Summer School on Methods and Applications of Neutron Spectroscopy
NIST Center for Neutron Research, June 19-23, 2011

A Study of the Singlet-Triplet Dispersion in the Geometrically Frustrated $S = 1$ Antiferromagnetic Dimer $Ba_3Mn_2O_8$: An experiment using the SPINS cold-neutron, triple-axis spectrometer

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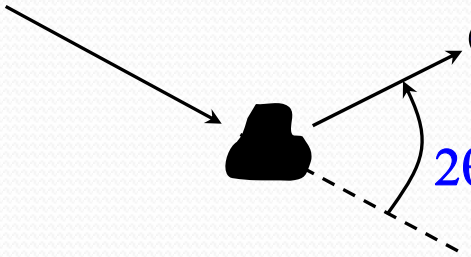
Basics of Neutron Scattering

Neutron scattering experiments measure the flux Φ_s of neutrons scattered by a sample into a detector as a function of the change in neutron wave vector ($\vec{Q}$) and energy ($\hbar\omega$).

$\Phi_s(Q,\hbar\omega) = \frac{\text{neutrons}}{\text{sec–cm}^2}$

Momentum	Energy
$\hbar k = \hbar(2\pi/\lambda)$	$\hbar\omega_n = \hbar^2 k_n^2/2m$
$\hbar Q = \hbar\vec{k}_i - \hbar\vec{k}_f$	$\hbar\omega = \hbar\omega_i - \hbar\omega_f$



The expressions for the scattered neutron flux Φ_s involve the positions and motions of atomic nuclei or unpaired electron spins.

$$\Phi_s = \mathbb{F}\{\vec{r}_i(t), \vec{r}_j(t), \vec{S}_i(t), \vec{S}_j(t)\}$$

$\Rightarrow$ Φ_s provides information about <u>all</u> of these quantities!

Neutron Scattering Cross Sections

The "cross sections" are what we measure experimentally.

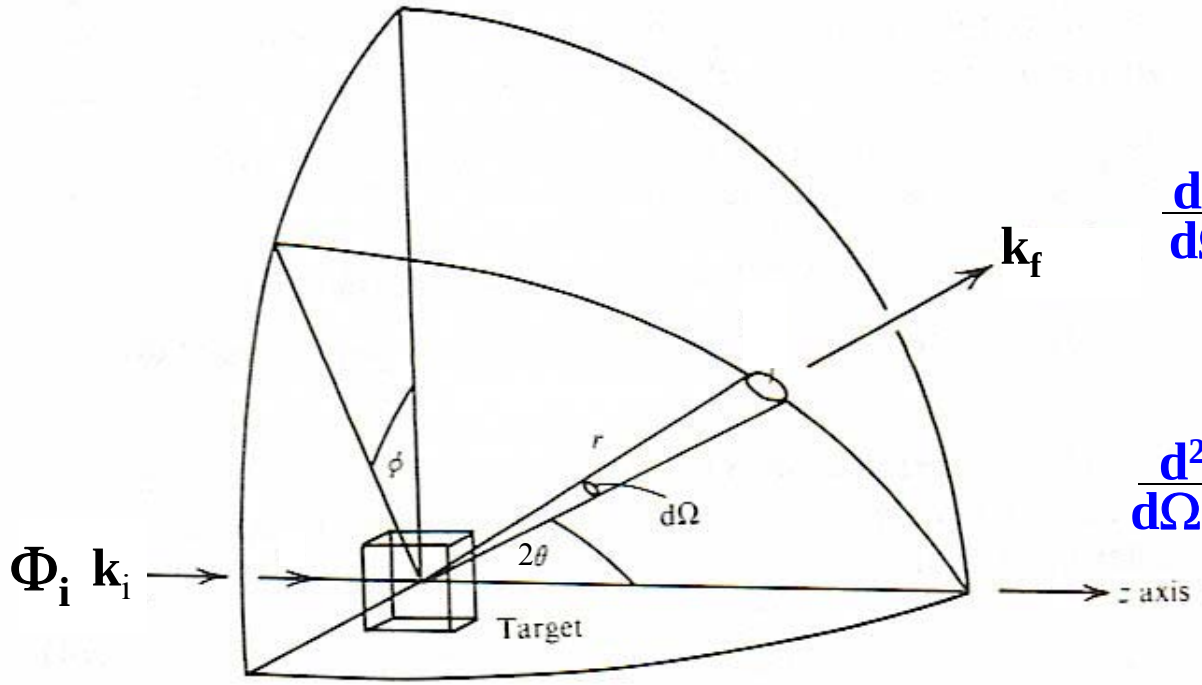
Consider an incident neutron beam with flux Φ_i (neutrons/sec/cm^2) and wave vector $\mathbf{k}_i$ on a sample.

We define three cross sections:

σ = Total cross section

$\frac{d\sigma}{d\Omega}$ = Differential cross section

$\frac{d^2\sigma}{d\Omega dE_f}$ = Partial differential cross section

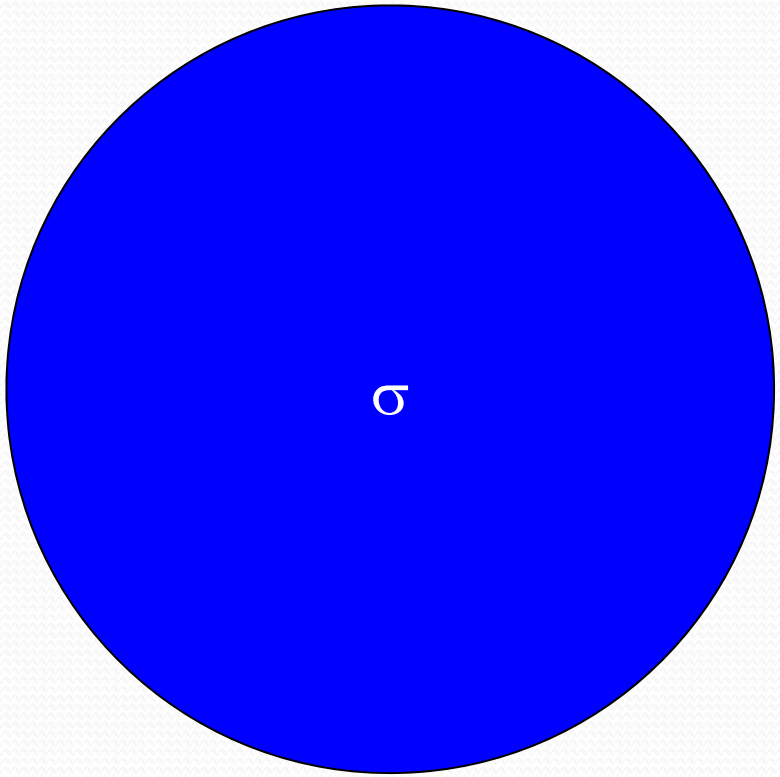


Neutron Scattering Cross Sections

What are the relative sizes of the cross sections?

Clearly: $\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int \frac{d^2\sigma}{d\Omega\, dE} d\Omega\, dE$

Thus: $\sigma >> \frac{d\sigma}{d\Omega} >> \frac{d^2\sigma}{d\Omega\, dE}$



$\leftarrow \frac{d^2\sigma}{d\Omega\, dE}$

Typically, $\frac{d\sigma}{d\Omega} \sim 10^6 \text{ x } \frac{d^2\sigma}{d\Omega\, dE}$

Neutron Scattering Cross Sections

What are the physical meanings of these three cross sections?

σ Probability that the nucleus will scatter a neutron.

$\frac{d\sigma}{d\Omega}$ Probability that the nucleus will scatter a neutron into $d\Omega$.
(Diffraction – structure. Signal is summed over all energies.)

$\frac{d^2\sigma}{d\Omega\, dE}$ Probability that the nucleus will scatter a neutron into $d\Omega$, having a final energy between E and dE.
(Inelastic scattering – dynamics. Small, but contains much info.)

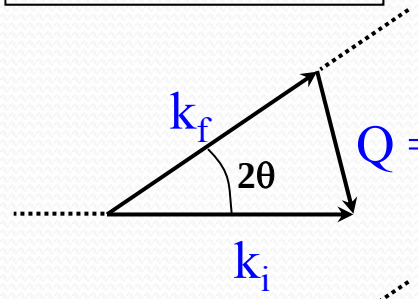
Basics of Neutron Scattering

Note that both of these cases are described by $\frac{d^2\sigma}{d\Omega\, dE}$

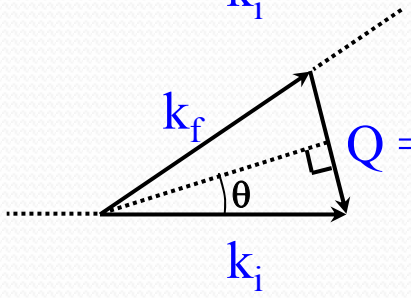
ELASTIC ($k_i=k_f$) $\neq \frac{d\sigma}{d\Omega}$

Elastic Scattering

- No change in neutron energy
- Probes changes in momentum only



$Q = k_i - k_f$



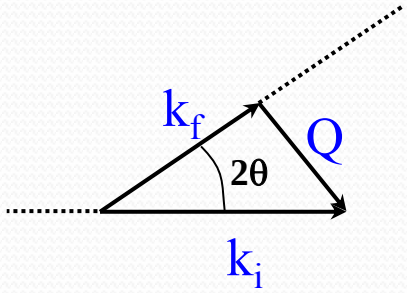
$\sin\theta = (Q/2)/k$

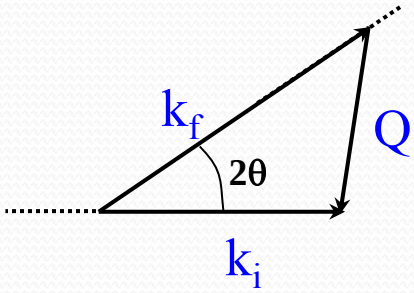
$Q = 2k\sin\theta = 4\pi\sin\theta/\lambda$

INELASTIC ($k_i \neq k_f$)

Inelastic Scattering

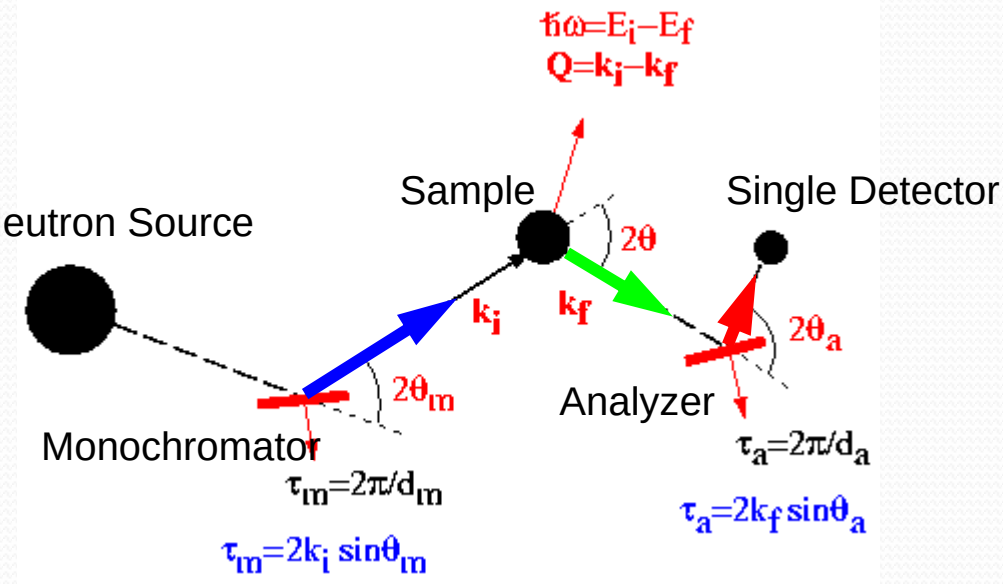
- Change in neutron energy
- Probes both momentum and energy changes

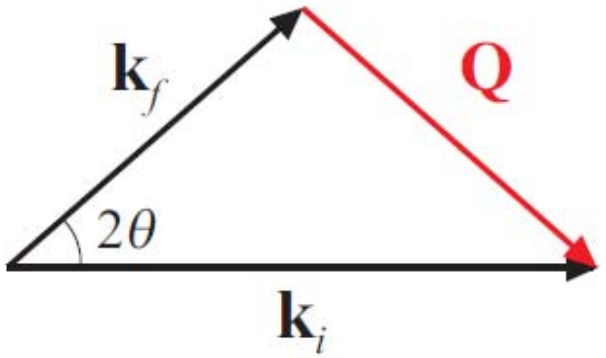




$\hbar\omega = \hbar\omega_i - \hbar\omega_f$ Energy gain ($\hbar\omega>0$) Energy loss ($\hbar\omega<0$)

Triple-Axis Spectroscopy

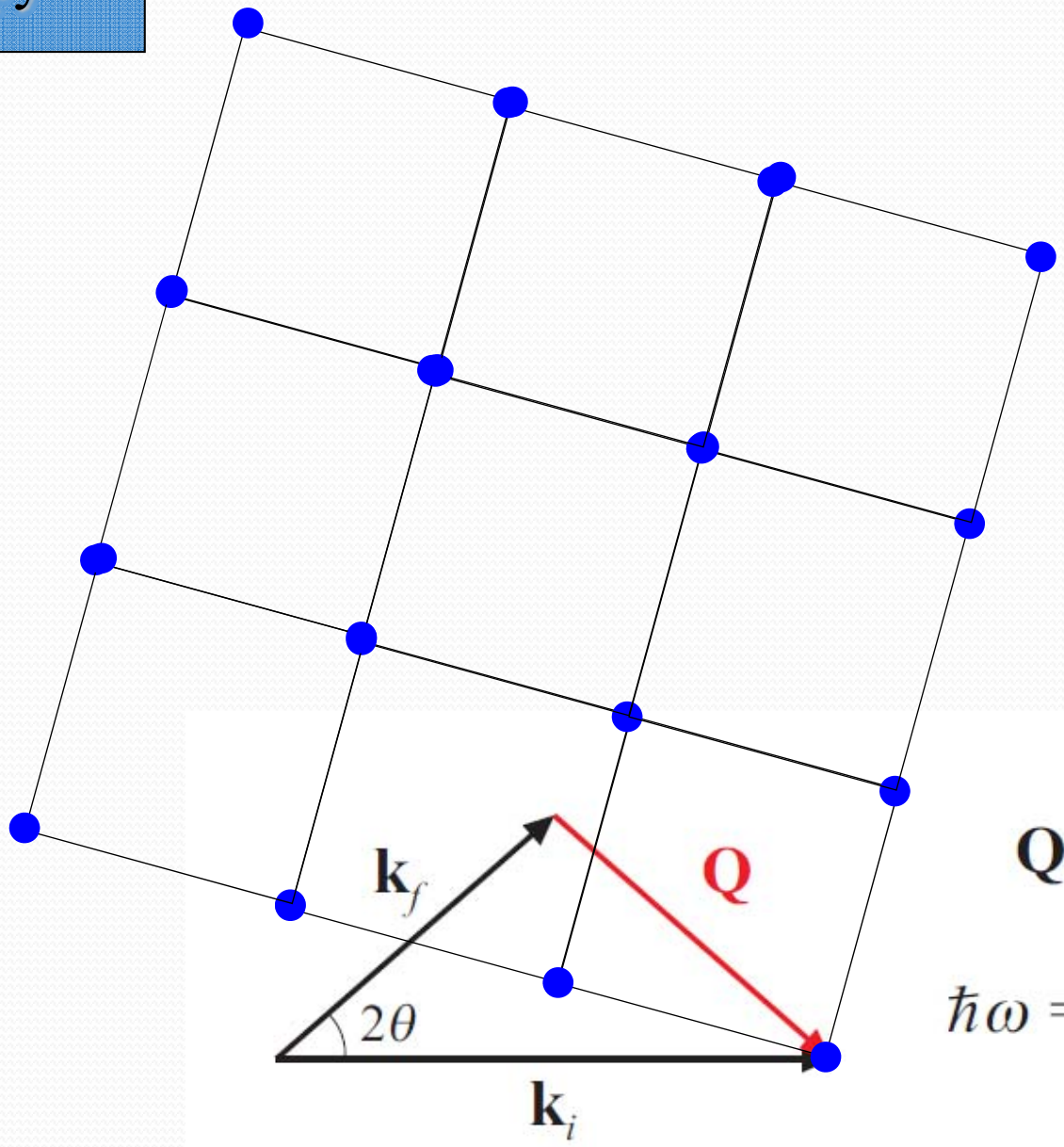




$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$$

$$\hbar\omega = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$$

Triple-Axis Spectroscopy

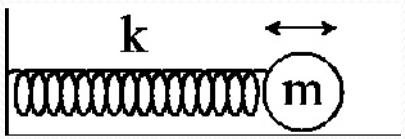


$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$$

$$\hbar\omega = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$$

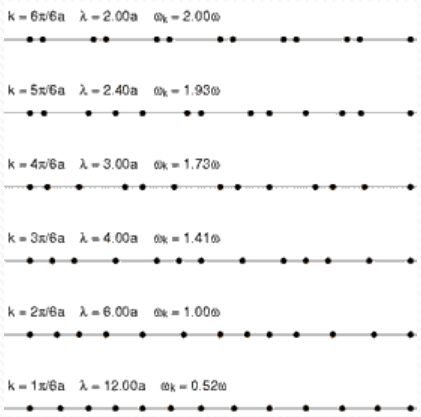
Dynamics of Solids

Correlated Motion in Ordered Solids



$$m\frac{d^2}{dt^2}x(t)+kx(t)=0 \qquad x(t)=A\cos\omega t=A\cos\left(\sqrt{\frac{k}{m}}\,t\right)$$

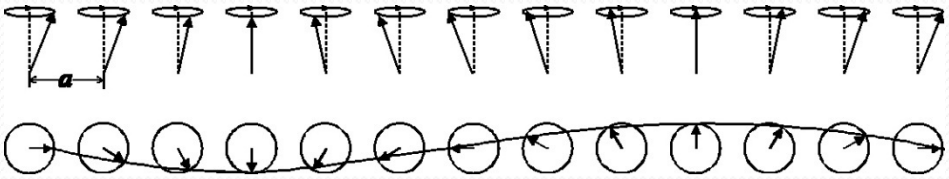
- Lattice vibrations: phonons



These vibrational modes occur as a result of the balance between the fluctuations (thermal or kinetic energy) and restoring forces (potential energy).
They are long-ranged in space and long-lived in time.

What happens if there are no restoring forces?
What happens if the spatial pattern changes with time?

- Spin precessions: magnons



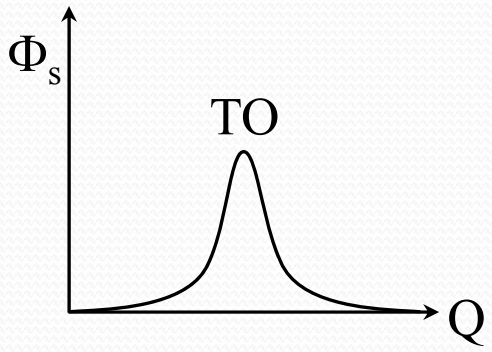
We use neutron spectroscopy to study the dynamics of solids

Neutron Inelastic Scattering

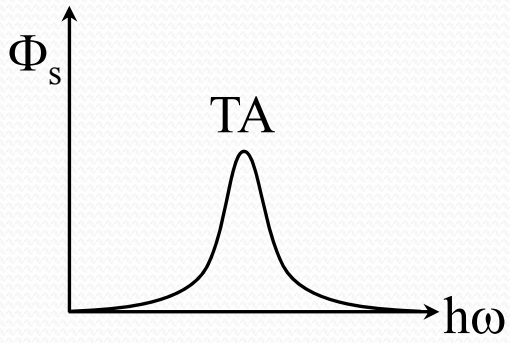
Neutron Measurements of Phonon Dispersions.

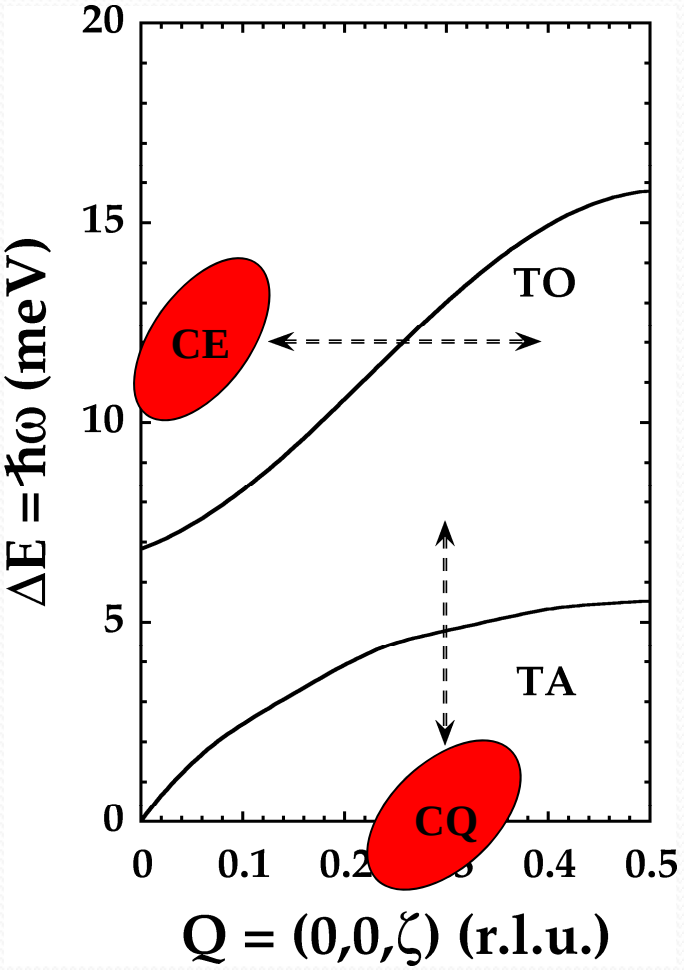
There are two primary methods of measuring the neutron scattering cross section S(Q,ω).

- Constant-E scans: vary Q at fixed hω.



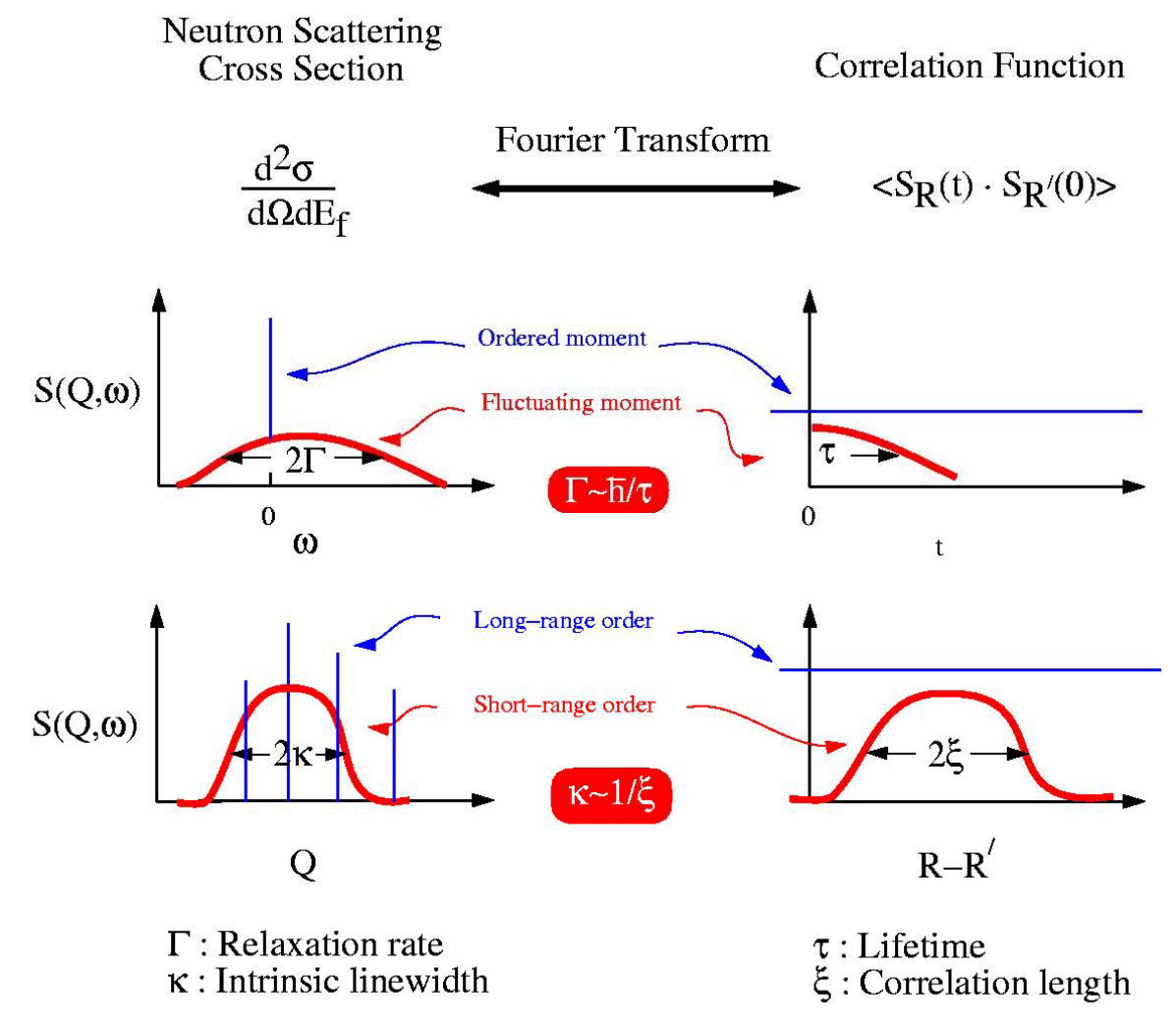
- Constant-Q scans: vary hω at fixed Q.





Neutron Inelastic Scattering

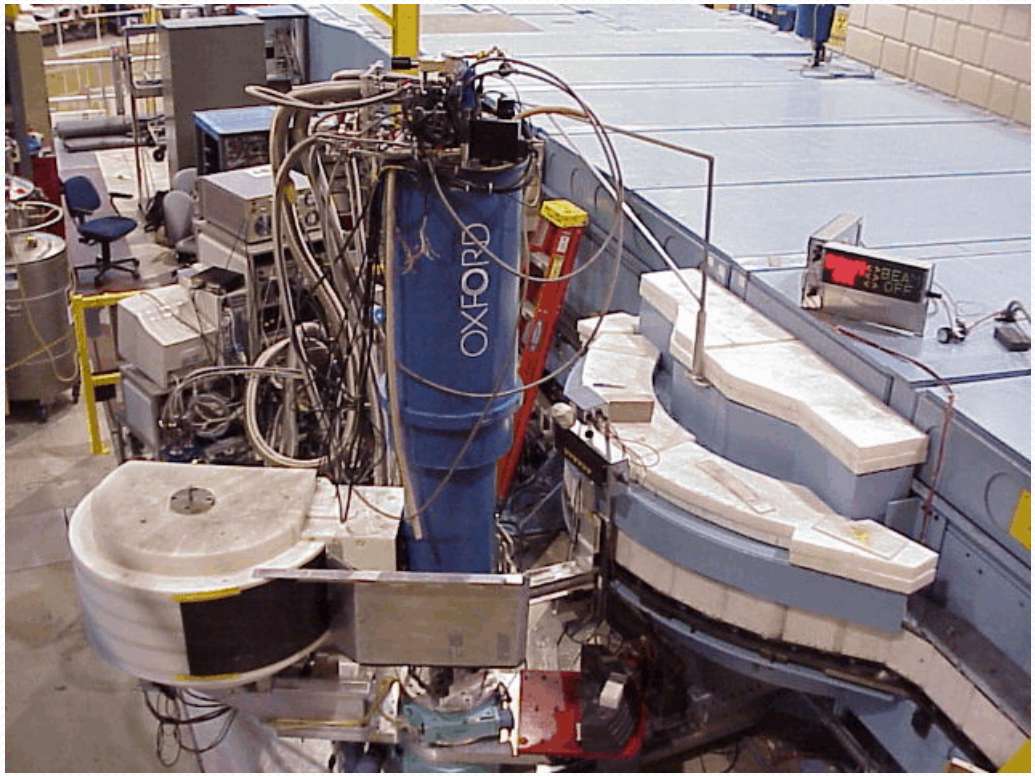
Spin-Spin Correlations



frequency (energy) vs. time

wave vector (momentum) vs. length

The Instrument SPINS

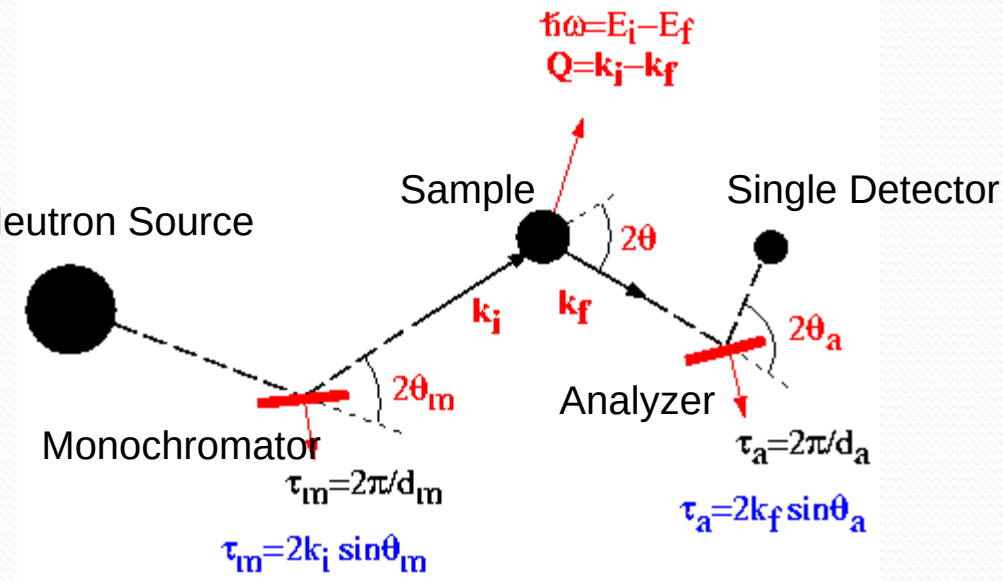


Why use SPINS for this study?
Because SPINS can

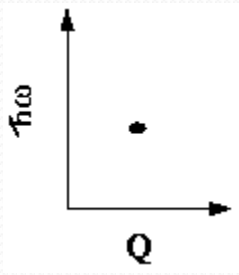
- easily access desired Q and $h\omega$
- cover the range $0.1<h\omega<10$ meV
- perform diffraction
- provide a flexible choice between high resolution or high intensity

The Instrument SPINS

SPINS Operation Mode I: Conventional Triple Axis (TAS)



A single point at a time



TAS is ideally suited for probing small regions of phase space

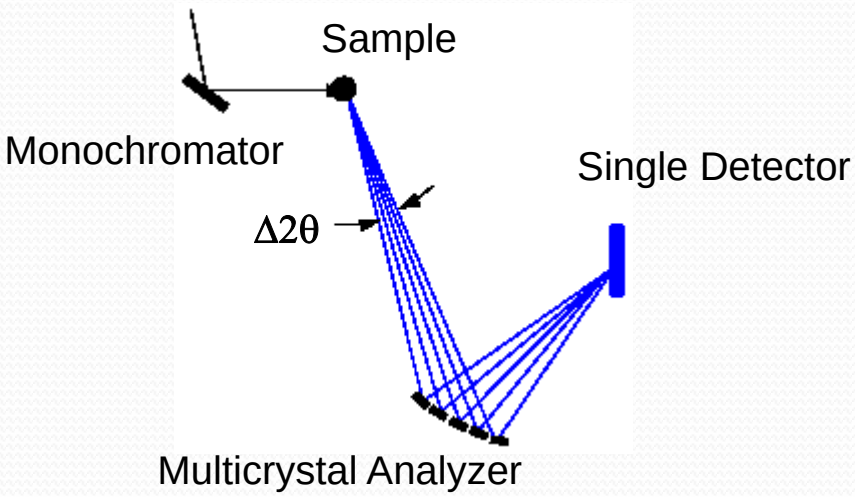
Shortcoming: Low data collection rate

Improvement

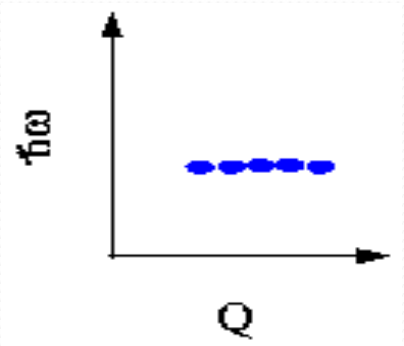
Multicrystal analyzer and position-sensitive detector

The Instrument SPINS

SPINS Operation Mode II: Horizontally Focusing Analyzer



Relaxed Q-resolution



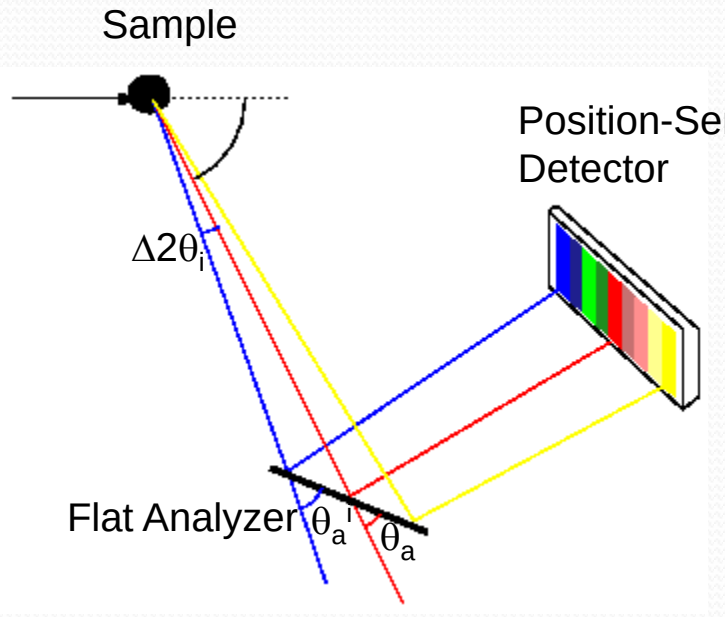
L = distance from sample to HF analyzer
w_a = total width of HF analyzer

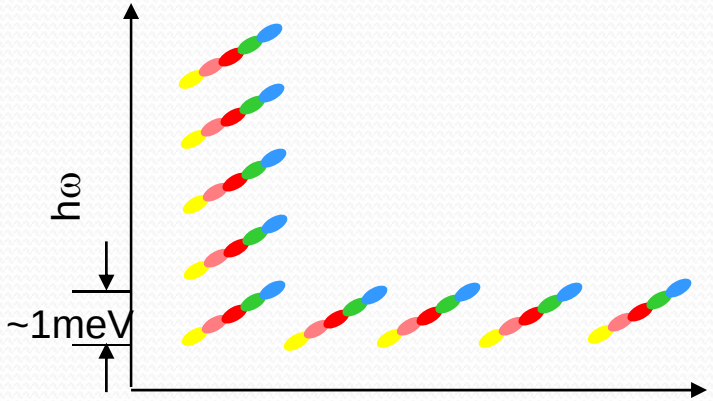
$\Delta 2\theta = w_a \sin\theta_a / L \sim 9$ degree for E_f=5 meV at SPINS

Useful for studying systems with short-range correlations

The Instrument SPINS

SPINS Operation Mode III: Multiplexing Detection System

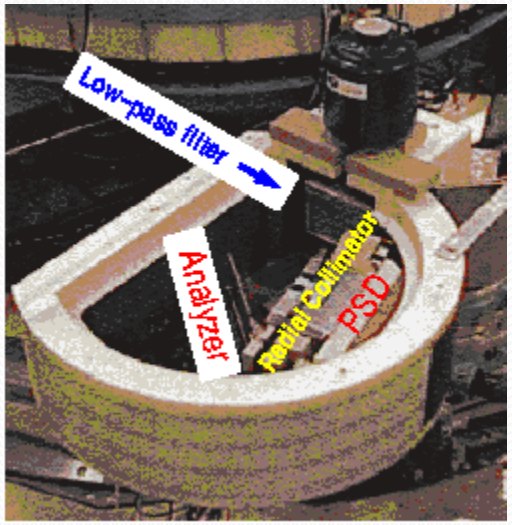




$\theta_a^i = \theta_a + \Delta 2\theta_i = \theta_a - \text{atan}(x \sin\theta_a/(L+x\cos\theta_a))$

$k_f^i = \tau_a/2\sin\theta_a^i$

$\mathbf{Q_i = k_i - k_f^i}$

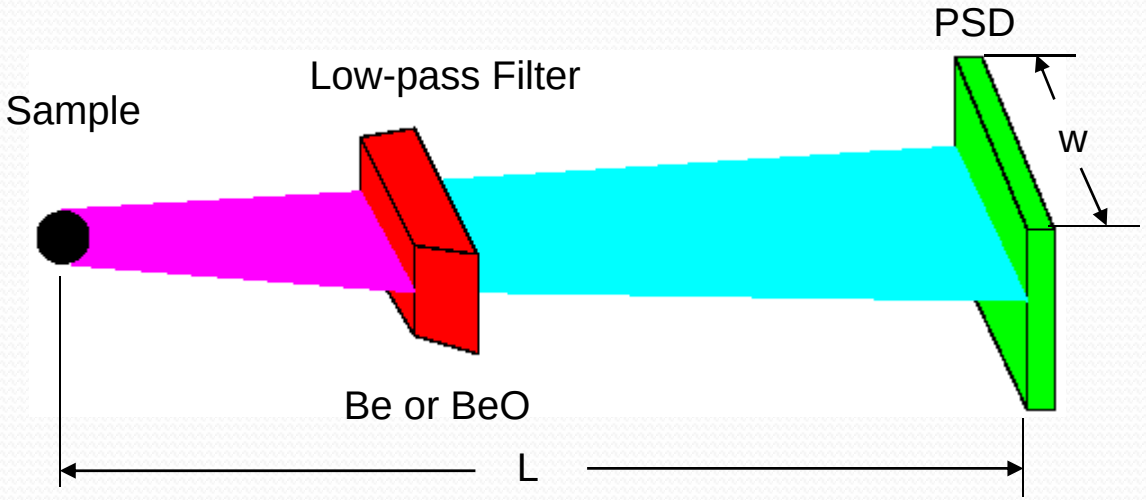


Probes scattering events at different energy and momentum transfers simultaneously

Survey (hω-Q) space by changing the incident energy and scattering angle

The Instrument SPINS

SPINS Operation Mode IV: Position Sensitive Detector in 2-Axis Mode



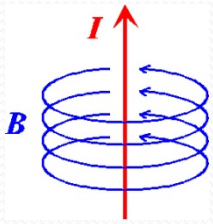
The filter passes only those neutrons with $0 < E_f < E_{cutoff}$

The PSD measures $\int_{E_i-E_{cutoff}}^{E_i} S(Q,\omega)\, d\omega$

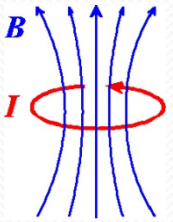
Large angular acceptance = w / L ~ 11^o for SPINS

Basics of Magnetism

- Why are some materials magnetic? Because of the electrons!
  - In classical physics, a flow of charges (i.e. current) will generate a magnetic field. (Ampere's Law) Therefore, a closed loop of current will generate a magnetic field just like a magnetic dipole.
  - In quantum physics, electrons exhibit an intrinsic magnetic field without angular motion. This quantized magnetic moment is called a "spin", and the eigenstates of spin can be either up or down w.r.t an arbitrary axis. (↑ = ½ or ↓ = -½)

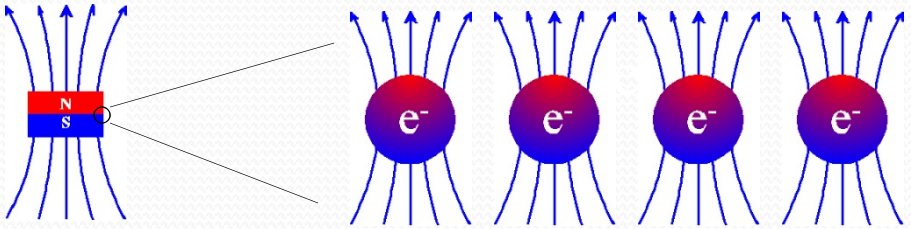


Interestingly, though neutrons are charge neutral, they exhibit a magnetic moment. This is why neutrons are able to scatter from the magnetic moments of electrons.



$$\vec{\mu} = \pi r^2 I \hat{n}$$

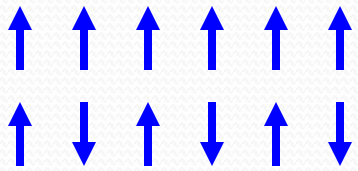
electromagnet

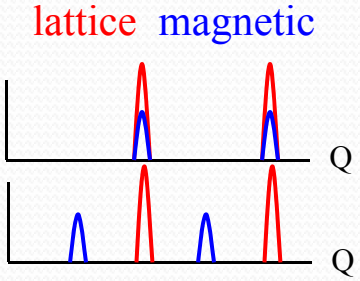


permanent magnet

Magnetic Order

- Magnetic interaction energy
  - Isotropic Heisenberg type: $E = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$
    - $J_{ij} < 0$ for the nearest neighbors:
    - $J_{ij} > 0$ for the nearest neighbors:





  - Noncollinear order may also exist due to the combinations of ferromagnetic/antiferromagnetic interactions and/or antisymmetric exchange interactions of the type:

$$E = \sum_{i,j} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$$

- Paramagnetic phase
  - If temperature is greater than the interaction energy ($kT >> J\,|\mathbf{S}|^2$), thermal energy will overcome the binding energy for the magnetic order.
  - As a result, spins will lose long-range order and fluctuate rapidly. In other words, they become disordered.

- Other types of disordered phases
  - Spin glass: frozen disordered magnetic moments
  - Geometrical frustration

Calculation of Magnetic Neutron Scattering Intensity

- Magnetic neutron scattering cross section

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}\omega} = r_o^2 \frac{k_f}{k_i} S(\mathbf{Q},\omega)$$

$$\text{where, } S(\mathbf{Q},\omega) = \sum_{\alpha,\beta}(\delta_{\alpha\beta} - \tilde{Q}_\alpha \tilde{Q}_\beta) \sum_{\lambda,\lambda'} p_\lambda \sum_{l,d}\sum_{l',d'} f_d^*(\mathbf{Q}) f_{d'}(\mathbf{Q}) \exp\{i\mathbf{Q}\cdot(\mathbf{R}_{l'd'} - \mathbf{R}_{ld})\}$$

$$\times \left\langle \lambda \left| \hat{S}_{ld}^{\alpha} \right| \lambda' \right\rangle \left\langle \lambda' \left| \hat{S}_{l'd'}^{\beta} \right| \lambda \right\rangle \delta(\hbar\omega + \hbar\omega_\lambda - \hbar\omega_{\lambda'})$$

- But if we consider only up and down spins for diffuse quasi-elastic scattering, all we need is the following simple equation:

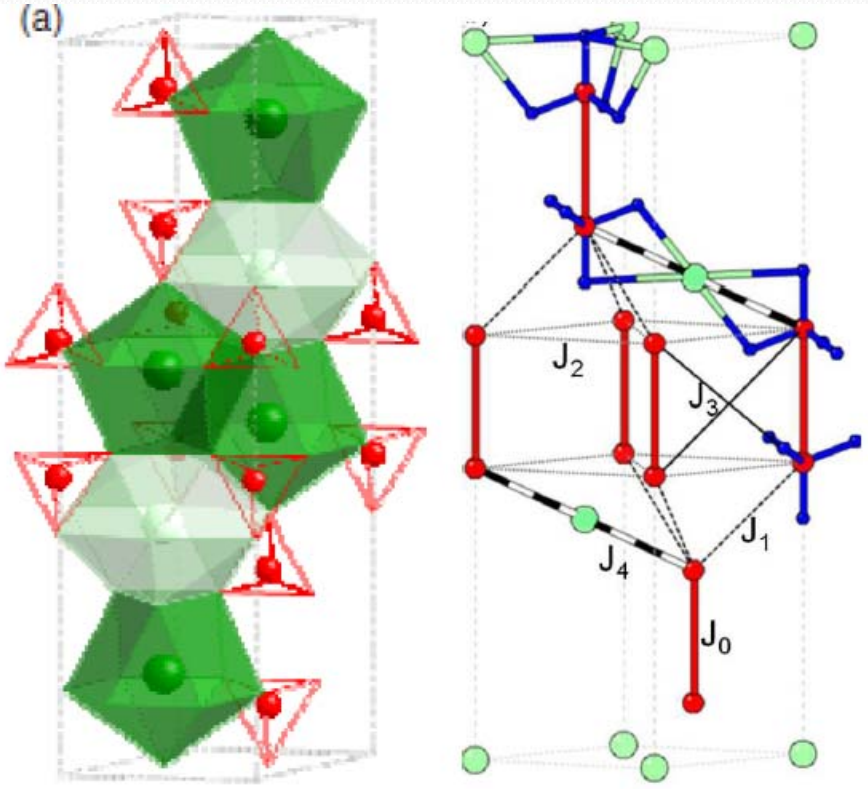
$$I(\mathbf{Q}) \propto \left| \sum_{\mathbf{R}} f_{\mathbf{R}}(\mathbf{Q}) \sigma_{\mathbf{R}} e^{i\mathbf{Q}\cdot\mathbf{R}} \right|^2$$

f : magnetic form factor

$\sigma = -1, \text{ or } 1$

Magnetic Properties of $Ba_3Mn_2O_8$

- The chemical structure of BMO involves double-layered triangular lattices in the basal plane, stacked along the c-axis with a periodicity of three.



- The hexagonal antiferromagnetic bilayer $Ba_3Mn_2O_8$ is a quasi-2D frustrated antiferromagnet with a quantum critical phase diagram (H vs. T).

- In applied magnetic field, BMO has two sequential magnetically ordered phases (separated by 4 quantum critical points)

Magnetic Properties of $Ba_3Mn_2O_8$

In order to understand the quantum critical phase diagram of BMO, we need to understand the zero-field exchange paths and constants.

(The critical field value is directly related to the magnetic excitation energy)

Now the question are:

(1) What do we need to measure in order to determine the exchange paths and exchange constants between a single dimer and interdimer ?

(2) What type of sample (powder or single crystal) we should use?

While the measurements of powder sample provide important information about the underlying physics of the system, measurements of single crystal sample can uncover the hidden information.

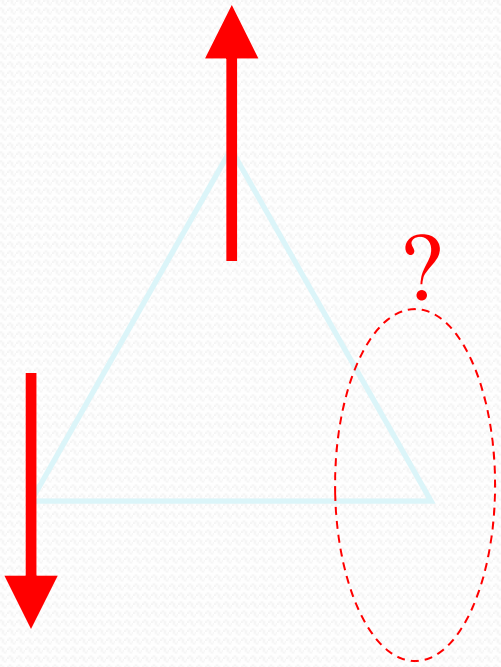
In the case of BMO, you will see that measurements on a single crystal sample are essential to determine the correct exchange paths and constants.

What is Geometrical Frustration?

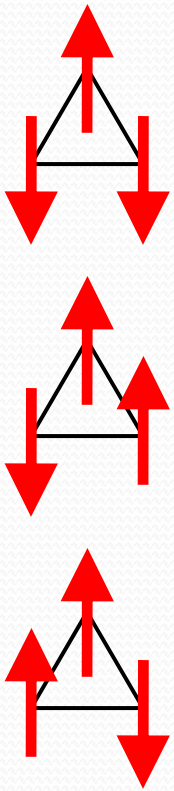
- Definition according to Wikipedia
  - "a phenomenon in which the geometrical properties of the atomic lattice forbid the existence of a unique ground state, resulting in a nonzero residual entropy"

- To put it simply, it means a situation in which things do not order because of their geometrical property, even when the temperature is low enough to induce order of some sort.
  - Degenerate ground states: there are many possible ways to satisfy the condition of the lowest energy.
  - Zero-energy fluctuations: since the degenerate ground states are equal in energy, the system will easily move from one state to another and experience no restoring force.
  - Residual entropy at T = 0 K: configurational entropy due to multiple possible choices

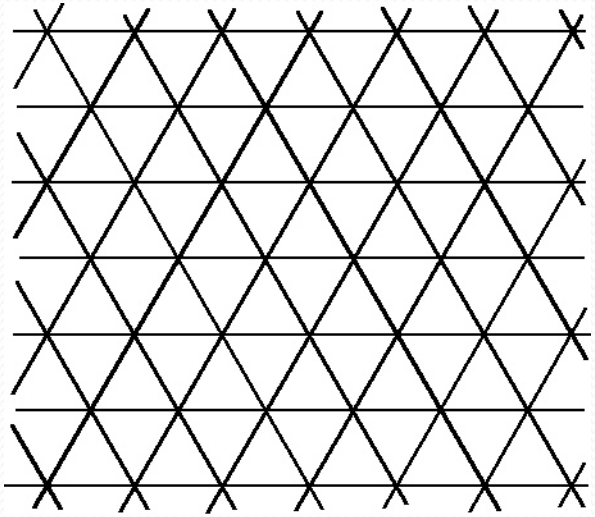
Example of Geometrical Frustration



Antiferromagnetic Ising spins
(if only up or down
orientations are allowed)



infinite lattice



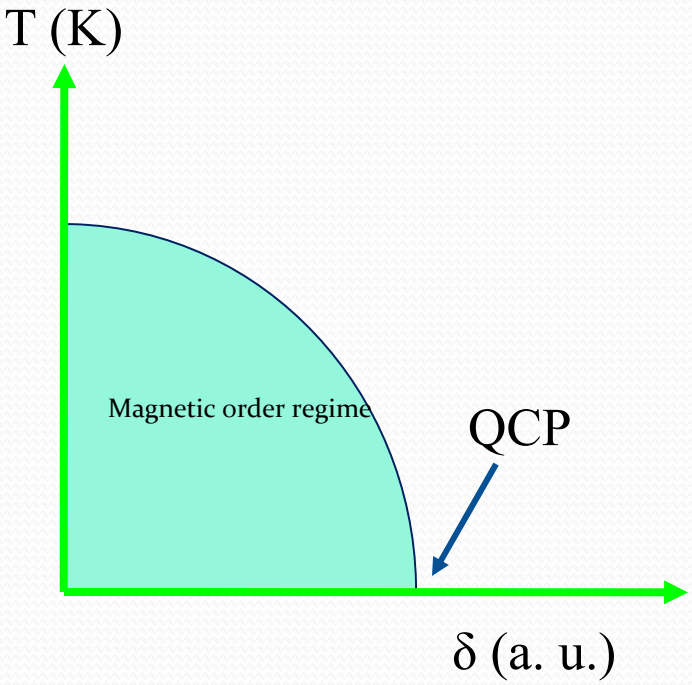
Infinite number of
degenerate ground strates!

Quantum Magnetic Phase

- A magnetic system enters into a quantum magnetic phase at T = 0 K via second order phase transition.

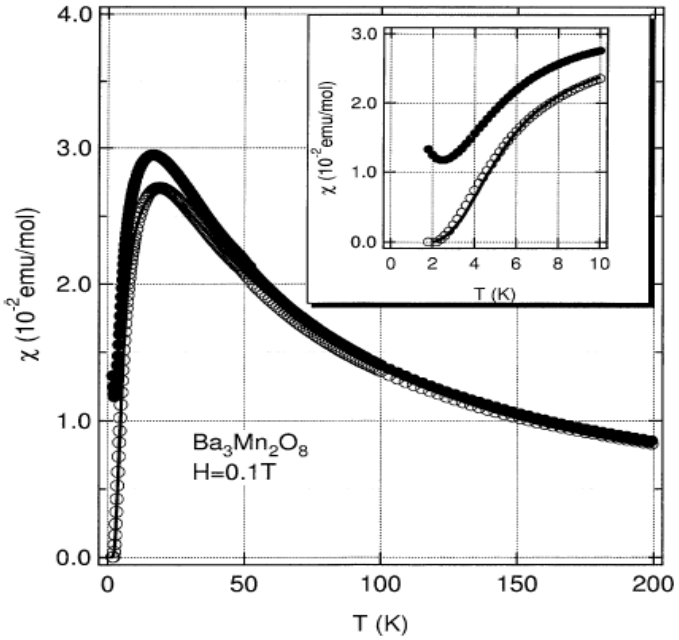
- The quantum phase is described by the divergence of the order parameter in both space and time.

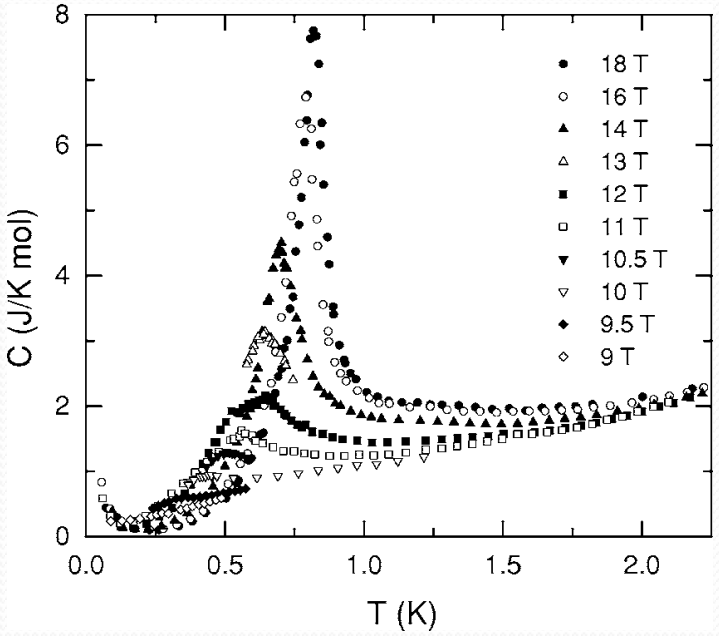
- The system can be driven to a quantum critical point using an external tuning parameter, such as magnetic field, pressure, or chemical doping of the crystal structure.

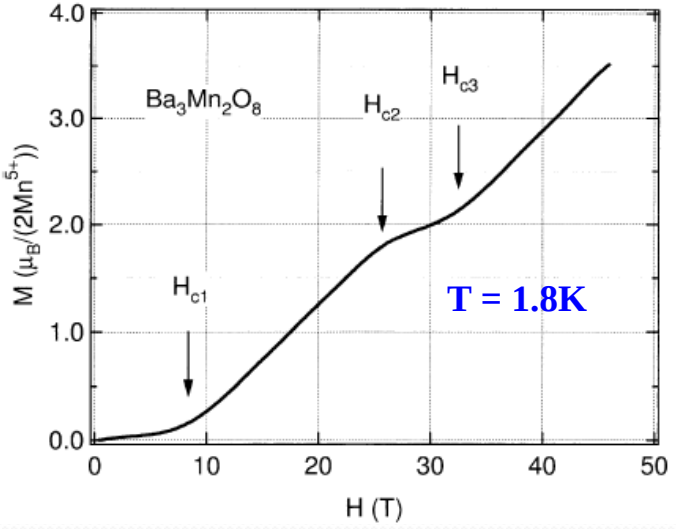


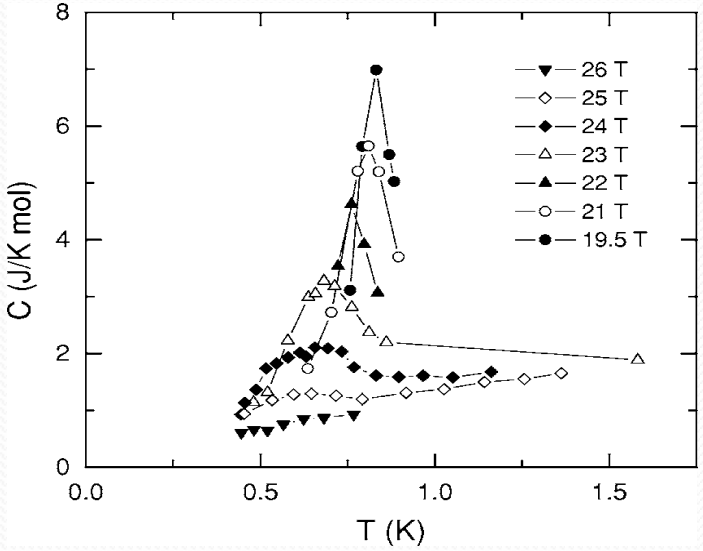
- Neutron scattering is a powerful technique with which to explore the dynamic properties of the system in quantum critical state.

Magnetic Properties of $Ba_3Mn_2O_8$ …









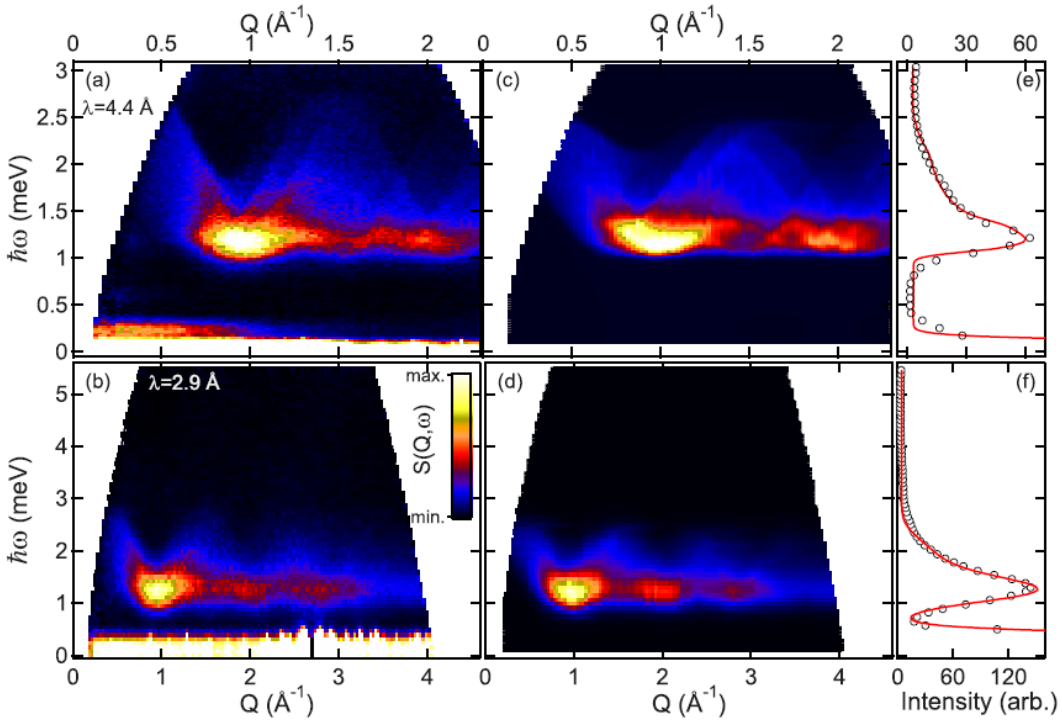
Neutron Scattering Measurements of BMO

Measurements using powder sample:

T = 1.4 K

- At T = 1.4 K, a single dispersion curve is observed, indicating singlet ground state

- Measurements on powder sample also suggest a spin gap of ~ 1 meV



The Heisenberg Hamiltonian describing the dimer and interdimer magnetic interaction is given by,

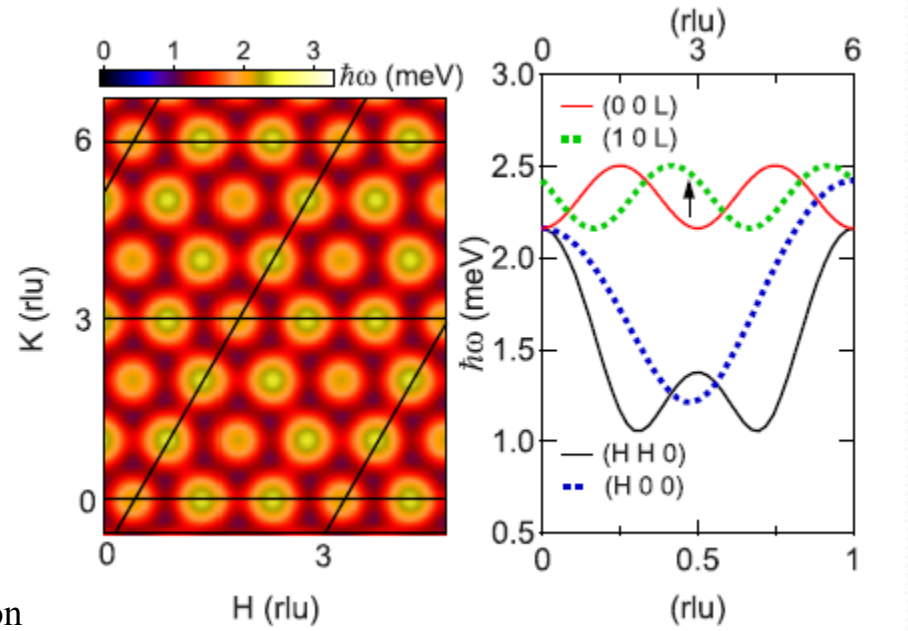
$$\aleph = \sum_{i,j} \frac{J_{i,j}}{2} S_i \bullet S_j + D \sum_i \left(S_i^z\right)^2 - g\mu_B H \sum_i S_i^z$$

where D is single-ion anisotropy determined from the μSR measurement.

Calculations suggest triplet excitation

The calculations were performed using RPA dispersion for Heisenberg exchange coupled dimers, given by

$$\hbar\omega(\mathrm{Q}) = \sqrt{\Delta^2 + M^2 \Delta \zeta(Q) R(T)}$$



(Where Δ is the spin gap, R(T) is the thermal population Difference between ground state and excited state, M is the Transition matrix element and ζ(Q) is the Fourier sum over interactions beyond dimer exchange.)

$$S(\mathrm{Q},\omega) = \frac{4e^{2J\beta}\left[1-\cos(\mathrm{Q.d})\right]}{\left(e^{2J\beta}+3e^{J\beta}+5e^{-J\beta}\right)\hbar\omega(\mathrm{Q})}\,\delta\left[\hbar\omega-\hbar\omega(\mathrm{Q})\right]$$

Calculation includes weak inter-dimer interaction that is believed to propagate triplet excitations.

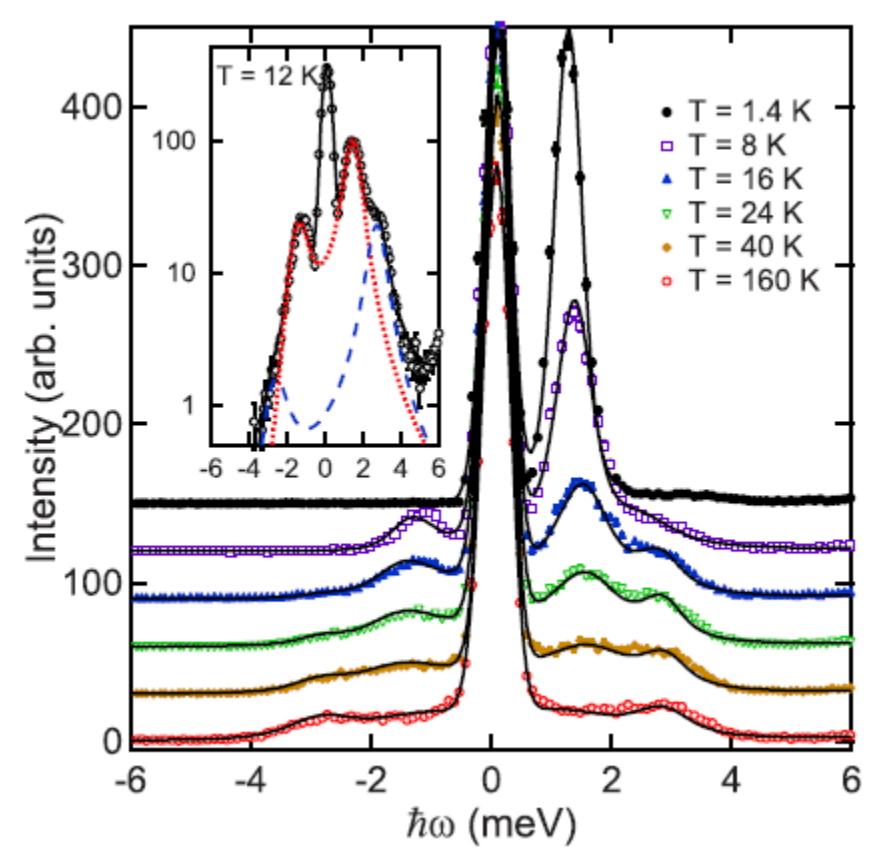
(M. Stone et al., PRB 77, 134406 (2008))

Measurements using powder sample continued …

- Interestingly, measurements at relatively higher temperature show the singlet peak at ~ 1.25 meV splits into two peaks at ~ 1.5 and 2.9 meV

- Singlet-triplet excitations ??

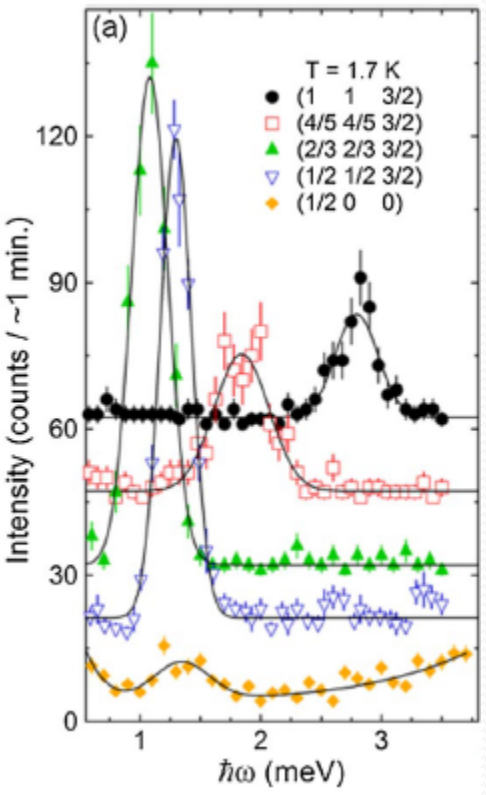
Data are fitted by two Lorentzian functions,

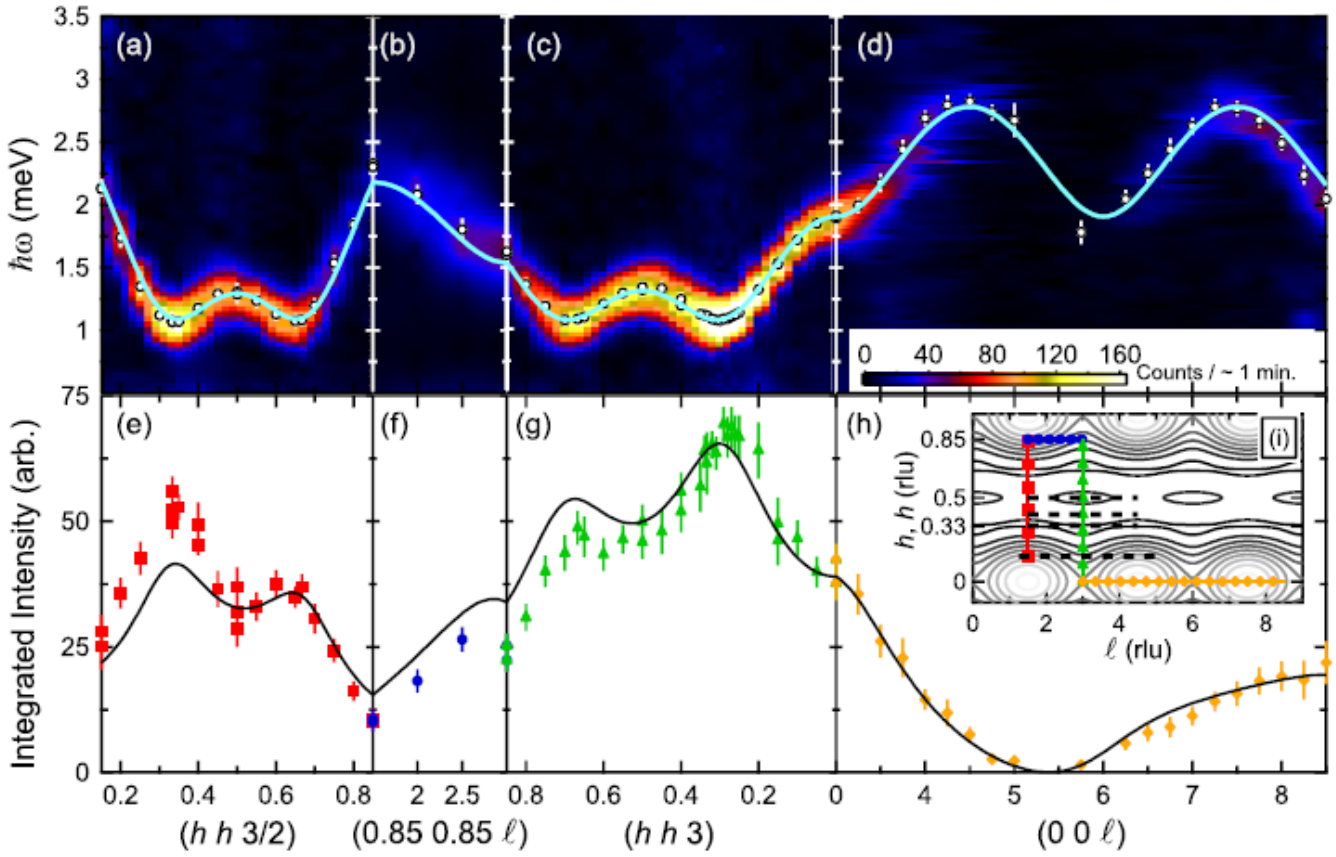


$$I(\omega)=(n(\omega)+1)\left(\frac{A\Gamma_1}{(\omega-\omega_1)^2+\Gamma_1^2}-\frac{A\Gamma_1}{(\omega+\omega_1)^2+\Gamma_1^2}+\frac{B\Gamma_2}{(\omega+\omega_2)^2+\Gamma_2^2}-\frac{B\Gamma_2}{(\omega+\omega_2)^2+\Gamma_2^2}\right)$$

Measurements on single crystal samples are necessary to confirm this.

Measurements using single crystal sample: (M. Stone et al., PRL 100, 237201 (2008))





Clearly, the dispersion curve is different from the one obtained from the powder sample

Instead of a single dispersion curve, suggesting singlet state, multiple branches are observed.

Good fit of the data is obtained by including the NNN interaction in the Hamiltonian, given by

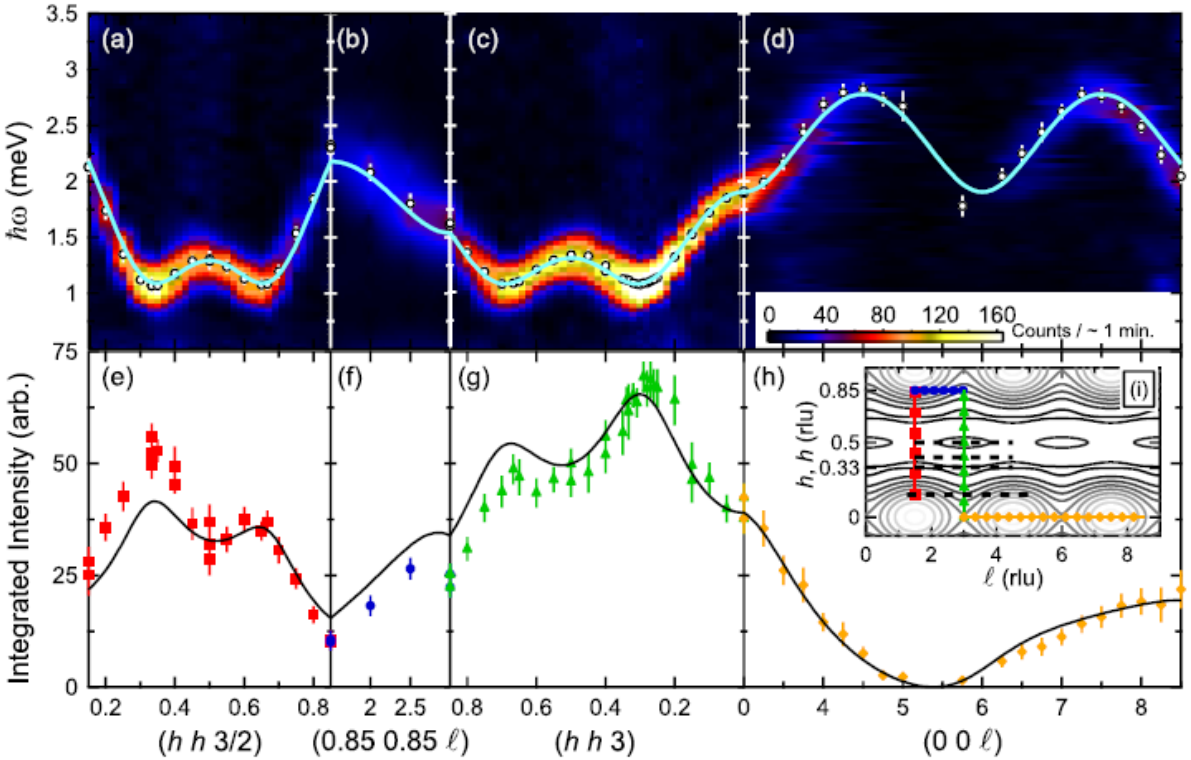
$$\hbar\omega^{\nu}(\mathbf{Q}) = \sqrt{\Delta_{\nu}^2 + \tfrac{8}{3}\Delta_{\nu}\mathcal{J}(\mathbf{Q})R(T)},$$

where

$$R(T) = \frac{1 - \exp(-J_0\beta)}{1 + 3\exp(-J_0\beta) + 5\exp(-3J_0\beta)}$$

$$\Delta_0 = J_0 + 2D/3 \qquad J_0 - D/3$$

$$\mathcal{J}(\mathbf{Q}) = J_1\omega_1 + 2(J_2 - J_3)\omega_2 + J_4\omega_4$$



$$\omega_1 = \cos\left(\frac{2\pi}{3}[-h + k + l]\right) + \cos\left(\frac{2\pi}{3}[-h - 2k + l]\right) + \cos\left(\frac{2\pi}{3}[2h + k + l]\right)$$

$$\omega_2 = \cos(2\pi k) + \cos(2\pi[h + k]) + \cos(2\pi h)$$

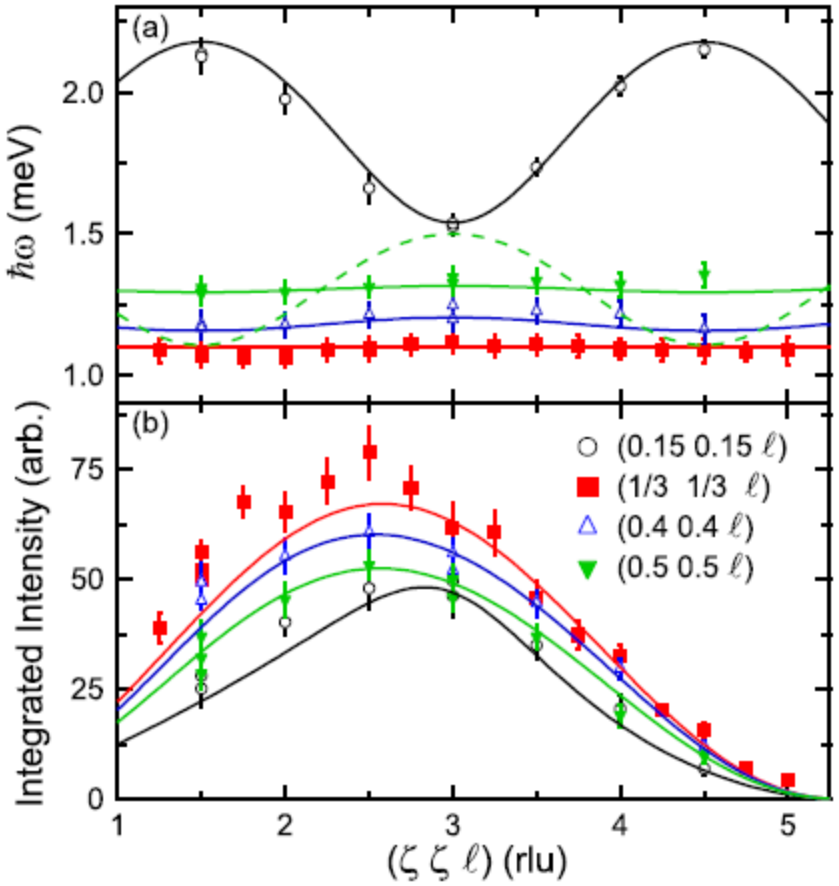
$$\omega_4 = \cos\left(\frac{2\pi}{3}[2h - 2k + l]\right) + \cos\left(\frac{2\pi}{3}[2h + 4k + l]\right) + \cos\left(\frac{2\pi}{3}[-4h - 2k + l]\right)$$

Note the ω_4 term (resulting from NNN interaction)

- Inclusion of NNN interactions is necessary to explain the dispersion curve

- The NNN interaction term in the Hamiltonian suggests that the interdimer interaction plays an important role in this system, thus *extends the exchange path along c**

- If we set $J_4 = 0$ in the previous equation, the dispersion behavior cannot be explained correctly (as shown by the dashed green curve in upper panel)



SUMMARY

A cold-neutron, triple-axis spectrometer, such as SPINS, is a vital tool for explorations of low-energy magnetic phenomena.

Magnetic properties of a system are governed by the underlying magnetic exchange couplings and the connecting paths.

Measurements of single crystal samples can provide the most information about the underlying spin dynamics.