Some answers for the practical ESM2017:
Neutron diffraction for magnetic structure determination

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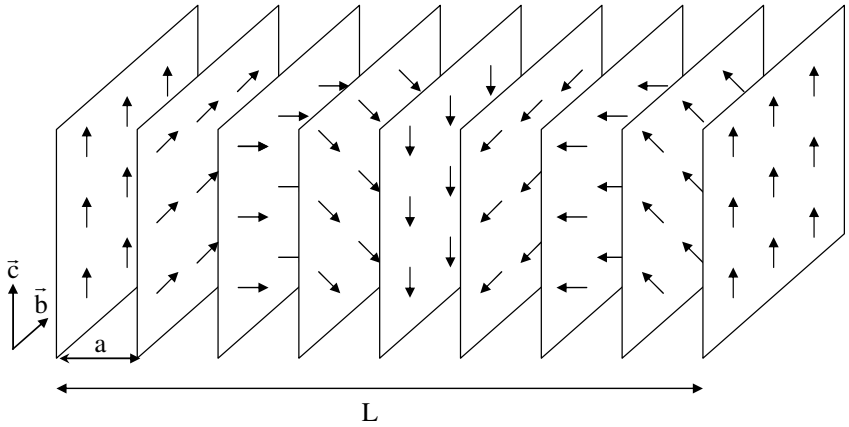
Bibliography:

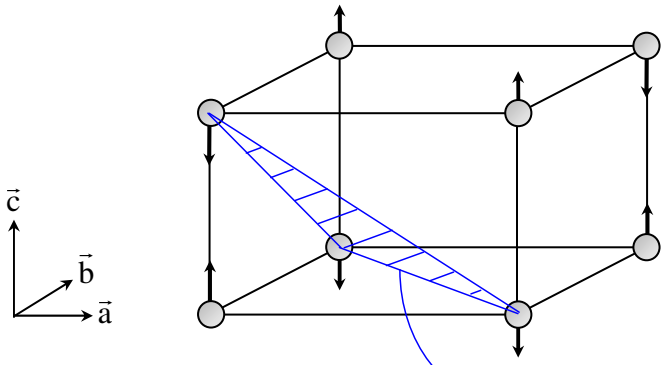
Reminder: Magnetic structures description and determination by neutron diffraction
E. Ressouche, *Collection SFN* 13, 02001 (2014),
DOI: https://doi.org/10.1051/sfn/20141302001

Exercise 1: What is a propagation vector?

A- Give the propagation vector of the two magnetic structures depicted below.

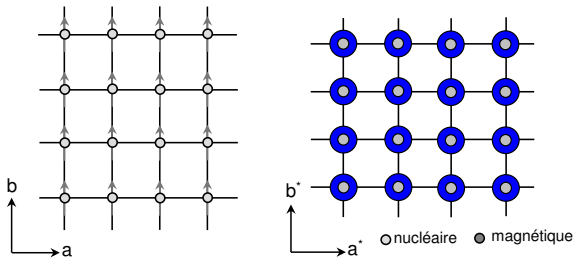


L=8, (b, c) ferromagnetic planes, **k**=(0, 0, 1/8)

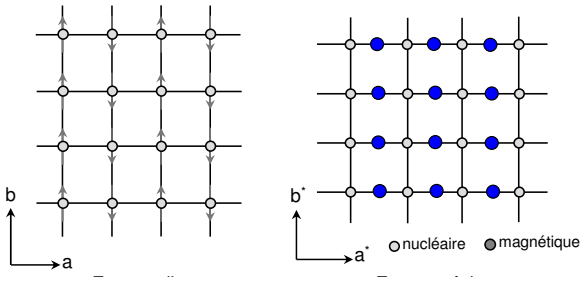


Doubling of the unit cell along a, b, and c, ferromagnetic planes perpendicular to a*+b*+c*, **k**=(1/2, 1/2, 1/2)

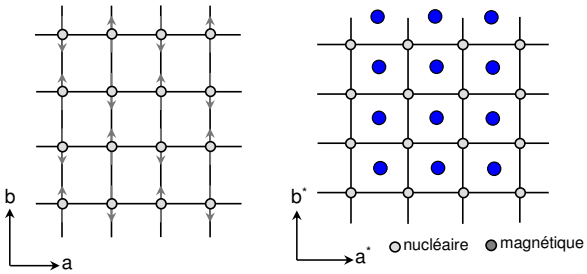
B- Indicate in all the cases below, (i) the propagation vectors (sometimes there are several), (ii) the type of magnetic structure (ex. ferromagnetic, antiferromagnetic...), and (iii) draw in the reciprocal space the magnetic Bragg peaks. Note that in all cases, the coupling along the 3rd direction (c-axis) is ferromagnetic.



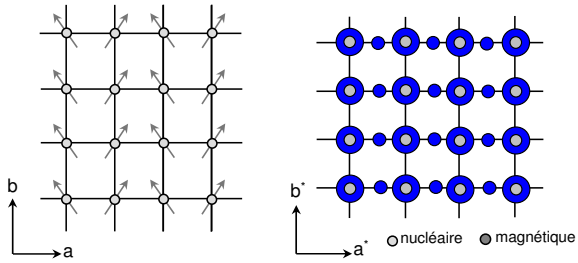
Ferromagnetic **k**=(0, 0, 0)



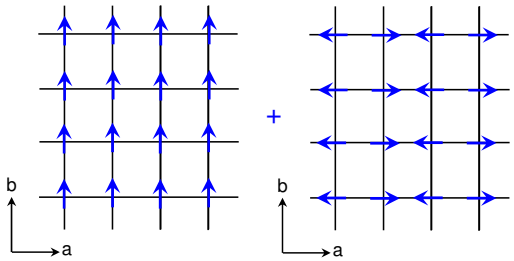
Antiferromagnetic **k**=(1/2, 0, 0)



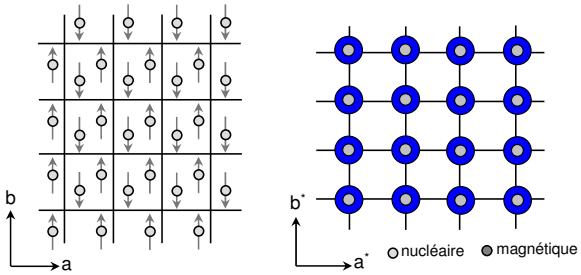
Antiferromagnetic **k**=(1/2, 1/2, 0)



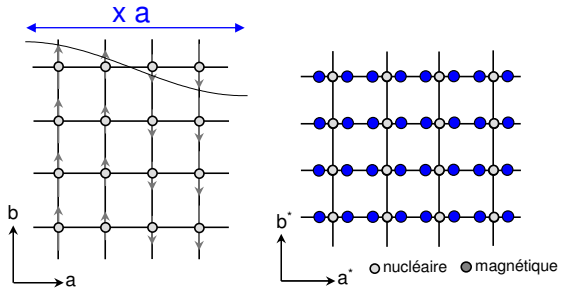
Canted antiferromagnetic **k**=(1/2, 1/2, 0)

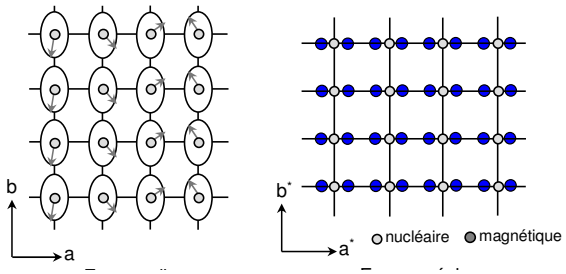


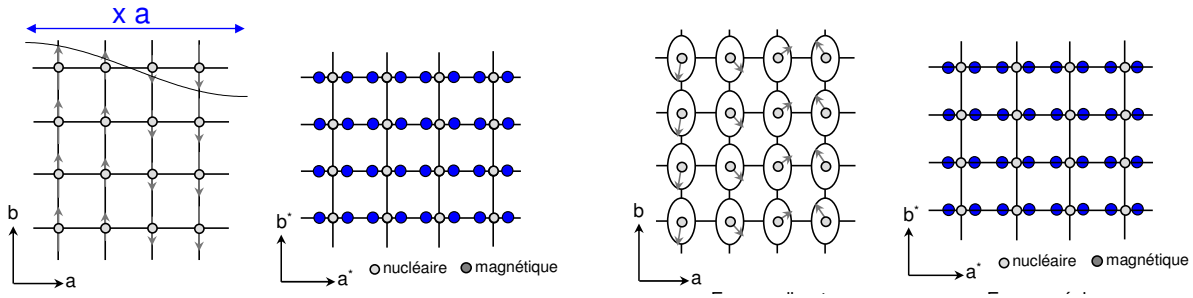
k$_1$=(0, 0, 0) **k**$_2$=(1/2, 0, 0)



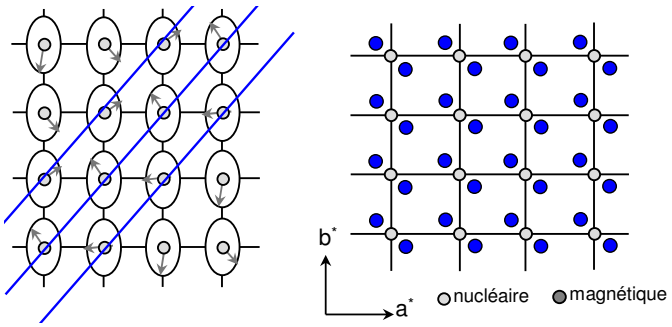
Antiferromagnetic k=(0, 0, 0), 2 atoms per unit cell: no doubling of the unit cell but antiferromagnetic arrangement within the unit cell.





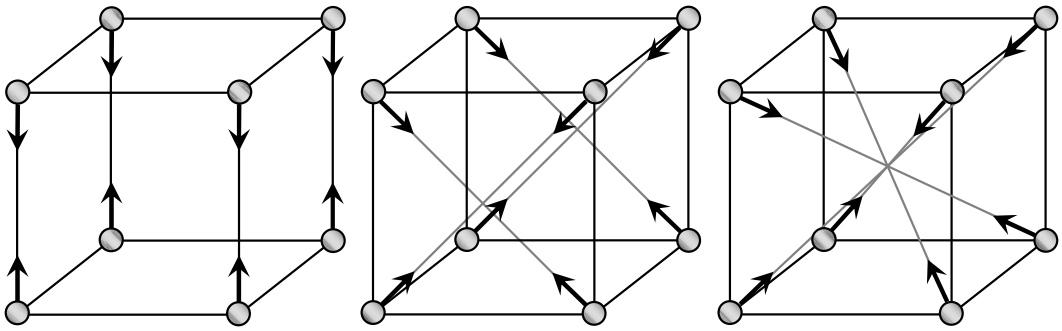


sinewave amplitude modulation **k**=(1/x, 0, 0) helix (cycloid) **k**=(1/x, 0, 0)
If x is identical, we can discriminate between the two thanks to the integrated intensities of the magnetic Bragg reflections



helix (cycloid) with k=(1/x, -1/x, 0)

C- Possible magnetic structures in a simple cubic lattice. Give the propagation vector(s) for each of these structures.



k=(0, 1/2, 0) simple-k

k=(0, 1/2, 0) double-k
k=(1/2, 0, 0)

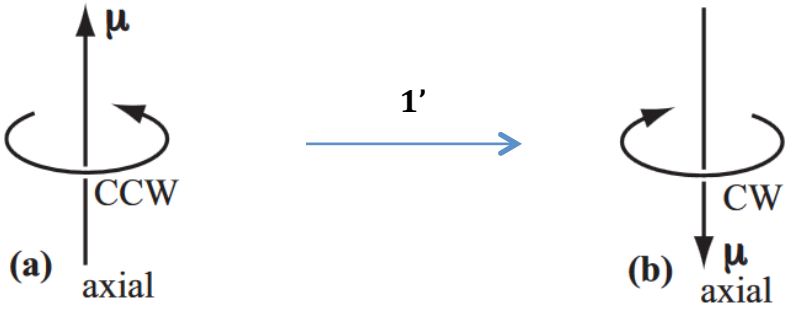
k=(0, 1/2, 0) triple-k
k=(1/2, 0, 0)
k=(0, 0, 1/2)

It is often very difficult to distinguish between these three structures because of the existence of magnetic domains. One has to use an external constraint, such as an applied magnetic field along a particular axis or a pressure to validate one model or the other.

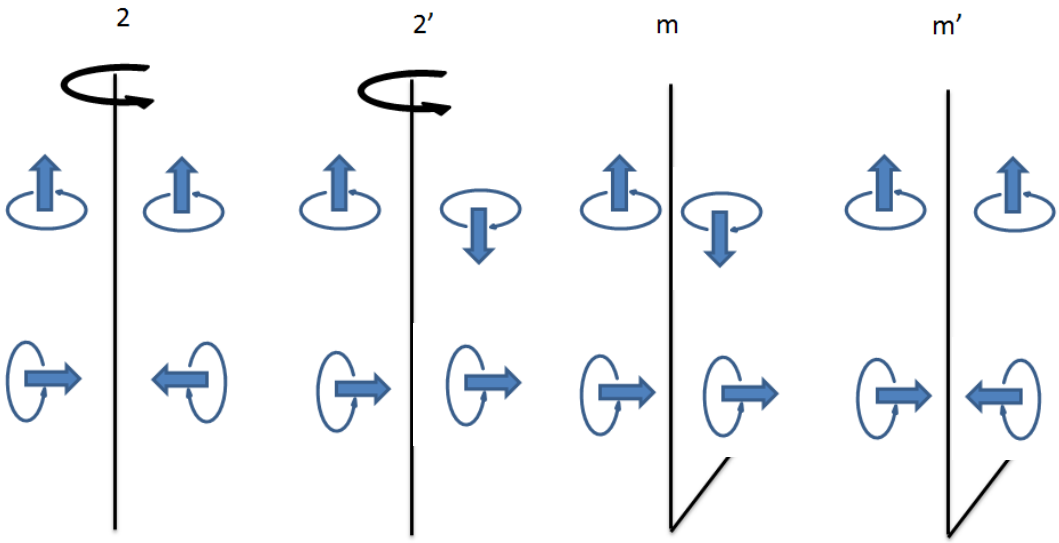
Exercise 2: magnetic symmetry

A magnetic moment originates from a current loop and can therefore be represented by an axial or pseudo vector. The direction of the moment vector is determined by the direction of the current; for a counter-clockwise current (a), the moment vector points

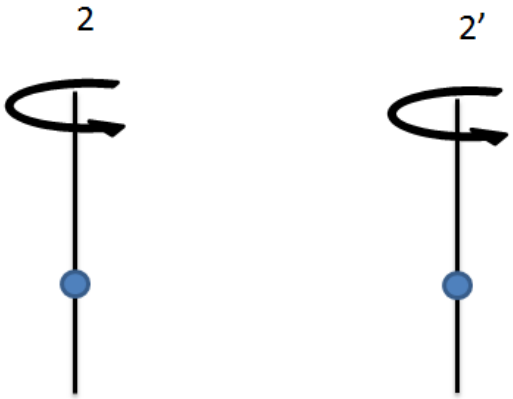
up, whereas for a clockwise current (b) the moment points down. Time reversal symmetry (1') inverses the magnetic moment direction.



A. Magnetic symmetry operations can be described as « usual » crystallographic operations (rotation, mirror, inversion) plus time reversal symmetry (1'). Draw the magnetic moment on the figure below. Which component of the magnetic moment is conserved/inverted by 2 and m symmetry operation, combines or not to time reversal?



B. Magnetic moments on special Wyckoff positions have less degree of freedom. Examine the possible orientation of the moment of an atom on a 2 and 2' fold-axis.



parallel to the rotation axis perpendicular to the rotation axis

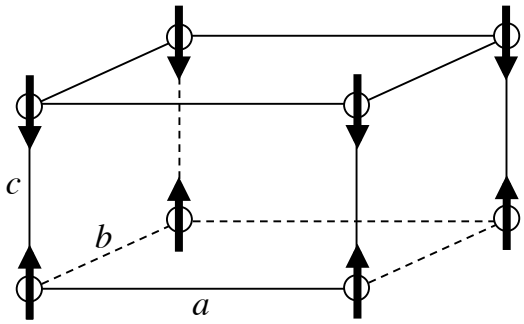
Exercise 3: simple antiferromagnetic arrangement

Antiferromagnetic compound, with one atom per unit cell (orthorhombic) located at the origin. The magnetic moments are along the c axis. The magnetic Bragg peaks appear at the position **Q**=(H, K, L+1/2) with H, K, L integers.

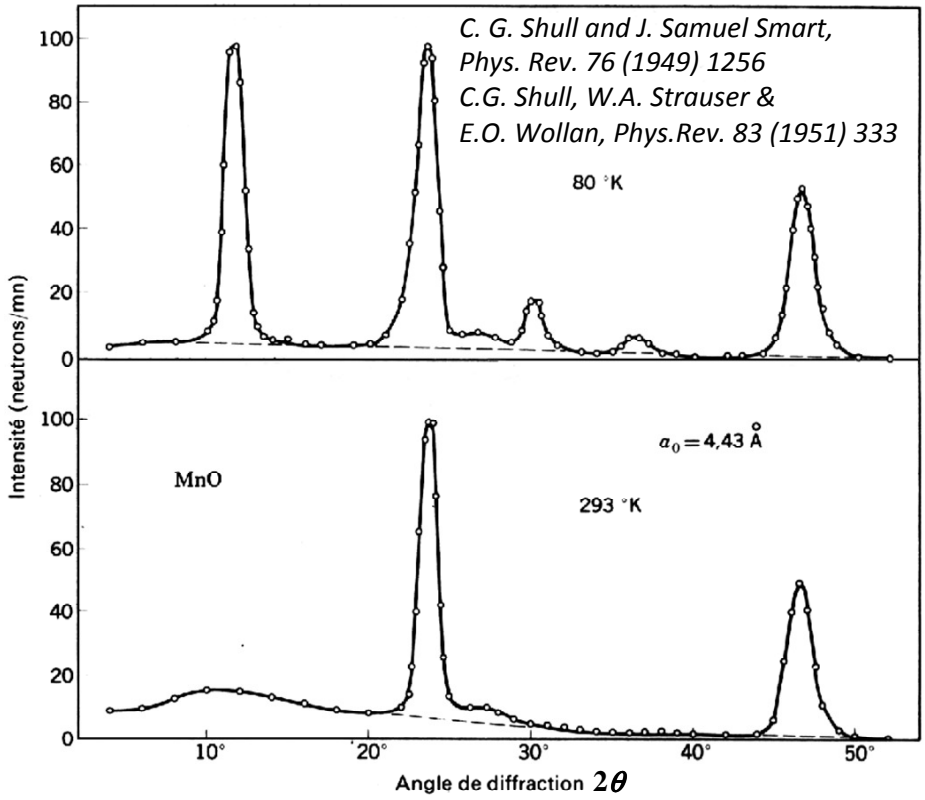
A-What is the periodicity of the magnetic structure compared to the nuclear one along the a, b, and c directions? The same in the a and b direction, doubled along c.

B-What is the spin arrangement? Complete the figure below.

C-What is the intensity of the 0 0 1/2 reflection? Zero since the neutron only probes the magnetic component perpendicular to the scattering vector



Exercise 4: historical example MnO



A-Nuclear diffraction

MnO crystallizes in a cubic system (cell parameter a=4.43 Å). First look at the room temperature diffractogram.

a-Knowing that the first measured reflection is the first reflection of the series, is the system primitive, centred or face centred? Index the observed reflections. Note that some reflections are very weak.

Help:
-Recall the extinction conditions of the 3 types of lattice (primitive P, centred C, face centred F) using the expression of the nuclear structure factor: $F_N(hkl) = \sum_{j=1}^{N} e^{i2\pi(hx_j+ky_j+hz_j)}$
-Show that for any *h k l* reflection of a cubic lattice, at the Bragg angle 2θ: $h^2+k^2+l^2 = A\sin^2\theta$. Use the Bragg law $\lambda = 2d_{hkl}\sin\vartheta$ and $d_{hkl} = a/\sqrt{h^2+k^2+l^2}$ for a cubic lattice.
-The proportionality coefficient *A* depends on the wavelength, not known at this stage. A way to proceed then is to compare the ratio of the $(h^2+k^2+l^2)/(h_1^2+k_1^2+l_1^2)$ compared to the ratio of $(\sin^2\theta)/(\sin^2\theta_1)$, the index 1 standing for the first observed reflection. They must be equal! which should give you the lattice type and allow you to index the diffractogram.

Extinction rules :

For a primitive lattice (P), no conditions:

$\forall\ h, k, l,\ F_N(hkl) \neq 0$

For a centred lattice (I):

$$F_N(hkl) = \sum_{j=1}^{N/2} b_j \left[e^{2i\pi(hx_j+ky_j+lz_j)} + e^{2i\pi(h(x_j+1/2)+k(y_j+1/2)+l(z_j+1/2))} \right]$$

$$F_N(hkl) = \sum_{j=1}^{N/2} b_j\, e^{2i\pi(hx_j+ky_j+lz_j)} \left[1 + e^{i\pi(h+k+l)} \right]$$

$$F_N(hkl) = \begin{cases} 2\sum_{j=1}^{N/2} b_j\, e^{2i\pi(hx_j+ky_j+lz_j)} & \text{si } h+k+l \quad \text{even} \\ 0 & \text{si } h+k+l \quad \text{odd} \end{cases}$$

$\Rightarrow F_N(hkl) \neq 0$ if $h+k+l = 2n$

For a face centred lattice (F):

$$F_N(hkl) = \sum_{j=1}^{N/4} b_j \left[\begin{array}{l} e^{2i\pi(hx_j+ky_j+lz_j)} + e^{2i\pi(h(x_j+1/2)+k(y_j+1/2)+lz_j)} \\ + e^{2i\pi(h(x_j+1/2)+ky_j+l(z_j+1/2))} + e^{2i\pi(hx_j+k(y_j+1/2)+l(z_j+1/2))} \end{array} \right]$$

$$F_N(hkl) = \sum_{j=1}^{N/4} b_j\, e^{2i\pi(hx_j+ky_j+lz_j)} \left[1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \right]$$

$$F_N(hkl) = \begin{cases} 4\sum_{j=1}^{N/4} b_j\, e^{2i\pi(hx_j+ky_j+lz_j)} & \text{If } h, k, l \text{ of same parity} \\ 0 & \text{If } h, k, l \text{ of different parity} \end{cases}$$

$\Rightarrow F_N(hkl) \neq 0$ If *h, k, l* of same parity

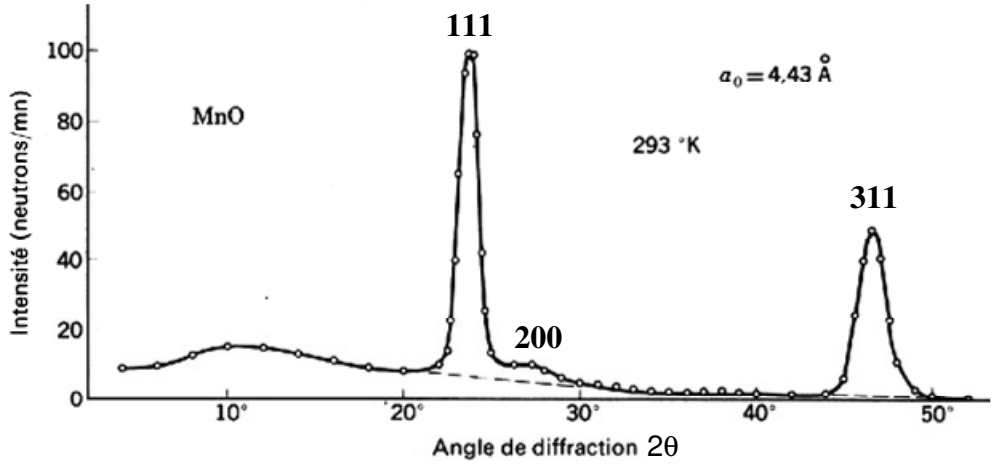
We can then get the following table:

	cubique P	Cubique I (*h*+*k*+*l* pair)		Cubique F (*h*,*k*,*l* même parité)	
hkl	$h^2+k^2+l^2$	$h^2+k^2+l^2$	$\frac{h^2+k^2+l^2}{h_1^2+k_1^2+l_1^2}$	$h^2+k^2+l^2$	$\frac{h^2+k^2+l^2}{h_1^2+k_1^2+l_1^2}$
100	**1**				
110	**2**	2	**1**		
111	**3**			3	**1**
200	**4**	4	**2**	4	**1.33**
210	**5**				
211	**6**	6	**3**		
220	**8**	8	**4**	8	**2.67**
221 - 300	**9**				
310	**10**	10	**5**		
311	**11**			11	**3.67**
222	**12**	12	**6**	12	**4**
320	**13**				
321	**14**	14	**7**		
400	16	16	8	16	**5.33**

Compared to the observed reflections:

$2\theta_i$	$\sin^2\theta_i$	$\frac{\sin^2\theta_i}{\sin^2\theta_1}$
$2\theta_1 \approx 23.7°$	0.0422	1
$2\theta_2 \approx 27.3°$	0.0557	1.32
$2\theta_3 \approx 46.5°$.	0.1558	3.70

We then deduce that MnO crystallizes in the face centred cubic space group. We can index the magnetic reflections as follows (note the 220 reflection is absent)



b- What was the neutron wavelength used in the measurements?
It is then easy to calculate the wavelength which is equal to 1.5 Å.

c- Mn occupies the (0, 0, 0) position and the O atoms the (1/2, 0, 0) position. Calculate the nuclear structure factor F_N(h, k, l) with the Fermi lengths b_O=5.8 and b_{Mn}=-3.73 fm. (note Debye-Waller neglected). Comment on the results.

$$F_N(hkl) = 4 \sum_{j=1}^{N/4} b_j \; e^{2i\pi(hx_j + ky_j + lz_j)} = 4\left[\bar{b}_{Mn} + \bar{b}_O \, e^{i\pi h}\right]$$

$$F_N(hkl) = \begin{cases} 4\left[\bar{b}_{Mn} + \bar{b}_O\right] = 8.3 & \text{For even } h, \text{ and thus for even } h, k, l \\ 4\left[\bar{b}_{Mn} - \bar{b}_O\right] = 38.1 & \text{For odd } h \text{ and thus for odd } h, k, l \end{cases}$$

Then the integrated intensities with odd indices are around 21 times more intense than those with even indices, which is in agreement with the observations.

B-Magnetic diffraction

A transition from a paramagnetic state to a magnetic ordered state occurs at 120 K. We then look at the neutron diffractogram measured below the transition temperature.

a-Is the ordered phase ferromagnetic or antiferromagnetic?

It is antiferromagnetic as new reflections appear.

b-Index the magnetic Bragg reflections and give the propagation vector k=(h_0, k_0, l_0) with h_0, k_0, l_0= 0 or 1/2

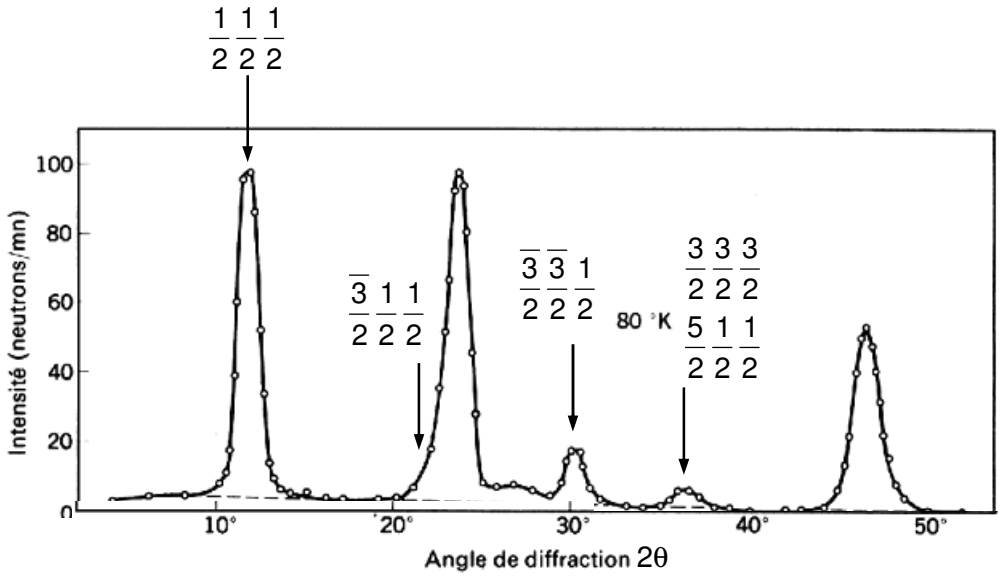
According to Bragg's law, the first magnetic reflection is observed at 2θ=11.8°
so that

$$h^2 + k^2 + l^2 = 0.7523 \approx \frac{3}{4} = \frac{1}{4} + \frac{1}{4} + \frac{1}{4}$$

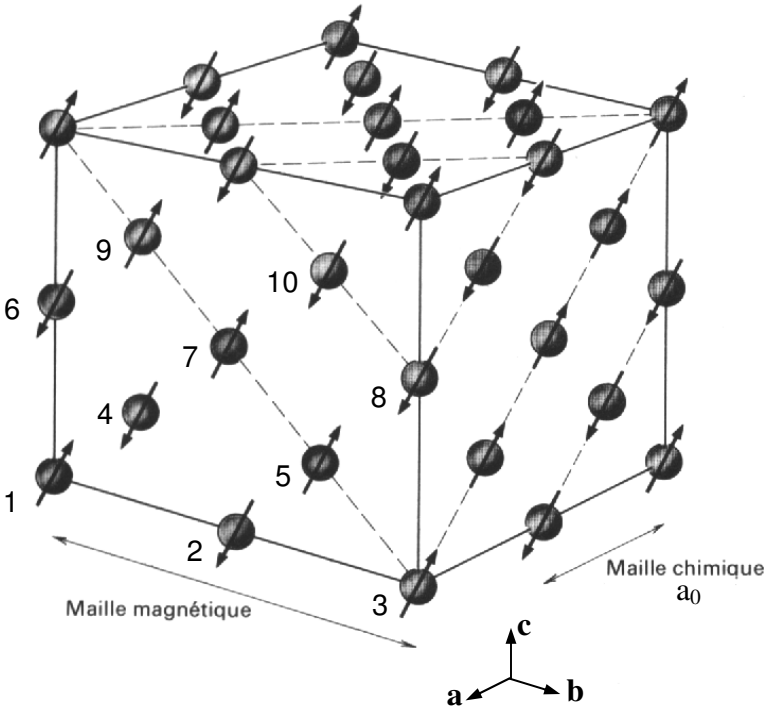
then the propagation vector is **k**=(1/2, 1/2, 1/2) (arbitrary choice for the sign).
Then all the magnetic reflections will be on **Q**=**H**+**k** of the form (h+1/2, k+1/2, l+1/2), with *h, k, l* of same parity.

Below is the indexation of the magnetic reflections:

2θ	$h^2 + k^2 + l^2$	$\vec{Q} = \vec{H} + \vec{k}$
11.8°	$0.75 = \frac{3}{4} = \frac{1}{4} + \frac{1}{4} + \frac{1}{4}$	$\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right) = (0\,0\,0) + \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$
≈ 22°	$2.59 \approx \frac{11}{4} = \frac{9}{4} + \frac{1}{4} + \frac{1}{4}$	$\left(\frac{\bar{3}}{2}\frac{1}{2}\frac{1}{2}\right) = (\bar{2}\,0\,0) + \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$
≈ 30°	$3.71 \approx \frac{19}{4} = \frac{9}{4} + \frac{9}{4} + \frac{1}{4}$	$\left(\frac{\bar{3}}{2}\frac{\bar{3}}{2}\frac{1}{2}\right) = (\bar{2}\,\bar{2}\,0) + \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$
≈ 36°	$4.77 \approx \frac{27}{4} = \frac{9}{4} + \frac{9}{4} + \frac{9}{4}$ ou $\frac{25}{4} + \frac{1}{4} + \frac{1}{4}$	$\left(\frac{3}{2}\frac{3}{2}\frac{3}{2}\right) = (1\,1\,1) + \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$ $\left(\frac{5}{2}\frac{1}{2}\frac{1}{2}\right) = (2\,0\,0) + \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$



c-Draw in the cube of 2aX2ax2a size the magnetic moments of the Mn for an arbitrary direction of the magnetic moments.



d-Why do the intensities of the magnetic Bragg reflection decrease so fast when 2θ increases? It decreases faster than the nuclear part since it is proportional to the square of the magnetic form factor (FT of the electron cloud density) that decreases rapidly with Q.

e-Are the $(-h_0, k_0, l_0)$, $(h_0, -k_0, l_0)$, $(h_0, k_0, -l_0)$ vectors also propagation vectors of the observed magnetic arrangement?

For a F cubic system, the (-1/2, 1/2, 1/2), (1/2, -1/2, 1/2) and (1/2, 1/2, -1/2) propagation vectors do not describe the observed magnetic structure. They belong, with (1/2, 1/2, 1/2) to the star of k and corresponds to 4 magnetic domains.

Note : In October 1949, Clifford Shull and Samuel Smart published the first magnetic neutron diffraction pattern (1949). Their experimental observation that the magnetic structure of MnO had a unit cell that was twice that of the nuclear along each of the crystallographic axis was conclusive proof that the predictions of antiferromagnetism by Louis Néel were correct.

Exercise 5: Rietveld analysis using FullProf on a powder sample of Fe langasite $Ba_3NbFe_3Si_2O_{14}$

Fullprof software developed by Juan Rodriguez-Carvajal (ILL)

Step 1: Refine the crystal structure of the sample in its paramagnetic state, and get all the relevant structural and profile parameters, including the scale factor (**FULLPROF** and **WINPLOTR**)

Step 2: Refine the crystal structure of the sample in its magnetically ordered state, without a magnetic model. This is important to see clearly the magnetic contribution to the diffraction data (such as additional peaks, etc.).

Step 3: Determine the propagation vector(s) **k** of the magnetic structure using the **k-SEARCH** program within **WINPLOTR2006**.

Step 4: Once the propagation vector is known, perform a symmetry analysis (**BASIREPS**) in order to get the basis vectors of the irreducible representations of the little group G_k.

Step 5: Solve the magnetic structure by using the symmetry information obtained in step 4 using trial and error methods (**FULLPROF**).

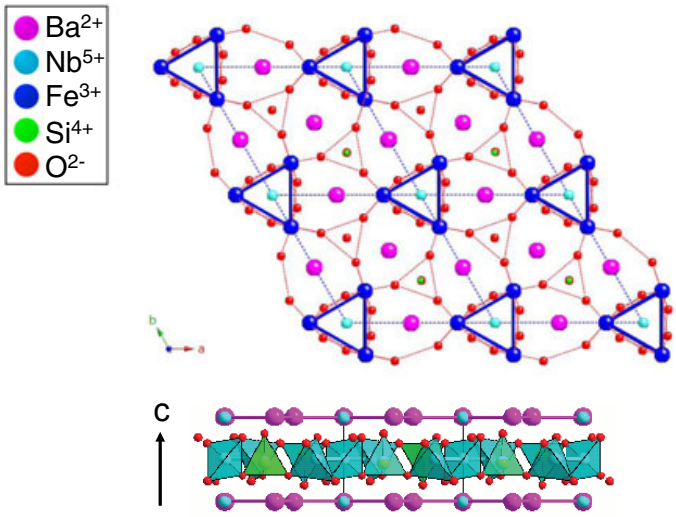
Determination of the magnetic structure of $Ba_3NbFe_3Si_2O_{14}$

We provide two powder diffraction patterns of $Ba_3NbFe_3Si_2O_{14}$ (diffractometer D1B@ILL), recorded with λ = 2.52 Å. The space group is trigonal **P321**, the cell parameters are $a = b = 8.505$ Å, and $c = 5.213$ Å, γ = 120°. A magnetic transition is observed at T_N =28 K. A 1.5 K pattern (in the magnetically ordered phase) has been recorded in the same conditions as that of the paramagnetic phase at 30 K.

atomic positions:

Ba	0.42806	0.00000	0.00000
Nb	0.00000	0.00000	0.00000
Si	0.33330	0.66670	0.39020
Fe	0.75632	0.00000	0.50000
O	0.33330	0.66670	0.75491
O	0.48242	0.30599	0.66076
O	0.21774	0.08759	0.22922

What are their Wyckoff letter and site multiplicity?

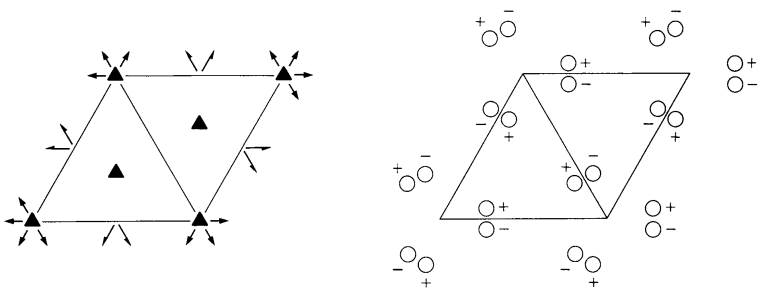


The format of the data corresponds to Ins = 3 (high temperature, lang30K.dat file) and Ins = 10 (low temperature, norm1p5K.dat file) in FULLPROF. A complete .pcr file, adapted for the refinement of the crystal structure of $Ba_3NbFe_3Si_2O_{14}$ at 30K is provided for easy start. The two diffraction patterns can be opened with WINPLOTR/WINPLOTR-2006 for easy visualisation.

International Tables for Crystallography (2006). Vol. A, Space group 150, pp. 506–507.

$P321$ D_3^2 321 Trigonal

No. 150 $P321$ Patterson symmetry $P\bar{3}m1$



Origin at 321

Asymmetric unit $0 \le x \le \frac{2}{3}$; $0 \le y \le \frac{2}{3}$; $0 \le z \le \frac{1}{2}$; $x \le (1+y)/2$; $y \le \min(1-x, (1+x)/2)$

Vertices $0,0,0$ $\frac{1}{2},0,0$ $\frac{2}{3},\frac{1}{3},0$ $\frac{1}{3},\frac{2}{3},0$ $0,\frac{1}{2},0$ $0,0,\frac{1}{2}$ $\frac{1}{2},0,\frac{1}{2}$ $\frac{2}{3},\frac{1}{3},\frac{1}{2}$ $\frac{1}{3},\frac{2}{3},\frac{1}{2}$ $0,\frac{1}{2},\frac{1}{2}$

Symmetry operations

(1) 1 (2) 3^+ $0,0,z$ (3) 3^- $0,0,z$
(4) 2 $x,x,0$ (5) 2 $x,0,0$ (6) 2 $0,y,0$

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		
6	*g*	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$
			(4) $y,x,\bar{z}$	(5) $x-y,\bar{y},\bar{z}$	(6) $\bar{x},\bar{x}+y,\bar{z}$
3	*f*	. 2 .	$x,0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$
3	*e*	. 2 .	$x,0,0$	$0,x,0$	$\bar{x},\bar{x},0$
2	*d*	3 . .	$\frac{1}{3},\frac{2}{3},z$	$\frac{2}{3},\frac{1}{3},\bar{z}$	
2	*c*	3 . .	$0,0,z$	$0,0,\bar{z}$	
1	*b*	3 2 .	$0,0,\frac{1}{2}$		
1	*a*	3 2 .	$0,0,0$		

Step 1 :
Refine the crystal structure of $Ba_3NbFe_3Si_2O_{14}$ by completing the provided .pcr file (Nucd1b.pcr) with input file lang30K.dat.

Step 2 :
Once the refinement is satisfactory, copy the .pcr into a new one (nuc_LT.pcr for example) that you will use with the 1.5 K data. Make sure all the parameters are fixed before you start running Fullprof. You will have to change the background. Which parameters do you think you could refine?
Visualise the .prf with Winplotr to better observe the magnetic peaks.

Step 3 :
Some magnetic peaks seem to appear on top of Bragg peaks: do you know what it means?
We will use the k-search program to identify the propagation vector.
On the .prf file, select a few magnetic peaks at low angles (nb : it is better to use a refined plot because the selection of magnetic peaks gives automatically corrected positions). Save the peak positions with the format needed by the program k-search (k-search.sat).
Then run the k-search program: what is the best solution?
What can you say about the magnetic structure corresponding to this propagation vector?

Step 4:
The whole symmetry analysis can be performed by hand or by using one of the available computing programs (Basireps, Sarah, Isodistort, etc..). The program BASIREPS will be used here, as it can be used efficiently with a minimal knowledge of group theory. Perform the symmetry analysis with Basireps: you only need the space group, the propagation vector, and the position(s) of the magnetic atom(s) (input file felang.smb to be completed). This is a complicated case with complex irreducible representations. Discuss what you can learn with it about the possible magnetic structures.

Step 5 :

Try now to refine the low temperature pattern with the nuclear and magnetic structures. We recall :

- **Helical structures**

In this kind of ordering, the magnetic moments rotate in a plane $(\hat{u}, \hat{v})$ when propagating along the $\boldsymbol{k}$ direction (Fig. 7) according to:

$$\boldsymbol{\mu}_{n\nu} = \mu_{1\nu} \cdot \hat{u} \ \cos(\boldsymbol{k} \cdot \boldsymbol{R}_n + \Phi_\nu) + \mu_{2\nu} \cdot \hat{v} \ \sin(\boldsymbol{k} \cdot \boldsymbol{R}_n + \Phi_\nu). \tag{3.6}$$

When $\mu_{1\nu} = \mu_{2\nu}$ the helix is circular, but examples of elliptic helixes $\mu_{1\nu} \neq \mu_{2\nu}$ can also be found. One should notice that the sine-wave modulated structures defined in the previous section are just particular cases of helical structures for which $\mu_{2\nu} = 0$. The distribution is described by two complex conjugate Fourier components $\boldsymbol{m}_{\nu,\boldsymbol{k}}$ and $\boldsymbol{m}_{\nu,-\boldsymbol{k}}$ associated to $\boldsymbol{k}$ and $-\boldsymbol{k}$:

$$\boldsymbol{m}_{\nu,\boldsymbol{k}} = [\frac{\mu_{1\nu} \cdot \hat{u} \ + i \ \mu_{2\nu} \cdot \hat{v}}{2}] \ e^{-i\Phi_\nu} \tag{3.7}$$

$$\boldsymbol{m}_{\nu,-\boldsymbol{k}} = [\frac{\mu_{1\nu} \cdot \hat{u} \ - i \ \mu_{2\nu} \cdot \hat{v}}{2}] \ e^{i\Phi_\nu} \tag{3.8}$$

and the magnetic structure factor can be written as:

$$\boldsymbol{F}_M(\boldsymbol{Q} = \boldsymbol{H} + \boldsymbol{k}) = p \sum_\nu f_\nu(\boldsymbol{Q}) \left[\frac{\mu_{1\nu} \cdot \hat{u} \ + j \ \mu_{2\nu} \cdot \hat{v}}{2}\right] e^{-i\Phi_\nu} \ e^{i\boldsymbol{Q}\cdot\boldsymbol{r}_\nu}. \tag{3.9}$$

You can refine the magnetic pattern in P1 symmetry with the three Fe magnetic atoms of the cell.

Important points for constructing a PCR file with a magnetic contribution to a powder diffraction pattern.

- A magnetic structure phase requires describing only the magnetic atoms in the unit cell.

- On the magnetic atoms lines, the magnetic form factor symbol follows the label of the atom. The real and imaginary parts of the Fourier coefficients of magnetic moments are provided after the coordinates in polar coordinates, isotropic temperature factor and occupation factor.

Comment on the magnetic structure of the Fe langasite: magnetic helices propagating along the c axis and magnetic triangular arrangement within the (a, b) plane. Very original magnetic structure with chiral properties. cf. Marty et al. Phys. rev. lett. 101 (2008) 247201.