Argonne NATIONAL LABORATORY

Magnetic Powder Scattering Intensities

Magnetic structure factor theory

Magnetic scattering factor

Magnetic "extinctions" & magnetic structure

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Magnetic structure factor (& nuclear one, too)

Some basic assumptions:

1. ***Neutron beam – unpolarized***
2. ***Polycrystalline sample – ideal random orientations (no texture)***
3. ***Elastic scattering only – ignore inelastic magnetic scattering***

→ Simplification!

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Intensities =
coherent nuclear scattering +coherent magnetic scattering
(i.e. no cross terms)

$$d\sigma = b^2+2bp\lambda\cdot\mathbf{q}+p^2q^2$$

Missing
ave = 0

(λ = unit vector in neutron spin direction)

Nuclear structure factor — Magnetic structure factor

$$|F_{\mathbf{h}}|^2 = \left|\sum_n b_n \exp\{2\pi i(\mathbf{h}\cdot\mathbf{r})\}\right|^2 + \left|\sum_m \mathbf{q}_m p_m \exp\{2\pi i(\mathbf{h}\cdot\mathbf{r})\}\right|^2$$

All atoms — Magnetic ions only

Structure factor – powders & no polarization – p's&q's?

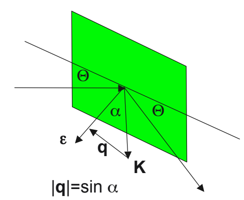
(after Bacon, 1975)

$$\mathbf{q}_m = \mathring{\mathbf{a}}_{\mathbf{h}}(\mathring{\mathbf{a}}_{\mathbf{h}}\cdot\mathbf{K}_m) - \mathbf{K}_m$$

$$p_m = \left(e^2\gamma / m_N c^2\right) S_m f_m$$

$\varepsilon_{\mathbf{h}}$ – *unit vector* || **h** – diffraction vector
$\mathbf{K}_m$ – *unit vector* || *magnetic moment on atom m*
∴ **q** *small for* **h** || ***K*** *& large for* **h** ⊥ **K**

0.54x10^{-12}cm – similar to b_n
e – electron charge
γ – neutron magnetic moment
m_N *– neutron mass*
c – speed of light



S – magnetic moment (Bohr magnetons)
f – 1-electron magnetic form factor

Magnetic form factor - f_m

Fourier transform of unpaired e^- density:
valence e^-; outer shell
Sharp fall off with Q (small d, etc.)

In GSAS:

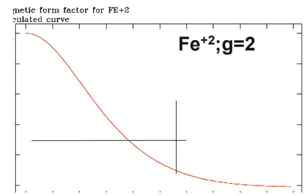
1. ***Tabulated by user***
2. ***Form factor coefficients $<j_0>$ and $<j_2>$ (higher terms ignored)***

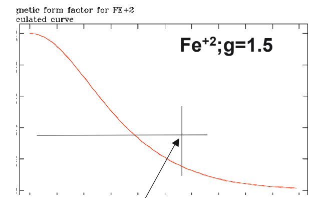
$$f_m = C + \sum_{i=1}^{4} A_i \exp\left(-B_i \sin^2\Theta/\lambda^2\right) + \left(\frac{2}{g}-1\right)\left[C' + \sum_{i=1}^{4} A'_i \exp\left(-B'_i \sin^2\Theta/\lambda^2\right)\right]\sin^2\Theta/\lambda^2$$

Landé g factor = 2 for 1st row transition elements:
quenched orbital contribution

In general $f_m \rightarrow 0$ for $\sin\Theta/\lambda > 0.5$; $d<1.0$

Magnetic form factors – from valence shell electrons





Orbital contribution quenched (typical 1st row)

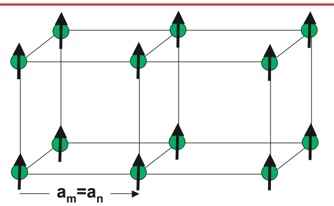
$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$\mu = g\sqrt{J(J+1)} \quad \textit{magnetic moment}$$

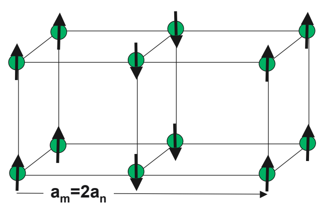
not quenched (v. slightly fatter)

Fe^{+2}; d^6: S=2, L=2, J=4
g=1.5; μ_J=6.7, μ_S=4.9
(μ_{obs}=5.2 in $FeCl_2$)

Magnetic structures



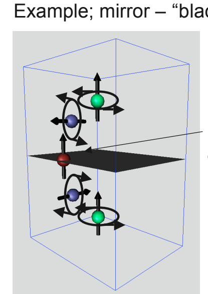
Ferromagnetic
No extra reflections



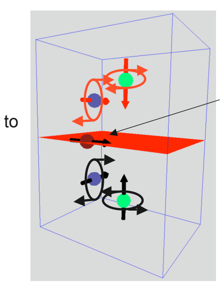
Antiferromagnetic
Extra reflections

Magnetic symmetry – spins & moments?

How do magnetic moments/spins transform via symmetry operations?
Operation is on spin (not moment) – physical object
Antioperation – spin reversal ("time reversal")
Example; mirror – "black" antimirror – "red"



NB: moment must be perpendicular to "black" plane

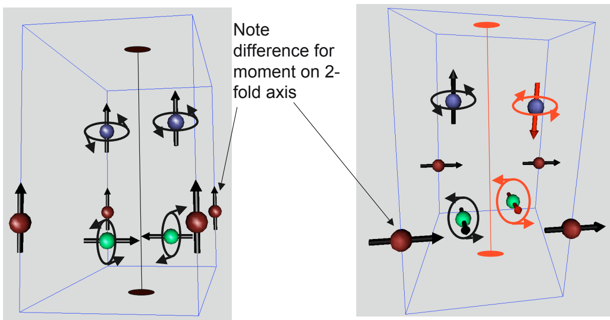


NB: moment must be in "red" mirror

Result depends on orientation & position

Rotations & antirotations

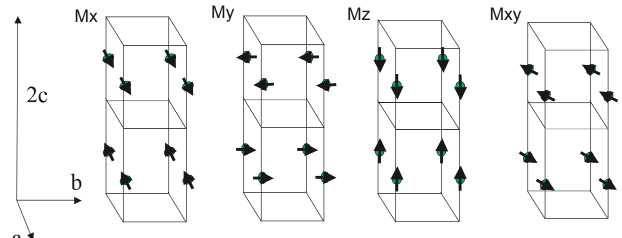
2-fold – "black"   anti 2-fold – "red"



NB: switch "black" to "red" is NOT ferro to antiferro!!

Extinctions – moment direction |**q**|=sin α

Possible antiferromagnets (assume orthorhombic?):



Pmm'm   Pm'mm   Pm'm'm'   P112'/m

(Note ¼ shift along z – to get atoms with moments in right places wrt symm operations)

Magnetic extinctions

Pmmm – no extinctions
Pm'mm – h00 all absent
Pmm'm – 0k0 all absent
Pm'm'm' – h00, 0k0, & 00l all absent
P112'/m – no extinctions
BUT, MOMENT DIRECTION MATTERS! (remember **q**)
(similar to extinctions for atoms in special positions)

NB: these rules are for magnetic atom in general position with moment pointed in a general MxMyMz direction.

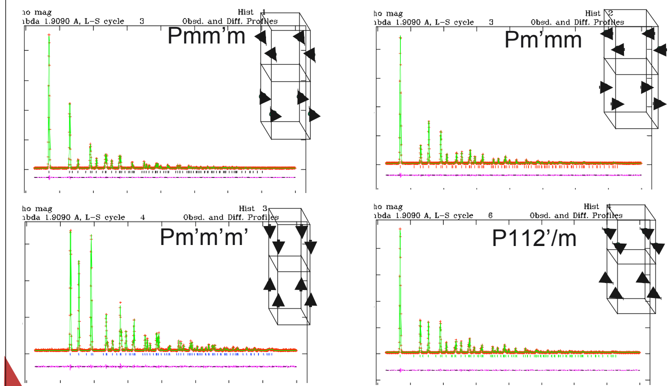
Magnetic extinctions, cont.

1st 10 nonzero magnetic reflections for antiferromagnetic cases

Pmm'm	Pm'mm	Pm'm'm'	P112'/m
0 0 1	0 0 1	- - -	0 0 1
0 1 1	0 1 1	0 1 1	0 1 1
1 0 1	1 0 1	1 0 1	1 0 1
1 1 1	1 1 1	1 1 1	1 1 1, -1 1 1
0 0 3	0 0 3	- - -	0 0 3
0 2 1	0 2 1	0 2 1	0 2 1
0 1 3	0 1 3	0 1 3	0 1 3
1 0 3	1 0 3	1 0 3	1 0 3
1 2 1	1 2 1	1 2 1	1 2 1, -1 2 1
1 1 3	1 1 3	1 1 3	1 1 3, -1 1 3

different

Different powder patterns – all CW neutron (ILL d1a) distinguish by intensities – only magnetic part



(different)

So how choose magnetic symmetry/structure?

Trial & error!! (A.J. Wills – SARAh)
In GSAS – use tools
1. SPCGROUP
2. EXPEDT – magnetic operator ("black"/"red")
3. VRSTPLOT – draw result; shows moment directions
4. Calculate pattern – check with observed data!

See tutorial….