Magnetic Neutron Scattering

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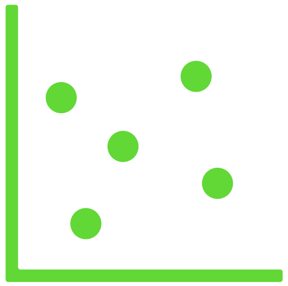
2019 Neutron and X-ray Scattering Summer School Lecture
Oak Ridge National Lab

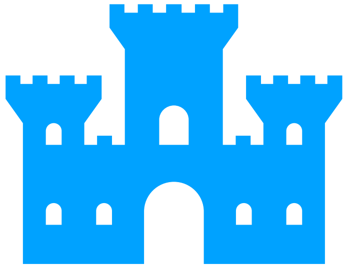
Outline

- Magnetism: Brief Overview

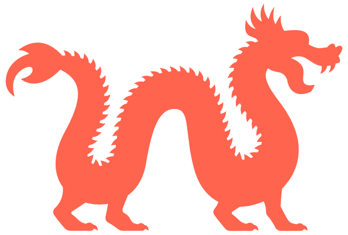
- Magnetic Neutron Scattering



- Elastic Scattering Examples



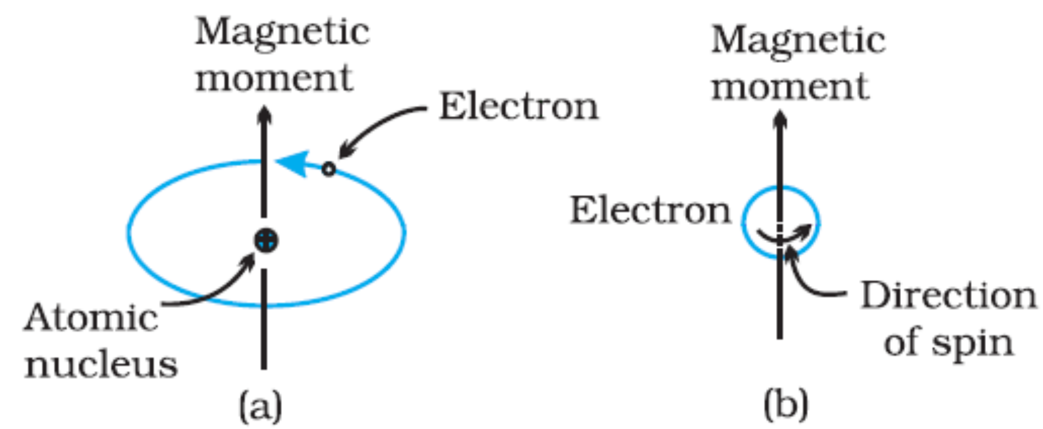
- Inelastic Scattering Examples



Magnetism: Brief Overview

Magnetic Moments from Electrons

- Electronic magnetic dipole moments arise from:



  - spin angular momentum, **S**

$$\boldsymbol{\mu}_{\mathrm{S}} = -g_{\mathrm{S}}\mu_{\mathrm{B}}\frac{\mathbf{S}}{\hbar}.$$

(g_S almost exactly 2)

  - orbital angular momentum, **L**

$$\boldsymbol{\mu}_{L} = -g_{\mathrm{L}}\mu_{\mathrm{B}}\frac{\mathbf{L}}{\hbar}.$$

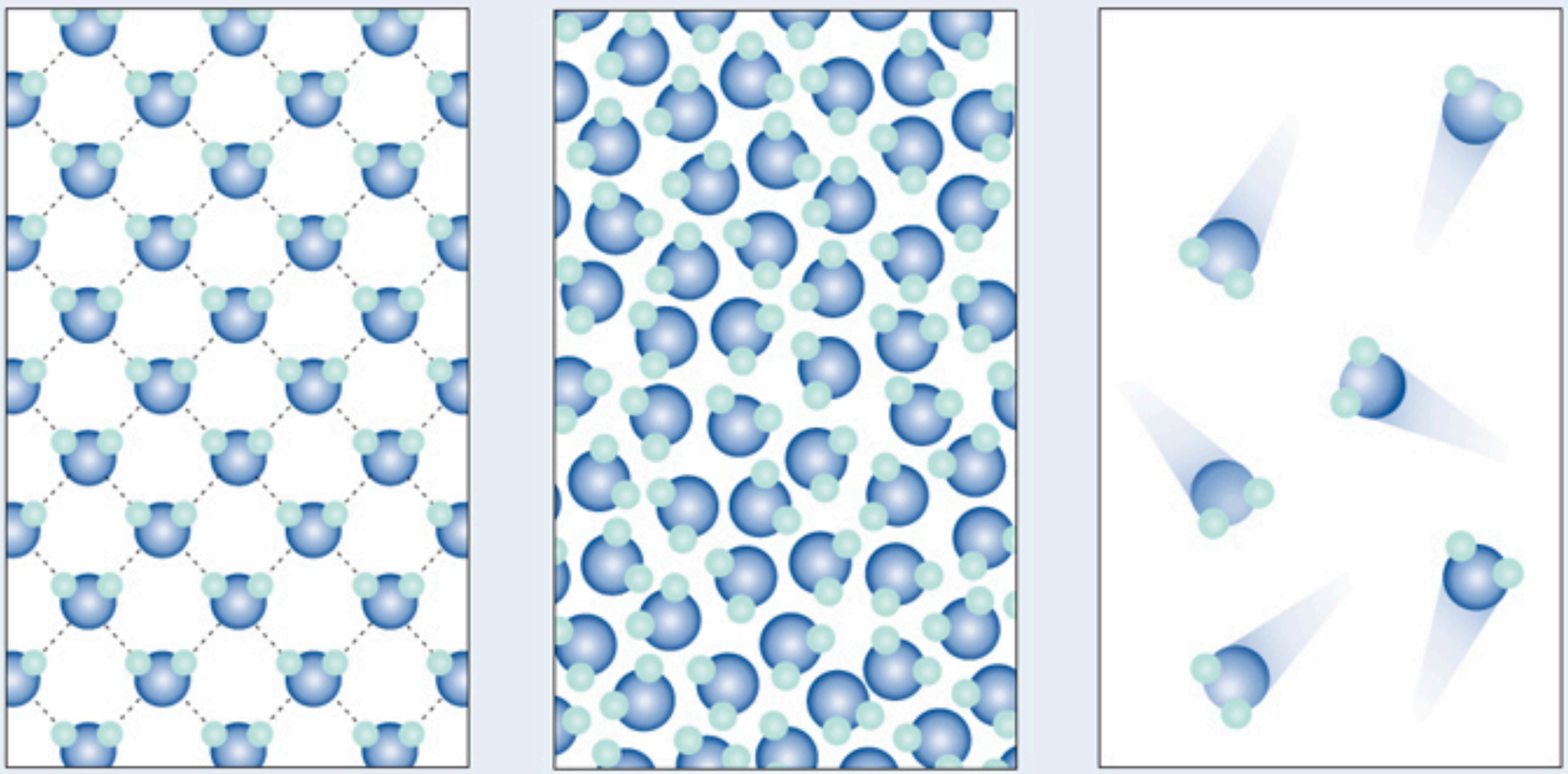
(g_L = 1)

Solid, Liquid, Gas

**Breaks "Translational Symmetry"
Atoms are fixed on average but can move coherently**

Free to move, correlated positions, can move coherently and incoherently

Free to move, uncorrelated positions, breaks no symmetry



Water molecules in solid ice.

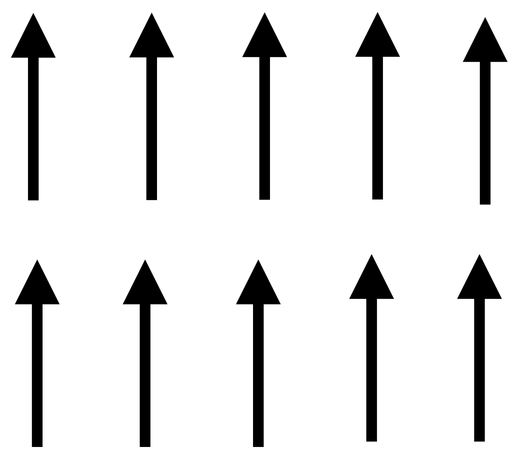
Water molecules in liquid water.

Water molecules in water vapour – a gas.

https://www.sciencelearn.org.nz/resources/607-solids-liquids-and-gases

Magnetic ordering

Ferromagnet



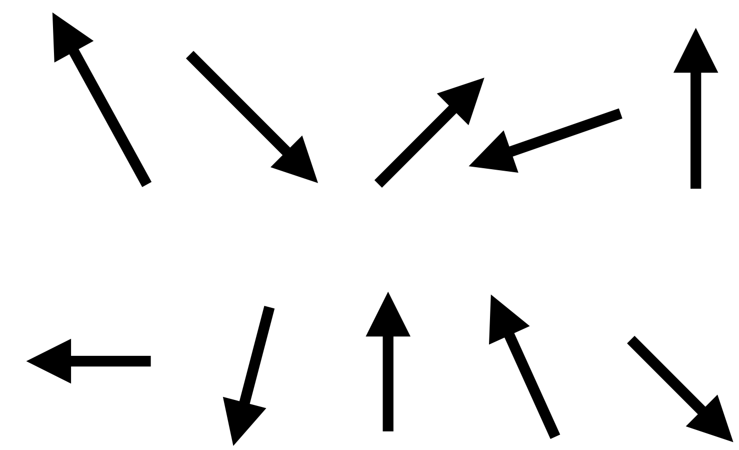
$T<T_c$

"Spin Solid"

Rotational symmetry Broken

coherent dynamics (spin waves)

Paramagnet

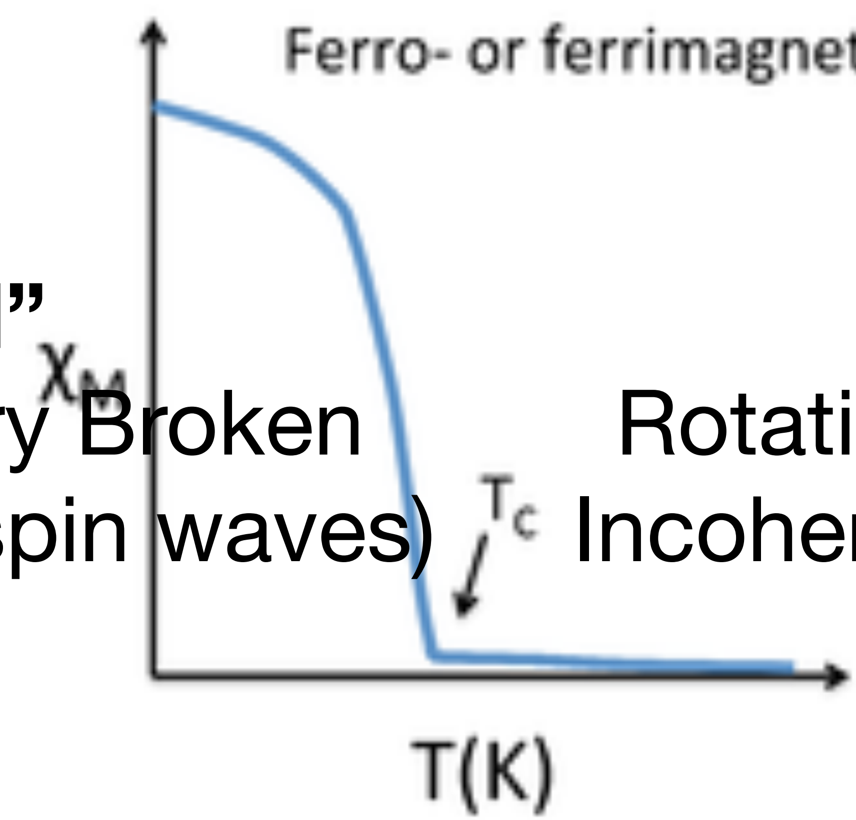


$T>T_c$

"Spin Gas"

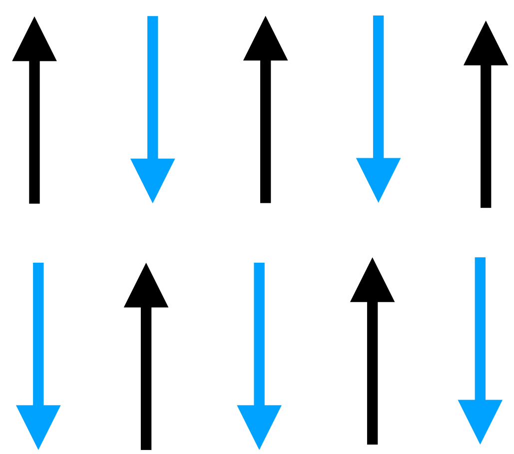
Rotational symmetry intact

Incoherent dynamics present



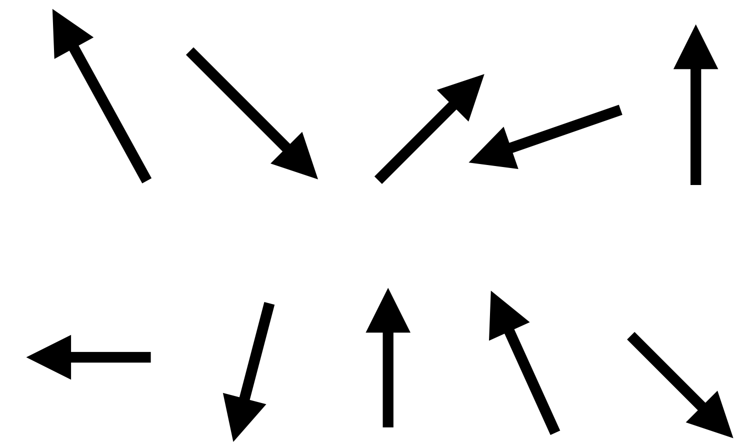
Magnetic ordering

Antiferromagnet

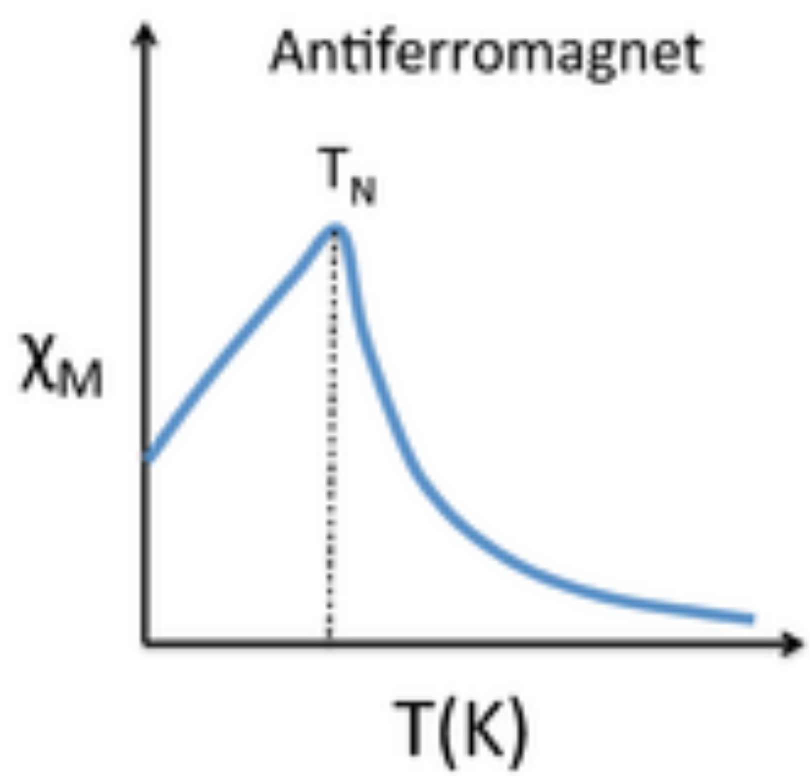


$T<T_N$

Paramagnet



$T>T_N$

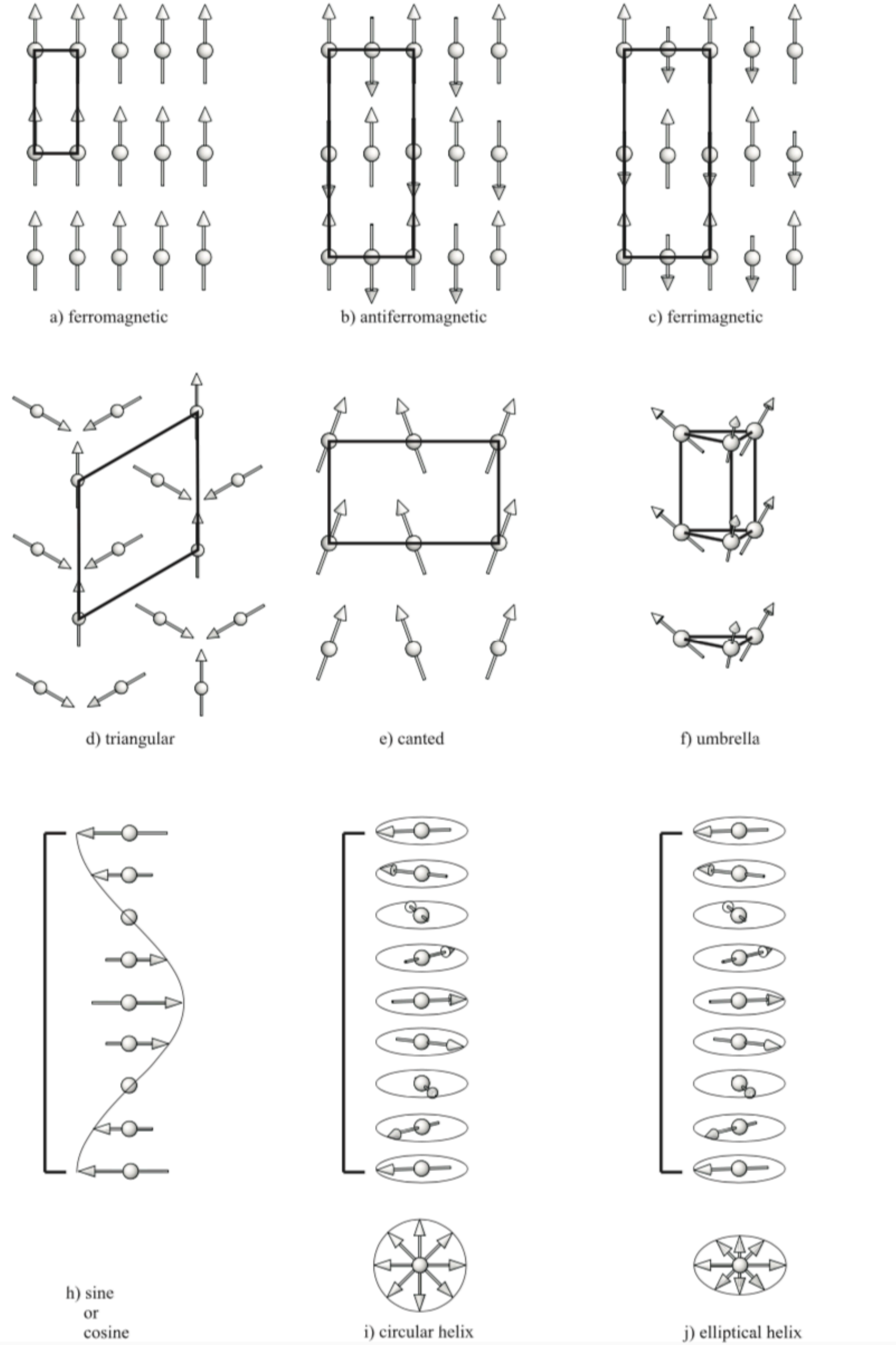


Other Types of Magnetic Order…

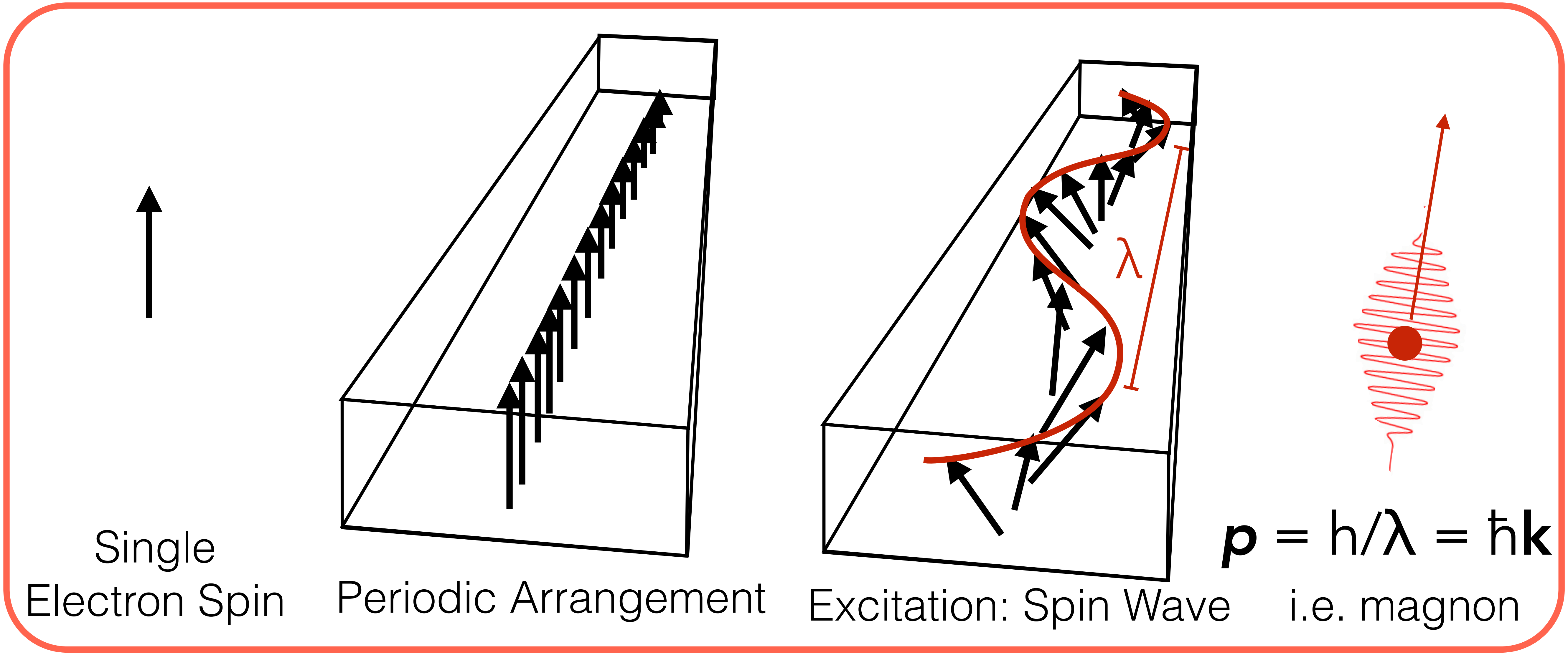
Magnetic structures and their determination using Group Theory

Andrew S. Wills*

These kinds of complicated structures can be identified using neutron scattering



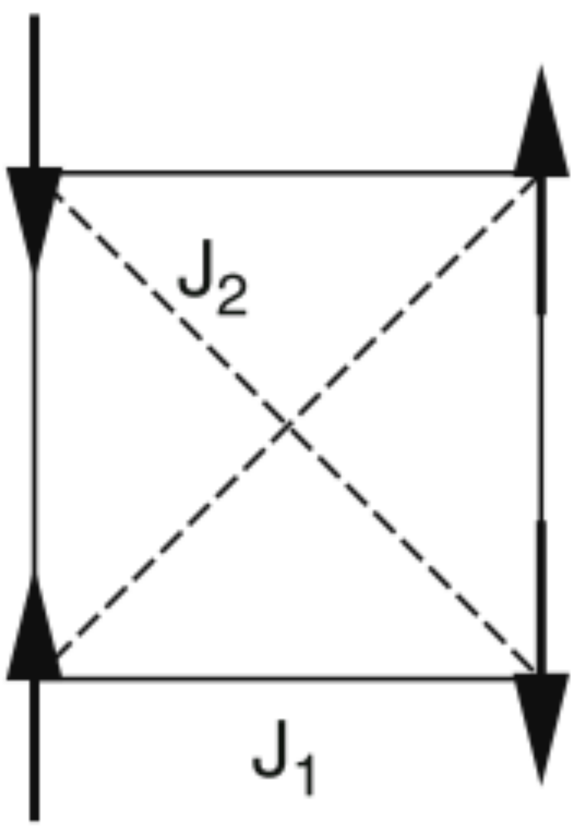
Spin Waves (magnons): emergent quasi-particles



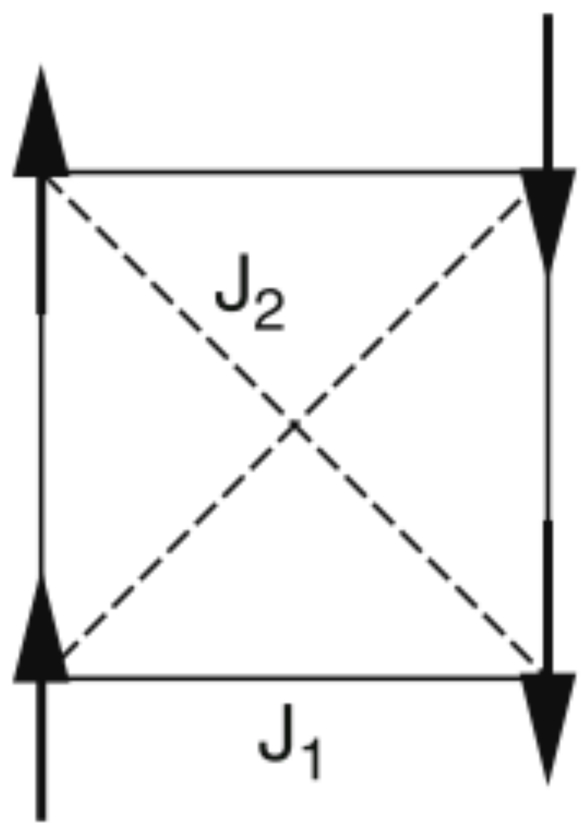
Using neutrons, we can understand the underlying interactions between spins by measuring spin wave dispersions

Example of a Magnetic Hamiltonian

$$H = J_1 \sum_{\langle i,j \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle k,l \rangle\rangle} S_k \cdot S_l$$



$2J_1 > J_2$



$2J_1 < J_2$

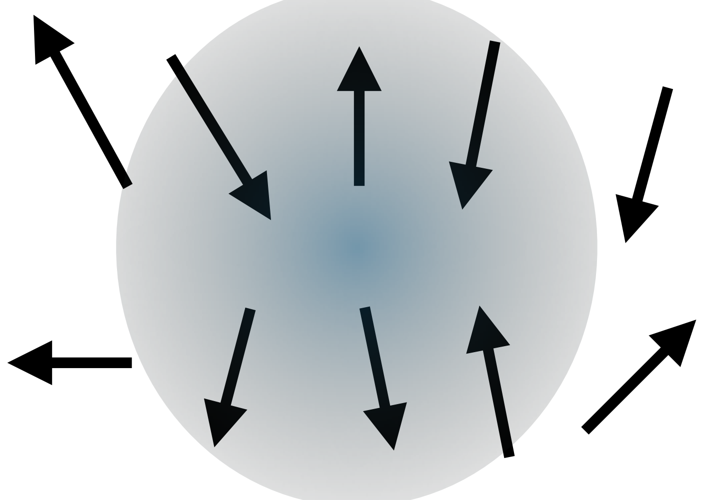
The exchange parameters (J_1, J_2) are like the "springs" between spins in analogy to the phonon models discussed by Bruce in the Previous lecture

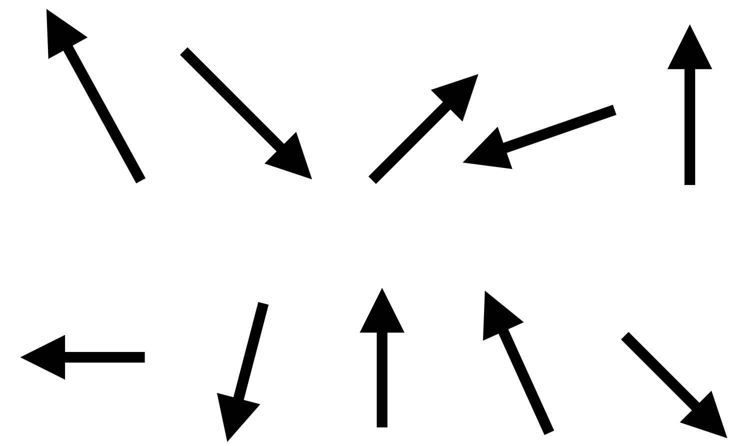
Spin liquid

Spin liquid

$2J_1 = J_2$?

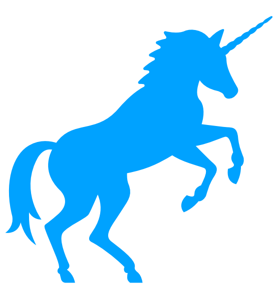
Paramagnet





$T<\theta_{CW}$

$T>\theta_{CW}$



"Spin liquid"

Rotational symmetry intact (like a paramagnet)

BUT spins are correlated over some region

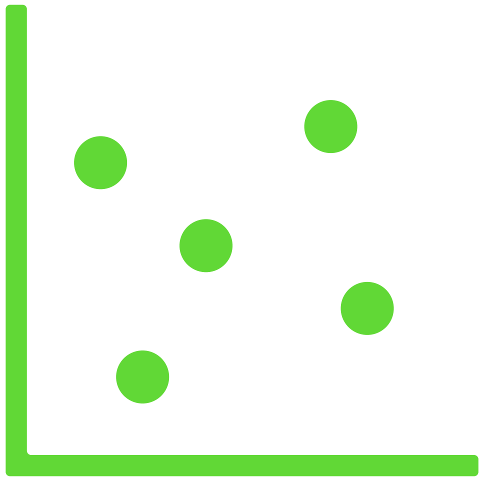
incoherent dynamics (*thermal* spin liquid)

or **coherent dynamics** (*quantum* spin liquid): Fractionalized excitations

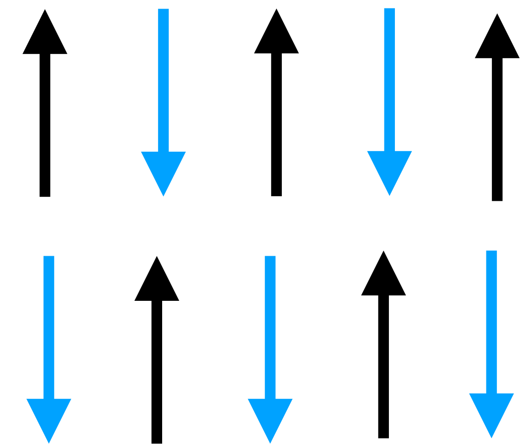
Magnetism is good for…

- **Technology, present and future**
  - magnetic storage (multiferroics next? Skyrmions?)
  - topological materials (protected edge states)
- **Fundamental inquiry**
  - what quantum phases are exist in a many body correlated spin system? (superconductivity, quantum spin liquids….)

Magnetic Neutron Scattering

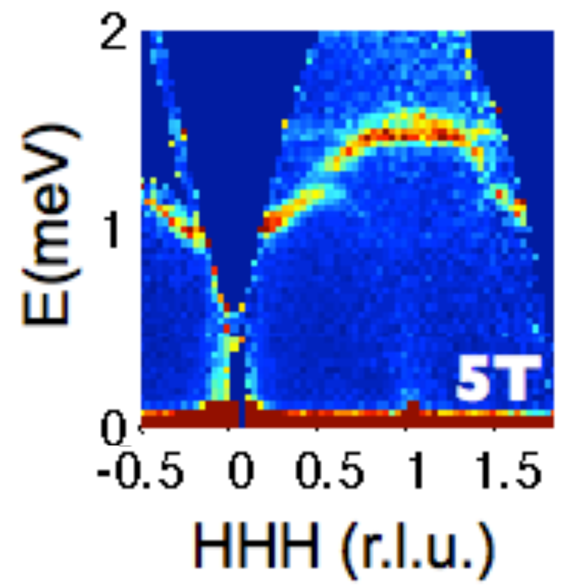


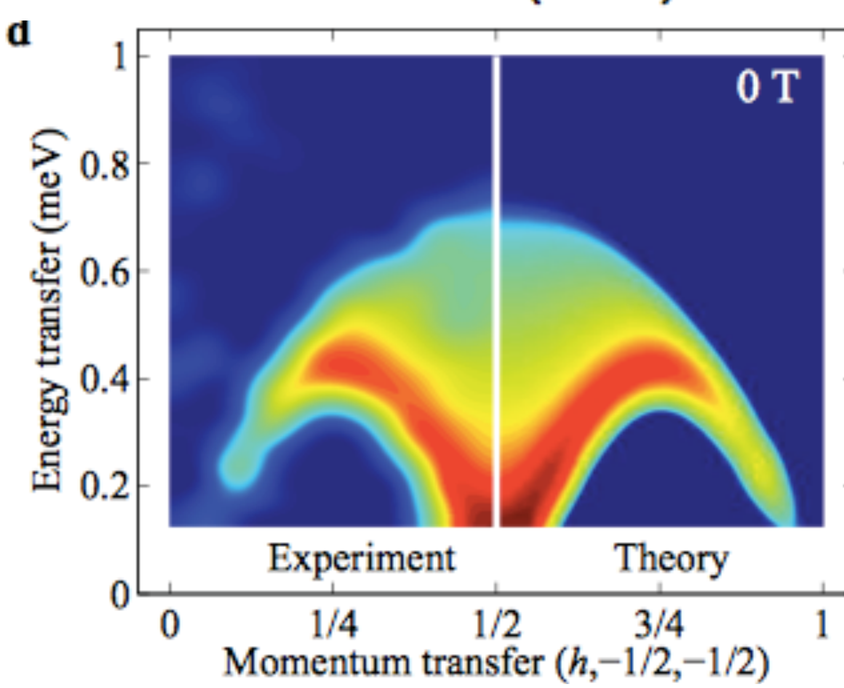
Neutron scattering is *essential* for the study of magnetic materials



Can measure (incomplete list!):

- Type of magnetic order (antiferromagnet, spiral, etc.)
- Spin wave dispersions - can use to get quantitative values of spin-spin interactions (“exchange interactions”)
- Presence of short range spin correlations through diffuse scattering
- Presence of exotic quasi-particles (fractionalization)





Magnetic Scattering

Elastic

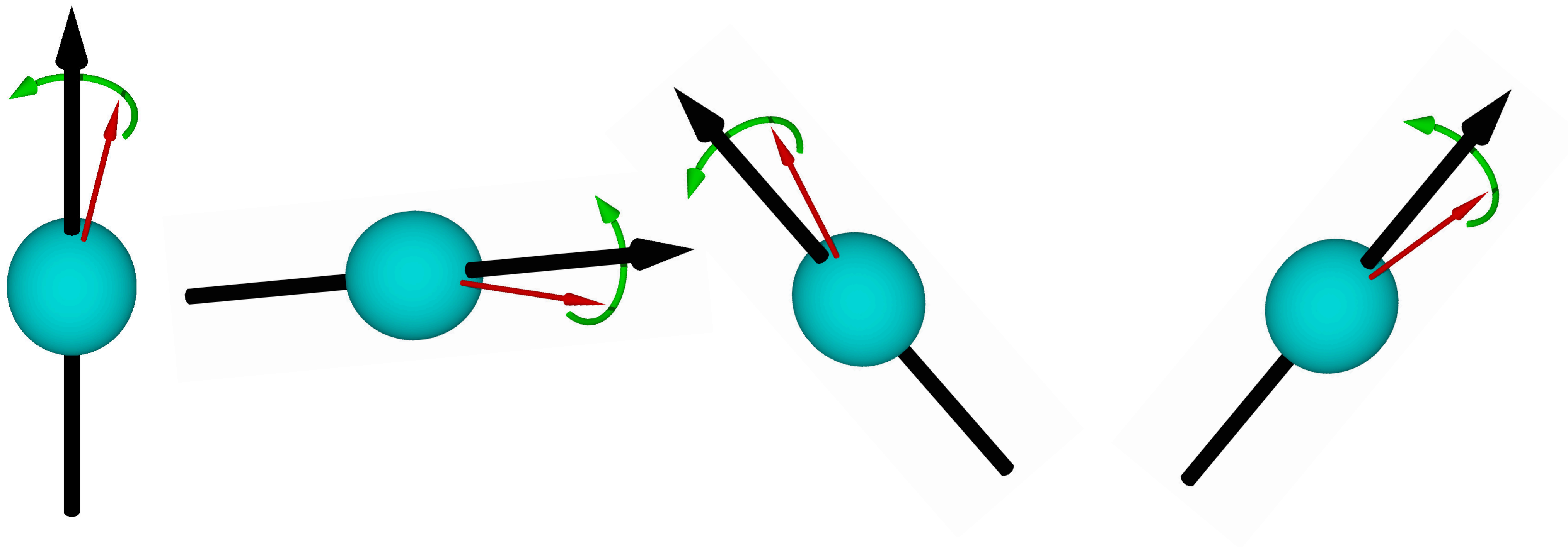
- Bragg peaks from Long Range Order
- Diffuse elastic scattering from short range correlations

Inelastic

- Spin waves
- Diffuse inelastic scattering
- Crystal Electric Field levels
- Exotic quasi-particles (possibly fractionalized?)

Quasi-Elastic

- Relaxational dynamics: Broad in energy but centered at $E = 0$



Magnetic cross section for ***unpolarized*** neutron beam

You can also learn more using spin-polarized neutrons … see Kathryn Krycka's lecture tomorrow

Interaction of neutron with unpaired electrons

- Neutrons are S=1/2 particles and carry a magnetic dipole moment, thus they are sensitive to magnetic potentials

$$\mu_n = -g_n \mu_N S_n$$

- Neutron scatters from the magnetic potential generated by electronic spin and orbital angular momentum

Table 2-1. Basic properties of a neutron (mainly in Gauss CGS units). σ_n denotes the neutron's angular momentum, $\mu_N = e\hbar/(2m_pc) = 5.0508 \cdot 10^{-24}$ erg/Gs is the nuclear magneton.

Electric charge	Spin $S_n = \sigma_n/\hbar$	Mass m_n (g)	m_nc^2/e (V)	Magnetic moment μ_n (erg/Gs)	Gyromagnetic ratio γ_n, $\mu_n = \gamma_n\sigma_n$ (s^{-1}/Gs)	g-factor g_n, $\mu_n = -g_n\mu_N S_n$	Lifetime (s)	Decay reaction
0	1/2	$1.675 \cdot 10^{-24}$	$0.94 \cdot 10^{9}$	$9.662 \cdot 10^{-24}$	$-1.832 \cdot 10^{4}$	3.826	887	$n \rightarrow p\, e^-\, \bar{\nu}_e$

Inelastic Magnetic Cross Section (proportional to measured intensity)

Magnetic form factor: suppresses magnetic intensity as Q increases

Polarization Factor: only sensitive to components perpendicular to Q

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}(\gamma r_0)^2 N(\frac{1}{2}gF(Q))^2 e^{-2W} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta)$$

$$\times \frac{1}{2\pi\hbar} \int dt\ e^{-i\omega t} \sum_{ll'} e^{i\vec{Q}\cdot(\vec{r_l} - \vec{r_{l'}})} \langle S_l^\alpha(0) S_{l'}^\beta(t) \rangle$$

Spin-Spin correlation function: what we are usually interested in

See Squires Eqn. 7.73

Magnetic Form Factor: F(Q)

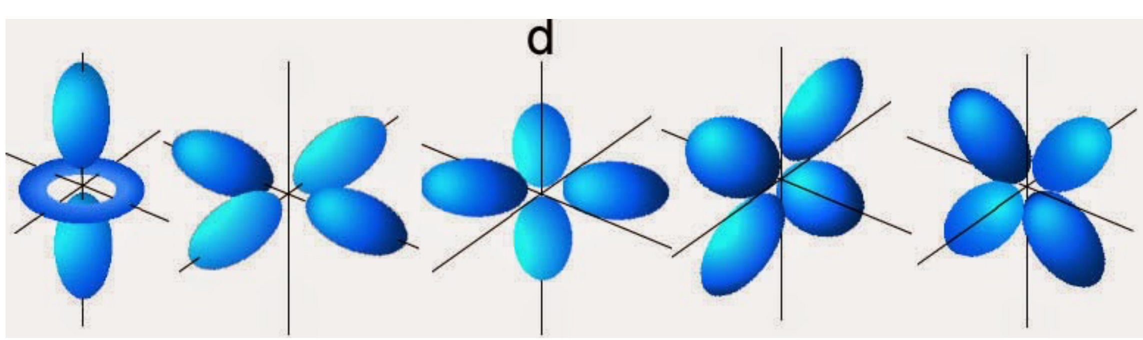
PHYSICAL REVIEW VOLUME 83, NUMBER 2 JULY 15, 1951

Neutron Diffraction by Paramagnetic and Antiferromagnetic Substances

C. G. SHULL, W. A. STRAUSER, AND E. O. WOLLAN
Oak Ridge National Laboratory, Oak Ridge, Tennessee
(Received March 2, 1951)

$$F(\vec{Q}) = \int S(\vec{r})e^{i\vec{Q}\cdot\vec{r}}d^3r$$

F(Q) is the Fourier transform of the spin distribution in real space



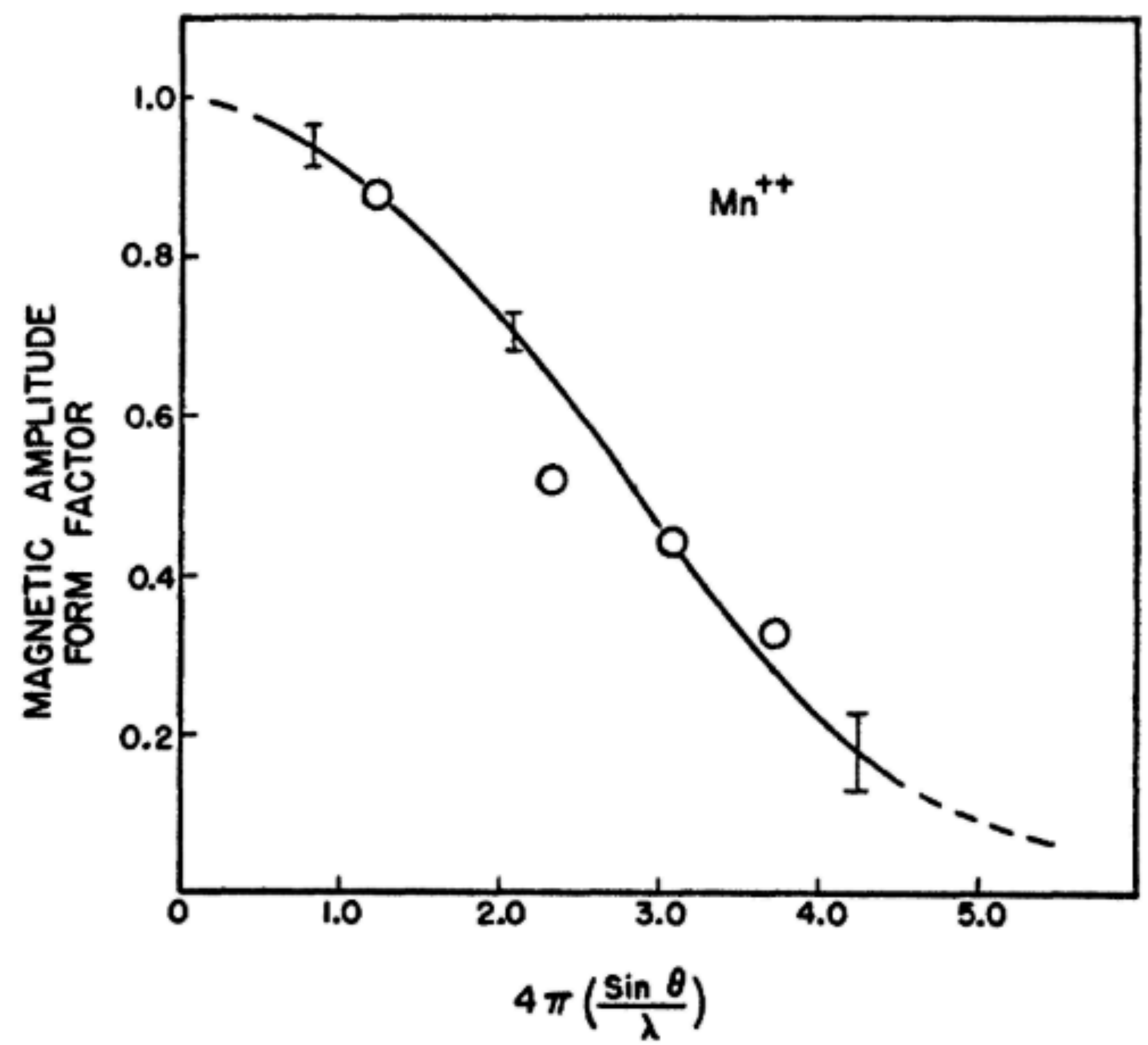


FIG. 2. Magnetic amplitude form factor for Mn^{++} ions. The curve is that obtained from paramagnetic diffuse scattering with estimated error as shown. The points represent values of the form factor obtained from the low temperature antiferromagnetic reflections of MnO.

Dynamic Structure Factor, S(Q,ω)

We often re-write the cross section from before as:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k}(\gamma r_0)^2 N(\frac{1}{2}gF(Q))^2 e^{-2W} \sum_{\alpha\beta}(\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \boxed{\mathcal{S}^{\alpha\beta}(Q,\omega)}$$

Encapsulates all the interesting stuff (i.e. the spin -spin correlations) into the **Dynamic Structure Factor,** *S*(Q,ω), which is the Fourier transform in space and time of the Pair Correlation Function

G(**r**,t) = Pairwise Correlations in Space and Time

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar}\int\int G(\mathbf{r},t)e^{i\mathbf{Q}\cdot\mathbf{r}}e^{-i\omega t}d^3r dt$$

Fluctuation Dissipation Theorem

General linear response susceptibility:

$$\chi(Q,\omega) = \chi'(Q,\omega) + \chi''(Q,\omega)$$

Energy absorbing response

Fluctuation Dissipation Theorem

$$S(Q,\omega) = \frac{1}{1-e^{-\beta\hbar\omega}}\frac{\chi''(Q,\omega)}{\pi(g\mu_B)^2}$$

With inelastic neutron scattering,
we are measuring the imaginary part of the susceptibility

Elastic Magnetic Scattering from a magnetically ordered crystal

$$\frac{d\sigma}{d\Omega}_{el} = (\gamma r_0)^2 N (\frac{1}{2} g F(Q))^2 e^{-2W} |\vec{\mathcal{F}}_{\perp}(Q)|^2$$

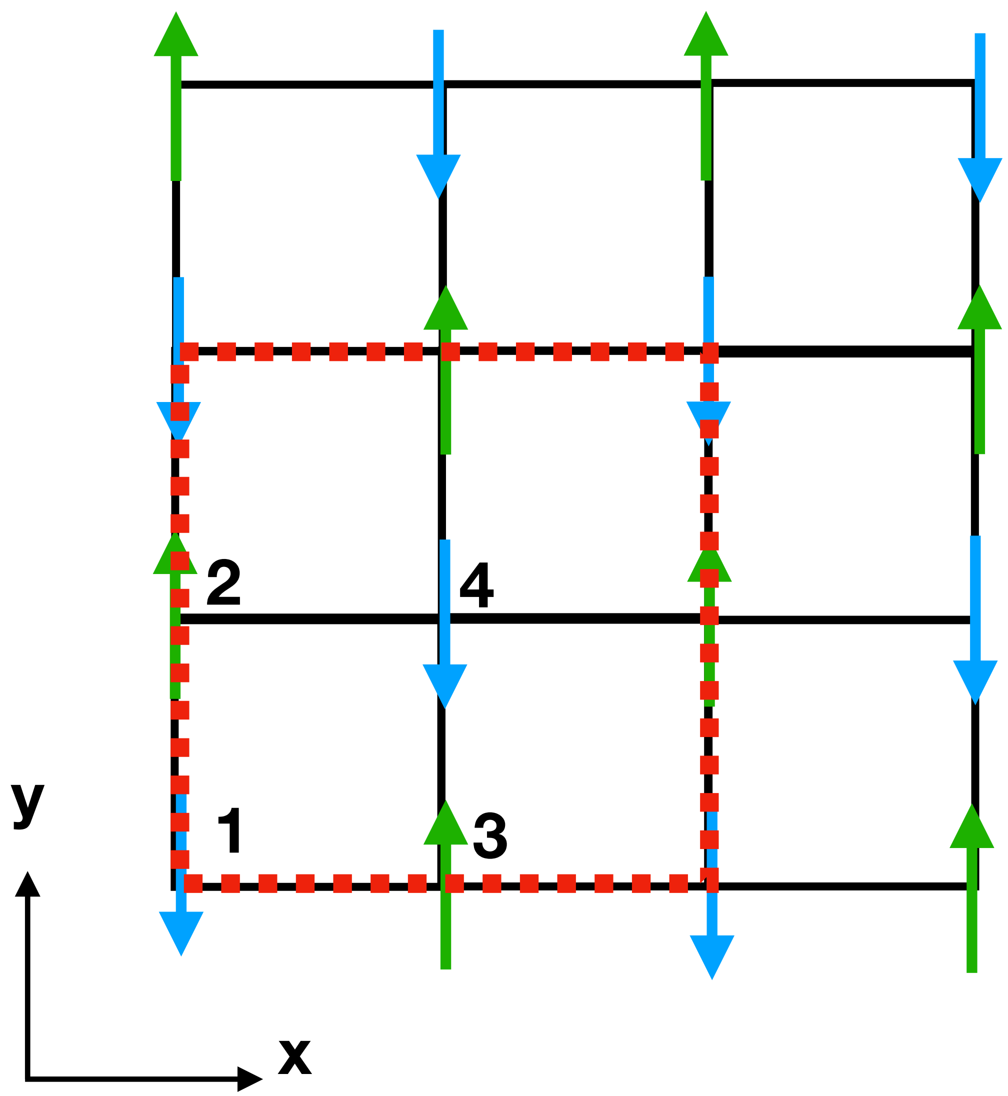
$$\vec{\mathcal{F}}(\vec{Q}) = \sum_m \vec{S}_m e^{i\vec{Q}\cdot\vec{r_m}}$$

Vector Magnetic Structure Factor: Sum over the *magnetic* unit cell

$$\vec{\mathcal{F}}_{\perp}(\vec{Q}) = \vec{\mathcal{F}}(\vec{Q}) - \hat{Q} \cdot \vec{\mathcal{F}}(\vec{Q})$$

take only component perpendicular to Q

Example: determine relative Bragg peak intensities



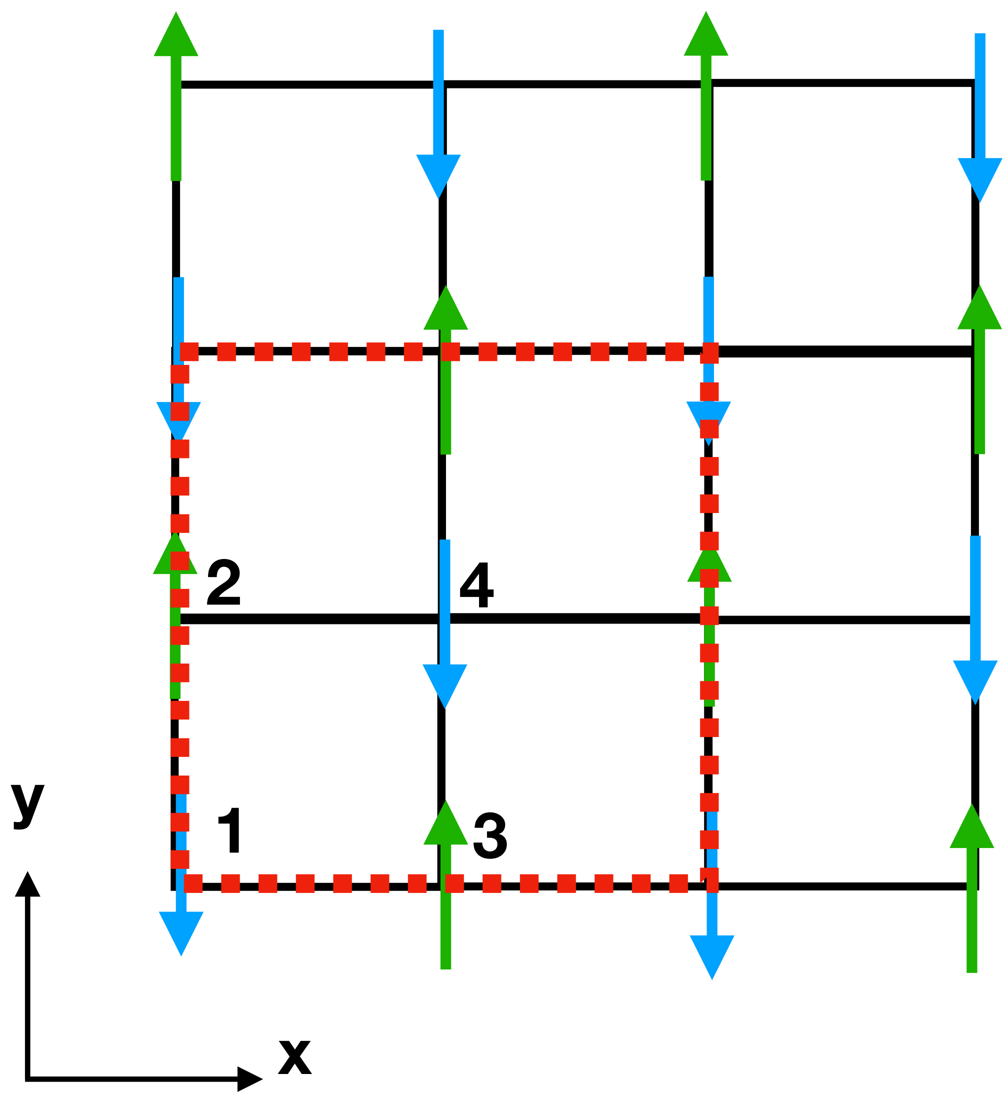
Test: Q = (0,0)

$$\vec{\mathcal{F}}(0,0) = \vec{S}_1 e^{2\pi i(0,0)\cdot(0,0)} + \vec{S}_2 e^{2\pi i(0,0)\cdot(0,1)} + \vec{S}_3 e^{2\pi i(0,0)\cdot(1,0)} + \vec{S}_4 e^{2\pi i(0,0)\cdot(1,1)}$$

$$\vec{\mathcal{F}}(0,0) = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4 = 0$$

Example: determine relative Bragg peak intensities

Test: Q = (0, 1/2)

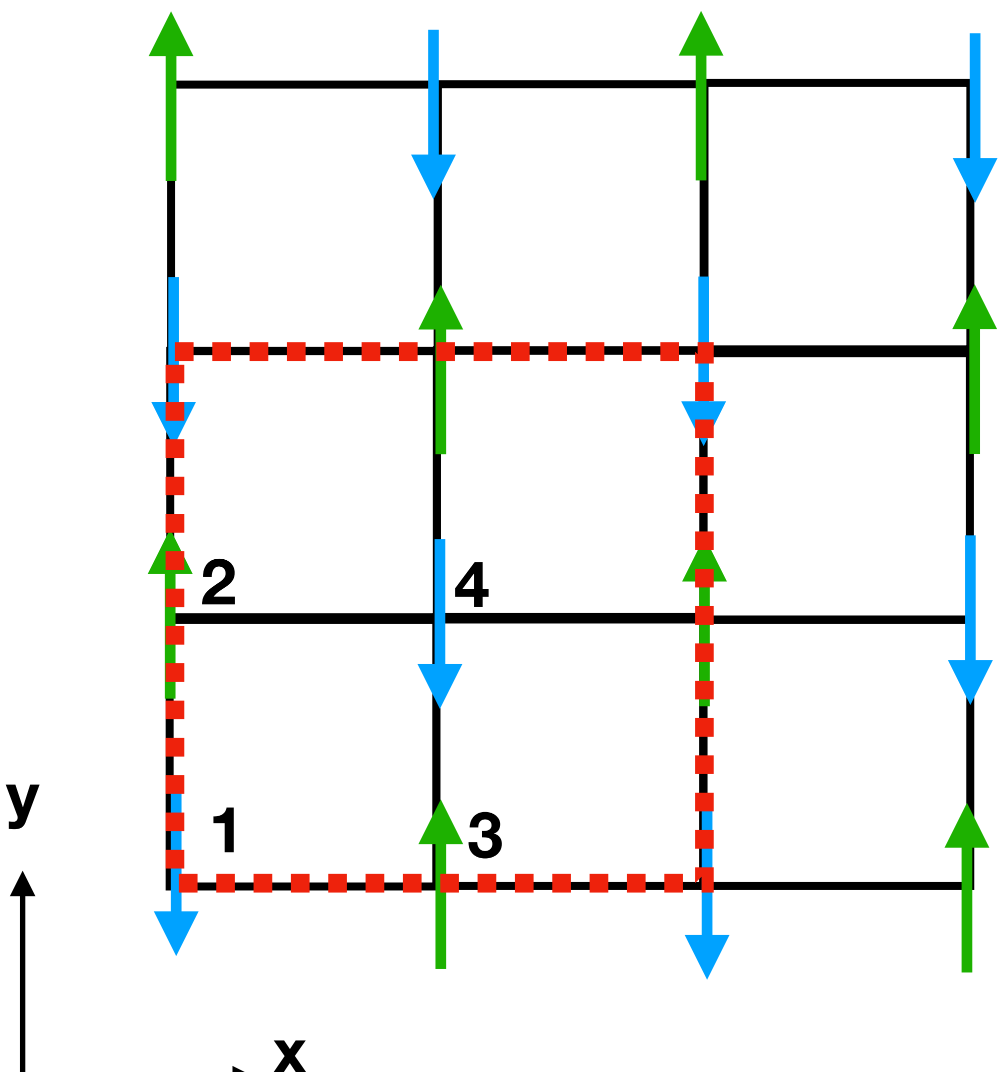


$$\vec{\mathcal{F}}(0, \frac{1}{2}) = \vec{S}_1 e^{2\pi i (0,\frac{1}{2})\cdot(0,0)} + \vec{S}_2 e^{2\pi i (0,\frac{1}{2})\cdot(0,1)} + \vec{S}_3 e^{2\pi i (0,\frac{1}{2})\cdot(1,0)} + \vec{S}_4 e^{2\pi i (0,\frac{1}{2})\cdot(1,1)}$$

$$\vec{\mathcal{F}}(0, \frac{1}{2}) = \vec{S}_1 - \vec{S}_2 + \vec{S}_3 - \vec{S}_4 = 0$$

Example: determine relative Bragg peak intensities

Test: Q = (0, 1/2)



$$\vec{\mathcal{F}}(\frac{1}{2},\frac{1}{2}) = \vec{S}_1 e^{2\pi i(\frac{1}{2},\frac{1}{2})\cdot(0,0)} + \vec{S}_2 e^{2\pi i(\frac{1}{2},\frac{1}{2})\cdot(0,1)} + \vec{S}_3 e^{2\pi i(\frac{1}{2},\frac{1}{2})\cdot(1,0)} + \vec{S}_4 e^{2\pi i(\frac{1}{2},\frac{1}{2})\cdot(1,1)}$$

$$\vec{\mathcal{F}}(\frac{1}{2},\frac{1}{2}) = \vec{S}_1 - \vec{S}_2 - \vec{S}_3 + \vec{S}_4 = -4(0, S)$$

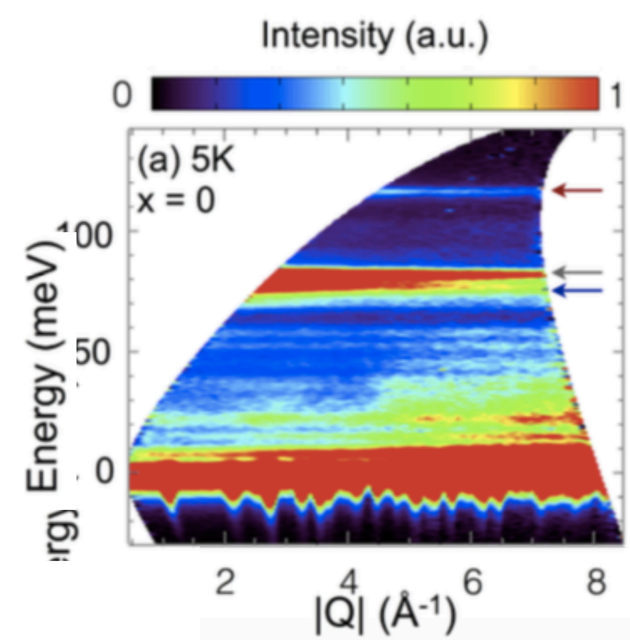
Therefore, intensity is proportional to:

$$|\vec{\mathcal{F}}_\perp(\frac{1}{2},\frac{1}{2})|^2 = \frac{4}{\sqrt{2}} S^2$$

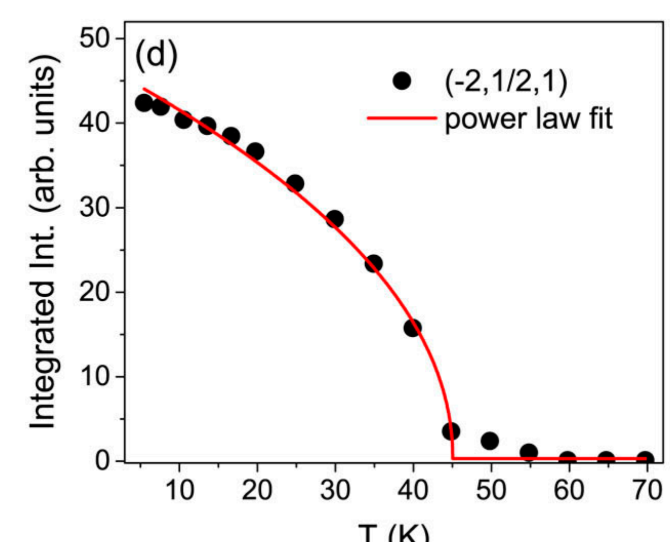
Rules for identifying magnetic scattering

In a given magnetic material, you will see both magnetic and nuclear scattering: How to distinguish?

1. Magnetic scattering **gets stronger as *Q* decreases** due to the "magnetic form factor", *F(Q)*. This conveniently contrasts with inelastic nuclear scattering (e.g. phonons), which increases intensity as *Q* increases.



2. Bragg Peaks and Spin Waves **should depend on temperature** / other external parameters (like magnetic field) in a way that is consistent with thermodynamic data. e.g. onset at T_N or T_c



Total Moment Sum Rule

- Intensity integrated over all Q and ω is constant.
- Scattering gets reorganized into different Q, ω as e.g. temperature changes, but the total amount is fixed

$$\frac{1}{d^3Q}\sum_{\alpha}\int d^3Q \int \hbar \, d\omega \, \boxed{\mathcal{S}^{\alpha\alpha}(\vec{Q},\omega)} = \langle \vec{S}(0)\cdot\vec{S}(0)\rangle = \boxed{S(S+1)}$$

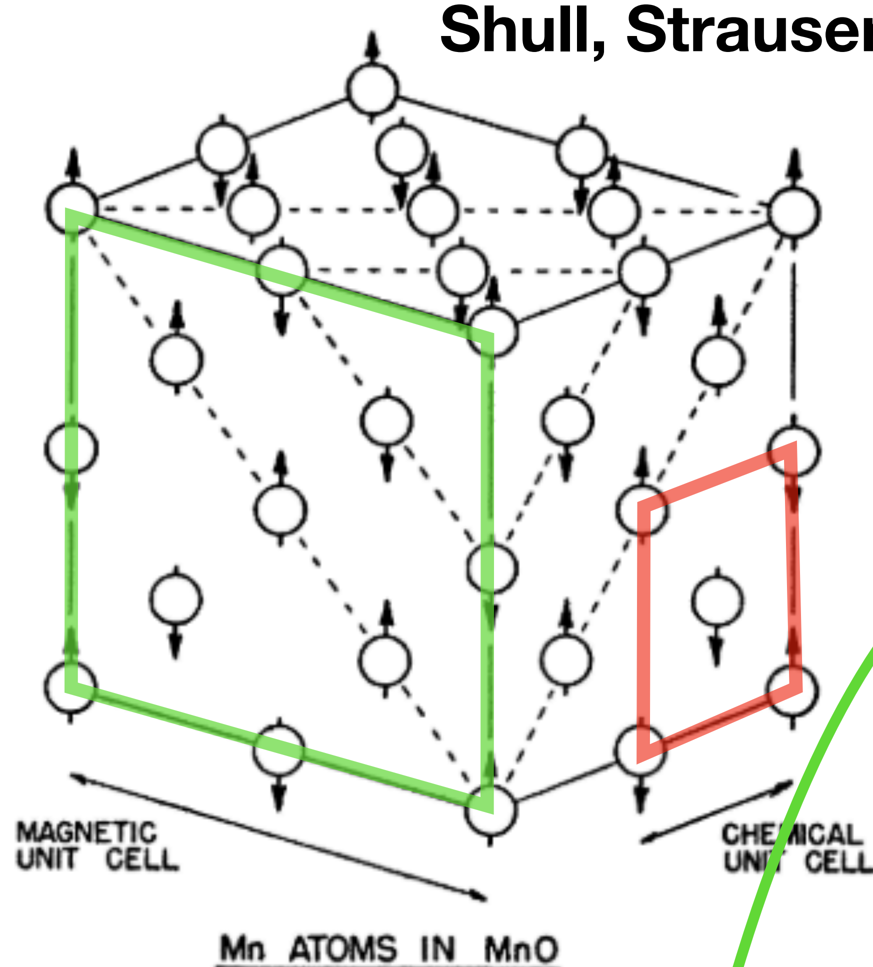
integrate over the dynamic structure factor

total amount is set by the length of the spins, *S*

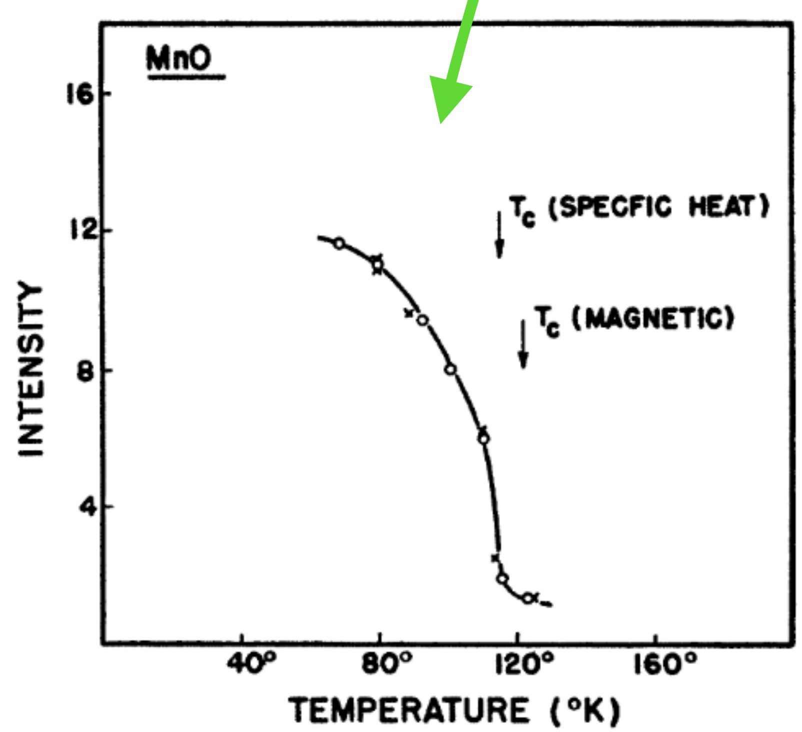
Magnetic **Elastic** Scattering Examples

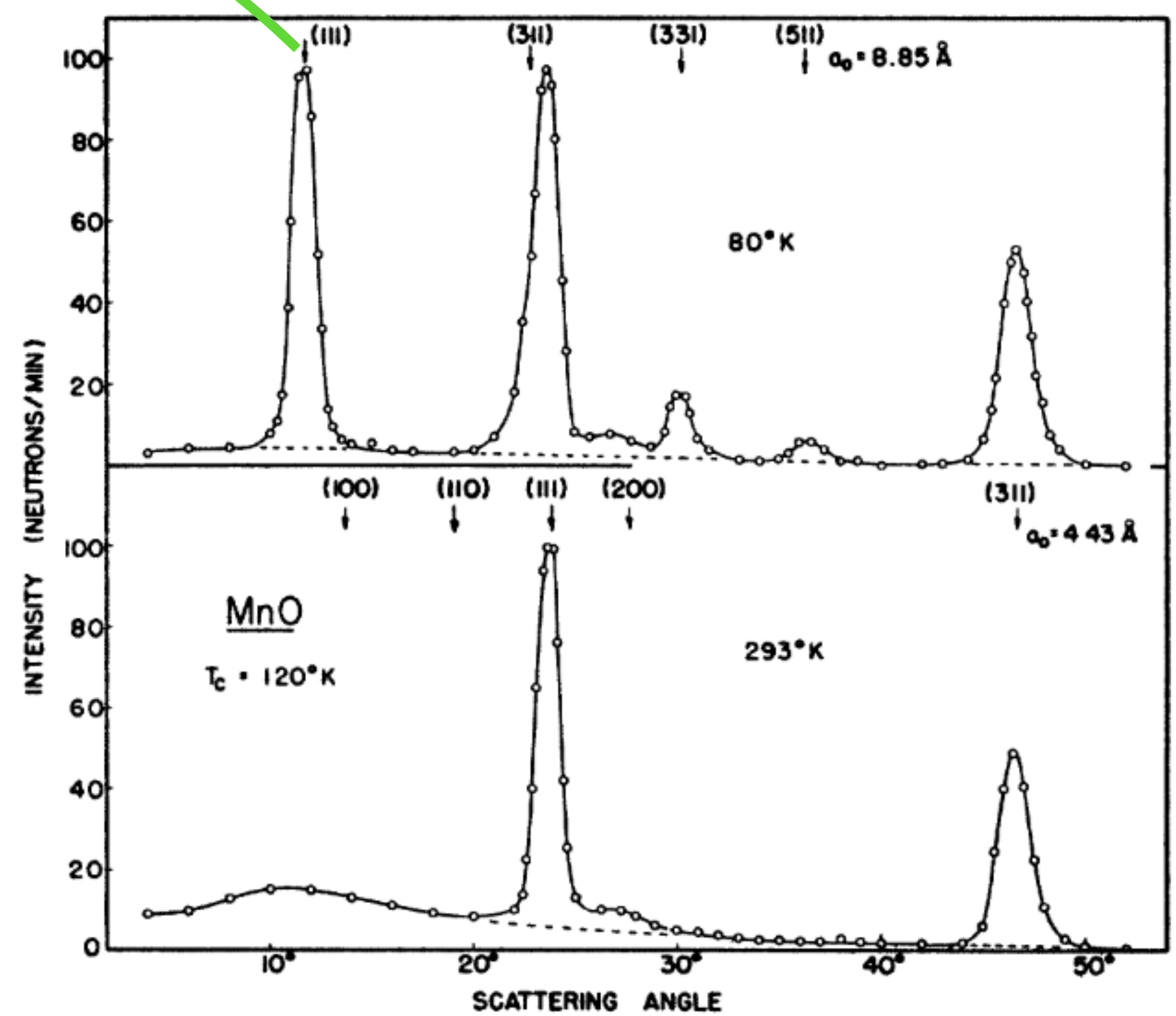
Magnetic order MnO

Shull, Strauser, Wollan, Physical Review 1951



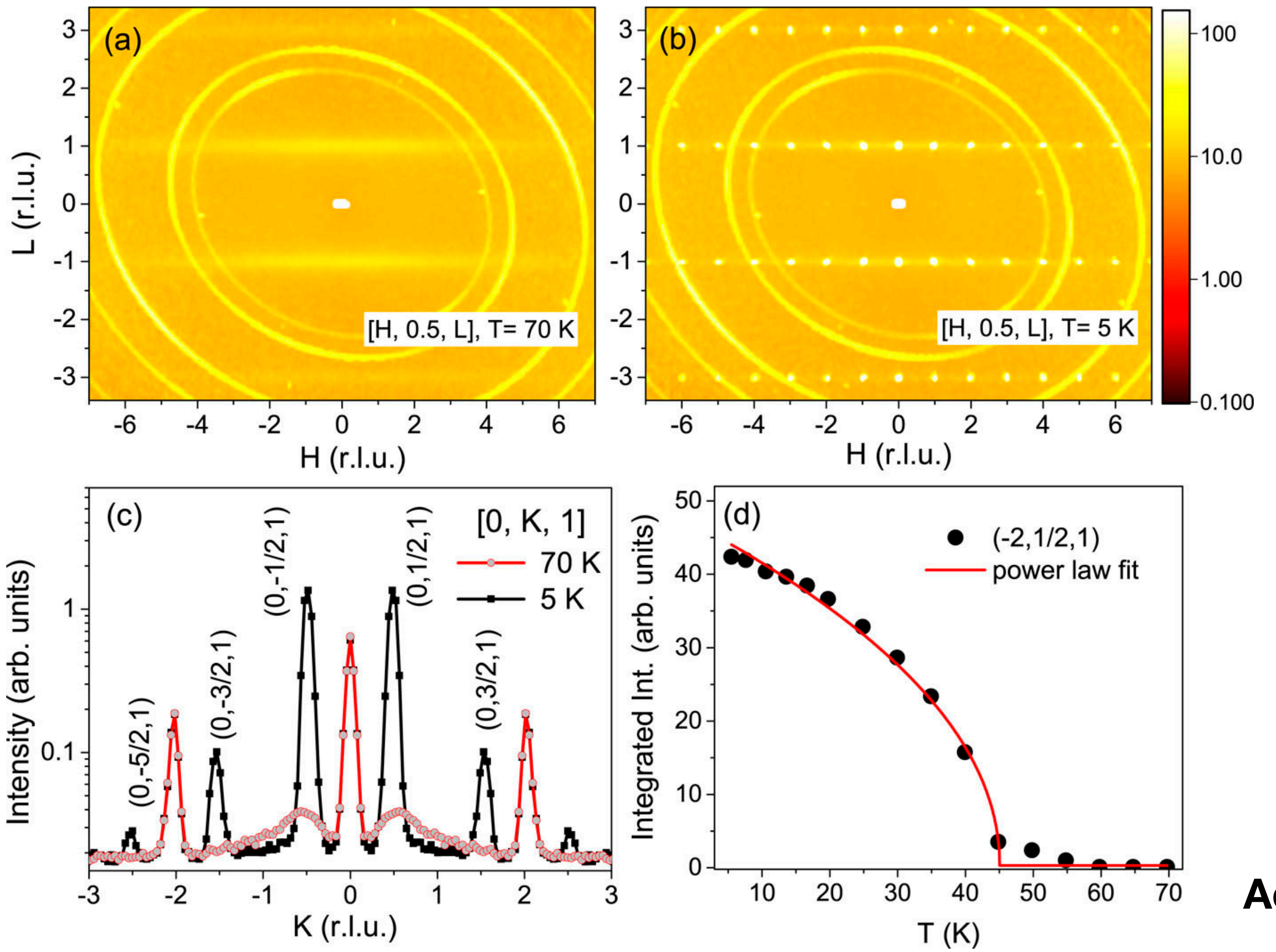
Polycrystalline Sample





Elastic magnetic scattering from crystals on CORELLI

$Mn_5(VO_4)_2(OH)_4$ single crystal

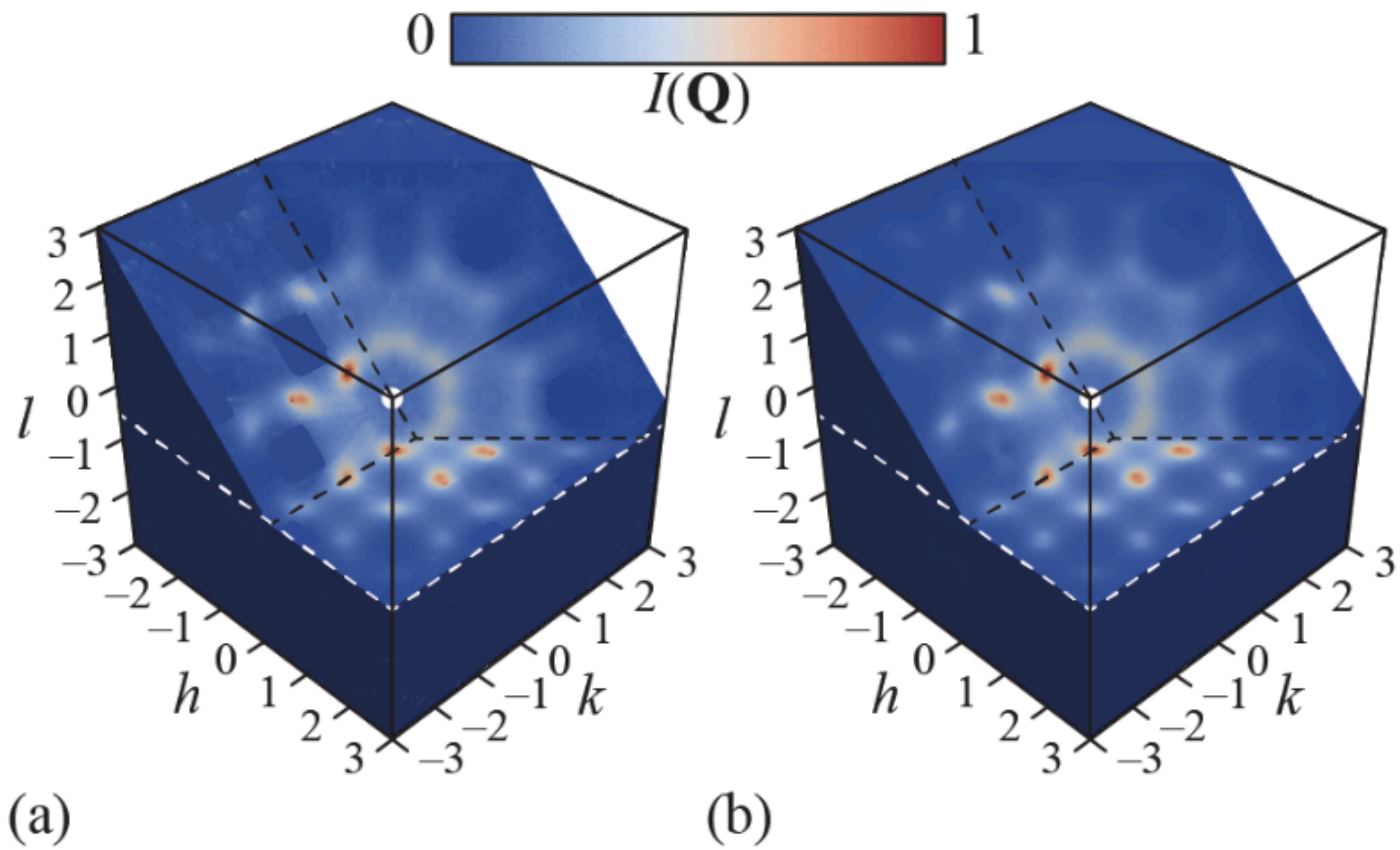


Above T_N, "rods" of diffuse magnetic scattering - 2D correlations

Below T_N, Bragg peaks

V. O. Garlea et al, AIP Advances 8, 101407 (2018)

Back to an oldie: Diffuse Scattering in MnO Above T_N



Data (taken at SXD, ISIS)

Reverse Monte Carlo fit ("Spinvert" program)

Above T_N, analysis of diffuse scattering shows longer range correlations than expected based on simple "width of diffuse scattering" trick. Correlations are not the same as the ordered state.

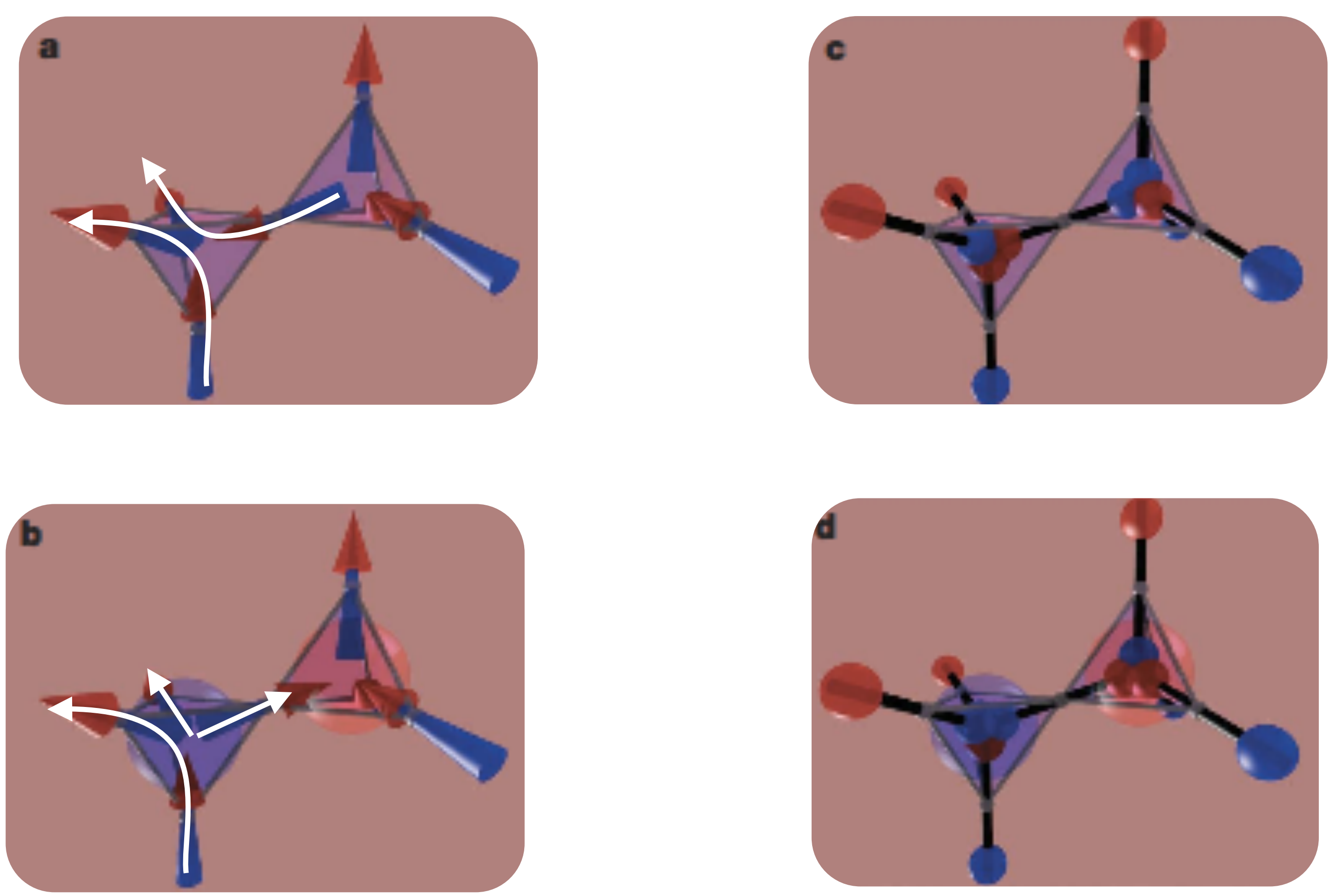
J. A. M. Paddison et al, Phys. Rev. B 97, 014429 (2018)

Spin Ice "pinch points"

Pinch points from "Spin Ice", a *disordered but highly correlated* spin structure

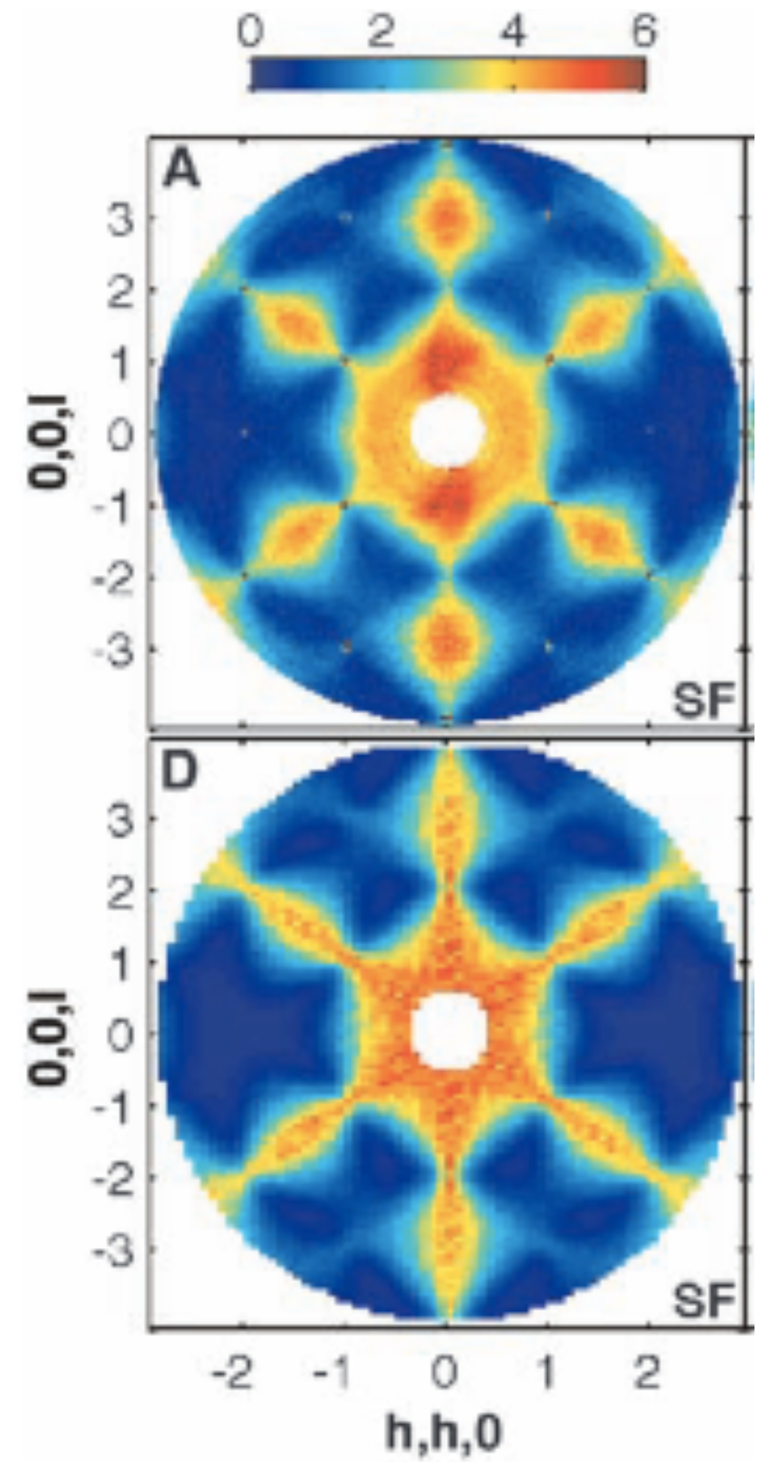
Spin Language

"Dumbell" Language



Castelnovo, Moessner, Sondhi. Nature, 451 (2008)

T. Fennell, *et al*, Science,vol. **326**, p. 415, 2009

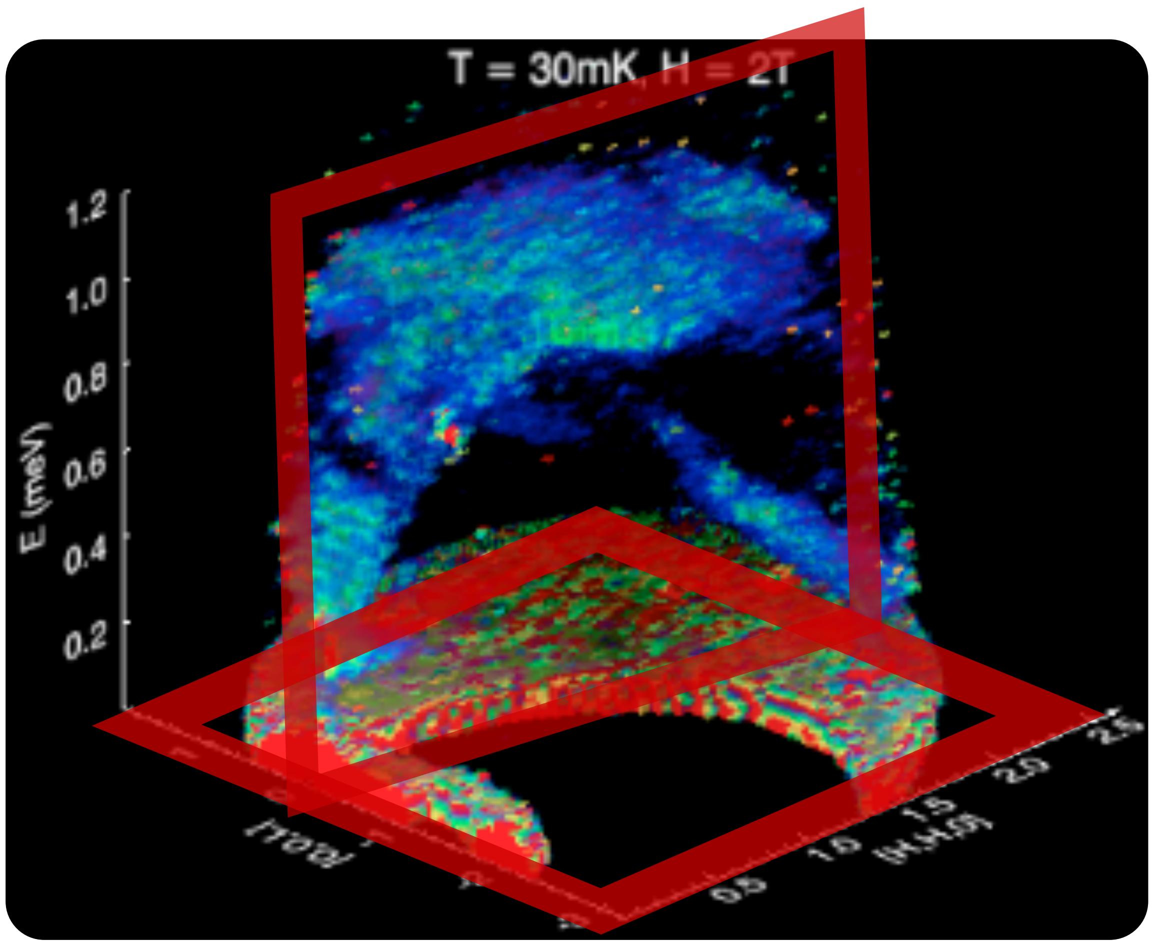


Measured ($Ho_2Ti_2O_7$, (taken at D7, ILL)

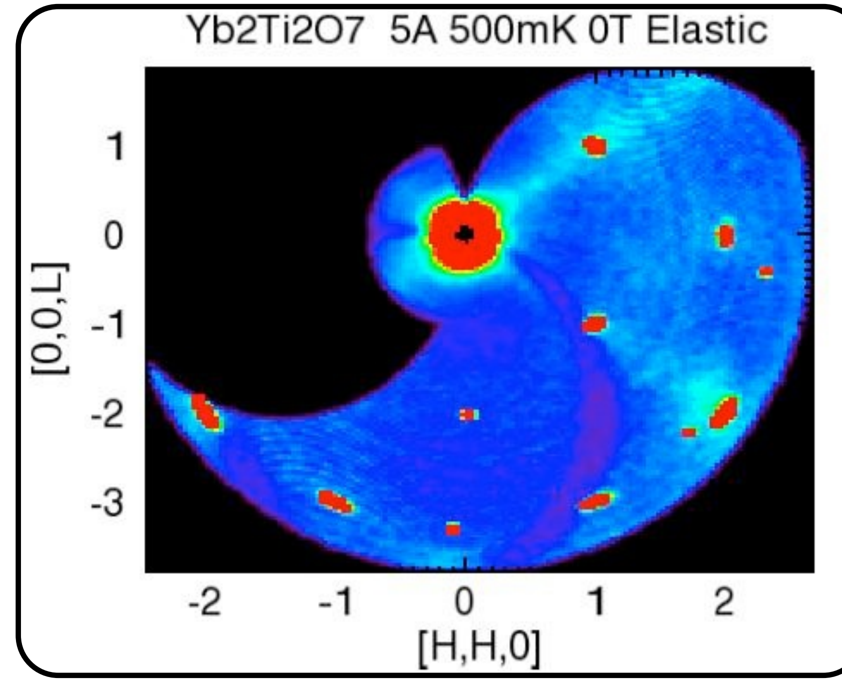
Predicted

Magnetic **Inelastic** Scattering Examples

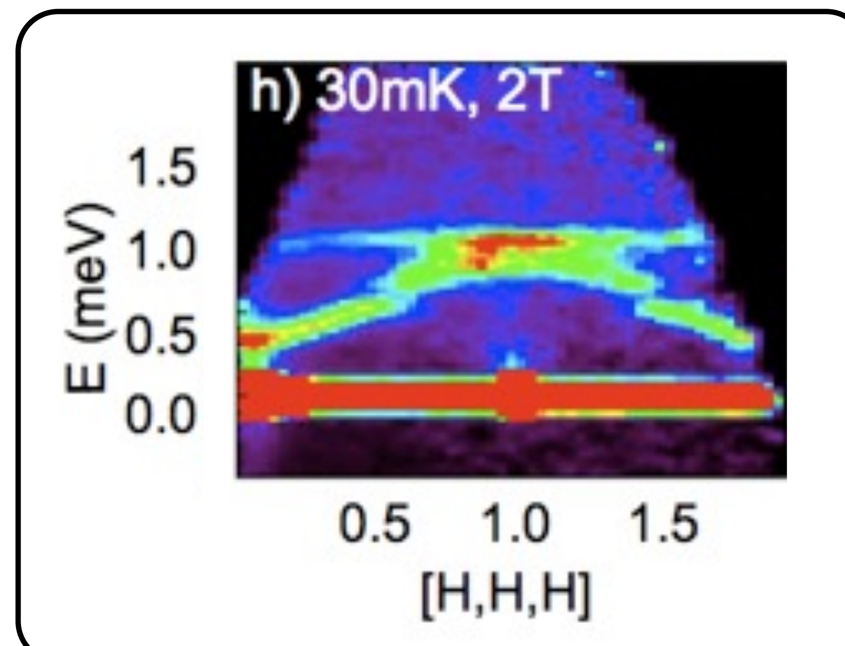
Volume of "Time of Flight" Data



Elastic:
Static
Correlations



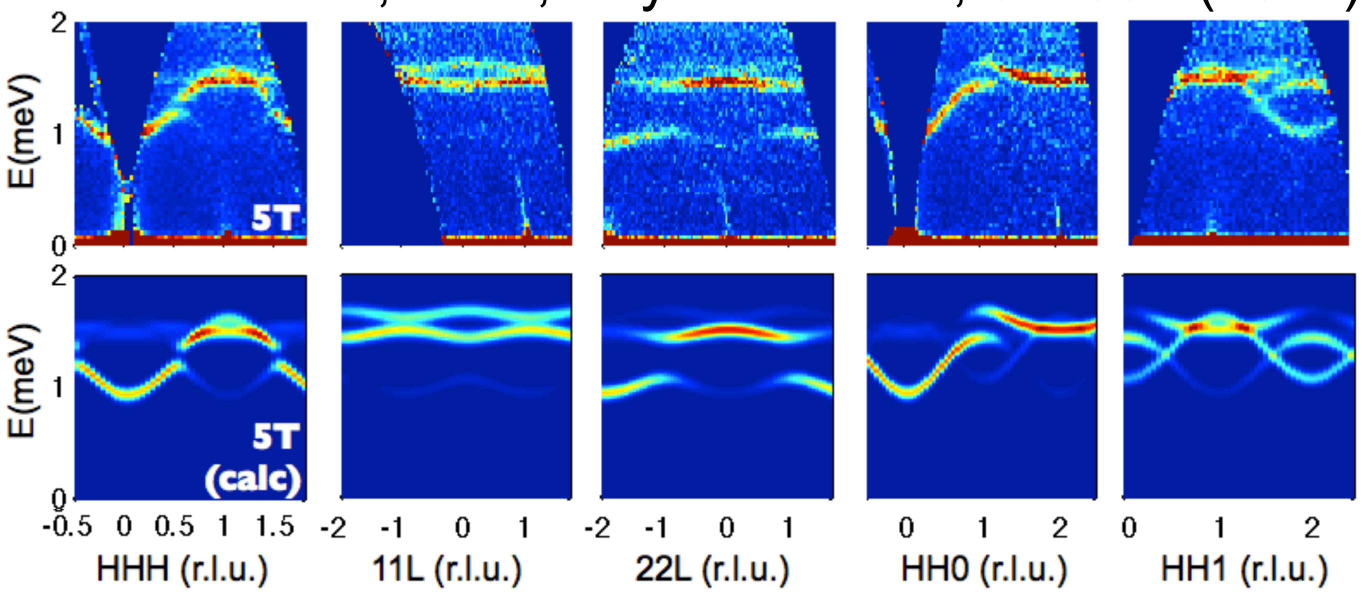
Inelastic:
Dynamic
Correlations



Determining exchange interactions with spin waves from field polarized state

$Yb_2Ti_2O_7$

K.A. Ross, et al., Phys. Rev. X **1**, 021002 (2011)



data, H=5T

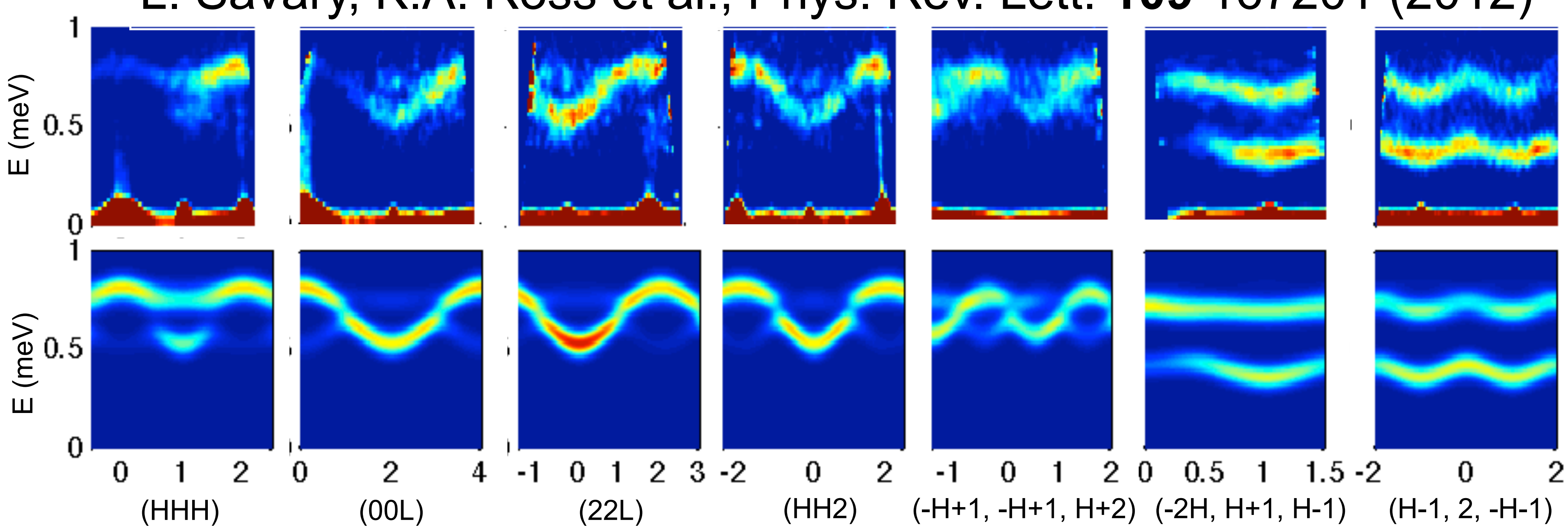
fit

	$Yb_2Ti_2O_7$	$Er_2Ti_2O_7$
J1	-0.09	0.11
J2	-0.22	-0.06
J3	-0.29	-0.10
J4	0.01	0.00

Params lead to "Order by Disorder"

$Er_2Ti_2O_7$

L. Savary, K.A. Ross et al., Phys. Rev. Lett. **109** 167201 (2012)



data, H=3T

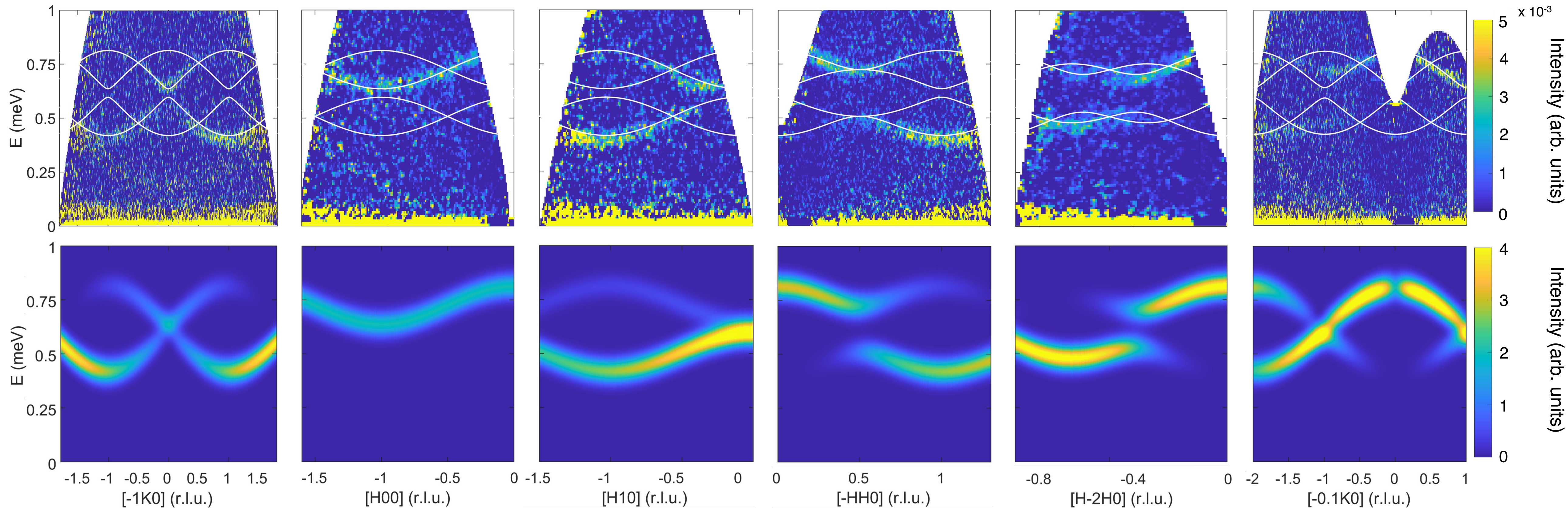
fit

H || to [1-10]

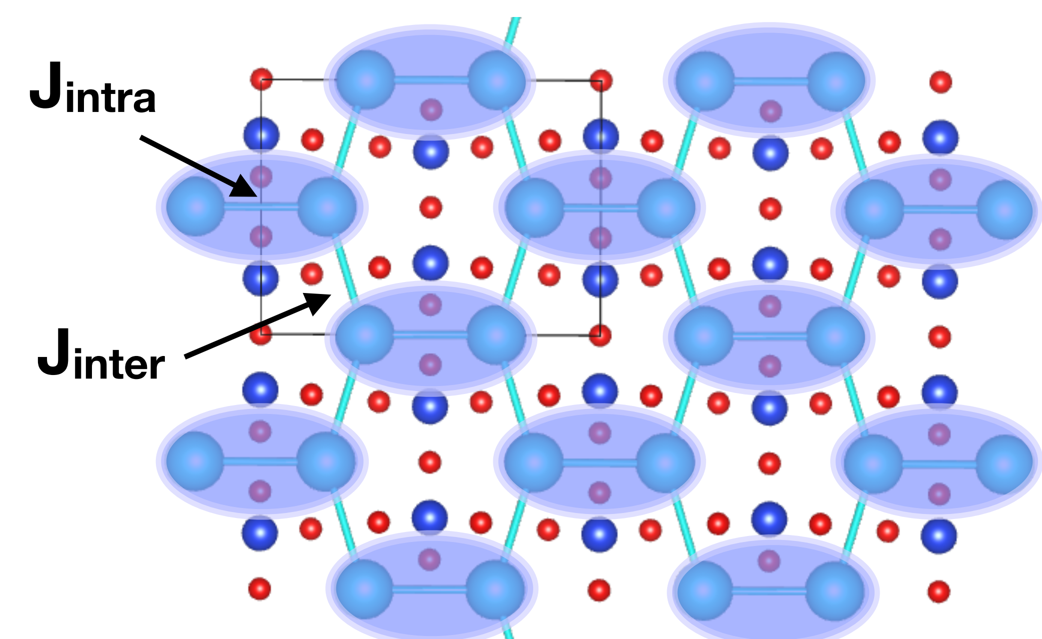
H || to [111]

(data taken at DCS, NCNR)

SpinW - handy tool for calculating spin waves!

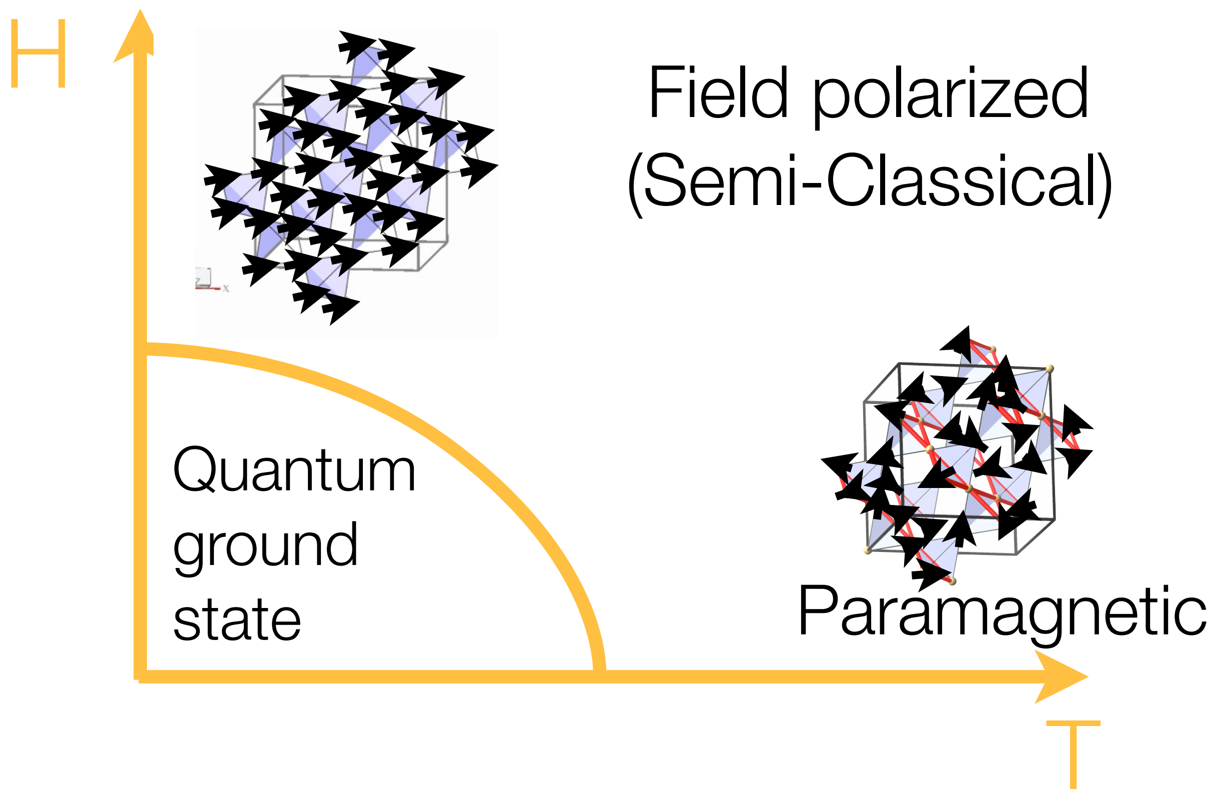


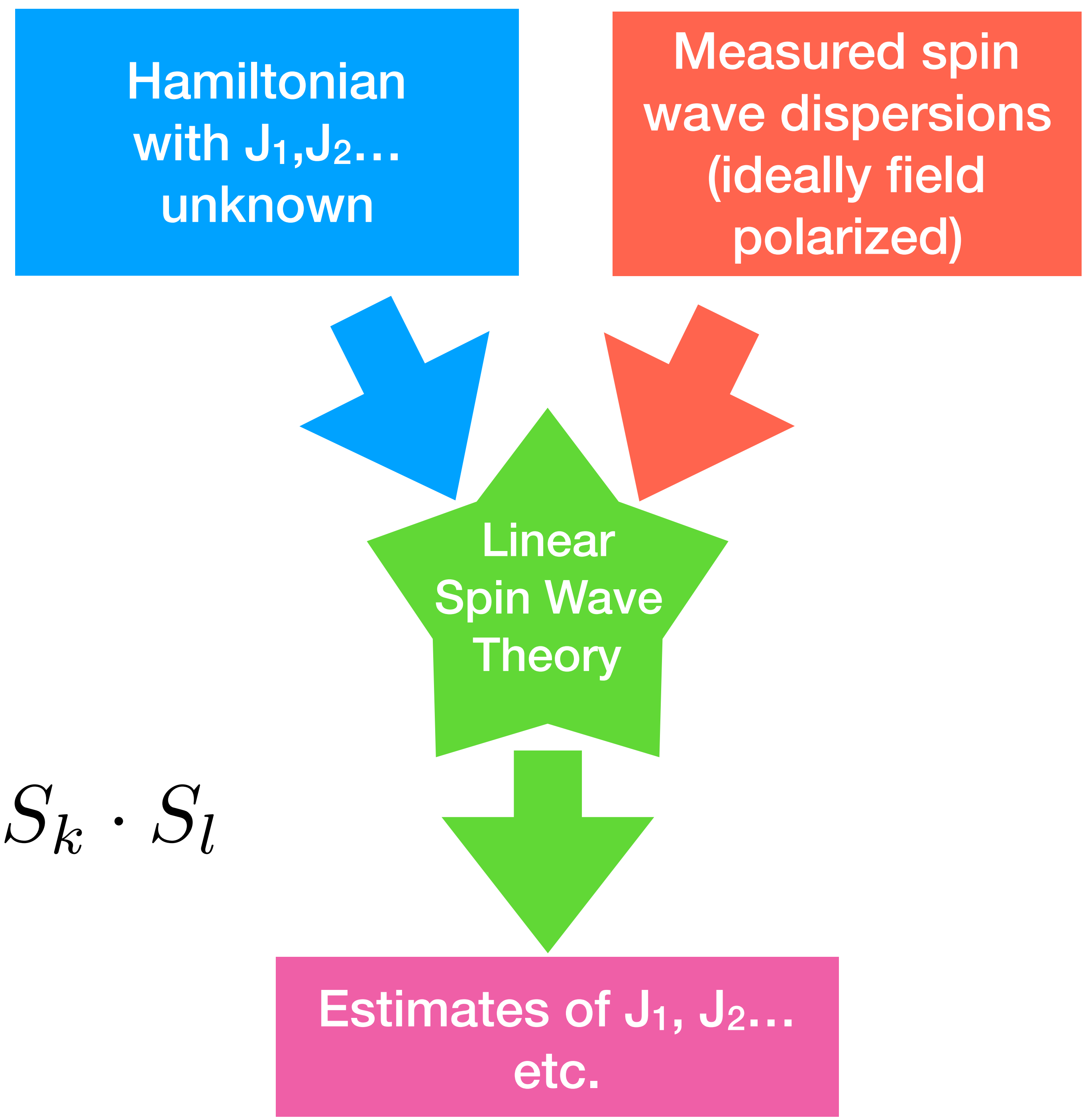
- $Yb_2Si_2O_7$ (Quantum Dimer Magnet) field-polarized — Data taken at CNCS (SNS)



- www.spinw.org

Extracting exchange parameters





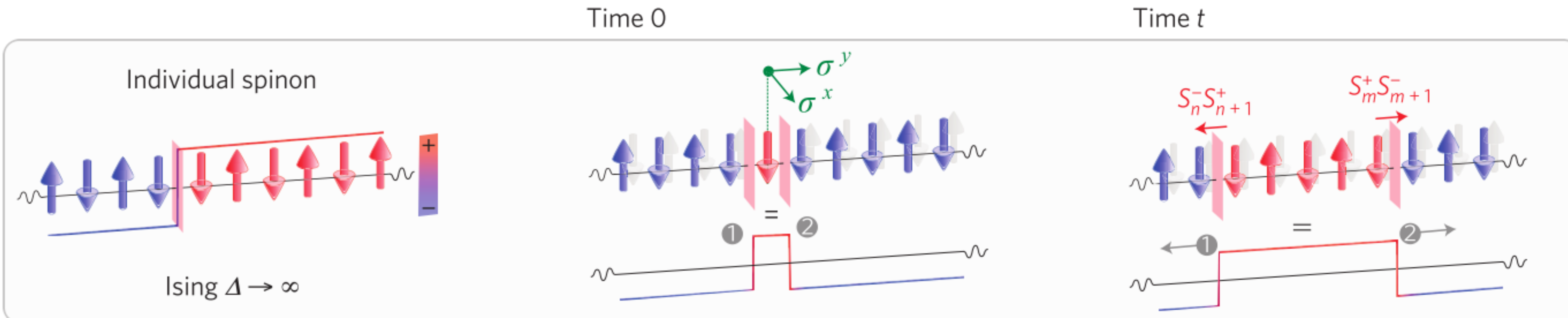
$$H = J_1 \sum_{\langle i,j \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle k,l \rangle\rangle} S_k \cdot S_l$$

Fractionalization / two particle scattering

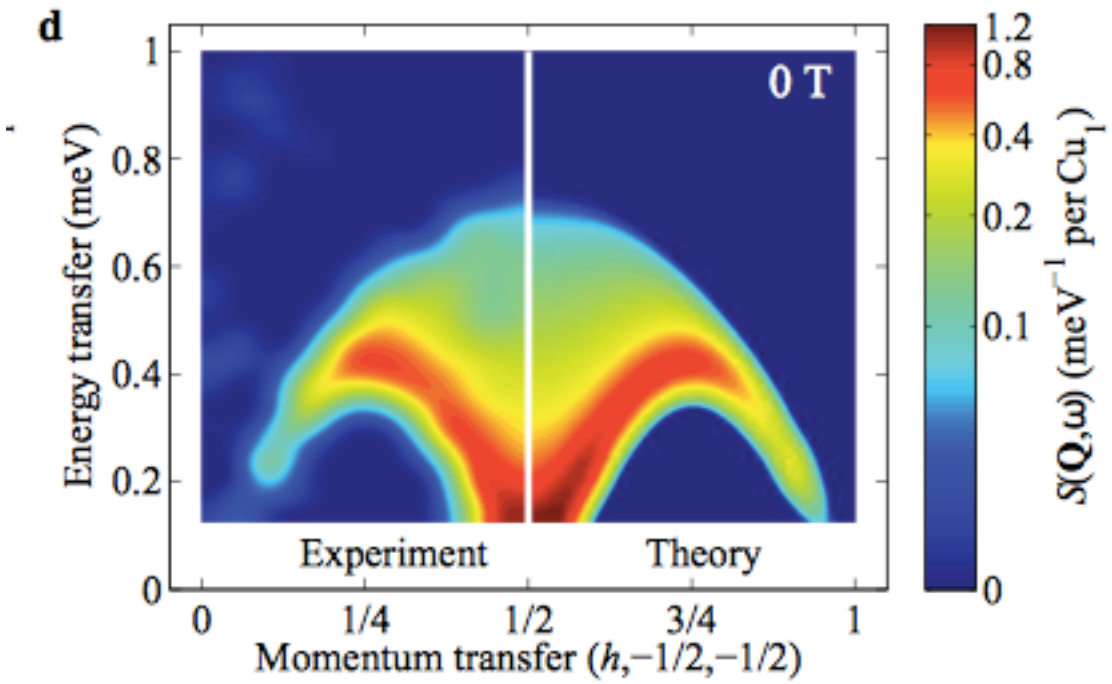
- Quantum Spin Liquids are predicted to have many body entanglement which leads to ***fractionalized excitations*** (e.g. a magnon splits into two spinons)

- Inelastic Neutron Scattering reveals two-particle scattering as a ***continuum*** (see extra slides at the end to see why this forms a continuum)

Two-Spinon continuum in Spin 1/2 Chain



e.g. $CuSO_4 \cdot 5D_2O$: spin 1/2 Chain



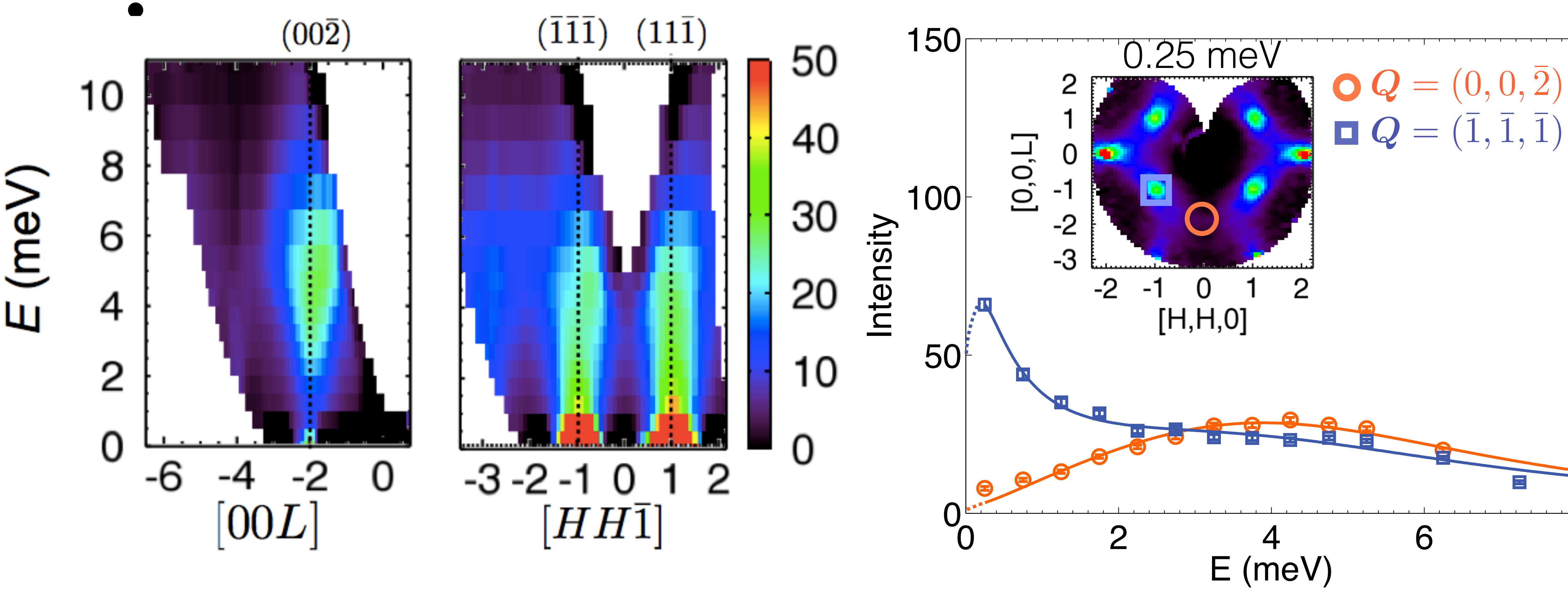
Already observed in 1D chains: entropy wins at finite *T*, domain walls persist and propagate

New challenge: are there 2D or 3D materials in which we can see this "fractionalization"?

Mourigal et al, Nature Physics 9, 435–441 (2013)

Diffuse Inelastic Scattering

- $NaCaCo_2F_7$: S=1/2 *spin frozen* state. Data taken at MACS (NCNR).
- Gapped excitation at (002)
    - Fit to **damped harmonic oscillator (DHO) at 3.4 meV**
- Gapless excitations at the magnetic Bragg features (111)
    - **Quasi-elastic relaxation** plus DHO at 3.4 meV
-



Summary

- Neutron Scattering is the definitive probe for magnetism in materials
- Elastic scattering can give access to magnetic long range ordered states, or short range magnetic correlations
- Inelastic scattering allows the measurement of spin waves (which can be used to extract exchange parameters), diffusive excitations from disordered states, or fractionalized excitations
- Main components of the cross section: Magnetic form factor, Dynamic structure factor, Polarization factor

Good references for a "deep dive" into magnetic neutron scattering

- G.L. Squires, "Introduction to the Theory of Thermal Neutron Scattering" (book)
- Stephen W. Lovesey, "The Theory of Neutron Scattering from Condensed Matter Volume II" (book)
- Randy S Fishman, Jaime A Fernandez-Baca and Toomas Rõõm, "Spin-Wave Theory and its Applications to Neutron Scattering and THz Spectroscopy", (book)
- Collin Broholm's lecture on magnetic neutron scattering, online: http://cins.ca/docs/ss2013/lectures/Broholm.pdf

How do we understand the two-particle continuum?

e.g. **two “spinons”** OR two “phonons”, “magnons”, etc…

First, single particle inelastic scattering:

Inelastic Neutron Scattering measures the "Dynamic Structure Factor"

Dynamic structure factor

$$\frac{d^2\sigma}{d\Omega dE'} \propto S(Q, \hbar\omega)$$

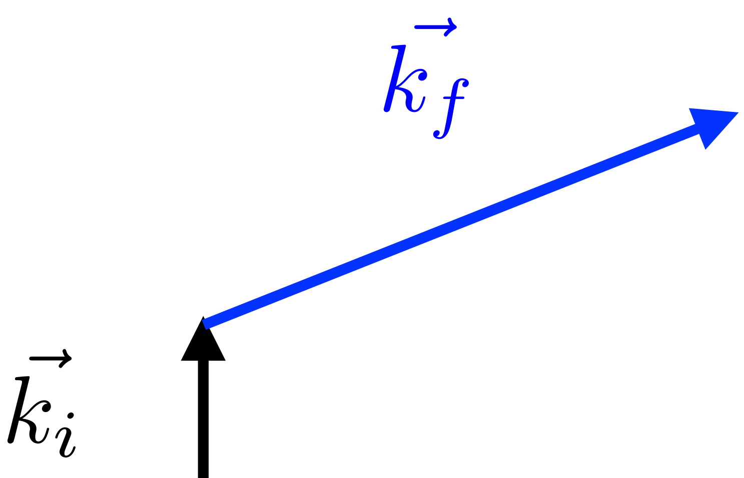
final neutron energy

$$\hbar\omega = E' - E$$

energy transfer

incident neutron energy

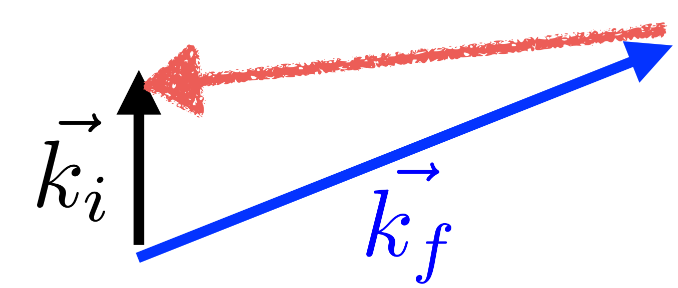
Momentum transfer and energy transfer are linked



$$E' = \frac{1}{2}mv_f^2 = \frac{\hbar^2 k_f^2}{2m}$$

$$E = \frac{1}{2}mv_i^2 = \frac{\hbar^2 k_i^2}{2m}$$

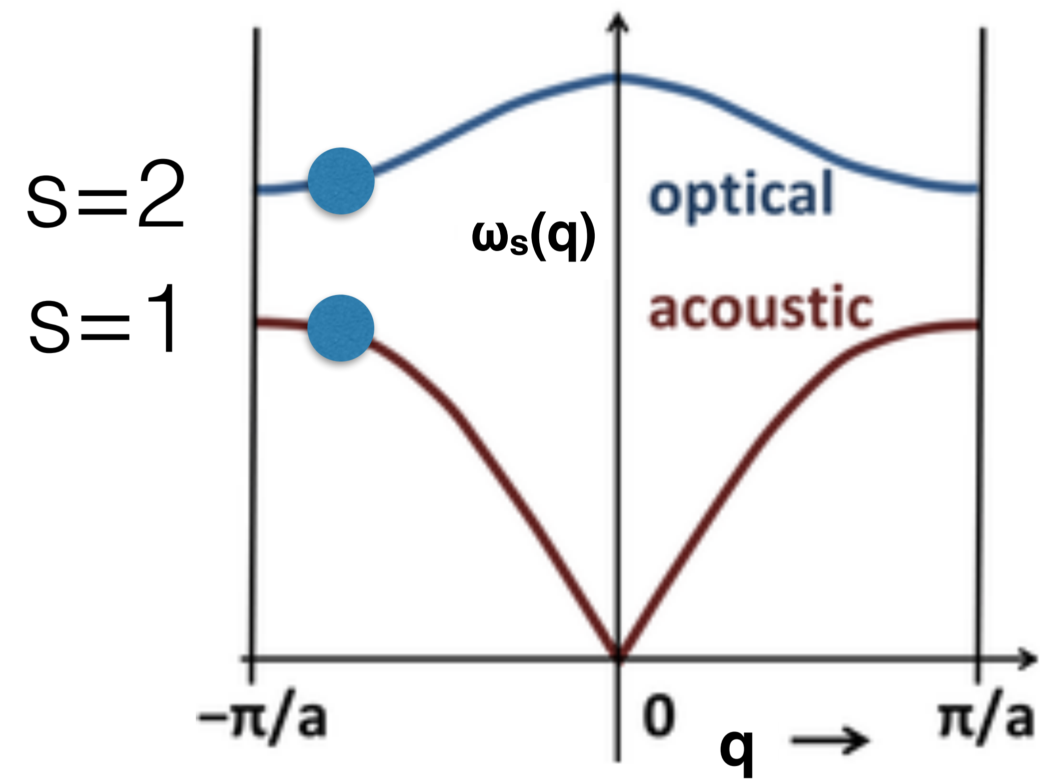
$$\vec{Q} = \vec{k_i} - \vec{k_f}$$

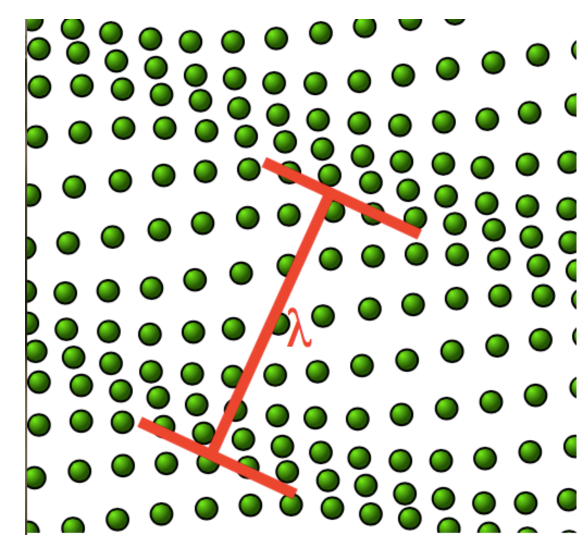


Scattering triangle

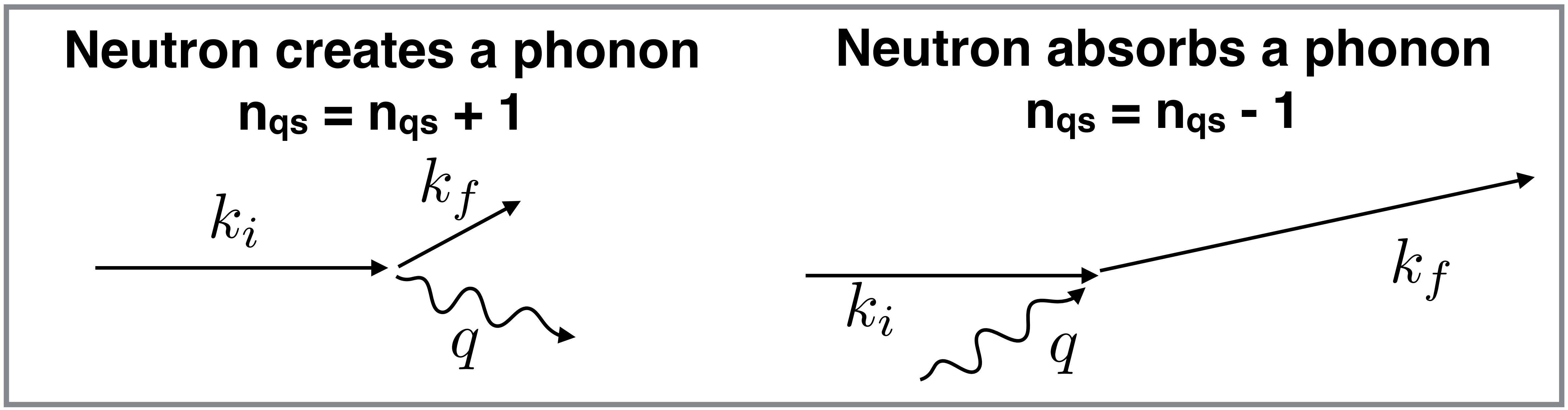
Example: Phonons

- Each point along the dispersion curve is a normal mode
- Quantum theory of lattice vibrations:
  - The **waves are treated as particles**
  - Each mode, designated by momentum ***q*** and branch *s* has an **occupation number n_{qs}, energy ω_s(*q*)**
  - The occupation number counts the number of "phonons"





Neutron Scattering from Phonons



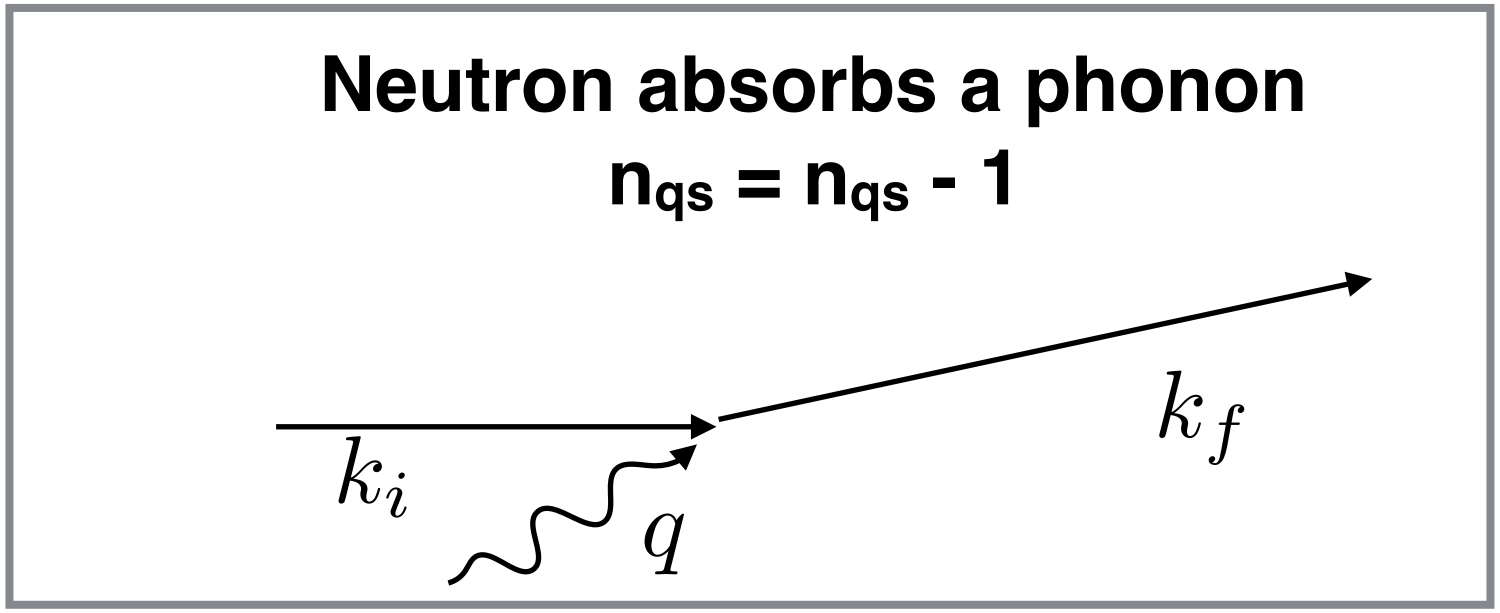
$$E' - E = -\sum_{qs} \hbar\omega_{qs}\Delta n_{qs}$$

Conservation of energy

$$\hbar\vec{k_f} - \hbar\vec{k_i} = -\sum_{qs} \hbar\vec{q}\Delta n_{qs} + \hbar\vec{G}$$

Conservation of "crystal momentum" (G is a reciprocal lattice vector)

One Phonon Absorption



$$E' = E + \hbar\omega_s(q)$$

Conservation of energy

$$\vec{k}_f = \vec{k}_i + \vec{q} + \vec{G}$$

Conservation of
"crystal momentum"
(G is a reciprocal lattice vector)

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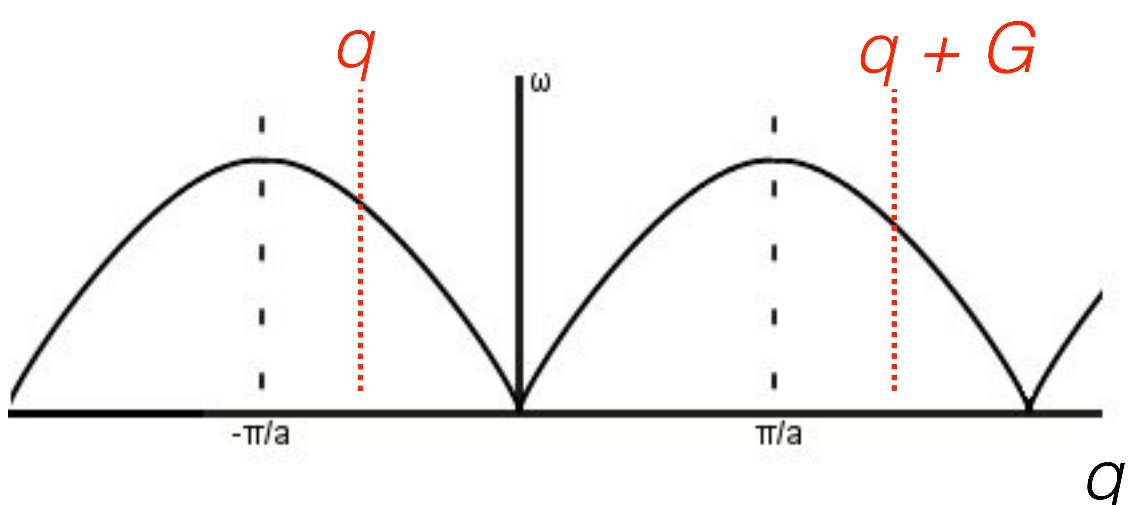


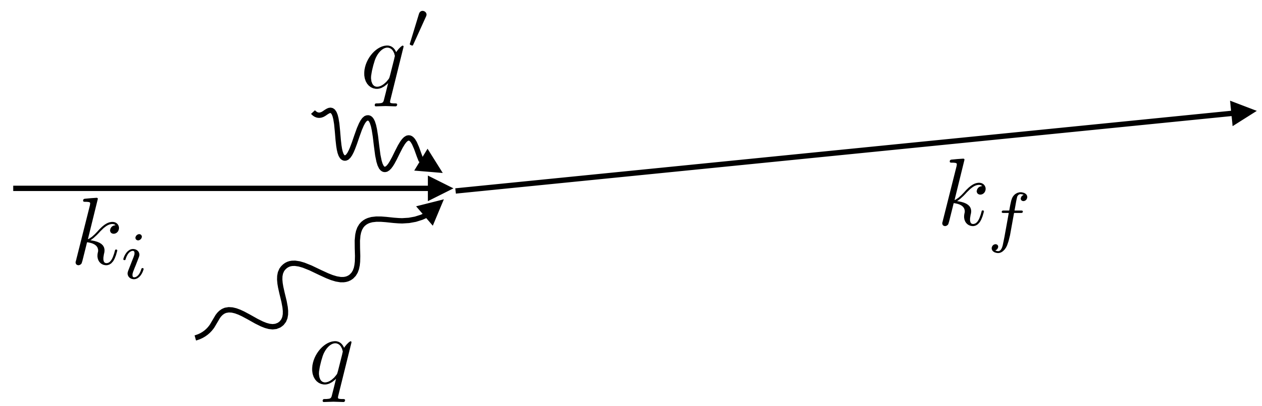
$$E' - E = \hbar\omega_s(\vec{k_f} - \vec{k_i})$$

Each 'ω_s' Specifies a *surface*
if we concentrate on a single direction for
k$_f$, and scan through different
lengths of $|k_f|$ (i.e. scan through *E'*),
we can measured one point on this surface

Two Phonon Process

Neutron absorbs two phonons

$\mathbf{n_{qs} = n_{qs} - 1, n_{q's'} = n_{q's'} - 1}$



$$E' = E + \hbar\omega_s(q) + \hbar\omega_{s'}(q')$$

Conservation of energy

$$\vec{k}_f = \vec{k}_i + \vec{q} + \vec{q}' + \vec{G}$$

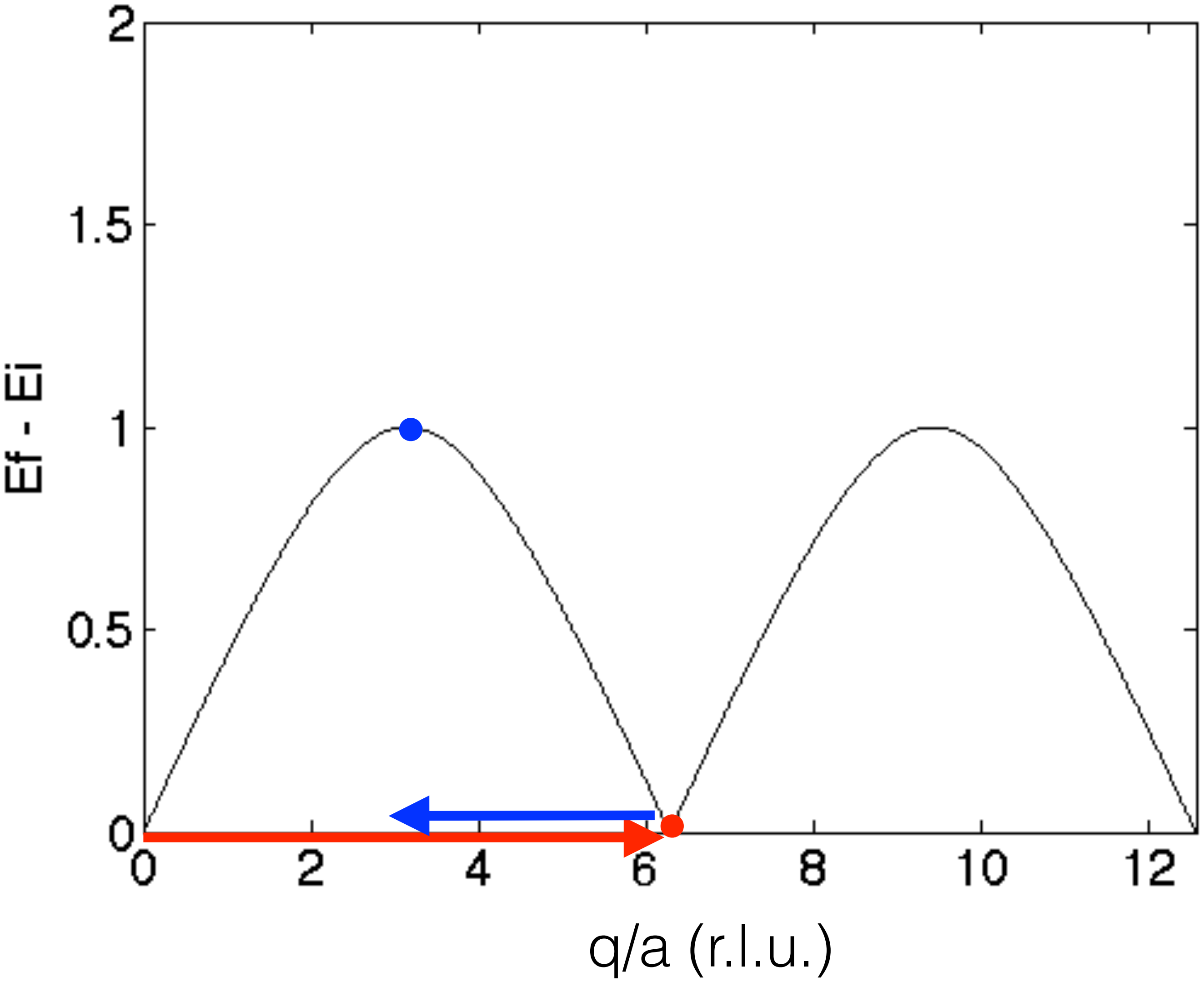
Conservation of
"crystal momentum"
(G is a reciprocal lattice vector)

$$E' = E + \hbar\omega_s(\vec{q}) + \hbar\omega_{s'}(\vec{k_f} - \vec{k_i} - \vec{q})$$

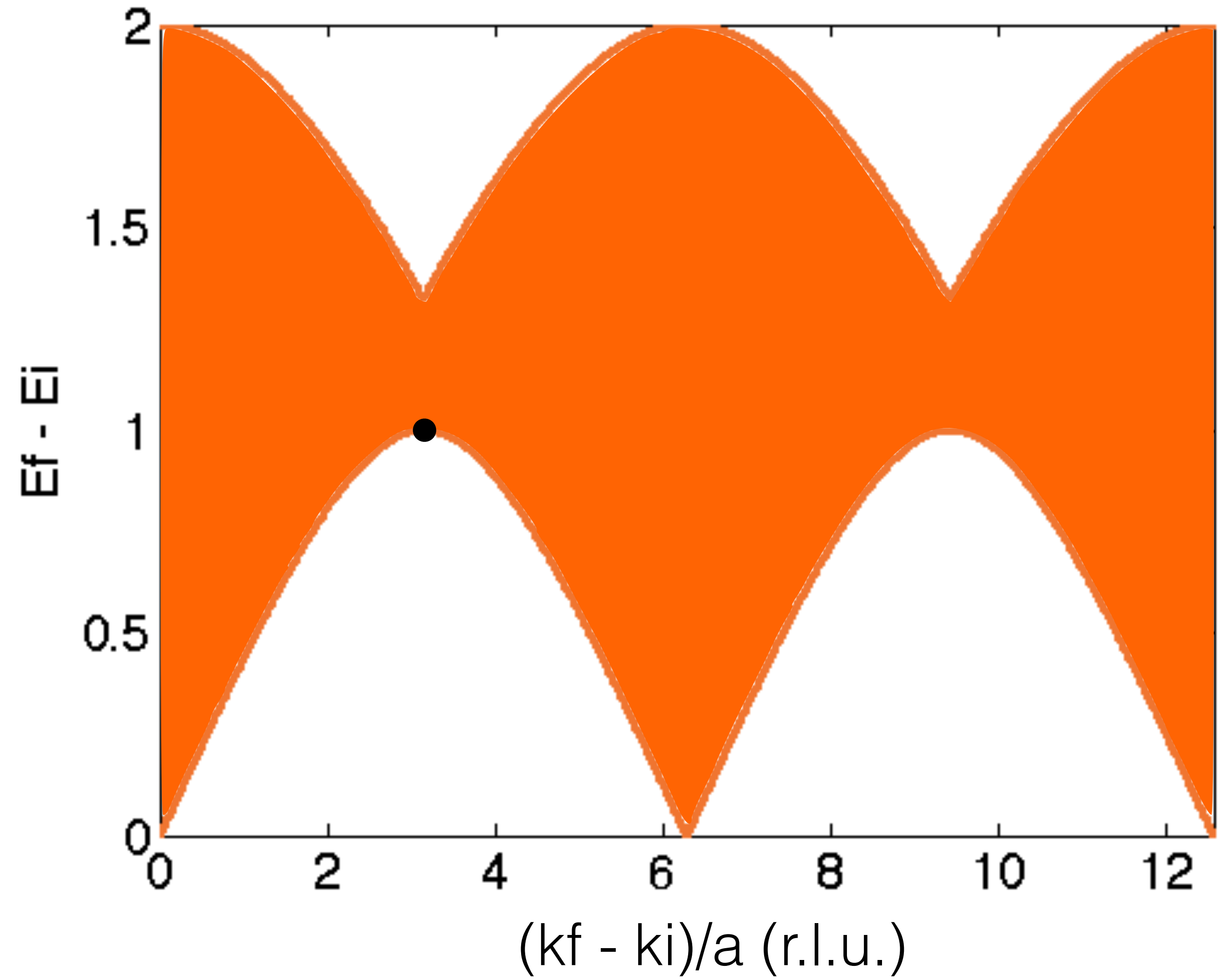
Now a given k_f does *not* uniquely correspond to a given $w_s(q)$
continuum of scattering observed

Multiphonon Continuum
e.g. 1D chain

Acoustic Phonon Dispersion

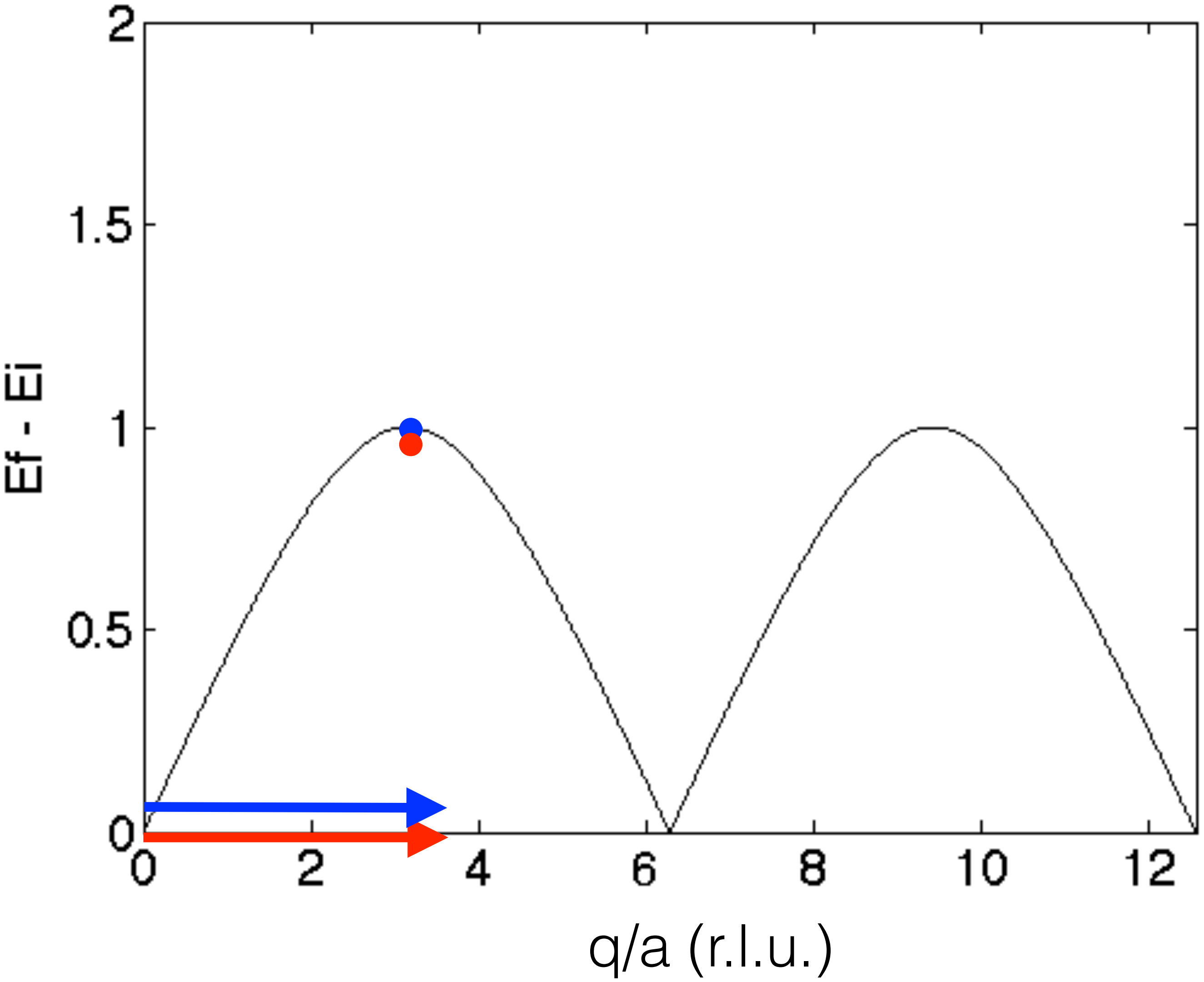


Region of measured intensity

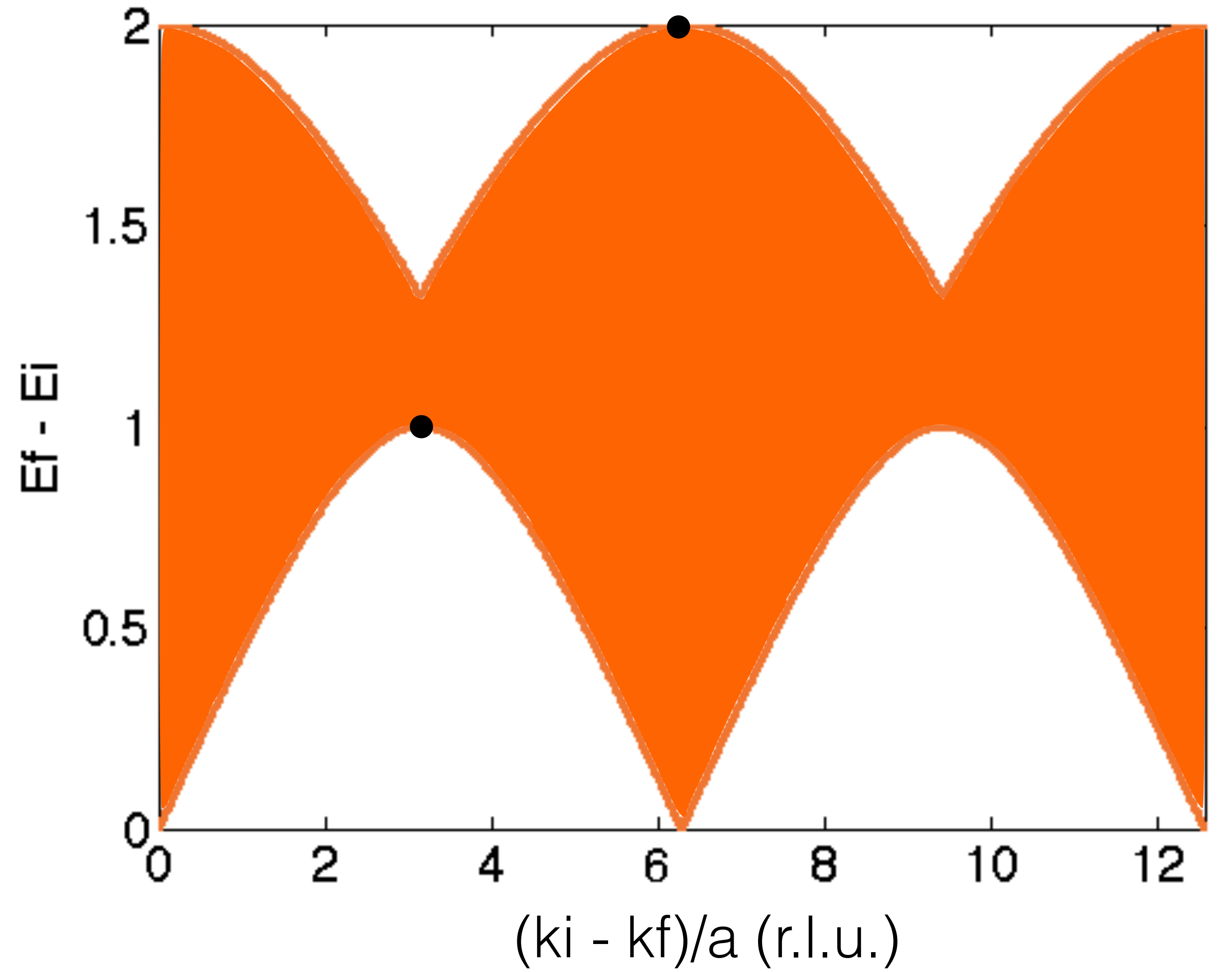


Multiphonon Continuum
e.g. 1D chain

Acoustic Phonon Dispersion



Region of measured intensity



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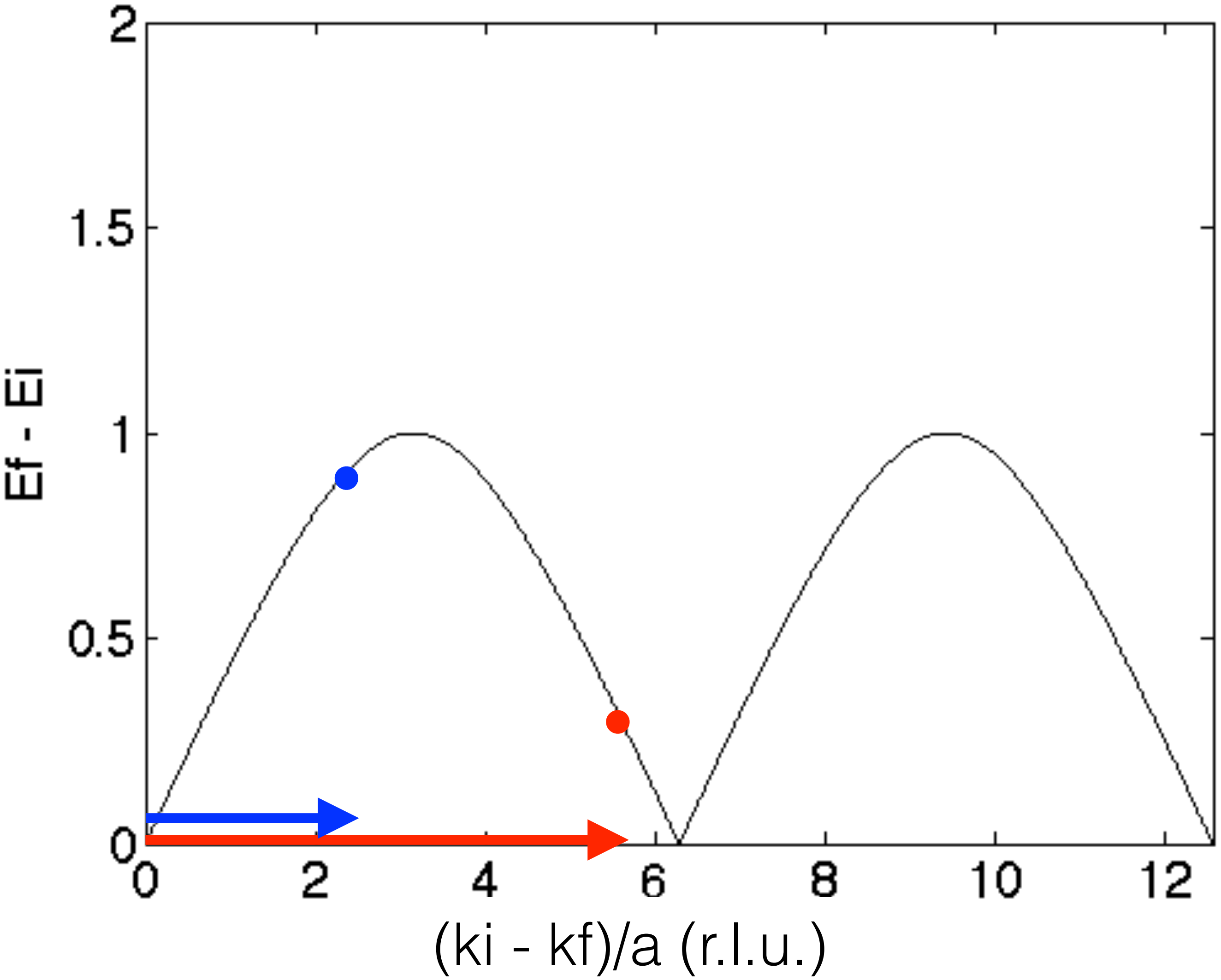

Region of measured intensity