Symmetry constraints on the electrical polarization in novel multiferroic materials

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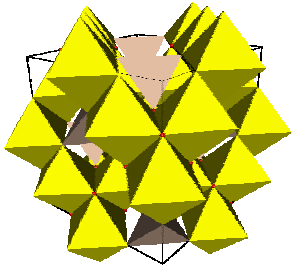
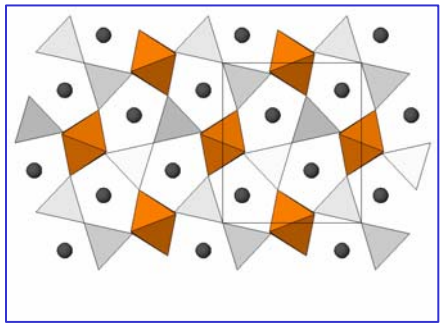
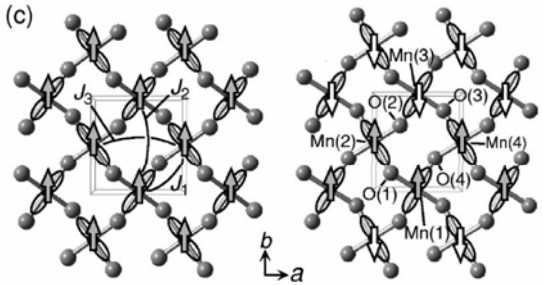
“Novel” multiferroic materials





- Improper ferroelectrics. Primary order parameter is magnetic.
- “Complex” magnetic structures.
- |**P**| is much smaller than for ordinary FE.



$LaMnO_3$ (*A*-type AF) $HoMnO_3$ (*E*-type AF)

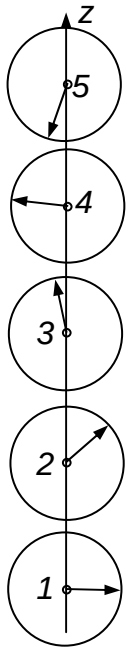
$RE Mn_2O_5$
CM,ICM

$RE MnO_3$
$Ni_3V_2O_8$
ICM

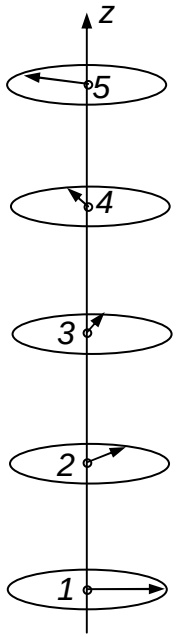
$HgCr_2S_4$ (?)
CM,ICM

Common Ingredient?

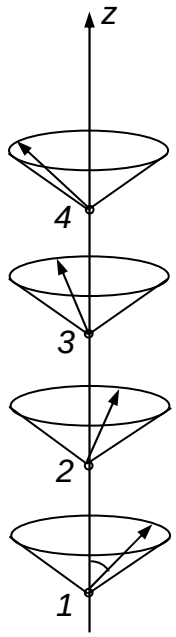
Sine-SDW



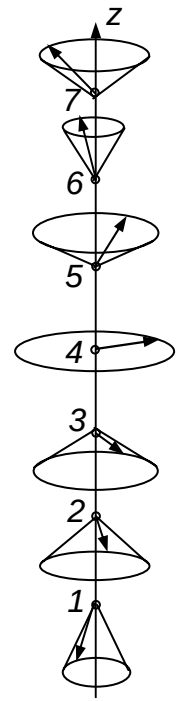
Cycloidal



Helical



Conical



Variable-β Conical

From: Yu. A. Izyumov and R. Ozerov, “Magnetic Neutron Diffraction”, Plenum Press, NY, 1970, pp. 3

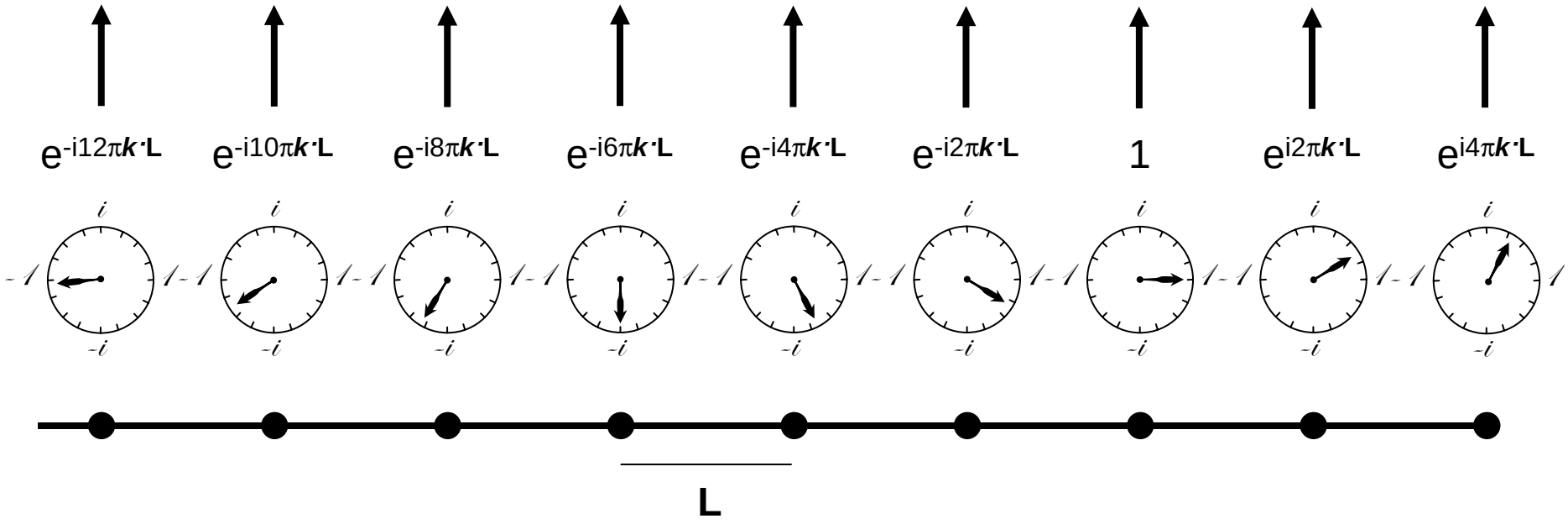
Programme of Work

1. Determine the **symmetry** of the magnetic structure (subgroup of the *paramagnetic* SG).
2. Extract the **rotational** (proper/improper) part of the surviving symmetry operators and “unprime” if necessary.
3. The resulting group ***S*** is one of the *32 three-dimensional crystallographic point groups.*

Common Ingredient: *S* must be one of the 10 *pyroelectric groups*.

1, 2, m, mm2, 4, 4mm, 3, 3m, 6, 6mm

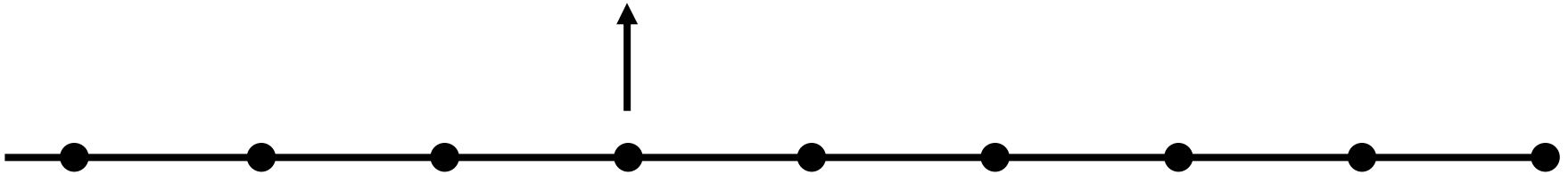
Propagation Vector



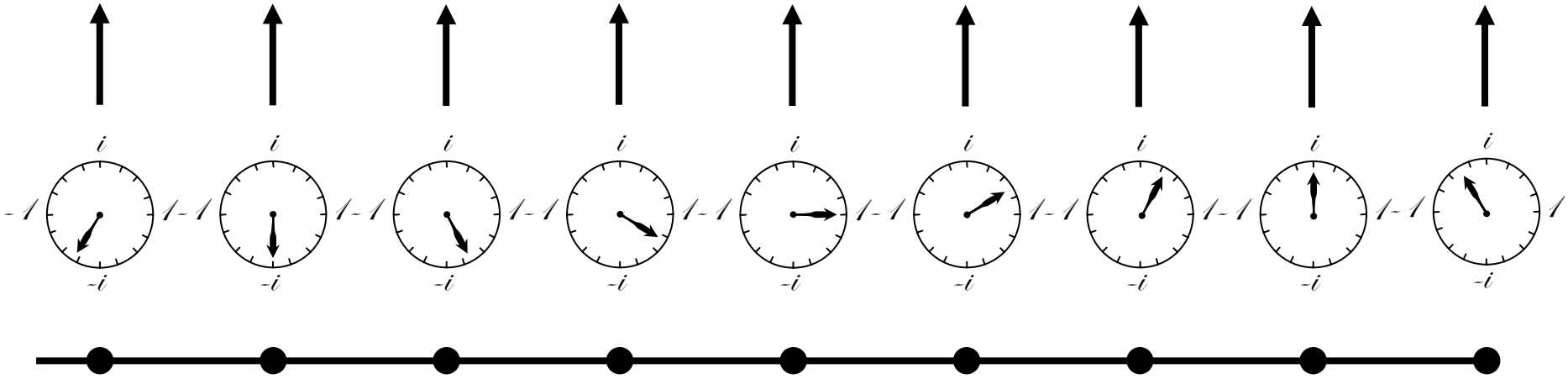
Fourier Components (complex)

$\boldsymbol{k}$

The effect of translations upon the basis vectors

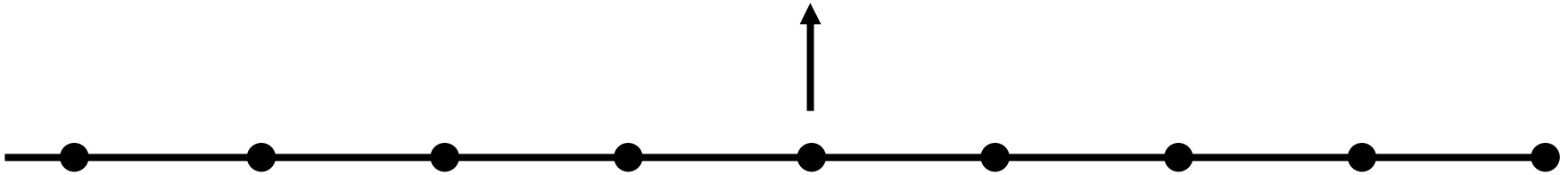


Generic basis vectors (real)

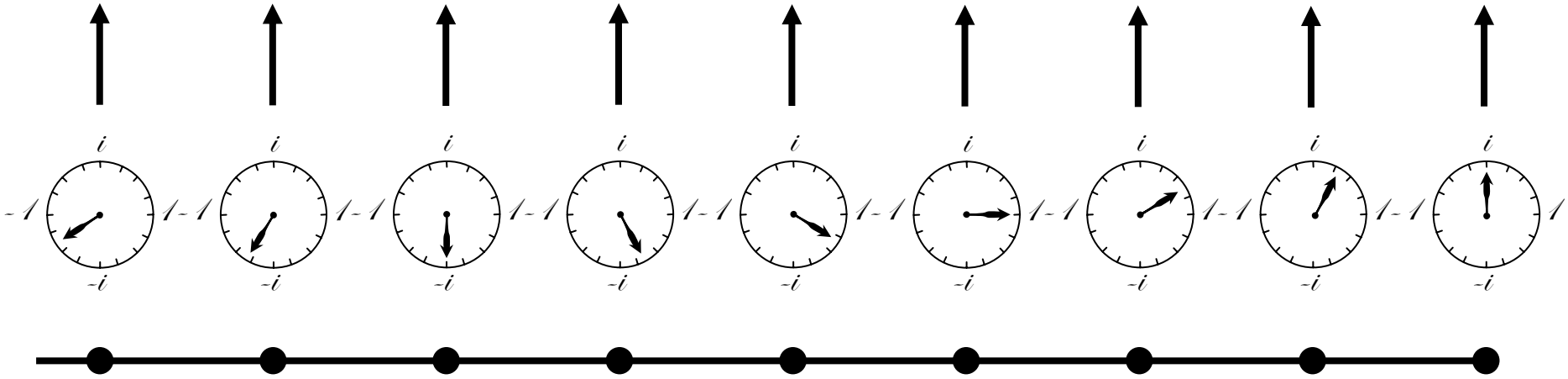


Fourier Components (complex)

The effect of translations upon the basis vectors

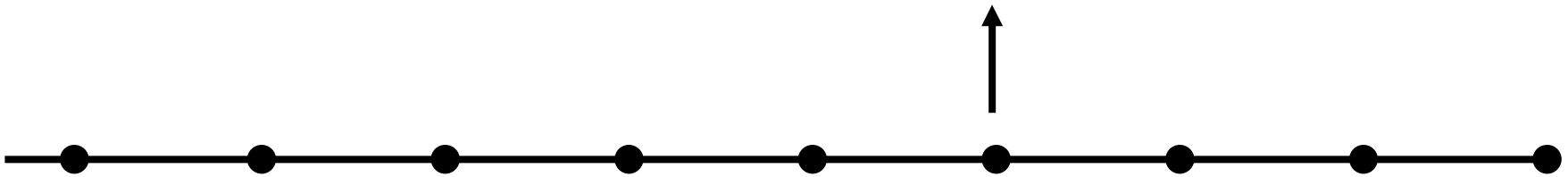


Generic basis vectors (real)

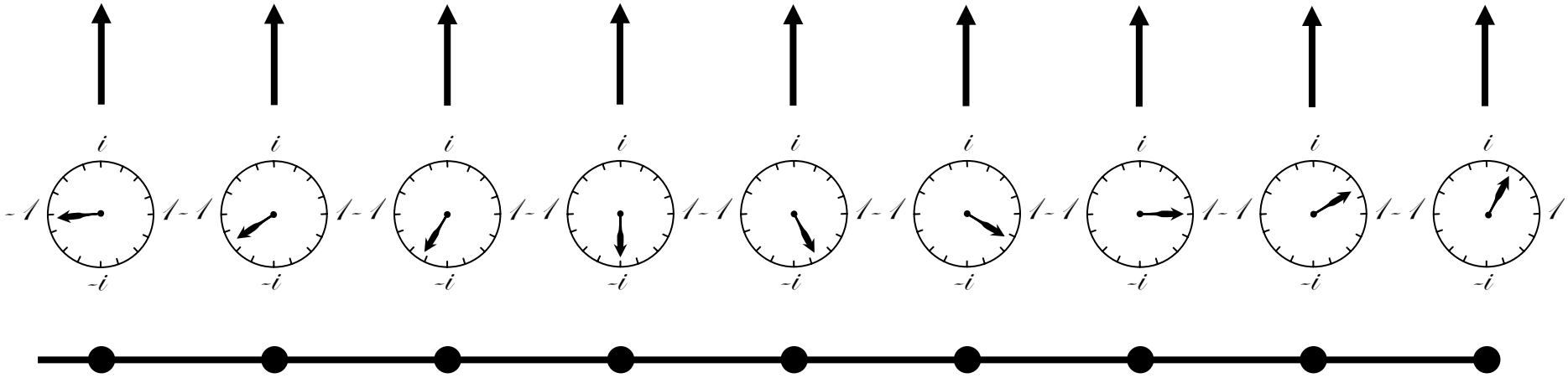


Fourier Components (complex)

The effect of translations upon the basis vectors

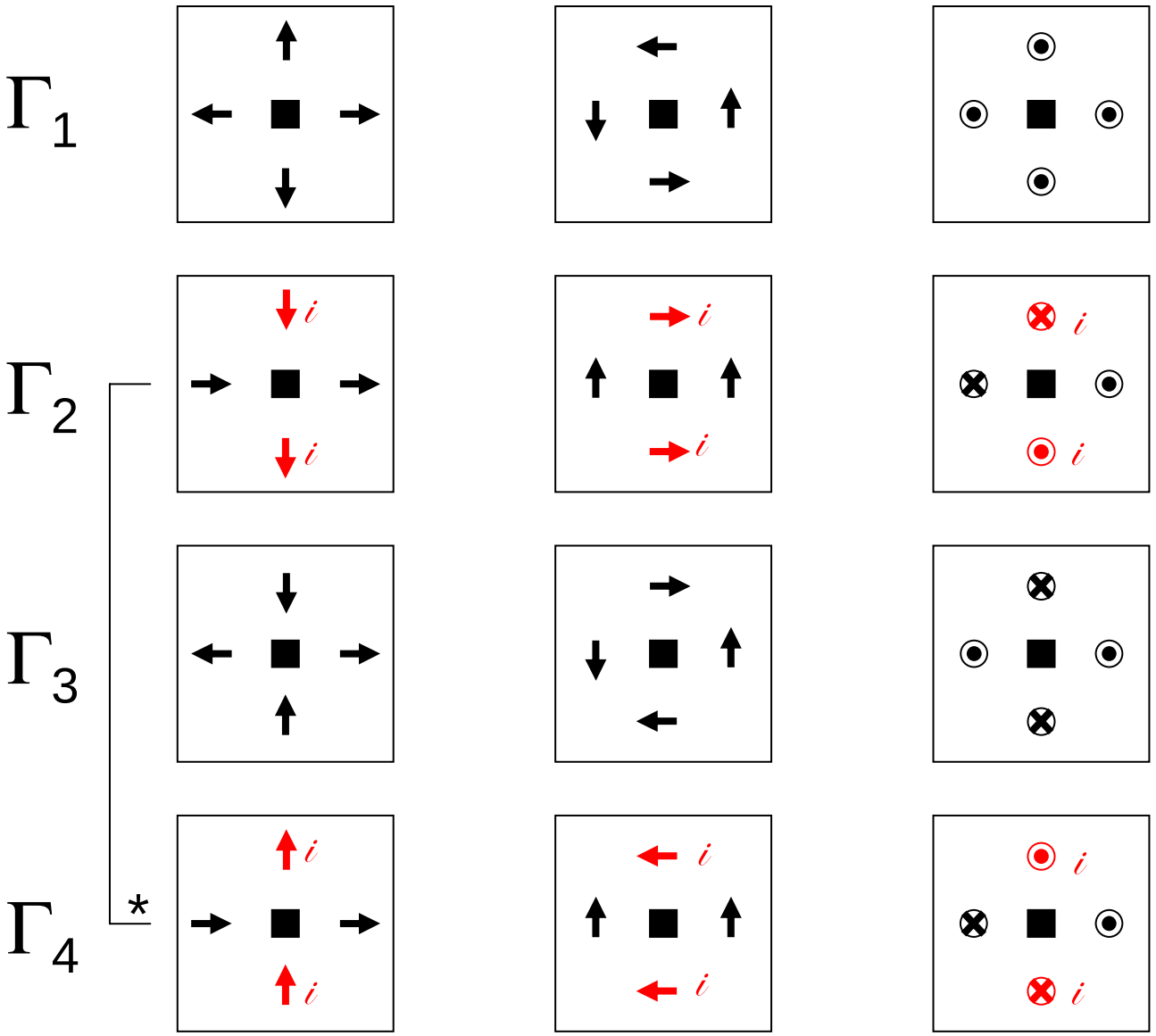


Generic basis vectors (real)



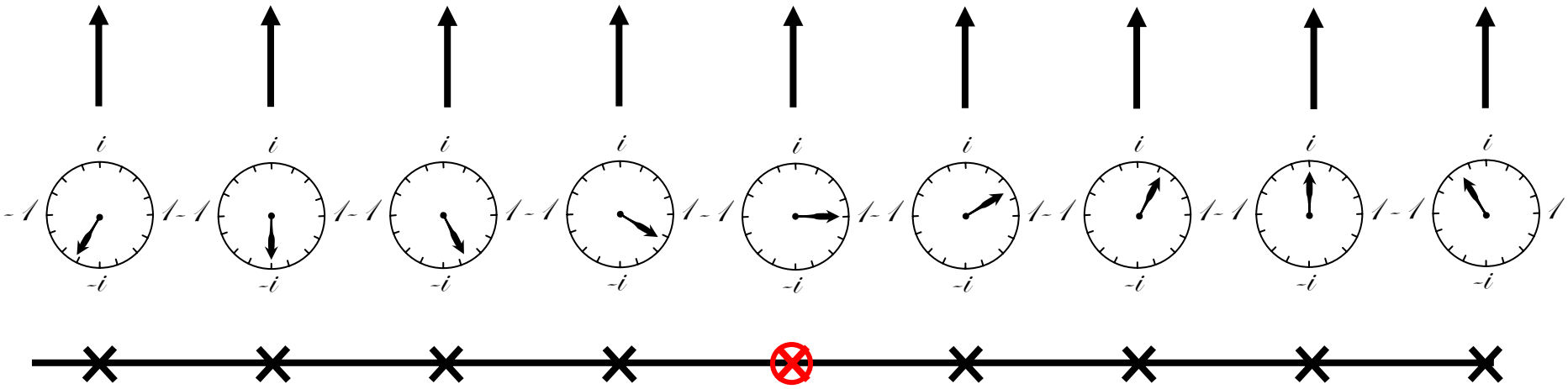
Fourier Components (complex)

Space Group $P4=C_4^1$ $k=(0,0,\mu)$

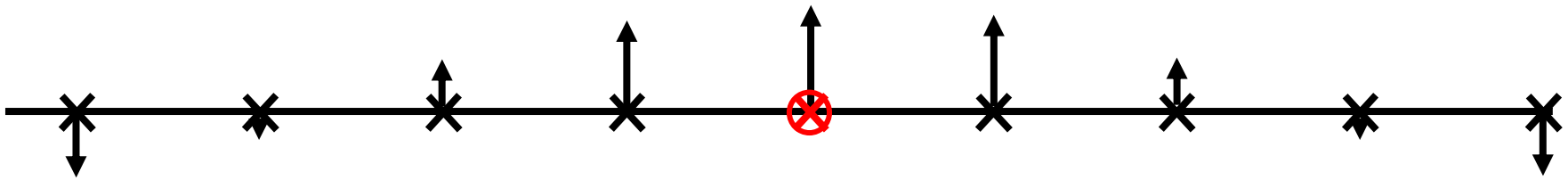


	1	180	-90	+90
Γ_1	1	1	1	1
Γ_2	1	-1	*i*	-*i*
Γ_3	1	1	-1	-1
Γ_4	1	-1	-*i*	*i*

The effect of the inversion operator *I*

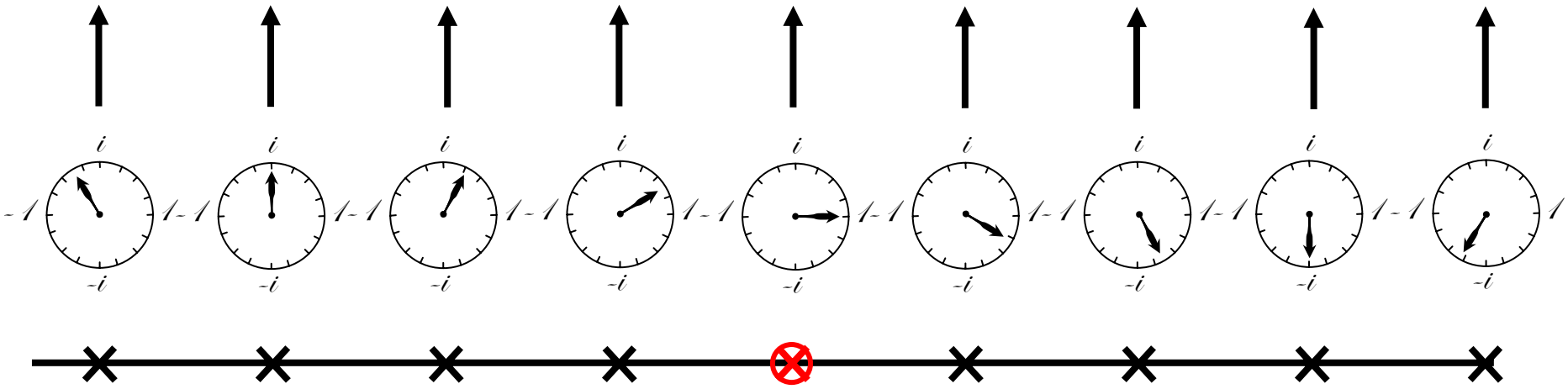


Fourier Components

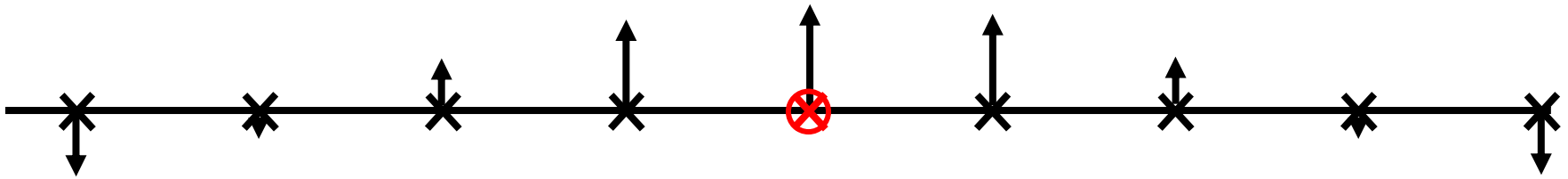


Magnetic Structure

The effect of the inversion operator *I*

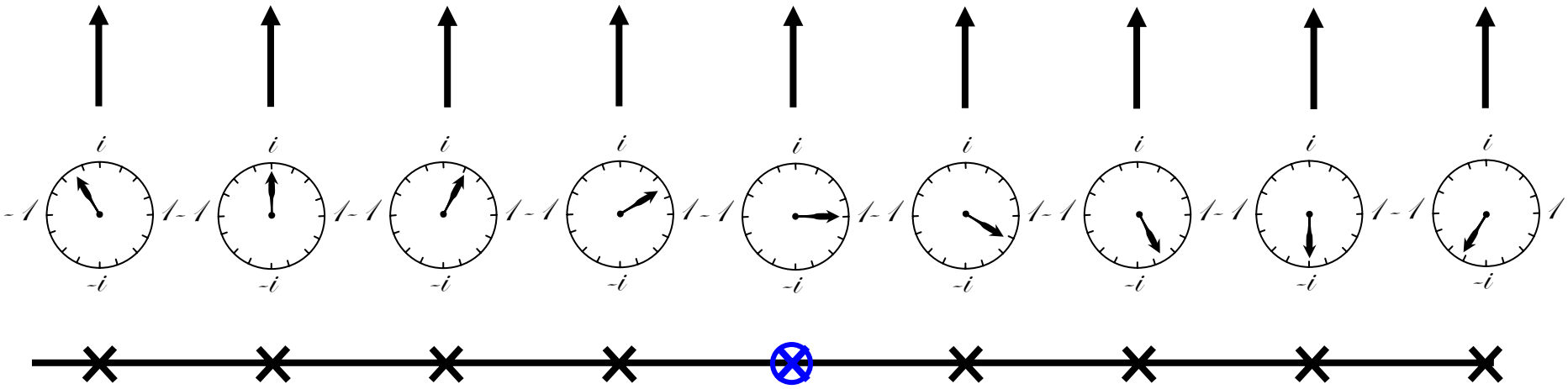


Fourier Components

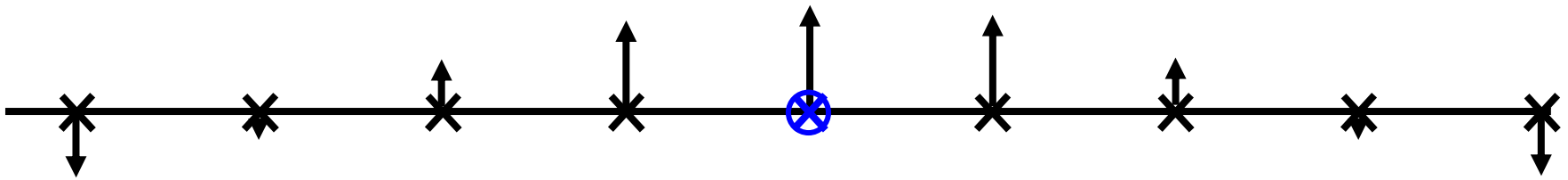


Magnetic Structure

The effect of the c.c.+inversion operator *KI*



Fourier Components

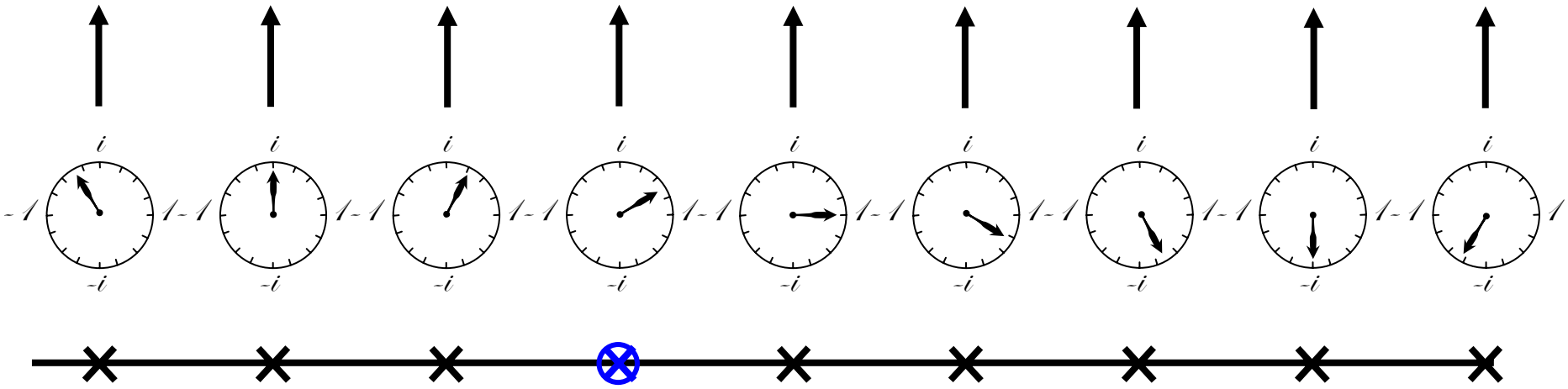


Magnetic Structure

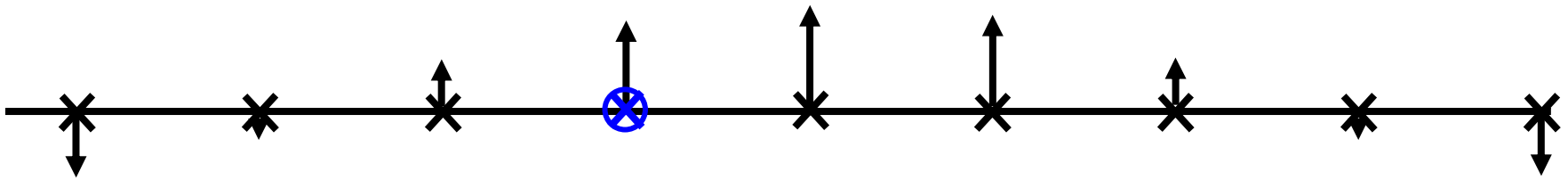
Co-representations and anti-symmetry

1. "Conventional" *irreps* discard a set of operators (e.g., the inversion *I* for *k* inside the Brillouin zone) that can still be symmetry operators for the *magnetic structure* (as opposed to its Fourier components).
2. Full symmetry properties of emerge only by combining normal SG operators with the complex conjugation operator *K* (e.g., *KI*).
3. Operators of the form *Kg* act as **anti-linear**, **anti-unitary** operators (cfr. Wigner). Their "corepresentation" theory has been extensively developed.

The effect of *KI* on a generic lattice point

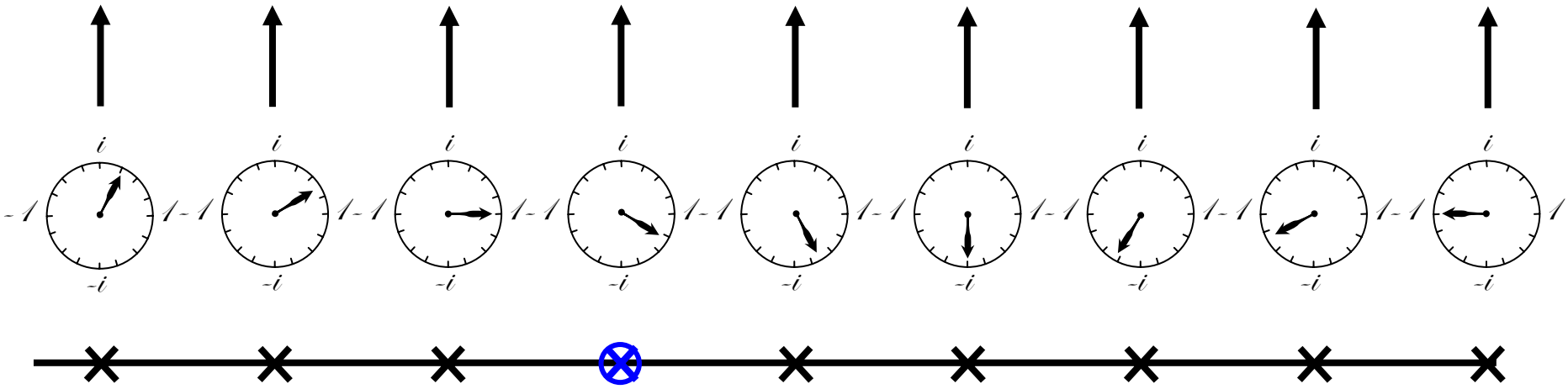


Fourier Components

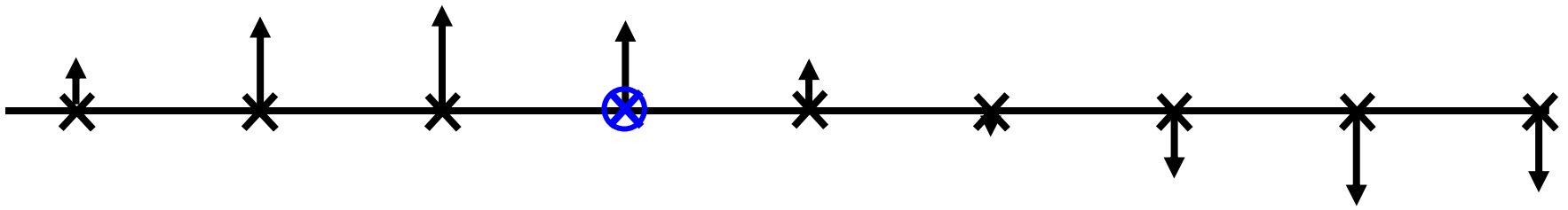


Magnetic Structure

The effect of *KI* on a generic lattice point

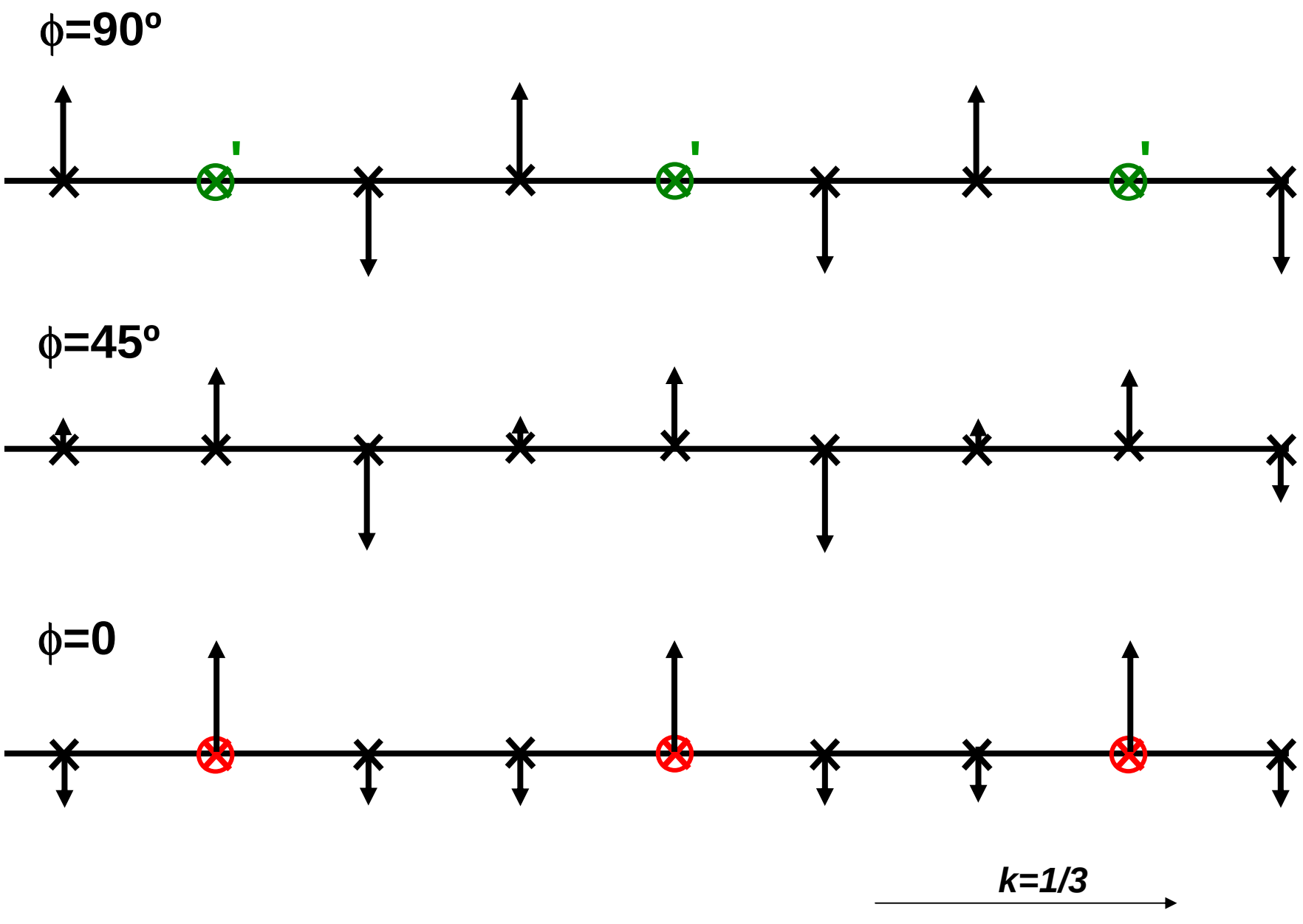


Fourier Components



Magnetic Structure

Importance of the overall phase



Magnetic control of ferroelectric polarization

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[1]*Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan*
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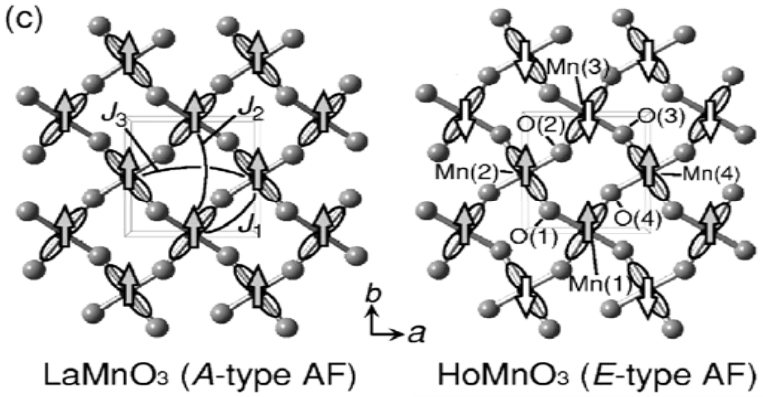
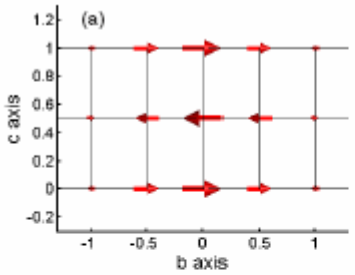
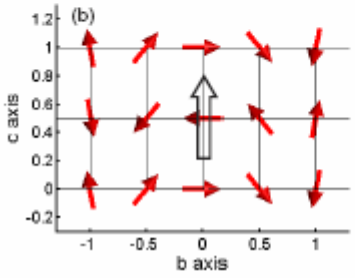
sinusoidal antiferromagnetic ordering. The modulated magnetic structure is accompanied by a magnetoelastically induced lattice modulation, and with the emergence of a spontaneous polarization. In the magnetic ferroelectric $TbMnO_3$, we found gigantic magnetoelectric and magnetocapacitance effects, which can be attributed to switching of the electric polarization induced by magnetic fields. Frustrated spin systems therefore provide a new area to search for magnetoelectric media.

The room-temperature crystal structure of $TbMnO_3$ investigated here is the orthorhombically c
group *Pbnm*; Fig. 1a). We pr

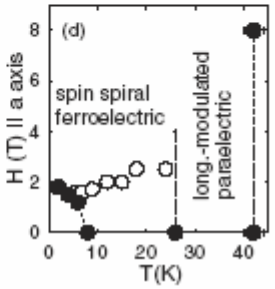


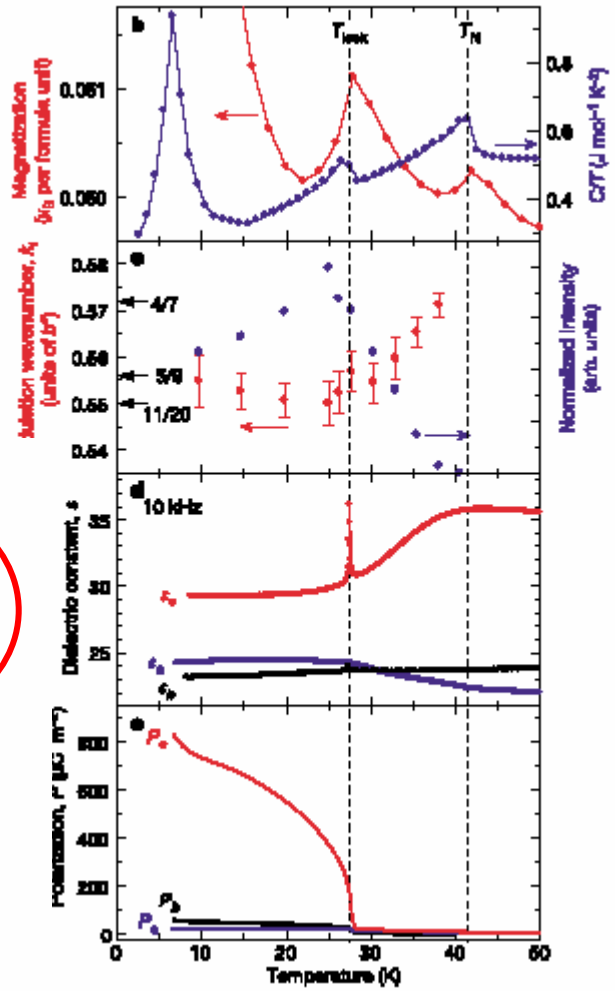




(c)

	1	2_y	m_{xy}	m_{yz}
Γ_1	1	1	1	1
Γ_2	1	1	-1	-1
Γ_3	1	-1	1	-1
Γ_4	1	-1	-1	1





Kenzelnamm *et al.*_PRL**95**_087206

$REMnO_3$ - *Pnma*, $k = (\mu,0,0)$

Cycloidals: $D_i + iD_j$

	1	2_x	m_{xz}	m_{xy}
	KI	Km_{yz}	$K2_y$	$K2_z$
Δ_1/D_1	1	ϵ	1	ϵ
Δ_2/D_2	1	ϵ	-1	$-\epsilon$
Δ_3/D_3	1	$-\epsilon$	1	$-\epsilon$
Δ_4/D_4	1	$-\epsilon$	-1	ϵ

$m2m \rightarrow \boldsymbol{P} \,/\!/\, y$

$REMnO_3$ - *Pnma*, $k = (\mu,0,0)$

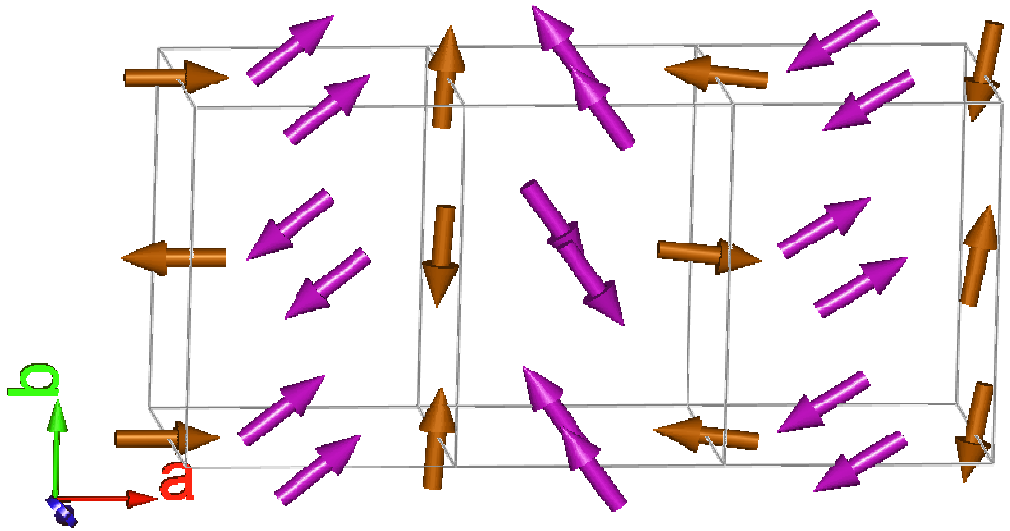
Cycloidals: $D_i + iD_j$

		1	2_x	m_{xz}	m_{xy}
		KI	Km_{yz}	$K2_y$	$K2_z$
Δ_1/D_1	A_x	1	ϵ	1	ϵ
Δ_2/D_2	A_y	1	ϵ	-1	$-\epsilon$
Δ_3/D_3	A_z	1	$-\epsilon$	1	$-\epsilon$
Δ_4/D_4	G_x	1	$-\epsilon$	-1	ϵ

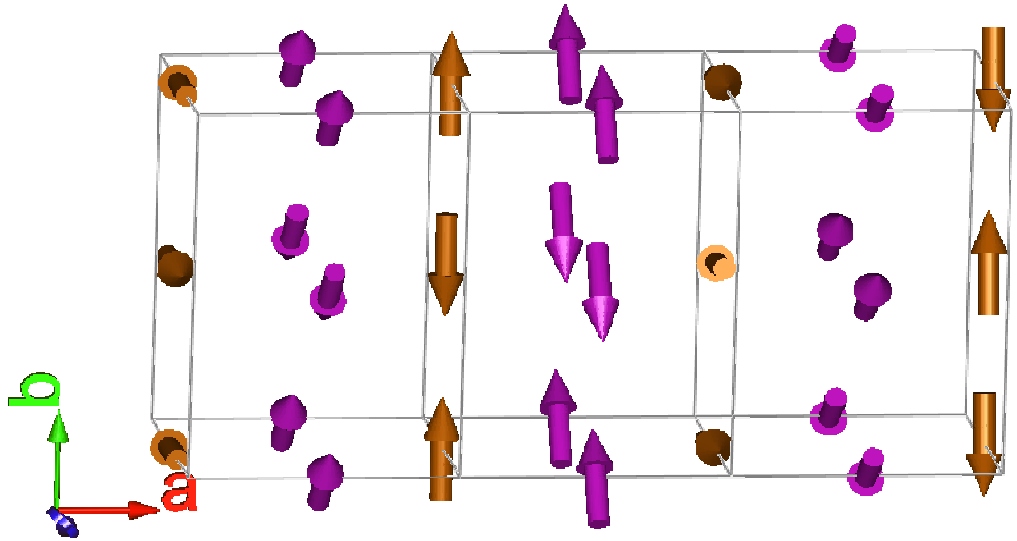
$222 \rightarrow \mathbf{P} = 0$

$REMnO_3$ - *Pnma*, $k = (\mu,0,0)$

	D_1	D_2	D_3	D_4
iD_1	$2mm(x)$	$222(.)$	$mm2(z)$	$m2m(y)$
iD_2	$222(.)$	$2mm(x)$	$m2m(y)$	$mm2(z)$
iD_3	$mm2(z)$	$m2m(y)$	$2mm(x)$	$222(.)$
iD_4	$m2m(y)$	$mm2(z)$	$222(.)$	$2mm(x)$

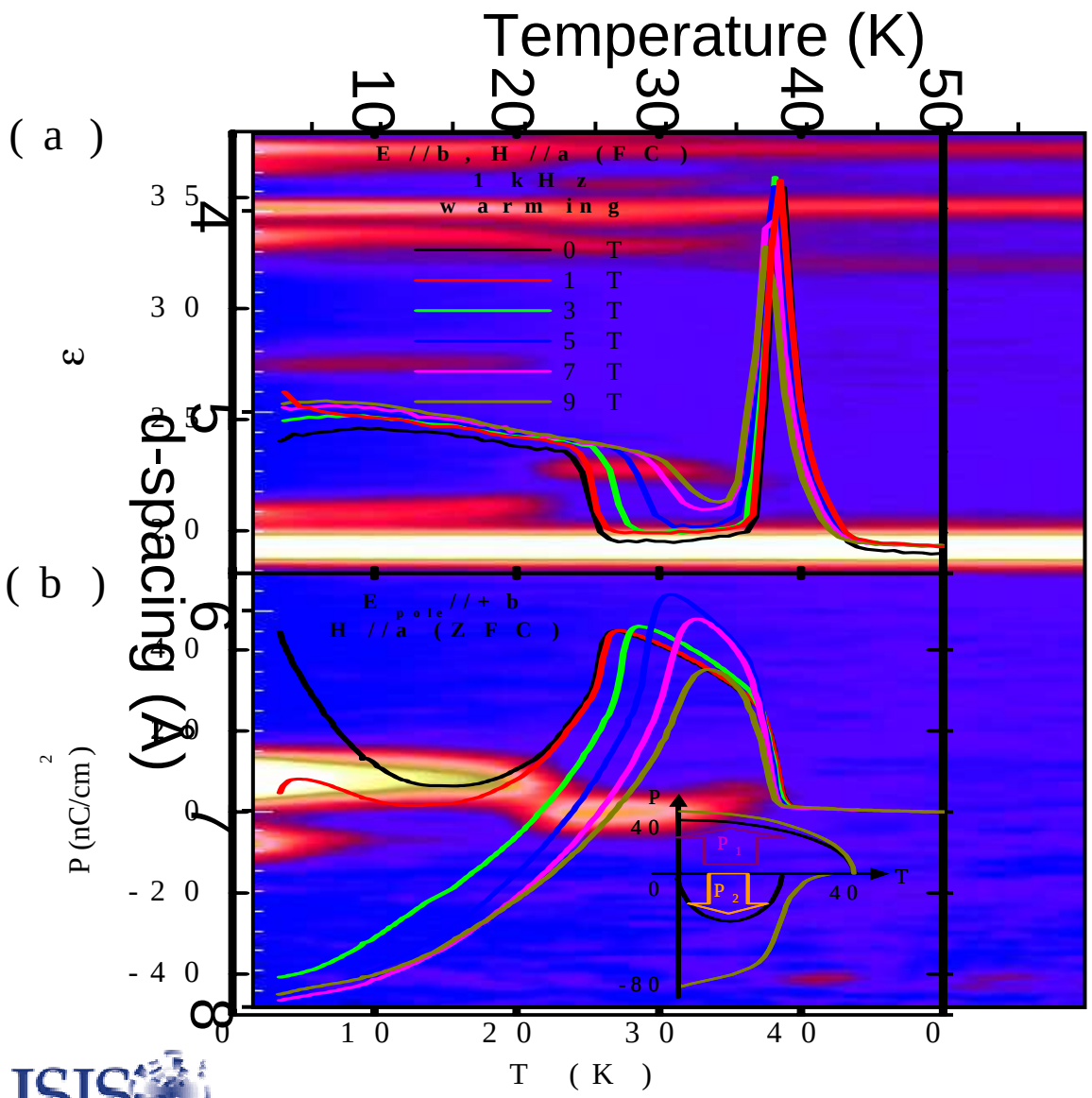


$m_x(D_3)+im_y(D_2)$

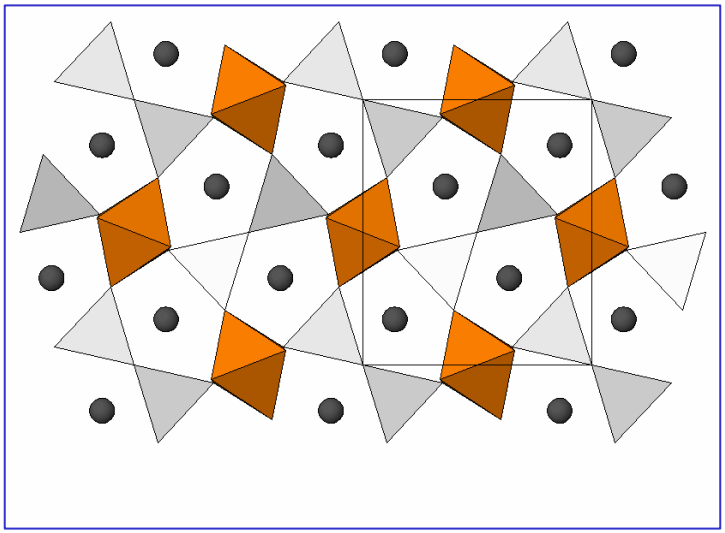


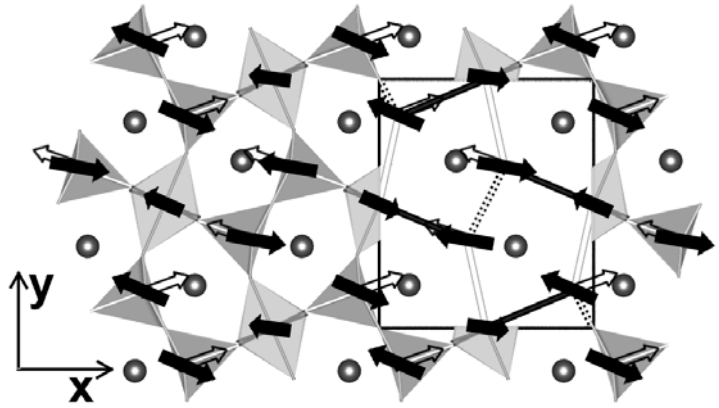
$m_z(D_3)+im_y(D_2)$

$TbMn_2O_5$



***ab*-plane**





$REMn_2O_5$ - Pbam, $k = (1/2,0,\mu)$

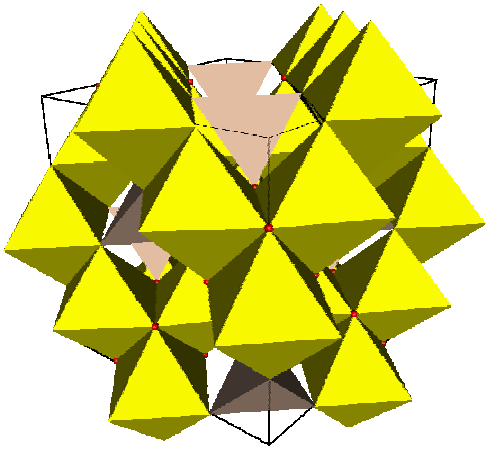
$m2m \rightarrow \mathbf{P} \,/\!/\, y$

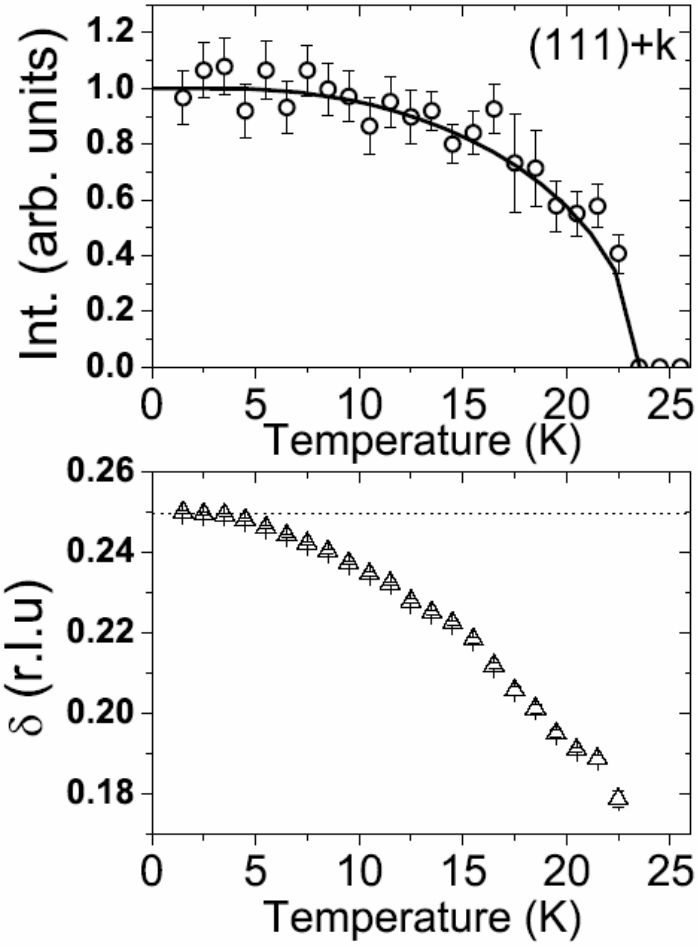
Coreps	1	2_z	m_{yz}	m_{xz}	KI	$K2_x$	$K2_y$	Km_z
D_1	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

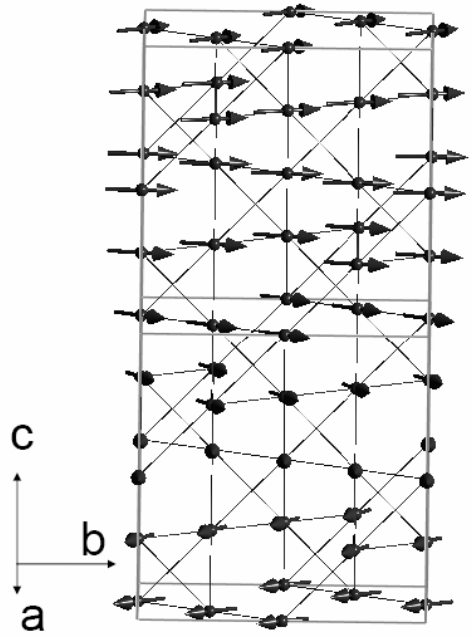
$$\psi_x(Mn^{4+}) = \gamma^*(m1_x + m1'_x) = \gamma^* [m1_x, m1'_x] \cdot \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

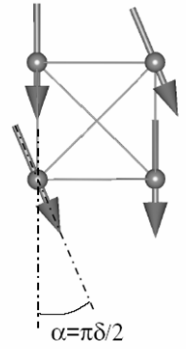
$$\psi_x(Mn^{3+}) = (m1_x + m1'_x) = [m1_x, m1'_x] \cdot \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$HgCr_2S_4$









ISIS

$HgCr_2S_4 - Fd\bar{3}m$, $k = (0,0,\mu)$

Coreps	1 / KI	2_z / Km_z	4_3 / $\bar{4}_3$	4_1 / $\bar{4}_1$	m_{yz} / $K2_x$	m_{xz} / $K2_y$	m_{d3} / $K2_{-11}$	m_{d4} / $K2_{11}$
$\tilde{\Gamma}_5$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} i\epsilon & 0 \\ 0 & -i\epsilon \end{pmatrix}$	$\begin{pmatrix} -i\epsilon & 0 \\ 0 & i\epsilon \end{pmatrix}$	$\begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\epsilon \\ -\epsilon & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$
	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i\epsilon* \\ -i\epsilon* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i\epsilon* \\ i\epsilon* & 0 \end{pmatrix}$	$\begin{pmatrix} \epsilon* & 0 \\ 0 & \epsilon* \end{pmatrix}$	$\begin{pmatrix} -\epsilon* & 0 \\ 0 & -\epsilon* \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$

$$\psi = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$422 \rightarrow \mathbf{P} = 0$$

Magnetic Symmetry - Shubnikov Groups

Paolo G. Radaelli

Objectives of this module

- To learn the relevance of time reversal for magnetic structures.
- To learn how PG and SG operators act on spins.
- To learn how magnetic groups can be constructed from subgroups of index 2.
- To learn how to find those on the International Tables for PG and SG.
- To learn about magnetic lattices.
- To be able to construct invariant spin arrangements for magnetic SG, with specific examples.
- To learn the relation between Shubnikov groups and representations.

Reference: W. Opechowski and R. Guccione, "Magnetic Symmetry", in *Magnetism*, Vol II part A, ed. By G.T. Rado and H. Suhl. Academic Press (New York and London), 1965, pp 105-165.

Notation-1

Element of Space group $\{F\}$: $F=(R|\boldsymbol{\tau}(R)+\mathbf{t})$,
where R is a proper or improper rotation, $\mathbf{t}$ is a primitive translation and $\boldsymbol{\tau}(R)$ is a non-primitive translation.

$\{R\}$ is the *point group* associated with $\{F\}$. If $\{(R|0)\}$ is a subgroup of $\{F\}$, then $\{F\}$ is called *symmorphic*.

Given a position $\boldsymbol{r}$ on the lattice, the subgroup $\{F(\boldsymbol{r})\}$ for which $(R|\boldsymbol{\tau}(R)+\mathbf{t})\,\boldsymbol{r} = \mathbf{t'}+\boldsymbol{r}$ is called *site space group*, and its point group $\{R(\boldsymbol{r})\}$.

We shall call $\{A\}=\{E, E'\}$ the 2-elements group of the *time identity* (E) and *time inversion* (E'). Because crystal structures are static, $\{F\}\otimes\{A\}$ is also a symmetry group of the crystal.

Notation-2

However, if we add spins (i.e., magnetic moments) to some of the atoms, time reversal will *switch* the direction of the spins. So $\{F\}\otimes\{A\}$ cannot be a symmetry group of the magnetic structure, and the magnetic symmetry group, $\{M\}$, *must* be a subgroup of $\{F\}\otimes\{A\}$. In particular, $(I|E')$ cannot belong to it.

Forward time Backward time

Purpose of the study of magnetic symmetry is to generate systematically *all* the magnetic groups associated with a particular space group of the crystal structure.

Caveat

Magnetic space groups, also known as *Shubnikov* groups, are perhaps the most elegant description of magnetic structures. However, in the presence of magnetic ordering, the crystallographic space group is often *not known* a priori, because the symmetry subtly is lowered by magnetic ordering itself. One has therefore to lower the symmetry in a systematic way, which is the purpose of representation theory. The study of Shubnikov groups with therefore serve as an introduction to the more general methods to be described in the remainder of the workshop.

‘Coloured’ groups

We have just seen that the magnetic space group $\{M\}$ *must* be a subgroup of $\{F\}\otimes\{A\}$, and cannot contain $(I|\mathrm{E}')$. However, it can contain elements of the form $(F|\mathrm{E}')$, which will be called *primed* (F'). If *it does not*, it is called a *trivial* (or *colourless)* group. Trivial groups *can* describe magnetic structures. Groups of the type $\{F\}\otimes\{A\}$ are called *gray* or *paramagnetic* groups. All non-trivial subgroups of $\{F\}\otimes\{A\}$ are called *black and white* groups.

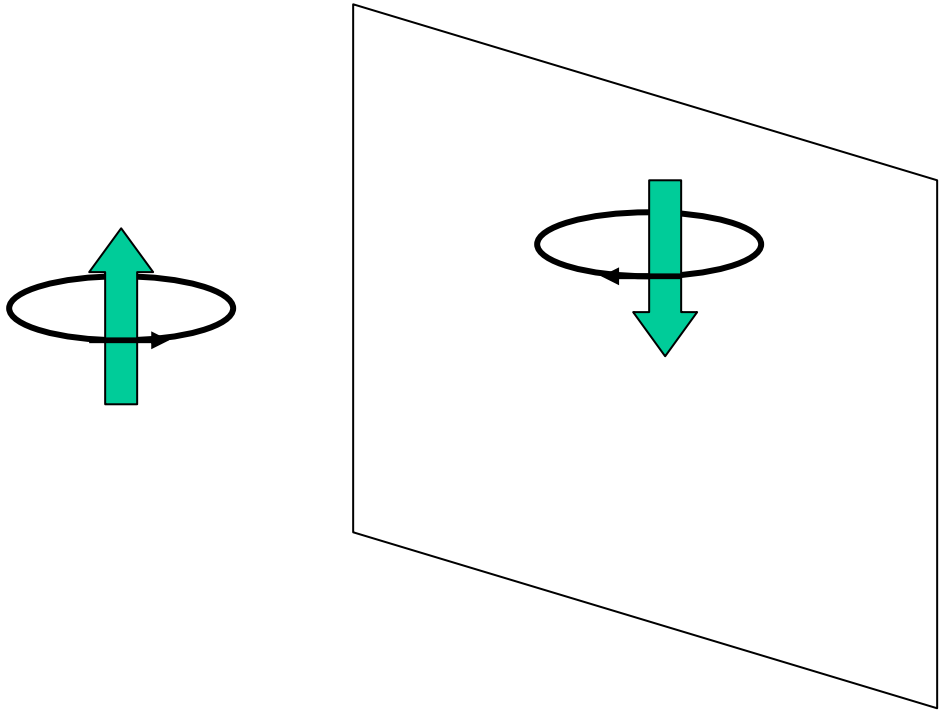
The original concepts and terminology were developed by Heesch (1930) and later by Belov and by Zamorzaev (~1955, including a complete list of the magnetic SG). The original aim was purely mathematical or crystallographic (study of coloured patterns on lattices, with *A* being colour inversion). The application to magnetism is due to Landau & Lifshitz (1958). These concept can be extended to *multicoloured* SG, which are also of some interest for magnetism. Aleksei Vasil'evich Shubnikov was the founder and first director of IC-RAS.

Colour vs. Spin

The analogy between colour and spin can be made by replacing the meaning of E' from *time reversal* to *colour change*. However, colour and spin differ fundamentally in the way the regular *space group* operators act upon them. Colours are *scalars*, whereas spins are *axial vectors*.

It is important to remember that **an axial vector is left invariant by centering**. Therefore, *proper* rotations act on spins in the same way as on normal (*polar*) vectors, whereas for *mirror operations and centering* there is an additional *spin flip*.

On top of this, *priming* any operator will entail and additional *spin flip*.



	m_x	2_z, 3_z, 4_z, 6_z	$\bar{1}$	1
Unprimed	Flip $s_y s_z$	Rotate s_x, s_y	No effect	No effect
Primed	Flip s_x	Rotate s_x, s_y Flip s_x, s_y, s_z	Flip s_x, s_y, s_z	Does not occur

Constructive theorem

We will give here the 'fundamental lemma' to construct magnetic groups. It will apply equally well to SG, PG or lattices. Let $\{G\}$ be a crystallographic group, $\{M\}$ a derived magnetic group (subgroup of $\{G\}\otimes\{A\}$) and $\{G_M\}$ the group of the elements of $\{G\}$ that are *unprimed* in $\{M\}$. It can be easily shown that

$$\{G\}= \{G_M\} + p\ \{G_M\}$$

where p *does* not belong to $\{G_M\}$, which is therefore a *subgroup of index 2* in $\{G\}$.

This simply has to do with the fact that the product of 2 primed elements must be unprimed.

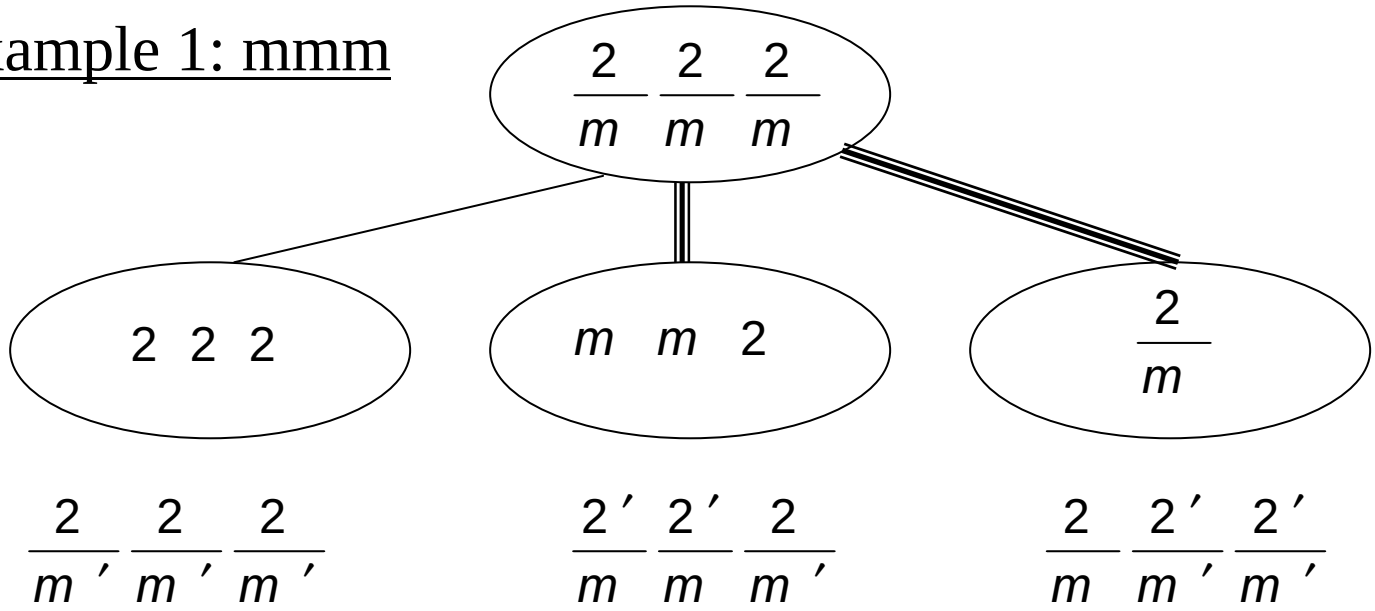
Follows $\{M\}= \{(G_M|E)\} + p\ \{(G_M|E')\}$

So, the problem of finding *all* magnetic groups arising from a crystallographic group $\{G\}$ is reduced to that of finding all subgroups of index 2 of $\{G\}$.

Example: magnetic point groups

To apply this rule to magnetic point groups, one needs to look no further that page 781 of the International Tables (copied overleaf). Subgroups of index 2 are those that have exactly half the number of elements of the original group. Elements of the subgroup will be *unprimed*, all the remaining elements being *primed*.

Example 1: mmm



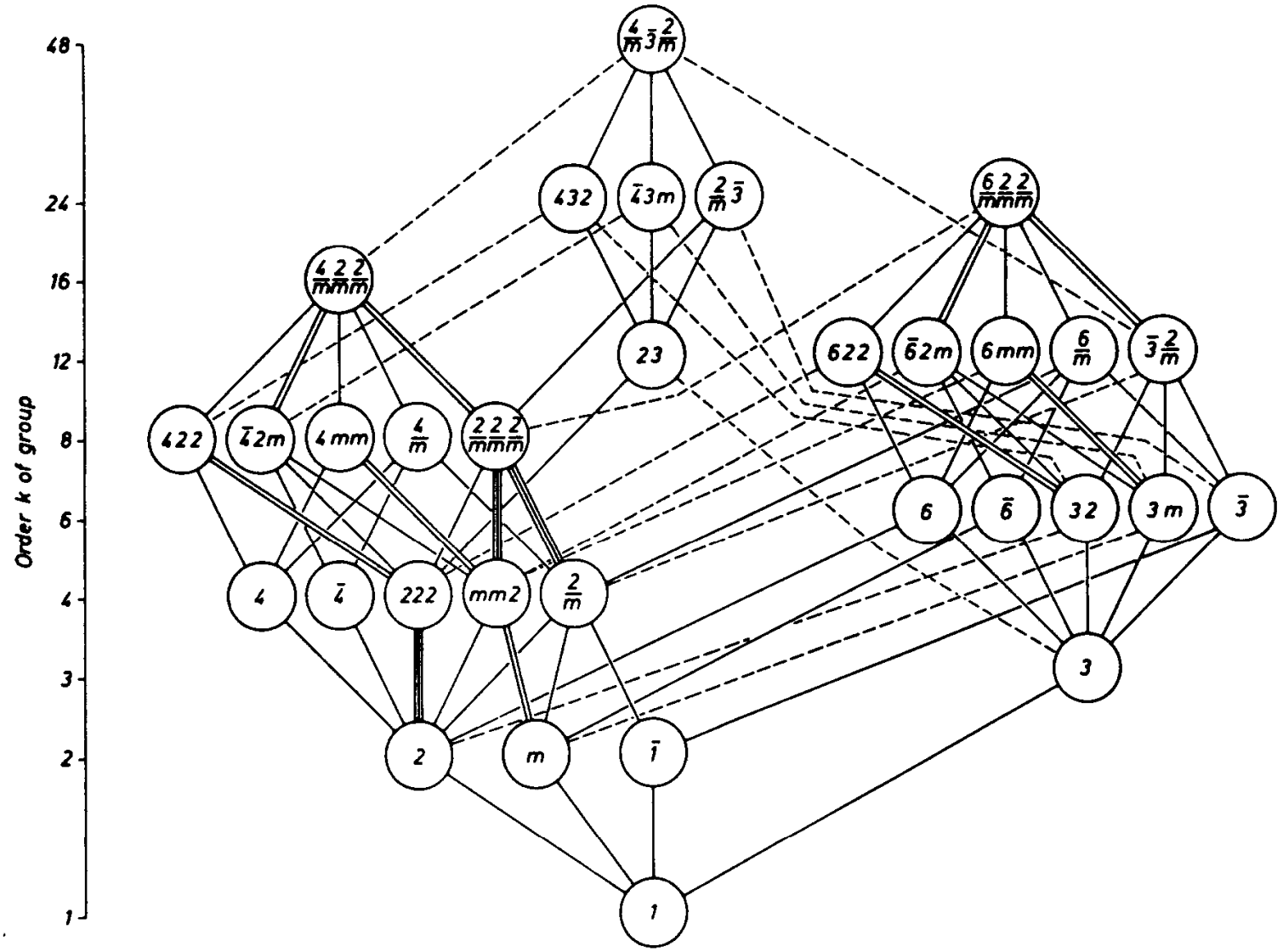
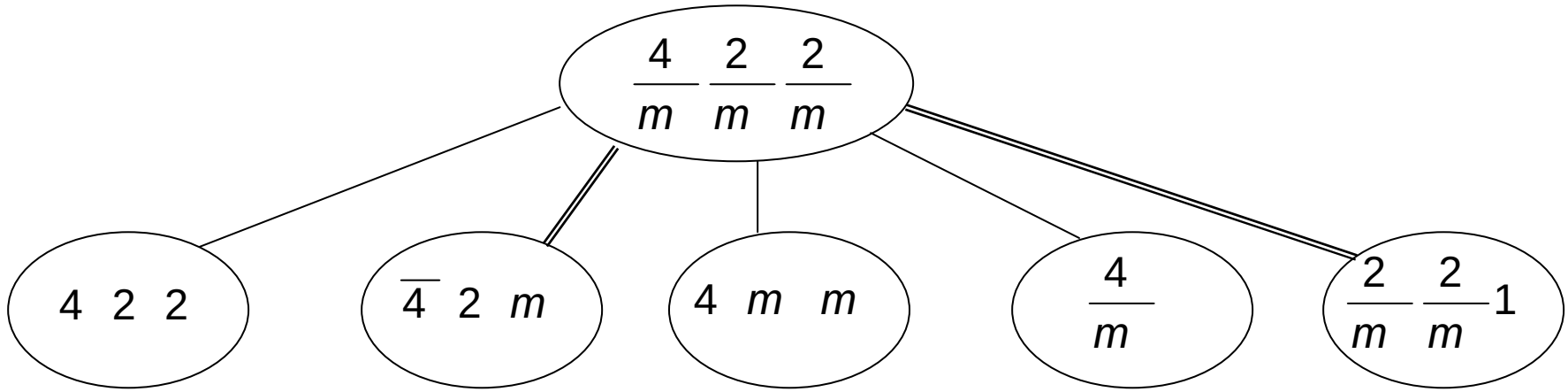


Fig. 10.3.2. Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. Solid lines indicate maximal normal subgroups; double or triple solid lines mean that there are two or three maximal normal subgroups with the same symbol. Dashed lines refer to sets of maximal conjugate subgroups. The group orders are given on the left. Full Hermann–Mauguin symbols are used.

Example 2: 4/m m m



4/m′ 2/m′ 2/m′ 4′/m′ 2/m′ 2′/m 4/m′ 2′/m 2′/m 4/m 2′/m′ 2′/m′ 4'/m 2/m 2′/m′

Admissible magnetic point groups

A point group is called *admissible* if all its operators leave *at least one* spin component invariant. Admissible MPG are marked with an asterisk in OG, Table I.

As we shall see,admissible point groups (AMPG) have two very important applications.

- The site symmetry of a magnetic atom *must be* a AMPG.
- A *Ferromagnetic* MSP *must have* a AMPG as its MPG.

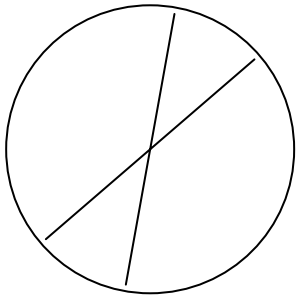
The second is a *necessary but not sufficient* condition for the MSP to support FM. The other condition is that its lattice is a trivial magnetic lattice (see below).

TABLE I

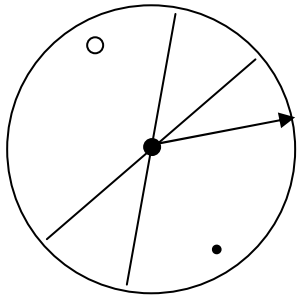
List of the Magnetic Point Groups

*1					
*$\bar{1}$	$\bar{1}'$				
*2	*2′				
*m	*m'				
*2/m	2′/m	2/m'	*2′/m'		
222	*2′2′2				
$mm2$	*$m'm2'$	*$m'm'2$			
mmm	$m'mm$	*$m'm'm$	$m'm'm'$		
*4	4′				
*$\bar{4}$	$\bar{4}'$				
*4/m	4′/m	4/m'	4′/m'		
422	4′22′	*42′2′			
4mm	4′$m'm$	*4$m'm'$			
$\bar{4}2m$	$\bar{4}'2'm$	$\bar{4}'2m'$	*$\bar{4}2'm'$		
4/mmm	4/$m'mm$	4′/$mm'm$	4′/$m'm'm$	*4/$mm'm'$	4/$m'm'm'$
*3					
*$\bar{3}$	$\bar{3}'$				
32	*32′				
3m	*3m'				
$\bar{3}m$	$\bar{3}'m$	$\bar{3}'m'$	*$\bar{3}m'$		
*6	6′				
*$\bar{6}$	$\bar{6}'$				
*6/m	6′/m	6/m'	6′/m'		
622	6′2′2	*62′2′			
6mm	6′$m'm$	*6$m'm'$			
$\bar{6}m2$	$\bar{6}'m'2$	$\bar{6}'m2'$	*$\bar{6}m'2'$		
6/mmm	6/$m'mm$	6′/$mm'm$	6′/$m'm'm$	*6/$mm'm'$	6/$m'm'm'$
23					
$m3$	$m'3$				
432	4′32′				
$\bar{4}3m$	$\bar{4}'3m'$				
$m3m$	$m'3m$	$m3m'$	$m'3m'$		

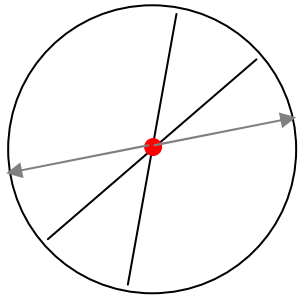
Examples of admissible PG



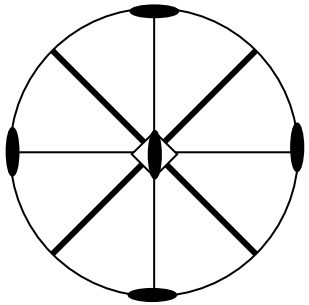
1^{*}



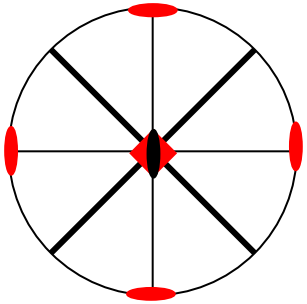
$\bar{1}^{*}$ (any direction)



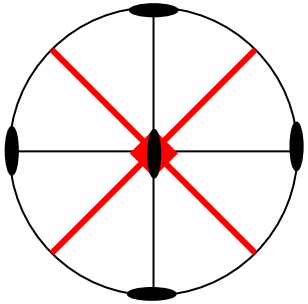
$\bar{1}'$



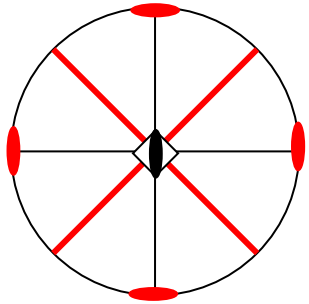
$\bar{4}2m$



$\bar{4}'2'm$



$\bar{4}'2m'$



$\bar{4}2'm'^{*}$

Spin along z

Things to remark about the $\bar{4}2m$ example

- Spin must be parallel to the 4-fold axis (*always* true except for 2-fold axes).
- $\bar{4}$ *must be black*. In fact, for spins, $\bar{4} = 4$
- If a spin is in a plane, that plane *must be red*.
- If a spin is perpendicular to a 2-fold axis, that axis *must be red.*
- Note that the central 2-fold axis of $\bar{4}'$ or *4' is always black*. This is because the product of two primed 45-degree rotations is an unprimed 90-degree rotation.

TABLE IV

LIST OF THE ADMISSIBLE MAGNETIC POINT GROUPS

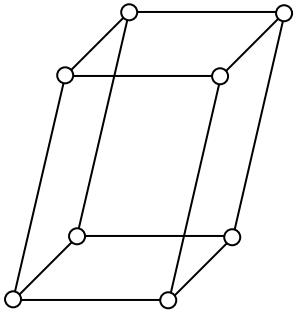
Magnetic point groups	Admissible spin directions
	$n_1 = 3$
$1 \quad \bar{1}$	Any direction
	$n_1 = 2$
$2' \quad 2'/m' \quad m'm2'$	Perpendicular to the axis
m'	Any direction in the plane
	$n_1 = 1$
m	Perpendicular to the plane
$m'm'm$	Perpendicular to the unprimed plane
$2'2'2$	Along the unprimed axis
$2 \quad 2/m \quad m'm'2$	Along the axis
$4 \quad \bar{4} \quad 4/m \quad 42'2'$	Along the axis of higher order
$4m'm' \quad \bar{4}2'm' \quad 4/mm'm'$	Along the axis of higher order
$3 \quad \bar{3} \quad 32' \quad 3m' \quad \bar{3}m'$	Along the axis of higher order
$6 \quad \bar{6} \quad 6/m \quad 62'2'$	Along the axis of higher order
$6m'm' \quad \bar{6}m'2' \quad 6/mm'm'$	Along the axis of higher order

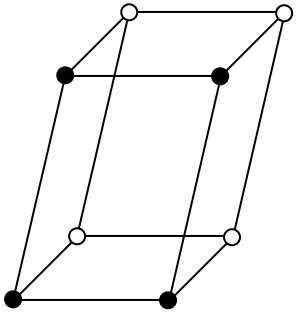
Magnetic Bravais Lattices

The constructive theorem we have used to generate the magnetic point groups , based on the identification of subgroups of index 2, can be applied to generate magnetic lattices $\{T_M\}$ from Bravais lattices $\{T\}$.

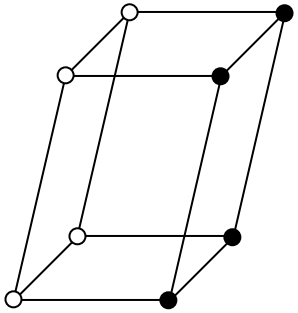
In general, a group of lattice translations generated by a set of primitive vectors $\boldsymbol{a_1}$, $\boldsymbol{a_2}$, $\boldsymbol{a_3}$ has exactly *seven* subgroups of index 2. However, they do not always generate independent MBL, as some of them can be equivalent by interchange of the axes. Also, we are only interested in MBL that *belong to the same holoedry* of the original BL.

In fact, as we shall see in the remainder, MSG either share the *same lattice* with the original SG (trivial ML) or the same *point group* (and therefore, necessarily, the same holoedry).

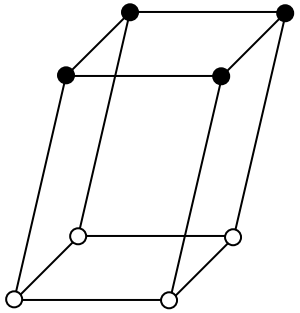




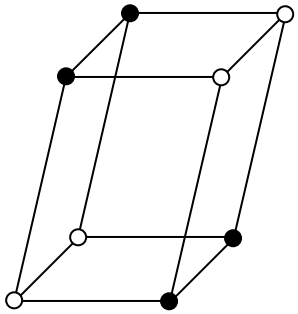
2a, b, c



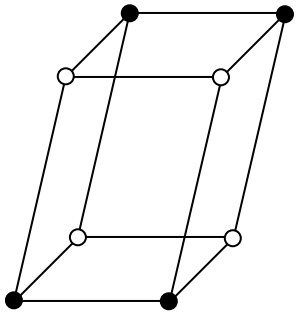
a, 2b, c



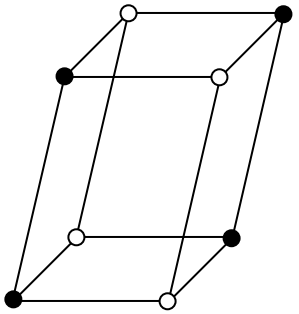
a, b, 2c



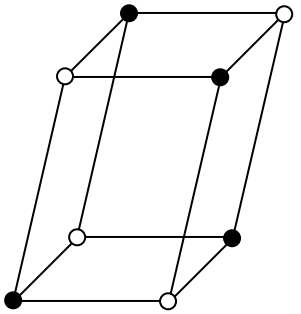
a, b+c, 2c



2a, b, a+c



2a, a+b, c



2a, a+b, a+c

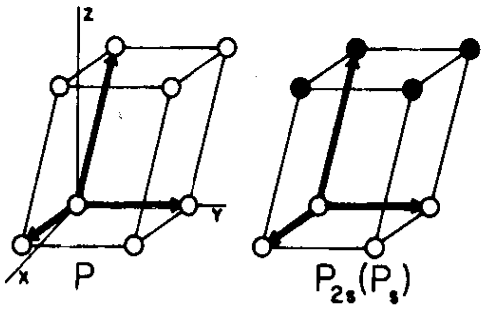


FIG. 1. Magnetic lattices of the triclinic system.

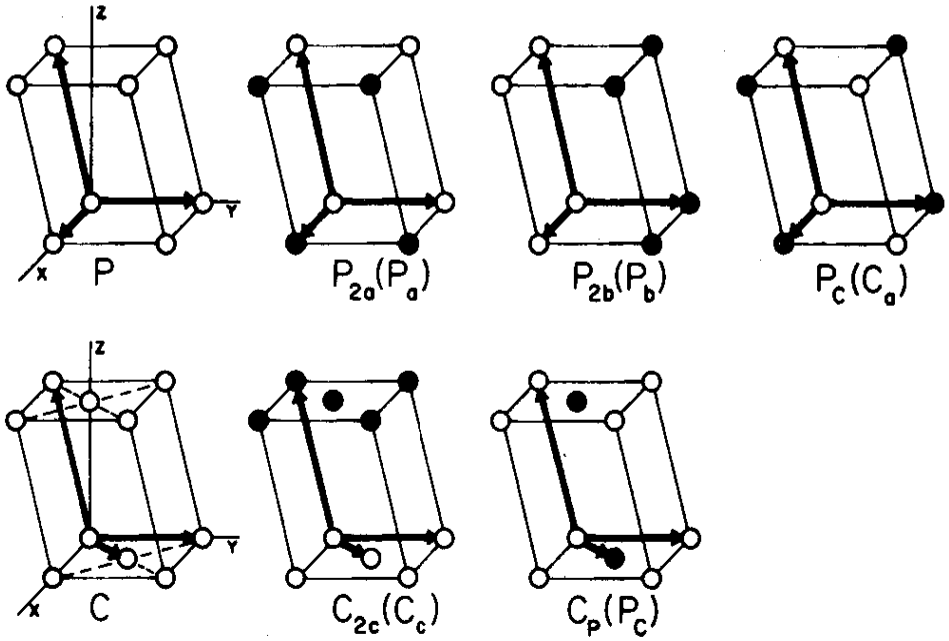


FIG. 2. Magnetic lattices of the monoclinic system (the twofold axis has been chosen as the y-axis).

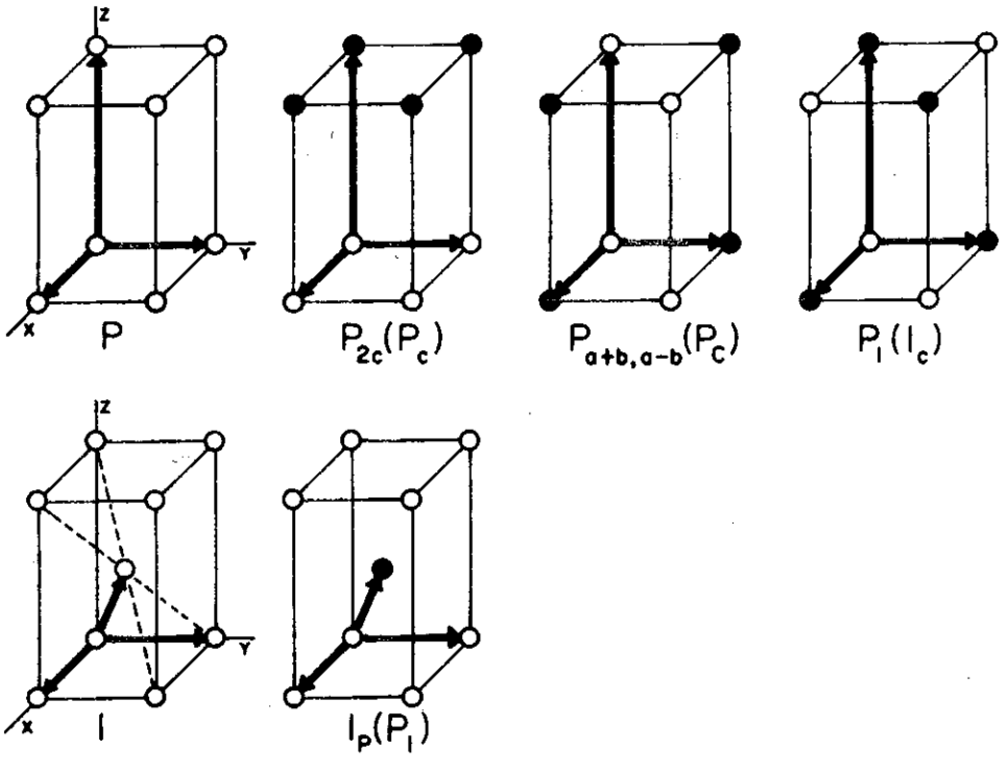


FIG. 4. Magnetic lattices of the tetragonal system.

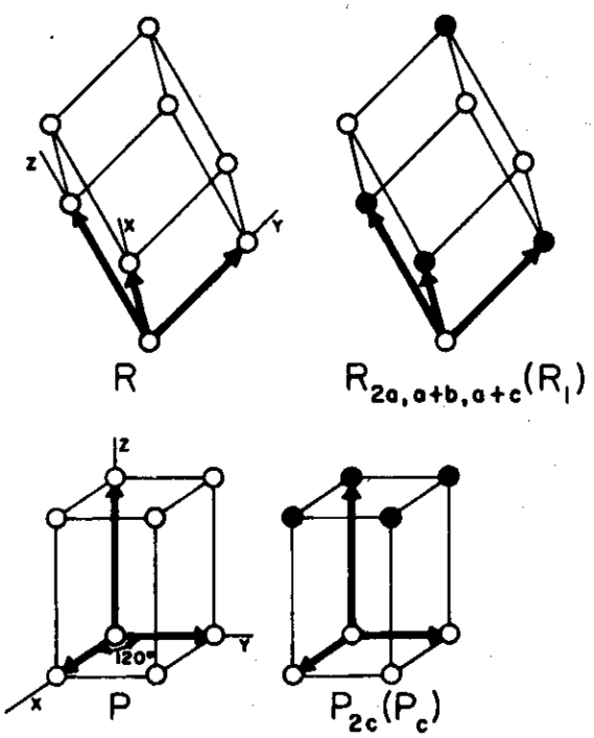


FIG. 5. Magnetic lattices of the trigonal and hexagonal systems.

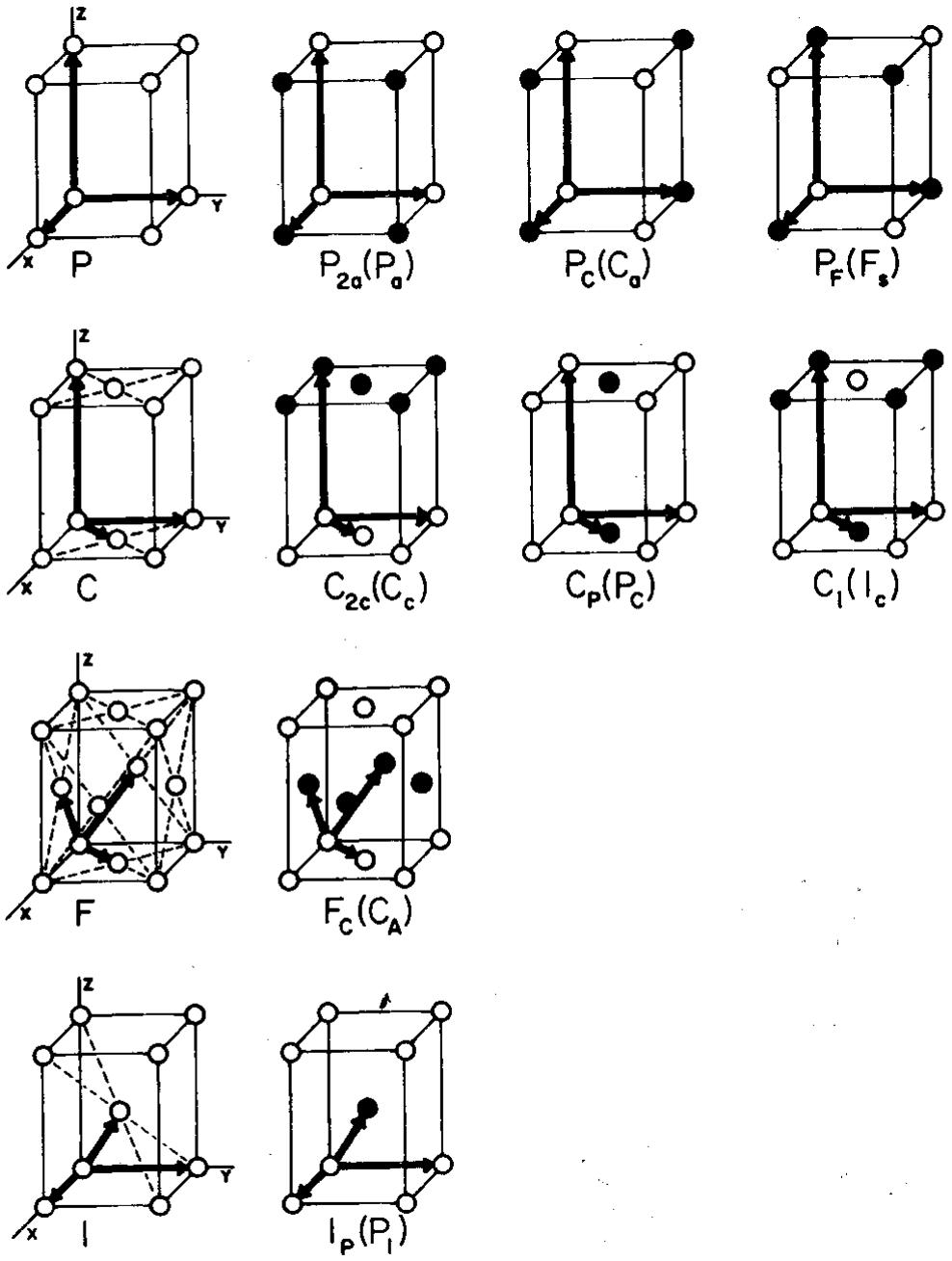


FIG. 3. Magnetic lattices of the orthorhombic system.

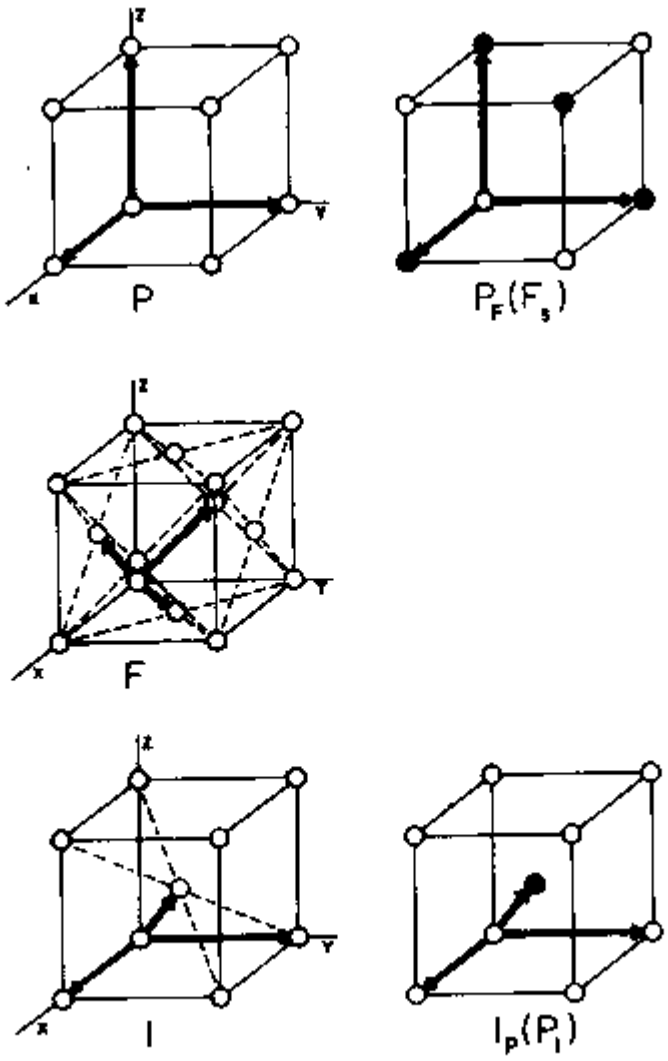


FIG. 6. Magnetic lattices of the cubic system.

Magnetic Space Groups

Once again, the constructive theorem, based on the identification of subgroups of index 2, can be applied to generate magnetic lattices $\{F_M\}$ from space groups $\{F\}$.

The method to generate all the MSG systematically is explained in OG. We will limit ourselves to use the International Tables volume A. In there, for each SG, there is a list of *minimal non-isomorphic subgroups* (Types I, IIa and IIb), and *minimal isomorphic subgroups of lowest index* (Type IIc). The index is indicated in brackets (e.g., [2]).

Therefore, each subgroup listed as [2] will generate a non-trivial magnetic space group. There are 1421 of them in total, 1191 of which are non-trivial. All SG except F23 and $P2_13$ generate at least 1 non-trivial MSG.

Rules to construct Magnetic Space Groups

1. Identify the subgroups of type I. They share the same lattice (trivial MBL) but have different PG, so they correspond to all the subgroups of index [2] of the associated PG (with multiplicity). For these, it is sufficient to prime the generators that correspond to missing operators.
2. Identify all the other subgroups of index 2 (IIa, IIb and IIc, no distinction). Then
   - Identify the MBL based on the supercell, and write its symbol.
   - For the Belov symbol (right column in OG), one simply need to complete the H-M symbol with that of the subgroup.
   - For the OG symbol, the modified operators with respect to the original symbol will be primed (e.g. m->n=m')

TABLE III

LIST OF MAGNETIC SPACE GROUPS[a]

Triclinic system

1

*$P1$

$P_{2a}1$ P_a1

$\bar{1}$

*$P\bar{1}$

$P\bar{1}'$

$P_{2a}\bar{1}$ $P_a\bar{1}$

Monoclinic system

2

*$P2$

*$P2'$

$P_{2a}2$ P_a2

$P_{2b}2$ P_b2

P_C2 C_a2

$P_{2b}2'$ P_b2_1

*$P2_1$

*$P2_1'$

$P_{2a}2_1$ P_a2_1

*$C2$

*$C2'$

$C_{2c}2$ C_c2

C_P2 P_C2

C_P2' P_C2_1

m

*Pm

*Pm'

$P_{2a}m$ P_am

$P_{2b}m$ P_bm

P_Cm C_am

$P_{2c}m'$ P_cc

*Pc

*Pc'

$P_{2a}c$ P_ac

$P_{2b}c$ P_bc

P_Cc C_ac

*Cm

*Cm'

$C_{2c}m$ C_cm

C_Pm P_Cm

$C_{2c}m'$ C_cc

C_Pm' P_Ac

*Cc

*Cc'

C_Pc P_Cc

$2/m$

*$P2/m$

$P2'/m$

$P2/m'$

*$P2'/m'$

$P_{2a}2/m$ P_a2/m

$P_{2b}2/m$ P_b2/m

P_C2/m C_a2/m

$P_{2b}2'/m$ P_b2_1/m

$P_{2c}2/m'$ P_c2/c

*$P2_1/m$

$P2_1'/m$

$P2_1/m'$

*$P2_1'/m'$

$P_{2a}2_1/m$ P_a2_1/m

$P_{2c}2_1/m'$ P_c2_1/c

*$C2/m$

$C2'/m$

$C2/m'$

*$C2'/m'$

$C_{2c}2/m$ C_c2/m

C_P2/m P_C2/m

$C_{2c}2/m'$ C_c2/c

C_P2'/m P_C2_1/m

C_P2/m' P_A2/c

C_P2'/m' P_A2_1/c

*$P2/c$

$P2'/c$

$P2/c'$

*$P2'/c'$

$P_{2a}2/c$ P_a2/c

$P_{2b}2/c$ P_b2/c

P_C2/c C_a2/c

$P_{2b}2'/c$ P_b2_1/c

*$P2_1/c$

$P2_1'/c$

$P2_1/c'$

*$P2_1'/c'$

$P_{2a}2_1/c$ P_a2_1/c

*$C2/c$

$C2'/c$

$C2/c'$

[a] Every page of Table III should be read first from the top to the bottom of the left-hand double column, then from the top to the bottom of the middle double column, and finally from the top to the bottom of the right-hand double column.

TABLE III (*continued*)

Monoclinic system

*$C2/c$

*$C2'/c'$

C_P2/c P_C2/c

C_P2'/c P_C2_1/c

Orthorhombic system

222

$P222$

*$P2'2'2$

$P_{2a}222$ P_a222

P_C222 C_a222

P_F222 F_c222

$P_{2a}22'2'$ P_a222_1

$P222_1$

*$P2'2'2_1$

*$P22'2_1'$

$P_{2a}222_1$ P_a222_1

P_C222_1 C_a222_1

$P_{2a}2'2'2_1$ $P_a2_12_12$

$P2_12_12$

*$P2_1'2_1'2$

*$P2_12_1'2'$

$P_{2c}2_12_12$ $P_c2_12_12$

$P_{2c}2_12_1'2'$ $P_a2_12_12_1$

$P2_12_12_1$

*$P2_1'2_1'2_1$

$C222_1$

*$C2'2'2_1$

*$C22'2_1'$

C_P222_1 P_C222_1

$C_P2'2'2_1$ $P_C2_12_12_1$

$C_P22'2_1'$ $P_A2_12_12$

$C222$

*$C2'2'2$

*$C22'2'$

$C_{2c}222$ C_c222

C_P222 P_C222

C_I222 I_c222

$C_{2c}22'2'$ C_c222_1

$C_P2'2'2$ $P_C2_12_12$

$C_P22'2'$ P_A222_1

$C_I2'22'$ $I_c2_12_12_1$

$F222$

*$F2'2'2$

F_C222 C_A222

$F_C22'2'$ C_A222_1

$I222$

*$I2'2'2$

I_P222 P_I222

$I_P2'2'2$ $P_I2_12_12$

$I2_12_12_1$

*$I2_1'2_1'2_1$

$I_P2_12_12_1$ $P_I2_12_12_1$

$I_P2_1'2_1'2_1$ P_I222_1

$mm2$

$Pmm2$

*$Pm'm2'$

*$Pm'm'2$

$P_{2c}nm2$ P_cmm2

$P_{2a}mm2$ P_amm2

P_Cmm2 C_amm2

P_Amm2 A_cmm2

P_Fmm2 F_cmm2

$P_{2c}mm'2'$ P_cmc2_1

$P_{2c}m'm'2$ P_ccc2

$P_{2a}m'm'2$ P_ama2

$P_Am'm'2$ A_cbm2

$Pmc2_1$

*$Pm'c2_1'$

*$Pmc'2_1'$

*$Pm'c'2_1$

$P_{2a}mc2_1$ P_amc2_1

$P_{2b}mc2_1$ P_bmc2_1

P_Cmc2_1 C_amc2_1

$P_{2a}mc'2_1'$ P_amn2_1

$P_{2b}m'c'2_1$ P_cca2_1

$Pcc2$

*$Pc'c2'$

*$Pc'c'2$

$P_{2a}cc2$ P_acc2

P_Ccc2 C_acc2

$P_{2b}c'c2'$ P_bnc2

$Pma2$

*$Pm'a2'$

*$Pma'2'$

*$Pm'a'2$

$P_{2b}ma2$ P_bma2

$P_{2c}ma2$ P_cma2

P_Ama2 A_cma2

$P_{2b}m'a2'$ P_aba2

$P_{2c}m'a2'$ P_cca2_1

$P_{2c}ma'2'$ P_cmn2_1

$P_{2c}m'a'2$ P_cnc2

$P_Am'a'2$ A_cba2

$Pca2_1$

*$Pc'a2_1'$

*$Pca'2_1'$

TABLE III (*continued*)

Orthorhombic system

$Pca2_1$

$*Pc'a'2_1$
$P_{3b}ca2_1$ $P_{b}ca2_1$
$P_{2b}c'a'2_1$ $P_{b}na2_1$

$Pnc2$

$*Pn'c2'$
$*Pnc'2'$
$*Pn'c'2$
$P_{2a}nc2$ $P_{a}nc2$
$P_{2a}nc'2'$ $P_{a}nn2$

$Pmn2_1$

$*Pm'n2_1'$
$*Pmn'2_1'$
$*Pm'n'2_1$
$P_{2b}mn2_1$ $P_{b}mn2_1$
$P_{2b}m'n2_1'$ $P_{a}na2_1$

$Pba2$

$*Pb'a2'$
$*Pb'a'2$
$P_{2c}ba2$ $P_{c}ba2$
$P_{2c}b'a2'$ $P_{c}na2_1$
$P_{2c}b'a'2$ $P_{c}nn2$

$Pna2_1$

$*Pn'a2_1'$
$*Pna'2_1'$
$*Pn'a'2_1$

$Pnn2$

$*Pn'n2'$
$*Pn'n'2$
$P_{F}nn2$ $F_{d}d2$

$Cmm2$

$*Cm'm2'$
$*Cm'm'2$
$C_{2c}mm2$ $C_{c}mm2$
$C_{P}mm2$ $P_{C}mm2$
$C_{I}mm2$ $I_{c}mm2$
$C_{2c}m'm2'$ $C_{c}mc2_1$
$C_{2c}m'm'2$ $C_{c}cc2$
$C_{P}m'm2'$ $P_{C}ma2$
$C_{P}m'm'2$ $P_{C}ba2$
$C_{I}m'm2'$ $I_{c}ma2$
$C_{I}m'm'2$ $I_{c}ba2$

$Cmc2_1$

$*Cm'c2_1'$
$*Cmc'2_1'$
$*Cm'c'2_1$
$C_{P}mc2_1$ $P_{C}mc2_1$
$C_{P}m'c2_1'$ $P_{C}ca2_1$
$C_{P}mc'2_1'$ $P_{C}mn2_1$
$C_{P}m'c'2_1$ $P_{C}na2_1$

$Ccc2$

$*Cc'c2'$
$*Cc'c'2$
$C_{P}cc2$ $P_{C}cc2$
$C_{P}c'c2'$ $P_{C}nc2$
$C_{P}c'c'2$ $P_{C}nn2$

$Amm2$

$*Am'm2'$
$*Amm'2'$
$*Am'm'2$
$A_{2a}mm2$ $A_{a}mm2$
$A_{P}mm2$ $P_{A}mm2$
$A_{I}mm2$ $I_{a}mm2$
$A_{2a}mm'2'$ $A_{a}ma2$
$A_{P}m'm2'$ $P_{B}mn2_1$
$A_{P}mm'2'$ $P_{A}mc2_1$
$A_{P}m'm'2$ $P_{A}nc2$
$A_{I}m'm'2$ $I_{a}ma2$

$Abm2$

$*Ab'm2'$
$*Abm'2'$
$*Ab'm'2$
$A_{2a}bm2$ $A_{a}bm2$
$A_{P}bm2$ $P_{B}ma2$
$A_{I}bm2$ $B_{I}ma2$
$A_{2a}b'm'2$ $A_{a}ba2$
$A_{P}b'm2'$ $P_{B}mc2_1$
$A_{P}bm'2'$ $P_{B}ca2_1$
$A_{P}b'm'2$ $P_{A}cc2$
$A_{I}b'm'2$ $I_{a}ba2$

$Ama2$

$*Am'a2'$
$*Ama'2'$
$*Am'a'2$
$A_{P}ma2$ $P_{A}ma2$
$A_{P}m'a2'$ $P_{A}na2_1$
$A_{P}ma'2'$ $P_{A}mn2_1$
$A_{P}m'a'2$ $P_{A}nn2$

$Aba2$

$*Ab'a2'$
$*Aba'2'$
$*Ab'a'2$
$A_{P}ba2$ $P_{A}ba2$
$A_{P}b'a2'$ $P_{A}ca2_1$
$A_{P}ba'2'$ $P_{B}na2_1$
$A_{P}b'a'2$ $P_{B}nc2$

$Fmm2$

$*Fm'm2'$
$*Fm'm'2$

TABLE III (*continued*)

Orthorhombic system

Fmm2

F_Cmm2 C_Amm2
F_Amm2 A_Cmm2
$F_Cmm'2'$ C_Amc2_1
$F_Cm'm'2$ C_Acc2
$F_Am'm2'$ A_Cbm2
$F_Amm'2'$ A_Cma2
$F_Am'm'2$ A_Cba2

Fdd2

*$Fd'd2'$
*$Fdd'2$

Imm2

*$Im'm2'$
*$Im'm'2$
I_Pmm2 P_Imm2
$I_Pmm'2'$ P_Imn2_1
$I_Pm'm'2$ P_Inn2

Iba2

*$Ib'a2'$
*$Ib'a'2$
I_Pba2 P_Icc2
$I_Pba'2'$ P_Ica2_1
$I_Pb'a'2$ P_Iba2

Ima2

*$Im'a2'$
*$Ima'2'$
*$Im'a'2$
I_Pma2 P_Ima2
$I_Pm'a2'$ P_Ina2_1
$I_Pma'2'$ P_Imc2_1
$I_Pm'a'2$ P_Inc2

mmm

Pmmm

$Pm'mm$
*$Pm'm'm$
$Pm'm'm'$
$P_{2c}mmm$ P_ammm
P_Cmmm C_ammm
P_Fmmm F_ammm
$P_{2a}mmm'$ P_cmma
$P_{2c}m'm'm$ P_ccm
P_Cmmm' C_amma

Pnnn

$Pn'nn$
*$Pn'n'n$
$Pn'n'n'$
P_Fnnn F_cddd

Pccm

$Pc'cm$
$Pccm'$
*$Pc'c'm$
*$Pc'cm'$
$Pc'c'm'$
$P_{2a}ccm$ P_accm
P_Cccm C_accm
$P_{2a}ccm'$ P_acca
$P_{2a}c'c'm$ P_cmna
$P_{2a}c'c'm'$ P_aban
P_Cccm' C_acca

Pban

$Pb'an$
$Pban'$
*$Pb'a'n$
*$Pb'an'$
$Pb'a'n'$

$P_{2c}ban$ P_cban
$P_{2c}b'an$ P_bnna
$P_{2c}b'a'n$ P_annn

Pmma

$Pm'ma$
$Pmm'a$
$Pmma'$
*$Pm'm'a$
*$Pmm'a'$
*$Pm'ma'$
$Pm'm'a'$
$P_{2b}mma$ P_bmma
$P_{2c}mma$ P_cmma
P_Amma C_amcm
$P_{2b}m'ma$ P_bbcm
$P_{2b}mma'$ P_annn
$P_{2b}m'ma'$ P_anna
$P_{2c}m'ma$ P_abam
$P_{2c}mm'a$ P_bbcm
$P_{2c}m'm'a$ P_ecca
$P_Am'ma$ C_anca

Pnna

$Pn'na$
$Pnn'a$
$Pnna'$
*$Pn'n'a$
*$Pnn'a'$
*$Pn'na'$
$Pn'n'a'$

Pmna

$Pm'na$
$Pmn'a$
$Pmna'$
*$Pm'n'a$
*$Pmn'a'$

TABLE III (*continued*)

Orthorhombic system

Pmna

$*Pm'na'$
$Pm'n'a'$
$P_{2b}mna$ $P_{b}mna$
$P_{2b}m'na$ $P_{c}bcn$
$P_{2b}mna'$ $P_{a}nmm$
$P_{2b}m'na'$ $P_{a}nna$

Pcca

$Pc'ca$
$Pcc'a$
$Pcca'$
$*Pc'c'a$
$*Pcc'a'$
$*Pc'ca'$
$Pc'c'a'$
$P_{2b}cca$ $P_{b}cca$
$P_{2b}c'ca$ $P_{a}bcn$
$P_{2b}cca'$ $P_{a}ccn$
$P_{2b}c'ca$ $P_{c}nna$

Pbam

$Pb'am$
$Pbam'$
$*Pb'a'm$
$*Pb'am'$
$Pb'a'm'$
$P_{2c}bam$ $P_{c}bam$
$P_{2c}b'am$ $P_{b}nma$
$P_{2c}b'a'm$ $P_{c}nmm$

Pccn

$Pc'cn$
$Pccn'$
$*Pc'c'n$
$*Pc'cn'$
$Pc'c'n'$

Pbcm

$Pb'cm$
$Pbc'm$
$Pbcm'$
$*Pb'c'm$
$*Pbc'm'$
$*Pb'cm'$
$Pb'c'm'$
$P_{2a}bcm$ $P_{a}bcm$
$P_{2a}bc'm$ $P_{c}nma$
$P_{2a}bcm'$ $P_{a}bca$
$P_{2a}bc'm'$ $P_{b}bcn$

Pnnm

$Pn'nm$
$Pnnm'$
$*Pn'n'm$
$*Pnn'm'$
$Pn'n'm'$

Pmmn

$Pm'mn$
$Pmmn'$
$*Pm'm'n$
$*Pmm'n'$
$Pm'm'n'$
$P_{2c}mmn$ $P_{c}mmn$
$P_{2c}m'mn$ $P_{a}nma$
$P_{2c}m'm'n$ $P_{c}ccn$

Pbcn

$Pb'cn$
$Pbc'n$
$Pbcn'$
$*Pb'c'n$
$*Pbc'n'$
$*Pb'cn'$
$Pb'c'n'$

Pbca

$Pb'ca$
$*Pb'c'a$
$Pb'c'a'$

Pnma

$Pn'ma$
$Pnm'a$
$Pnma'$
$*Pn'm'a$
$*Pnm'a'$
$*Pn'ma'$
$Pn'm'a'$

Cmcm

$Cm'cm$
$Cmc'm$
$Cmcm'$
$*Cm'c'm$
$*Cmc'm'$
$*Cm'cm'$
$Cm'c'm'$
$C_{P}mcm$ $P_{A}mma$
$C_{P}m'cm$ $P_{C}bcm$
$C_{P}mc'm$ $P_{C}mmn$
$C_{P}mcm'$ $P_{B}nma$
$C_{P}m'c'm$ $P_{C}nma$
$C_{P}mc'm'$ $P_{C}nnm$
$C_{P}m'cm'$ $P_{C}bcn$
$C_{P}m'c'm'$ $P_{C}nna$

Cmca

$Cm'ca$
$Cmc'a$
$Cmca'$
$*Cm'c'a$
$*Cmc'a'$

TABLE III (*continued*)

Orthorhombic system

Cmca

*$Cm'ca'$
$Cm'c'a'$
C_Pmca P_Cbam
$C_Pm'ca$ P_Ccca
$C_Pmc'a$ P_Cnma
C_Pmca' P_Cbcm
$C_Pm'c'a$ P_Cccn
$C_Pmc'a'$ P_Cmna
$C_Pm'ca'$ P_Cbca
$C_Pm'c'a'$ P_Cbcn

Cmmm

$Cm'mm$
$Cmmm'$
*$Cm'm'm$
*$Cmm'm'$
$Cm'm'm'$
$C_{2c}mmm$ C_cmmm
C_Pmmm P_Cmmm
C_Immm I_cmmm
$C_{2c}m'm'm$ C_cccm
$C_{2c}mm'm'$ C_cmcm
$C_Pm'mm$ P_Cmma
C_Pmmm' P_Cmmn
$C_Pm'm'm$ P_Cbam
$C_Pmm'm'$ P_Cmna
$C_Pm'm'm'$ P_Cban
$C_Im'mm$ I_cmma
$C_Im'm'm$ I_cbam

Cccm

$Cc'cm$
$Cccm'$
*$Cc'c'm$
*$Ccc'm'$
$Cc'c'm'$
C_Pccm P_Cccm
$C_Pc'cm$ P_Cmna
C_Pccm' P_Ccccn
$C_Pc'c'm$ P_Cnnm
$C_Pcc'm'$ P_Cnna
$C_Pc'c'm'$ P_Cnnn

Cmma

$Cm'ma$
$Cmma'$
*$Cm'm'a$
*$Cmm'a'$
$Cm'm'a'$
$C_{2c}mma$ C_cmma
C_Pmma P_Cccm
C_Immma I_cbam
$C_{2c}m'ma$ C_cmca
$C_{2c}m'm'a$ C_ccca
$C_Pm'ma$ P_Ccca
$C_Pmm'a$ P_Cmma
C_Pmma' P_Cbcm
$C_Imm'a$ I_cmma
$C_Im'm'a'$ I_cbca

Ccca

$Cc'ca$
$Ccca'$
*$Cc'c'a$
*$Ccc'a'$
$Cc'c'a'$
C_Pcca P_Cban
$C_Pc'ca$ P_Ccca
C_Pcca' P_Cbcn
$C_Pcc'a'$ P_Cnna

Fmmm

$Fm'mm$
*$Fm'm'm$
$Fm'm'm'$
F_Cmmm C_Ammm
$F_Cm'mm$ C_Amcm
F_Cmmm' C_Amma
$F_Cm'm'm$ C_Accm
$F_Cmm'm'$ C_Amca
$F_Cm'm'm'$ C_Acca

Fddd

$Fd'dd$
*$Fd'd'd$
$Fd'd'd'$

Immm

$Im'mm$
*$Im'm'm$
$Im'm'm'$
I_Pmmm P_Immm
$I_Pm'mm$ P_Immn
$I_Pm'm'm$ P_Innm
$I_Pm'm'm'$ P_Innn

Ibam

$Ib'am$
$Ibam'$
*$Ib'a'm$
*$Iba'm'$
$Ib'a'm'$
I_Pbam P_Iccm
$I_Pb'am$ P_Ibcm
I_Pbam' P_Iccn
$I_Pb'a'm$ P_Ibam
$I_Pb'am'$ P_Ibcn
$I_Pb'a'm'$ P_Iban

Ibca

$Ib'ca$
*$Ib'c'a$

TABLE III (*continued*)

Orthorhombic system

Ibca

$Ib'c'a'$
I_Pbca P_Ibca
$I_Pb'ca$ P_Icca

Imma

$Im'ma$
$Imma'$
$*Im'm'a$
$*Imm'a'$
$Im'm'a'$
I_Pmma P_Imma
$I_Pm'm'a$ P_Imna
$I_Pmm'a'$ P_Imna
$I_Pm'ma'$ P_Inma

Tetragonal system

4

$P4$

$P4'$
$P_{2c}A$ P_cA
P_P4 P_C4
P_I4 I_cA
$P_{2c}A'$ P_cA_2

$P4_1$

$P4_1'$
P_P4_1 P_C4_1

$P4_2$

$P4_2'$
$P_{2c}A_2$ P_cA_1
P_P4_2 P_C4_2
P_I4_2 I_cA_1
$P_{2c}A_2'$ P_cA_2

$P4_3$

$P4_3'$
P_P4_3 P_C4_3

$I4$

$I4'$
I_P4 P_I4
I_P4' P_I4_2

$I4_1$

$I4_1'$
I_P4_1 P_I4_1
I_P4_1' P_I4_3

$\bar{4}$

$P\bar{4}$

$P\bar{4}'$
$P_{2c}\bar{4}$ $P_c\bar{4}$
$P_P\bar{4}$ $P_C\bar{4}$
$P_I\bar{4}$ $I_c\bar{4}$

$I\bar{4}$

$I\bar{4}'$
$I_P\bar{4}$ $P_I\bar{4}$

$4/m$

$P4/m$

$P4'/m$
$P4/m'$
$P4'/m'$
$P_{2c}A/m$ P_cA/m
P_P4/m P_C4/m
P_I4/m I_cA/m
$P_{2c}A'/m$ P_cA_2/m
P_P4/m' P_C4/n

$P4_2/m$

$P4_2'/m$
$P4_2/m'$
$P4_2'/m'$
P_P4_2/m P_C4_2/m
P_P4_2/m' P_C4_2/n

$P4/n$

$P4'/n$
$P4/n'$
$P4'/n'$
$P_{2c}A/n$ P_cA/n
$P_{2c}A'/n$ P_cA_2/n

$P4_2/n$

$P4_2'/n$
$P4_2/n'$
$P4_2'/n'$
P_I4_2/n I_cA_1/a

$I4/m$

$I4'/m$
$I4/m'$
$I4'/m'$
I_P4/m P_I4/m
I_P4'/m P_I4_2/m
I_P4/m' P_I4/n
I_P4'/m' P_I4_2/n

$I4_1/a$

$I4_1'/a$
$I4_1/a'$
$I4_1'/a'$

422

P422

$P4'22'$
$*P42'2'$

TABLE III (*continued*)

Tetragonal system

*P*422

*P*4′2′2
$P_{2c}422$ P_c422
P_P422 P_C422
P_I422 I_c422
$P_{2c}4'22'$ P_c4_222
$P_P4'22'$ P_C42_12

*P*42$_1$2

*P*4′2$_1$2′
**P*42$_1'$2′*
*P*4′2$_1'$2
$P_{2c}42_12$ P_c42_12
$P_{2c}4'2_1'2$ $P_c4_22_12$

*P*4$_1$22

*P*4$_1'$22′
**P*4$_1$2′2′*
*P*4$_1'$2′2
P_P4_122 P_C4_122
$P_P4_1'22'$ $P_C4_12_12$

*P*4$_1$2$_1$2

*P*4$_1'$2$_1$2′
**P*4$_1$2$_1'$2′*
*P*4$_1'$2$_1'$2
P_P4_222 P_C4_222
$P_P4_2'22'$ $P_C4_2_12$

*P*4$_2$2$_1$2

*P*4$_2'$2$_1$2′
**P*4$_2$2$_1'$2′*
*P*4$_2'$2$_1'$2
$I422$

*I*4′22′
**I*42′2′*
*I*4′2′2
I_P422 P_I422
$I_P4'22'$ P_I4_222
$I_P42'2'$ P_I42_12
$I_P4'2'2$ $P_I4_2_12$

*I*4$_1$22

*I*4$_1'$22′
**I*4$_1$2′2′*
*I*4$_1'$2′2
I_P4_122 P_I4_122
$I_P4_1'22'$ P_I4_222
$I_P4_12'2'$ $P_I4_12_12$
$I_P4_1'2'2$ $P_I4_2_12$

4*mm*

*P*4*mm*

*P*4′*m*′*m*
*P*4′*mm*′
**P*4*m*′*m*′*
$P_{2c}4mm$ P_c4mm
P_P4mm P_C4mm
P_I4mm I_c4mm
$P_{2c}4'm'm$ P_cA_2cm
$P_{2c}4'mm'$ P_cA_2mc
$P_{2c}4m'm'$ P_c4cc
$P_P4'mm'$ P_C4bm
$P_I4m'm'$ I_c4cm

*P*4*bm*

*P*4′*b*′*m*
*P*4′*bm*′
**P*4*b*′*m*′*
$P_{2c}4bm$ P_cAbm
$P_{2c}4'b'm$ P_cA_2nm
$P_{2c}4'bm'$ P_cA_2bc
$P_{2c}4b'm'$ P_cAnc

*P*4$_2$*cm*

*P*4$_2'c'm$
*P*4$_2'cm'$
**P*4$_2c'm'*
P_P4_2cm P_C4_2mc
$P_P4_2'cm'$ P_C4_2bc

*P*4$_2$*nm*

*P*4$_2'n'm$
*P*4$_2'nm'$
**P*4$_2n'm'*
P_I4_2nm I_cA_1md
$P_I4_2n'm'$ I_cA_1cd

TABLE III (*continued*)

Tetragonal system

$P4cc$

$P4'c'c$
$P4'cc'$
$*P4c'c'$
P_P4cc P_C4cc
$P_P4'cc'$ P_C4nc

$P4nc$

$P4'n'c$
$P4'nc'$
$*P4n'c'$

$P4_2mc$

$P4_2'm'c$
$P4_2'mc'$
$*P4_2m'c'$
P_P4_2mc P_C4_2cm
$P_P4_2'mc'$ P_C4_2nm

$P4_2bc$

$P4_2'b'c$
$P4_2'bc'$
$*P4_2b'c'$

$I4mm$

$I4'm'm$
$I4'mm'$
$*I4m'm'$
I_P4mm P_I4mm
$I_P4'm'm$ P_I4_2nm
$I_P4'mm'$ P_I4_2mc
$I_P4m'm'$ P_I4nc

$I4cm$

$I4'c'm$
$I4'cm'$
$*I4c'm'$
I_P4cm P_I4bm
$I_P4'c'm$ P_I4_2cm
$I4'cm'$ P_I4_2bc
$I4c'm'$ P_I4cc

$I4_1md$

$I4_1'm'd$
$I4_1'md'$
$*I4_1m'd'$

$I4_1cd$

$I4_1'c'd$
$I4_1'cd'$
$*I4_1c'd'$

$\bar{4}2m$

$P\bar{4}2m$

$P\bar{4}'2'm$
$P\bar{4}'2m'$
$*P\bar{4}2'm'$
$P_{2c}\bar{4}2m$ $P_c\bar{4}2m$
$P_P\bar{4}2m$ $P_C\bar{4}m2$
$P_I\bar{4}2m$ $I_c\bar{4}m2$
$P_{2c}\bar{4}2'm'$ $P_c\bar{4}2c$
$P_P\bar{4}'2m'$ $P_C\bar{4}b2$
$P_I\bar{4}'2m'$ $I_c\bar{4}c2$

$P\bar{4}2c$

$P\bar{4}'2'c$
$P\bar{4}'2c'$
$*P\bar{4}2'c'$
$P_P\bar{4}2c$ $P_C\bar{4}c2$
$P_P\bar{4}'2c'$ $P_C\bar{4}n2$

$P\bar{4}2_1m$

$P\bar{4}'2_1'm$
$*P\bar{4}2_1'm'$
$P_{2c}\bar{4}2_1m$ $P_c\bar{4}2_1m$
$P_{2c}\bar{4}'2_1m'$ $P_c\bar{4}2_1c$

$P\bar{4}2_1c$

$P\bar{4}'2_1'c$
$P\bar{4}'2_1c'$
$*P\bar{4}2_1'c'$

$P\bar{4}m2$

$P\bar{4}'m'2$
$P\bar{4}'m2'$
$*P\bar{4}m'2'$
$P_{2c}\bar{4}m2$ $P_c\bar{4}m2$
$P_P\bar{4}m2$ $P_C\bar{4}2m$
$P_I\bar{4}m2$ $I_c\bar{4}2m$
$P_{2c}\bar{4}'m'2$ $P_c\bar{4}c2$
$P_P\bar{4}'m2'$ $P_C\bar{4}2_1m$

$P\bar{4}c2$

$P\bar{4}'c'2$
$P\bar{4}'c2'$
$*P\bar{4}c'2'$
$P_P\bar{4}c2$ $P_C\bar{4}2c$
$P_P\bar{4}'c2'$ $P_C\bar{4}2_1c$

$P\bar{4}b2$

$P\bar{4}'b'2$
$P\bar{4}'b2'$
$*P\bar{4}b'2'$
$P_{2c}\bar{4}b2$ $P_c\bar{4}b2$
$P_{2c}\bar{4}'b'2$ $P_c\bar{4}n2$

$P\bar{4}n2$

$P\bar{4}'n'2$
$P\bar{4}'n2'$
$*P\bar{4}n'2'$
$P_I\bar{4}n2$ $I_c\bar{4}2d$

TABLE III (*continued*)

Tetragonal system

$I\bar{4}m2$

$I\bar{4}'m'2$
$I4'm2'$
$*I\bar{4}m'2'$
$I_P\bar{4}m2$ $P_I\bar{4}m2$
$I_P\bar{4}'m'2$ $P_I\bar{4}n2$

$I\bar{4}c2$

$I\bar{4}'c'2$
$I\bar{4}'c2'$
$*I\bar{4}c'2'$
$I_P\bar{4}c2$ $P_I\bar{4}c2$
$I_P\bar{4}c'2'$ $P_I\bar{4}b2$

$I\bar{4}2m$

$I\bar{4}'2'm$
$I\bar{4}'2m'$
$*I\bar{4}2'm'$
$I_P\bar{4}2m$ $P_I\bar{4}2m$
$I_P\bar{4}'2'm$ $P_I\bar{4}2_1m$
$I_P\bar{4}'2m'$ $P_I\bar{4}2c$
$I_P\bar{4}2'm'$ $P_I\bar{4}2_1c$

$I\bar{4}2d$

$I\bar{4}'2'd$
$I\bar{4}'2d'$
$*I\bar{4}2'd'$

$4/mmm$

$P4/mmm$

$P4/m'mm$
$P4'/mm'm$
$P4'/mmm'$
$P4'/m'm'm$
$*P4/mm'm'$
$P4'/m'mm'$
$P4/m'm'm'$
$P_{2c}4/mmm$ P_c4/mmm
P_P4/mmm P_C4/mmm
P_I4/mmm I_c4/mmm
$P_{2c}4'/mm'm$ P_c4_2/mcm
$P_{2c}4'/mmm'$ P_c4_2/mmc
$P_{2c}4/mm'm'$ P_c4/mcc
$P_P4/m'mm$ P_C4/nmm
P_P4'/mmm' P_C4/mbm
$P_P4'/m'mm'$ P_C4/nbm
$P_I4/mm'm'$ I_c4/mcm

$P4/mcr$

$P4/m'cc$
$P4'/mc'c$
$P4'/mcc'$
$P4'/m'c'c$
$*P4/mc'c'$
$P4'/m'cc'$
$P4/m'c'c'$
P_P4/mcc P_C4/mcc
$P_P4/m'cc$ P_C4/ncc
P_P4'/mcc' P_C4/mnc
$P_P4'/m'cc'$ P_C4/nnc

$P4/nbm$

$P4/n'bm$
$P4'/nb'm$
$P4'/nbm'$
$P4'/n'b'm$
$*P4/nb'm'$
$P4'/n'bm'$
$P4/n'b'm'$
$P_{2c}4/nbm$ P_c4/nbm
$P_{2c}4'/nb'm$ P_c4_2/nnm
$P_{2c}4'/nbm'$ P_c4_2/nbc
$P_{2c}4/nb'm'$ P_c4/nnc

$P4/nnc$

$P4/n'nc$
$P4'/nn'c$
$P4'/nnc'$
$P4'/n'n'c$
$*P4/nn'c'$
$P4'/n'nc'$
$P4/n'n'c'$

$P4/mbm$

$P4/m'bm$
$P4'/mb'm$
$P4'/mbm'$
$P4'/m'b'm$
$*P4/mb'm'$
$P4'/m'bm'$
$P4/m'b'm'$
$P_{2c}4/mbm$ P_c4/mbm
$P_{2c}4'/mb'm$ P_c4_2/mnm
$P_{2c}4'/mbm'$ P_c4_2/mbc
$P_{2c}4/mb'm'$ P_c4/mnc

$P4/mnc$

$P4/m'nc$
$P4'/mn'c$
$P4'/mnc'$
$P4'/m'n'c$
$*P4/mn'c'$
$P4'/m'nc'$
$P4/m'n'c'$

$P4/nmm$

$P4/n'mm$
$P4'/nm'm$
$P4'/nmm'$
$P4'/n'm'm$
$*P4/nm'm'$
$P4'/n'mm'$
$P4/n'm'm'$
$P_{2c}4/nmm$ P_c4/nmm

TABLE III (*continued*)

Tetragonal system

$P4/nmm$

$P_{2c}4'/nm'm$ P_c4_2/ncm
$P_{2c}4'/nmm'$ P_c4_2/nmc
$P_{2c}4/nm'm'$ P_c4/ncc

$P4/ncc$

$P4/n'cc$
$P4'/nc'c$
$P4'/ncc'$
$P4'/n'c'c$
$*P4/nc'c'$
$P4'/n'cc'$
$P4/n'c'c'$

$P4_2/mmc$

$P4_2/m'mc$
$P4_2'/mm'c$
$P4_2'/mmc'$
$P4_2'/m'm'c$
$*P4_2/mm'c'$
$P4_2'/m'mc'$
$P4_2/m'm'c'$
P_P4_2/mmc P_C4_2/mcm
$P_P4_2/m'mc$ P_C4_2/ncm
$P_P4_2/mm'c'$ P_C4_2/mnm
$P_P4_2'/m'mc$ P_C4_2/nnm

$P4_2/mcm$

$P4_2/m'cm$
$P4_2'/mc'm$
$P4_2/mcm'$
$P4_2'/m'c'm$
$*P4_2/mc'm'$
$P4_2'/m'cm'$
$P4_2/m'c'm'$
P_P4_2/mcm P_C4_2/mmc
$P_P4_2/m'cm$ P_C4_2/nmc
P_P4_2'/mcm' P_C4_2/mbc
$P_P4_2'/m'cm'$ P_C4_2/nbc

$P4_2/nbc$

$P4_2/n'bc$
$P4_2'/nb'c$
$P4_2'/nbc'$
$P4_2'/n'b'c$
$*P4_2/nb'c'$
$P4_2'/n'bc'$
$P4_2/n'b'c'$

$P4_2/nnm$

$P4_2/n'nm$
$P4_2'/nn'm$
$P4_2'/nnm'$
$P4_2'/n'n'm$
$*P4_2/nn'm'$
$P4_2'/n'nm'$
$P4_2/n'n'm'$
P_I4_2/nnm I_c4_1/amd
$P_I4_2/nn'm'$ I_c4_1/acd

$P4_2/mbc$

$P4_2/m'bc$
$P4_2'/mb'c$
$P4_2'/mbc'$
$P4_2'/m'b'c$
$*P4_2/mb'c'$
$P4_2'/m'bc'$
$P4_2/m'b'c'$

$P4_2/mnm$

$P4_2/m'nm$
$P4_2'/mn'm$
$P4_2'/mnm'$
$P4_2'/m'n'm$
$*P4_2/mn'm'$
$P4_2'/m'nm'$
$P4_2/m'n'm'$

$P4_2/nmc$

$P4_2/n'mc$
$P4_2'/nm'c$
$P4_2'/nmc'$
$P4_2'/n'm'c$
$*P4_2/nm'c'$
$P4_2'/n'mc'$
$P4_2/n'm'c'$

$P4_2/ncm$

$P4_2/n'cm$
$P4_2'/nc'm$
$P4_2'/ncm'$
$P4_2'/n'c'm$
$*P4_2/nc'm'$
$P4_2'/n'cm'$
$P4_2/n'c'm'$

$I4/mmm$

$I4/m'mm$
$I4'/mm'm$
$I4'/mmm'$
$I4'/m'm'm$
$*I4/mm'm'$
$I4'/m'mm'$
$I4/m'm'm'$
I_P4/mmm P_I4/mmm
$I_P4/m'mm$ P_I4/nmm
$I_P4'/mm'm$ P_I4_2/mnm
I_P4'/mmm' P_I4_2/mmc
$I_P4'/m'm'm$ P_I4_2/nnm
$I_P4/mm'm'$ P_I4/mnc
$I_P4'/m'mm'$ P_I4_2/nmc
$I_P4/m'm'm'$ P_I4/nnc

TABLE III (*continued*)

Tetragonal system		Trigonal system		$P3_121$	
		3			
$I4/mcm$		$*P3$		$*P3_12'1$	
				$P_{2c}3_221$	P_c3_221
$I4/m'cm$		$P_{2c}3$	P_c3	$P3_112$	
$I4'/mc'm$					
$I4'/mcm'$		$*P3_1$		$*P3_112'$	
$I4'/m'c'm$				$P_{2c}3_112$	P_c3_112
$*I4/mc'm'$		$P_{2c}3_2$	P_c3_2	$P3_221$	
$I4'/m'cm'$		$*P3_2$			
$I4/m'c'm'$				$*P3_22'1$	
I_P4/mcm	P_I4/mcc	$P_{2c}3_1$	P_c3_1	$P_{2c}3_121$	P_c3_121
$I_P4/m'cm$	P_I4/ncc	$*R3$		$R32$	
$I_P4'/mc'm$	P_I4_2/mbc				
I_P4'/mcm'	P_I4_2/mcm	R_R3		$*R32'$	
$I_P4'/m'c'm$	P_I4_2/nbc	$\bar{3}$		R_R32	
$I_P4/mc'm'$	P_I4/mbm	$*P\bar{3}$		$3m$	
$I_P4'/m'cm'$	P_I4_2/ncm			$P3m1$	
$I_P4/m'c'm'$	P_I4/nbm	$P\bar{3}'$			
		$P_{2c}\bar{3}$	$P_c\bar{3}$	$*P3m'1$	
$I4_1/amd$		$*R\bar{3}$		$P_{2c}3m1$	P_c3m1
$I4_1/a'md$				$P_{2c}3m'1$	P_c3c1
$I4_1'/am'd$		$R\bar{3}'$		$P31m$	
$I4_1'/amd'$		$R_R\bar{3}$			
$I4_1'/a'm'd$		32		$*P31m'$	
$*I4_1/am'd'$		$P312$		$P_{2c}31m$	P_c31m
$I4_1'/a'md'$				$P_{2c}31m'$	P_c31c
$I4_1/a'm'd'$		$*P312'$		$P3c1$	
$I4_1/acd$		$P_{2c}312$	P_c312		
		$P321$		$*P3c'1$	
$I4_1/a'cd$				$P31c$	
$I4_1'/ac'd$		$*P32'1$			
$I4_1/acd'$		$P_{2c}321$	P_c321	$*P31c'$	
$I4_1'/a'c'd$		$P3_112$		$R3m$	
$*I4_1/ac'd'$					
$I4_1'/a'cd'$		$*P3_112'$			
$I4_1/a'c'd'$		$P_{2c}3_212$	P_c3_212	$*R3m'$	

TABLE III (*continued*)

Trigonal system

$R3m$

R_R3m
R_R3m' R_I3c

$R3c$

$*R3c'$

$\bar{3}m$

$P\bar{3}1m$

$P\bar{3}'1m$
$P\bar{3}'1m'$
$*P\bar{3}1m'$
$P_{2c}\bar{3}1m$ $P_c\bar{3}1m$
$P_{2c}\bar{3}1m'$ $P_c\bar{3}1c$

$P\bar{3}1c$

$P\bar{3}'1c$
$P\bar{3}'1c'$
$*P\bar{3}1c'$

$P\bar{3}m1$

$P\bar{3}'m1$
$P\bar{3}'m'1$
$*P\bar{3}m'1$
$P_{2c}\bar{3}m1$ $P_c\bar{3}m1$
$P_{2c}\bar{3}m'1$ $P_c\bar{3}c1$

$P\bar{3}c1$

$P\bar{3}'c1$
$P\bar{3}'c'1$
$*P\bar{3}c'1$

$R\bar{3}m$

$R\bar{3}'m$
$R\bar{3}'m'$
$*R\bar{3}m'$
$R_R\bar{3}m$
$R_R\bar{3}m'$ $R_I\bar{3}c$

$R\bar{3}c$

$R\bar{3}'c$
$R\bar{3}'c'$
$*R\bar{3}c'$

Hexagonal system

6

$*P6$

$P6'$
$P_{2c}6$ P_c6
$P_{2c}6'$ P_c6_3

$*P6_1$

$P6_1'$

$*P6_5$

$P6_5'$

$*P6_2$

$P6_2'$
$P_{2c}6_2$ P_c6_1
$P_{2c}6_2'$ P_c6_4

$*P6_4$

$P6_4'$
$P_{2c}6_4$ P_c6_2
$P_{2c}6_4'$ P_c6_5

$*P6_3$

$P6_3'$

$\bar{6}$

$*P\bar{6}$

$P\bar{6}'$
$P_{2c}\bar{6}$ $P_c\bar{6}$

$6/m$

$*P6/m$

$P6'/m$
$P6/m'$
$P6'/m'$
$P_{2c}6/m$ P_c6/m
$P_{2c}6'/m$ P_c6_3/m

$*P6_3/m$

$P6_3'/m$
$P6_3/m'$
$P6_3'/m'$

622

$P622$

$P6'2'2$
$P6'22'$
$*P62'2'$
$P_{2c}622$ P_c622
$P_{2c}6'22$ P_c6_322

$P6_122$

$P6_1'2'2$
$P6_1'22'$
$*P6_12'2'$

$P6_522$

$P6_5'2'2$
$P6_5'22'$
$*P6_52'2'$

$P6_222$

$P6_2'2'2$
$P6_2'22'$
$*P6_22'2'$
$P_{2c}6_222$ P_c6_122
$P_{2c}6_2'22$ P_c6_422

TABLE III (*continued*)

Hexagonal system

$P6_422$

$P6_42'2$
$P6_422'$
$*P6_42'2'$
$P_{2c}6_422$ P_c6_222
$P_{2c}6_42'2$ P_c6_522

$P6_322$

$P6_32'2$
$P6_322'$
$*P6_32'2'$

$6mm$

$P6mm$

$P6'm'm$
$P6'mm'$
$*P6m'm'$
$P_{2c}6mm$ P_c6mm
$P_{2c}6'm'm$ P_c6_3cm
$P_{2c}6'mm'$ P_c6_3mc
$P_{2c}6m'm'$ P_c6cc

$P6cc$

$P6'c'c$
$P6'cc'$
$*P6c'c'$

$P6_3cm$

$P6_3'c'm$
$P6_3'cm'$
$*P6_3c'm'$

$P6_3mc$

$P6_3'm'c$
$P6_3'mc'$
$*P6_3m'c'$

$\bar{6}m2$

$P\bar{6}m2$

$P\bar{6}'m'2$
$P\bar{6}'m2'$
$*P\bar{6}m'2'$
$P_{2c}\bar{6}m2$ $P_c\bar{6}m2$
$P_{2c}\bar{6}'m'2$ $P_c\bar{6}c2$

$P\bar{6}c2$

$P\bar{6}'c'2$
$P\bar{6}'c2'$
$*P\bar{6}c'2'$

$P\bar{6}2m$

$P\bar{6}'2'm$
$P\bar{6}'2m'$
$*P\bar{6}2'm'$
$P_{2c}\bar{6}2m$ $P_c\bar{6}2m$
$P_{2c}\bar{6}'2m'$ $P_c\bar{6}2c$

$P\bar{6}2c$

$P\bar{6}'2'c$
$P\bar{6}'2c'$
$*P\bar{6}2'c'$

$6/mmm$

$P6/mmm$

$P6/m'mm$
$P6'/mm'm$
$P6'/mmm'$
$P6'/m'm'm$
$P6'/m'mm'$
$*P6/mm'm'$
$P6/m'm'm'$
$P_{2c}6/mmm$ P_c6/mmm
$P_{2c}6'/mm'm$ P_c6_3/mcm
$P_{2c}6'/mmm'$ P_c6_3/mmc
$P_{2c}6/mm'm'$ P_c6/mcc

$P6/mcc$

$P6/m'cc$
$P6'/mc'c$
$P6'/mcc'$
$P6'/m'c'c$
$P6'/m'cc'$
$*P6/mc'c'$
$P6/m'c'c'$

$P6_3/mcm$

$P6_3/m'cm$
$P6_3'/mc'm$
$P6_3'/mcm'$
$P6_3'/m'c'm$
$P6_3'/m'cm'$
$*P6_3/mc'm'$
$P6_3/m'c'm'$

$P6_3/mmc$

$P6_3/m'mc$
$P6_3'/mm'c$
$P6_3'/mmc'$
$P6_3'/m'm'c$
$P6_3'/m'mc'$
$*P6_3/mm'c'$
$P6_3/m'm'c'$

Cubic system

23

$P23$

P_F23 F_z23

$F23$

$I23$

I_P23 P_I23

TABLE III (*continued*)

Cubic system

$P2_13$

$I2_13$

I_P2_13 P_I2_13

$m3$

$Pm3$

$Pm'3$

P_Fm3 F_sm3

$Pn3$

$Pn'3$

P_Fn3 F_sd3

$Fm3$

$Fm'3$

$Fd3$

$Fd'3$

$Im3$

$Im'3$

I_Pm3 P_Im3

$I_Pm'3$ P_In3

$Pa3$

$Pa'3$

$Ia3$

$Ia'3$

I_Pa3 P_Ia3

432

$P432$

$P4'32'$

P_F432 F_s432

$P4_232$

$P4_2'32'$

P_F4_232 F_s4_132

$F432$

$F4'32'$

$F4_132$

$F4_1'32'$

$I432$

$I4'32'$

I_P432 P_I432

$I_P4'32'$ P_I4_232

$P4_332$

$P4_3'32'$

$P4_132$

$P4_1'32'$

$I4_132$

$I4_1'32'$

I_P4_132 P_I4_332

$I_P4_1'32'$ P_I4_132

$\bar{4}3m$

$P\bar{4}3m$

$P\bar{4}'3m'$

$P_F\bar{4}3m$ $F_s\bar{4}3m$

$P_F\bar{4}'3m'$ $F_s\bar{4}3c$

$F\bar{4}3m$

$F\bar{4}'3m'$

$I\bar{4}3m$

$I\bar{4}'3m'$

$I_P\bar{4}3m$ $P_I\bar{4}3m$

$I_P\bar{4}'3m'$ $P_I\bar{4}3n$

$P\bar{4}3n$

$P\bar{4}'3n'$

$F\bar{4}3c$

$F\bar{4}'3c'$

$I\bar{4}3d$

$I\bar{4}'3d'$

$m3m$

$Pm3m$

$Pm'3m$

$Pm3m'$

$Pm'3m'$

P_Fm3m F_sm3m

P_Fm3m' F_sm3c

$Pn3n$

$Pn'3n$

$Pn3n'$

$Pn'3n'$

$Pm3n$

$Pm'3n$

$Pm3n'$

$Pm'3n'$

$Pn3m$

$Pn'3m$

$Pn3m'$

$Pn'3m'$

TABLE III (*continued*)

Cubic system			
$Pn3m$		$Fm3c'$	$Im3m$
P_Fn3m	F_ed3m	$Fm'3c'$	$Im'3m$
P_Fn3m'	F_ed3c	$Fd3m$	$Im3m'$
$Fm3m$		$Fd'3m$	$Im'3m'$
$Fm'3m$		$Fd3m'$	I_Pm3m P_Im3m
$Fm3m'$		$Fd'3m'$	$I_Pm'3m$ P_In3m
$Fm'3m'$		$Fd3c$	I_Pm3m' P_Im3n
$Fm3c$		$Fd'3c$	$I_Pm'3m'$ P_In3n
$Fm'3c$		$Fd3c'$	$Ia3d$
		$Fd'3c'$	$Ia'3d$
			$Ia3d'$
			$Ia'3d'$

Rules to construct invariant spin arrangements

- Define a magnetic space group generated by the SG of the crystal structure.
- Identify the magnetic site, and define its magnetic point symmetry. A *graphic* representation of the MG is useful.
- Check that the site MPG is *admissible* for at least one spin component. Otherwise, the MSG does not support any magnetic structure on that site.
- Pick one admissible component, and apply in turn all the MSG operators on that component, propagating it to all equivalent sites.

Rules to determine the MSG from a given structure

- Check that the magnetic structure Γ is Shubnikov-compatible. This is easily done by applying the operators of the *crystal* space group $\{F\}$ upon Γ (including lattice doublings). Γ is Shubnikov-compatible if and only if, the structure is either invariant ($\times$ 1) or reversed ($\times$ -1) for each and every F in $\{F\}$.
- Prime all the operators in $\{F\}$ for which Γ is reversed, and identify the new primitive translations. This completes the process.

Shubnikov groups and representations

To make a link with the more powerful representation analysis, we can simply think of how a magnetic structure Γ, which is invariant under a particular magnetic groups $\{F_M\}$, will transform under the 'parent' space group $\{F\}$. It is apparent that Γ will be invariant ($\times 1$) under the operators which are *unprimed* in $\{F_M\}$, whereas all the spins will be switched ($\times -1$) for the operators that are *primed* in $\{F_M\}$. In other words, the set of numbers 1 or –1 is a *representation* of $\{F\}$ onto the linear space generated by Γ. We can easily prove that the reverse is also true.

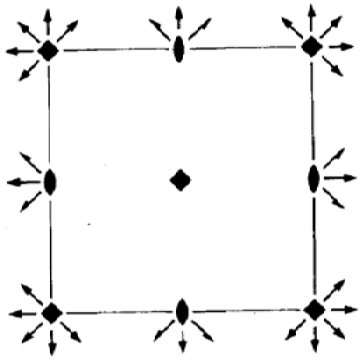
We can conclude the Shubnikov groups are *equivalent to 1-dimensional real representations* of $\{F\}$, with the invariant Γ*s* being their basis sets. In general, if we relax the requirement for invariance of the crystal structure, there is no reason to prefer these to all the (infinite) others, whence the need for extending the analysis to the *full expansion in irreducible representations*.

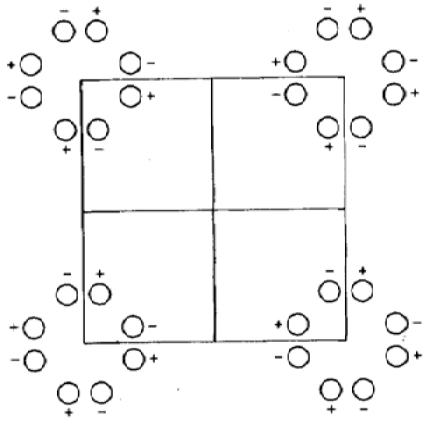
Pnma

P 2_1/n 2_1/m 2_1/a

Irrep	Shubn.	{1 |000}	{2_00z |½0½}	{2_0y0 |0½0}	{2_x00 |½½½}	{-1 |000}	{m_xy0 |½0½}	{m_x0z |0½0}	{m_0yz |½½½}
Γ_1	Pnma	1	1	1	1	1	1	1	1
Γ_2	Pn'm'a'	1	1	1	1	-1	-1	-1	-1
Γ_3	Pn'm'a	1	1	-1	-1	1	1	-1	-1
Γ_4	Pnma'	1	1	-1	-1	-1	-1	1	1
Γ_5	Pn'ma'	1	-1	1	-1	1	-1	1	-1
Γ_6	Pnm'a	1	-1	1	-1	-1	1	-1	1
Γ_7	Pnm'a'	1	-1	-1	1	1	-1	-1	1
Γ_8	Pn'ma	1	-1	-1	1	-1	1	1	-1

No. 89 $P422$ Patterson symmetry $P4/mmm$





Origin at 422

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 1	(2) 2 0,0,z	(3) 4^+ 0,0,z	(4) 4^- 0,0,z
(5) 2 0,y,0	(6) 2 x,0,0	(7) 2 x,x,0	(8) 2 x,$\bar{x}$,0

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	p	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	
							Special:
4	o	.2.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	n	.2.	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	m	.2.	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	l	.2.	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	k	..2	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	j	..2	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	i	2..	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k=2n$
2	h	4..	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g	4..	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f	222.	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $h+k=2n$
2	e	222.	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$			hkl : $h+k=2n$
1	d	422	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c	422	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b	422	$0,0,\frac{1}{2}$				no extra conditions
1	a	422	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p4mm$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p2mm$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [110] $p2mm$
$\boldsymbol{a}'=\frac{1}{2}(-\boldsymbol{a}+\boldsymbol{b})$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,x,0$

Maximal non-isomorphic subgroups

I [2]$P411$ ($P4$) 1; 2; 3; 4
[2]$P221$ ($P222$) 1; 2; 5; 6
[2]$P212$ ($C222$) 1; 2; 7; 8

IIa none

IIb [2]$P4_222$ ($\boldsymbol{c}'=2\boldsymbol{c}$); [2]$C422_1$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}$)($P42_12$); [2]$F422$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}, \boldsymbol{c}'=2\boldsymbol{c}$)($I422$)

Maximal isomorphic subgroups of lowest index

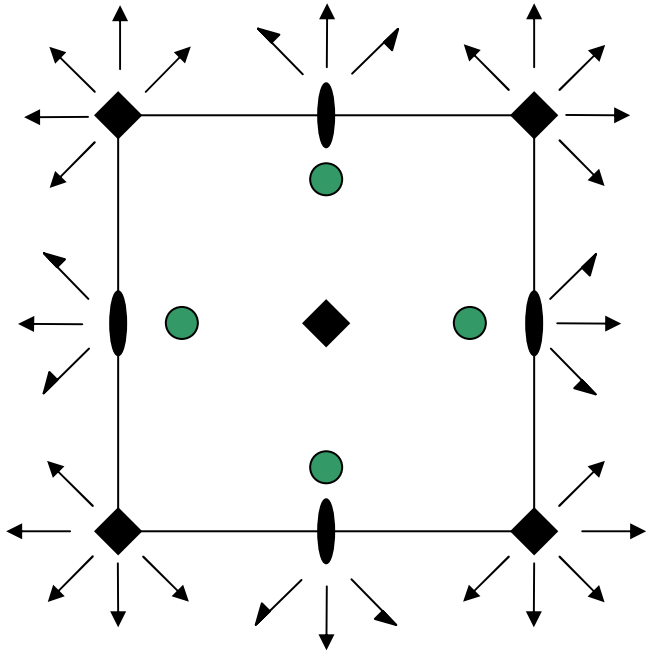
IIc [2]$P422$ ($\boldsymbol{c}'=2\boldsymbol{c}$); [2]$C422$ ($\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{b}'=2\boldsymbol{b}$)($P422$)

Minimal non-isomorphic supergroups

I [2]$P4/mmm$; [2]$P4/mcc$; [2]$P4/nbm$; [2]$P4/nnc$; [3]$P432$

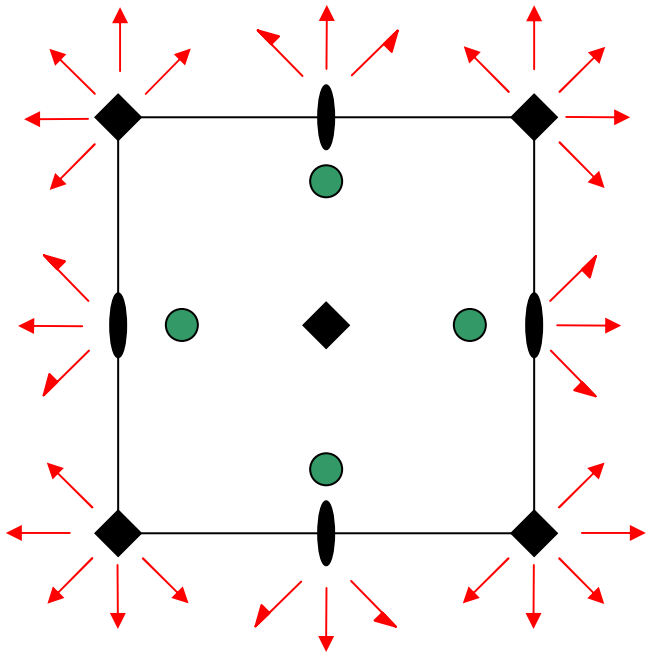
II [2]$I422$

P422 (No 89)



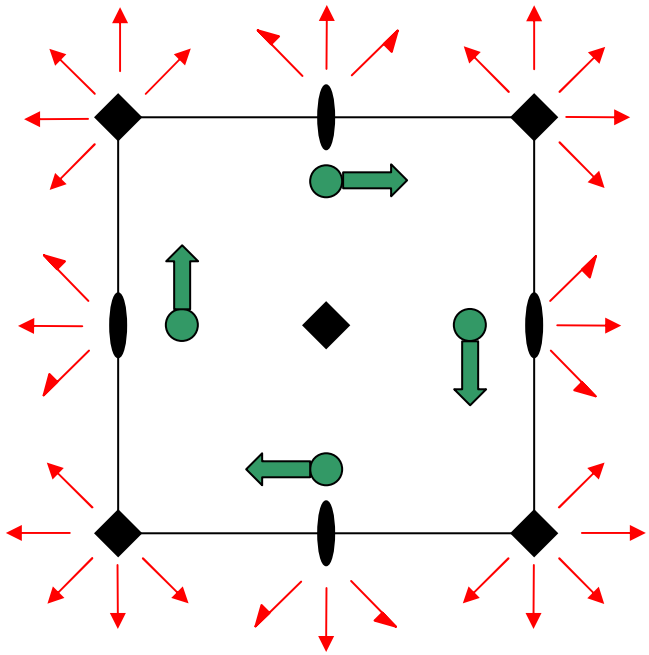
Special position: 4o [.2.] x, ½, 0

P42’2’



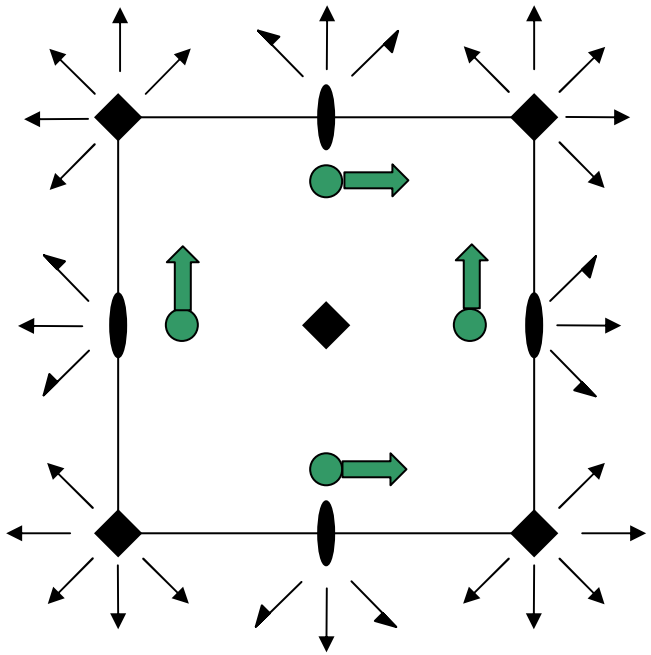
Special position: 4o [.2.] x, ½, 0

P42’2’

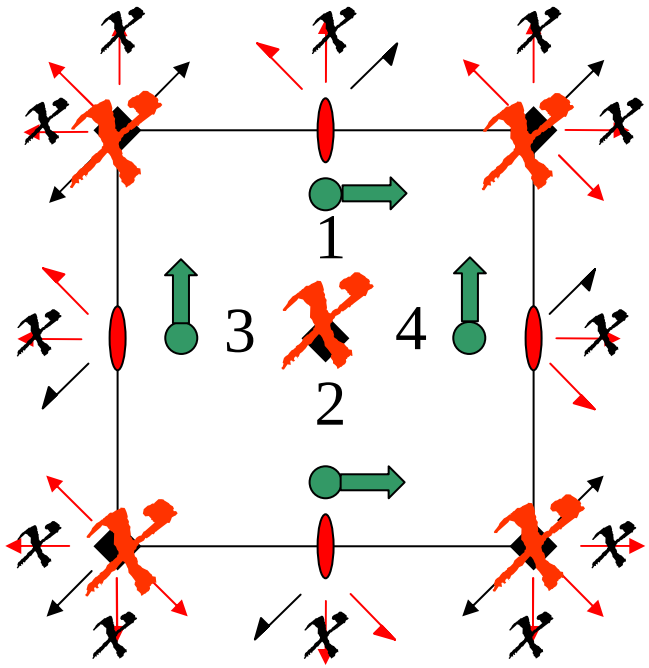


Special position: 4o [.2.] x, ½, 0

P422 →?

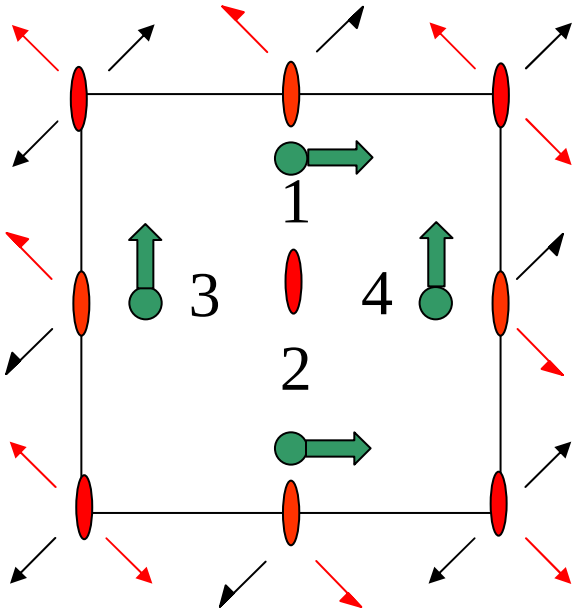


Special position: 4o [.2.] x, ½, 0



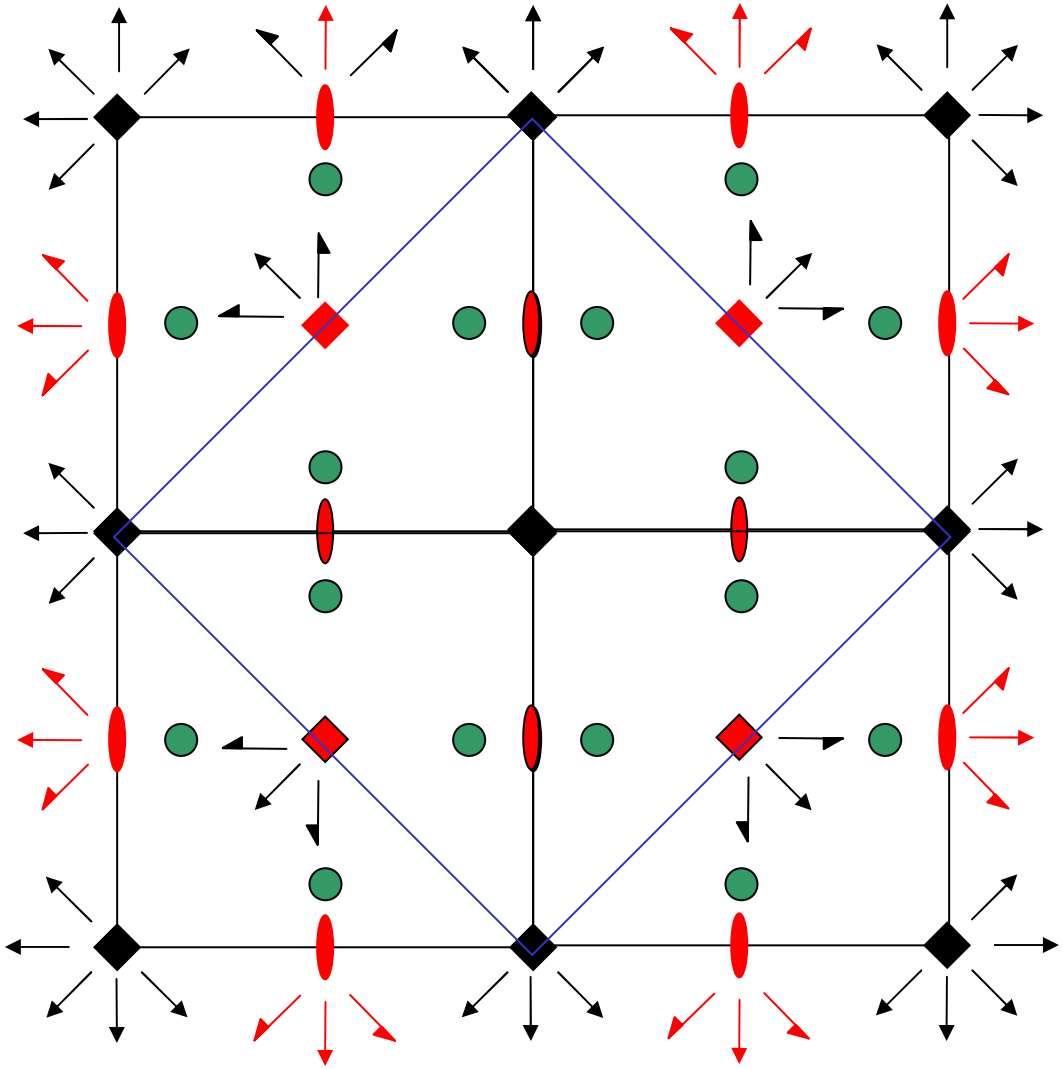
Special position: 4o [.2.] x, ½, 0

C22'2'

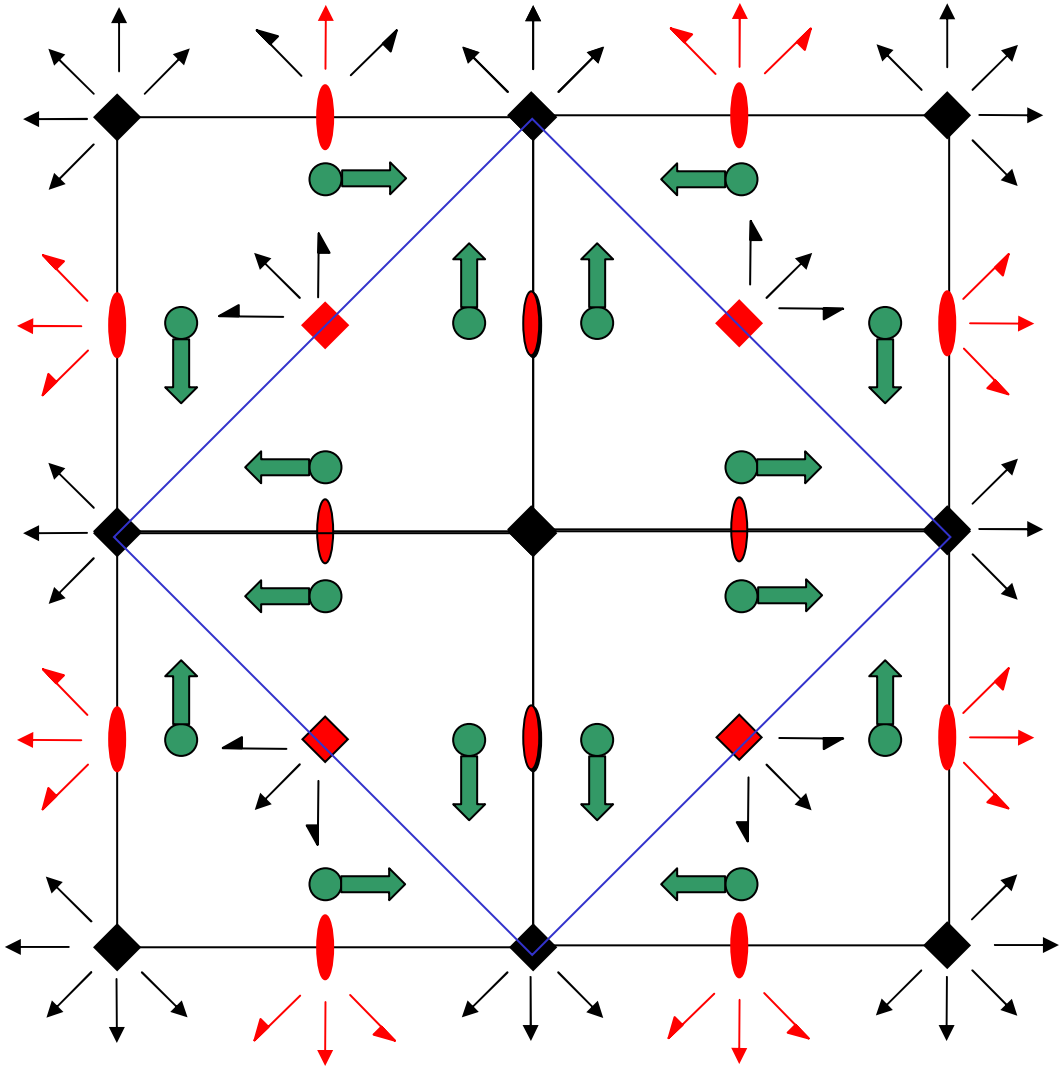


Special position: 4o [.2.] x, ½, 0

P_P422

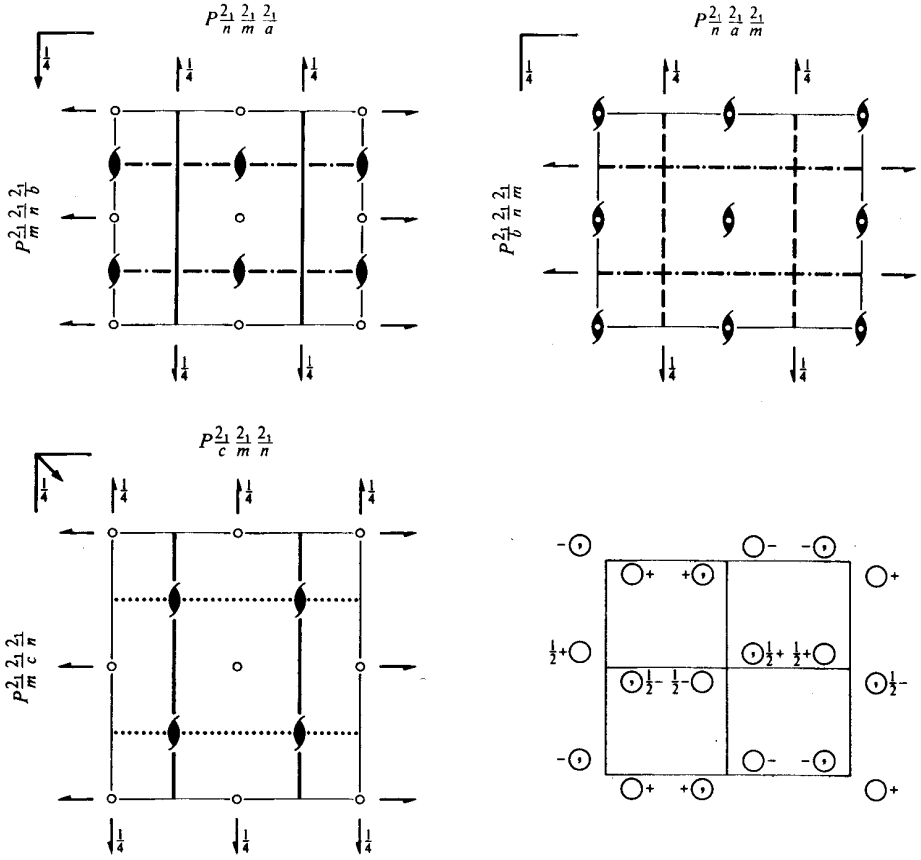


P_P422



$Pnma$ D_{2h}^{16} mmm Orthorhombic

No. 62 $P\,2_1/n\,2_1/m\,2_1/a$ Patterson symmetry $Pmmm$



Origin at $\bar{1}$ on $1\,2_1\,1$

Asymmetric unit $0\le x\le \frac{1}{2};\ 0\le y\le \frac{1}{4};\ 0\le z\le 1$

Symmetry operations

(1) 1
(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$
(3) $2(0,\frac{1}{2},0)$ $0,y,0$
(4) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$
(5) $\bar{1}$ $0,0,0$
(6) a $x,y,\frac{1}{4}$
(7) m $x,\frac{1}{4},z$
(8) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	*d*	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$ (6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}$ (7) $x,\bar{y}+\frac{1}{2},z$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$ (8) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2}$	$0kl$: $k+l=2n$ $hk0$: $h=2n$ $h00$: $h=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
4	*c*	$.m.$	$x,\frac{1}{4},z$	$\bar{x}+\frac{1}{2},\frac{3}{4},z+\frac{1}{2}$	$\bar{x},\frac{3}{4},\bar{z}$	$x+\frac{1}{2},\frac{1}{4},\bar{z}+\frac{1}{2}$	no extra conditions
4	*b*	$\bar{1}$	$0,0,\frac{1}{2}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	hkl : $h+l,k=2n$
4	*a*	$\bar{1}$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	hkl : $h+l,k=2n$

Symmetry of special projections

Along [001] $p\,2g\,m$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $c\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,\frac{1}{4},\frac{1}{4}$

Along [010] $p\,2g\,g$
$\boldsymbol{a}'=\boldsymbol{c}$ $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I
[2]$P\,2_1\,2_1\,2_1$ 1; 2; 3; 4
[2]$P\,1\,1\,2_1/a$ ($P\,2_1/c$) 1; 2; 5; 6
[2]$P\,1\,2_1/m\,1$ ($P\,2_1/m$) 1; 3; 5; 7
[2]$P\,2_1/n\,1\,1$ ($P\,2_1/c$) 1; 4; 5; 8
[2]$P\,n\,m\,2_1$ ($P\,m\,n\,2_1$) 1; 2; 7; 8
[2]$P\,n\,2_1\,a$ ($P\,n\,a\,2_1$) 1; 3; 6; 8
[2]$P\,2_1\,m\,a$ ($P\,m\,c\,2_1$) 1; 4; 6; 7

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

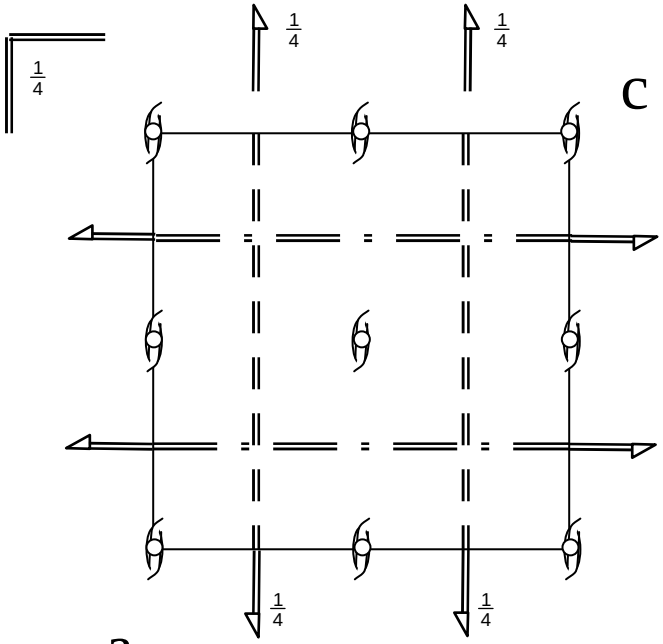
IIc [3]$P\,n\,m\,a$($\boldsymbol{a}'=3\boldsymbol{a}$); [3]$P\,n\,m\,a$($\boldsymbol{b}'=3\boldsymbol{b}$); [3]$P\,n\,m\,a$($\boldsymbol{c}'=3\boldsymbol{c}$)

Minimal non-isomorphic supergroups

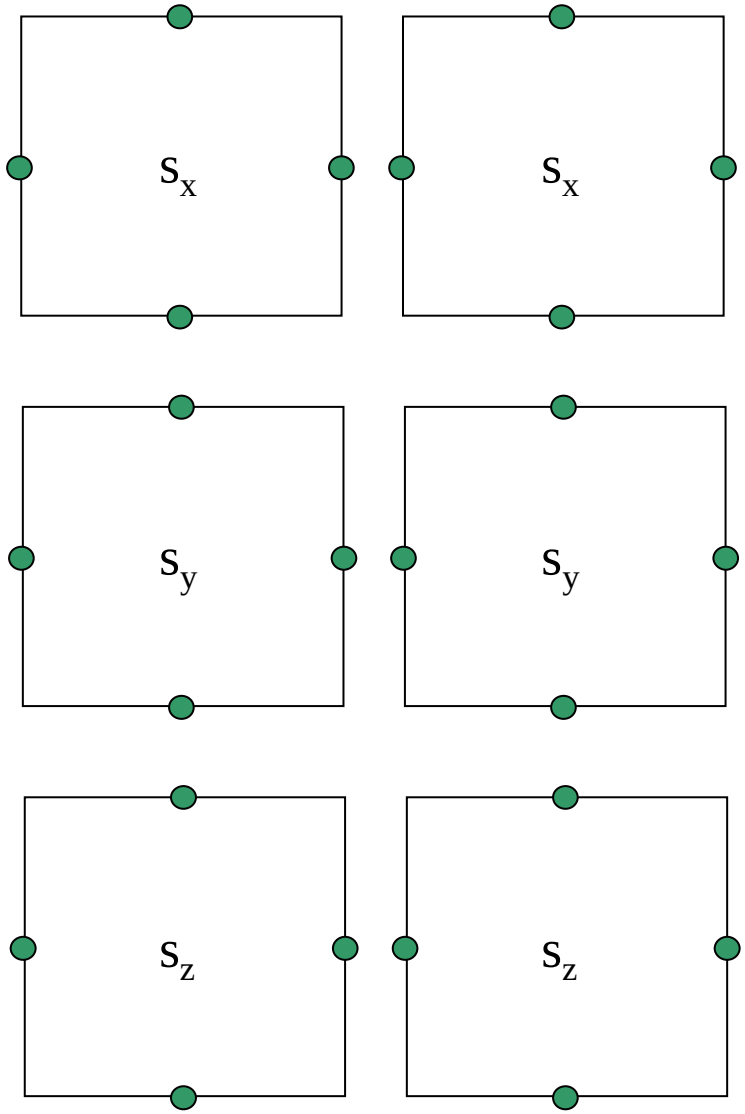
I none

II [2]$A\,m\,m\,a$($C\,m\,c\,m$); [2]$B\,b\,m\,m$($C\,m\,c\,m$); [2]$C\,c\,m\,b$($C\,m\,c\,a$); [2]$I\,m\,m\,a$; [2]$P\,n\,m\,m$($2\boldsymbol{a}'=\boldsymbol{a}$)($P\,m\,m\,n$); [2]$P\,c\,m\,a$($2\boldsymbol{b}'=\boldsymbol{b}$)($P\,b\,a\,m$); [2]$P\,b\,m\,a$($2\boldsymbol{c}'=\boldsymbol{c}$)($P\,b\,c\,m$)

Pnma (Pbnm)

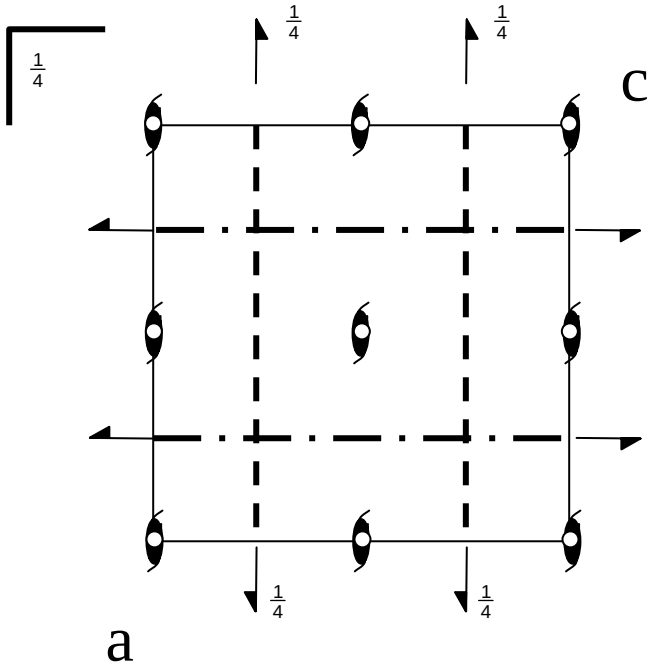


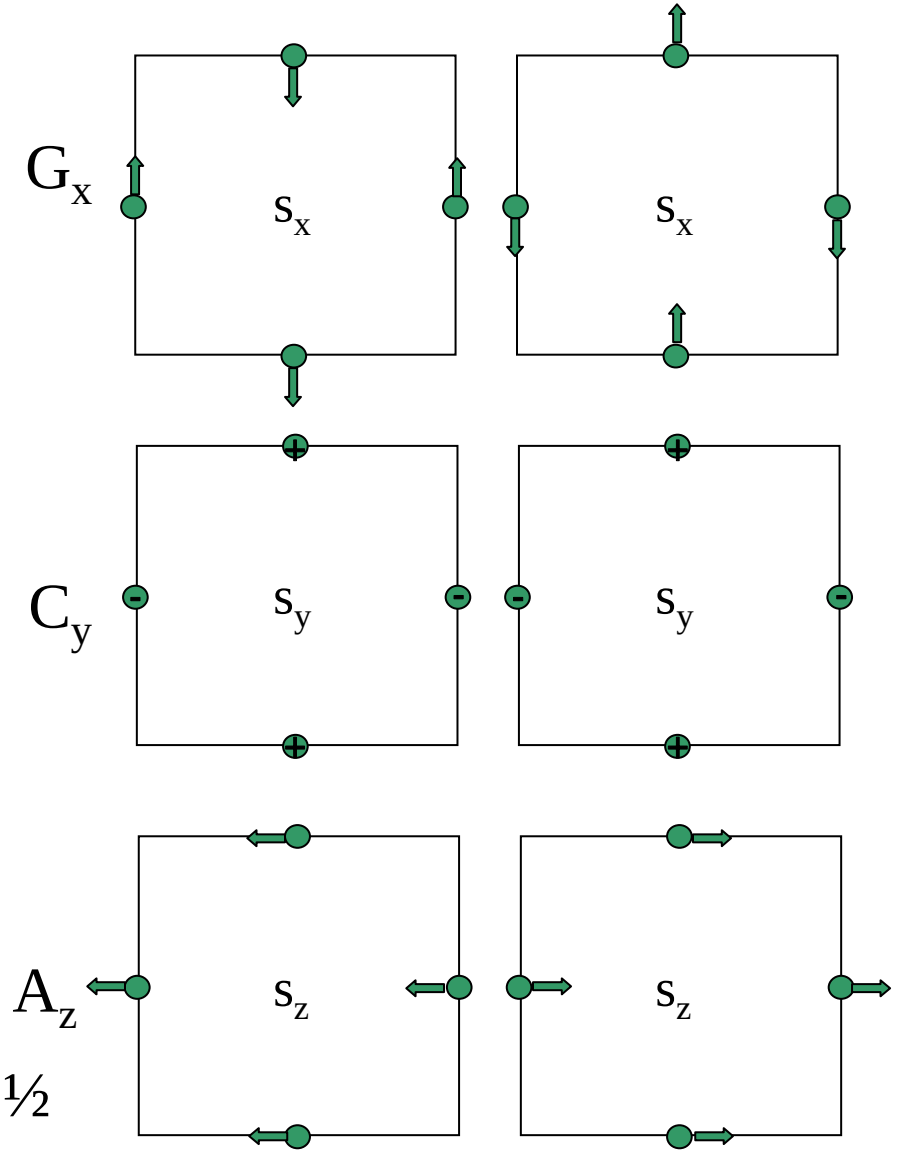
Special position: 4b [$\bar{1}$] 0,0, ½



y=0 y= ½

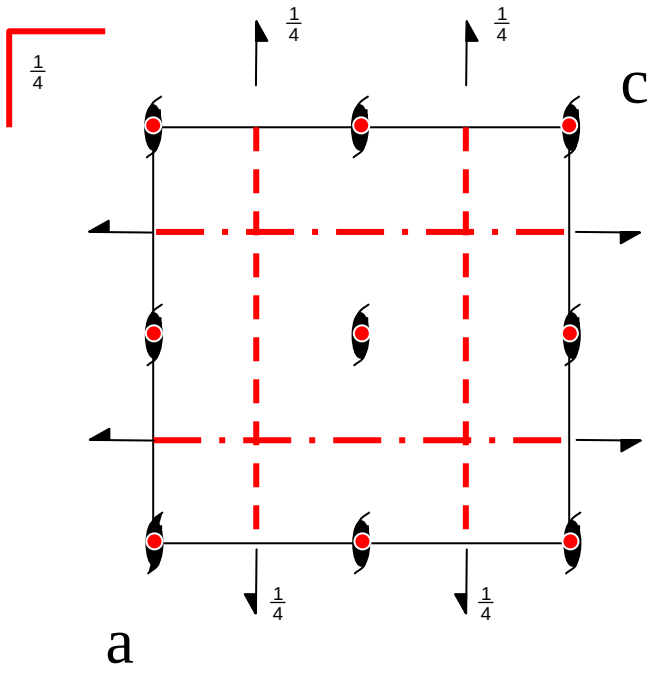
Pnma (Pbnm)



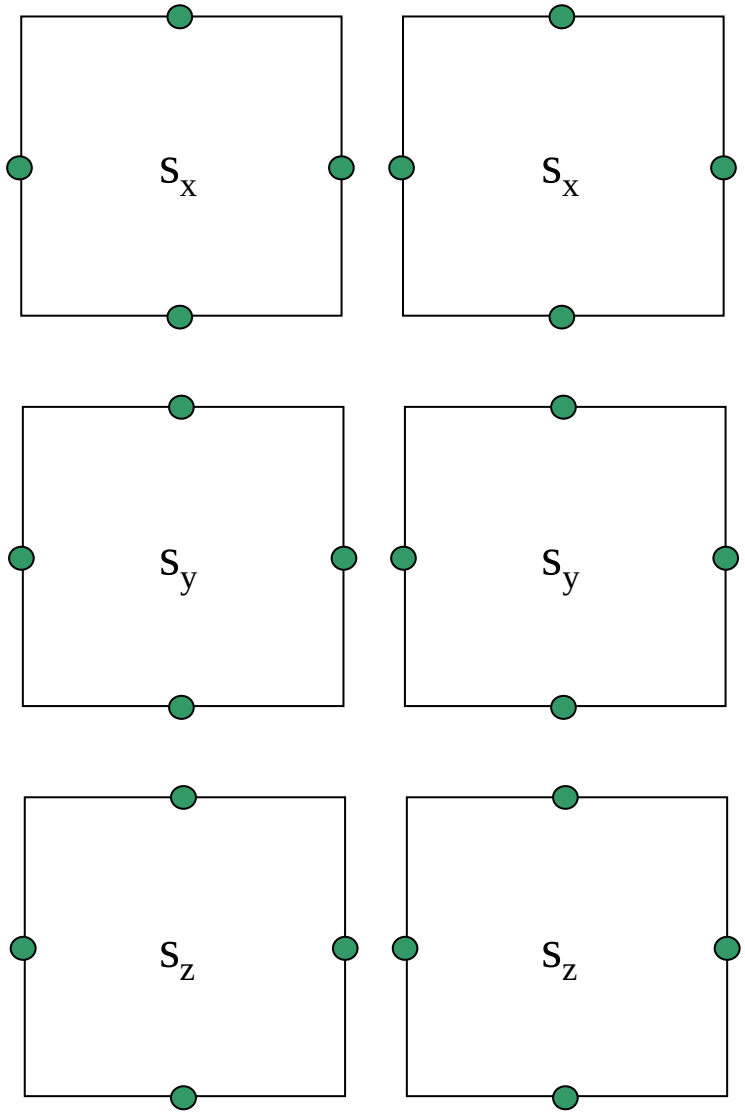


Special position: 4b [$\bar{1}$] 0,0, ½

Pn'm'a' (Pb'n'm')

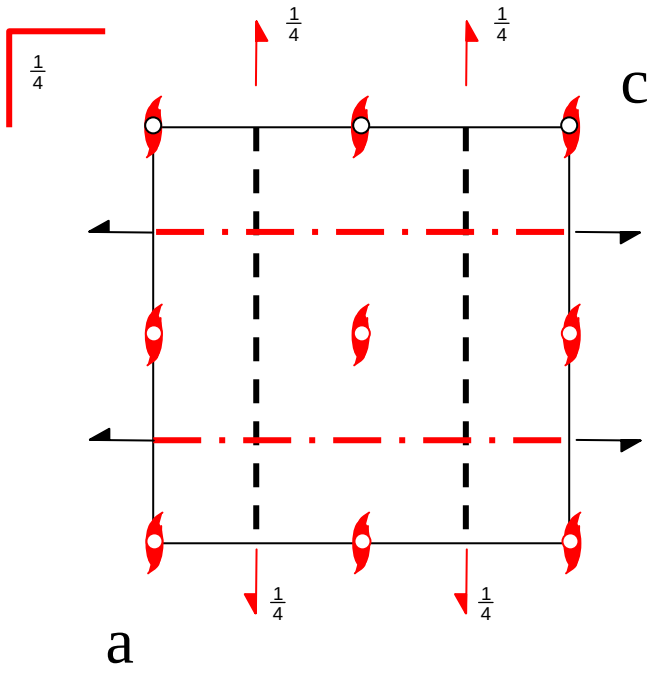


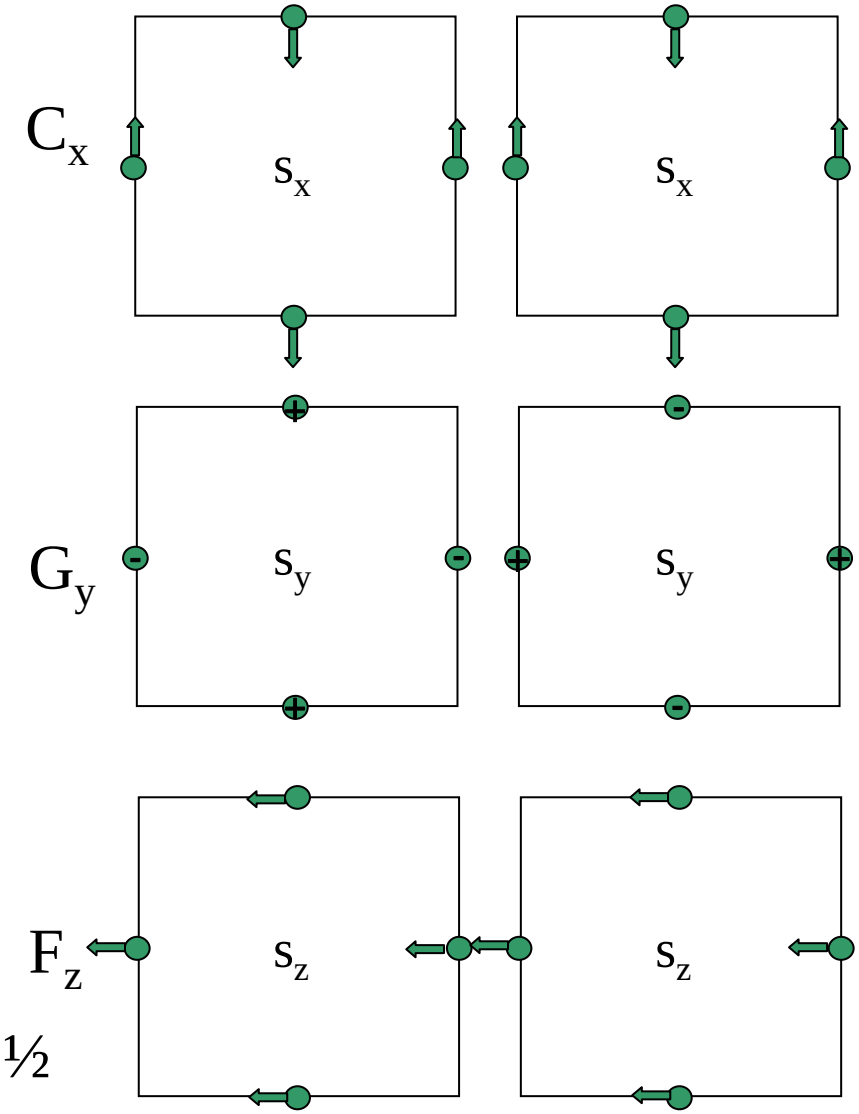
Special position: 4b [$\bar{1}$] 0,0, ½



y=0 y= ½

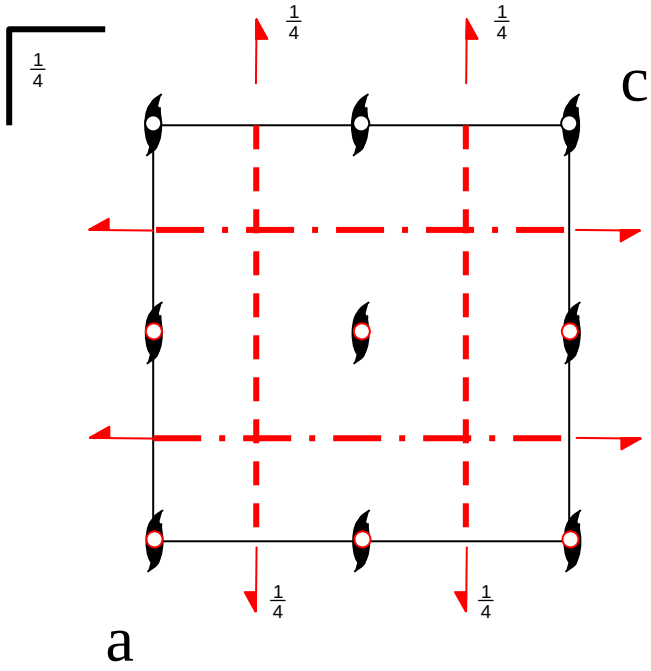
Pn'm'a (Pb n'm')

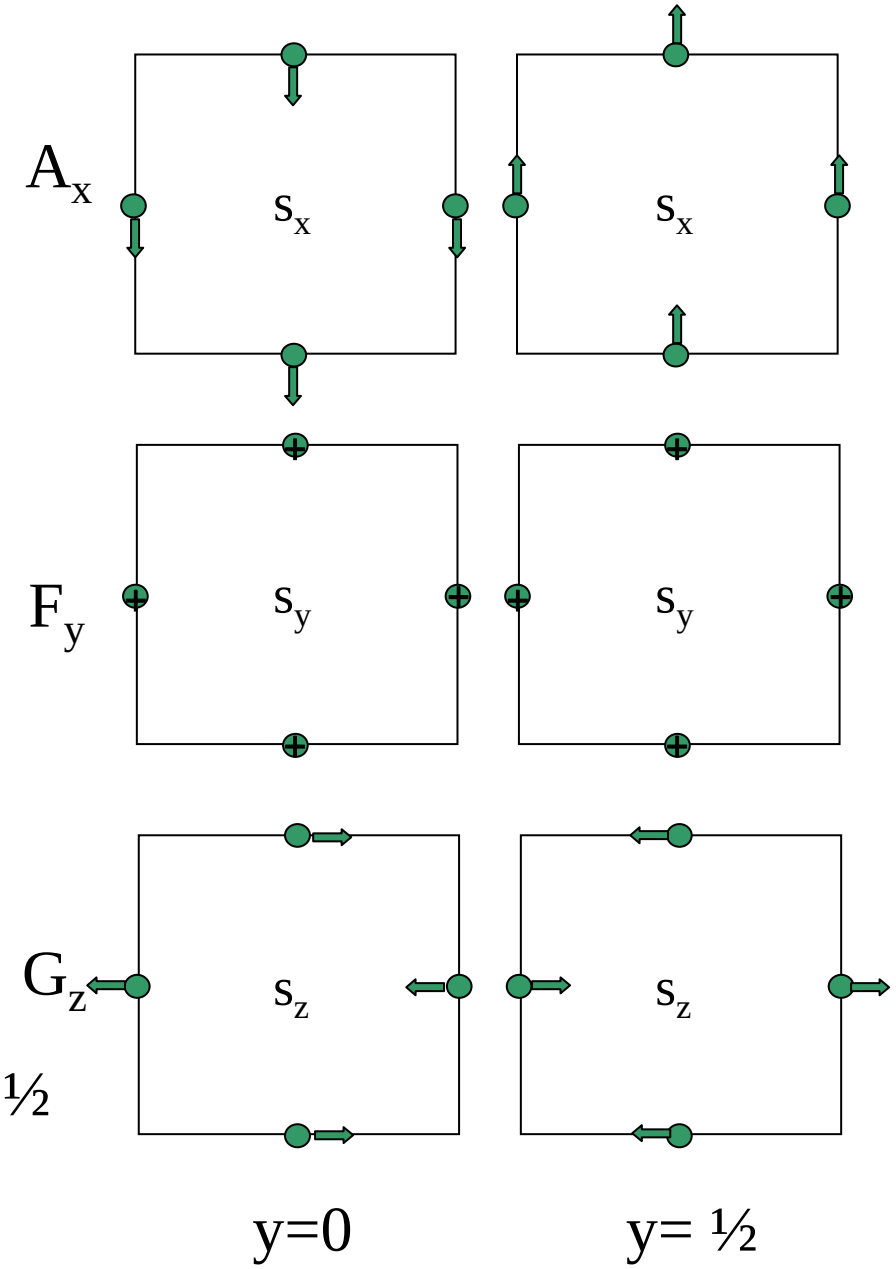




Special position: 4b [$\bar{1}$] 0,0, ½

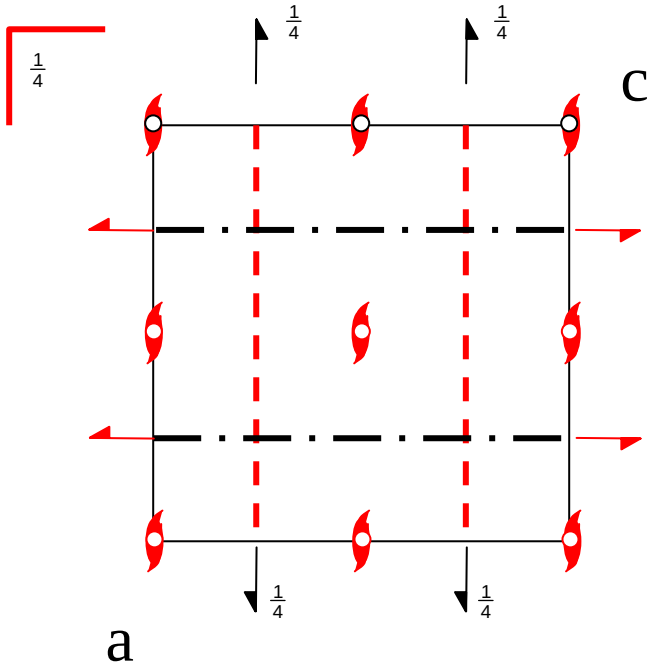
Pn'ma' (Pb' n'm)

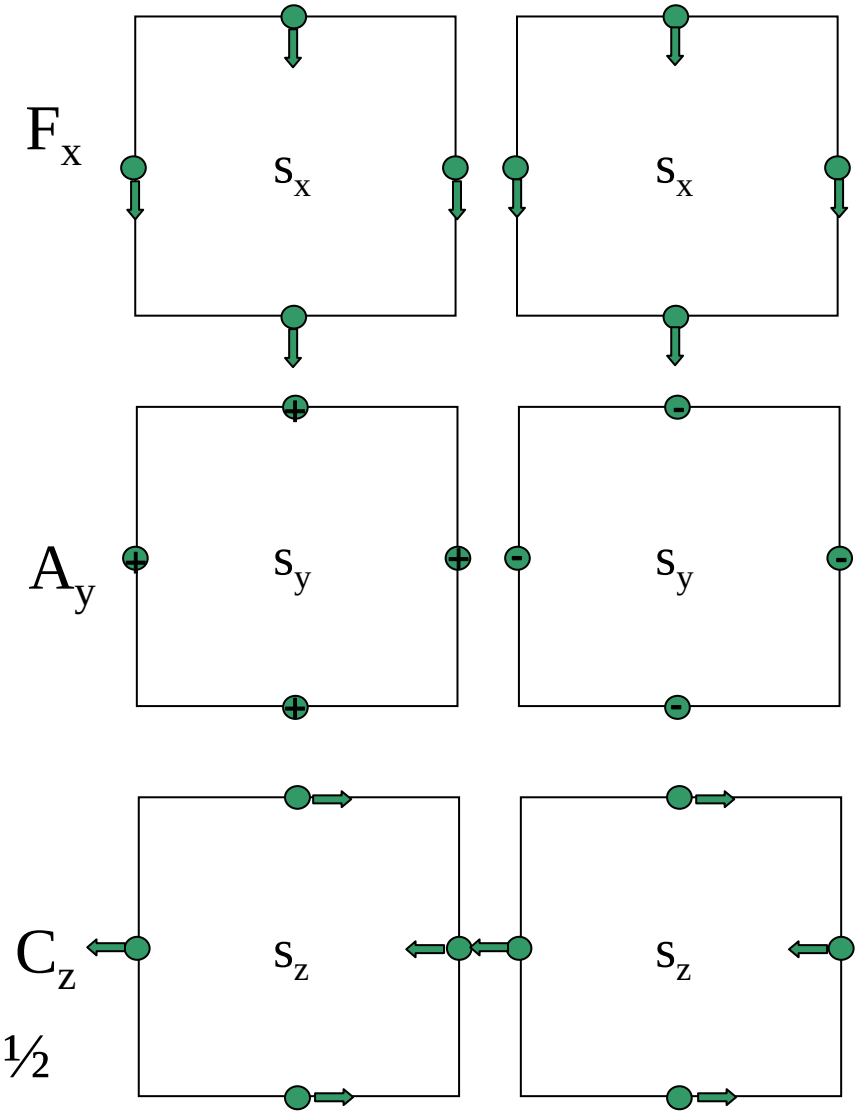




Special position: 4b [$\bar{1}$] 0,0, ½

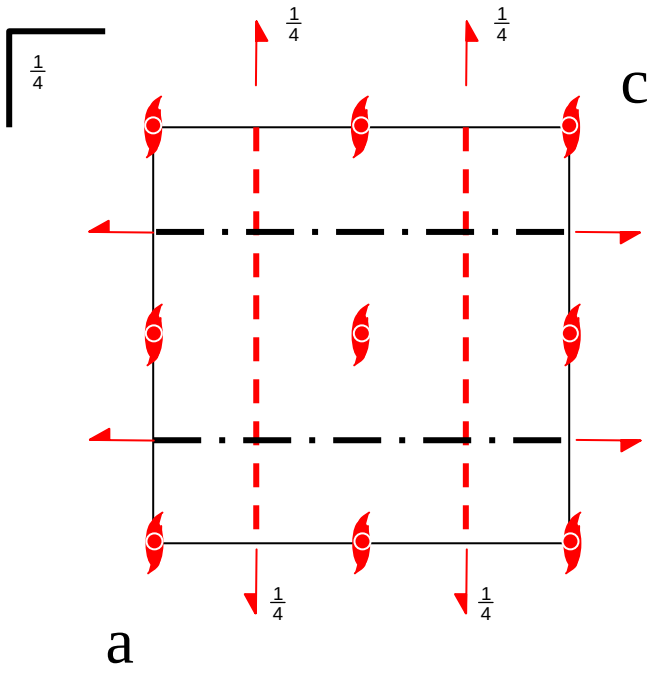
Pnm'a' (Pb'nm')



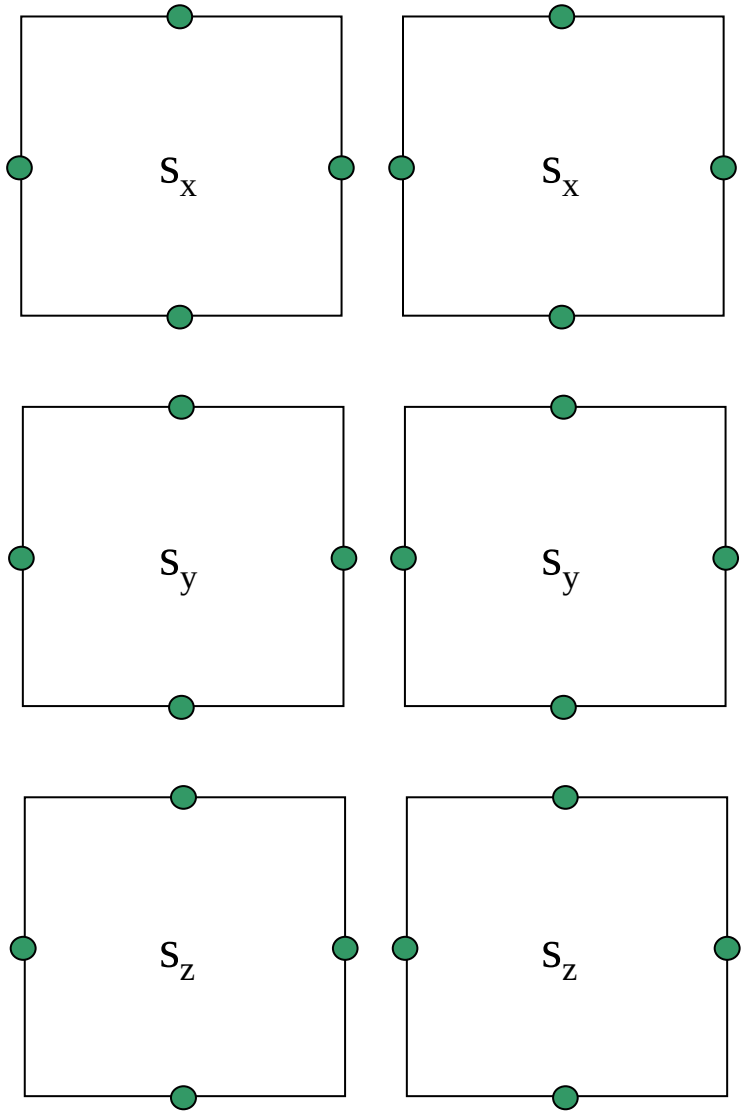


Special position: 4b [$\bar{1}$] 0,0, ½

Pnma' (Pb'nm)

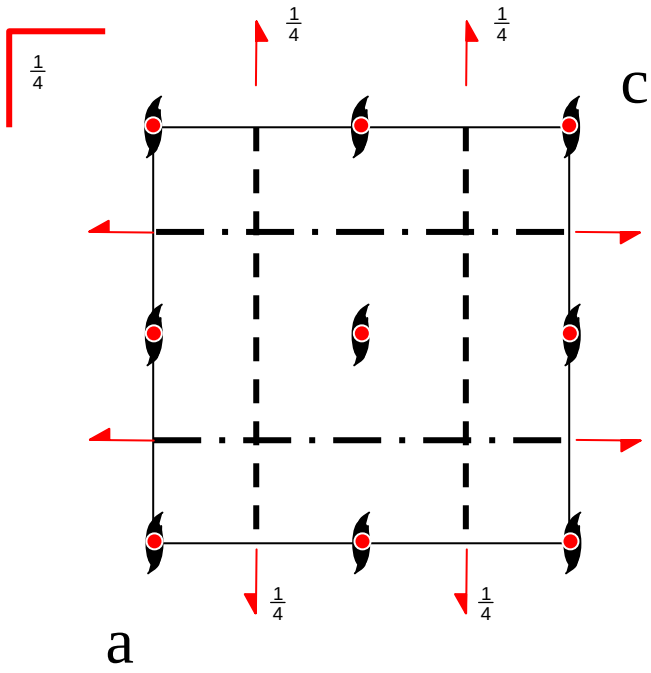


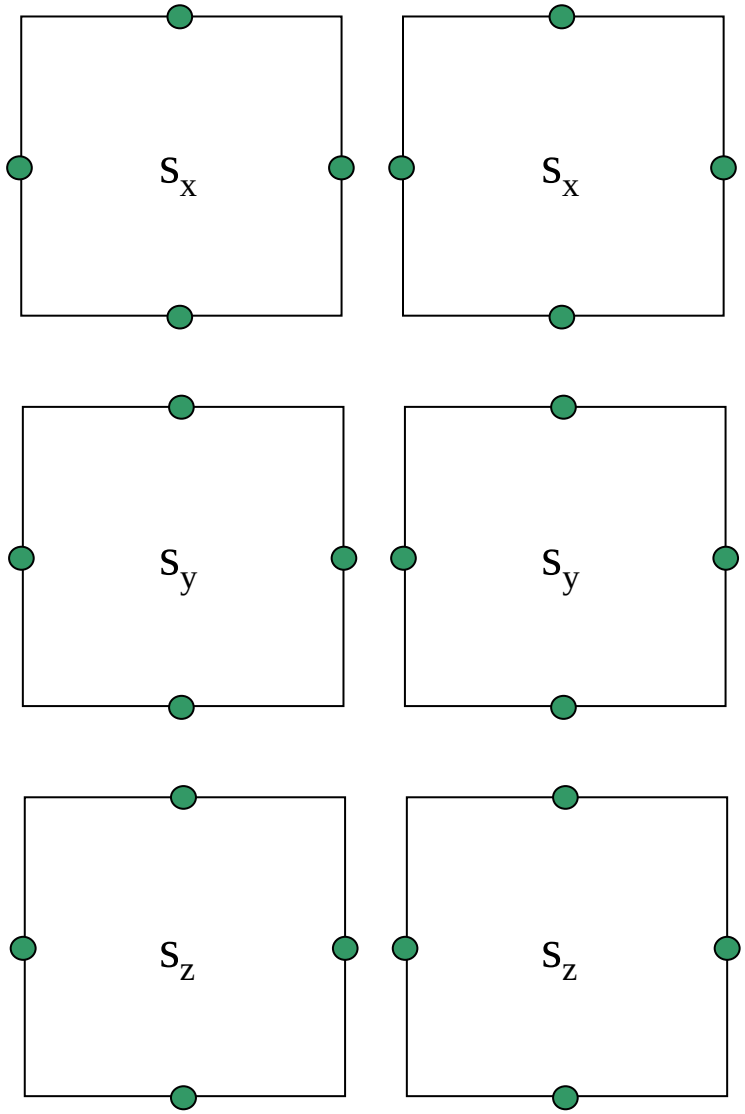
Special position: 4b [$\bar{1}$] 0,0, ½



y=0 y= ½

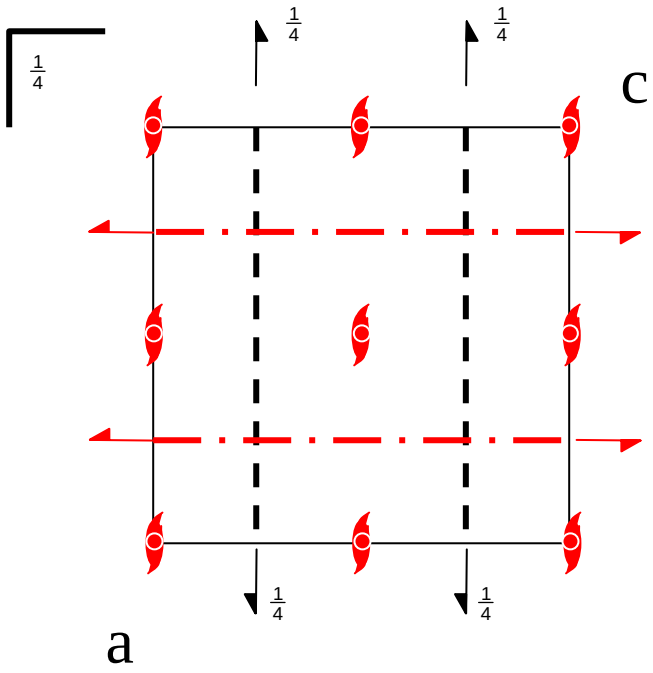
Pnm'a (Pbnm')

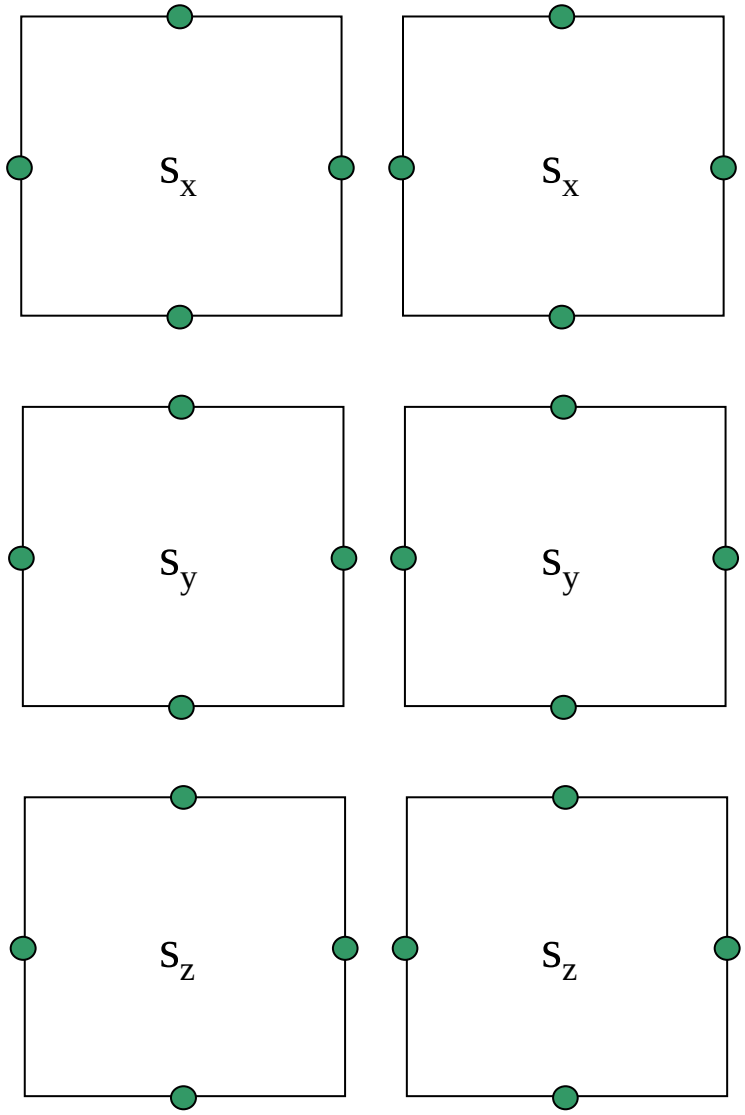




Special position: 4b [$\bar{1}$] 0,0, ½

Pn'ma (Pbn'm)





Special position: 4b [$\bar{1}$] 0,0, ½

y=0 y= ½

Magnetic Refinements in GSAS

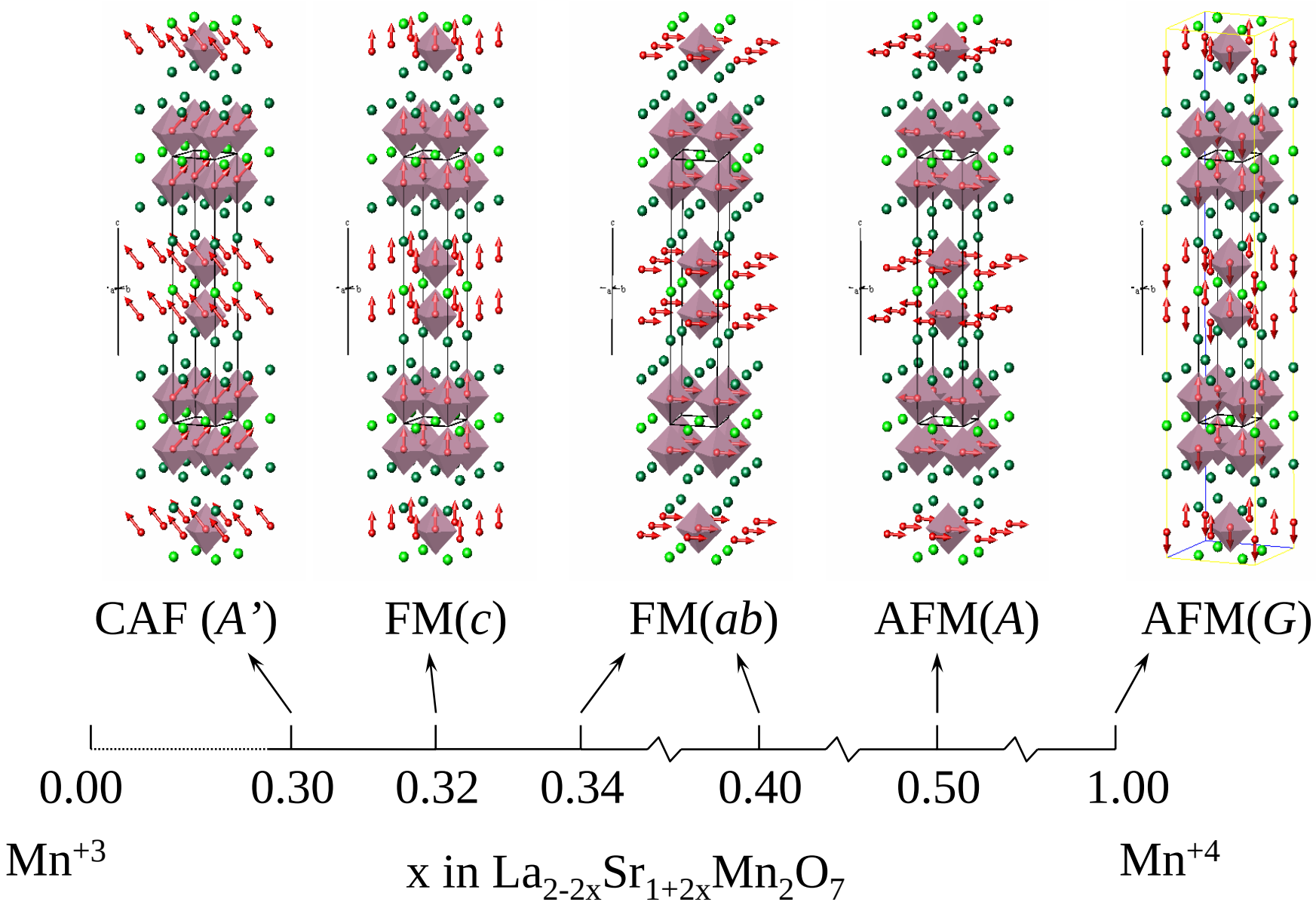
Paolo G. Radaelli

GSAS magnetic options

- The approach of GSAS to magnetic structures is loosely based on Shubnikov groups.
- However, for each space group, not all Shubnicov groups generated from it are possible. The only possible ones are those corresponding to subgroups of index 2 of types I and IIa. In other words, the *conventional* unit cell must be in common between the parent group and the subgroup.
- In GSAS there is a straight implementation of the OG formalism, where 'primed' operators (or lattices) correspond to 'red' operators.
- Alternatively, one can always generate an additional magnetic phase with appropriate constraints.

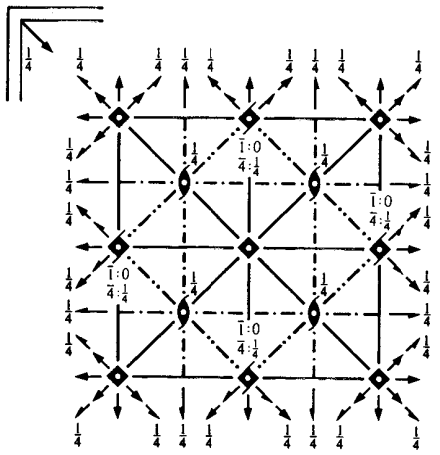
GSAS magnetic entries

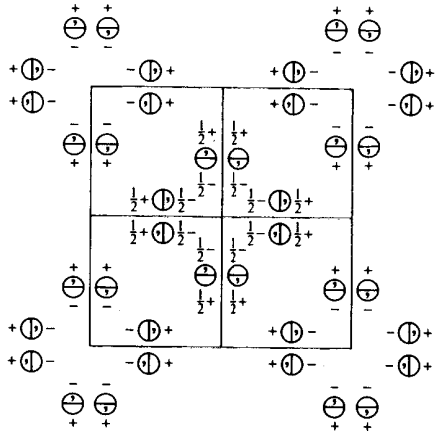
- **Phase**: in the "phase" menu (keystrokes **k-p-p**), one has the option of selecting (**m**) whether the phase is nuclear, nuclear *and* magnetic or purely magnetic (**a, b, c,** respectively).
- **Form factor**: in the form factor editing menu (**k-p-f**) there is an option (**m**) to edit magnetic form factors. One can use the default values (warning! They are different for different oxidation states) or input user values (see ITC, volume C).
- **Atoms**: in the atom editing menu (**k-l-a**) there is an option (**m**) to assign magnetic moments to individual atoms. Within that menu, there is an option (**s**) to 'prime' the group generators. GSAS automatically determines if the magnetic point group of the site is admissible, and, if so, for which spin directions. One can change colours with the **c** option. Once out of the **s** menu, one can change the spin components with the **m** option.


CAF (A')
FM(c)
FM(ab)
AFM(A)
AFM(G)
0.00
0.30
0.32
0.34
0.40
0.50
1.00
Mn+3
x in La2-2xSr1+2xMn2O7
Mn+4

$I\,4/m\,m\,m$ D_{4h}^{17} $4/m\,m\,m$ Tetragonal

No. 139 $I\,4/m\,2/m\,2/m$ Patterson symmetry $I\,4/m\,m\,m$





Origin at centre $(4/m\,m\,m)$

Asymmetric unit $0\le x\le\frac{1}{2};\ 0\le y\le\frac{1}{2};\ 0\le z\le\frac{1}{4};\ x\le y$

Symmetry operations

For (0,0,0)+ set

(1) 1	(2) 2 0,0,z	(3) 4^+ 0,0,z	(4) 4^- 0,0,z
(5) $\bar{2}$ 0,y,0	(6) 2 x,0,0	(7) $\bar{2}$ x,x,0	(8) $\bar{2}$ x,$\bar{x}$,0
(9) $\bar{1}$ 0,0,0	(10) m x,y,0	(11) $\bar{4}^+$ 0,0,z; 0,0,0	(12) $\bar{4}^-$ 0,0,z; 0,0,0
(13) m x,0,z	(14) m 0,y,z	(15) m x,$\bar{x}$,z	(16) m x,x,z

For $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$ set

(1) $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	(2) $2(0,0,\frac{1}{2})$ $\frac{1}{4},\frac{1}{4},z$	(3) $4^+(0,0,\frac{1}{2})$ $0,\frac{1}{4},z$	(4) $4^-(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$
(5) $\bar{2}(0,\frac{1}{2},0)$ $\frac{1}{4},y,\frac{1}{4}$	(6) $2(\frac{1}{2},0,0)$ $x,\frac{1}{4},\frac{1}{4}$	(7) $\bar{2}(\frac{1}{2},\frac{1}{2},0)$ $x,x,\frac{1}{4}$	(8) $\bar{2}$ $x,\bar{x}+\frac{1}{2},\frac{1}{4}$
(9) $\bar{1}$ $\frac{1}{4},\frac{1}{4},\frac{1}{4}$	(10) $n(\frac{1}{2},\frac{1}{2},0)$ $x,y,\frac{1}{4}$	(11) $\bar{4}^+$ $\frac{1}{2},0,z$; $\frac{1}{2},0,\frac{1}{4}$	(12) $\bar{4}^-$ $0,\frac{1}{2},z$; $0,\frac{1}{2},\frac{1}{4}$
(13) $n(\frac{1}{2},0,\frac{1}{2})$ $x,\frac{1}{4},z$	(14) $n(0,\frac{1}{2},\frac{1}{2})$ $\frac{1}{4},y,z$	(15) c $x+\frac{1}{2},\bar{x},z$	(16) $n(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ x,x,z

---

Maximal non-isomorphic subgroups (*continued*)

IIa	[2]$P\,4/m\,m\,m$	1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16
	[2]$P\,4/n\,n\,c$	1; 2; 3; 4; 5; 6; 7; 8; (9; 10; 11; 12; 13; 14; 15; 16)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4/m\,n\,c$	1; 2; 3; 4; 9; 10; 11; 12; (5; 6; 7; 8; 13; 14; 15; 16)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4/n\,m\,m$	1; 2; 3; 4; 13; 14; 15; 16; (5; 6; 7; 8; 9; 10; 11; 12)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4_2/n\,n\,m$	1; 2; 5; 6; 11; 12; 15; 16; (3; 4; 7; 8; 9; 10; 13; 14)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4_2/n\,m\,c$	1; 2; 7; 8; 11; 12; 13; 14; (3; 4; 5; 6; 9; 10; 15; 16)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4_2/m\,m\,c$	1; 2; 5; 6; 9; 10; 13; 14; (3; 4; 7; 8; 11; 12; 15; 16)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2]$P\,4_2/m\,n\,m$	1; 2; 7; 8; 9; 10; 15; 16; (3; 4; 5; 6; 11; 12; 13; 14)+$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [3]$I\,4/m\,m\,m\,(\boldsymbol{c}'=3\boldsymbol{c})$; [9]$I\,4/m\,m\,m\,(\boldsymbol{a}'=3\boldsymbol{a},\boldsymbol{b}'=3\boldsymbol{b})$

Minimal non-isomorphic supergroups

I [3]$F\,m\,\bar{3}\,m$; [3]$I\,m\,\bar{3}\,m$

II [2]$C\,4/m\,m\,m\,(2\boldsymbol{c}'=\boldsymbol{c})\,(P\,4/m\,m\,m)$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5); (9)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates (0,0,0)+		(½,½,½)+		Reflection conditions
							General:
32	*o*	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	hkl : $h+k+l=2n$
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(7) $y,x,\bar{z}$	(8) $\bar{y},\bar{x},\bar{z}$	$hk0$: $h+k=2n$
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x,y,\bar{z}$	(11) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	$0kl$: $k+l=2n$
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	hhl : $l=2n$
							$00l$: $l=2n$
							$h00$: $h=2n$
							Special: as above, plus
16	*n*	.*m*.	$0,y,z$	$0,\bar{y},z$	$\bar{y},0,z$	$y,0,z$	no extra conditions
			$0,y,\bar{z}$	$0,\bar{y},\bar{z}$	$y,0,\bar{z}$	$\bar{y},0,\bar{z}$	
16	*m*	..*m*	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
			$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
16	*l*	*m*..	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
			$\bar{x},y,0$	$x,\bar{y},0$	$y,x,0$	$\bar{y},\bar{x},0$	
16	*k*	..2	$x,x+\frac{1}{2},\frac{1}{4}$	$\bar{x},\bar{x}+\frac{1}{2},\frac{1}{4}$	$\bar{x}+\frac{1}{2},x,\frac{1}{4}$	$x+\frac{1}{2},\bar{x},\frac{1}{4}$	hkl : $l=2n$
			$\bar{x},\bar{x}+\frac{1}{2},\frac{3}{4}$	$x,x+\frac{1}{2},\frac{3}{4}$	$x+\frac{1}{2},\bar{x},\frac{3}{4}$	$\bar{x}+\frac{1}{2},x,\frac{3}{4}$	
8	*j*	*m*2*m*.	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
8	*i*	*m*2*m*.	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
8	*h*	*m*.2*m*	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
8	*g*	2*mm*.	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $l=2n$
8	*f*	..2/*m*	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{1}{4}$	$\frac{3}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{3}{4},\frac{1}{4}$	hkl : $k,l=2n$
4	*e*	4*mm*	$0,0,z$	$0,0,\bar{z}$			no extra conditions
4	*d*	$\bar{4}m2$	$0,\frac{1}{2},\frac{1}{4}$	$\frac{1}{2},0,\frac{1}{4}$			hkl : $l=2n$
4	*c*	*mmm*.	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			hkl : $l=2n$
2	*b*	4/*mmm*	$0,0,\frac{1}{2}$				no extra conditions
2	*a*	4/*mmm*	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4m\,m$
$\boldsymbol{a}'=\frac{1}{2}(\boldsymbol{a}-\boldsymbol{b})$ $\boldsymbol{b}'=\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b})$
Origin at $0,0,z$

Along [100] $c\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [110] $p\,2m\,m$
$\boldsymbol{a}'=\frac{1}{2}(-\boldsymbol{a}+\boldsymbol{b})$ $\boldsymbol{b}'=\frac{1}{2}\boldsymbol{c}$
Origin at $x,x,0$

Maximal non-isomorphic subgroups

I	[2]$I\,4\,2\,2$	(1; 2; 3; 4; 5; 6; 7; 8)+
	[2]$I\,4/m\,1\,1$ ($I\,4/m$)	(1; 2; 3; 4; 9; 10; 11; 12)+
	[2]$I\,4m\,m$	(1; 2; 3; 4; 13; 14; 15; 16)+
	[2]$I\,\bar{4}\,2m$	(1; 2; 5; 6; 11; 12; 15; 16)+
	[2]$I\,\bar{4}m\,2$	(1; 2; 7; 8; 11; 12; 13; 14)+
	[2]$I\,2/m\,2/m\,1$ ($I\,m\,m\,m$)	(1; 2; 5; 6; 9; 10; 13; 14)+
	[2]$I\,2/m\,1\,2/m$ ($F\,m\,m\,m$)	(1; 2; 7; 8; 9; 10; 15; 16)+

(*Continued on preceding page*)

Notes on the Layered Manganite example

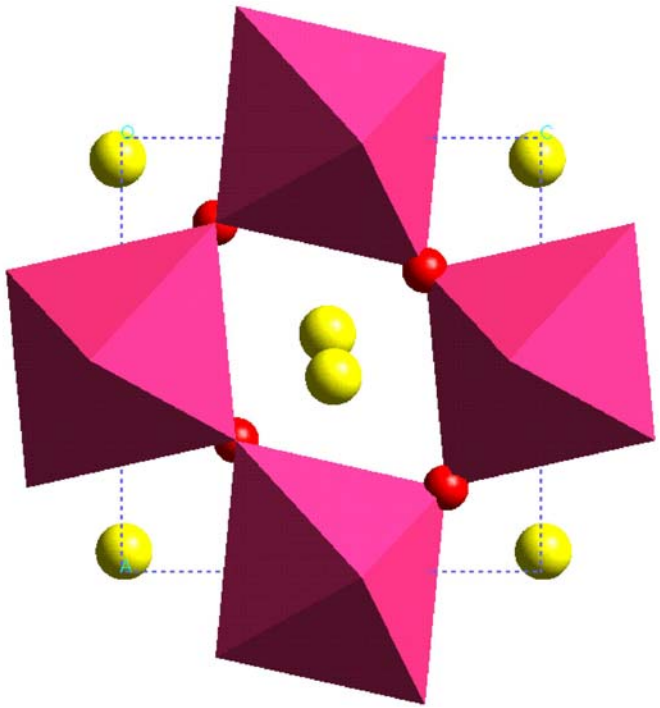
- The manganite site is 4e [4mm]. Of the magnetic subgroups of [4mm], the only admissible one is 4m'm'. Consequently, the only possible magnetic space groups are *I4/mm'm' I4/m'm'm', I_P4/mm'm' and I_P4/m'm'm'. Note that the first one is a ferromagnetic group.
- An immediate consequence of the site symmetry of the Mn site is that the spin *has* to be directed along the 4-fold axis.
- There are therefore only 4 magnetic structures generated with the Shubnikov approach. The layers are *always* FM, with the intra- and inter-bilayer coupling being FM or AFM.
- Note the significant number of magnetic structures which are observed, but cannot be generated with the Shubnikov approach.

Magnetic refinements - multi-phase approach

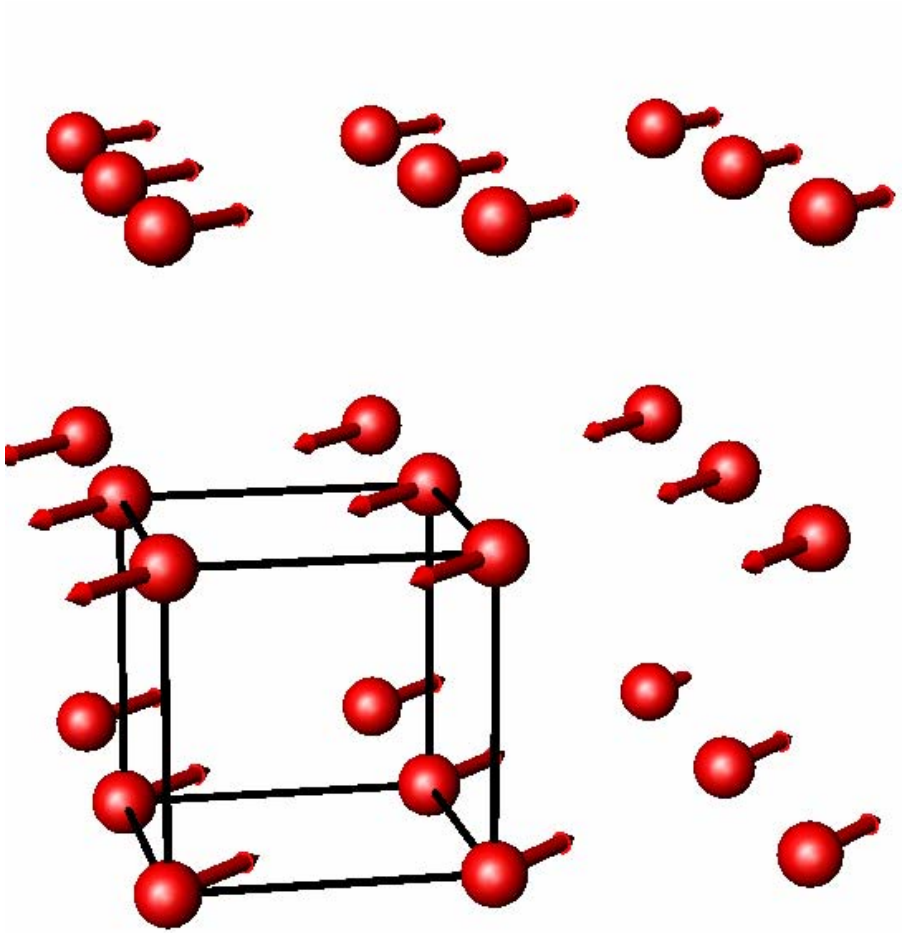
Should the Shubnikov approach be insufficient to describe the magnetic structure, one can resort to introducing a second *purely magnetic* phase with appropriate constraints but lower symmetry This enables one to deal with any kind of commensurate structure, including the representation analysis. Here are a few tips:

1. If the magnetic phase has the same conventional cell as the nuclear one, the lattice and phase fraction constraints are straightforward.
2. If the magnetic cell is *larger* than the nuclear one, one has to remember that the phase fraction is proportional to the number of unit cells in the sample. So, if the the volume of the MP is doubled, its phase fraction must be halved.
3. One can also set constraints on the lattice when the two cells are different. However, remember that the constraints are on the reciprocal metric tensor, *not* on lattice parameters. Consult a crystallography book to see how they are related for the various lattices.

Shubnikov Groups: a GSAS application



Pnma



Magnetic powder diffraction and instrumentation

Paolo G. Radaelli

Spin Density

Unit-Cell Spin Density (localised and isotropic approx.):

$$\mathbf{M}_u(\mathbf{r}) = \sum_{j=1}^{\text{n atoms}} \hat{\mathbf{m}}_j \mu_j G_j\left(\left|\mathbf{r}-\mathbf{r}_j\right|\right) \qquad \tilde{\mathbf{M}}_u(\mathbf{k}) = \sum_{j=1}^{\text{n atoms}} \hat{\mathbf{m}}_j \mu_j f_j(k) \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_j}$$

Lattice Spin Density (simple translational symmetry):

$$\mathbf{M}(\mathbf{r}) = \sum_{\mathbf{r}_n} \mathbf{M}_u\left(\mathbf{r}-\mathbf{r}_n\right) \qquad \tilde{\mathbf{M}}(\mathbf{k}) = \sum_{\boldsymbol{\kappa}\in\Gamma^*} \delta\left(\boldsymbol{\kappa}-\mathbf{k}\right) \sum_{j=1}^{\text{n atoms}} \hat{\mathbf{m}}_j \mu_j f_j(k) \mathrm{e}^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_j}$$

Lattice Spin Density (1-dimensional modulation):

$$\mathbf{M}(\mathbf{r}) = \sum_{\mathbf{r}_n} \overline{\overline{P}}\left(\mathbf{r}_n\cdot\boldsymbol{\tau}\right)\cdot\mathbf{M}_u\left(\mathbf{r}-\mathbf{r}_n\right) \quad \tilde{\mathbf{M}}(\mathbf{k}) = \sum_{\substack{\boldsymbol{\kappa}\in\Gamma^* \\ l=-\infty,+\infty}} \delta\left(\boldsymbol{\kappa}-l\boldsymbol{\tau}-\mathbf{k}\right) \sum_{j=1}^{\text{n atoms}} \left(\overline{\overline{A}}_l\cdot\hat{\mathbf{m}}_j\right)\mu_j f_j(k) \mathrm{e}^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_j}$$

where $\overline{\overline{P}}(x) = \sum_{l=-\infty}^{+\infty} \overline{\overline{A}}_l \, \mathrm{e}^{ilx}$ has a periodicity of 1.

Magnetic Scattering of Neutrons

Neutrons are strongly scattered from magnetic moments. The scattering <u>amplitude</u> from an ion is of the order of $\gamma r_e \mu$, where:

$\gamma = -1.91$ Neutron magnetic moment in nuclear magnetons (spin + orbital).

$r_e = 0.282 \cdot 10^{-12}$ *cm* Electron classical radius ($e^2/m_e c^2$)

μ = ion magnetic moment in Bohr magnetons.

For comparison, typical nuclear scattering amplitudes for neutrons are of the order of $0.5\text{-}1.0 \cdot 10^{-12}$ *cm*.

Magnetic Scattering of Neutrons- II

Let's recall the formula for the lattice spin density and its Fourier transform:

$$\mathbf{M}(\mathbf{r}) = \sum_{\mathbf{r}_n} \mathbf{M}_u(\mathbf{r} - \mathbf{r}_n) \qquad \tilde{\mathbf{M}}(\mathbf{k}) = \sum_{\boldsymbol{\kappa} \in \Gamma^*} \delta(\boldsymbol{\kappa} - \mathbf{k}) \sum_{j=1}^{\text{n atoms}} \hat{\mathbf{m}}_j \mu_j f_j(k) \mathrm{e}^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_j}$$

The Fourier transform $\tilde{\mathbf{M}}(\mathbf{k})$ is called magnetic structure factor. Unlike the nuclear structure factor, it is an axial vector quantity, and it has to be combined with the other vector quantity in the problem in order to obtain the cross section, which is a scalar. The other vector quantities are the momentum transfer **k** (a conventional vector) and the neutron spin $\mathbf{s}_n$ (an axial vector).

The Magnetic Form Factor

$$f(\mathbf{k}) = \frac{\left\langle q \left| \int \mathbf{M}(\mathbf{r}) \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}}\, dr^3 \right| q \right\rangle}{\left\langle q \left| \int \mathbf{M}(\mathbf{r}) dr^3 \right| q \right\rangle}$$ **over a single atom**

In the isotropic case:

$$f(\mathbf{k}) = f(k) = \langle j_0(k) \rangle + \left(1 - \tfrac{2}{g}\right) \langle j_2(k) \rangle$$

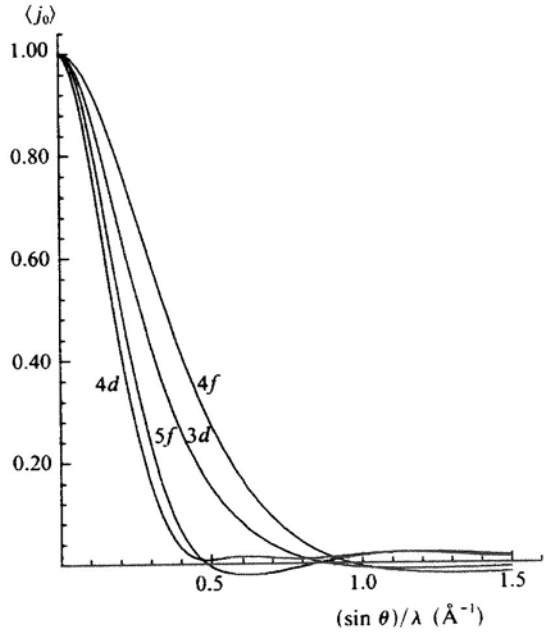


Fig. 6.1.2.2. Comparison of 3*d*, 4*d*, 4*f*, and 5*f* form factors. The 3*d* form factor is for Co, and the 4*d* for Rh, both calculated from wavefunctions given by Clementi & Roetti (1974). The 4*f* form factor is for Gd^{3+} calculated by Freeman & Desclaux (1972) and the 5*f* is that for U^{3+} given by Desclaux & Freeman (1978).

From: International Tables of Crystallography, Volume C, ed. by AJC Wilson, Kluwer Ac. Pub., 1998, p. 513

Scattering of Neutrons from MS

It is useful to introduce the quantity $\mathbf{Q}(\mathbf{k})$, known as magnetic interaction vector, and defined as:

$$\mathbf{Q}(\mathbf{k}) = \hat{\mathbf{k}} \times \tilde{\mathbf{M}}(\mathbf{k}) \times \hat{\mathbf{k}}$$

$\mathbf{Q}(\mathbf{k})$ is the projection of the magnetic structure factor upon the plane perpendicular to the momentum transfer $\mathbf{k}$. Magnetic neutron scattering cross sections only contain $\mathbf{Q}(\mathbf{k})$. In other words, scattering of neutrons through $\mathbf{k}$ is only determined by the components of the magnetic moments $\perp$ to $\mathbf{k}$. Note that $\mathbf{Q}(\mathbf{k})$ can be complex.

Magnetic Scattering Formulæ

Polarised neutrons - polarisation analysis

Non-flip $$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{++} = (\gamma r_e)^2\left\{\left|\hat{\mathbf{s}}_n \cdot \mathbf{Q}(\mathbf{k})\right|^2 + \left|F'(\mathbf{k})\right|^2 + \hat{\mathbf{s}}_n \cdot \left[\mathbf{Q}^*(\mathbf{k})F'(\mathbf{k}) + \mathbf{Q}(\mathbf{k})F'^*(\mathbf{k})\right]\right\}$$

Flip $$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{+-} = (\gamma r_e)^2\left\{\left[\hat{\mathbf{s}}_n \times \mathbf{Q}(\mathbf{k})\right] \cdot \left[\hat{\mathbf{s}}_n \times \mathbf{Q}^*(\mathbf{k})\right] + i\hat{\mathbf{s}}_n \cdot \left[\mathbf{Q}(\mathbf{k})^* \times \mathbf{Q}(\mathbf{k})\right]\right\}$$

Total $$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{\uparrow} = (\gamma r_e)^2\left\{\left|\mathbf{Q}(\mathbf{k})\right|^2 + \left|F'(\mathbf{k})\right|^2 + \hat{\mathbf{s}}_n \cdot \left[\mathbf{Q}^*(\mathbf{k})F'(\mathbf{k}) + \mathbf{Q}(\mathbf{k})F'^*(\mathbf{k}) + i\mathbf{Q}(\mathbf{k})^* \times \mathbf{Q}(\mathbf{k})\right]\right\}$$

Unpolarised neutrons

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{Unpol} = (\gamma r_e)^2\left\{\left|\mathbf{Q}(\mathbf{k})\right|^2 + \left|F'(\mathbf{k})\right|^2\right\}$$

Formulæ Explained

Non-flip: In addition to the nuclear scattering, it contains the components of **Q**(**k**) parallel to the neutron spin and a magneto-structural interference term.

Flip: It contains the components of **Q**(**k**) perpendicular to the neutron spin, plus an additional term which is present only if **Q**(**k**) is complex.

Total: It contains the nuclear term, the module square of **Q**(**k**) and the two terms which are linear in $\mathbf{s}_n$.

Unpolarised: It contains only the nuclear term and the module square of **Q**(**k**), since the two terms which are linear in $\mathbf{s}_n$ cancel upon averaging.

Neutron beam polarisation

As we have seen, the scattering cross section depends on the initial spin direction $\mathbf{s}_i$. Also, in general, the final direction of the neutron spin $\mathbf{s}_f$ is not parallel to the initial one $\mathbf{s}_i$. Therefore, the population of spins in a neutron beam is generally altered by magnetic scattering. One defines the neutron beam polarisation as $\mathbf{P} = \langle \hat{\mathbf{s}}_n \rangle$, where $\hat{\mathbf{s}}_n$ is the neutron spin direction and the average is taken over all the neutrons in the beam. The transformation of the neutron polarisation upon scattering is given by:

$$\mathbf{P}_f = \overline{\overline{\mathbf{D}}}\mathbf{P}_i + \mathbf{P}_C$$

Where $\overline{\overline{\mathbf{D}}}$ is a tensor describing the effects of rotation and depolarisation and $\mathbf{P}_C$ describes the creation of new polarisation.

The simplest case-I

Scattering of unpolarised neutrons from a collinear unmodulated structure. Here, $\boldsymbol{\kappa}$ is a reciprocal lattice vector.

For collinear structures (all moments // $\hat{\mathbf{m}}$)

$$\left|\mathbf{Q}(\boldsymbol{\kappa})\right|^2 = \sin^2(\alpha)\left|\sum_{j=1}^{\text{n atoms}} \mu_j f_j(\kappa) \mathrm{e}^{-i\boldsymbol{\kappa}\cdot\mathbf{r}_j}\right|^2$$

where α is the angle between $\hat{\boldsymbol{\kappa}}$ and $\hat{\mathbf{m}}$

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\boldsymbol{\kappa})\right)^{Unpol} = (\gamma r_e)^2\left\{\left|\mathbf{Q}(\boldsymbol{\kappa})\right|^2 + \left|F'(\boldsymbol{\kappa})\right|^2\right\}$$

The simplest case-II

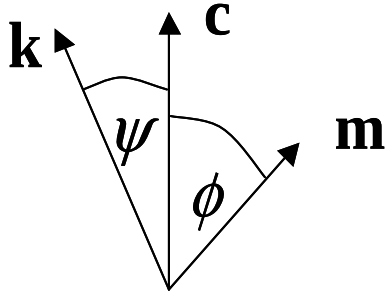
It looks like all the information is there to solve the structure even with unpolarised neutrons and powder diffraction. All the magnetic moment magnitudes are contained in $\mathbf{Q}(\boldsymbol{\kappa})$ with the appropriate phase factors and signs. Also, the information about the direction of the magnetic moments is there through the prefactor $\sin^2(\alpha)$. So, why bother with polarised neutrons and single-crystal techniques?

Magnetic Powder Diffraction

Averaging of the $\sin^2(\alpha)$ term over the (quasi)-degenerate reflections:

- For Uniaxial Groups (3-fold, 4-fold, 6-fold) we can only determine the angle ϕ:

$$\overline{\sin^2\alpha} = 1 - \tfrac{1}{2}\sin^2\psi\sin^2\varphi - \cos^2\psi\cos^2\varphi$$



- For Cubic Structures, the direction of the magnetic moments is undetermined:

$$\overline{\sin^2\alpha} = 2/3$$

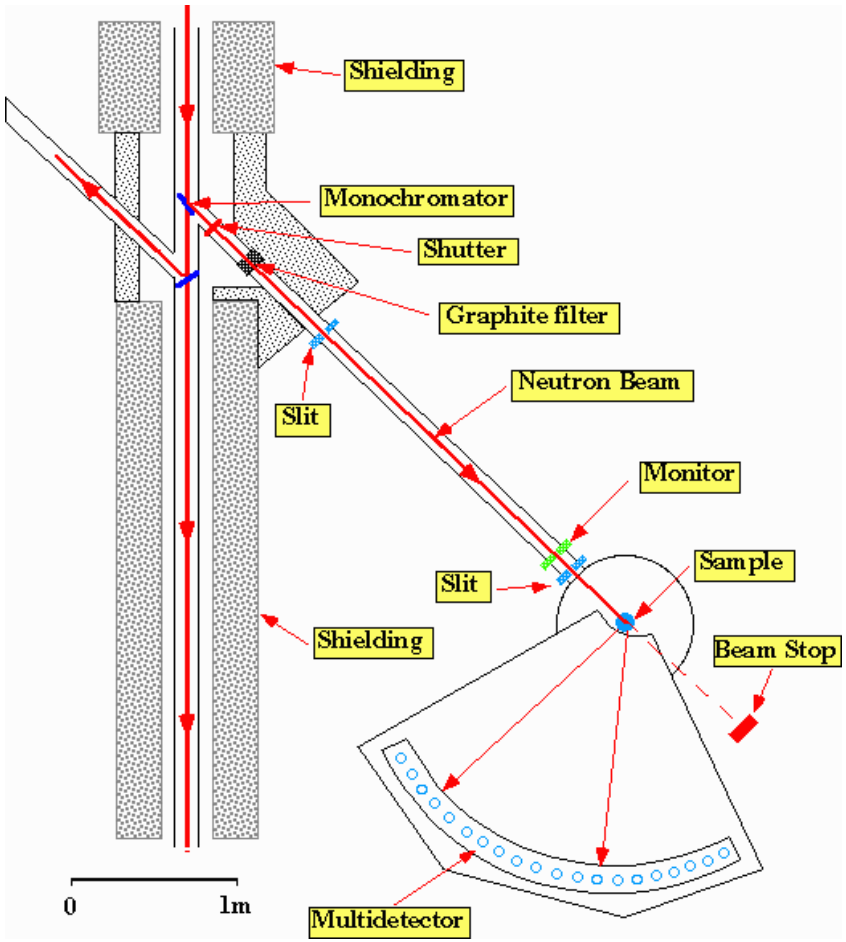
Magnetic Powder Diffractometers-I

- High-*k* range: For magnetic structure analysis, one rarely needs to go beyond $\sin(\theta)/\lambda=0.5$. Wavelengths > 2 Å are ideal.
- Low-*k* range: It is essential to have good coverage at low *k*, as many helimagnetic structures have very long periodicity. $k=0.5$ Å^{-1} is the minimum acceptable to do any sensible work. $k=0.1$ Å^{-1} is ideal.
- Resolution: it is desirable especially in structure with low crystallographic symmetry, because it enables to reduce the accidental degeneracy.

CW Powder Diffractometers

- Most magnetic structure problems are first tackled using high-intensity CW powder diffractometers (e.g., D1B). The biggest advantages are the excellent coverage at low k, the high flux (that can be further enhanced through focussing) and the simplicity of the data structure. Resolution is generally quite poor.
- The use of high-resolution machines (e.g., D2B) is becoming more common, especially when the magnetic moments are large, the structure has low symmetry and there is an interplay between magnetism and structural properties.

The High-Intensity CW Powder diffractometer D1B at the ILL



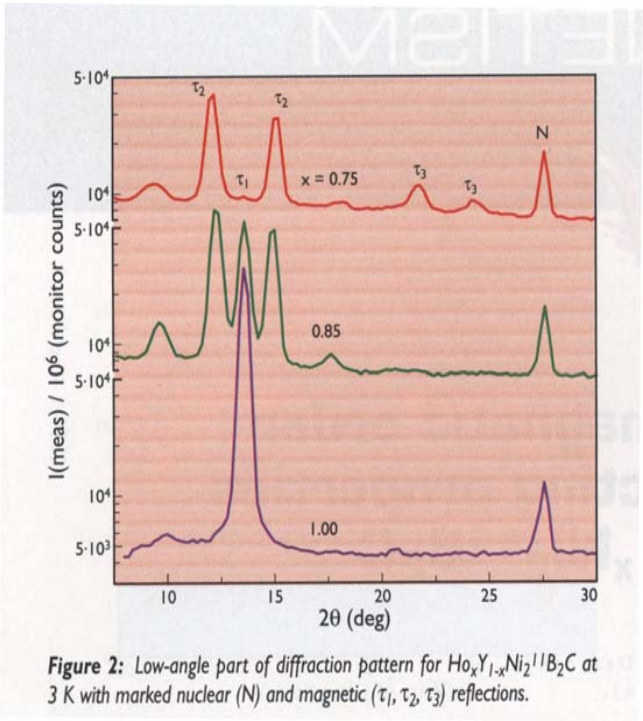
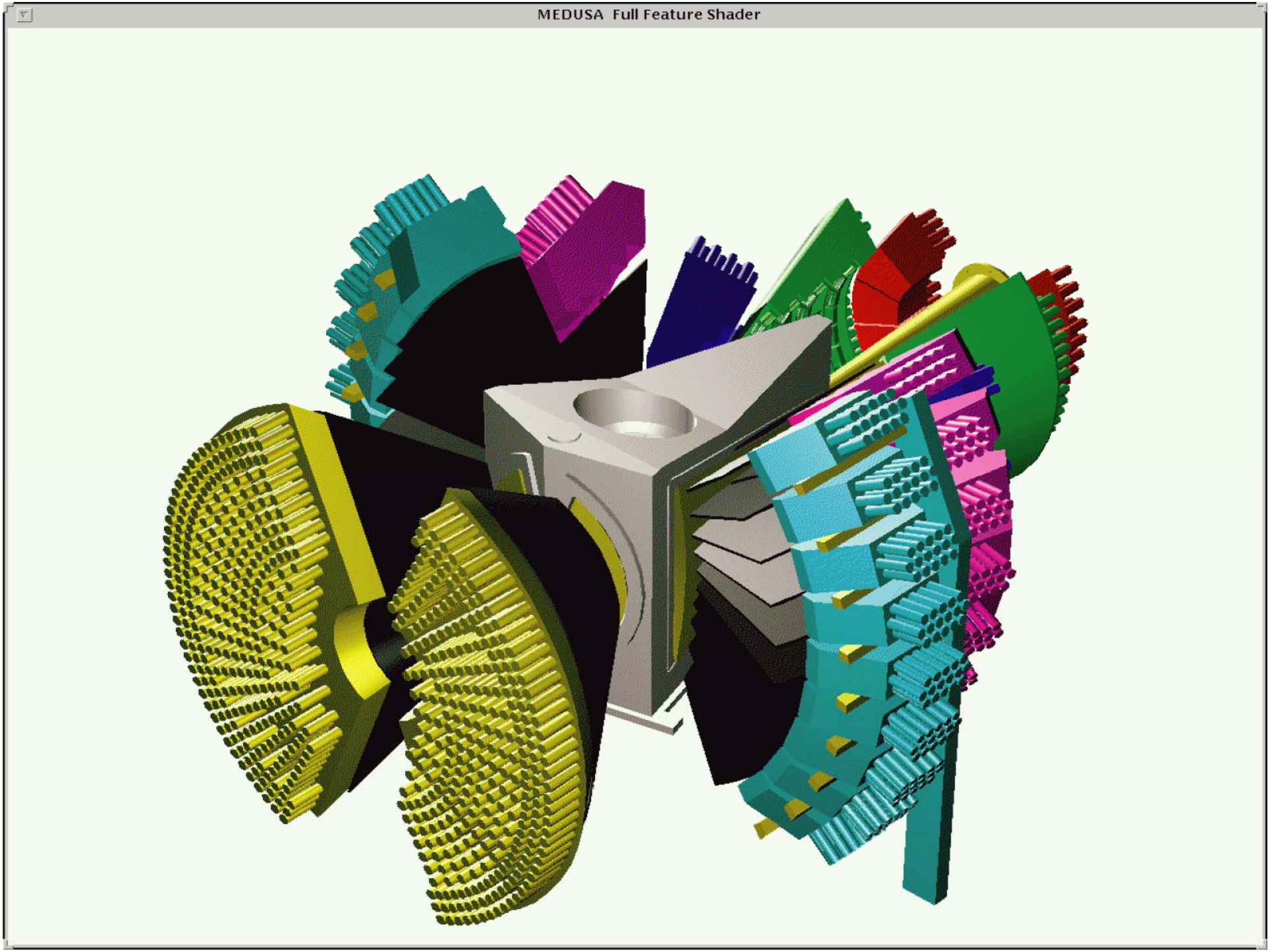
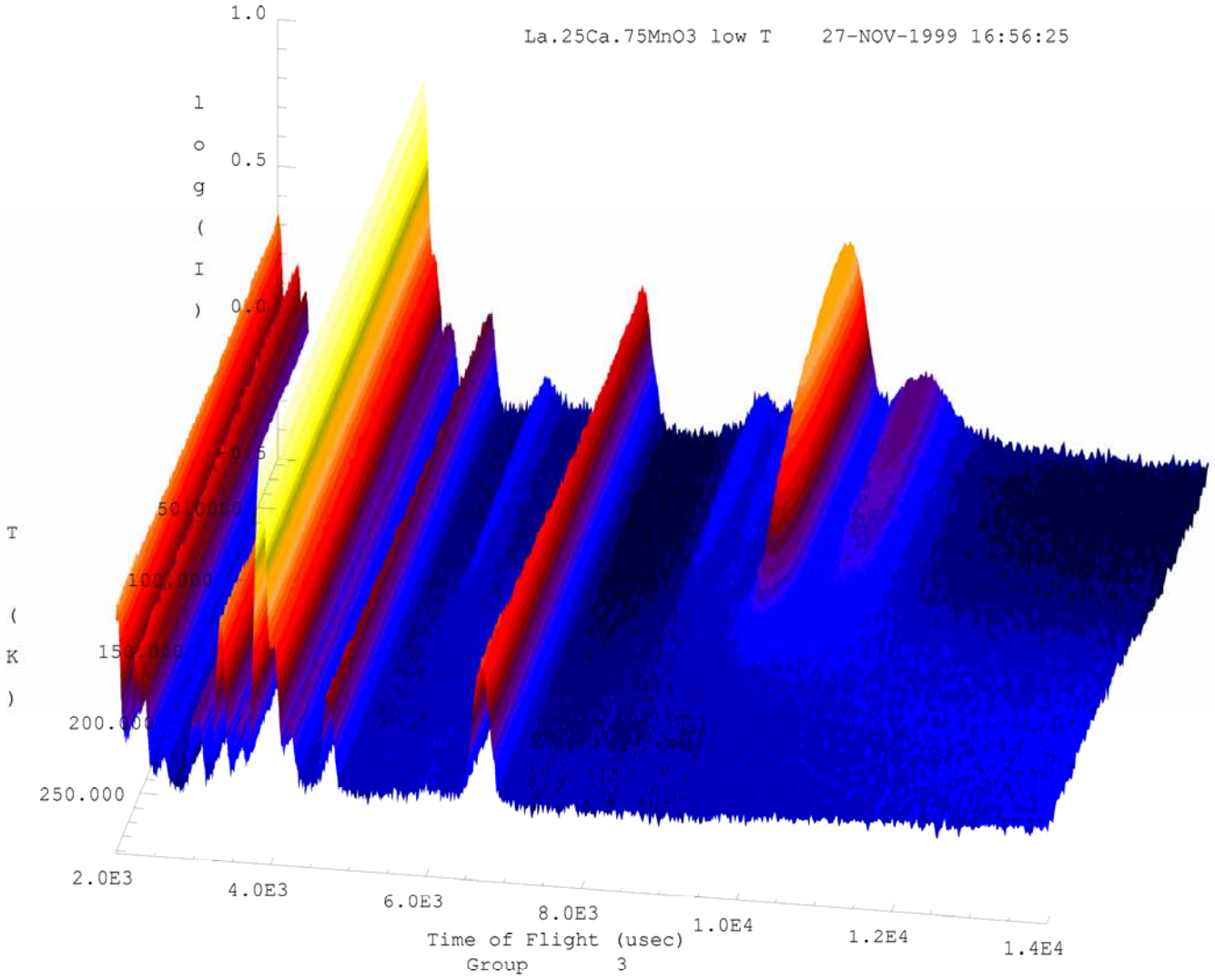
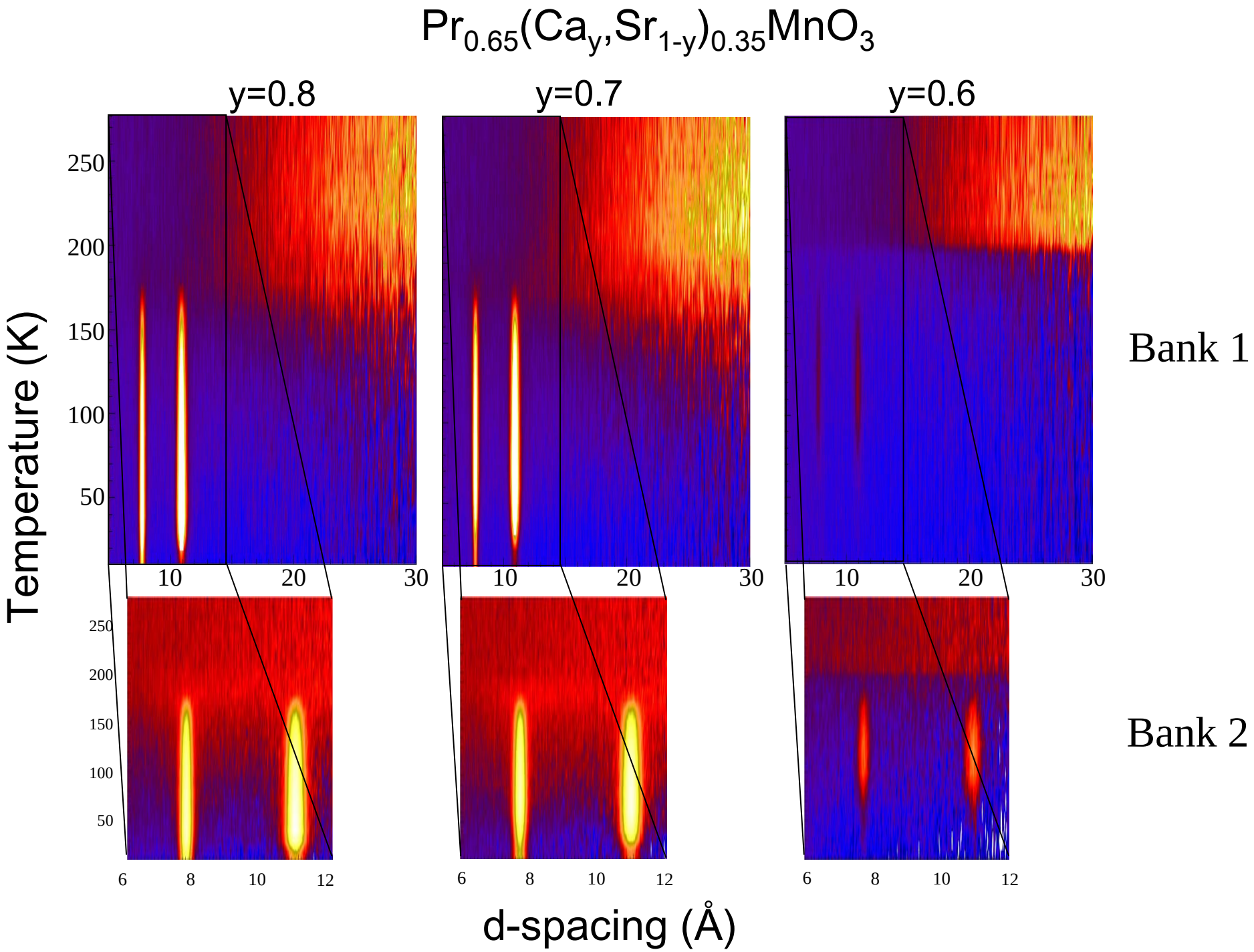
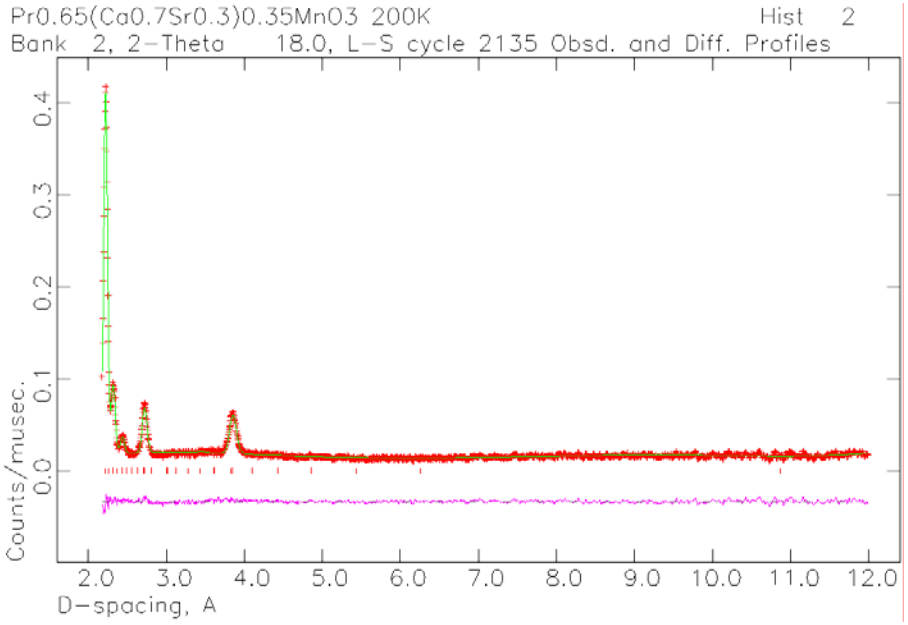


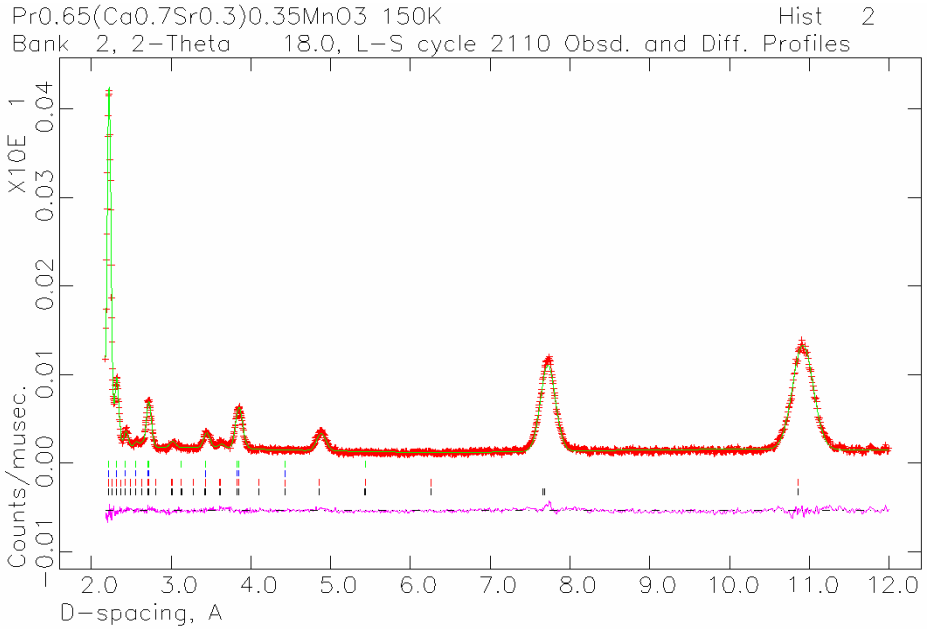
Figure 2: *Low-angle part of diffraction pattern for $Ho_xY_{1-x}Ni_2{}^{11}B_2C$ at 3 K with marked nuclear (N) and magnetic (τ_1, τ_2, τ_3) reflections.*

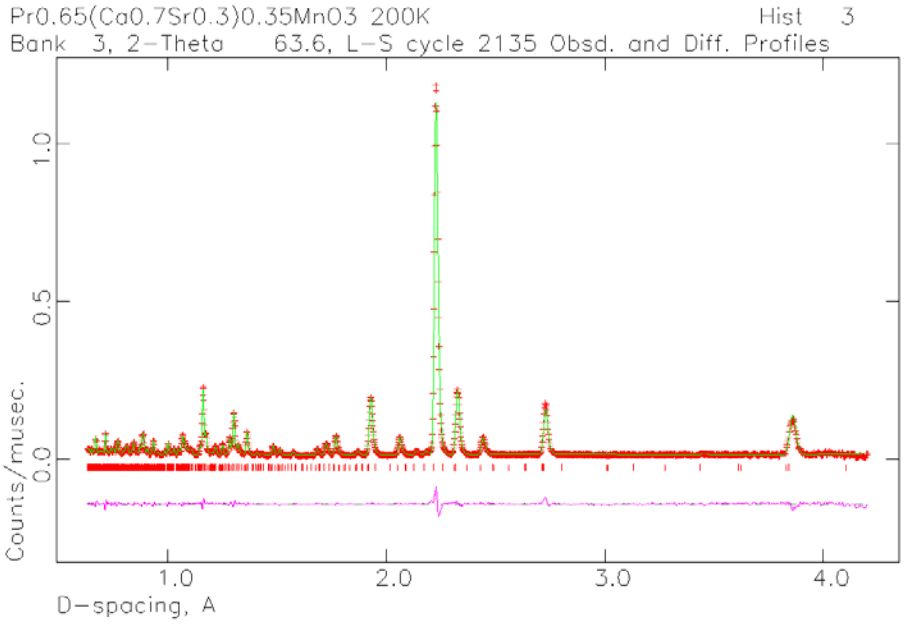

MEDUSA Full Feature Shader

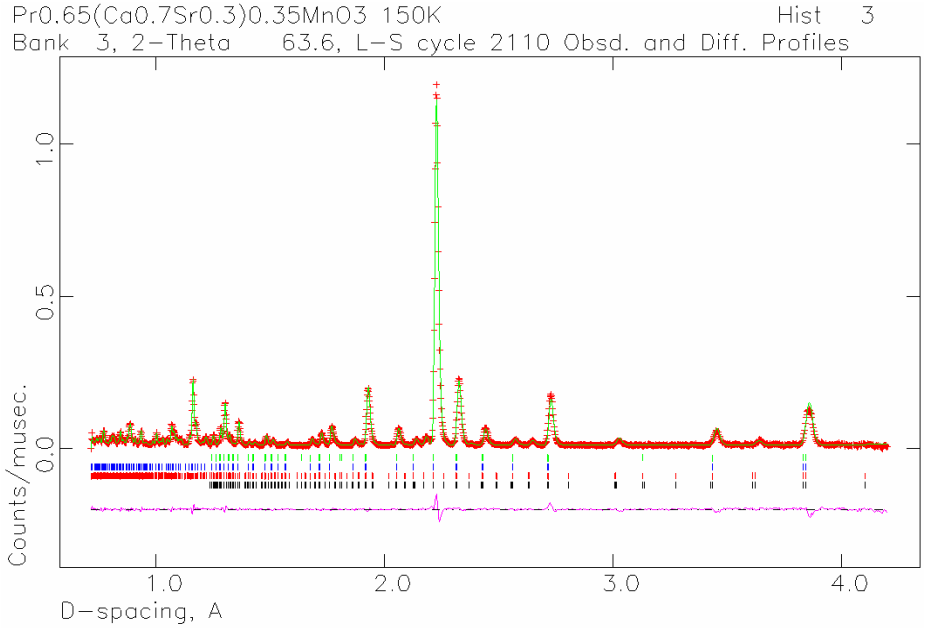

La.25Ca.75MnO3 low T 27-NOV-1999 16:56:25
log(I)
1.0
0.5
0.0
T (K)
50.000
100.000
150.000
200.000
250.000
2.0E3
4.0E3
6.0E3
8.0E3
1.0E4
1.2E4
1.4E4
Time of Flight (usec)
Group 3

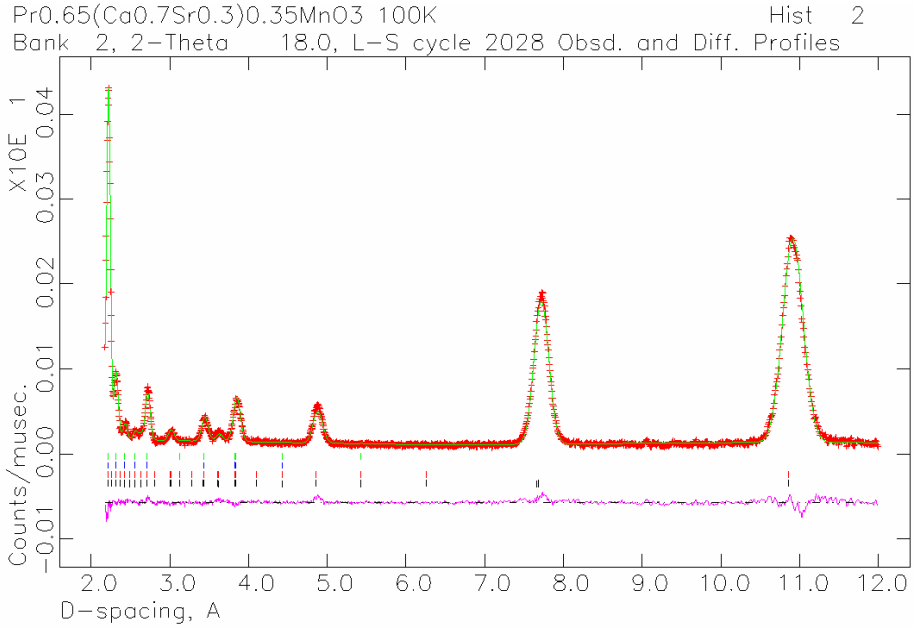

$Pr_{0.65}(Ca_y,Sr_{1-y})_{0.35}MnO_3$
y=0.8
y=0.7
y=0.6
Temperature (K)
250
200
150
100
50
10
20
30
6
8
10
12
d-spacing (Å)
Bank 1
Bank 2

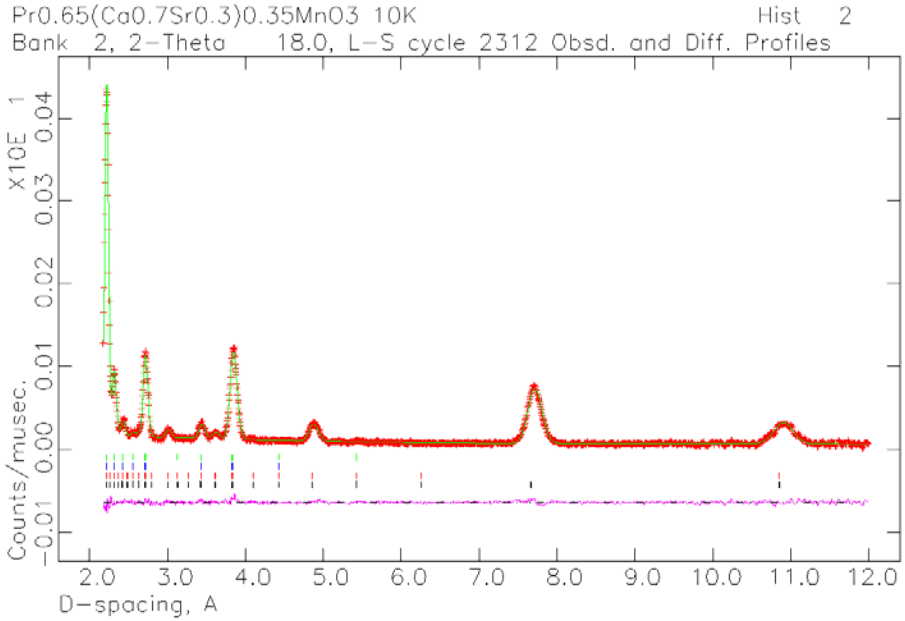

Pr0.65(Ca0.7Sr0.3)0.35MnO3 200K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2135 Obsd. and Diff. Profiles
Counts/musec.
0.0
0.1
0.2
0.3
0.4
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
D-spacing, A

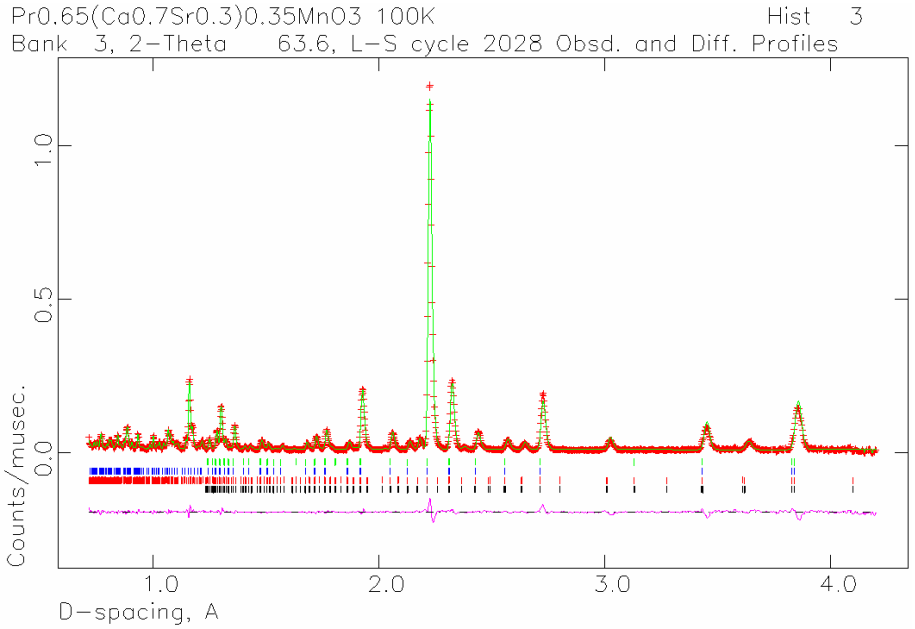

Pr0.65(Ca0.7Sr0.3)0.35MnO3 150K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2110 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
-0.01
0.00
0.01
0.02
0.03
0.04
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
D-spacing, A

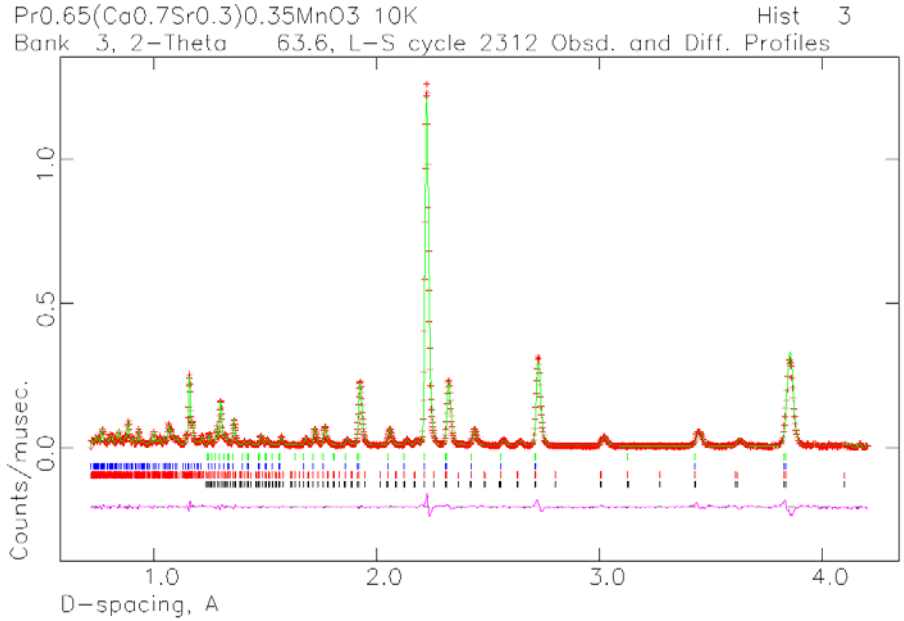

Pr0.65(Ca0.7Sr0.3)0.35MnO3 200K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2135 Obsd. and Diff. Profiles
Counts/musec.
0.0
0.5
1.0
1.0
2.0
3.0
4.0
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 150K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2110 Obsd. and Diff. Profiles
Counts/musec.
0.0
0.5
1.0
1.0
2.0
3.0
4.0
D-spacing, A

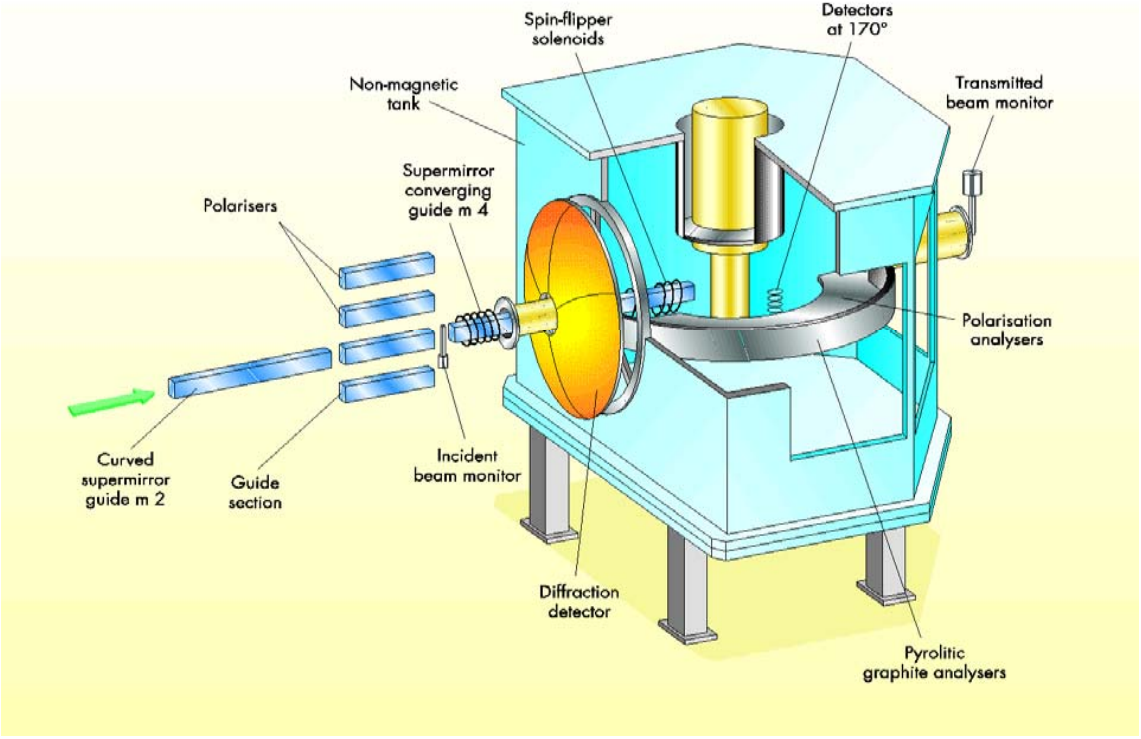

Pr0.65(Ca0.7Sr0.3)0.35MnO3 100K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2028 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
D-spacing, A

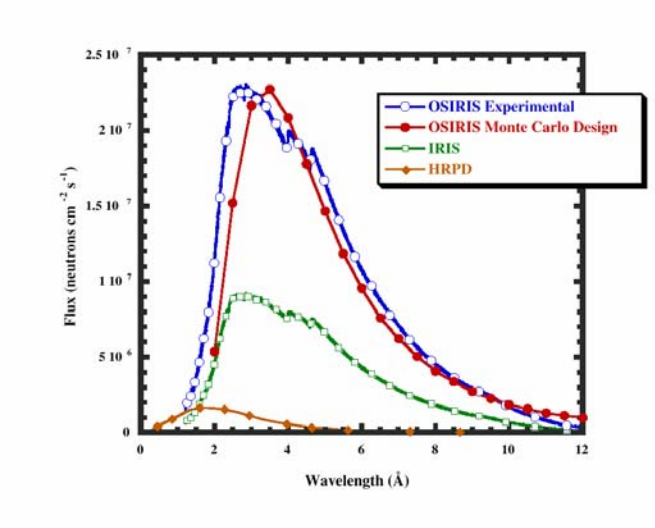

Pr0.65(Ca0.7Sr0.3)0.35MnO3 10K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2312 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 100K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2028 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 10K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2312 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A

OSIRIS





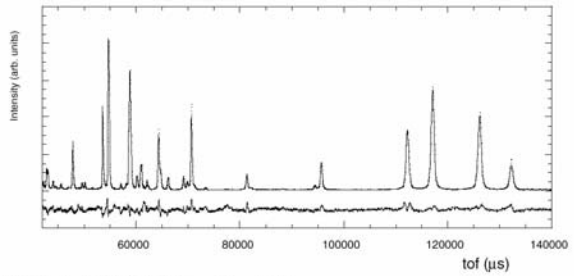
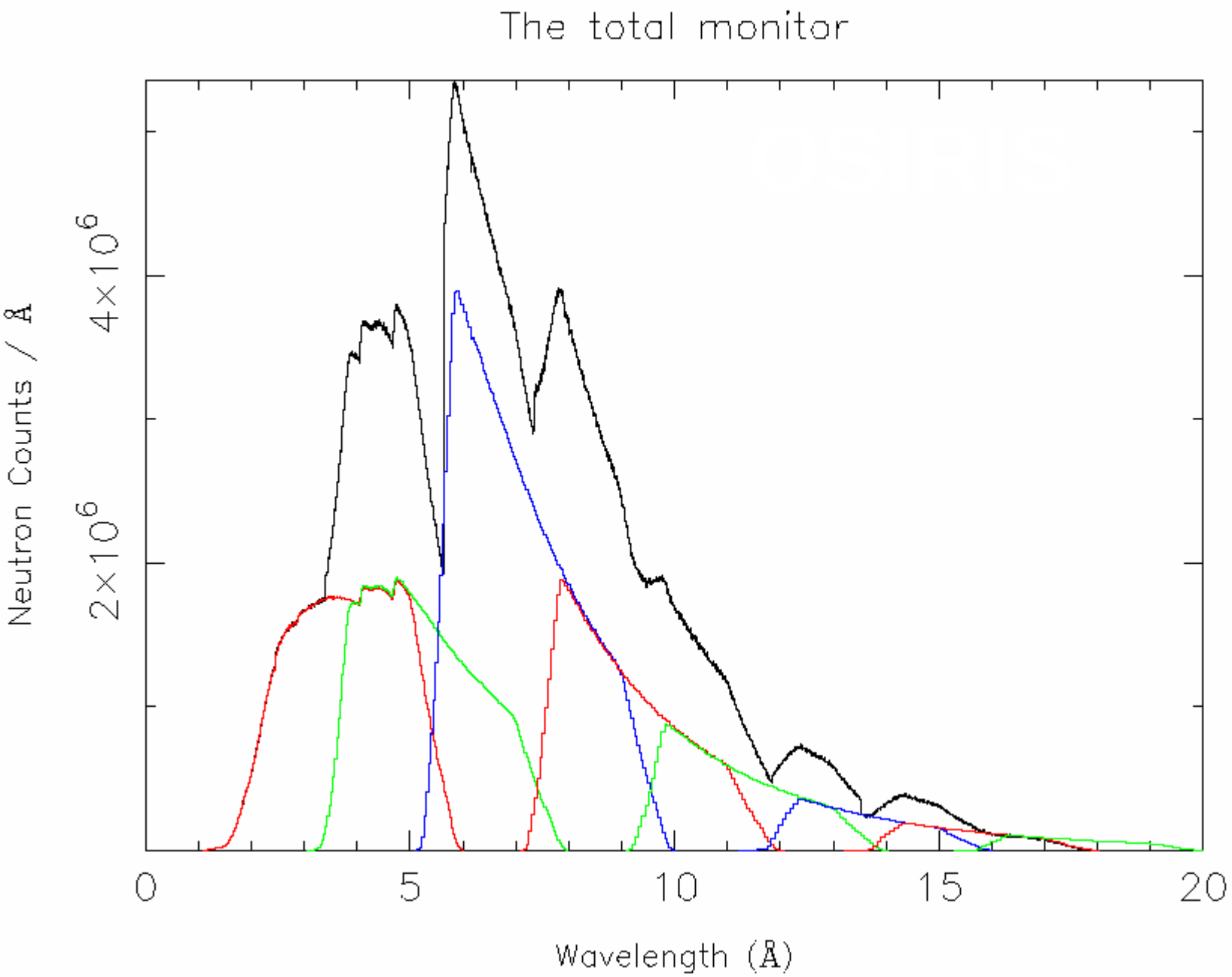
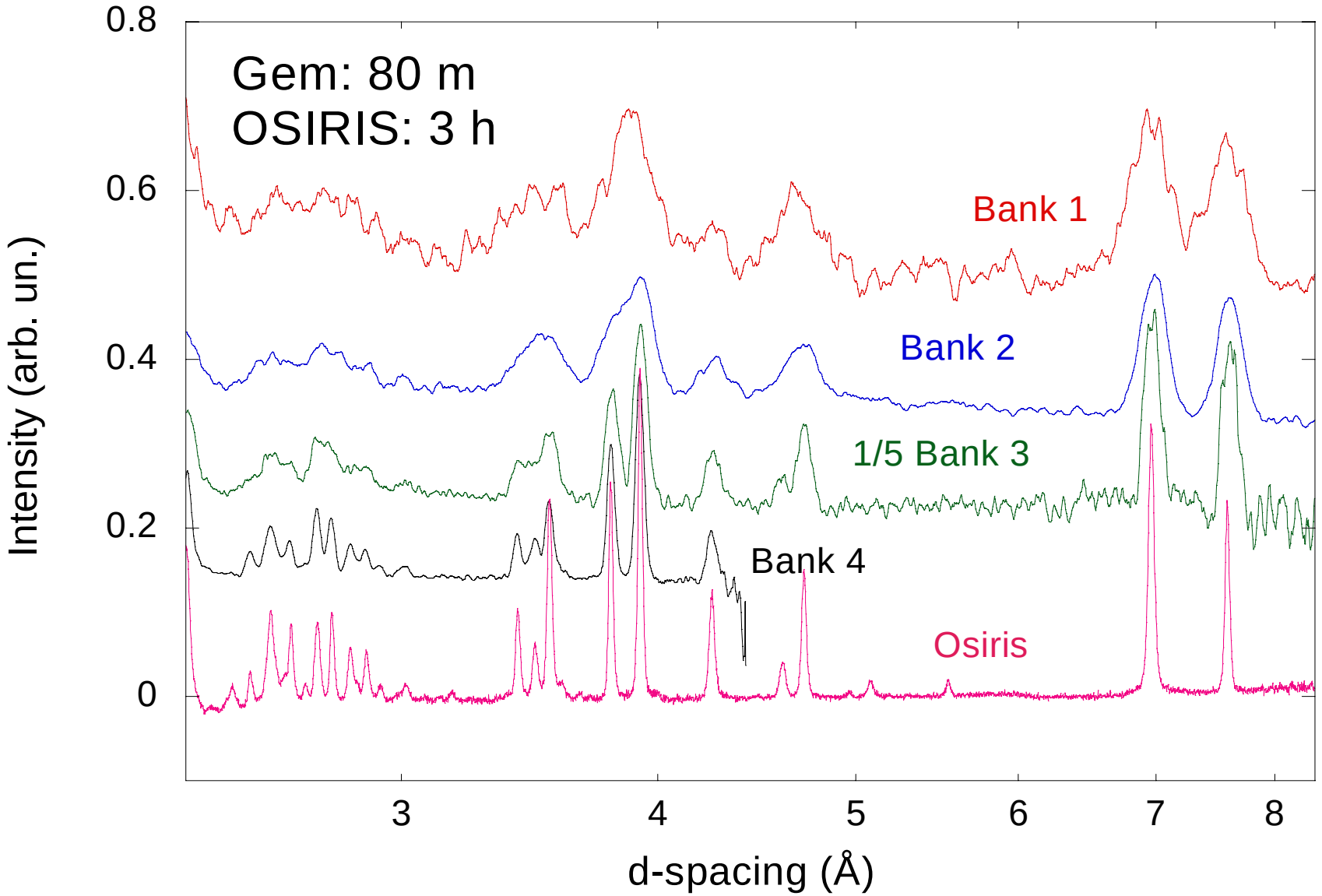
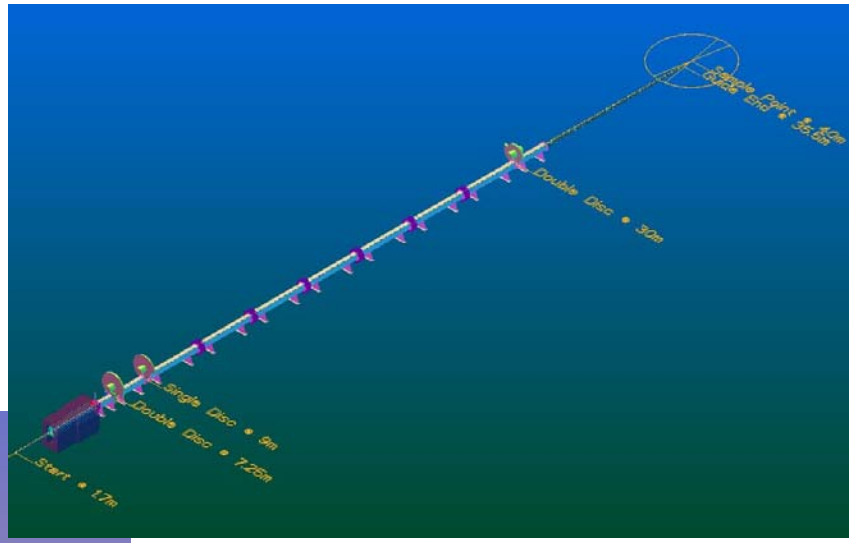


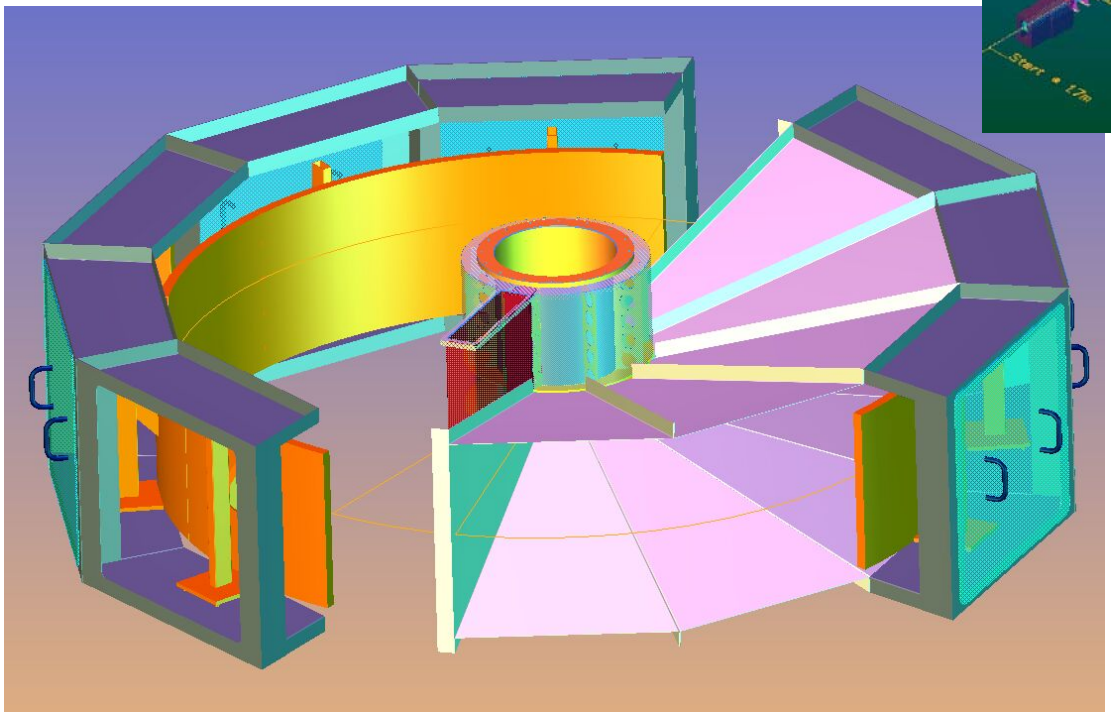
Fig. 2. Rietveld fit for $Ga_{0.08}Fe_{0.92}AsO_4$.

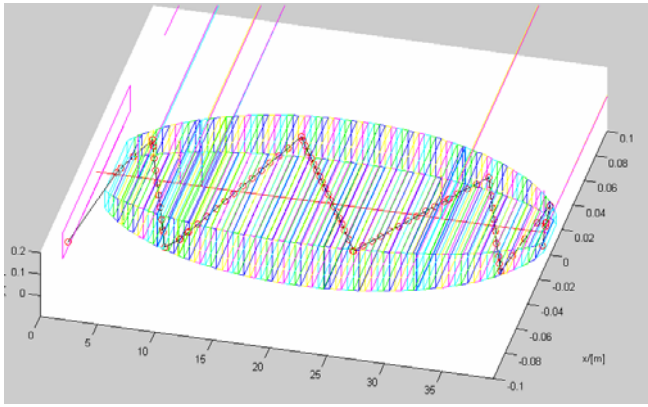

The total monitor
Neutron Counts / Å
2×10^6
4×10^6
0
5
10
15
20
Wavelength (Å)


GEM-OSIRIS Comparison
Magnetic Diffraction
Gem: 80 m
OSIRIS: 3 h
Bank 1
Bank 2
1/5 Bank 3
Bank 4
Osiris
Intensity (arb. un.)
0.8
0.6
0.4
0.2
0
3
4
5
6
7
8
d-spacing (Å)

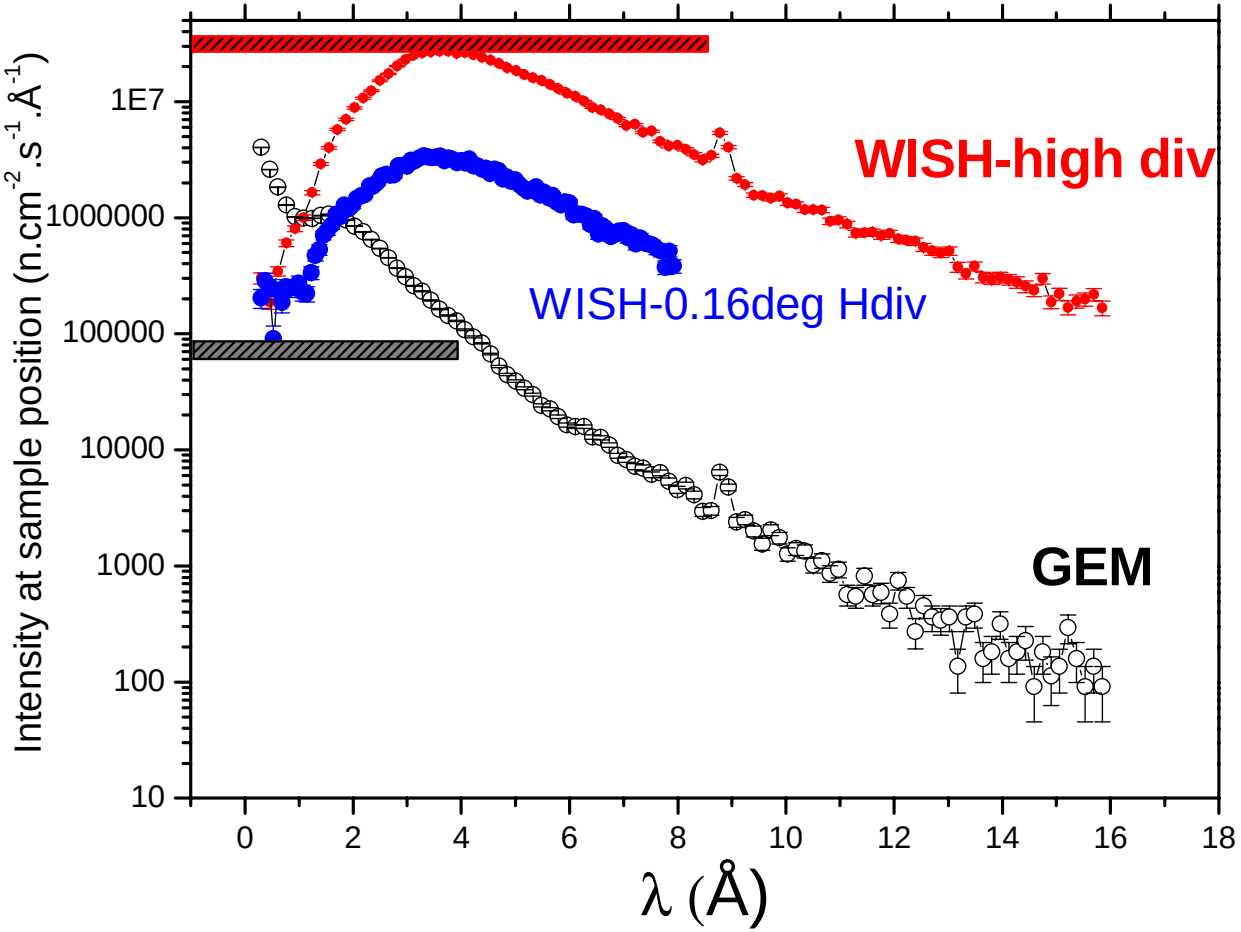
WISH


Single Point
Double Disc • 30m
Single Disc • 9m
Double Disc • 7.25m
Start • 17m




0.2
0.1
0
0
5
10
15
20
25
30
35
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
-0.06
-0.08
-0.1
x/[m]

Monte-Carlo simulations



Means to obtain a polarised beam

- Scattering from a magnetic crystal (monochromatic): Cu_2MnAl (Heusler), (Co,Fe)

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{\uparrow} = (\gamma r_e)^2 \left\{ |\mathbf{Q}(\mathbf{k})|^2 + |F'(\mathbf{k})|^2 + 2\hat{\mathbf{s}}_n \cdot [\mathbf{Q}(\mathbf{k}) F'(\mathbf{k})] \right\}$$

cancels out for spins antiparallel to the magnetic interaction vector and $|\mathbf{Q}(\mathbf{k})|=F'(\mathbf{k})$

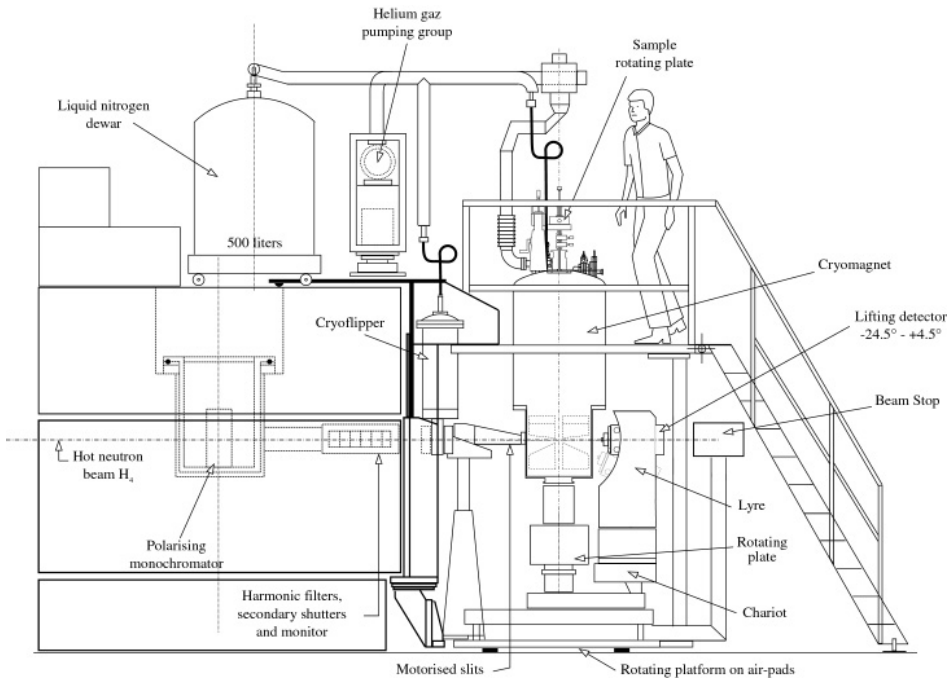
- Magnetic multilayers (white beam)

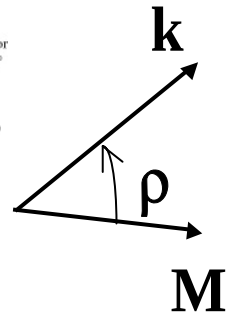
- ^{3}He polarising filters (white beam)

Uses of the neutron polarisation

Technique	Materials	Method	Applications	Instruments (examples)
Unpolarised neutrons	Powders and single crystals	Measure total cross section for unpolarised neutrons	Survey. Simple collinear structures	D1B, D20 (CWP) OSIRIS, GEM(TOFP) D10, D15 (CWSX)
Polarised neutrons	Usu. single crystals, typically FM.	Set **M**, measure with **P** parallel or antiparallel to **M**, to obtain "Flipping ratios"	Form factors, spin density distributions.	D3
Uniaxial polarimetry	Powders and single crystals	Set $\mathbf{P}_i$ along any direction and measure the projection of $\mathbf{P}_f$ onto $\mathbf{P}_i$.	Separate magnetic from nuclear scattering. Some non-collinear structures	D7 TAS + polariser + analyser. OSIRIS (future)
Spherical polarimetry.	Single crystals	Set $\mathbf{P}_i$ along any direction and measure the full $\mathbf{P}_f$.	Complex non-collinear AFM strcutures.	TAS + polariser + analyser +Cryopad

D3 (ILL)





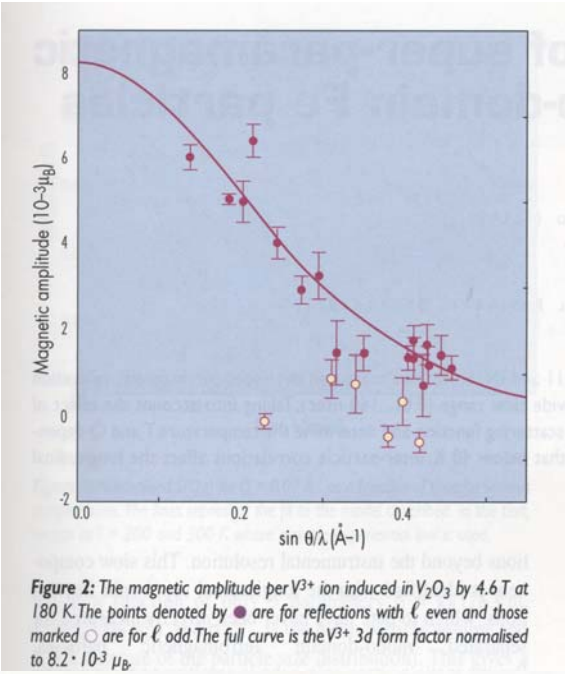


Figure 2: *The magnetic amplitude per V^{3+} ion induced in V_2O_3 by 4.6 T at 180 K. The points denoted by ● are for reflections with ℓ even and those marked ○ are for ℓ odd. The full curve is the V^{3+} 3d form factor normalised to $8.2 \cdot 10^{-3}\ \mu_B$.*

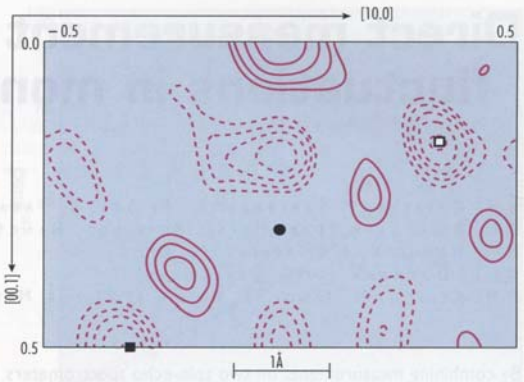


Figure 3: *The section, parallel to (01.0) passing through the origin, of the maximum entropy reconstruction of the difference between the observed magnetisation distribution and that due to spherically symmetric V^{3+} ions. The ● marks the position of the V^{3+} ion, the ■ that of the O^{2-} ion in the plane of the section and the □ that of the O^{2-} which is 0.1 Å below it. The contours are logarithmically spaced with a factor of two between successive levels. The highest contour is at $0.33 \cdot 10^{-3}\ \mu_B$ Å^{-3}.*

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{k})\right)^{\uparrow} = (\gamma r_e)^2\left\{|\mathbf{Q}(\mathbf{k})|^2 + |F'(\mathbf{k})|^2 + 2\hat{\mathbf{s}}_n \cdot [\mathbf{Q}(\mathbf{k})F'(\mathbf{k})]\right\}$$

$$R = \frac{1 + 2Py\sin^2\rho + y^2\sin^2\rho}{1 - 2Py\sin^2\rho + y^2\sin^2\rho} \quad ; \quad y = (\gamma r_e)M(\mathbf{k})/F(\mathbf{k})$$

Uniaxial Polarisation Analysis

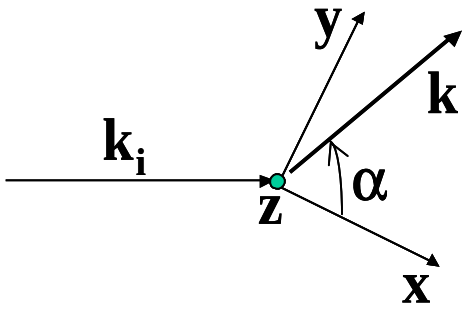
- One-detector setup

	Non spin-flip	Spin-flip
$\vec{P}_i \parallel \mathbf{k}$	$\sigma_c + \frac{1}{3}\sigma_i$	$\frac{2}{3}\sigma_i + \sigma_m$
$\vec{P}_i \perp \mathbf{k}$	$\sigma_c + \frac{1}{3}\sigma_i + \frac{1}{2}\sigma_m$	$\frac{2}{3}\sigma_i + \frac{1}{2}\sigma_m$

σ_c: Nuclear Coherent
σ_i: Nuclear spin-incoherent
σ_m: Magnetic (electrons)

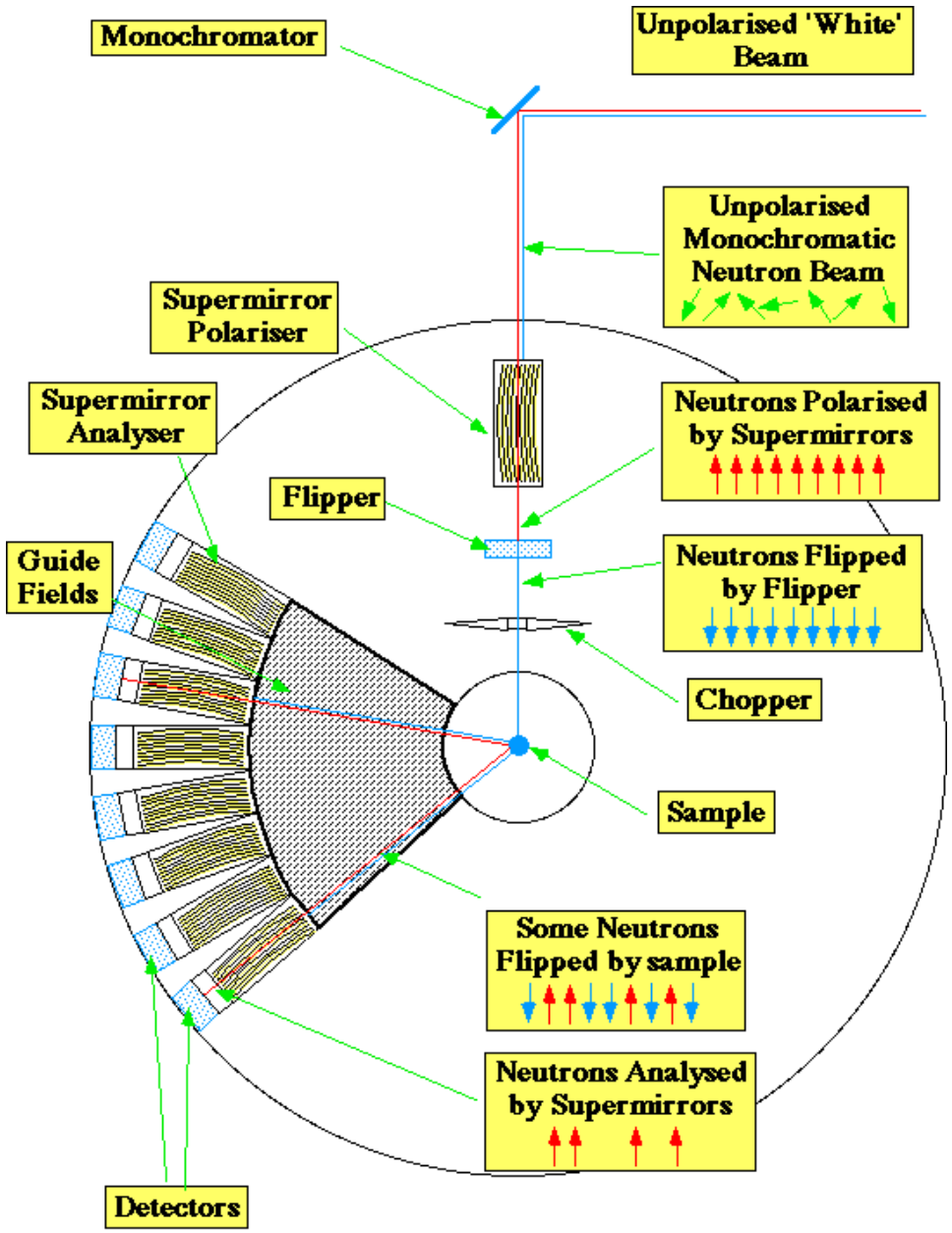
- Multidetector setup

	Non spin-flip	Spin-flip
$\vec{P}_i \parallel \vec{x}$	$\sigma_c + \frac{1}{3}\sigma_i + \frac{1}{2}\sigma_m \sin^2\alpha$	$\frac{2}{3}\sigma_i + \frac{1}{2}\sigma_m (1+\cos^2\alpha)$
$\vec{P}_i \parallel \vec{y}$	$\sigma_c + \frac{1}{3}\sigma_i + \frac{1}{2}\sigma_m \cos^2\alpha$	$\frac{2}{3}\sigma_i + \frac{1}{2}\sigma_m (1+\sin^2\alpha)$
$\vec{P}_i \parallel \vec{z}$	$\sigma_c + \frac{1}{3}\sigma_i + \frac{1}{2}\sigma_m$	$\frac{2}{3}\sigma_i + \frac{1}{2}\sigma_m$



D7 (ILL)

- Diffuse scattering
- Cold neutrons
- Supermirror polarisers
- 32 detectors
- 1-directional polarisation analysis: Separation of coherent and incoherent scattering
- 3-directional polarisation analysis:Separation also of magnetic scattering
- Time-of-flight option



General Layout of D7 for Polarisation Analyses

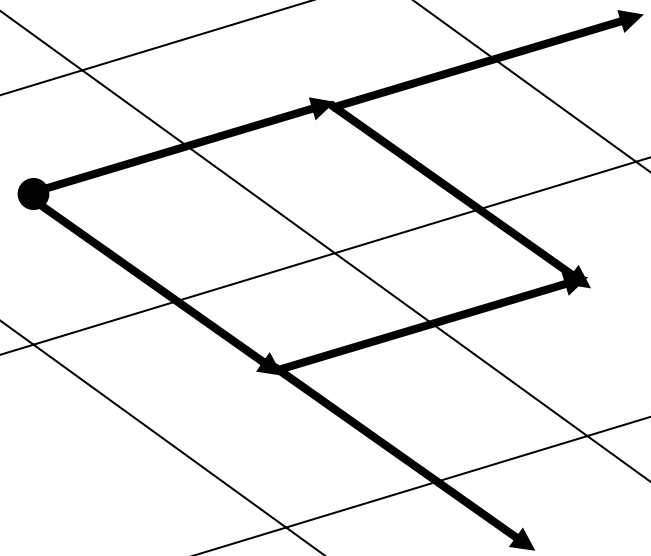
Magnetic Symmetry

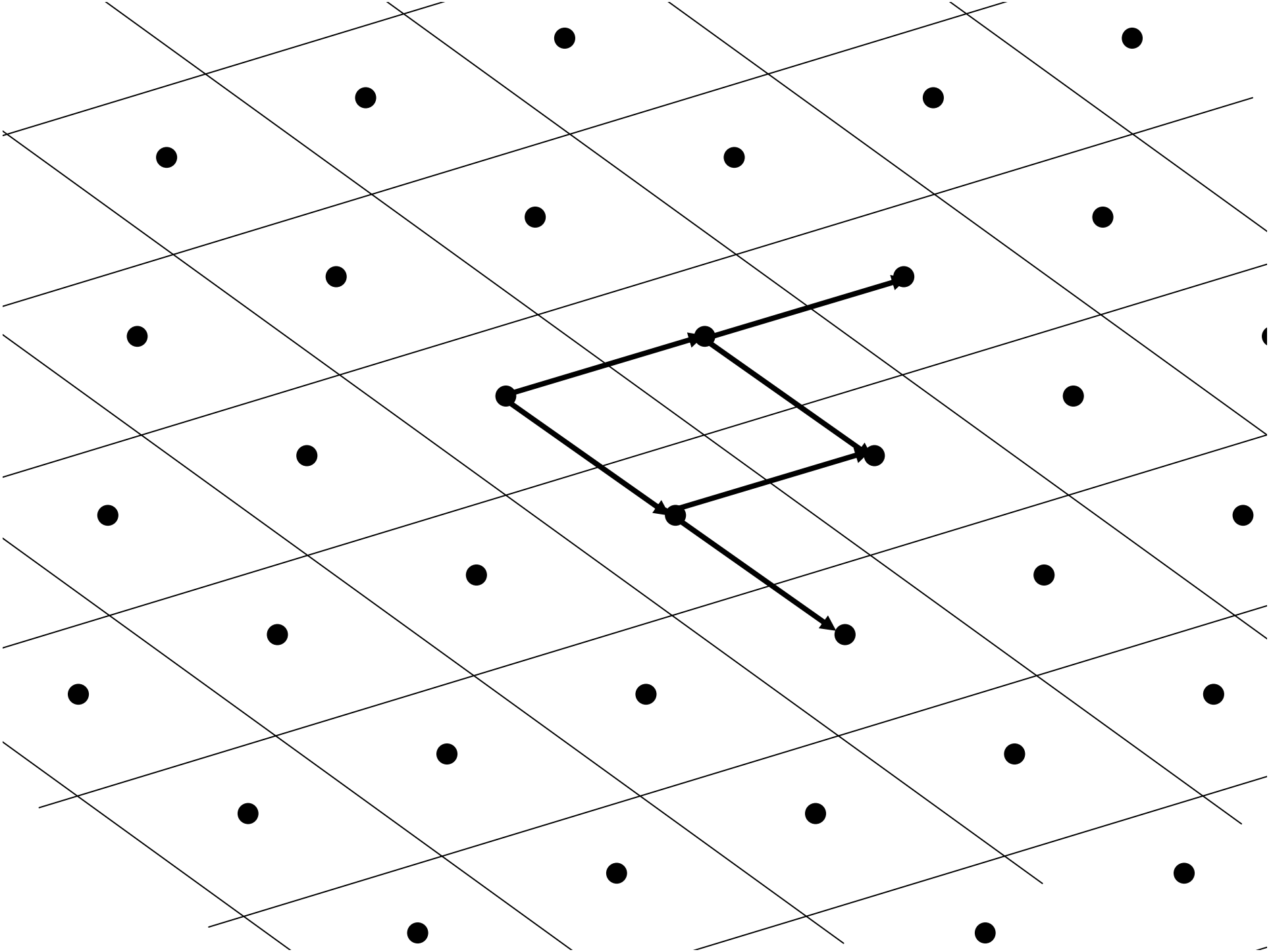
Paolo G. Radaelli

Symmetry in the solid state

- Symmetry = invariance
- *Think active! – everything is affected*
- Ordering = symmetry breaking (lowering)
- Crystalline state = Translational invariance

Symmetry operators form a group





Other types of symmetry

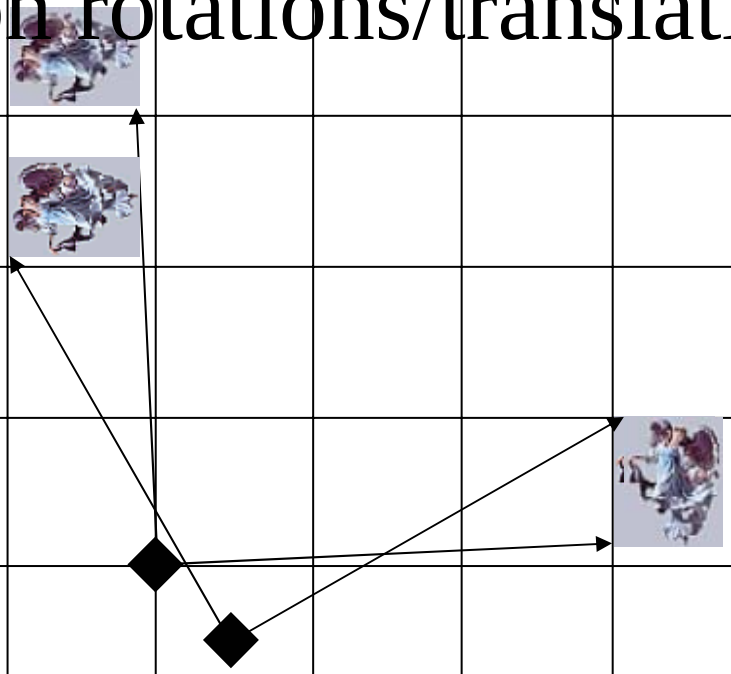
- Rotations

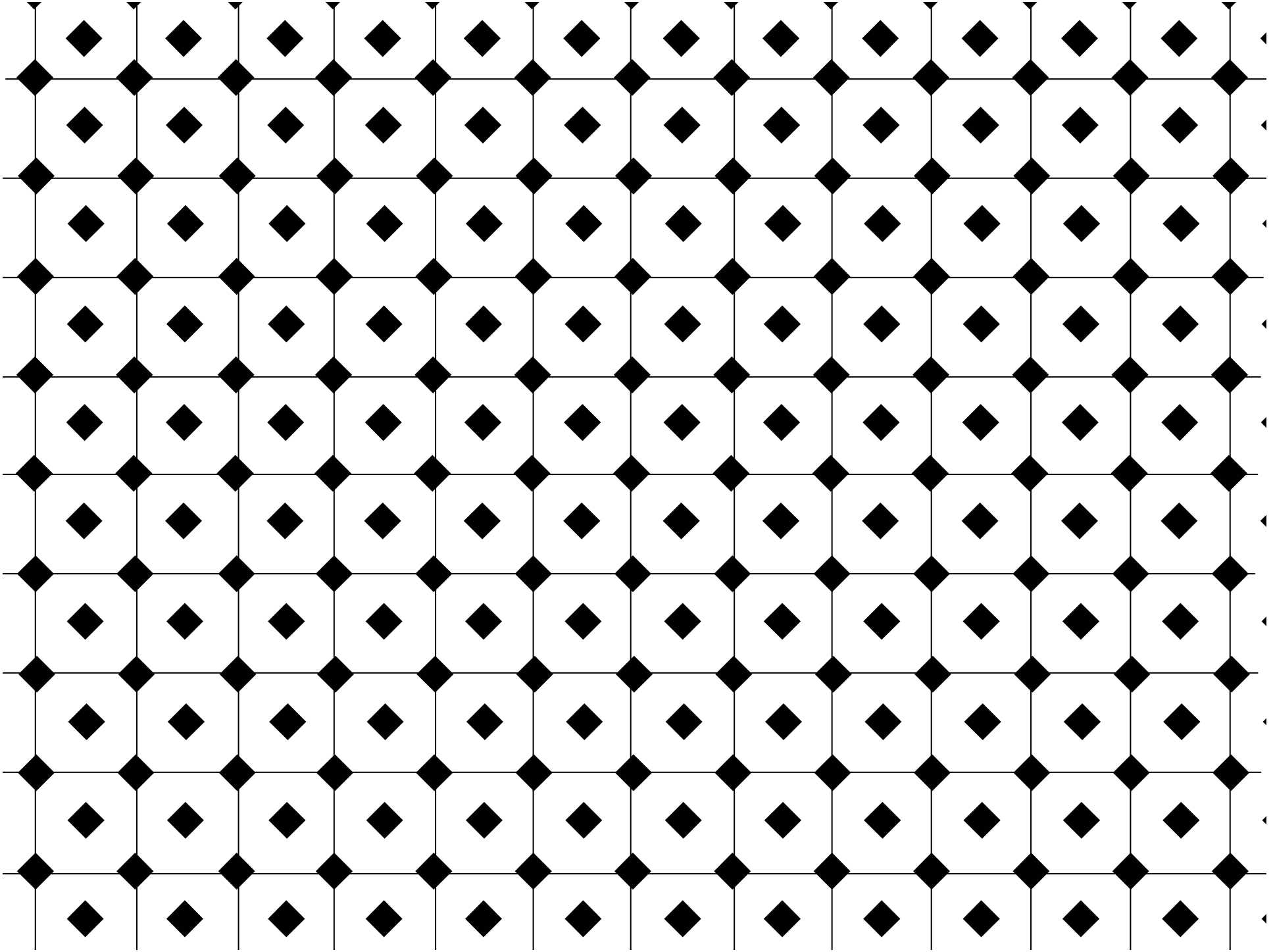
2-fold 3-fold 4-fold 6-fold

- Inversion ○
- Mirror, $\bar{3}$ ..

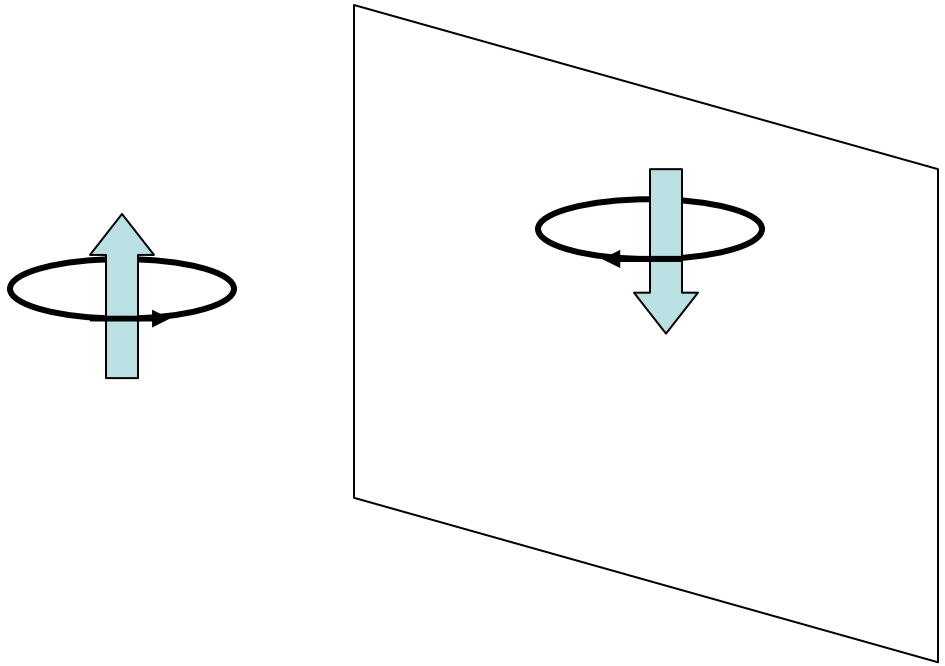
- + non-primitive translations….= 230 SG

Composition rotations/translations





Effect of symmetry on magnetic moments

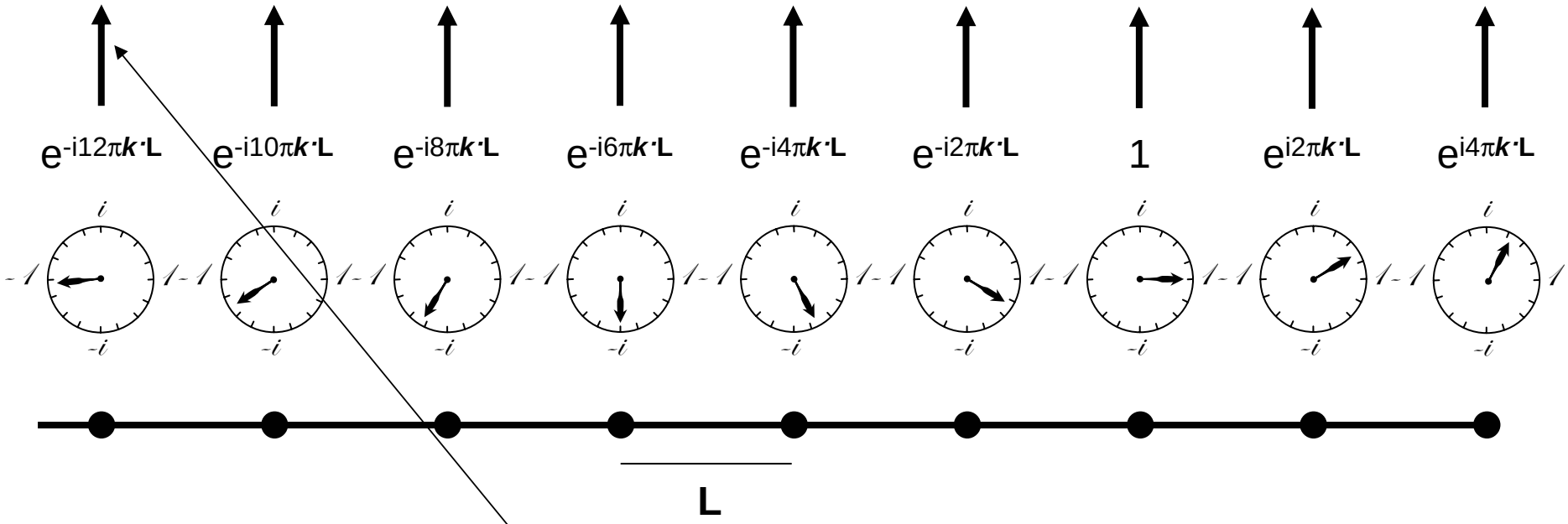


	m_x	2_z, 3_z, 4_z, 6_z	$\bar{1}$	1
Unprimed	Flip $s_y s_z$	Rotate s_x, s_y	No effect	No effect
Primed	Flip s_x	Rotate s_x, s_y Flip s_x, s_y, s_z	Flip s_x, s_y, s_z	Does not occur

Basis Vectors

- *Stop thinking at vectors as arrows!*
- "Vectors" are elements of a linear space, where we define **addition** and **multiplication by a scalar** (complex or real). E.g., wavefunction.
- We can define a **basis** of linearly independent vectors.
- Description of magnetic structures = find "suitable" (highly symmetric) bases….

Propagation Vector

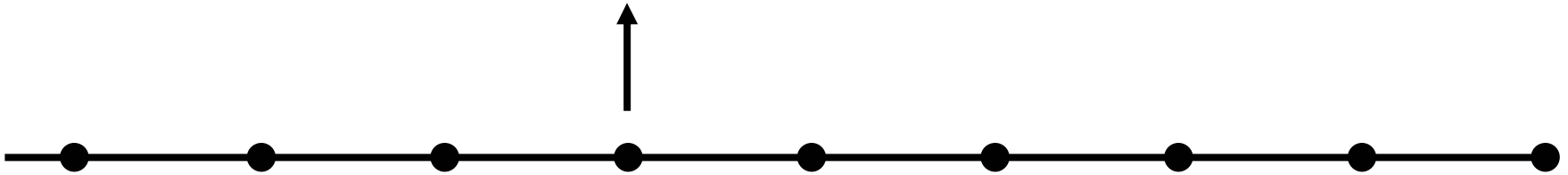


Fourier Components (complex)

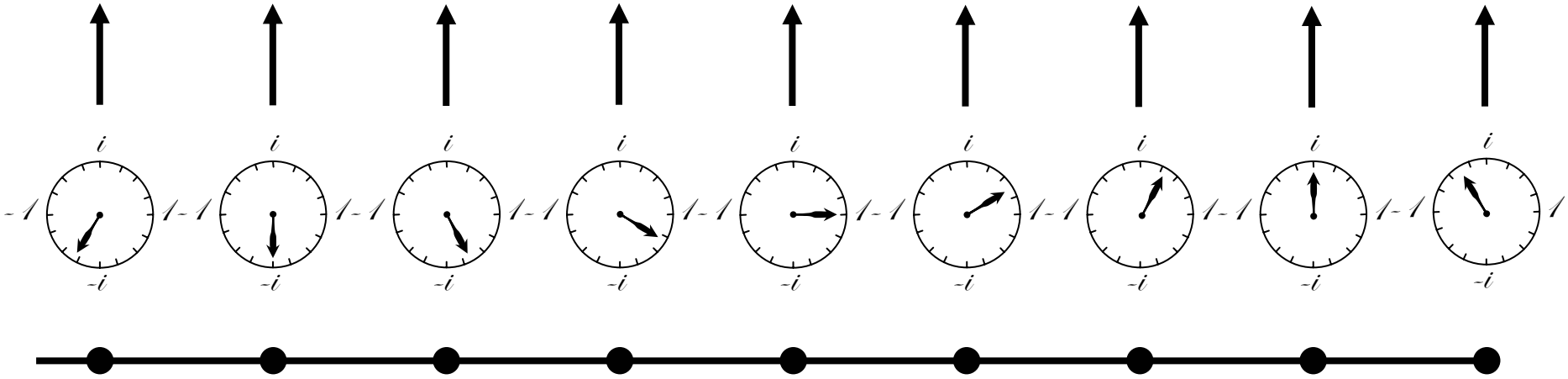
k

Moments are classical, real axial vectors

The effect of translations upon the basis vectors

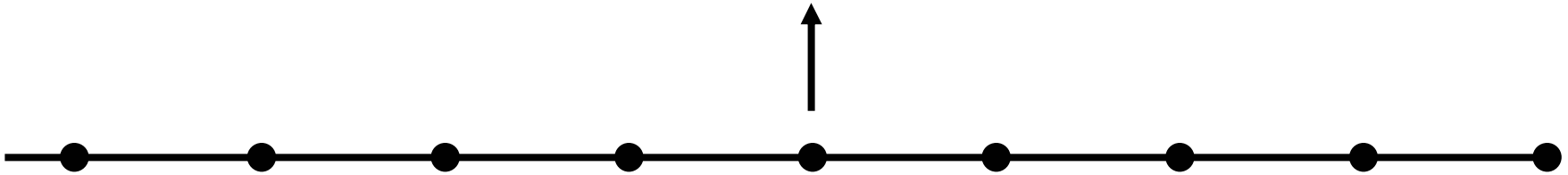


Generic basis vectors (real)

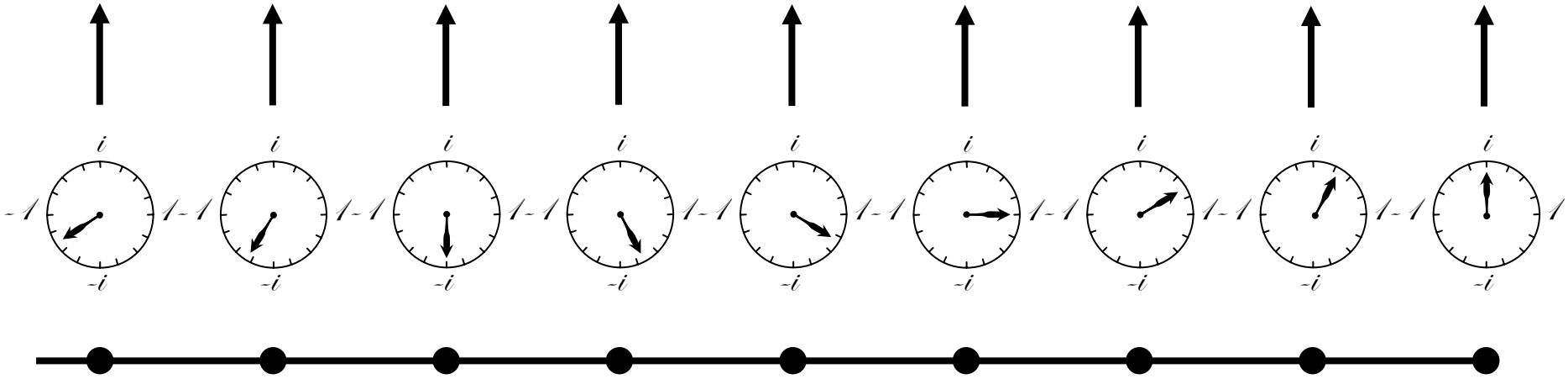


Fourier Components (complex)

The effect of translations upon the basis vectors

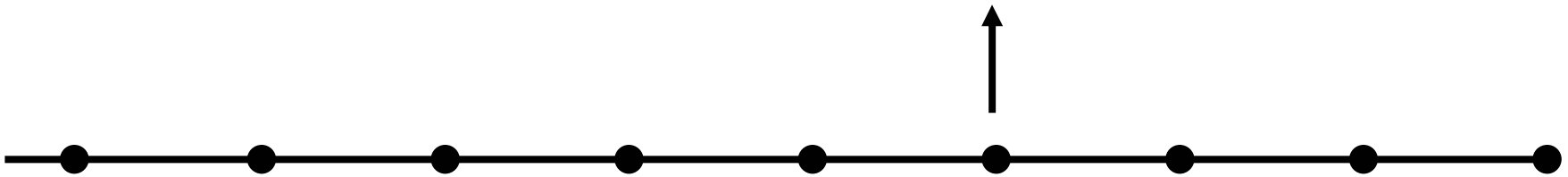


Generic basis vectors (real)

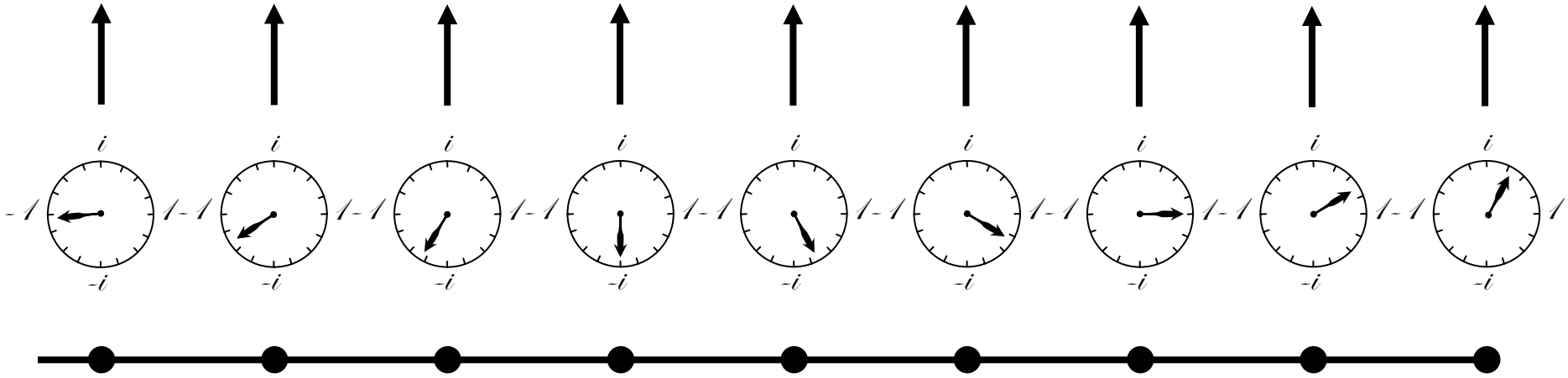


Fourier Components (complex)

The effect of translations upon the basis vectors

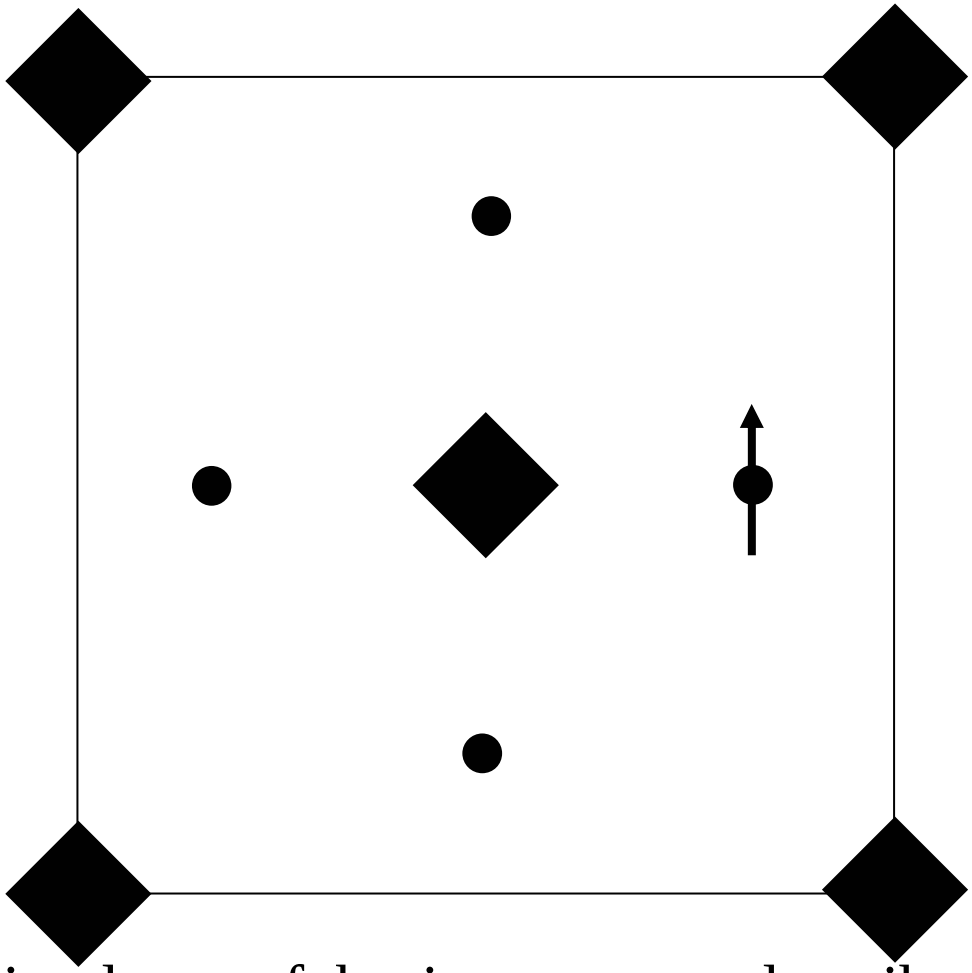


Generic basis vectors (real)



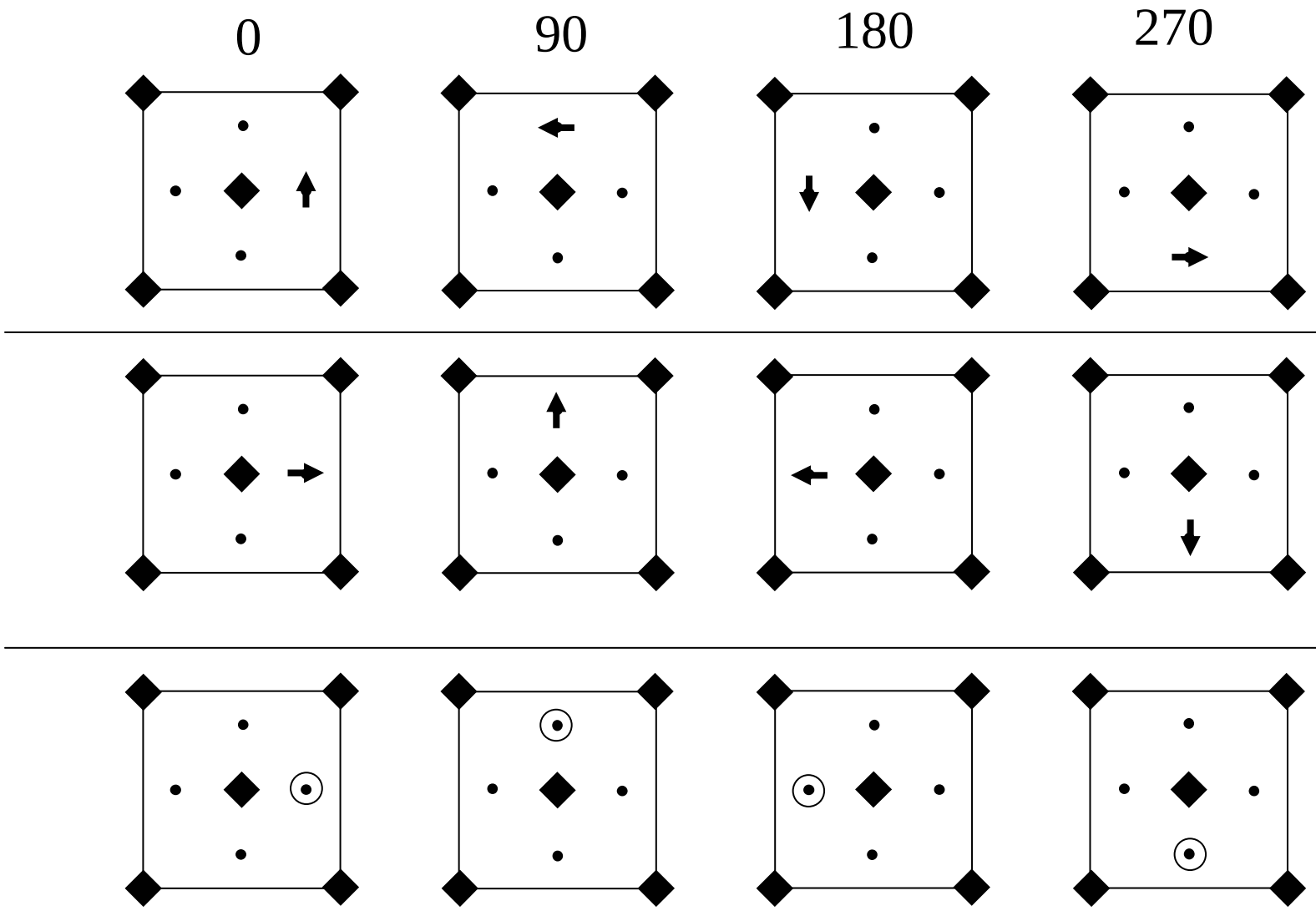
Fourier Components (complex)

Space Group $P4=C_4^1$ $k=(0,0,\mu)$



1. Find a simple set of basis vectors to describe *all* magnetic structures.
2. Find out how they are related by symmetry
3. Express this in matrix form.

Space Group $P4=C_4^1$ $k=(0,0,\mu)$



Matrix *representation*

0			
1	0	0	0
0	1	0	0
0	0	1	0
0	0	0	1

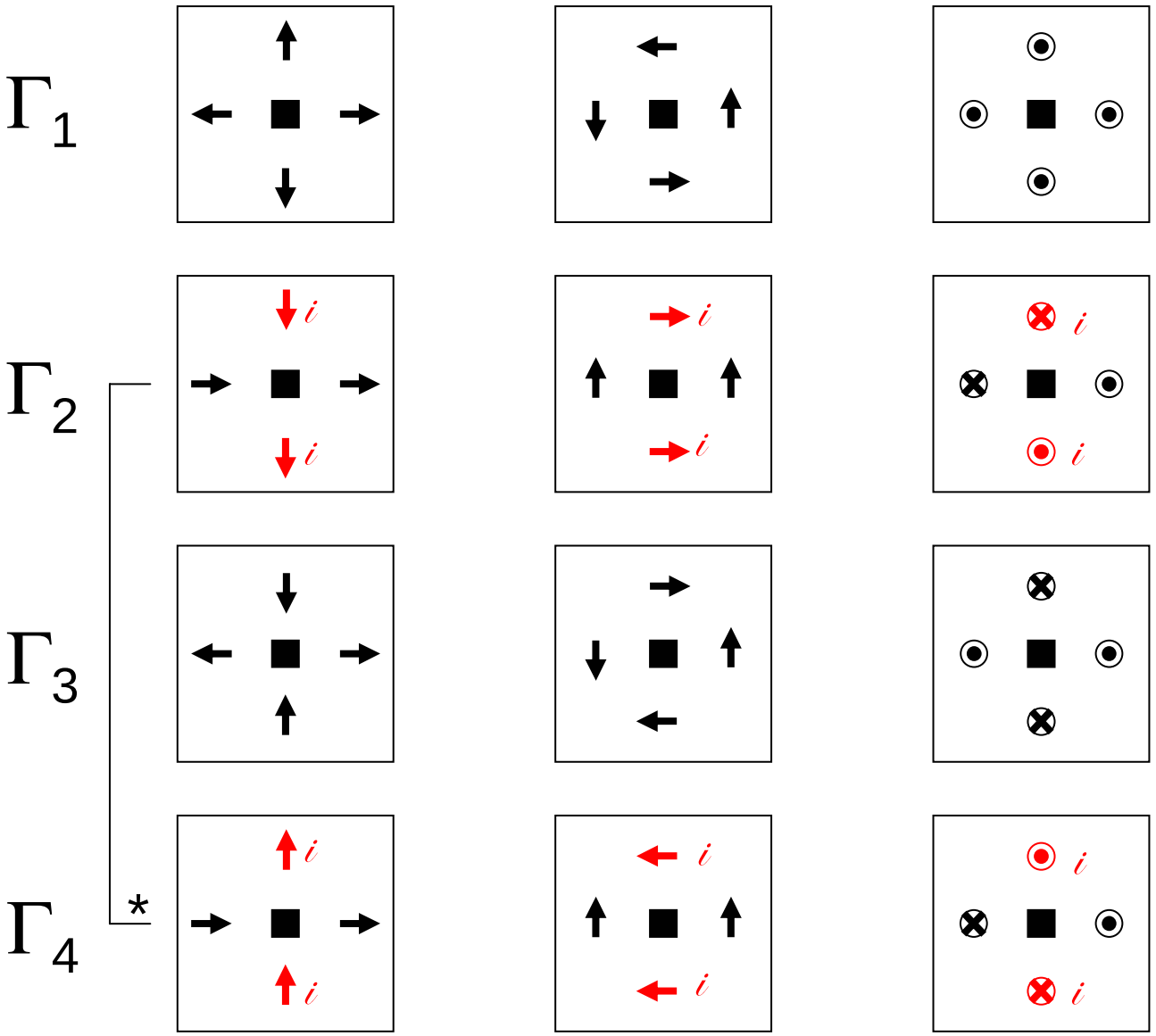
90			
0	0	0	1
1	0	0	0
0	1	0	0
0	0	1	0

180			
0	0	1	0
0	0	0	1
1	0	0	0
0	1	0	0

270			
0	1	0	0
0	0	1	0
0	0	0	1
1	0	0	0

1. Fully reduce this to *1-dimensional* representations.
2. Remember you have the following numbers at your disposal: 1, -1, i, -i. One of the *irreps* is totally symmetric.
3. Remember composition rules….

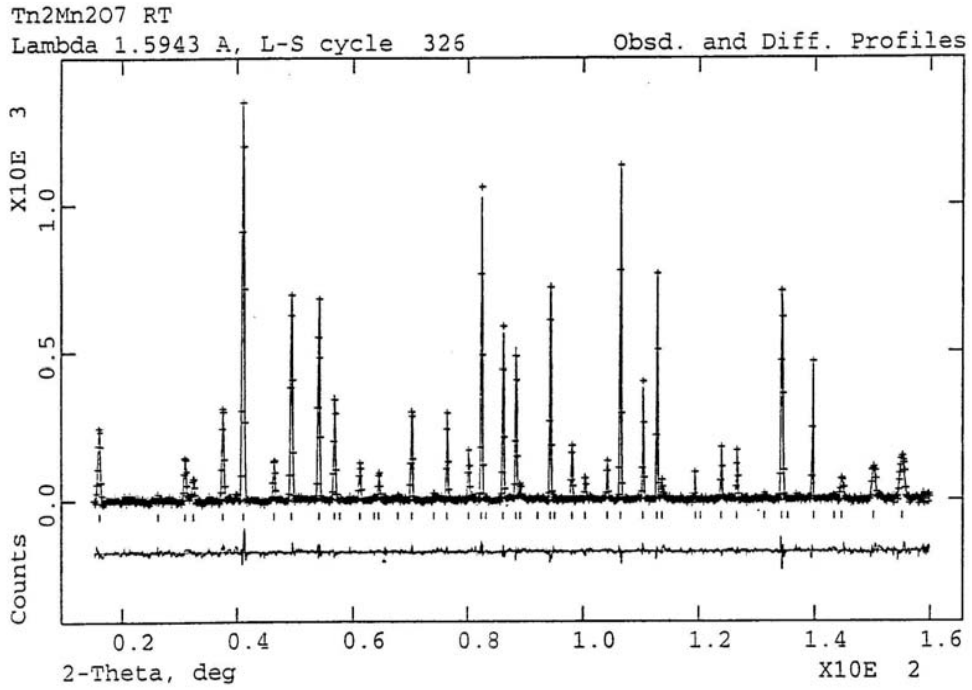
Space Group $P4=C_4^1$ $k=(0,0,\mu)$



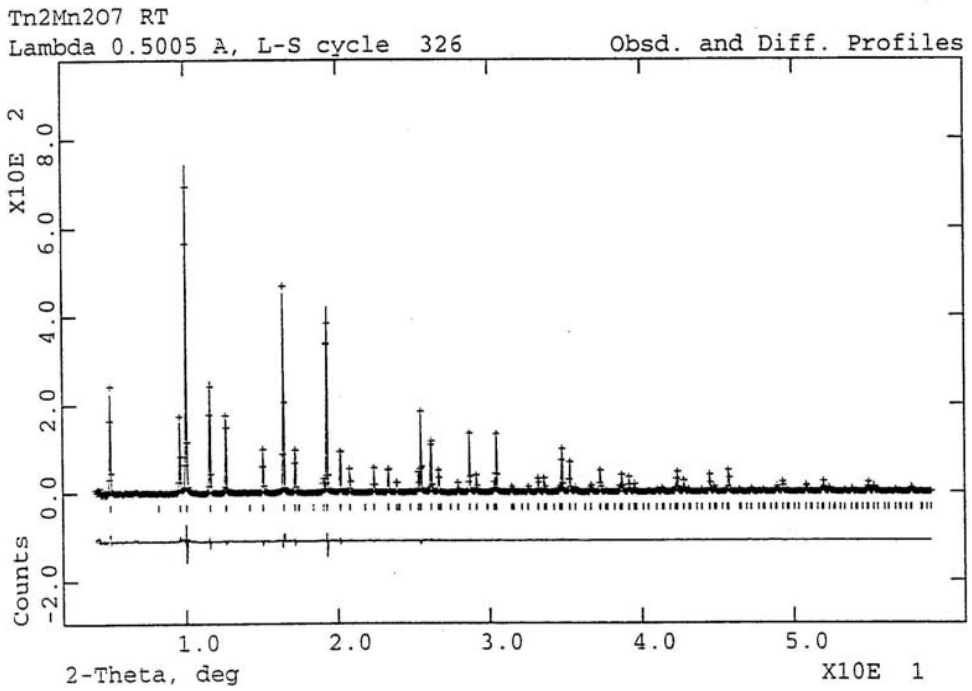
	1	180	-90	+90
Γ_1	1	1	1	1
Γ_2	1	-1	*i*	-*i*
Γ_3	1	1	-1	-1
Γ_4	1	-1	-*i*	*i*

Magnetic powder diffraction and instrumentation

Paolo G. Radaelli



neutrons



X-rays

Scattering condition for a single crystal

$$\mathbf{k}_i = \frac{2\pi}{\lambda}\hat{\mathbf{s}}_i \qquad \mathbf{k}_f = \frac{2\pi}{\lambda}\hat{\mathbf{s}}_f \qquad \mathbf{p} = \hbar\mathbf{k} \quad \Rightarrow \quad \text{De Broglie}$$

$$(\mathbf{k}_f - \mathbf{k}_i)\cdot\mathbf{a}_j = \mathbf{Q}\cdot\mathbf{a}_j = 2\pi h_j$$

$h_j = h,k,l$ (Miller indices) $\Rightarrow$ Laue equation

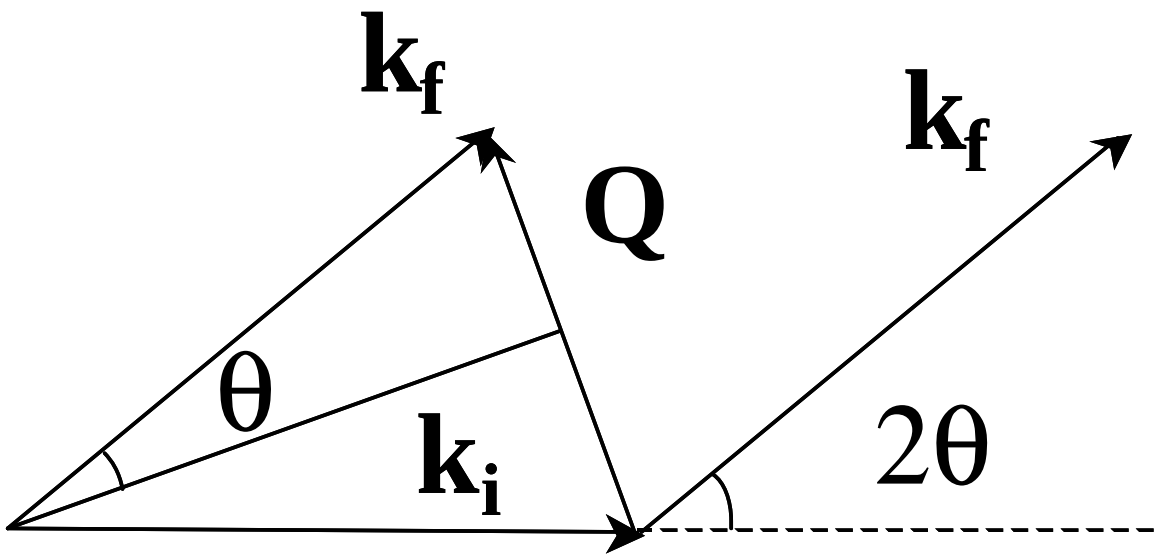
$$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i = \boldsymbol{\tau} = 2\pi\sum_i \mathbf{a}_i^* h_i$$

$\Rightarrow$ Reciprocal lattice

$$\mathbf{a}_1^* = \frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\cdots$$

Note: often people use $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$

Scattering triangle and Bragg law



$$Q = \frac{2\pi}{d} = \frac{4\pi \sin\theta}{\lambda} \qquad p_i = \hbar k_i = \frac{2\pi\hbar}{\lambda} \qquad d = \frac{\lambda}{2\sin\theta}$$

$$\lambda v = \frac{2\pi\hbar}{m_n} = 3.96 \times 10^3 \quad [\text{Å m sec}^{-1}]$$

TOF

$$\tau\,[\mu\text{sec}] = d\,[\text{Å}] \times 505.4 \cdot L\,[m] \cdot \sin\theta$$

Spacing formulae

$$\frac{1}{d_{hlk}^{\ 2}} = \frac{1}{\left(1+2\cos\alpha\cos\beta\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma\right)}$$

$$\times\left\{\frac{h^2\sin^2\alpha}{a^2}+\frac{k^2\sin^2\beta}{b^2}+\frac{l^2\sin^2\gamma}{c^2}+\frac{2hk}{ab}\left(\cos\alpha\cos\beta-\cos\gamma\right)\right.$$

$$\left.+\frac{2kl}{bc}\left(\cos\beta\cos\gamma-\cos\alpha\right)+\frac{2hl}{ac}\left(\cos\alpha\cos\gamma-\cos\beta\right)\right\}$$

The Scattering Function

$$\mathrm{P} = \varepsilon_{\mathrm{det}} \Phi \, V n_u \cdot \int S(\mathbf{Q}) d\Omega \quad [particles / \mathrm{sec}]$$

n_u ["*units*"/ Å^3] number density

$S(\mathbf{Q})$ [$barns = 10^{-24}\, cm^2$] Scattering function

Sometimes $S(\mathbf{Q})$ is normalised to $S_\infty(\mathbf{Q})$

Magnetic Scattering of Neutrons

Neutrons are strongly scattered from magnetic moments. The scattering <u>amplitude</u> from an ion is of the order of $\gamma r_e \mu$, where:

$\gamma = -1.91$ Neutron magnetic moment in nuclear magnetons (spin + orbital).

$r_e = 0.282 \cdot 10^{-12}$ *cm* Electron classical radius ($e^2/m_e c^2$)

μ = ion magnetic moment in Bohr magnetons.

For comparison, typical nuclear scattering amplitudes for neutrons are of the order of $0.5\text{-}1.0 \cdot 10^{-12}$ *cm*.

Single-atom magnetic scattering factors

$$\vec{\mathbf{A}}_{mag} = r_e \cdot \gamma \cdot f_m(Q)\,\mu \cdot \frac{1}{Q^2}\left(Q \times \hat{\mathbf{m}} \times Q\right)$$

$$\left(\frac{\partial \sigma}{\partial \Omega}\right)_{mag}^{unpol} = \left(r_e \cdot \gamma \cdot f_m(Q) \cdot \mu\right)^2 \cdot \frac{1}{Q^4}\left|Q \times \hat{\mathbf{m}} \times Q\right|^2$$

$$f_m(Q) = \frac{\int d\mathbf{r} M(\mathbf{r})\, e^{iQ\cdot\mathbf{r}}}{\int d\mathbf{r} M(\mathbf{r})}$$

$$\gamma = -1.91\,\mu_n \;;\; \mu_n = 1/966\;\mu_B \quad ;\; \mu_B = \frac{\hbar e}{2m} = 9.25 \times 10^{-24} JT^{-1}$$

The Magnetic Form Factor

$$f(\mathbf{Q}) = \frac{\left\langle \psi \left| \int \hat{\mathbf{M}}(\mathbf{r})\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}}\, dr^3 \right| \psi \right\rangle}{\left\langle \psi \left| \int \hat{\mathbf{M}}(\mathbf{r}) dr^3 \right| \psi \right\rangle}$$ over a single atom

In the isotropic case:

$$f(\mathbf{Q}) = f(Q) = \langle j_0(Q) \rangle + \left(1 - \tfrac{2}{g}\right) \langle j_2(Q) \rangle$$

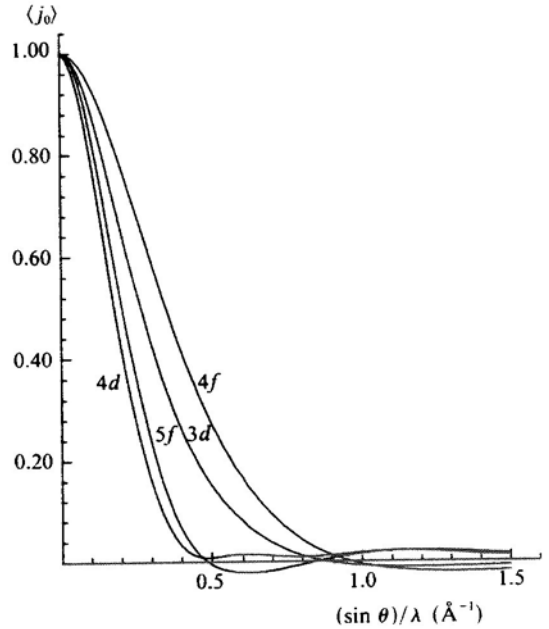


Fig. 6.1.2.2. Comparison of 3*d*, 4*d*, 4*f*, and 5*f* form factors. The 3*d* form factor is for Co, and the 4*d* for Rh, both calculated from wavefunctions given by Clementi & Roetti (1974). The 4*f* form factor is for Gd^{3+} calculated by Freeman & Desclaux (1972) and the 5*f* is that for U^{3+} given by Desclaux & Freeman (1978).

From: International Tables of Crystallography, Volume C, ed. by AJC Wilson, Kluwer Ac. Pub., 1998, p. 513

Atomic scattering factors

$$A_{\text{Atom}} = r_e \cdot \left[P + (1-P)\cos^2 2\theta\right]^{1/2} \cdot f(\mathbf{Q})$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{Atom}} = r_e{}^2 \cdot \left[P + (1-P)\cos^2 2\theta\right] \cdot \left|f(\mathbf{Q})\right|^2$$

X-rays

$$r_e = \frac{e^2}{mc^2} = 0.2818\ 10^{-14}\ \text{m} \qquad r_e{}^2 = 7.94\times10^{-2}\ \text{barns}$$

$$f(\mathbf{q}) = \int d\mathbf{r}\rho(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$A_{coh} = b_{coh}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} = \left|b_{coh}\right|^2 \quad [\text{barns}]$$

Neutrons (nuclear)

$$\mathbf{A}_{mag} = r_e \cdot \gamma \cdot f_m(\mathbf{Q})\,\mu \cdot \hat{\mathbf{m}}$$

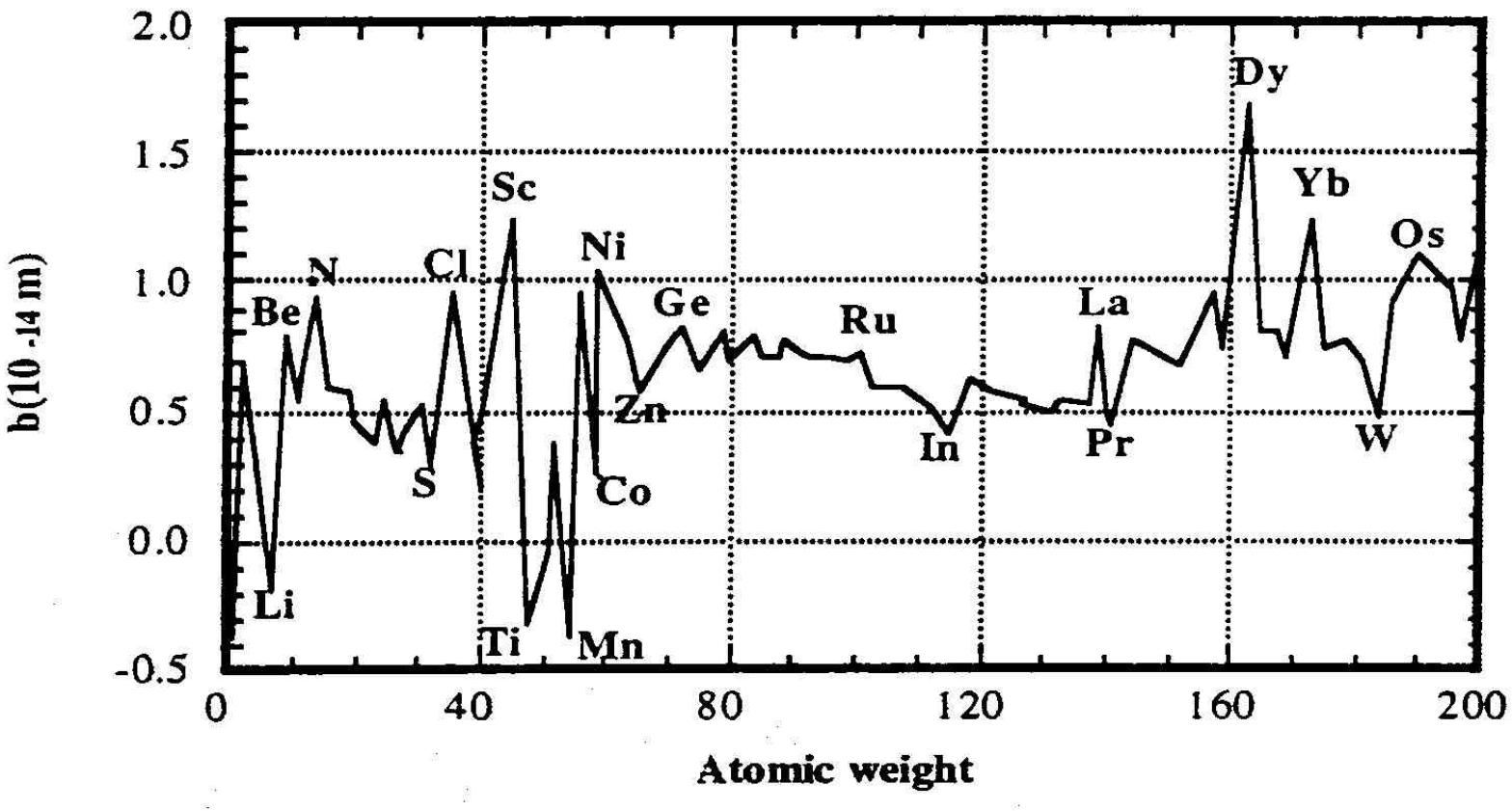
$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{mag}^{unpol} = \left(r_e \cdot \gamma \cdot f_m(\mathbf{Q}) \cdot \mu\right)^2 \cdot \frac{1}{Q^4}\left|\mathbf{Q}\times\hat{\mathbf{m}}\times\mathbf{Q}\right|^2$$

Neutrons (magnetic)

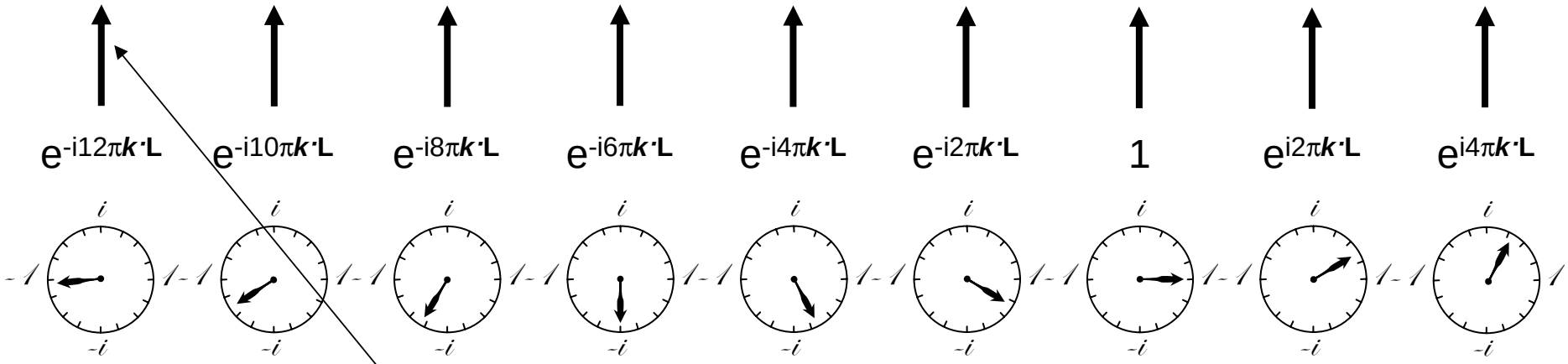
$$f_m(\mathbf{Q}) = \frac{\int d\mathbf{r}M(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}}}{\int d\mathbf{r}M(\mathbf{r})}$$

$$\gamma = -1.91\,\mu_n\ ;\ \mu_n = 1/966\ \mu_B \quad ;\ \mu_B = \frac{\hbar e}{2m} = 9.25\times10^{-24}\,JT^{-1}$$

Fermi lengths vs atomic weight



Propagation Vector



Fourier Components (complex)

k

Moments are classical, real axial vectors

Scattering of neutrons from magnetic structures

$$\vec{\mathbf{m}}_{j,n} = \vec{\mathbf{m}}_j e^{i\varphi_j} e^{i\mathbf{k}\cdot\mathbf{R}_n} + c.c.$$

$$\vec{\mathbf{A}}(\mathbf{Q}) = r_e \cdot \gamma \cdot \sum_{n,j} f_j(\mathbf{Q}) \frac{\mathbf{Q}\times\vec{\mathbf{m}}_{j,n}\times\mathbf{Q}}{Q^2} e^{i\mathbf{Q}\cdot\mathbf{R}_n - W_j(Q)} =$$

$$= r_e \cdot \gamma \cdot \sum_n \vec{\mathbf{M}}_p e^{i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_n} + \vec{\mathbf{M}}_p{}^* e^{i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_n}$$

$$\vec{\mathbf{M}}_p = \sum_j f_j(\mathbf{Q}) \frac{\mathbf{Q}\times\vec{\mathbf{m}}_j e^{i\varphi_j}\times\mathbf{Q}}{Q^2} e^{-W_j(Q)}$$

It is useful to define **Q,** the *magnetic interaction vector*

Scattering of neutrons from magnetic structures-II

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{mag}^{unpol} = \vec{\mathbf{A}}(\mathbf{Q})\cdot\vec{\mathbf{A}}^{*}(\mathbf{Q}) =$$

$$= \left(r_e\cdot\gamma\right)^2 \sum_{n,n'}\left[\vec{\mathbf{M}}_p\, e^{i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_n} + \vec{\mathbf{M}}_p{}^{*}\, e^{i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_n}\right]\cdot\left[\vec{\mathbf{M}}_p{}^{*} e^{-i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_n} + \vec{\mathbf{M}}_p\, e^{-i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_{n'}}\right]$$

$$= \left(r_e\cdot\gamma\right)^2 N\sum_{n}\vec{\mathbf{M}}_p\cdot\vec{\mathbf{M}}_p{}^{*}\left[e^{i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_n} + e^{i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_n}\right] +$$

$$+\left(r_e\cdot\gamma\right)^2 \sum_{n,n'}\left[\vec{\mathbf{M}}_p\cdot\vec{\mathbf{M}}_p\; e^{i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_n - i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_{n'}} + \vec{\mathbf{M}}_p{}^{*}\cdot\vec{\mathbf{M}}_p{}^{*} e^{i(\mathbf{Q}-\mathbf{k})\cdot\mathbf{R}_n - i(\mathbf{Q}+\mathbf{k})\cdot\mathbf{R}_{n'}}\right]$$

Case 1: **k** is a generic point in the Brillouin zone

$$2\mathbf{k} \neq \boldsymbol{\kappa}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{mag}^{unpol} = \left(r_e \cdot \gamma\right)^2 N \vec{\mathbf{M}}_p \cdot \vec{\mathbf{M}}_p^{\,*} \left[\delta\left(\mathbf{Q}-\boldsymbol{\kappa}+\mathbf{k}\right)+\delta\left(\mathbf{Q}-\boldsymbol{\kappa}-\mathbf{k}\right)\right]$$

$$\mathbf{q} := \mathbf{Q}-\boldsymbol{\kappa}$$

Case 2: **k** is a Lifshits vector (special point of symmetry)

$$2\mathbf{k} = \boldsymbol{\kappa}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{mag}^{unpol} = \left(r_e \cdot \gamma\right)^2 N\,\delta\left(\mathbf{Q}-\boldsymbol{\kappa}+\mathbf{k}\right)\left[2\vec{\mathbf{M}}_p \cdot \vec{\mathbf{M}}_p{}^* + \vec{\mathbf{M}}_p \cdot \vec{\mathbf{M}}_p + \vec{\mathbf{M}}_p{}^* \cdot \vec{\mathbf{M}}_p{}^*\right]$$

$$= 4\left(r_e \cdot \gamma\right)^2 N\,\delta\left(\mathbf{Q}-\boldsymbol{\kappa}+\mathbf{k}\right)\left|\mathrm{Re}\,\vec{\mathbf{M}}_p\right|^2$$

$$\vec{\mathbf{m}}_{j,n} = \vec{\mathbf{m}}_j e^{i\varphi_j}\left(-1\right)^{n//} + c.c. = 2\vec{\mathbf{m}}_j \cos\varphi_j \left(-1\right)^{n//}$$

Magnetic Scattering Formulæ

Polarised neutrons - polarisation analysis

Non-flip

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q})\right)^{++} = (\gamma r_e)^2 \left\{ \left|\hat{\mathbf{s}}_n \cdot \vec{\mathbf{M}}_p(\mathbf{Q})\right|^2 + \left|F'(\mathbf{Q})\right|^2 + \hat{\mathbf{s}}_n \cdot \left[\vec{\mathbf{M}}_p{}^*(\mathbf{Q}) F'(\mathbf{Q}) + \vec{\mathbf{M}}_p(\mathbf{Q}) F'^*(\mathbf{Q})\right] \right\}$$

Flip $$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q})\right)^{+-} = (\gamma r_e)^2 \left\{ \left[\hat{\mathbf{s}}_n \times \vec{\mathbf{M}}_p(\mathbf{Q})\right] \cdot \left[\hat{\mathbf{s}}_n \times \vec{\mathbf{M}}_p{}^*(\mathbf{Q})\right] + i\hat{\mathbf{s}}_n \cdot \left[\vec{\mathbf{M}}_p(\mathbf{Q})^* \times \vec{\mathbf{M}}_p(\mathbf{Q})\right] \right\}$$

Total

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q})\right)^{\uparrow} = (\gamma r_e)^2 \left\{ \left|\vec{\mathbf{M}}_p(\mathbf{Q})\right|^2 + \left|F'(\mathbf{Q})\right|^2 + \hat{\mathbf{s}}_n \cdot \left[\vec{\mathbf{M}}_p{}^*(\mathbf{Q}) F'(\mathbf{Q}) + \vec{\mathbf{M}}_p(\mathbf{Q}) F'^*(\mathbf{Q}) + i\vec{\mathbf{M}}_p(\mathbf{Q})^* \right.\right.$$

Unpolarised neutrons

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q})\right)^{Unpol} = (\gamma r_e)^2 \left\{ \left|\vec{\mathbf{M}}_p(\mathbf{Q})\right|^2 + \left|F'(\mathbf{Q})\right|^2 \right\}$$

Formulæ Explained

Non-flip: In addition to the nuclear scattering, it contains the components of $\mathbf{M}_{\boldsymbol{p}}(\mathbf{Q})$ parallel to the neutron spin and a magneto-structural interference term.

Flip: It contains the components of $\mathbf{M}_{\boldsymbol{p}}(\mathbf{Q})$ perpendicular to the neutron spin, plus an additional term which is present only if $\mathbf{M}_{\boldsymbol{p}}(\mathbf{Q})$ is complex.

Total: It contains the nuclear term, the module square of $\mathbf{M}_{\boldsymbol{p}}(\mathbf{Q})$ and the two terms which are linear in $\mathbf{s}_{\mathrm{n}}$.

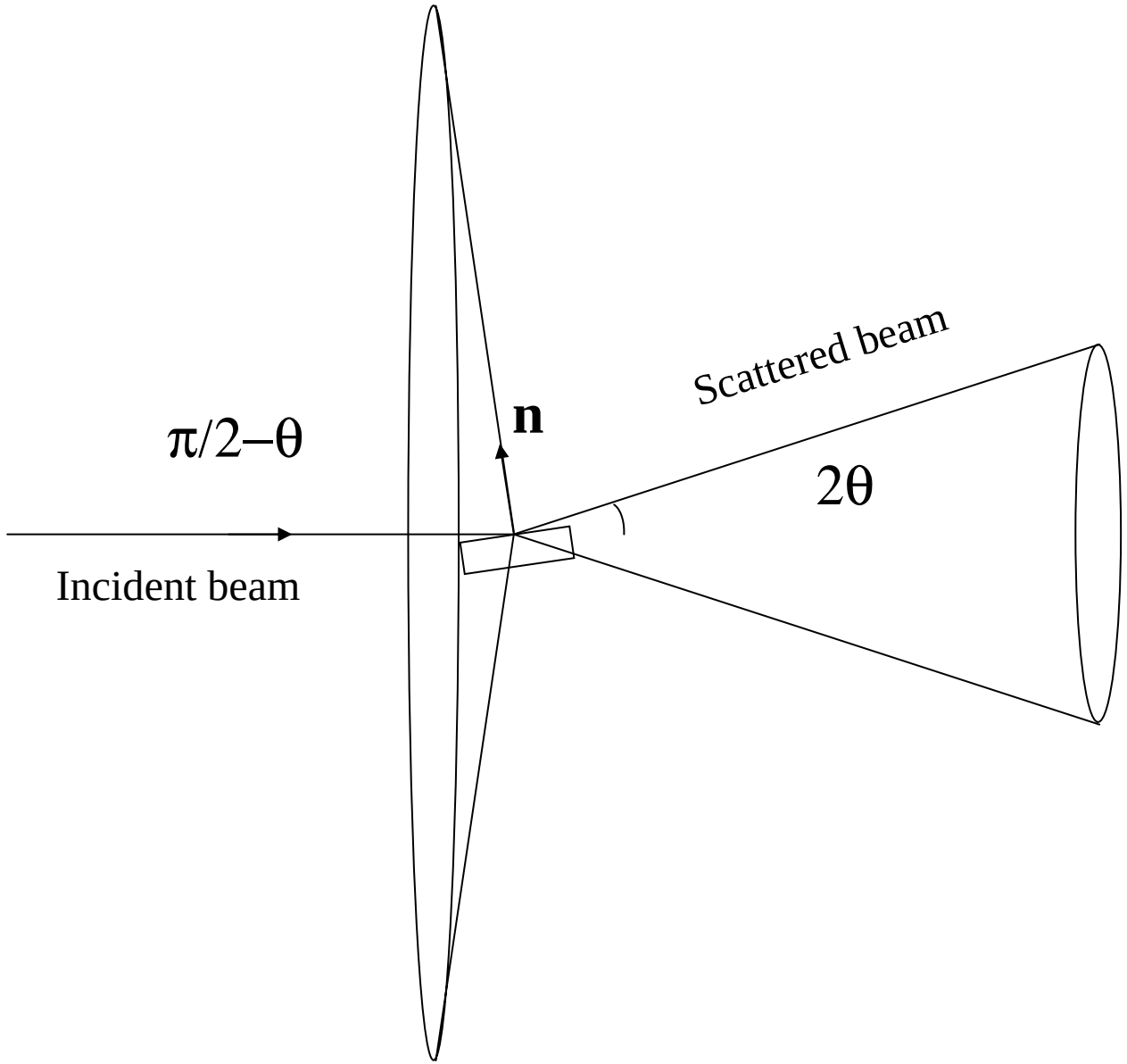
Unpolarised: It contains only the nuclear term and the module square of $\mathbf{M}_{\boldsymbol{p}}(\mathbf{Q})$, since the two terms which are linear in $\mathbf{s}_{\mathrm{n}}$ cancel upon averaging.

SX Scattering Function

$$S(\mathbf{Q}) = \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta^{(3)}(\mathbf{Q} - \boldsymbol{\tau}) \left| F(\boldsymbol{\tau}) \right|^2 \quad [\text{barns}]$$

v_0	[Å^3]	unit cell volume
$n_u = \frac{1}{v_0}$	[*u.c.*/Å^3]	number density
$\boldsymbol{\tau}$		R.L. nodes

Debye-Scherrer cones and powder stats



Powder Scattering Function

$$S(Q) = \frac{2\pi^2}{v_0} \sum_{\mathrm{mod}\,\tau} m_\tau \frac{\delta(Q-\tau)}{Q^2} \left|F(\tau)\right|^2 \quad [\mathrm{barns}]$$

v_0	[Å^3]	unit cell volume
$n_u = \frac{1}{v_0} p$	[*u.c.*/Å^3]	number density
τ		R.L. nodes
m_τ		multiplicity
p		packing fraction

The simplest case-I

Scattering of unpolarised neutrons from a collinear unmodulated structure. Here, $\boldsymbol{\kappa}$ is a reciprocal lattice vector.

For collinear structures (all moments // $\hat{\mathrm{m}}$)

$$\left|\vec{\mathbf{M}}_p(\mathbf{Q})\right|^2 = \sin^2(\alpha)\left|\sum_{j=1}^{\text{n atoms}} \mu_j f_j(Q)\mathrm{e}^{-i\mathbf{Q}\cdot r_j - W}\right|^2$$

where α is the angle between $\mathbf{Q}$ and $\hat{\mathrm{m}}$

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(\mathbf{Q})\right)^{Unpol} = (\gamma r_e)^2\left\{\left|\vec{\mathbf{M}}_p(\mathbf{Q})\right|^2 + \left|F'(\mathbf{Q})\right|^2\right\}$$

The simplest case-II

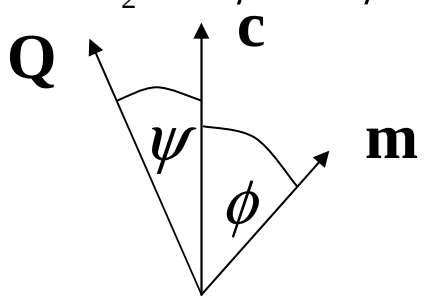
It looks like all the information is there to solve the structure even with unpolarised neutrons and powder diffraction. All the magnetic moment magnitudes are contained in $\mathbf{M}_p(\mathbf{Q})$ with the appropriate phase factors and signs. Also, the information about the direction of the magnetic moments is there through the prefactor $\sin^2(\alpha)$. So, why bother with polarised neutrons and single-crystal techniques?

Magnetic Powder Diffraction

Averaging of the $\sin^2(\alpha)$ term over the (quasi)-degenerate reflections:

- For Uniaxial Groups (3-fold, 4-fold, 6-fold) we can only determine the angle ϕ:

$$\overline{\sin^2\alpha} = 1 - \tfrac{1}{2}\sin^2\psi\sin^2\varphi - \cos^2\psi\cos^2\varphi$$



- For Cubic Structures, the direction of the magnetic moments is undetermined:

$$\overline{\sin^2\alpha} = 2/3$$

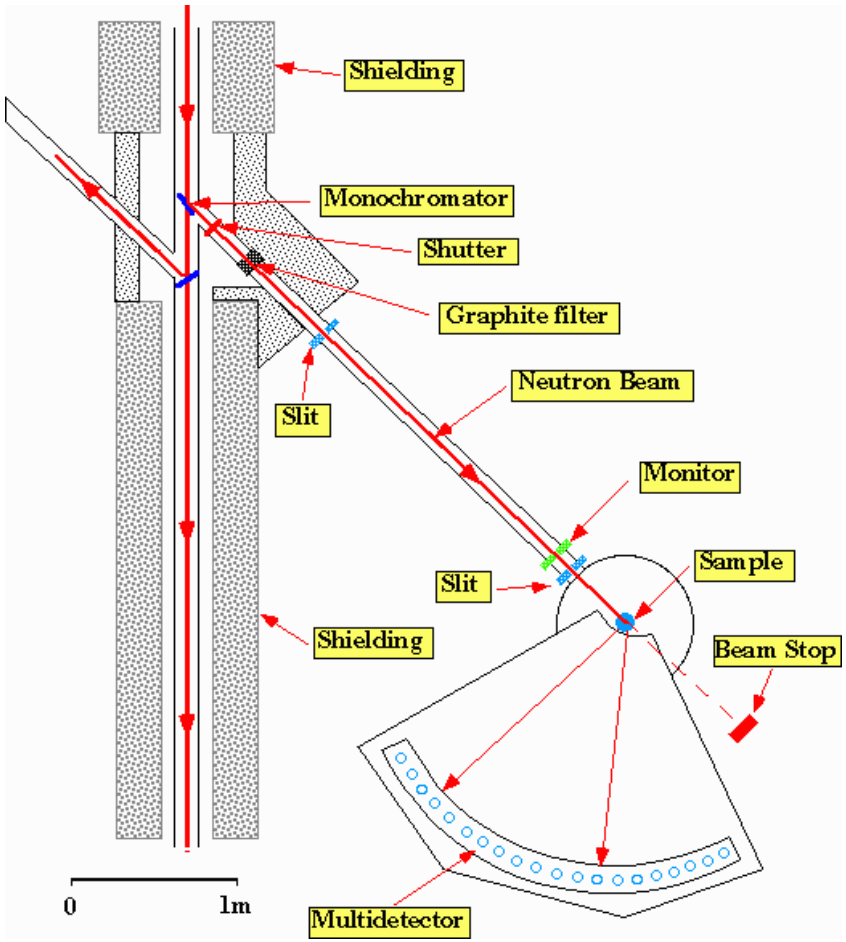
Magnetic Powder Diffractometers-I

- High-*Q* range: For magnetic structure analysis, one rarely needs to go beyond $\sin(\theta)/\lambda=0.5$. Wavelengths > 2 Å are ideal.
- Low-*Q* range: It is essential to have good coverage at low *k*, as many helimagnetic structures have very long periodicity. $Q=0.5$ Å^{-1} is the minimum acceptable to do any sensible work. $Q=0.1$ Å^{-1} is ideal.
- Resolution: it is desirable especially in structure with low crystallographic symmetry, because it enables to reduce the accidental degeneracy.

CW Powder Diffractometers

- Most magnetic structure problems are first tackled using high-intensity CW powder diffractometers (e.g., D1B). The biggest advantages are the excellent coverage at low Q, the high flux (that can be further enhanced through focussing) and the simplicity of the data structure. Resolution is generally quite poor.
- The use of high-resolution machines (e.g., D2B) is becoming more common, especially when the magnetic moments are large, the structure has low symmetry and there is an interplay between magnetism and structural properties.

The High-Intensity CW Powder diffractometer D1B at the ILL



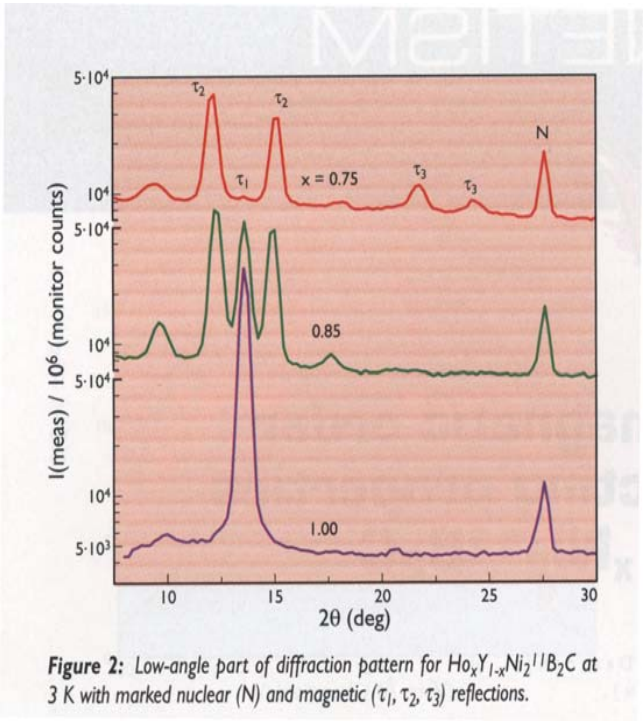
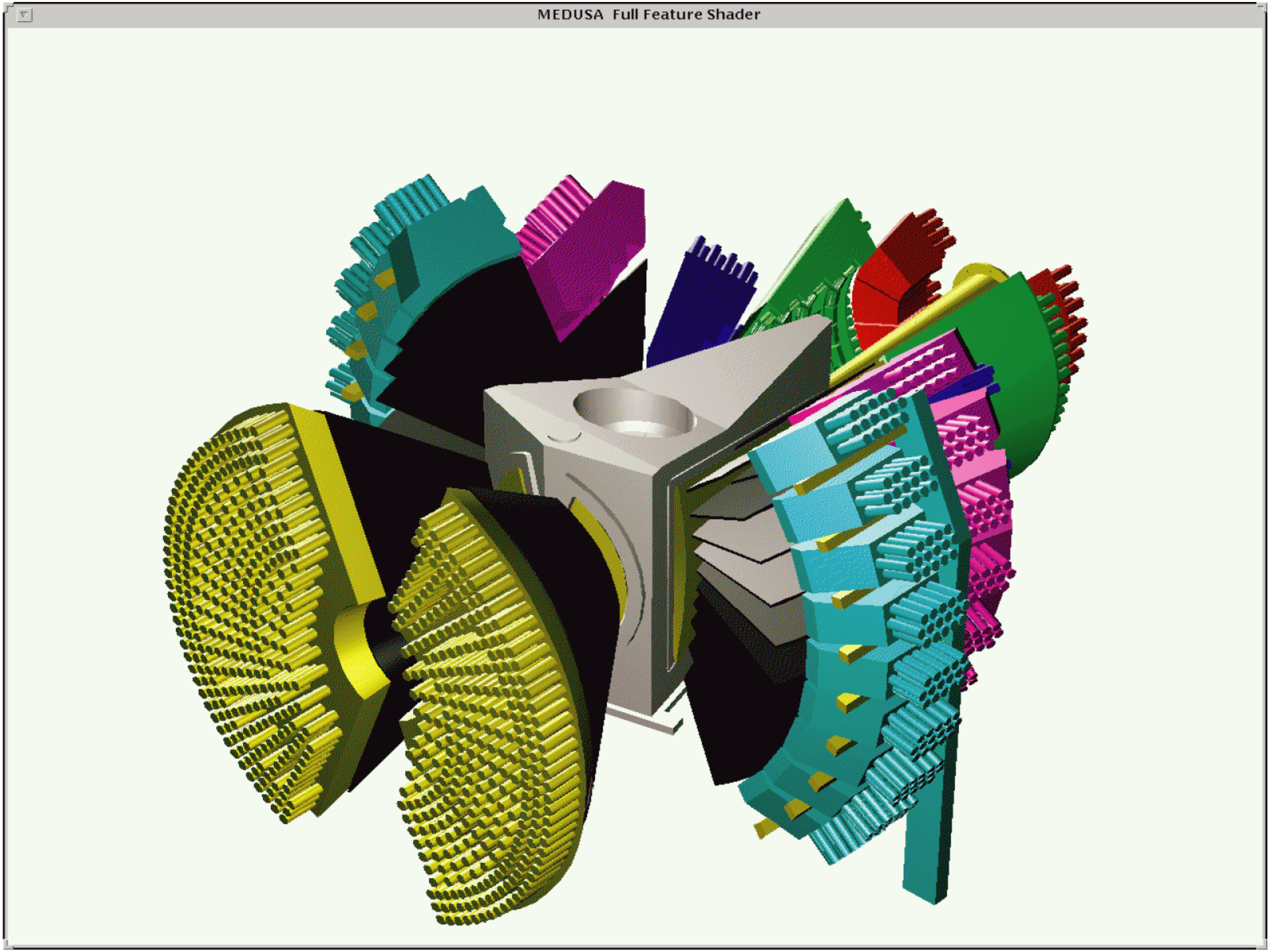
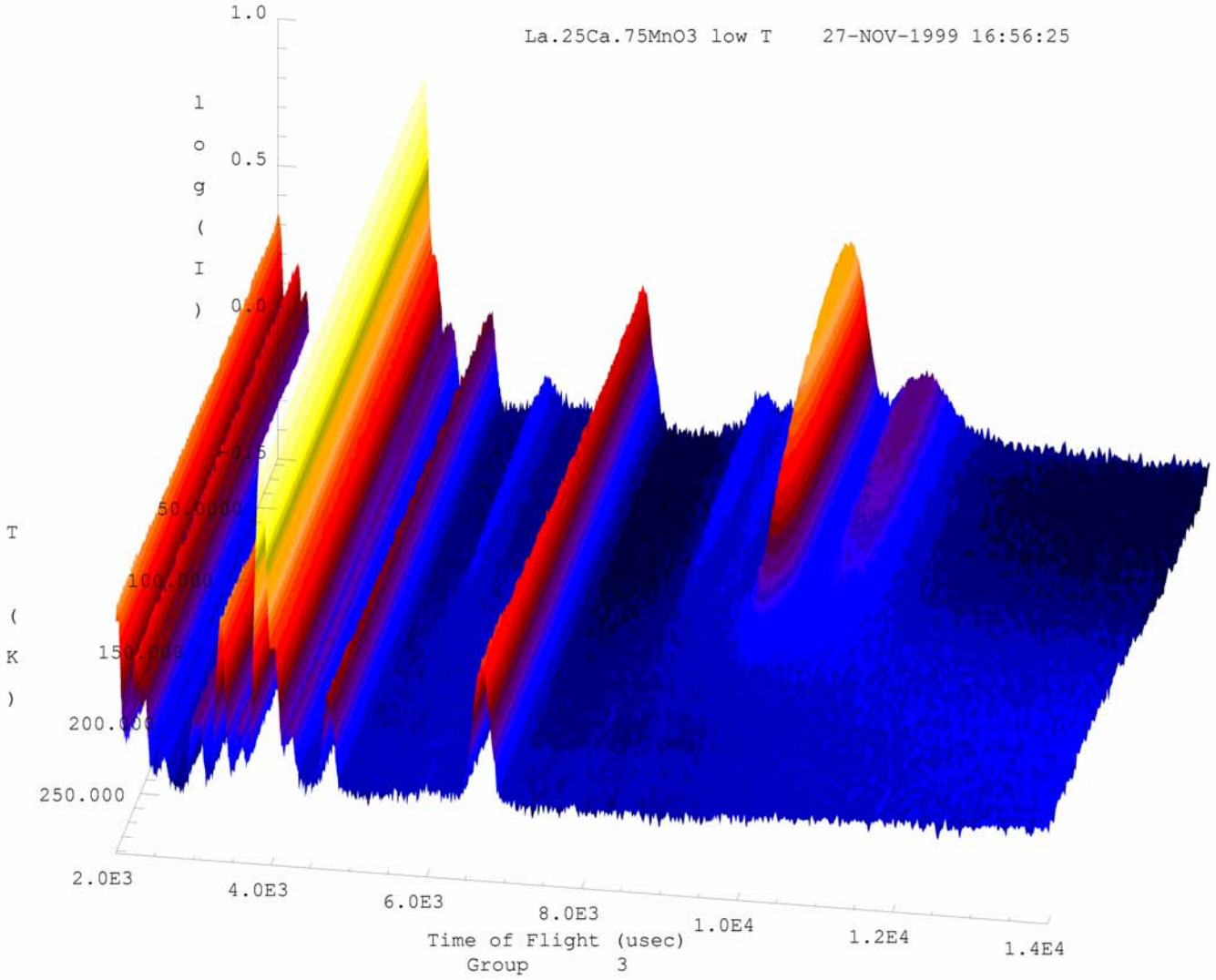
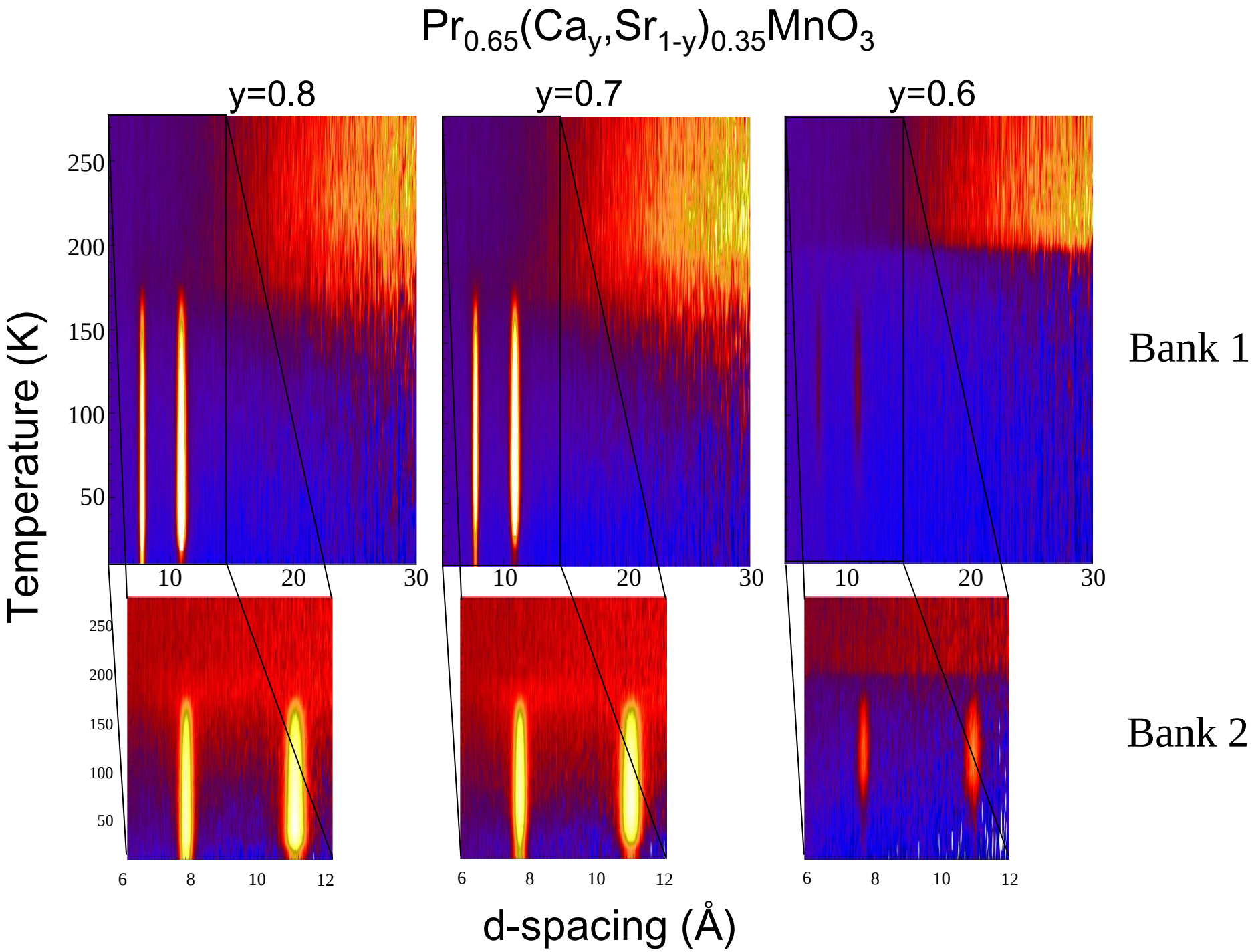
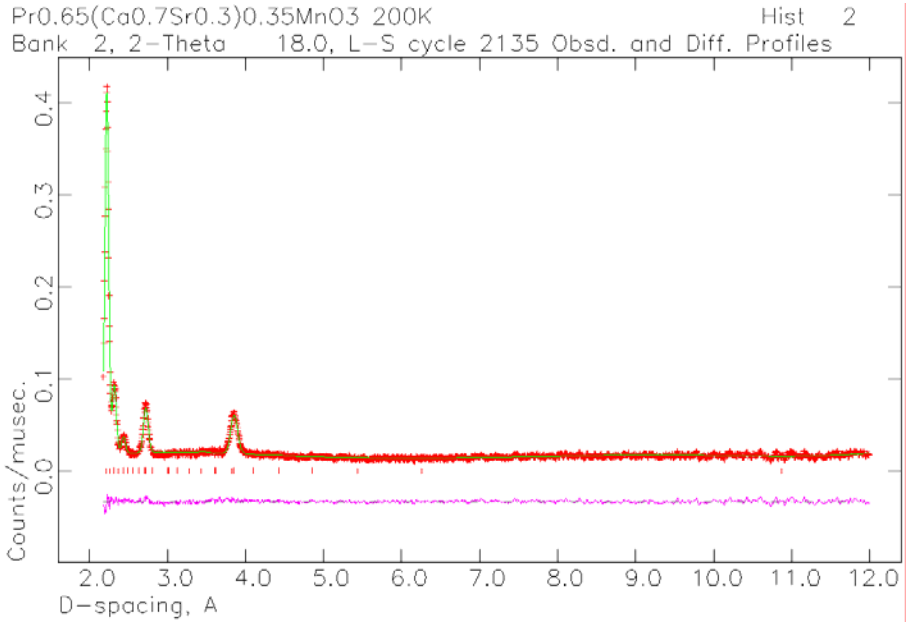


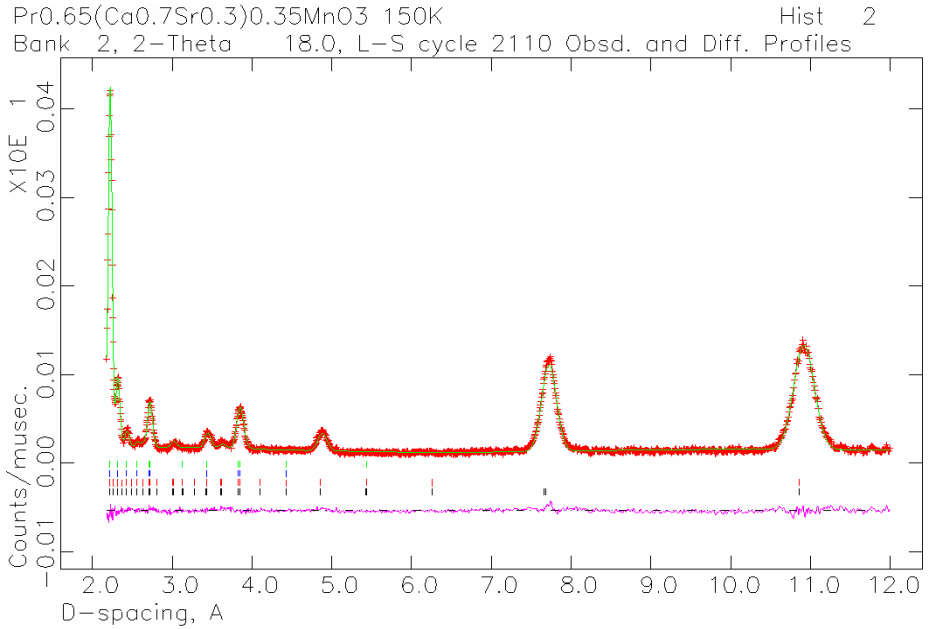
Figure 2: *Low-angle part of diffraction pattern for $Ho_xY_{1-x}Ni_2{}^{11}B_2C$ at 3 K with marked nuclear (N) and magnetic (τ_1, τ_2, τ_3) reflections.*

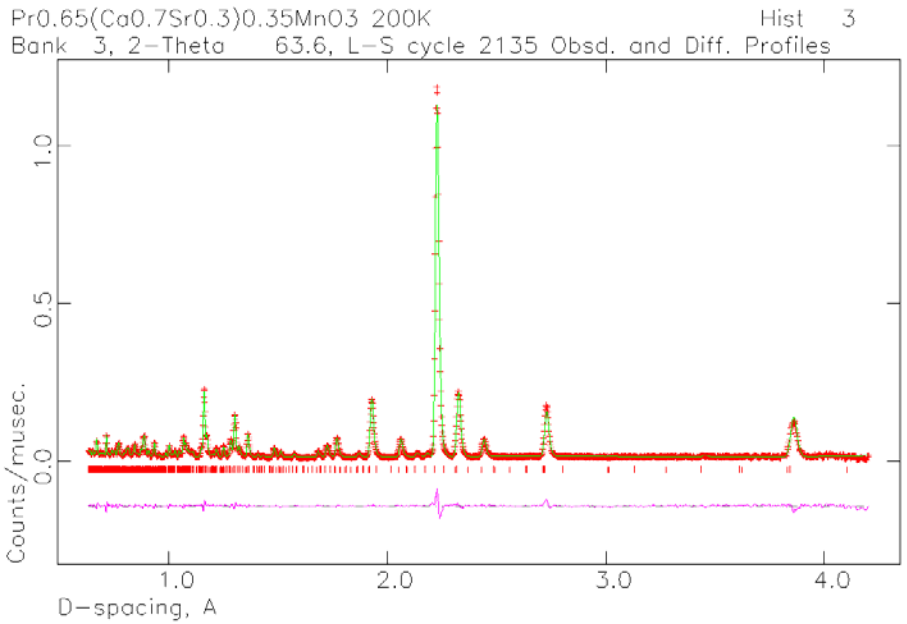

MEDUSA Full Feature Shader

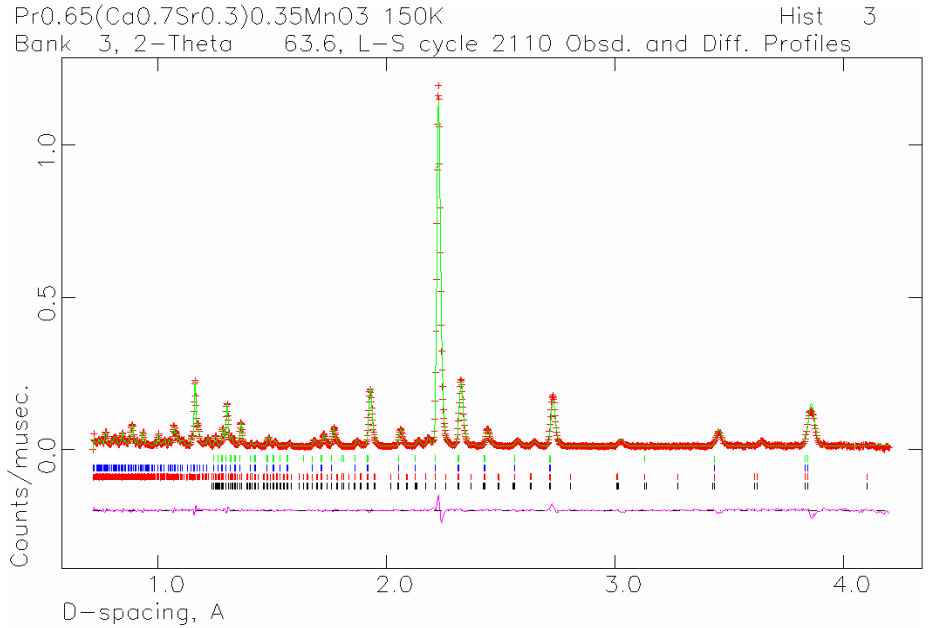

La.25Ca.75MnO3 low T 27-NOV-1999 16:56:25
log(I)
1.0
0.5
0.0
T (K)
50.000
100.000
150.000
200.000
250.000
2.0E3
4.0E3
6.0E3
8.0E3
1.0E4
1.2E4
1.4E4
Time of Flight (usec)
Group 3

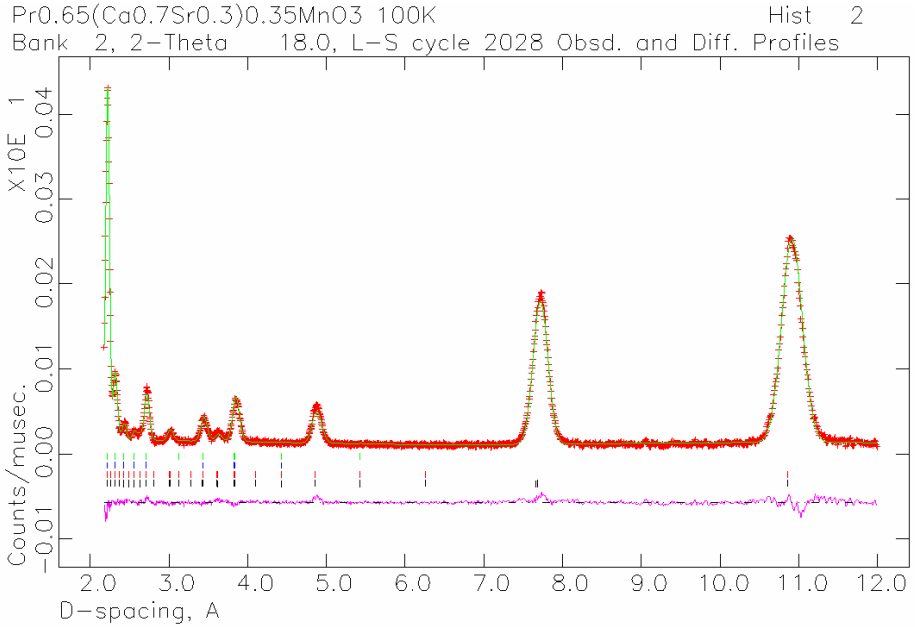

$Pr_{0.65}(Ca_y,Sr_{1-y})_{0.35}MnO_3$
y=0.8
y=0.7
y=0.6
Temperature (K)
250
200
150
100
50
10
20
30
Bank 1
Bank 2
6
8
10
12
d-spacing (Å)

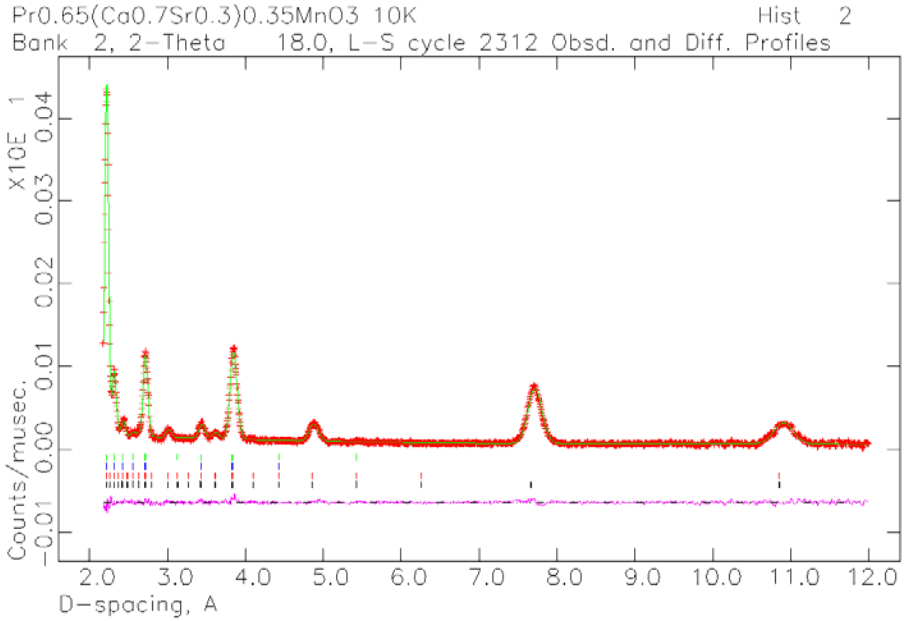

Pr0.65(Ca0.7Sr0.3)0.35MnO3 200K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2135 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A

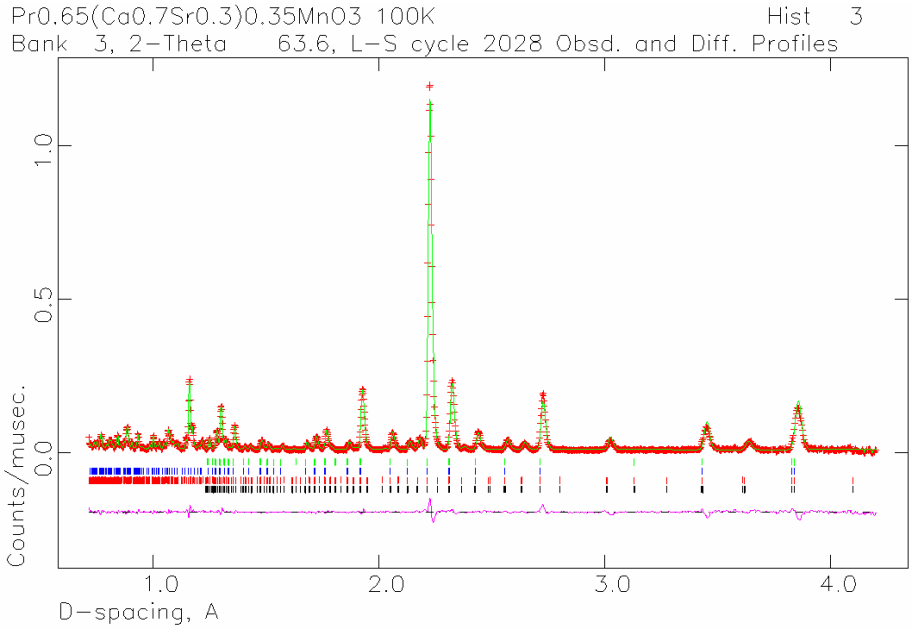

Pr0.65(Ca0.7Sr0.3)0.35MnO3 150K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2110 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
D-spacing, A

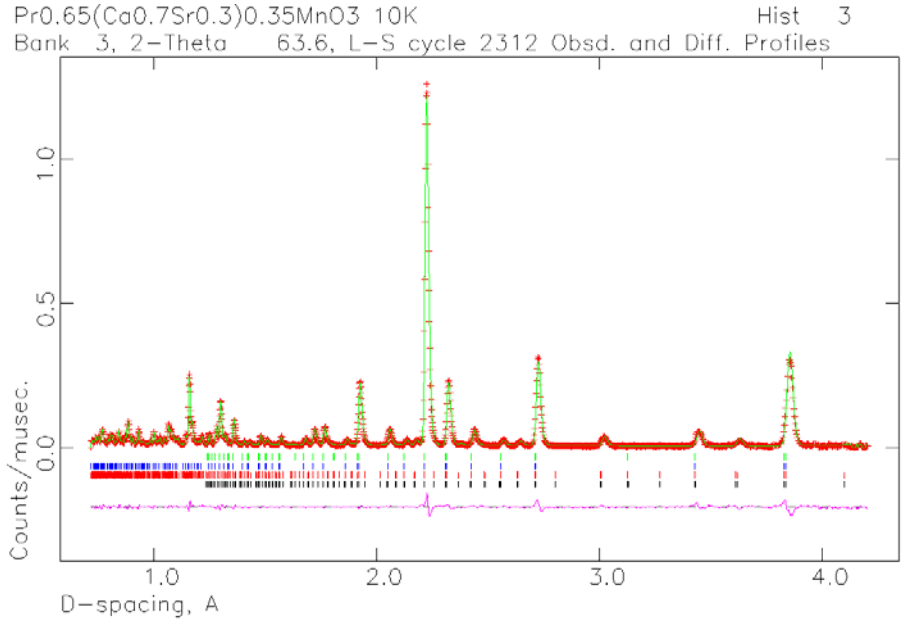

Pr0.65(Ca0.7Sr0.3)0.35MnO3 200K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2135 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 150K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2110 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A

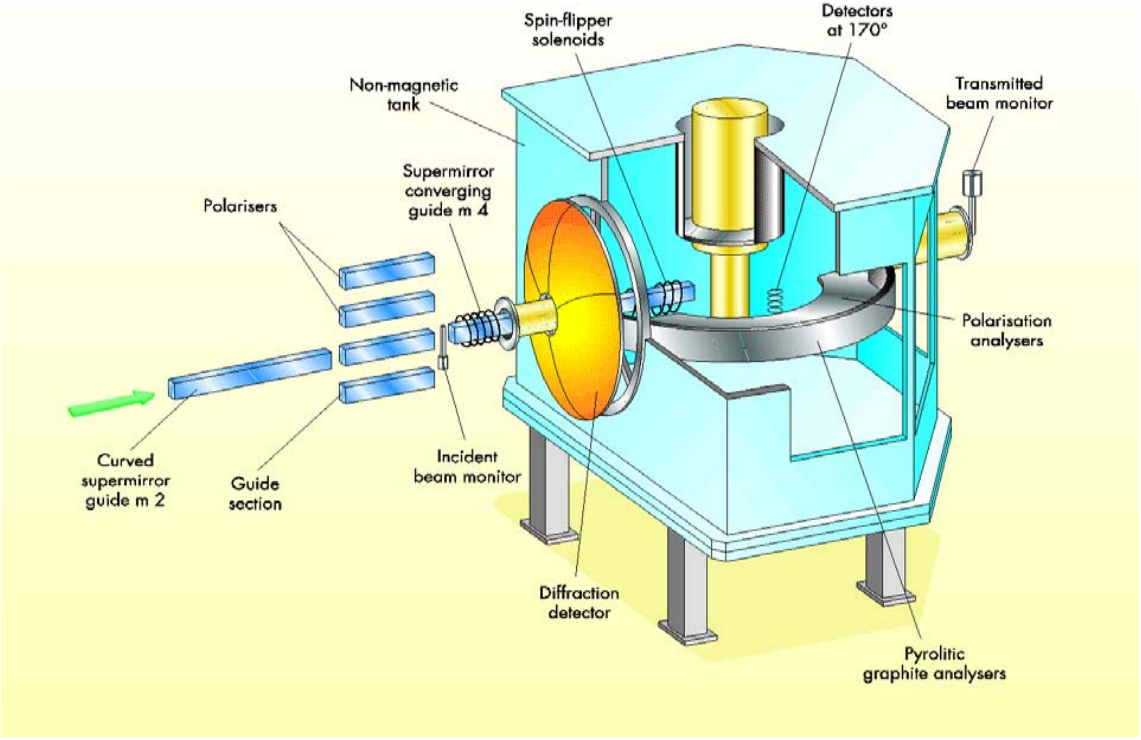

Pr0.65(Ca0.7Sr0.3)0.35MnO3 100K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2028 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
D-spacing, A

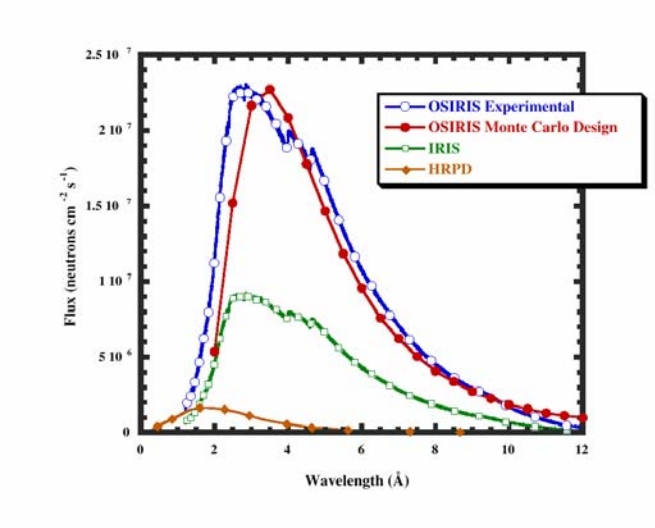

Pr0.65(Ca0.7Sr0.3)0.35MnO3 10K Hist 2
Bank 2, 2-Theta 18.0, L-S cycle 2312 Obsd. and Diff. Profiles
X10E 1
Counts/musec.
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 100K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2028 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A


Pr0.65(Ca0.7Sr0.3)0.35MnO3 10K Hist 3
Bank 3, 2-Theta 63.6, L-S cycle 2312 Obsd. and Diff. Profiles
Counts/musec.
D-spacing, A

OSIRIS





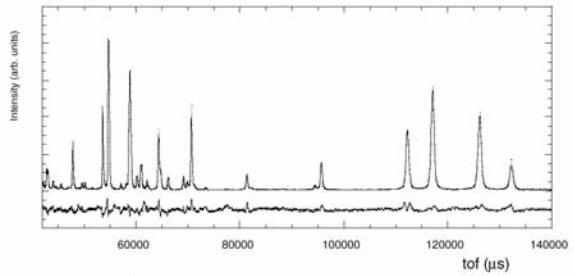
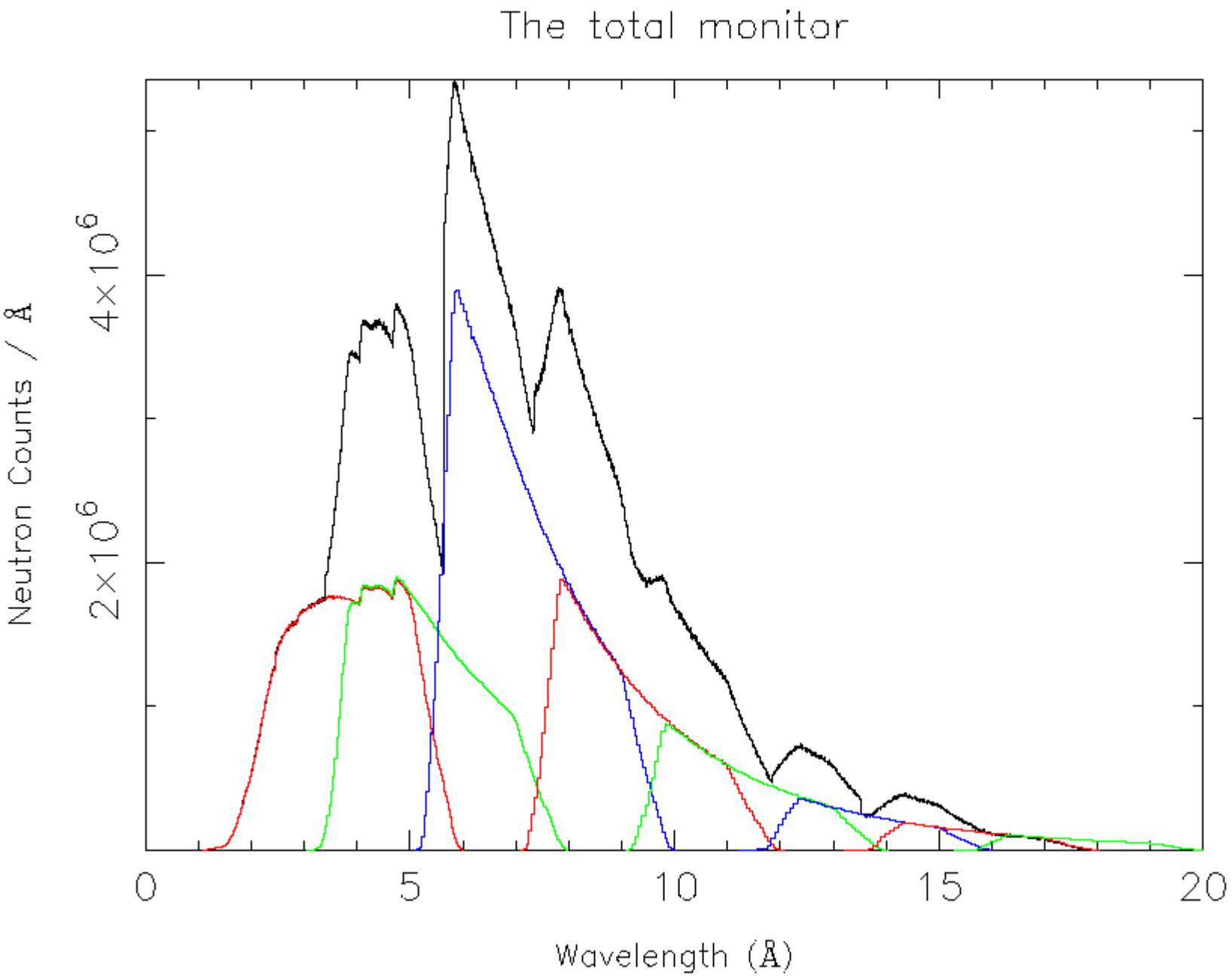
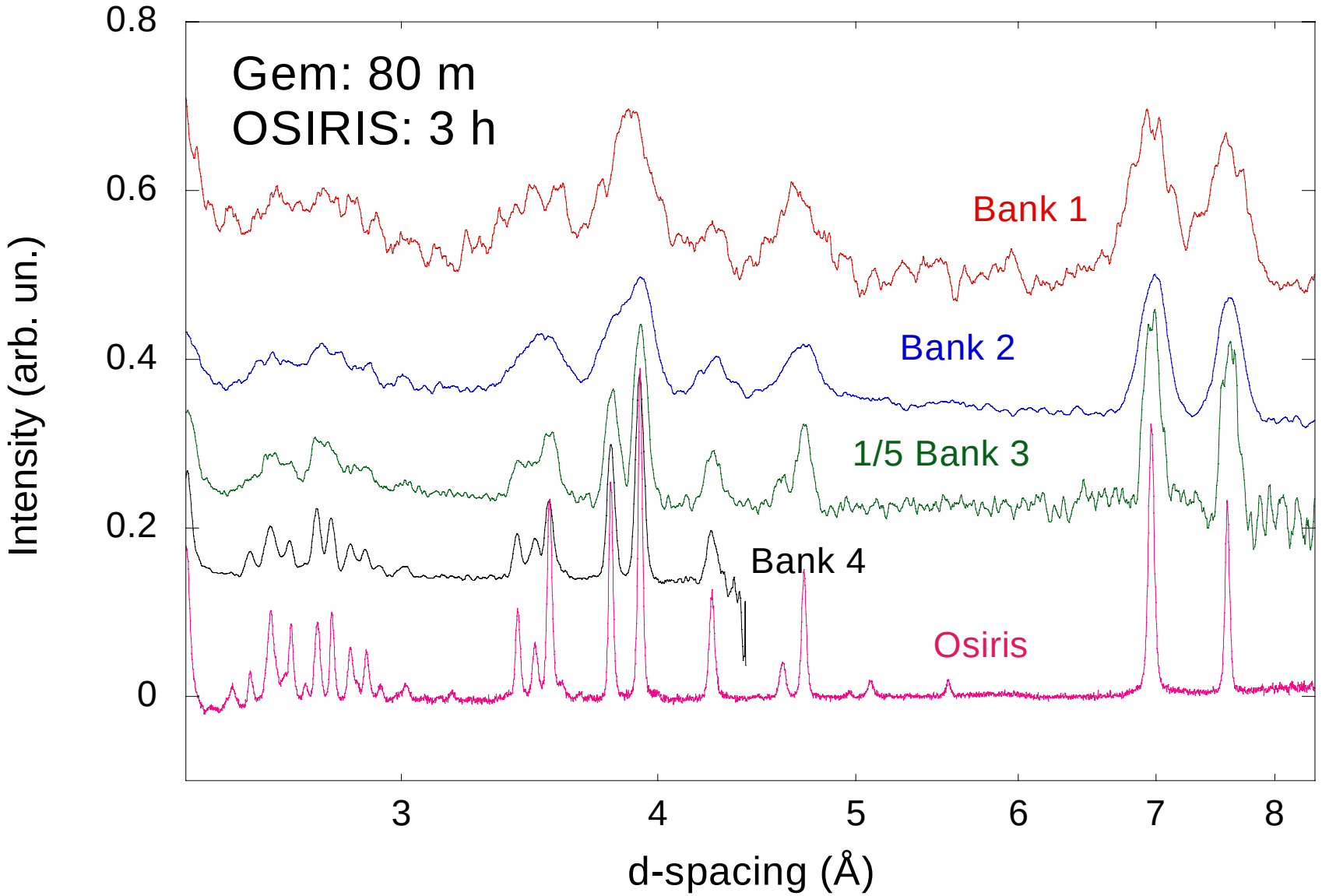
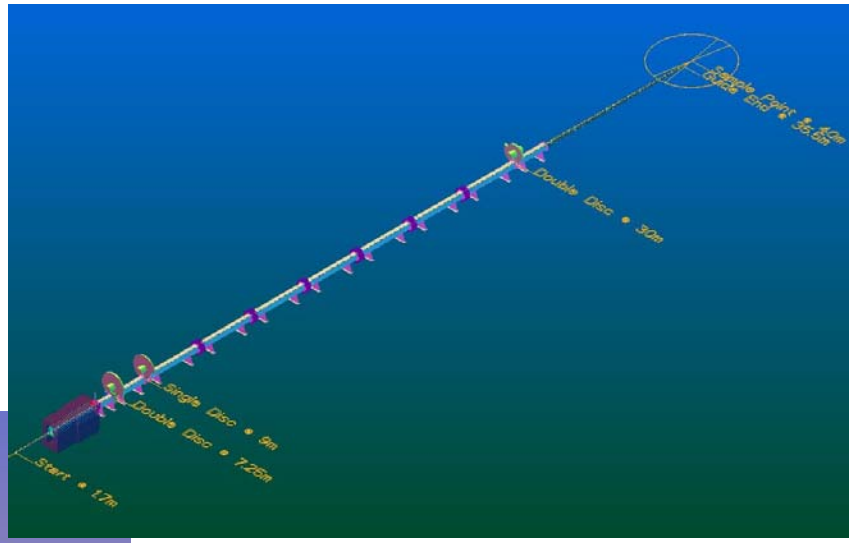


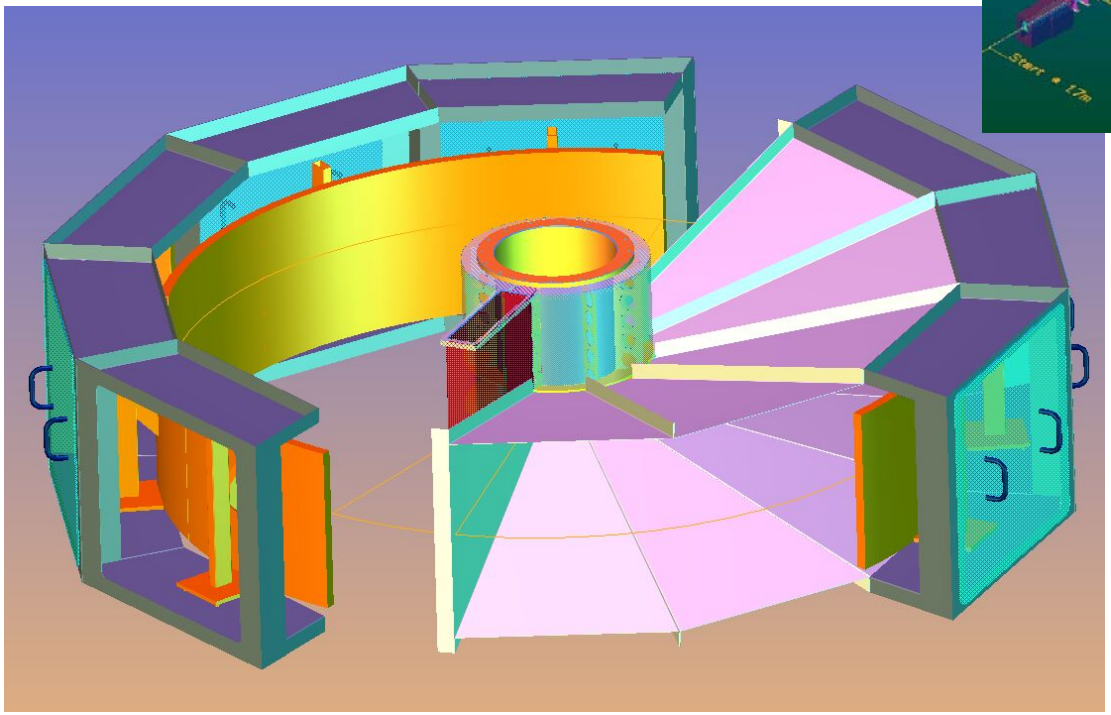
Fig. 2. Rietveld fit for $Ga_{0.08}Fe_{0.92}AsO_4$.

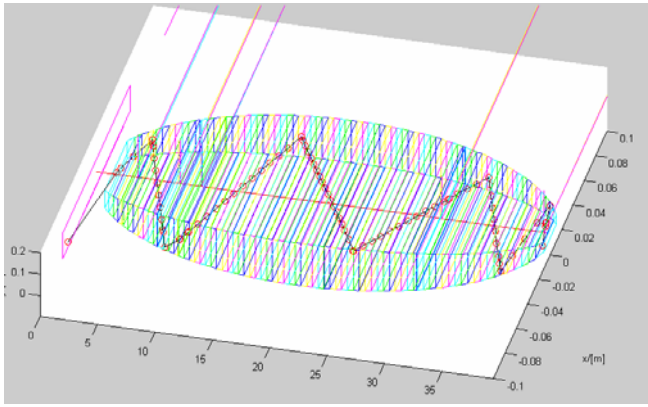

The total monitor
Neutron Counts / Å
2×10^6
4×10^6
0
5
10
15
20
Wavelength (Å)


GEM-OSIRIS Comparison
Magnetic Diffraction
Gem: 80 m
OSIRIS: 3 h
Bank 1
Bank 2
1/5 Bank 3
Bank 4
Osiris
Intensity (arb. un.)
0.8
0.6
0.4
0.2
0
3
4
5
6
7
8
d-spacing (Å)

WISH


Single Point
Double Disc • 30m
Single Disc • 9m
Double Disc • 7.25m
Start • 17m




0.2
0.1
0
0
5
10
15
20
25
30
35
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
-0.06
-0.08
-0.1
x/[m]

Monte-Carlo simulations