Unraveling the Mysteries in Complex Oxides by Neutron Scattering

Seung-Hun Lee
University of Virginia

Condensed Matter Science and Neutron Scattering

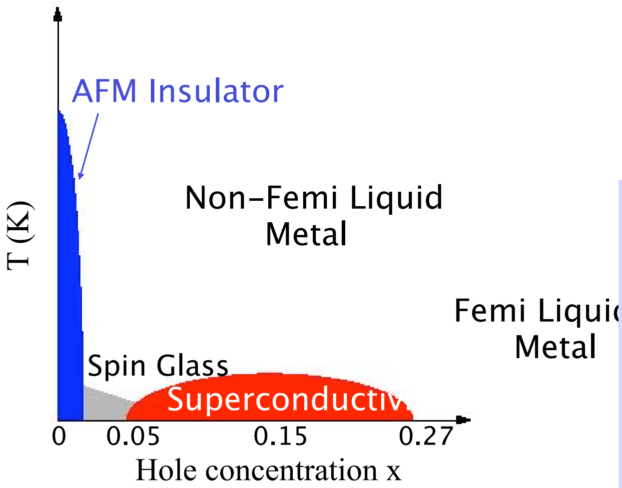
Why neutron scattering is a powerful tool in CMS?

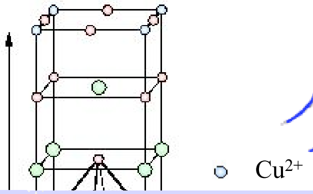
What Is Condensed Matter Science about?

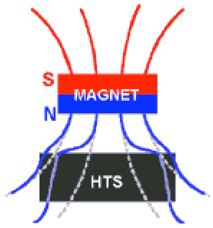
- Study **Emergent phenomena** that are **collective effects** of a huge number of particles

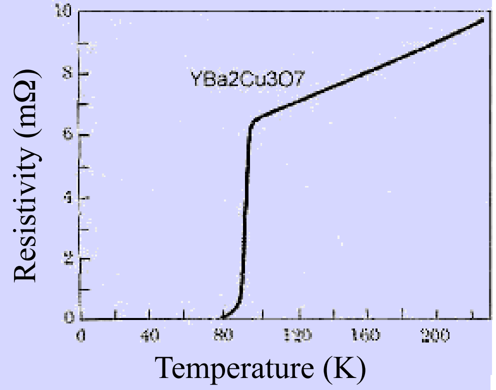
High T_c Superconductivity

$La_{2-x}Sr_xCuO_4$







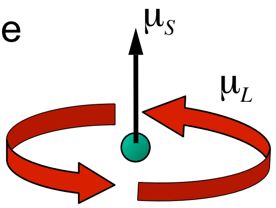


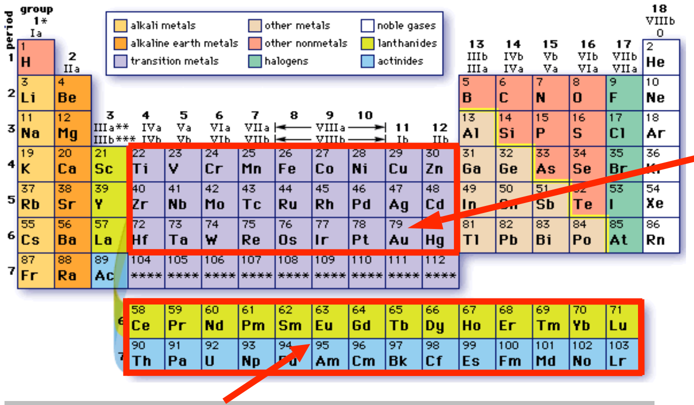
Outline

- **Introduction:**
  1. Collective phenomena in Condensed Matter Physics
  2. Magnetism and Neutron Scattering
- **Example: Neutron scattering studies on geometrically frustrated magnets ACr_2O_4 (A=Zn, Cd)**
  1. Composite spin degrees of freedom
  2. Spin-Peierls-like phase transitions
- **Summary**

Origin of Magnetism

- Unpaired electrons of ions in solids have
  1) electronic spin μ_S
  2) orbital momentum μ_L



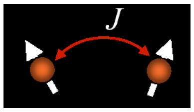


Transition metals:
unfilled d shells
Quenched orbital moments
Small moments

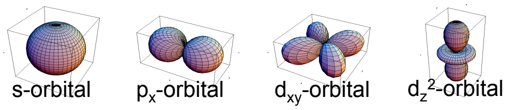
Rare earth metals: unfilled f shells
Strong spin-orbit coupling J=S+L
Large magnetic moments

Spin interactions of localized moments

$$\mathcal{H} = \Sigma_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j$$



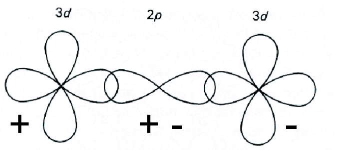
- Exchange interactions arise from the overlap of electronic orbitals of neighboring sites and the Pauli exclusion principle



Crystal fields lead to spatially oriented electron orbitals

- Direct exchange arising from direct overlap of neighboring electron orbitals

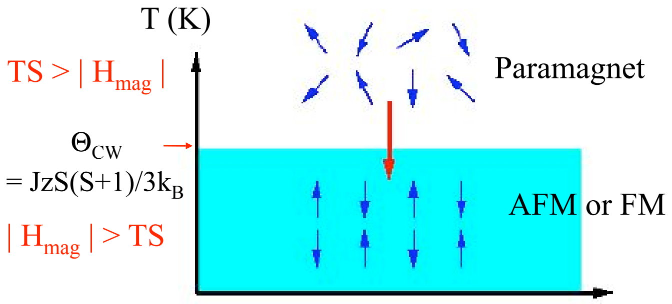
- Superexchange is mediated by a diamagnetic anion such as O^{-2} or F^{-1}



- Indirect exchange mediated by conduction electrons, RKKY interaction

Phase Diagram for a Three-Dimensional Ordinary Magnet

$$F = H_{mag} - TS = - \Sigma J S_i S_j - TS$$



T (K)

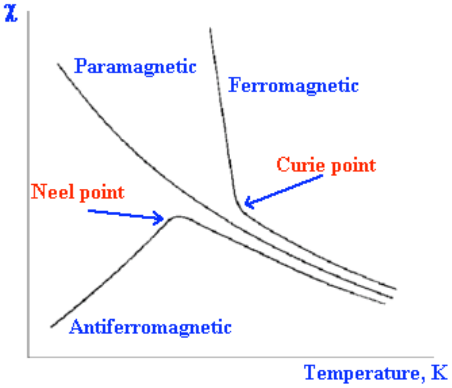
$TS > | H_{mag} |$

$\Theta_{CW} = JzS(S+1)/3k_B$

$| H_{mag} | > TS$

Paramagnet

AFM or FM



- The Ground State is a Long range (anti)ferromagnetically ordered state.
- Low Energy Excitations can be explained by Long range linear spin waves.

Magnetic Neutron Scattering

Neutron:

- Wavelength comparable to interatomic spacing
- Penetrating → bulk properties are measured
- has spin *s* = ½ and interacts with atomic moments

Scattering by atomic magnetic moments: $I = (0.54)^2 S (S+1)$

Magnetic scattering intensities can be comparable to nuclear scattering !!

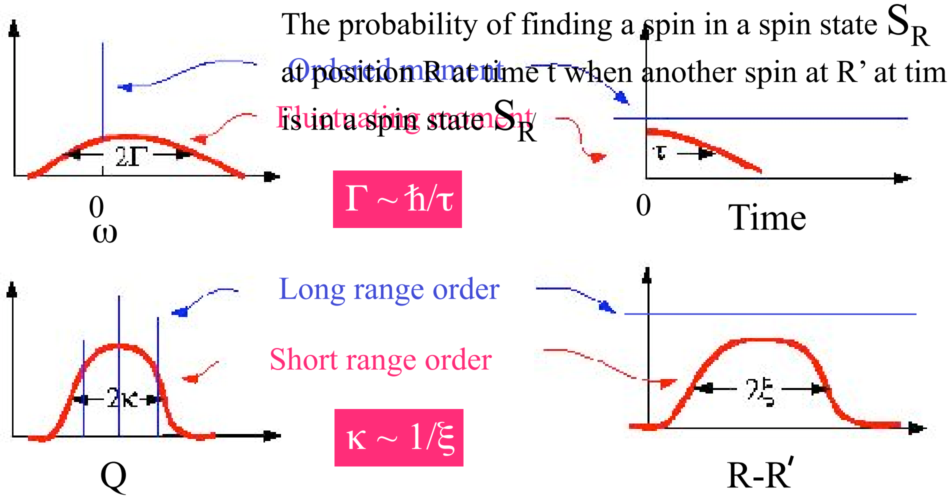
Magnetic Neutron Scattering Cross Section

Spin-Spin Correlation Function

Fourier Transform

$$\frac{d^2\sigma}{d\Omega d\omega} \longleftrightarrow < S_R(t)\, S_{R'}(0) >$$

The probability of finding a spin in a spin state S_R at position R at time t when another spin at R’ at time t=0 is in a spin state S_R



$\Gamma \sim \hbar/\tau$

$\kappa \sim 1/\xi$

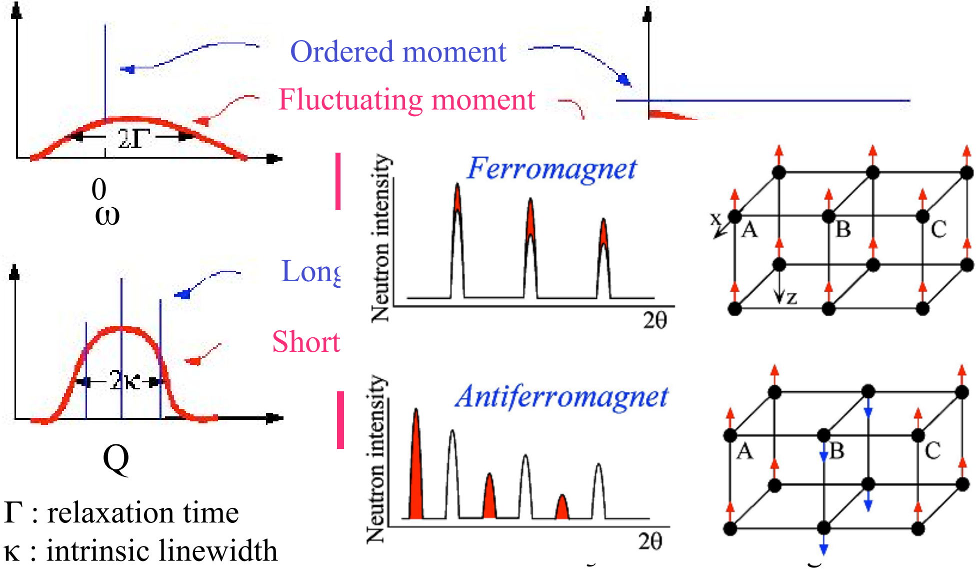
Γ : relaxation time
κ : intrinsic linewidth

τ : lifetime
ξ : correlation length

Neel phase:
What kind of magnetic scattering signal in Q and ω space would you expect?

(1) Any Elastic signal?

(2) Any Inelastic signal? If any, what kind of shape in the ω- and Q-space?



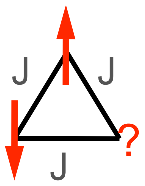
Γ : relaxation time
κ : intrinsic linewidth

Do all magnetic systems order at low temperatures?

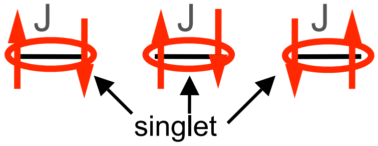
Systems with Quantum Fluctuations at T=0K

Low dimensional spin systems

Frustration



Dimerization

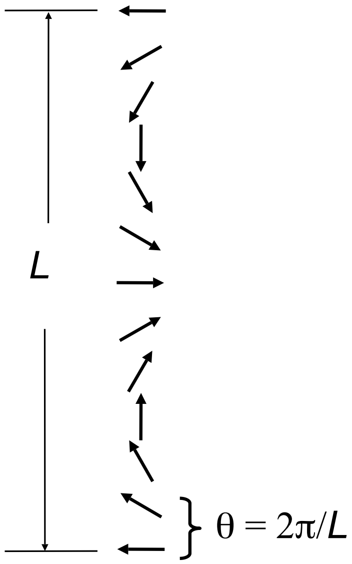


Quantum fluctuations are important in low dimensions, systems with frustrated interactions or dimerization

➡ *Novel quantum-coherent ground states with non-conventional spin correlations*

Low dimensionality suppresses magnetic long range order

Spin wave in an XY spin system $\mathcal{H} = \Sigma_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j$



Energy cost to create such a spin wave

a. In three-dimensions: $E \propto L^3 \left(\frac{2\pi}{L}\right)^2 \xrightarrow{L\to\infty} \infty$
presence of LRO

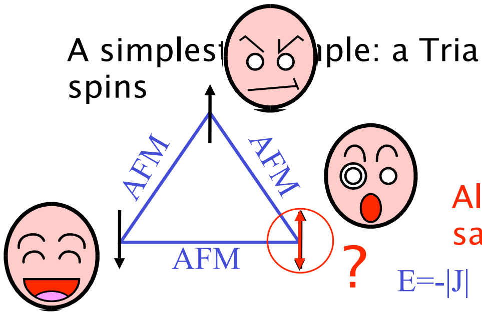
b. In two-dimensions: $E \propto L^2 \left(\frac{2\pi}{L}\right)^2 \xrightarrow{L\to\infty} const$

borderline case: Kosterlitz-Thouless transition

c. In one-dimension: $E \propto L \left(\frac{2\pi}{L}\right)^2 \xrightarrow{L\to\infty} 0$
Absence of LRO

Geometrical Frustration

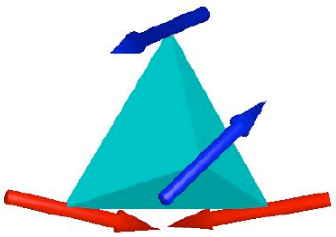
A simplest ple: a Triangle of three antiferromagnetic Ising spins



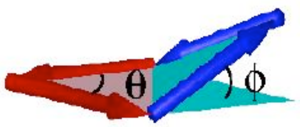
$H = -J \, \Sigma \, \mathbf{S}_i \cdot \mathbf{S}_j$

All exchange interactions can not be satisfied.

A tetrahedron with four isotropic spins



$\Sigma \, \mathbf{S}_i = 0$

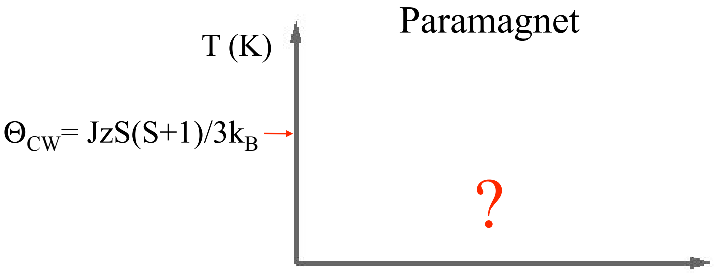


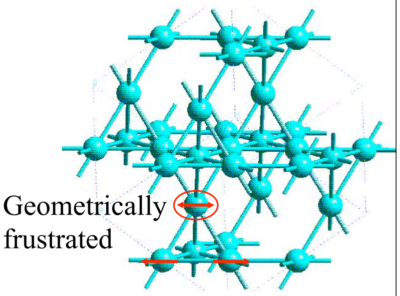
Zero energy modes
in the ground state manifold

Geometrical frustration leads to a large degeneracy in the ground state

Phase Diagram for Geometrical Frustration

$H = -J\,\Sigma\,\mathbf{S_i} \cdot \mathbf{S_j}$

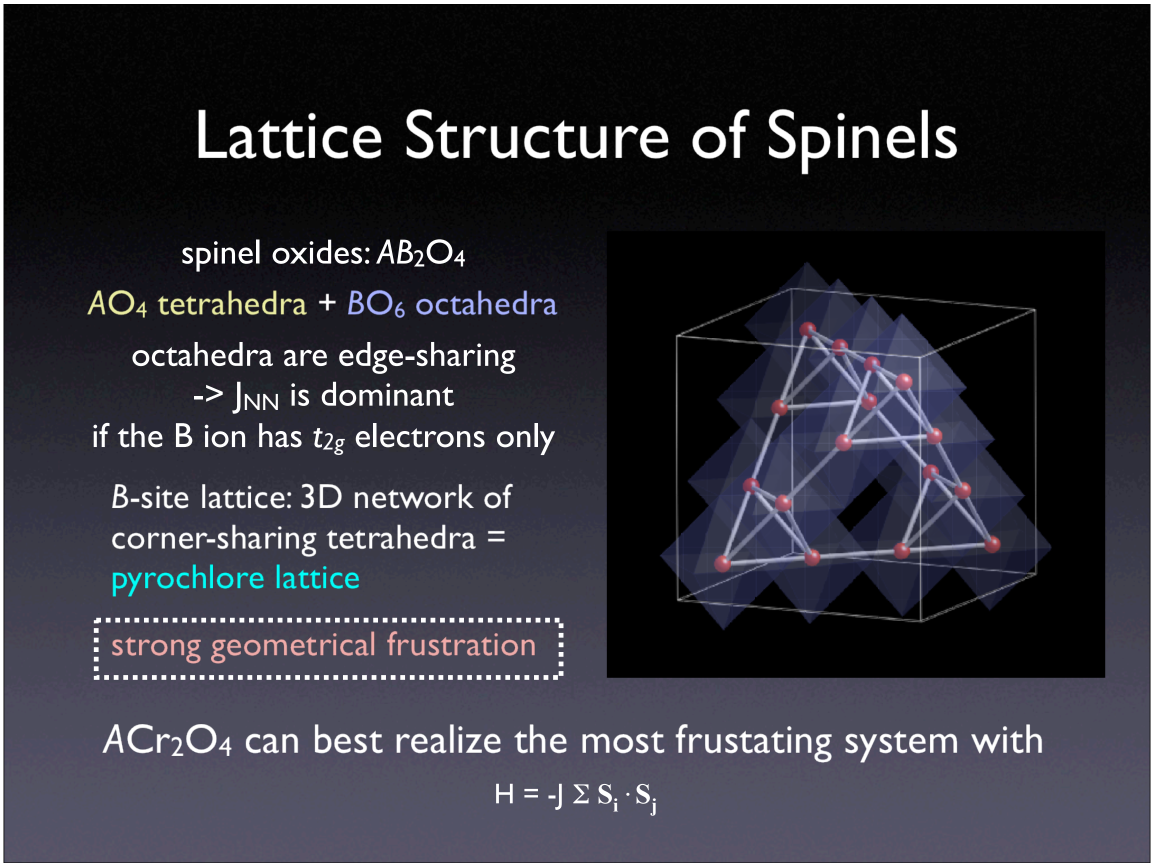




What is the nature of the ground state ?
How are the spins correlated with each other ?

Outstanding Issues

- What is the nature of spin liquid phase?
- GF vs the third law of thermodynamics, entropy -> 0 at T -> 0?



Lattice Structure of Spinels

spinel oxides: AB_2O_4

AO_4 tetrahedra + BO_6 octahedra

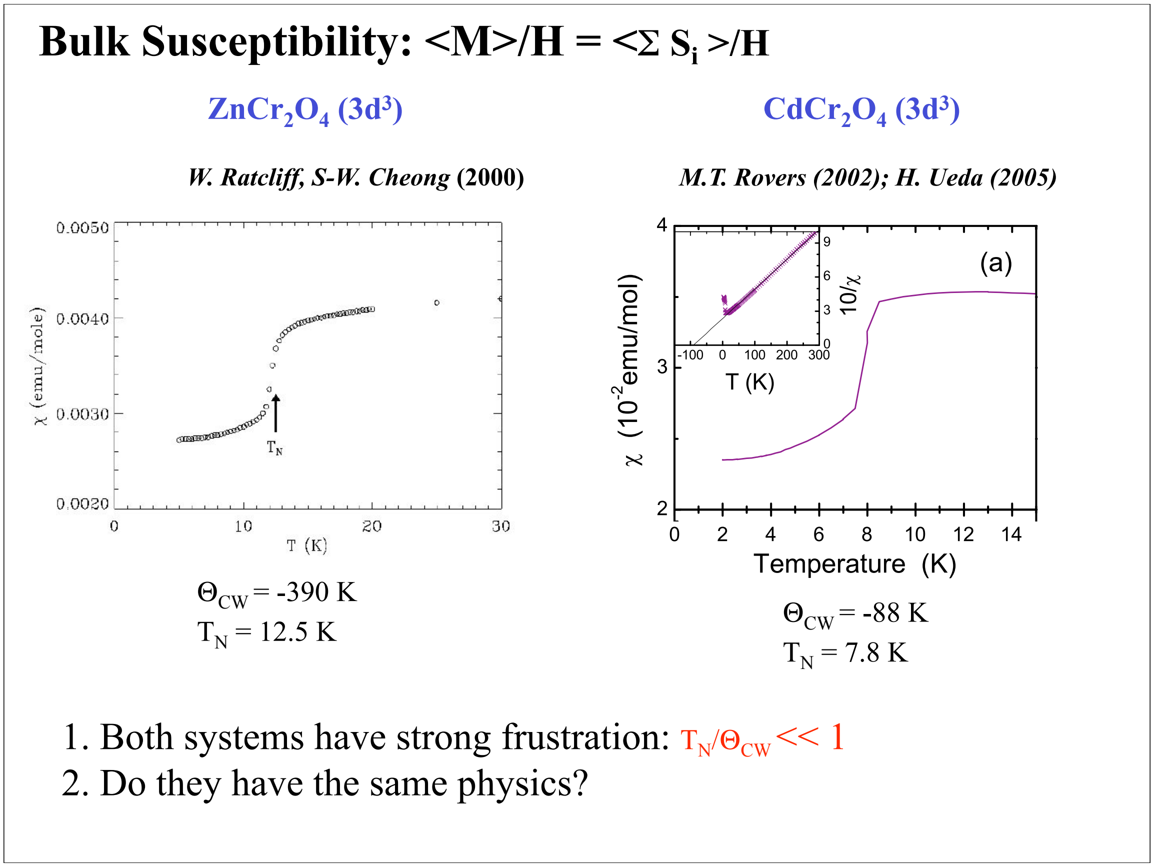
octahedra are edge-sharing
-> J_{NN} is dominant
if the B ion has t_{2g} electrons only

B-site lattice: 3D network of corner-sharing tetrahedra = pyrochlore lattice

strong geometrical frustration

ACr_2O_4 can best realize the most frustating system with

$$H = -J \sum S_i \cdot S_j$$



Bulk Susceptibility: $\langle M\rangle/H = \langle \Sigma\, S_i \rangle/H$

$ZnCr_2O_4$ ($3d^3$)

***W. Ratcliff, S-W. Cheong* (2000)**

Θ_{CW} = -390 K
T_N = 12.5 K

$CdCr_2O_4$ ($3d^3$)

M.T. Rovers (2002); H. Ueda (2005)

Θ_{CW} = -88 K
T_N = 7.8 K

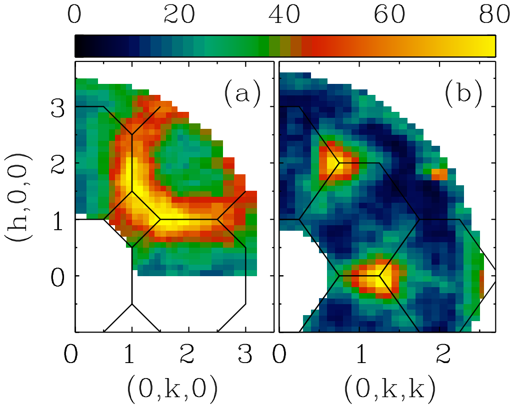
1. Both systems have strong frustration: $T_N/\Theta_{CW} << 1$
2. Do they have the same physics?

Nature of the Spin Liquid State in GF magnets

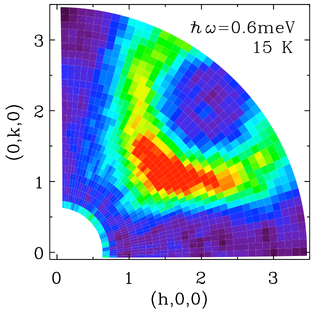
Emergence of Composite Spin Excitations

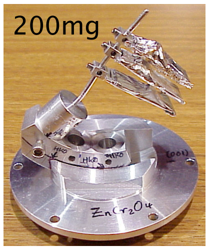
Spin fluctuations in the Spin liquid phase (T > T_N)

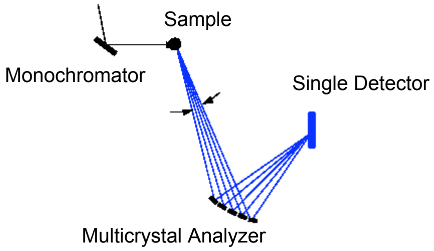
$ZnCr_2O_4$ (3d^3)



$CdCr_2O_4$ (3d^3)







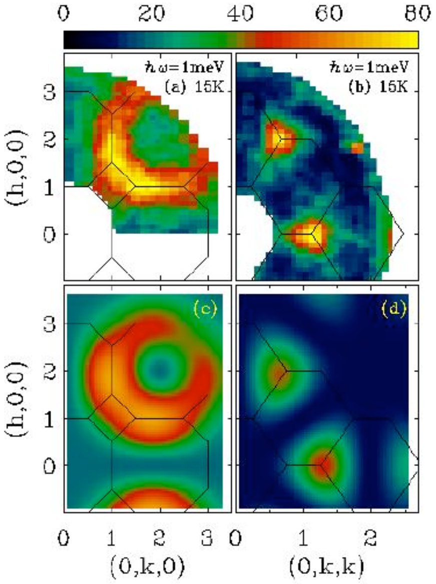
$ZnCr_2O_4$ and $CdCr_2O_4$ have the identical spin fluctuations in the spin liquid phase!

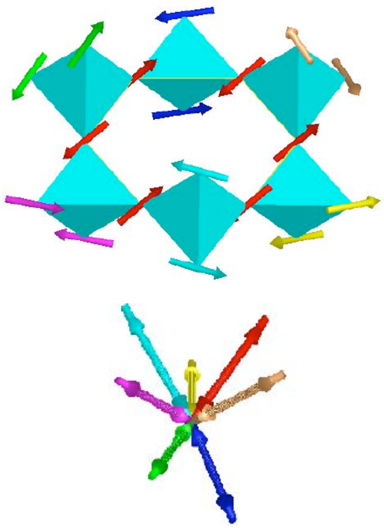
Composite Spin Excitations in ACr_2O_4

SHL et al., Nature Vol 418, 856 (2002)

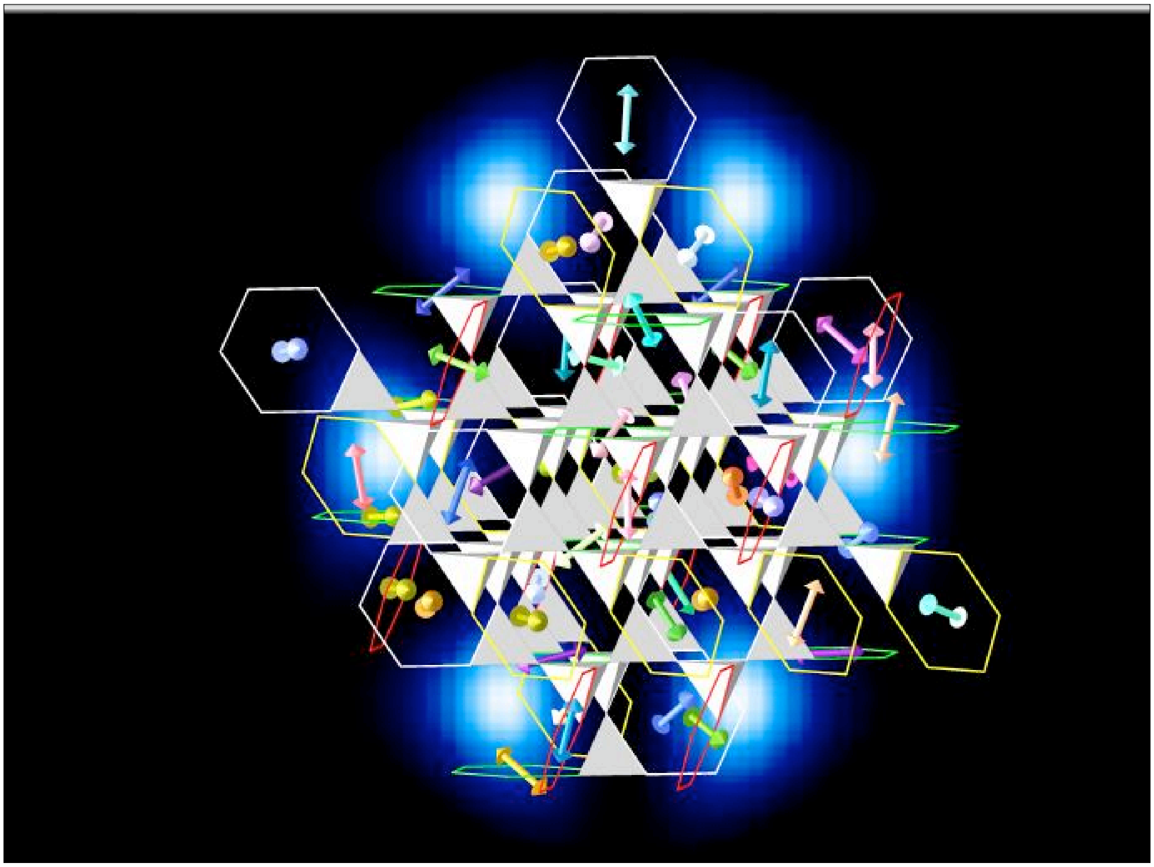
Spin liquid phase

$T > T_N$





The fundamental spin degree of freedom is an Antiferromagnetic hexagonal spin loop !



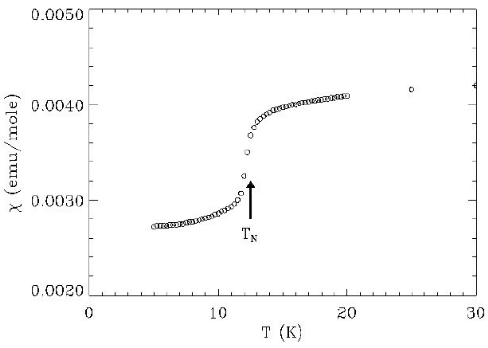
Nature of the Phase Transitions in GF magnets

Spin-Lattice Couplings

Phase Transitions

$ZnCr_2O_4$ ($3d^3$)

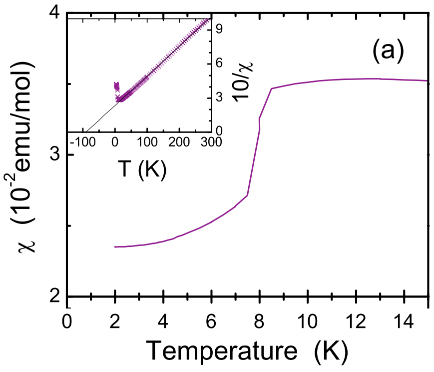
***W. Ratcliff, S-W. Cheong* (2000)**



$\Theta_{CW} = -390$ K
$T_N = 12.5$ K

$CdCr_2O_4$ ($3d^3$)

M.T. Rovers (2002); H. Ueda (2005)



$\Theta_{CW} = -88$ K
$T_N = 7.8$ K

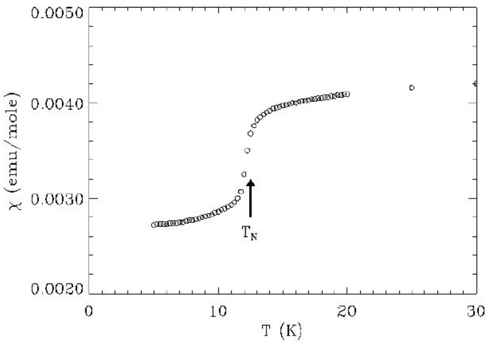
1. Both systems have strong frustration: $T_N/\Theta_{CW} << 1$
2. Do they have the same physics?

Phase Transition due to Spin-Lattice coupling

$ZnCr_2O_4$ ($3d^3$)

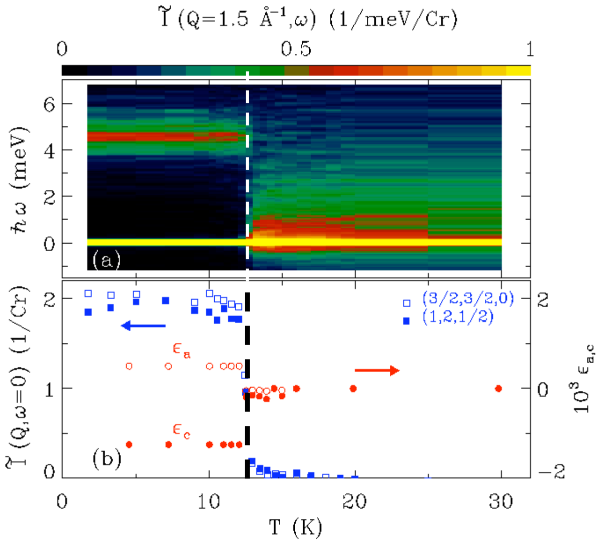
***SHL* et al., PRL (2000)**

***W. Ratcliff, S-W. Cheong* (2000)**



$\Theta_{CW} = -390$ K

$T_N = 12.5$ K



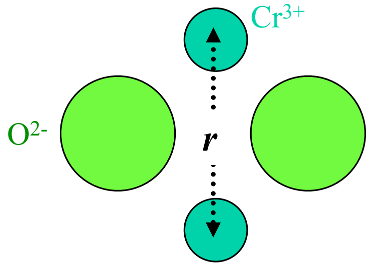
Contraction along the c-axis (c < a)

Commensurate spin structure below T_N

Spin-Peierls-like (spin-lattice) transition

Why does tetragonal strain encourage Néel order ?

Edge sharing n-n exchange in $ZnCr_2O_4$ depends strongly on Cr-Cr distance, ***r*** :



From series of Cr-compounds:

$$\frac{dJ}{dr} \approx 40\ \text{meV}/\text{Å}$$

$$\begin{cases} \Delta J_{\parallel} = \dfrac{\varepsilon_a + \varepsilon_c}{2} r_0 \dfrac{dJ}{dr} = -0.04\ \text{meV} \\ \Delta J_{\perp} = \varepsilon_a r_0 \dfrac{dJ}{dr} = 0.06\ \text{meV} \end{cases}$$

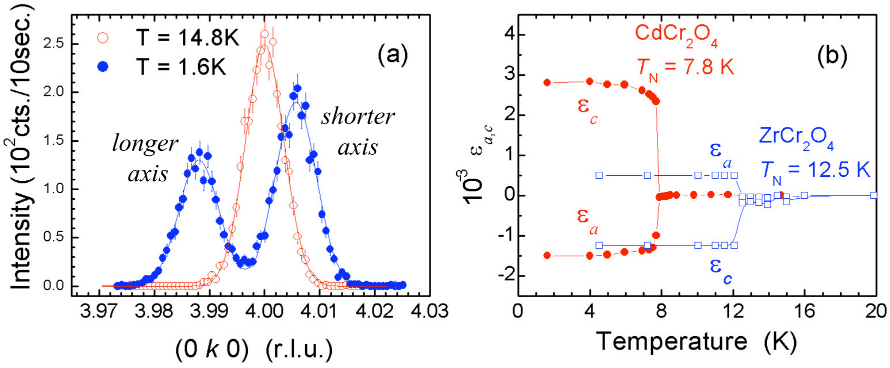
The effects on a single tetrahedron is to make 4 bonds more AFM and two bonds less AFM. This relieves frustration!

Lattice distortions in $CdCr_2O_4$ at $T < T_N$

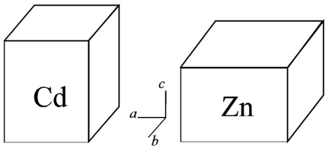
Single crystal diffraction

$(4\ 0\ 0)_{cubic}$

J.-H. Chung et al., submitted to PRL



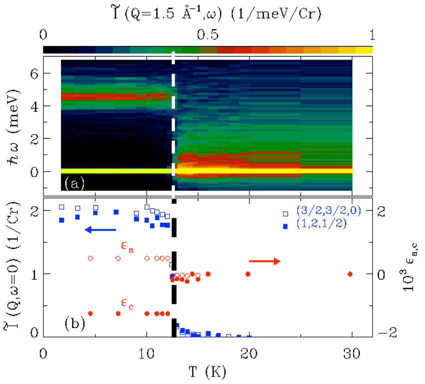
Elongation along the c-axis (c > a)



Phase Transitions due to Spin-Lattice Coupling

$ZnCr_2O_4$ ($3d^3$)

SHL/CB et al., PRL (2000)

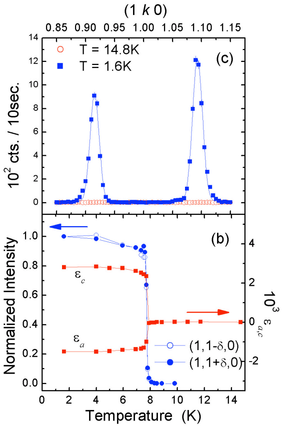


Contraction along the c-axis (c < a)

Commensurate spin structure below T_N

$CdCr_2O_4$ ($3d^3$)

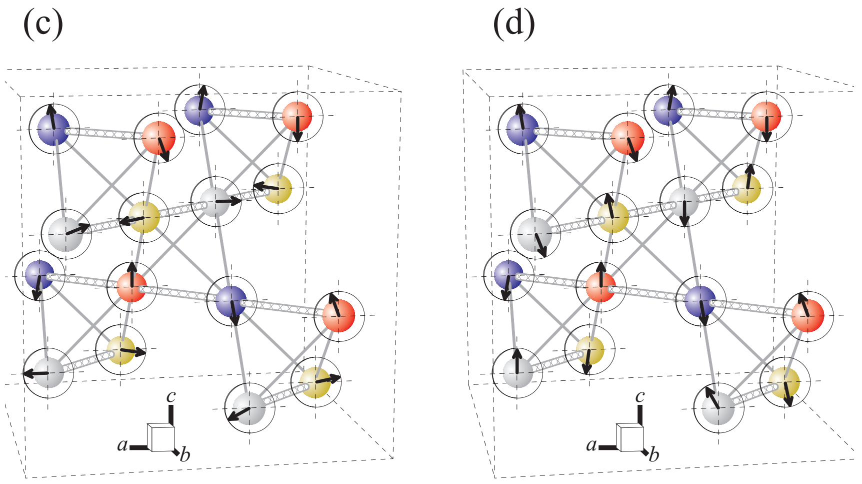
***Cheong/Matsuda/SHL* et al. (2005)**



Elongation along the c-axis (c > a)

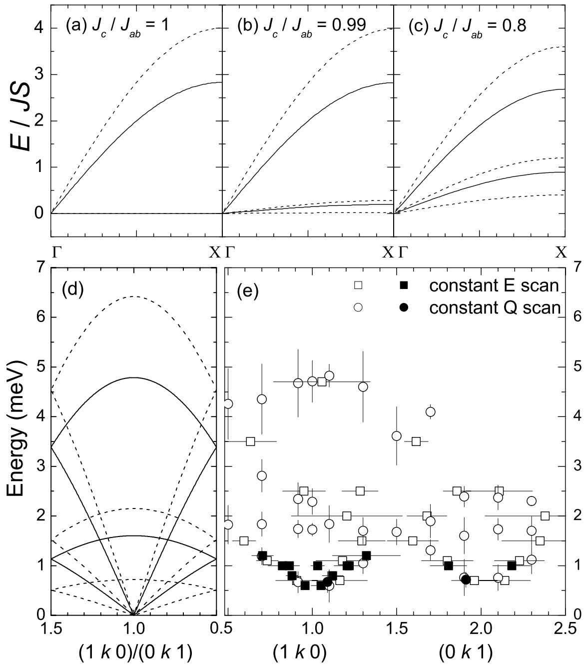
Incommensurate spin structure below T_N

Spin Structure in the Tetragonal Phase of $CdCr_2O_4$



1. Incommensurate spin ordering with Q=(0,d,1)
2. Spins are lying on the ac-plane

Spin Fluctuations in the Neel Phase of $CdCr_2O_4$



Collaborators on $ZnCr_2O_4$, $CdCr_2O_4$

C. Broholm (Johns Hopkins Univ.)
S-W. Cheong (Rutgers Univ.)
J.-H. Chung (NIST)
G. Gasparovic (Johns Hopkins Univ.)
K.-P. Hong (HANARO, KAERI, Korea)
Q. Huang (NIST)
K. Kakurai (JAERI, Japan)
T.H. Kim (Ewha Woman's Univ.)
Y.J. Kim (University of Toronto)
M. Matsuda (JAERI, Japan)
S. Park (HANARO, KAERI, Korea)
W. Ratcliff (Rutgers Univ., now at NIST)
T. Sato (NIST, now at ISSP, U of Tokyo, Japan)
H. Ueda (ISSP, U of Tokyo, Japan)

Summary

- **Neutron scattering is the most powerful tool in magnetism**
- **Example: Neutron scattering studies on geometrically frustrated magnets ACr_2O_4 (A=Zn, Cd)**
  1. Composite spin degrees of freedom
  2. Spin-Peierls-like phase transitions different in nature
- **Modern neutron spectroscopy allows new science**