Magnetic phase transitions and symmetry

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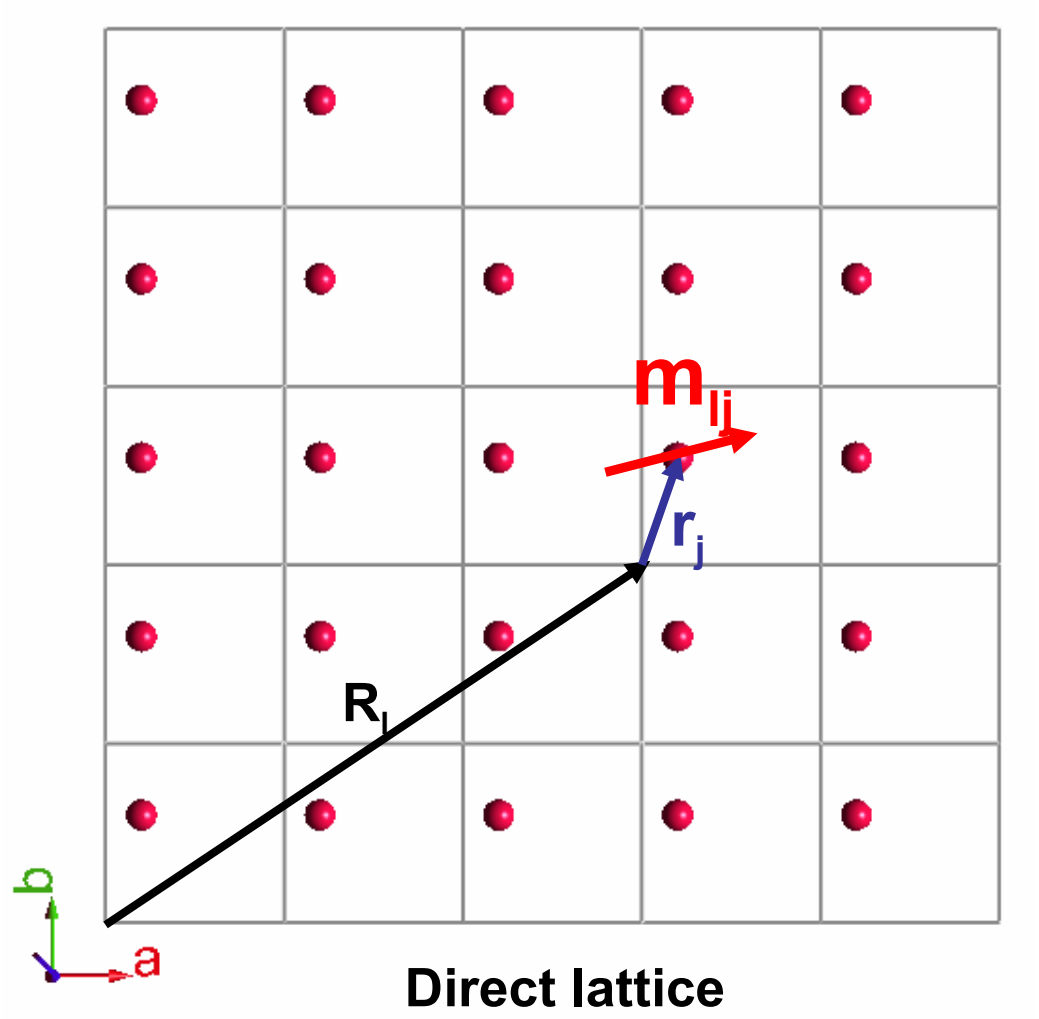
Outline

- Will discuss exclusively the magnetically ordered state
- Different type of magnetic structures and how to describe them
- Magnetic symmetry, representation analysis, and magnetic space groups.
- Landau theory of phase transitions
- Symmetry breaking and types of domains

Description of magnetic structures

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

$R_{lj}=R_l+r_j$ where R_l is a pure lattice translation

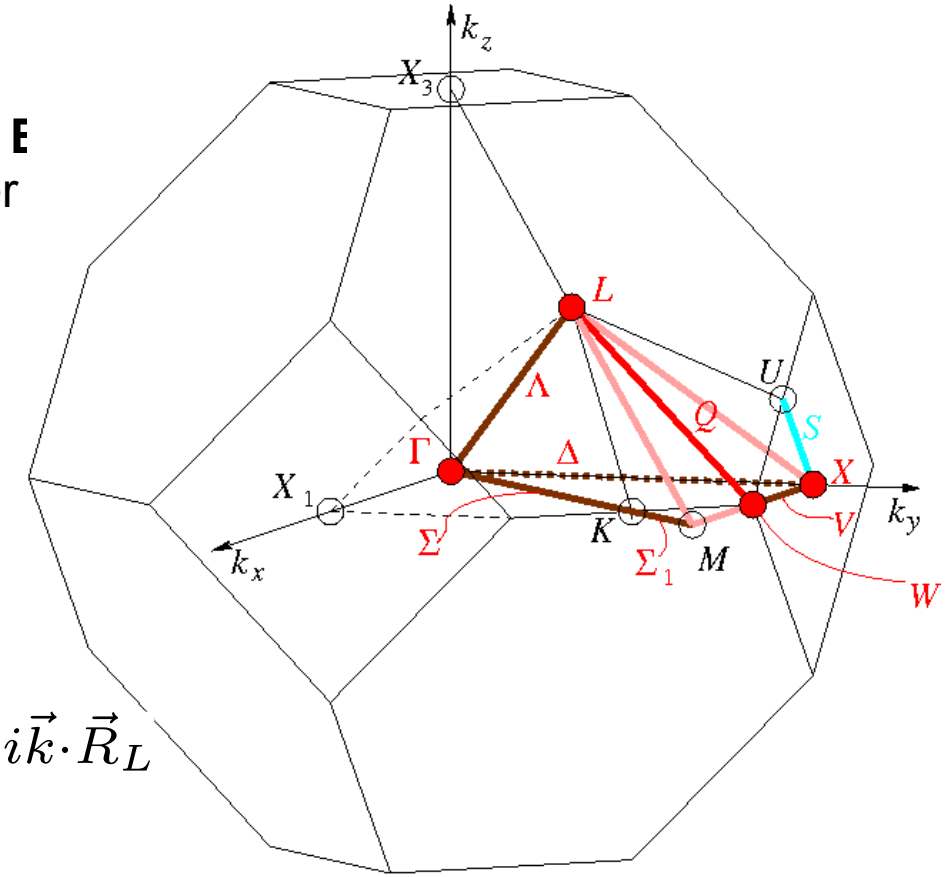


Formalism of propagation vector

For simplicity, in particular for wave-vector inside the B
one usually describe magnetic structures with Fourier

$$\vec{m}_{lj}(\vec{R}_L) = \sum_k \vec{S}_{kj} e^{-2\pi i \vec{k}\cdot\vec{R}_L}$$

$$\vec{m}_{lj}(\vec{R}_L) = \vec{S}_{kj} e^{-2\pi i \vec{k}\cdot\vec{R}_L} + \vec{S}_{-kj} e^{2\pi i \vec{k}\cdot\vec{R}_L}$$



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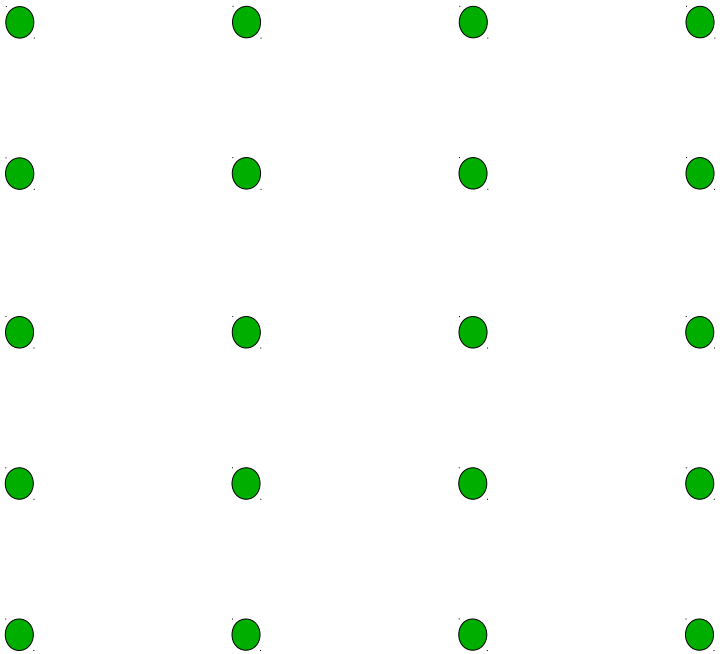
http://www.cryst.ehu.es

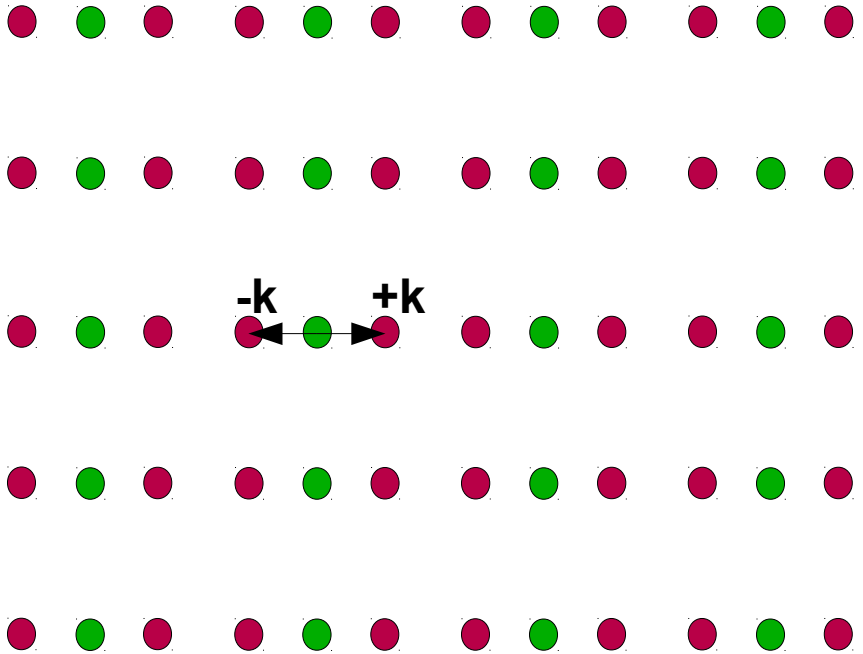
Since $\mathbf{m}_{lj}$ is a real vector,
one must imposes the condition $\mathbf{S}_{-kj}^{*}=\mathbf{S}_{kj}$

Here $\mathbf{S}_{kj}$ is a complex vector !

Formalism of propagation vector

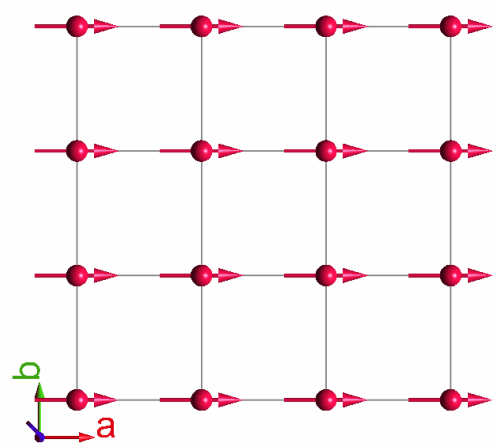


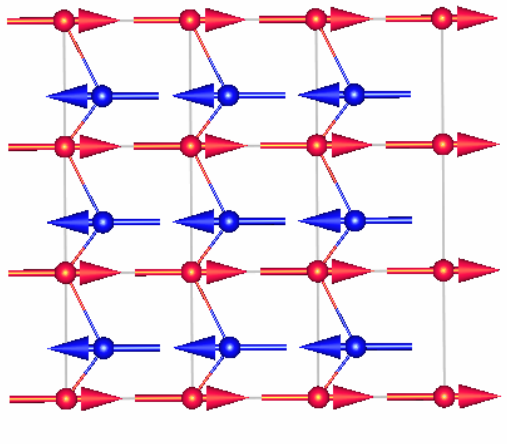
Reciprocal lattice



Reciprocal lattice (magnetic superlattices)

k=0

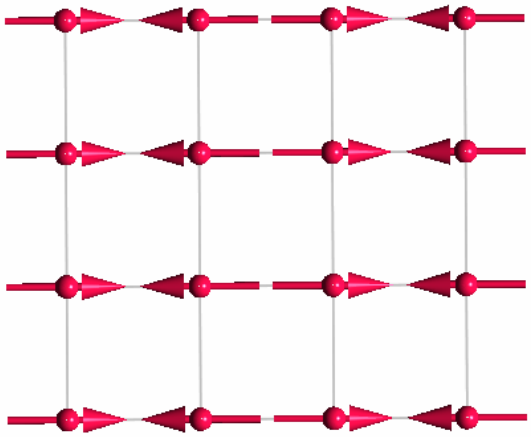




$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j}$$

- The magnetic structure may be described within the crystallographic unit cell
- Magnetic symmetry: conventional crystallography plus time reversal operator: crystallographic magnetic groups

K=1/2 r.l.v



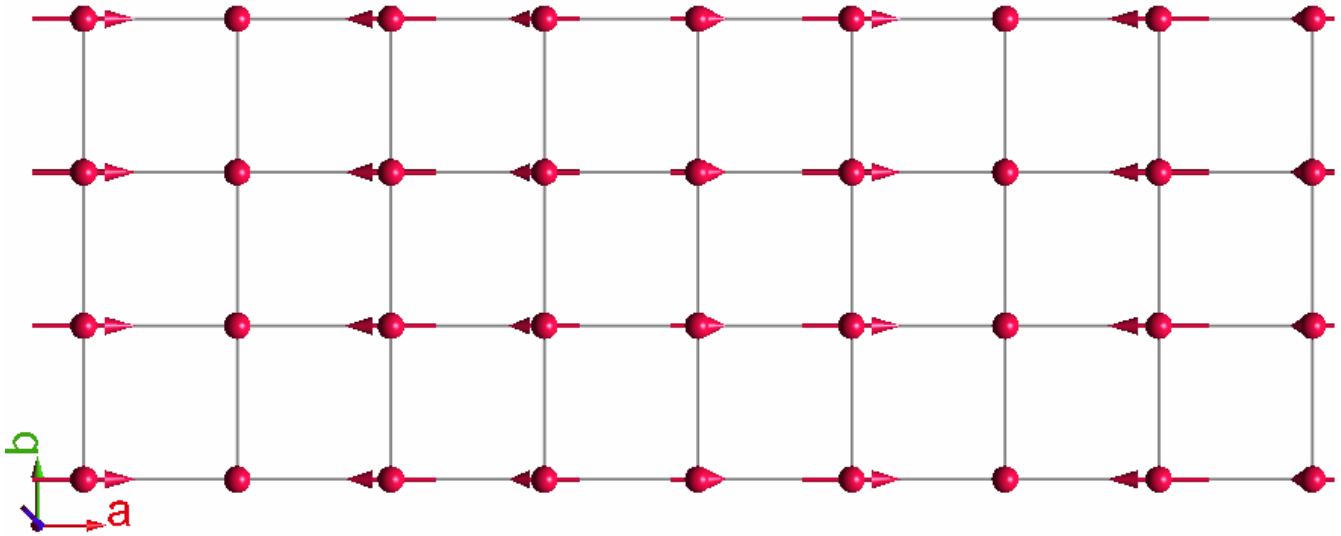
$$\mathbf{m}_{lj} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{\mathbf{k}j} \; exp\{-2\pi i \mathbf{k}\mathbf{R}_l\} = \mathbf{S}_{\mathbf{k}j} \left(-1\right)^{n(l)}$$

- REAL Fourier coefficients = magnetic moments
- The magnetic symmetry may also be described using crystallographic magnetic space groups

K is inside the Brillouin Zone, amplitude modulation

- k interior of the Brillouin zone (pair k, -k)

- Real S_k, or imaginary component in the same direction as the real one



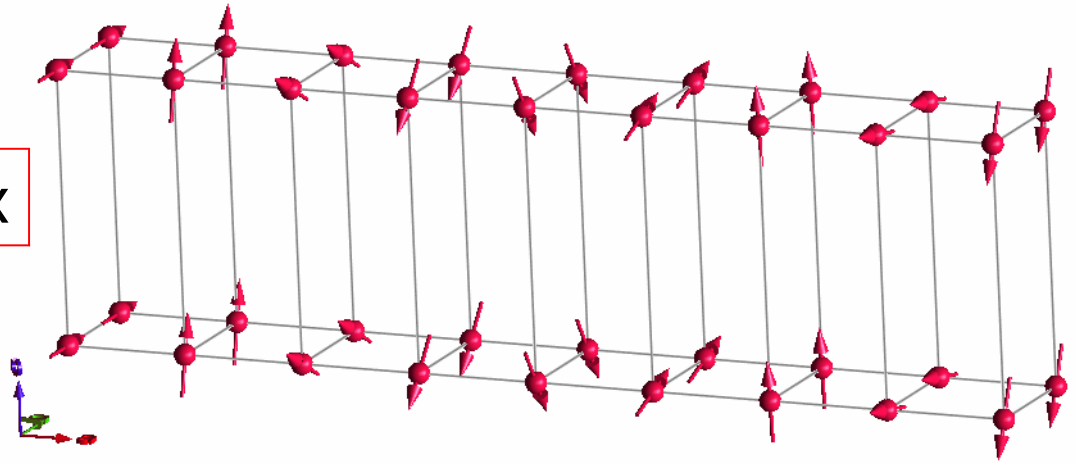
"Longitudinal"

$$\mathbf{S}_{\mathbf{kj}} = \frac{1}{2} m_j \mathbf{u}_j exp(-2\pi i \phi_{\mathbf{kj}})$$

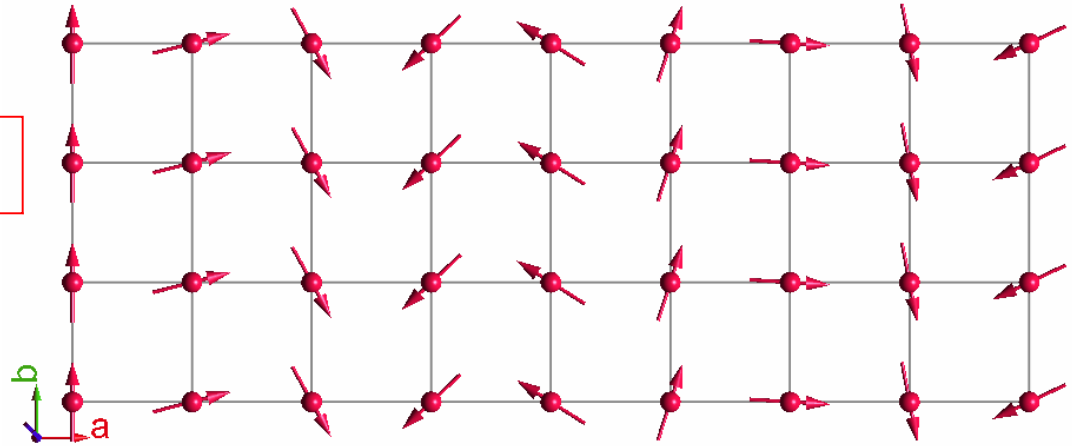
$$\mathbf{m}_{lj} = m_j \mathbf{u}_j \cos 2\pi(\mathbf{kR}_l + \phi_{\mathbf{kj}})$$

K is inside the Brillouin Zone, cycloids and spirals

Helix



Cycloid

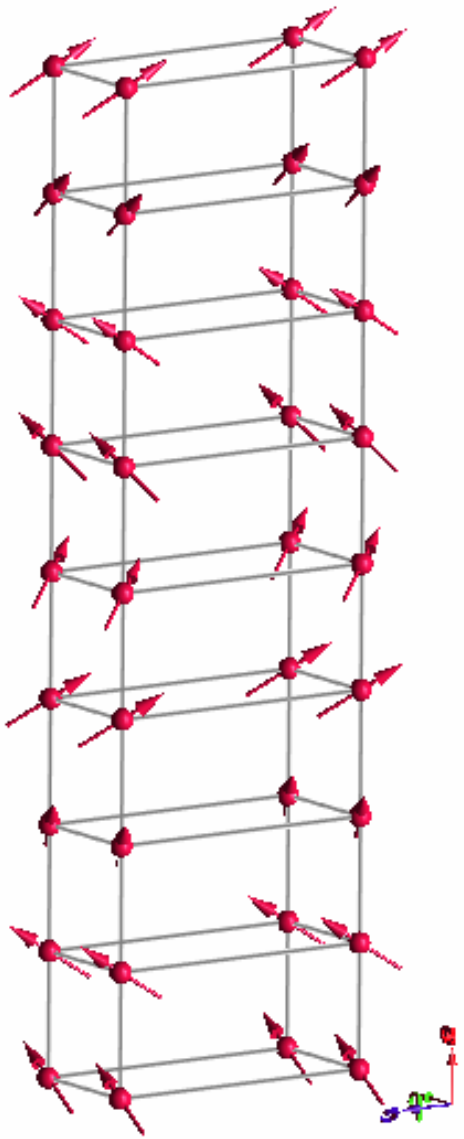


$$\mathbf{S}_{\mathbf{kj}} = \frac{1}{2}\left[m_{uj}\mathbf{u}_j + i m_{vj}\mathbf{v}_j \right] \; exp(-2\pi i \phi_{\mathbf{kj}})$$

$$\mathbf{m}_{lj} = m_{uj}\mathbf{u}_j \cos 2\pi(\mathbf{kR}_l + \phi_{\mathbf{kj}}) + m_{vj}\mathbf{v}_j \sin 2\pi(\mathbf{kR}_l + \phi_{\mathbf{kj}})$$

Multi-k structures : Conical structures

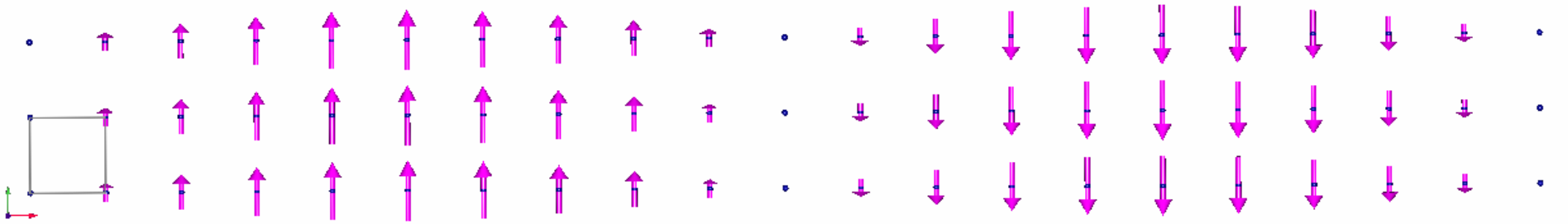
Conical



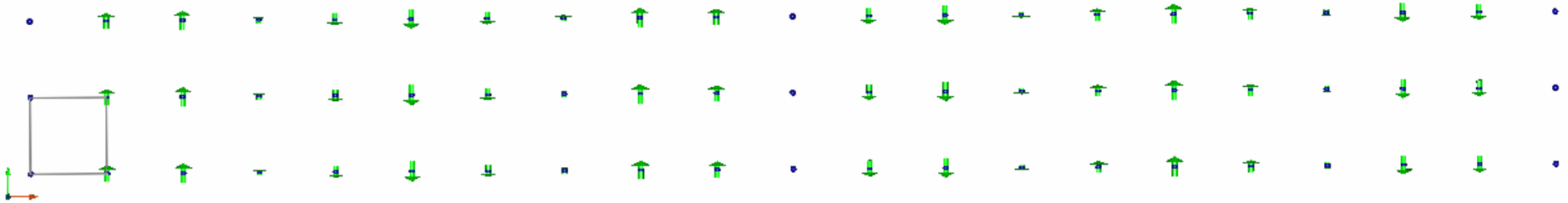
Multi-k structure with:

- **Helical modulation**
- **Ferromagnetic component**

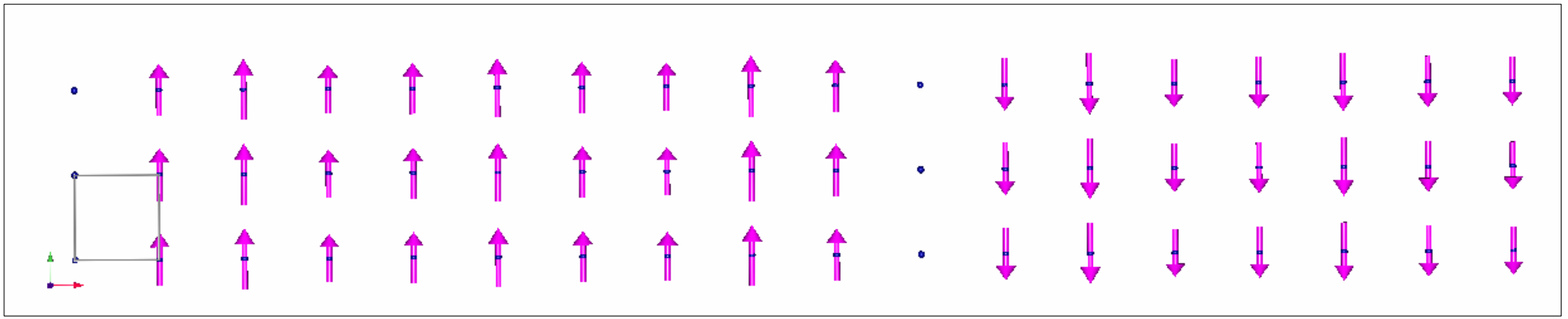
Multi-k structures : Bunched modulations



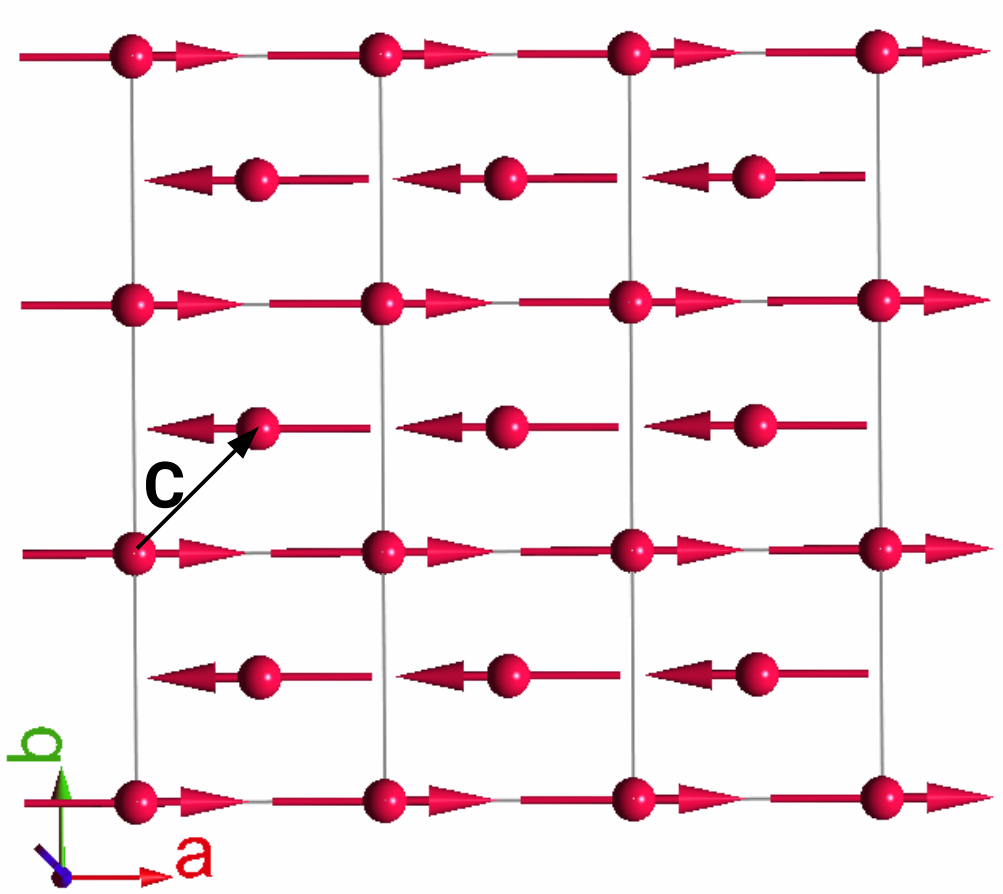
k=(d,0,0)



+ k=(3d,0,0) + … + k=((2n+1)d,0,0)



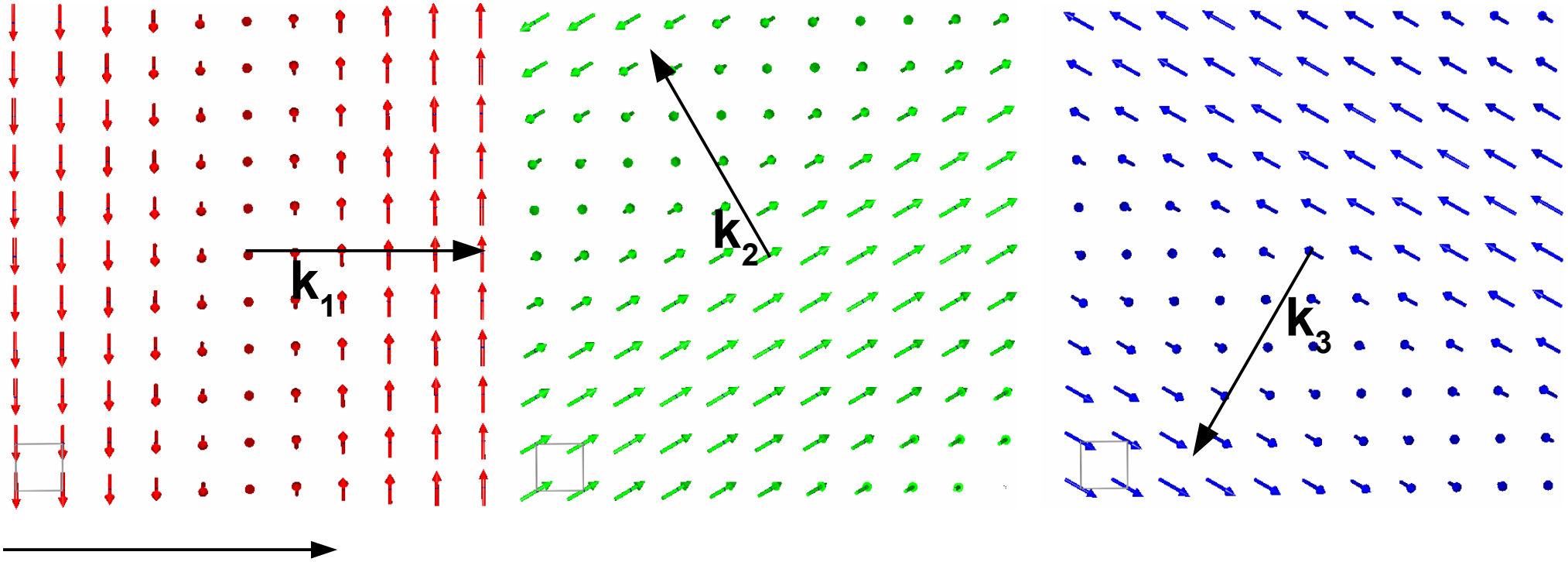
Wave-vector formalism and centered cells



Beware when working with non-primitive unit-cells.
If in doubt always think in the primitive setup

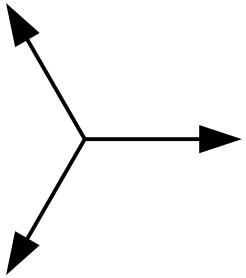
k=(1,0,0) or (0,1,0) !!!!!

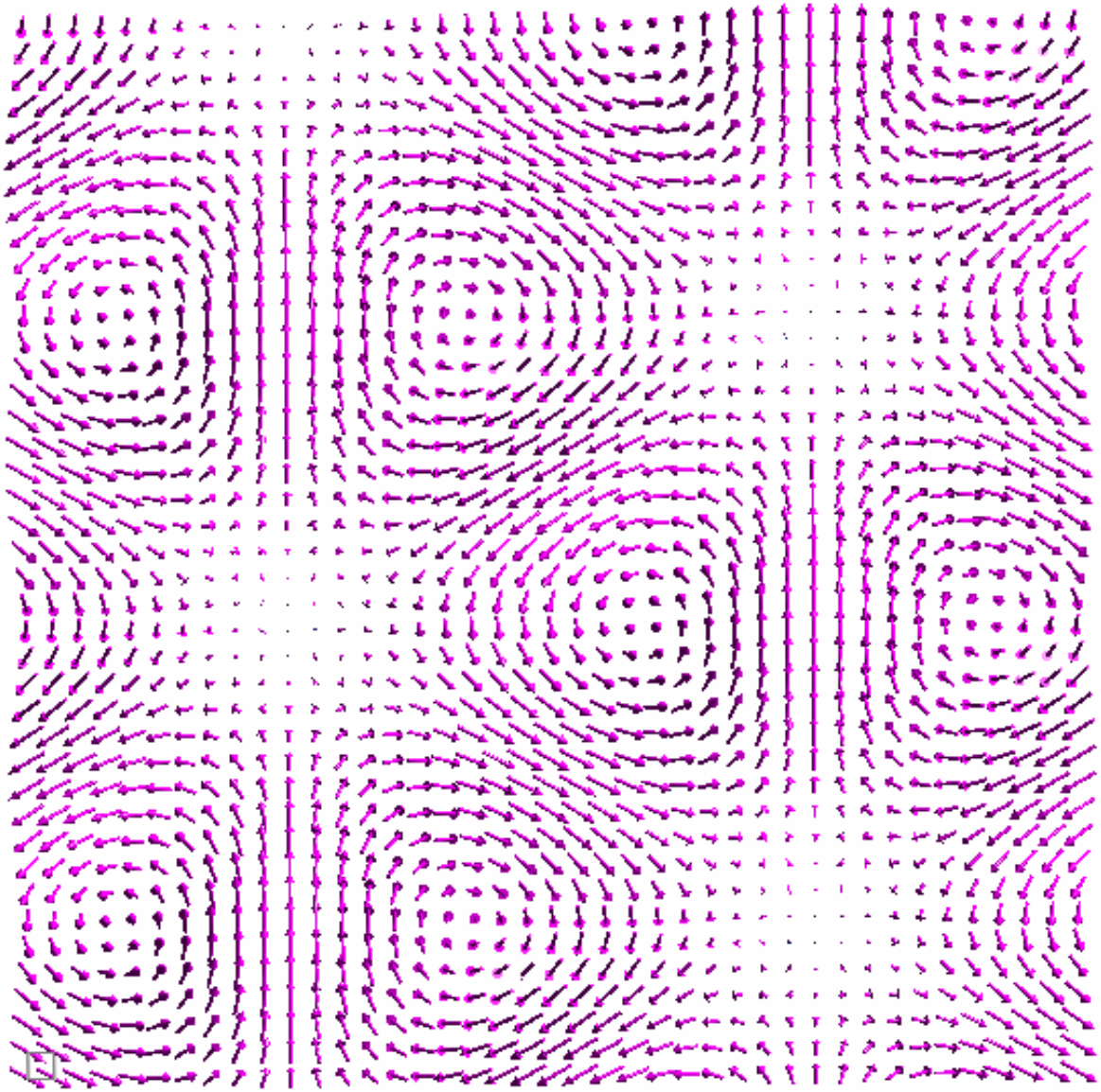
Example of a 4-k structure: the skyrmion lattice



- **$k_1+k_2+k_3=0$, same chirality for k_1, k_2, k_3**
  - **Ferromagnetic component**

Multi-k structures





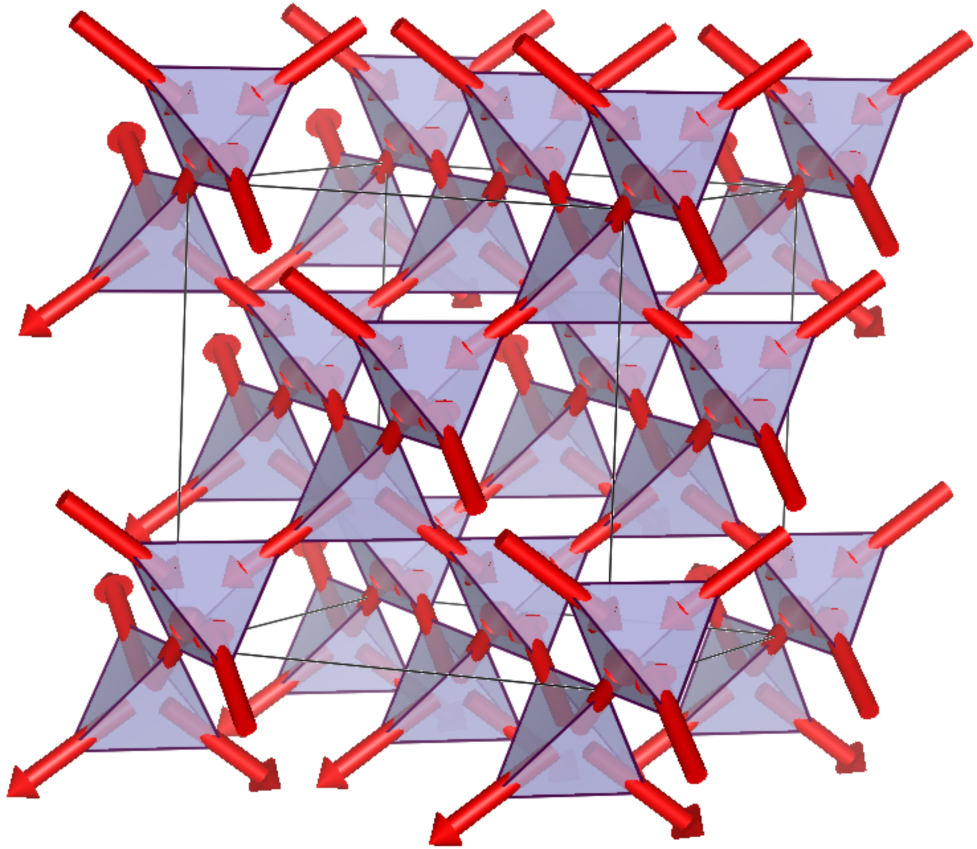
"Skyrmion"-type lattice stabilized by energy terms of the type:

$$F = \ldots + S_1 e^{ik_1 + \phi_1} . S_2 e^{ik_2 + \phi_2} . S_3 e^{ik_3 + \phi_3} . M$$

Crystal symmetries

So far, we have only considered translation symmetry to describe the different types of magnetic structures.

In addition we will need to take into account all the crystallographic symmetries and time-reversal symmetry.



Example: Pyrochlore Fd-3m

- Space group: infinite number of symmetry operations

Symmetry axis or symmetry point	Graphical symbol*	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed *symbol* (partial elements in parentheses)
Identity	None	None	1
Twofold rotation axis Twofold rotation point (two dimensions)		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Threefold rotation axis Threefold rotation point (two dimensions)		None	3
Threefold screw axis: '3 sub 1'		$\frac{1}{3}$	3_1
Threefold screw axis: '3 sub 2'		$\frac{2}{3}$	3_2
Fourfold rotation axis Fourfold rotation point (two dimensions)		None	4 (2)
Fourfold screw axis: '4 sub 1'		$\frac{1}{4}$	4_1 (2_1)
Fourfold screw axis: '4 sub 2'		$\frac{1}{2}$	4_2 (2)
Fourfold screw axis: '4 sub 3'		$\frac{3}{4}$	4_3 (2_1)
Sixfold rotation axis Sixfold rotation point (two dimensions)		None	6 (3,2)
Sixfold screw axis: '6 sub 1'		$\frac{1}{6}$	6_1 (3_1,2_1)
Sixfold screw axis: '6 sub 2'		$\frac{1}{3}$	6_2 (3_2,2)
Sixfold screw axis: '6 sub 3'		$\frac{1}{2}$	6_3 (3,2_1)
Sixfold screw axis: '6 sub 4'		$\frac{2}{3}$	6_4 (3_1,2)
Sixfold screw axis: '6 sub 5'		$\frac{5}{6}$	6_5 (3_2,2_1)
Centre of symmetry, inversion centre: '1 bar' Reflection point, mirror point (one dimension)		None	$\bar{1}$
Inversion axis: '3 bar'		None	$\bar{3}$ (3,$\bar{1}$)
Inversion axis: '4 bar'		None	$\bar{4}$ (2)
Inversion axis: '6 bar'		None	$\bar{6} = 3/m$
Twofold rotation axis with centre of symmetry		None	$2/m$ ($\bar{1}$)
Twofold screw axis with centre of symmetry		$\frac{1}{2}$	$2_1/m$ ($\bar{1}$)
Fourfold rotation axis with centre of symmetry		None	$4/m$ ($\bar{4}$, 2, $\bar{1}$)
'4 sub 2' screw axis with centre of symmetry		$\frac{1}{2}$	$4_2/m$ ($\bar{4}$, 2, $\bar{1}$)
Sixfold rotation axis with centre of symmetry		None	$6/m$ ($\bar{6}$, $\bar{3}$, 3, 2, $\bar{1}$)
'6 sub 3' screw axis with centre of symmetry		$\frac{1}{2}$	$6_3/m$ ($\bar{6}$, $\bar{3}$, 3, 2_1, $\bar{1}$)

Symmetry plane or symmetry line	Graphical symbol	Glide vector in units of lattice translation vectors parallel and normal to the projection plane	Printed symbol
Reflection plane, mirror plane Reflection line, mirror line (two dimensions)	———	None	*m*
'Axial' glide plane Glide line (two dimensions)	– – – –	$\frac{1}{2}$ lattice vector along line in projection plane $\frac{1}{2}$ lattice vector along line in figure plane	*a*, *b* or *c* *g*
'Axial' glide plane	·····	$\frac{1}{2}$ lattice vector normal to projection plane	*a*, *b* or *c*
'Double' glide plane* (in centred cells only)	··–·–·–	*Two* glide vectors: $\frac{1}{2}$ along line parallel to projection plane and $\frac{1}{2}$ normal to projection plane	*e*
'Diagonal' glide plane	–·–·–·	*One* glide vector with *two* components: $\frac{1}{2}$ along line parallel to projection plane, $\frac{1}{2}$ normal to projection plane	*n*
'Diamond' glide plane† (pair of planes; in centred cells only)	–·–·◂·– –·–·▸·–	$\frac{1}{4}$ along line parallel to projection plane, combined with $\frac{1}{4}$ normal to projection plane (arrow indicates direction parallel to the projection plane for which the normal component is positive)	*d*

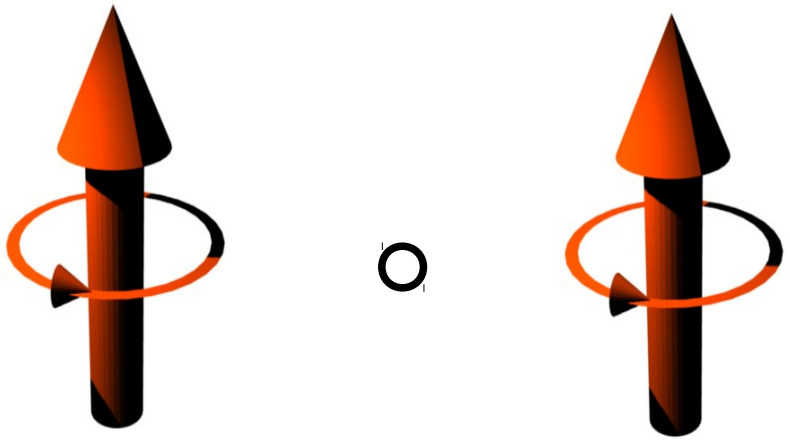
- Use the Seitz notation $\{\alpha|\mathbf{t}_\alpha\}$

– α rotational part (proper or improper)

– $\mathbf{t}_\alpha$ translational part

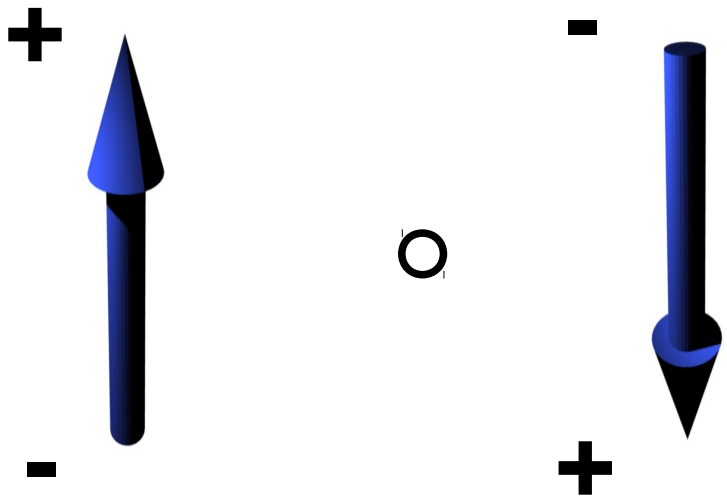
$$\{\alpha|\tau_\alpha\}\ \{\beta|\tau_\beta\}=\{\alpha\beta|\alpha t_\beta+t_\alpha\}$$

Isnversion symmetry on vectors and pseudo-vector



Axial or 'pseudo' vector

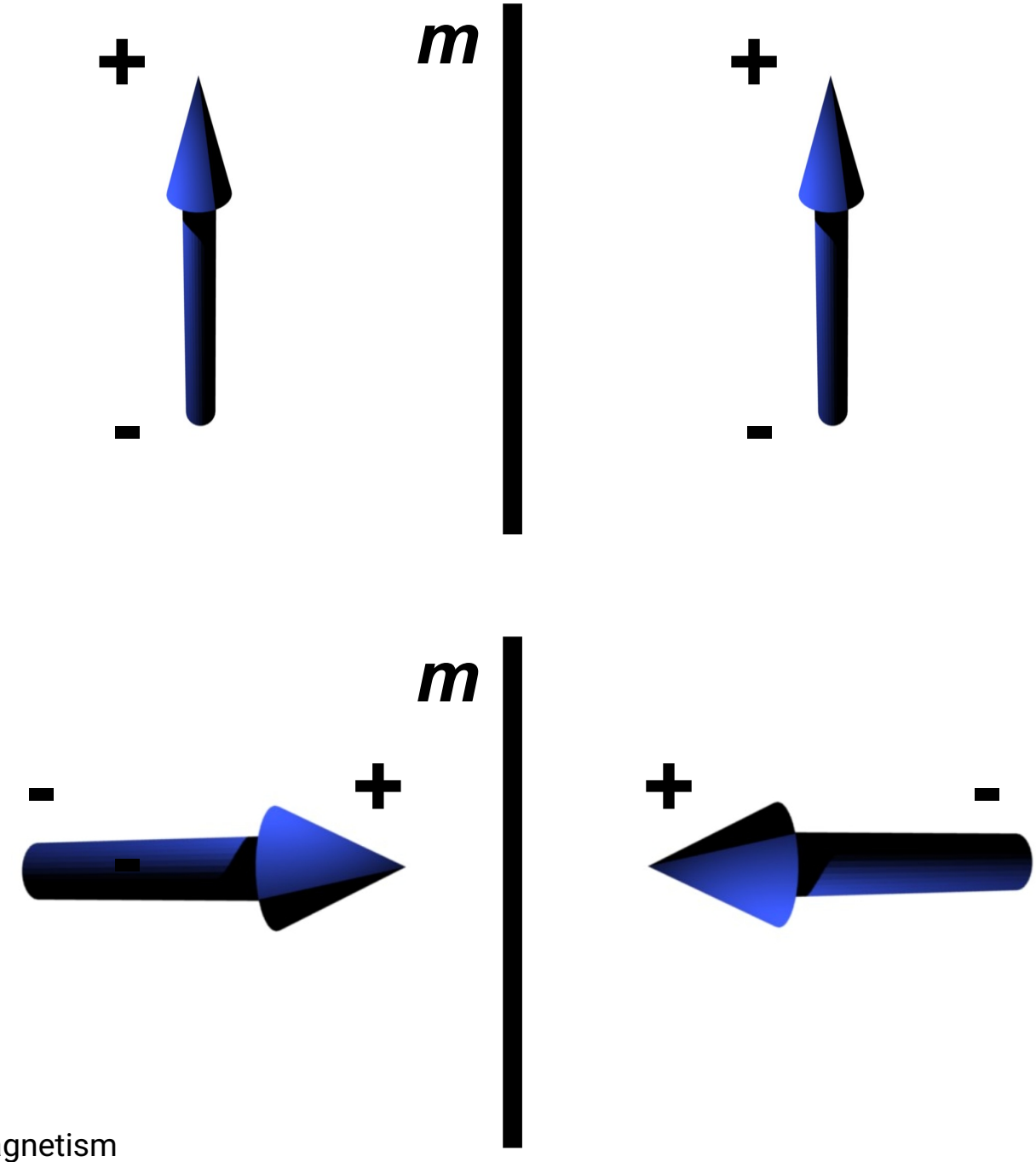
- **Parity even, time-odd**



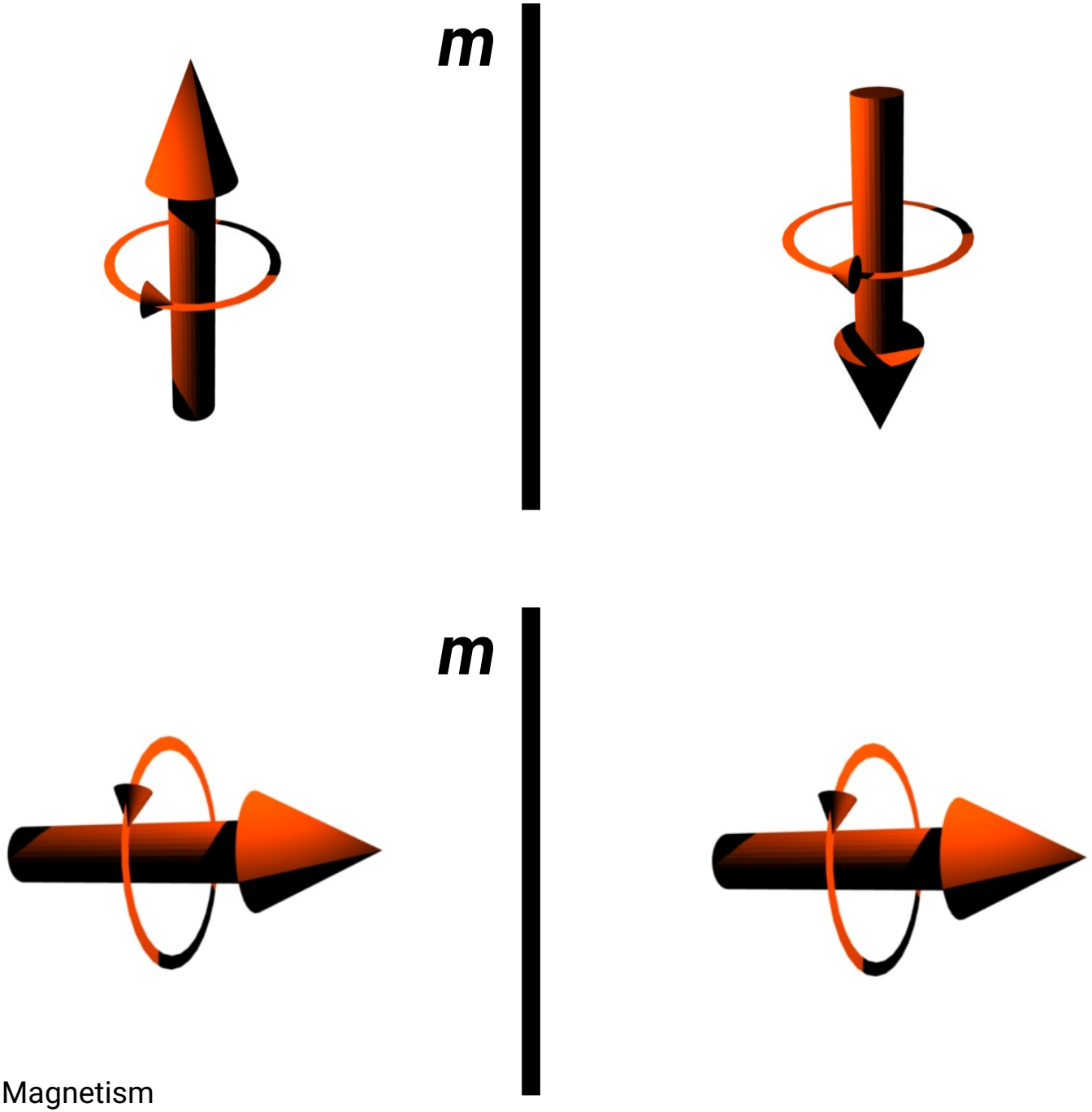
Polar vector

- **Parity odd, time even**

Mirror symmetry on vectors

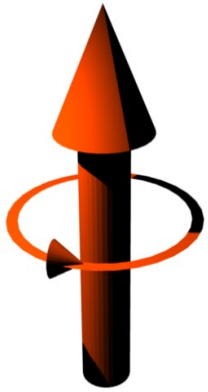


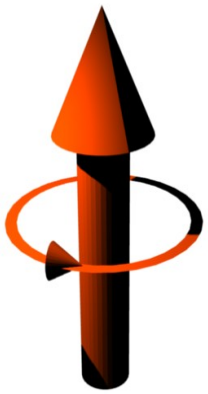
Mirror symmetry on pseudo-vectors



Magnetic crystallographic symmetry

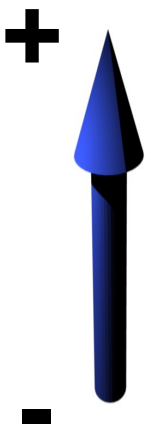
We need to take into account all the “usual” crystallographic symmetries + the time-reversal symmetry (as a linear “classical” operator)

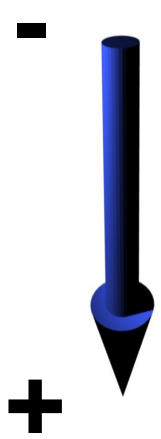




Axial or 'pseudo' vector

- **Parity even, time-odd**





Polar vector

- **Parity odd, time even**

Prime symmetry operator, i.e. the combination of a conventional crystallographic symmetry + time reversal will be noted $\{\alpha'|\tau_\alpha\}$ **(primed)**

Note about time-reversal operator

In QM, one needs to introduce the time reversal operator Θ
as defined by Wigner,sometimes noted T*.
This operator comes about in QM, from the time-dependent Schrodinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

« Whenever the Hamiltonian of the problem is real, the complex conjugate of any eigenfunction is also an eigenfunction with the same energy ».

The operator Θ is the combimation of T (t -> -t) and complex conjugation (K).

In the rest of the lecture, I will use time-reversal as a unitary linear operator, also called the "prime" operator.

Why symmetry is important ?

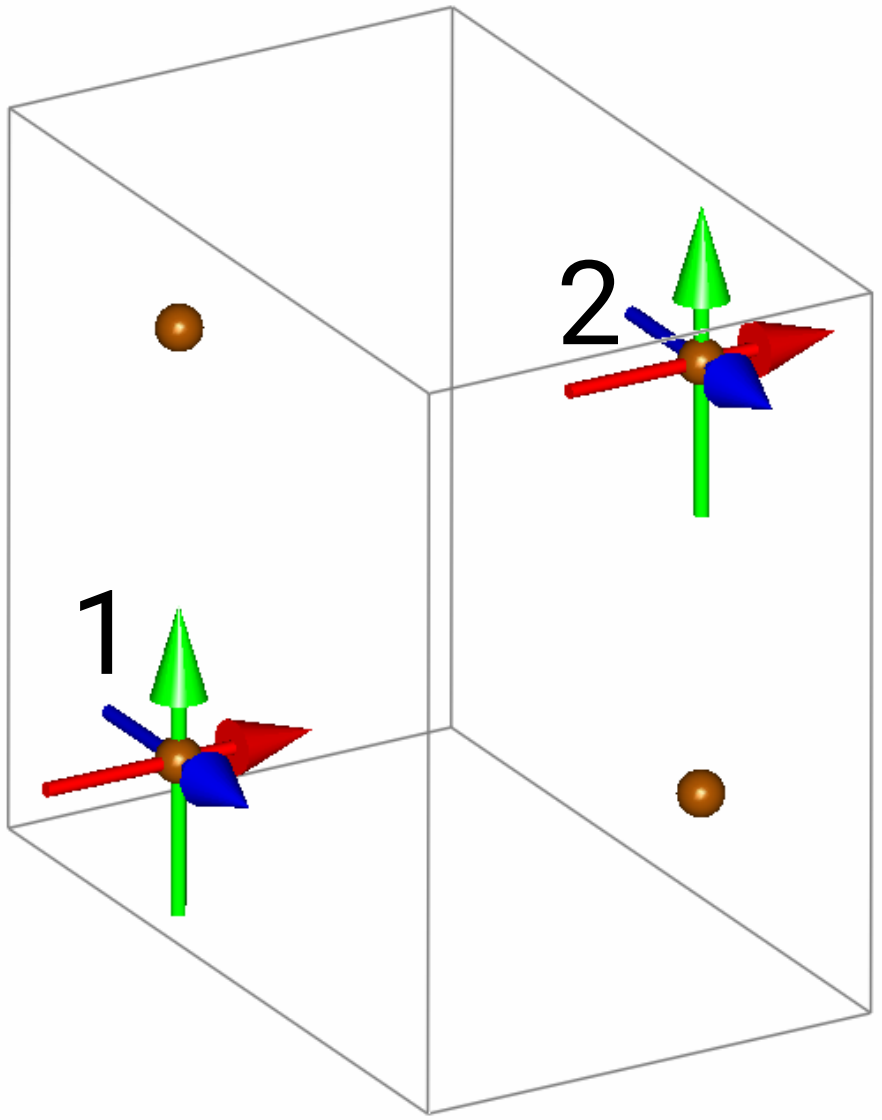
- Neumann's principle: If a crystal is invariant under a symmetry operation, its physical properties must also be invariant under the same symmetry operation (and generally under all the symmetry operations of the point group)

- Symmetry dictates what is allowed and what is forbidden/constrained

- Unless there is a "phase transition", what is forbidden/restricted by symmetry is **"protected", i.e. it will remain forbidden unless the symmetry changes.**

[Neumann, F. E. (1885), Vorlesungen über die Theorie der Elastizität der festen Körper und des Lichtäthers, edited by O. E. Meyer. Leipzig, B. G. Teubner-Verlag]

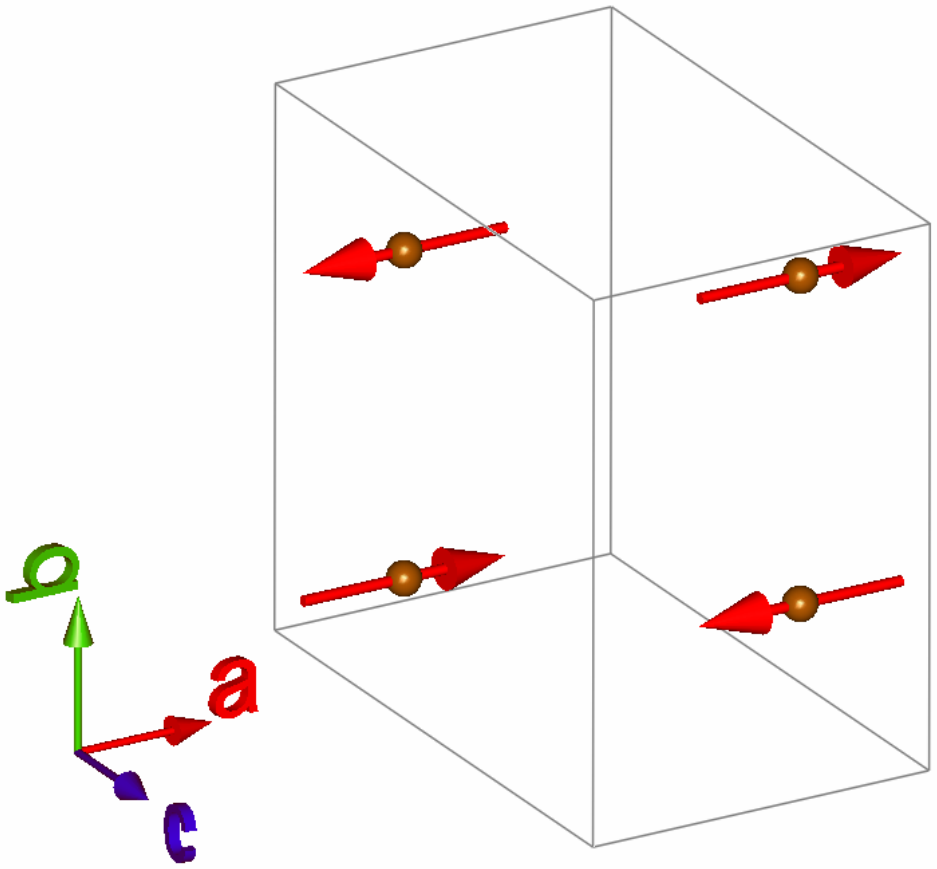
Why symmetry is important ? Example 1 DM interaction

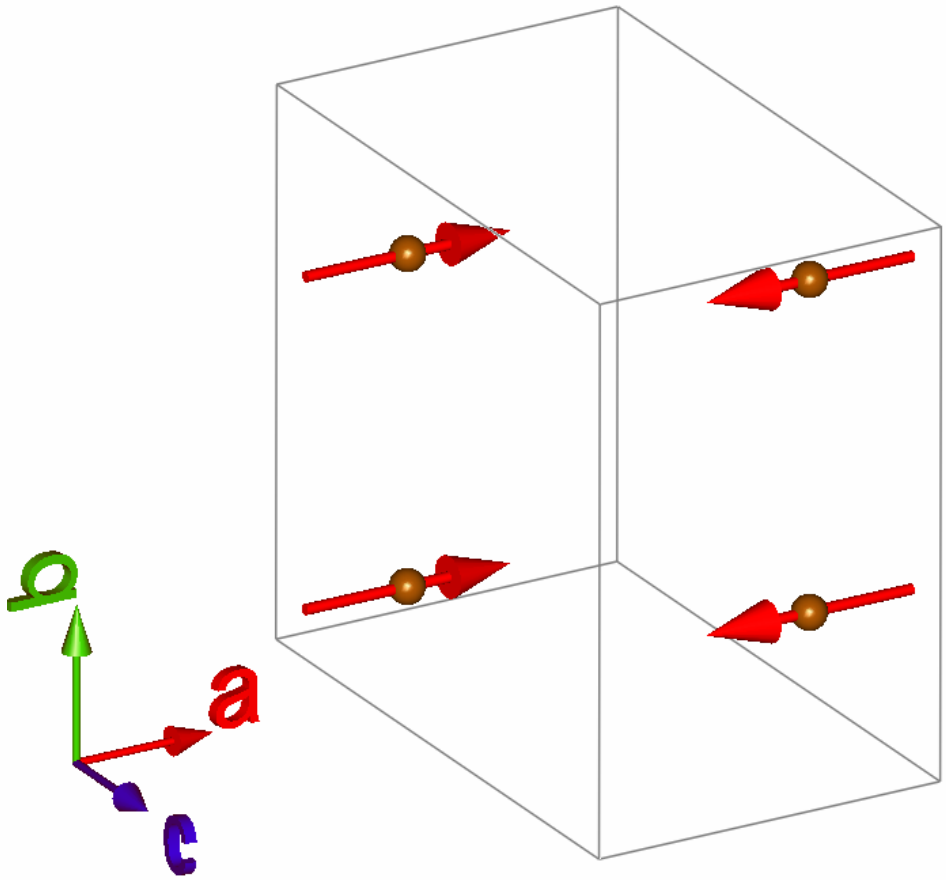


$$\vec{D} \cdot \left(\vec{S_1} \times \vec{S_2} \right)$$

Why symmetry is important ? Example 2 Linear ME effect

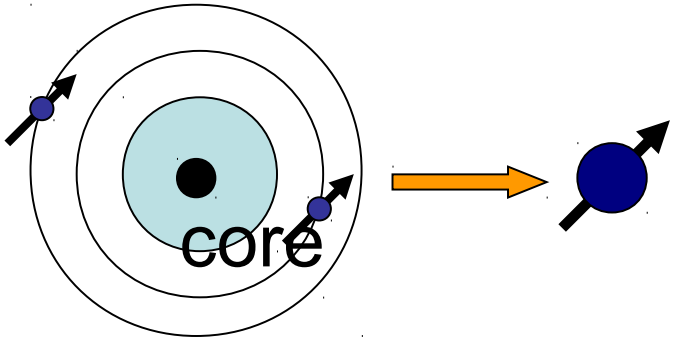
Which of these two AFM structures support a linear magnetoelectric effect?



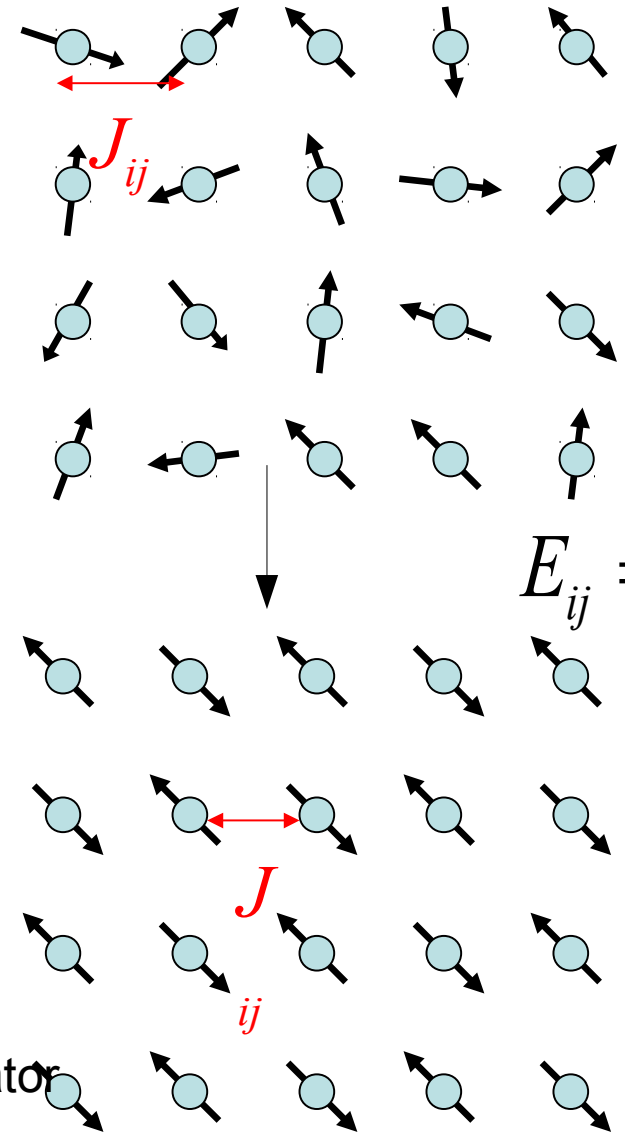


Ordered magnetic state

- In some crystals, some of the atoms/ions have unpaired electrons (transition metals, rare-earths).
- The intra-atomic electron correlation, Hund's rule, favors a state with maximum S/J, the ions posses a localized magnetic moment



Ni^{2+}



$$\langle \mathbf{S}_i \rangle = 0$$

$$E_{ij} = -J_{ij}\ \mathbf{S}_i \cdot \mathbf{S}_j$$

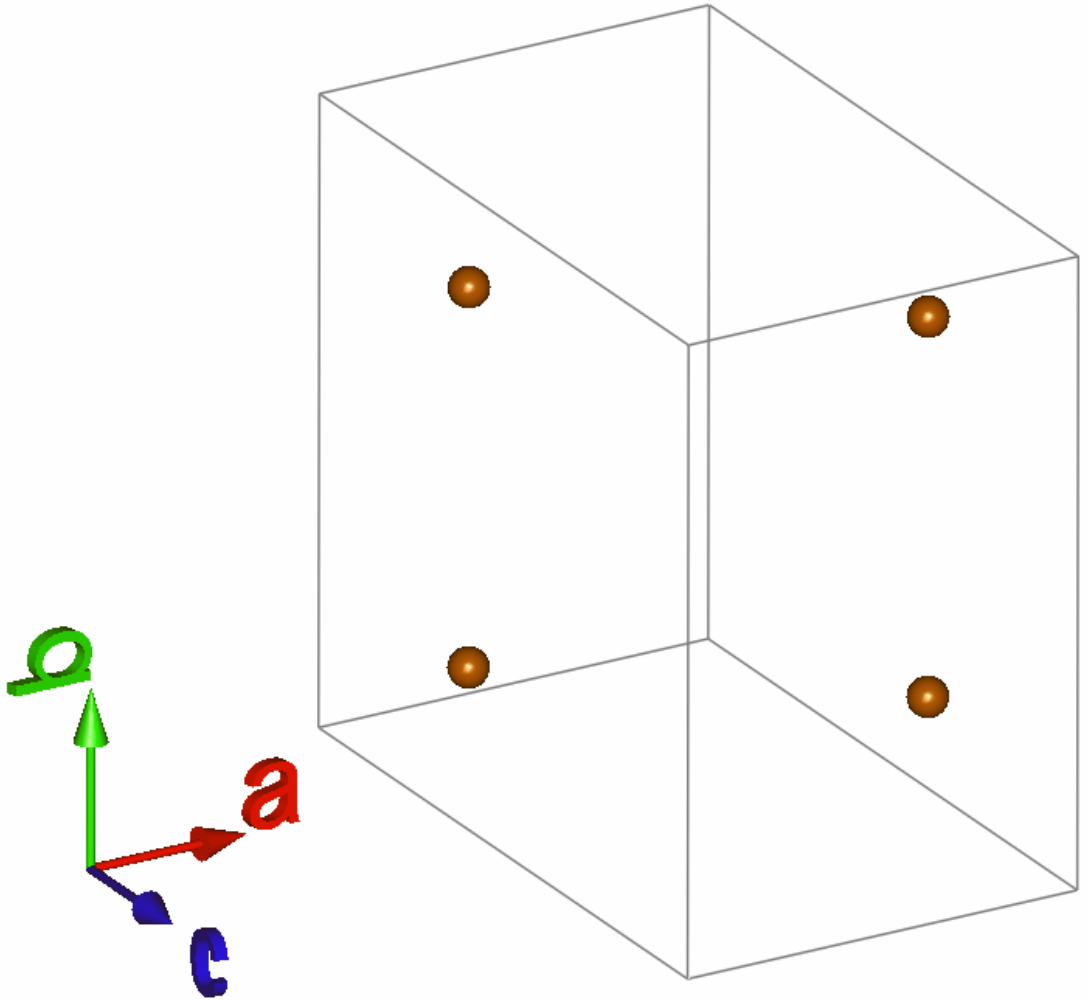
$$\langle \mathbf{S}_i \rangle \neq 0$$

- Exchange interactions (direct, superexchange, double exchange, RKKY,dipolar ….) often stabilizes a long range magnetic order.
- Time-reversal symmetry is a valid symmetry operator of the paramagnetic phase, but is broken in the ordered phase.

Paramagnetic group

Example: Monoclinic SG *P2/m1'*

Magnetic atom in general position x,y,z



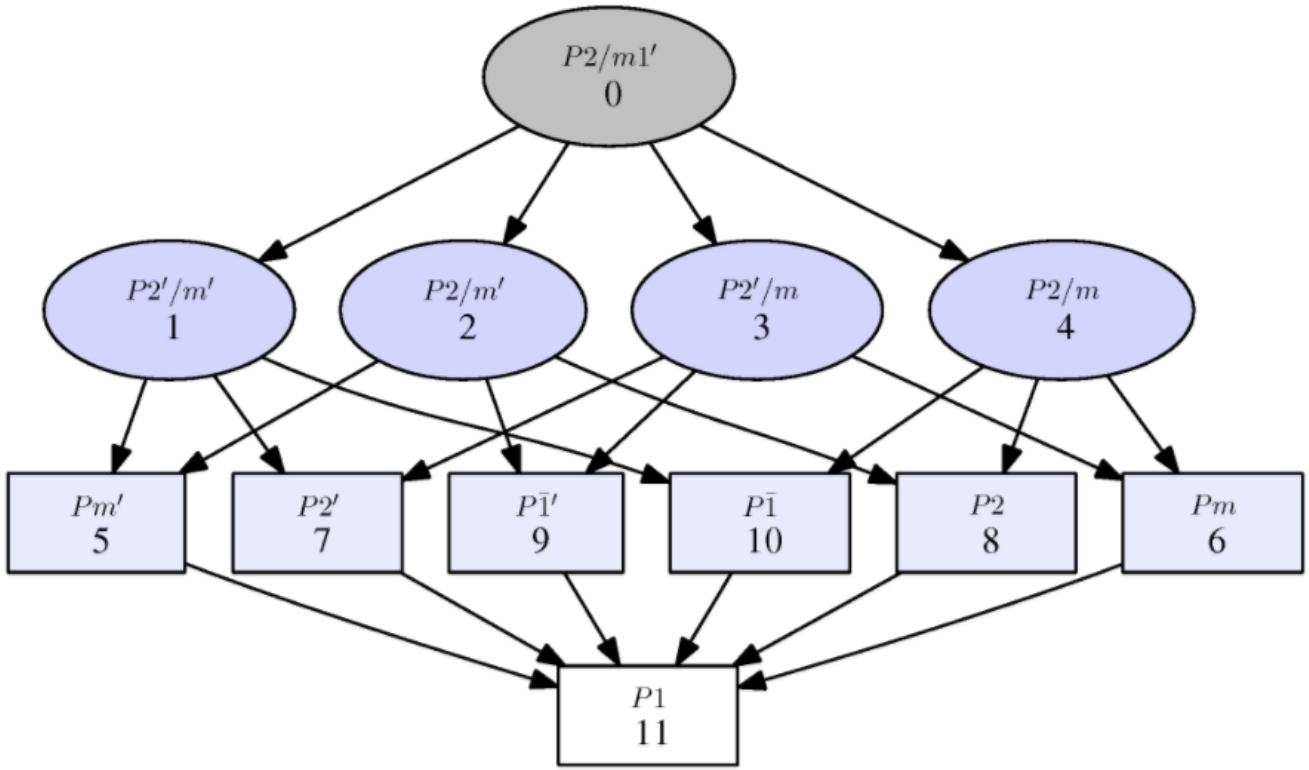
$$\{1|000\}$$
$$\{\bar{1}|000\}$$
$$\{2_y|000\}$$
$$\{m_{xz}|000\}$$

$$\{1'|000\}$$
$$\{\bar{1}'|000\}$$
$$\{2'_y|000\}$$
$$\{m'_{xz}|000\}$$

Paramagnetic group is what is called a grey group *P2/m1'*

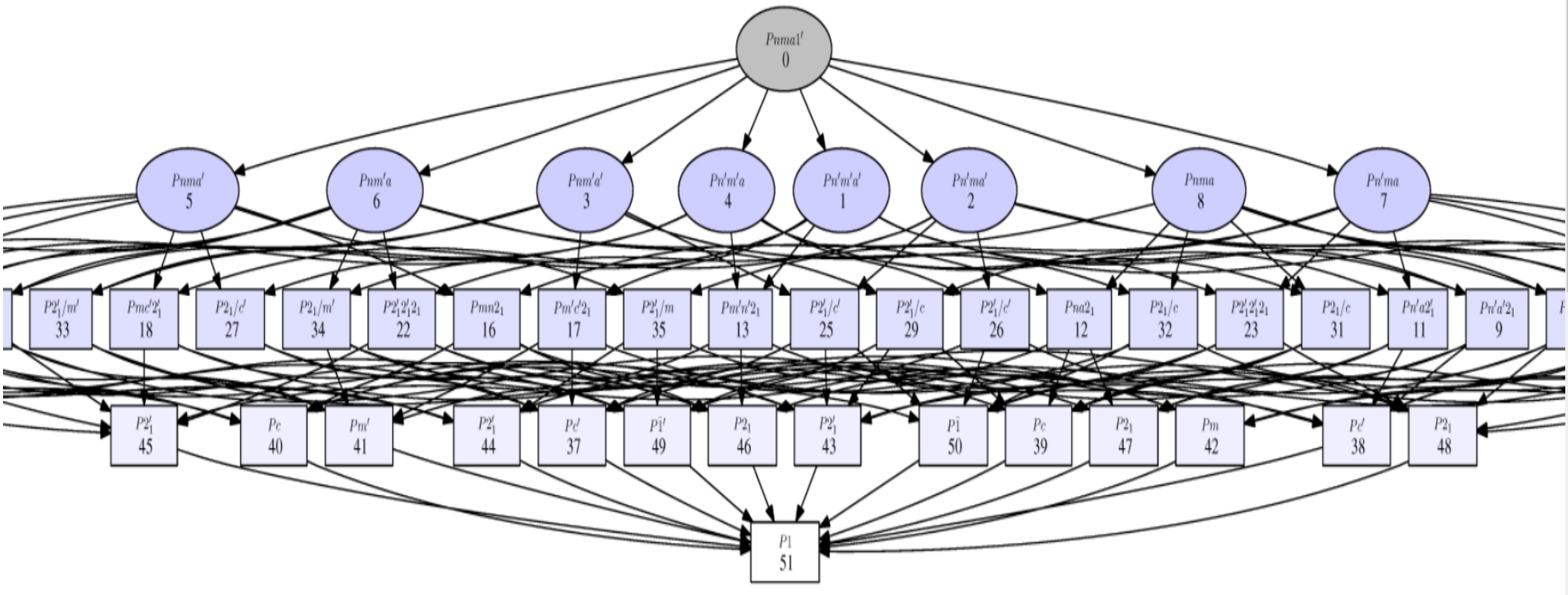
Transitions to magnetically ordered phases with k=0

Example: Monoclinic SG *P2/m1'*
Magnetic atom in general position x,y,z



Perez-Mato, JM; Gallego, SV; Elcoro, L; Tasci, E and Aroyo, MI
J. of Phys.: Condens Matter (2016), 28:28601

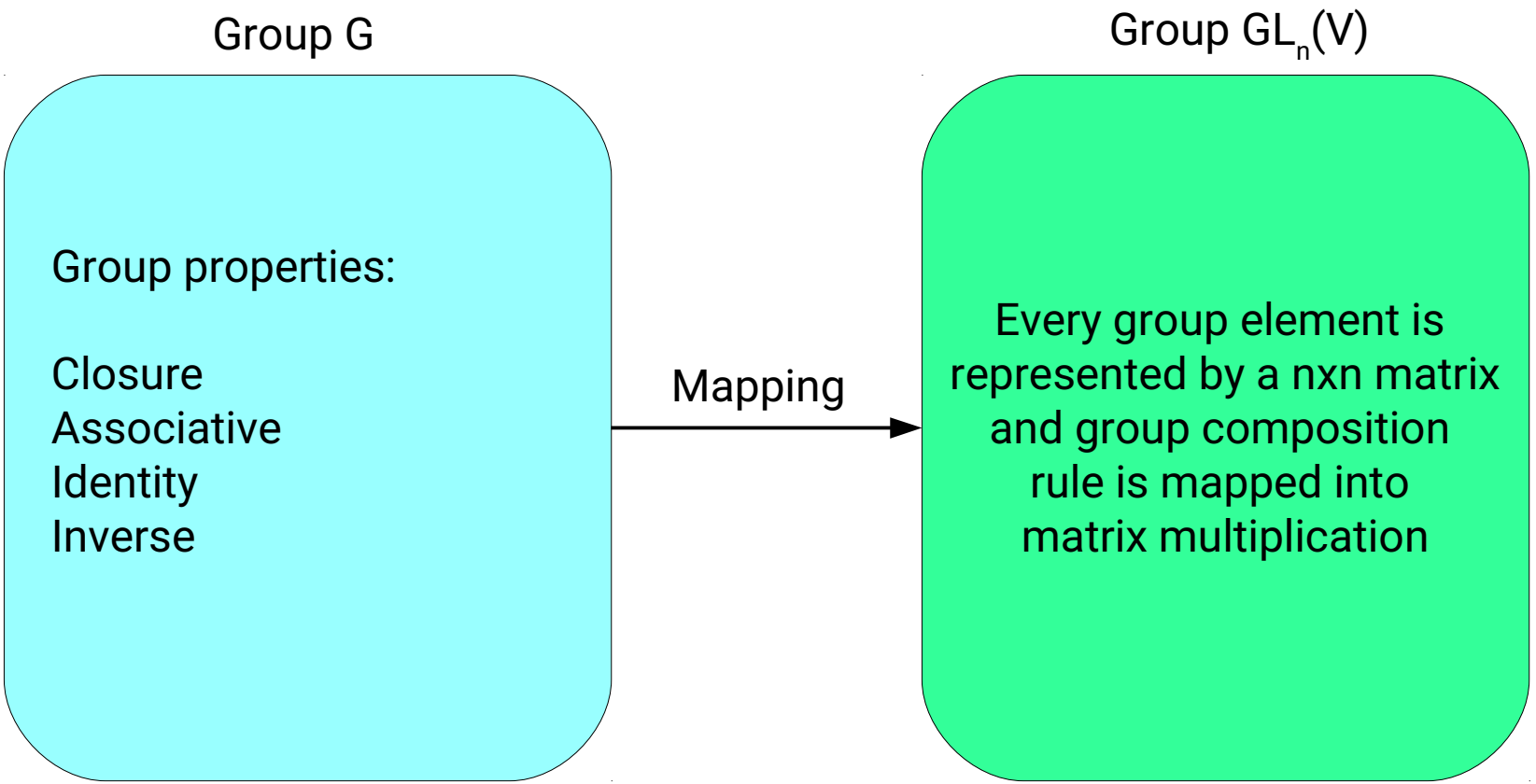
Symmetry descent Pnma1’



Perez-Mato, JM; Gallego, SV; Elcoro, L; Tasci, E and Aroyo, MI
J. of Phys.: Condens Matter (2016), 28:28601

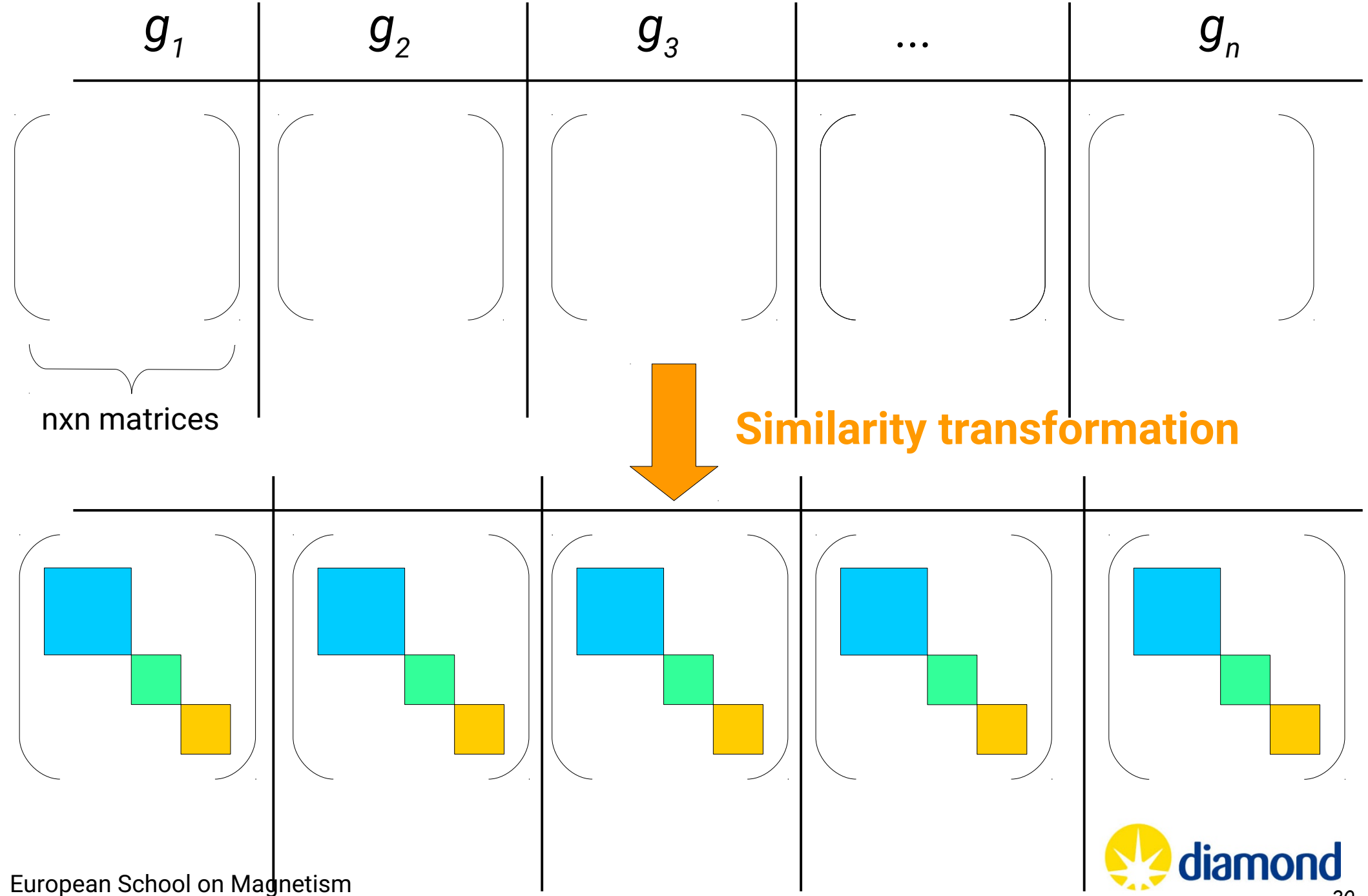
Representation theory

Vector space V that contains all the possible degrees of freedom of my system.



$$V = V_1 \oplus V_2 \oplus \ldots \oplus V_n$$

Representation theory



Group of pure translations

	$\{1\|000\}\{1\|100\}\{1\|010\}\{1\|t\}\{1\|200\}\ldots\ldots\ldots$
Γ^K	$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$ e^{-ikt}

- Infinite abelian group
- Infinite number of irreducible representations, and consists of the complex root of unity.
- Basis are Bloch functions.

$$\phi^k(\mathbf{r}) = u_k(\mathbf{r}).e^{i\mathbf{k}\cdot\mathbf{r}}$$

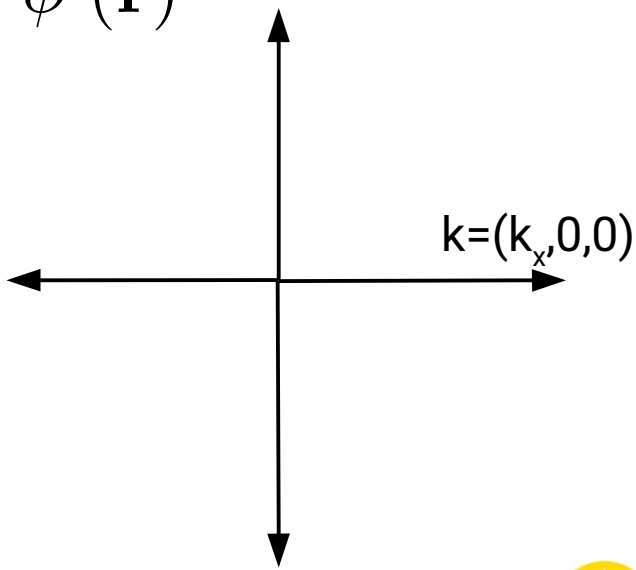
$$u_k(\mathbf{r}+\mathbf{t}) = u_k(\mathbf{r})$$

$$\{1|t\}\phi^k(\mathbf{r}) = \phi^k(\mathbf{r}-\mathbf{t}) = u_k(\mathbf{r}-\mathbf{t})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{t})} = e^{-i\mathbf{k}\cdot\mathbf{t}}\phi^k(\mathbf{r})$$

Space group

Consider a symmetry element g={h|t} and a Bloch-function ⎯':

$$\phi^k(\mathbf{r}) = u_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$$
$$\phi' = \{h|t\}\phi^k(\mathbf{r})$$
$$\{1|u\}\phi' = \{1|u\}\{h|t\}\phi^k(\mathbf{r})$$
$$= \{h|t\}\{1|h^{-1}u\}\phi^k(\mathbf{r})$$
$$= e^{-i\mathbf{k}\cdot\mathbf{h}^{-1}\mathbf{u}}\{h|t\}\phi^k(\mathbf{r}) = e^{-i(hk)u}\phi'(\mathbf{r})$$



Φ' is a Block-function with index (hk)

Little group G_k

- By applying the rotational part of the symmetry elements of the paramagnetic group, one founds a set of k vectors, known as the “star of k”
- Two vectors k_1 and k_2 are *equivalent* if they equal or related by a reciprocal lattice vector.
- In the general case, all vectors k_1, k_2,……k_i in the star are not equivalent
- The group generated from the point group operations that leave k invariant elements + translations is called the group of the propagation vector k or little group and noted G_k..

Representation of (infinite) space groups

Despite the **infinite** number of atomic positions in a crystal symmetry elements in a space group

…a representation theory of space groups is feasible using **Bloch functions** associated to k points of the reciprocal space. This means that the group properties can be given by matrices of finite dimensions for the:

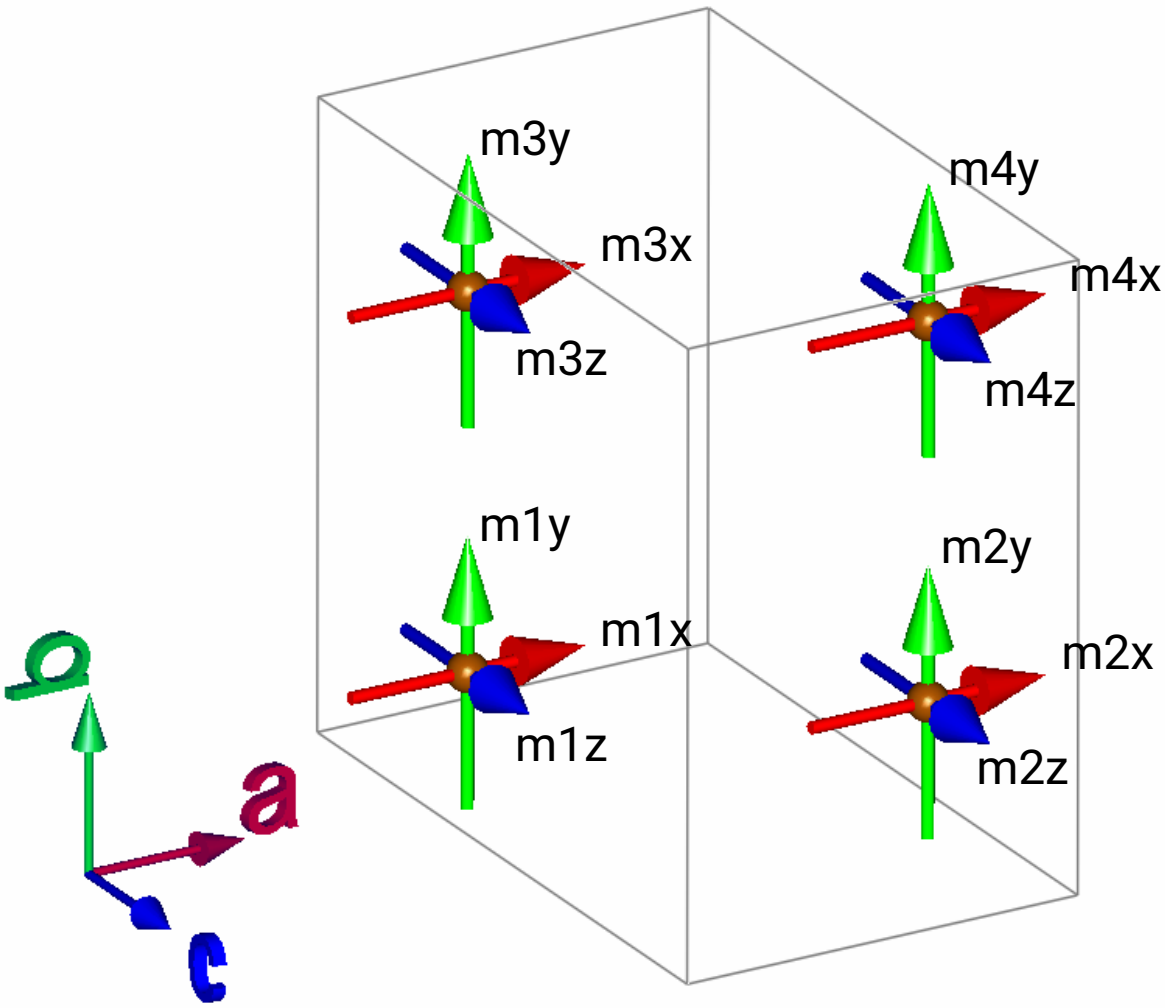
- Reducible (physical) representations can be constructed on the space of the components of a set of generated points in the zero cell.

- **Irreducible representations** of the Group of vector **k** are constructed from a finite set of elements of the zero-block.

Representation theory, example

Example: Monoclinic SG *P2/m*

Magnetic atom in general position x,y,z



$$\begin{pmatrix} m1x \\ m1y \\ m1z \\ m2x \\ m2y \\ m2z \\ m3x \\ m3y \\ m3z \\ m4x \\ m4y \\ m4z \end{pmatrix}$$

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

Symmetry operators ->				
1	2 0,y,0	-1 0,0,0	m x,0,z	
{1|000}	{2_0y0|000}	{-1|000}	{m_x0z|000}	
Γ_1	1	1	1	1	**P2/m**
Γ_2	1	1	-1	-1	**P2/m'**
Γ_3	1	-1	1	-1	**P2'/m'**
Γ_4	1	-1	-1	1	**P2'/m**

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

Symmetry operators ->			
1	2 0,y,0	-1 0,0,0	m x,0,z
{1|000}	{2_0y0|000}	{-1|000}	{m_x0z|000}

Γ_1	1	1	-1	-1

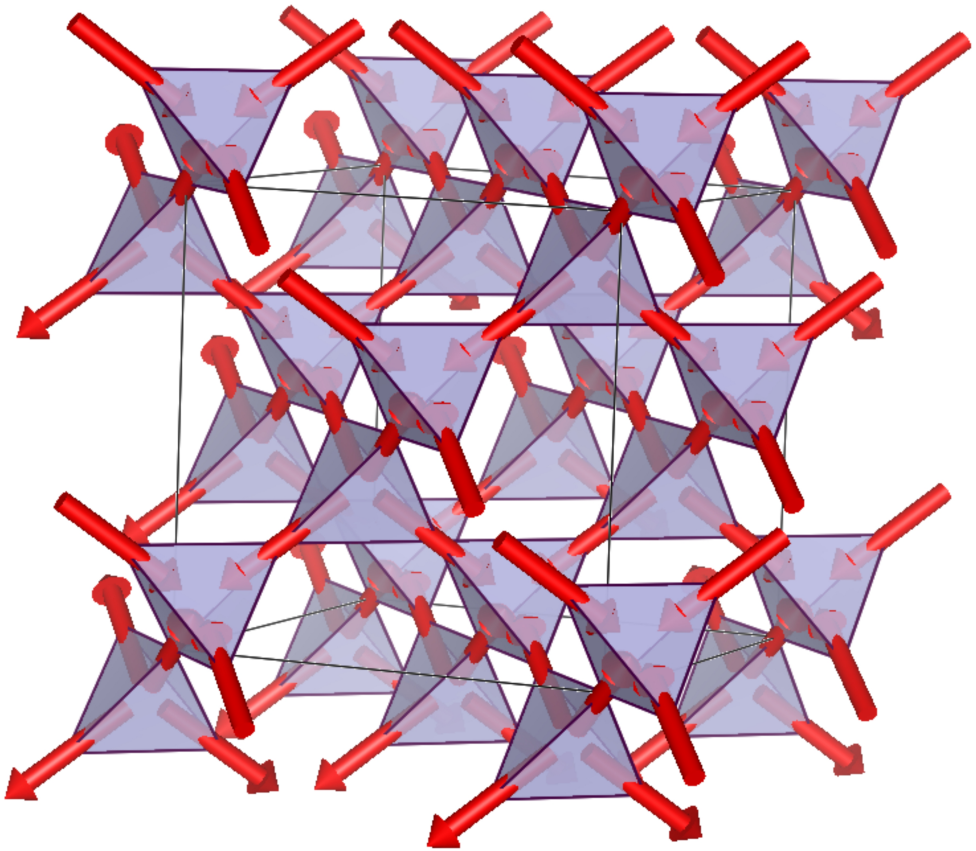
P2/m'

Representation theory

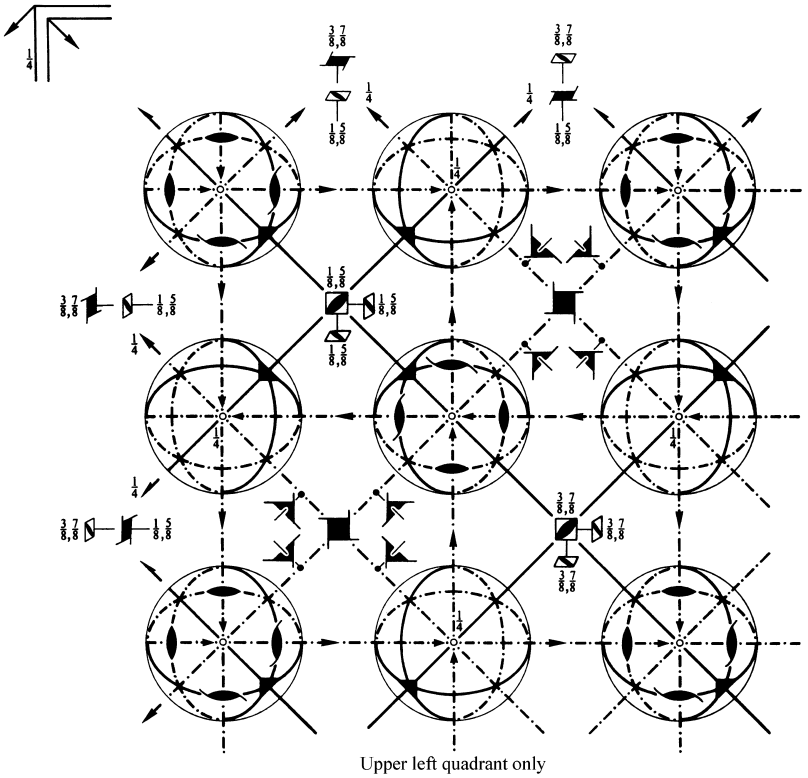
Magnetic space group

If irreducible representation is one-dimensional, there is a 1 to 1 correspondence between representation theory and magnetic space groups !

Representation theory, irreducible representation dim > 1



Pyrochlore
Space group *Fd-3m*
Setting 2, inversion at origin
Magnetic atom in position 16c (0,0,0)



Representation theory, irreducible representation dim > 1

$$\Gamma=\Gamma_3+\Gamma_6+\Gamma_8+2\Gamma_{10}$$

Fd-3m’

Ireps	Symmetry operators →					
v	1	2 (0,0,1/2) 3/8,1/8,z	2 (0,1/2,0) 1/8,y,3/8	2 (1/2,0,0) x,3/8,1/8	3+ x,x,x	3- x,-x+3/4,x-1/2
v	{1|000}	{2_00z|tsp}	{2_0y0|spt}	{2_x00|pts}	{3+_xxx|000}	{3+_-xx-x|pts}
v	Symm(1)	Symm(2)	Symm(3)	Symm(4)	Symm(5)	Symm(6)
IRrep(1):	1	1	1	1	1	1
IRrep(2):	1	1	1	1	1	1
IRrep(3):	1	1	1	1	1	1
IRrep(4):	1	1	1	1	1	1
IRrep(5):	1 0 0 1	0 1 1 0	1 0 0 1	0 1 1 0	a 0 0 b	0 b a 0
IRrep(6):	1 0 0 1	0 1 1 0	1 0 0 1	0 1 1 0	a 0 0 b	0 b a 0
IRrep(7):	1 0 0 0 1 0 0 0 1	1 0 0 0 -1 0 0 0 -1	-1 0 0 0 -1 0 0 0 1	-1 0 0 0 1 0 0 0 -1	0 0 1 1 0 0 0 1 0	0 0 -1 0 0 1 0 -1 0
IRrep(8):	1 0 0 0 1 0 0 0 1	1 0 0 0 -1 0 0 0 -1	-1 0 0 0 -1 0 0 0 1	-1 0 0 0 1 0 0 0 -1	0 0 1 1 0 0 0 1 0	0 0 -1 0 0 1 0 -1 0
IRrep(9):	1 0 0 0 1 0 0 0 1	1 0 0 0 -1 0 0 0 -1	-1 0 0 0 -1 0 0 0 1	-1 0 0 0 1 0 0 0 -1	0 0 1 1 0 0 0 1 0	0 0 -1 0 0 1 0 -1 0
IRrep(10):	1 0 0 0 1 0 0 0 1	1 0 0 0 -1 0 0 0 -1	-1 0 0 0 -1 0 0 0 1	-1 0 0 0 1 0 0 0 -1	0 0 1 1 0 0 0 1 0	0 0 -1 0 0 1 0 -1 0

For irreducible representations of dimension 2 or 3 , the magnetic space group (and full symmetry) depends on the *direction of the order parameter*

Irreducible representation dim >1

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

ISODISTORT SUITE HELP

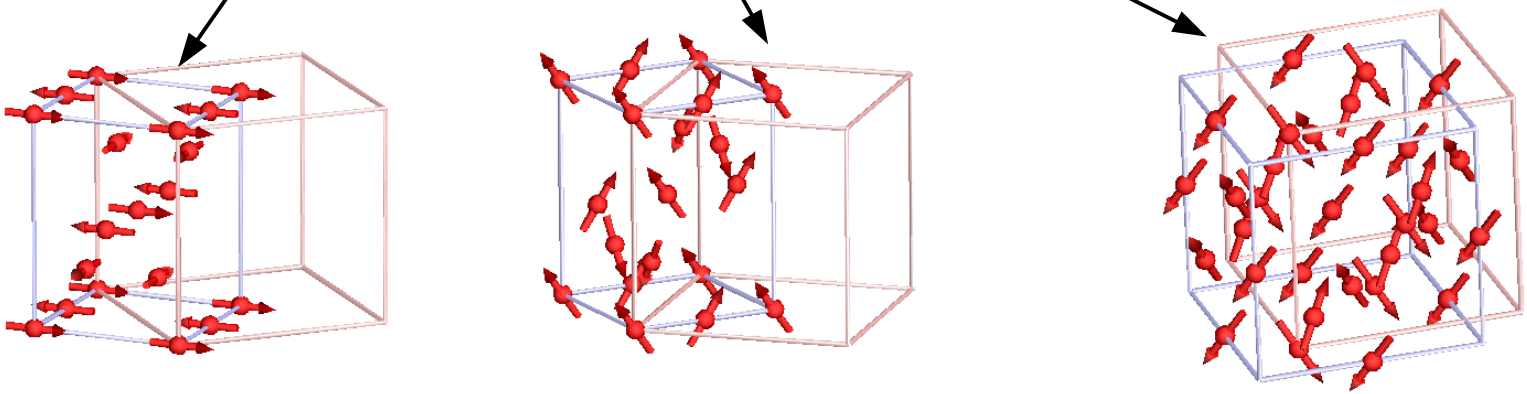
ISODISTORT: order parameter direction

Space Group: 227 Fd-3m Oh-7, Lattice parameters: a=9.00000, b=9.00000, c=9.00000, alpha=90.00000, beta=90.00000, gamma=90.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
Ir 16c (0,0,0)
Include magnetic distortions
k point: GM, k11 (0,0,0)
IR: mGM3+, mk11t5

Finish selecting the distortion mode by choosing an order parameter direction

- P1 (a,0) 141.551 I4_1/amd, basis={(-1/2,1/2,0),(-1/2,-1/2,0),(0,0,1)}, origin=(0,1/2,-1/2), s=1, i=6, k-active= (0,0,0)
- P2 (0,a) 141.554 I4_1'/am'd, basis={(-1/2,1/2,0),(-1/2,-1/2,0),(0,0,1)}, origin=(0,1/2,-1/2), s=1, i=6, k-active= (0,0,0)
- C1 (a,b) 70.527 Fddd, basis={(1,0,0),(0,0,1),(0,-1,0)}, origin=(-1/4,1/2,-1/4), s=1, i=12, k-active= (0,0,0)

OK



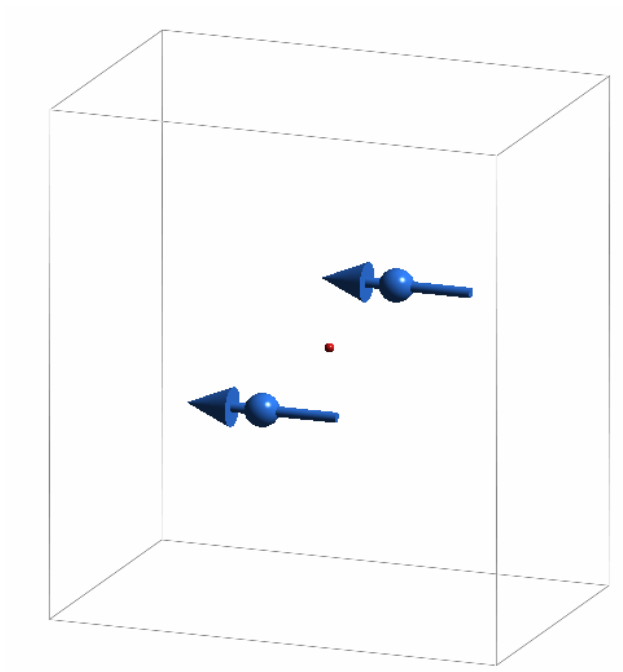
In this case, there can be **more symmetry constraints** (by choosing special direction of the order parameter) than simply mixing all basis vectors of the irrep.

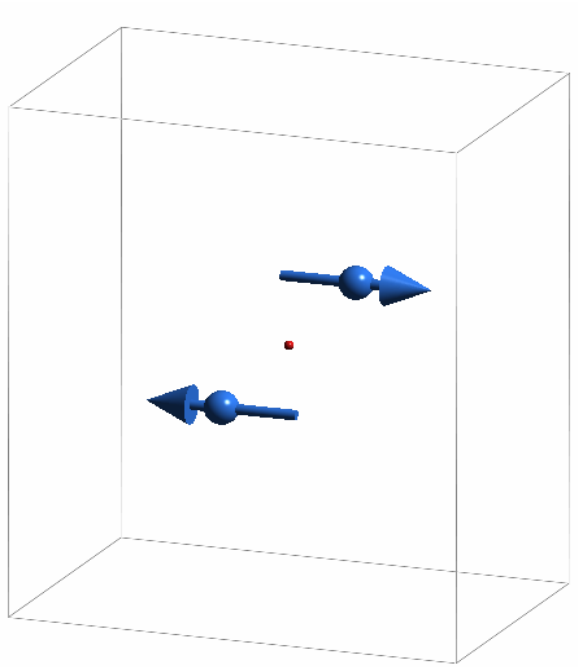
Magnetic point group

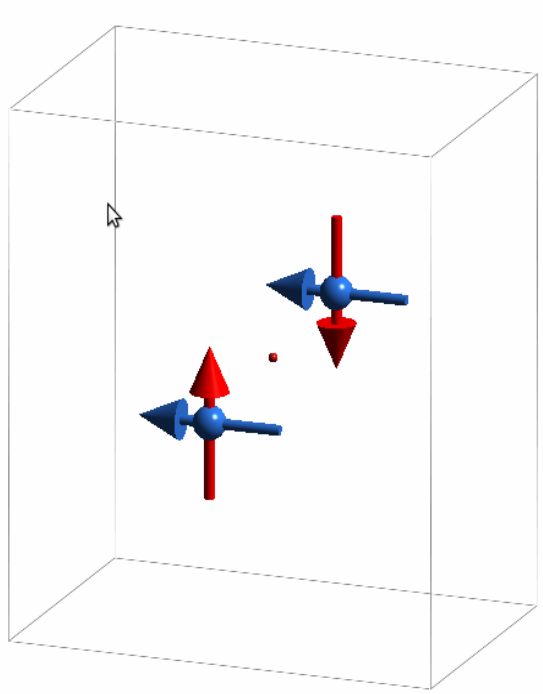
Determine the point group S in the magnetically ordered phase.

For any symmetry operator g={R|τ} of the paramagnetic group:

$R \in S$ if and only if $g.m = \pm m$







diamond

The 122 magnetic point groups

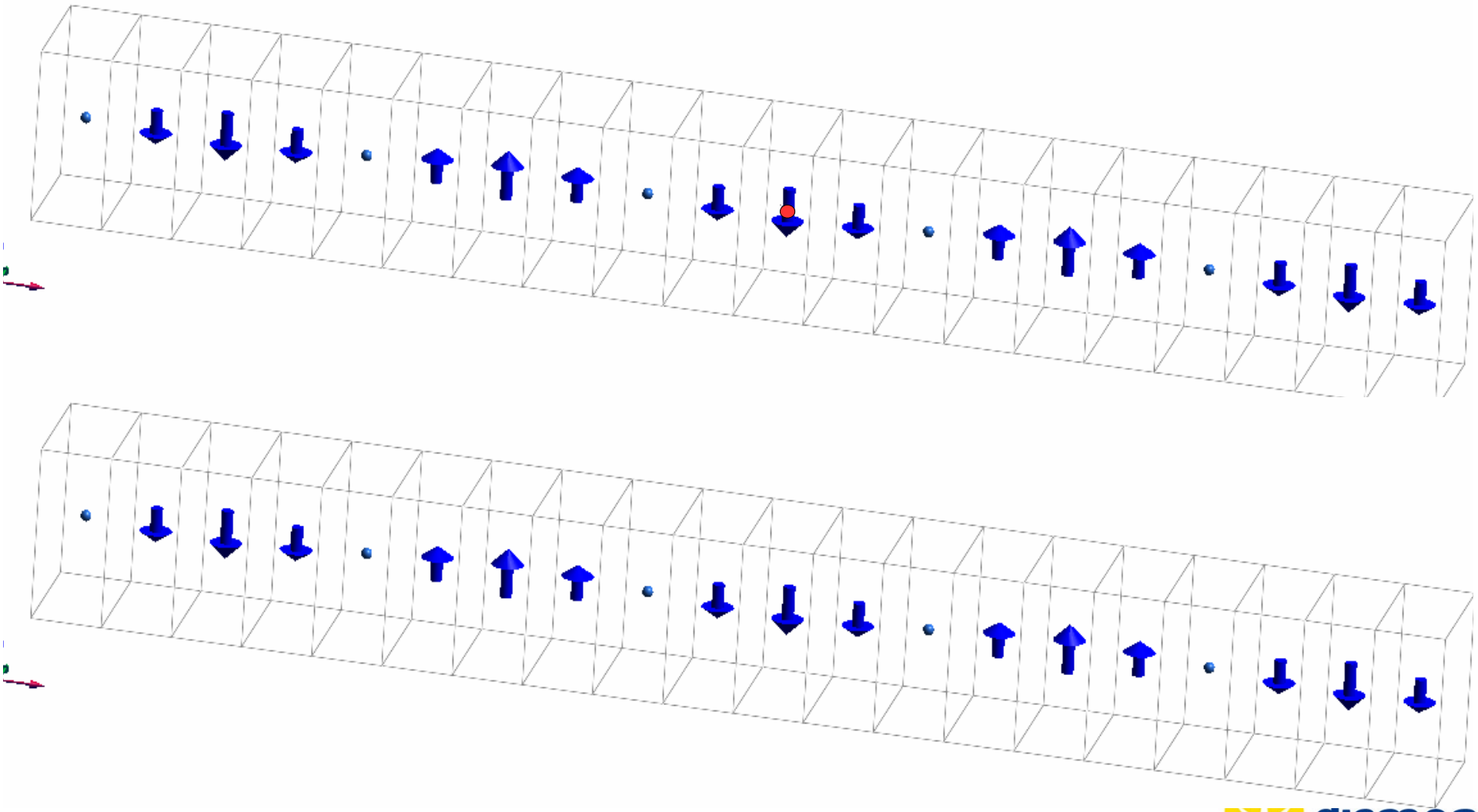
***International Tables for Crystallography* (2006). Vol. D, Section 1.5.8, pp. 137–142.**

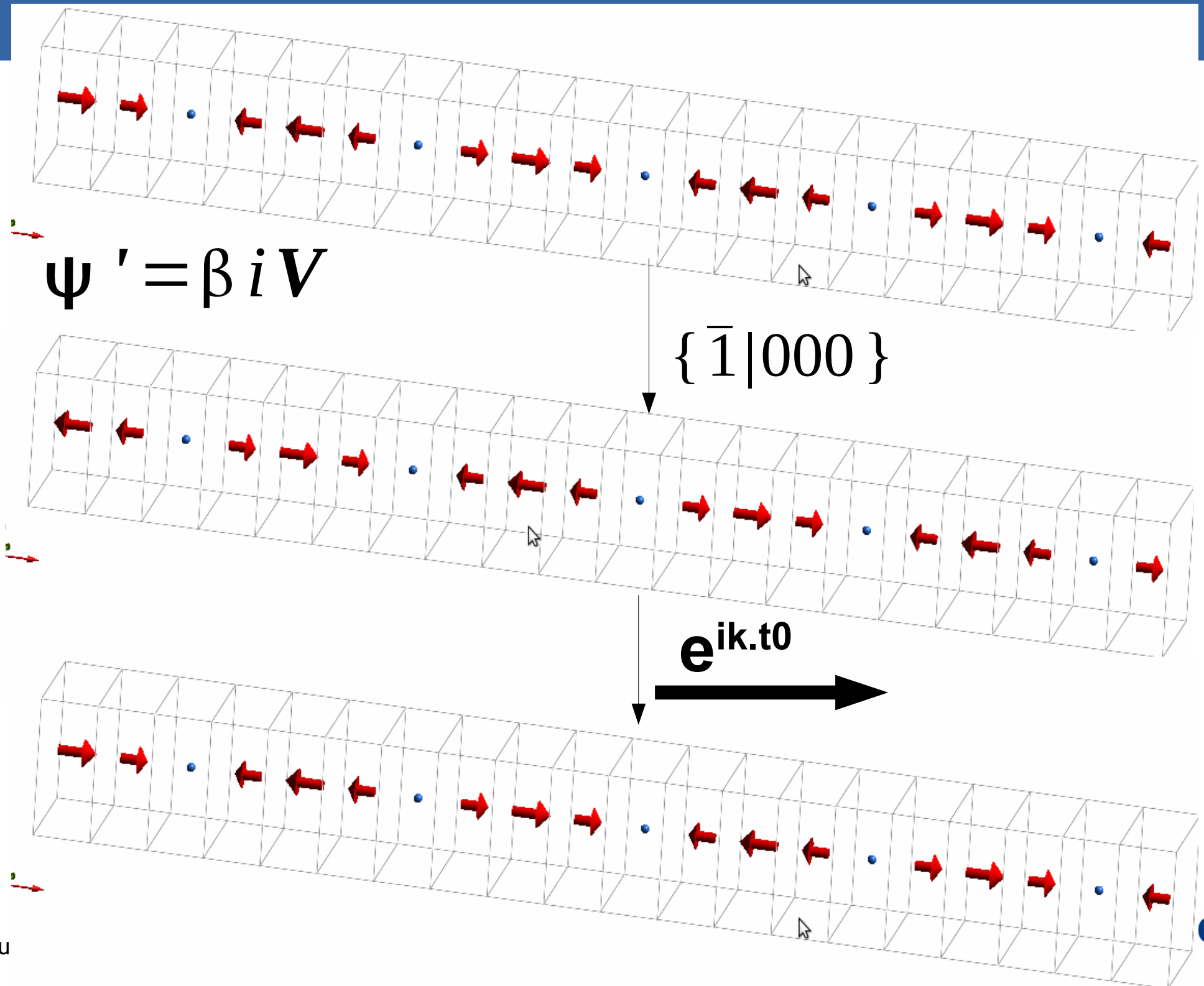
Table 1.5.8.3. *Classification of the 122 magnetic point groups according to magnetoelectric types*

Type	Inversions in the group	Permitted terms in thermodynamic potential	Magnetic point groups	Number of magnetic point groups				
1	$1'$	E EHH	$1'$, $21'$, $m1'$, $mm21'$, $41'$, $4mm1'$, $31'$, $3m1'$, $61'$, $6mm1'$	10	31		49	122
2		E EHH HEE	$6'$, $6'mm'$	2				
3		E EH EHH HEE	$mm2$, $4mm$, $4'$, $4'mm'$, $3m$, $6mm$	6				
4		E H EH EHH HEE	1, 2, m, $2'$, m', $m'm2'$, $m'm'2$, 4, $4m'm'$, 3, $3m'$, 6, $6m'm'$	13		31		
5		H EH EHH HEE	$2'2'2$, $42'2'$, $\bar{4}$, $\bar{4}2'm'$, $32'$, $62'2'$	6				
6		H EHH HEE	$\bar{6}$, $\bar{6}m'2'$	2				
7	$\bar{1}$	H HEE	$\bar{1}$, $2/m$, $2'/m'$, $m'm'm$, $4/m$, $4/mm'm'$, $\bar{3}$, $\bar{3}m'$, $6/m$, $6/mm'm'$	10				
8		EH EHH HEE	222, $\bar{4}'$, 422, $\bar{4}2m$, $4'22'$, $\bar{4}'2m'$, $\bar{4}'2'm$, 32, $\bar{6}'$, 622, $\bar{6}'m'2$, $\bar{6}m'2'$, 23, $\bar{4}'3m'$	14			73	
9		EHH HEE	$\bar{6}m2$, $6'22'$	2				
10		EH	432	1		19		
11	$\bar{1}'$	EH	$\bar{1}'$, $2/m'$, $2'/m$, mmm', $m'm'm'$, $4/m'$, $4'/m'$, $4/m'm'm'$, $4/m'mm$, $4'/m'm'm$, $\bar{3}'$, $\bar{3}'m'$, $\bar{3}'m$, $6/m'$, $6/m'm'm'$, $6/m'mm$, $m'\bar{3}'$, $m'\bar{3}'m'$	18				
12		EHH	$\bar{4}3m$	1		11		
13	$1'$	EHH	$2221'$, $\bar{4}1'$, $4221'$, $\bar{4}2m1'$, $321'$, $\bar{6}1'$, $6221'$, $\bar{6}m21'$, $231'$, $\bar{4}3m1'$	10				
14		HEE	$4'32'$	1		11		
15	$\bar{1}$	HEE	mmm, $4'/m$, $4/mmm$, $4'/mmm'$, $\bar{3}m$, $6'/m'$, $6/mmm$, $6'/m'm'm$, $m\bar{3}$, $m\bar{3}m'$	10				
16	$\bar{1}'$		$6'/m$, $6'/mmm'$, $m'\bar{3}'m$	3		16		
17	$1'$		$4321'$	1				
18	$\bar{1}$		$m\bar{3}m$	1				
19	$\bar{1}$, $1'$, $\bar{1}'$		$\bar{1}1'$, $2/m1'$, $mmm1'$, $4/m1'$, $4/mmm1'$, $\bar{3}1'$, $\bar{3}m1'$, $6/m1'$, $6/mmm1'$, $m\bar{3}1'$, $m\bar{3}m1'$	11				

Let's consider an inversion centre in the zeroth cell, marked by a red point.
in the case of a single-k magnetic structure with k inside the BZ.
If one considers an amplitude modulation of the form:

$$\psi = \alpha U$$

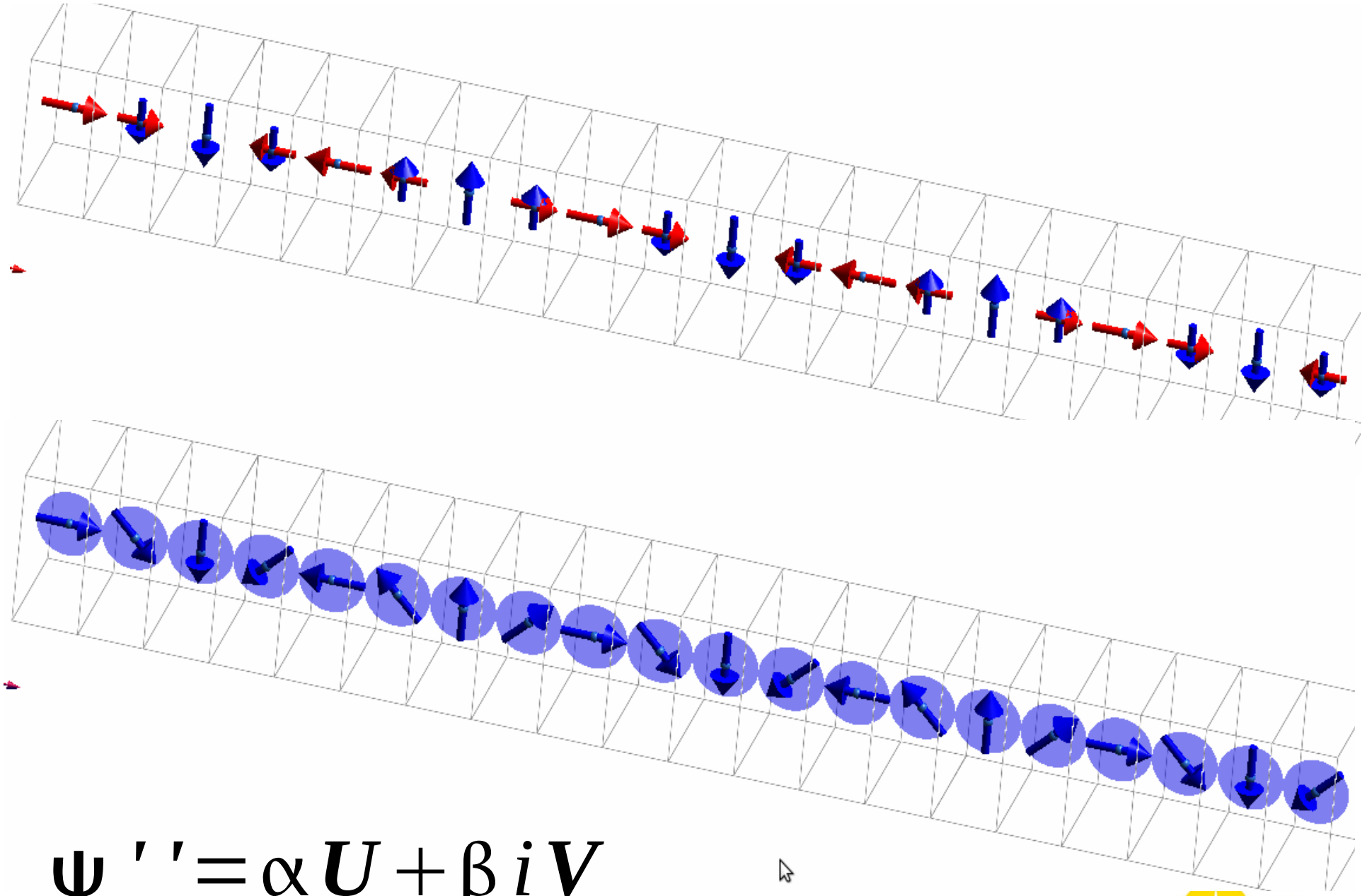




Eu

ond

Mixture of two modes



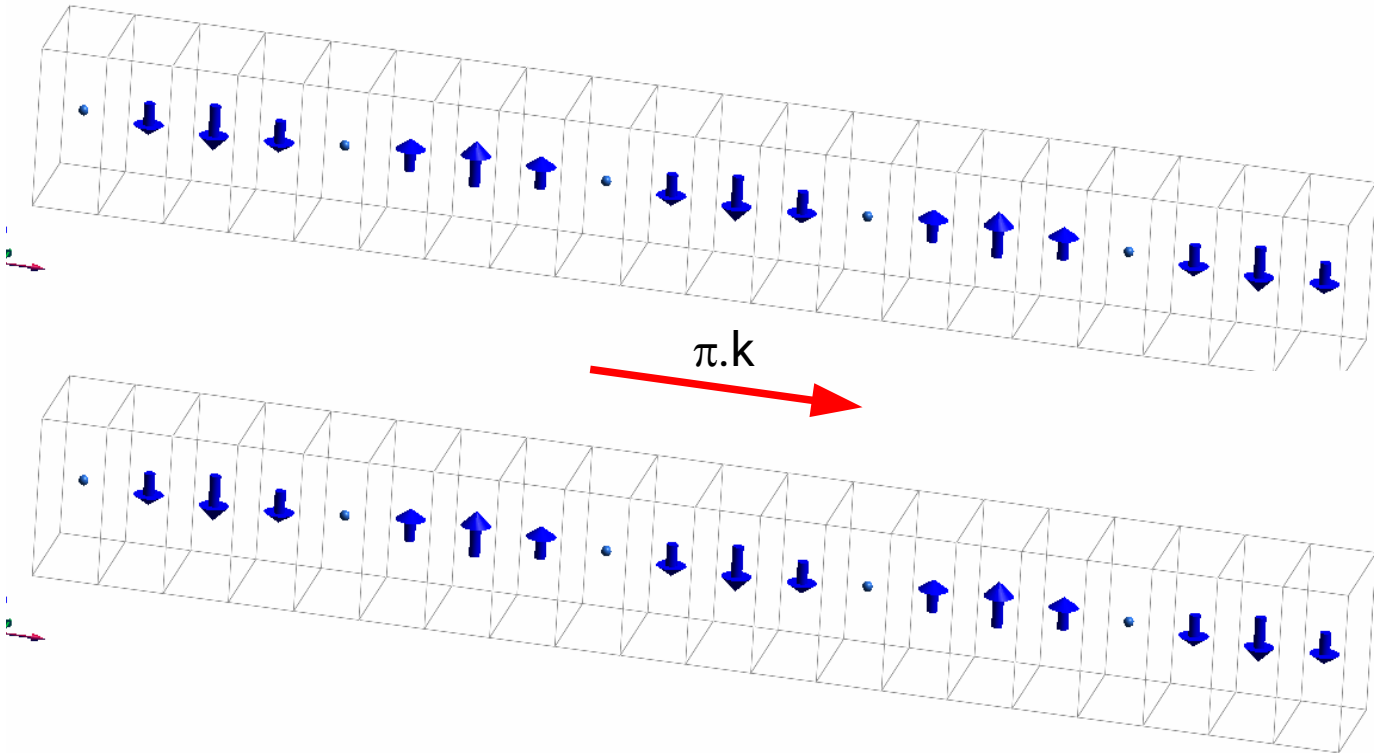
$$\psi'' = \alpha U + \beta i V$$

Operator 1'

Note about the **linear time-reversal operator, the 'prime' operator.**

1' is present in this case with a single k vector and no harmonics

In the previous example, application of 1', flip all the spins, irrespective of the components of the modulations, i.e is equivalent to a simultaneous phase shift of $\pi.k$.



Magnetic point group (k inside BZ)

In the cases where the magnetic wavevector is inside the BZ, to which all incommensurate structure belongs:

For any symmetry operator g={R|τ} of the paramagnetic group:

$$If\ we\ note\ \psi = S_{kj}.e^{-2\pi i k.R_L}$$

$$R \in S \Leftrightarrow$$

$$g[\psi] = \pm e^{-2\pi i k.R_0}[\psi] \qquad g[\psi] = \pm e^{-2\pi i k.R_0'}[\psi^*]$$

$$\Leftrightarrow$$

$$g[\psi] = \pm e^{-2\pi i k.R_0}[\psi] \qquad Kg[\psi] = \pm e^{2\pi i k.R_0'}[\psi]$$

Essentially, R belongs to S, if and only if psi is an eigenvector of the operator g or Kg.

The 122 magnetic point groups

***International Tables for Crystallography* (2006). Vol. D, Section 1.5.8, pp. 137–142.**

Table 1.5.8.3. *Classification of the 122 magnetic point groups according to magnetoelectric types*

Type	Inversions in the group	Permitted terms in thermodynamic potential	Magnetic point groups	Number of magnetic point groups				
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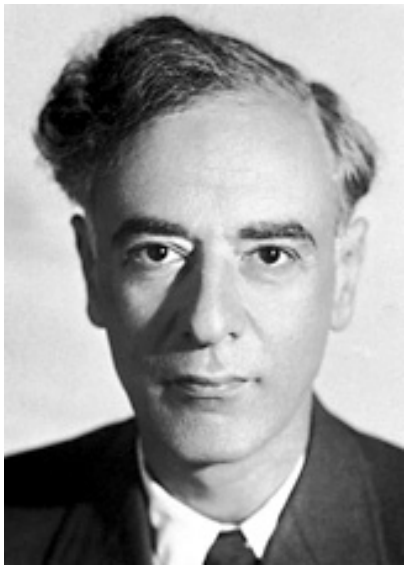
2		E EHH HEE	$6'$, $6'mm'$	2				
3		E EH EHH HEE	$mm2$, $4mm$, $4'$, $4'mm'$, $3m$, $6mm$	6				
4		E H EH EHH HEE	1, 2, m, $2'$, m', $m'm2'$, $m'm'2$, 4, $4m'm'$, 3, $3m'$, 6, $6m'm'$	13		31		
5		H EH EHH HEE	$2'2'2$, $42'2'$, $\bar{4}$, $\bar{4}2'm'$, $32'$, $62'2'$	6				
6		H EHH HEE	$\bar{6}$, $\bar{6}m'2'$	2				
7	$\bar{1}$	H HEE	$\bar{1}$, $2/m$, $2'/m'$, $m'm'm$, $4/m$, $4/mm'm'$, $\bar{3}$, $\bar{3}m'$, $6/m$, $6/mm'm'$	10				
8		EH EHH HEE	222, $\bar{4}'$, 422, $\bar{4}2m$, $4'22'$, $\bar{4}'2m'$, $\bar{4}'2'm$, 32, $\bar{6}'$, 622, $\bar{6}'m'2$, $\bar{6}m'2'$, 23, $\bar{4}'3m'$	14			73	
9		EHH HEE	$\bar{6}m2$, $6'22'$	2				
10		EH	432	1		19		
11	$\bar{1}'$	EH	$\bar{1}'$, $2/m'$, $2'/m$, mmm', $m'm'm'$, $4/m'$, $4'/m'$, $4/m'm'm'$, $4/m'mm$, $4'/m'm'm$, $\bar{3}'$, $\bar{3}'m'$, $\bar{3}'m$, $6/m'$, $6/m'm'm'$, $6/m'mm$, $m'\bar{3}'$, $m'\bar{3}'m'$	18				
12		EHH	$\bar{4}3m$	1		11		
13	$1'$	EHH	$2221'$, $\bar{4}1'$, $4221'$, $\bar{4}2m1'$, $321'$, $\bar{6}1'$, $6221'$, $\bar{6}m21'$, $231'$, $\bar{4}3m1'$	10				
14		HEE	$4'32'$	1		11		
15	$\bar{1}$	HEE	mmm, $4'/m$, $4/mmm$, $4'/mmm'$, $\bar{3}m$, $6'/m'$, $6/mmm$, $6'/m'm'm$, $m\bar{3}$, $m\bar{3}m'$	10				
16	$\bar{1}'$		$6'/m$, $6'/mmm'$, $m'\bar{3}'m$	3		16		
17	$1'$		$4321'$	1				
18	$\bar{1}$		$m\bar{3}m$	1				
19	$\bar{1}$, $1'$, $\bar{1}'$		$\bar{1}1'$, $2/m1'$, $mmm1'$, $4/m1'$, $4/mmm1'$, $\bar{3}1'$, $\bar{3}m1'$, $6/m1'$, $6/mmm1'$, $m\bar{3}1'$, $m\bar{3}m1'$	11				

Landau's theory of phase transitions



- **Idea : to explain second order (continuous) phase transitions, i.e. transitions for which thermodynamic variables varies smoothly but characterized by an 'abrupt' breaking of symmetry**

- **Close to the transition, the free energy is analytic and can be expanded in powers of order parameter(s)**

- **The free energy obeys the symmetry of the Hamiltonian**

- **Magnetic transitions, ferroelectric(elastic), superfluids, superconductors**

Lev Landau, Nobel Prize 1962
"for his pioneering theories for condensed matter, especially liquid helium"

Landau theory of phase transitions

L. Landau, Eine mogliche Erklarung der Feldabhangigkeit der Suszeptibilitat bei niedrigen Temperaturen, *Phys. Z. Sowjet.* 4, 675 (1933)

Lev. LANDAU

only the first terms:

$$F_1 = \frac{1}{2} a m_1^2 + \frac{1}{4} b m_1^4, \tag{1}$$

(odd powers naturally do not occur on symmetry grounds), and the analogous expression

$$F_2 = \frac{1}{2} a m_2^2 + \frac{1}{4} b m_2^4 \tag{2}$$

for the layers of the second kind.

2. The exchange energy of the two kinds layers of per pair of atoms:

$$F_3 = A(\boldsymbol{m}_1 \cdot \boldsymbol{m}_2). \tag{3}$$

3. The free energy for the interaction of the moment with the lattice

$$F_4 = \frac{1}{2}\alpha(m_{1x}^2 + m_{1y}^2), \quad F_5 = \frac{1}{2}\alpha(m_{2x}^2 + m_{2y}^2), \tag{4}$$

and, finally, the energy in the external field

$$F_6 = -(\boldsymbol{H} \cdot \boldsymbol{m}_1), \quad F_7 = -(\boldsymbol{H} \cdot \boldsymbol{m}_2). \tag{5}$$

The total free energy per atom is thus equal to

$$F = \frac{1}{2}(F_1 + F_2 + F_3 + F_4 + F_5 + F_6 + F_7) \tag{6}$$

we now put

$$\frac{1}{2}(\boldsymbol{m}_1 + \boldsymbol{m}_2) = \boldsymbol{m}; \quad \frac{1}{2}(\boldsymbol{m}_1 - \boldsymbol{m}_2) = \boldsymbol{l}. \tag{7}$$

Then, as is readily calculated, we have:

$$F = \frac{1}{2}(a - A) l^2 + \frac{1}{4} b l^4 + \frac{1}{2}\alpha(l_x^2 + l_y^2) + \frac{1}{2}(a + A) m^2 + \frac{1}{2}\alpha(m_z^2 + m_y^2) + \frac{1}{2} b m^2 l^2 + b(\boldsymbol{m} \cdot \boldsymbol{l})^2 + \frac{1}{4} b m^4 - (\boldsymbol{H} \cdot \boldsymbol{m}).$$

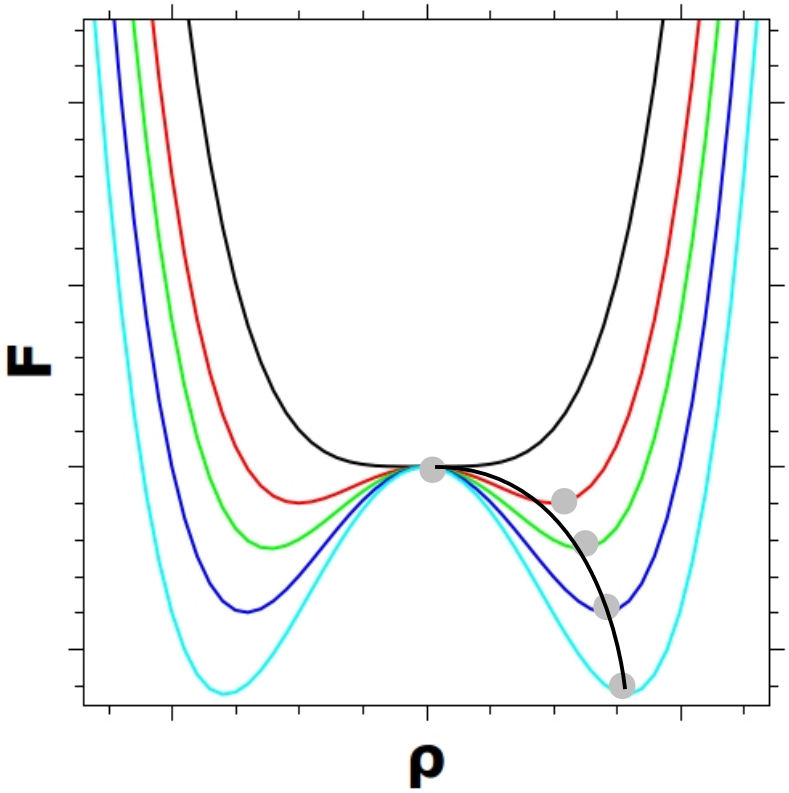
$$\chi_x = \chi_y = \frac{1/\beta}{\alpha + (2A/\beta)}, \qquad \chi_z = \frac{1/\beta}{2(\Theta - T) + (2A/\beta)}.$$

diamond

Landau theory of phase transitions

"Phase transitions of the second kind and critical phenomena", Chapter 14
Course of theoretical physics, Volume 5, Statistical Physics
L. D. Landau and E.M. Lifshitz

- Phase transitions of the second kind, where the state of the body changes continuously.
- Very important general property: the symmetry of one phase is higher than that of the other
- Whilst the change is continuous, the symmetry change is not
- Thermodynamic functions vary continuously.



$$F = F_0 + \alpha . \rho^2 + \beta . \rho^4$$

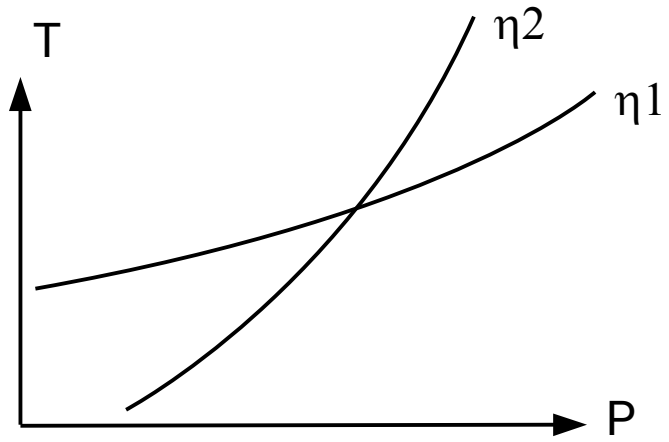
$$\alpha = \alpha_0 (T - T_c), \alpha_0 > 0$$

$$\beta > 0$$

Landau theory

- Free energy is expanded in **powers** of the **order parameter**(s), polarization, strain...
- Allowed terms must be **invariant by all operations** of the high-symmetry group
- Once F is constructed, one can calculate the variation of physical quantities, **relation between domains**...

In a second order phase transition, a single symmetry mode is involved (single irreducible representation).



Formalism of propagation vector

$$\mathbf{S}_{\mathbf{k}js} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{\mathbf{k}\,\nu}_{n\lambda}(js)$$

The coefficients $C^{\nu}_{n\lambda}$ are the free parameters of the magnetic structure (order parameters of the phase transition in the Landau theory)

$\mathbf{k}$: reference to the propagation vector

ν : reference to the irreducible representation Γ_{ν}

n : index running from 1 up to $n_{\nu} \Rightarrow \Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu}\, \Gamma_{\nu}$

λ : index running from 1 up to $\dim(\Gamma_{\nu})$

Domains

- Because the **symmetry** of the ordered magnetic state **is lower** than that of the paramagnetic state (loss of certain symmetry elements)

- If the order of the paramagnetic group $\mathbf{G_0}$ **is g** and the order of the ordered group $\mathbf{G_1}$ **is h**, there will be **g/h domains**.

- The different types of domains:

  - configuration domains (k-domains) : loss of translational symmetry
  - orientation domains (S-domains): loss of rotational symmetry
  - 180 degrees domains (time-reversed domains): loss of time-reversal symmetry
  - chiral domains: loss of inversion symmetry

k-domains

- The symmetry operations of the paramagnetic group (their rotational parts) transforms the wave-vector **k** either :

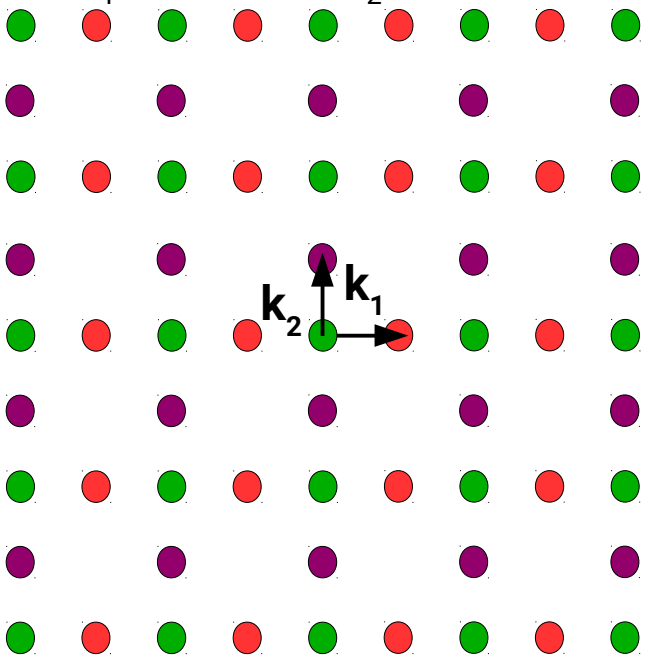
  - in an equivalent vector (related to **k** by a r.l.v)
  - in a new vector

- The set of independent **k** vectors generated by the symmetry operators of the paramagnetic group is named the star of **k** and noted **{k}**

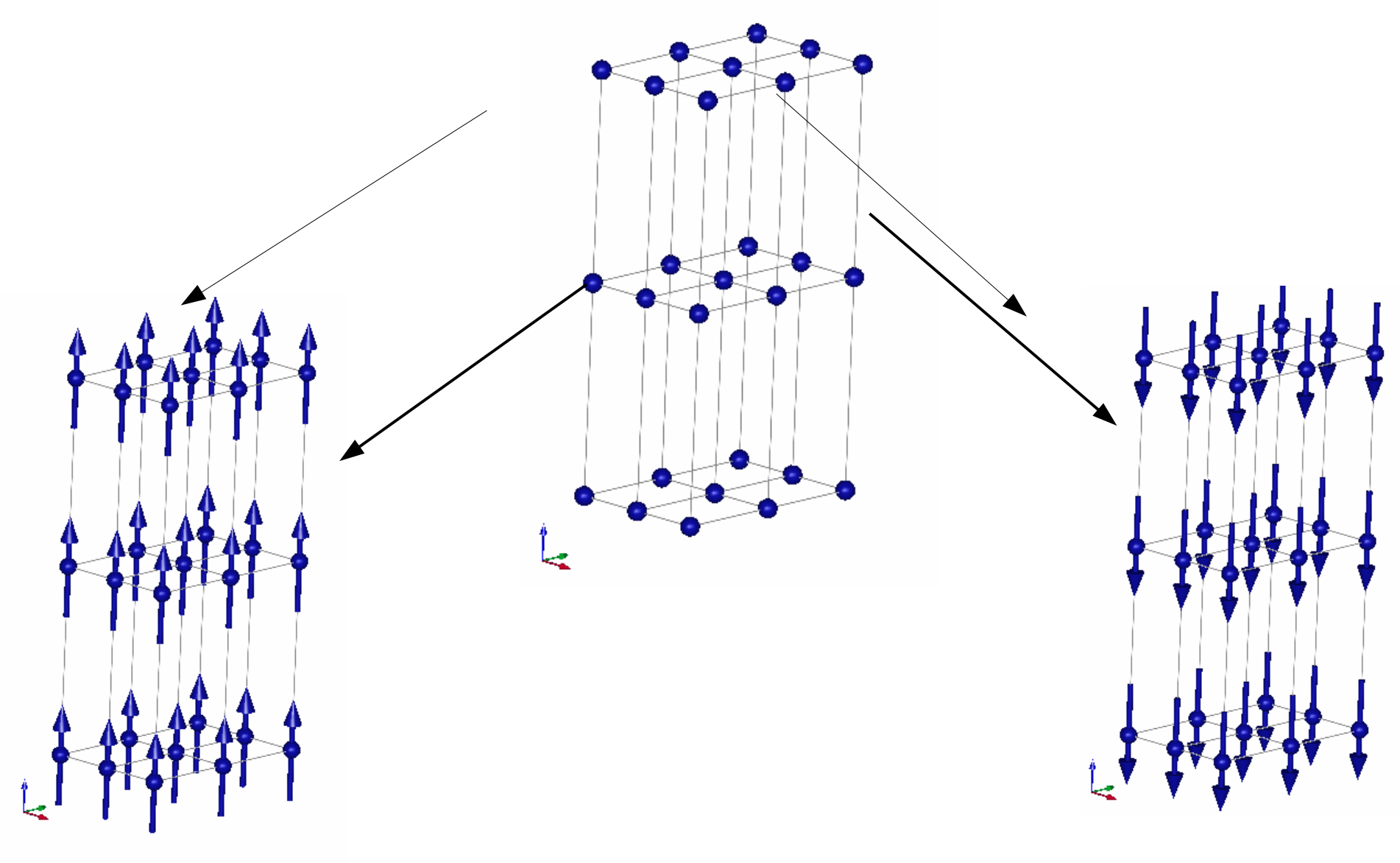
- If the magnetic configuration is **single-k,** then there will be as many domains as arms in **{k}**

Example : tetragonal system

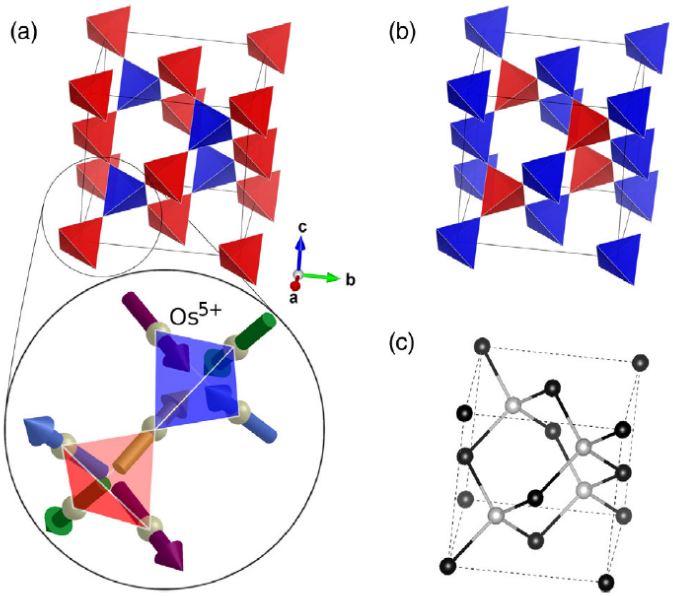
$k_1=(1/2,0,0)$, $k_2=(0,1/2,0)$



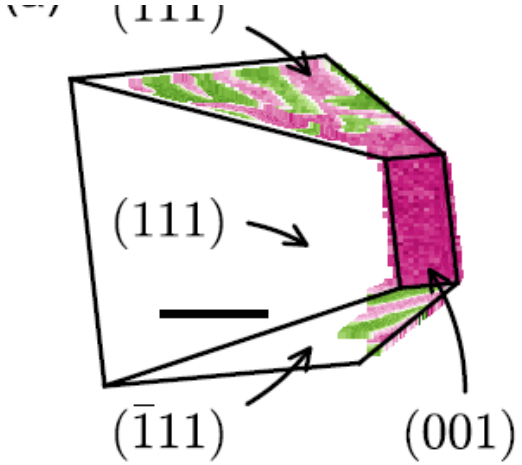
180 degrees (time-reversed)-domains

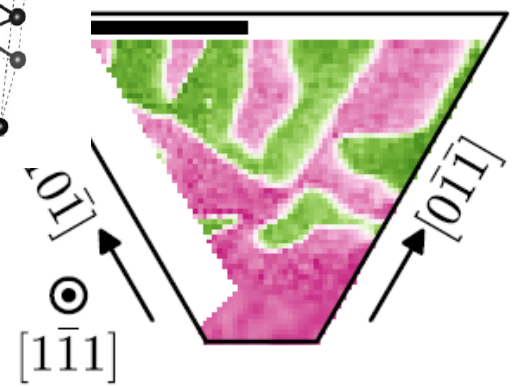


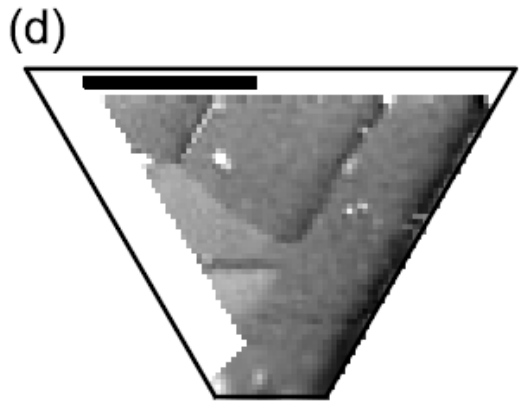
Time-reversed domains in pyrochlores

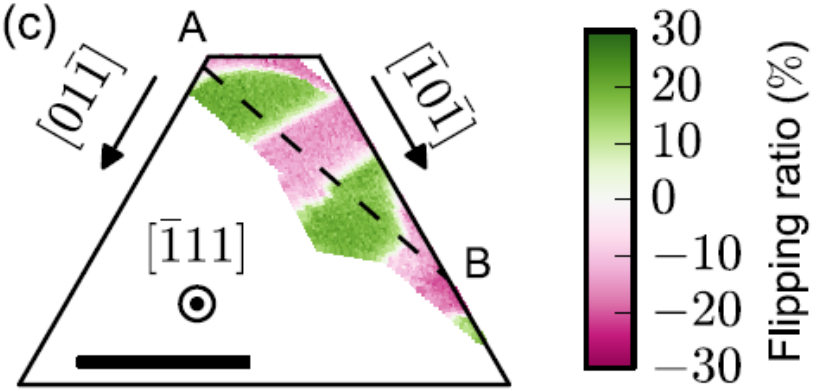


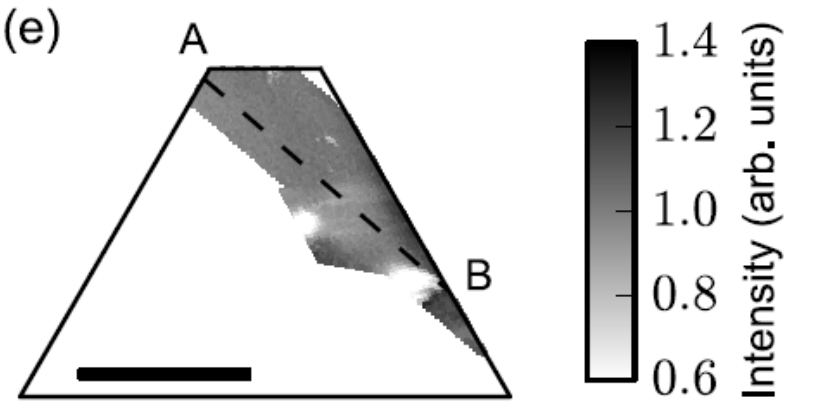
[1] S. Tardif et al., "All-In–All-Out Magnetic Domains: X-Ray Diffraction Imaging and Magnetic Field Control," Phys. Rev. Lett., vol. 114, no. 14, p. 147205, 2015.



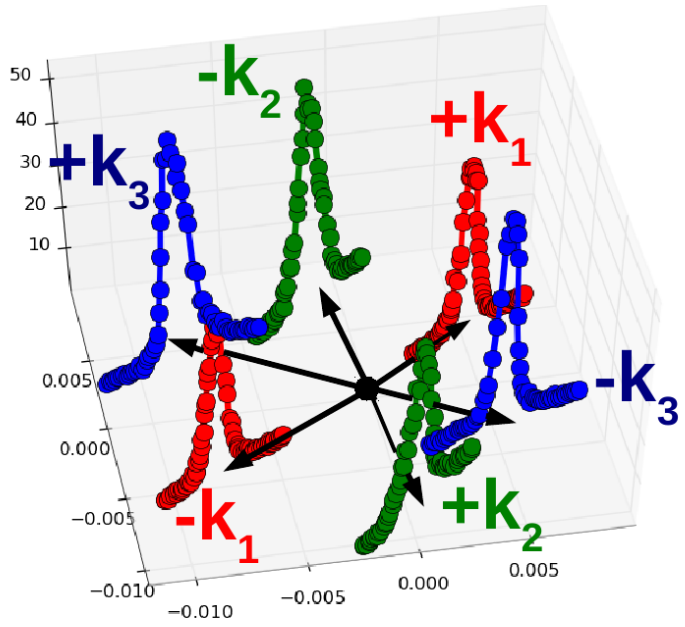


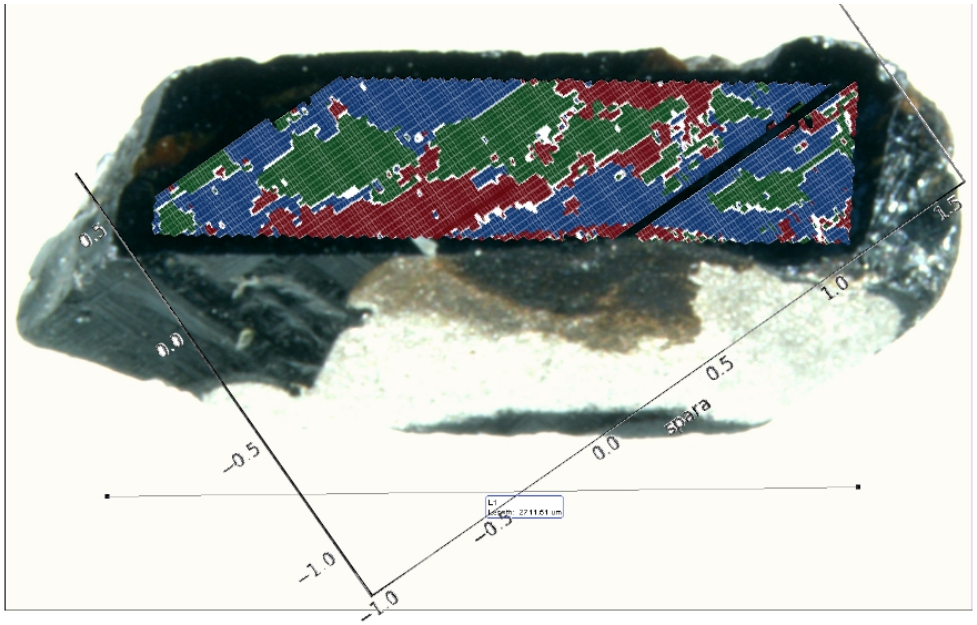


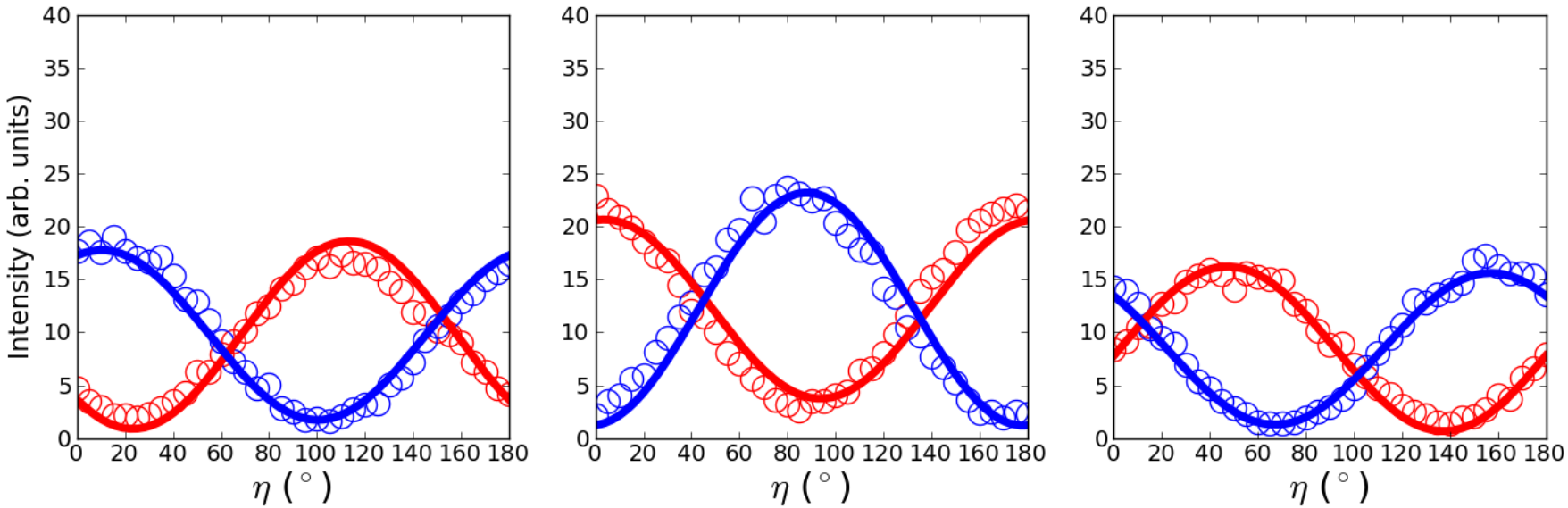




K-domains in BiFeO3 single crystals

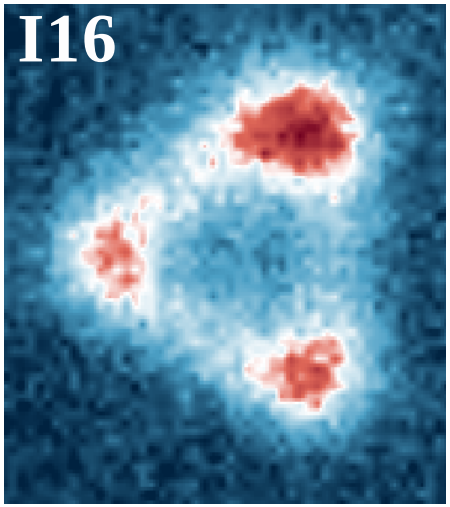


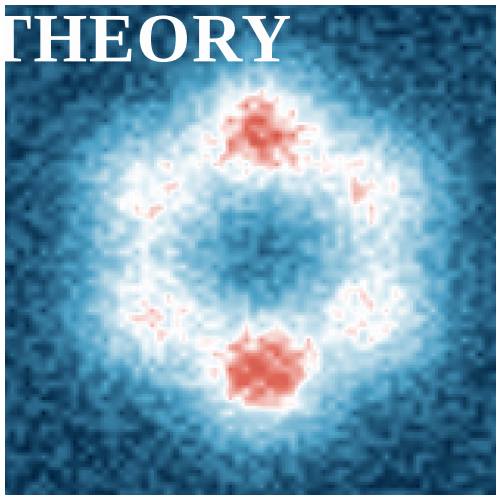


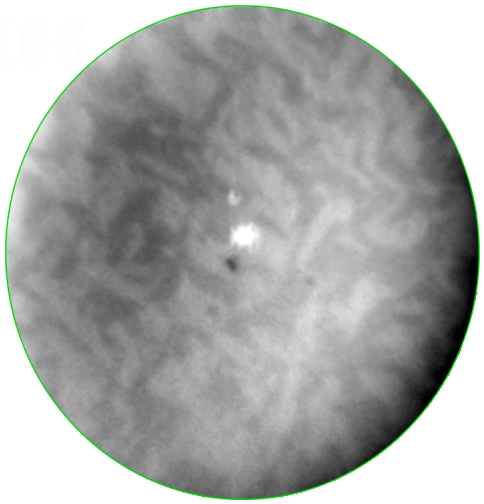


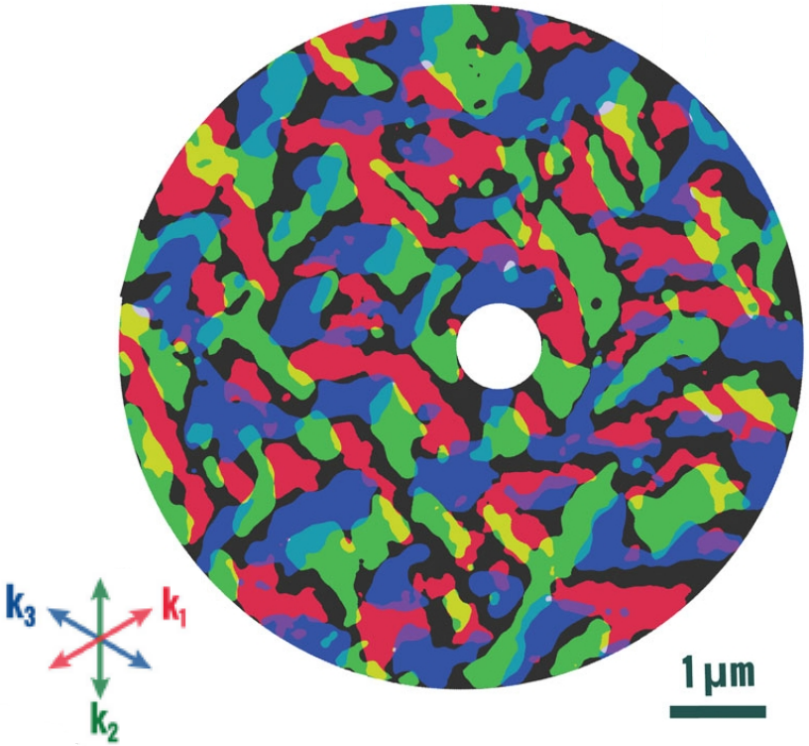
R. Johnson et al., PRL 2012

K-domains in BiFeO3 thin films









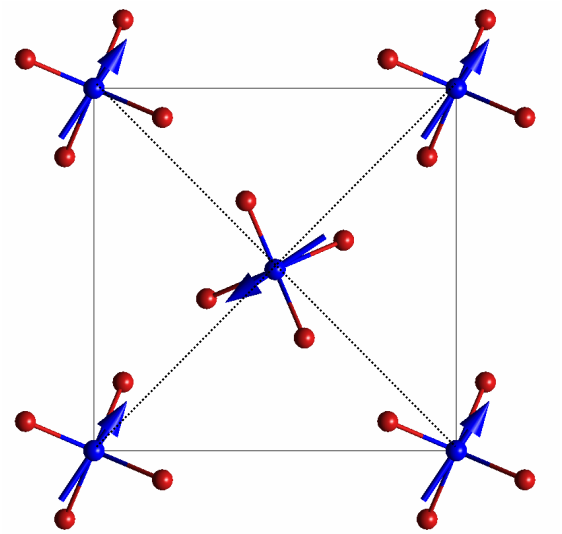
Neutron and X-Ray Diffraction results all pointed towards a monoclinic distortion generating magnetic domains less than 1µm in size for the $BiFeO_3$ thin films.

PhotoEmission Electron Microscopy (PEEM) eventually uncovered the elusive magnetic domain structure in the strained $BiFeO_3$ films.

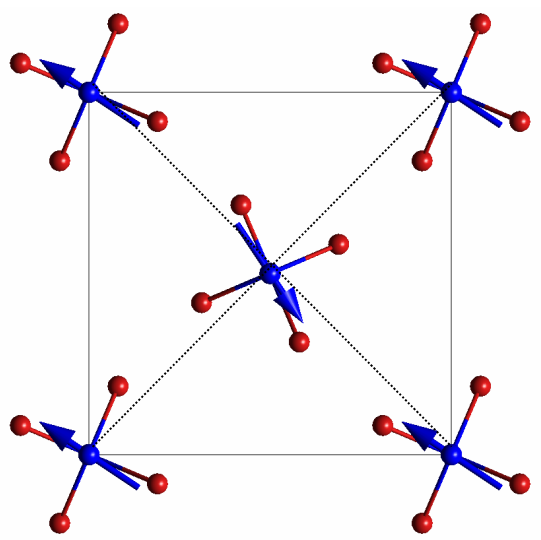
N. Waterfield-Price *et al.*, Phys. Rev. Lett. **117,** 117601 (2016)

S-domains

a)



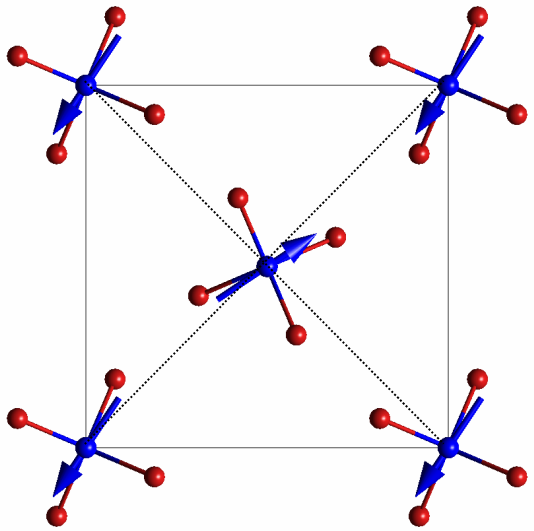
b)



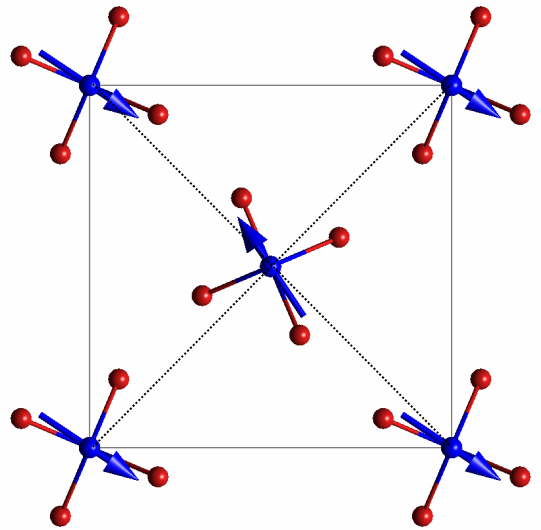
$BaCo_2Ge_2O_7$
Space group *P -4 2_1 m*

k=0

c)

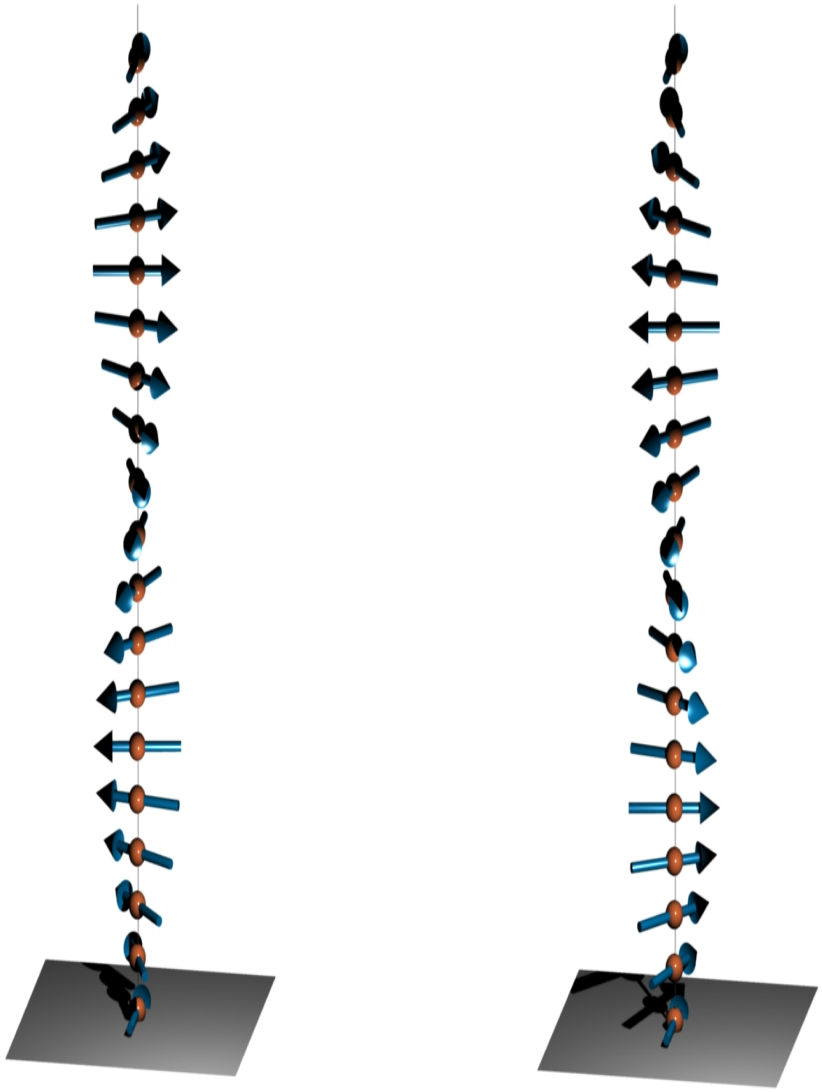


d)



In this case, there is no loss of translational symmetry but a loss of rotational invariance (4-fold axis since the moments are in-plane)

Chiral-domains



- Loss of inversion symmetry generates two domains of opposite handedness
- Note however that this is not the case if the paramagnetic group is a chiral group, in which case a single handedness is stabilized (no energy degeneracy)

The use of symmetry

1945:Shubnikovre-introduces the time reversal group {1,1’} first described by **Heesch in 1929**, Z. Krist. **71**, 95.

1951:Shubnikovdescribes the bi-colourpoint groups

1955:Belov, **Neronova**& **Smirnova** provide for the first time the full list of 1651 Shubnikov space groups. Sov. Phys. Crystallogr. **1**, 487-488

1957:Zamorzaevderives, using group theory, the Shubnikov groups. Kristallografiya**2**, 15 (Sov. Phys. Cryst., **3**, 401)

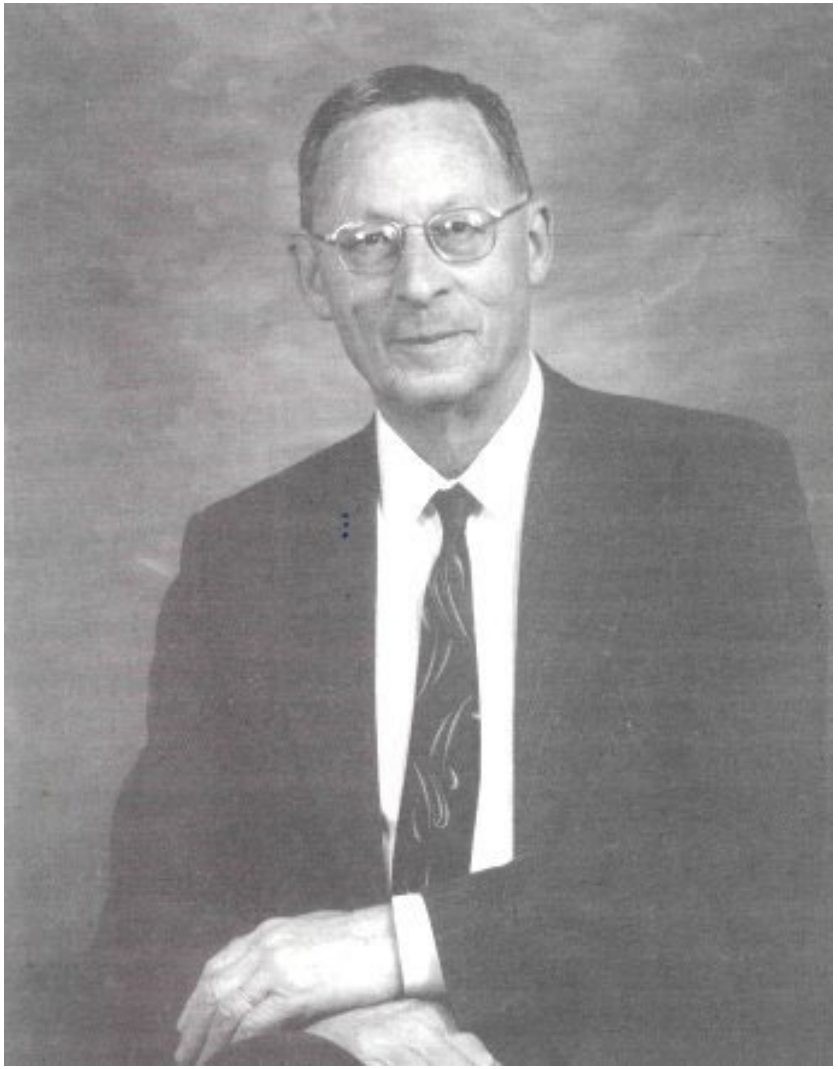
1965:Opechowski and **Guccione** derive and enumerate the full list of magnetic space groups (Shubnikov groups)

1968: Describing 3-dimensional Periodic Magnetic Structures by Shubnikov Groups **Koptsik, V.A.**
Soviet Physics Crystallography, **12**(5) , 723 (1968)

2001:Daniel B. Litvin provides for the first time the full description of all Shubnikov (Magnetic Space) Groups. Acta Cryst. **A57**, 729-730

2010: Magnetic Space Groups on computer programs
Compiled by Harold T. Stokes and BrantonJ. Campbell
Brigham Young University, Provo, Utah, USA June 2010

Key work

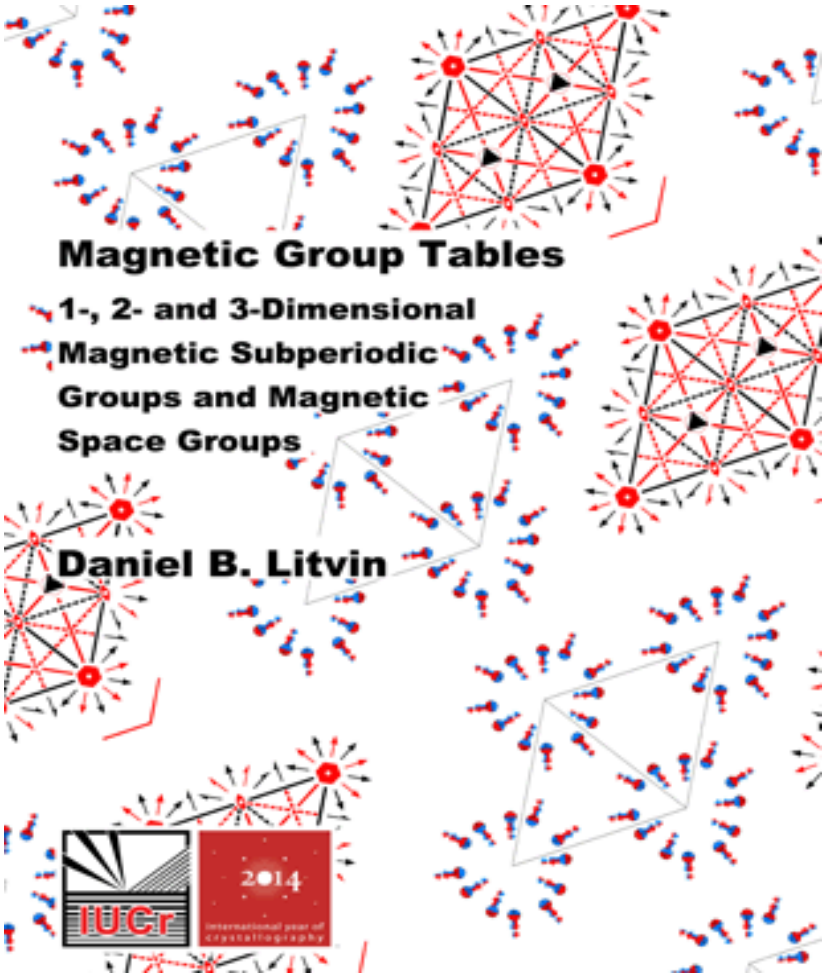


Representation analysis of magnetic structures

F. Bertaut, Acta Cryst. (1968). A24, 217-231

'Felix Bertaut is a mathematician who does crystallography'. Andre Guinier

https://www.iucr.org/publ/978-0-9553602-2-0



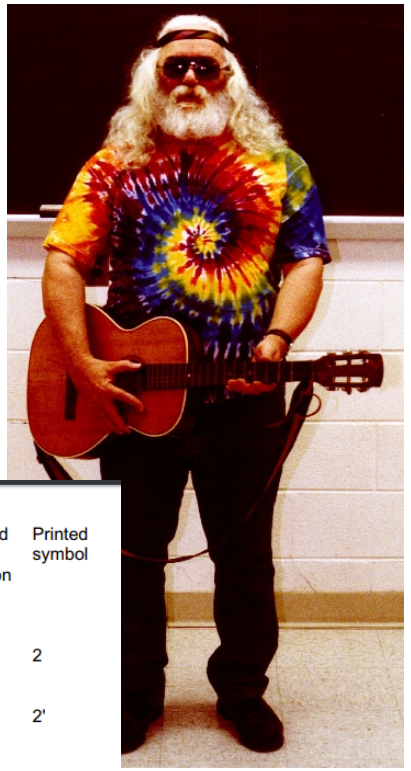
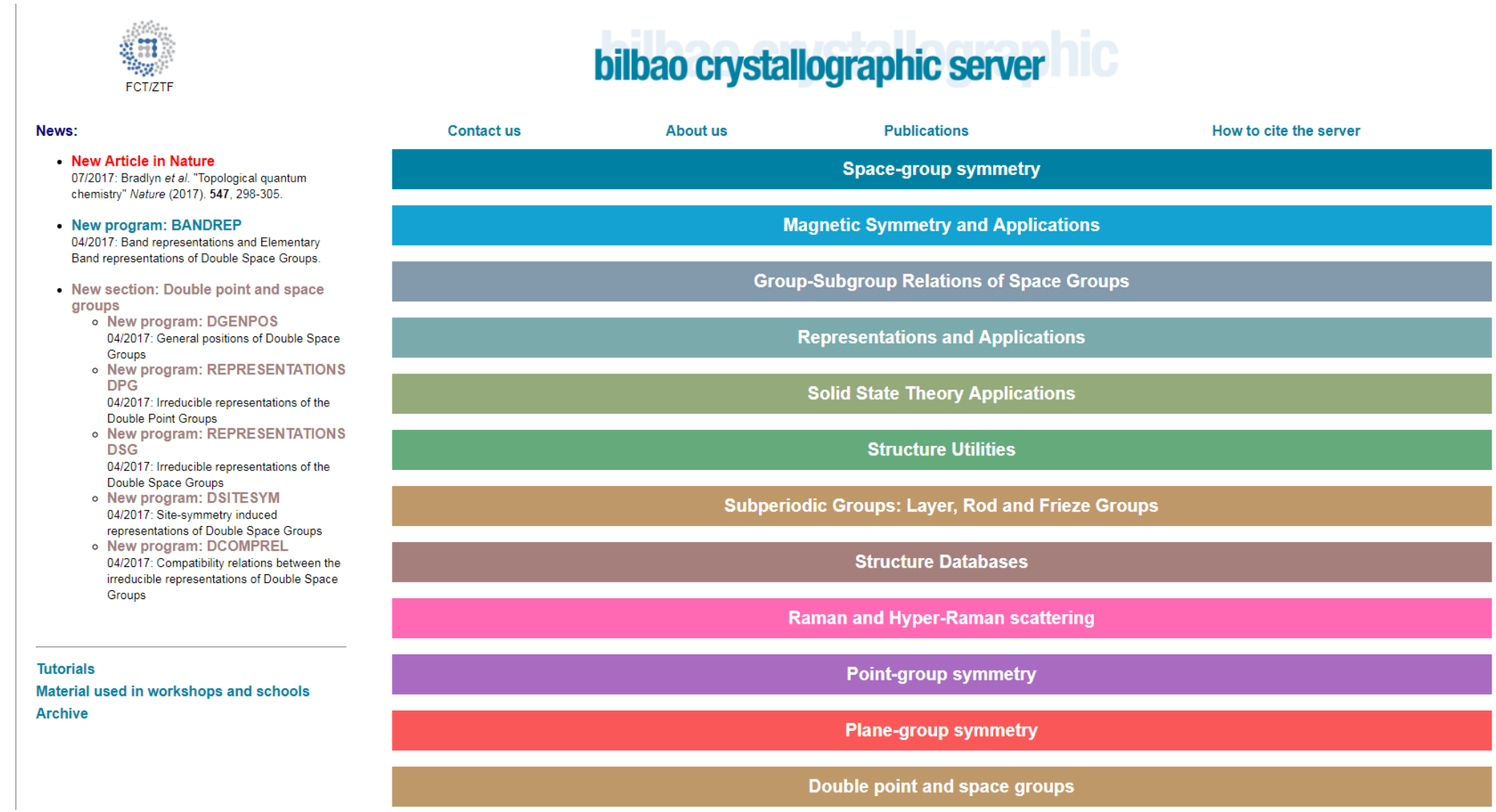


Table 2.2.3.1: Symmetry axes parallel to the plane of projection

Symmetry Axis	Graphical symbol	Screw vector of a right-handed screw rotation in units of the shortest non-primed translation vector parallel to the axis.	Printed symbol
Twofold unprimed rotation axis,		None	2
Twofold primed rotation axis		None	2'
Twofold unprimed screw axis, 2 sub 1		½	2_1
Twofold primed screw axis, 2 sub 1 primed		½	$2_1'$
Fourfold unprimed rotation axis		None	4
Fourfold primed rotation axis		None	4'
Fourfold unprimed screw axis, 4 sub 1		1/4	4_1
Fourfold primed screw axis, 4 sub 1 primed		1/4	$4_1'$

Software for magnetic symmetry

http://www.cryst.ehu.es/



Software for magnetic symmetry

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

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.
- **New!** 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

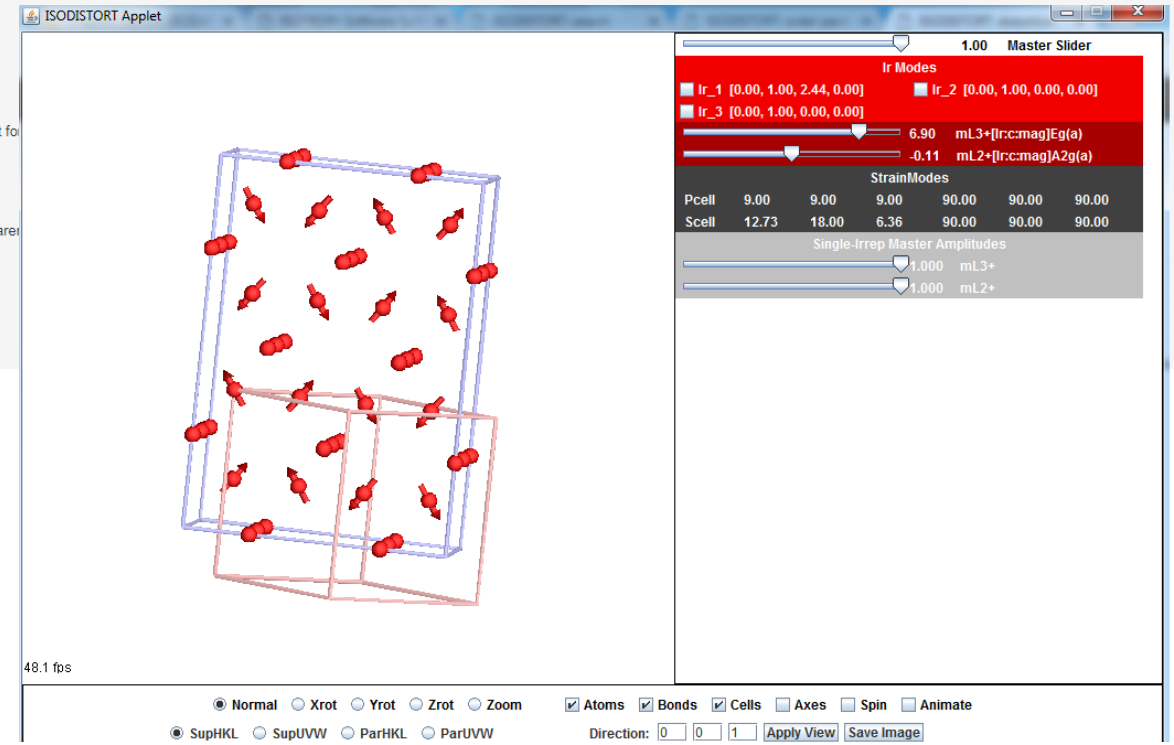
- ISO(3+d)D: (3+d)-Dimensional Superspace Groups for d=1,2,3
- ISO(3+1)D: Isotropy Subgroups for Incommensurately Modulated Distortions in Crystalline Solids: A Complete List fo
- FINDSSG: Identify the superspace group symmetry given a list of symmetry operators.
- TRANSFORMSSG: Transform a superspace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



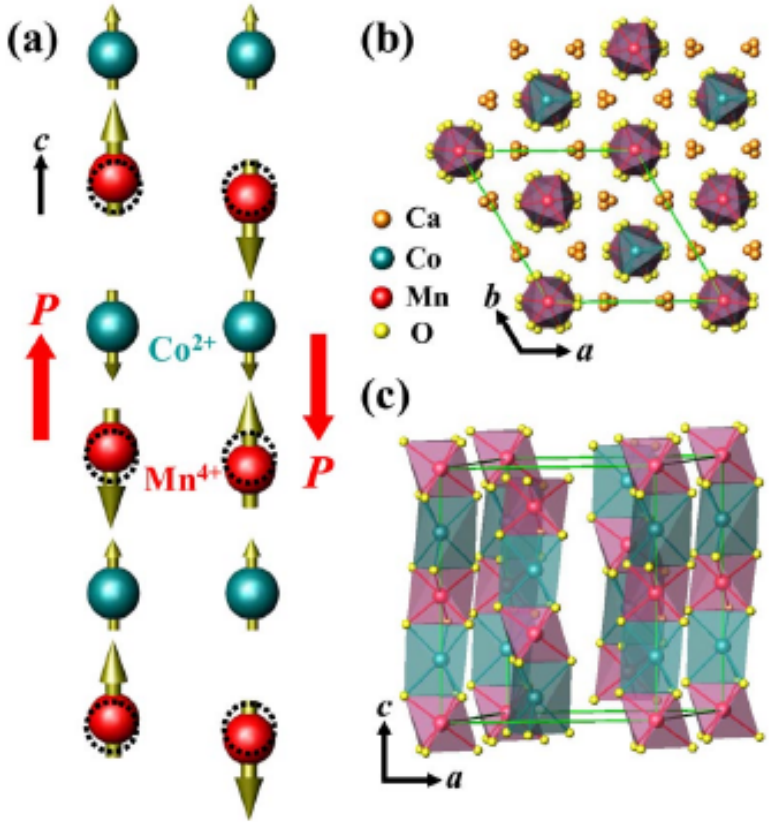
The Isodistort applet is extremely useful for commensurate/incom. structures

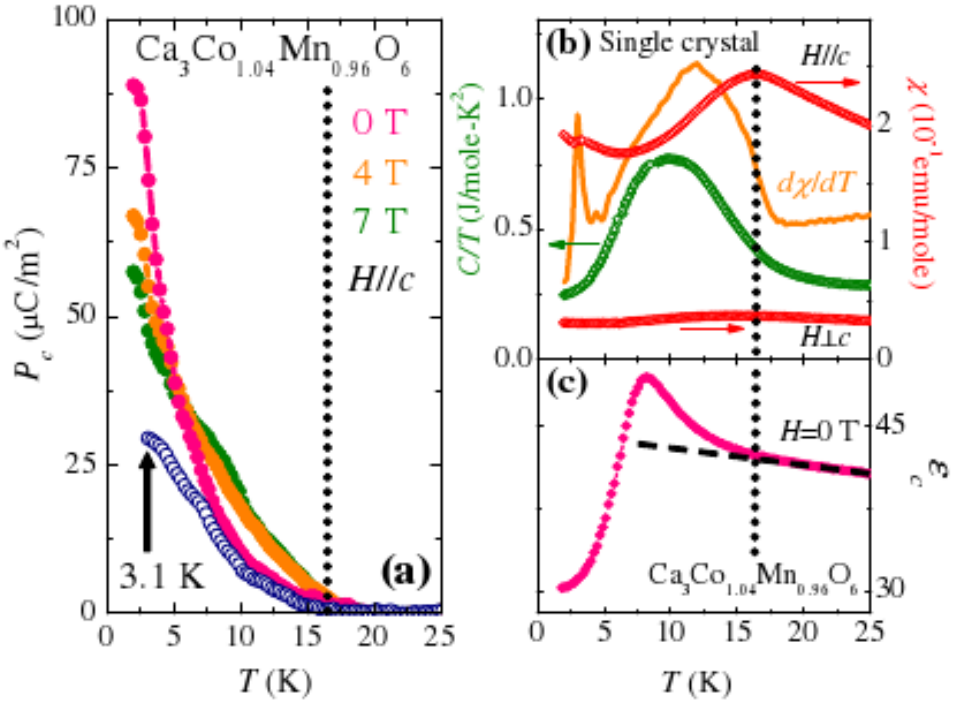
A more complex example: Ca_3CoMnO_6

PRL 100, 047601 (2008) PHYSICAL REVIEW LETTERS week ending 1 FEBRUARY 2008

Ferroelectricity in an Ising Chain Magnet

Y. J. Choi,[1] H. T. Yi,[1] S. Lee,[1] Q. Huang,[2] V. Kiryukhin,[1] and S.-W. Cheong[1]

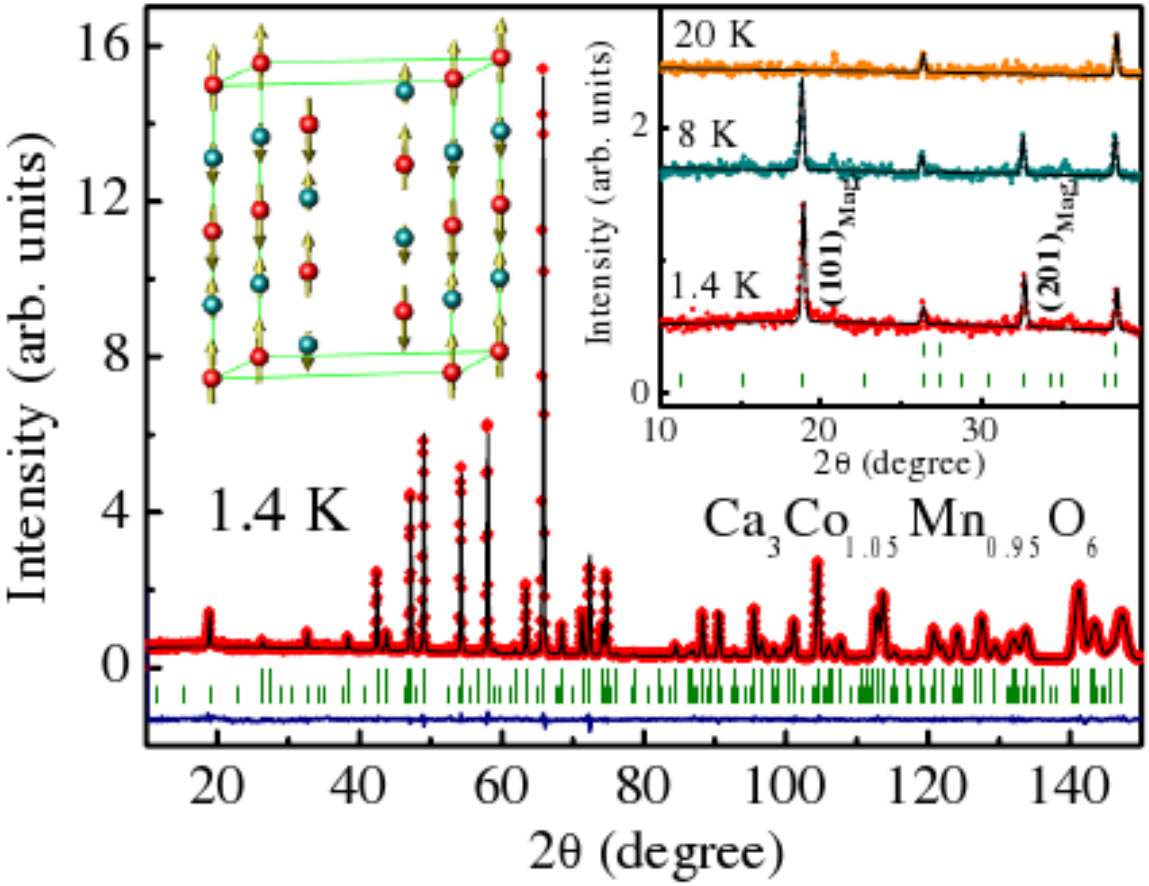




diamond

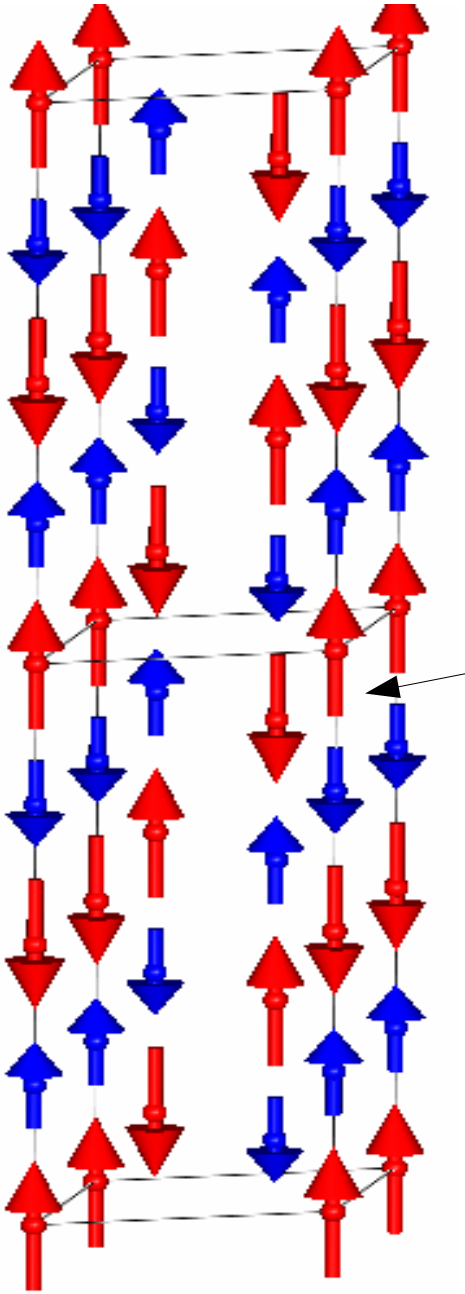
Ca_3CoMnO_6

Space group: *R-3c*
Charge ordered:
Mn^{4+} position (0,0,0)
Co^{2+} position (0,0,1/4)
Magnetic propagation vector k=0



diamond

Ca_3CoMnO_6



It is obvious that the 3-fold symmetry axis is preserved.
However, for example the inversion center is lost.
It can not be simultaneously

- $\bar{1}$ (Mn moments red)
- $\bar{1}$,(Co moments blue)

The magnetic modes belongs to:
- Irep(1) for Mn
- Irep(4) for Co (see next slide)

Ca_3CoMnO_6

	1	3+ 0,0,z	3- 0,0,z	2 x,x,1/4	2 x,0,1/4	2 0,y,1/4	-1 0,0,0	-3+ 0,0,z; 0,0-3- 0,0,z; 0,0c	x,-x,z	c x,2x,z	c 2x,x,2z
v	{1|000}	{3+_00z|000}	{3-_00z|000}	{2_xx0|00p}	{2_x00|00p}	{2_0y0|00p}	{-1|000}	{-3+_00z|000} {-3-_00z|000}	{m_x-xz|00p}	{m_x2xz|00p}	{m_2xxz|00p}
v	Symm(1)	Symm(2)	Symm(3)	Symm(4)	Symm(5)	Symm(6)	Symm(7)	Symm(8) Symm(9)	Symm(10)	Symm(11)	Symm(12)
IRrep(1):	1	1	1	1	1	1	1	1 1	1	1	1
IRrep(2):	1	1	1	1	1	1	-1	-1 -1	-1	-1	-1
IRrep(3):	1	1	1	-1	-1	-1	1	1 1	-1	-1	-1
IRrep(4):	1	1	1	-1	-1	-1	-1	-1 -1	1	1	1
IRrep(5):	1 0 0 1	a 0 0 b	b 0 0 a	0 1 1 0	0 b a 0	0 a b 0	-1 0 0 -1	-a 0 0 -b	-b 0 0 -a	0 -1 -1 0	0 -b -a 0	0 -a -b 0
IRrep(6):	1 0 0 1	a 0 0 b	b 0 0 a	0 1 1 0	0 b a 0	0 a b 0	1 0 0 1	a 0 0 b	b 0 0 a	0 1 1 0	0 b a 0	0 a b 0

r1

r2

P_z P_z P_z $-P_z$ $-P_z$ $-P_z$ $-P_z$ $-P_z$ $-P_z$ P_z P_z P_z

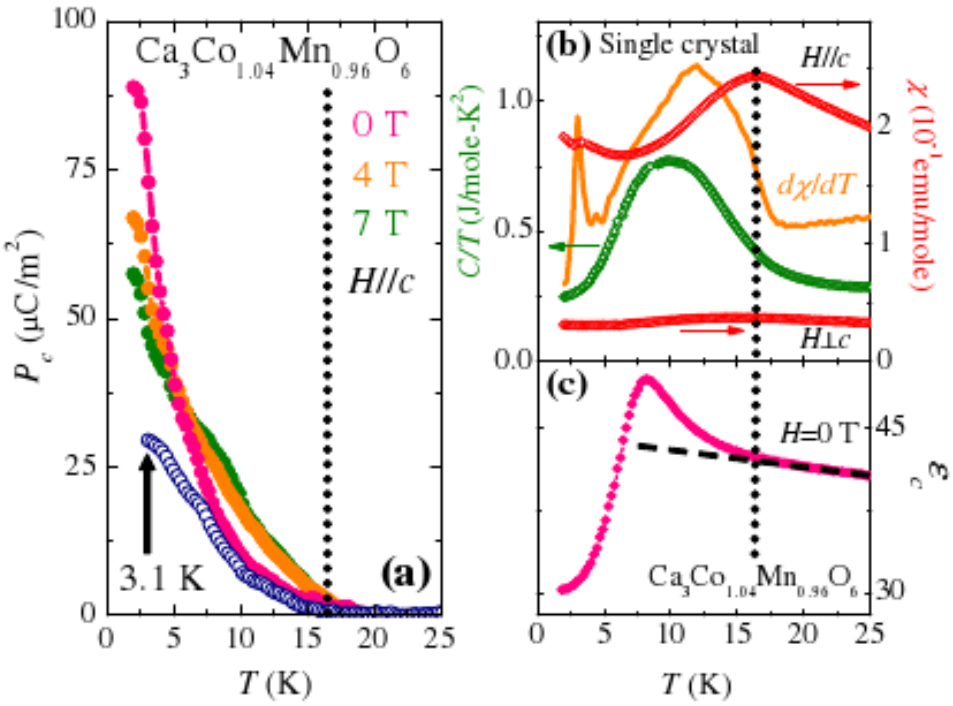
Point group 3m (C3v) ⇒ **Electric P allowed along c.**

diamond

$$F = F_0 + \alpha_1 \rho_1^2 + \beta_1 \rho_1^4 + \alpha_2 \rho_2^2 + \beta_2 \rho_2^4 + \gamma \rho_1 \rho_2 P_z + \frac{P_z^2}{\chi_{zz}}$$

Stability condition : $\frac{\partial F}{\partial P_z} = 0$

$$P_z = -\gamma \rho_1 \rho_2 \chi_{zz}$$



diamond