Physics of Materials

Chapter 2: Crystallography

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Masters Course PHYS-307

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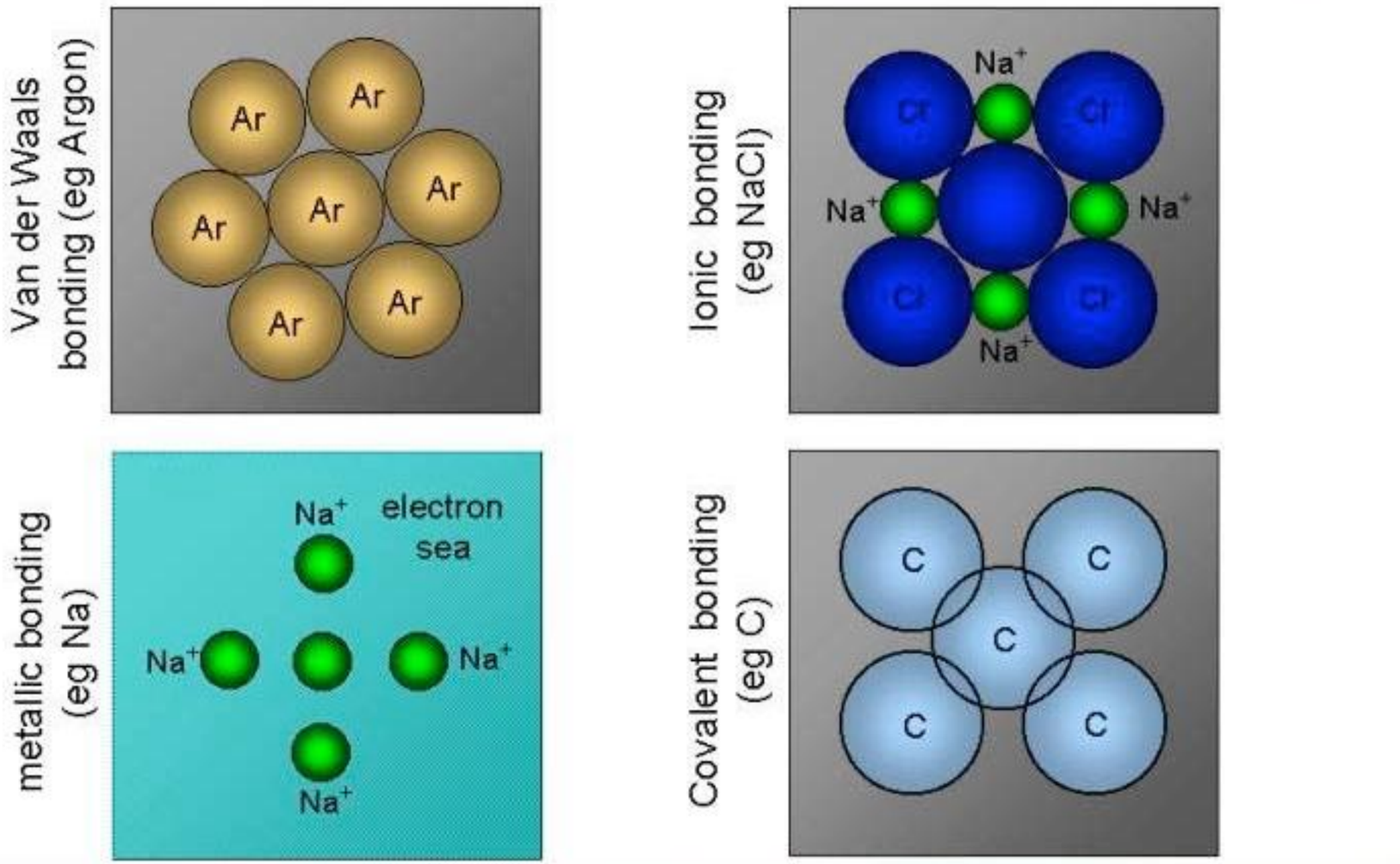
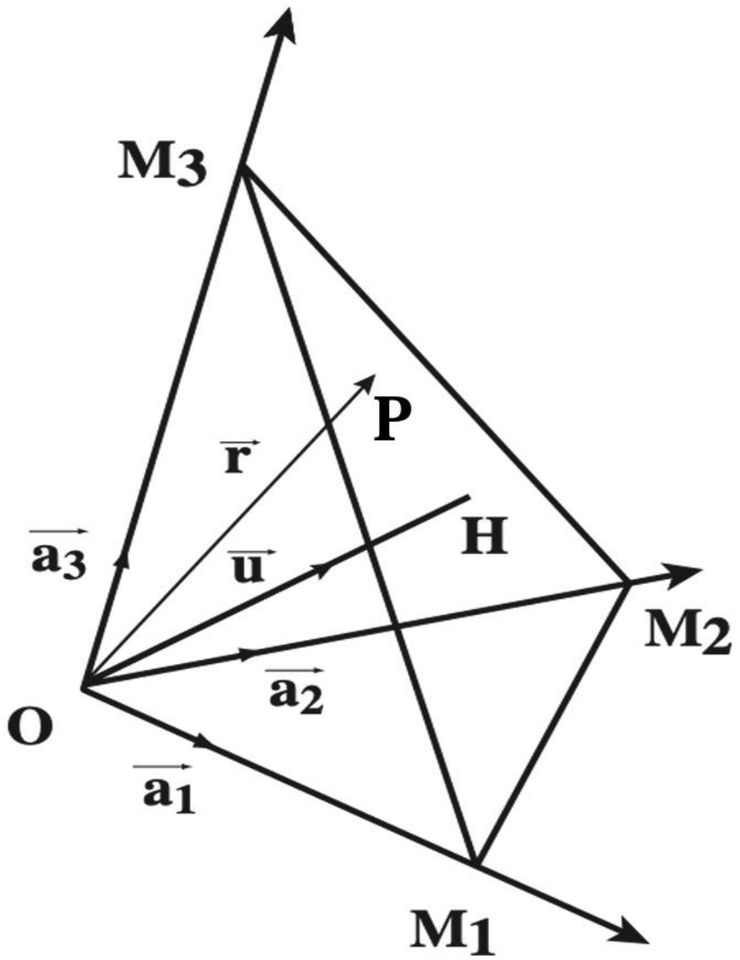
Atomic bonding: structures



Nodes of the periodic lattice



$$\overrightarrow{OM} = m_1\vec{a}_1 + m_2\vec{a}_2 + m_3\vec{a}_3$$

$$\overrightarrow{OM} = m\left(m'_1\vec{a}_1 + m'_2\vec{a}_2 + m'_3\vec{a}_3\right) = m\overrightarrow{OM}' \quad \text{with } m \text{ the GCD}$$

$$\overrightarrow{OM_1} = n_1\vec{a}_1$$
$$\overrightarrow{OM_2} = n_2\vec{a}_2$$
$$\overrightarrow{OM_3} = n_3\vec{a}_3$$

equation of the plane M_1, M_2, M_3

$$\vec{r} = x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3 = \overrightarrow{OP}$$

$$\vec{r}\cdot\vec{u} = OH$$

$$OH = x\left(\vec{a}_1\cdot\vec{u}\right) + y\left(\vec{a}_2\cdot\vec{u}\right) + z\left(\vec{a}_3\cdot\vec{u}\right)$$

$$\overrightarrow{M_1M_2} = n_2\vec{a}_2 - n_1\vec{a}_1$$
$$\overrightarrow{M_2M_3} = n_3\vec{a}_3 - n_2\vec{a}_2$$
$$\overrightarrow{M_1M_3} = n_3\vec{a}_3 - n_1\vec{a}_1$$

but $\overrightarrow{OM_1}\cdot\vec{u} = n_1\vec{a}_1\cdot\vec{u} = OH$ .....

$$\left(\vec{a}_1\cdot\vec{u}\right) = \frac{OH}{n_1} \quad \left(\vec{a}_2\cdot\vec{u}\right) = \frac{OH}{n_2} \quad \left(\vec{a}_3\cdot\vec{u}\right) = \frac{OH}{n_3}$$

The equation of the plane becomes:

$$\frac{x}{n_1}+\frac{y}{n_2}+\frac{z}{n_3}=1$$

let n be their GCD so that:

$$n_1 = nn_1' \quad n_2 = nn_2' \quad n_3 = nn_3'$$

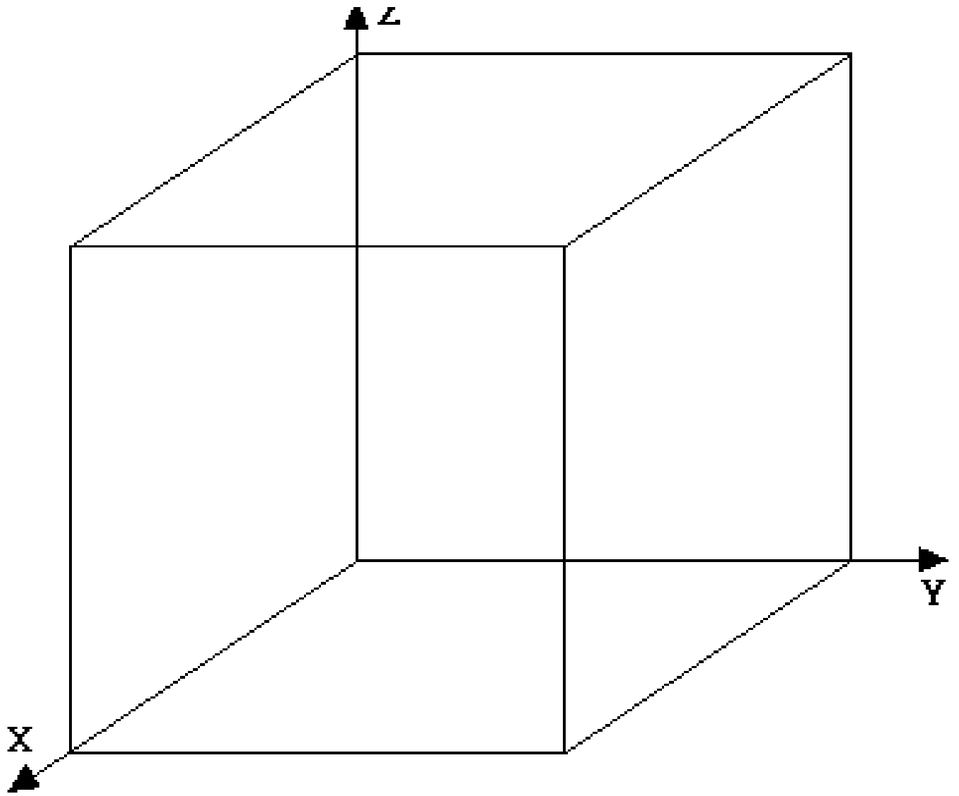
or $\frac{x}{n'_1}+\frac{y}{n'_2}+\frac{z}{n'_3}=1$ $n'_1, n'_2 n'_3$ are prime numbers

$$n'_2 n'_3 x + n'_1 n'_3 y + n'_1 n'_2 z = n'_1 n'_2 n'_3$$

Miller indices

$$h = n'_2 n'_3 \quad k = n'_1 n'_3 \quad l = n'_1 n'_2$$

Examples equation of the plane



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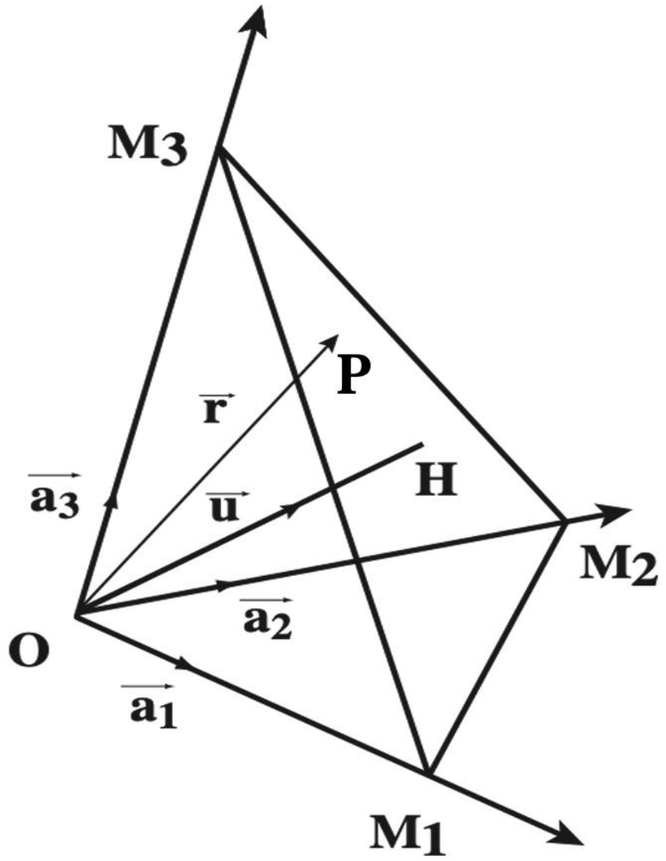
Normal vectors to crystallographic planes

$$\vec{u} = \left(n'_2 \vec{a_2} - n'_1 \vec{a_1}\right) \times \left(n'_3 \vec{a_3} - n'_1 \vec{a_1}\right)$$

$$\vec{u} = n'_2 n'_3 \left(\vec{a_2} \times \vec{a_3}\right) + n'_3 n'_1 \left(\vec{a_3} \times \vec{a_1}\right) + n'_1 n'_2 \left(\vec{a_1} \times \vec{a_2}\right)$$

$$\vec{u} = \quad h\left(\vec{a_2} \times \vec{a_3}\right) \quad + \quad k\left(\vec{a_3} \times \vec{a_1}\right) \quad + \quad l\left(\vec{a_1} \times \vec{a_2}\right)$$

$$\vec{u} = \quad h\vec{a_1^*} \quad + \quad k\vec{a_2^*} \quad + \quad l\vec{a_3^*} = \vec{r^*}$$



It would be better to normalize $\vec{a_i} \cdot \vec{a_i^*} = 1$

$$\vec{a_1^*} = \frac{\left(\vec{a_2} \times \vec{a_3}\right)}{\vec{a_1} \cdot \left(\vec{a_2} \times \vec{a_3}\right)} = \frac{\left(\vec{a_2} \times \vec{a_3}\right)}{V}$$

but also $\vec{a_1^*} \times \vec{a_2^*} = \frac{\vec{a_3}}{V}$

Distance between crystalline planes $\left\| \vec{r_{hkl}^*} \right\| = \frac{1}{d_{hkl}}$

The intersection of two crystalline planes

$$h_1 x + k_1 y + l_1 z = 0$$
$$h_2 x + k_2 y + l_2 z = 0$$

plane through origin

The common line between the two planes is given on the basis $\left(\vec{a_1}, \vec{a_2}, \vec{a_3}\right)$ by the vector

$$\left(k_1 l_2 - l_1 k_2\right)\vec{a_1} + \left(l_1 h_2 - h_1 l_2\right)\vec{a_2} + \left(h_1 k_2 - h_2 k_1\right)\vec{a_3}$$

Reciprocally by taking two vectors of the direct lattice

$$x\vec{a_1} + y\vec{a_2} + z\vec{a_3} \quad \text{and} \quad x'\vec{a_1} + y'\vec{a_2} + z'\vec{a_3}$$

The normal to the plane formed by these vectors is given by

$$\left(yz' - y'z\right)\vec{a_1^*} + \left(x'z - xz'\right)\vec{a_2^*} + \left(xy' - x'y\right)\vec{a_3^*}$$

Matrix math for non-orthonormal basis

$$\left(x\vec{a_1}+y\vec{a_2}+z\vec{a_3}\right)\cdot\left(x'\vec{a_1}+y'\vec{a_2}+z'\vec{a_3}\right)=\begin{pmatrix} x & y & z \end{pmatrix}\begin{pmatrix} a_1^2 & \vec{a_1}\cdot\vec{a_2} & \vec{a_1}\cdot\vec{a_3} \\ \vec{a_1}\cdot\vec{a_2} & a_2^2 & \vec{a_2}\cdot\vec{a_3} \\ \vec{a_1}\cdot\vec{a_3} & \vec{a_2}\cdot\vec{a_3} & a_3^2 \end{pmatrix}\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}=\vec{r_T}M\vec{r}$$

M is called metric tensor; its determinant is the Volume^2

$$\left(h\vec{a^*_1}+k\vec{a^*_2}+l\vec{a^*_3}\right)\cdot\left(h'\vec{a^*_1}+k'\vec{a^*_2}+l'\vec{a^*_3}\right)=\begin{pmatrix} h & k & l \end{pmatrix}\begin{pmatrix} a^{*2}_1 & \vec{a^*_1}\cdot\vec{a^*_2} & \vec{a^*_1}\cdot\vec{a^*_3} \\ \vec{a^*_1}\cdot\vec{a^*_2} & a^{*2}_2 & \vec{a^*_2}\cdot\vec{a^*_3} \\ \vec{a^*_1}\cdot\vec{a^*_3} & \vec{a^*_2}\cdot\vec{a^*_3} & a^{*2}_3 \end{pmatrix}\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix}$$

$$=\vec{h_T}M^*\vec{h} \qquad and\ M^*=M^{-1}$$

Bragg diffraction

If we consider X-rays (and electrons) as plane waves $E = E_0 \exp(kx - \omega t)$

Wave vector $\vec{S}$ with amplitude $k = \frac{2\pi}{\lambda}$

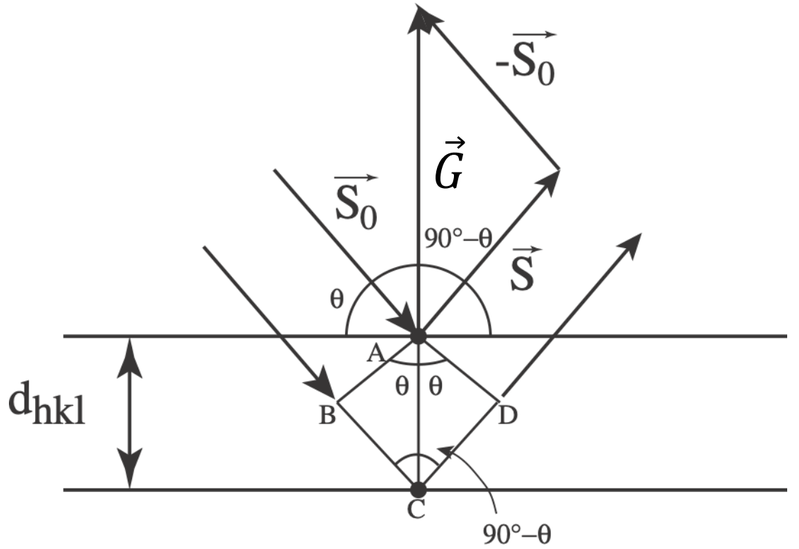
Constructive interference if $BC + CD = n\lambda$

$$2d_{hkl}\cos(90-\theta) = 2d_{hkl}\sin\theta = n\lambda$$

In effect this can be written as:

$\vec{S} - \vec{S}_0 = \vec{G}$ G is a reciprocal lattice vector

$$\left\|\vec{S} - \vec{S}_0\right\| = \left\|\vec{G}\right\| \Rightarrow 2\|S\|\sin\theta = 2\left(\frac{2\pi}{\lambda}\right)\sin\theta = \frac{2\pi}{d_{hkl}}$$

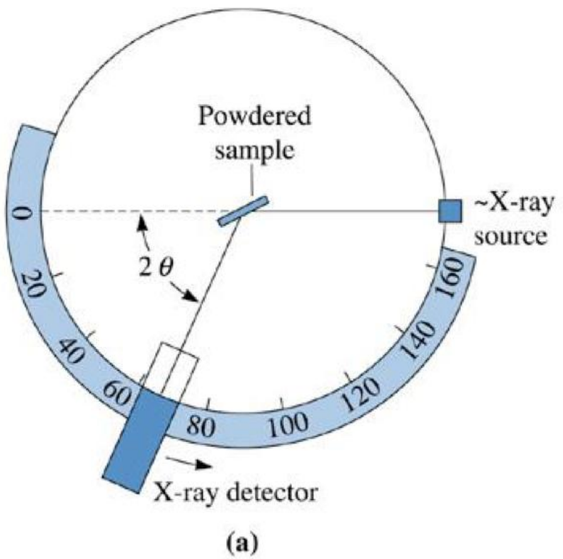


$$\left\|\vec{S}\right\| = \left\|\vec{S}_0\right\|$$

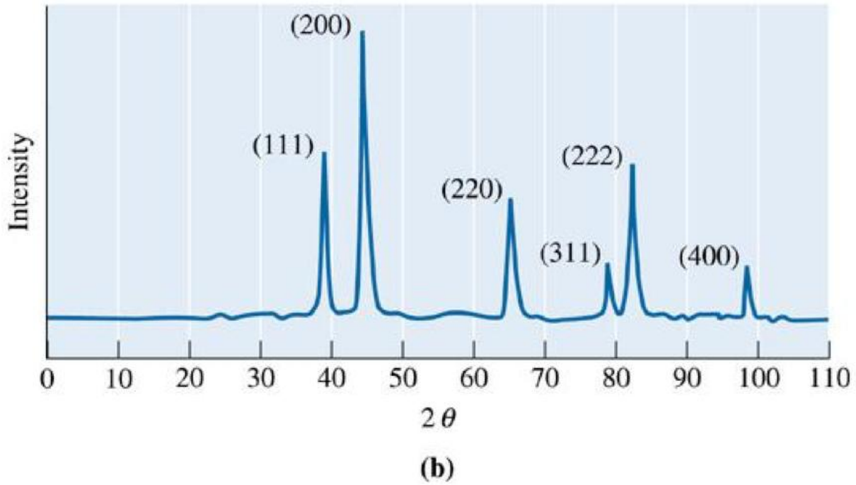
conservation of momentum

$$G = \frac{2\pi}{d_{hkl}} = \left\|\vec{r}^{\,*}_{hkl}\right\| = \frac{1}{d_{hkl}}$$

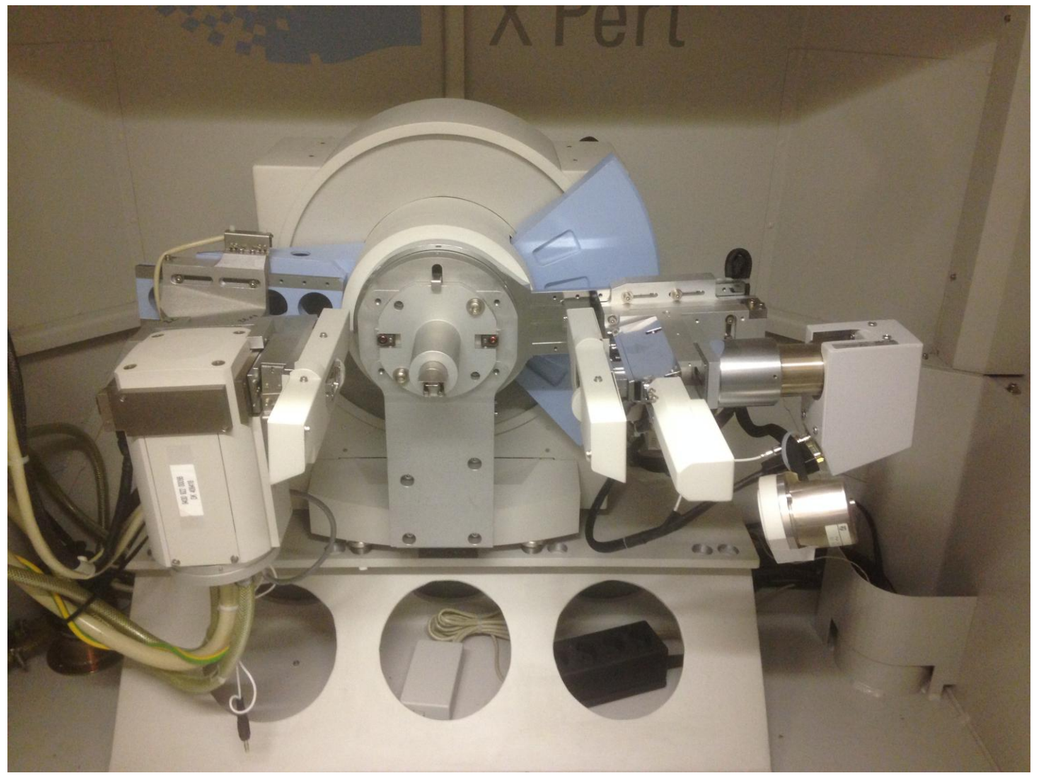
X-ray diffraction



(a)



(b)



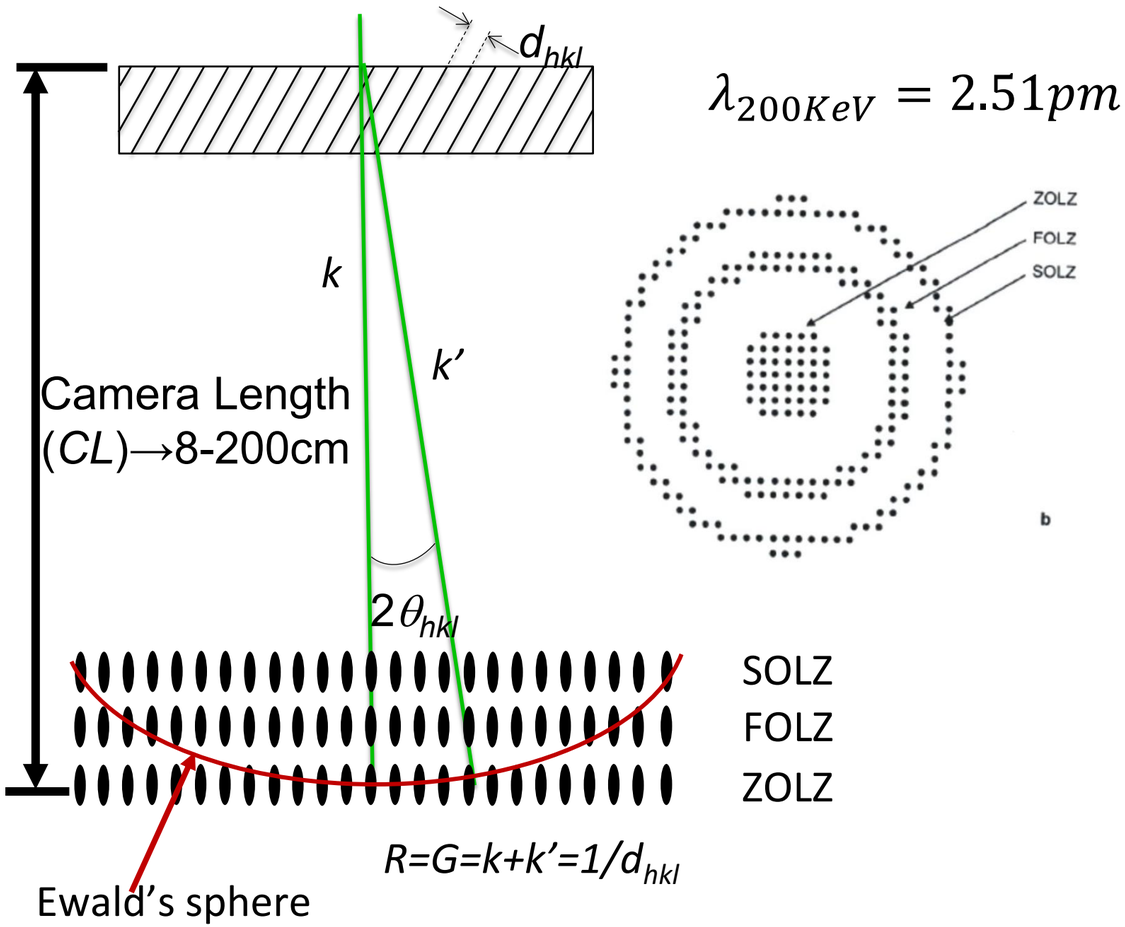
fcc Au

$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2 + k^2 + l^2}$$

Transmission Electron Diffraction

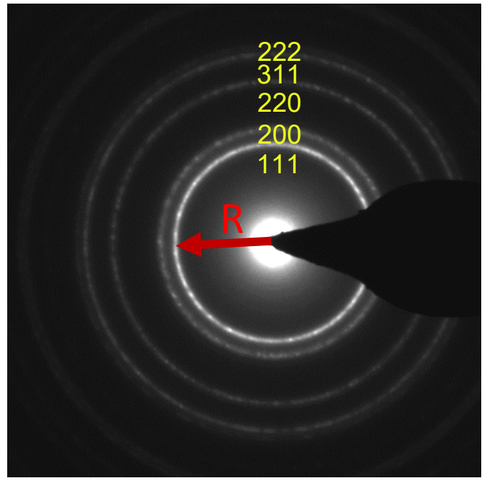
$$2dsin\theta = 2\theta d = n\lambda$$

$$R\lambda = 2\theta = R/CL,\ d_{hkl} = \lambda CL/R$$

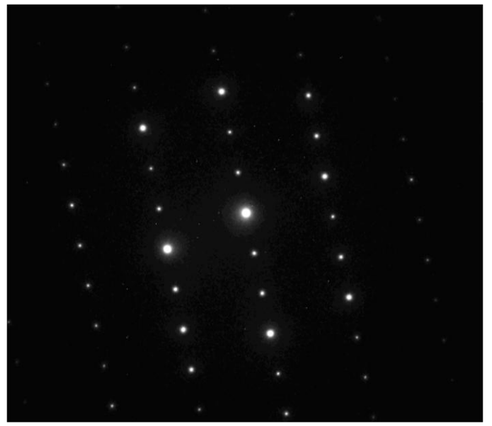


$$\lambda_{200KeV} = 2.51pm$$

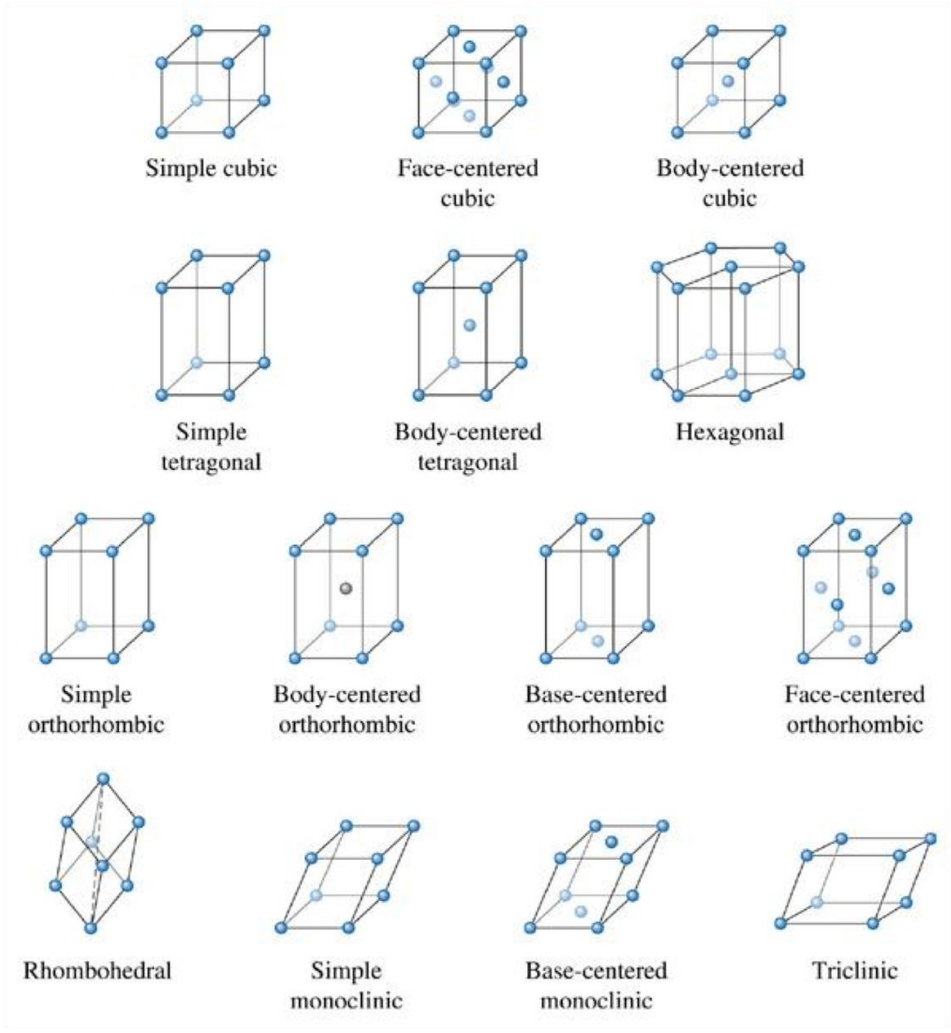
Bragg Diffraction Powder Pattern



Single Crystal Spot Pattern



Crystallography



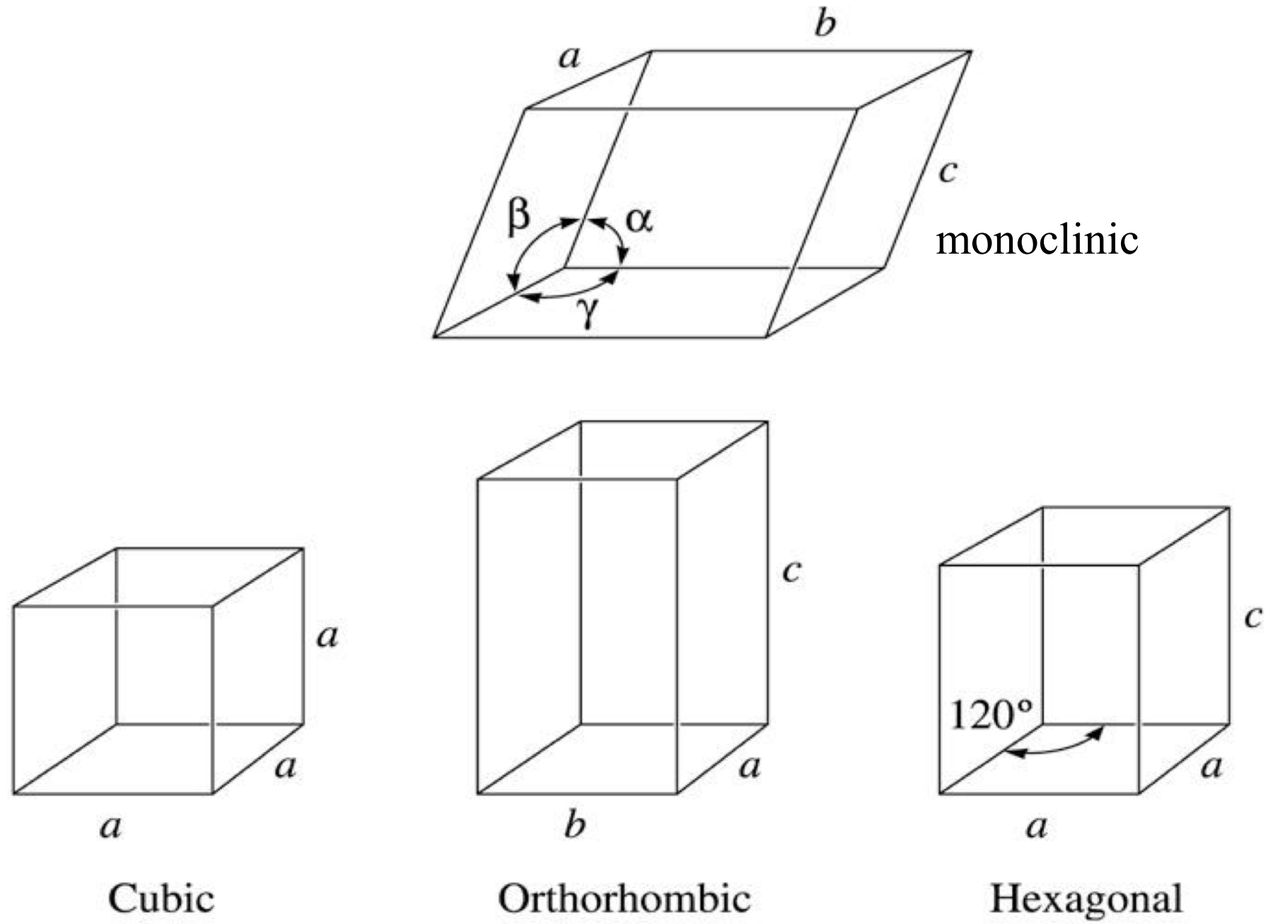
Metals

Ceramics
(ionic bonds)

Polymers
(covalent bonding)

14 Bravais lattices

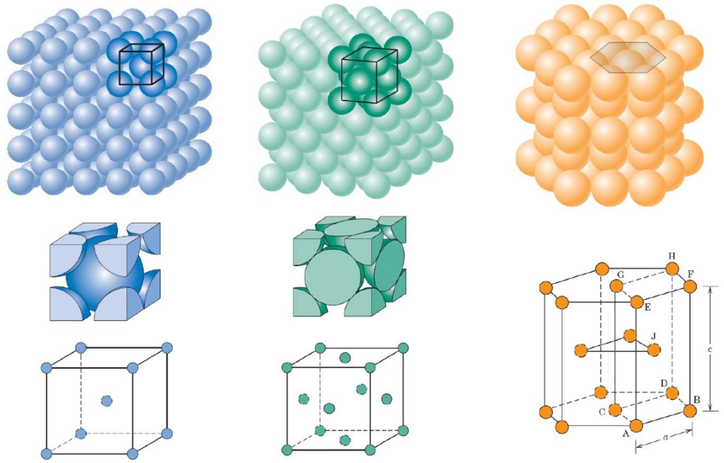
Definition of crystalline cell angles and edges



Characteristics of 7 crystalline systems

Structure	Axis	Angles between axis	Volume of the cell
Cubic	$a=b=c$	$all = 90°$	a^3
Tetrahedral	$a=b\neq c$	$all = 90°$	$a^2 \cdot c$
Orthorhombic	$a\neq b\neq c$	$all = 90°$	$a \cdot b \cdot c$
Hexagonal	$a=b\neq c$	$\alpha=\beta=90°, \gamma=120°$	$\sqrt{3}/2 \cdot a^2 c$
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$	$a^3\sqrt{1-3(\cos\alpha)^2+2(\cos\alpha)^3}$
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°, \beta\neq 90°$	$a \cdot b \cdot c \sin\beta$
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	$abc\sqrt{1-(\cos\alpha)^2-(\cos\beta)^2-(\cos\gamma)^2+2\cos\alpha\cos\beta\cos\gamma}$

Structure of metals



Metal Elements from the Periodic Table

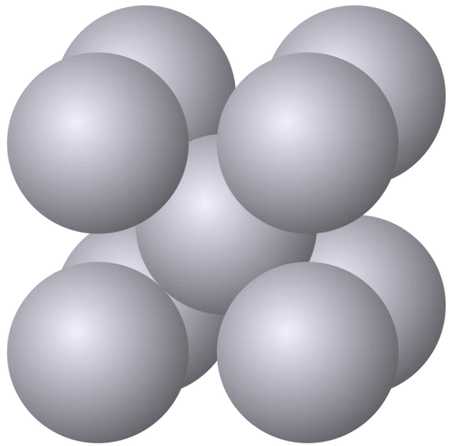
Li	Be																
Na	Mg														Al		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn				
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb				
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		

CCP (Cubic Close Packing) · HCP (Hexagonal Close Packing) · BCC (Body Centered Cubic) · HC (4H) · ? (Other)

19/08/2008 chemtips.com

Compact Structures

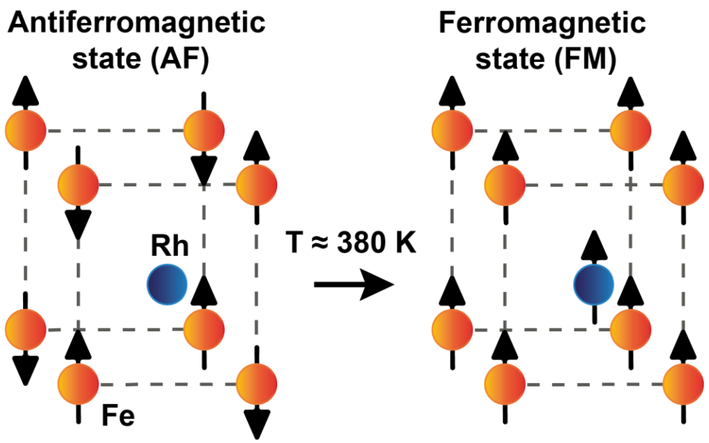
Body centered cubic structure

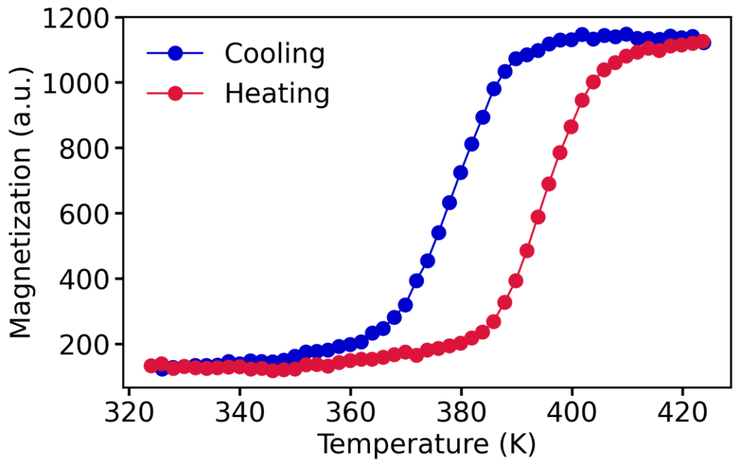


iron, chromium, tungsten.....

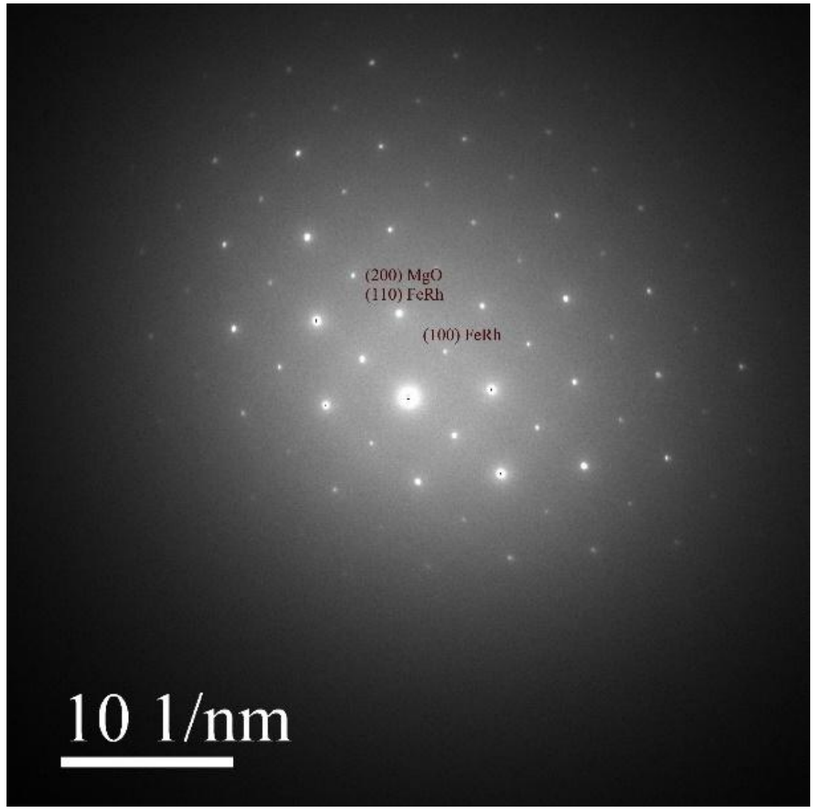
Electron Diffraction Example ordered BCC

$Fe_xRh_{1-x}; x \in (0.48; 0.52)$

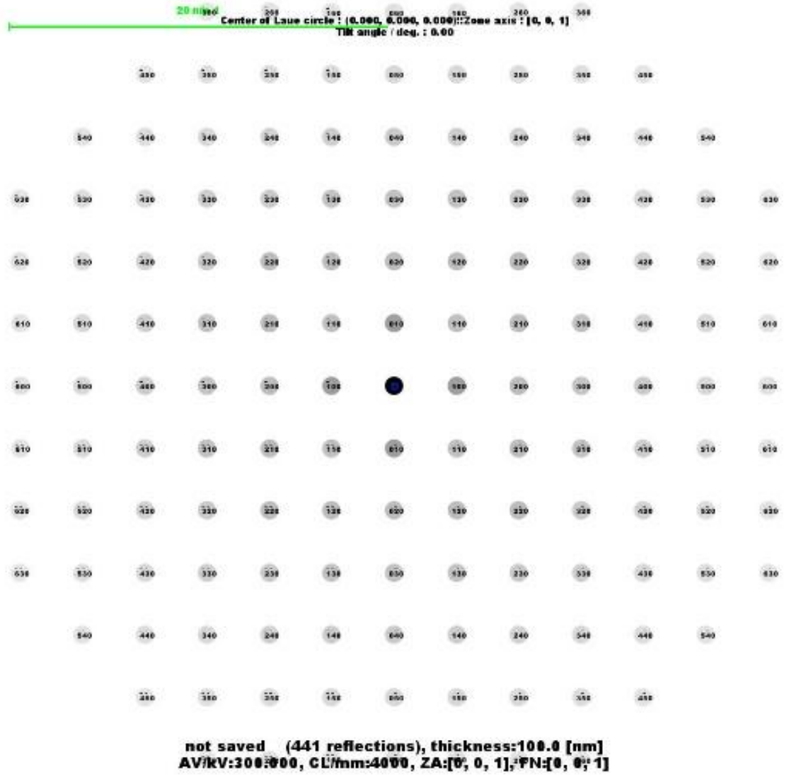




TEM diffraction



FeRh [100]ZA simulation



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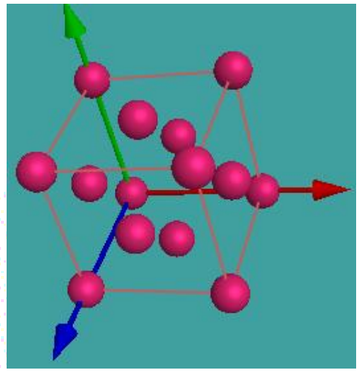
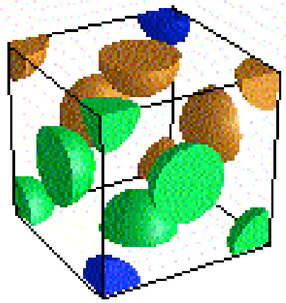
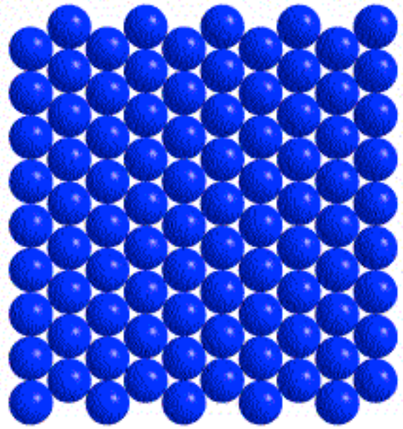
Compact Structures

Face centered cubic structure





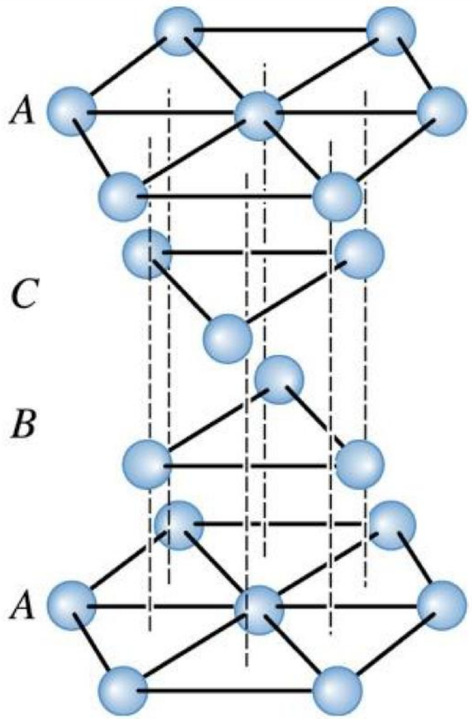
Stacking A-B-C-A-B sequence

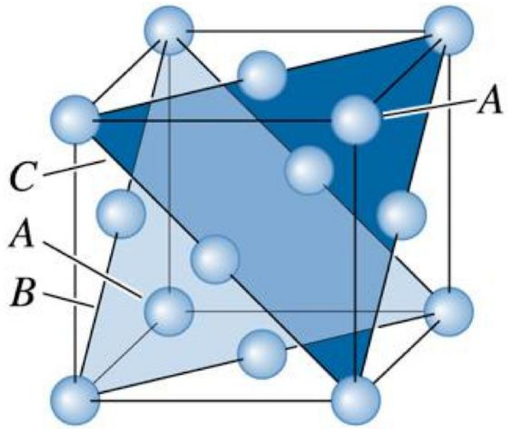


aluminum, nickel, gold.....

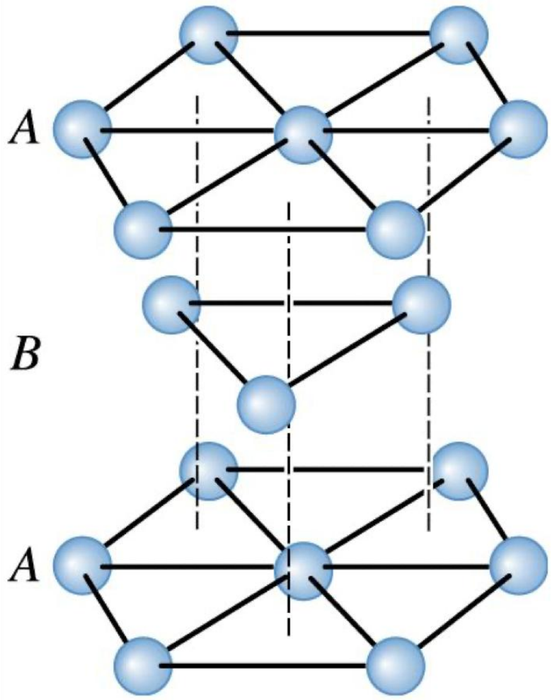
Compact Structures

Stacking in the FCC



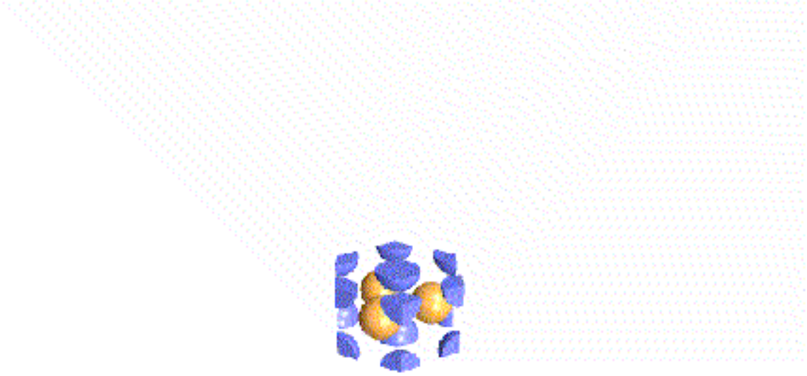


HCP

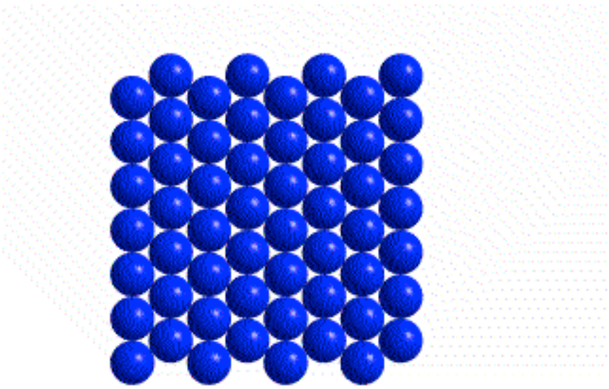


Compact Structures

Hexagonal compact structure



A-B-A-B structure

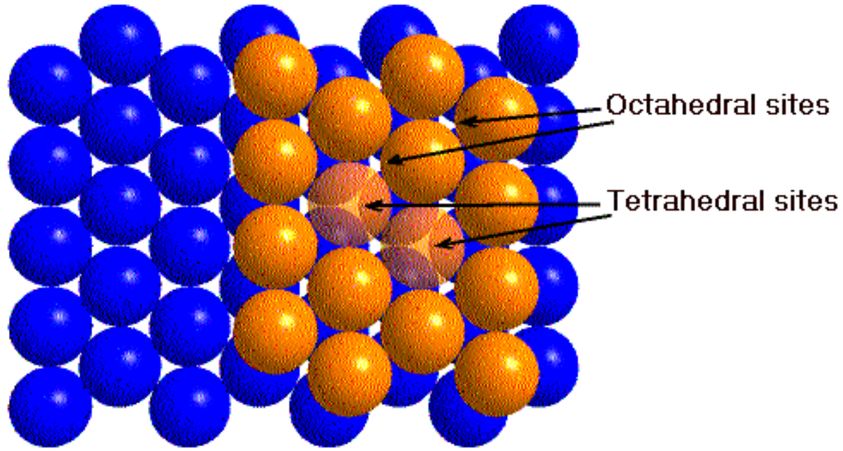


Comparison between structures

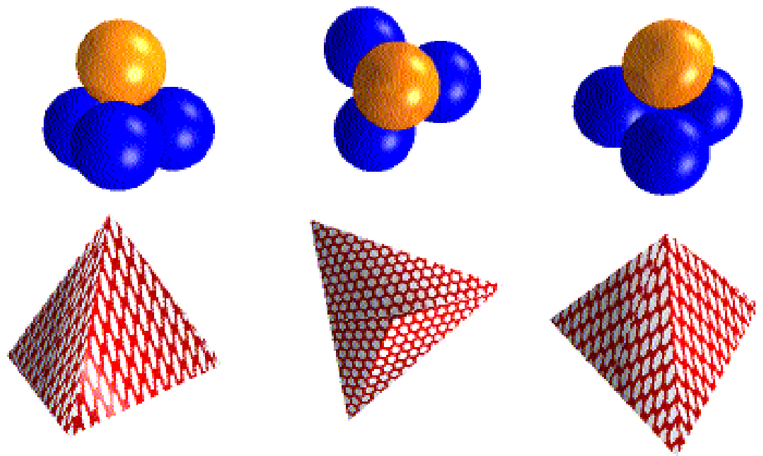
HCP FCC

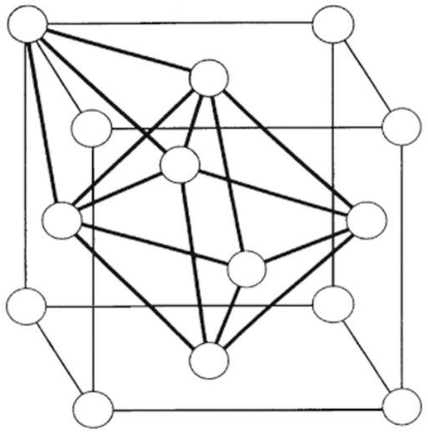
(001) (111)

Interstitial sites in FCC metals

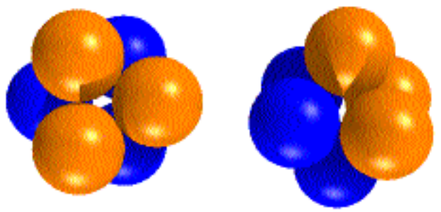


Tetrahedral sites

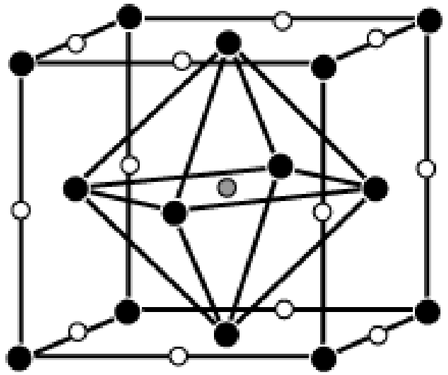




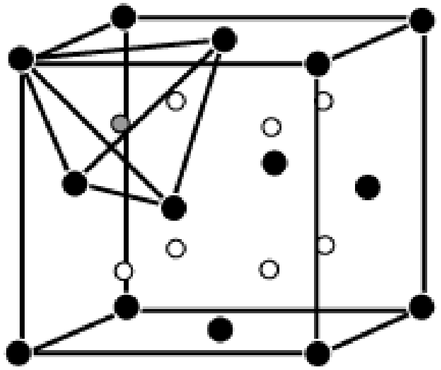
Octahedral sites

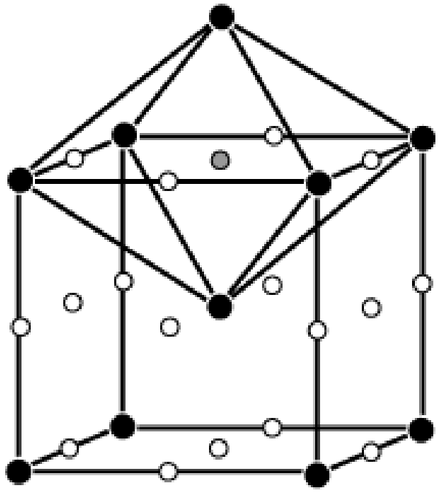


Interstitial sites

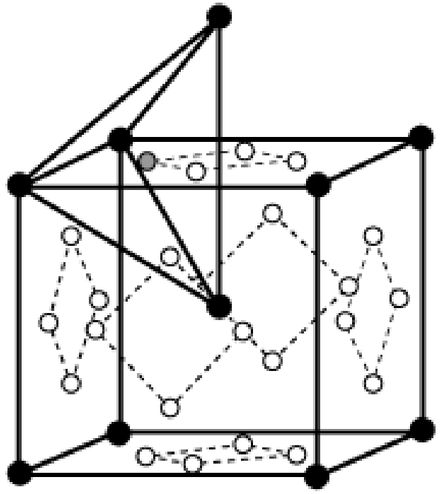


fcc





bcc



octahedral

tetrahedral

Coordination number
atomic radius

Table 9 Atomic and ionic radius

Approximative values. For origin references, consult W.B. Pearson, *Crystal chemistry and physics of metals and alloys,* Wiley, 1972.

Units: 1 Å = 10^{-10} m

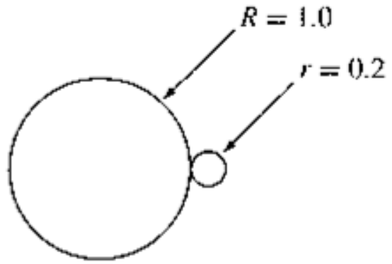
Symbole — Mg
0,65 — Standard radii for ions in the configuration of neutral gases (filled layer)
1,40 — Radius of atoms in the case of tetrahedral covalent bonds
1,60 — Radius of ions for coordination number of 12 (metals)

H 2,08																	He
Li 0,68 1,56	Be 0,35 1,06 1,13											B 0,23 0,88 0,98	C 0,15 0,77 0,92	N 1,71 0,70	O 1,40 0,66	F 1,36 0,64	Ne 1,58
Na 0,97 1,91	Mg 0,65 1,40 1,60											Al 0,50 1,26 1,43	Si 0,41 1,17 1,32	P 2,12 1,10	S 1,84 1,04	Cl 1,81 0,99	Ar 1,88
K 1,33 2,38	Ca 0,99 1,98	Sc 0,81 1,64	Ti 0,68 1,46	V 1,35	Cr 1,28	Mn 1,26	Fe 1,27	Co 1,25	Ni 1,25	Cu 1,35 1,28	Zn 0,74 1,31 1,39	Ga 0,62 1,26 1,41	Ge 0,53 1,22 1,37	As 2,22 1,18 1,39	Se 1,98 1,14	Br 1,95 1,11	Kr 2,00
Rb 1,48 2,55	Sr 1,13 2,15	Y 0,93 1,80	Zr 0,80 1,60	Nb 0,67 1,47	Mo 1,40	Tc 1,36	Ru 1,34	Rh 1,35	Pd 1,38	Ag 1,26 1,52 1,45	Cd 0,97 1,48 1,57	In 0,81 1,44 1,66	Sn 0,71 1,40 1,55	Sb 2,45 1,36 1,59	Te 2,21 1,32	I 2,16 1,28	Xe 2,17
Cs 1,67 2,73	Ba 1,35 2,24	La 1,15 1,88	Hf 1,58	Ta 1,47	W 1,41	Re 1,38	Os 1,35	Ir 1,36	Pt 1,39	Au 1,37 1,44	Hg 1,10 1,48 1,57	Tl 0,95 1,72	Pb 0,84 1,75	Bi 1,70	Po 1,76	At	Rn
Fr 1,75 	Ra 1,37 	Ac 1,11 															

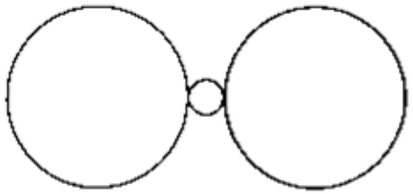
Ce 1,01 1,71– 1,82	Pr 1,83	Nd 1,82	Pm 1,81	Sm 1,80	Eu $2,04^{2+}$– $1,80^{3+}$	Gd 1,80	Tb 1,78	Dy 1,77	Ho 1,77	Er 1,76	Tm 1,75	Yb $1,94^{2+}$– $1,74^{3+}$	Lu
Th 0,99 1,80	Pa 0,90 1,63	U 0,83 1,56	Np 1,56	Pu 1,58– 1,64	Am 1,81	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Coordination number

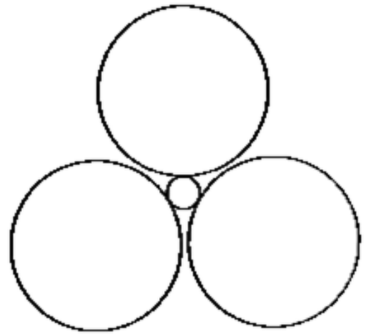
CN	*r/R*	geometry
2	$0 < \frac{r}{R} < 0.155$	
3	$0.155 \leq \frac{r}{R} < 0.225$	Triangle
4	$0.225 \leq \frac{r}{R} < 0.414$	Tetrahedron
6	$0.414 \leq \frac{r}{R} < 0.732$	Octahedron
8	$0.732 \leq \frac{r}{R} < 1$	Body Centered Cubic
12	1	or[a] Face Centered Cubic and Hexagonal Close Packed



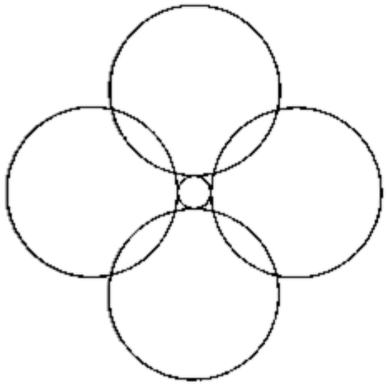
CN = 1 possible



CN = 2 possible

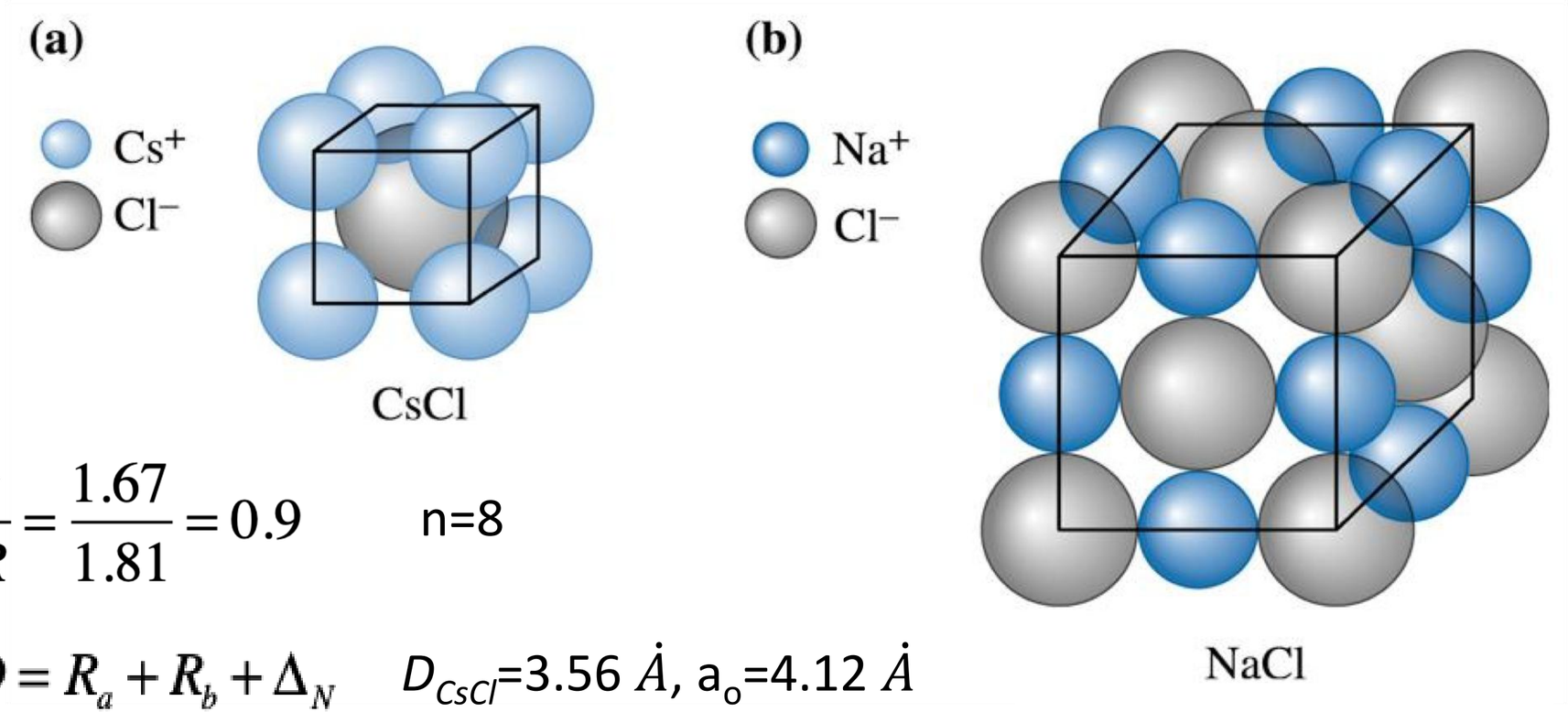


CN = 3 maximum



CN = 4 unstable

Composite structures



$$\frac{r}{R} = \frac{1.67}{1.81} = 0.9$$ n=8

$$D = R_a + R_b + \Delta_N$$ D_{CsCl}=3.56 $\dot{A}$, a_o=4.12 $\dot{A}$

N	Δ_N(Å)	N	Δ_N(Å)	N	Δ_N(Å)
1	-0.50	5	-0.05	9	0.11
2	-0.31	6	0	10	0.14
3	-0.19	7	0.04	11	0.17
4	-0.11	8	0.08	12	0.19

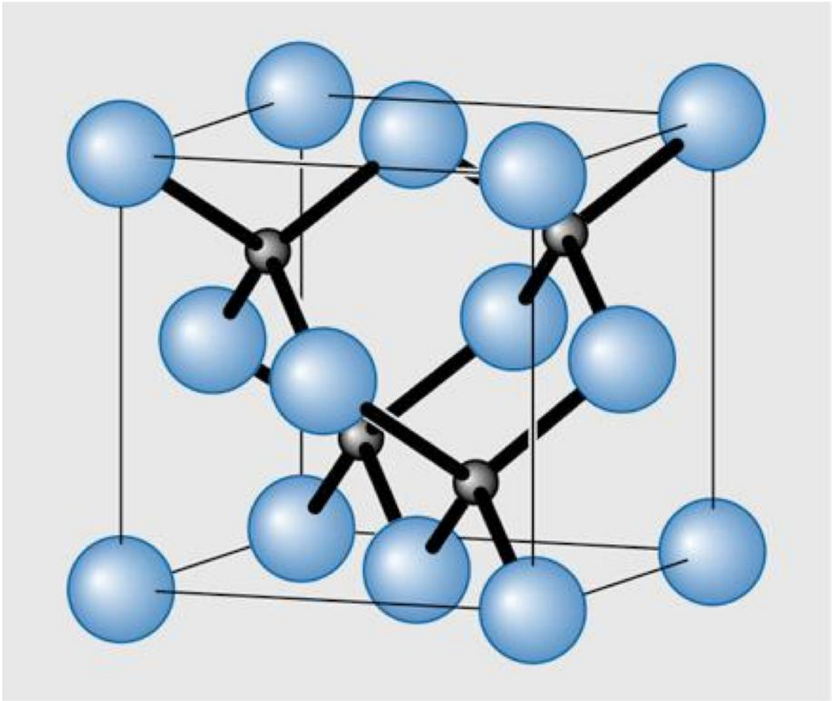
$$\frac{r}{R} = \frac{0.97}{1.81} = 0.5$$ n=6

Composite structures

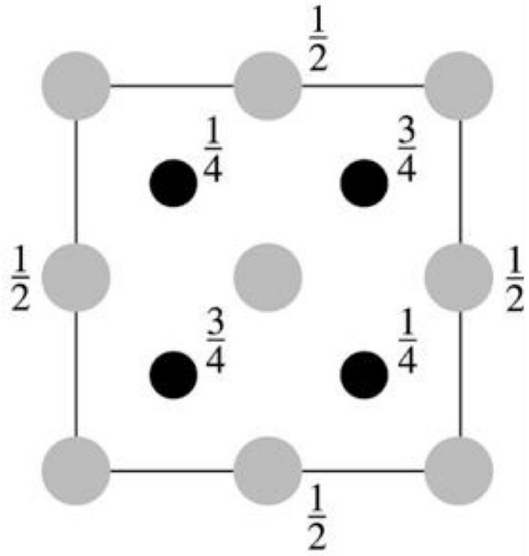
Sphalerite (zincblende)

$$\frac{r}{R} = \frac{0.74}{1.84} = 0.4$$

n=4



(a)



(b)

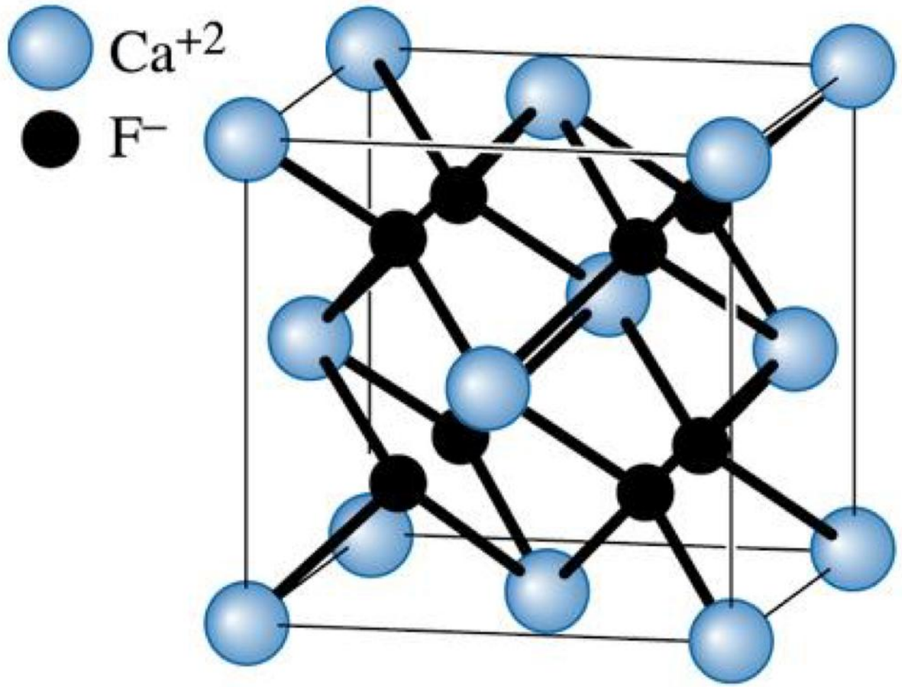
ZnS

Composite structures

Fluorite CaF_2

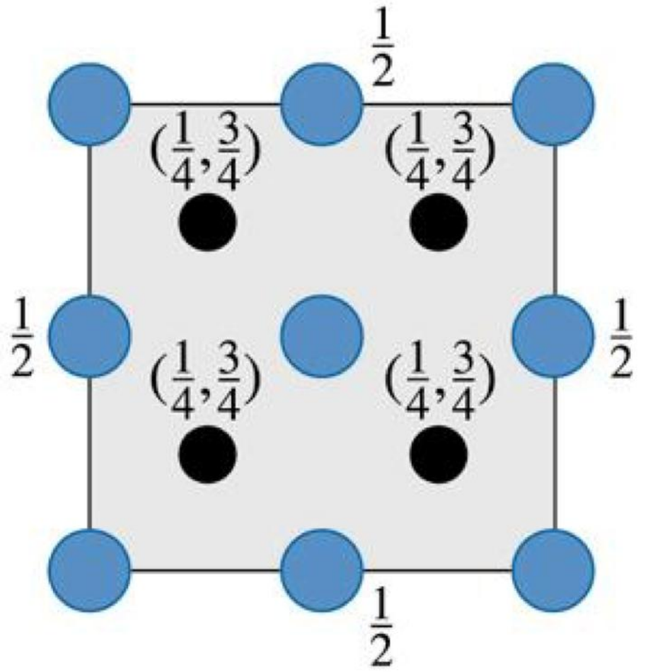
$n_{Ca}=8$

$$\frac{r}{R}=\frac{0.99}{1.36}=0.73$$



Flourite cell

(a)

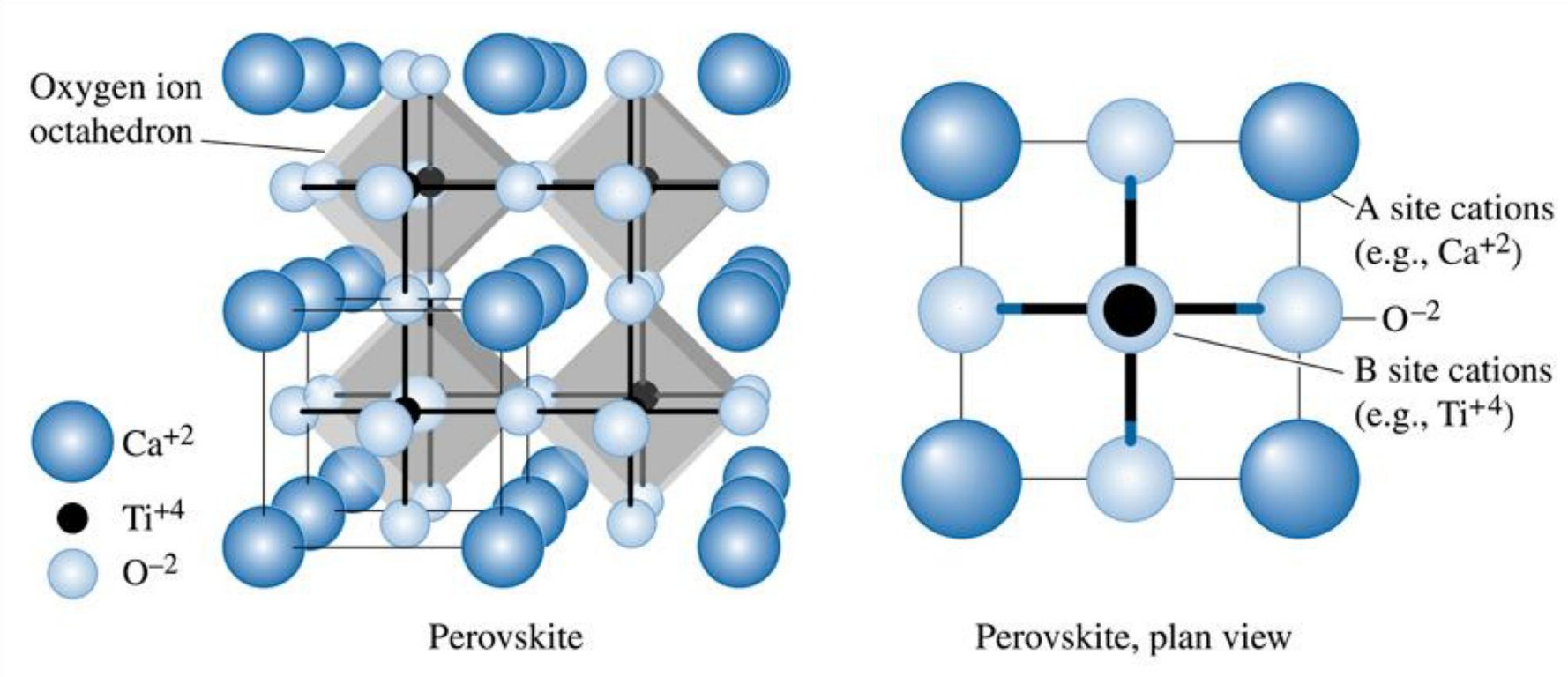


Plan view

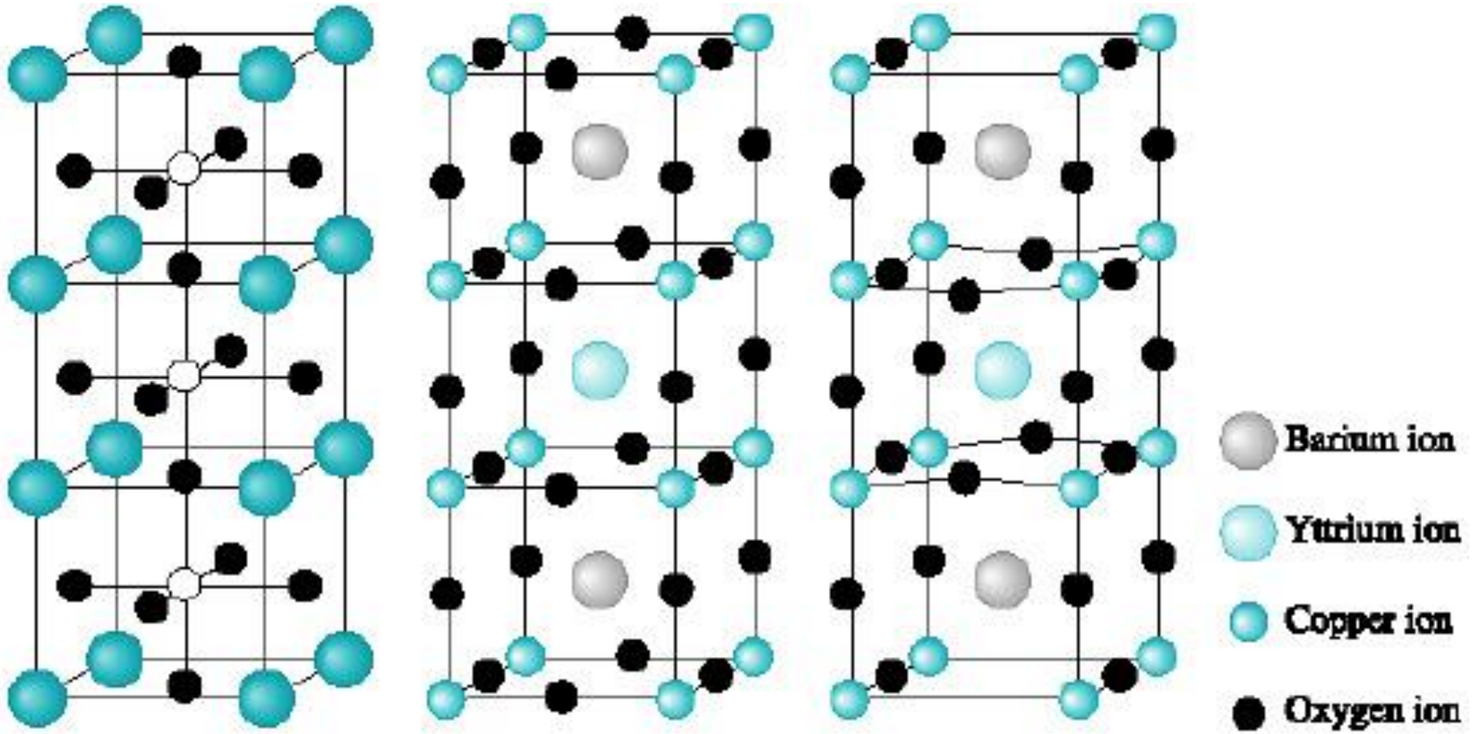
(b)

Composite structures

Perovskite $CaTiO_3$



Perovskite superconductor



Perovskite $YBa_2Cu_3O_7$