

Minicurso 1: Caracterização de materiais por difração e espalhamento de raios X e neutrons a baixo ângulo

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Prof. Guinther Kellermann
LORXI: Laboratório de Ótica de Raios X e Instrumentação

Outline:

- Propriedades e produção do raios X
- Propriedades e produção de nêutrons
- Geometria dos Cristais
- Lei de Bragg
- Difração de Pó
- Método Rietveld
- Difratometros

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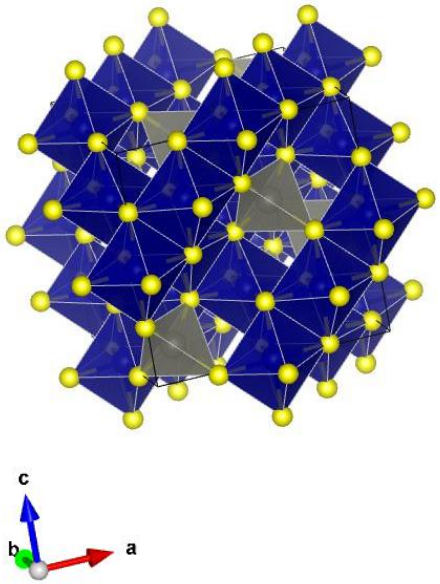
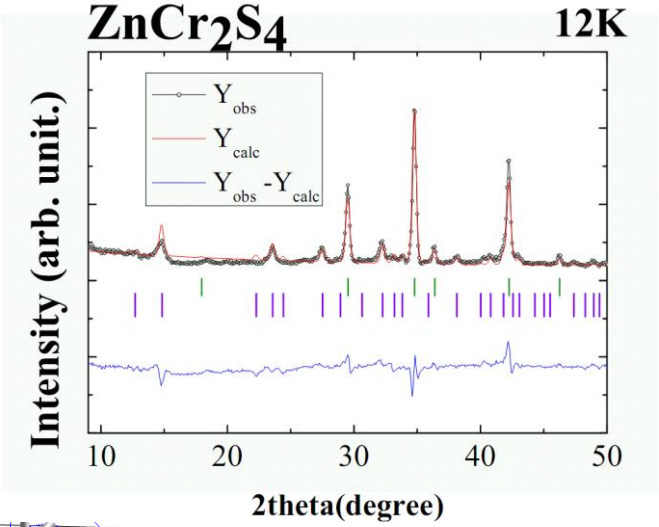
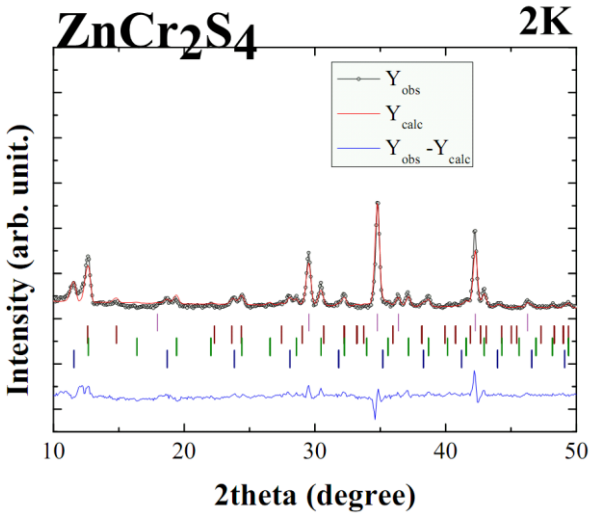
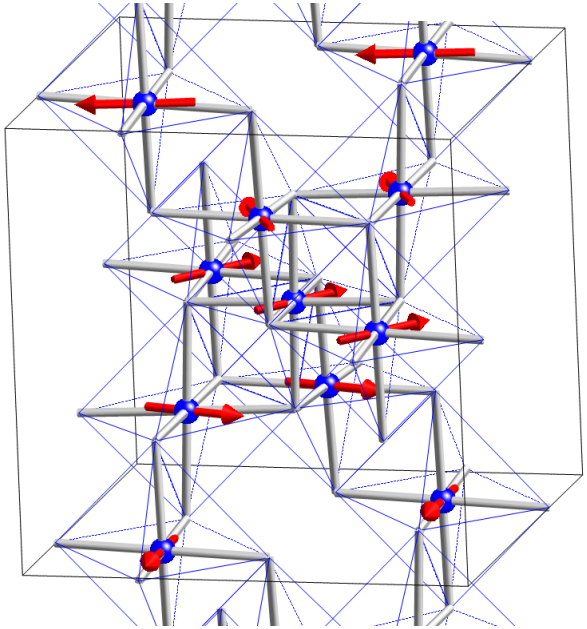
PHYSICAL REVIEW B 79, 064423 (2009)

Spin-driven phase transitions in $ZnCr_2Se_4$ and $ZnCr_2S_4$ probed by high-resolution synchrotron x-ray and neutron powder diffraction

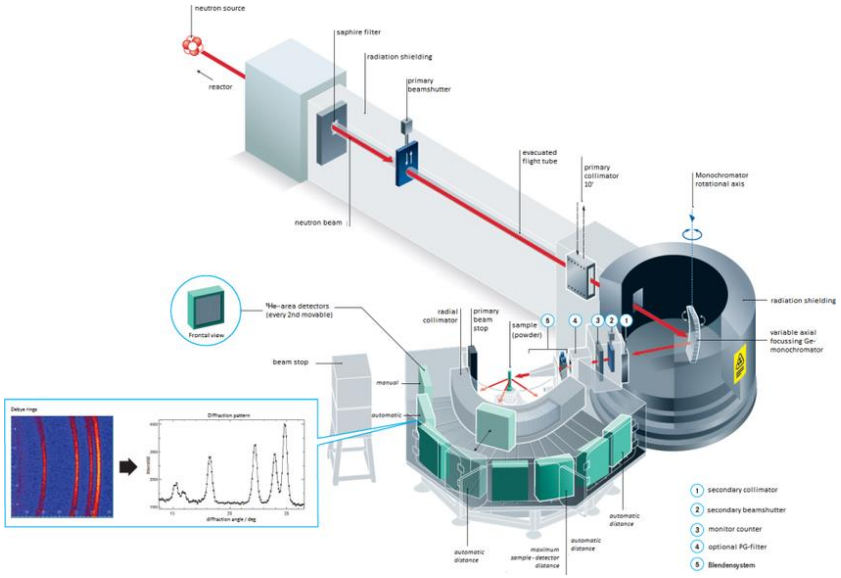




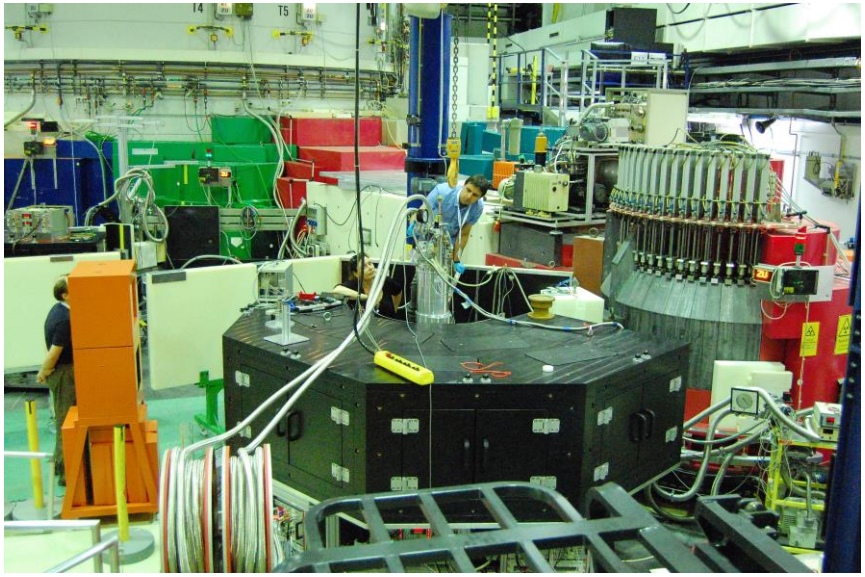




- Neutron diffraction data
- Crystal Structure consistent with Fd-3m below T_{N1}~15 K
- Incommensurate helical AFM structure with FM (001) planes with a propagation vector k_1~(0,0,0.78) along [001] axis below T_{N1}~15 K
- Below T_{N2}~ 8 K: coexistence of 2 additional commensurate collinear AFM (k_2=(1,0.5,0) and k_3=(0.5,0.5,0)) and IC helical AFM structures.



E9 – FIREPOD - HZB





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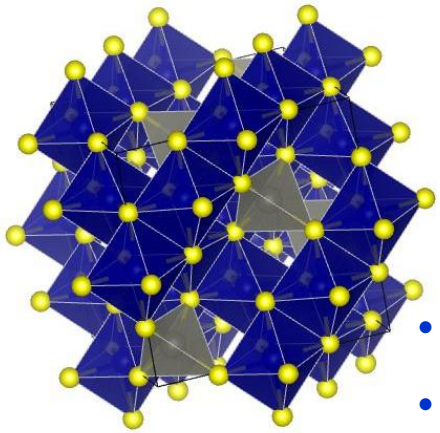
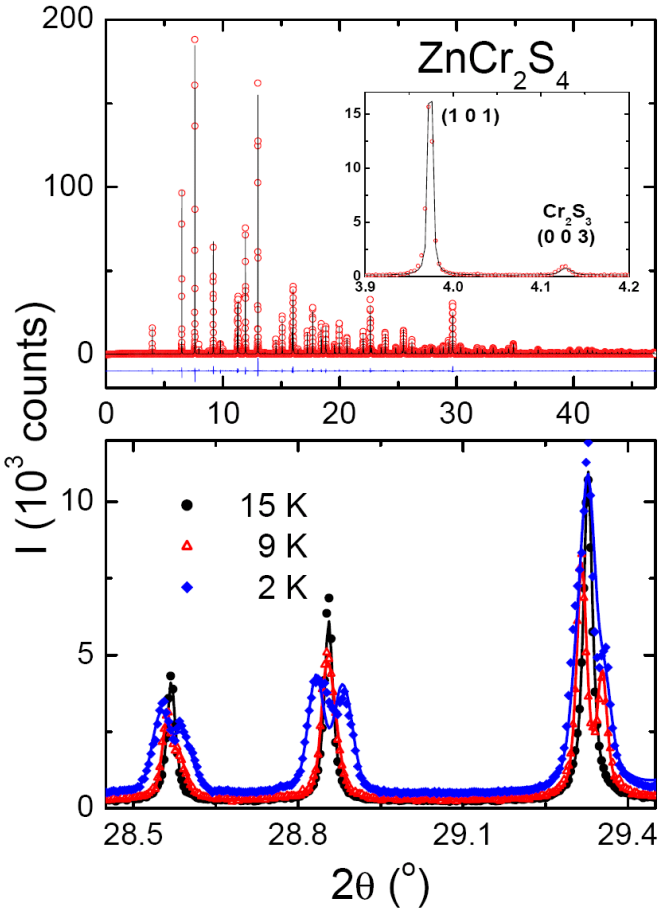
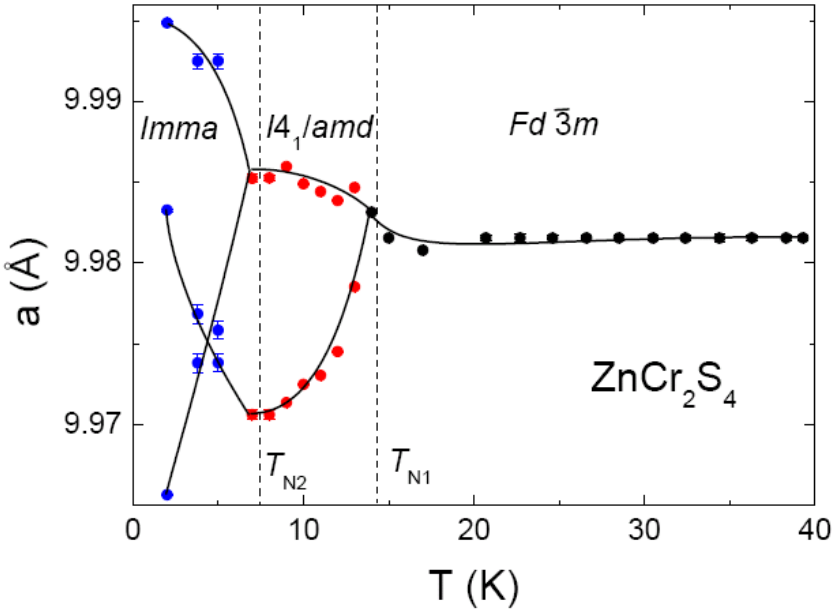


- Measured at ESRF ID31
- Wavelength of λ=0.39950 Å
- Rietveld refinement





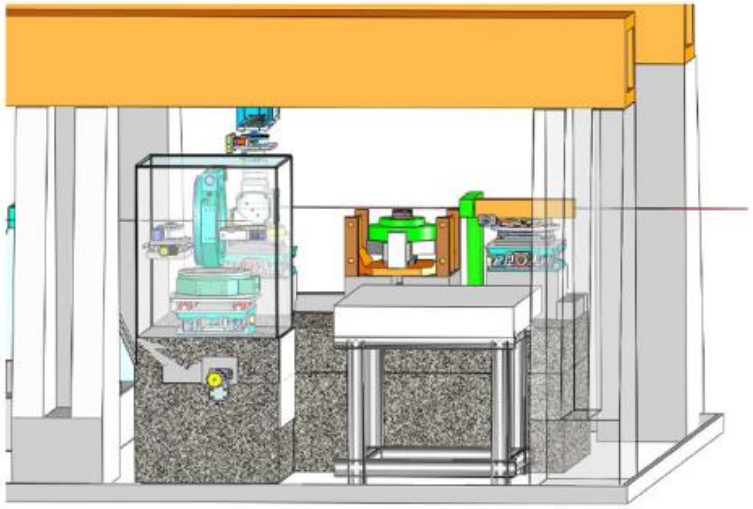
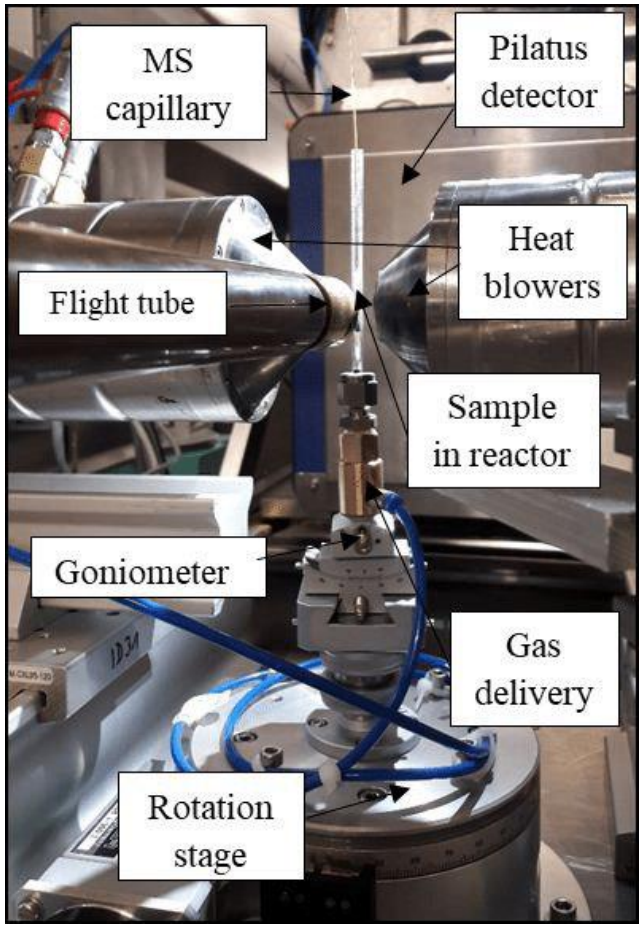


Figure 6. High resolution diffraction and imaging instrument.

ID31 ESRF



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Similarities between structural distortions under pressure and chemical doping in superconducting $BaFe_2As_2$

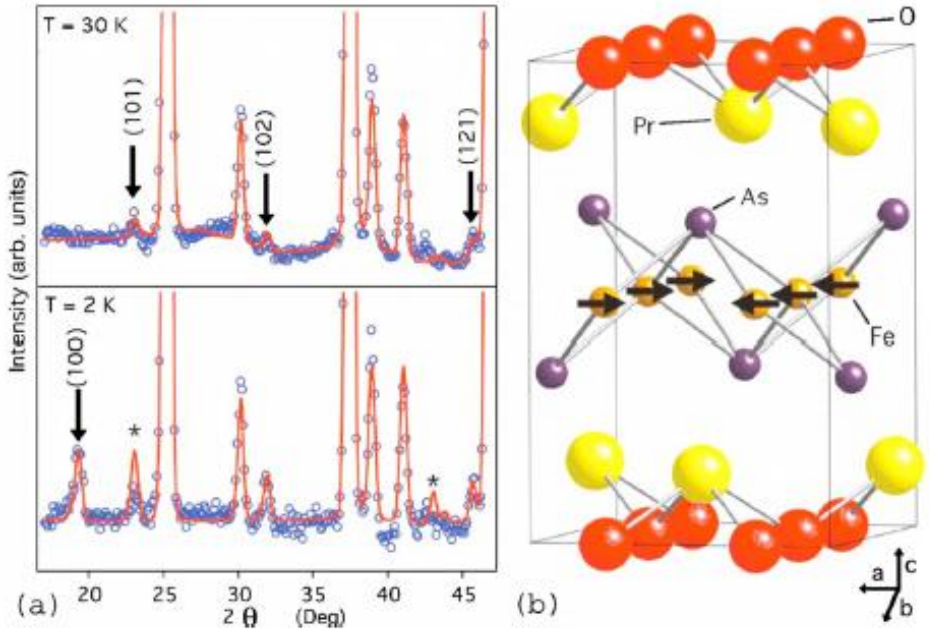

FIG. 4. (Color online) (a) Low angle region of neutron powder-diffraction patterns for PrFeAsO, recorded using D20. Top pattern shows fit at 30 K in Fe-spin ordered regime while bottom pattern shows combined Fe and Pr fit at 1.4 K. Stars mark areas of disagreement between observed and calculated patterns; (b) Refined Fe magnetic structure of PrFeAsO at 30 K.

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Assessing the pozzolanic activity of cements with added sugar cane straw ash by synchrotron X-ray diffraction and Rietveld analysis

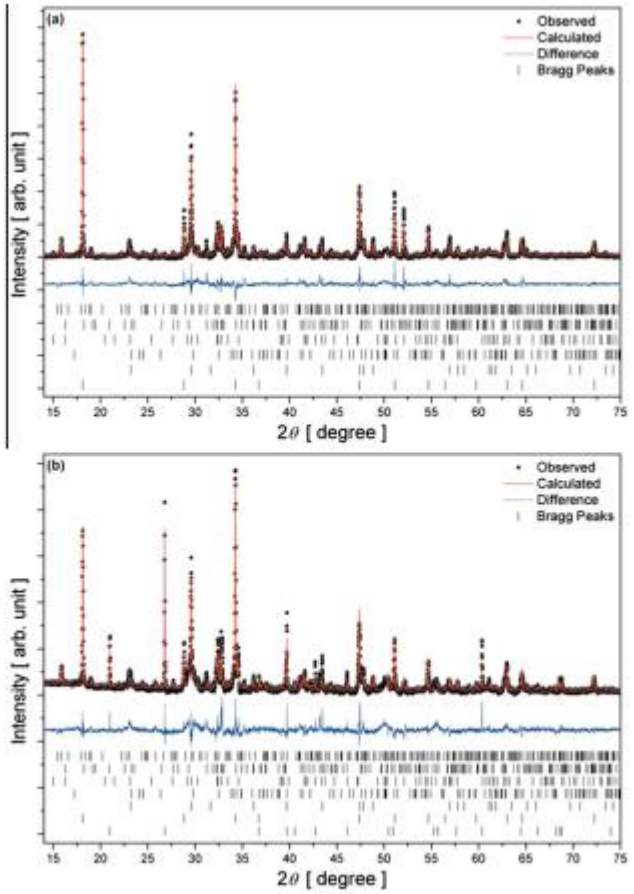


Fig. 5. Diffractograms of OPC (a) and OPC/SCSA (700 °C) (b) samples appear also with the angular position of the identified phases from top to bottom: Ettringite, Belite, Alite, Brownmillerite, Calcite, Portlandite and Quartz (present only in OPC/SCSA sample). Both samples were taken for 3 days of curing time.



XPD-LNLS

Softwares para refinamento:

Disponíveis na Internet:

- FULLPROF
- GSAS
- JANA
- RIETAN

Pagos:

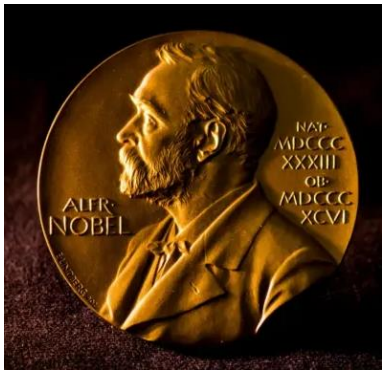
- TOPAS (Brucker)
- Malvern Panalytical’s XRD software suite

Softwares para refinamento:

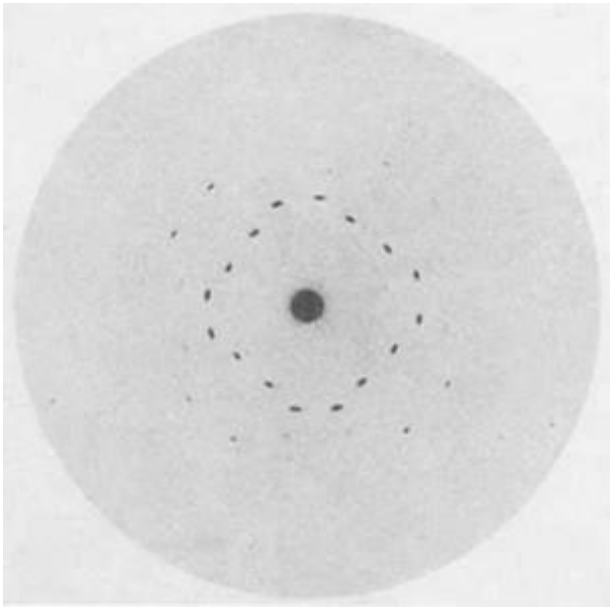
Disponíveis na Internet (onde achar):

- FULLPROF (https://www.ill.eu/sites/fullprof/)
- GSAS (https://subversion.xray.aps.anl.gov/trac/pyGSAS#:~:text=GSAS%2DII%20is%20a%20unique,x%2Dray%20and%20neutron%20probes.)
- JANA (http://jana.fzu.cz/)
- RIETAN (http://www.cristal.org/DU-SDPD/nexus/rietveld/fatriet/angle_dispersive.html)

The Nobel Prize in Physics 1914



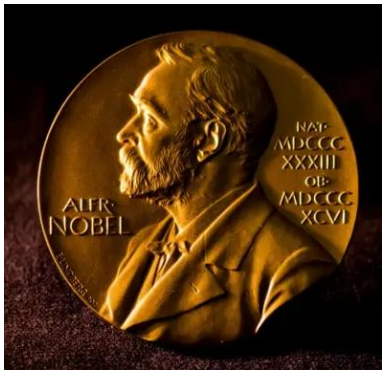


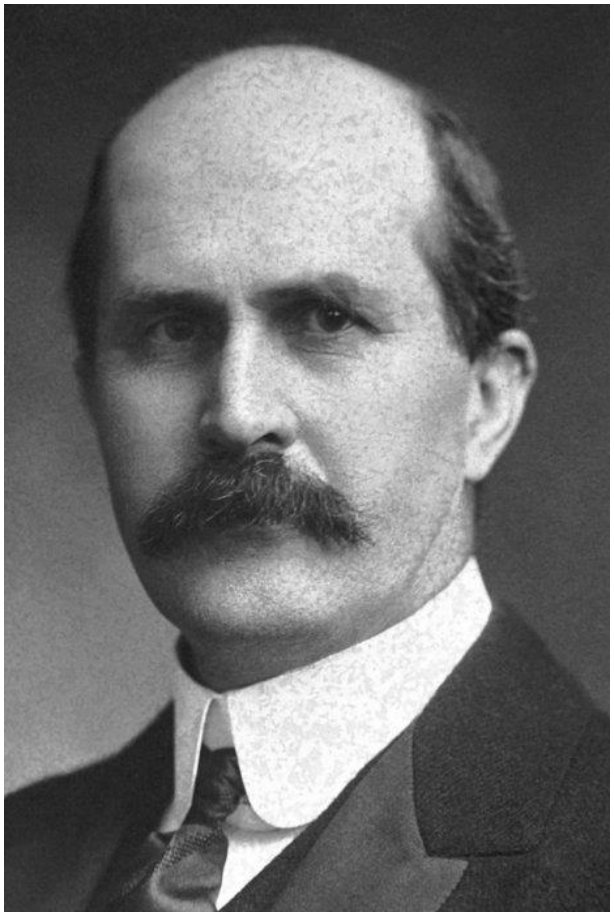


Max von Laue

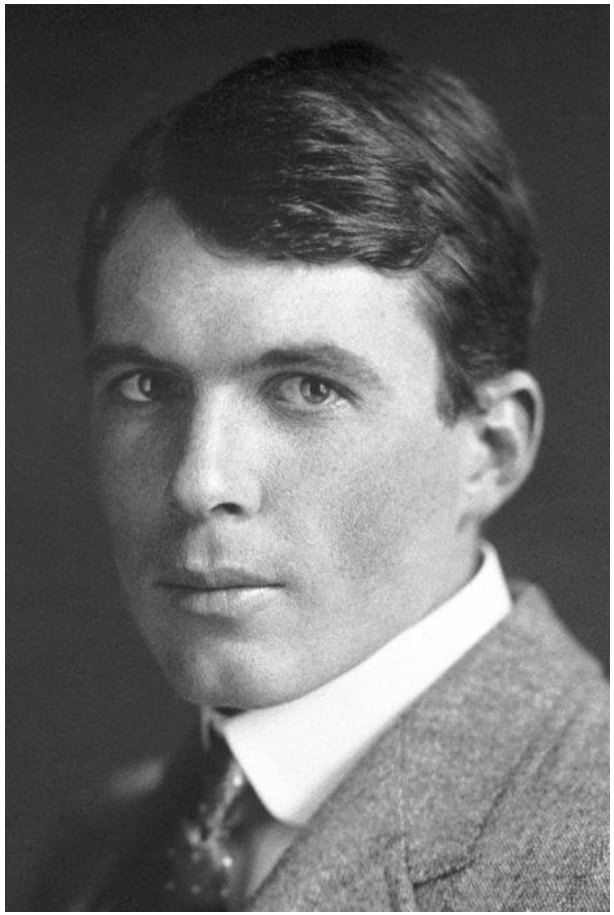
The Nobel Prize in Physics 1914 was awarded to Max von Laue "for his discovery of the diffraction of X-rays by crystals."

The Nobel Prize in Physics 1915





Sir William Henry Bragg



William Lawrence Bragg

The Nobel Prize in Physics 1915 was awarded jointly to Sir William Henry Bragg and William Lawrence Bragg "for their services in the analysis of crystal structure by means of X-rays."

Bragg's Law

$$n\lambda = 2d\sin\theta$$

The Nobel Prize in Physiology or Medicine 1962



Photo from the Nobel Foundation archive.

Francis Harry Compton Crick

Prize share: 1/3



Photo from the Nobel Foundation archive.

James Dewey Watson

Prize share: 1/3



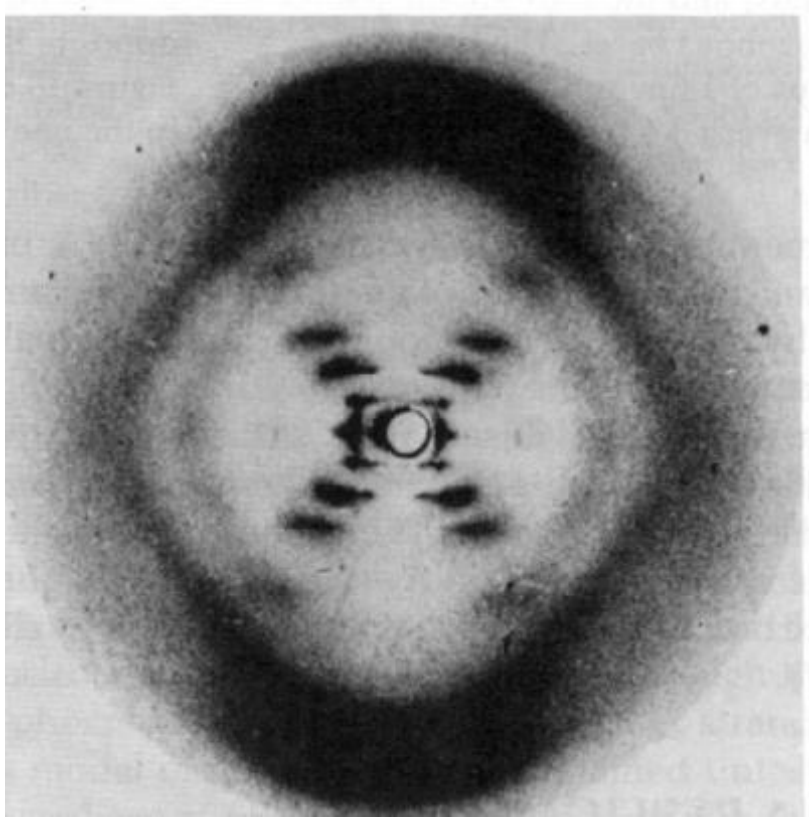
Photo from the Nobel Foundation archive.

Maurice Hugh Frederick Wilkins

Prize share: 1/3

The Nobel Prize in Physiology or Medicine 1962 was awarded jointly to Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material."

The Nobel Prize in Physiology or Medicine 1962





Rosalind Franklin

25 July 1920 – 16 April 1958

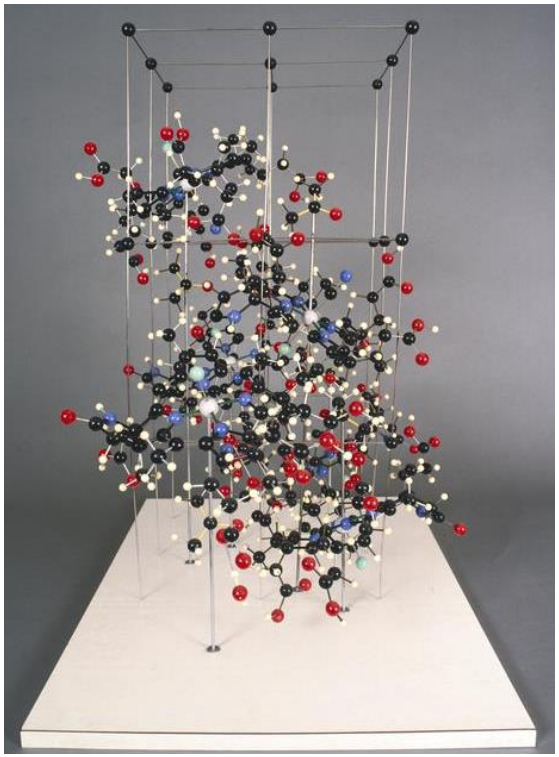
Photo 51- The x-ray diffraction image that allowed Watson and Crick to solve the structure of DNA





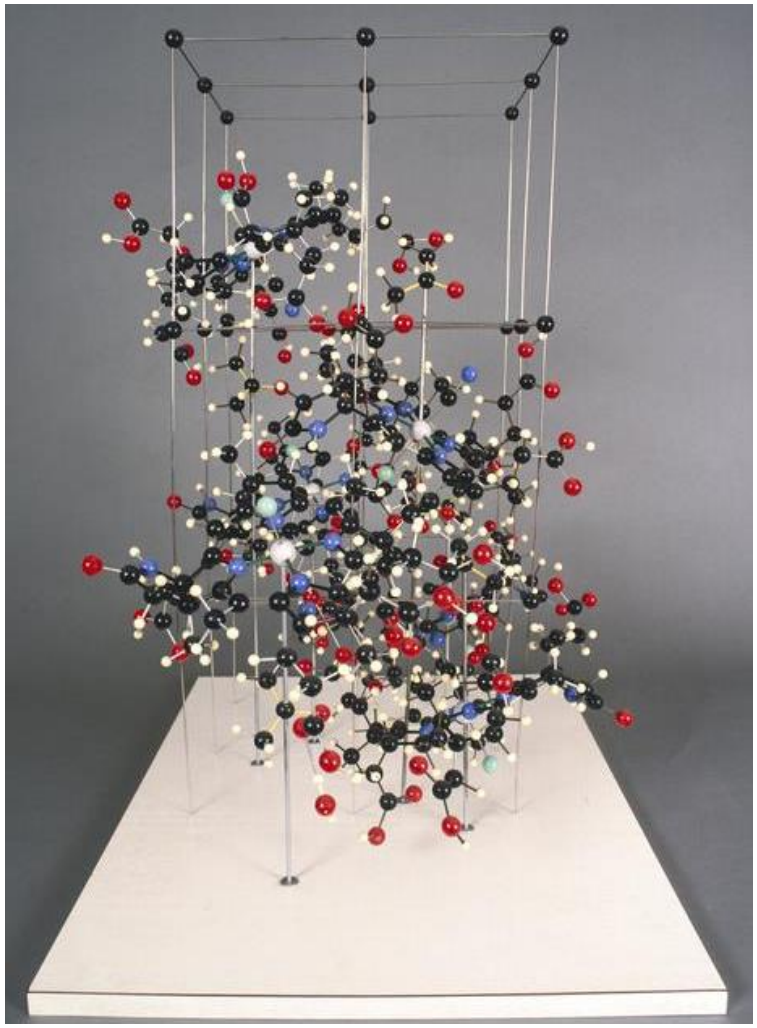
Dorothy Crowfoot Hodgkin

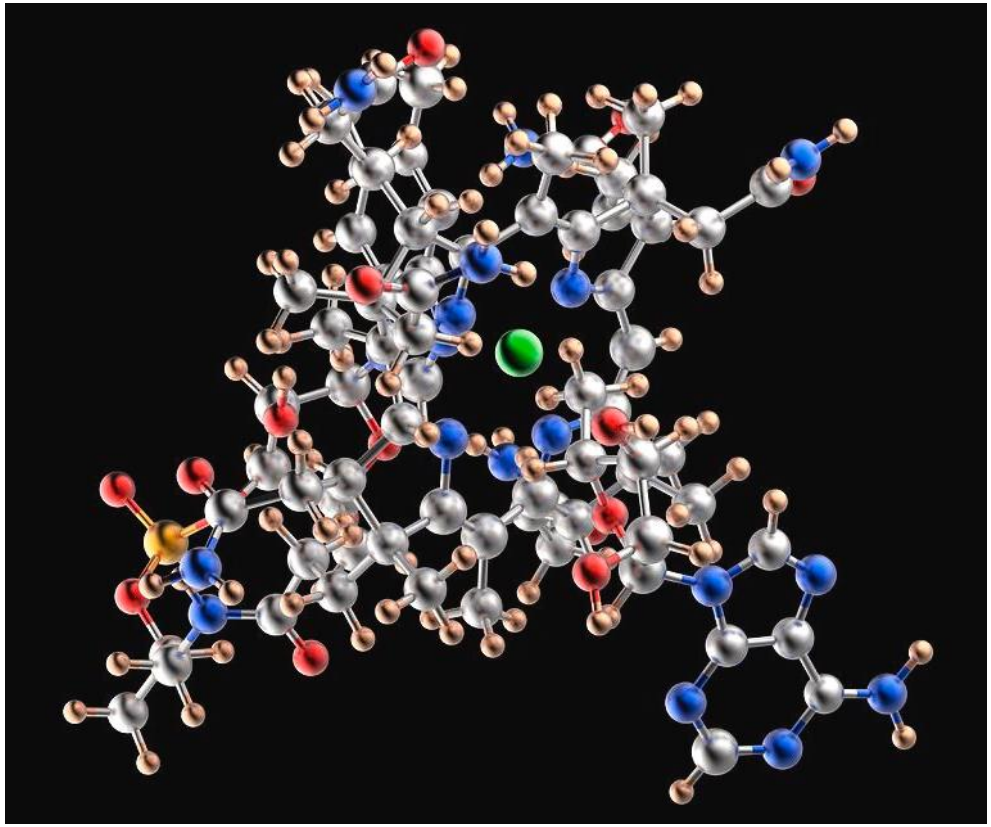
The Nobel Prize in Chemistry 1964
Born: 12 May 1910, Cairo, Egypt
Died: 29 July 1994, Shipston-on-Stour, United Kingdom
Affiliation at the time of the award: University of Oxford, Royal Society, Oxford, United Kingdom
Prize motivation: “for her determinations by X-ray techniques of the structures of important biochemical substances”

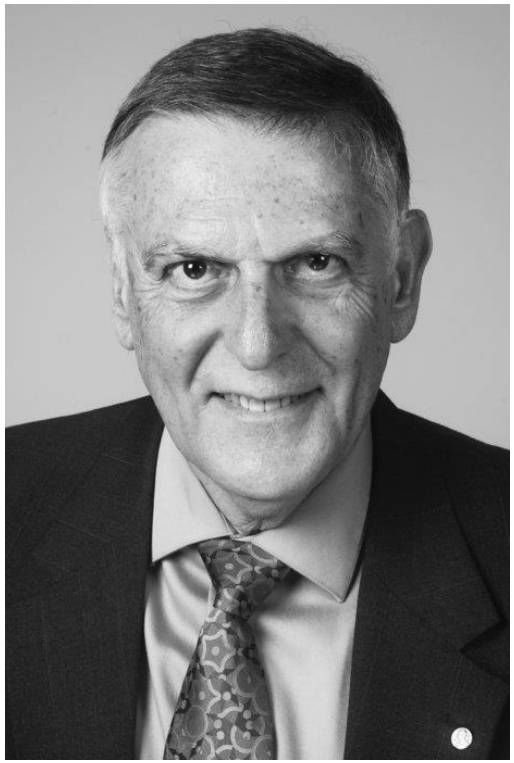


Vitamina B12

Vitamina B12



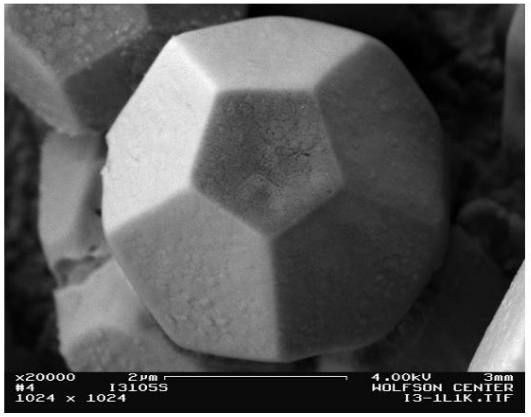


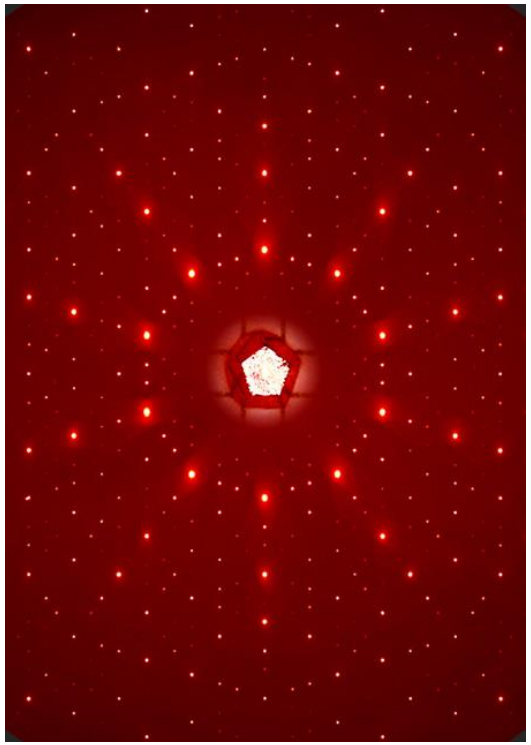


Dan Shechtman

The Nobel Prize in Chemistry 2011
Born: 24 January 1941, Tel Aviv, British Mandate of Palestine (now Israel)
Affiliation at the time of the award: Technion - Israel Institute of Technology, Haifa, Israel
Prize motivation: “for the discovery of quasicrystals”
Prize share: 1/1

A quasi-periodic crystal of the system Mg-Zn-Ce





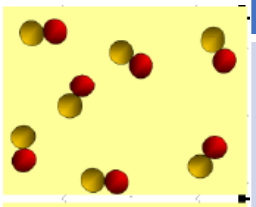
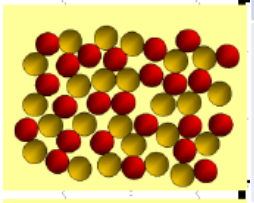
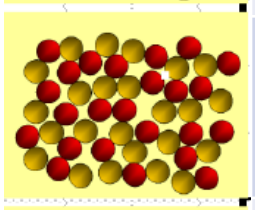
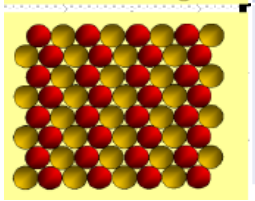
V escola de verão

Geometria dos Cristais

Cristal é um sólido composto de átomos, íons ou moléculas que demonstram ordem periódica de longo alcance em três dimensões



O estado cristalino

	Estado da matéria	Volume Fixo	Forma Fixa	Ordem	Properties
	Gás	Não	Não	Não	isotrópico
	Líquido	Sim	Não	Curto alcance	isotrópico
	Sólido (amorfo)	Sim	Sim	Curto alcance	isotrópico
	Sólido (cristalino)	Sim	Sim	Longo alcance	Anisotrópico

Crystalline vs. Amorphous Solids



Galena
(PbS)
a crystalline solid



Obsidian
(typically $KAlSi_3O_8$)
an amorphous solid

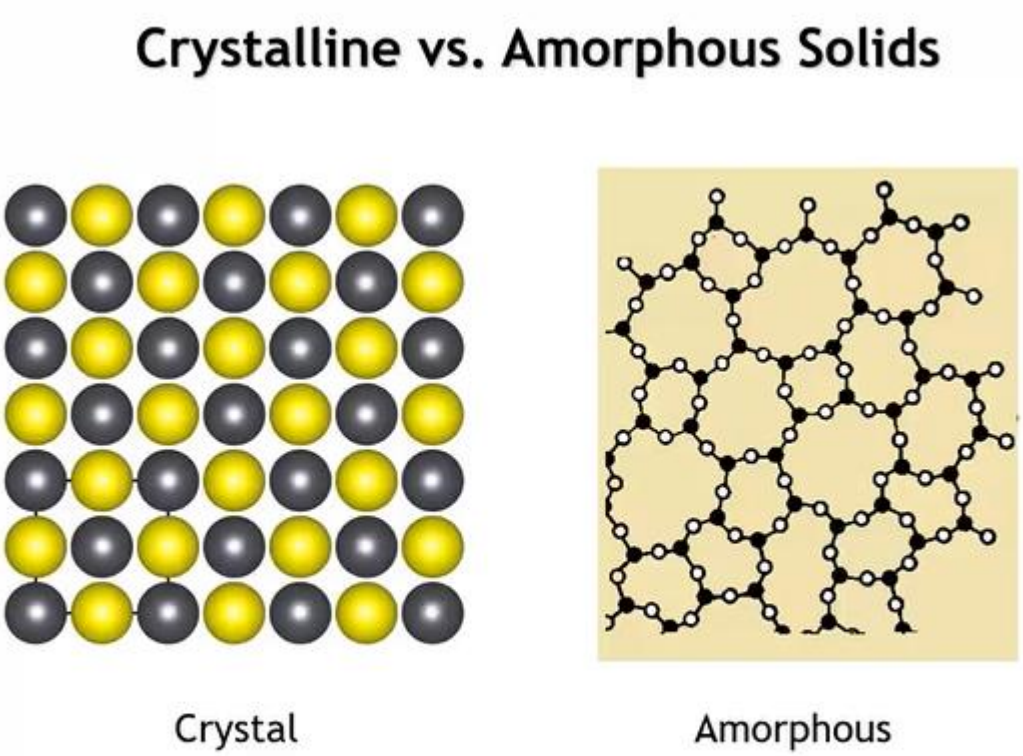
Crystalline solids possess translational symmetry, amorphous solids do not
(they are like frozen liquids)

Entender simetria de translação

Sulfato de chumbo

Vidro vulcânico
Silicato de alumínio com potassio

V escola de verão



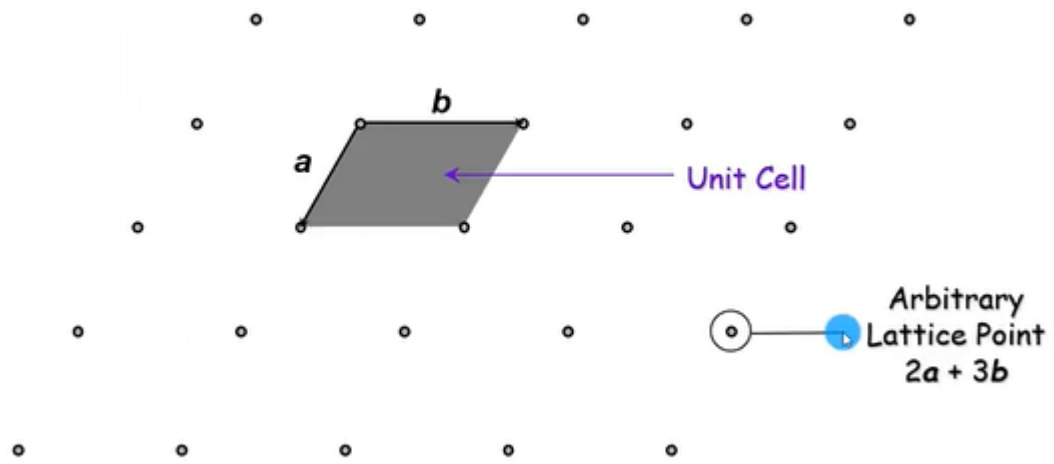
Entender simetria de translação

Observando em escala atômica

Um pouco de Matemática:

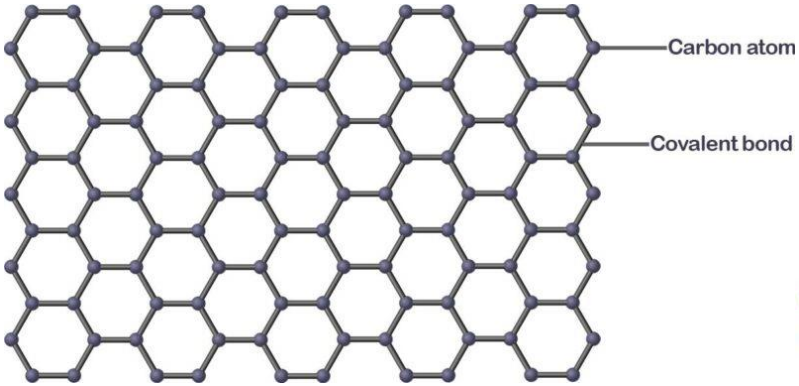
Simetria translacional (em 2D)

Entender simetria de translação

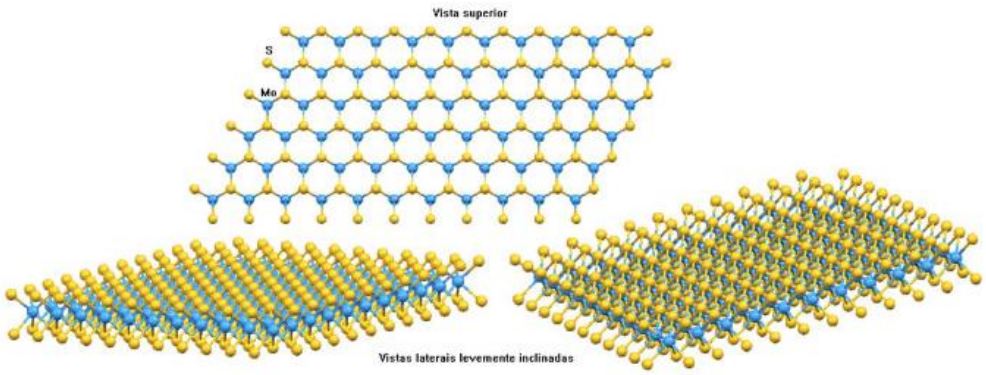


- a e b são vetores da rede. Todo o ponto da rede pode ser definido ao adicionarmos os 2 vetores (2D).
- A célula unitária é o paralelogramo definido pelos vetores da rede. Todo o espaço pode ser preenchido pela célula unitária.

V escola de verão

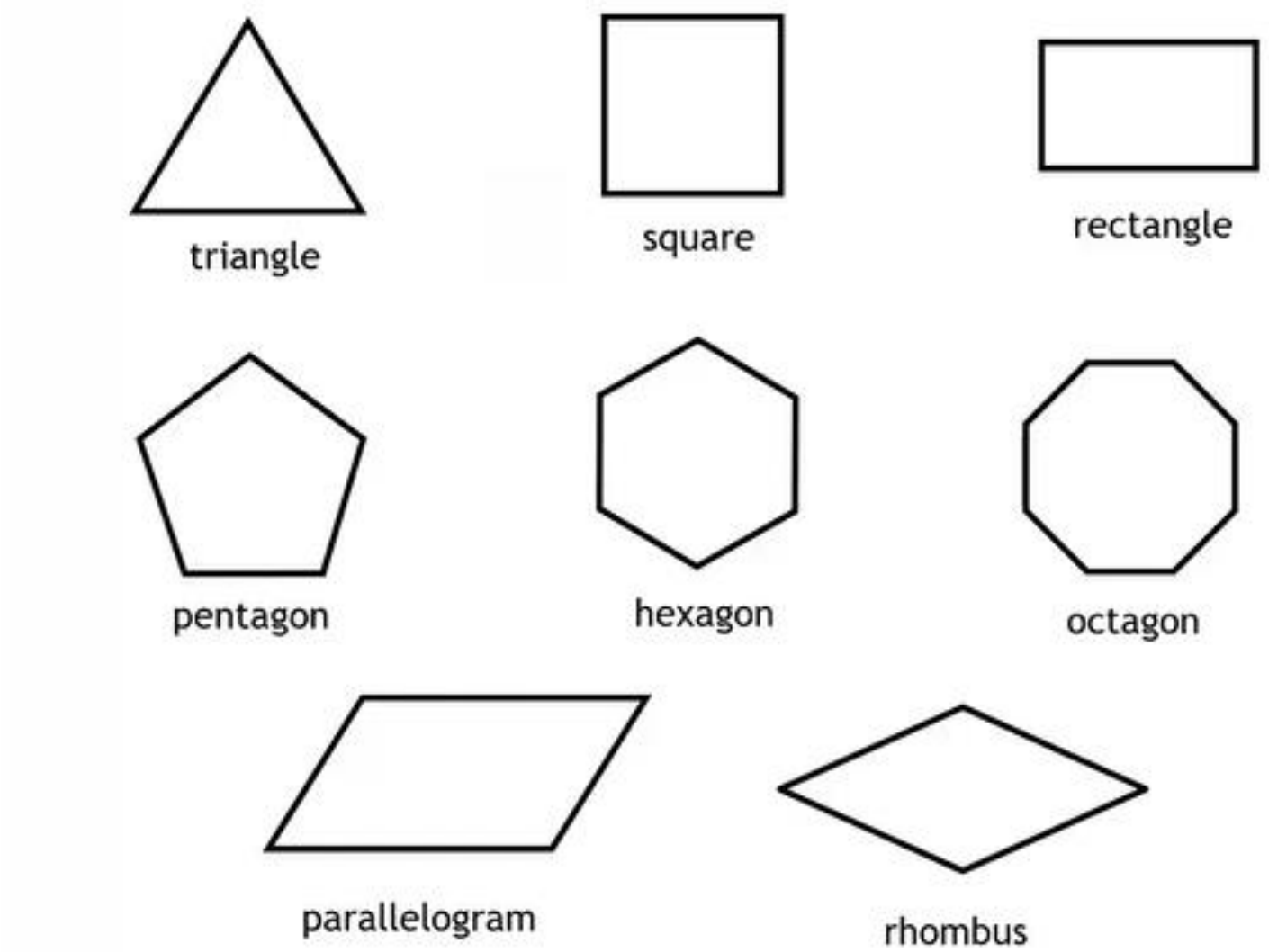


Grafeno



Dissulfeto de Molibdênio

Quais formas preenchem o espaço?



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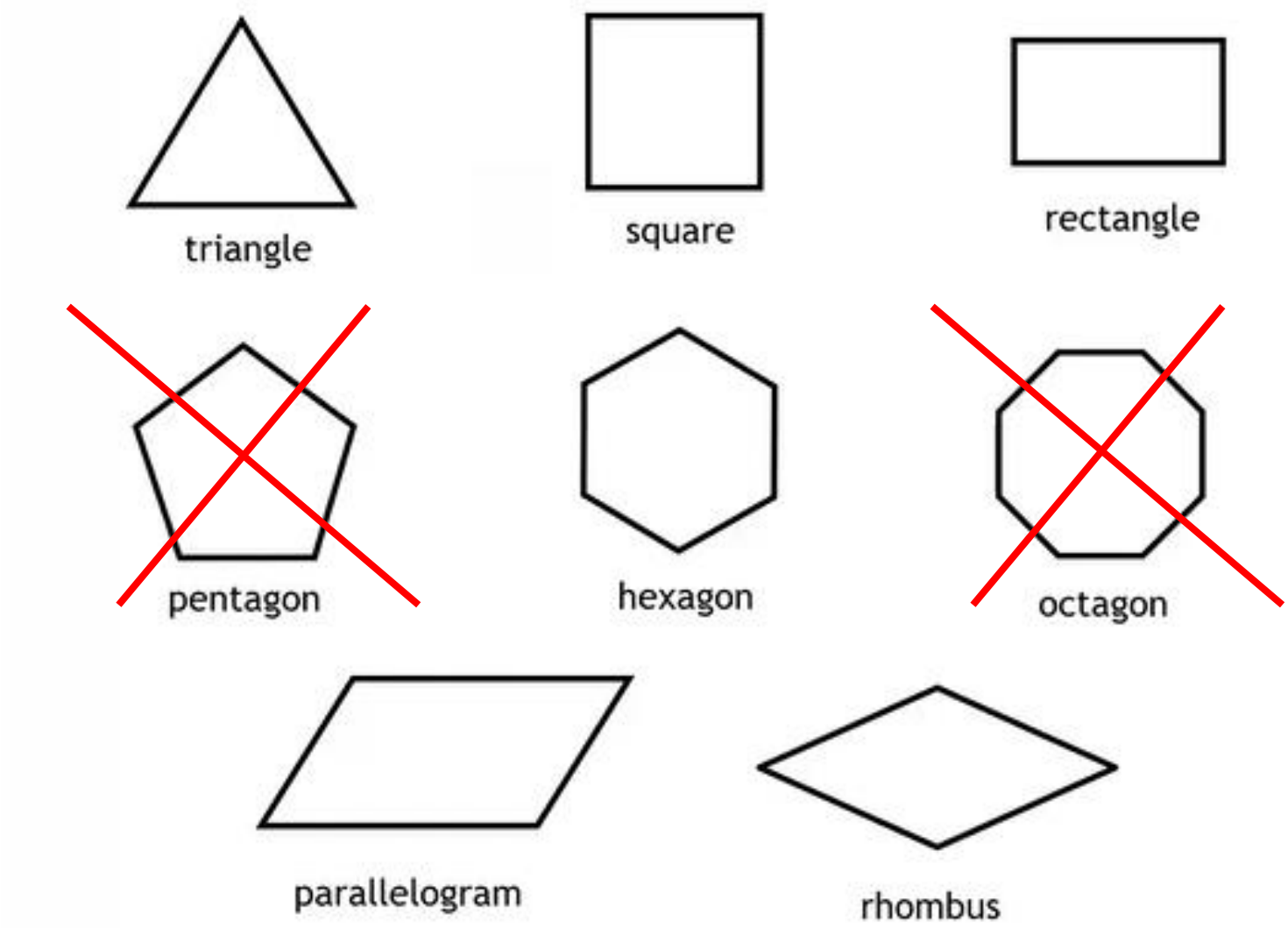

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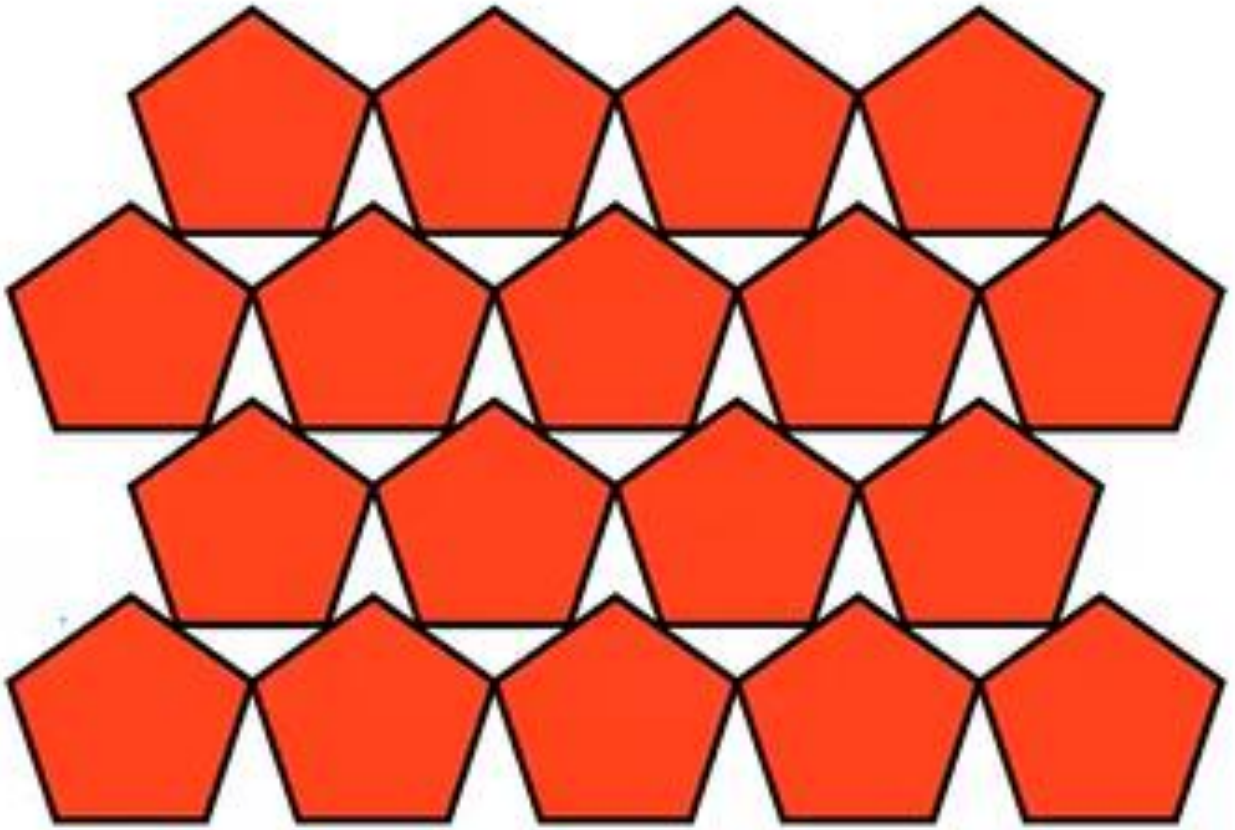
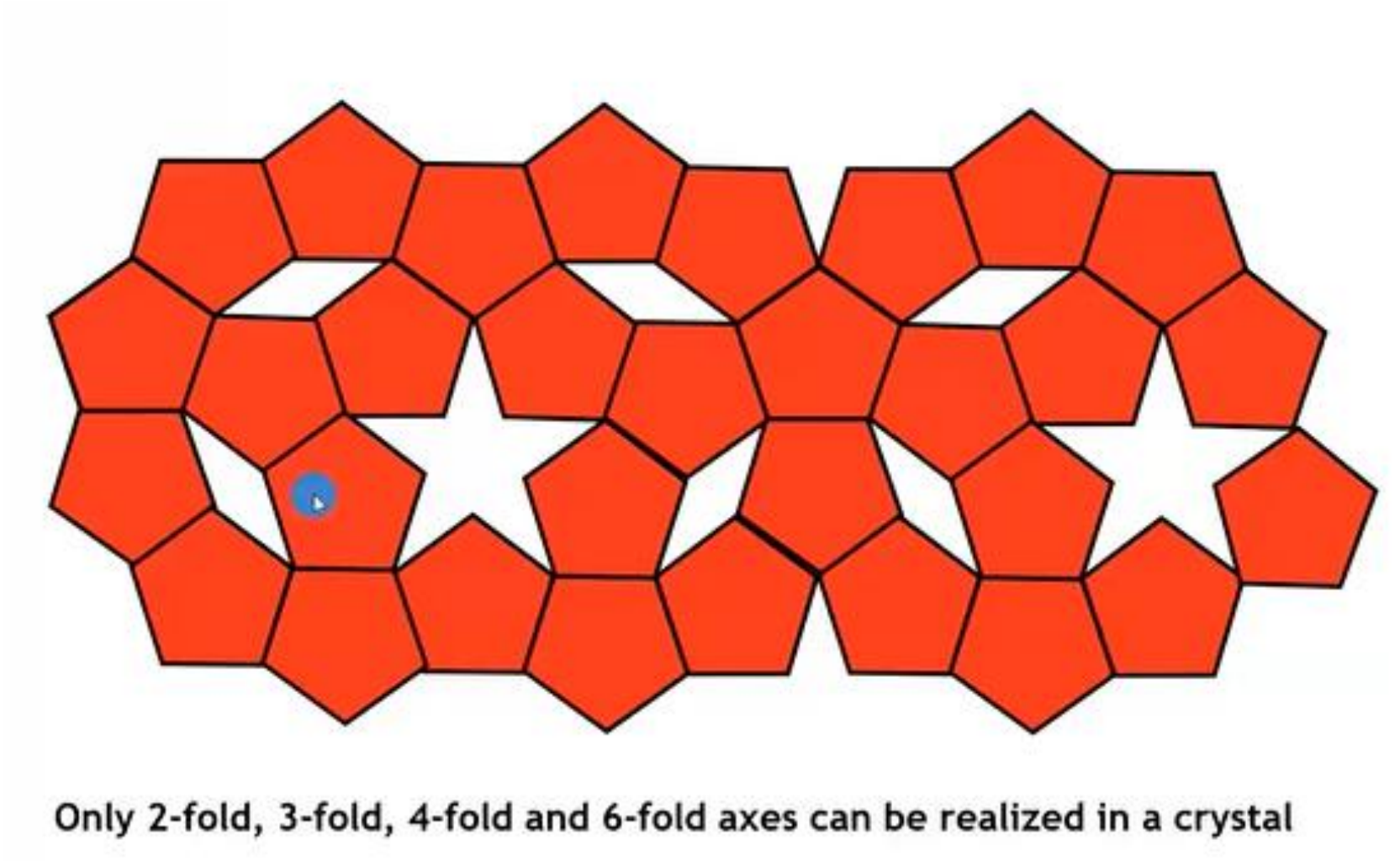
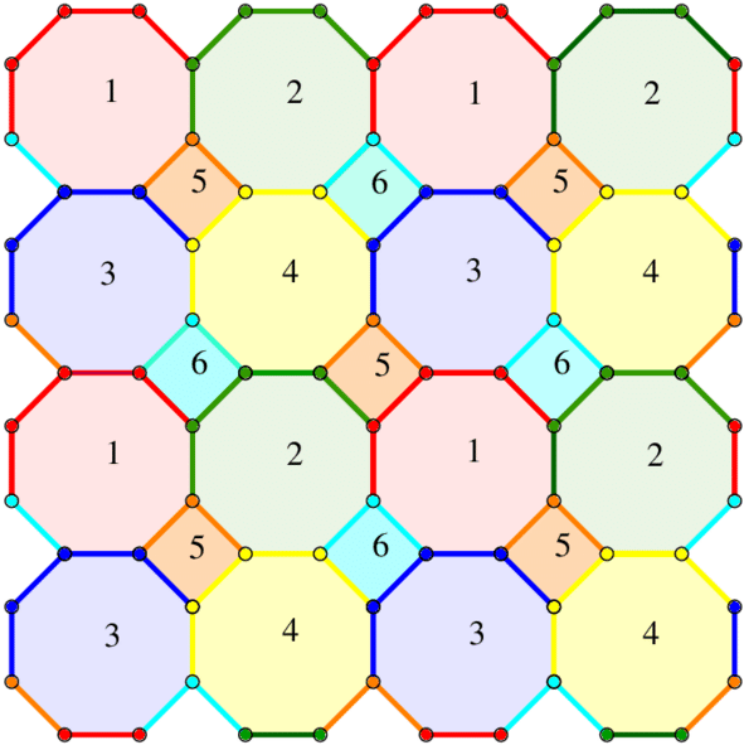
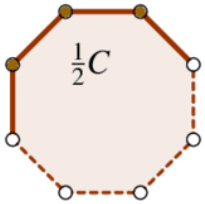




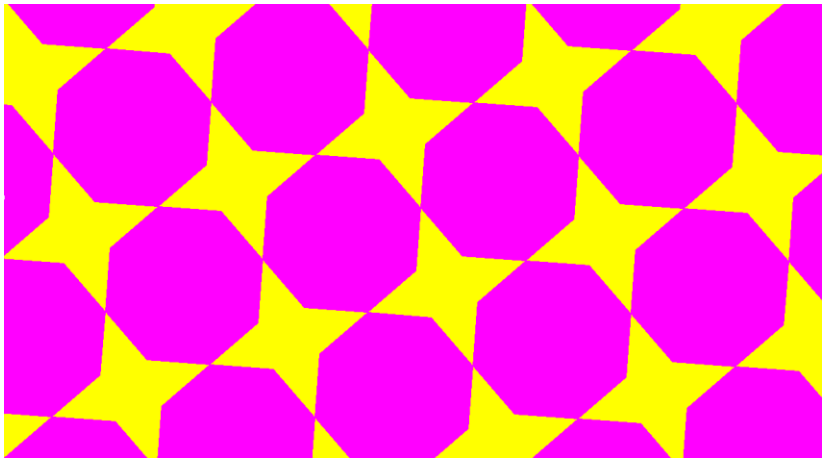
Only 2-fold, 3-fold, 4-fold and 6-fold axes can be realized in a crystal

V escola de verão









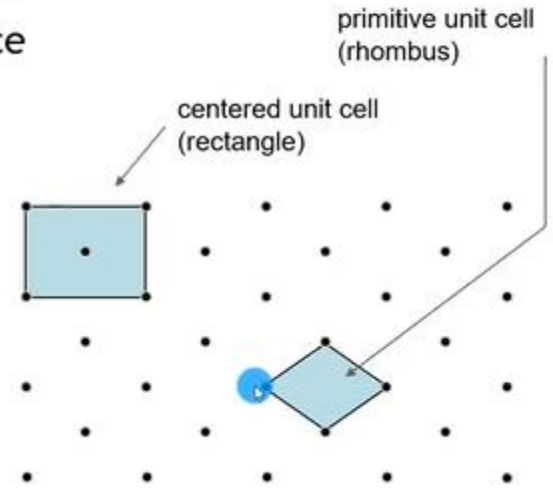
2D Bravais Lattices

- Primitive hexagonal lattice
- Primitive square lattice
- Primitive rectangular lattice
- Centered rectangular lattice
- Primitive oblique lattice

The centered rectangular lattice contains an extra lattice point at

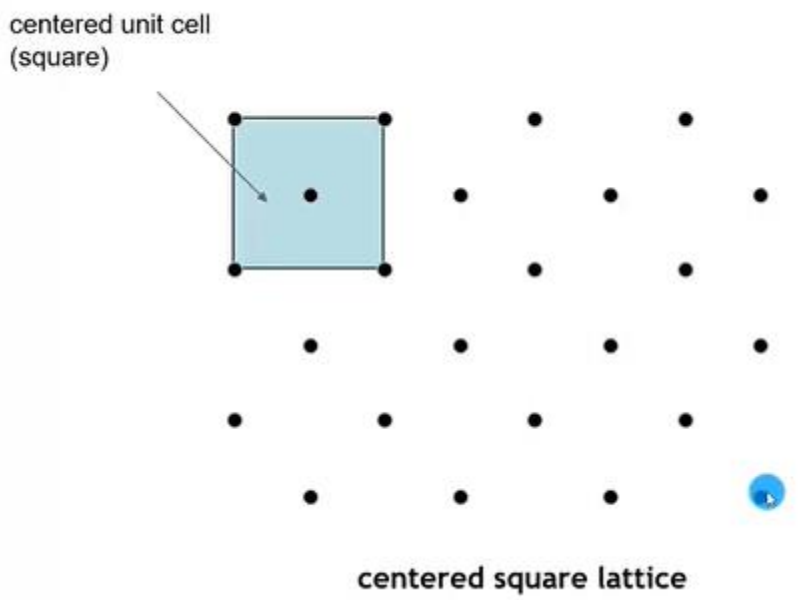
½ ***a*** + ½ ***b***

Making 2 lattice points per unit cell



centered rectangular lattice

Por que não há outras redes de Bravais centradas?



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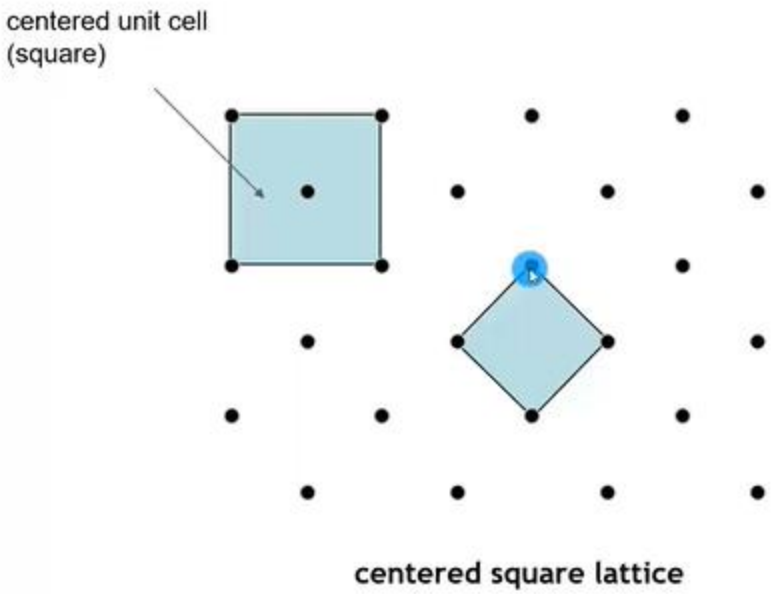

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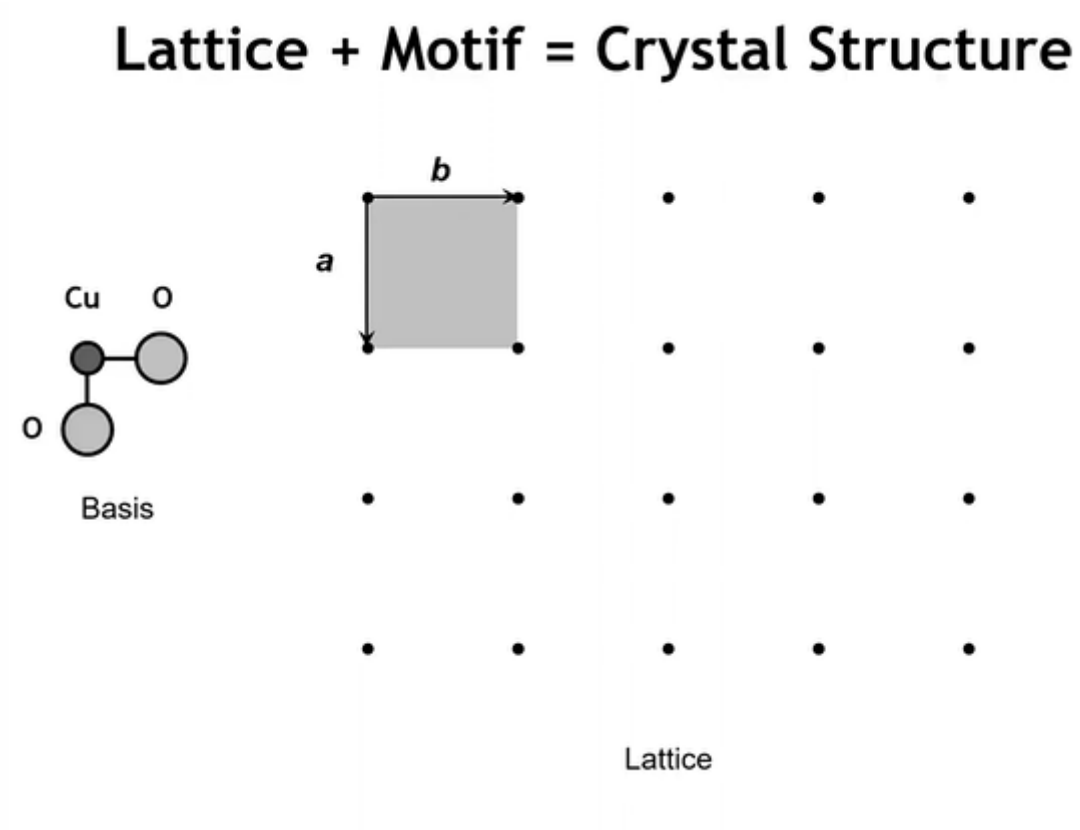

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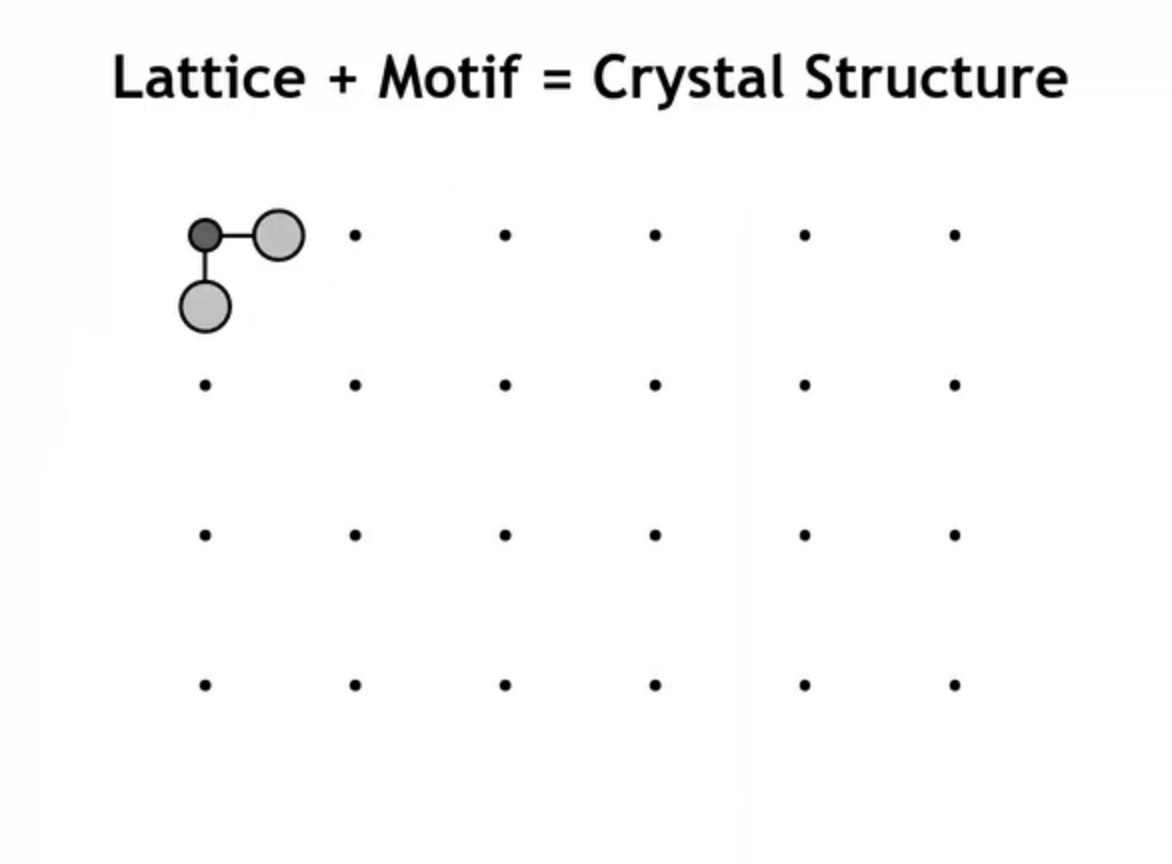
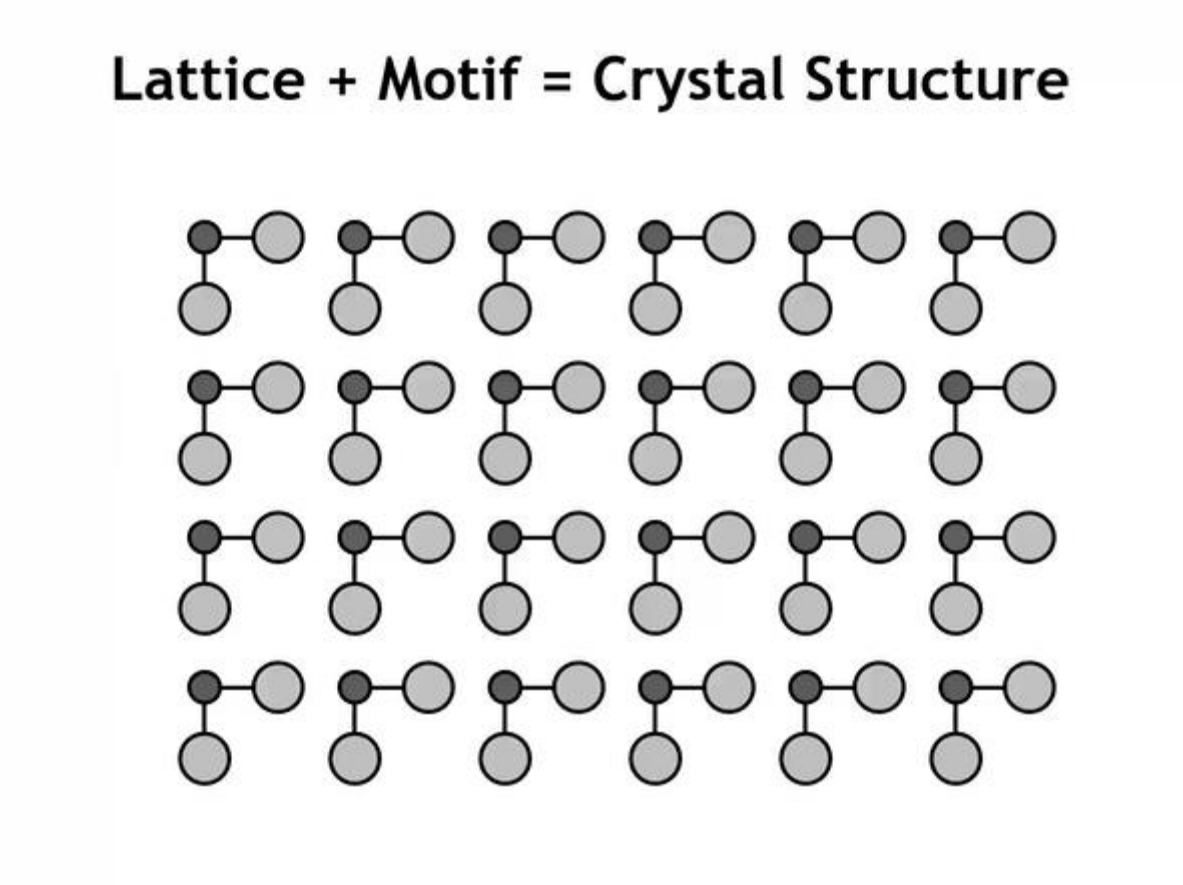
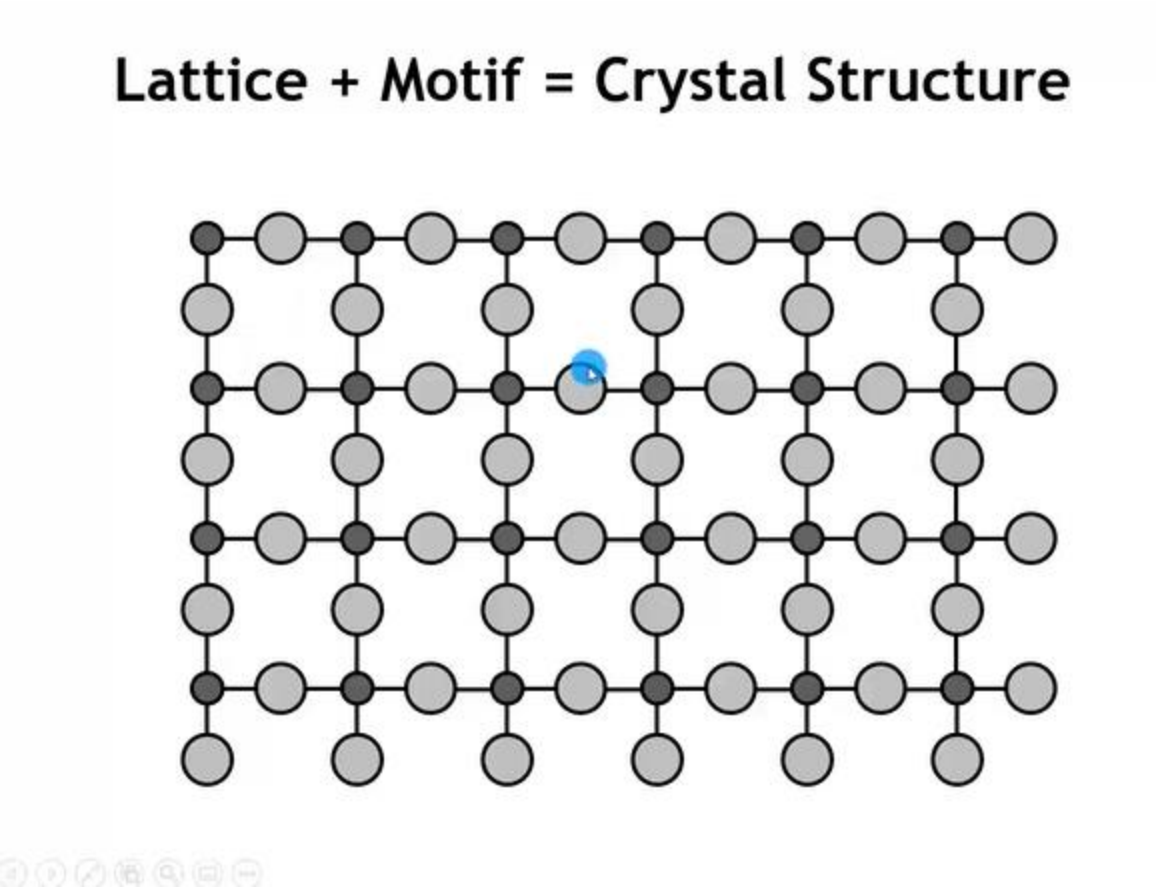
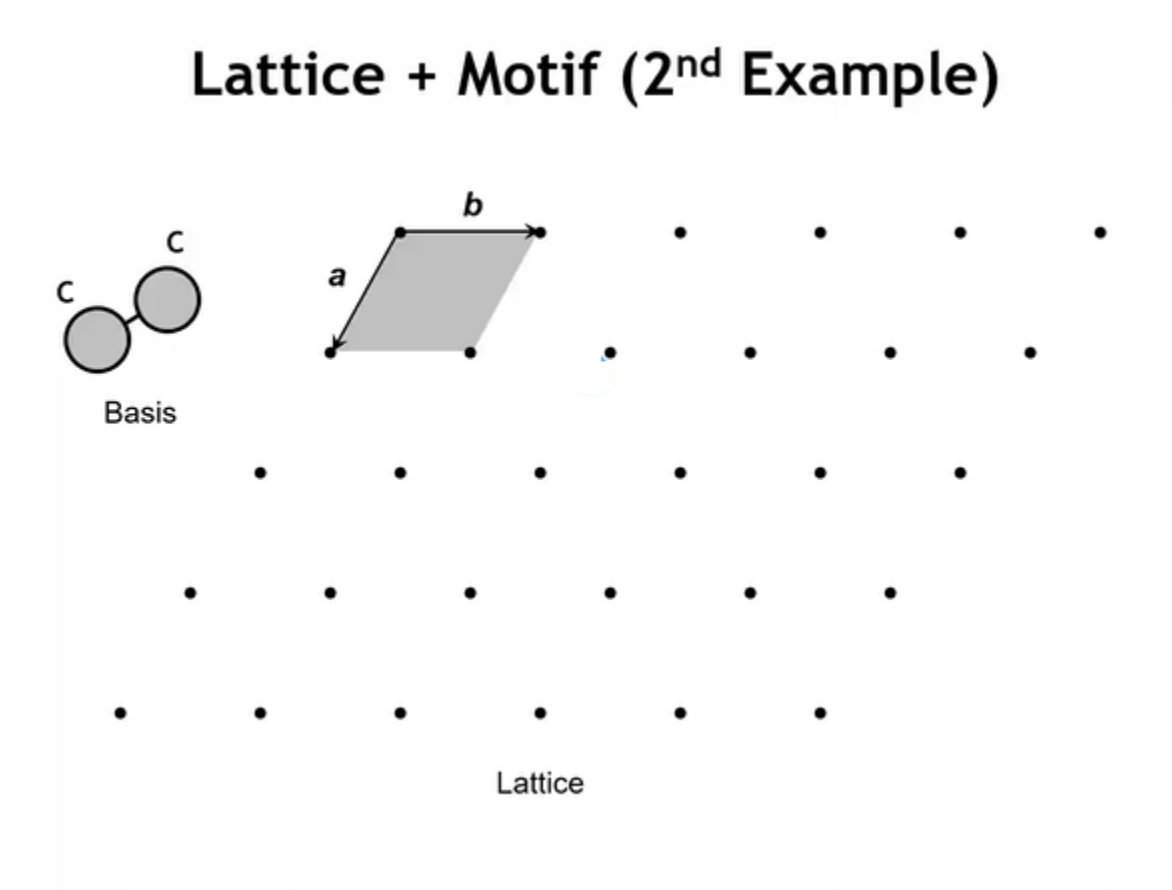


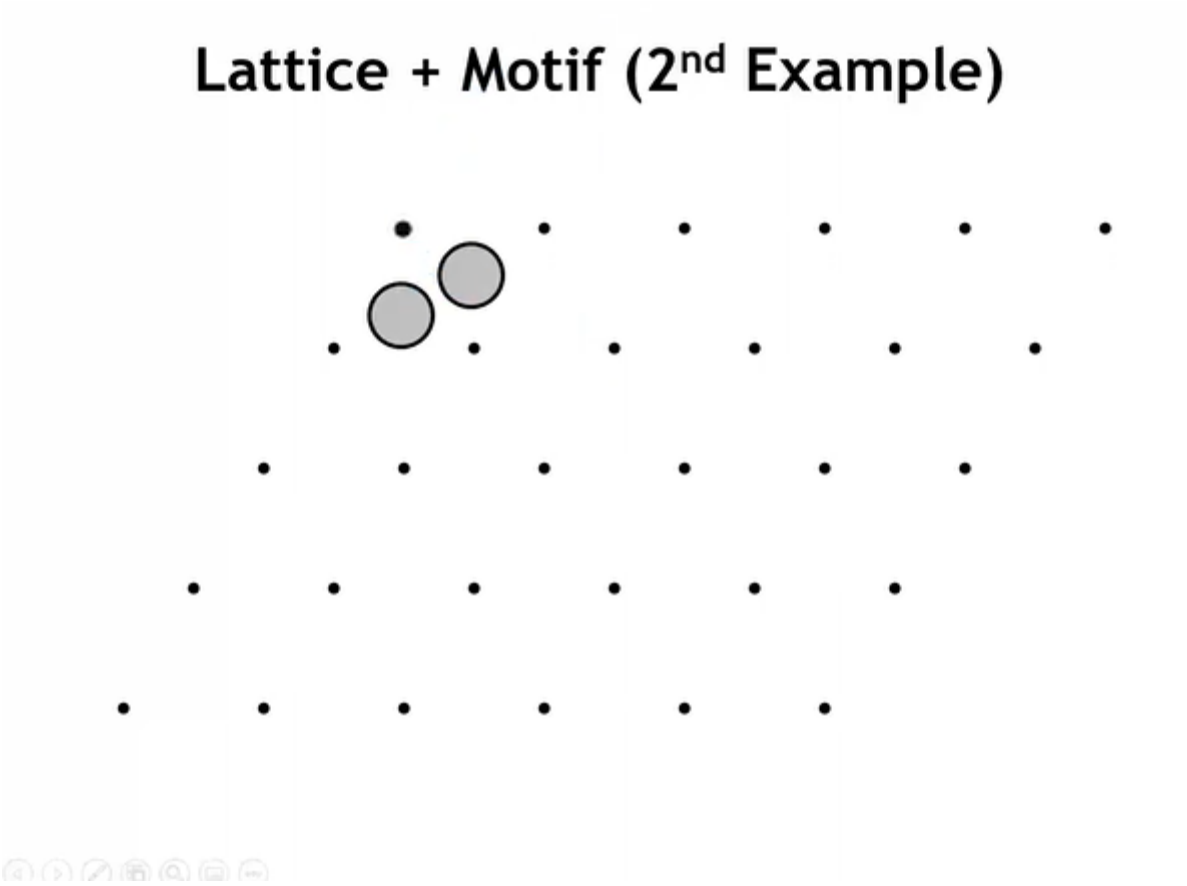
V escola de verão

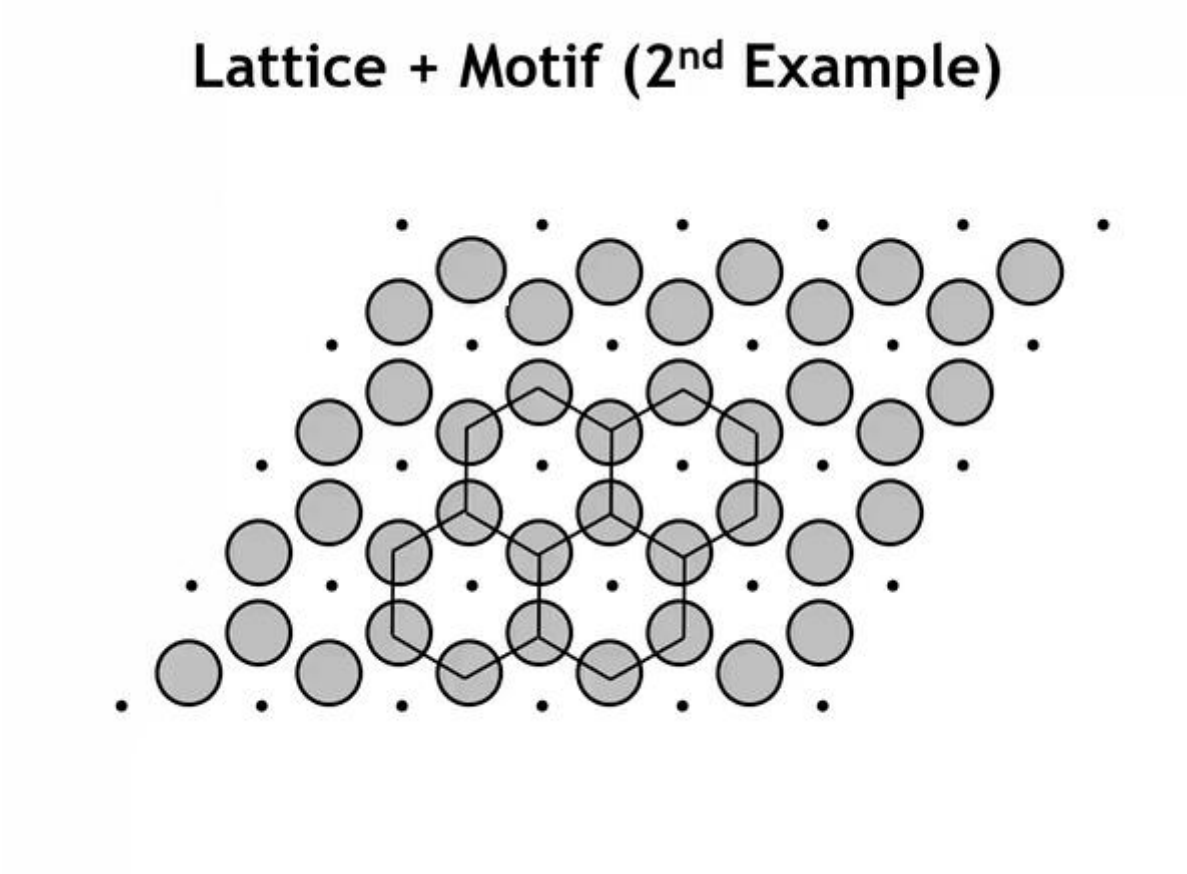


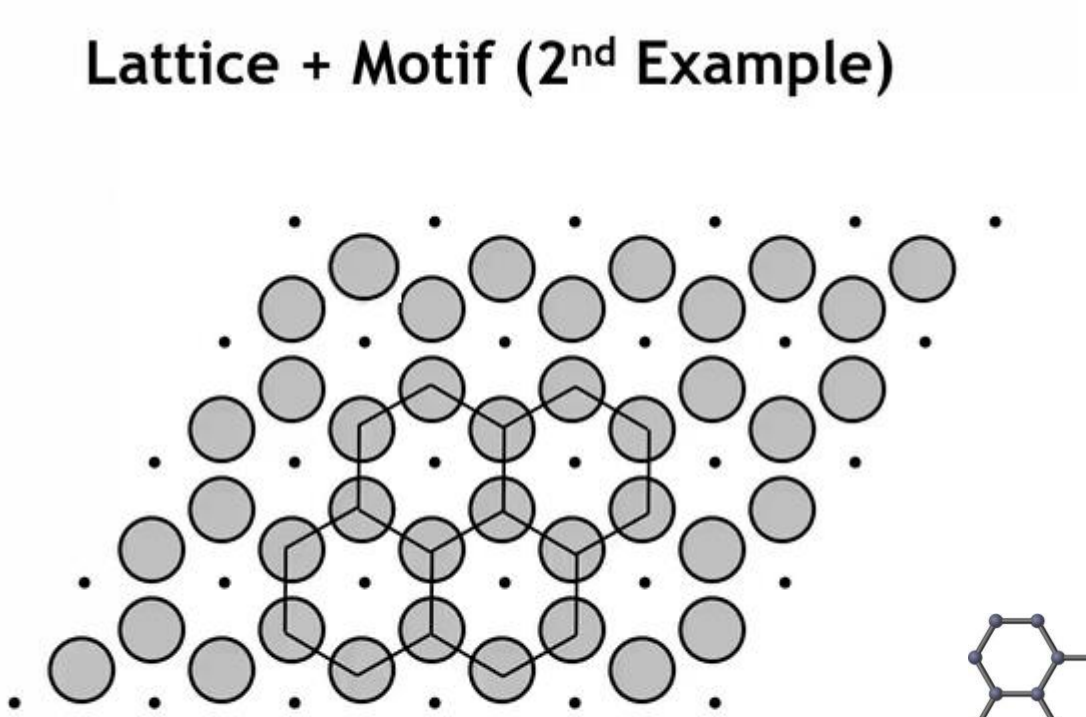
V escola de verão

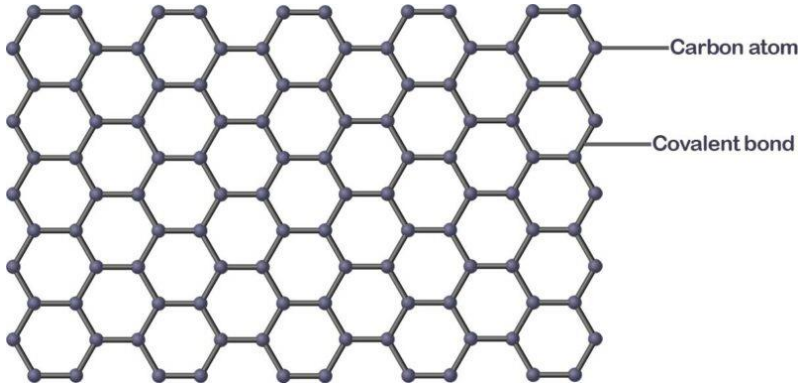



Lattice + Motif (2nd Example)
C
C
Basis
a
b
Lattice


Lattice + Motif (2nd Example)

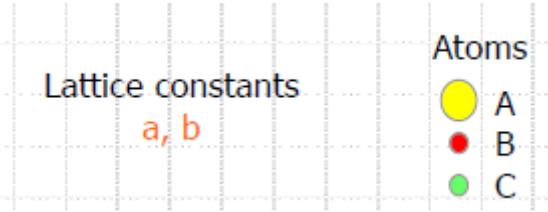

Lattice + Motif (2nd Example)



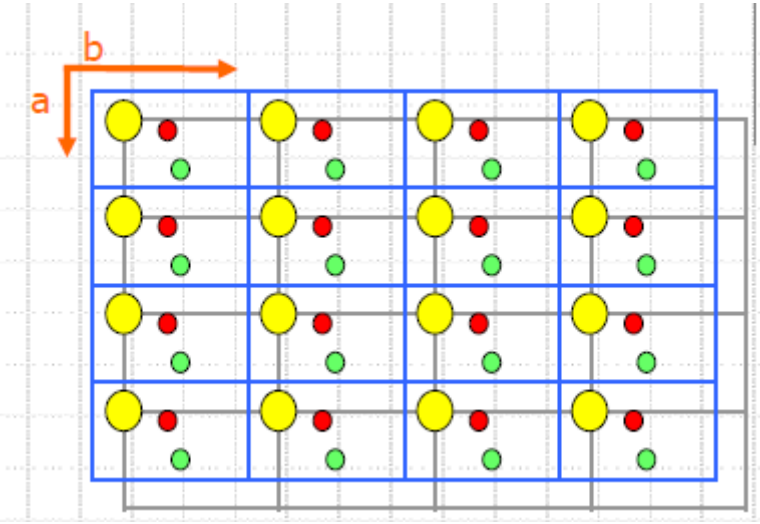


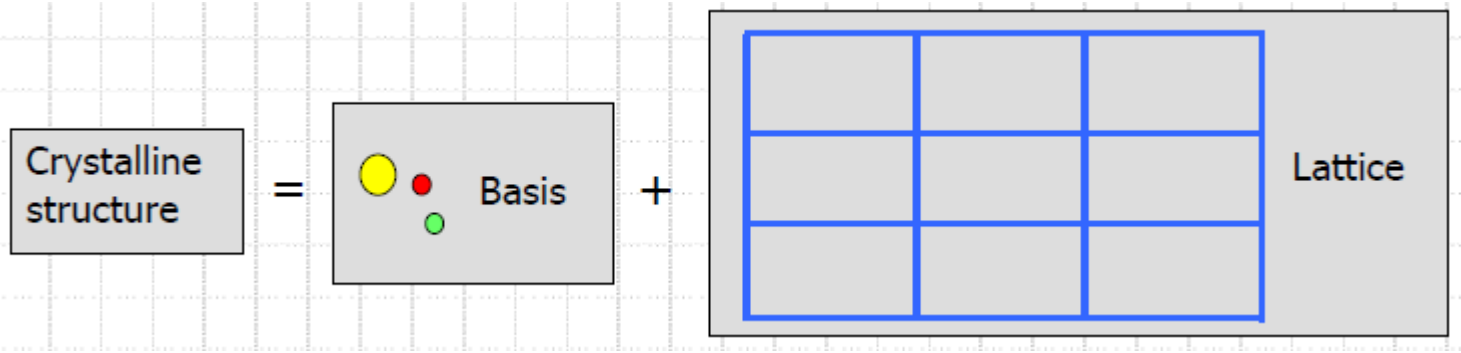
Grafeno

Estrutura de cristal

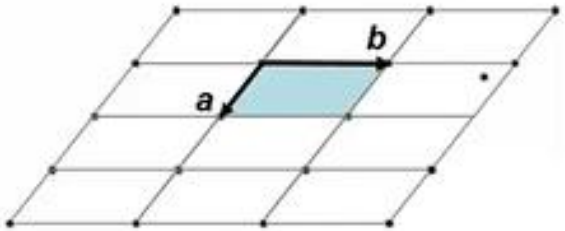


Não apenas as posições de átomos, íons ou moléculas são repetitivas – existem certas relações de simetria em seu arranjo.

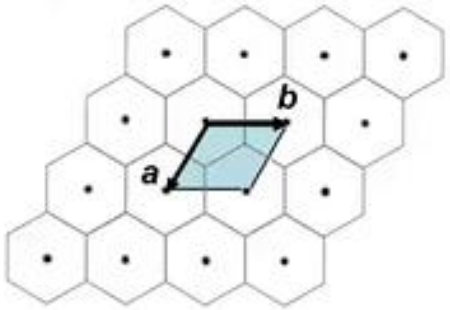




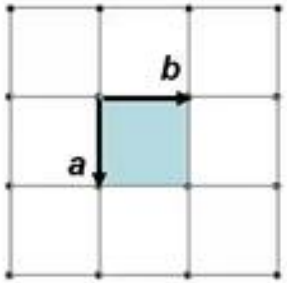
2D Bravais Lattices



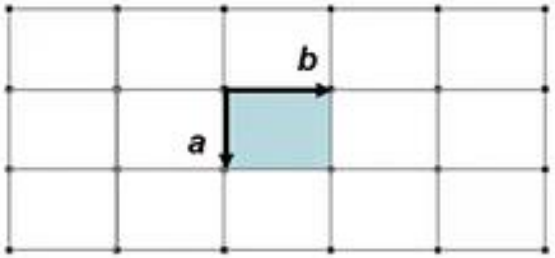
Oblique



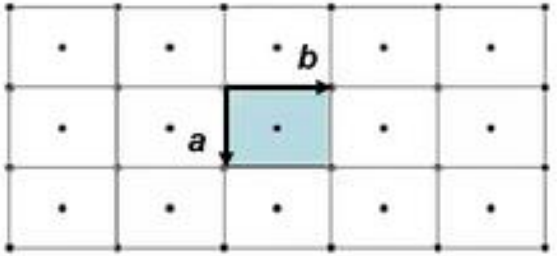
Hexagonal



Square

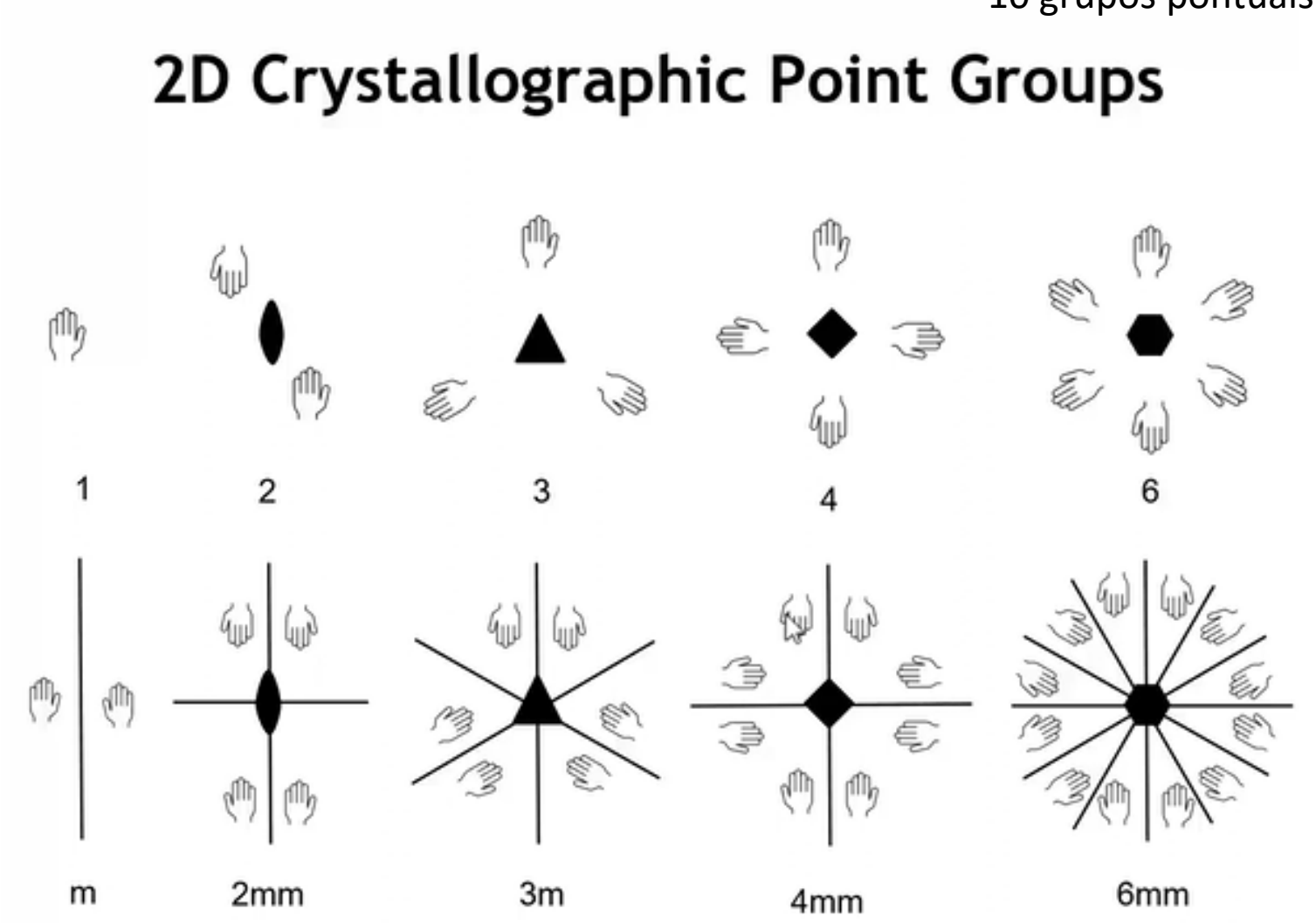


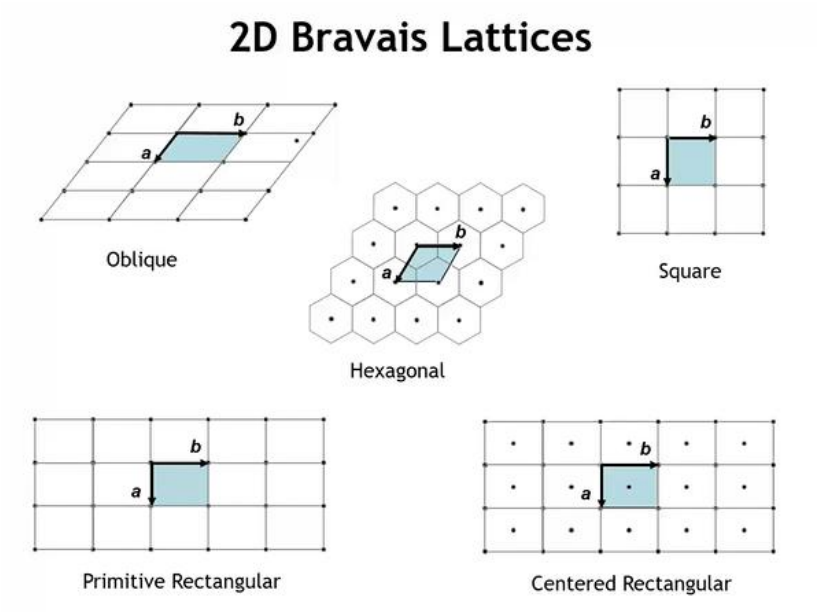
Primitive Rectangular



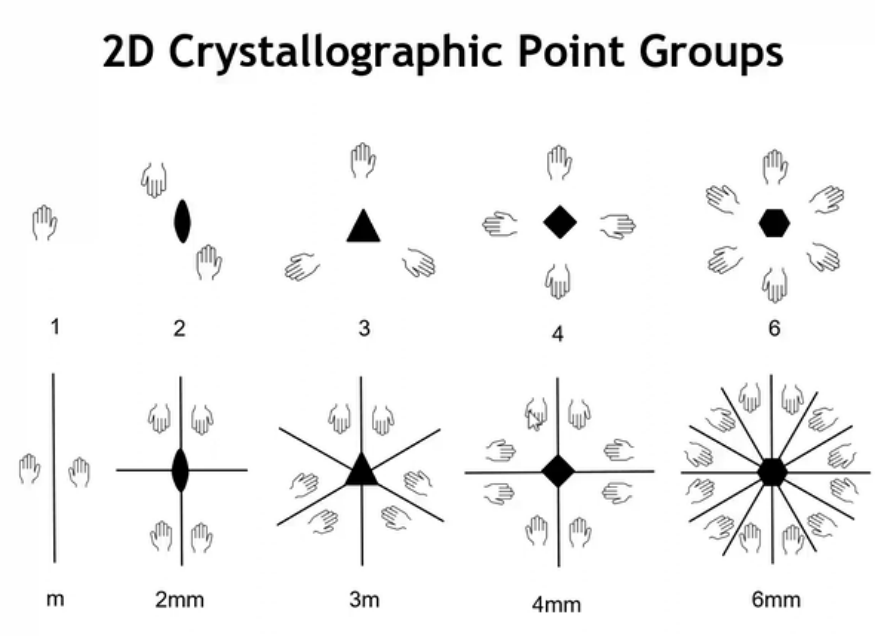
Centered Rectangular

10 grupos pontuais





X

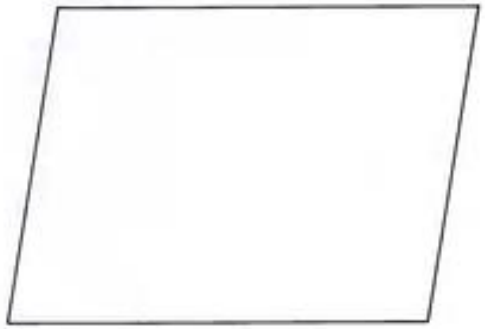


5 x 10=17 Space groups

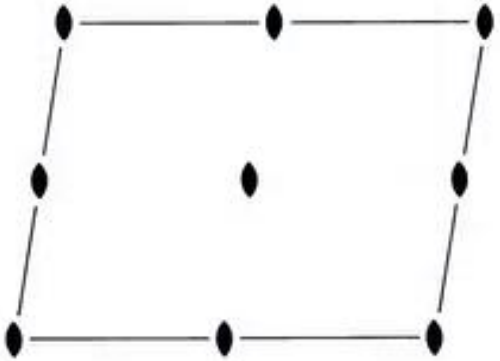
Bravais Lattice Symmetry

Bravais Lattice	Centering Types	Required symmetry	Point groups
Oblique	Primitive	none	1, 2
Rectangular	Primitive, Centered	mirror and/or glide plane	m, 2mm
Square	Primitive	4-fold rotation axis	4, 4mm
Hexagonal	Primitive	3-fold and/or 6-fold rotation axis	6, 3, 3m, 6mm

Oblique Plane Groups

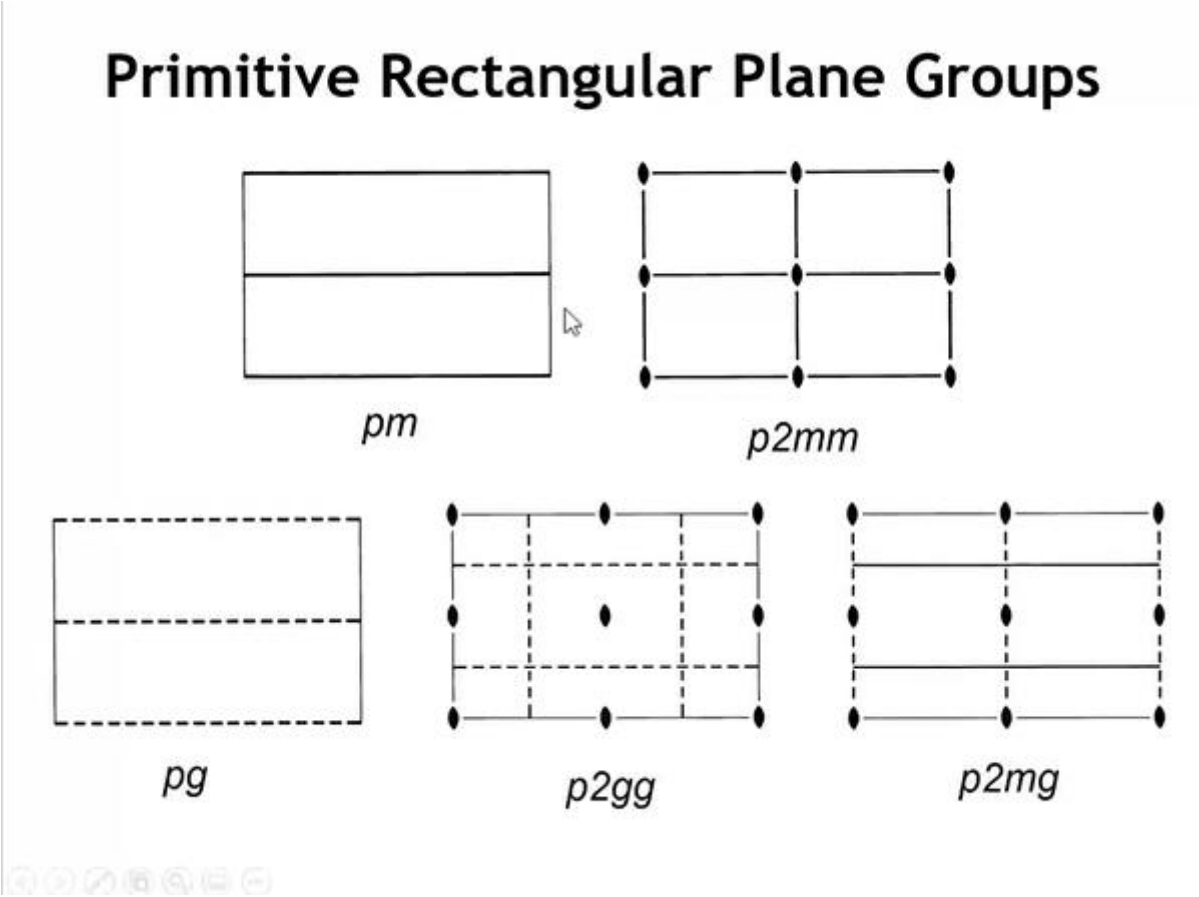


p1



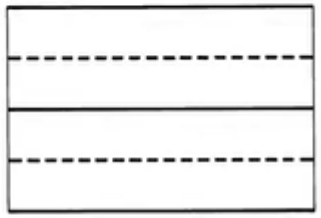
p2

V escola de verão

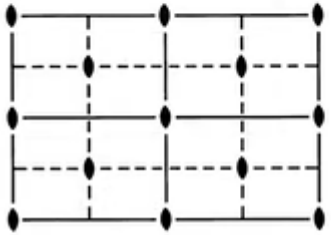


V escola de verão

Centered Rectangular Plane Groups

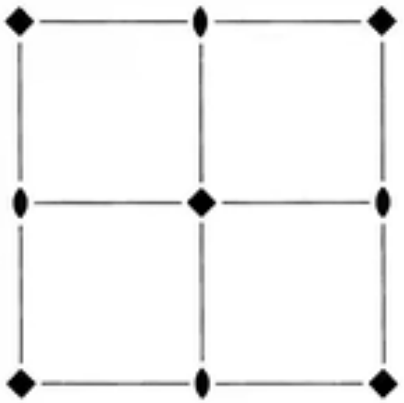


cm

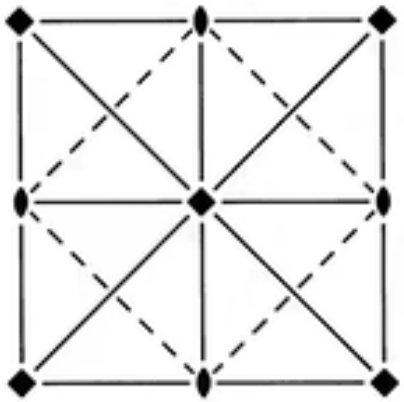


c2mm

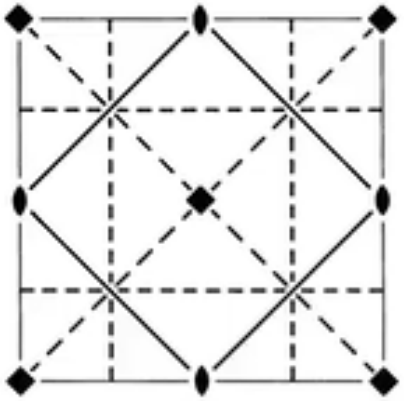
Square Plane Groups



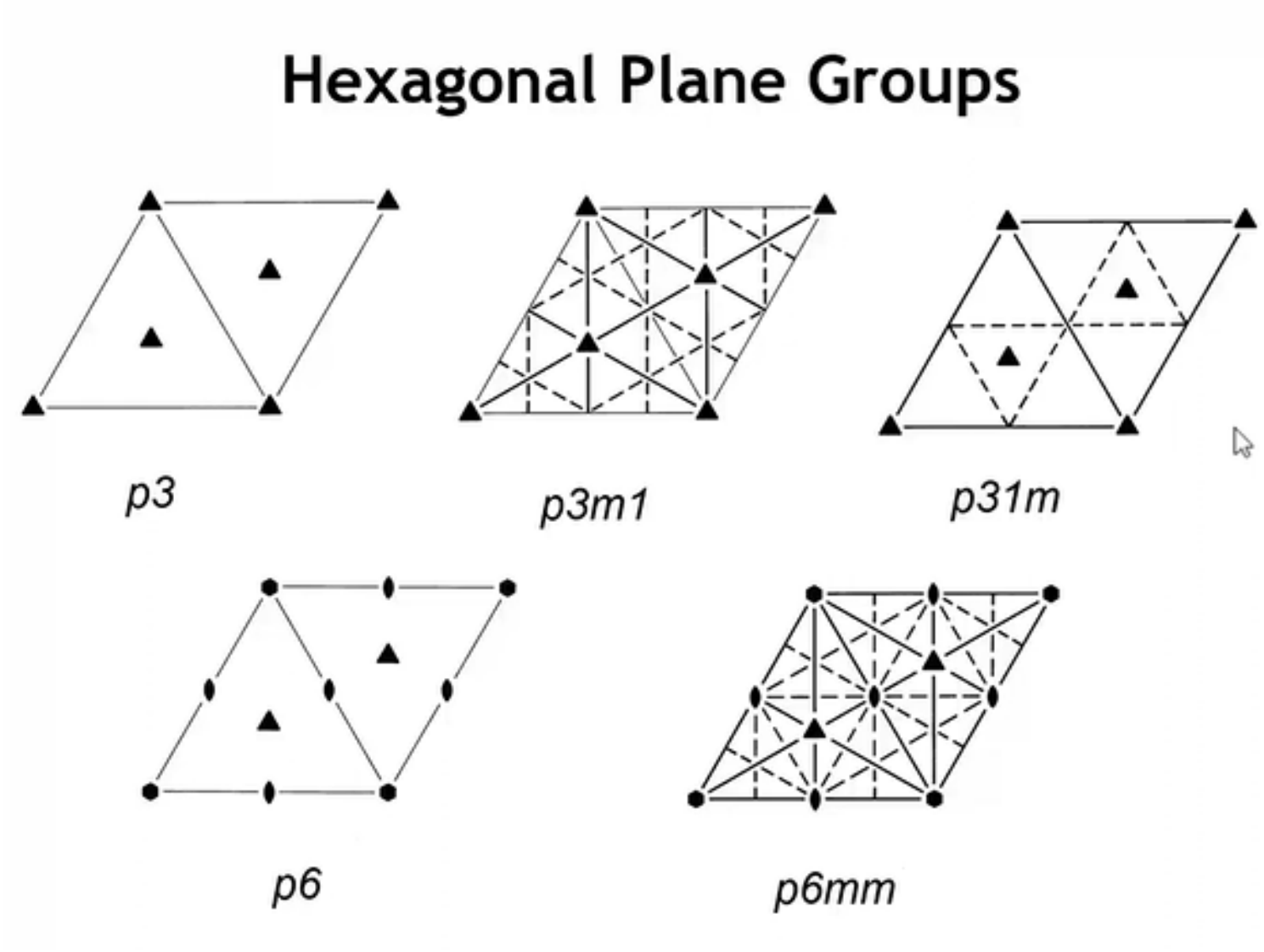
p4



p4mm

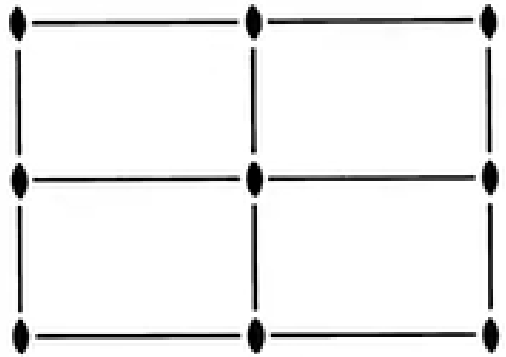


p4gm

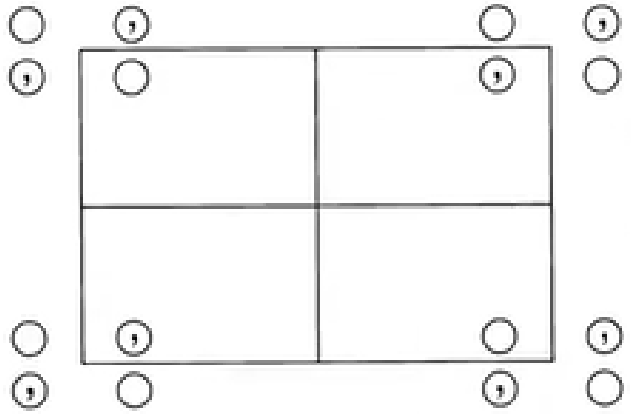

Hexagonal Plane Groups
p3
p3m1
p31m
p6
p6mm

Wyckoff Sites

P2mm



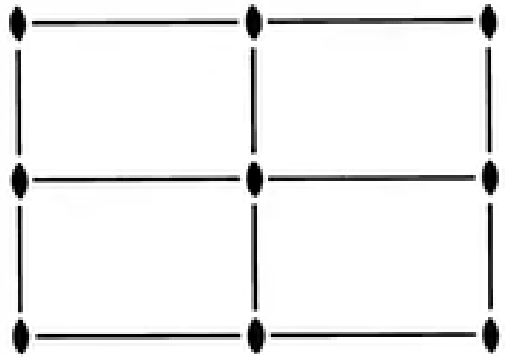
Posições equivalentes



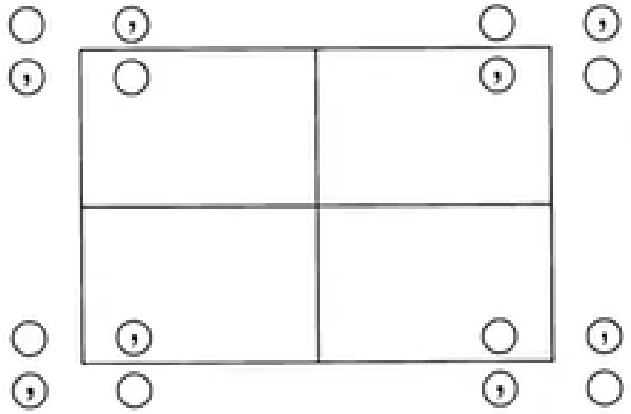
Multiliplicity	Wyckoff site	Site symmetry	Coordinates
4	i	1	(x,y), (−x,y), (x,−y), (−x,−y)
2	h	m	(½,y), (½,−y)
2	g	m	(0,y), (0,−y)
2	f	m	(x,½), (−x,½)
2	e	m	(x,0), (−x,0)
1	d	2mm	(½,½)
1	c	2mm	(½,0)
1	b	2mm	(0,½)
1	a	2mm	(0,0)

Wyckoff Sites

P2mm



Posições equivalentes

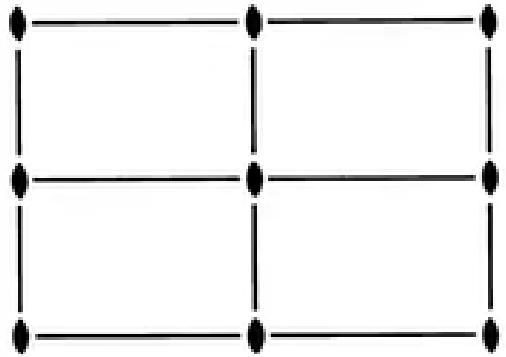


General Position

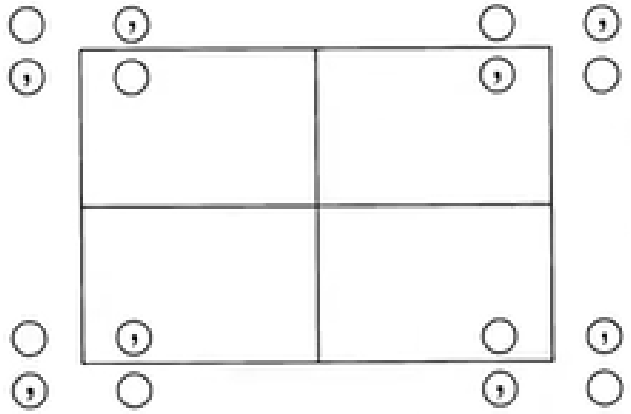
Multiliplicity	Wyckoff site	Site symmetry	Coordinates
4	i	1	(x,y), (−x,y), (x,−y), (−x,−y)
2	h	m	(½,y), (½,−y)
2	g	m	(0,y), (0,−y)
2	f	m	(x,½), (−x,½)
2	e	m	(x,0), (−x,0)
1	d	2mm	(½,½)
1	c	2mm	(½,0)
1	b	2mm	(0,½)
1	a	2mm	(0,0)

Wyckoff Sites

P2mm



Posições equivalentes



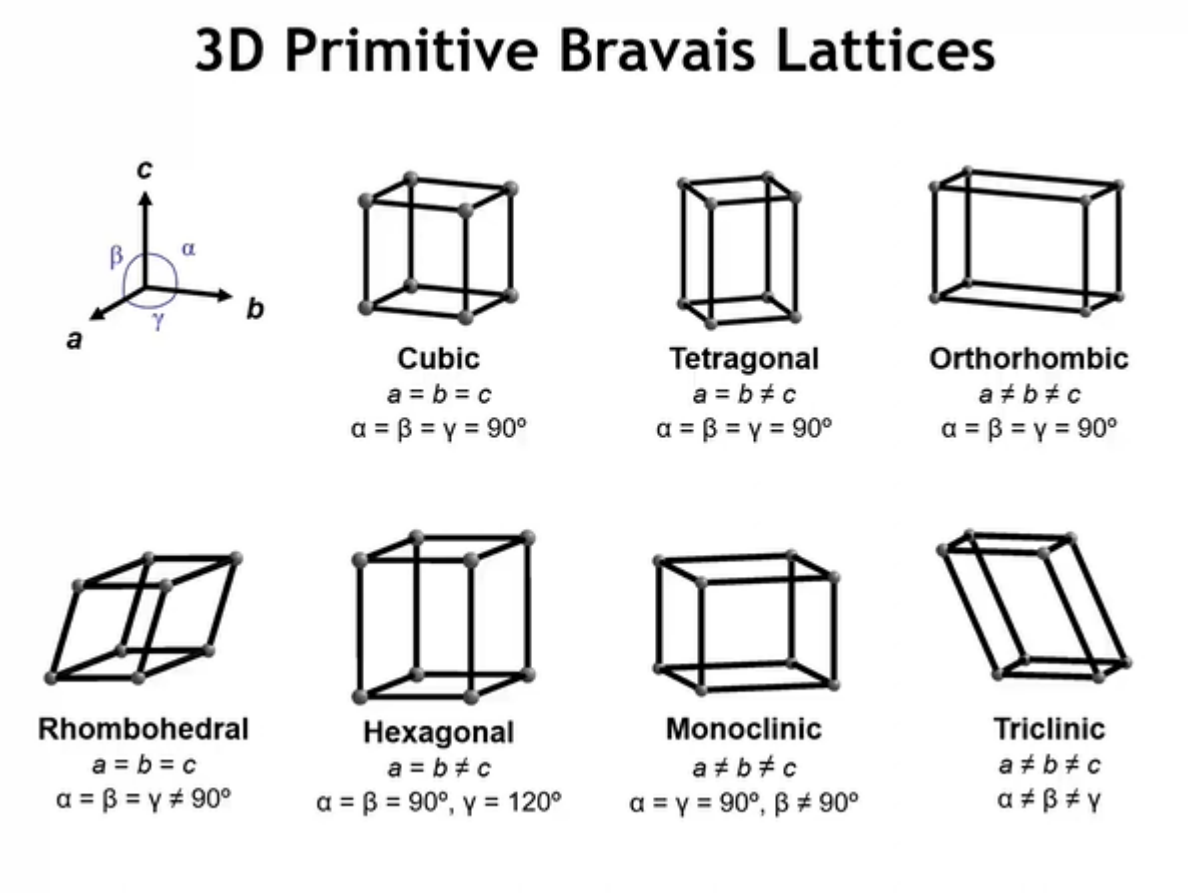
Multiliplicity	Wyckoff site	Site symmetry	Coordinates
4	i	1	(x,y), (−x,y), (x,−y), (−x,−y)
2	h	m	(½,y), (½,−y)
2	g	m	(0,y), (0,−y)
2	f	m	(x,½), (−x,½)
2	e	m	(x,0), (−x,0)
1	d	2mm	(½,½)
1	c	2mm	(½,0)
1	b	2mm	(0,½)
1	a	2mm	(0,0)

Posições Especiais

V escola de verão

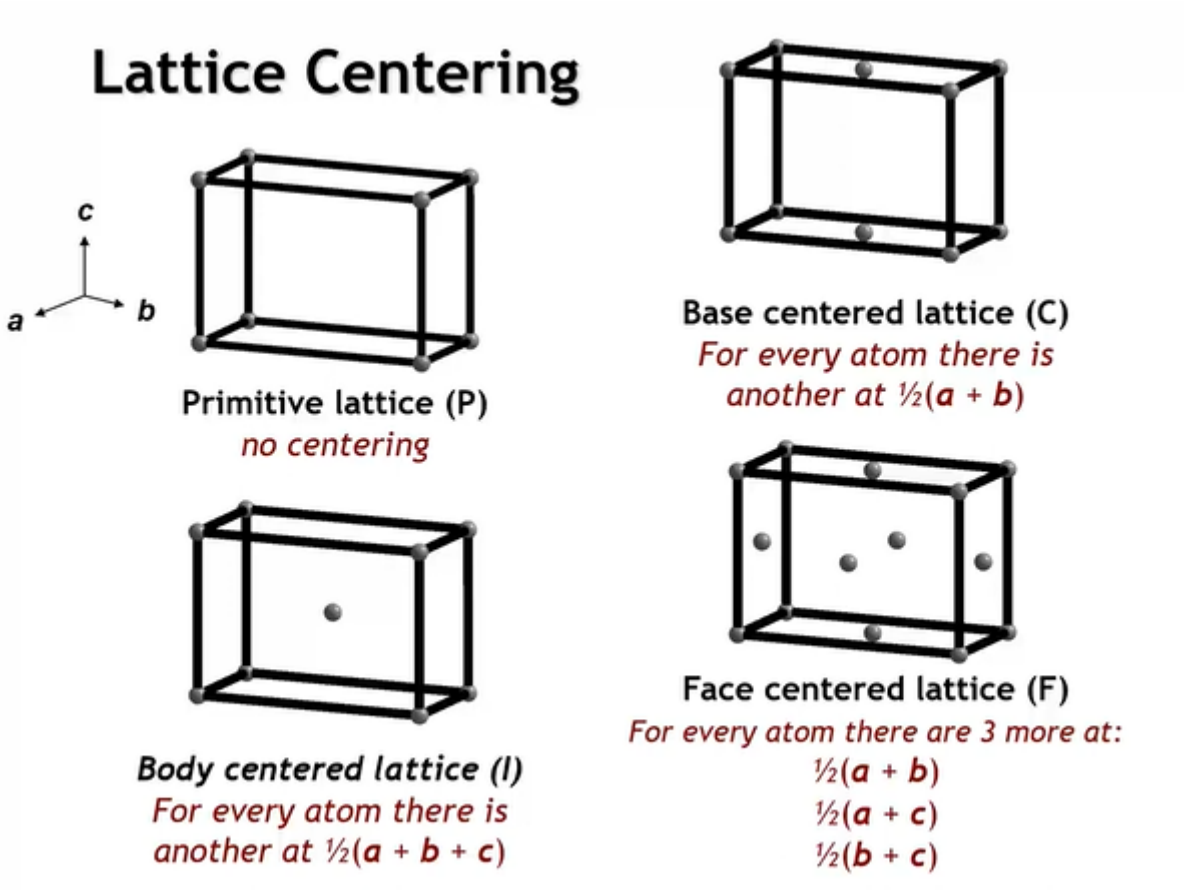
Grupo de Simetria Espacial 3D

Simetrias de Translação em três dimensões

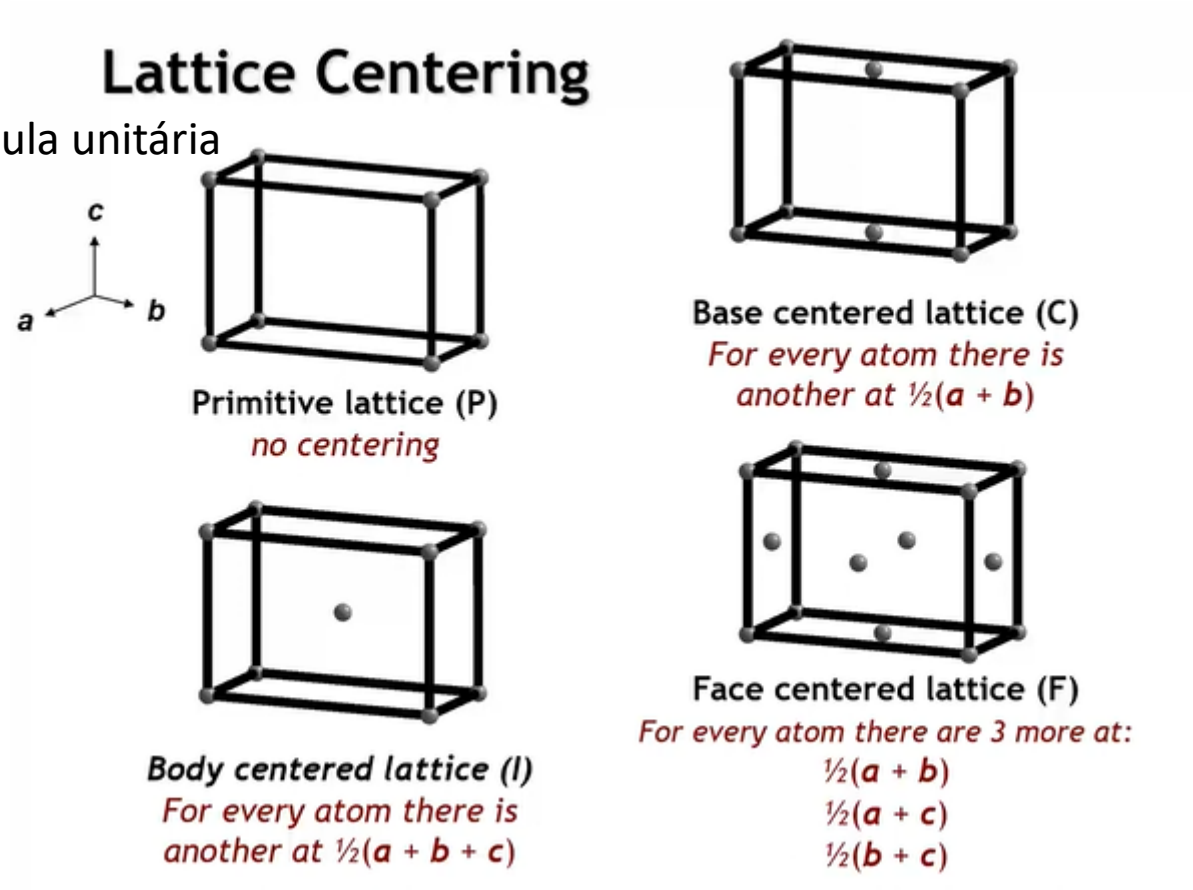


7 redes de Bravais Primitivas

V escola de verão

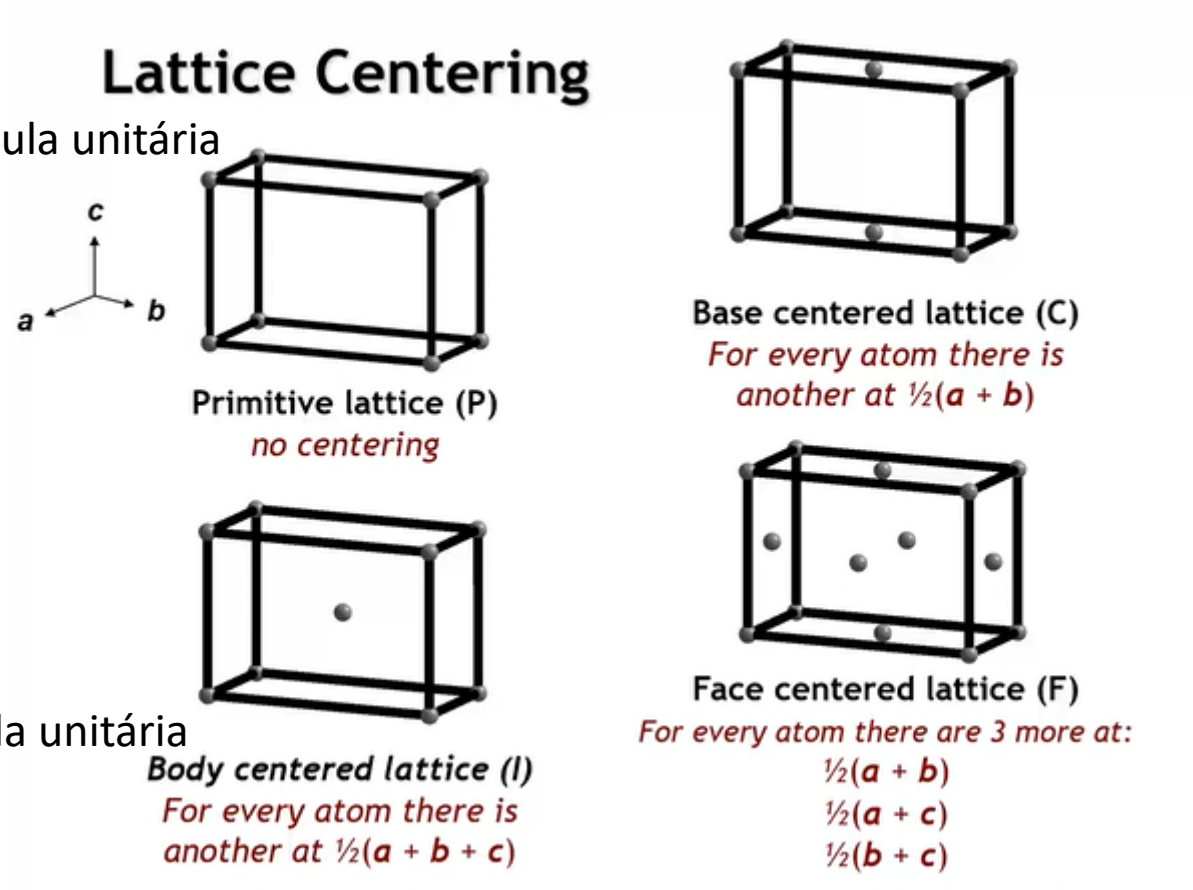


1 átomo por célula unitária



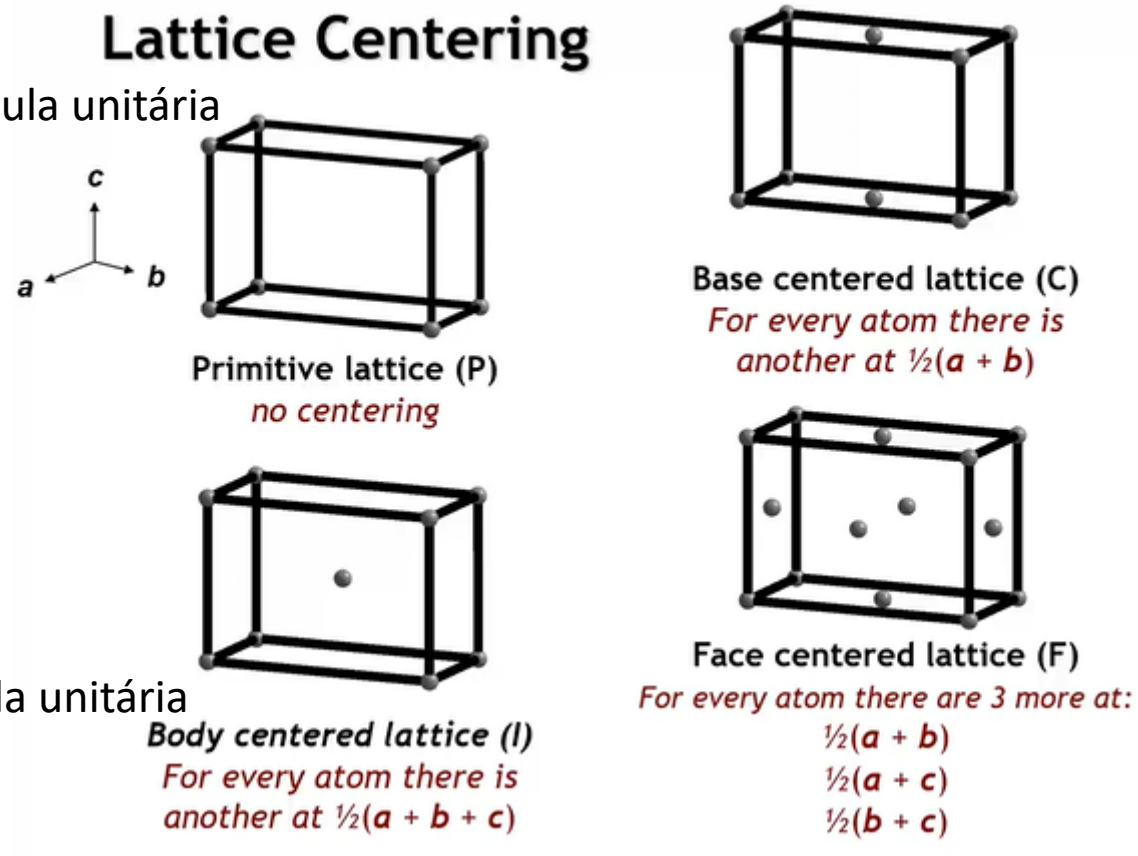
1 átomo por célula unitária

2 átomo por célula unitária

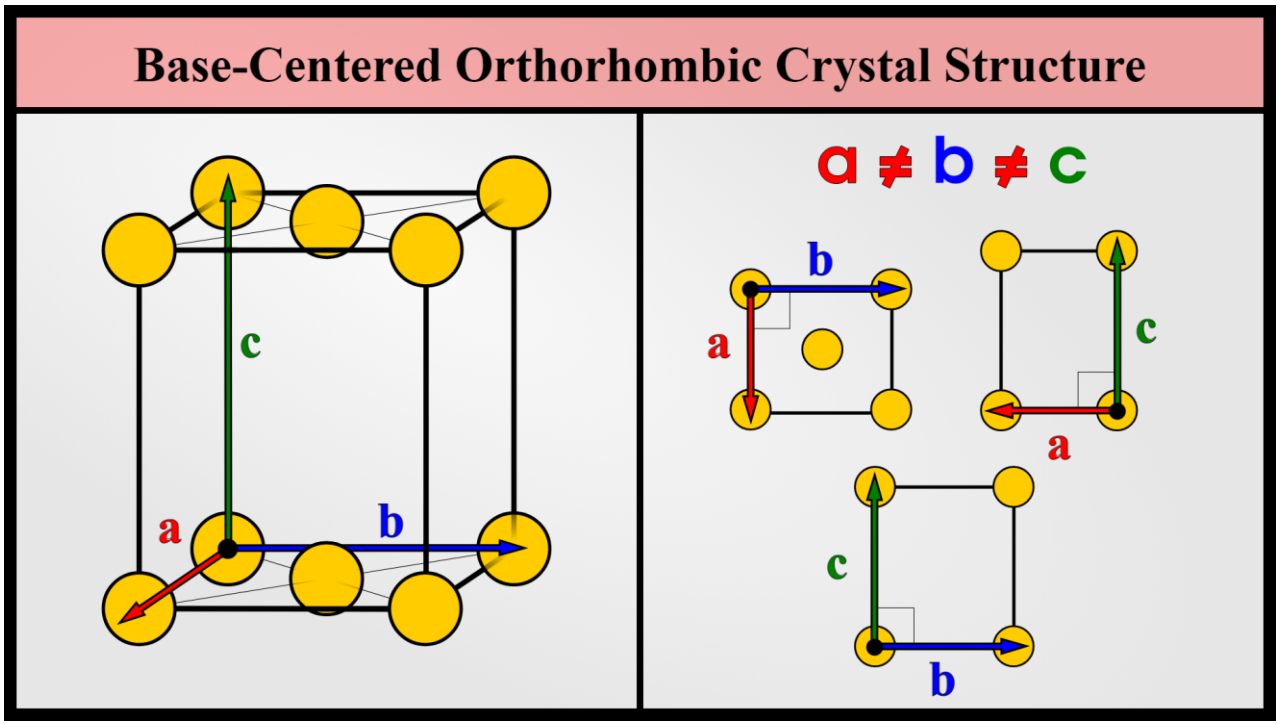


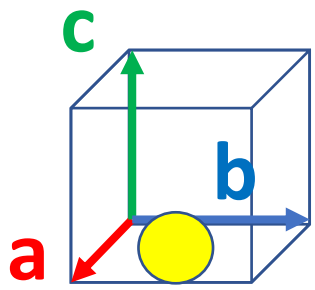
2 átomo por célula unitária

1 átomo por célula unitária

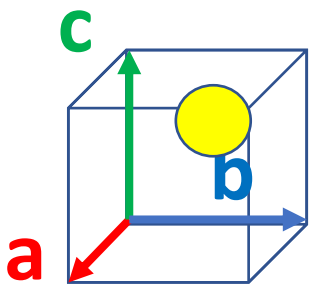


2 átomo por célula unitária

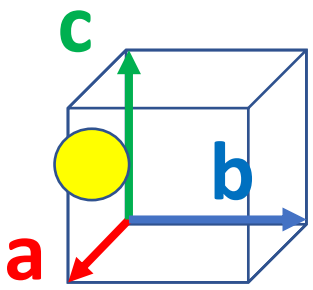




Base c centered lattice

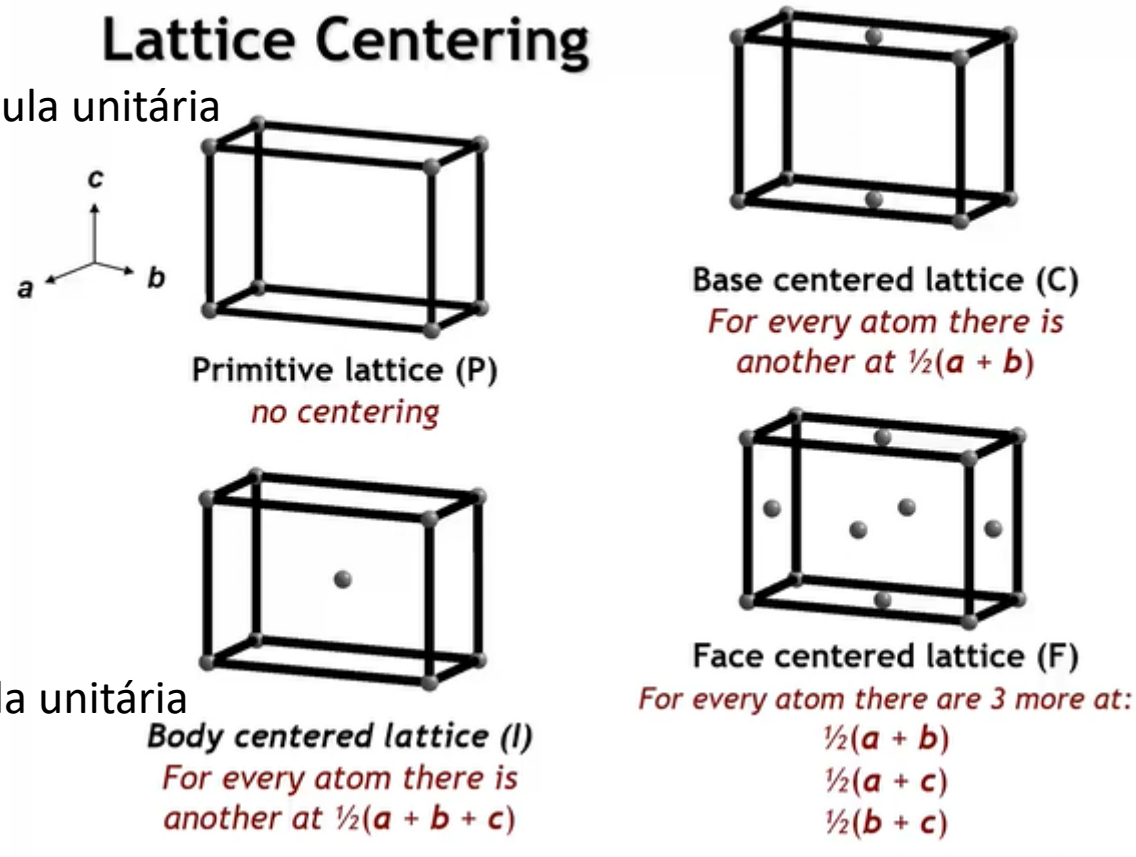


Base a centered lattice



Base b centered lattice

2 átomo por célula unitária



1 átomo por célula unitária

2 átomo por célula unitária

3 átomo por célula unitária

Fourteen 3D Bravais Lattices

Crystal System	P	C	I	F	Examples
Triclinic ($a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$)	X				Primitive triclinic
Monoclinic ($a \neq b \neq c$; $\alpha = \gamma = 90^\circ \beta \neq 90$)	X	X			Base-centered monoclinic
Orthorhombic ($a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$)	X	X	X	X	Face-centered orthorhombic
Rhombohedral ($a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$)	X				Primitive rhombohedral
Hexagonal ($a = b \neq c$; $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$)	X				Primitive hexagonal
Tetragonal ($a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$)	X		X		Body-centered tetragonal
Cubic ($a = b = c$; $\alpha = \beta = \gamma = 90^\circ$)	X		X	X	Face-centered cubic

The 14 3D Bravais Lattices

P = Primitive lattice

I = Body centered lattice

½ (**a** + **b** + **c**)

F = Face centered lattice

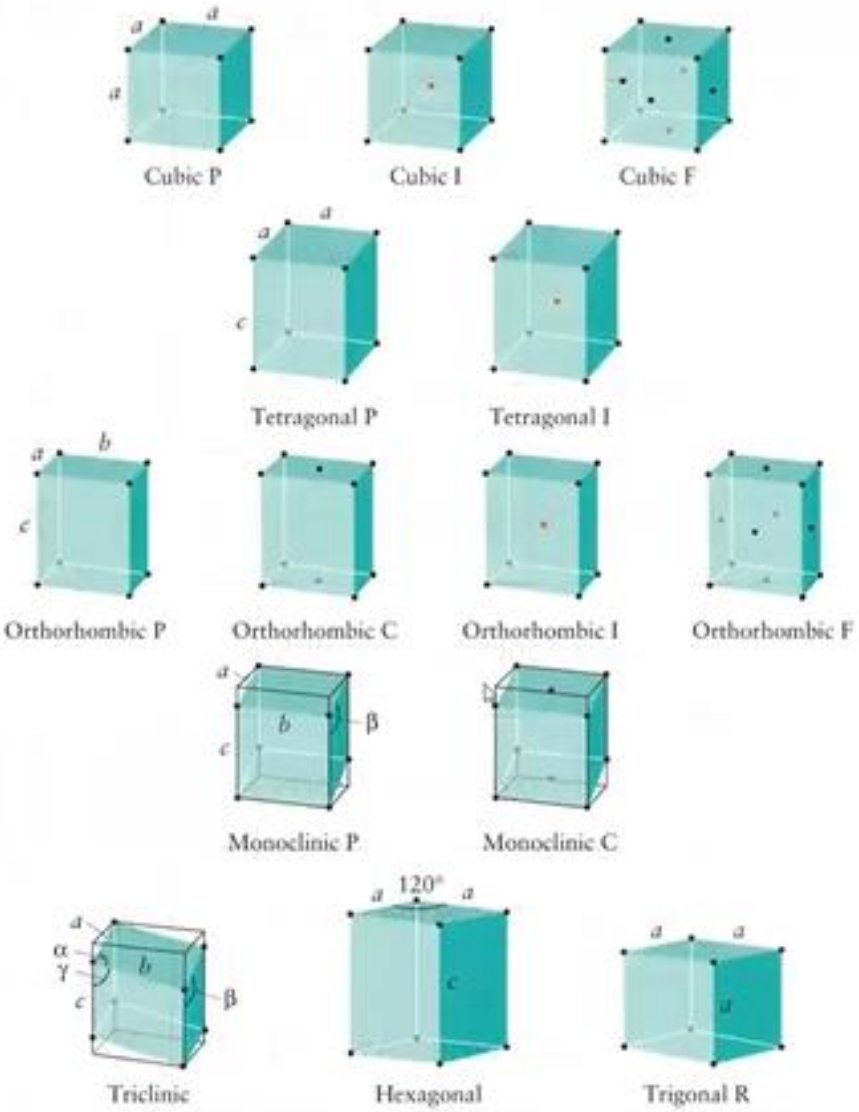
½ (**a** + **b**)

½ (**a** + **c**)

½ (**b** + **c**)

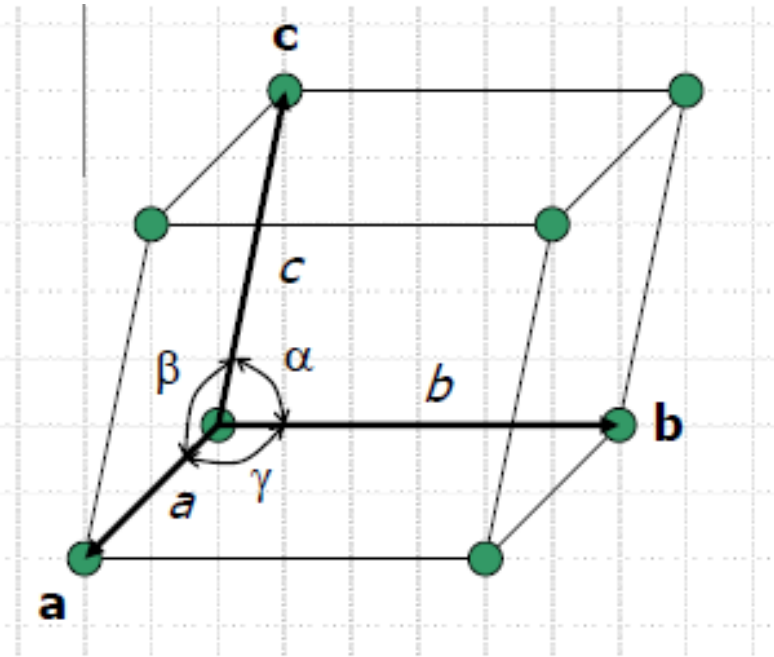
C = Base centered lattice

½ (**a** + **b**)



Estrutura de cristal

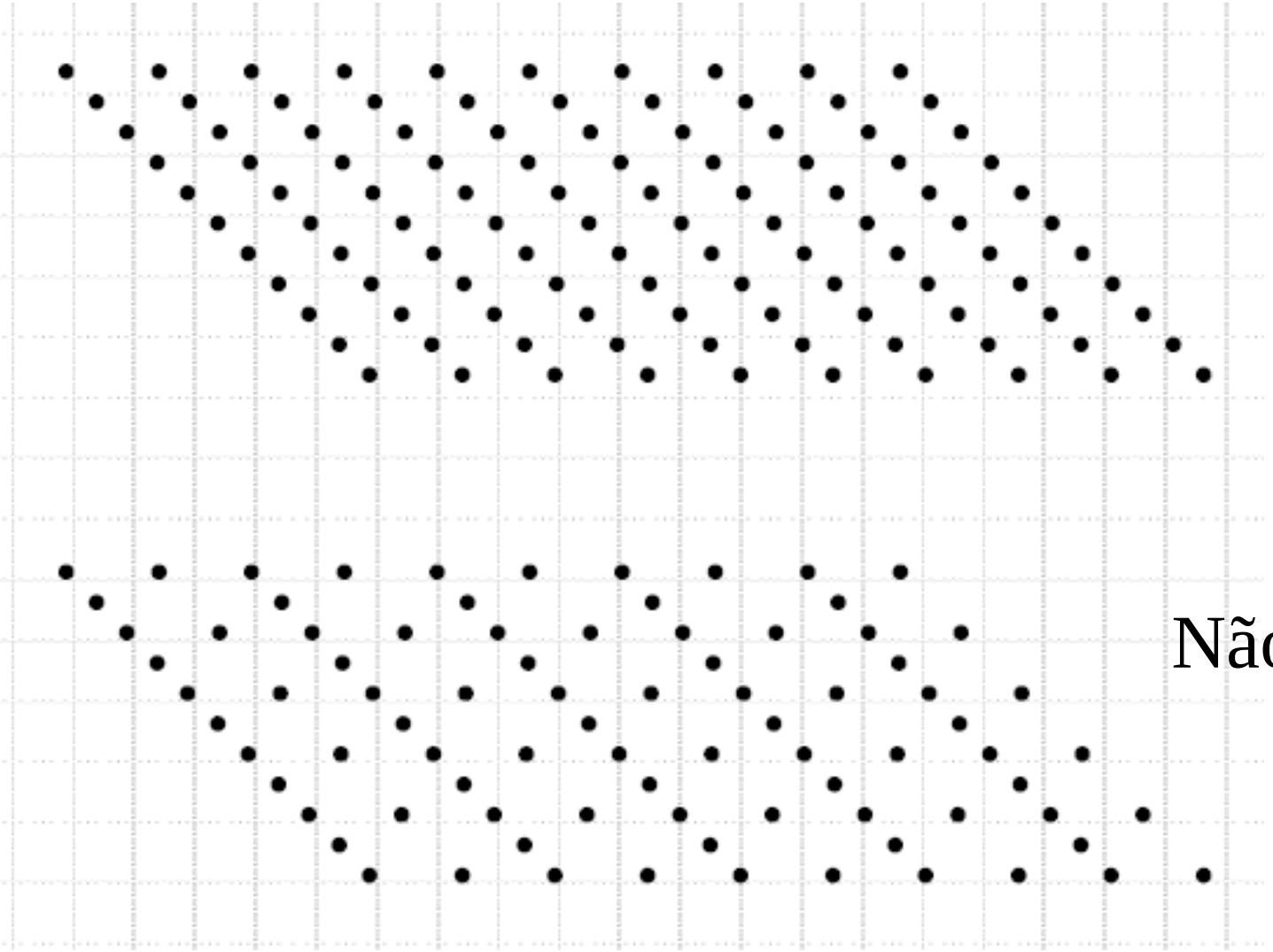
Vetores de rede, parâmetros de rede e ângulos inter-axiais



Lattice vector	**a**	**b**	**c**
Lattice parameter	*a*	*b*	*c*
Interaxial angle	α	β	γ

rede é uma matriz de pontos no espaço em que o ambiente de cada ponto é idêntico

Estrutura de cristal



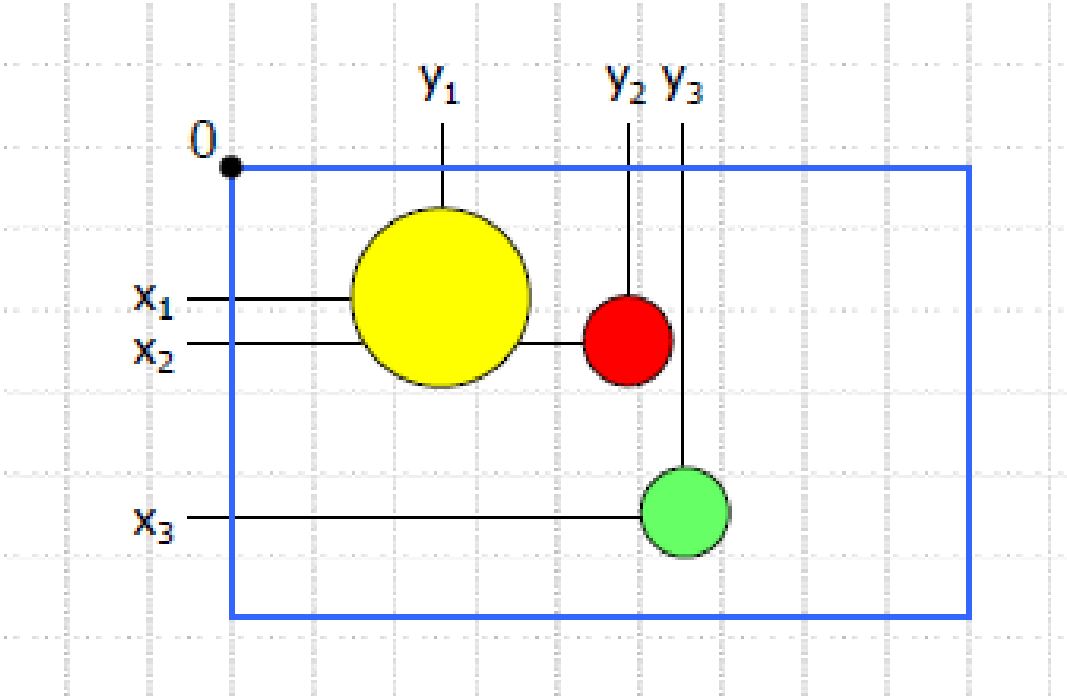
Rede

Não é Rede

Estrutura de cristal

Conteúdo da célula unitária

- Coordenadas de todos os átomos
- tipos de átomos
- Ocupação do local
- Parâmetros de deslocamento individuais



Operações de Simetria

Point Symmetry Elements

Point Symmetry Element	Symmetry Operation
1. Identity (1)	Nothing changes
2. Inversion center ($\bar{1}$)	Inversion through a point
3. Mirror plane (*m*)	Reflect through the plane
4. Proper rotation axis (N)	Rotate by 360/N degrees about the axis
5. Rotoinversion axis ($\bar{N}$)	Rotate by 360/N degrees about the axis, followed by inversion operation

5 classes de simetria

Operações de Simetria

Point Symmetry Elements

Point Symmetry Element	Symmetry Operation
1. Identity (1)	Nothing changes
2. Inversion center ($\bar{1}$)	Inversion through a point
3. Mirror plane (*m*)	Reflect through the plane
4. Proper rotation axis (N)	Rotate by 360/N degrees about the axis
5. Rotoinversion axis ($\bar{N}$)	Rotate by 360/N degrees about the axis, followed by inversion operation

5 classes de simetria

Sempre presente!!

Operações de Simetria

Point Symmetry Elements

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5 classes de simetria

Hermann-Mauguin

Schoenflies – Rotaciona 360/N e reflete num espelho m

Operações de Simetria

Point Symmetry Elements

Point Symmetry Element	Symmetry Operation
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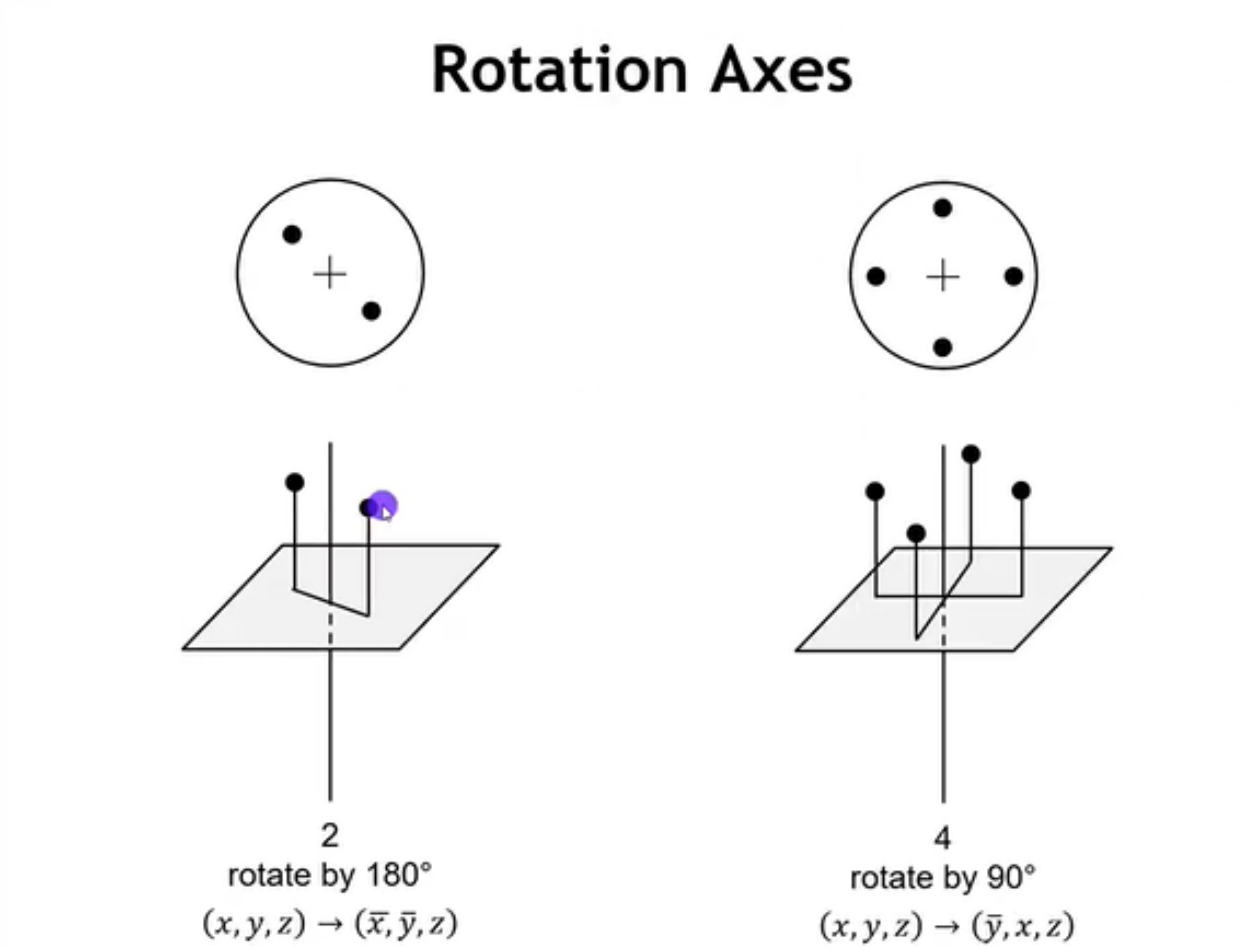
5 classes de simetria

1 fold proper rotation axis (360/1)

1 fold proper rotation axis (360/1)+ inversão

$\bar{2}$ rotoinversion axis

V escola de verão



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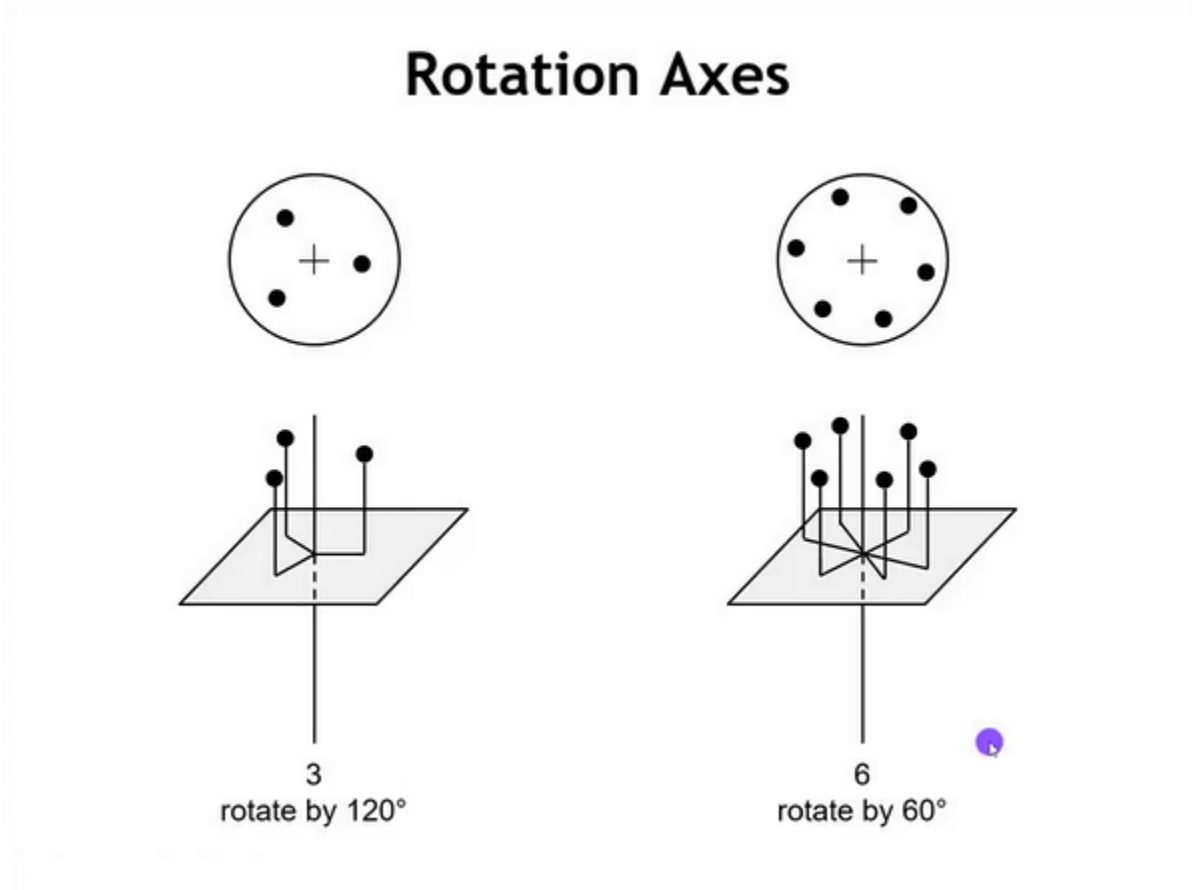

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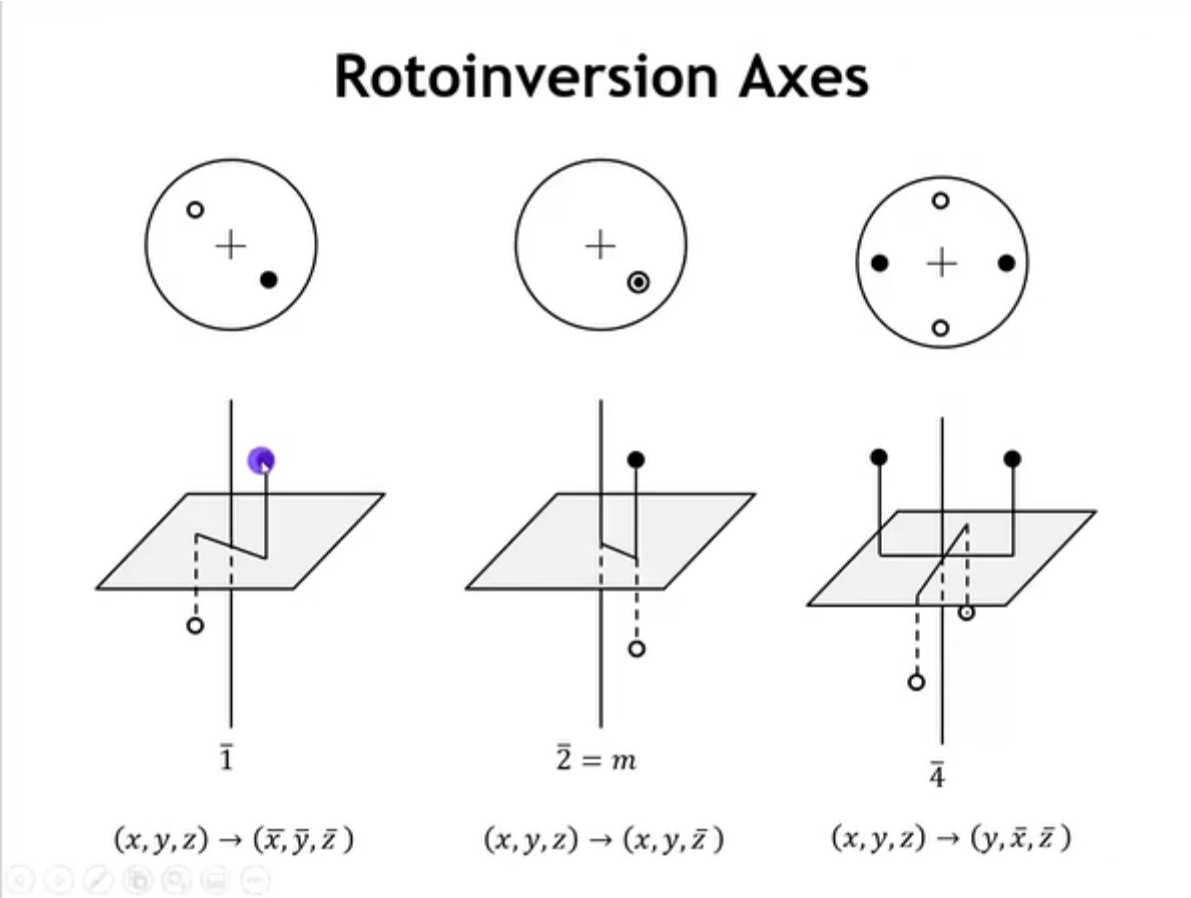

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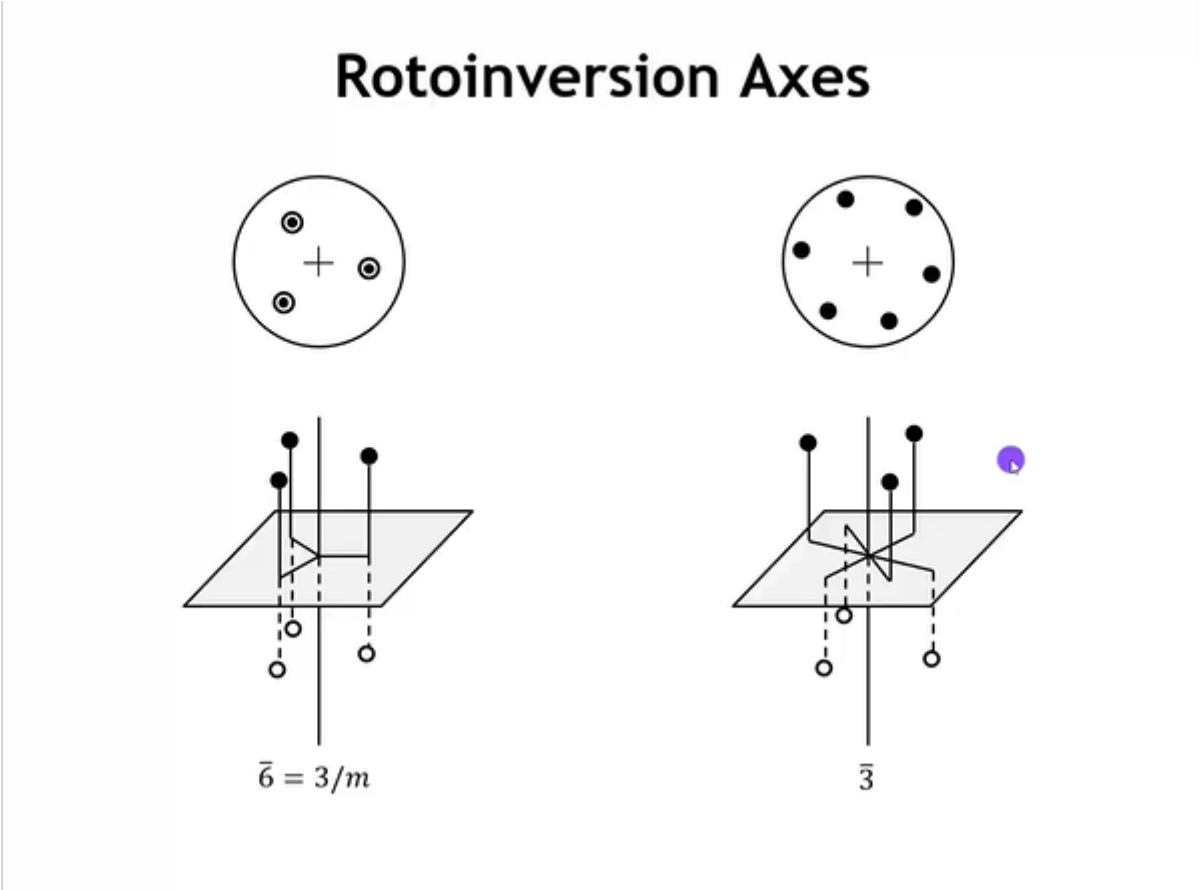
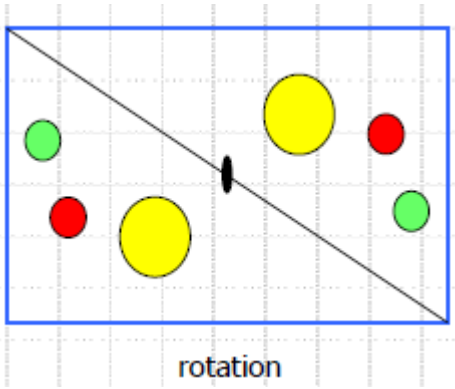
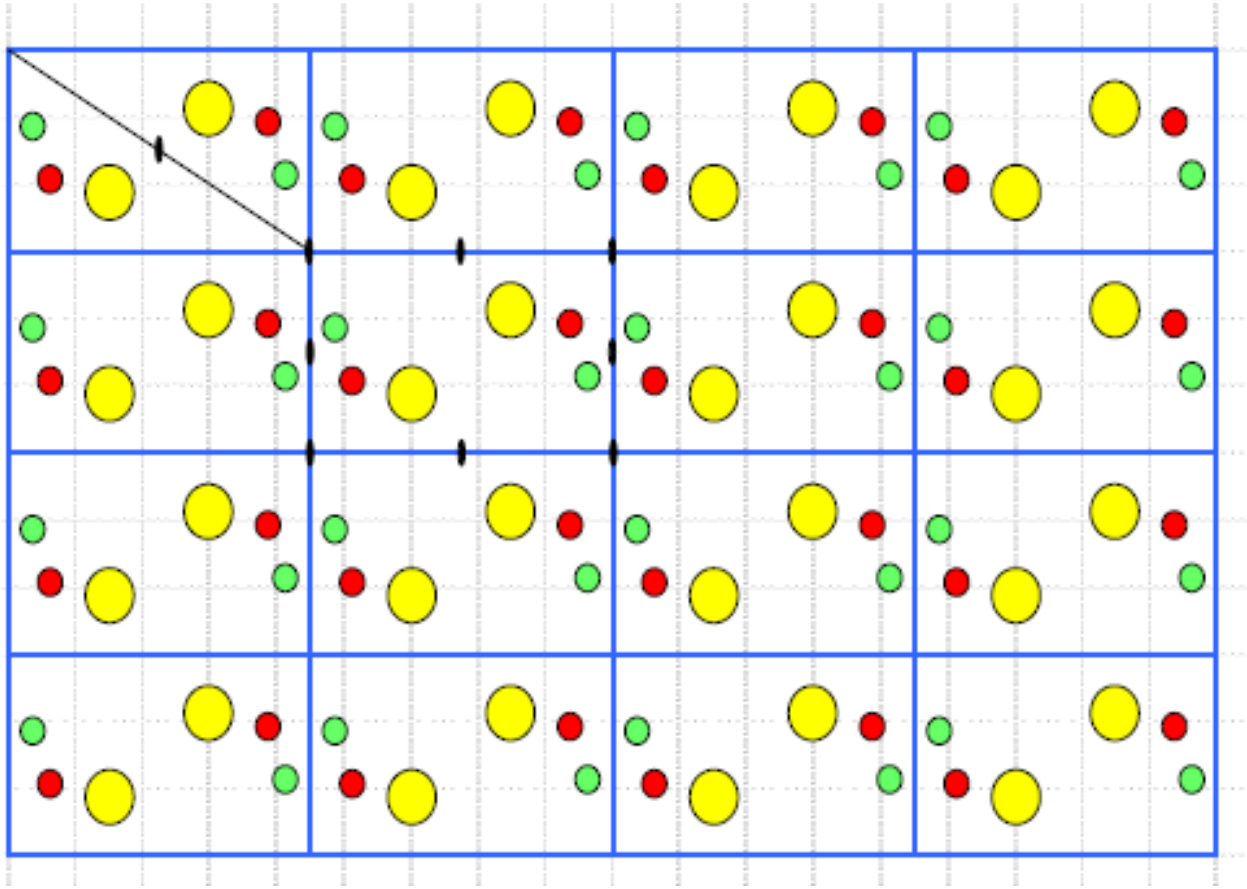


Estrutura de cristal

Normalmente, a célula unitária tem mais de uma molécula ou grupo de átomos
Eles podem ser representados por operadores de simetria





Travel symmetry operation

Travel Symmetry Operations

All point symmetry operations leave at least one point in the same place [there is at least one point for which $p = f(p)$]

Travel symmetry operations have a translational component and therefore do not map any point back onto itself [there is no point p for which $p = f(p)$].

Symmetry Element	Symmetry Operation
1. Glide plane (*a*, *b*, *c*, *e*, *n*, *d*)	Reflect through a plane, then translate parallel to the plane
2. Screw axis (N_M)	Rotate by 360/N degrees about the axis, followed by a translation by M/N of the unit cell parallel to the axis

Híbrido = simetria de ponto + simetria de translação

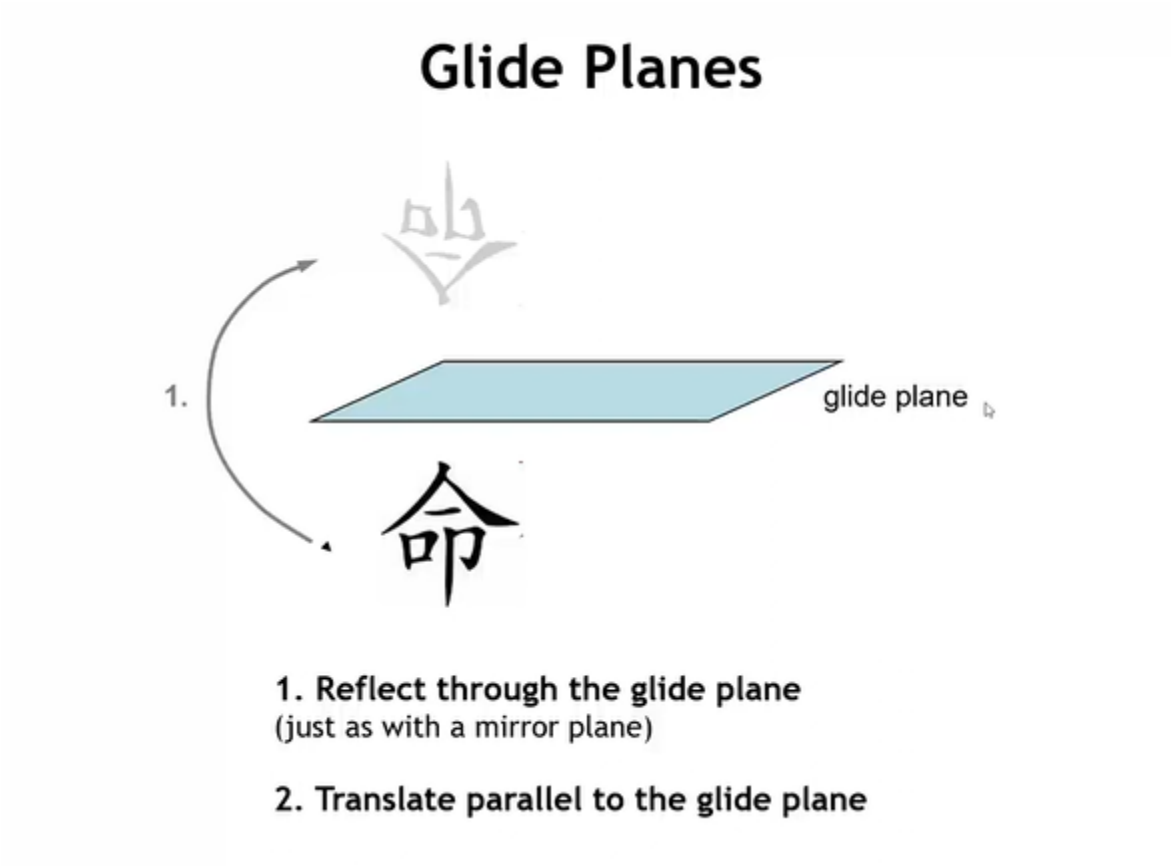
Glide Planes



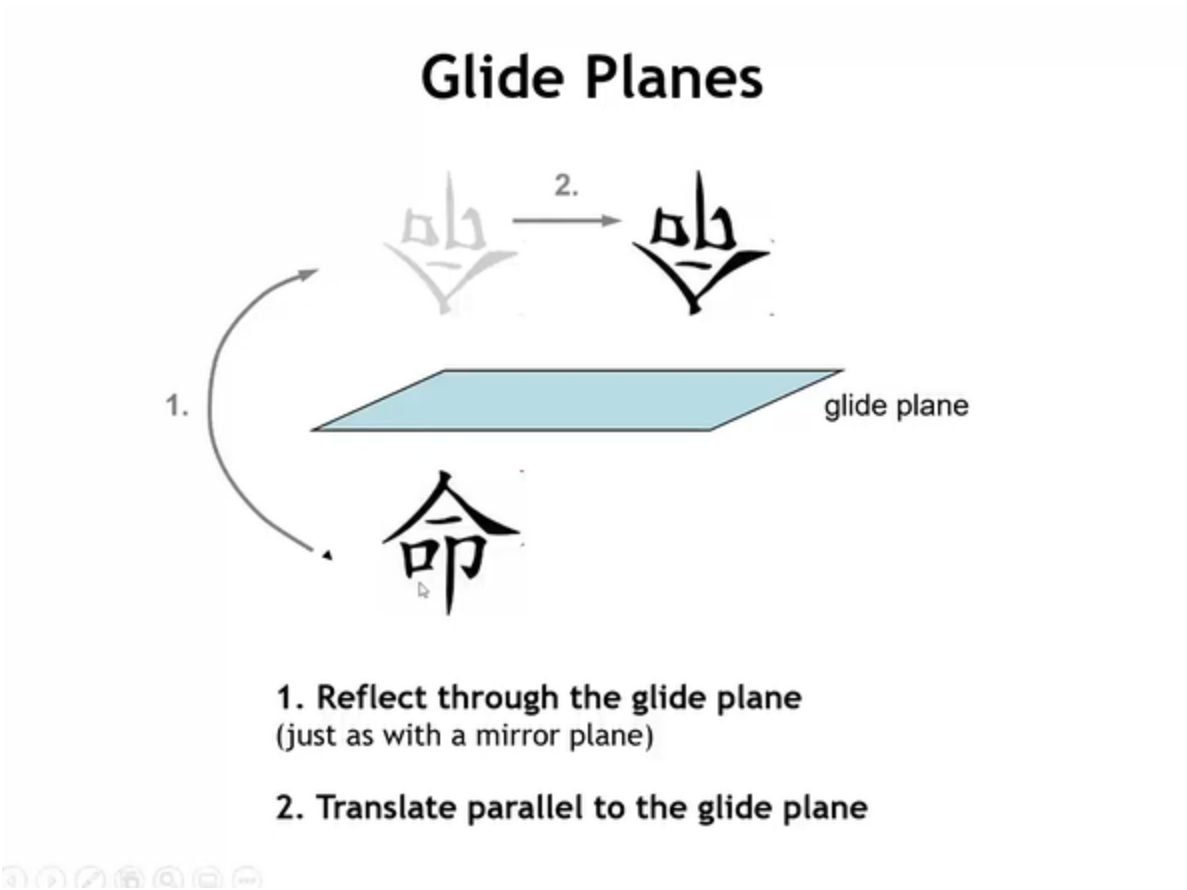


1. Reflect through the glide plane
(just as with a mirror plane)

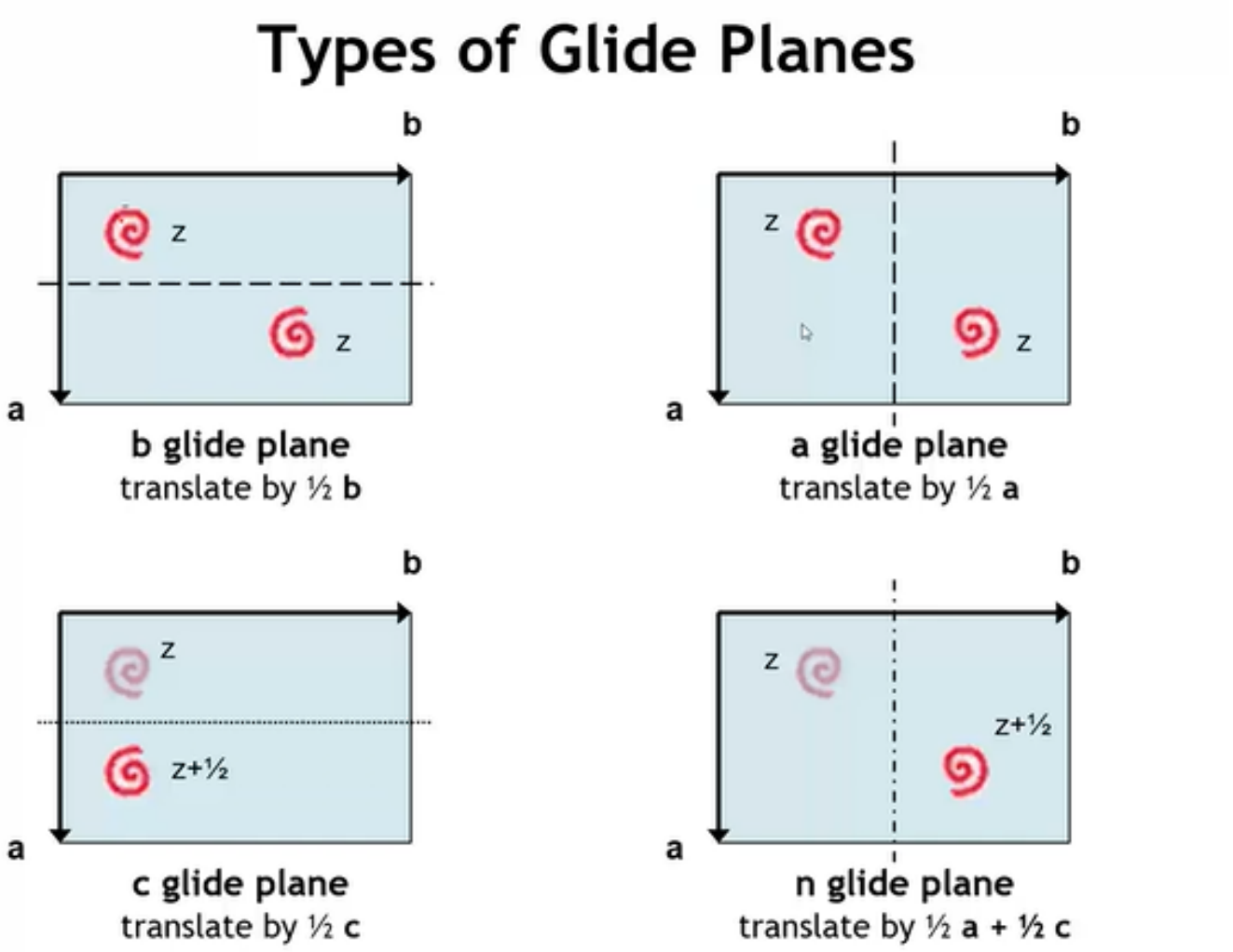
2. Translate parallel to the glide plane

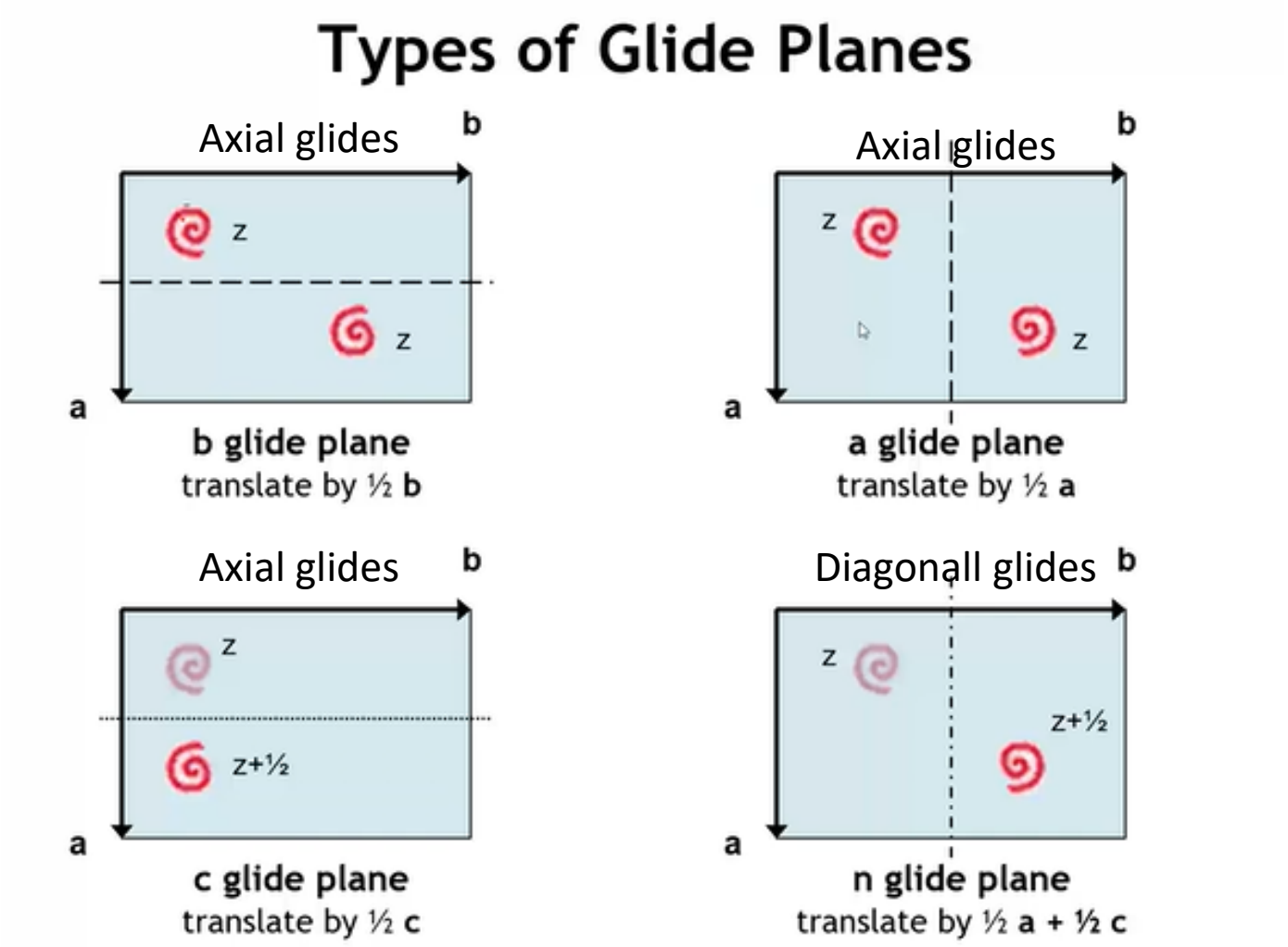

Glide Planes
1.
glide plane
1. Reflect through the glide plane
(just as with a mirror plane)
2. Translate parallel to the glide plane

V escola de verão



Axial glides



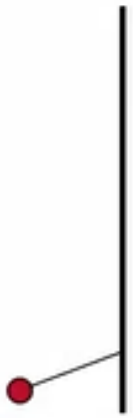

Types of Glide Planes
Axial glides
b
z
z
a
b glide plane
translate by ½ b
Axial glides
b
z
z
a
a glide plane
translate by ½ a
Axial glides
b
z
z+½
a
c glide plane
translate by ½ c
Diagonall glides
b
z
z+½
a
n glide plane
translate by ½ a + ½ c

Types of Glide Planes

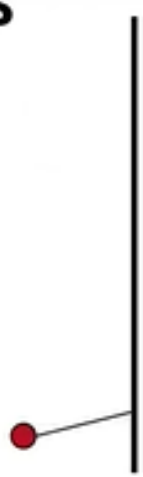
Herman-Mauguin Symbol	Plane ⊥ to which axis	Translation vector
Axial Glides		
a	b or c	½ **a**
b	a or c	½ **b**
c	a or b	½ **c**
Diagonal glides, *n*	a	½ **b** + ½ **c**
	b	½ **a** + ½ **c**
	c	½ **a** + ½ **b**
Diamond glides, *d*	a	¼ **b** + ¼ **c**
	b	¼ **a** + ¼ **c**
	c	¼ **a** + ¼ **b**

Face centered

N_M Screw Axes



2_1 screw axis
Rotate by 180°
Translate by ½ **c**

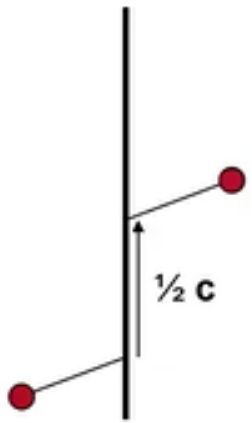


4_1 screw axis
Rotate by 90°
Translate by ¼ **c**

1. **Rotate by 360/N** (just as with a N-fold proper rotation axis)

2. **Translate by M/N of a unit cell vector parallel to the screw axis**

N_M Screw Axes



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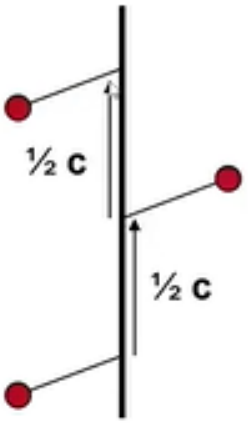
N_M Screw Axes



2_1 screw axis
Rotate by 180°
Translate by ½ **c**



4_1 screw axis
Rotate by 90°
Translate by ¼ **c**

1. Rotate by 360/N (just as with a N-fold proper rotation axis)

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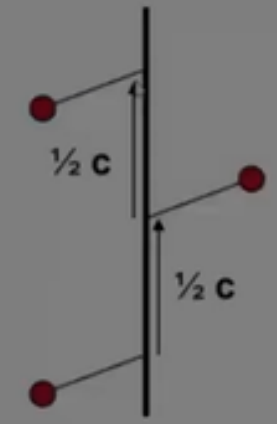
N_M Screw Axes



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Translate by ½ **c**



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Rotate by 90°
Translate by ¼ **c**

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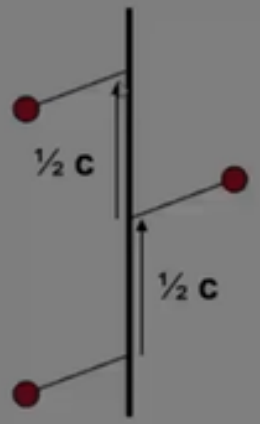
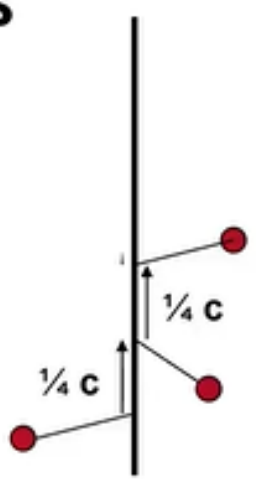
N_M Screw Axes



2_1 screw axis
Rotate by 180°
Translate by ½ **c**

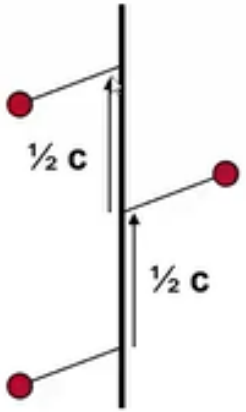


4_1 screw axis
Rotate by 90°
Translate by ¼ **c**

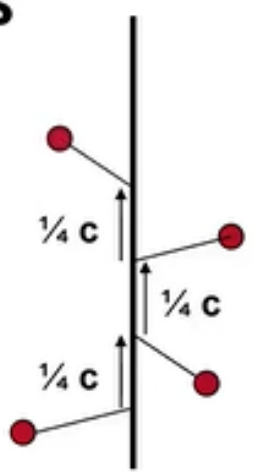
1. Rotate by 360/N (just as with a N-fold proper rotation axis)

2. Translate by M/N of a unit cell vector parallel to the screw axis

N_M Screw Axes



2_1 screw axis
Rotate by 180°
Translate by ½ **c**

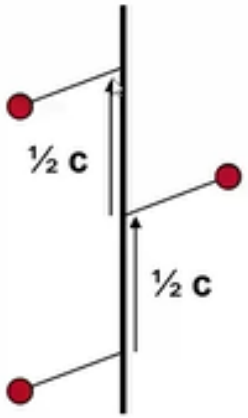


4_1 screw axis
Rotate by 90°
Translate by ¼ **c**

1. Rotate by 360/N (just as with a N-fold proper rotation axis)

2. Translate by M/N of a unit cell vector parallel to the screw axis

N_M Screw Axes



2_1 screw axis
Rotate by 180°
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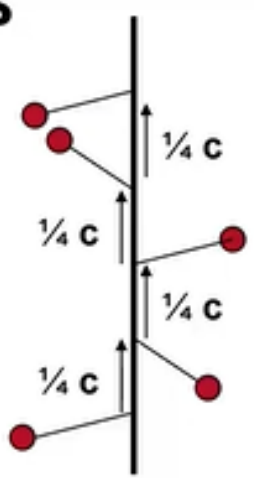
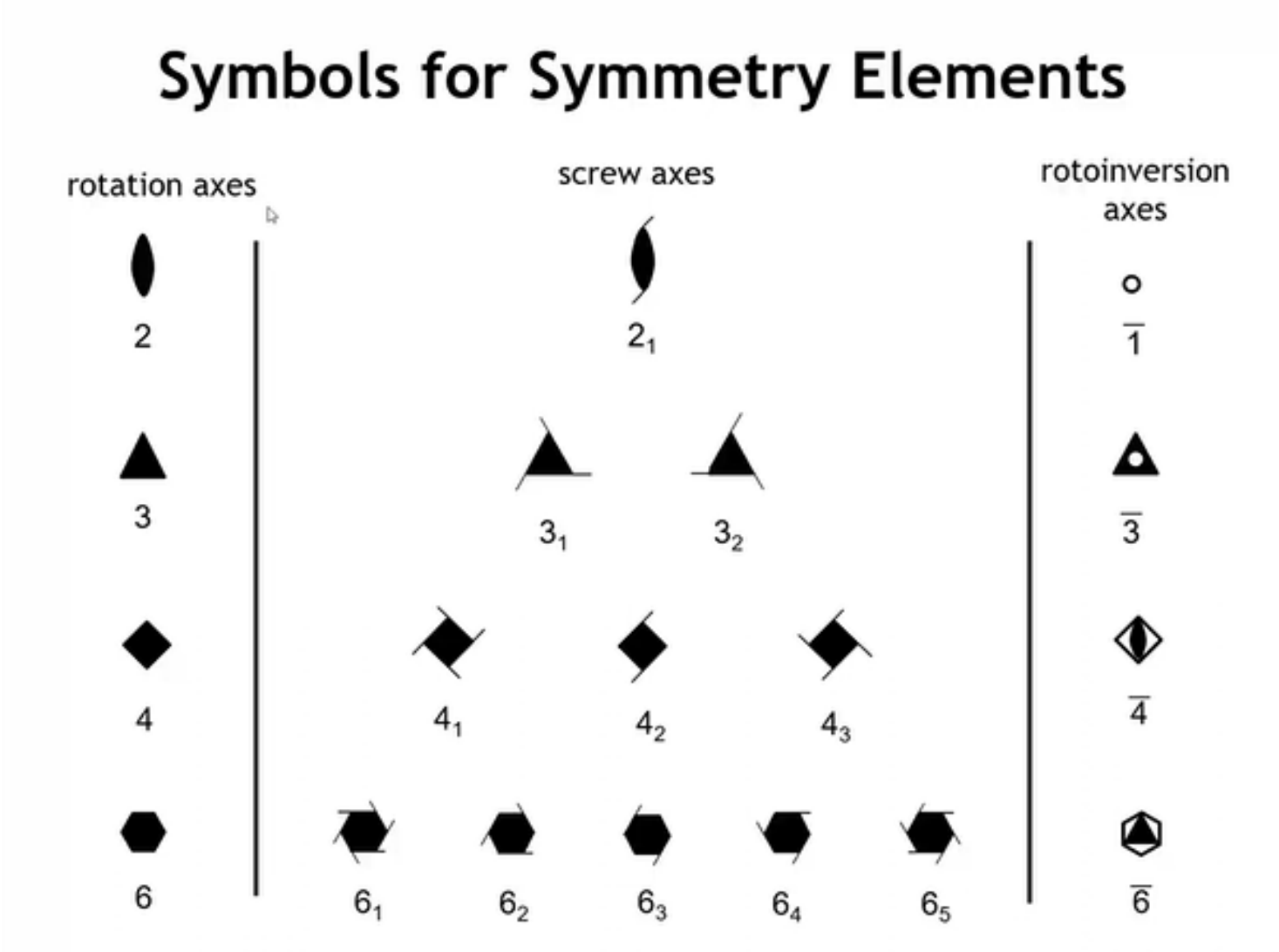


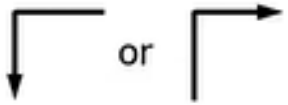
4_1 screw axis
Rotate by 90°
Translate by ¼ **c**

1. **Rotate by 360/N** (just as with a N-fold proper rotation axis)

2. **Translate by M/N of a unit cell vector parallel to the screw axis**


Symbols for Symmetry Elements
rotation axes
screw axes
rotoinversion axes
2
3
4
6
2_1
3_1
3_2
4_1
4_2
4_3
6_1
6_2
6_3
6_4
6_5
$\bar{1}$
$\bar{3}$
$\bar{4}$
$\bar{6}$

Symbols for Symmetry Elements

	View ⊥ to plane	View ∥ to plane
mirror ***m***		
a-, *b*- or *c*-glide ***a***, ***b***, ***c***	 or	Glide in plane Glide ⊥ to plane
n-glide ***n***		
d-glide ***d***		
e-glide ***e***		

Combinação de dois glide planes

Grupos Pontuais

Teoria de grupos

Point Groups

A point group is a set of operations (point symmetry elements) that fulfil the mathematical requirements of being a group and act on an isolated object.

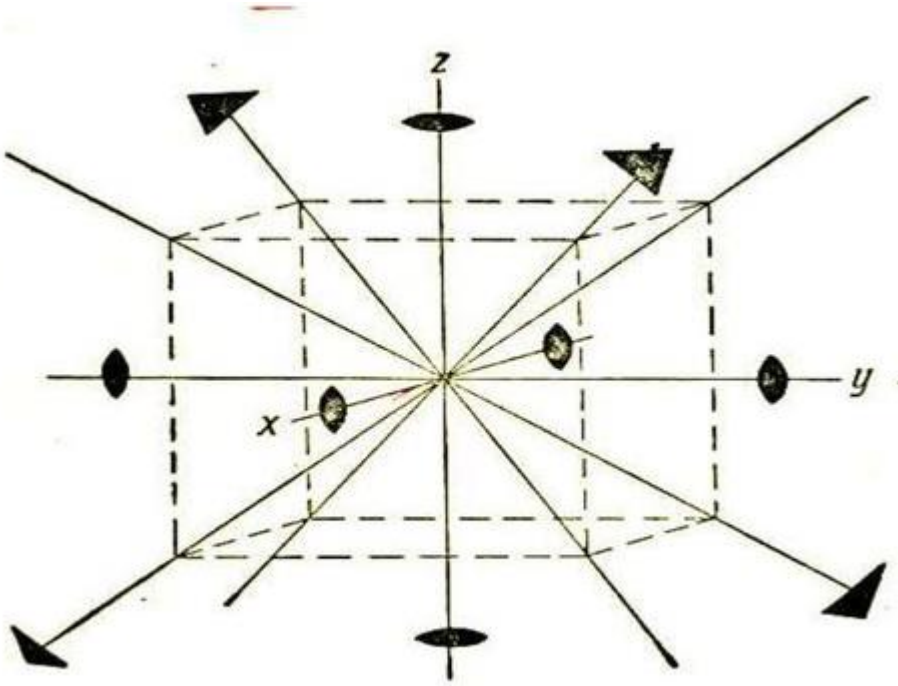
A group must have the following properties

- **Identity** (one operation in the group, the identity, has the property that it maps every point back onto itself)
- **Fixed point** (there is at least one point for which every operation in the group maps this point back onto itself)
- **Closure** (the combination of any two operations yields an operation that is also part of the group),
- **Inverse** (for every operation in the group f_1 there is an inverse operation f_2 such that $f_1 \cdot f_2 = f_2 \cdot f_1 = 1$, note that some operations are their own inverse)

32 Crystallographic Point Groups

	Triclinic	Mono/ Ortho	Trigonal	Tetragonal	Hexagonal	Cubic
Rotation	1	2	3	4	6	23
Rotoinversion	$\bar{1}$	$\bar{2} = m$	$\bar{3}$	$\bar{4}$	$\bar{6}$	
Rotation + perp mirror		$2/m$	$3/m = \bar{6}$	$4/m$	$6/m$	$m\bar{3}$
Rotation + perp 2-fold		222	32	422	622	432
Rotation + parallel mirrors		$mm2$	$3m$	$4mm$	$6mm$	
Rotoinversion + parallel mirrors		$mm2$	$\bar{3}m$	$\bar{4}2m$	$\bar{6}2m$	$\bar{4}3m$
Rotation + parallel & perp mirrors		mmm	$3/mmm = \bar{6}2m$	$4/mmm$	$6/mmm$	$m\bar{3}m$

Entries in red are duplicates



Grupo pontual 23:
Intersecção de eixos de rotação de 3-fold que aparece ao longo das diagonais do cubo

32 Crystallographic Point Groups

Crystal System	Lattice	Required symmetry	Point groups
Cubic	Cubic	3-fold axes along body diagonals	23, $m\bar{3}$, $\bar{4}3m$, 432, $m\bar{3}m$
Tetragonal	Tetragonal	4-fold axis	4, $\bar{4}$, $4/m$, 422, $4mm$, $\bar{4}m2$, $4/mmm$
Hexagonal	Hexagonal	6-fold axis	6, $\bar{6}$, $6/m$, 622, $6mm$, $\bar{6}m2$, $6/mmm$
Trigonal	Hexagonal or Rhombohedral	3-fold axis	3, $\bar{3}$, 32, $3m$, $\bar{3}m$
Orthorhombic	Orthorhombic	Three mutually perpendicular 2-fold axes or mirror planes	222, $2mm$, mmm
Monoclinic	Monoclinic	2-fold axis or mirror plane	2, m, $2/m$
Triclinic	Triclinic	none	1, $\bar{1}$

Schoenflies & Hermann Mauguin

Crystal System	Lattice	Hermann-Mauguin Point groups	Schoenflies Point groups
Cubic	Cubic	$23, m\bar{3}, \bar{4}3m, 432, m\bar{3}m$	$T\ T_h\ T_d\ O\ O_h$
Tetragonal	Tetragonal	$4, \bar{4}, 4/m, 422, 4mm, \bar{4}m2, 4/mmm$	$C_4\ S_4\ C_{4h}\ D_4\ C_{4v}\ D_{2d}\ D_{4h}$
Hexagonal	Hexagonal	$6, \bar{6}, 6/m, 622, 6mm, \bar{6}m2, 6/mmm$	$C_6\ C_{3h}\ C_{6h}\ D_6\ C_{6v}\ D_{3h}\ D_{6h}$
Trigonal	Hexagonal or Rhombohedral	$3, \bar{3}, 32, 3m, \bar{3}m$	$C_3\ C_{3i}\ D_3\ C_{3v}\ D_{3d}$
Orthorhombic	Orthorhombic	$222, 2mm, mmm$	$D_2\ C_{2v}\ D_{2h}$
Monoclinic	Monoclinic	$2, m, 2/m$	$C_2\ C_s\ C_{2h}$
Triclinic	Triclinic	$1, \bar{1}$	$C_1\ C_i$

V escola de verão

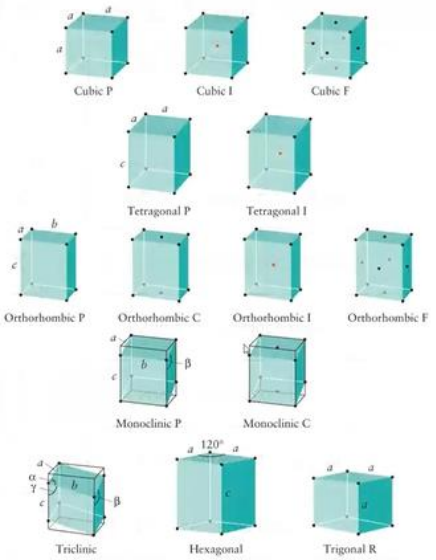
The 14 3D Bravais Lattices

P = Primitive lattice

I = Body centered lattice
½ (**a** + **b** + **c**)

F = Face centered lattice
½ (**a** + **b**)
½ (**a** + **c**)
½ (**b** + **c**)

C = Base centered lattice
½ (**a** + **b**)



X

32 Crystallographic Point Groups

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Rotation	1	2	3	4	6	23
Rotoinversion	$\bar{1}$	$\bar{2} = m$	$\bar{3}$	$\bar{4}$	$\bar{6}$	
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Rotoinversion + parallel mirrors		$mm2$	$\bar{3}m$	$\bar{4}2m$	$\bar{6}2m$	$\bar{4}3m$
Rotation + parallel & perp mirrors		mmm	$\frac{3/mmm}{= \bar{6}2m}$	$4/mmm$	$6/mmm$	$m\bar{3}m$

Entries in red are duplicates

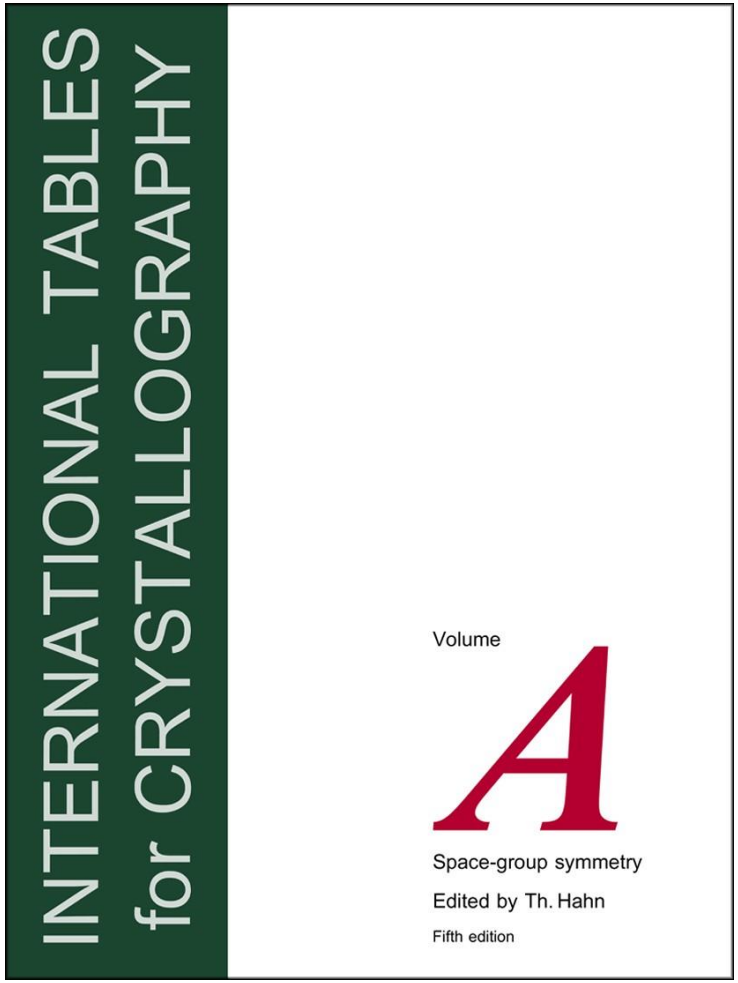
14 X 32=230 grupos Espaciais

Fourteen 3D Bravais Lattices

Crystal System	P	C	I	F	Examples
Triclinic ($a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$)	X				Primitive triclinic
Monoclinic ($a \neq b \neq c$; $\alpha = \gamma = 90^\circ \beta \neq 90$)	X	X			Base-centered monoclinic
Orthorhombic ($a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$)	X	X	X	X	Face-centered orthorhombic
Rhombohedral ($a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$)	X				Primitive rhombohedral
Hexagonal ($a = b \neq c$; $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$)	X				Primitive hexagonal
Tetragonal ($a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$)	X		X		Body-centered tetragonal
Cubic ($a = b = c$; $\alpha = \beta = \gamma = 90^\circ$)	X		X	X	Face-centered cubic

International Tables for Crystallography Volume A

- This reference source contains the symmetry information for all 230 three-dimensional space groups (and more)
- You can access an online version of this reference at https://onlinelibrary.wiley.com/iucr/itc/Ac/



V escola de verão

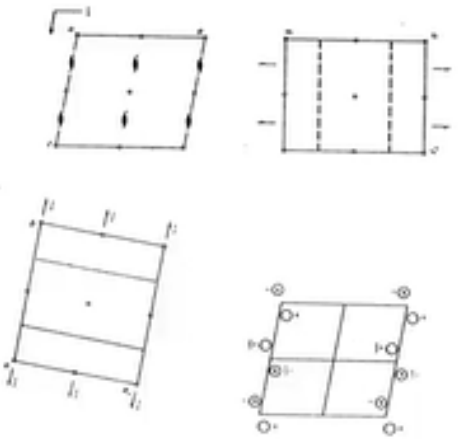
International Tables for Crystallography – Volume A
Entry for Space Group $P2_1/c$ (#14)

Page 1

$P\,2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1$; $0 \le y \le 1$; $0 \le z \le 1$

Symmetry operations

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

Page 2

CONTINUED No. 14 $P\,2_1/c$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	General: $h0l$: $l=2n$; $0k0$: $k=2n$; $00l$: $l=2n$
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			Special: as above, plus hkl: $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl: $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl: $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl: $k+l=2n$

Symmetry of special projections

Along [001] $p\,2\,g\,m$; $a'=a_x$ $b'=b$; Origin at $0,0,z$

Along [100] $p\,2\,g\,g$; $a'=b$ $b'=c_x$; Origin at $x,0,0$

Along [010] $p\,2$; $a'=\frac{1}{2}c$ $b'=a$; Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2]$P\,1\,2_1\,1$ ($P\,2_1$) 1; 2
[2]$P\,\bar{1}$ 1; 3
[2]$P\,1\,c\,1$ ($P\,c$) 1; 4

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]$P\,1\,2_1/c\,1$ ($b'=3b$) ($P\,2_1/c$); [2]$P\,1\,2_1/c\,1$ ($a'=2a$ or $a'=2a$, $c'=2a+c$) ($P\,2_1/c$)

Minimal non-isomorphic supergroups

I [2]$P\,n\,n\,a$; [2]$P\,m\,n\,a$; [2]$P\,c\,c\,a$; [2]$P\,b\,a\,m$; [2]$P\,c\,c\,n$; [2]$P\,b\,c\,m$; [2]$P\,n\,n\,m$; [2]$P\,b\,c\,n$; [2]$P\,b\,c\,a$; [2]$P\,n\,m\,a$; [2]$C\,m\,c\,a$

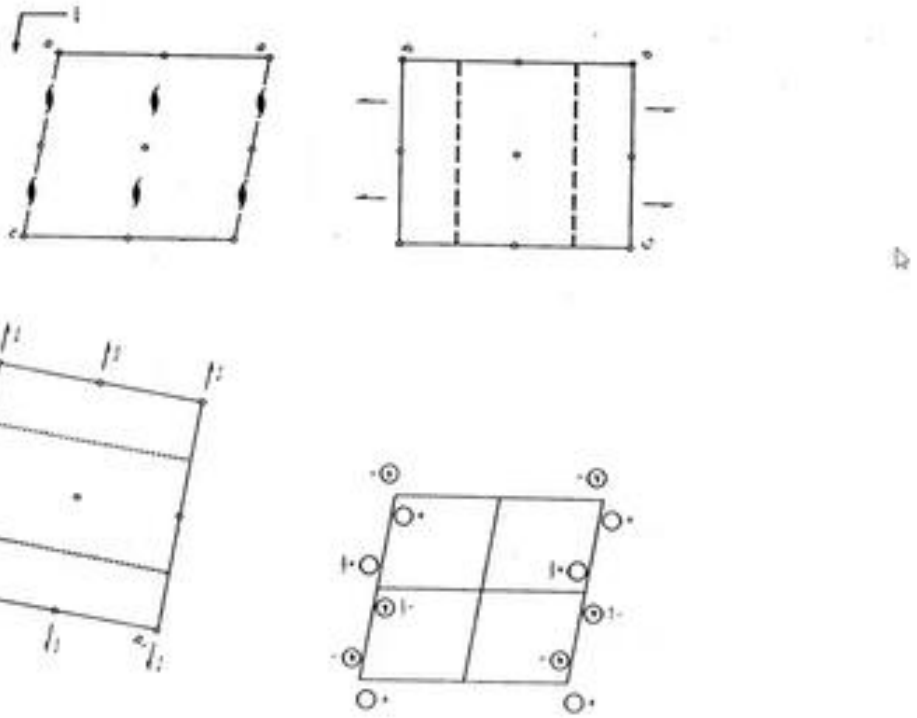
II [2]$C\,1\,2/c\,1$ ($C\,2/c$); [2]$A\,1\,2/m\,1$ ($C\,2/m$); [2]$F\,1\,2/c\,1$ ($C\,2/c$); [2]$P\,1\,2_1/m\,1$ ($2c'=c$) ($P\,2_1/m$); [2]$P\,1\,2/c\,1$ ($2b'=b$) ($P\,2/c$)

V escola de verão

$P\,2_1/c$ C_{2h}^5 2/m Monoclinic

No. 14 $P\,1\,2_1/c\,1$ Patterson symmetry $P\,1\,2/m\,1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

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

Symmetry operations

(1) 1 (2) $2(0,\tfrac{1}{4},0)$ $0,y,\tfrac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,\tfrac{1}{4},z$

V escola de verão

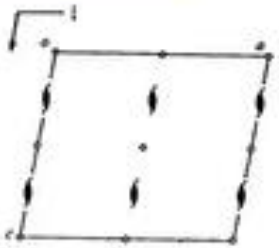
$P\,2_1/c$ C_{2h}^5 2/m Monoclinic

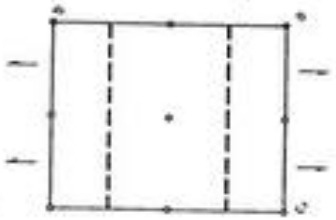
No. 14 $P\,1\,2_1/c\,1$

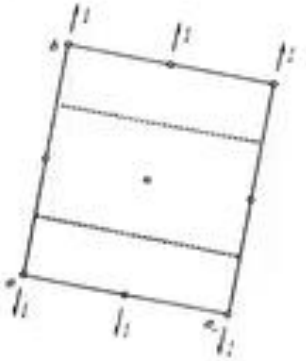
Patterson symmetry $P\,1\,2/m\,1$

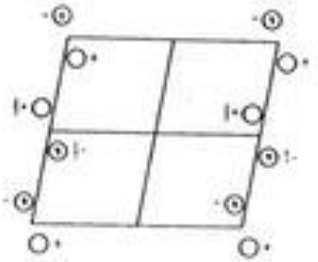
UNIQUE AXIS b, CELL CHOICE 1

Hermann-Mauguin Space Group Symbols (Short & Long)









Origin at $\bar{1}$

Asymmetric unit $0\le x\le 1;\ 0\le y\le 1;\ 0\le z\le 1$

Symmetry operations

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

V escola de verão

Schoenflies Space Group

$P\,2_1/c$

C_{2h}^5

2/m

Monoclinic

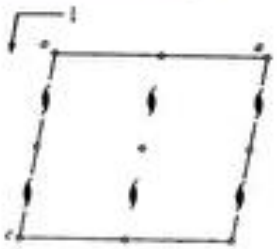
No. 14

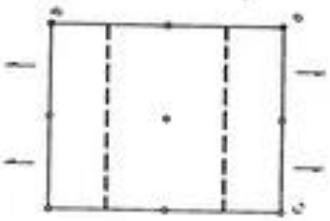
$P\,1\,2_1/c\,1$

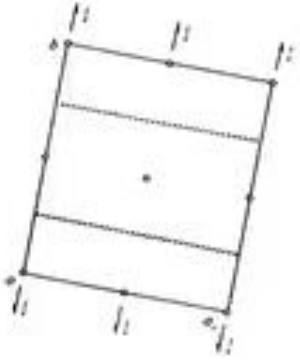
Patterson symmetry $P\,1\,2/m\,1$

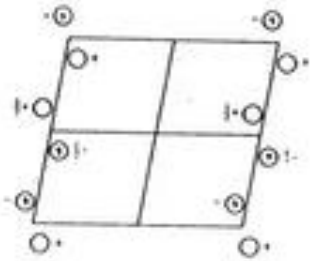
UNIQUE AXIS b, CELL CHOICE 1

Hermann-Mauguin Space Group Symbols (Short & Long)









Origin at $\bar{1}$

Asymmetric unit $0\le x\le 1;\ 0\le y\le 1;\ 0\le z\le 1$

Symmetry operations

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

V escola de verão

Schoenflies Space Group

$P\,2_1/c$

C_{2h}^5

$2/m$

Crystal System

Monoclinic

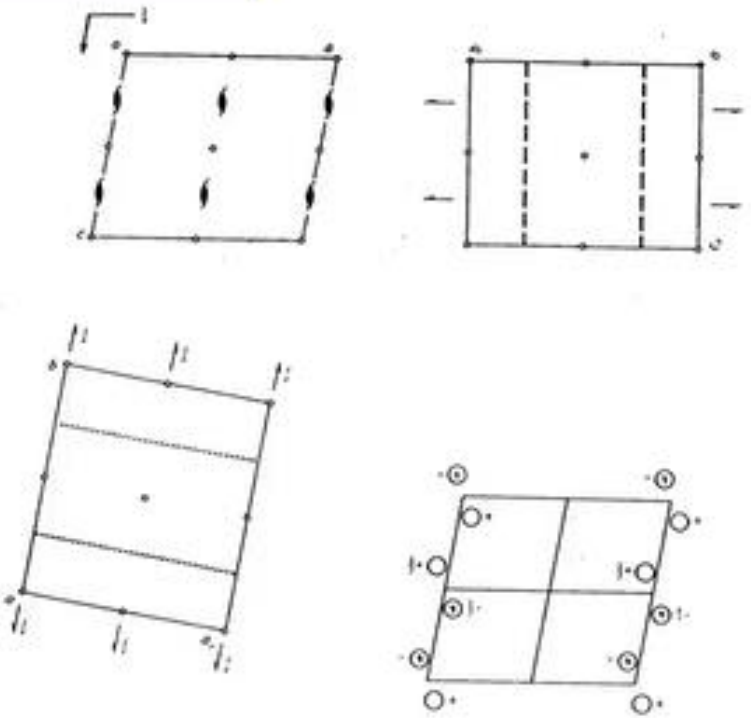
No. 14

$P\,1\,2_1/c\,1$

UNIQUE AXIS b, CELL CHOICE 1

Patterson symmetry $P\,1\,2/m\,1$

Hermann-Mauguin Space Group Symbols (Short & Long)



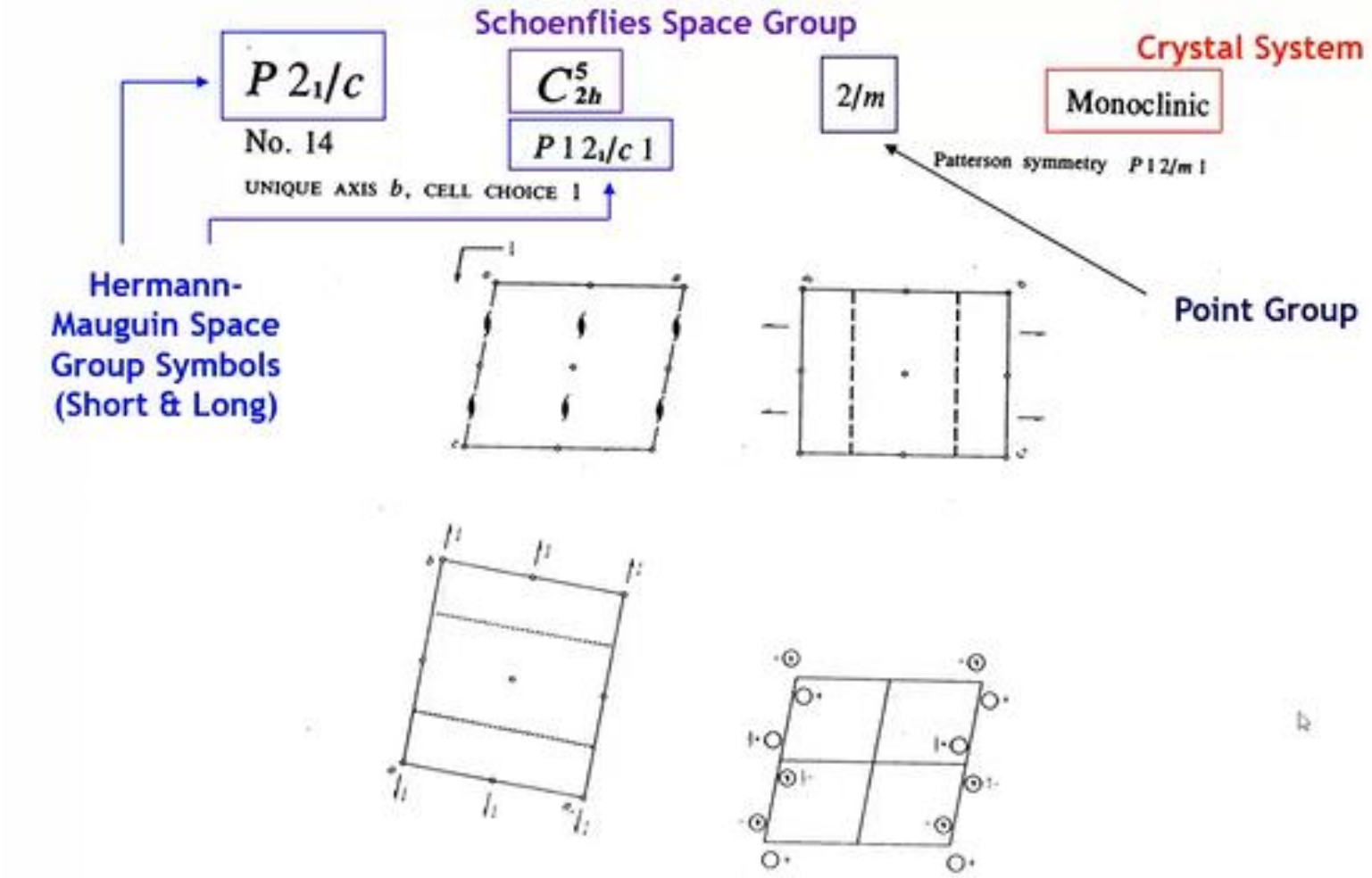
Origin at $\bar{1}$

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

Symmetry operations

(1) 1 (2) $2(0,\tfrac{1}{4},0)\ 0,y,\tfrac{1}{4}$ (3) $\bar{1}\ 0,0,0$ (4) $c\ x,\tfrac{1}{4},z$

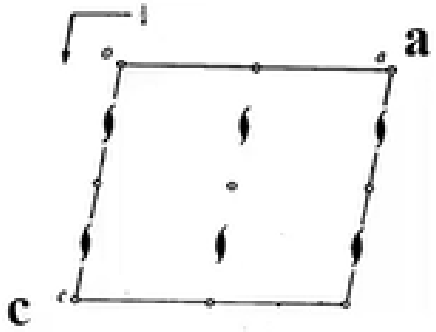
V escola de verão

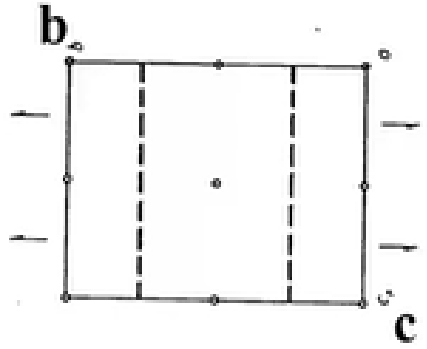


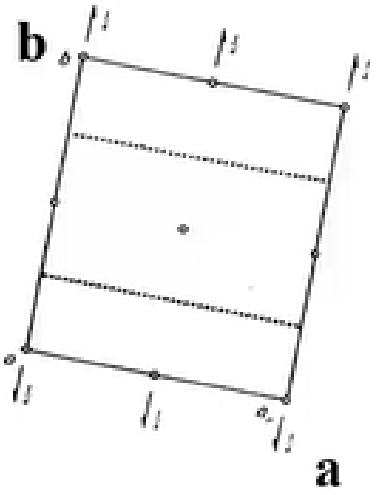
V escola de verão

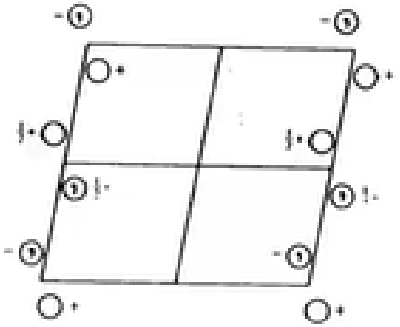
P 1 2_1/c 1

Axes parallel to or planes perpendicular to the b-axis









Origin at $\bar{1}$

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

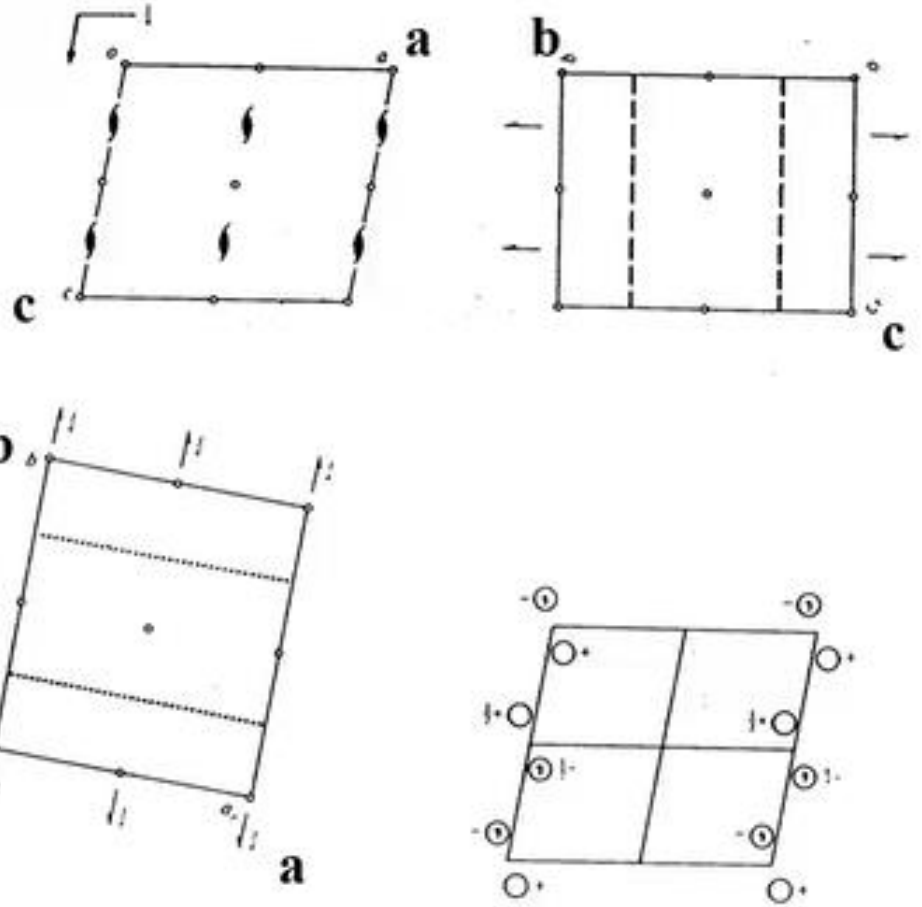
Symmetry operations

(1) 1 (2) 2(0,¼,0) 0,*y*,¼ (3) $\bar{1}$ 0,0,0 (4) *c* *x*,¼,*z*

V escola de verão

P 1 2_1/c 1

Axes parallel to or planes perpendicular to the b-axis



Origin at $\bar{1}$

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

Symmetry operations

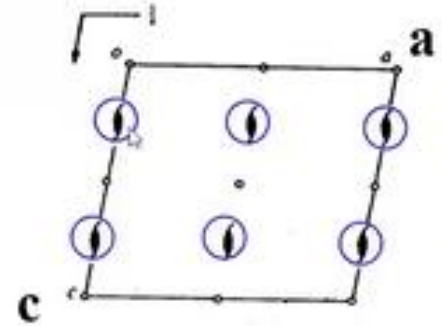
(1) 1 (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,\frac{1}{4},z$

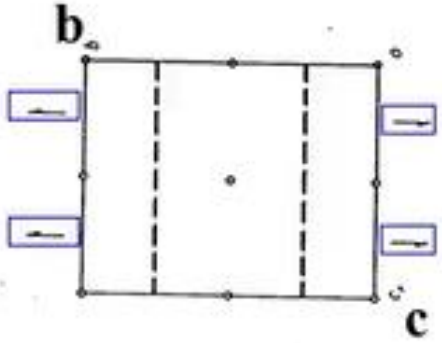
2_1 Screw Axis

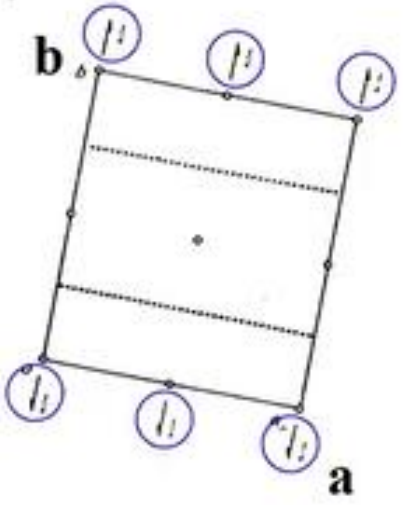
V escola de verão

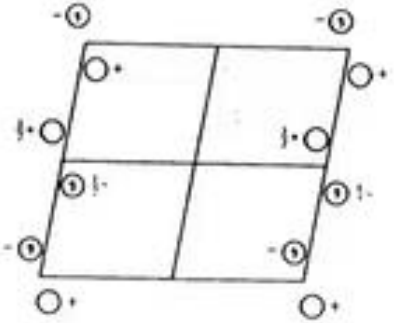
P 1 $2_1/c$ 1

Axes parallel to or planes perpendicular to the b-axis









Origin at $\bar{1}$

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

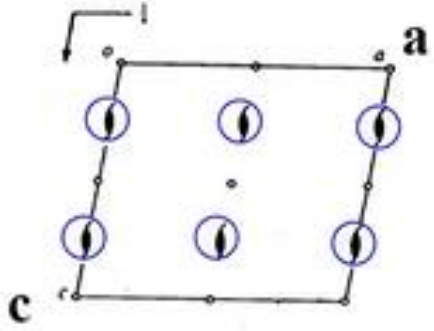
Symmetry operations

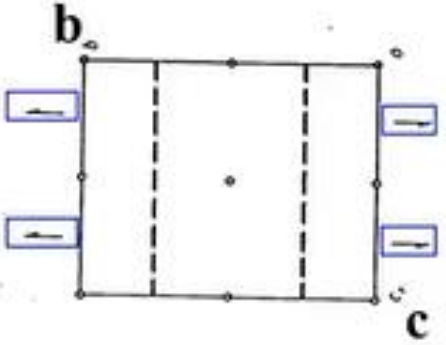
(1) 1 | (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ | (3) $\bar{1}$ 0,0,0 | (4) c $x,\frac{1}{4},z$

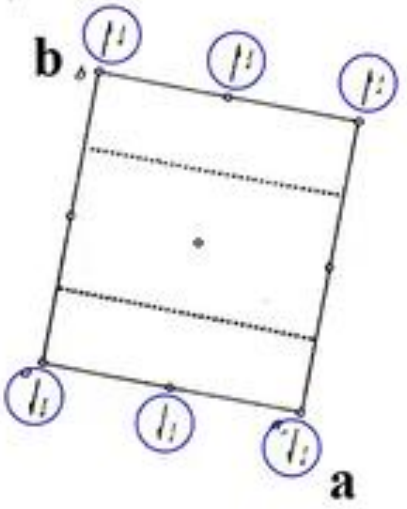
2_1 Screw Axis

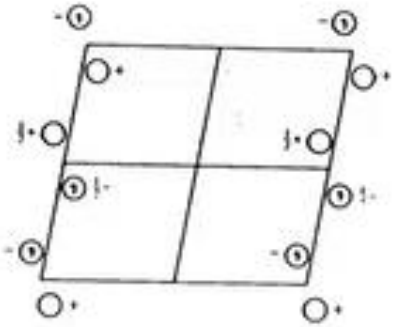
P 1 $2_1/c$ 1

Axes parallel to or planes perpendicular to the b-axis









Origin at $\bar{1}$

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

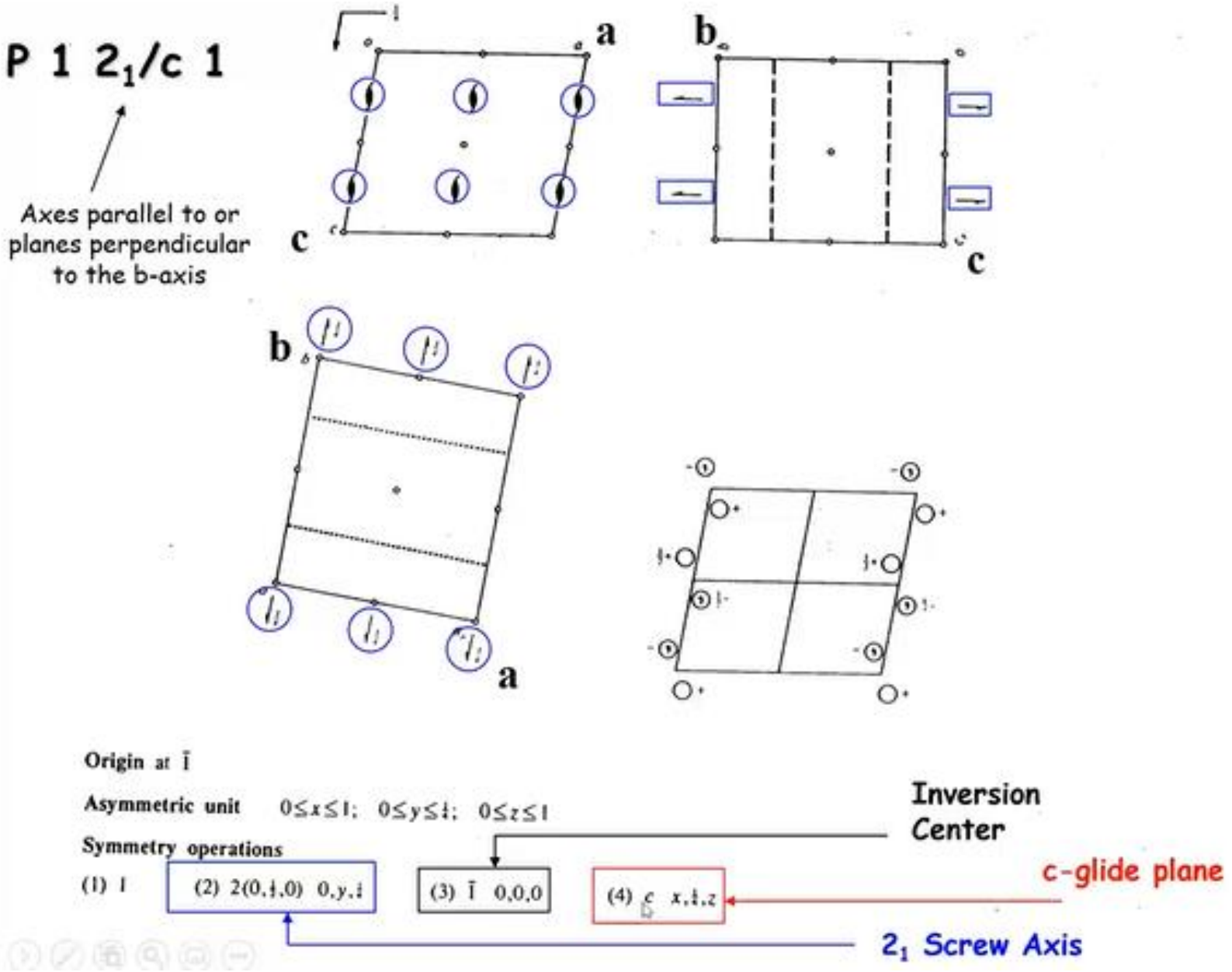
Symmetry operations

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

Inversion Center

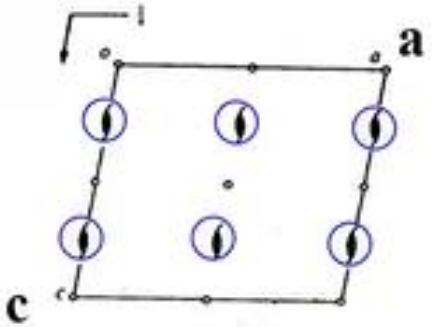
2_1 Screw Axis

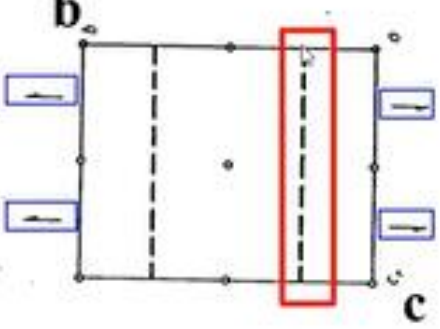
V escola de verão

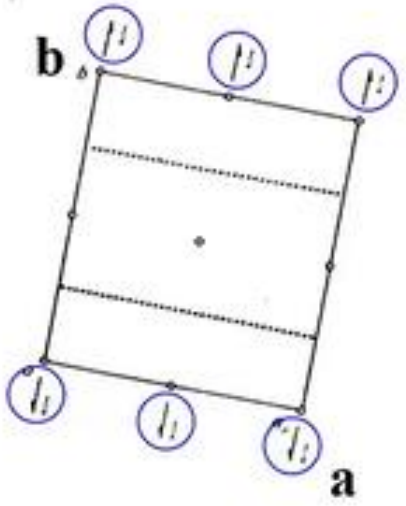


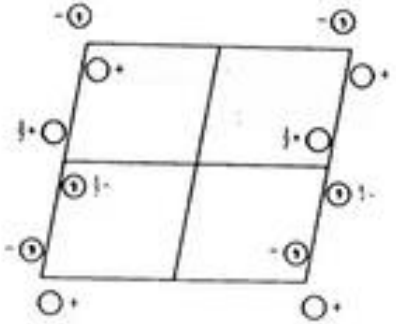
P 1 $2_1/c$ 1

Axes parallel to or planes perpendicular to the b-axis









Origin at $\bar{1}$

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

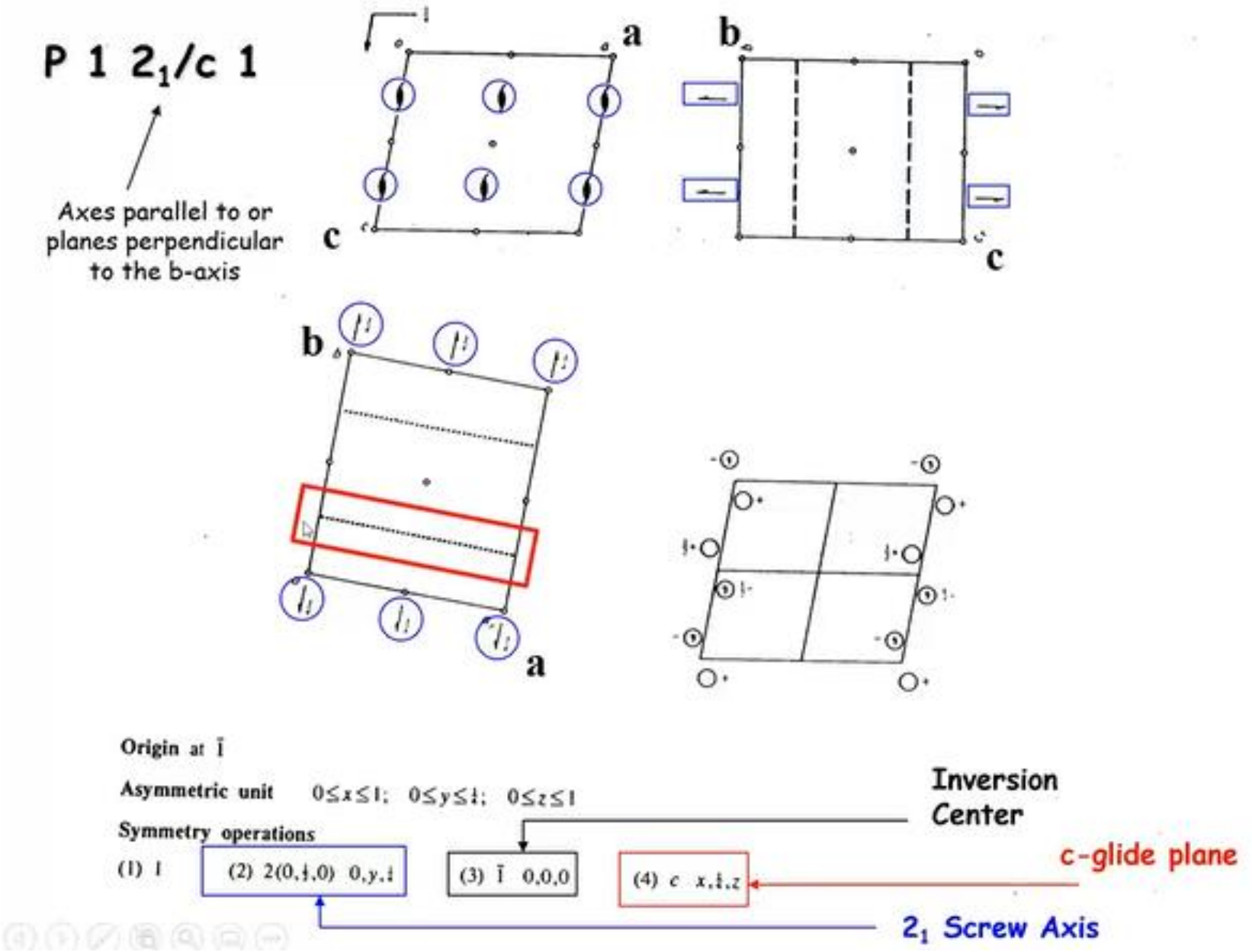
Symmetry operations

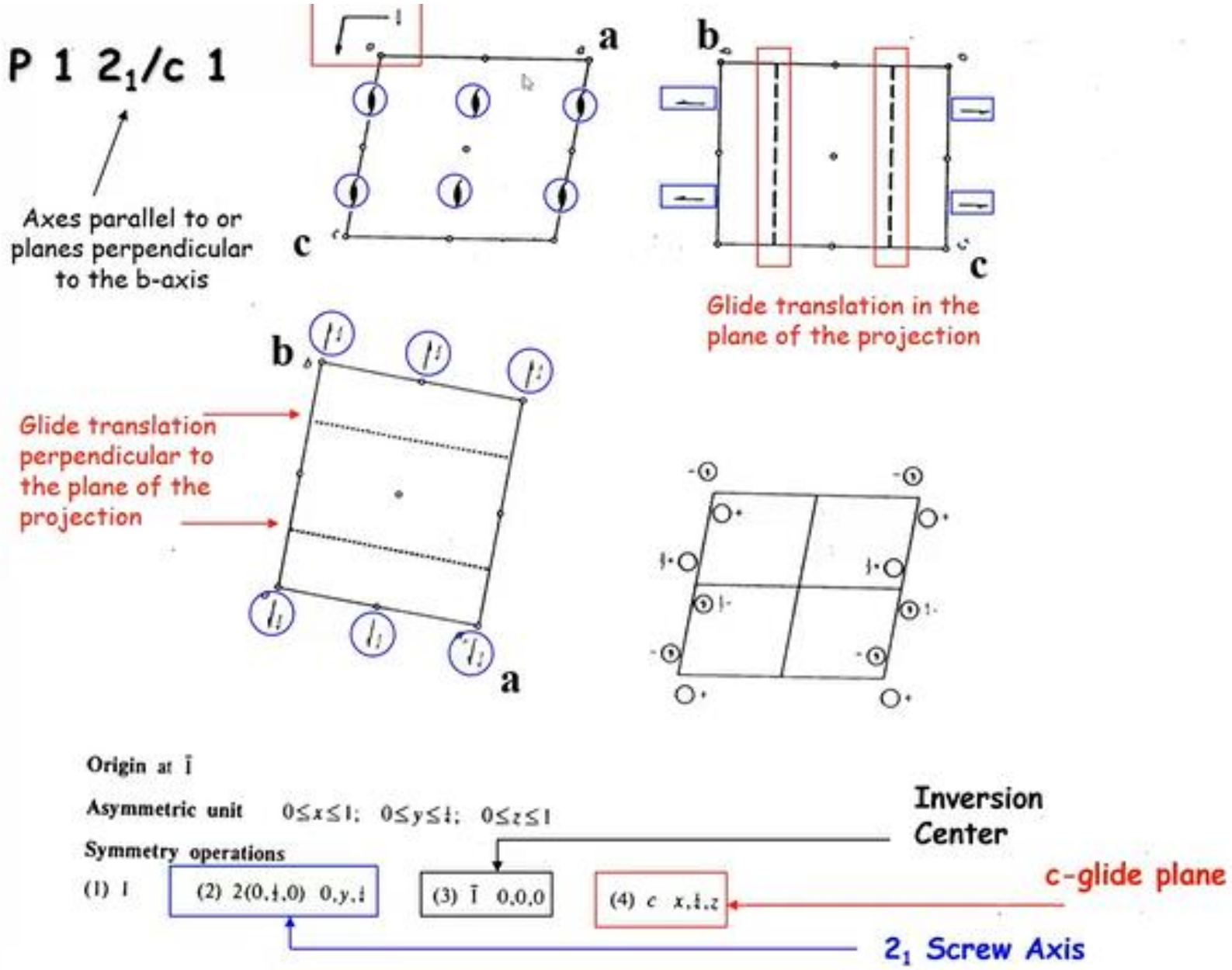
(1) 1 | (2) $2(0,\frac{1}{4},0)$ $0,y,\frac{1}{4}$ | (3) $\bar{1}$ 0,0,0 | (4) c $x,\frac{1}{4},z$

Inversion Center

c-glide plane

2_1 Screw Axis


P 1 2₁/c 1
Axes parallel to or planes perpendicular to the b-axis
a
c
b
c
b
a
Origin at 1̄
Asymmetric unit 0≤x≤1; 0≤y≤¼; 0≤z≤1
Symmetry operations
(1) 1
(2) 2(0,¼,0) 0,y,¼
(3) 1̄ 0,0,0
(4) c x,¼,z
Inversion Center
c-glide plane
2₁ Screw Axis


P 1 2₁/c 1
Axes parallel to or planes perpendicular to the b-axis
a
c
b
c
Glide translation in the plane of the projection
b
Glide translation perpendicular to the plane of the projection
a
Origin at 1̄
Asymmetric unit 0≤x≤1; 0≤y≤¼; 0≤z≤1
Symmetry operations
(1) 1
(2) 2(0,¼,0) 0,y,¼
(3) 1̄ 0,0,0
(4) c x,¼,z
Inversion Center
c-glide plane
2₁ Screw Axis

V escola de verão

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

Symmetry of special projections

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

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

Along [010] $p\,2$
$\boldsymbol{a'=\frac{1}{2}c}$ $\boldsymbol{b'=a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2]$P\,1\,2_1\,1\,(P\,2_1)$ 1; 2
[2]$P\,\bar{1}$ 1; 3
[2]$P\,1\,c\,1\,(P\,c)$ 1; 4

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]$P\,1\,2_1/c\,1\,(\boldsymbol{b'=3b})(P\,2_1/c)$; [2]$P\,1\,2_1/c\,1\,(\boldsymbol{a'=2a}$ or $\boldsymbol{a'=2a, c'=2a+c})(P\,2_1/c)$

Minimal non-isomorphic supergroups

I [2]$Pnna$; [2]$Pmna$; [2]$Pcca$; [2]$Pbam$; [2]$Pccn$; [2]$Pbcm$; [2]$Pnnm$; [2]$Pbcn$; [2]$Pbca$; [2]$Pnma$; [2]$Cmca$

II [2]$C\,1\,2/c\,1\,(C\,2/c)$; [2]$A\,1\,2/m\,1\,(C\,2/m)$; [2]$I\,1\,2/c\,1\,(C\,2/c)$; [2]$P\,1\,2_1/m\,1\,(2\boldsymbol{c'=c})(P\,2_1/m)$; [2]$P\,1\,2/c\,1\,(2\boldsymbol{b'=b})(P\,2/c)$

V escola de verão

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
4	*e*	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},z$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$
2	*d*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$		
2	*c*	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$		
2	*b*	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
2	*a*	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$		

General position

Wyckoff Sites

Reflection conditions

General:

$h0l$: $l=2n$
$0k0$: $k=2n$
$00l$: $l=2n$

Special: as above, plus

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

Symmetry of special projections

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

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

Along [010] $p\,2$
$\boldsymbol{a}'=\frac{1}{2}\boldsymbol{c}$, $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2]*P* 1 2_1 1 (*P* 2_1)	1; 2
	[2]*P* $\bar{1}$	1; 3
	[2]*P* 1*c* 1 (*Pc*)	1; 4
IIa	none	
IIb	none	

Maximal isomorphic subgroups of lowest index

IIc [3]*P* 1 $2_1/c$ 1 ($\boldsymbol{b}'=3\boldsymbol{b}$)(*P* $2_1/c$); [2]*P* 1 $2_1/c$ 1 ($\boldsymbol{a}'=2\boldsymbol{a}$ or $\boldsymbol{a}'=2\boldsymbol{a}, \boldsymbol{c}'=2\boldsymbol{a}+\boldsymbol{c}$)(*P* $2_1/c$)

Minimal non-isomorphic supergroups

I [2]*Pnna*; [2]*Pmna*; [2]*Pcca*; [2]*Pbam*; [2]*Pccn*; [2]*Pbcm*; [2]*Pnnm*; [2]*Pbcn*; [2]*Pbca*; [2]*Pnma*; [2]*Cmca*

II [2]*C* 1 2/*c* 1 (*C* 2/*c*); [2]*A* 1 2/*m* 1 (*C* 2/*m*); [2]*I* 1 2/*c* 1 (*C* 2/*c*); [2]*P* 1 $2_1/m$ 1 ($2\boldsymbol{c}'=\boldsymbol{c}$)(*P* $2_1/m$); [2]*P* 1 2/*c* 1 ($2\boldsymbol{b}'=\boldsymbol{b}$)(*P* 2/*c*)

V escola de verão

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

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates			
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},z$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$

General position

2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$

Wyckoff Sites

Reflection Conditions/ Systematic Absences

Reflection conditions

General:

$h0l$: $l=2n$
$0k0$: $k=2n$
$00l$: $l=2n$

Special: as above, plus

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

hkl : $k+l=2n$

Symmetry of special projections

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

Along [100] $p\,2g\,g$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p\,2$
$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2]$P\,1\,2_1\,1$ $(P2_1)$ 1; 2
[2]$P\,\bar{1}$ 1; 3
[2]$P\,1\,c\,1$ (Pc) 1; 4

IIa none

IIb none

Subgroups = Space group symmetry if certain symmetry operations are eliminated

Supergroups = Space group symmetry if certain symmetry operations are added

Maximal isomorphic subgroups of lowest index

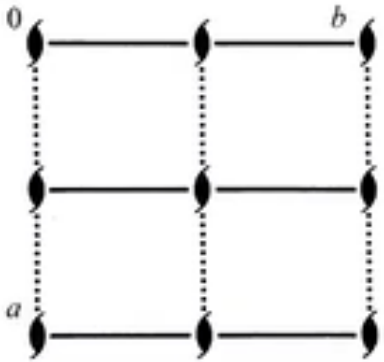
IIc [3]$P\,1\,2_1/c\,1$ $(\mathbf{b}'=3\mathbf{b})$ $(P2_1/c)$; [2]$P\,1\,2_1/c\,1$ $(\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c})$ $(P2_1/c)$

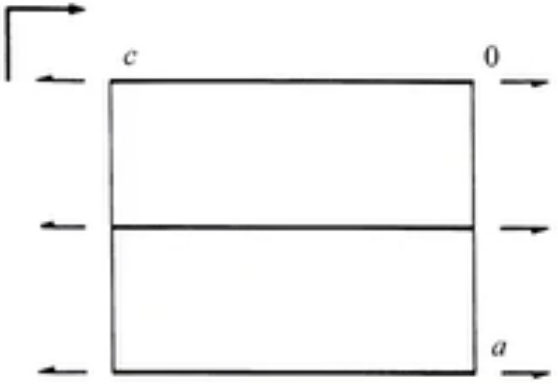
Minimal non-isomorphic supergroups

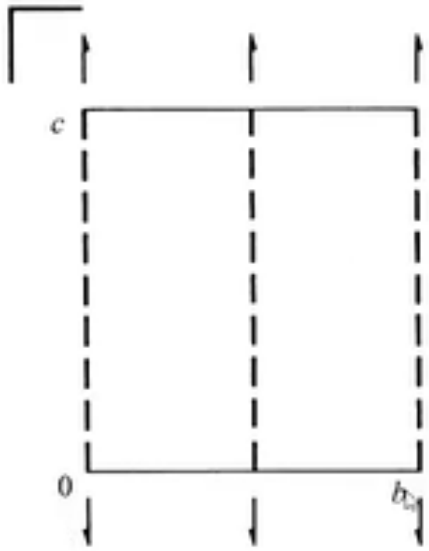
I [2]$Pnna$; [2]$Pmna$; [2]$Pcca$; [2]$Pbam$; [2]$Pccn$; [2]$Pbcm$; [2]$Pnnm$; [2]$Pbcn$; [2]$Pbca$; [2]$Pnma$; [2]$Cmca$

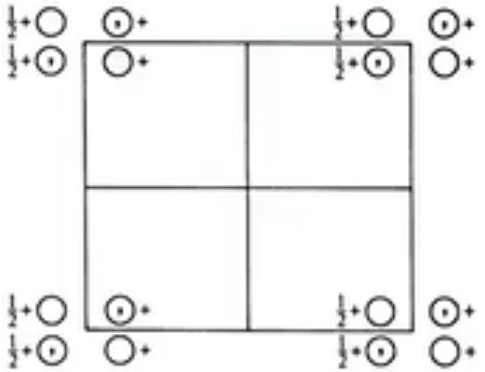
II [2]$C\,1\,2/c\,1$ $(C2/c)$; [2]$A\,1\,2/m\,1$ $(C2/m)$; [2]$I\,1\,2/c\,1$ $(C2/c)$; [2]$P\,1\,2_1/m\,1$ $(2\mathbf{c}'=\mathbf{c})$ $(P2_1/m)$; [2]$P\,1\,2/c\,1$ $(2\mathbf{b}'=\mathbf{b})$ $(P2/c)$

Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.



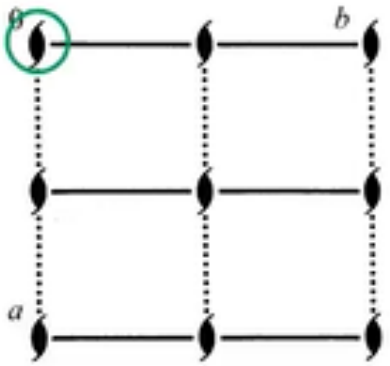


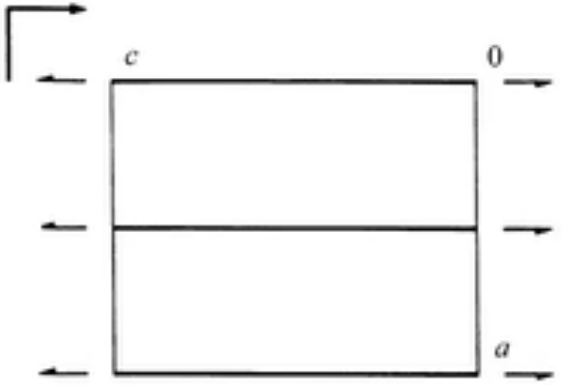


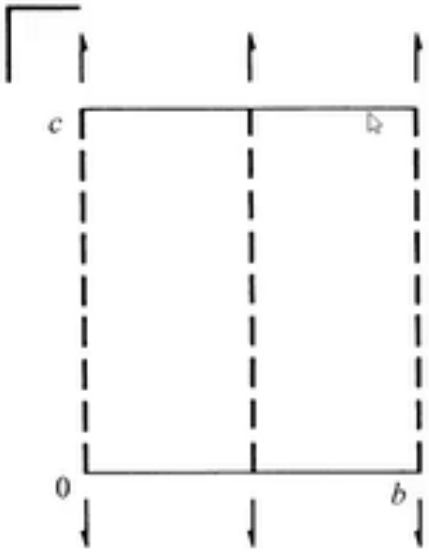


Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c





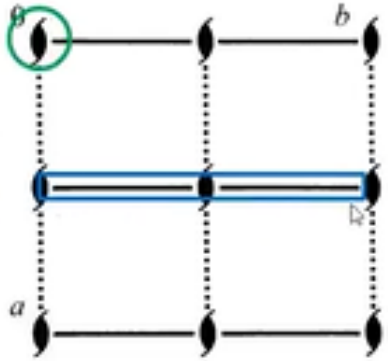


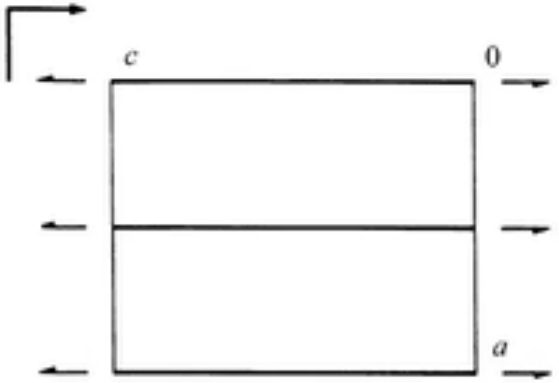
V escola de verão

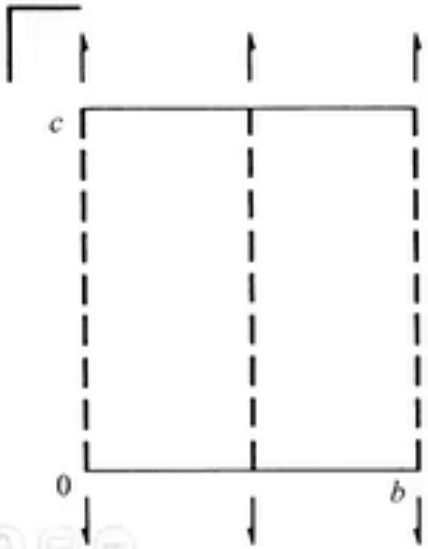
Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c

mirror plane perpendicular to a





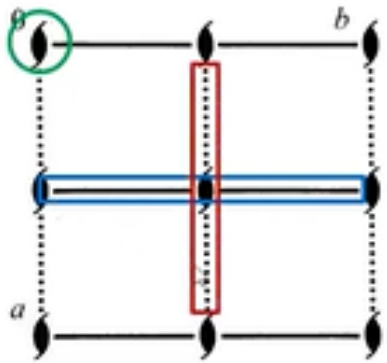


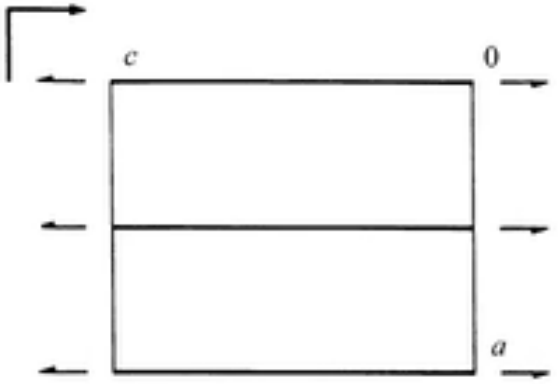
Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

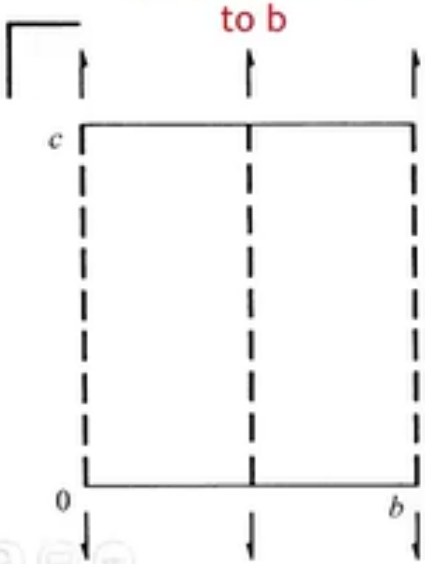
2_1 screw axis parallel to c

mirror plane perpendicular to a

glide plane perpendicular to b



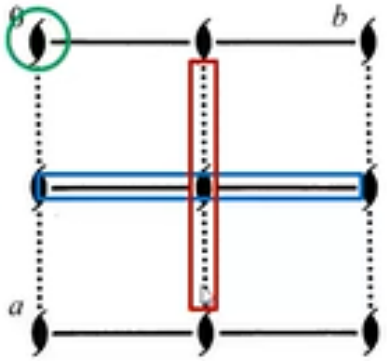




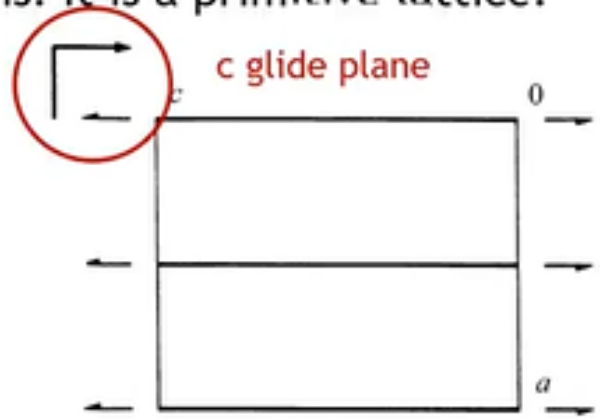
Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c

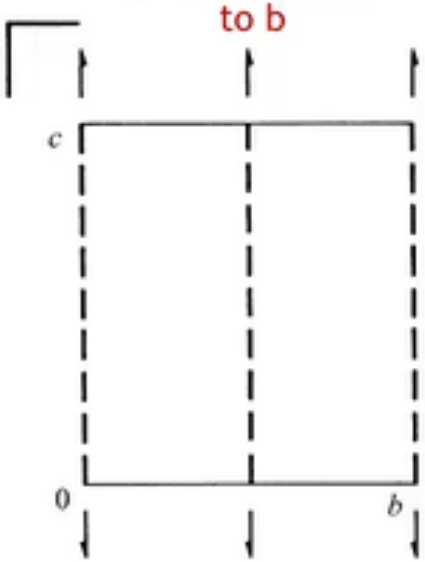
mirror plane perpendicular to a



c glide plane



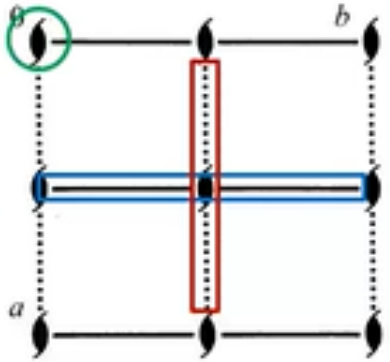
glide plane perpendicular to b



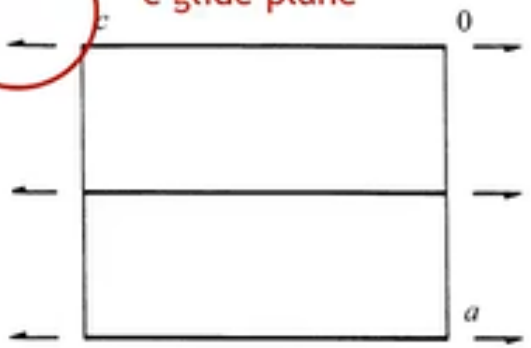
Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c

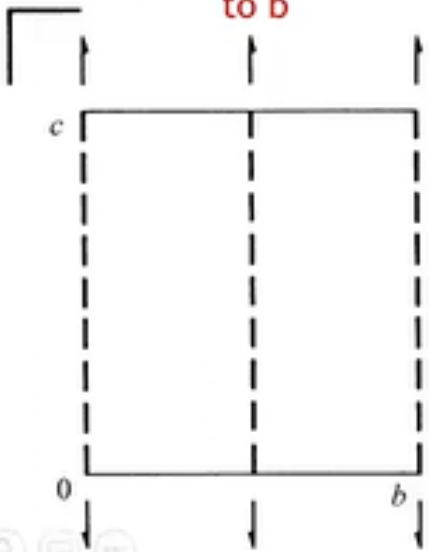
mirror plane perpendicular to a



c glide plane



glide plane perpendicular to b

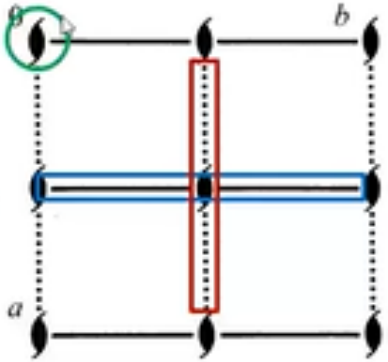


Space Group: $Pmc2_1$

Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c

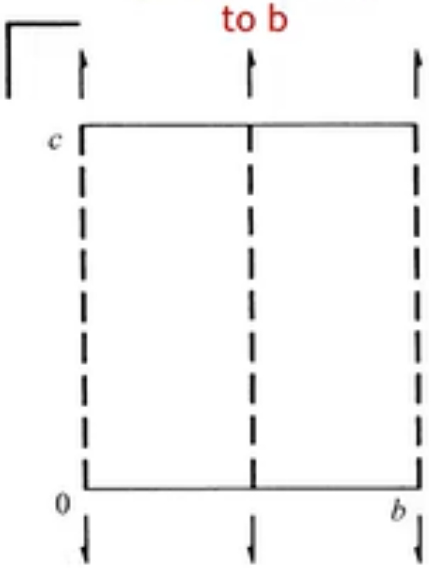
mirror plane perpendicular to a



c glide plane



glide plane perpendicular to b



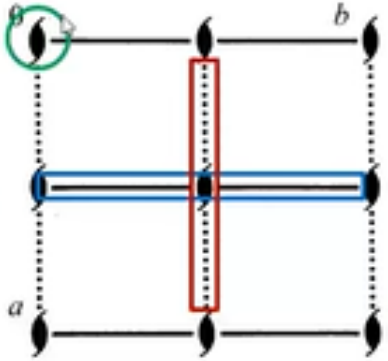
Space Group: $Pmc2_1$

Point Group: mm2

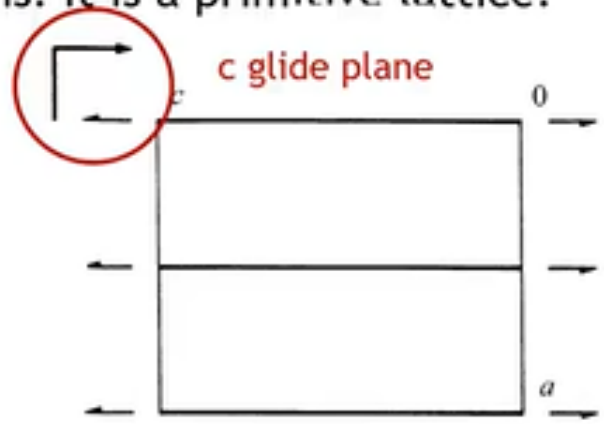
Identify the space group, point group and crystal system from these symmetry diagrams. It is a primitive lattice.

2_1 screw axis parallel to c

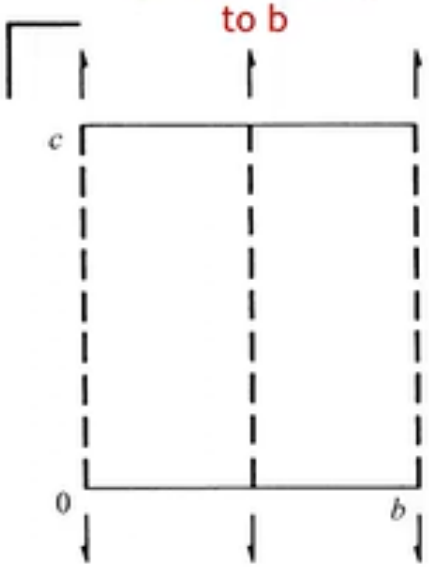
mirror plane perpendicular to a



c glide plane



glide plane perpendicular to b



Space Group: $Pmc2_1$

Point Group: mm2

Crystal System: orthorhombic

Space Group Notation by Crystal System

		Crystal axis referred to by symmetry labels			
Crystal System	**Short Space Group Name***	**1st position (s_1)**	**2nd position (s_2)**	**3rd position (s_3)**	**Examples**
Triclinic	$P1$ *or* $P\bar{1}$	---	---	---	$P1, P\bar{1}$
Monoclinic	$\mathbf{L}s_1$	*b* axis			$P2_1$ $C\,2/c$
Orthorhombic	$\mathbf{L}s_1\mathbf{s_2}\mathbf{s_3}$	*a*-axis	*b*-axis	*c*-axis	$Pnma$ $Cmc2_1$
Tetragonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 4**	*a*- and *b*-axes	*ab* face diagonals	$P\bar{4}2_1m$ $I\,4/m$
Trigonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 3**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P31c$ $R3$
Hexagonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 6**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P\,6_3/mmc$ $P6_4$
Cubic	$\mathbf{L}s_1\mathbf{s_2}s_3$	*a*-, *b*- and *c*-axes	body diagonals **contains a 3**	face diagonals	$Pm\bar{3}m$ $Ia\bar{3}$

*L = P (primitive), F (face centered), I (body centered), R (rhombohedral), A, B, C (base centered).
Only symbols shown in bold are present for all space groups in a given crystal system.

Space Group Notation by Crystal System

		Crystal axis referred to by symmetry labels			
Crystal System	**Short Space Group Name***	**1st position (s_1)**	**2nd position (s_2)**	**3rd position (s_3)**	**Examples**
Triclinic	$P1$ *or* $P\bar{1}$	---	---	---	$P1, P\bar{1}$
Monoclinic	$\mathbf{L}s_1$	*b* axis			$P2_1$ $C2/c$
Orthorhombic	$\mathbf{L}s_1s_2s_3$	*a*-axis	*b*-axis	*c*-axis	$Pnma$ $Cmc2_1$
Tetragonal	$\mathbf{L}s_1s_2s_3$	***c*-axis contains a 4**	*a*- and *b*-axes	*ab* face diagonals	$P\bar{4}2_1m$ $I\,4/m$
Trigonal	$\mathbf{L}s_1s_2s_3$	***c*-axis contains a 3**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P31c$ $R3$
Hexagonal	$\mathbf{L}s_1s_2s_3$	***c*-axis contains a 6**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P\,6_3/mmc$ $P6_4$
Cubic	$\mathbf{L}s_1s_2s_3$	*a*-, *b*- and *c*-axes	**body diagonals contains a 3**	face diagonals	$Pm\bar{3}m$ $Ia\bar{3}$

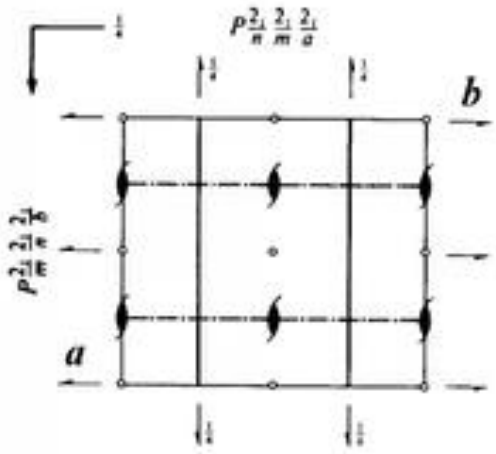
*L = *P* (primitive), *F* (face centered), *I* (body centered), *R* (rhombohedral), *A*, *B*, *C* (base centered).
Only symbols shown in bold are present for all space groups in a given crystal system.

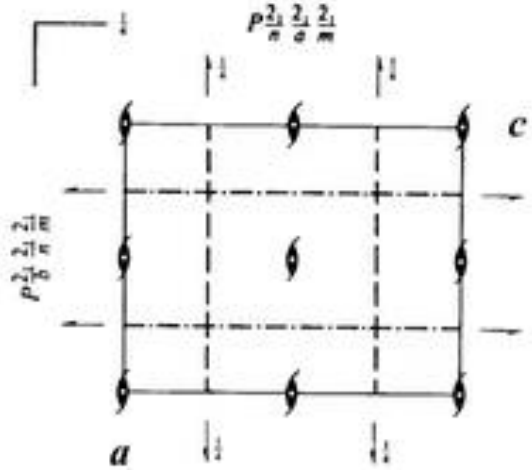
Orthorhombic

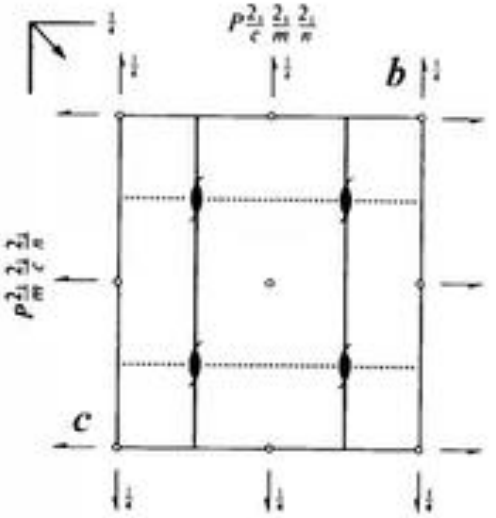
$P\,n\,m\,a$ D_{2h}^{16}

No. 62

$P\,2_1/n\,2_1/m\,2_1/a$







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

2_1 screw axis parallel to the a-axis
+
n-glide plane ⊥ to the a-axis

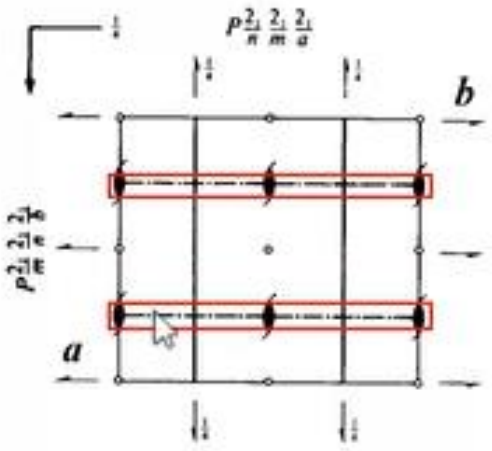
2_1 screw axis parallel to the b-axis
+
mirror plane ⊥ to the b-axis

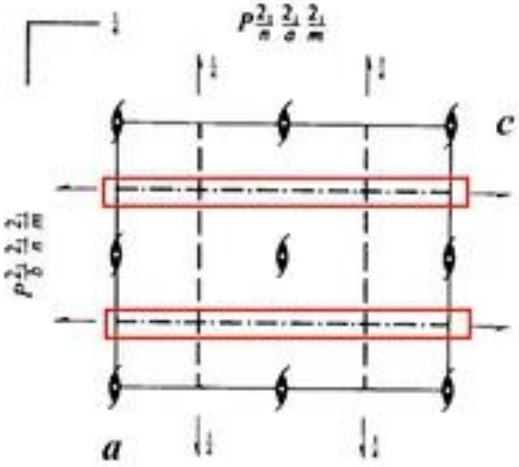
2_1 screw axis parallel to the c-axis
+
a-glide plane ⊥ to the c-axis

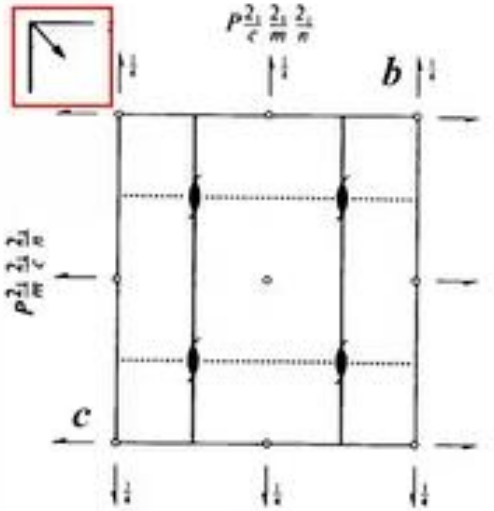
$P\,n\,m\,a$ D_{2h}^{16} **Orthorhombic**

No. 62

$P\,2_1/n\,2_1/m\,2_1/a$







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

2_1 screw axis parallel to the a-axis
+
n-glide plane ⊥ to the a-axis

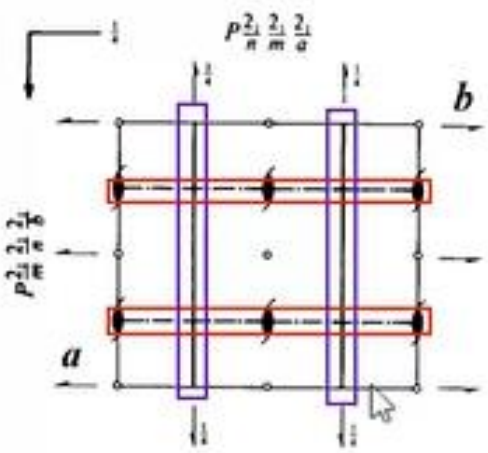
2_1 screw axis parallel to the b-axis
+
mirror plane ⊥ to the b-axis

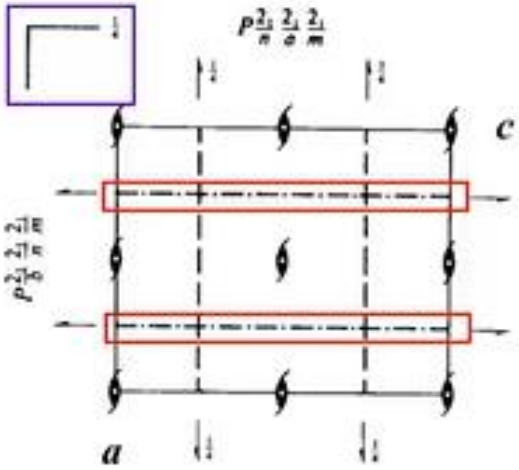
2_1 screw axis parallel to the c-axis
+
a-glide plane ⊥ to the c-axis

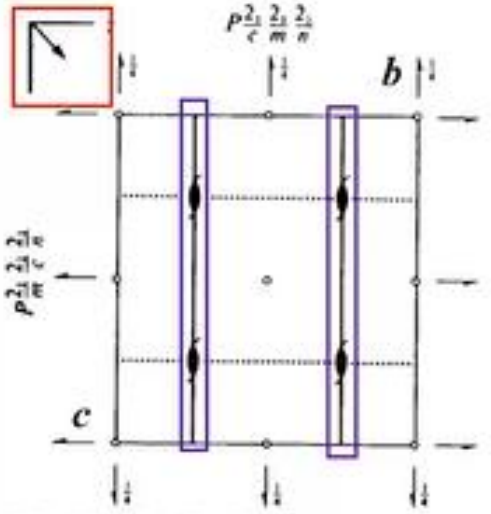
P n m a D_{2h}^{16} Orthorhombic

No. 62

$P\,2_1/n\,2_1/m\,2_1/a$





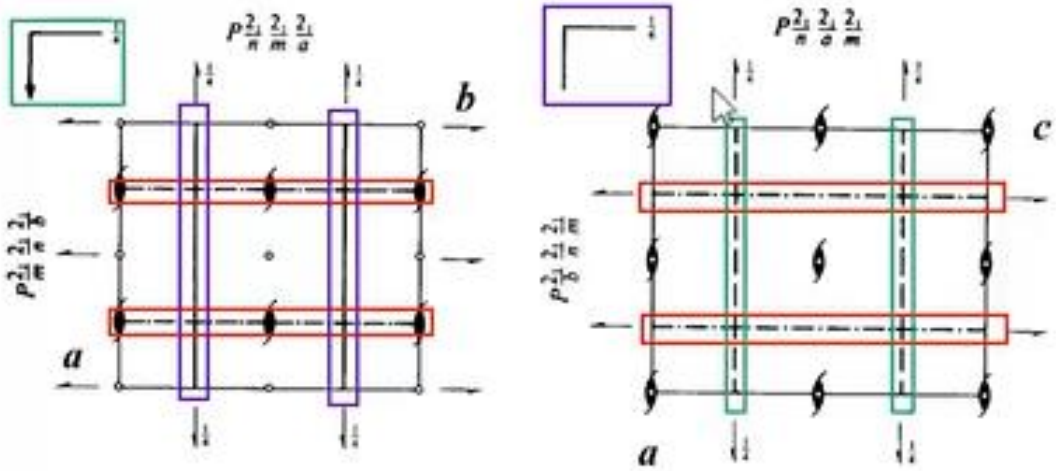


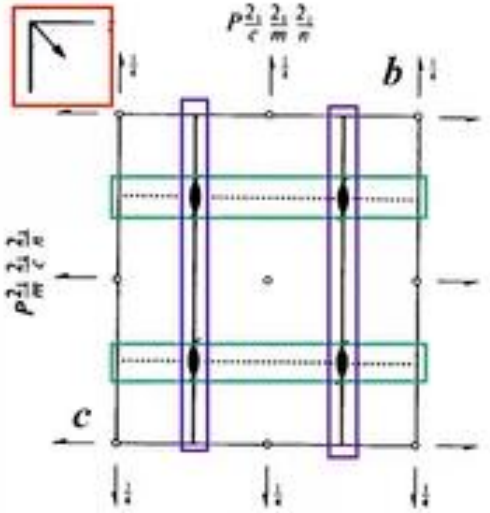
P 2_1/n 2_1/m 2_1/a

- 2_1 screw axis parallel to the a-axis + n-glide plane ⊥ to the a-axis
- 2_1 screw axis parallel to the b-axis + mirror plane ⊥ to the b-axis
- 2_1 screw axis parallel to the c-axis + a-glide plane ⊥ to the c-axis

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

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





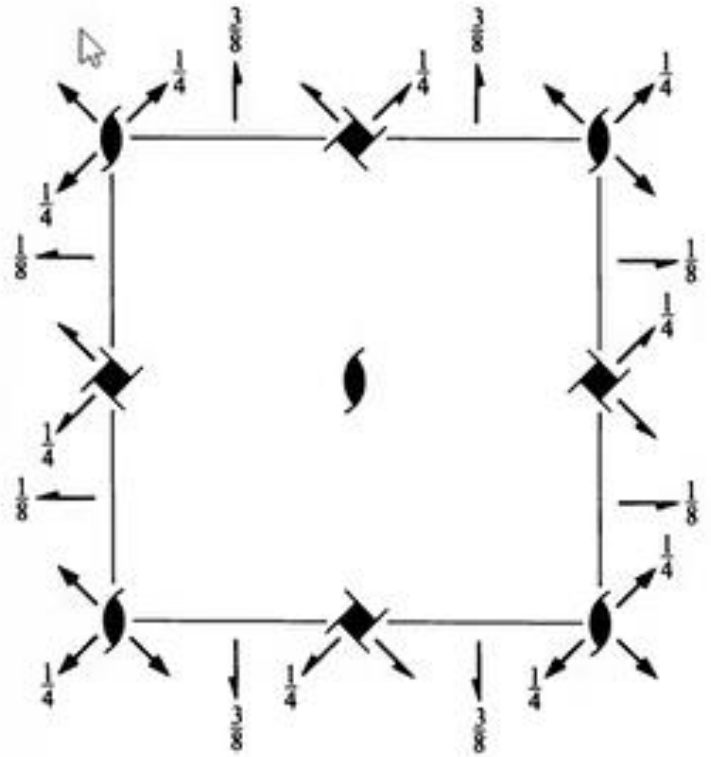
P 2_1/n 2_1/m 2_1/a

- 2_1 screw axis parallel to the a-axis + n-glide plane ⊥ to the a-axis
- 2_1 screw axis parallel to the b-axis + mirror plane ⊥ to the b-axis
- 2_1 screw axis parallel to the c-axis + a-glide plane ⊥ to the c-axis

Space Group Notation by Crystal System

		Crystal axis referred to by symmetry labels			
Crystal System	**Short Space Group Name***	**1st position (s_1)**	**2nd position (s_2)**	**3rd position (s_3)**	**Examples**
Triclinic	$P1$ *or* $P\bar{1}$	---	---	---	$P1, P\bar{1}$
Monoclinic	$\mathbf{L}s_1$	*b* axis			$P2_1$ $C\,2/c$
Orthorhombic	$\mathbf{L}s_1s_2s_3$	*a*-axis	*b*-axis	*c*-axis	$Pnma$ $Cmc2_1$
Tetragonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 4**	*a*- and *b*-axes	*ab* face diagonals	$P\bar{4}2_1m$ $I\,4/m$
Trigonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 3**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P31c$ $R3$
Hexagonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 6**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P\,6_3/mmc$ $P6_4$
Cubic	$\mathbf{L}s_1s_2s_3$	*a*-, *b*- and *c*-axes	body diagonals **contains a 3**	face diagonals	$Pm\bar{3}m$ $Ia\bar{3}$

*L = P (primitive), F (face centered), I (body centered), R (rhombohedral), A, B, C (base centered).
Only symbols shown in bold are present for all space groups in a given crystal system.



Tetragonal

2_1 screw axis parallel to the a- & b-axes, No glides or mirrors ⊥ to these axes

P 4_1 2_1 2

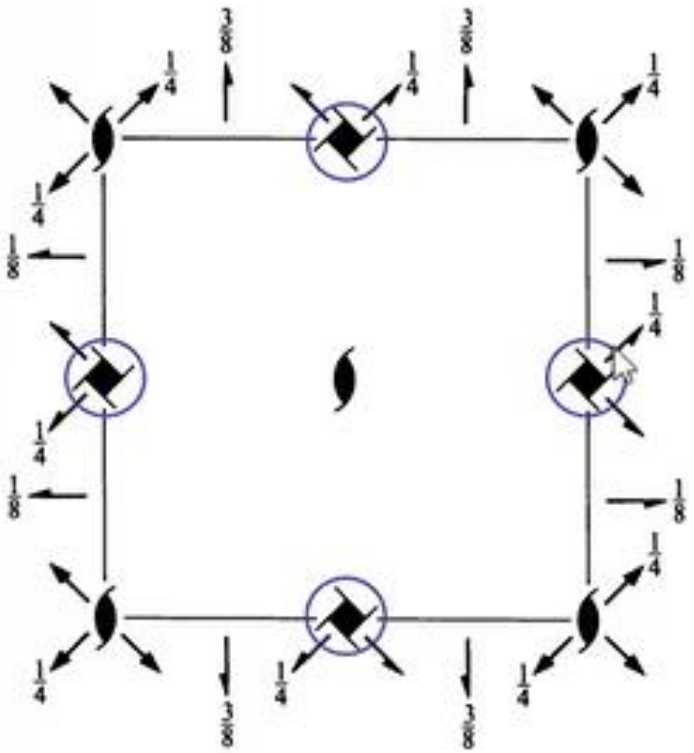
4_1 screw axis parallel to c. No glides or mirrors ⊥ to the c-axis

2-fold axes parallel to the face diagonals in the ab plane No glides or mirrors ⊥ to these axes

Tetragonal

$P\,4_1\,2_1\,2$ $\quad D_4^4$

No. 92 $\quad P\,4_1\,2_1\,2$



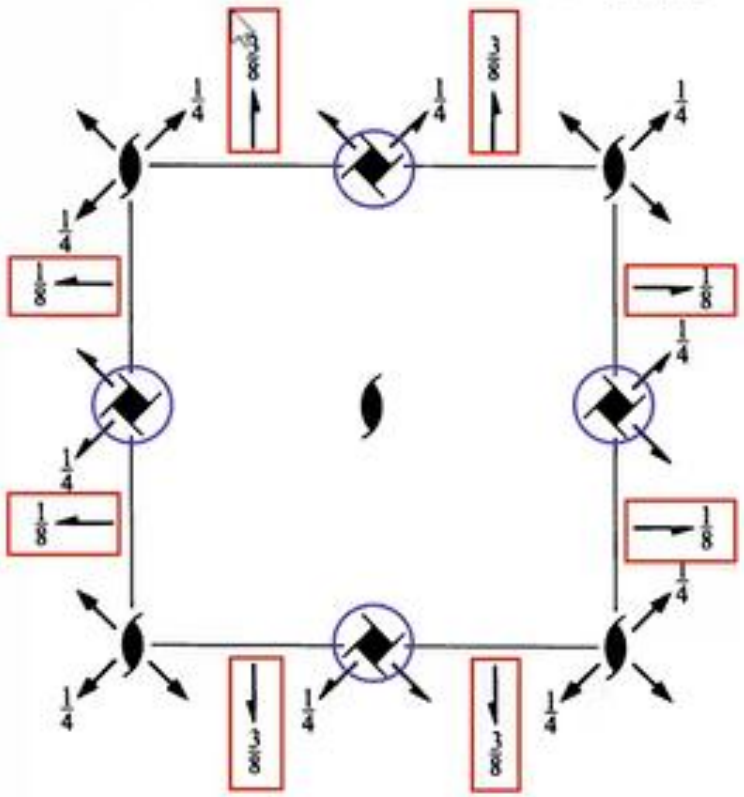
2_1 screw axis parallel to the a- & b-axes, No glides or mirrors $\perp$ to these axes

$P\,4_1\,2_1\,2$

4_1 screw axis parallel to c. No glides or mirrors $\perp$ to the c-axis

2-fold axes parallel to the face diagonals in the ab plane No glides or mirrors $\perp$ to these axes

V escola de verão



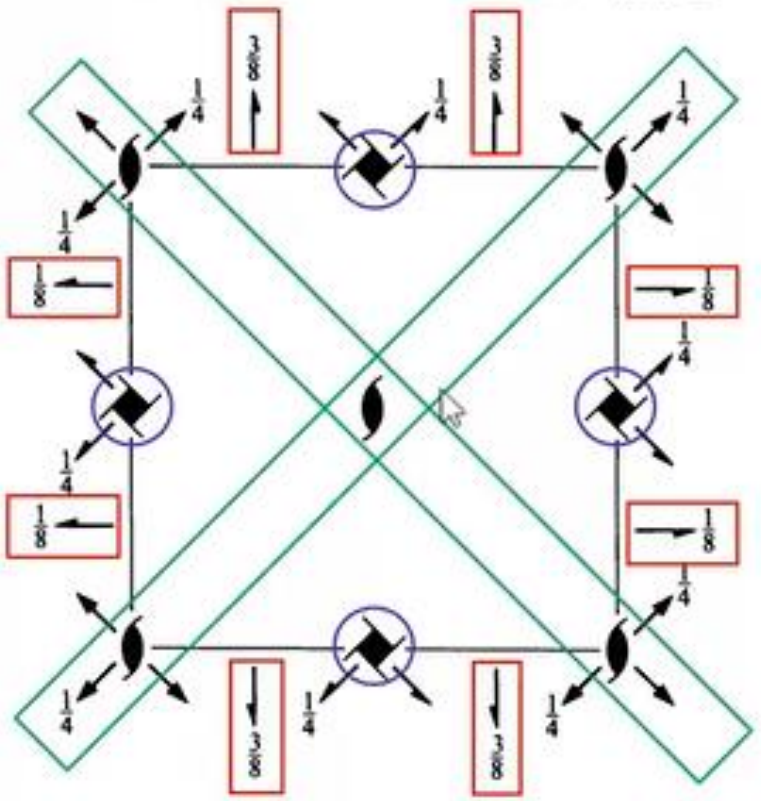
Tetragonal

2_1 screw axis parallel to the a- & b-axes, No glides or mirrors ⊥ to these axes

$P\,4_1\,2_1\,2$

4_1 screw axis parallel to c. No glides or mirrors ⊥ to the c-axis

2-fold axes parallel to the face diagonals in the ab plane No glides or mirrors ⊥ to these axes



Tetragonal

2_1 screw axis parallel to the a- & b-axes, No glides or mirrors ⊥ to these axes

$P\,4_1\,2_1\,2$

4_1 screw axis parallel to c. No glides or mirrors ⊥ to the c-axis

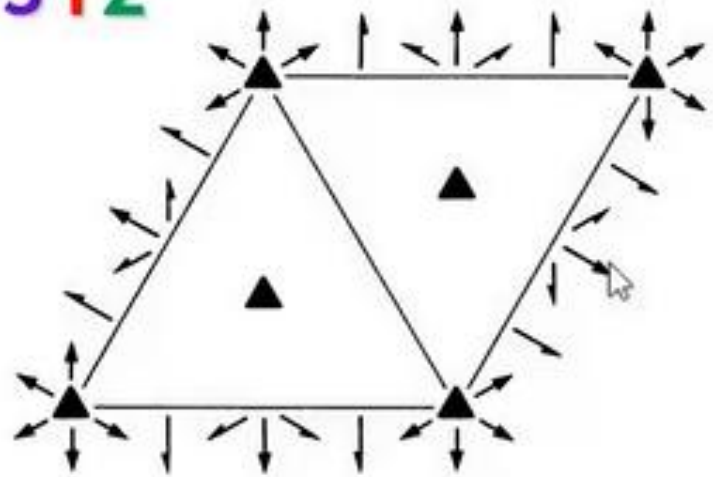
2-fold axes parallel to the face diagonals in the ab plane No glides or mirrors ⊥ to these axes

Space Group Notation by Crystal System

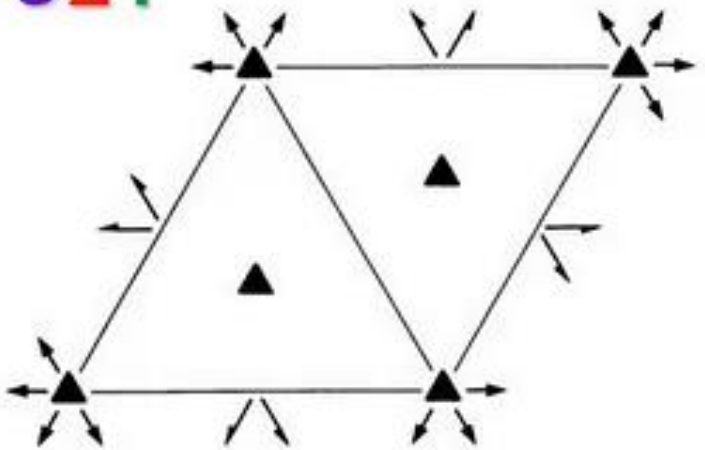
		Crystal axis referred to by symmetry labels			
Crystal System	**Short Space Group Name***	**1st position (s_1)**	**2nd position (s_2)**	**3rd position (s_3)**	**Examples**
Triclinic	$P1$ *or* $P\bar{1}$	---	---	---	$P1, P\bar{1}$
Monoclinic	$\mathbf{L}s_1$	*b* axis			$P2_1$ $C\,2/c$
Orthorhombic	$\mathbf{L}s_1s_2s_3$	*a*-axis	*b*-axis	*c*-axis	$Pnma$ $Cmc2_1$
Tetragonal	$\mathbf{L}s_1s_2s_3$	*c*-axis contains a 4	*a*- and *b*-axes	*ab* face diagonals	$P\bar{4}2_1m$ $I4/m$
Trigonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 3**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P31c$ $R3$
Hexagonal	$\mathbf{L}s_1s_2s_3$	*c*-axis **contains a 6**	*a*- and *b*-axes	in-plane ⊥ to *a*- and *b*-axes	$P\,6_3/mmc$ $P6_4$
Cubic	$\mathbf{L}s_1s_2s_3$	*a*-, *b*- and *c*-axes	body diagonals **contains a 3**	face diagonals	$Pm\bar{3}m$ $Ia\bar{3}$

*L = *P* (primitive), *F* (face centered), *I* (body centered), *R* (rhombohedral), *A*, *B*, *C* (base centered).
Only symbols shown in bold are present for all space groups in a given crystal system.

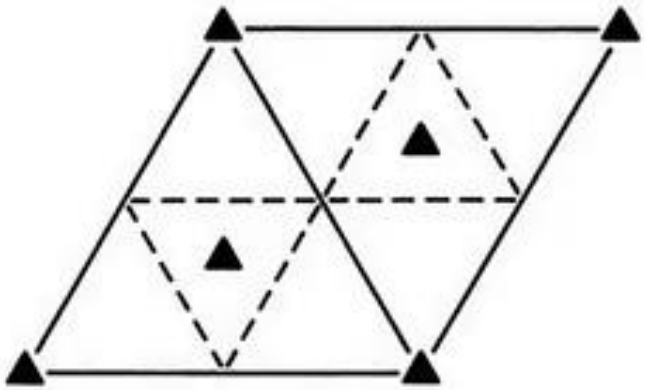
P312



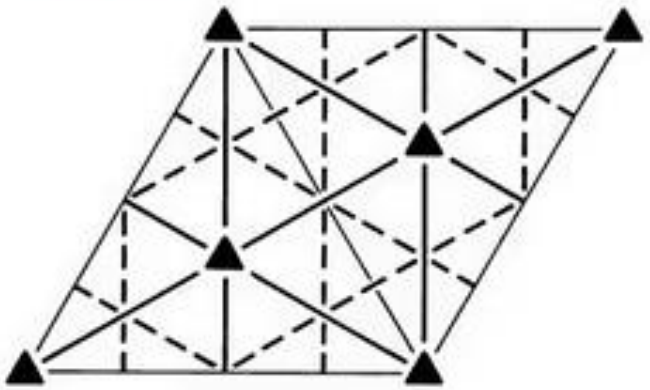
P321

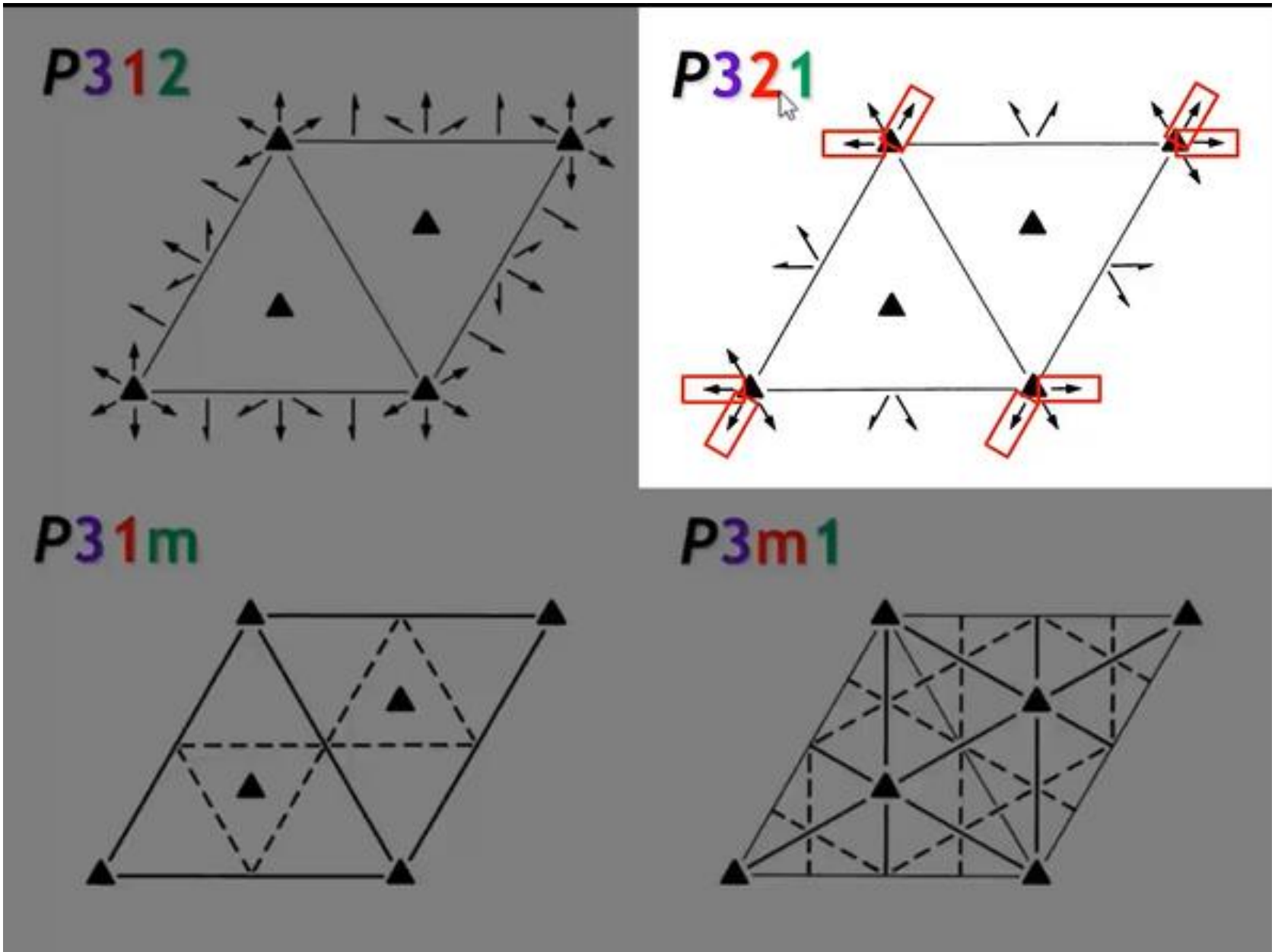


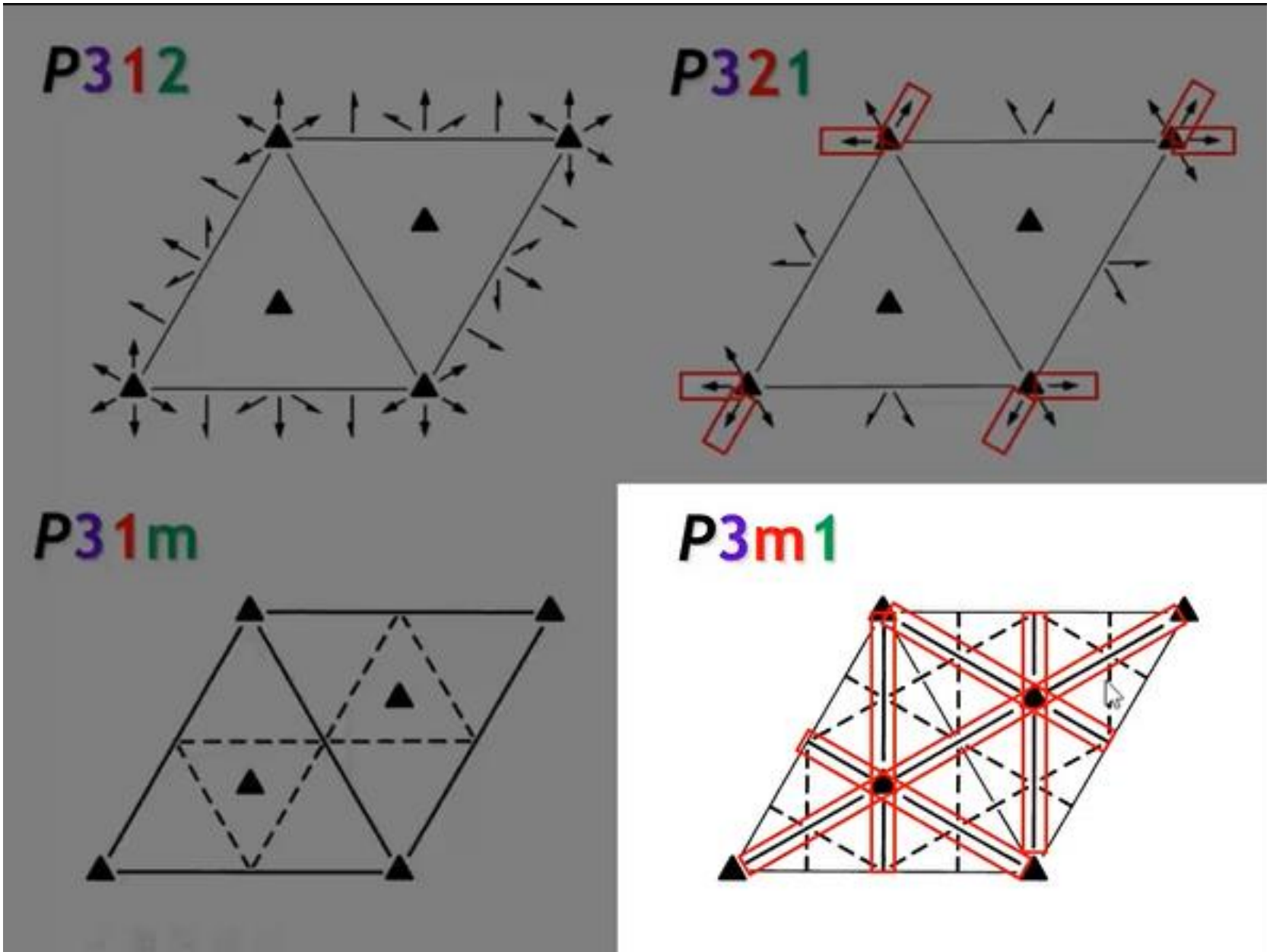
P31m



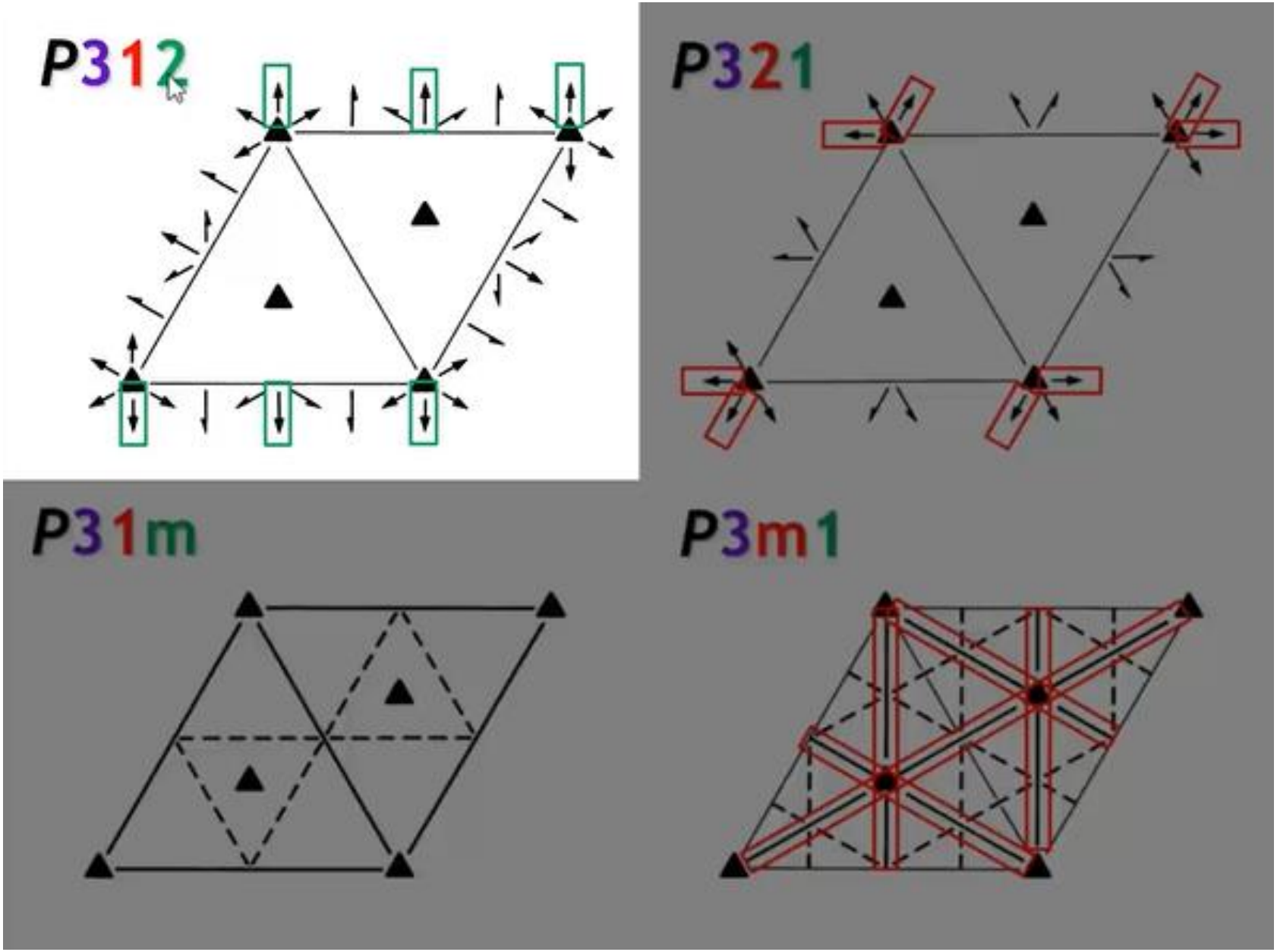
P3m1




P312
P321
P31m
P3m1


P312
P321
P31m
P3m1

V escola de verão



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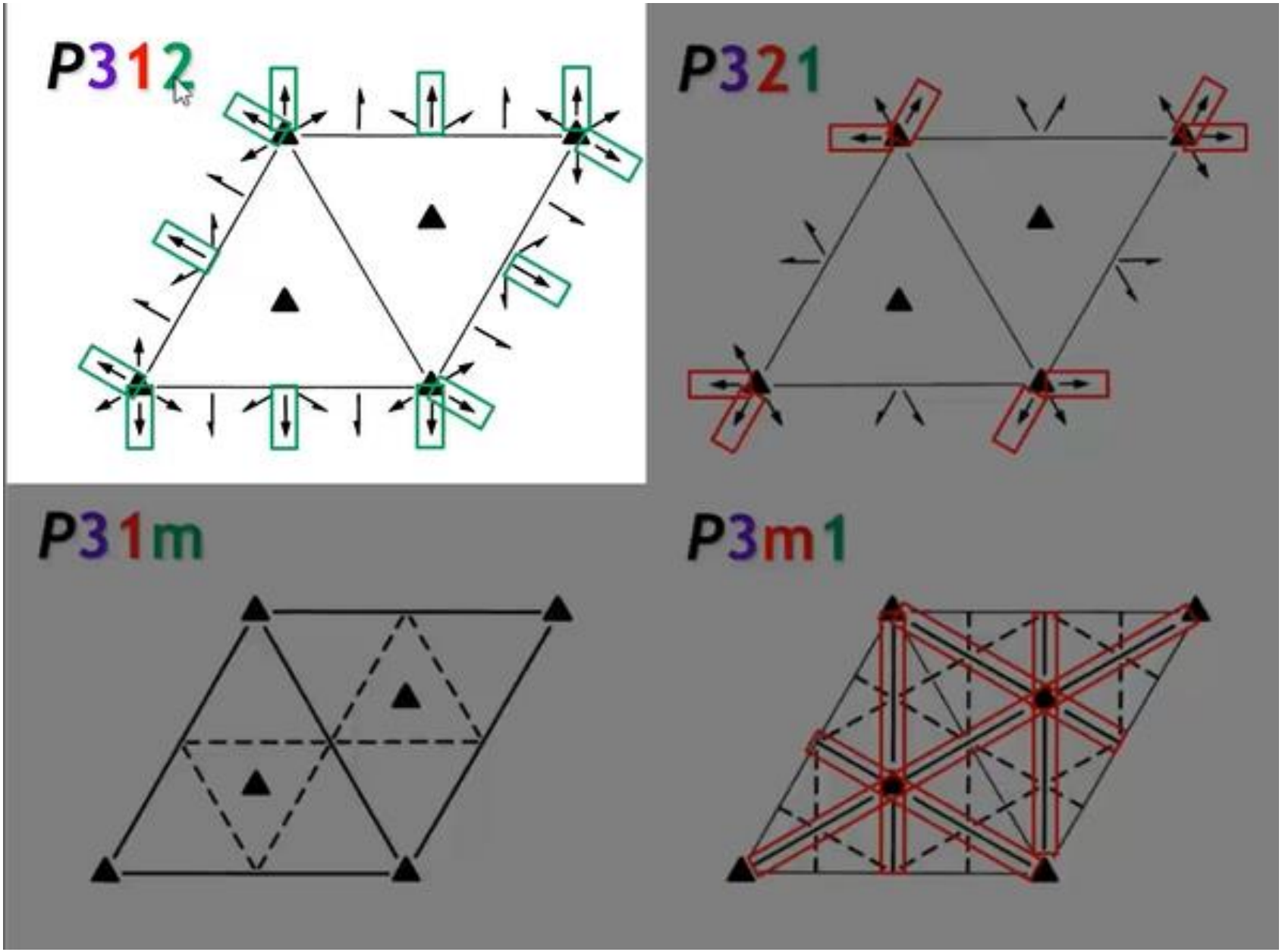

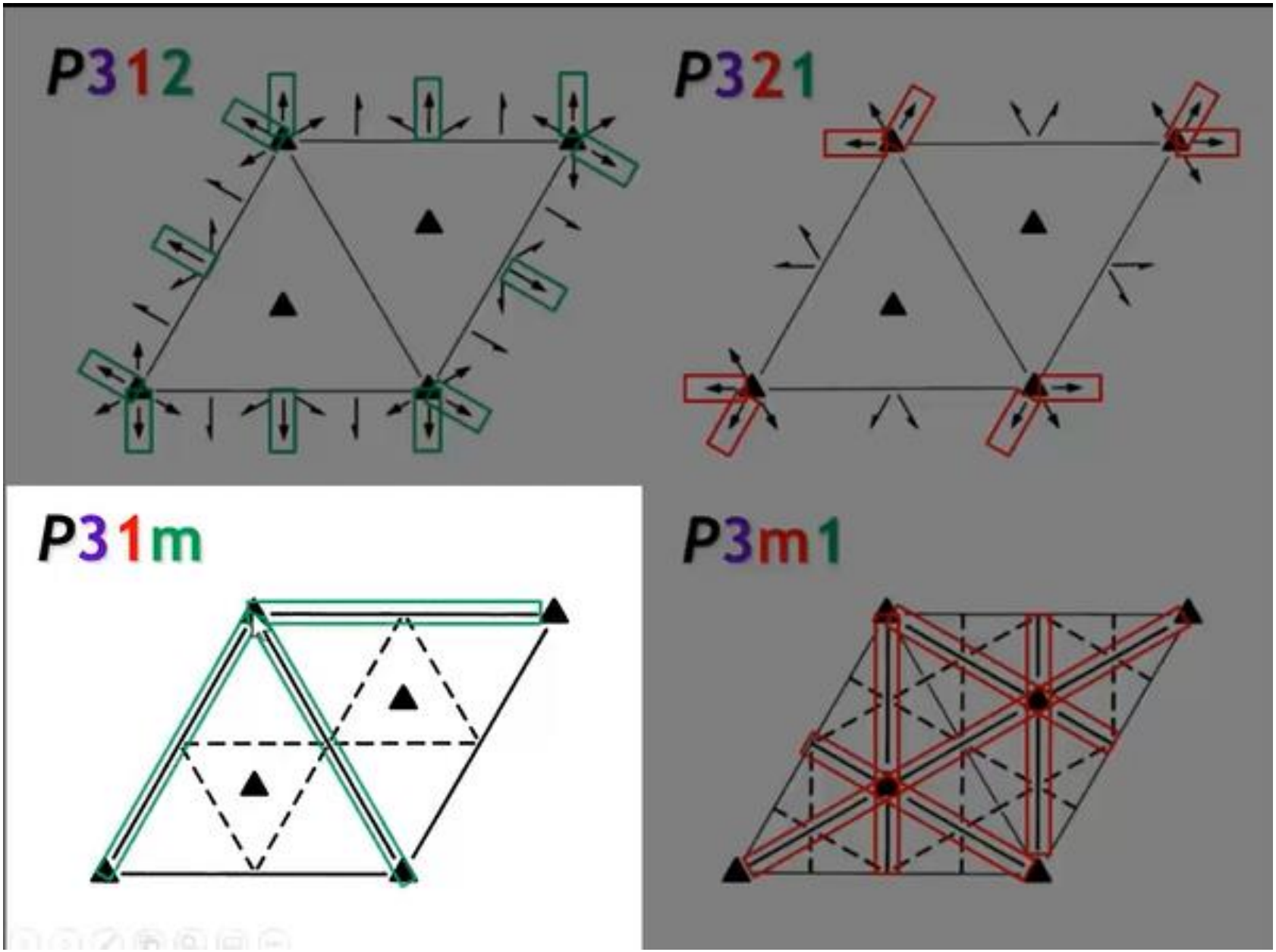
P312
P321
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Orthorhombic	$\mathbf{L}s_1\mathbf{s_2}\mathbf{s_3}$	*a*-axis	*b*-axis	*c*-axis	$Pnma$ $Cmc2_1$
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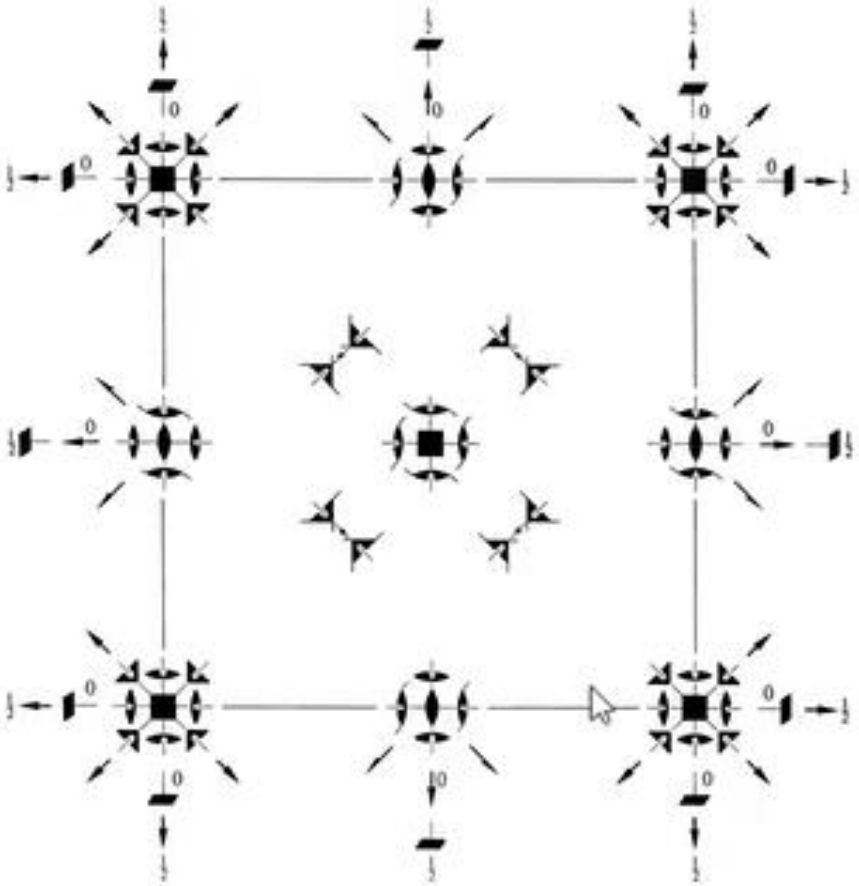
Cubic	$\mathbf{L}s_1\mathbf{s_2}s_3$	*a*-, *b*- and *c*-axes	body diagonals **contains a 3**	face diagonals	$Pm\bar{3}m$ $Ia\bar{3}$

*L = P (primitive), F (face centered), I (body centered), R (rhombohedral), A, B, C (base centered).
Only symbols shown in bold are present for all space groups in a given crystal system.

Cubic



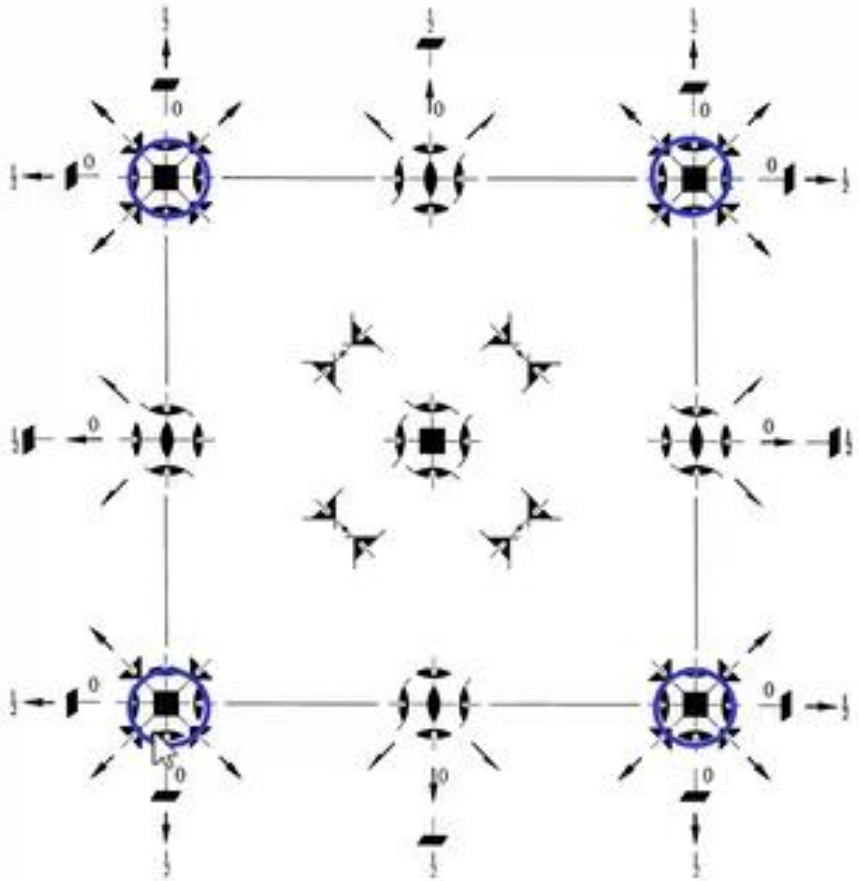
3-fold axis parallel to body diagonals

P432

4-fold axis parallel to *a*,*b*,*c*

2-fold axes parallel to the face diagonals

Cubic



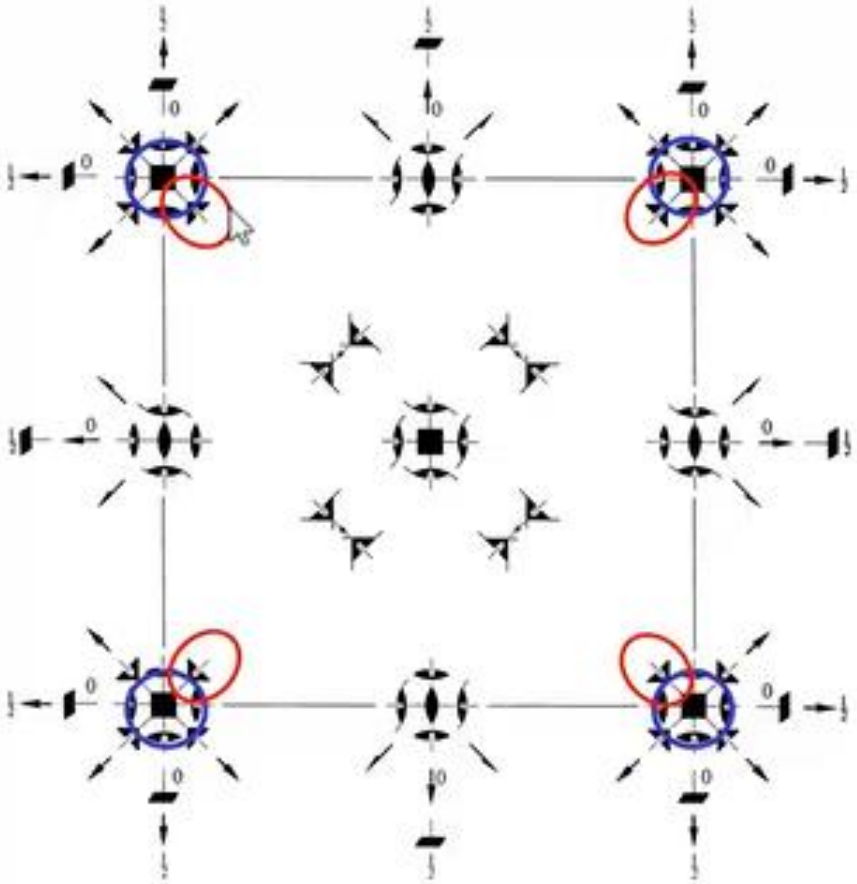
3-fold axis parallel to body diagonals

P432

4-fold axis parallel to *a*,*b*,*c*

2-fold axes parallel to the face diagonals

Cubic



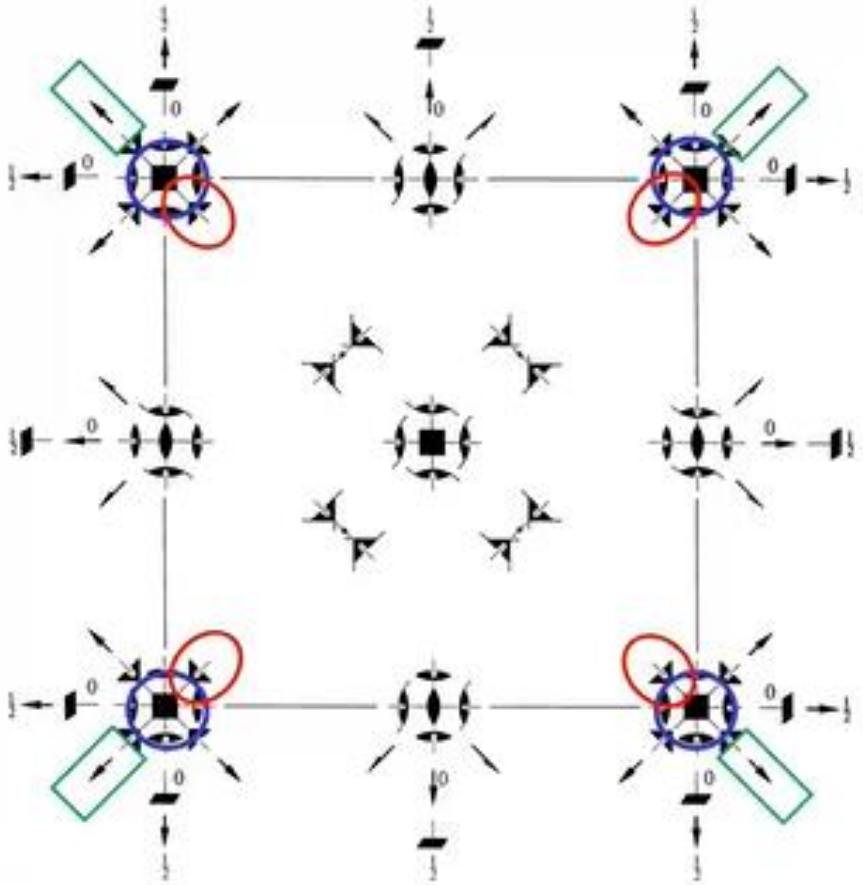
3-fold axis parallel to body diagonals

P432

4-fold axis parallel to *a*,*b*,*c*

2-fold axes parallel to the face diagonals

Cubic



3-fold axis parallel to body diagonals

P432

4-fold axis parallel to *a*,*b*,*c*

2-fold axes parallel to the face diagonals

Name the crystal system, Bravais lattice and point group from the following short Hermann-Mauguin space group symbols.

Pmma

$I4_1/a$

Name the crystal system, Bravais lattice and point group from the following short Hermann-Mauguin space group symbols.

Pmma

Crystal system: *orthorhombic*
Bravais lattice: *primitive orthorhombic*
Point group: *mmm* (D_{2h})
nonsymmorphic space group

$I4_1/a$

Name the crystal system, Bravais lattice and point group from the following short Hermann-Mauguin space group symbols.

Pmma

Crystal system: *orthorhombic*
Bravais lattice: *primitive orthorhombic*
Point group: *mmm* (D_{2h})
nonsymmorphic space group

$I4_1/a$

Crystal system: *tetragonal*
Bravais lattice: *body centered tetragonal*
Point group: $4/m$ (C_{4h})
nonsymmorphic space group

Name the crystal system, Bravais lattice, and point group from the following short Hermann-Mauguin space group symbols.

Iba2

I23

Name the crystal system, Bravais lattice, and point group from the following short Hermann-Mauguin space group symbols.

Iba2

Crystal system: *orthorhombic*
Bravais lattice: *body centered orthorhombic*
Point group: 2mm (C_{2v})
nonsymmorphic space group

*I*23

Name the crystal system, Bravais lattice, and point group from the following short Hermann-Mauguin space group symbols.

Iba2

Crystal system: *orthorhombic*
Bravais lattice: *body centered orthorhombic*
Point group: 2mm (C_{2v})
nonsymmorphic space group

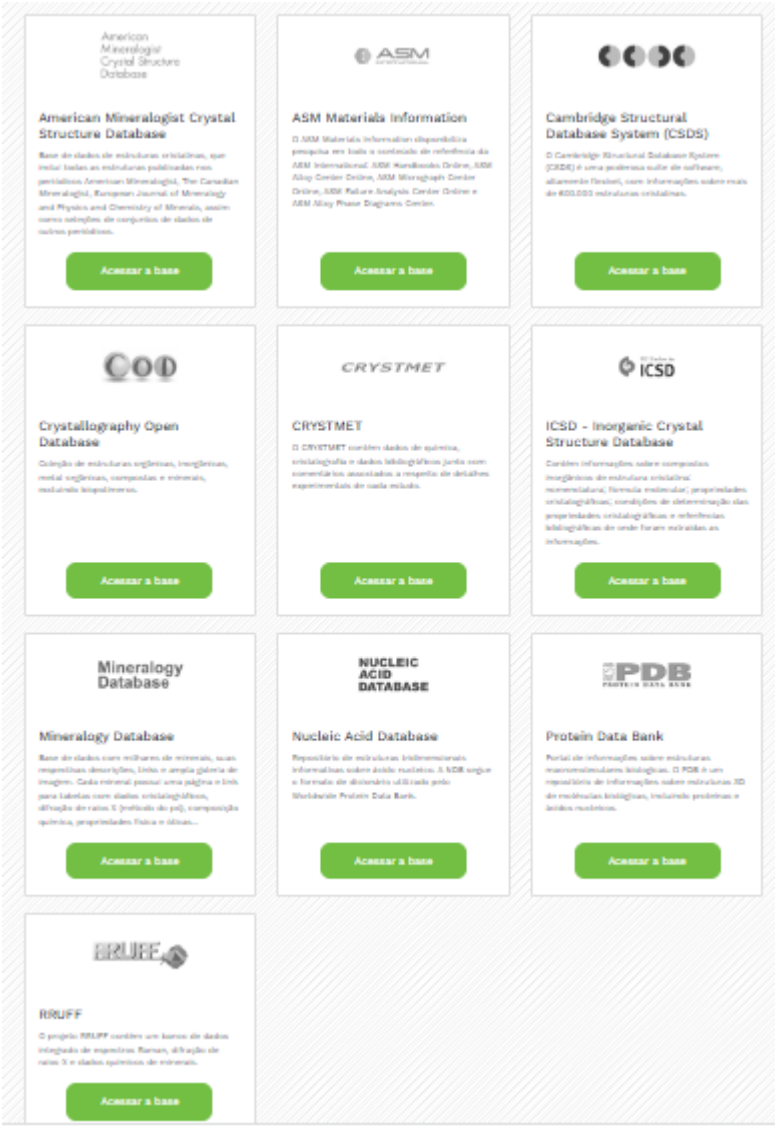
*I*23

Crystal system: *cubic*
Bravais lattice: *body centered cubic*
Point group: 23 (T)
symmorphic space group

Simetria de grupos Espaciais e a Estrutura de cristais iônicos e metálicos

Frequentemente adotam grupos de alta simetria

V escola de verão



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Crystal Structure Databases

- Inorganic Crystal Structure Database (ICSD)
  - www.fiz-Karlsruhe.de/icsd.html
- Cambridge Structural Database (CSD)
  - www.ccdc.cam.ac.uk
- Protein Data Bank (PDB)
  - www.rcsb.org/pdb







V escola de verão



Frequencies of Space Groups

Crystal System	Number of Space Groups	% organic structures	% inorganic structures	% protein structures
Triclinic	2	24%	4%	4%
Monoclinic	13	53%	17%	25%
Orthorhombic	59	18%	21%	37%
Tetragonal	68	2.2%	15%	13%
Trigonal	25	1.7%	10%	12%
Hexagonal	27	0.5%	11%	8%
Cubic	36	0.4%	22%	1.6%

Most Common Inorganic Space Groups

Space Group	Crystal System	% organic structures
$P2_1/c$	Monoclinic	6.7%
$Fm\text{-}3m$	Cubic	5.6%
$Fd\text{-}3m$	Cubic	5.4%
$Pnma$	Orthorhombic	5.4%
$I4/mmm$	Tetragonal	4.2%
$P\text{-}1$	Triclinic	3.7%

- These six space groups account for 31% of all inorganic crystal structures (much more variety than seen for organics).
- Efficient packing of spherical objects (atoms, ions) favors high symmetry structures that often contain mirror planes and rotation axes.

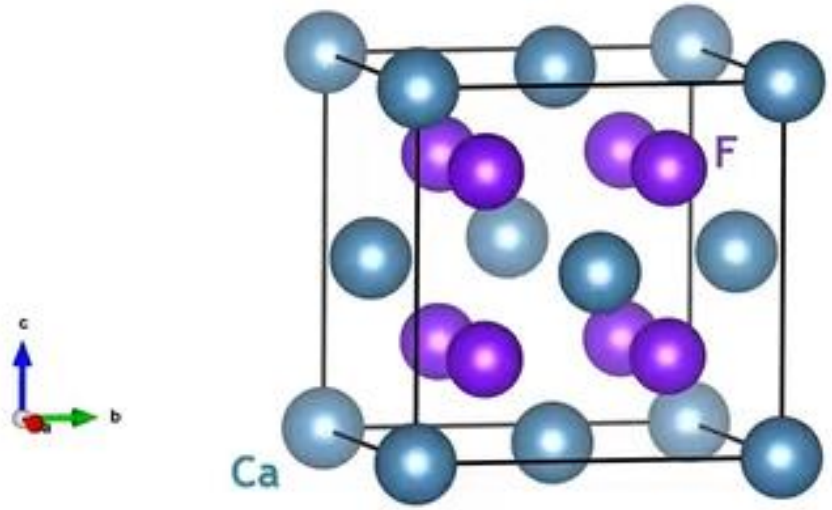
Representing Crystal Structures

Examples of crystal structure visualization programs

- Vesta (Freeware)
  - https://jp-minerals.org/vesta/en/
- Diamond
  - https://www.crystalimpact.com/diamond/
- CrystalMaker
  - http://www.crystalmaker.com/

V escola de verão

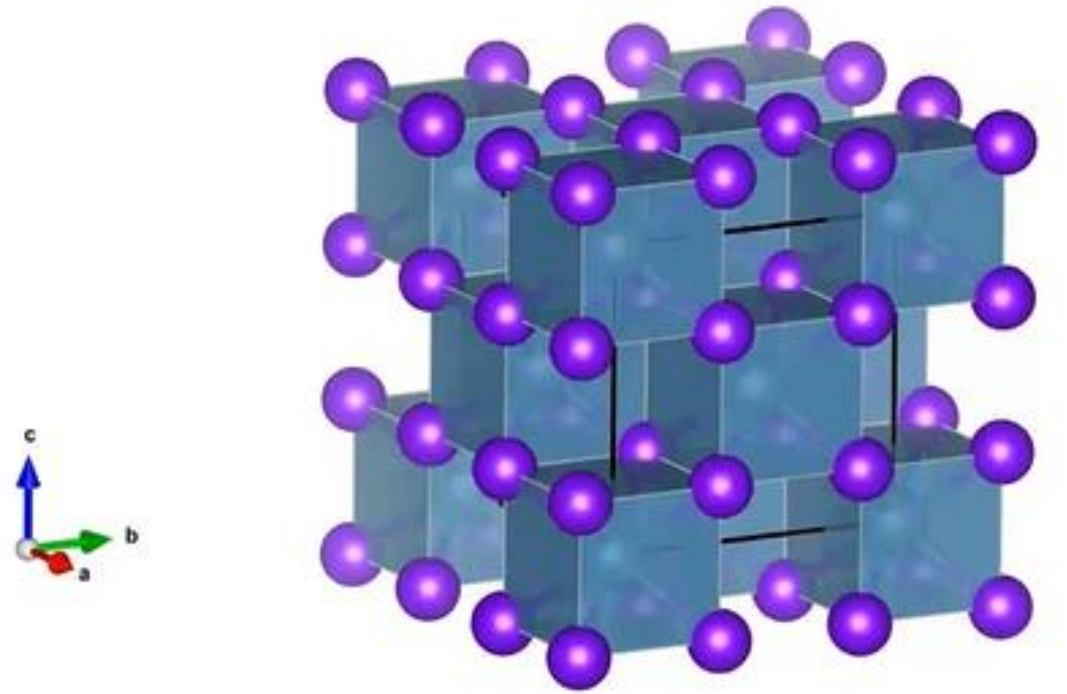
Space Group:	$Fm\bar{3}m$ (#225)			
Lattice parameters:	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Ca (4a)	0,0,0	½,½,0	½,0,½	0,½,½
F (8c)	¼,¼,¼	¾,¾,¼	¾,¼,¾	¼,¾,¾
	¼,¼,¾	¾,¾,¾	¾,¼,¼	¼,¾,¼

V escola de verão

Space Group	$Fm\bar{3}m$ (#225)			
Lattice parameters	$a = 5.46$ Å			
Atom	Wyckoff Site	x	y	z
Ca	4a	0	0	0
F	8c	1/4	1/4	1/4



Calculations of Theoretical Density

density = (mass of atoms within unit cell)/(unit cell volume)

From the site multiplicities we see that there are four CaF_2 formula units within the unit cell (Z = 4) → 4 Ca + 8 F

$$FW = (40.08\ \text{g/mol}) + 2(19.00\ \text{g/mol}) = 78.08\ \text{g/mol}$$

$$mass = \frac{Z \times FW}{N_A} = \frac{4 \times (78.08\ \text{g/mol})}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 5.186 \times 10^{-22}\ \text{g}$$

$$volume = (5.46 \times 10^{-8}\ \text{cm})^3 = 1.628 \times 10^{-22}\ \text{cm}^3$$

$$density = \frac{mass}{volume} = \frac{5.186 \times 10^{-22}\ \text{g}}{1.628 \times 10^{-22}\ \text{cm}^3} = 3.19\ \text{g/cm}^3$$

Unit Cell Volume Formulas

Cubic: $V = a^3$

Tetragonal: $V = a^2c$

Orthorhombic: $V = abc$

Trigonal/Hexagonal: $V = a^2c[\sin(60°)]$

Monoclinic: $V = abc[\sin(\beta)]$

Triclinic:

$$V = abc[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2(\cos\alpha \cdot \cos\beta \cdot \cos\gamma)]^{1/2}$$

Calculating Z

As we will see often times we will want to work backwards from the density and unit cell dimensions to calculate the number of formula units per unit cell, *Z*.

$$\rho = \frac{mass}{volume}$$

$$\rho = \frac{(FW \times Z)/N_A}{V_{cell}}$$

$$Z = \frac{V_{cell} \times \rho \times N_A}{FW}$$

The formula weight (*FW*) can be calculated from the empirical formula, and V_{cell} can be determined from a diffraction experiment. This allows us to calculate *Z* from the density, ρ.

Constraints Imposed by Space Group Symmetry

Let's say we are given the following experimentally determined parameters

Empirical Formula: $ZnCr_2O_4$

Space Group: $Fd\bar{3}m$

Unit cell parameters: a = 8.327 Å

Density: ρ = 5.4 g/cm^3

What can you say about the structure of this compound? Can we determine the occupied Wyckoff sites from this data? Can we fully determine the structure?

Step 1: Calculate Z

The first step is to determine the number of atoms in the unit cell.

$$V_{cell} = a^3 = \left(8.327\ \text{Å}\right)^3 = (8.327 \times 10^{-8}\ \text{cm})^3 = 5.77 \times 10^{-22}\ \text{cm}^3$$

$$FW = 65.4\frac{g}{mol} + 2\left(52.0\frac{g}{mol}\right) + 4\left(16.0\frac{g}{mol}\right) = 233.4\frac{g}{mol}$$

$$Z = \frac{V_{cell} \times \rho \times N_A}{FW} = \frac{(5.77 \times 10^{-22}\ \text{cm}^3)(5.4\ \text{g/cm}^3)(6.02 \times 10^{23}\ \text{mol}^{-1})}{233.4\ \text{g/mol}}$$

$$Z = 8.04 \approx 8$$

Therefore, the unit cell contains 8 Zn, 16 Cr, and 32 O atoms.

Step 2: Examine Site Multiplicities

Multiliplicity	Wyckoff site	Site symmetry	Coordinates
192	i	1	(x, y, z) ...
96	h	2	(1/8, y, 1/4–y) ...
96	g	m	(x, x, z) ...
48	f	2mm	(x, 0, 0) ...
32	e	3m	(x, x, x) ...
16	d	–3m	(5/8, 5/8, 5/8) ...
16	c	–3m	(1/8, 1/8, 1/8) ...
8	b	–43m	(1/2, 1/2, 1/2) ...
8	a	–43m	(0, 0, 0) ...

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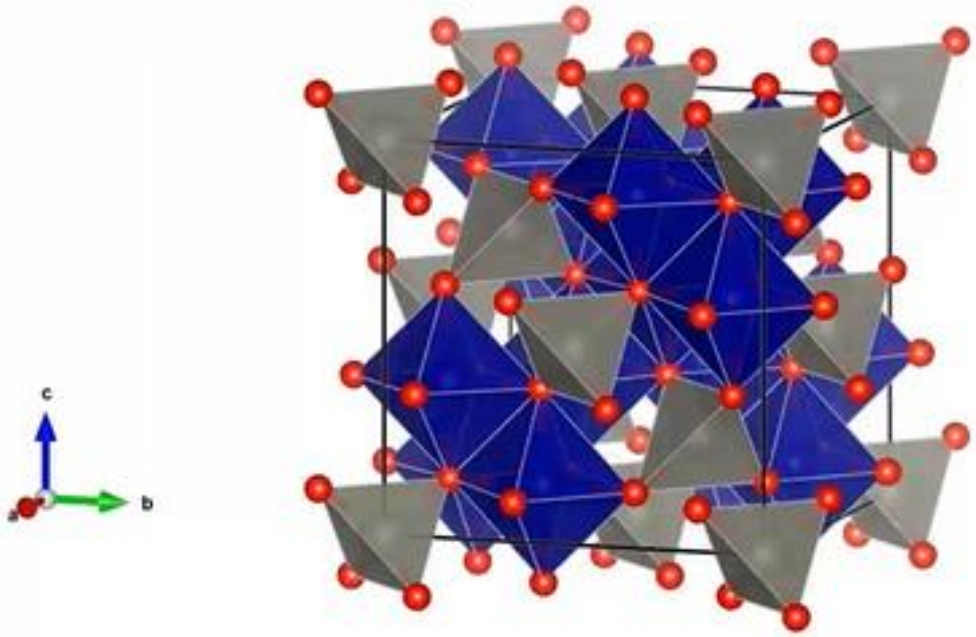
16	d	–3m	(5/8, 5/8, 5/8) ...
16	c	–3m	(1/8, 1/8, 1/8) ...
8	b	–43m	(1/2, 1/2, 1/2) ...
8	a	–43m	(0, 0, 0) ...

Assuming the crystal does not exhibit disorder, we can narrow down the occupied Wyckoff site by considering multiplicities

- Zn sits on either Wyckoff site 8a or 8b
- Cr sits on either Wyckoff site 16c or 16d
- O sits on Wyckoff site 32e

V escola de verão

Space Group	$Fd\bar{3}m$ (#227)			
Lattice parameters	$a = 8.327$ Å			
Atom	Wyckoff Site	x	y	z
Zn	8a	0	0	0
Cr	16d	5/8	5/8	5/8
O	32e	0.3815	0.3815	0.3815



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Trigonal	25	1.7%	10%	12%
Hexagonal	27	0.5%	11%	8%
Cubic	36	0.4%	22%	1.6%

Most Common Organic Space Groups

Space Group	Crystal System	% organic structures
$P2_1/c$	Monoclinic	35%
$P\bar{1}$	Triclinic	23%
$C2/c$	Monoclinic	8%
$P2_12_12_1$	Orthorhombic	8%
$P2_1$	Monoclinic	5%
$Pbca$	Orthorhombic	4%

- These six space groups account for 83% of all organic crystal structures
- Efficient packing of non-spherical objects is best accomplished by inversion, screw and glide operations (not mirrors)

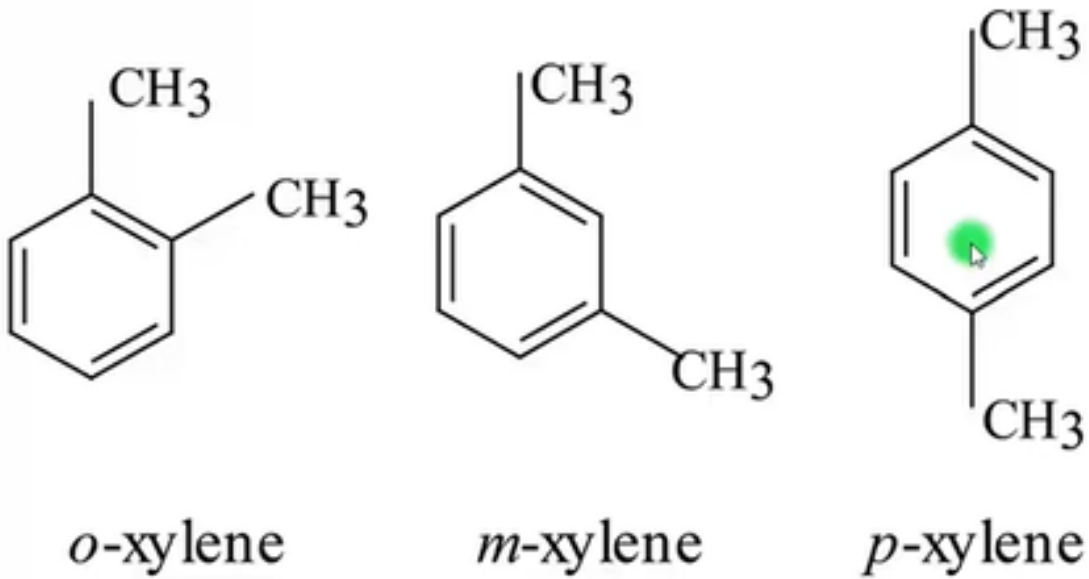
Taken from "X-ray Crystallography" by G. S. Girolami, University Science Books (2016).

Frequencies of Space Group with Point Group 222

Space Group	Structures in CSD†	Structures in ICSD
P222 (#16)	18	13
$P2_122$ (#17)	39	31
$P2_12_12$ (#18)	847	276
$P2_12_12_1$ (#19)	16,256	1862

†Taken from Powder Diffraction Course, Birkbeck College, London
http://pd.chem.ucl.ac.uk/pdnn/symm3/sgpfreq.htm

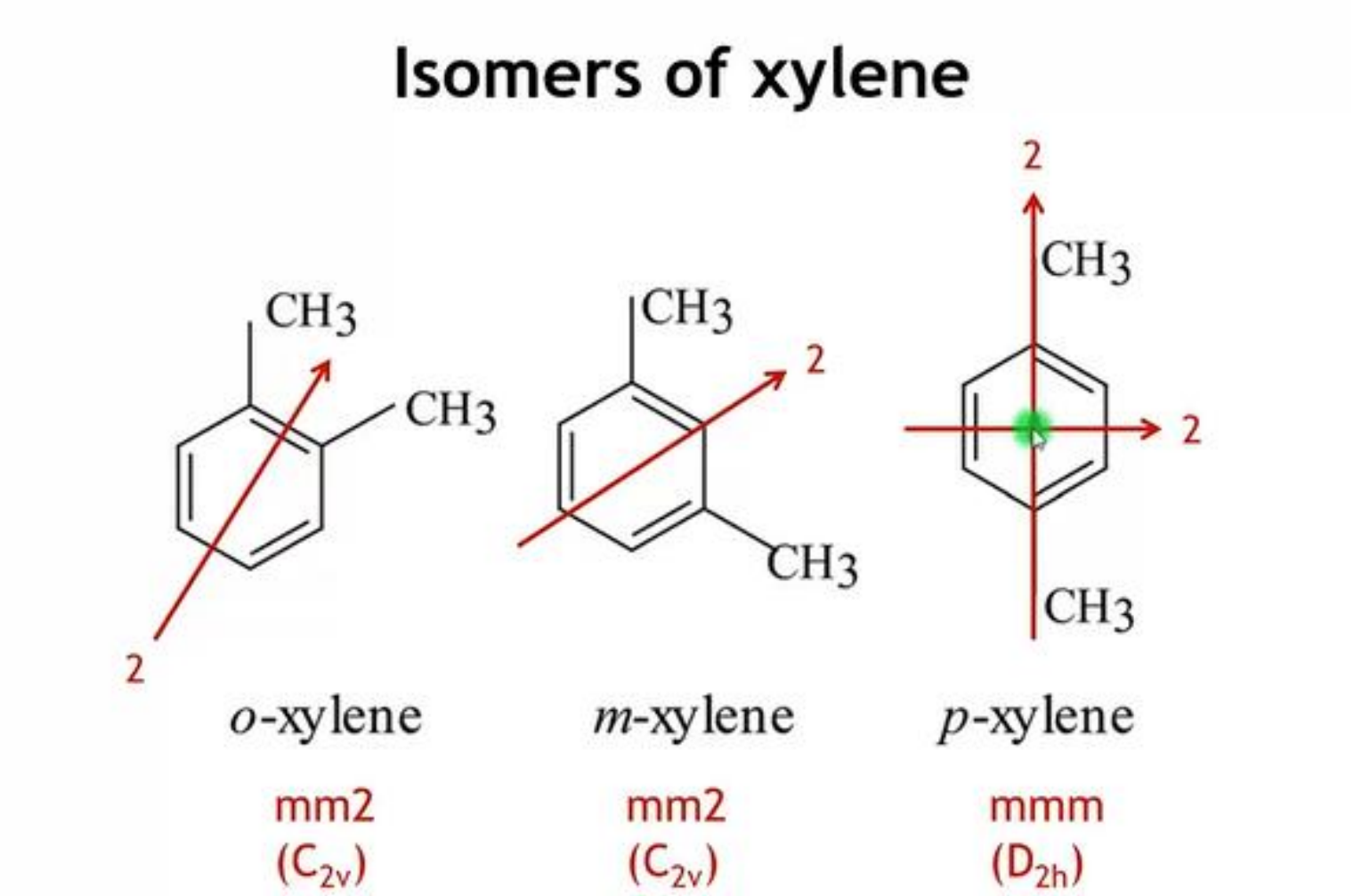
Isomers of xylene



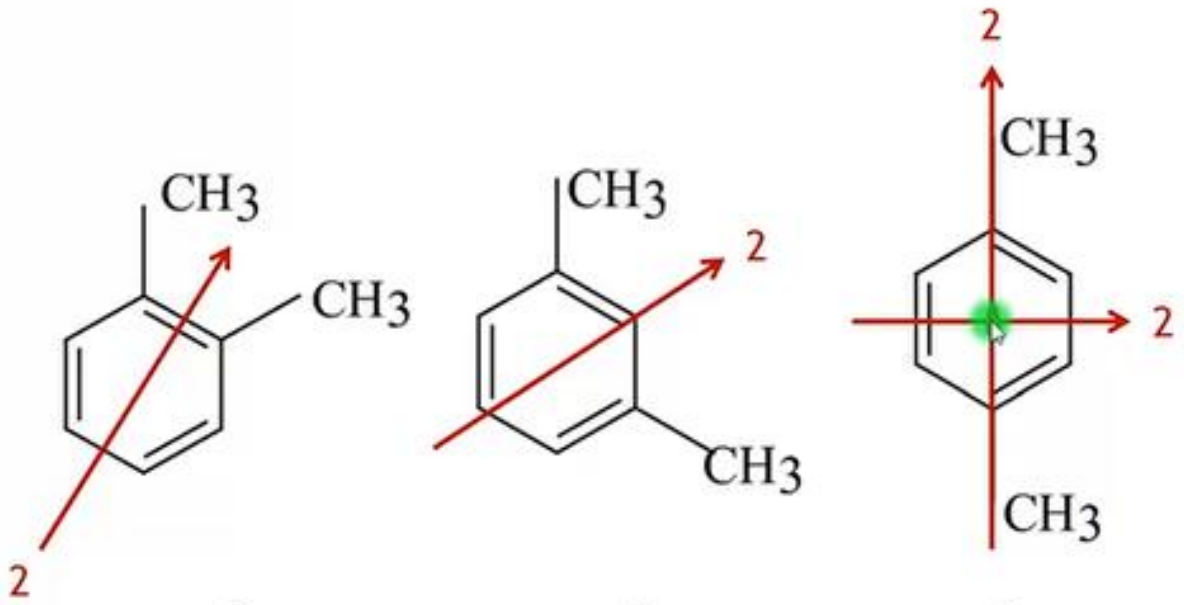
o-xylene *m*-xylene *p*-xylene

What is the point group symmetry of each molecule? Assume free rotation of the methyl groups.

V escola de verão



Isomers of xylene



o-xylene	*m*-xylene	*p*-xylene
mm2 (C_{2v})	mm2 (C_{2v})	mmm (D_{2h})

How do these symmetries relate to the space group symmetries found when these molecules crystallize?

meta-xylene

Space Group: *Pbca*

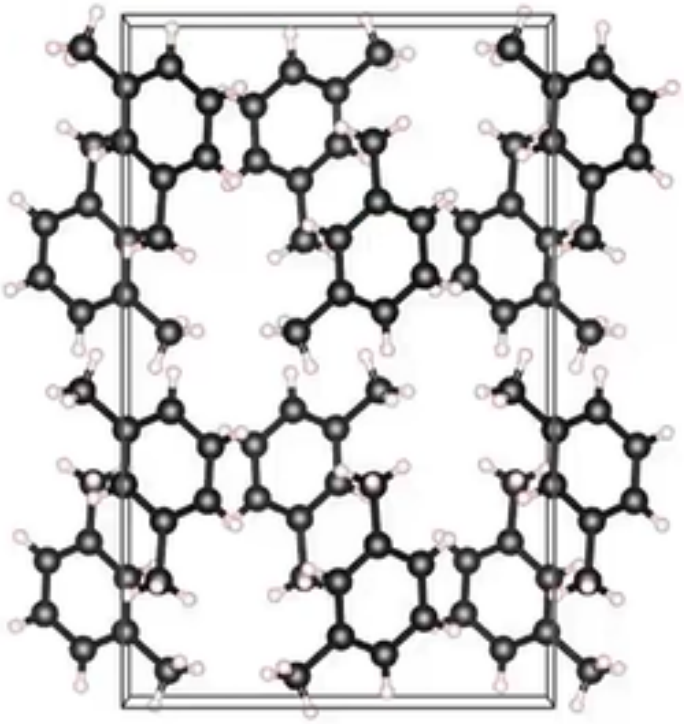
a = 10.516 Å

b = 7.596 Å

c = 16.868 Å

Volume = 1347 Å^3

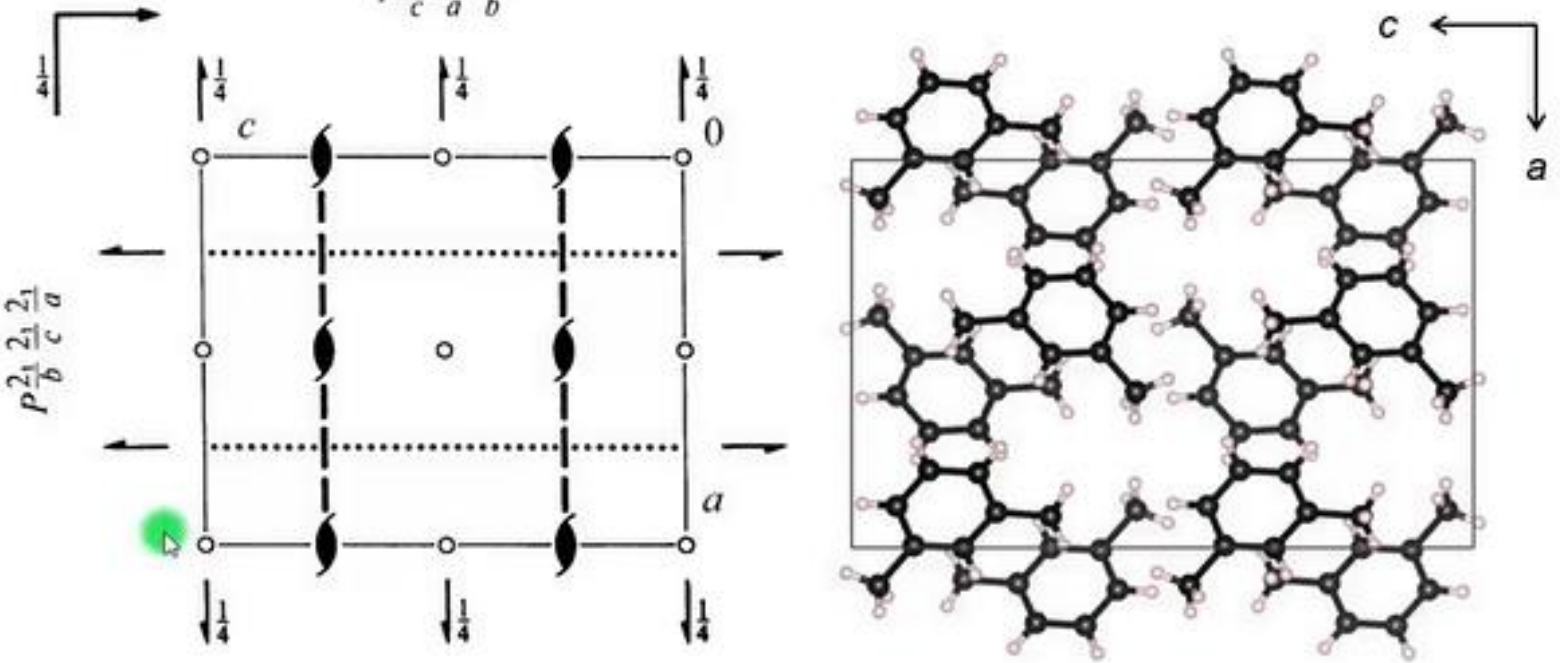
Z = 8 (64 C, 80 H per unit cell)



Ibberson, David, Parsons, Prager, Shankland, *J. Molecular Structure*, **524** (2000), 121-128.

V escola de verão

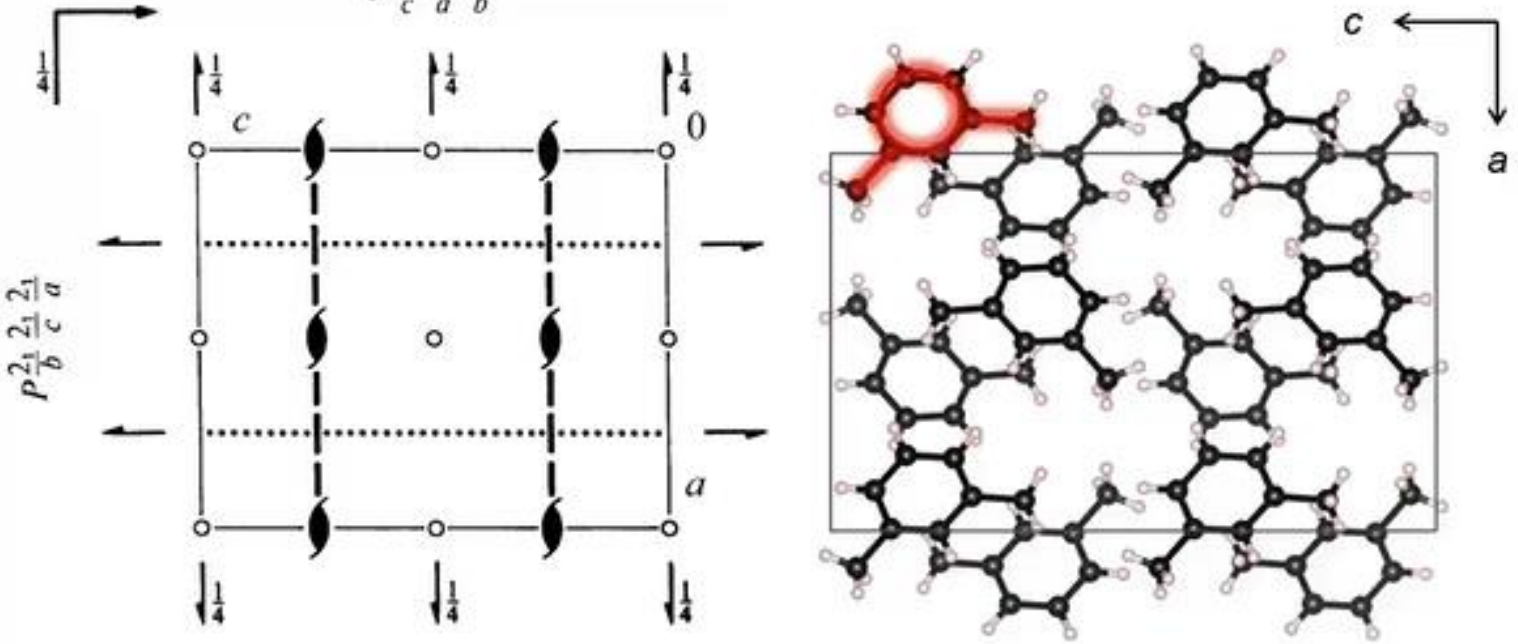
Pbca



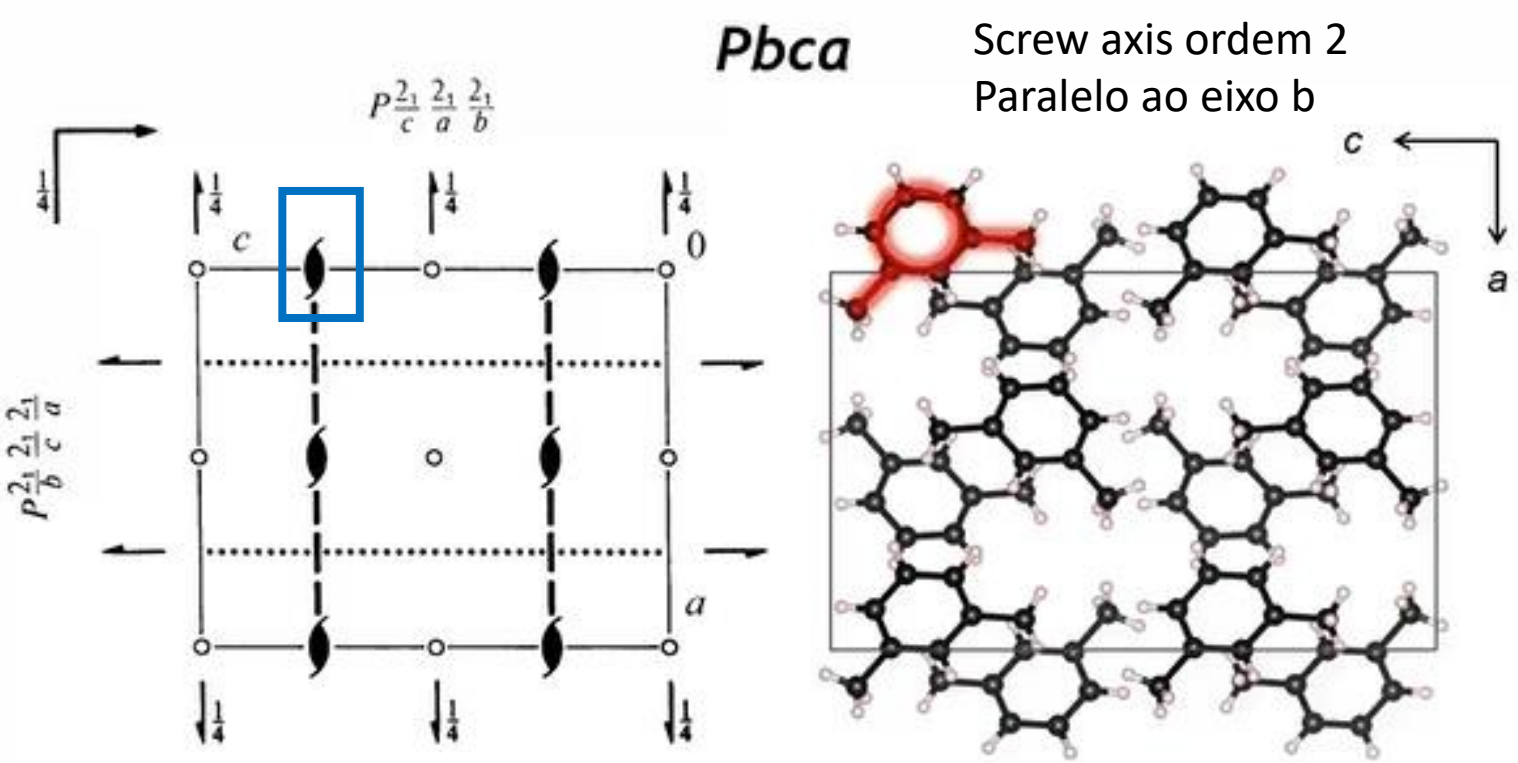
Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

V escola de verão

Pbca



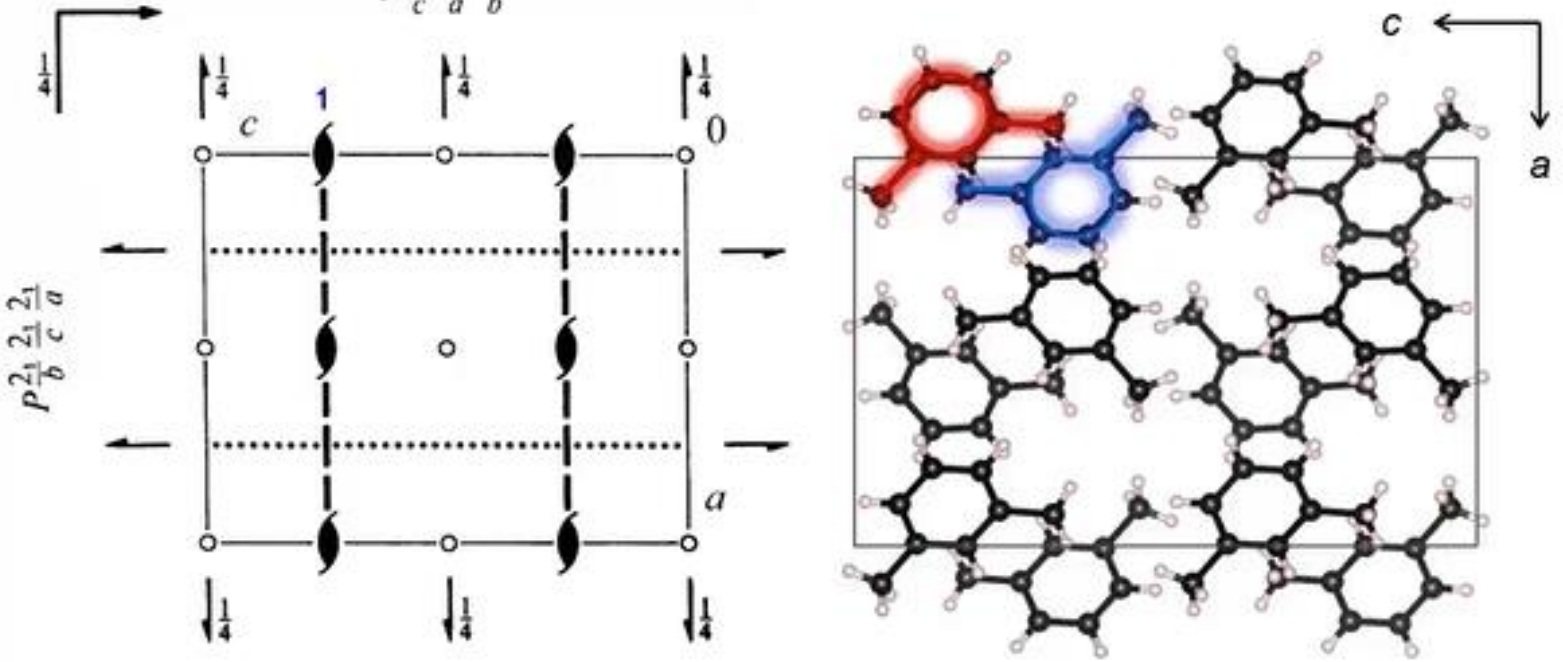
Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)



Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

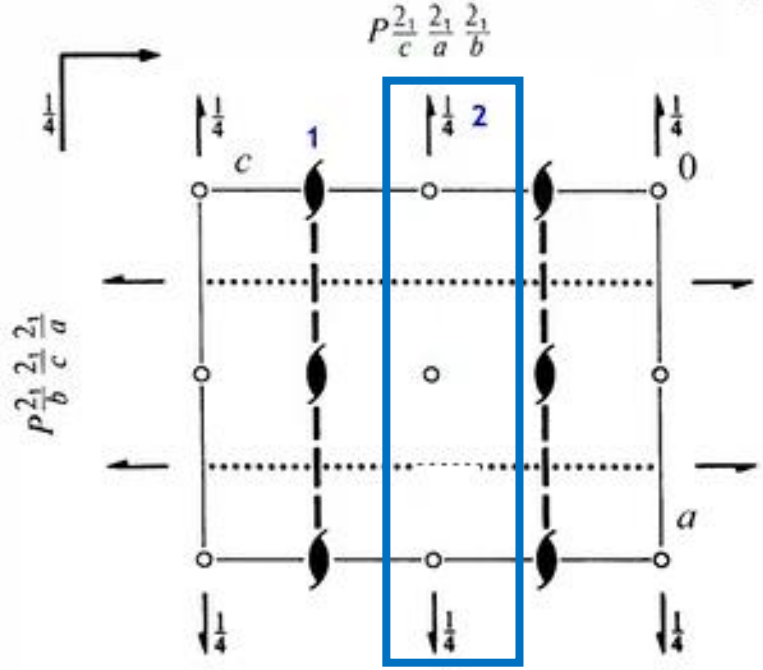
V escola de verão

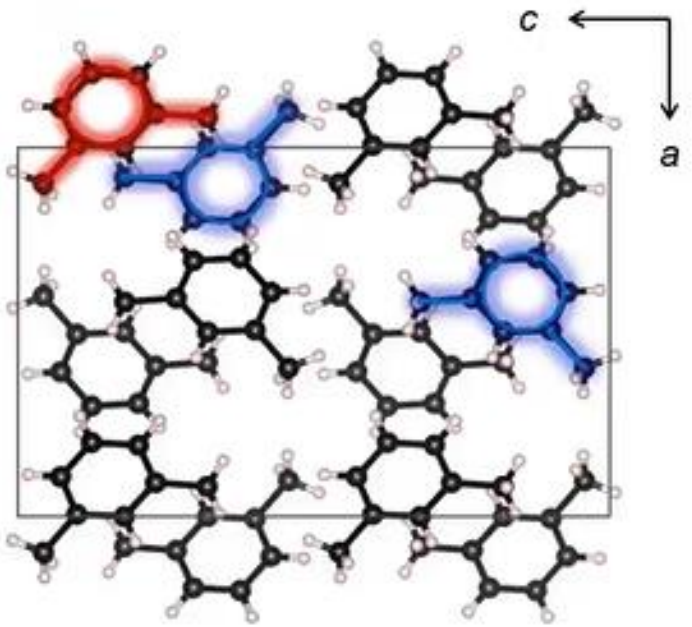
Pbca



Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

Screw axis ordem 2
Paralelo ao eixo a

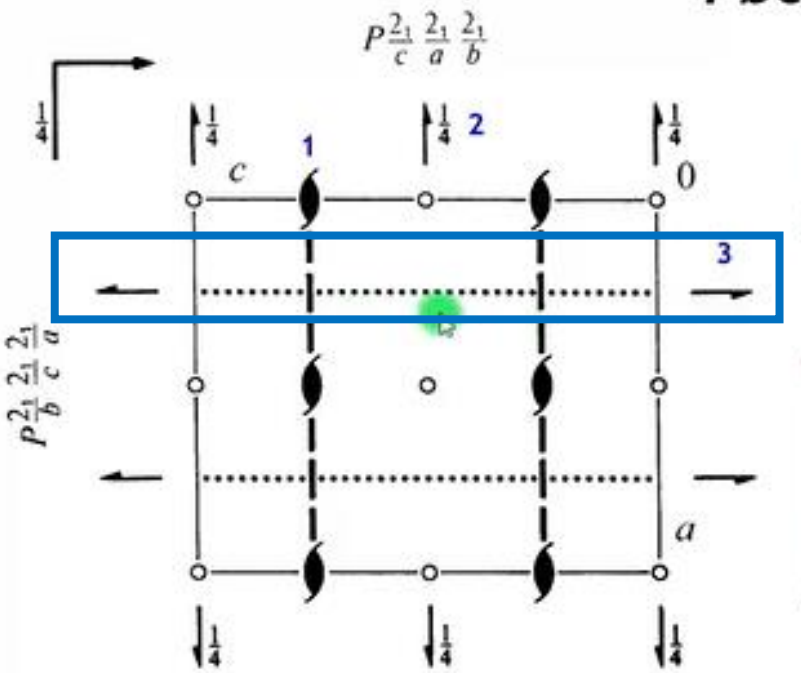


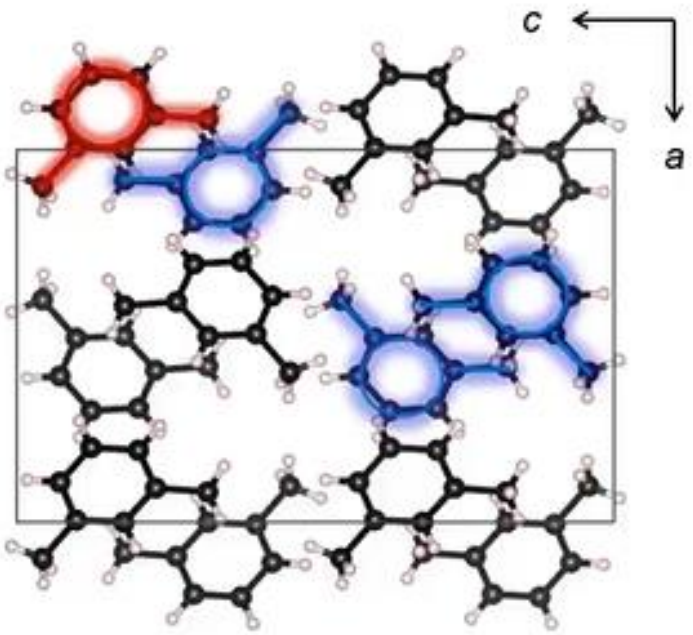


Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

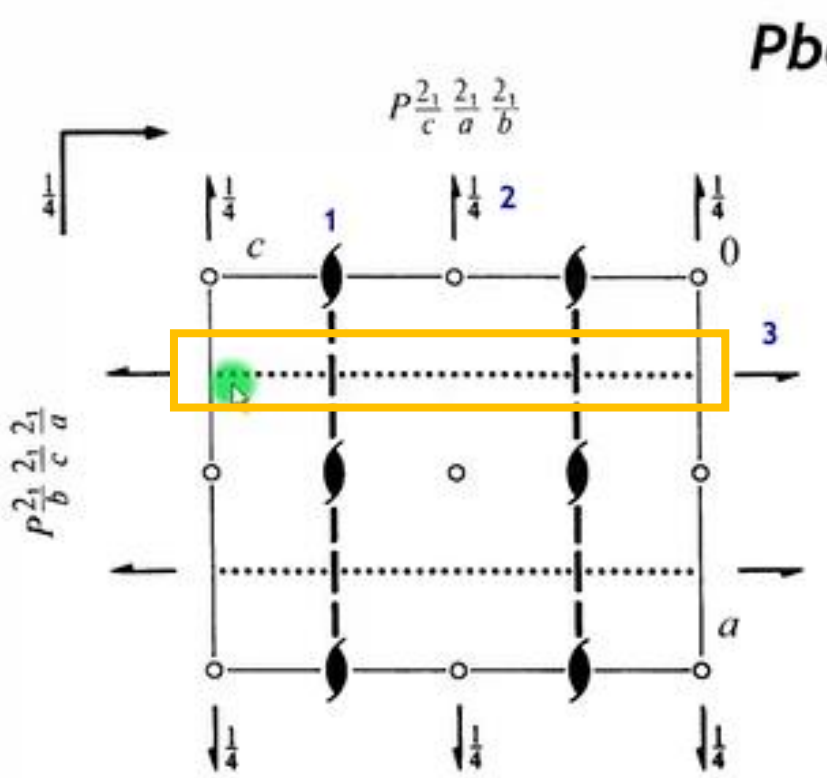
Pbca

Screw axis ordem 2
Paralelo ao eixo c

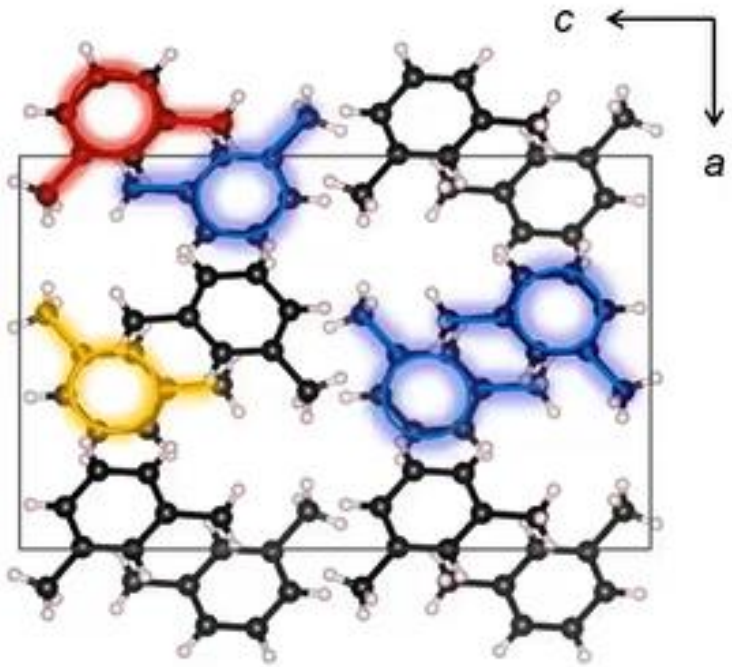




Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)



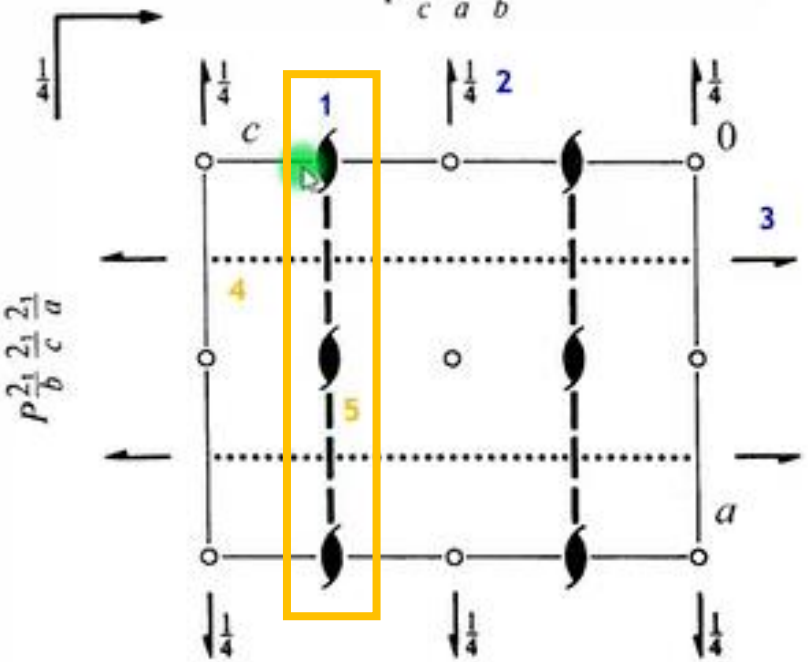
B-glide plane
Perpendicular ao eixo a

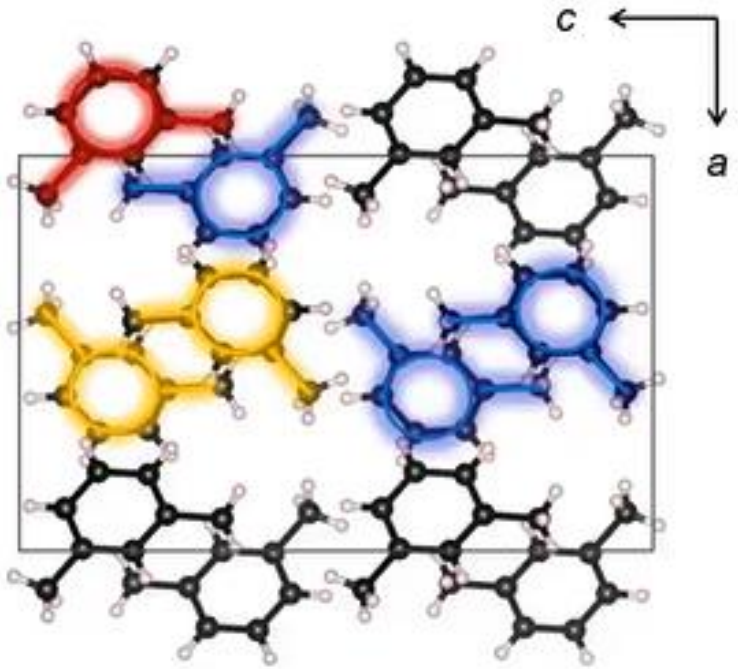


Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

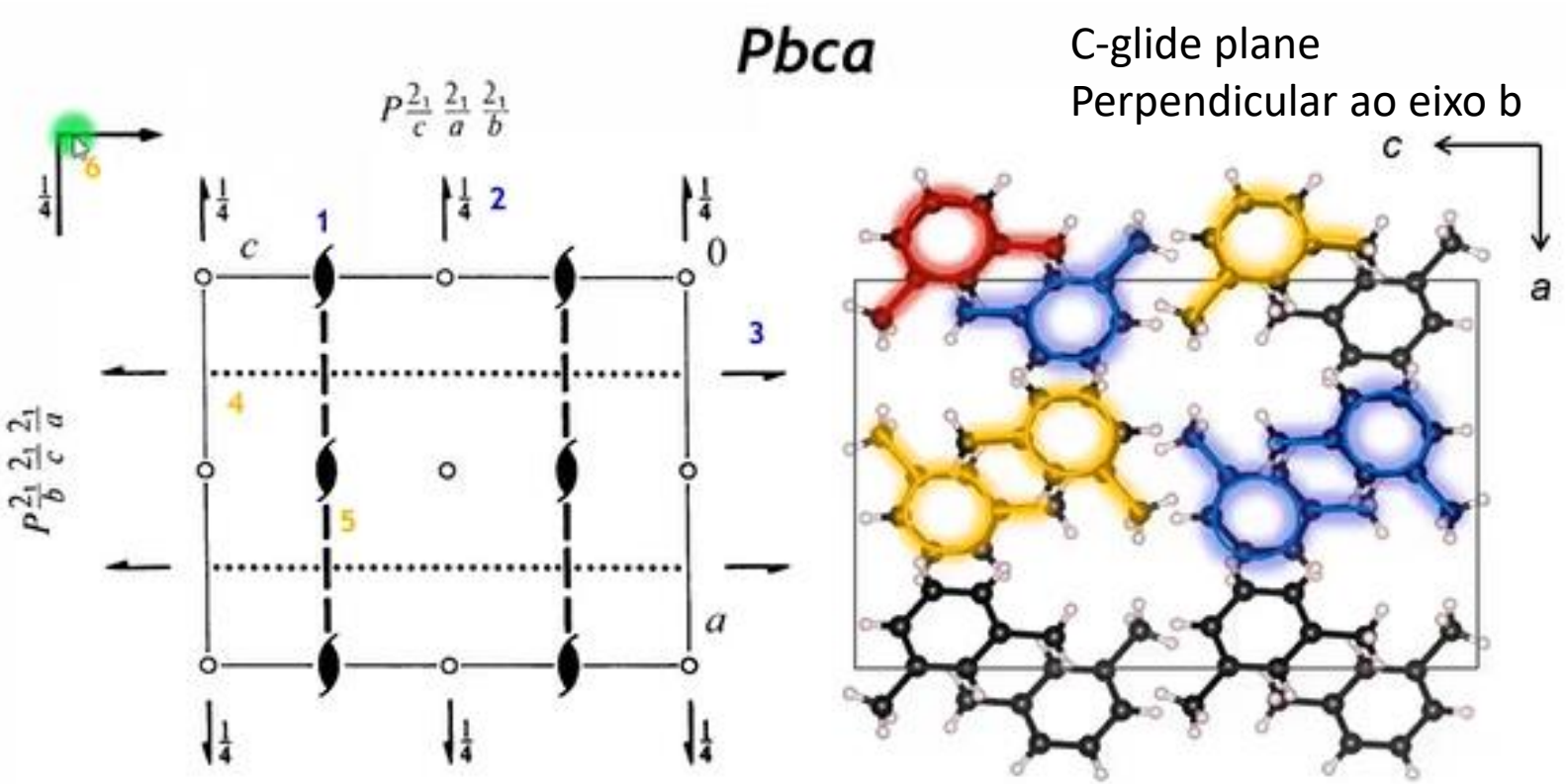
Pbca

A-glide plane
Perpendicular ao eixo c



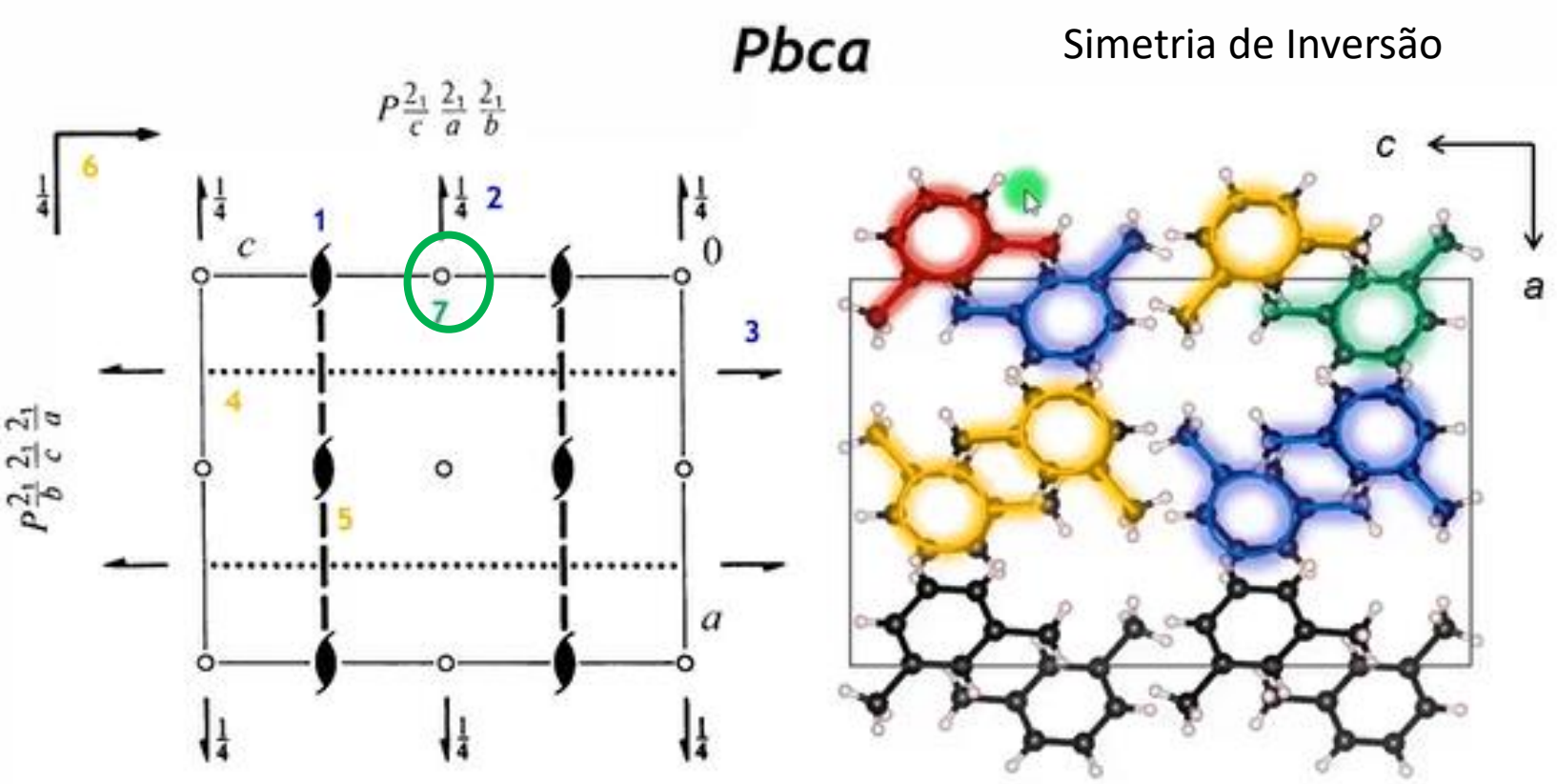


Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)



Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

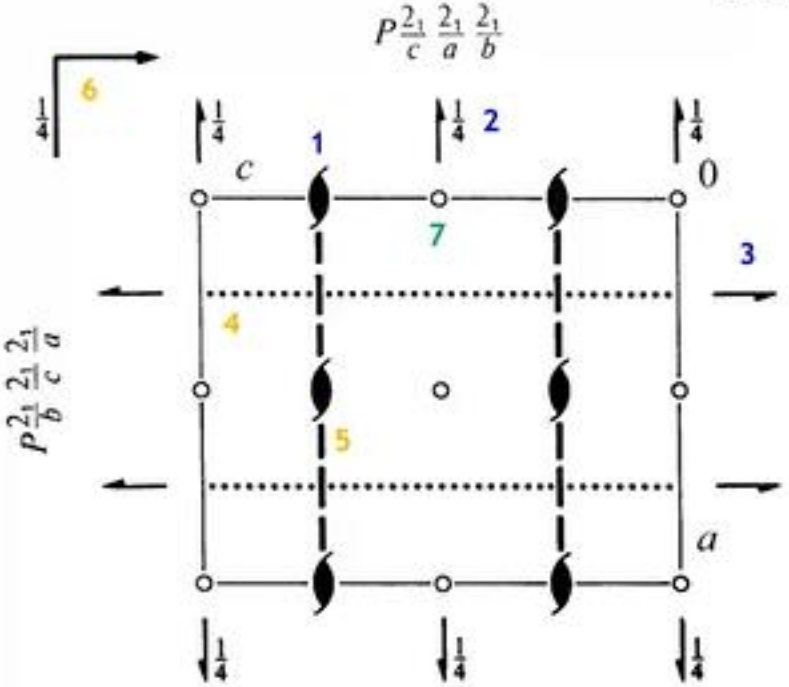
Simetria de Inversão

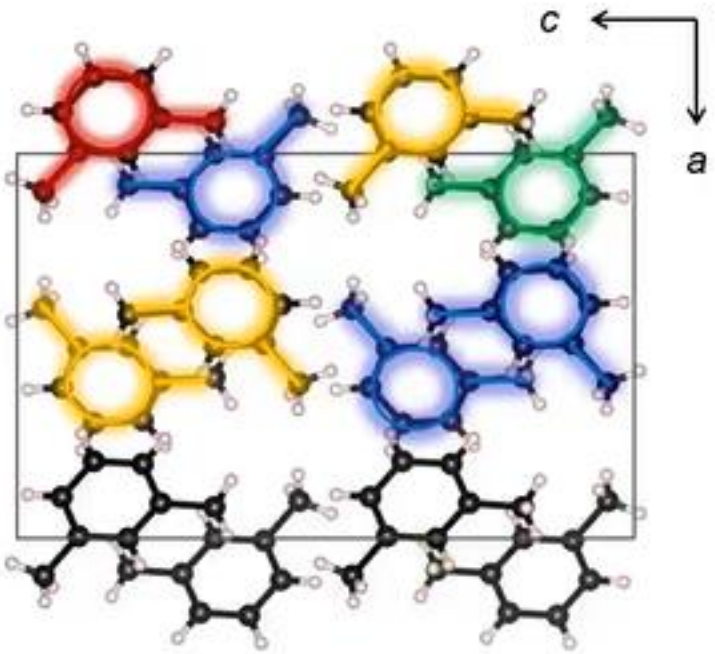


Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

Pbca

8 moléculas

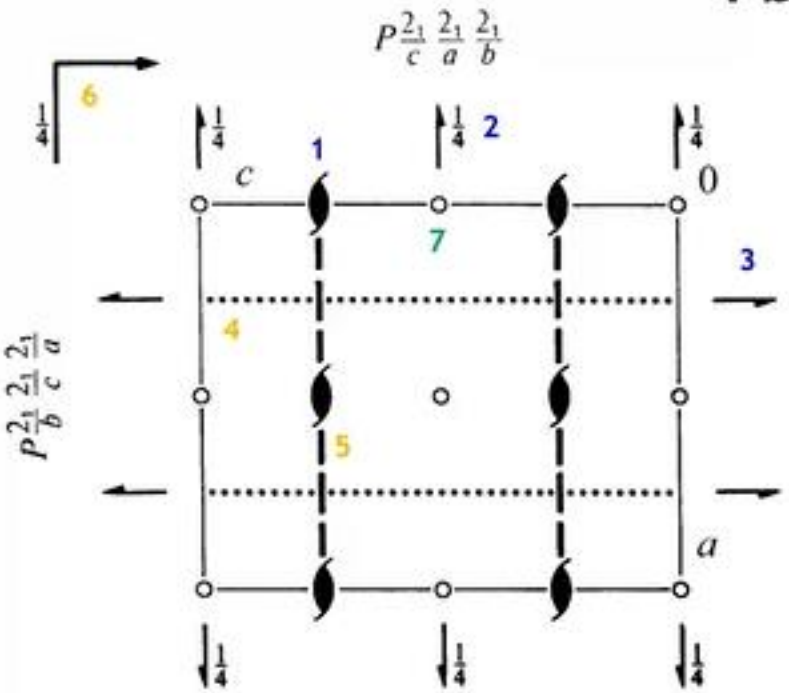


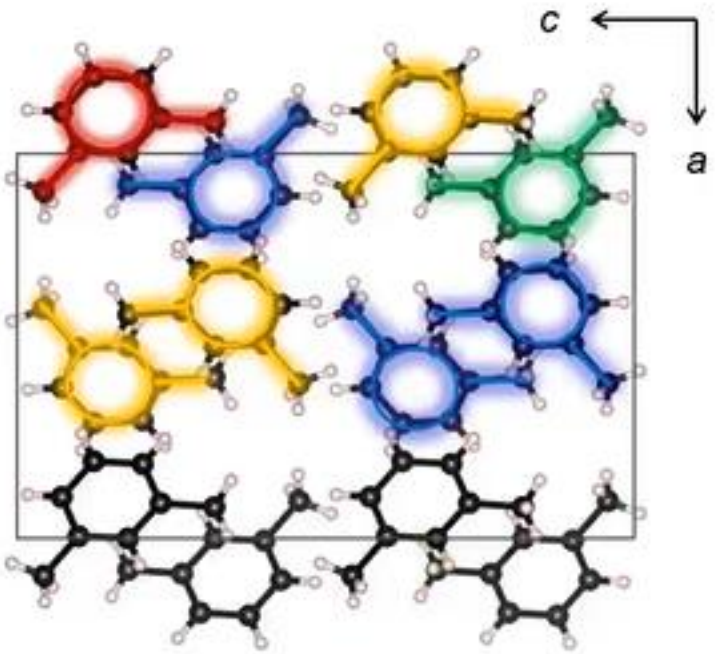


Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

3 screw axis (azul)
3 glide planes (amarelo)
1 inversão (verde)

Pbca





Mult.	Site	Sym.	Coordinates
8	c	1	(x,y,z), (½-x,-y,½+z), (-x,½+y,½+z), (½+x,½+y,-z), (-x,-y,-z), (½+x,y, ½+z), (x,½-y,½+z), (½-x,½+y,z)
4	b	-1	(½,0,0), (0,0,½), (0,½,0), (½,½,½)
4	a	-1	(0,0,0), (½,0, ½), (½,½,0), (0,½,½)

meta-xylene

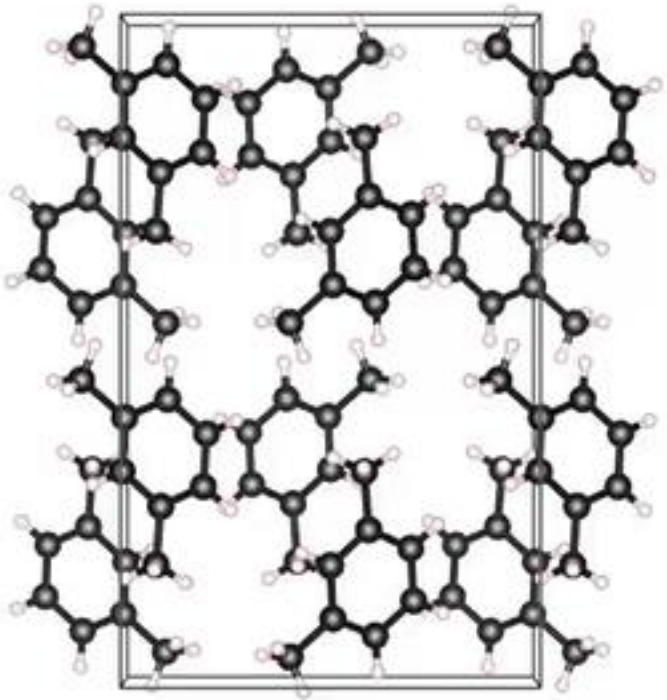
Space Group: *Pbca*

Z = 8 molecules

General position multiplicity = 8

1 molecule in the asymmetric unit

The symmetry operations of the space group don't impose any symmetry on the molecule



para-xylene

Space Group: $P2_1/n$

a = 5.734 Å

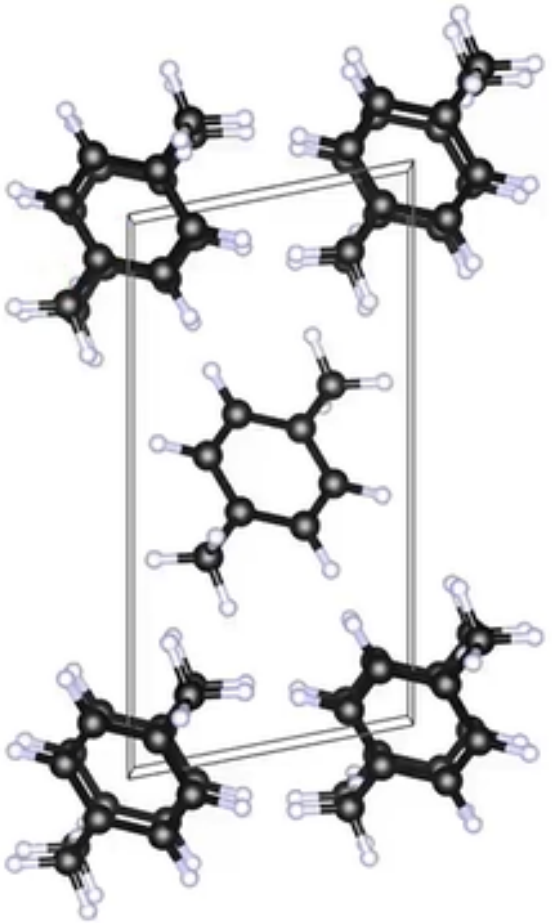
b = 4.949 Å

c = 11.138 Å

β = 100.71°

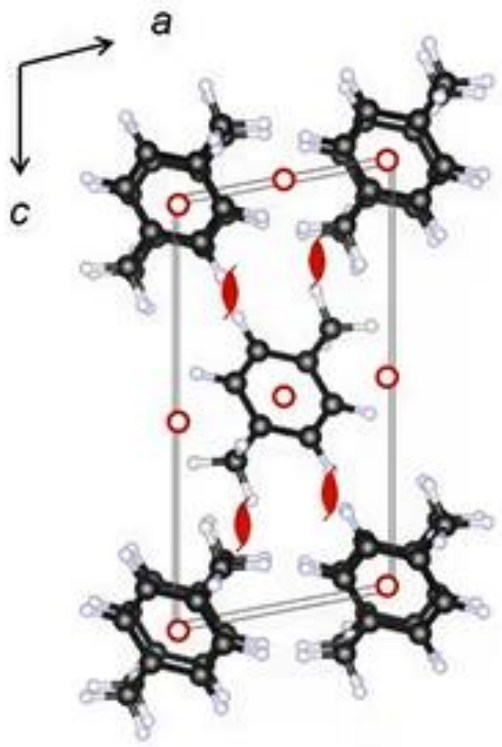
Volume = 310.6 Å^3

Z = 2 (16 C, 20 H per unit cell)



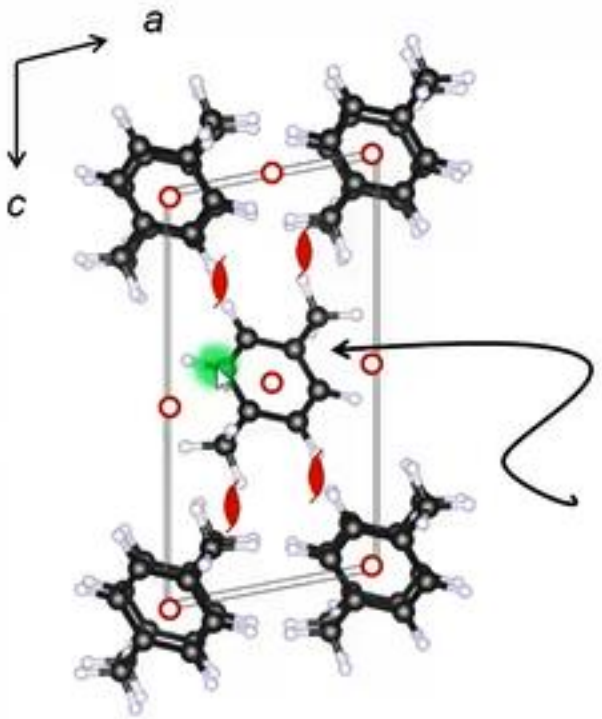
Ibberson, David, Parsons, Prager, Shankland, *J. Molecular Structure*, **524** (2000), 121-128.

V escola de verão



$P2_1/n$

Mult.	Site	Sym.	Coordinates
4	e	1	(x,y,z), (½-x,½+y,½-z), (-x,-y,-z), (½+x,½-y,½+z)
2	d	-1	(½,0,0), (0,½,½)
2	c	-1	(½,0,½), (0,½,0)
2	b	-1	(0,0,½), (½,½,0)
2	a	-1	(0,0,0), (½,½,½)



$P2_1/n$

There is an inversion center at the center of the aromatic ring. The molecule must have inversion symmetry.

Molecule generated by either the 2_1 screw or the n-glide

Mult.	Site	Sym.	Coordinates
4	e	1	(x,y,z), (½-x,½+y,½-z), (-x,-y,-z), (½+x,½-y,½+z)
2	d	-1	(½,0,0), (0,½,½)
2	c	-1	(½,0,½), (0,½,0)
2	b	-1	(0,0,½), (½,½,0)
2	a	-1	(0,0,0), (½,½,½)

para-xylene

Space Group: $P2_1/n$

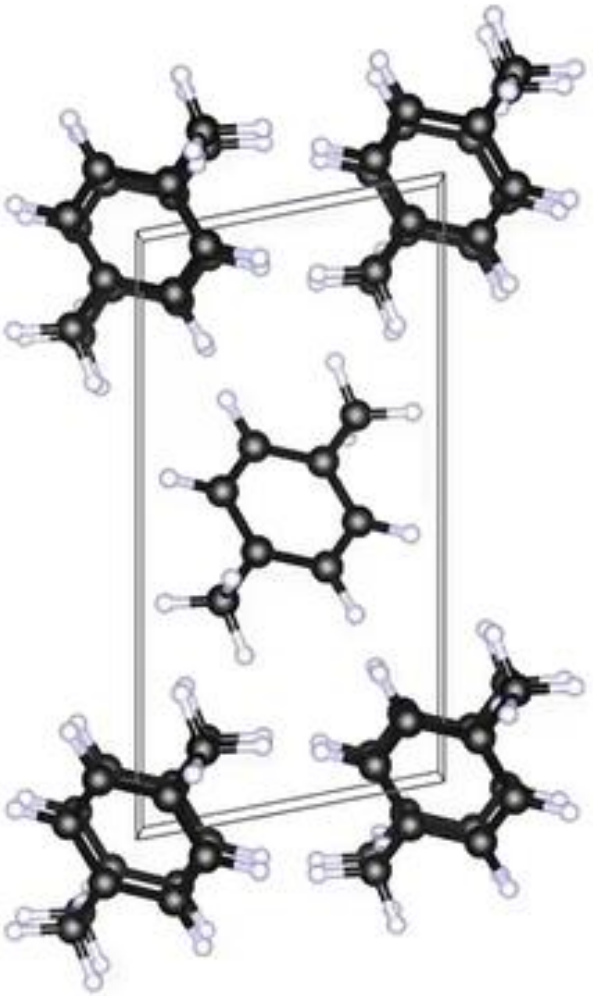
Z = 2 molecules

General position multiplicity = 4

(Z′ = ½)

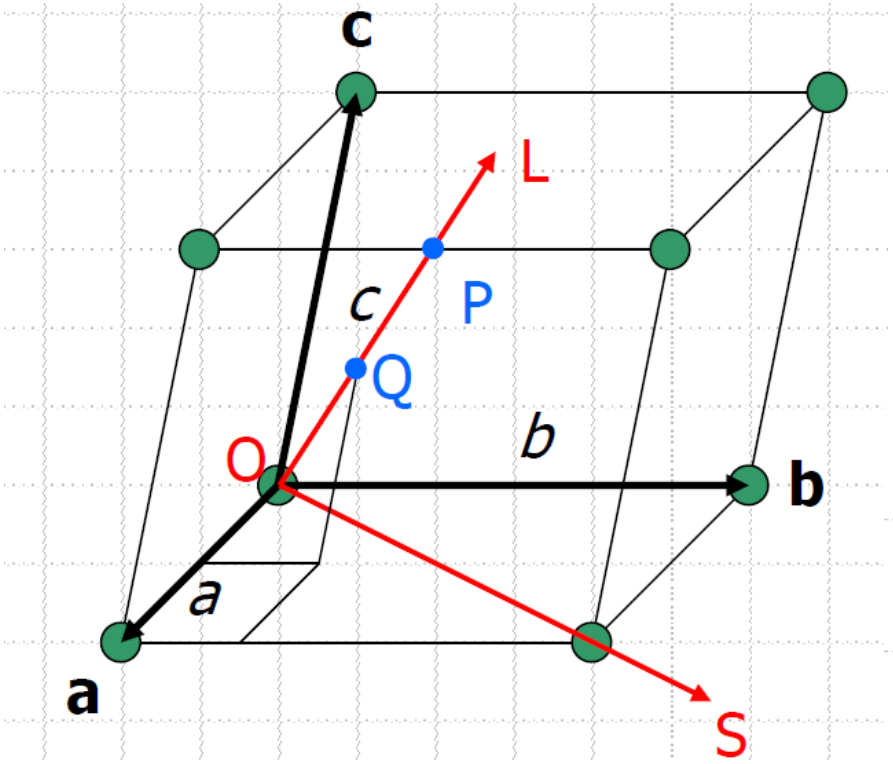
½ molecule in the asymmetric unit

The symmetry operations of the space group impose an inversion center on the molecular



Indexando as Direções da Rede

A direção deve passar pela origem
As coordenadas do ponto P (em frações de a, b e c) são 1, ½, 1 → [212]
Para as coordenadas do ponto Q são ½, ¼, ½ → [212]



[212] - define a direção para OL

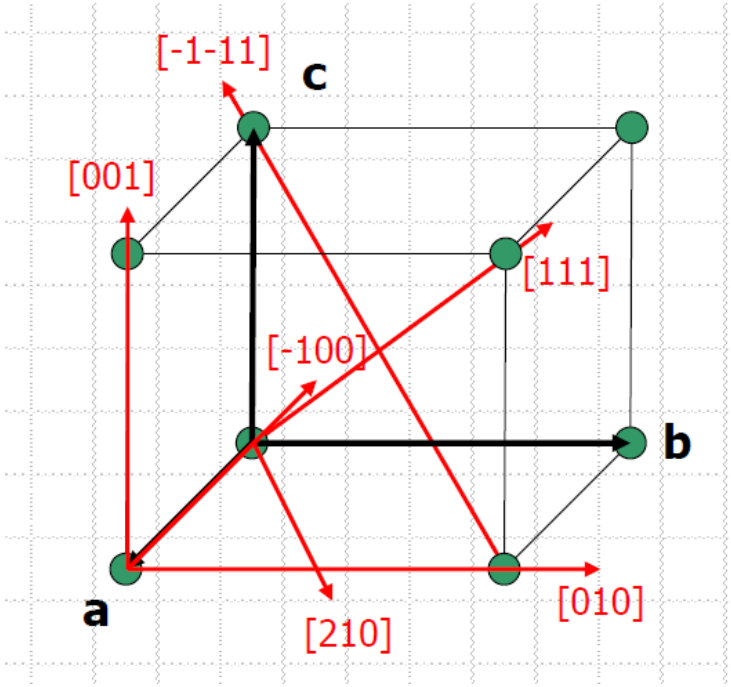
Para OS – a direção é [110]

$$\mathbf{r}_{102} = 2\mathbf{a} + 1\mathbf{b} + 2\mathbf{c}$$

$$\mathbf{r}_{110} = 1\mathbf{a} + 1\mathbf{b} + 0\mathbf{c}$$

Indexando as Direções da Rede

As direções relacionadas por simetria são chamadas de direções de uma forma.



Temos: [111], [-111], [-1-1-1], [11-1], ...

<111>

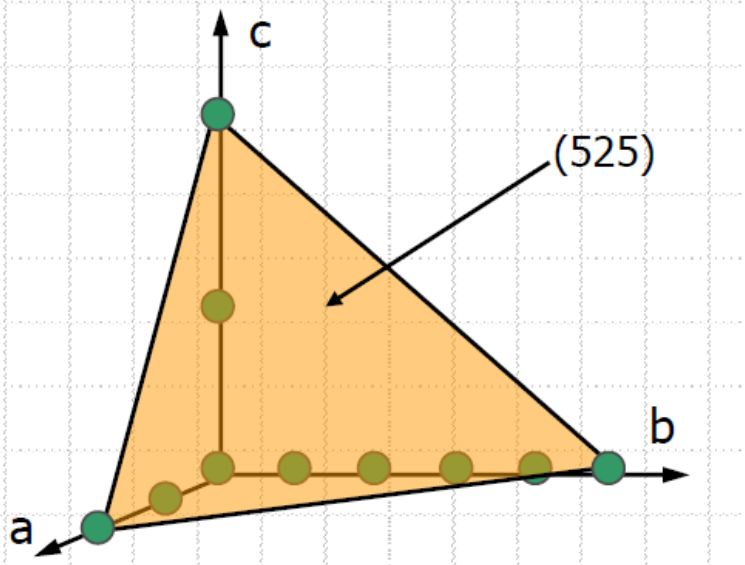
Direção específica →[uvw]

Família de direções → <uvw>

Definição dos Índices de Miller

Vamos desenhar um plano em 2xa, 5xb, 2xc.

	a	b	c
The intercepts	2	5	2
The reciprocals	1/2	1/5	1/2
Multiply by 10	5	2	5
The Miller indices	(525)		

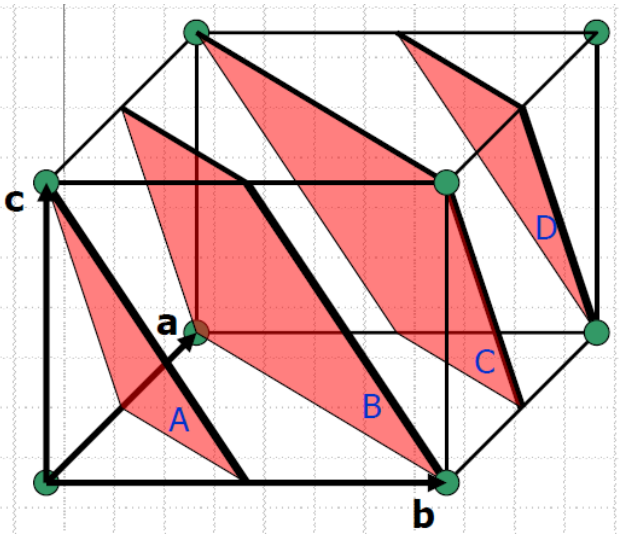


Plano específico →(hkl)

Família de planos →{hkl }

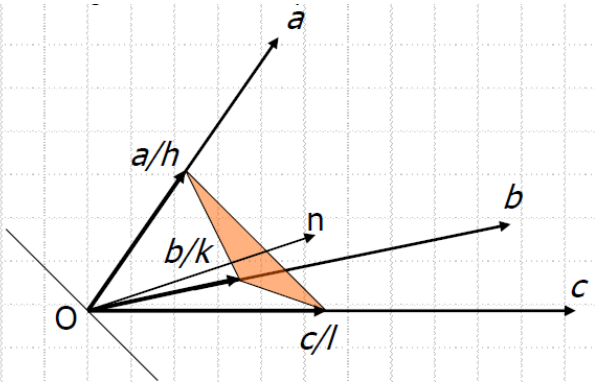
Definição dos Índices de Miller

- For plane A $a/2$, $b/2$, and $1c \Rightarrow 2, 2, 1 \Rightarrow$ plane is (221)
- For plane B $1a$, $1b$, and $2c \Rightarrow 1, 1, 1/2 \Rightarrow 2, 2, 1 \Rightarrow$ plane is (221)
- For plane C $3a/2$, $3b/2$, and $3c \Rightarrow 2/3, 2/3, 1/3 \Rightarrow 2, 2, 1 \Rightarrow$ plane is (221)
- For plane D $2a$, $2b$, and $4c \Rightarrow 1/2, 1/2, 1/4 \Rightarrow 2, 2, 1 \Rightarrow$ plane is (221)

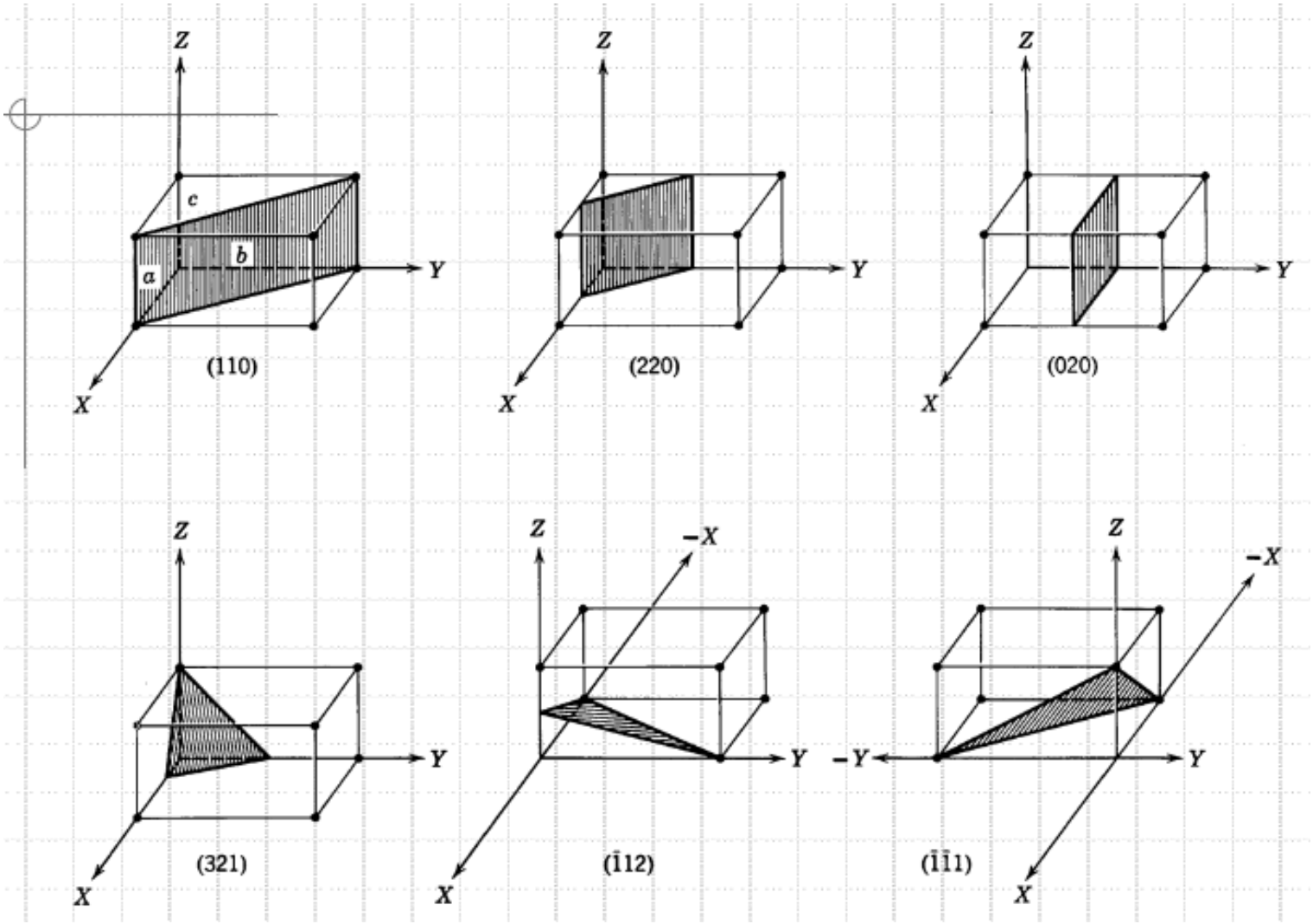


Por conjunto de planos cristalográficos hkl, queremos dizer um conjunto de planos equidistantes paralelos, um dos quais passa pela origem e o próximo mais próximo faz interceptações a/h, b/k e c/l nos três eixos cristalográficos.

Os inteiros hk são geralmente chamados de índices de Miller.



índices de Miller



Miller Indices and Zone Axis Symbols

Conclusão para índices cristalográficos

[uvw] = colchetes designam uma direção na rede desde a origem até um ponto. Usado para incluir coletivamente todas as faces de cristais cujas interseções (ou seja, arestas) são paralelas entre si. Estes são referidos como zonas cristalográficas e representam uma direção na rede cristalina.

<uvw> –designa família de direções.

(hkl) = parênteses designam uma face cristalina ou uma família de planos ao longo de uma rede cristalina.

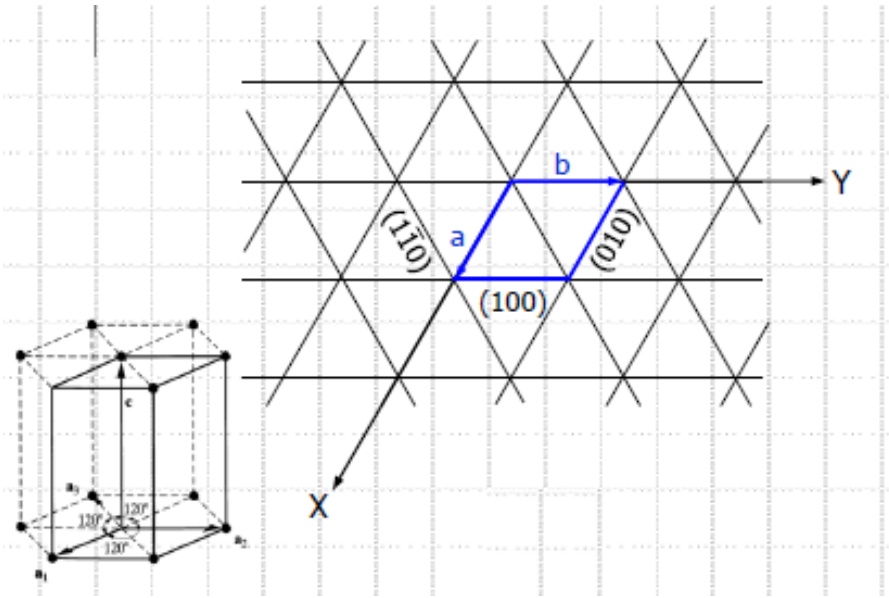
{hkl} = colchetes ou colchetes "ondulados" designam um conjunto de faces que são equivalentes pela simetria do cristal. O conjunto de planos de face resulta na forma cristalina. {100} na classe isométrica inclui (100), (010), (001), (-100), (0-10) e (00-1), enquanto para a triclínica {100} apenas o (100) é incluído.

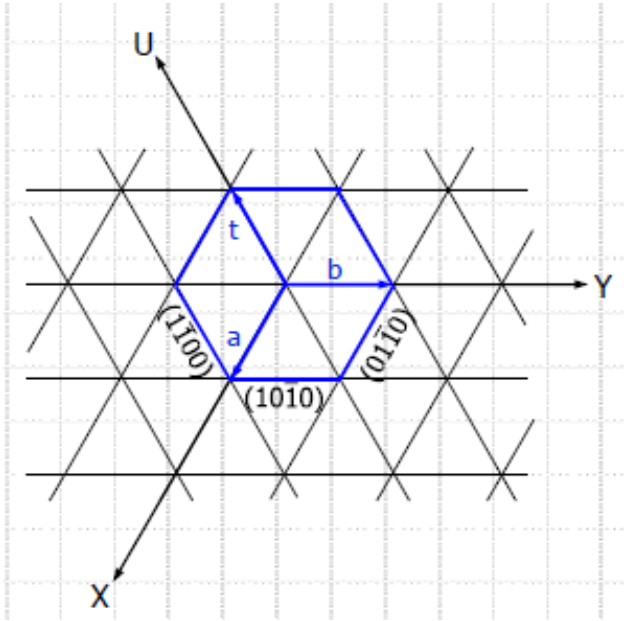
O espaçamento d é definido como a distância entre planos adjacentes. Quando os raios X difratam devido à interferência entre uma família de planos atômicos semelhantes, cada plano de difração pode ser referenciado por seus índices d_{hkl}

Caso Especial: Redes Trigonais e Hexagonais

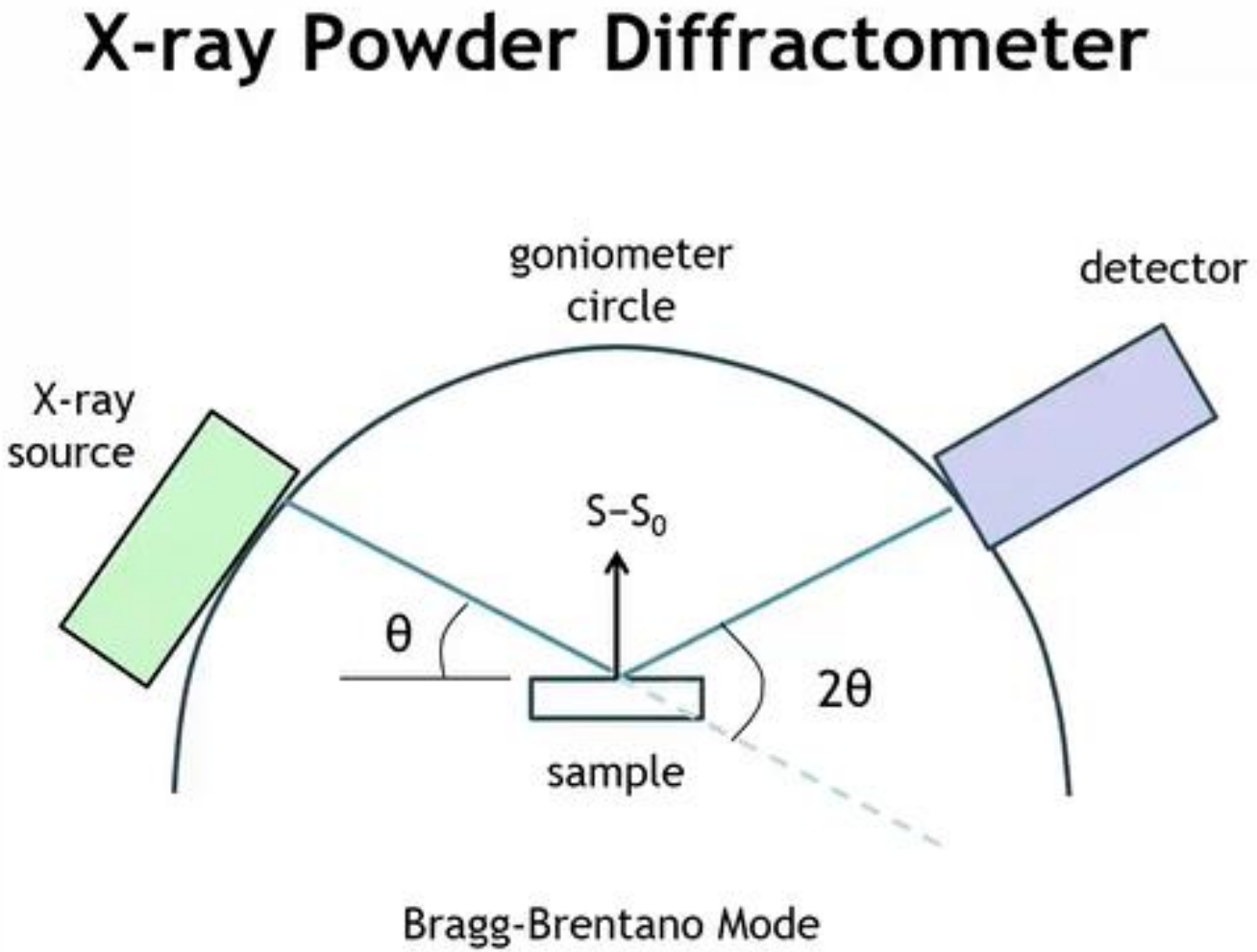
(1 -10), (100) e (010) são índices de tipos diferentes, mas descrevem planos de rede cristalograficamente equivalentes.
Apresentando o quarto eixo –U. Temos índices de Miller-Bravais (hkil).
Todos os índices dos planos são da mesma forma –{10 -10}.

$$h+ k+ i = 0 \rightarrow \quad i= -(h+ k) \rightarrow \quad \{hk.l\}$$

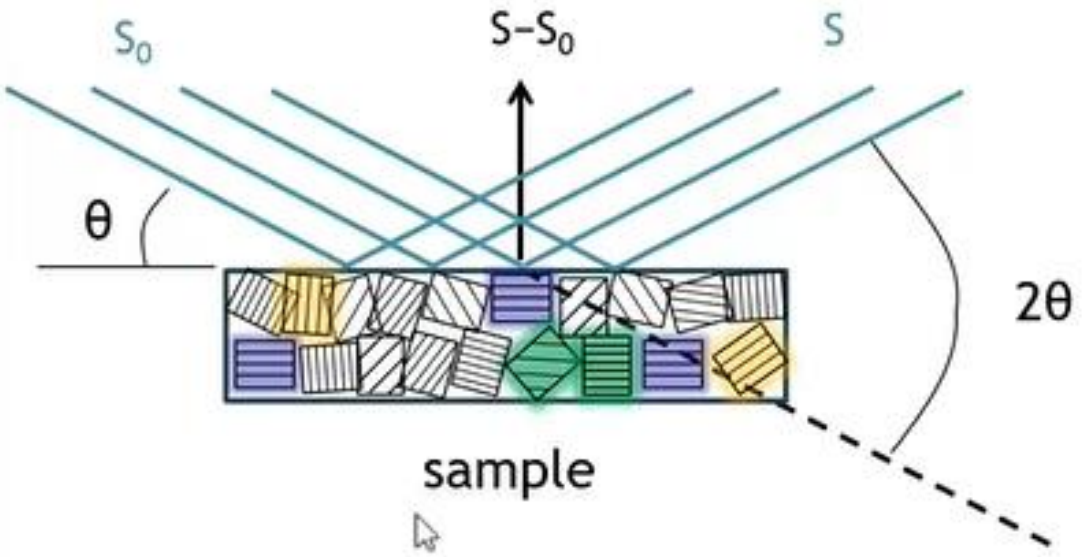




V escola de verão


X-ray Powder Diffractometer
goniometer circle
detector
X-ray source
S–S0
θ
2θ
sample
Bragg-Brentano Mode

X-ray Powder Diffractometer

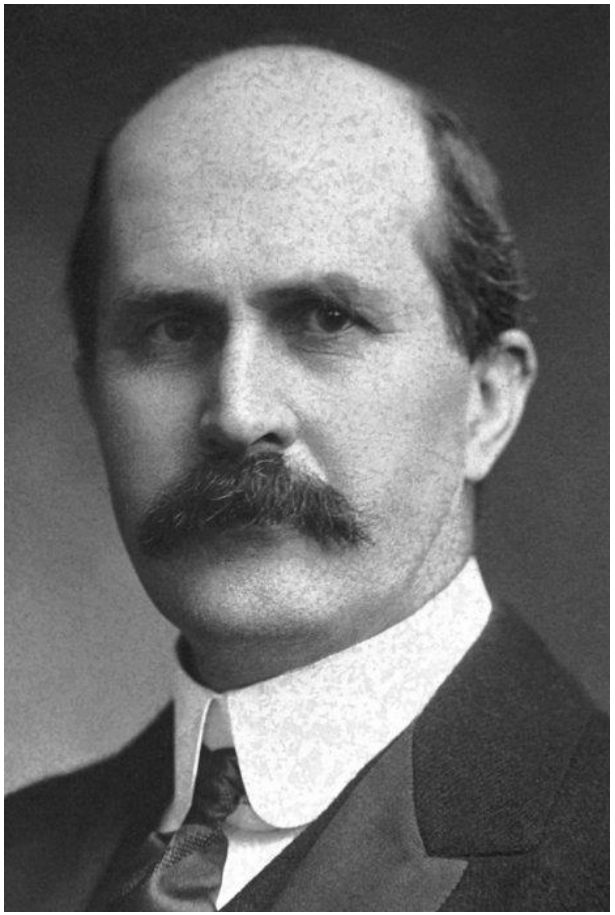


For constructive interference to occur we need:

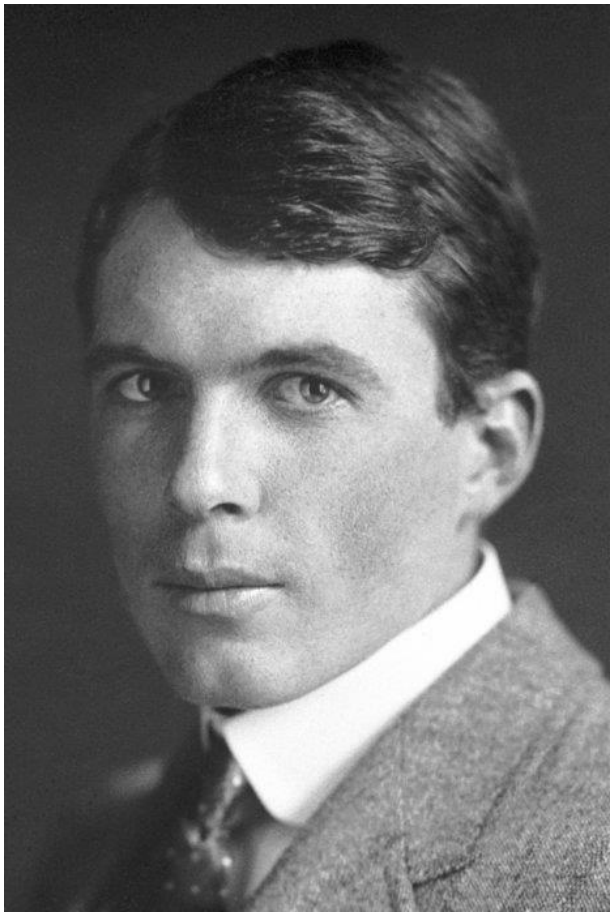
- The θ/2θ angle should satisfies Bragg's Law for a given set of (hkl) lattice planes.
- Have a crystal oriented so that its lattice planes are perpendicular to $S - S_0$

The Nobel Prize in Physics 1915

Lei de Bragg



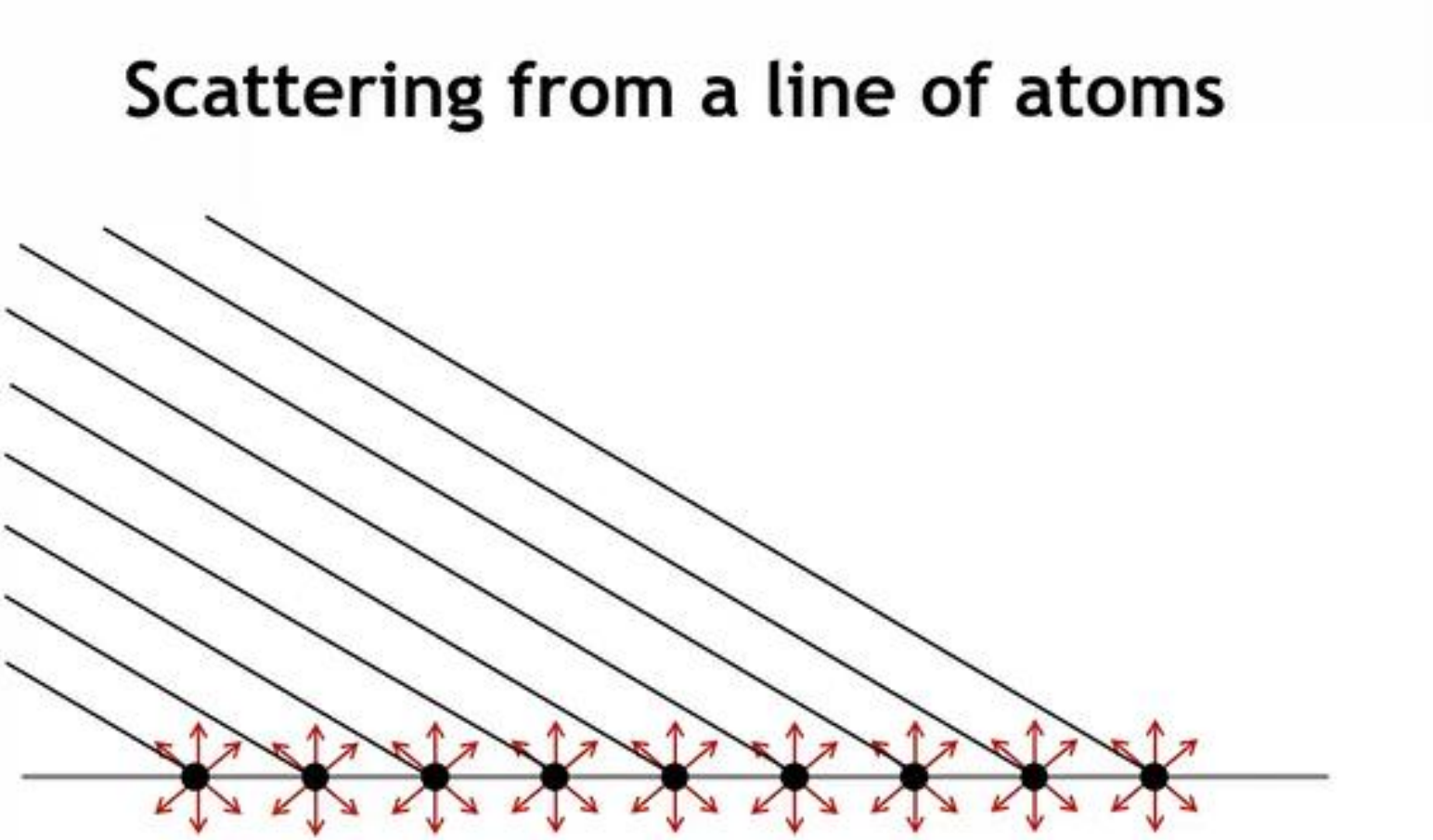
Sir William Henry Bragg



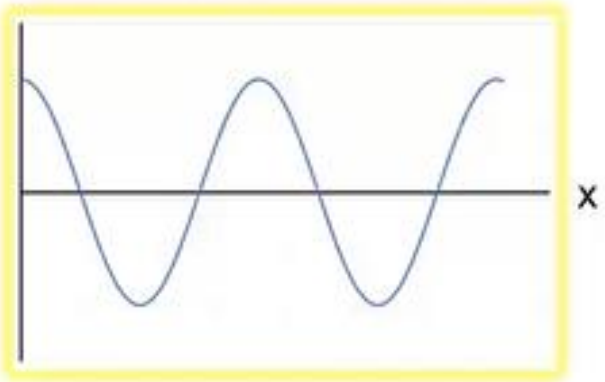
William Lawrence Bragg

Scattering from a line of atoms




Scattering from a line of atoms

Interference Effects



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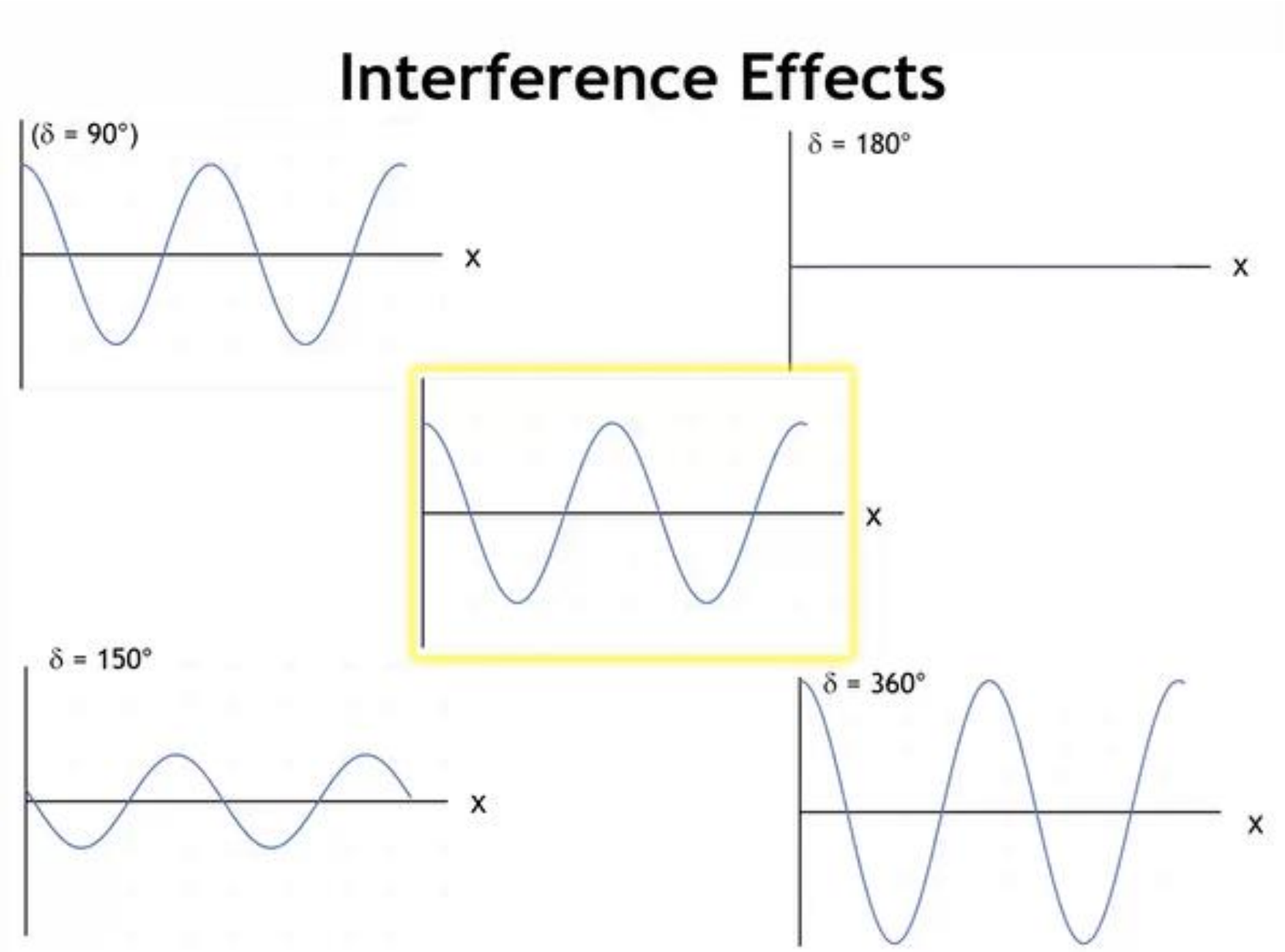
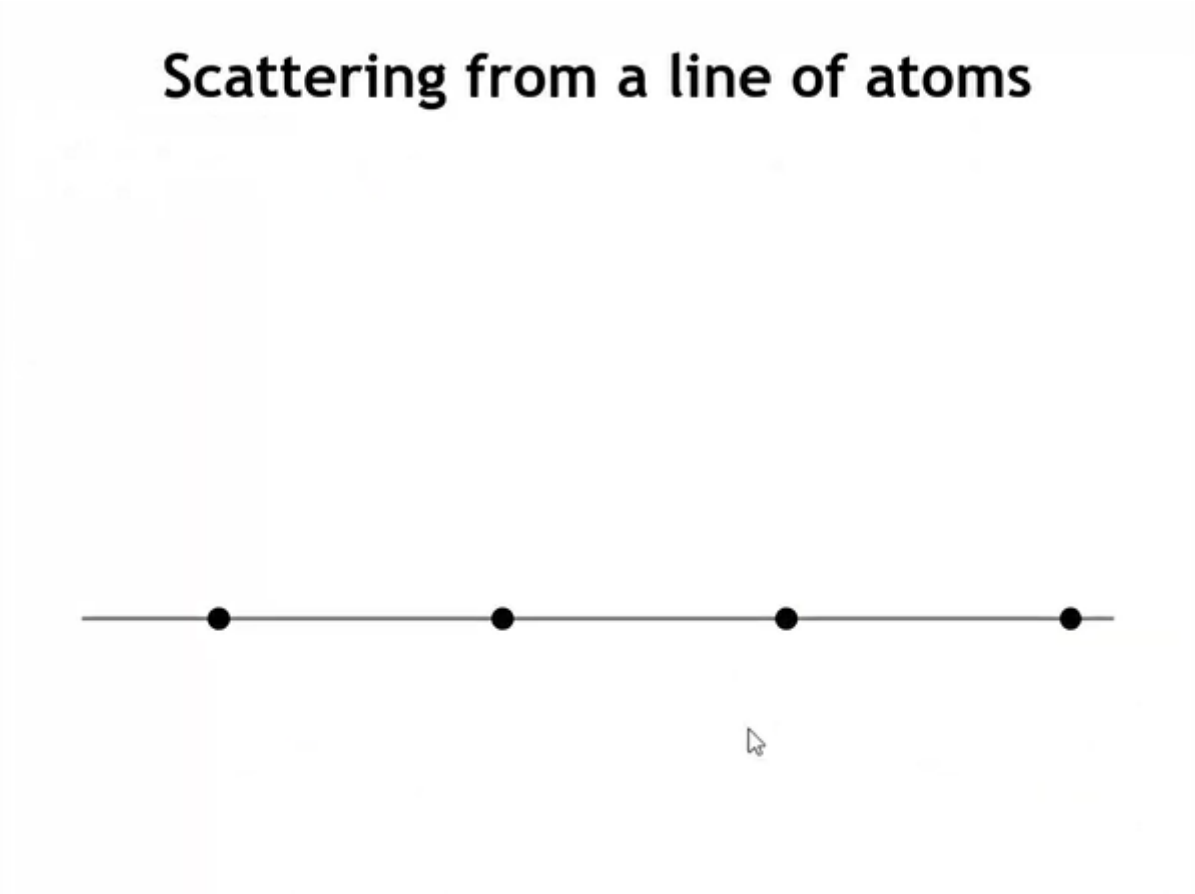
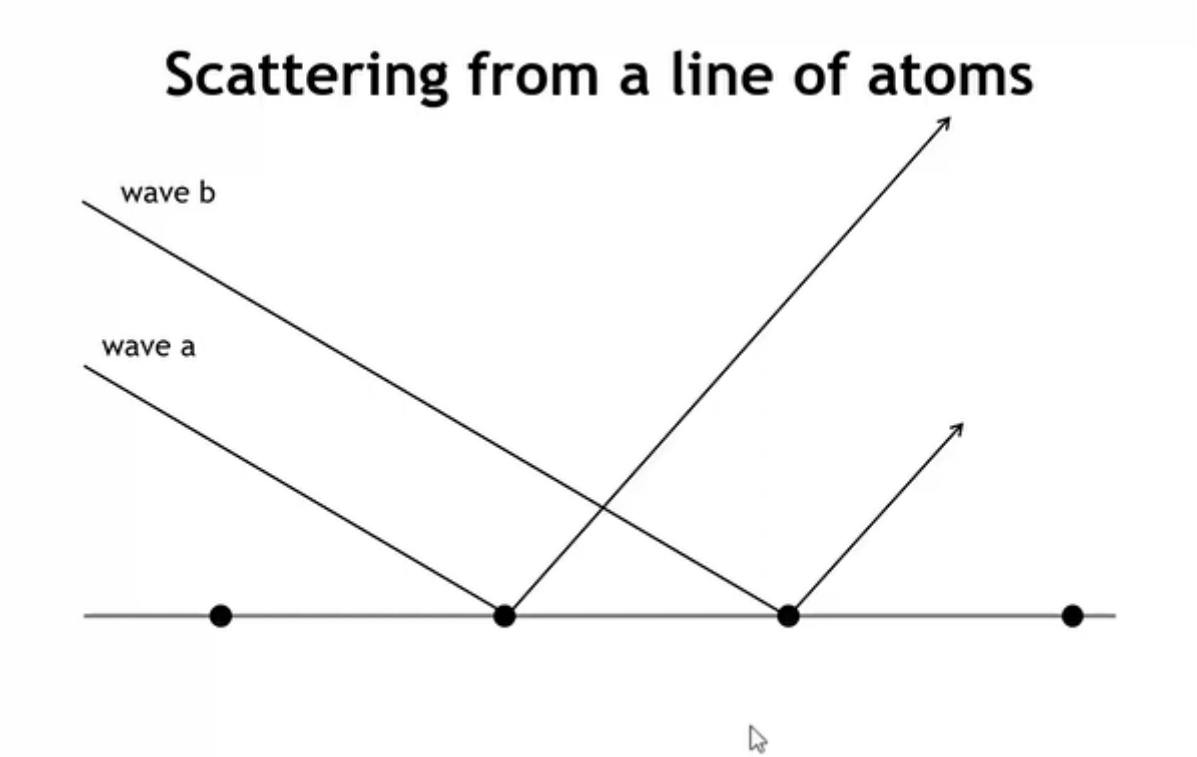



Scattering from a line of atoms

V escola de verão



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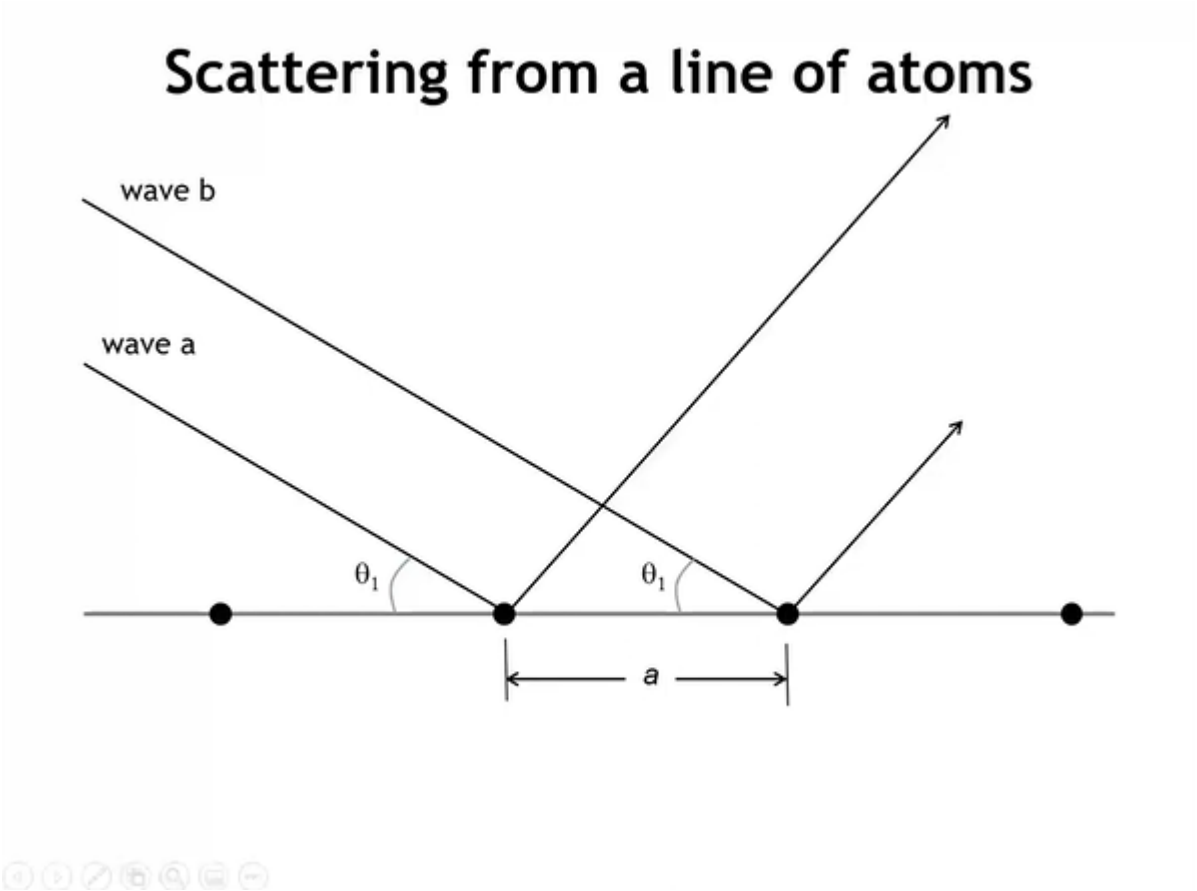

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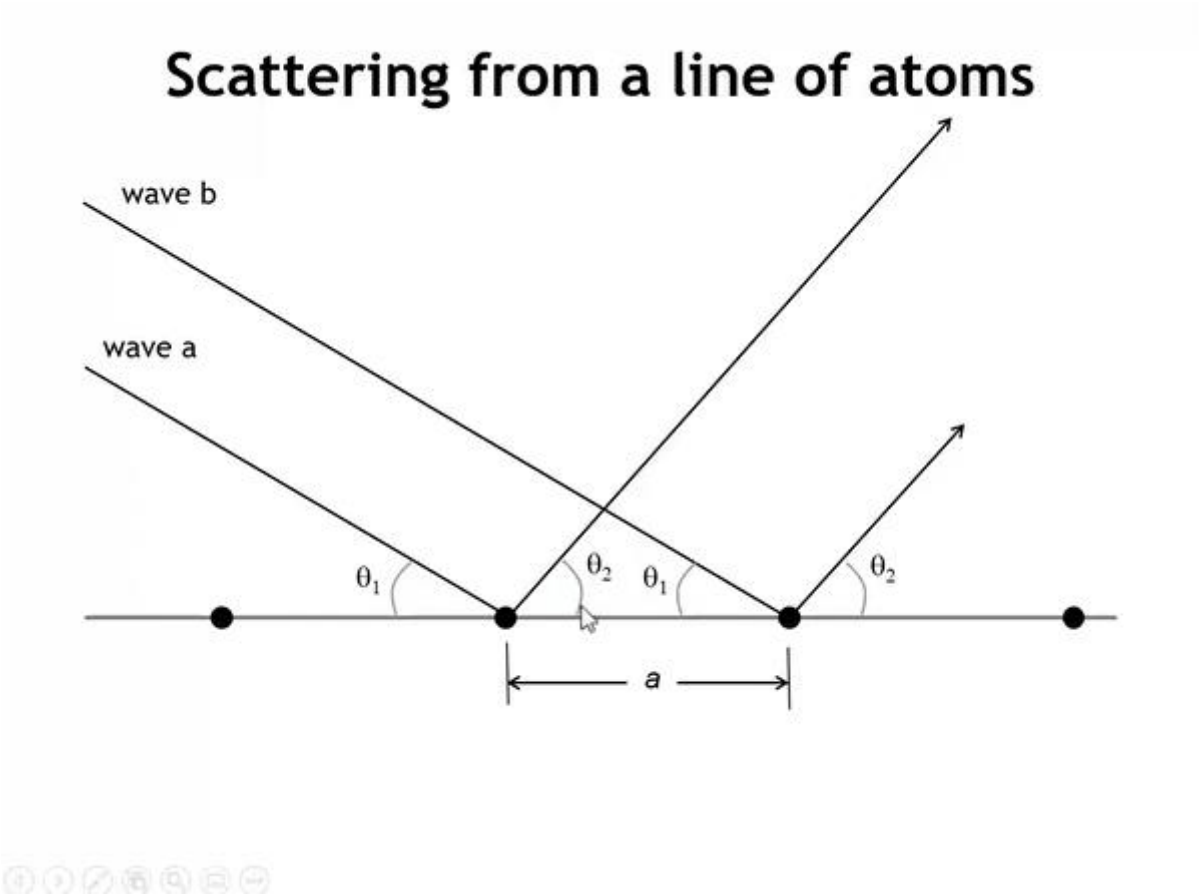

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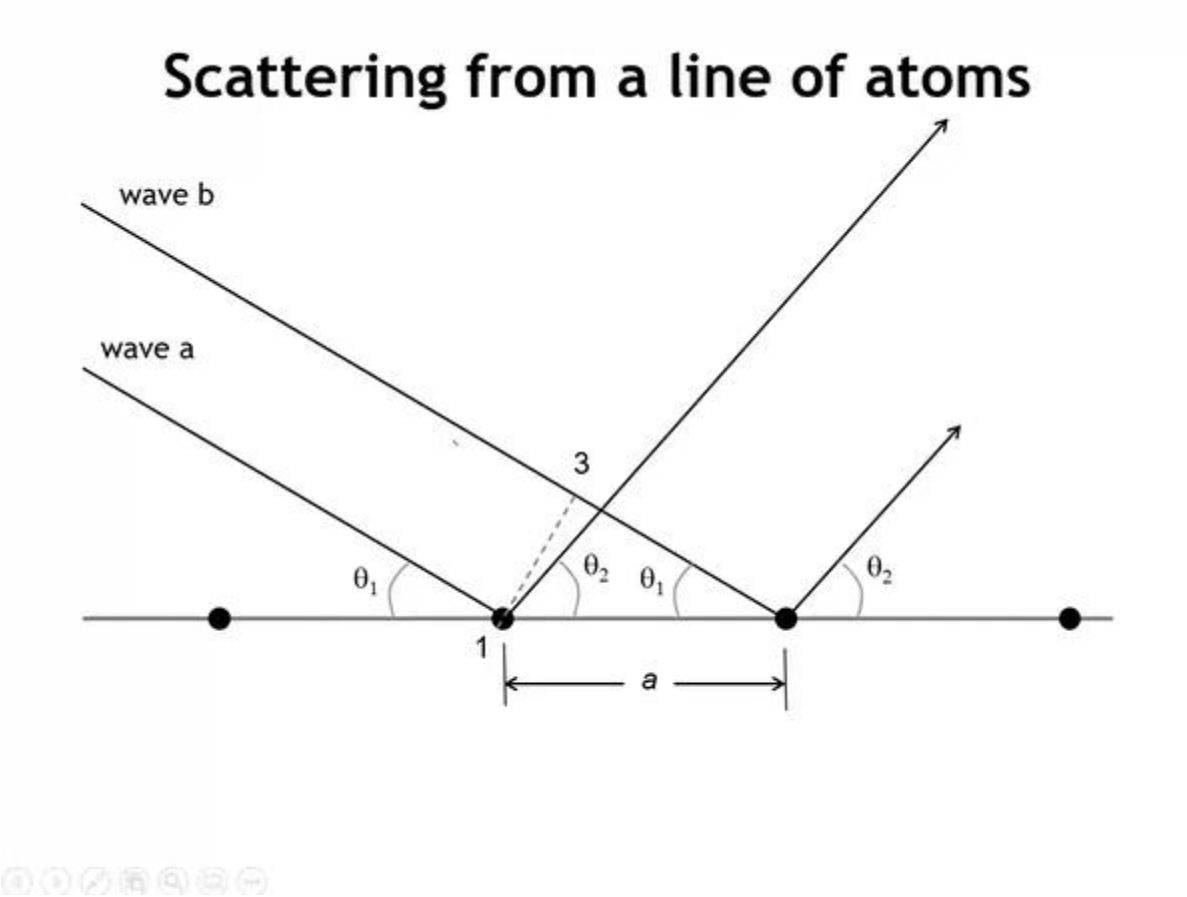
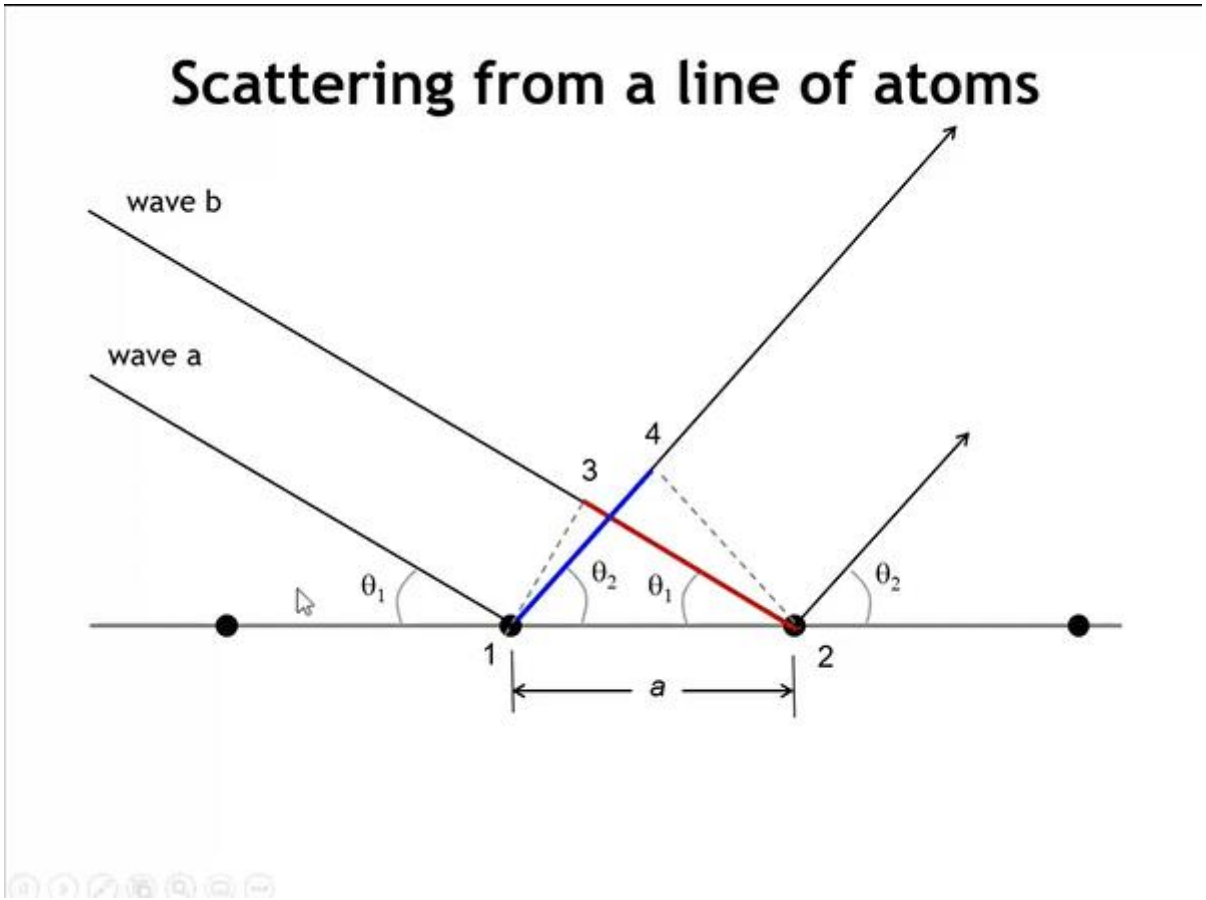
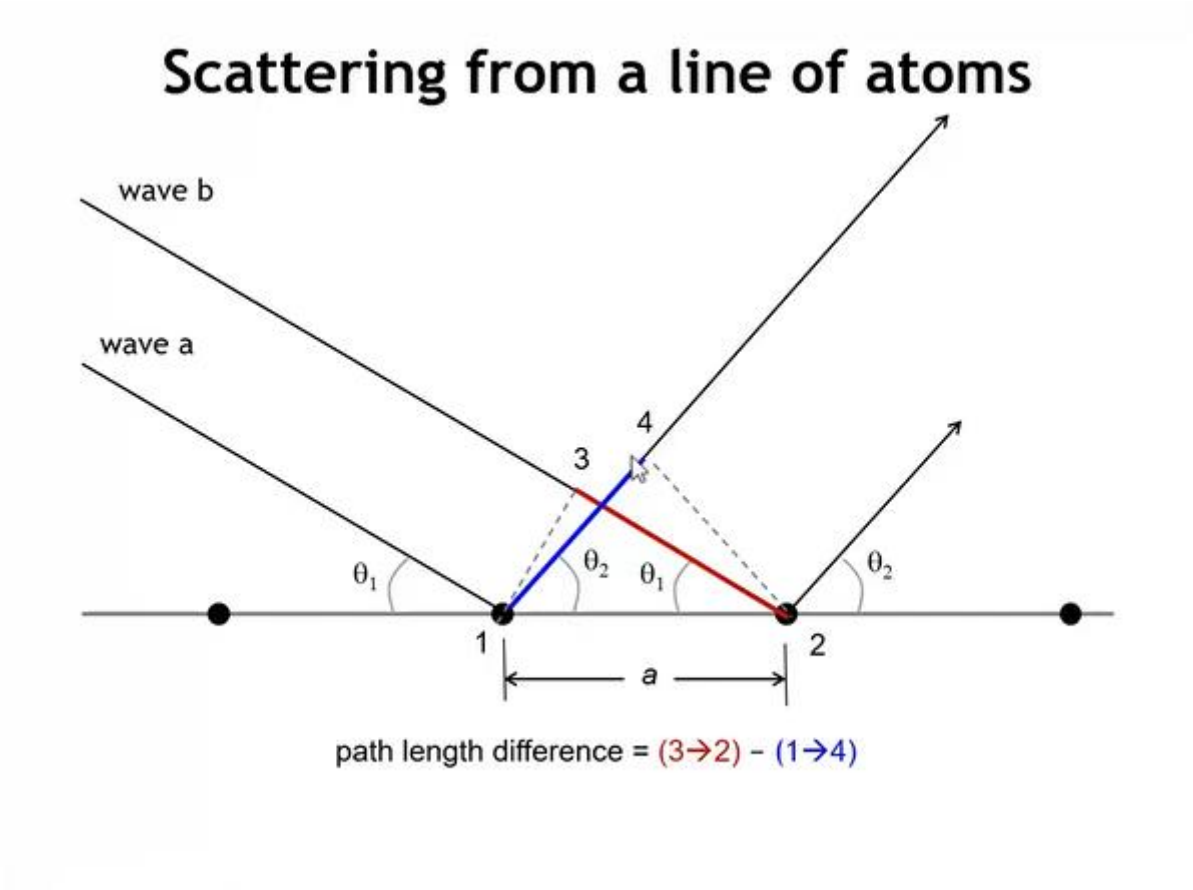



Scattering from a line of atoms
wave b
wave a
4
3
θ1
θ2
θ1
θ2
1
2
a

V escola de verão



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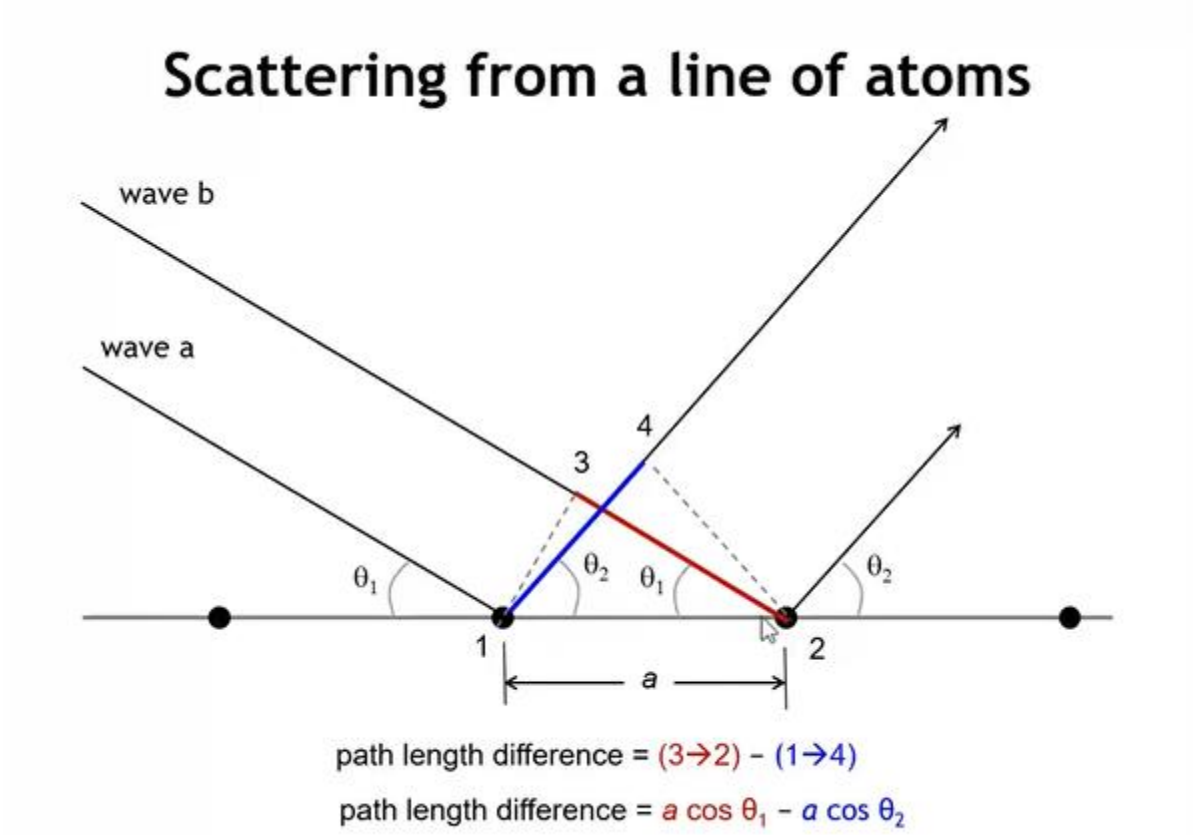
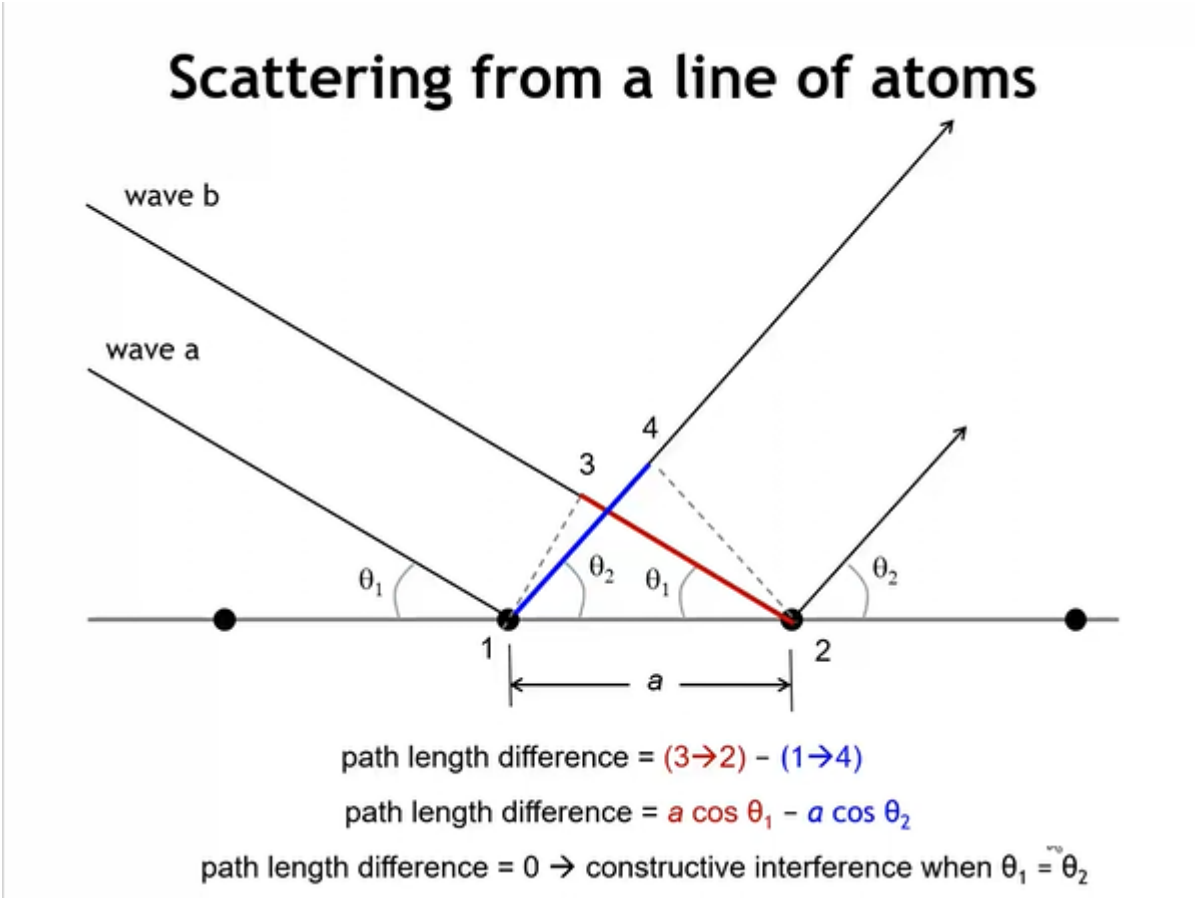
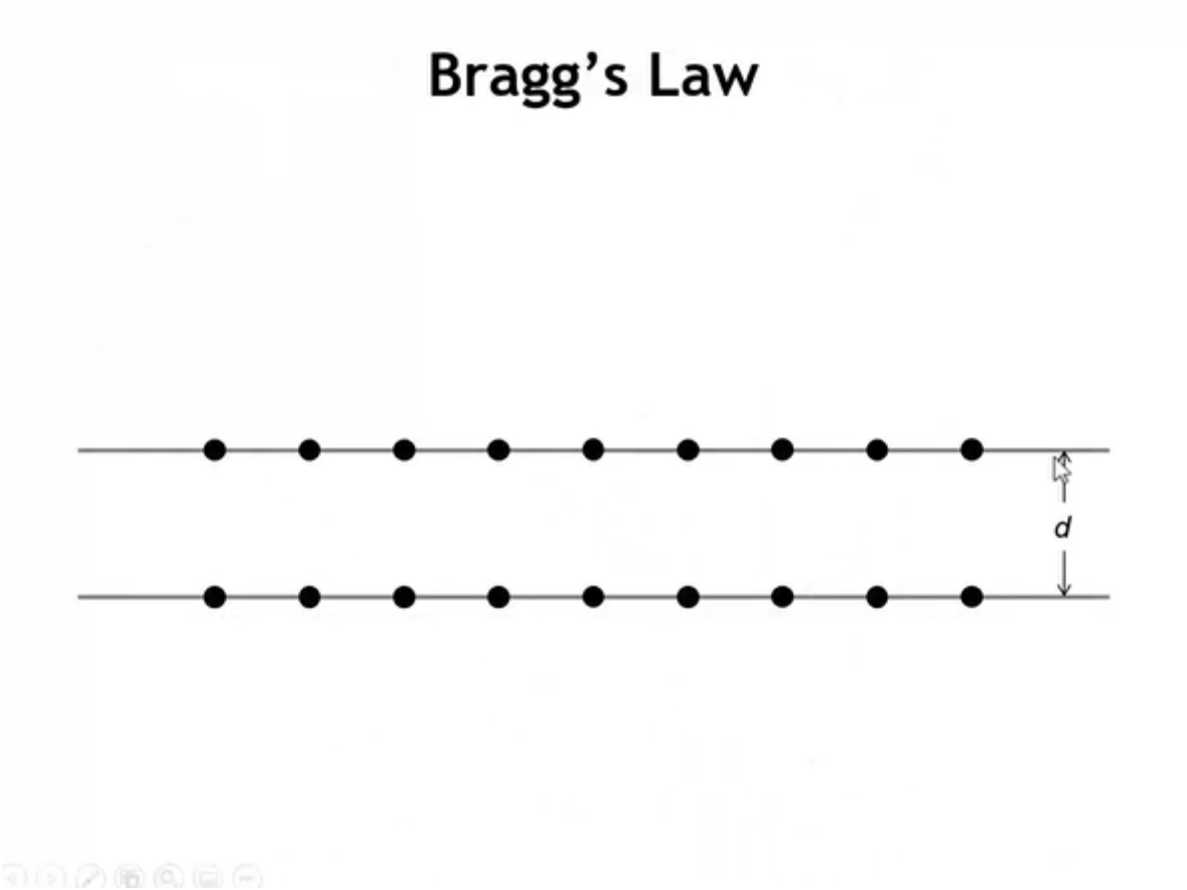



Scattering from a line of atoms
wave b
wave a
4
3
θ1
θ2
θ1
θ2
1
2
a
path length difference = (3→2) – (1→4)
path length difference = a cos θ1 – a cos θ2
path length difference = 0 → constructive interference when θ1 = θ2

V escola de verão



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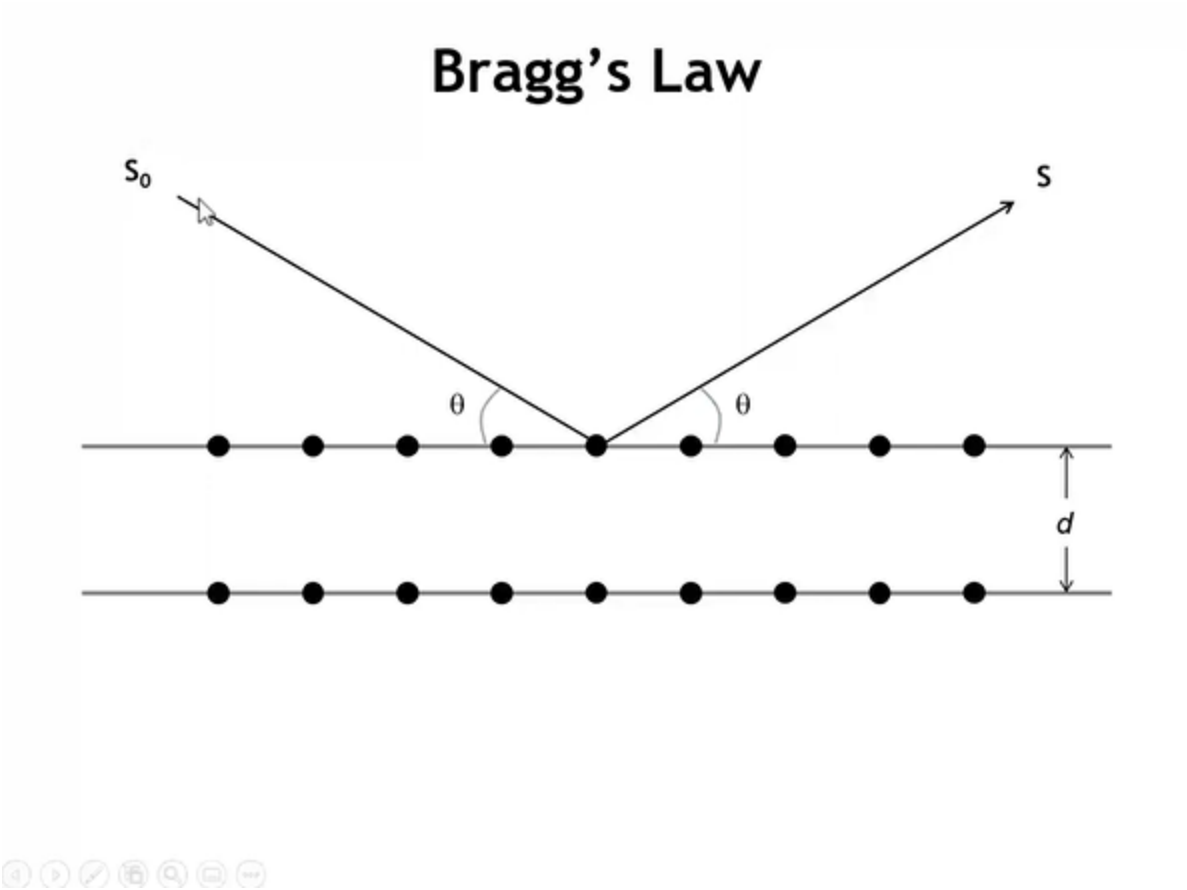

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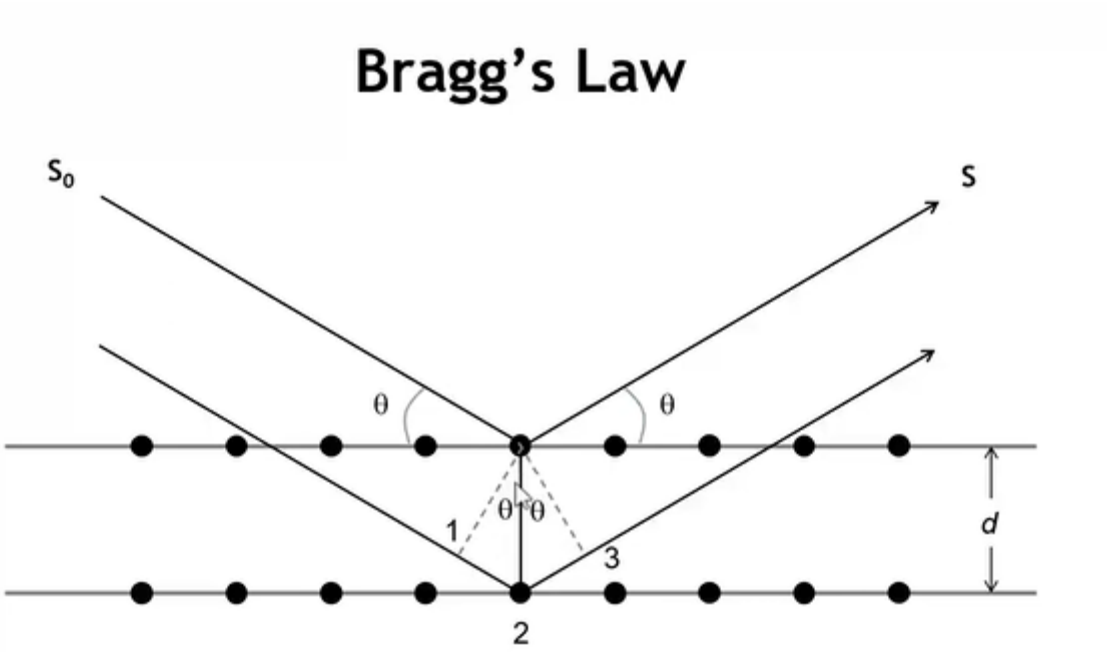

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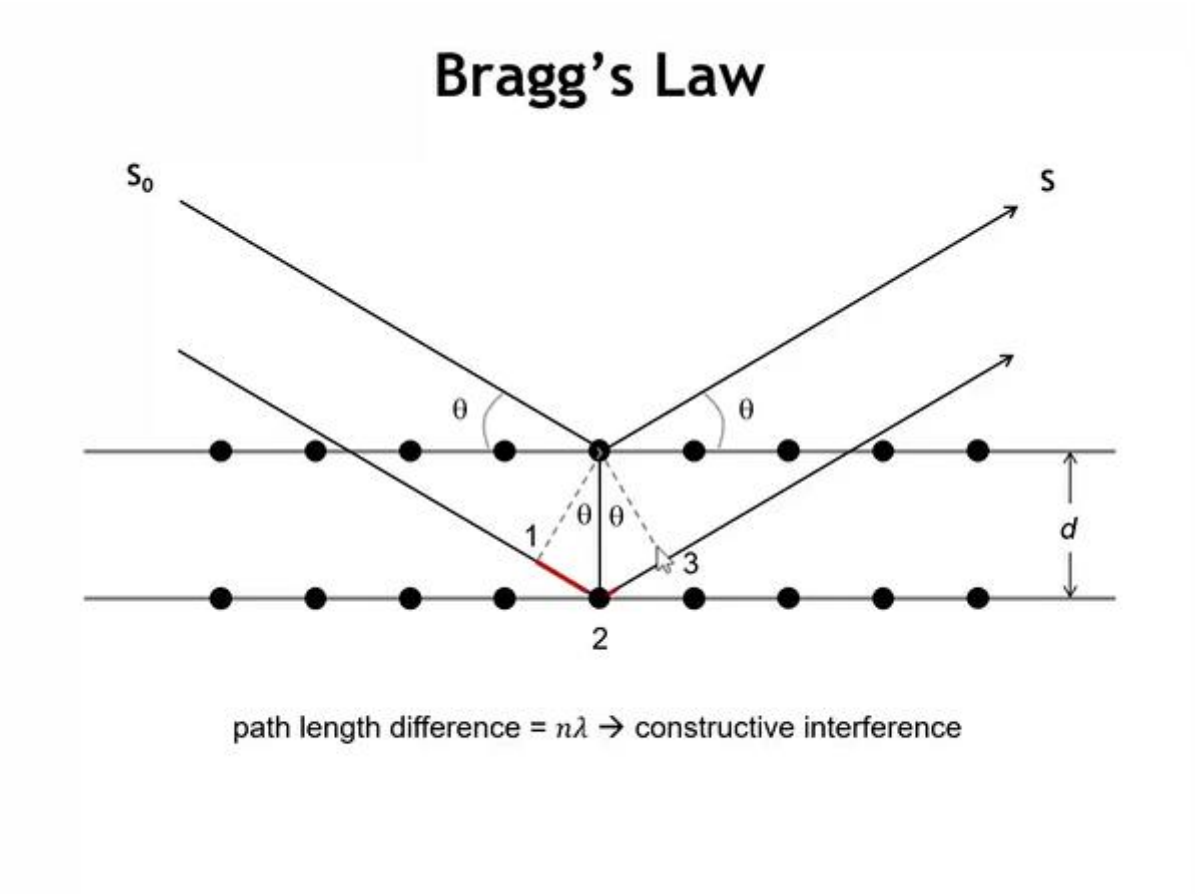

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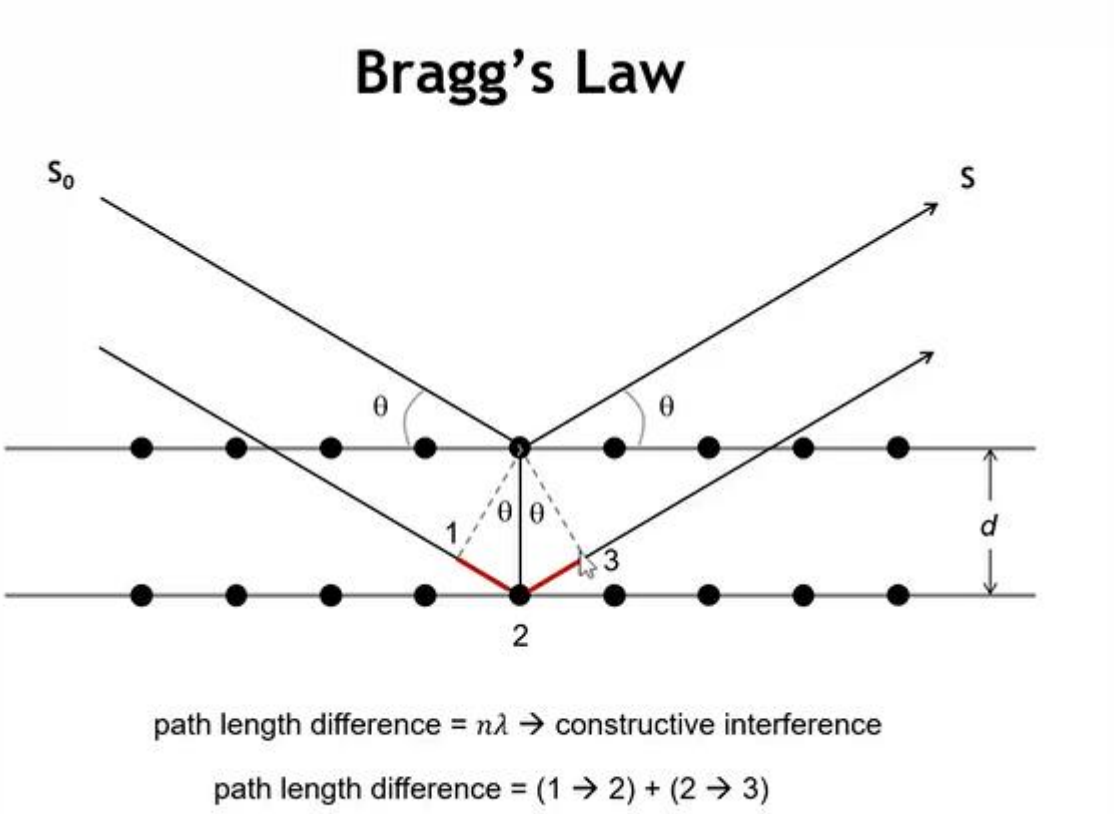
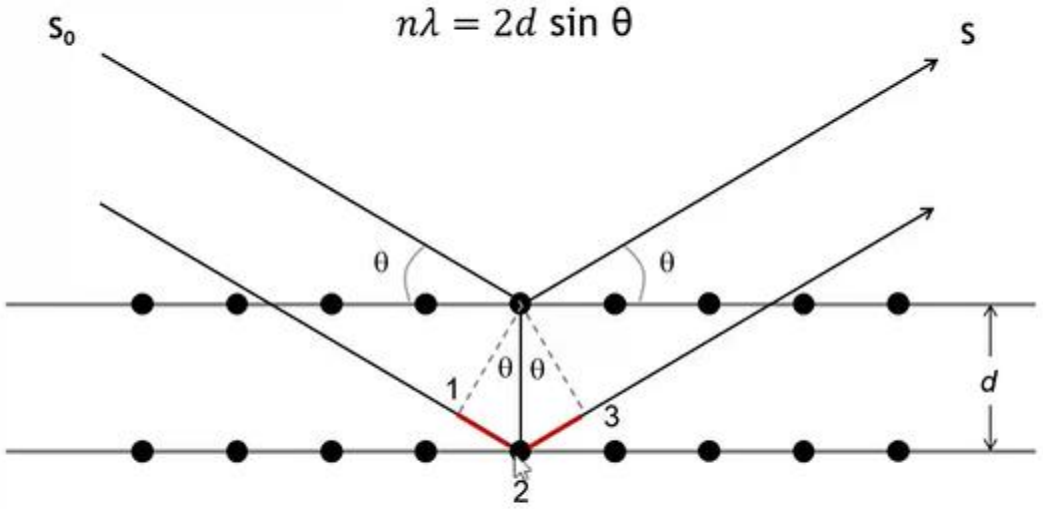


V escola de verão

Bragg's Law

$n\lambda = 2d \sin\theta$



path length difference = $n\lambda$ → constructive interference

path length difference = (1 → 2) + (2 → 3)

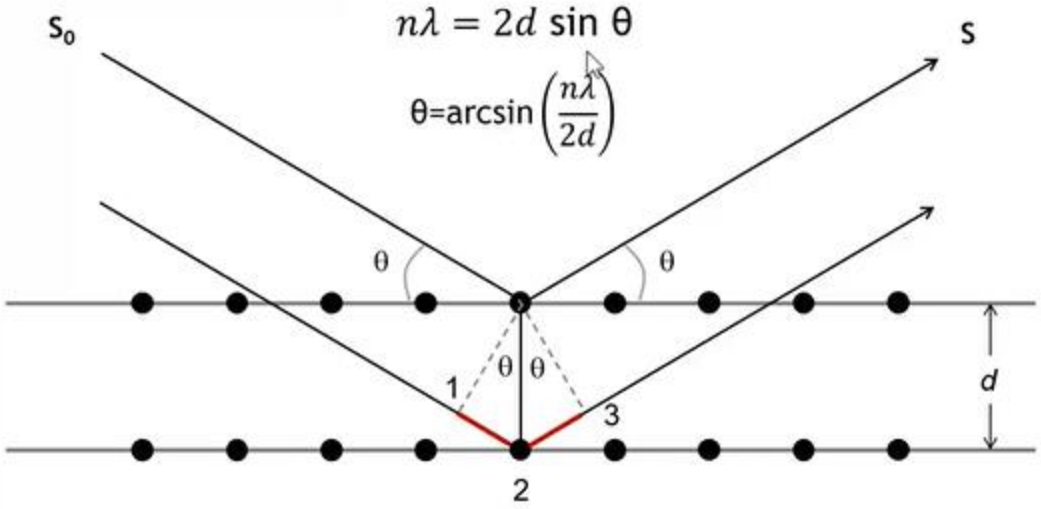
$d \sin\theta + d \sin\theta = 2d \sin\theta = n\lambda$

V escola de verão

Bragg's Law

$n\lambda = 2d \sin\theta$

$\theta = \arcsin\left(\frac{n\lambda}{2d}\right)$



path length difference = $n\lambda$ → constructive interference

path length difference = (1 → 2) + (2 → 3)

$d \sin\theta + d \sin\theta = 2d \sin\theta = n\lambda$

Collaboration for Neutrons

ISIS - UK / BR

Collaboration for Neutrons

ISIS - UK / BR

Science and Technology Facilities Council

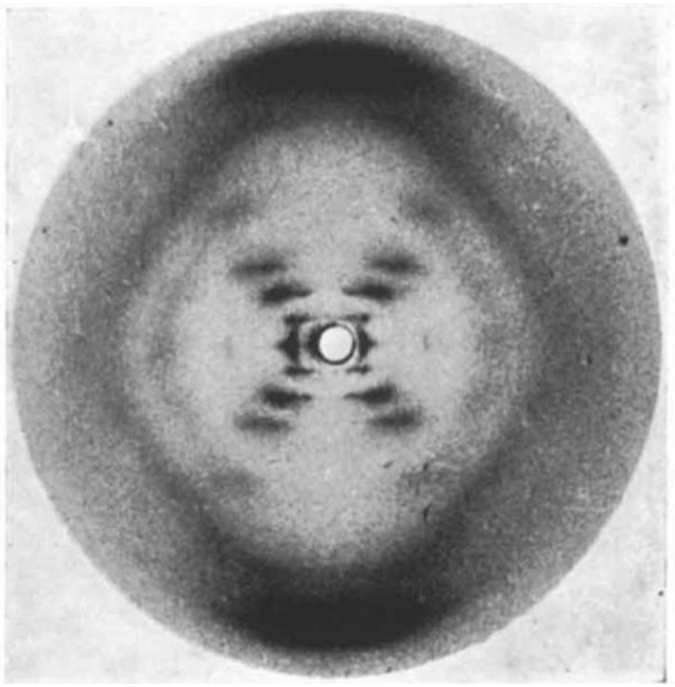
ISIS Neutron and Muon Source

LORXI

I Neutron Techniques Workshop Collaboration ISIS-UK / Brazil

Descoberta da Estrutura do DNA





DNA

"Deoxyribonucleic acid"



What is DNA?

- “Code of Life” -an organism’s information code for making proteins or traits.
- Controls all of the activities of the cell.
- Found in the nucleus of EVERY cell in our bodies.

Composition

- What are the components?
- What is a base?
- What is a nucleo**s**ide?
- What is a nucleo**t**ide?
  - What are the bases?
  - What is the sugar?
  - What is phosphate?

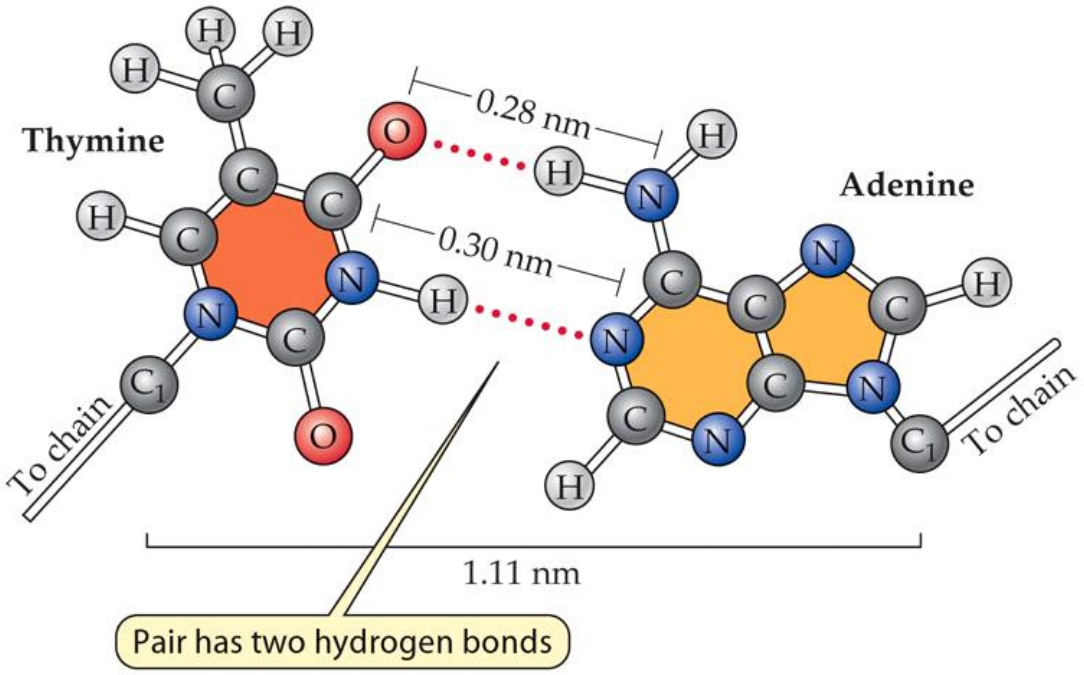
OK… what did they know

- Composition
- Hydrogen bonding
    - What is this?
    - How did they know this?
    - *What* hydrogen bonds?
- Helical structure
    - How did they know this?

Let’s look at each of these circumstances…..

On to composition

- Why not “hydrogen bonding”?
  - Investigators did not know what hydrogen bonded.
  - There were ***lots*** of possibilities….
  - Here’s a textbook example….



MICROBIAL LIFE, Figure 3.6 (Part 1) © 2002 Sinauer Associates, Inc.

But there are *other* possibilities….

- Hoogstein pairs
- *reversed* Hoogstein pairs
- *reversed* Watson-Crick pairs

An example….

So, it was not obvious…

And who was Jerry Donohue and why was he important?

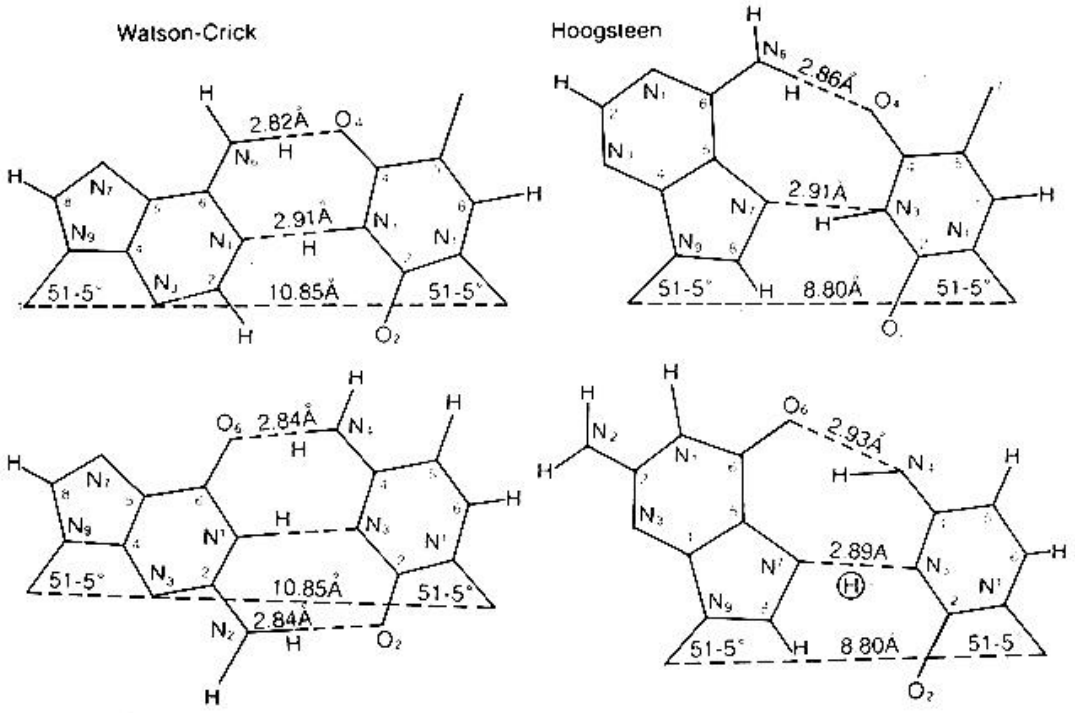
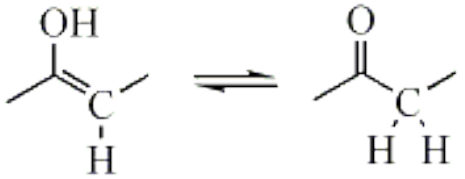
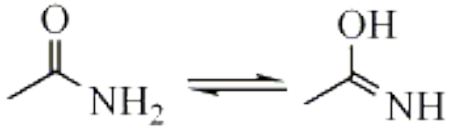


FIGURE 4.2. Coordinates of Watson–Crick and Hoogsteen pairs. (After Ref. 20.)

Enol form ⇌ Keto form



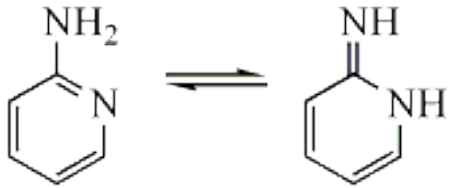
Lactam form ⇌ Lactim form

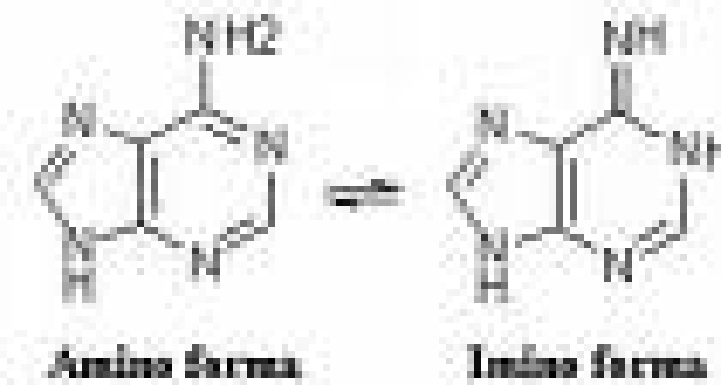


Amide form ⇌ Imidic acid form



Amine form ⇌ Imine form





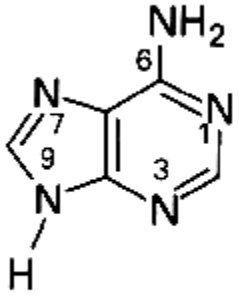
Here's the problem…

You need the structure on the left.

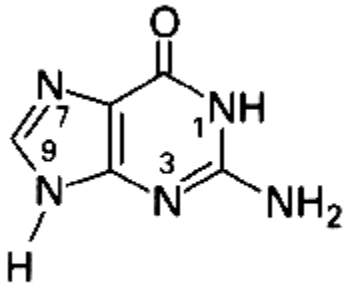
Watson and Crick originally worked with the structure on the right.

Composition

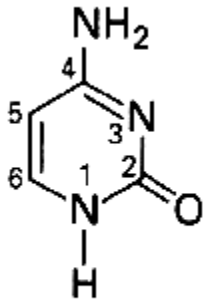
- So composition *alone* is insufficient!
- One must use the “correct” tautomers.
- Even knowing the “correct” tautomers is not sufficient.
- Distributing them in space becomes important.
  - Let’s look at the problem…



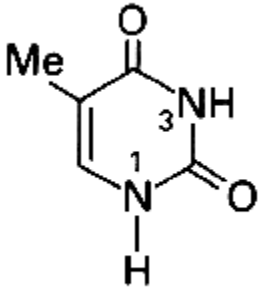
adenine



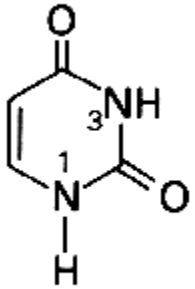
guanine



cytosine



thymine



uracil

COMPOSITION: What about Chargaff's "rules"?

A + G = T + C purines = pyrimidines

A + C = G + T amino's = keto's

Some algebra:

A = T + C – G
G = A + C –T
A = T + C – (A + C – T)
A = T + C – A – C + T
A = T – A + T
2A = 2T
A = T

Similarly, G = C

But Chargaff *never* reported that A = T or G = C….

COMPOSITION…

- Components were known
- Tautomeric forms not certain
- Significance of abundances of forms (as demonstrable by algebra) not known

- HOW WAS A=T G=C BONDING ESTABLISHED?

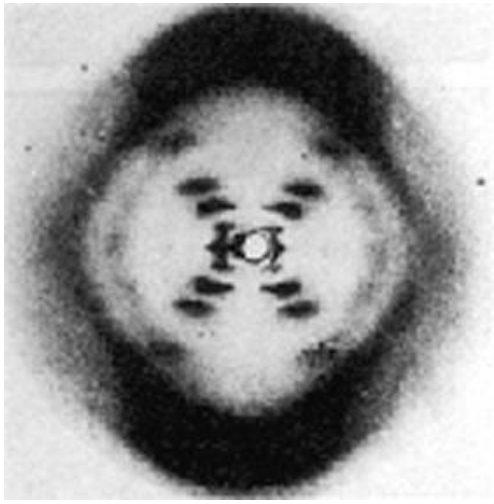
  - That in a moment… first hydrogen bonding

That hydrogen bonds were important in the structure of DNA was known *before* Watson (James Dewey Watson) and Crick (Francis Harry Compton Crick) initiated their "MODEL BUILDING"

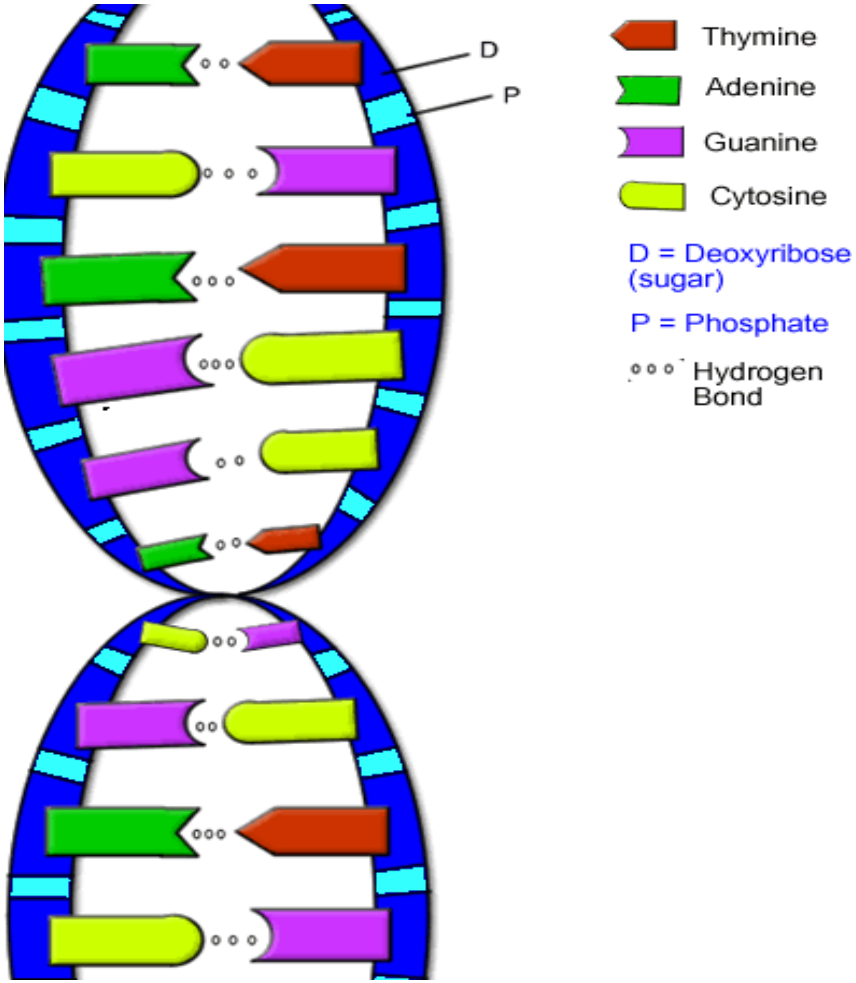
- What are hydrogen bond?
- What is the strength of hydrogen bonds?
- How was it known *before* the structure of DNA was known that hydrogen bonds contributed to the structure of DNA?

History of DNA

- By mid 1800's, scientists knew that nuclei contained chemicals called nucleic acids.
- Rosalind Franklin used x-ray crystallography to discover that DNA is the shape of a twisted ladder called a "double helix"
  - 1953- James Watson and Francis Crick made model of DNA
  - Won the Nobel Prize

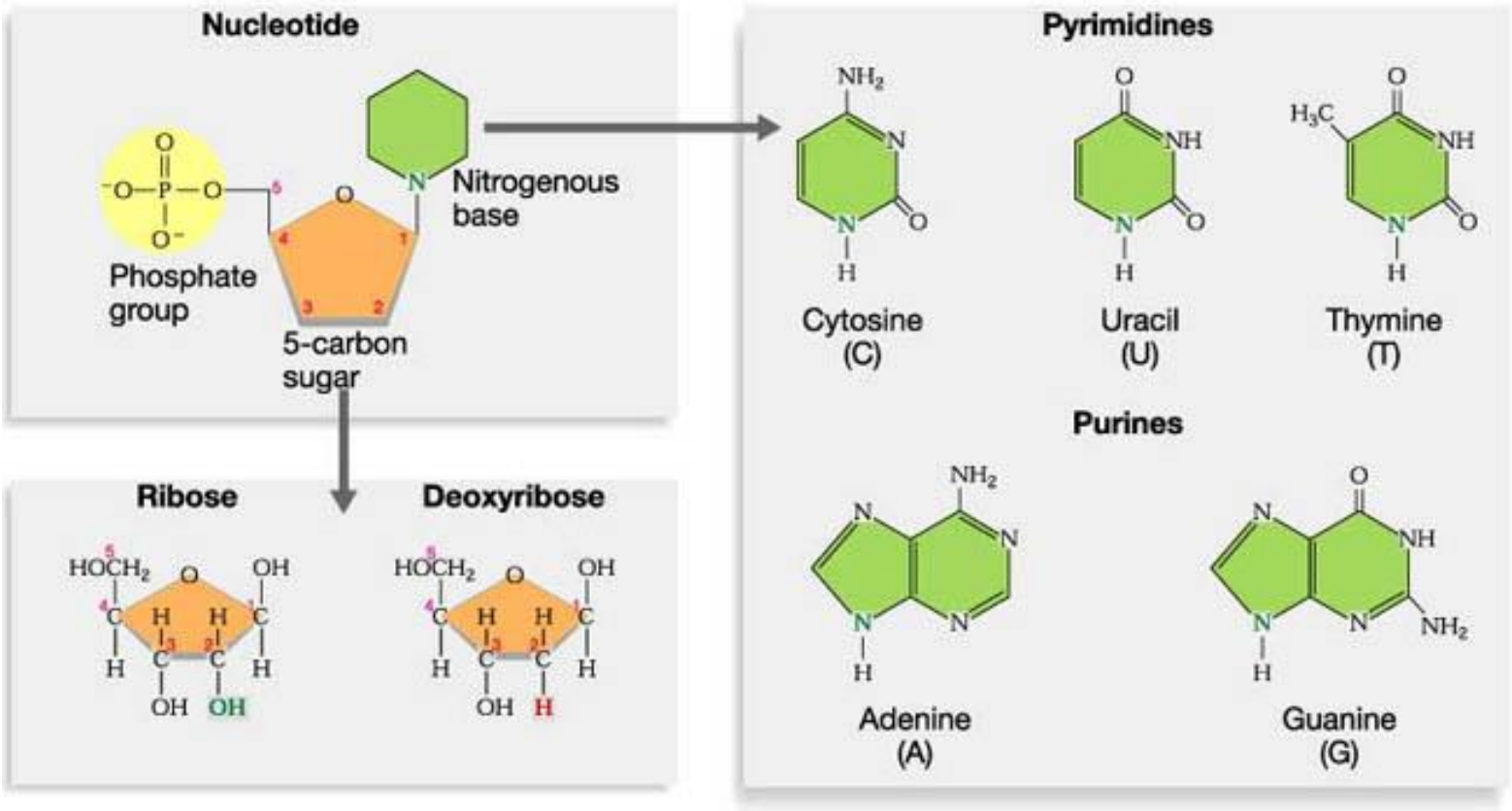


DNA Model



- Sides of Ladder: Sugar (deoxyribose) and phosphates
- Rungs of ladder: Nitrogen bases (adenine, thymine, guanine, and cytosine)

DNA structure



DNA is made up of four bases. RNA also has four bases, but has uracil instead of thymine.

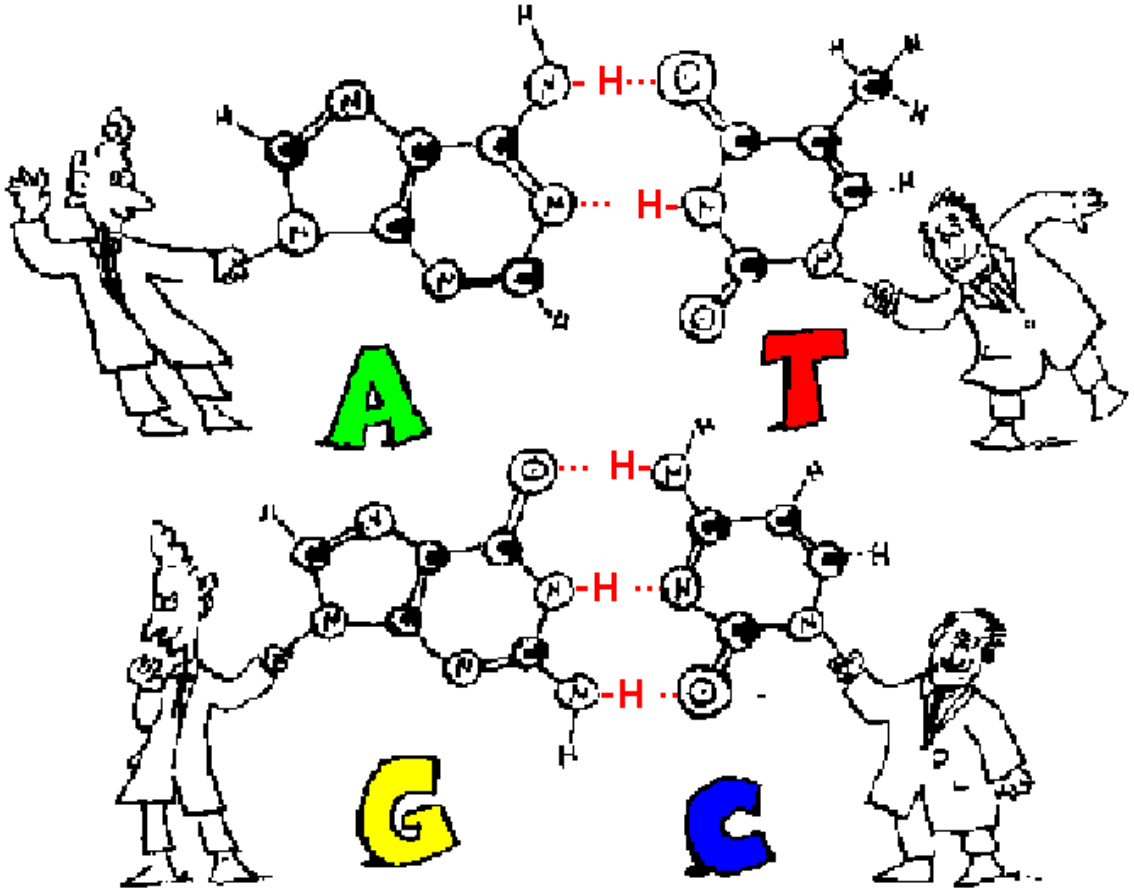
Chargaff's Rules

- The amount of cytosine always equals the amount of guanine.
- The amount of adenine always equals the amount of thymine.
- Therefore, they exist as pairs that match up with each other.

A=T

C=G

DNA structure



Across the DNA double-ladder, A always pairs with T, C always pairs with G because of the number of hydrogen bonds the bases form.

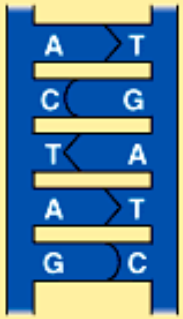
How is DNA Copied?

- By DNA Replication (occurs in interphase)
- Steps:

  1. Two sides of DNA molecule unwind and separate.

  2. Nitrogen bases floating in the nucleus pair up with original bases on each separated strand.

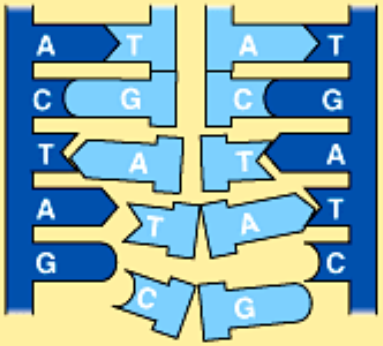
  3. Two new identical DNA strands are formed



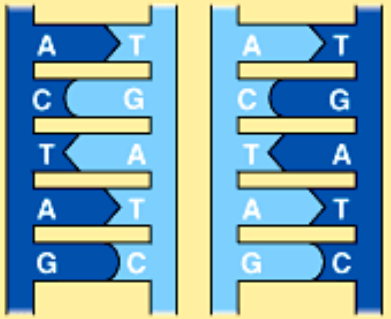
(a) The parent molecule has two complementary strands of DNA. Each base is paired by hydrogen bonding with its specific partner, A with T and G with C.



(b) The first step in replication is separation of the two DNA strands.



(c) Each parental strand now serves as a template that determines the order of nucleotides along a new complementary strand.



(d) The nucleotides are connected to form the sugar-phosphate backbones of the new strands. Each "daughter" DNA molecule consists of one parental strand and one new strand.

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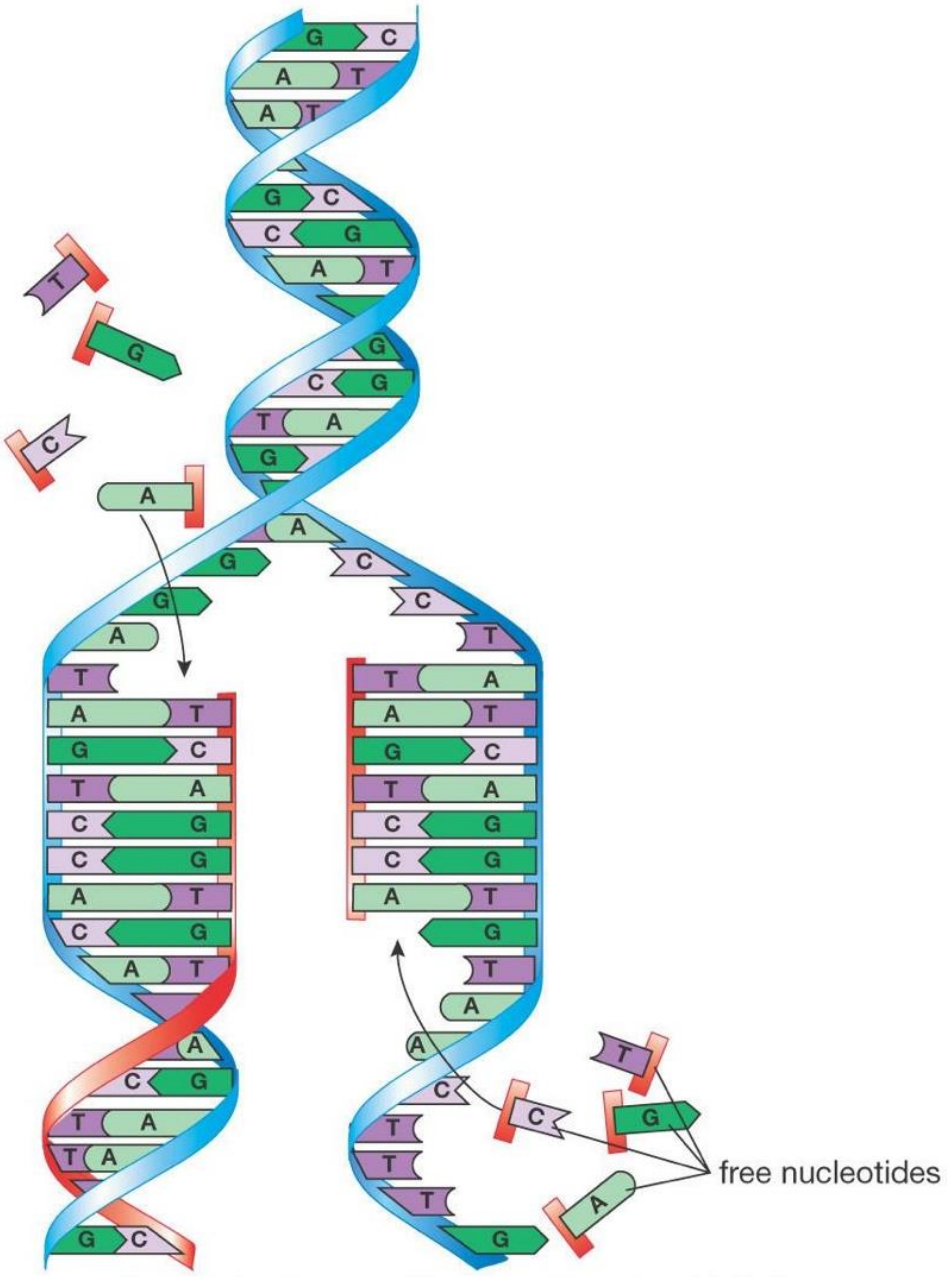
Overview of DNA replication. The hydrogen bonds break to “unzip” the DNA strand. Enzymes guide free nucleotides to the exposed single strands and match the nucleotides.



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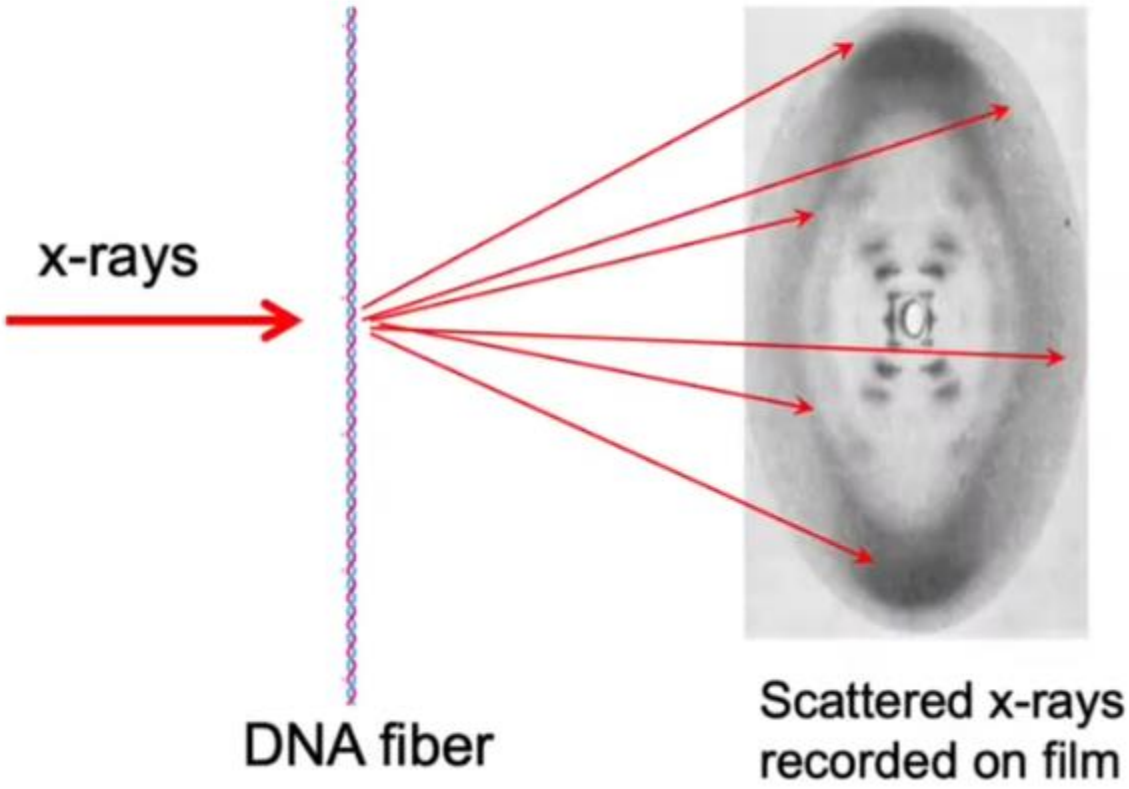
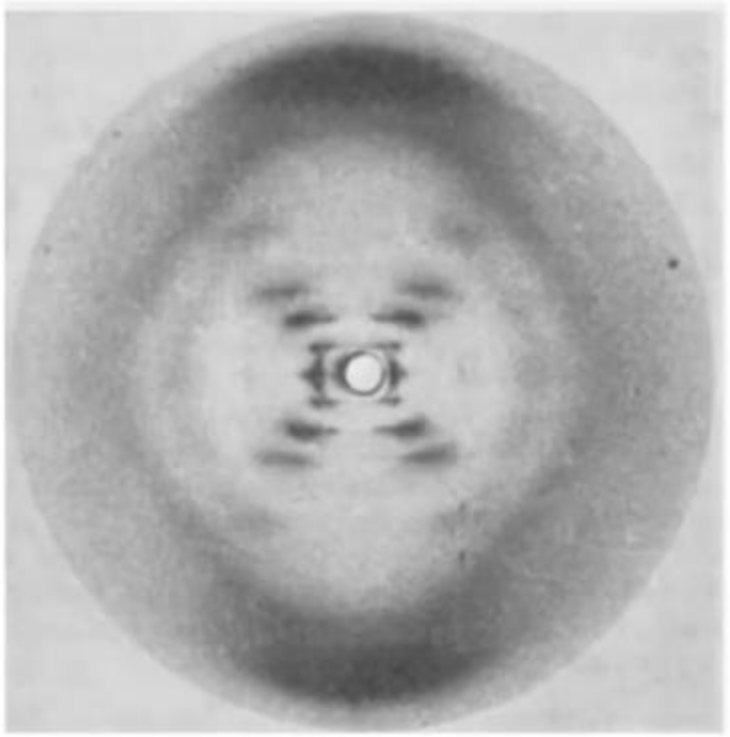
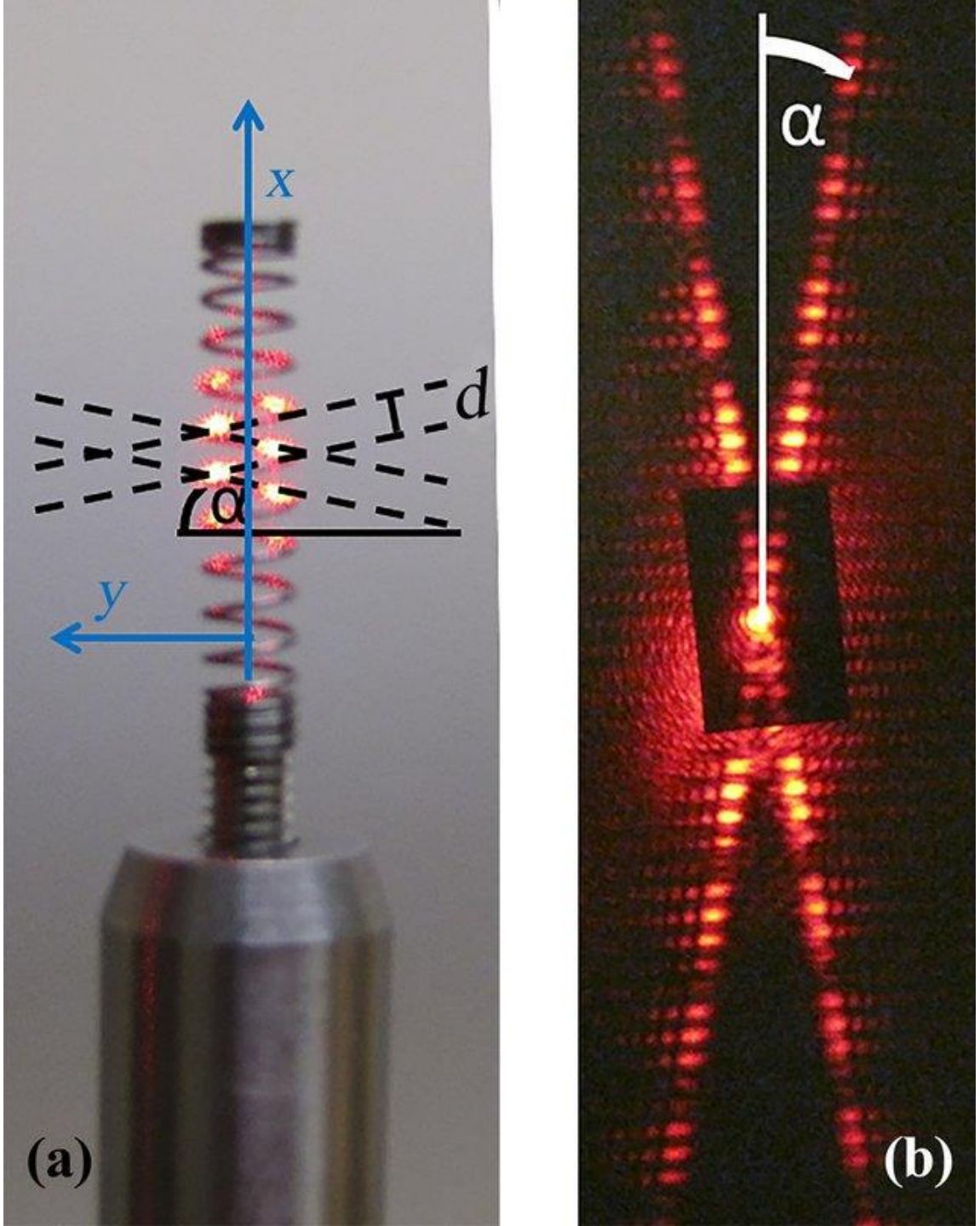
Franklin's experiment: DNA fiber diffraction

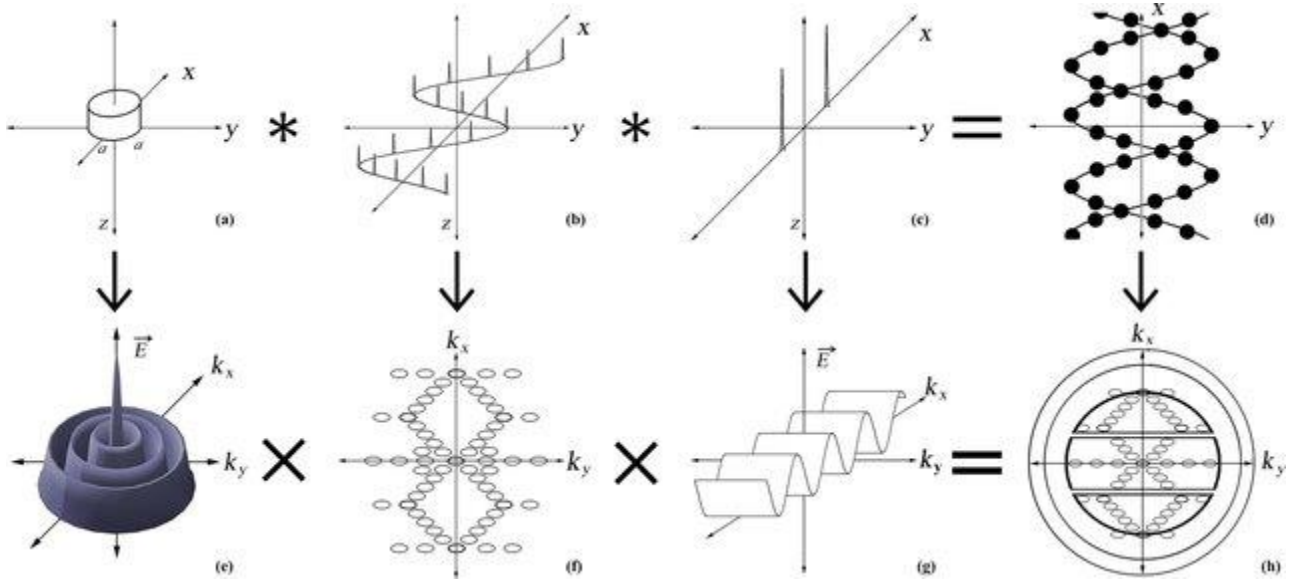


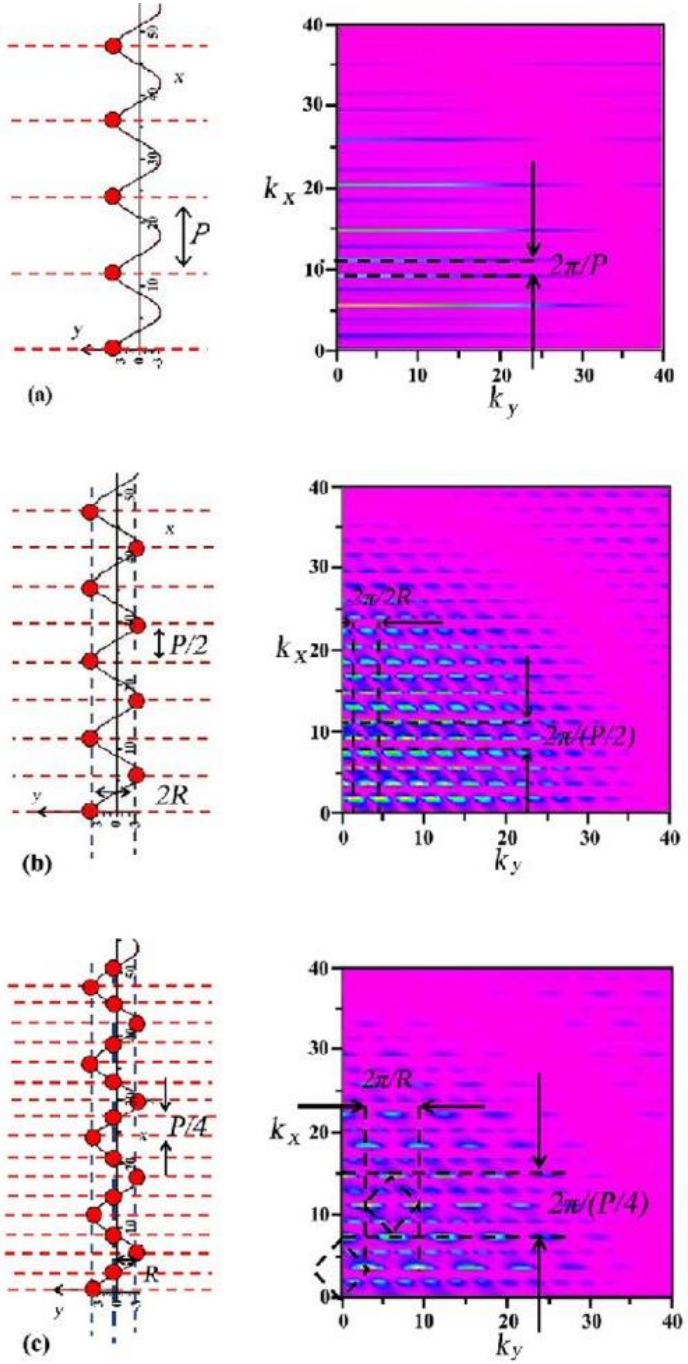
Interpreting photograph 51



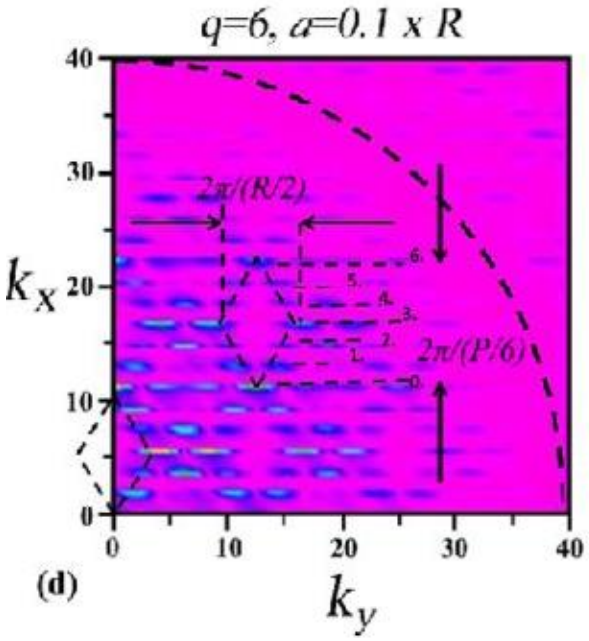


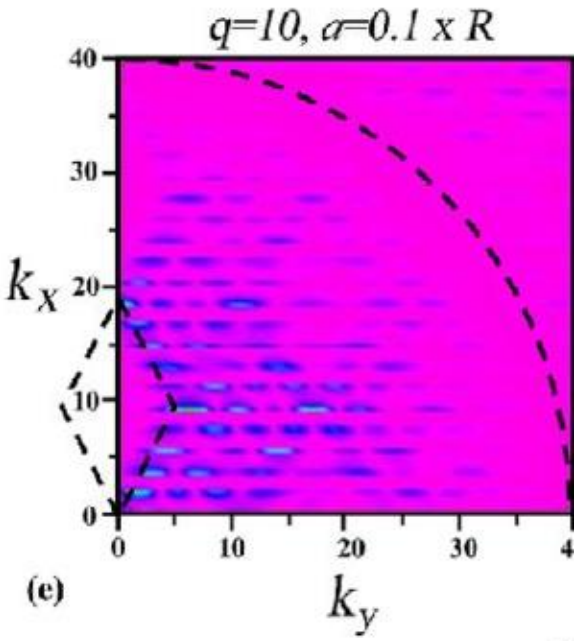

x
y
d
α
(a)
α
(b)

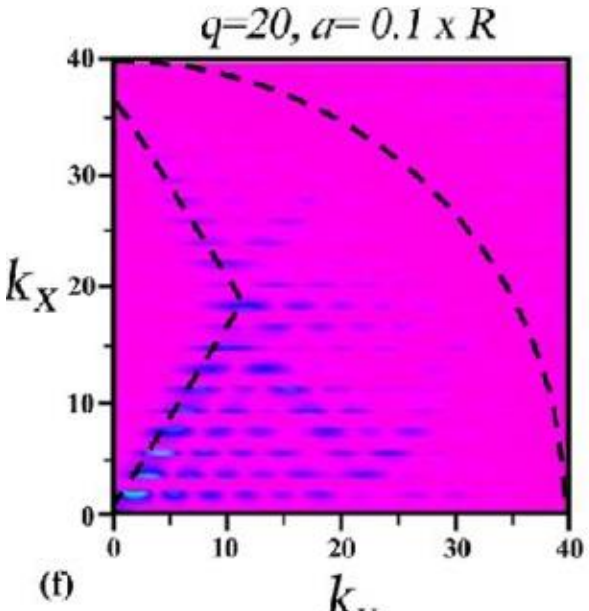

x
y
z
a
a
(a)
*
x
y
z
(b)
*
x
y
z
(c)
=
x
y
(d)
$\vec{E}$
k_x
k_y
(e)
×
k_x
k_y
(f)
×
$\vec{E}$
k_x
k_y
(g)
=
k_x
k_y
(h)

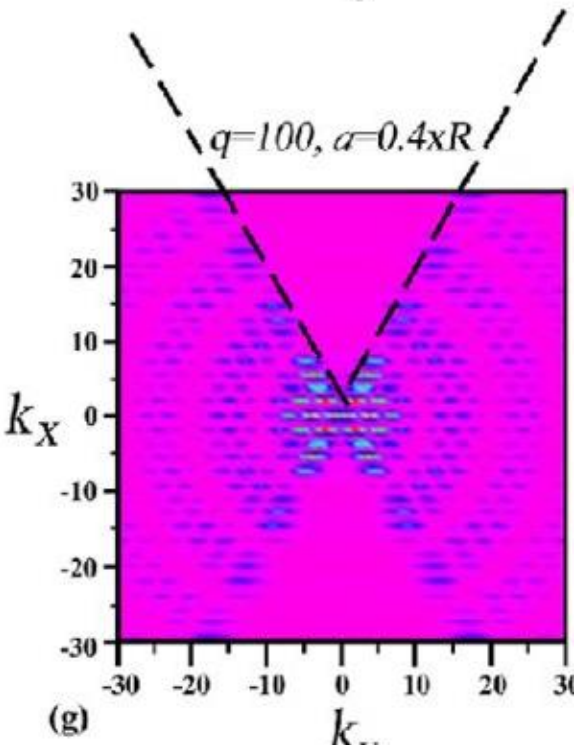


First quadrant of the diffraction pattern for (a) one hole (q ¼ 1), (b) two holes (q ¼ 2), and (c) four holes (q ¼ 4) per pitch. The dotted lines and arrows show how the pattern is related to the diffracting structure. (Note the first minimum of the Airy disk that suppresses the pattern in an area outlining a quarter of a circle.)



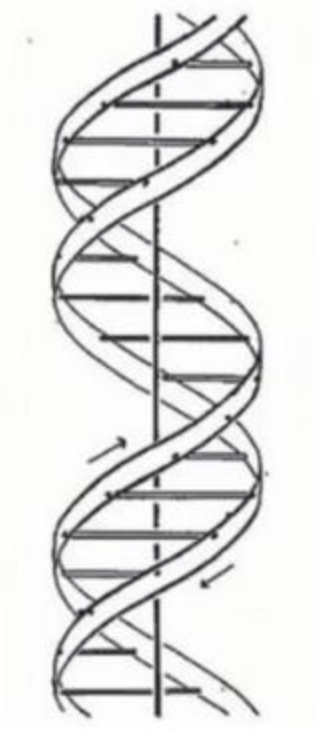


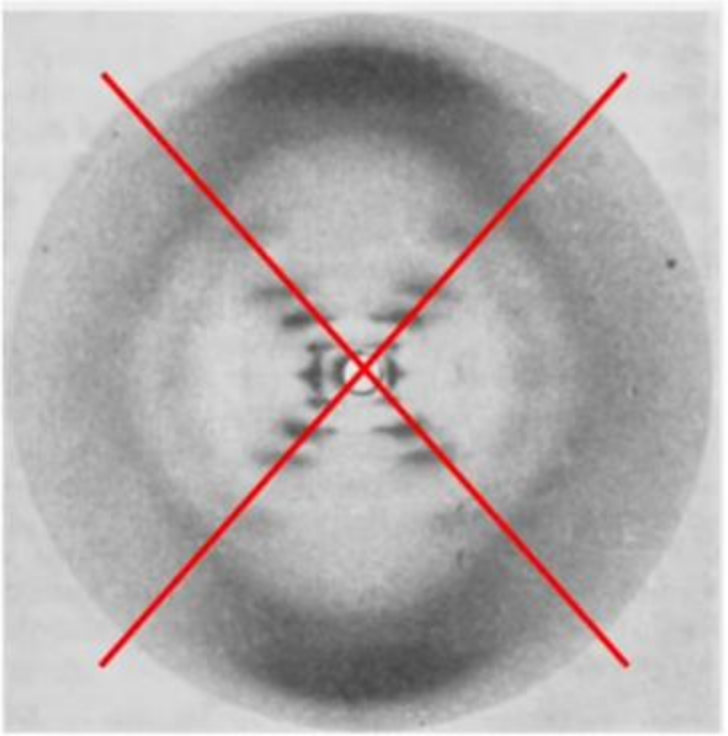




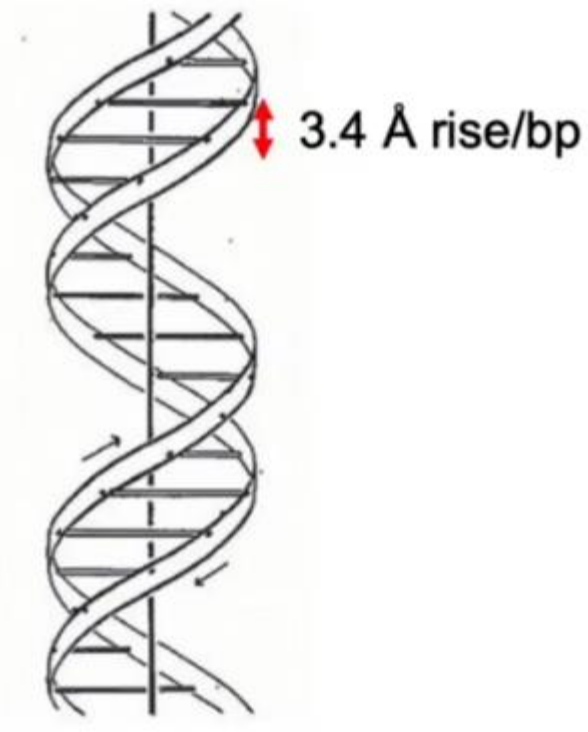
Panels (d)-(g) were all made using P ¼ 3.4, R ¼ 1, and 5 illuminated pitches. The dashed quarter circle outlines the first minimum of the Airy disk. Panel (g) shows that when the holes overlap, the rhombus grows into an X

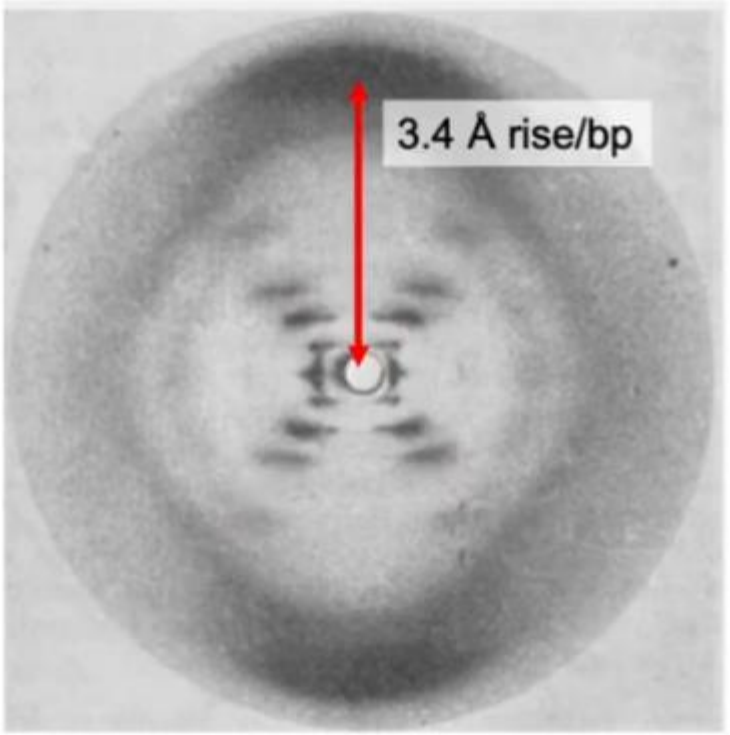
Interpreting photograph 51



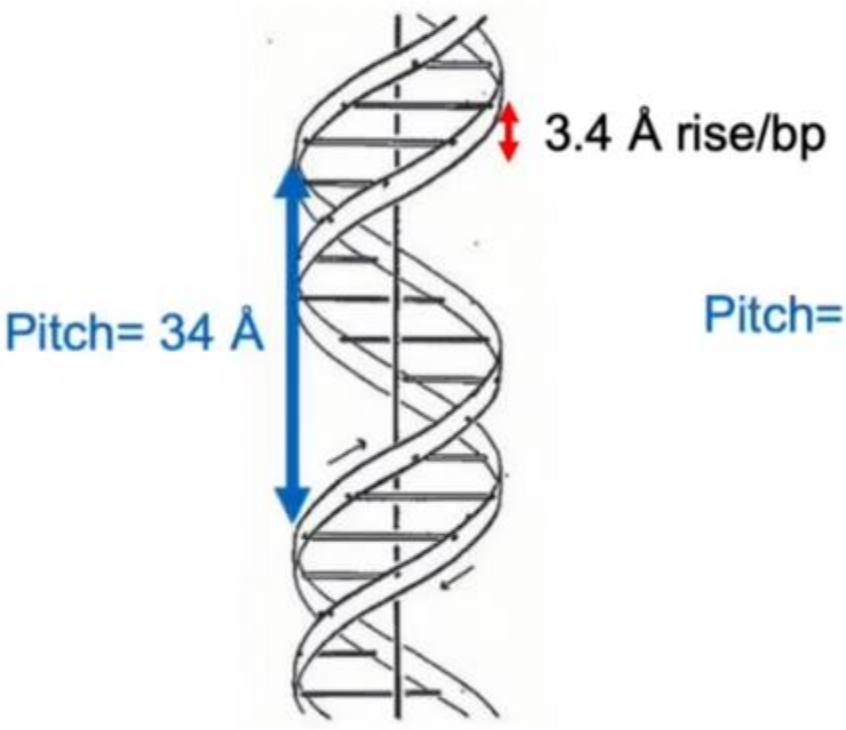


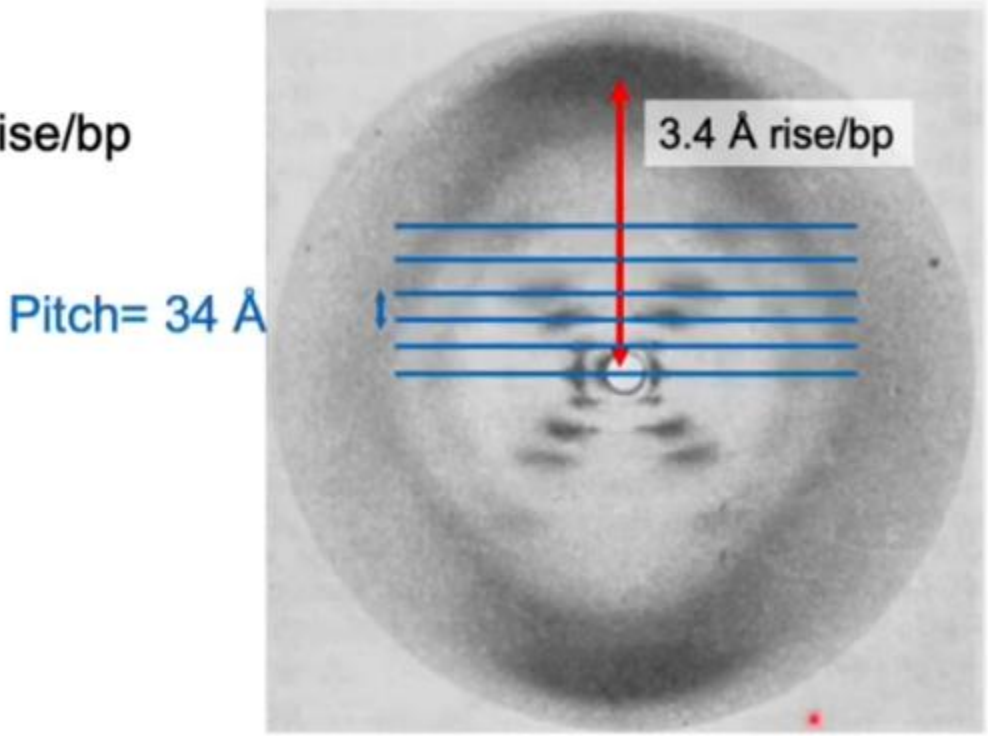
Interpreting photograph 51





Interpreting photograph 51





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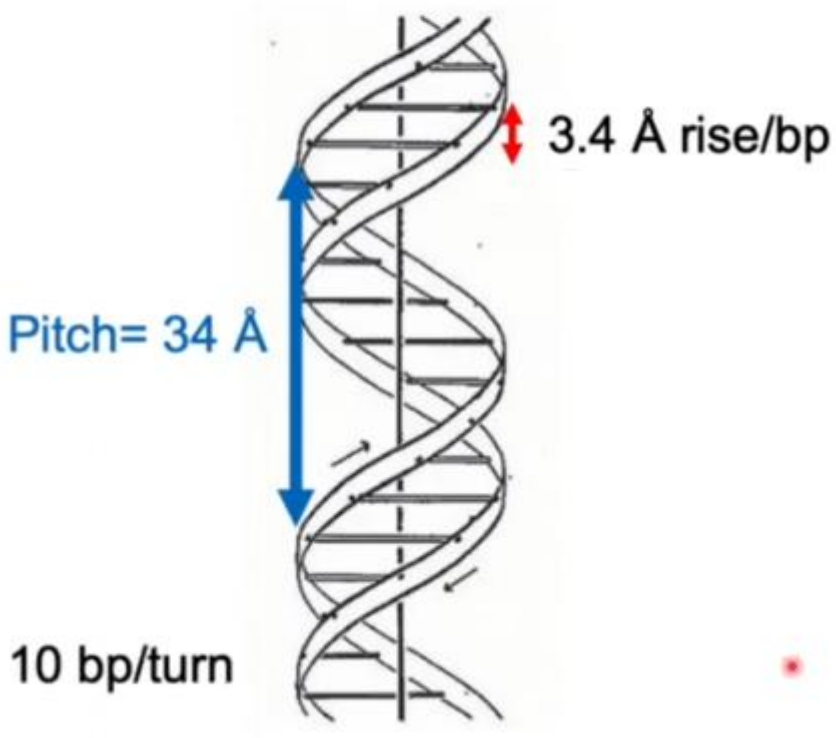

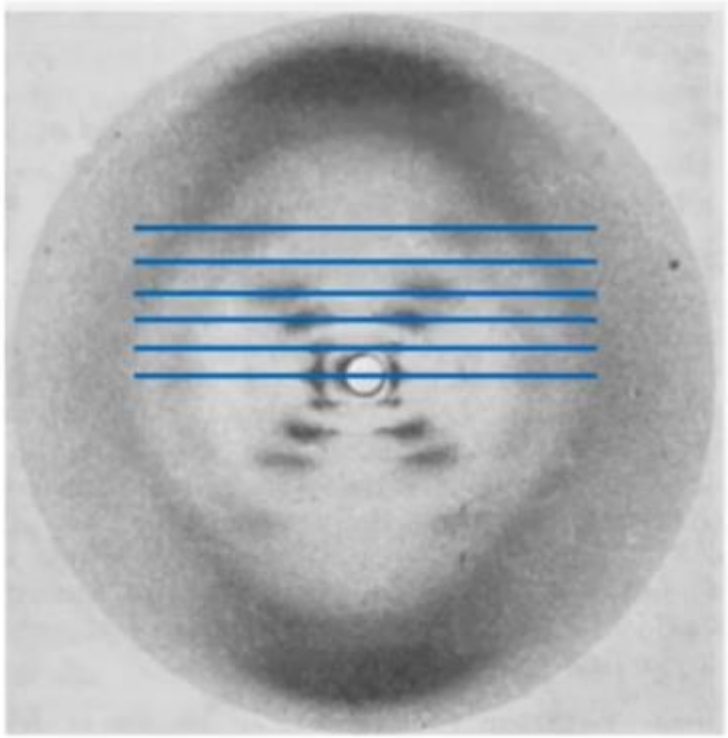

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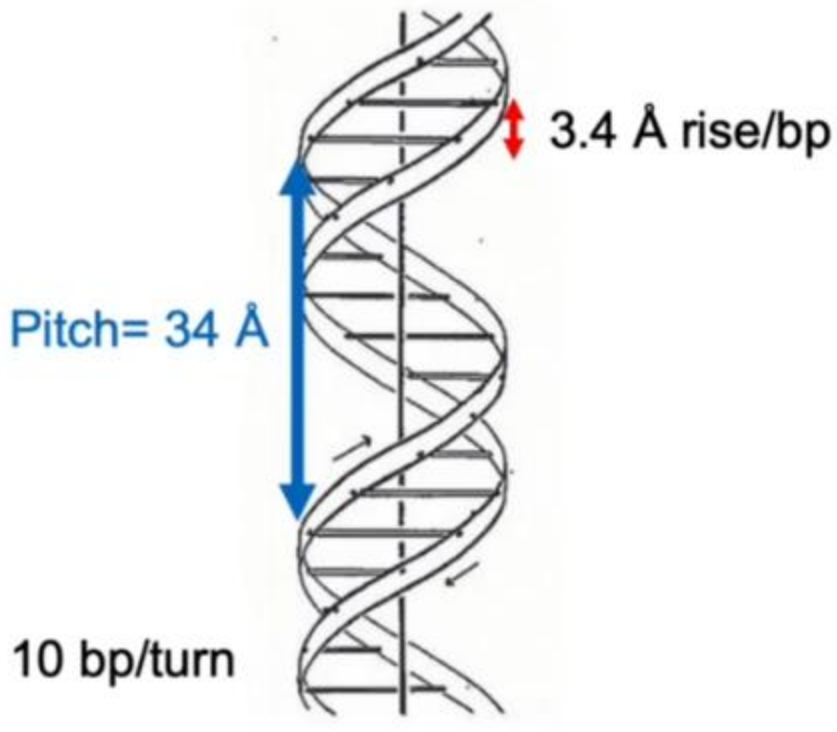

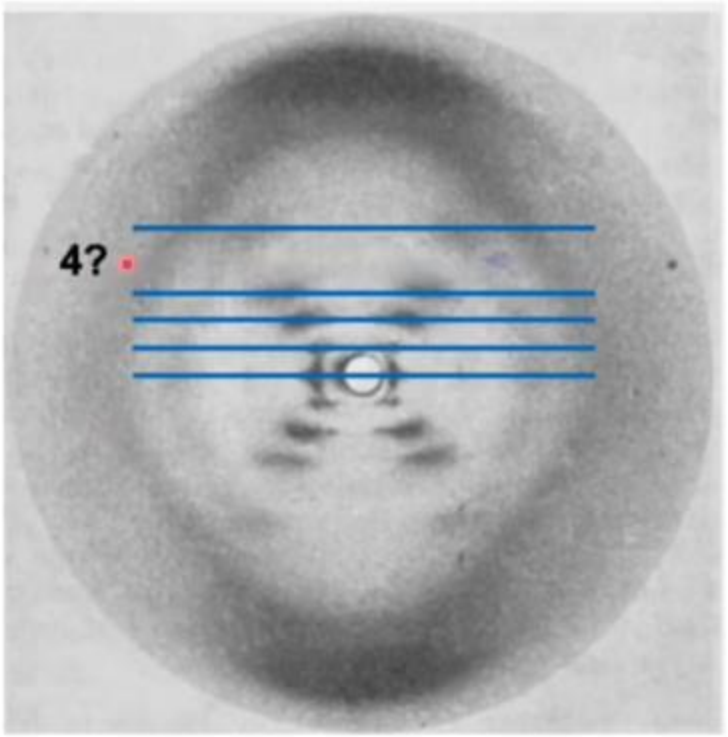

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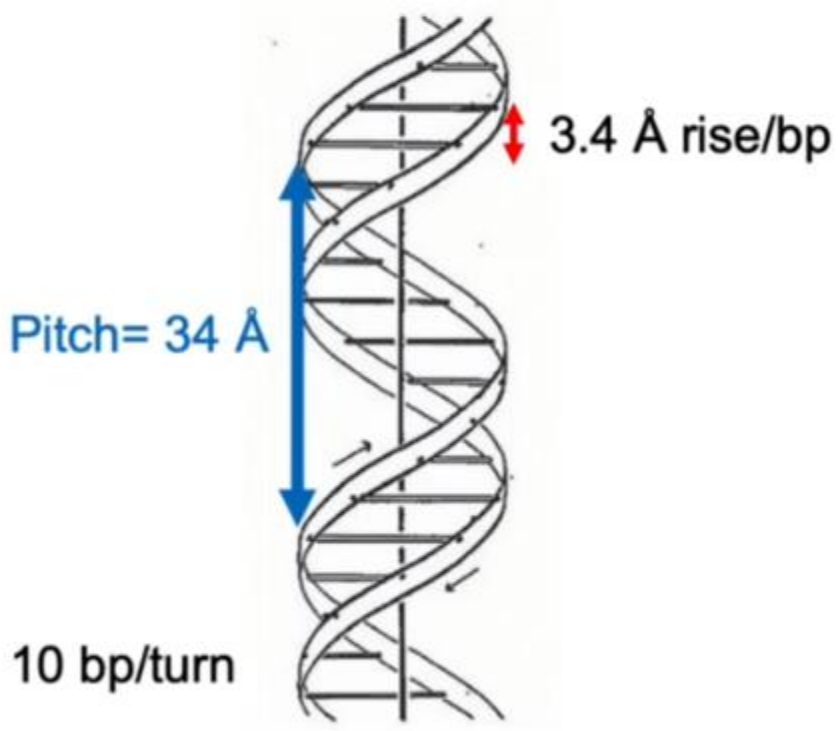

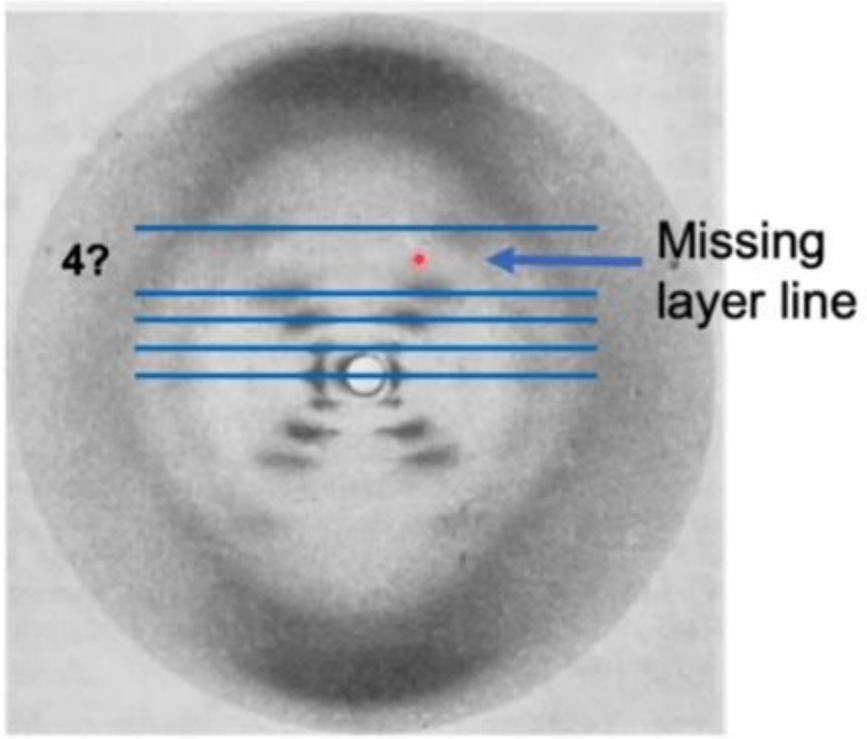

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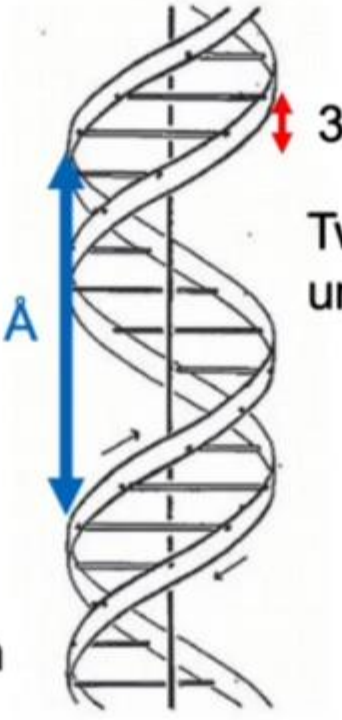
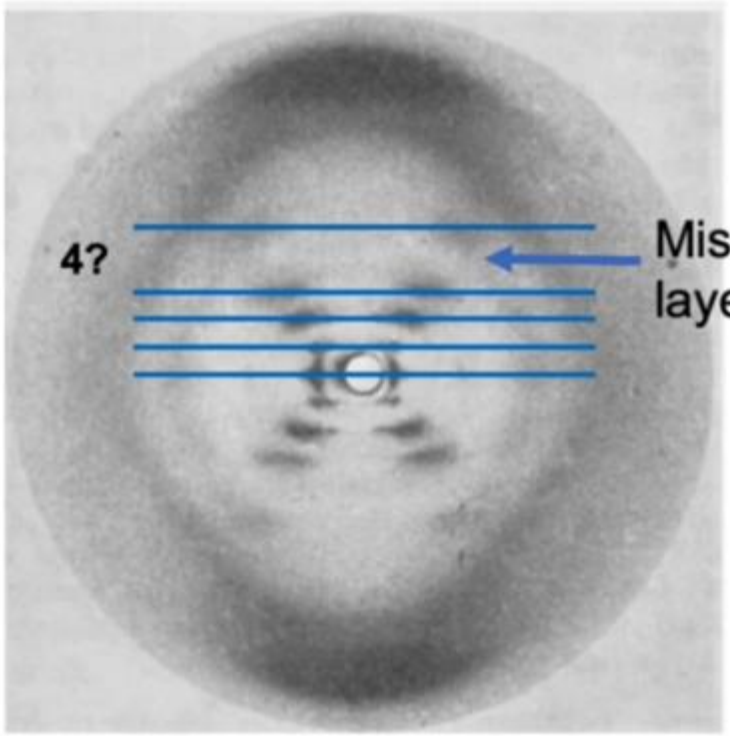


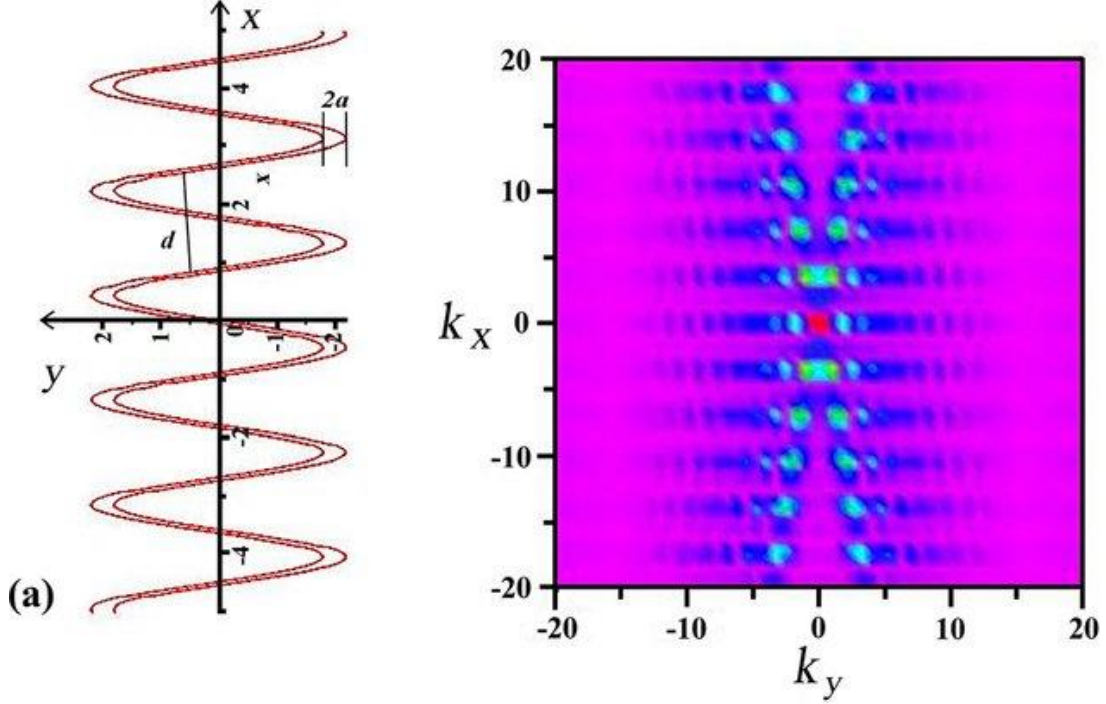
3.4 Å rise/bp

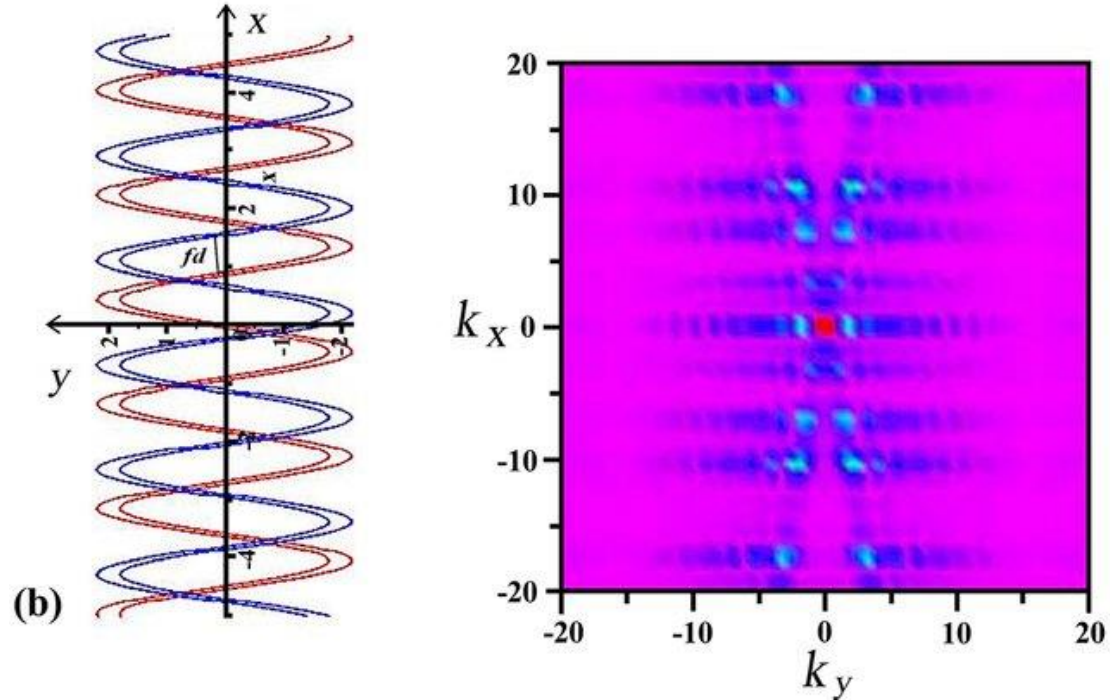
Two strands
unequally spaced

Pitch= 34 Å

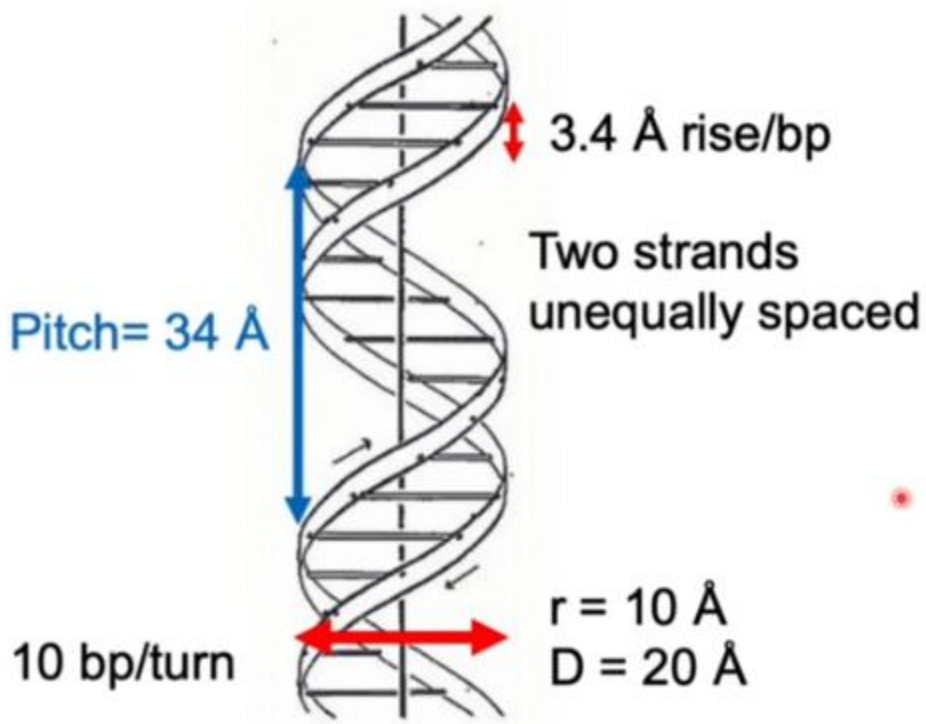
10 bp/turn

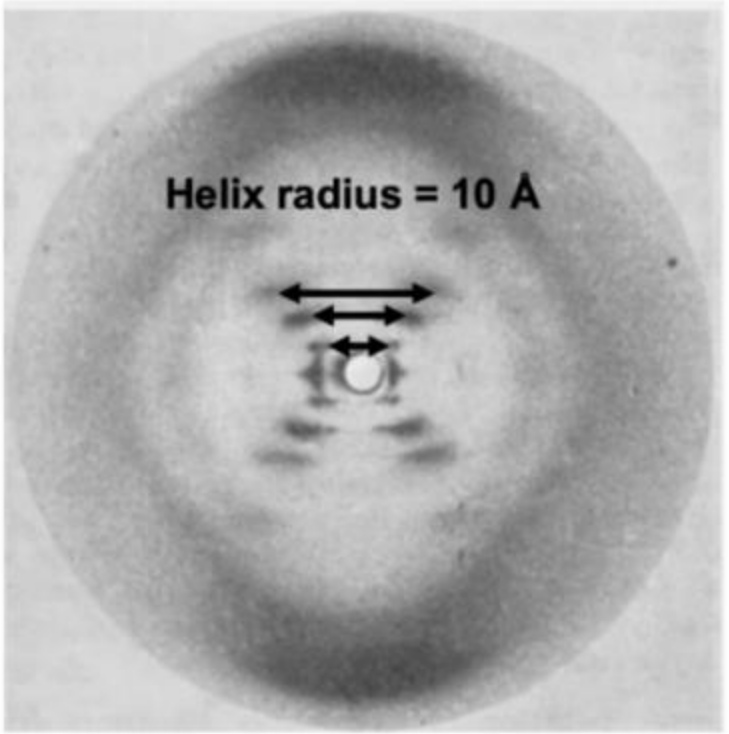



X
2a
x
d
y
(a)
20
10
0
-10
-20
k_X
-20
-10
0
10
20
k_y

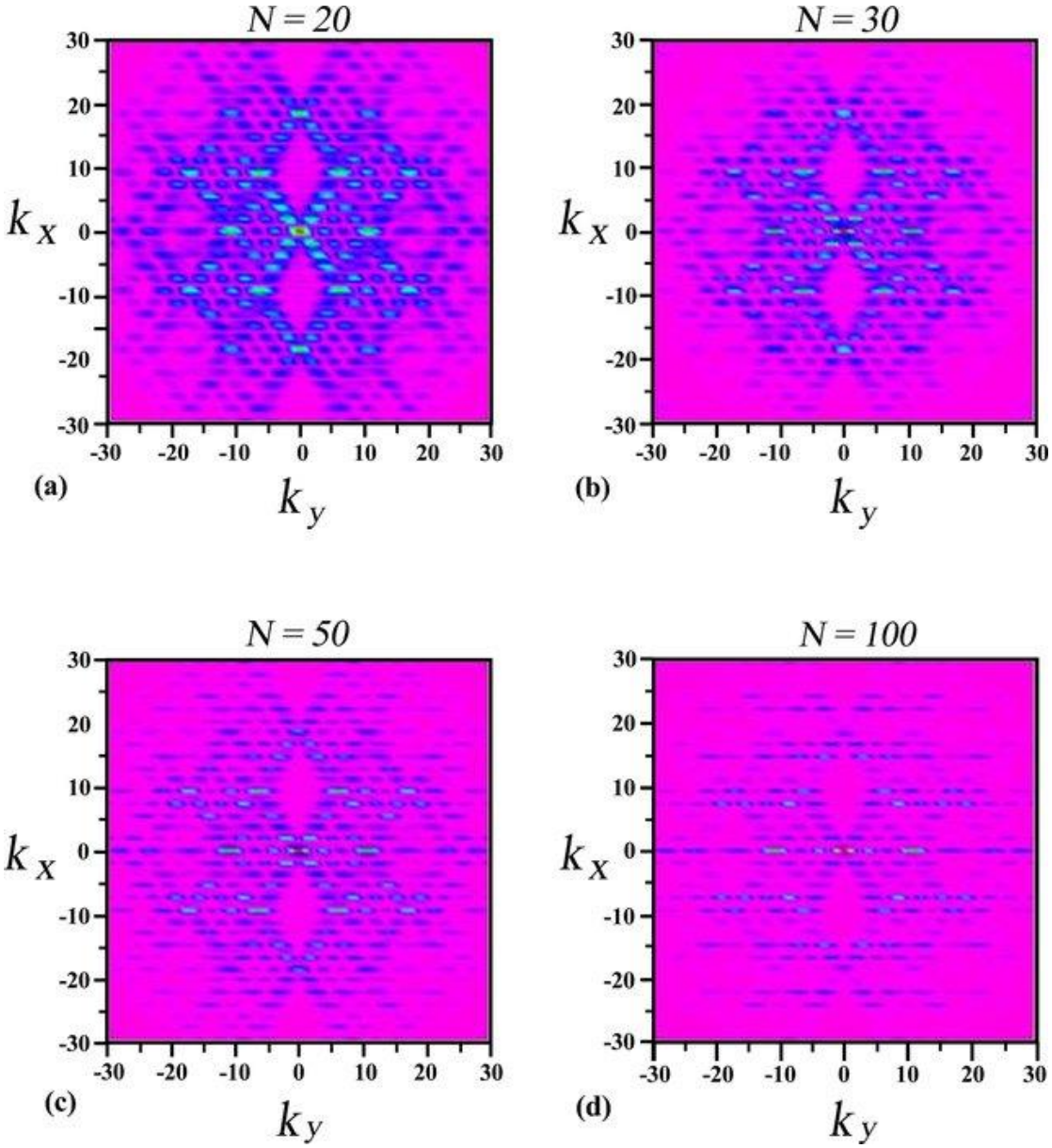

X
x
fd
y
(b)
20
10
0
-10
-20
k_X
-20
-10
0
10
20
k_y

Interpreting photograph 51

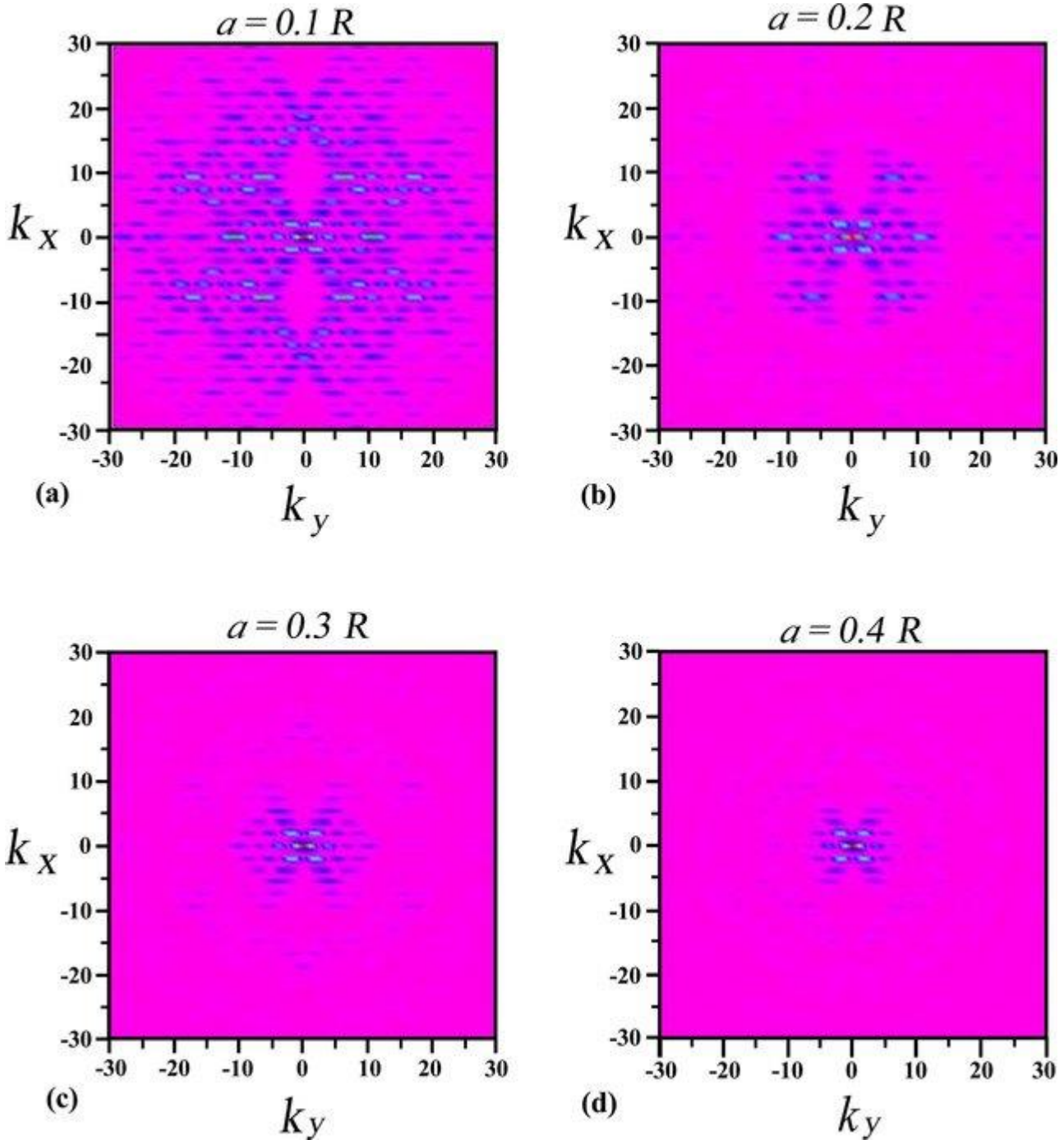


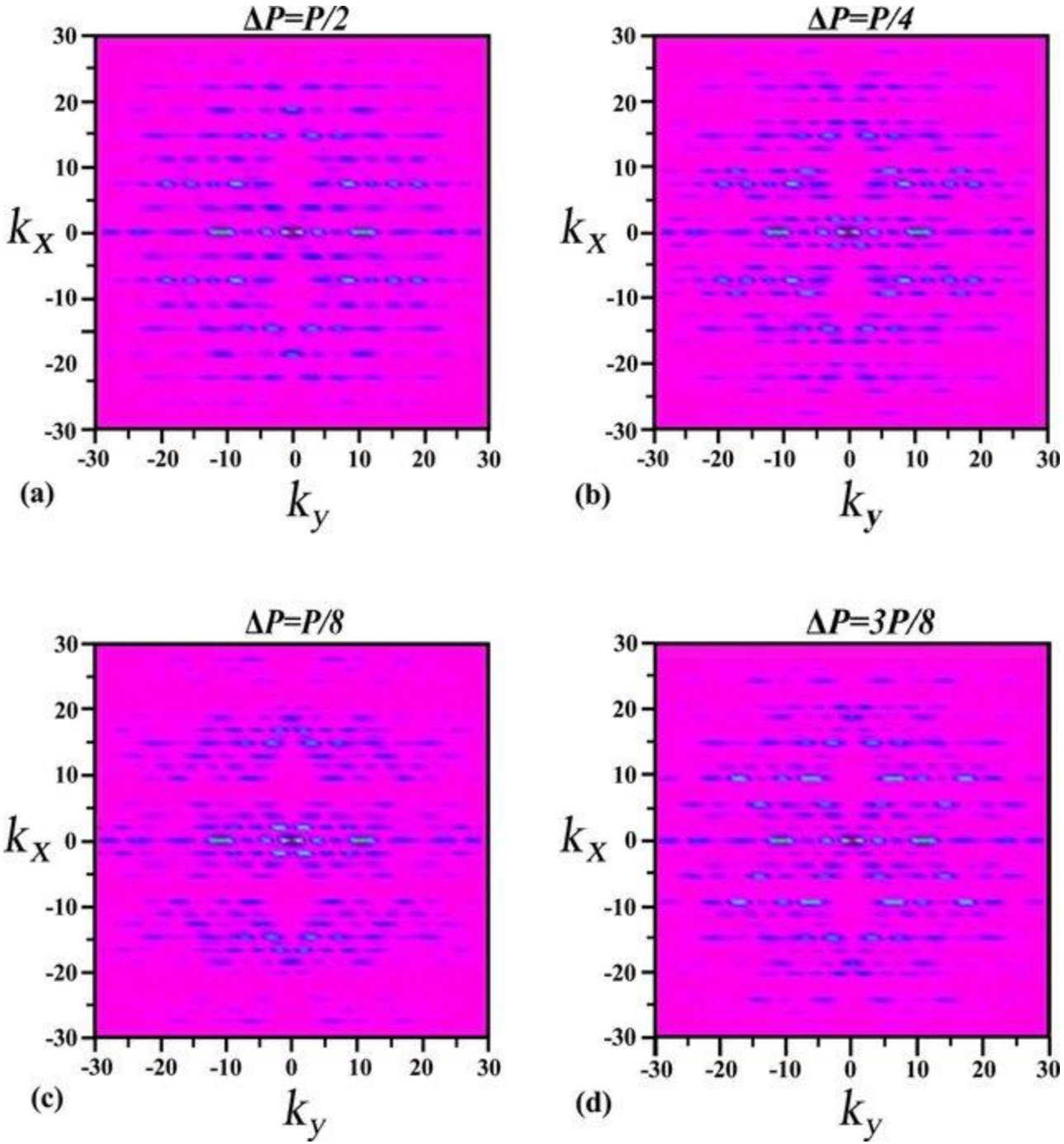


Franklin & Gosling (1953) Nature 171:740-741

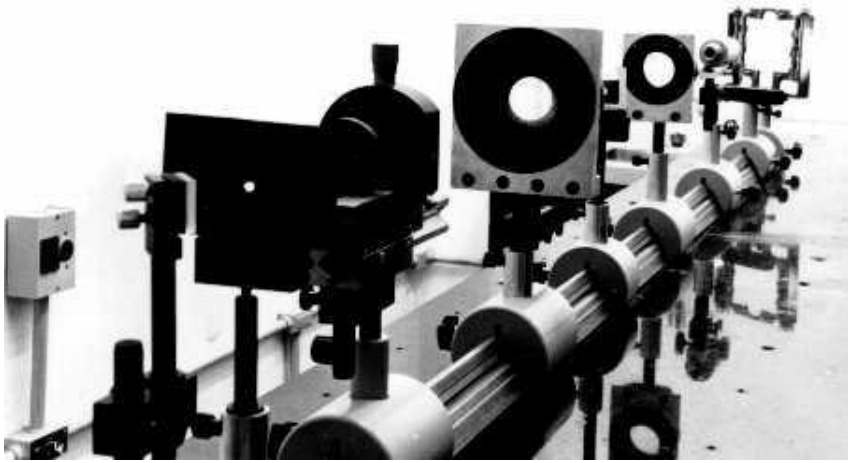


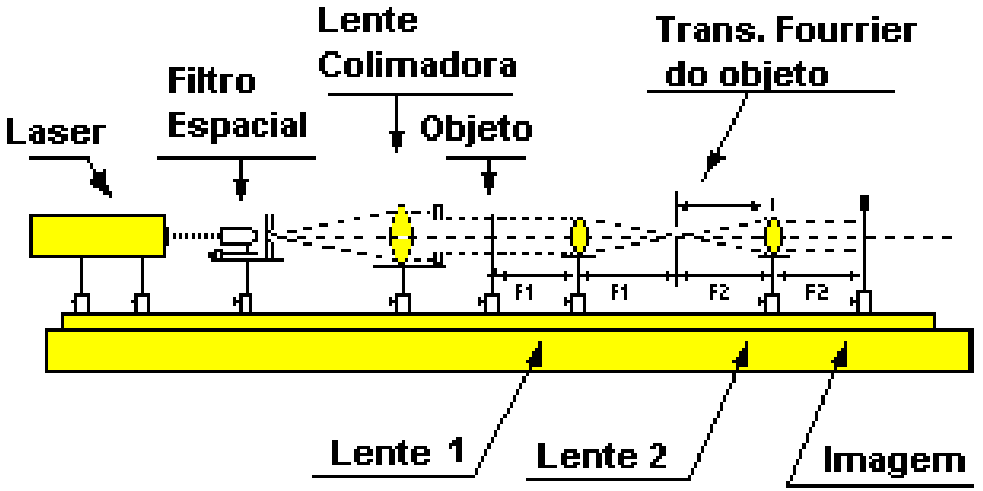
As the number of illuminated pitches (N) increases, the diffraction pattern becomes sharper (similar to two-beam versus multiple-beam interference).


a = 0.1 R
a = 0.2 R
a = 0.3 R
a = 0.4 R
k_x
k_y
30
20
10
0
-10
-20
-30
(a)
(b)
(c)
(d)


ΔP=P/2
ΔP=P/4
ΔP=P/8
ΔP=3P/8
30
20
10
0
-10
-20
-30
k_X
k_y
(a)
(b)
(c)
(d)

Processamento de Imagem









Transformada de Fourier

$$F(\omega) = \mathcal{F}\{f(t)\} = \int_{-\infty}^{\infty} f(t)e^{-j\omega t}\,dt.$$

Collaboration for Neutrons

ISIS - UK / BR

Collaboration for Neutrons

ISIS - UK / BR

Science and Technology Facilities Council

ISIS Neutron and Muon Source

LORXI

I Neutron Techniques Workshop Collaboration ISIS-UK / Brazil