Advanced magnetic structures: classification and determination by neutron diffraction

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Lecture course 402-0543-00L:
Neutron Scattering in Condensed Matter Physics
24.03.10 Lecture 12: Advanced magnetic structures

Purpose of this lecture

1. You need to acquaint yourself with the classification of the magnetic structures that are used in the literature, such as Shubnikov (or black-white) groups and irreducible representation notations.
2. You need to be able to construct all possible symmetry adapted magnetic structures for a given crystal structure and a propagation vector (a point on the Brilloine zone) using *representation (rep) analysis of magnetic structures*. This way of description/construction is related to the Landau theory of second order phase transitions and applies not only to magnetic ordering, but generally to any type of phase transitions. For example, using the *rep*-analysis one can analyze displacive crystal structure transitions.

Overview of Lecture

- Long range magnetic order seen by ND. Two ways of magnetic structure classification: “Shubnikov” vs. “reps analysis” -- *introduction* 9
- Point groups. Intro to group representations (reps) 12
- Irreducible representations (irreps) 8
- Basic crystallography. Symmetry elements. Space groups (SG) 5
- Irreps of SG. Reciprocal lattice. Propagation k-vector of <magnetic> structure/Brillouine zone points 8
- Case study of magnetic structure determination using k-vector reps formalism for classifying symmetry adopted magnetic modes 12
- Magnetic Shubnikov groups. Comparison of two ways of magnetic structure classification/determination: “Shubnikov” vs. “reps analysis” 4

Literature on (magnetic) symmetry and magnetic neutron diffraction

All you need to know about magnetic neutron diffraction. Magnetic symmetry, representation analysis

Yu. A. Izyumov, V. E. Naish and R. P. Ozerov, ”*Neutron diffraction of magnetic materials*”, New York [etc.]: Consultants Bureau, 1991.

and

Groups, representation analysis, point groups and simple applications, e.g. molecular vibrations, crystal field theory.

J.P Elliott and P.G. Dawber “*Symmetry in physics*”, vol. 1, 1979 The Macmillan press LTD

Notes, papers, talks and computer programs, etc. on magnetic structures, (magnetic) symmetry and magnetic neutron diffraction

- Andrew S. Wills (UCL) http://www.chem.ucl.ac.uk/people/wills/magnetic_structures/magnetic_structures.html
- Juan Rodríguez-Carvajal (ILL) et al, http://www.ill.fr/sites/fullprof/ `program BasIreps`
- Wiesława Sikora et al, http://www.ftj.agh.edu.pl/~sikora/modyopis.htm
- Bilbao Crystallographic Server is a web site with crystallographic programs and databases accessible via Internet
  bilbao crystallographic server http://www.cryst.ehu.es/

V. Pomjakushin , "*Determination of the magnetic structure from powder neutron diffraction.*" Lecture given at the "Workshop on X-rays, Synchrotron Radiation and Neutron Diffraction Techniques, June 18-22, 2008, PSI, http://sinq.web.psi.ch/sinq/instr/hrpt/praktikum

Magnetic structure seen by ND

Magnetic interactions are described by QM Hamiltonian with quantum spin operators

$$\hat{H} = -\sum_{i,j} J_{ij} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j + \sum_i D_i \hat{s}_z^2 + \ldots$$

In a diffraction experiment (coherent Bragg scattering), however, the problem is reduced and we observe only the following correlators. <> averaging over all initial states of the scatterer. i,j=1..N

$$\sim \sum \left\langle \hat{\mathbf{s}}_i \right\rangle \cdot \left\langle \hat{\mathbf{s}}_j \right\rangle$$ = Fourier sum of ***classical*** axial vectors

Magnetic structure that we observe is an ordered set of ***classical*** axial vectors $\mathbf{s}_i = \left\langle \hat{\mathbf{s}}_i \right\rangle$ that can be directed at any angle with respect to crystal axes and field.

In the symmetry analysis we deal with the classical spins (*no coreprs*).

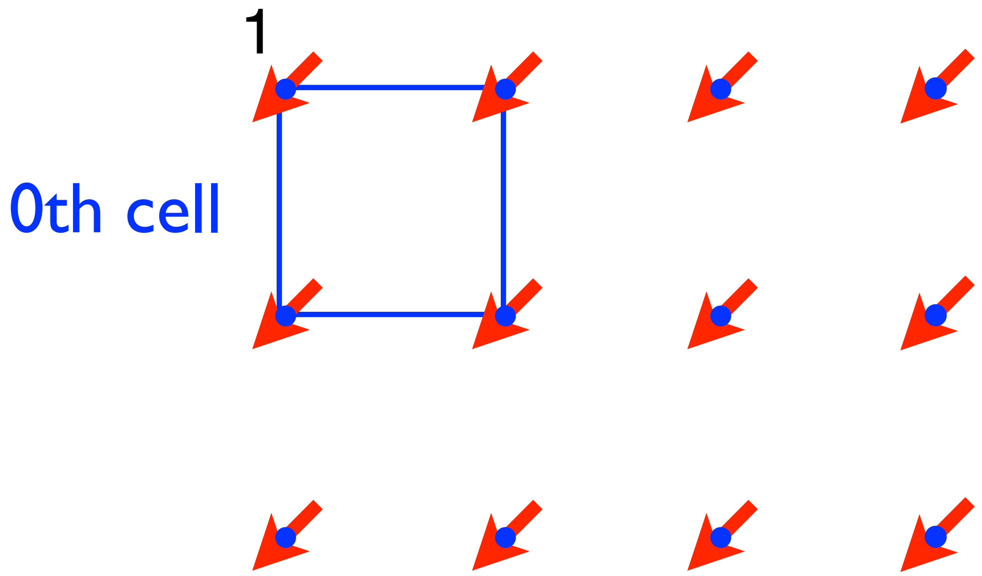
$$\mathbf{s}_i = \left\langle \hat{\mathbf{s}}_i \right\rangle = s_x \mathbf{e}_{\boldsymbol{x}} + s_y \mathbf{e}_{\boldsymbol{y}} + s_z \mathbf{e}_{\boldsymbol{z}}$$

$$\xcancel{\left\langle \hat{s}_z \right\rangle, \left\langle \widehat{\mathbf{s}^2} \right\rangle}$$

Magnetic structure

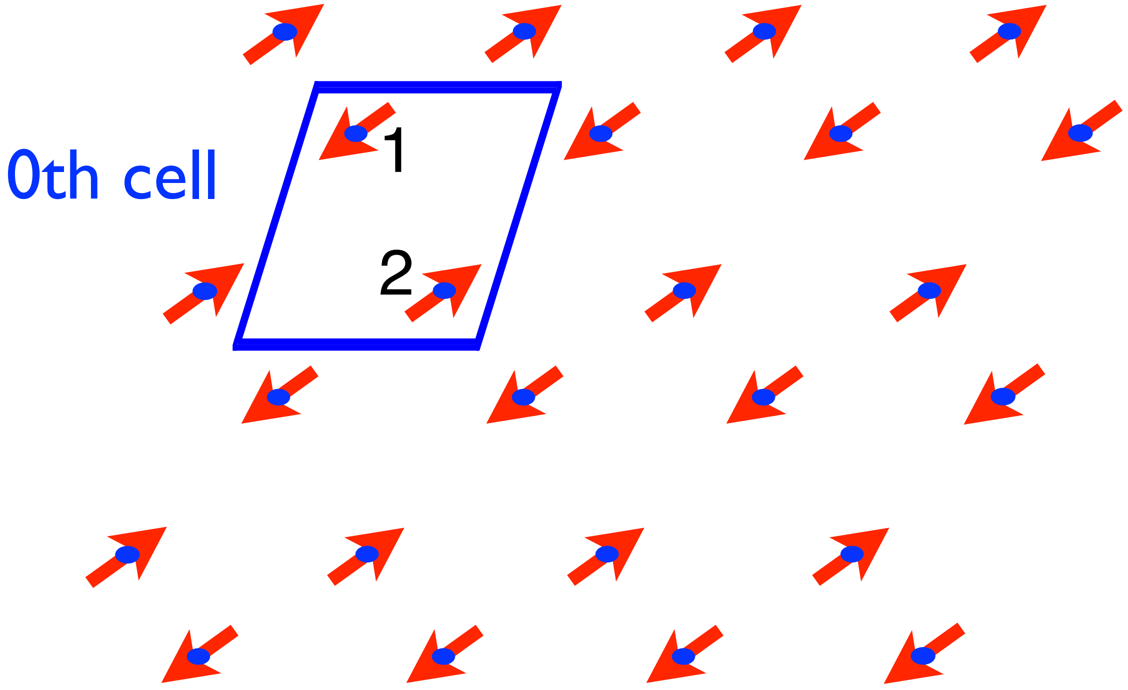
Examples

k=[0,0]
FM



$$\mathbf{S}_{01} = \mathbf{S}_x + \mathbf{S}_y$$

k=[0,0]
AFM



$$\mathbf{S}_{01} = \mathbf{S}_x + \mathbf{S}_y$$

$$\mathbf{S}_{02} = -\mathbf{S}_{01}$$

Examples of magnetic structures.
Propagation vector k≠0

Magnetic moment
is a real quantity

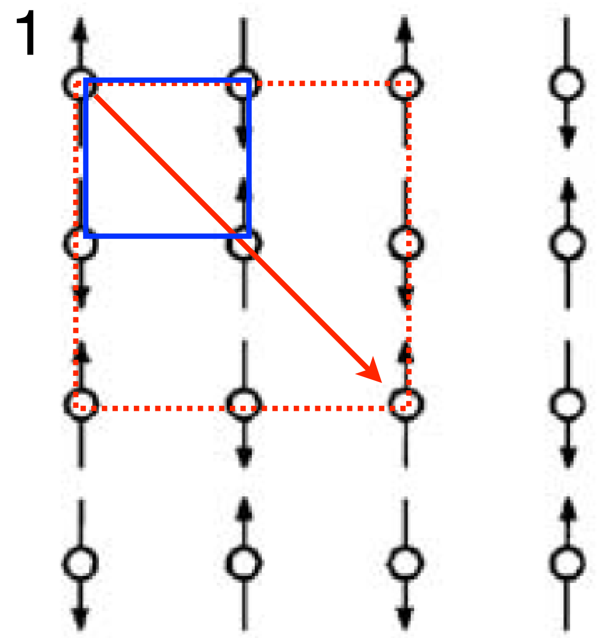
$$\mathbf{S}(\mathbf{r}_j) = \frac{1}{2}(\mathbf{S}_0 e^{+2\pi i \mathbf{r}_j \mathbf{k}} + \mathbf{S}_0^* e^{-2\pi i \mathbf{r}_j \mathbf{k}})$$

Bloch waves

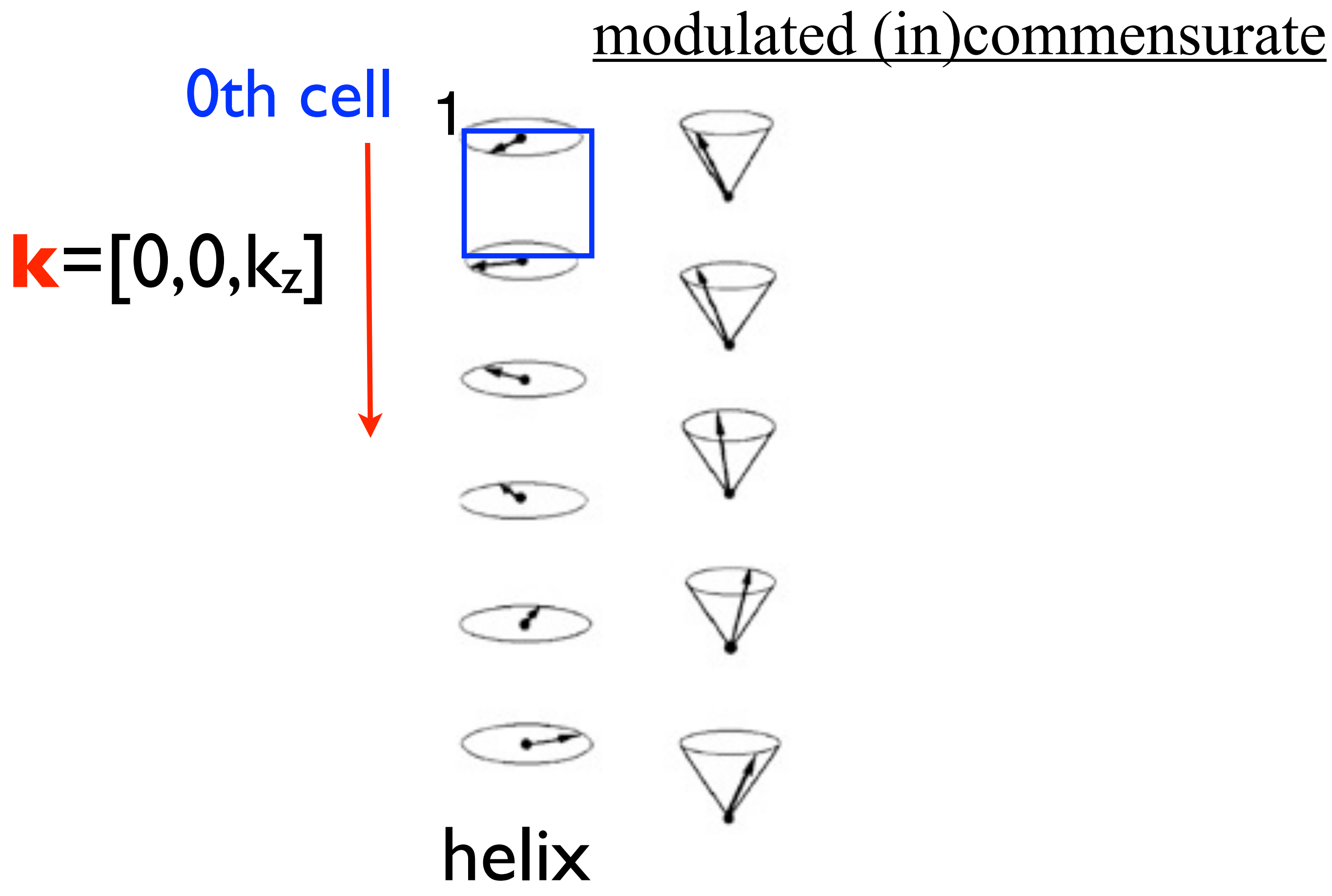
Amplitude is complex
(one can not avoid this)

$$\mathbf{S}_0 = \mathbf{S}_x e^{i\phi_x} + \mathbf{S}_y e^{i\phi_y} + \mathbf{S}_z e^{i\phi_z}$$

k=[1/2,1/2] AFM



$$\mathbf{S}_{01} = \mathbf{S}_y$$



$$\mathbf{S}_{01} = \mathbf{S}_x + \mathbf{S}_y e^{\frac{i\pi}{2}} = \mathbf{S}_x + i\mathbf{S}_y$$

$$\mathbf{S}_{01} = \mathbf{S}_x + i\mathbf{S}_y + \mathbf{S}_z e^{i\phi_z}$$

Interference between nuclear and magnetic scattering (slide skipped)

General note:

When the magnetic unit cell is larger than the nuclear one (propagation vector $k \neq 0$) the interference between nuclear and magnetic scattering is absent in any (un)polarized neutron diffraction experiment.

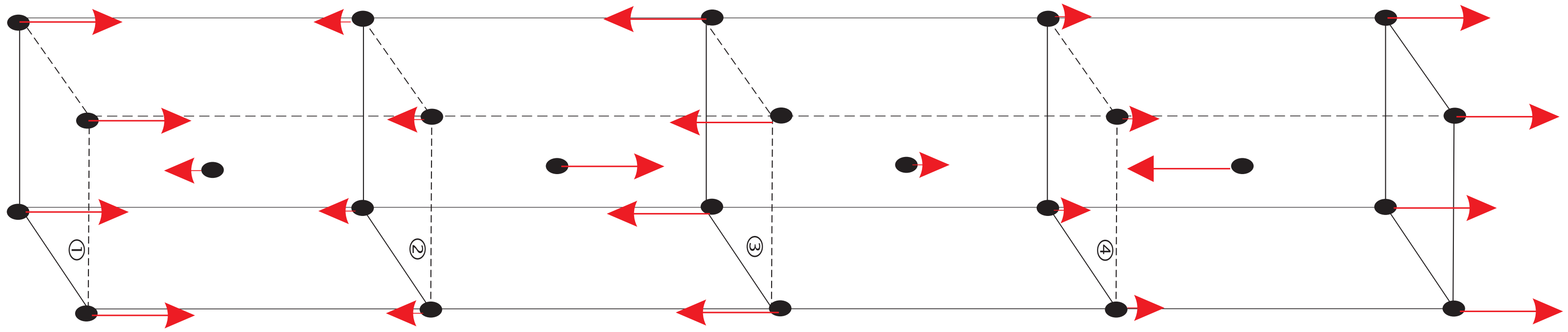
Reason: Magnetic Bragg peaks appear at different from nuclear peaks positions in reciprocal space

Only amplitudes can be determined (slide skipped)

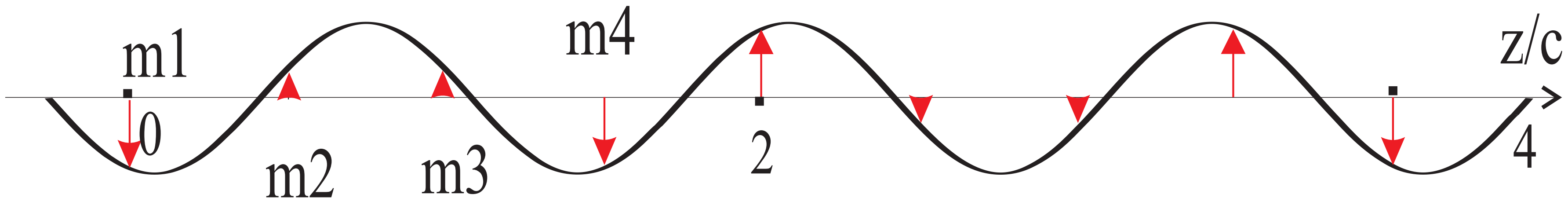
$$\mathbf{S} = \mathbf{S}_0 \cos(2\pi k z + \phi), k = \frac{3}{4} \qquad I \sim S_0^2 + S_0 F \xcancel{\cos(\phi)}$$

Spin/atom magnetic moment

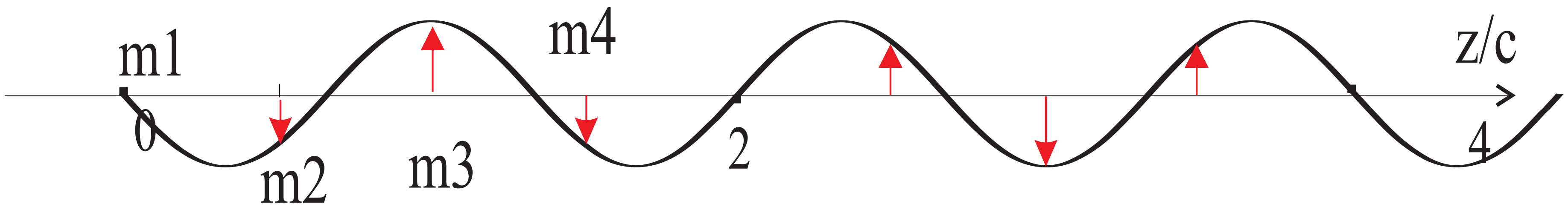
Amplitude



$\phi = 7\pi/8$



$\phi = \pi/2$



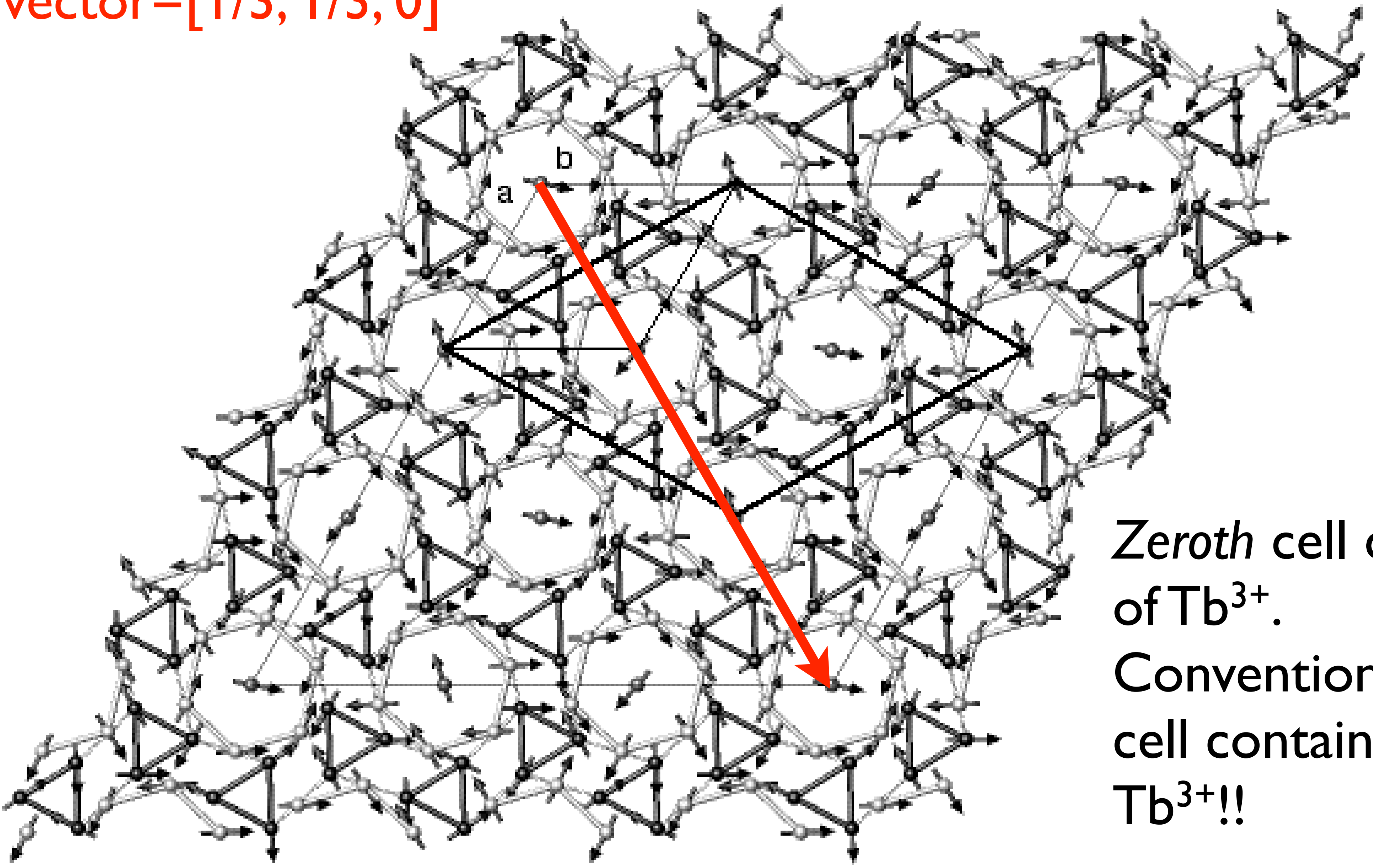
The phase Φ is not accessible and the magnetic moments on the atoms cannot be determined.

Example of complex magnetic structure

Antiferromagnetic three sub-lattice ordering in $Tb_{14}Au_{51}$

P6/m

k-vector=[1/3, 1/3, 0]



Zeroth cell contains **14** spins of Tb^{3+}.

Conventional magnetic unit cell contains 126 spins of Tb^{3+}!!

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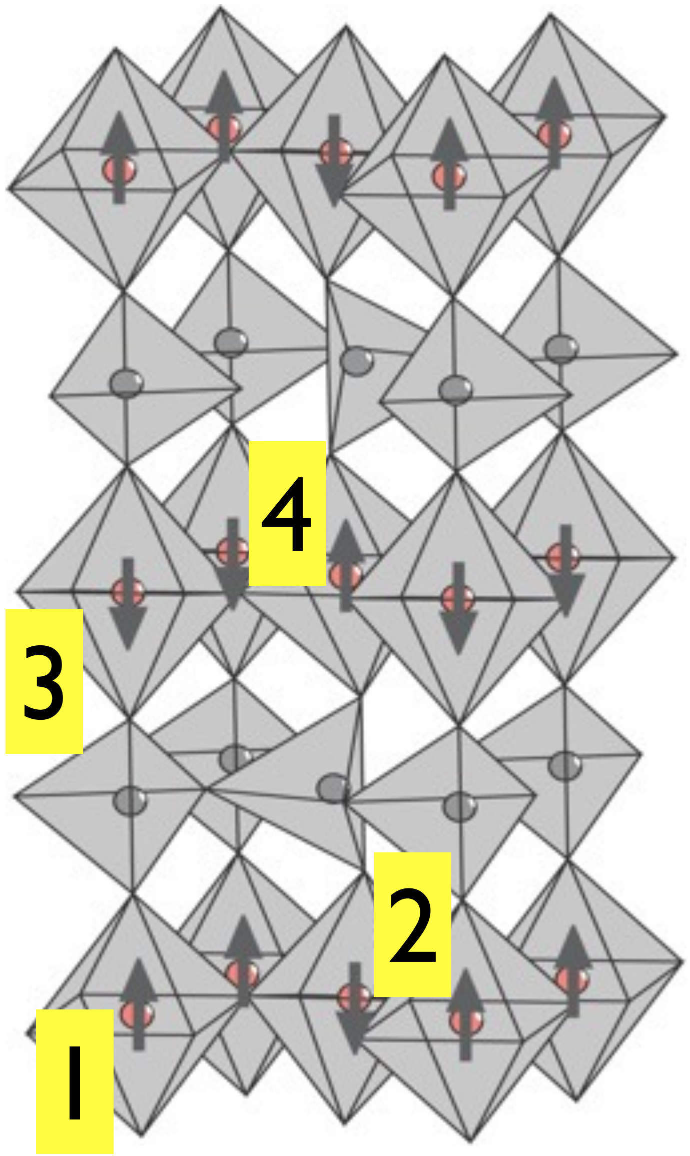
Some legitimate questions

1. How do we describe/classify/predict magnetic symmetries and structures?
2. How do we construct all symmetry allowed magnetic structures for a given crystal structure?

Description vs. determination/constructiveness

Two ways of description of magnetic structures

Magnetic structure is an axial vector function **S**(**r**) defined on the discreet system of points (atoms), e.g. $\mathbf{S}(\mathbf{r}) = \mathbf{s}(\mathbf{r}_1) \oplus \mathbf{s}(\mathbf{r}_2) \oplus \mathbf{s}(\mathbf{r}_3) \oplus \mathbf{s}(\mathbf{r}_4)$



1. g**S**(**r**) = **S**(**r**) to itself, where g∈ subgroup of SG⊗1’, 1’=spin reversal, SG (space group)

   or

2. g**S**(**r**) = **S**’(**r**) to different function defined on the same system of points, g∈ SG

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r) = **S**(**r**) to itself, where g ∈ subgroup of
⊗1', 1'=spin reversal, SG (space group)

r) = **S'**(**r**) to different function defined on the
e system of points, g ∈ SG

Two ways of description of magnetic structures

1. **Magnetic or Shubnikov groups.** Historically the first way of description. A group that leaves **S**(**r**) invariant under a subgroup of G⊗1'. Identifying those symmetry elements that leave S(r) invariant.
   Similar to the space groups (SG 230). Defining of all possible magnetic space groups MSG: a crystallographer dream. The MSG symbol looks similar to SG one, e.g. *Pn'ma*

SG 62 ***Pnma***

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

MSG

2. Representation analysis. How does **S**(**r**) transform under g ∈ G (space group)?

S(**r**) that is transformed under g ∈ G according to a single irreducible representation τ_i of *G.* Identifying/classifying all the functions **S'**(**r**) that appears under all symmetry operators of the space group G

$d^{\mathbf{k}\nu}(g)$

g	$/2$	$/3$	$/4$	$/25$	$/26$	$/27$	$/28$
$\hat{\tau}1$	1	1	1	1	1	1	1
$\hat{\tau}2$	1	1	1	−1	−1	−1	−1
$\hat{\tau}3$	1	−1	−1	1	1	−1	−1
$\hat{\tau}5$	−1	1	−1	1	−1	1	−1
$\hat{\tau}7$	−1	−1	1	1	−1	−1	1

$\hat{\tau}4 = \hat{\tau}3 \times \hat{\tau}2,\ \hat{\tau}6 = \hat{\tau}5 \times \hat{\tau}2,\ \hat{\tau}8 = \hat{\tau}7 \times \hat{\tau}2$

Introduction to representation theory

Four group axioms

A set G of elements is G_1, G_2, G_3, G_4, ... said to form a group if a low of multiplication of the elements is defined that satisfies certain conditions

Closure

For all G_a, G_b in G, the result of the operation $G_a \bullet G_b$ is also in G.

Associativity

For all G_a, G_b and G_c in G, the equation $(G_a \bullet G_b) \bullet G_c = G_a \bullet (G_b \bullet G_c)$ holds.

Identity element

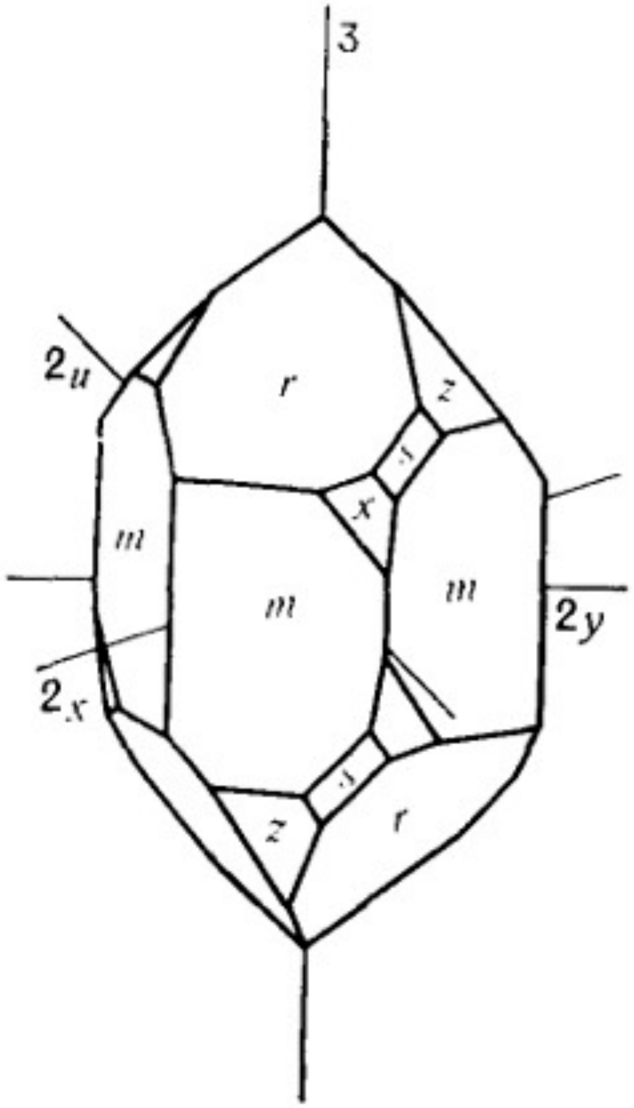
One element of the set E called identity must have the properties $G_a \bullet E = G_a$ and $E \bullet G_a = G_a$

Inverse element

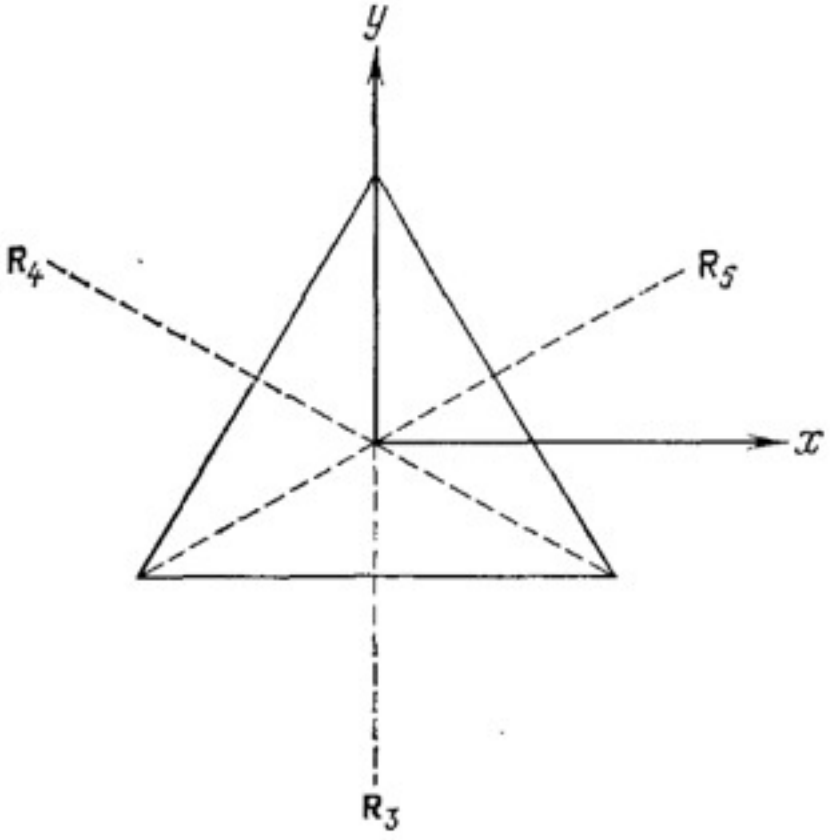
For each G_a in G, there exists an element G_a^{-1} in G such that $G_a \bullet G_a^{-1} = G_a^{-1} \bullet G_a = E$

Example: point group 32

Point group Hermann–Mauguin symbol *32* (D_3 Schoenflies symbol)
e.g Quartz



or regular triangle

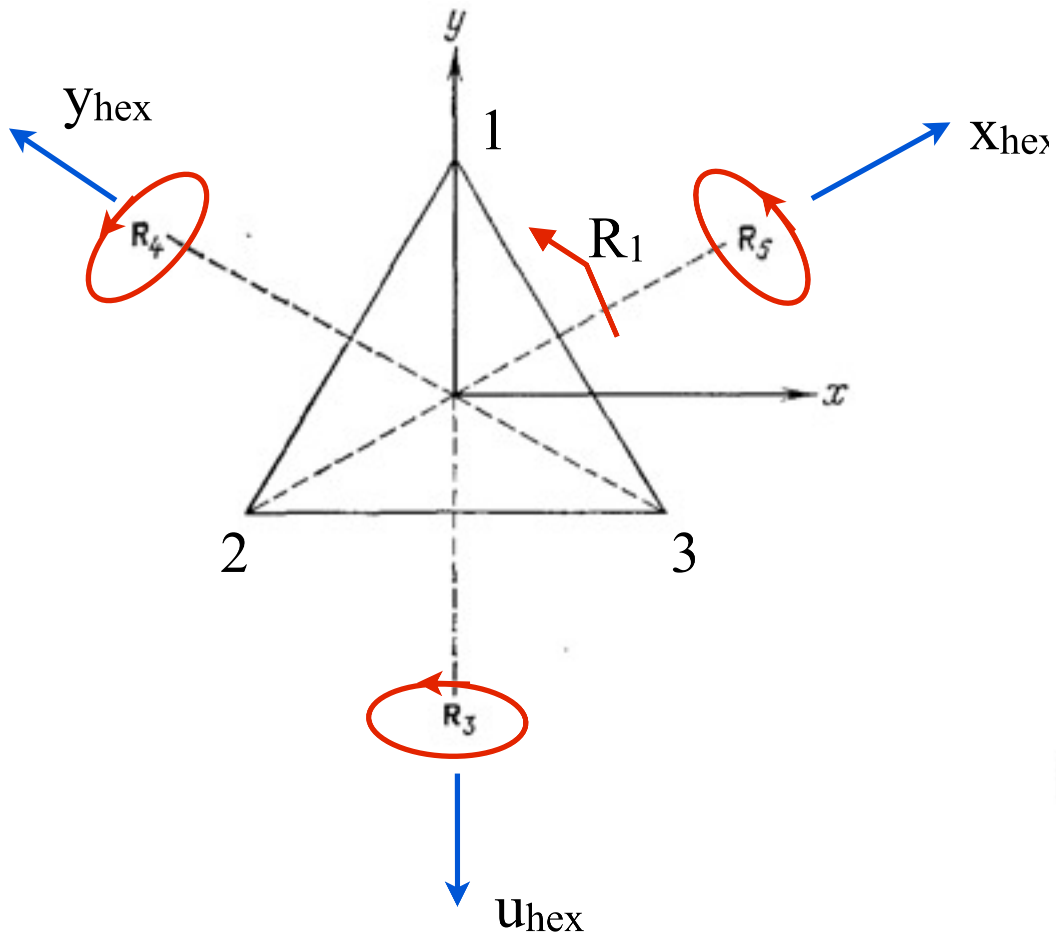


Multiplication table, isomorphism

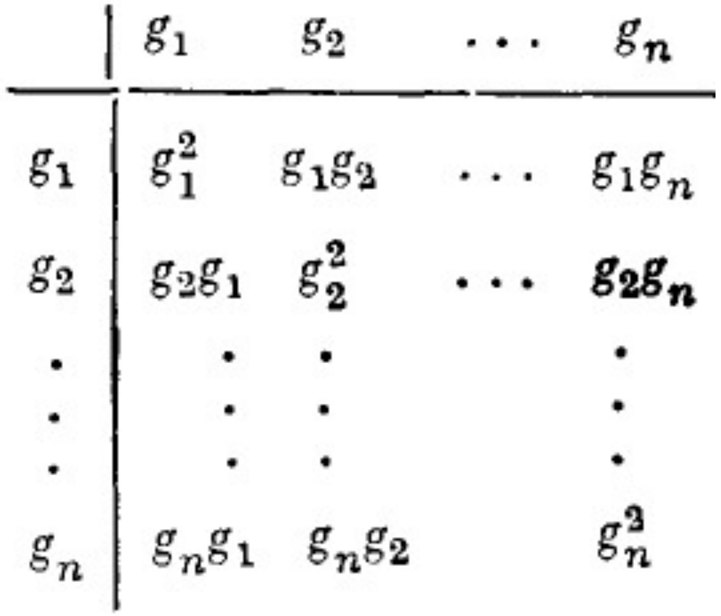
Point group 32 (D_3 Schoenflies symbol)
e.g regular triangle

6 symmetry elements (rotations):
R0=E, R_1=2π/3, R_2=4π/3 around z, R_3, R_4, R_5, = π around resp. axes in xy-plane

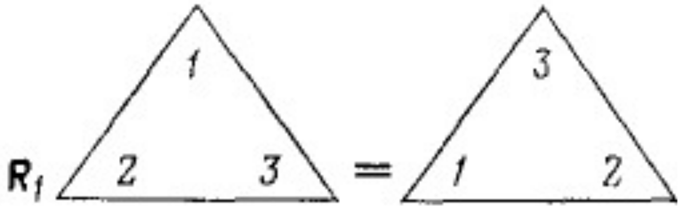
hex → 1 3^1 3^2 2_u 2_y 2_x

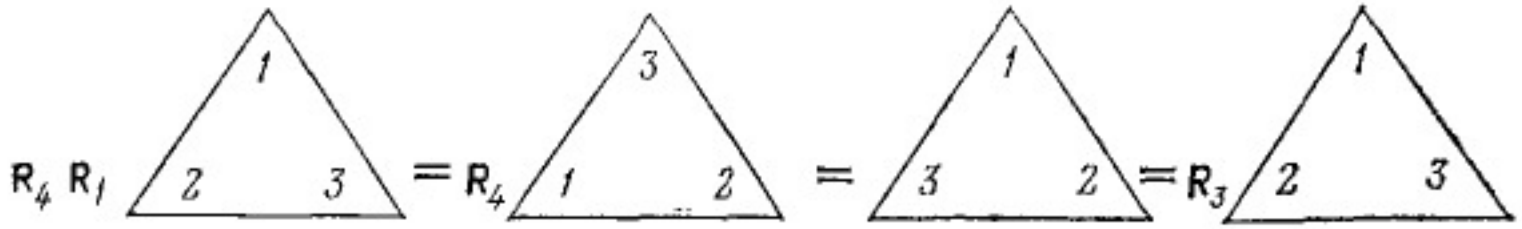


multiplication table



	g_1	g_2	$\cdots$	g_n
g_1	g_1^2	g_1g_2	$\cdots$	g_1g_n
g_2	g_2g_1	g_2^2	$\cdots$	g_2g_n
$\vdots$	$\vdots$	$\vdots$		$\vdots$
g_n	g_ng_1	g_ng_2		g_n^2



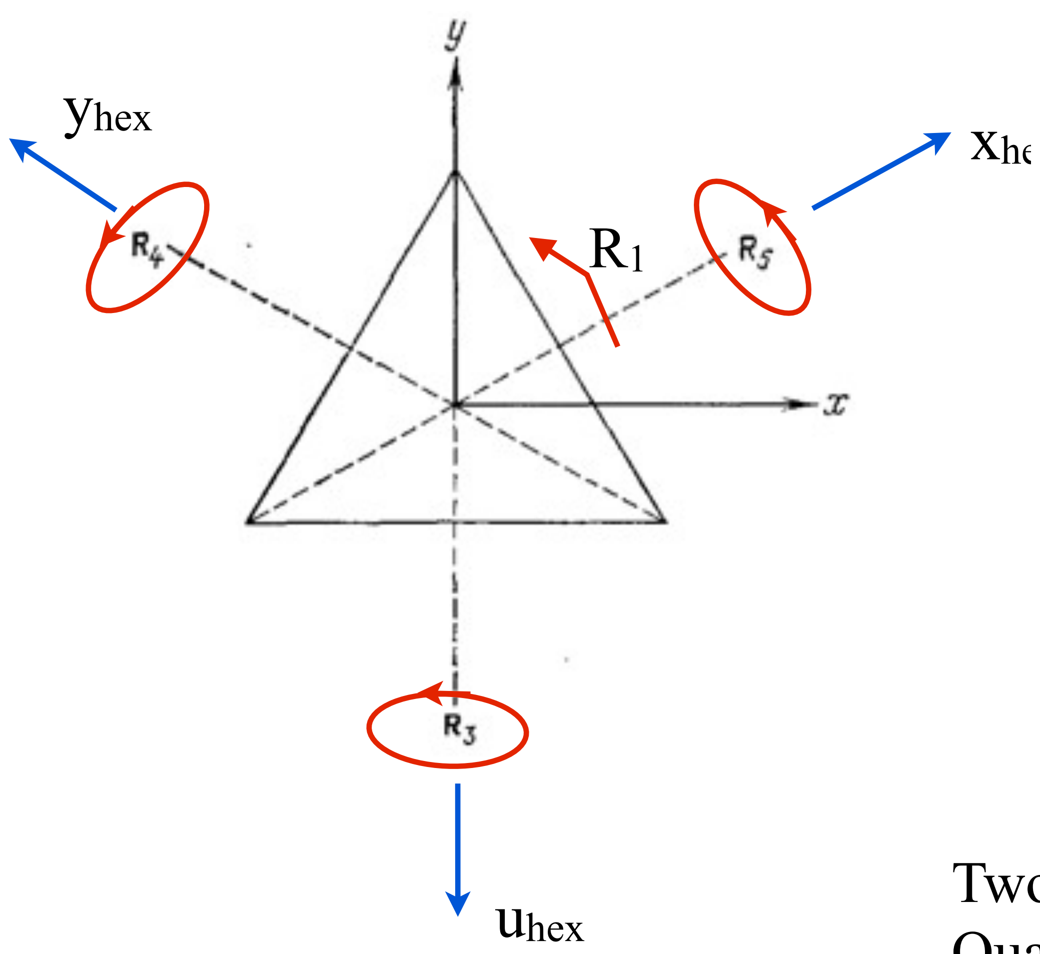


$$R_4R_1=R_3$$

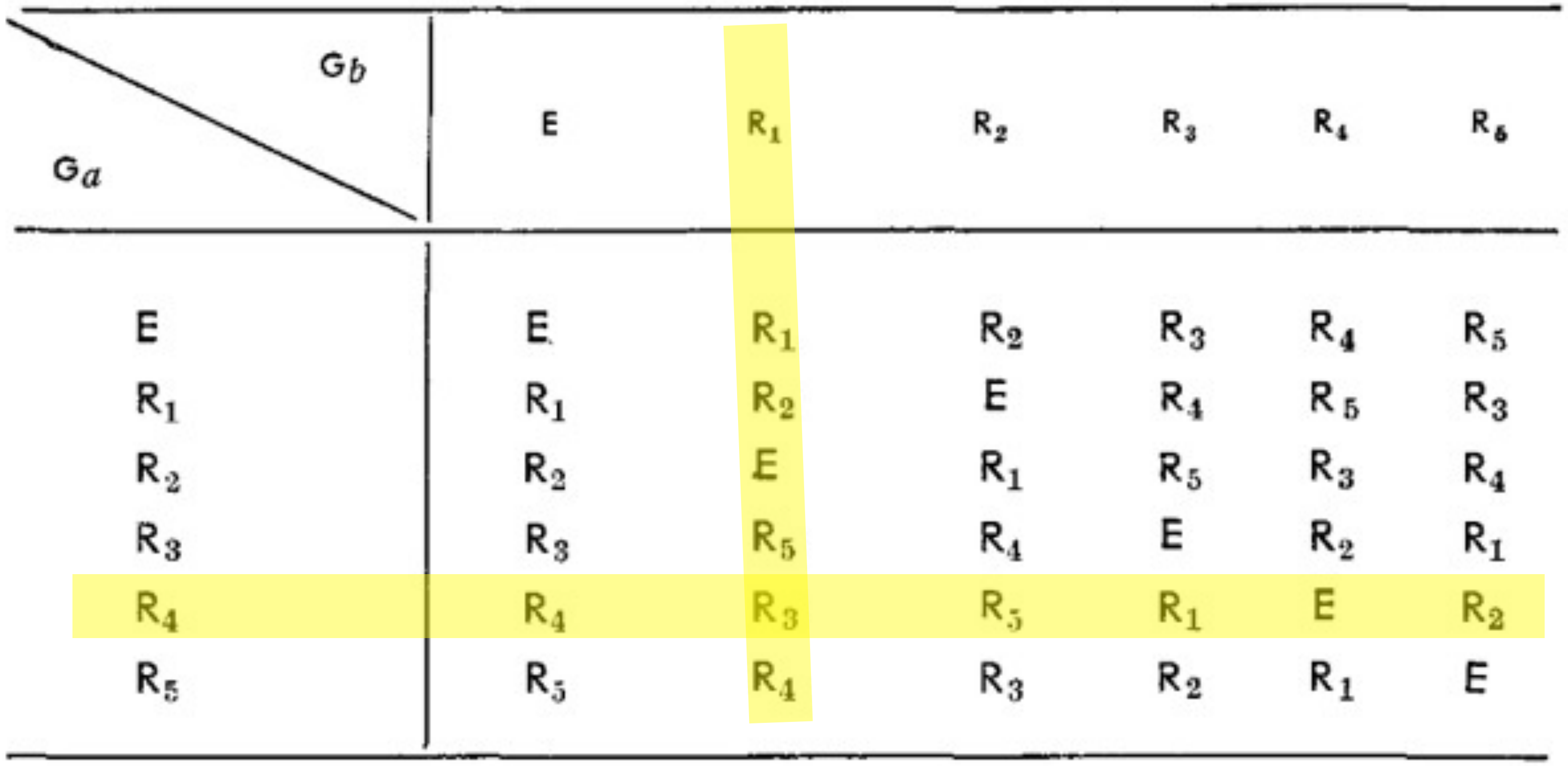
Multiplication table, isomorphism

Point group 32 (D_3 Schoenflies symbol)
e.g regular triangle

6 symmetry elements (rotations):
$R0=E$, $R_1=2\pi/3$, $R_2=4\pi/3$ around z, R_3, R_4, R_5, $= \pi$ around resp. axes in xy-plane
hex → 1 3^1 3^2 2_u 2_y 2_x



hex → 1 3^1 3^2 2_u 2_y 2_x



G_a \ G_b	E	R_1	R_2	R_3	R_4	R_6
E	E	R_1	R_2	R_3	R_4	R_5
R_1	R_1	R_2	E	R_4	R_5	R_3
R_2	R_2	E	R_1	R_5	R_3	R_4
R_3	R_3	R_5	R_4	E	R_2	R_1
R_4	R_4	R_3	R_5	R_1	E	R_2
R_5	R_5	R_4	R_3	R_2	R_1	E

Two groups are **isomorphous** if they have the same multiplication table
Quartz *32* D_3
Ammonia molecule *3m* C_{3v}

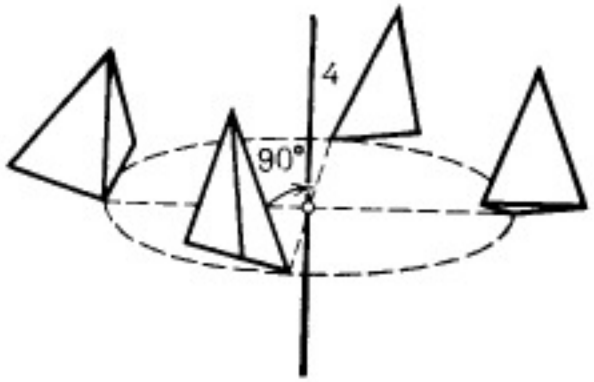
Isomorphism. Abstract group. (slide skipped)

cyclic group of ordinary complex numbers

$i^k \quad k=0, 1, 2, 3$

Gb Ga	1	−1	i	−i	
1	1	−1	i	−i	
−1	−1	1	−i	i	π
i	i	−i	−1	1	π/2
−i	−i	i	1	−1	-π/2
		π	π/2	-π/2	

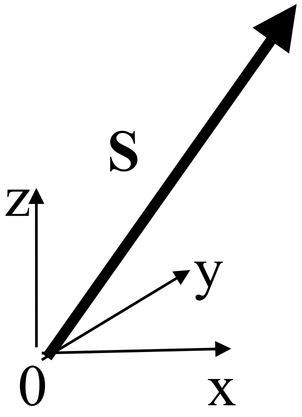
crystallographic point group C_4



Linear vector spaces I. Vectors

Vector of dimension 3:

position (or magnetic moment) of a particle in 3D:

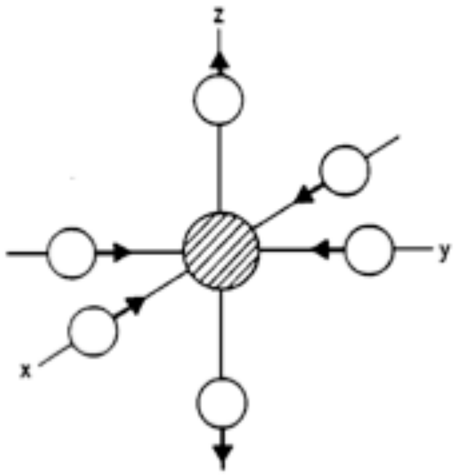


$$\begin{pmatrix} s_x \\ s_y \\ s_z \end{pmatrix}$$

Vector of dimension 3N:

positions (or magnetic moments) of **N** particles in 3D:

$$\begin{pmatrix} s_{x1} \\ s_{y1} \\ s_{z1} \\ s_{x2} \\ s_{y2} \\ s_{z2} \\ \dots \\ \dots \\ \dots \\ s_{xN} \\ s_{yN} \\ s_{zN} \end{pmatrix}$$



Linear vector spaces II. Basis

A set r_1 , r_2, ... is said to form a **'linear vector space *L*'** if the sum of any two members produces another in the set and a multiplication by a complex number *c* also produces another in the set.

$r_j + r_i$

$c\, r_i$

A set of vectors r_1 , r_2, ... r_p is said to be **'linearly independent'** if the members are not related by an equation:

$$\sum_{k=1}^{p} c_k \mathbf{r}_k = 0$$

The **'dimension'** (*l*) of *L* = greatest number of vectors which form a linearly independent set.

In *l*-dimensional vector space *L* any set of o *l* linearly independent vectors are said to form a **'basis'** $\mathbf{e}_j$.

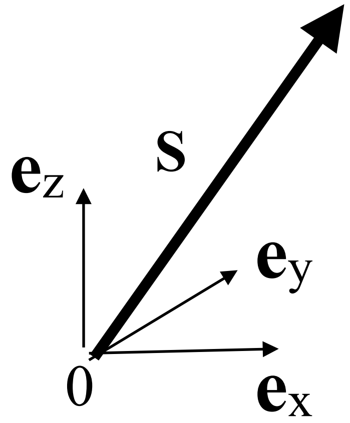
any vector **r** in *l*-dimensional vector space *L* can be written as:

$$\mathbf{r} = \sum_{j=1}^{l} c_j \mathbf{e}_j$$

Linear vector spaces III. Basis. Examples

3-dimensional space of particle displacement (or magnetic moment)

$$\mathbf{s} = \sum_{j=x,y,z} s_j \mathbf{e}_j$$



3N-dimensional space of all possible displacements (or magnetic moments)
Function ψ=**s**(s_{11}, $s_{12, \ldots}$) is defined on N discreet points

$$\psi = \sum_{n=1}^{N} \sum_{j=x,y,z} s_{jn} \mathbf{e}_{jn}$$

$$\begin{pmatrix} s_{x1} \\ s_{y1} \\ s_{z1} \\ s_{x2} \\ s_{y2} \\ s_{z2} \\ \ldots \\ \ldots \\ \ldots \\ s_{xN} \\ s_{yN} \\ s_{zN} \end{pmatrix}$$

6-dimensional function space

$$\psi = \sum_{j=1}^{6} c_j \mathbf{e}_j$$

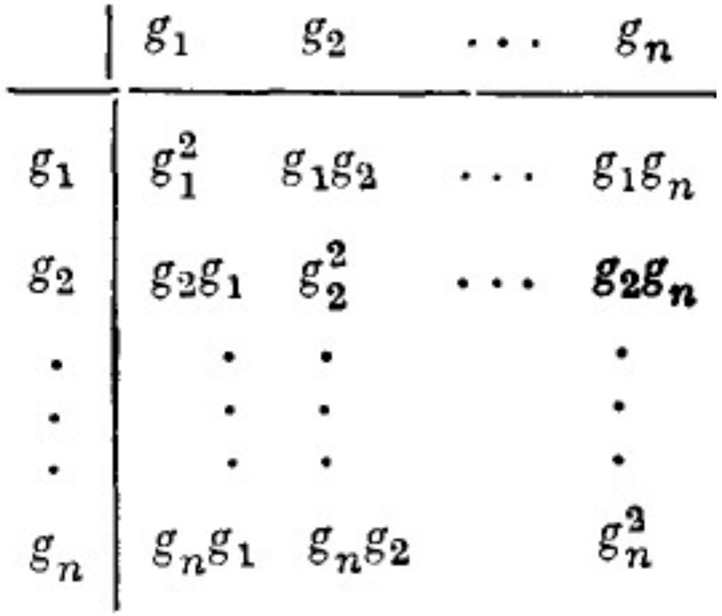
$$e_1 = x^2$$
$$e_2 = y^2$$
$$e_3 = z^2$$
$$e_4 = yz$$
$$e_5 = zx$$
$$e_6 = xy$$

Group representations (reps) I

If we can find **a set of square matrices** (in general linear operators) T(g_a) in a **vector space** ***L*,** which correspond to the elements g_a of group *G* and have the same multiplication table, i.e. T(g_a) T(g_b)= T(g_a g_b) then this set of matrices is said to form a matrix **'representation'** of the group *G* in space *L*.

n matrices *l*x*l*. *n* is order of *G*

multiplication table



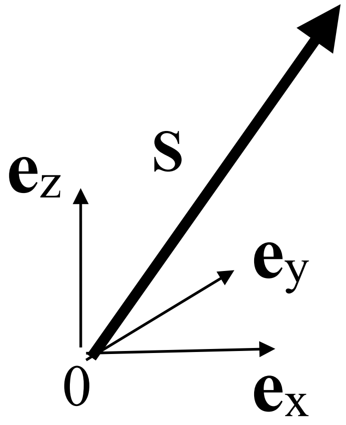
	g_1	g_2	$\cdots$	g_n
g_1	g_1^2	$g_1 g_2$	$\cdots$	$g_1 g_n$
g_2	$g_2 g_1$	g_2^2	$\cdots$	$g_2 g_n$
$\cdot$	$\cdot$	$\cdot$		$\cdot$
$\cdot$	$\cdot$	$\cdot$		$\cdot$
$\cdot$	$\cdot$	$\cdot$		$\cdot$
g_n	$g_n g_1$	$g_n g_2$		g_n^2

$$T(g_1) = \begin{pmatrix} t^1_{11} & t^1_{12} & t^1_{13} & ... & t^1_{1l} \\ t^1_{21} & t^1_{22} & t^1_{23} & ... & t^1_{2l} \\ . & . & . & & . \\ . & . & . & & . \\ . & . & . & & . \\ t^1_{l1} & t^1_{l2} & t^1_{l3} & ... & t^1_{ll} \end{pmatrix}, T(g_2) = \begin{pmatrix} t^2_{11} & t^2_{12} & t^2_{13} & ... & t^2_{1l} \\ t^2_{21} & t^2_{22} & t^2_{23} & ... & t^2_{2l} \\ . & . & . & & . \\ . & . & . & & . \\ . & . & . & & . \\ t^2_{l1} & t^2_{l2} & t^2_{l3} & ... & t^2_{ll} \end{pmatrix}, T(g_3) = ...$$

Dimension of representation is equal to the dimension of the vector space

Reps II. Point groups. Real 3D space

3-dimensional vector space of particle spin $\mathbf{s} = \sum_{j=x,y,z} s_j \mathbf{e}_j$

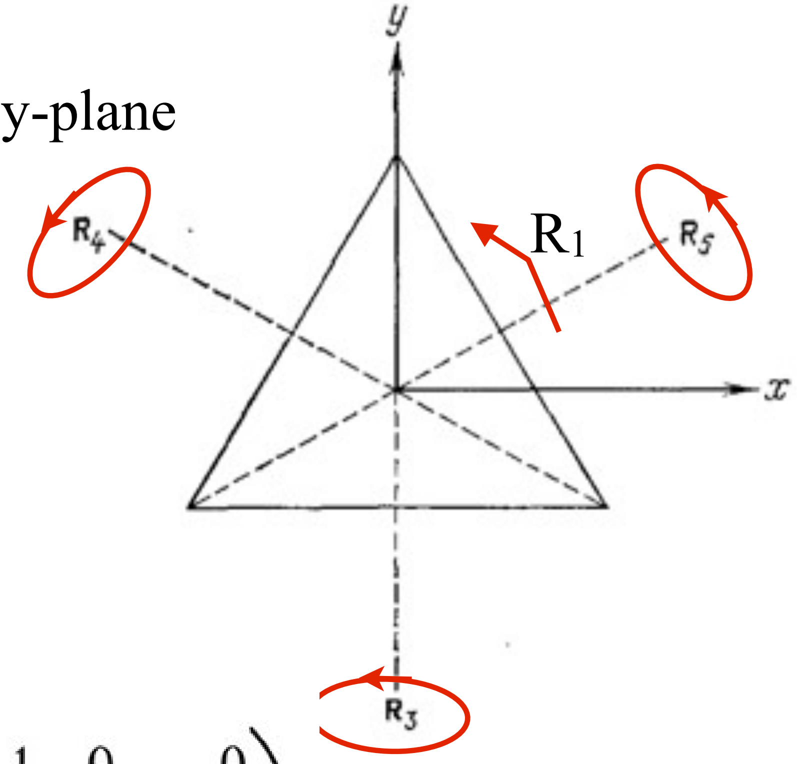


Rotation matrices for point groups can be used to construct 3-dimensional representations

$$\varphi_z \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Reps II. Point groups. Real 3D space
Example Point group 32

6 symmetry elements (rotations):
$R0=E$, $R_1=2\pi/3$, $R_2=4\pi/3$ around z, R_3, R_4, R_5, $= \pi$ around resp. axes in xy-plane



$$\varphi_z \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

1. **<u>3-</u>**dimensional representation

$$T(R_1) = \begin{pmatrix} -\frac{1}{2} & -\sqrt{\frac{3}{4}} & 0 \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad T(R_2) = \begin{pmatrix} -\frac{1}{2} & \sqrt{\frac{3}{4}} & 0 \\ -\sqrt{\frac{3}{4}} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad T(R_3) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$ ... etc

2. By taking the one dimensional space of vector $\mathbf{e}_z$ alone we may generate very simple **<u>one-</u>**dimensional representation

$$T^{(2)}(R_1) = 1,\ T^{(2)}(R_2) = 1,\ T^{(2)}(R_3) = -1,\ T^{(2)}(R_4) = -1,$$
$$T^{(2)}(R_5) = -1,\ T^{(2)}(E) = 1$$

representation with dim=6 for point group 32. Induced transformation of functions (skipped)

6-dimensional function space

$$\psi = \sum_{j=1}^{6} c_j \psi_j$$

$$\psi_1 = x^2$$
$$\psi_2 = y^2$$
$$\psi_3 = z^2$$
$$\psi_4 = yz$$
$$\psi_5 = zx$$
$$\psi_6 = xy$$

Let's construct the rep-matrix for element R₁=2π/3 rotation around *z*
$T(G_a)\psi(\mathbf{r}) = \psi'(\mathbf{r}) = \psi(G_a^{-1}\mathbf{r})$

$$\bar{x} = x\cos(-2\pi/3) + y\sin(-2\pi/3) = -(\frac{1}{2})x - (\frac{3}{4})^{1/2}y$$

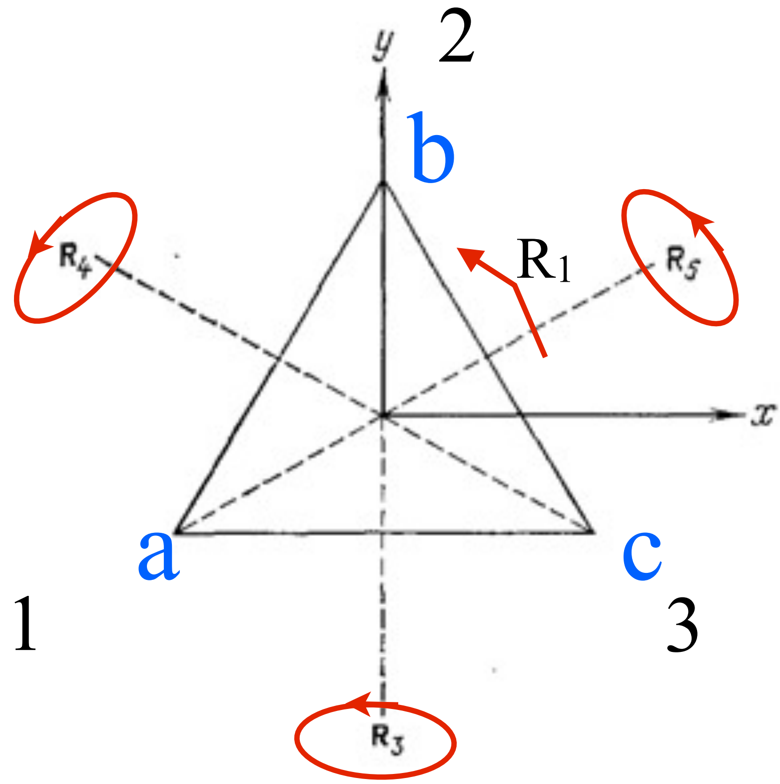
$$T(R_1)\psi_1 = \bar{x}^2 = (\frac{1}{4})x^2 + (\frac{3}{4})^{1/2}xy + (\frac{3}{4})y^2$$

$$T(R_1)\psi_1 = \bar{x}^2 = (\frac{1}{4})\psi_1 + (\frac{3}{4})^{1/2}\psi_6 + (\frac{3}{4})\psi_2$$

$$\mathrm{T(R_1)} = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \sqrt{\frac{3}{4}} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & -\sqrt{\frac{3}{4}} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & \sqrt{\frac{3}{4}} & 0 \\ 0 & 0 & 0 & -\sqrt{\frac{3}{4}} & -\frac{1}{2} & 0 \\ -\sqrt{\frac{3}{4}} & \sqrt{\frac{3}{4}} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix}$$

Reps III. Sites space.
Example Point group 32

6 symmetry elements (rotations):
$R0=E$, $R_1=2\pi/3$, $R_2=4\pi/3$ around z, R_3, R_4, R_5, $= \pi$ around resp. axes in xy-plar

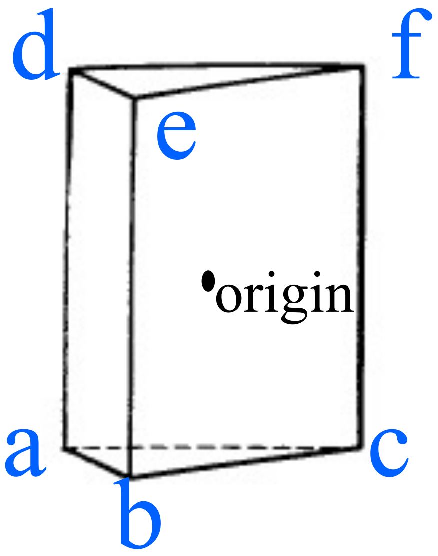


3-dimensional vector space of particle sites.
Note, not the xyz, but labeled sites.

element R_1 permutes the sites

b ⇒ a
c ⇒ b
a ⇒ c

$$\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} b \\ c \\ a \end{pmatrix}$$



permutation (n=3) representation of group 32

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

Product of two representations of group

Direct (tensor) matrix product $U\otimes V = \begin{bmatrix} u_{1,1}V & u_{1,2}V & \cdots \\ u_{2,1}V & u_{2,2}V & \\ \vdots & & \ddots \end{bmatrix} = \begin{bmatrix} u_{1,1}v_{1,1} & u_{1,1}v_{1,2} & \cdots & u_{1,2}v_{1,1} & u_{1,2}v_{1,2} & \cdots \\ u_{1,1}v_{2,1} & u_{1,1}v_{2,2} & & u_{1,2}v_{2,1} & u_{1,2}v_{2,2} & \\ \vdots & & \ddots & & & \\ u_{2,1}v_{1,1} & u_{2,1}v_{1,2} & & & & \\ u_{2,1}v_{2,1} & u_{2,1}v_{2,2} & & & & \\ \vdots & & & & & \end{bmatrix}.$

dimension *m* *n*

$$T^{(\alpha\times\beta)}_{ij,\,kl}(\mathsf{G}_a) = T^{(\alpha)}_{ik}(\mathsf{G}_a)\, T^{(\beta)}_{jl}(\mathsf{G}_a).$$

gives a new rep with dimension m×n and new vector space!

permutation (n=3) representation of group 32

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$\otimes$$

Rotation matrices for point group 32

$$\varphi_z \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \ldots$$

= 9 by 9 matrices: 9 dimensional representation

Reducibility

A study of possible representations of even a simple group like D3 seems to be a scaring task.

BUT!

For a finite group all representations can be built up from a finite number of ‘distinct‘ irreducible representations

$$\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \text{[illegible]} & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 & 0 & 0 & 0 & \text{[illegible]} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} & 0 & 0 & \text{[illegible]} & \text{[illegible]} & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & \text{[illegible]} & \text{[illegible]} & 0 & 0 & 0 \\ 0 & \bar{b} & 0 & 0 & 0 & 0 & 0 & \text{[illegible]} & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{b} & 0 & 0 & 0 & \text{[illegible]} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \text{[illegible]} & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \text{[illegible]} & \text{[illegible]} & 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & \text{[illegible]} & \text{[illegible]} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 0 & \text{[illegible]} & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \text{[illegible]} & 0 & 0 & 0 & 0 & \bar{b} & 0 & 0 & 0 & 0 \\ 0 & \text{[illegible]} & 0 & 0 & 0 & 0 & 0 & 0 & \bar{b} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} s_{x1} \\ s_{y1} \\ s_{z1} \\ s_{x2} \\ s_{y2} \\ s_{z2} \\ s_{x3} \\ s_{y3} \\ s_{z3} \\ s_{x4} \\ s_{y4} \\ s_{z4} \end{pmatrix}$$

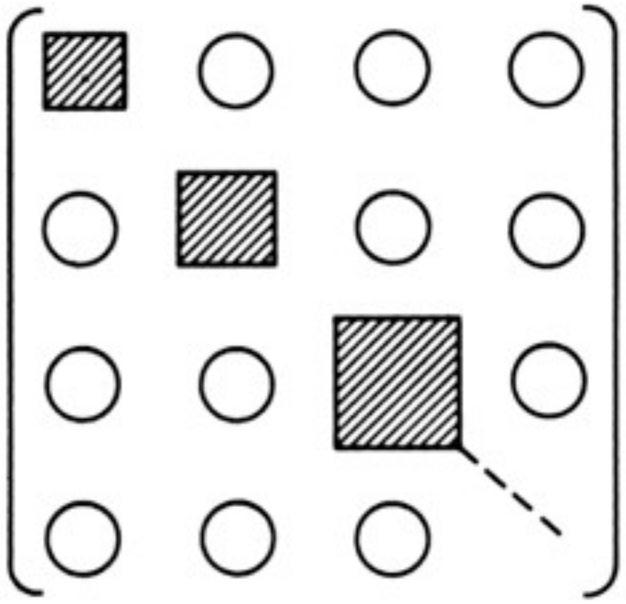
representation is reducible!

Reduction of any representation of group to block diagonal shape

Representation (dimension=n) of a group G in linear space L is reducible to a block-diagonal shape that is a direct sum of irreducible square matrices τ_1, τ_2, ... For each element G_a the representation has the shape:

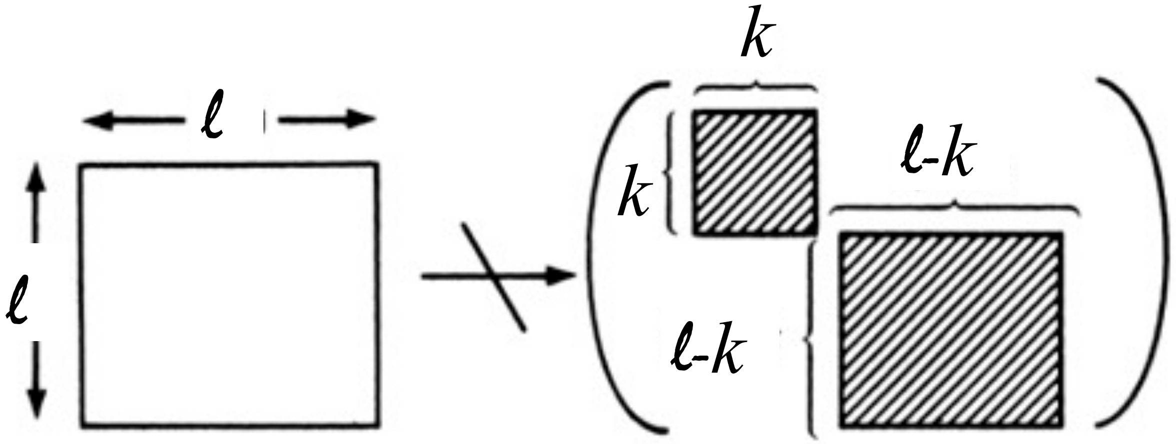
One can divide space L into the sum of subspaces L_i each of which is invariant and irreducible. $S_{\tau i}$ is a vector from L_i and is transformed by matrices $\tau_i(G_a)$.

$$\tau_1 \oplus \tau_2 \oplus \tau_3 \oplus \ldots =$$

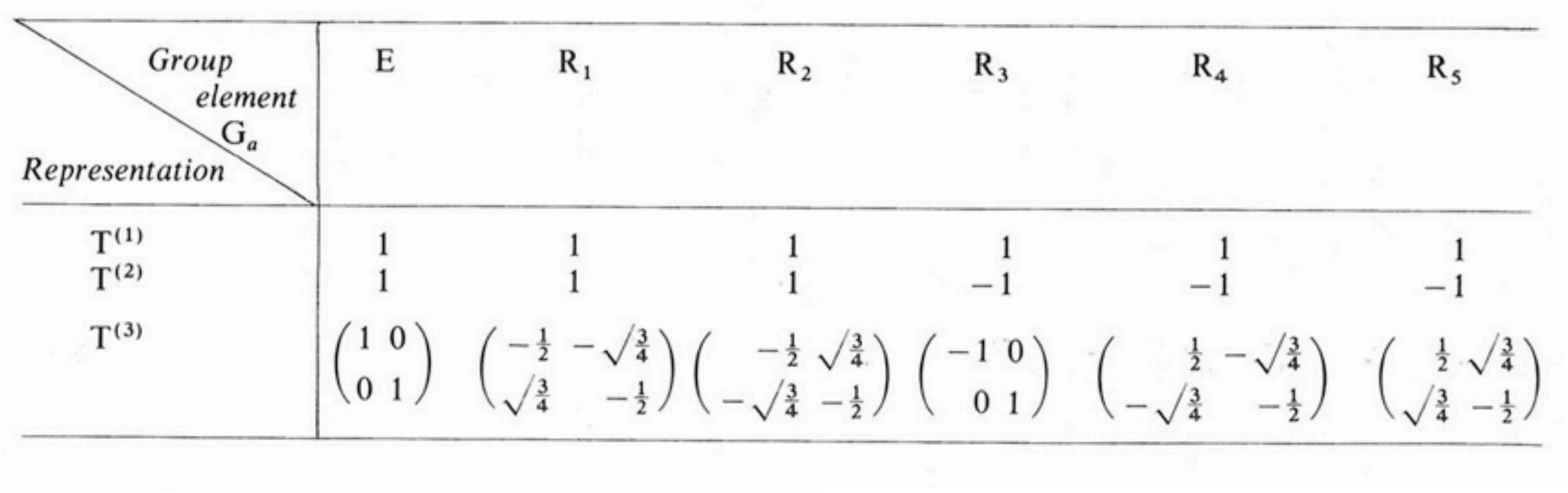


$$\begin{pmatrix} S_{\tau 1} \\ S_{\tau 2} \\ S_{\tau 3} \\ . \\ . \end{pmatrix}$$

τ_i is irreducible if: It is impossible to find a new basis such that non-diagonal elements of any τ_i in the new basis are zero for all elements G_a



Example: Irreducible representations (irreps) of point group 32 (D_3)

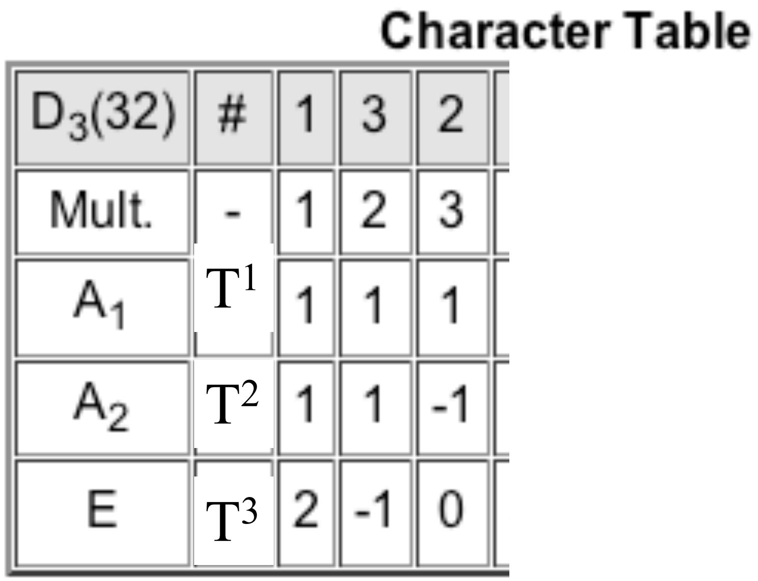


	1	3^1	3^2	2_u	2_y	2_x
Group element G_a / *Representation*	E	R_1	R_2	R_3	R_4	R_5
$T^{(1)}$	1	1	1	1	1	1
$T^{(2)}$	1	1	1	-1	-1	-1
$T^{(3)}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \sqrt{\frac{3}{4}} \\ -\sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\sqrt{\frac{3}{4}} \\ -\sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$

Characters of representations

Character = trace of rep matrix $\chi(G_a) = \sum_{i=1}^{l} T_{ii}(G_a)$

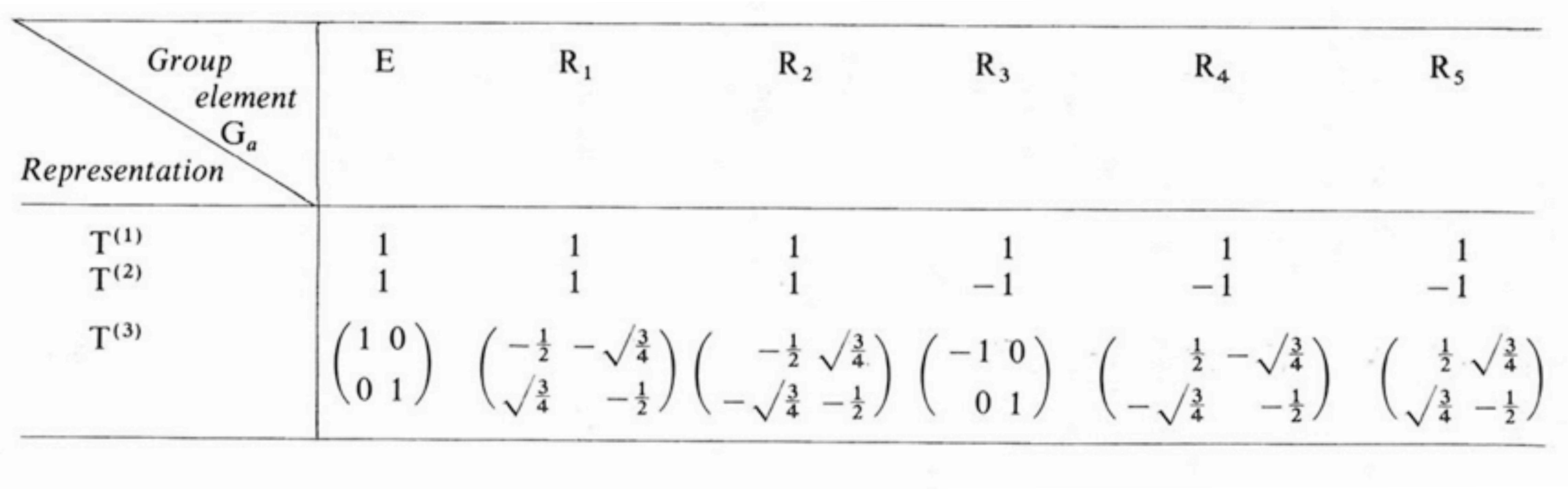
Character Table



D$_3$(32)	#	1	3	2
Mult.	-	1	2	3
A$_1$	T^1	1	1	1
A$_2$	T^2	1	1	-1
E	T^3	2	-1	0

Conjugated class = elements with the same character

1 3^1 3^2 2_u 2_y 2_x



Group element G_a / *Representation*	E	R_1	R_2	R_3	R_4	R_5
$T^{(1)}$	1	1	1	1	1	1
$T^{(2)}$	1	1	1	-1	-1	-1
$T^{(3)}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \sqrt{\frac{3}{4}} \\ -\sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\sqrt{\frac{3}{4}} \\ -\sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \sqrt{\frac{3}{4}} \\ \sqrt{\frac{3}{4}} & -\frac{1}{2} \end{pmatrix}$

Reduction formulae. Projection.

rep $\Rightarrow_{\Sigma_\oplus}$ irreps:

$$T_{ij} = \sum_{\oplus} n_\nu T_{ij}^{\nu}$$

$$\begin{array}{c|c|c|c}
T_{ij}{}^{1} & 0 & 0 & 0 \\ \hline
0 & T_{ij}{}^{1} & 0 & 0 \\ \hline
0 & 0 & T_{ij}{}^{2} & 0 \\ \hline
0 & 0 & 0 & \ldots
\end{array}$$

$$n_\nu = \frac{1}{n(G)} \sum_{g \subset G} \chi(g) \chi^{*\nu}(g)$$

n(G) order of *G*

basis functions: projection operator *P* technique

$$\psi_i = \hat{P}\varphi = \frac{1}{n(G)} \sum_{g \subset G} T_{ij}^{*\nu}(g) T(g) \varphi$$

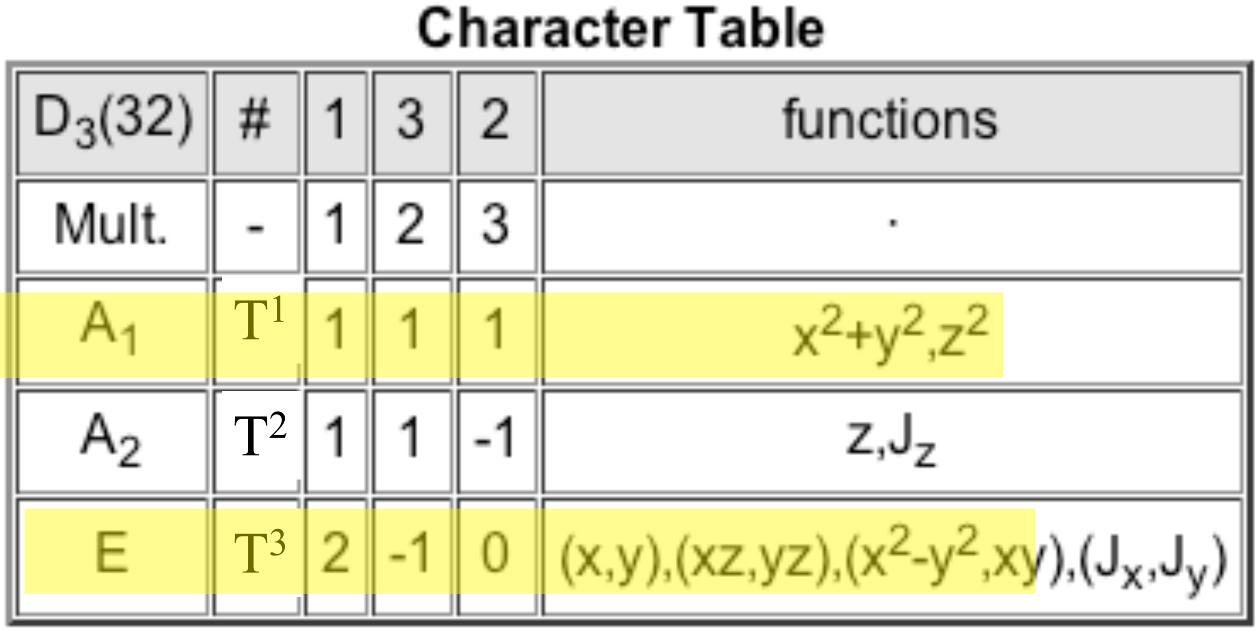
Example:
6-dimensional function space in point group D_3 (32) defines 6D-representation *T*

$$\psi = \sum_{j=1}^{6} c_j \psi_j$$

$$\psi_1 = x^2$$
$$\psi_2 = y^2$$
$$\psi_3 = z^2$$
$$\psi_4 = yz$$
$$\psi_5 = zx$$
$$\psi_6 = xy$$

decomposed
to

$T = 2T^1 \oplus 2T^2$



Character Table

D_3(32)	#	1	3	2	functions
Mult.	-	1	2	3	.
A_1	T^1	1	1	1	x^2+y^2,z^2
A_2	T^2	1	1	-1	z,J_z
E	T^3	2	-1	0	$(x,y),(xz,yz),(x^2-y^2,xy),(J_x,J_y)$

Symmetry in QM. Theorem.

$\hat{H}(\mathbf{r})$, $\mathbf{r} = (r_1, r_2, r_3, \dots r_n)$, vector space with n degree of freedoms (dimension n)
$\psi(\mathbf{r})$ arbitrary wave function

G - group of coordinate transformation, T(G_a) - induced transformations in ψ-*space*
$T(G_a)\psi(\mathbf{r}) = \psi'(\mathbf{r}) = \psi(G_a^{-1}\mathbf{r})$

$T(G_a)HT^{-1}(G_a) = H'$

if H=H': G is called symmetry group of the Hamiltonian
potential energy $V(\mathbf{r}) = V(G_a\mathbf{r})$

eigenvalues/functions

$$\hat{H}\psi_v = E_v\psi_v \quad \Rightarrow E_v, \psi_v^{\,1}, \psi_v^{\,2}, \dots \psi_v^{\,l_v}$$

E_v, $\psi_v^{\,lv}$ can be classified by irreps t_{ij}^{v}
dimension of t_{ij}^{v} $\equiv$ degeneracy l_v

!

rep $\Rightarrow_{\Sigma_\oplus}$ irreps: $T_{ij} = \sum_{\oplus} n_\nu T_{ij}^\nu$

T_{ij}^1	0	0	0
0	T_{ij}^1	0	0
0	0	T_{ij}^2	0
0	0	0	...

Illustration. Single molecular “classical” magnet or molecular vibrations

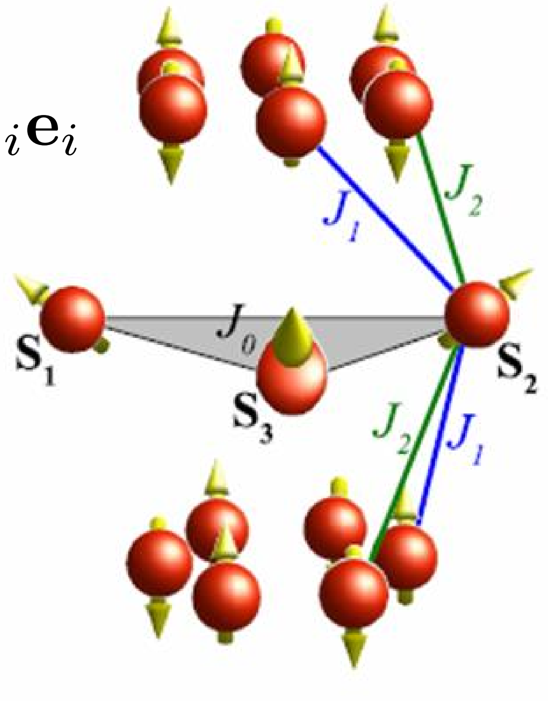
$$H = \sum_{\mathbf{R},\mathbf{R}',\alpha,\beta} A_{\alpha,\beta}(\mathbf{R},\mathbf{R}')S_\alpha(\mathbf{R})S_\beta(\mathbf{R}') \quad (\alpha,\beta = x,y,z)$$

3N-dimensional space of spins. Function ψ=**s**(s11, s12, ...) is defined on N discreet points

$$\hat{A}\mathbf{e}_j = \sum_{i=1}^{3N} A_{ji}\mathbf{e}_i$$

def of potential energy operator
i runs on both α and **R**

$$\psi = \sum_{i=1}^{3N} s_i \mathbf{e}_i$$



$$H = (\psi \cdot \hat{A}\psi) \ = \sum_{i,j} s_i s_j (\mathbf{e}_i \cdot A\mathbf{e}_j) \ = \sum_{i,j} s_i s_j A_{ij}$$

The molecule has symmetry group *G* ⇒ *A* must be invariant under symmetry elements of *G*

Representation of group G in 3N-dimensional space of spins

$$\mathbf{e}_i{}' = T(G_a)\mathbf{e}_i = \sum_j T_{ij}(G_a)\mathbf{e}_j$$

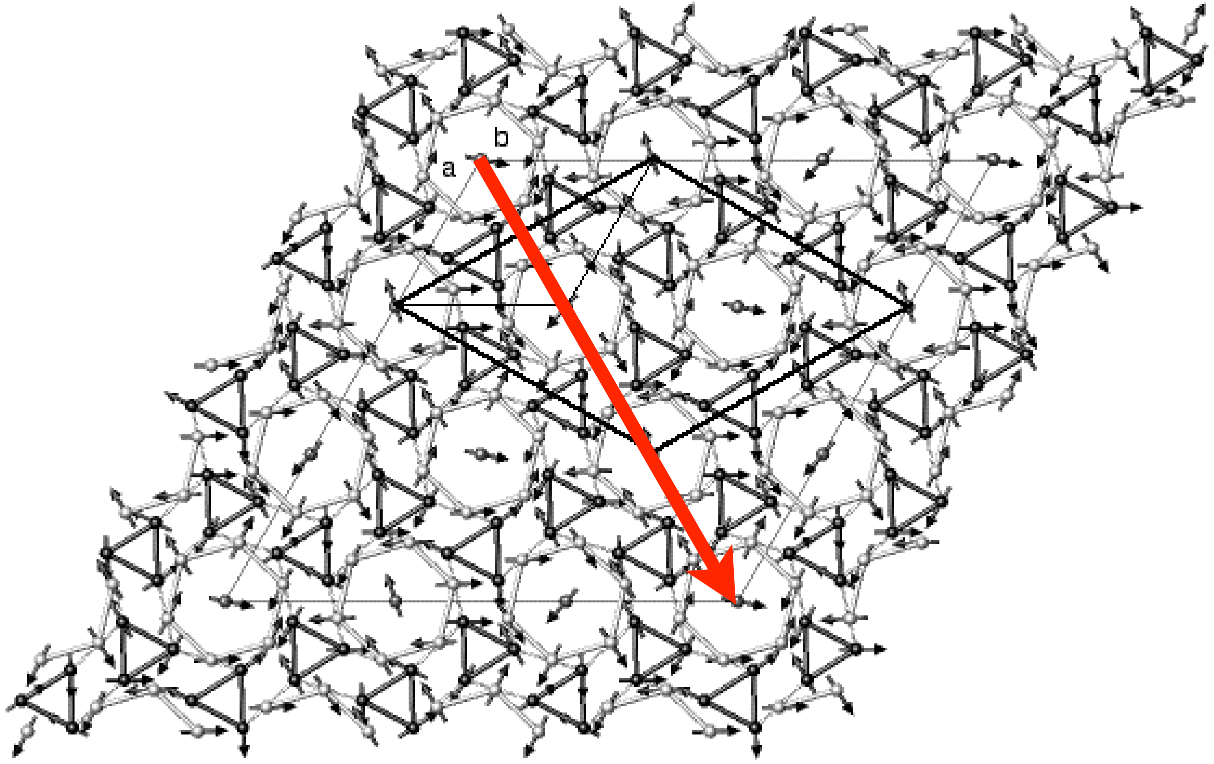
rep $\Rightarrow_{\Sigma_\oplus}$ irreps: !

$$T_{ij} = \sum_{\oplus} n_\nu T_{ij}^\nu$$

E_ν, $\psi_\nu{}^{l\nu}$ can be classified by irreps $t_{ij}{}^\nu$ Normal modes $\psi_\nu{}^{l\nu}$ can be found without diagonalization of *H*!

Landau theory of phase transitions says that only one irrep (+c.c.) is becoming critical and is needed to describe the ordered structure

Great simplification!



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Zeroth cell contains **14** spins
=> 14*3=42 parameters.

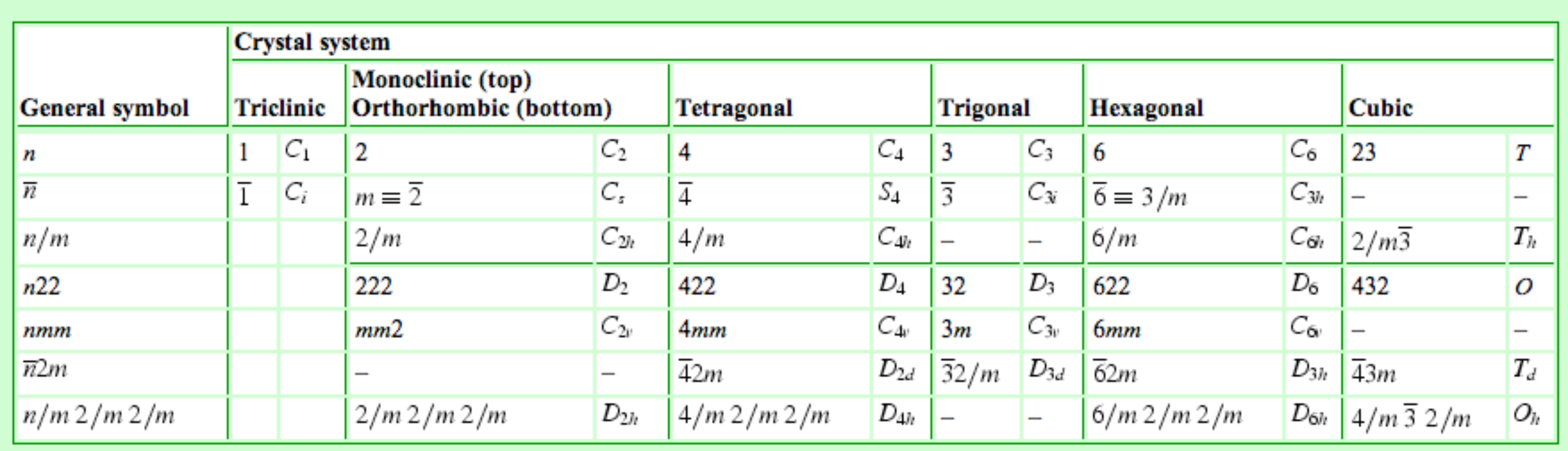
$\big\downarrow$ one irrep

Only 3 independent spins are needed!

Basic crystallography

32 crystallographic point groups

A *crystallographic* point group is a point group that maps a point lattice onto itself. Consequently, rotations and rotoinversions are restricted to the well known crystallographic cases 1, 2, 3, 4, 6 and $\bar{1}$, $\bar{2} = m$, $\bar{3}$, $\bar{4}$, $\bar{6}$



	Crystal system											
General symbol	**Triclinic**		**Monoclinic (top)** **Orthorhombic (bottom)**		**Tetragonal**		**Trigonal**		**Hexagonal**		**Cubic**	
n	1	C_1	2	C_2	4	C_4	3	C_3	6	C_6	23	T
$\bar{n}$	$\bar{1}$	C_i	$m \equiv \bar{2}$	C_s	$\bar{4}$	S_4	$\bar{3}$	C_{3i}	$\bar{6} \equiv 3/m$	C_{3h}	–	–
n/m			$2/m$	C_{2h}	$4/m$	C_{4h}	–	–	$6/m$	C_{6h}	$2/m\bar{3}$	T_h
$n22$			222	D_2	422	D_4	32	D_3	622	D_6	432	O
nmm			$mm2$	C_{2v}	$4mm$	C_{4v}	$3m$	C_{3v}	$6mm$	C_{6v}	–	–
$\bar{n}2m$			–	–	$\bar{4}2m$	D_{2d}	$\bar{3}2/m$	D_{3d}	$\bar{6}2m$	D_{3h}	$\bar{4}3m$	T_d
$n/m\,2/m\,2/m$			$2/m\,2/m\,2/m$	D_{2h}	$4/m\,2/m\,2/m$	D_{4h}	–	–	$6/m\,2/m\,2/m$	D_{6h}	$4/m\,\bar{3}\,2/m$	O_h

Hermann–Mauguin (left) and Schoenflies symbols (right).

3D Space* groups

Groups of transformations/motions of three dimensional homogeneous discreet space into itself

Two kinds of
transformations/motions = 1. rotations (32 point groups)

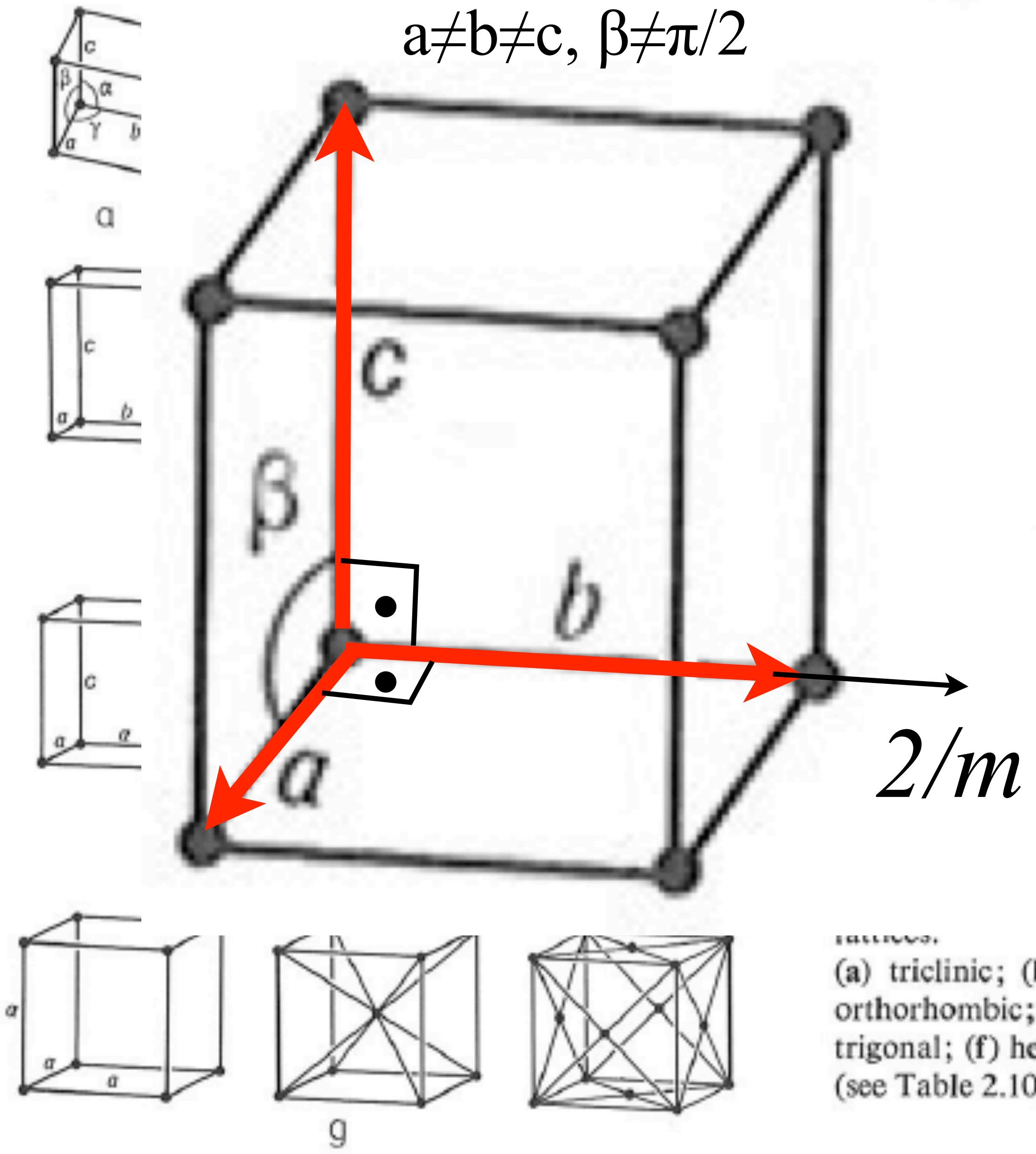
2. translations $\mathbf{t} = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3$

---

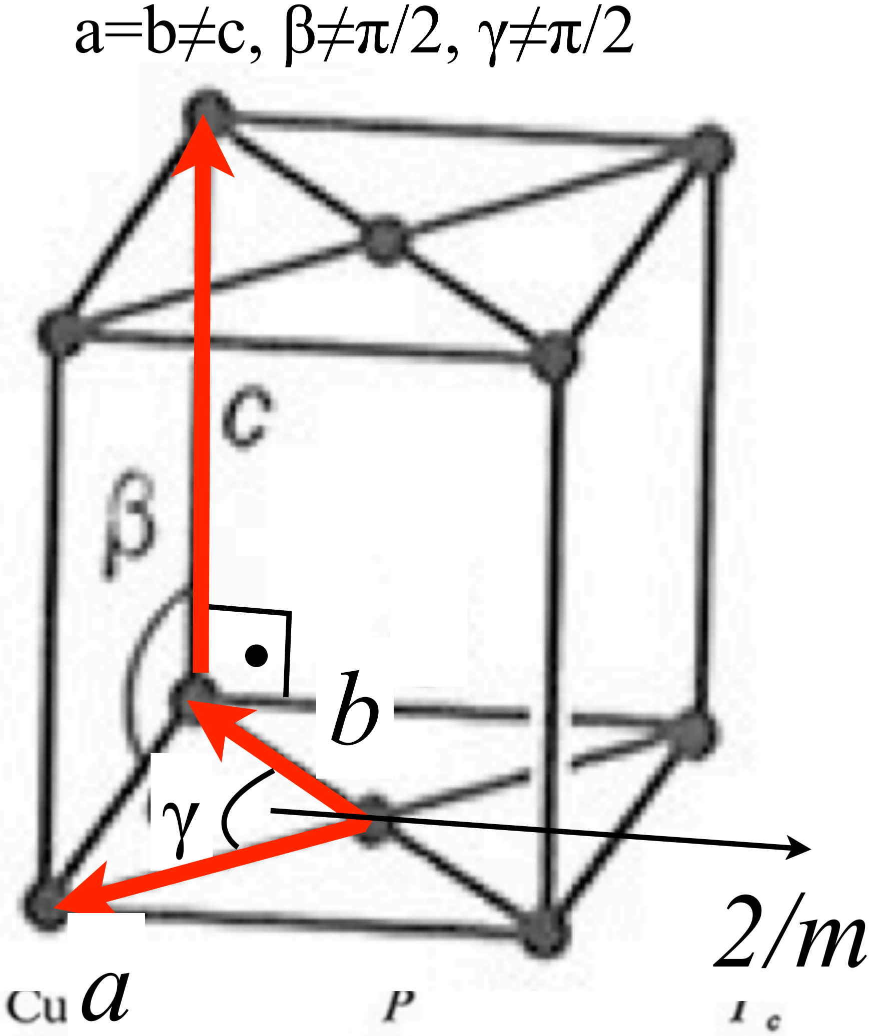
* E.S. Fedorov (1890) A.Schoenflies (1890)

14 Bravias* groups.

A full group of motions (of both kinds) that bring the lattice into self-coincidence, i.e., which contains both point symmetry operations and translations, is called a *Bravais group*, and an infinite lattice derived from one point by a Bravais group, a *Bravais lattice*.



lattices.
(a) triclinic; (b) monoc
orthorhombic; (d) tetra
trigonal; (f) hexagonal;
(see Table 2.10)



		group notation)	International symbol
			$P\bar{1}$
			$P2/m$
			$B(C)2/m$
			$Pmmm$
			$C(B,A)mmm$
			$Immm$
			$Fmmm$
			$P4/mmm$
			$I4/mmm$
			$R\bar{3}m$
			$P6/mmm$
Cu	P	Γ_c	$Pm\bar{3}m$
	I	Γ_c^v	$Im\bar{3}m$
	F	Γ_c^f	$Fm\bar{3}m$

*A. Bravias (1848)

230 space groups

Product of 32 point crystallographic groups and 14 Bravias groups

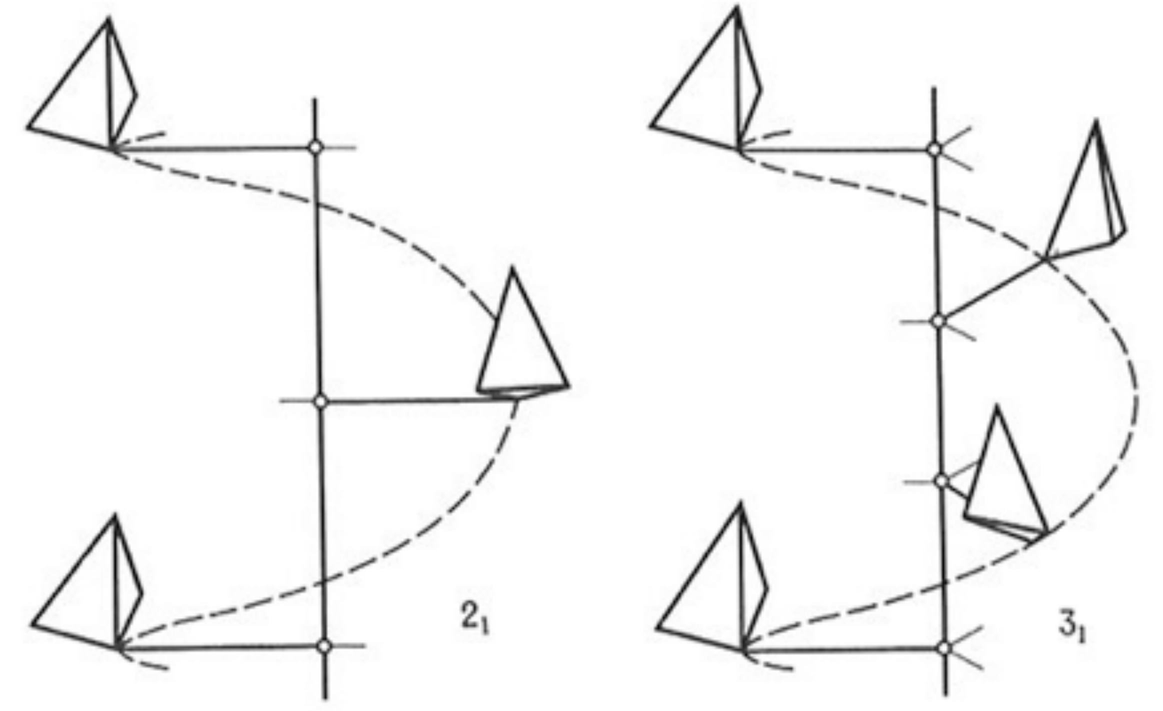
New symmetry elements

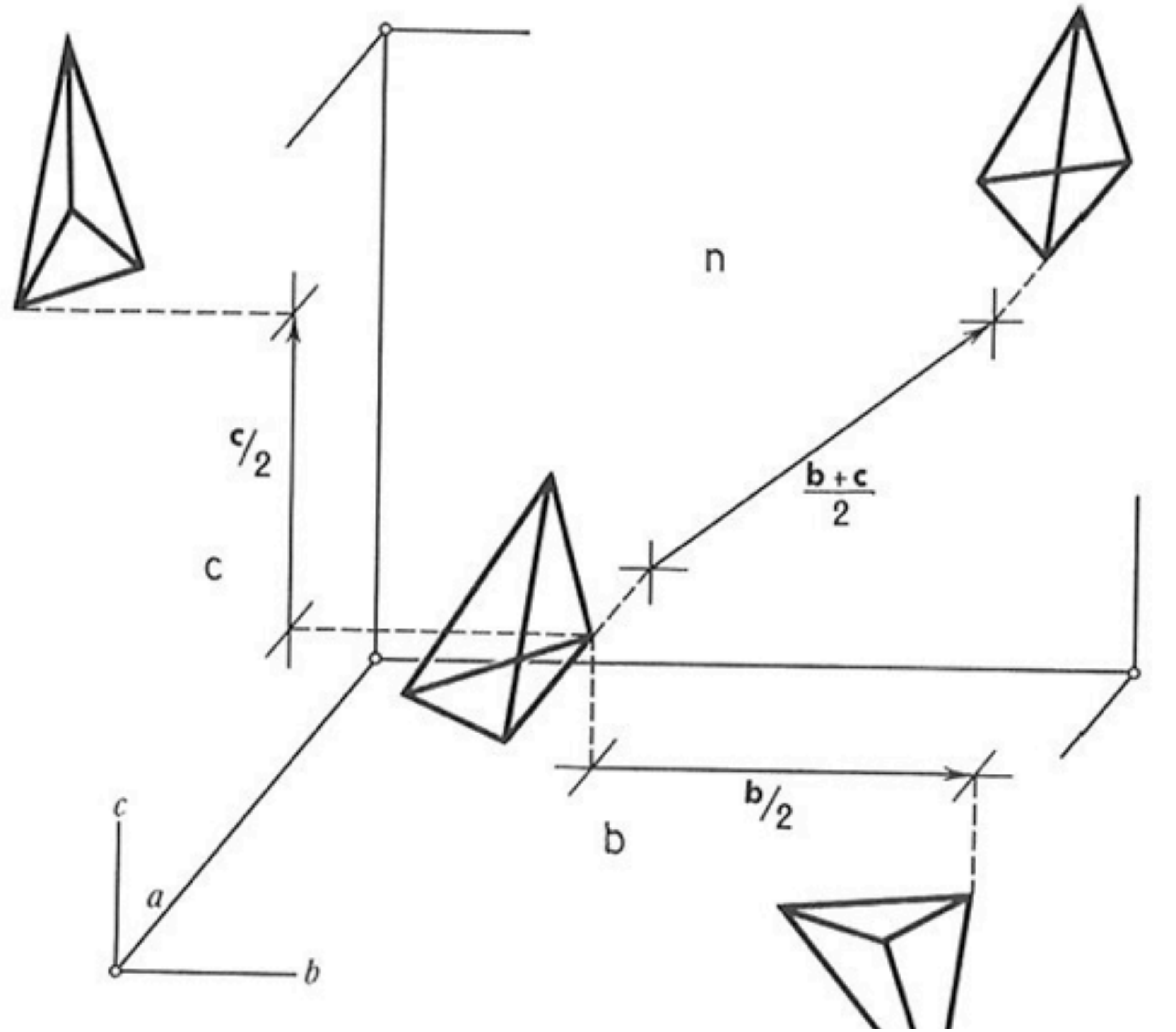
Screw axes or axes of screw rotations = rotation + translation. e.g. 2_1, 3_1,3_2, ...

Glide-reflection planes = mirror reflection + translation by *t/2*, *a*, *b*, *n*

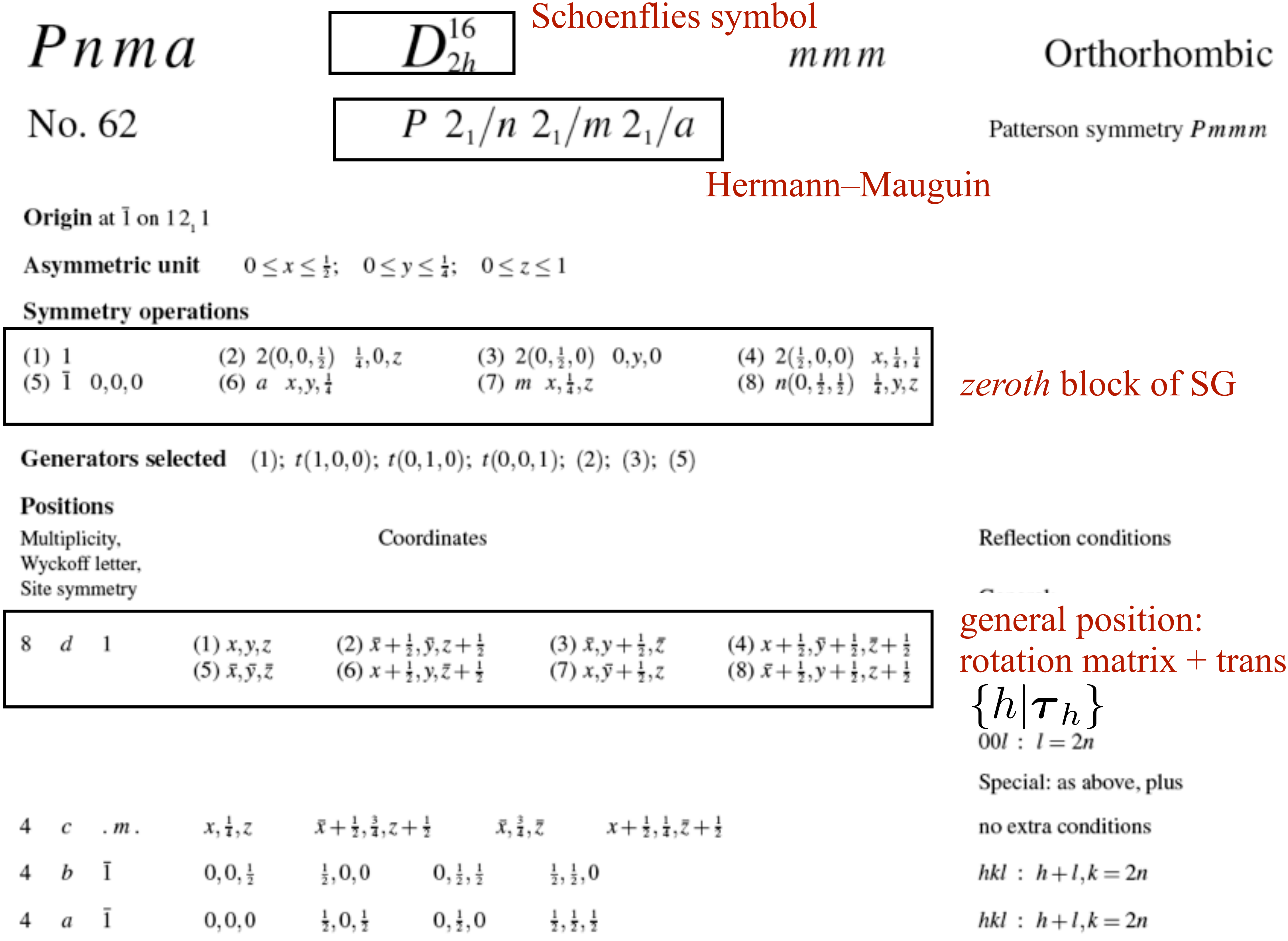
$$\alpha_s = 2\pi/N, \; N = 2, 3, 4, 6,$$

$$t_s = \frac{q}{N}\, t, \quad q = 1, 2, 3, 4, 6.$$





International Tables



$Pnma$ $\boxed{D_{2h}^{16}}$ Schoenflies symbol mmm Orthorhombic

No. 62 $\boxed{P\ 2_1/n\ 2_1/m\ 2_1/a}$ Patterson symmetry $Pmmm$

Hermann–Mauguin

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

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

Symmetry operations

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

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

zeroth block of SG

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

Positions

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

general position:
rotation matrix + translation
$\{h|\boldsymbol{\tau}_h\}$

V. Pomjakushin, Advanced magnetic structures ETHZ '10

Thursday, 25 March 2010

irreps of SG

O. V. Kovalev, *“Representations of the Crystallographic Space Groups: irreducible representations, induced representations, and corepresentations”* (Gordon and Breach Science Publishers, 1993), 2nd ed.

Bloch waves, irreps of Bravias Lattice group

Bloch wave **ψ**(**r**) is a solution of Hamiltonian having periodic symmetry of Bravias Lattice BL ($\mathbf{t}_L$), (e.g. **ψ**(**r**) can describe magnetic structure)

$$\psi(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{kr}},\ u(\mathbf{r}+\mathbf{t}_L) = u(\mathbf{r})$$

Representation theory

Space group *G* contains translation (*t*) BL group *T*. $\mathbf{t} = n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3$

What are irreps and basis functions (b.f) of *T* ?

Two properties of T-elements: $T(\mathbf{t}) = T(\mathbf{t_1})^{n_1}T(\mathbf{t_2})^{n_2}T(\mathbf{t_3})^{n_3} = T(n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3)$

$T(\mathbf{t}_j)^{N_j+1} = T(\mathbf{t}_j), j = 1,2,3$

Born–von Karman

$\Downarrow$

1D matrixes

N=*N*$_1$ *N*$_2$ *N*$_3$ irreps of *T* enumerated by ordinary numbers p_j

$$exp\left[-2\pi i\left(\frac{p_1n_1}{N_1}+\frac{p_2n_2}{N_2}+\frac{p_3n_3}{N_3}\right)\right], 0 \le p_j \le N_j - 1$$

Bloch waves = basis functions

$N_1\,N_2\,N_3$ irreps of T enumerated by ordinary numbers p_j $$exp\left[-2\pi i\left(\frac{p_1n_1}{N_1}+\frac{p_2n_2}{N_2}+\frac{p_3n_3}{N_3}\right)\right],0\leq p_j\leq N_j-1$$

Reciprocal lattice ($\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$) allows us conveniently sort out/enumerate all irreps of $T\in G$
$\mathbf{b}_j\mathbf{t}_k=2\pi\delta_{jk}$

$$\mathbf{b}=p_1\mathbf{b}_1+p_2\mathbf{b}_2+p_3\mathbf{b}_3$$

$$T(\mathbf{t})\rightarrow\exp(-i\mathbf{kt})$$

wave vector or *propagation vector* $$\mathbf{k}=\left(\frac{p_1}{N_1}\mathbf{b}_1+\frac{p_2}{N_2}\mathbf{b}_2+\frac{p_3}{N_3}\mathbf{b}_3\right)$$

$$\mathbf{t}=n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3$$

Matrices of irrep number **k:** $D^{\mathbf{k}}(\mathbf{t})=\exp(-i\mathbf{kt})$

$$T(\mathbf{t})\psi^{\mathbf{k}}(\mathbf{r})=\exp(-i\mathbf{kt})\psi^{\mathbf{k}}(\mathbf{r})$$

operator

b.f.

Most general basis function of the **k***th* irrep of translation group $T\in G$ is Bloch function $$\psi^{\mathbf{k}}(\mathbf{r})=u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}$$ $$u_{\mathbf{k}}(\mathbf{r}+\mathbf{t})=u_{\mathbf{k}}(\mathbf{r})$$

Symmetry group of propagation vector, star {k}

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

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

Symmetry operations

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

$+T(n_1\mathbf{t}_1 + n_2\mathbf{t}_2 + n_3\mathbf{t}_3)$

How does b.f. $\psi^{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}$ transform under any element of SG $T(g)$?

1. Recap- under pure translation

$$T(\mathbf{t})\psi^{\mathbf{k}}(\mathbf{r}) = \exp(-i\mathbf{kt})\psi^{\mathbf{k}}(\mathbf{r})$$

2. under general element g

rotation

$$g\psi^{\mathbf{k}}(\mathbf{r}) = \{h|\boldsymbol{\tau}_h + \mathbf{t}_n\}\psi^{\mathbf{k}}(\mathbf{r}) = \psi'(\mathbf{r})$$

accompanying translation

To find ψ' consider pure translation again

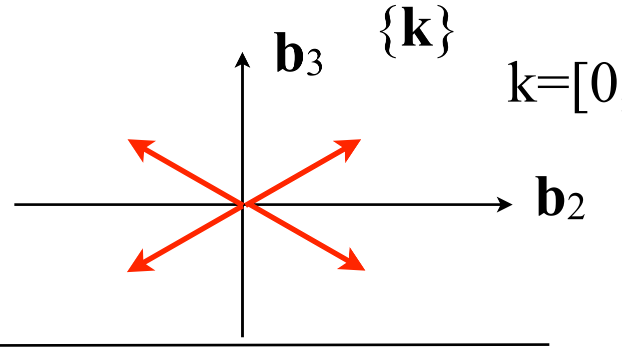
$$T(\mathbf{t})\psi'(\mathbf{r}) = \text{...some math...} = \exp(-i\hat{h}\mathbf{kt})\psi'(\mathbf{r})$$

$$\{h|\boldsymbol{\tau}_h + \mathbf{t}_n\}\psi^{\mathbf{k}}(\mathbf{r}) = \psi^{\hat{h}\mathbf{k}}(\mathbf{r})$$

$h\mathbf{k}$ = or ≠ $\mathbf{k} + \mathbf{b}$

Manyfold of all non-equivalent* $h\mathbf{k}$ = propagation vector star $\{\mathbf{k}\}$

Little group $G_k \in G$ leave ***k*** *invariant*



k=[0,u,v]

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*non-equivalent h**k** ≠ **k** + **b**

Symmetry group of propagation vector, examples of star {k}

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

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

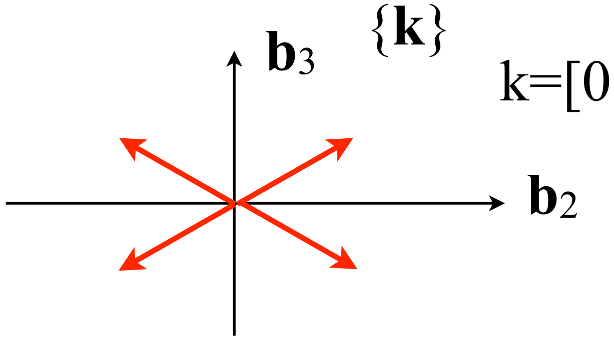
Symmetry operations

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

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

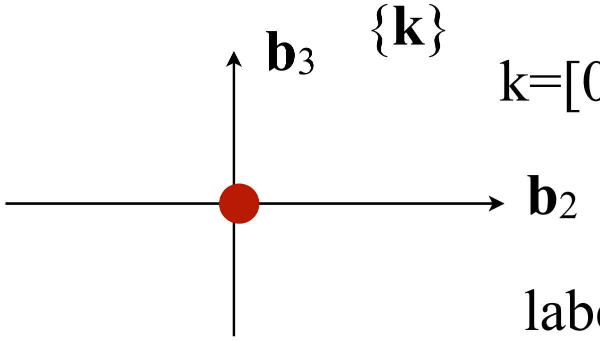
$+T(n_1\mathbf{t}_1+n_2\mathbf{t}_2+n_3\mathbf{t}_3)$

Manyfold of all non-equivalent $h\mathbf{k}$ = propagation vector star $\{\mathbf{k}\}$



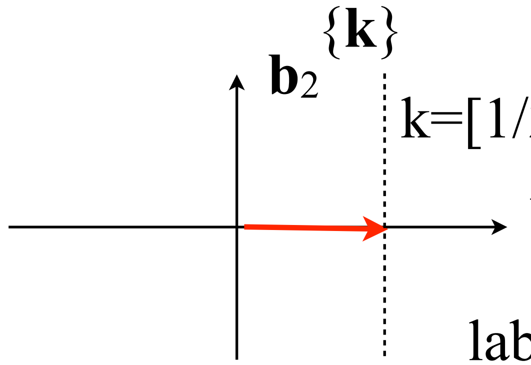
k=[0,u,v]

label *K*



k=[0,0,0]

label *Γ*



k=[1/2,0,0]

label *X*

Little group G

Little group $G_k \in G$ leave ***k*** *invariant*

(1) 1

(8) $n(0,\frac{1}{2},\frac{1}{2})\quad \frac{1}{4},y,z$

$G_k =$ '*P1n1*'

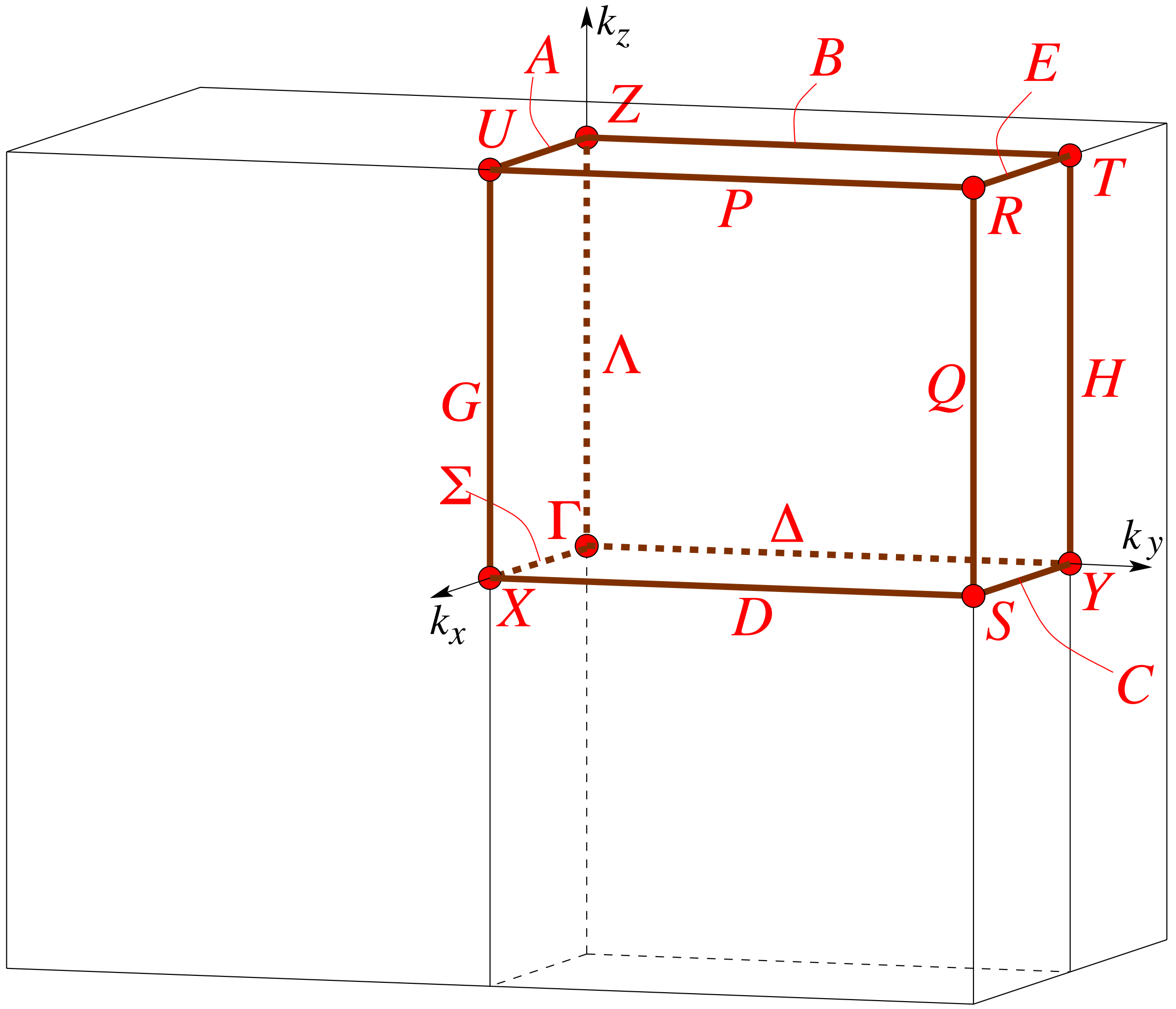
$G_k = G$

$G_k = G$

The k-vector types and Brillouin zones of the space groups

propagation vector = a point on/inside Brillouine zone

Brillouine zone of *Pmmm* (Γ_0)

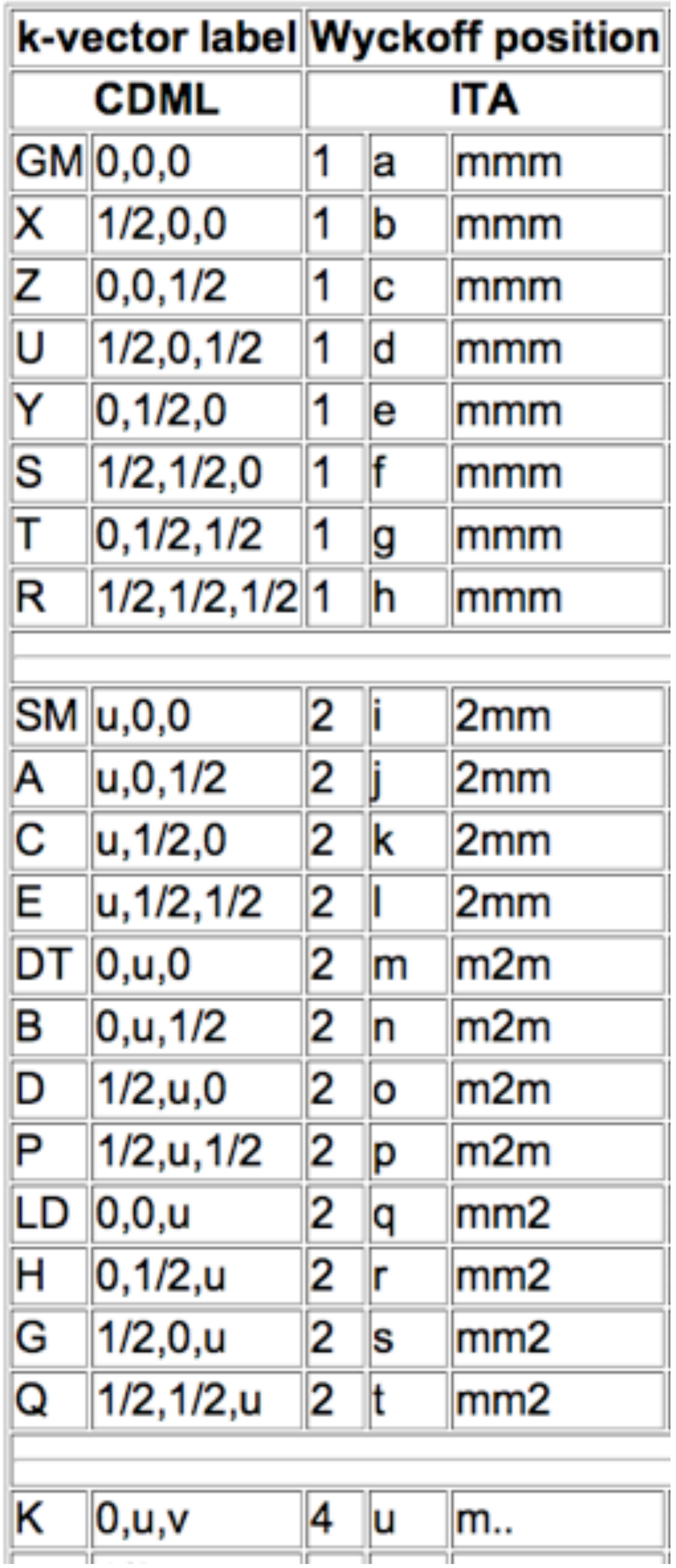


A.P. Cracknell, B.L. Davis, S.C. Miller and W.F. Love (1979) (abbreviated as **CDML**)

Kovalev O.V (1986) (1993) *Representations of the Crystallographic Space Groups* (London: Gordon and Breach)

Kovalev

k_{19}
k_{20}
k_{22}
k_{24}
k_{21}
k_{25}
…
…



k-vector label		Wyckoff position		
CDML		ITA		
GM	0,0,0	1	a	mmm
X	1/2,0,0	1	b	mmm
Z	0,0,1/2	1	c	mmm
U	1/2,0,1/2	1	d	mmm
Y	0,1/2,0	1	e	mmm
S	1/2,1/2,0	1	f	mmm
T	0,1/2,1/2	1	g	mmm
R	1/2,1/2,1/2	1	h	mmm
SM	u,0,0	2	i	2mm
A	u,0,1/2	2	j	2mm
C	u,1/2,0	2	k	2mm
E	u,1/2,1/2	2	l	2mm
DT	0,u,0	2	m	m2m
B	0,u,1/2	2	n	m2m
D	1/2,u,0	2	o	m2m
P	1/2,u,1/2	2	p	m2m
LD	0,0,u	2	q	mm2
H	0,1/2,u	2	r	mm2
G	1/2,0,u	2	s	mm2
Q	1/2,1/2,u	2	t	mm2
K	0,u,v	4	u	m..

Γ_c^f face centered cubic. Brillouine zone, {k}

Classification symbol, number, etc.

IPHS	*W*	8	1	0	½
	L	9	½	½	½
	X	10	0	0	1

CMDL   Kovalev   **B**$_1$, **B**$_2$, **B**$_3$

k-vector star {k}

$\boldsymbol{k}_1 = ¼(\boldsymbol{b}_1 + \boldsymbol{b}_2) + ½(\boldsymbol{b}_2 + \boldsymbol{b}_3),\ \boldsymbol{k}_2 = -\boldsymbol{k}_1$

$\boldsymbol{k}_3 = ¼(\boldsymbol{b}_1 + \boldsymbol{b}_3) + ½(\boldsymbol{b}_1 + \boldsymbol{b}_2),\ \boldsymbol{k}_4 = -\boldsymbol{k}_3$

$\boldsymbol{k}_5 = ¼(\boldsymbol{b}_2 + \boldsymbol{b}_3) + ½(\boldsymbol{b}_1 + \boldsymbol{b}_3),\ \boldsymbol{k}_6 = -\boldsymbol{k}_5$

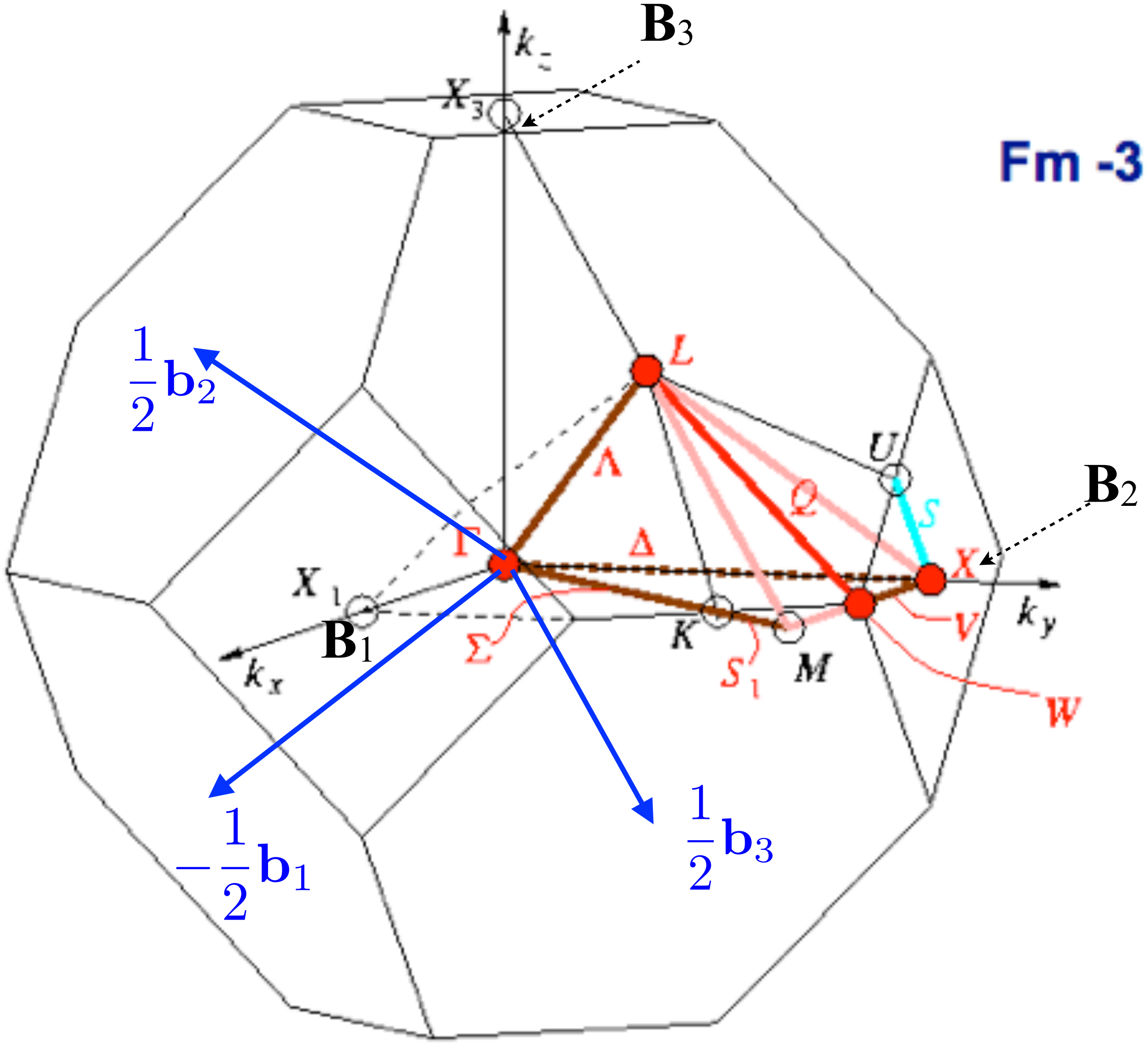
$\boldsymbol{k}_1 = ½(\boldsymbol{b}_1 + \boldsymbol{b}_2 + \boldsymbol{b}_3),\ \boldsymbol{k}_2 = ½\boldsymbol{b}_1,\ \boldsymbol{k}_3 = ½\boldsymbol{b}_2,\ \boldsymbol{k}_4 = ½\boldsymbol{b}_3$

$\boldsymbol{k}_1 = ½(\boldsymbol{b}_1 + \boldsymbol{b}_2),\ \boldsymbol{k}_2 = ½(\boldsymbol{b}_1 + \boldsymbol{b}_3),\ \boldsymbol{k}_3 = ½(\boldsymbol{b}_2 + \boldsymbol{b}_3)$

B$_1$, **B**$_2$, **B**$_3$ edges of Bravias cell of reciprocal lattice

b$_1$, **b**$_2$, **b**$_3$ reciprocal lattice periods

$$\begin{bmatrix} \mathbf{b1} \\ \mathbf{b2} \\ \mathbf{b3} \end{bmatrix} = \begin{bmatrix} -\mathbf{B1}+\mathbf{B2}+\mathbf{B3} \\ \mathbf{B1}-\mathbf{B2}+\mathbf{B3} \\ \mathbf{B1}+\mathbf{B2}-\mathbf{B3} \end{bmatrix}$$



Fm -3 m-O$_h^5$ (225)

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Kovalev book (slide skipped)

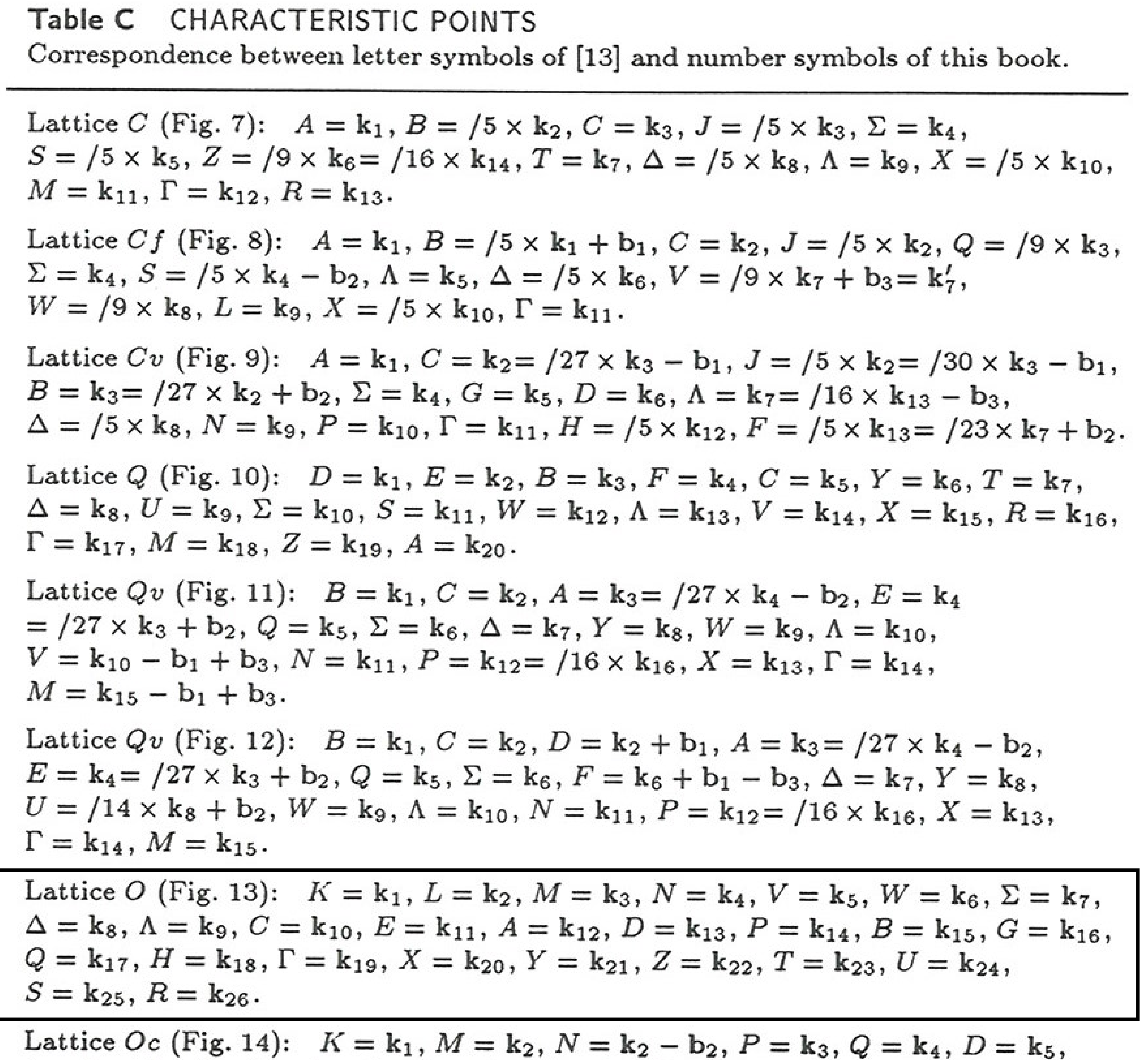


Table C CHARACTERISTIC POINTS

Correspondence between letter symbols of [13] and number symbols of this book.

Lattice C (Fig. 7): $A = \mathbf{k}_1$, $B = /5 \times \mathbf{k}_2$, $C = \mathbf{k}_3$, $J = /5 \times \mathbf{k}_3$, $\Sigma = \mathbf{k}_4$, $S = /5 \times \mathbf{k}_5$, $Z = /9 \times \mathbf{k}_6 = /16 \times \mathbf{k}_{14}$, $T = \mathbf{k}_7$, $\Delta = /5 \times \mathbf{k}_8$, $\Lambda = \mathbf{k}_9$, $X = /5 \times \mathbf{k}_{10}$, $M = \mathbf{k}_{11}$, $\Gamma = \mathbf{k}_{12}$, $R = \mathbf{k}_{13}$.

Lattice Cf (Fig. 8): $A = \mathbf{k}_1$, $B = /5 \times \mathbf{k}_1 + \mathbf{b}_1$, $C = \mathbf{k}_2$, $J = /5 \times \mathbf{k}_2$, $Q = /9 \times \mathbf{k}_3$, $\Sigma = \mathbf{k}_4$, $S = /5 \times \mathbf{k}_4 - \mathbf{b}_2$, $\Lambda = \mathbf{k}_5$, $\Delta = /5 \times \mathbf{k}_6$, $V = /9 \times \mathbf{k}_7 + \mathbf{b}_3 = \mathbf{k}'_7$, $W = /9 \times \mathbf{k}_8$, $L = \mathbf{k}_9$, $X = /5 \times \mathbf{k}_{10}$, $\Gamma = \mathbf{k}_{11}$.

Lattice Cv (Fig. 9): $A = \mathbf{k}_1$, $C = \mathbf{k}_2 = /27 \times \mathbf{k}_3 - \mathbf{b}_1$, $J = /5 \times \mathbf{k}_2 = /30 \times \mathbf{k}_3 - \mathbf{b}_1$, $B = \mathbf{k}_3 = /27 \times \mathbf{k}_2 + \mathbf{b}_2$, $\Sigma = \mathbf{k}_4$, $G = \mathbf{k}_5$, $D = \mathbf{k}_6$, $\Lambda = \mathbf{k}_7 = /16 \times \mathbf{k}_{13} - \mathbf{b}_3$, $\Delta = /5 \times \mathbf{k}_8$, $N = \mathbf{k}_9$, $P = \mathbf{k}_{10}$, $\Gamma = \mathbf{k}_{11}$, $H = /5 \times \mathbf{k}_{12}$, $F = /5 \times \mathbf{k}_{13} = /23 \times \mathbf{k}_7 + \mathbf{b}_2$.

Lattice Q (Fig. 10): $D = \mathbf{k}_1$, $E = \mathbf{k}_2$, $B = \mathbf{k}_3$, $F = \mathbf{k}_4$, $C = \mathbf{k}_5$, $Y = \mathbf{k}_6$, $T = \mathbf{k}_7$, $\Delta = \mathbf{k}_8$, $U = \mathbf{k}_9$, $\Sigma = \mathbf{k}_{10}$, $S = \mathbf{k}_{11}$, $W = \mathbf{k}_{12}$, $\Lambda = \mathbf{k}_{13}$, $V = \mathbf{k}_{14}$, $X = \mathbf{k}_{15}$, $R = \mathbf{k}_{16}$, $\Gamma = \mathbf{k}_{17}$, $M = \mathbf{k}_{18}$, $Z = \mathbf{k}_{19}$, $A = \mathbf{k}_{20}$.

Lattice Qv (Fig. 11): $B = \mathbf{k}_1$, $C = \mathbf{k}_2$, $A = \mathbf{k}_3 = /27 \times \mathbf{k}_4 - \mathbf{b}_2$, $E = \mathbf{k}_4 = /27 \times \mathbf{k}_3 + \mathbf{b}_2$, $Q = \mathbf{k}_5$, $\Sigma = \mathbf{k}_6$, $\Delta = \mathbf{k}_7$, $Y = \mathbf{k}_8$, $W = \mathbf{k}_9$, $\Lambda = \mathbf{k}_{10}$, $V = \mathbf{k}_{10} - \mathbf{b}_1 + \mathbf{b}_3$, $N = \mathbf{k}_{11}$, $P = \mathbf{k}_{12} = /16 \times \mathbf{k}_{16}$, $X = \mathbf{k}_{13}$, $\Gamma = \mathbf{k}_{14}$, $M = \mathbf{k}_{15} - \mathbf{b}_1 + \mathbf{b}_3$.

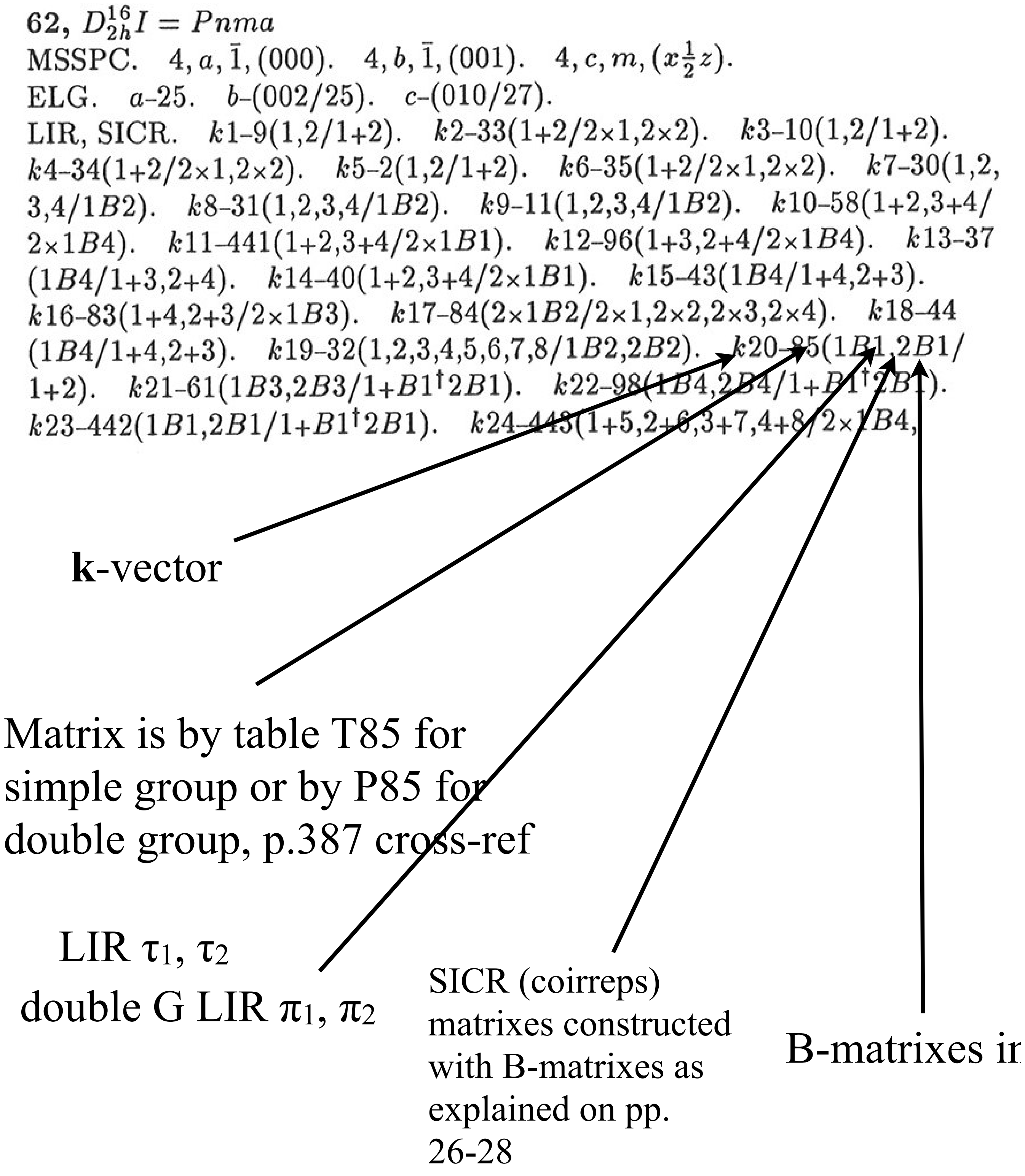
Lattice Qv (Fig. 12): $B = \mathbf{k}_1$, $C = \mathbf{k}_2$, $D = \mathbf{k}_2 + \mathbf{b}_1$, $A = \mathbf{k}_3 = /27 \times \mathbf{k}_4 - \mathbf{b}_2$, $E = \mathbf{k}_4 = /27 \times \mathbf{k}_3 + \mathbf{b}_2$, $Q = \mathbf{k}_5$, $\Sigma = \mathbf{k}_6$, $F = \mathbf{k}_6 + \mathbf{b}_1 - \mathbf{b}_3$, $\Delta = \mathbf{k}_7$, $Y = \mathbf{k}_8$, $U = /14 \times \mathbf{k}_8 + \mathbf{b}_2$, $W = \mathbf{k}_9$, $\Lambda = \mathbf{k}_{10}$, $N = \mathbf{k}_{11}$, $P = \mathbf{k}_{12} = /16 \times \mathbf{k}_{16}$, $X = \mathbf{k}_{13}$, $\Gamma = \mathbf{k}_{14}$, $M = \mathbf{k}_{15}$.

Lattice O (Fig. 13): $K = \mathbf{k}_1$, $L = \mathbf{k}_2$, $M = \mathbf{k}_3$, $N = \mathbf{k}_4$, $V = \mathbf{k}_5$, $W = \mathbf{k}_6$, $\Sigma = \mathbf{k}_7$, $\Delta = \mathbf{k}_8$, $\Lambda = \mathbf{k}_9$, $C = \mathbf{k}_{10}$, $E = \mathbf{k}_{11}$, $A = \mathbf{k}_{12}$, $D = \mathbf{k}_{13}$, $P = \mathbf{k}_{14}$, $B = \mathbf{k}_{15}$, $G = \mathbf{k}_{16}$, $Q = \mathbf{k}_{17}$, $H = \mathbf{k}_{18}$, $\Gamma = \mathbf{k}_{19}$, $X = \mathbf{k}_{20}$, $Y = \mathbf{k}_{21}$, $Z = \mathbf{k}_{22}$, $T = \mathbf{k}_{23}$, $U = \mathbf{k}_{24}$, $S = \mathbf{k}_{25}$, $R = \mathbf{k}_{26}$.

Lattice Oc (Fig. 14): $K = \mathbf{k}_1$, $M = \mathbf{k}_2$, $N = \mathbf{k}_2 - \mathbf{b}_2$, $P = \mathbf{k}_3$, $Q = \mathbf{k}_4$, $D = \mathbf{k}_5$,

Brillouine zone of *Pmmm* (Γ_0)

Kovalev book (slide skipped)



62, $D_{2h}^{16}I = Pnma$
MSSPC. $4, a, \bar{1}, (000)$. $4, b, \bar{1}, (001)$. $4, c, m, (x\frac{1}{2}z)$.
ELG. a–25. b–(002/25). c–(010/27).
LIR, SICR. k1–9(1,2/1+2). k2–33(1+2/2×1,2×2). k3–10(1,2/1+2). k4–34(1+2/2×1,2×2). k5–2(1,2/1+2). k6–35(1+2/2×1,2×2). k7–30(1,2,3,4/1$B$2). k8–31(1,2,3,4/1$B$2). k9–11(1,2,3,4/1$B$2). k10–58(1+2,3+4/2×1$B$4). k11–441(1+2,3+4/2×1$B$1). k12–96(1+3,2+4/2×1$B$4). k13–37(1$B$4/1+3,2+4). k14–40(1+2,3+4/2×1$B$1). k15–43(1$B$4/1+4,2+3). k16–83(1+4,2+3/2×1$B$3). k17–84(2×1$B$2/2×1,2×2,2×3,2×4). k18–44(1$B$4/1+4,2+3). k19–32(1,2,3,4,5,6,7,8/1$B$2,2$B$2). k20–85(1$B$1,2$B$1/1+2). k21–61(1$B$3,2$B$3/1+$B1^\dagger$2$B$1). k22–98(1$B$4,2$B$4/1+$B1^\dagger$2$B$1). k23–442(1$B$1,2$B$1/1+$B1^\dagger$2$B$1). k24–443(1+5,2+6,3+7,4+8/2×1$B$4,

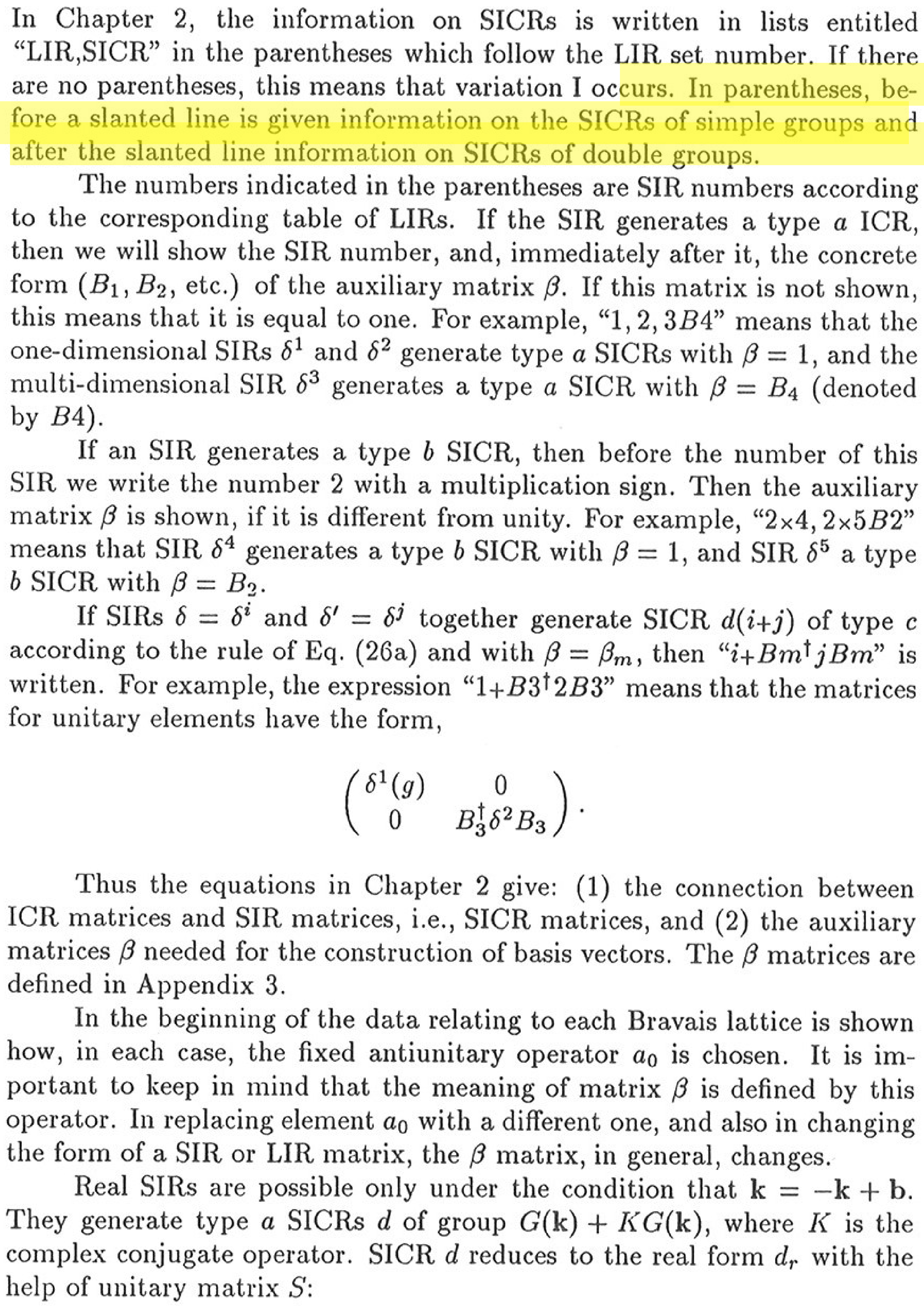
k-vector

Matrix is by table T85 for simple group or by P85 for double group, p.387 cross-ref

LIR τ_1, τ_2
double G LIR π_1, π_2

SICR (coirreps) matrixes constructed with B-matrixes as explained on pp. 26-28

B-matrixes ir



In Chapter 2, the information on SICRs is written in lists entitled "LIR,SICR" in the parentheses which follow the LIR set number. If there are no parentheses, this means that variation I occurs. In parentheses, before a slanted line is given information on the SICRs of simple groups and after the slanted line information on SICRs of double groups.

The numbers indicated in the parentheses are SIR numbers according to the corresponding table of LIRs. If the SIR generates a type a ICR, then we will show the SIR number, and, immediately after it, the concrete form (B_1, B_2, etc.) of the auxiliary matrix β. If this matrix is not shown, this means that it is equal to one. For example, "$1, 2, 3B4$" means that the one-dimensional SIRs δ^1 and δ^2 generate type a SICRs with $\beta = 1$, and the multi-dimensional SIR δ^3 generates a type a SICR with $\beta = B_4$ (denoted by $B4$).

If an SIR generates a type b SICR, then before the number of this SIR we write the number 2 with a multiplication sign. Then the auxiliary matrix β is shown, if it is different from unity. For example, "2×4, 2×5$B$2" means that SIR δ^4 generates a type b SICR with $\beta = 1$, and SIR δ^5 a type b SICR with $\beta = B_2$.

If SIRs $\delta = \delta^i$ and $\delta' = \delta^j$ together generate SICR $d(i+j)$ of type c according to the rule of Eq. (26a) and with $\beta = \beta_m$, then "$i{+}Bm^\dagger jBm$" is written. For example, the expression "$1{+}B3^\dagger 2B3$" means that the matrices for unitary elements have the form,

$$\begin{pmatrix} \delta^1(g) & 0 \\ 0 & B_3^\dagger \delta^2 B_3 \end{pmatrix}.$$

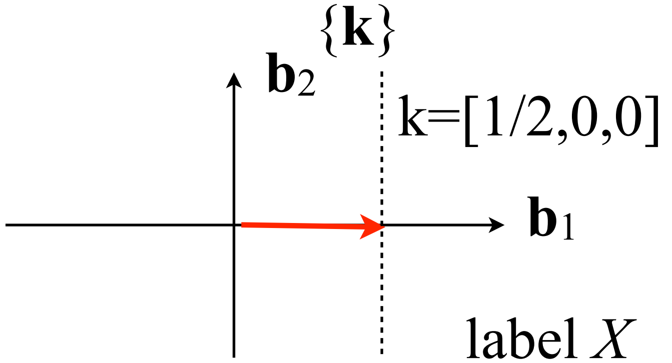
Thus the equations in Chapter 2 give: (1) the connection between ICR matrices and SIR matrices, i.e., SICR matrices, and (2) the auxiliary matrices β needed for the construction of basis vectors. The β matrices are defined in Appendix 3.

In the beginning of the data relating to each Bravais lattice is shown how, in each case, the fixed antiunitary operator a_0 is chosen. It is important to keep in mind that the meaning of matrix β is defined by this operator. In replacing element a_0 with a different one, and also in changing the form of a SIR or LIR matrix, the β matrix, in general, changes.

Real SIRs are possible only under the condition that $\mathbf{k} = -\mathbf{k} + \mathbf{b}$. They generate type a SICRs d of group $G(\mathbf{k}) + KG(\mathbf{k})$, where K is the complex conjugate operator. SICR d reduces to the real form d_r with the help of unitary matrix S:

♕ Space group irreps ♕

Representation of SG for star {**k**} are characterized by irreps of little group G_k of any arm of propagation vector **k.**



$G_k = G$

Pnma k=[1/2,0,0], k20, *X*
irreps: two 2D τ_1, τ_2

Consider one irrep $d^{\mathbf{k}\nu}$ ($l_\nu \times l_\nu$ matrixes) with dim=l_ν with number ν

Its basis: l_ν functions

$$\psi_\lambda^{\mathbf{k}\nu} = \boxed{u^{\nu}_{\mathbf{k}\lambda}(\mathbf{r})} e^{i\mathbf{k}\mathbf{r}} (\lambda = 1, ..., l_\nu)$$

that are transformed by symmetry elements *g* by matrixes $d^{\mathbf{k}\nu}(g)$

!

Not yet defined. A linear combination of vectors of some linear vector space LVS

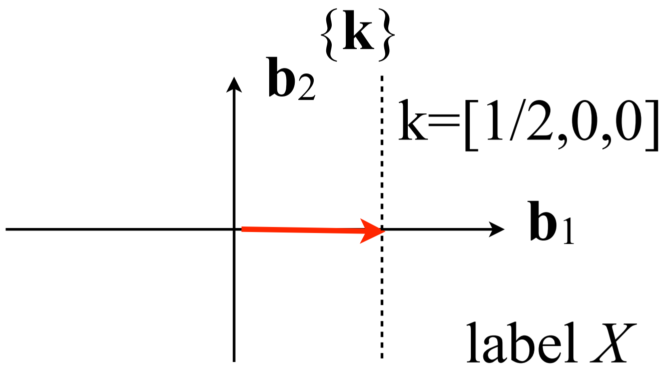
$$\begin{pmatrix} \psi_\lambda^{\mathbf{k}1} \\ \psi_\lambda^{\mathbf{k}2} \\ \dots \\ \dots \\ \dots \\ \psi_\lambda^{\mathbf{k}l_\nu} \end{pmatrix}$$

Example (LIR)

$d^{\mathbf{k}\nu}(g)$

IT	2_x	2_y	2_z	$\bar{1}$	n_x	m_y	a_z
g Kovalev	/2	/3	/4	/25	/26	/27	/28
$\hat{\tau}1$	$\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$
$\hat{\tau}2 = \hat{\tau}1 \times$	1	1	1	-1	-1	-1	-1

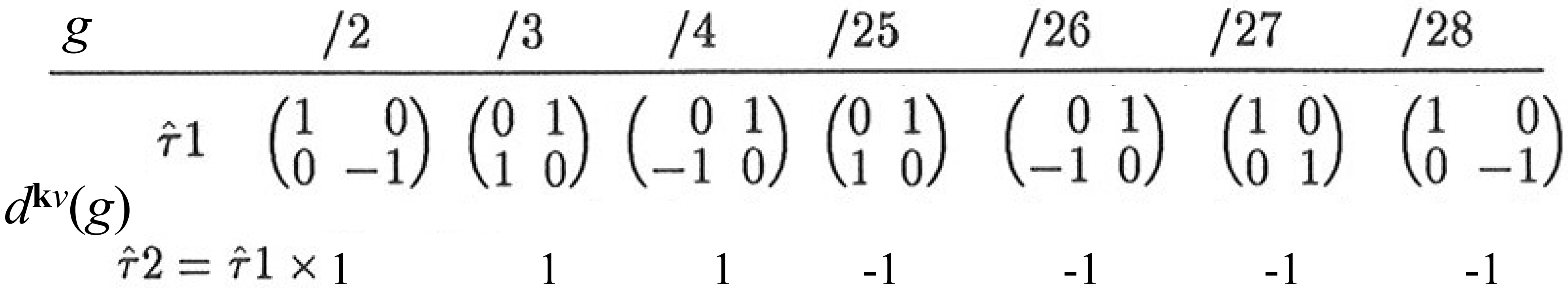
Space group irreps, examples
dimensions up to 6 (cf. 3 for point groups)



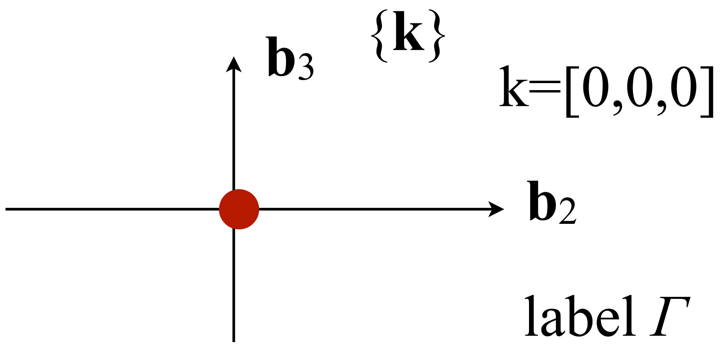
$G_k = G$

Example 1 *Pnma* k=[1/2,0,0], k20

irreps: two 2D τ_1, τ_2



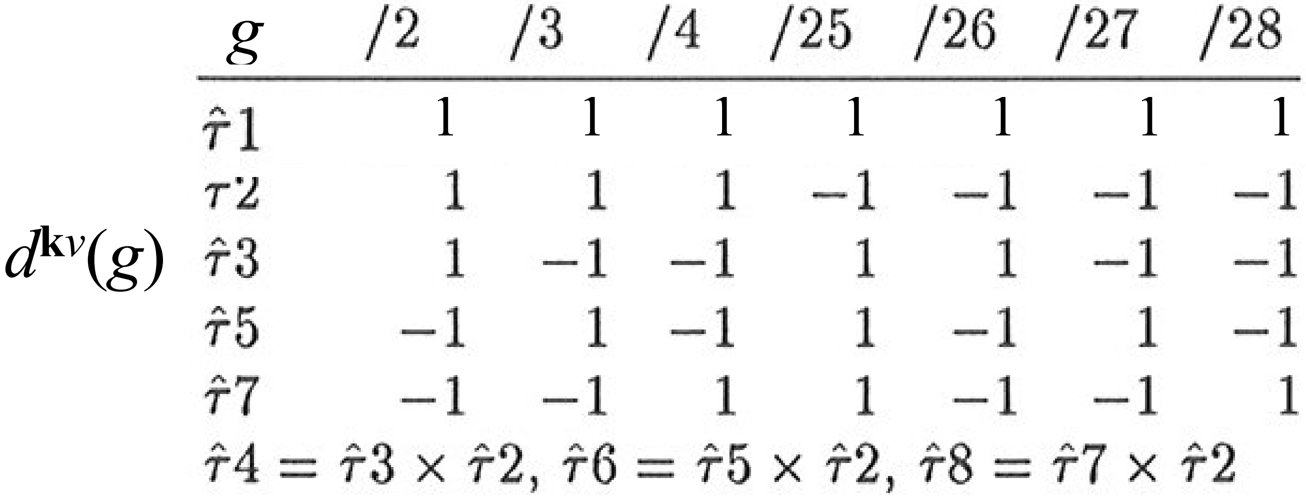
	g	/2	/3	/4	/25	/26	/27	/28
$d^{\mathbf{k}\nu}(g)$	$\hat{\tau}1$	$\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}$	$\begin{pmatrix}0 & 1\\-1 & 0\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}$	$\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}$
	$\hat{\tau}2 = \hat{\tau}1 \times$	1	1	1	-1	-1	-1	-1



$G_k = G$

Example 2 *Pnma* k=[0,0,0], k19

irreps: eight 1D τ_1, τ_2, τ_3, τ_4, τ_5, τ_6, τ_7, τ_8



	g	/2	/3	/4	/25	/26	/27	/28
$d^{\mathbf{k}\nu}(g)$	$\hat{\tau}1$	1	1	1	1	1	1	1
	$\hat{\tau}2$	1	1	1	−1	−1	−1	−1
	$\hat{\tau}3$	1	−1	−1	1	1	−1	−1
	$\hat{\tau}5$	−1	1	−1	1	−1	1	−1
	$\hat{\tau}7$	−1	−1	1	1	−1	−1	1

$\hat{\tau}4 = \hat{\tau}3 \times \hat{\tau}2,\ \hat{\tau}6 = \hat{\tau}5 \times \hat{\tau}2,\ \hat{\tau}8 = \hat{\tau}7 \times \hat{\tau}2$

Example 3

Higher dimensions: Ia3d (#230) k=[1,0,0]: 1(6D) ⊕ 3(2D)

k=[1/2,1/2,1/2]: 1(4D) ⊕ 2(2D)

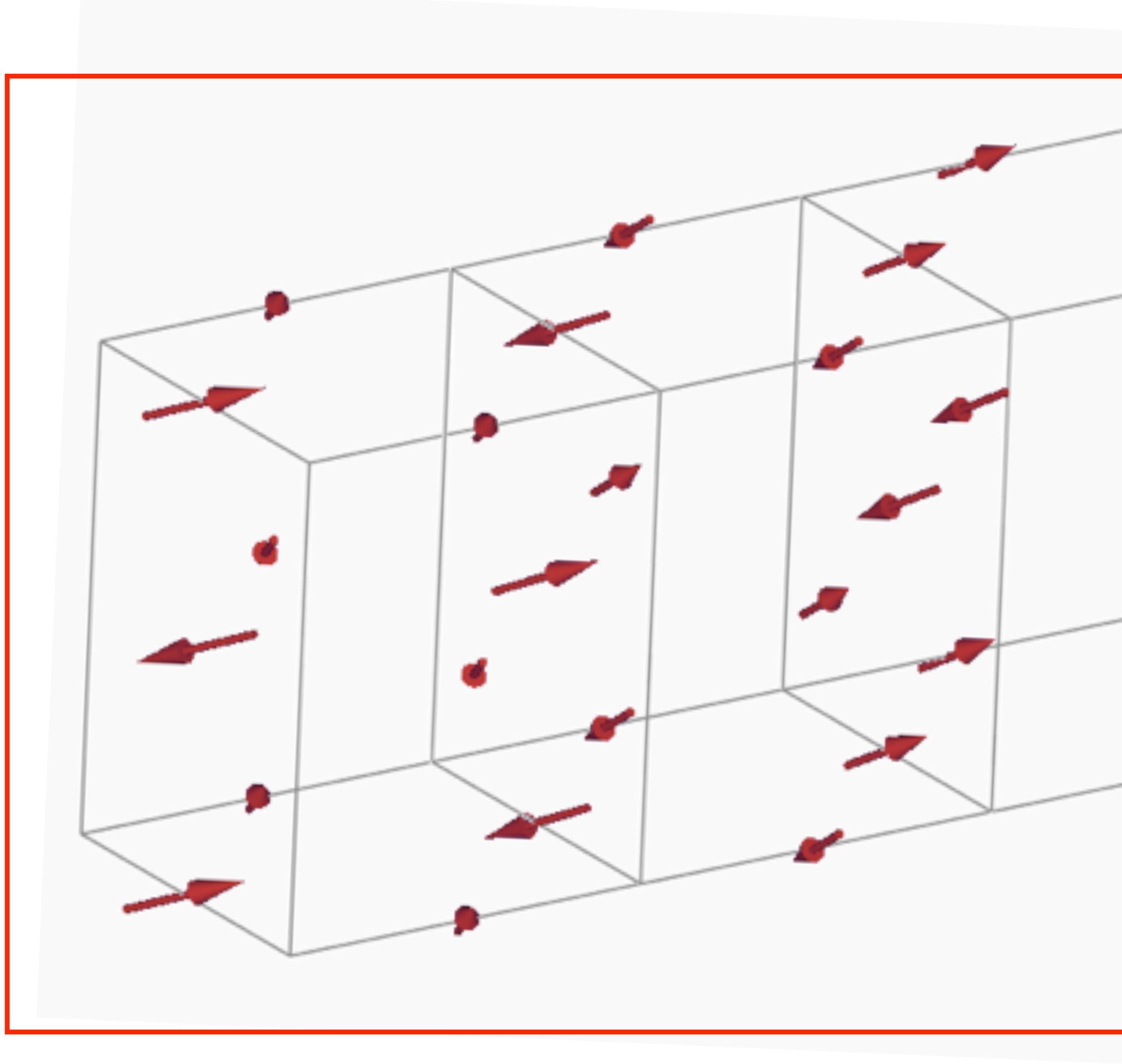
Constructing of vector space of magnetic structure and reducible magnetic representation

Case study of magnetic structure of multiferroic $TbMnO_3$

Space Group *G: Pnma,* no.62
propagation vector k=[μ,0,0]

↓

has 4 1D irreducible representations



symmetry
irreps

linear space
reps of *G* in LS

New Journal of Physics 11, 043019 (2009)

k-vector group

Group *G: Pnma,* no.62: 8 symmetry operators

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

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

Little group G_k, k=[0.45,0,0]=[q,0,0]

Little group of propagation vector G_k contains only the elements of G that do not change **k**

$P2_1ma\,(Pmc2_1, 26)$

(1) x,y,z | (4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}+\frac{1}{2}$ | (7) $x,\bar{y}+\frac{1}{2},z$ | (6) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$

rotation+ translation

$$E\begin{pmatrix}100\\010\\001\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}\quad 2_x\begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}\quad m_y\begin{pmatrix}100\\0\bar{1}0\\001\end{pmatrix}\begin{pmatrix}0\\\frac{1}{2}\\0\end{pmatrix}\quad m_z\begin{pmatrix}100\\010\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{pmatrix}$$

vector space and representation for an atom in position (0,0,1/2) for k-vector group

Mn-position	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$
position number	a	b	c	d
k-group element	g_1	g_2	g_3	g_4

rotation+ translation

$$E \begin{pmatrix}100\\010\\001\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix} \quad 2_x \begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix} \quad m_y \begin{pmatrix}100\\0\bar{1}0\\001\end{pmatrix}\begin{pmatrix}0\\\frac{1}{2}\\0\end{pmatrix} \quad m_y \begin{pmatrix}100\\010\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{pmatrix}$$

Permutation representation

element g_2 changes atomic position:

element g_2 is represented by 4x4 matrix

a ⇒ b

b ⇒ a

c ⇒ d

d ⇒ c

$$\begin{pmatrix}0100\\1000\\0001\\0010\end{pmatrix}\begin{pmatrix}a\\b\\c\\d\end{pmatrix} = \begin{pmatrix}b\\a\\d\\c\end{pmatrix}$$

$$b = e^{2\pi i(\mathbf{k}\mathbf{a}_p)}$$

in addition, element g_2 sometimes moves the atom outside of the *zero*cell. We have to return the atom back with **-a**$_p$:

	-a$_p$
a ⇒ b	(000)
b ⇒ a	(-100)
c ⇒ d	(000)
d ⇒ c	(-100)

$$\psi^{\mathbf{k}\nu}(\mathbf{r}) = u^{\nu}_{\mathbf{k}}(\mathbf{r})e^{2\pi i\mathbf{k}\mathbf{r}}$$

Classifying possible magnetic structures

Magnetic representation

group element	g_1	g_2	g_3	g_4
rotation+ translation	$E\begin{pmatrix}100\\010\\001\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}$	$2_x\begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}$	$m_y\begin{pmatrix}100\\0\bar{1}0\\001\end{pmatrix}\begin{pmatrix}0\\\frac{1}{2}\\0\end{pmatrix}$	$m_y\begin{pmatrix}100\\010\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{pmatrix}$
Mn-position	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$
position number	a	b	c	d

Permutation representation

4x4 matrices (P)	$\begin{pmatrix}1000\\0100\\0010\\0001\end{pmatrix}$	$\begin{pmatrix}0100\\b000\\0001\\00b0\end{pmatrix}$	$\begin{pmatrix}0010\\0001\\1000\\0100\end{pmatrix}$	$\begin{pmatrix}0001\\00b0\\0100\\b000\end{pmatrix}$

Axial vector (spin) representation

For instance:
rotational part of element g_2: $R(g_2)$ changes atomic spin direction:

element g_2 is represented by 3x3 matrix

$$R(g_2)\times\det(R)\begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}\begin{pmatrix}S_x\\S_y\\S_z\end{pmatrix}=\begin{pmatrix}S_x\\-S_y\\-S_z\end{pmatrix}$$

Classifying possible magnetic structures

Magnetic representation

group element	g1	g2	g3	g4
rotation+ translation	$E\begin{pmatrix}100\\010\\001\end{pmatrix}\begin{pmatrix}0\\0\\0\end{pmatrix}$	$2_x\begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix}$	$m_y\begin{pmatrix}100\\0\bar{1}0\\001\end{pmatrix}\begin{pmatrix}0\\\frac{1}{2}\\0\end{pmatrix}$	$m_y\begin{pmatrix}100\\010\\00\bar{1}\end{pmatrix}\begin{pmatrix}\frac{1}{2}\\0\\\frac{1}{2}\end{pmatrix}$
Mn-position	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$
position number	a	b	c	d

Permutation representation

4x4 matrices (P)	$\begin{pmatrix}1000\\0100\\0010\\0001\end{pmatrix}$	$\begin{pmatrix}0100\\b000\\0001\\00b0\end{pmatrix}$	$\begin{pmatrix}0010\\0001\\1000\\0100\end{pmatrix}$	$\begin{pmatrix}0001\\00b0\\0100\\b000\end{pmatrix}$

Axial vector (spin) representation

3x3 matrices (A) *R(g₂)×det (R)*	$\begin{pmatrix}100\\010\\001\end{pmatrix}$	$\begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix}$	$\begin{pmatrix}\bar{1}00\\010\\00\bar{1}\end{pmatrix}$	$\begin{pmatrix}\bar{1}00\\0\bar{1}0\\001\end{pmatrix}$

Classifying possible magnetic structures

Magnetic representation

group element	g_1	g_2	g_3	g_4
Mn-position	$0, 0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, 0$
position number	a	b	c	d
spin	**S_1**	**S_2**	**S_3**	**S_4**

Vector spaces

Permutation representation

4x4 matrices (P)

$$\begin{pmatrix}1000\\0100\\0010\\0001\end{pmatrix} \quad \begin{pmatrix}0100\\b000\\0001\\00b0\end{pmatrix} \quad \begin{pmatrix}0010\\0001\\1000\\0100\end{pmatrix} \quad \begin{pmatrix}0001\\00b0\\0100\\b000\end{pmatrix} \qquad \begin{pmatrix}a\\b\\c\\d\end{pmatrix}$$

Axial vector (spin) representation

3x3 matrices (A) *R(g_2)×det (R)*

$$\begin{pmatrix}100\\010\\001\end{pmatrix} \quad \begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix} \quad \begin{pmatrix}\bar{1}00\\010\\00\bar{1}\end{pmatrix} \quad \begin{pmatrix}\bar{1}00\\0\bar{1}0\\001\end{pmatrix} \qquad \begin{pmatrix}S_x\\S_y\\S_z\end{pmatrix}$$

Magnetic representation

direct (tensor) product
P⊗A
12x12 matrices

e.g. for group element g_2

$$\begin{pmatrix}0100\\b000\\0001\\00b0\end{pmatrix} \otimes \begin{pmatrix}100\\0\bar{1}0\\00\bar{1}\end{pmatrix} = \begin{pmatrix}
0&0&0&1&0&0&0&0&0&0&0&0\\
0&0&0&0&\bar{1}&0&0&0&0&0&0&0\\
0&0&0&0&0&\bar{1}&0&0&0&0&0&0\\
1&0&0&0&0&0&0&0&0&0&0&0\\
0&\bar{b}&0&0&0&0&0&0&0&0&0&0\\
0&0&\bar{b}&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&1&0&0\\
0&0&0&0&0&0&0&0&0&0&\bar{1}&0\\
0&0&0&0&0&0&0&0&0&0&0&\bar{1}\\
0&0&0&0&0&0&1&0&0&0&0&0\\
0&0&0&0&0&0&0&\bar{b}&0&0&0&0\\
0&0&0&0&0&0&0&0&\bar{b}&0&0&0
\end{pmatrix}$$

$TmMnO_3$: Classifying possible magnetic structures basis vectors/functions $S_{\tau 1}$, $S_{\tau 2}$, $S_{\tau 3}$, ...

Pnma, k=[0.45,0,0] Mn in (4a)-position

12D magnetic representation is reduced to four one-dimensional irreps

$$d = \sum_{\oplus} n_\nu d^\nu = 3\tau_1 \oplus 3\tau_2 \oplus \boxed{3\tau_3} \oplus 3\tau 4$$

$$n_\nu = \frac{1}{n(G)} \sum_{g \subset G} \chi(g) \chi^{*\nu}(g)$$

Tm in (4c)-position (x,1/4,z) Different decomposition!

$1\tau_1 \oplus 2\tau_2 \oplus 2\tau_3 \oplus 1\tau_4$

	E	2_x	m_y	m_z
	g_1	g_2	g_3	g_4
τ_1	1	a	1	a
τ_2	1	a	-1	$-a$
τ_3	1	$-a$	1	$-a$
τ_4	1	$-a$	-1	a

$a = e^{\pi i k_x}$

recap: irrep: 1D matrixes d_τ(g) that define how basis functions b.f. should be changed/transformed under action of **abstract group** elements g_i. The permutations and spin rotations, *or whatever meaning of* g_i *is*, **are not** yet here!

Projection method: to find basis functions b.f. transforming according to a specific irrep τ

Axial basis construction. Projection method.

Basis functions.
$3\sigma_M N$-dimention column

$$\psi_\lambda^{\kappa\nu} = \sum_n^{\oplus} \sigma_\lambda^{\kappa\nu} \exp(i\kappa \mathbf{t}_n),$$

$3\sigma_M$-dimention column in *zeroth*-cell.

$$\sigma_\lambda^{\kappa\nu} = \sum_{i=1}^{\sigma_M}{}^{\oplus} S\begin{pmatrix} \kappa\nu \\ \lambda \end{pmatrix}\Bigg|\, i\Bigg),$$

$$S\begin{pmatrix} \kappa\nu \\ \lambda \end{pmatrix}\Bigg|\, i\Bigg) = \sum_{h \in G_\kappa^0} d_{\lambda[\mu]}^{*\kappa\nu}(g) \exp[-i\kappa \mathbf{a}_p(g,j)]\, \delta_{i,g[j]}\, \delta_h \begin{pmatrix} R^h_{x[\beta]} \\ R^h_{y[\beta]} \\ R^h_{z[\beta]} \end{pmatrix}$$

Start function.
$3\sigma_M$ N-dimension column

$$\varphi_\kappa^{j\beta} = \sum_n^{\oplus} \sigma_0^{j\beta} \exp(i\kappa \mathbf{t}_n),$$

$3\sigma_M$-dimension column in *zeroth*-cell. All components = 0, except the one for atom *j* and direction β

[...] the values, that must be fixed, define a start for the basis function construction. Choosing different start values for "[...]" one obtains either different linear independent b.f. or zero

---

$R_{\alpha\beta}^h$ rotation matrix of rotational part of group element $\{h|\tau_h\}$

$d_{\lambda\mu}^\nu$ matrix of irrep number ν

$\mathbf{a}_p(g,j)$ returning translation after action of g on atom j

$\delta_h = \det(R_{\alpha\beta}^h)$

Verifying invariance of b.f. under irrep τ3

Pnma, k=[0.45,0,0] Mn in (4a)-position

12D magnetic representation is reduced to four one-dimensional irreps

$$d = \sum_{\oplus} n_\nu d^\nu = 3\tau_1 \oplus 3\tau_2 \oplus \boxed{3\tau_3} \oplus 3\tau 4$$

recap: irrep: 1D matrixes d_τ(g) that define how basis functions b.f. should be changed/ transformed under action of **abstract group** elements g_i. The permutations and spin rotations, *or whatever meaning of* g_i *is*, **are not** yet here!

	E	2_x	m_y	m_z
	g_1	g_2	g_3	g_4
τ_1	1	a	1	a
τ_2	1	a	-1	$-a$
τ_3	1	$-a$	1	$-a$
τ_4	1	$-a$	-1	a

$a = e^{\pi i k_x}$

Projection method: to find basis functions b.f. transforming according to a specific irrep τ

	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$
Mn-position	1	2	3	4

$$S'_{\tau 3} = +1\mathbf{e}_{1x} - a^*\mathbf{e}_{2x} - 1\mathbf{e}_{3x} + a^*\mathbf{e}_{4x}$$

$$\boxed{S''_{\tau 3} = +1\mathbf{e}_{1y} + a^*\mathbf{e}_{2y} + 1\mathbf{e}_{3y} + a^*\mathbf{e}_{4y}}$$

$$S'''_{\tau 3} = +1\mathbf{e}_{1z} + a^*\mathbf{e}_{2z} - 1\mathbf{e}_{3z} - a^*\mathbf{e}_{4z}$$

Example: ferromagnetic mode $S''_{\tau 3}$. Element g_2

---

action of g_2 =(rotation 2_x ; swap 1 ⇔ 2, 3 ⇔ 4, phase $2\pi i k_x$ for 2⇒1, 4⇒3)

$a^{*2} = e^{-2\pi i k_x}$

$$S''_{\tau 3} \rightarrow g_2^{2x} S''_{\tau 3} = -1\mathbf{e}_{1y} - a^*\mathbf{e}_{2y} - 1\mathbf{e}_{3y} - a^*\mathbf{e}_{4y} \ : \text{ spin space}$$

$$S''_{\tau 3} \rightarrow g_2^{\text{swap}} S''_{\tau 3} = -a^*\mathbf{e}_{1y} - 1\mathbf{e}_{2y} - a^*\mathbf{e}_{3y} - 1\mathbf{e}_{4y} \ : \text{ cite space}$$

$$S''_{\tau 3} \rightarrow g_2^{\text{phase}} S''_{\tau 3} = -a^*\mathbf{e}_{1y} - a^{*2}\mathbf{e}_{2y} - a^*\mathbf{e}_{3y} - a^{*2}\mathbf{e}_{4y} \ : \text{ to } 0th$$

$$d(g_2)^{irrep\ \tau 3} S''_{\tau 3} = -a \cdot S''_{\tau 3} \boxed{\overset{\text{Invariant!}}{=} +1\mathbf{e}_{1y} + a^*\mathbf{e}_{2y} + 1\mathbf{e}_{3y} + a^*\mathbf{e}_{4y}}$$

Classifying possible magnetic structures
Great simplification!

Pnma, k=[0.45,0,0] Mn in (4a)-position

12D magnetic representation is reduced to four one-dimensional irreps

$$3\tau_1 \oplus 3\tau_2 \oplus 3\tau_3 \oplus 3\tau 4$$

	E	2_x	m_y	m_z
	g_1	g_2	g_3	g_4
τ_1	1	a	1	a
τ_2	1	a	-1	$-a$
τ_3	1	$-a$	1	$-a$
τ_4	1	$-a$	-1	a

$$a = e^{\pi i k_x}$$

	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,0$
Mn-position	1	2	3	4

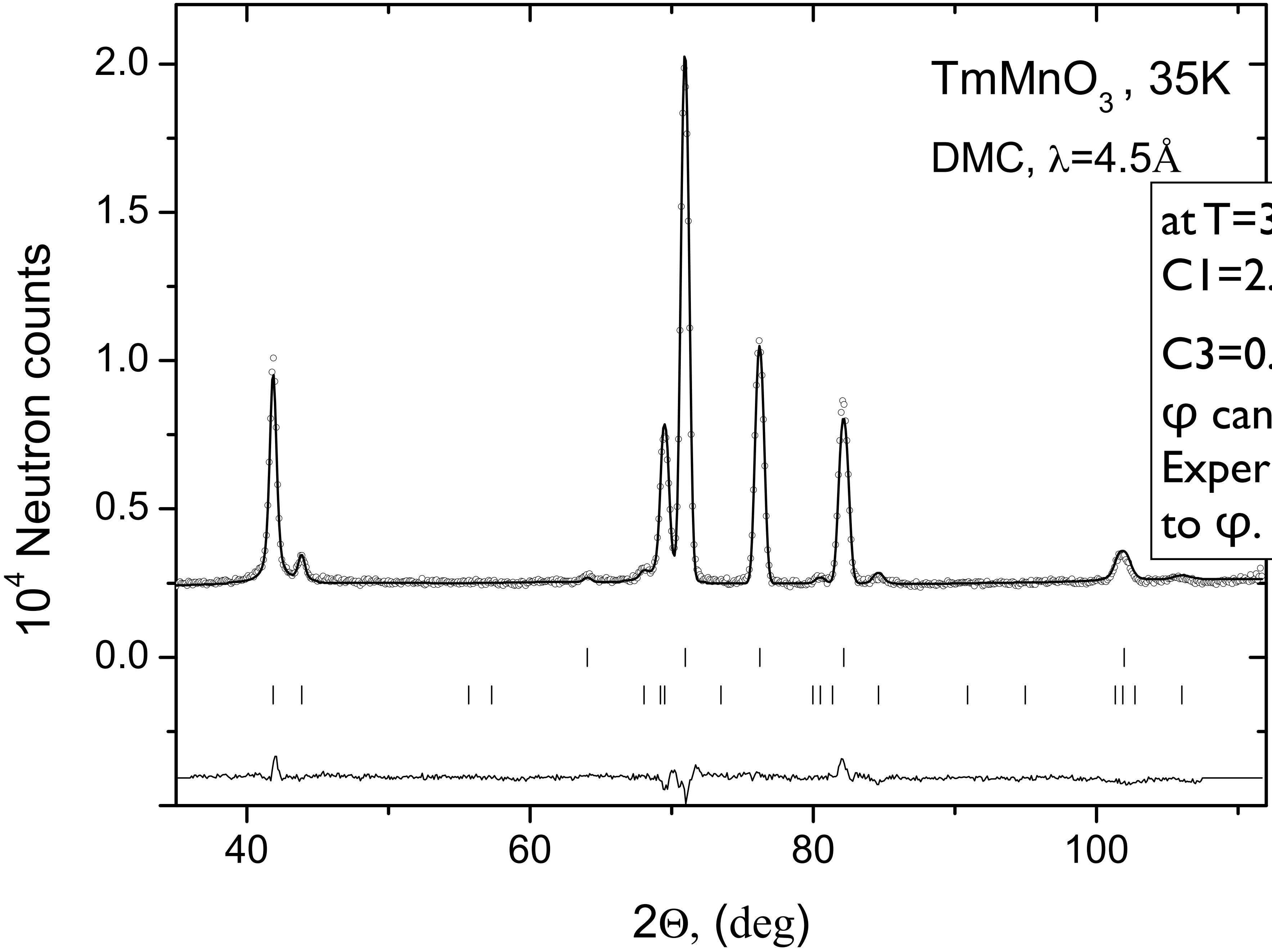
$$S'_{\tau 3} = +1\mathbf{e}_{1x} - a^*\mathbf{e}_{2x} - 1\mathbf{e}_{3x} + a^*\mathbf{e}_{4x}$$
$$S''_{\tau 3} = +1\mathbf{e}_{1y} + a^*\mathbf{e}_{2y} + 1\mathbf{e}_{3y} + a^*\mathbf{e}_{4y}$$
$$S'''_{\tau 3} = +1\mathbf{e}_{1z} + a^*\mathbf{e}_{2z} - 1\mathbf{e}_{3z} - a^*\mathbf{e}_{4z}$$

Assuming that the phase transition goes according to one irreducible representation τ3 the spins of all four atoms are set only by 3 variables instead of 12!

$$C_1 S'_{\tau 3} + C_2 S''_{\tau 3} + C_3 S'''_{\tau 3}$$

Refinement of the data for τ₃

$$\mathbf{S}(\mathbf{r}) = \frac{1}{2}(C_1 S'_{\tau 3} + C_2 S''_{\tau 3} + C_3 S'''_{\tau 3})e^{2\pi i \mathbf{k}\boldsymbol{r}} + c.c.$$

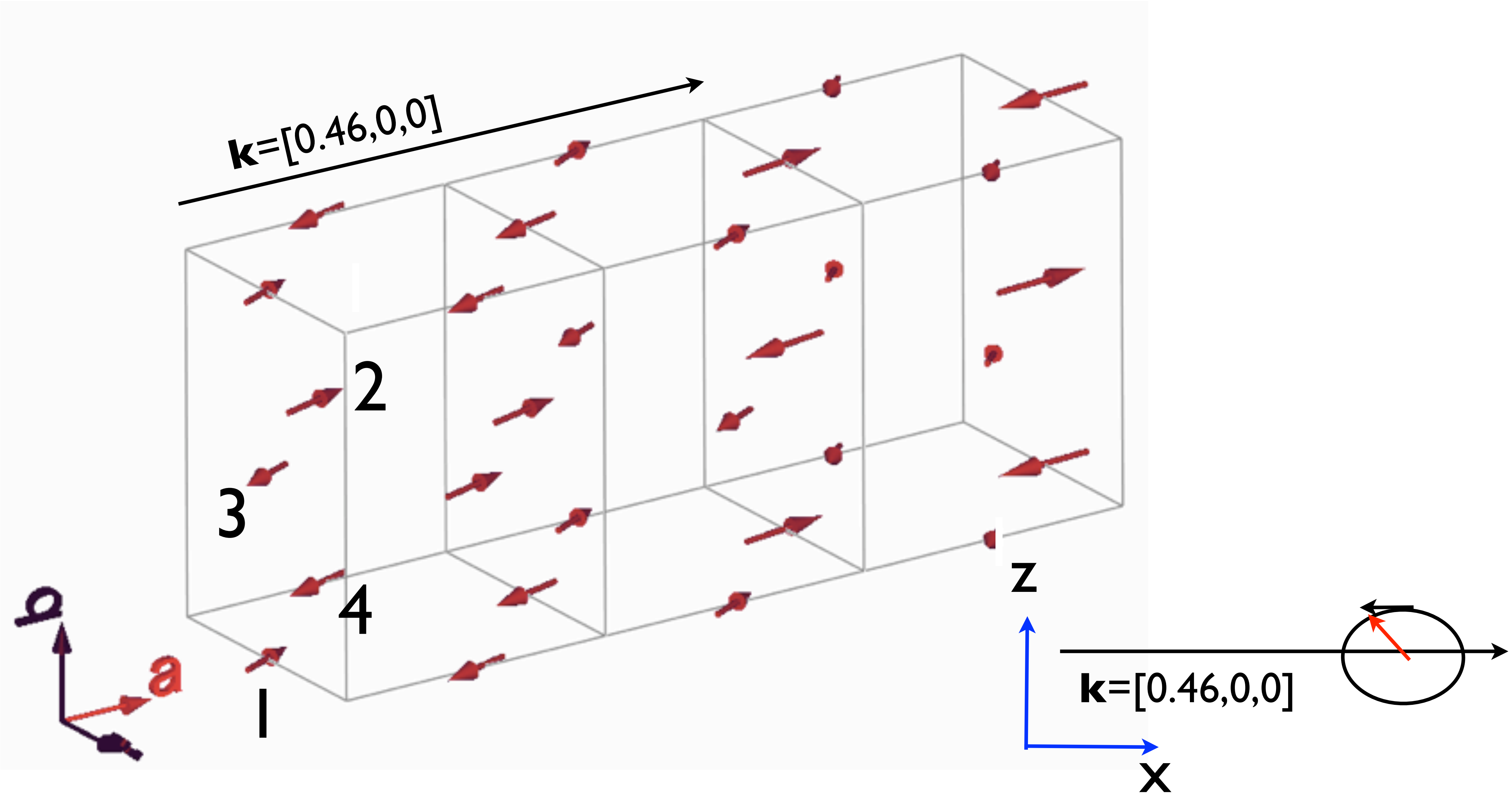


at T=35K
C1=2.11(1)μ_B, C2=0,
C3=0.67(2) $e^{i\varphi}$ μ_B
φ can be fixed to any value.
Experiment data are insensitive to φ.

Visualization of the magnetic structure

a cycloid structure propagating along x-direction

$$\mathbf{S}(\mathbf{r}) = Re\left[(C_1 S'_{\tau 3} + |C_3|\exp(i\varphi) S'''_{\tau 3})\exp(2\pi i \mathbf{k}\boldsymbol{r})\right]$$



V. Pomjakushin, Advanced magnetic structures ETHZ '10

Magnetic symmetry. 1651 3D-Shubnikov (Sh or Ш) space groups

230 space groups (SG)

an additional element:
spin inversion operator *R* or color change.
R-group (1,R)

⇒

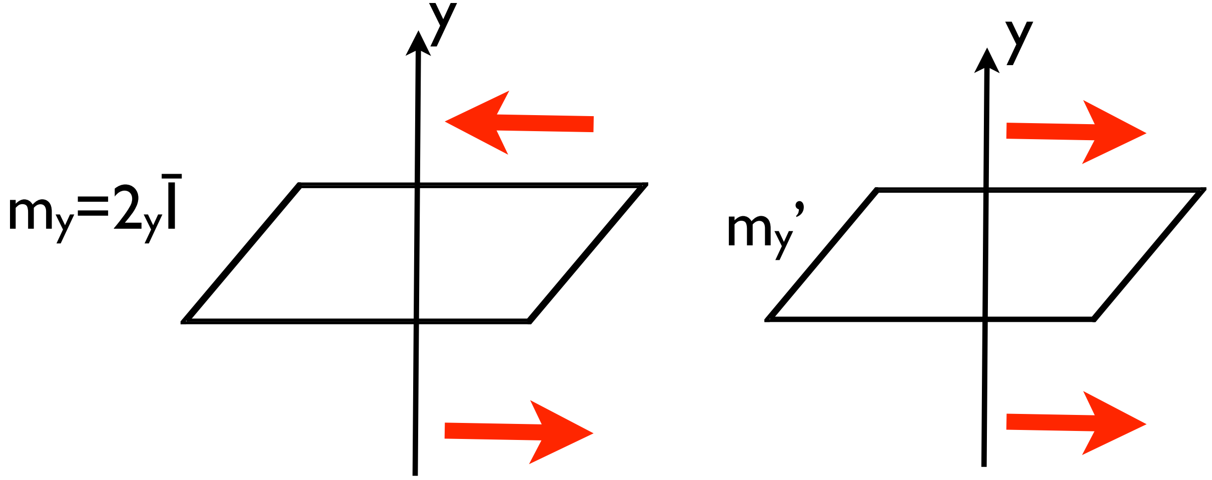
R(♖) = ♜

R(☺)=☹

R(↑) = ↓

Magnetic Groups = (subgroup of) space group *G* ⊗ R-group

additional elements:
'anti-elements' g'=(*g*·*R*), *g*∈*G*



$$\mathbf{S} = "[\mathbf{v} \times \mathbf{r}]"$$

230 (gray) paramagnetic groups Sh_p
<u>1,1' ∈ Sh_p</u> ⇒ **S**=0 , e.g. *Pnma1'*

230 Single-color magnetic groups
<u>no antielements</u>

1191 black/white magnetic groups that contain additional 'anti-elements' g'=(*g*·*R*) except *g*=1 (identity). <u>No primed 1'</u>

---

antisymmetry: Heesh (1929), Shubnikov (1945).
groups: Zamorzaev (1953, 1957); Belov, Neronova, Smirnova (1955)
spin reversal: Landau and Lifschitz (1957)

Isomorphism between Sh-groups and 1D irreps of SG. Niggli-Indenbom theorem

Consider *1D real* irrep of space group

$g_1, g_2, g_3, ...$
1, -1, 1, ...

1D real irrep and *Sh* group are isomorphous
Niggli-Indenbom theorem
↔

formally we can
$g_1, g_2', g_3, ...$

magnetic *Sh* space groups

same multiplication table

identity representations
1, 1, 1, 1, ...
↔
230 Single-color magnetic groups
no antielements

non-identity 1D irreps
↔
1191 black/white magnetic subgroups that contain additional 'antielements' $g'=(g{\cdot}R)$ except $g=1$ (identity). No primed 1'

Examples of Sh groups

59 <u>$Pmmn$</u>

$Pm'mn$

$Pmmn'$

*$Pm'm'n$

*$Pmm'n'$

$Pm'm'n'$

$P_{2c}mmn$

$P_{2c}m'mn$

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

62 <u>$Pnma$</u>

$Pn'ma$

$Pnm'a$

$Pnma'$

*$Pn'm'a$

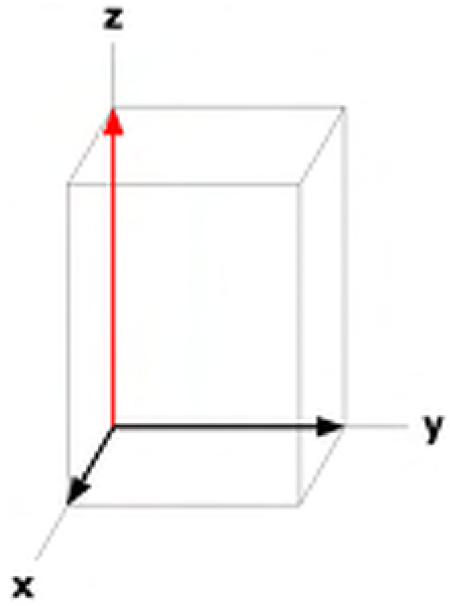
*$Pnm'a'$

*$Pn'ma'$

$Pn'm'a'$

Ferromagnetic groups: point symmetry allows FM orientation of spins

recap:
for ‘anti-elements’ g’=(g·*R*), *g*∈*G*
g can be a pure translation *t*, so *t’* gives centering/doubling



$P_{2c} = P_{a,b,2c}$
$t_\alpha = c = (0,0,1)$

!

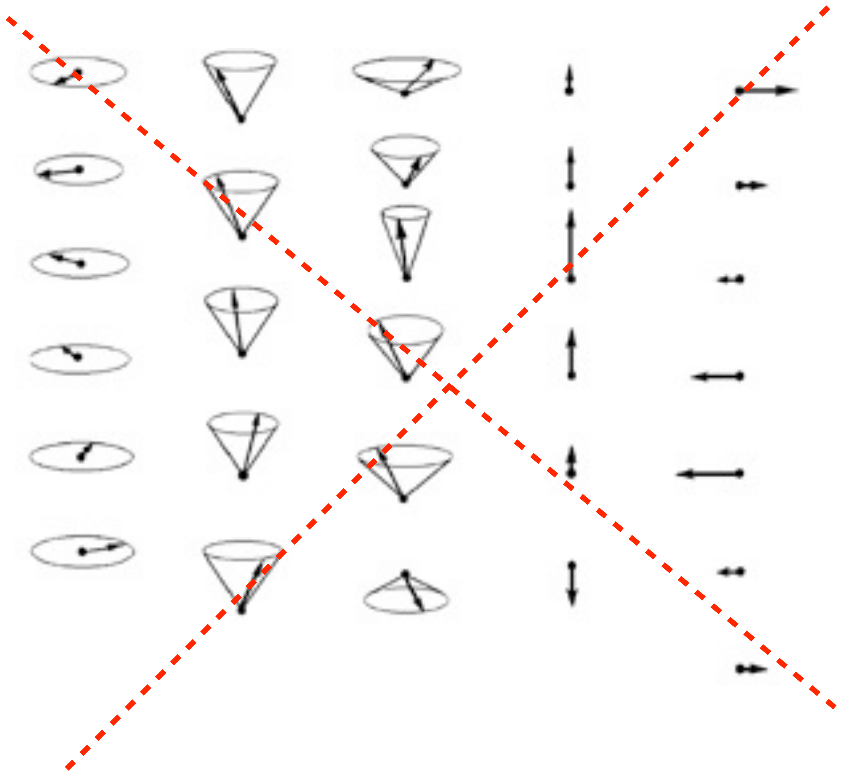
k≠[0,0,0] structures for *Pnma* correspond to either complex *irreps* or/and muti-dimensional *irreps* and cannot be derived from *Pnma*

Disadvantages of Sh-group description

Sh groups do not give a constructive way of deducing all symmetry allowed magnetic modes.

Reason 1: *Sh* group is not necessarily made from the parent *G*. Thus, it is not an ultimate practical tool for obtaining all allowed spin configurations

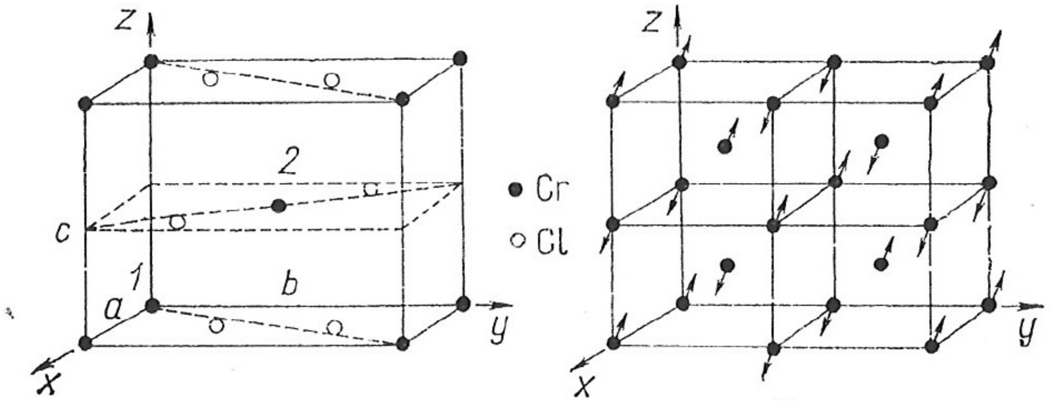
Reason 2: 3D *Sh* not describe modulated structures. No rotations on non-crystallographic angle - no helix. Linear orthogonal transformations preserve the spin size - no SDW



Example 1: there are no cubic ferromagnetic Sh-groups. "problems" with cubic ferromagnets Fe, EuO, EuS, ...

Example 2:
$CrCl_2$ space group: *Pnnm.*
Sh groups*: Pnnm Pn'nm, Pnnm', Pn'n'm, Pnn'm', Pn'n'm'*

No one describes $CrCl_2$ magnetic structure
Cr-atoms in 2(a)-position
k=[0 1/2 1/2]



One can still find less symmetric *Sh* group
Magnetic symbol
{*Pnnm;* 2(a) $Sh^7_2=P_s\bar{I}$;
$\mathbf{S}_1$=(uvw), $\mathbf{S}_2$=(-u-v-w)}

The End

further complications

1. several irreps involved, e.g. exchange multiplet
2. multi-k structures
3. spin domains, k-domains, chiral domains for single crystal data

Literature on (magnetic) neutron scattering

Neutron scattering (general)

Albert Furrer, Joel Mesot , and Thierry Strassle, "*Neutron scattering in condensed matter physics*". World Scientific, 2008

S.W. Lovesey, "*Theory of Neutron Scattering from Condensed Matter*", Oxford Univ. Press, 1987. Volume 2 for magnetic scattering. Definitive formal treatment

G.L. Squires, "*Intro. to the Theory of Thermal Neutron Scattering*", C.U.P., 1978, Republished by Dover, 1996. Simpler version of Lovesey.