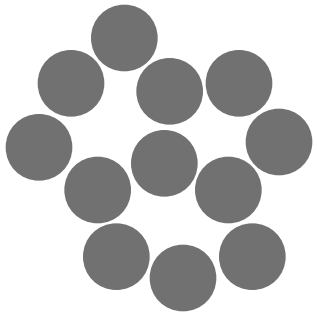
Lecture Outline Crystallography

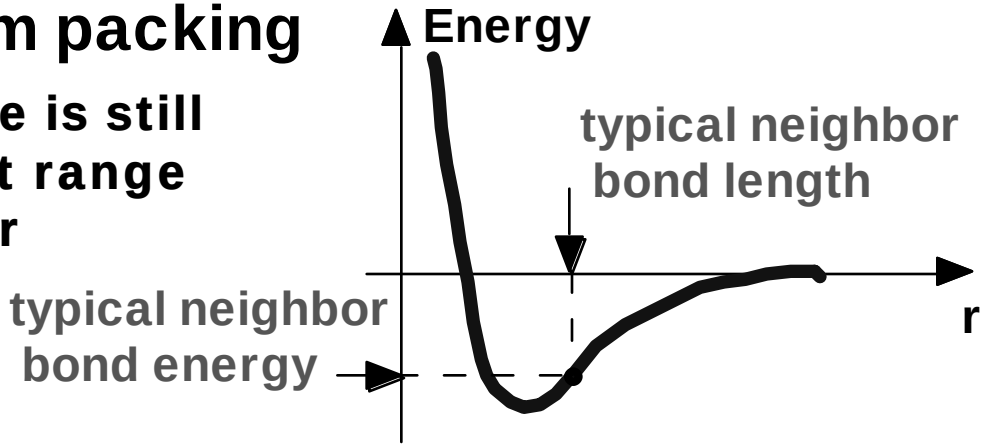
- Short and long range Order
- Poly- and single crystals, anisotropy, polymorphy
- Allotropic and Polymorphic Transitions
- Lattice, Unit Cells, Basis, Packing, Density, and Crystal Structures
- Points, Directions, and Planes in the Unit Cell
- Structures with more than one atoms per lattice point
- Interstitial Sites
- Ionic Crystal Structures
- Covalent Crystal Structures
- Metallic Crystal structures
- Diffraction and modern microscopy

Lowest ENERGY state at each temperature

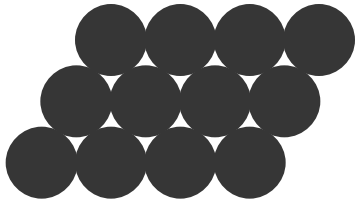
- **Non dense, random packing**



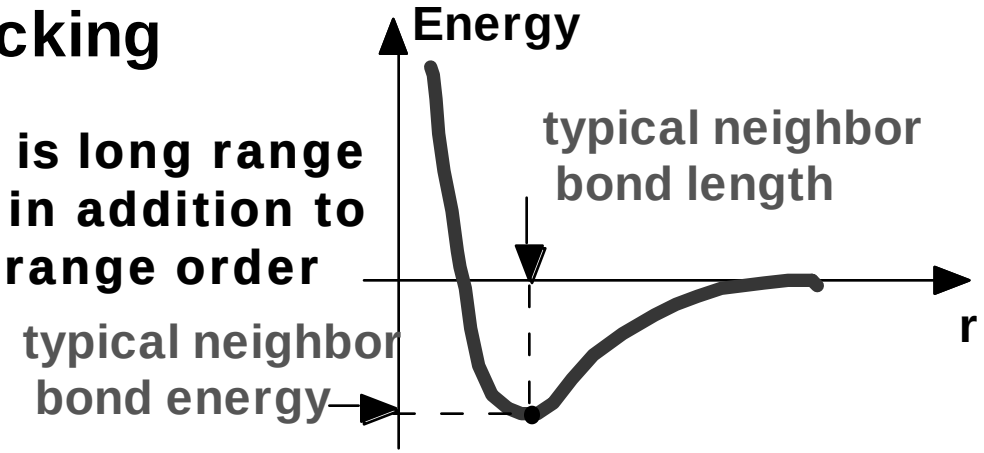
There is still short range order



- **Dense, regular packing**



There is long range order in addition to short range order



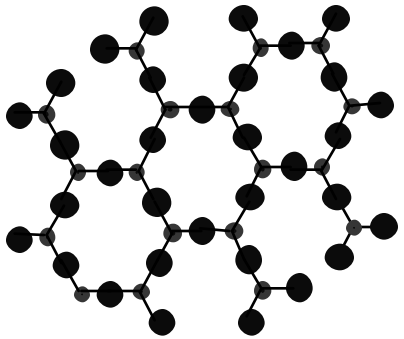
Dense, regular-packed structures tend to have lower energy, of course everything depends on temperature, at low enough temperatures many materials crystallize

MATERIALS AND PACKING

Crystalline materials...

- **atoms pack in periodic, 3D arrays**
- **typical of: -metals**
  -many ceramics
  - semiconductors
  -some polymers

Glass is actually a cold melt, over long enough times, it crystallizes, old church windows are thicker at the bottom



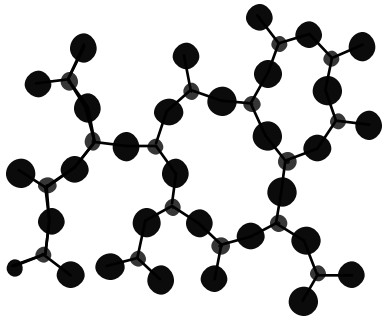
One of many forms of crystalline SiO_2

• **Si** ● **Oxygen**

Noncrystalline materials...

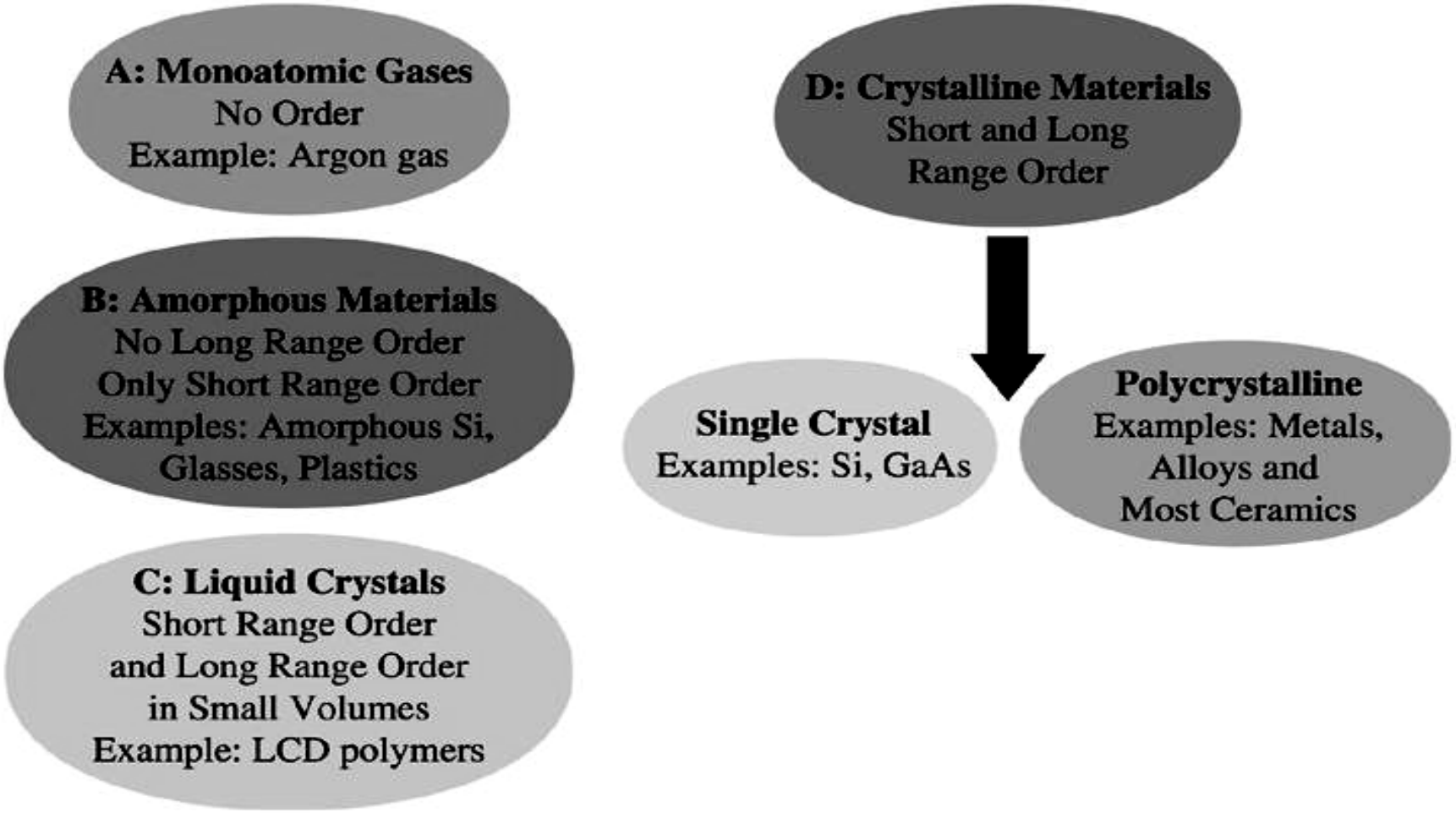
- **atoms have no periodic packing**
- **occurs for: -complex structures**
  - rapid cooling

"Amorphous" = Noncrystalline

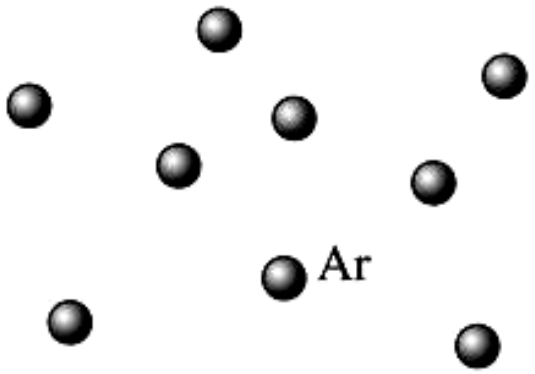


noncrystalline SiO_2

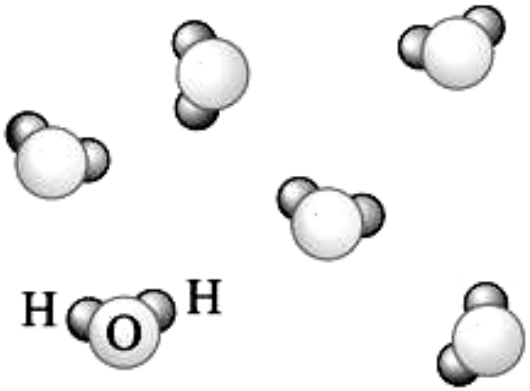
Quartz glass, a cold melt



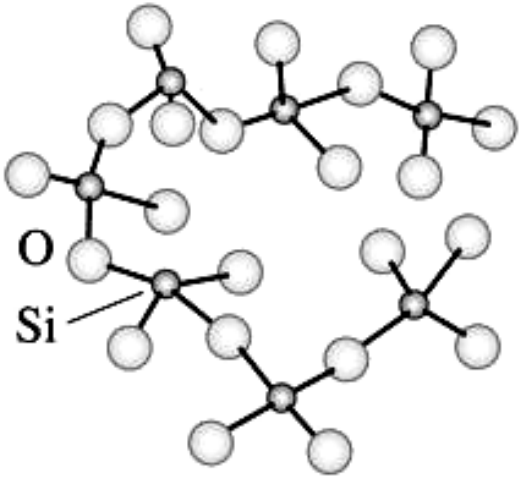
Classification of materials based on type of atomic order.



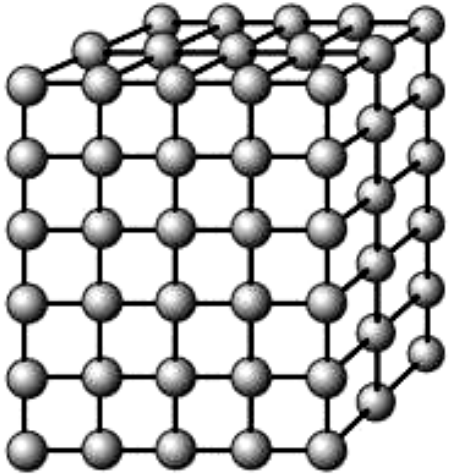
(a)



(b)



(c)



(d)

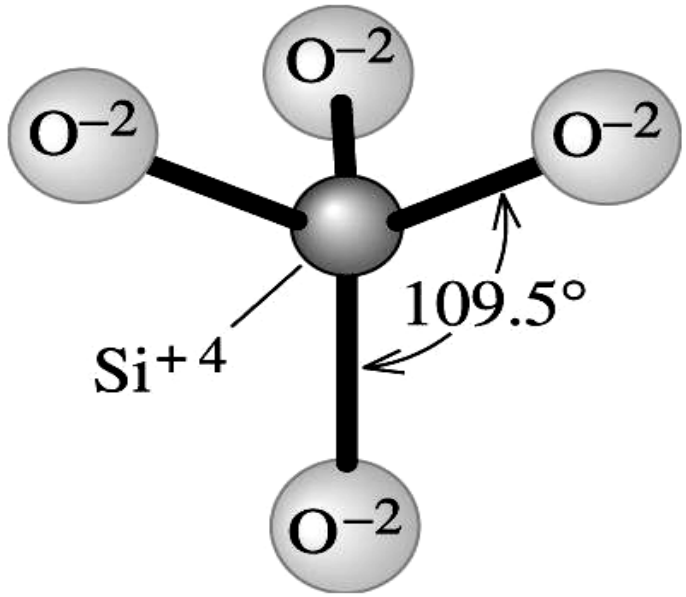
Levels of atomic arrangements in materials:

(a) Inert monoatomic gases have no regular ordering of atoms:

(b,c) Some materials, including water vapor, nitrogen gas, amorphous silicon and silicate glass have short-range order.

(d) Metals, alloys, many ceramics, semiconductors and some polymers have regular ordering of atoms/ions that extends through the material

= crystals



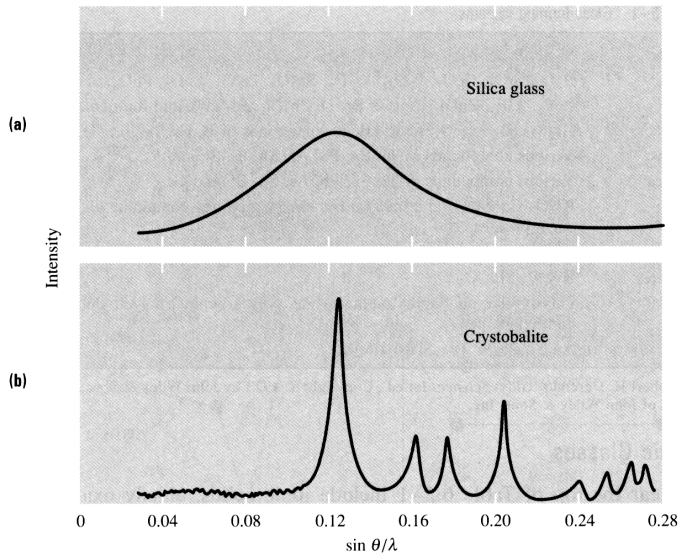


FIGURE 6.5–1
A comparison of the X-ray scans for **(a)** amorphous silica and **(b)** a crystalline polymorph of silica (crystobalite). *(Source: Adapted from B. E. Warren and J. Biscal,* Journal of American Ceramic Society, *2149, 1938.)*

Basic "*Si-0*" tetrahedron in silicate glass. X-ray diffraction shows only short range order.

Note that this cannot exist in quartz at room temperature, there the tetrahedron is distorted resulting in pronounced anisotropy effects such as piezoelectricity.

In ß-cristobalite, a high temperature phase of quartz, we have an undistorted tetrahedron again, X-ray diffraction shows long range order

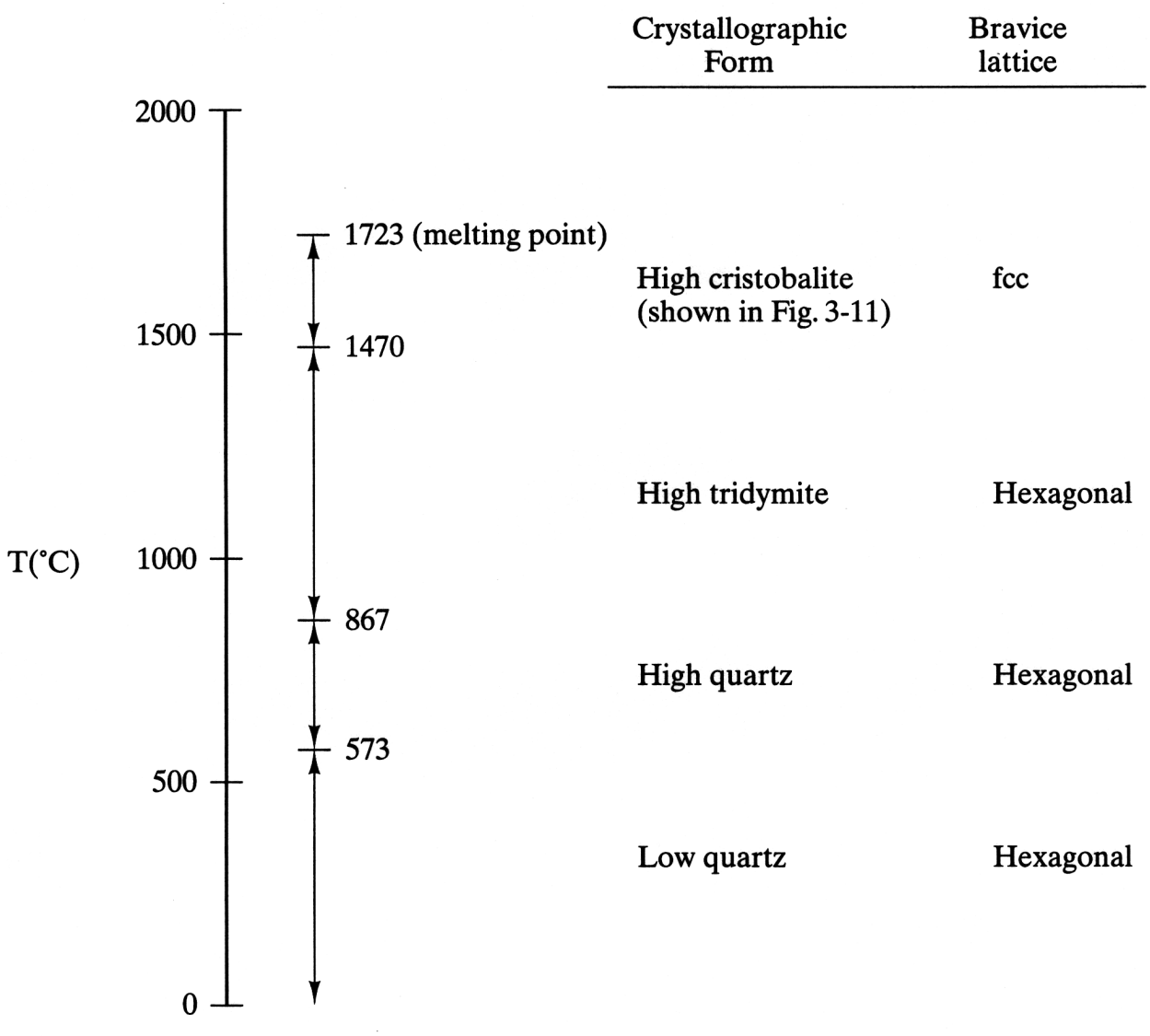
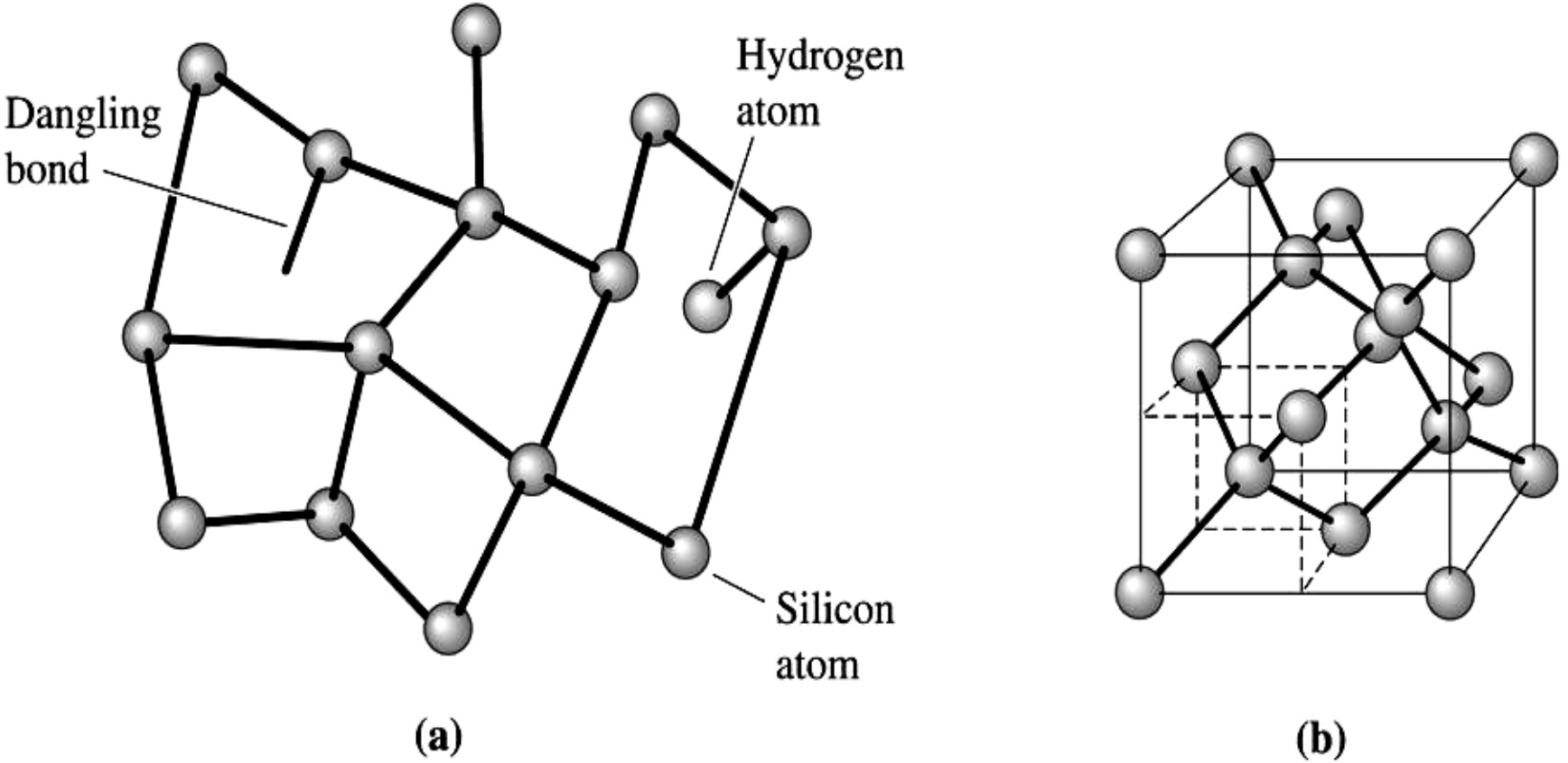


Figure 3-12 *Many crystallographic forms of SiO_2 are stable as they are heated from room temperature to the melting temperature. Each form represents a different way to connect adjacent SiO_4^{4-} tetrahedra.*

Again there are different crystallographic phases, i.e. long range order structures until the crystal melts and only short range order remains



Atomic arrangements in (a) Amorphous silicon with H (b) Crystalline silicon. Note the variation in the inter-atomic distance for amorphous silicon, but there still is short-range order

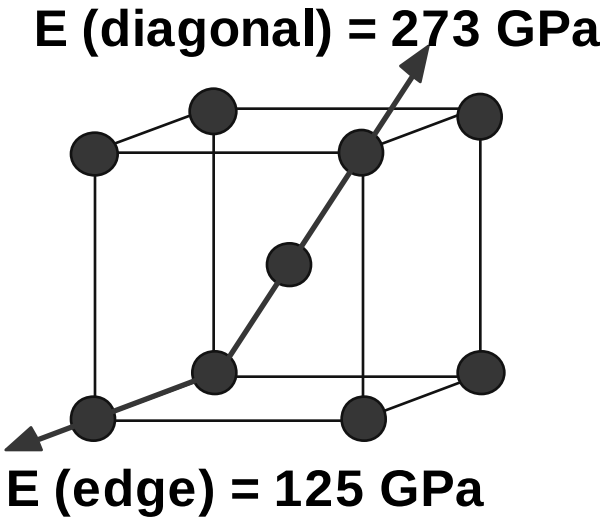
POLY-CRYSTALS

- ***Most*** **engineering materials are poly-crystalline !**

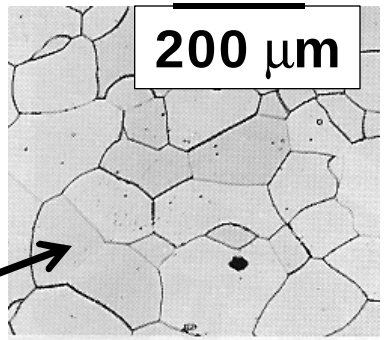
- **Nb-Hf-W plate with an electron beam weld.**
- **Each "grain" is a single crystal.**
- **If crystals are randomly oriented, component properties are not directional, *but frequently we have texture, preferred orientation of poly-crystals resulting in pronounced anisotropy***
- **Crystal sizes range from 1 nm to 2 cm, (i.e., from a few to millions of atomic layers).**

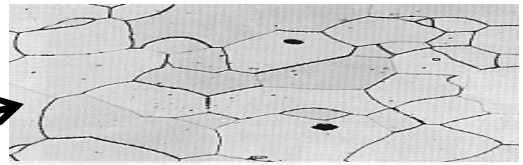
SINGLE versus POLY-CRYSTALS

- **Single (Mono-)crystals**
  - **Properties vary with direction: anisotropy.**
  - **Example: the modulus of elasticity (E) in BCC iron:**



- **Poly-crystals**
  - **Properties may/may not vary with direction, depending on degree of texture.**
  - **If grains are randomly oriented: isotropic. ($E_{poly\ iron}$ = 210 GPa)**
  - **If grains are textured, anisotropic.**

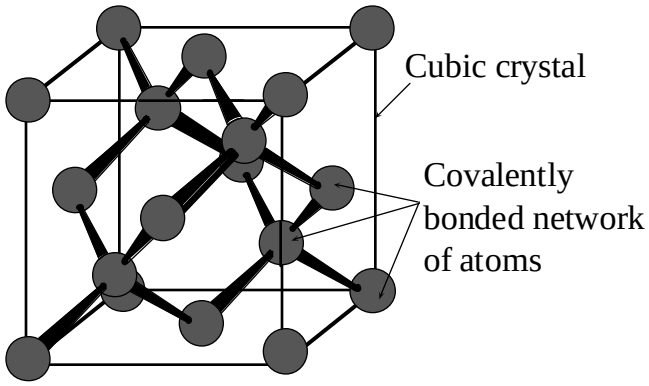




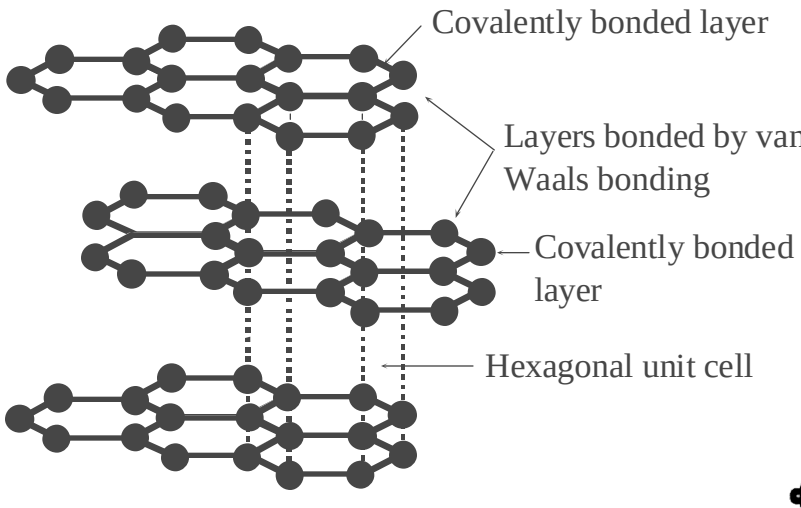
Allotropic and Polymorphic Transitions

- Allotropy - The characteristic of an element being able to exist in more than one crystal structure, depending on temperature and pressure.
- Polymorphism - Compounds exhibiting more than one type of crystal structure.

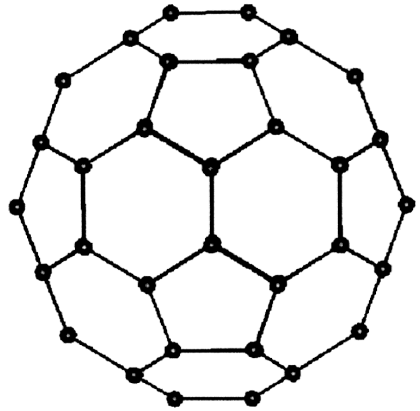
- **Everything depends on temperature and pressure**, e.g. coefficient of thermal expansion can, therefore, only be defined over a certain region of temperature



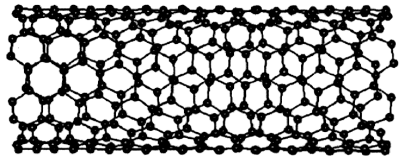
(a) Diamond unit cell



(b) Graphite

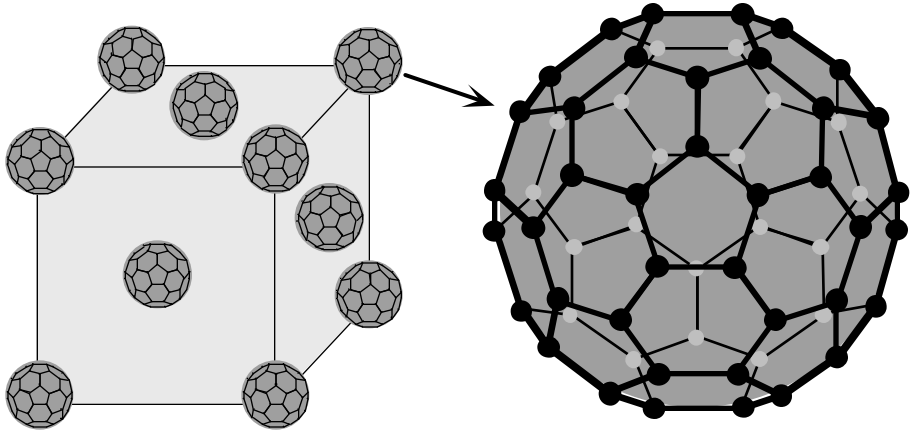


(a)



(b)

Figure 3-19 *(a) C_{60} molecule, or buckyball. (b) Cylindrical array of hexagonal rings of carbon atoms, or buckytube. (Courtesy of Molecular Simulations, Inc.)*



The FCC unit cell of the Buckminsterfullerene crystal. Each lattice point has a C_{60} molecule

Buckminsterfullerene (C_{60}) molecule (the "buckyball" molecule)

(c) Buckminsterfullerene

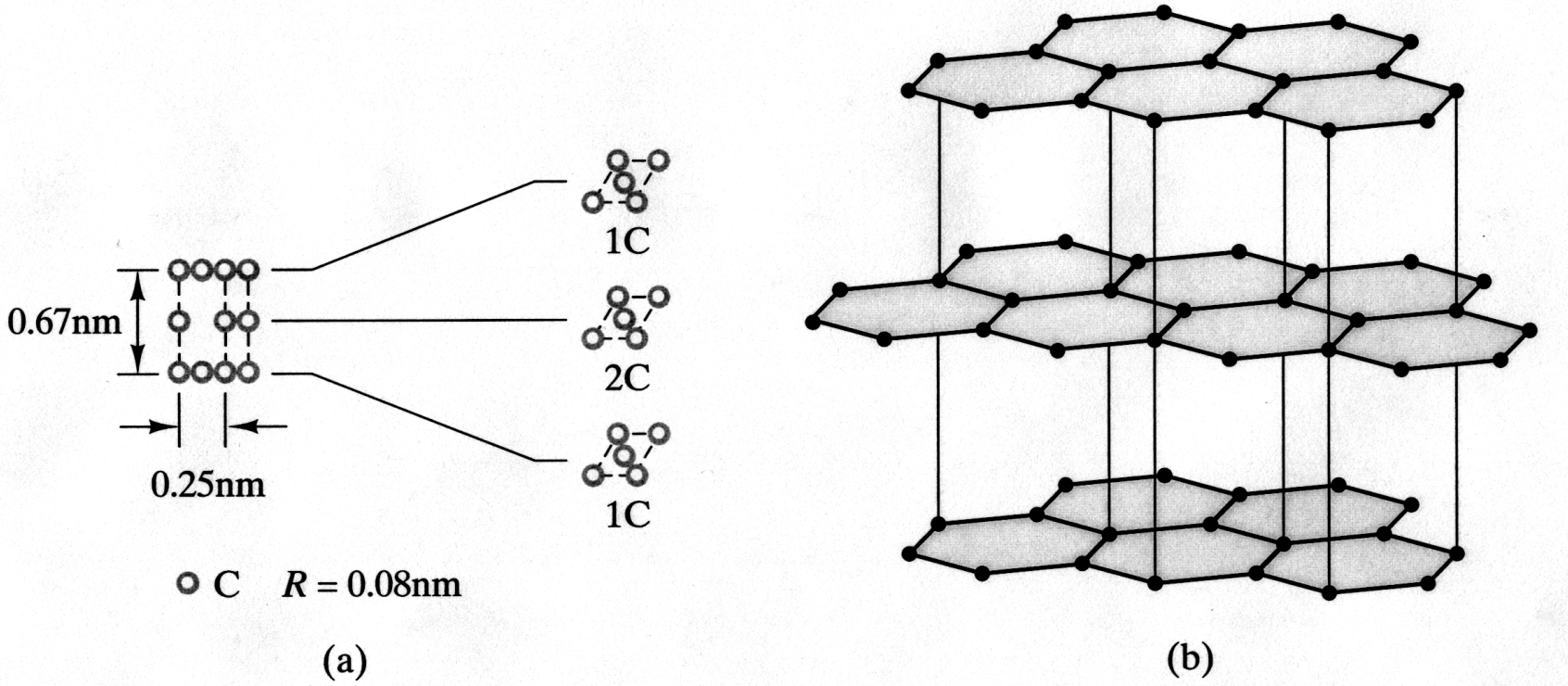


Figure 3-18 *(a) An exploded view of the graphite (C) unit cell. (From F. H. Norton,* Elements of Ceramics, *2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1974.) (b) A schematic of the nature of graphite's layered structure. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann,* Introduction to Ceramics, *2nd ed., John Wiley & Sons, Inc., New York, 1976.)*

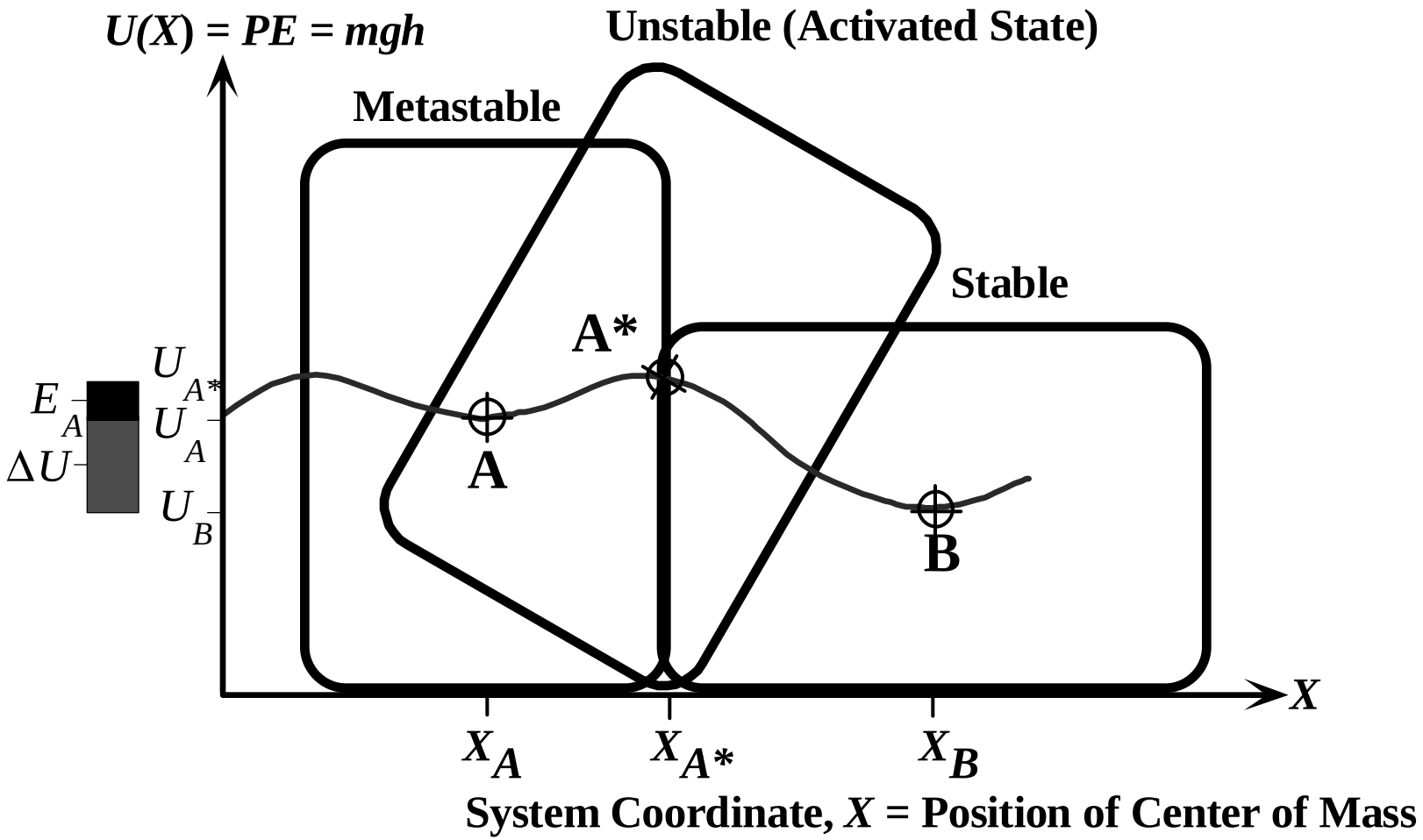
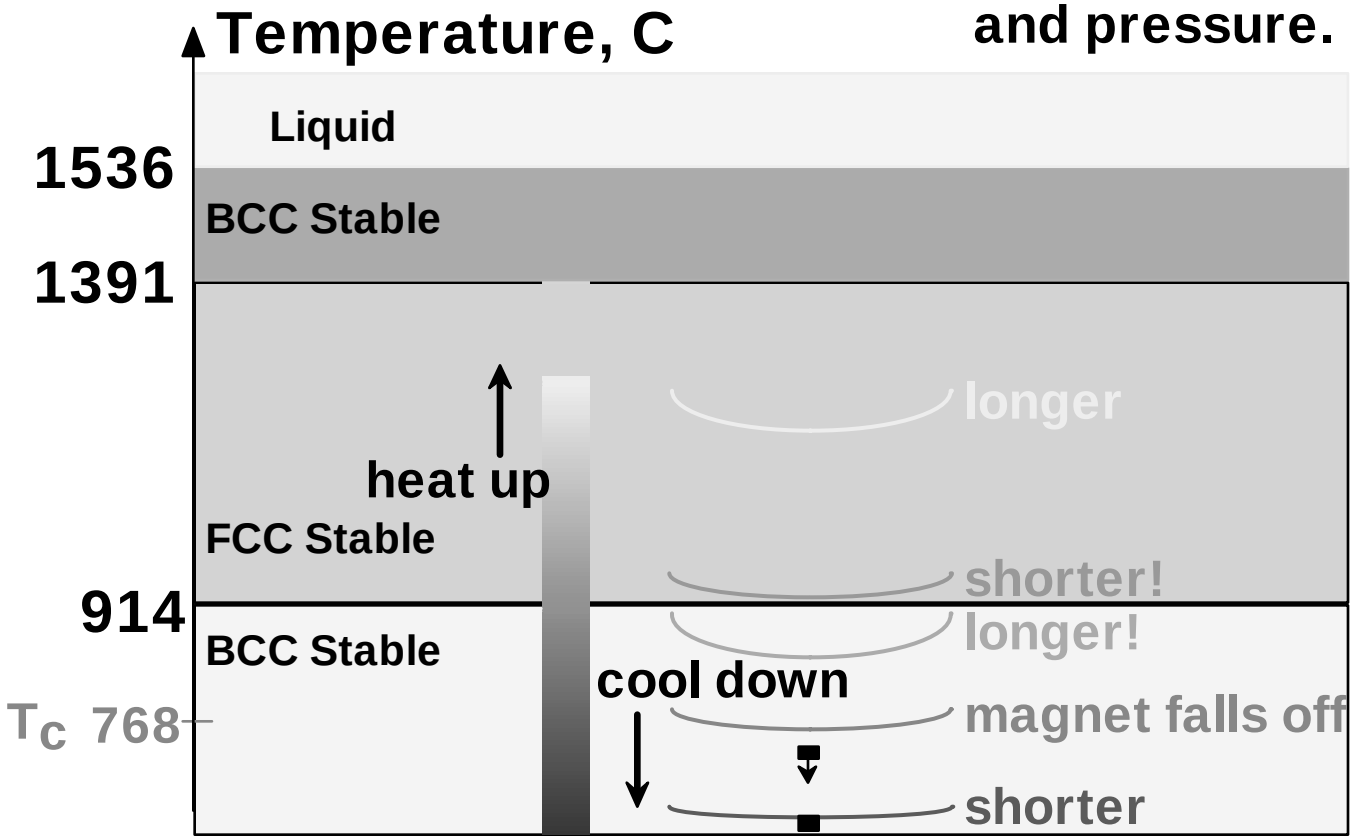


Fig. 1.27: Tilting a filing cabinet from state A to its edge in state A^* requires an energy E_A. After reaching A^*, the cabinet spontaneously drops to the stable position B. PE of state B is lower than A and therefore state B is more stable than A.

Example: heating and cooling of a hanging iron wire

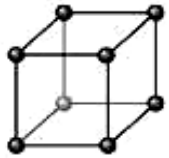
- **Demonstrates "polymorphism"**

The same group of atoms has more than one crystal structure.
The actual structure depends on temperature and pressure.

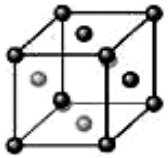


Lattice, Unit Cells, Basis, and Crystal Structures

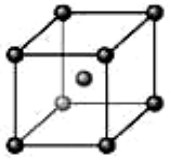
- Lattice - a 3D collection of points that divide space into smaller equally sized units.
- Basis - a group of atoms associated with a lattice point. This may be one single atom or a group of atoms.
- Unit cell - a subdivision of the lattice that still retains the overall characteristics of the entire lattice, contains at least one atom may contain many atoms.
- Atomic radius - apparent radius of an atom, typically calculated from the dimensions of the unit cell, using close-packed directions (depends upon type of bonding, coordination number, quantum mechanics).
- Packing factor - The fraction of space in a unit cell occupied by atoms.



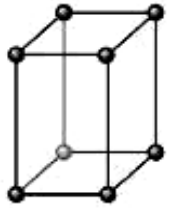
Simple cubic



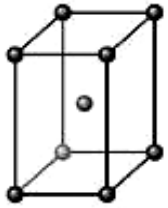
Face-centered cubic



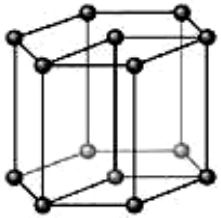
Body-centered cubic



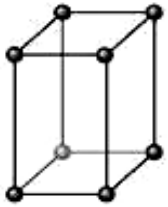
Simple tetragonal



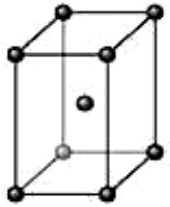
Body-centered tetragonal



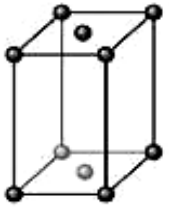
Hexagonal



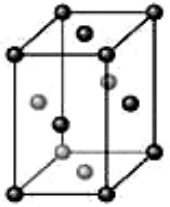
Simple orthorhombic



Body-centered orthorhombic

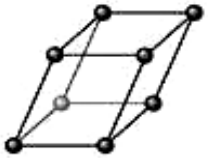


Base-centered orthorhombic

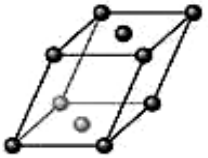


Face-centered orthorhombic

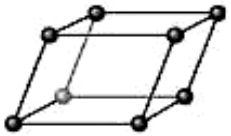
Rhombohedral



Simple monoclinic



Base-centered monoclinic



Triclinic

The fourteen types of Bravais) lattices grouped in seven crystal systems:

triclinic

monocline

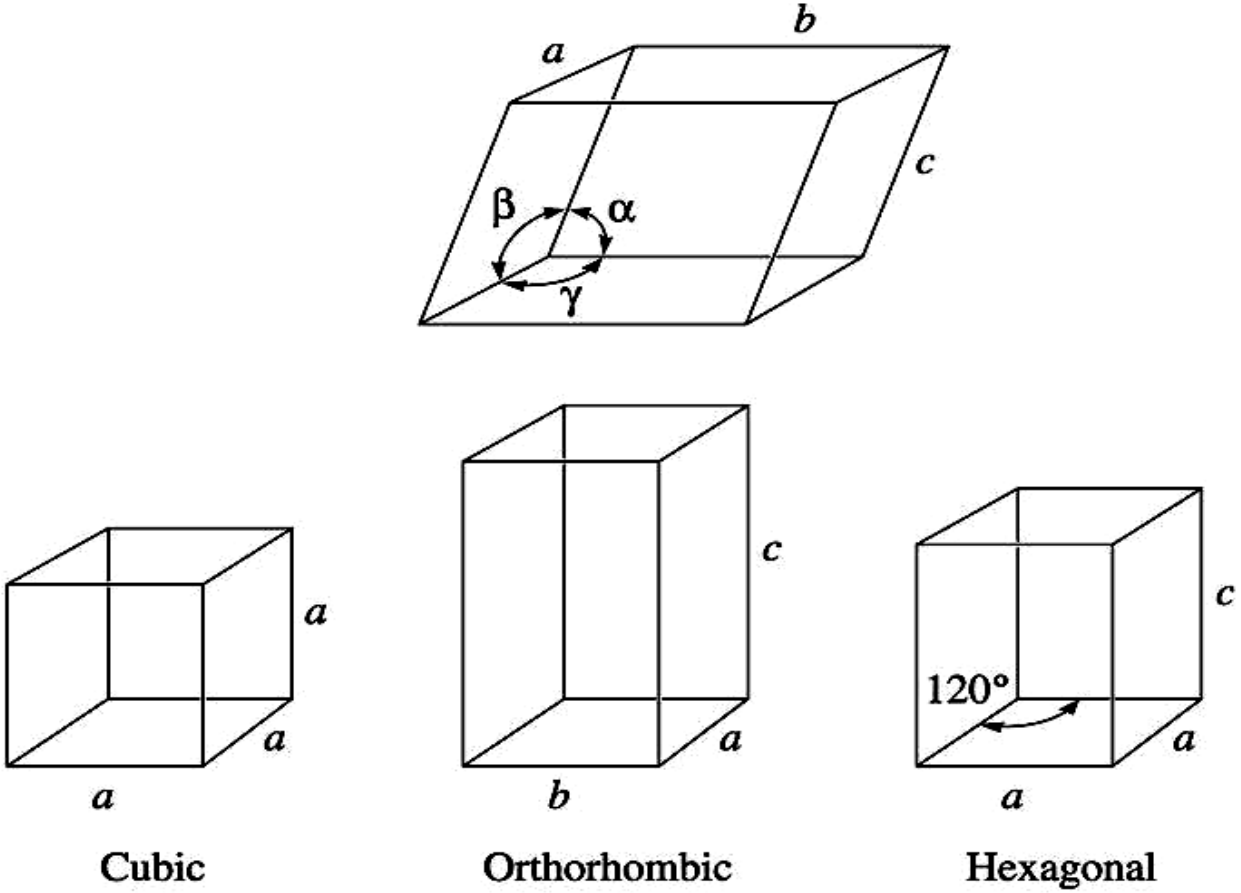
rhombohedral = (trigonal)

orthorhombic

tetragonal

hexagonal

cubic



Definition of lattice parameters in cubic, orthorhombic, and hexagonal crystal systems.

Note that angles are not always 90° degrees and coordination axis lengths are not necessarily all equal, as you know them to be from Cartesian coordinates

For cubic crystals, however, calculations are just like with Cartesian coordinates

TABLE 3-1 ■ *Characteristics of the seven crystal systems*

Structure	Axes	Angles between Axes	Volume of the Unit Cell
Cubic	$a = b = c$	All angles equal 90°	a^3
Tetragonal	$a = b \neq c$	All angles equal 90°	a^2c
Orthorhombic	$a \neq b \neq c$	All angles equal 90°	abc
Hexagonal	$a = b \neq c$	Two angles equal 90°. One angle equals 120°.	$0.866a^2c$
Rhombohedral or trigonal	$a = b = c$	All angles are equal and none equals 90°	$a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$
Monoclinic	$a \neq b \neq c$	Two angles equal 90°. One angle (β) is not equal to 90°	$abc \sin\beta$
Triclinic	$a \neq b \neq c$	All angles are different and none equals 90°	$abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$

Lattice Points and Directions in the Unit Cell

- Miller-indices - A shorthand notation to describe certain crystallographic directions and planes in a material.

Lattice directions are in direct space and are denoted by [ ] brackets. A negative number is represented by a bar over the number.

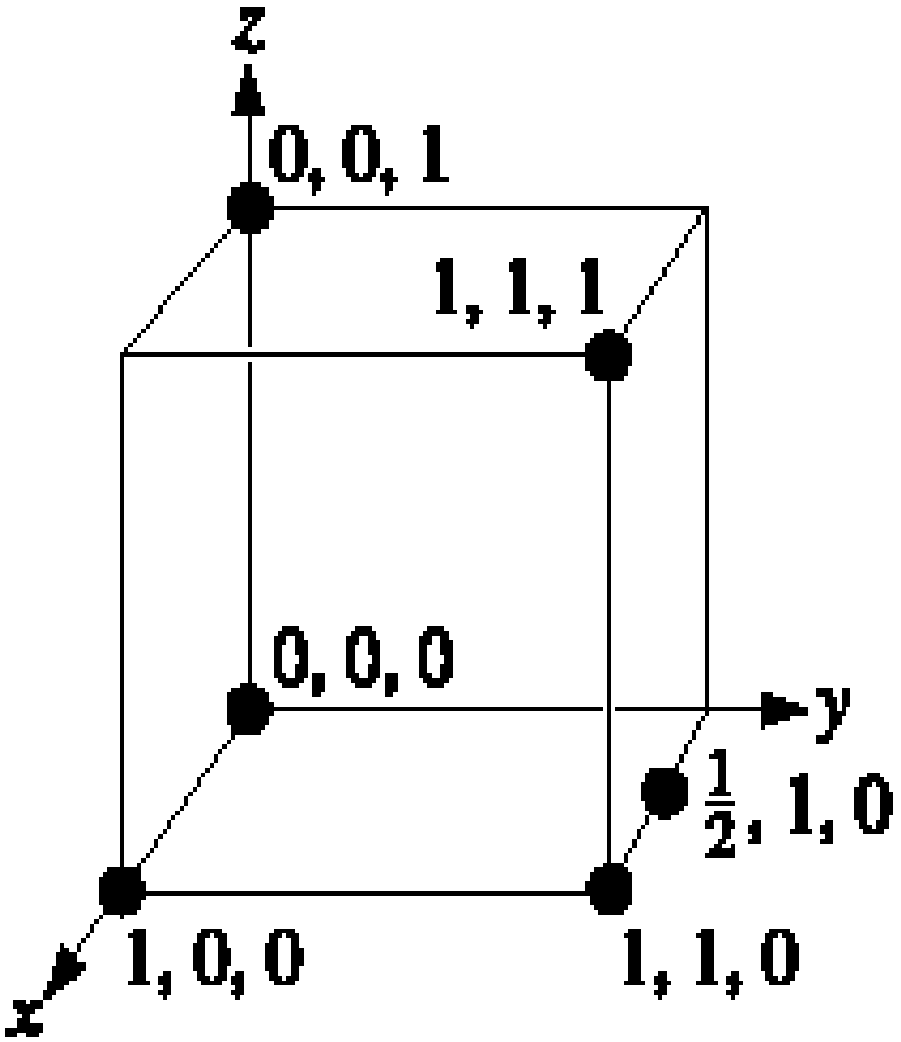
Directions of a form (also called family) - Crystallographic directions that all have the same characteristics, although their ‘‘sense’’ may be different. Denoted by < > brackets, they are symmetrically equivalent

Lattice Planes in the Unit Cell **are an altogether different matter !**

- Miller-indices - A shorthand notation to describe certain crystallographic directions and planes in a material.

Lattice planes are represented by the vector that is normal (perpendicular to them), these are 3D vectors in reciprocal (or dual) space (reciprocal space is nothing fancy - it is just a mathematical convenience !)

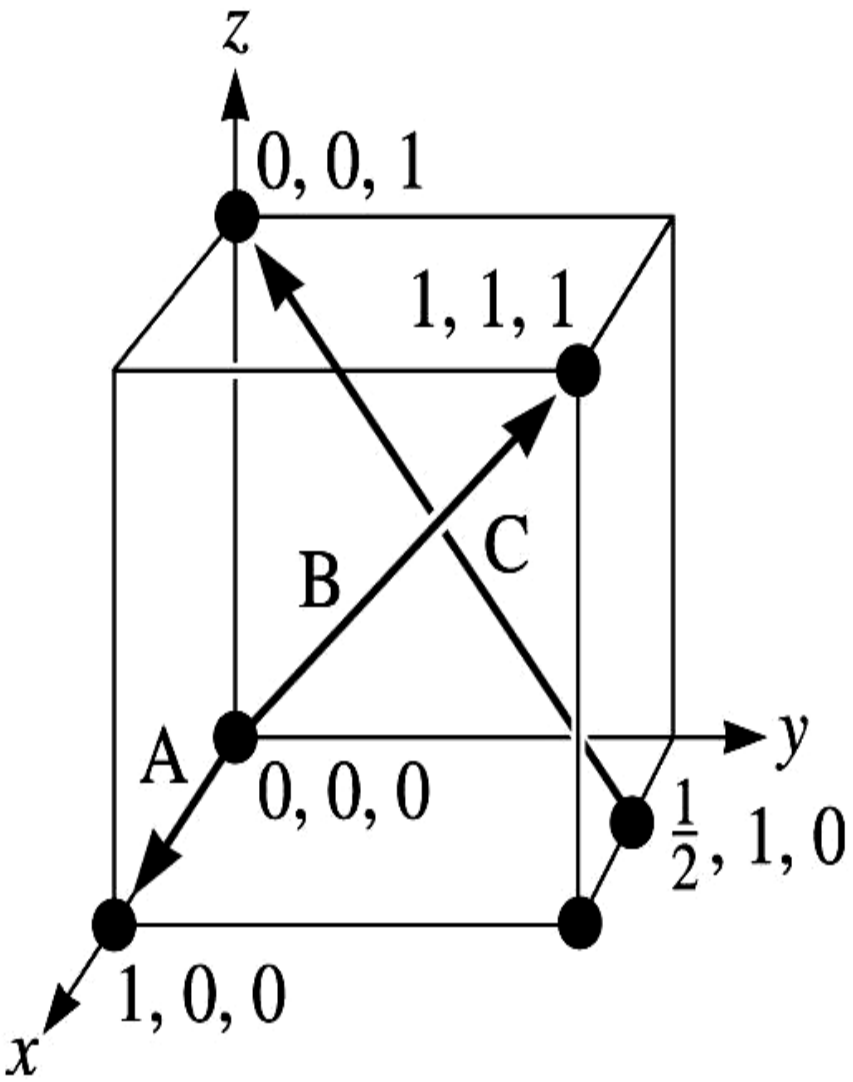
Directions of a form (also called family) – lattice planes that all have the same characteristics, although their ‘‘sense’’ may be different. Denoted by { } brackets, they are symmetrically equivalent. Now if the lattice point represents more than one point the front side and the back side of one and the same plane may have very different chemical properties as different atoms will be exposed, e.g. ZnS structure



We start with the coordinates of lattice points in order to define the Miller indices of lattice directions

Coordinates of selected points in the unit cell. The number refers to the distance from the origin in terms of lattice parameters.

Determining Miller Indices of Directions



Determine coordinates of two points that lie in direction of interest,
$u_1\ v_1\ w_1$ and $u_2\ v_2\ w_2$

calculations are simplified if the second point corresponds with the origin of the coordinate system

Subtract coordinates of second point from those of first point
$u' = u_1-u_2$, $v' = v_1-v_2$, $w' = w_1-w_2$

Clear fractions from the differences to give indices in lowest integer values. Write indices in [] brackets. Negative integer values are indicated with a bar over the integer,

[uvw] and $[\bar{u}\bar{v}\bar{w}]$ are running in opposite directions

Direction *A*

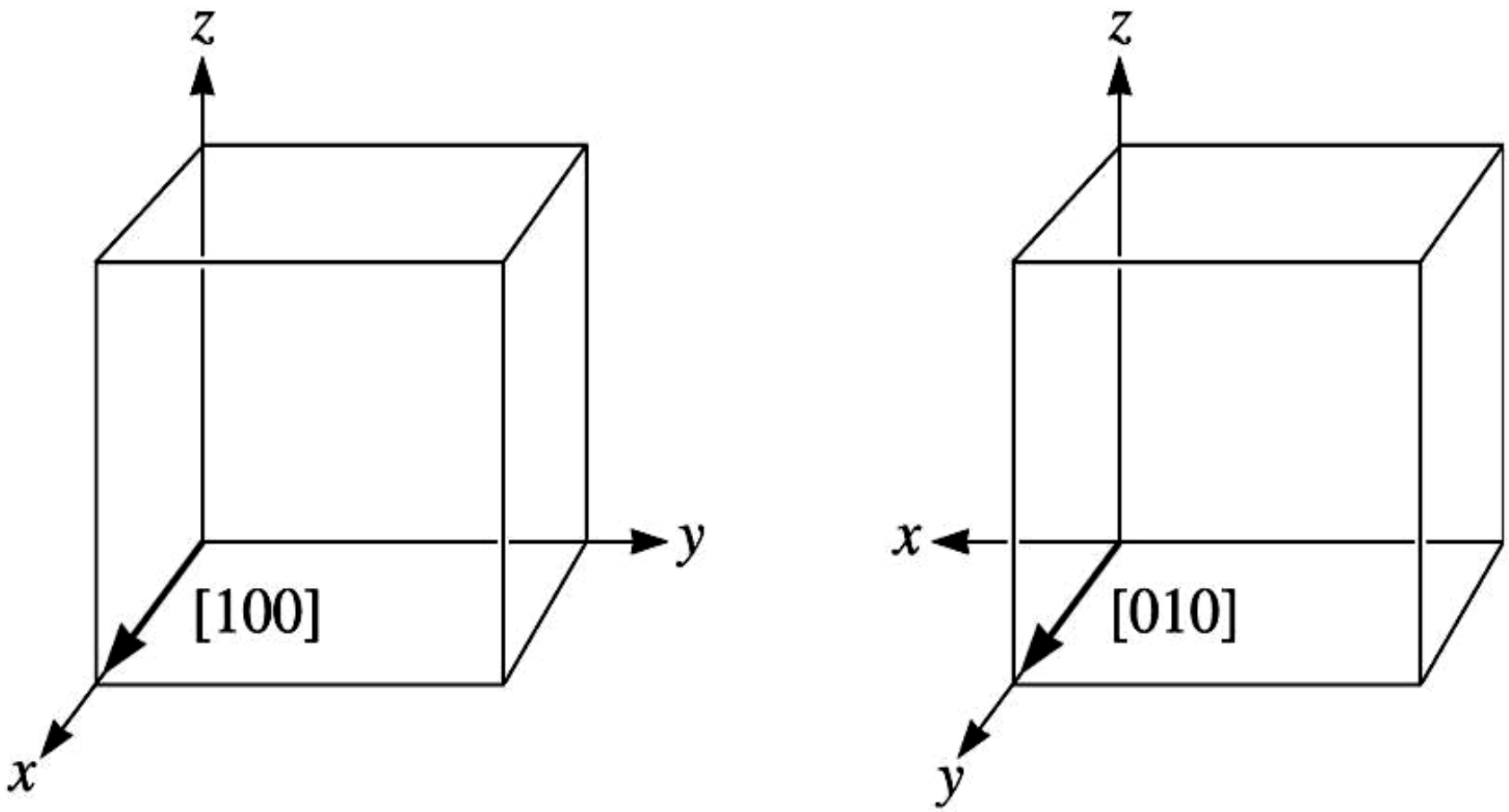
1. Two points are 1, 0, 0, and 0, 0, 0
2. 1, 0, 0, - (0, 0, 0) = 1, 0, 0
3. No fractions to clear or integers to reduce
4. [100]

Direction *B*

1. Two points are 1, 1, 1 and 0, 0, 0
2. 1, 1, 1, - (0, 0, 0) = 1, 1, 1
3. No fractions to clear or integers to reduce
4. [111]

Direction *C*

1. Two points are 0, 0, 1 and 1/2, 1, 0
2. 0, 0, 1 –(1/2, 1, 0) = -1/2, -1, 1
3. 2 (-1/2, -1, 1) = -1,-2, 2
4. $[\bar{1}\bar{2}2]$

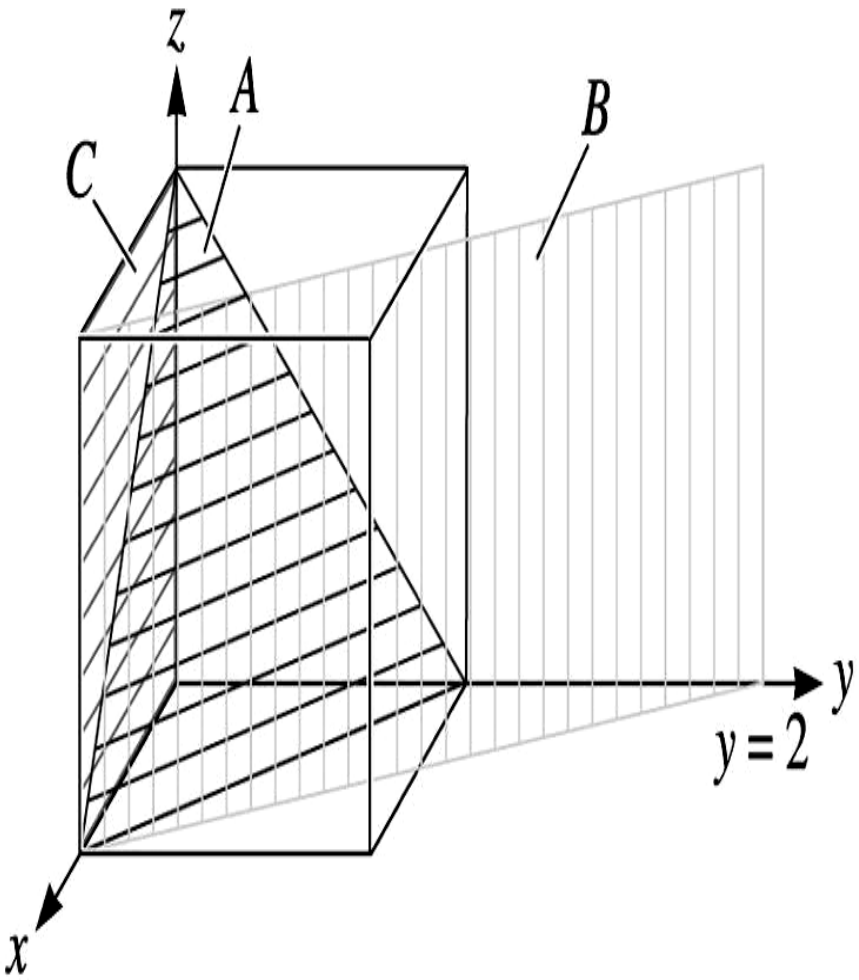


Equivalency of crystallographic directions of a form in cubic systems.

TABLE 3-3 ■ *Directions of the form* ⟨110⟩ *in cubic systems*

$$\langle 110 \rangle = \begin{cases} [110] & [\bar{1}\bar{1}0] \\ [101] & [\bar{1}0\bar{1}] \\ [011] & [0\bar{1}\bar{1}] \\ [1\bar{1}0] & [\bar{1}10] \\ [10\bar{1}] & [\bar{1}01] \\ [01\bar{1}] & [0\bar{1}1] \end{cases}$$

Determining Miller Indices of Planes



Identify the coordinate intersects of the plane, if plane is parallel to one of the axes, this intercept is taken to be infinite

Take the reciprocal of the intercept

Clear fractions, but do not reduce to lowest integers

Cite in (h k l) parentheses

Negative integer values are indicated with a bar over the integer

$(\bar{h}\ \bar{k}\ \bar{l})$ is the same plane as (h k l) , just its back side

Plane *A*

1. $x = 1$, $y = 1$, $z = 1$
2. $1/x = 1$, $1/y = 1$, $1/z = 1$
3. No fractions to clear
4. **(111)**

Plane *B*

1. The plane never intercepts the z axis, so $x = 1$, $y = 2$, and $z = \infty$
2. $1/x = 1$, $1/y = 1/2$, $1/z = 0$
3. Clear fractions: $1/x = 2$, $1/y = 1$, $1/z = 0$
4. **(210)**

Plane *C*

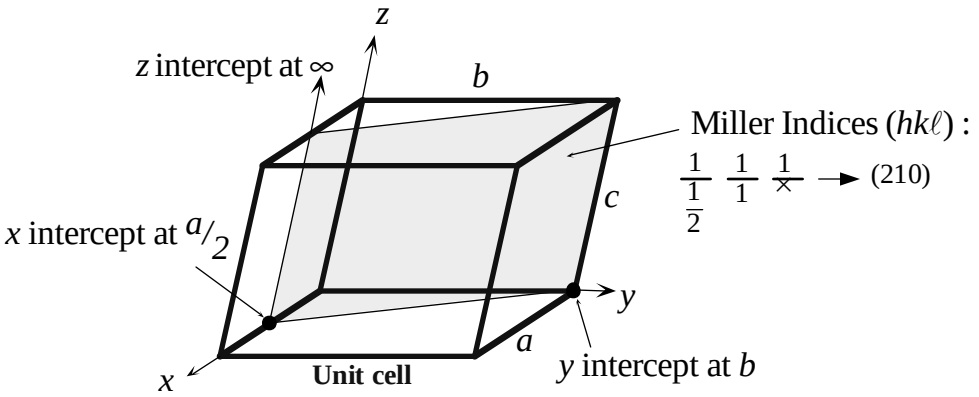
1. We shall move the origin, since the plane passes through 0, 0, 0. Let's move the origin one lattice parameter in the y-direction. Then,

$x = \infty$, $y = -1$, and $z = \infty$

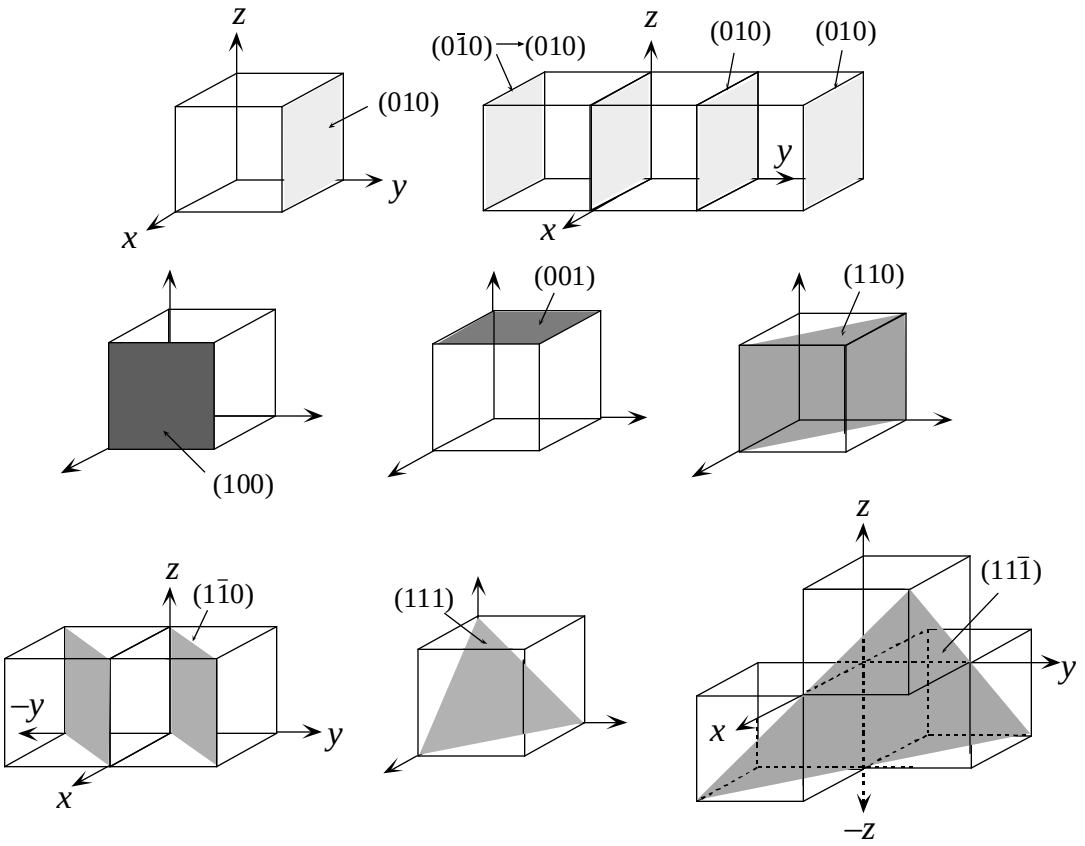
2. $1/x = 0$, $-1/y = -1$, $1/z = 0$
3. No fractions to clear.

4. $(0\bar{1}0)$

that seemed a bit arbitrary, we could have moved the origin in the –y direction as well, then we would have gotten (010), which is just the back side of $(0\bar{1}0)$



(a) Identification of a plane in a crystal



(b) Various planes in the cubic lattice

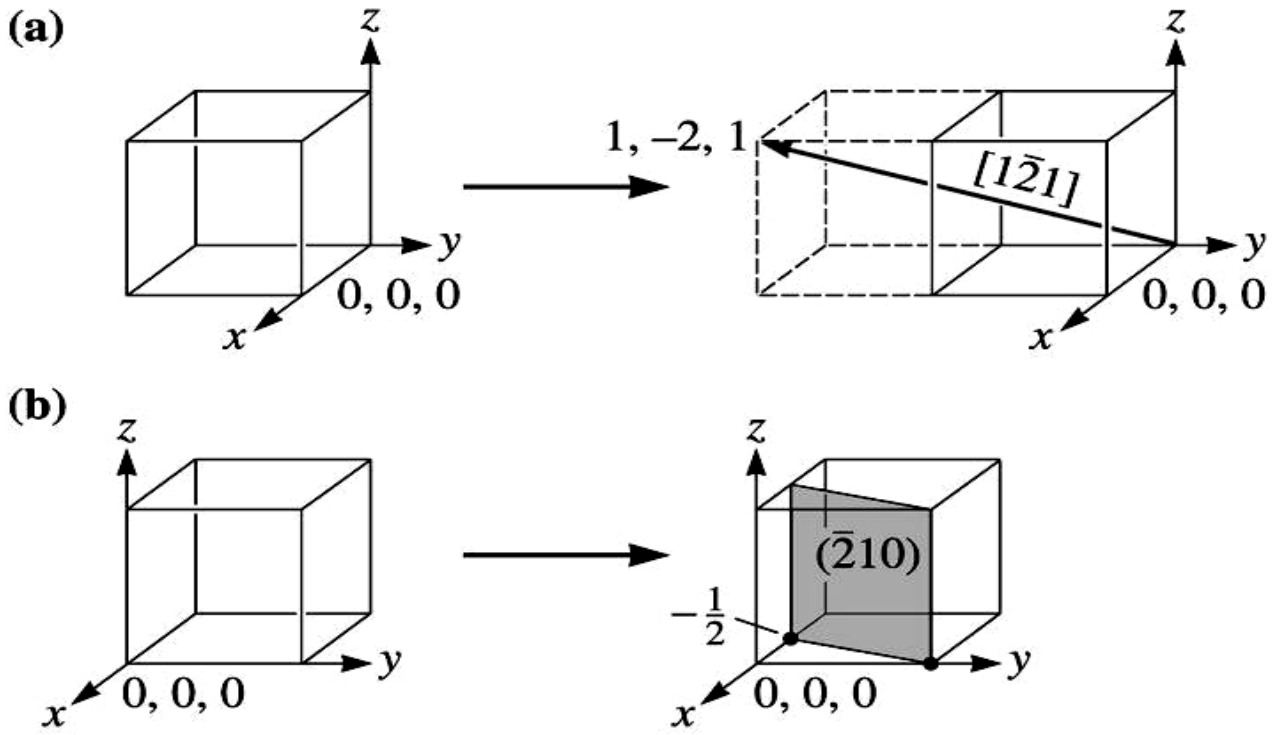
TABLE 3-4 ■ *Planes of the form {110} in cubic systems*

$$\{110\}\begin{cases}(110)\\(101)\\(011)\\(1\bar{1}0)\\(10\bar{1})\\(01\bar{1})\end{cases}$$

Note: The negatives of the planes are not unique planes.

Drawing Direction and Plane

Draw (a) the $[1\bar{2}1]$ direction and (b) the $[\bar{2}10]$ plane in a cubic unit cell.



Construction of a (a) direction and (b) plane within a unit cell

SOLUTION

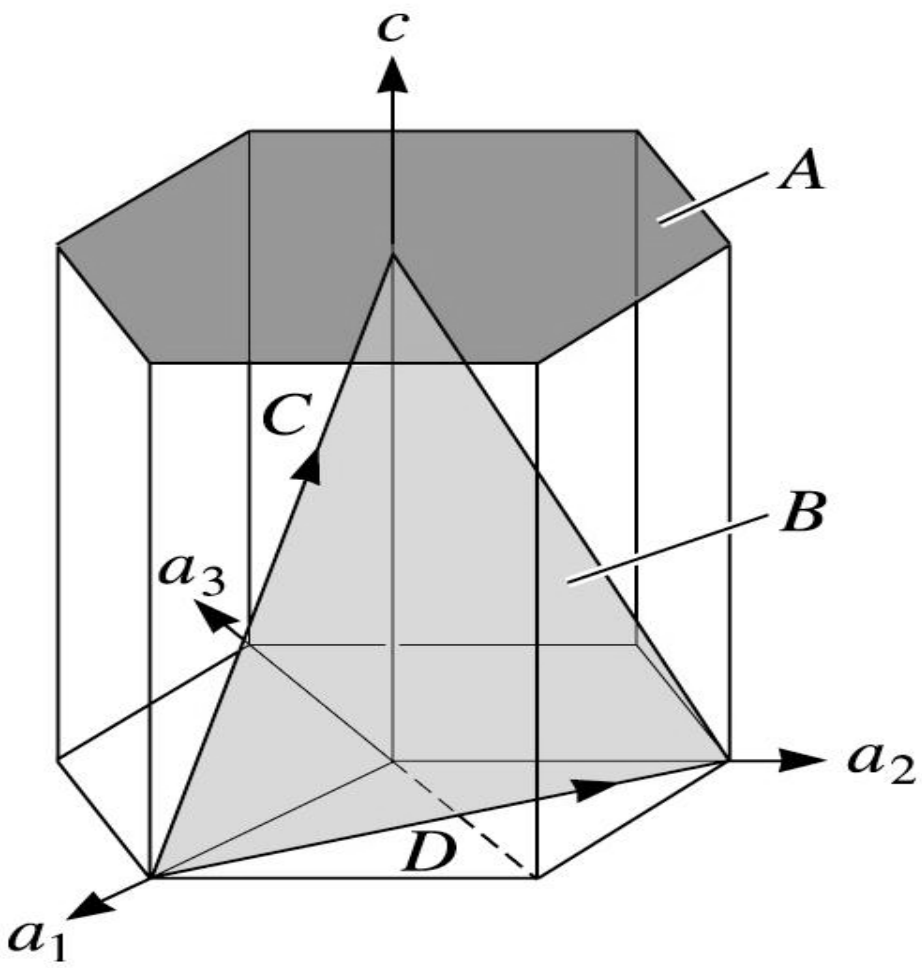
a. Because we know that we will need to move in the negative *y*-direction, let's locate the origin at 0, +1, 0. The ''tail'' of the direction will be located at this new origin. A second point on the direction can be determined by moving +1 in the *x*-direction, 2 in the negative y-direction, and +1 in the z direction.

b. To draw in the $[\bar{2}10]$ plane, first take reciprocals of the indices to obtain the intercepts, that is:

$$x = 1/-2 = -1/2 \quad y = 1/1 = 1 \quad z = 1/0 = \infty$$

Since the *x*-intercept is in a negative direction, and we wish to draw the plane within the unit cell, let's move the origin +1 in the *x*-direction to 1, 0, 0. Then we can locate the *x*-intercept at 1/2 and the *y*-intercept at +1. The plane will be parallel to the *z*-axis.

Determining Miller-Bravais Indices for Planes and Directions in hexagonal system



Miller-Bravais indices are obtained for crystallographic planes, directions, and points in hexagonal unit cells by using a **four-axis coordinate system**.

For planes (hk*i*l), the index $i = -(h+k)$, i.e. $h+k = -i$

For directions [uv*t*w], we have also $t = (u+v)$, i.e. $u+v = -t$

Miller-Bravais indices for planes are straightforward, just as we obtained the intersects for 3 axes, we have to obtain them now for 4 axes

SOLUTION

Plane *A*

1. $a_1 = a_2 = a_3 = \infty$, $c = 1$
2. $1/a_1 = 1/a_2 = 1/a_3 = 0$, $1/c = 1$
3. No fractions to clear
4. (0001)

Plane *B*

1. $a_1 = 1$, $a_2 = 1$, $a_3 = -1/2$, $c = 1$
2. $1/a_1 = 1$, $1/a_2 = 1$, $1/a_3 = -2$, $1/c = 1$
3. No fractions to clear
4. $(11\bar{2}1)$

***Determining directions in the hexagonal system is a bit more challenging* it is easier to calculate with 3 indices and then simply make up the forth**

SOLUTION (Continued)

Direction *C*

1. Two points are 0, 0, 1 and 1, 0, 0.
2. 0, 0, 1, - (1, 0, 0) = -1, 0, 1
3. No fractions to clear or integers to reduce.
4. $[\bar{1}01]\text{or}[\bar{2}113]$

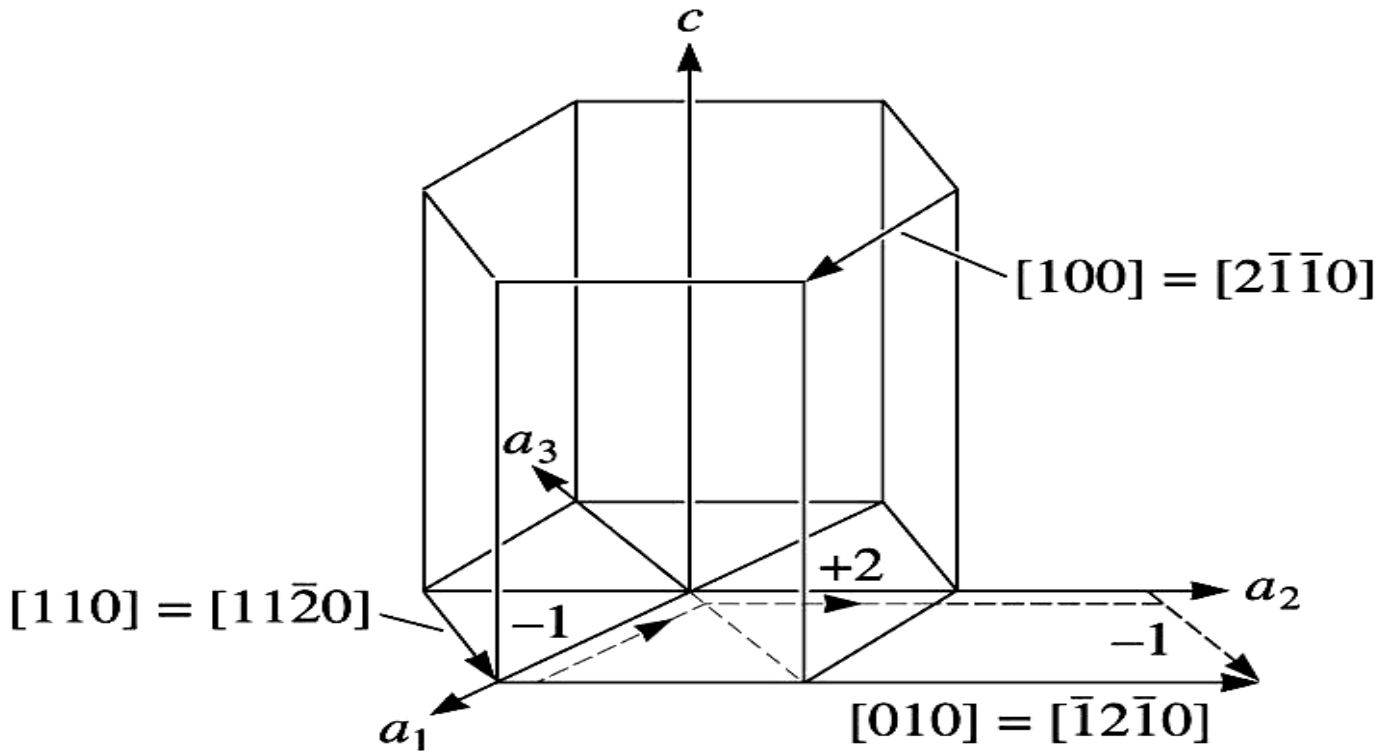
Direction *D*

1. Two points are 0, 1, 0 and 1, 0, 0.
2. 0, 1, 0, - (1, 0, 0) = -1, 1, 0
3. No fractions to clear or integers to reduce.
4. $[\bar{1}10]\text{or}[\bar{1}100]$ extension to 4 indices looks easy, but is not !

How did we get the forth index ? All have to be relabeled, say [UVW] are the three indexes, u = $^1/_3$ (2U –V),

v = $^1/_3$ (2V-U), t = - $^1/_3$ (u+v), w = W

Miller-Bravais Indices of important directions



Typical directions in the hexagonal unit cell, using both three-and-four-axis systems. The dashed lines show that the [$\bar{1}$2$\bar{1}$0] direction is equivalent to a [010] direction.

Densely packed lattice directions in the basal plane (0001), e.g. [100], [010], and [110] have similar Miller-Bravais indices, important for dislocation slip systems

Now as we have coordinates for lattice points, lattice directions and lattice planes, we can start making crystallographic calculations

Good news: everything is easy in the cubic system angle between two different direct [uvw] (or reciprocal – (hkl)) space directions

$$a = \arccos \frac{u_1 u_2 + v_1 v_2 + z_1 z_2}{\sqrt{u_1^2 + v_1^2 + z_1^2} \cdot \sqrt{u_2^2 + v_2^2 + z_2^2}}$$

$$b = \arccos \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

So angle between planes is calculated as angle between their normals, if you were to use a protractor (or contact goniometer), you would just measure an angle 180 ° - ß

Bad news: **everything gets a bit more difficult in non cubic systems for two reasons, the coordinate axes are no longer perpendicular to each other, the unit vectors of coordinate axes have different length**

No problem: we have the metric tensor G, a 3 by 3 matrix

$$\begin{pmatrix} a^2 & ab\cos g & ac\cos b \\ ab\cos g & b^2 & bc\cos a \\ ac\cos b & bc\cos a & c^2 \end{pmatrix}$$

If cubic simply

$$\begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & a^2 \end{pmatrix}$$

So angle between lattice directions become

$$a = \arccos \frac{u'Gv}{\sqrt{u'Gu}\sqrt{v'Gv}}$$

Example: what is the angle between [100] and [111] in (tetragonal) ß-Sn?

a = 0.583 nm, c = 0.318nm, *Solution:*

$$(1 \quad 0 \quad 0)\begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = (1 \quad 0 \quad 0)\begin{pmatrix} a^2 \\ a^2 \\ c^2 \end{pmatrix} = a^2$$

$$\sqrt{u'Gu} = a = 0.583nm$$

$$\sqrt{(1 \quad 1 \quad 1)\cdot G \cdot \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}} = \sqrt{a^2 + a^2 + c^2} = 0.8836nm$$

Putting into relation from above

$$a = \arccos \frac{u'Gv}{\sqrt{u'Gu}\sqrt{v'Gv}}$$

$$a = \arccos \frac{a^2}{a \cdot 0.8836} = 27.91°$$

So that was not all that difficult !!!

***Same basic idea for lattice planes*, i.e. their normals which are vectors in reciprocal (or dual) space**
everything is easy in cubic systems, in other crystal systems we use reciprocal metric tensor, the reciprocal 3 by 3 matrix of the metric tensor

$$\begin{pmatrix} b^2c^2\sin^2 a & abc^2(\cos a\cos b-\cos g & ab^2c(\cos a\cos g-\cos b \\ abc^2(\cos a\cos b-\cos g) & a^2c^2\sin^2 b & a^2bc(\cos b\cos g-\cos a \\ ab^2c(\cos a\cos g-\cos b & a^2bc(\cos b\cos g-\cos a & a^2b^2\sin^2 g \end{pmatrix}$$

If cubic simply,

this also defines the reciproc al lattice

$$\begin{pmatrix} 1/a^2 & 0 & 0 \\ 0 & 1/a^2 & 0 \\ 0 & 0 & 1/a^2 \end{pmatrix}$$

So angle between normals of lattice planes become

$$a=\arccos\frac{h'Gk}{\sqrt{h'Gh}\sqrt{k'Gk}}$$

Metric tensor (and its reciprocal) also define reciprocal lattice

$$a^* = (\sqrt{b^2c^2\sin^2 a}\,)^{-1} = b \times c$$

$$b^* = (\sqrt{a^2c^2\sin^2 b}\,)^{-1} = a \times c$$

$$c^* = (\sqrt{b^2a^2\sin^2 g}\,)^{-1} = b \times a$$

It is just a mathematical convenience, particularly useful for interpretation of (X-ray and electron diffraction) data

$$d^* = H = h\,a_1^* + k a_2^* + l\,a_3^* = {}^1/_d$$

In cubic systems simply: $d_{hkl} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

Other geometric considerations, valid for all crystal systems, that is the great thing about Miller indices !!!

When does a direction lie in a plane?

If their dot product is zero, e.g. $[\bar{1}01]$ **and (111) , -1 + 0 +1 = 0**

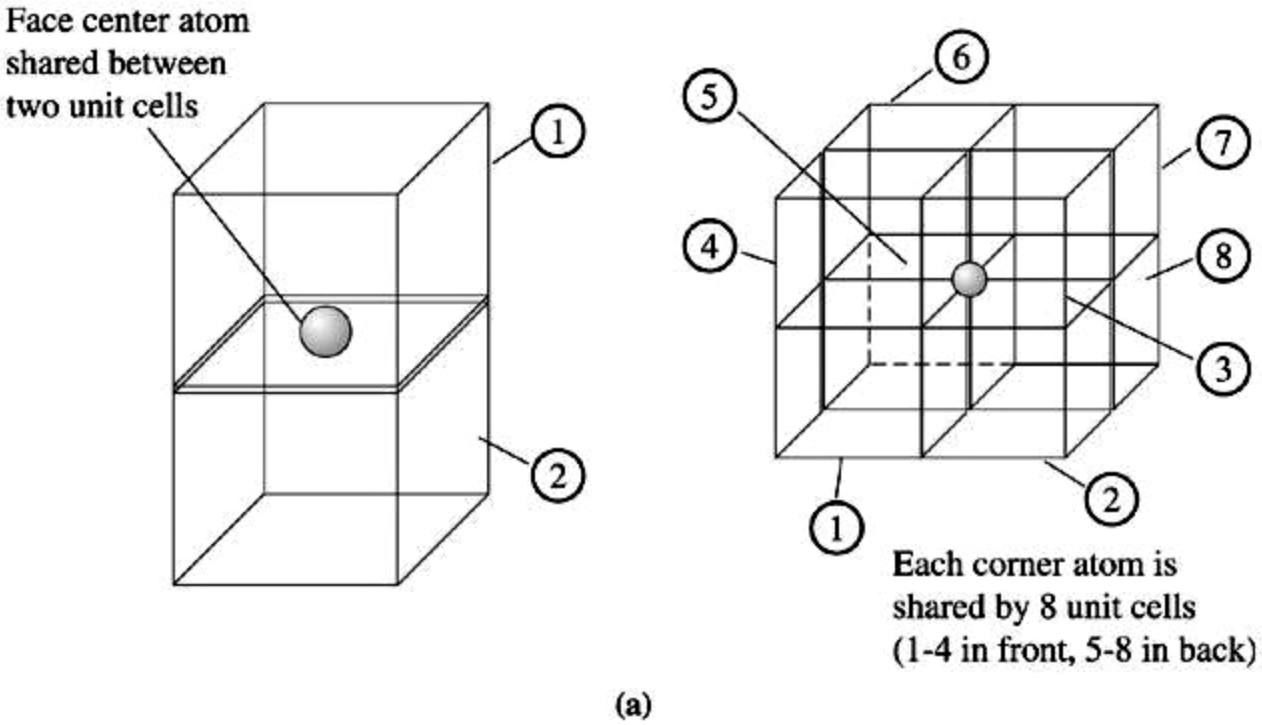
But $[\bar{1}01]$ **does not lie in** $(\bar{1}31)$ **as 1 + 0 + 1 ? 0**

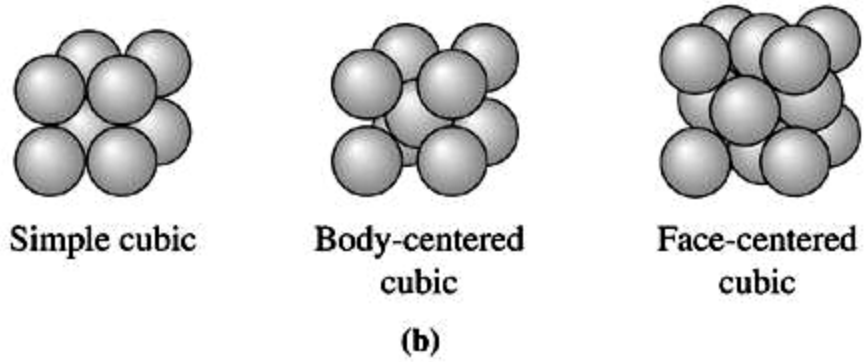
What are the indices of the direction that mediated the intersection of two plane?

We have to determine cross products

(111) x $(\bar{1}2\bar{3})$ = $[\bar{5}23]$

Centered lattices and structures with more than one lattice point per unit cell





(a) Illustration showing sharing of face and corner atoms.

(b) The models for simple cubic (SC), body centered cubic (BCC), and face-centered cubic (FCC) unit cells,

assuming only one atom per lattice point.

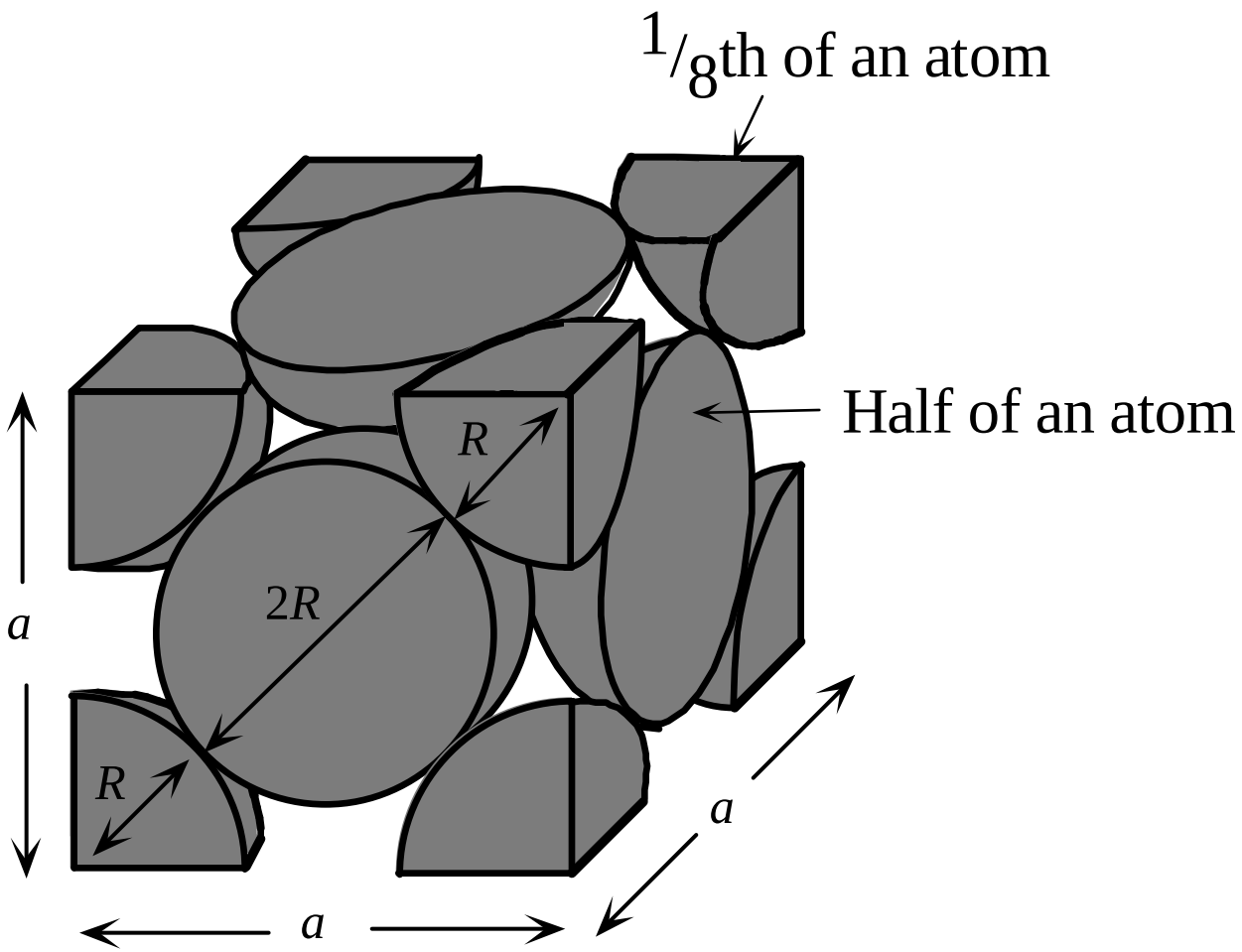


Fig. 1.38: The FCC unit cell. The atomic radius is *R* and the lattice parameter is *a*

Determining the Number of Lattice Points in Cubic Crystal Systems

Determine the number of lattice points per cell in the cubic crystal systems. If there is only one atom located at each lattice point, calculate the number of atoms per unit cell.

SOLUTION

In the SC unit cell: lattice point / unit cell = (8 corners)1/8 = 1

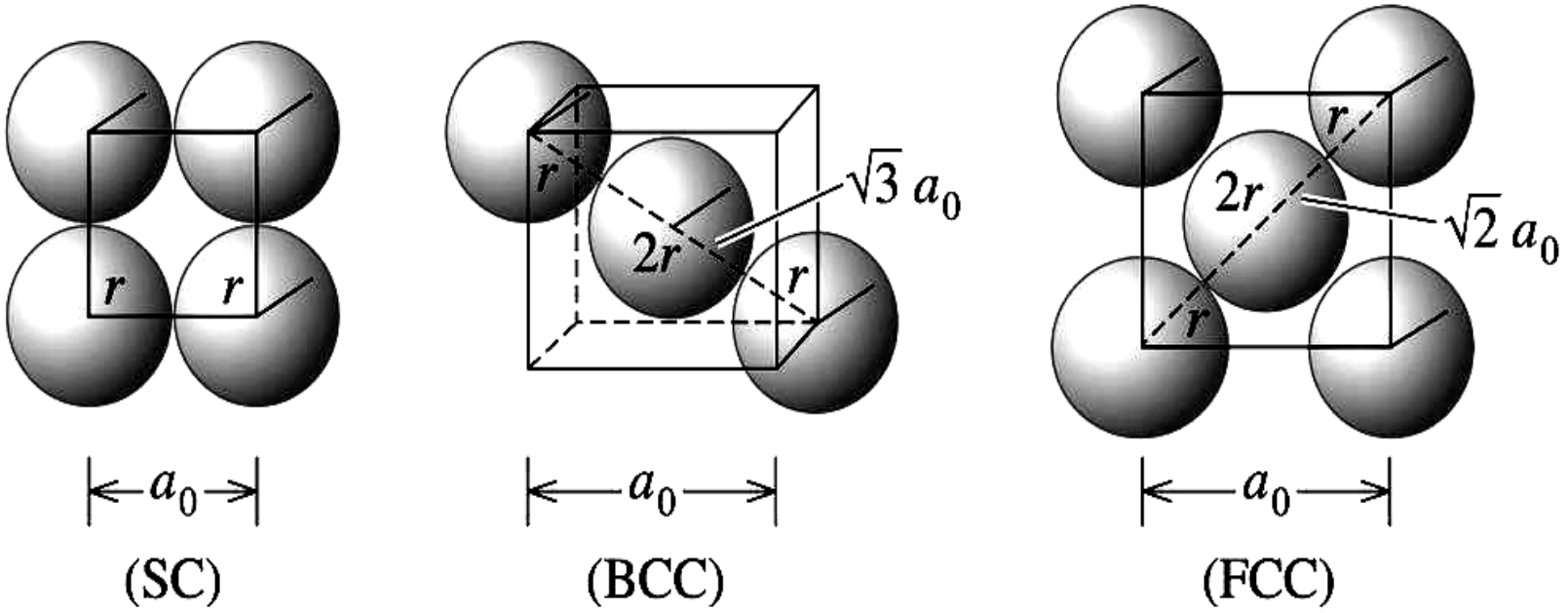
In BCC unit cells: lattice point / unit cell
= (8 corners)1/8 + (1 center)(1) = 2

In FCC unit cells: lattice point / unit cell
= (8 corners)1/8 + (6 faces)(1/2) = 4

If there is only on atom per lattice point, as in typical metal structures, the number of atoms per unit cell would be 1, 2, and 4, for the simple cubic, body-centered cubic, and face-centered cubic, unit cells, respectively. ***But there are also many structures with more than one atom per lattice point***

Determining the Relationship between Atomic Radius and Lattice Parameters

Determine the relationship between the atomic radius and the lattice parameter in SC, BCC, and FCC structures when one atom is located at each lattice point.



The relationships between the atomic radius and the lattice parameter in cubic systems

SOLUTION

Referring to Figure above, we find that atoms touch along the edge of the cube in SC structures.

$$a_0 = 2r$$

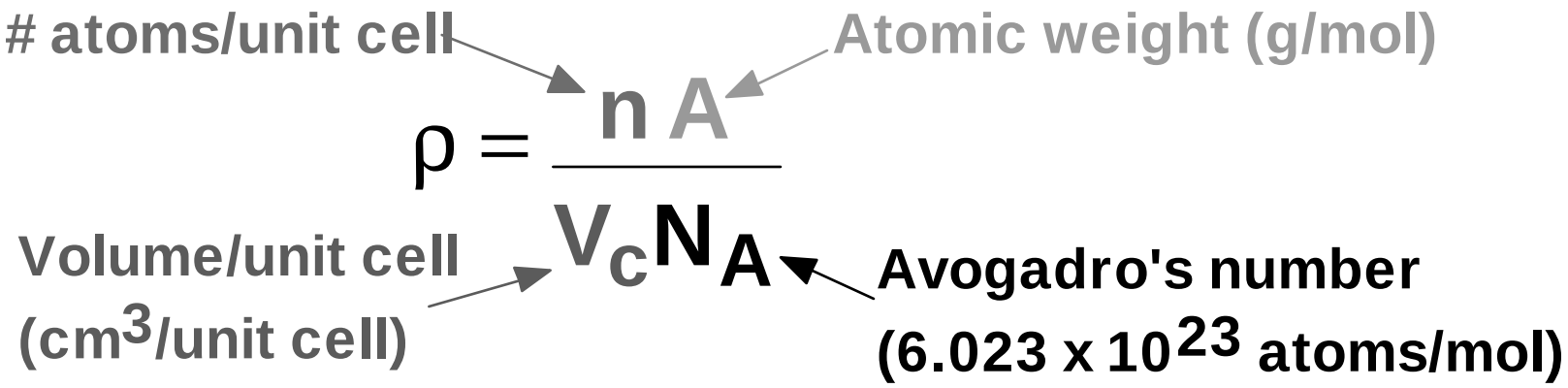
In BCC structures, atoms touch along the body diagonal. There are two atomic radii from the center atom and one atomic radius from each of the corner atoms on the body diagonal, so

$$a_0 = \frac{4r}{\sqrt{3}}$$

In FCC structures, atoms touch along the face diagonal of the cube. There are four atomic radii along this length—two radii from the face-centered atom and one radius from each corner, so:

$$a_0 = \frac{4r}{\sqrt{2}}$$

THEORETICAL DENSITY, ρ



Example: Copper

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius R = 0.128 nm (1 nm = 10^{-7}cm)

$V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23} cm^3$

Result: theoretical $\rho_{Cu} = 8.89$ g/cm^3

Compare to actual: $\rho_{Cu} = 8.94$ g/cm^3

So there must be some real structure in addition !

Determining the Density of BCC Iron

Determine the density of BCC iron, which has a lattice parameter of 0.2866 nm.

SOLUTION

Atoms/cell = 2, a_0 = 0.2866 nm = 2.866 ´ 10^{-8} cm

Atomic mass = 55.847 g/mol

Volume of unit cell = a_0^3 = (2.866 ´ 10^{-8} cm)^3 = 23.54 ´ 10^{-24} cm^3/cell

Avogadro's number N_A = 6.023 ´ 10^{23} atoms/mol

$$\text{Density } r = \frac{(\text{number of atoms/cell})(\text{atomic mass of iron})}{(\text{volume of unit cell})(\text{Avogadro's number})}$$

$$r = \frac{(2)(55.847)}{(23.54 \times 10^{-24})(6.02 \times 10^{23})} = 7.882 g/cm^3$$

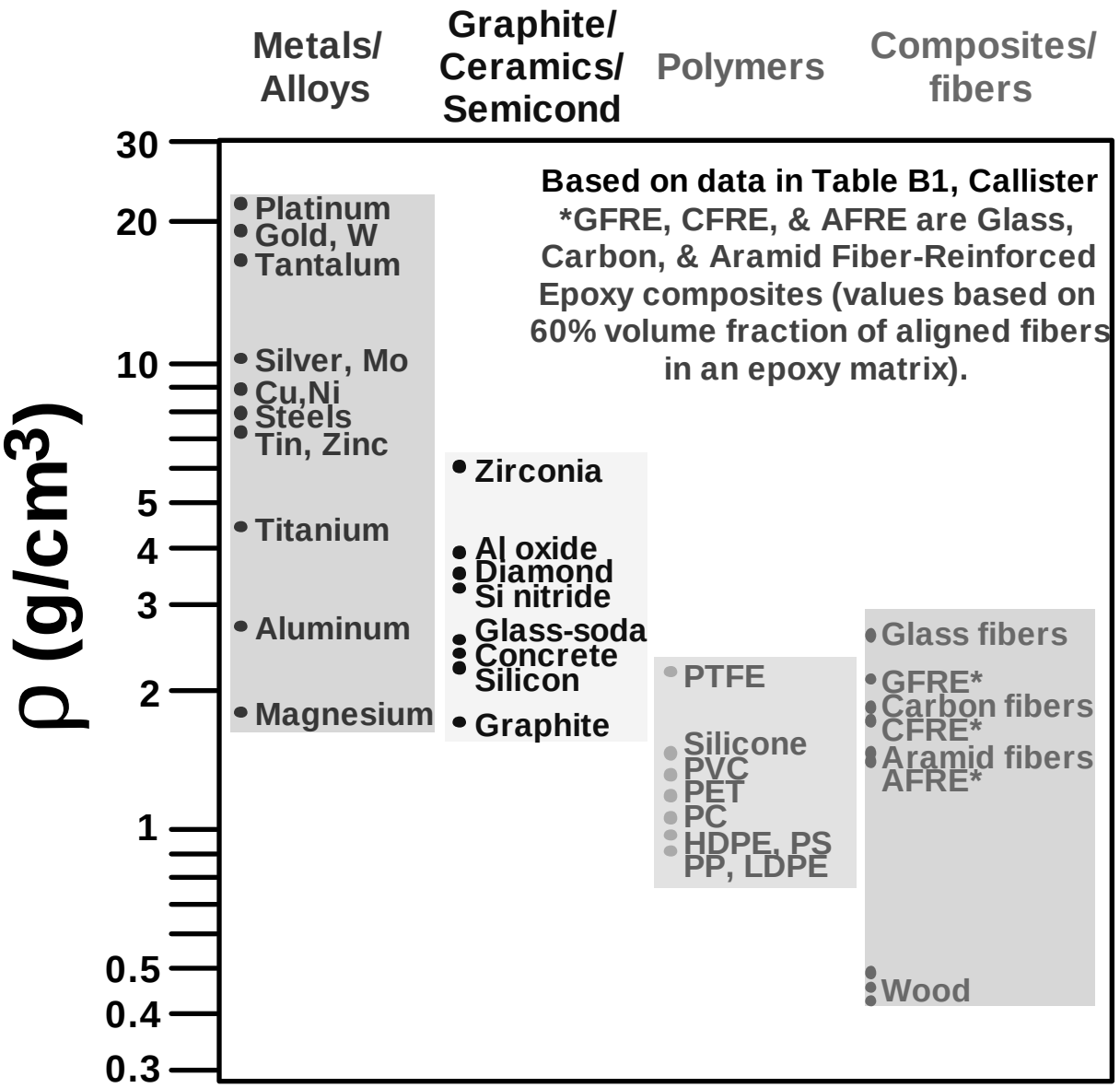
DENSITIES OF MATERIAL CLASSES

Metals typically have
- close-packing (metallic bonding)
- large atomic mass

Ceramics have
- less dense packing (covalent bonding)
- often lighter elements

Polymers have…
- poor packing (parts often amorphous)
- lighter elements (C,H,O)

Composites have…
- intermediate values

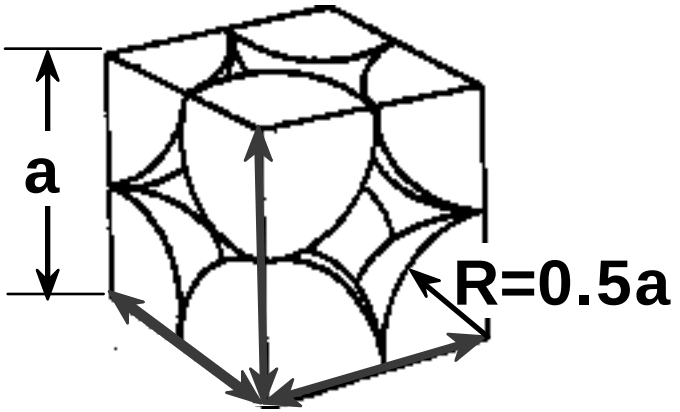


ATOMIC PACKING FACTOR

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

*assume hard spheres

- **APF for a simple cubic structure = 0.52**



close-packed directions

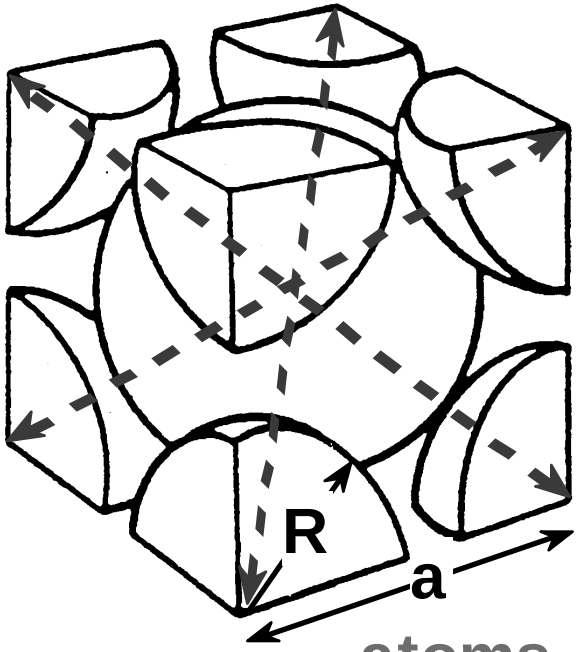
contains 8 x 1/8 =

1 atom/unit cell

$$APF = \frac{\frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}}}{\frac{\text{volume}}{\text{unit cell}}} = \frac{1 \cdot \frac{4}{3}\pi (0.5a)^3}{a^3}$$

ATOMIC PACKING FACTOR: BCC

- **APF for a body-centered cubic structure = 0.68**



Close-packed directions:

length = 4R

$= \sqrt{3}\, a$

Unit cell contains:

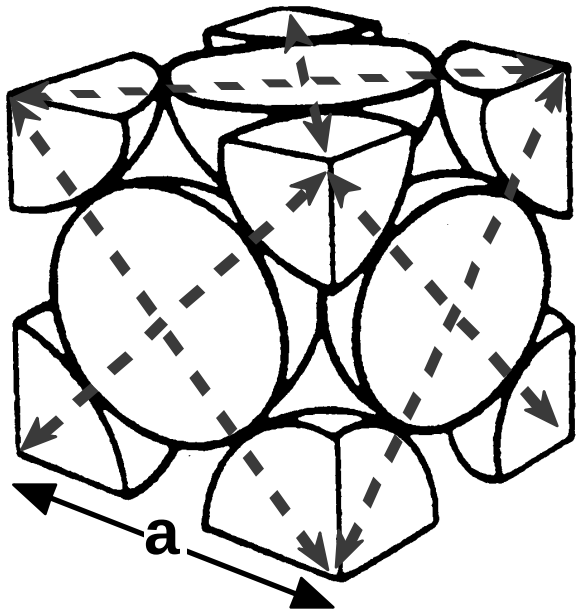
1 + 8 x 1/8

= 2 atoms/unit cell

$$APF = \frac{\text{atoms}}{\text{unit cell}} \cdot \frac{\text{volume}}{\text{atom}} \Big/ \frac{\text{volume}}{\text{unit cell}} = \frac{2 \cdot \frac{4}{3}\pi (\sqrt{3}a/4)^3}{a^3}$$

ATOMIC PACKING FACTOR: FCC

- **APF for a body-centered cubic structure = 0.74**



Close-packed directions:

length = 4R

$= \sqrt{2}\, a$

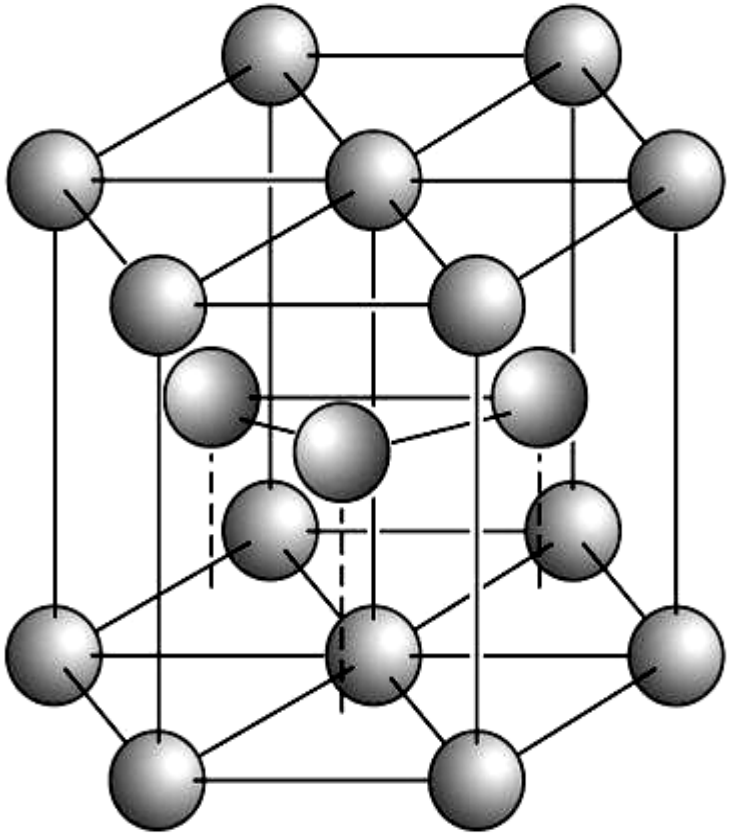
Unit cell contains:

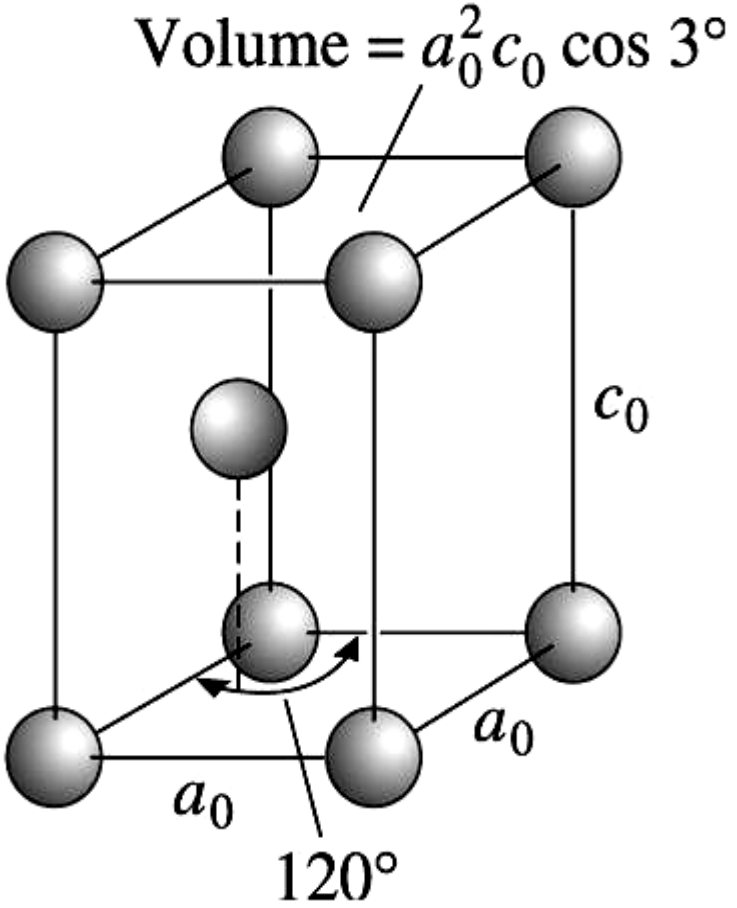
6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

That is the highest possible packing factor !!

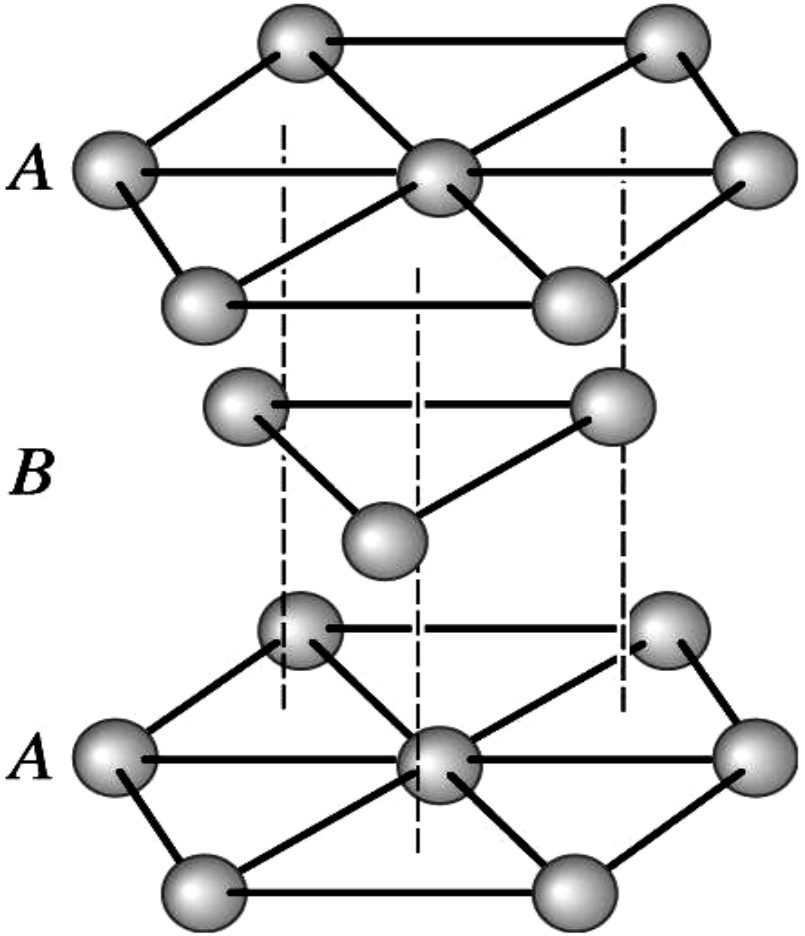
$$APF = \frac{\dfrac{\text{atoms}}{\text{unit cell}} \cdot \dfrac{\text{volume}}{\text{atom}}}{\dfrac{\text{volume}}{\text{unit cell}}} = \frac{4 \cdot \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3}{a^3}$$



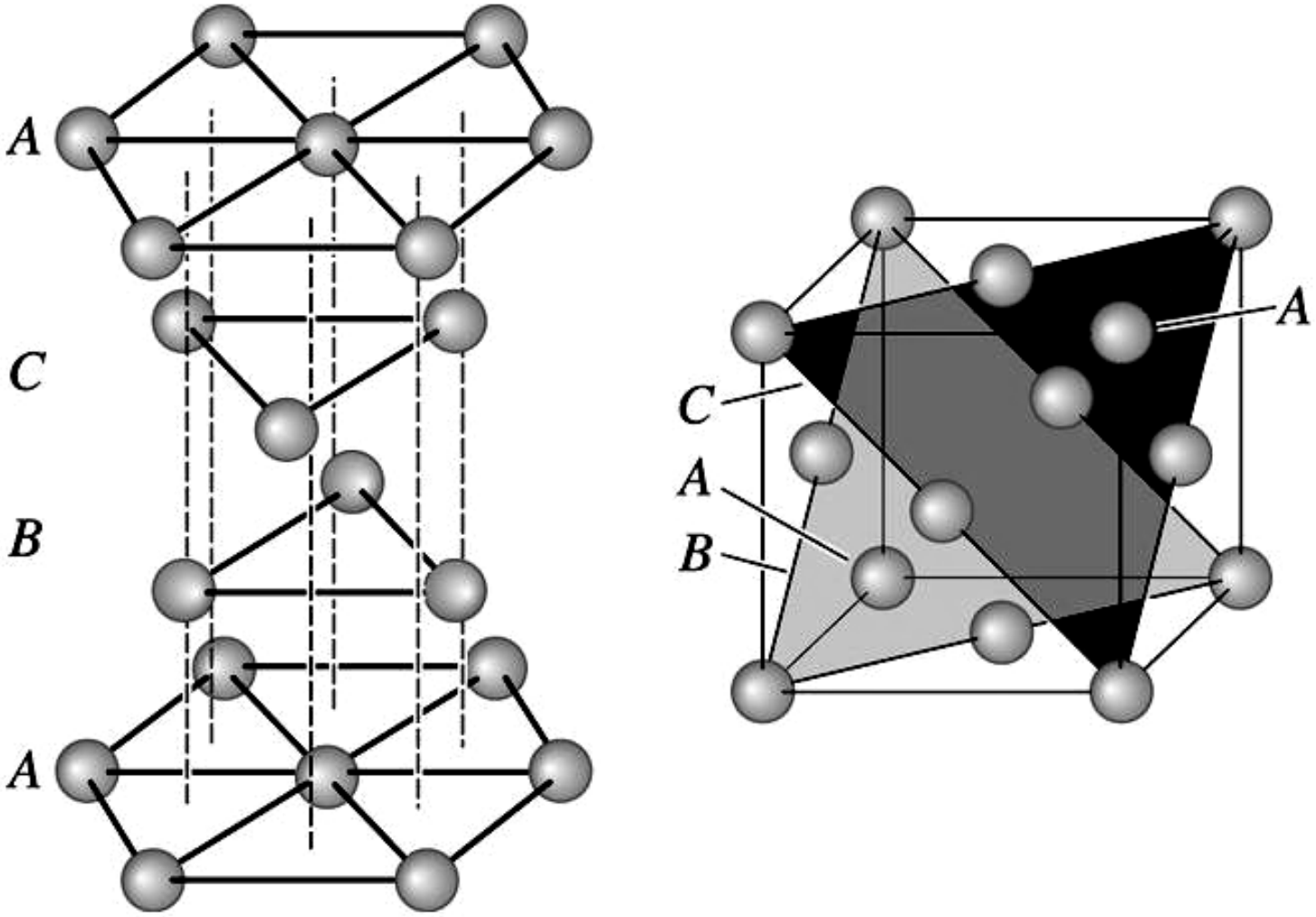


The hexagonal close-packed (HCP) structure (left) and its unit cell. The packing factor is also 74 %, i.e. the highest possible, just as we had for FCC spheres

Stacking sequences of closed packed structures, i.e. those with 74 % Packing factor



The *ABABAB* stacking sequence of close-packed planes produces the HCP structure.



The *ABCABCABC* stacking sequence of close-packed planes produces the FCC structure.

Coordination and nearest neighbors

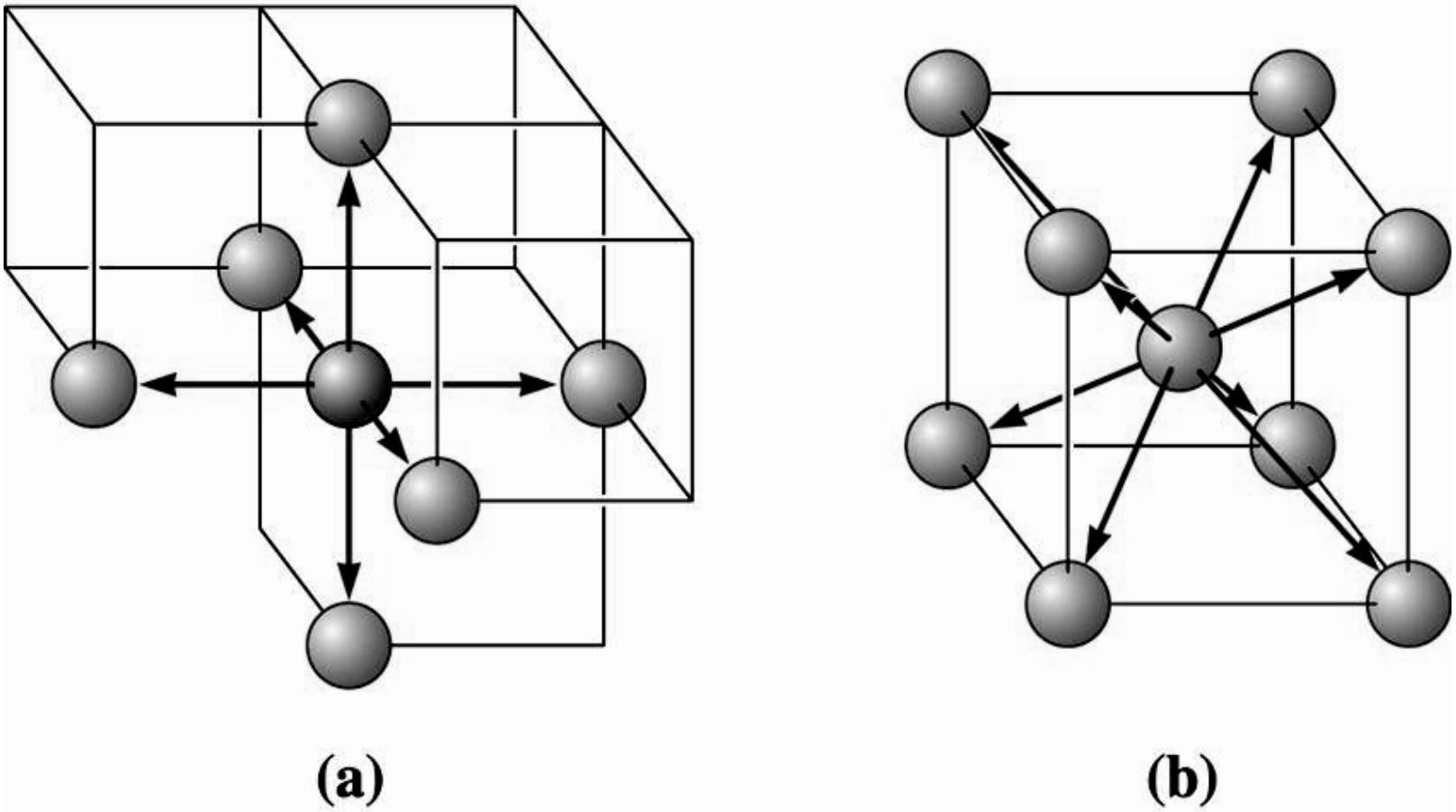


Illustration of coordinations in (a) SC- six fold and (b) BCC – 8 fold unit cells. Six atoms touch each atom in SC, while the eight atoms touch each atom in the BCC unit cell.

TABLE 3-2 ■ *Crystal structure characteristics of some metals*

Structure	a_0 versus r	Atoms per Cell	Coordination Number	Packing Factor	Examples
Simple cubic (SC)	$a_0 = 2r$	1	6	0.52	Polonium (Po), α-Mn
Body-centered cubic	$a_0 = 4r/\sqrt{3}$	2	8	0.68	Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Zr, Cr
Face-centered cubic	$a_0 = 4r/\sqrt{2}$	4	12	0.74	Fe, Cu, Au, Pt, Ag, Pb, Ni
Hexagonal close-packed	$a_0 = 2r$ $c_0 \approx 1.633a_0$	2	12	0.74	Ti, Mg, Zn, Be, Co, Zr, Cd

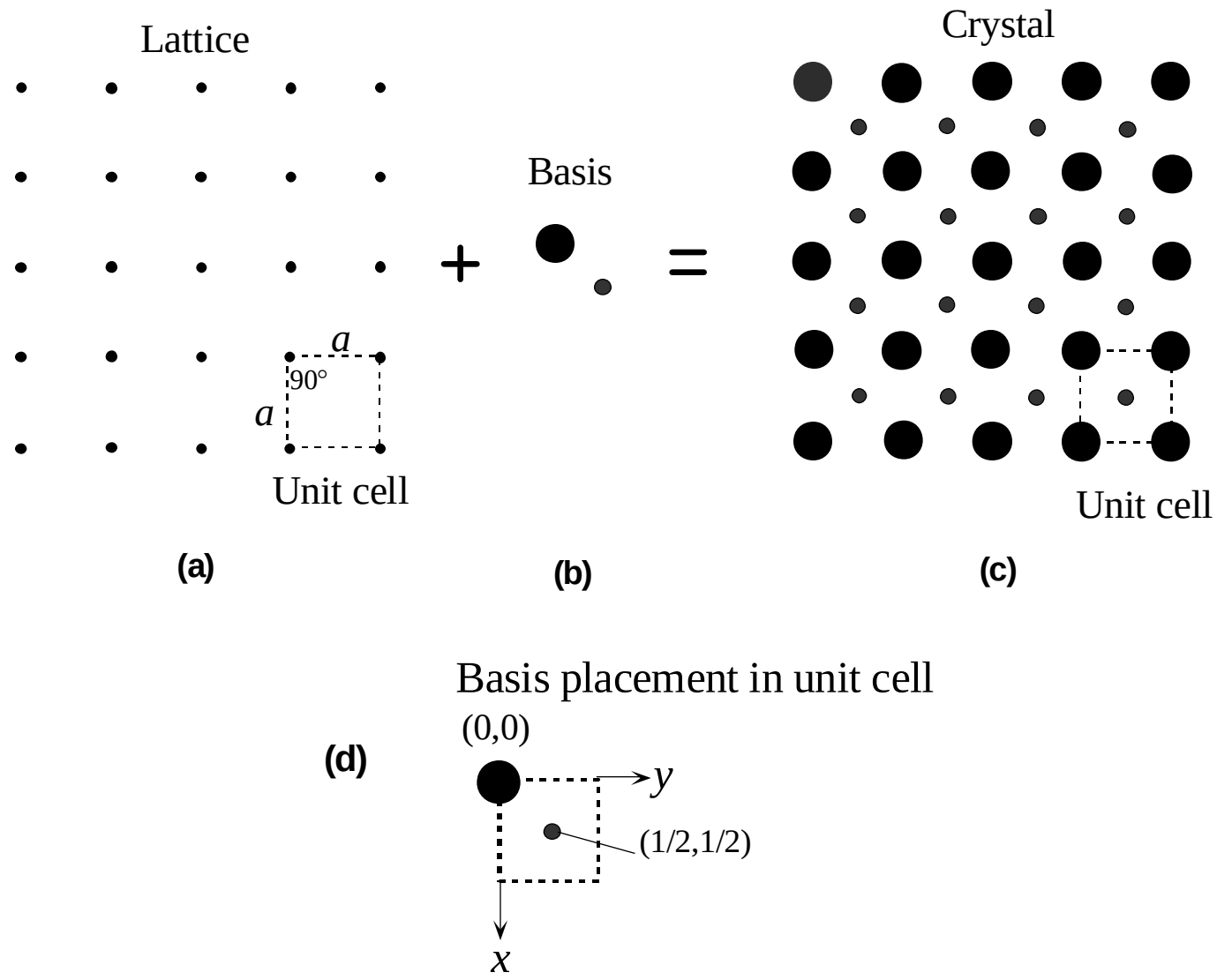


Fig. 1.70: (a) A simple square lattice. The unit cell is a square with a side *a*. (b) Basis has two atoms. (c) Crystal = Lattice + Basis. The unit cell is a simple square with two atoms. (d) Placement of basis atoms in the crystal unit cell.

Figure 3.7.1a

Figure 3.7.1b

M.C. Escher's two dimensional patterns are filling the whole 2D space. We can determine a unit cell which happened to be composed off many details, regardless of which periodic detail we use for the choice of the unit cell, these cells will always be identical. So we can think about it in a way that all the details are shrunk into a lattice points and all that remains is the geometrical array of lattice points we had in the previous slide

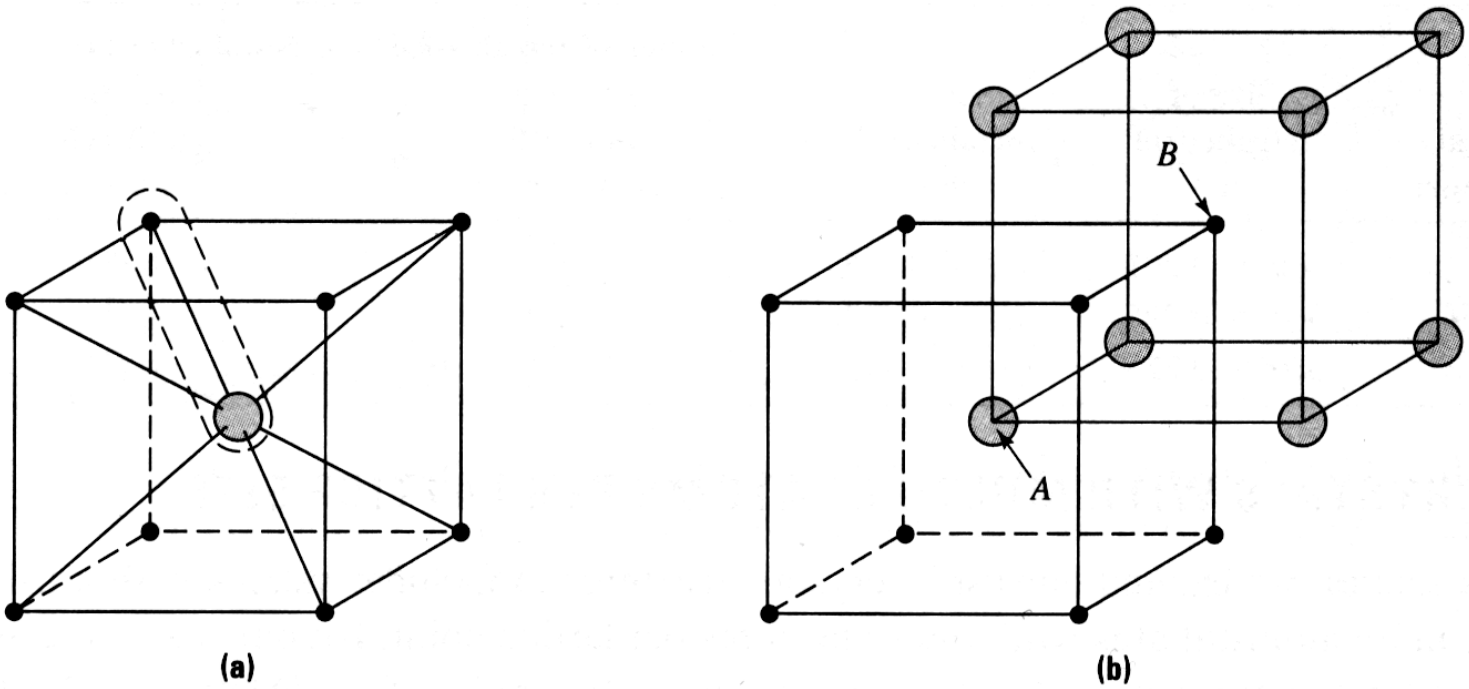


FIGURE 3.7–2 The CsCl crystal structure: **(a)** A simple cubic lattice with two different atoms per lattice point; **(b)** Alternatively, the structure can be viewed as a pair of interwoven simple cubic lattices.

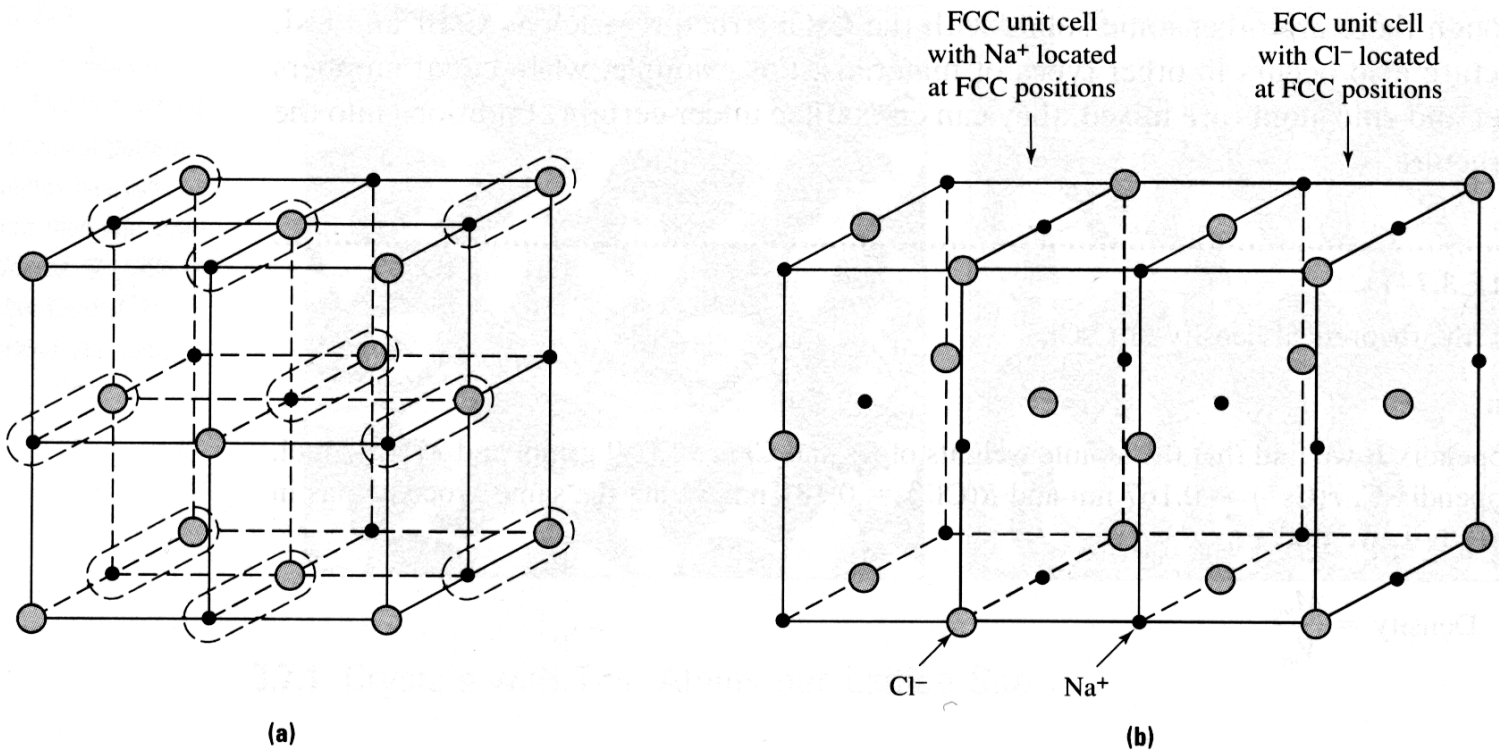


FIGURE 3.7–3 The NaCl crystal structure: **(a)** An FCC lattice with two different atoms per lattice point; **(b)** Alternatively, the structure can be viewed as a pair of interwoven FCC lattices.

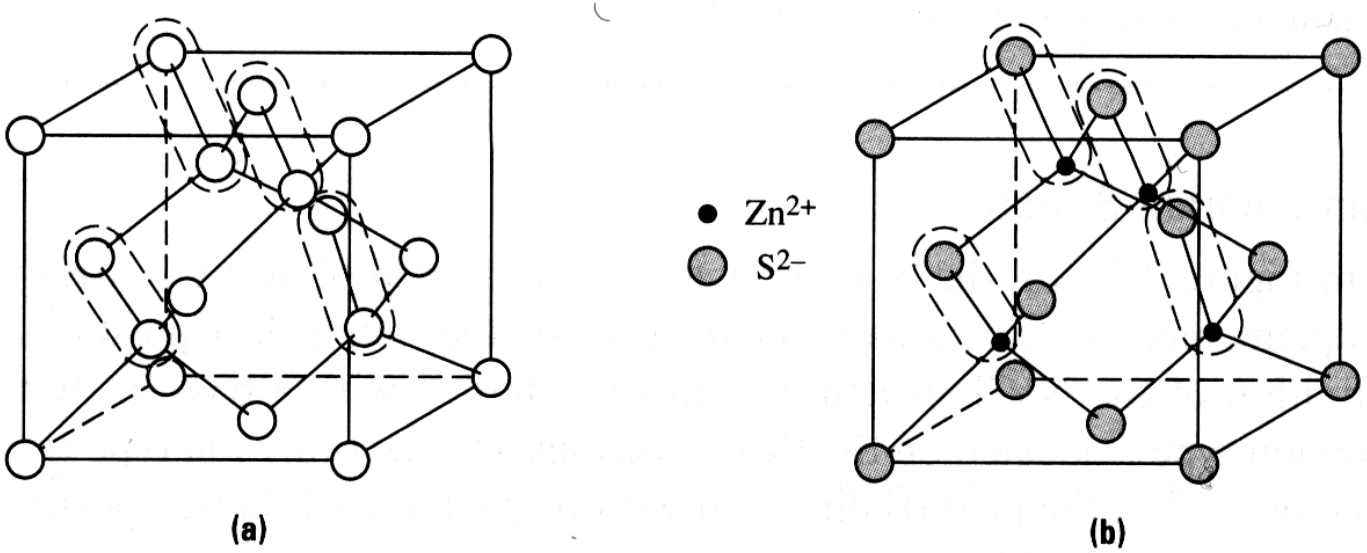


FIGURE 3.7–4 **(a)** The diamond cubic crystal structure is composed of an FCC lattice with two atoms per lattice point. One atom from each pair is centered on each lattice point, and the second atom is positioned at $(a_0\sqrt{3}/4)$ $[1\ 1\ \bar{1}]$. **(b)** The zinc blende crystal structure is similar to the diamond cubic structure, except that the basis is composed of two different atoms.

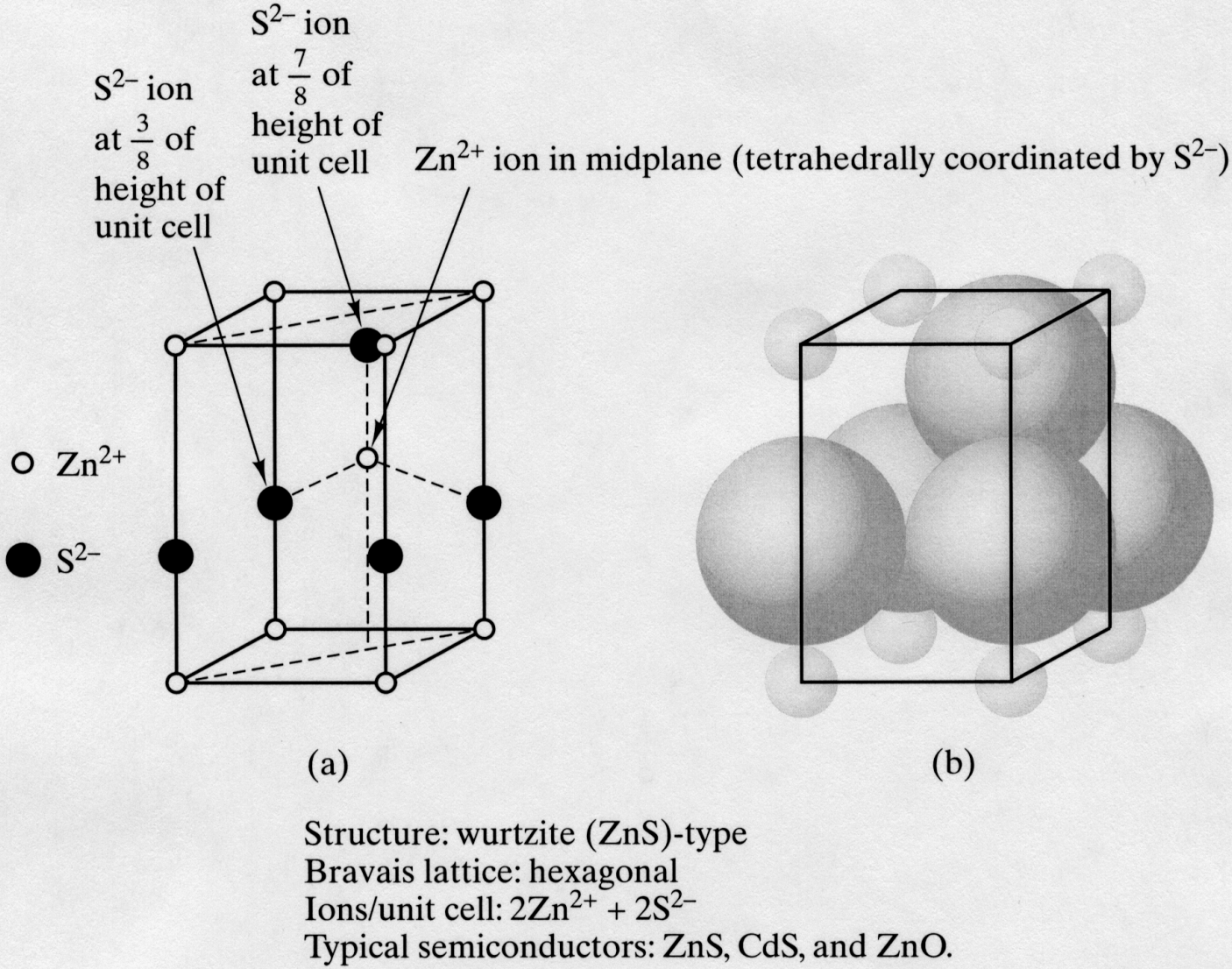


Figure 3-25 *Wurtzite (ZnS) unit cell showing (a) ion positions and (b) full-size ions.*

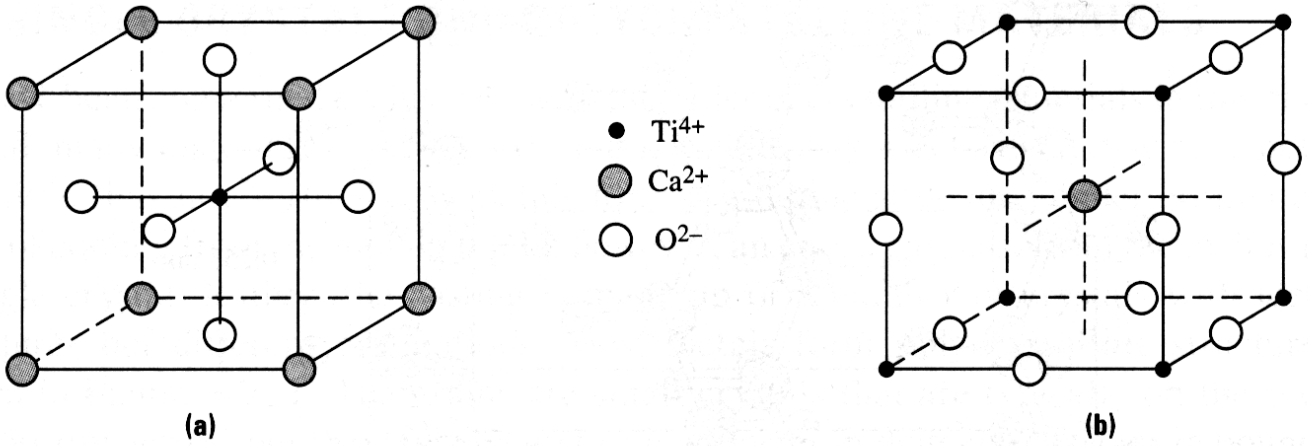


FIGURE 3.7–7 The perovskite unit cell for $CaTiO_3$ drawn **(a)** with the origin coinciding with a Ca^{2+} ion, and **(b)** with the origin coinciding with a Ti^{4+} ion.

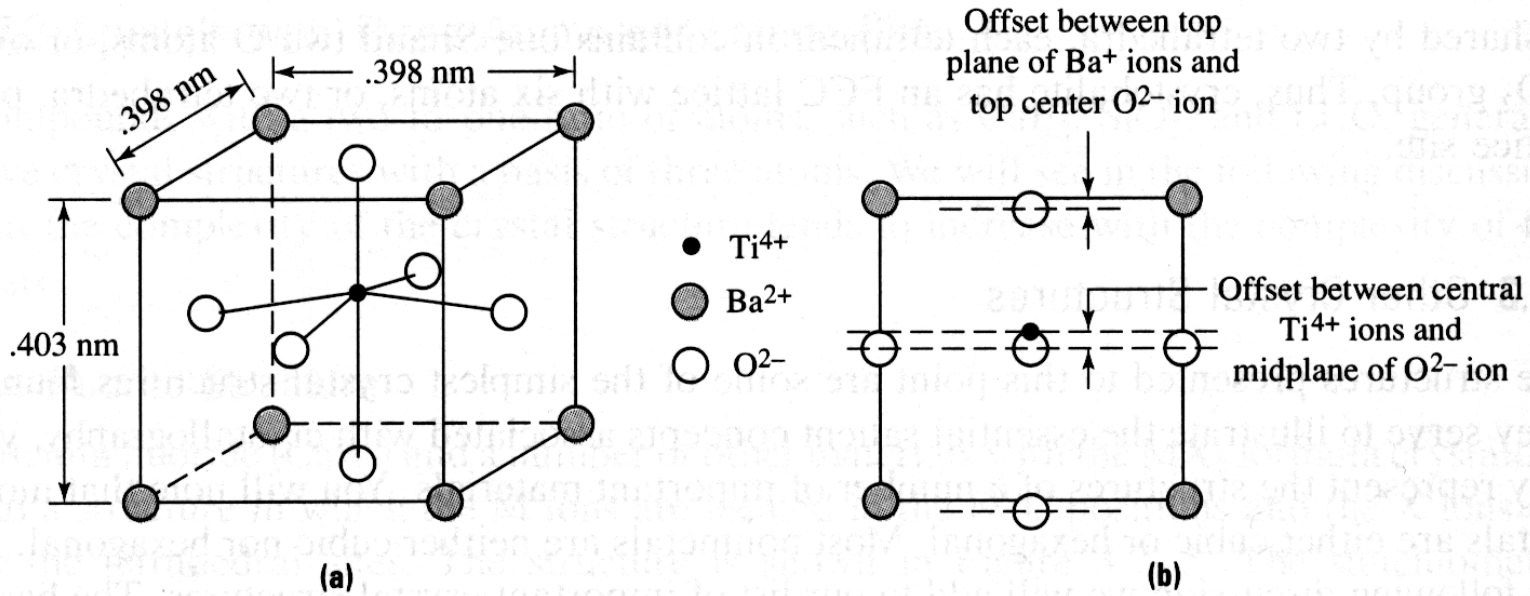
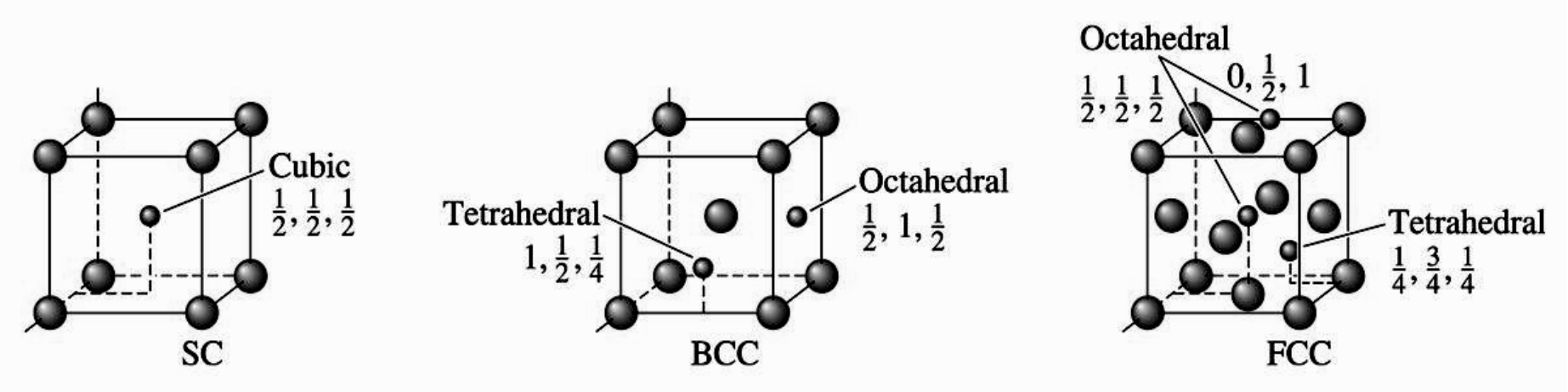


FIGURE 3.7–8 The tetragonal unit cell of $BaTiO_3$ shown **(a)** in 3-D, and **(b)** in 2-D.

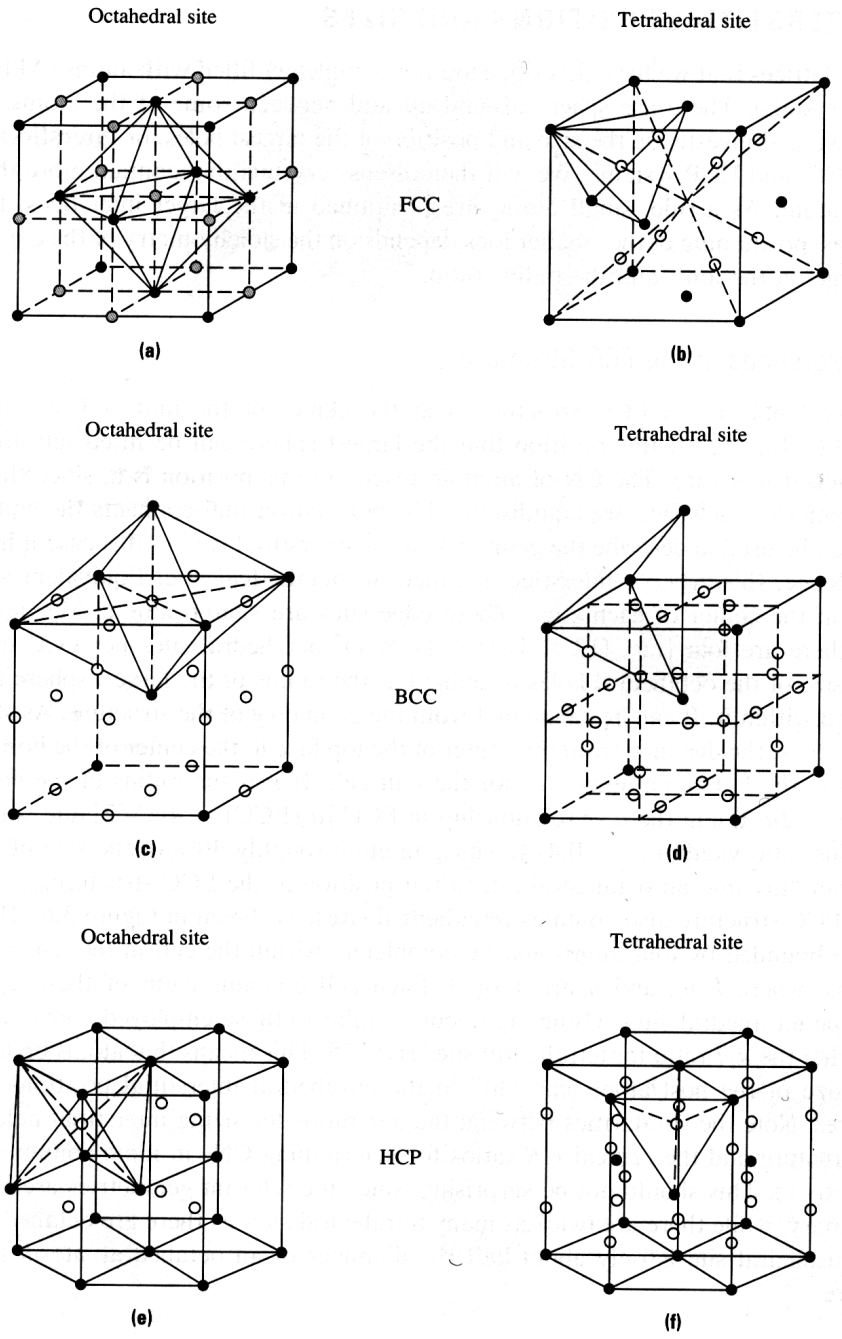
Interstitial Sites

- Interstitial sites - Locations between the ‘‘normal’’ atoms or ions in a crystal into which another - usually different - atom or ion is placed. Typically, the size of this interstitial location is smaller than the atom or ion that is to be introduced.
- Cubic site - An interstitial position that has a coordination number of eight. An atom or ion in the cubic site touches eight other atoms or ions.
- Octahedral site - An interstitial position that has a coordination number of six. An atom or ion in the octahedral site touches six other atoms or ions.
- Tetrahedral site - An interstitial position that has a coordination number of four. An atom or ion in the tetrahedral site touches four other atoms or ions.



The location of the interstitial sites in cubic unit cells. Only representative sites are shown.

FIGURE 3.6–1
The locations of the interstitial sites in the common crystal structures: **(a)** octahedral sites in FCC, **(b)** tetrahedral sites in FCC, **(c)** octahedral sites in BCC, **(d)** tetrahedral sites in BCC, **(e)** octahedral sites in HCP, and **(f)** tetrahedral sites in HCP.



Interstitial sites are important because we can derive more structures from these basic FCC, BCC, HCP structures by partially or completely different sets of these sites

Calculating Octahedral Sites

How many octahedral sites are there in one FCC unit cell?

SOLUTION

The octahedral sites include the 12 edges of the unit cell, with the coordinates

$$\frac{1}{2},0,0 \quad \frac{1}{2},1,0 \quad \frac{1}{2},0,1 \quad \frac{1}{2},1,1$$

$$0,\frac{1}{2},0 \quad 1,\frac{1}{2},0 \quad 1,\frac{1}{2},1 \quad 0,\frac{1}{2},1$$

$$0,0,\frac{1}{2} \quad 1,0,\frac{1}{2} \quad 1,1,\frac{1}{2} \quad 0,1,\frac{1}{2}$$

plus the center position, 1/2, 1/2, 1/2.

SOLUTION (Continued)

Each of the sites on the edge of the unit cell is shared between four unit cells, so only $^1/_4$ of each site belongs uniquely to each unit cell.

Therefore, the number of sites belonging uniquely to each cell is:

(12 edges) ($^1/_4$ per cell) + 1 center location

= 4 octahedral sites

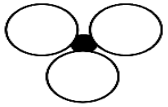
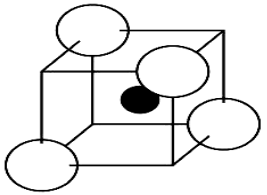
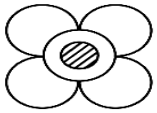
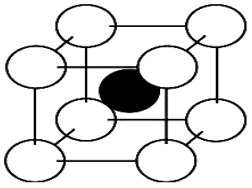
How much space is there available to fill the different sites with "hard sphere" atoms?

TABLE 3.6–1 The size and number of tetrahedral and octahedral interstitial sites in the BCC, FCC, and HCP crystal structures. The sizes of the interstitial sites are given in terms of the radius ratio (κ/r) where κ is the radius of the largest atom that can "fit" into the interstitial position and r is the radius of the host atoms. The number of interstitial sites is given in terms of both the number of sites per cell and, in parentheses, the number of sites per host atom.

Crystal structure	Size of tetrahedral sites	Size of octahedral sites	Number of tetrahedral sites per unit cell (per host atom)	Number of octahedral sites per unit cell (per host atom)
BCC	$\kappa/r = 0.291$	$\kappa/r = 0.155$	12 (6)	6 (3)
FCC	$\kappa/r = 0.225$	$\kappa/r = 0.414$	8 (2)	4 (1)
HCP	$\kappa/r = 0.225$	$\kappa/r = 0.414$	12 (2)	6 (1)

The radios ratios have to be of course the same as the once we discussion in connection with coordination

TABLE 3-6 ■ ***The coordination number and the radius ratio***

Coordination Location of Number	Interstitial	Radius Ratio	Representation
2	Linear	0–0.155	
3	Center of triangle	0.155–0.225	
4	Center of tetrahedron	0.225–0.414	
6	Center of octahedron	0.414–0.732	
8	Center of cube	0.732–1.000	

Crystal Structures of Ionic Materials

- Factors that need to be considered in order to understand crystal structures of ionically bonded solids:
  - Ionic Radii for filling of various interstitial sites
  - Electrical Neutrality as a structural principle

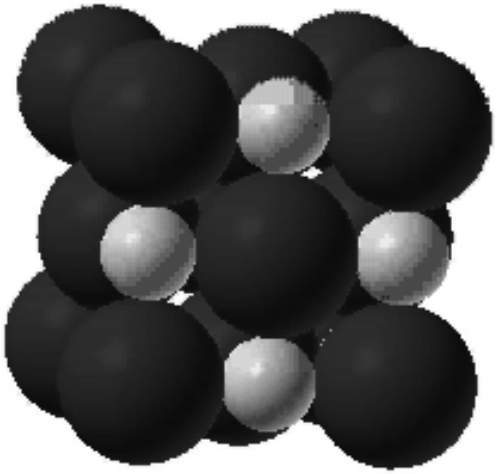
STRUCTURE OF NaCl

- **Compounds: Often have close-packed structures**

– there is more than one atom per lattice point.

- **Structure of NaCl**

- **FCC + octahedral Interstitial site filled**



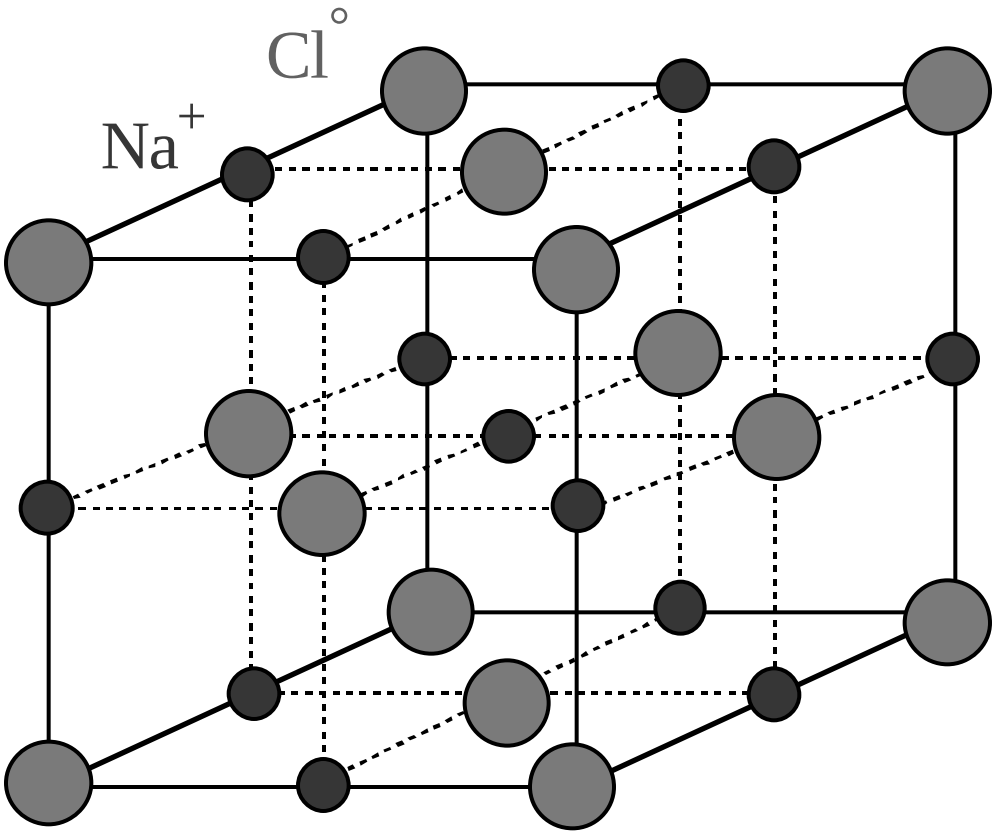


Fig. 1.36: A possible reduced sphere unit cell for the NaCl (rock salt) crystal. An alternative unit cell may have Na^+ and Cl° interchanged. Examples: AgCl, CaO, CsF, LiF, LiCl, NaF, NaCl, KF, KCl, MgO

Simple cubic packing with the cube interstitial site filled by another atom, note that there are two atoms per lattice point, i.e. the lattice as such is still simple cubic

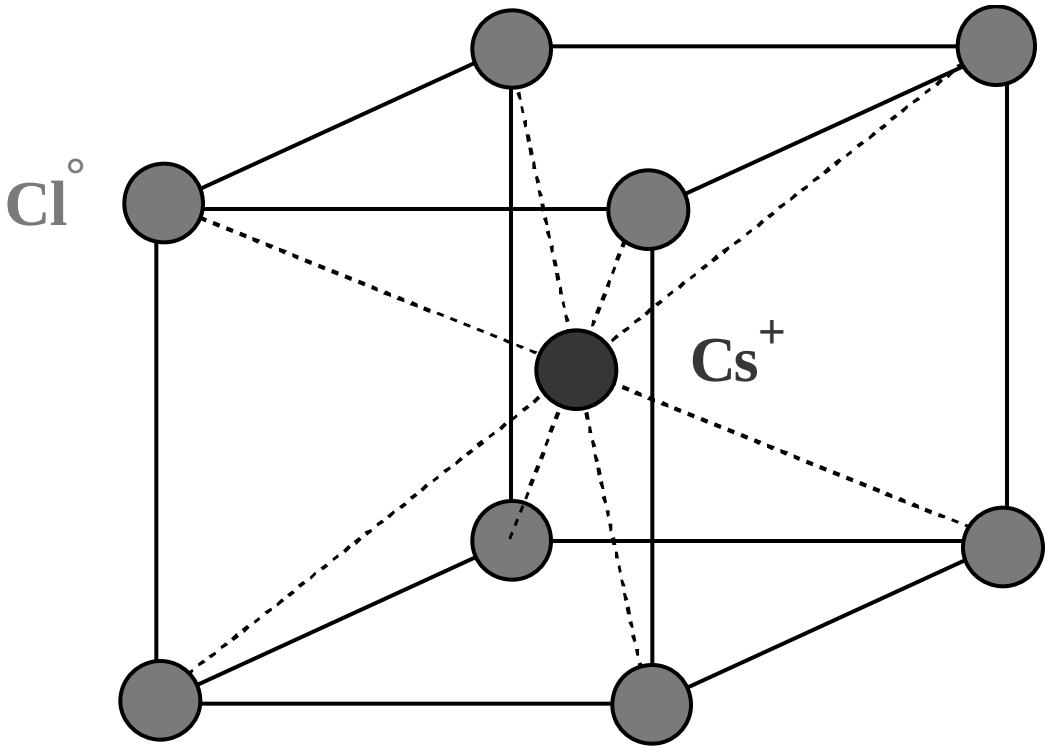
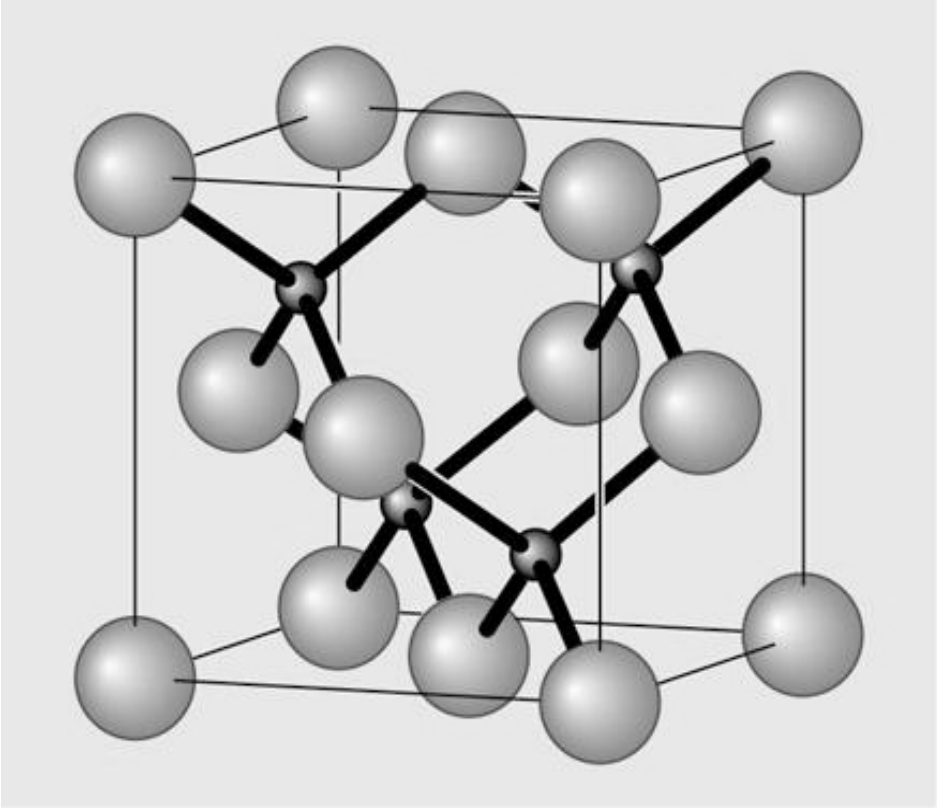
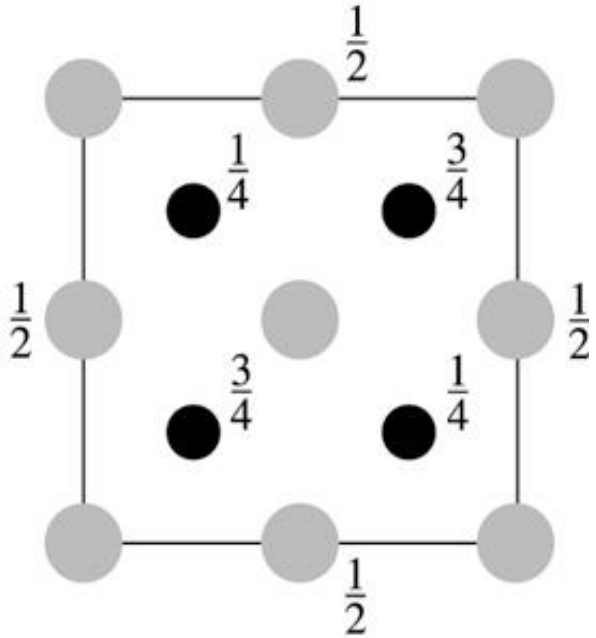


Fig. 1.37: A possible reduced sphere unit cell for the CsCl crystal. An alternative unit cell may have Cs^+ and Cl° interchanged. Examples: CsCl, CsBr, CsI, TlCl, TlBr, TlI.

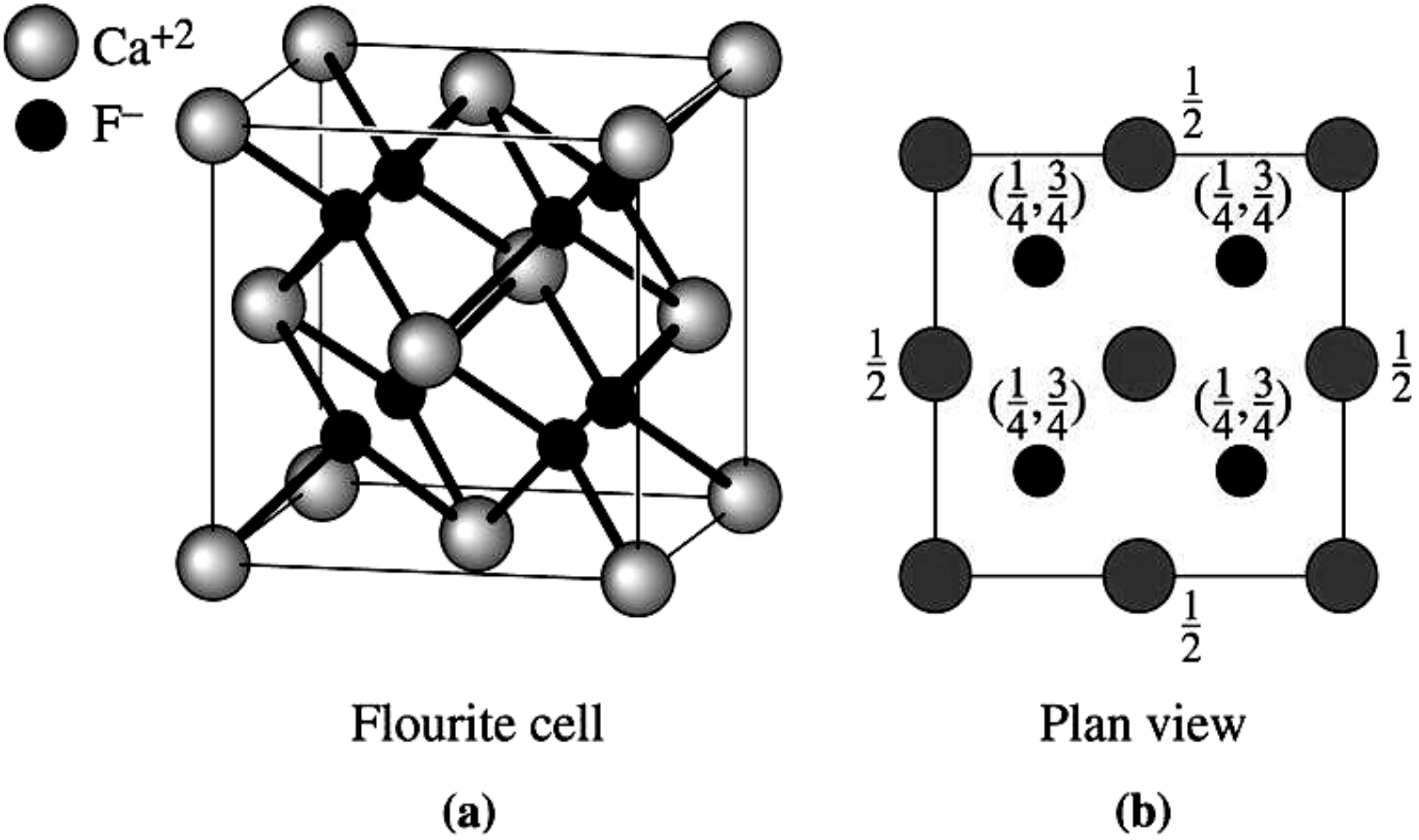


(a)

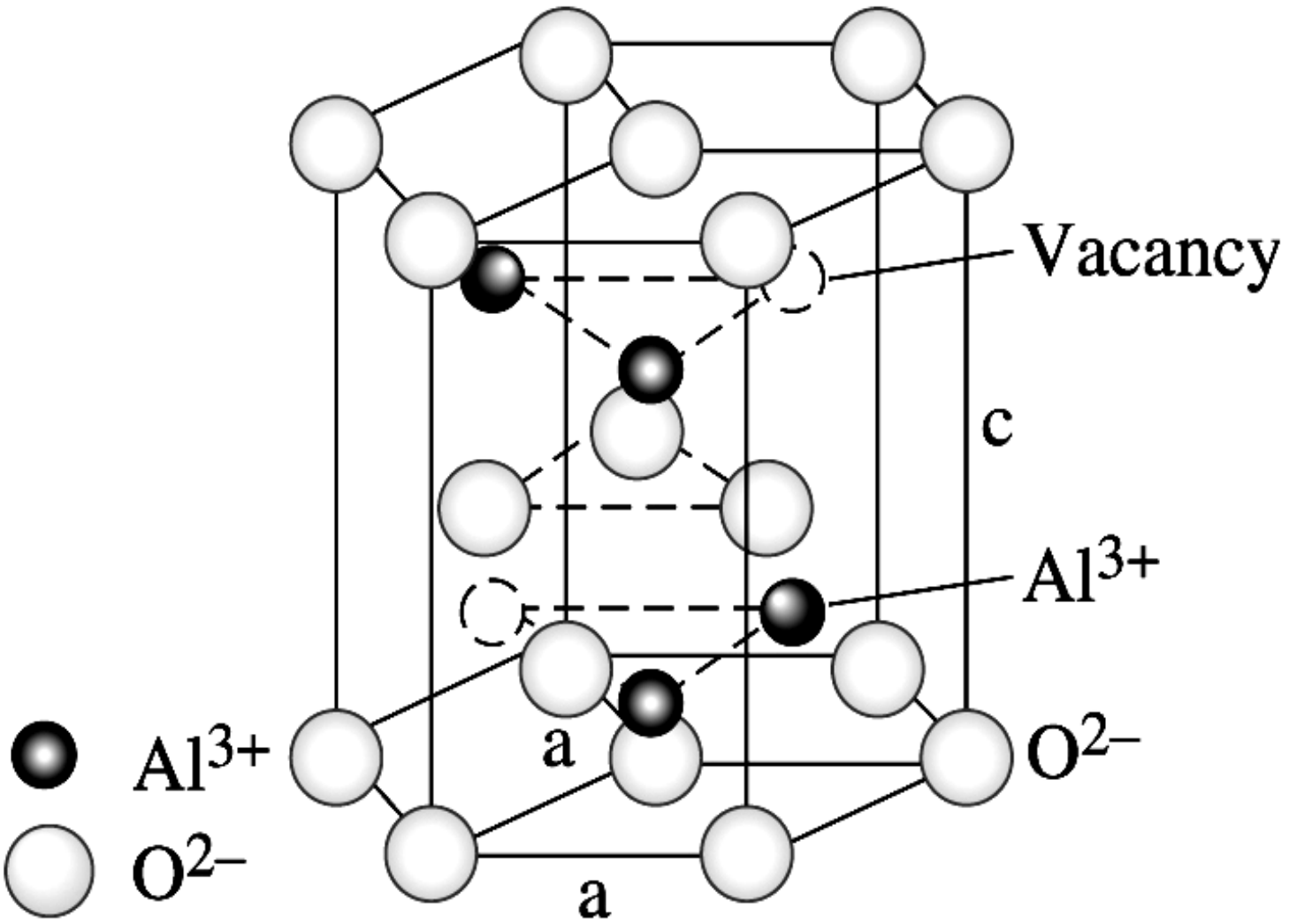


(b)

(a) The zinc blende unit cell, (b) plan view. There is usually a large covalent contribution to these bonds. The coordination is quite low for ionic bonds.



(a) Fluorite unit cell, (b) plan view. All 8 tetrahedral interstitial sites are filled by F anions, as the formula is CsF_2, there is three atoms per lattice point. U)2, ThO2 and ZrO2 have the same structure, there is also the "antifluorite" structure for Li_2O, Na_2O, K_2O with cations and anions reversed



Corundum structure of alpha-alumina (a-Al_2O_3), O in HCP and Al in some of the octahedral interstitial sites, possibly the most widely used ceramic

Covalent Structures

- Covalently bonded materials frequently have complex structures in order to satisfy the directional restraints imposed by the bonding.
- Diamond cubic (DC) - A special type of face-centered cubic crystal structure found in carbon, silicon, α-Sn, and other covalently bonded materials.

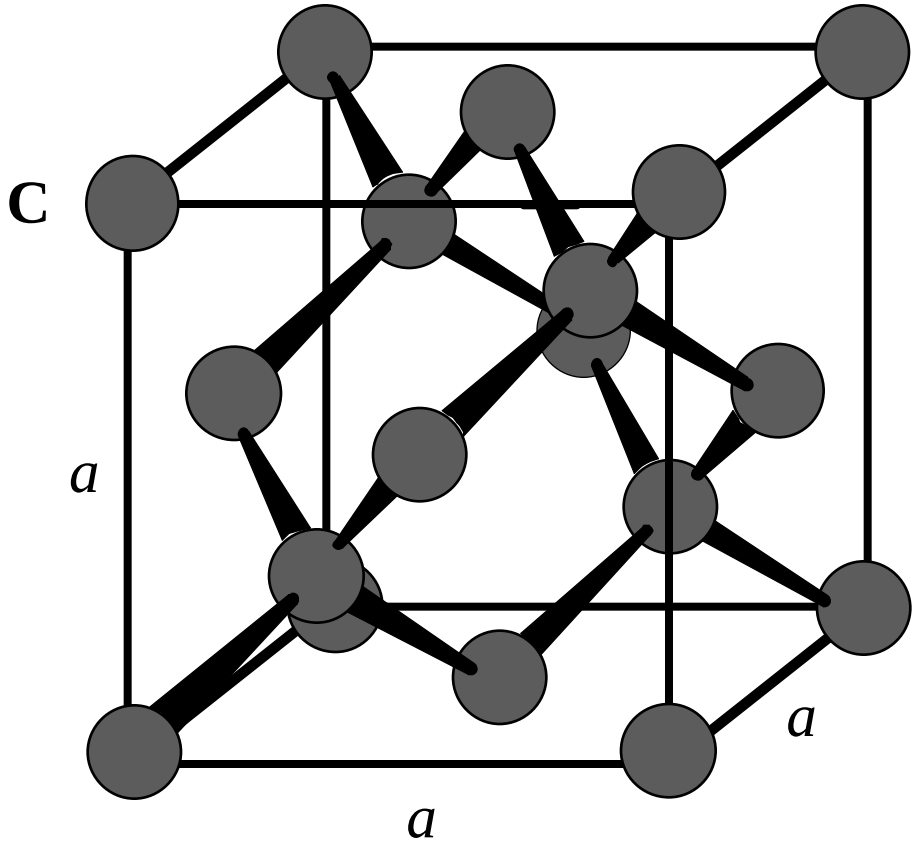


Fig. 1.33: The diamond unit cell is cubic. The cell has eight atoms. Grey Sn (α-Sn) and the elemental semiconductors Ge and Si have this crystal structure.

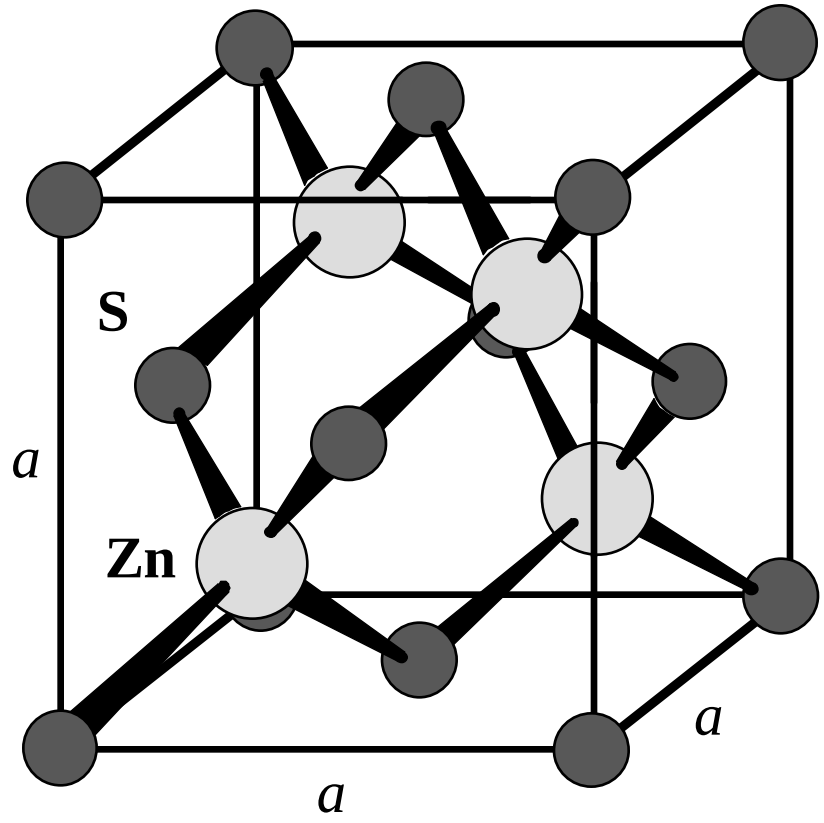
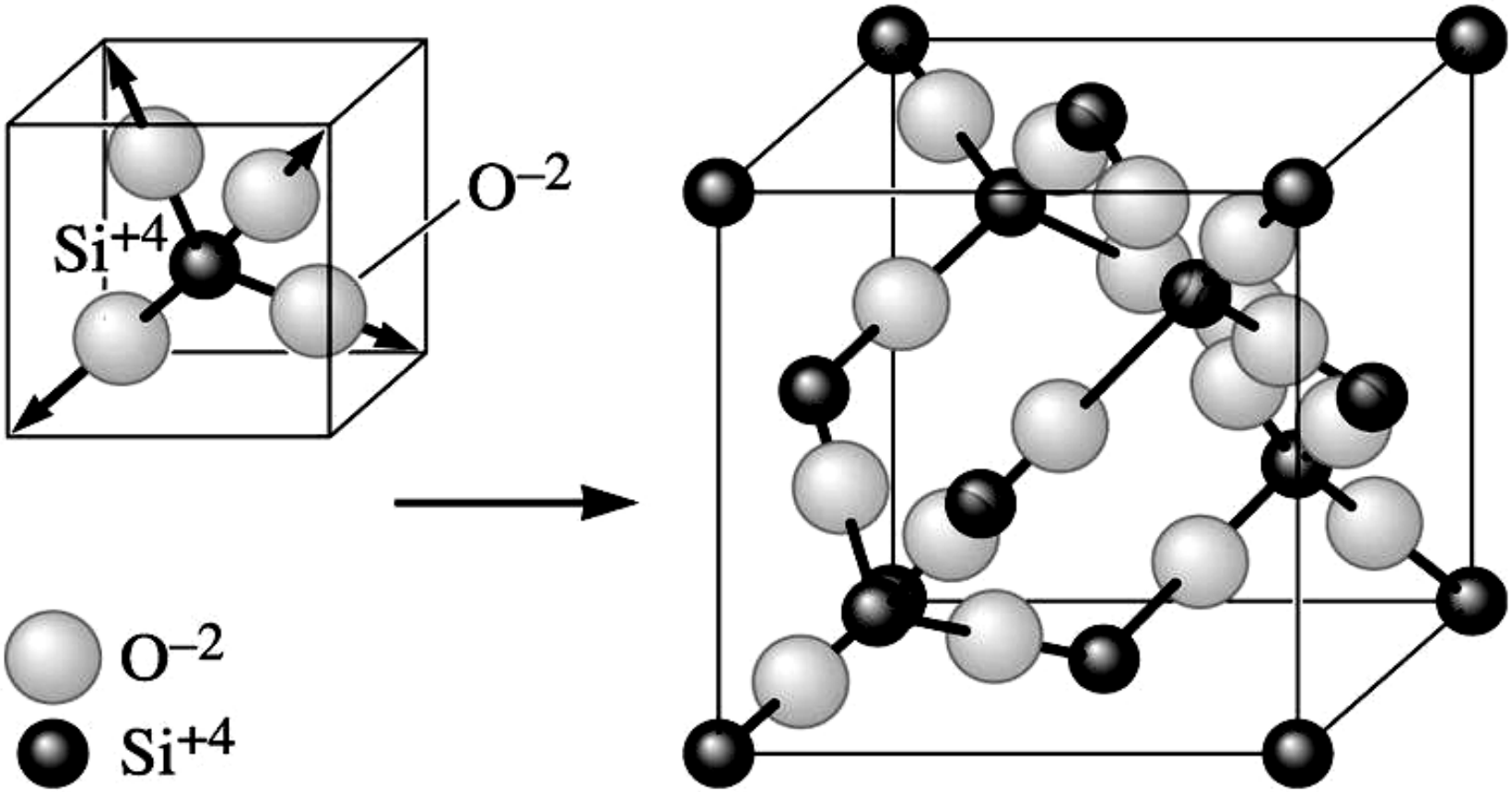
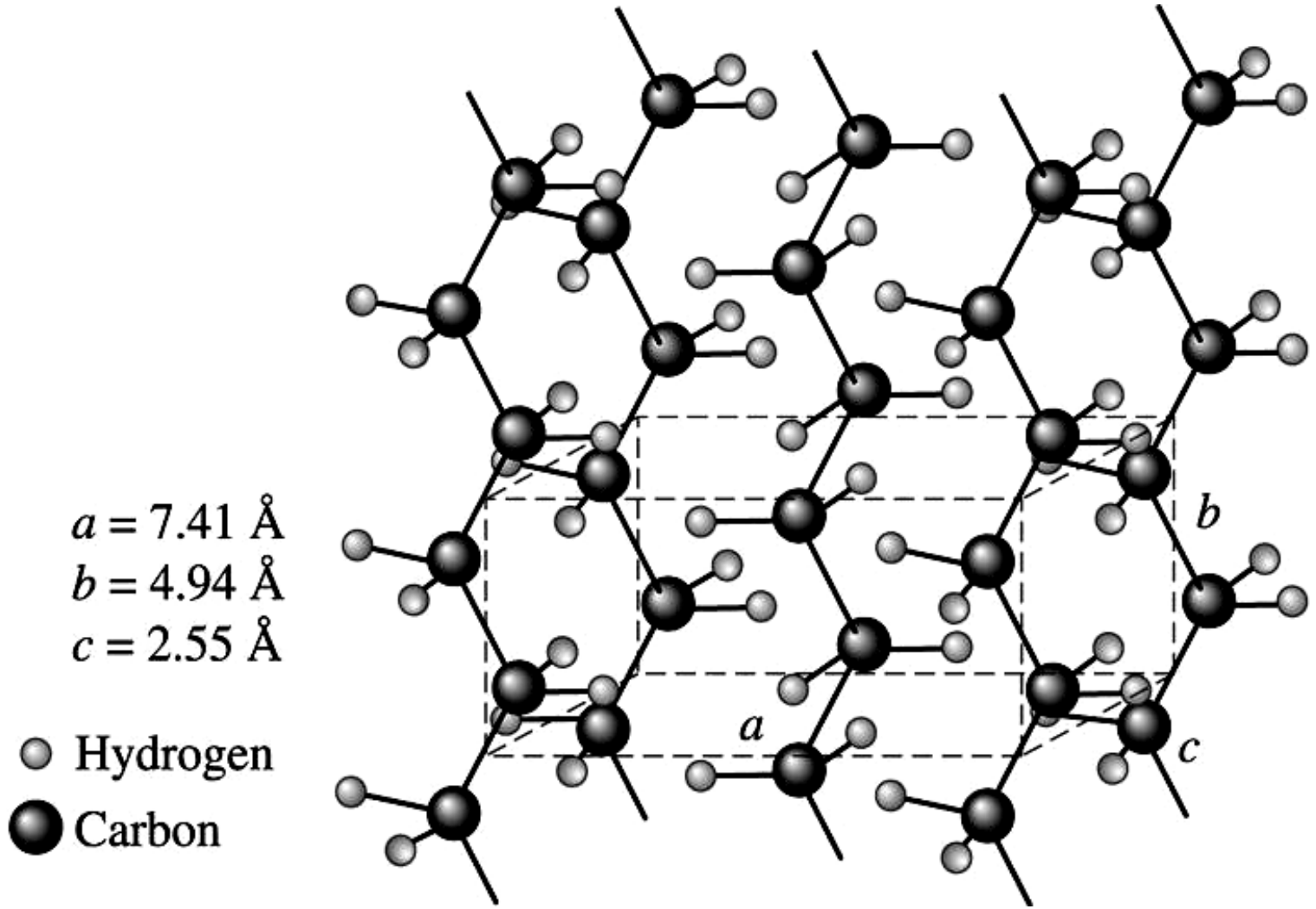


Fig. 1.34: The Zinc blende (ZnS) cubic crystal structure. Many important compound crystals have the zinc blende structure. Examples: AlAs, GaAs, GaP, GaSb, InAs, InP, InSb, ZnS, ZnTe.



The silicon-oxygen tetrahedron and the resultant *ß*-cristobalite form of silica. Note: there is six atom at every lattice point, i.e. one Si in the center, 4 O within the tetrahedron and 4 times ¼ Si at the apexes of each tetrahedron



The unit cell of crystalline polyethylene, Orthorhombic, there are typically many defects in polymer crystals

METALLIC CRYSTALS

- **tend to be densely packed.**
- **have several reasons for dense packing:**
  -Typically, only one element is present, so all atomic radii are the same.
  -Metallic bonding is not directional.
  -Nearest neighbor distances tend to be small in order to lower bond energy.
- **have the simplest crystal structures.**

We will revisit the two closest packed structures and give some examples for each of them

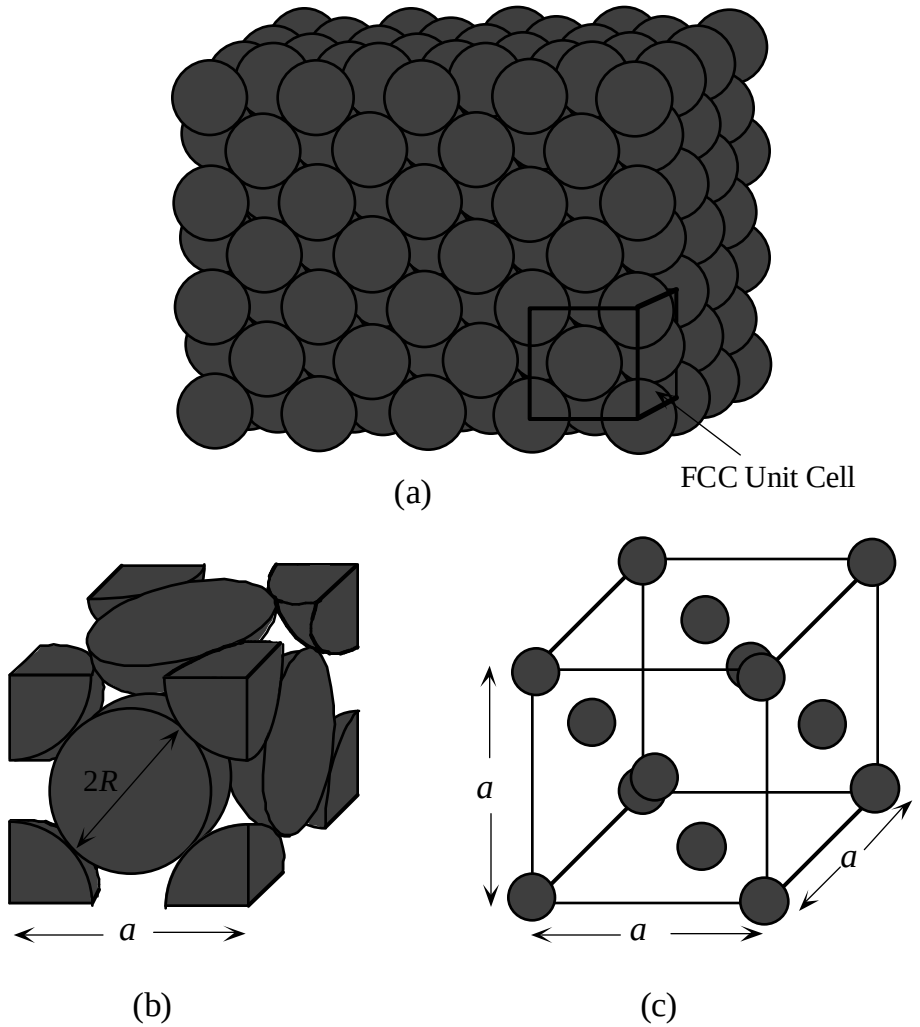
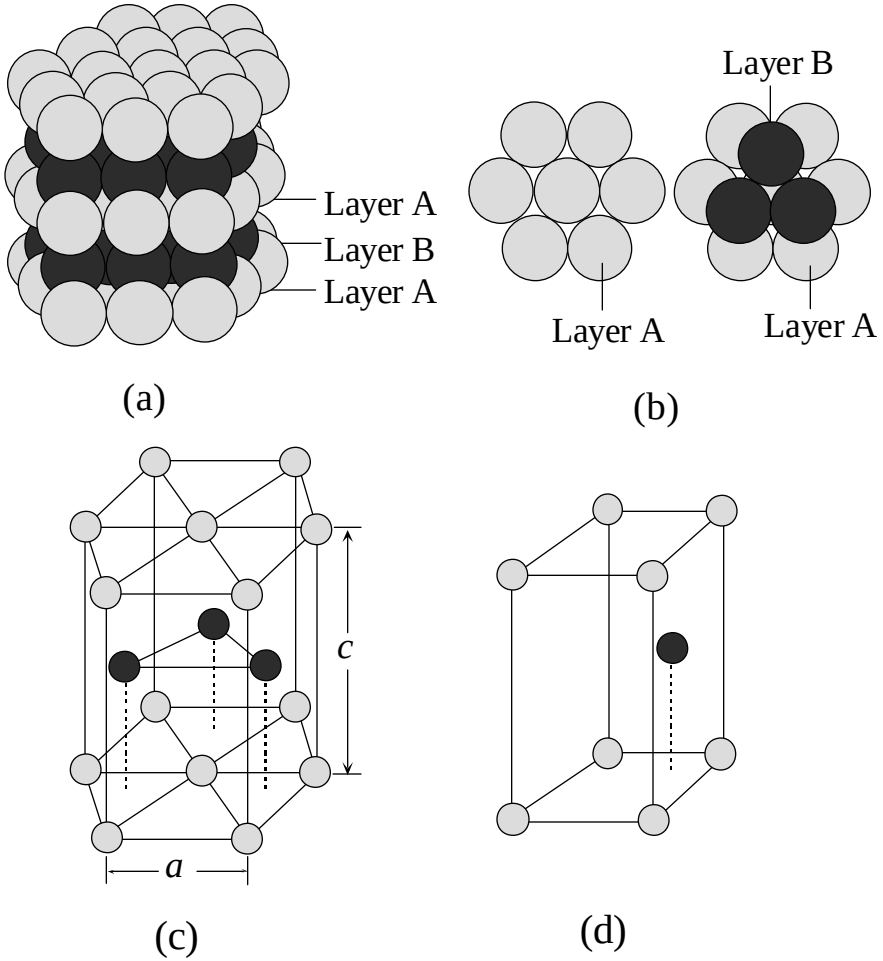


Fig. 1.30: (a) The crystal structure of copper is Face Centered Cubic (FCC). The atoms are positioned at well defined sites arranged periodically and there is a long range order in the crystal. (b) An FCC unit cell with closed packed spheres. (c) Reduced sphere representation of the FCC unit cell. Examples: Ag, Al, Au, Ca, Cu, γ-Fe (>912• C), Ni, Pd, Pt, Rh



Examples: Be, Mg, α-Ti (< 882°C), Cr, Co, Zn, Zr, Cd

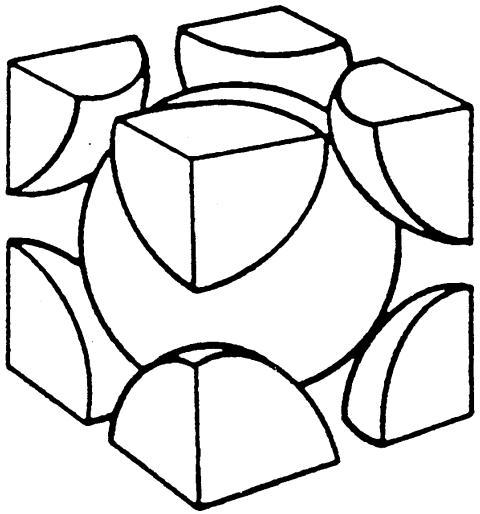
Be very careful, the yellow and blue spheres represent one and the same type of atoms

Fig. 1.32: The Hexagonal Close Packed (HCP) Crystal Structure. (a) The Hexagonal Close Packed (HCP) Structure. A collection of many Zn atoms. Color difference distinguishes layers (stacks). (b) The stacking sequence of closely packed layers is ABAB (c) A unit cell with reduced spheres (d) The smallest unit cell with reduced spheres.

What is steel?

It's not an element, it's an intestinal alloy,

about 1 C atom every 50 Fe atoms, i.e. 0.4 weight % C



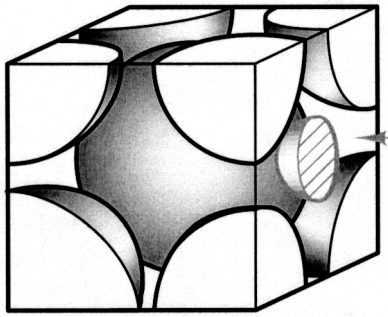


Figure 4-4 *Interstitial solid solution of carbon in α-iron. The carbon atom is small enough to fit with some strain in the interstice (or opening) among adjacent Fe atoms in this structure of importance to the steel industry. [This unit cell structure can be compared with Figure 3–4b.]*

So the crystal structure is BCC, as it is Fe at room temperature, every now and then a much smaller c atom fits into one of the cubic interstitial sites and this increases the strength from about 15 MPa to more than 1500 MPa

How is that little amount of C accomplishing so much ?

More about things such as this in next lecture on lattice defects

SUMMARY Crystals

- **Atoms typically assemble into crystals some materials e.g. glass are amorphous, i.e. have only short range order**

- **We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).**

- **Material properties generally vary with single crystal orientation (i.e., they are anisotropic),**

but properties are frequently quite non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains as e.g. in steel and other engineering materials

Diffraction Techniques for Crystal Structure Analysis

- Diffraction - The constructive interference, or reinforcement, of a beam of x-rays or electrons interacting with a material. The diffracted beam provides useful information concerning the structure of the material.
- Bragg's law - The relationship describing the angle ? at which a beam of x-rays of a particular wavelength diffracts from crystallographic planes of a given interplanar spacing.
- In a diffractometer a moving x-ray detector records the 2? angles at which the beam is diffracted, giving a characteristic diffraction pattern

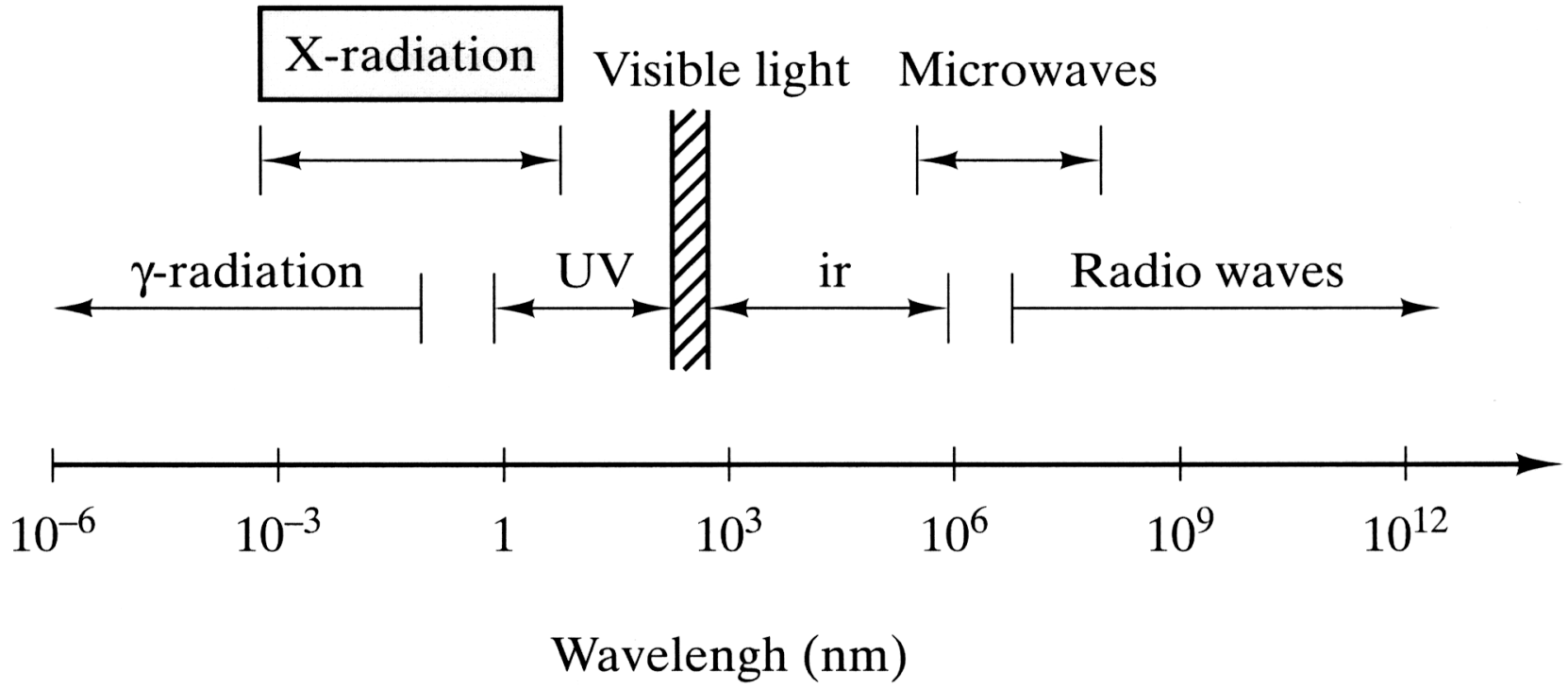


Figure 3-34 *Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.*

Lattice constants range from about 0.1 nm to some 50 - 100 nm. Most crystals' lattice constants are in the 1-5 nm range, since crystals are periodic, they are the ideal diffraction grating for X-rays, Max von Laue's 1914 Nobel prize that proved both, crystals are periodic 3D arrangements of atoms and X-rays are waves (well wave-particles actually)

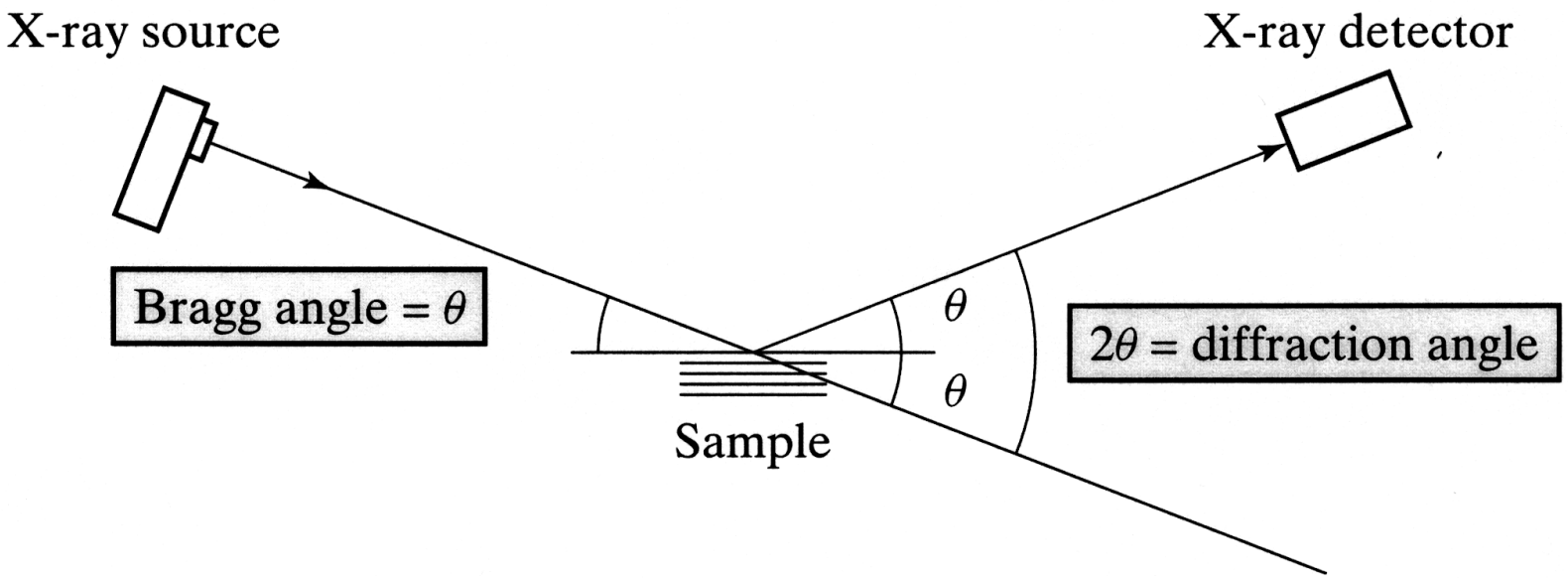
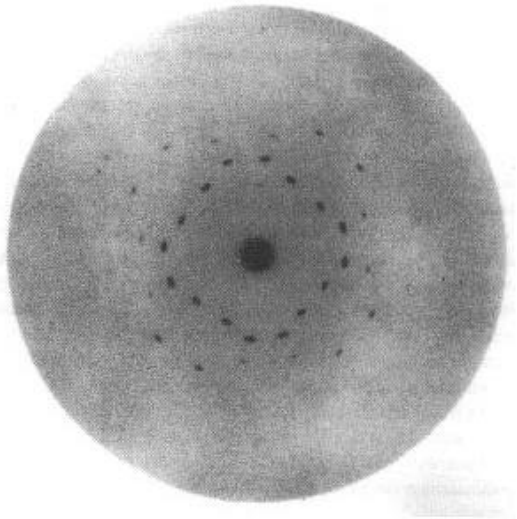


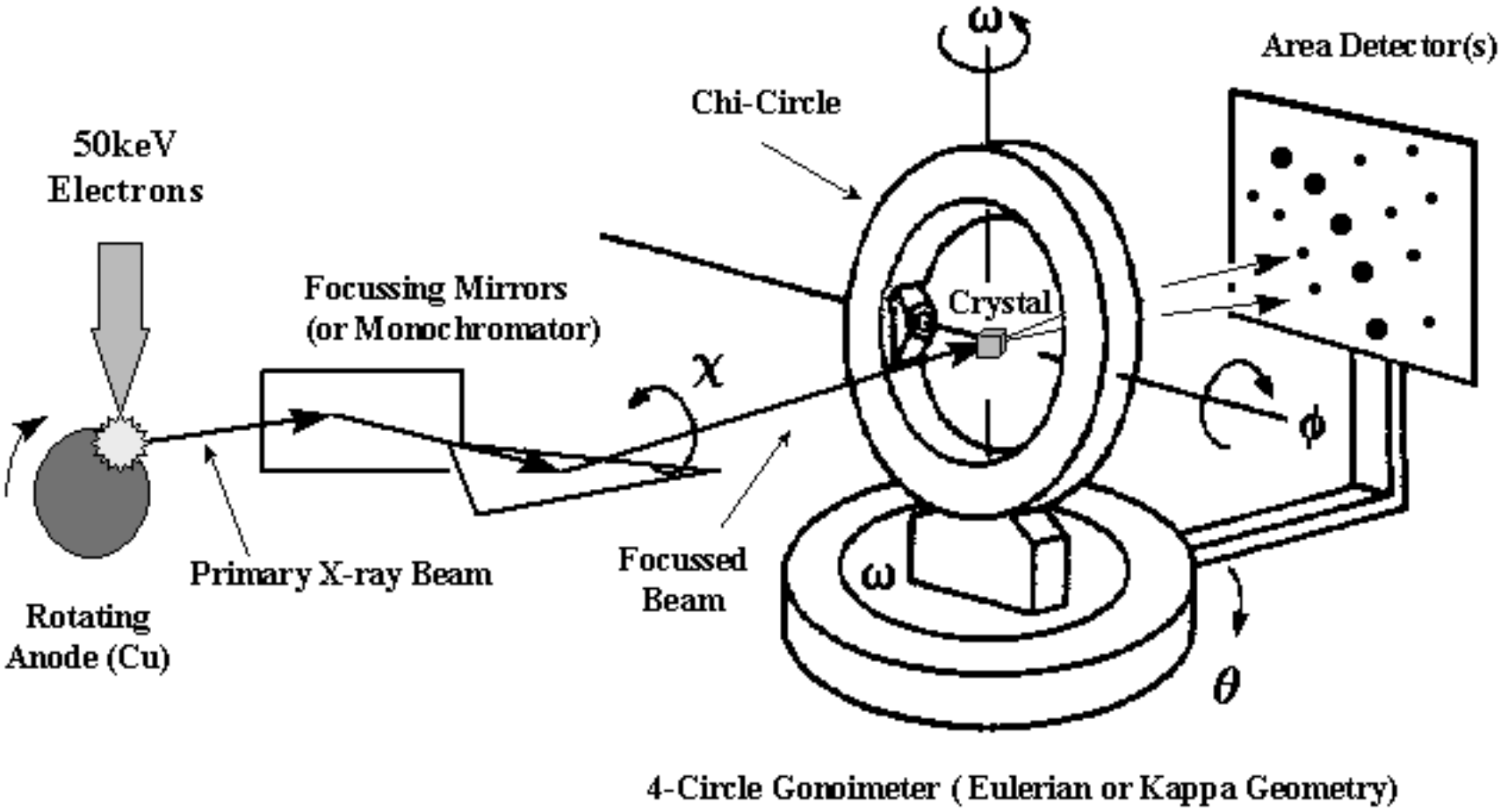
Figure 3-36 *Relationship of the Bragg angle (θ) and the experimentally measured diffraction angle (2θ).*



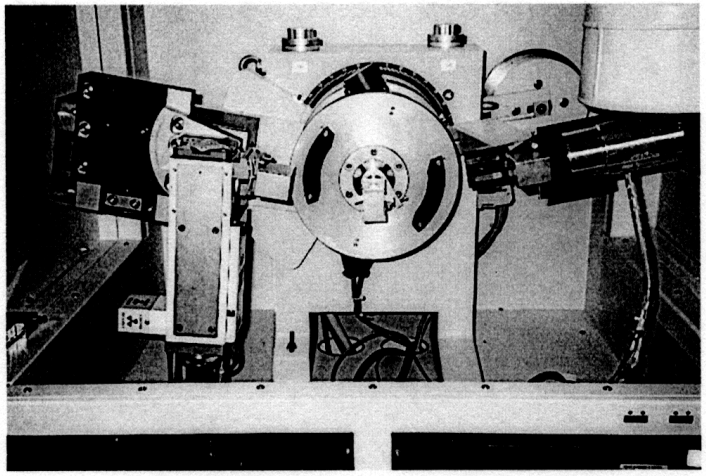
The diffraction angle is always 2?

Bragg's law: n λ = 2 d_{hkl} sin ?

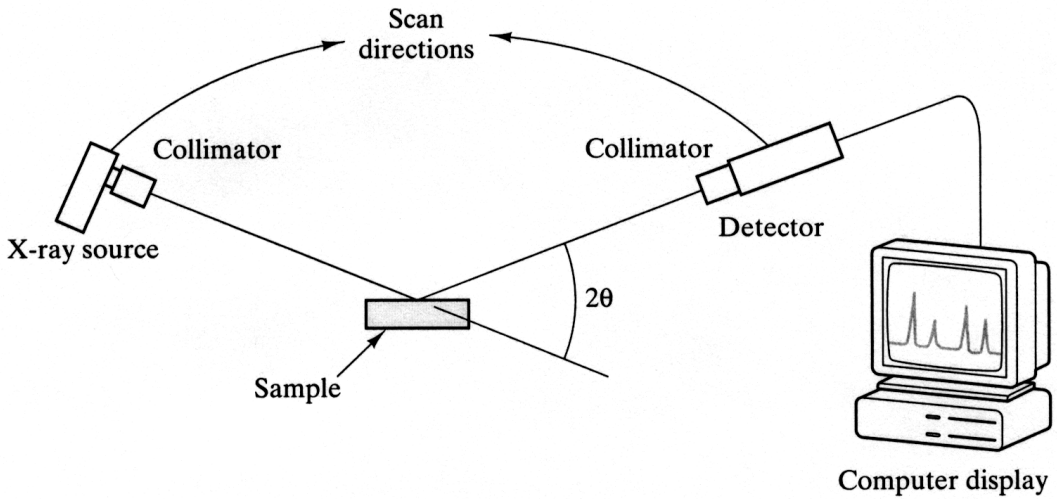
n – the order of reflection can be dropped by allowing indices for hkl that are not smallest integers, i.e. HKL



Single crystal diffractometers are more sophisticated



(a)

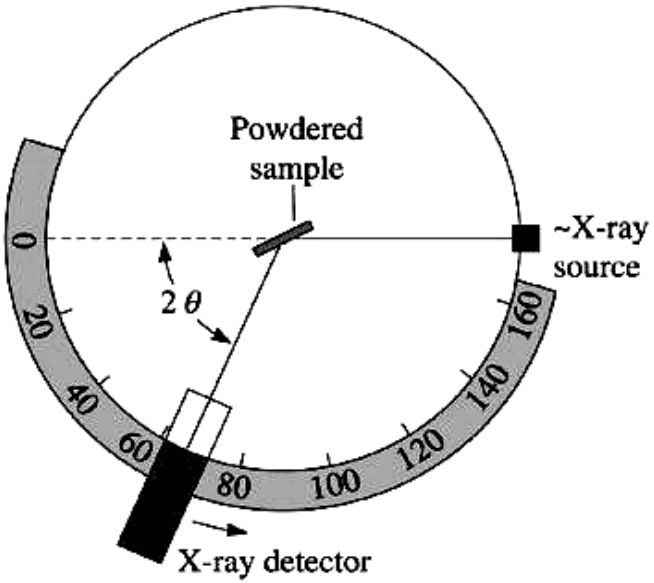


(b)

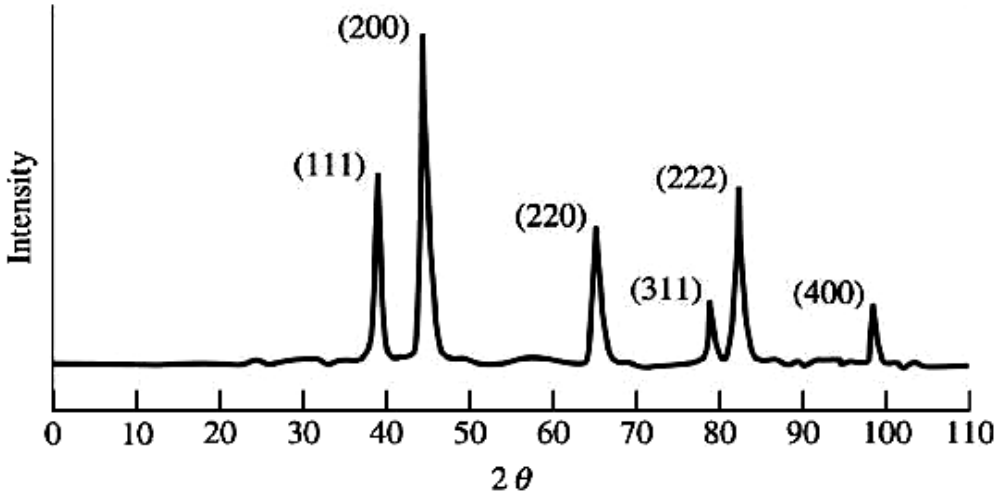
Figure 3-40 *(a) An x-ray diffractometer. (Courtesy of Scintag, Inc.) (b) A schematic of the experiment.*

Powder diffractometers (for polycrystalline powder)

are less sophisticated and can be found in many places



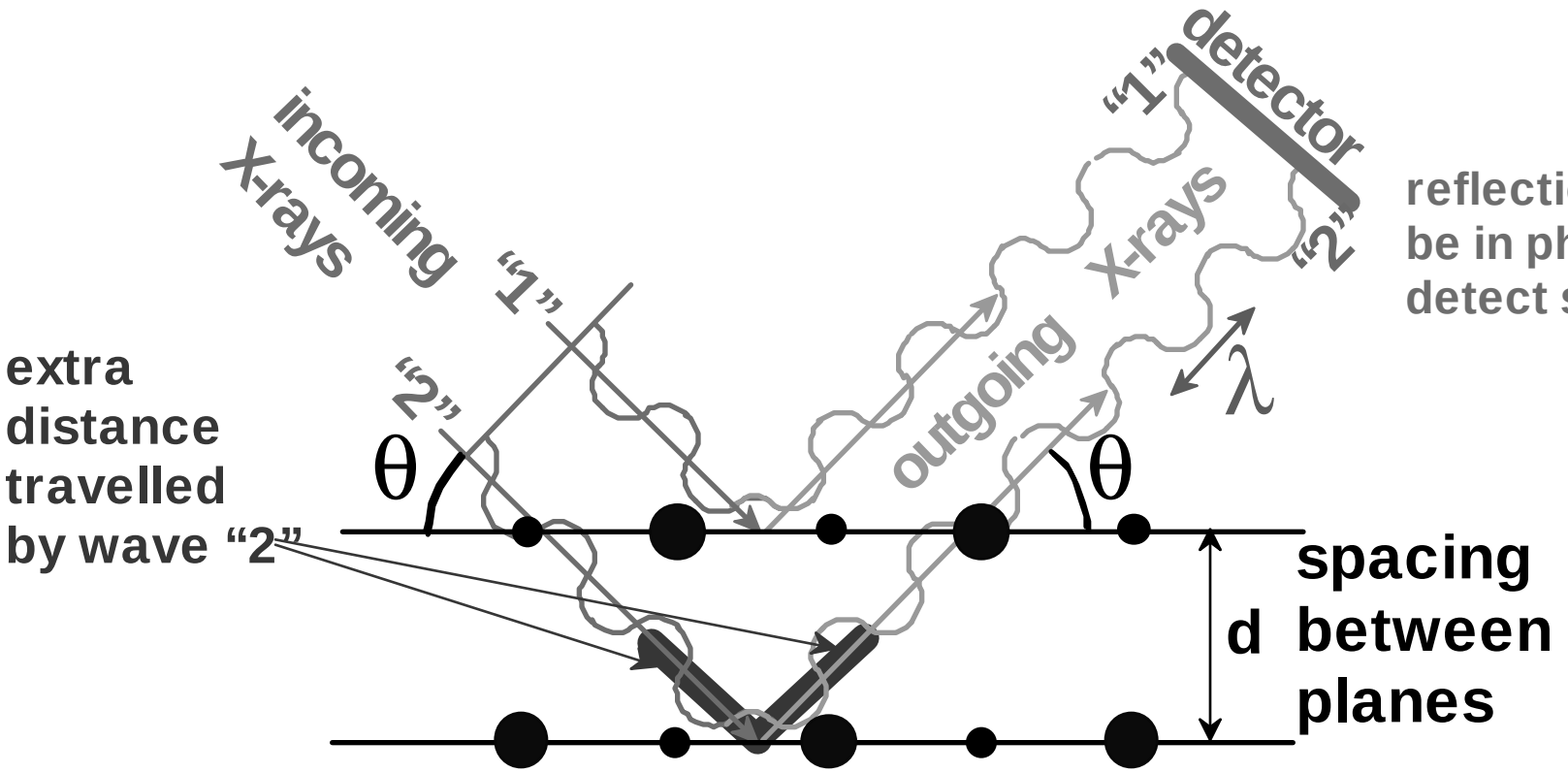
(a)



(b)

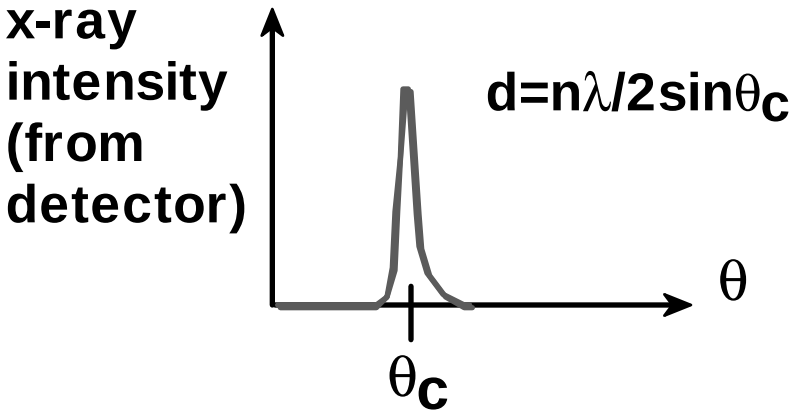
(a) sketch of a diffractometer viewed from above, showing powder sample, incident and diffracted beams.

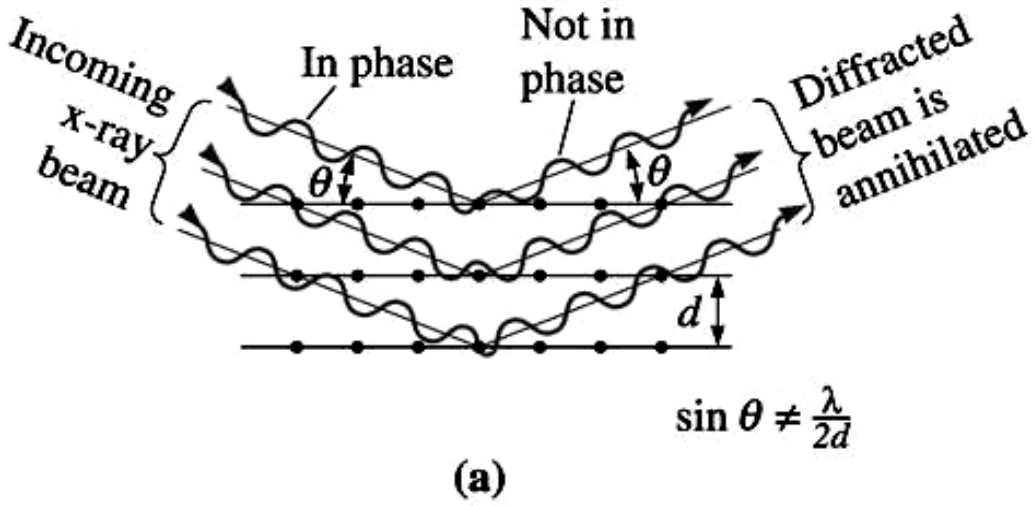
(b) diffraction pattern obtained from a sample of gold powder, notice the Miller indices of the diffracting crystal planes

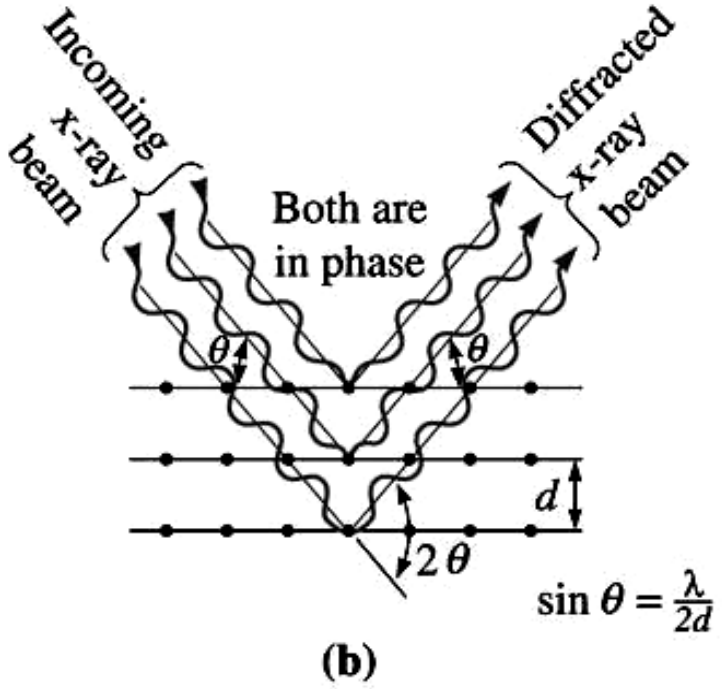


reflections must be in phase to detect signal

- **Measurement of: "reflection" angles (Bragg angles), θ, for X-rays provide atomic spacing, d.**







(a) Destructive and (b) reinforcing (constructive) interference between x-rays "reflected on a set of planes. Reinforcement occurs only at angles that satisfy Bragg's law.

$\lambda = 2\, d_{HKL} \sin\theta$

No other X-ray diffraction peaks occur

X-ray Diffraction for an forensic examination

The results of a x-ray diffraction experiment on some metal powder found at a crime scene using characteristic x-rays with ? = 0.7107 Å (a radiation obtained from molybdenum (Mo) target) show that diffracted peaks occur at the following 2? angles:

Peak	2θ	Peak	2θ
1	20.20	5	46.19
2	28.72	6	50.90
3	35.36	7	55.28
4	41.07	8	59.42

Determine the indices of the plane producing each peak, and from that the lattice parameter of the material and from that identify the material (you know it is some metal so it is a good guess to assume the crystals in the powder are cubic)

SOLUTION

$\lambda = 2\, d_{HKL} \sin\theta$ $\qquad$ $\left(\frac{l}{2d_{HKL}}\right)^2 = \sin^2 q$

$$d_{HKL} = \frac{1}{\sqrt{H^2 + K^2 + L^2}} = (Ha^* + Kb^* + Lc^*)^{-1} = (d^*_{HKL})^{-1} = \vec{g}$$

We first determine the $\sin^2\theta$ value for each peak, then divide through by the lowest denominator, 0.0308, "guess" the indices

Peak	2θ	$\sin^2\theta$	$\sin^2\theta/0.0308$	$h^2 + k^2 + l^2$	(hkl)
1	20.20	0.0308	1	2	(110)
2	28.72	0.0615	2	4	(200)
3	35.36	0.0922	3	6	(211)
4	41.07	0.1230	4	8	(220)
5	46.19	0.1539	5	10	(310)
6	50.90	0.1847	6	12	(222)
7	55.28	0.2152	7	14	(321)
8	59.42	0.2456	8	16	(400)

SOLUTION (Continued)

We could then use 2? values for any of the peaks to calculate the interplanar spacing and thus the lattice parameter. Picking peak 8:

2? = 59.42 or ? = 29.71

$$d_{400} = \frac{l}{2\sin q} = \frac{0.7107}{2\sin(29.71)} = 0.71699\text{Å}$$

$$a_0 = d_{400}\sqrt{h^2 + k^2 + l^2} = (0.71699)(4) = 2.868\,\text{Å}$$

This is the lattice parameter for body-centered cubic iron.

So the gardener did steal the cookies – only kidding

Since out of all metals only Po has the simple cubic structure, and we do know our material was not radioactive and difficult to obtain, we didn't check for an indexing scheme for a single cubic lattice, it would have gotten us nowhere anyway

There are certain systematic absences of reflections

You may have noticed that there are no (hkl) triplets with h+k+l = odd.

Laue's kinematical theory of X-ray diffraction (1912) explains why,

different structures have forbidden reflections, i.e. reflections that do not show up in diffraction but these planes do of course exist in the crystals, it is just that diffraction on them is destructive

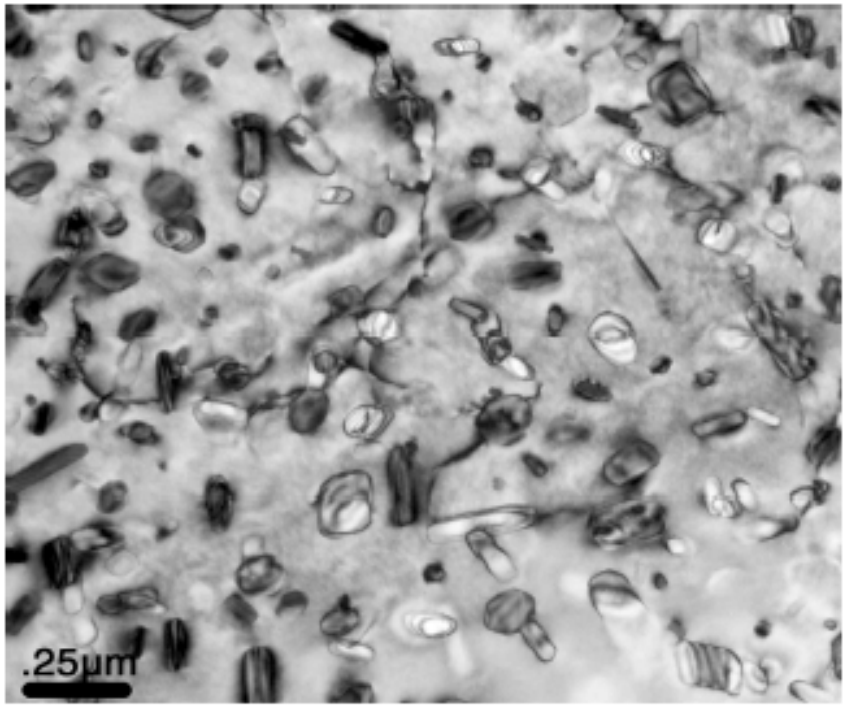
Simple cubic crystals have no forbidden reflections

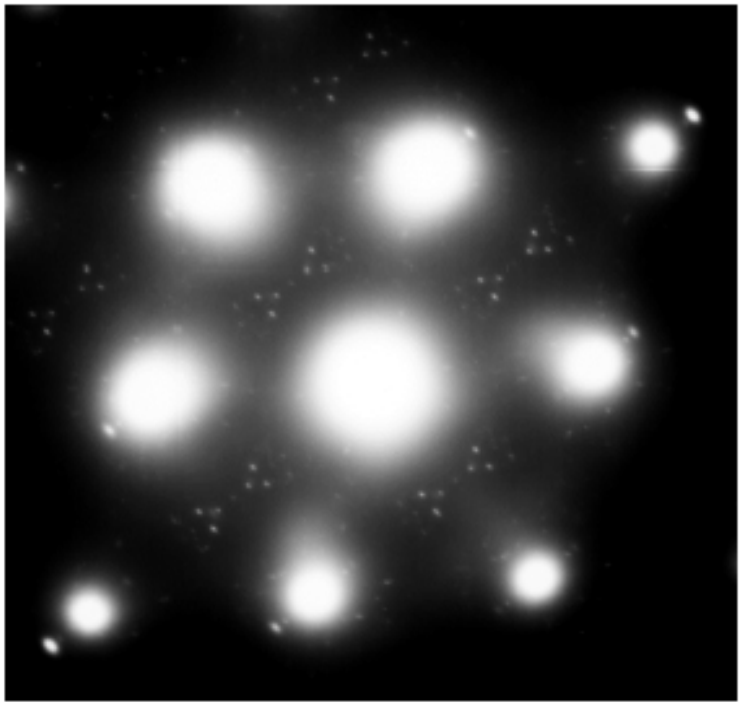
Rules for Determining the Diffracting {*hkl*} Planes in Cubic Crystals

Bravais lattice	Reflections present	Reflections absent
BCC	$(h + k + l)$ = even	$(h + k + l)$ = odd
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

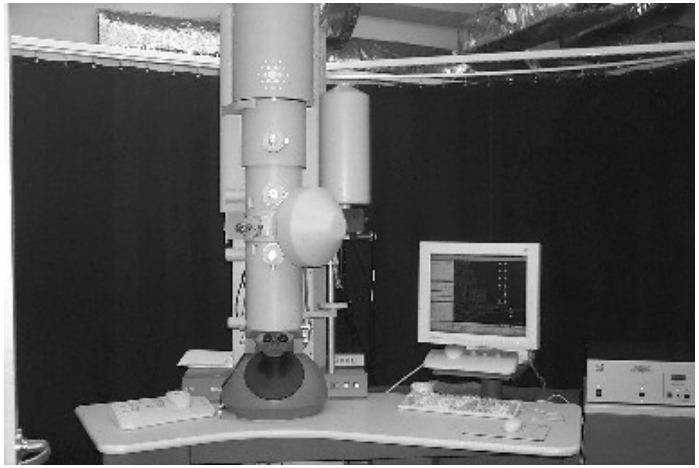
Miller Indices of the Diffracting Planes for BCC and FCC Lattices

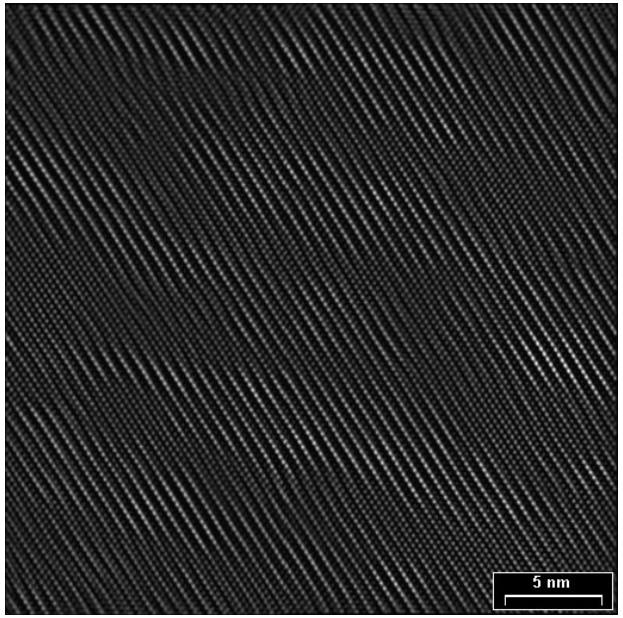
Cubic planes {*hkl*}	$h^2 + k^2 + l^2$	Sum $\Sigma(h^2 + k^2 + l^2)$	Cubic diffracting planes {*hkl*} FCC	Cubic diffracting planes {*hkl*} BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2	...	110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6	...	211
...		7		
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10	...	310

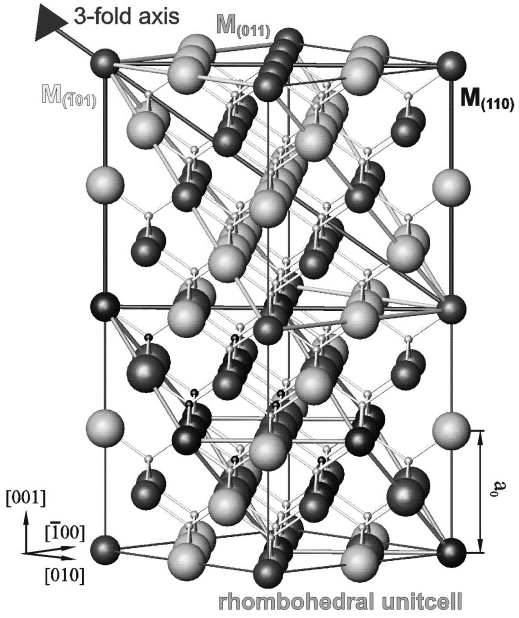




A TEM micrograph of an aluminum alloy (Al-7055) sample. The diffraction pattern at the right shows large bright spots that represent diffraction from the main aluminum matrix grains. The smaller spots originate from the nano-scale crystals of another compound that is present in the aluminum alloy.







(In,Ga)P, an important semiconductor for visible light lasers can show a variety of atomic ordering

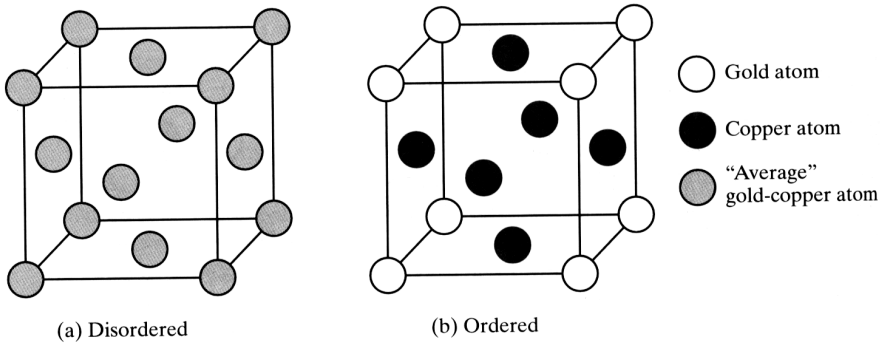
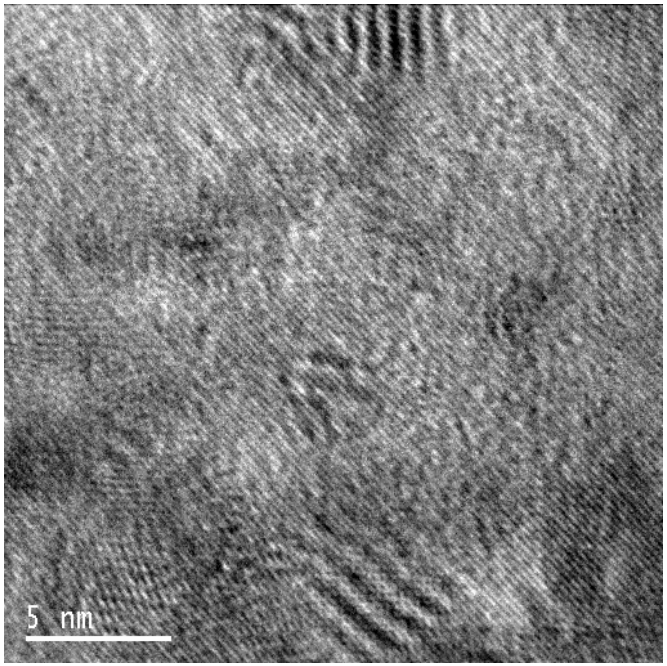
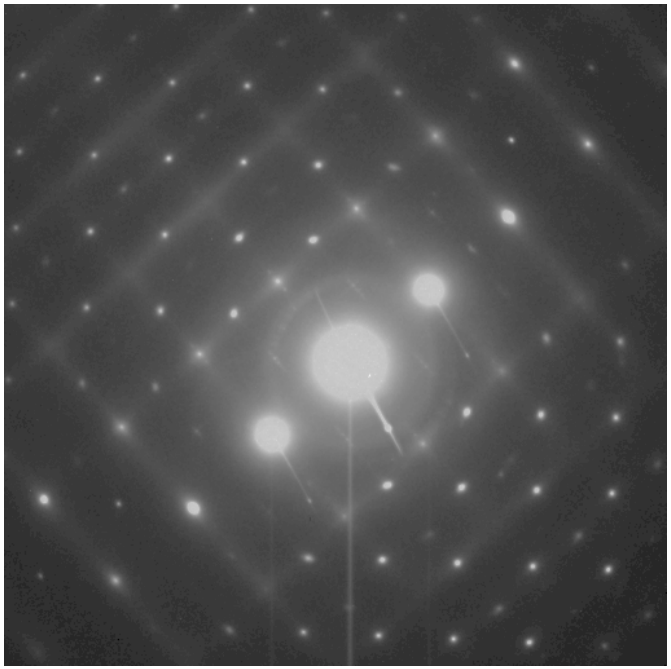
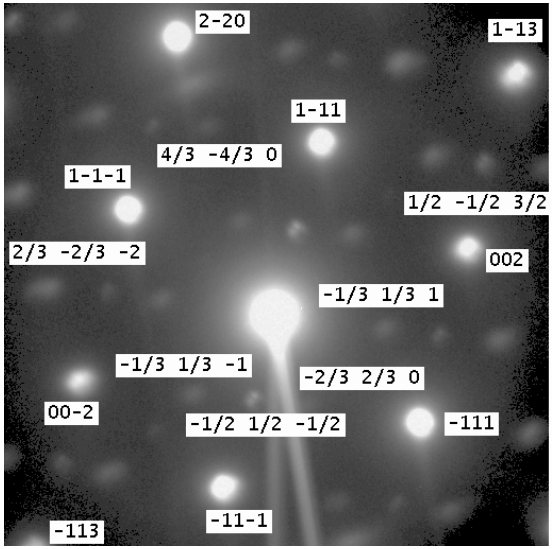


Figure 4-3 *Ordering of the solid solution in the $AuCu_3$ alloy system. (a) Above ~ 390°C, there is a random distribution of the Au and Cu atoms among the fcc sites. (b) Below ~ 390°C, the Au atoms preferentially occupy the corner positions in the unit cell, giving a simple cubic Bravais lattice. (From B. D. Cullity,* Elements of X-Ray Diffraction, *2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1978.)*

The very same thing, i.e. atomic ordering exist in metals as well

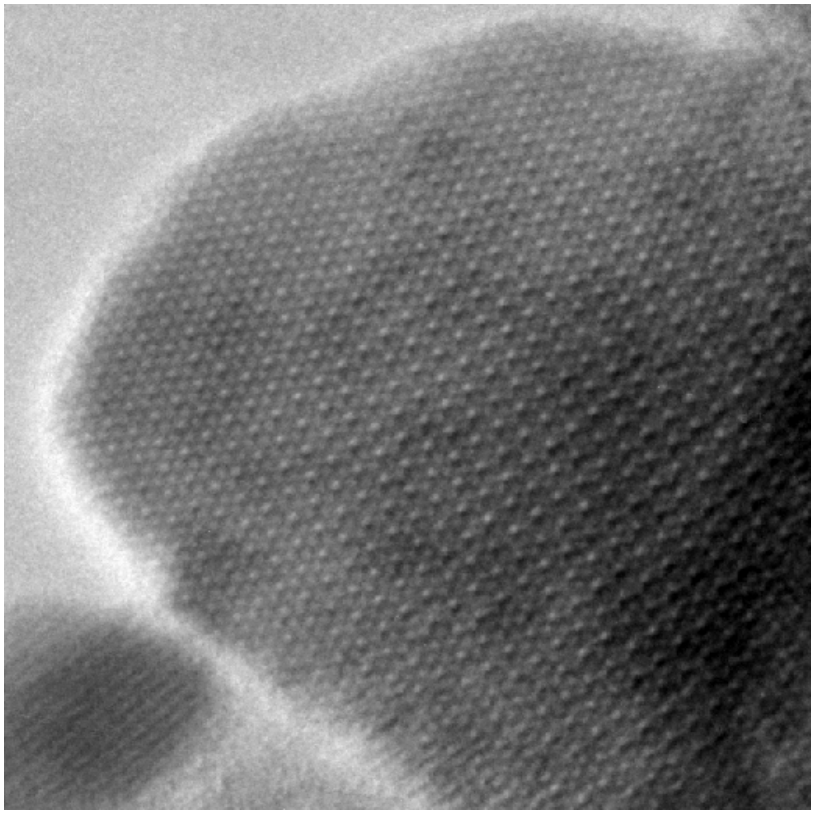


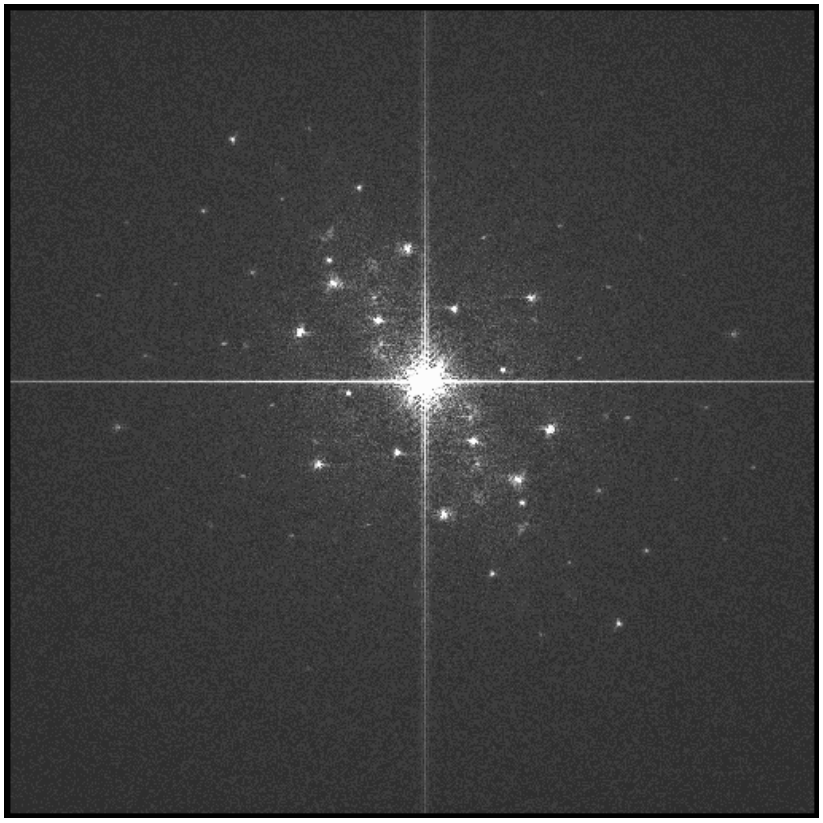




II-VI semiconductors with atomic ordering, (Cd,Zn)Se quantum dots in ZnSe, [001] plan view

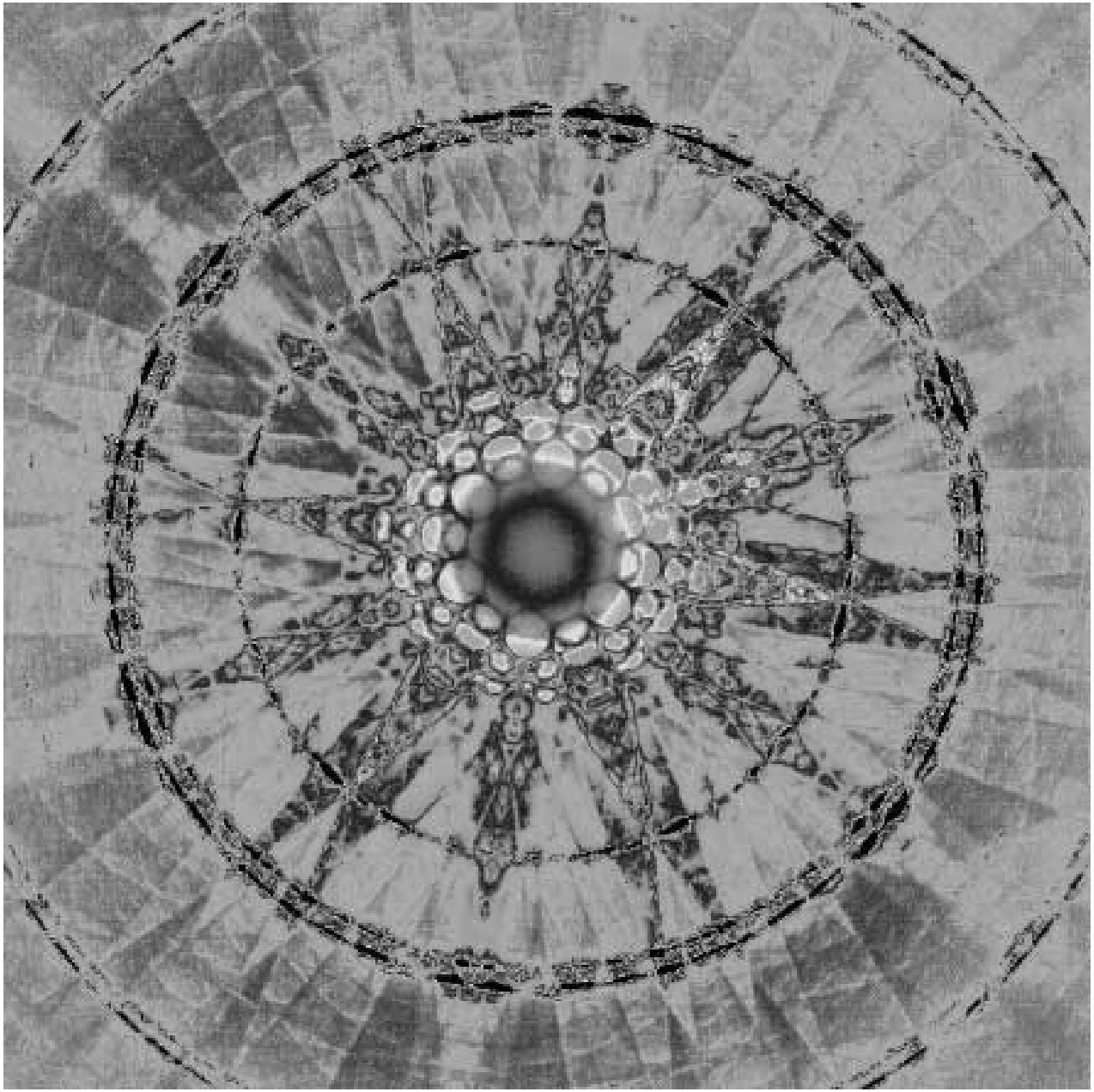
(Cd,Mn,Zn)Se quantum dots in <110> cross section





Unknown crystallographic phase in (In,Ga)(Sb,As) quantum dots in InAs matrix,

a Fourier transform power spectrum of a high resolution TEM images replaces frequently a diffraction pattern as much of the information is contained in such calculated images



False color convergent beam electron diffraction pattern,

From the symmetry of the lines (Kikuchi lines), the crystal system can be determined

From the fine structure of the diffraction disk, the space group can be determined

Works for extremely tiny specs of matter, perhaps 2 nm across

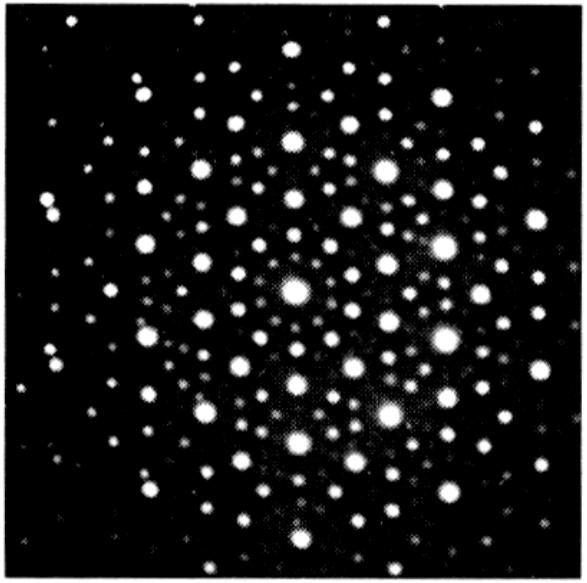
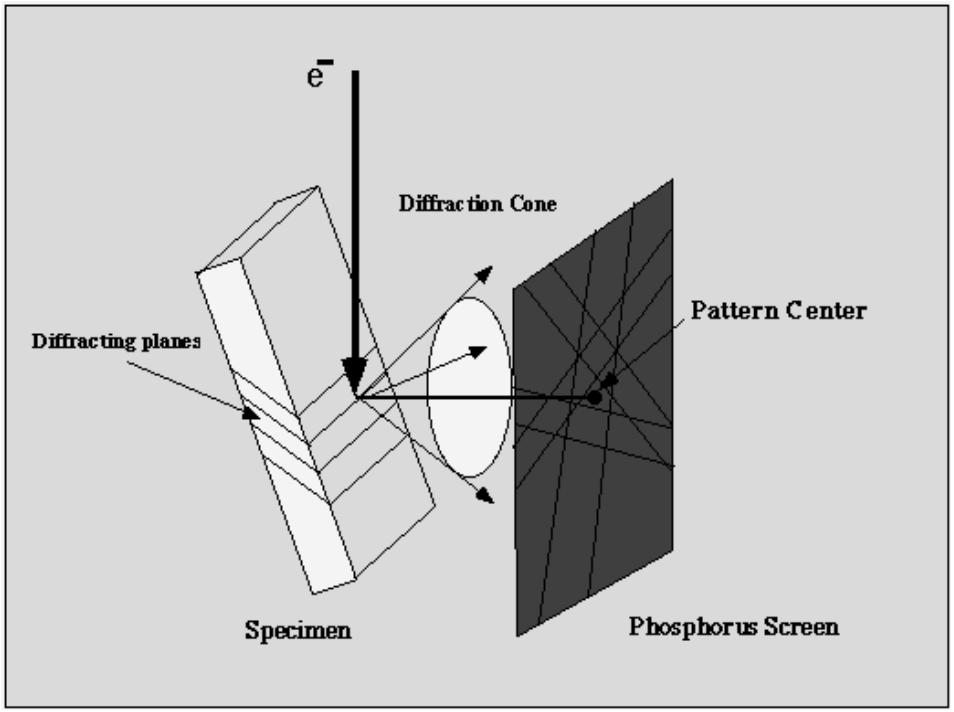


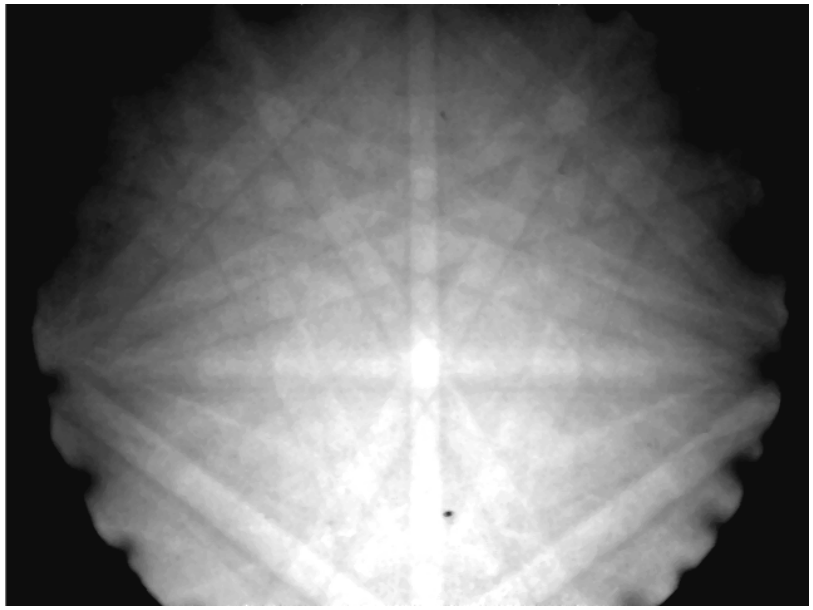
Figure 4-27 *Electron diffraction pattern of a rapidly cooled Al_6Mn alloy showing fivefold symmetry; that is, the pattern is identical with each rotation of 360°/5, or 72°, about its center. Such symmetry is impossible in traditional crystallography. [After D. Schechtman et al.,* Phys. Rev. Letters 53, *1951 (1984).]*

Wow, what is that?

It can't be a crystal as it obviously has a five fold symmetry, it is not amorphous either as it clearly has a diffraction pattern?

It's a **quasi-crystal, i.e.** and entity with short range order (as amorphous and crystalline materials) and long range order (as a crystal), the crucial difference is, the long range order is **non periodic**





Crystallographic work can also be done in modern SEMs !

Electron backscatter (Kikuchi) diffraction (EBSD), here of a Si crystal

scanning probe microscopy, STM, AFM, …

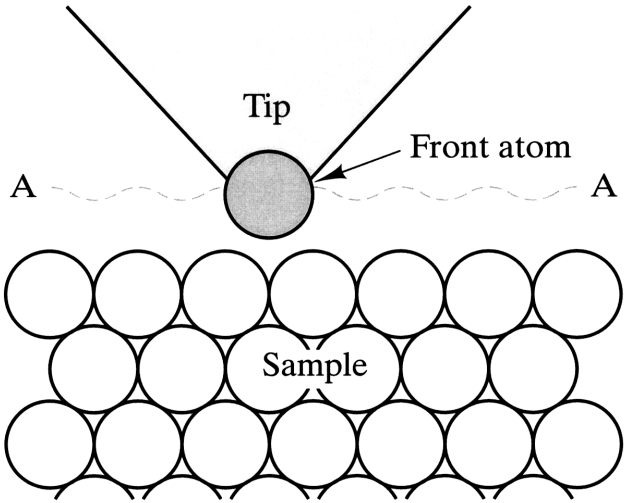
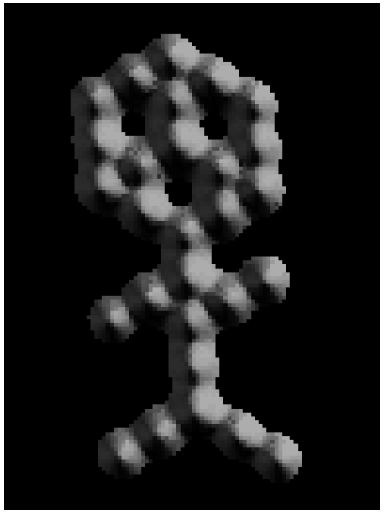
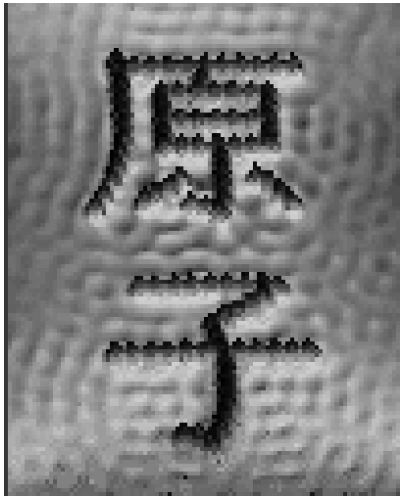


Figure 4-41 *Schematic of the principle by which the probe tip of either a scanning tunneling microscope (STM) or an atomic force microscope (AFM) operates. The sharp tip follows the contour A-A as it maintains either a constant tunneling current (in the STM) or a constant force (in the AFM). The STM requires a conductive sample while the AFM can also inspect insulators.*

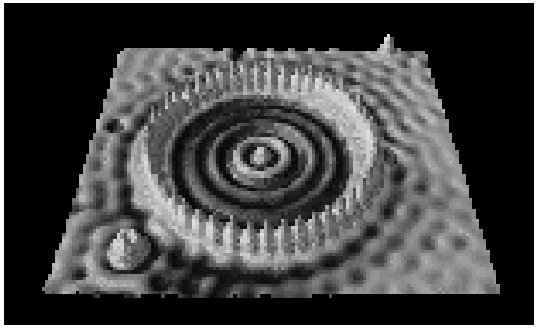
Atoms can be arranged and imaged!



Carbon monoxide molecules arranged on a platinum (111) surface.



Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.



Something more useful, the square of the quantum mechanical wave function of an electron that is trapped in a “cage” of Cu atoms