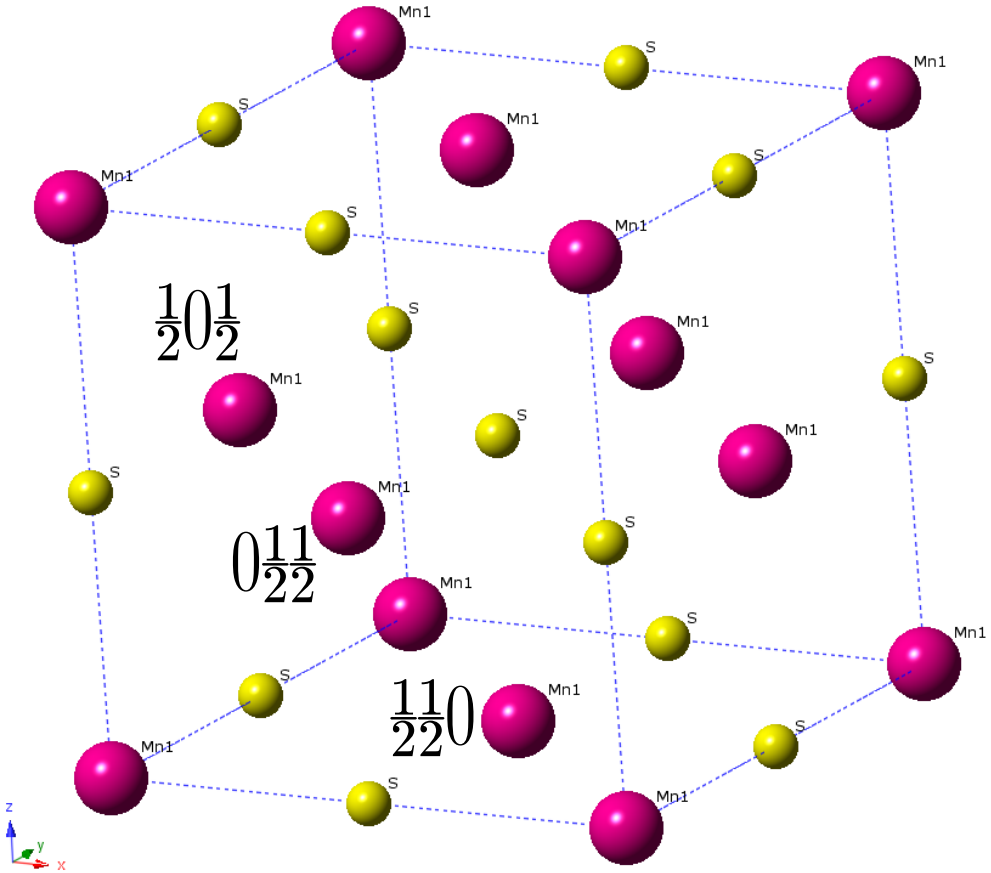
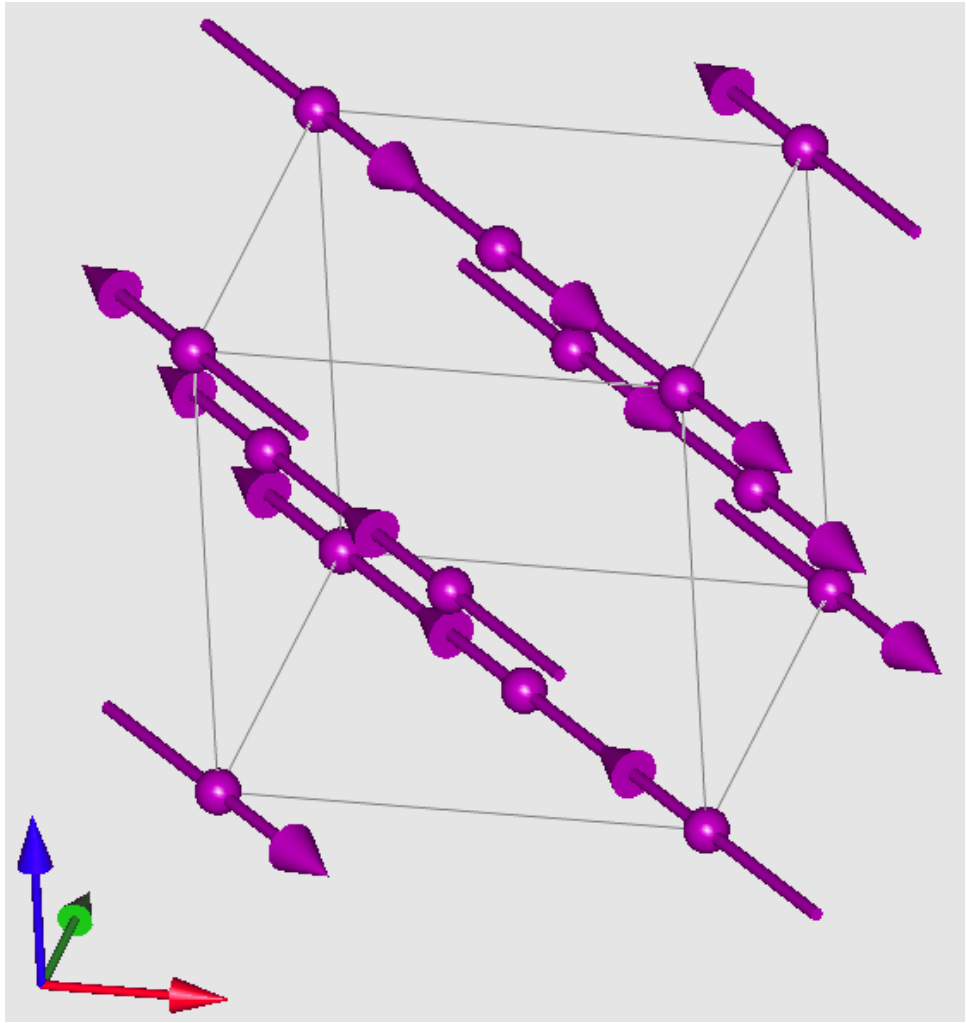
Approximate crystal and magnetic structures of MnS below Néel temperature

single propagation vector
k=[1/2,1/2,1/2]





cubic, Fm-3m: Mn-atom in (000),
three other Mn-atoms are generated
by F-centering translations

Scattering from magnetic structure with propagation vector k

In ND experiment we measure correlators of Fourier transform of magnetic lattice

$$\frac{d\sigma}{d\Omega} \propto (\mathbf{F}(\mathbf{q}) \cdot \mathbf{F}^*(\mathbf{q}) + i\mathbf{P} \cdot [\mathbf{F}(\mathbf{q}) \times \mathbf{F}^*(\mathbf{q})]) \cdot \delta(\mathbf{H} \pm \mathbf{k} - \mathbf{q})$$

structure factor

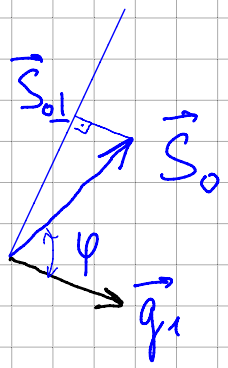
polarized neutron (chiral) term.

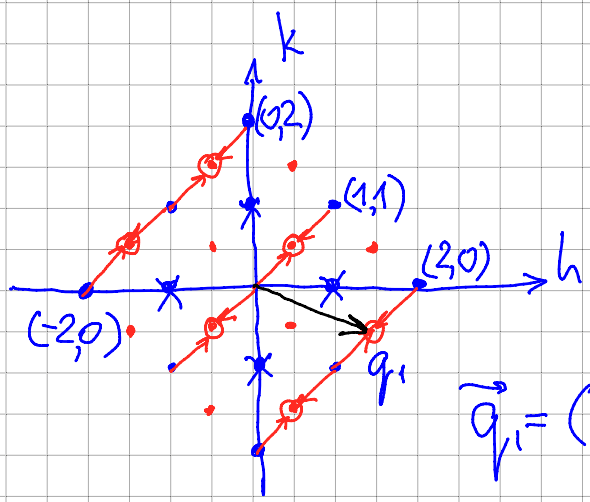
Bragg peak at $\mathbf{q} = \mathbf{H} \mp \mathbf{k}$

$$\mathbf{F}(\mathbf{q}) \propto \sum_j \mathbf{S}_{0\perp j} \cdot \exp(i\mathbf{q}\mathbf{r}_j)$$

$$\vec{S}_\perp = \frac{\vec{q} \times \vec{S} \times \vec{q}}{|\vec{q}|^2}$$

$$|\vec{S}_\perp| = |\vec{S}_0| |\sin\varphi|$$





$\vec{H} = (h,k)$

$\vec{k} = (\frac{1}{2}, \frac{1}{2})$

new peaks at $\vec{H} \pm \vec{k}$

$\vec{q}_1 = (2,0) - \vec{k} = (\frac{3}{2}, -\frac{1}{2})$

....

Practicum problems

MAGNETIC ORDER IN MnS

5. Practical course at SINQ

5.1 Manganese sulfide MnS

- rock salt crystal structure
- ionic crystal: Mn^{2+}, S^{2-}
- lattice constant a = 5.199 Å at T = 4.2 K
- space group $Fm\bar{3}m$
- electronic configuration of Mn^{2+}: $3d^5$
- Néel temperature T_N = 161 K
- long-range antiferromagnetic order: antiferromagnetic stacking along (111) of ferromagnetic planes
- therefore doubling of the magnetic unit cell with respect to the crystallographic unit cell

Task 1: positions of nuclear Bragg peaks, indexing of the peaks

5.2 Neutron diffraction of MnS at room temperature

For all measurements at HRPT we will use $\lambda = 1.886$ Å

$$\lambda = 2d_{hkl} \sin\theta_{hkl}$$ Bragg law (1)

λ: neutron wavelength, d_{hkl}: d-spacing of scattering plane hkl
θ_{hkl}: (half) scattering angle of reflection hkl in diffraction pattern

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$ (2)

a: cubic lattice constant, h, k, l indices of scattering plane

$$\vec{\tau}_{hkl} = \frac{2\pi}{a}(h, k, l)$$ $\vec{\tau}_{hkl} \equiv \vec{H}$ (3)

corresponding vector in reciprocal space: a node of reciprocal lattice

(1)

Tasks: $I(2\theta)$

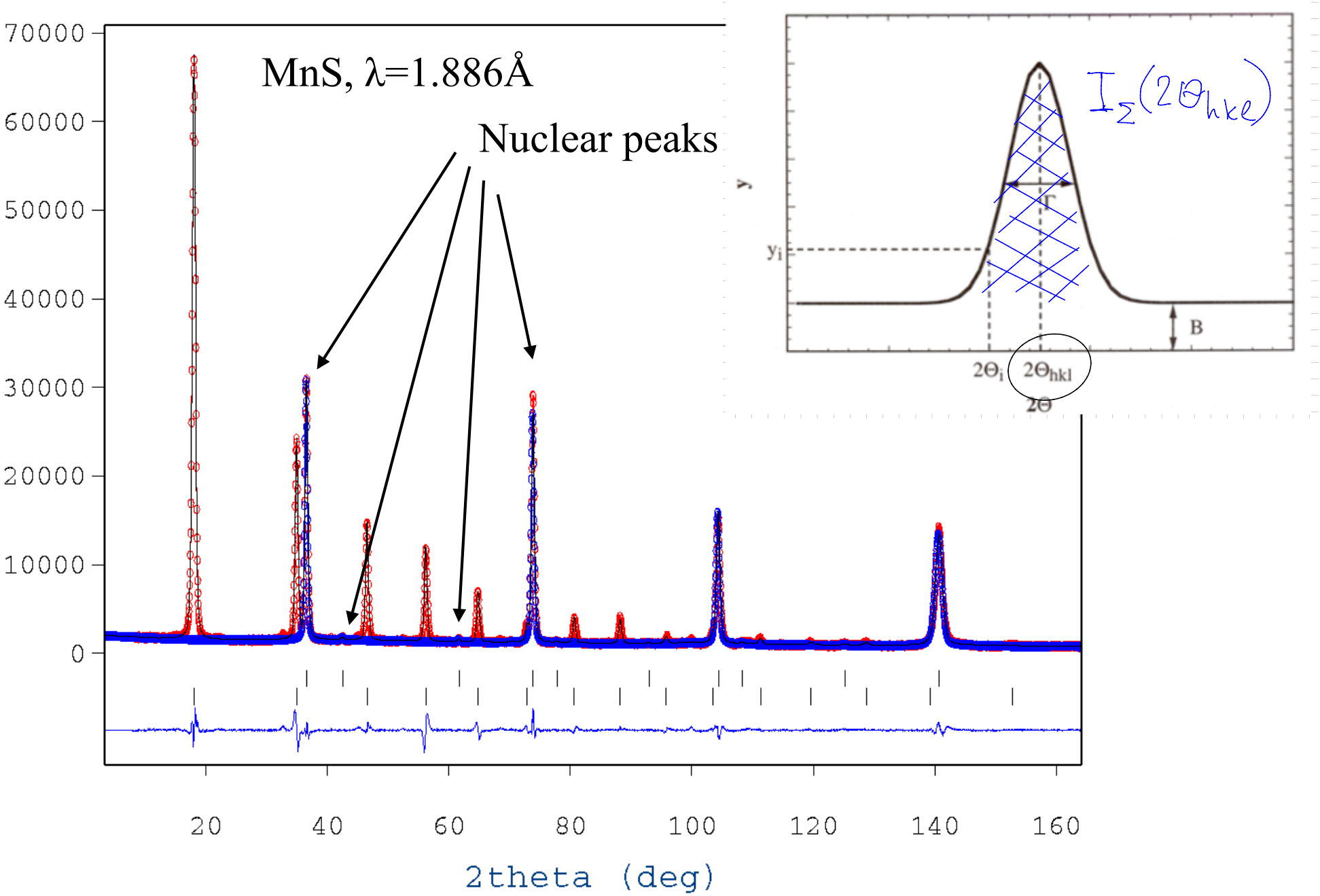
- measure a diffraction pattern of MnS at T = 300 K in the paramagnetic state ($> T_N \simeq 150$ K)
- -determine peak positions Θ, *d*-spacings and indices (h, k, l) for ~~all~~ first 4 observed peaks

Coherent elastic cross section for nuclear neutron diffraction:

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{hkl}} |F_{\vec{\tau}_{hkl}}|^2 \delta(\vec{Q} - \vec{\tau}_{hkl})$$ (4) $\rightarrow \vec{Q} = \vec{\tau}_{hkl}$ $\quad |\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$

$\vec{Q}$: scattering vector, $\vec{\tau}_{hkl}$: reciprocal lattice vector defining scattering planes
$\delta(\vec{Q} - \vec{\tau}_{hkl})$ → **peak position given by crystal lattice (unit cell)**

All the calculations/fits of experimental integrated intensities and peak positions will be done with ‘fit’ program under HRPT linux-computer



Task 2a: Calculation of structure factors and Bragg peak intensities and comparison with experiment

Coherent elastic cross section for nuclear neutron diffraction:

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{hkl}} \left|F_{\vec{\tau}_{hkl}}\right|^2 \delta(\vec{Q} - \vec{\tau}_{hkl}) \qquad (4) \rightarrow \vec{Q} = \vec{\tau}_{hkl} \qquad |\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$$

$\vec{Q}$: scattering vector, $\vec{\tau}_{hkl}$: reciprocal lattice vector defining scattering planes

$\delta(\vec{Q} - \vec{\tau}_{hkl})$ → **peak position given by crystal lattice (unit cell)**

$F_{\vec{\tau}_{hkl}}$: structure factor of unit cell

$$F_{\vec{\tau}_{hkl}} = \sum_{\vec{d}_i} \left(b_{\vec{d}_i} e^{i\vec{\tau}_{hkl}\cdot\vec{d}_i} \cdot e^{-B_i (Q/4\pi)^2} \right) \qquad (5)$$

we assume $B = 0$, but actually $B \simeq 0.8\,\text{Å}^2$ @ RT

$\vec{d}_i$: atomic coordinate of i-th atom in real space, sum runs over all atoms in unit cell

$b_{\vec{d}_i}$: scattering length of atom at position $\vec{d}_i$

Intensity ~ $\left|F_{\vec{\tau}_{hkl}}\right|^2$ → **peak intensity is mainly given by arrangement of atoms in unit cell**

The sum runs over all atoms in unit cell.

femto or fermi

$1\,\text{fm} = 10^{-13}\,\text{cm} = 10^{-15}\,\text{m}$

For MnS: b_{Mn} = -3.73 fm, b_S = 2.85 fm

$\vec{d}$-vectors:

Mn:	$\vec{d}_1$= a(0, 0, 0)	$\vec{d}_2$= a(0, ½, ½)	F-centering. (8)
	$\vec{d}_3$= a(½, 0, ½)	$\vec{d}_4$= a(½, ½, 0)	
S:	$\vec{d}_5$= a(½, ½, ½)	$\vec{d}_6$= a(½, 0, 0)	
	$\vec{d}_7$= a(0, ½, 0)	$\vec{d}_8$= a(0, 0, ½)	

Task 2b: Calculation of structure factors and Bragg peak intensities and comparison with experiment

$I_\Sigma(2\theta)$ is measured in the experiment $|\vec{Q}| = \frac{4\pi \sin\theta}{\lambda}$

For cylindrical geometry of the powder sample container the integrated intensity of the scattered neutrons of the Bragg peak at $|\vec{Q}|$ is given by

$$I(Q) = C \cdot A(\theta) \cdot L(\theta) \cdot \frac{d\sigma}{d\Omega} = C \cdot A(\theta) \cdot L(\theta) \cdot |F\ (Q)|^2 \cdot mult \quad (6)$$

assume: $A(\theta) \simeq 1$

C: scale factor, $A(\theta)$: absorption factor, $L(\theta)$: Lorentz factor, *mult*: multiplicity

$$L(\theta) = \frac{1}{\sin\theta \sin 2\theta} \quad (7)$$

The Lorentz factor $L(\theta)$ is a geometrical correction depending on the scattering geometry.

2

Tasks:

- calculate $|F_{\vec{\tau}_{hkl}}|^2$ for (h,k,l) = (1,1,1), calculate the multiplicity → (111), (-111), ...
- calculate $|F_{\vec{\tau}_{hkl}}|^2$ for (h,k,l) = (2,0,0), calculate the multiplicity
- compare ratio of $I(\vec{\tau}_{111})$ / $I(\vec{\tau}_{200})$ with the measured intensity ratio

Task 3: Indexing of the magnetic Bragg peaks. Calculation of magnetic structure factors and determination of the value and direction of the Mn-spins.

5.3 Neutron diffraction of MnS in the magnetically ordered state

3

Tasks:

- measure a neutron diffraction pattern of MnS at T = 50 K in the magnetically ordered state (or lower T)
- compare this date with the paramagnetic pattern at room temperature
- index the magnetic peaks, i.e. find (h, k, l) for ~~each~~ first 3 magnetic peak
- based on the indices, what is the magnetic unit cell compared to the crystallographic one
- Using eq. (6) for (111)-peak and eq. (10) for $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ magnetic peak determine $\vec{\mu}$.

Consider $\vec{\mu} \parallel (111)$ in calculations

- Which direction of $\vec{\mu}$ can be excluded?

Task 3: Indexing of the magnetic Bragg peaks. Calculation of magnetic structure factors and determination of the value and direction of the Mn-spins.

Coherent elastic cross section for antiferromagnetic order

$$\frac{d\sigma}{d\Omega} \sim \sum_{\vec{\tau}_{M,hkl}} |F_{M,hkl}|^2 \delta(\vec{Q} - \vec{\tau}_{M,hkl})$$

$F_{M,hkl}$: antiferromagnetic structure factor

Formula (10) is actually formula (6) with $|\vec{F}_{M\perp}|$ instead of $|F|^2$ with the same scale factor C

The intensity of the magnetic Bragg peak at $|\vec{Q}_M|$ is

$$I(Q_M) = C \cdot A(\theta) \cdot L(\theta) \cdot |F_{M\perp}|^2 \cdot mult \quad (10) \quad A(\theta) = 1$$

multiplicity is 2 for $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak. Can you explain why?

where

$$\vec{F}_{M\perp} = \frac{1}{2} r_0 \sum_{j=1}^{4} e^{i\vec{Q}_M \vec{d}_j} \vec{\mu}_{j\perp} \quad (11) \quad \text{and} \quad \vec{\mu}_\perp = \left(\vec{\mu} - \frac{\vec{Q}_M(\vec{\mu} \cdot \vec{Q}_M)}{Q_M{}^2}\right) \quad (12)$$

where $\vec{\mu}$ is the magnetic moment in units μ_B and r_0 = -0.54·10^{-12} cm, $\vec{Q}_M \equiv \vec{\tau}_{M,hkl}$

The sum runs over Mn-atoms.

$\vec{\mu}_1 \uparrow\downarrow \vec{\mu}_{2,3,4}$ Can you explain why?