Nanoparticle Technology

Lecture 03: Fundamentals of Nanotechnology

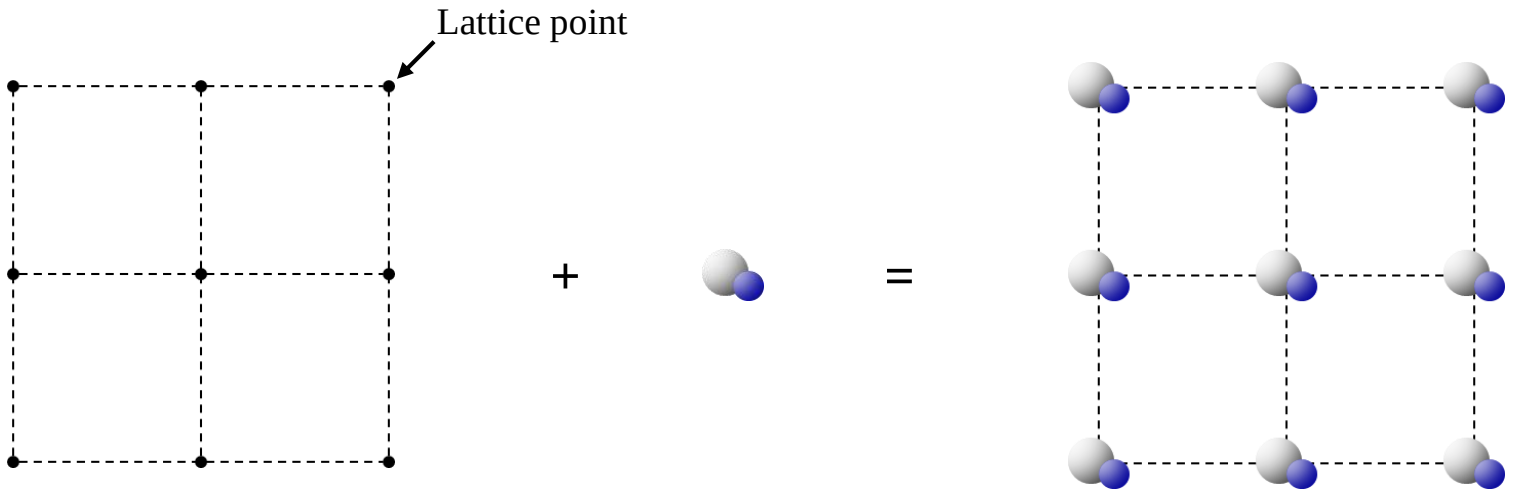
Lecture 03: table of contents

Crystal structures

Atomic arrangement of solid

- Crystalline (or single crystal): periodic arrangement of atoms, infinitely repetitive pattern
- Polycrystalline (or poly crystal): mixture of several single crystals
- Amorphous (or non-crystal): random arrangement of atoms

Crystal structure = lattice + basis



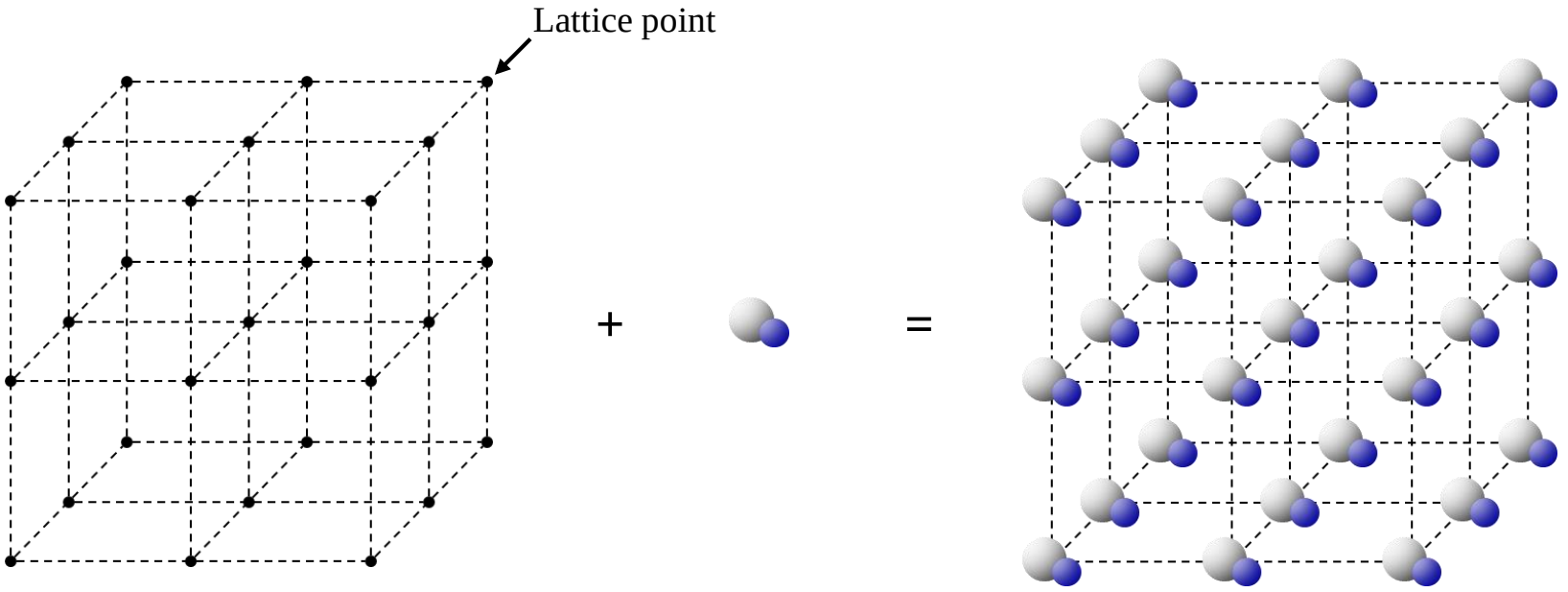
2-dimensional lattice

Basis

2-dimensional crystal structure

- Lattice is an array of lattice points, which are infinitely repeated.
- Crystal structure is formed by adding basis (atom or ion or molecule) to every lattice points of the lattice.

Crystal structure = lattice + basis



3-dimensional lattice

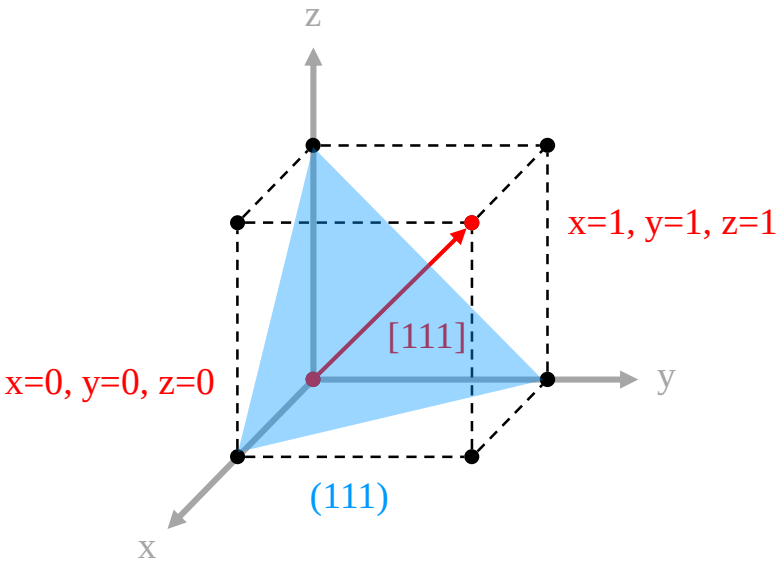
Basis

3-dimensional crystal structure

- Lattice is an array of lattice points, which are infinitely repeated.
- Crystal structure is formed by adding basis (atom or ion or molecule) to every lattice points of the lattice.

Lattice direction and plane

- How to get lattice direction and plane?



Lattice direction is defined as a vector between two points.

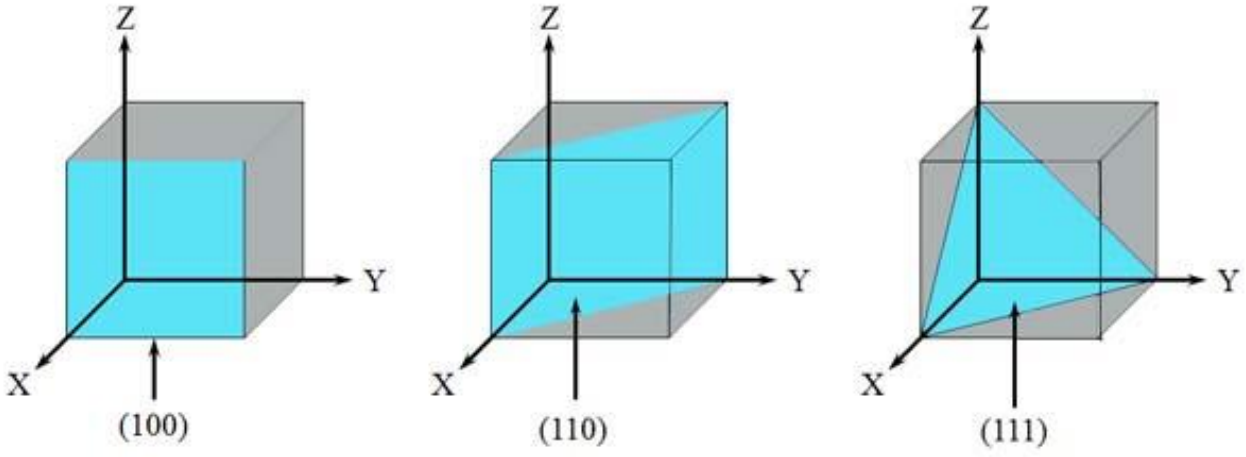
Lattice direction [*uvw*]: $u = u_2\text{-}u_1$, $v = v_2\text{-}v_1$, $w = w_2\text{-}w_1$

Lattice plane is described by Miller indices: *h k l*, which are given by the reciprocal of the intercepts of the plane on the three axis.

Lattice plane (*hkl*): $h=1/u$, $k=1/v$, $l=1/w$

Lattice direction and plane

- To find the Miller indices of a plane…



h	k	l	
$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$=(100)$

h	k	l	
$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{\infty}$	$=(110)$

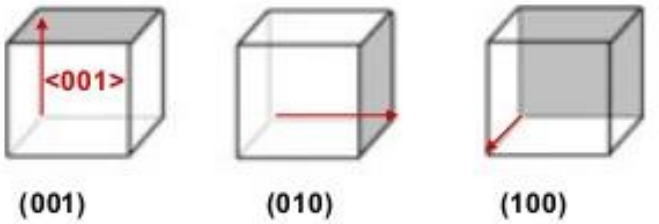
h	k	l	
$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$	$=(111)$

1. Determine the intercepts of the plane with axes
2. Take the reciprocals of intercepts
3. Reduce to the smallest integer values
4. Enclose in brackets

Lattice direction and plane

- Family of directions: < >, and planes: { }

<100>
{100}



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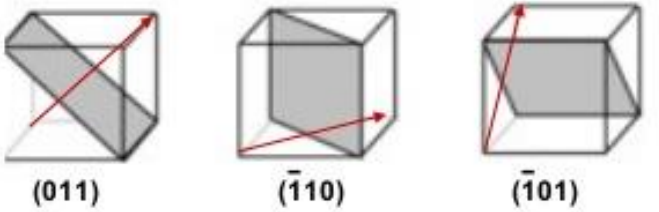
<110>
{110}



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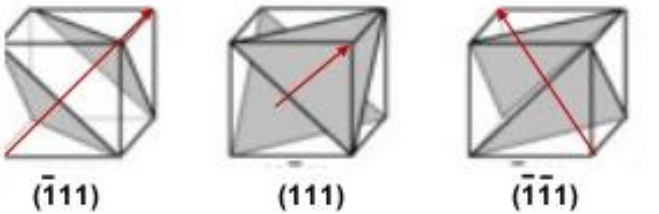
<111>
{111}



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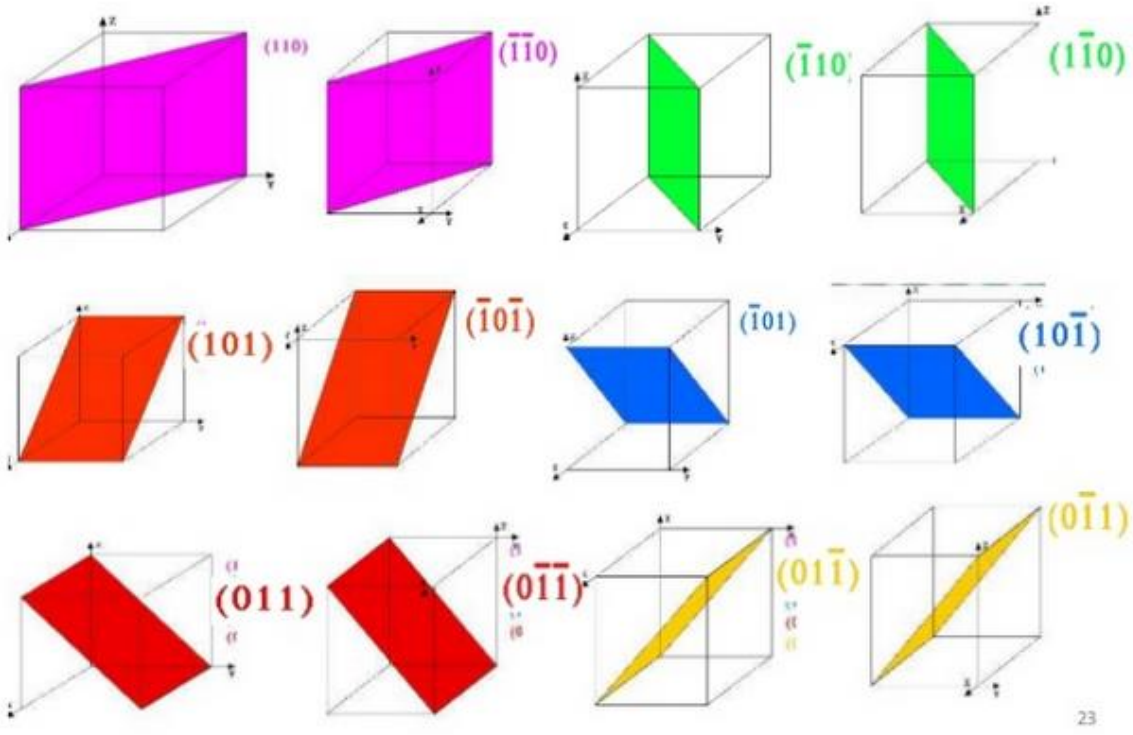
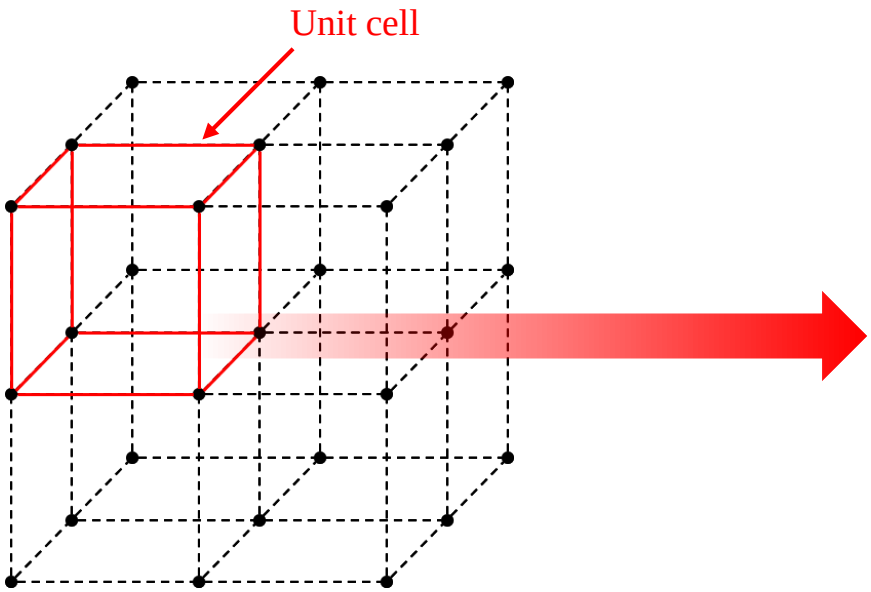
Lattice direction and plane

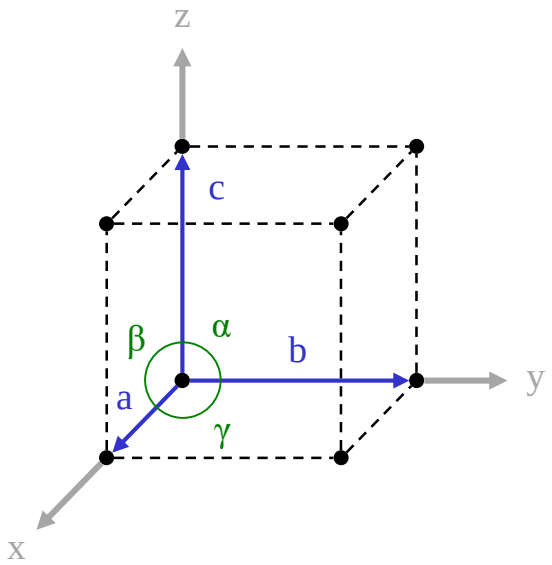
- Family of planes {110}



Unit cell



3-dimensional lattice



Unit cell on x-y-z axis

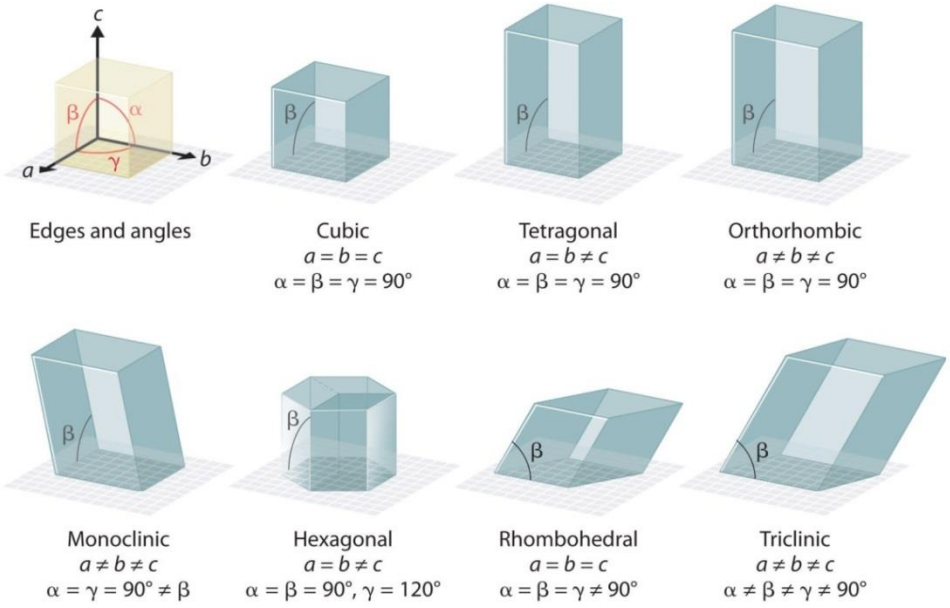
Lattice parameters

Vector lengths: a, b, c

Angles between vectors: α, β, γ

Lattice systems

7 lattice systems



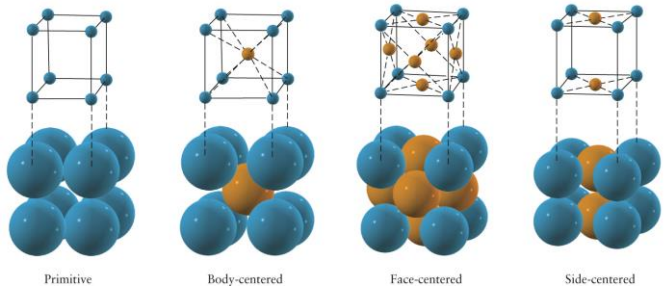
4 types of unit cell

P: Primitive (or simple)

I: Body-Centered

F: Face-Centered

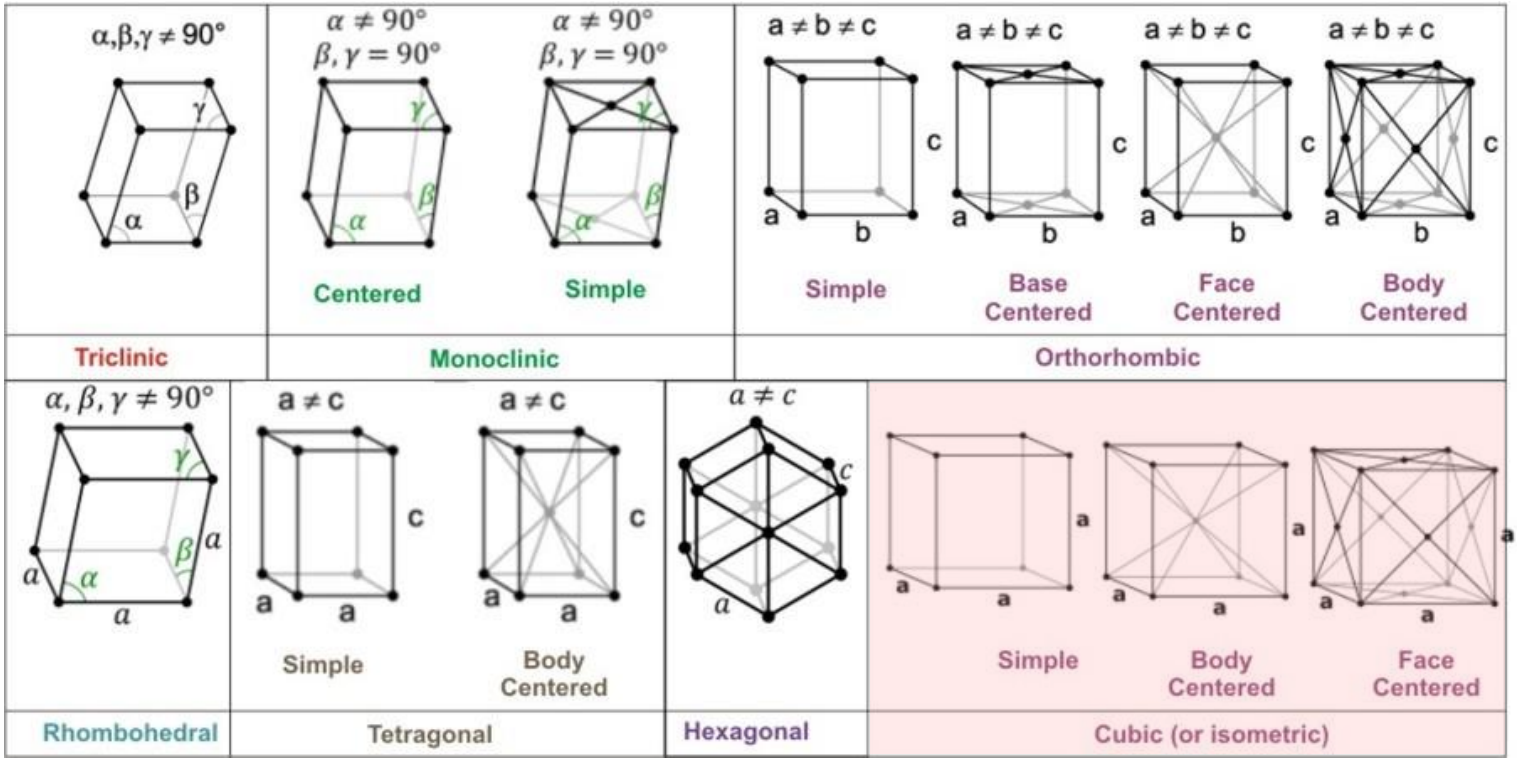
C: Base-Centered (or side-)



Possible crystal systems: 7 × 4 = 28

The 14 Bravais lattices

A. Bravais (1811 ~ 1863)
- French physicist



Examples

- Crystal structure of metals

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

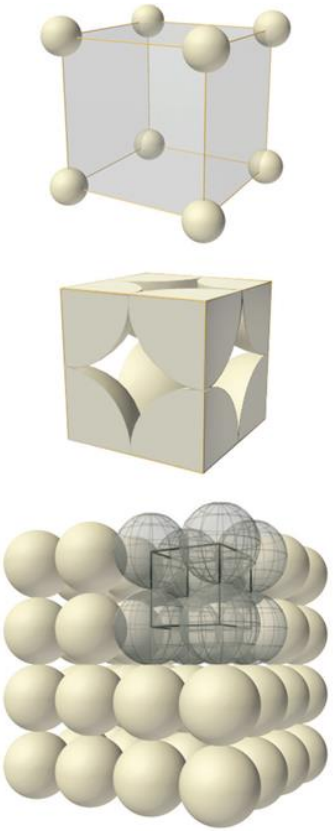
Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

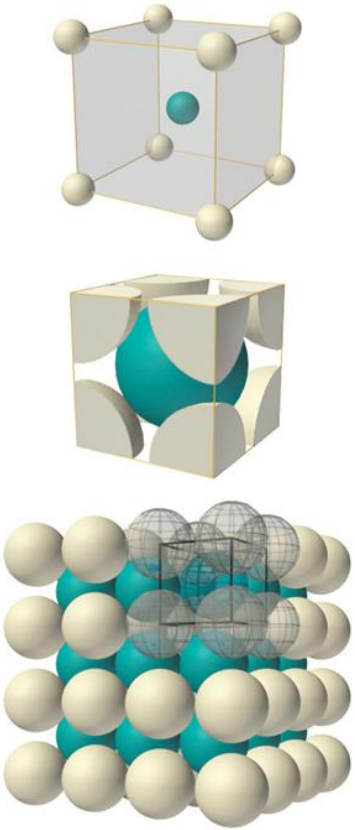
[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

Cubic structures

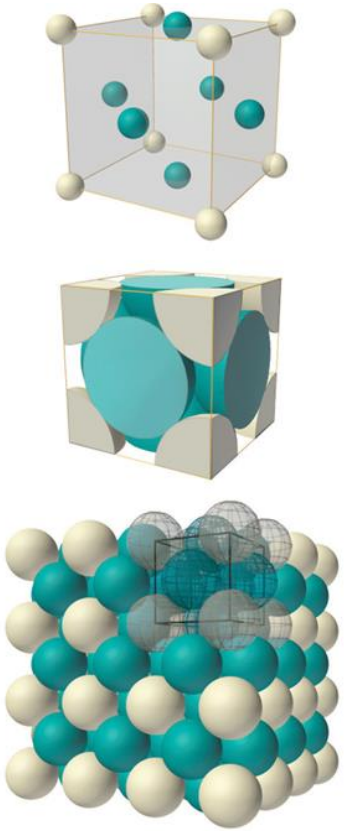
Simple cubic (SC)



Body-centered cubic (BCC)



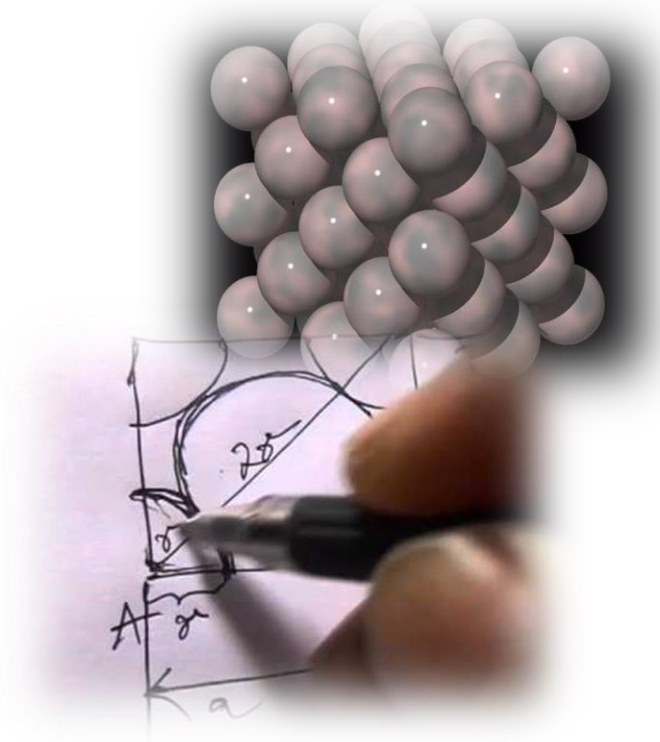
Face-centered cubic (FCC)



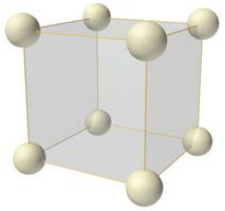
Atomic packing factor (APF)

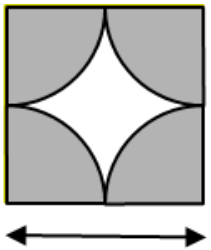
- Atomic packing factor (APF) or packing efficiency indicates how closely atoms are packed in a unit cell and it is given by the ratio of volume of atoms in the unit cell and volume of the unit cell.

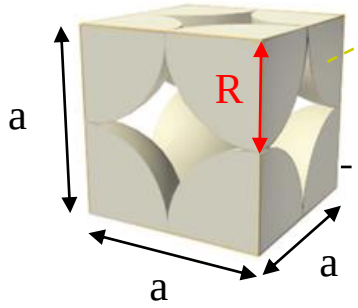
$$\text{APF} = \frac{\text{Volume of atoms in the unit cell}}{\text{Volume of the unit cell}}$$



Atomic packing factor: simple cubic (SC)





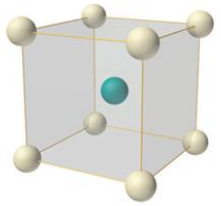


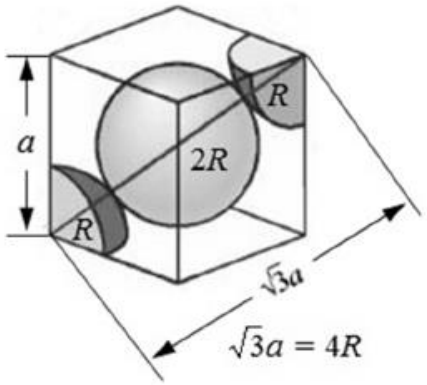
Number of atom: 8 × 1/8 = 1

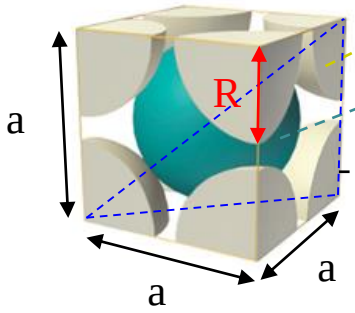
Volume of unit cell: a × a × a = a^3

$$APF = \frac{1 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{4}{3}\pi \times \left(\frac{a}{2}\right)^3}{a^3} = 0.52$$

Atomic packing factor: body-centered cubic (BCC)







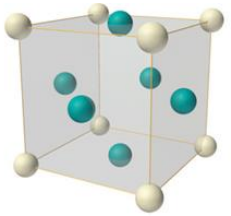
Number of atom: 8 × 1/8 = 1

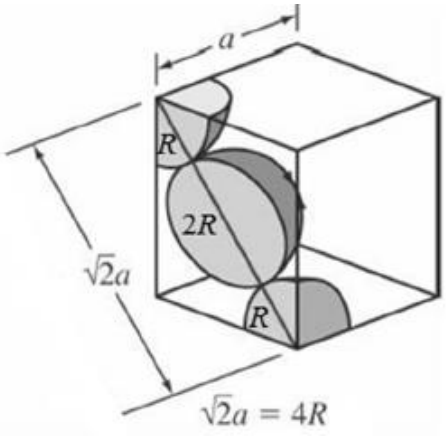
Number of atom: 1

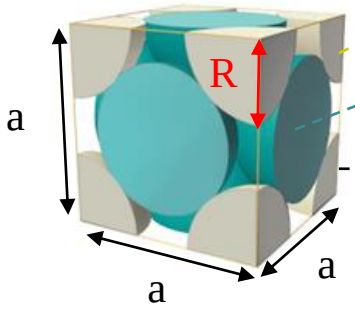
Volume of unit cell: a × a × a = a^3

$$APF = \frac{2 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{8}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3}{a^3} = 0.68$$

Atomic packing factor: face-centered cubic (FCC)







Number of atom: 8 × 1/8 = 1

Number of atom: 6 × 1/2 = 3

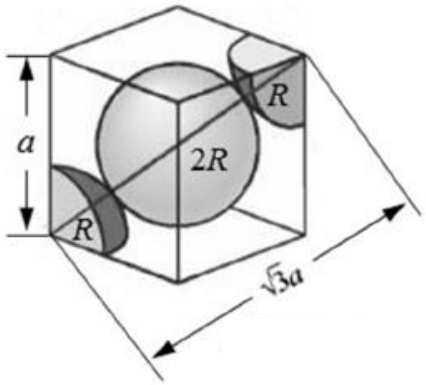
Volume of unit cell: a × a × a = a^3

$$APF = \frac{4 \times \frac{4}{3}\pi R^3}{a^3} = \frac{\frac{16}{3}\pi \times \left(\frac{\sqrt{2}}{4}a\right)^3}{a^3} = 0.74$$

Examples (calculation)

Ex. 1) Find the lattice parameter (a) of iron (Fe)

For iron (Fe),
Crystal structure: body-centered cubic (BCC) at room temperature
Atomic radius (R): 0.124 nm



$$\sqrt{3}a = 4R$$

$$a = \frac{4R}{\sqrt{3}} = \frac{4 \times 0.124\ nm}{\sqrt{3}} = 0.286\ nm$$

Examples (calculation)

Ex. 2) Theoretical density (ρ) calculation of aluminum (Al)

$$\rho = \frac{nA}{V_c N_A}$$

n = number of atoms in the unit cell
A = atomic weight
V_c = volume of the unit cell
N_A = Avogadro's number (6.023×10^{23} atoms/mol)

For aluminum (Al),
Crystal structure: face-centered cubic (FCC)
Lattice parameter: 0.405 nm

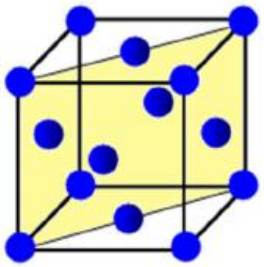
$$\rho = \frac{4\ atoms \times 26.98\ g/mol}{(0.405\ nm)^3 \times 6.023 \times 10^{23}\ atoms/mol} = 2.697\ g/cm^3$$

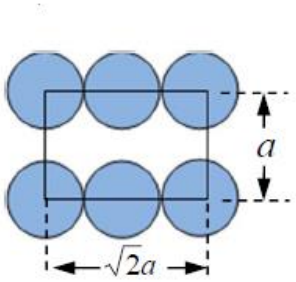
Cubic structures: planar density (PD)

- Planar density (PD) refers to density of atomic packing on a particular plane.

$$\text{PD} = \frac{\text{Number of atoms on a plane}}{\text{Area of plane}}$$

Ex. 1) PD of FCC structure on (110) plane





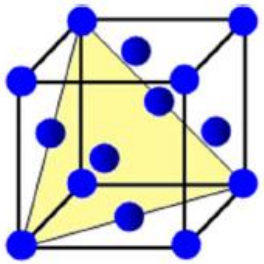
$$PD_{(110)} = \frac{2}{a\sqrt{2}a} = \frac{\sqrt{2}}{a^2}$$

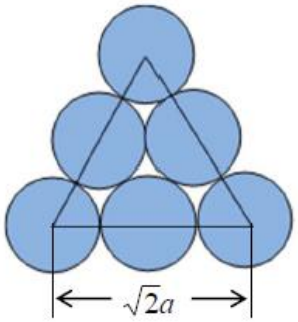
Cubic structures: planar density (PD)

- Planar density (PD) refers to density of atomic packing on a particular plane.

$$\text{PD} = \frac{\text{Number of atoms on a plane}}{\text{Area of plane}}$$

Ex. 2) PD of FCC structure on (111) plane





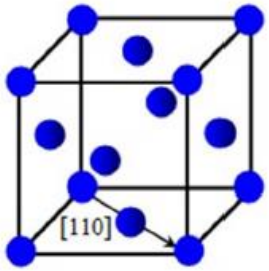
$$PD_{(111)} = \frac{2}{\frac{1}{2}\sqrt{2}a \times \sqrt{3}\frac{\sqrt{2}a}{2}} = \frac{4}{\sqrt{3}a^2}$$

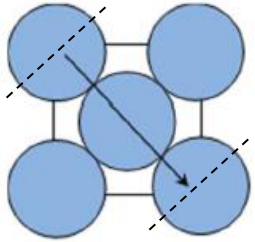
Cubic structures: linear density (LD)

- Linear density (LD) is the number of atoms per unit length along a particular direction.

$$\text{LD} = \frac{\text{Number of atoms on the direction vector}}{\text{Length of the direction vector}}$$

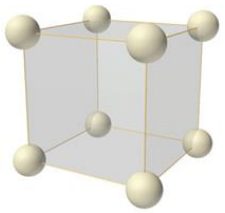
Ex. 1) LD of FCC structure on [110] direction



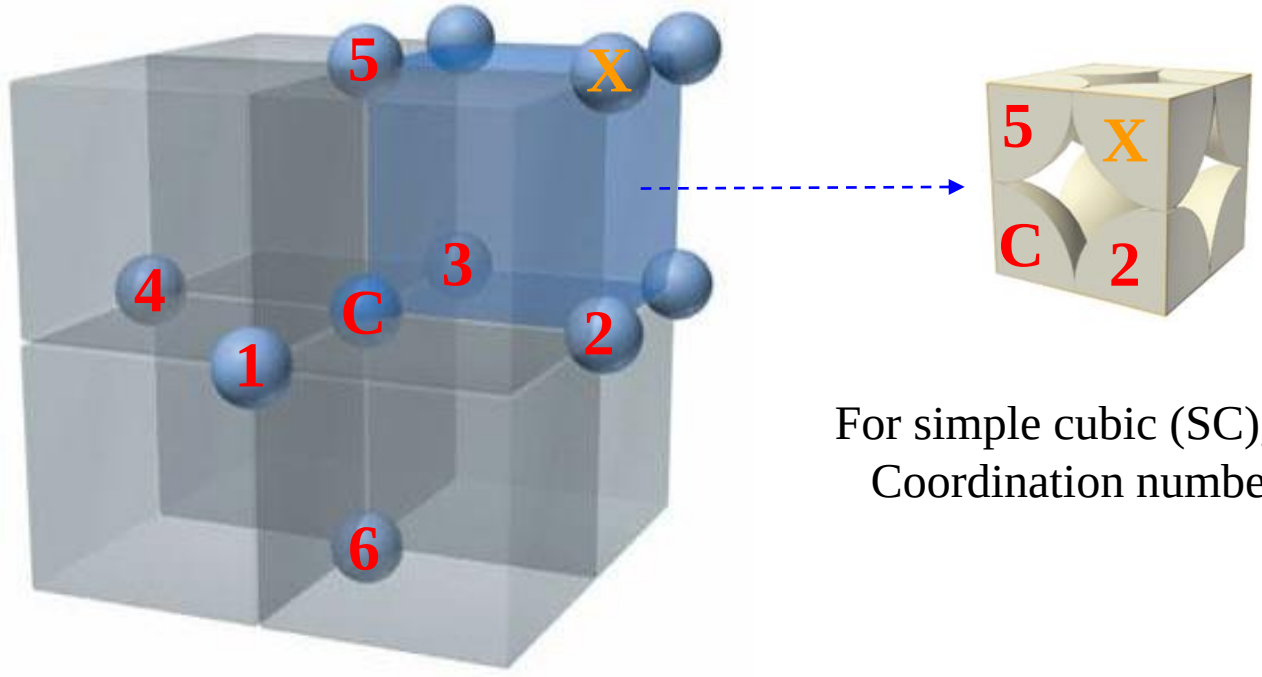


$$LD_{(110)} = \frac{2}{\sqrt{2}a} = \frac{\sqrt{2}}{a}$$

Coordination number of simple cubic (SC)

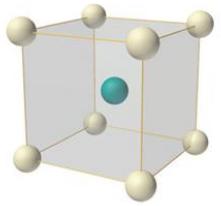


- Coordination number (CN): number of nearest-neighbor atoms

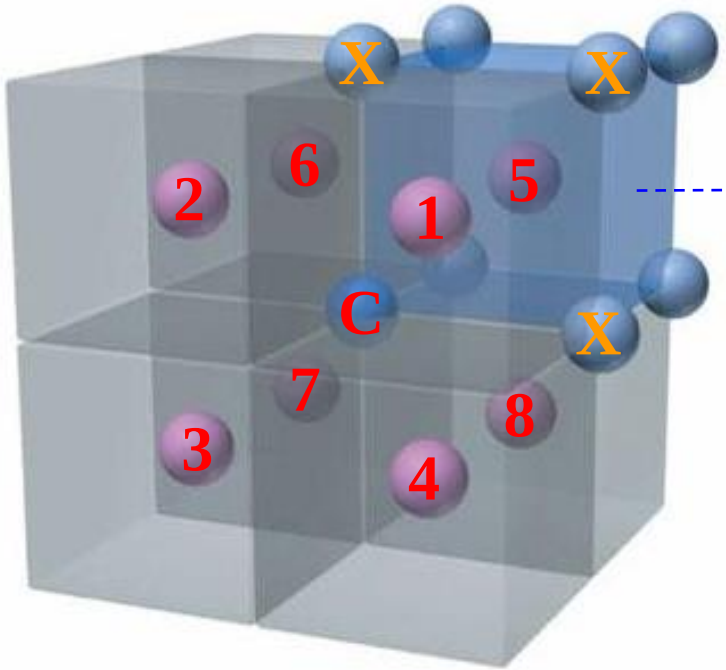


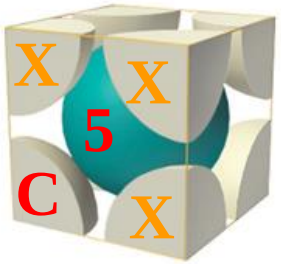
For simple cubic (SC),
Coordination number (CN) = 6

Coordination number of body-centered cubic (BCC)



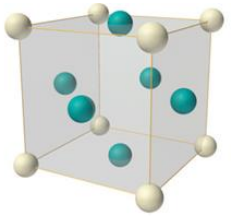
- Coordination number (CN): number of nearest-neighbor atoms



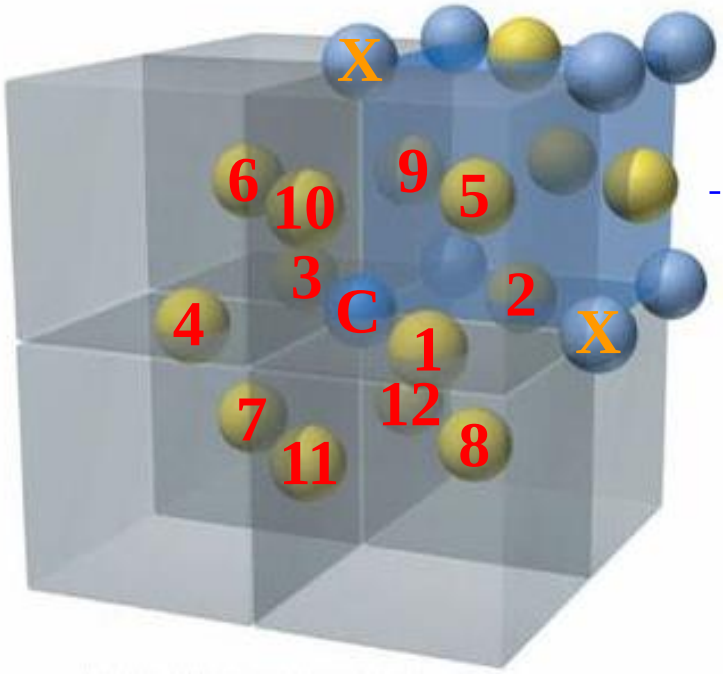


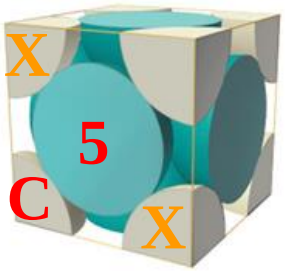
For body-centered cubic (BCC),
Coordination number (CN) = 8

Coordination number of face-centered cubic (FCC)



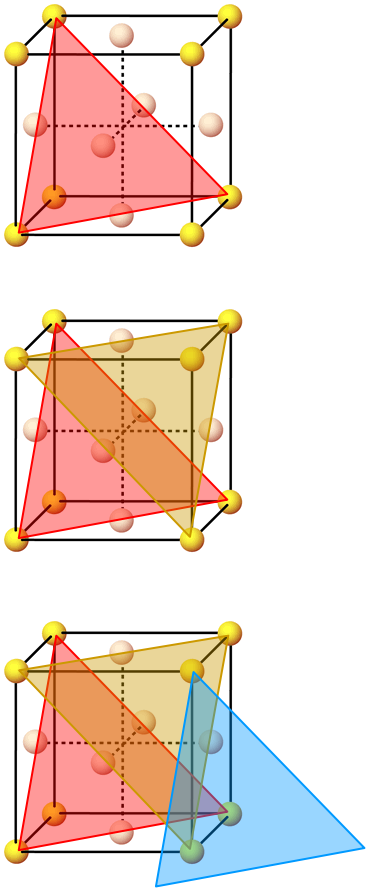
- Coordination number (CN): number of nearest-neighbor atoms

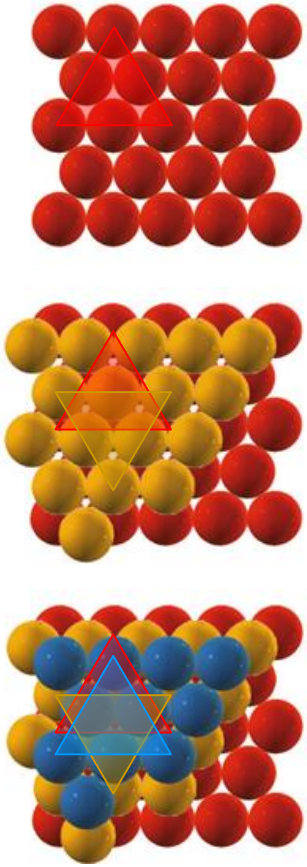




For face-centered cubic (FCC),
Coordination number (CN) = 12

Close-packed structure: FCC (111) plane

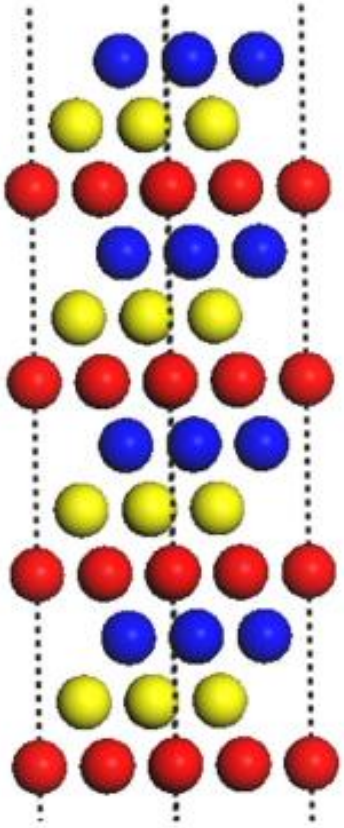




1st layer

2nd layer

3rd layer



12th=3rd (C)

11th=2nd (B)

10th=1st (A)

9th=3rd (C)

8th=2nd (B)

7th=1st (A)

6th=3rd (C)

5th=2nd (B)

4th=1st (A)

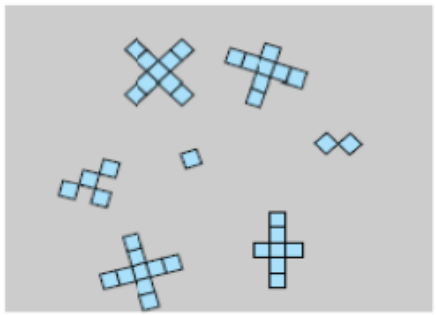
3rd (C)

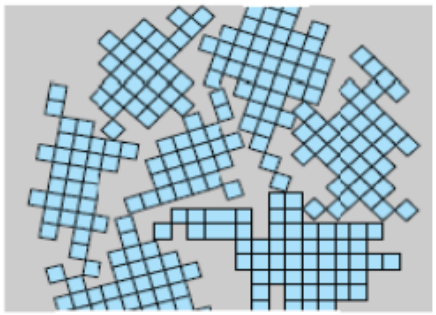
2nd (B)

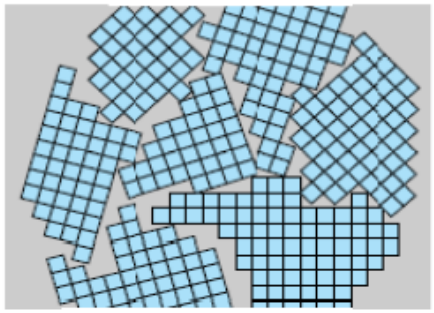
1st (A)

Crystal structure of common metals

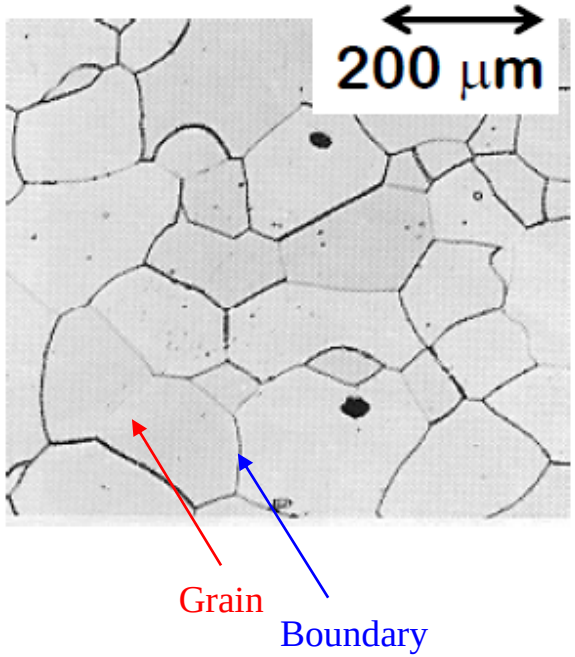
- Most of common metals have poly crystal structure which is consisted of many single crystals.







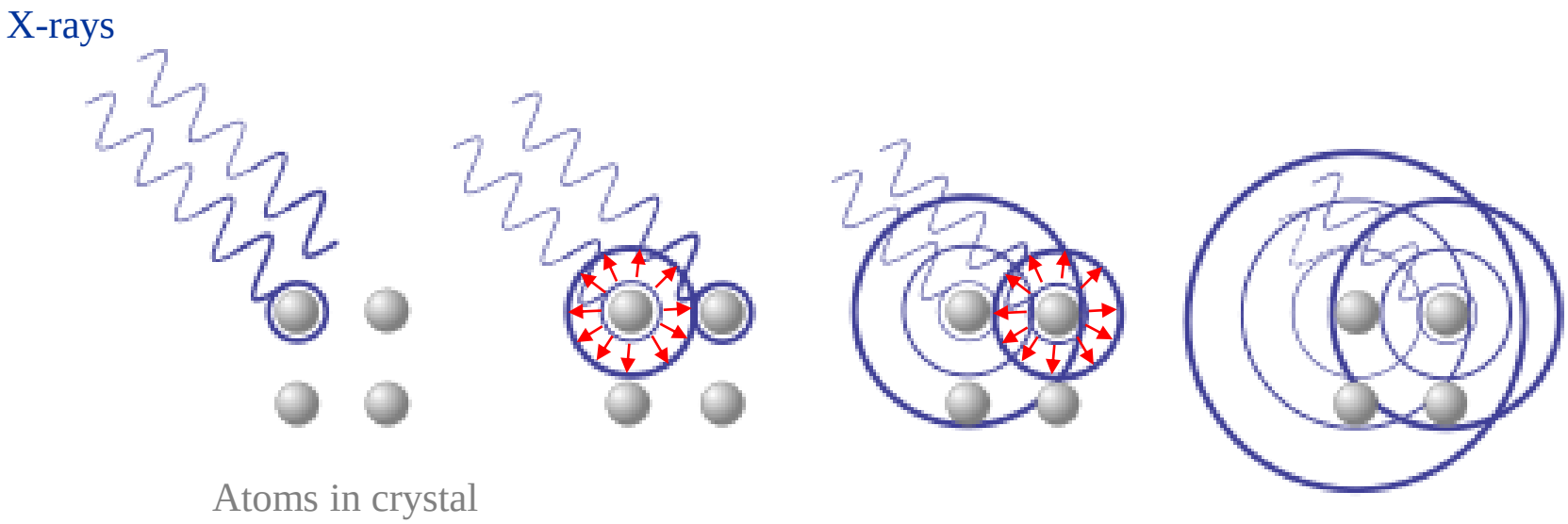
Crystal structure of common metal



X-ray diffraction (XRD)

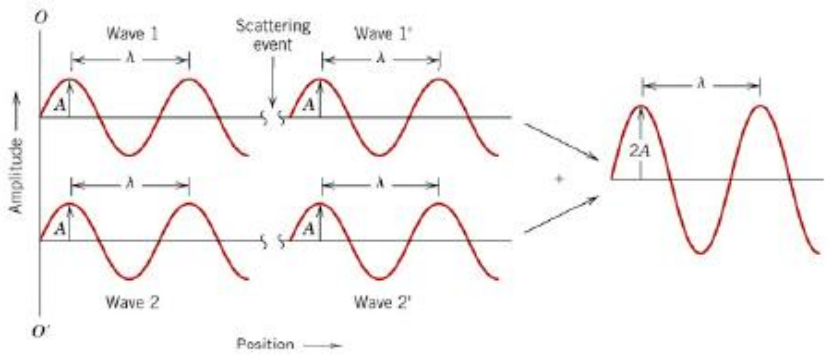
X-ray diffraction (XRD): Bragg's Law

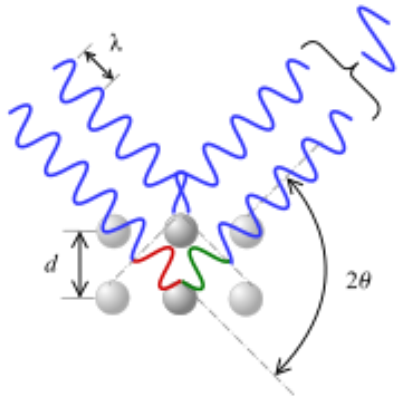
- X-rays interact with the atoms in a crystal structure.



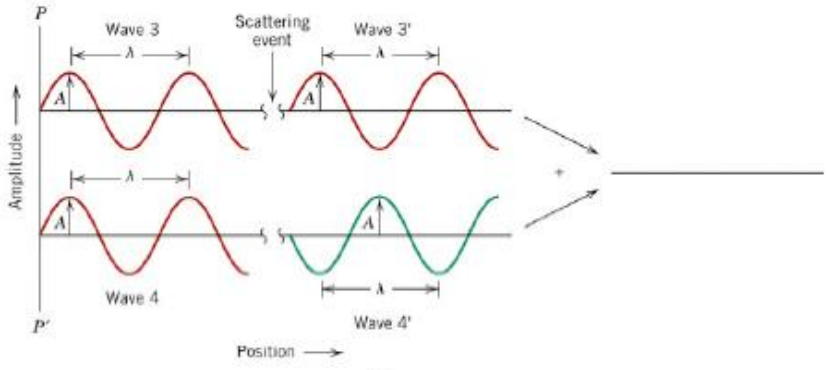
X-ray diffraction (XRD): Bragg's Law

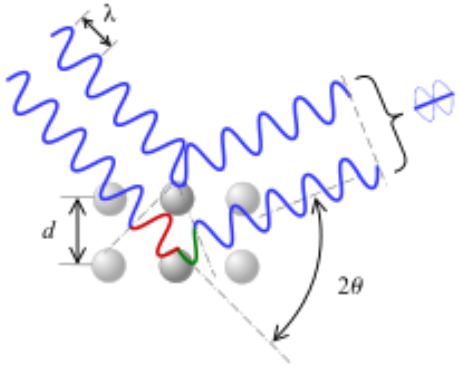
Constructive interference





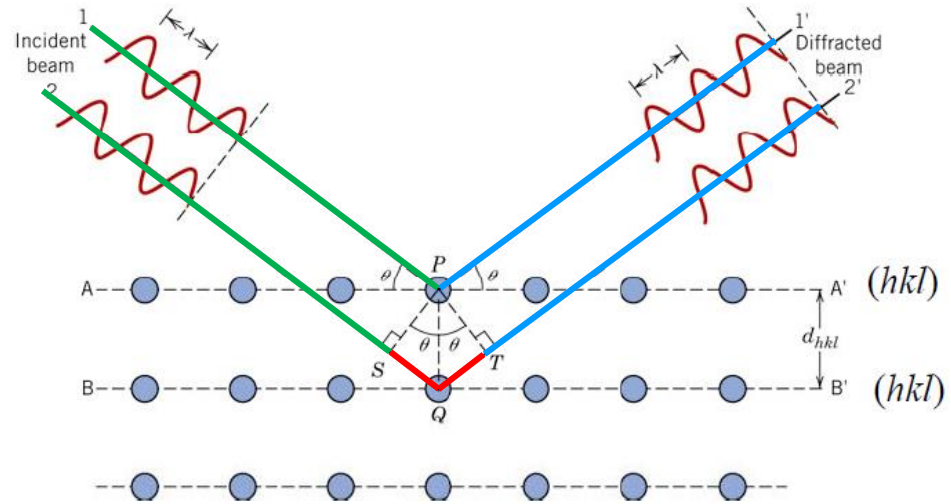
Destructive interference





X-ray diffraction (XRD): Bragg's Law

- For a crystalline, the waves are scattered from lattice planes separated by the interplanar distance d_{hkl}. When the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integer multiple of the wavelength.



Bragg's Law

$$n\lambda = SQ + QT = d_{hkl}\sin\theta + d_{hkl}\sin\theta = 2d_{hkl}\sin\theta$$

X-ray diffraction (XRD): examples (calculation)

Ex.) For analysis of iron (Fe) crystal structure, X-ray diffraction (XRD) measurement is conducted. Calculated the distance of plane (220) and its diffraction angle with the provided information as shown in below.

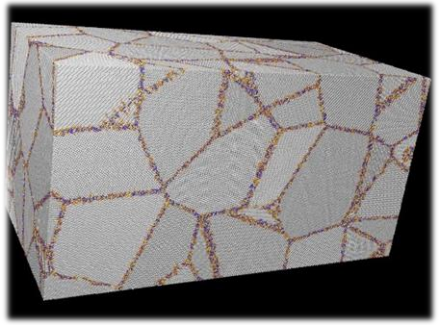
For iron (Fe),
Crystal structure: body-centered cubic (BCC)
Lattice parameter: 0.2866 nm
For XRD measurement
Wavelength of X-ray: 0.1790 nm (n = 1)

Distance of plane (220): $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.2866\ nm}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013\ nm$

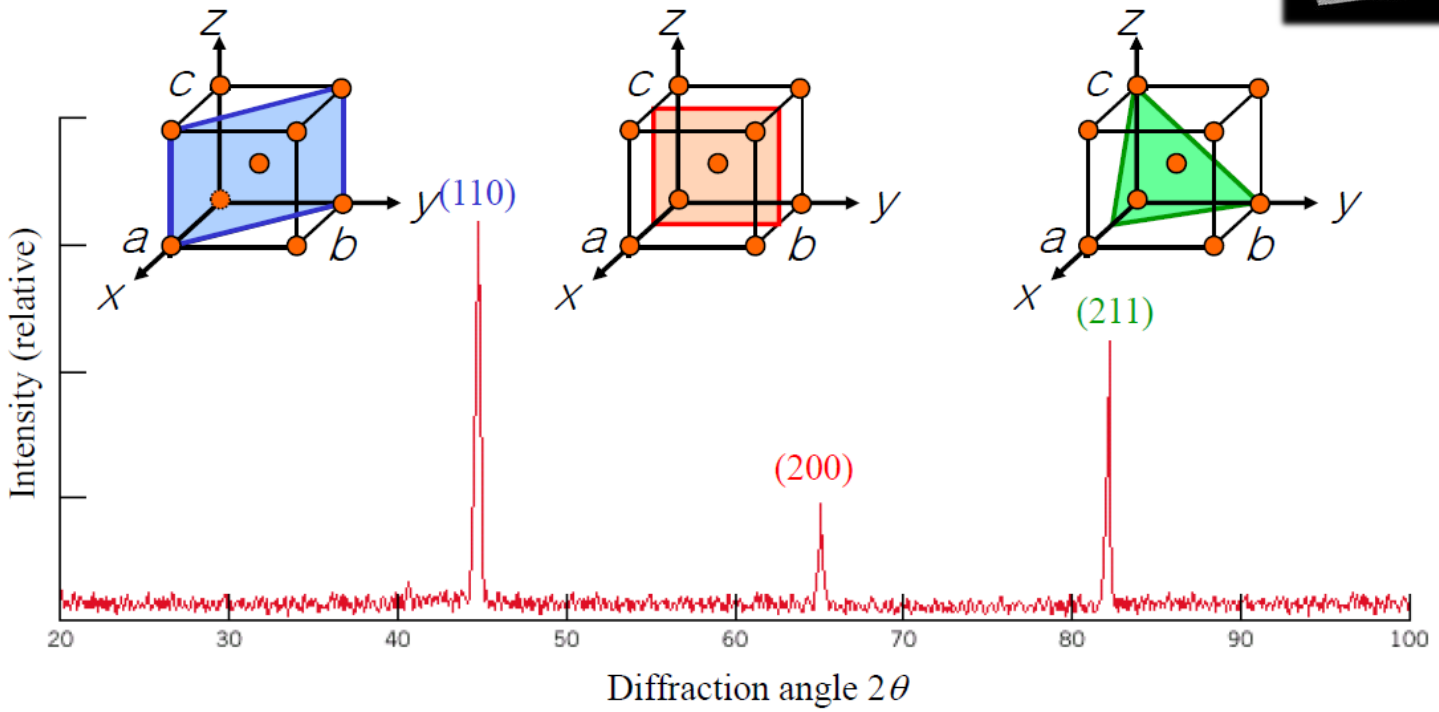
Diffraction angle of plane (220): $\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{1 \times 0.1790\ nm}{2 \times 0.1013\ nm} = 0.884$

$\theta = 62.13^{\circ}$

X-ray diffraction (XRD): examples (data)

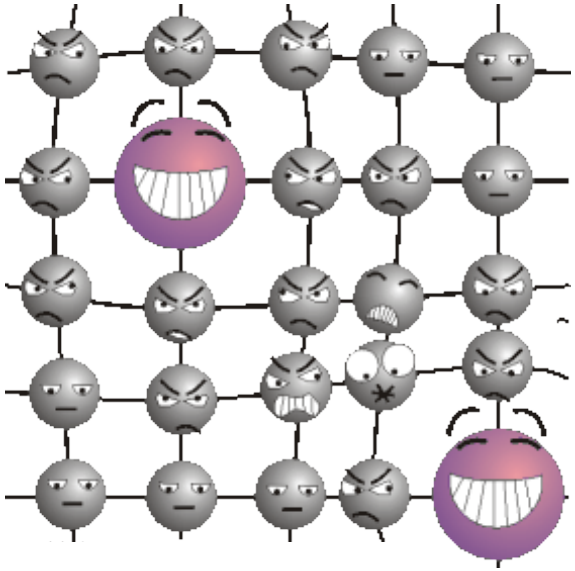


- Diffraction pattern for Fe poly crystal

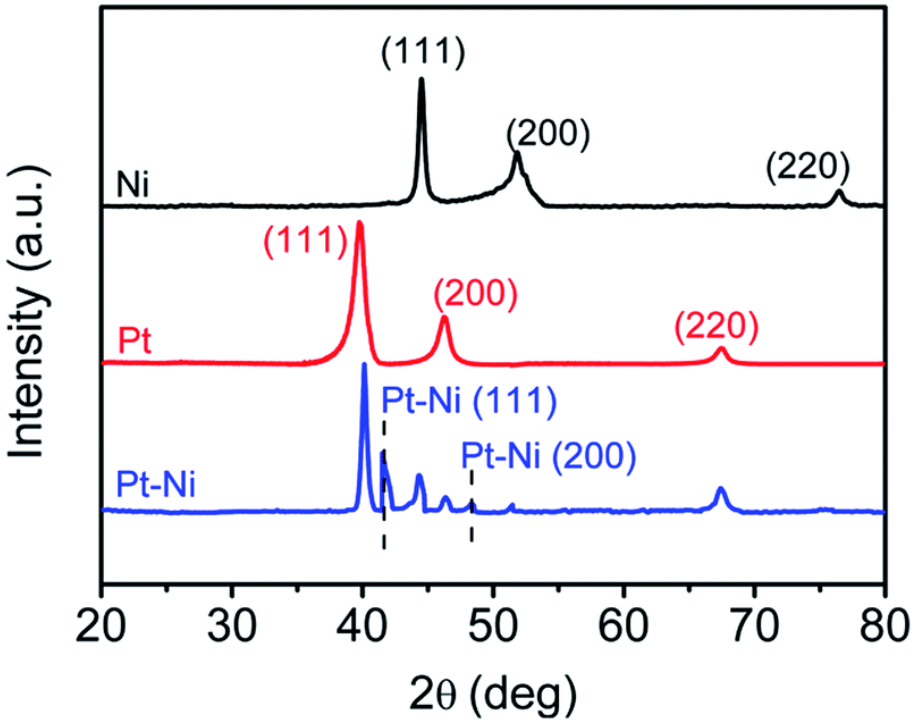


X-ray diffraction (XRD): examples (data)

- Diffraction patterns for Pt-Ni alloy

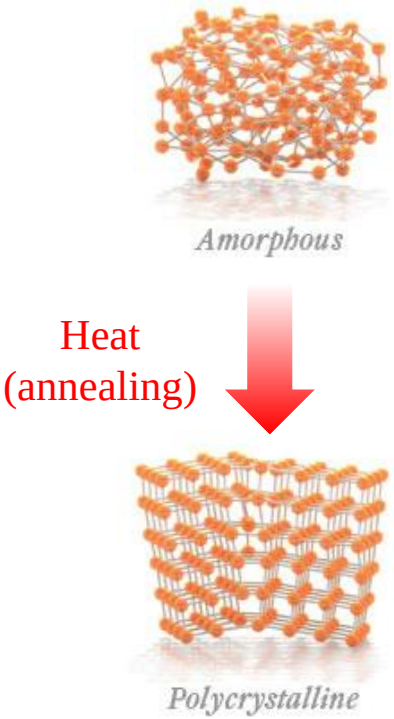


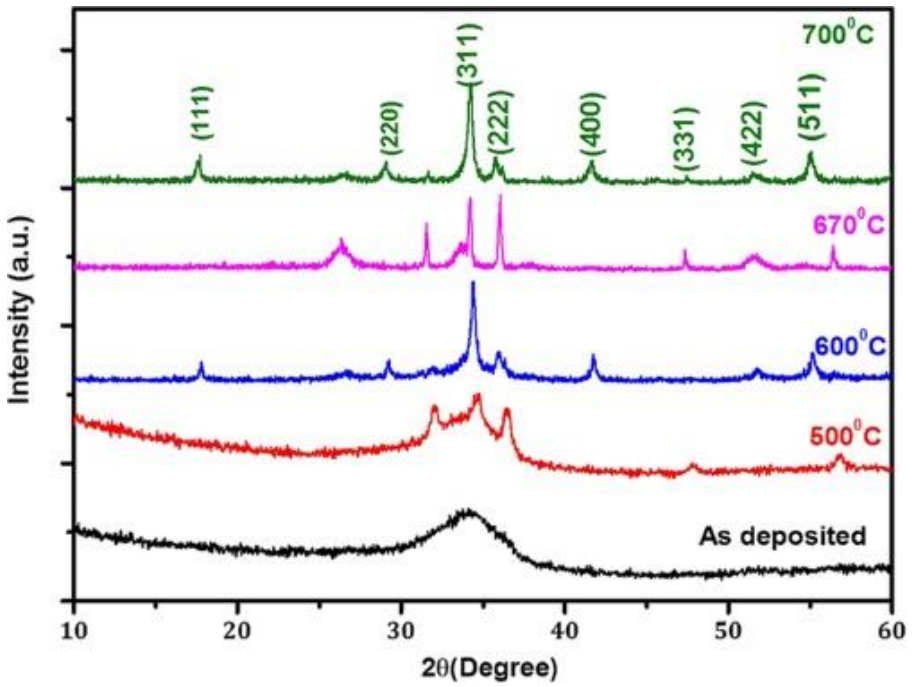
	Crystal structure	Atomic radius
Nickel (Ni)	FCC	124 pm
Platinum (Pt)	FCC	139 pm



X-ray diffraction (XRD): examples (data)

- Diffraction patterns for Zn_2SnO_4 poly crystal after heat treatment

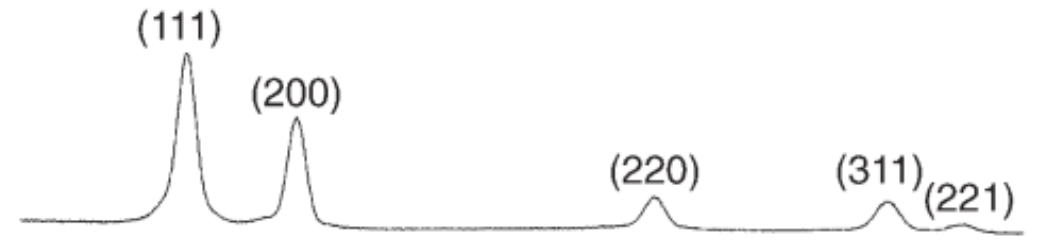


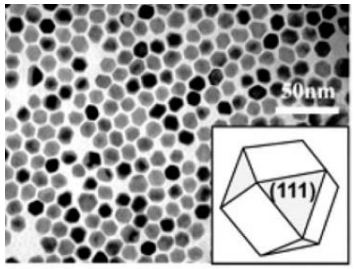


X-ray diffraction (XRD): examples (data)

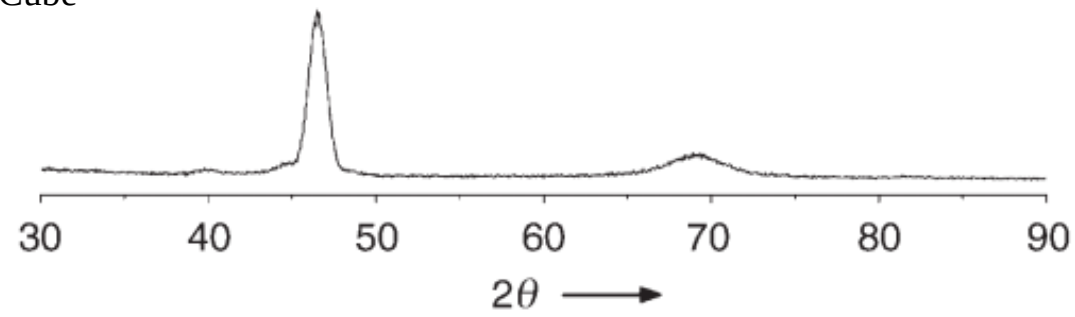
- Diffraction patterns of shape-controlled Au nanoparticles

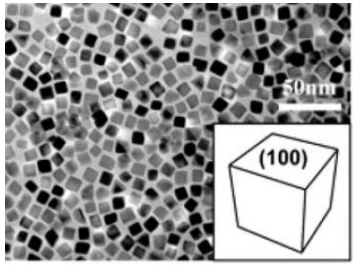
Truncated cube





Cube

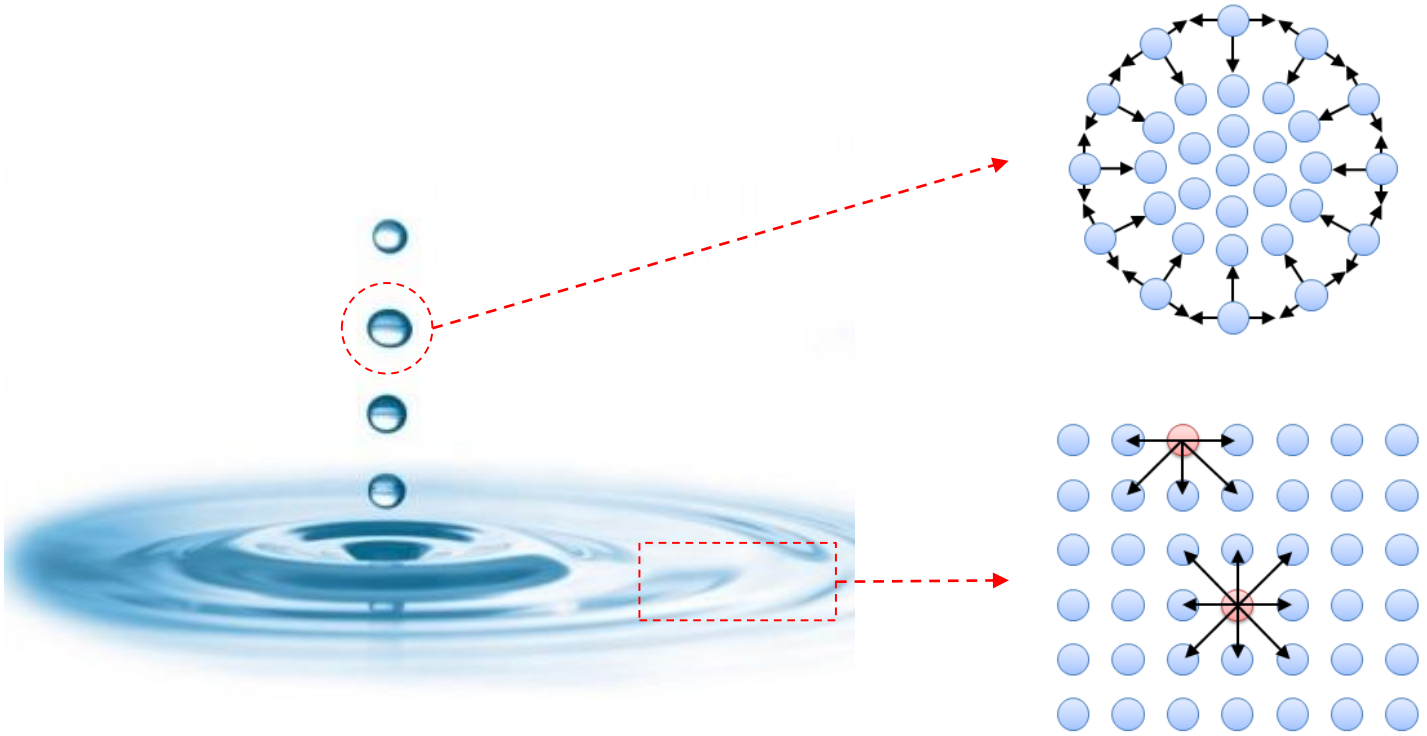




Surface energy

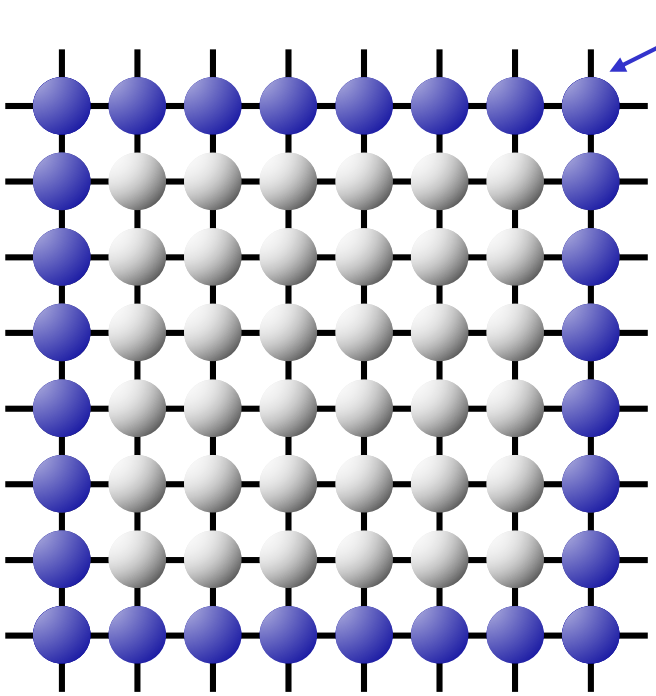
What is surface energy?

- Surface energy quantifies the disruption of intermolecular bonds that occur when a surface is created.



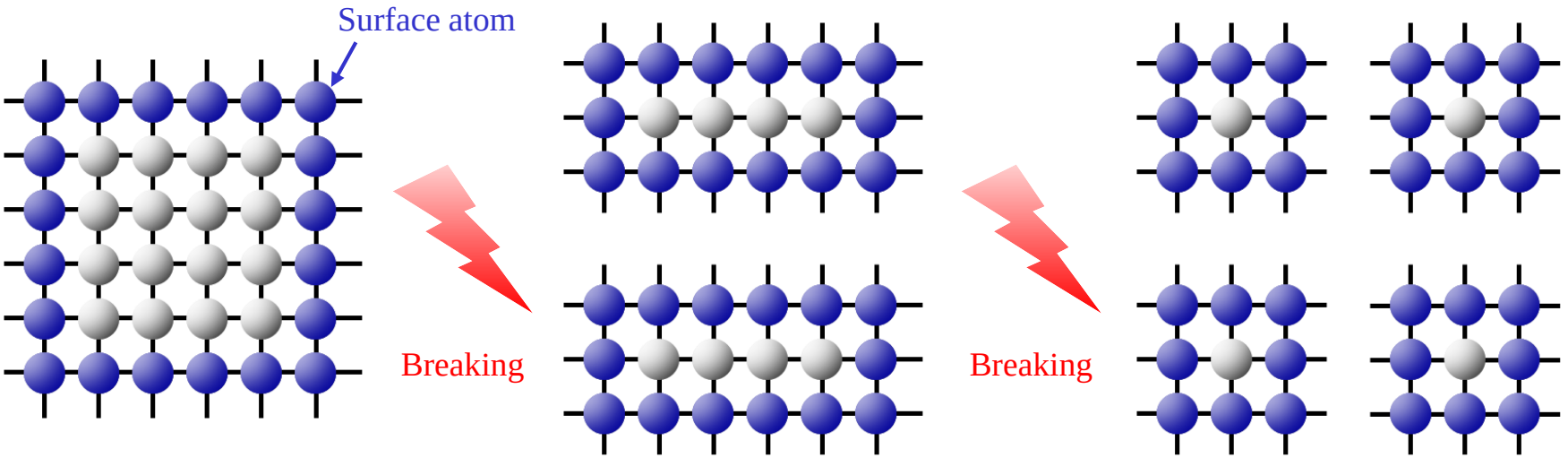
What is surface of solid?

- Theoretically, the surface of solid means the outermost atoms.



Surface atom (%)
= (Surface atom # / Total atom #) × 100
= (28 / 64) × 100
= 43.7 %

Surface atom (%)



Surface atom (%)
= (20 / 36) ×100
= 55.5 %

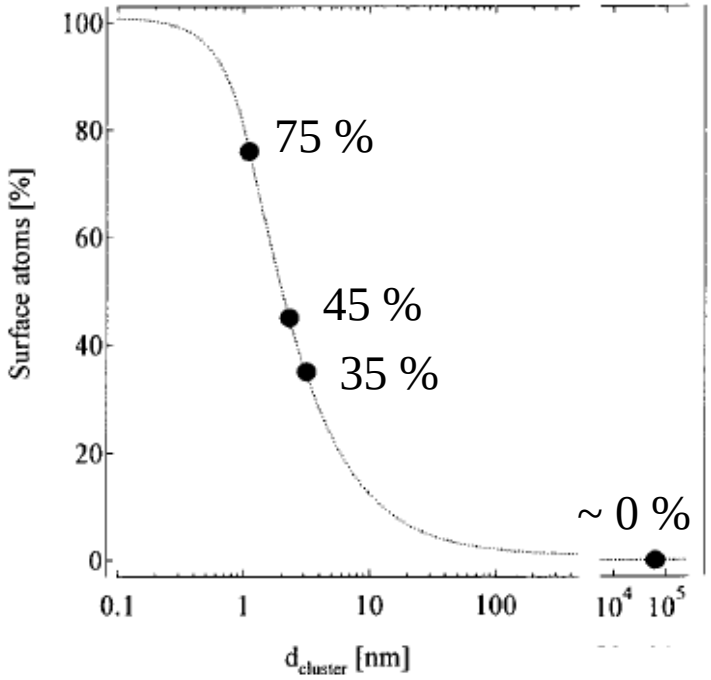
Surface atom (%)
= (14 / 18) ×100
= 77.8 %

Surface atom (%)
= (8 / 9) ×100
= 88.9 %

Surface atoms (%) of Pd and Au clusters

- The surface atoms (%) is significantly increased when the cluster size is decreased to nanometer scale.

Pd clusters

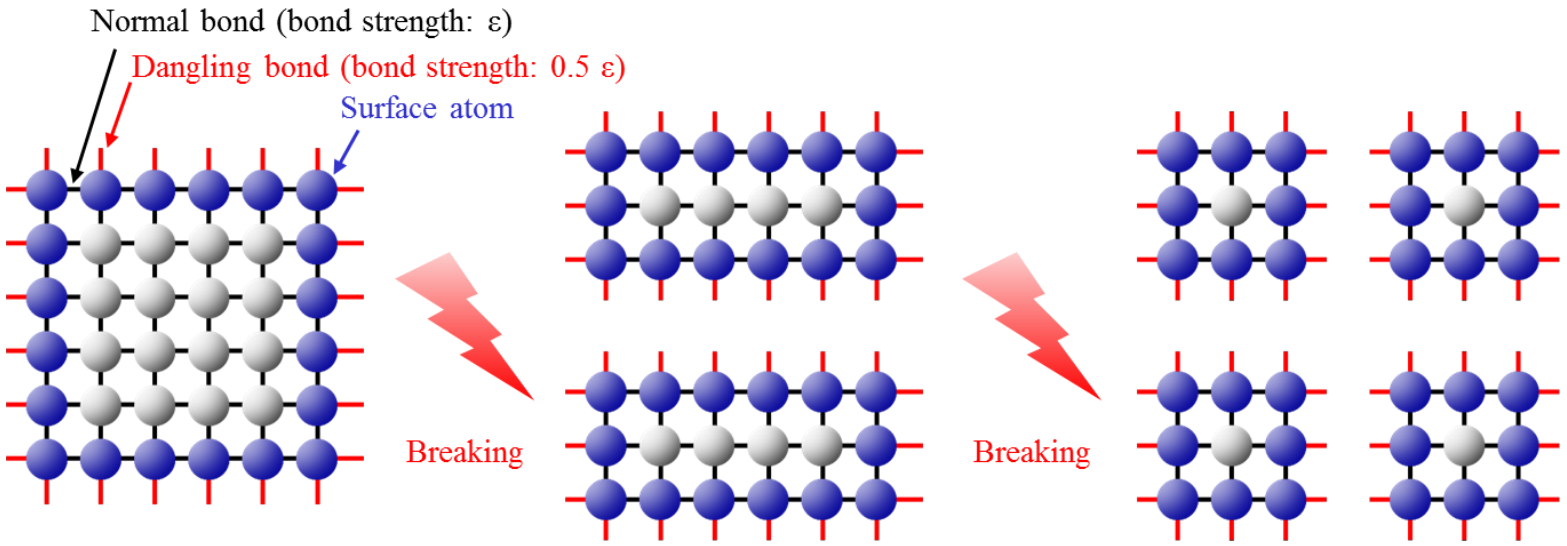


Au clusters

Number of shell		Size	Total number of Atoms	Surface Atoms (%)
1 shell		6Å	13	92
2 shells		10Å	55	76
3 shells		14Å	147	63
4 shells		18Å	309	52
5 shells		22Å	561	45
7 shells		26Å	1415	35

Dangling bond and surface energy

- Dangling bond (or broken bond): an unsatisfied valence on an immobilized atom



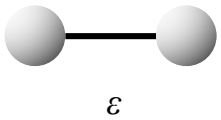
Surface energy: $\gamma = 0.5\varepsilon\rho_a N_b$
(without surface relaxation)

ε: bond strength
ρ_a: number density of atoms at surface
N_b: number of broken bond

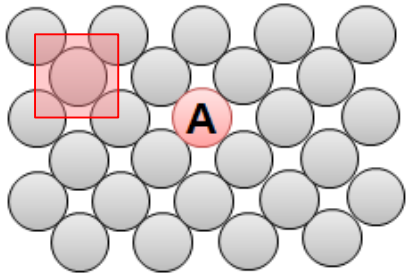
Surface energy calculation: FCC (100) plane

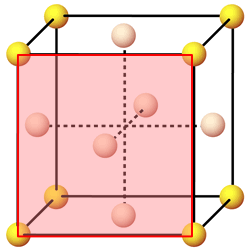
Surface energy = Dangling bond strength × Number of broken bond × Number density of atoms at surface

Normal bond



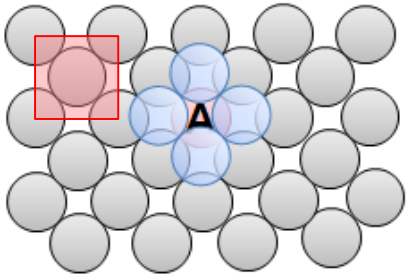
1st layer of (100)



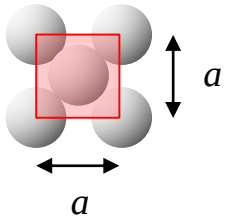


Dangling bond

2nd layer of (100)



Planar density of (100)

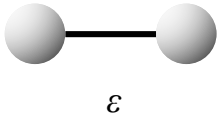


Surface energy = $0.5\,\varepsilon$ × 4 × $\frac{2}{a^2}$ = $\frac{4\varepsilon}{a^2}$

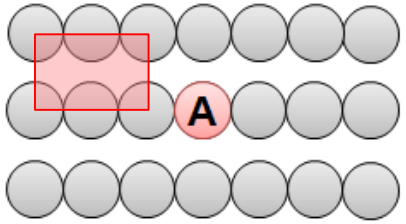
Surface energy calculation: FCC (110) plane

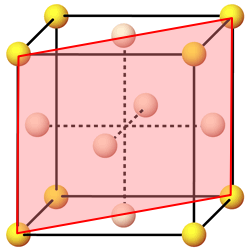
Surface energy = Dangling bond strength × Number of broken bond × Number density of atoms at surface

Normal bond



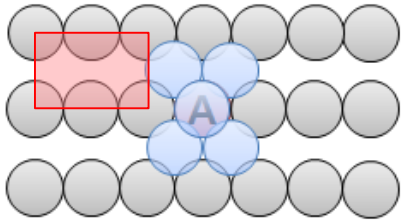
1st layer of (110)



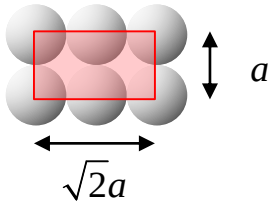


Dangling bond

2nd, 3rd layers of (110)



Planar density of (110)



Surface energy = $0.5\,\varepsilon$ × 5 × $\frac{2}{\sqrt{2}a^2}$ = $\frac{5\varepsilon}{\sqrt{2}a^2}$

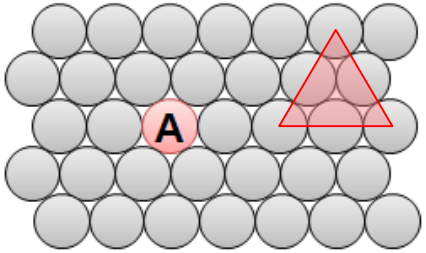
Surface energy calculation: FCC (111) plane

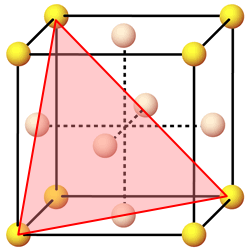
Surface energy = Dangling bond strength × Number of broken bond × Number density of atoms at surface

Normal bond

ε

1st layer of (111)

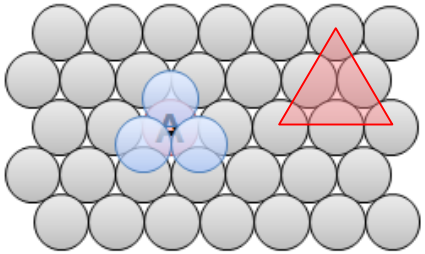




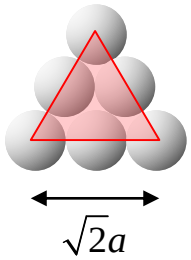
Dangling bond

$0.5\ \varepsilon$

2nd layer of (111)



Planar density of (111)



$\sqrt{2}a$

Surface energy = $0.5\ \varepsilon$ × 3 × $\frac{4}{\sqrt{3}a^2}$ = $\frac{2\sqrt{3}\varepsilon}{a^2}$

Surface energy calculation: FCC

FCC planes | Number of broken bond

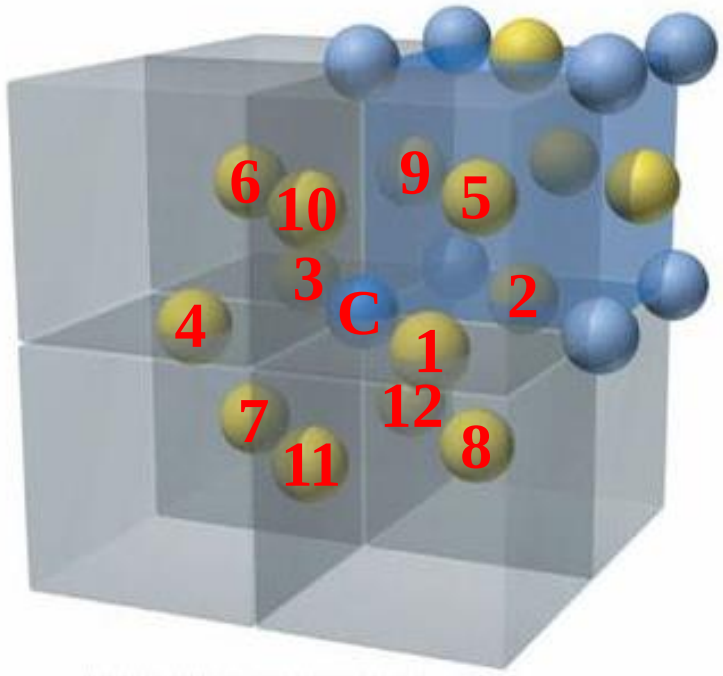
(100) — 4

(110) — 5

(111) — 3

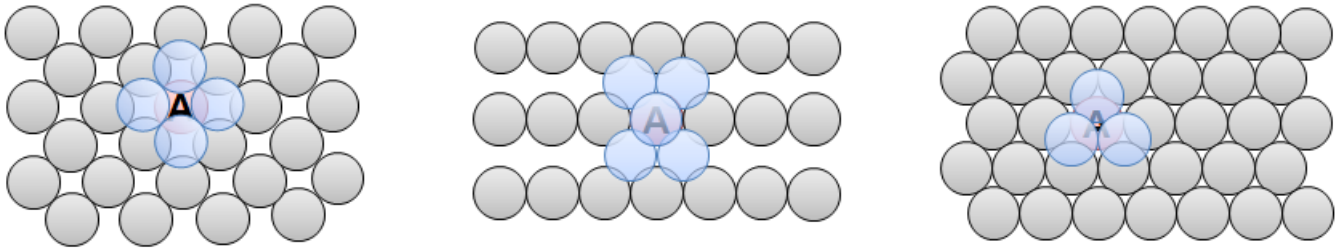
12

For FCC, Coordination number (CN) = 12



Surface energy calculation: FCC

(100) (110) (111)



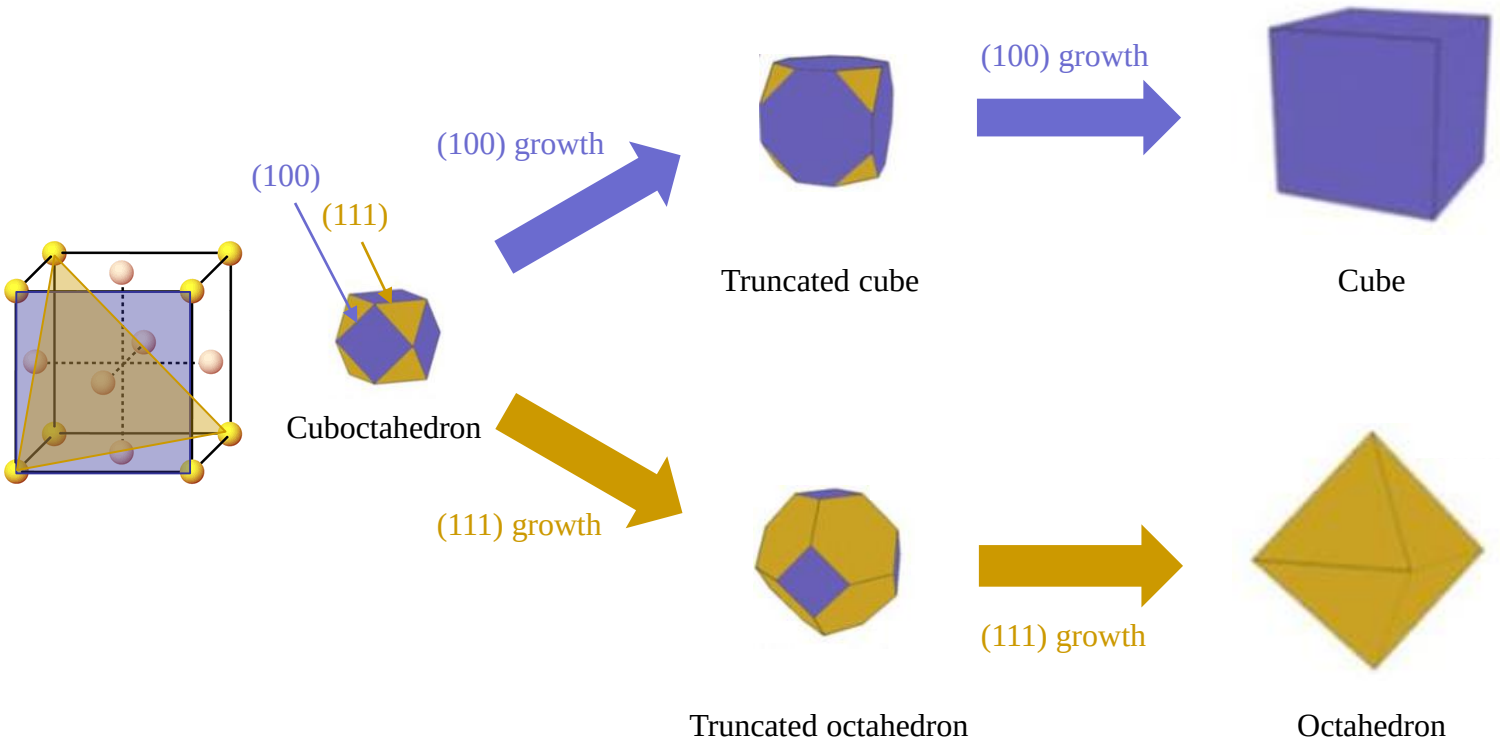
Surface energy (γ) $\frac{4\varepsilon}{a^2} = 4.00 \times \frac{\varepsilon}{a^2}$ $\frac{5\varepsilon}{\sqrt{2}a^2} \approx 3.54 \times \frac{\varepsilon}{a^2}$ $\frac{2\sqrt{3}\varepsilon}{a^2} \approx 3.46 \times \frac{\varepsilon}{a^2}$

$\gamma_{100} > \gamma_{110} > \gamma_{111}$

Unstable → Stable

Surface energy calculation: FCC

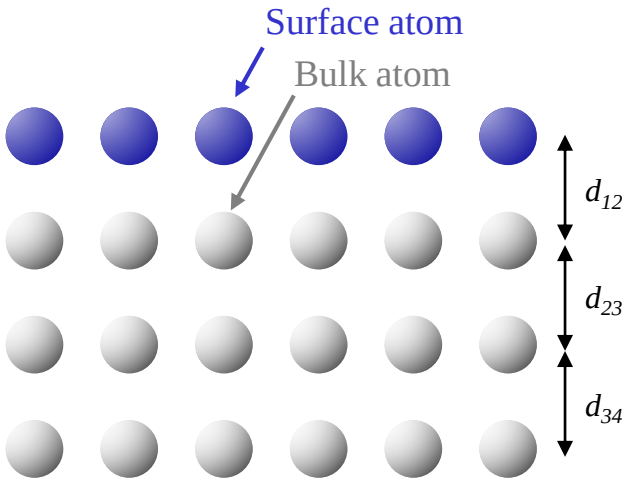
- To decrease the surface energy of cubotahedron nanoparticle, the growth of (111) plane is mostly advantageous to form the octahedron nanoparticle.



How to reduce surface energy? 1. surface relaxation

- Surface relaxation

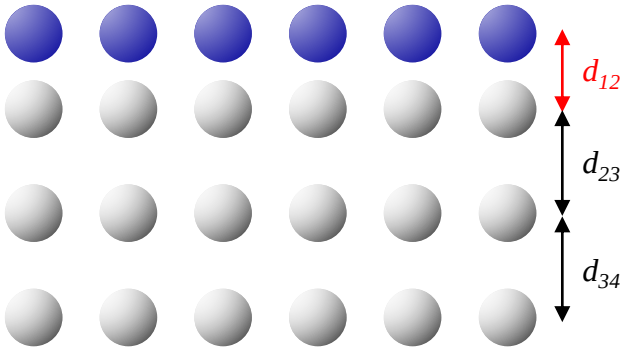
Side view



Original surface

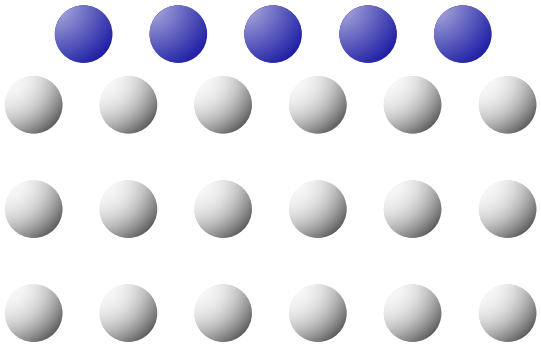
$d_{12} = d_{23} = d_{34}$

Inward shift



$d_{12} < d_{23} = d_{34}$

Lateral shift



How to reduce surface energy? 2. surface reconstruction

- Surface reconstruction of Si surface

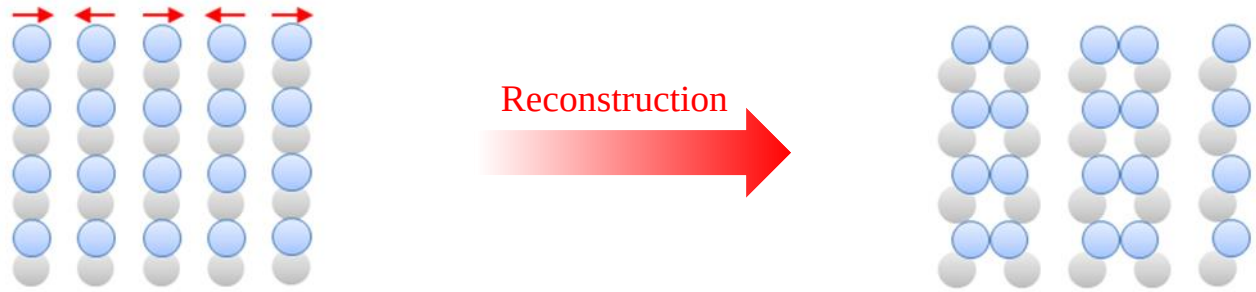
Side view

Decreasing the number of dangling bond

Original Si surface

Reconstructed Si surface

Top view



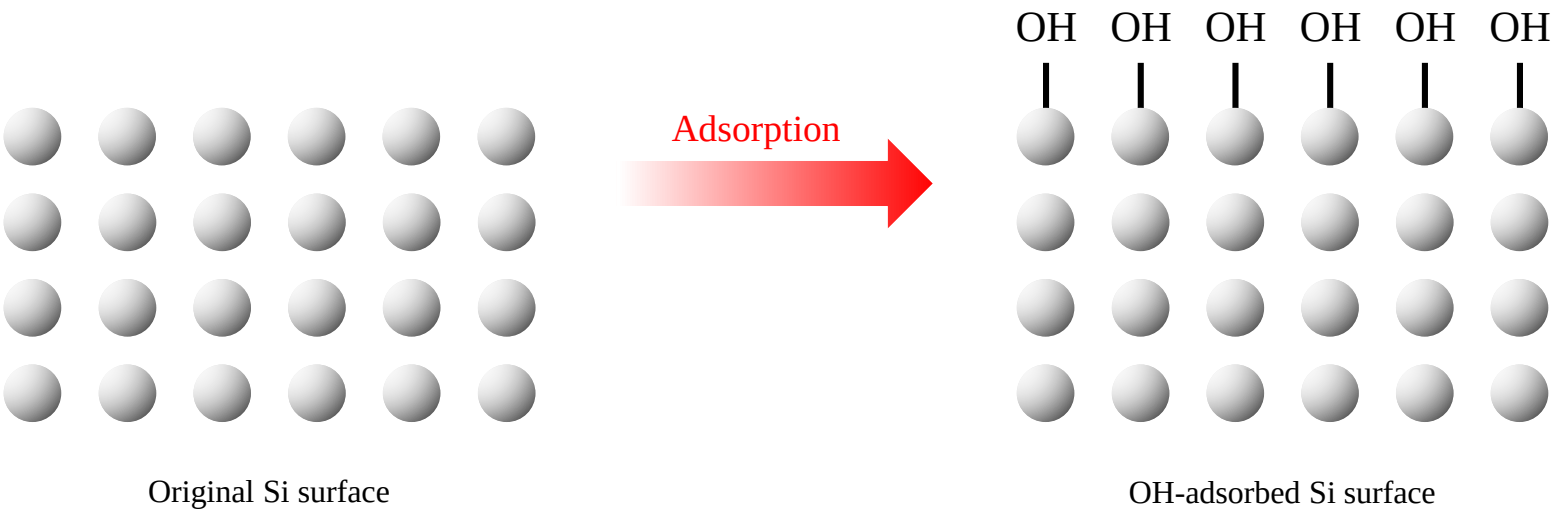
Original Si surface

Reconstructed Si surface

How to reduce surface energy? 3. surface adsorption

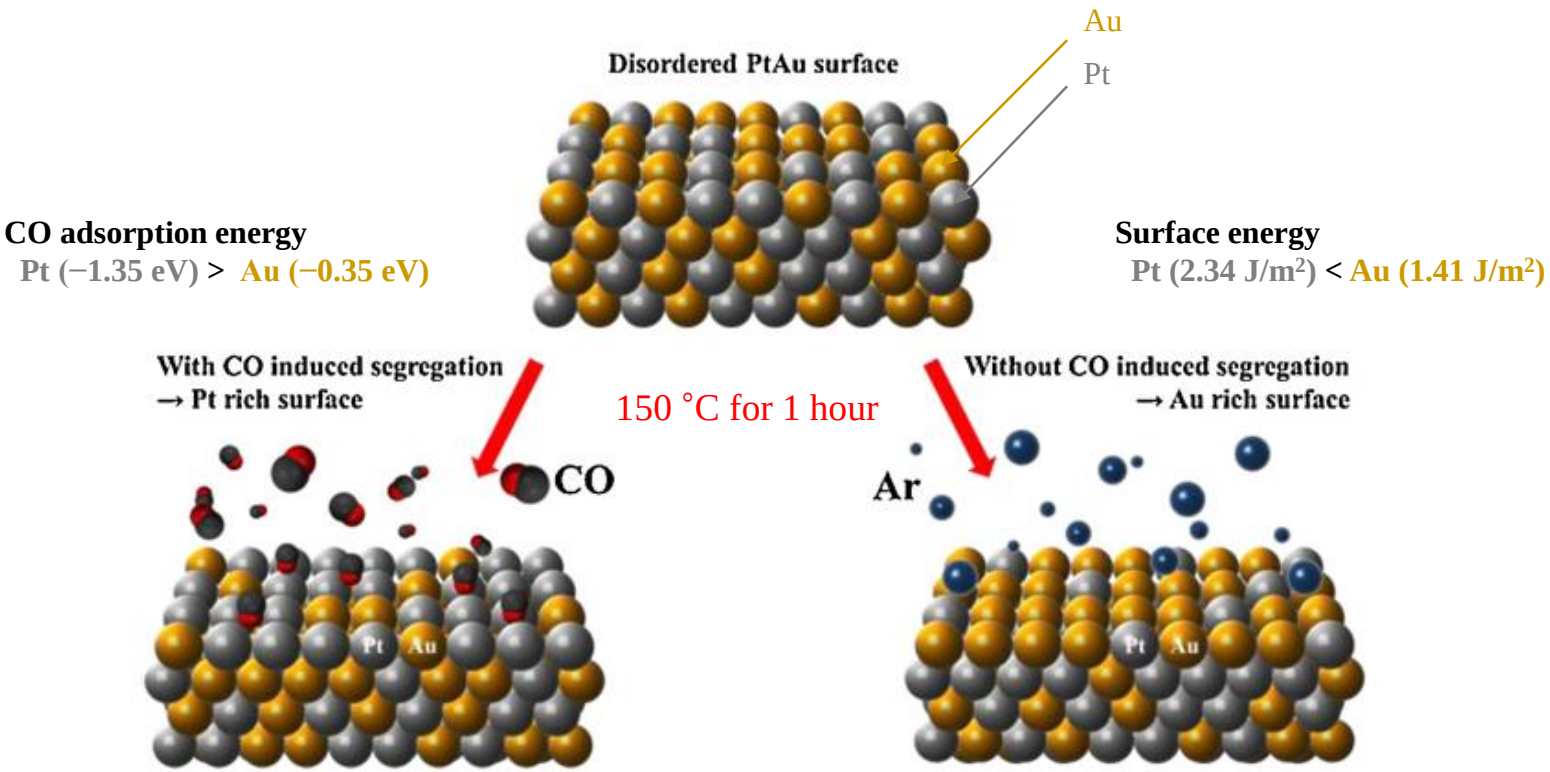
- Surface adsorption of hydroxyl group on silicon surface

Side view



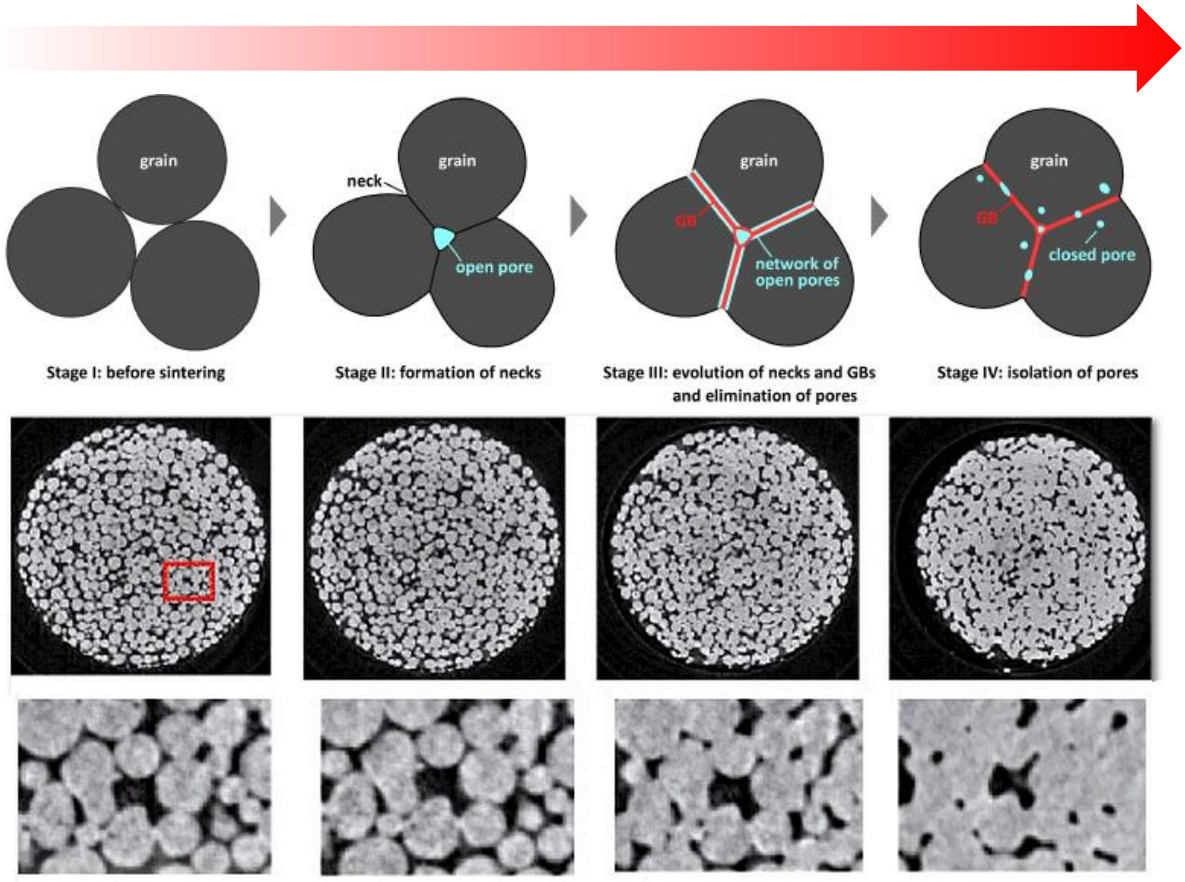
How to reduce surface energy? 4. surface segregation

- Surface segregation of disordered PtAu surface



How to reduce surface energy? 5. sintering

- Sintering of Cu clusters



How to reduce surface energy? 6. Ostwald ripening

- Ostwald ripening of Pd nanoparticles