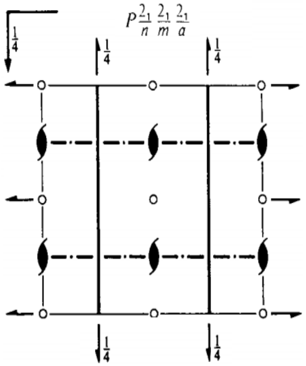
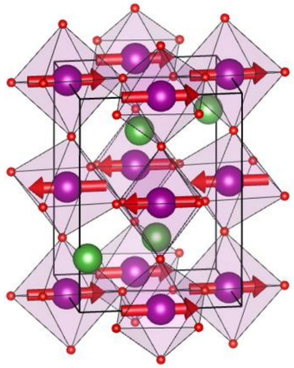
GDR MEETICC

Matériaux, Etats ElecTroniques, Interaction et Couplages non Conventionnels

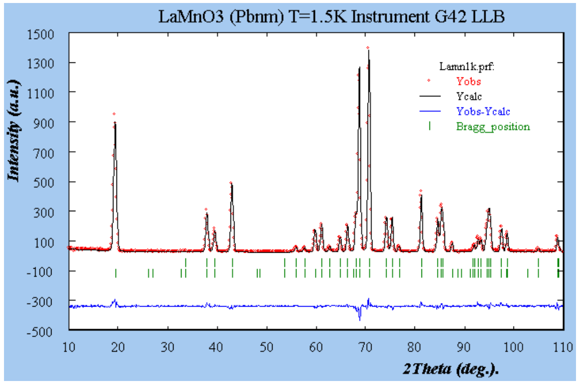




Winter school

4 – 10 February 2018,

Banyuls-sur-Mer, France



CRYSTALLOGRAPHIC and MAGNETIC STRUCTURES from NEUTRON DIFFRACTION: the POWER of SYMMETRIES (Lecture II)

Béatrice GRENIER & **Gwenaëlle ROUSSE**

UGA & CEA, INAC/MEM/MDN
Grenoble, France

UPMC & Collège de France,
Paris, France

Global outline *(Lectures II, and III)*

II- Magnetic structures

Description in terms of propagation vector: *the various orderings, examples*

Description in terms of symmetry:

- **Magnetic point groups**: *time reversal, the 122 magnetic point groups*
- **Magnetic lattices:** *translations and anti-translations, the 36 magnetic lattices*
- **Magnetic space groups** = Shubnikov groups

III- Determination of nucl. and mag. structures from neutron diffraction

Nuclear and magnetic neutron diffraction: *structure factors, extinction rules*

Examples in powder neutron diffraction

Examples in single-crystal neutron diffraction

Interest of magnetic structure determination ?

Some material from: J. Rodriguez-Carvajal, L. Chapon and M. Perez-Mato was used to prepare Lectures II and III

Interest of magnetic structure determination

1. A PROFILE REFINEMENT METHOD FOR NUCLEAR AND MAGNETIC STRUCTURES
By: RIETVELD, HM
JOURNAL OF APPLIED CRYSTALLOGRAPHY Volume: 2 Pages: 65-& Part: 2 Published: 1969
Full Text from Publisher
Times Cited: 9,529 *(from Web of Science Core Collection)*
Usage Count

2. RECENT ADVANCES IN MAGNETIC-STRUCTURE DETERMINATION BY NEUTRON POWDER DIFFRACTION
EN
By: RODRIGUEZCARVAJAL, J
Conference: WORKSHOP ON THE USE OF NEUTRONS AND X-RAYS IN THE STUDY OF MAGNETISM Location: GRENOBLE, FRANCE Date: JAN 21-23, 1993
Sponsor(s): INST LAUE LANGEVIN; EUROPEAN SYNCHROTRON RADIAT FACIL
PHYSICA B Volume: 192 Issue: 1-2 Pages: 55-69 Published: OCT 1993
Full Text from
Times Cited: 6,185 *(from Web of Science Core Collection)*
Usage Count

Methods and Computing Programs

3. Magnetic control of ferroelectric polarization
By: Kimura, T; Goto, T; Shintani, H; et al.
NATURE Volume: 426 Issue: 6962 Pages: 55-58 Published: NOV 6 2003
Full Text from Publisher | View Abstract
Times Cited: 2,562 *(from Web of Science Core Collection)*
Usage Count

Multiferroics

4. Physics and Applications of Bismuth Ferrite
By: Catalan, Gustau; Scott, James F.
ADVANCED MATERIALS Volume: 21 Issue: 24 Pages: 2463-2485 Published: JUN 26 2009
Full Text from Publisher | View Abstract
Times Cited: 1,548 *(from Web of Science Core Collection)*
Usage Count

5. Magnetic order close to superconductivity in the iron-based layered LaO(1-x)F(x)FeAs systems
By: de la Cruz, Clarina; Huang, Q.; Lynn, J. W.; et al.
NATURE Volume: 453 Issue: 7197 Pages: 899-902 Published: JUN 12 2008
Full Text from Publisher | View Abstract
Times Cited: 1,404 *(from Web of Science Core*
Usage Count

Superconductors

Interest of magnetic structure determination

Nano particles

6. **Magnetic nanoparticles**
By: Kodama, RH
JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS Volume: 200 Issue: 1-3 Pages: 359-372 Published: OCT 1999
Full Text from Publisher | View Abstract
Times Cited: 986 *(from Web of Science Core Collection)*
Usage Count

7. **Charge, orbital, and magnetic ordering in La0.5Ca0.5MnO3**
By: Radaelli, PG; Cox, DE; Marezio, M; et al.
PHYSICAL REVIEW B Volume: 55 Issue: 5 Pages: 3015-3023 Published: FEB 1 1997
Full Text from Publisher | View Abstract
Times Cited: 751 *(from Web of Science Core Collection)*
Usage Count

Multiferroics

8. **Magnetic inversion symmetry breaking and ferroelectricity in TbMnO3**
By: Kenzelmann, M; Harris, AB; Jonas, S; et al.
PHYSICAL REVIEW LETTERS Volume: 95 Issue: 8 Article Number: 087206 Published: AUG 19 2005
Full Text from Publisher | View Abstract
Times Cited: 526 *(from Web of Science Core Collection)*
Usage Count

Computing Methods

9. **Crystallographic Computing System JANA2006: General features**
By: Petricek, Vaclav; Dusek, Michal; Palatinus, Lukas
ZEITSCHRIFT FUR KRISTALLOGRAPHIE Volume: 229 Issue: 5 Pages: 345-352 Published: 2014
Full Text from Publisher | View Abstract
Times Cited: 489 *(from Web of Science Core Collection)*
Usage Count

Manganites, charge ordering orbital ordering

10. **Direct observation of charge and orbital ordering in La0.5Sr1.5MnO4**
By: Murakami, Y; Kawada, H; Kawata, H; et al.
PHYSICAL REVIEW LETTERS Volume: 80 Issue: 9 Pages: 1932-1935 Published: MAR 2 1998
Times Cited: 444 *(from Web of Science Core Collection)*

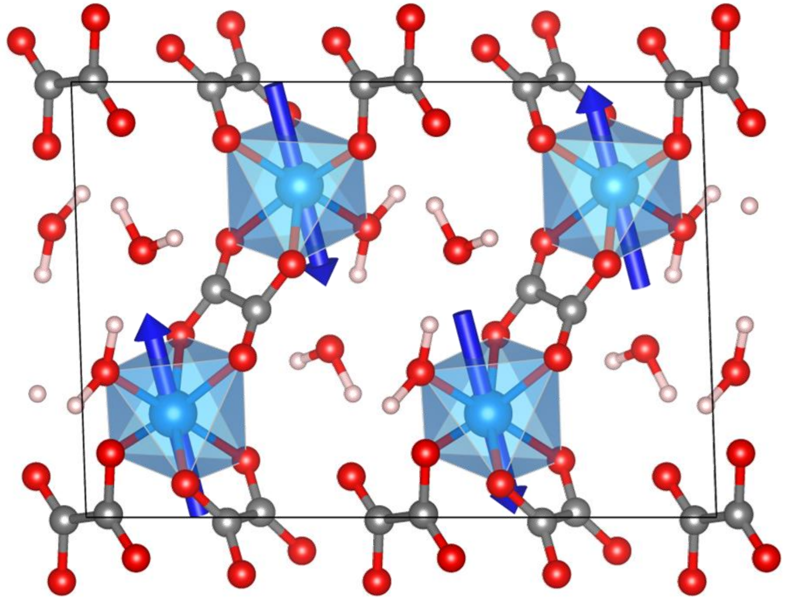
11. **Magnetic ordering and relation to the metal-insulator transition in Pr1-xSrxMnO3 and Nd1-xSrxMnO3 with x similar to 1/2**
By: Kawano, H; Kajimoto, R; Yoshizawa, H; et al.
PHYSICAL REVIEW LETTERS Volume: 78 Issue: 22 Pages: 4253-4256 Published: JUN 2 1997
Full Text from Publisher | View Abstract
Times Cited: 420 *(from All Databases)*

Heavy Fermions

13. **Onset of antiferromagnetism in heavy-fermion metals**
By: Schroder, A; Aeppli, G; Coldea, R; et al.
NATURE Volume: 407 Issue: 6802 Pages: 351-355 Published: SEP 21 2000
Times Cited: 380 *(from All Databases)*

1. What is a magnetic structure ?

A crystallographic structure consists in a long-range order of atoms, described by a unit cell, a space group, and atomic positions of the asymmetry unit.

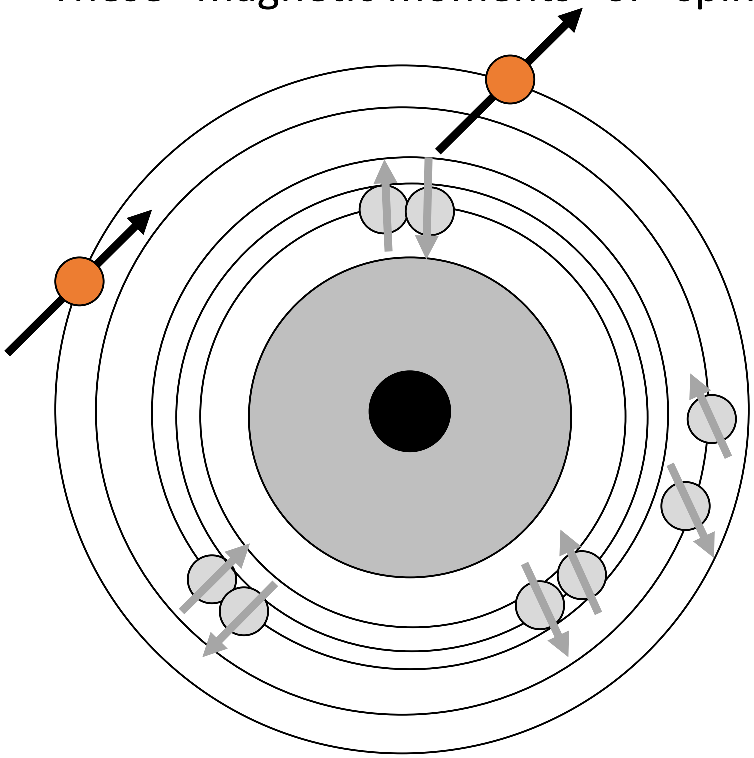


A magnetic structure corresponds to the long range ordering of “magnetic moments” or “spins”.

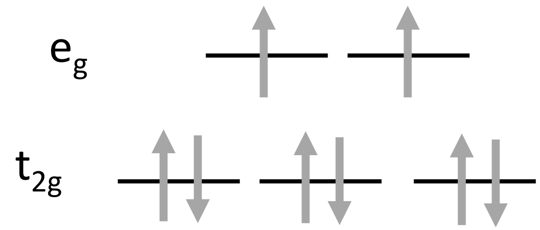
These “magnetic moments” or “spins” correspond to the spin of the unpaired electrons

1. What is a magnetic structure ?

These “magnetic moments” or “spins” correspond to the spin of the unpaired electrons

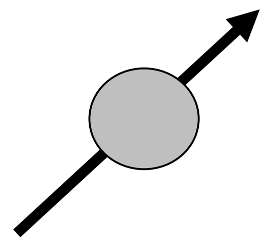


Example Ni^{2+} $3d^8$ in an octahedral environment



Hund’s and Pauli’s rules

This is represented as a magnetic moment carried by Ni^{2+}



2 unpaired electrons $\Rightarrow S = 1$

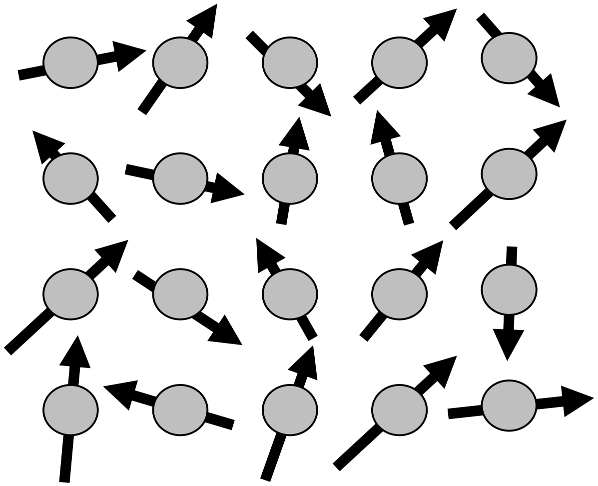
$$m = 2\,\mu_B$$

$$\mu_B = \frac{q\hbar}{2m_e}$$

$\vec{m} = -g_S\,\mu_B\,\vec{S}$ (transition metals)

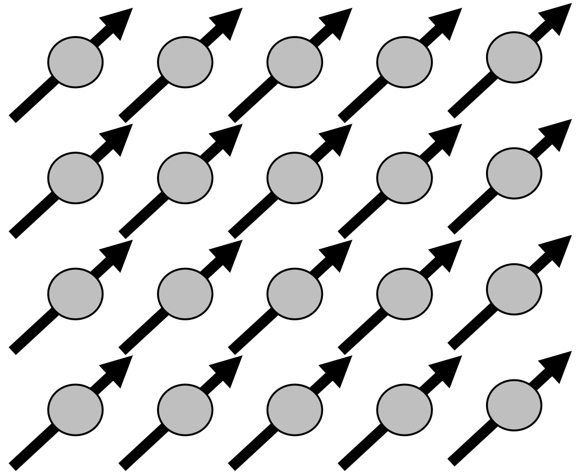
$\vec{m} = -g_J\,\mu_B\,\vec{J}$ (rare earths)

1. What is a magnetic structure ?

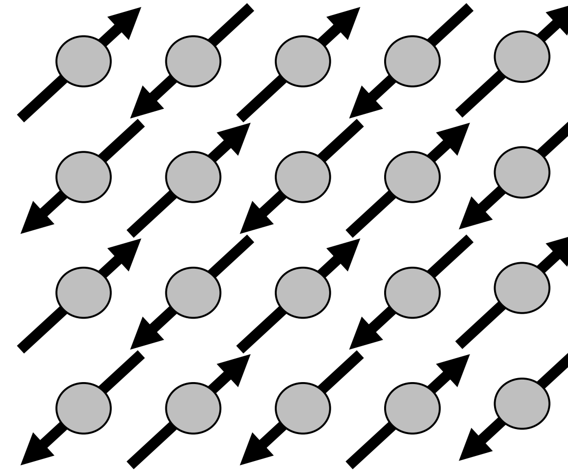


paramagnetic state

$$< \vec{S}_i > = \vec{0}$$

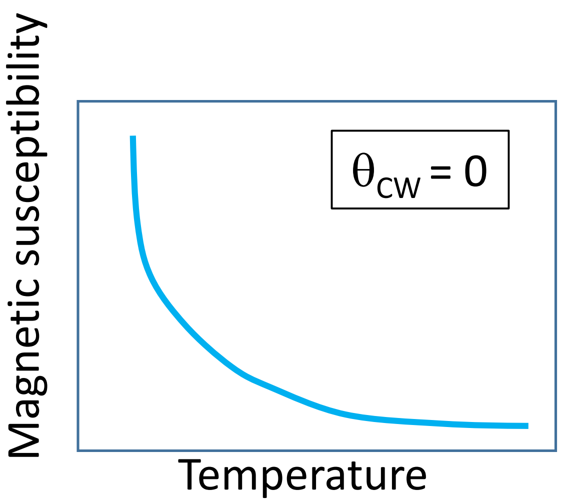


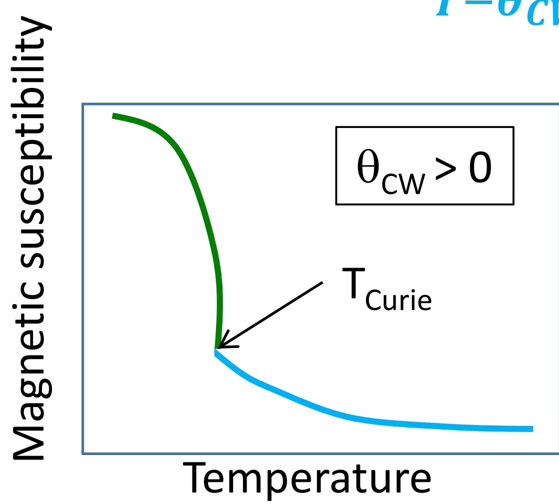
ferromagnetic state

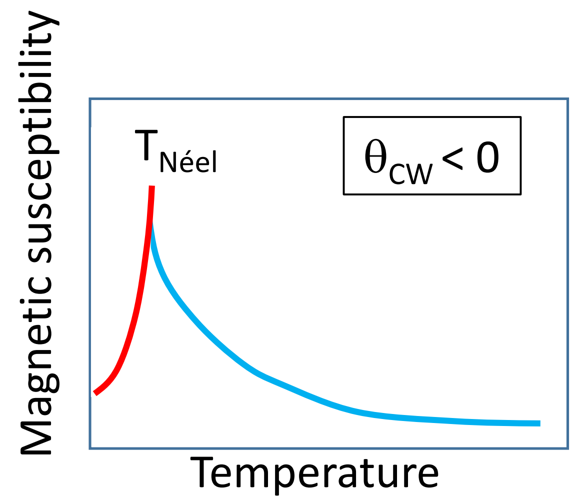


antiferromagnetic state

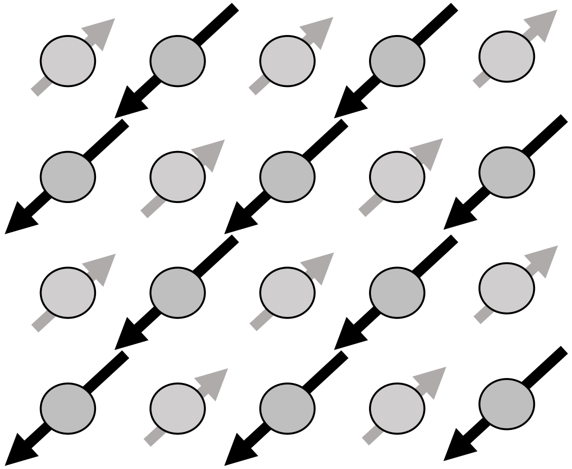
Curie-Weiss: $\chi = \frac{C}{T - \theta_{CW}}$



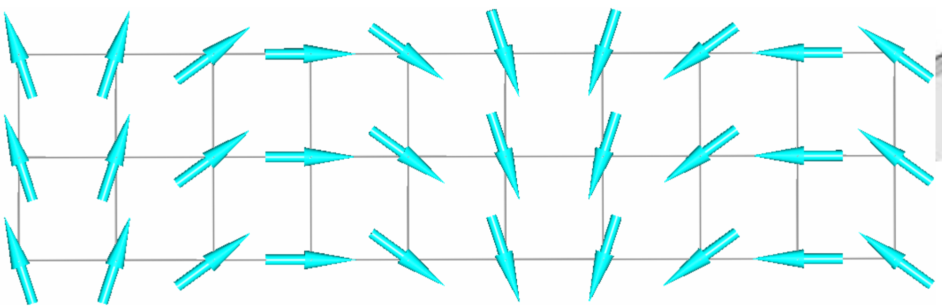




What is a magnetic structure ?



There are also plenty of more complex magnetic structures, arising e. g. from frustration :
Helical
Sinusoidal
Incommensurate …



ferrimagnetic state
When different magnetic atoms (or different oxidation states for the same atom)
=> Non-zero total magnetic moment

Knowing a magnetic structure means being able to say, *in whatever magnetic atom of whatever unit cell*, <u>what is the direction and value of the magnetic moment</u>

Tools to describe a magnetic structure ?

There exist 2 approaches:

• **Group representation theory** applied to conventional crystallographic space groups and **using the concept of propagation vector $\vec{k}$**
→ the most general (any $\vec{k}$ vectors, incommensurate ones included)

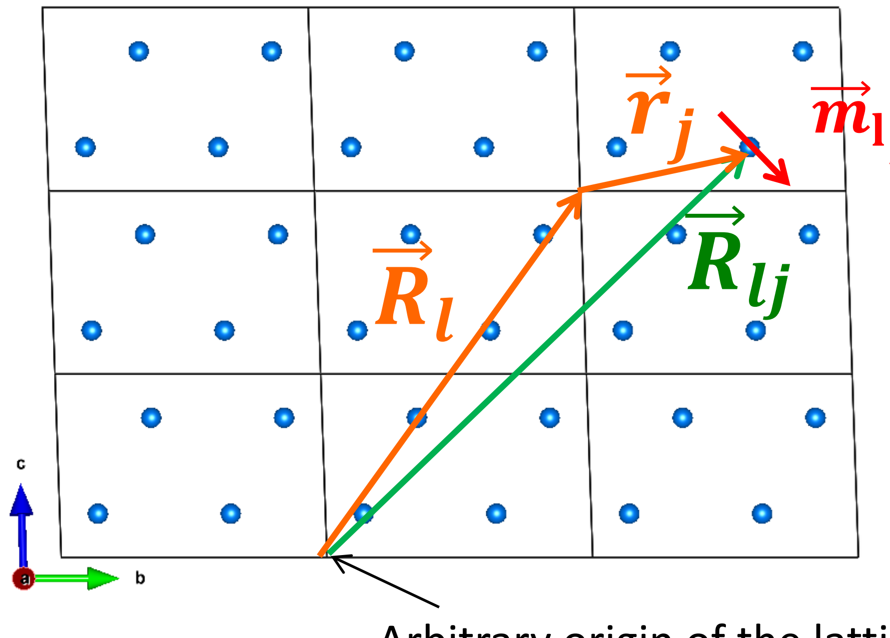
• **Magnetic symmetry approach:** symmetry invariance of magnetic configurations (Magnetic Space Groups, often called Shubnikov groups)
→ only $\vec{k} = \vec{0}$, $\vec{k} = \frac{1}{2}\vec{H}$, or $\vec{k} = \vec{H}$

Béatrice Grenier in the second part of this talk

The position of atom j in unit-cell l is given by:

$$\vec{R}_{lj} = \vec{R}_l + \vec{r}_j$$

Where $\vec{R}_l$ is a pure lattice translation



$$\vec{R}_{l_j} = \vec{R}_l + \vec{r}_j = l_1\,\vec{a} + l_2\,\vec{b} + l_3\,\vec{c} + x_j\vec{a} + y_j\,\vec{b} + z_j\,\vec{c}$$

Whatever kind of magnetic structure in a crystal can be described mathematically by using a Fourier series

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\; e^{-2i\pi(\vec{k}.\vec{R}_l)}$$

$\vec{k}$ is a vector belonging to the Reciprocal Lattice

The reciprocal lattice is defined as a network of points in the Fourier space (Q-space)

which are the extremities of vectors: $\boxed{\vec{H} = h\vec{a}^\star + k\vec{b}^\star + l\vec{c}^\star}$

with $\vec{a}^\star$, $\vec{b}^\star$, and $\vec{c}^\star$ the unit vectors of the reciprocal lattice, and h, k, l integers.

$$\vec{a}^\star = C\,\frac{\vec{b}\times\vec{c}}{V} \quad\rightarrow\quad \vec{a}^\star \perp \vec{b} \text{ and } \vec{c}$$

$$\vec{b}^\star = C\,\frac{\vec{c}\times\vec{a}}{V} \quad\rightarrow\quad \vec{b}^\star \perp \vec{a} \text{ and } \vec{c}$$

$$\vec{c}^\star = C\,\frac{\vec{a}\times\vec{b}}{V} \quad\rightarrow\quad \vec{c}^\star \perp \vec{a} \text{ and } \vec{b}$$

In solid state physics, $C = 2\pi$
In crystallography, $C = 1$

for $C = 1$

$$\vec{a}^\star.\vec{a} = \vec{b}^\star.\vec{b} = \vec{c}^\star.\vec{c} = 1$$
$$\vec{a}^\star.\vec{b} = \vec{a}^\star.\vec{c} = 0$$
$$\vec{b}^\star.\vec{a} = \vec{b}^\star.\vec{c} = 0$$
$$\vec{c}^\star.\vec{a} = \vec{c}^\star.\vec{b} = 0$$

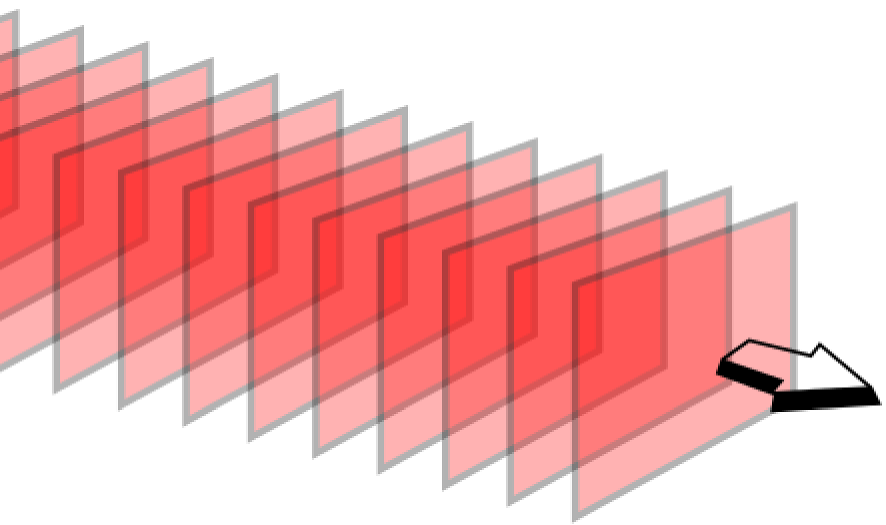
where C is a constant
and V is the volume of the unit cell
in direct space:

$$V = (\vec{a},\vec{b},\vec{c}) = (\vec{a}\times\vec{b}).\vec{c} = \vec{a}.(\vec{b}\times\vec{c})$$

Propagation vector formalism

meaning of the propagation vector : analogy with plane waves

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)}$$



$\vec{k}$

The propagation vector $\vec{k}$ of a magnetic structure reflects:

- its periodicity L ($k = 1/L$)
- the direction it propagates

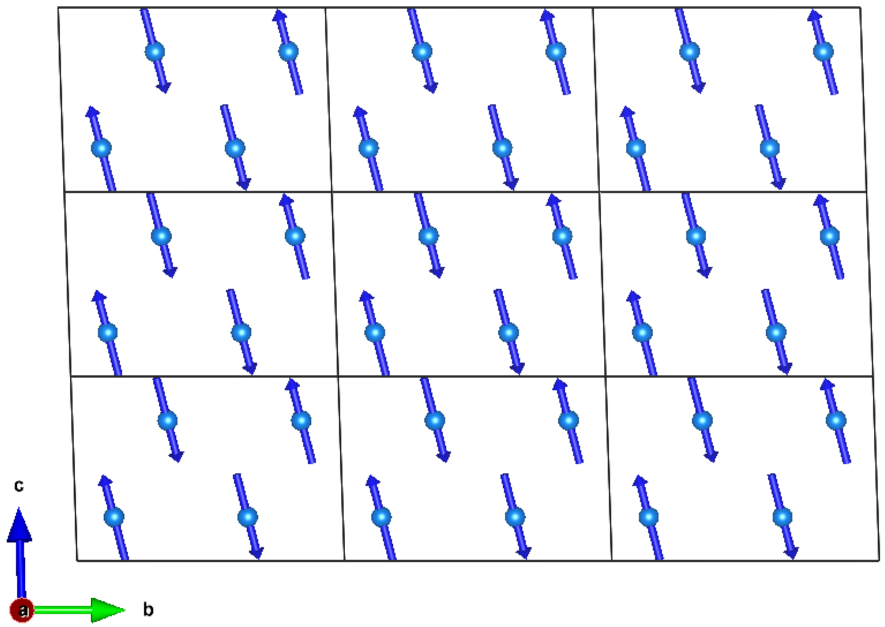
For a magnetic atom j, the magnetic moments $\vec{m}_{lj}$ (cell l) form planes of parallel moments that are perpendicular to the direction of the propagation vector

1. Propagation vectors formalism ; $\vec{k}$ = (0, 0, 0)

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)}$$

Let us examine the simple case $\vec{k}$= (0, 0, 0)

$$\vec{m}_{lj} = \vec{S}_{\vec{k}j} \text{ ; both are real}$$



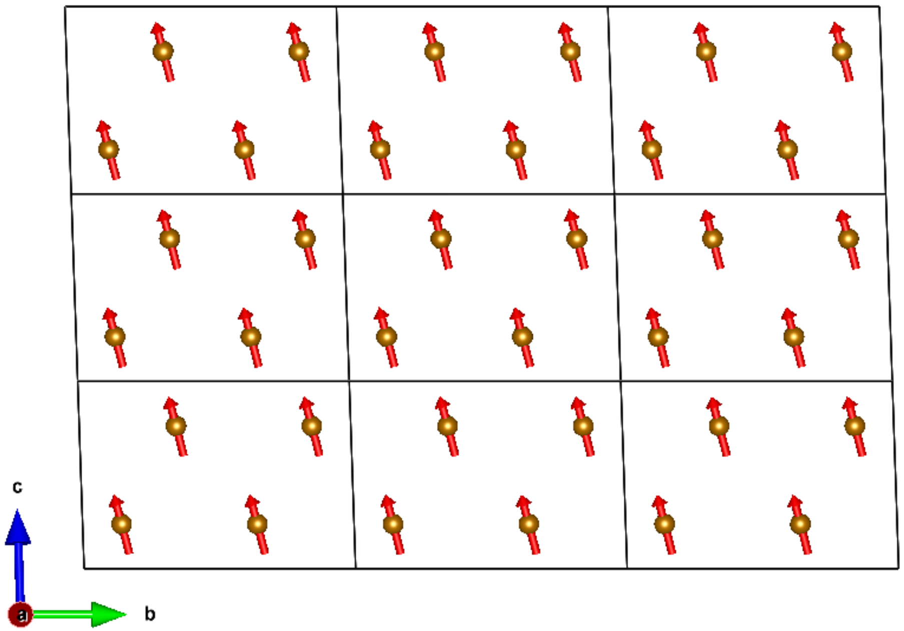
In this case the **magnetic cell** is the *same* as the **nuclear cell**

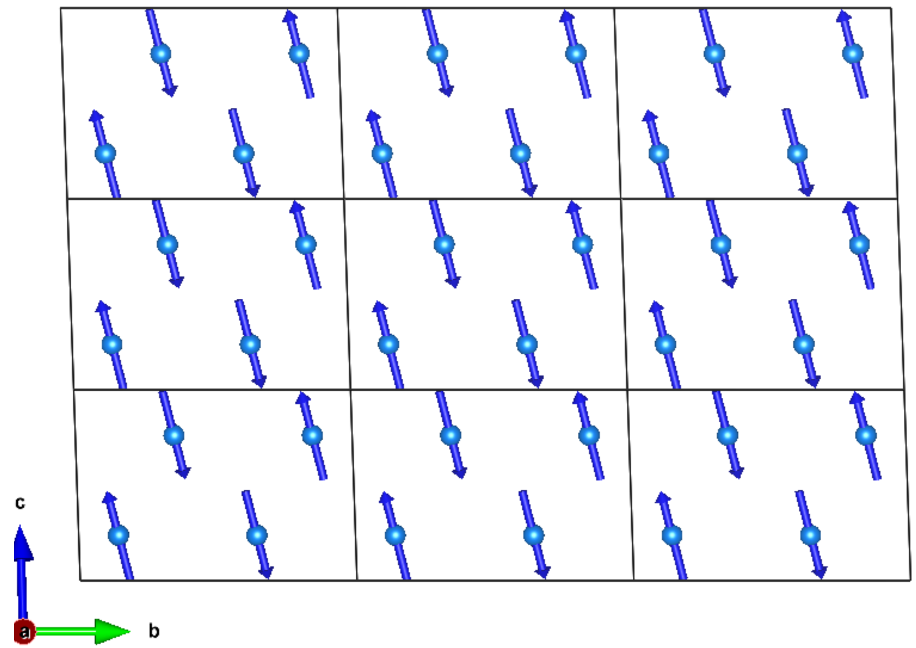
Propagation vectors formalism ; $\vec{k}$ = (0, 0, 0)

Remark : any ferromagnetic structure has $\vec{k} = (0,0,0)$

However the reverse is not true.

Many AF structures have $\vec{k} = (0,0,0)$

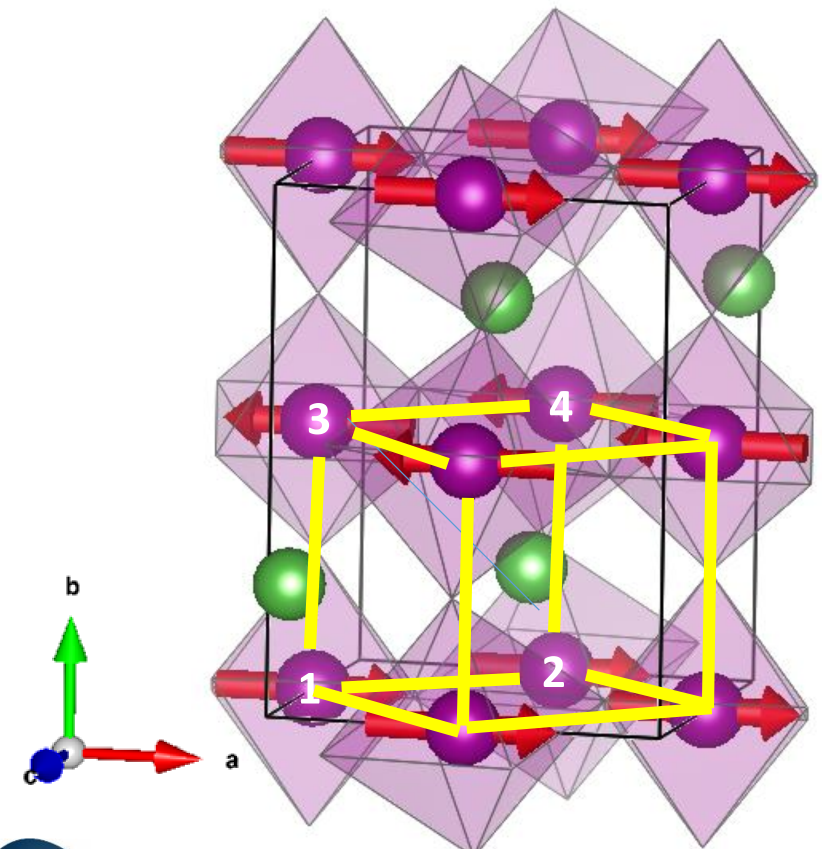




A notation useful in perovskites

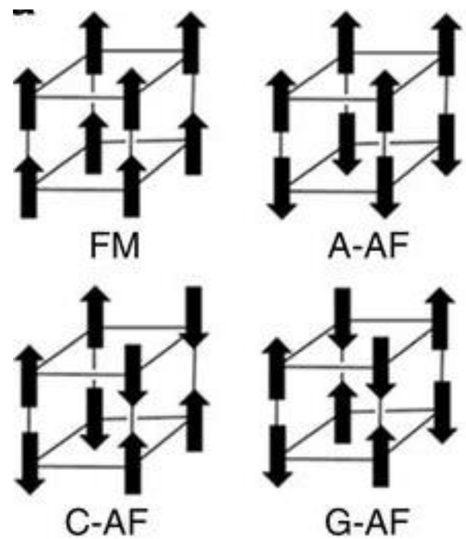
TABLE I. Crystallographic and magnetic parameters of $LaMnO_3$ obtained by Rietveld refinement at the diffractometer G4.2 using neutrons of $\lambda=2.59$ Å at $T=1.4$ K. The space group is *Pbnm*. The numbering of Mn atoms in the unit cell is Mn1 (1/2,0,0), Mn2 (1/2,0,1/2), Mn3 (0,1/2,1/2), and Mn4 (0,1/2,0). The basis function describing the magnetic structure is $[G_x, A_y, F_z] \approx [0, A_y, 0]$, corresponding to the irreducible representation $\Gamma_{4g}(--)$ of *Pbnm* for $\mathbf{k}=0$ (Ref. 17). The magnetic moments of the four Mn atoms follow the sequence $A_y(+--+)$. So constituting ferromagnetic (**a**,**b**) planes of magnetic moments aligned along **b** coupled antiferromagnetically along **c**.

Moussa et al., 10.1103/PhysRevB.54.15149



Pnma, position 4*b*

$0, 0, \frac{1}{2}$ $\quad \frac{1}{2}, 0, 0$ $\quad 0, \frac{1}{2}, \frac{1}{2}$ $\quad \frac{1}{2}, \frac{1}{2}, 0$



$F = + \; + \; + \; +$

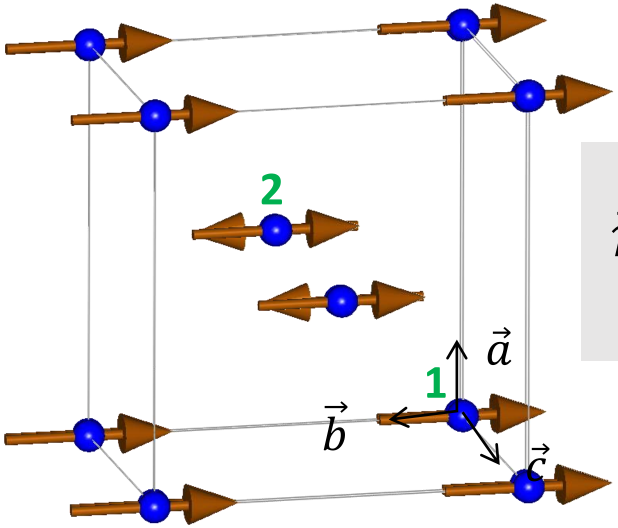
$A = + \; - \; - \; +$

$C = + \; + \; - \; -$

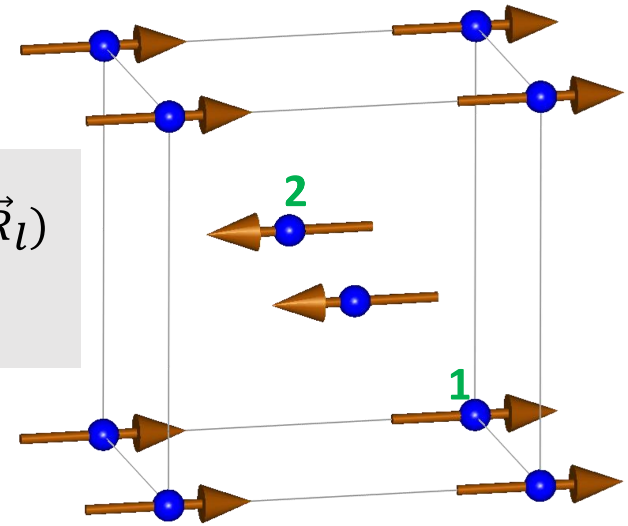
$G = + \; - \; + \; -$

Constraints on the directions and couplings given by **symmetry analysis** (see later)

2. Note on centered cells: C-centered cell



$$\overrightarrow{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)}$$



$\vec{k}$ = (0, 0, 0) ?

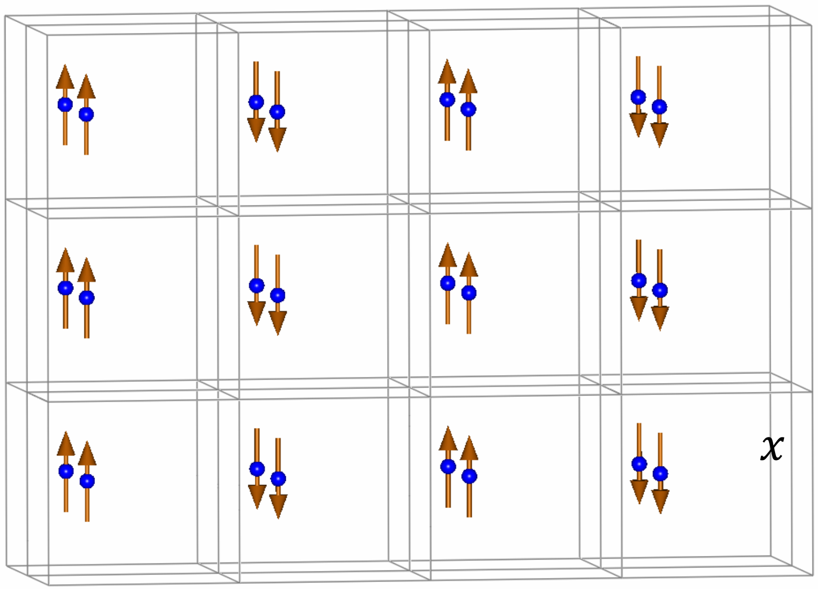
$\vec{k}$ = (1, 0, 0)

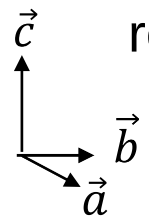
$$\overrightarrow{m_1} = +m\,\vec{u}$$
$$\overrightarrow{m_2} = +m\,\vec{u}$$

For centered cells, we sum over atoms j of the primitive cell and values of $\vec{k}$ may be $> \frac{1}{2}$

$$\overrightarrow{m_1} = +m\,\vec{u}$$
$$\overrightarrow{m_2} = +me^{-2i\pi((1,0,0).(\frac{1}{2},\frac{1}{2},0))}\,\vec{u}$$
$$\overrightarrow{m_2} = +me^{-2i\pi\frac{1}{2}}\,\vec{u}$$
$$\overrightarrow{m_2} = -m\,\vec{u}$$

3. Propagation vector formalism ; $\vec{k} = ½\,\vec{H}$





The propagation vector is a special point of the Brillouin Zone surface and $\vec{k} = ½\,\vec{H}$, where $\vec{H}$ is a reciprocal lattice vector.

$$\vec{R}_l = l_1\vec{a} + l_2\vec{b} + l_3\vec{c}$$

$$\vec{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)} = \vec{S}_{\vec{k}j}\, e^{-i\pi(\vec{H}.\vec{R}_l)} = \vec{S}_{\vec{k}j}\,(-1)^{n_l}$$

$$\boxed{\vec{m}_{lj} = \vec{m}_{0j}\,(-1)^{n_l}}$$

The structure is antiferromagnetic

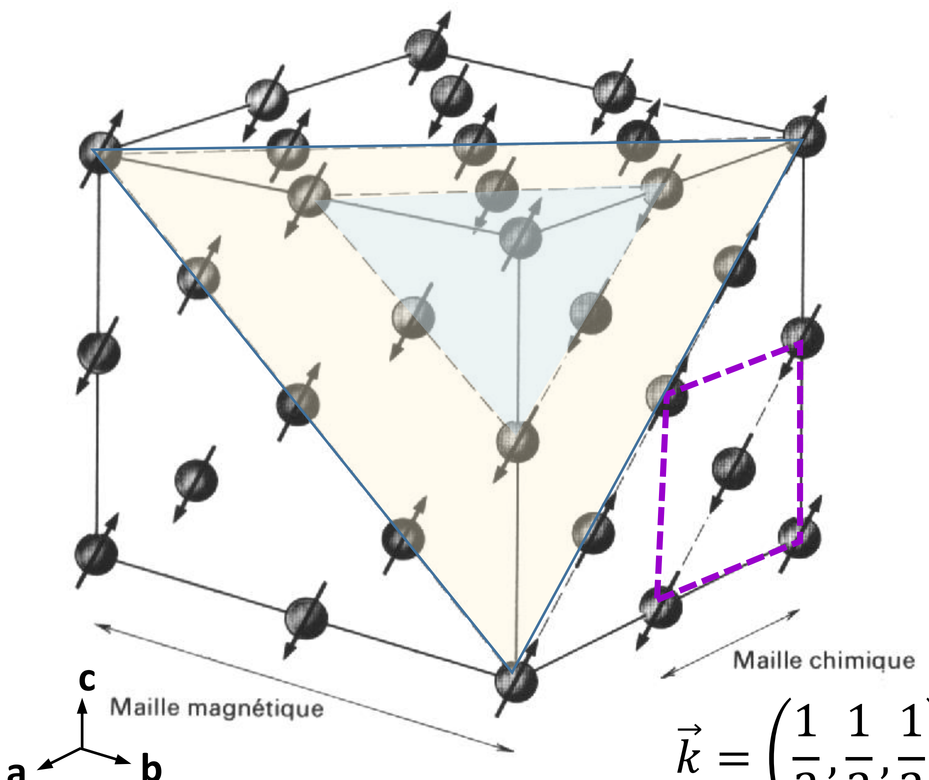
The magnetic symmetry may also be described using Shubnikov magnetic space groups

Example (see Figure): $\vec{k} = \left(0, \frac{1}{2}, 0\right) \Rightarrow \vec{m}_{lj} = \vec{m}_{0j}(-1)^{l_2}$

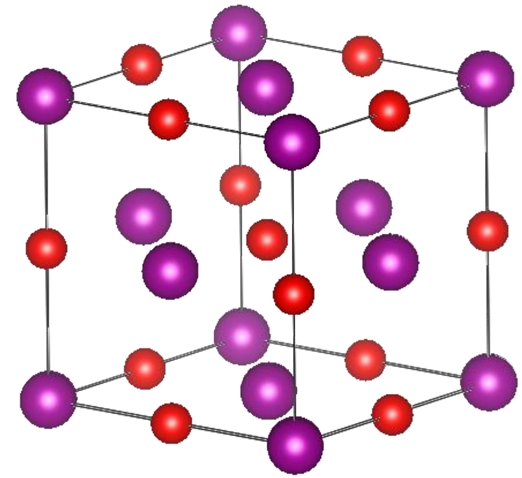
First magnetic neutron diffraction experiments: MnO

Detection of Antiferromagnetism by Neutron Diffraction*

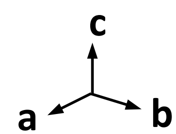
C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee
AND
J. SAMUEL SMART
Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland
August 29, 1949

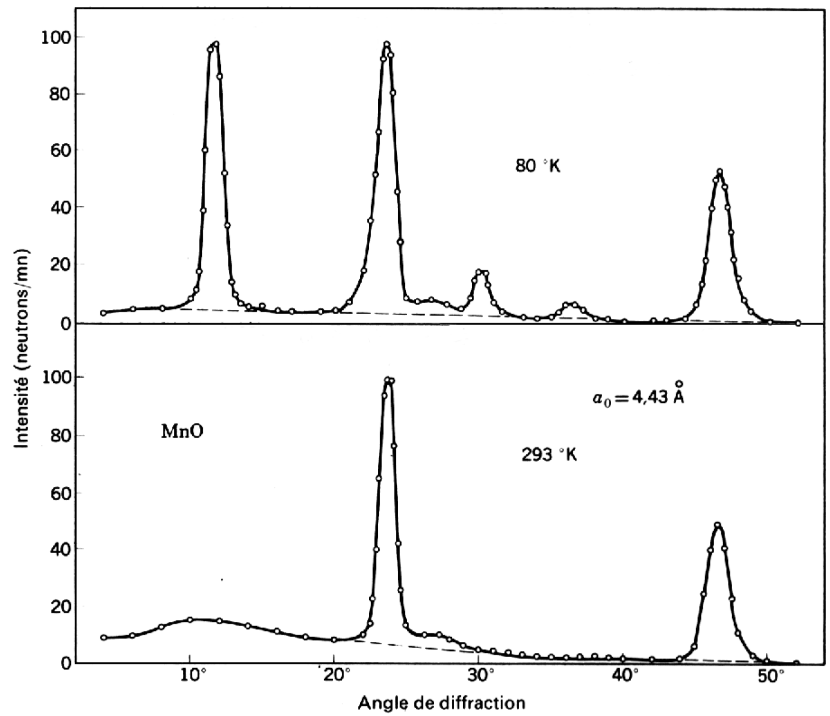


$$\vec{k} = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$$



MnO structure
$a = 4.45$ Å
$Fm\bar{3}m$





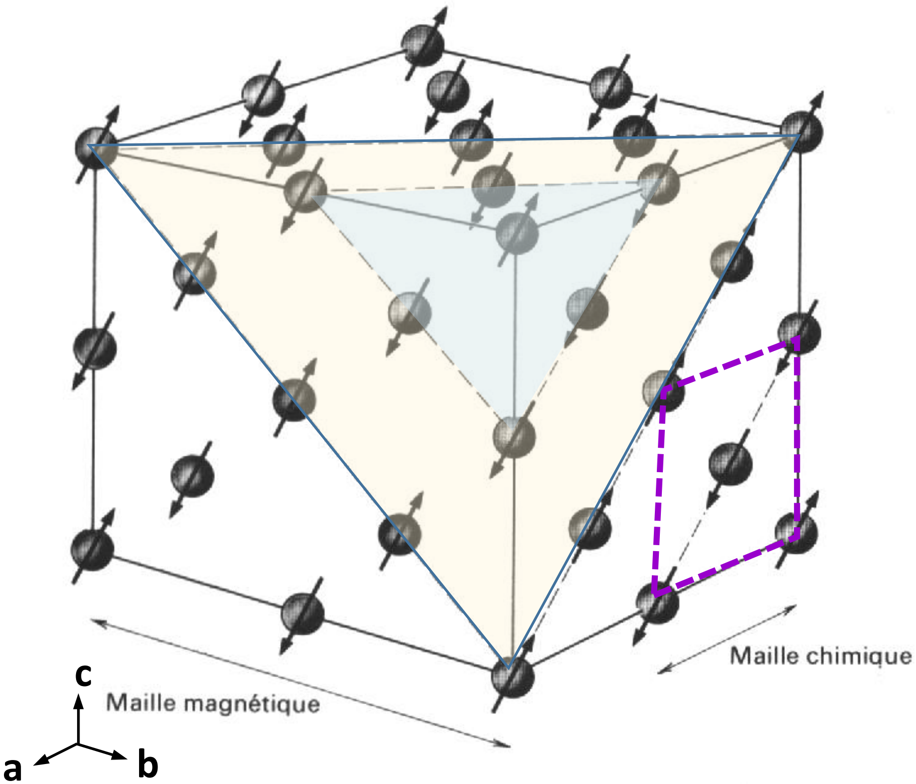
First magnetic neutron diffraction experiments: MnO

$\vec{k}_1 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

Note: what about $\vec{k}_2 = \left(\frac{\bar{1}}{2}, \frac{1}{2}, \frac{1}{2}\right)$, $\vec{k}_3 = \left(\frac{1}{2}, \frac{\bar{1}}{2}, \frac{1}{2}\right)$ and $\vec{k}_4 = \left(\frac{1}{2}, \frac{1}{2}, \frac{\bar{1}}{2}\right)$?

Are they equivalent ?

$\vec{k}_1$ and $\vec{k}_2$ are equivalent if $\vec{k}_2 - \vec{k}_1$ is a reciprocal lattice vector $\vec{H}$



$$\vec{k}_2 - \vec{k}_1 = \left(\frac{\bar{1}}{2}, \frac{1}{2}, \frac{1}{2}\right) - \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) = (\bar{1}, 0, 0)$$

This is not a reciprocal lattice vector (lattice F), therefore these 4 propagation vectors are not equivalent

=> they constitute the star of k-vectors.

Single-crystal: 4 different $\vec{k}$ −domains

Note on multi-$\vec{k}$ structures

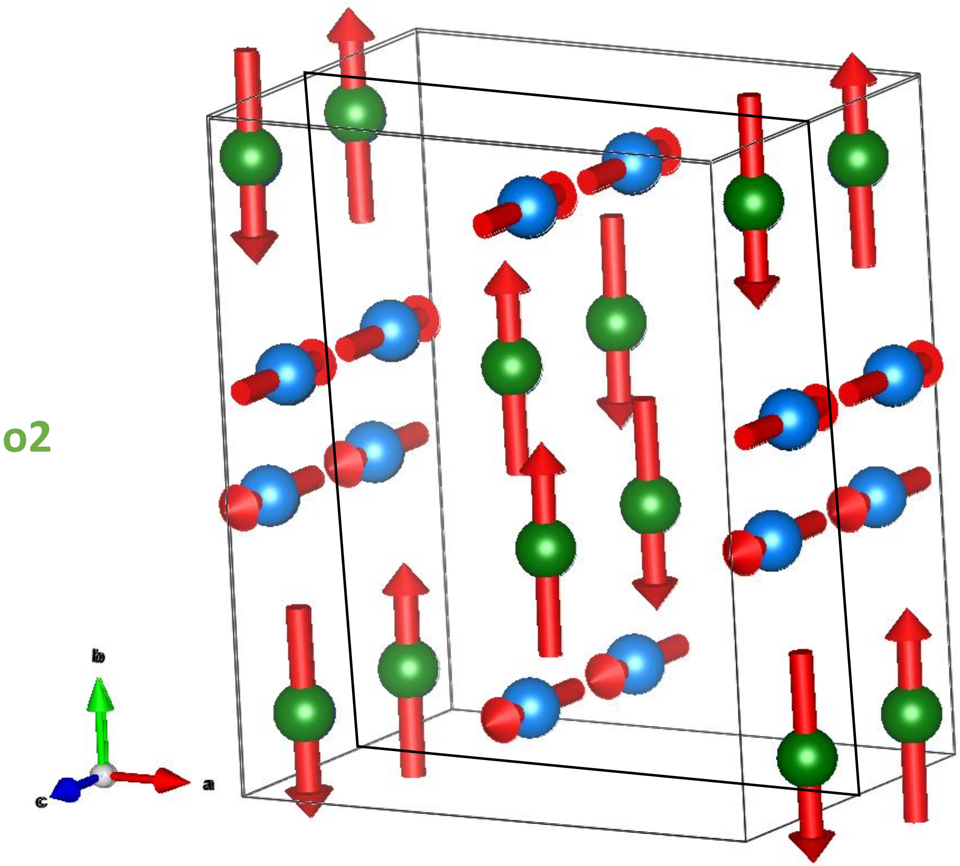
Example 1: $SrHo_2O_4$

$$\vec{k_1} = (0,0,0)$$
$$\vec{k_2} = \left(0,0,\frac{1}{2}\right)$$

Holmium distributed on 2 sites **Ho1**, **Ho2**

$$\vec{k_1} = (0,0,0)$$

$$\vec{k_2} = \left(0,0,\frac{1}{2}\right)$$

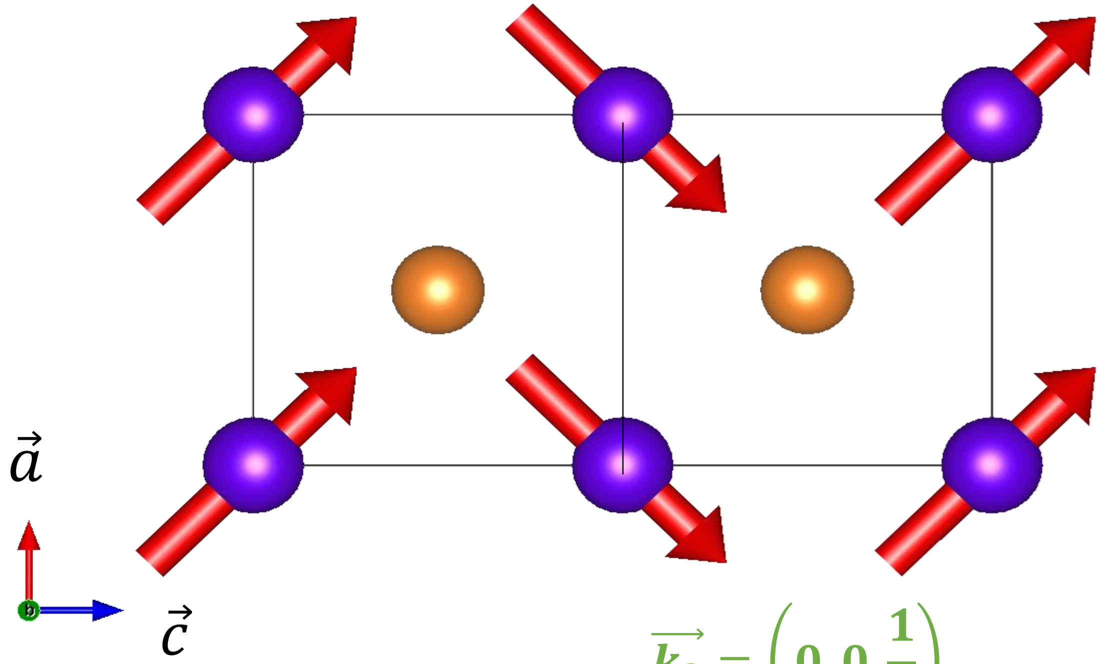


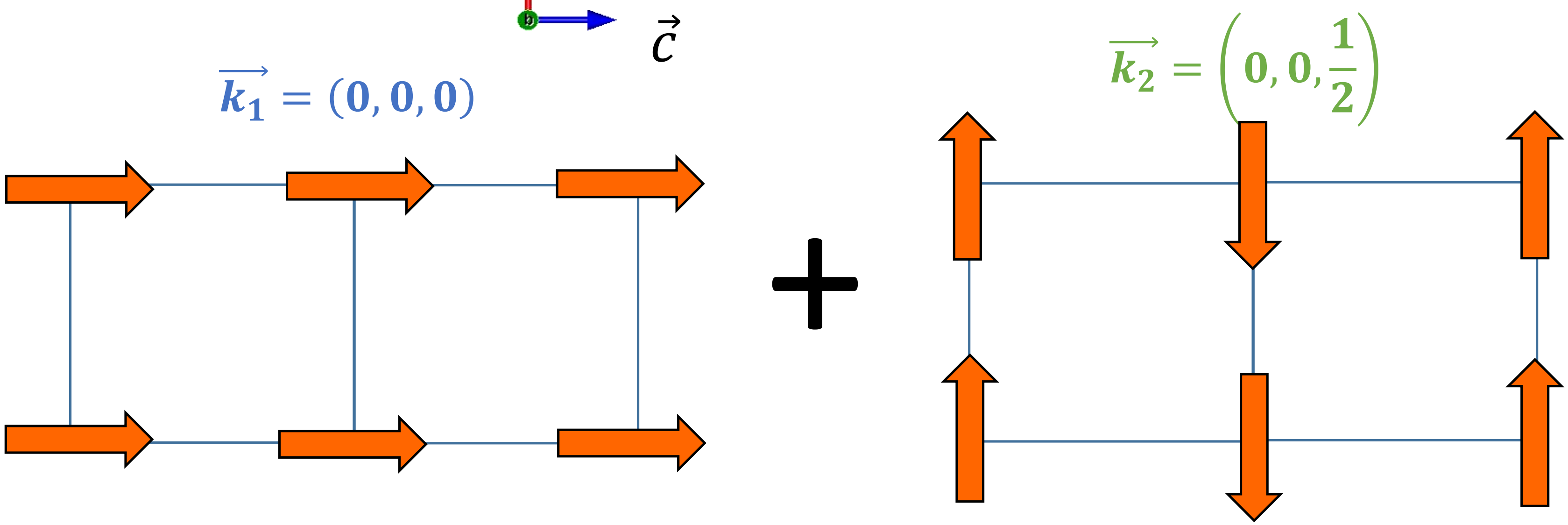
Note on multi-$\vec{k}$ structures

Example 2: TbMg

Tb is the magnetic ion

This allows a **canting** (net ferromagnetic component)





$$\overrightarrow{m}_{lj} = \sum_{\vec{k}} \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)}$$

$\vec{k}$ and $-\vec{k}$ should be considered ($\vec{k}$ and $-\vec{k}$ are not equivalent)

$$\overrightarrow{m}_{lj} = \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)} + \vec{S}_{-\vec{k}j}\, e^{-2i\pi(-\vec{k}.\vec{R}_l)}$$

$$\vec{S}_{\vec{k}j} = \frac{1}{2}\left(\overrightarrow{Re}_{\vec{k}j} + i\,\overrightarrow{Im}_{\vec{k}j}\right) e^{-2i\pi\varphi_{\vec{k}j}}$$

six parameters are independent

Necessary condition for real $\overrightarrow{m}_{lj}$: $\vec{S}_{-\vec{k}j} = \vec{S}_{\vec{k}j}{}^*$

2 simple cases:

1) Real $\vec{S}_{\vec{k}j}$: $\vec{S}_{\vec{k}j} = \frac{1}{2}\left(\overrightarrow{Re}_{\vec{k}j}\right) e^{-2i\pi\varphi_{\vec{k}j}}$

2) Imaginary component $\left(\overrightarrow{Im}_{\vec{k}j}\right)$ perpendicular to the real one $(\overrightarrow{Re}_{\vec{k}j})$

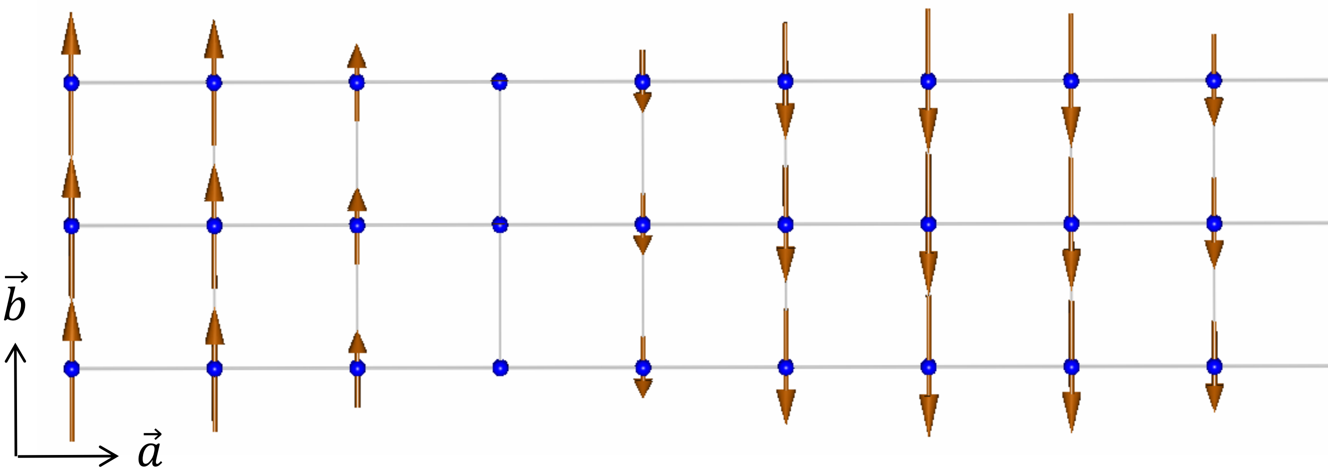
Sinusoidal magnetic structures

$$\vec{m}_{lj} = \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)} + \vec{S}_{-\vec{k}j}\, e^{-2i\pi(-\vec{k}.\vec{R}_l)}$$

$$\vec{S}_{\vec{k}j} = \frac{1}{2}\overrightarrow{Re}_{\vec{k}j}\, e^{-2i\pi\varphi_{\vec{k}j}}$$

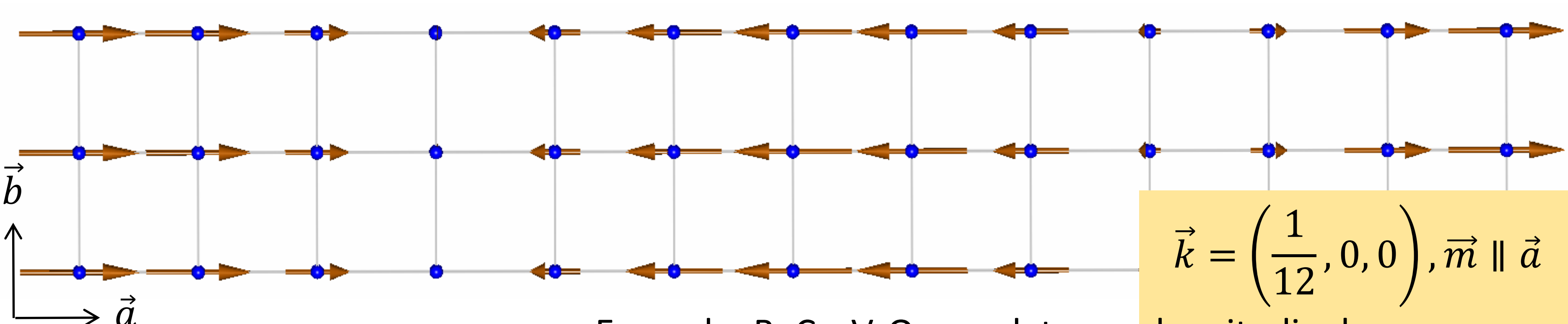
$$\vec{S}_{\vec{k}j} = \frac{1}{2} m_j \vec{u_j}\, e^{-2i\pi\varphi_{\vec{k}j}}$$

$$\vec{m}_{lj} = m_j \vec{u_j} \cos\left(2\pi\left(\vec{k}.\vec{R}_l + \varphi_{\vec{k}j}\right)\right)$$



$\vec{k} = \left(\frac{1}{12}, 0, 0\right), \vec{m} \parallel \vec{b}$

transverse



$\vec{k} = \left(\frac{1}{12}, 0, 0\right), \vec{m} \parallel \vec{a}$

longitudinal

Example: $BaCo_2V_2O_8$, see later

Helical magnetic structures

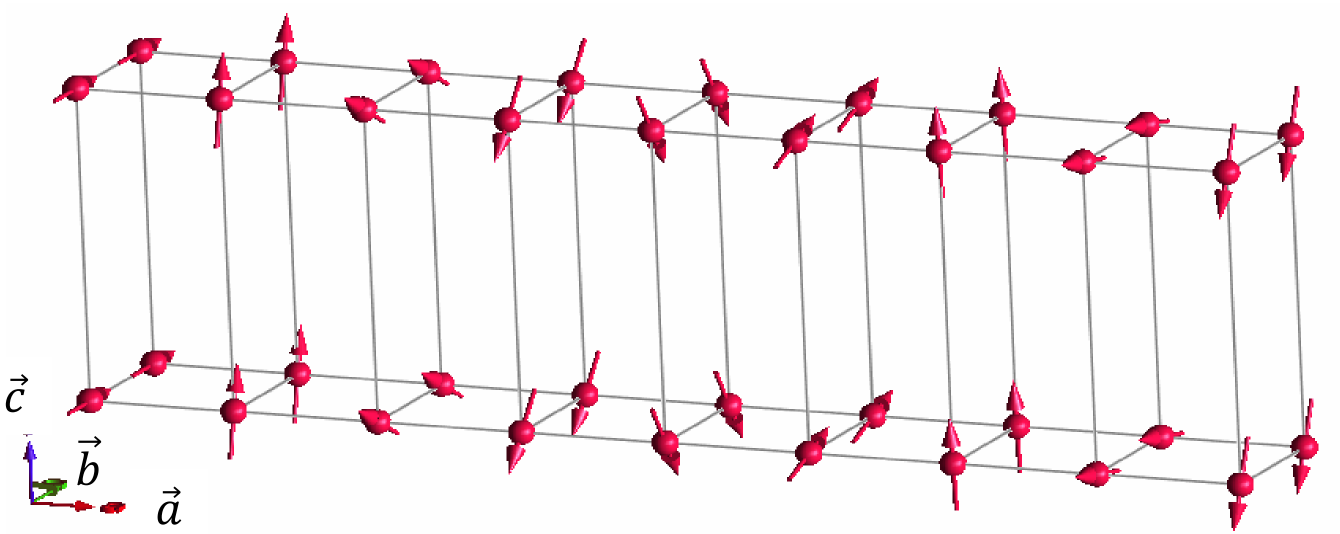
$$\vec{m}_{lj} = \vec{S}_{\vec{k}j}\, e^{-2i\pi(\vec{k}.\vec{R}_l)} + \vec{S}_{-\vec{k}j}\, e^{-2i\pi(-\vec{k}.\vec{R}_l)}$$

$$\vec{S}_{\vec{k}j} = \frac{1}{2}(m_{uj}\ \vec{u}_j + i\, m_{vj}\ \vec{v}_j)e^{-2i\pi\varphi_{\vec{k}j}} \qquad with\ \vec{u}_j \perp \vec{v}_j$$

$$\vec{S}_{-\vec{k}j} = \vec{S}^{*}_{\vec{k}j} = \frac{1}{2}(m_{uj}\ \vec{u}_j - i\, m_{vj}\ \vec{v}_j)e^{+2i\pi\varphi_{\vec{k}j}}$$

$$\vec{m}_{lj} = \frac{1}{2}m_{uj}\vec{u}_j\left(e^{-2i\pi(\vec{k}.\vec{R}_l+\varphi_{\vec{k}j})} + e^{2i\pi(\vec{k}.\vec{R}_l+\varphi_{\vec{k}j})}\right) + \frac{1}{2}m_{vj}\vec{v}_j\, i\left(e^{-2i\pi(\vec{k}.\vec{R}_l+\varphi_{\vec{k}j})} - e^{2i\pi(\vec{k}.\vec{R}_l+\varphi_{\vec{k}j})}\right)$$

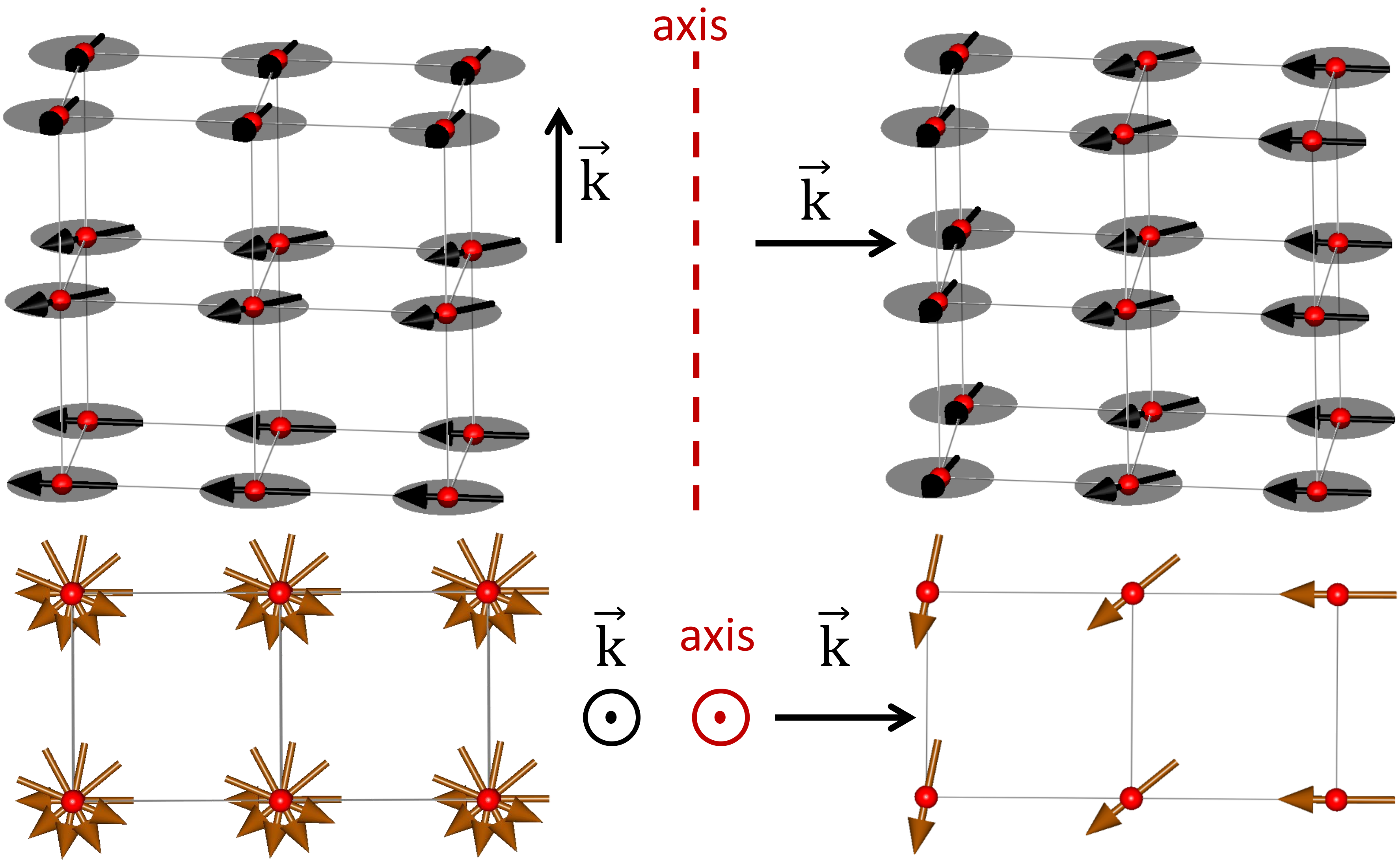
$$\vec{m}_{lj} = m_{uj}\vec{u}_j \cos\left(2\pi\left(\vec{k}.\vec{R}_l + \varphi_{\vec{k}j}\right)\right) + m_{vj}\vec{v}_j \sin\left(2\pi\left(\vec{k}.\vec{R}_l + \varphi_{\vec{k}j}\right)\right)$$



$\vec{k} \parallel \vec{a}$

$\vec{m} \in (\vec{b}, \vec{c})$

Helix ($\vec{k} \parallel axis$) Cycloid ($\vec{k} \perp axis$)



Global outline

II- Magnetic structures

Description in terms of propagation vector: *the various orderings, examples*

- $\vec{k} = (0, 0, 0)$ Magnetic cell = nuclear cell
- $\vec{k} = (1, 0, 0)$ Centered cells
- $\vec{k} = \frac{1}{2}\vec{H}$ Magnetic cell 2 x, 4x, 8x bigger than nuclear cell

Shubnikov groups

- Pair $(\vec{k}, -\vec{k})$ Complex magnetic structures (helical, sinusoidal and more)

Description in terms of symmetry:

Magnetic point groups: *time reversal, the 122 magnetic point groups*

Magnetic lattices: *translations and anti-translations, the 36 magnetic lattices*

Magnetic space groups = Shubnikov groups

Tools to describe a magnetic structure ?

There exist 2 approaches:

• **Group representation theory** applied to conventional crystallographic space groups and using the concept of propagation vector $\vec{k}$
→ the most general (any $\vec{k}$ vectors, incommensurate ones included)

tools based on this approach presented at the end of this lecture
but theory not explained at all ("black box")

• **Magnetic symmetry approach:** symmetry invariance of magnetic configurations (Magnetic Space Groups, often called Shubnikov groups)
→ only $\vec{k} = \vec{0}$, $\vec{k} = \frac{1}{2}\vec{H}$, or $\vec{k} = \vec{H}$

main purpose of the following

→ Magnetic point groups
Magnetic lattices
Magnetic space groups

Magnetic point groups: *Axial vs polar vectors*

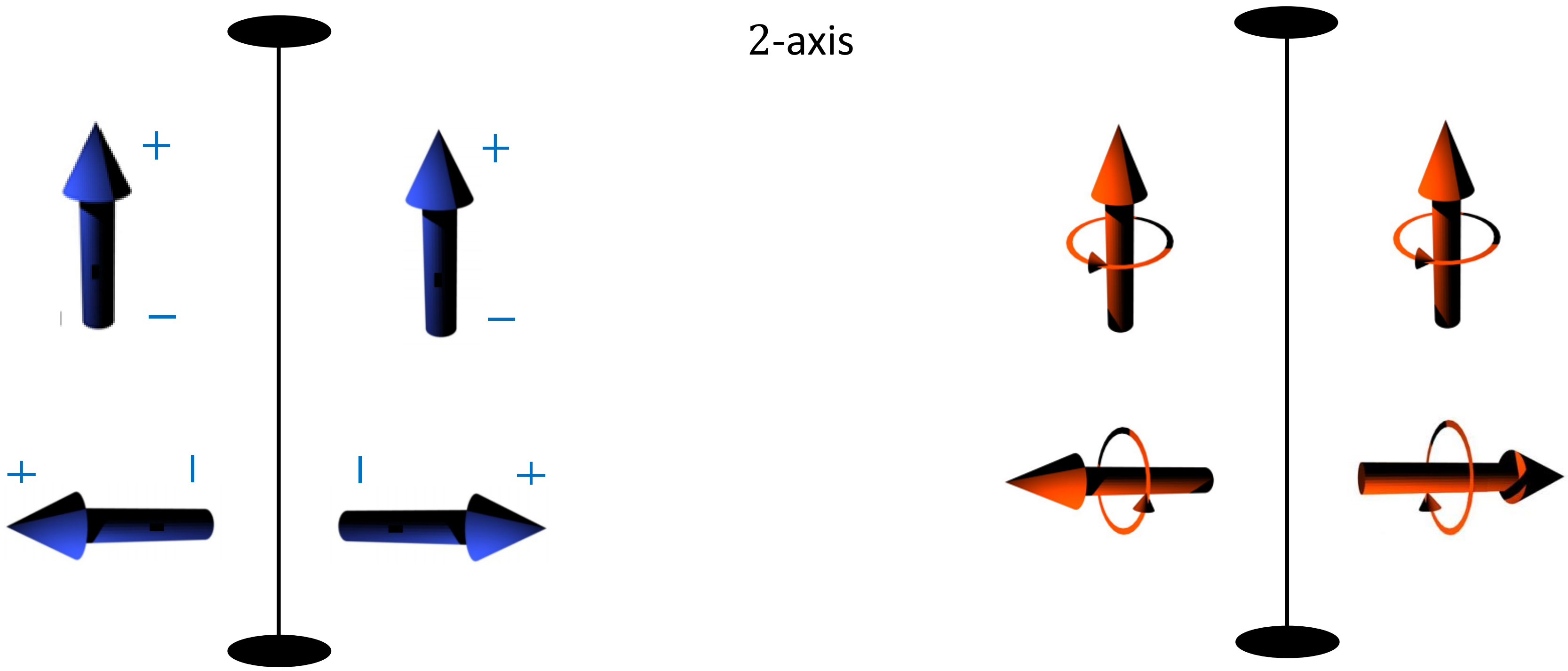
Effect of the crystallographic point group symmetries α on polar and axial vectors

Proper symmetry operations ($\det\alpha = +1$)

Electrical dipole $\vec{p}$
Polar vector

Magnetic moment $\vec{m}$
Axial vector
(current loop symmetry)

2-axis



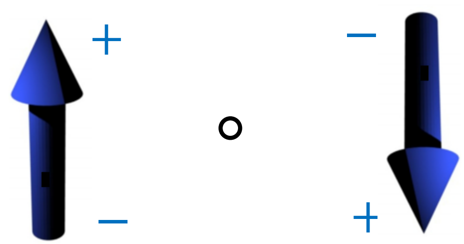
Magnetic point groups: *Axial vs polar vectors*

Effect of the crystallographic point group symmetries α on polar and axial vectors

Improper symmetry operations ($\det \alpha = -1$)

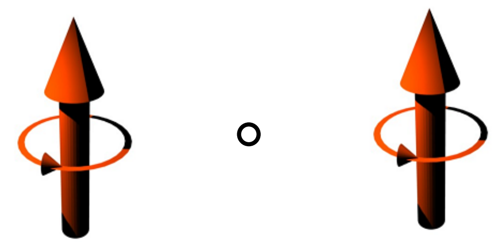
Electrical dipole $\vec{p}$
Polar vector

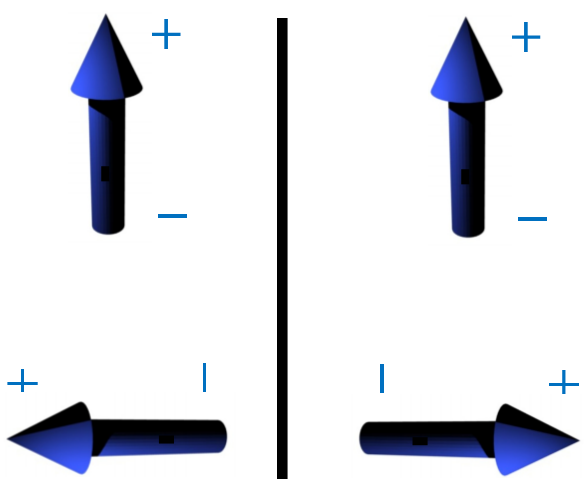
Magnetic moment $\vec{m}$
Axial vector



Inversion

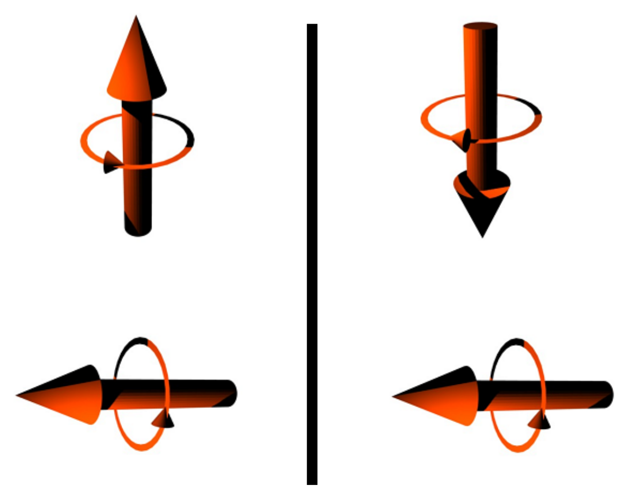
$\bar{1}$





Mirror plane

m

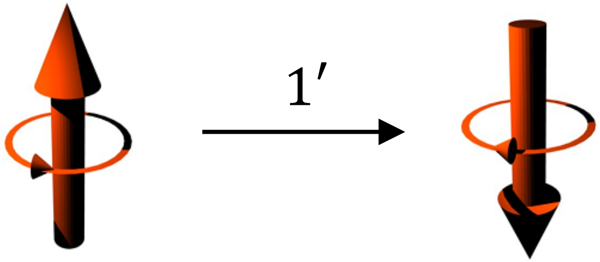


Magnetic point groups: *Spin reversal and primed symmetries*

To describe magnetic point symmetries, we need to introduce a new operator …

"**spin reversal**" = **time-reversal** or **anti-identity**: $1'$

→ changes the sense of the current and thus flips the magnetic moment



$\rightarrow\ \Theta = \{1, 1'\}$ time reversal group

$1'$ does not change nuclear positions and changes the sign of **all** magnetic moments

⇒ always present in non magnetic structures but **absent** in magnetically ordered ones !

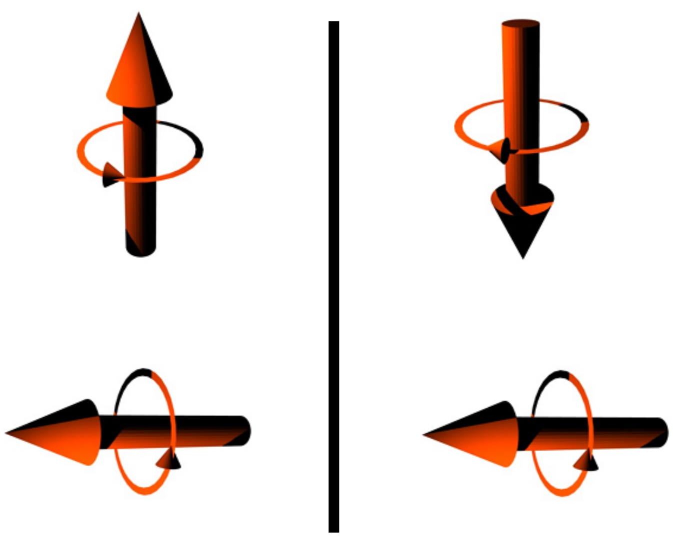
N.B.: $1'$ does not change neither the direction of a polar vector (i.e., an electrical dipole)

Magnetic point groups: *Spin reversal and primed symmetries*

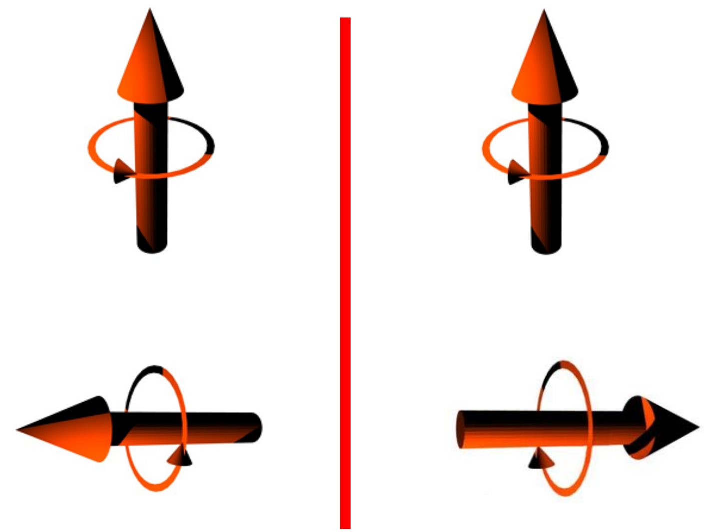
We can define new symmetry operations =

combination of a crystallographic point group sym. with $1'$ = "**primed**" symmetry

m (mirror)



m' (primed mirror)



When a magnetic ordering occurs:

some point symmetries may be lost and become primed

Magnetic point groups: *Classification*

G: crystallographic point group

M: magnetic point group → subgroup of the direct product of G with $\Theta = \{1, 1'\}$

$$M \subset G \otimes \Theta$$

3 types of magnetic point groups:

1/ 32 **colorless** groups: $M = G$ (Fedorov groups)

2/ 32 **gray** groups: $M = G \cup G1'$ (paramagnetic groups)

3/ 58 **black-white** groups: $M = H \cup (G - \mathrm{H})1'$

with H: subgroup of index 2 of G (**halving** group)

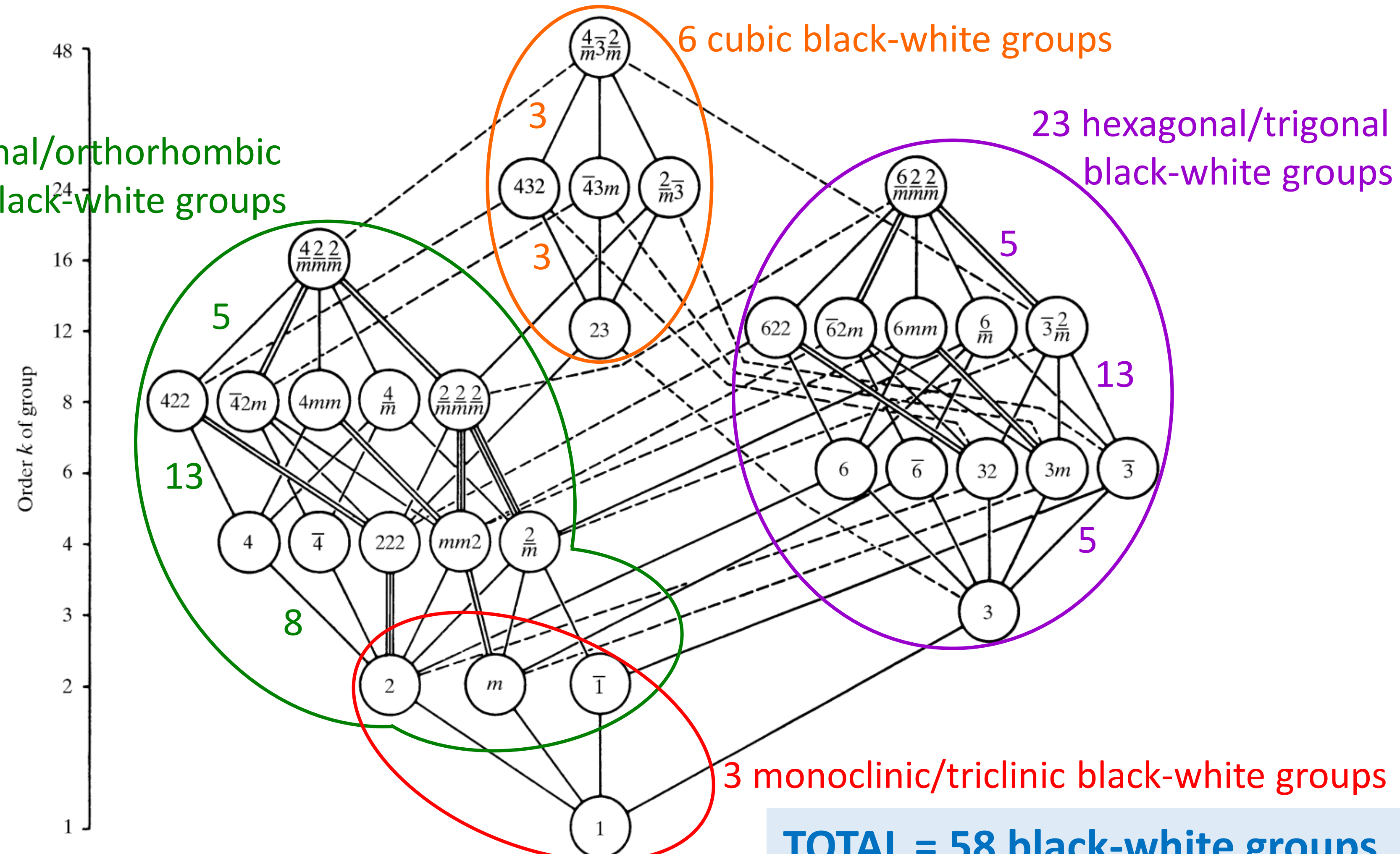
and $G - H$: the remaining operators, i.e. those not in H

⇒ 122 magnetic point groups

N.B.: **Colorless** groups are also called **monochrome** groups

Analogy **spin-reversal** / **color change**

Maximal subgroups and minimal supergroups of point groups



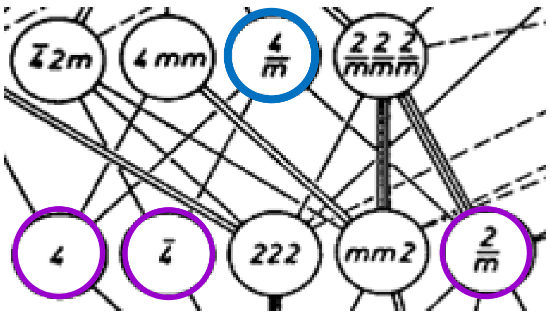
TOTAL = 58 black-white groups

Fig. 10.1.3.2. Maximal subgroups and minimal supergroups of the three-dimensional crystallographic point groups. Solid lines indicate maximal normal

Taken from: International Tables for Crystallography, volume A, p. 796

Magnetic point groups: *Classification*

Example: **black-white magnetic point groups derived from $\boldsymbol{4/m}$**



$G = 4/m$ has 3 subgroups of index 2:

$$H_1 = 4 = \{1, 4_z^+, 2_z, 4_z^-\}$$
$$H_2 = \bar{4} = \{1, \overline{4_z^+}, 2_z, \overline{4_z^-}\}$$
$$H_3 = 2/m = \{1, 2_z, \bar{1}, m_z\}$$

⇒ There are 4 possible magnetic groups:

$$M_0 = G = 4/m = \left\{1, 4_z^+, 2_z, 4_z^-, \bar{1}, \overline{4_z^+}, m_z, \overline{4_z^-}\right\}$$ colorless group

$$M_1 = H_1 + (G - H_1)1' = \left\{1, 4_z^+, 2_z, 4_z^-, \bar{1}', \overline{4_z^+}', m_z', \overline{4_z^-}'\right\} = 4/m'$$
$$M_2 = H_2 + (G - H_2)1' = \left\{1, 4_z^{+\prime}, 2_z, 4_z^{-\prime}, \bar{1}', \overline{4_z^+}, m_z', \overline{4_z^-}\right\} = 4'/m'$$
$$M_3 = H_2 + (G - H_2)1' = \left\{1, 4_z^{+\prime}, 2_z, 4_z^{-\prime}, \bar{1}, \overline{4_z^+}', m_z, \overline{4_z^-}'\right\} = 4'/m$$

black-white groups

Magnetic point groups: *Classification*

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Magnetic Symmetry and Applications

MPOINT — Magnetic Point Group Tables

$$M_1 = \left\{1, 4_z^+, 2_z, 4_z^-, \overline{1}', \overline{4_z^+}', m_z', \overline{4_z^-}'\right\} = 4/m'$$

Magnetic Point Group Tables of 4/m' (#11.4.38)

Useful data about magnetic point group 4/m'

Number of elements of the group (order): **8**
This group is **centrosymmetric**
This group is **not polar**
This group is **not compatible with ferromagnetism**

Symmetry operations of the group

N	(x,y,z) form	matrix form	Seitz symbol
1	x,y,z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	1
2	-x,-y,z, +1 $-m_x,-m_y,m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	2_z
3	-y,x,z, +1 $-m_y,m_x,m_z$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	4_z
4	y,-x,z, +1 $m_y,-m_x,m_z$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	4_z^{-1}
5	-x,-y,-z, -1 $-m_x,-m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	-1'
6	x,y,-z, -1 $m_x,m_y,-m_z$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	m_z'
7	y,-x,-z, -1 $m_y,-m_x,-m_z$	$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	$-4_z'$
8	-y,x,-z, -1 $-m_y,m_x,-m_z$	$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}'$	$-4_z^{-1\prime}$

Magnetic point groups: *Classification*

Not all of the magnetic point groups can be realized in a magnetically ordered system

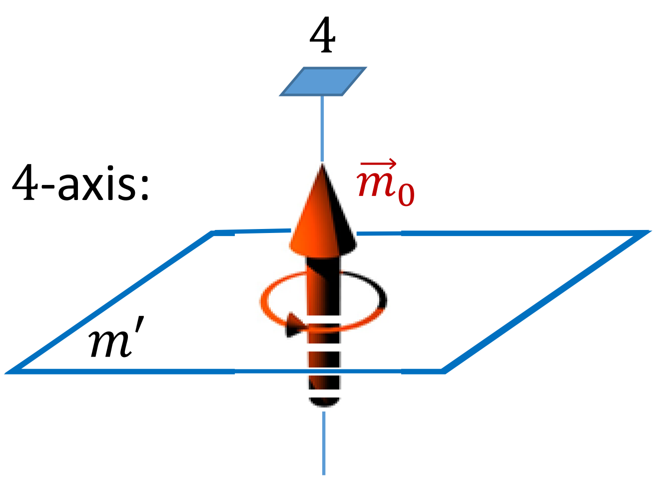
→ **Admissible magnetic point groups:** *(for a magnetic atom placed at the origin)*

all the operators leave at least one spin component invariant

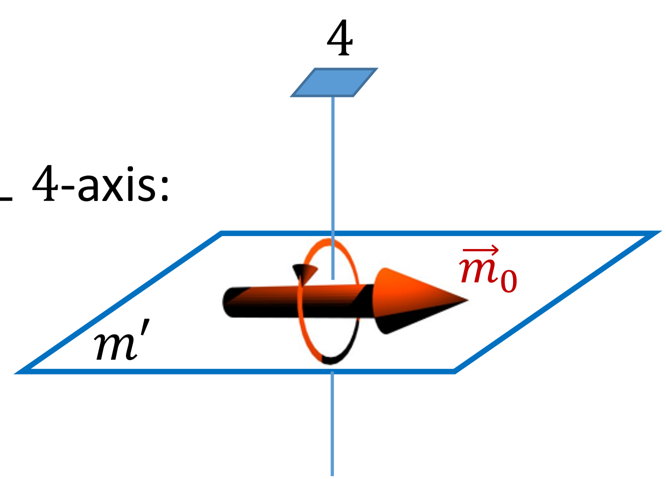
- none of the gray groups is admissible,
- many of the colorless and black-white groups are not admissible.

Example: $M_1 = 4/m'$ → $4/m'$ not admissible but $4/m$ is admissible if $\vec{m}_0 \parallel$ 4-axis

If $\vec{m}_0 \parallel$ 4-axis:



If $\vec{m}_0 \perp$ 4-axis:



$4: \quad \vec{m}_0 \rightarrow \vec{m}_0$

$m': \quad \vec{m}_0 \rightarrow -\vec{m}_0$

$4 \times 4: \quad \vec{m}_0 \rightarrow -\vec{m}_0$

$m': \quad \vec{m}_0 \rightarrow \vec{m}_0$

Magnetic point groups: *Classification*

The 31 admissible magnetic point groups:

Admissible magnetic point groups					Admissible spin direction
1	$\bar{1}$				any direction
$2'$	$2'/m'$	$m'm2'$			⊥ 2'-axis (and ⊥ m-plane for $m'm2'$)
m'					any direction within the m'-plane
m					⊥ m-plane
$m'm'm$					⊥ m-plane
$2'2'2$					‖ 2-axis
2	$2/m$	$m'm'2$			‖ 2-axis
4	$\bar{4}$	$4/m$	$42'2'$		‖ 4 or $\bar{4}$ -axis
$4m'm'$	$\bar{4}2m'$		$4/mm'm'$		‖ 4 or $\bar{4}$ -axis
3	$\bar{3}$	$32'$	$3m'$	$\bar{3}m'$	‖ 3 or $\bar{3}$ -axis
6	$\bar{6}$	$6/m$	$62'2'$		‖ 6 or $\bar{6}$ -axis
$6m'm'$	$\bar{6}m'2'$		$6/mm'm'$		‖ 6 or $\bar{6}$ -axis

Magnetic point groups: *Prediction for macroscopic properties*

- Example 1: **Ferromagnetoelectrics**

(spontaneous dielectric polarization $\vec{P}$ & magnetic polarization $\vec{M}$)

polar vector — axial vector

Among the 31 admissible point groups (compatible with ferromagnetism),
only 13 are also compatible with ferroelectricity

Table 1.5.8.4. *List of the magnetic point groups of the ferromagnetoelectrics*

Symbol of symmetry group		Allowed direction of	
Schoenflies	Hermann–Mauguin	**P**	**M**
C_1	1	Any	Any
C_2	2	∥ 2	∥ 2
$C_2(C_1)$	$2'$	∥ $2'$	⊥ $2'$
$C_s = C_{1h}$	m	∥ m	⊥ m
$C_s(C_1)$	m'	∥ m'	∥ m'
$C_{2v}(C_2)$	$m'm'2$	∥ 2	∥ 2
$C_{2v}(C_s)$	$m'm2'$	∥ $2'$	⊥ m
C_4	4	∥ 4	∥ 4
$C_{4v}(C_4)$	$4m'm'$	∥ 4	∥ 4
C_3	3	∥ 3	∥ 3
$C_{3v}(C_3)$	$3m'$	∥ 3	∥ 3
C_6	6	∥ 6	∥ 6
$C_{6v}(C_6)$	$6m'm'$	∥ 6	∥ 6

International tables for crystallography (2006), Vol. D, Section 1.5.8.3, pp. 141-142

Magnetic point groups: *Prediction for macroscopic properties*

- <u>Example 2</u>: **Linear magnetoelectric effect**

A magnetic field $\vec{H}$ applied in a crystal can produce an electric polarization $\vec{P}$: $P_i = \alpha_{ij} H_j$

An electric field $\vec{E}$ applied in a crystal can produce a magnetic moment $\vec{M}$: $M_i = \alpha_{ij} E_j$

→ possible in 58 magnetic point groups

→ predictions on the form of the $\tilde{\alpha}$ tensor:

Hermann–Mauguin	Matrix representation of the property tensor α_{ij}
1 $\bar{1}'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$
$2 (= 121)$ $m' (= 1m'1)$ $2/m' (= 1\,2/m'\,1)$ (unique axis y)	$\begin{bmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{bmatrix}$
$m (= 1m1)$ $2' (= 12'1)$ $2'/m (= 1\,2'/m\,1)$ (unique axis y)	$\begin{bmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{bmatrix}$
222 $m'm'2\,[2m'm',\ m'2m']$ $m'm'm'$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$
$mm2$ $2'2'2$ $2'mm'\,[m2'm']$ mmm'	$\begin{bmatrix} 0 & \alpha_{12} & 0 \\ \alpha_{21} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$4,\ \bar{4}',\ 4/m'$ $3,\ \bar{3}'$ $6,\ \bar{6}',\ 6/m'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & 0 \\ -\alpha_{12} & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$
$\bar{4}$ $4'$ $4'/m'$	$\begin{bmatrix} \alpha_{11} & \alpha_{12} & 0 \\ \alpha_{12} & -\alpha_{11} & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$422,\ 4m'm'$ $\bar{4}'2m'\,[\bar{4}'m'2],\ 4/m'm'm'$ $32,\ 3m',\ \bar{3}'m'$ $622,\ 6m'm'$ $\bar{6}'m'2\,[\bar{6}'2m'],\ 6/m'm'm'$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{bmatrix}$
$4mm,\ 42'2'$ $\bar{4}'2'm\,[\bar{4}'m2'],\ 4/m'mm$ $3m,\ 32',\ \bar{3}'m$ $6mm,\ 62'2'$ $\bar{6}'m2'\,[\bar{6}'2'm],\ 6/m'mm$	$\begin{bmatrix} 0 & \alpha_{12} & 0 \\ -\alpha_{12} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$\bar{4}2m,\ \bar{4}m'2'$ $4'22',\ 4'm'm$ $4'/m'm'm$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & -\alpha_{11} & 0 \\ 0 & 0 & 0 \end{bmatrix}$
$23,\ m'\bar{3}'$ $432,\ \bar{4}'3m',\ m'\bar{3}'m'$	$\begin{bmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{11} \end{bmatrix}$

Taken from the ITC, Volume D, p. 138

Magnetic point groups: *Prediction for macroscopic properties*

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Magnetic Symmetry and Applications

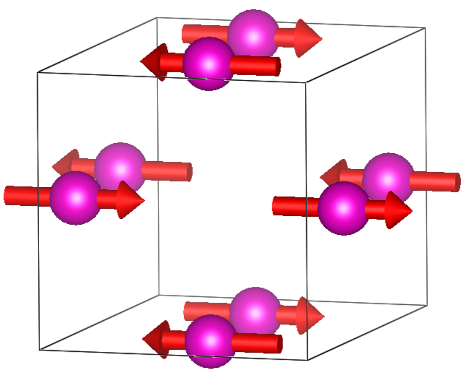
MAGNDATA ⚠ A collection of magnetic structures with transportable cif-type files

$Pnm'a \rightarrow mm'm$

$EuZrO_3$

$Pn'm'a' \rightarrow m'm'm'$

MTENSOR ⚠ Symmetry-adapted form of crystal tensors in magnetic phases



Information about the selected tensor

- 2 nd rank Magnetoelectric tensor α_{ij} (direct effect)
- Axial tensor which inverts under time-reversal symmetry operation
- Defining equation: $\mathbf{M_i=\alpha_{ij}E_j}$
- Relates Electric field **E** with Magnetization **M**
- Intrinsic symmetry symbol: **aeV^2**

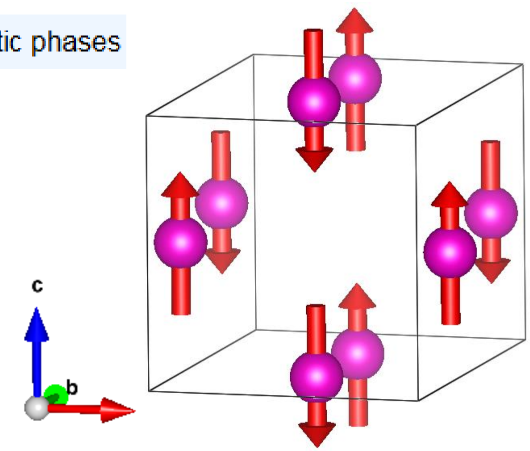


Table of tensor components

α_{ij}	j		
i	1	2	3
1	0	0	α_{13}
2	0	0	0
3	α_{31}	0	0

Number of independent coefficients: 2

Table of tensor components

α_{ij}	j		
i	1	2	3
1	α_{11}	0	0
2	0	α_{22}	0
3	0	0	α_{33}

Number of independent coefficients: 3

Magnetic Bravais lattices

To describe magnetic translation symmetries, we introduce a new operator …

Anti-translation $\vec{t}' = \vec{t}1'$ (replaces the propagation vector formalism)

→ limitation of the Shubnikov symmetry: only $\vec{k} = \vec{0}$, $\vec{k} = \vec{H}/2$, or $\vec{k} = \vec{H}$

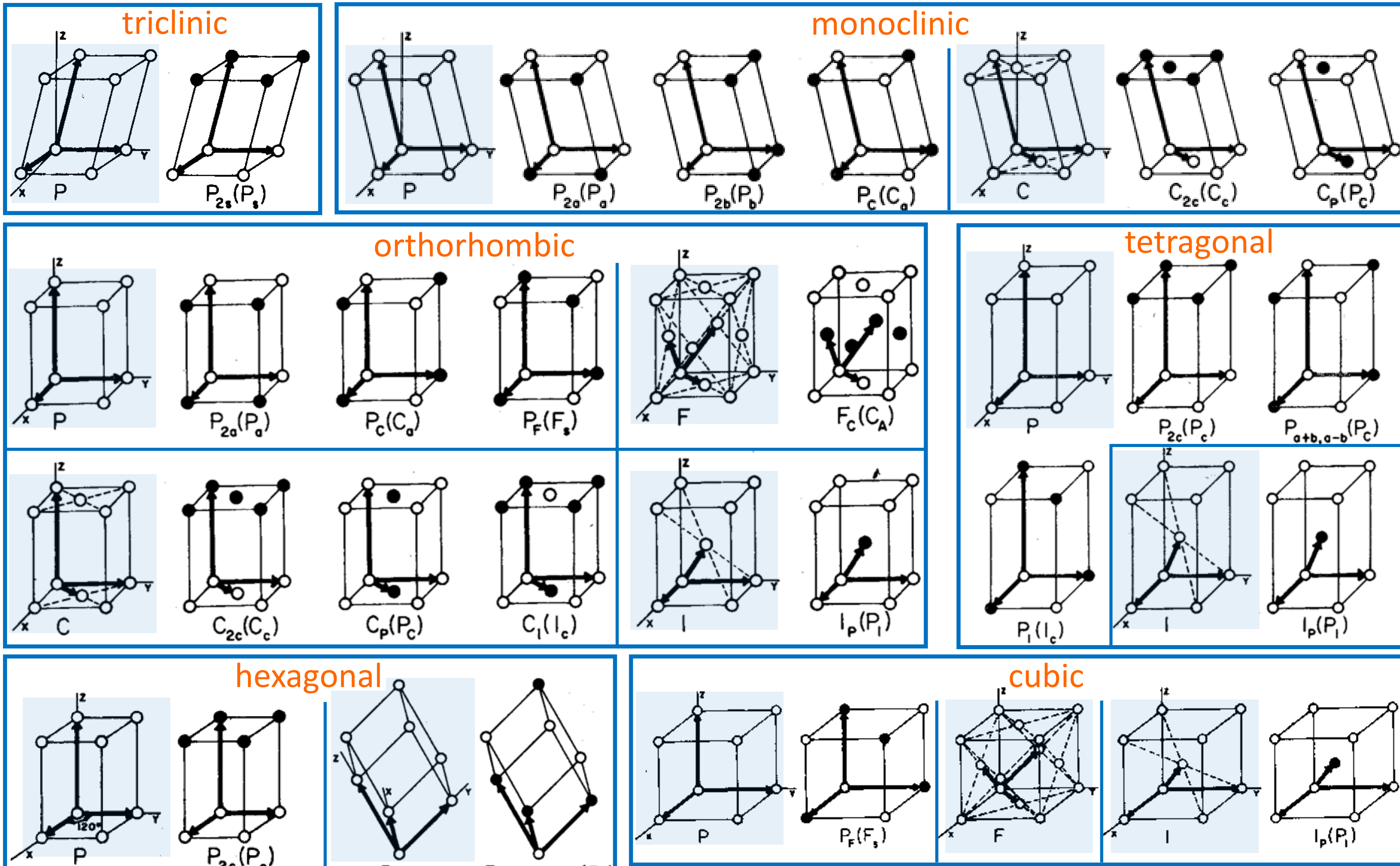
- **Gray** translation groups: not considered (incompatible with magnetic order)
- **Colorless** translation groups: same as the 14 Bravais lattices (only translations)
- **Black-white** translation groups: contain translations and anti-translations

$$M_L = H_L \cup (T - H_L)1'$$

with H_L: subgroup of index 2 of the translation group T
and $T - H_L$: the remaining operators, i.e. those not in H_L

→ 22 black-white Bravais lattices

The 36 magnetic Bravais lattices



o: *translations*, •: *anti-translations, OG(BNS)*

Magnetic Bravais lattices: *OG vs BNS notations*

BNS: N. V. Belov, N. N. Neronova, and T.S. Smirnova (1957)
OG: W. Opechowski and R. Guccione (1965)

→ same lattice symbol X for colorless translation groups: $X = P, I, F, A, B, C, R$
→ different lattice symbol X_Y for black-white translation groups $H_L \cup (T - H_L)1'$

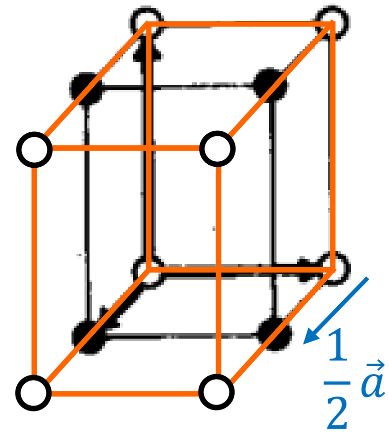
BNS: X = symbol of subgroup H_L (decorated by white points only)
Y = type of colored lattice (fractional anti-translation in H_L)

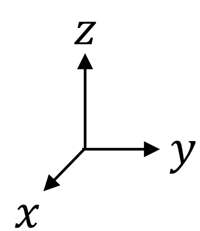
Symbol	Fractional	Symbol	Fractional
P_S	(0,0,1/2) triclinic only	B_b	(0,1/2,0)
P_a	(1/2,0,0)	B_a	(1/2,0,0)
P_b	(0,1/2,0)	B_A	(0,1/2,1/2)
P_c	(0,0,1/2)	C_c	(0,0,1/2)
P_A	(0,1/2,1/2)	C_a	(1/2,0,0)
P_B	(1/2,0,1/2)	C_A	(0,1/2,1/2)
P_C	(1/2,1/2,0)	F_S	(1/2,1/2,1/2)
P_I	(1/2,1/2,1/2)	I_a	(1/2,0,0)
A_a	(1/2,0,0)	I_b	(0,1/2,0)
A_b	(0,1/2,0)	I_c	(0,0,1/2)
A_B	(1/2,0,1/2)	R_I	(0,0,1/2)

http://stokes.byu.edu/iso/magneticspacegroupshelp.php

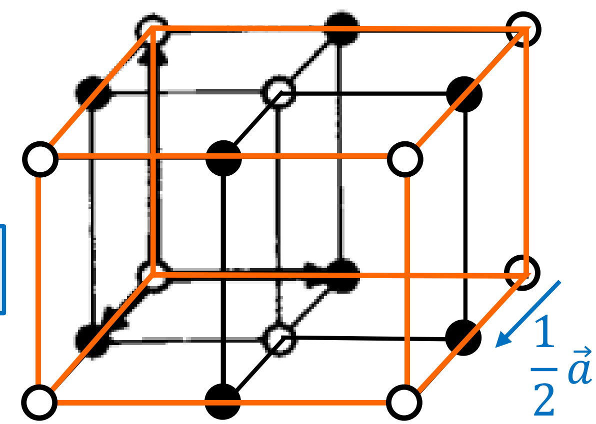
Examples:

P_a





C_a



Magnetic Bravais lattices: *OG vs BNS notations*

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→ same lattice symbol X for colorless translation groups: $X = P, I, F, A, B, C, R$
→ different lattice symbol X_Y for black-white translation groups $H_L \cup (T - H_L)1'$

OG: X = symbol of parent group T (decorated by black and white point
Y = type of colored lattice (translations in T)

Symbol	Sublattice
P_{2s}	(1,0,0,),(0,1,0),(0,0,2) triclinic only
P_{2a}	(2,0,0,),(0,1,0),(0,0,1)
P_{2b}	(1,0,0),(0,2,0),(0,0,1)
P_{2c}	(1,0,0),(0,1,0),(0,0,2)
P_A	(1,0,0),(0,1,1),(0,-1,1)
P_B	(1,0,1),(0,1,0),(-1,0,1)
P_C	(1,1,0),(-1,1,0),(0,0,1) non-tetragonal only
P_P	(1,1,0),(-1,1,0),(0,0,1) tetragonal only
P_F	(0,1,1),(1,0,1),(1,1,0) non-tetragonal only
P_I	(0,1,1),(1,0,1),(1,1,0) tetragonal only
A_{2a}	(2,0,0),(0,1/2,1/2),(0,-1/2,1/2)
A_P	(1,0,0),(0,1,0),(0,0,1)
A_I	(1,1/2,1/2),(0,1,0),(0,0,1)

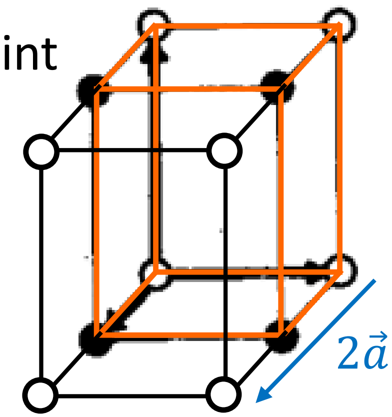
B_{2b}	..(1/2,0,1/2),
B_P	(1,0,0),(0,1
B_I	(1,0,0),(1/2
C_{2c}	(1/2,1/2,0),
C_P	(1,0,0),(0,1
C_I	(1,0,0),(0,1
F_A	(1,0,0),(0,1
F_B	(1/2,0,1/2),
F_C	(1/2,1/2,0),
I_P	(1,0,0),(0,1
I_A	(1/2,1/2,1/2
I_B	(1,0,1),(1/2
I_C	(1,1,0),(-1,
R_R	(1/3,2/3,2/3

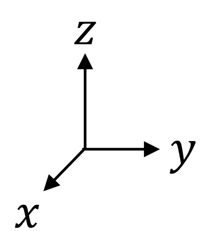
http://stokes.byu.edu/iso/magneticspacegroupshelp.php

Examples:

P_{2a}

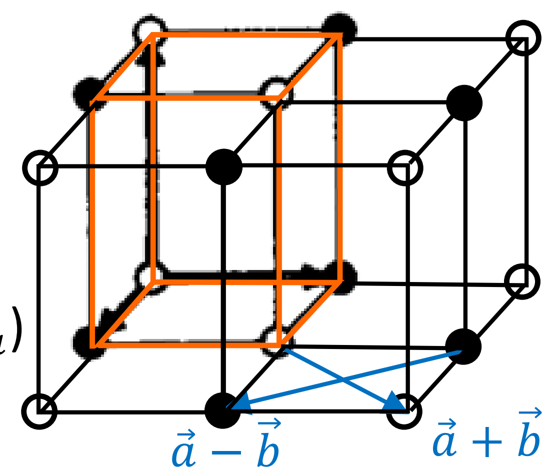
(BNS: P_a)





P_C

(BNS: C_a)



Magnetic space groups: *Primed and unprimed symmetries*

As for magnetic point groups and translation groups,
magnetic space group symmetries can be primed (g') or not (g)

Example:

Glide plane $a \perp \vec{c}$ at $z = 1/4$ in $Pnma$

$$\left\{m_z \middle| \frac{1}{2}, 0, \frac{1}{2}\right\}$$

$$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1/2 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

unprimed sym. $\delta = 1$

Glide plane $a' \perp \vec{c}$ at $z = 1/4$ in $Pn'ma'$

$$\left\{m_z \middle| \frac{1}{2}, 0, \frac{1}{2}\right\}'$$

$$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1/2 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

spin reversal $\delta = -1$

Atomic coordinates: $\vec{r}_j' = g\vec{r}_j = \{\alpha|\vec{t}_\alpha\}\vec{r}_j = \alpha\vec{r}_j + \vec{t}_\alpha$

$$x, y, z \quad \rightarrow \quad x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$$

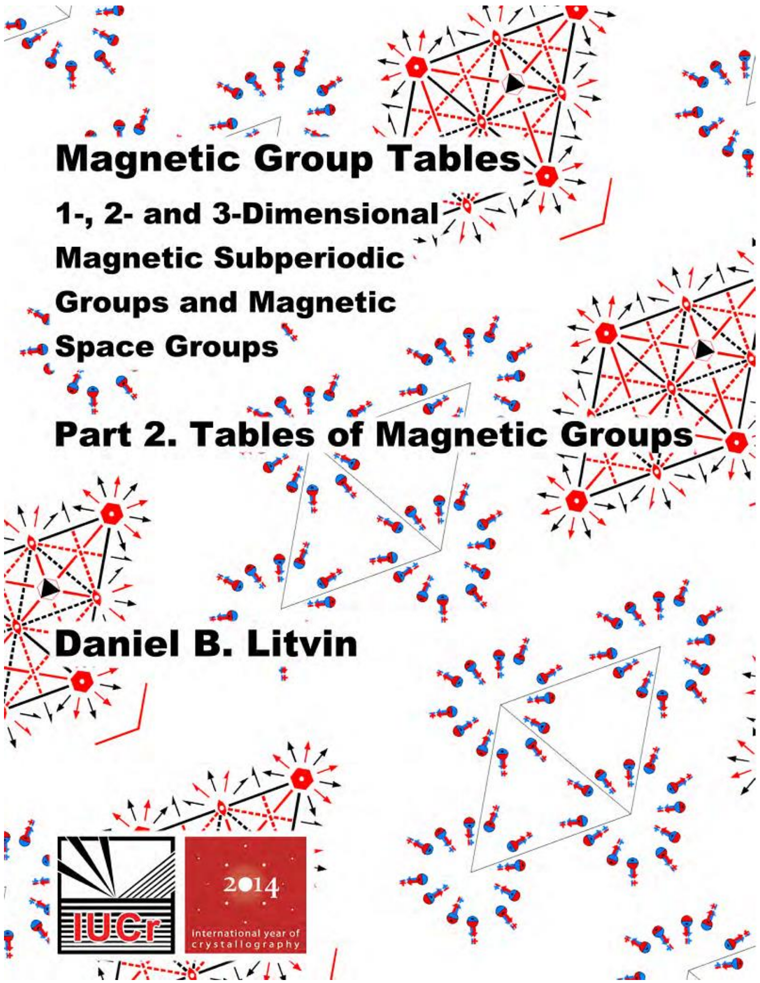
Magnetic moment: $\vec{m}_j' = g\vec{m}_j = \det(\alpha)\ \delta\ \alpha\vec{m}_j$

$$m_x, m_y, m_z \quad \rightarrow \quad -m_x, -m_y, m_z$$

$$m_x, m_y, m_z \quad \rightarrow \quad m_x, m_y, -m_z$$

Magnetic space groups: *Classification*

Using the same procedure as for magnetic point groups and translation groups allows to obtain and classify the **1651 magnetic space groups = Shubnikov groups**



- **Daniel B. Litvin** (2001)

Pennsylvania State University, Reading, USA
Magnetic group tables electronic book

Full description of all Shubnikov groups (in a form similar to that of the ITC, volume A, for crystallographic space groups), using the OG notation.

http://sites.psu.edu/ecsphysicslitvin/

Magnetic space groups: *Classification*

ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA, stokesh@byu.edu

Description: The ISOTROPY software suite is a collection of software which applies group theoretical methods to the analysis of phase transitions in crystalline solids.
How to cite: ISOTROPY Software Suite, iso.byu.edu.

References and Resources

Isotropy subgroups and distortions

- ISODISTORT: Explore and visualize distortions of crystalline structures. Possible distortions include atomic displacements, atomic ordering, strain, and magnetic moments.
- ISOSUBGROUP: Interactive program using user-friendly interface to list isotropy subgroups.
- ISOTROPY: Interactive program using command lines to explore isotropy subgroups and their associated distortions.
- SMODES: Find the displacement modes in a crystal which brings the dynamical matrix to block-diagonal form, with the smallest possible blocks.
- FROZSL: Calculate phonon frequencies and displacement modes using the method of frozen phonons.

Space groups and irreducible representations

- ISOCIF: Create or modify CIF files.
- FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell.
- ISO-IR: Tables of Irreducible Representations. The 2011 version of IR matrices.
- ISO-MAG: Tables of magnetic space groups, both in human-readable and computer-readable forms.

Superspace Groups

- ISO(3+d)D: (3+d)-Dimensional Superspace Groups for d=1,2,3
- ISO(3+1)D: Isotropy Subgroups for Incommensurately Modulated Distortions in Crystalline Solids: A Complete List for One-Dimensional Modulations
- FINDSSG: Identify the superspace group symmetry given a list of symmetry operators.
- TRANSFORMSSG: Transform a superspace group to a new setting.

Phase Transitions

- COPL: Find a complete list of order parameters for a phase transition, given the space-group symmetries of the parent and subgroup phases.
- INVARIANTS: Generate invariant polynomials of the components of order parameters.
- COMSUBS: Find common subgroups of two structures in a reconstructive phase transition

Linux

- ISOTROPY Software Suite for Linux: includes ISOTROPY, FINDSYM, SMODES, COMSUBS.

- **Harold T. Stokes and Branton J. Campbell** (2010)

Brigham Young University, Provo, Utah, USA

Isotropy software suite

Compiled by using the data of D. B. Litvin

(OG and BNS notations)

http://iso.byu.edu/iso/isotropy.php

Magnetic space groups: *Classification*

bilbao crystallographic server

Magnetic Symmetry and Applications	
MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MNORMALIZER	Normalizers of Magnetic Space Groups
IDENTIFY MAGNETIC GROUP	Identification of a Magnetic Space Group from a set of generators in an arbitrary setting
BNS2OG ⚠	Transformation of symmetry operations between BNS and OG settings
mCIF2PCR ⚠	Transformation from mCIF to PCR format (FullProf).
MPOINT ⚠	Magnetic Point Group Tables
MAGNEXT	Extinction Rules of Magnetic Space Groups
MAXMAGN ⚠	Maximal magnetic space groups for a given space group and a propagation vector
MAGMODELIZE	Magnetic structure models for any given magnetic symmetry
k-SUBGROUPSMAG ⚠	Magnetic subgroups consistent with some given propagation vector(s) or a supercell
MAGNDATA ⚠	A collection of magnetic structures with transportable cif-type files
MVISUALIZE ⚠	3D Visualization of magnetic structures with Jmol
MTENSOR ⚠	Symmetry-adapted form of crystal tensors in magnetic phases

- **Mois I. Aroyo, J. Manuel Perez-Mato, G. de la Flor, E. S. Tasci, S. V. Gallego, …**

Many tools dealing with magnetic space groups (from 2010)

http://www.cryst.ehu.es

Magnetic space groups: *Classification*

G: crystallographic space group, H: subgroup of index 2 of G
M: magnetic space group

4 types of magnetic space groups:

- Type I: 230 **colorless** groups: $M = G$ (Fedorov groups)
- Type II: 230 **gray** groups: $M = G \cup G1'$ (paramagnetic groups)
- 1191 **black-white** groups: $M = H \cup (G - H)1'$ (BW groups)

Type III:
674 BW groups such that
H is an **equi-translation** subgroup
(H has the **same translation group** T as G: ∃ translations only)
→ **first kind, BW1**

$\vec{k} = \vec{0}$

Type IV:
517 BW groups such that
H is an **equi-class** subgroup
(M has a **colored lattice**:
∃ translations and anti-translations)
→ **second kind, BW2**

$\vec{k} = \vec{H}$ (for centered cells) or $\vec{k} = \frac{1}{2}\vec{H}$

Magnetic space groups: *Classification*

BNS vs OG notations for the Shubnikov groups:

→ **types I, II, and III: same notation**

→ **type IV: different notation**

$M = H \cup (G - H)1'$

with translation group T split between H and $G - H$ (∃ anti-translations)

$M_L = H_L \cup (T - H_L)1'$

Lattice symbol: see previous part (magnetic Bravais lattices)

Symbols for the planes and axes of symmetry:

BNS notation: those belonging to subgroup H

→ always unprimed

→ can be different from those given for parent group G

OG notation: those given for parent group G

→ can be primed or unprimed

The magnetic space groups can be constructed using the International tables for Crystallography, Volume A

Example: space group $Ima2$ (No. 46)

Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 0,0,z (3) a x,0,z (4) m $\frac{1}{4}$,y,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) c $x,\frac{1}{4},z$ (4) $n(0,\frac{1}{2},\frac{1}{2})$ $0,y,z$

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)

Maximal non-isomorphic subgroups

I	[2] $I1a1$ (Cc, 9)	(1; 3)+
	[2] $Im11$ (Cm, 8)	(1; 4)+
	[2] $I112$ ($C2$, 5)	(1; 2)+
IIa	[2] $Pna2_1$ (33)	1; 3; (2; 4) + ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$)
	[2] $Pnc2$ (30)	1; 2; (3; 4) + ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$)
	[2] $Pma2$ (28)	1; 2; 3; 4
	[2] $Pmc2_1$ (26)	1; 4; (2; 3) + ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$)
IIb	none	

Colorless trivial magnetic space group:

$Ima2 = \{1, m_x, a_y, 2_z\}\, T$

For simplicity, we drop off the translation group T in the following

BW1 magnetic space groups:

$M = H \cup (G - H)1'$ with all translations of G in H

$I1a1 \cup (Ima2 - I1a1)1' = \{1, a_y\} + \{m_x, 2_z\}1' = Im'a2'$

$Im11 \cup (Ima2 - Im11)1' = \{1, m_x\} + \{a_y, 2_z\}1' = Ima'2'$

$I112 \cup (Ima2 - I112)1' = \{1, 2_z\} + \{m_x, a_y\}1' = Im'a'2$

BW2 magnetic space groups

<u>Example</u>: space group $Ima2$ (No. 46) - *continuation*

Symmetry operations

For $(0,0,0)+$ set

(1) 1	(2) 2 $\quad 0,0,z$	(3) a $\quad x,0,z$	(4) m $\quad \frac{1}{4},y,z$

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

(1) $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	(2) $2(0,0,\frac{1}{2})$ $\quad \frac{1}{4},\frac{1}{4},z$	(3) c $\quad x,\frac{1}{4},z$	(4) $n(0,\frac{1}{2},\frac{1}{2})$ $\quad 0,y,z$

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)

Maximal non-isomorphic subgroups

I	[2] $I1a1$ (Cc, 9)	(1; 3)+
	[2] $Im11$ (Cm, 8)	(1; 4)+
	[2] $I112$ ($C2$, 5)	(1; 2)+
IIa	[2] <u>$Pna2_1$</u> (33)	1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2] <u>$Pnc2$</u> (30)	1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
	[2] <u>$Pma2$</u> (28)	1; 2; 3; 4
	[2] <u>$Pmc2_1$</u> (26)	1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
IIb	none	

BW2 magnetic space groups:

$M = H \cup (G-H)1'$ with H_L in H and $T-H_L$ in $G-H$

$\vec{t}_I = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ becomes an anti-translation

$$H_L = \{\vec{t}\,|\,\vec{t} = u\vec{a} + v\vec{b} + w\vec{c};\, u,v,w \in \mathbb{Z}\}$$

$$T - H_L = \{\vec{t}\,|\,\vec{t} = u\vec{a} + v\vec{b} + w\vec{c} + \vec{t}_I;\, u,v,w \in \mathbb{Z}\} = H'_L$$

			BNS	OG
<u>$Pna2_1$</u>:	$\{1, n_x, a_y, 2_{1z}\}H_L + \{1, m_x, c_y, 2_z\}H'_L$	=	P_Ina2_1	$I_Pm'a2'$
<u>$Pnc2$</u>:	$\{1, n_x, c_y, 2_z\}H_L + \{1, m_x, a_y, 2_{1z}\}H'_L$	=	P_Ina2_1	$I_Pm'a2'$
<u>$Pma2$</u>:	$\{1, m_x, a_y, 2_z\}H_L + \{1, n_x, c_y, 2_{1z}\}H'_L$	=	P_Ina2_1	$I_Pm'a2'$
<u>$Pmc2_1$</u>:	$\{1, m_x, c_y, 2_{1z}\}H_L + \{1, n_x, a_y, 2_z\}H'_L$	=	P_Ina2_1	$I_Pm'a2'$

Magnetic space groups: *Example using the ITC – volume A*

Bilbao Crystallographic Server → MGENPOS → Table of Magnetic Space Group Symbols

The magnetic space groups derived from the Fedorov space group: Ima2 (#46)

Listed with respect to the BNS setting:

- #46.241 Ima2 [OG: Ima2 #46.1.338] *Type I (Fedorov)*
- #46.242 Ima21' [OG: Ima21' #46.2.339] *Type II (grey group)*
- #46.243 Im'a2' [OG: Im'a2' #46.3.340] *Type III (translationgleiche)*
- #46.244 Ima'2' [OG: Ima'2' #46.4.341] *Type III (translationgleiche)*
- #46.245 Im'a'2 [OG: Im'a'2 #46.5.342] *Type III (translationgleiche)*
- #46.246 $I_c$ma2 [OG: C_Im'm2' #35.12.247] *Type IV (klassengleiche)*
- #46.247 $I_a$ma2 [OG: A_Im'm'2 #38.13.277] *Type IV (klassengleiche)*
- #46.248 $I_b$ma2 [OG: $A_I$bm2 #39.8.285] *Type IV (klassengleiche)*

Listed with respect to the OG setting:

- #46.1.338 Ima2 [BNS: Ima2 #46.241] *Type I (Fedorov)*
- #46.2.339 Ima21' [BNS: Ima21' #46.242] *Type II (grey group)*
- #46.3.340 Im'a2' [BNS: Im'a2' #46.243] *Type III (translationgleiche)*
- #46.4.341 Ima'2' [BNS: Ima'2' #46.244] *Type III (translationgleiche)*
- #46.5.342 Im'a'2 [BNS: Im'a'2 #46.245] *Type III (translationgleiche)*
- #46.6.343 $I_P$ma2 [BNS: $P_I$ma2 #28.98] *Type IV (klassengleiche)*
- #46.7.344 I_Pm'a2' [BNS: $P_I$na2_1 #33.155] *Type IV (klassengleiche)*
- #46.8.345 $I_P$ma'2' [BNS: $P_I$mc2_1 #26.77] *Type IV (klassengleiche)*
- #46.9.346 I_Pm'a'2 [BNS: $P_I$nc2 #30.122] *Type IV (klassengleiche)*

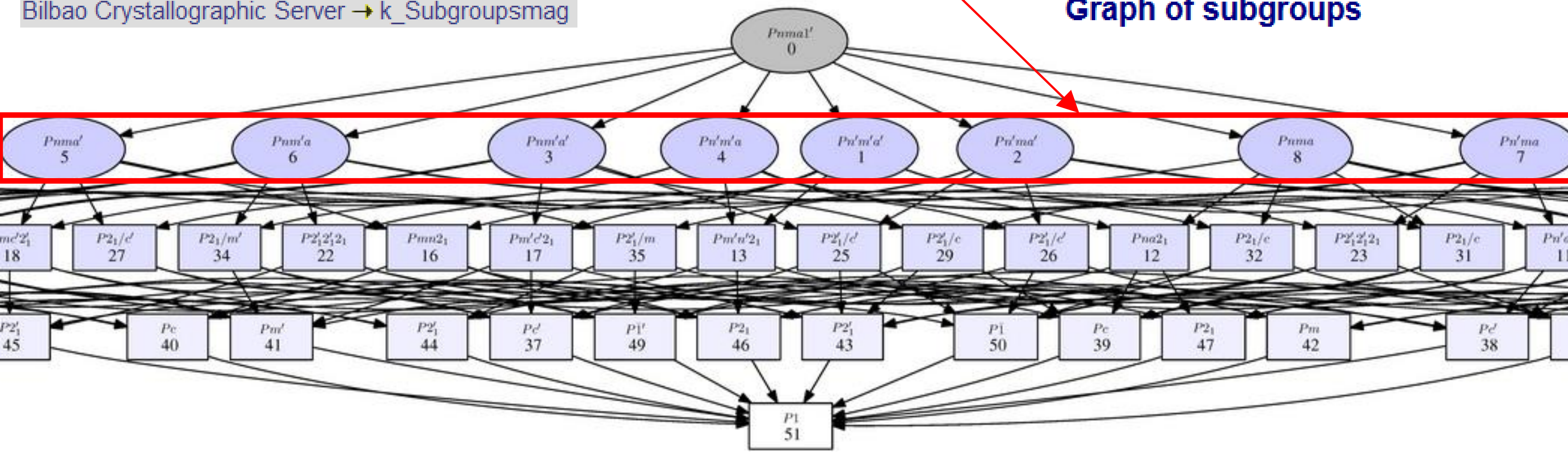
Magnetic space groups: *Application to $LaMnO_3$*

Above T_N: magnetic space group = $Pnma1'$ (gray group)

Below T_N: $\vec{k} = (0,0,0) \Rightarrow$ possible maximal subgroups (index 2)?

Bilbao Crystallographic Server → k_Subgroupsmag

Graph of subgroups



Mn: 4 a $\bar{1}$ $0,0,0$ $\frac{1}{2},0,\frac{1}{2}$ $0,\frac{1}{2},0$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

$\Rightarrow$ possible space groups: those containing $\bar{1}$ and not $\bar{1}'$

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

neutron diffraction experiment

Magnetic space groups: *Application to $LaMnO_3$*

Pn'ma	m'mm	Orthorhombic
62.3.504	$P2_1/n'2_1'/m2_1'/a$	

Positions

Coordinates

Multiplicity,
Wyckoff letter,
Site Symmetry.

Magnetic components

8	d	1	(1) x,y,z [u,v,w]	(2) $\bar{x}$+1/2,$\bar{y}$,z+1/2 [u,v,$\bar{w}$]	(3) $\bar{x}$,y+1/2,$\bar{z}$ [u,$\bar{v}$,w]	(4) x+1/2,$\bar{y}$+1/2,$\bar{z}$+1/2 [u,$\bar{v}$,$\bar{w}$]
			(5) $\bar{x}$,$\bar{y}$,$\bar{z}$ [$\bar{u}$,$\bar{v}$,$\bar{w}$]	(6) x+1/2,y,$\bar{z}$+1/2 [$\bar{u}$,$\bar{v}$,w]	(7) x,$\bar{y}$+1/2,z [$\bar{u}$,v,$\bar{w}$]	(8) $\bar{x}$+1/2,y+1/2,z+1/2 [$\bar{u}$,v,w]
4	c	.m.	x,1/4,z [0,v,0]	$\bar{x}$+1/2,3/4,z+1/2 [0,v,0]	$\bar{x}$,3/4,$\bar{z}$ [0,$\bar{v}$,0]	x+1/2,1/4,$\bar{z}$+1/2 [0,$\bar{v}$,0]
4	b	$\bar{1}'$	0,0,1/2 [0,0,0]	1/2,0,0 [0,0,0]	0,1/2,1/2 [0,0,0]	1/2,1/2,0 [0,0,0]
4	a	$\bar{1}'$	0,0,0 [0,0,0]	1/2,0,1/2 [0,0,0]	0,1/2,0 [0,0,0]	1/2,1/2,1/2 [0,0,0]

$\vec{m}$ cannot be on a Wyckoff position whose symmetry is $\bar{1}'$!!!
($\bar{1}'$ is not an admissible magnetic point group)

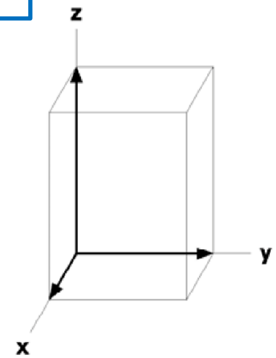
Parts of pages 1 and 2 (/2) of $Pn'ma$ Shubnikov group, D. B. Litvin

Magnetic space groups: *Application to* $LaMnO_3$

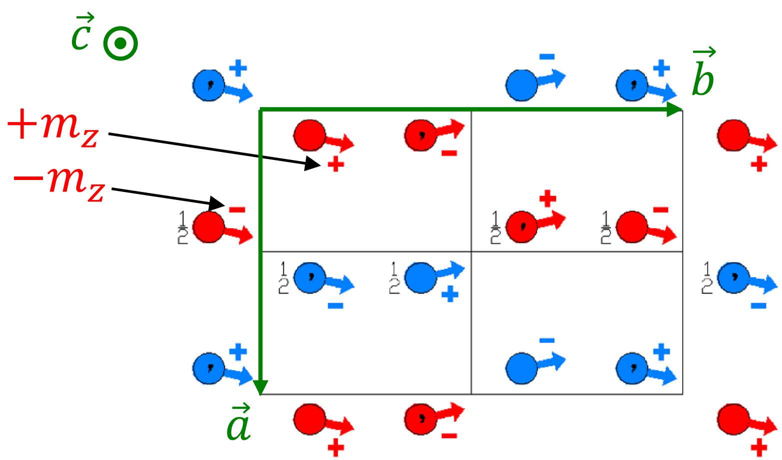
$Pn'ma'$ Shubnikov group

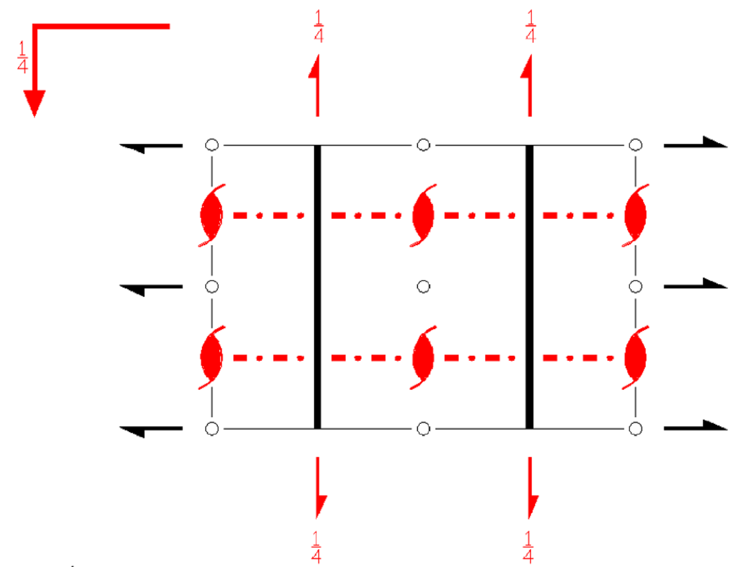
Black: unprimed sym. op.
Red: primed sym. op.

$Pn'ma'$
$= \{1, 2_{1y}, \bar{1}, m_y\}$
$\cup \{2_{1x}, n_x, 2_{1z}, a_z\}1'$



Pn'ma'	m'mm'	Orthorhombic
62.8.509	$P2_1'/n'2_1/m2_1'/a'$	





Origin at $\bar{1}$ on 12_11

Asymmetric unit $0 \le x \le 1/2$; $0 \le y \le 1/4$; $0 \le z \le 1$

Symmetry Operations

(1) 1
(1|0,0,0)

(5) $\bar{1}$ 0,0,0
($\bar{1}$|0,0,0)

(2) 2' (0,0,1/2) 1/4,0,z
(2_z|1/2,0,1/2)'

(6) a' (1/2,0,0) x,y,1/4
(m_z|1/2,0,1/2)'

(3) 2 (0,1/2,0) 0,y,0
(2_y|0,1/2,0)

(7) m x,1/4,z
(m_y|0,1/2,0)

(4) 2' (1/2,0,0) x,1/4,1/4
(2_x|1/2,1/2,1/2)'

(8) n' (0,1/2,1/2) 1/4,y,z
(m_x|1/2,1/2,1/2)'

page 1/2 of $Pn'ma'$
D. B. Litvin

Magnetic space groups: *Application to $LaMnO_3$*

Continued	62.8.509	Pn'ma'

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			
8	d	1	(1) x,y,z [u,v,w]	(2) $\bar{x}$+1/2,$\bar{y}$,z+1/2 [u,v,$\bar{w}$]	(3) $\bar{x}$,y+1/2,$\bar{z}$ [$\bar{u}$,v,$\bar{w}$]	(4) x+1/2,$\bar{y}$+1/2,$\bar{z}$+1/2 [$\bar{u}$,v,w]
			(5) $\bar{x}$,$\bar{y}$,$\bar{z}$ [u,v,w]	(6) x+1/2,y,$\bar{z}$+1/2 [u,v,$\bar{w}$]	(7) x,$\bar{y}$+1/2,z [$\bar{u}$,v,$\bar{w}$]	(8) $\bar{x}$+1/2,y+1/2,z+1/2 [$\bar{u}$,v,w]
4	c	.m.	x,1/4,z [0,v,0]	$\bar{x}$+1/2,3/4,z+1/2 [0,v,0]	$\bar{x}$,3/4,$\bar{z}$ [0,v,0]	x+1/2,1/4,$\bar{z}$+1/2 [0,v,0]
4	b	$\bar{1}$	0,0,1/2 [u,v,w]	1/2,0,0 [u,v,$\bar{w}$]	0,1/2,1/2 [$\bar{u}$,v,$\bar{w}$]	1/2,1/2,0 [$\bar{u}$,v,w]
4	a	$\bar{1}$	0,0,0 [u,v,w]	1/2,0,1/2 [u,v,$\bar{w}$]	0,1/2,0 [$\bar{u}$,v,$\bar{w}$]	1/2,1/2,1/2 [$\bar{u}$,v,w]

Mn

Symmetry of Special Projections

Along [0,0,1] p 2'mg'
a* = -b b* = a/2
Origin at 0,0,z

Along [1,0,0] c 2'mm'
a* = b b* = c
Origin at x,1/4,1/4

Along [0,1,0] p 2gg1'
a* = c b* = a
Origin at 0,y,0

page 2/2 of $Pn'ma'$
D. B. Litvin

Continued

Generators selected (1); t(1,0,0

Admissible magnetic point groups					Admissible spin direction
1	$\bar{1}$				any direction
$2'$	$2'/m'$	$m'm2'$			⊥ 2'-axis (and ⊥ m-plane for $m'm2'$)
m'					any direction within the m'-plane
m					⊥ m-plane

Positions

Multiplicity,
Wyckoff letter,
Site Symmetry.

8	d	1	(1) x,y,z [u,v,w]	(2) $\bar{x}$+1/2,$\bar{y}$,z+1/2 [u,v,$\bar{w}$]	(3) $\bar{x}$,y+1/2,$\bar{z}$ [$\bar{u}$,v,$\bar{w}$]	(4) x+1/2,$\bar{y}$+1/2,$\bar{z}$+1/2 [$\bar{u}$,v,w]
			(5) $\bar{x}$,$\bar{y}$,$\bar{z}$ [u,v,w]	(6) x+1/2,y,$\bar{z}$+1/2 [u,v,$\bar{w}$]	(7) x,$\bar{y}$+1/2,z [$\bar{u}$,v,$\bar{w}$]	(8) $\bar{x}$+1/2,y+1/2,z+1/2 [$\bar{u}$,v,w]
4	c	.m.	x,1/4,z [0,v,0]	$\bar{x}$+1/2,3/4,z+1/2 [0,v,0]	$\bar{x}$,3/4,$\bar{z}$ [0,v,0]	x+1/2,1/4,$\bar{z}$+1/2 [0,v,0]
4	b	$\bar{1}$	0,0,1/2 [u,v,w]	1/2,0,0 [u,v,$\bar{w}$]	0,1/2,1/2 [$\bar{u}$,v,$\bar{w}$]	1/2,1/2,0 [$\bar{u}$,v,w]
4	a	$\bar{1}$	0,0,0 [u,v,w]	1/2,0,1/2 [u,v,$\bar{w}$]	0,1/2,0 [$\bar{u}$,v,$\bar{w}$]	1/2,1/2,1/2 [$\bar{u}$,v,w]

Mn

Symmetry of Special Projections

Along [0,0,1] p 2'mg'
a* = -b b* = a/2
Origin at 0,0,z

Along [1,0,0] c 2'mm'
a* = b b* = c
Origin at x,1/4,1/4

Along [0,1,0] p 2gg1'
a* = c b* = a
Origin at 0,y,0

page 2/2 of $Pn'ma'$
D. B. Litvin

The symmetry of this Wyckoff position imposes $\vec{m} \parallel \vec{b}$
($\vec{m}$ must be ⊥ to the mirror plane)

Magnetic space groups: *Application to $LaMnO_3$*

bilbao crystallographic server

Magnetic Symmetry and Applications

MGENPOS General Positions of Magnetic Space Groups

General Positions of the Group *Pn'ma'* (#62.448)

For this space group, BNS and OG settings coincide.
Its label in the OG setting is given as: Pn'ma' (#62.8.509)

N	Standard/Default Setting			
	(x,y,z) form	Matrix form	Geom. interp.	Seitz notation
1	x, y, z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	1 +1	{ 1 | 0 }
2	-x, y+1/2, -z, +1 $-m_x,m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	2 (0,1/2,0) 0,y,0 +1	{ 2_{010} | 0 1/2 0 }
3	-x, -y, -z, +1 m_x,m_y,m_z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	-1 0,0,0 +1	{ -1 | 0 }
4	x, -y+1/2, z, +1 $-m_x,m_y,-m_z$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	m x,1/4,z +1	{ m_{010} | 0 1/2 0 }
5	x+1/2, -y+1/2, -z+1/2, -1 $-m_x,m_y,m_z$	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & -1 & 1/2 \\ 0 & 0 & 0 & -1 \end{pmatrix}'$	2 (1/2,0,0) x,1/4,1/4 -1	{ $2'_{100}$ | 1/2 1/2 1/2 }
6	-x+1/2, -y, z+1/2, -1 $m_x,m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}'$	2 (0,0,1/2) 1/4,0,z -1	{ $2'_{001}$ | 1/2 0 1/2 }
7	-x+1/2, y+1/2, z+1/2, -1 $-m_x,m_y,m_z$	$\begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}'$	n (0,1/2,1/2) 1/4,y,z -1	{ m'_{100} | 1/2 1/2 1/2 }
8	x+1/2, y, -z+1/2, -1 $m_x,m_y,-m_z$	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1/2 \end{pmatrix}'$	a x,y,1/4 -1	{ m'_{001} | 1/2 0 1/2 }

MWYCKPOS Wyckoff Positions of Magnetic Space Groups

Wyckoff Positions of the Group *Pn'ma'* (#62.448)

For this space group, BNS and OG settings coincide.
Its label in the OG setting is given as: Pn'ma' (#62.8.509)

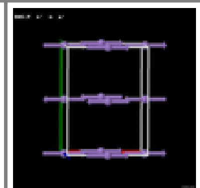
Multiplicity	Wyckoff letter	Coordinates
8	d	(x,y,z | m_x,m_y,m_z) (x+1/2,-y+1/2,-z+1/2 | $-m_x,m_y,m_z$) (-x,y+1/2,-z | $-m_x,m_y,-m_z$) (-x+1/2,-y,z+1/2 | $m_x,m_y,-m_z$) (-x,-y,-z | m_x,m_y,m_z) (-x+1/2,y+1/2,z+1/2 | $-m_x,m_y,m_z$) (x,-y+1/2,z | $-m_x,m_y,-m_z$) (x+1/2,y,-z+1/2 | $m_x,m_y,-m_z$)
4	c	(x,1/4,z | $0,m_y,0$) (x+1/2,1/4,-z+1/2 | $0,m_y,0$) (-x,3/4,-z | $0,m_y,0$) (-x+1/2,3/4,z+1/2 | $0,m_y,0$)
4	b	(0,0,1/2 | m_x,m_y,m_z) (1/2,1/2,0 | $-m_x,m_y,m_z$) (0,1/2,1/2 | $-m_x,m_y,-m_z$) (1/2,0,0 | $m_x,m_y,-m_z$)
4	a	(0,0,0 | m_x,m_y,m_z) (1/2,1/2,1/2 | $-m_x,m_y,m_z$) (0,1/2,0 | $-m_x,m_y,-m_z$) (1/2,0,1/2 | $m_x,m_y,-m_z$)

Magnetic space groups: *Application to $LaMnO_3$*

bilbao crystallographic server

Magnetic Symmetry and Applications

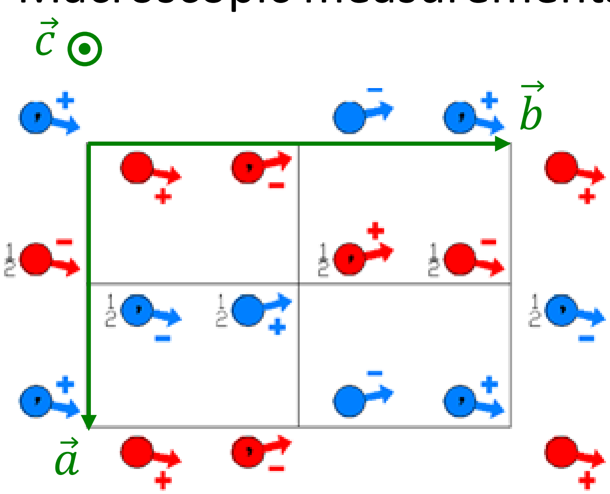
MAGNDATA ⚠ A collection of magnetic structures with transportable cif-type files

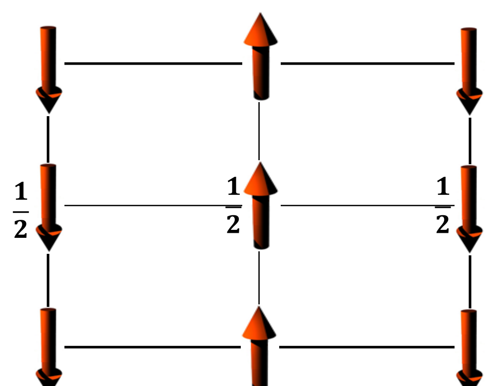
N	Entry	Structure	Propagation vector(s)	Parent space group	Transformation from parent	Magnetic (super)space group	Magnetic point group
1	0.1 $LaMnO_3$		0,0,0	Pnma (62) (standard)	(**a**,**b**,**c**;0,0,0)	Pn'ma' (62.448) (standard)	m'm'm (8.4.27)

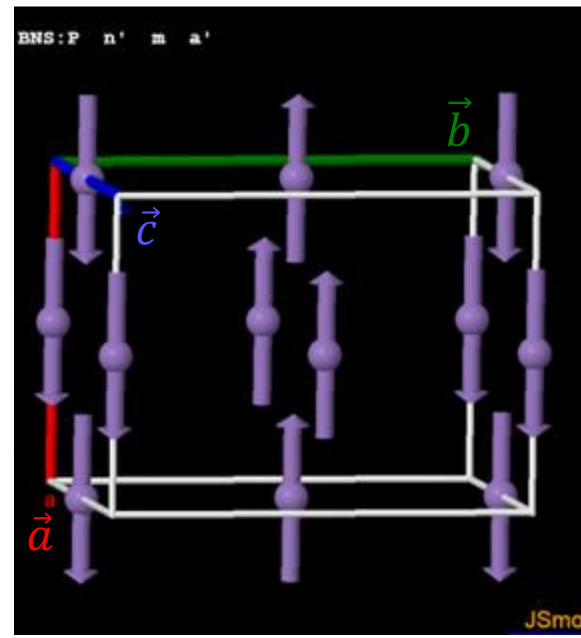
$LaMnO_3$:

Mn located at (0,0,0), i.e. on $\bar{1}$

Macroscopic measurements → AF with $\vec{m} \parallel \vec{a}$-axis







origin shift by (1/2, 0, 0) in this Fig.

Magnetic space groups: *Application to $LaMnO_3$*

.mcif file for $LaMnO_3$

```
_space_group_magn.number_BNS  62.448
_space_group_magn.name_BNS  "P  n'  m  a'  "
_space_group_magn.point_group_name  "m'm'm"
_space_group_magn.point_group_number  "8.4.27"
_cell_length_a                  5.7461(2)
_cell_length_b                  7.6637(4)
_cell_length_c                  5.5333(2)
_cell_angle_alpha               90.0000
_cell_angle_beta                90.0000
_cell_angle_gamma               90.0000

loop_
_space_group_symop_magn.id
_space_group_symop_magn_operation.xyz
1 x,y,z,+1
2 -x,y+1/2,-z,+1
3 -x,-y,-z,+1
4 x,-y+1/2,z,+1
5 x+1/2,-y+1/2,-z+1/2,-1
6 -x+1/2,-y,z+1/2,-1
7 -x+1/2,y+1/2,z+1/2,-1
8 x+1/2,y,-z+1/2,-1

loop_
_space_group_symop_magn_centering.id
_space_group_symop_magn_centering.xyz
1 x,y,z,+1

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
La La 0.0513(7) 0.25000 -0.0095(5) 1
Mn Mn 0.00000 0.00000 0.50000 1
O1 O 0.48493(80) 0.25000 0.0777(7) 1
O2 O 0.3085(5) 0.0408(4) 0.7227(5) 1

loop_
_atom_site_moment.label
_atom_site_moment.crystalaxis_x
_atom_site_moment.crystalaxis_y
_atom_site_moment.crystalaxis_z
_atom_site_moment.symmform
Mn 3.87(3) 0.0 0.0 mx,my,mz
```

$\delta = \pm 1$ whether the sym. op. is unprimed or primed

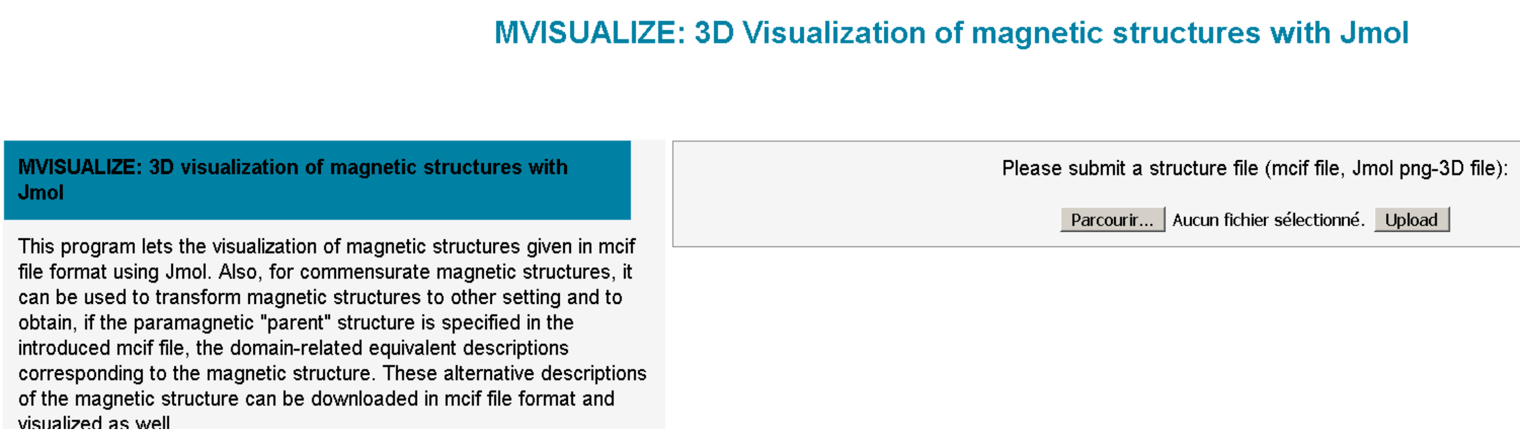
$m_x = 3.87(3)\mu_B/\mathrm{Mn}^{3+}, m_y = 0, m_z = 0$

Visualization of *.mcif files

- **FpStudio** (FullProf Suite) – J. Rodriguez-Carvajal and L. Chapon

- **Bilbao Crystallographic Server**

[http://webbdcrista1.ehu.es/magndata/**mvisualize.php**](http://webbdcrista1.ehu.es/magndata/mvisualize.php)



MVISUALIZE: 3D Visualization of magnetic structures with Jmol

MVISUALIZE: 3D visualization of magnetic structures with Jmol

This program lets the visualization of magnetic structures given in mcif file format using Jmol. Also, for commensurate magnetic structures, it can be used to transform magnetic structures to other setting and to obtain, if the paramagnetic "parent" structure is specified in the introduced mcif file, the domain-related equivalent descriptions corresponding to the magnetic structure. These alternative descriptions of the magnetic structure can be downloaded in mcif file format and visualized as well

Please submit a structure file (mcif file, Jmol png-3D file):

Parcourir... Aucun fichier sélectionné. Upload

- **Vesta**

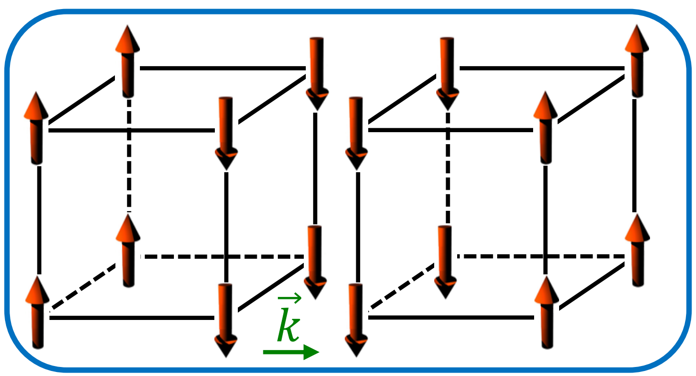
Magnetic domains

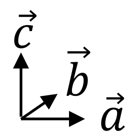
Symmetry of the ordered magnetic state lower than that of the paramagnetic state

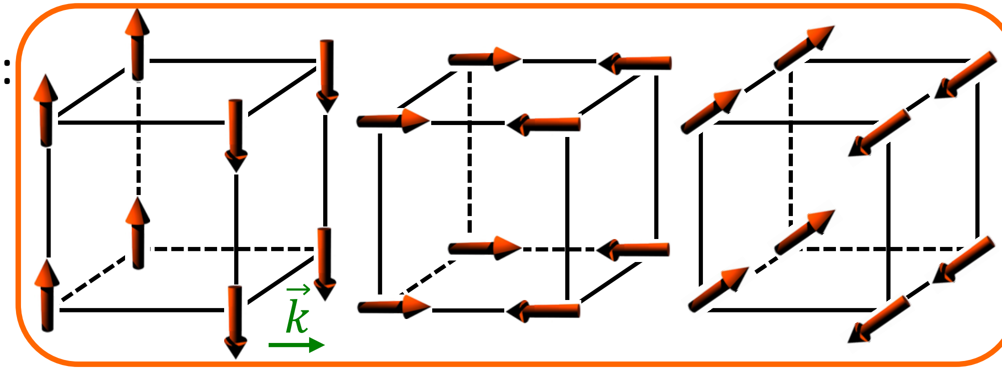
G_0: paramagnetic Shubnikov group of order n_0
G: ordered Shubnikov group of order n
$\Rightarrow \frac{n_0}{n}$ magnetic domains

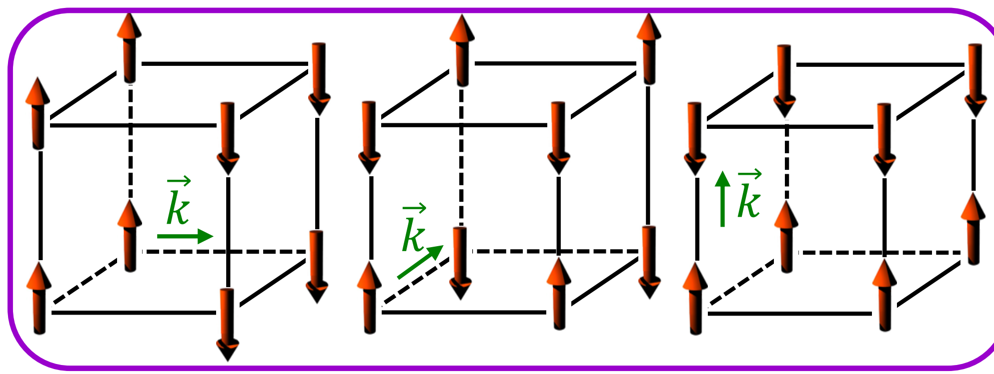
There exist **4 types of magnetic domains**:

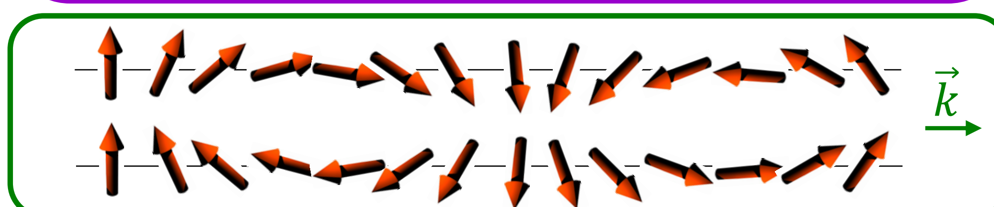
- Time-reversed domains: 180° domains
- Orientation domains: s-domains
- Configuration domains: k-domains
- Chiral domains (if $\bar{1}$ is lost)











Group representation theory

How to find the possible magnetic structures using group theory?

- Determine experimentally the propagation vector $\vec{k}$
- Select in the crystallographic space group G the sym. op. g that leave $\vec{k}$ invariant
  → Little group G_k (subgroup of G) = $\{g \in G | \alpha\vec{k} = \vec{k} + \vec{H}\}$ with $g = \{\alpha|\vec{t}_\alpha\}$
- Write the magnetic representation Γ = set of $3n \times 3n$ matrices for all sym. op. of G_k describing how each magnetic component is transformed

  n equivalent magnetic atoms, 3 magnetic components u, v, w for each atom
  d such matrices with d the order of G_k

- Reduce Γ into **Irreducible representations** (Ireps) Γ_ν
  (i.e., block diagonalize the matrices as much as possible): $\Gamma = a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus \ldots$
- For each IRep Γ_ν appearing in the decomposition of Γ, find its basis vectors $\psi_\nu^1, \psi_\nu^2, \ldots$
- **Landau theory (for 2nd order transition)**: The magnetic structure that establishes at the phase transition corresponds to an IRep that persists while all other IReps cancel

⇒ **the magnetic structure is described by the basis vectors of the IRep that persists, while the basis vectors associated to all the other IReps cancel.**

Group representation theory (= representation analysis) developped by E. F. Bertaut

Most frequently used softwares to determine the IReps and thus the possible magnetic orderings:

Basireps (from the Fullprof suite) – Juan Rodriguez-Carvajal

Sarah – Andrew Wills

MODY – W. Sikora, F. Białas, L. Pytlik

ISOTROPY - Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell

Input file: crystallographic space group

propagation vector

atomic coordinates of the magnetic atom(s)

Input: crystallographic space group $Pnma$

propagation vector $\vec{k} = (0,0,0)$

atomic coordinates of the magnetic atom $x = 0, y = 0, z = 0$

Output: 4 irreducible representations of dimension 1, each contained 3 times in Γ

$$\Gamma = 3\Gamma_1 \oplus 3\Gamma_2 \oplus 3\Gamma_3 \oplus 3\Gamma_4$$

	Γ_1	Γ_2	Γ_3	Γ_4
Mn $(0,0,0)$	$u, \quad v, \quad w$	$u, \quad v, \quad w$	$u, \quad v, \quad w$	$u, \quad v, \quad w$
Mn $\left(\frac{1}{2},0,\frac{1}{2}\right)$	$-u, -v, \quad w$	$-u, -v, \quad w$	$u, \quad v, -w$	$u, \quad v, -w$
Mn $\left(0,\frac{1}{2},0\right)$	$-u, \quad v, -w$	$u, -v, \quad w$	$-u, \quad v, -w$	$u, -v, \quad w$
Mn $\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$	$u, -v, -w$	$-u, \quad v, \quad w$	$-u, \quad v, \quad w$	$u, -v, -w$
	⇕	⇕	⇕	⇕
	$Pnma$	$Pn'm'a$	$Pn'ma'$	$Pnm'a'$

Summary

Magnetic point groups:

As for crystallographic point groups, magnetic point groups are very important to **make predictions on macroscopic magnetic properties**

Magnetic space groups *vs* Propagation vectors & IReps:

A magnetic structure can be described in two ways:

1/ **Propagation vector** and irreducible representations (**IReps**)
or
2/ **Magnetic space group** *(like crystallographic space groups with an additional symmetry operator:* $1'$ *= spin reversal)*

Both descriptions can be used for softwares refining a magnetic structure

N.B.: 1st approach: more general
propagation vector: very useful for diffraction → see lecture III

Nevertheless, the 2nd approach can be generalized to incommensurate structures → superspace groups