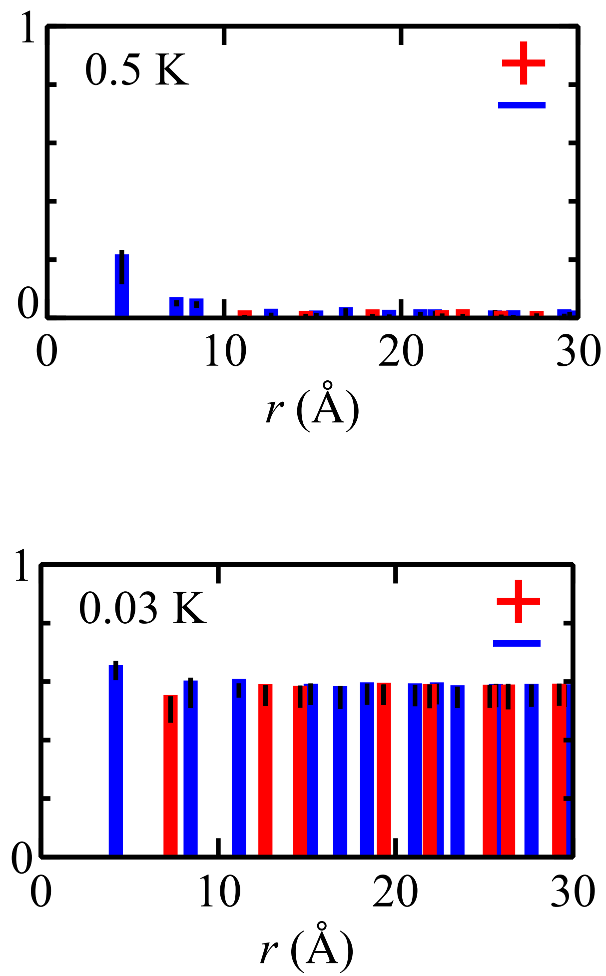
Diffuse scattering



Local magnetic structure



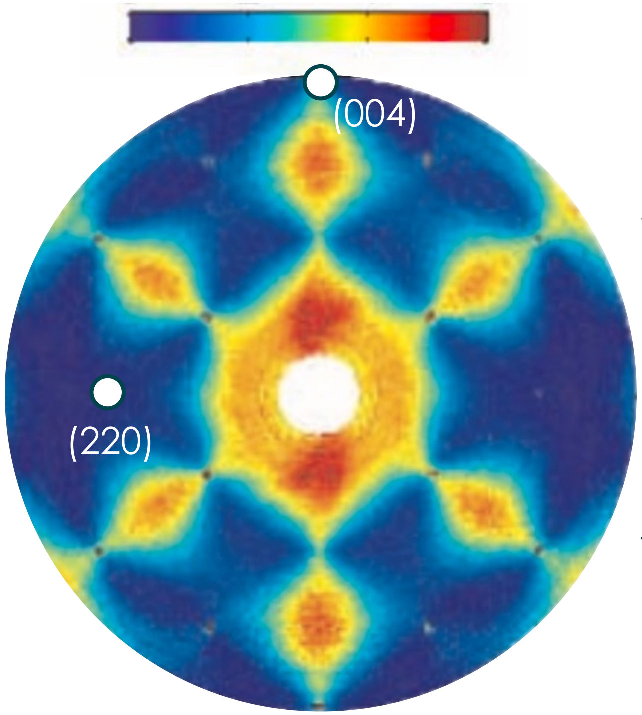
“Emergent charge” correlations



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

How can we analyze diffuse scattering data?

Data*

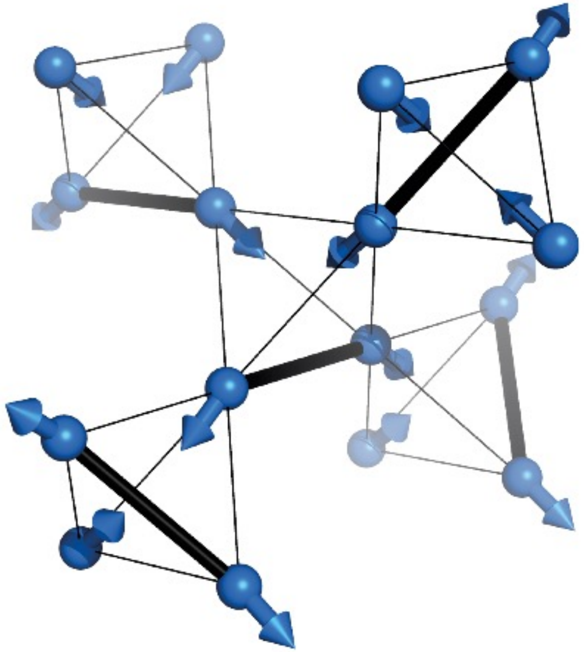


Reciprocal space

structure refinement

interaction modelling

Model**



Real space

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

Interaction refinement

Define Hamiltonian and guess interaction values

$$H = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j$$

Calculate diffuse scattering (e.g. using field theory or Monte Carlo simulations)

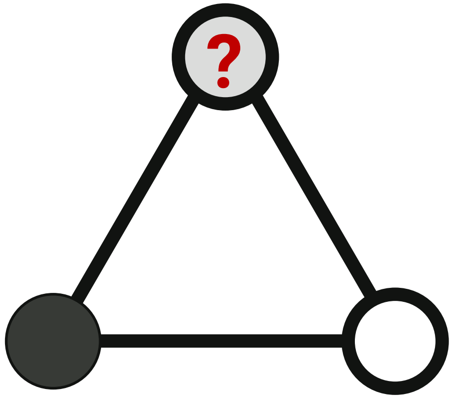
Send goodness-of-fit to least-squares optimizer

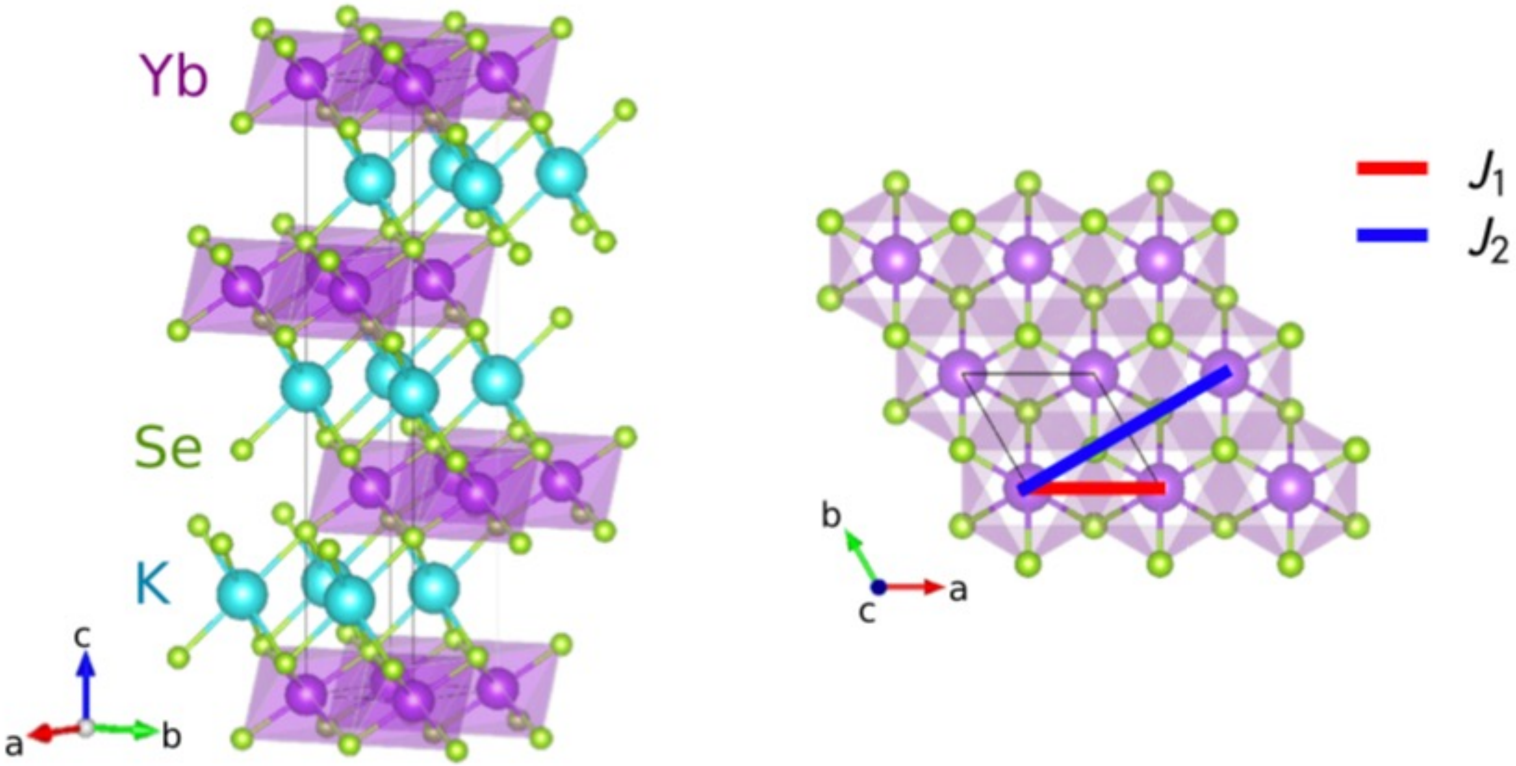
Receive new values of interactions from optimizer

Spinteract software: Paddison, *J Phys Cond Matt* **35,** 495802 (2023). **www.joepaddison.com/software**
Sunny software: Dahlbom *et al., arXiv:2501.13095* (2025). **https://github.com/SunnySuite/Sunny.jl**

Magnetic example: Spin-liquid candidate $KYbSe_2$

- Magnetic Yb^{3+} with effective spin-½ occupy a triangular lattice
- Antiferromagnetic interactions → frustration

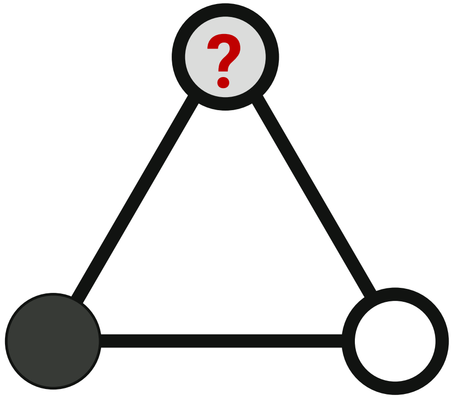


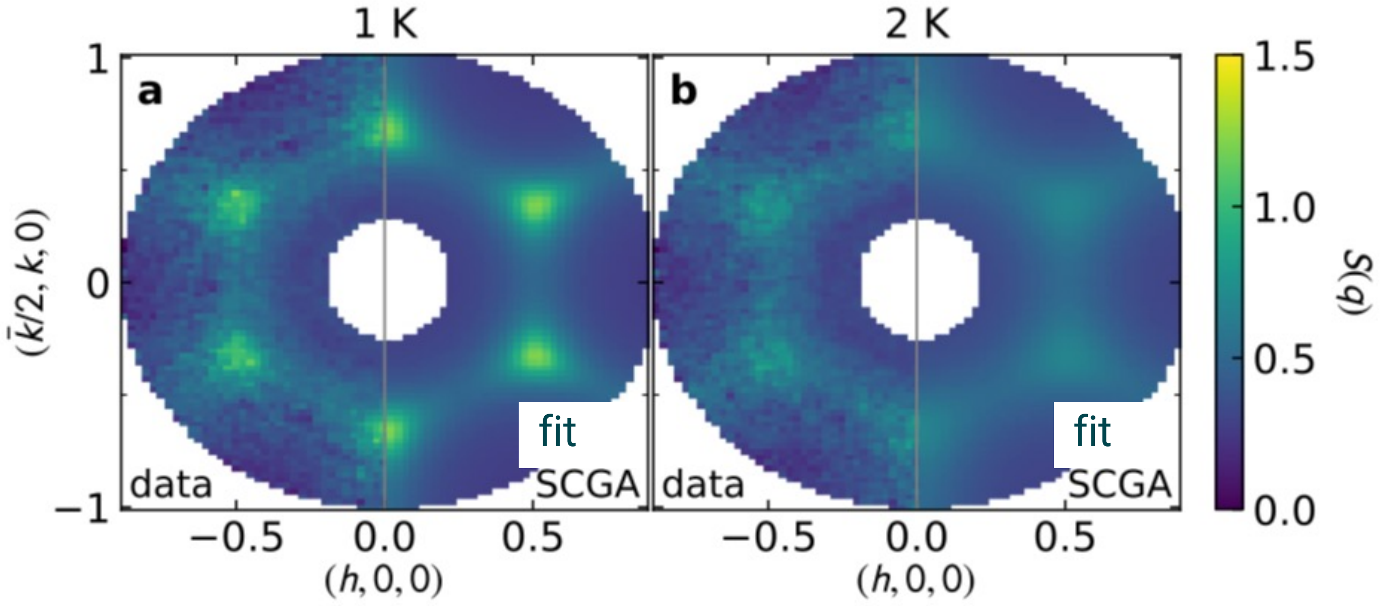


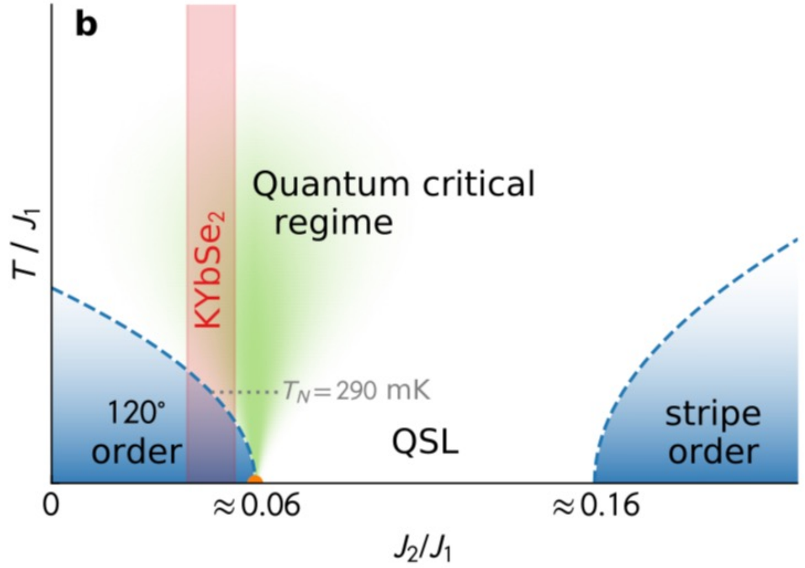
Scheie *et al.*, *Nat. Phys.* **20**, 74 (2024)

Magnetic example: Spin-liquid candidate $KYbSe_2$

- Neutron data from CNCS @ ORNL
- Fitted interactions place material near quantum spin-liquid phase



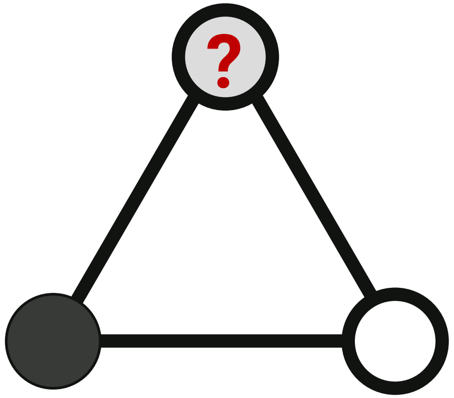




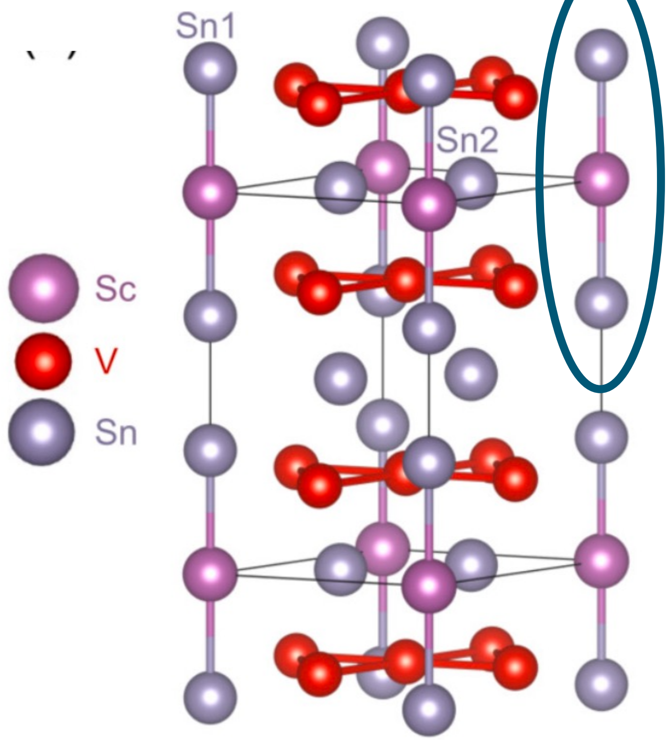
Scheie *et al.*, *Nat. Phys.* **20**, 74 (2024)

Intermetallic example: Kagome metal ScV_6Sn_6

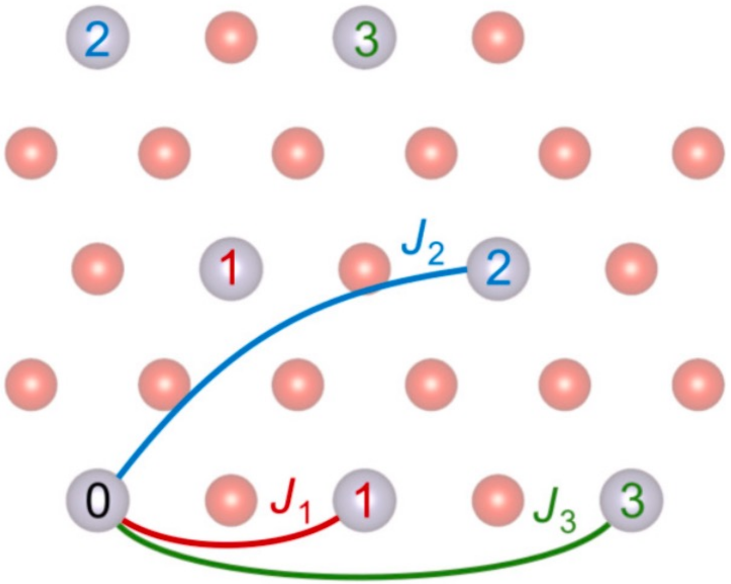
- Trimers of **Sn-Sc-Sn** occupy a triangular lattice
- Each trimer occupies one of two positions along **z** → frustration?



Sn-Sc-Sn trimer



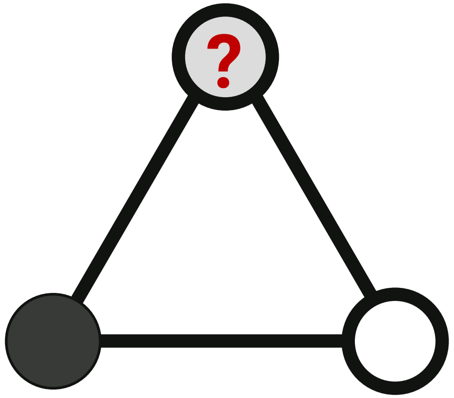
Trimer-trimer interactions

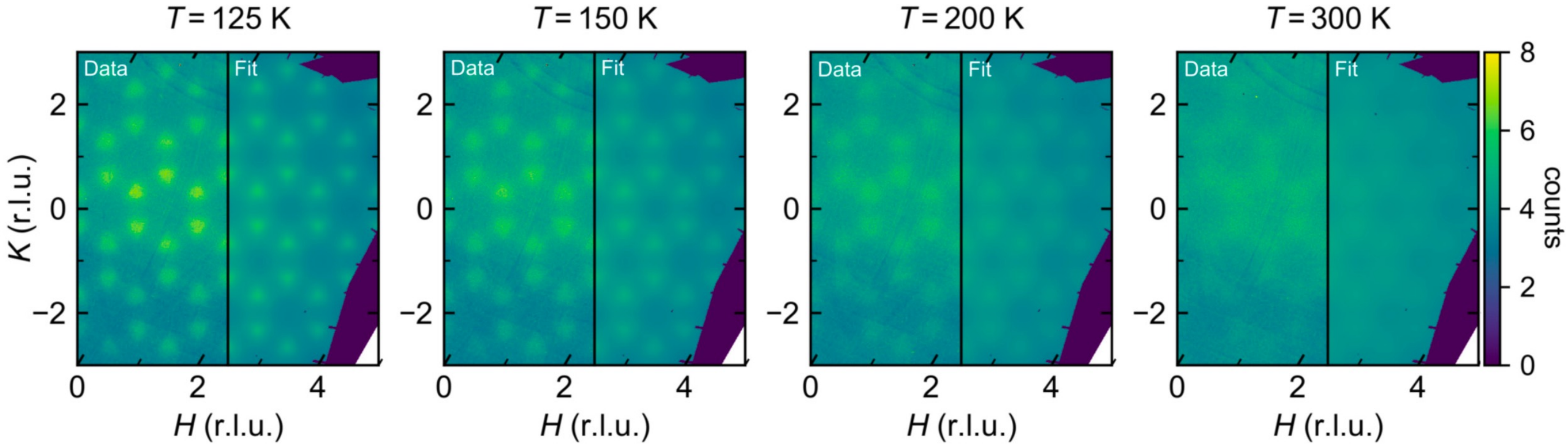


Gomez Alvarado *et al.*, *PRB* **110**, L140304 (2024)

Intermetallic example: Kagome metal ScV_6Sn_6

- Frustrated antiferro interactions between trimers explain temperature and **Q**-dependence of diffuse scattering

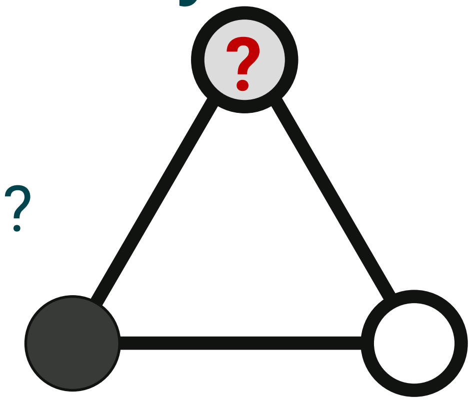




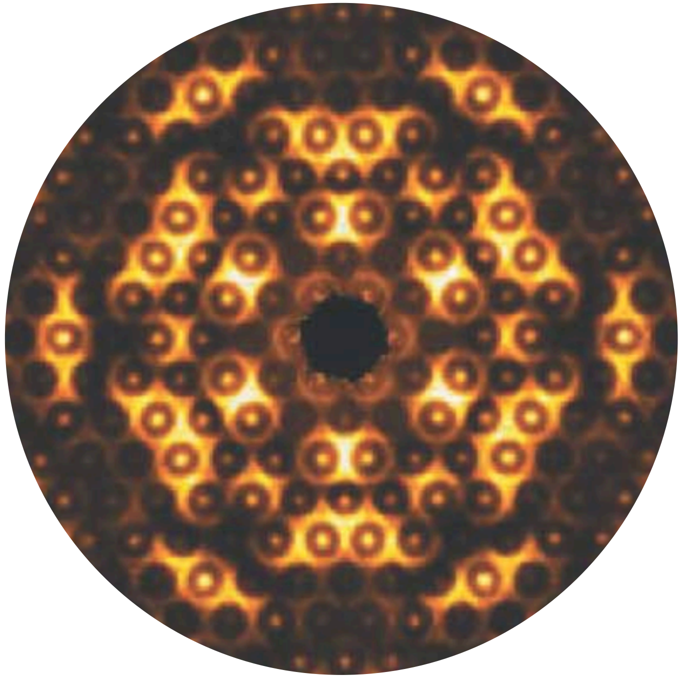
Gomez Alvarado *et al.*, *PRB* **110**, L140304 (2024)

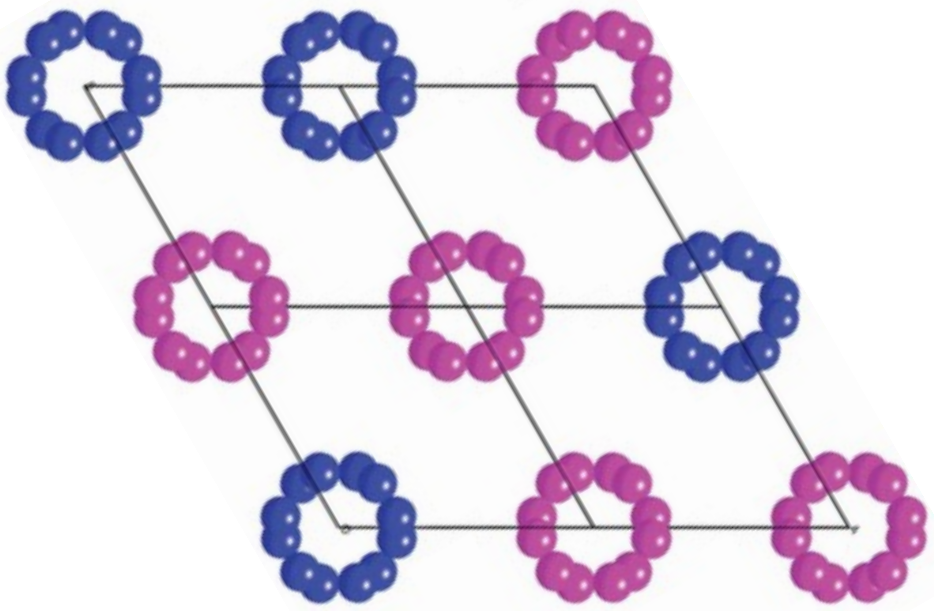
Macromolecular example: Gag protein from Feline Foamy virus

- Protein molecules occupy a triangular lattice
- Each molecule occupies one of two positions along **z** → frustration?



X-ray diffuse data*.

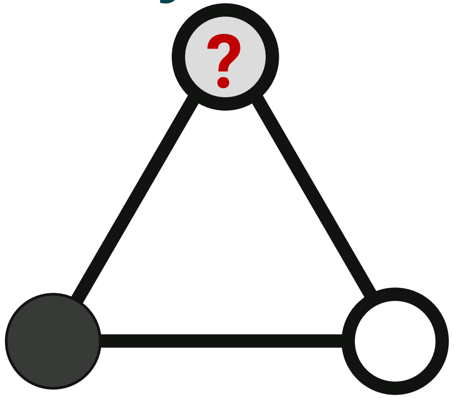




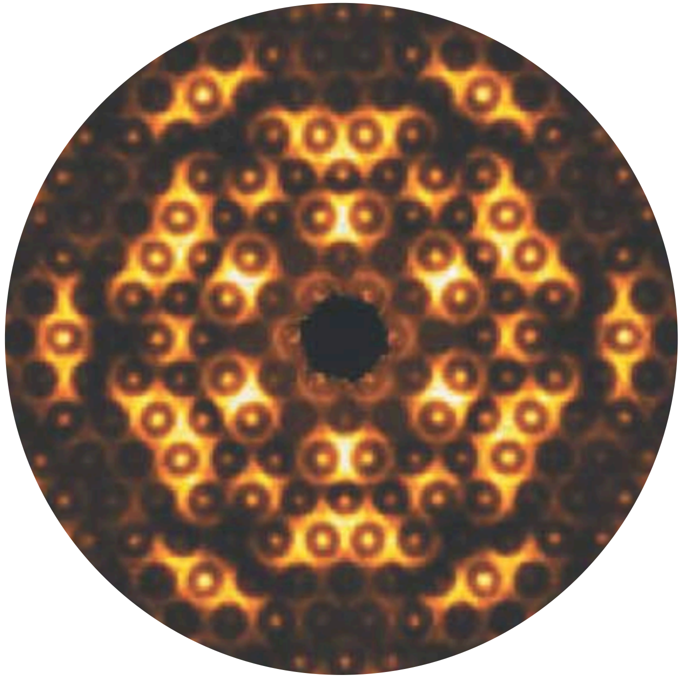
*Welberry, Heerdegen, Goldstone & Taylor, *Acta Cryst.* B **67**, 516 (2011)

Macromolecular example: Gag protein from Feline Foamy virus

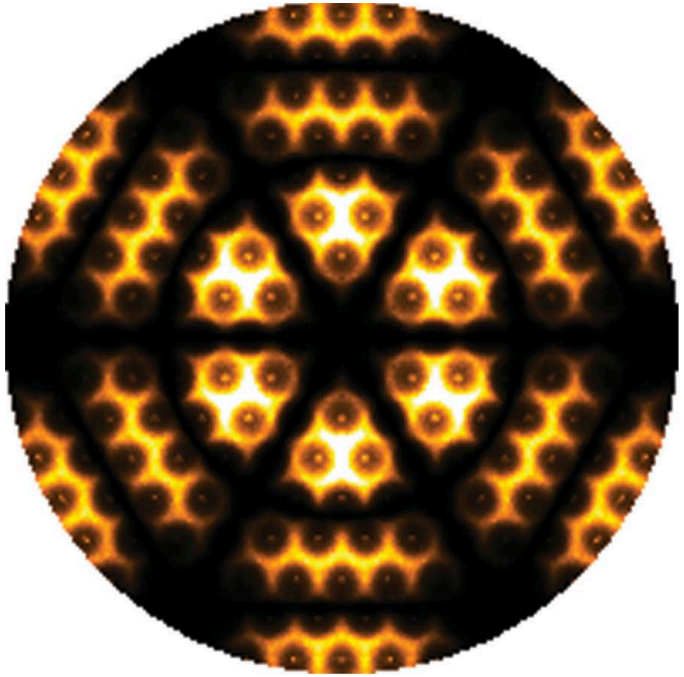
- Frustrated antiferro interactions between molecules explain **Q**-dependence of diffuse scattering



X-ray diffuse data*.



Model
Nearest + next-nearest neighbor



*Welberry, Heerdegen, Goldstone & Taylor, *Acta Cryst.* B **67**, 516 (2011)

Summary

- Diffuse scattering arises from **correlated disorder**
  - Disordered species can be atoms, spins, molecules, or collective objects
- Instruments at SNS and HFIR can measure diffuse scattering accurately
  - Powder and single-crystal data both information-rich
- Lots of useful software, much of it co-developed at ORNL
  - **RMCProfile**: Matt Tucker ***tuckermg@ornl.gov***, Yuanpeng Zhang ***zhangy@ornl.gov***
  - **RMCDiscord:** Zach Morgan ***morganzj@ornl.gov***
  - **Spinvert & Spinteract:** Joe Paddison ***paddisonja@ornl.gov***
  - **Su(n)ny:** David Dahlbom ***dahlbomda@ornl.gov***
  - **Discus:** Thomas Proffen ***tproffen@ornl.gov***
- Don't hesitate to contact instrument scientists or developers!

Email: paddisonja@ornl.gov