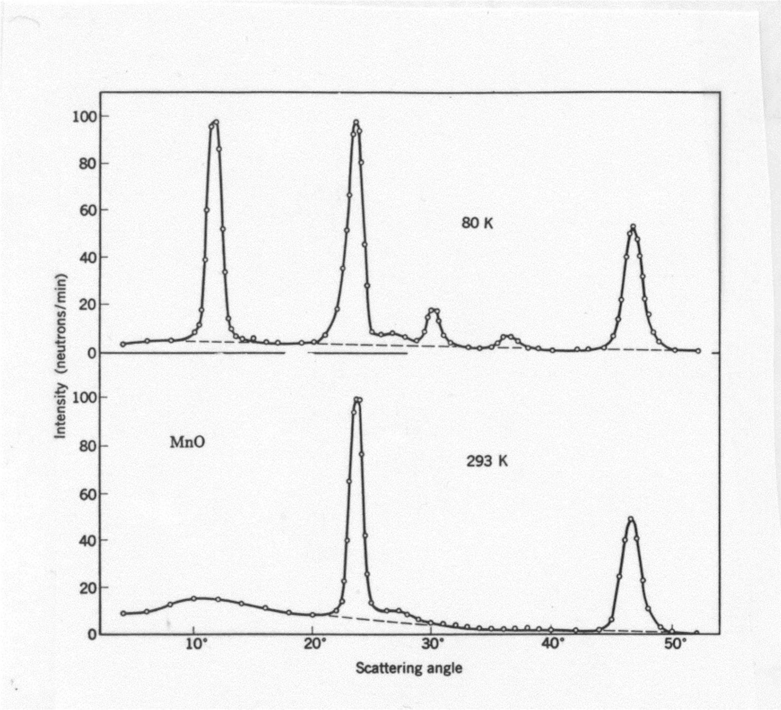
Magnetic Neutron Scattering

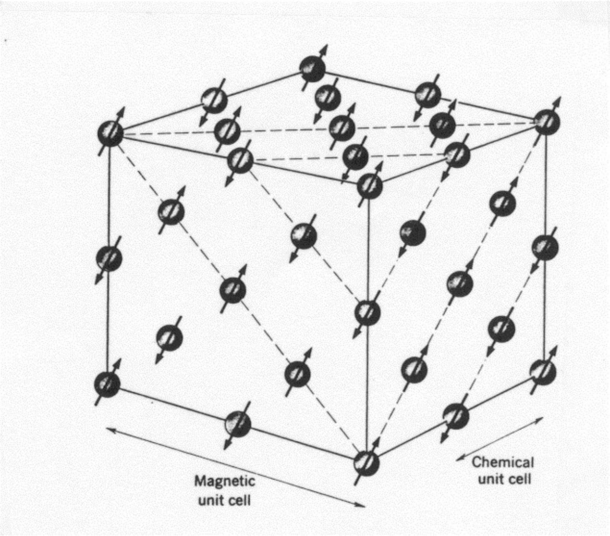
Bruce D. Gaulin

McMaster University

Brockhouse Institute for Materials Research

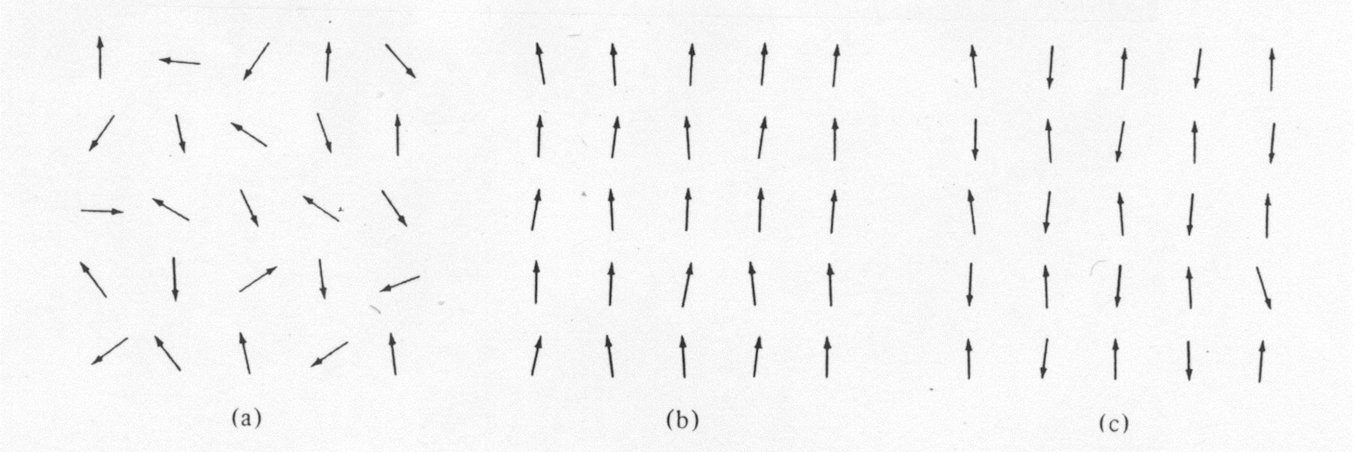
- **Magnetism and Neutron Scattering – A Killer Application**
- **Magnetism in Solids**
- **Bottom lines on magnetic neutron scattering**
- **Examples**





C. G. Shull et al, 1951

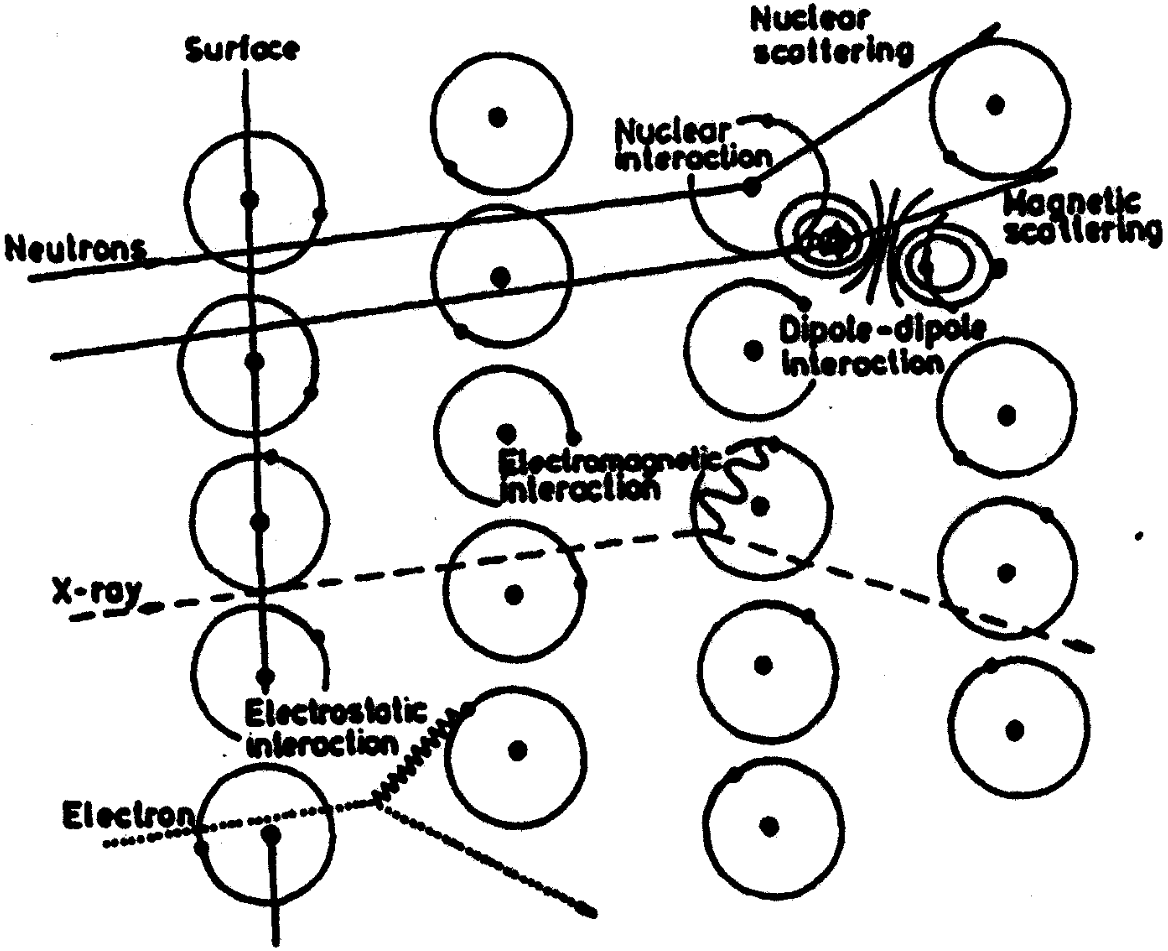
Magnetic Structure of MnO



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

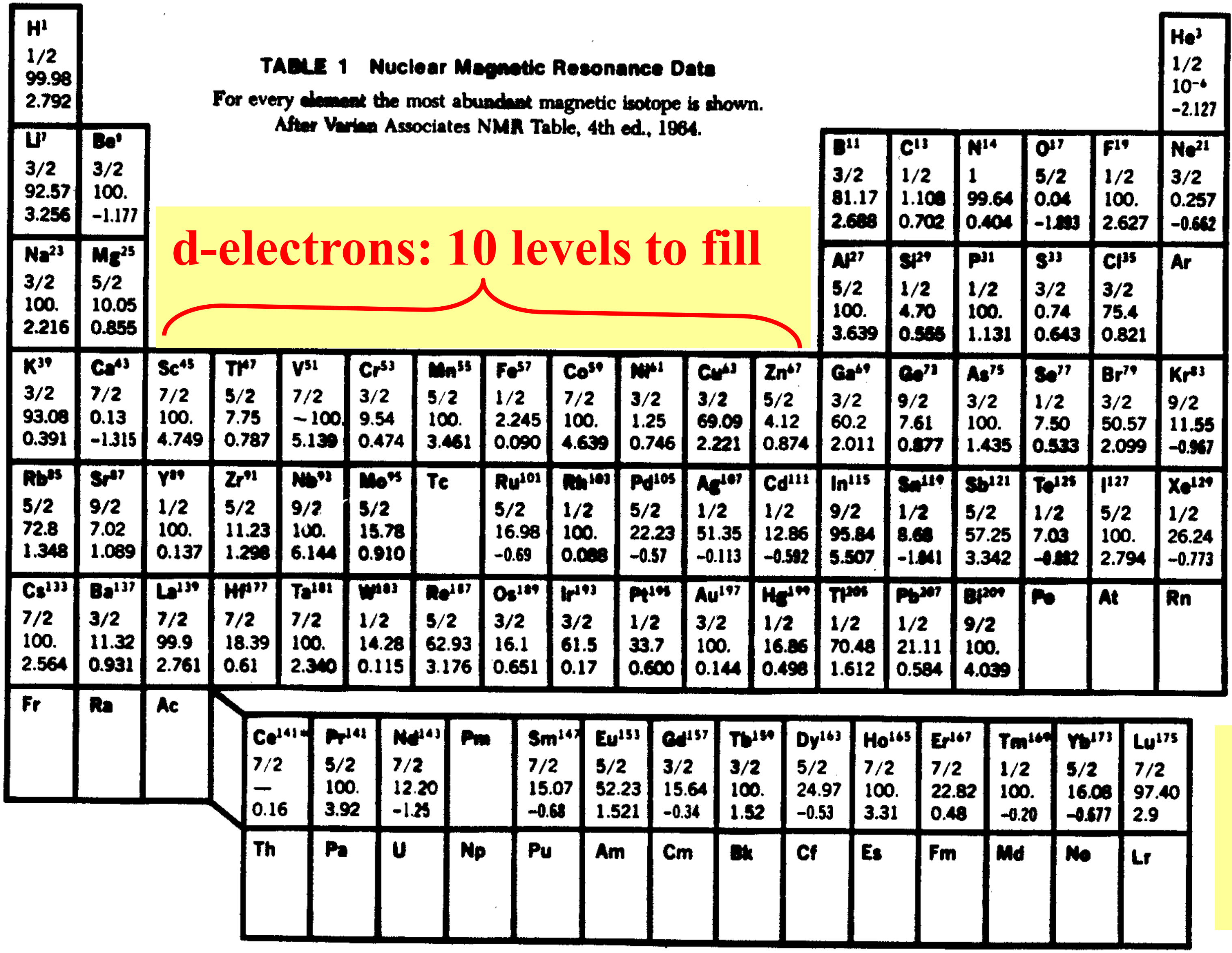


TABLE 1 Nuclear Magnetic Resonance Data

For every element the most abundant magnetic isotope is shown.
After Varian Associates NMR Table, 4th ed., 1964.

d-electrons: 10 levels to fill

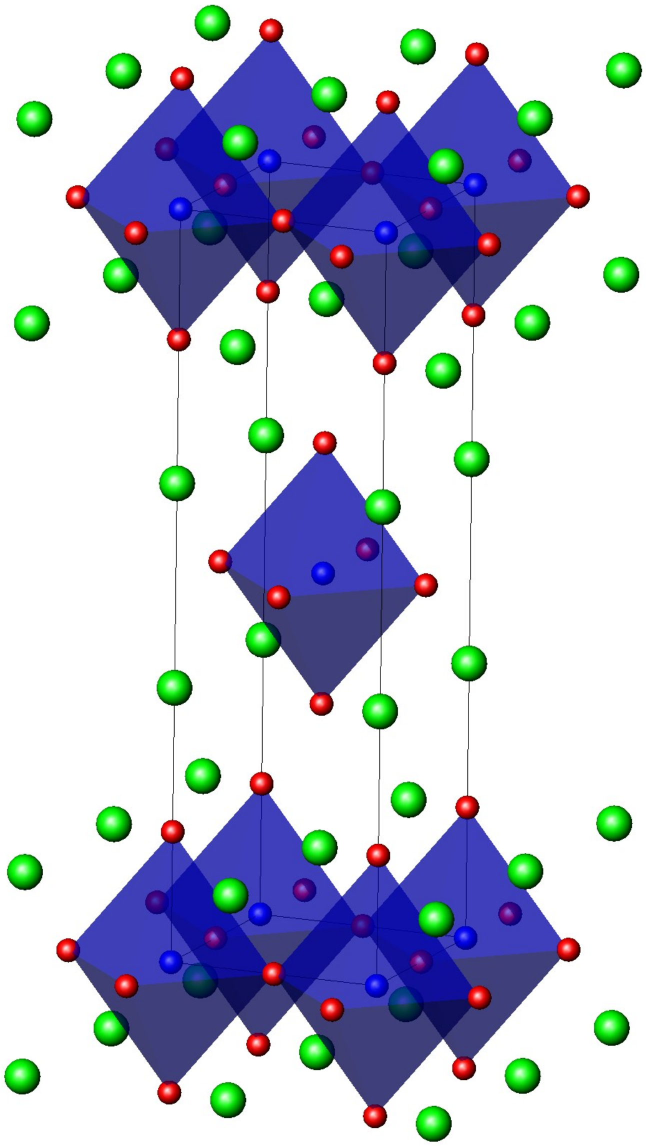
H^{1} 1/2 99.98 2.792																	He^{3} 1/2 10^{-6} −2.127
Li^{7} 3/2 92.57 3.256	Be^{9} 3/2 100. −1.177											B^{11} 3/2 81.17 2.688	C^{13} 1/2 1.108 0.702	N^{14} 1 99.64 0.404	O^{17} 5/2 0.04 −1.893	F^{19} 1/2 100. 2.627	Ne^{21} 3/2 0.257 −0.662
Na^{23} 3/2 100. 2.216	Mg^{25} 5/2 10.05 0.855											Al^{27} 5/2 100. 3.639	Si^{29} 1/2 4.70 0.555	P^{31} 1/2 100. 1.131	S^{33} 3/2 0.74 0.643	Cl^{35} 3/2 75.4 0.821	Ar
K^{39} 3/2 93.08 0.391	Ca^{43} 7/2 0.13 −1.315	Sc^{45} 7/2 100. 4.749	Ti^{47} 5/2 7.75 0.787	V^{51} 7/2 ~100. 5.139	Cr^{53} 3/2 9.54 0.474	Mn^{55} 5/2 100. 3.461	Fe^{57} 1/2 2.245 0.090	Co^{59} 7/2 100. 4.639	Ni^{61} 3/2 1.25 0.746	Cu^{63} 3/2 69.09 2.221	Zn^{67} 5/2 4.12 0.874	Ga^{69} 3/2 60.2 2.011	Ge^{73} 9/2 7.61 0.877	As^{75} 3/2 100. 1.435	Se^{77} 1/2 7.50 0.533	Br^{79} 3/2 50.57 2.099	Kr^{83} 9/2 11.55 −0.967
Rb^{85} 5/2 72.8 1.348	Sr^{87} 9/2 7.02 1.089	Y^{89} 1/2 100. 0.137	Zr^{91} 5/2 11.23 1.298	Nb^{93} 9/2 100. 6.144	Mo^{95} 5/2 15.78 0.910	Tc	Ru^{101} 5/2 16.98 −0.69	Rh^{103} 1/2 100. 0.088	Pd^{105} 5/2 22.23 −0.57	Ag^{107} 1/2 51.35 −0.113	Cd^{111} 1/2 12.86 −0.592	In^{115} 9/2 95.84 5.507	Sn^{119} 1/2 8.68 −1.041	Sb^{121} 5/2 57.25 3.342	Te^{125} 1/2 7.03 −0.882	I^{127} 5/2 100. 2.794	Xe^{129} 1/2 26.24 −0.773
Cs^{133} 7/2 100. 2.564	Ba^{137} 3/2 11.32 0.931	La^{139} 7/2 99.9 2.761	Hf^{177} 7/2 18.39 0.61	Ta^{181} 7/2 100. 2.340	W^{183} 1/2 14.28 0.115	Re^{187} 5/2 62.93 3.176	Os^{189} 3/2 16.1 0.651	Ir^{193} 3/2 61.5 0.17	Pt^{195} 1/2 33.7 0.600	Au^{197} 3/2 100. 0.144	Hg^{199} 1/2 16.86 0.498	Tl^{205} 1/2 70.48 1.612	Pb^{207} 1/2 21.11 0.584	Bi^{209} 9/2 100. 4.039	Po	At	Rn
Fr	Ra	Ac															

Ce^{141*} 7/2 — 0.16	Pr^{141} 5/2 100. 3.92	Nd^{143} 7/2 12.20 −1.25	Pm	Sm^{147} 7/2 15.07 −0.68	Eu^{153} 5/2 52.23 1.521	Gd^{157} 3/2 15.64 −0.34	Tb^{159} 3/2 100. 1.52	Dy^{163} 5/2 24.97 −0.53	Ho^{165} 7/2 100. 3.31	Er^{167} 7/2 22.82 0.48	Tm^{169} 1/2 100. −0.20	Yb^{173} 5/2 16.08 −0.677	Lu^{175} 7/2 97.40 2.9
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

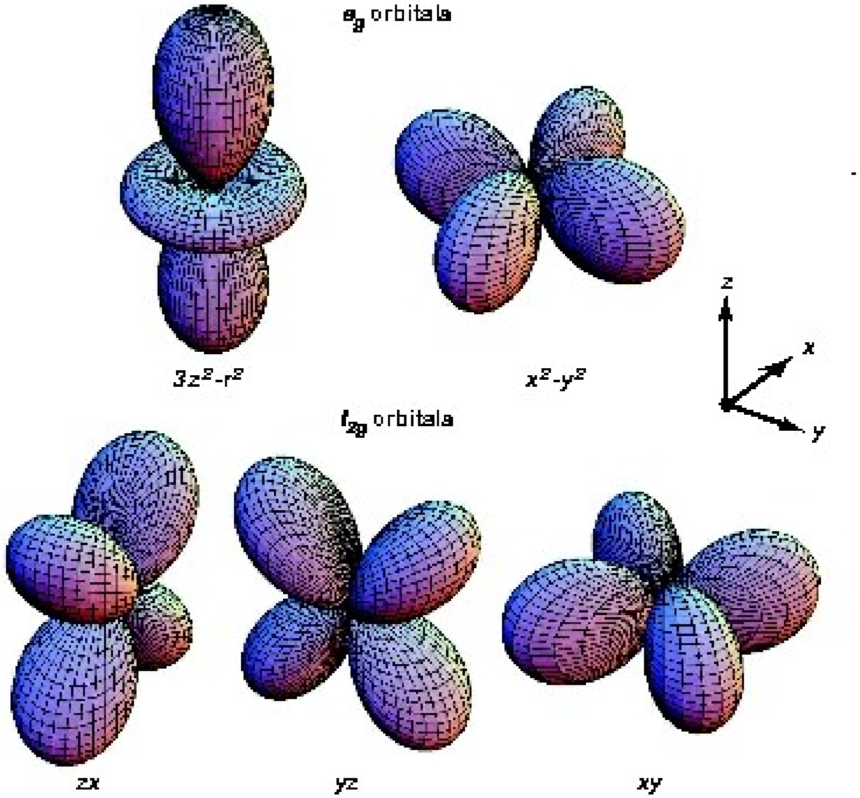
4f

14 levels

5f



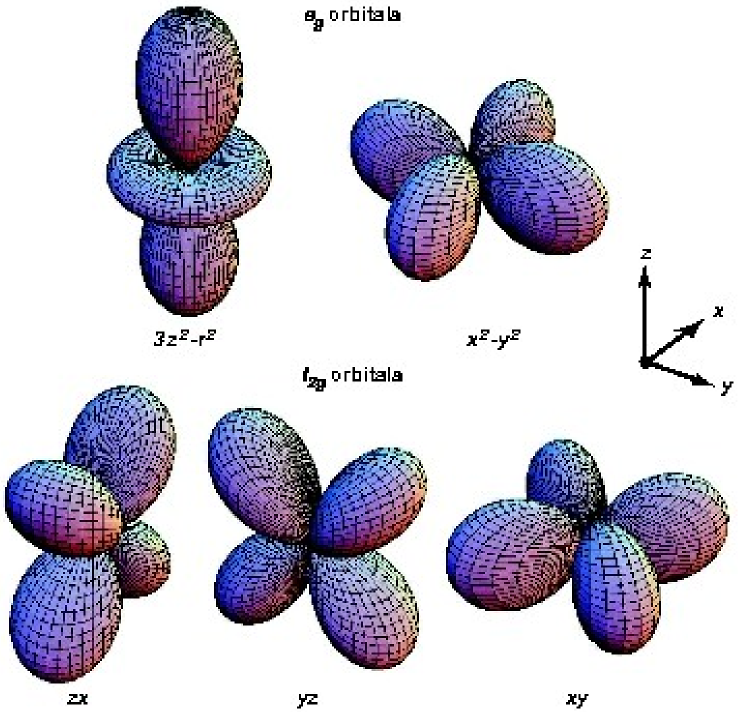
e_g orbitals



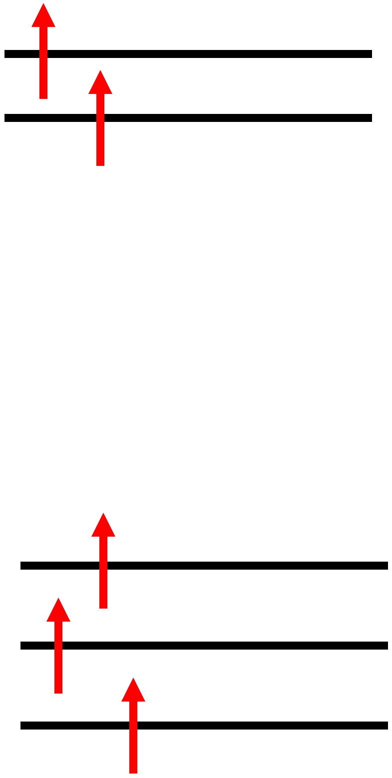
t_{2g} orbitals

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

e_g orbitals

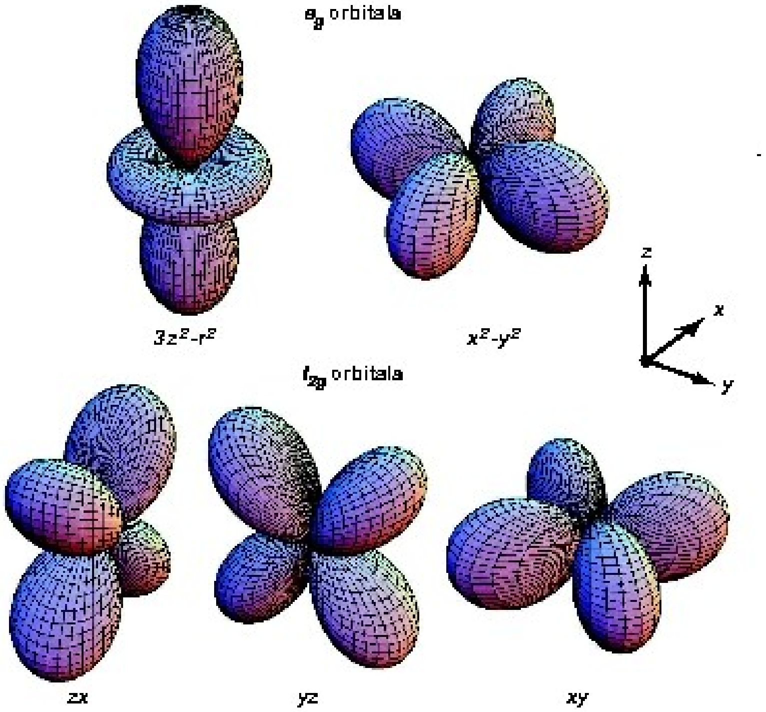


t_{2g} orbitals

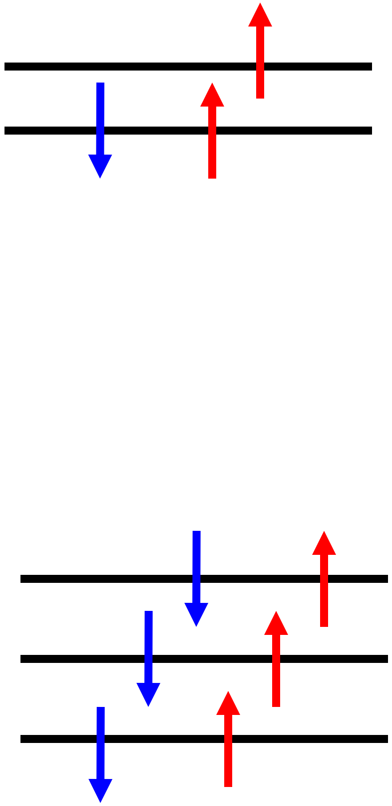


$3d^9$: Cu^{2+}

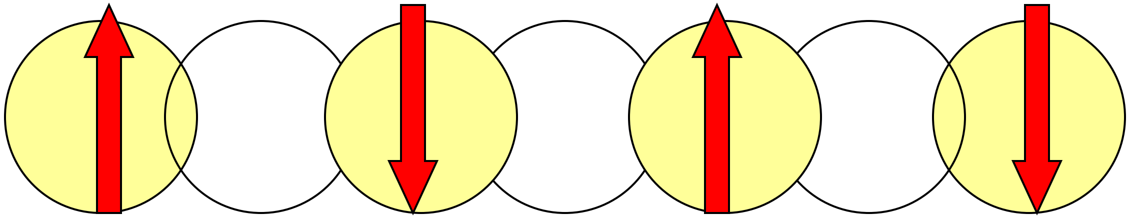
e_g orbitals



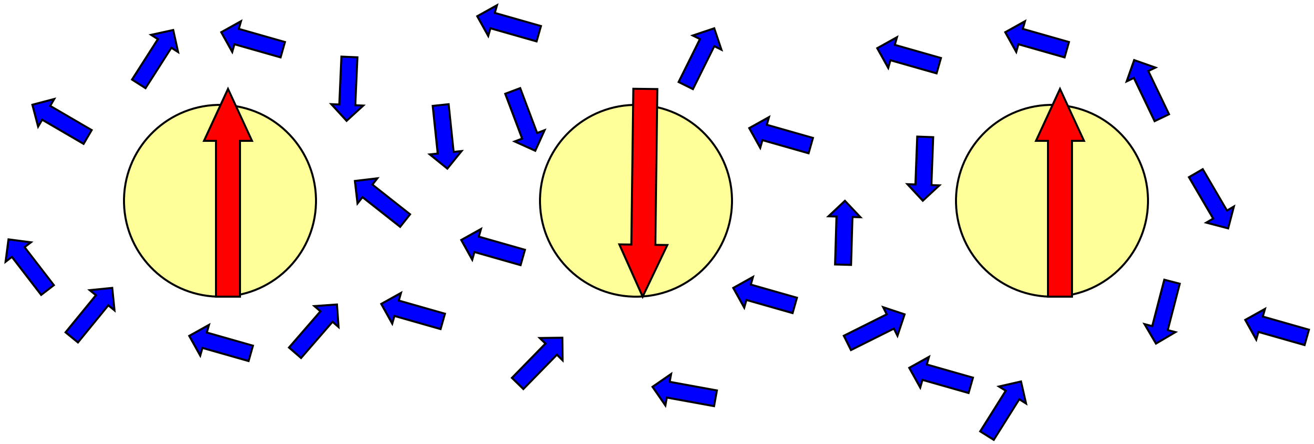
t_{2g} orbitals



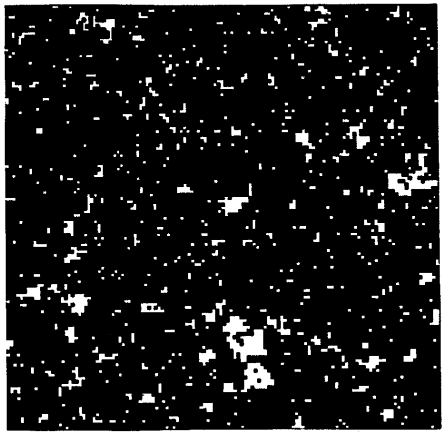
Superexchange Interactions in Magnetic Insulators



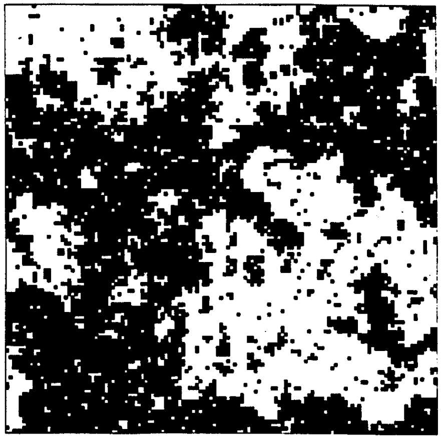
$$H = \mathbf{J}\ \Sigma_{i,j}\ \mathbf{S}_i \bullet \mathbf{S}_j$$



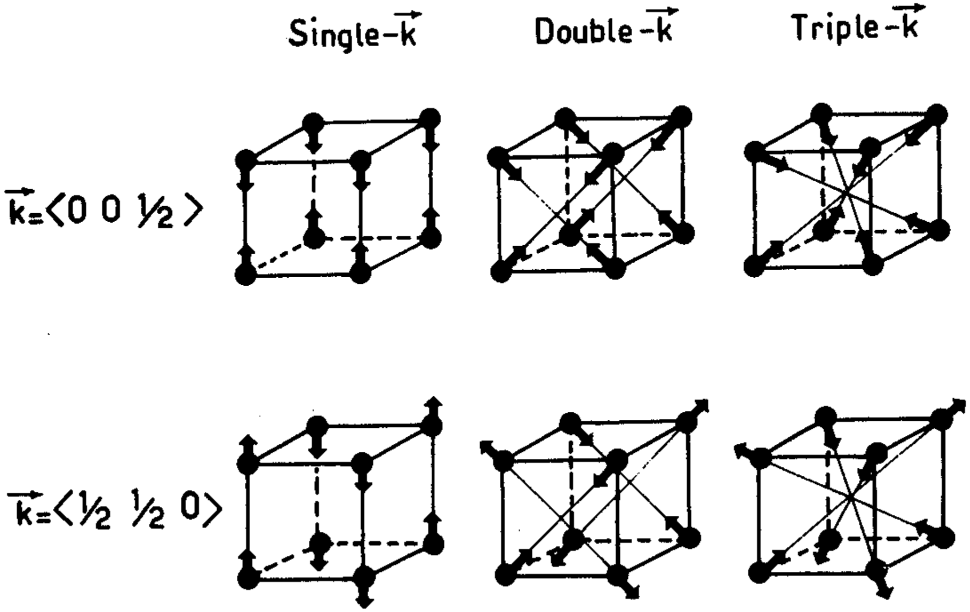
RKKY exchange in Itinerant Magnets (eg. Rare Earth Metals)

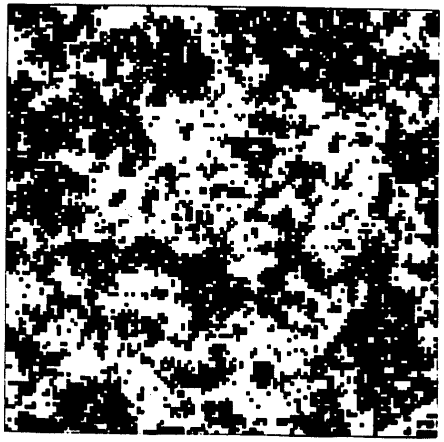


$T = 0.9\ T_C$



$T = T_C$





$T = 1.1\ T_C$

Magnetic Neutron Scattering

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

Only couple to electrons in solids via magnetic interactions

$$\boldsymbol{\mu}_n = - \gamma \mu_N \boldsymbol{\sigma}$$

$\gamma = 1.913$ **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**
  1^{st} Order Perturbation Theory

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

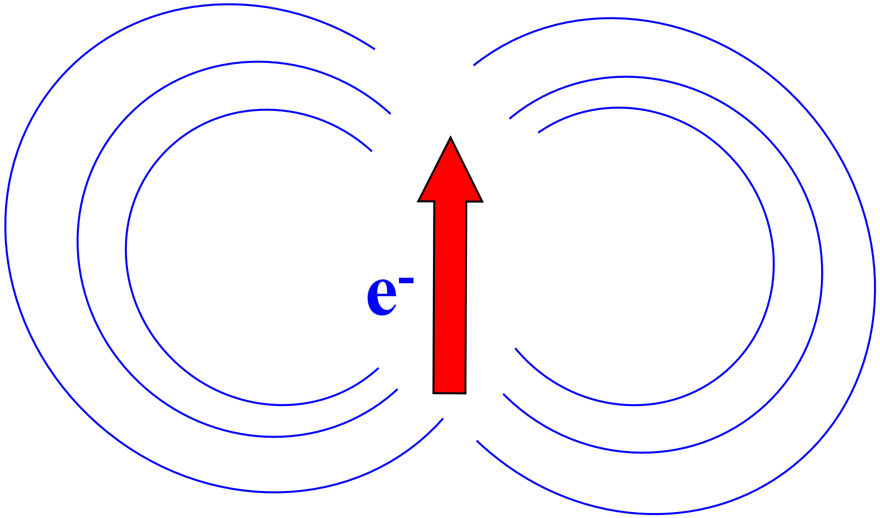
$$= k'/k \;(m/2\pi\hbar^2)^2 \;\; |< \mathbf{k}'\sigma'\lambda' \,|\, V_M \,|\, \mathbf{k}\,\sigma\,\lambda > |^2 \;\; \delta\,(E_\lambda - E_\lambda' + \hbar\omega)$$

kinematic *interaction matrix element* *energy conservation*

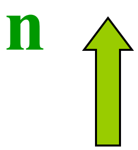
Understanding this means understanding:

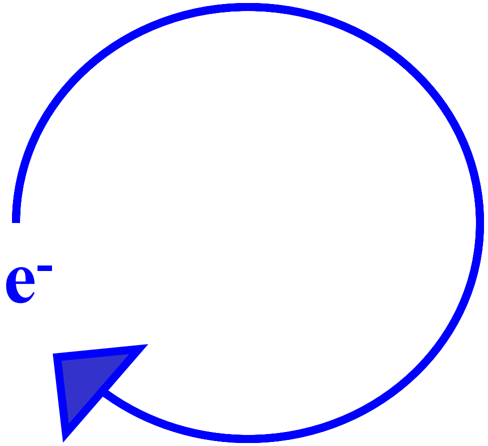
V_M: The potential between the neutron and all the unpaired electrons in the material

$$V_M = -\mu_n B$$



Magnetic Field
from spin ½ of Electron: B_S





Magnetic Field
from Orbital Motion of Electrons: B_L

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

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

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

$$\times\;\; \Sigma_{\,\lambda\,\lambda'}\; p_\lambda < \lambda\, |\, \exp(\text{-}i\boldsymbol{\kappa}\, \mathbf{R}_{d'})S^\alpha{}_{d'}\,|\, \lambda' >< \lambda'\, |\, \exp(i\boldsymbol{\kappa}\, \mathbf{R}_d)S^\beta{}_d\, |\, \lambda >$$

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

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 $\delta\,(E_\lambda - E_{\lambda}{}^{\prime} + \hbar\omega)$ to obtain $d^2\sigma/d\Omega\, dE^{\prime}$ in terms of ***spin correlation functions***:

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

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

$$\times\ \ \int <\exp(-i\boldsymbol{\kappa}\cdot\mathbf{u_0}))\exp(i\boldsymbol{\kappa}\cdot\mathbf{u}_l(t))>$$

$$\times\ \ \underbrace{<S_0{}^{\alpha}(0)\ S_l{}^{\beta}(t)>}_{}\ \exp(-i\omega\ t)\ dt$$

Dynamic Spin Pair Correlation Function

Fourier tranform: S(κ, ω)

Bottom Lines:

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

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

Diffraction type experiments:

Add up spin correlations with phase set by $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}'$

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

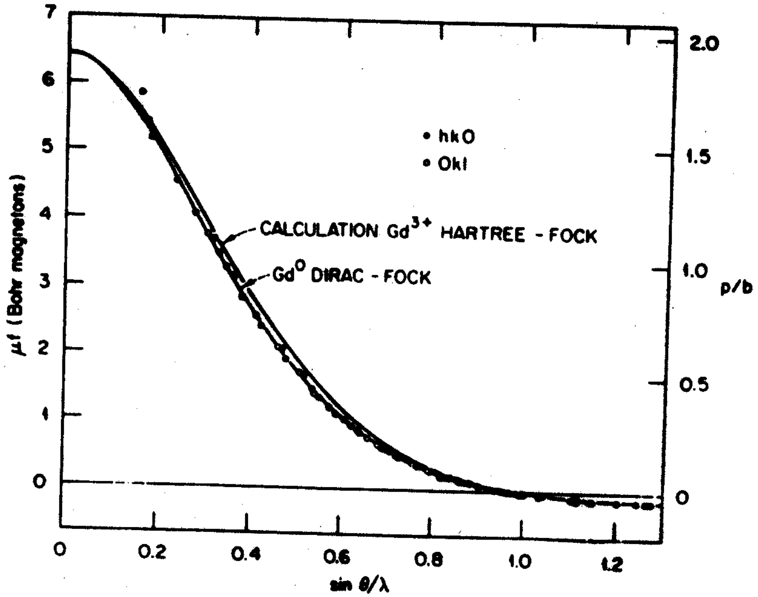
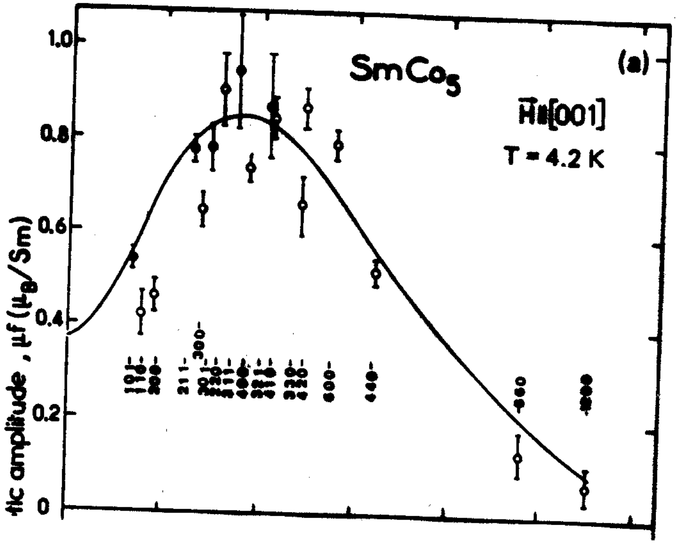
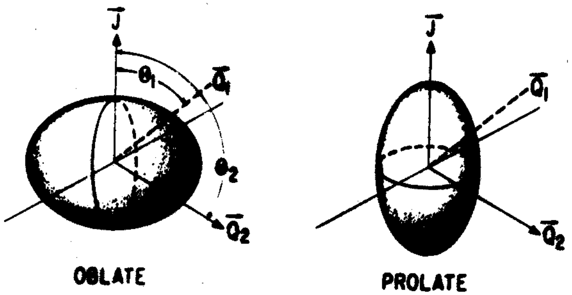


FIG. 13. Comparison of the experimental ^{160}Gd form factor at 96 K as measured by Moon *et al.*[47] with nonrelativistic Hartree–Fock and relativistic Dirac–Fock calculations by Freeman and Desclaux.[36]

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

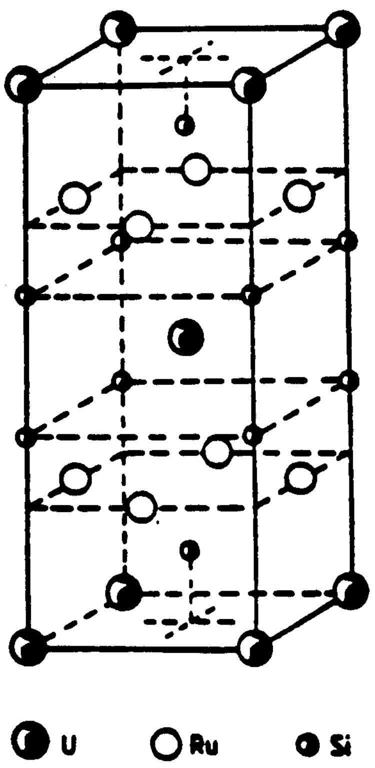
$$\hbar\omega = (\hbar k)^2/2m - (\hbar k')^2/2m = 0$$

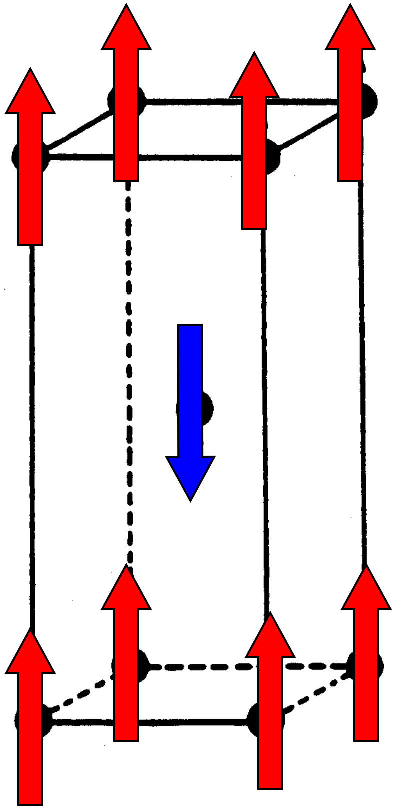
measures time-independent magnetic structure

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

$$\times\; \underbrace{\Sigma_{\alpha\,\beta}\;\; (\delta_{\alpha\,\beta} - \kappa_\alpha\, \kappa_\beta}_{\textbf{S } \perp \boldsymbol{\kappa} \textbf{ only}})\; \Sigma_l\; \underbrace{\exp(i\boldsymbol{\kappa}\cdot\mathbf{l})\; {<}S_0^{\alpha}{>}}_{\textbf{Add up spins with exp(i}\boldsymbol{\kappa}\cdot\textbf{l) phase factor}}\; {<}S_l^{\beta}{>}$$

URu$_2$Si$_2$





κ = 0,0,1

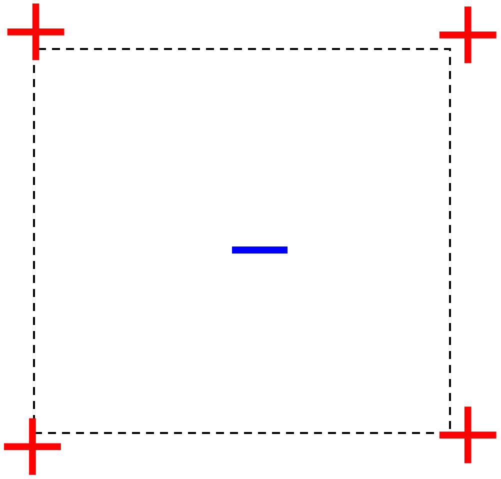
a*=b*=0:
everything within a basal plane (a-b) adds up in phase

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:

μ ⊥ κ good!

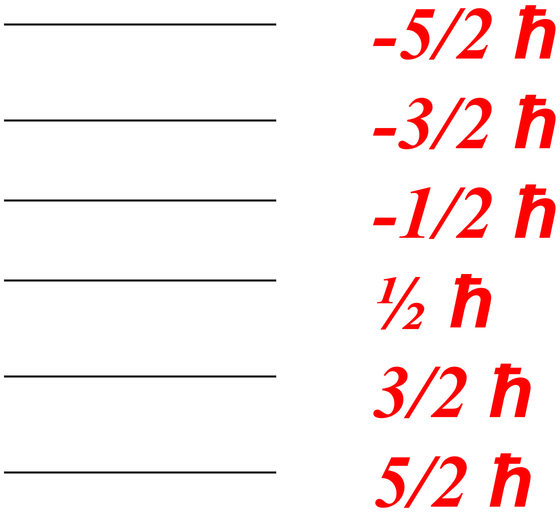


Mn^{2+} as an example: ½ filled 3d shell S=5/2

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

m_z = +5/2 ħ, +3/2 ħ, +1/2 ħ, -1/2 ħ, -3/2 ħ ,–5/2 ħ

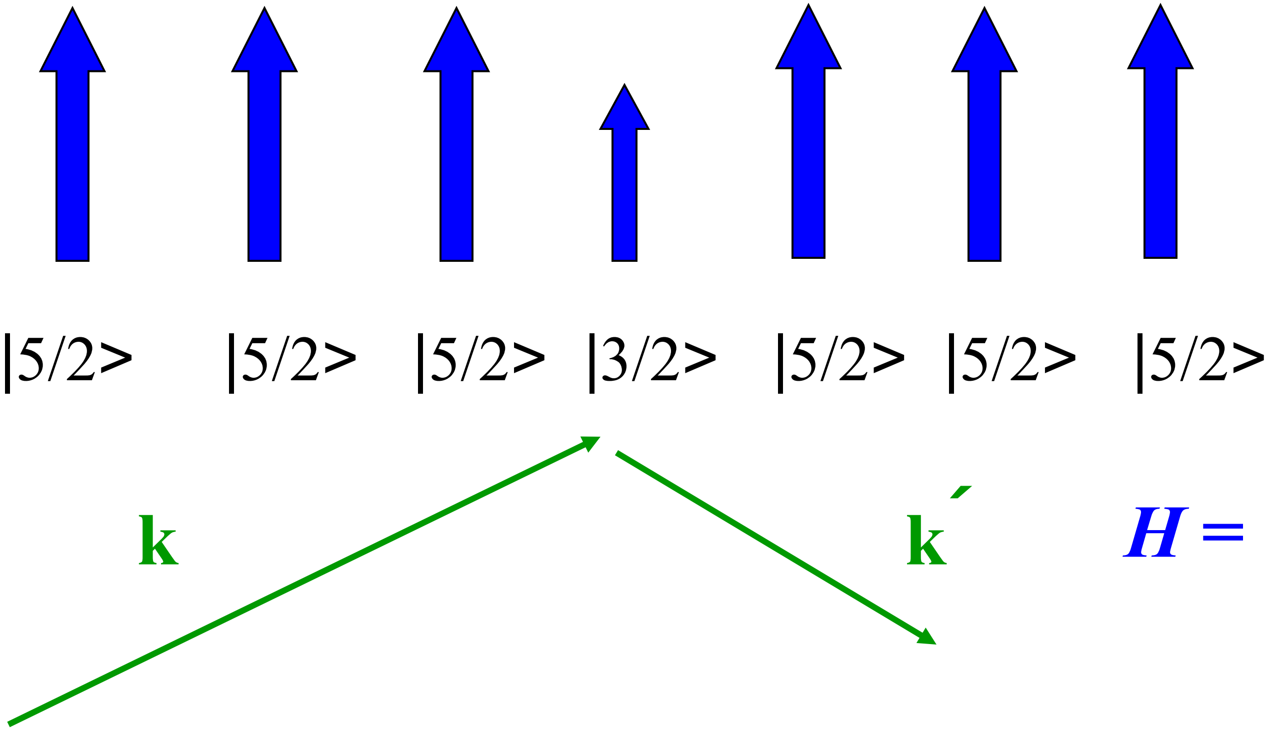
H=0; 6 degenerate states



H ≠ 0; 6 non-degenerate states

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

Magnetic sites are coupled by exchange interactions:



|5/2>　|5/2>　|5/2>　|3/2>　|5/2>　|5/2>　|5/2>

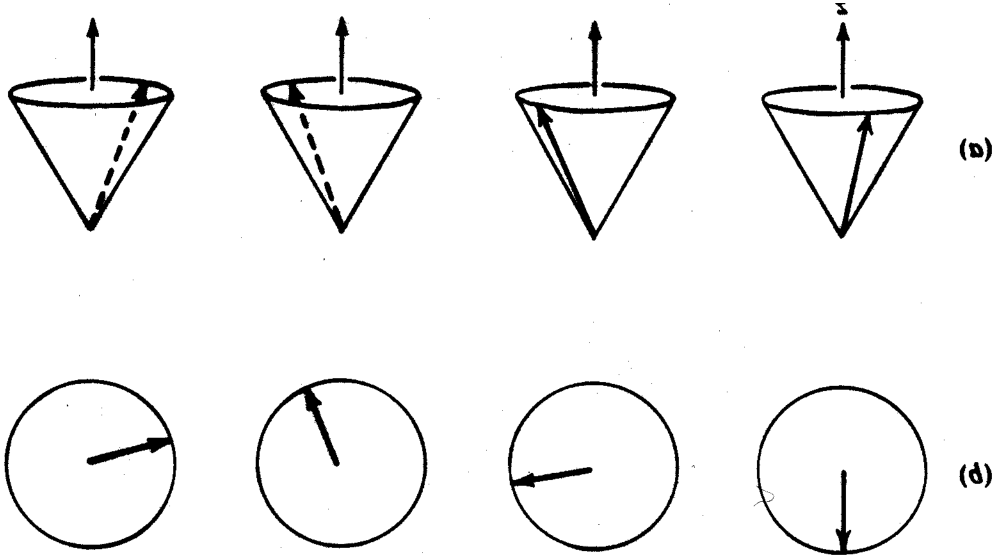
k

k´

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

Spin Wave Eigenstate:

“Defect” is distributed over all possible sites



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

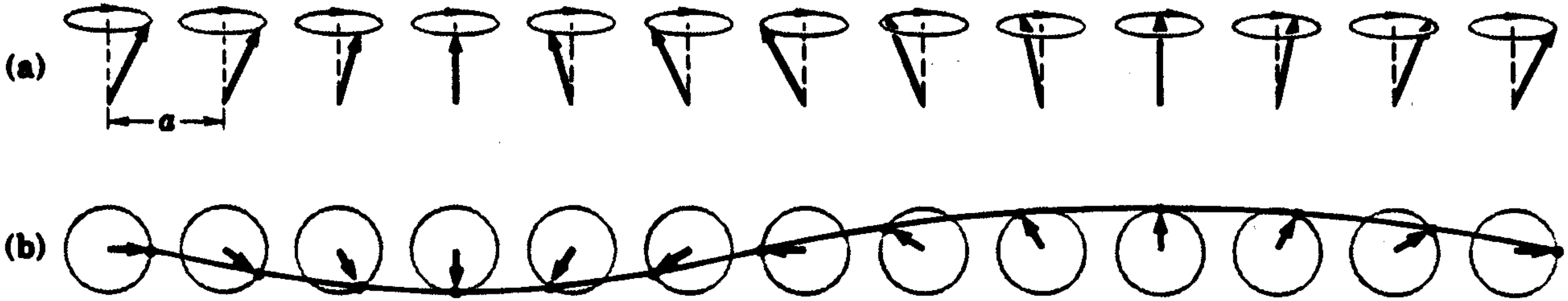


Figure 9 A spin wave on a line of spins. (a) The spins viewed in perspective. (b) Spins viewed from above, showing one wavelength. The wave is drawn through the ends of the spin vectors.

Study magnetic excitations (eg. spin waves)

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

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

Bose (temperature) factor

Imaginary part of the dynamic susceptibility

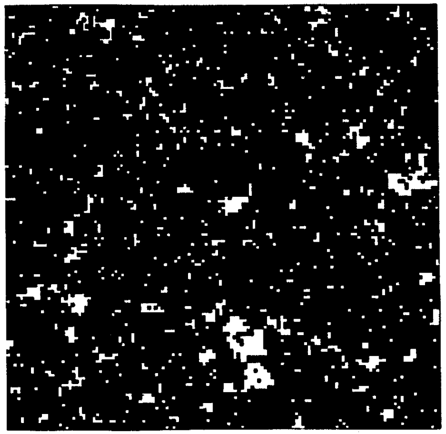
Sum Rules:

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

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

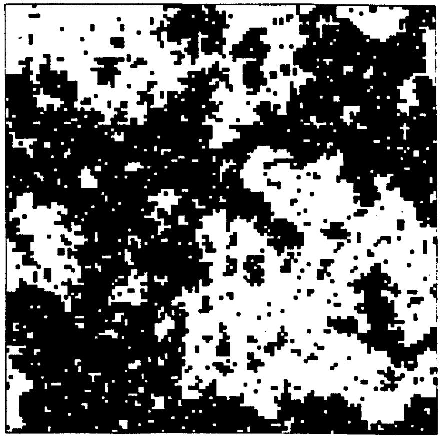
   where χ_{DC} is the χ measured with a SQUID

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



$T = 0.9\ T_C$

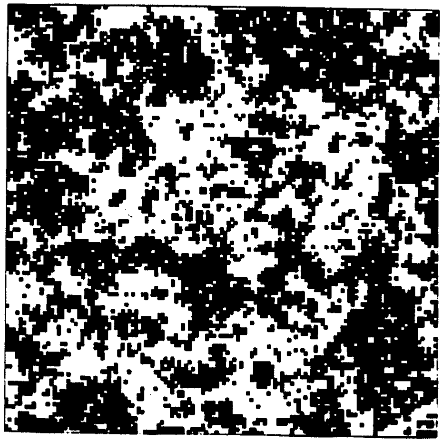
Symmetry broken



$T = T_C$

ξ~ very large

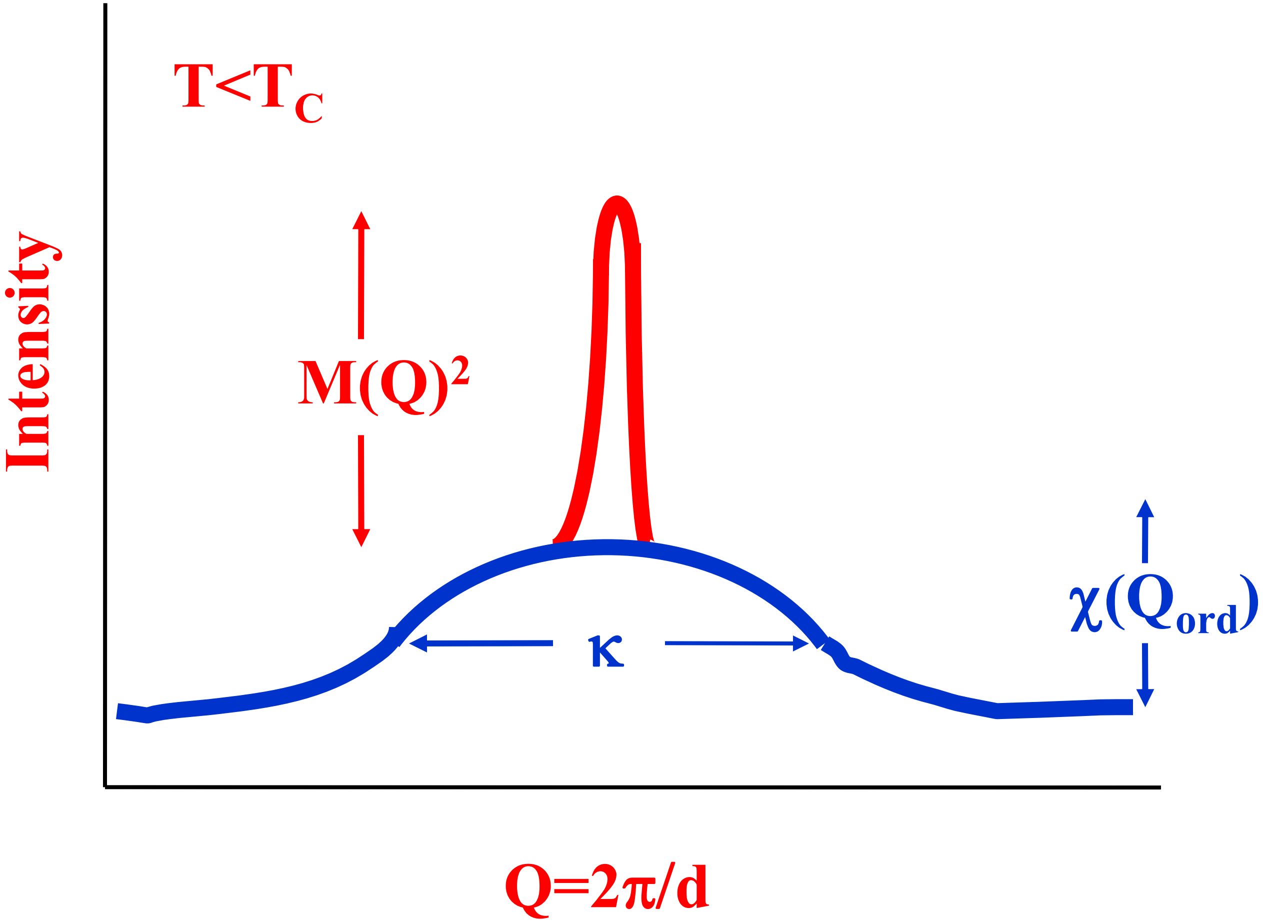
Origin of universality

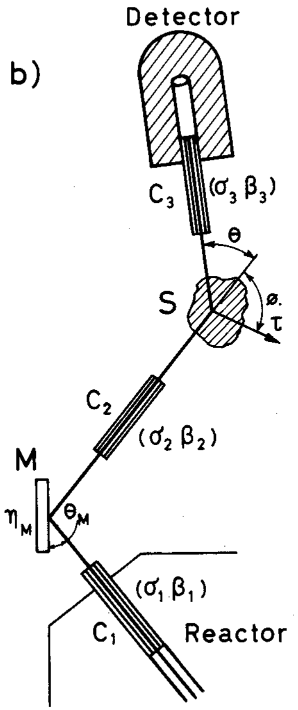


$T = 1.1\ T_C$

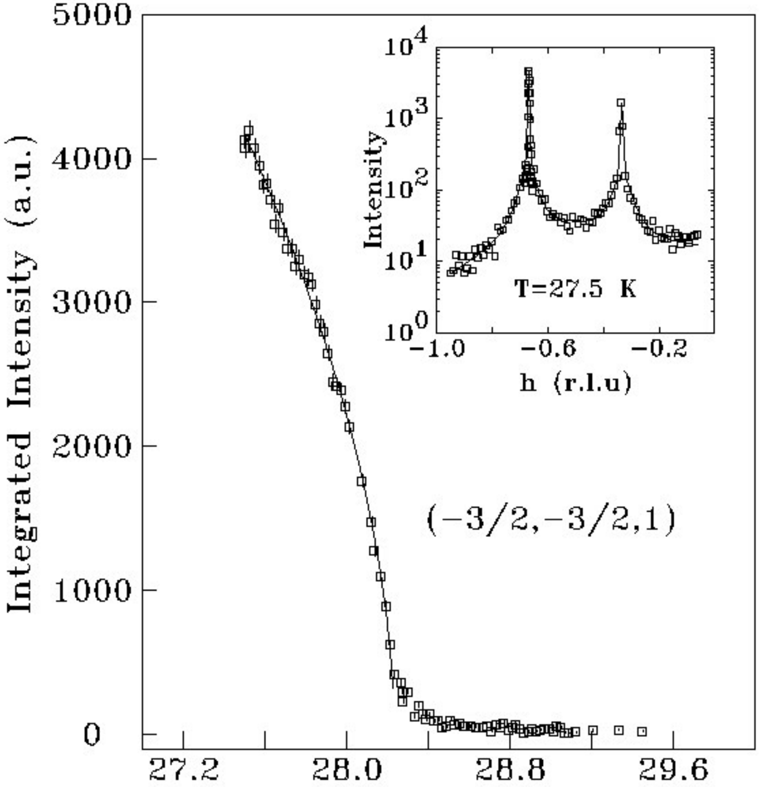
- Bragg scattering gives square of order parameter; symmetry breaking

- Diffuse scattering gives fluctuations in the order parameter





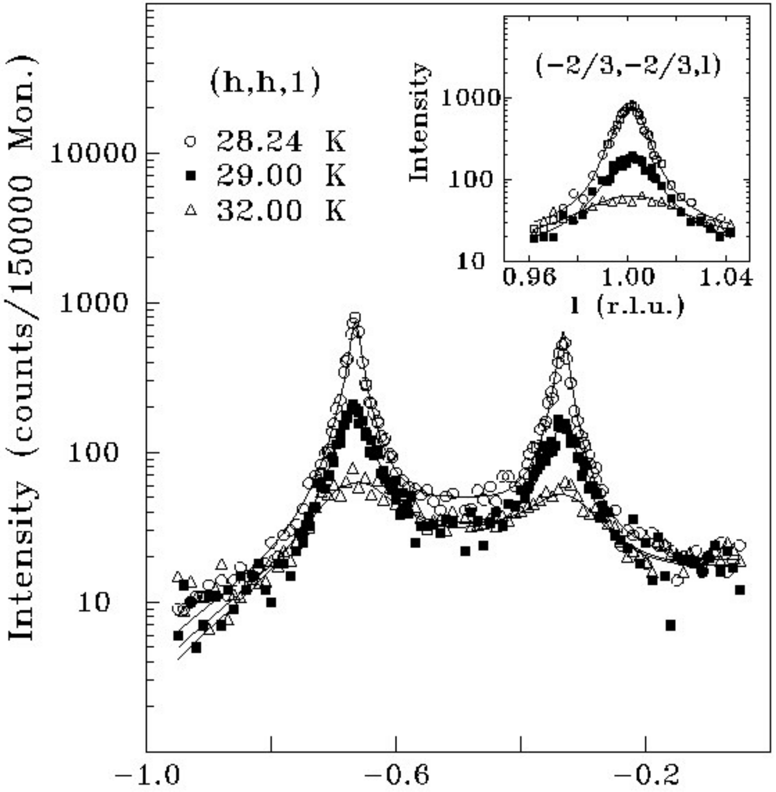
$CsCoBr_3$



Bragg scattering

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

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

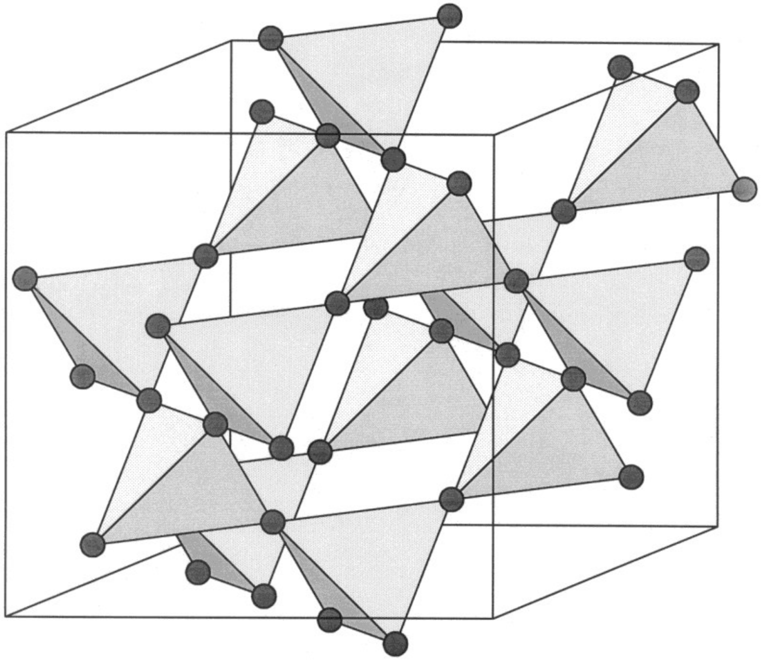


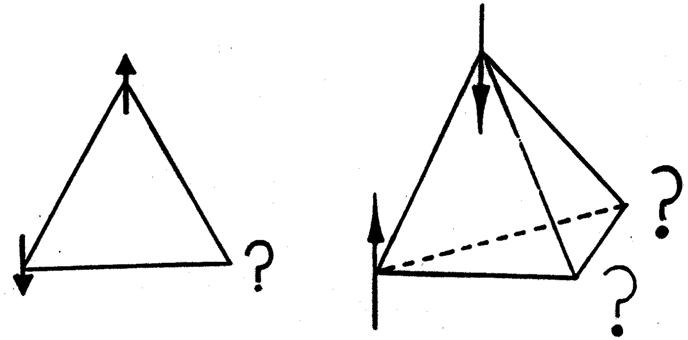
Energy-integrated critical scattering

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

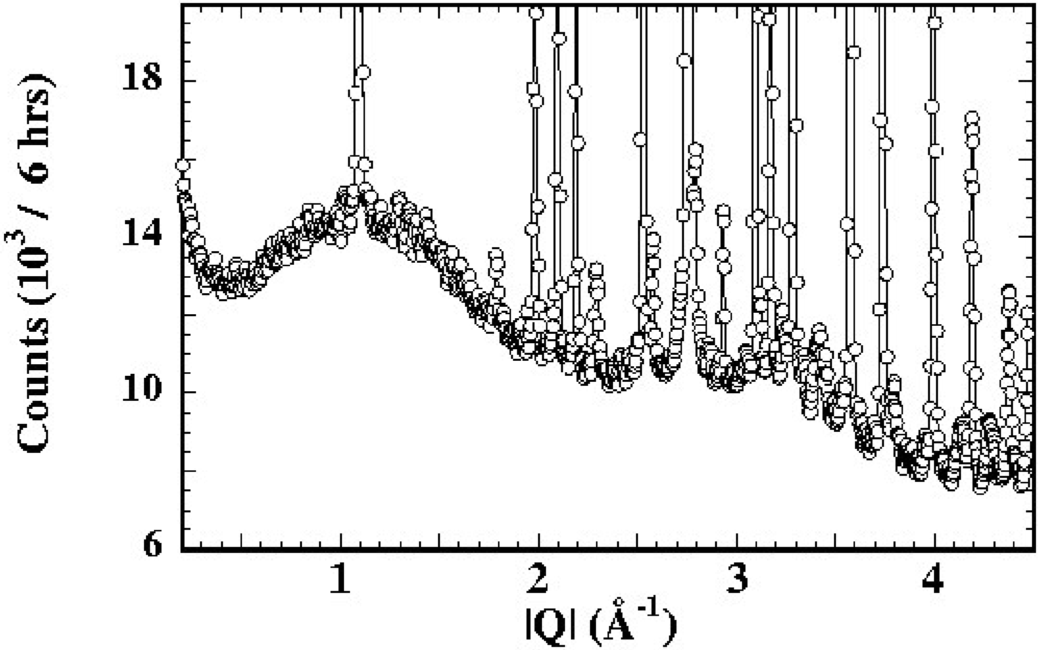
Geometrical Frustration:

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

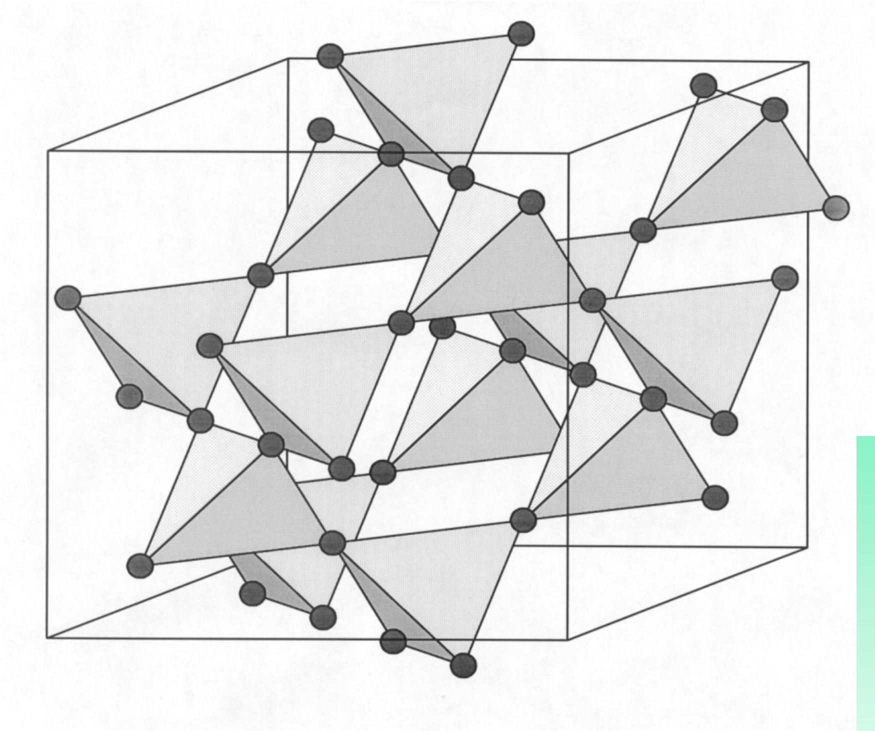




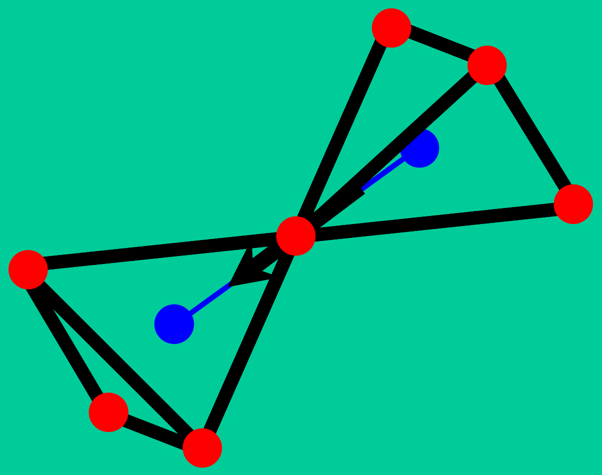
Low temperature powder neutron diffraction from $Tb_2Ti_2O_7$



A^{3+} site within a distorted cube of 8 O^{2-} ions – unique direction pointing into or out of tetrahedra



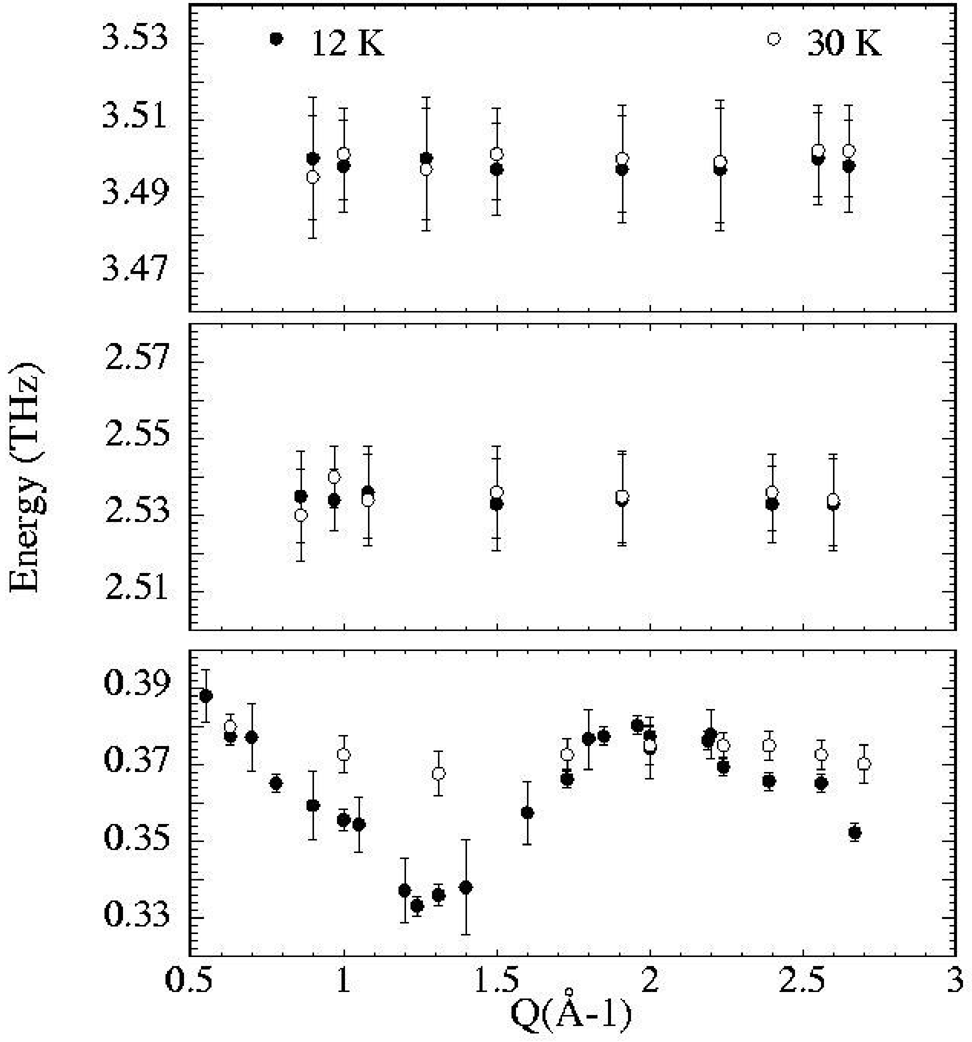
Local Ising anisotropy

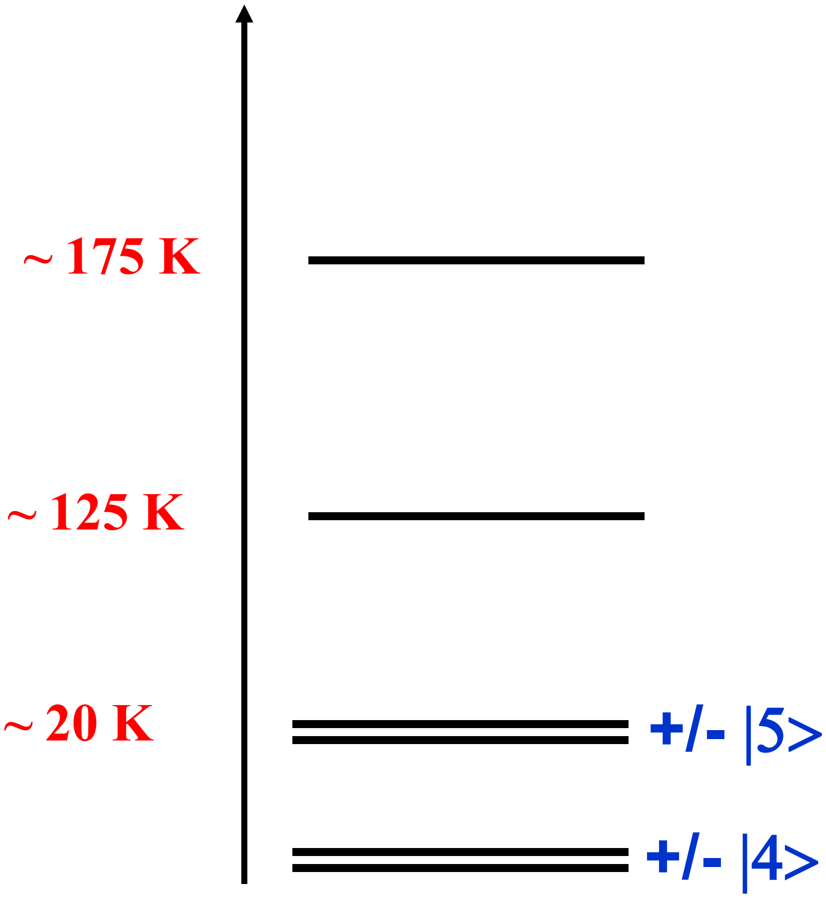


Tb^{3+} : S=3, L=3, J=6

(2J+1) = 13 states split by the crystalline electric field

Inelastic neutron scattering on polycrystalline $Tb_2Ti_2O_7$





~ 175 K

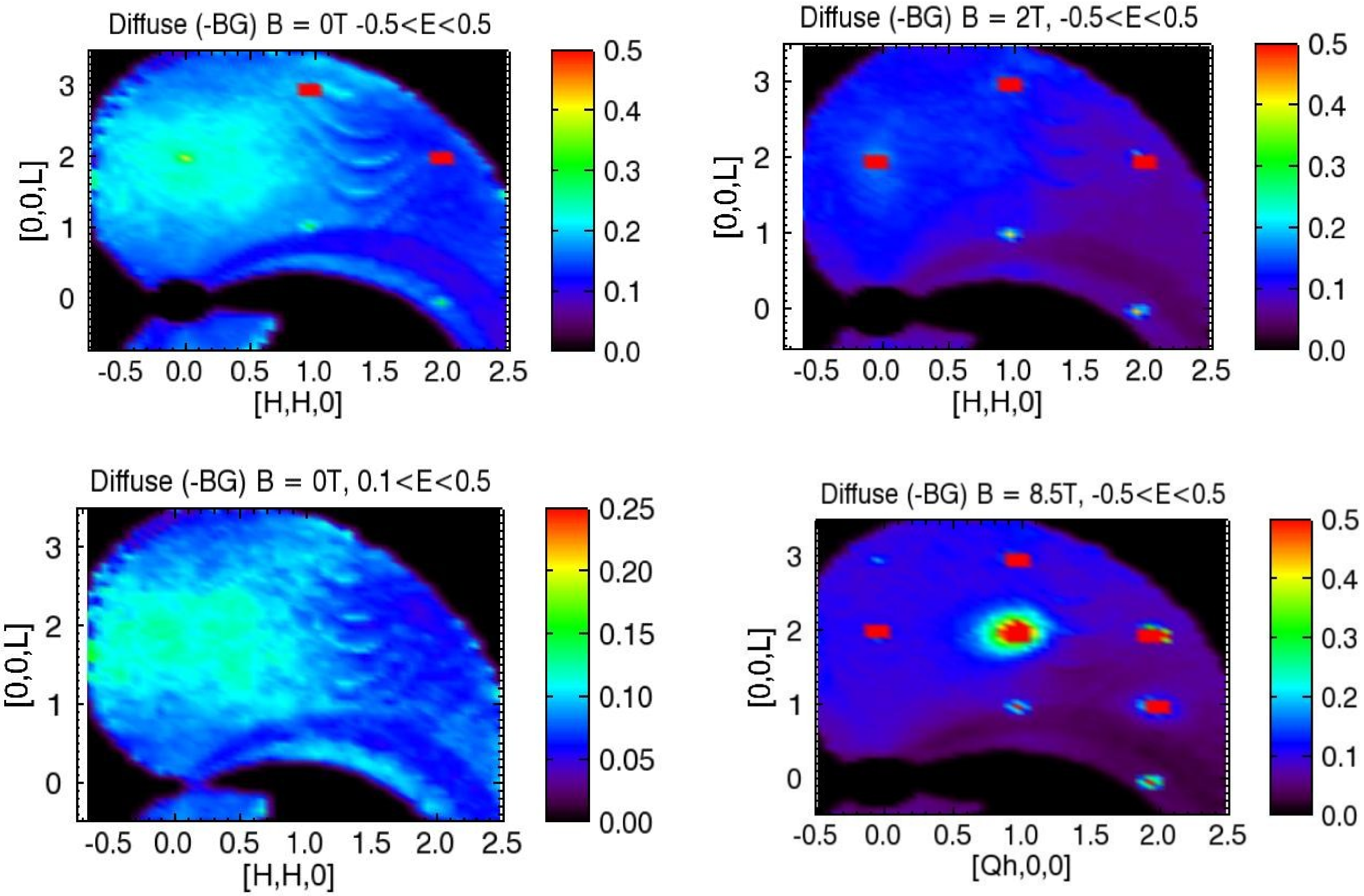
~ 125 K

~ 20 K

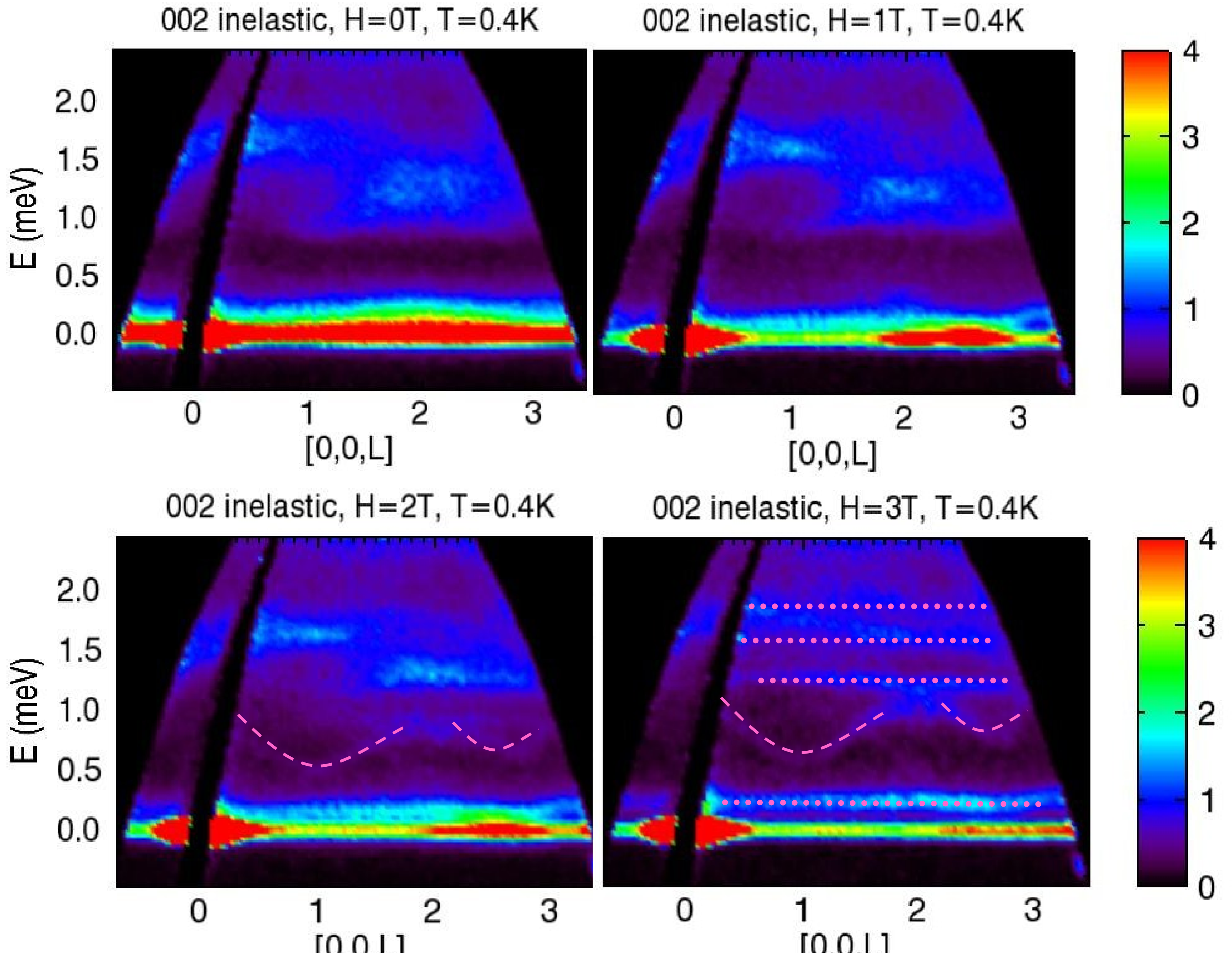
+/- |5>

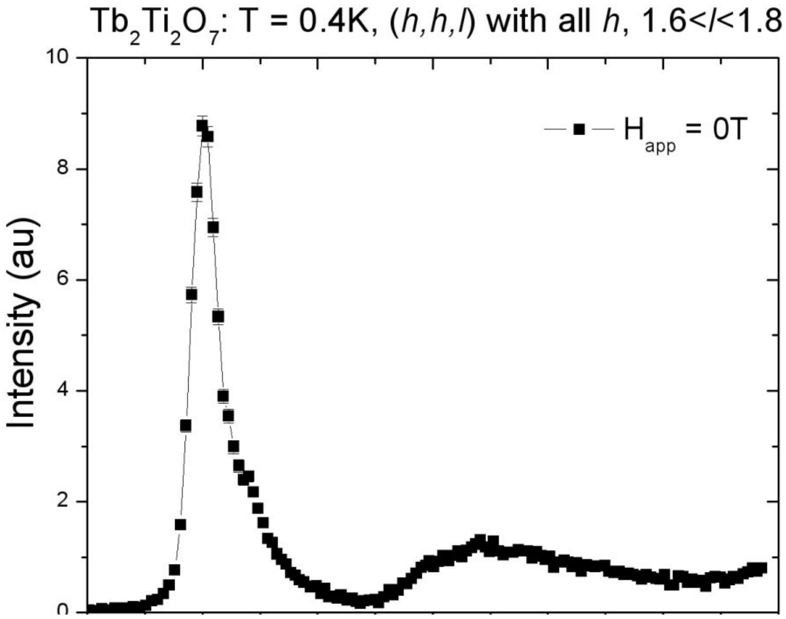
+/- |4>

(Δ : $Ho_2Ti_2O_7$ ~ 240 K ; $Dy_2Ti_2O_7$ ~ 380 K)

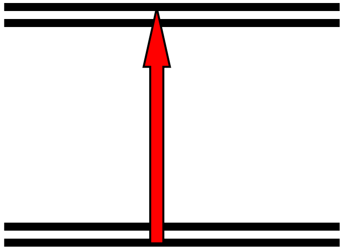


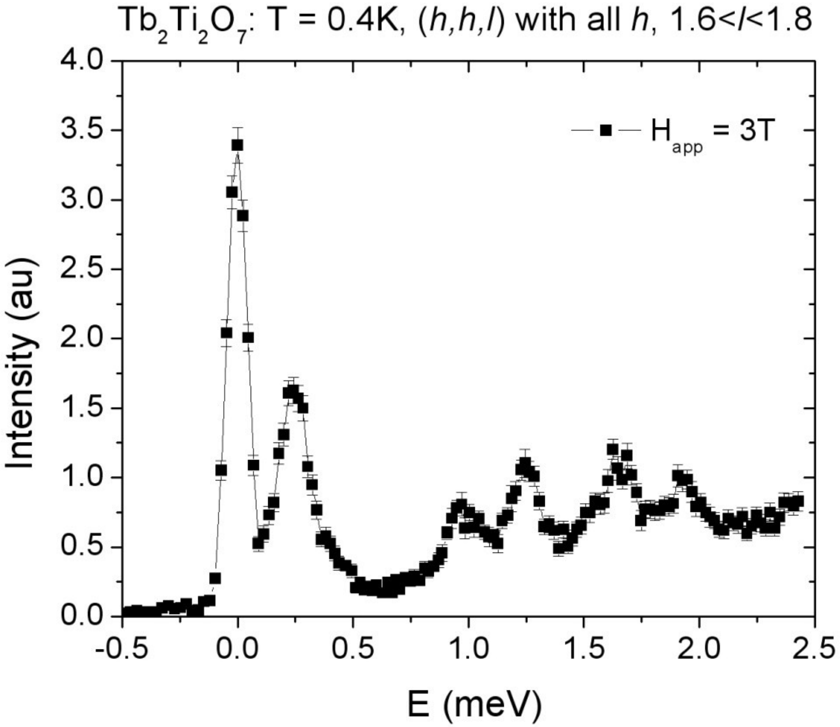
Time-of-flight neutron scattering from DCS on $Tb_2Ti_2O_7$


002 inelastic, H=0T, T=0.4K
002 inelastic, H=1T, T=0.4K
002 inelastic, H=2T, T=0.4K
002 inelastic, H=3T, T=0.4K
E (meV)
2.0
1.5
1.0
0.5
0.0
0
1
2
3
[0,0,L]
4
3
2
1
0

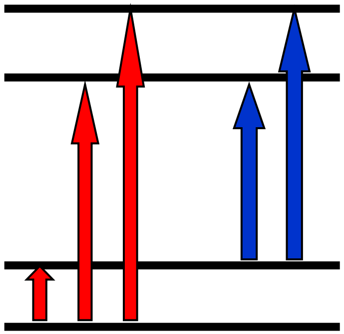


One Transition in Zero Field





Five Transitions in Non-Zero Field



Conclusions:

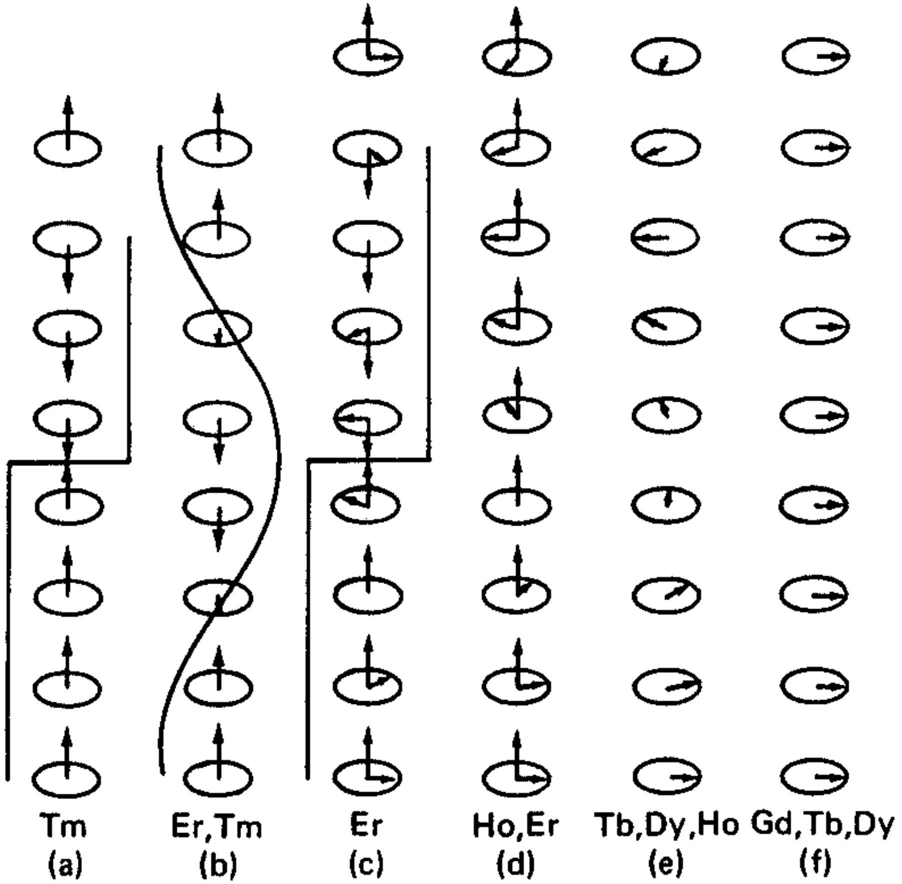
- **Neutrons probe magnetism on length scales from 1 – 100 A, and on time scales from 10^{-9} to 10^{-12} seconds**

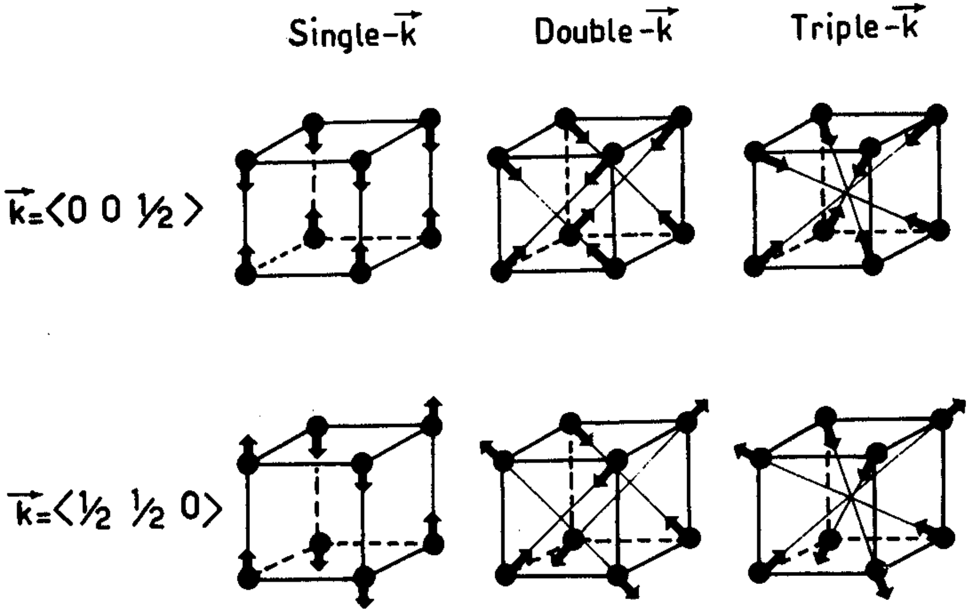
- **Magnetic neutron scattering goes like the form factor squared (small κ), follows dipole selection rules $< \lambda' \mid S^{+,-,z} \mid \lambda >$, and is sensitive only to components of moments ⊥ to κ.**

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

Magnetic Structures can be complicated

Incommensurate structures in rare earth metals





Muliple-k structures in high-symmetry antiferromagnets