III. Crystal Structures II

Recall: Crystal structure = Lattice + Basis

Lattice $\uparrow$ 14 types in 3D

Basis $\uparrow$ The smallest structural unit, when attached to each lattice point, gives the crystal structure

- Recall that $(\vec{a}_1, \vec{a}_2, \vec{a}_3)$ defines a primitive cell.
- In describing the locations of the atoms in the basis, we need to give the positions relative to a lattice point:

$$\vec{r}_i = x_i\vec{a}_1 + y_i\vec{a}_2 + z_i\vec{a}_3$$

$$(0 \leq x_i, y_i, z_i \leq 1)$$

for the i^{th} atom in the basis.

Note: These are equilibrium positions.
Due to various effects (e.g. temperature), they may be oscillating slightly about the equilibrium positions.

Here, we discuss some crystal structures of general interest.

+ The number of atoms in a basis varies from system to system. Many have only a few atoms, but some (e.g. biochemical structures) have many (few hundreds) atoms.

A. Many simple metals have bcc structure with a basis of one atom

e.g.

	a(Å)		a(Å)
Li	3.49	Rb	5.59
Na	4.23	Cs	6.05
K	5.23	Fe	2.87

Note: The lattice constant "a" here is the length of the edge of the cube^{+}. Recall that the cube is not the primitive cell for bcc.

B. There are also monoatomic (basis of 1 atom) fcc crystals

e.g.

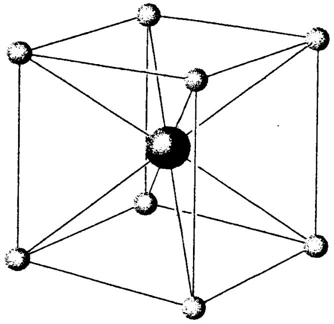
	a(Å)		a(Å)
Ag	4.09	Cu	3.61
Al	4.05	Pb	4.95
Au	4.08	Pd	3.89
Ca	5.58	Pt	3.92

Notes: (i) "a" refers to the edge of the cube.$^{+}$
The cube is not the primitive cell for fcc.
(ii) The fcc lattice is related to close packing of spheres.

[Note: Note the typical value of a]

+ i.e., conventional unit cell

C. Cesium Chloride Structure



The cesium chloride crystal structure. The space lattice is simple cubic, and the basis has one Cs^+ ion at 000 and one Cl^- ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Description

- Simple cubic lattice
- A basis of two ions

○ Cs^+ ion

● Cl^- ion

Relative to a lattice point,

Cs^+ ion is at $\underbrace{000}$

meaning: at $0\hat{x} + 0\hat{y} + 0\hat{z}$

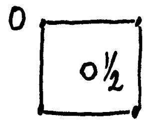
Cl^- ion is at $\underbrace{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$

meaning: at $\frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$

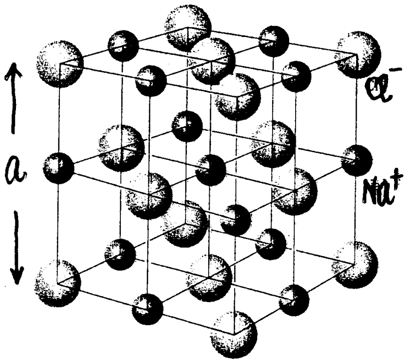
Other examples of CsCl structure

Crystal	a
BeCu	2.70 Å
AlNi	2.88 Å
CsCl	4.11 Å
NH_4Cl	3.87 Å
LiHg	3.29 Å
TlBr	3.97 Å

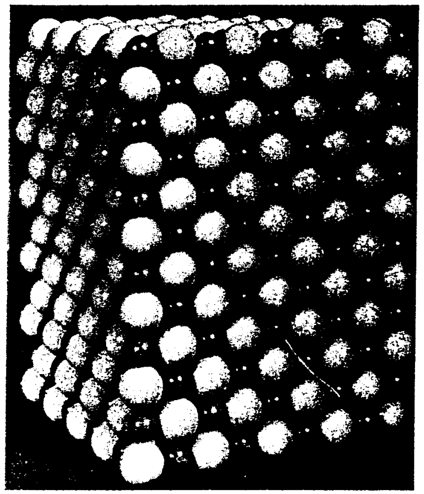
The structure is also represented by:



D. Sodium Chloride Structure



We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.



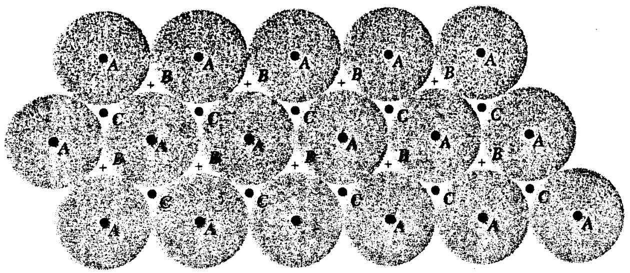
Model of sodium chloride. The sodium ions are smaller than the chlorine ions.

[figures from Kittel]

- The Bravais lattice is fcc.
- Basis of 2 ions: one Na^+ and one Cl^-
- Na^+ ions form a fcc lattice and Cl^- ions form another fcc lattice, displaced from the first lattice by half a cube edge, i.e. by $a/2$.

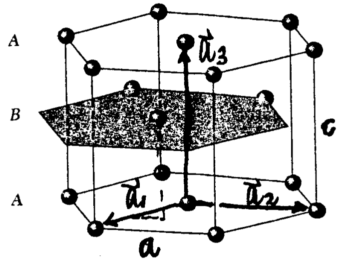
Crystal	a
NaCl	5.63 Å
MgO	4.20 Å
KBr	6.59 Å
PbS	5.92 Å

E. Hexagonal Close-packed (hcp) structure



A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed on top of this, above and parallel to the plane of the drawing, with centers over the points marked *B*. There are two choices for a third layer. It can go in over *A* or over *C*. If it goes in over *A*, the sequence is *ABABAB* . . . and the structure is hexagonal close-packed. If the third layer goes in over *C*, the sequence is *ABCABCABC* . . . and the structure is face-centered cubic.

Layers of closed packed spheres stacked up as ABABAB⋯



The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point. The lattice parameters *a* and *c* are indicated, where *a* is in the basal plane and *c* is the magnitude of the axis $\mathbf{a}_3$

Bravais lattice: hexagonal

Ideal hcp: $\frac{c}{a} = 1.633$

Basis of 2 atoms

one atom at 000

Another atom at $\frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$

or $\frac{2}{3}\frac{1}{2}\frac{1}{2}$.

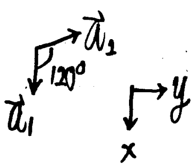
Examples:	He	Mg	Zn	Y	Zr	Cd	Co
c/a	1.633	1.623	1.861	1.570	1.594	1.886	1.622

If the layers are stacked as ABCABC⋯, then the structure is fcc.

For hcp, if we express $\vec{a}_1, \vec{a}_2, \vec{a}_3$ in terms of $\hat{x}, \hat{y}, \hat{z}$, we have

$$\begin{cases} \vec{a}_1 = a\hat{x}, \quad \vec{a}_2 = -\frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y} \\ \vec{a}_3 = c\hat{z} \end{cases}$$

x-y plane



Note that: $|\vec{a}_1| = |\vec{a}_2|$ (hexagonal)

- Basis of 2 atoms:

  One at the origin (lattice pt) 000,

  the other at $\vec{r} = \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$

  $$= \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{6}a\hat{y} + \frac{c}{2}\hat{z}$$

In the so-called "ideal hcp", (stacking of identical spheres, we require $|\vec{r}| = a$, (i.e. distance between centers of neighboring spheres is the same)

[∵ close-pack]

but $|\vec{r}| = \sqrt{\frac{a^2}{4} + \frac{3}{36}a^2 + \frac{c^2}{4}}$.

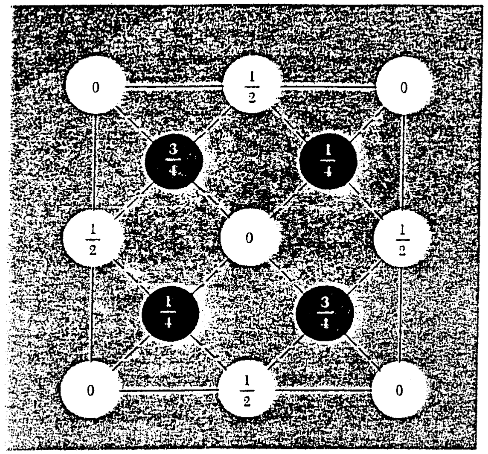
∴ In ideal hcp, $\frac{a^2}{4} + \frac{1}{12}a^2 + \frac{1}{4}c^2 = a^2$

$$\Rightarrow \frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$ for ideal hcp.

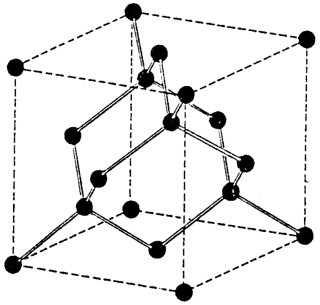
F. Diamond Structure

- Lattice : fcc
- Basis of 2 atoms : 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (referring to the conventional cube)

(identical atoms) (diamond)



Atomic positions in the cubic cell of the diamond structure projected on a cube face; fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the fcc lattice; those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced along the body diagonal by one-fourth of its length. With a fcc space lattice, the basis consists of two identical atoms at 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

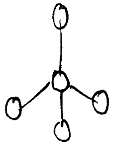


Crystal structure of diamond, showing the tetrahedral bond arrangement.

Each atom has 4 nearest neighbors.

In a unit cube, 4 lattice pts ⇒ 8 atoms in a unit cube for diamond structure.

Angle between any two of the bonds joining a site to its neighbors $= 109°28'$



Recall: sp^3 hybridization

$\therefore$ directional covalent bonding prefers the diamond (zinc blende) Structure.

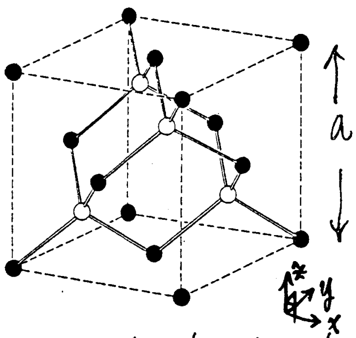
E.g., Carbon (diamond), $\underbrace{\text{Si, Ge,}}_{\text{important semiconductors}}$

G. Cubic Zinc Sulfide Structure ("Zinc Blende" structure)

- Similar to diamond structure. But Basis of 2 different atoms.

All with zinc blende structure

Crystal	a	Crystal	a
CuF	4.26 Å	ZnSe	5.65 Å
SiC	4.35	GaAs	5.65
CuCl	5.41	AlAs	5.66
ZnS	5.41	CdS	5.82
AlP	5.45	InSb	6.46
GaP	5.45	AgI	6.47



Crystal structure of cubic zinc sulfide.

[In a unit cube, 4 molecules.]

An important structure as many of the compound semiconductors take on the zinc blende structure.

Q: Take a black dot sitting at (0,0,0), where are the 4 nearest neighboring white dots?

black	white neighbors	Meaning
(0,0,0)	$(+\frac{1}{4},+\frac{1}{4},+\frac{1}{4})$	a neighbor at $\vec{d}_1=\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$
	$(-\frac{1}{4},+\frac{1}{4},-\frac{1}{4})$	a neighbor at $\vec{d}_2=\frac{a}{4}(-\hat{x}+\hat{y}-\hat{z})$
	$(+\frac{1}{4},-\frac{1}{4},-\frac{1}{4})$	a neighbor at $\vec{d}_3=\frac{a}{4}(\hat{x}-\hat{y}-\hat{z})$
	$(-\frac{1}{4},-\frac{1}{4},+\frac{1}{4})$	a neighbor at $\vec{d}_4=\frac{a}{4}(-\hat{x}-\hat{y}+\hat{z})$

E.g. GaAs and many useful semiconductors

H. Remarks

(a) Packing Fraction

- how tightly atoms are packed in a given structure?
- Idea: replace atoms by the largest spheres consistent with the cell size (no overlap)

$$F = \frac{Z\,\frac{4\pi}{3}\left(\frac{r_1}{2}\right)^3}{v}$$

Z = # atoms in unit cell
r_1 = nearest neighbor separation
v = volume of unit cell
If primitive cell, $v = \Omega_c$.

SC: $v = a^3$, $r_1 = a$, $Z = 1 \Rightarrow F = \frac{\pi}{6} = 0.52$

[i.e. packing identical spheres in SC structure, the spheres occupy 52% of the volume, 48% are voids.]

bcc: $v = a^3$, $r_1 = \frac{\sqrt{3}}{2}a$, $Z = 2$, $F = 0.68$

fcc: $v = a^3$, $r_1 = \frac{\sqrt{2}}{2}a$, $Z = 4$, $F = 0.74$ \ same as

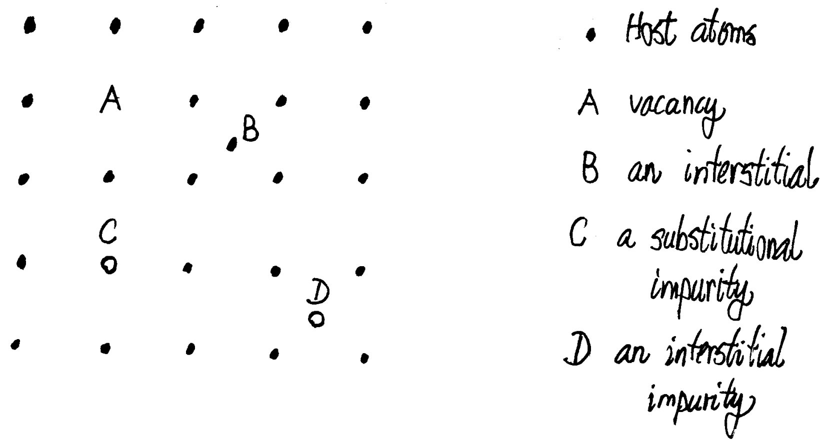
hcp: $v = \sqrt{2}a^3$, $r_1 = a$, $Z = 2$, $F = 0.74$ / both are close-packed structures

(b) Defects

- Deviations from ideal structure are known as defects.

Point Defects

Vacancy, interstitial, impurity



- Vacancies and interstitials are thermally excited.

From Statistical mechanics, if N = atoms in crystal, E_v = energy to create a vacancy, then at temperature T, we have

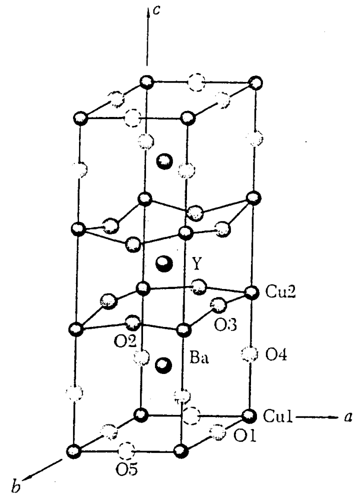
$$\frac{N_v}{N} = e^{-\frac{\beta E_v}{2}} \qquad \text{(Ex.) [Stat. Mech.]}$$

for $N_v \ll N$

- Non-equilibrium vacancies and interstitials can be created by quenching, or by bombardment by particles.

High-temperature Superconductors

YBCO : $YBa_2Cu_3O_7$ (Parent compound)



Superconducting when some oxygen positions are vacant.

$T_c = 90K$

$a = 0.388\,nm$
$b = 0.384\,nm$ } very close ⇓ very close to a tetragonal lattice.
$c = 1.163\,nm$

The crystal structure of $YBa_2Cu_3O_7$, showing a primitive cell. The planes containing sites marked Cu2, O2, and O3 form the conducting pathways.

Refs:

Kittel: Ch.1

Read Kittel Ch.3 (early sections) on bonding.
↳ and review relevant topics in Quantum Physics.

Students should be able to:

- describe crystal structures systematically
- recognize CsCl, NaCl, hcp, diamond, zinc blende structures and state their properties
- realize the use of conventional unit cells in describing crystal structures, when the Bravais lattice is either bcc or fcc

Remark:

- Only when one becomes familiar with the description of crystal structures in real space, one can appreciate the construction of a reciprocal space and its usefulness.