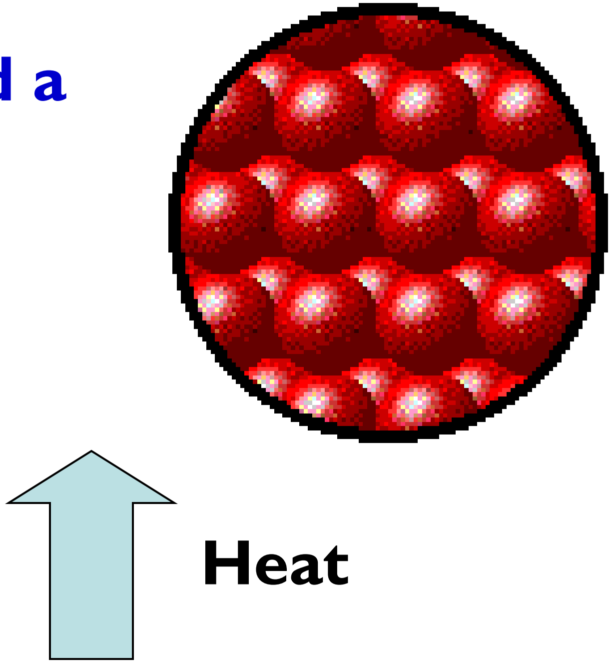
Solid states of matter

- Particles of solids are tightly packed, vibrating about a fixed position.
- Solids have a definite shape and a definite volume.
- Strong cohesive forces
- Minimal compressibility
- Little thermal expansion



Types of solids

- **Crystalline** a well defined arrangement of atoms; this arrangement is often seen on a macroscopic level.
  - *Ionic solids* **–** ionic bonds hold the solids in a regular three dimensional arrangement.
  - *Molecular solid* – solids like ice that are held together by intermolecular forces.
  - *Covalent network* – a solid consists of atoms held together in large networks or chains by covalent networks.
  - *Metallic* – similar to covalent network except with metals. Provides high conductivity.
- **Amorphous** – atoms are randomly arranged. No order exists in the solid.

Isotropy and anisotropy

- Amorphous substances are said to be isotropic because they exhibit the same value of any property in all directions
- Crystalline substances, on the other hand, are anisotropic and the magnitude of a physical property varies with directions
- Polymorphism is the occurrence of multiple crystalline forms of a material.
- Allotropy occurs in chemical elements

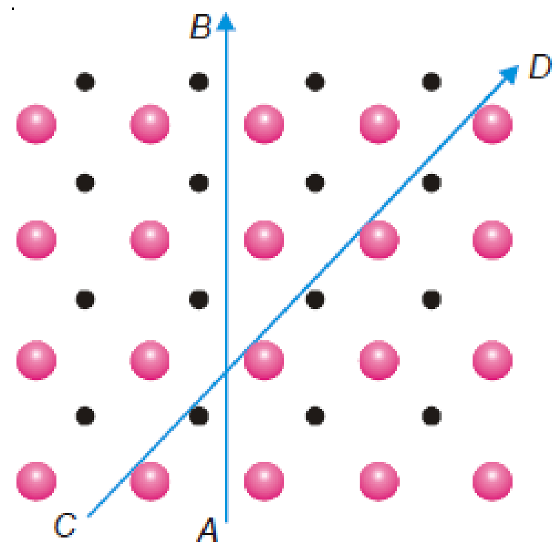
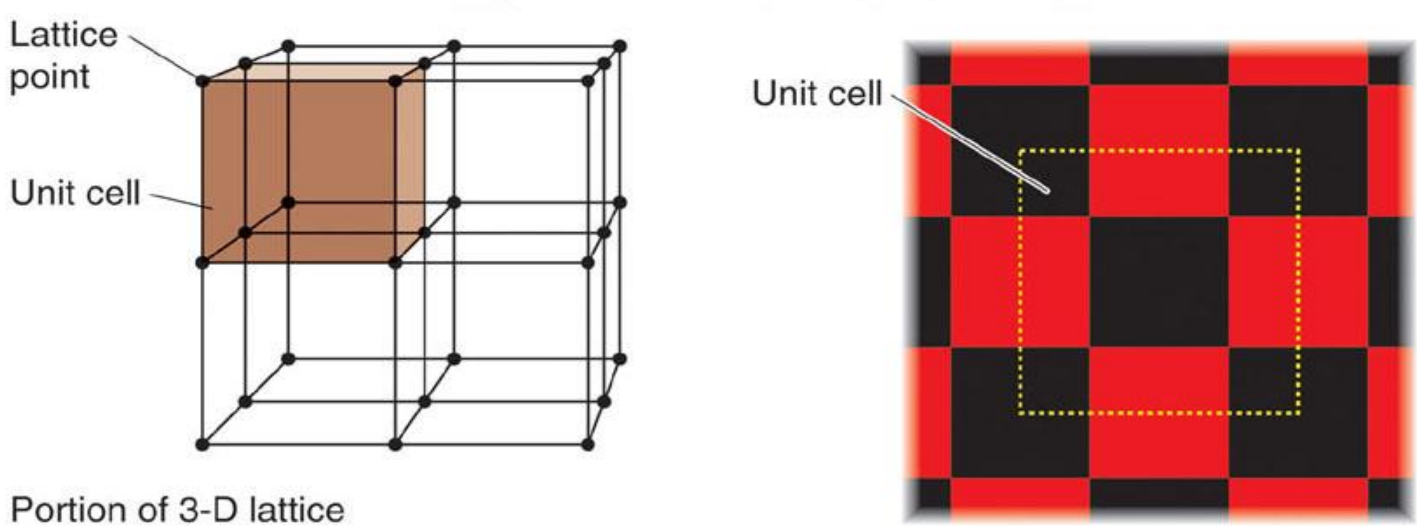


Figure 12.2
Anisotropy in crystals is due to different arrangements of particles in different directions.

Unit cells in crystalline solids

- Unit cell- the smallest repeating array of atoms.
- Lattice point- the position of particles of a substance in space.
- The external shape is called the habit of the crystal.
- The plane surfaces of the crystal are called faces. The angles between the faces are referred to as the interfacial angles.

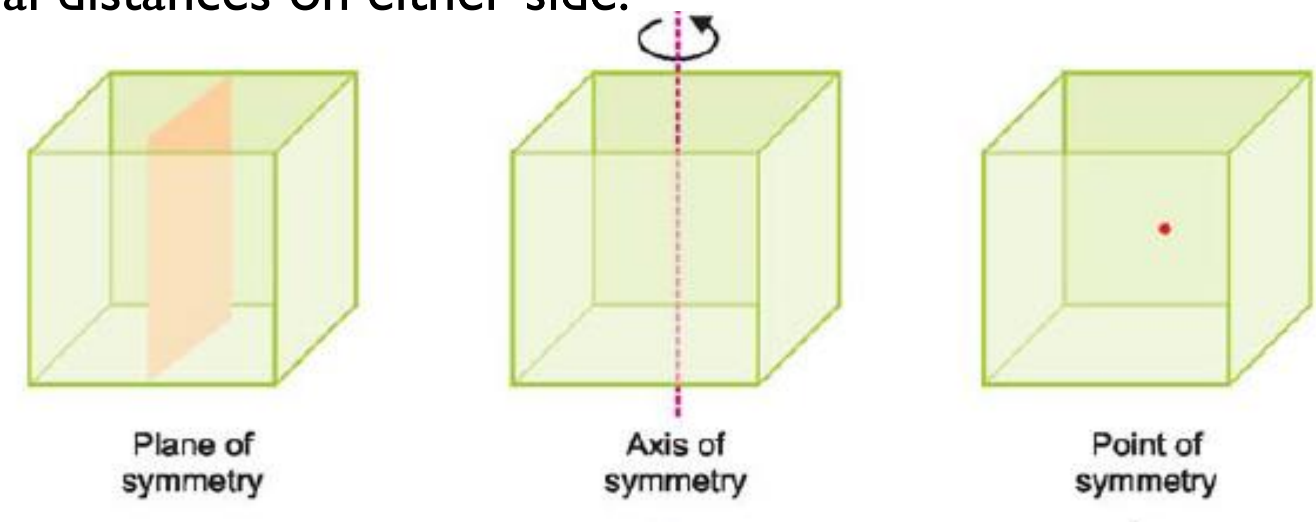


A Portion of 3-D lattice

B Portion of 2-D lattice

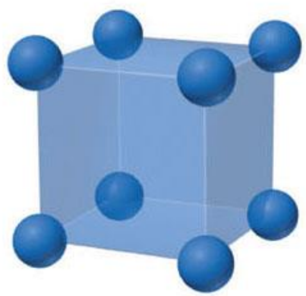
Crystal symmetry

- Plane of symmetry, a crystal is said to have a plane of symmetry if it can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other.
- Axis symmetry, an imaginary line drawn through the crystal such that during rotation of the crystal through 360º, the crystal presents exactly the same appearance more than once.
- Centre of symmetry, a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side.

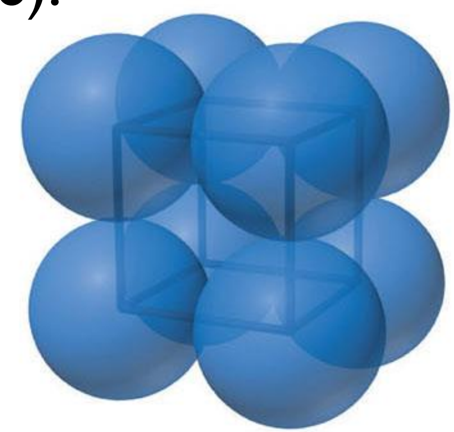


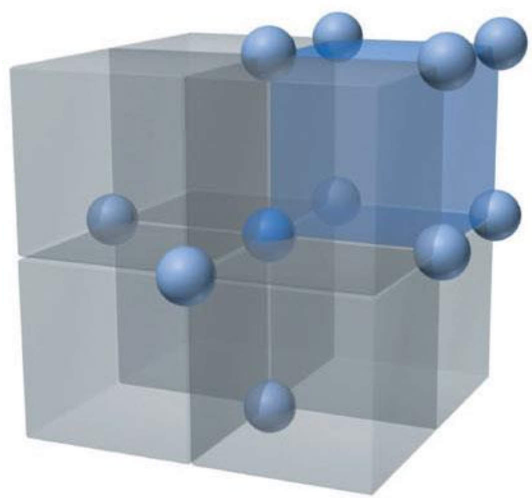
Cubic unit cells

- **Primitive-cubic** shared atoms are located only at each of the corners. 1 atom per unit cell. Each atom has 6 nearest neighbors (coordination number of 6).



simple cubic





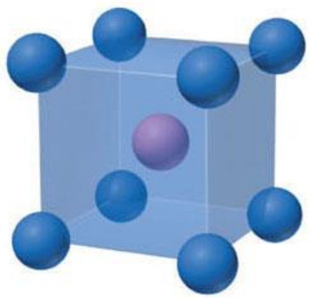
coordination number = 6

1/8 atom at 8 corners

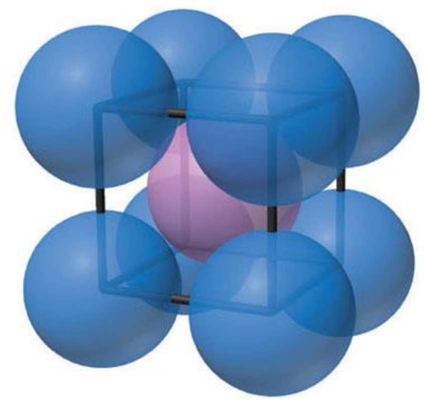
Atoms/unit cell = 1/8 x 8 = 1

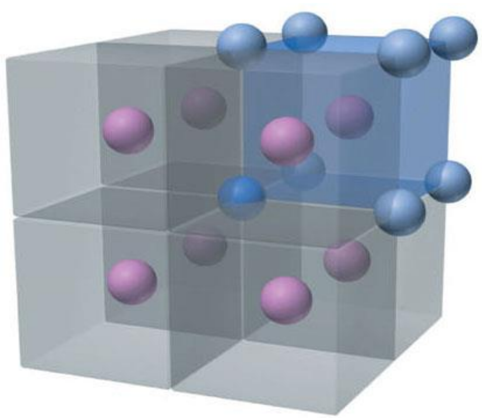
Cubic unit cells

Body-centered cubic shared1 atom in center and the corner atoms give a net of 2 atoms per unit cell. Produces a-b-a-b arrangement & takes 2 layers to define arrangements. (coordination number 8).

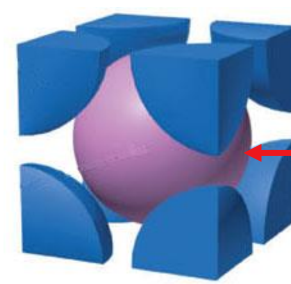


body-centered cubic





coordination number = 8



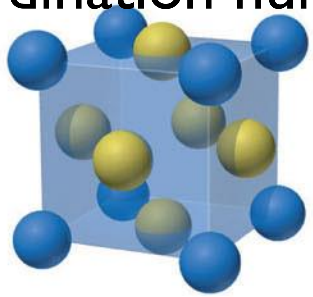
1/8 atom at 8 corners

1 atom at center

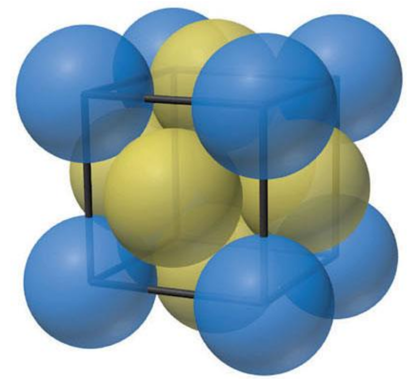
Atoms/unit cell = (1/8 x 8) + 1 = 2

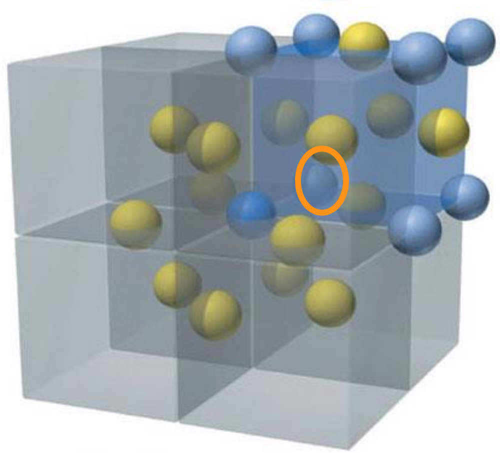
Cubic unit cells

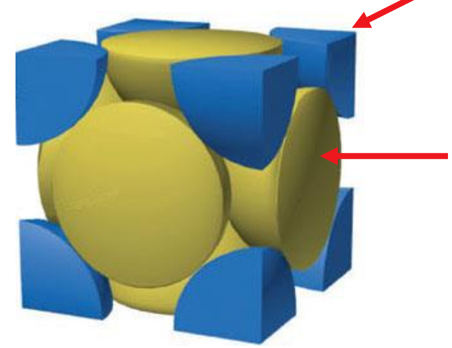
Face-centered cubic corner atoms plus half-atoms in each face give 4 atoms per unit cell. FCC structure has a-b-c-a-b-c stacking & takes 3 layers to establish the repeating pattern. (coordination number 12).



face-centered cubic







1/8 atom at 8 corners

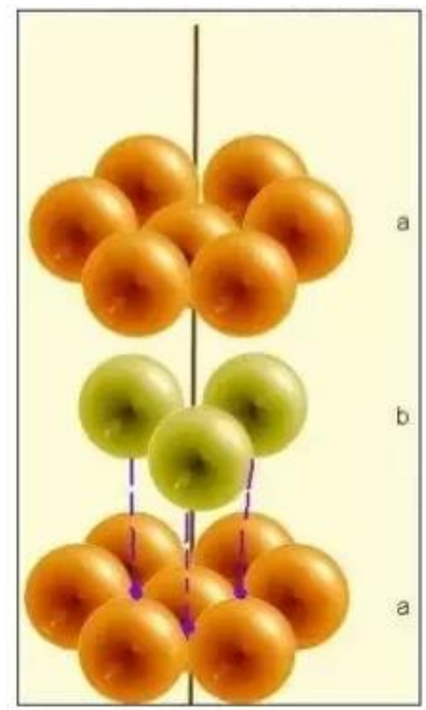
1/2 atom at 6 faces

Coordination number = 12

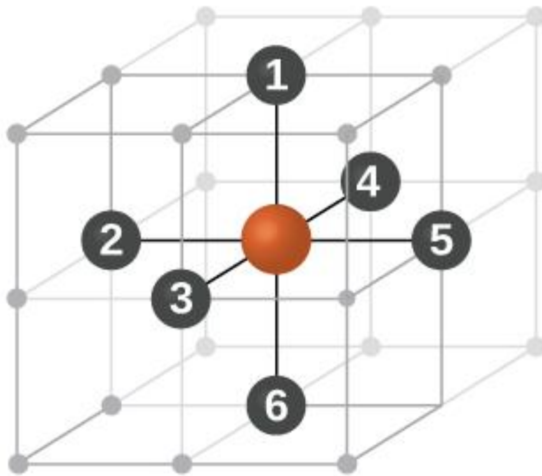
Atoms/unit cell = (1/8 x 8) + (1/2 x 6) = 4

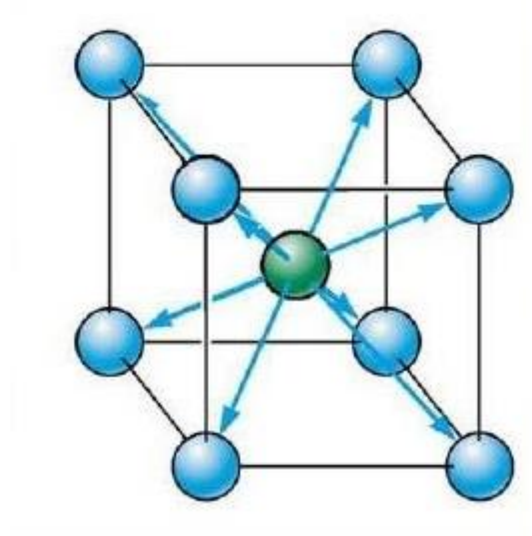
HCP unit cells

The hexagonal closed packed (hcp) structure has a coordination number of 12 and contains 6 atoms per unit cell

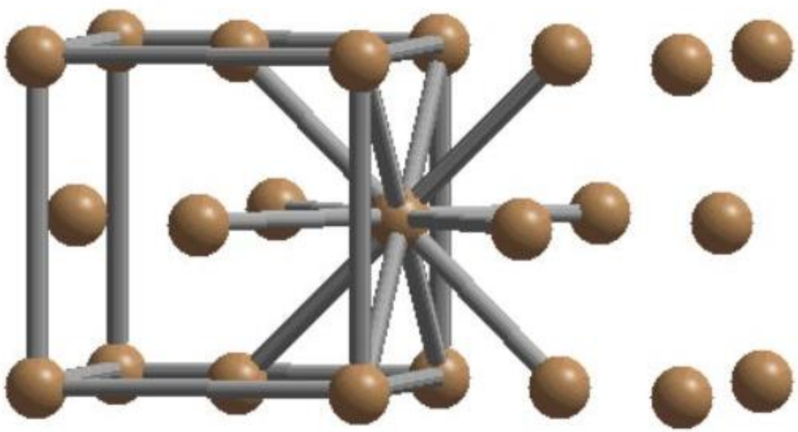


Unit cells

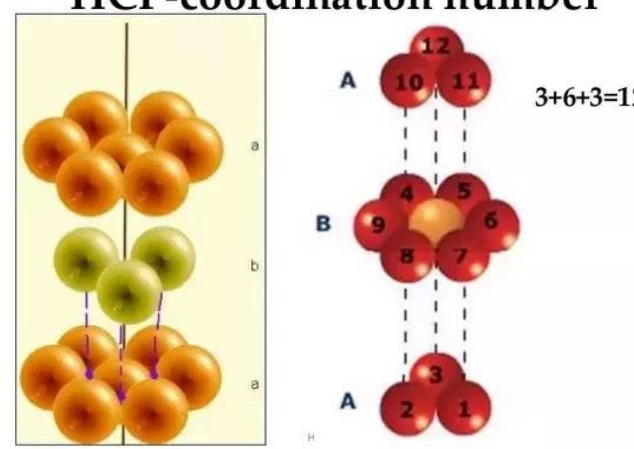




FCC-coordination number



HCP-coordination number



Cubic unit cells

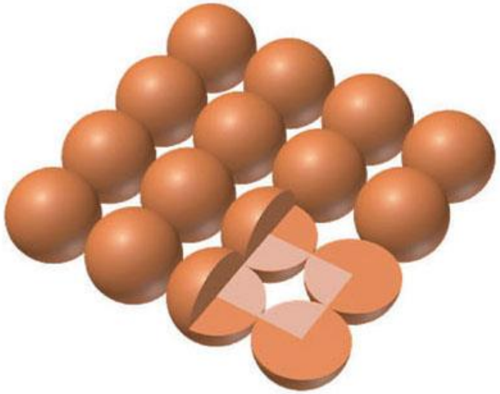
Problem-1: The unit cell of metallic gold is face centred cubic.

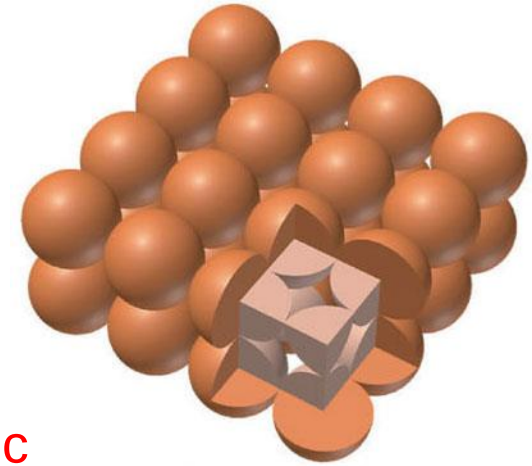
(a) How many atoms occupy the gold unit cell ?

(b) What is the mass of a gold unit cell ?

Problem-2: By X-ray diffraction it is found that nickel crystals are face-centred cubic. The edge of the unit cell is 3.52 Å. The atomic mass of nickel is 58.7 and its density is 8.94 g/cm3. Calculate Avogadro's number from the data.

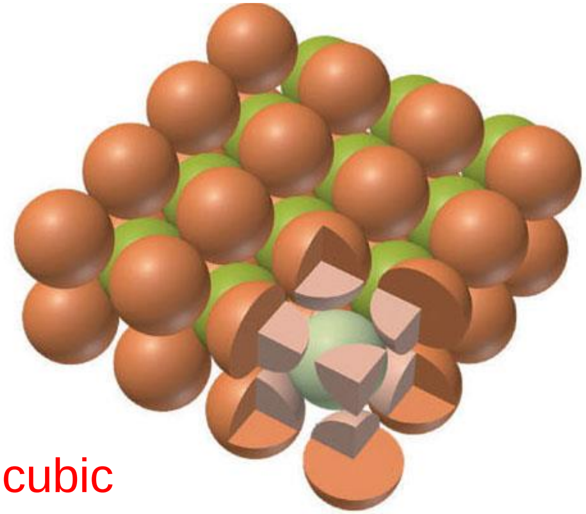
Packing of spheres





simple cubic

52% packing efficiency



body-centered cubic

68% packing efficiency

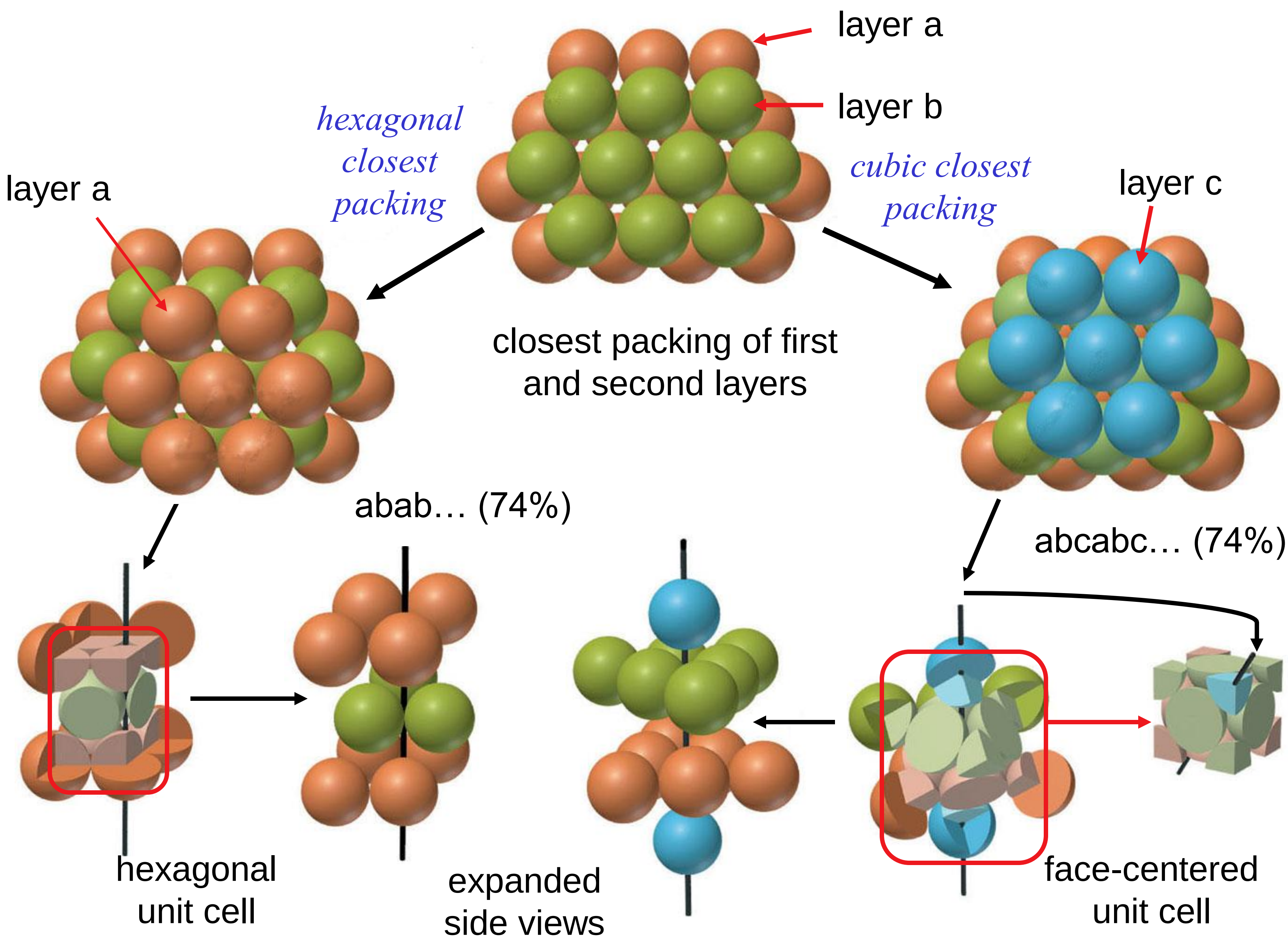
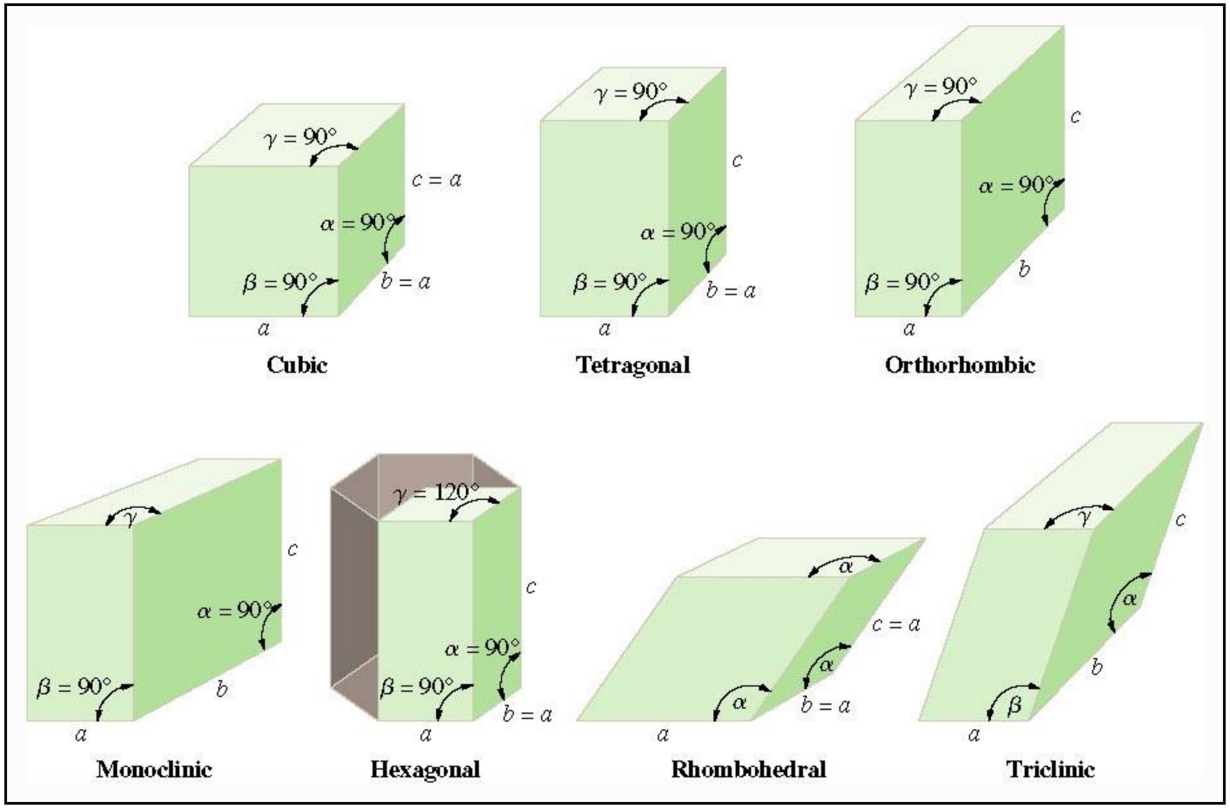

layer a
layer b
hexagonal closest packing
cubic closest packing
layer a
layer c
closest packing of first and second layers
abab… (74%)
abcabc… (74%)
hexagonal unit cell
expanded side views
face-centered unit cell

Figure 11.31

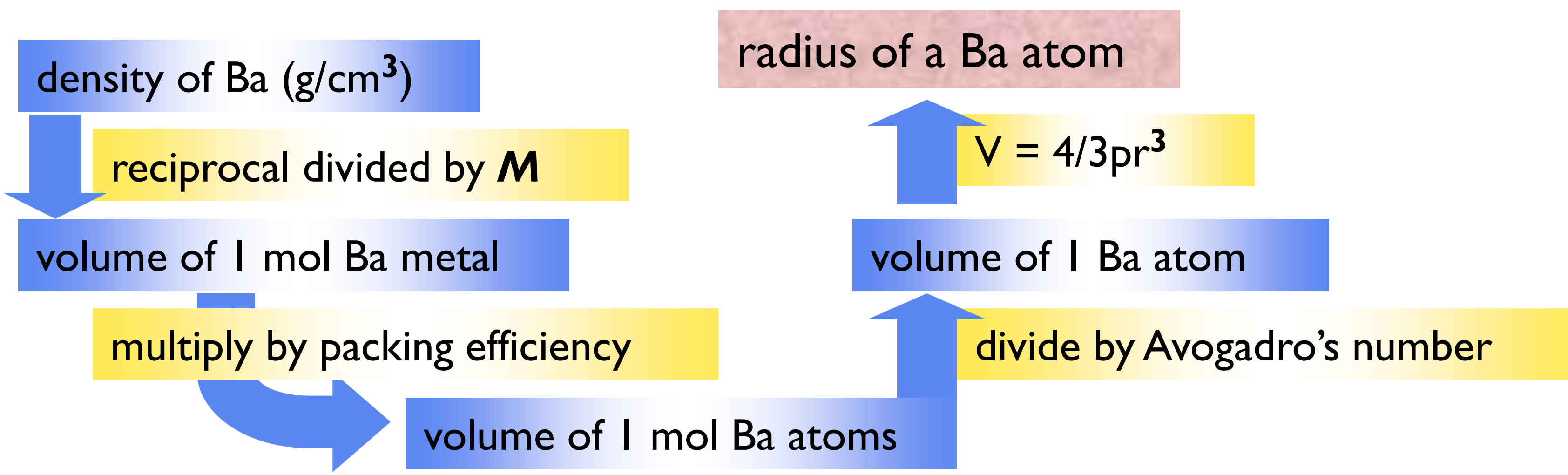
- Length of sides a, b, and c as well as angles α, β, γ vary to give most of the unit cells. Return to unit cells



SAMPLE PROBLEM 12.4 **Determining atomic radius from crystal structure**

PROBLEM: Barium is the largest non-radioactive alkaline earth metal. It has a body-centered cubic unit cell and a density of 3.62 g/cm^3. What is the atomic radius of barium? (volume of a sphere: $V = 4/3pr^3$)

PLAN: Use the density and molar mass to find the volume of 1 mol of Ba. Since 68% (for a body-centered cubic) of the unit cell contains atomic material, dividing by Avogadro's number will give the volume of one atom of Ba. Using the volume of a sphere, the radius can be calculated.



SAMPLE PROBLEM 12.4 (continued)

SOLUTION:

$$\text{volume of Ba metal} = \frac{1\ cm^3}{3.62\ g} \times \frac{137.3\ g\ Ba}{mol\ Ba} = 37.9\ cm^3/mol\ Ba$$

$$37.9\ cm^3/mol\ Ba \quad \times 0.68 \quad = 26\ cm^3/mol\ Ba\ atoms$$

$$\frac{26\ cm^3}{mol\ Ba\ atoms} \times \frac{mol\ Ba\ atoms}{6.022 \times 10^{23}\ atoms} = 4.3 \times 10^{-23}\ cm^3/atom$$

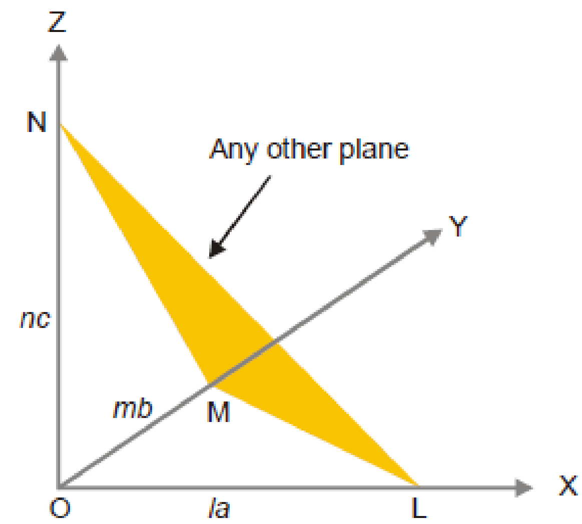
$$r^3 = 3V/4p \qquad r = \sqrt[3]{\frac{3V}{4\pi}} = \sqrt[3]{\frac{3(4.3x10^{-23}\ cm^3)}{4 \times 3.14}} \boxed{= 2.2 \times 10^{-8}\ cm}$$

Miller indices

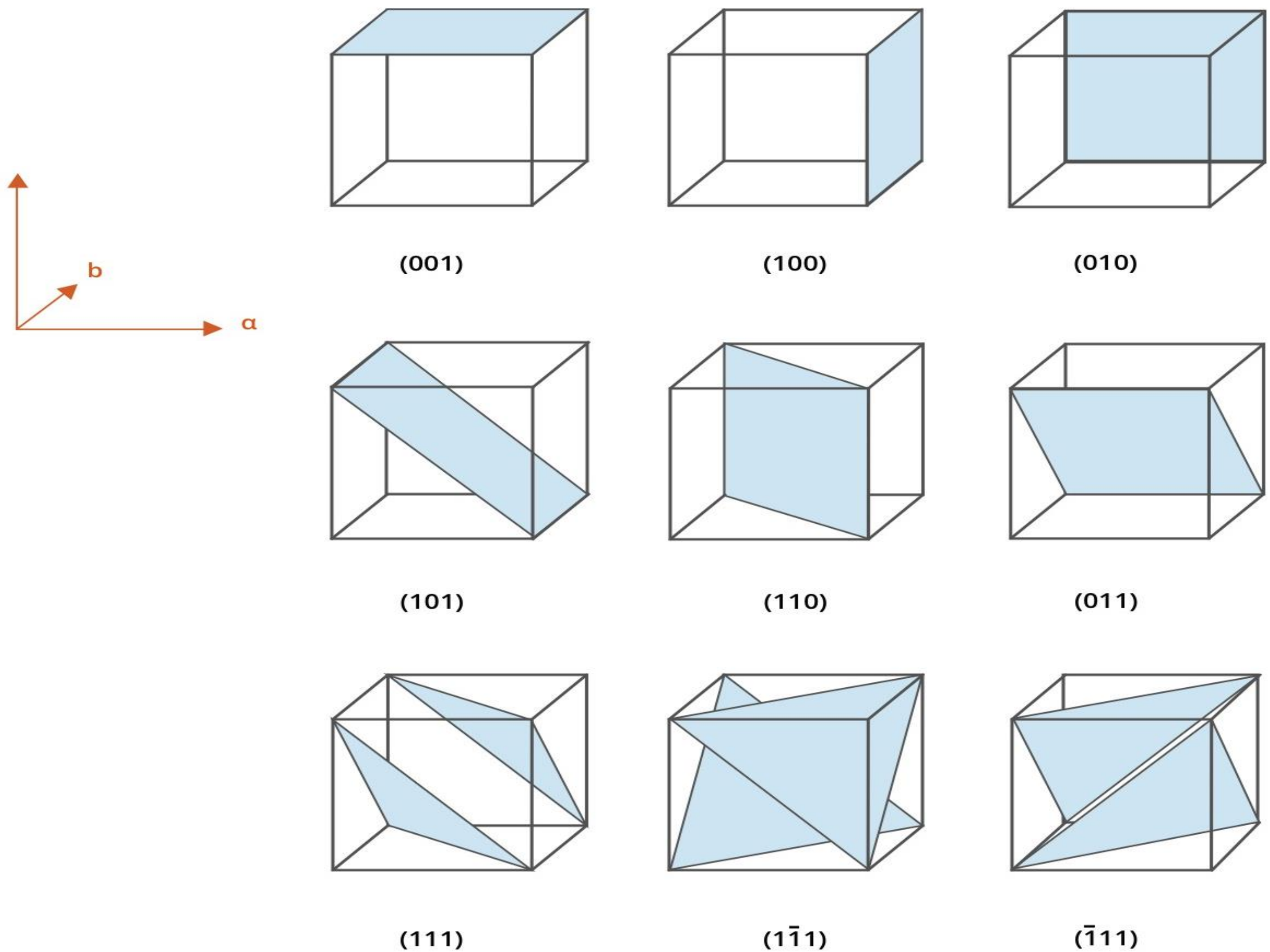
The miller indices definition can be stated as the mathematical representation of the crystallographic planes in three dimensions. Miller indices are used to specify directions and planes.

Calculation of Miller Indices:

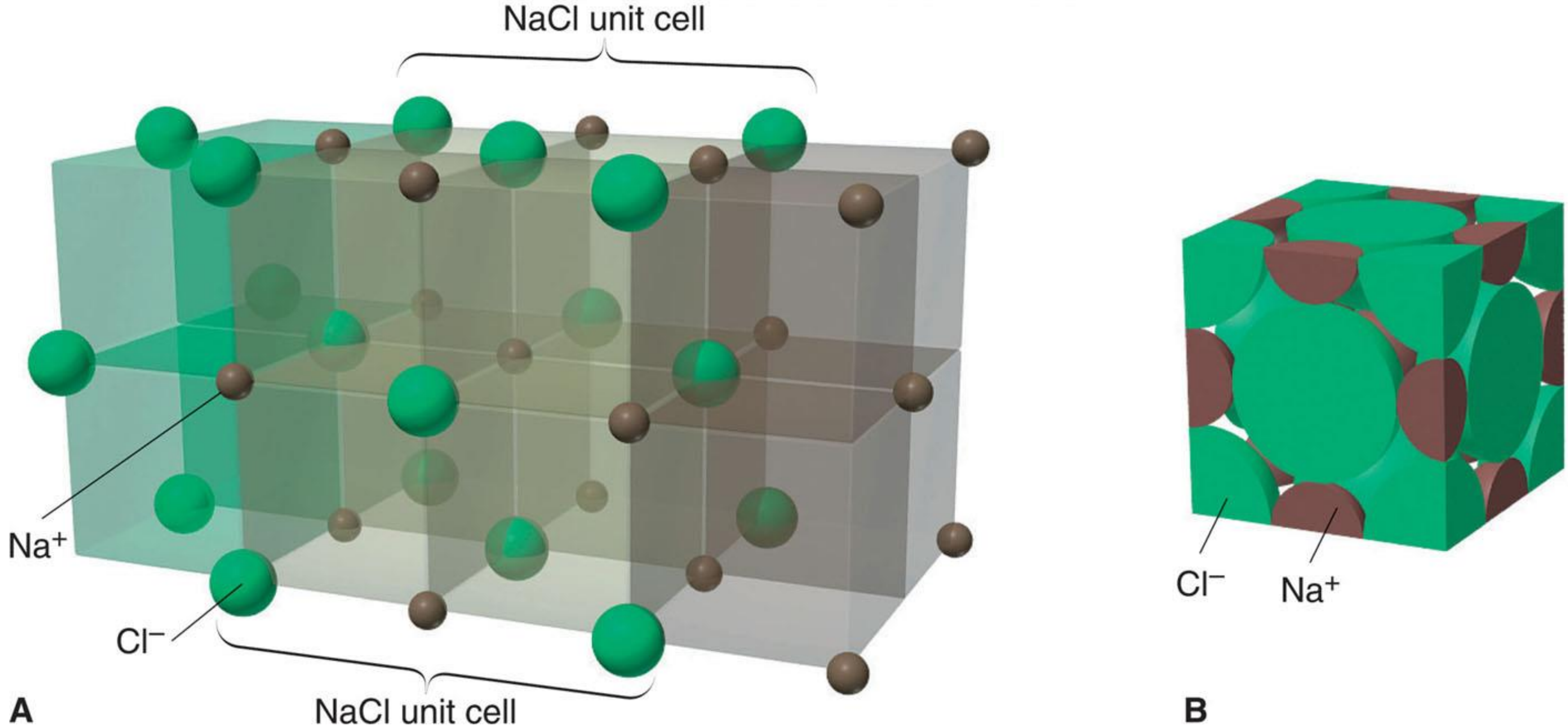
- Write the intercepts as multiples of a, b, c, say, la, mb and nc.
- Take reciprocals of l, m, and n,
- Clear fractions to get whole numbers h, k, l,
- Miller indices of the plane are (h, k, l).



Examples of Miller indices



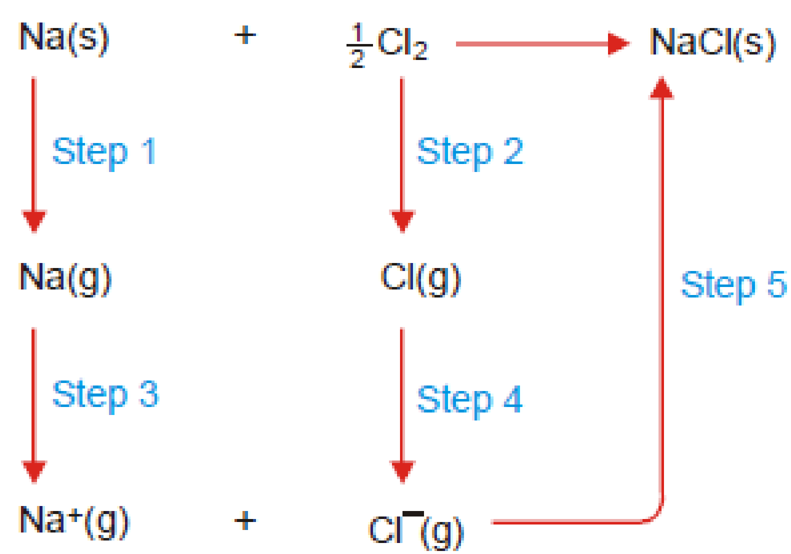
The sodium chloride structure



Lattice energy of ionic crystal

The change in enthalpy (heat change) that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.

Born Haber cycle is the application of Hess's law "at constant temperature, heat energy changes (enthalpy – ΔHrec) accompanying a chemical reaction will remain constant, irrespective of the way the reactants react to form product".



A Born-Haber cycle for the formation of NaCl crystal from its elements.

Lattice energy of NaCl crystal

Enthalpy change for direct formation. 2

$Na(s) + \frac{1}{2} Cl_2(g) \longrightarrow NaCl(s)$; $\Delta H° = -411$ kJ

Enthalpy change by indirect steps.

Step 1: $Na(s) \longrightarrow Na(g)$ $\Delta H_1° = +108$ kJ (sublimation)

Step 2: $\frac{1}{2} Cl_2 \longrightarrow Cl(g)$ $\Delta H_2° = +121$ kJ (dissociation)

Step 3: $Na(g) \longrightarrow Na^+(g) + e^-$ $\Delta H_3° = +495$ kJ (ionization)

Step 4. $Cl + e^- \longrightarrow Cl^-(g)$ $\Delta H_4° = -348$ kJ (ionization)

Step 5: $Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$ $\Delta H_5° = -$ (lattice energy)

According to Hess's law

$\Delta H°_1 + \Delta H°_2 + \Delta H°_3 + \Delta H°_4 + \Delta H°_5 = -411$ kJ

108 kJ + 121 kJ + 495 kJ – 348 kJ – lattice energy = – 411 kJ

So, lattice energy = +787 kJ mol^{-1}

Diffraction of x-rays by crystal

1) the X-ray diffracted from atoms in crystal planes obey the laws of reflection.
(2) the two rays reflected by successive planes will be in phase if the extra distance travelled by the second ray is an integral number of wavelengths.

According to Bragg's,
$n\lambda = CB + BD$...(i)

Geometry shows that
$CB = BD = AB \sin\theta$...(ii)

From (i) and (ii)
$n\lambda = 2AB \sin\theta$.
or
$n\lambda = 2d \sin\theta$.

This is known as the Bragg equation.

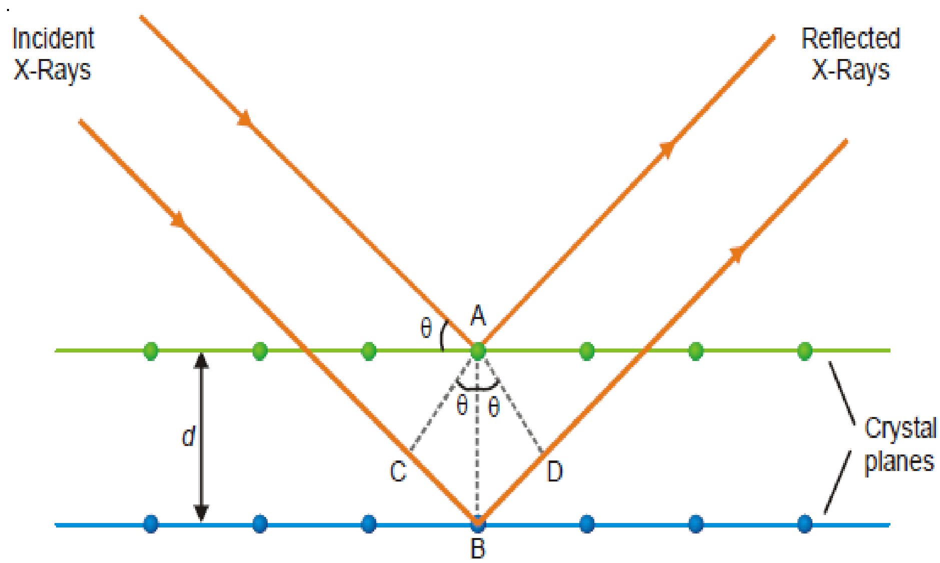


Figure 12.14
Reflection of X-Rays from two different planes of a crystal.

Application of Bragg's equation

Problem-1: Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a copper X-ray tube (λ = 1.539 Å) at an angle of 22.5°C. (2.01 A)

Problem-2: Diffraction angle 2θ equal to 16.8° for a crystal having inter planar distance in the crystal is 0.400 nm when second order diffraction was observed. Calculate the wavelength of X-rays used. (0.584 A)