Summer School on Methods and Applications of Neutron Spectroscopy
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Magnetic phase transition and spin fluctuations in the geometrically frustrated antiferromagnetic spinel $CdCr_2O_4$: An experiment using the SPINS cold-neutron triple axis spectrometer

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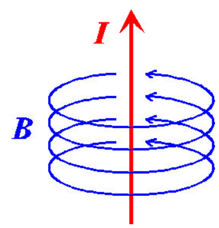
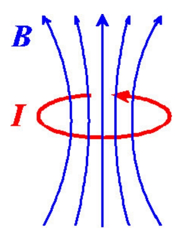
Basics of magnetism

- Why some materials are magnetic? It's electrons!
  - In classical physics, a flow of charges (or current) will generate magnetic field. (Ampere's Law) Therefore, a closed loop of current will have a magnetic field just like a magnetic dipole.
  - In quantum physics, electrons have intrinsic magnetic field with no angular motion. This quantized magnetic moment is called a "spin", and their eigenstates can be either up or down. (↑ = $\frac{1}{2}$ or ↓ = -$\frac{1}{2}$)



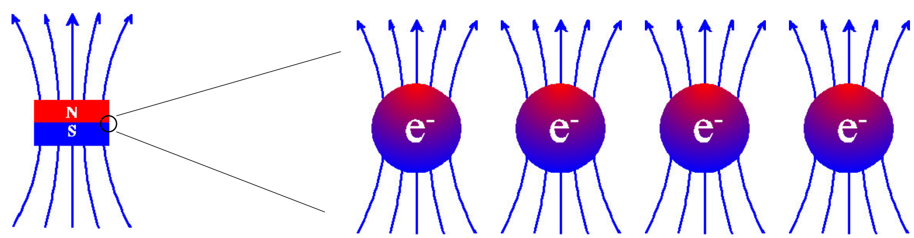
There are more, but let's not worry about these for now:

- Orbital motions of electrons may also add to the electronic magnetic moment
- Protons and neutrons in nuclei also have magnetic moments.



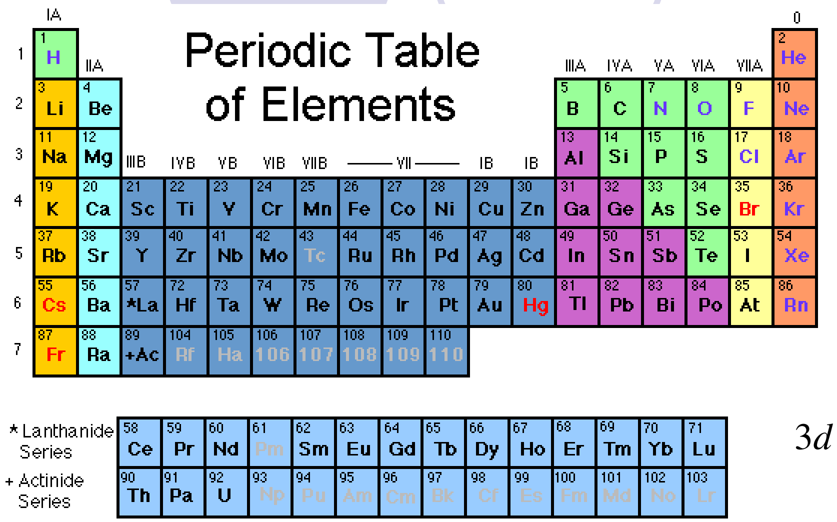
$$\vec{\mu} = \pi r^2 I \hat{n}$$

electromagnet

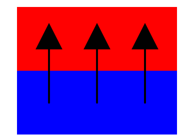


permanent magnet

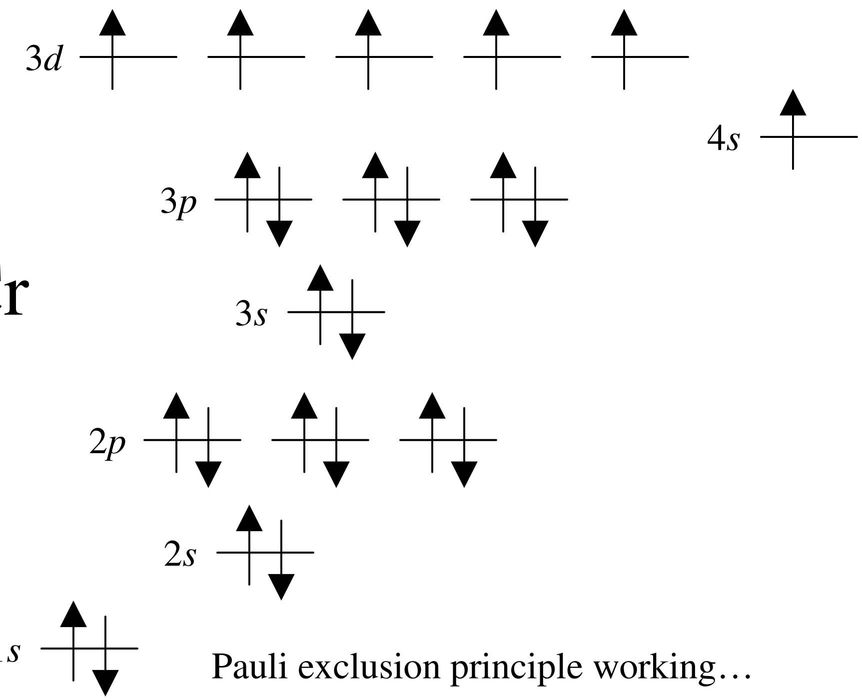
Electron energy levels



Cr^{3+}: $3d^3 4s^0$



Cr

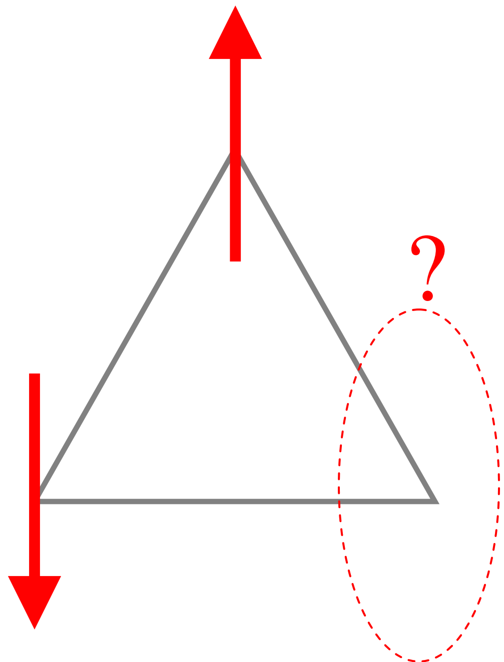


Pauli exclusion principle working…

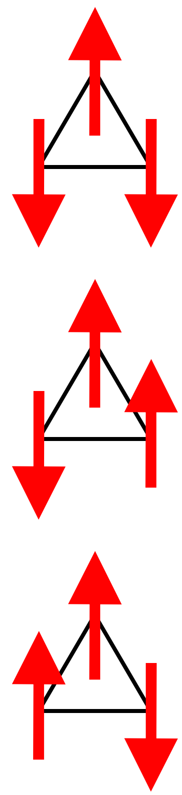
What is geometrical frustration?

- 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 there is a driving force to order
  - 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

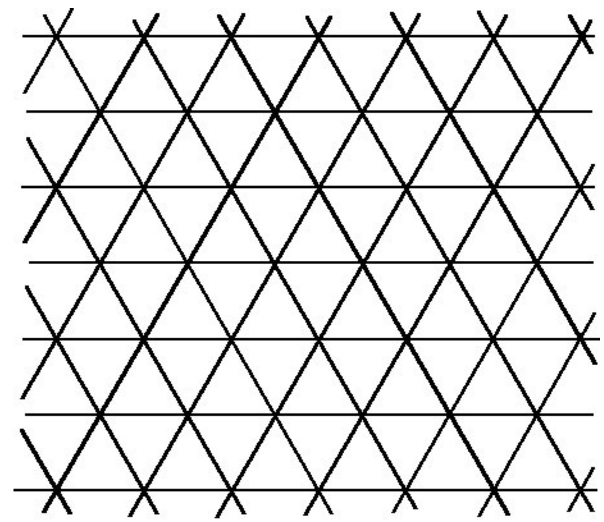
Example of geometrical frustration: antiferromagnet



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

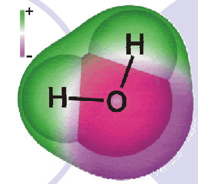


infinite lattice

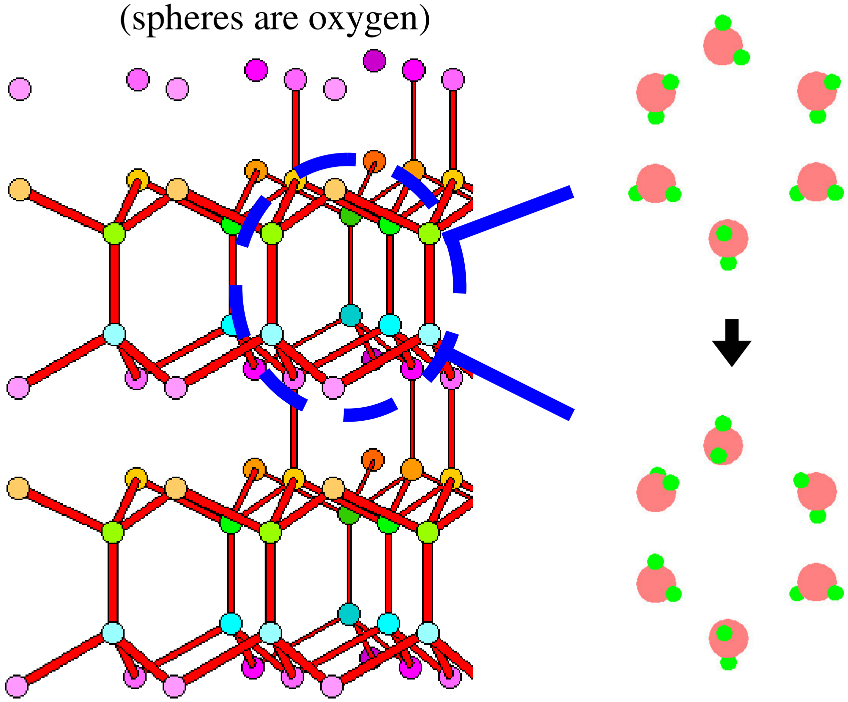


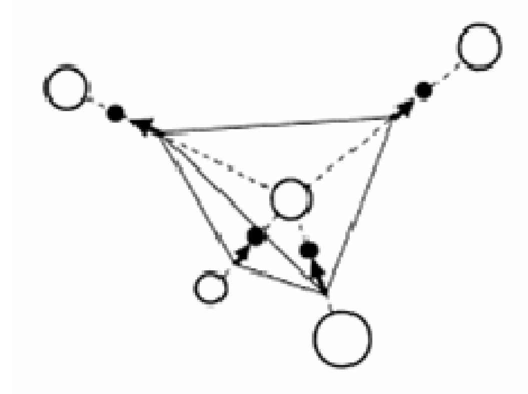
Infinite number of
degenerate ground strates!

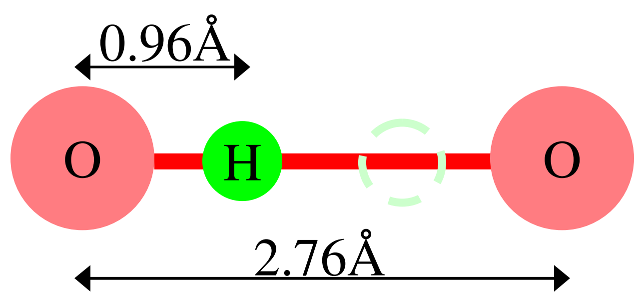
Example of geometrical frustration (II):



Structure of ice
(spheres are oxygen)





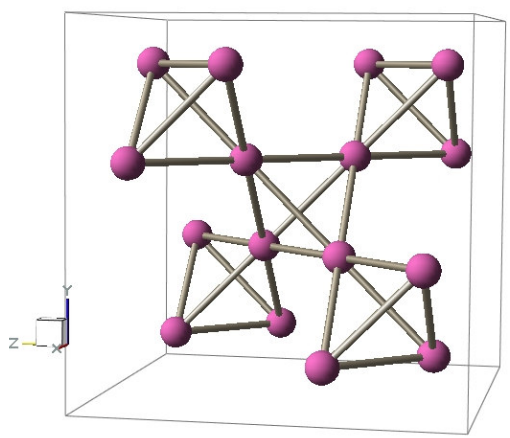


Residual entropy due to proton disorder

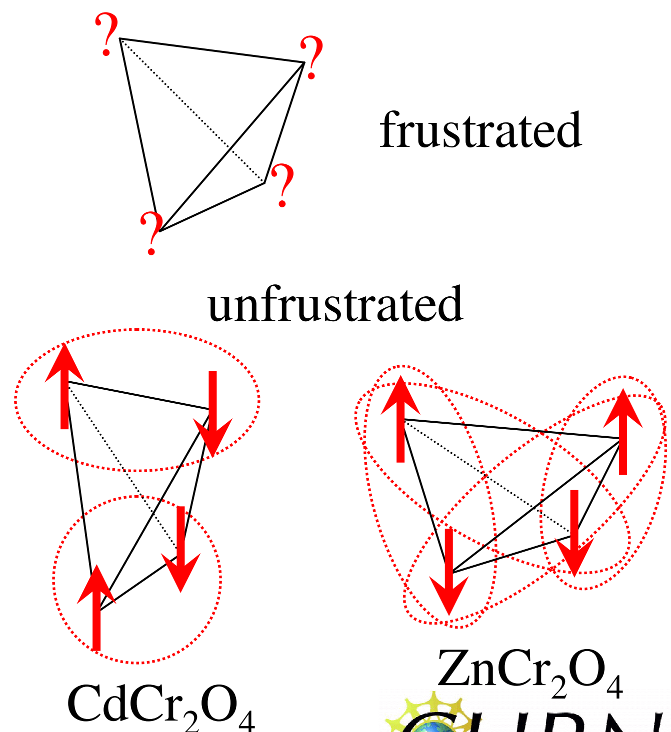
$$S_o \cong k_B \ln\left[2^{2N_A} \times (6/16)^{N_A}\right]$$
$$= N_A k_B \ln(3/2)$$
$$= 0.81\ \mathrm{cal/K \cdot mol}$$

$CdCr_2O_4$: Cr^{3+} ($3d^3$, $S = 3/2$)

Magnetic Cr^{3+} ions form a lattice of corner-shared tetrahedra
Similar lattices are found in spinel (AB_2O_4) B-sites or pyrochlores ($A_2B_2O_7$)
If the lattice is cubic, antiferromagnetic spins won't order down to 0 K!



But $CdCr_2O_4$ eventually orders at very low temperatures. How?



Magnetic exchange energy between a pair of spins is $E = J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j$. If $J_{ij} > 0$, then $\mathbf{S}_i$ and $\mathbf{S}_j$ will become antiparallel to each other

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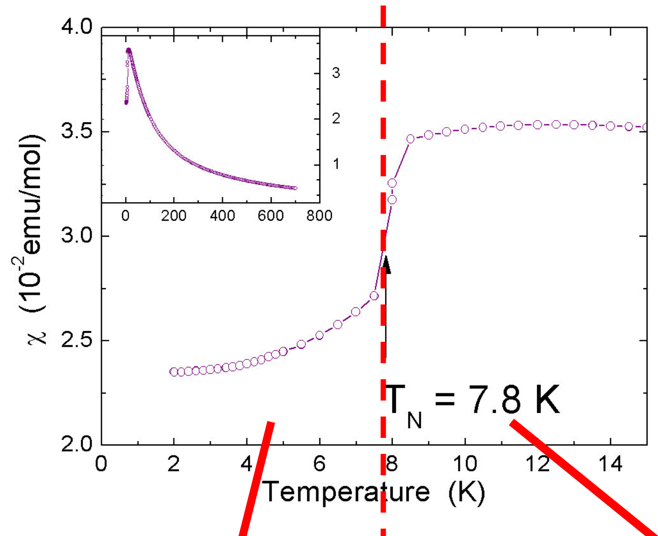
Magnetic phase transition in $CdCr_2O_4$

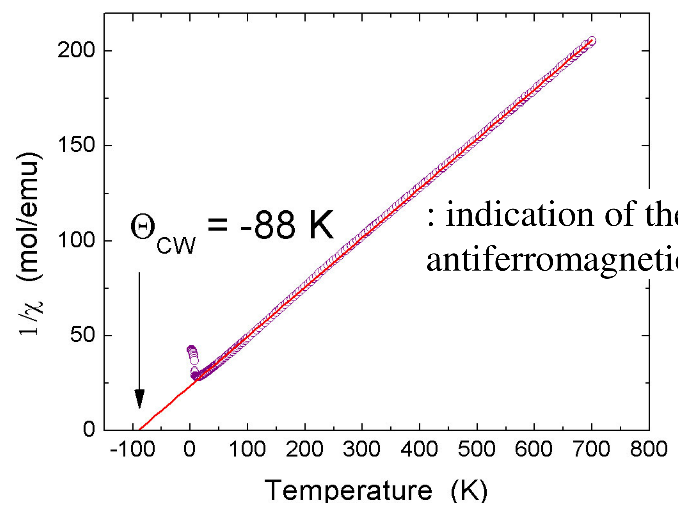
Magnetic susceptibility
$\chi = dM/dH$

M: magnetization of the material
H: applied magnetic field

susceptibility

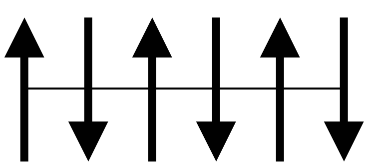


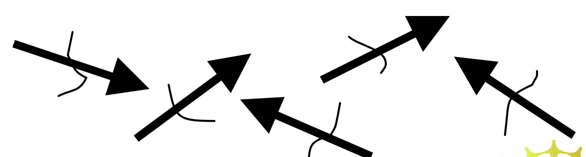
inverse susceptibility



: indication of the strength of the antiferromagnetic interaction

$$\frac{|\Theta_{CW}|}{T_N} >> 1$$: strong frustration





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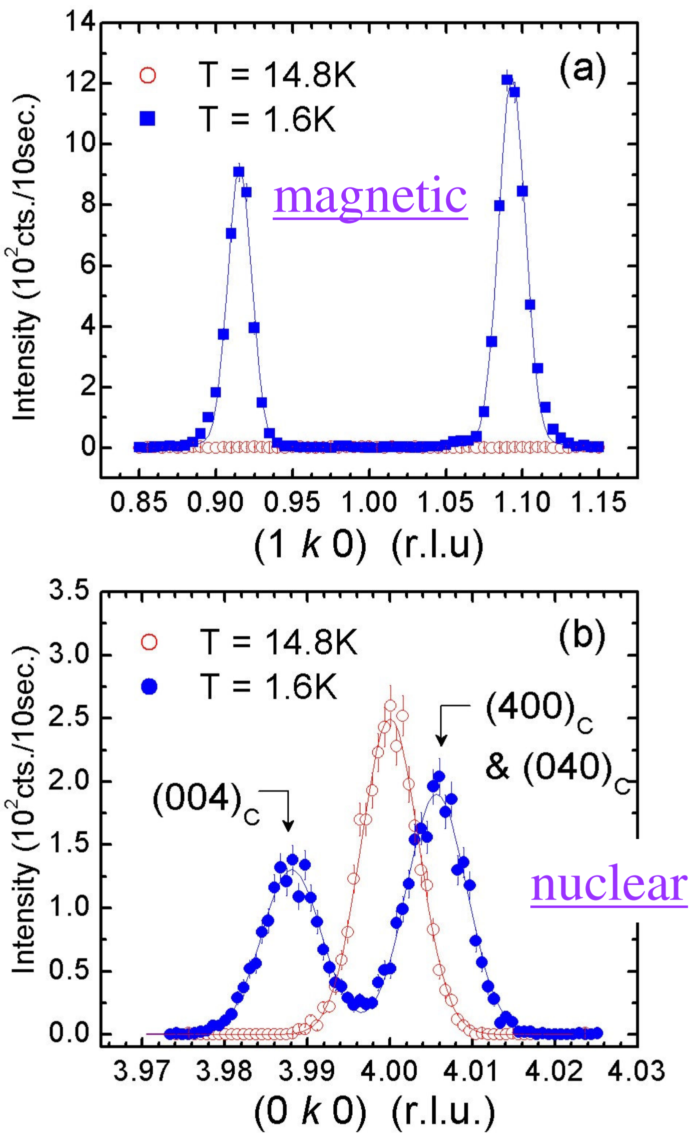
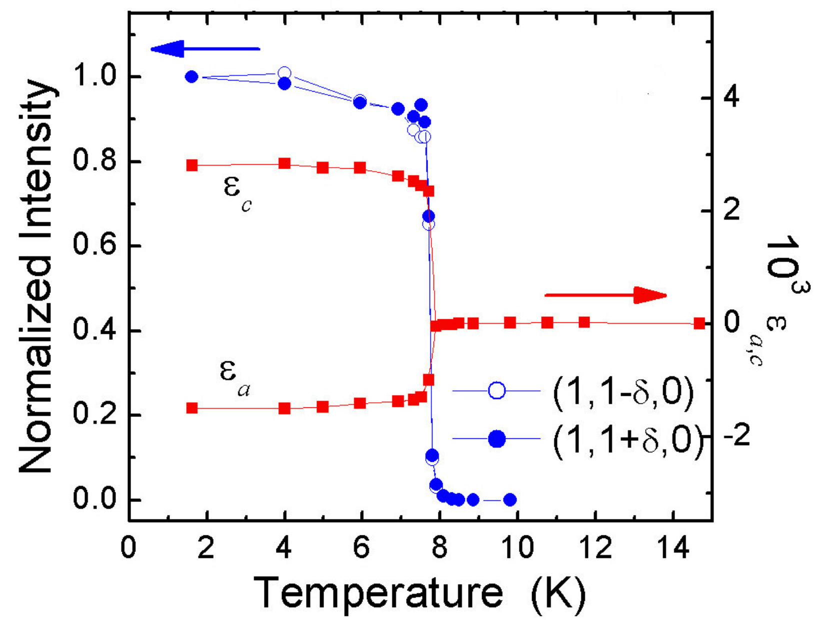
Magnetic and crystallographic phase transitions

Elastic neutron scattering



Magnetic diffraction intensity

Lattice strain $\varepsilon = (a-a_o)/a_o$



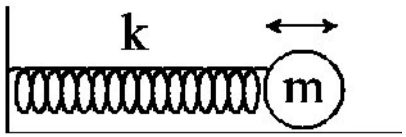
ordered | frustrated

A few things to learn from the experiment

- Ordered vs. disordered magnetic phases
  - How are they different in dynamics?
  - How do we interpret inelastic neutron scattering data in terms of time scales of order?
- Disorder due to geometrical frustration
  - How is it different from disorder due to temperature? Is it truly random or correlated in short-range?
  - What is the most likely ground state of the geometrically frustrated phase? How is it similar to or different from the ground state in the ordered phase?
  - How do we calculate magnetic structure factor that can be used for the analysis of neutron scattering intensity?
- And, of course, how to use a triple-axis spectrometer

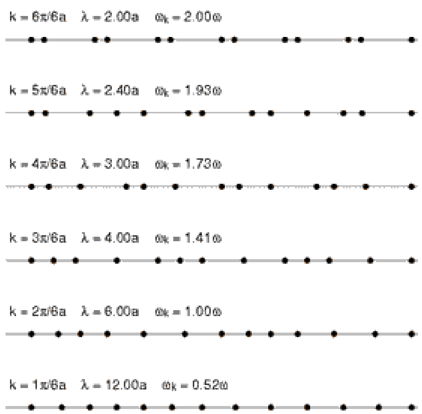
Correlated motion in ordered solids

- Ball & spring: harmonic oscillator



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

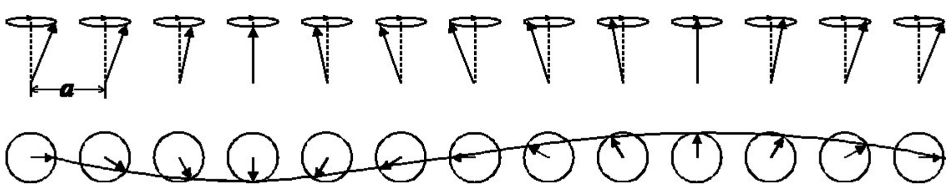
- Lattice vibrations: phonons



These vibrational modes occur as a result of the balance between a tendency for fluctuation (thermal or kinetic energy) and a restoring force (potential energy).
They are long-range in space and long-lived in time.

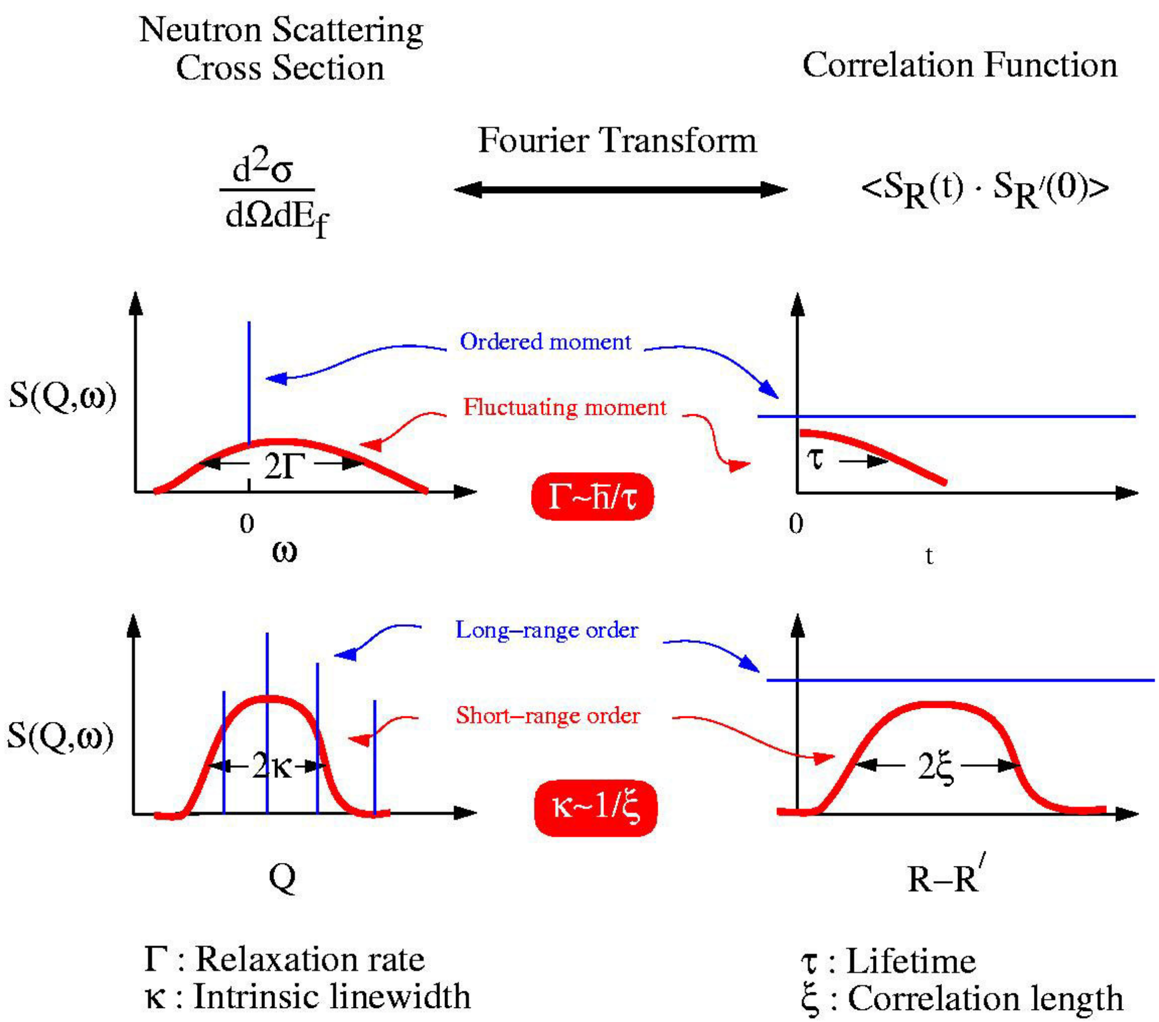
Question:
What if there are no restoring forces?
What if the ordered pattern changes with time?

- Spin precessions: magnons



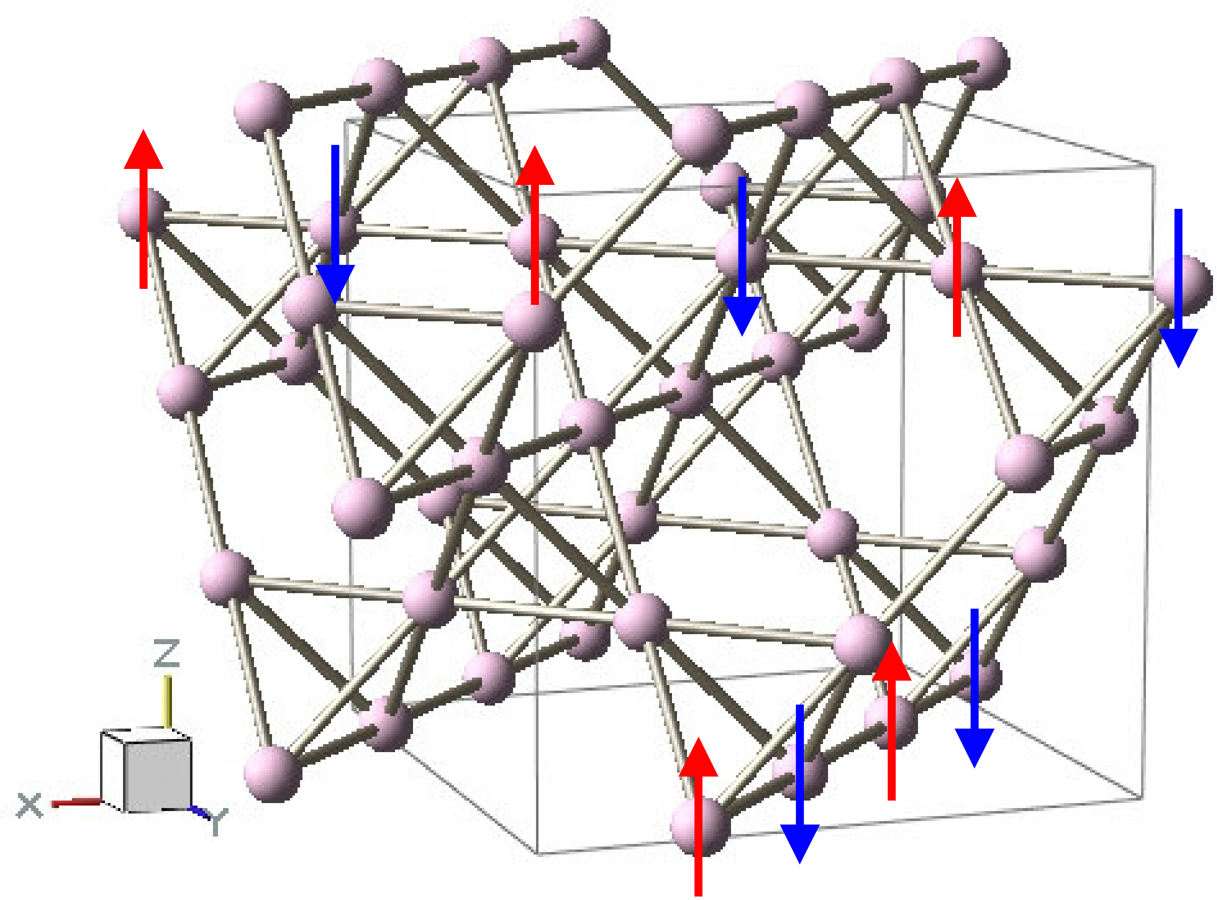
We use neutron spectroscopy to study the dynamics of solids

Magnetic neutron scattering: spin-spin correlations



Looking for the degenerate ground states in the geometrically frustrate phase

How can we place antiferromagnetic spins on this lattice and get the lowest energy? The reasonable approach is to have as many antiparallel pairs as possible.



IF this is how the degenerate ground states look like, how do we calculate the corresponding **Q**-dependence of the neutron scattering intensity?

Magnetic neutron scattering cross section

- General equation for the scattering intensity

$$I(\mathbf{Q}) \propto \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \propto \left| \int \boldsymbol{\rho}(\mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{R}} d\mathbf{R} \right|^2$$

$\boldsymbol{\rho}(\mathbf{R})$: scattering strength density

- Magnetic neutron scattering cross section

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

$$\text{where, } S(\mathbf{Q},\omega) = \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \tilde{Q}_\alpha \tilde{Q}_\beta) \sum_{\lambda,\lambda'} p_\lambda \sum_{l,d} \sum_{l',d'} f_d^*(\mathbf{Q}) f_{d'}(\mathbf{Q}) \exp\{i\mathbf{Q}\cdot(\mathbf{R}_{l'd'} - \mathbf{R}_{ld})\}$$
$$\times \langle \lambda | \hat{S}_{ld}^{\alpha} | \lambda' \rangle \langle \lambda' | \hat{S}_{l'd'}^{\beta} | \lambda \rangle \, \delta(\hbar\omega + \hbar\omega_\lambda - \hbar\omega_{\lambda'})$$

  - 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

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

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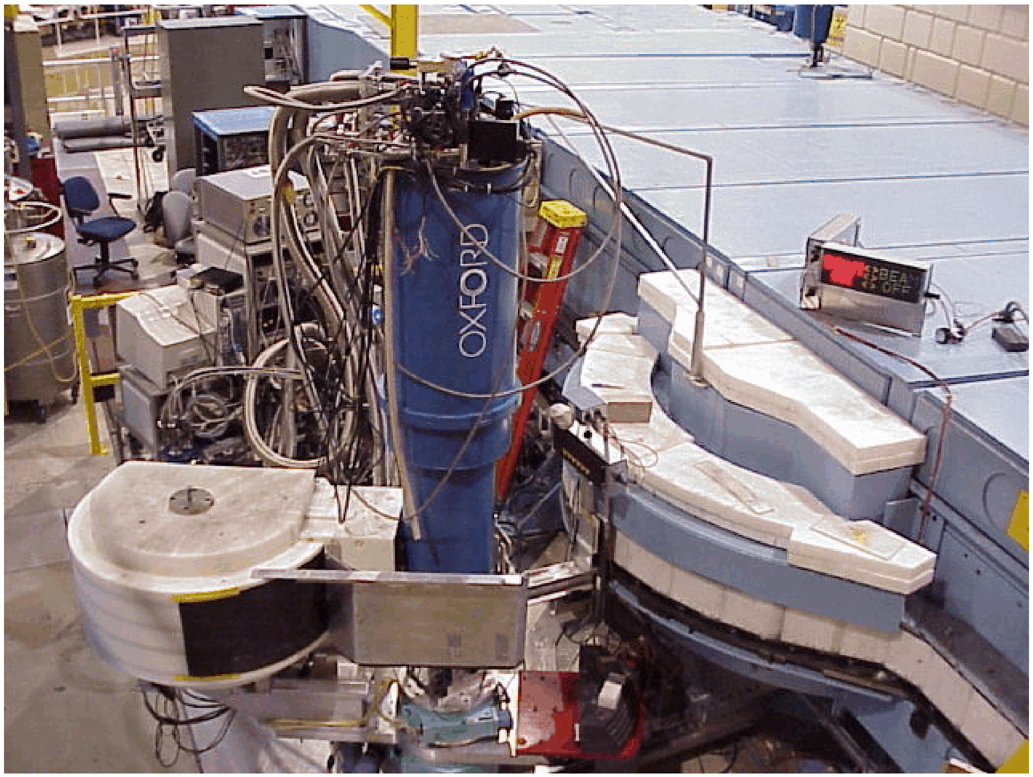
SPINS cold neutron triple axis spectrometer



Why SPINS for this study? Because SPINS

- can precisely access desired Q and $\hbar\omega$
- covers $\hbar\omega$ in the range 0.1 ~ 10 meV
- can also perform diffraction measurement
- provides a flexible choice of high resolution or high intensity

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Summary

- In this experiment, we are going to study the magnetic phase transitions in $CdCr_2O_4$, which is a spinel with antiferromagnetic interactions between Cr^{3+} ions on B sites.

- While its magnetic exchange interaction strength is comparable to $|\Theta_{CW}|$ ~ 88 K, the magnetic phase transition occurs at much lower temperature, T_N = 7.8 K, due to the geometrical frustration.

- Below the magnetic phase transition, there is a well-defined ground state with long-range magnetic order. On the other hand, above the transition the magnetic structure is disordered, not because of thermal fluctuations, but because of the multiplicity of ground states.

- In order to characterize two different magnetic phases below and above the magnetic phase transition, we are going to use neutron triple axis spectroscopy technique. By measuring energy and momentum dependence of the neutron scattering spectra, we expect to reveal the time and the length scales of the magnetic correlations of the two distinct phases.