Magnetic Neutron Scattering

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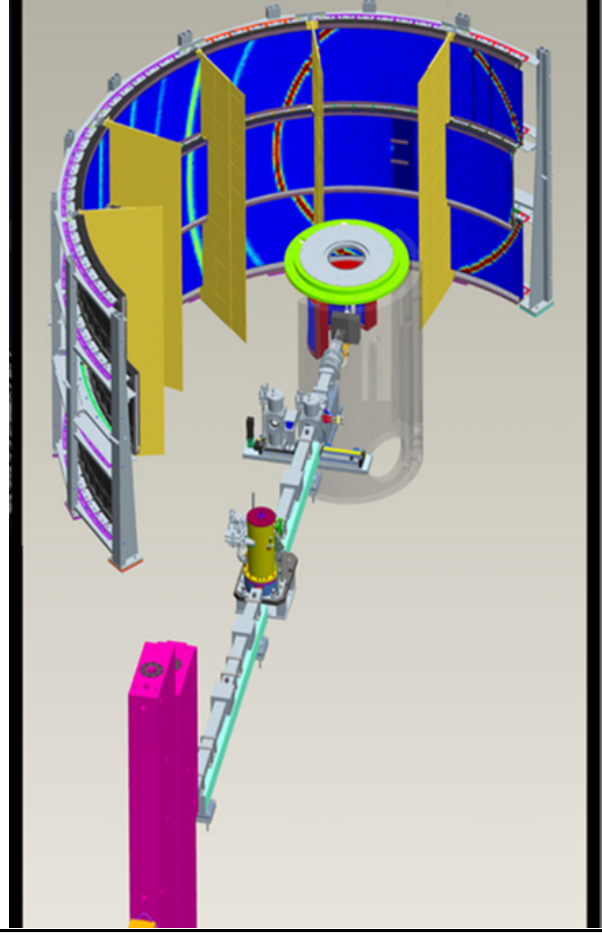
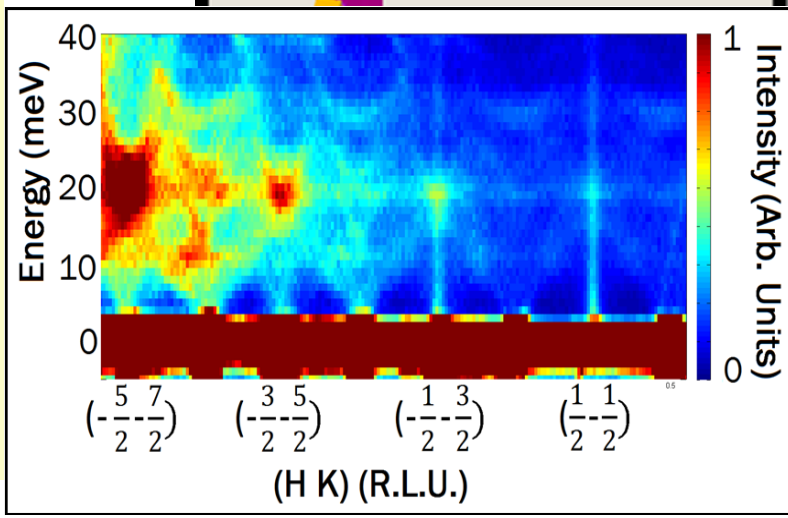


- Magnetism and Neutron Scattering: A Killer Application
- Magnetism in solids
- Bottom Lines on Magnetic Neutron Scattering
- Examples



A brief history of magnetism

~ 500 BC:

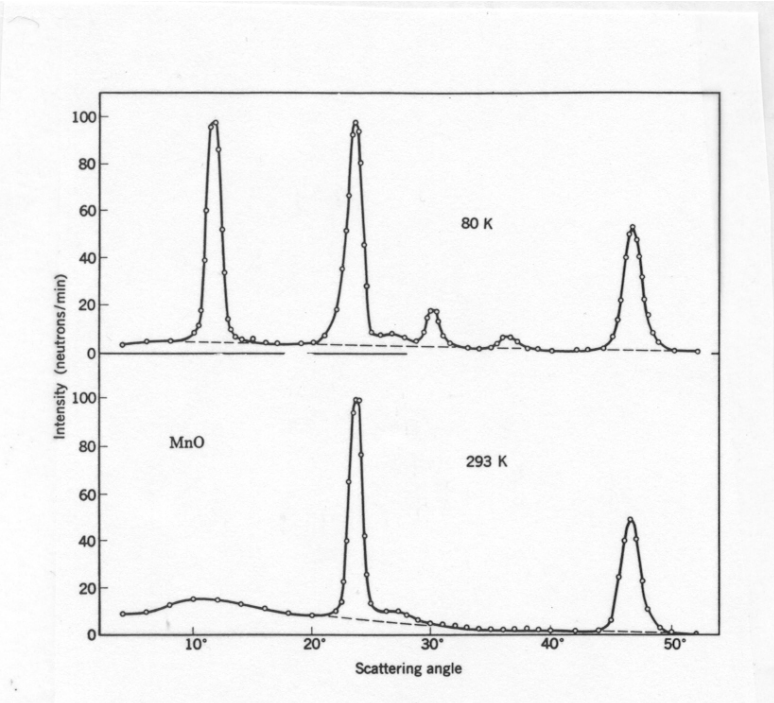
Ferromagnetism documented in Greece, India, used in China

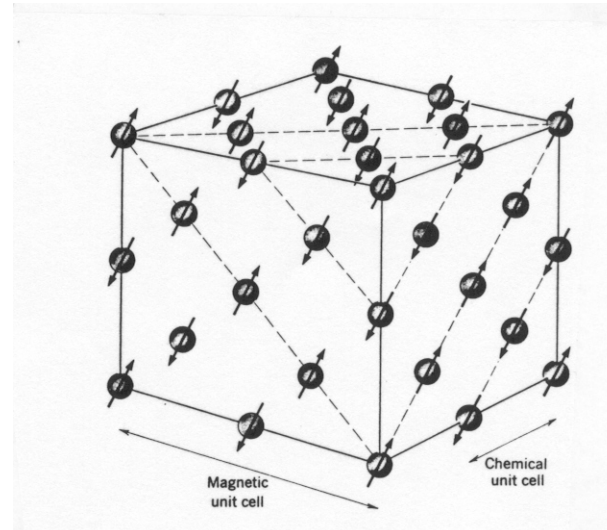
sinan, ~200BC

time

1949 AD:

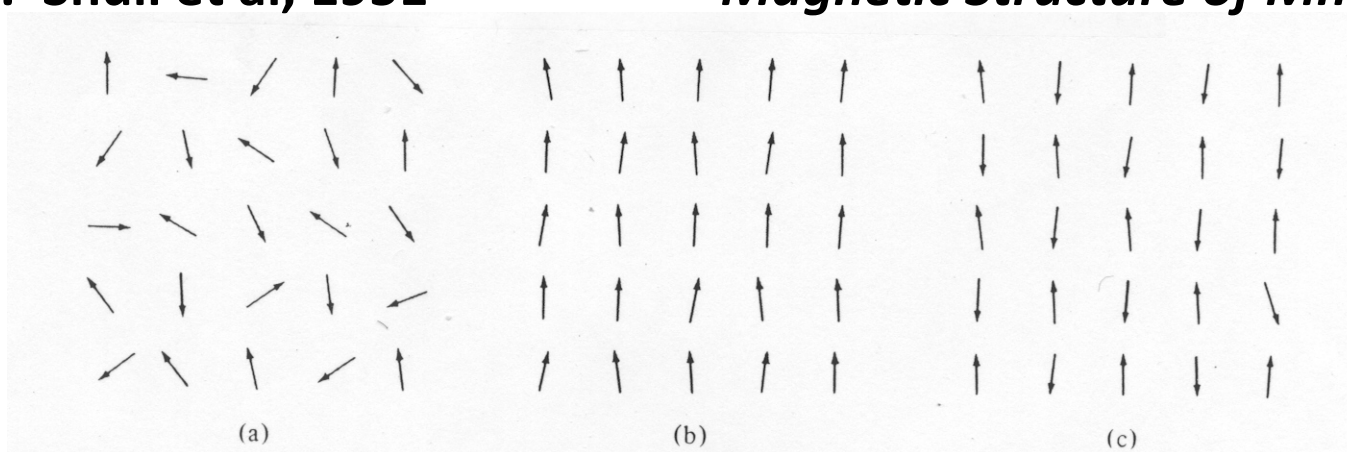
Antiferromagnetism proven experimentally





C. G. Shull et al, 1951

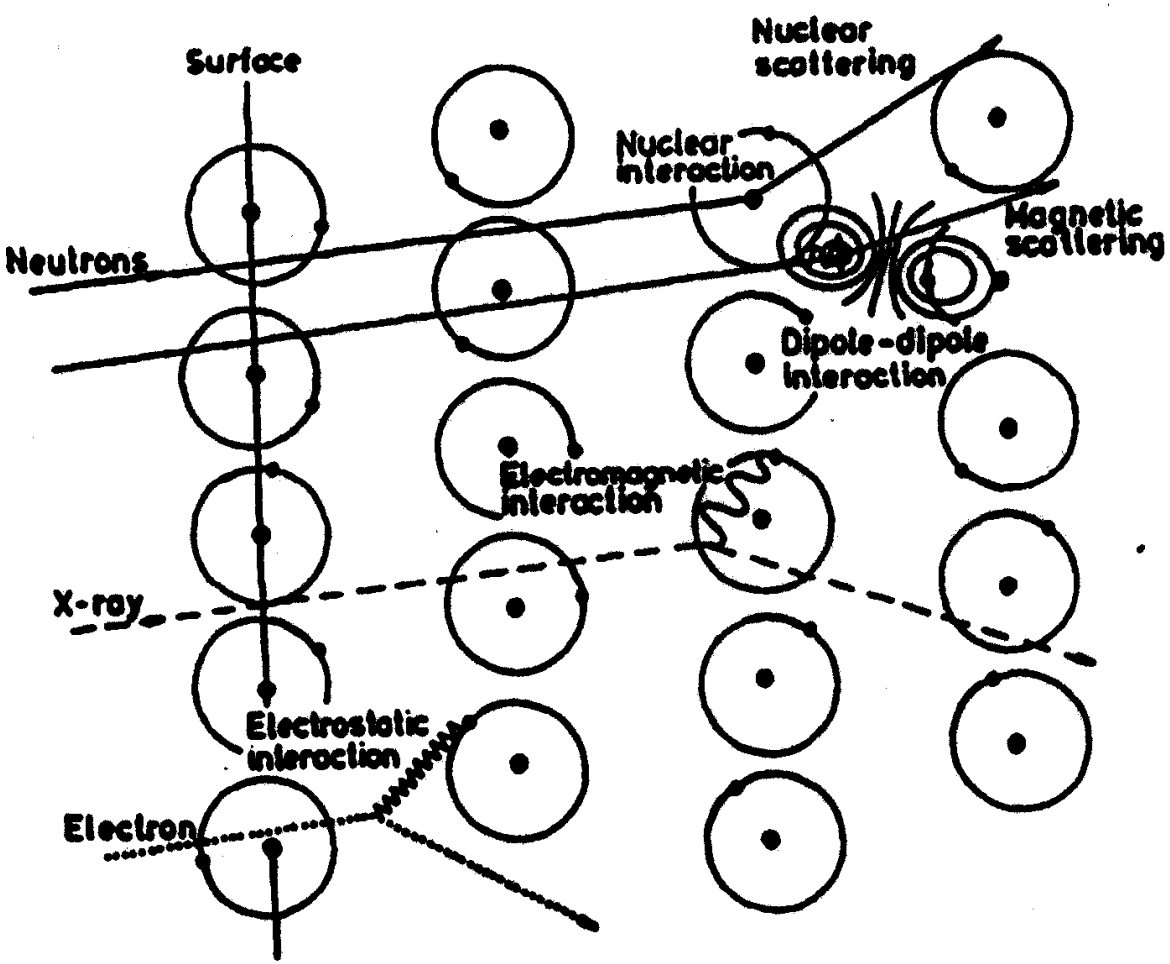
Magnetic Structure of MnO



Paramagnet $T>T_C$

Ferromagnet $T<T_C$

Antiferromagnet $T<T_N$



Magnetic Neutron Scattering directly probes the electrons in solids

Killer Application: Most powerful probe of magnetism in solids!

Magnetism = Net Angular Momentum

d-electrons: 10 levels to fill

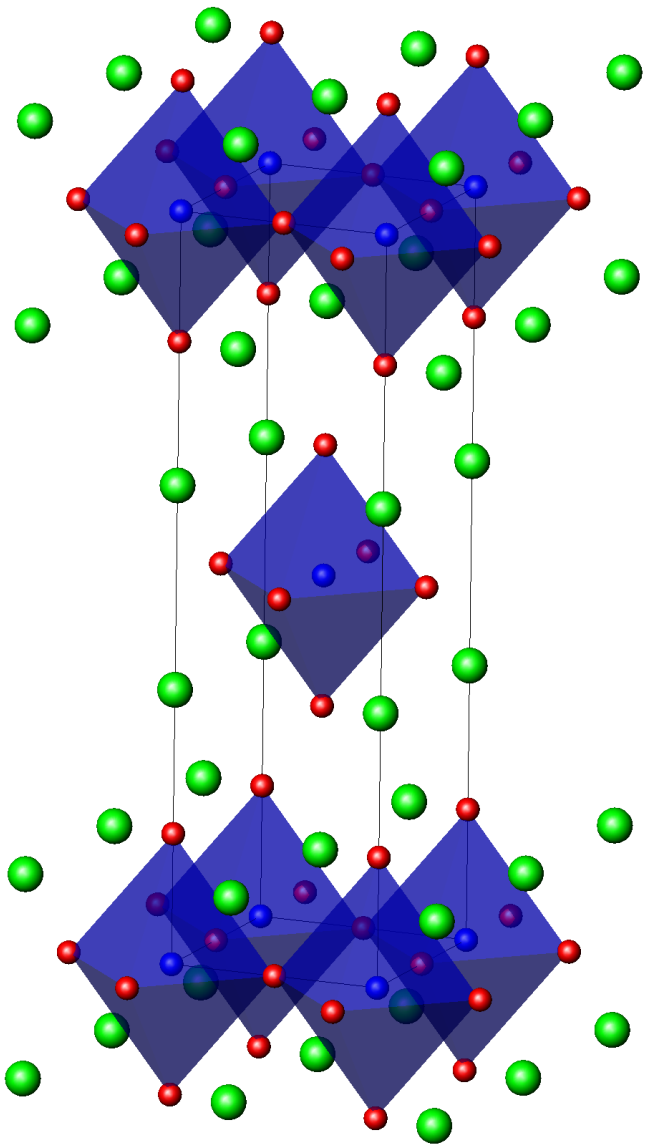
hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

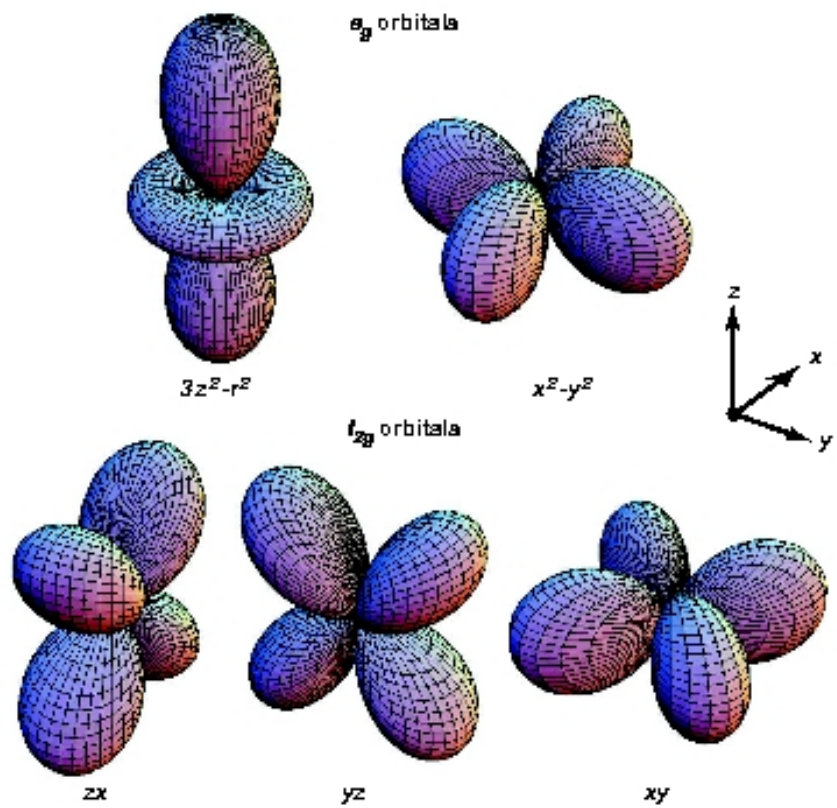
4f

14 levels

5f



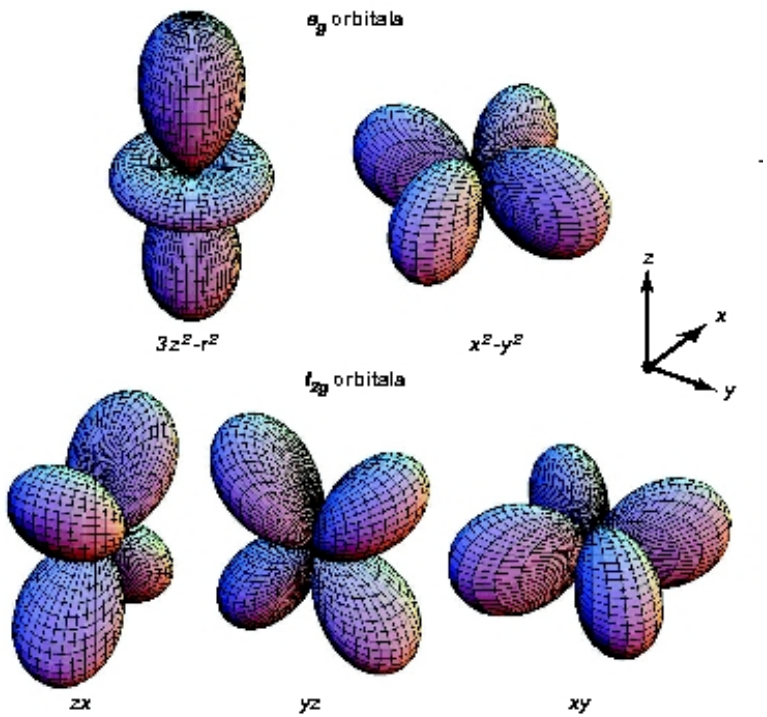
e_g orbitals

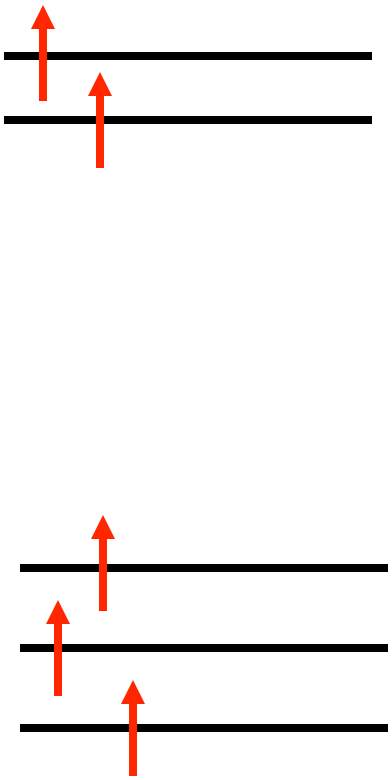


t_{2g} orbitals

$3d^5$: Mn^{2+}

e_g orbitals

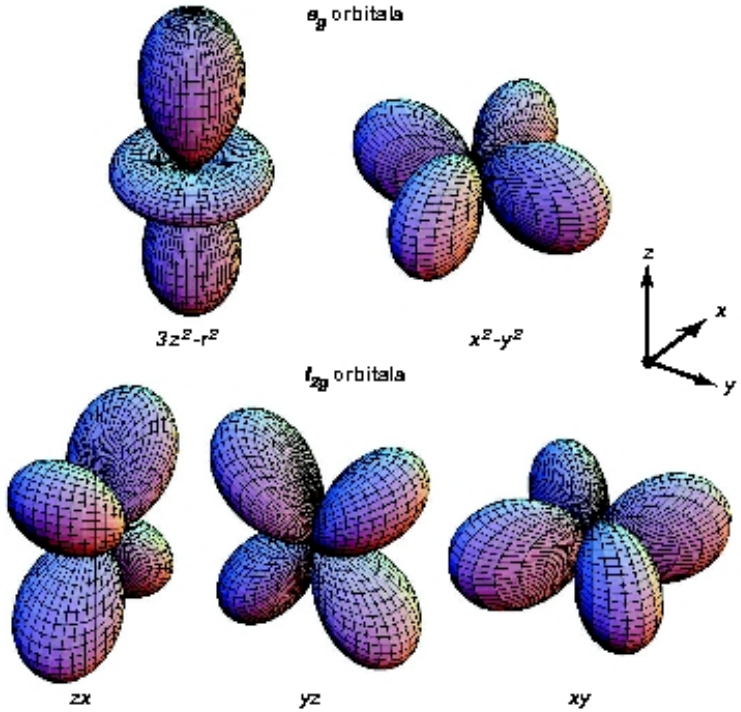


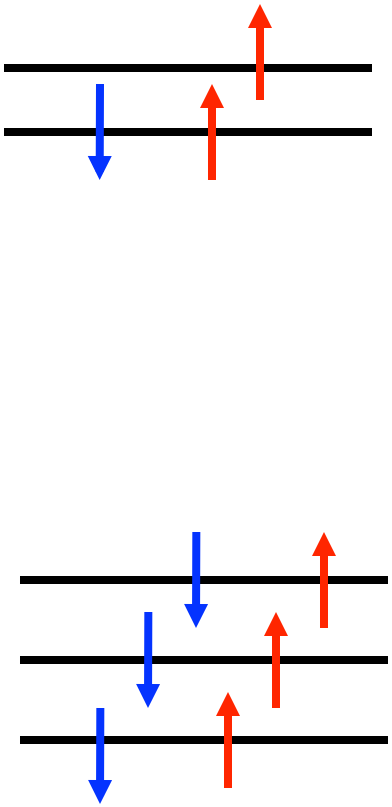


t_{2g} orbitals

$3d^9 : Cu^{2+}$

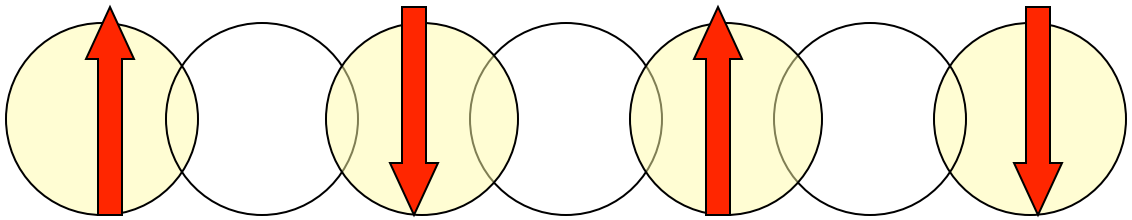
e_g orbitals



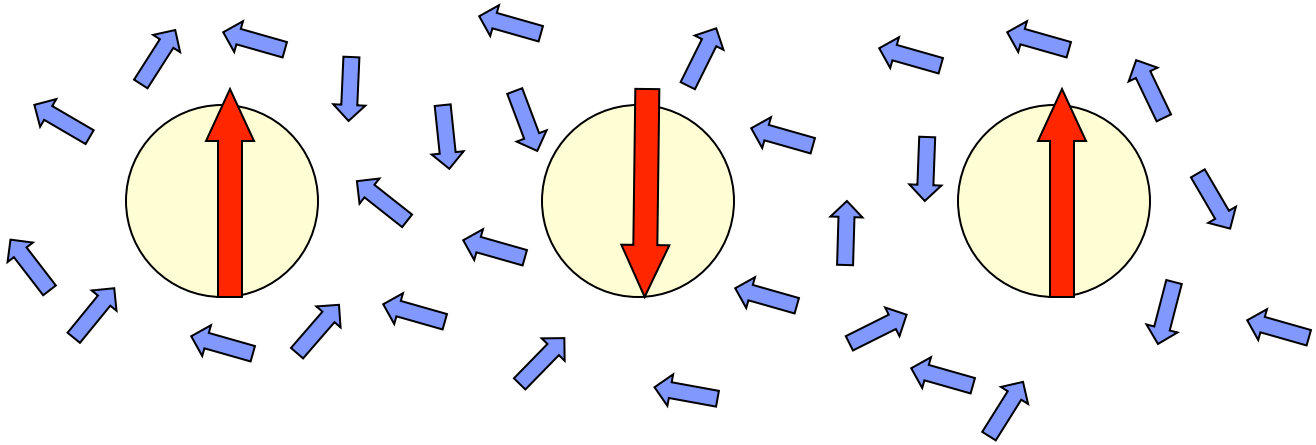


t_{2g} orbitals

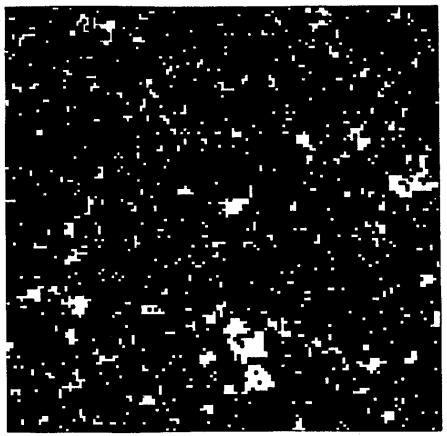
Superexchange Interactions in Magnetic Insulators



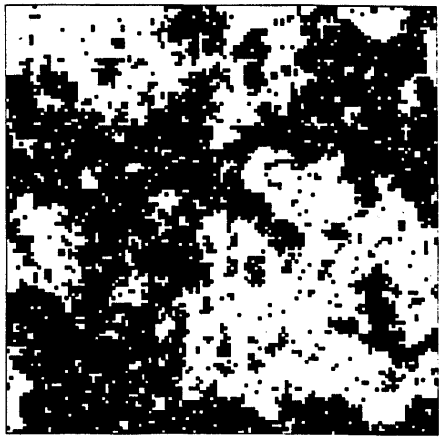
$$H = J \sum_{i,j} S_i \bullet S_j$$



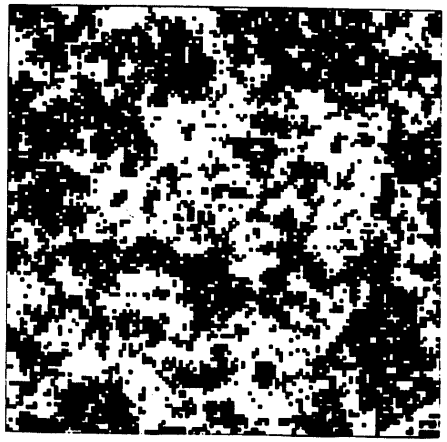
RKKY exchange in Itinerant Magnets (eg. Rare Earth Metals)



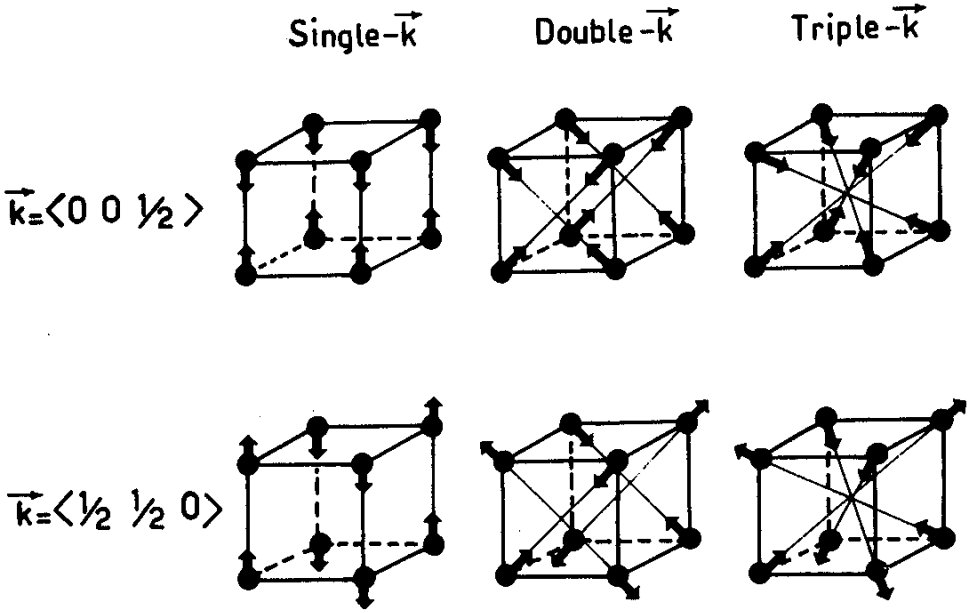
$T = 0.9\ T_C$



$T = T_C$



$T = 1.1\ T_C$



Magnetic Neutron Scattering

Neutrons carry no charge; carry s=1/2 magnetic moment

Only couple to electrons in solids via magnetic interactions

$$\mu_n = -\gamma\, \mu_N\, \sigma$$

$\gamma = 1.913$ **nuclear magneton=$e\hbar/2m_n$** **Pauli spin operator**

How do we understand what occurs when a beam of mono-energetic neutrons falls incident on a magnetic material?

Calculate a "cross section":

What fraction of the neutrons scatter off the sample with a particular:

a) Change in momentum: $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}'$

b) Change in energy: $\hbar\omega = \hbar^2 k^2/2m - \hbar^2 k'^2/2m$

- **Fermi's Golden Rule**
  1st Order Perturbation Theory

$d^2\sigma/d\Omega\, dE' \;:\; \mathbf{k}, \sigma, \lambda \rightarrow \mathbf{k}', \sigma', \lambda'$

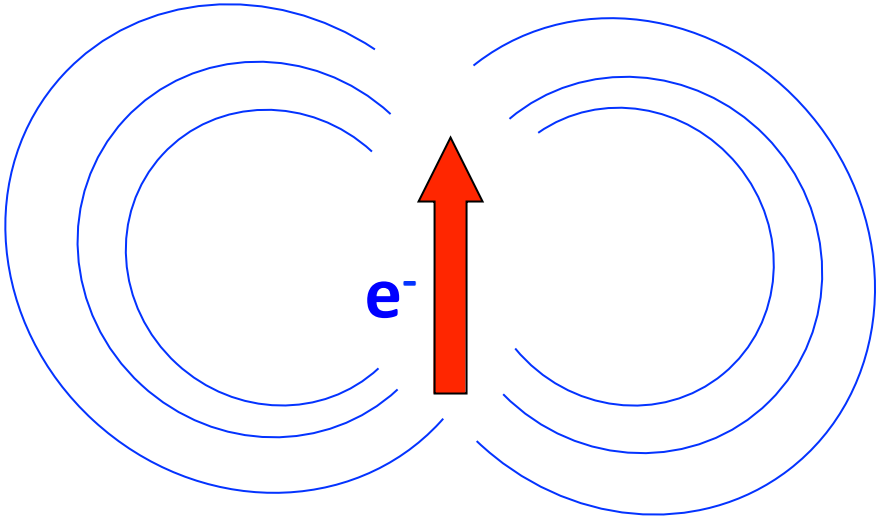
$$= k'/k \; (m/2\pi\hbar^2)^2 \; |\langle \mathbf{k}'\sigma'\lambda' | V_M | \mathbf{k}\sigma\lambda \rangle|^2 \; \delta(E_\lambda - E_{\lambda'} + \hbar\omega)$$

kinematic ***interaction matrix element*** ***energy conservation***

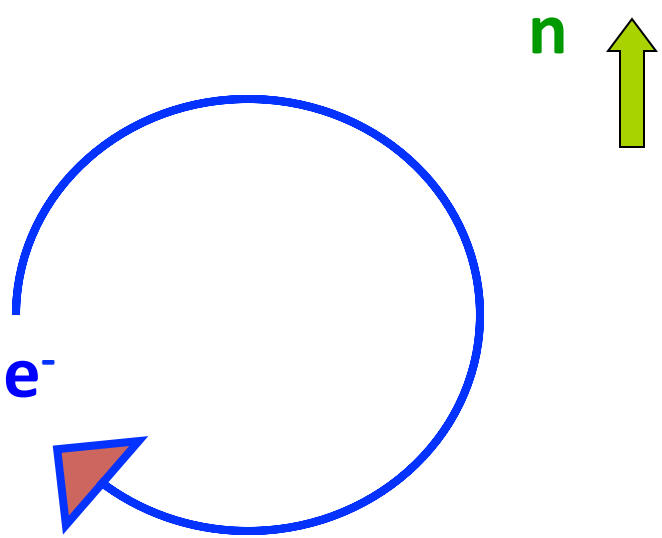
Understanding this means understanding:

V_M: The potential between the neutron and all the unpaired electrons in the material

$V_M = -\mu_n B$



Magnetic Field
from spin ½ of Electron: B_S



Magnetic Field
from Orbital Motion of Electrons: B_L

The evaluation of $|\langle \mathbf{k}' \sigma' \lambda' | V_M | \mathbf{k} \sigma \lambda \rangle|^2$ is somewhat complicated, and I will simply jump to the result:

$$d^2\sigma/d\Omega\, dE' = (\gamma r_0)^2\, k'/k\, \Sigma_{\alpha\beta}\, (\delta_{\alpha\beta} - \kappa_\alpha \kappa_\beta)$$

$$\times\ \Sigma\, \Sigma_{\text{All magnetic atoms at d and d}'}\ F_{d'}^*(\boldsymbol{\kappa}) F_d(\boldsymbol{\kappa})$$

$$\times\ \Sigma_{\lambda\lambda'}\, p_\lambda \langle \lambda | \exp(-i\boldsymbol{\kappa}\, \mathbf{R}_{d'}) S^\alpha_{d'} | \lambda' \rangle \langle \lambda' | \exp(i\boldsymbol{\kappa}\, \mathbf{R}_d) S^\beta_d | \lambda \rangle$$

$$\times\ \delta\,(E_\lambda - E_{\lambda'} + \hbar\omega)$$

With $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}'$

This expression can be useful in itself, and explicitly shows the salient features of magnetic neutron scattering

We often use the properties of $\delta\,(E_\lambda - E_\lambda' + \hbar\omega)$ to obtain $d^2\sigma/d\Omega\, dE'$ in terms of ***spin correlation functions***:

$$d^2\sigma/d\Omega\, dE' = (\gamma\, r_0)^2/(2\pi\hbar)\;\; k'/k\;\; N\{1/2\; g\; F_d(\boldsymbol{\kappa})\}^2$$

$$\times\;\; \Sigma_{\alpha\beta}\;\; (\delta_{\alpha\beta} - \kappa_\alpha\, \kappa_\beta)\; \Sigma_l\, \exp(i\boldsymbol{\kappa}\cdot\mathbf{l})$$

$$\times\;\; \int \langle \exp(-i\boldsymbol{\kappa}\cdot\mathbf{u_0}))\exp(i\boldsymbol{\kappa}\cdot\mathbf{u}_l(t))\rangle$$

$$\times\;\; \langle S_0^{\alpha}(0)\; S_l^{\beta}(t)\rangle\; \exp(-i\omega\, t)\; dt$$

Dynamic Spin Pair Correlation Function

Fourier tranform: $S(\kappa, \omega)$

Bottom Lines:

- **Comparable in strength to nuclear scattering**
- $\{1/2\, g\, F(\kappa)\}^2$: **goes like the magnetic form factor squared**
- $\Sigma_{\alpha\beta}\ (\delta_{\alpha\beta} - \kappa_\alpha \kappa_\beta)$: **sensitive only to those components of spin $\perp \kappa$**
- **Dipole selection rules, goes like:** $< \lambda' \mid S^\beta_d \mid \lambda >$;

where $S^\beta = S^x, S^y\ (S^+, S^-)$ or S^z

Diffraction type experiments:

Add up spin correlations with phase set by $\kappa = k - k'$

$\Sigma_l \exp(i\kappa\cdot l) <S_0^\alpha(0)\, S_l^\beta(t)>$ **with t=0**

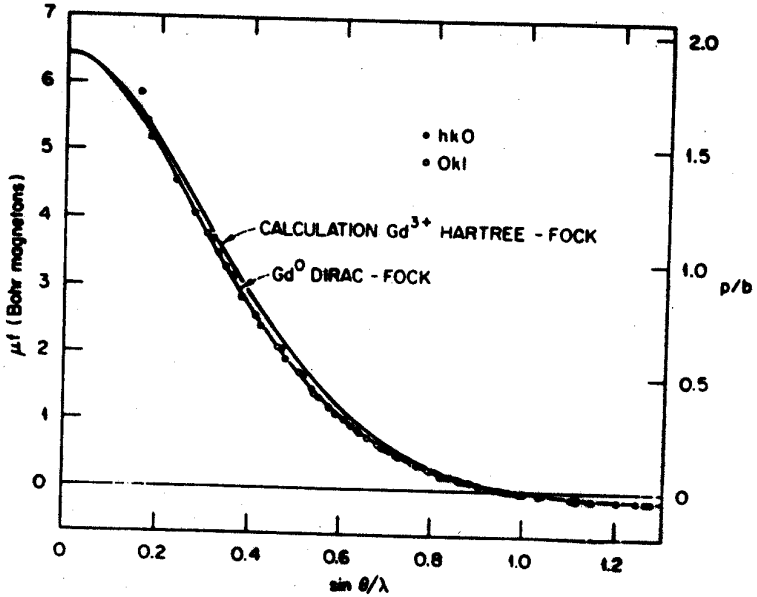
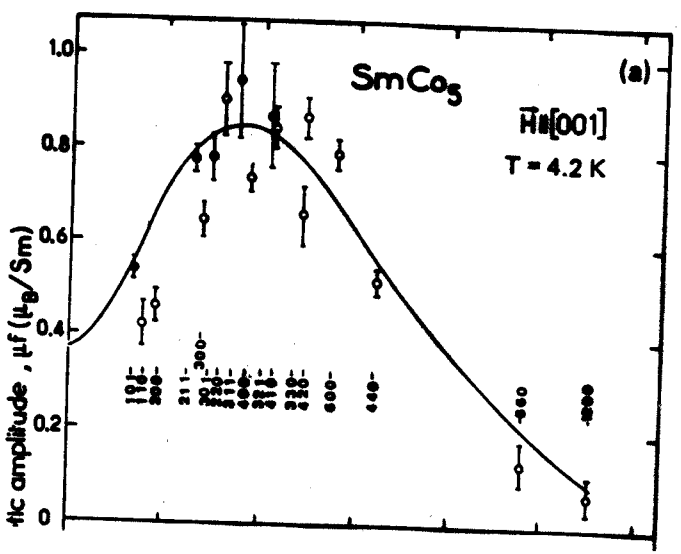
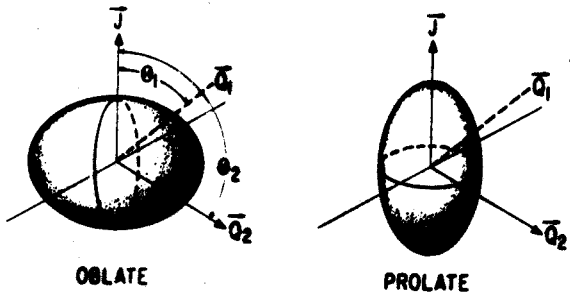


FIG. 13. Comparison of the experimental ^{160}Gd form factor at 96 K as measured by Moon *et al.*[47] with nonrelativistic Hartree–Fock and relativistic Dirac–Fock calculations by Freeman and Desclaux.[36]



Magnetic form factor, F(κ), is the Fourier transform of the spatial distribution of magnetic electrons –

usually **falls off monotonically with κ as π/(1 A) ~ 3 A^{-1}**



Three types of scattering experiments are typically performed:

- **Elastic scattering**
- **Energy-integrated scattering**
- **Inelastic scattering**

Elastic Scattering

$$\hbar\omega = (\hbar k)^2/2m - (\hbar k')^2/2m = 0$$

measures time-independent magnetic structure

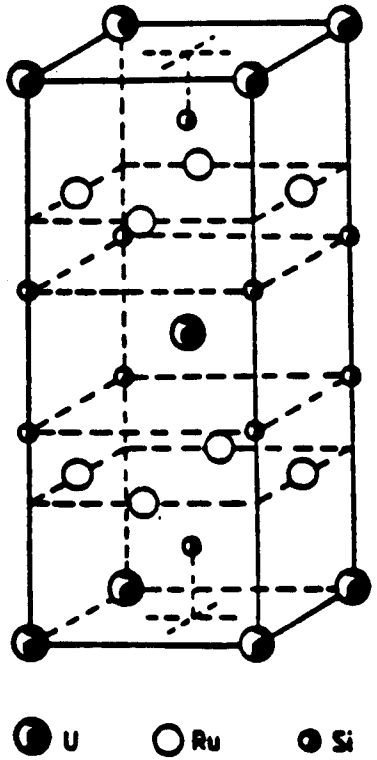
$$d\sigma/d\Omega = (\gamma\, r_0)^2\{1/2\, g\, F(\kappa)\}^2 \quad \exp(-2W)$$

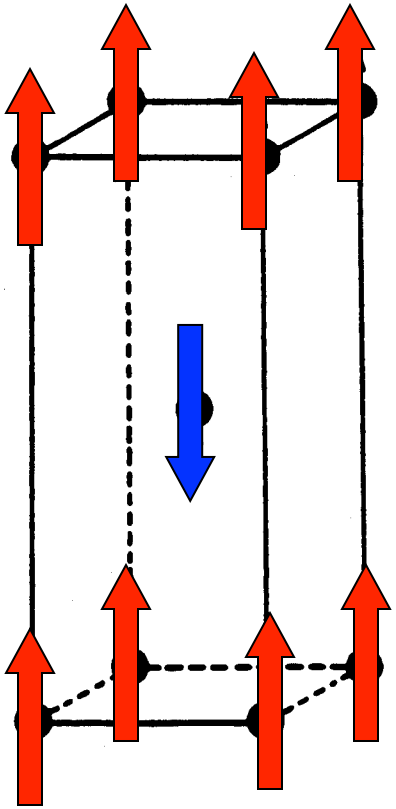
$$\times \Sigma_{\alpha\beta}\ (\delta_{\alpha\beta} - \kappa_\alpha \kappa_\beta)\ \Sigma_l \exp(i\kappa\cdot l) \langle S_0^\alpha\rangle \langle S_l^\beta\rangle$$

S ⊥κ only

Add up spins with exp(iκ·l) phase factor

URu_2Si_2





κ = 0,0,1

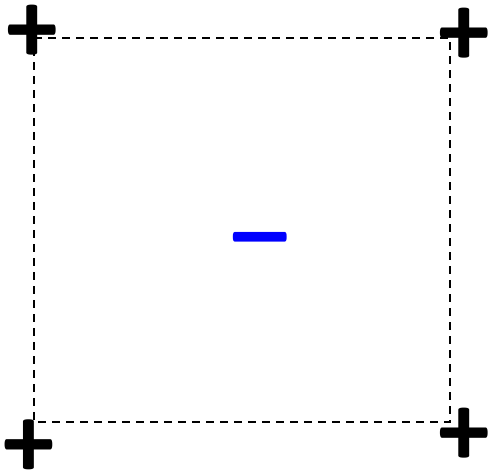
$a^*=b^*=0$:
everything within a basal plane (a-b) adds up in phase

$c^*=1$:
2π phase shift from top to bottom of unit cell

π phase shift from corners to body-centre –good …..
but μ // κ kills off intensity!

Try κ = 1,0,0:

$\mu \perp \kappa$ good!

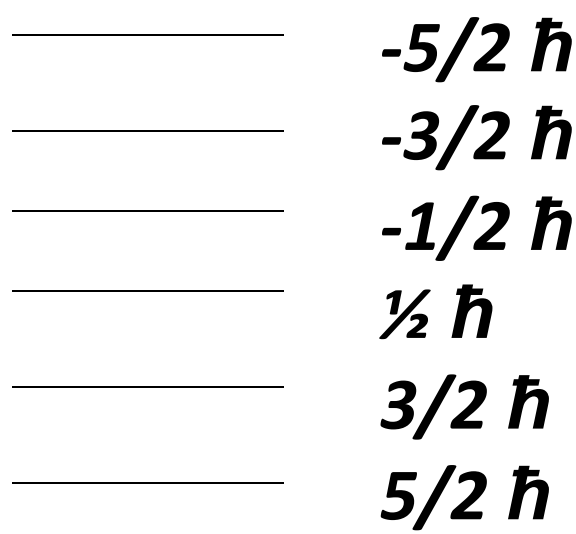


Mn^{2+} as an example: ½ filled 3d shell S=5/2

(2S+1) = 6 states : $|S(S+1), m_z>$

$m_z = +5/2\,\hbar, +3/2\,\hbar, +1/2\,\hbar, -1/2\,\hbar, -3/2\,\hbar, -5/2\,\hbar$

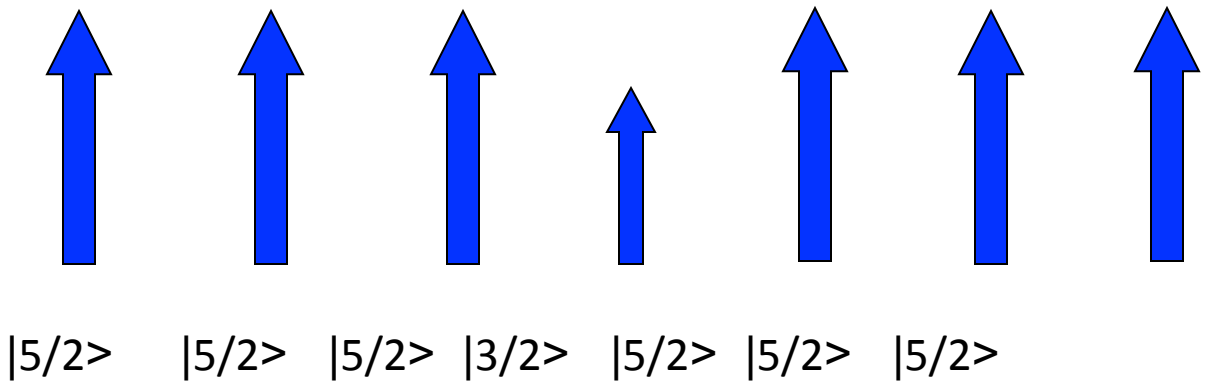
H=0; 6 degenerate states

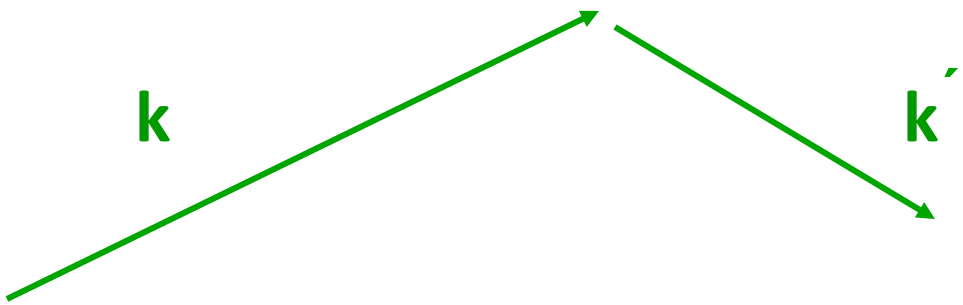


H ≠ 0; 6 non-degenerate states

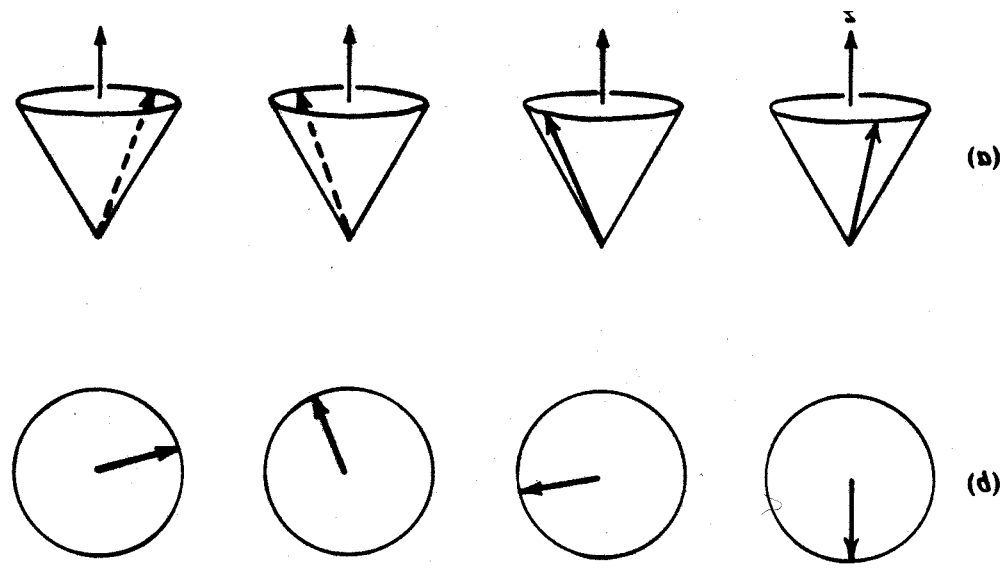
$< 3/2 | S^- | 5/2 > \neq 0 \rightarrow$ inelastic scattering

Magnetic sites are coupled by exchange interactions:





$$H = J \sum_{i,j} S_i \bullet S_j$$



Spin Wave Eigenstate:

"Defect" is distributed over all possible sites

Inelastic Magnetic Scattering : $|k| \neq |k^0|$

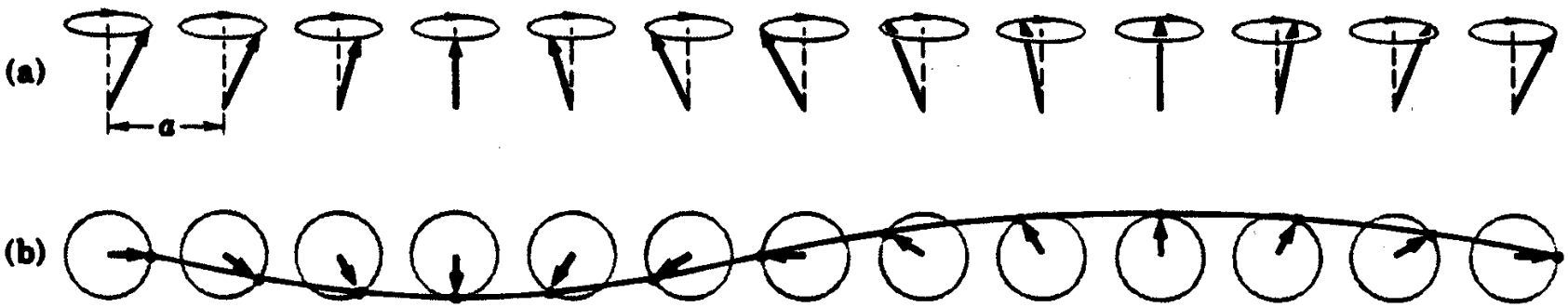


Figure 9 A spin wave on a line of spins. (a) The spins viewed in perspective. (b) Spins viewed from above, showing one wavelength. The wave is drawn through the ends of the spin vectors.

Study magnetic excitations (eg. spin waves)

Dynamic magnetic moments **on time scale 10^{-9} to 10^{-12} sec**

$$S(\kappa, \omega) = n(\omega)\, \chi''(\kappa, \omega)$$

Bose (temperature) factor

Imaginary part of the dynamic susceptibility

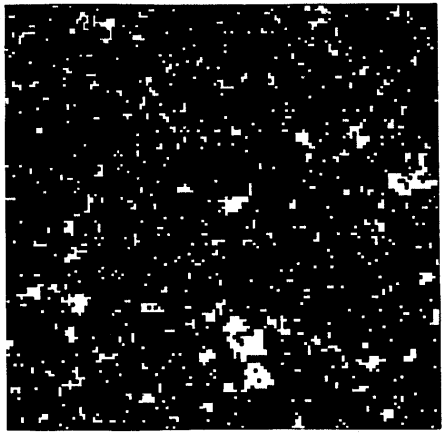
Sum Rules:

One can understand very general features of the magnetic neutron Scattering experiment on the basis of "sum rules".

1. $\chi_{DC} = \int (\chi''(\kappa=0, \omega)/\omega)\, d\omega$;

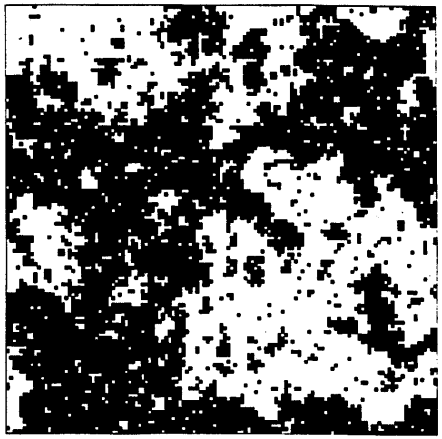
where χ_{DC} is the χ measured with a SQUID

2. $\int d\omega \int_{BZ} d\kappa\, S(\kappa, \omega) = S(S+1)$



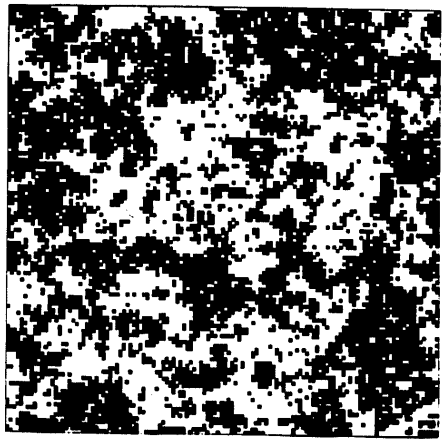
$T = 0.9\ T_C$

Symmetry broken



$T = T_C$

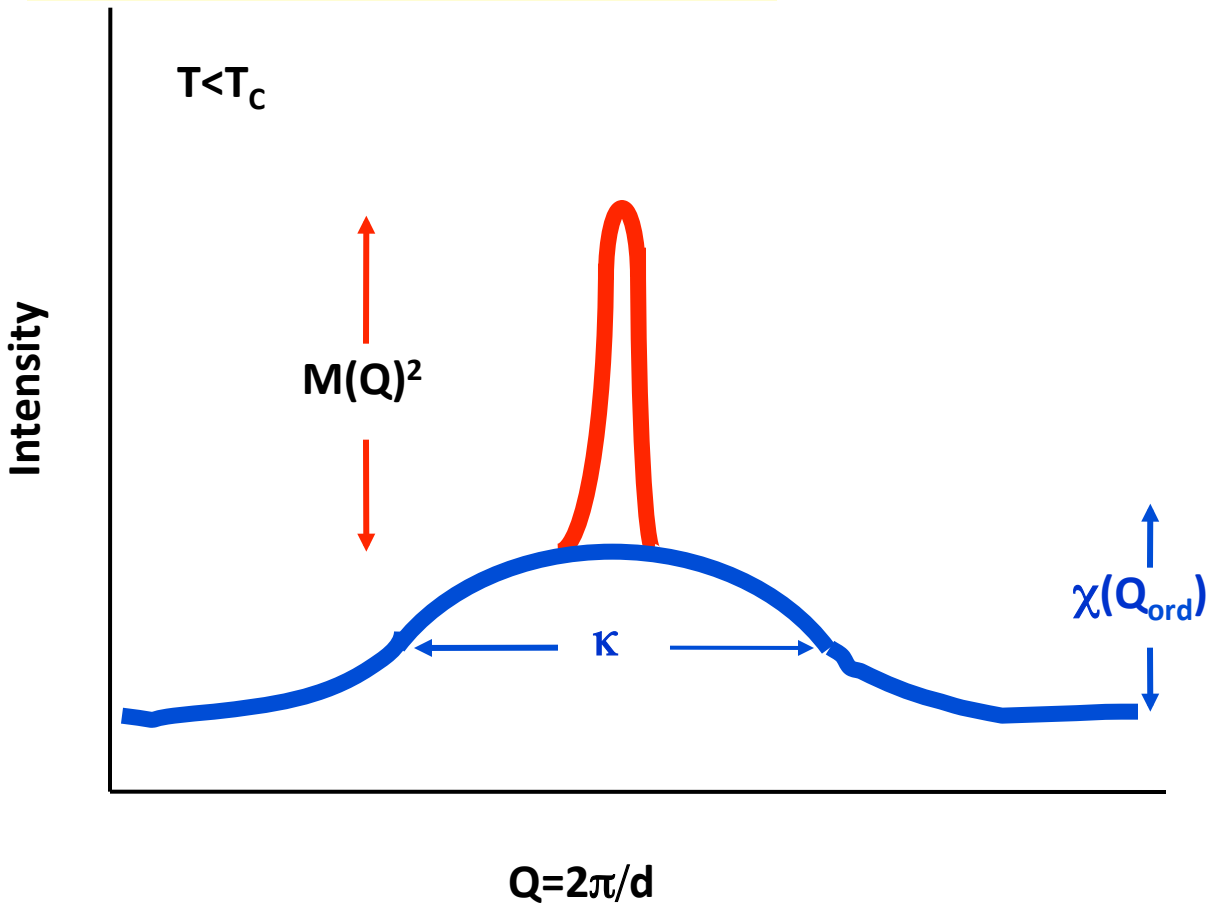
$\xi \sim$ very large
Origin of universality

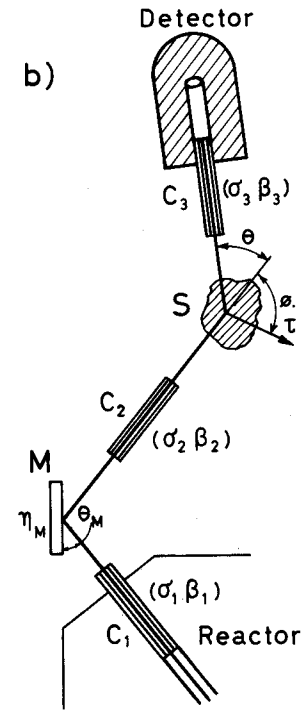


$T = 1.1\ T_C$

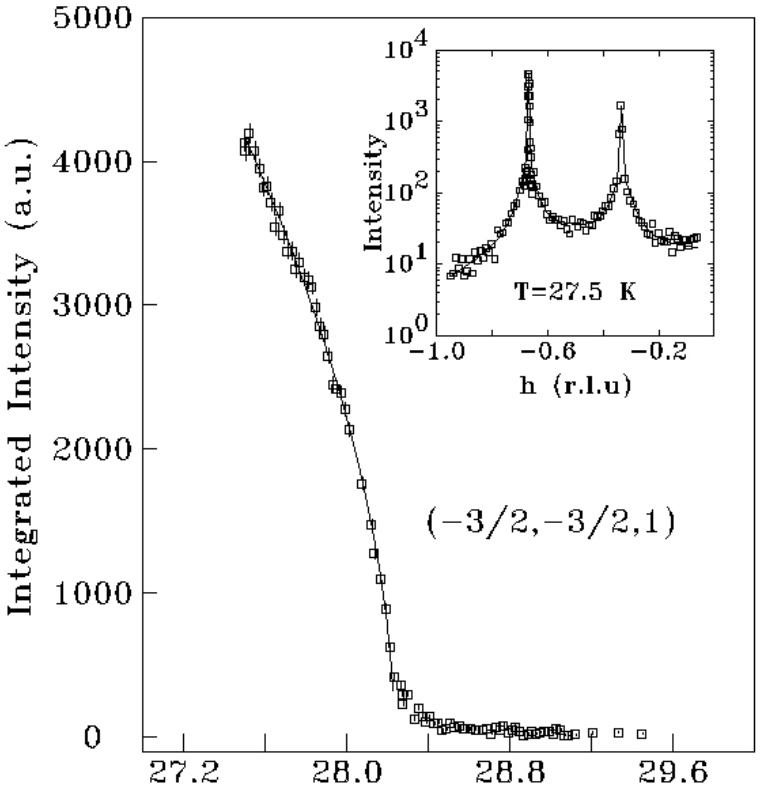
- **Bragg scattering gives square of order parameter; symmetry breaking**

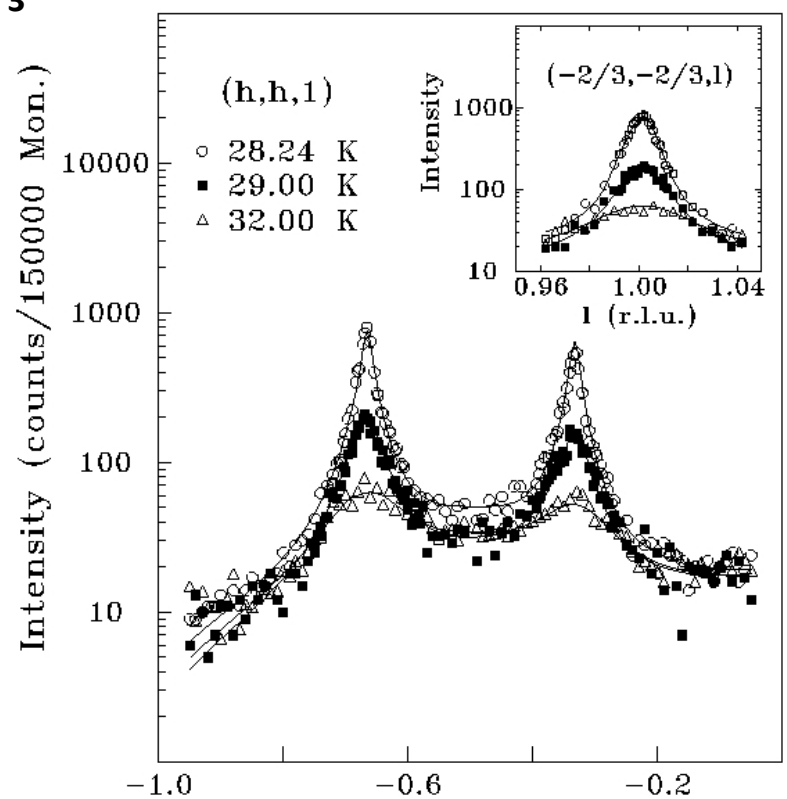
- **Diffuse scattering gives fluctuations in the order parameter**





$CsCoBr_3$





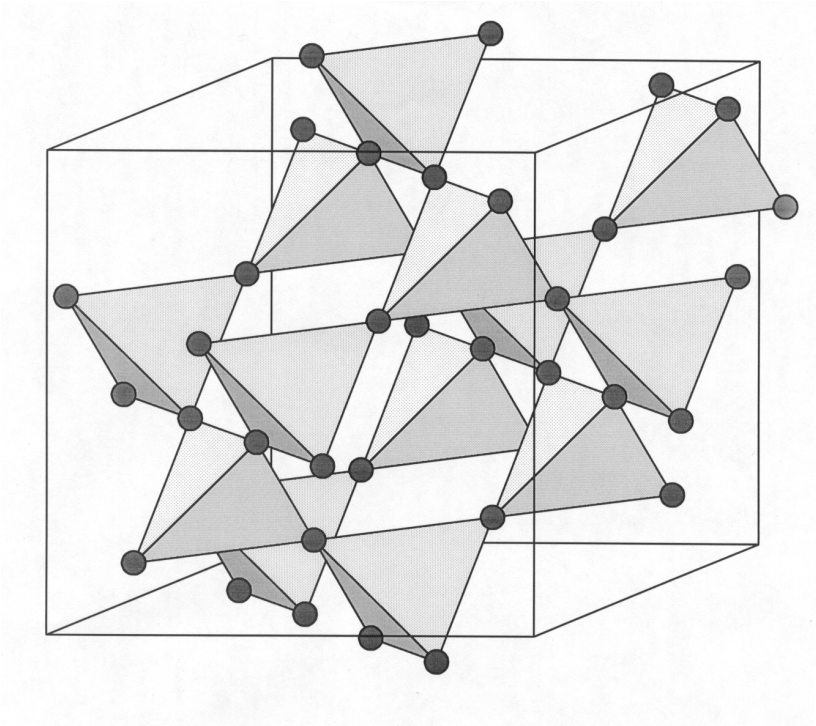
Bragg scattering

Q=(2/3, 2/3, 1)

Energy-integrated critical scattering

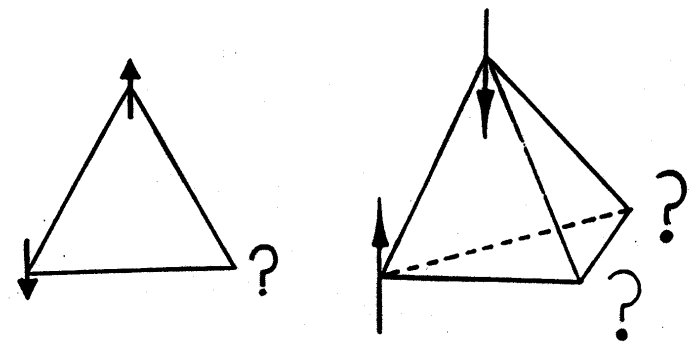
$$I=M^2=M_0^2(1-T/T_C)^{2\beta}$$

$$\frac{d\sigma(\vec{Q})}{d\Omega} = \frac{\chi(\vec{Q}_{ord})}{1+\frac{q_a^2+q_b^2}{\kappa_{ab}^2}+\frac{q_c^2}{\kappa_c^2}},$$

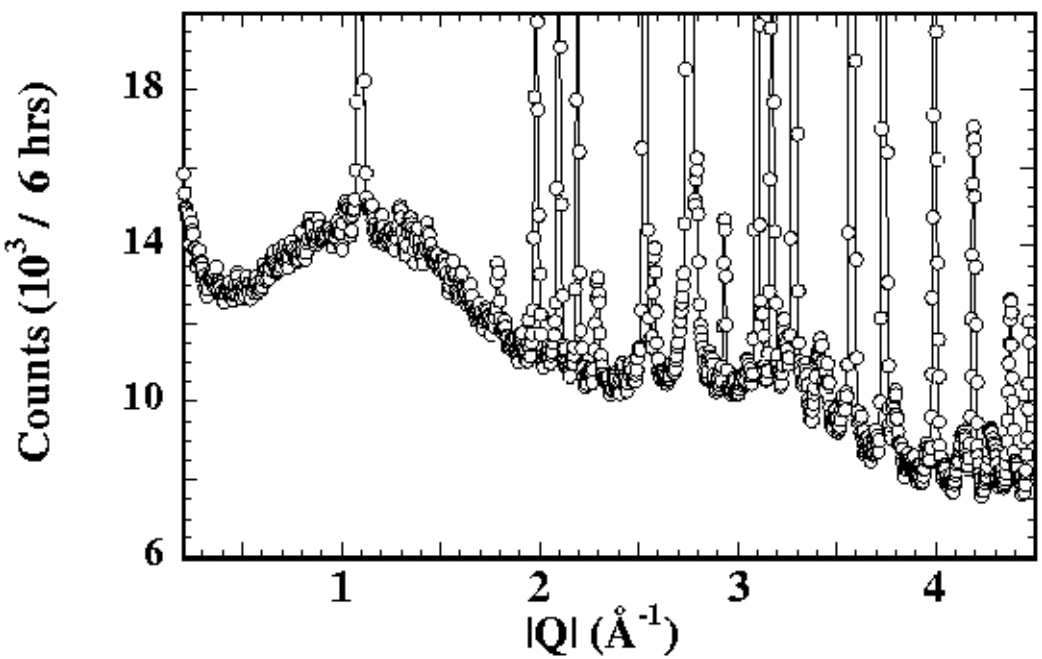


Geometrical Frustration:

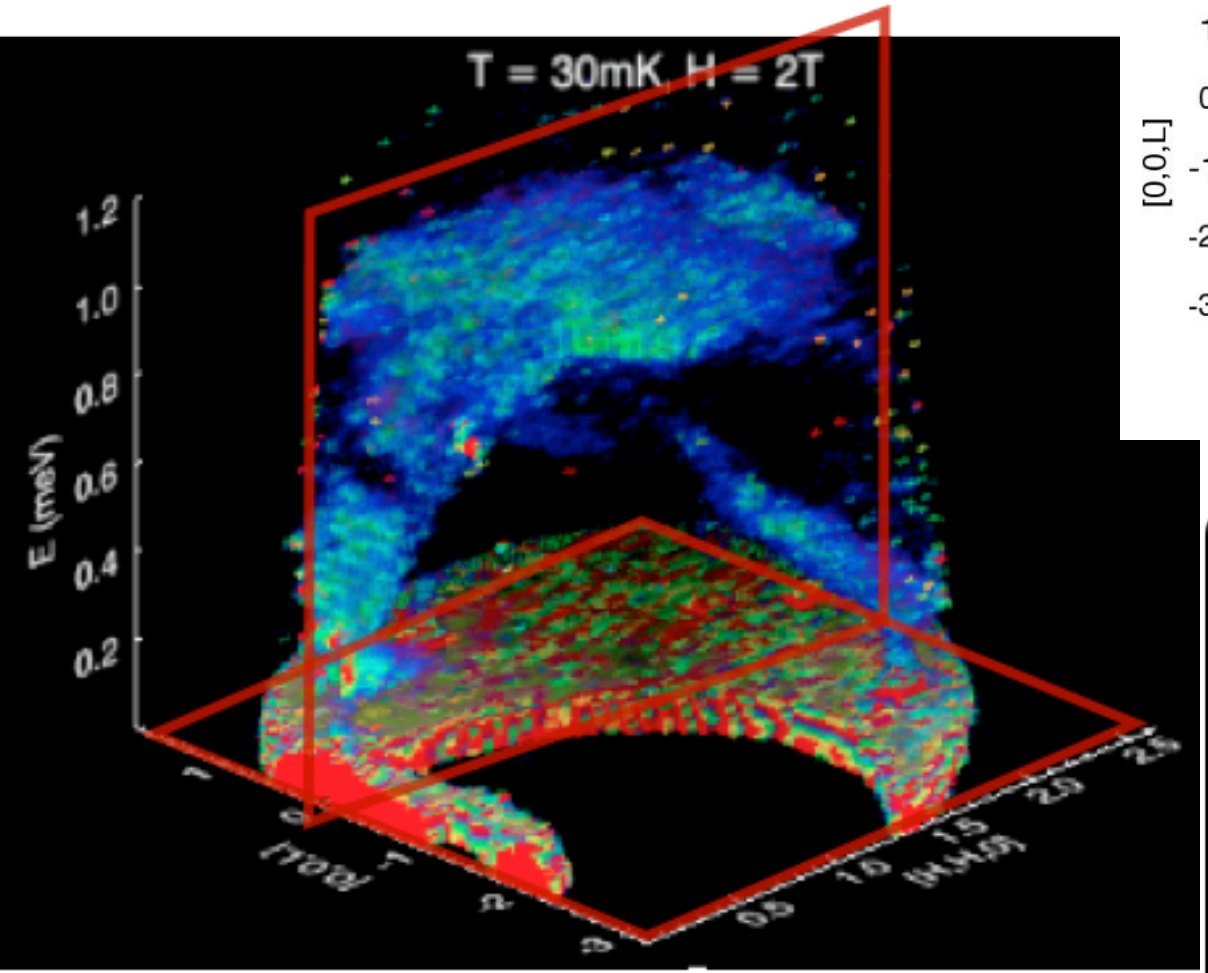
The cubic pyrochlore structure;
A network of corner-sharing tetrahedra

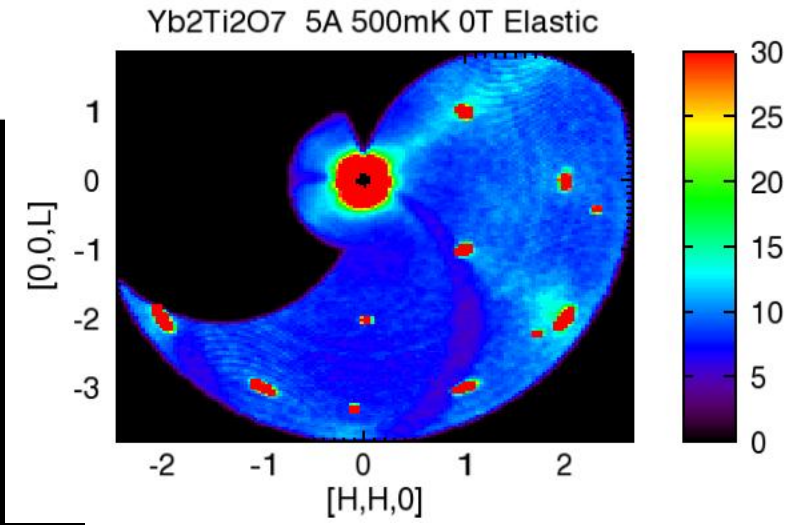


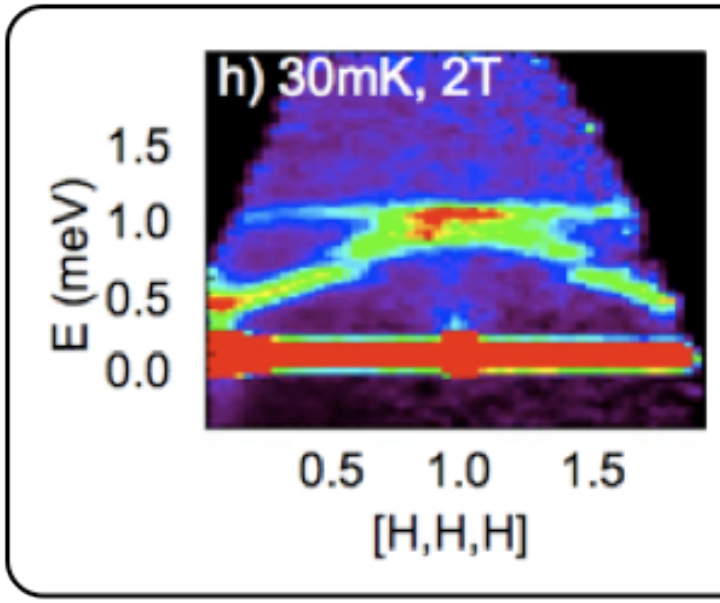
Low temperature powder neutron diffraction from $Tb_2Ti_2O_7$



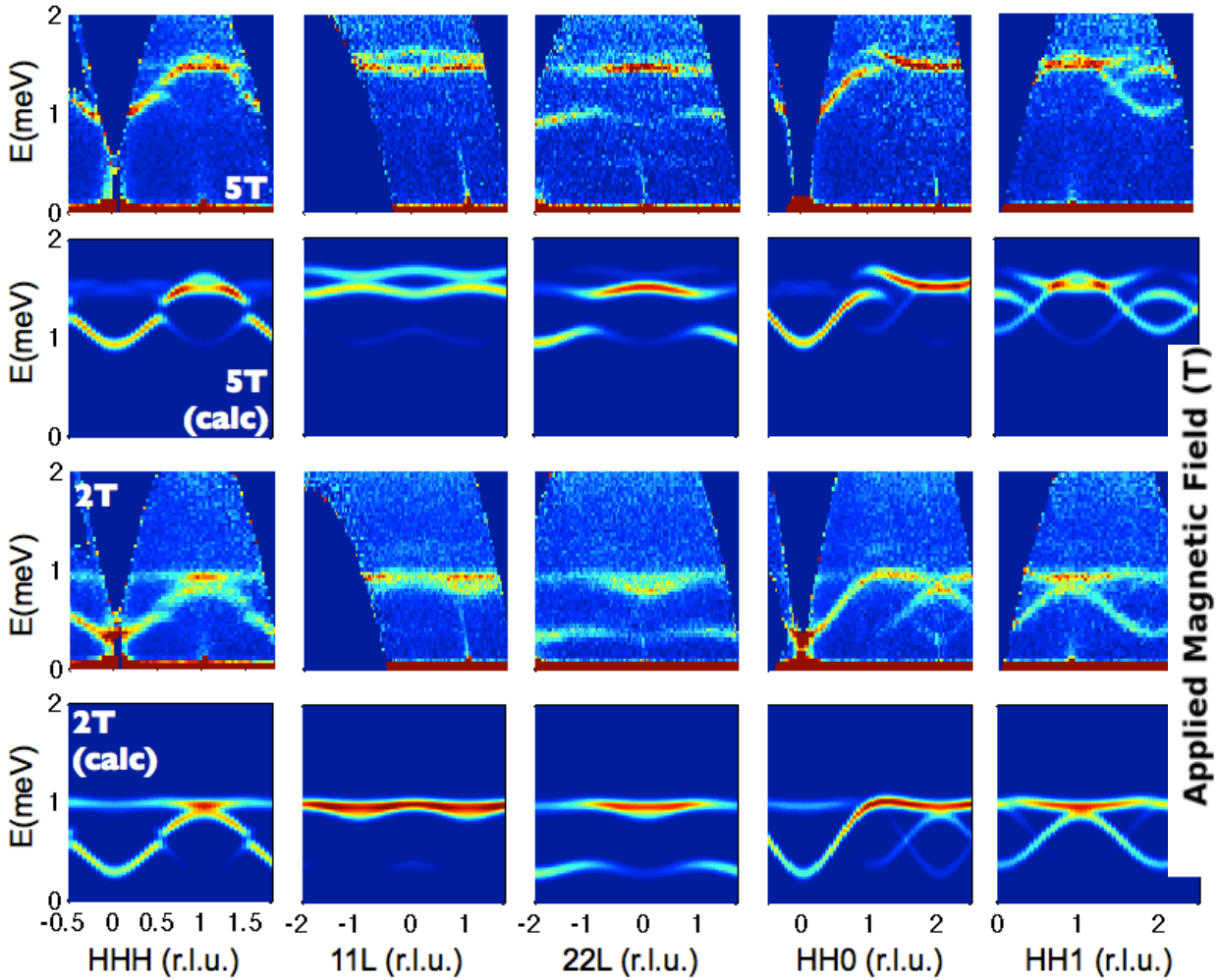
$Yb_2Ti_2O_7$ field polarized state

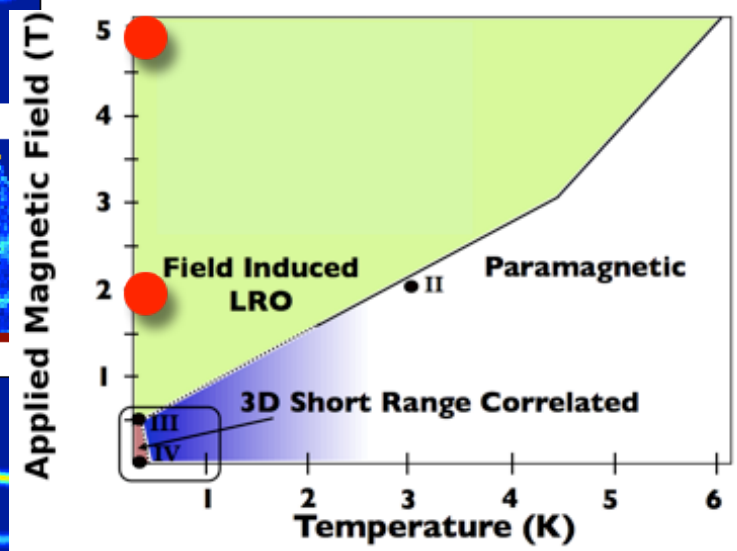






$Yb_2Ti_2O_7$ field polarized state





"Quantum Spin Ice"

K.A. Ross, L. Savary, B. D. Gaulin, and L. Balents, *Quantum Excitations in Quantum Spin Ice, Phys. Rev. X* ***1, 021002 (2011).***

$$J_{zz} = 0.17 \pm 0.04,\ J_{\pm} = 0.05 \pm 0.01,\ J_{\pm\pm} = 0.05 \pm 0.01,\ J_{z\pm} = -0.14 \pm 0.01 \text{ (meV)}$$

Conclusions:

- **Neutrons probe magnetism on length scales from 1 – 100 A, and on time scales from 10^{-9} to 10^{-12} seconds**

- **Magnetic neutron scattering goes like the form factor squared (small κ), follows dipole selection rules $< \lambda' \mid S^{+,-,z} \mid \lambda >$, and is sensitive only to components of moments $\perp$ to κ.**

- **Neutron scattering is the most powerful probe of magnetism in materials; magnetism is a killer application of neutron scattering (1 of 3).**