Fundamentals of Solid State Physics

Materials and Crystal Structures

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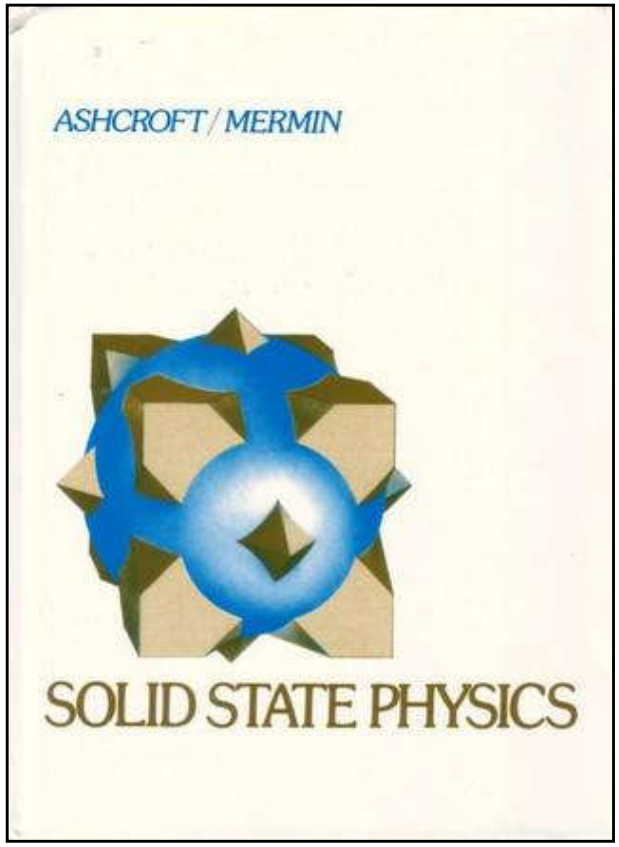
This Class

- Introduction (Week 1)
- **Materials and Crystal Structures (Week 2–3)**
  - **Crystal structures, lattices**
  - **Reciprocal space, Brillouin zones**
  - **Materials Characterization: Wave diffraction, the Bragg law**
- Electronic Properties (Week 4–12)
- Thermal Properties (Week 13)
- Optical Properties (Week 14)
- Magnetic Properties (Week 15)

Further Reading

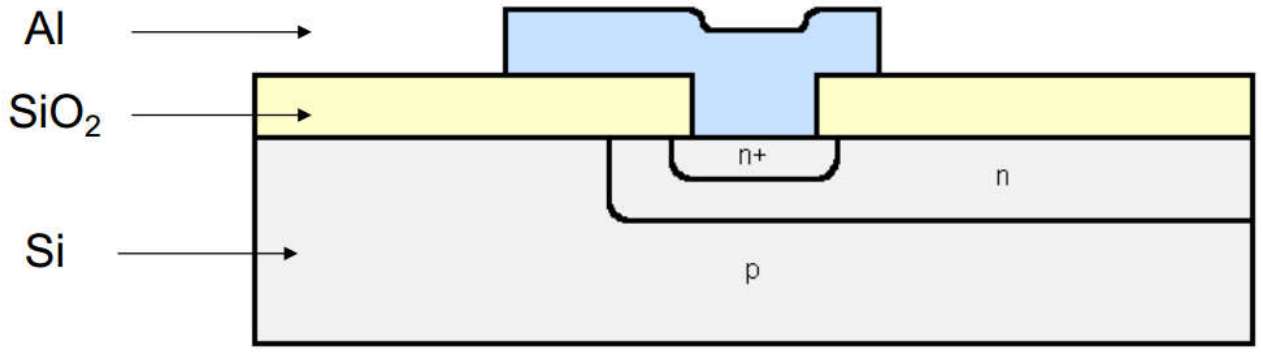
- **Ashcroft & Mermin, Chapter 4, 5, 6**

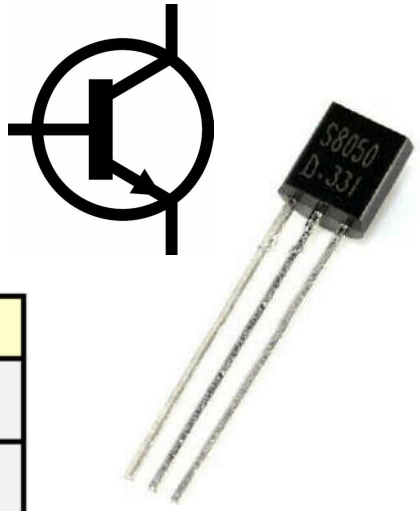


Importance of Materials

CMOS transistor

- Complementary Metal-Oxide-Semiconductor





Importance of Materials

CMOS transistor
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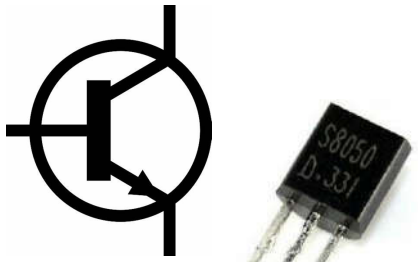
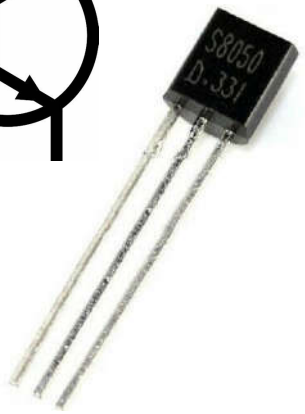
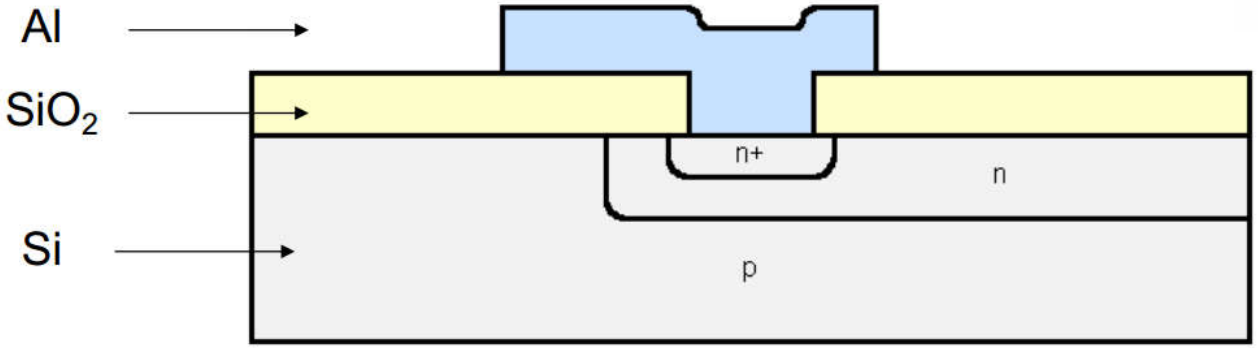






Metal

SiO_2

Silicon

Importance of Materials

Metal

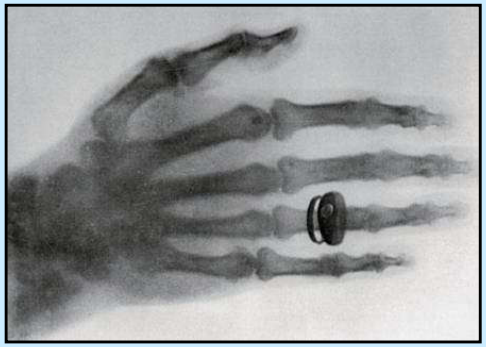
SiO_2

Silicon

- Crystal Structures
  - polycrystalline, amorphous, single crystalline
- Electronics
  - conductor, insulator, semiconductor
- Optics (in the visible range)
  - reflective, transparent, absorbing

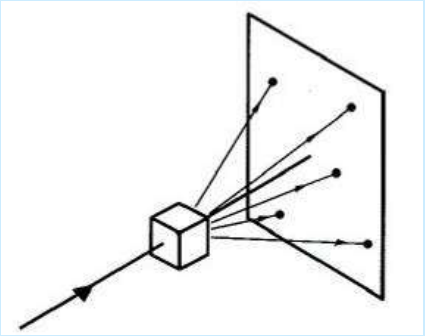
History of Crystal Structures

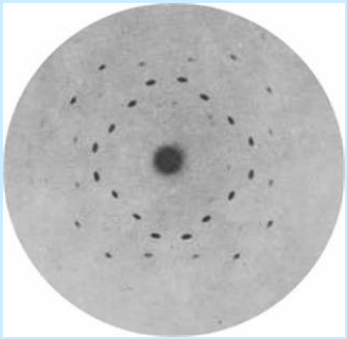
Discovery of X-ray



W. Rontgen (伦琴)
Nobel Prize in 1901

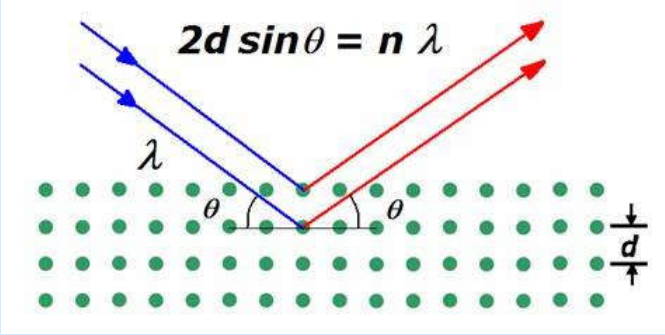
X-ray diffraction of crystals





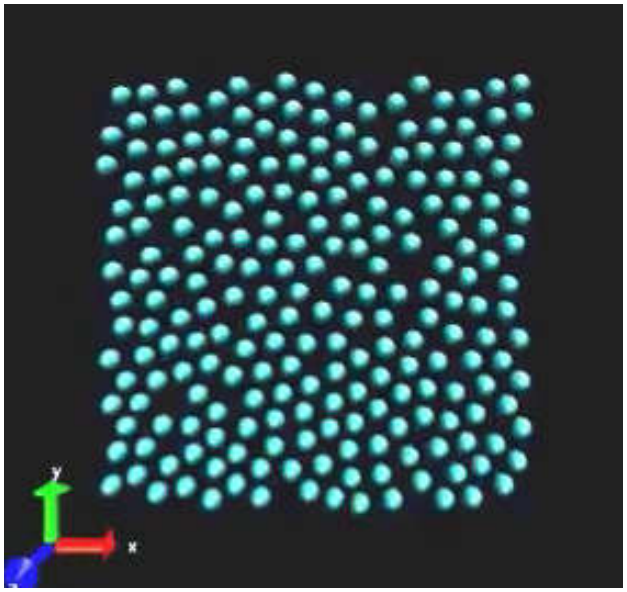
M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law

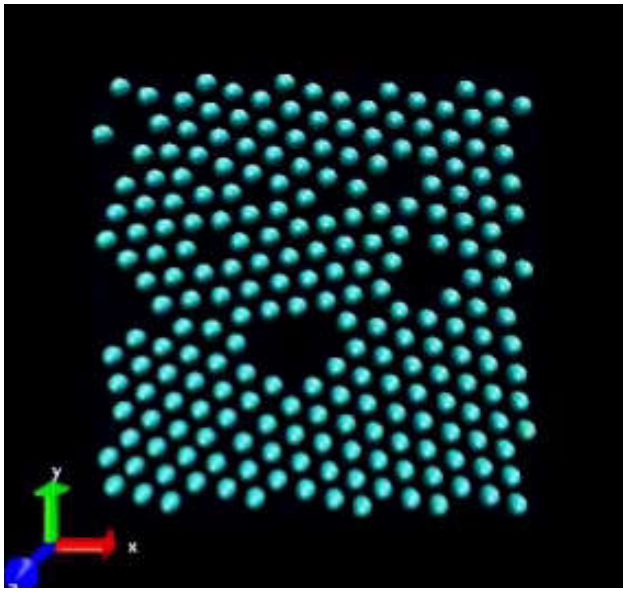


Bragg & Bragg (布拉格父子)
Nobel Prize in 1915

Crystal Structures



Video

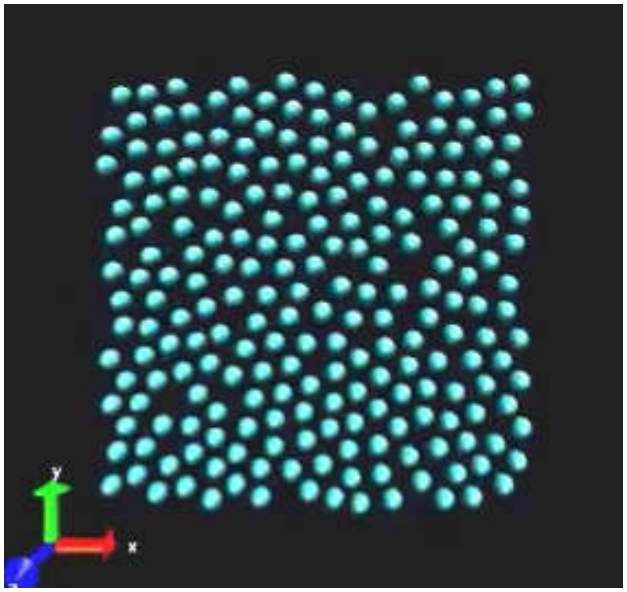


molecular dynamics simulation

crystal structure:
ordered, periodic arrays of atoms
(with translational symmetry)

Crystal is a microscopic (微观) concept,
not a macroscopic (宏观) concept.

Crystal Structures



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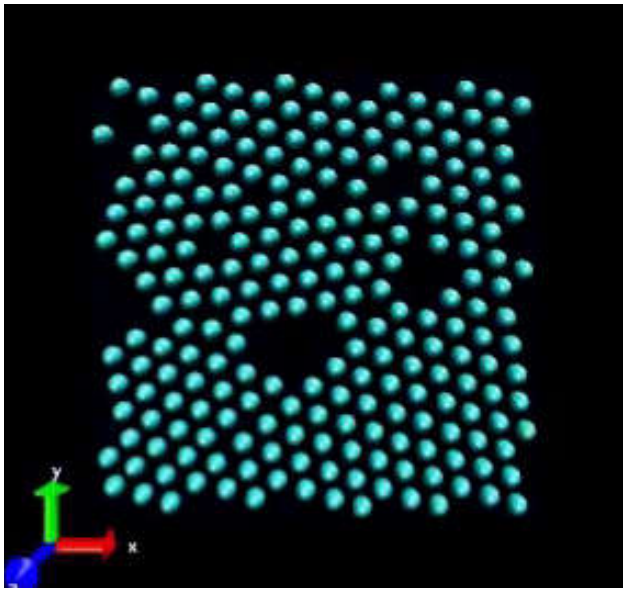
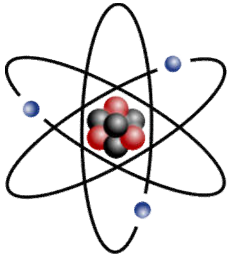


our macroscopic world

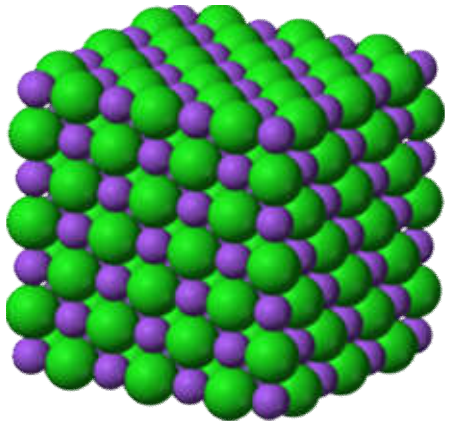
?

Chemical Bonding 化学键

- **Solids are formed by chemical bonding between atoms**
  - Metallic Bonding 金属键
  - Ionic Bonding 离子键
  - Covalent Bonding 共价键
  - Van der Waals Bonding 范德华键
  - Hydrogen Bonding 氢键
  - ...



atom

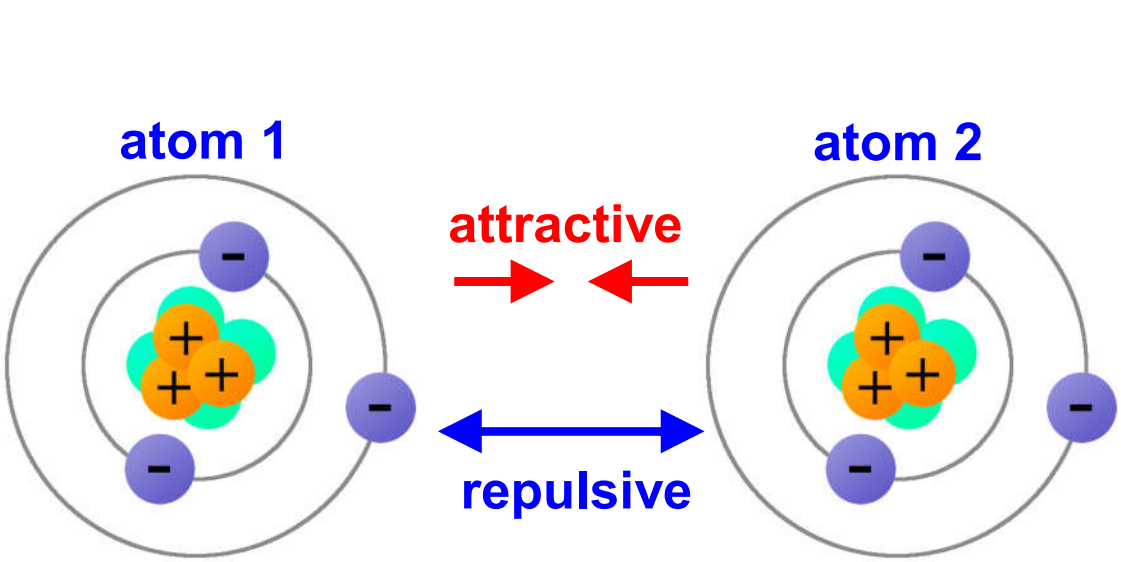


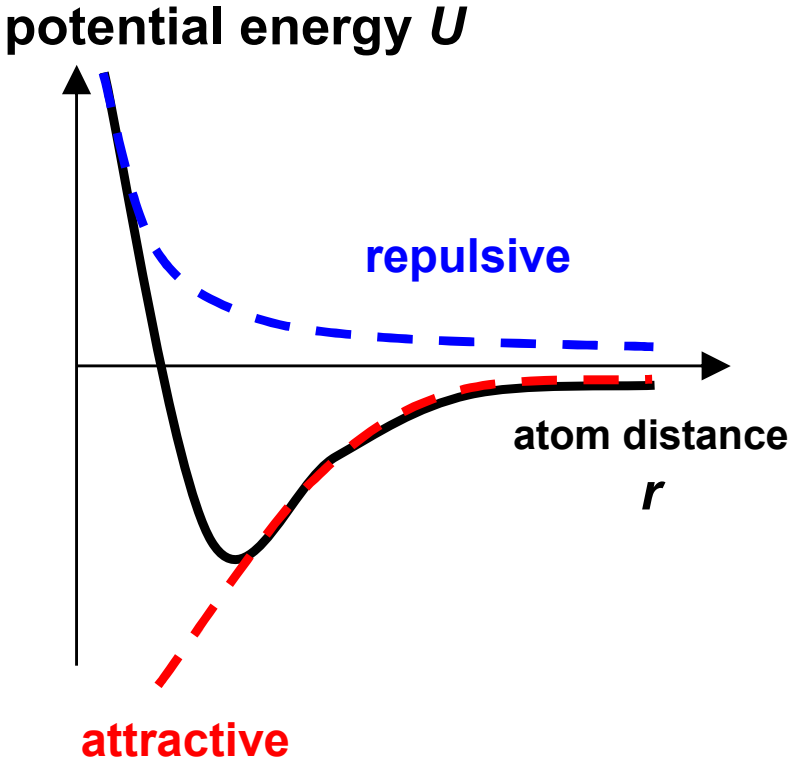
solid

- **Valence electrons form bonds**
  - Silicon (Si) $[1s^2\ 2s^2\ 2p^6]\ 3s^2\ 3p^2$

https://www.chemguide.co.uk/atoms/bondingmenu.html

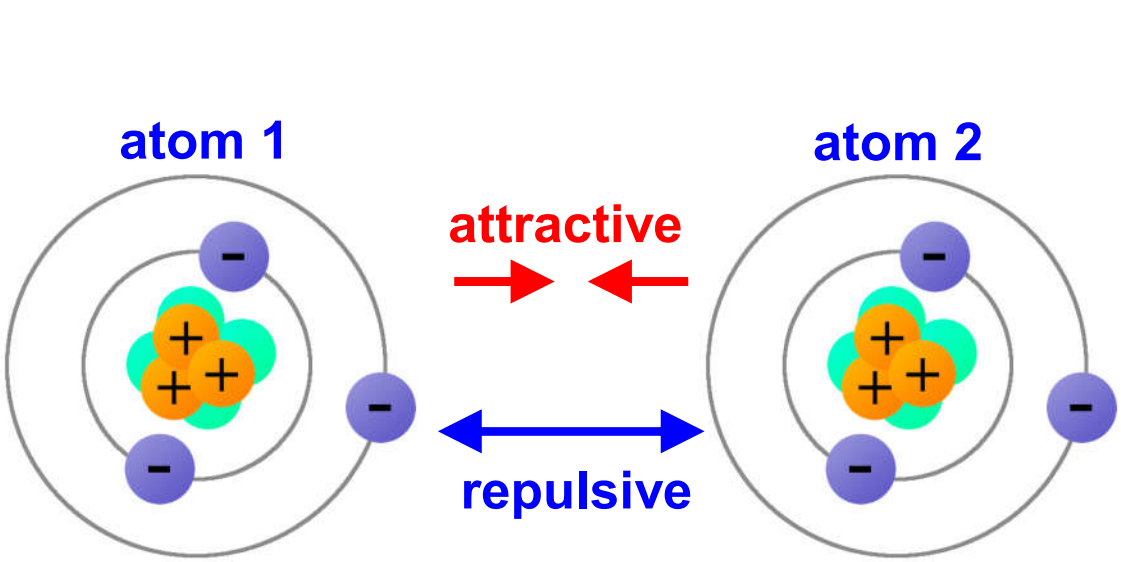
Atomic Interactions

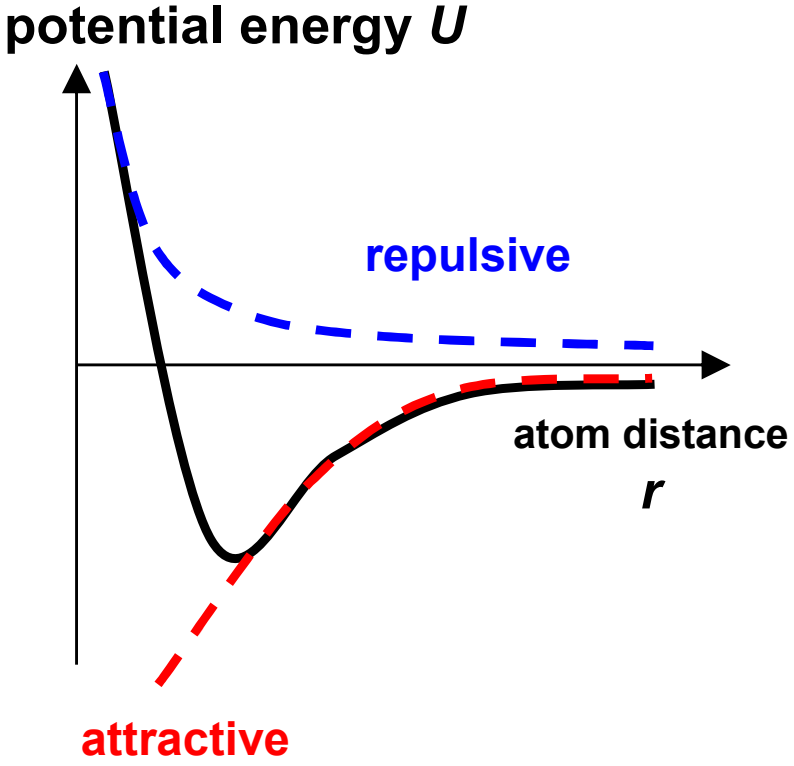




- **Interatomic Potential *U***
  - attraction: electrostatic (+ –)
  - repulsion: electrostatic (+ + /– –)
    and Pauli exclusion principle

Atomic Interactions



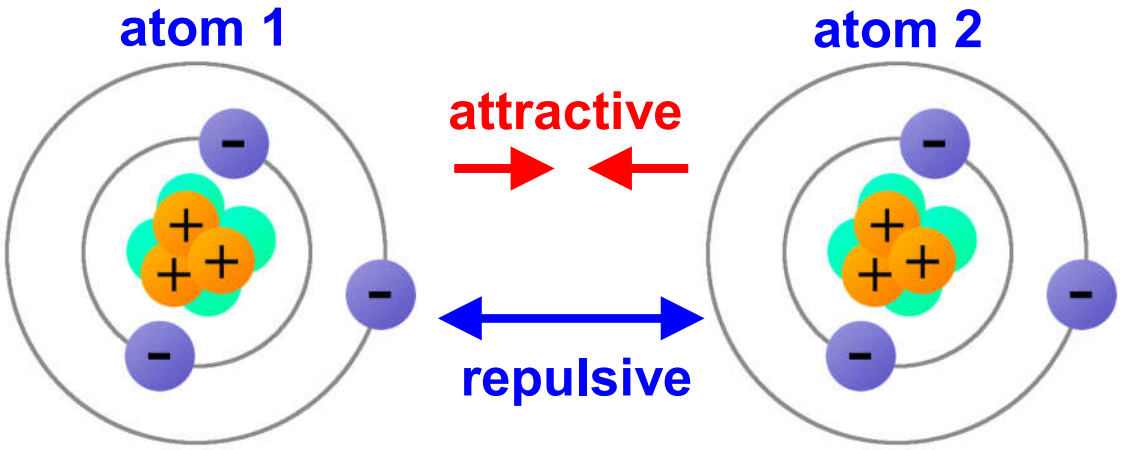


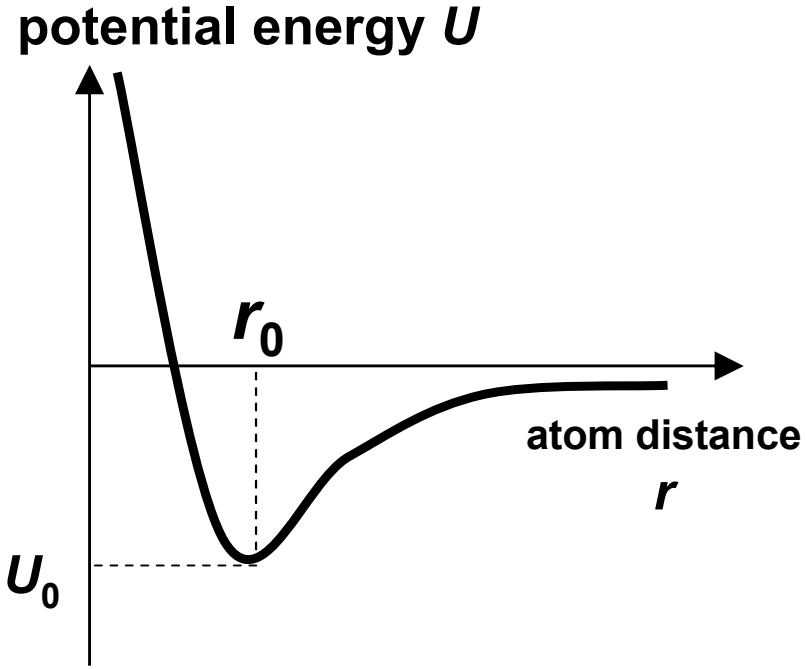
- **Interatomic Potential *U***

$$U(r) = U_{\text{repulsion}}(r) - U_{\text{attaction}}(r)$$

U **- potential energy (J, eV)**
r **- atomic distance (nm, Å)**

Atomic Interactions





- **Interatomic Potential *U***

$-U_0$ - cohesive energy (结合能)
lowest energy state

$$U(r) = U_{\text{repulsion}}(r) - U_{\text{attaction}}(r)$$

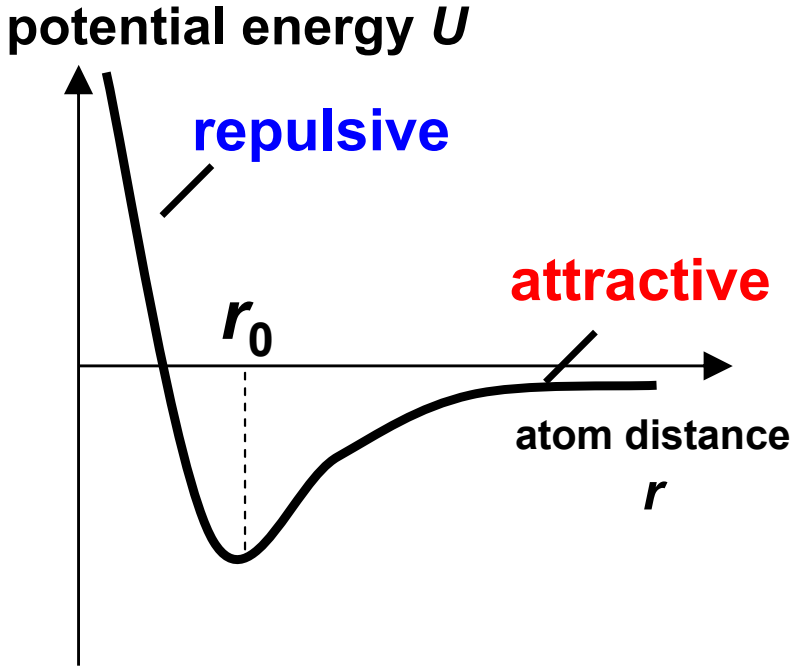
***U* - potential energy (J, eV)**
***r* - atomic distance (nm, Å)**

Interatomic Potential: Examples

- **Lennard-Jones (L-J)**

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$

repulsive attractive



- **Buckingham Potential**

$$U(r) = A\exp\left(-\frac{r}{\rho}\right) - \frac{B}{r^{6}}$$

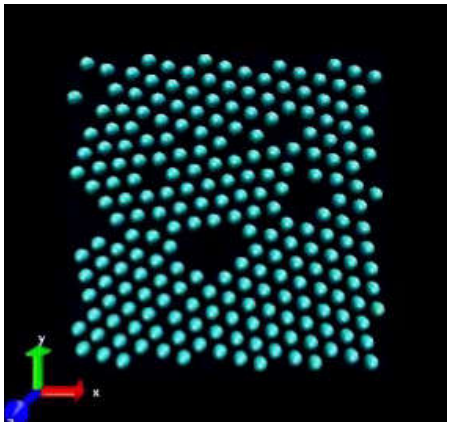
repulsive attractive

- **Morse Potential**

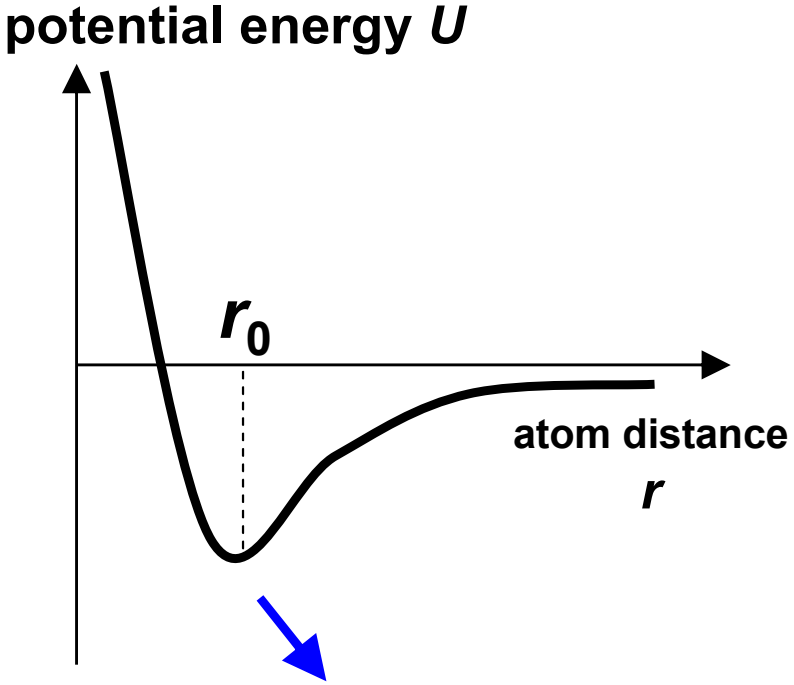
$$U(r) = D\left(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\right)$$

repulsive attractive

Atomic Interactions



optimal distance r_0:
periodicity of crystals



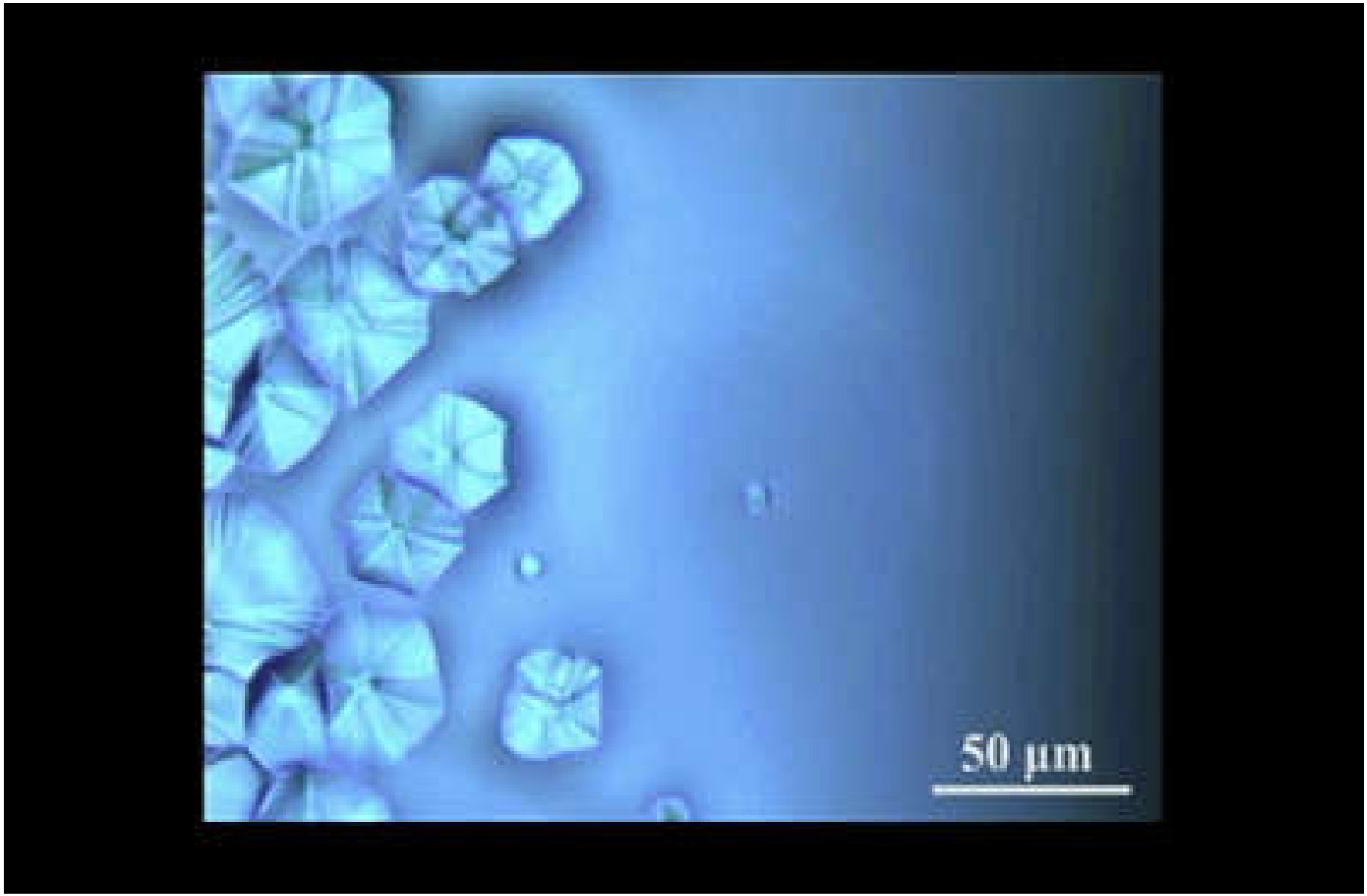
bonding length
(equilibrium distance)

- **Interatomic Potential *U***

$$U(r) = U_{\text{repulsion}}(r) - U_{\text{attaction}}(r)$$

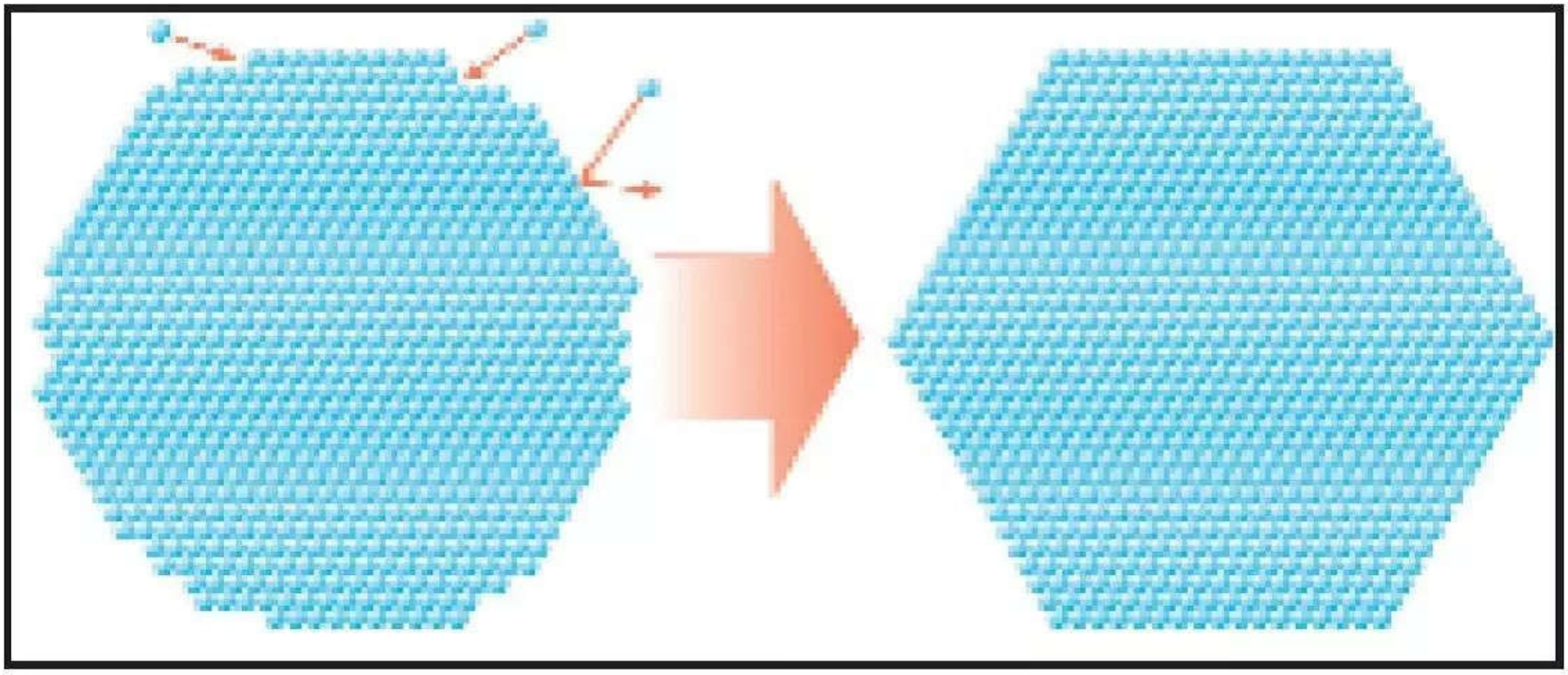
U **- potential energy (J, eV)**
r **- atomic distance (nm, Å)**

Macroscopic Crystals



M. He, *Nat. Comm.* **8,** 16045 (2017)

Macroscopic Crystals



Macroscopic Crystals

金刚石 diamond (C)

石英 quartz (SiO_2)

红宝石 ruby (Al_2O_3:Cr)

食盐 salt (NaCl)

Macroscopic Crystals

Silicon Crystal

石英 quartz (SiO_2)

Crystal Cave, Mexico

Crystal Structures

- Vectors
  - Translational vectors
  - Primitive vectors
- Cells
  - Unit Cell, Conventional Cell
  - Primitive Cell, Wigner-Seitz Cell
- Lattice
  - Bravais Lattice
  - SC, BCC, FCC, HCP, ...
- Packing
  - Atomic Packing Factor
- Miller Index
- Coordination Number

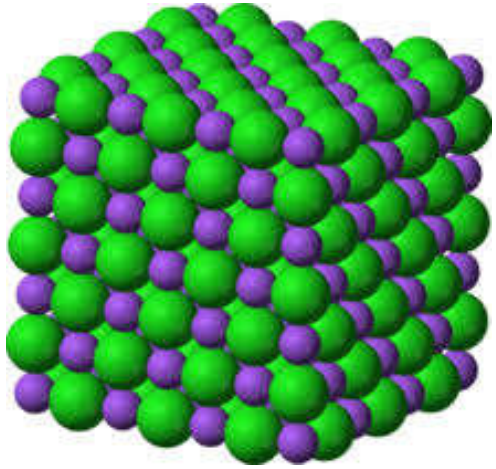
Crystal, Basis and Lattice

- Crystal 晶体
  - real material structures - physical concept, finite
- Basis 基元
  - single unit of an group of atoms
- Lattice 晶格/点阵
  - arrangement of points - mathematical concept, infinite
  - one point can represent *one or more* atoms

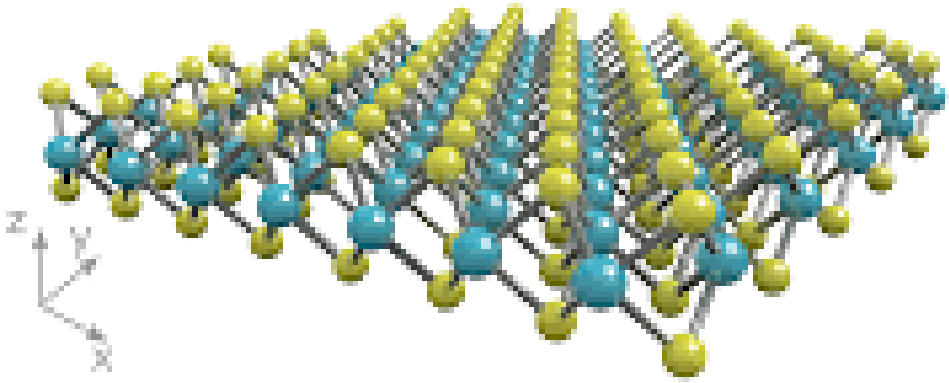
Crystal Basis Lattice

Crystal, Basis and Lattice

Crystal

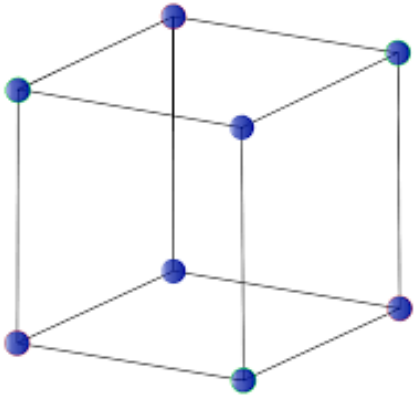


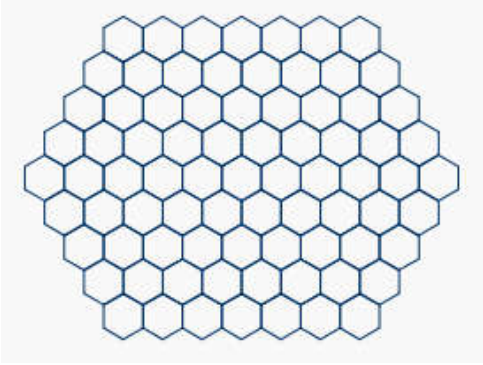
NaCl



monolayer MoS_2

Lattice





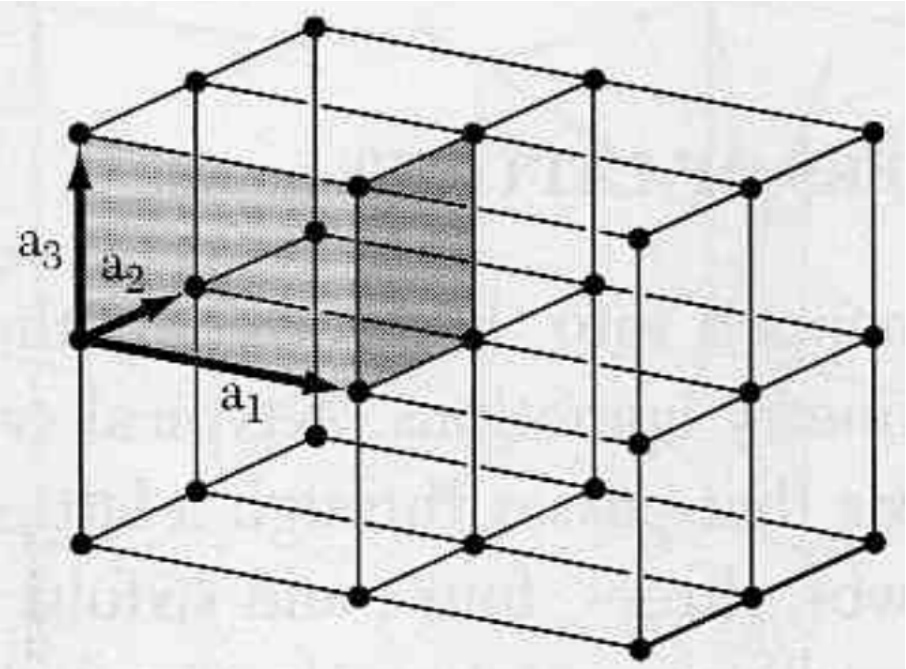
Bravais Lattice 布拉菲点阵

- Each point is ***exactly*** the same
- Position of each point

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

n_1, n_2, n_3 cover ***all*** the integers

- (a_1, a_2, a_3) primitive vectors 基矢量



translational symmetry
平移对称性

Bravais Lattice 布拉菲点阵

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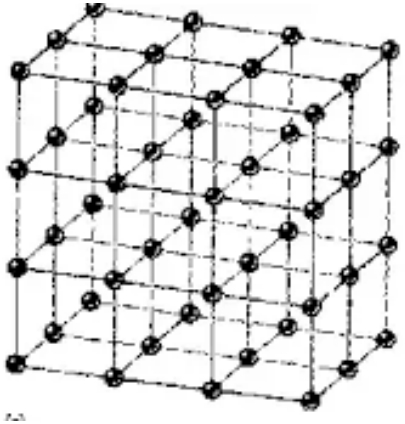
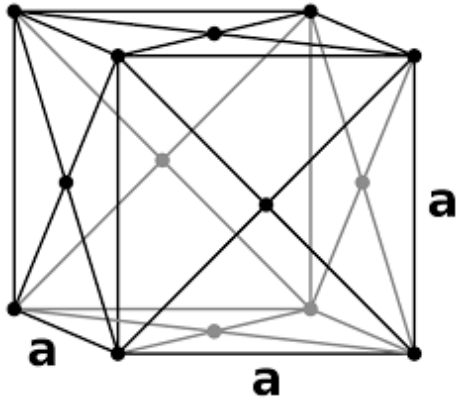
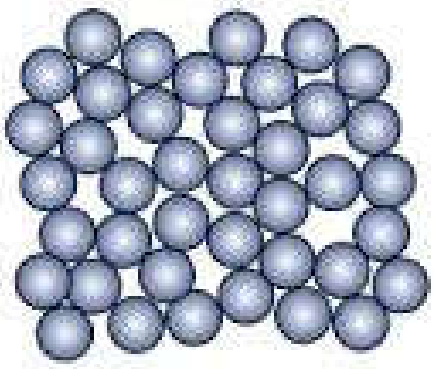
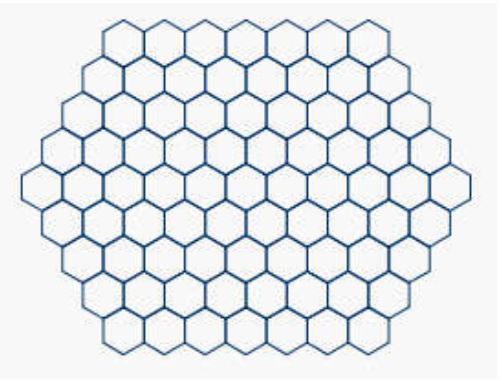
n_1, n_2, n_3 cover ***all*** the integers

Q: which is Bravais lattice, which is not?









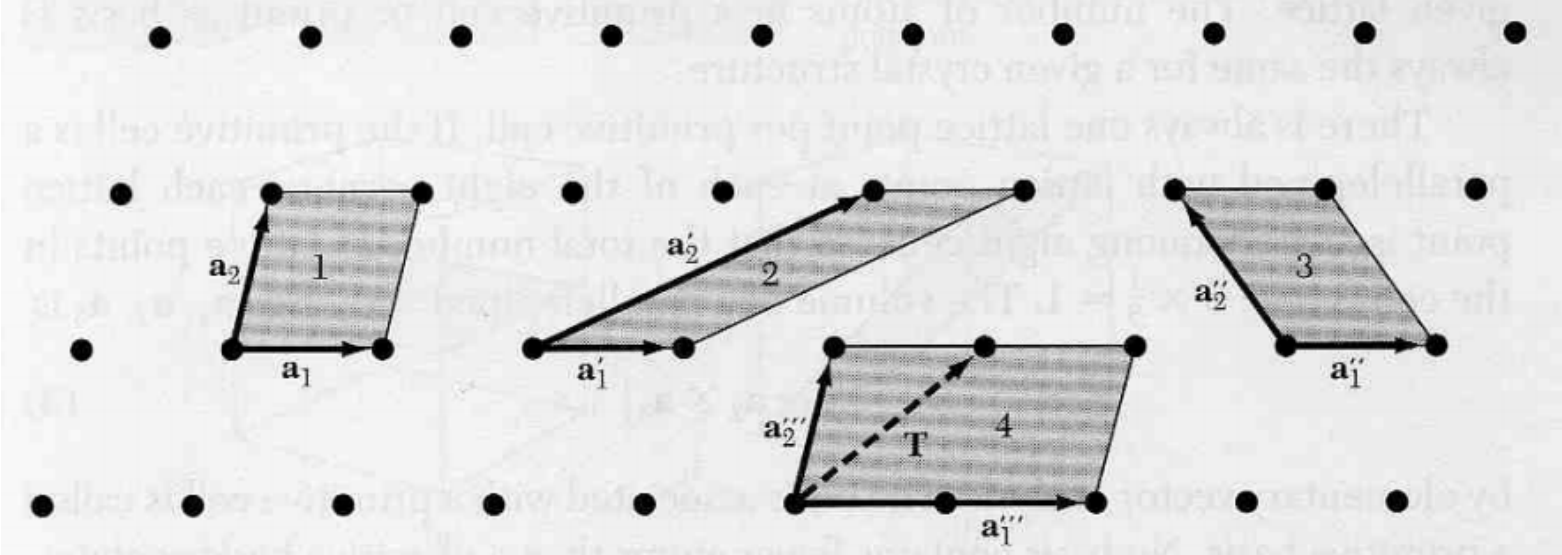
Bravais Lattice 布拉菲点阵

- Each point is ***exactly*** the same
- Position of each point

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

n_1, n_2, n_3 cover ***all*** the integers

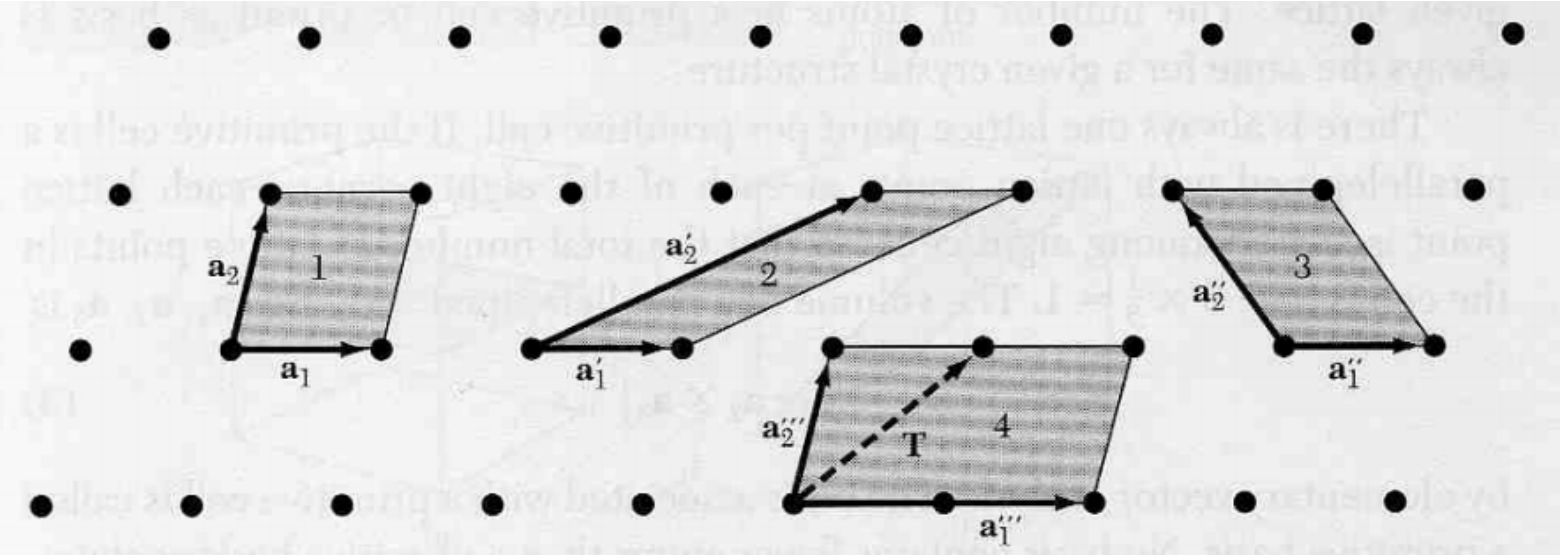
- ($\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$) primitive vectors 基矢量



Q: which are primitive vectors, which are not?

Lattice Cells 晶胞

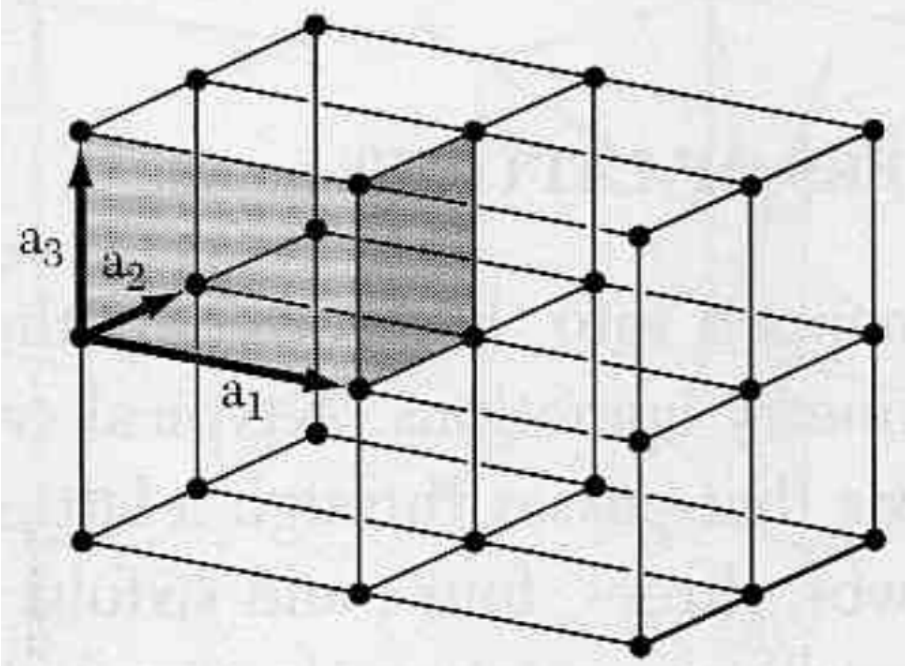
- **Repetitive Units to form the infinite lattice**



Lattice Cells 晶胞

- **Primitive Cell 原胞/素胞**
  - **A cell with the *smallest* volume**
  - **A cell with *only one* lattice point**

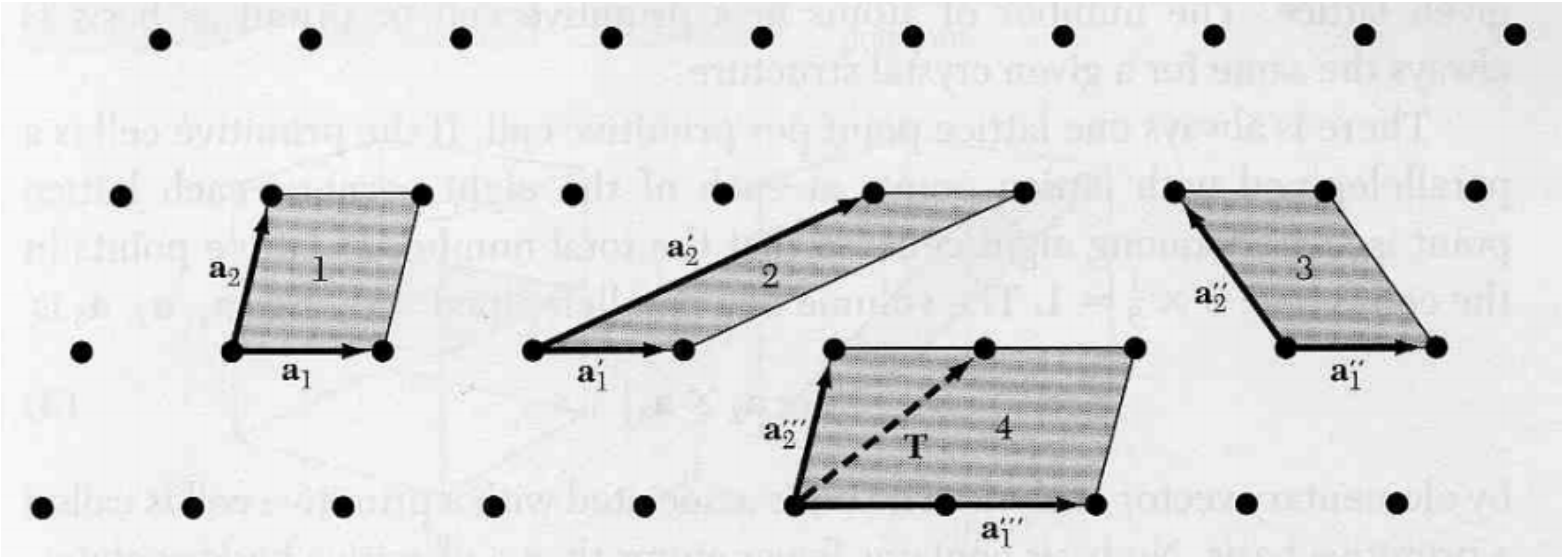
$$V_{\mathrm{R}} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$



Q: how many atoms are in this primitive cell?

Lattice Cells 晶胞

- **Primitive Cell 原胞/素胞**
  - **A cell with the *smallest* volume**
  - **A cell with *only one* lattice point**



Q: which are primitive cells, which are not?

Lattice Cells 晶胞

- **Primitive Cell 原胞/素胞**
  - **A cell with the *smallest* volume**
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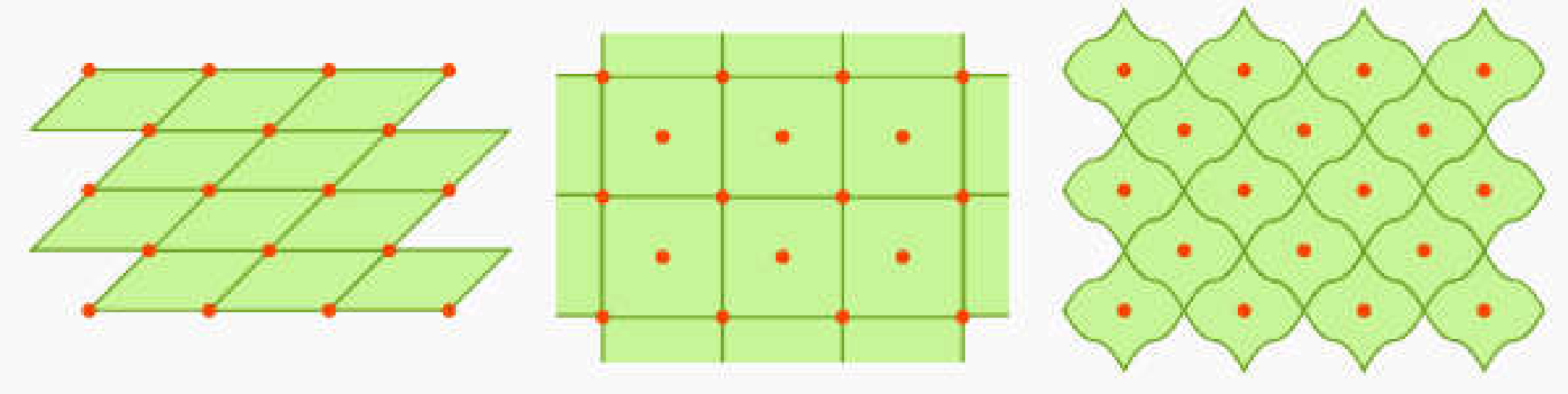
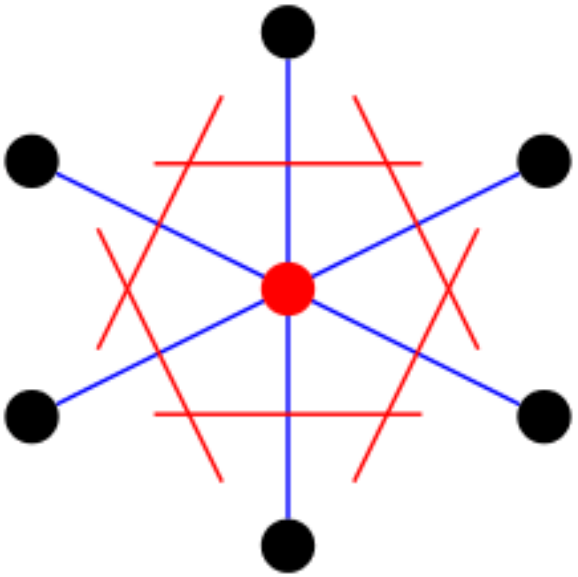
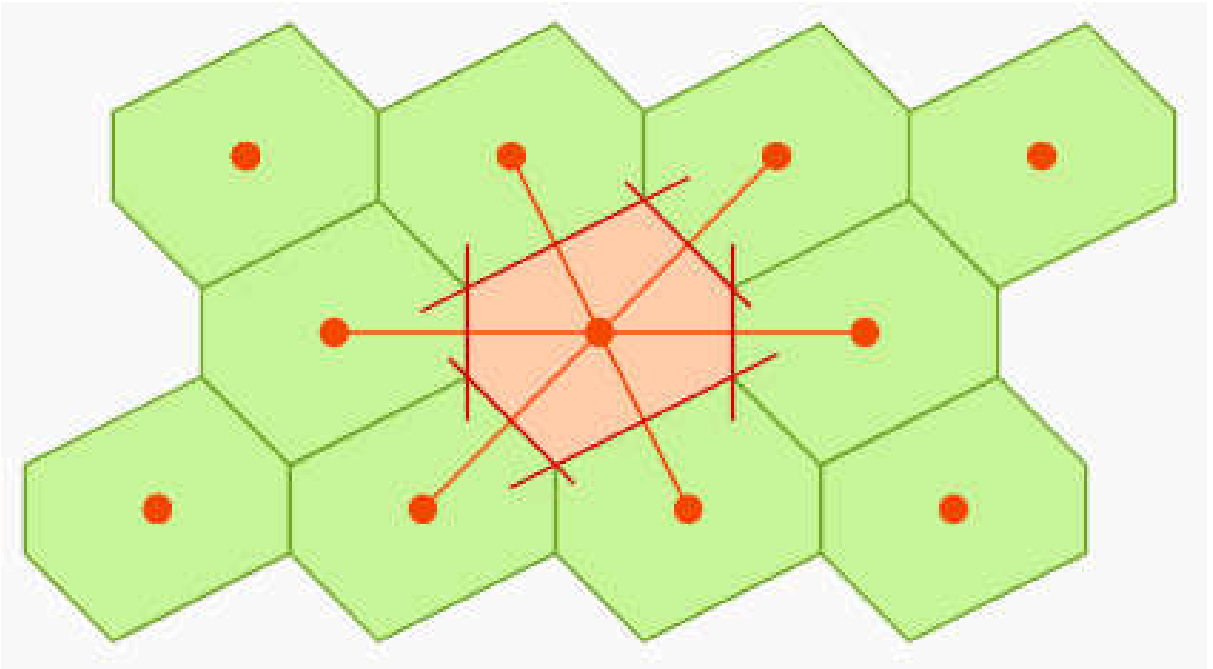


Q: which are primitive cells, which are not?

Lattice Cells 晶胞

- **Wigner-Seitz cell**
  - **A very special primitive cell**

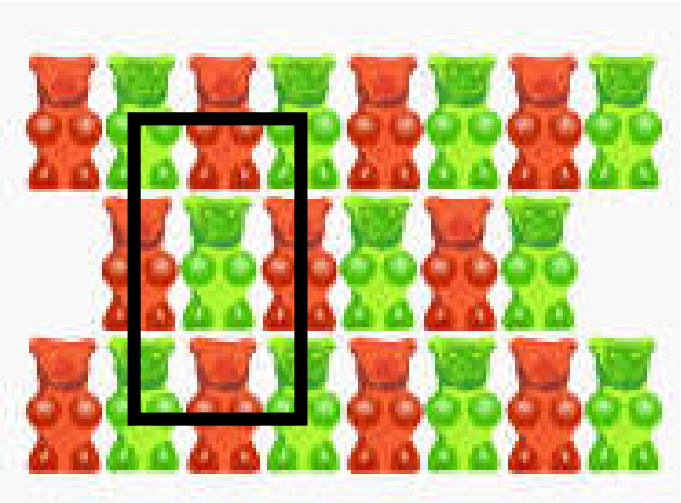


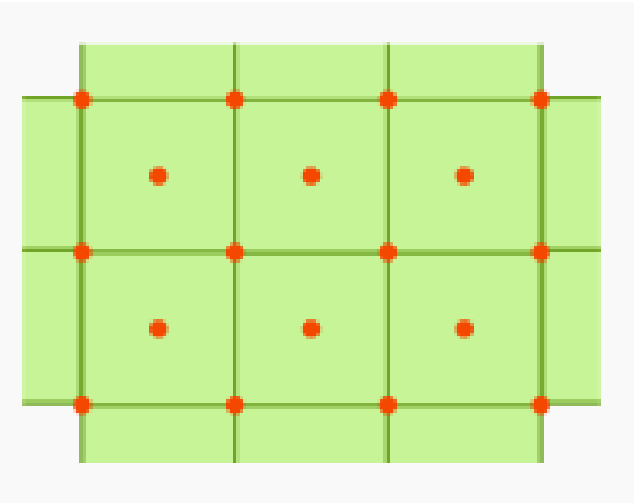


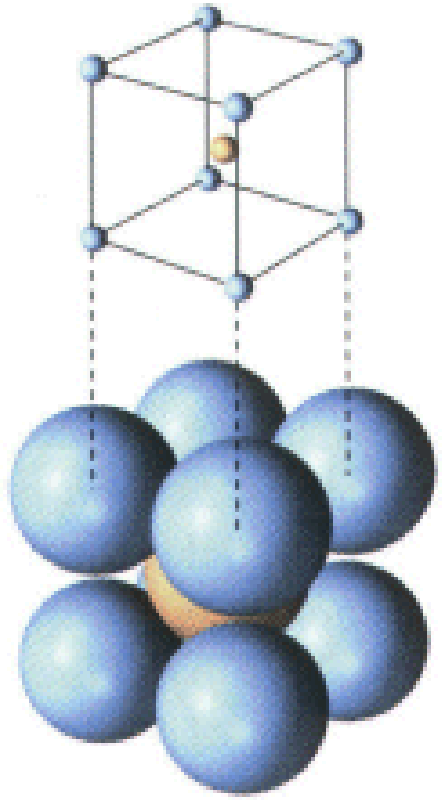
1. draw lines to connect nearby points
2. at the midpoint and normal to these lines draw new lines/planes

Lattice Cells 晶胞

- **Compound Cell 复胞**
  - **A cell with *more than one* lattice point**

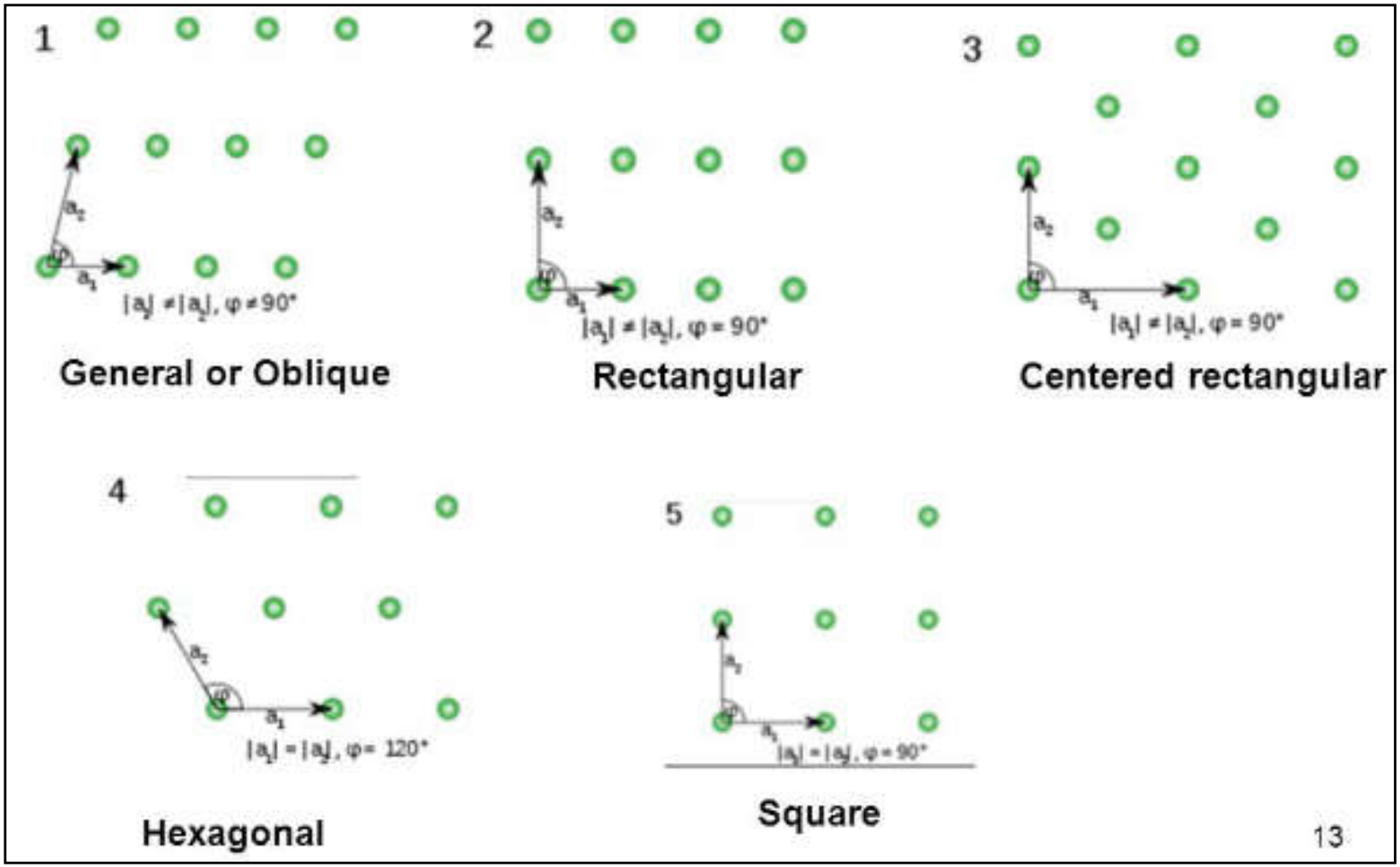






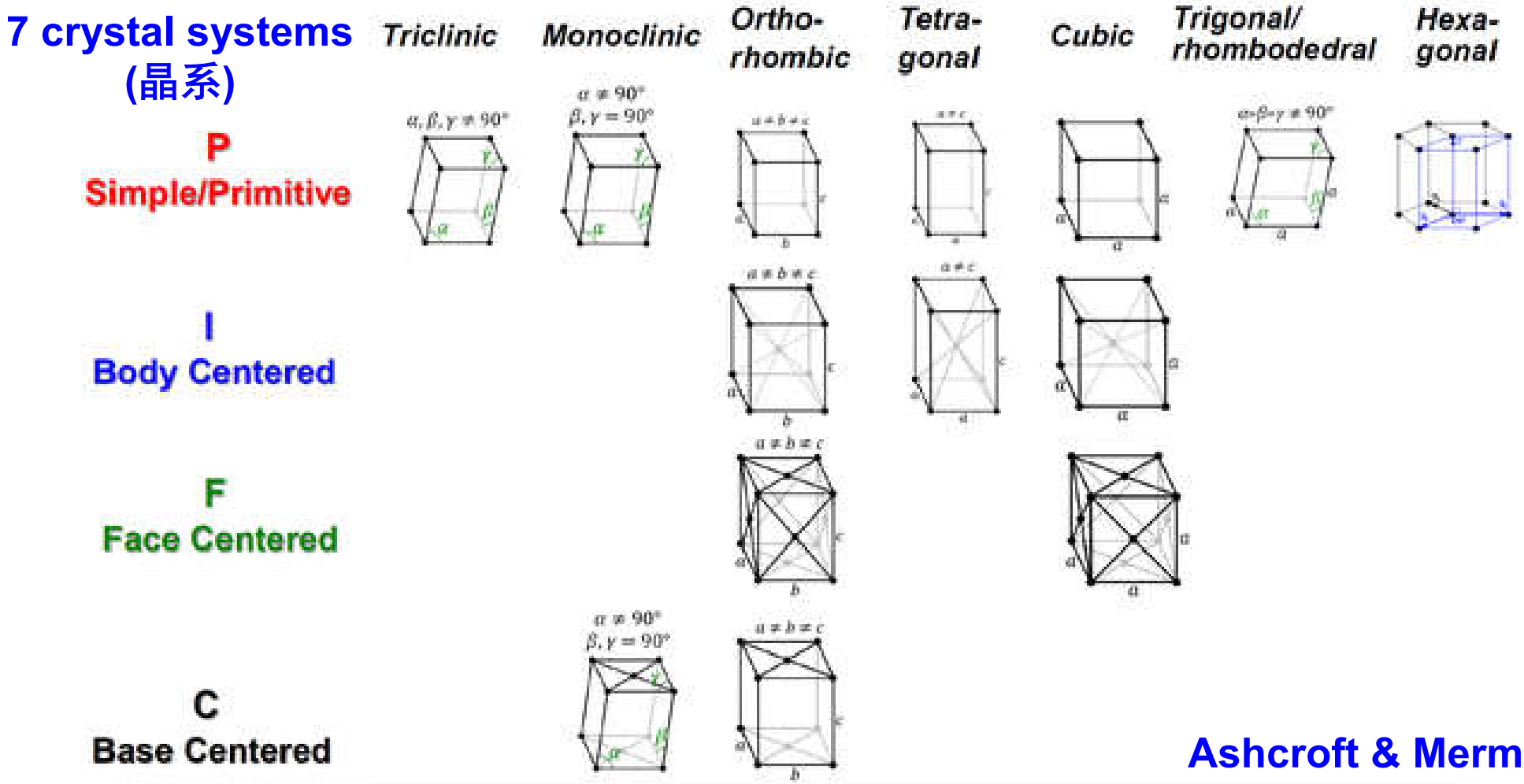
2D Bravais Lattice

- There are 5 Bravais lattices in 2D



3D Bravais Lattice

- There are 14 Bravais lattices in 3D

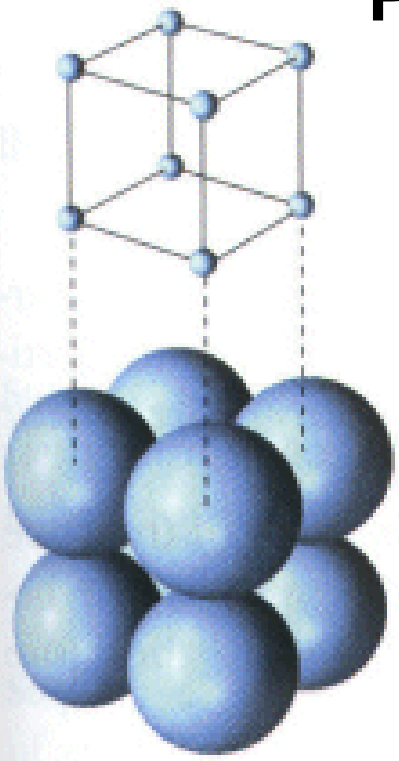


Ashcroft & Mermin
Chapter 7

Bravais Lattice for Cubics 立方晶格

简单立方 SC

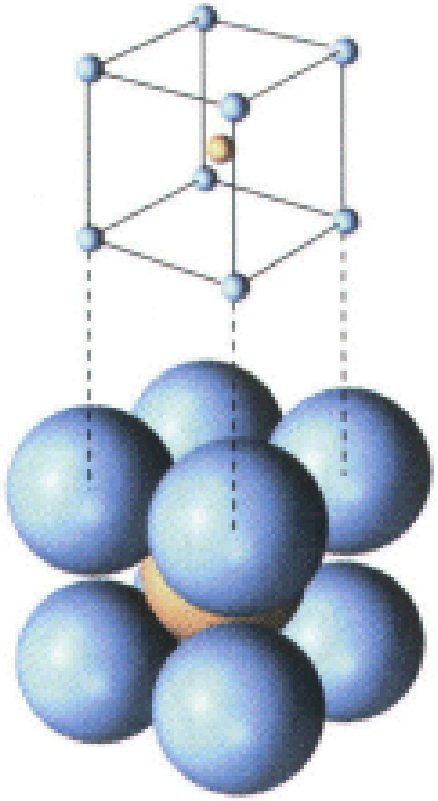
Simple cubic



Po

体心立方 BCC

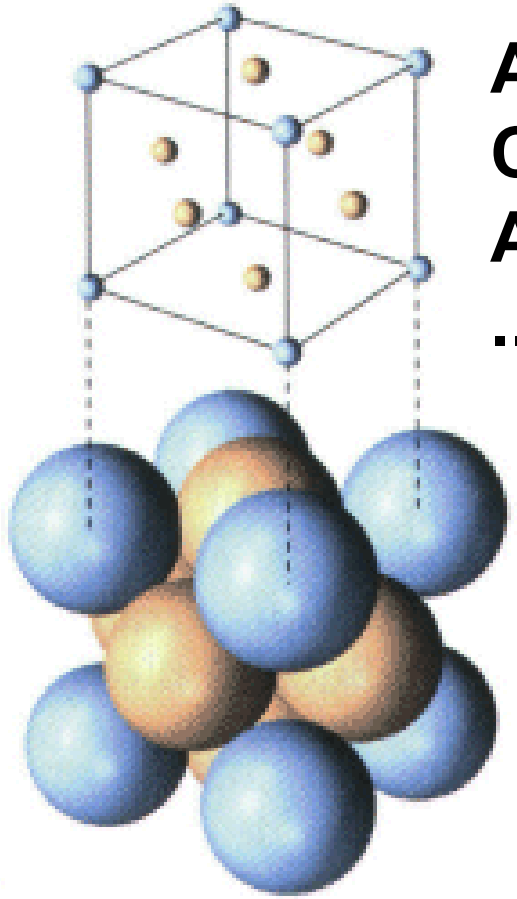
Body-centered cubic



Li
Na
Cr
...

面心立方 FCC

Face-centered cubic

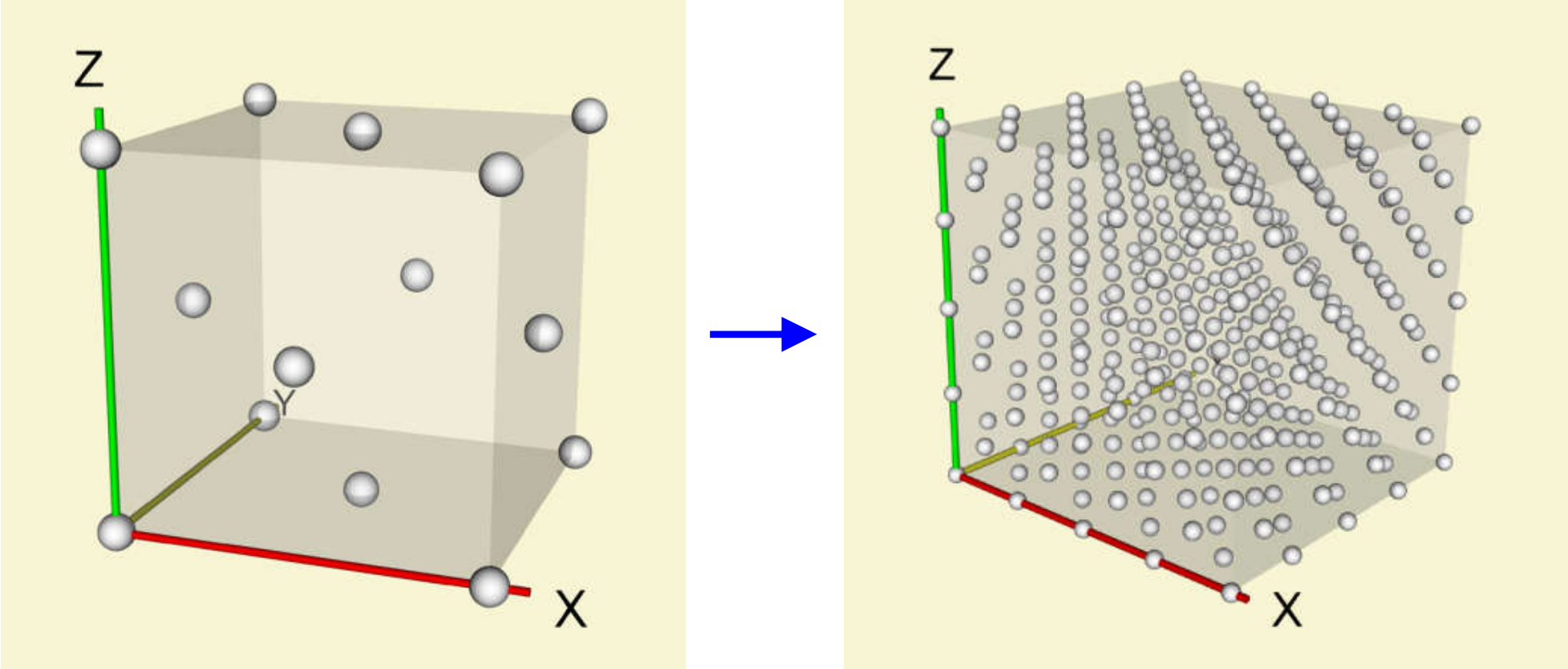


Al
Cu
Au
...

Q: Crystals with SC are not common, why?

FCC is a Bravais Lattice

Each point is *exactly* the same



https://quantumwise.com/documents/manuals/ATK-2008.10/chap.audtb.html

2D Packing

- ***Atomic Packing Factor (APF)*** **填充因子**
- **APF = (area of circles) / (area of unit cell)**

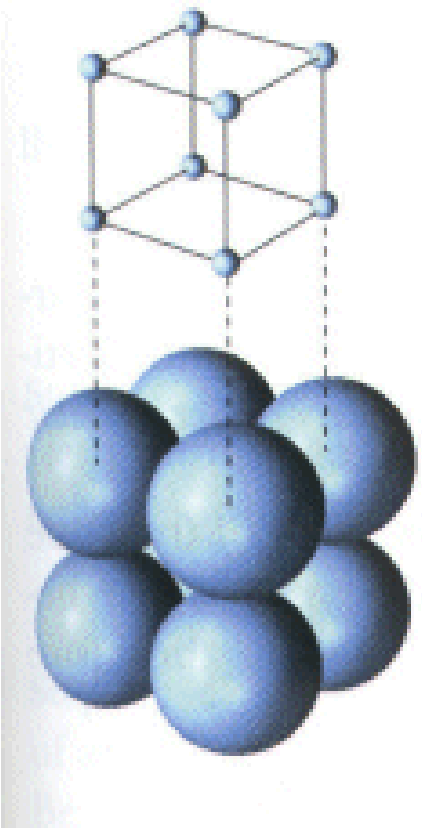
$$APF = \frac{\pi(0.5a)^2}{a^2} = \frac{\pi}{4} = 0.785$$

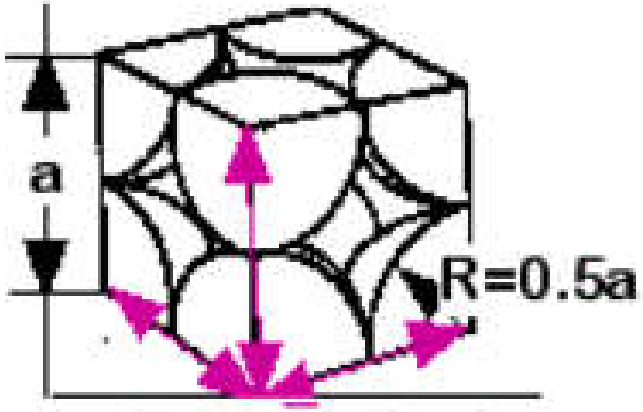
<

$$APF = \frac{\pi(0.5a)^2}{a * a * \sqrt{3}/2} = \frac{\pi}{2\sqrt{3}} = 0.906$$

简单立方 SC

- APF = (volume of spheres) / (volume of unit cell)





close-packed directions

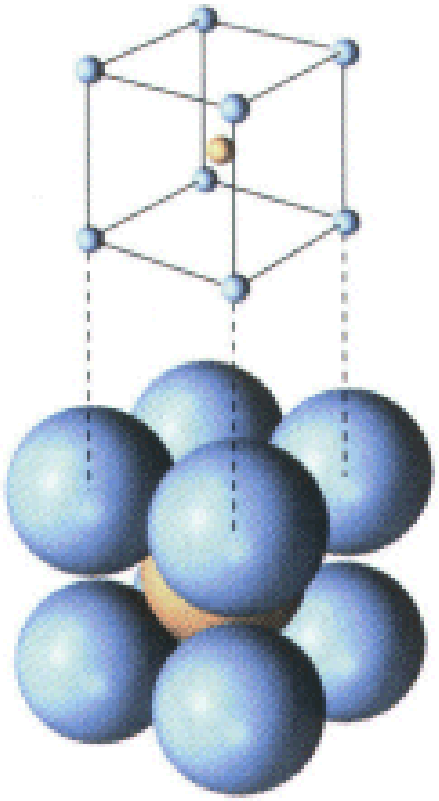
contains 8 x 1/8 = 1atom/unit cell

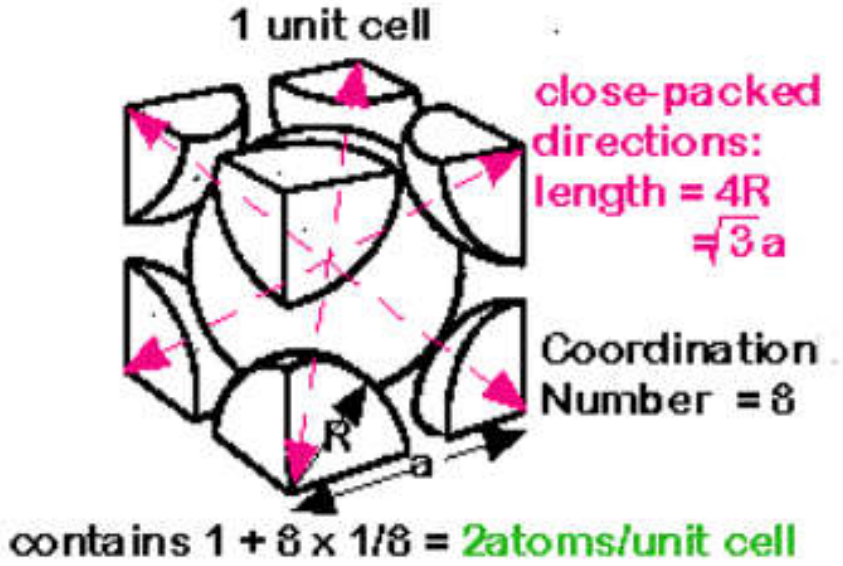
$$APF = \frac{1 * \frac{4}{3}\pi(0.5a)^3}{a^3} = \frac{\pi}{6} = 0.523$$

简单立方 SC

体心立方 BCC

- APF = (volume of atoms) / (volume of unit cell)



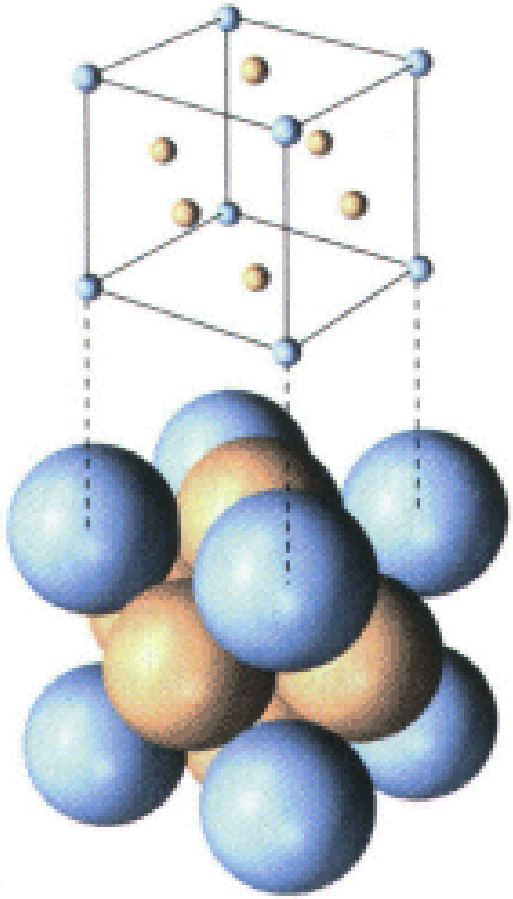


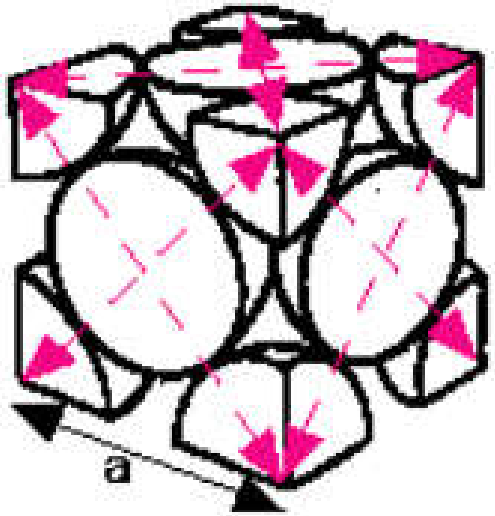
体心立方 BCC

$$APF = \frac{2 * \frac{4}{3}\pi(\frac{\sqrt{3}}{4}a)^3}{a^3} = \frac{\sqrt{3}}{8}\pi = 0.681$$

面心立方 FCC

- APF = (volume of atoms) / (volume of unit cell)





close-packed directions:
length = 4R
= √2 a

Coordination Number = 12

contains 6 x 1/2 + 8 x 1/8 = 4atoms/unit cell

$$APF = \frac{4 * \frac{4}{3}\pi(\frac{\sqrt{2}}{4}a)^3}{a^3} = \frac{\sqrt{2}}{6}\pi = 0.740$$

面心立方 FCC

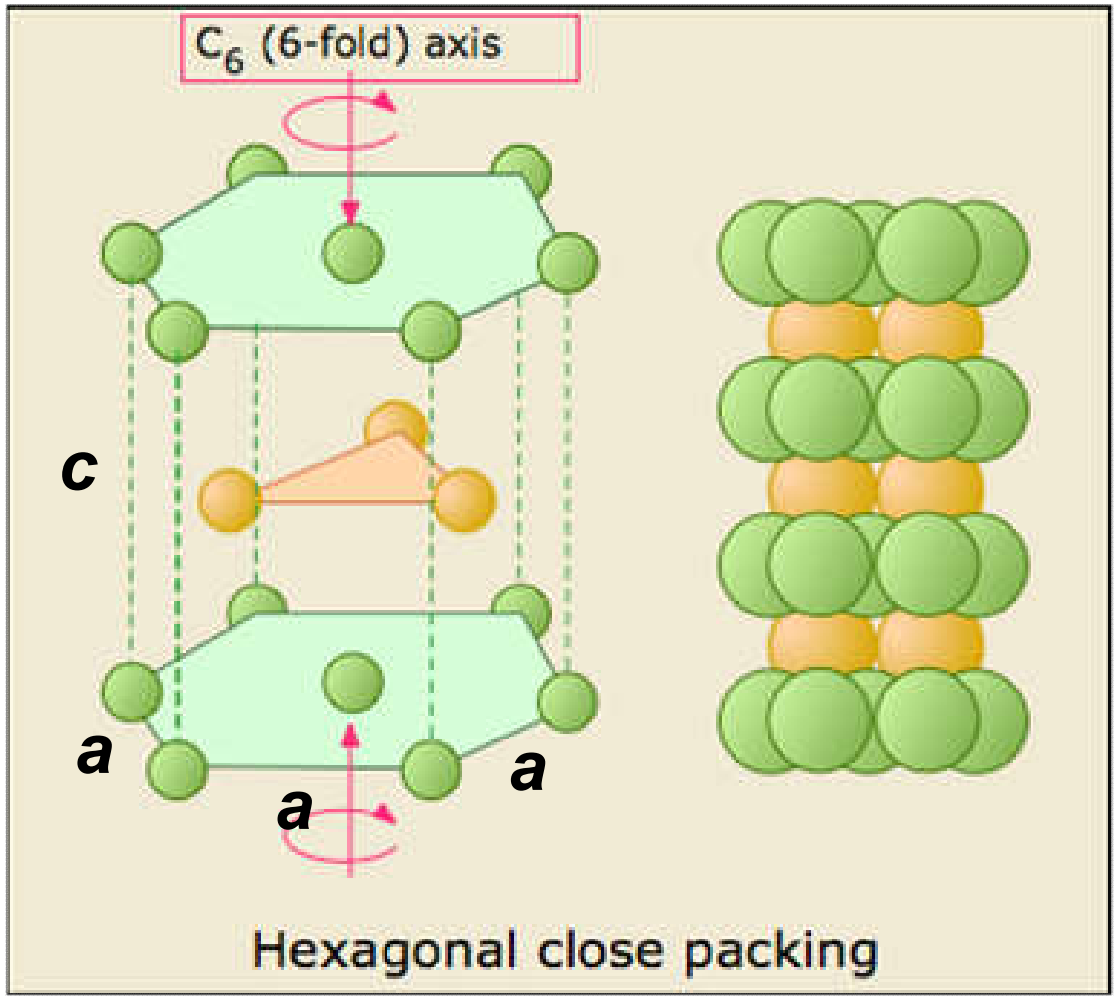
Cubic Lattices

	SC	BCC	FCC
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}\,a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction[a]	$\frac{1}{6}\pi$ $=0.524$	$\frac{1}{8}\pi\sqrt{3}$ $=0.680$	$\frac{1}{6}\pi\sqrt{2}$ $=0.740$

***a*: lattice constant / lattice parameter (晶格常数 / 晶格参数)**

Atoms tend to pack closely

Hexagonal Close Packing (HCP) 六角密排



Mg, Zn, Ti,...

APF for HCP

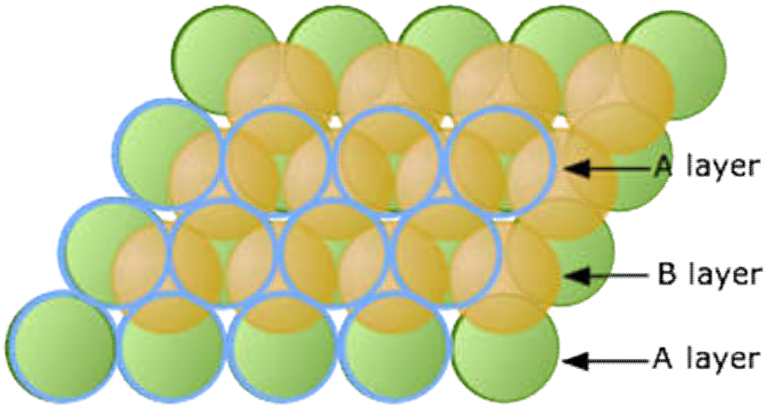
$$APF = 0.740$$

same as FCC

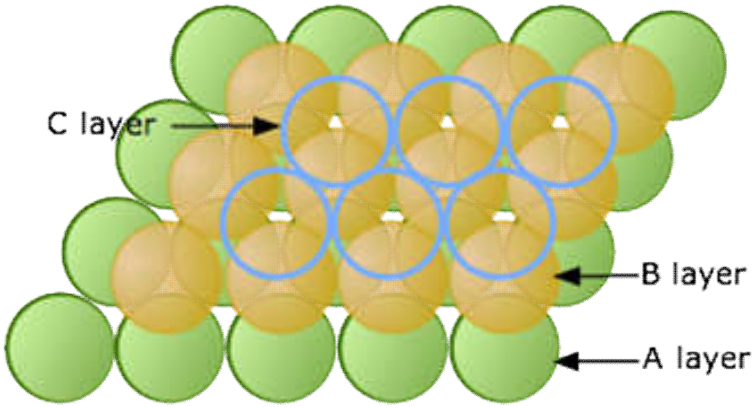
Q: Is HCP a Bravais lattice?

c/a = ???

HCP and FCC

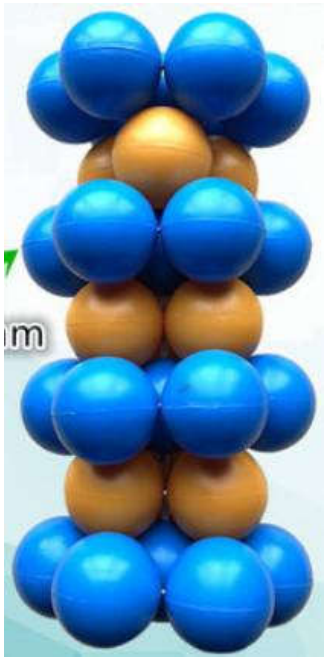


ABA hexagonal close packed



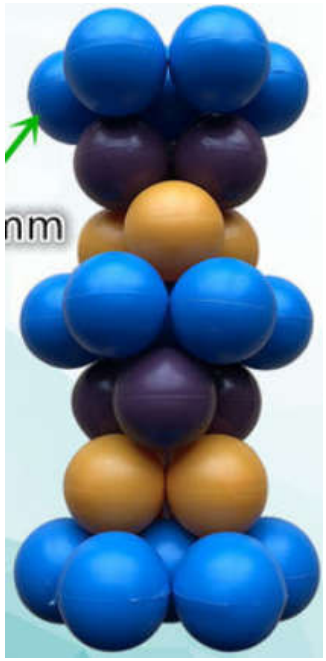
ABC face-centered cubic

A
B
A
B
A
B
A



HCP

A
C
B
A
C
B
A



FCC

HCP and FCC - A Little Story

cannonball pack

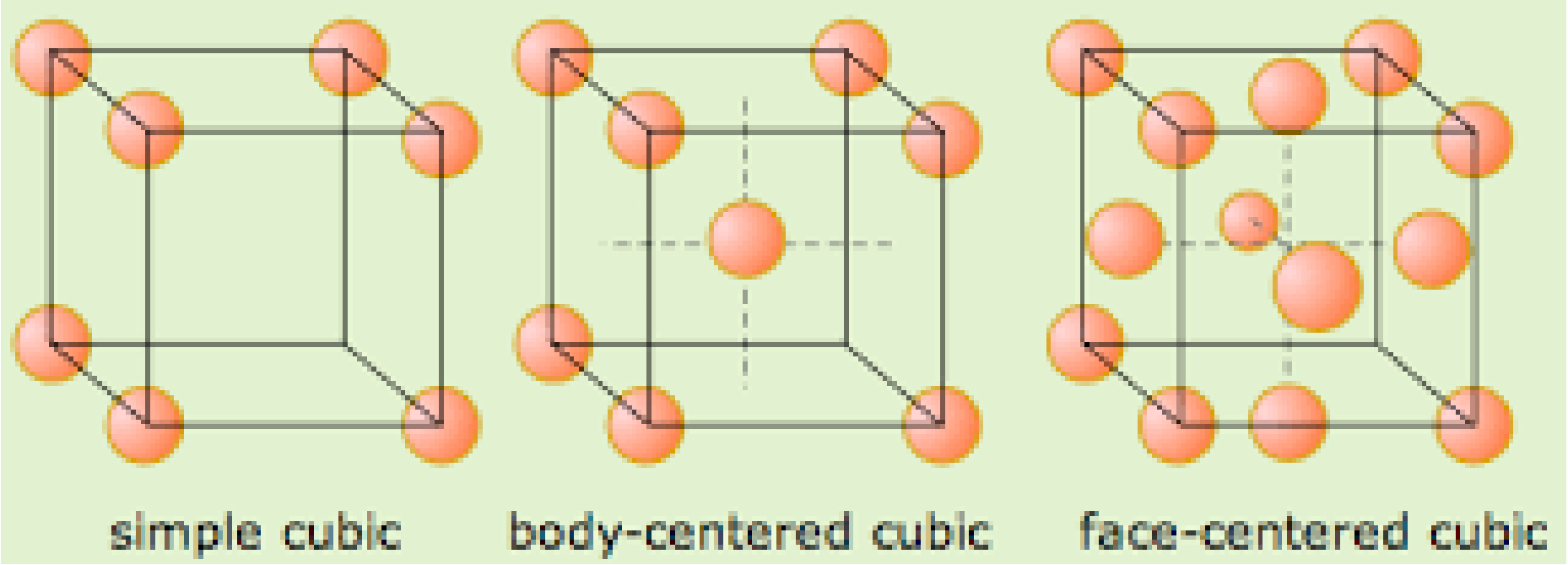
Q: FCC, or HCP?

- HCP and FCC are the densest way to pack equal-sized spheres in 3D space
  - J. Kepler's conjecture (开普勒猜想) in 1611
  - Everyone believes that it should be true, but no proof until ...
- T. Hales in Univ. Pittsburgh proved it in 1998

T. C. Hales, *Annals Math.* **162,** 1065 (2005)

Cubic Lattices

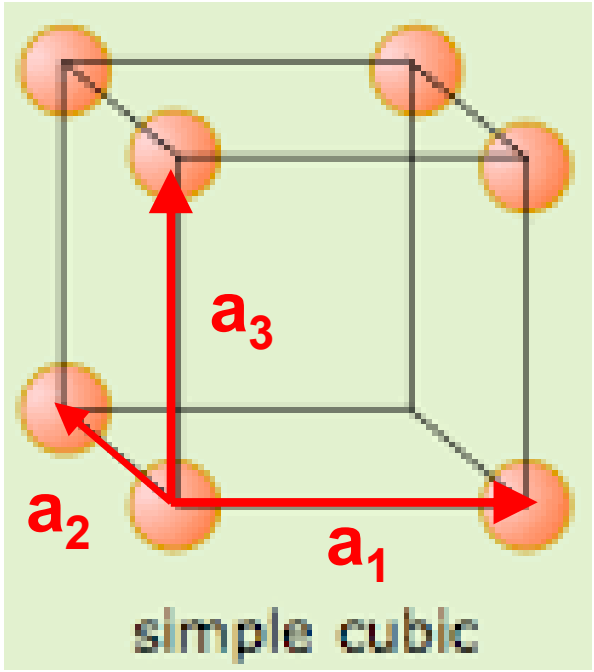
- These are *conventional cells* 惯用晶胞
- They are *not primitive cells* for BCC and FCC. *Why?*



简单立方 SC　　体心立方 BCC　　面心立方 FCC

Q: How to draw primitive cells for BCC and FCC?

A Primitive Cell for SC

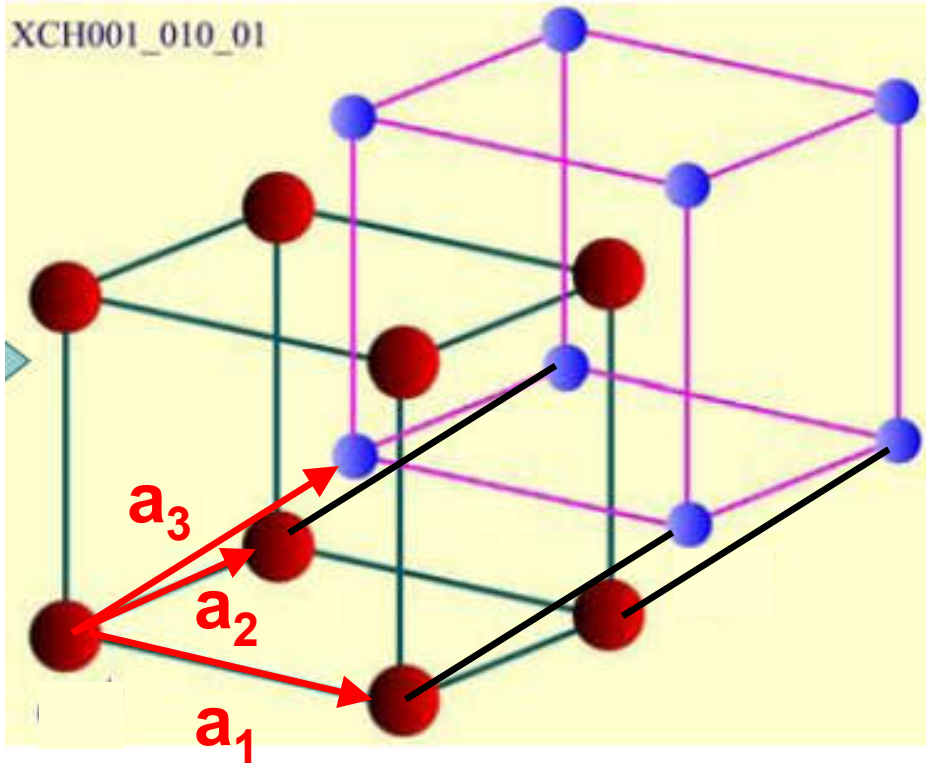


$$\mathbf{a}_1 = a\hat{\mathbf{x}}$$
$$\mathbf{a}_2 = a\hat{\mathbf{y}}$$
$$\mathbf{a}_3 = a\hat{\mathbf{z}}$$

$(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$ are Cartesian coordinates

The volume of this primitive cell = a^3

A Primitive Cell for BCC



$$\mathbf{a}_1 = a\hat{\mathbf{x}}$$

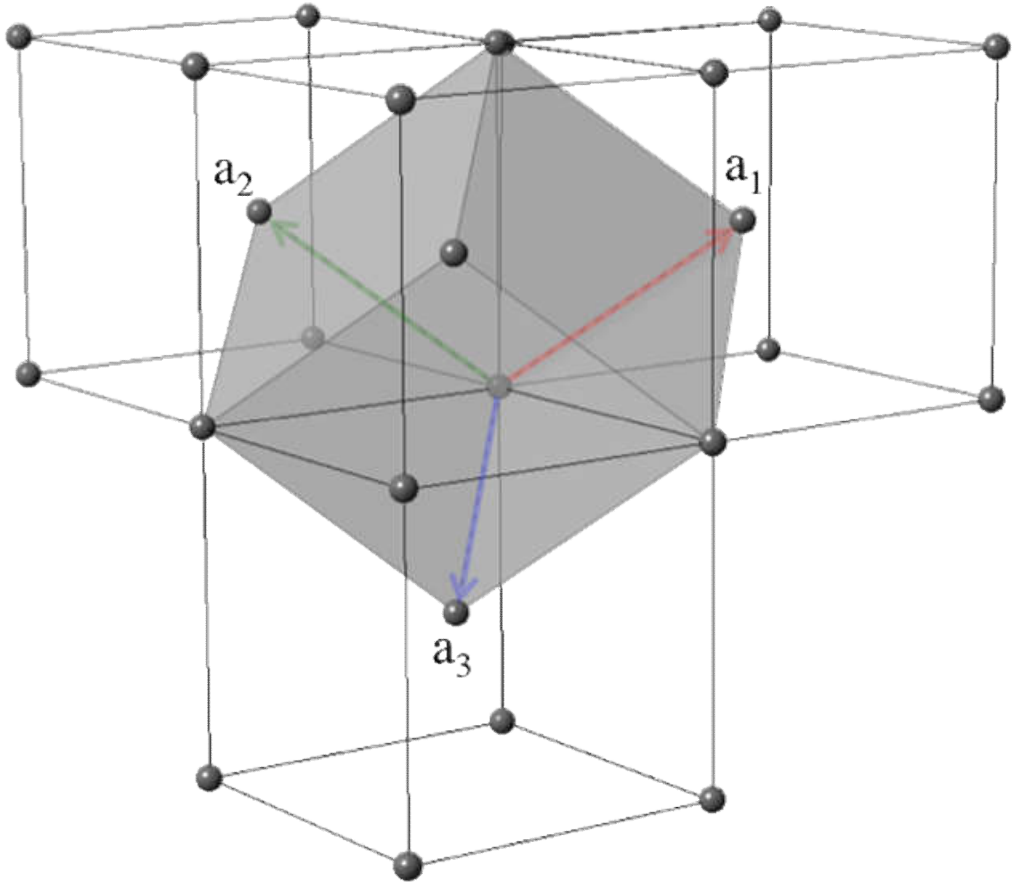
$$\mathbf{a}_2 = a\hat{\mathbf{y}}$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})$$

Q: What is the volume of the primitive cell?

Another Primitive Cell for BCC

a more symmetric one



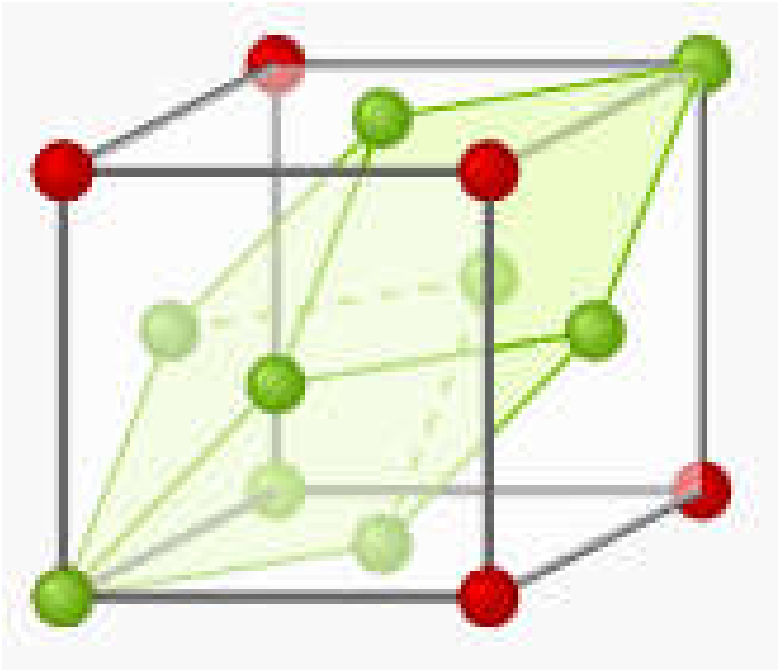
$$\mathbf{a}_1 = \frac{a}{2}\left(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{a}_2 = \frac{a}{2}\left(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}\right)$$

$$\mathbf{a}_3 = \frac{a}{2}\left(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}\right)$$

Q: What is the volume of the primitive cell?

A Primitive Cell for FCC



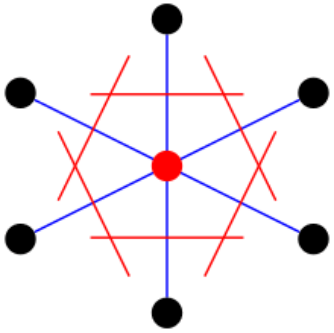
$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

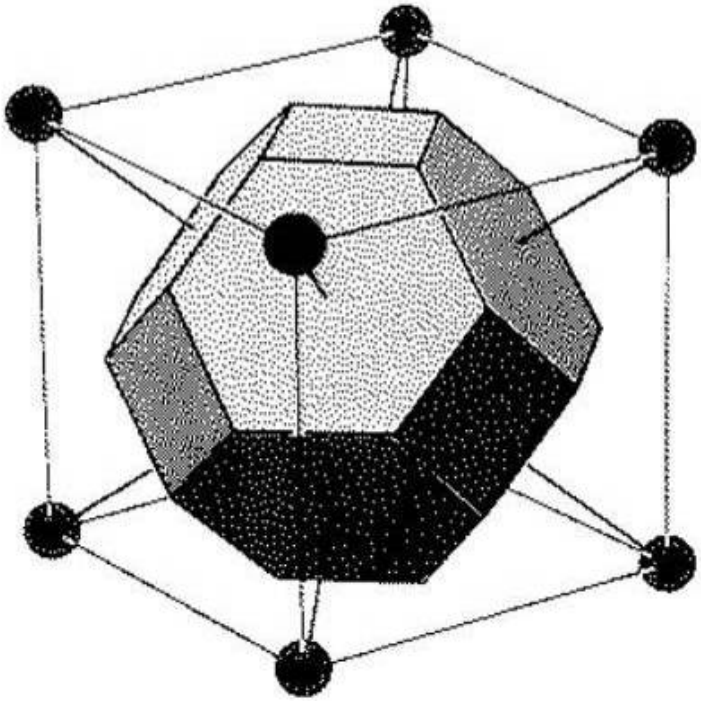
$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

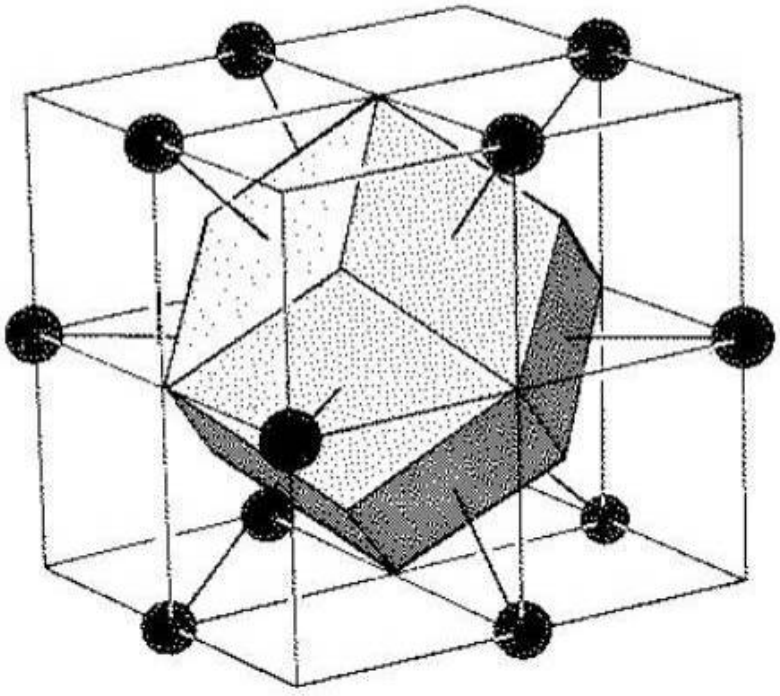
Q: What is the volume of the primitive cell?

Wigner-Seitz cells for BCC and FCC





体心立方 BCC

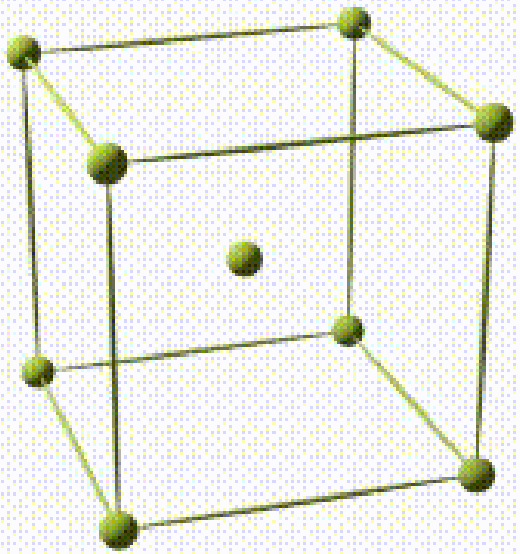


面心立方 FCC

Q: What is the volume of the Wigner-Seitz cell?

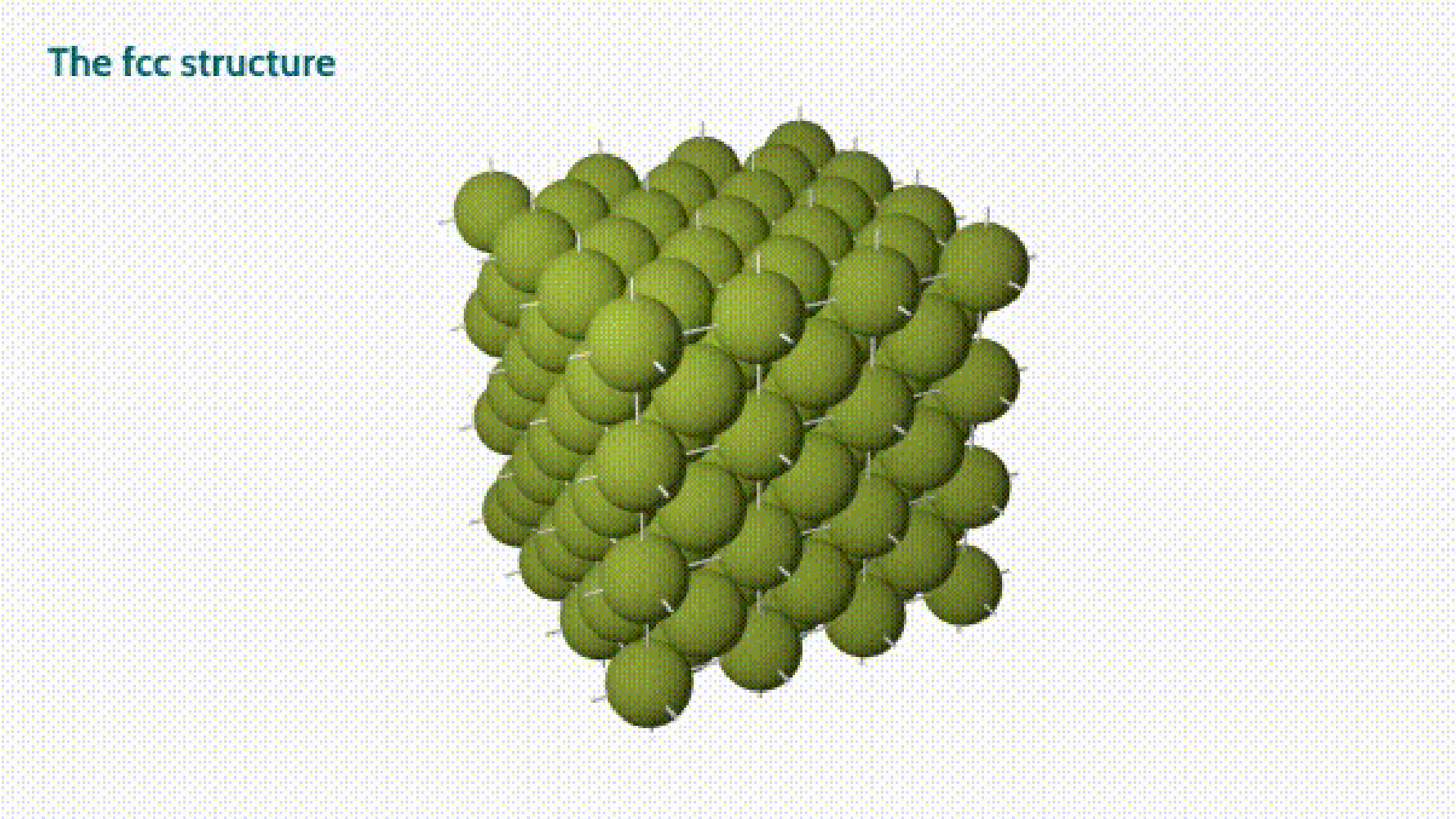
Review: BCC and FCC

The bcc structure



https://www.physics-in-a-nutshell.com/article/12/body-centered-cubic-bcc

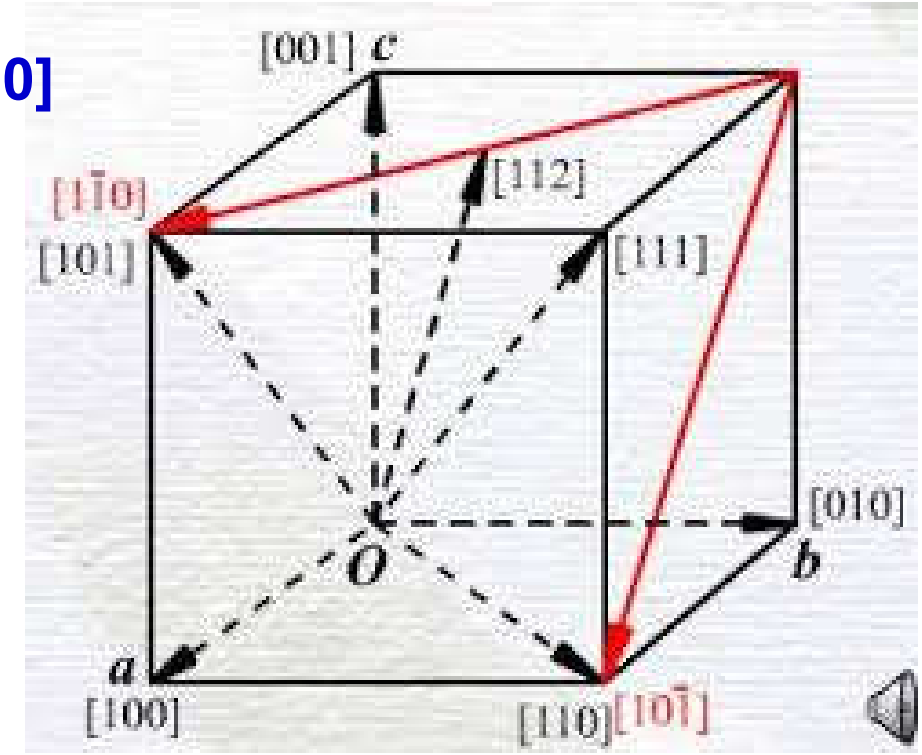
Review: BCC and FCC



https://www.physics-in-a-nutshell.com/article/11/close-packed-structures-fcc-and-hcp

Miller Indices - Direction 晶向

- crystal direction [*hkl*]
  - in cubic lattices, [*hkl*] direction ⊥ (*hkl*) plane
- <*hkl*>
  - a group of similar directions
  - <001> includes [001], [010], [100]

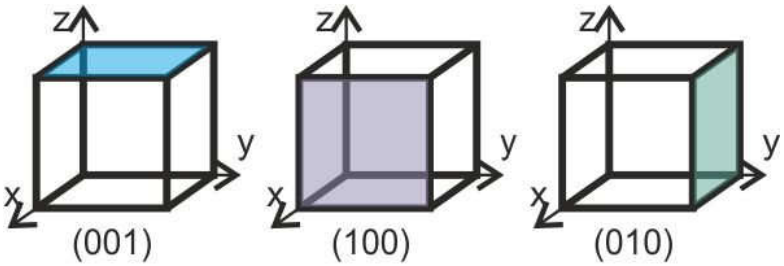


h, k, l **are integers with no common factors**

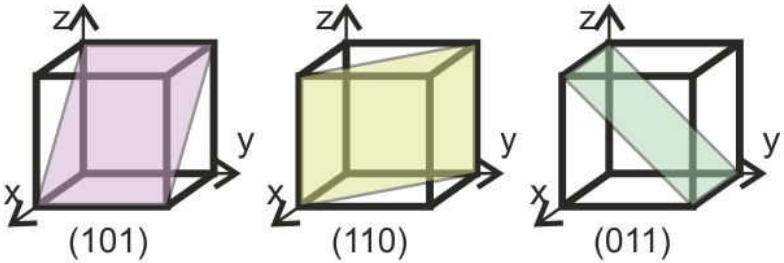
Miller Indices - Plane 晶面

- crystal plane (*hkl*)
  - intercepts at (a_1/h, a_2/k, a_3/l)
- {*hkl*}
  - a group of similar planes

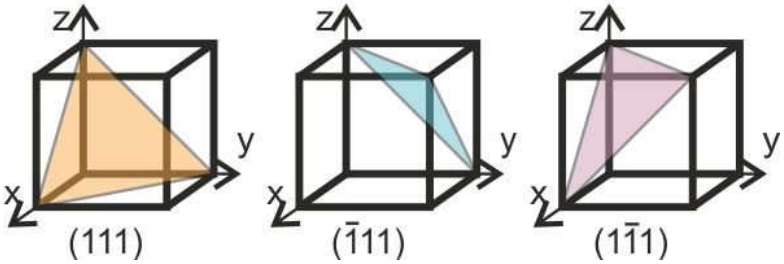
{001}



{011}



{111}



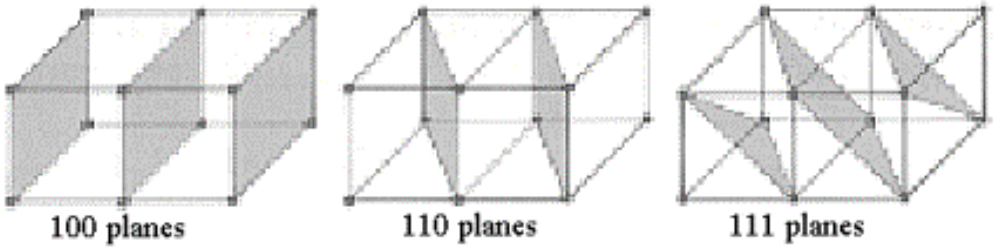
***h, k, l* are integers with no common factors**

Q: Draw planes: (120), (112), (131)

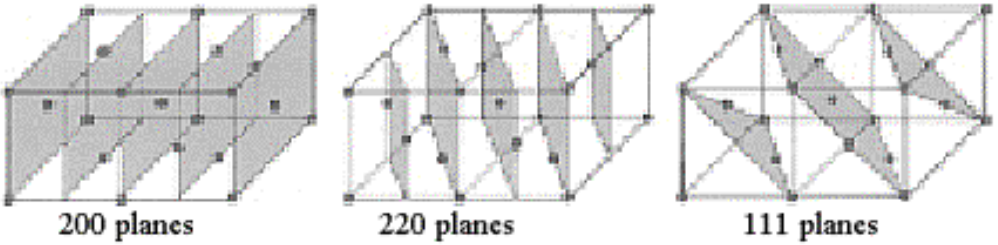
Lattice Plane 晶面

- any plane with at least 3 noncollinear Bravais lattice points
  - not always planes with Miller index, e.g., (200), (220), (222)

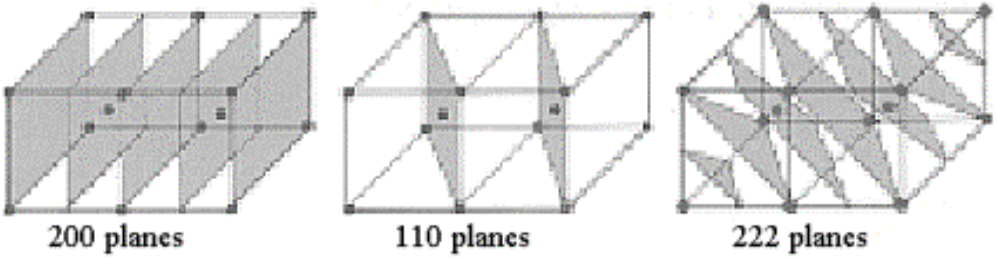
SC



FCC

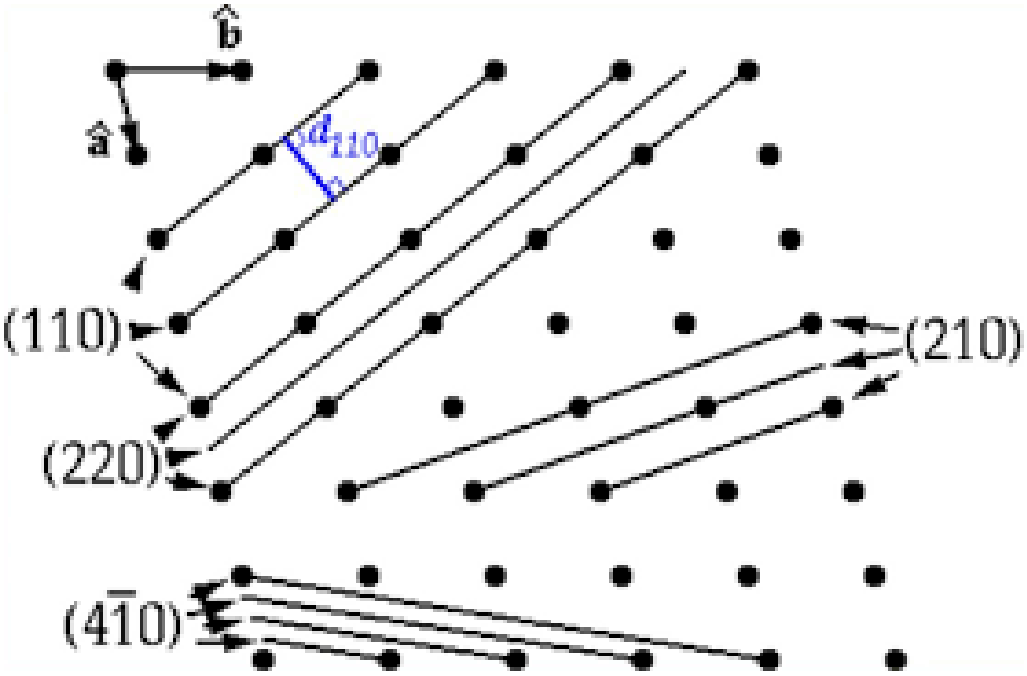


BCC



Interplanar Spacing 晶面间距

- **Distance between adjacent lattice planes**



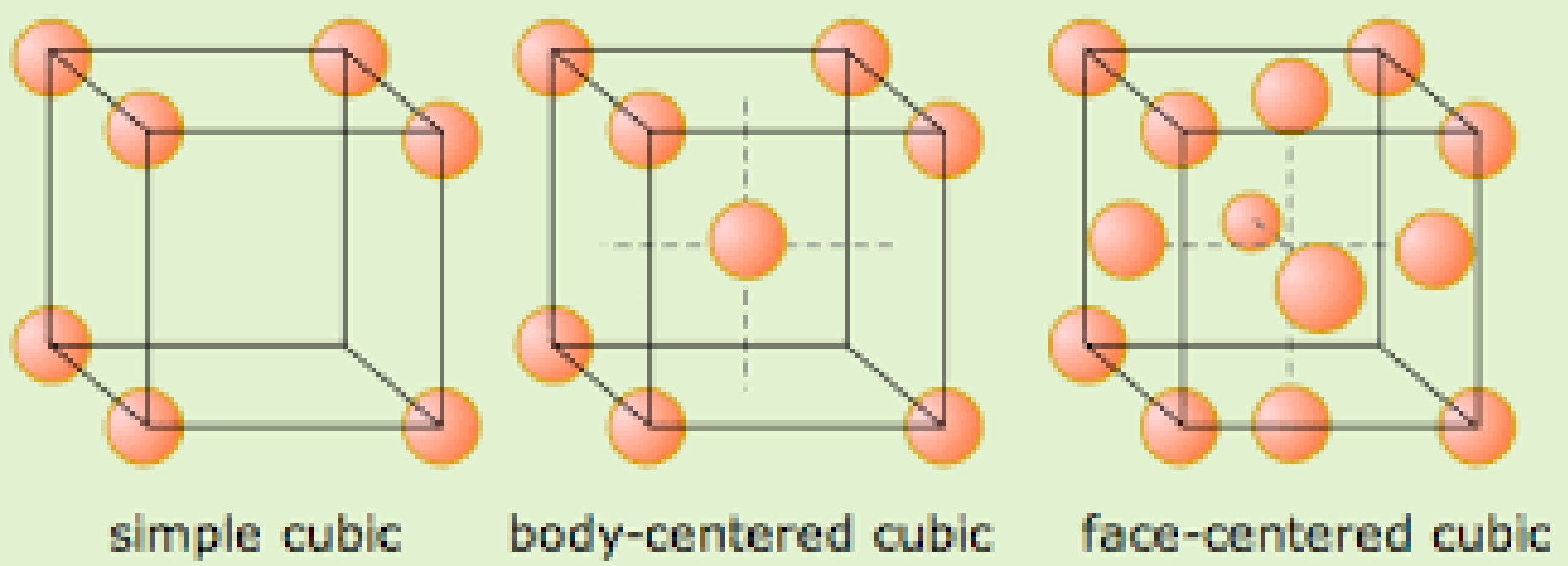
For cubic systems (SC, BCC, FCC)

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Q: Interplanar Spacing for (120), (112), (131)

Coordination Number 配位数

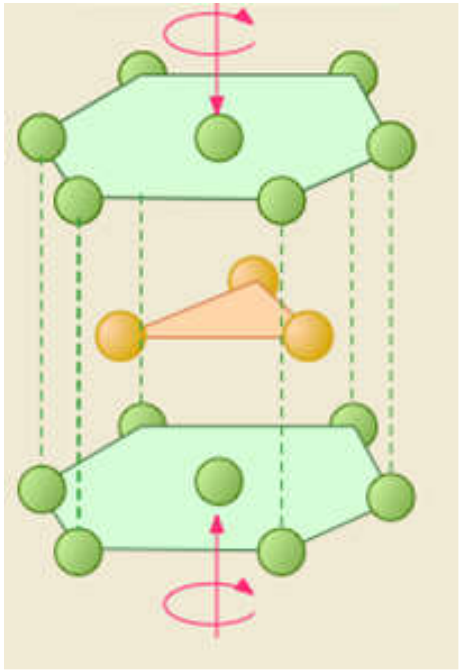
- The number of the nearest neighbors
  - 'kissing' number



简单立方 SC	体心立方 BCC	面心立方 FCC
6	8	12

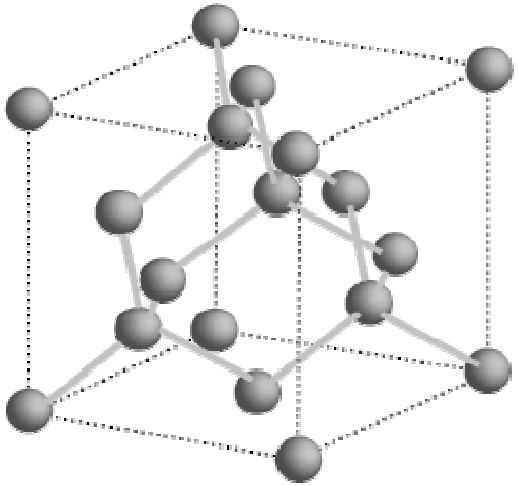
Coordination Number 配位数

- The number of the nearest neighbors
  - 'kissing' number



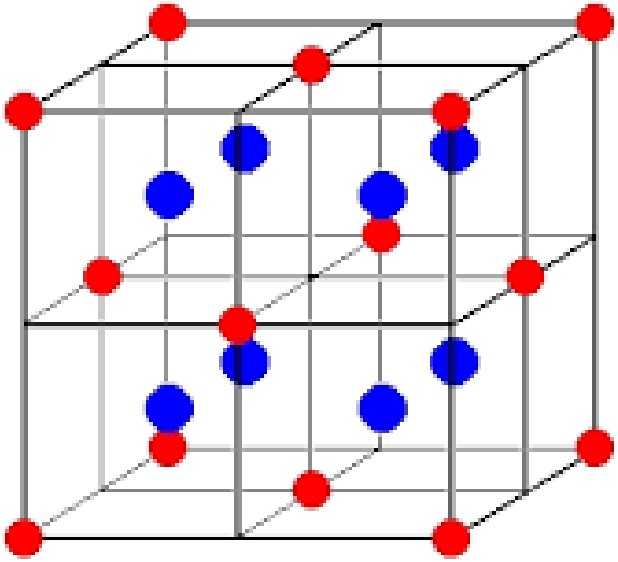
HCP

?



diamond

?



CaF_2

? and ?

Common Crystal Structures

- BCC, FCC, HCP

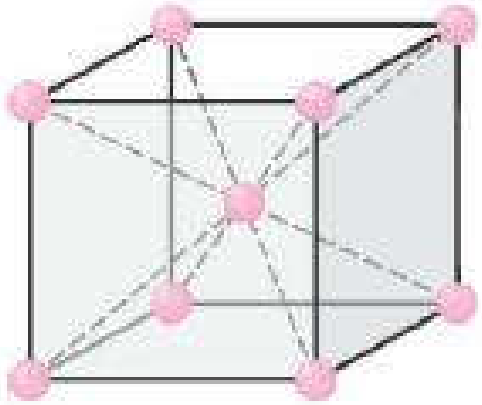
- Diamond 金刚石
  - C, Si, Ge
- Zinc Blende 闪锌矿
  - GaAs, InP, ZnS
- Halite / Rock Salt 岩盐
  - NaCl, KCl
- CsCl

- Fluorite 萤石
  - CaF_2
- Wurtzite 纤锌矿
  - GaN, ZnO
- Perovskite 钙钛矿
  - $CaTiO_3$, $CsPbBr_3$

- 1D, 2D structures
- ...

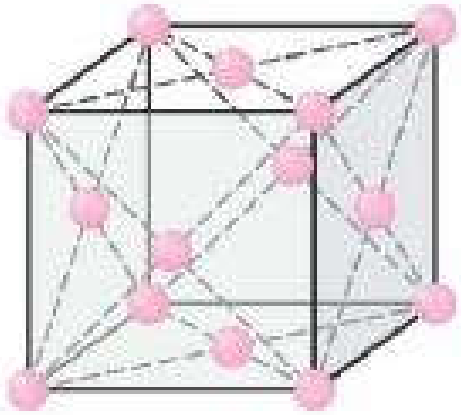
BCC, FCC, HCP

Li, Na, Cr, ...



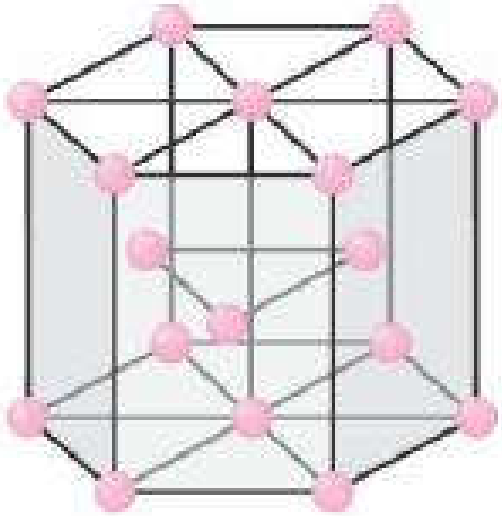
BCC

Al, Cu, Au, ...



FCC

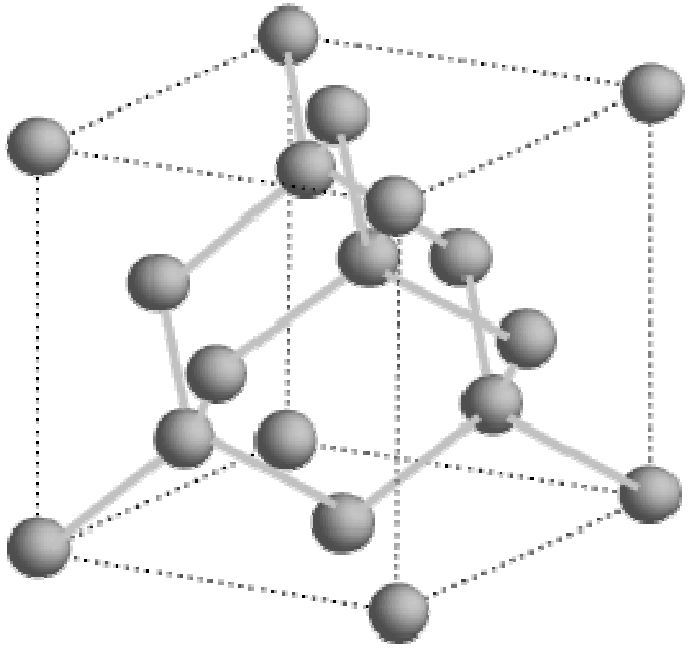
Mg, Zn, Ti, ...



HCP

Diamond Structure

- C, Si, Ge, ...



a

					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

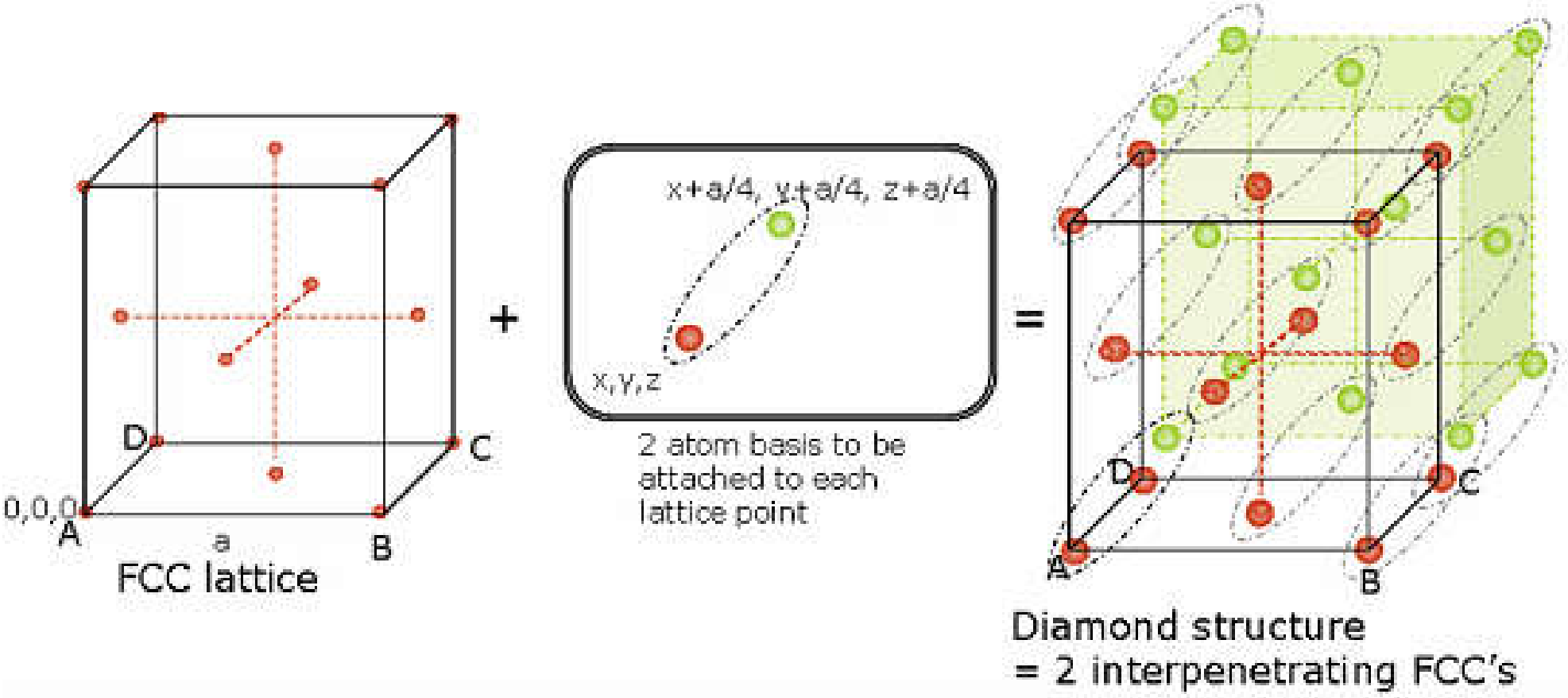
lattice parameters for diamond structures

	a (Å)
C (diamond)	3.57
Si	5.43
Ge	5.66
α-Sn	6.49

Q:
What is the Bravais lattice?
What is the atomic distance?
How many atoms in the cubic cell?
What is the APF?

Diamond Structure

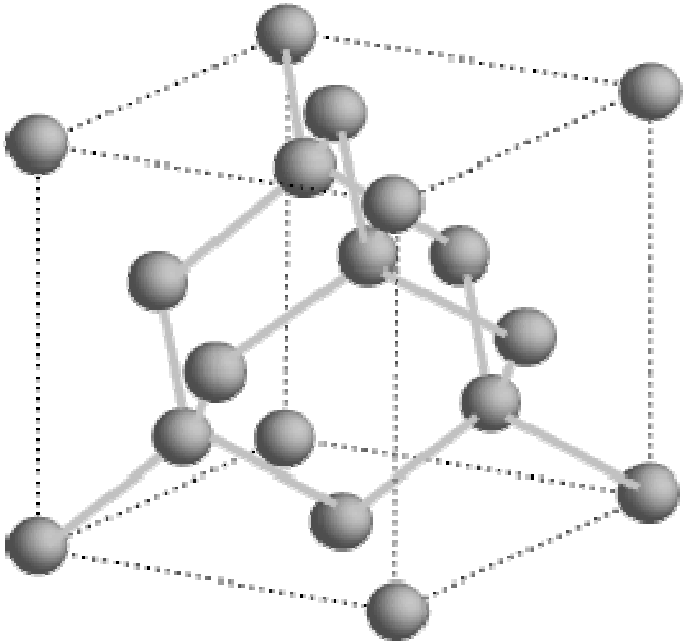
- C, Si, Ge, ...

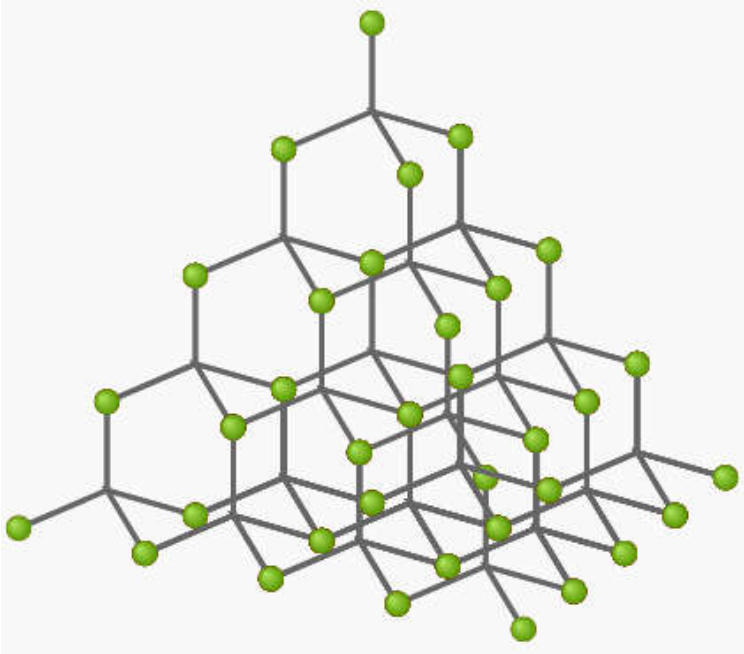


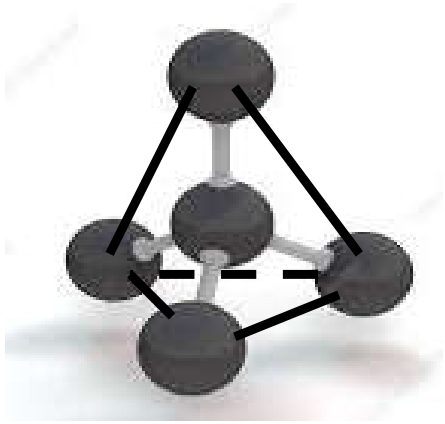
Lattice **Basis** **Crystal**

Diamond Structure

- C, Si, Ge, ...



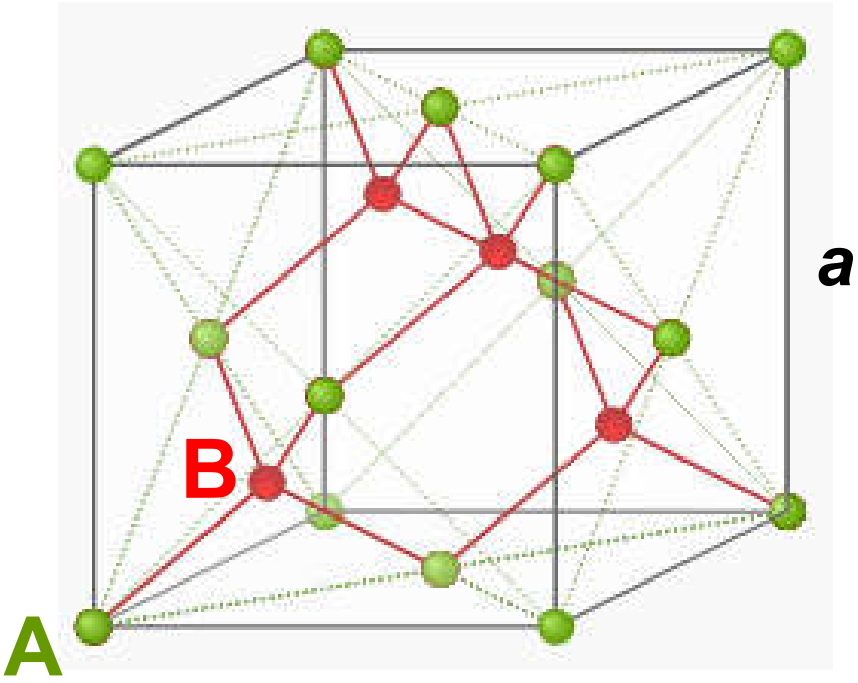




tetrahedron
(正四面体)

Zinc Blende 闪锌矿

- GaAs, InP, ZnS, ...

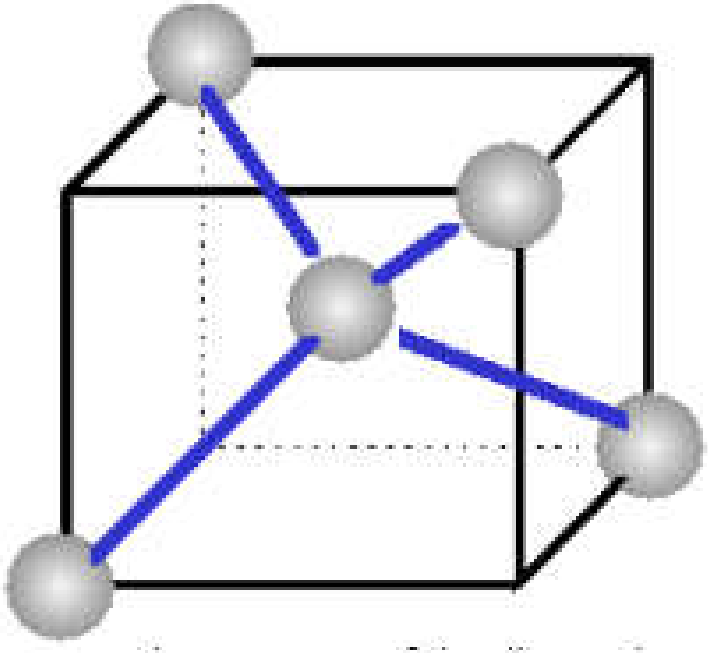


					2 He
5 B	6 C	7 N	8 O	9 F	10 Ne
13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn

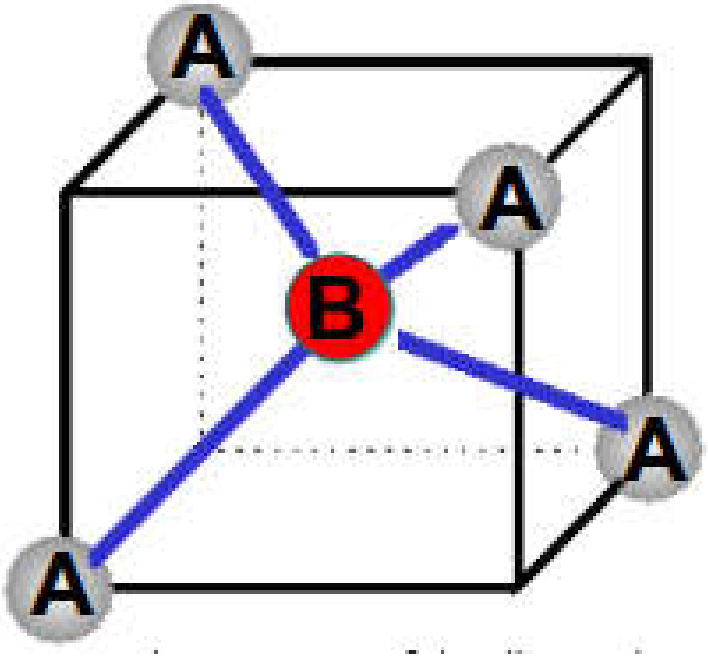
Q:
How many A and B atoms in the cubic cell?

Diamond vs. Zinc Blende

- FCC lattice



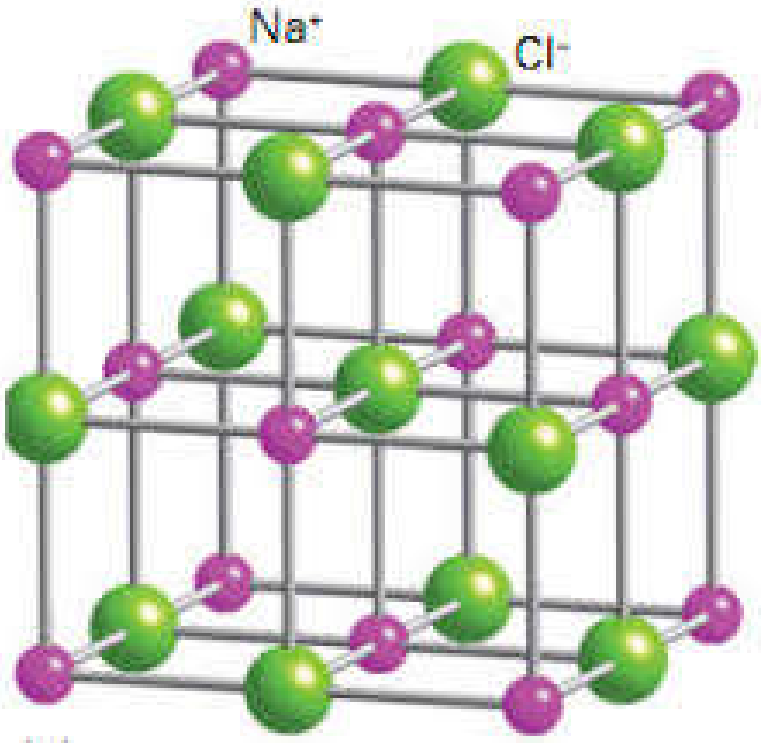
Si

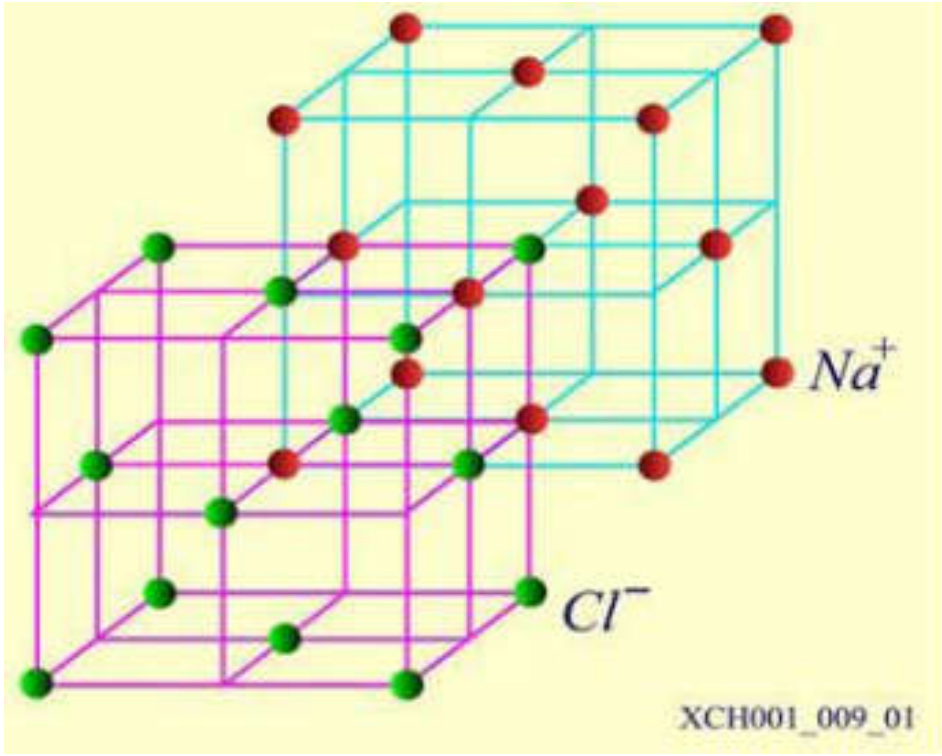


GaAs

Halite / Rock Salt 岩盐

- NaCl, ...

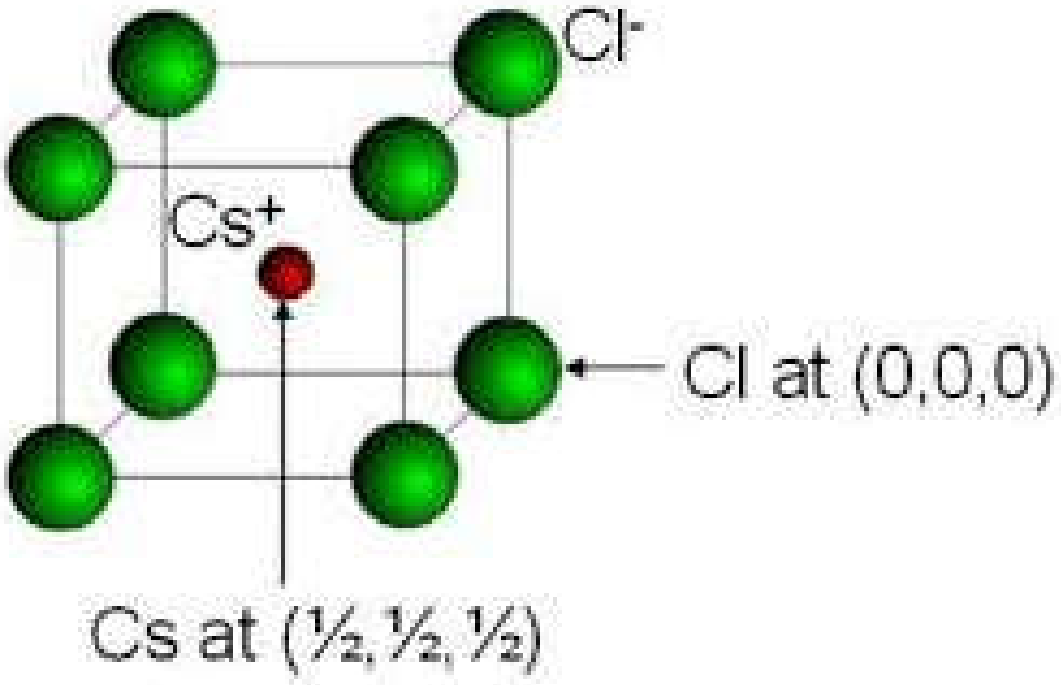


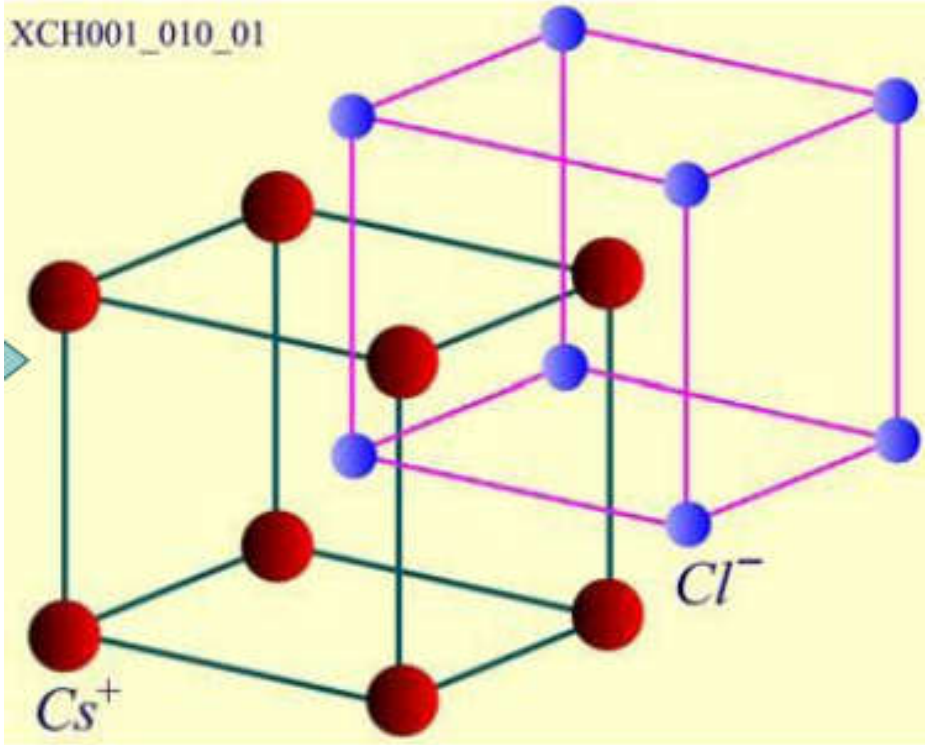


Q:
What is the Bravais lattice?
How many A and B atoms in the cubic cell?

CsCl

- **CsCl, ...**

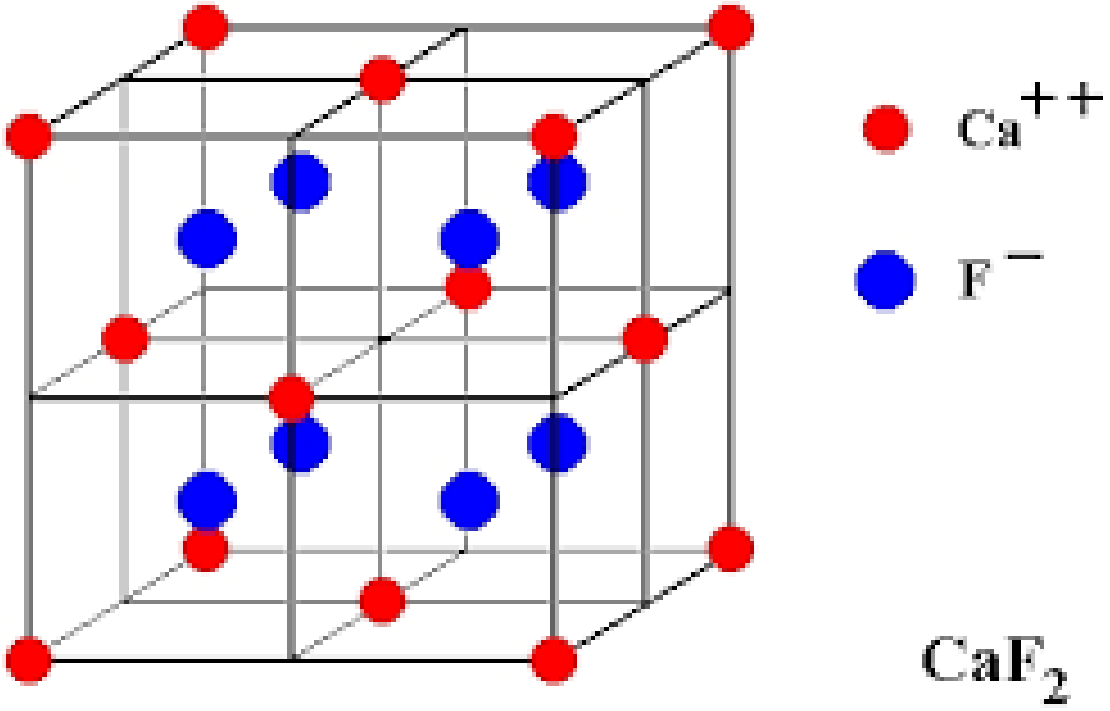




Q:
What is the Bravais lattice?
How many A and B atoms in the cubic cell?

Fluorite 萤石

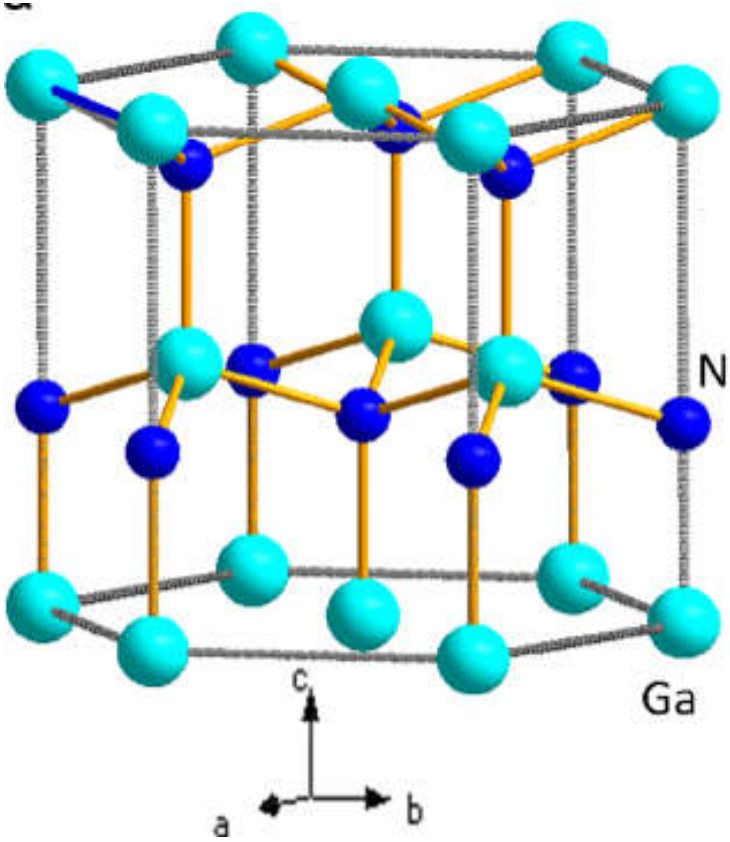
- CaF_2, ...

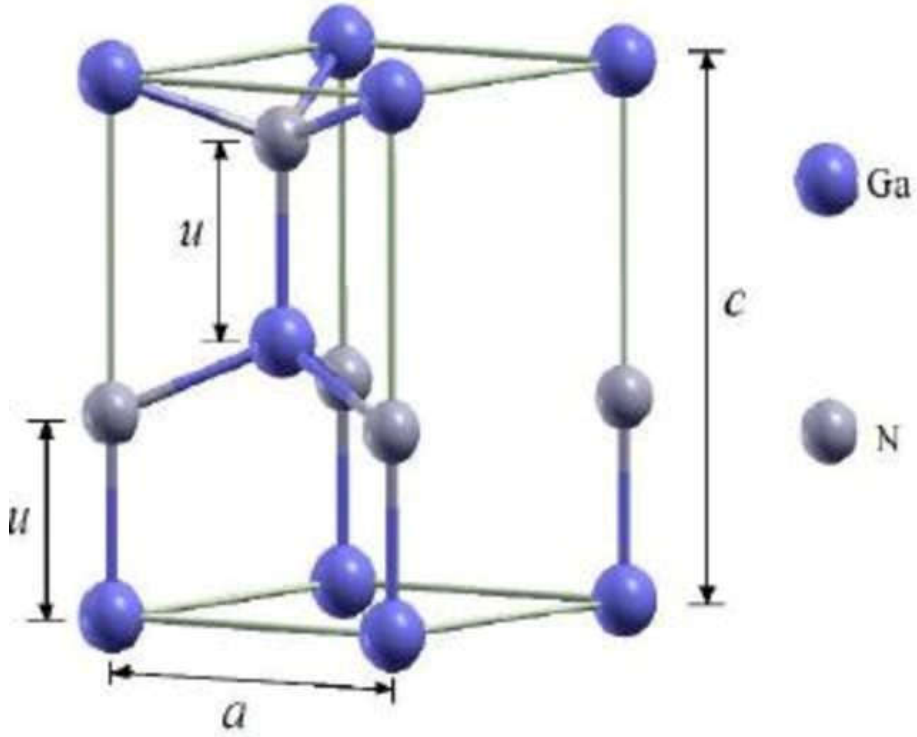


Q:
What is the Bravais lattice?
How many Ca and F atoms in the cubic cell?

Wurtzite 纤锌矿

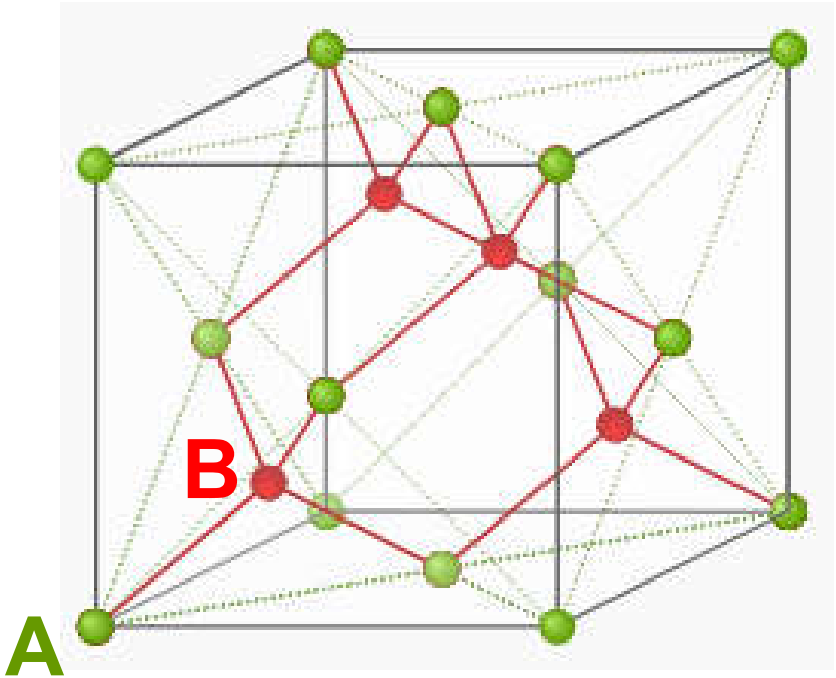
- GaN, ZnO, ...

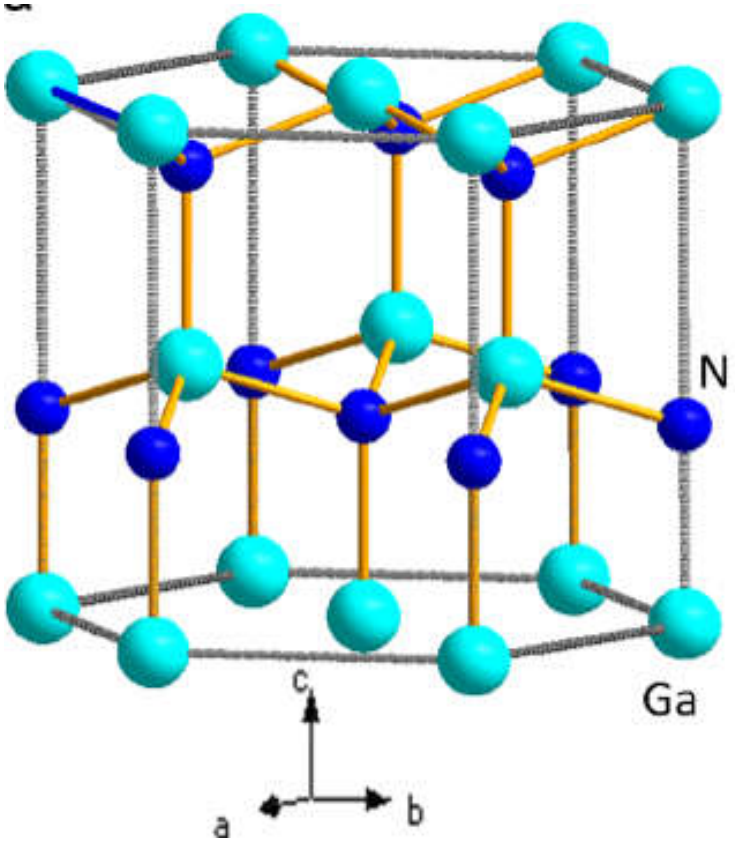




Allotrope 同素异构体

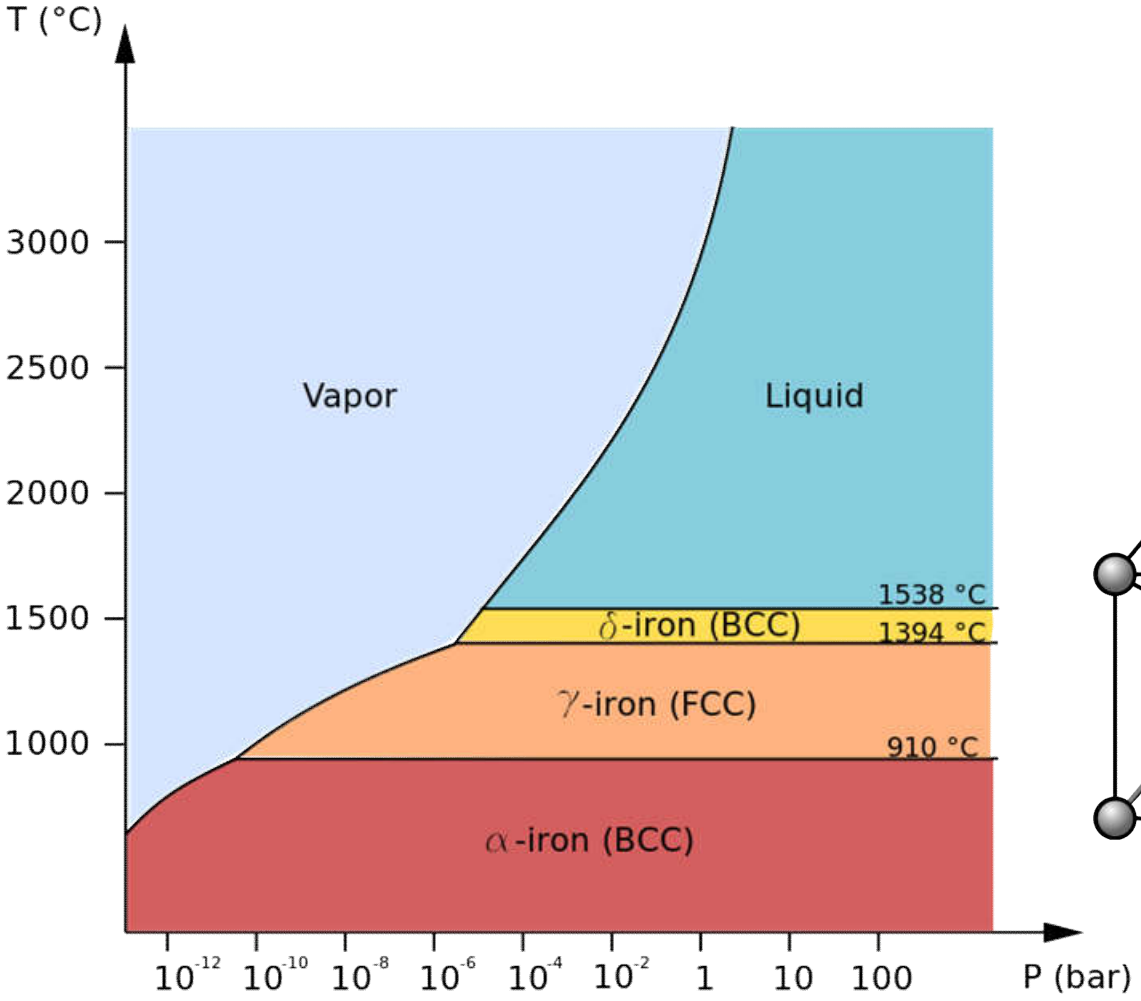
- ZnO can have Zinc Blende or Wurtzite structures

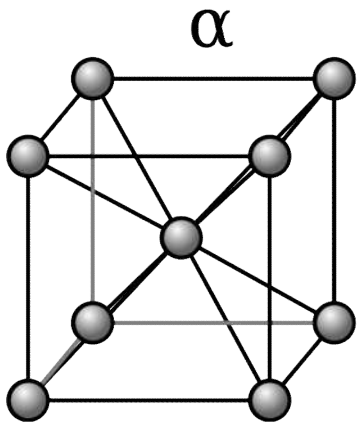


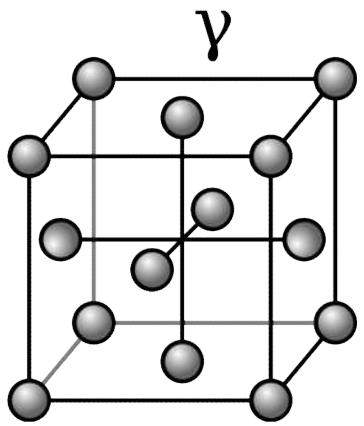


Allotrope 同素异构体

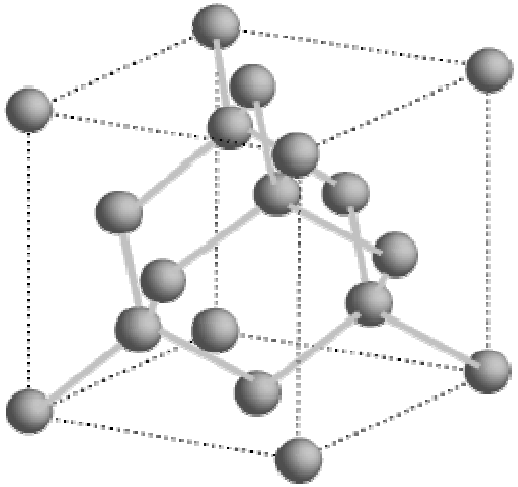
- Fe can have BCC or FCC structures

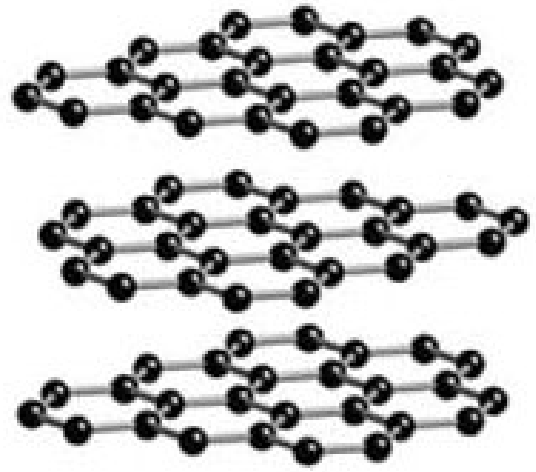


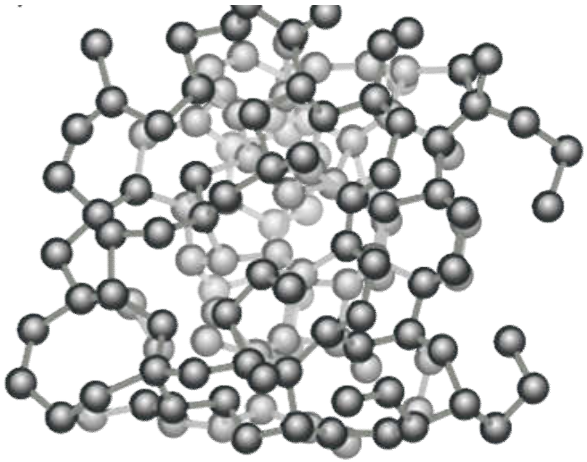




Allotropes for Carbon







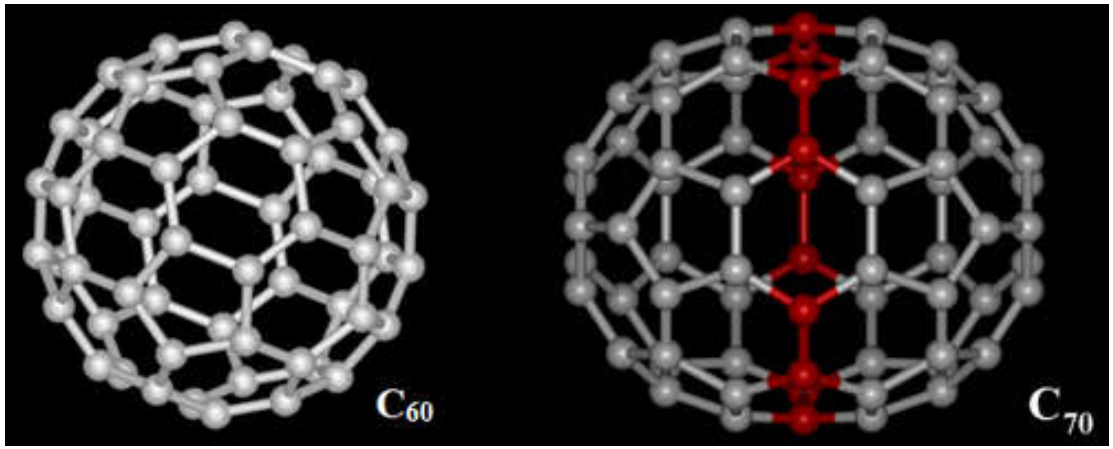
diamond

graphite

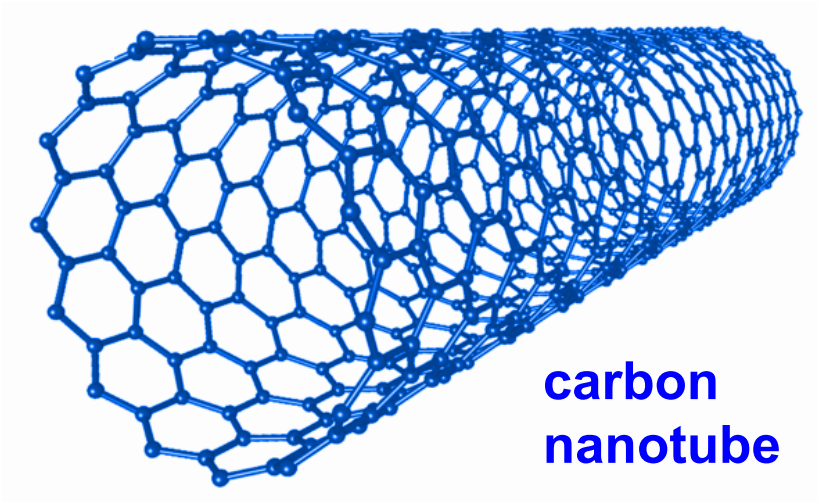
amorphous carbon

Q: which one is electrically conductive, diamond or graphite?

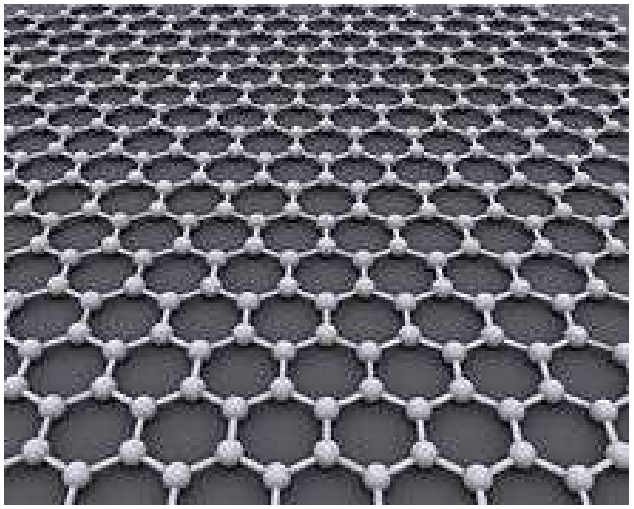
Allotropes for Carbon



H. Kroto, R. Curl, R. Smalley
1996 Nobel Prize in Chemistry



S. Iijima, *Nature* **354,** 56 (1991)

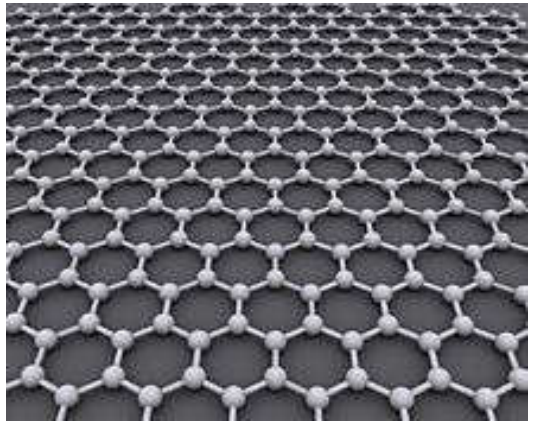


graphene

A. Geim, K. Novoselov
2010 Nobel Prize in Physics

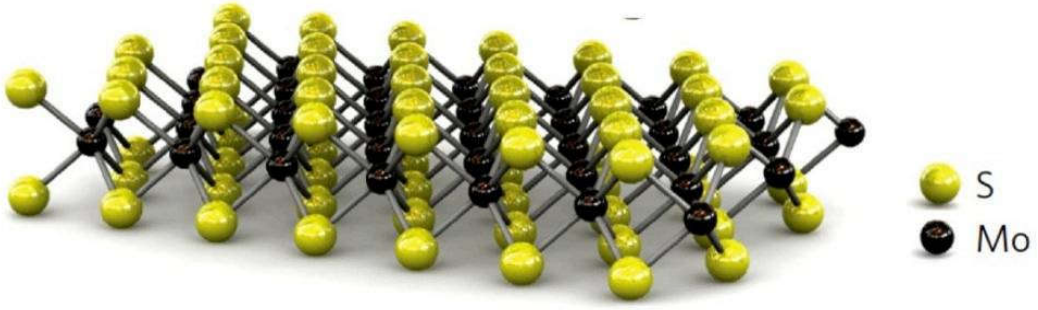
2D Materials

- **Single atomic layer crystal**

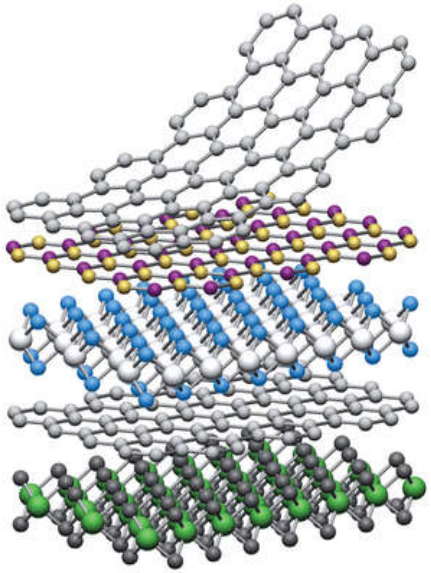


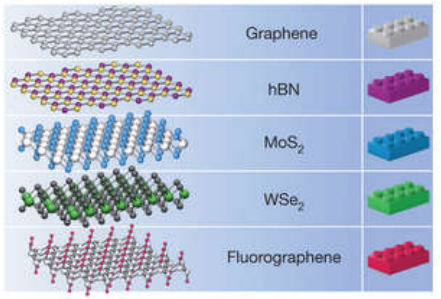
graphene

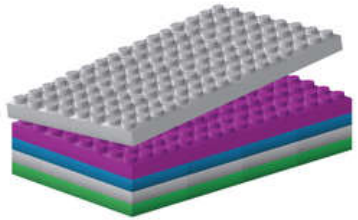
A. Geim, K. Novoselov
2010 Nobel Prize in Physics



Transition metal dichalcogenide (TMDC)
MoS_2, WSe_2, ...







Materials are Imperfect

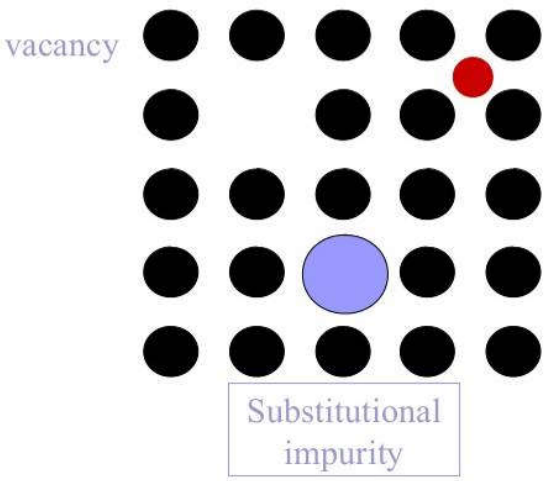
"Crystals are like people, it is the defects in them which tend to make them interesting. "

---- Colin Humphreys

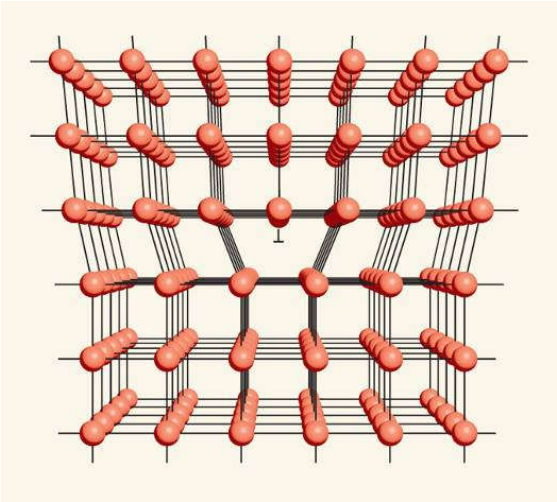
- Defects
  - 0D, 1D, 2D, 3D
- Crystallinity
  - Single Crystal, Polycrystal, Amorphous
  - Quasi-Crystal
  - Liquid Crystal

Defects in Crystals 缺陷

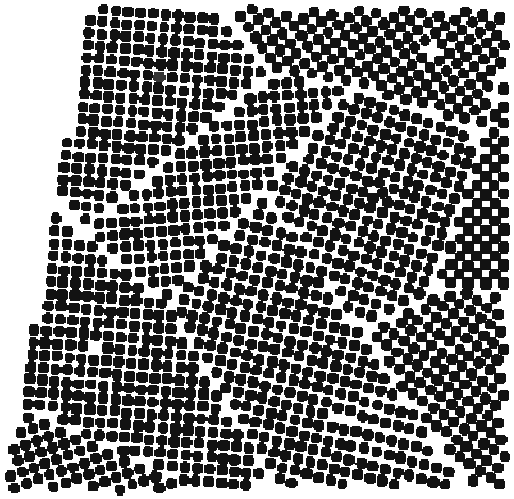
- 0D point defect 点缺陷
- 1D line defect 线缺陷
- 2D plane defect 面缺陷
- 3D volume defect 体缺陷



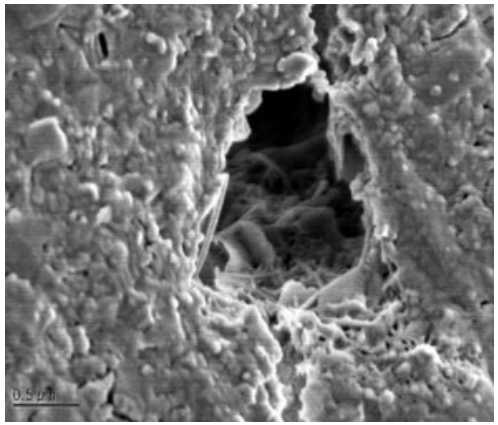
0D
point defect



1D
dislocation

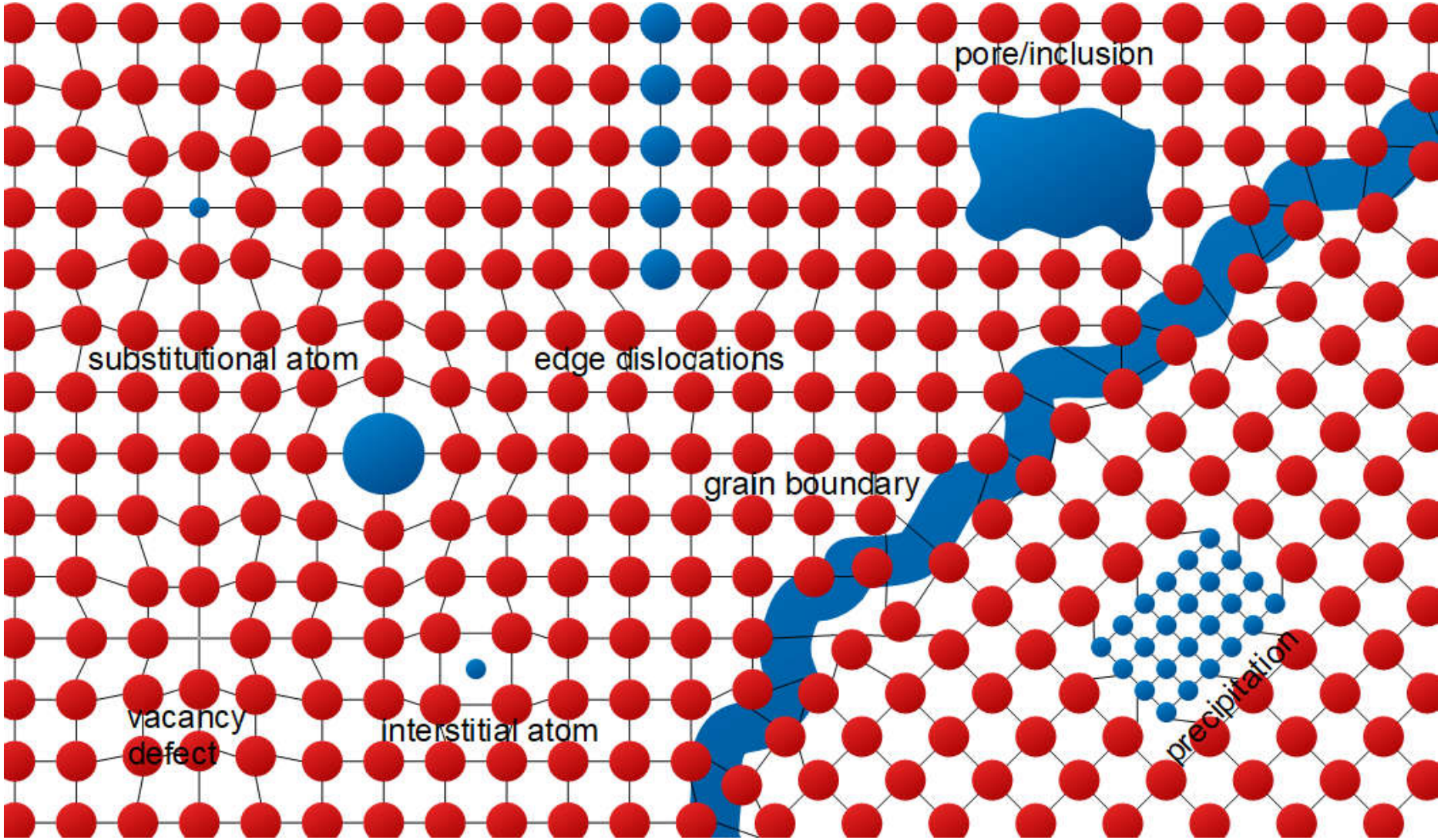


2D
grain boundary



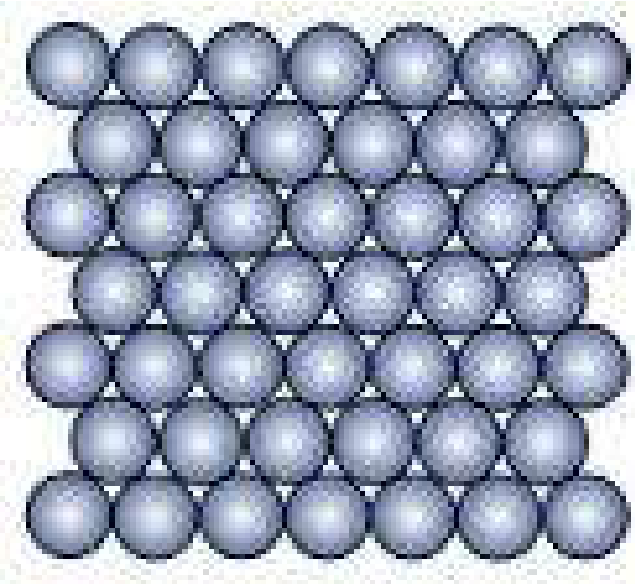
3D
void / precipitate

Defects in Crystals 缺陷

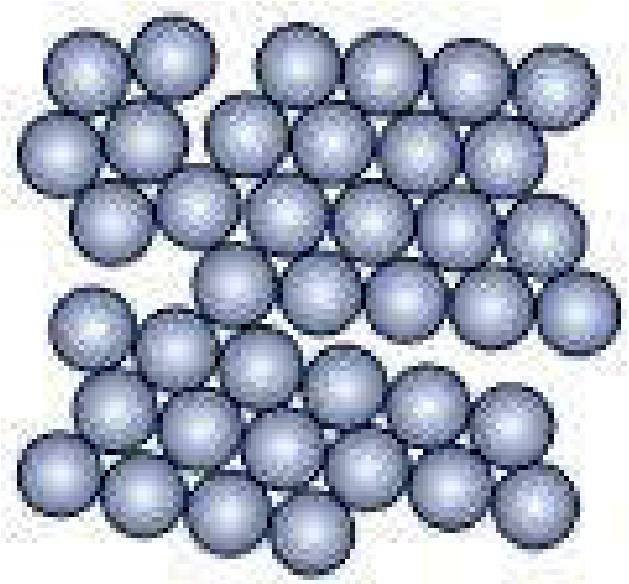


https://www.tec-science.com/material-science/structure-of-metals/crystallographic-defects/

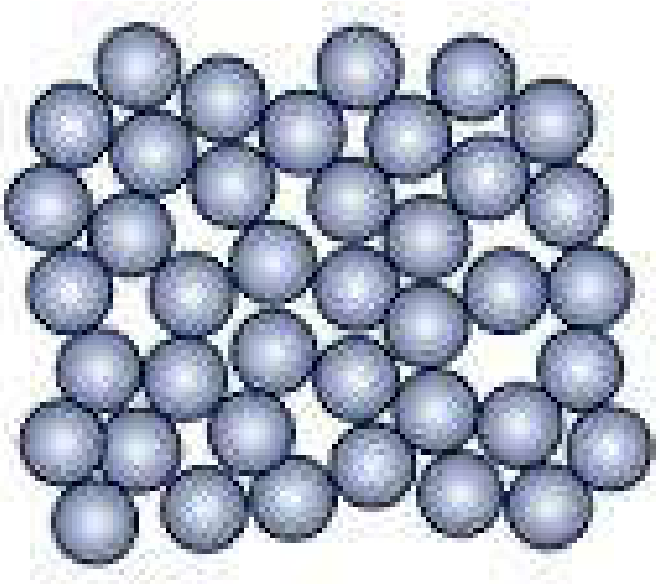
Crystallinity



single crystalline
monocrystalline
单晶

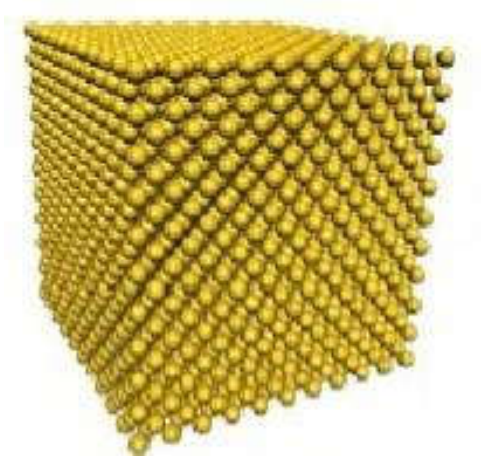


polycrystalline
multicrystalline
多晶



amorphous
非晶

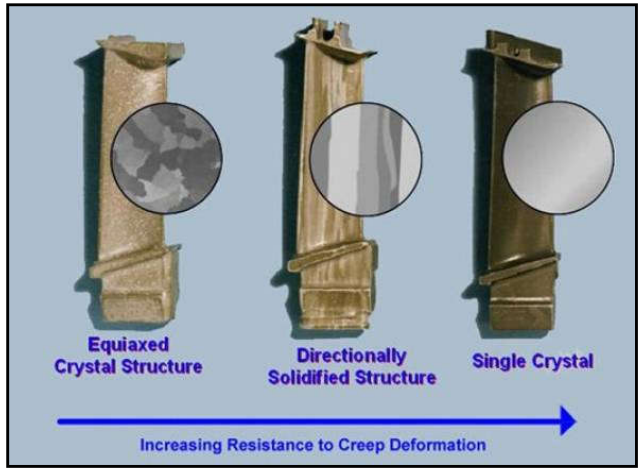
Single Crystal / Mono Crystal



Quartz

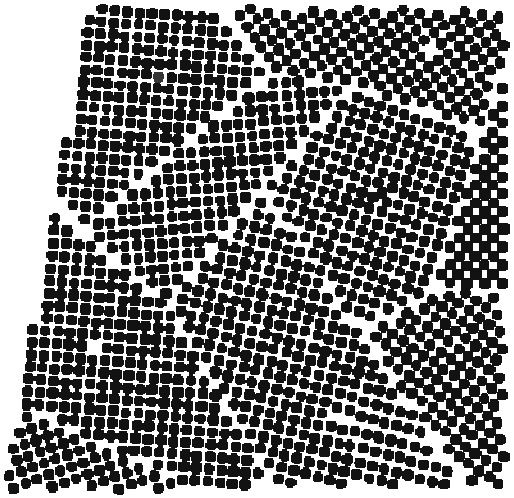
Sugar

Silicon wafers,
GaAs, GaN, sapphire, ...

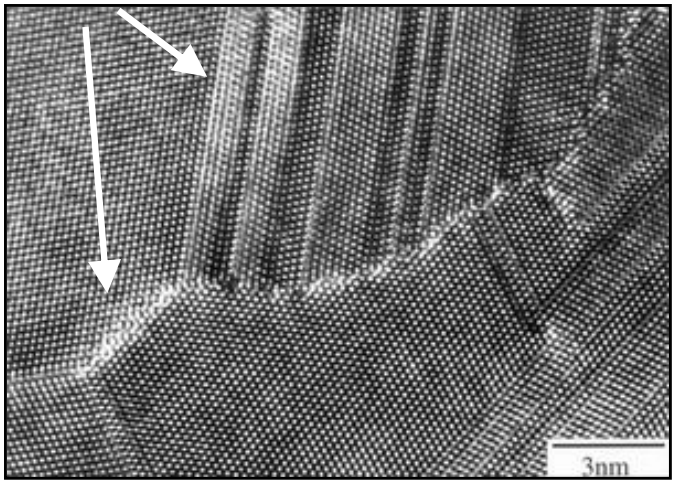


turbine blade

Polycrystal / Multicrystal



grain boundary



polycrystalline silicon

Poly-Crystalline
Solar Cell

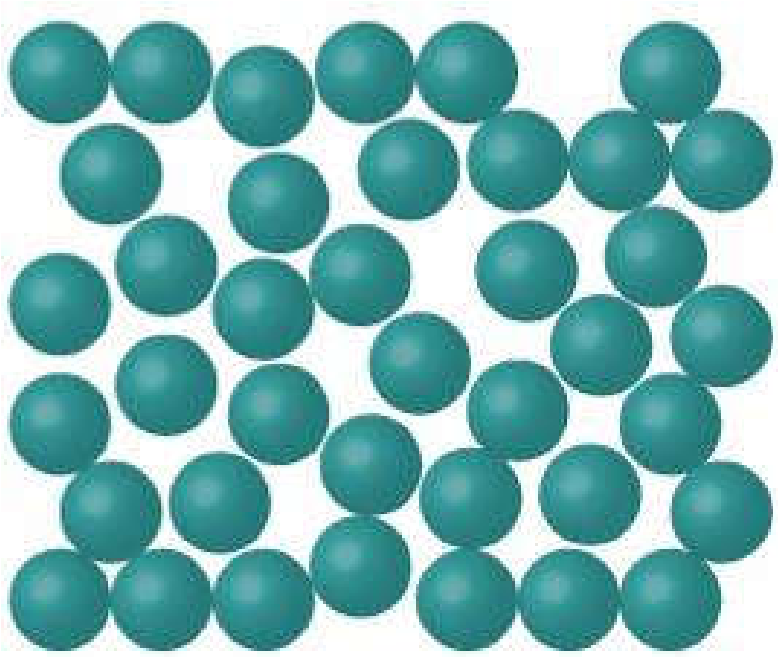
Mono-Crystalline
Solar Cell

metals

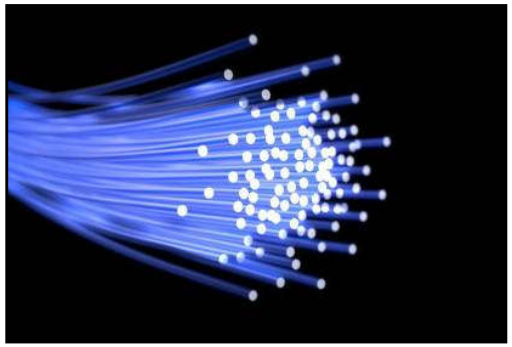
ceramics

Amorphous Materials

- **Defects are everywhere ...**



Amorphous



silica fiber

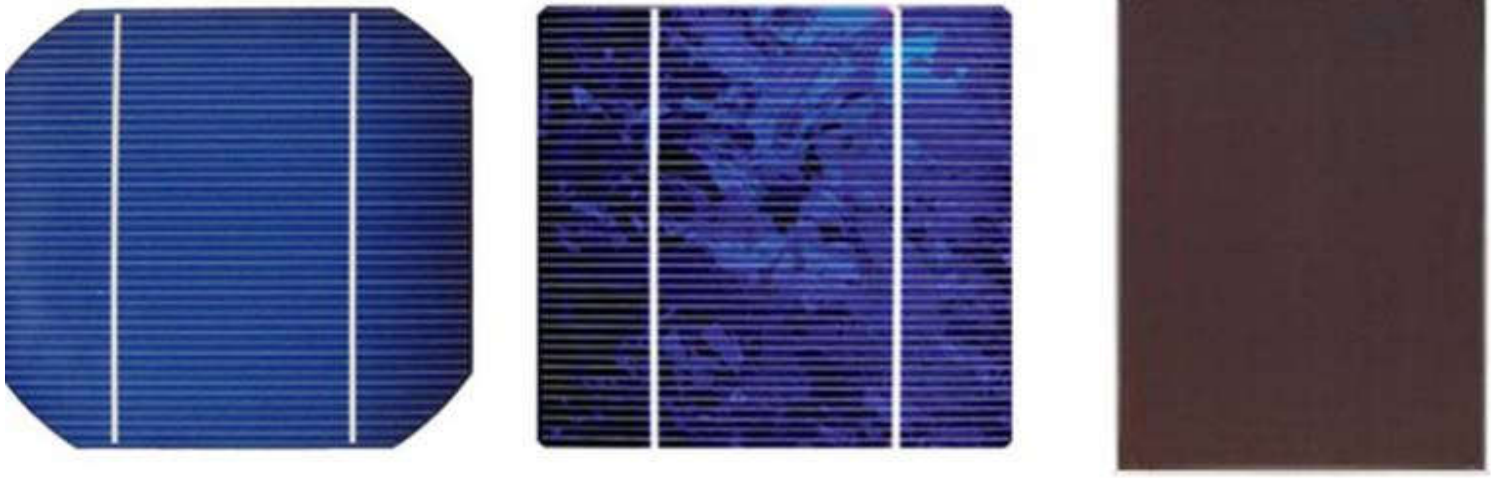
glass

plastics

Crystallinity

Silicon Solar Cells

Monocrystalline **Polycrystalline** **Amorphous**



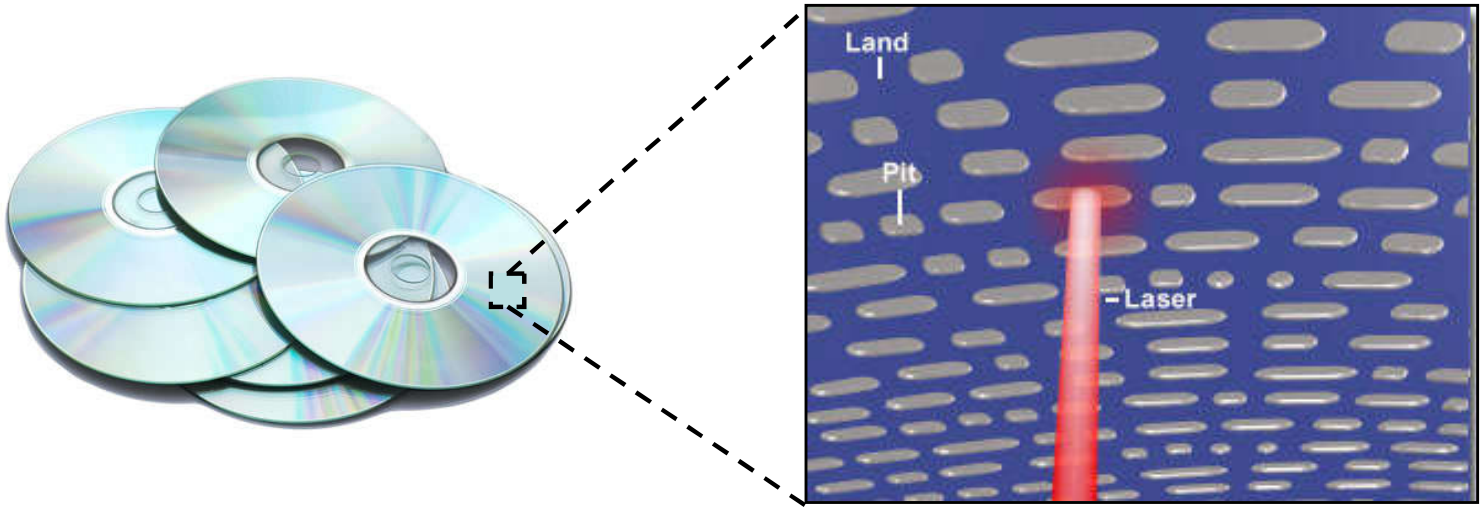
temperature

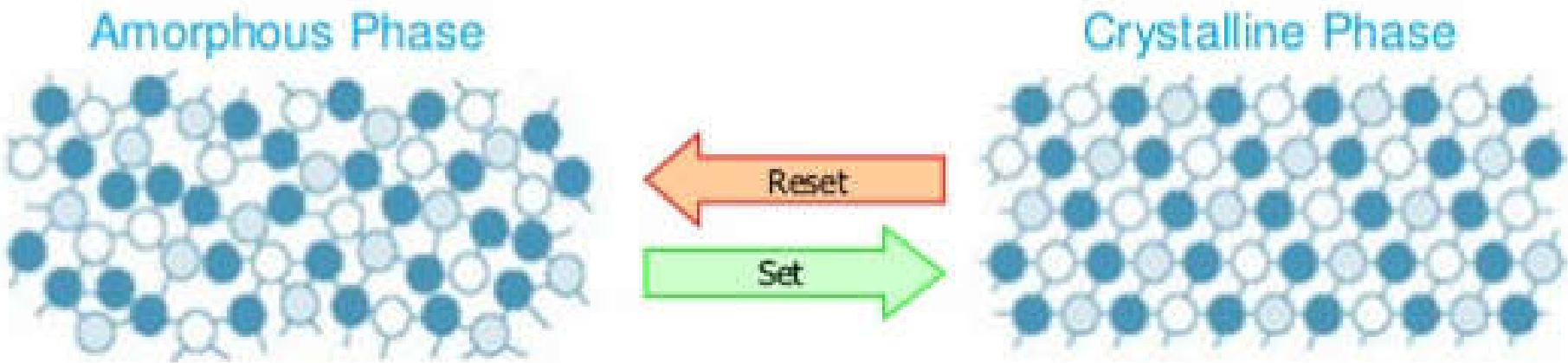
efficiency

price

Optical Disc

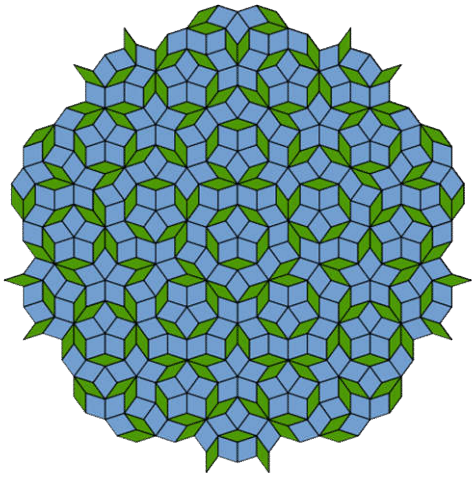
- **Phase Change Memory**



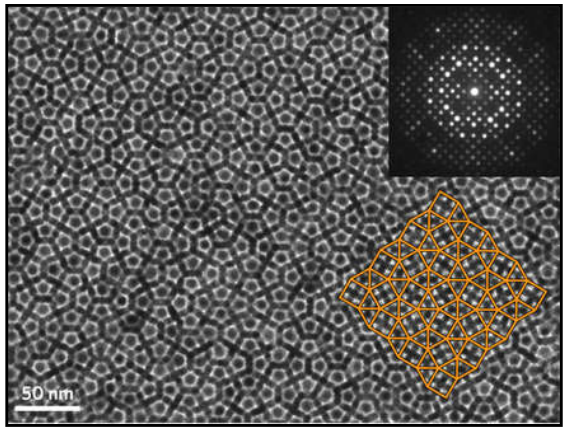


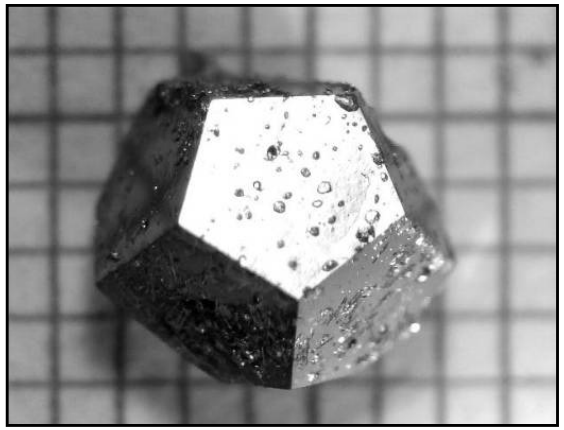
Quasi-Crystal 准晶

- Neither crystalline nor amorphous
  - 5, 8, 10, or 12-fold rotational symmetry
  - no translational symmetry



Penrose tiling

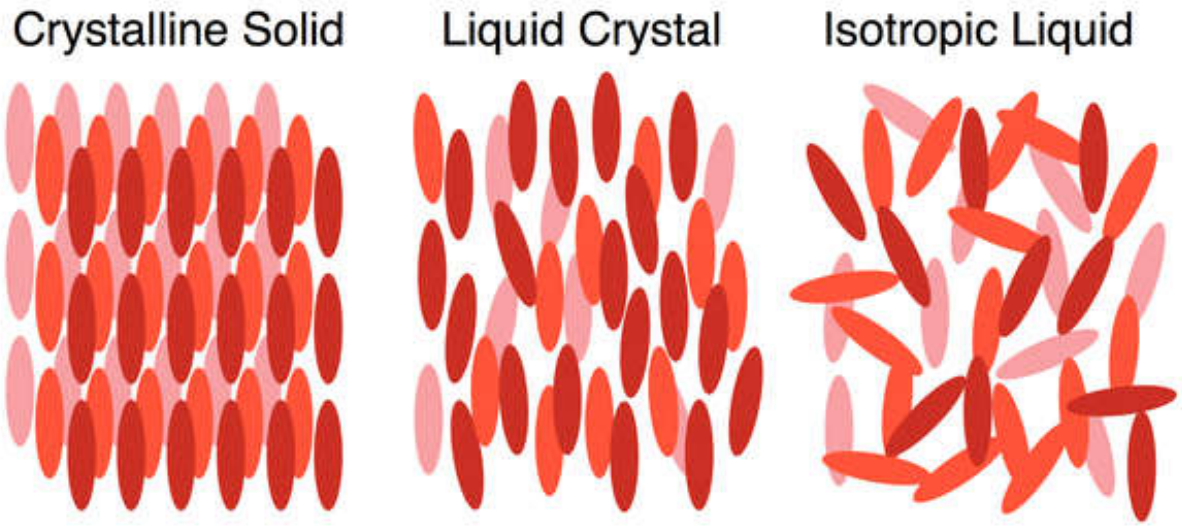




A Ho-Mg-Zn quasicrystal

D. Shechtman
2011 Nobel Prize in Chemistry

Liquid Crystals 液晶



Liquid crystal display (LCD)

P. de Gennes
1991 Nobel Prize in Physics

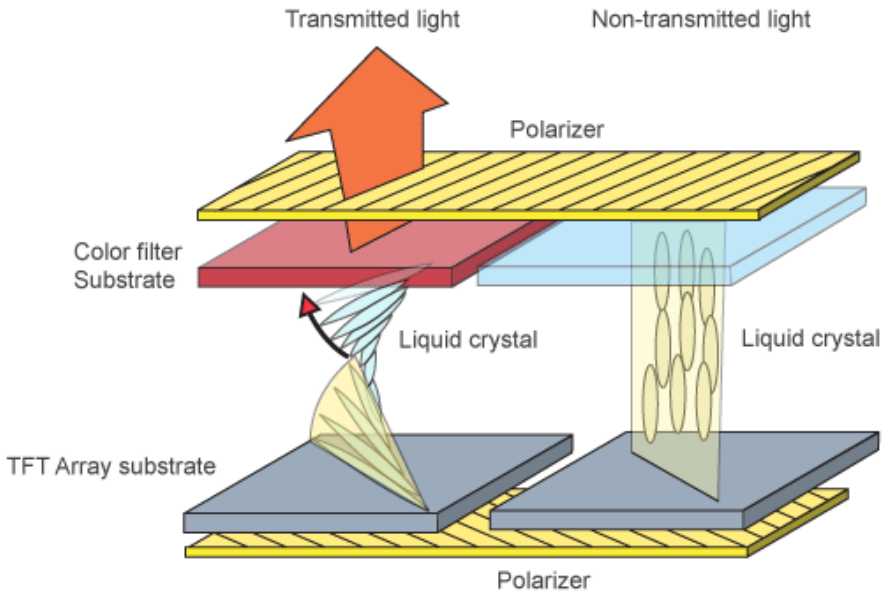


Diagram 2: The Fundamental Photonics of Liquid Crystal (Twisted Nematics)

Thank you for your attention