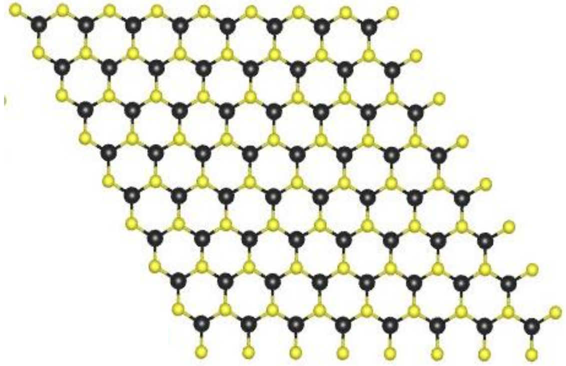
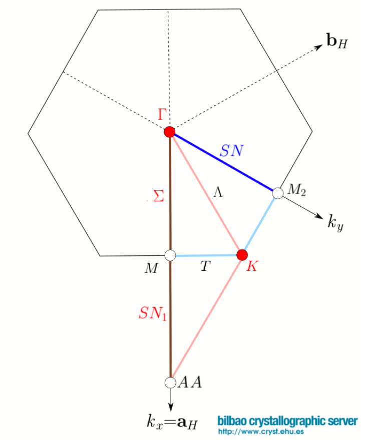
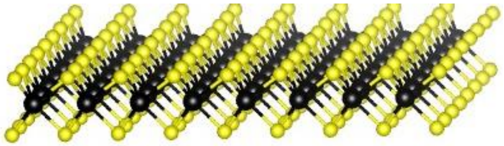
Study of layer and multilayer materials using the Bilbao Crystallographic Server

G. de la Flor, R. A. Evarestov, Y. E. Kitaev, E. Tasci, L. Elcoro G. Madariaga, M. I. Aroyo







Content

- Bilbao Crystallographic Server
- Subperiodic Groups: Layer, Rod and Frieze Groups
  - Crystallographic database available at the BCS
- Relationship between layer and space groups
  - Layer groups Brillouin-zone database
- Identification of layer symmetry of periodic sections
- The site-symmetry induced representations of layer groups
- Conclusions

Bilbao Crystallographic Server

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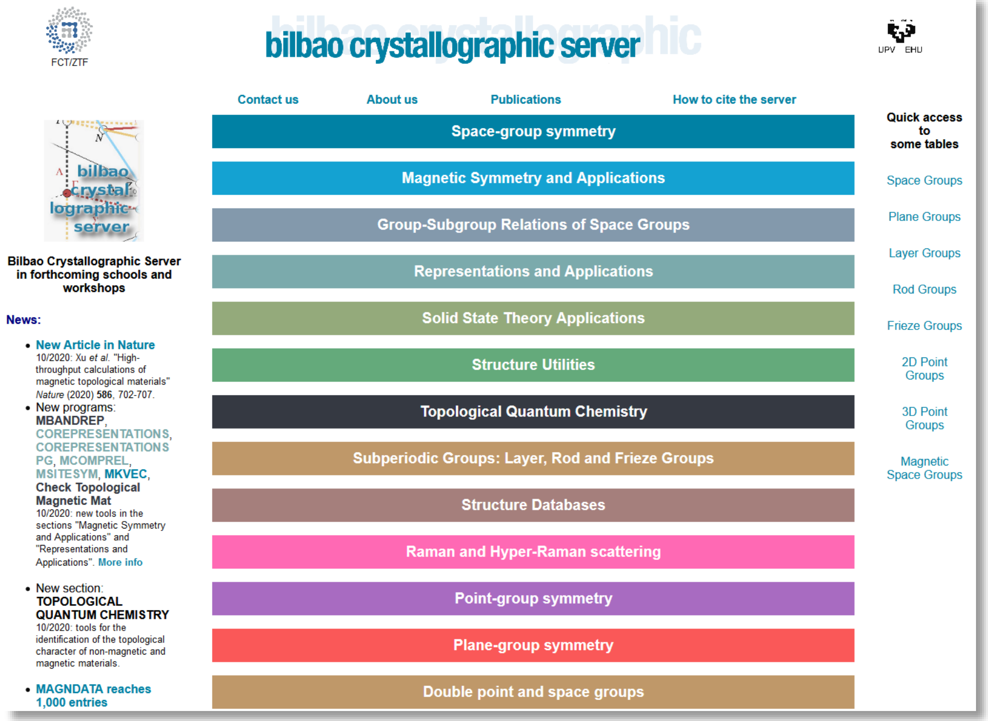

BCS-Team

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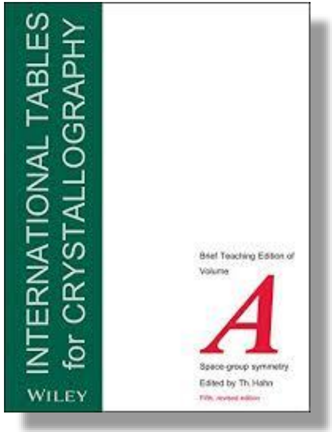
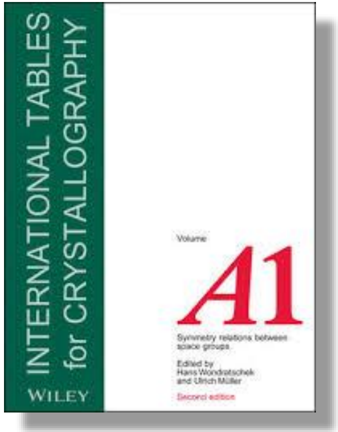
Crystallographic Databases





Point groups

Plane groups

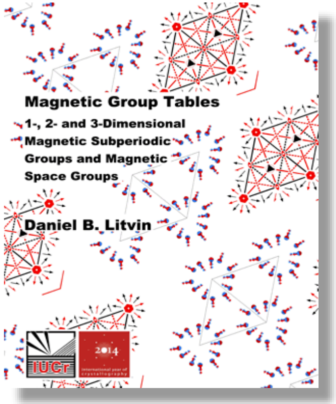
Space groups

Space groups

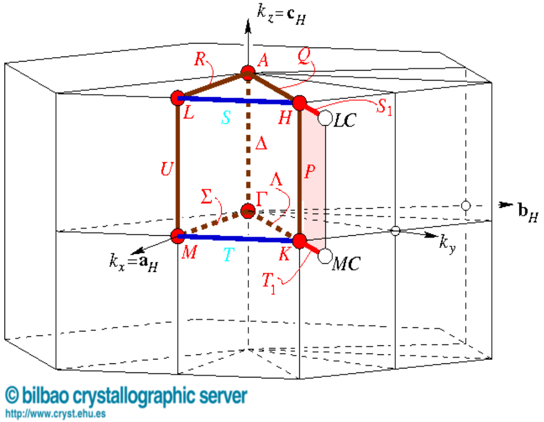
Subperiodic groups

- Frieze groups
- Rod groups
- Layer groups

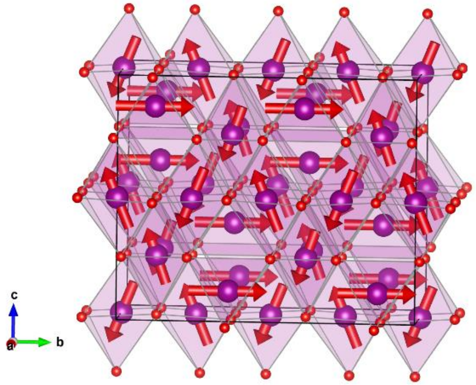
Crystallographic Databases



Magnetic groups



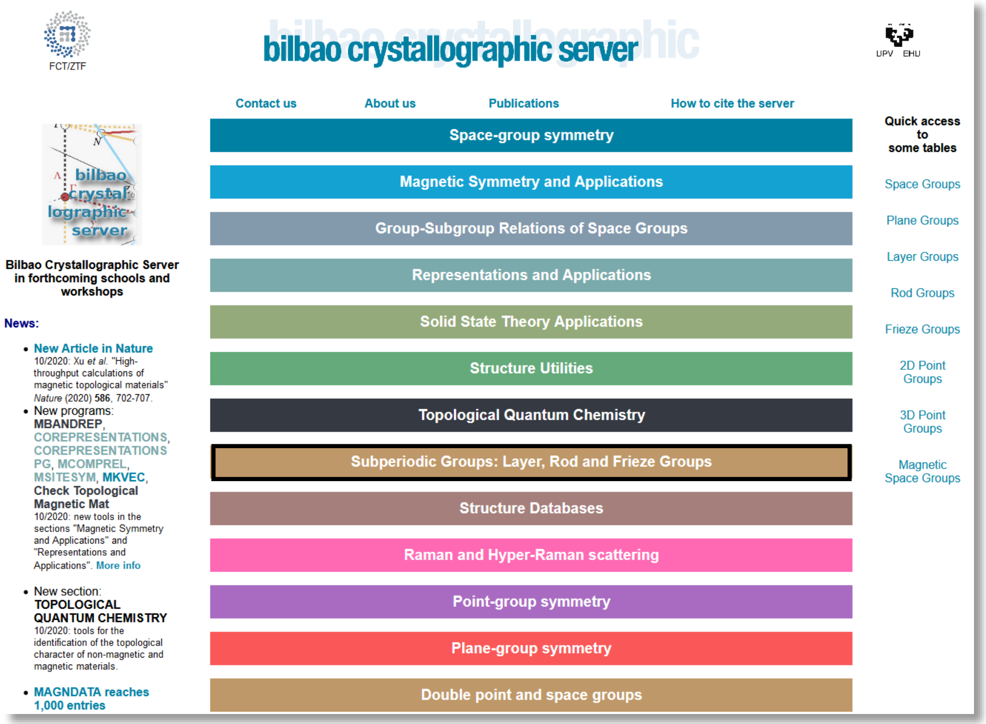
Brillouin zones and ***k***-vector



Magnetic structures database

Double groups

Subperiodic Groups: Layer, Rod and Frieze Groups



Subperiodic Groups: Layer, Rod and Frieze Groups	
GENPOS	Generators and General Positions of Subperiodic Groups
WPOS	Wyckoff Positions of Subperiodic Groups
MAXSUB	Maximal Subgroups of Subperiodic Groups
LKVEC ⚠	The k-vector types and Brillouin zones of Layers Groups
SECTIONS ⚠	Identification of Layer Symmetry of Periodic Sections
LSITESYM ⚠	Site-symmetry induced representations of Layer Groups

- Crystallographic information
- Brillouin-zone database for layer groups
- Identification of layer symmetry of periodic sections
- Site-symmetry induced representations of layer groups

Subperiodic Groups: Layer, Rod and Frieze Groups

- There are <u>three types</u> of subperiodic groups:

Frieze groups

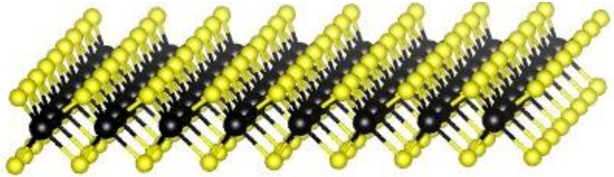
2D groups with 1D translations

Rod groups

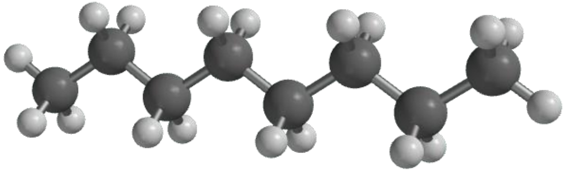
3D groups with 1D translations

Layer groups

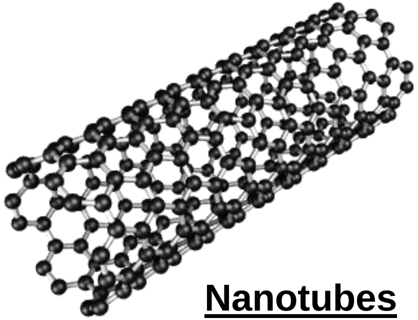
3D groups with 2D translations



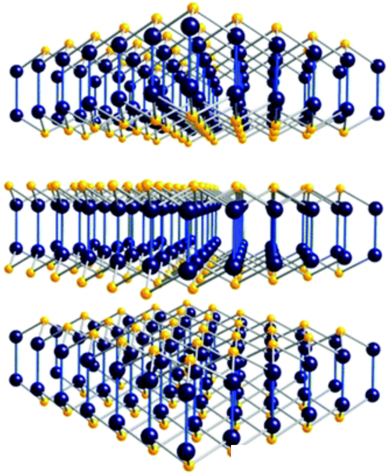
Subperiodic Groups: Layer, Rod and Frieze Groups

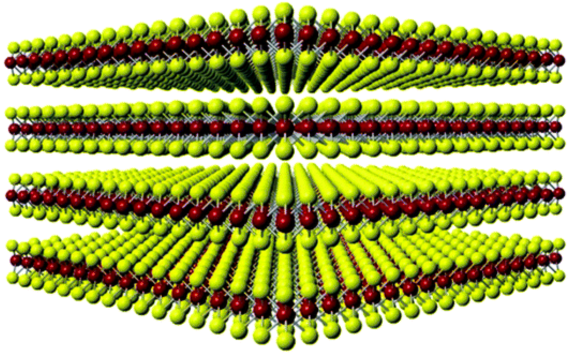


Polymers



Nanotubes

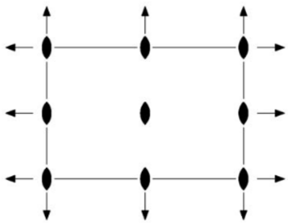


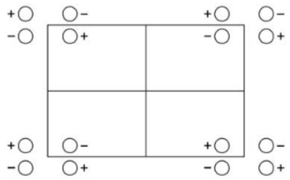


Layered materials

Volume E – International Tables

$p222$	222	Orthorhombic/Rectangular
No. 19	$p222$	Patterson symmetry $pmmm$





Origin at 222

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

Symmetry operations

(1) 1 (1|0,0,0)　(2) 2 0,0,z (2$_z$|0,0,0)　(3) 2 0,y,0 (2$_y$|0,0,0)　(4) 2 x,0,0 (2$_x$|0,0,0)

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

Positions

GENPOS

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

WYCKPOS

Symmetry of special projections

Along [001] $p2mm$
a′ = **a**　**b**′ = **b**
Origin at $0,0,z$

Along [100] $p2mm$
a′ = **b**
Origin at $x,0,0$

Along [010] $p2mm$
a′ = **a**
Origin at $0,y,0$

Maximal non-isotypic subgroups

I　[2] $p121$ ($p211$, 8)　1; 3
　[2] $p211$ (8)　1; 4
　[2] $p112$ (3)　1; 2

IIa　none

IIb　[2] $c222$ (**a**′ = 2**a**, **b**′ = 2**b**) (22); [2] $p22_12$ (**b**′ = 2**b**) ($p2_122$, 20); [2] $p2_122$ (**a**′ = 2**a**) (20)

MAXSUB

Maximal isotypic subgroups of lowest index

IIc　[2] $p222$ (**a**′ = 2**a** or **b**′ = 2**b**) (19)

Minimal non-isotypic supergroups

I　[2] $pmmm$ (37); [2] $pmaa$ (38); [2] $pban$ (39); [2] $p422$ (53); [2] $p\bar{4}2m$ (57)

II　[2] $c222$ (22)

MINSUP

Programs: GENPOS, WYCKPOS & MAXSUB

GENPOS

General Positions of the Layer Group *p* 2 2 2 (No. 19)

No.	Coordinate triplets	Matrix form	Symmetry operation	
			ITE	Seitz
1	x,y,z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	1	{ 1 | 0 }
2	-x,-y,z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	2 0,0,z	{ 2_{001} | 0 }
3	-x,y,-z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	2 0,y,0	{ 2_{010} | 0 }
4	x,-y,-z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	2 x,0,0	{ 2_{100} | 0 }

WYCKPOS

Wyckoff Positions of Layer Group *p* 2 2 2 (No. 19)

Multiplicity	Wyckoff Letter	Site Symmetry	Coordinates
4	m	1	(x,y,z) (-x,-y,z) (-x,y,-z) (x,-y,-z)
2	l	..2	(1/2,1/2,z) (1/2,1/2,-z)
2	k	..2	(0,1/2,z) (0,1/2,-z)
2	j	..2	(1/2,0,z) (1/2,0,-z)
2	i	..2	(0,0,z) (0,0,-z)
2	h	.2.	(1/2,y,0) (1/2,-y,0)
2	g	.2.	(0,y,0) (0,-y,0)
2	f	2..	(x,1/2,0) (-x,1/2,0)
2	e	2..	(x,0,0) (-x,0,0)
1	d	222	(1/2,1/2,0)
1	c	222	(0,1/2,0)
1	b	222	(1/2,0,0)
1	a	222	(0,0,0)

Wyckoff position and site symmetry group of a specific point

Specify the point by its relative coordinates (in fractions or decimals)
Variable parameters (x,y,z) are also accepted

x = ☐ y = ☐ z = ☐

Show

MAXSUB

Maximal Subgroups of Layer Group *p* 2 2 2 (No. 19)

Note: The program uses the default settings

In the following table the list of maimal subgroups is given. Click over "show.." to see the possible setting(s) for the given subgroup.

N	Subgroup	HM Symbol	Index	Type	Tranformations
1	3	*p* 1 1 2	2	t	show..
2	8	*p* 2 1 1	2	t	show..
3	19	*p* 2 2 2	2	k	show..
4	19	*p* 2 2 2	3	k	show..
5	20	*p* 2_1 2 2	2	k	show..
6	22	*c* 2 2 2	2	k	show..

t represents the *translationengleichen subgroups*
k represents the *klassengleichen subgroups*

GENPOS & WPOS provide the data in standard and non-standard settings

Relationship between layer and space groups

- Layer groups ($\mathcal{L}$) form a subgroup of space groups ($\mathcal{G}$): $\mathcal{L} < \mathcal{G}$
- $\mathcal{L} < \mathcal{G}$ is essential to derive the layer groups ***k*** vectors and Brillouin zones
- The space group $\mathcal{G}$ can be expressed as $\mathcal{G} = \mathcal{L} \wedge T_3$ ➡ $\mathcal{L} \simeq G/T_3$
- The ***k*** vectors of $\mathcal{L}$ can be deduced from $\mathcal{G}$ based on the *isomorphism* $\mathcal{L} \simeq G/T_3$
- The *reciprocal-group approach* is applied to classified the ***k*** vectors of $\mathcal{L}$
- The reciprocal space of layer groups is described by *reciprocal-plane groups*

Procedure: k-vector and BZ figures derivation

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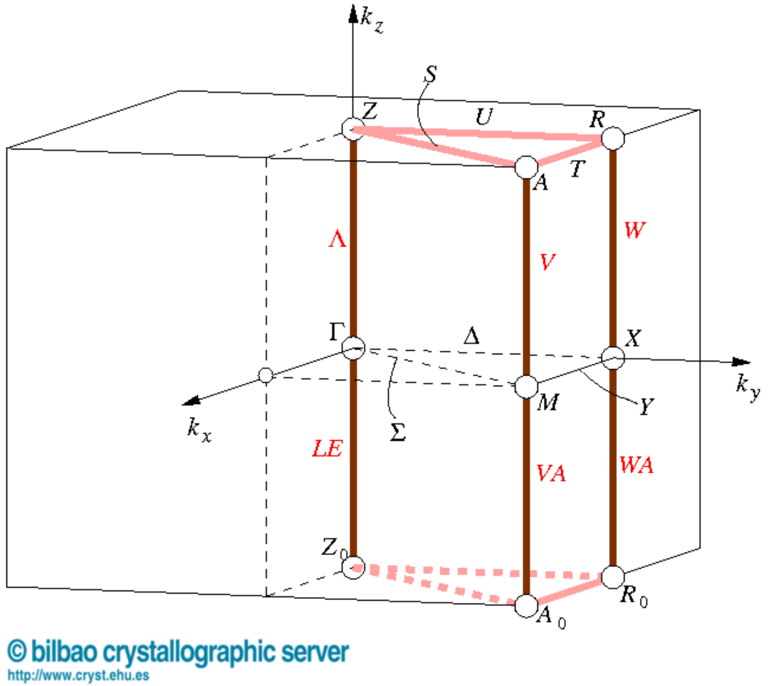
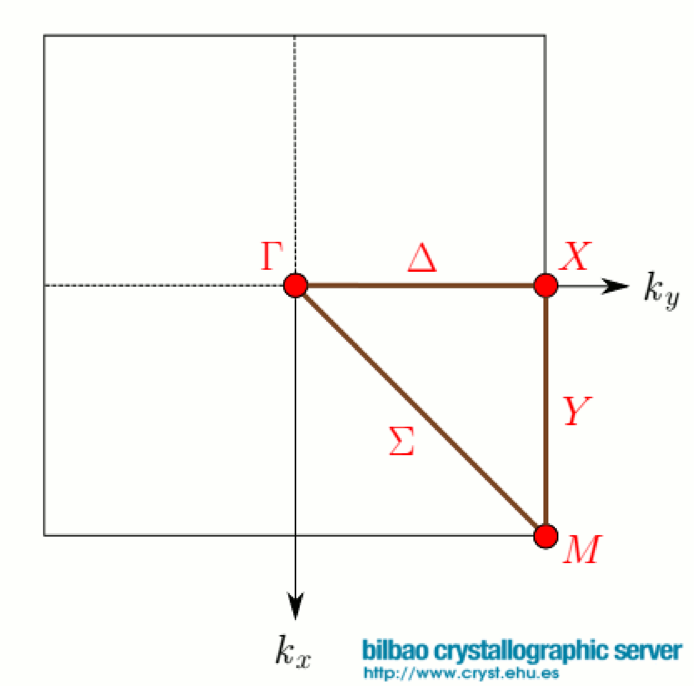
Brillouin Zone of the space group P4mm (No. 99)



Brillouin Zone of the layer group *p*4mm (No. 55)



Procedure: k-vector and BZ figures derivation

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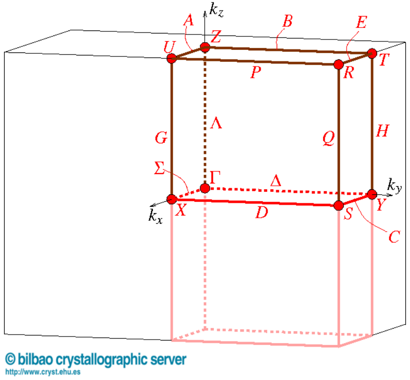
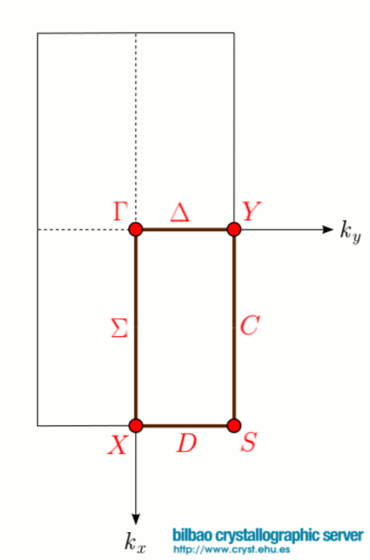


Brillouin Zone of the space group *P222* (No.16)

Brillouin Zone of the layer group *p222* (No.19)



1. Identify the space group $\mathcal{G}$ to which the layer group $\mathcal{L}$ is related to
2. Identify the reciprocal-space-group $(\mathcal{G})^*$ of $\mathcal{G}$
3. Calculate the section of $(\mathcal{G})^*$ along (001) → $(\mathcal{L}_{\text{section}})$
4. Determine the reciprocal plane group of $\mathcal{L}$: the [001] projection of $\mathcal{L}_{\text{section}}$ is calculated

- The classification scheme of the **k** vectors derived in this work is compared with the classification of Litvin & Wike in *Character Tables and Compatibility Relations of the Eighty Layer Groups*

The program LKVEC

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Input of the program: layer group number

The k-vector types of layers group *p* 4 m m (No. 55)

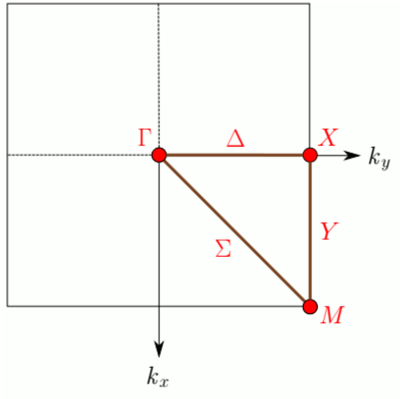
(Table for arithmetic crystal class 4mm*p*)

*p*4mm (No. 55), *p*4bm (No. 56)

Reciprocal plane group (*p*4mm)* (No. 11)

Brillouin zone

k-vector description			Plane-group description			
Label[(1)]	Coefficients	Little layer co-group	Wyckoff Position			Coordinates
GM	0,0	4mm	1	a	4mm	0,0
M	1/2,1/2	4mm	1	b	4mm	1/2,1/2
X	0,1/2	2mm.	2	c	2mm.	0,1/2
DT	0,u	.m.	4	d	.m.	0,y : 0 < y < 1/2
Y	u,1/2	.m.	4	e	.m.	x,1/2 : 0 < x < 1/2
SM	u,u	..m	4	f	..m	x,x : 0 < x < 1/2
D=[GM X M]	u,v	1	8	g	1	x,y : 0 < x < y < 1/2



The program LKVEC

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Input of the program: layer group number

The k-vector types of layers group *p* 4 m m (No. 55)

(Table for arithmetic crystal class 4mm*p*)

*p*4mm (No. 55), *p*4bm (No. 56)

Reciprocal plane group (*p*4mm)* (No. 11)

Brillouin zone

k-vector description			Plane-group description			
Label(1)	Coefficients	Little layer co-group	Wyckoff Position			Coordinates
GM	0,0	4mm	1	a	4mm	0,0
M	1/2,1/2	4mm	1	b	4mm	1/2,1/2
X	0,1/2	2mm.	2	c	2mm.	0,1/2
DT	0,u	.m.	4	d	.m.	0,y : 0 < y < 1/2
Y	u,1/2	.m.	4	e	.m.	x,1/2 : 0 < x < 1/2
SM	u,u	..m	4	f	..m	x,x : 0 < x < 1/2
D=[GM X M]	u,v	1	8	g	1	x,y : 0 < x < y < 1/2

k-vector identification tool

If you want to identify a **k**-vector you have to introduce:

1. The reciprocal bases: Primitive(*)

2. The **k**-vector: k_x 0 k_y 1

identify

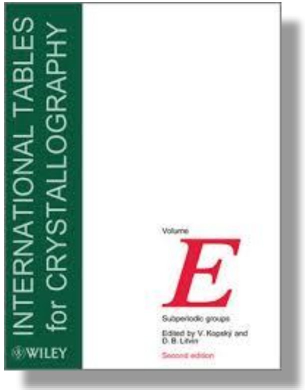
The k-vector types of layers group *p* 4 m m (No. 55)

• Layer Group: *p* 4 m m (No. 55) • The reciprocal bases: primitive • The **k**-vector coordinates: 0, 1	• **k**-vector label: GM • The star of the **k**-vector has 1 arm: ◦ 0.000 1.000 • GM is a **k**-vector point. • Layer little co-group: 4mm • ITA classification: 1a • Site-symmetry group: 4mm

Identification of layer symmetry of periodic sections

- The symmetries of planes intersecting the crystal are called the *sectional layer groups*

Scanning tables



$$\mathcal{G} = P4mm$$

Orientation orbit (hkl)	Conventional basis of the scanning group $\mathbf{a}'$	$\mathbf{b}'$	$\mathbf{d}$	Scanning group $\mathcal{H}$	Linear orbit $s\mathbf{d}$	Sectional layer group $\mathcal{L}(s\mathbf{d})$	
(001)	$\mathbf{a}$	$\mathbf{b}$	$\mathbf{c}$	$P4mm$	$s\mathbf{d}$	$p4mm$	L55
(100)	$\mathbf{b}$	$\mathbf{c}$	$\mathbf{a}$	$Pm2m$	$0\mathbf{d}, \frac{1}{2}\mathbf{d}$	$pm2m$	L27
(010)	$-\mathbf{a}$	$\mathbf{c}$	$\mathbf{b}$		$[s\mathbf{d}, -s\mathbf{d}]$	$pm11$	L11
(110)	$(-\mathbf{a}+\mathbf{b})$	$\mathbf{c}$	$(\mathbf{a}+\mathbf{b})$	$Bm2m$	$[0\mathbf{d}, \frac{1}{2}\mathbf{d}]$	$pm2m$	L27
$(1\bar{1}0)$	$(\mathbf{a}+\mathbf{b})$	$\mathbf{c}$	$(\mathbf{a}-\mathbf{b})$		$[\frac{1}{4}\mathbf{d}, \frac{3}{4}\mathbf{d}]$	$pm2a$ $(\mathbf{a}'/4)$	L31
					$[\pm s\mathbf{d}, (\pm s+\frac{1}{2})\mathbf{d}]$	$pm11$	L11

The program SECTIONS

For a given space group the program identifies the full set of possible layer symmetries of periodic sections defined by their common normal vector

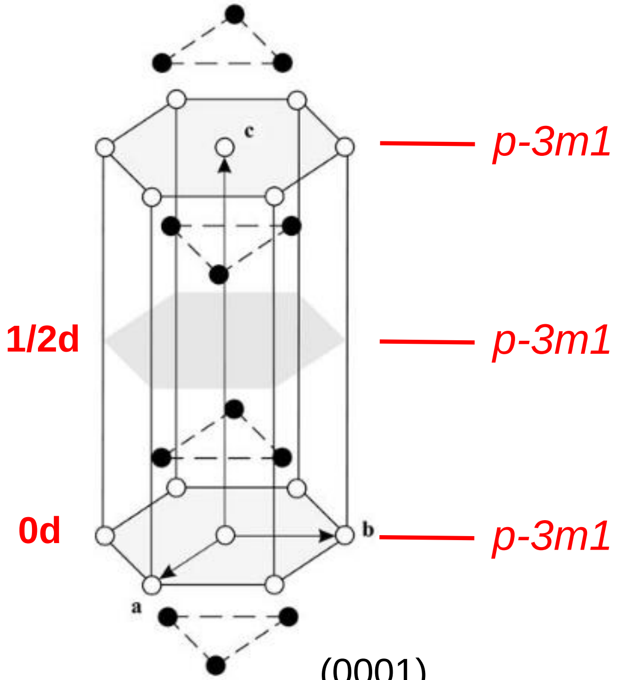
Scanning tables for the space group *P4mm* (No. 99) along (*1 0 0*)

Scanning group	Conventional basis of the scanning group **a'**,**b'**,**d**; p_1,p_2,p_3	Linear orbit *sd*	Sectional layer group
*Pmm*2 (No. 25)	**b**,**c**,**a** ; 0,0,0	±s**d**	*pm*11 (No.11) **-a**,**-b**,**c** ; 0,0,0
		[0**d**,1/2**d**]	*pm*2*m* (No.27) **a**,**b**,**c** ; 0,0,0

$\mathcal{G} = P4mm$

Orientation orbit (hkl)	Conventional basis of the scanning group $\mathbf{a}'$	$\mathbf{b}'$	$\mathbf{d}$	Scanning group $\mathcal{H}$	Linear orbit $s\mathbf{d}$	Sectional layer group $\mathcal{L}(s\mathbf{d})$	
(001)	$\mathbf{a}$	$\mathbf{b}$	$\mathbf{c}$	$P4mm$	$s\mathbf{d}$	$p4mm$	L55
(100)	$\mathbf{b}$	$\mathbf{c}$	$\mathbf{a}$	$Pm2m$	$0\mathbf{d}, \frac{1}{2}\mathbf{d}$	$pm2m$	L27
(010)	$-\mathbf{a}$	$\mathbf{c}$	$\mathbf{b}$		$[s\mathbf{d}, -s\mathbf{d}]$	$pm11$	L11
(110)	$(-\mathbf{a}+\mathbf{b})$	$\mathbf{c}$	$(\mathbf{a}+\mathbf{b})$	$Bm2m$	$[0\mathbf{d}, \frac{1}{2}\mathbf{d}]$	$pm2m$	L27
$(1\bar{1}0)$	$(\mathbf{a}+\mathbf{b})$	$\mathbf{c}$	$(\mathbf{a}-\mathbf{b})$		$[\frac{1}{4}\mathbf{d}, \frac{3}{4}\mathbf{d}]$	$pm2a$ ($\mathbf{a}'/4$)	L31
					$[\pm s\mathbf{d}, (\pm s+\frac{1}{2})\mathbf{d}]$	$pm11$	L11

Example: Program SECTIONS – CdI_2



$P\bar{3}m1\ (No. 164)$

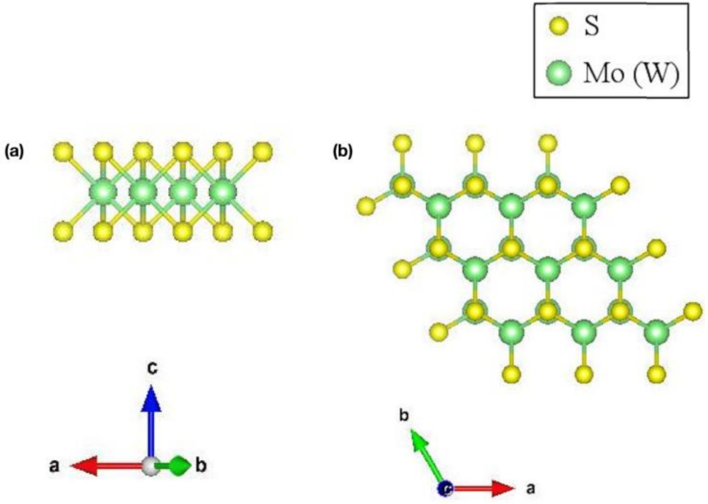
Scanning tables for the space group *P*-3*m*1 (No. 164)

Scanning group	Conventional basis of the scanning group **a'**,**b'**,**d**; p_1,p_2,p_3	Linear orbit *s***d**	Sectional layer group
P-3*m*1 (No. 164)	**a**,**b**,**c** ; 0,0,0	±*s***d**	*p*3*m*1 (No.69) **a**,**b**,**c** ; 0,0,0
		[0**d**,1/2**d**]	*p*-3*m*1 (No.72) **a**,**b**,**c** ; 0,0,0

For planes of this orientation at any other height p3m1

The program LSITESYM

- Site-symmetry approach: It establishes the local properties of atoms in crystals with the symmetry of states of the whole crystalline system



- **Bulk crystal**: $P6_3/mmc$ (No. 194)

  Mo 2c (1/3, 2/3, 1/4)
  S 4f (1/3,2/3,z)

- **Single layer**: *p-6m2* (No. 78)

  Mo 1c (2/3, 1/3, 0)
  S 2e (1/3,2/3,z)

The program LSITESYM

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- Site-symmetry approach: It establishes the local properties of atoms in crystals with the symmetry of states of the whole crystalline system

Atom	Wyckoff position	$\mathbf{D}_\sigma$	Γ (0, 0) $\bar{6}2m$	K ($\frac{1}{3}$, $\frac{1}{3}$) $\bar{6}..$	M ($\frac{1}{2}$, 0) $m2m$
Mo	$1c$ ($\frac{2}{3}$, $\frac{1}{3}$, 0) $\bar{6}m2$	A_2'' (z) E' (x, y)	3 5	6 1, 3	3 1, 2
S	$2e$ ($\frac{1}{3}$, $\frac{2}{3}$, z) $3m.$	A_1 (z) E (x, y)	1, 3 5, 6	3, 4 1, 2, 5, 6	1, 3 1, 2, 3, 4

- **Bulk crystal**: $P6_3/mmc$ (No. 194)

  Mo 2c (1/3, 2/3, 1/4)

  S 4f (1/3,2/3,z)

- **Single layer**: *p-6m2* (No. 78)

  Mo 1c (2/3, 1/3, 0)

  S 2e (1/3,2/3,z)

Conclusions

Karlsruhe Institute of Technology

- The *Bilbao Crystallographic Server* is in constant development
- New features and programs have been recently included in the section dedicated to Subperiodic Groups: layer, rod and frieze groups
- Set of tools dedicated to the study of layered and multilayered materials
- New tools are under development and will be soon available in the server

THANK YOU FOR YOUR ATTENTION

Questions

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