Chapter 2

Three-dimensional Lattices

in 3D, a Bravais lattice is an infinite array of discrete points that can be connected by a lattice translation vector

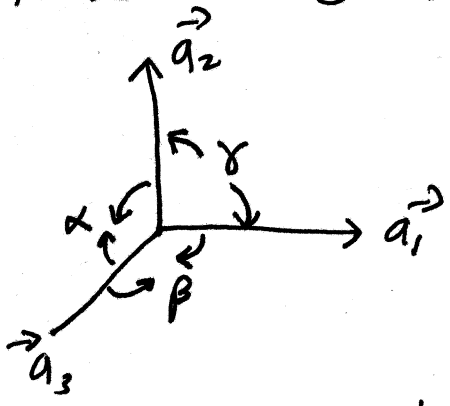
$$\vec{R} = n_1 \vec{a_1} + n_2 \vec{a_2} + n_3 \vec{a_3} \quad ; \quad n_1, n_2, n_3 : 0, \pm 1, \pm 2, \cdots$$

$\vec{a_1}, \vec{a_2}, \vec{a_3}$: primitive vectors which are non-coplanar and not necessary to be orthogonal

The volume of the primitive cell (parallelepiped) is given by

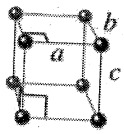
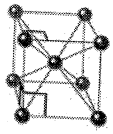
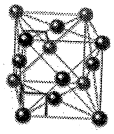
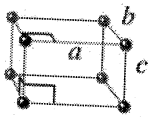
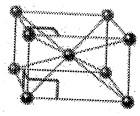
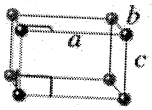
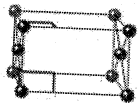
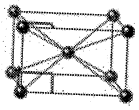
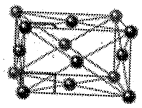
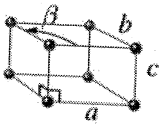
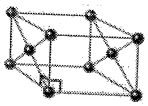
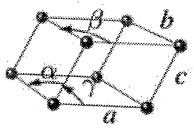
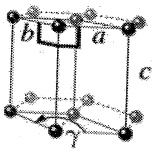
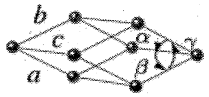
$$V = |\vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})|$$

↳ does not depend on the choice of $\vec{a_1}, \vec{a_2}, \vec{a_3}$



as mentioned earlier, and based on symmetries, there are 230 different lattices with a basis in 3D. However there are only 14 Bravais lattice among them that are fallen into 7 - crystal systems. In this course, we will restrict ourselves in studying the 14 Bravais lattices. The next table summarizes the 3D - 14 Bravais lattices.

Table 2.8. The seven crystal systems and fourteen Bravais lattices in three dimensions

	Simple	Base-Centered	Body-Centered	Face-Centered
Cubic $a=b=c$ $\alpha=\beta=\gamma=90°$				
Tetragonal $a\neq b=c$ $\alpha=\beta=\gamma=90°$				
Orthorhombic $a\neq b\neq c$ $\alpha=\beta=\gamma=90°$				
Monoclinic $a\neq b\neq c$ $\alpha=\gamma=90°$ $\beta\neq 90°$				
Triclinic $a\neq b\neq c$ $\alpha,\beta,\gamma\neq 90°$				
Hexagonal $a=b\neq c$ $\alpha=\beta=90°$ $\gamma = 120°$				
Rhombohedral $a=b=c$ $\alpha=\beta=\gamma\neq 90°$				

Monoatomic Lattices: lattices composed of atoms of a single element.

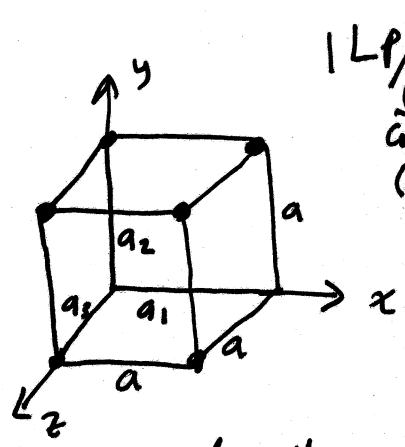
① The simple cubic lattice (SC)

$\vec{a_1} = a\hat{i}$; $\vec{a_2} = a\hat{j}$; $\vec{a_3} = a\hat{k}$

$V = a^3$; # of nearest neighbors = 6

There is only one element that adapts this structure: Vp = Vc

Polonium



1 LP/unit ce
↓
conven
(0,0,0)

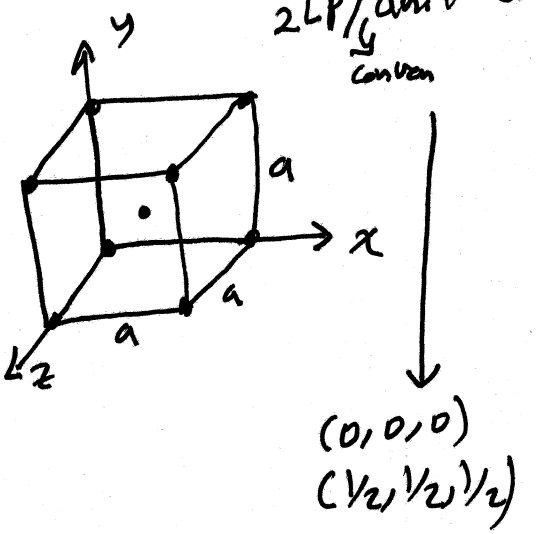
conventional cell ≡ primitive cell

② The body-centered cubic lattice (BCC)

$\vec{a_1} = \frac{a}{2}(\hat{i}+\hat{j}-\hat{k}) = \frac{a}{2}(1\ 1\ -1)$

$\vec{a_2} = \frac{a}{2}(-\hat{i}+\hat{j}+\hat{k}) = \frac{a}{2}(-1\ 1\ 1)$

$\vec{a_3} = \frac{a}{2}(\hat{i}-\hat{j}+\hat{k}) = \frac{a}{2}(1\ -1\ 1)$



Volume of primitive cell = $|\vec{a_1}\cdot(\vec{a_2}\times\vec{a_3})|$

$= \frac{a^3}{2}$, Vp = Vc /2

# of nearest neighbors = 8

Typical elements with BCC structure: Fe, Li, Na, K, Rb, Cs

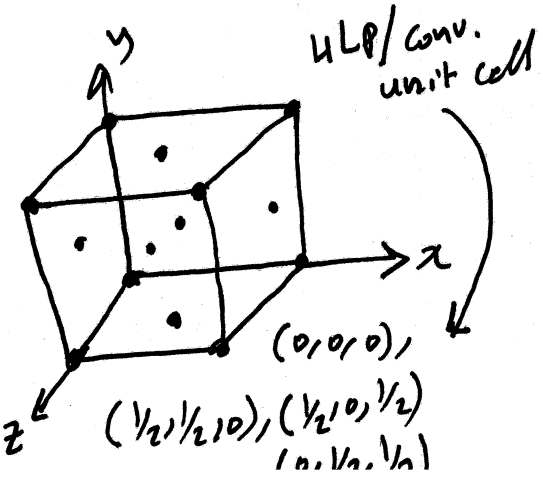
③ The face-centered cubic (FCC)

$\vec{a_1} = \frac{a}{2}(1\ 1\ 0)$; $V_p = \frac{a^3}{4}$, Vp = Vc /4

$\vec{a_2} = \frac{a}{2}(1\ 0\ 1)$; # of near. neighb = 12

$\vec{a_3} = \frac{a}{2}(0\ 1\ 1)$

Ag, Au, Al, Cu, Pb, ---



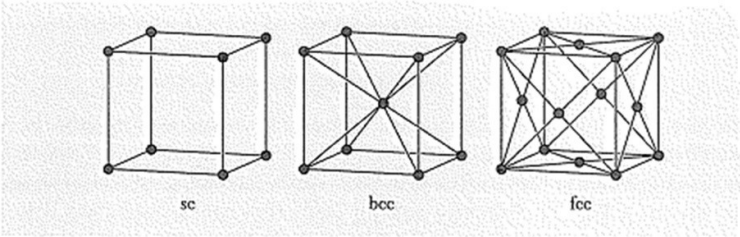
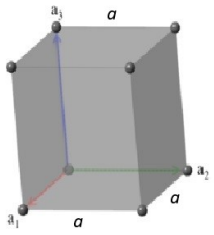


Figure 8 The cubic space lattices. The cells shown are the conventional cells.

Table 2 Characteristics of cubic lattices[a]

	Simple	Body-centered	Face-centered
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]	$\frac{1}{6}\pi$	$\frac{1}{8}\pi\sqrt{3}$	$\frac{1}{6}\pi\sqrt{2}$
	=0.524	=0.680	=0.740

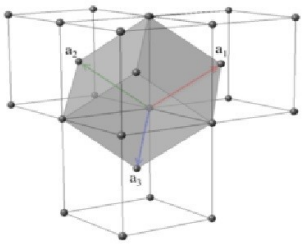
[a]The packing fraction is the maximum proportion of the available volume that can be filled with hard spheres.



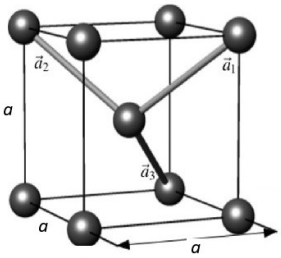
Primitive unit cell = conventional unit cell
($V_p = V_c$)

$\vec{a_1} = a\,\hat{i}\;;\; \vec{a_2} = a\,\hat{j}\;;\; \vec{a_3} = a\,\hat{k}$

SC : Primitive unit cell = conventional unit cell (Vp = Vc)



Or

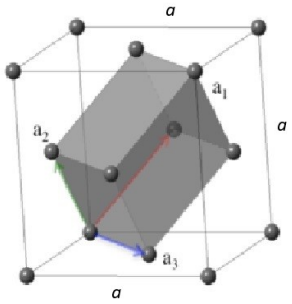


$\vec{a_1} = \frac{a}{2}(1\ 1\ -1)$

$\vec{a_2} = \frac{a}{2}(-1\ 1\ 1)$

$\vec{a_3} = \frac{a}{2}(1\ -1\ 1)$

BCC : Primitive unit cell # conventional unit cell ($V_p = V_c/2$)



$\vec{a_1} = \frac{a}{2}(1\ 1\ 0)$

$\vec{a_2} = \frac{a}{2}(1\ 0\ 1)$

$\vec{a_3} = \frac{a}{2}(0\ 1\ 1)$

FCC : Primitive unit cell # conventional unit cell ($V_p = V_c/4$)

see problem 1 in HW#2 for calculation of V_P for both fcc and bcc structures

④ The hexagonal lattice (simple hexagonal)

This structure does not occur among the elements, except as the starting point for the hexagonal close-packed structure.

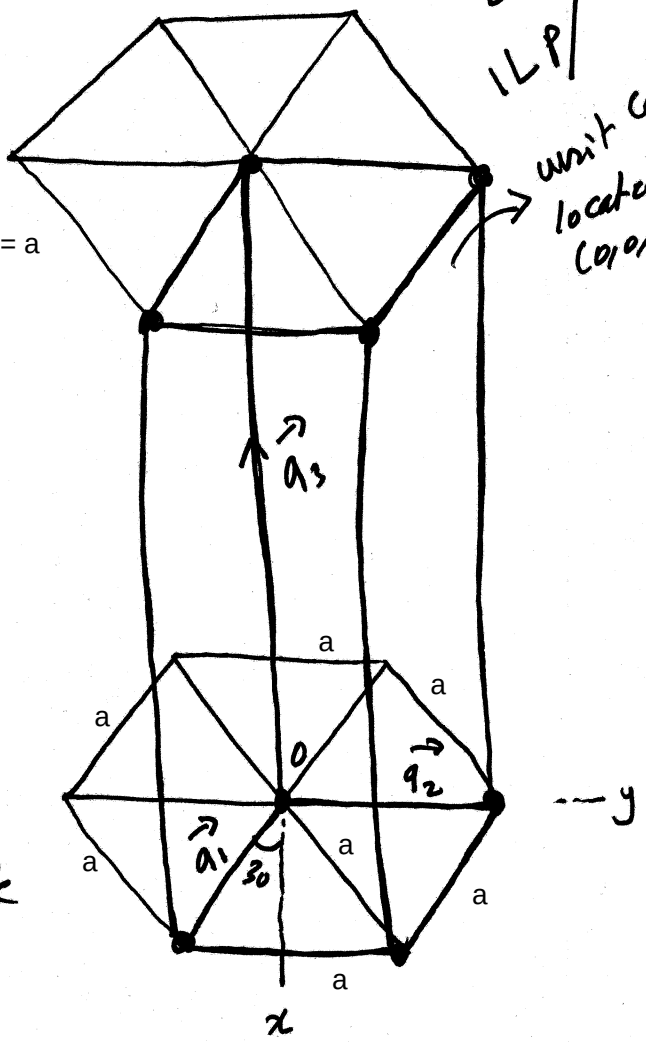
$\vec{a_1} = a\cos 30\,\hat{i} - a\sin 30\,\hat{j}$

$= a\frac{\sqrt{3}}{2}\hat{i} - \frac{a}{2}\hat{j}$

$\vec{a_2} = a\hat{j}$; $\vec{a_3} = c\hat{k}$, $|a1| = |a2| = a$

# of 1st NN = 6 ; take the one sitting in the center of hexagon.

$V_c = V_p = |\vec{a_1}\cdot\vec{a_2}\times\vec{a_3}| = \frac{a^2 c\sqrt{3}}{2}$



⑤ The hexagonal close-packed (hcp)

This structure is like the honeycomb lattice, a lattice with a basis. (See Fig 2.5)

# of LPs = $8\times\frac{1}{8} + 1$

$(0,0,0) \xrightarrow{\vec{r}} \left(\frac{2}{3}a, \frac{1}{3}a, \frac{c}{2}\right)$

the distance between the two lattice points is a where $\vec{r} = \frac{2}{3}\vec{a_1} + \frac{1}{3}\vec{a_2} + \frac{1}{2}\vec{a_3}$

$= \frac{2}{3}\frac{\sqrt{3}}{2}a\hat{i} - \frac{2}{3}\frac{a}{2}\hat{j} + \frac{1}{3}a\hat{j} + \frac{c}{2}\hat{k}$

$= \frac{\sqrt{3}}{3}a\hat{i} + \frac{c}{2}\hat{k}$

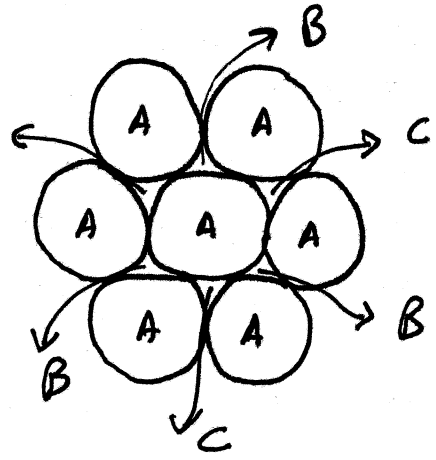
$|\vec{r}| = \sqrt{\frac{3}{9}a^2 + \frac{c^2}{4}}$; for an ideal hcp ; $\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$

see problem 2 and problem 4 in HW#2 for proof

so $|\vec{r}| = \sqrt{\frac{3}{9}a^2 + \frac{8}{12}a^2} = a\sqrt{\frac{108}{108}} = a$

the hcp structure is constructed as follows

- 1st layer with centers at A
- a 2nd identical layer of spheres is placed above the first layer with centers over the points B



- There are two choices for a third layer. it can go over A or over C
  - i) if it goes over A, the sequence is ABABAB--- and the structure is hexagonal close-packed.
  - ii) if it goes over C, the sequence is ABCABCABC, and the structure is fcc

- note that for hcp, the # of 1st NN = 12

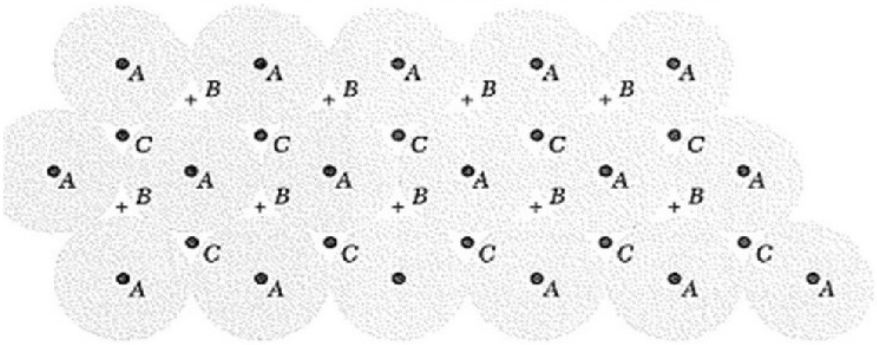
hint: start counting from the atom located at (0,0,0)

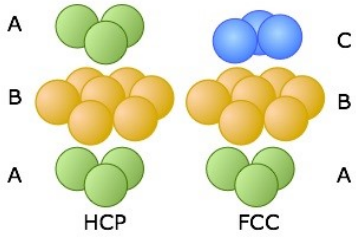
- 6 atoms in plane A
- 3 atoms in plane B from above
- 3 " " " " below

all atoms in plane B have the same distance $|r| = a$ to the origin

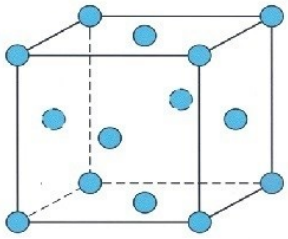
Examples: Co, Zn, Cd, Mg, Y

Close-Packed Structures





ABCABCABC.... (fcc structure)

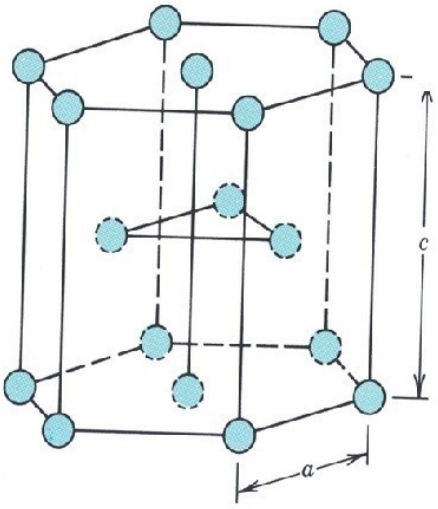


4 LP / unit cell

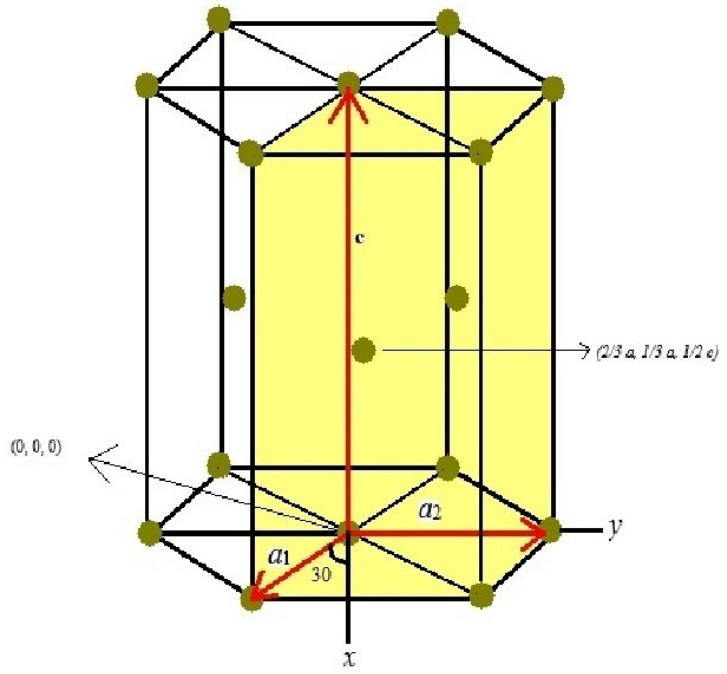
Table 4.1
ELEMENTS WITH THE MONATOMIC FACE-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ-Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β-Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

ABABAB..... (hcp structure)

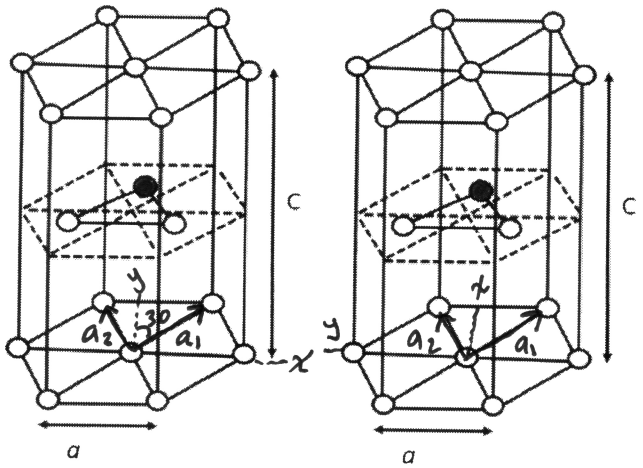


Crystal	c/a	Crystal	c/a	Crystal	c/a
He	1.633	Zn	1.861	Zr	1.594
Be	1.581	Cd	1.886	Gd	1.592
Mg	1.623	Co	1.622	Lu	1.586
Ti	1.586	Y	1.570		



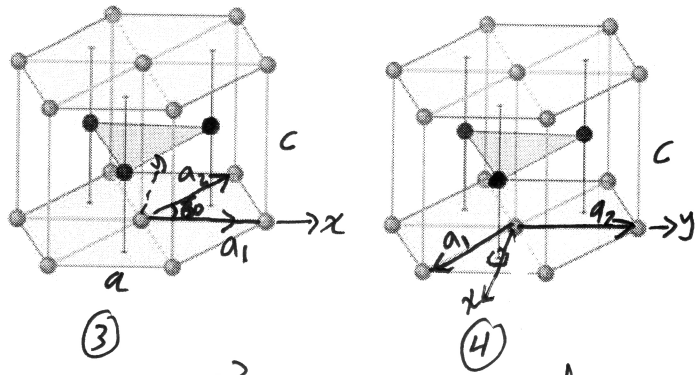
2 LP / primitive cell located at (0,0,0) and (2/3 *a*. 1/3 *a*, 1/2 c)

How to choose the two basis of the hcp structure



① ②

$\vec{a_3} = c(0,0,1)$



③ ④

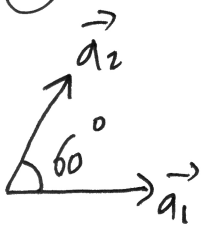
There are two basis. The first one is ab $\vec{d_1} = (0,0,0)$ and the second base $\vec{d_2}$ depends on $\vec{a_1}$ and $\vec{a_2}$ selection. Here I give few examples.

① $\vec{a_1} = a(1/2, \frac{\sqrt{3}}{2}, 0)$, $\vec{a_2} = a(-1/2, \frac{\sqrt{3}}{2}, 0)$, $\vec{a_3} = c(0,0,1)$

$\Rightarrow \vec{d_2} = \frac{1}{3}\vec{a_1} + \frac{1}{3}\vec{a_2} + \frac{1}{2}\vec{a_3} = (0, \frac{a}{\sqrt{3}}, \frac{c}{2})$

② if you now switch the x and y axes as show in ②

$\vec{d_2} = \frac{1}{3}\vec{a_1} + \frac{1}{3}\vec{a_2} + \frac{1}{2}\vec{a_3} = (\frac{a}{\sqrt{3}}, 0, \frac{c}{2})$

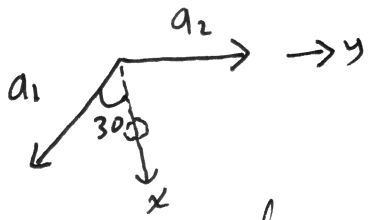


③ $\vec{a_1} = a(1,0,0)$, $\vec{a_2} = a(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$, $\vec{a_3} = c(0,0,1)$

$\vec{d_2} = \frac{1}{3}\vec{a_1} + \frac{1}{3}\vec{a_2} + \frac{\vec{a_3}}{2} = (\frac{a}{2}, \frac{a}{2\sqrt{3}}, \frac{c}{2})$

④ $\vec{a_1} = a(\frac{\sqrt{3}}{2}, -1/2, 0)$, $\vec{a_2} = a(0,1,0)$, $\vec{a_3} = c(0,0,1)$

$\vec{d_2} = \frac{2}{3}\vec{a_1} + \frac{1}{3}\vec{a_2} + \frac{1}{2}\vec{a_3} = (\frac{a}{\sqrt{3}}, 0, \frac{c}{2})$

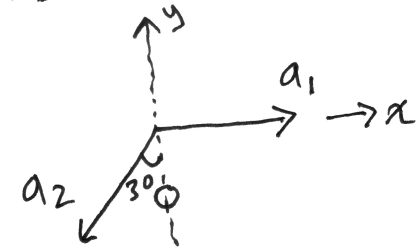


which similar to case ②

⑤ if $\vec{a_1}$ and $\vec{a_2}$ are exchanged and the (x,y) has also changed

$\vec{a_1} = a(1,0,0)$, $\vec{a_2} = a(-1/2, -\frac{\sqrt{3}}{2}, 0)$, $\vec{a_3} = c(0,0,1)$

$\Rightarrow \vec{d_2} = \frac{1}{3}\vec{a_1} + \frac{2}{3}\vec{a_2} + \frac{1}{2}\vec{a_3} = (0, -\frac{a}{\sqrt{3}}, \frac{c}{2})$



(6) The diamond lattice:

this structure is not a Bravais lattice because there are two types of lattice points with different environme

the underlying lattice is an fcc lattice with a two-atomic basis. Thus there are 2 atoms attached to each lattice point located at $(0,0,0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. since the # of LPs for an fcc lattic is 4 and each point contains two atoms, then the # of atoms per conventional unit cell is 8 located at $(0,0,0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$

$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$.

i.e 8 atoms on the corners, 6 atoms on the faces, and 4 atoms inside the cube. This structure can be viewed as two inter-penetrating fcc lattices, where the origin of the 1st lattice is at $(0,0,0)$ and the origin of the 2nd lattice is shifted to $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$ along a body diagonal of the cube.

- # of 1st NN = 4 sitting on the vertices of regular tetrahedron.

basis primitive vectors is the same of those for an fcc lattice

$\vec{a}_1 = \frac{a}{2}(1\,1\,0)$

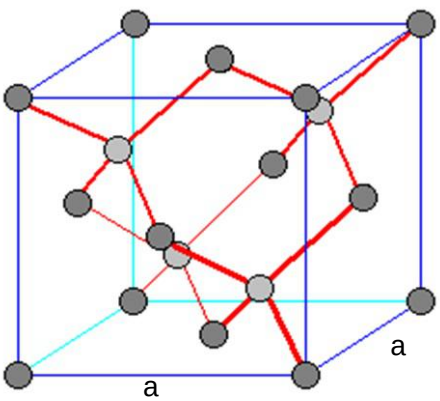
$\vec{a}_2 = \frac{a}{2}(1\,0\,1)$

$\vec{a}_3 = \frac{a}{2}(0\,1\,1)$

Examples

C, Si, Ge, Sn

↓ diamond ↓ Tin



Compounds: Crystals made of more than one element. Therefore, can't be Bravais lattices. There are Hundreds of thousands of different crystal that have been cataloged. Here we discuss a few common types.

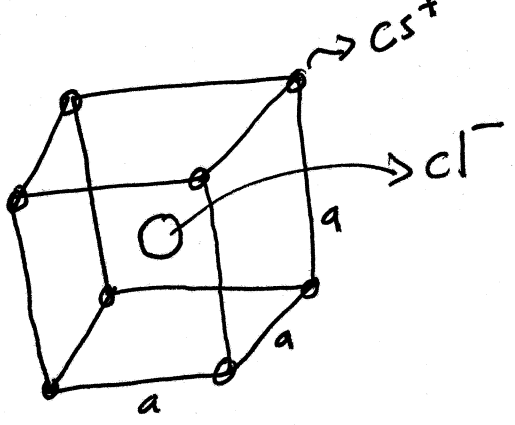
① Rocksalt – Sodium Chloride (NaCl)

can be viewed as an fcc lattice with two basis; Na^+ at $(0,0,0)$ and Cl^- at $(1/2, 1/2, 1/2)a$; i.e two inter-penetrating fcc lattices; the Na^+ ions form the first lattice and the Cl^- ions form another fcc lattice, displaced from the first lattice by half a cube edge, $a/2$. Note that there are 4 units of NaCl in the unit cell. # of 1^{st} NN = 6

Examples: MgO, KBr, PbS, AgF, AgCl, BaO, ---

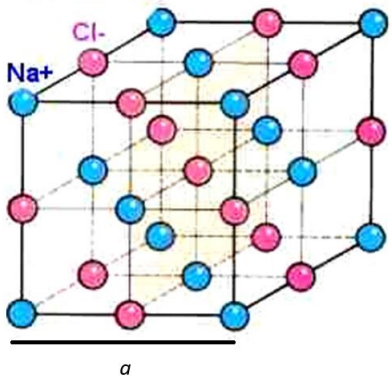
② Cesium Chloride (CsCl)

Can be described as a SC lattice with two basis; Cs^+ ion at $(0,0,0)$ and Cl^- ion at $(1/2, 1/2, 1/2)a$. or it can be viewed as the Cs^+ and Cl^- ions alternate in a bcc lattice. # of 1^{st} NN = 8



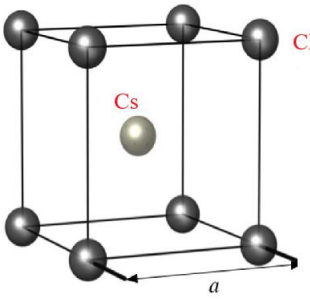
Examples: BeCu, AlNi, LiHg, ---

Rocksalt—Sodium Chloride structure (NaCl)



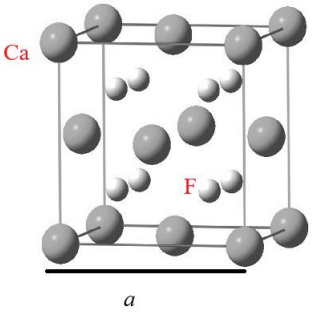
Crystal	a	Crystal	a	Crystal	a	Crystal	a	Crystal	a
AgBr	5.77	CrN	4.14	LiI	6.00	NiO	4.17	SrS	6.02
AgCl	5.55	CsF	6.01	MgO	4.21	PbS	5.93	SrSe	6.23
AgF	4.92	FeO	4.31	MgS	5.20	PbSe	6.12	SrTe	6.47
BaO	5.52	KBr	6.60	MgSe	5.45	PbTe	6.45	TiC	4.32
BaS	6.39	KCl	6.30	MnO	4.44	RbBr	6.85	TiN	4.24
BaSe	6.60	KF	5.35	MnS	5.22	RbCl	6.58	TiO	4.24
BaTe	6.99	KI	7.07	MnSe	5.49	RbF	5.64	VC	4.18
CaS	5.69	LiBr	5.50	NaBr	5.97	RbI	7.34	VN	4.13
CaSe	5.91	LiCl	5.13	NaCl	5.64	SnAs	5.68	ZrC	4.68
CaTe	6.35	LiF	4.02	NaF	4.62	SnTe	6.31	ZrN	4.61
CdO	4.70	LiH	4.09	NaI	6.47	SrO	5.16		

Cesium Chloride structure (CsCl)



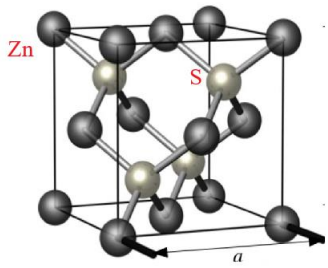
Crystal	a	Crystal	a	Crystal	a
AgCd	3.33	CsCl	4.12	NiAl	2.88
AgMg	3.28	CuPd	2.99	TiCl	3.83
AgZn	3.16	CuZn	2.95	TlI	4.20
CsBr	4.29	NH_4Cl	3.86	TlSb	3.84

Fluorite—Calcium Fluoride structure (CaF2)



Crystal	a	Crystal	a	Crystal	a
BaF_2	6.20	$CoSi_2$	5.36	Mg_2Si	6.39
CaF_2	5.46	HfO_2	5.12	Mg_2Sn	6.77
CdF_2	5.39	Li_2O	4.62	Na_2S	6.53
CeO_2	5.41	Li_2S	5.71	$SrCl_2$	6.98
CmO_2	5.37	Mg_2Pb	6.84	UO_2	5.47

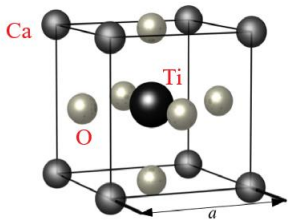
Zincblende (Zinc Sulfide) structure (ZnS)



Crystal	a	Crystal	a	Crystal	a
AgI	6.47	CdTe	6.48	HgSe	6.08
AlAs	5.62	CuBr	5.69	HgTe	6.43
AlP	5.45	CuCl	5.41	InAs	6.04
AlSb	6.13	CuI	6.04	InP	5.87
BeS	4.85	GaAs	5.63	InSb	6.48
BeSe	5.07	GaP	5.45	SiC	4.35
BeTe	5.54	GaSb	6.12	ZnS	5.41
CdS	5.82	HgS	5.85	ZnTe	6.09

Similar to diamond; but dimond is composed of one type of atoms (carbon), while Zincblende is composed of two types of atoms (Zn and S)

The perovskite structure (CaTiO3)



Crystal	a	Crystal	a		
$BaTiO_3$	4.01	$CsHgCl_3$	5.44	$LaAlO_3$	3.78
$CaSnO_3$	3.92	$CsIO_3$	4.66	$LaGaO_3$	3.88
$CaTiO_3$	3.84	KIO_3	4.41	$RbIO_3$	4.52
$CaZrO_3$	4.02	$KMgF_3$	3.97	$SrTiO_3$	3.91
$CsCdBr_3$	5.33	$KNiF_3$	4.01	$SrZrO_3$	4.10
$CsHgBr_3$	5.77	$KZnF_3$	4.05	$YAlO_3$	3.68

③ Fluorite – calcium Fluoride (CaF_2)

the unit cell has 4 Ca^{+2} ions, one at the origin and the others are located at the face centers of the cube; similar to an fcc lattice of Ca^{+2} ions.

$(0,0,0)$, $(0,\frac{1}{2},\frac{1}{2})a$, $(\frac{1}{2},0,\frac{1}{2})a$, $(\frac{1}{2},\frac{1}{2},0)a$.

The F^- ions are located at the vertices of a SC

↓

8

having only half the lattice spacing of the unit cell. The SC is inside the fcc lattice of the Ca^{+2} ions. The positions of the F^- ions are

$(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{1}{4},\frac{3}{4},\frac{3}{4})$, $(\frac{3}{4},\frac{1}{4},\frac{3}{4})$, $(\frac{3}{4},\frac{3}{4},\frac{1}{4})$

$(\frac{3}{4},\frac{3}{4},\frac{3}{4})$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, $(\frac{1}{4},\frac{3}{4},\frac{1}{4})$, $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$

See Fig 2.9

Examples:

BaF_2, CdF_2, CeO_2, CmO_2,

④ Zincblende – Zinc sulfide (ZnS):

similar to diamond structure, but basis of two different atoms. The unit cell contains 4 units of (ZnS). The Zn^{+2} ions are positioned on an fcc lattice points and the S^{-2} ions are positioned inside the cube in a similar positions of the interior atoms in diamond. so diamond structure: involves one type of atoms

zincblend structure: " two different types of atoms

Examples: AgI, AlP, —

- **Packing Fraction:** not covered in textbook

- how tightly atoms are packed in a given structure?

- idea: replace atoms by the largest spheres consistant with the cell size (with no overlaps).

$$F = \frac{Z\ \frac{4}{3}\pi R^3}{a^3} \equiv \frac{[\#\text{ of atoms/unit cell}][\text{volume/atom}]}{V \leftarrow \text{volume of conventional unit cell}}$$

R: radius of the atom (see problem 2.6 Marder in HW#2)

SC: $V = a^3$; $R = \frac{a}{2}$; $Z = 1$ $\Rightarrow$ $F = \frac{\pi}{6} = 0.52$

spheres occupy 52% of the volume of the cube and 48% are voids

bcc: $V = a^3$, $R = \frac{\sqrt{3}}{4}a$; $Z = 2$ $\Rightarrow$ $F = 0.68$

fcc: $V = a^3$, $R = \frac{\sqrt{2}}{4}a$; $Z = 4$ $\Rightarrow$ $F = 0.74$

hcp: $V = \frac{a^2 c\sqrt{3}}{2}$; $\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.66$; $R = \frac{a}{2}$; $Z = 2$ $\Rightarrow$ $F = 0.74$

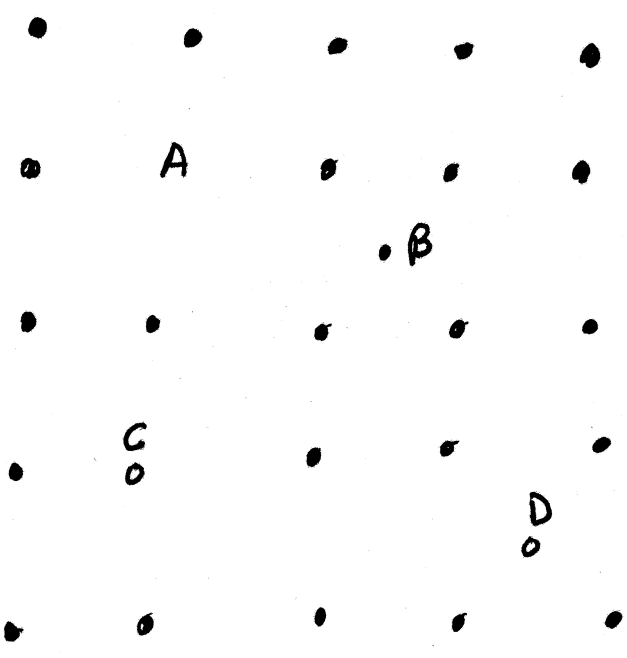
diamond: $V = a^3$; $R = \frac{\sqrt{3}}{8}a$; $Z = 8$ $\Rightarrow F = 0.34$ } the same as they both hcp structure

detailed calculations of packing fractions are given in the solution of problem 2.6 of Marder textbook

- Defects : not covered in textbook

Deviations from ideal structure

Point defects : vacancy, interstitial, impurity



•: host atoms

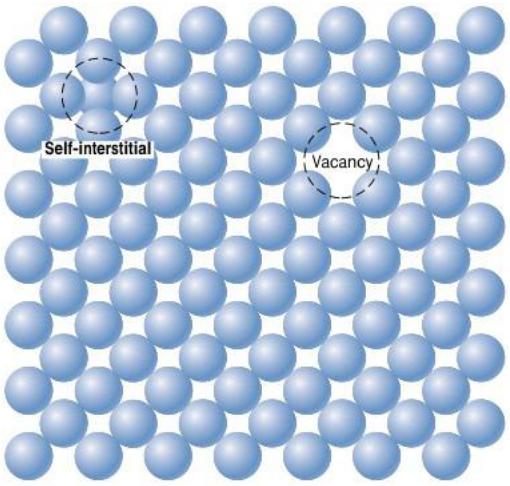
A: vacancy

B: interstitial

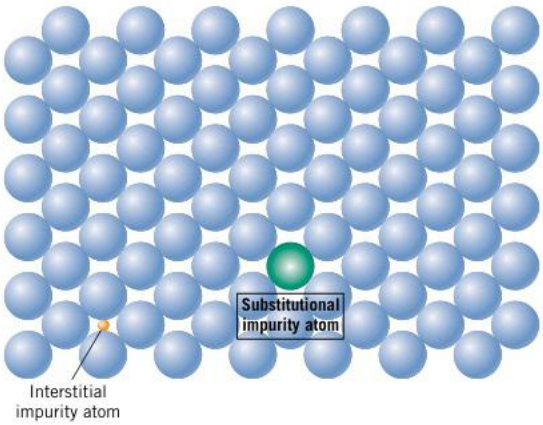
C: a substitutional impurity

D: an interstitial impurity

vacancies and interstitials are thermally excited.



Two-dimensional representations of a vacancy and a self-interstitial.



Two-dimensional schematic representations of substitutional and interstitial impurity atoms.

(Adapted from Callister - Materials Science and Engineering An Introduction 9th c2014 textbook)