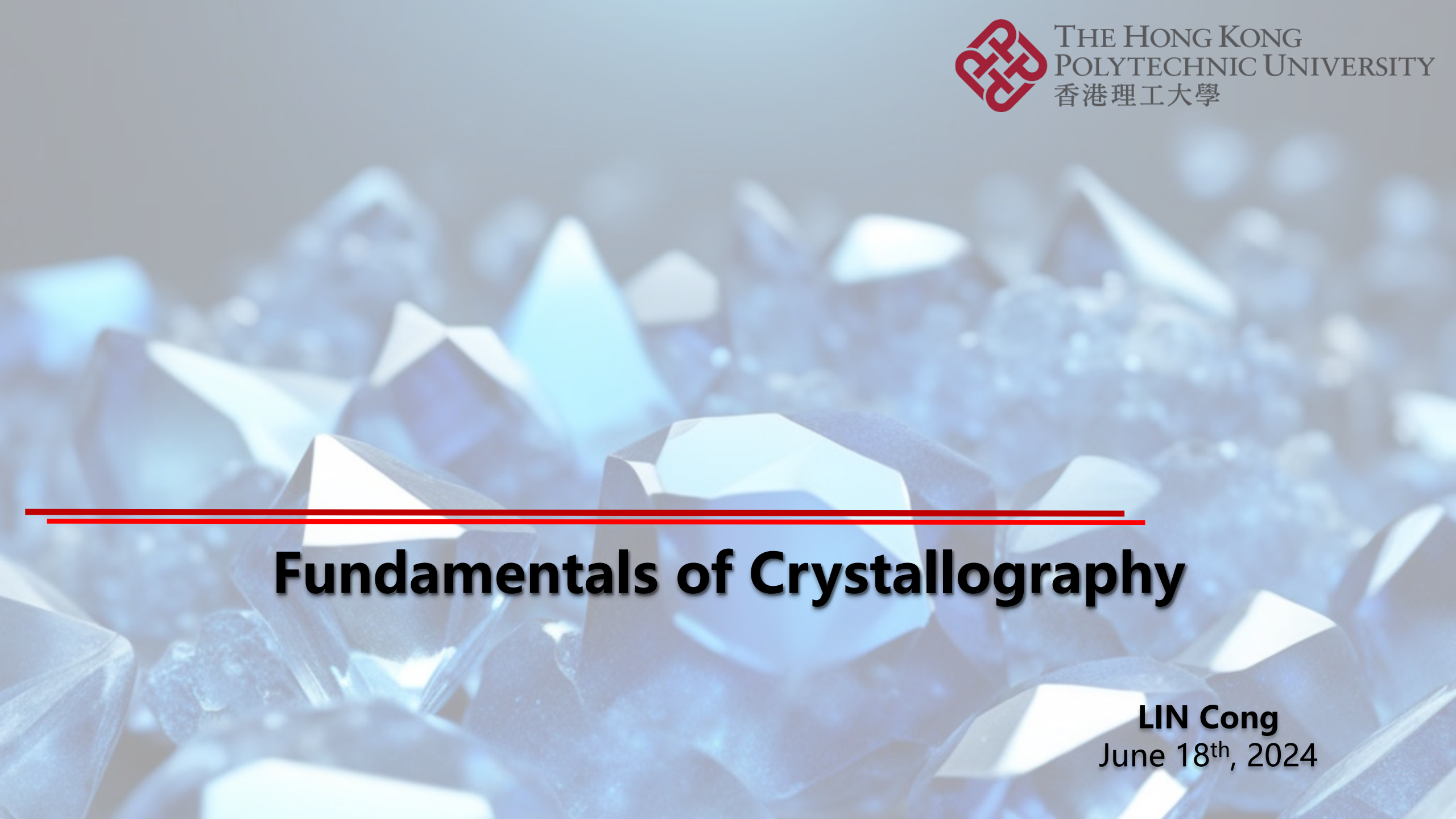


THE HONG KONG POLYTECHNIC UNIVERSITY
香港理工大學

Fundamentals of Crystallography

LIN Cong

June 18th, 2024

Some Nice Crystals



Fluorite (CaF_2)



Snowflake (H_2O)



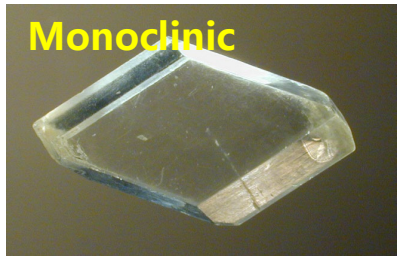
Rutile (TiO_2)



Cinnabarite (HgS)



Natrolite
($Na_2Al_2Si_3O_{10}•2H_2O$)



Gypsum
($CaSO_4•2H_2O$)



Albite
($NaAlSi_3O_8$)







Crystal Palace

In the Naica mines of northern Mexico, near the city of Chihuahua, an underground city of giant crystals form a truly unreal landscape. Hundreds of thousands of years old, the giant selenite crystals existed for millennia in a completely closed environment; a true geode, the Naica Cuevo de los Cristales is completely covered in the transparent "macrocrystals," some of which have grown up to 12 meters in length. Discovered in 2000 by two brothers working in the Naica silver and gold mine 1,000 feet below the surface of the earth, the crystals in this cave are some of the largest ever to be found.

Solids and Crystallography

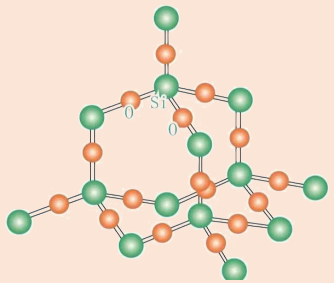
Normal States of Matter

Gas | **Solid** | Liquid

Crystal

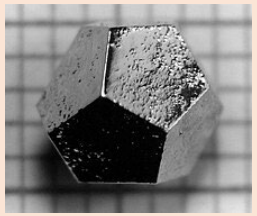


Quartz

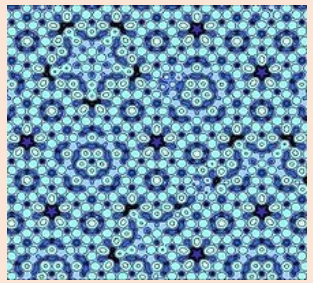


Long-range Order

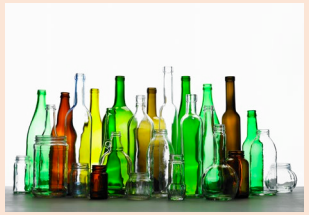
Quasicrystal



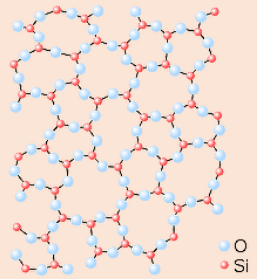
Dy-Mg-Zn
Dodecahedral Quasicrystal



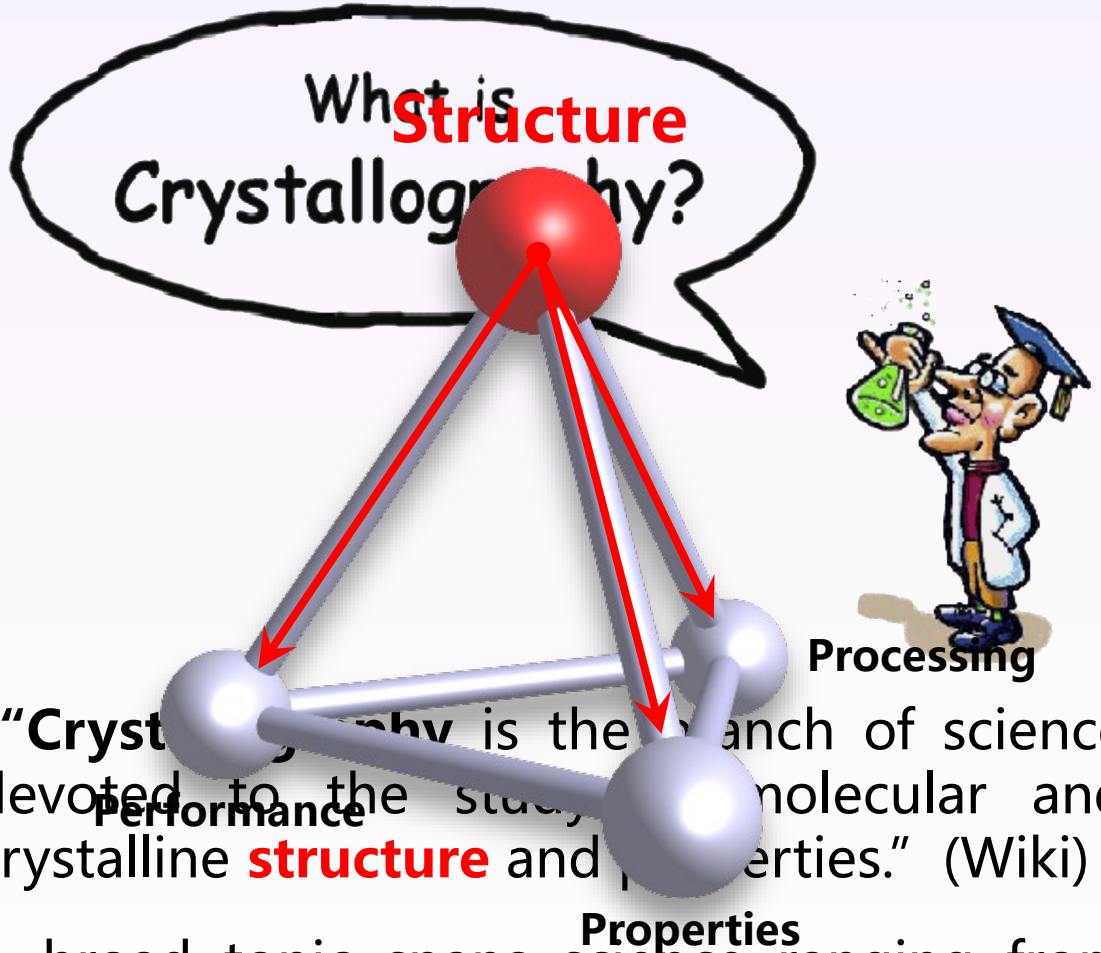
Non-Crystal (Amorphous)



Glass Bottle



Short-range Order



"Crystallography is the branch of science devoted to the study of molecular and crystalline **structure** and properties." (Wiki)

A broad topic spans science ranging from the fundamentals of crystal structure to the mathematics of crystal geometry, including those which are not periodic or quasicrystals.

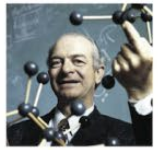
Importance of Crystallography in Fundamental Science

Highlights of the Many Nobel Prizes **Awarded to Crystallographers**

See a complete list of winners at iucr.org/people/nobel-prize



Wilhelm Röntgen
Discovery of X-rays
1901



Linus Pauling
Alpha-helical structure of proteins, nature of chemical bonds
1954



Francis Crick, James Watson & Maurice Wilkins
Created DNA model: double-helical structure for biological information storage
1962



Herbert Hauptman & Jerome Karle
Direct mathematical methods of determining crystallized materials
1985



Clifford Shull & Bertram Brockhouse
Electron diffraction and neutron diffraction
1994



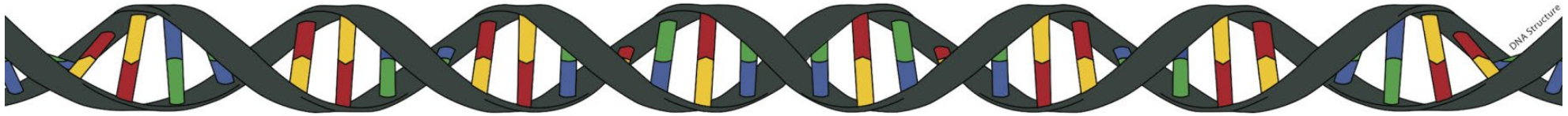
Venki Ramakrishnan, Tom Steitz & Ada Yonath
Studies of the structure and function of the ribosome
2009



Dan Shechtman
Discovery of quasicrystals
2011



Jean-Pierre Sauvage, J. Fraser Stoddart & Ben Feringa
Design and synthesis of molecular machines
2016



1914 **Max von Laue**
First demonstrated X-ray diffraction through crystals



1915 **Sir William H. & Sir William L. Bragg**
First atomic crystal structure



1962 **John Kendrew & Max Perutz**
Hemoglobin: Transport protein, which led to the understanding of Sickle Cell Anemia



1964 **Dorothy Hodgkin**
Structures of cholesterol, penicillin, vitamin B12, and insulin



1976 **William Lipscomb**
The structure of boranes, illuminating problems of chemical bonding



1988 **Johann Deisenhofer, Robert Huber & Hartmut Michel**
First membrane protein that is essential to photosynthesis



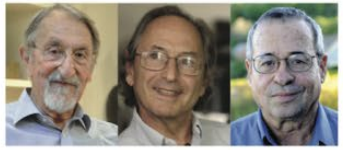
2003 **Peter Agre & Roderick MacKinnon**
Discoveries concerning channels in cell membranes



2006 **Roger Kornberg**
Studies of the molecular basis of eukaryotic transcription



2013 **Martin Karplus, Michael Levitt & Arieh Warshel**
Development of sophisticated computer simulations for complex chemical processes



33 related Nobel Prizes with 56 Nobel laureates in crystallography!

Additional Important Contributors to Crystallography



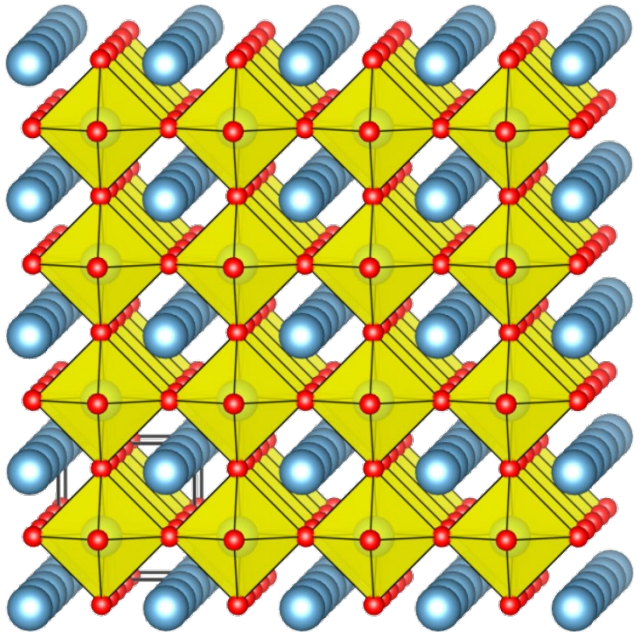
Arthur Patterson
The Patterson Function (equation) gives a map of the vectors between atoms



David Harker
Applied Patterson's map to identify planes and sections on different axes in molecular structures

Understanding Crystal Structure

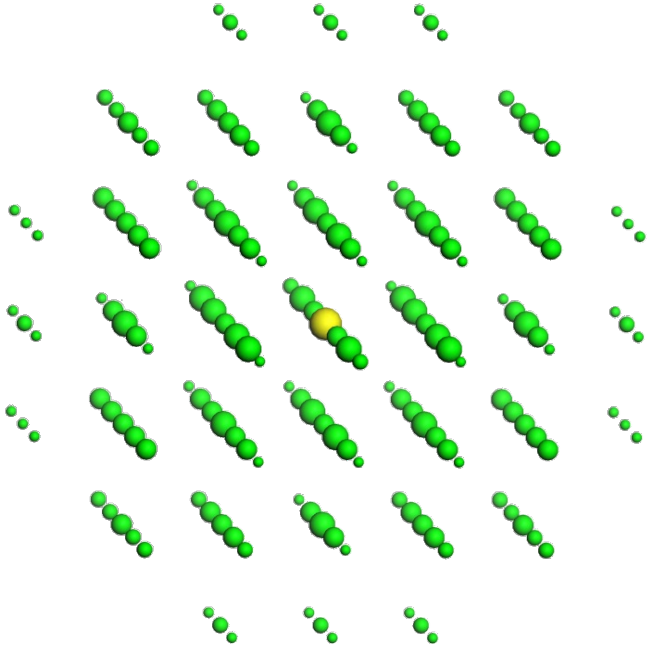
Real Space



Atom	*x*	*y*	*z*
Ca	0.5	0.5	0.5
Ti	0	0	0
O	0.5	0	0

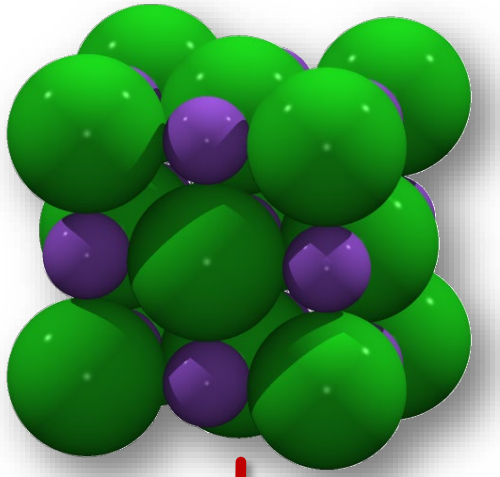
FT

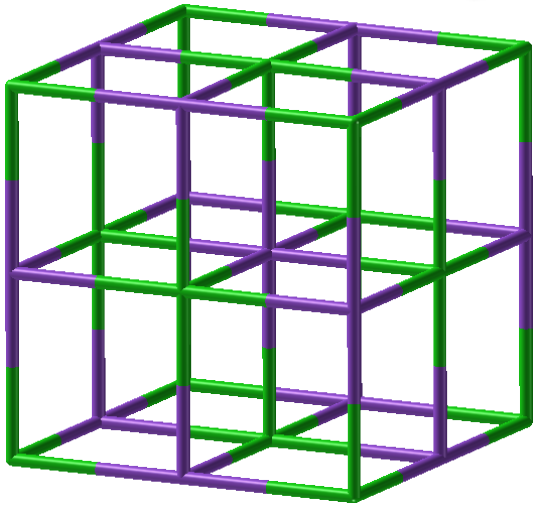
Reciprocal Space



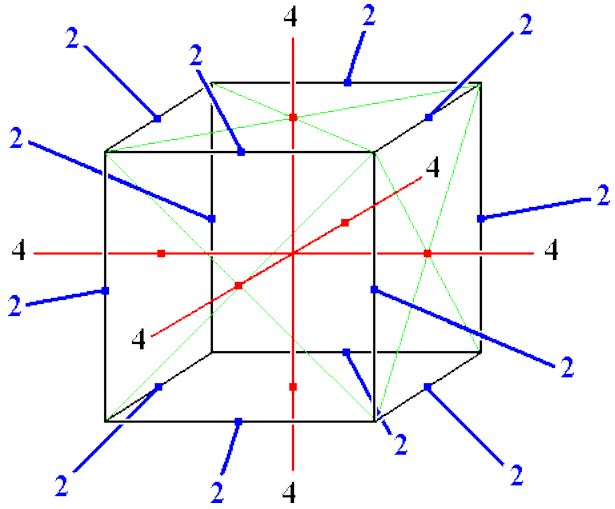
h	*k*	*l*	F_{hkl}	*Pha*
0	0	1	8.4	0
0	1	1	23.9	0
1	1	1	15.5	180
0	0	2	41.0	0
0	1	2	5.5	0
1	1	2	19.8	0
			...	

Outline

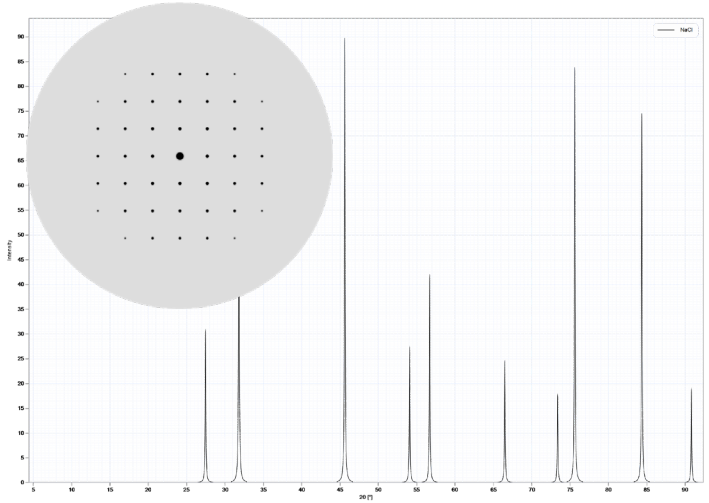




Lattice



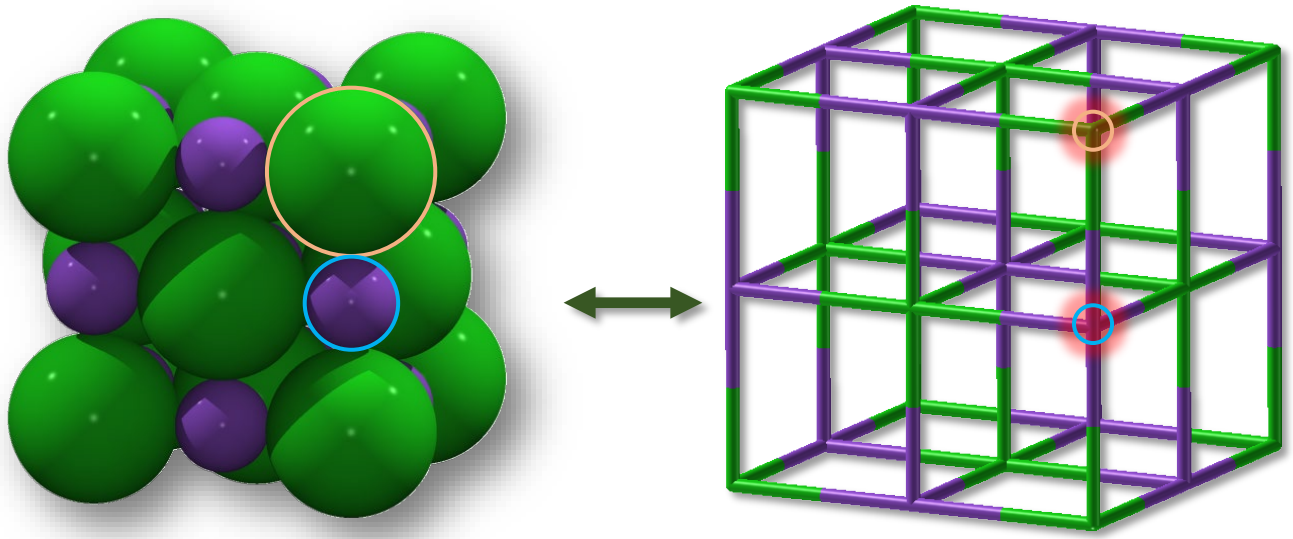
Symmetry



Diffraction (briefly)

Lattice

- **Lattice**: the mathematically **abstract**, **ordered**, and **periodic** arrangement of points in space that represents the internal crystal structure.



- **Lattice points**: **abstract** points, with specific contents called **structural motif**/**unit** that involves the **kinds**, **number**, and **arrangement pattern** of the **atoms**, **ions**, **molecules**, or **clusters** that make up the crystal structure.

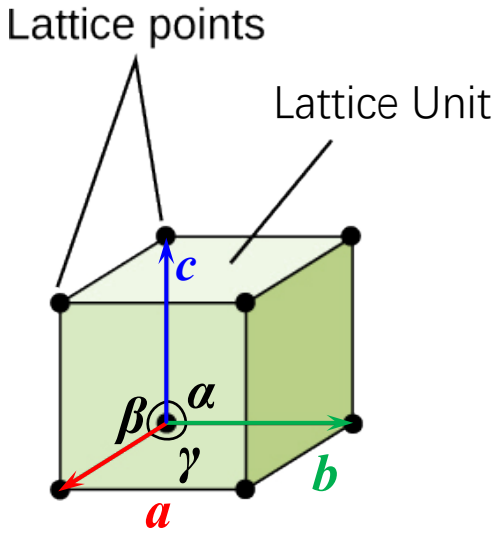
- **Crystal structure = Lattice + Structural Motif**

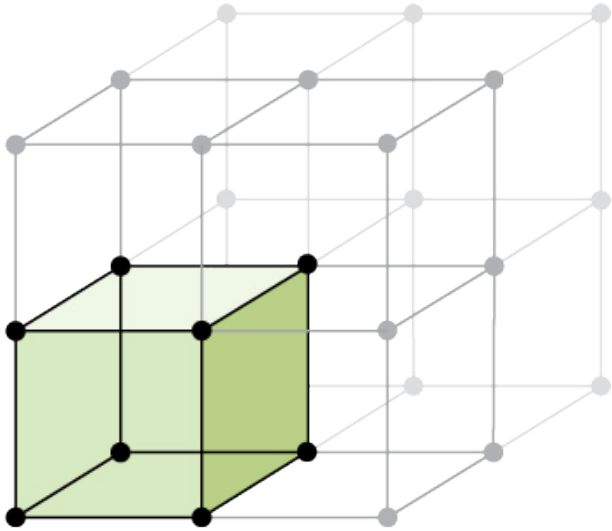
Spatial (Three-Dimensional) Lattice

- **Lattice unit**: the **parallel hexahedron** in juxtaposition that are divided by three **independent** and **unparallel** fundamental vectors ***a***, ***b***, and ***c***.

- **Translation group** (the set of all translation vectors that can restore the lattice unit):

$$\boldsymbol{T} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c} \qquad m, n, p = 0, \pm 1, \pm 2, \ldots$$



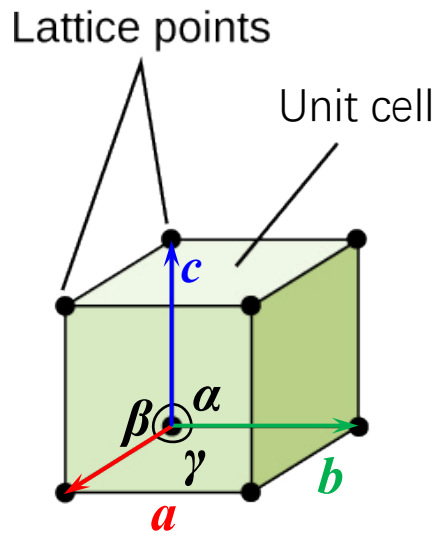


- **Unit cell**: the **parallel hexahedron** divided according to the periodicity of crystal structure.
  - Lattice unit and unit cell both describes structural periodicity.
  - Lattice unit is abstract, reflecting the **repeat pattern**, but unit cell is proposed on actual crystal, involving the **symmetry** and **structural contents** (atomic kinds, number, position, occupancy, anisotropic factors, and others).

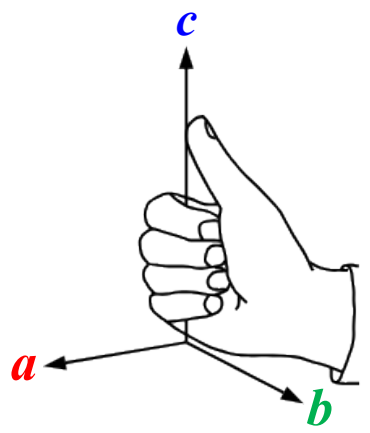
Spatial (Three-Dimensional) Lattice

- Lattice parameters / Unit cell parameters:

$$a = |\boldsymbol{a}|,\ b = |\boldsymbol{b}|,\ c = |\boldsymbol{c}|,\ \alpha = \boldsymbol{b}\wedge\boldsymbol{c},\ \beta = \boldsymbol{a}\wedge\boldsymbol{c},\ \gamma = \boldsymbol{a}\wedge\boldsymbol{b},\ V = \boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})$$



- Selection of lattice: choosing one point as the **origin** and **three unparallel fundamental vectors** ($\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$) from the origin, following **Right-Hand Rule**.

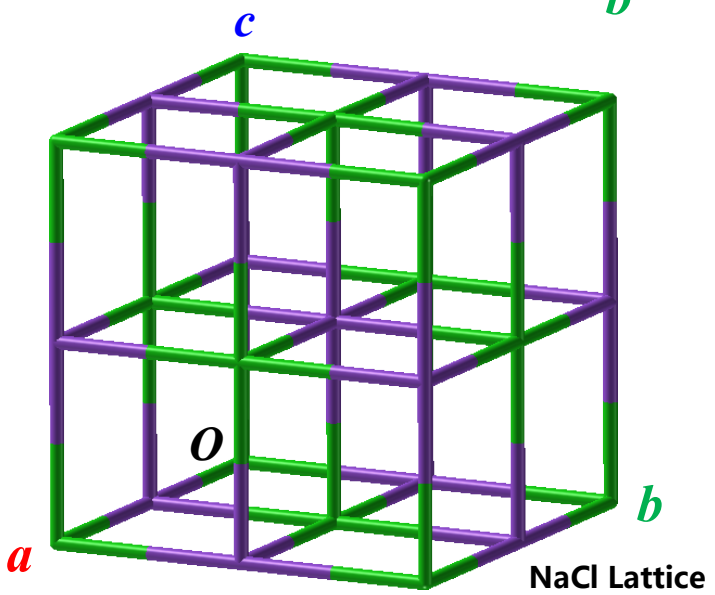


- Coordinates of atom (x, y, z) in unit cell refers to the vector $\boldsymbol{r}$ from origin to the atom:

$$\boldsymbol{r} = x\boldsymbol{a} + y\boldsymbol{b} + z\boldsymbol{c}$$

Cl^-: (0, 0, 0), (½, 0, ½), (0, ½, ½), (½, ½, 0)

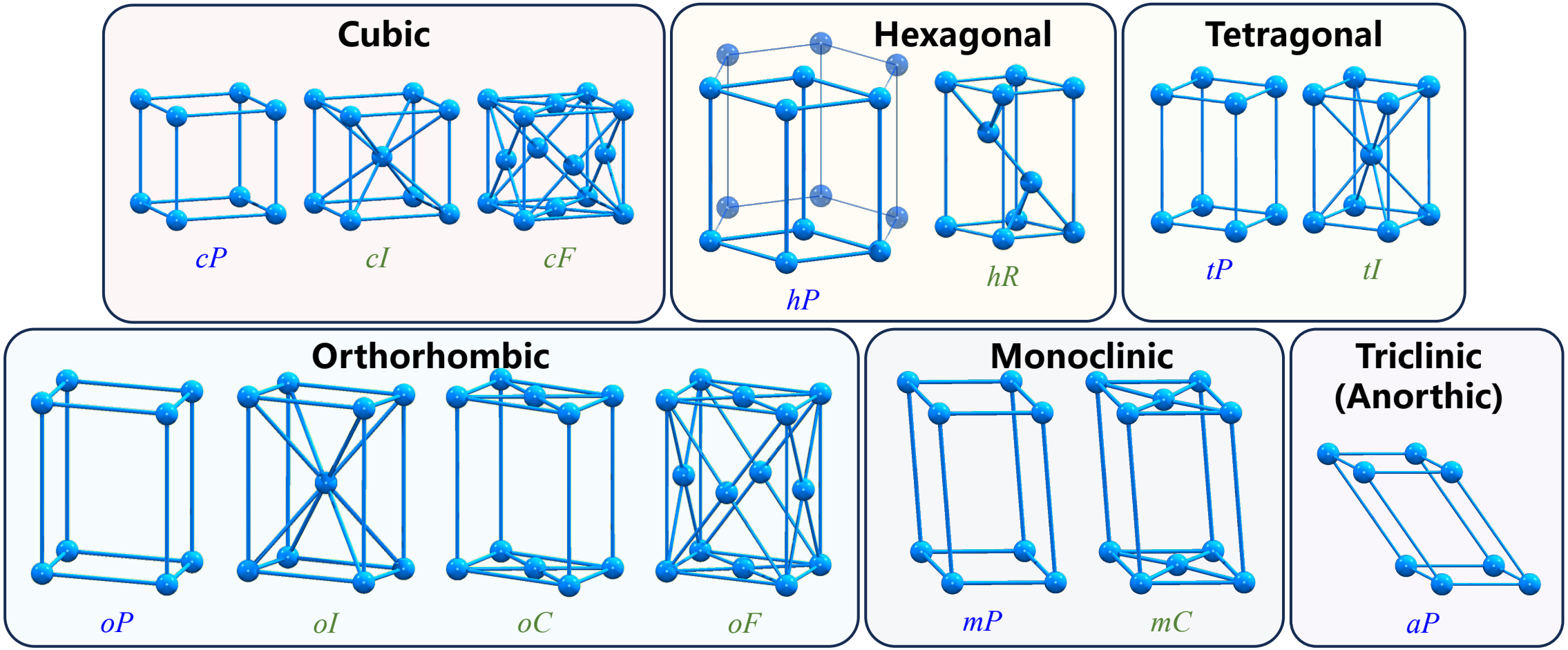
Na^+: (½, 0, 0), (0, ½, 0), (0, 0, ½), (½, ½, ½)



NaCl Lattice

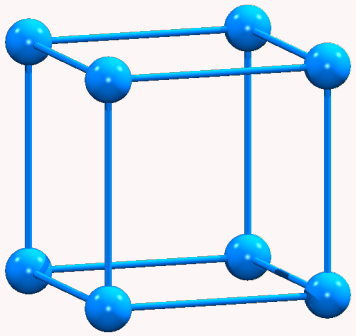
Bravais Lattices

- The collection of **14** different spatial lattices considering the lattice parameters and translation symmetry, into which atoms can be arranged in crystals.

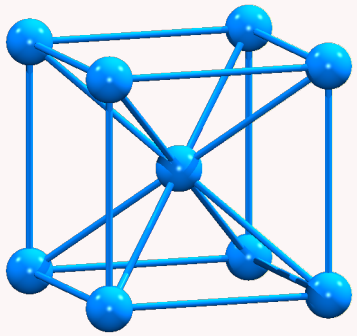


- **Primitive lattice**: the lattice with **one** lattice point.
- **Multiple lattice**: the lattice with **more than one** lattice point.

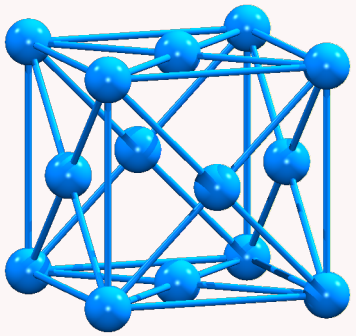
Cubic and Hexagonal Lattices



cP



cI



cF

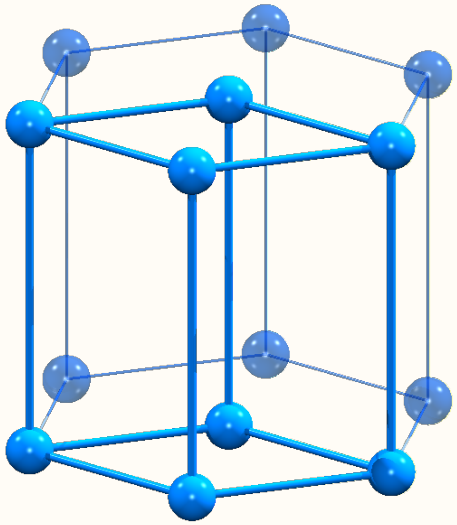
Cubic, $a = b = c$, $\alpha = \beta = \gamma = 90°$

P = Primitive

I = Body-entered

F = Face-centered

C = Side-centered



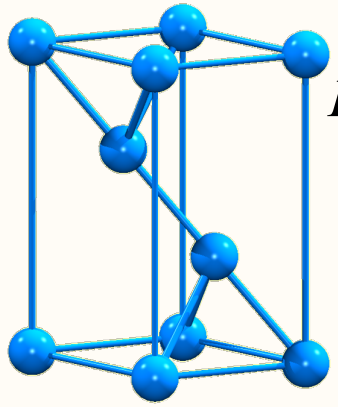
hP

Hexagonal *P*

$a = b \neq c$

$\alpha = \beta = 90°$,

$\gamma = 120°$



hR

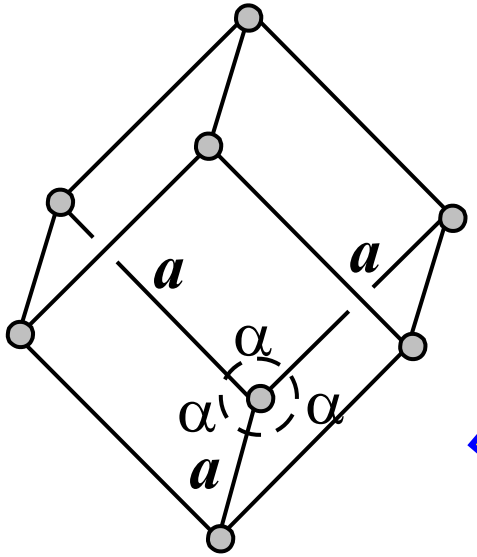
***R*-Centered Hexagonal**

$a = b \neq c$

$\alpha = \beta = 90°$,

$\gamma = 120°$

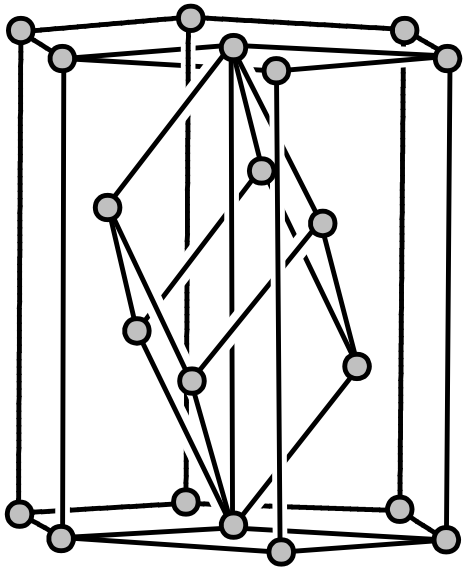
R-Centered Hexagonal Lattice



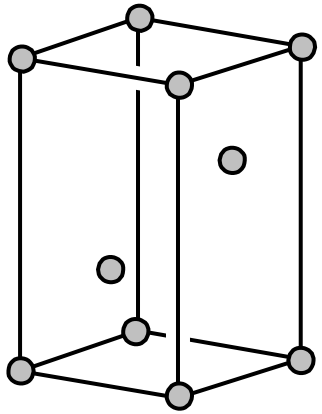
Rhombohehra

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$



Rhombohedra in hexagonal lattices



hR

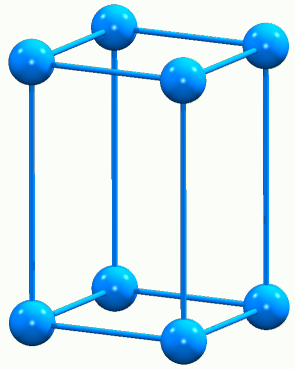
***R*-Centered Hexagonal**

$a = b \neq c$

$\alpha = \beta = 90°,$

$\gamma = 120°$

Tetragonal and Orthorhombic Lattices

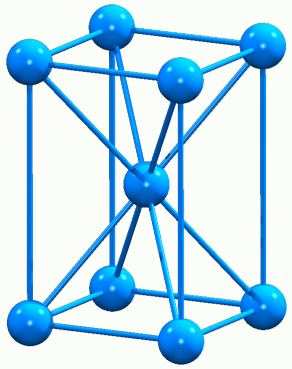


tP

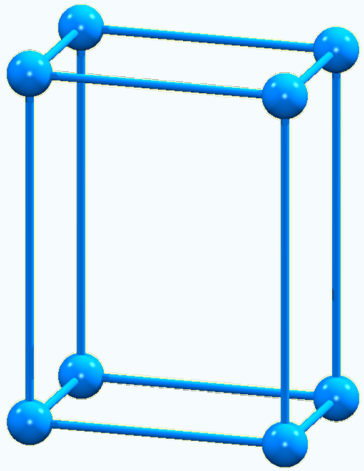
Tetragonal

$a = b \neq c$

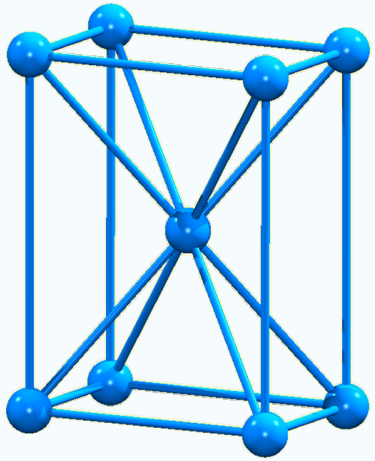
$\alpha = \beta = \gamma = 90°$



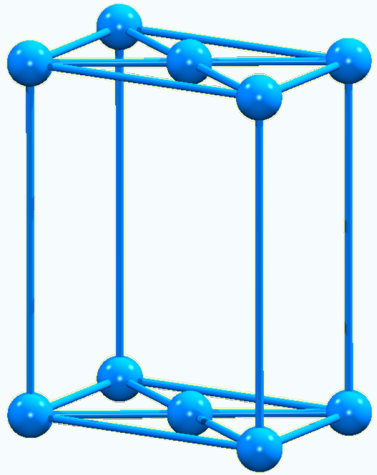
tI



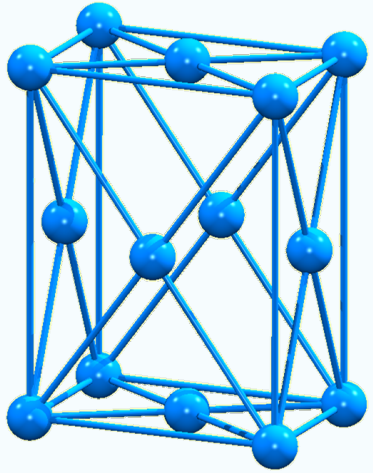
oP



oI



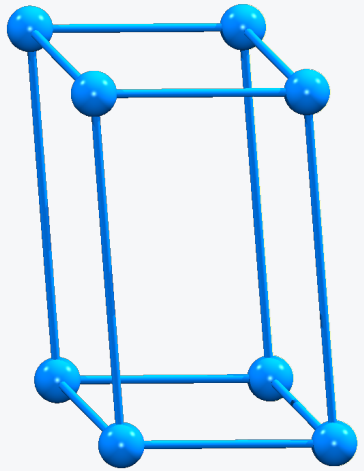
oC



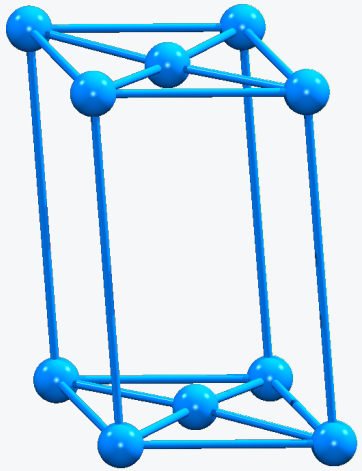
oF

Orthorhombic, $a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$

Monoclinic and Triclinic Lattices



mP



mC

Monoclinic

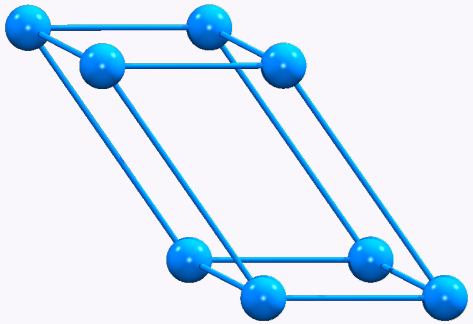
$a \neq b \neq c$

$\alpha = \gamma = 90°, \beta \neq 90°$

Triclinic (Anorthic)

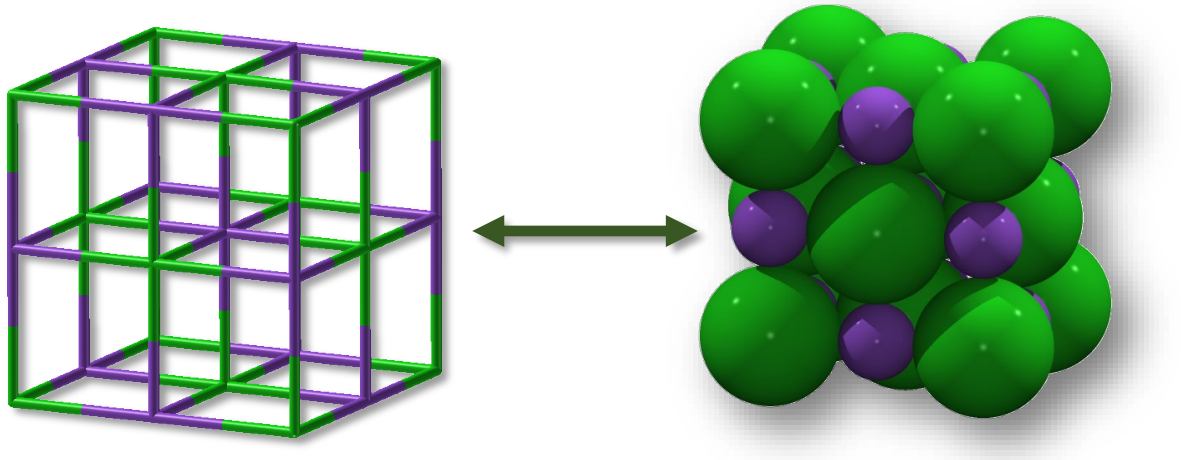
$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$



aP

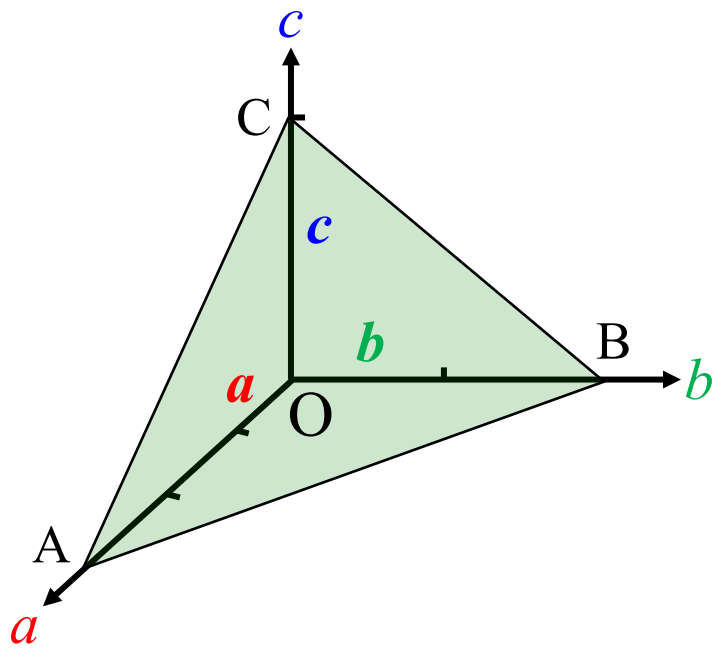
Relationship of Elements in Lattice and Crystal



Mathematical Abstract	Actual Content
Lattice	Crystal
Lattice unit	Unit cell
Lattice point	Structural motif
Linear lattice	Crystal edge
Planar lattice	Crystal plane
Spatial lattice	Crystal structure
6 kinds of shape	6 kinds of crystal family
14 kinds of Bravais lattice	14 kinds of Bravais crystal lattice

Crystal Plane and Its Index

- **Crystal plane**: the lattice plane in structure, with actual contents of periodically arranged atoms.
- **Crystal plane index**: **ratio of the inverse intercepts** of the lattice plane along the lattice vectors.



$OA/a = 3 \quad OB/b = 2 \quad OC/c = 1$

Ratio of inverse intercepts:

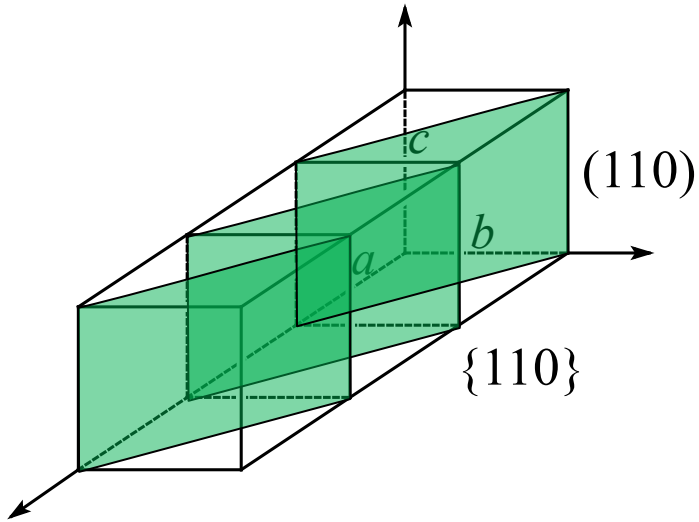
$1/OA : 1/OB : 1/OC = 1/3 : 1/2 : 1/1$

$= 2 : 3 : 6$

Crystal plane index (lattice plane index):

(236)

- **Miller index**: the coprime crystal plane index, expressed by ***(hkl)***.
- Parallel to a lattice vector → index of **0** in that direction.
- Crystal plane family: a group of parallel crystal planes, expressed by ***{hkl}***.



Crystal Plane Spacing

- The vertical distance between adjacent lattice planes in a crystal plane family, expressed by d_{hkl}.

Crystal System	Expression for d_{hkl}
Cubic	$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\left[\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right]$
Triclinic	$\frac{1}{d_{hkl}^2} = \frac{1}{V^2}\left[h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)\right]$ where $V = abc\left[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma\right]^{\frac{1}{2}}$

Symmetry

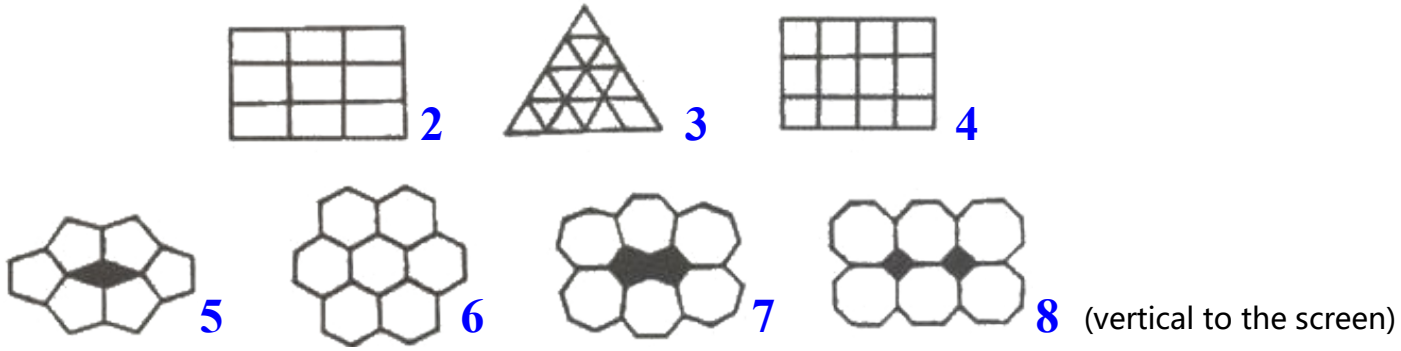
- **Symmetry** plays the fundamental and crucial role in crystallography, referring to the collection of **operations** and **elements** that can **restore** the crystal structure.

Symmetry Operation	Symmetry Element	Feature
Rotation $L(\alpha)$	Rotation axis n	Point symmetry Macroscopic symmetry Molecular symmetry Related to 32 point groups
Reflection M	Mirror m	
Inversion I	Symmetry center i	
Rotation-inversion $L(\alpha)I$	Inversion axis $\overline{n}$	
Translation T	Lattice T_{mnp}	Spatial symmetry Microscopic symmetry Related to 230 space groups
Screw rotation $L(\alpha)T$	Screw axis n_m	
Glide reflection MT	Glide plane mT_{mnp}	

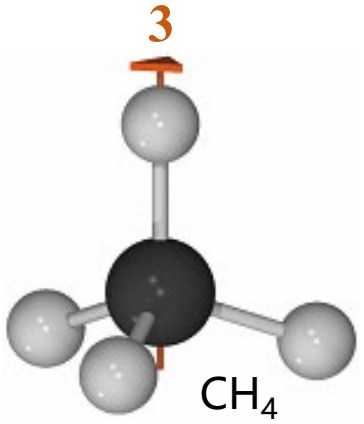
Point/Macroscopic Symmetry

➢ Rotation $L(\alpha)$

- Rotation around n axis by the smallest angle $\alpha = 2\pi/n$ can restore the structure.
- In crystal structure, only **1**, **2**, **3**, **4**, and **6**-fold axes are allowed.

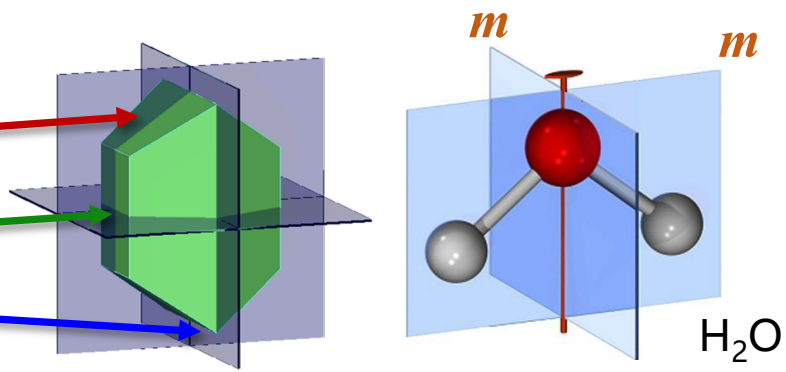


(vertical to the screen)



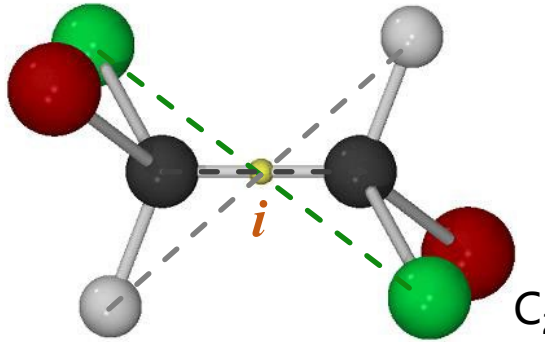
➢ Reflection M

- The operation to mirror the structure across a plane (so-called mirror m), resulting in a symmetrical configuration.
- In macroscopic symmetry, m can only be
  - ✓ Vertical to and bisecting crystal plane;
  - ✓ Vertical to crystal edge and passing through its midpoint;
  - ✓ Passing through the crystal edge.



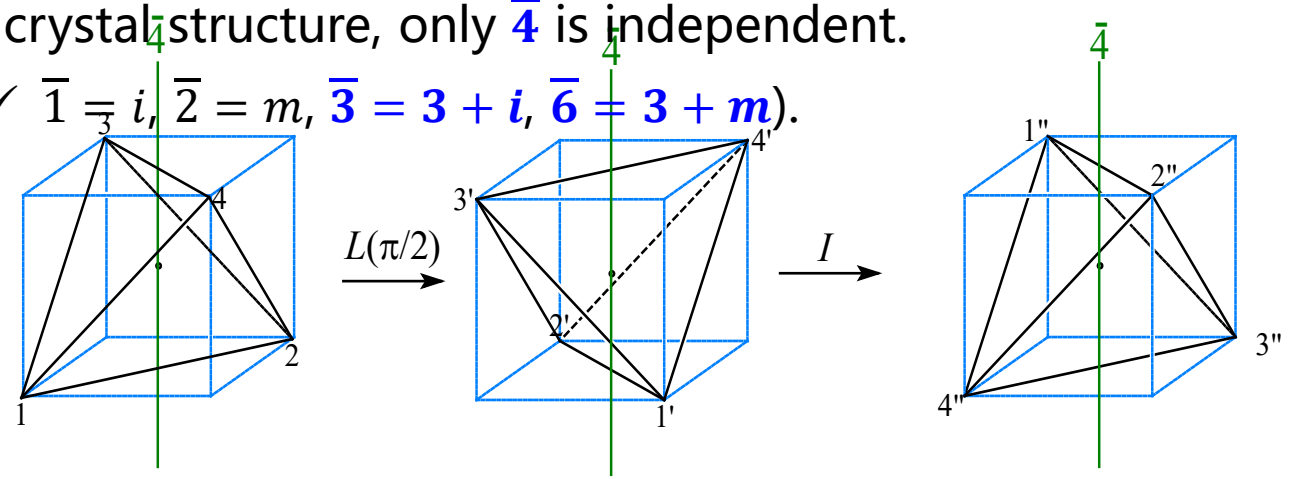
Point/Macroscopic Symmetry

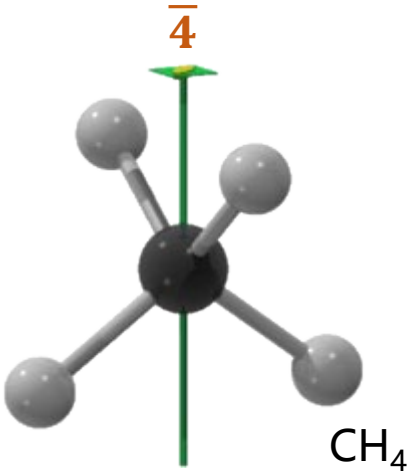
- **Inversion I**
  - The structure is symmetrical along the center point (symmetry center i).



$C_2H_2Cl_2Br_2$

- **Rotation-Inversion (Rotoinversion) $L(\alpha)I$**
  - The compound operation ($\bar{n}$) of rotation (n) and inversion (i) to restore the structure.
  - In crystal structure, only $\bar{4}$ is independent.
    - ✓ $\bar{1} = i$, $\bar{2} = m$, $\bar{3} = 3 + i$, $\bar{6} = 3 + m$).





CH_4

7 Crystal Systems

Crystal Family	Crystal System	Characteristic Symmetry Element	Unit Cell Feature	
c	Cubic	Four **3**	$a=b=c,\ \alpha=\beta=\gamma=90°$	
h	Hexagonal	**6** or $\overline{\mathbf{6}}$	$a=b\neq c,\ \alpha=\beta=90°,\ \gamma=120°$	
	Trigonal	**3** or $\overline{\mathbf{3}}$	H cell	$a=b\neq c,\ \alpha=\beta=90°,\ \gamma=120°$
			R cell	$a=b=c,\ \alpha=\beta=\gamma\neq 90°$
t	Tetragonal	**4** or $\overline{\mathbf{4}}$	$a=b\neq c,\ \alpha=\beta=\gamma=90°$	
o	Orthorhombic	Two mutually perpendicular ***m*** or three mutually perpendicular **2**	$a\neq b\neq c,\ \alpha=\beta=\gamma=90°$	
m	Monoclinic	**2** or ***m***	$a\neq b\neq c,\ \alpha=\gamma=90°\neq\beta$	
a	Triclinic	***i*** or none	$a\neq b\neq c,\ \alpha\neq\beta\neq\gamma\neq 90°$	

32 Point Groups

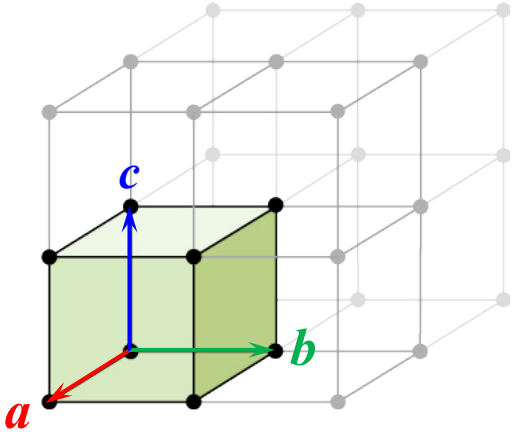
Position in symbol	First	Second	Third
Cubic	<100>	<111>	<110>
Tetragonal, hexagonal, trigonal	<001>	<100>	$<\bar{1}10>$
Orthorhombic	[100]	[010]	[001]
Monoclinic	[010]	–	

Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin
C_1	1	C_4	4	$C_{3i} = S_6$	$\bar{3}$	C_{6h}	$6/m$
C_i	$\bar{1}$	S_4	$\bar{4}$	D_3	32	C_{6v}	$6mm$
C_2	2	D_4	422	C_{3v}	$3m$	D_{6h}	$6/mmm$
$C_s = C_{1v}$	m	C_{4v}	$4mm$	D_{3d}	$\bar{3}m$	T	23
C_{2h}	$2/m$	C_{4h}	$4/m$	C_6	6	T_h	$m\bar{3}$
C_{2v}	$mm2$	D_{2d}	$\bar{4}2m$	C_{3h}	$\bar{6}$	T_d	$\bar{4}3m$
D_2	222	D_{4h}	$4/mmm$	D_6	622	O	432
D_{2h}	mmm	C_3	3	D_{3h}	$\bar{6}m2$	O_h	$m\bar{3}m$

$m3$, $m3m$)

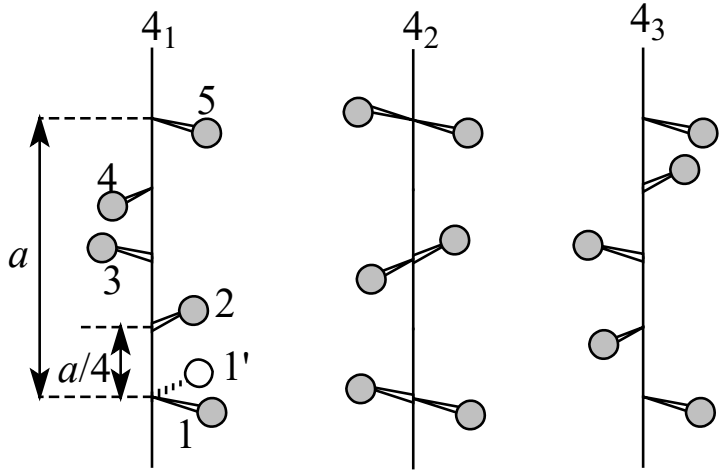
Spatial/Microscopic Symmetry

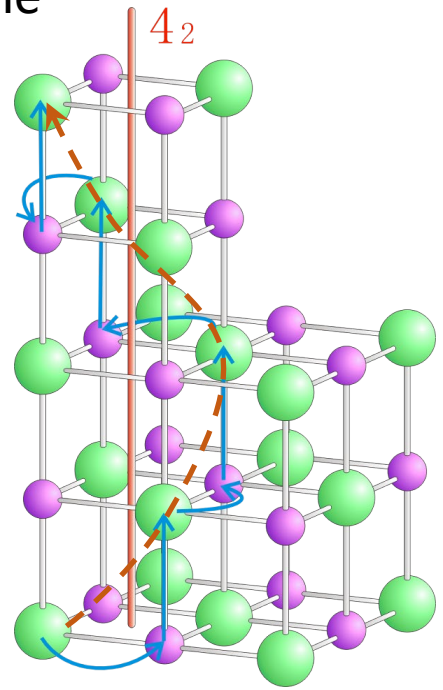
- The symmetry **within** the lattice structure.



- **Translation** T
  - The lattice structure repeats itself along the fundamental directions.

- **Screw rotation** $L(\alpha)T$
  - The compound operation (n_m) of rotation (n) and translation (T_{mnp}, with translation amount of m/n ($m < n$) with respect to the fundamental vector magnitude) along the rotation axis.
  - Typical screw axes: 2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, and 6_5.



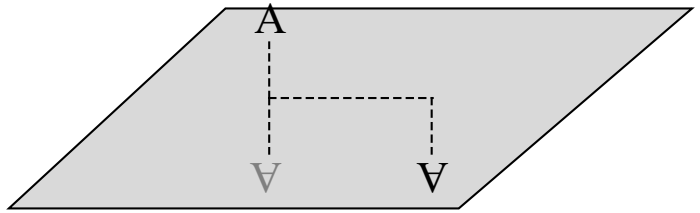


NaCl

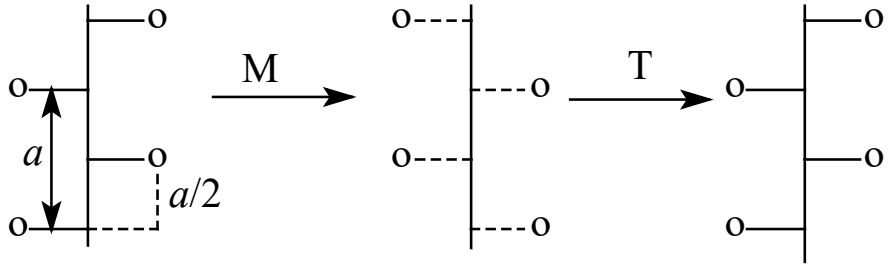
Spatial/Microscopic Symmetry

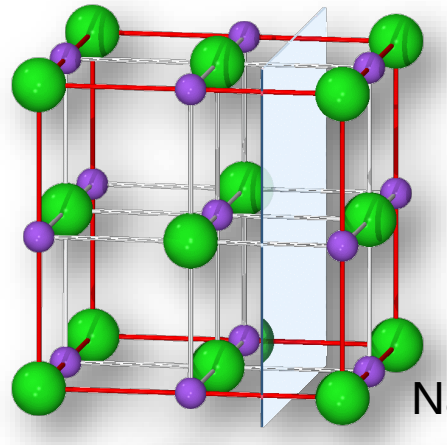
➢ Glide reflection MT

- The compound operation (mT_{mnp}) of reflection (m) and translation (T_{mnp}, with diverse translation direction (parallel to m) and amount.



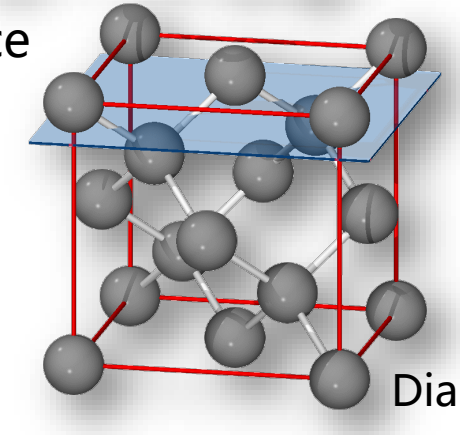
- Glide plane kinds:
  - ✓ a (b or c) glide: reflection and translation along a (b or c) axis with a distance of $a/2$ ($b/2$ or $c/2$).





NaCl

  - ✓ n glide: reflection and translation along $a+b$ ($a+c$ or $b+c$) (face diagonal) with a distance of $(a+b)/2$ ($(a+c)/2$ or $(b+c)/2$).
  - ✓ d glide (diamond glide) : reflection and translation along $a+b$ ($a+c$ or $b+c$) (face diagonal) with a distance of $(a+b)/4$ ($(a+c)/4$ or $(b+c)/4$).



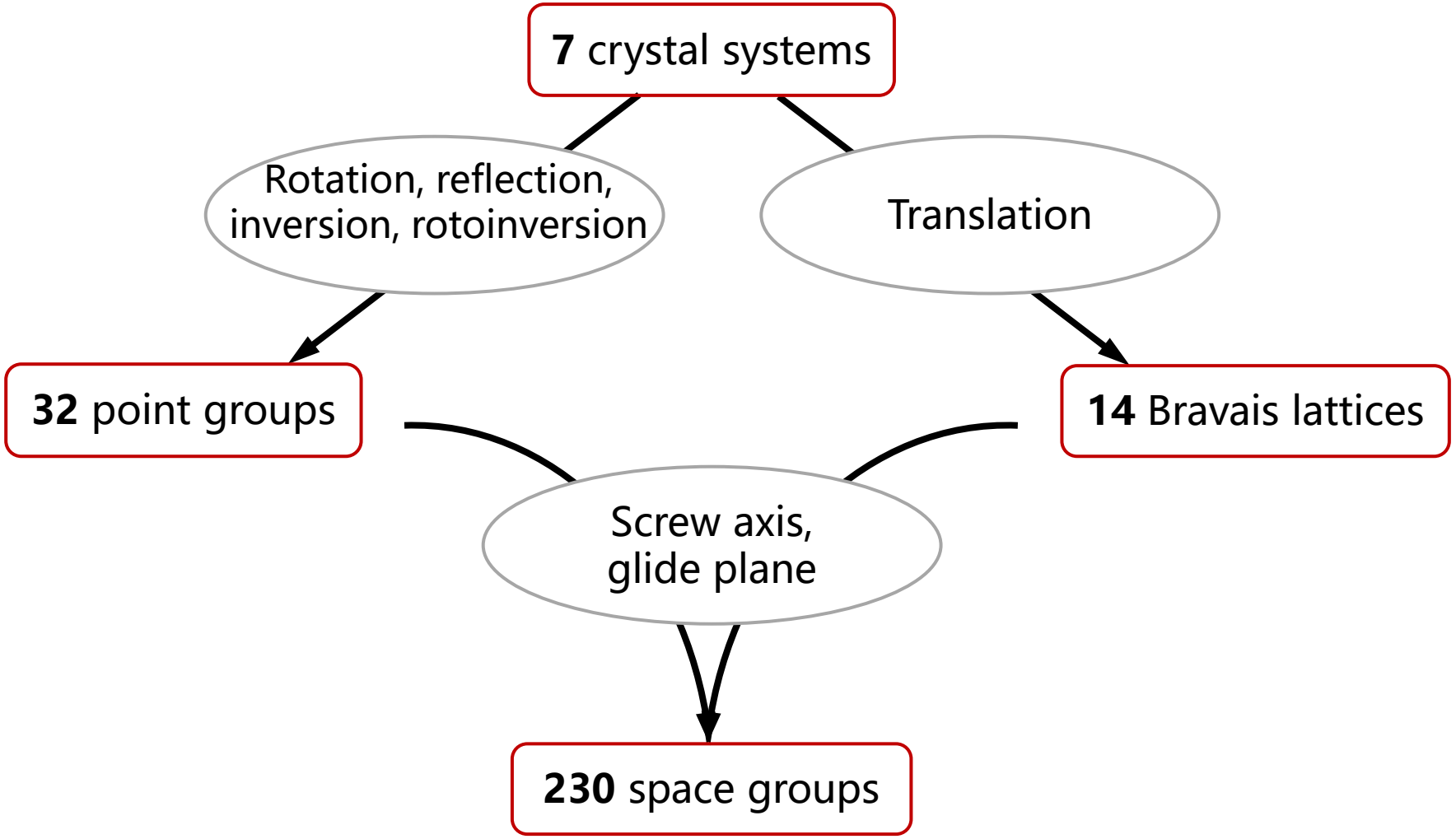
Diamond

Symmetry Elements in Crystal Structure

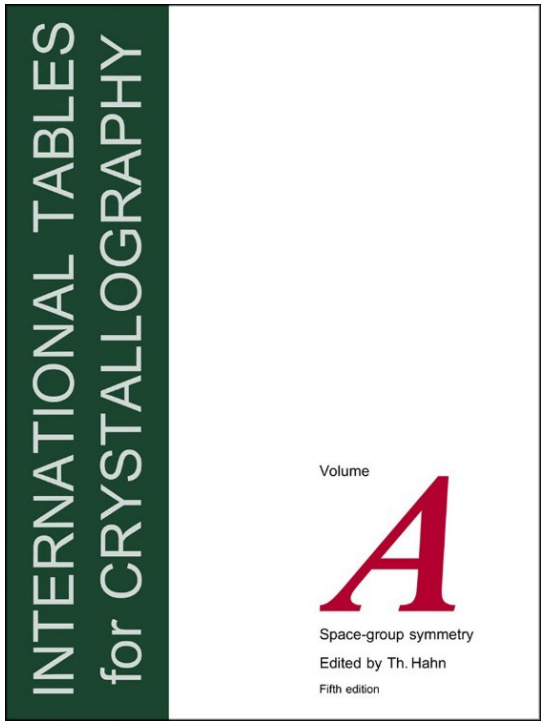
Element	Symbol	⊥ to Projection Plane	In or ∥ to Projection Plane
Simple mirror	m	———	or
Axial glide	$a,b,c,$	---------- (glide in projection plane) ..... (glide ⊥ to projection plane)	or or
Diagonal glide	n	-·-·-·-	
Diamond glide	d		
Center of inversion	$\bar{1}$	○	
Rotation axis	2, 3, 4, 6		
Rotation–inversion axis	$\bar{3}$, $\bar{4}$, $\bar{6}$		
Screw axis	2_1 3_1, 3_2 4_1, 4_2, 4_3 6_1, 6_2, 6_3, 6_4, 6_5		

230 Space Groups

- From crystal systems to space groups:



230 Space Groups



Herman-Mauguin symbols

Long symbols	Short symbols
$C\,1\,2/m\,1$	$C2/m$
$P\,2_1\,2_1\,2$	$P21212$
$P\,2/m\,2/n\,2_1/a$	$Pmna$
$I\,4_1/a\,2/m\,2/d$	$I41/amd$
$P\,6_3/m\,2/m\,2/c$	$P63/mmc$
$F\,4/m\,\bar{3}\,2/m$	$Fm\bar{3}m$



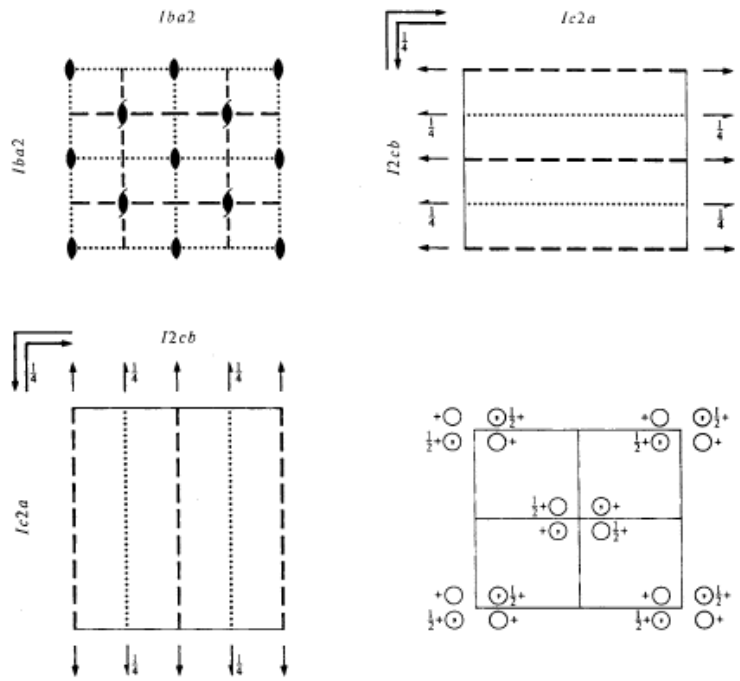
The Space Group List Project '230'

230 Space Groups

$Iba2$ C_{2v}^{21} $mm2$ Orthorhombic

No. 45 $Iba2$

Patterson symmetry $Immm$



Origin on $cc2$

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

Symmetry operations

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

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

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

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

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates $(0,0,0)+$	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$		Reflection conditions
8	c	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x+\frac{1}{2},\bar{y}+\frac{1}{2},z$	(4) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$	General:
							hkl : $h+k+l=2n$
							$0kl$: $k,l=2n$
							$h0l$: $h,l=2n$
							$hk0$: $h+k=2n$
							$h00$: $h=2n$
							$0k0$: $k=2n$
							$00l$: $l=2n$
							Special: as above, plus
4	b	..2	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$			hkl : $l=2n$
4	a	..2	$0,0,z$	$\frac{1}{2},\frac{1}{2},z$			hkl : $l=2n$

Symmetry of special projections

Along [001] $c2mm$
$\mathbf{a}' = \mathbf{a}$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p1m1$
$\mathbf{a}' = \frac{1}{2}\mathbf{b}$ $\mathbf{b}' = \frac{1}{2}\mathbf{c}$
Origin at $x,0,0$

Along [010] $p11m$
$\mathbf{a}' = \frac{1}{2}\mathbf{c}$ $\mathbf{b}' = \frac{1}{2}\mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I
[2] $I1a1$ $(Cc, 9)$ (1; 3)+
[2] $Ib11$ $(Cc, 9)$ (1; 4)+
[2] $I112$ $(C2, 5)$ (1; 2)+

IIa
[2] $Pba2$ (32) 1; 2; 3; 4
[2] $Pca2_1$ (29) 1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
[2] $Pbc2_1$ $(Pca2_1, 29)$ 1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
[2] $Pcc2$ (27) 1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3] $Iba2$ ($\mathbf{a}' = 3\mathbf{a}$ or $\mathbf{b}' = 3\mathbf{b}$) (45); [3] $Iba2$ ($\mathbf{c}' = 3\mathbf{c}$) (45)

Minimal non-isomorphic supergroups

I [2] $Ibam$ (72); [2] $Ibca$ (73); [2] $I4cm$ (108); [2] $I4_1cd$ (110); [2] $I\bar{4}c2$ (120)

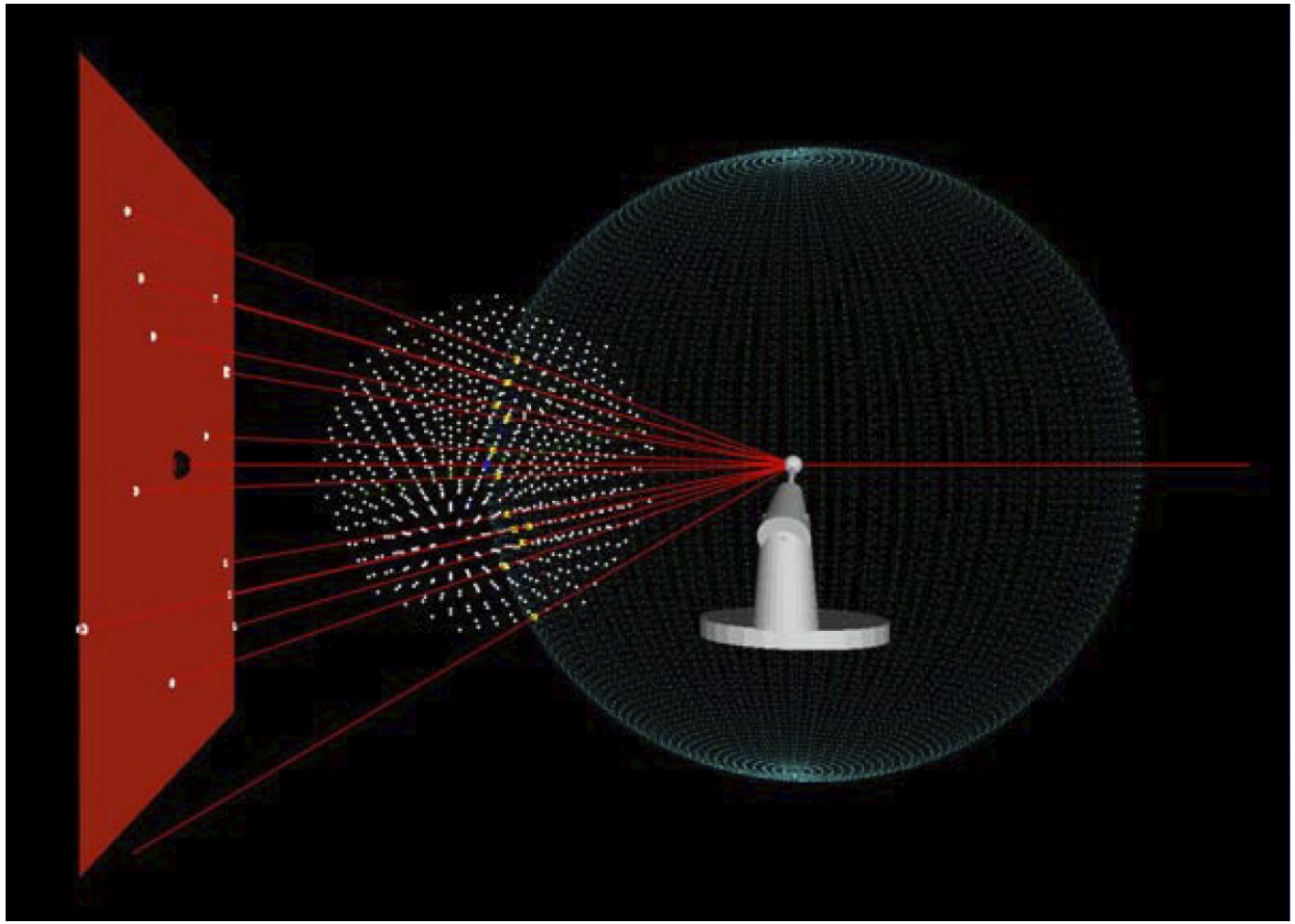
II [2] $Cmm2$ ($\mathbf{c}' = \frac{1}{2}\mathbf{c}$) (35); [2] $Aem2$ ($\mathbf{a}' = \frac{1}{2}\mathbf{a}$) (39); [2] $Bme2$ ($\mathbf{b}' = \frac{1}{2}\mathbf{b}$) ($Aem2$, 39)

11 Laue Symmetry

- Laue symmetry = diffraction pattern symmetry
- The symmetry of a diffraction pattern (weighted reciprocal lattice) tells you about the symmetry of the crystal
- Laue symmetry is the point symmetry of the solid plus an additional center of symmetry
- Friedel' s law: $|\mathbf{F}(hkl)| = |\mathbf{F}(\text{-}h\text{-}k\text{-}l)|$, $\Phi(hkl) = \text{-}\Phi(\text{-}h\text{-}k\text{-}l)$
- 11 of the 32 point groups contain a center of symmetry
- Add a center of symmetry to all non-centro-symmetric classes to give the 11 Laue classes:

$$\text{-}1,\ 2/m,\ mmm,\ 4/m,\ 4/mmm,\ \text{-}3,\ \text{-}3m,\ 6/m,\ 6/mmm,\ m\text{-}3,\ m\text{-}3m$$

Diffraction



- Diffraction is the basis of modern crystallography

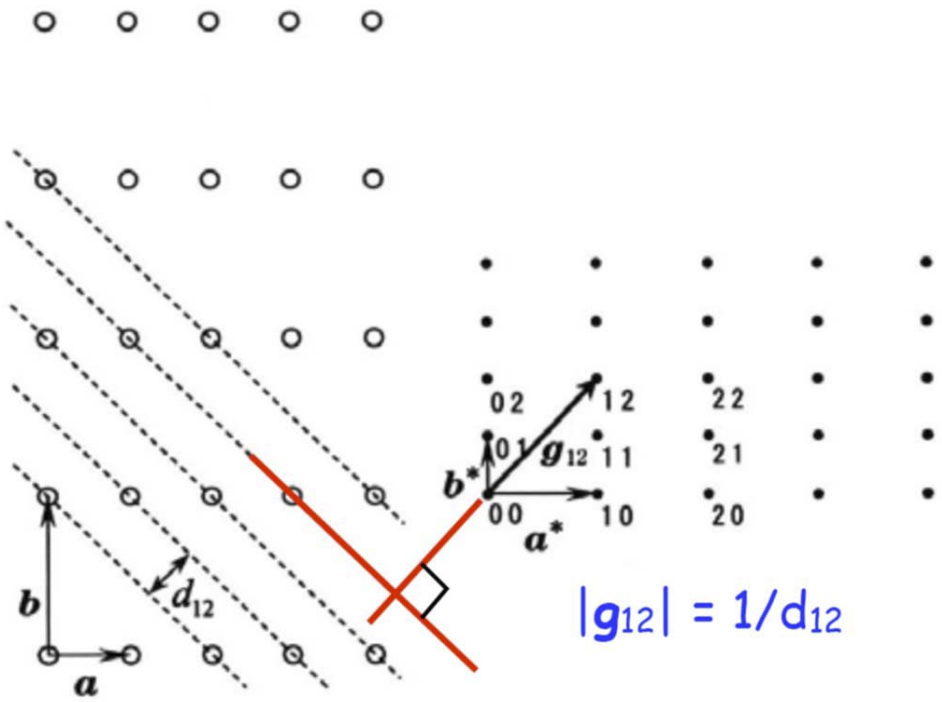
Crystal in Reciprocal Space

- Laue symmetry = diffraction pattern symmetry
- This concept gives a physical picture of diffraction geometries.
- Each reciprocal lattice point (hkl) (diffraction spot) represents a set of parallel planes in real space. These planes are perpendicular to the reciprocal lattice vector

$$\mathbf{g}_{hkl} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*.$$

- The interplaner distance d_{hkl} is inversely proportional to the magnitude of the reciprocal lattice vector, $\mathbf{g}_{hkl}$.

$$|\mathbf{g}_{hkl}| = 1/d_{hkl}$$

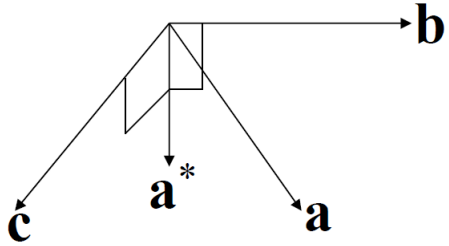


2D real space 2D reciprocal space

Relationship between Real and Reciprocal Space

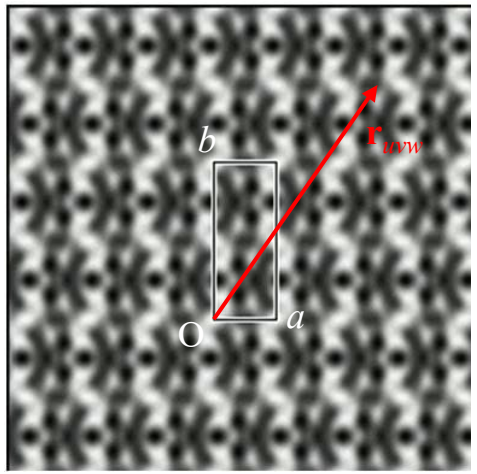
$\boldsymbol{a}^* = \boldsymbol{b}\times\boldsymbol{c} / V_c \qquad \boldsymbol{b}^* = \boldsymbol{c}\times\boldsymbol{a} / V_c \qquad \boldsymbol{c}^* = \boldsymbol{a}\times\boldsymbol{b} / V_c$

V_c is the volume of the unit cell, $\boldsymbol{a}\cdot(\boldsymbol{b}\times\boldsymbol{c})$



- $\boldsymbol{a}^*$ is orthogonal to $\boldsymbol{b}$ and $\boldsymbol{c}$ but not necessarily parallel to $\boldsymbol{a}$.
- $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$ need not be normal to one another.

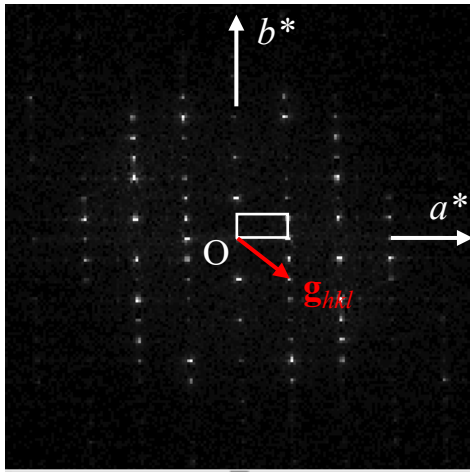
Real space



$\mathbf{r}_{uvw} = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$

$[uvw]$ is called a zone axis, which represents the direction along which an image or an ED pattern is taken.

Reciprocal

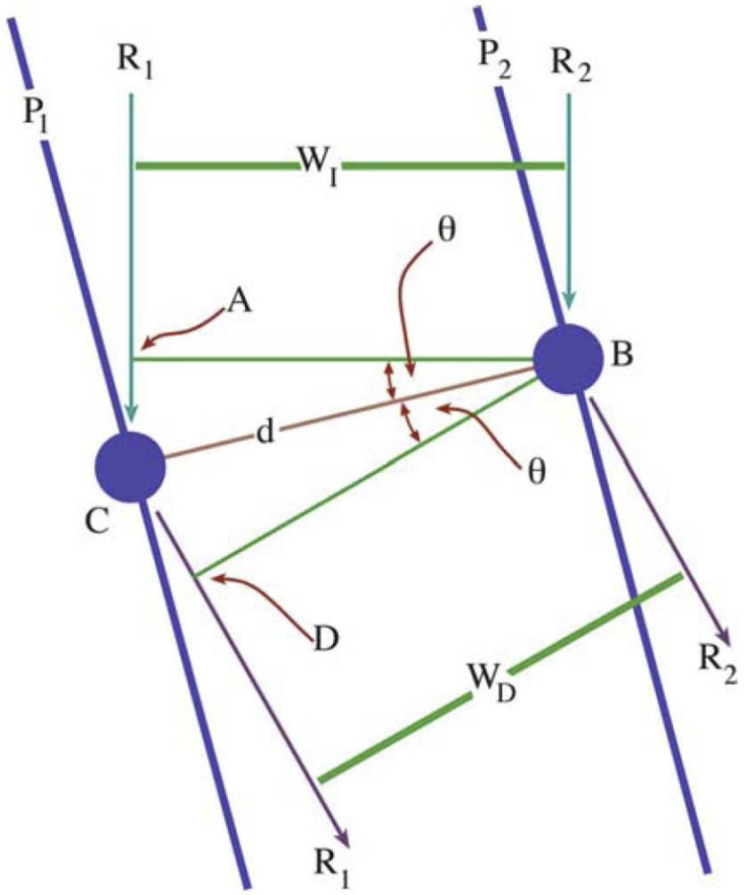


$\mathbf{g}_{(hkl)} = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^*$

hkl are called Miller indices.

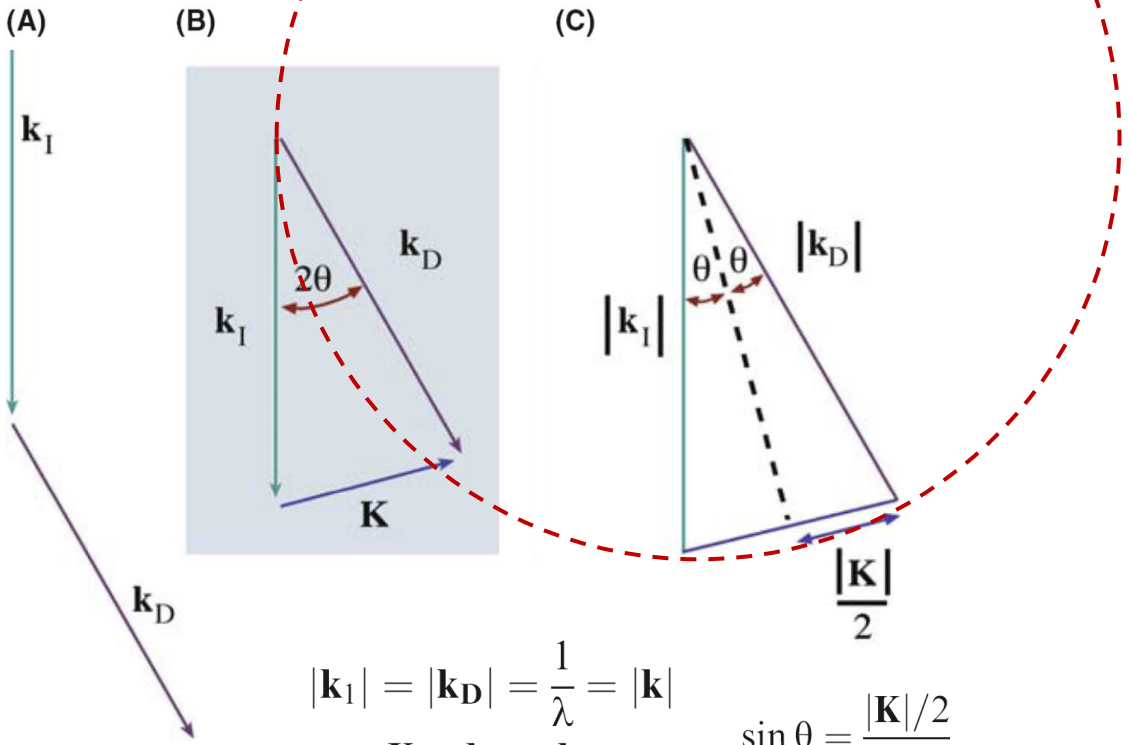
Bragg's Law and Ewald Sphere

Real space



$2d_{hkl}*\sin\theta = n\lambda$

Reciprocal space



$$|\mathbf{k}_I| = |\mathbf{k}_D| = \frac{1}{\lambda} = |\mathbf{k}|$$

$$\mathbf{K} = \mathbf{k}_D - \mathbf{k}_I$$

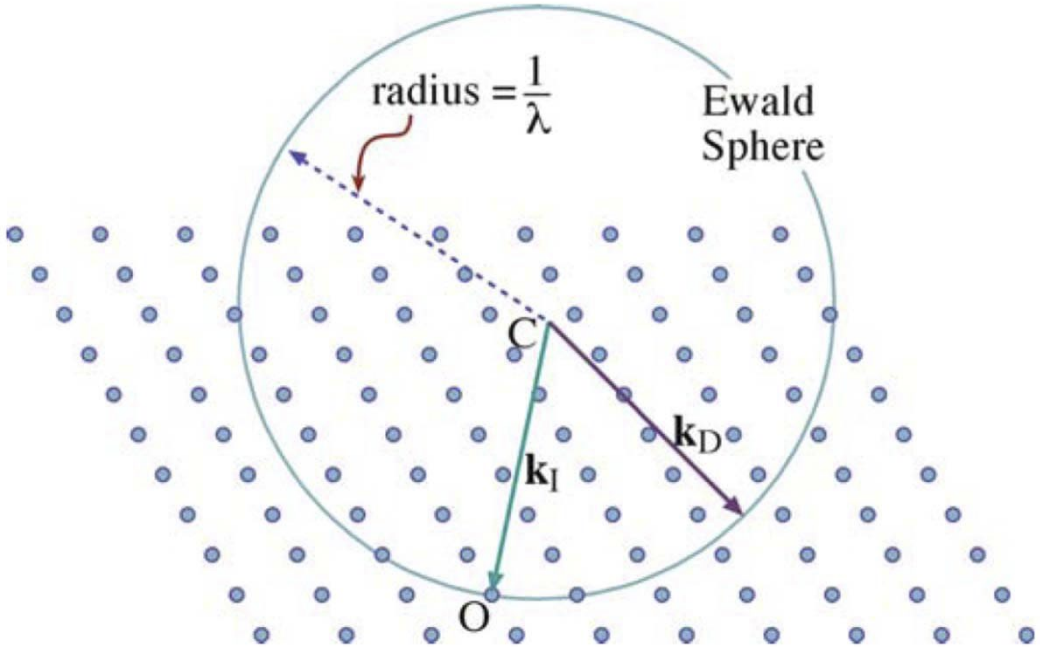
$$\sin\theta = \frac{|\mathbf{K}|/2}{|\mathbf{k}_I|}$$

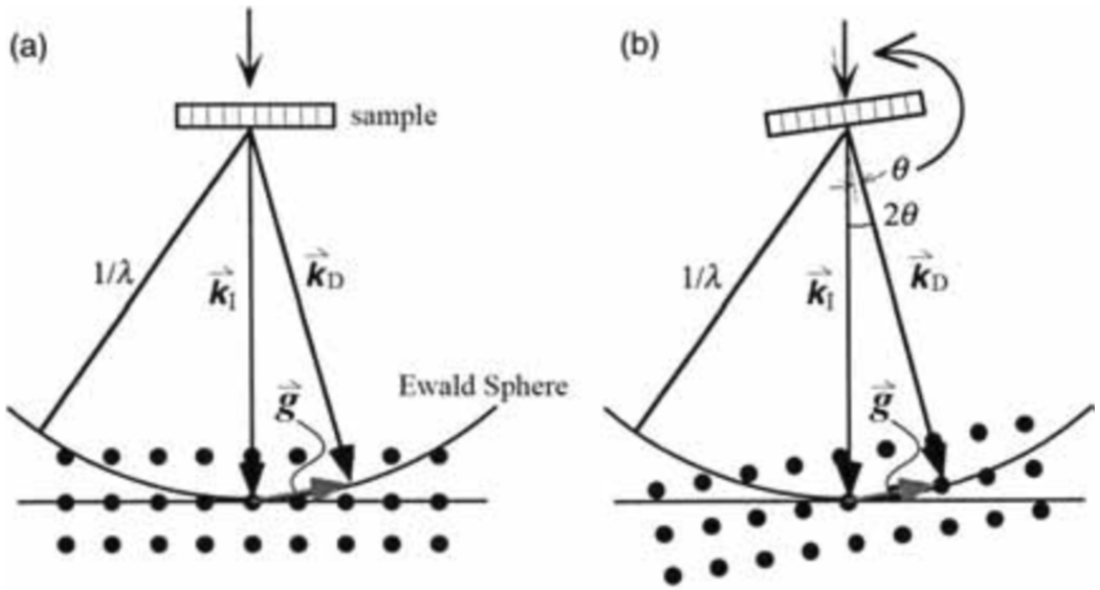
$$|\mathbf{K}| = \frac{2\sin\theta}{\lambda}$$

- **k** is the wave vector for the plane wave function.
- All $\mathbf{k_D}$ form a sphere, i.e., the so-called Ewald sphere.

Bragg's in Reciprocal Space

- Ewald sphere: the sphere of radius $1/\lambda$.
- Bragg diffraction: Bragg condition is satisfied when the sphere cuts through the reciprocal lattice point.

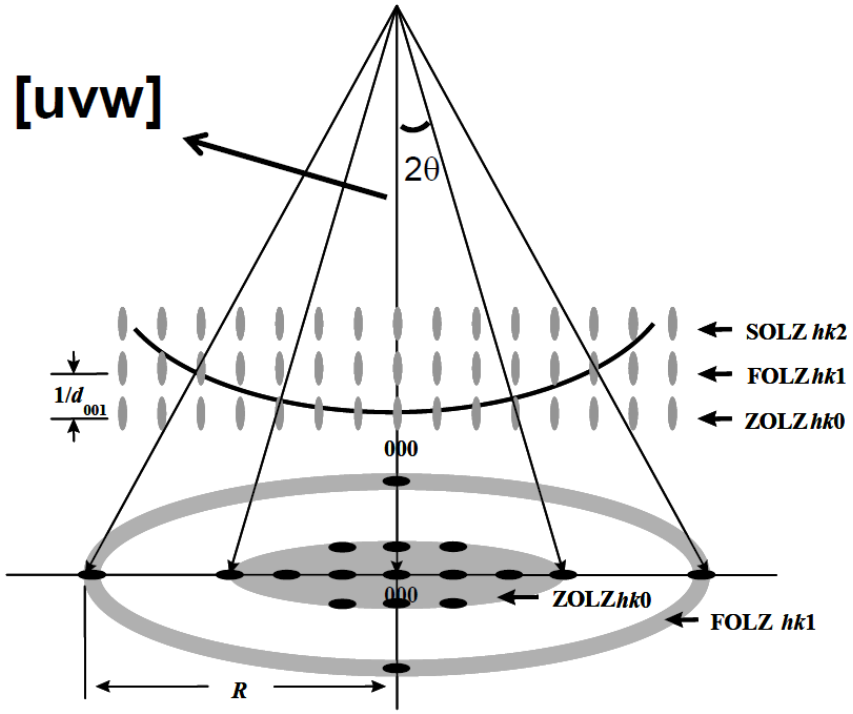


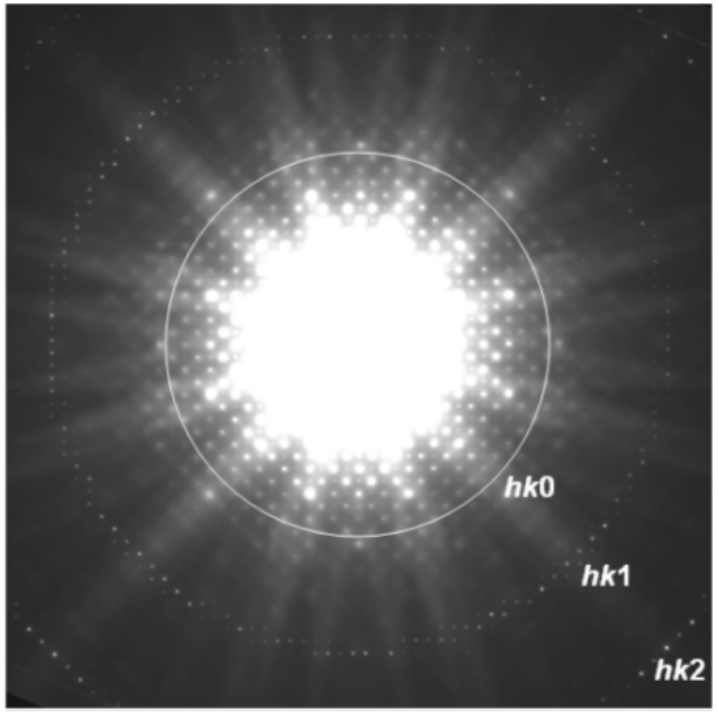


Laue Equation

$$u \cdot h + v \cdot k + w \cdot l = n \quad (n = 0, \pm 1, \pm 2 \ldots)$$

$n = 0$: zero order (ZOLZ); $n = 1$: first order (FOLZ), …





- All reflections shown in the ED pattern taken along the $[uvw]$ direction will obey the Laue equation.


THANKS