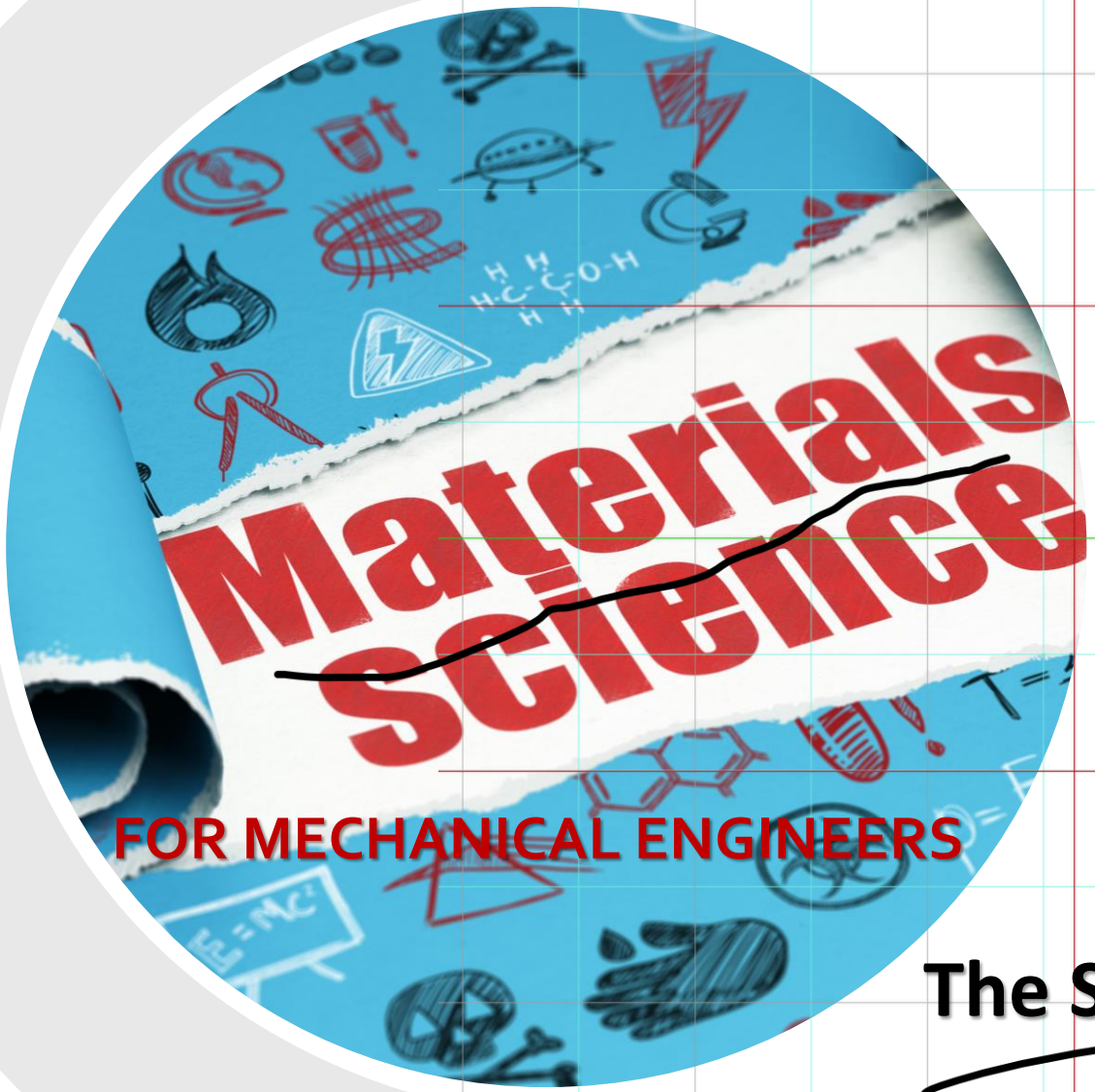


FOR MECHANICAL ENGINEERS

The Structure of Crystalline Solids

SPRING 2022-2023

INTRODUCTION

Learning Objectives

- Describe the difference in atomic/molecular structure between crystalline and noncrystalline materials.
- Draw unit cells for face-centred cubic, bodycentered cubic, and hexagonal close-packed crystal structures.
- Derive the relationships between unit cell edge length and atomic radius for face-centred cubic and body-centred cubic crystal structures.
- Compute the densities for metals having facecentered cubic and body-centred cubic crystal structures given their unit cell dimensions.
- Given three direction index integers, sketch the direction corresponding to these indices within a unit cell.
- Specify the Miller indices for a plane that has been drawn within a unit cell.
- Describe how face-centred cubic and hexagonal close-packed crystal structures may be generated by the stacking of close-packed planes of atoms.
- Distinguish between single crystals and polycrystalline materials.
- Define *isotropy* and *anisotropy* with respect to material properties.

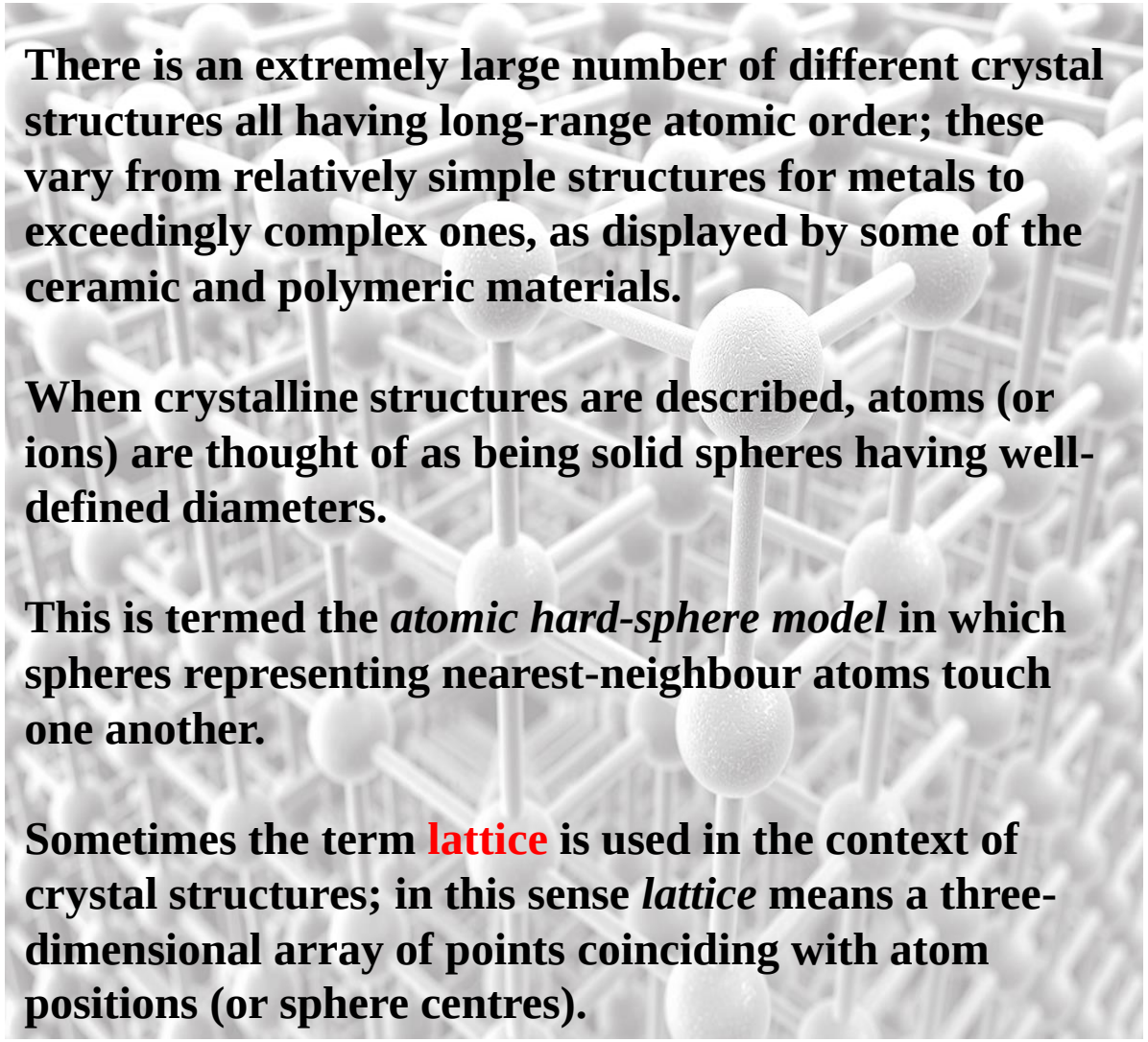
FUNDAMENTAL CONCEPTS

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another.

A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances—that is, long-range order exists, such that upon solidification, the atoms will position themselves in a repetitive three dimensional pattern, in which each atom is bonded to its nearest neighbour atoms.

All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent.

Some of the properties of crystalline solids depend on the crystal structure of the material, the manner in which atoms, ions, or molecules are spatially arranged.



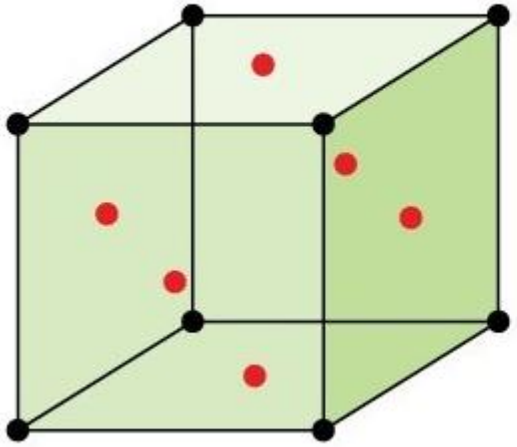
There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials.

When crystalline structures are described, atoms (or ions) are thought of as being solid spheres having well-defined diameters.

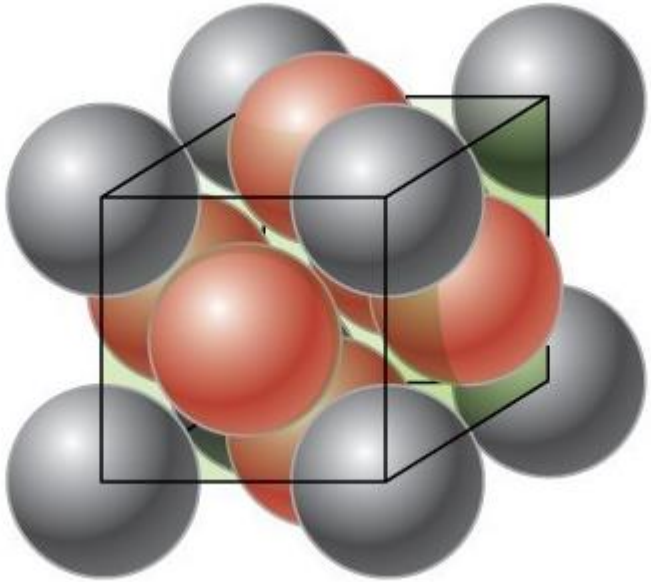
This is termed the *atomic hard-sphere model* in which spheres representing nearest-neighbour atoms touch one another.

Sometimes the term lattice is used in the context of crystal structures; in this sense *lattice* means a three-dimensional array of points coinciding with atom positions (or sphere centres).

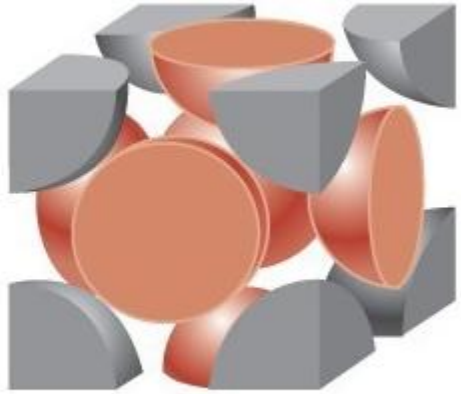
FUNDAMENTAL CONCEPTS



Reduced sphere



Aggregate of many atoms



Hard-sphere unit cell representation

- The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells.**

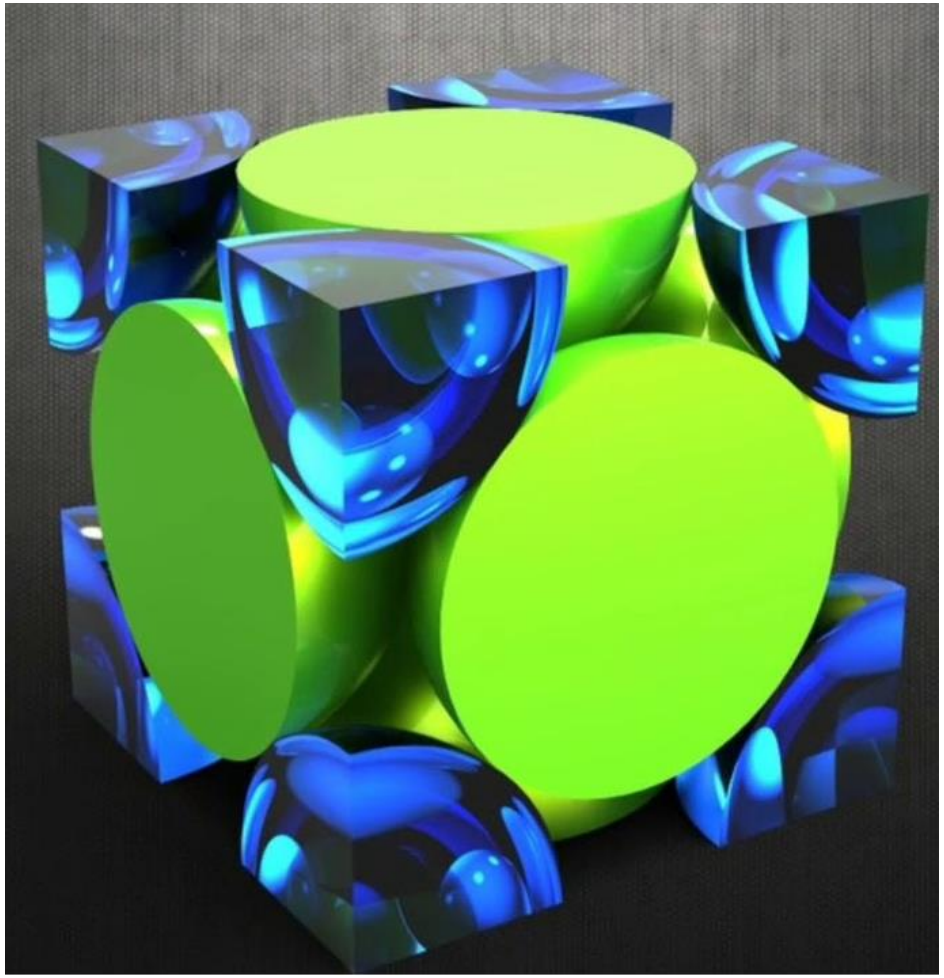
- Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres, which in this case happens to be a cube.

- A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges.

FUNDAMENTAL CONCEPTS

- The unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.

- Convenience usually dictates that parallelepiped corners coincide with centres of the hard-sphere atoms. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest level of geometrical symmetry.



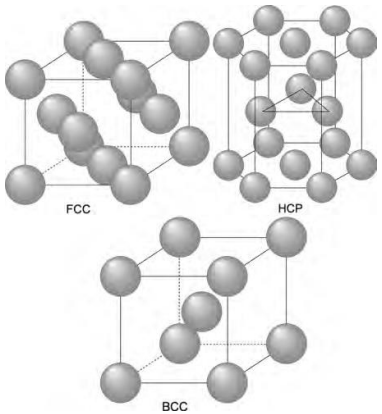
METALLIC CRYSTAL STRUCTURES

The atomic bonding in this group of materials is metallic and thus nondirectional in nature.

Consequently, there are minimal restrictions as to the number and position of nearest-neighbour atoms; this leads to relatively large numbers of nearest neighbours and dense atomic packings for most metallic crystal structures.

Also, for metals, when we use the hard-sphere model for the crystal structure, each sphere represents an ion core.

Three relatively simple crystal structures are found for most of the common metals: face-centred cubic, bodycentered cubic, and hexagonal close-packed.



Atomic Radii and Crystal Structures for 16 Metals

Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

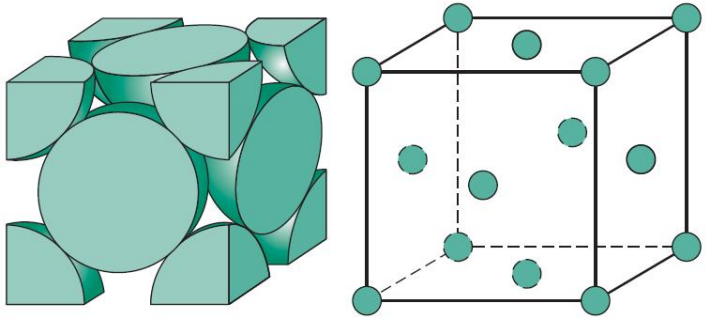
METALLIC CRYSTAL STRUCTURES

The Face-Centred Cubic Crystal Structure

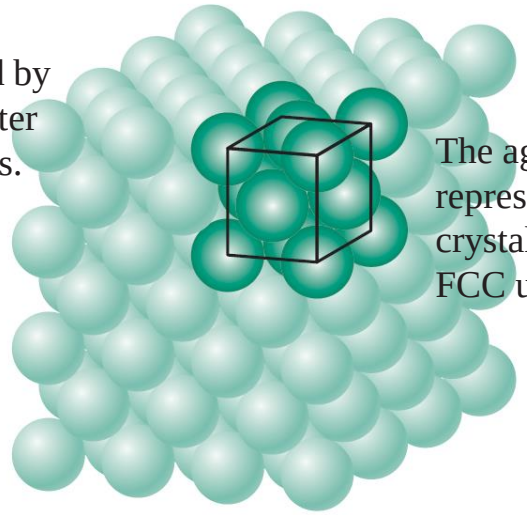
The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centres of all the cube faces. It is aptly called the **face-centred cubic (FCC)** crystal structure.

Some of the familiar metals having this crystal structure are copper, aluminium, silver, and gold.

Hard-sphere model for the FCC unit cell



Atom centres are represented by small circles to provide a better perspective on atom positions.



The aggregate of atoms represents a section of crystal consisting of many FCC unit cells.

These spheres or ion cores touch one another across a face diagonal; the cube edge length a and the atomic radius R are related through:

$$a = 2R\sqrt{2}$$

METALLIC CRYSTAL STRUCTURES

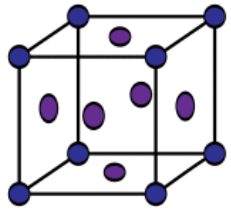
The number of atoms associated with each unit cell can also be determined. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell.

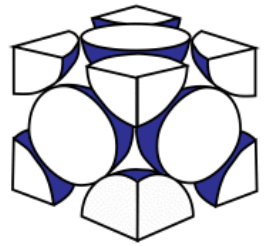
For example, for cubic unit cells, an atom completely within the interior "belongs" to that unit cell, one at a cell face is shared with one other cell, and an atom residing at a corner is shared among eight.

The number of atoms per unit cell, N, can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

where
N_i = the number of interior atoms
N_f = the number of face atoms
N_c = the number of corner atoms





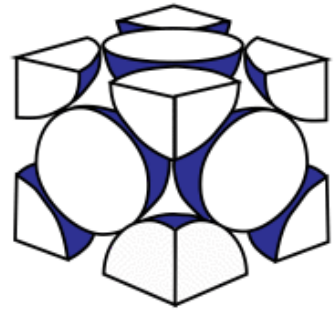
For the FCC crystal structure, there are eight corner atoms (N_c = 8), six face atoms (N_f = 6), and no interior atoms (N_i = 0). Thus, N = 4 (a total of four whole atoms may be assigned to a given unit cell).

METALLIC CRYSTAL STRUCTURES

The cell is composed of the volume of the cube that is generated from the centres of the corner atoms. Corner and face positions are really equivalent—that is, translation of the cube corner from an original corner atom to the centre of a face atom will not alter the cell structure.

Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF).**

For metals, each atom has the same number of nearest-neighbour or touching atoms, which is the coordination number. For facecentered cubics, the coordination number is 12.



Here the front face atom has four corner nearest-neighbour atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front (not shown).

The APF is the sum of the sphere volumes of all atoms within a unit cell (assuming the atomic hard-sphere model) divided by the unit cell volume:

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

METALLIC CRYSTAL STRUCTURES

Determination of FCC Unit Cell Volume

Calculate the volume of an FCC unit cell in terms of the atomic radius R.

Solution

In the FCC unit cell illustrated, the atoms touch one another across a face-diagonal, the length of which is $4R$. Because the unit cell is a cube, its volume is a^3, where a is the cell edge length. From the right triangle on the face,

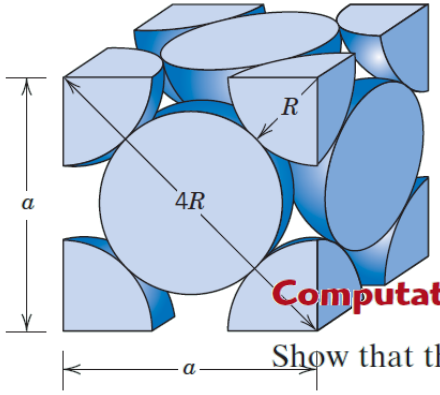
$$a^2 + a^2 = (4R)^2$$

or, solving for a,

$$a = 2R\sqrt{2}$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2}$$



Computation of the Atomic Packing Factor for FCC

Show that the atomic packing factor for the FCC crystal structure is 0.74.

Solution

The APF is defined as the fraction of solid sphere volume in a unit cell, or

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

Both the total atom and unit cell volumes may be calculated in terms of the atomic radius R. The volume for a sphere is $\frac{4}{3}\pi R^3$, and because there are four atoms per FCC unit cell, the total FCC atom (or sphere) volume is

$$V_S = (4)\tfrac{4}{3}\pi R^3 = \tfrac{16}{3}\pi R^3$$

The total unit cell volume is $V_C = 16R^3\sqrt{2}$

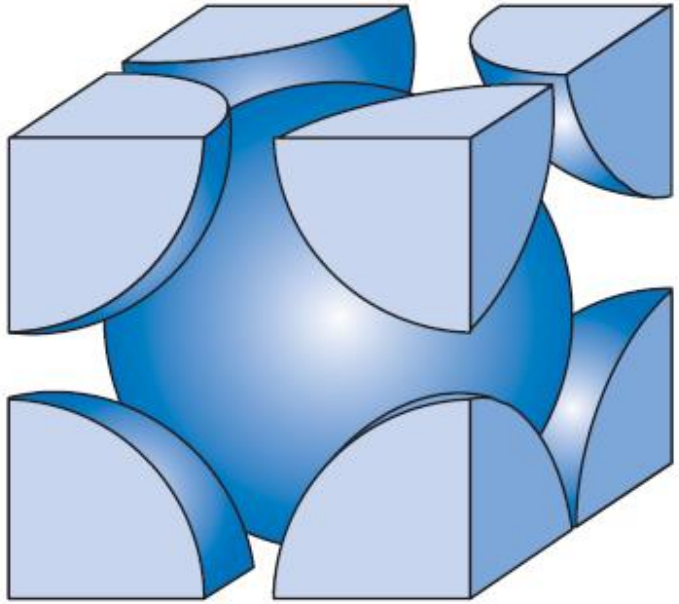
Therefore, the atomic packing factor is

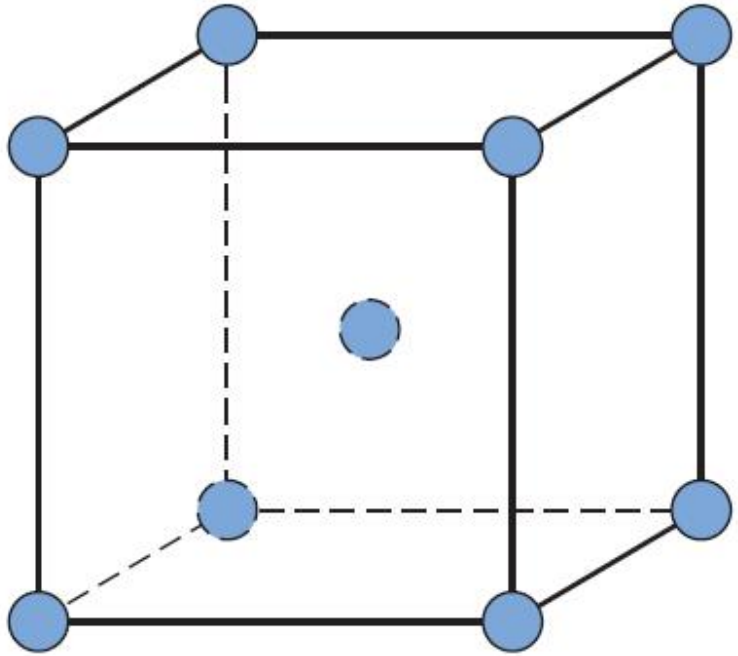
$$\text{APF} = \frac{V_S}{V_C} = \frac{\left(\frac{16}{3}\right)\pi R^3}{16R^3\sqrt{2}} = 0.74$$

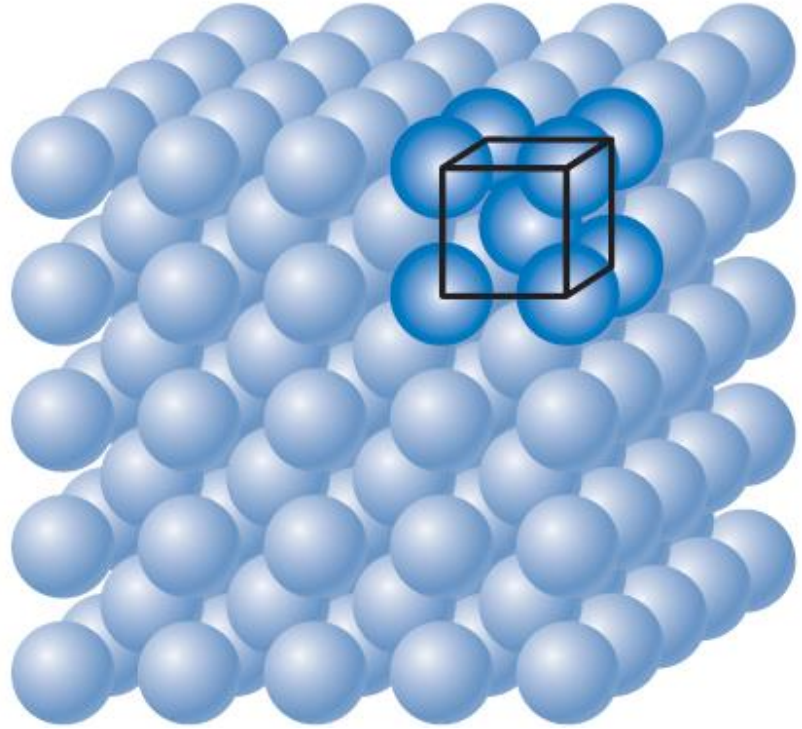
METALLIC CRYSTAL STRUCTURES

The body-Centred Cubic Crystal Structure

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube centre. This is called a **body-centred cubic (BCC)** crystal structure.







$$a = \frac{4R}{\sqrt{3}}$$

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8}$$

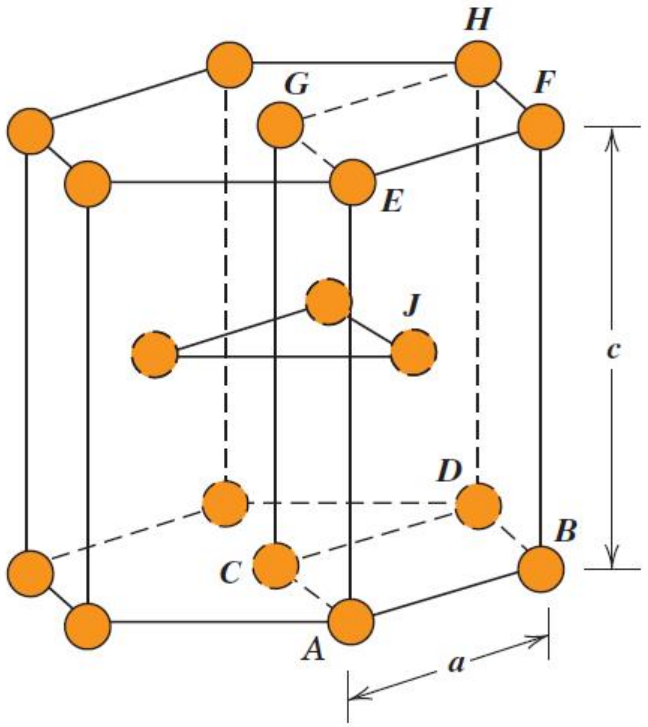
The atomic packing factor for BCC is 0.68

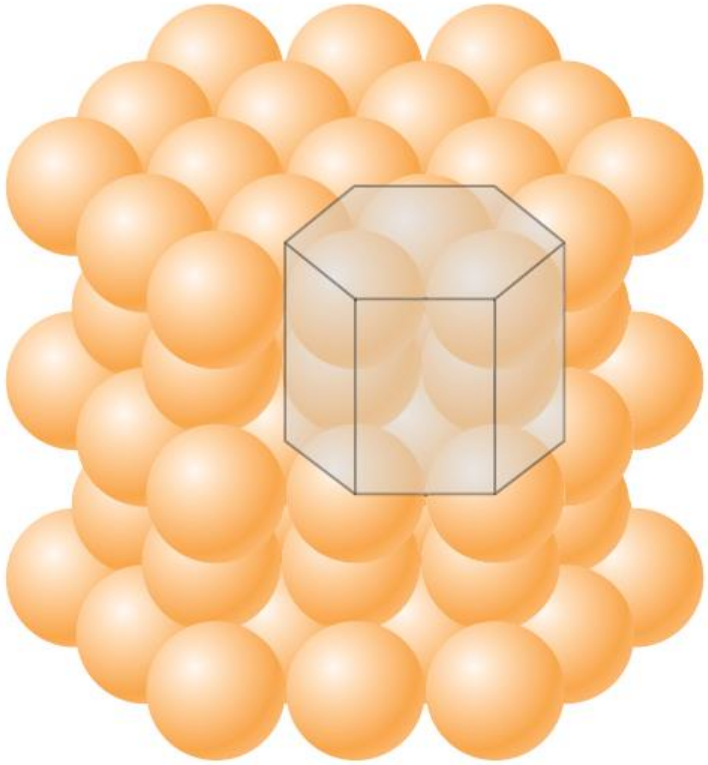
METALLIC CRYSTAL STRUCTURES

The Hexagonal Close-Packed Crystal Structure

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal or **hexagonal close-packed (HCP).**

If *a* and *c* represent, respectively, the short and long unit cell dimensions, the *c*/*a* ratio should be 1.633; however, for some HCP metals, this ratio deviates from the ideal value.





$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6}$$

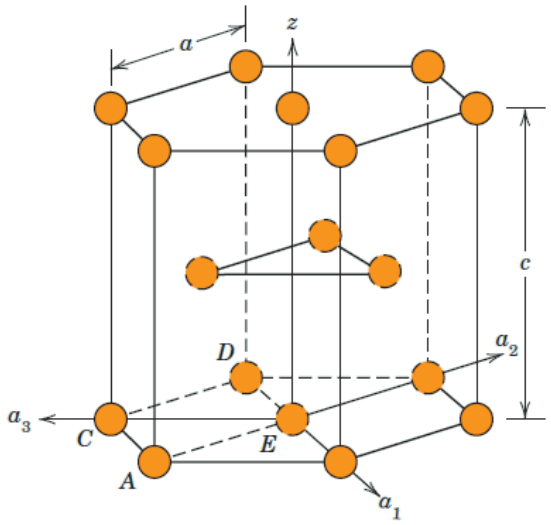
The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively.

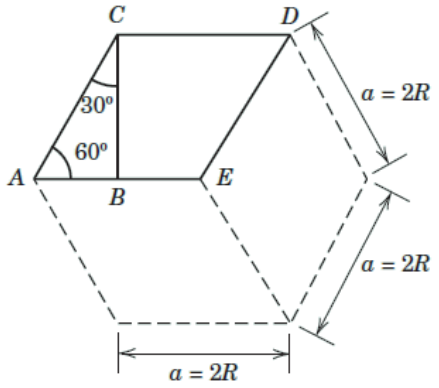
METALLIC CRYSTAL STRUCTURES

Determination of HCP Unit Cell Volume

(a) Calculate the volume of an HCP unit cell in terms of its a and c lattice parameters.

(b) Now provide an expression for this volume in terms of the atomic radius, R, and the c lattice parameter.





Solution

(a) We use the adjacent reduced-sphere HCP unit cell to solve this problem.

Now, the unit cell volume is just the product of the base area times the cell height, c. This base area is just three times the area of the parallelepiped $ACDE$ shown below. (This $ACDE$ parallelepiped is also labeled in the above unit cell.)

The area of $ACDE$ is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just a, and $\overline{BC}$ is equal to $\overline{BC} = a\cos(30°) = \dfrac{a\sqrt{3}}{2}$

Thus, the base area is just $$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2\sqrt{3}}{2}$$

Again, the unit cell volume V_C is just the product of the AREA and c; thus, $$V_C = \text{AREA}(c) = \left(\frac{3a^2\sqrt{3}}{2}\right)(c) = \frac{3a^2c\sqrt{3}}{2}$$

(b) For this portion of the problem, all we need do is realize that the lattice parameter a is related to the atomic radius R as

$$a = 2R$$

Now making this substitution for a in Equation 3.7a gives

$$V_C = \frac{3(2R)^2c\sqrt{3}}{2}$$
$$= 6R^2c\sqrt{3}$$

METALLIC CRYSTAL STRUCTURES

DENSITY COMPUTATIONS

A knowledge of the crystal structure of a metallic solid permits computation of its theoretical density ρ through the relationship:

$$\rho = \frac{nA}{V_C N_A}$$

where

n = number of atoms associated with each unit cell, A = atomic weight

V_C = volume of the unit cell. N_A = Avogadro's number (6.022×10^{23} atoms/mol)

Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density, and compare the answer with its measured density.

METALLIC CRYSTAL STRUCTURES

DENSITY COMPUTATIONS

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Theoretical Density Computation for Copper

Copper has an atomic radius of 0.128 nm, an FCC crystal structure, and an atomic weight of 63.5 g/mol. Compute its theoretical density, and compare the answer with its measured density.

Solution

Because the crystal structure is FCC, n, the number of atoms per unit cell, is 4.
Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol.
The unit cell volume V_C for FCC is $16R^3\sqrt{2}$, where R, the atomic radius, is 0.128 nm.

Substitution yields

$$\rho_{Cu} = \frac{nA_{Cu}}{V_C N_A} = \frac{nA_{Cu}}{(16R^3\sqrt{2})N_A}$$

$$= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8} \text{ cm})^3/\text{unit cell}](6.022 \times 10^{23} \text{ atoms/mol})}$$

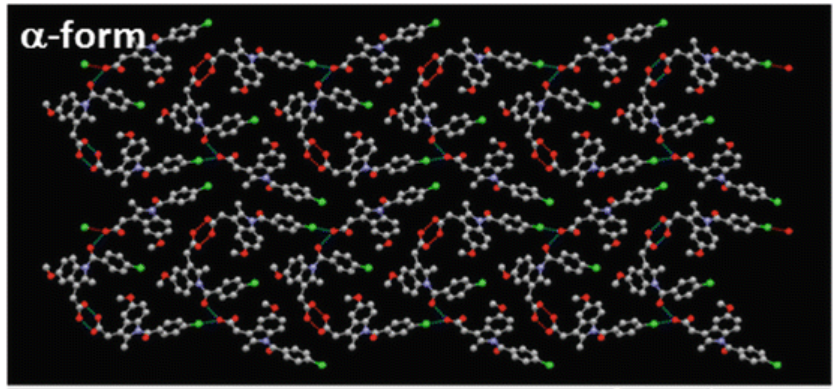
$$= 8.89 \text{ g/cm}^3$$

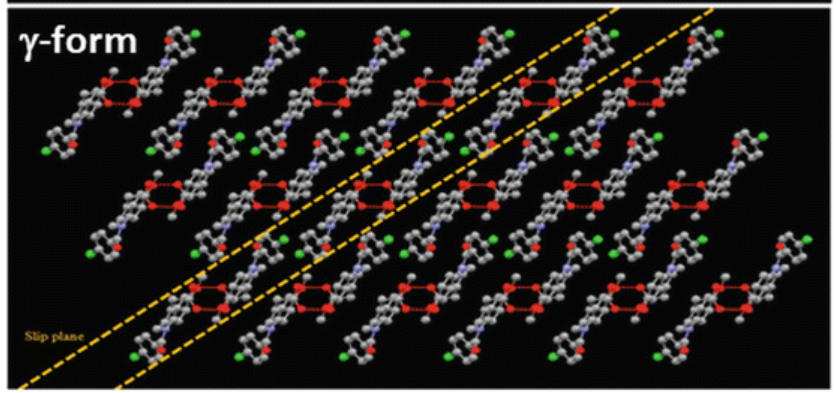
The literature value for the density of copper is 8.94 g/cm^3, which is in very close agreement with the foregoing result.

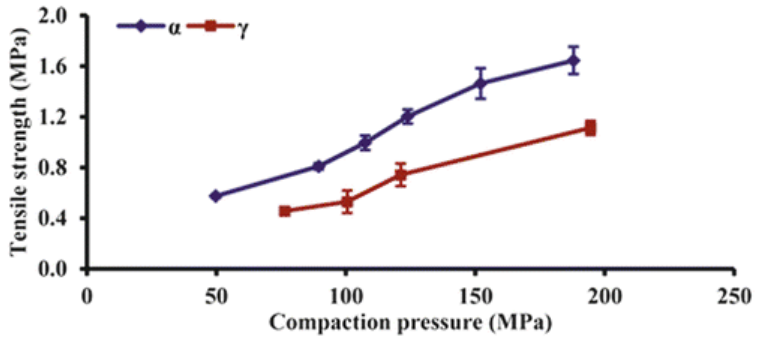
METALLIC CRYSTAL STRUCTURES

POLYMORPHISM AND ALLOTROPY

Some metals, as well as nonmetals, may have **more than one crystal structure**, a phenomenon known as **polymorphism**.







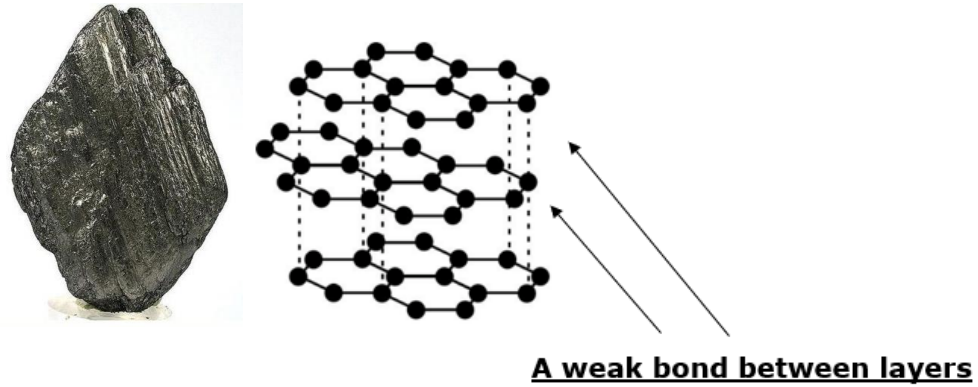
METALLIC CRYSTAL STRUCTURES

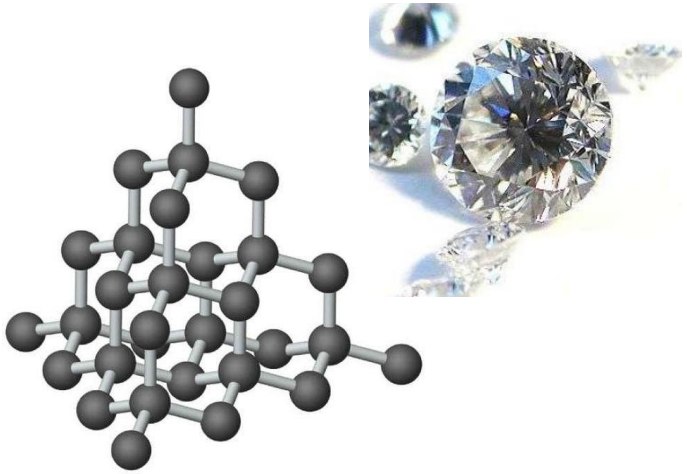
When found in elemental solids, the condition is often termed **allotropy.** The prevailing crystal structure depends on both the temperature and the external pressure.

One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures.

Also, pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F).

Most often a modification of the density and other physical properties accompanies a polymorphic transformation.





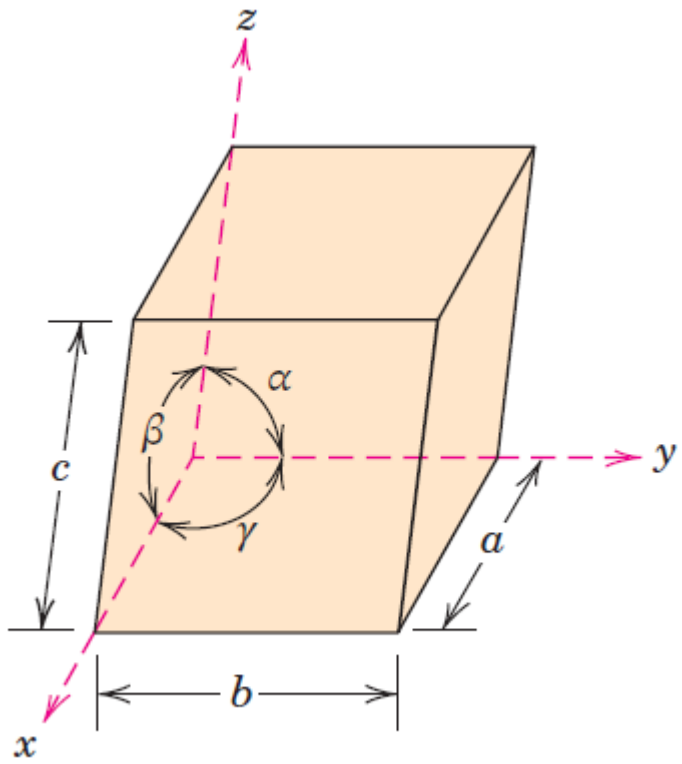
CRYSTAL SYSTEMS

Because there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements.

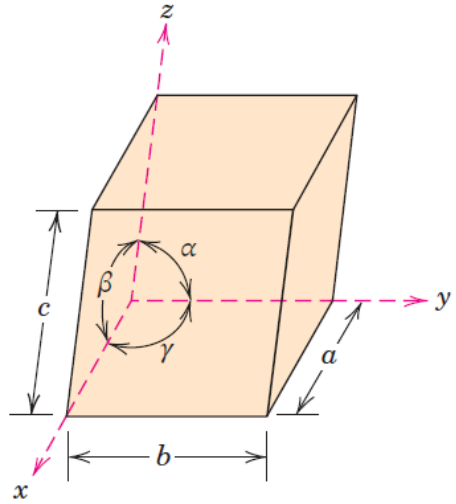
One such scheme is based on the unit cell geometry, that is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell.

Within this framework, an *x*-*y*-*z* coordinate system is established with its origin at one of the unit cell corners; each of the *x*, *y*, and *z* axes coincides with one of the three parallelepiped edges that extend from this corner, as illustrated.

The unit cell geometry is completely defined in terms of six parameters (**lattice parameters** of a crystal structure): the three edge lengths *a*, *b*, and *c*, and the three interaxial angles α, β, and γ.



CRYSTAL SYSTEMS



On this basis there are seven different possible combinations of a, b, and c and α, β, and γ, each of which represents a distinct **crystal system.**

These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral, monoclinic, and triclinic.

The cubic system, for which $a = b = c$ and $\alpha = \beta = \gamma = 90°$, has the greatest degree of symmetry.

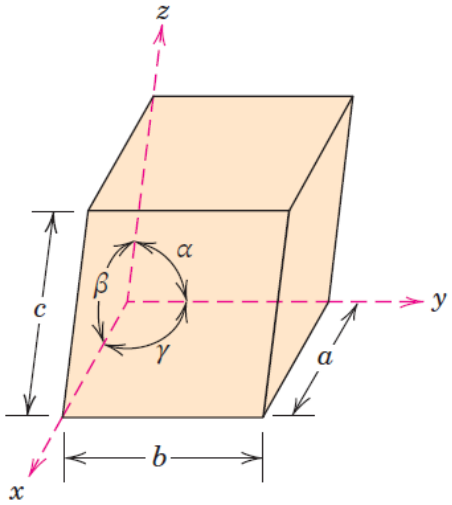
The least symmetry is displayed by the triclinic system, because $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

From the discussion of metallic crystal structures, it should be apparent that both FCC and BCC structures belong to the cubic crystal system, whereas HCP falls within the hexagonal system. The conventional hexagonal unit cell really consists of three parallelepipeds.

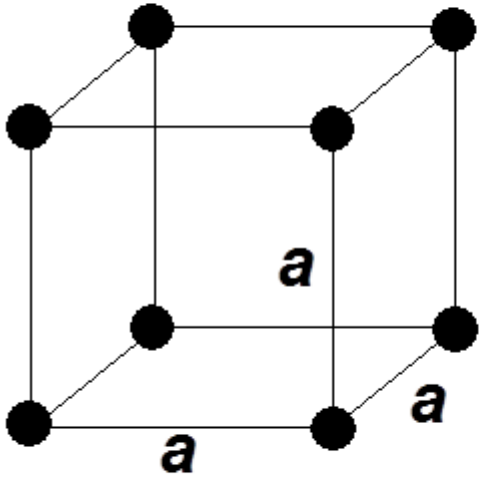
It is important to note that many of the principles and concepts addressed here also apply to crystalline ceramic and polymeric systems. For example, crystal structures are most often described in terms of unit cells, which are normally more complex than those for FCC, BCC, and HCP.

In addition, for these other systems, we are often interested in determining atomic packing factors and densities, using modified forms of the Equations presented earlier. Furthermore, according to unit cell geometry, crystal structures of these other material types are grouped within the seven crystal systems.

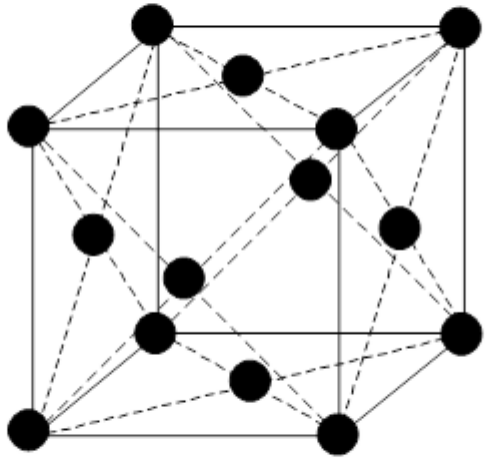
CRYSTAL SYSTEMS



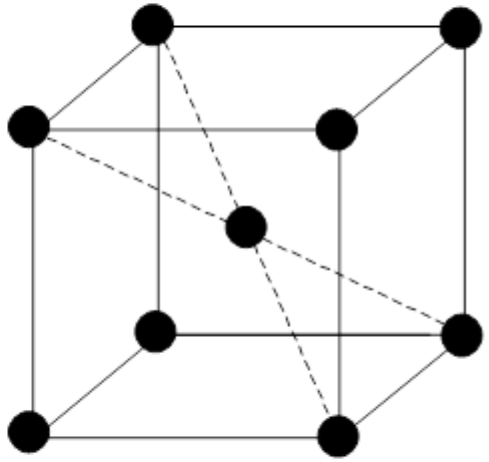
Crystal Structures - Cubic



Simple



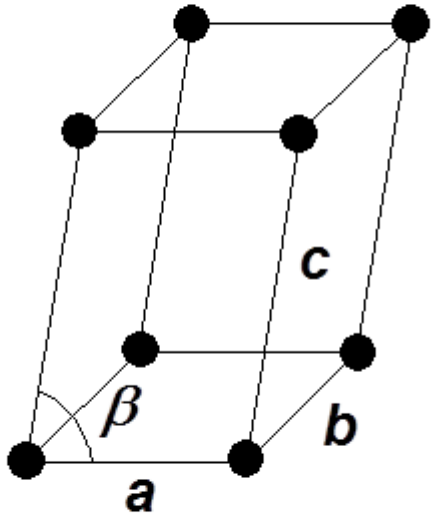
Face-Centered



Body-Centered

CRYSTAL SYSTEMS

Crystal Structures - Monoclinic



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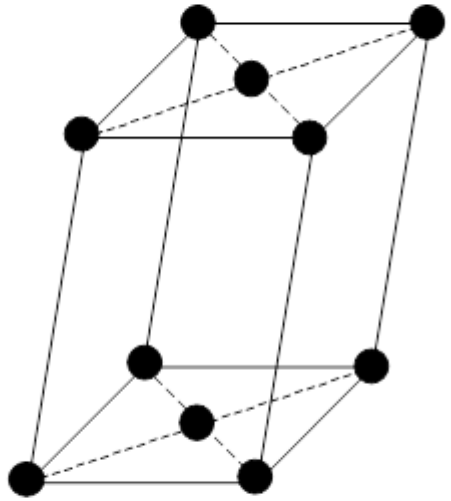
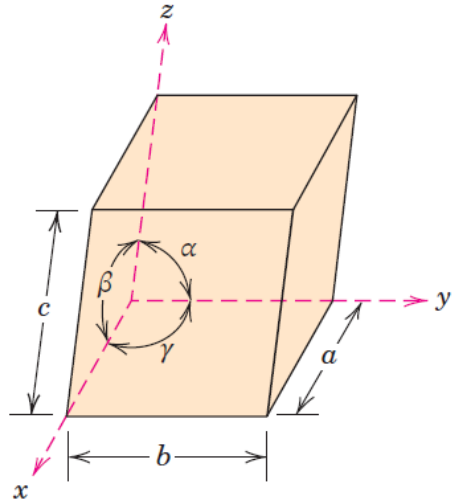
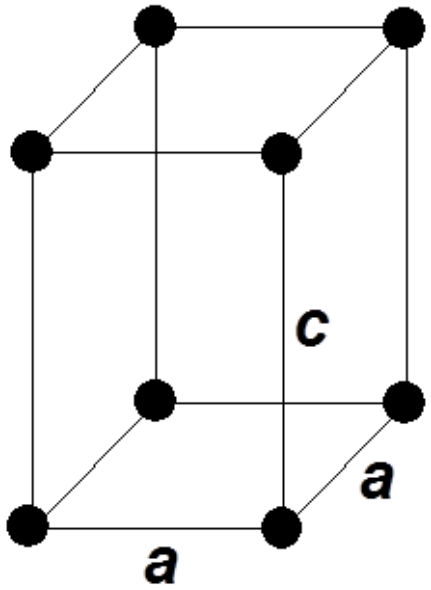


End Face-Centered

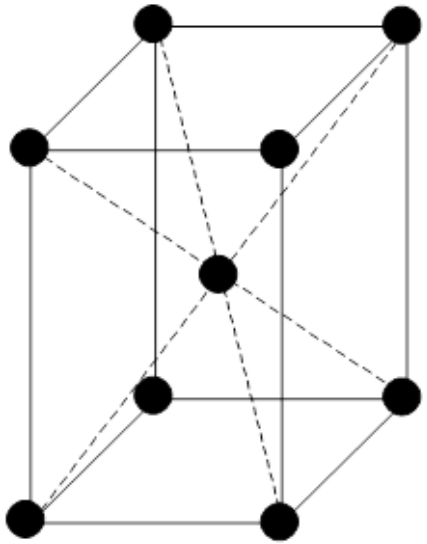


CRYSTAL SYSTEMS

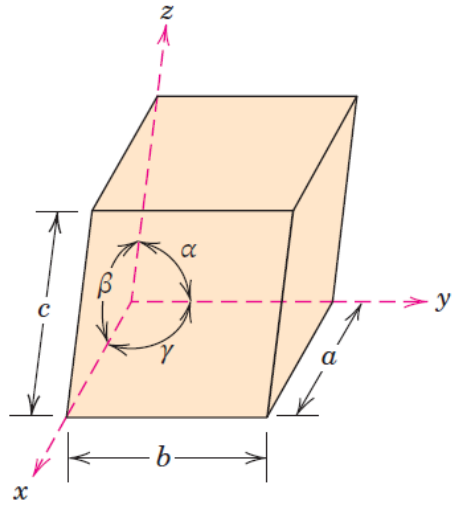
Crystal Structures - Tetragonal



Simple

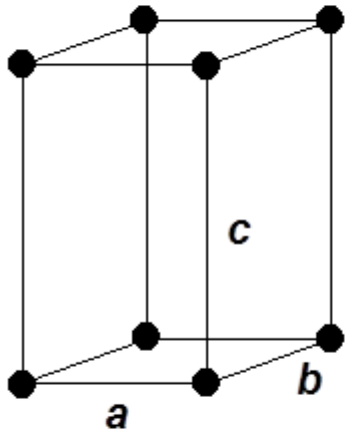


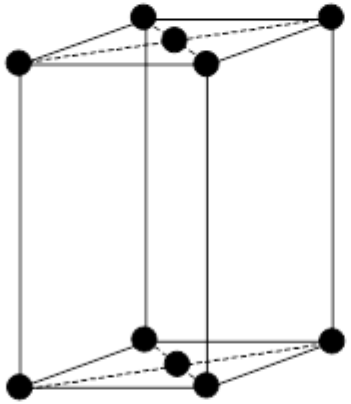
Body-Centered

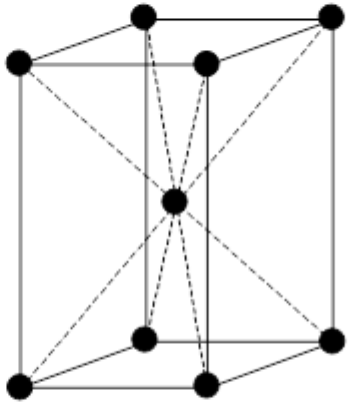


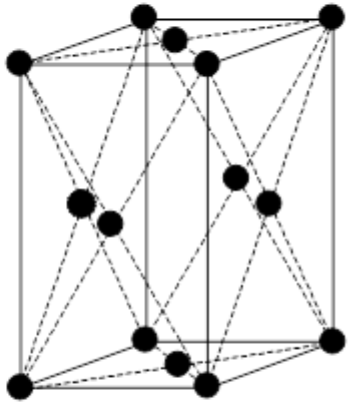
CRYSTAL SYSTEMS

Crystal Structures - Orthorhombic







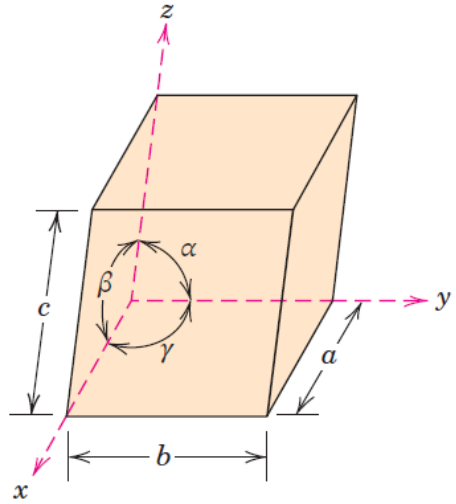


Simple

End Face-Centered

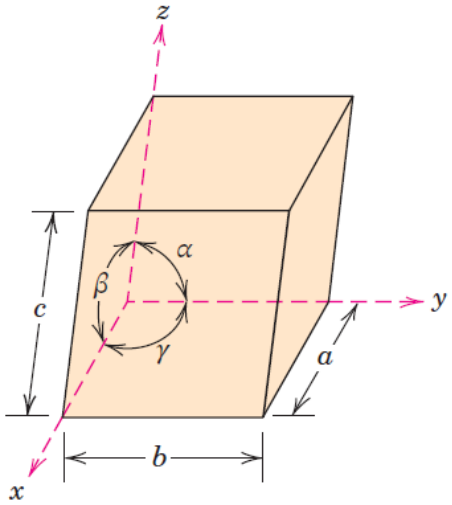
Body Centered

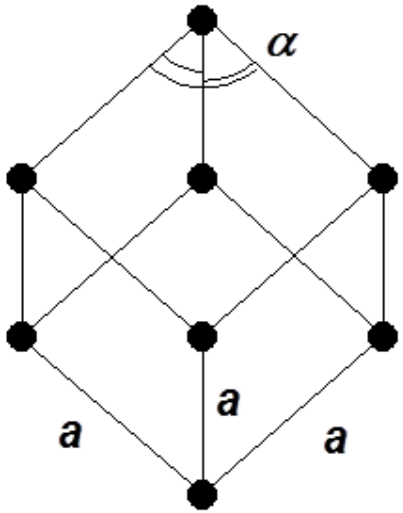
Face Centered



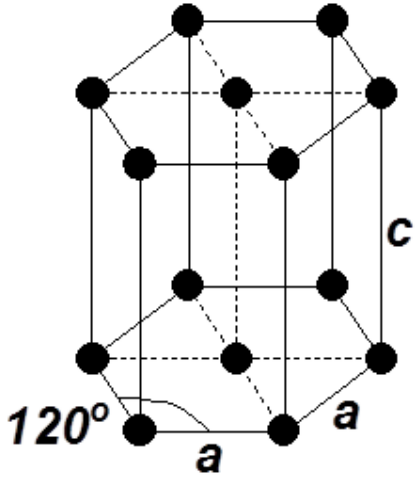
CRYSTAL SYSTEMS

Crystal Structures – Other Shapes

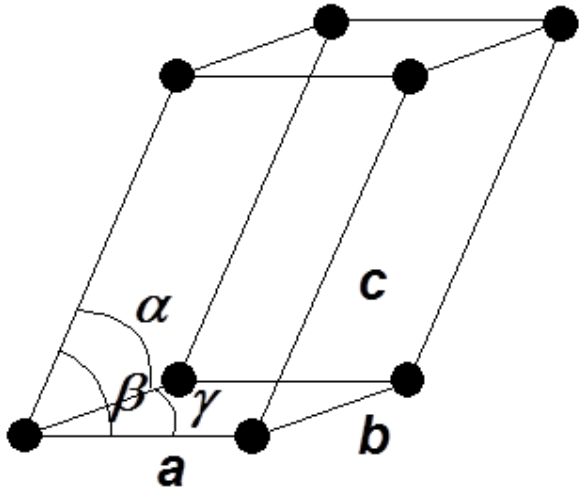




Rhombohedral



Hexagonal



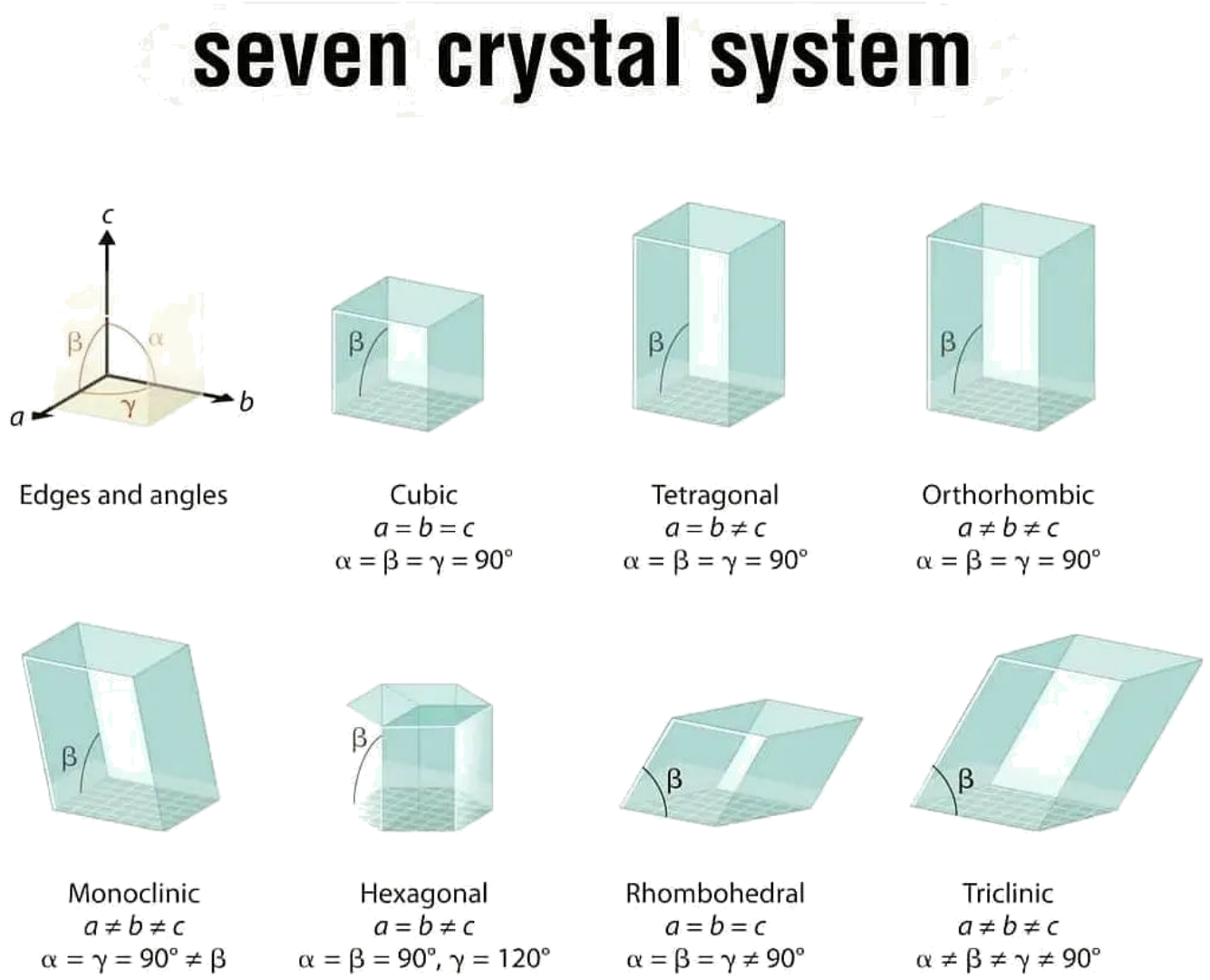
Triclinic

CRYSTAL SYSTEMS

Discussion Question:

What is the difference between crystal structure and crystal system?

A crystal structure is made of atoms. A crystal lattice is made of points. A crystal system is a set of axes. In other words, the structure is an ordered array of atoms, ions or molecules.



CRYSTAL SYSTEMS

Discussion Question:

Crystal Structure is obtained by attaching atoms, groups of atoms or molecules. This structure occurs from the intrinsic nature of the constituent particles to produce symmetric patterns.

A small group of a repeating pattern of the atomic structure is known as the unit cell of the structure.

A unit cell is the building block of the crystal structure and it also explains in detail the entire crystal structure and symmetry with the atom positions along with its principal axes. The length, edges of principal axes and the angle between the unit cells are called lattice constants or lattice parameters.

CRYSTAL SYSTEMS

What is the difference between crystal structure and crystal system?

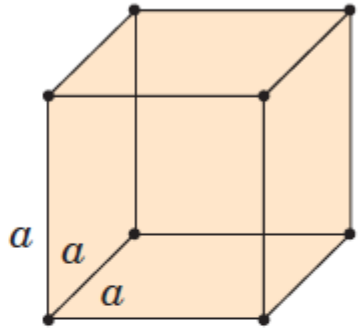
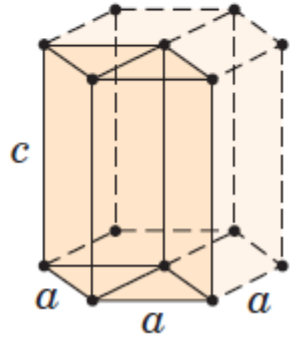
Crystal Structure: A crystal structure can be described in terms of its lattice and motif. We say, loosely:

Crystal = lattice + motif

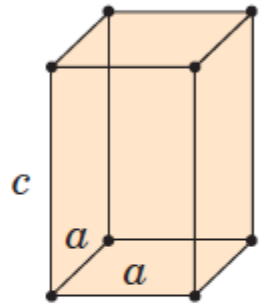
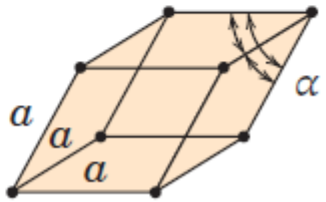
A lattice is a periodic arrangement of points. It is a geometrical construct that gives the periodicity of the crystal, or in other words, tells us how the atoms are repeated. It is still not a crystal as there are no atoms. Atoms come from motif. Motif (or basis) is an atom or a group of atoms associated with each lattice point.

Crystal System: A crystal structure is classified into 32 crystal classes based on its point group symmetry (Rotation or Roto-reflection axes). These 32 point groups are then classified into 7 crystal systems based on certain characteristic symmetry.

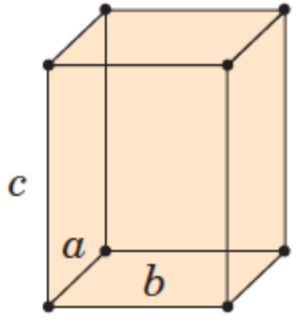
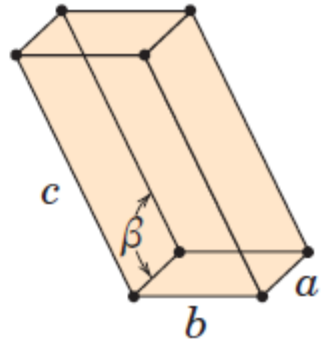
CRYSTAL SYSTEMS

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	

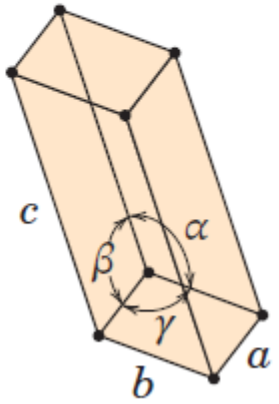
CRYSTAL SYSTEMS

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	

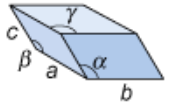
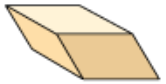
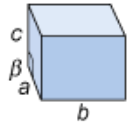
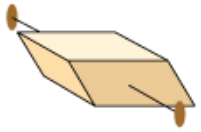
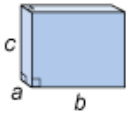
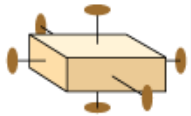
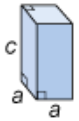
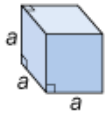
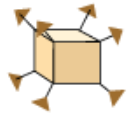
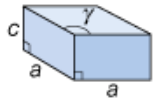
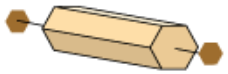
CRYSTAL SYSTEMS

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	

CRYSTAL SYSTEMS

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

CRYSTAL SYSTEMS

Crystal system	Unit cell	Essential symmetry	Example of everyday object with essential symmetry	Mineral example
triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ 	none	a packet of envelopes pushed askew in two directions 	plagioclase feldspar, kyanite
monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$ 	one two-fold axis	a partially squashed matchbox cover, flattened to one side 	gypsum, biotite mica, muscovite mica, orthoclase feldspar, hornblende (amphibole), augite (pyroxene), talc
orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$ 	three two-fold axes (at 90° to each other)	a matchbox 	barite, topaz, olivine, andalusite
tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$ 	one four-fold axis	two sugar cubes stuck together 	chalcopyrite, zircon
cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$ 	four three-fold axes (through corners)	a sugar cube 	galena, halite, pyrite, fluorite, garnet, diamond, sphalerite, magnetite, silver, gold
trigonal	$a = b = c$ $120° > \alpha = \beta = \gamma \neq 90°$ 	one three-fold axis	a triangular prism 	calcite, tourmaline, hematite, corundum (e.g. ruby, sapphire)
hexagonal	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$ 	one six-fold axis	unsharpened pencil 	graphite, apatite, beryl (e.g. emerald, aquamarine)

[Crystal Structure - Definition, 7 Types of Crystal Structure with Videos (byjus.com)]

Crystallographic Points, Directions, and Planes

When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms.

Labelling conventions have been established in which three numbers or indices are used to designate point locations, directions, and planes.

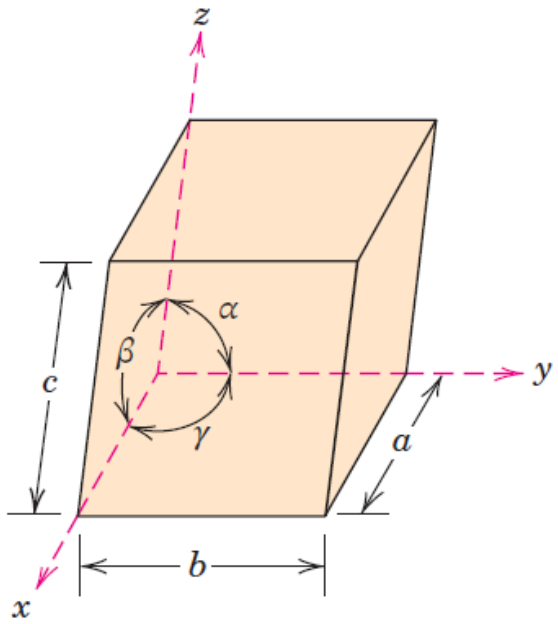
The basis for determining index values is the unit cell, with a right-handed coordinate system consisting of three (x, y, and z) axes situated at one of the corners and coinciding with the unit cell edges, as shown.

For some crystal systems—namely, hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not* mutually perpendicular, as in the familiar Cartesian coordinate scheme.

Crystallographic Directions, and Planes

we need a way to identify directions and planes of atoms. Why?

- Deformation under loading (*slip*) occurs on certain crystalline planes and in certain crystallographic directions.
- Before we can predict how materials fail, we need to know what modes of failure are more likely to occur.
- Other properties of materials (*electrical conductivity, thermal conductivity, elastic modulus*) can vary in a crystal with orientation.



Crystallographic Points, Directions, and Planes

POINT COORDINATES

Sometimes it is necessary to specify a lattice position within a unit cell. Lattice position is defined in terms of three *lattice position coordinates*, which are associated with the *x*, *y*, and *z* axes—we have chosen to label these coordinates as P_x, P_y, and P_z.

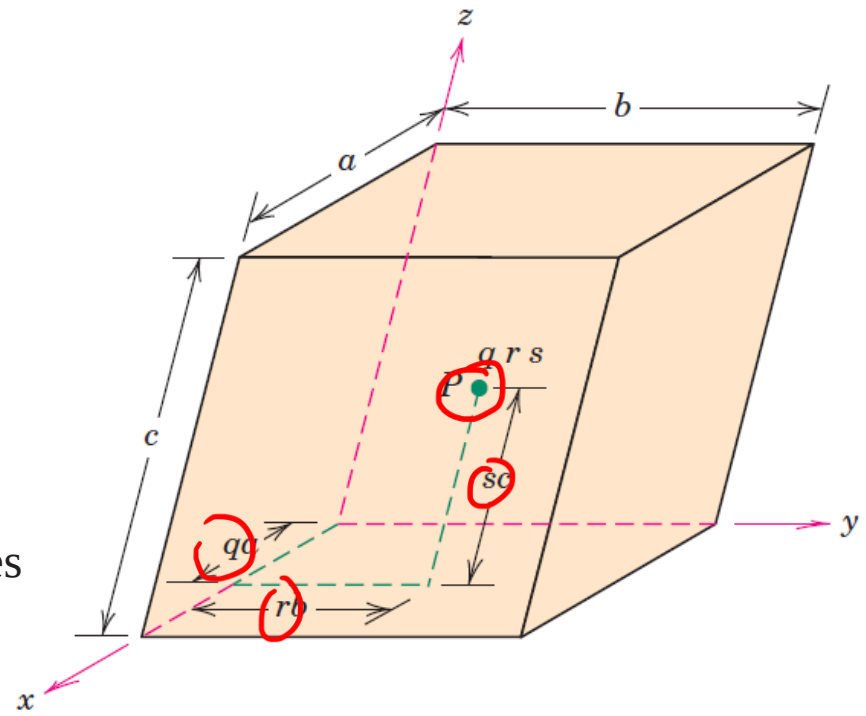
Coordinate specifications are possible using three *point indices*: *q*, *r*, and *s*. These indices are fractional multiples of *a*, *b*, and *c* unit cell lengths—that is, *q* is some fractional length of *a* along the *x* axis, *r* is some fractional length of *b* along the *y* axis, and similarly for *s*.

In other words, lattice position coordinates (i.e., the *P*s) are equal to the products of their respective point indices and the unit cell edge lengths—viz.

$$P_x = qa \qquad P_y = rb \qquad P_z = sc$$

To illustrate, consider the unit cell as shown, the *x*-*y*-*z* coordinate system with its origin located at a unit cell corner, and the lattice site located at point *P*.

Note how the location of *P* is related to the products of its *q*, *r*, and *s* point indices and the unit cell edge lengths

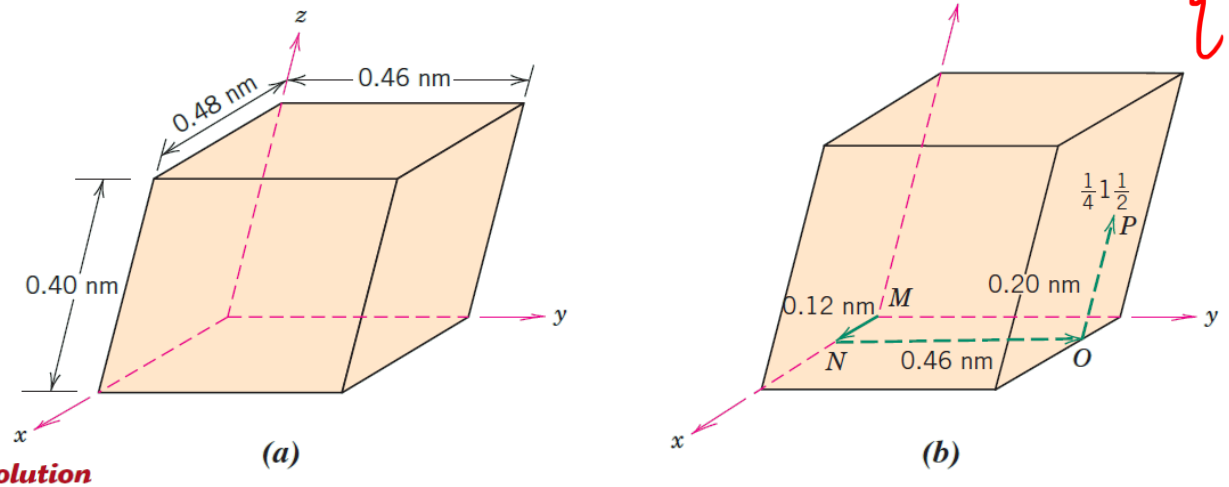


Crystallographic Points, Directions, and Planes

Example

Location of Point Having Specified Coordinates

For the unit cell shown in the accompanying sketch (*a*), locate the point having indices $\frac{1}{4}\ 1\ \frac{1}{2}$.



Solution

From sketch (*a*), edge lengths for this unit cell are as follows: $a = 0.48$ nm, $b = 0.46$ nm, and $c = 0.40$ nm. Furthermore, in light of the preceding discussion, the three point indices are $q = \frac{1}{4}$, $r = 1$, and $s = \frac{1}{2}$. We use Equations 3.9a through 3.9c to determine lattice position coordinates for this point as follows:

$$P_x = qa$$

$$= \left(\frac{1}{4}\right)a = \frac{1}{4}(0.48\ \text{nm}) = 0.12\ \text{nm}$$

$$P_y = rb$$

$$= (1)b = 1(0.46\ \text{nm}) = 0.46\ \text{nm}$$

$$P_z = sc$$

$$= \left(\frac{1}{2}\right)c = \frac{1}{2}(0.40\ \text{nm}) = 0.20\ \text{nm}$$

To locate the point having these coordinates within the unit cell, first use the *x* lattice position coordinate and move from the origin (point *M*) 0.12 nm units along the *x* axis (to point *N*), as shown in (*b*).

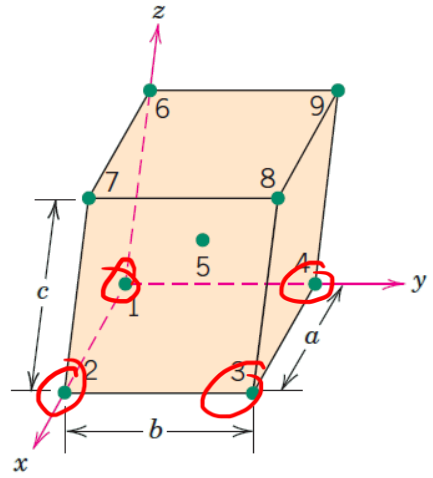
Similarly, using the *y* lattice position coordinate, proceed 0.46 nm parallel to the *y* axis, from point *N* to point *O*. Finally, move from this position 0.20 nm units parallel to the *z* axis to point *P* (per the *z* lattice position), as noted again in (*b*). Thus, point *P* corresponds to the $\frac{1}{4}\ 1\ \frac{1}{2}$ point indices.

Crystallographic Points, Directions, and Planes

Example

Specification of Point Indices

Specify indices for all numbered points of the unit cell in the illustration.



Solution

For this unit cell, lattice points are located at all eight corners with a single point at the center position.

Point 1 is located at the origin of the coordinate system, and, therefore, its lattice position coordinates referenced to the x, y, and z axes are $0a$, $0b$, and $0c$, respectively.

$$P_x = qa = 0a$$
$$P_y = rb = 0b$$
$$P_z = sc = 0c$$

Solving the above three expressions for values of the q, r, and s indices leads to

$$q = \frac{0a}{a} = 0$$

$$r = \frac{0b}{b} = 0$$

$$s = \frac{0c}{c} = 0$$

Therefore this is the 0 0 0 point.

Because point number 2 lies one unit cell edge length along the x axis, its lattice position coordinates referenced to the x, y, and z axes are a, $0b$, and $0c$, and

$$P_x = qa = a$$
$$P_y = rb = 0b$$
$$P_z = sc = 0c$$

Thus we determine values for the q, r, and s indices as follows:

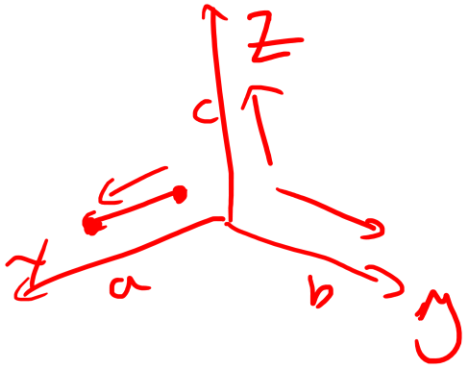
$$q = 1 \qquad r = 0 \qquad s = 0$$

Hence, point 2 is 1 0 0.

This same procedure is carried out for the remaining seven points in the unit cell. Point indices for all nine points are listed in the following table.

Point Number	q	r	s
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

Crystallographic Points, Directions, and Planes



CRYSTALLOGRAPHIC DIRECTIONS

A *crystallographic direction* is defined as a line directed between two points, or a *vector*.

The following steps are used to determine the three directional indices: A right-handed *x*-*y*-*z* coordinate system is first constructed. As a matter of convenience, its origin may be located at a unit cell corner.

1. The coordinates of two points that lie on the direction vector (referenced to the coordinate system) are determined—for example, for the vector tail, point 1: x_1, y_1, and z_1; whereas for the vector head, point 2: x_2, y_2, and z_2.
2. Tail point coordinates are subtracted from head point components—that is, $x_2 - x_1$, $y_2 - y_1$, and $z_2 - z_1$.
3. These coordinate differences are then normalized in terms of (i.e., divided by) their respective *a*, *b*, and *c* lattice parameters—that is,

$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$

which yields a set of three numbers.

5. If necessary, these three numbers are multiplied or divided by a common factor to reduce them to the smallest integer values.
6. The three resulting indices, not separated by commas, are enclosed in square brackets, thus: [uvw]. The u, v, and w integers correspond to the normalized coordinate differences referenced to the x, y, and z axes, respectively.

Crystallographic Points, Directions, and Planes

In summary, the *u*, *v*, and *w* indices may be determined using the following equations:

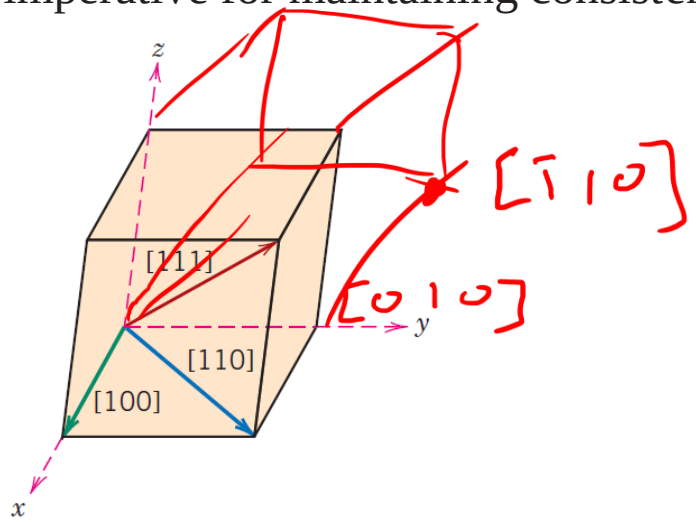
$$u = n\left(\frac{x_2 - x_1}{a}\right) \qquad v = n\left(\frac{y_2 - y_1}{b}\right) \qquad w = n\left(\frac{z_2 - z_1}{c}\right)$$

In these expressions, *n* is the factor that may be required to reduce *u*, *v*, and *w* to integers.

For each of the three axes, there are both positive and negative coordinates. Thus, negative indices are also possible, which are represented by a bar over the appropriate index. For example, the [$1\bar{1}1$] direction has a component in the $-y$ direction.

Also, changing the signs of all indices produces an antiparallel direction; that is, [$\bar{1}\bar{1}\bar{1}$] is directly opposite to [$1\bar{1}1$]. If more than one direction (or plane) is to be specified for a particular crystal structure, it is imperative for maintaining consistency that a positive– negative convention, once established, not be changed.

The [100], [110], and [111] directions are common ones (shown in the unit cell)

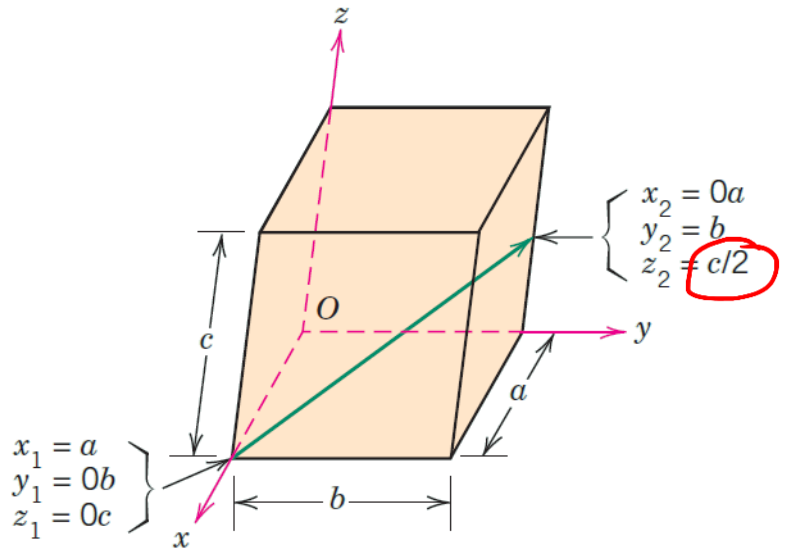


Crystallographic Points, Directions, and Planes

Example

Determination of Directional Indices

Determine the indices for the direction shown in the accompanying figure.



Solution

It is first necessary to take note of the vector tail and head coordinates. From the illustration, tail coordinates are as follows:

$$x_1 = a \qquad y_1 = 0b \qquad z_1 = 0c$$

For the head coordinates,

$$x_2 = 0a \qquad y_2 = b \qquad z_2 = c/2$$

Now taking point coordinate differences,

$$x_2 - x_1 = 0a - a = -a$$
$$y_2 - y_1 = b - 0b = b$$
$$z_2 - z_1 = c/2 - 0c = c/2$$

Crystallographic Points, Directions, and Planes

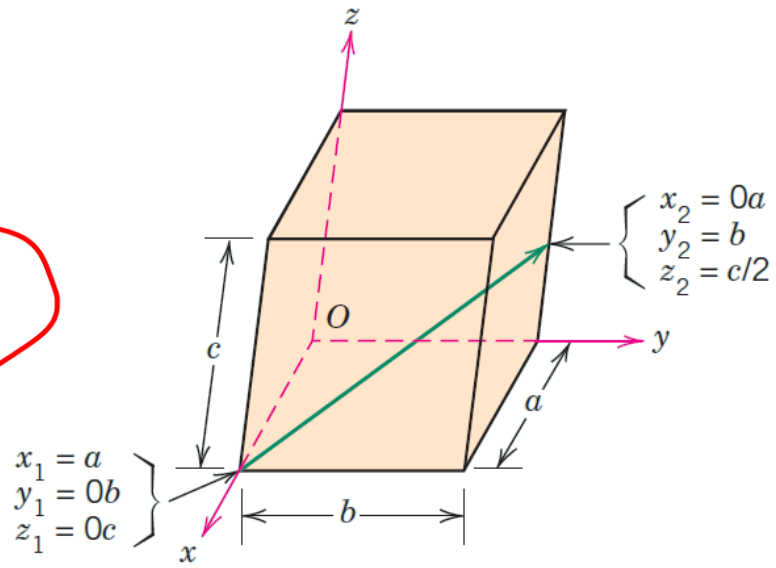
Example

$$u = n\left(\frac{x_2 - x_1}{a}\right) = 2\left(\frac{-a}{a}\right) = -2$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) = 2\left(\frac{b}{b}\right) = 2$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) = 2\left(\frac{c/2}{c}\right) = 1$$

$[\bar{2}21]$



And, finally enclosure of the −2, 2, and 1 indices in brackets leads to $[\bar{2}21]$ as the direction designation.

This procedure is summarized as follows:

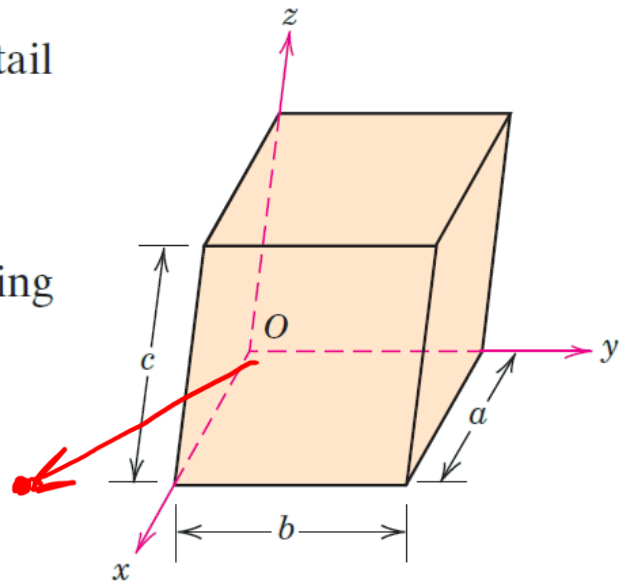
	x	*y*	*z*
Head coordinates $(x_2, y_2, z_2,)$	$0a$	b	$c/2$
Tail coordinates $(x_1, y_1, z_1,)$	a	$0b$	$0c$
Coordinate differences	$-a$	b	$c/2$
Calculated values of u, v, and w	$u = -2$	$v = 2$	$w = 1$
Enclosure		$[\bar{2}21]$	

Crystallographic Points, Directions, and Planes

Example

Construction of a Specified Crystallographic Direction

Within the following unit cell draw a $[1\bar{1}0]$ direction with its tail located at the origin of the coordinate system, point O.



Solution

This problem is solved by reversing the procedure of the preceding example. For this $[1\bar{1}0]$ direction,

$$u = 1$$
$$v = -1$$
$$w = 0$$

Because the tail of the direction vector is positioned at the origin, its coordinates are as follows:

$$x_1 = 0a$$
$$y_1 = 0b$$
$$z_1 = 0c$$

Crystallographic Points, Directions, and Planes

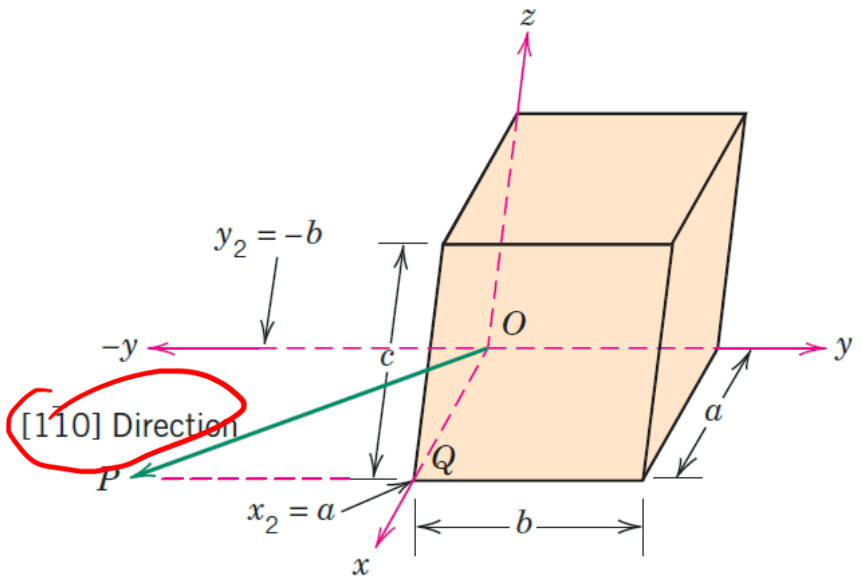
Example

$$x_2 = ua + x_1 = (1)(a) + 0a = a$$
$$y_2 = vb + y_1 = (-1)(b) + 0b = -b$$
$$z_2 = wc + z_1 = (0)(c) + 0c = 0c$$

(n = 1)

The construction process for this direction vector is shown in the following figure.

Because the tail of the vector is positioned at the origin, we start at the point labeled O and then move in a stepwise manner to locate the vector head. Because the x head coordinate (x_2) is a, we proceed from point O, a units along the x axis to point Q. From point Q, we move b units parallel to the $-y$ axis to point P, because the y head coordinate (y_2) is $-b$. There is no z component to the vector inasmuch as the z head coordinate (z_2) is $0c$. Finally, the vector corresponding to this $[1\bar{1}0]$ direction is constructed by drawing a line from point O to point P, as noted in the illustration.



Crystallographic Points, Directions, and Planes

For some crystal structures, several nonparallel directions with different indices are *crystallographically equivalent*, meaning that the spacing of atoms along each direction is the same.

For example, in cubic crystals, all the directions represented by the following indices are equivalent: [100], [$\bar{1}$00], [010], [0$\bar{1}$0], [001], and [00$\bar{1}$]. As a convenience, equivalent directions are grouped together into a *family*, which is enclosed in angle brackets, thus: ⟨100⟩.

Furthermore, directions in cubic crystals having the same indices without regard to order or sign—for example, [123] and [213]—are equivalent.

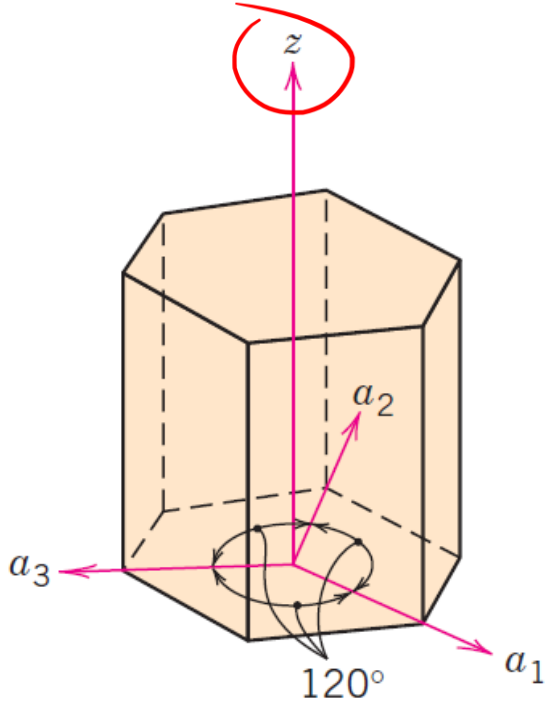
This is, in general, not true for other crystal systems. For example, for crystals of tetragonal symmetry, the [100] and [010] directions are equivalent, whereas the [100] and [001] are not.

Crystallographic Points, Directions, and Planes

Directions in Hexagonal Crystals

A problem arises for crystals having hexagonal symmetry in that some equivalent crystallographic directions do not have the same set of indices.

This situation is addressed using a four-axis, or *Miller–Bravais*, coordinate system, as shown.



The three a_1, a_2, and a_3 axes are all contained within a single plane (called the *basal plane*) and are at 120° angles to one another. The z axis is perpendicular to this basal plane. Directional indices, which are obtained as described earlier, are denoted by four indices, as [*uvtw*]; by convention, the *u*, *v*, and *t* relate to vector coordinate differences referenced to the respective a_1, a_2, and a_3 axes in the basal plane; the fourth index pertains to the z axis.

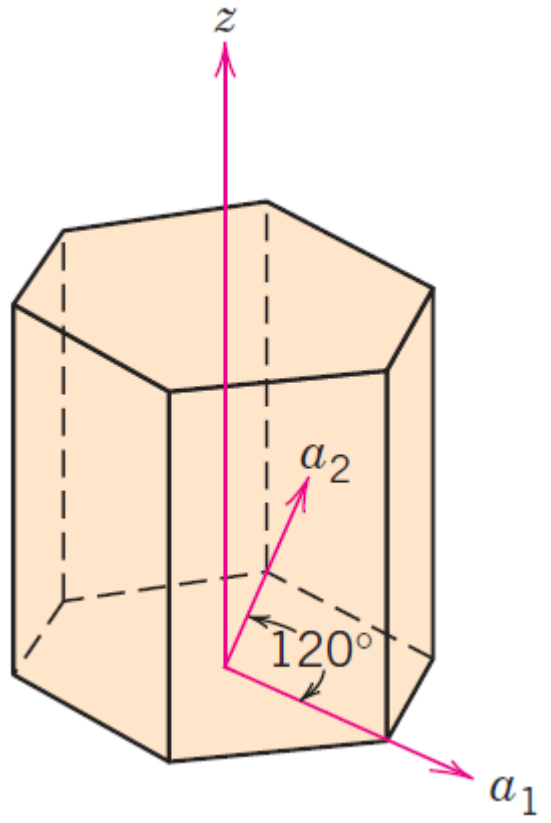
Crystallographic Points, Directions, and Planes

Conversion from the three-index system to the four-index system as [*UVW*]→[*uvtw*] is accomplished using the following formulas:

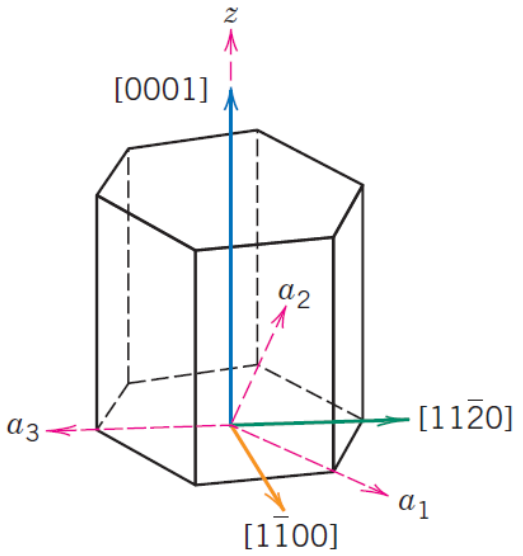
$$u = \frac{1}{3}(2U - V) \qquad v = \frac{1}{3}(2V - U) \qquad t = -(u + v) \qquad w = W$$

Here, uppercase *U*, *V*, and *W* indices are associated with the three-index scheme (instead of *u*, *v*, and *w* as previously), whereas lowercase *u*, *v*, *t*, and *w* correlate with the Miller–Bravais four-index system.

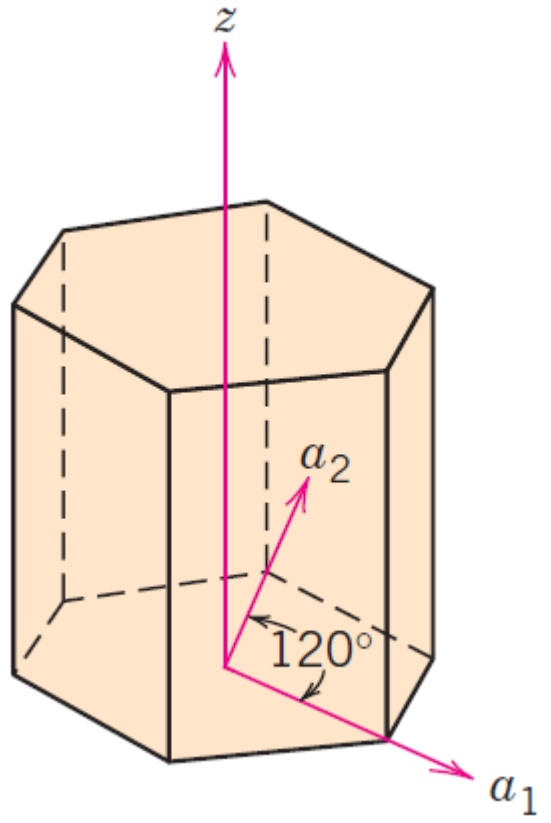
For example, using these equations, the [010] direction becomes [$1\bar{2}10$]; furthermore, [$1\bar{2}10$] is also equivalent to the following: [$1\bar{2}10$], [$\bar{1}2\bar{1}0$], [$\bar{1}\bar{2}10$].



For the hexagonal crystal system, the [0001], [$\bar{1}100$], and [$11\bar{2}0$] directions.



Crystallographic Points, Directions, and Planes



Determination of directional indices is carried out using a procedure similar to the one used for other crystal systems—by the subtraction of vector tail point coordinates from head point coordinates.

To simplify the demonstration of this procedure, first determine the *U*, *V*, and *W* indices using the three-axis a_1–a_2–z coordinate system and then convert to the *u*, *v*, *t*, and *w* indices Using:

$$u = \frac{1}{3}(2U - V) \qquad v = \frac{1}{3}(2V - U) \qquad t = -(u + v) \qquad w = W$$

The designation scheme for the three sets of head and tail coordinates is as follows:

Axis	Head Coordinate	Tail Coordinate
a_1	a_1''	a_1'
a_2	a_2''	a_2'
z	z''	z'

Using this scheme, the *U*, *V*, and *W* hexagonal index equivalents are as follows:

$$U = n\left(\frac{a_1'' - a_1'}{a}\right) \qquad V = n\left(\frac{a_2'' - a_2'}{a}\right) \qquad W = n\left(\frac{z'' - z'}{c}\right)$$

the parameter *n* is included to facilitate, if necessary, reduction of the *U*, *V*, and *W* to integer values.

Crystallographic Points, Directions, and Planes

Example

Determination of Directional Indices for a Hexagonal Unit Cell

For the direction shown in the accompanying figure, do the following:

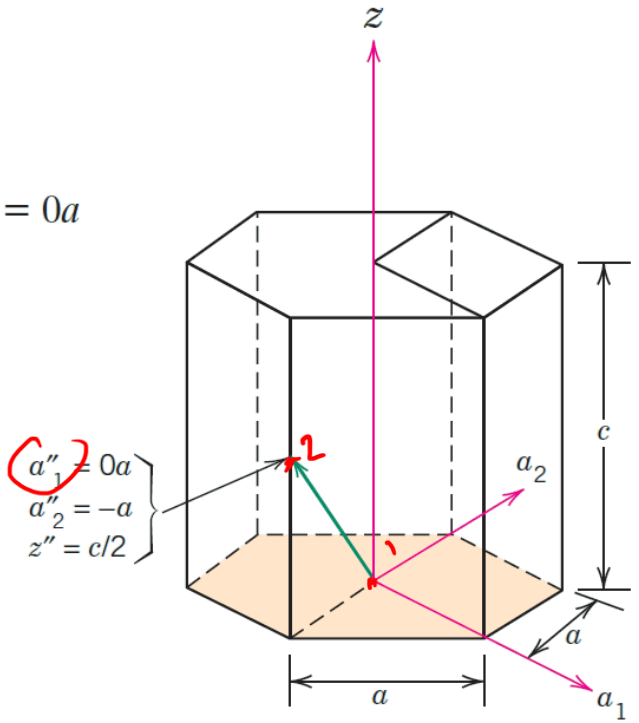
(a) Determine the directional indices referenced to the three-axis coordinate system of
(b) Convert these indices into an index set referenced to the four-axis scheme

Solution

The first thing we need to do is determine U, V, and W indices for the vector referenced to the three-axis scheme represented in the sketch;
Because the vector passes through the origin, $a_1' = a_2' = 0a$ and $z' = 0c$.
Furthermore, from the sketch, coordinates for the vector head are as follows:

$$a_1'' = 0a \qquad a_2'' = -a \qquad z'' = \frac{c}{2}$$

Because the denominator in z'' is 2, we assume that $n = 2$. Therefore,



$$U = n\left(\frac{a_1'' - a_1'}{a}\right) = 2\left(\frac{0a - 0a}{a}\right) = 0$$

$$V = n\left(\frac{a_2'' - a_2'}{a}\right) = 2\left(\frac{-a - 0a}{a}\right) = -2$$

$$W = n\left(\frac{z'' - z'}{c}\right) = 2\left(\frac{c/2 - 0c}{c}\right) = 1$$

This direction is represented by enclosing the above indices in brackets—namely, $[0\bar{2}1]$.

Crystallographic Points, Directions, and Planes

Example

For this $[0\bar{2}1]$ direction $U = 0$ $V = -2$ $W = 1$

and

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}[(2)(0) - (-2)] = \frac{2}{3} \qquad v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(-2) - 0] = -\frac{4}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{4}{3}\right) = \frac{2}{3} \qquad w = W = 1$$

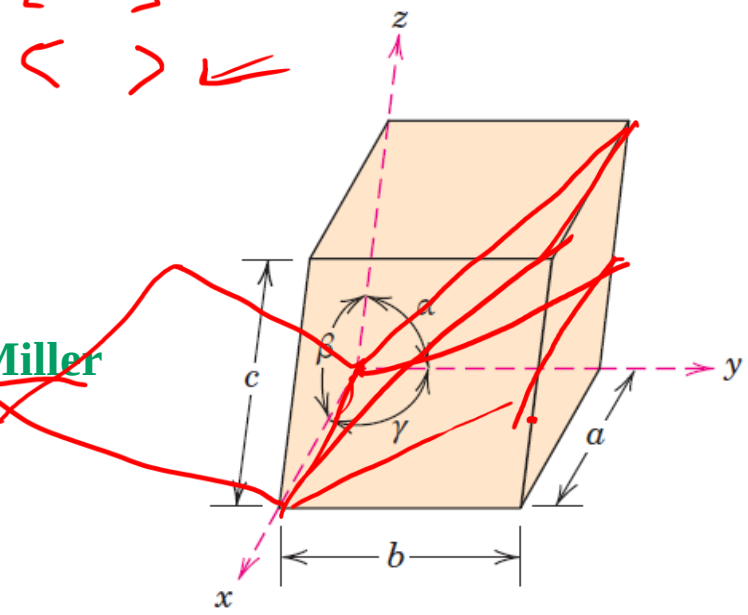
Multiplication of the preceding indices by 3 reduces them to the lowest set, which yields values for u, v, t, and w of 2, –4, 2, and 3, respectively. Hence, the direction vector shown in the figure is $[2\bar{4}23]$.

Crystallographic Points, Directions, and Planes

CRYSTALLOGRAPHIC PLANES

The orientations of planes for a crystal structure are represented in a similar manner. Again, the unit cell is the basis, with the three-axis coordinate system as represented.

In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as (*hkl*).



What are Miller indices?

Miller indices, group of three numbers that indicates the orientation of a plane or set of parallel planes of atoms in a crystal.

Any two planes parallel to each other are equivalent and have identical indices. The procedure used to determine the *h*, *k*, and *l* index numbers is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.

2. At this point, the crystallographic plane either intersects or parallels each of the three axes. The coordinate for the intersection of the crystallographic plane with each of the axes is determined (referenced to the origin of the coordinate system). These intercepts for the *x*, *y*, and *z* axes will be designed by *A*, *B*, and *C*, respectively.

Crystallographic Points, Directions, and Planes

3. The reciprocals of these numbers are taken. A plane that parallels an axis is considered to have an infinite intercept and therefore a zero index.
4. The reciprocals of the intercepts are then normalized in terms of (i.e., multiplied by) their respective *a*, *b*, and *c* lattice parameters. That is,

$$\frac{a}{A} \quad \frac{b}{B} \quad \frac{c}{C}$$

5. If necessary, these three numbers are changed to the set of smallest integers by multiplication or by division by a common factor.
6. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (*hkl*). The *h*, *k*, and *l* integers correspond to the normalized intercept reciprocals referenced to the *x*, *y*, and *z* axes, respectively.

In summary, the *h*, *k*, and *l* indices may be determined using the following equations:

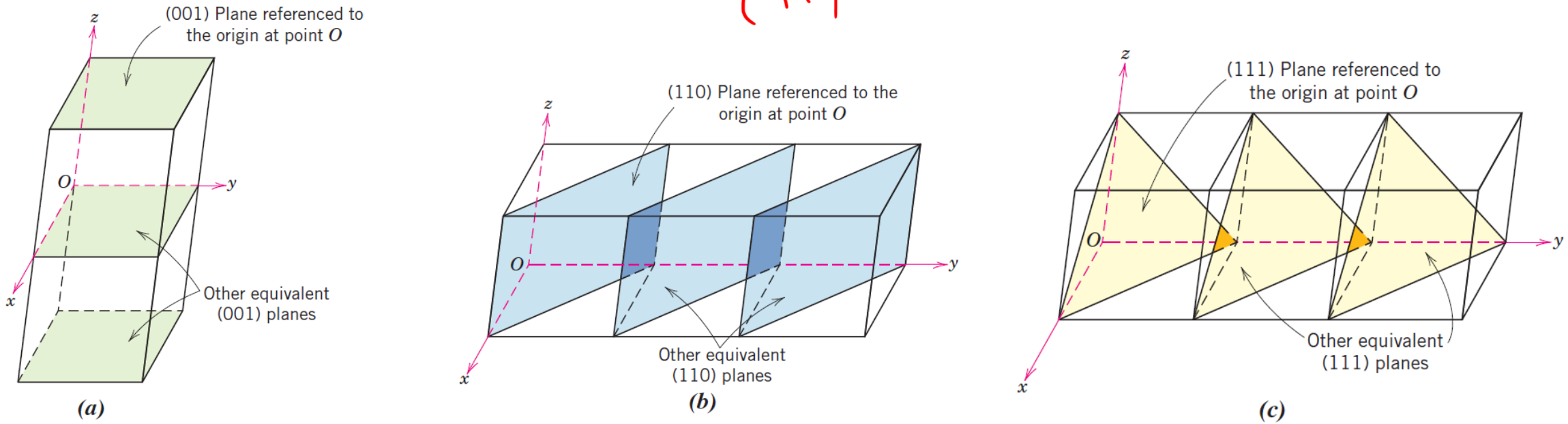
$$h = \frac{na}{A} \qquad k = \frac{nb}{B} \qquad l = \frac{nc}{C}$$

In these expressions, *n* is the factor that may be required to reduce *h*, *k*, and *l* to integers.

Crystallographic Points, Directions, and Planes

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index. Furthermore, reversing the directions of all indices specifies another plane parallel to, on the opposite side of, and equidistant from the origin. Several low-index planes are represented in the figure below.

An interesting and unique characteristic of cubic crystals is that planes and directions having the same indices are perpendicular to one another; however, for other crystal systems there are no simple geometrical relationships between planes and directions having the same indices.



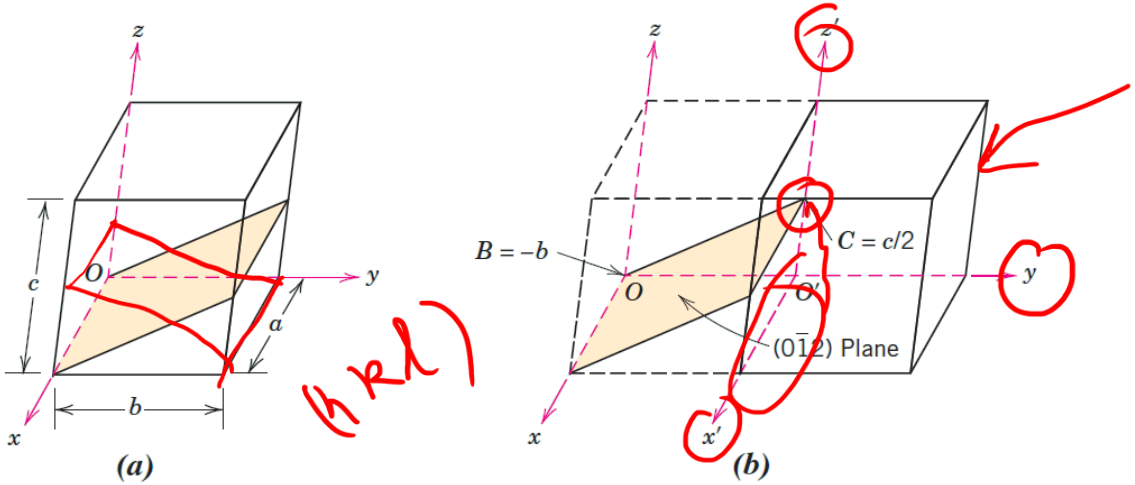
Representations of a series each of the (*a*) (001), (*b*) (110), and (*c*) (111) crystallographic planes.

Crystallographic Points, Directions, and Planes

Example

Determination of Planar (Miller) Indices

Determine the Miller indices for the plane shown in the accompanying sketch (*a*).



Solution

Because the plane passes through the selected origin *O*, a new origin must be chosen at the corner of an adjacent unit cell. In choosing this new unit cell, we move one unit-cell distance parallel to the *y*-axis, as shown in sketch (*b*). Thus x'-y-z' is the new coordinate axis system having its origin located at O'. Because this plane is parallel to the x' axis its intercept is ∞a—that is, $A = \infty a$. Furthermore, from illustration (*b*), intersections with the y and z' axes are as follows:

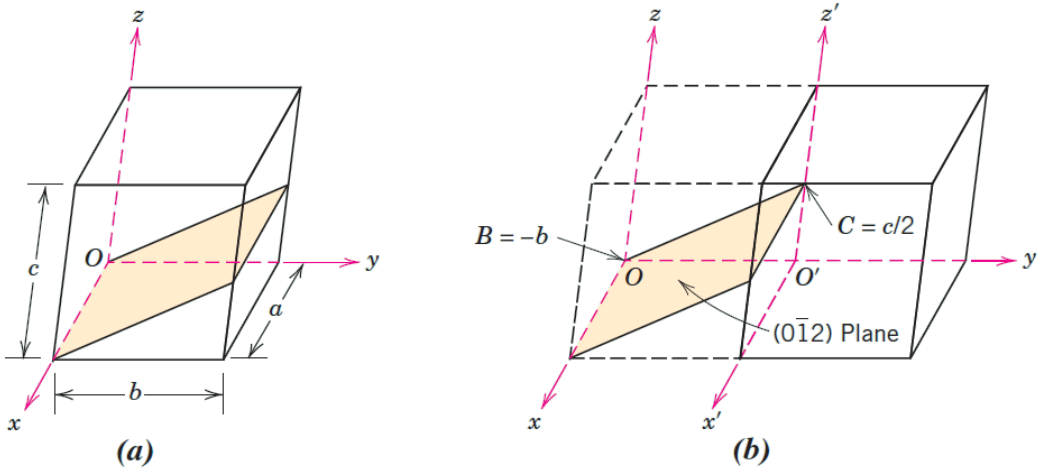
$B = -b$ $C = c/2$

Crystallographic Points, Directions, and Planes

Example

Determination of Planar (Miller) Indices

Determine the Miller indices for the plane shown in the accompanying sketch (*a*).



Solution

Because the plane passes through the selected origin O, a new origin must be chosen at the corner of an adjacent unit cell. In choosing this new unit cell, we move one unit-cell distance parallel to the y-axis, as shown in sketch (b). Thus x'-y-z' is the new coordinate axis system having its origin located at O'. Because this plane is parallel to the x' axis its intercept is ∞a—that is, $A = \infty a$. Furthermore, from illustration (b), intersections with the y and z' axes are as follows:

$$B = -b \qquad C = c/2$$

Crystallographic Points, Directions, and Planes

Example

$$h = \frac{na}{A} = \frac{1a}{\infty a} = 0$$

$$k = \frac{nb}{B} = \frac{1b}{-b} = -1$$

$$l = \frac{nc}{C} = \frac{1c}{c/2} = 2$$

And finally, enclosure of the 0, −1, and 2 indices in parentheses leads to $(0\bar{1}2)$ as the designation for this direction. This procedure is summarized as follows:

	x	*y*	*z*
Intercepts (A, B, C)	∞a	$-b$	$c/2$
Calculated values of h, k, and l (Equations 3.13a–3.13c)	$h = 0$	$k = -1$	$l = 2$
Enclosure		$(0\bar{1}2)$	

Crystallographic Points, Directions, and Planes

Example

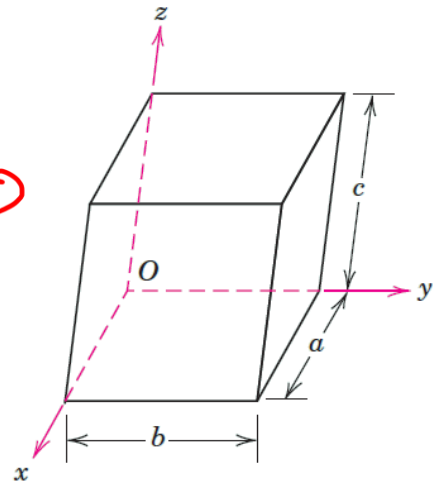
Construction of a Specified Crystallographic Plane

Construct a (101) plane within the following unit cell.

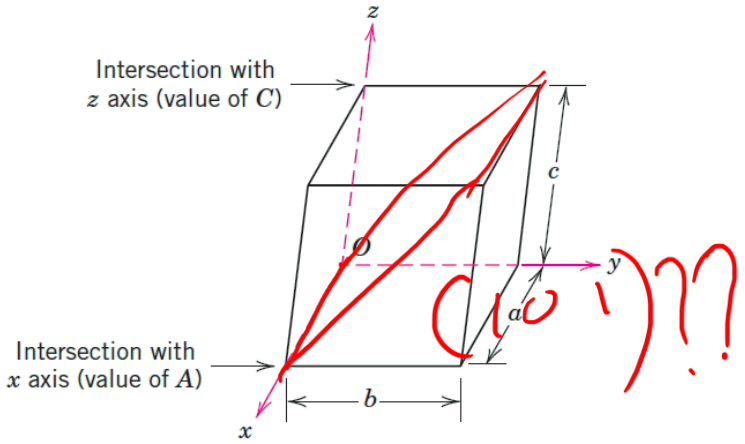
Solution

To solve this problem, carry out the procedure used in the preceding example in reverse order. For this (101) direction,

$$h = 1$$
$$k = 0$$
$$l = 1$$



(a)



(b)

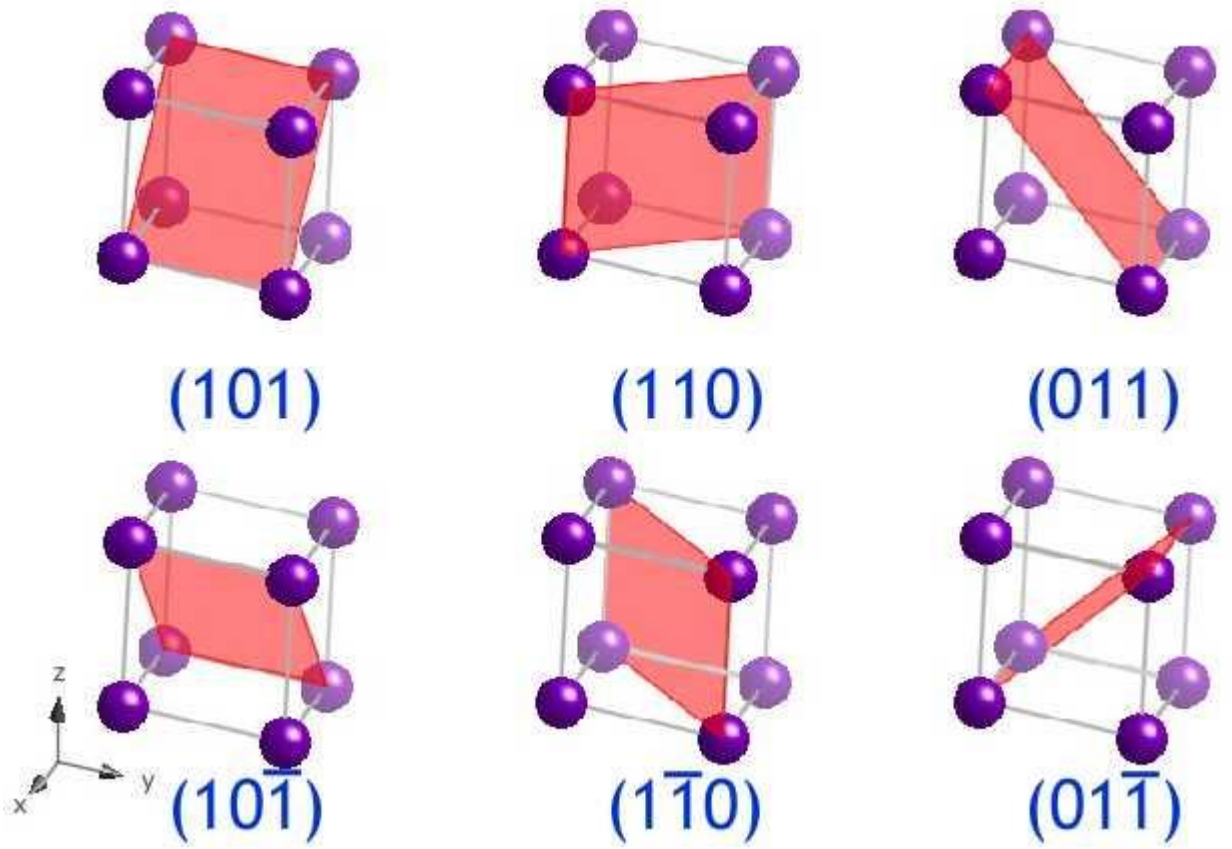
Using these h, k, and l indices, we want to solve for the values of A, B, and C
Taking the value of n to be 1—because these three Miller indices are all integers—leads to the following:

$$A = \frac{na}{h} = \frac{(1)(a)}{1} = a \qquad B = \frac{nb}{k} = \frac{(1)(b)}{0} = \infty b$$

$$C = \frac{nc}{l} = \frac{(1)(c)}{1} = c$$

Crystallographic Points, Directions, and Planes

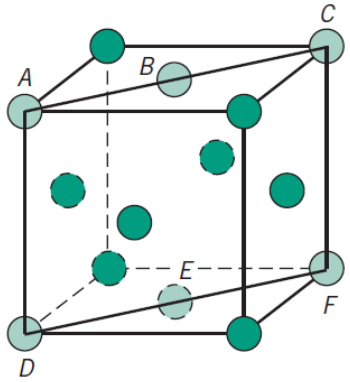
Example



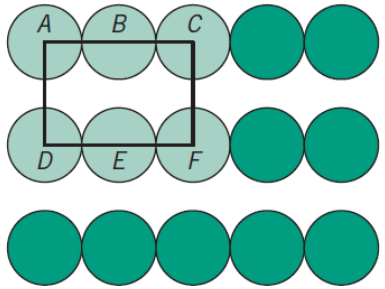
Crystallographic Points, Directions, and Planes

Atomic Arrangements

The atomic arrangement for a crystallographic plane, which is often of interest, depends on the crystal structure. The (110) atomic planes for FCC and BCC crystal structures are represented in the figures below, respectively. Reduced-sphere unit cells are also included.



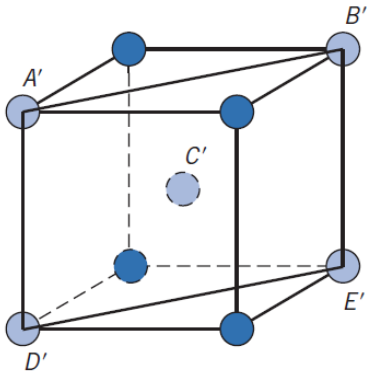
(a)



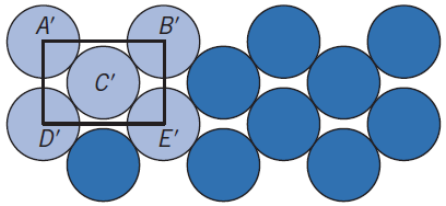
(b)

(*a*) Reduced-sphere FCC unit cell with the (110) plane. (*b*) Atomic packing of an FCC (110) plane.

Corresponding atom positions from (*a*) are indicated.



(a)



(b)

(*a*) Reduced-sphere BCC unit cell with the (110) plane. (*b*) Atomic packing of a BCC (110) plane.

Corresponding atom positions from (*a*) are indicated.

Crystallographic Points, Directions, and Planes

Note that the atomic packing is different for each case. The circles represent atoms lying in the crystallographic planes as would be obtained from a slice taken through the centres of the full-size hard spheres.

A “family” of planes contains all planes that are *crystallographically equivalent*— that is, having the same atomic packing; a family is designated by indices enclosed in braces—such as {100}.

For example, in cubic crystals, the (111), ($\bar{1}\,\bar{1}\,1$), ($\bar{1}11$), ($1\,\bar{1}\,1$), ($11\bar{1}$), ($\bar{1}\,1\bar{1}$), ($\bar{1}\bar{1}1$), and ($1\bar{1}\bar{1}$) planes all belong to the {111} family.

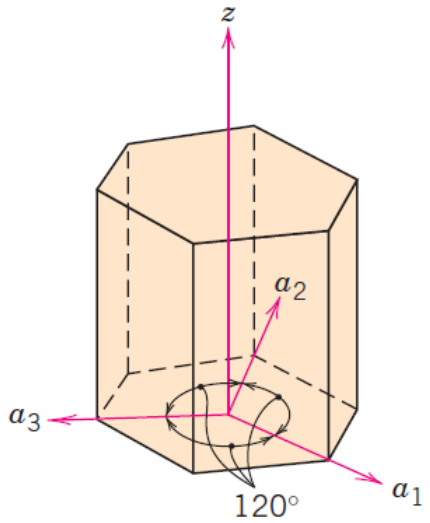
However, for tetragonal crystal structures, the {100} family contains only the (100), ($\bar{1}00$), (010), and ($0\bar{1}0$) planes because the (001) and ($00\bar{1}$) planes are not crystallographically equivalent.

Also, in the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent. For example, both (123) and ($3\bar{1}2$) belong to the {123} family.

Crystallographic Points, Directions, and Planes

Hexagonal Crystals

For crystals having hexagonal symmetry, it is desirable that equivalent planes have the same indices; as with directions, this is accomplished by the Miller–Bravais system.

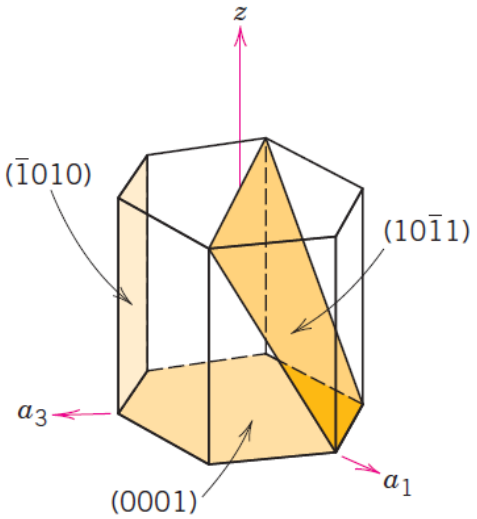


This convention leads to the four-index (*hkil*) scheme, which is favoured in most instances because it more clearly identifies the orientation of a plane in a hexagonal crystal.

There is some redundancy in that *i* is determined by the sum of *h* and *k* through

$$i = -(h + k)$$

Otherwise, the three *h*, *k*, and *l* indices are identical for both indexing systems.



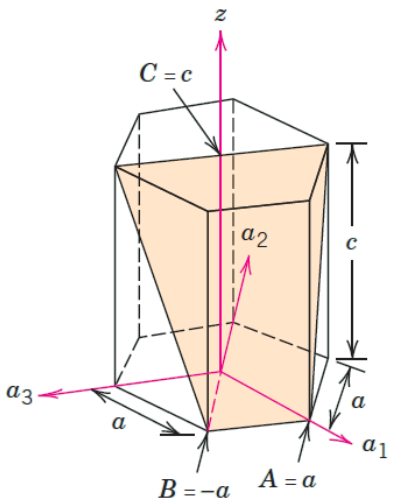
Several of the common planes that are found for crystals having hexagonal symmetry. The (0001), $(10\bar{1}1)$, and $(\bar{1}010)$ planes.

Crystallographic Points, Directions, and Planes

Example

Determination of the Miller–Bravais Indices for a Plane within a Hexagonal Unit Cell

Determine the Miller–Bravais indices for the plane shown in the hexagonal unit cell.



Solution

If we again take A, B, and C to represent intercepts on the respective a_1, a_2, and z axes, normalized intercept reciprocals may be written as

$$\frac{a}{A} \quad \frac{a}{B} \quad \frac{c}{C}$$

Now, because the three intercepts noted on the above unit cell are

$$A = a \qquad B = -a \qquad C = c$$

values of h, k, and l, may be determined using

$$h = \frac{na}{A} = \frac{(1)(a)}{a} = 1 \qquad k = \frac{na}{B} = \frac{(1)(a)}{-a} = -1 \qquad n = 1$$

$$l = \frac{nc}{C} = \frac{(1)(c)}{c} = 1$$

And, finally, the value of i is found as follows:

$$i = -(h + k) = -[1 + (-1)] = 0$$

Therefore, the $(hkil)$ indices are $(1\bar{1}01)$.

Notice that the third index is zero (i.e., its reciprocal = ∞), which means this plane parallels the a_3 axis. Inspection of the preceding figure shows that this is indeed the case.

Crystallographic Points, Directions, and Planes

Summary of Equations Used to Determine Crystallographic Point, Direction, and Planar Indices

Coordinate Type	*Index Symbols*	*Representative Equation*[a]	*Equation Symbols*
Point	$q\ r\ s$	$q = \dfrac{a}{P_x}$	P_x = lattice position coordinate
Direction			
Non-hexagonal	$[uvw]$	$u = n\left(\dfrac{x_2 - x_1}{a}\right)$	x_1 = tail coordinate—x axis x_2 = head coordinate—x axis
Hexagonal	$[UVW]$	$U = n\left(\dfrac{a_1'' - a_1'}{a}\right)$	a_1' = tail coordinate—a_1 axis a_1'' = head coordinate—a_1 axis
	$[uvtw]$	$u = \dfrac{1}{3}(2U - V)$	—
Plane			
Non-hexagonal	(hkl)	$h = \dfrac{na}{A}$	A = plane intercept—x axis
Hexagonal	$(hkil)$	$i = -(h + k)$	—

In these equations a and n denote, respectively, the x-axis lattice parameter, and a reduction-to-integer parameter.

LINEAR AND PLANAR DENSITIES

Linear and planar densities are important considerations relative to the process of *slip*— that is, the mechanism by which metals plastically deform. *Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing*.

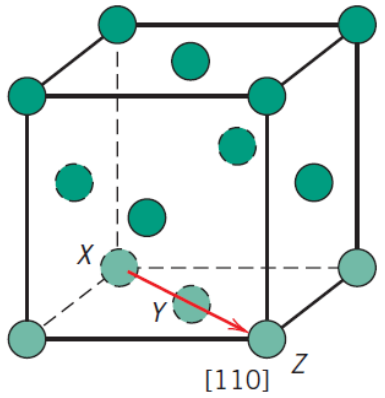
Directional equivalency is related to *linear density* in the sense that, for a particular material, equivalent directions have identical linear densities.

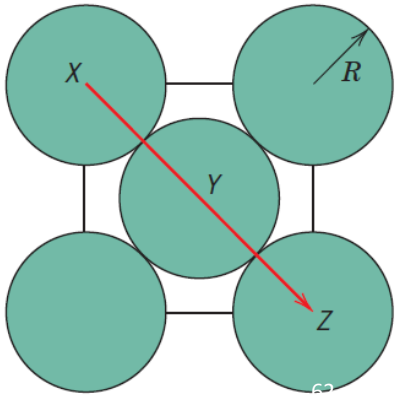
The corresponding parameter for crystallographic planes is *planar density*, and planes having the same planar density values are also equivalent.

Linear density ***LD*** (nm^{-1}, m^{-1}) is defined as the number of atoms per unit length whose centres lie on the direction vector for a specific crystallographic direction:

$$LD = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$$

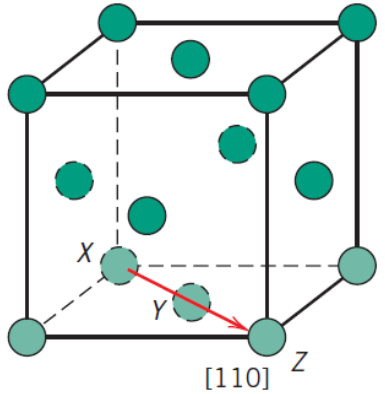
The linear density of the [110] direction for the FCC crystal structure:
The five atoms that lie on the bottom face of this unit cell are shown. The [110] direction vector passes from the centre of atom *X*, through atom *Y*, and finally to the centre of atom *Z*.

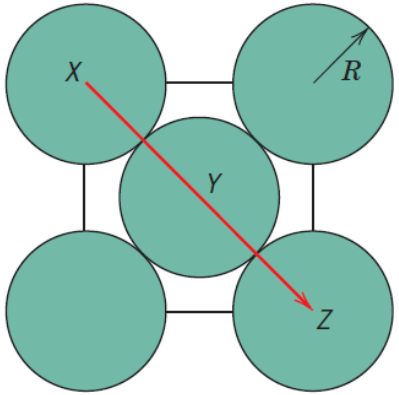




LINEAR AND PLANAR DENSITIES

With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells.





Each of the *X* and *Z* corner atoms is also shared with one other adjacent unit cell along this [110] direction (i.e., one-half of each of these atoms belongs to the unit cell being considered), whereas atom *Y* lies entirely within the unit cell.

Thus, there is an equivalence of two atoms along the [110] direction vector in the unit cell.

Now, the direction vector length is equal to $4R$; thus, the [110] linear density for FCC is:

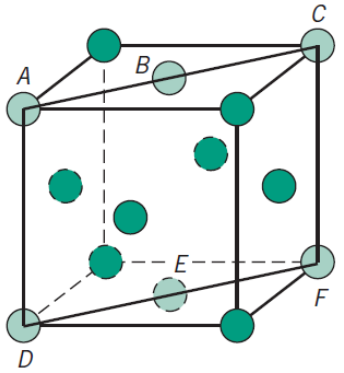
$$\mathrm{LD}_{110} = \frac{2 \text{ atoms}}{4R} = \frac{1}{2R}$$

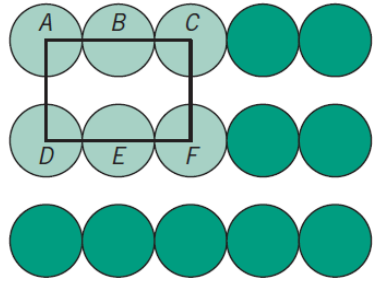
Planar density ***PD*** (nm^{-2}, m^{-2}) is taken as the number of atoms per unit area that are centred on a particular crystallographic plane:

$$\mathrm{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}}$$

LINEAR AND PLANAR DENSITIES

For example, consider the section of a (110) plane within an FCC unit cell:





Six atoms have centres that lie on this plane, only one-quarter of each of atoms *A*, *C*, *D*, and *F* and one-half of atoms *B* and *E*, for a total equivalence of just **2** atoms, are on that plane.

The area of this rectangular section is equal to the product of its length and width:
the length (horizontal dimension) is equal to 4*R*, whereas the width (vertical dimension) is equal to 2*R*√2 because it corresponds to the FCC unit cell edge length.

$$a = 2R\sqrt{2}$$

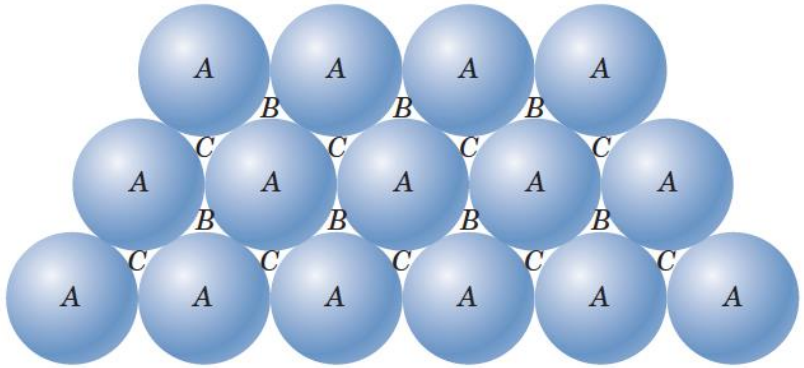
Thus, the area of this planar region is $(4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$, and the planar density is determined as follows:

$$PD_{110} = \frac{2 \text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}}$$

CLOSE-PACKED CRYSTAL STRUCTURES

Recall: FCC and HCP structures have atomic packing factors of 0.74, which is the most efficient packing of equal-size spheres or atoms.

These two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated.



Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centres of all the atoms in one close-packed plane be labelled ***A***.

Associated with this plane are two sets of equivalent triangular depressions formed by three adjacent atoms, into which the next close-packed plane of atoms may rest.

Those having the triangle vertex pointing up are arbitrarily designated as ***B*** positions, whereas the remaining depressions are those with the down vertices, which are marked ***C***.

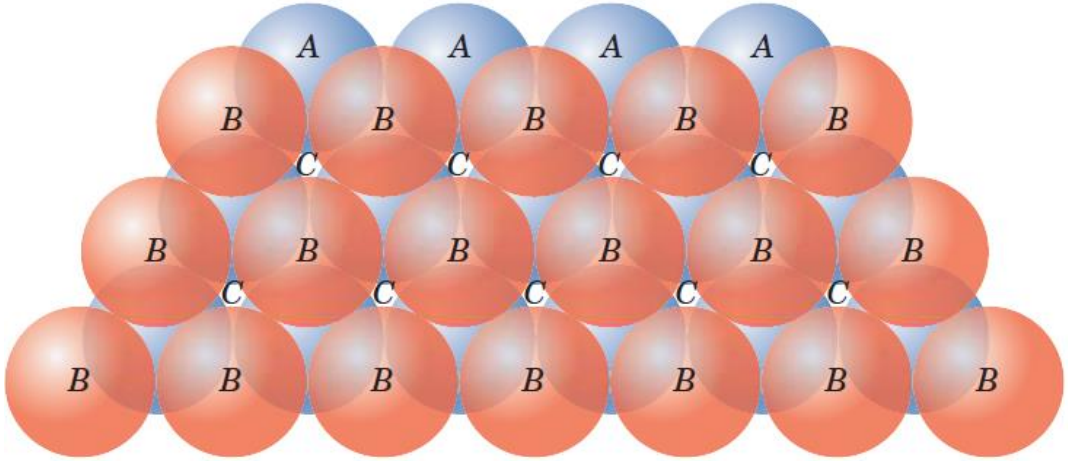
CLOSE-PACKED CRYSTAL STRUCTURES

A second close-packed plane may be positioned with the centres of its atoms over either *B* or *C* sites; at this point, both are equivalent.

Suppose that the *B* positions are arbitrarily chosen; the stacking sequence is termed *AB*.

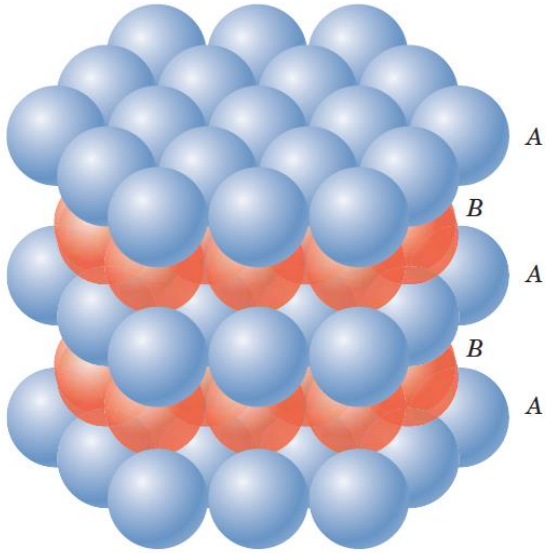
The real distinction between FCC and HCP lies in where the third close-packed layer is positioned.

For HCP, the centres of this layer are aligned directly above the original *A* positions.



This stacking sequence, *ABABAB* . . . , is repeated over and over. Of course, the *ACACAC* . . . arrangement would be equivalent.

These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown.

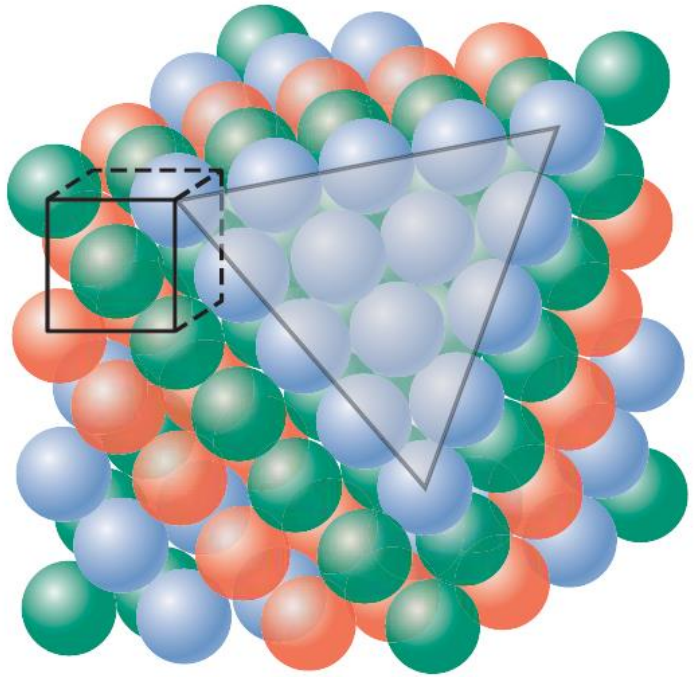


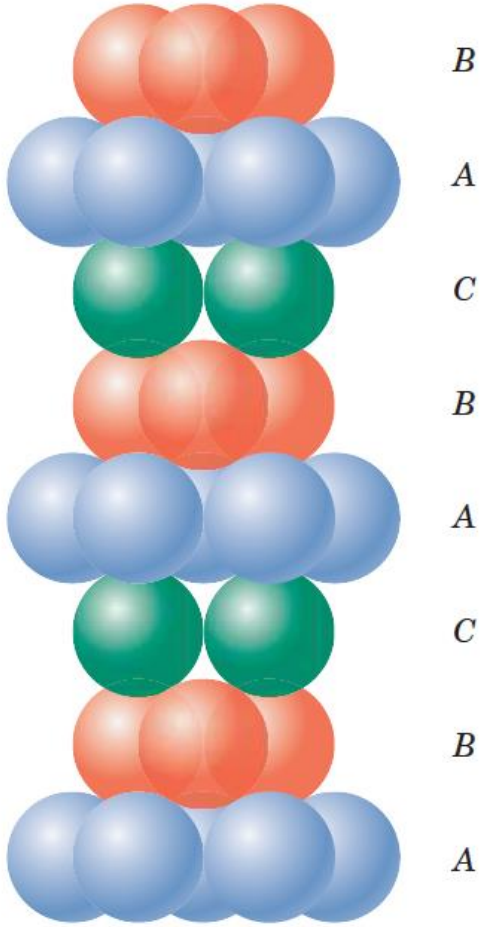
CLOSE-PACKED CRYSTAL STRUCTURES

For the face-centred crystal structure, the centres of the third plane are situated over the *C* sites of the first plane. This yields an *ABCABCABC* . . . stacking sequence; that is, the atomic alignment repeats every third plane.

It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell.

However, this relationship is demonstrated. These planes are of the (111) type; an FCC unit cell is outlined on the upper left-hand front face of to provide perspective.





Crystalline and Noncrystalline Materials

SINGLE CRYSTALS

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal.**

All unit cells interlock in the same way and have the same orientation.

Single crystals exist in nature, but they can also be produced artificially.
They are ordinarily difficult to grow because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal assumes a regular geometric shape having flat faces, as with some of the gemstones; the shape is indicative of the crystal structure.

Within the past few years, single crystals have become extremely important in many modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

Photograph of a garnet single crystal that was found in Tongbei, Fujian Province, China.

An iron pyrite single crystal that was found in Navajún, La Rioja, Spain.

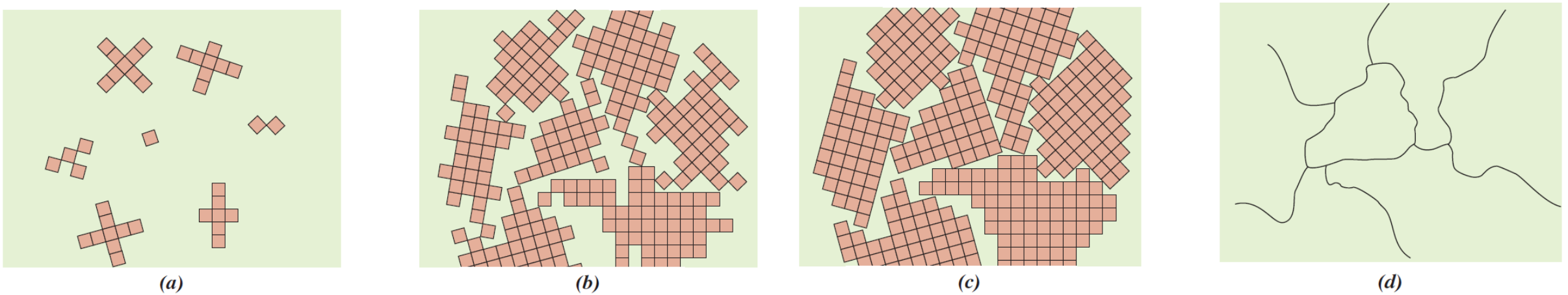
Crystalline and Noncrystalline Materials

POLYCRYSTALLINE MATERIALS

Most crystalline solids are composed of a collection of many small crystals or **grains;** such materials are termed **polycrystalline.**

Various stages in the solidification of a polycrystalline specimen are represented schematically below.

Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids.



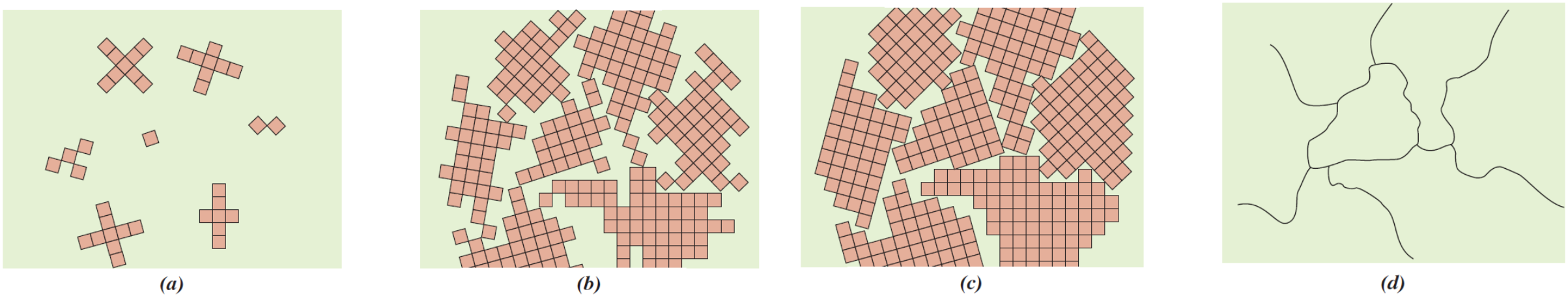
Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries.

Crystalline and Noncrystalline Materials

The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each.

The extremities of adjacent grains impinge on one another as the solidification process approaches completion.

The crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary.**



Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries.

Crystalline and Noncrystalline Materials

ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken.

For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. *This directionality of properties is termed* ***anisotropy,*** *and it is associated with the variance of atomic or ionic spacing with crystallographic direction.*

Substances in which measured properties are independent of the direction of measurement are ***isotropic.***

The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic.

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random.

Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically.

Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

	Modulus of Elasticity (GPa)		
Metal	***[100]***	***[110]***	***[111]***
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Crystalline and Noncrystalline Materials

Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a "texture."

The magnetic properties of some iron alloys used in transformer cores are anisotropic—that is, grains (or single crystals) magnetize in a ⟨100⟩-type direction easier than any other crystallographic direction.

Energy losses in transformer cores are minimized by utilizing polycrystalline sheets of these alloys into which have been introduced a *magnetic texture*: most of the grains in each sheet have a ⟨100⟩-type crystallographic direction that is aligned (or almost aligned) in the same direction, which is oriented parallel to the direction of the applied magnetic field.

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Historically, much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials.

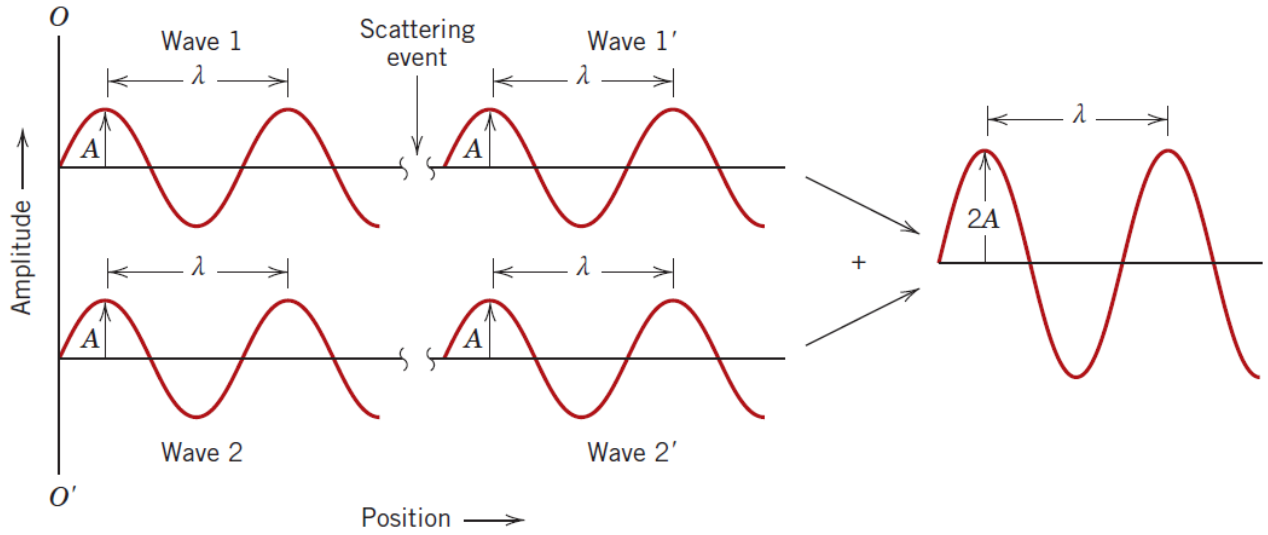
The Diffraction Phenomenon

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that
(1) are capable of scattering the wave, and
(2) have spacings that are comparable in magnitude to the wavelength.

Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

Consider waves 1 and 2, which have the same wavelength (λ) and are in phase at point O–O'.

Now let us suppose that both waves are scattered in such a way that they traverse different paths.



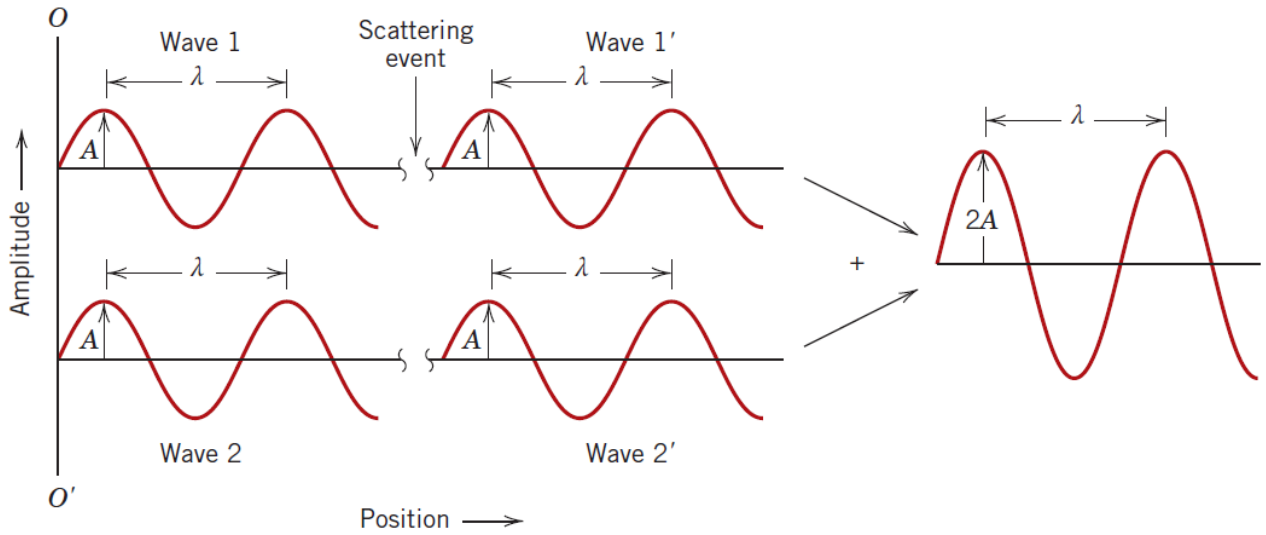
X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

The phase relationship between the scattered waves, which depends upon the difference in path length, is important.

One possibility results when this path length difference is an integral number of wavelengths.

These scattered waves (now labelled 1′ and 2′) are still in phase.

They are said to mutually reinforce (or constructively Interfere with) one another; when amplitudes are added, the wave shown on the right side of the figure results.



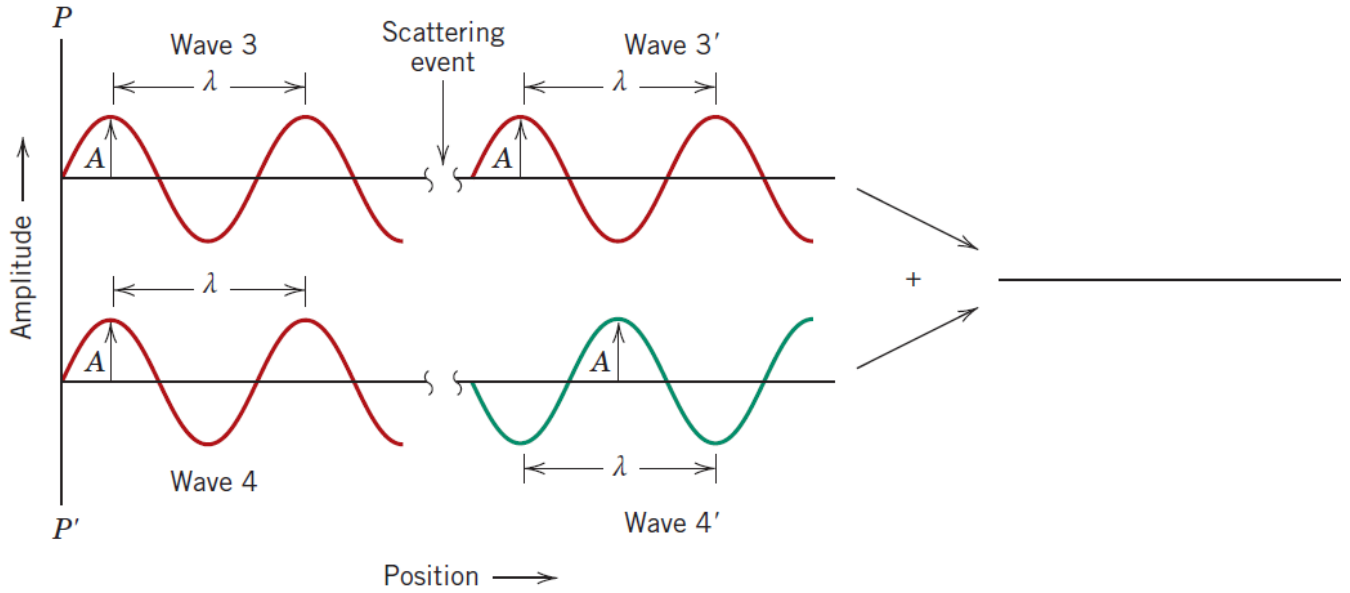
This is a manifestation of **diffraction,** and we refer to a *diffracted beam* as one composed of a large number of scattered waves that mutually reinforce one another.

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement.

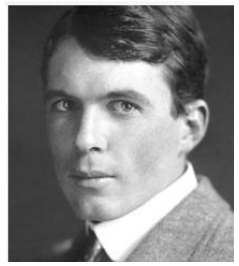
The other extreme is that demonstrated here, in which the path length difference after scattering is some Integral number of *half*-wavelengths.

The scattered waves are out of phase—that is, Corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the right side of the figure.



Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES



X-Ray Diffraction and Bragg's Law (Wulff–Bragg's condition)

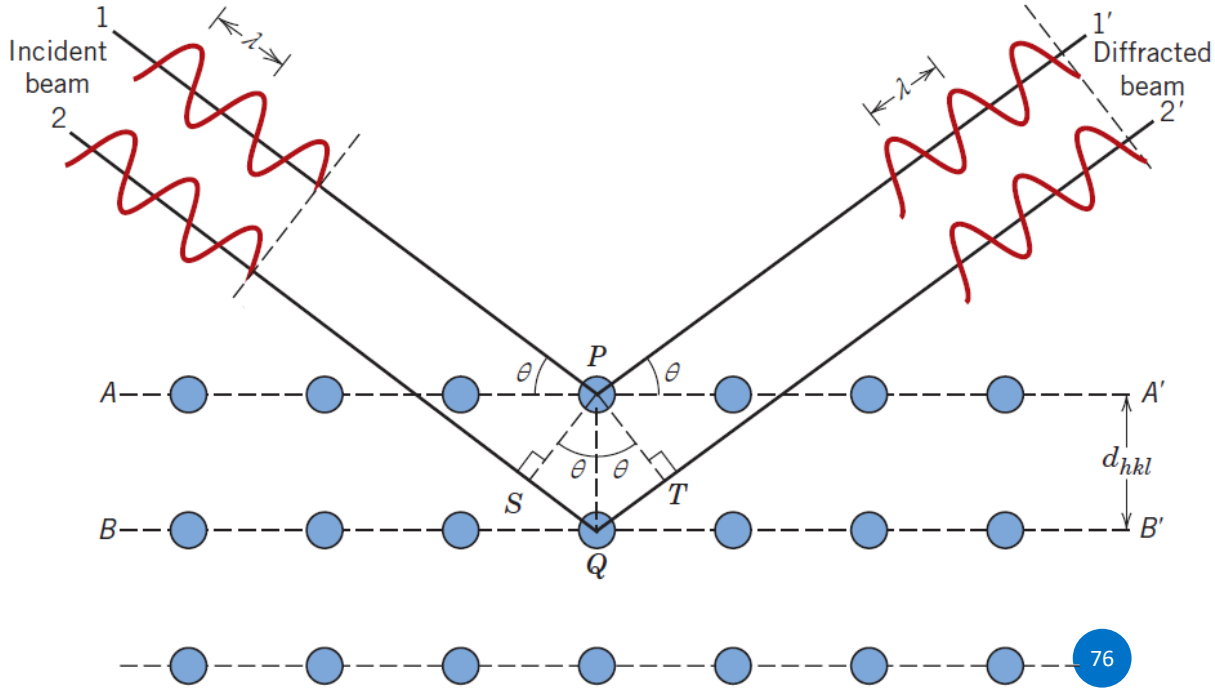
X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids.

When a beam of x-rays impinges on a solid material, a portion of this beam is scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path.

What are the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Consider the two parallel planes of atoms *A*–*A*′ and *B*–*B*′ , which have the same *h*, *k*, and *l* Miller indices and are separated by the interplanar spacing *dhkl*.

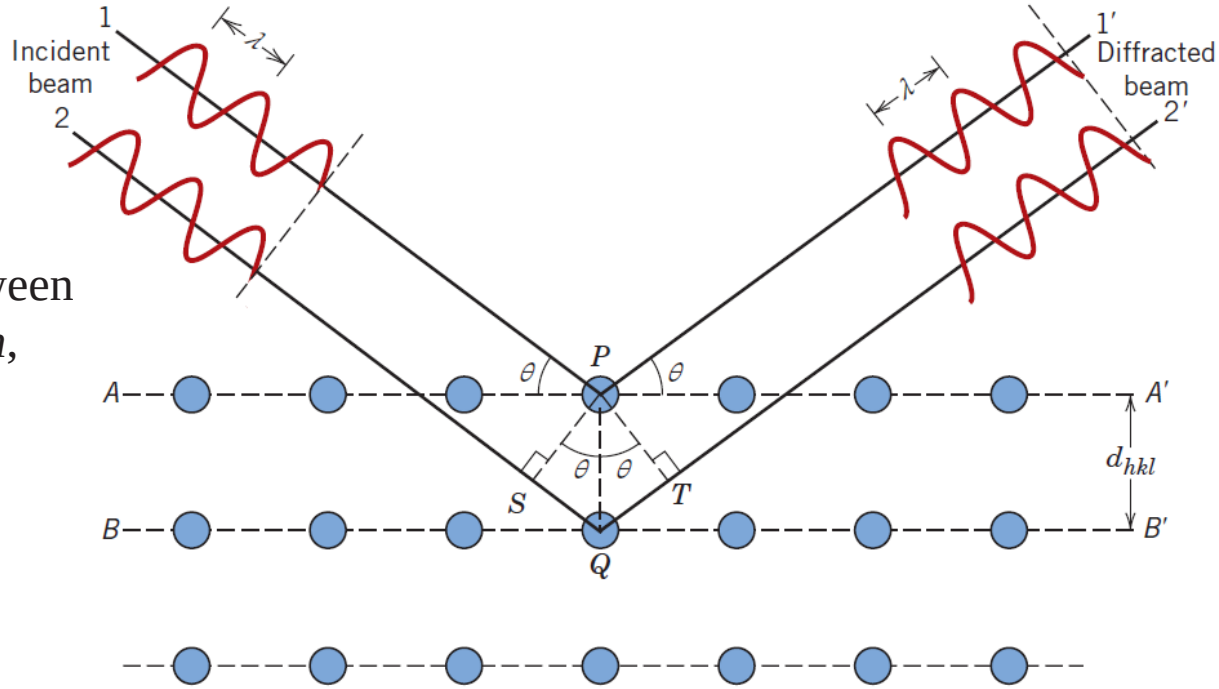
Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ.



X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Two rays in this beam, labelled 1 and 2, are scattered by atoms *P* and *Q*.

Constructive interference of the scattered rays 1′ and 2′ occurs also at an angle θ to the planes if the path length difference between 1–*P*–1′ and 2–*Q*–2′ (i.e., *SQ* + *QT*) is equal to a whole number, *n*, of wavelengths—that is, the condition for diffraction is:



$$n\lambda = \overline{SQ} + \overline{QT} \qquad n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$n\lambda = 2d_{hkl}\sin\theta \qquad \textbf{Bragg's law}$$

n is the order of reflection, which may be any integer (1, 2, 3, . . .) consistent with sin θ not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam.

If Bragg's law is not satisfied, then the interference will be nonconstructive so as to yield a very low-intensity diffracted beam. The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing *dhkl*) is a function of the Miller indices (*h*, *k*, and *l*) as well as the lattice parameter(s). For example, for crystal structures that have cubic symmetry: (*a* is the lattice parameter "unit cell edge length").

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Bragg's law is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners.

However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centres, which can produce out-of-phase scattering at certain Bragg angles.

The net result is the absence of some diffracted beams that should be present. Specific sets of crystallographic planes that do not give rise to diffracted beams depend on crystal structure.

For the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur, whereas for FCC, h, k, and l must all be either odd or even; diffracted beams for all sets of crystallographic planes are present for the simple cubic crystal structure.

These restrictions, called *reflection rules*, are summarized:

X-Ray Diffraction Reflection Rules and Reflection Indices for Body-Centered Cubic, Face-Centered Cubic, and Simple Cubic Crystal Structures

Crystal Structure	*Reflections Present*	*Reflection Indices for First Six Planes*
BCC	$(h + k + l)$ even	110, 200, 211, 220, 310, 222
FCC	h, k, and l either all odd or all even	111, 200, 220, 311, 222, 400
Simple cubic	All	100, 110, 111, 200, 210, 211

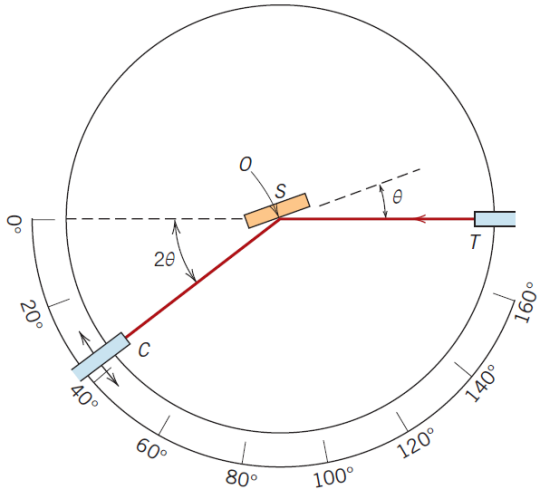
X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Diffraction Techniques

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation.

Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The *diffractometer* is an apparatus used to determine the angles at which Diffraction occurs for powdered specimens; its features are represented schematically.



A specimen *S* in the form of a flat plate is supported so that rotations about the axis labelled *O* are possible; this axis is perpendicular to the plane of the page.

The monochromatic x-ray beam is generated at point *T*, and the intensities of diffracted beams are detected with a counter labelled *C* in the figure. The specimen, x-ray source, and counter are coplanar

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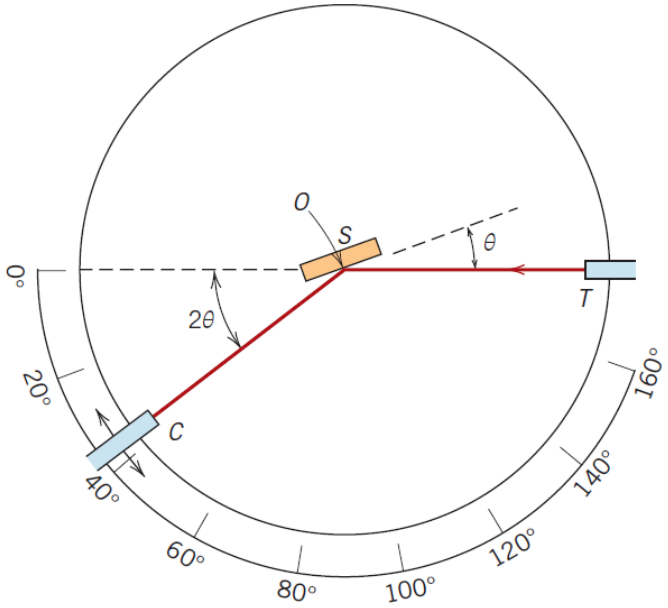
The counter is mounted on a movable The counter is mounted on a movable carriage that may also be rotated about the *O* axis; its angular position in terms of 2θ is marked on a graduated scale.

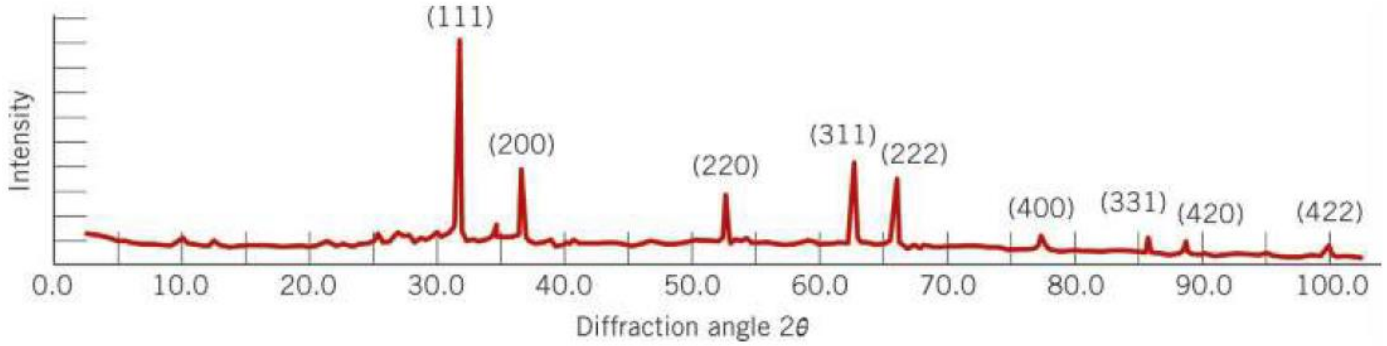


Carriage and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this ensures that the incident and Reflection angles are maintained equal to one another.

Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ; 2θ is termed the *diffraction angle*, which is measured experimentally.

The figure shows a diffraction pattern for a powdered specimen of lead.
The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes.



These peaks are plane-indexed in the figure.

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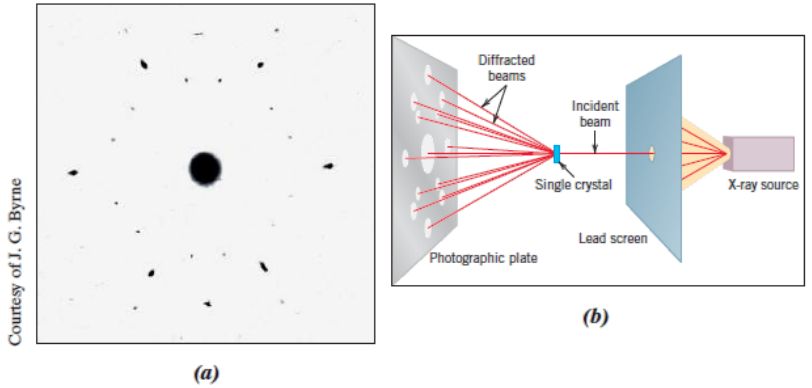
Other powder techniques have been devised in which diffracted beam intensity and position are recorded on a photographic film instead of being measured by a counter.

One of the primary uses of x-ray diffractometry is for the determination of crystal structure. The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks, whereas the arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs.

The figure here was generated using an incident x-ray beam that was directed on a magnesium crystal; each spot (with the exception of the darkest one near the centre) resulted from an x-ray beam that was diffracted by a specific set of crystallographic planes.



Other uses of x-rays include qualitative and quantitative chemical identifications and the determination of residual stresses and crystal size.

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Example

Interplanar Spacing and Diffraction Angle Computations

For BCC iron, compute **(a)** the interplanar spacing and **(b)** the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a) The value of the interplanar spacing d_{hkl} is determined , with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$ because we are considering the (220) planes. Therefore,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$= \frac{0.2866\ \text{nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013\ \text{nm}$$

(b) The value of θ may now be computed , with $n = 1$ because this is a first order reflection: -

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790\,\text{nm})}{(2)(0.1013\,\text{nm})} = 0.884 \qquad \theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = 124.26°$$

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Example

Interplanar Spacing and Lattice Parameter Computations for Lead

Figure shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also, determine the lattice parameter of Pb for each of the peaks. For all peaks, assume the order of diffraction is 1.

Solution

The first peak results from diffraction by the (111) set of planes, occurs at $2\theta = 31.3°$ the corresponding interplanar spacing is equal to

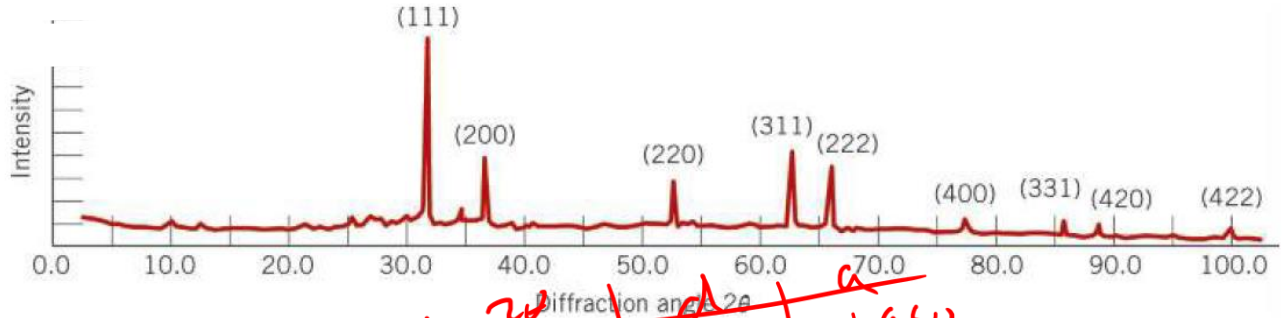
$$d_{111} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1542\text{ nm})}{(2)\left[\sin\left(\frac{31.3°}{2}\right)\right]} = 0.2858\text{ nm}$$

the lattice parameter a is determined as $a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$

$$= d_{111}\sqrt{(1)^2 + (1)^2 + (1)^2} \quad = (0.2858\text{ nm})\sqrt{3} = 0.4950\text{ nm}$$

Similar computations are made for the next four peaks; the results are tabulated below:

Peak Index	*2θ*	*d_{hkl} (nm)*	*a (nm)*
200	36.6	0.2455	0.4910
220	52.6	0.1740	0.4921
311	62.5	0.1486	0.4929
222	65.5	0.1425	0.4936



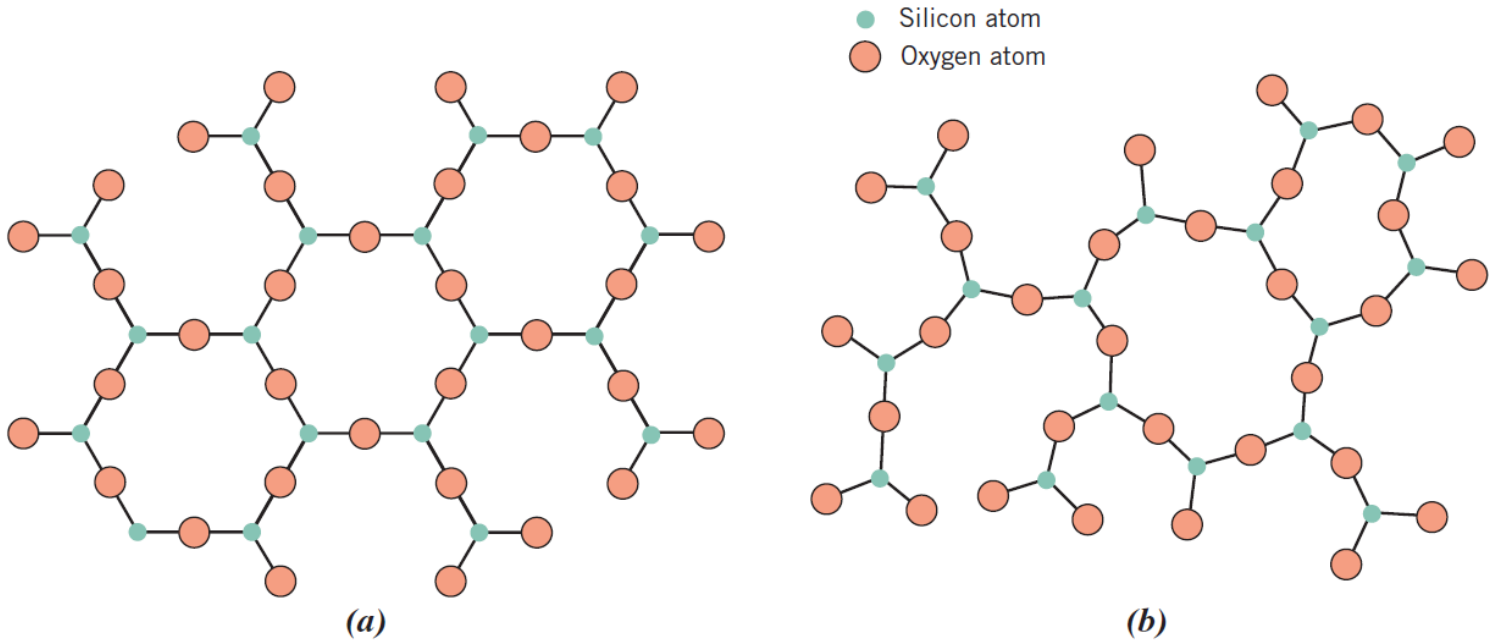
400 77° 0.1239 0.4950
331 84.9 0.1136 0.4951
422 88 0.1109 0.4959
422 100 0.1006 0.4924

NONCRYSTALLINE SOLIDS

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances.

Sometimes such materials are also called **amorphous** (meaning literally “without form”), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states.



Two-dimensional schemes of the structure of (*a*) crystalline silicon dioxide and (*b*) noncrystalline silicon dioxide.

NONCRYSTALLINE SOLIDS

Even though each silicon ion bonds to three oxygen ions (and a fourth oxygen ion above the plane) for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or an amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification.

Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty.

Furthermore, rapidly cooling through the freezing temperature favours the formation of a noncrystalline solid, because little time is allowed for the ordering process.

Metals normally form crystalline solids, but some ceramic materials are crystalline, whereas others—the inorganic glasses—are amorphous.

Polymers may be completely noncrystalline or semicrystalline consisting of varying degrees of crystallinity.

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