Foundations of

Materials Science and Engineering

WILLIAM SMITH | JAVAD HASHEMI

SIXTH EDITION

Mc Graw Hill Education

Foundations of Materials Science and Engineering

Sixth Edition

William F. Smith
Late Professor Emeritus of Engineering of
University of Central Florida

Javad Hashemi, Ph.D.
Professor of Mechanical Engineering
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FOUNDATIONS OF MATERIALS SCIENCE AND ENGINEERING, SIXTH EDITION

Published by McGraw-Hill Education, 2 Penn Plaza, New York, NY 10121.

This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 LCR 21 20 19 18

ISBN 978-1-259-69655-8
MHID 1-259-69655-3

Portfolio Manager: *Thomas Scaife Ph.D.*
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Cover Image: *Florida Atlantic University*
Compositor: *SPi Global*

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Library of Congress Cataloging-in-Publication Data

Names: Smith, William F. (William Fortune), 1931- author. | Hashemi, Javad, 1961- author.
Title: Foundations of materials science and engineering / William F. Smith, late professor emeritus of engineering of University of Central Florida, Javad Hashemi, Ph.D., professor of mechanical engineering, Florida Atlantic University.
Description: Sixth edition. | New York, NY: McGraw-Hill Education, c2019. | Includes answers to chapter exercises. | Includes index.
Identifiers: LCCN 2017048596 | ISBN 9781259696558 (alk. paper)
Subjects: LCSH: Materials science. | Materials science—Textbooks. | Materials. | Materials—Textbooks.
Classification: LCC TA403 .S5955 2019 | DDC 620.1/1—dc23 LC record available at https://lccn.loc.gov/2017048596

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Dr. Francisco Presuel-Moreno is an Associate Professor of Ocean and Mechanical Engineering at Florida Atlantic University and directs the Marine Materials and Corrosion Lab. **Dr. Presuel-Moreno** received his Ph.D. in Engineering Science from the University of South Florida. Prior to his tenure at Florida Atlantic University, **Dr. Presuel-Moreno** did a Postdoctoral stay at the Materials Science and Engineering department at the University of Virginia. Over the course of his career, **Dr. Presuel-Moreno** has accumulated extensive educational and research background, including marine materials, metallic corrosion in concrete, durability of reinforced concrete structures, non-destructive testing and experimental and computational modeling of corrosion processes.

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PREFACE

The subject of materials science and engineering is an essential course to engineers and scientists from all disciplines. With advances in science and technology, development of new engineering fields, and changes in the engineering profession, today's engineer must have a deeper, more diverse, and up-to-date knowledge of materials-related issues. At a minimum, all engineering students must have the basic knowledge of the structure, properties, processing, and performance of various classes of engineering materials. This is a crucial first step in the materials selection decisions in everyday rudimentary engineering problems. A more in-depth understanding of the same topics is necessary for designers of complex systems, forensic (materials failure) analysts, and research and development engineers/scientists.

Accordingly, to prepare materials engineers and scientists of the future, *Foundations of Materials Science and Engineering* is designed to present diverse topics in the field with appropriate breadth and depth. The strength of the book is in its balanced presentation of concepts in science of materials (basic knowledge) and engineering of materials (applied knowledge). The basic and applied concepts are integrated through concise textual explanations, relevant and stimulating imagery, detailed sample problems, electronic supplements, and homework problems. This textbook is therefore suitable for both an introductory course in materials at the sophomore level and a more advanced (junior/senior level) second course in materials science and engineering. Finally, the sixth edition and its supporting resources are designed to address a variety of student learning styles based on the well-known belief that not all students learn in the same manner and with the same tools.

The following improvements have been made to the sixth edition:

- Chapter 1, Introduction to Materials Science and Engineering, has been updated to reflect the most recent available data on the use of various classes of materials in diverse industries. The use of materials in aerospace and automotive industries is discussed in detail. The historical competition among major classes of materials has been discussed in more detail and updated.
- All chapters have been reviewed for accuracy of content, images, and tables. New images representing more recent engineering applications have been included in all chapters. Diffusivity data in Chapter 5 has been updated. The mechanical property discussion in Chapter 6 has been expanded to include modulus of resilience and toughness. The iron-carbon phase diagram in Chapter 9 has been updated and improved. The concept of glass transition temperature has been expanded upon in the discussion of polymers in Chapter 10. The classification of composite materials in Chapter 12 has been expanded and improved. In Chapter 13, the sign convention in reporting the half-cell potentials has been made consistent with IUPAC conventions. The state of the art in microprocessor manufacturing, capability, and design has been updated.

- The end-of-chapter problems have been classified according to the learning/understanding level expected from the student by the instructor. The classification is based on Bloom's Taxonomy and is intended to help students as well as instructors to set goals and standards for learning objectives. The first group in the classification is the Knowledge and Comprehension Problems. These problems will require students to show learning at the most basic level of recall of information and recognition of facts. Most problems ask the students to perform tasks such as define, describe, list, and name. The second group is the Application and Analysis Problems. In this group, students are required to apply the learned knowledge to the solution of a problem, demonstrate a concept, calculate, and analyze. Finally, the third class of problems is called Synthesis and Evaluation Problems. In this class of problems, the students are required to judge, evaluate, design, develop, estimate, assess, and in general synthesize new understanding based on what they have learned from the chapter. It is worth noting that this classification is not indicative of the level of difficulty, but simply different cognitive levels.
- For most chapters, new problems—mostly in the synthesis and evaluation category—have been developed. These problems are intended to make the students think in a more in-depth and reflective manner. This is an important objective of the authors to help instructors to train engineers and scientists who operate at a higher cognitive domain.
- The instructors' PowerPoint® lectures have been updated according to the changes made to various chapters. These detailed, yet succinct, PowerPoint lectures are highly interactive and contain technical video clips, tutorials for problem solving, and virtual laboratory experiments. The PowerPoint lectures are designed to address a variety of learning styles including innovative, analytic, common sense, and dynamic learners. Not only is this a great presentation tool for the instructor, it creates interest in the student to learn the subject more effectively. We strongly recommend that the instructors for this course view and test these PowerPoint lecture presentations. This could be especially helpful for new instructors.

Additional resources available through the Instructor Resources are interactive quizzing, and step-by-step, real-life processes; animations; and a searchable materials properties database.

ACKNOWLEDGMENTS

The co-author, Javad Hashemi, would like to dedicate his efforts on this textbook to the eternal-loving memory of his parents Seyed-Hashem and Sedigheh; to his wife, mentor, and friend, Eva; to his sons Evan Darius and Jonathon Cyrus; and last but not least to his siblings (thank you for your ceaseless love and support).

The authors would like to acknowledge with appreciation the numerous and valuable comments, suggestions, constructive criticisms, and praise from the following evaluators and reviewers:

Gerald Bourne
Wendy Dannels
Donna Ebenstein
Francesco Madaro
Sam Mil'shtein
Morteza Mohssenzadeh
Masoud Naghedolfeizi
Margaret Pinnell
Ranji Vaidyanathan

Javad Hashemi

ABOUT THE COVER

A race car is an example of a complex mechanical system that utilizes a variety of materials from all five classes in its structure. For instance, for the race car in the image, the body is made of lightweight carbon fiber composites to save weight, the chassis is made of strong and tough steel alloys, the tires are made of durable volcanized rubber, key components in the engine and brake system are either made of or coated with ceramic materials to withstand high temperature, and a variety of sensors as well as the on-board computer system uses electronic materials. The design and selection of materials for the race car is based on many factors including safety, performance, durability, and cost.

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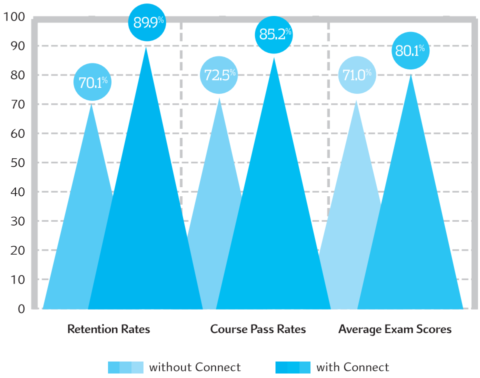

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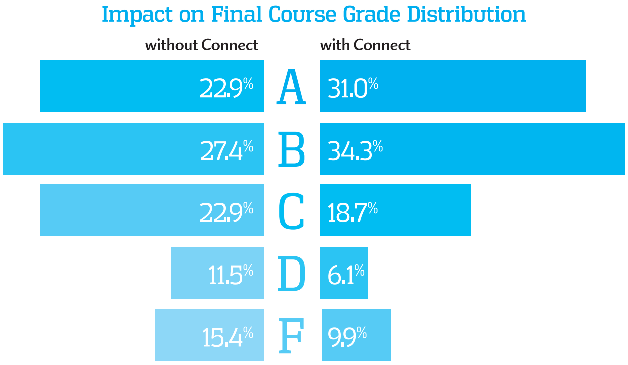

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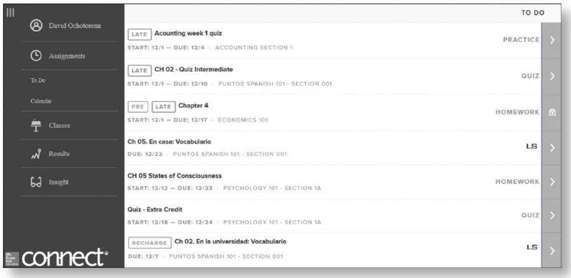

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PRACTICE

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QUIZ

PRE LATE Chapter 4
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HOMEWORK

Ch 05. En casa: Vocabulario
DUE: 12/22 · PUNTOS SPANISH 101 - SECTION 001
LS

CH 05 States of Consciousness
START: 12/12 — DUE: 12/23 · PSYCHOLOGY 101 - SECTION 1A
HOMEWORK

Quiz - Extra Credit
START: 12/18 — DUE: 12/24 · PSYCHOLOGY 101 - SECTION 1A
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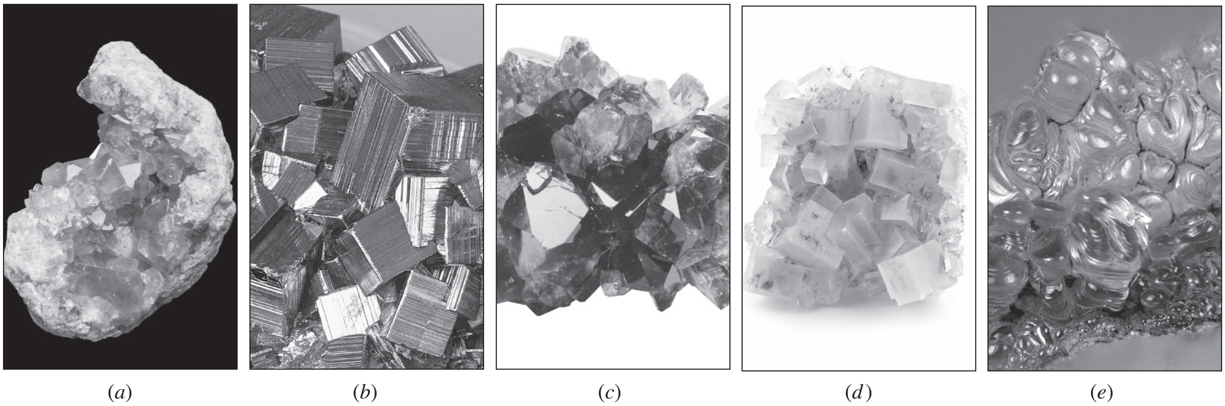
CHAPTER

3

Crystal and Amorphous Structure in Materials


(*a*) (*b*) (*c*) (*d*) (*e*)

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Solids may be categorized broadly into crystalline and amorphous solids. Crystalline solids, due to orderly structure of their atoms, molecules, or ions, possess well-defined shapes. Metals are crystalline and are composed of well-defined crystals or grains. The grains are small and are not clearly observable due to the opaque nature of metals. In minerals, mostly translucent to transparent in nature, the well-defined crystalline shapes are clearly observable. The following images show the crystalline nature of minerals such as (*a*) celestite ($SrSo_4$) with a sky blue or celestial color, (*b*) pyrite (FeS_2), also called "fool's gold" due to its brassy yellow color, (*c*) amethyst (SiO_2), a purple variety of quartz, and (*d*) halite (NaCl), better known as rock salt. In contrast, amorphous solids have poor or no long-range order and do not solidify with the symmetry and regularity of crystalline solids. As an example, the amorphous structure of hyalite opal or glass opal is shown in Figure e. Note the lack of symmetry and of sharp and well-defined crystal edges. ■

LEARNING OBJECTIVES

By the end of this chapter, students will be able to

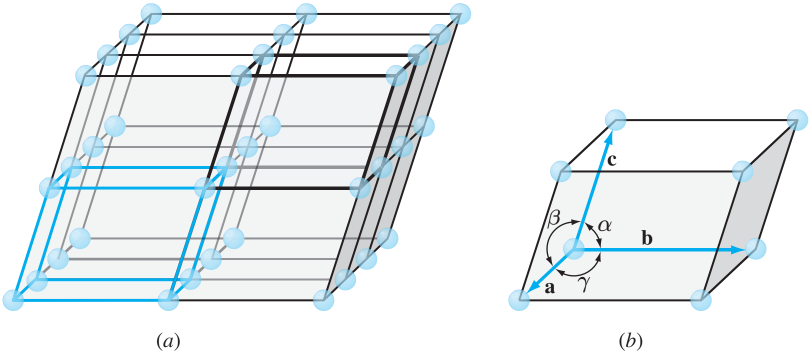
1. Describe what crystalline and noncrystalline (amorphous) materials are.
2. Learn how atoms and ions in solids are arranged in space and identify the basic building blocks of solids.
3. Describe the difference between atomic structure and crystal structure for solid material.
4. Distinguish between crystal structure and crystal system.
5. Explain why plastics cannot be 100 percent crystalline in structure.
6. Explain polymorphism or allotropy in materials.
7. Compute the densities for metals having body-centered and face-centered cubic structures.
8. Describe how to use the X-ray diffraction method for material characterization.
9. Write the designation for atom position, direction indices, and Miller indices for cubic crystals. Specify what are the three densely packed structures for most metals. Determine Miller-Bravais indices for hexagonal close-packed structure. Be able to draw directions and planes in cubic and hexagonal crystals.

3.1 THE SPACE LATTICE AND UNIT CELLS

The physical structure of solid materials of engineering importance depends mainly on the arrangements of the atoms, ions, or molecules that make up the solid and the bonding forces between them. If the atoms or ions of a solid are arranged in a pattern that repeats itself in three dimensions, they form a solid that has *long-range order* (LRO) and is referred to as a *crystalline solid* or *crystalline material.* Examples of crystalline materials are metals, alloys, and some ceramic materials. In contrast to crystalline materials, there are some materials whose atoms and ions are not arranged in a long-range, periodic, and repeatable manner and possess only *short-range order* (SRO). This means that order exists only in the immediate neighborhood of an atom or a molecule. As an example, liquid water has short-range order in its molecules in which one oxygen atom is covalently bonded to two hydrogen atoms. But this order disappears as each molecule is bonded to other molecules through weak secondary bonds in a random manner. Materials with only short-range order are classified as *amorphous* (without form) or noncrystalline. A more detailed definition and some examples of amorphous materials are given in Section 3.12.

Animation
Tutorial

Atomic arrangements in crystalline solids can be described by referring the atoms to the points of intersection of a network of lines in three dimensions. Such a network is called a **space lattice** (Fig. 3.1*a*), and it can be described as an infinite three-dimensional array of points. Each point in the space lattice has identical surroundings.



(*a*) (*b*)

Figure 3.1
(*a*) Space lattice of ideal crystalline solid. (*b*) Unit cell showing lattice constants.

In an ideal **crystal,** the grouping of **lattice points** about any given point are identical with the grouping about any other lattice point in the crystal lattice. Each space lattice can thus be described by specifying the atom positions in a repeating **unit cell,** such as the one heavily outlined in Figure 3.1*a*. The unit cell may be considered the smallest subdivision of the lattice that maintains the characteristics of the overall crystal. A group of atoms organized in a certain arrangement relative to each other and associated with lattice points constitutes the **motif** or basis. The crystal structure may then be defined as the collection of lattice and basis. It is important to note that atoms do not necessarily coincide with lattice points. The size and shape of the unit cell can be described by three lattice vectors **a, b,** and **c,** originating from one corner of the unit cell (Fig. 3.1*b*). The axial lengths a, b, and c and the interaxial angles α, β, and γ are the *lattice constants* of the unit cell.

3.2 CRYSTAL SYSTEMS AND BRAVAIS LATTICES

Tutorial

By assigning specific values for axial lengths and interaxial angles, unit cells of different types can be constructed. Crystallographers have shown that only seven different types of unit cells are necessary to create all space lattices. These crystal systems are listed in Table 3.1.

Many of the seven crystal systems have variations of the basic unit cell. A.J. Bravais[1] showed that 14 standard unit cells could describe all possible lattice networks. These Bravais lattices are illustrated in Figure 3.2. There are four basic types of unit cells: (1) simple, (2) body-centered, (3) face-centered, and (4) base-centered.

---

[1] August Bravais (1811–1863). French crystallographer who derived the 14 possible arrangements of points in space.

Table 3.1 Classification of space lattices by crystal system

Crystal System	Axial Lengths and Interaxial Angles	Space Lattice
Cubic	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90°$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90°$	Simple tetragonal Body-centered tetragonal
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90°$	Simple rhombohedral
Hexagonal	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Simple hexagonal
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90° \neq \mathrm{b}$	Simple monoclinic Base-centered monoclinic
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple triclinic

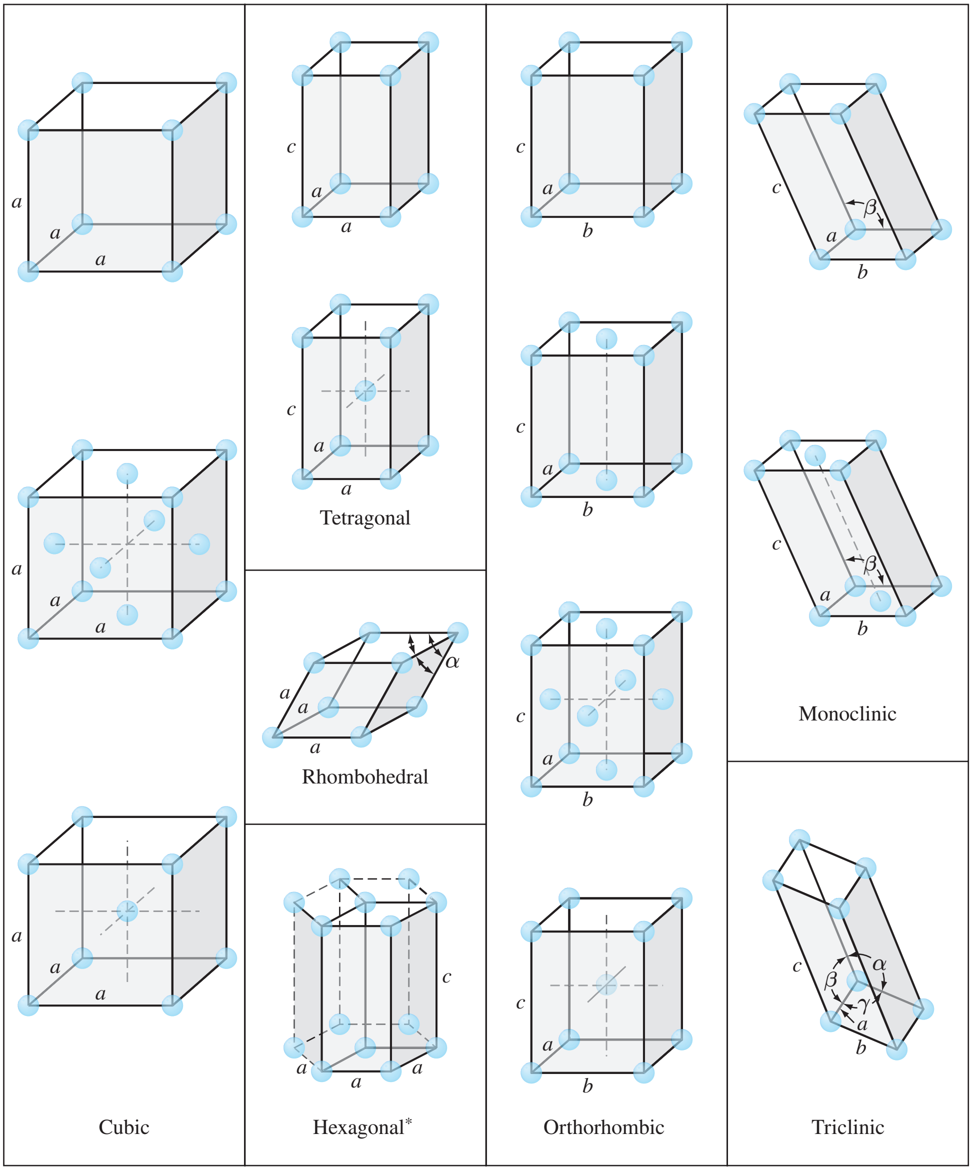
In the cubic system there are three types of unit cells: simple cubic, body-centered cubic, and face-centered cubic. In the orthorhombic system all four types are represented. In the tetragonal system there are only two: simple and body-centered. The face-centered tetragonal unit cell appears to be missing but can be constructed from four body-centered tetragonal unit cells. The monoclinic system has simple and base-centered unit cells, and the rhombohedral, hexagonal, and triclinic systems have only one simple type of unit cell.

3.3 PRINCIPAL METALLIC CRYSTAL STRUCTURES

In this chapter, the principal crystal structures of elemental metals will be discussed in detail. Most ionic and covalent materials also possess a crystal structure which will be discussed in detail in Chapter 11.

Most elemental metals (about 90%) crystallize upon solidification into three densely packed crystal structures: **body-centered cubic (BCC)** (Fig. 3.3*a*), **face-centered cubic (FCC)** (Fig. 3.3*b*), and **hexagonal close-packed (HCP)** (Fig. 3.3*c*). The HCP structure is a denser modification of the simple hexagonal crystal structure shown in Figure 3.2. Most metals crystallize in these dense-packed structures because energy is released as the atoms come closer together and bond more tightly with each other. Thus, the densely packed structures are in lower and more stable energy arrangements.

The extremely small size of the unit cells of crystalline metals that are shown in Figure 3.3 should be emphasized. The cube side of the unit cell of body-centered cubic iron, for

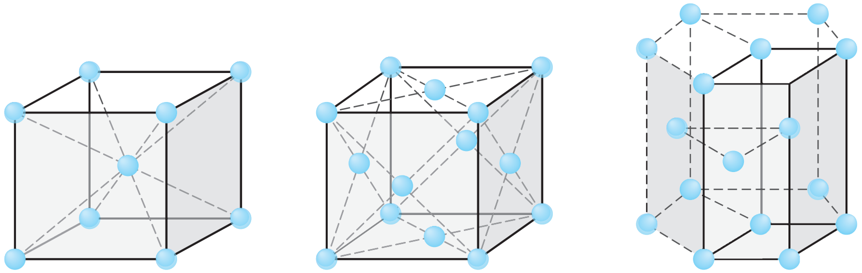


Tutorial Animation

Figure 3.2

The 14 Bravais conventional unit cells grouped according to crystal system. The dots indicate lattice points that, when located on faces or at corners, are shared by other identical lattice unit cells.

(Source: W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* vol. 1: "Structure," Wiley, 1964, p. 47.)



(*a*) (*b*) (*c*)

Figure 3.3
Principal metal crystal structure and unit cells: (*a*) body-centered cubic, (*b*) face-centered cubic, (c) hexagonal close-packed crystal structure (the unit cell is shown by solid lines).

example, at room temperature is equal to 0.287×10^{-9} m, or 0.287 nanometer (nm).[2] Therefore, if unit cells of pure iron are lined up side by side, in 1 mm there will be

$$1 \text{ mm} \times \frac{1 \text{ unit cell}}{0.287 \text{ nm} \times 10^{-6} \text{ mm/nm}} = 3.48 \times 10^{6} \text{ unit cells!}$$

Let us now examine in detail the arrangement of the atoms in the three principal crystal structure unit cells. Although an approximation, we shall consider atoms in these crystal structures to be hard spheres. The distance between the atoms (interatomic distance) in crystal structures can be determined experimentally by X-ray diffraction analysis.[3] For example, the interatomic distance between two neighboring aluminum atoms in a piece of pure aluminum at 20°C is 0.286 nm. The radius of the aluminum atom in the aluminum metal is assumed to be half the interatomic distance, or 0.143 nm. The atomic radii of selected metals are listed in Tables 3.2 to 3.4.

3.3.1 Body-Centered Cubic (BCC) Crystal Structure

First, consider the atomic-site unit cell for the BCC crystal structure shown in Figure 3.4*a*. In this unit cell, the solid spheres represent the centers where atoms are located and clearly indicate their relative positions. If we represent the atoms in this cell as hard spheres, then the unit cell appears as shown in Figure 3.4*b*. In this unit cell, we see that the central atom is surrounded by eight nearest neighbors and is said to have a coordination number of 8.

Animation
Tutorial

If we isolate a single hard-sphere unit cell, we obtain the model shown in Figure 3.4*c*. Each of these cells has the equivalent of two atoms per unit cell. One complete atom is located at the center of the unit cell, and an eighth of a sphere (an

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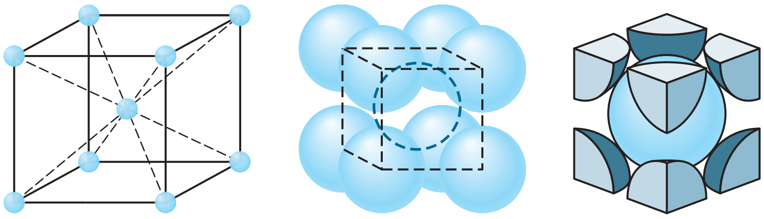
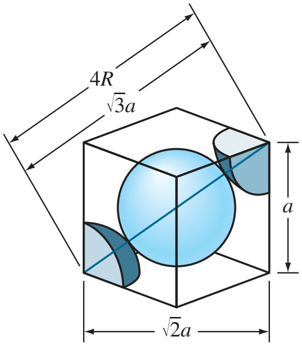
[2] 1 nanometer = 10^{-9} meter.

[3] Some of the principles of X-ray diffraction analysis will be studied in Section 3.11.



(*a*) (*b*) (*c*)

Figure 3.4
BCC unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (*c*) isolated unit cell.



$\sqrt{3}a = 4R$

Figure 3.5
BCC unit cell showing relationship between the lattice constant *a* and the atomic radius *R*.

Tutorial Animation

octant) is located at each corner of the cell, making the equivalent of another atom. Thus, there is a total of 1 (at the center) + 8 × $\frac{1}{8}$(at the corners) = 2 atoms per unit cell. The atoms in the BCC unit cell contact each other across the cube diagonal, as indicated in Figure 3.5, so the relationship between the length of the cube side *a* and the atomic radius *R* is

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

EXAMPLE PROBLEM 3.1

Iron at 20°C is BCC with atoms of atomic radius 0.124 nm. Calculate the lattice constant *a* for the cube edge of the iron unit cell.

■ **Solution**

From Figure 3.5 it is seen that the atoms in the BCC unit cell touch across the cube diagonals. Thus, if *a* is the length of the cube edge, then

$$\sqrt{3}a = 4R \tag{3.1}$$

where *R* is the radius of the iron atom. Therefore, considering that three significant digits should be used in all calculations, the answer will be (use three significant digits for $\sqrt{3}$)

$$a = \frac{4R}{\sqrt{3}} = \frac{4(0.124\text{ nm})}{\sqrt{3}} = 0.287\text{ nm} \blacktriangleleft$$

use three significant digits

Table 3.2 Selected metals that have the BCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

Metal	Lattice Constant a (nm)	Atomic Radius R* (nm)
Chromium	0.289	0.125
Iron	0.287	0.124
Molybdenum	0.315	0.136
Potassium	0.533	0.231
Sodium	0.429	0.186
Tantalum	0.330	0.143
Tungsten	0.316	0.137
Vanadium	0.304	0.132

*Calculated from lattice constants by using Eq. (3.1), $R = \sqrt{3}\,a/4$.

If the atoms in the BCC unit cell are considered to be spherical, an **atomic packing factor** (APF) can be calculated by using the equation

$$\text{APF} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}} \tag{3.2}$$

Using this equation, the APF for the BCC unit cell (Fig. 3.4*c*) is calculated to be 68% (see Example Problem 3.2). That is, 68% of the volume of the BCC unit cell is occupied by atoms and the remaining 32% is empty space. The BCC crystal structure is *not* a close-packed structure since the atoms could be packed closer together. Many metals such as iron, chromium, tungsten, molybdenum, and vanadium have the BCC crystal structure at room temperature. Table 3.2 lists the lattice constants and atomic radii of selected BCC metals.

EXAMPLE PROBLEM 3.2

Calculate the atomic packing factor (APF) for the BCC unit cell, assuming the atoms to be hard spheres.

■ Solution

$$\text{APF} = \frac{\text{volume of atoms in BCC unit cell}}{\text{volume of BCC unit cell}} \tag{3.2}$$

Since there are two atoms per BCC unit cell, the volume of atoms in the unit cell of radius R is

$$V_{\text{atoms}} = (2)\left(\frac{4}{3}\pi R^3\right) = 8.373\,R^3$$

The volume of the BCC unit cell is

$$V_{\text{unit cell}} = a^3$$

Tutorial

where a is the lattice constant. The relationship between a and R is obtained from Figure 3.5, which shows that the atoms in the BCC unit cell touch each other across the cubic diagonal. Thus,

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

Thus,

$$V_{\text{unit cell}} = a^3 = 12.32R^3$$

The atomic packing factor for the BCC unit cell is, therefore,

$$\text{APF} = \frac{V_{\text{atoms}}/\text{unit cell}}{V_{\text{unit cell}}} = \frac{8.373R^3}{12.32R^3} = 0.6796 \approx 0.68 \blacktriangleleft$$

3.3.2 Face-Centered Cubic (FCC) Crystal Structure

Consider next the FCC lattice-point unit cell of Figure 3.6*a*. In this unit cell, there is one lattice point at each corner of the cube and one at the center of each cube face. The hard-sphere model of Figure 3.6*b* indicates that the atoms in the FCC crystal structure are packed as close together as possible, and are thus called a close-packed structure. The APF for this close-packed structure is 0.74 as compared to 0.68 for the BCC structure, which is not close-packed.

The FCC unit cell as shown in Figure 3.6*c* has the equivalent of four atoms per unit cell. The eight corner octants account for one atom ($8 \times \frac{1}{8} = 1$), and the six half-atoms on the cube faces contribute another three atoms, making a total of four atoms per unit cell. The atoms in the FCC unit cell contact each other across the cubic face diagonal, as indicated in Figure 3.7, so the relationship between the length of the cube side a and the atomic radius R is

$$\sqrt{2}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

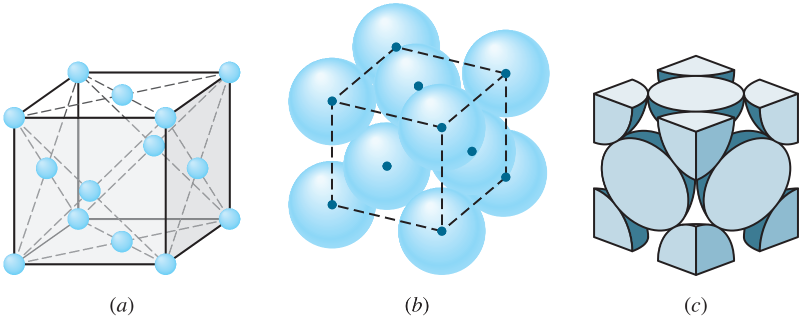


Figure 3.6
FCC unit cells: (*a*) atomic-site unit cell, (*b*) hard-sphere unit cell, and (*c*) isolated unit cell.

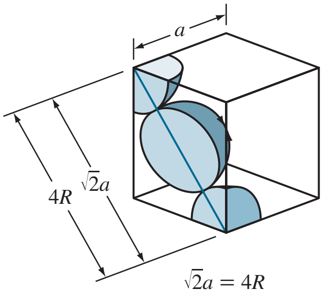


Figure 3.7
FCC unit cell showing relationship between the lattice constant *a* and atomic radius *R*. Since the atoms touch across the face diagonals, $\sqrt{2}a = 4R$.

Tutorial
Animation

The APF for the FCC crystal structure is 0.74, which is greater than the 0.68 factor for the BCC structure. The APF of 0.74 is for the closest packing possible of “spherical atoms.” Many metals such as aluminum, copper, lead, nickel, and iron at elevated temperatures (912°C to 1394°C) crystallize with the FCC crystal structure. Table 3.3 lists the lattice constants and atomic radii for some selected FCC metals.

3.3.3 Hexagonal Close-Packed (HCP) Crystal Structure

The third common metallic crystal structure is the hexagonal close-packed (HCP) structure shown in Figures 3.8*a* and *b*. Metals do not crystallize into the simple hexagonal crystal structure shown in Figure 3.2 because the APF is too low. The atoms can attain a lower energy and a more stable condition by forming the HCP structure of Figure 3.8*b*. The APF of the HCP crystal structure is 0.74, the same as that for the FCC crystal structure since in both structures the atoms are packed as tightly as

Table 3.3 Selected metals that have the FCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

Metal	Lattice Constant *a* (nm)	Atomic Radius *R** (nm)
Aluminum	0.405	0.143
Copper	0.3615	0.128
Gold	0.408	0.144
Lead	0.495	0.175
Nickel	0.352	0.125
Platinum	0.393	0.139
Silver	0.409	0.144

*Calculated from lattice constants by using Eq. 3.3, $R = \sqrt{2}a/4$.

Tutorial

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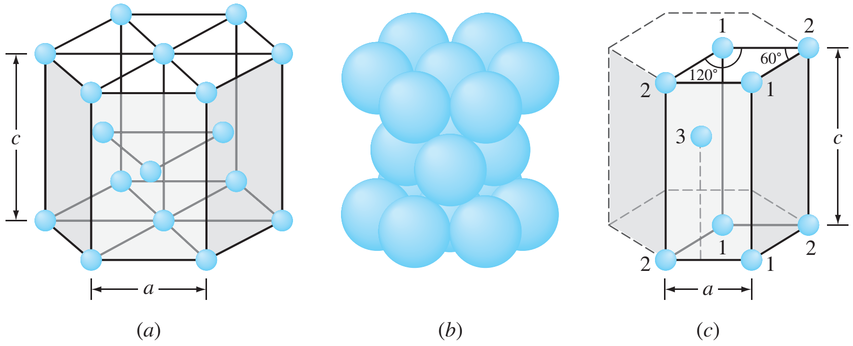


Figure 3.8

HCP crystal structure: (*a*) schematic of the crystal structure, (*b*) hard-sphere model, and (*c*) isolated unit cell schematic.

(Source: F.M. Miller *Chemistry: Structure and Dynamics,* McGraw-Hill, 1984, p. 296.)

possible. In both the HCP and FCC crystal structures, each atom is surrounded by 12 other atoms, and thus both structures have a coordination number of 12. The differences in the atomic packing in FCC and HCP crystal structures will be discussed in Section 3.8.

The isolated HCP unit cell, also called the *primitive cell,* is shown in Figure 3.8*c*. The atoms at locations marked "1" on Figure 3.8*c* contribute $\frac{1}{6}$ of an atom to the unit cell. The atoms at locations marked "2" contribute $\frac{1}{12}$ of an atom to the unit cell.

Thus, the atoms at the eight corners of the unit cell collectively contribute one atom $(4(\frac{1}{6}) + 4(\frac{1}{12}) = 1)$. The atom at location "3" is centered inside the unit cell but extends slightly beyond the boundary of the cell. The total number of atoms inside an HCP unit cell is therefore two (one at corners and one at center). In some textbooks the HCP unit cell is represented by Figure 3.8*a* and is called the "larger cell." In such a case, one finds six atoms per unit cell. This is mostly for convenience, and the true unit cell is presented in Figure 3.8*c* by the solid lines. When presenting the topics of crystal directions and planes we will also use the larger cell for convenience, in addition to the primitive cell.

The ratio of the height c of the hexagonal prism of the HCP crystal structure to its basal side a is called the *c/a ratio* (Fig. 3.8*a*). The *c/a ratio* for an ideal HCP crystal structure consisting of uniform spheres packed as tightly together as possible is 1.633. Table 3.4 lists some important HCP metals and their *c/a* ratios. Of the metals listed, cadmium and zinc have *c/a* ratios higher than the ideal ratio, which indicates that the atoms in these structures are slightly elongated along the c axis of the HCP unit cell. The metals magnesium, cobalt, zirconium, titanium, and beryllium have *c/a* ratios less than the ideal ratio. Therefore, in these metals, the atoms are slightly compressed in the direction along the c axis. Thus, for the HCP metals listed in Table 3.4, there is a certain amount of deviation from the ideal hard-sphere model.

Table 3.4 Selected metals that have the HCP crystal structure at room temperature (20°C) and their lattice constants, atomic radii, and *c/a* ratios

Metal	Lattice Constants (nm) *a*	Lattice Constants (nm) *c*	Atomic Radius *R* (nm)	*c/a* Ratio	% Deviation from Ideality
Cadmium	0.2973	0.5618	0.149	1.890	+15.7
Zinc	0.2665	0.4947	0.133	1.856	+13.6
Ideal HCP				1.633	0
Magnesium	0.3209	0.5209	0.160	1.623	−0.66
Cobalt	0.2507	0.4069	0.125	1.623	−0.66
Zirconium	0.3231	0.5148	0.160	1.593	−2.45
Titanium	0.2950	0.4683	0.147	1.587	−2.81
Beryllium	0.2286	0.3584	0.113	1.568	−3.98

EXAMPLE PROBLEM 3.3

a. Calculate the volume of the zinc crystal structure unit cell by using the following data: pure zinc has the HCP crystal structure with lattice constants $a = 0.2665$ nm and $c = 0.4947$ nm.

b. Find the volume of the larger cell.

■ **Solution**

The volume of the zinc HCP unit cell can be obtained by determining the area of the base of the unit cell and then multiplying this by its height (Fig. EP3.3).

a. The area of the base of the unit cell is area *ABDC* of Figure EP3.3*a* and *b*. This total area consists of the areas of two equilateral triangles of area *ABC* of Figure EP3.3*b*. From Figure EP3.3*c*,

$$\text{Area of triangle } ABC = \tfrac{1}{2}(\text{base})(\text{height})$$
$$= \tfrac{1}{2}(a)(a\ \sin 60°) = \tfrac{1}{2}a^2 \sin 60°$$

From Figure EP3.3*b*,

$$\text{Total area of HCP base, area } ABDC = (2)(\tfrac{1}{2}a^2 \sin 60°)$$
$$= a^2 \sin 60°$$

From Figure EP3.3*a*,

$$\text{Volume of zinc HCP unit cell} = (a^2 \sin 60°)(c)$$
$$= (0.2665\ \text{nm})^2(0.8660)(0.4947\ \text{nm})$$
$$= 0.03043\ \text{nm}^3 \blacktriangleleft$$

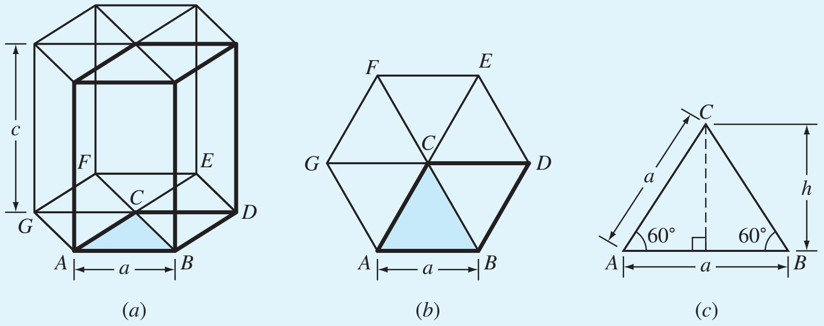


Figure EP3.3
Diagrams for calculating the volume of an HCP unit cell. (*a*) HCP unit cell. (*b*) Base of HCP unit cell. (*c*) Triangle ABC removed from base of unit cell.

b. From Figure EP3.3*a*,

$$\begin{aligned}\text{Volume of “large” zinc HCP cell} &= 3(\text{volume of the unit cell or primitive cell}) \\ &= 3(0.0304) = 0.09130\ \text{nm}^3\end{aligned}$$

3.4 ATOM POSITIONS IN CUBIC UNIT CELLS

To locate atom positions in cubic unit cells, we use rectangular *x*, *y*, and *z* axes. In crystallography, the positive *x* axis is usually the direction coming out of the paper, the positive *y* axis is the direction to the right of the paper, and the positive *z* axis is the direction to the top (Fig. 3.9). Negative directions are opposite to those just described.

Tutorial

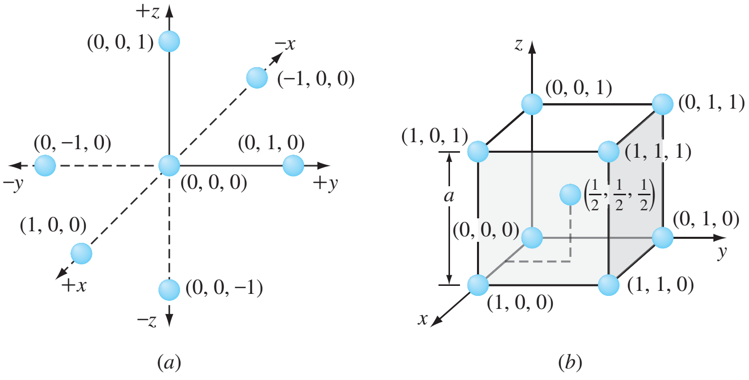


Figure 3.9
(*a*) Rectangular *x, y,* and *z* axes for locating atom positions in cubic unit cells. (*b*) Atom positions in a BCC unit cell.

Atom positions in unit cells are located by using unit distances along the *x, y,* and *z* axes, as indicated in Fig. 3.9*a*. For example, the position coordinates for the atoms in the BCC unit cell are shown in Fig. 3.9*b*. The atom positions for the eight corner atoms of the BCC unit cell are

$$(0, 0, 0)\ (1, 0, 0)\ (0, 1, 0)\ (0, 0, 1)$$
$$(1, 1, 1)\ (1, 1, 0)\ (1, 0, 1)\ (0, 1, 1)$$

The center atom in the BCC unit cell has the position coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. For simplicity, sometimes only two atom positions in the BCC unit cell are specified, which are (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The remaining atom positions of the BCC unit cell are assumed to be understood. In the same way, the atom positions in the FCC unit cell can be located.

3.5 DIRECTIONS IN CUBIC UNIT CELLS

Often it is necessary to refer to specific directions in crystal lattices. This is especially important for metals and alloys with properties that vary with crystallographic orientation. *For cubic crystals, the crystallographic* **direction indices** *are the vector components of the direction resolved along each of the coordinate axes and reduced to the smallest integers.*

To diagrammatically indicate a direction in a cubic unit cell, we draw a direction vector from an origin, which is usually a corner of the cubic cell, until it emerges from the cube surface (Fig. 3.10). The position coordinates of the unit cell where the direction vector emerges from the cube surface after being converted to integers are the direction indices. The direction indices are enclosed by square brackets with no separating commas.

For example, the position coordinates of the direction vector *OR* in Figure 3.10*a* where it emerges from the cube surface are (1, 0, 0), and so the direction indices for the direction vector *OR* are [100]. The position coordinates of the direction vector *OS* (Fig. 3.10*a*) are (1, 1, 0), and so the direction indices for *OS* are [110]. The position coordinates for the direction vector *OT* (Fig. 3.10*b*) are (1, 1, 1), and so the direction indices of *OT* are [111].

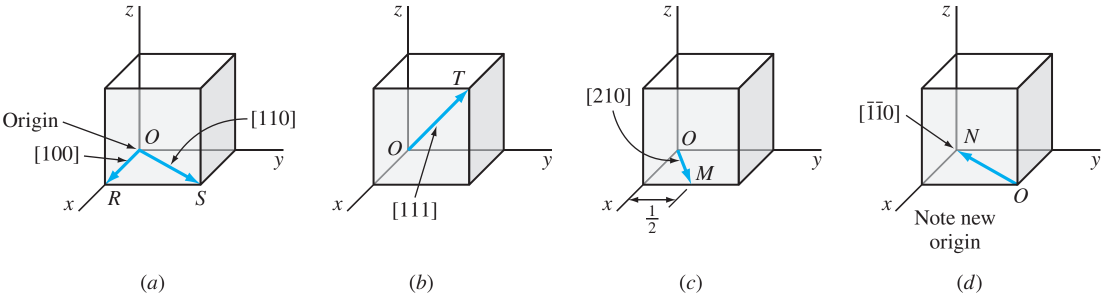


Figure 3.10
Some directions in cubic unit cells.

Tutorial

The position coordinates of the direction vector *OM* (Fig. 3.10*c*) are $(1, \frac{1}{2}, 0)$, and since the direction vectors must be integers, these position coordinates must be multiplied by 2 to obtain integers. Thus, the direction indices of *OM* become $2\left(1, \frac{1}{2}, 0\right) = [210]$. The position coordinates of the vector *ON* (Fig. 3.10*d*) are $(-1, -1, 0)$. A negative direction index is written with a bar over the index. Thus, the direction indices for the vector *ON* are $[\bar{1}\bar{1}0]$. Note that to draw the direction *ON* inside the cube, the origin of the direction vector had to be moved to the front lower-right corner of the unit cube (Fig. 3.10*d*). Further examples of cubic direction vectors are given in Example Problem 3.4.

Often it is useful to determine the angle between two crystal directions. In addition to geometrical analysis, we can use the definitions of dot product to determine the angles between any two direction vectors. Recall from your knowledge of vectors that

$$A \cdot B = \| A \| \, \| B \| \cos \theta; \; A = a_x i + a_y j + a_z k \text{ and } B = b_x i + b_y j + b_z k$$

$$\begin{aligned} & & & \textit{also,} \\ A \cdot B & = & & a_x b_x + a_y b_y + a_z b_z \\ & & & \textit{therefore,} \\ \cos \theta & = & & \frac{a_x b_x + a_y b_y + a_z b_z}{\| A \| \, \| B \|} \end{aligned} \tag{3.4}$$

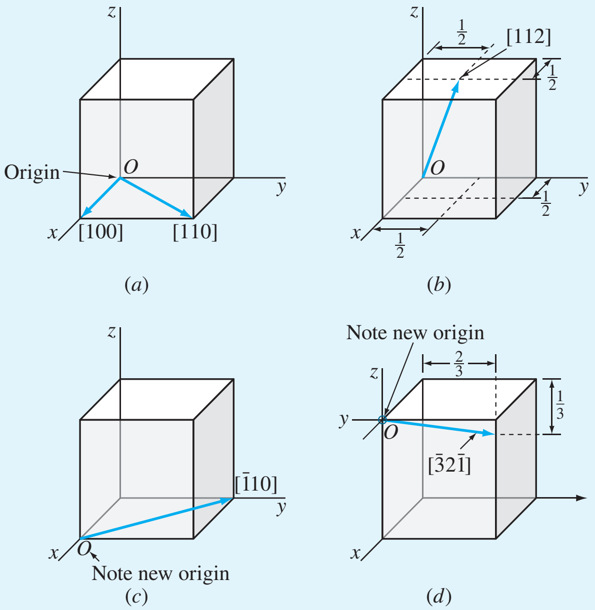
EXAMPLE PROBLEM 3.4

Draw the following direction vectors in cubic unit cells:

a. [100] and [110]
b. [112]
c. $[\bar{1}10]$
d. $[\bar{3}2\bar{1}]$
e. Find the angle between [100] and [110]
f. Find the angle between [112] and $[\bar{1}10]$

■ **Solution**

a. The position coordinates for the [100] direction are (1, 0, 0) (Fig. EP3.4*a*). The position coordinates for the [110] direction are (1, 1, 0) (Fig. EP3.4*a*).
b. The position coordinates for the [112] direction are obtained by dividing the direction indices by 2 so that they will lie within the unit cube. Thus, they are $(\frac{1}{2}, \frac{1}{2}, 1)$ (Fig. EP3.4*b*).
c. The position coordinates for the $[\bar{1}10]$ direction are $(-1, 1, 0)$ (Fig. EP3.4*c*). Note that the origin for the direction vector must be moved to the lower-left front corner of the cube.
d. The position coordinates for the $[\bar{3}2\bar{1}]$ direction are obtained by first dividing all the indices by 3, the largest index. This gives $-1, \frac{2}{3}, -\frac{1}{3}$ for the position coordinates of the exit point of the direction $[\bar{3}2\bar{1}]$, which are shown in Figure EP3.4*d*.



Tutorial

Figure EP3.4
Direction vectors in cubic unit cells.

e. The angle between directions [100] and [110] can be determined using Eq. 3.4 as follows:

$$\|\boldsymbol{A}\| = \sqrt{1^2 + 0^2 + 0^2} = 1$$

$$\|\boldsymbol{B}\| = \sqrt{1^2 + 1^2 + 0^2} = \sqrt{2}$$

$$\cos\theta = \frac{a_x b_x + a_y b_y + a_z b_z}{\|\boldsymbol{A}\|\,\|\boldsymbol{B}\|} = \frac{(1)(1) + (0)(1) + (0)(0)}{(1)\left(\sqrt{2}\right)} = \frac{1}{\sqrt{2}}$$

$$\theta = 45^\circ$$

f. The angle between directions [112] and [$\bar{1}$10] can be determined using Eq. 3.4 as follows:

$$\|\boldsymbol{A}\| = \sqrt{1^2 + 1^2 + 2^2} = \sqrt{6}$$

$$\|\boldsymbol{B}\| = \sqrt{-1^2 + 1^2 + 0^2} = \sqrt{2}$$

$$\cos\theta = \frac{a_x b_x + a_y b_y + a_z b_z}{\|\boldsymbol{A}\|\,\|\boldsymbol{B}\|} = \frac{(1)(-1) + (1)(1) + (2)(0)}{\left(\sqrt{6}\right)\left(\sqrt{2}\right)} = \frac{0}{\sqrt{12}}$$

$$\theta = 90^\circ$$

The letters *u, v,* and *w* are used in a general sense for the direction indices in the *x, y,* and *z* directions, respectively, and are written as [*uvw*]. It is also important to note that *all parallel direction vectors have the same direction indices.*

Directions are said to be *crystallographically equivalent* if the atom spacing along each direction is the same. For example, the following cubic edge directions are crystallographic equivalent directions:

$$[100],\ [010],\ [001],\ \left[0\bar{1}0\right],\ \left[00\bar{1}\right],\ \left[\bar{1}00\right] \equiv \langle 100\rangle$$

Equivalent directions are called *indices of a family* or *form.* The notation ⟨100⟩ is used to indicate cubic edge directions collectively. Other directions of a form are the cubic body diagonals ⟨111⟩ and the cubic face diagonals ⟨110⟩.

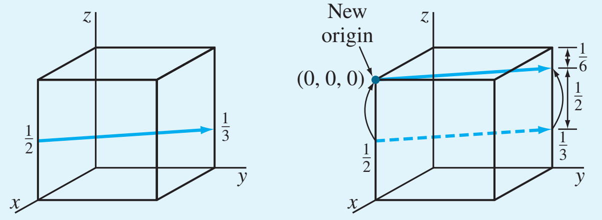
EXAMPLE PROBLEM 3.5

Determine the direction indices of the cubic direction shown in Figure EP3.5*a*.

■ **Solution**

Parallel directions have the same direction indices, and so we move the direction vector in a parallel manner until its tail reaches the nearest corner of the cube, still keeping the vector within the cube. Thus, in this case, the upper-left front corner becomes the new origin for the direction vector (Fig. EP3.5*b*). We can now determine the position coordinates where the direction vector leaves the unit cube. These are $x = -1$, $y = +1$, and $z = -\frac{1}{6}$. The position coordinates of the direction where it leaves the unit cube are thus $(-1, +1, -\frac{1}{6})$. The direction indices for this direction are, after clearing the fraction 6*x*, $(-1, +1, -\frac{1}{6})$, or $[\bar{6}6\bar{1}]$.

Tutorial



(*a*) (*b*)

Figure EP3.5

EXAMPLE PROBLEM 3.6

Determine the direction indices of the cubic direction between the position coordinates $\left(\frac{3}{4}, 0, \frac{1}{4}\right)$ and $\left(\frac{1}{4}, \frac{1}{2}, \frac{1}{2}\right)$.

■ **Solution**

First we locate the origin and termination points of the direction vector in a unit cube, as shown in Figure EP3.6. The fraction vector components for this direction are

$$x = -\left(\frac{3}{4} - \frac{1}{4}\right) = -\frac{1}{2}$$

$$y = \left(\frac{1}{2} - 0\right) = \frac{1}{2}$$

$$= \left(\frac{1}{2} - \frac{1}{4}\right) = \frac{1}{4}$$

Thus, the vector direction has fractional vector components of $-\frac{1}{2}, \frac{1}{2}, \frac{1}{4}$. The direction indices will be in the same ratio as their fractional components. By multiplying the fraction vector components by 4, we obtain $[\bar{2}21]$ for the direction indices of this vector direction.

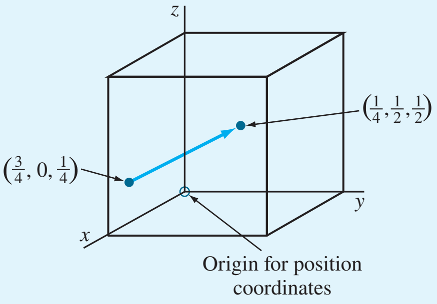


Figure EP3.6

3.6 MILLER INDICES FOR CRYSTALLOGRAPHIC PLANES IN CUBIC UNIT CELLS

Sometimes it is necessary to refer to specific lattice planes of atoms within a crystal structure, or it may be of interest to know the crystallographic orientation of a plane or group of planes in a crystal lattice. To identify crystal planes in cubic crystal structures, the *Miller notation system*[4] is used. The **Miller indices of a crystal plane** are defined as the *reciprocals of the fractional intercepts (with fractions cleared) that the plane makes with the crystallographic x, y, and z axes of the three nonparallel edges of the cubic unit cell.* The cube edges of the unit cell represent unit lengths, and the intercepts of the lattice planes are measured in terms of these unit lengths.

The procedure for determining the Miller indices for a cubic crystal plane is as follows:

1. Choose a plane that does *not* pass through the origin at (0, 0, 0).
2. Determine the intercepts of the plane in terms of the crystallographic *x, y,* and *z* axes for a unit cube. These intercepts may be fractions.

Tutorial

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[4] William Hallowes Miller (1801–1880). English crystallographer who published a "Treatise on Crystallography" in 1839, using crystallographic reference axes that were parallel to the crystal edges and using reciprocal indices.

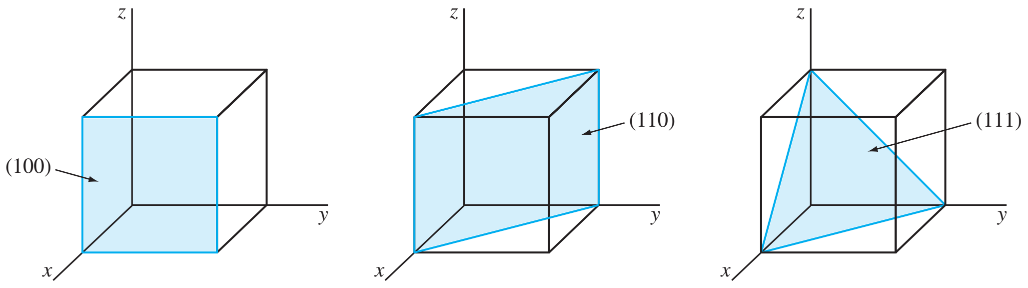
3. Form the reciprocals of these intercepts.
4. Clear fractions and determine the *smallest* set of whole numbers that are in the same ratio as the intercepts. These whole numbers are the Miller indices of the crystallographic plane and are enclosed in parentheses without the use of commas. The notation (hkl) is used to indicate Miller indices in a general sense, where h, k, and l are the Miller indices of a cubic crystal plane for the x, y, and z axes, respectively.

Figure 3.11 shows three of the most important crystallographic planes of cubic crystal structures. Let us first consider the shaded crystal plane in Figure 3.11*a*, which has the intercepts 1, ∞, ∞ for the x, y, and z axes, respectively. We take the reciprocals of these intercepts to obtain the Miller indices, which are therefore 1, 0, 0. Since these numbers do not involve fractions, the Miller indices for this plane are (100), which is read as the one-zero-zero plane. Next let us consider the second plane shown in Figure 3.11*b*. The intercepts of this plane are 1, 1, ∞. Since the reciprocals of these numbers are 1, 1, 0, which do not involve fractions, the Miller indices of this plane are (110). Finally, the third plane (Fig. 3.11*c*) has the intercepts 1, 1, 1, which give the Miller indices (111) for this plane.

Consider now the cubic crystal plane shown in Figure 3.12 that has the intercepts $\frac{1}{3}$, $\frac{2}{3}$, 1. The reciprocals of these intercepts are 3, $\frac{3}{2}$, 1. Since fractional intercepts are not allowed, these fractional intercepts must be multiplied by 2 to clear the $\frac{3}{2}$ fraction. Thus, the reciprocal intercepts become 6, 3, 2, and the Miller indices are (632). Further examples of cubic crystal planes are shown in Example Problem 3.7.

If the crystal plane being considered passes through the origin so that one or more intercepts are zero, the plane must be moved to an equivalent position in the same unit cell, and the plane must remain parallel to the original plane. This is possible because all equispaced parallel planes are indicated by the same Miller indices.

If sets of equivalent lattice planes are related by the symmetry of the crystal system, they are called *planes of a family or form,* and the indices of one plane of the family are enclosed in braces as $\{hkl\}$ to represent the indices of a family of symmetrical planes. For example, the Miller indices of the cubic surface planes (100), (010), and (001) are designated collectively as a family or form by the notation $\{100\}$.



(*a*) (*b*) (*c*)

Tutorial

Figure 3.11
Miller indices of some important cubic crystal planes: (*a*) (100), (*b*) (110), and (*c*) (111).

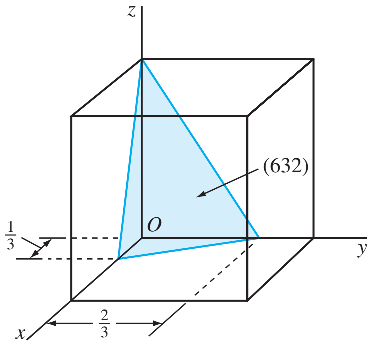


Figure 3.12
Cubic crystal plane (632), which has fractional intercepts.

EXAMPLE PROBLEM 3.7

Draw the following crystallographic planes in cubic unit cells:

a. (101)
b. $(1\bar{1}0)$
c. (221)
d. Draw a (110) plane in a BCC atomic-site unit cell, and list the position coordinates of the atoms whose centers are intersected by this plane.

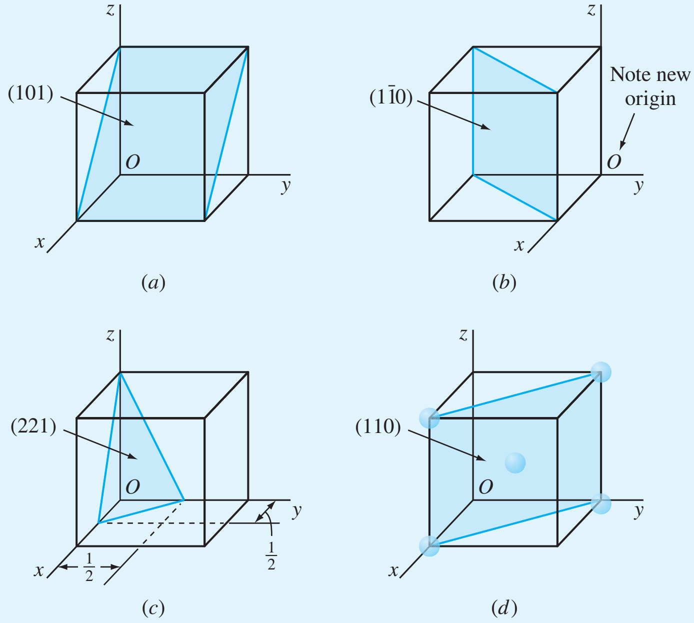


Figure EP3.7
Various important cubic crystal planes.

■ Solution

a. First determine the reciprocals of the Miller indices of the (101) plane. These are 1, ∞, 1. The (101) plane must pass through a unit cube at intercepts $x = 1$ and $z = 1$ and be parallel to the y axis (Fig. EP3.7*a*).

b. First determine the reciprocals of the Miller indices of the $(1\bar{1}0)$ plane. These are1, −1, ∞. The $(1\bar{1}0)$ plane must pass through a unit cube at intercepts $x = 1$ and $y = -1$ and be parallel to the z axis. Note that the origin of axes must be moved to the lower-right back side of the cube (Fig. EP3.7*b*).

c. First determine the reciprocals of the Miller indices of the (221) plane. These are $\frac{1}{2}, \frac{1}{2}, 1$. The (221) plane must pass through a unit cube at intercepts $x = \frac{1}{2}$, $y = \frac{1}{2}$, and $z = 1$ (Fig. EP3.7*c*).

d. Atom positions whose centers are intersected by the (110) plane are (1, 0, 0), (0, 1, 0), (1, 0, 1), (0, 1, 1), and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. These positions are indicated by the solid circles (Fig. EP3.7*d*).

An important relationship for the cubic system, and *only the cubic system,* is that the direction indices of a direction *perpendicular* to a crystal plane are the same as the Miller indices of that plane. For example, the [100] direction is perpendicular to the (100) crystal plane.

In cubic crystal structures, the *interplanar spacing* between two closest parallel planes with the same Miller indices is designated d_{hkl}, where h, k, and l are the Miller indices of the planes. This spacing represents the distance from a selected origin containing one plane and another parallel plane with the same indices that is closest to it. For example, the distance between (110) planes 1 and 2, d_{110}, in Figure 3.13 is AB.

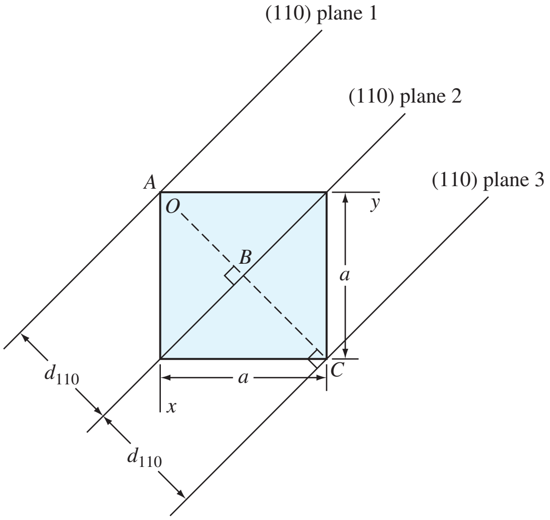


Figure 3.13
Top view of cubic unit cell showing the distance between (110) crystal planes, d_{110}.

Also, the distance between (110) planes 2 and 3 is d_{110} and is length BC in Figure 3.13. From simple geometry, it can be shown that for cubic crystal structures

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.5}$$

where d_{hkl} = interplanar spacing between parallel closest planes with Miller indices h, k, and l

a = lattice constant (edge of unit cube)

h, k, l = Miller indices of cubic planes being considered

EXAMPLE PROBLEM 3.8

Determine the Miller indices of the cubic crystallographic plane shown in Figure EP3.8*a*.

■ **Solution**

First, transpose the plane parallel to the z axis $\frac{1}{4}$ unit to the right along the y axis as shown in Figure EP3.8*b* so that the plane intersects the x axis at a unit distance from the new origin located at the lower-right back corner of the cube. The new intercepts of the transposed plane with the coordinate axes are now $(+1, -\frac{5}{12}, \infty)$. Next, we take the reciprocals of these intercepts to give $(1, -\frac{12}{5}, 0)$. Finally, we clear the $\frac{12}{5}$ fraction to obtain $(5\overline{12}0)$ for the Miller indices of this plane.

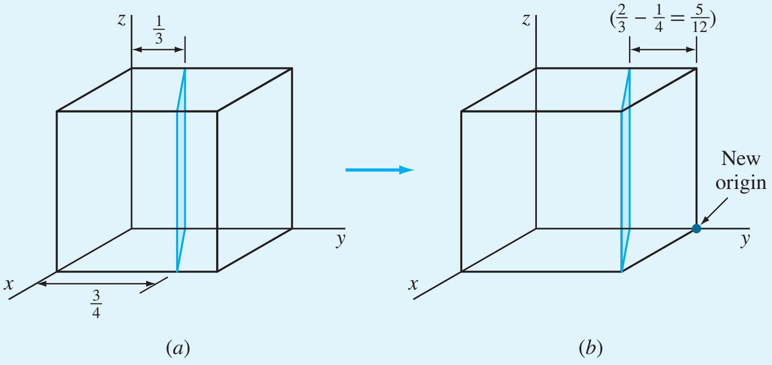


Figure EP3.8

EXAMPLE PROBLEM 3.9

Determine the Miller indices of the cubic crystal plane that intersects the position coordinates $(1, \frac{1}{4}, 0)$, $(1, 1, \frac{1}{2})$, $(\frac{3}{4}, 1, \frac{1}{4})$, and all coordinate axes.

■ **Solution**

First, we locate the three position coordinates as indicated in Figure EP3.9 at *A, B,* and *C.* Next, we join *A* and *B,* extend *AB* to *D,* and then join *A* and *C.* Finally, we join *A* to *C* to complete plane *ACD*. The origin for this plane in the cube can be chosen at *E,* which gives

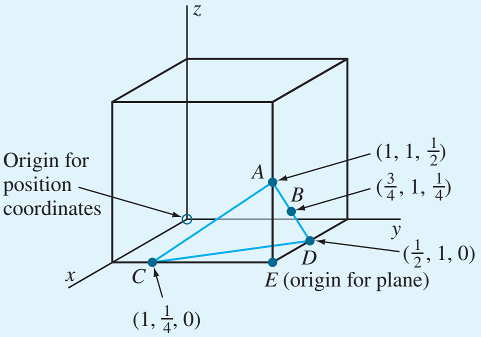


Figure EP3.9

axial intercepts for plane *ACD* at $x = -\frac{1}{2}$, $y = -\frac{3}{4}$, and $z = \frac{1}{2}$. The reciprocals of these axial intercepts are -2, $-\frac{4}{3}$, and 2. Multiplying these intercepts by 3 clears the fraction, giving Miller indices for the plane of $(\bar{6}46)$.

EXAMPLE PROBLEM 3.10

Copper has an FCC crystal structure and a unit cell with a lattice constant of 0.361 nm. What is its interplanar spacing d_{220}?

■ **Solution**

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.361 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.128 \text{ nm} \blacktriangleleft$$

3.7 CRYSTALLOGRAPHIC PLANES AND DIRECTIONS IN HEXAGONAL CRYSTAL STRUCTURE

3.7.1 Indices for Crystal Planes in HCP Unit Cells

Crystal planes in HCP unit cells are commonly identified by using four indices instead of three. The HCP crystal plane indices, called *Miller-Bravais indices,* are denoted by the letters *h, k, i,* and *l* and are enclosed in parentheses as (*hkil*). These four-digit hexagonal indices are based on a coordinate system with four axes, as shown in Figure 3.14 in an HCP unit cell. There are three basal axes, a_1, a_2, and a_3, which make 120° with each other. The fourth axis or *c* axis is the vertical axis located at the center of the unit cell. The *a* unit of measurement along the a_1, a_2, and a_3 axes is the distance between the atoms along these axes and is indicated in Figure 3.14. In the discussion of HCP planes and directions, we will use both the “unit cell” and the “larger cell” for the presentation of concepts. The unit of measurement along the *c* axis is the height of the unit cell. The reciprocals of the intercepts that a crystal plane makes with the a_1, a_2,

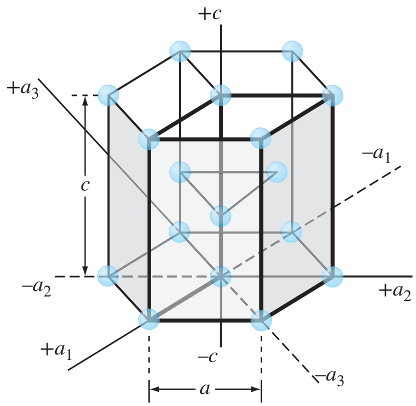
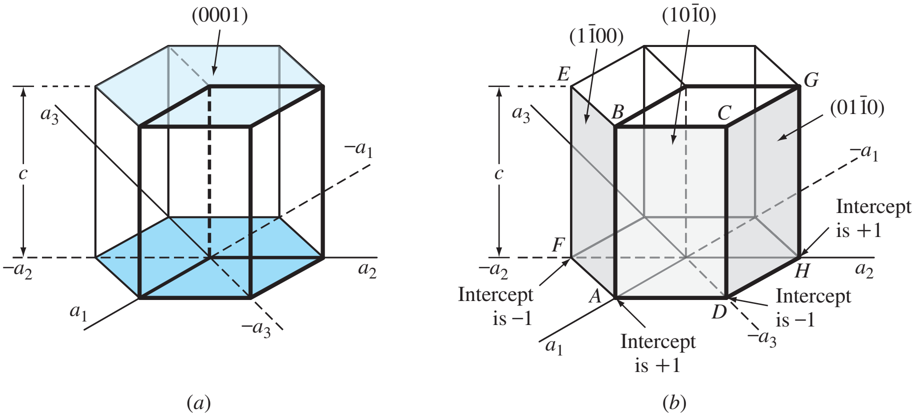


Figure 3.14
The four coordinate axes (a_1, a_2, a_3, and c) of the HCP crystal structure.

and a_3 axes give the h, k, and i indices, while the reciprocal of the intercept with the c axis gives the l index.

Basal Planes The basal planes of the HCP unit cell are very important planes for this unit cell and are indicated in Figure 3.15*a*. Since the basal plane on the top of the HCP unit cell in Figure 3.15*a* is parallel to the a_1, a_2, and a_3 axes, the intercepts of this plane with these axes will be at infinity. Thus, $a_{1\text{intercept}} = \infty$, $a_{2\text{intercept}} = \infty$, and $a_{3\text{intercept}} = \infty$. The c axis, however, is unity since the top basal plane intersects the c axis at unit distance, $c_{\text{intercept}} = 1$. Taking the reciprocals of these intercepts gives the Miller-Bravais indices for the HCP basal plane. Thus $h = 0$, $k = 0$, $i = 0$, and $l = 1$. The HCP basal plane is, therefore, a zero-zero-zero-one or (0001) plane.



(*a*) (*b*)

Figure 3.15
Miller-Bravais indices of hexagonal crystal planes: (*a*) basal planes and (*b*) prism planes.

Prism Planes Using the same method, the intercepts of the front prism plane (*ABCD*) of Figure 3.15*b* are $a_{1\text{intercept}} = +1$, $a_{2\text{intercept}} = \infty$, $a_{3\text{intercept}} = -1$, and $c_{intercept} = \infty$. Taking the reciprocals of these intercepts gives $h = 1$, $k = 0$, $i = -1$, and $l = 0$, or the $(10\bar{1}0)$ plane. Similarly, the *ABEF* prism plane of Figure 3.15*b* has the indices $(\bar{1}100)$ and the *DCGH* plane the indices $(01\bar{1}0)$. All HCP prism planes can be identified collectively as the $\{10\bar{1}0\}$ family of planes.

Sometimes HCP planes are identified only by three indices (*hkl*) since $h + k = -i$. However, the (*hkil*) indices are used more commonly because they reveal the hexagonal symmetry of the HCP unit cell.

3.7.2 Direction Indices in HCP Unit Cells[5]

Directions in HCP unit cells are also usually indicated by four indices *u, v, t,* and *w* enclosed by square brackets as [*uvtw*]. The *u, v,* and *t* indices are lattice vectors in the a_1, a_2, and a_3 directions, respectively (Fig. 3.16), and the *w* index is a lattice vector in the *c* direction. To maintain uniformity for both HCP indices for planes and directions, it has been agreed that $u + v = -t$ for directions.

Let us now determine the Miller-Bravais hexagonal indices for the directions a_1, a_2, and a_3, which are the positive basal axes of the hexagonal unit cell. The a_1 direction indices are given in Figure 3.16*a*, the a_2 direction indices in Figure 3.16*b*, and the a_3 direction indices in Figure 3.16*c*. If we need to indicate a *c* direction also for the a_3 direction, this is shown in Figure 3.16*d*. Figure 3.16*e* summarizes the positive and negative directions on the upper basal plane of the simple hexagonal crystal structure.

3.8 COMPARISON OF FCC, HCP, AND BCC CRYSTAL STRUCTURES

3.8.1 FCC and HCP Crystal Structures

As previously pointed out, both the HCP and FCC crystal structures are close-packed structures. That is, their atoms, which are considered approximate "spheres," are packed together as closely as possible so that an atomic packing factor of 0.74 is attained.[6] The (111) planes of the FCC crystal structure shown in Figure 3.17*a* have a packing arrangement identical to the (0001) planes of the HCP crystal structure shown in Figure 3.17*b*. However, the three-dimensional FCC and HCP crystal structures are not identical because there is a difference in the stacking arrangement of their atomic planes, which can best be described by considering the stacking of hard spheres representing atoms. As a useful analogy, one can imagine the stacking of planes of equal-sized marbles on top of each other, minimizing the space between the marbles.

---

[5] The topic of direction indices for hexagonal unit cells is not normally presented in an introductory course in materials but is included here for advanced students.

[6] As pointed out in Section 3.3, the atoms in the HCP structure deviate to varying degrees from ideality. In some HCP metals, the atoms are elongated along the *c* axis, and in other cases, they are compressed along the *c* axis (see Table 3.4).

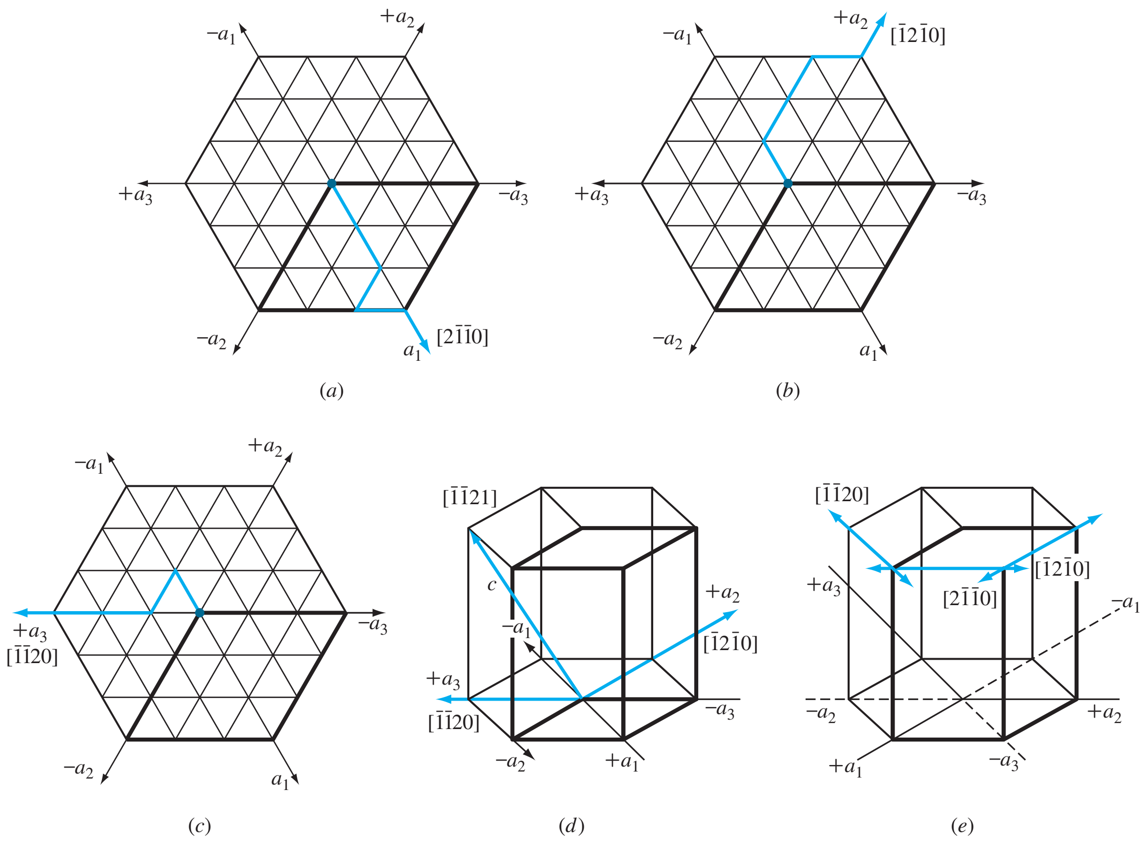


Figure 3.16

Miller-Bravais hexagonal crystal structure direction indices for principal directions: (*a*) $+a_1$ axis direction on basal plane, (*b*) $+a_2$ axis direction on basal plane, (*c*) $+a_3$ direction axis on basal plane, and (*d*) $+a_3$ direction axis incorporating *c* axis. (e) Positive and negative Miller-Bravais directions are indicated in simple hexagonal crystal structure on upper basal plane.

Consider first a plane of close-packed atoms designated the *A* plane, as shown in Figure 3.18. Note that there are two different types of empty spaces or voids between the atoms. The voids pointing to the top of the page are designated *a* voids and those pointing to the bottom of the page, *b* voids. A second plane of atoms can be placed over the *a* or *b* voids, and the same three-dimensional structure will be produced. Let us place plane *B* over the *a* voids, as shown in Figure 3.18*b*. Now if a third plane of atoms is placed over plane *B* to form a closest-packed structure, it is possible to form two different close-packed structures. One possibility is to place the atoms of the third plane in the *b* voids of the *B* plane. Then the atoms of this third plane will lie directly over those of the *A* plane and thus can be designated another *A* plane (Fig. 3.18*c*). If subsequent planes of atoms are placed in this same alternating stacking arrangement, then

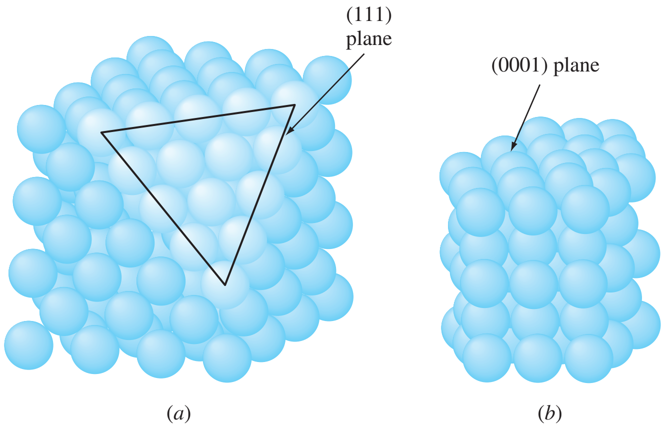


Figure 3.17

Comparison of the (*a*) FCC crystal structure showing a close-packed (111) plane and (*b*) an HCP crystal structure showing the close-packed (0001) plane.

(Source: W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* vol. 1: "Structure," Wiley, 1964, p. 51.)

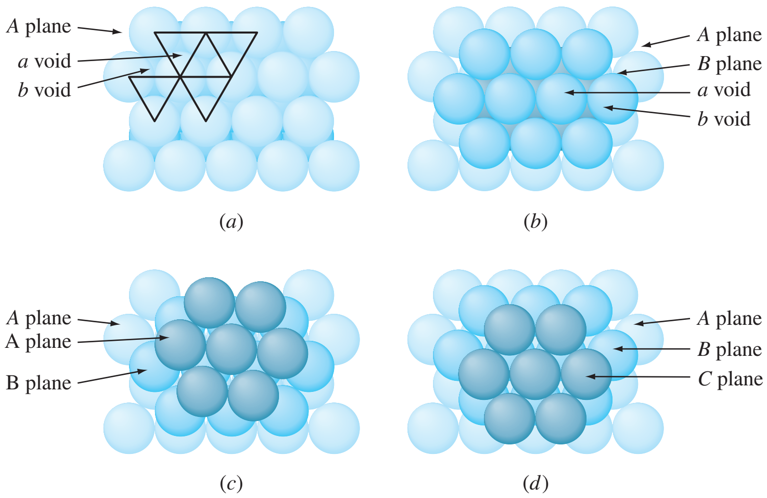
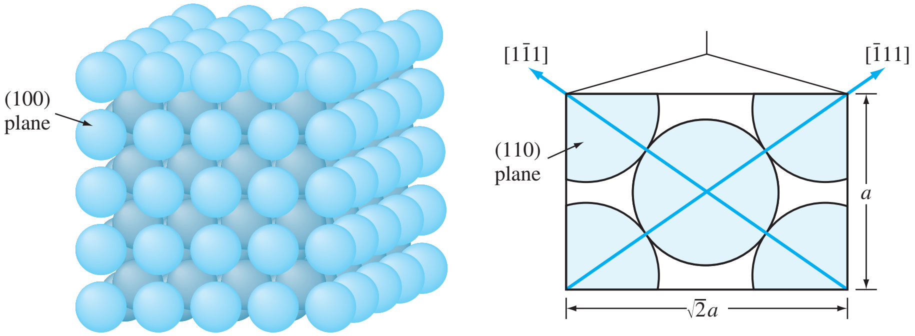


Figure 3.18

Formation of the HCP and FCC crystal structures by the stacking of atomic planes. (*a*) *A* plane showing the *a* and *b* voids. (*b*) *B* plane placed in *a* voids of plane *A*. (*c*) Third plane placed in *b* voids of *B* plane, making another *A* plane and forming the HCP crystal structure. (*d*) Third plane placed in the *a* voids of *B* plane, making a new *C* plane and forming the FCC crystal structure.

(Source: Ander, P.; Sonnessa, A.J., *Principles of Chemistry,* 1st ed.)

Animation



(*a*) (*b*)

Figure 3.19
BCC crystal structure showing (*a*) the (100) plane and (*b*) a section of the (110) plane. Note that this is not a close-packed structure, but that the diagonals have close-packed directions.

(Source: W.G. Moffatt, G.W. Pearsall and J. Wulff, *The Structure and Properties of Materials,* vol. 1: "Structure," Wiley, 1964, p. 51.)

the stacking sequence of the three-dimensional structure produced can be denoted by *ABABAB*. . . . Such a stacking sequence leads to the HCP crystal structure (Fig. 3.17*b*).

The second possibility for forming a simple close-packed structure is to place the third plane in the *a* voids of plane *B* (Fig. 3.18*d*). This third plane is designated the *C* plane since its atoms do not lie directly above those of the *B* plane or the *A* plane. The stacking sequence in this close-packed structure is thus designated *ABCABCABC*. . . and leads to the FCC structure shown in Figure 3.17*a*.

3.8.2 BCC Crystal Structure

The BCC structure is not a close-packed structure and hence does not have close-packed planes like the {111} planes in the FCC structure and the {0001} planes in the HCP structure. The most densely packed planes in the BCC structure are the {110} family of planes, of which the (110) plane is shown in Figure 3.19*b*. However, the atoms in the BCC structure do have close-packed directions along the cube diagonals, which are the ⟨111⟩ directions.

3.9 VOLUME, PLANAR, AND LINEAR DENSITY UNIT-CELL CALCULATIONS

3.9.1 Volume Density

Using the hard-sphere atomic model for the crystal structure unit cell of a metal and a value for the atomic radius of the metal obtained from X-ray diffraction analysis, a value for the **volume density** of a metal can be obtained by using the equation

$$\text{Volume density of metal} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \tag{3.6}$$

In Example Problem 3.11, a value of 8.933 $\mathrm{Mg/m^3}$ (8.933 $\mathrm{g/cm^3}$) is obtained for the theoretical density of copper. The handbook experimental value for the density of copper is 8.96 $\mathrm{Mg/m^3}$ (8.96 $\mathrm{g/cm^3}$). The slightly different density of the experimental value could be attributed to various defects, mismatch where grains meet (grain boundaries), and human error. These crystalline defects are discussed in Chapter 4. Another cause of the discrepancy could also be due to the atoms not being perfect spheres.

EXAMPLE PROBLEM 3.11

Copper has an FCC crystal structure and an atomic radius of 0.1278 nm. Assuming the atoms to be hard spheres that touch each other along the face diagonals of the FCC unit cell as shown in Figure 3.7, calculate a theoretical value for the density of copper in mega-grams per cubic meter. The atomic mass of copper is 63.54 g/mol.

■ **Solution**

For the FCC unit cell, $\sqrt{2}a = 4R$, where a is the lattice constant of the unit cell, and R is the atomic radius of the copper atom. Thus,

$$a = \frac{4R}{\sqrt{2}} = \frac{(4)(0.1278\ \text{nm})}{\sqrt{2}} = 0.3615\ \text{nm}$$

$$\text{Volume density of copper} = \rho_v = \frac{\text{mass/unit cell}}{\text{volume/unit cell}} \tag{3.6}$$

In the FCC unit cell, there are four atoms/unit cell. Each copper atom has a mass of (63.54 g/mol) (6.02×10^{23} atoms/mol). Thus, the mass m of Cu atoms in the FCC unit cell is

$$m = \frac{(4\ \text{atoms})(63.54\ \text{g/mol})}{6.022 \times 10^{23}\ \text{atoms/mol}}\left(\frac{10^{-6}\ \text{Mg}}{\text{g}}\right) = 4.220 \times 10^{-28}\ \text{Mg}$$

The volume V of the Cu unit cell is

$$V = a^3 = \left(0.361\ \text{nm} \times \frac{10^{-9}\ \text{m}}{\text{nm}}\right)^3 = 4.724 \times 10^{-29}\,\text{m}^3$$

Thus, the theoretical density of copper is

$$\rho_v = \frac{m}{V} = \frac{4.220 \times 10^{-28}\ \text{Mg}}{4.724 \times 10^{-29}\,\text{m}^3} = 8.933\ \text{Mg/m}^3(8.933\ \text{g/cm}^3) \blacktriangleleft$$

3.9.2 Planar Atomic Density

Sometimes it is important to determine the atomic densities on various crystal planes. To do this, a quantity called the **planar atomic density** is calculated by using the relationship

$$\text{Planar atomic density} = \rho_p = \frac{\begin{array}{c}\text{equiv. no. of atoms whose centers}\\ \text{are intersected by selected area}\end{array}}{\text{selected area}} \tag{3.8}$$

For convenience, the area of a plane that intersects a unit cell is usually used in these calculations, as shown, for example, in Figure 3.20 for the (110) plane in a BCC unit

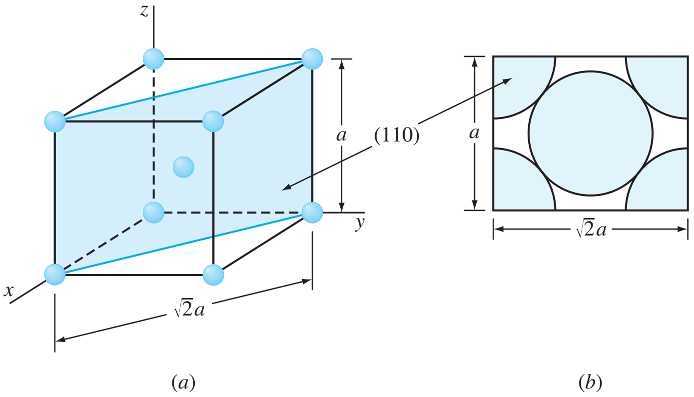


Figure 3.20
(*a*) A BCC atomic-site unit cell showing a shaded (110) plane.
(*b*) Areas of atoms in BCC unit cell cut by the (110) plane.

cell. In order for an atom area to be counted in this calculation, the plane of interest must intersect the center of an atom. In Example Problem 3.12, the (110) plane intersects the centers of five atoms, but the equivalent of only two atoms is counted since only one-quarter of each of the four corner atoms is included in the area inside the unit cell.

EXAMPLE PROBLEM 3.12

Calculate the planar atomic density ρ_p on the (110) plane of the α iron BCC lattice in atoms per square millimeter. The lattice constant of α iron is 0.287 nm.

■ **Solution**

$$\rho_P = \frac{\text{equiv. no. of atoms whose centers are intersected by selected area}}{\text{selected area}} \tag{3.7}$$

The equivalent number of atoms intersected by the (110) plane in terms of the surface area inside the BCC unit cell is shown in Figure 3.22 and is

$$1 \text{ atom at center} + 4 \times \frac{1}{4} \text{atoms at four corners of plane} = 2 \text{ atoms}$$

The area intersected by the (110) plane inside the unit cell (selected area) is

$$\left(\sqrt{2}a\right)(a) = \sqrt{2}a^2$$

Thus, the planar atomic density is

$$\rho_P = \frac{2 \text{ atoms}}{\sqrt{2}\,(0.287 \text{ nm})^2} = \frac{17.2 \text{ atoms}}{\text{nm}^2}$$

$$= \frac{17.2 \text{ atoms}}{\text{nm}^2} \times \frac{10^{12} \text{ nm}^2}{\text{mm}^2}$$

$$= 1.72 \times 10^{13} \text{ atoms/mm}^2 \blacktriangleleft$$

3.9.3 Linear Atomic Density and Repeat Distance

Sometimes it is important to determine the atomic densities in various directions in crystal structures. To do this, a quantity called the **linear atomic density** is calculated by using the relationship

$$\text{Linear atomic density} = \rho_l = \frac{\dfrac{\text{no. of atomic diam. intersected by selected}}{\text{length of line in direction of interest}}}{\text{selected length of line}} \tag{3.8}$$

The distance between two consecutive lattice points along a specific direction is called the **repeat distance**.

Example Problem 3.13 shows how the linear atomic density can be calculated in the [110] direction in a pure copper crystal lattice.

EXAMPLE PROBLEM 3.13

Calculate the linear atomic density ρ_l in the [110] direction in the copper crystal lattice in atoms per millimeter. Copper is FCC and has a lattice constant of 0.361 nm.

■ **Solution**

The atoms whose centers the [110] direction intersects are shown in Figure EP3.13. We shall select the length of the line to be the length of the face diagonal of the FCC unit cell, which is $\sqrt{2}\,a$. The number of atomic diameters intersected by this length of line are $\frac{1}{2} + 1 + \frac{1}{2} = 2$ atoms. Thus using Eq. 3.8, the linear atomic density is

$$\rho_l = \frac{2 \text{ atoms}}{\sqrt{2}\,a} = \frac{2 \text{ atoms}}{\sqrt{2}(0.361 \text{ nm})} = \frac{3.92 \text{ atoms}}{\text{nm}}$$

$$= \frac{3.92 \text{ atoms}}{\text{nm}} \times \frac{10^6 \text{ nm}}{\text{mm}}$$

$$= 3.92 \times 10^6 \text{ atoms/mm} \blacktriangleleft$$

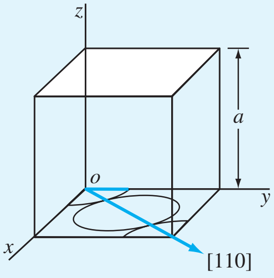


Figure EP3.13
Diagram for calculating the linear atomic density in the [110] direction in an FCC unit cell.

3.10 POLYMORPHISM OR ALLOTROPY

Many elements and compounds exist in more than one crystalline form under different conditions of temperature and pressure. This phenomenon is termed **polymorphism,** or *allotropy*. Many industrially important metals such as iron, titanium, and cobalt undergo allotropic transformations at elevated temperatures at atmospheric pressure. Table 3.5 lists some selected metals that show allotropic transformations and the structure changes that occur.

Iron exists in both BCC and FCC crystal structures over the temperature range from room temperature to its melting point at 1539°C as shown in Figure 3.21. Alpha (α) iron exists from −273°C to 912°C and has the BCC crystal structure. Gamma (γ)

Table 3.5 Allotropic crystalline forms of some metals

Metal	Crystal Structure at Room Temperature	At Other Temperatures
Ca	FCC	BCC (>447°C)
Co	HCP	FCC (>427°C)
Hf	HCP	BCC (>1742°C)
Fe	BCC	FCC (912–1394°C) BCC (>1394°C)
Li	BCC	HCP (<−193°C)
Na	BCC	HCP (<−233°C)
Tl	HCP	BCC (>234°C)
Ti	HCP	BCC (>883°C)
Y	HCP	BCC (>1481°C)
Zr	HCP	BCC (>872°C)

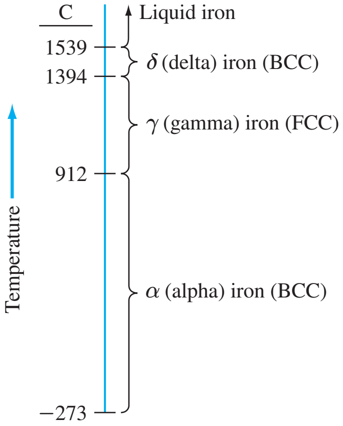


Figure 3.21
Allotropic crystalline forms of iron over temperature ranges at atmospheric pressure.

iron exists from 912°C to 1394°C and has the FCC crystal structure. Delta (δ) iron exists from 1394°C to 1539°C which is the melting point of iron. The crystal structure of δ iron is also BCC but with a larger lattice constant than α iron.

EXAMPLE PROBLEM 3.14

Calculate the theoretical volume change accompanying a polymorphic transformation in a pure metal from the FCC to BCC crystal structure. Assume the hard-sphere atomic model and that there is no change in atomic volume before and after the transformation.

■ **Solution**

In the FCC crystal structure unit cell, the atoms are in contact along the face diagonal of the unit cell, as shown in Figure 3.7. Hence,

$$\sqrt{2}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{2}} \tag{3.3}$$

In the BCC crystal structure unit cell, the atoms are in contact along the body diagonal of the unit cell as shown in Figure 3.5. Hence,

$$\sqrt{3}a = 4R \quad \text{or} \quad a = \frac{4R}{\sqrt{3}} \tag{3.1}$$

The volume per atom for the FCC crystal lattice, since it has four atoms per unit cell, is

$$V_{\text{FCC}} = \frac{a^3}{4} = \left(\frac{4R}{\sqrt{2}}\right)^3\left(\frac{1}{4}\right) = 5.66R^3$$

The volume per atom for the BCC crystal lattice, since it has two atoms per unit cell, is

$$V_{\text{BCC}} = \frac{a^3}{2} = \left(\frac{4R}{\sqrt{3}}\right)^3\left(\frac{1}{2}\right) = 6.16R^3$$

The change in volume associated with the transformation from the FCC to BCC crystal structure, assuming no change in atomic radius, is

$$\begin{aligned}\frac{\Delta V}{V_{\text{FCC}}} &= \frac{V_{\text{BCC}} - V_{\text{FCC}}}{V_{\text{FCC}}}\\ &= \left(\frac{6.16R^3 - 5.66R^3}{5.66R^3}\right)100\% = +8.83\% \blacktriangleleft\end{aligned}$$

3.11 CRYSTAL STRUCTURE ANALYSIS

Our present knowledge of crystal structures has been obtained mainly by X-ray diffraction techniques that use X-rays whose wavelength are the same as the distance between crystal lattice planes. However, before discussing the manner in

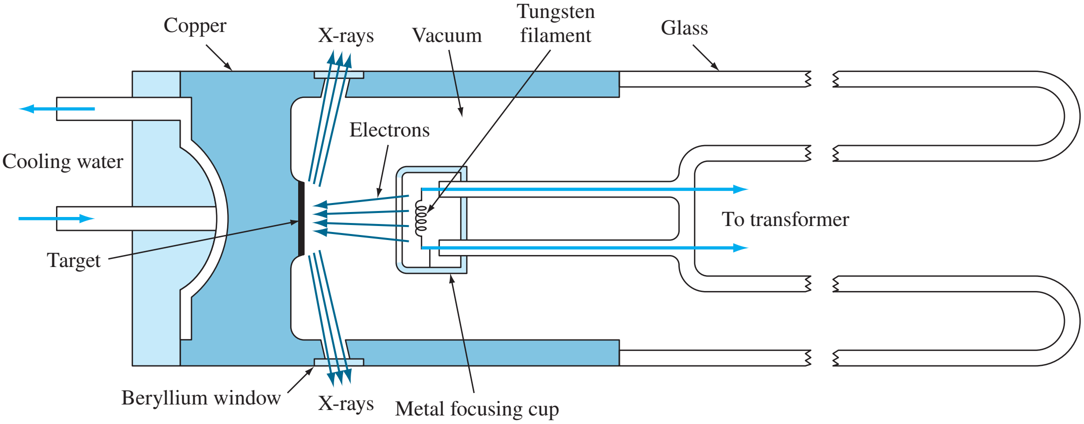


Figure 3.22
Schematic diagram of the cross section of a sealed-off filament X-ray tube.
(Source: B. D. Cullity, *Elements of X-Ray Diffraction* 2nd ed., Addison-Wesley, 1978, p. 23.)

which X-rays are diffracted in crystals, let us consider how X-rays are produced for experimental purposes.

3.11.1 X-Ray Sources

X-rays used for diffraction are electromagnetic waves with wavelengths in the range 0.05 to 0.25 nm (0.5 to 2.5 Å). By comparison, the wavelength of visible light is of the order of 600 nm (6000 Å). In order to produce X-rays for diffraction purposes, a voltage of about 35 kV is necessary and is applied between a cathode and an anode target metal, both of which are contained in a vacuum, as shown in Figure 3.22. When the tungsten filament of the cathode is heated, electrons are released by thermionic emission and accelerated through the vacuum by the large voltage difference between the cathode and anode, thereby gaining kinetic energy. When the electrons strike the target metal (e.g., molybdenum), X-rays are given off. However, most of the kinetic energy (about 98%) is converted into heat, so the target metal must be cooled externally.

The X-ray spectrum emitted at 35 kV using a molybdenum target is shown in Figure 3.23. The spectrum shows continuous X-ray radiation in the wavelength range from about 0.2 to 1.4 Å (0.02 to 0.14 nm) and two spikes of characteristic radiation that are designated the K_α and K_β lines. The wavelengths of the K_α and K_β lines are characteristic for an element. For molybdenum, the K_α line occurs at a wavelength of about 0.7 Å (0.07 nm). The origin of the characteristic radiation is explained as follows: first, K electrons (electrons in the $n = 1$ shell) are knocked out of the atom by highly energetic electrons bombarding the target, leaving excited atoms. Next, some electrons in higher shells (that is, $n = 2$ or 3) drop down to lower energy levels

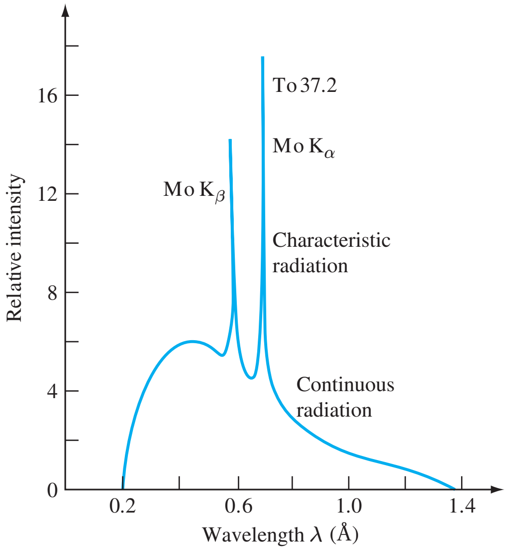


Figure 3.23
X-ray emission spectrum produced when molybdenum metal is used as the target metal in an X-ray tube operating at 35 kV.

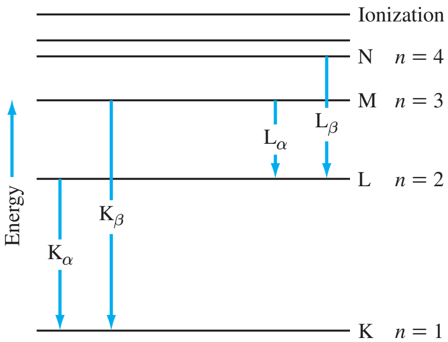


Figure 3.24
Energy levels of electrons in molybdenum showing the origin of K$_\alpha$ and K$_\beta$ radiation.

to replace the lost K electrons, emitting energy of a characteristic wavelength. The transition of electrons from the L ($n = 2$) shell to the K ($n = 1$) shell creates energy of the wavelength of the K$_\alpha$ line, as indicated in Figure 3.24.

3.11.2 X-Ray Diffraction

Since the wavelengths of some X-rays are about equal to the distance between planes of atoms in crystalline solids, reinforced diffraction peaks of radiation of varying intensities can be produced when a beam of X-rays strikes a crystalline solid. However, before considering the application of X-ray diffraction techniques to crystal structure analysis, let us examine the geometric conditions necessary to produce diffracted or reinforced beams of reflected X-rays.

Consider a monochromatic (single-wavelength) beam of X-rays to be incident on a crystal, as shown in Figure 3.25. For simplification, let us allow the crystal planes of atomic scattering centers to be replaced by crystal planes that act as mirrors in reflecting the incident X-ray beam. In Figure 3.25, the horizontal lines represent a set of parallel crystal planes with Miller indices (*hkl*). When an incident beam of monochromatic X-rays of wavelength λ strikes this set of planes at an angle such that the wave patterns of the beam leaving the various planes are *not in phase, no reinforced beam will be produced* (Figure 3.25*a*). Thus, destructive interference occurs. If the reflected wave patterns of the beam leaving the various planes are in phase, then reinforcement of the beam or constructive interference occurs (Fig. 3.25*b*).

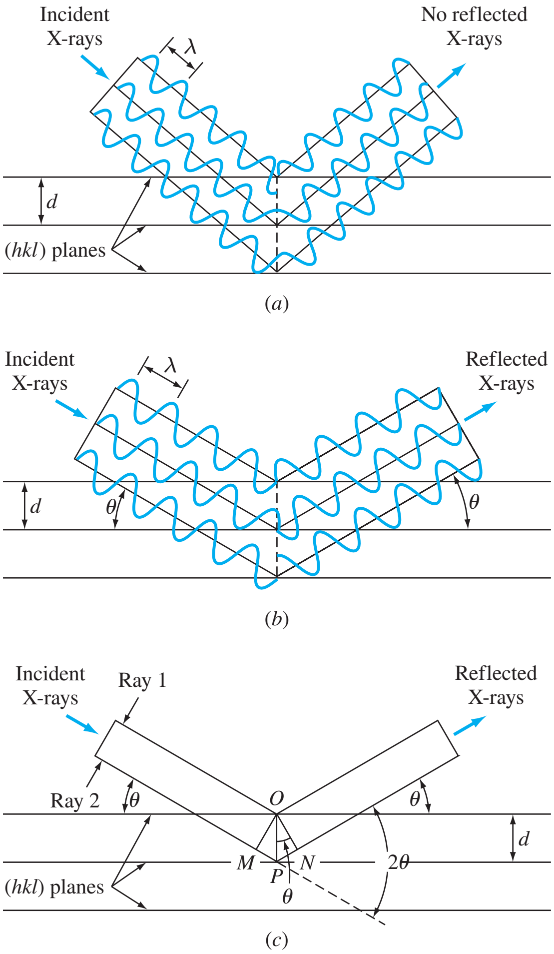


Figure 3.25

The reflection of an X-ray beam by the *(hkl)* planes of a crystal. (*a*) No reflected beam is produced at an arbitrary angle of incidence. (*b*) At the Bragg angle *θ,* the reflected rays are in phase and reinforce one another. (c) Similar to (*b*) except that the wave representation has been omitted.

(Source: A.G. Guy and J.J. Hren *Elements of Physical Metallurgy* (3rd ed.). Addison-Wesley, 1974, p. 201.)

Let us now consider incident X-rays 1 and 2 as indicated in Figure 3.25*c*. For these rays to be in phase, the extra distance of travel of ray 2 is equal to $MP + PN$, which must be an integral number of wavelengths λ. Thus,

$$n\lambda = MP + PN \tag{3.9}$$

where $n = 1, 2, 3, \ldots$ and is called the *order of the diffraction.* Since both MP and PN equal $d_{hkl} \sin \theta$, where d_{hkl} is the interplanar spacing of the crystal planes of indices (hkl), the condition for constructive interference (i.e., the production of a diffraction peak of intense radiation) must be

$$n\lambda = 2\,d_{hkl} = \sin \theta \qquad \textbf{(3.10)}$$

This equation, known as *Bragg's law,*[7] gives the relationship among the angular positions of the reinforced diffracted beams in terms of the wavelength λ of the incoming X-ray radiation and of the interplanar spacings d_{hkl} of the crystal planes. In most cases, the first order of diffraction where $n = 1$ is used, and so for this case, Bragg's law takes the form

$$\lambda = 2\,d_{hkl} = \sin \theta \qquad \textbf{(3.11)}$$

EXAMPLE PROBLEM 3.15

A sample of BCC iron was placed in an X-ray diffractometer using incoming X-rays with a wavelength $\lambda = 0.1541$ nm. Diffraction from the {110} planes was obtained at $2\theta = 44.70°$. Calculate a value for the lattice constant a of BCC iron. (Assume first-order diffraction with $n = 1$.)

■ **Solution**

$$2\theta = 44.704° \qquad \theta = 22.35°$$

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

$$d_{110} = \frac{\lambda}{2 \sin \theta} = \frac{0.1541 \text{ nm}}{2(\sin\ 22.35°)} \qquad \textbf{(3.11)}$$

$$= \frac{0.1541 \text{ nm}}{2(0.3803)} = 0.2026 \text{ nm}$$

Rearranging Eq. 3.5 gives

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

Thus,

$$a(\text{Fe}) = d_{110}\sqrt{1^2 + 1^2 + 0^2}$$

$$= (0.2026 \text{ nm})(1.414) = 0.2865 \text{ nm} \blacktriangleleft$$

3.11.3 X-Ray Diffraction Analysis of Crystal Structures

The Powder Method of X-Ray Diffraction Analysis The most commonly used X-ray diffraction technique is the *powder method.* In this technique, a powdered specimen is utilized so that there will be a random orientation of many crystals to ensure that some of the particles will be oriented in the X-ray beam to satisfy the diffraction conditions of

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[7] William Henry Bragg (1862–1942). English physicist who worked on X-ray crystallography.

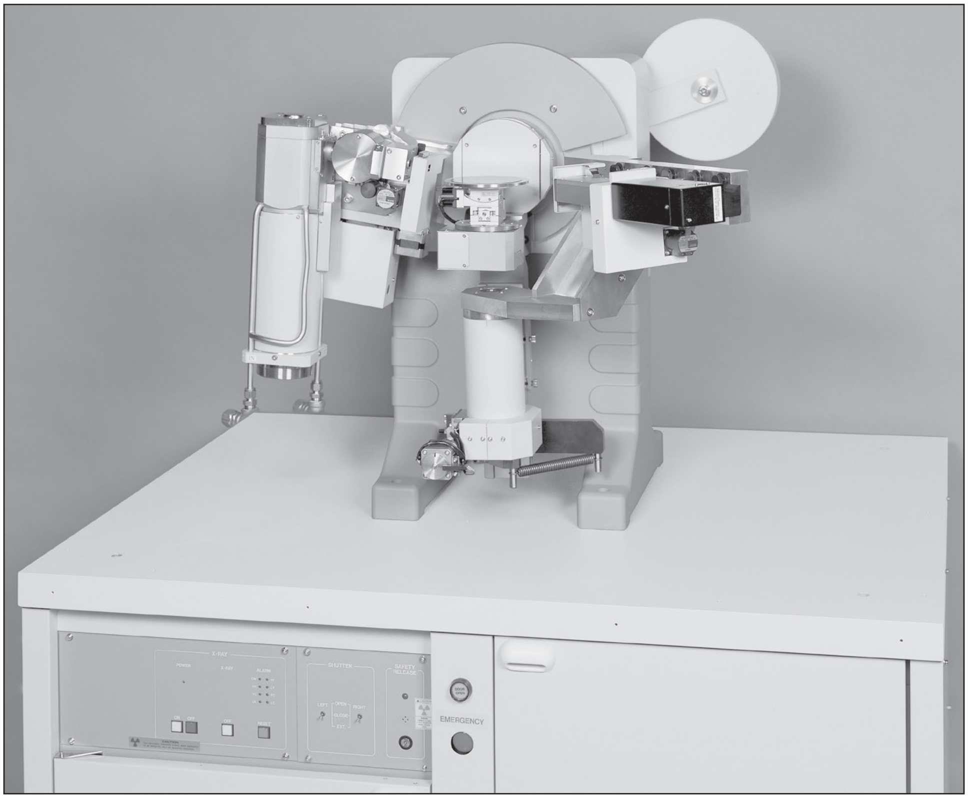

Figure 3.26

An X-ray diffractometer (with X-radiation shields removed).

(Courtesy of Rigaku)

Bragg's law. Modern X-ray crystal analysis uses an X-ray diffractometer that has a radiation counter to detect the angle and intensity of the diffracted beam (Fig. 3.26). A recorder automatically plots the intensity of the diffracted beam as the counter moves on a goniometer[8] circle (Fig. 3.27) that is in synchronization with the specimen over a range of 2θ values. Figure 3.28 shows an X-ray diffraction recorder chart for the intensity of the diffracted beam versus the diffraction angles 2θ for a powdered pure-metal specimen. In this way, both the angles of the diffracted beams and their intensities can be recorded at one time. Sometimes a powder camera with an enclosed filmstrip is used instead of the diffractometer, but this method is much slower and in most cases, less convenient.

Diffraction Conditions for Cubic Unit Cells X-ray diffraction techniques enable the structures of crystalline solids to be determined. The interpretation of X-ray diffraction data for most crystalline substances is complex and beyond the scope of this

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[8] A goniometer is an instrument for measuring angles.

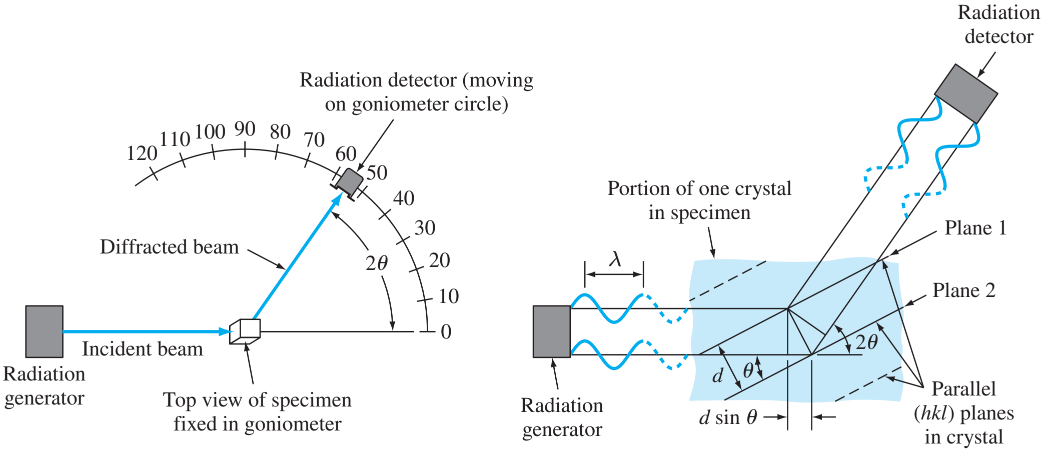


Figure 3.27

Schematic illustration of the diffractometer method of crystal analysis and of the conditions necessary for diffraction.

(Source: A.G. Guy, *Essentials of Materials Science,* McGraw-Hill, 1976.)

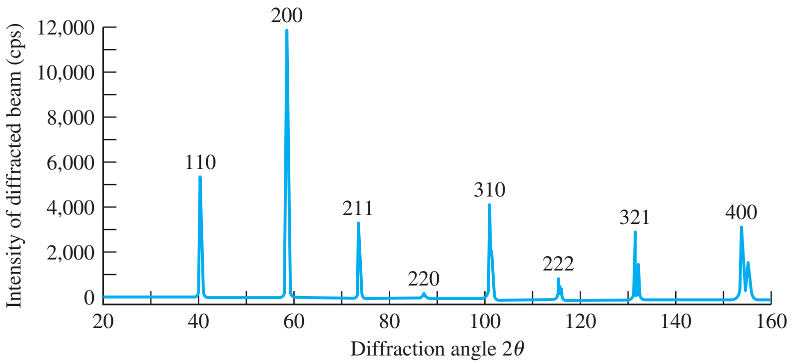


Figure 3.28

Record of the diffraction angles for a tungsten sample obtained by the use of a diffractometer with copper radiation.

(Source: A.G. Guy and J.J. Hren, *Elements of Physical Metallurgy* 3rd ed., Addison-Wesley, 1974, p. 208.)

book, and so only the simple case of diffraction in pure cubic metals will be considered. The analysis of X-ray diffraction data for cubic unit cells can be simplified by combining Eq. 3.4,

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

with the Bragg equation $\lambda = 2d \sin \theta$, giving

$$\lambda = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \tag{3.12}$$

This equation can be used along with X-ray diffraction data to determine if a cubic crystal structure is body-centered or face-centered cubic. The rest of this subsection will describe how this is done.

To use Eq. 3.12 for diffraction analysis, we must know which crystal planes are the diffracting planes for each type of crystal structure. For the simple cubic lattice, reflections from all (hkl) planes are possible. However, for the BCC structure, diffraction occurs only on planes whose Miller indices when added together ($h + k + l$) total to an even number (Table 3.6). Thus, for the BCC crystal structure, the principal diffracting planes are {110}, {200}, {211}, etc., which are listed in Table 3.7. In the case of the FCC crystal structure, the principal diffracting planes are those whose Miller indices are either all even or all odd (zero is considered even). Thus, for the FCC crystal structure, the diffracting planes are {111}, {200}, {220}, etc., which are listed in Table 3.7.

Interpreting Experimental X-Ray Diffraction Data for Metals with Cubic Crystal Structures We can use X-ray diffractometer data to determine crystal structures. A simple case to illustrate how this analysis can be used is to distinguish between the

Table 3.6 Rules for determining the diffracting {*hkl*} planes in cubic crystals

Bravais Lattice	Reflections Present	Reflections Absent
BCC	$(h + k + l)$ = even	$(h + k + l)$ = odd
FCC	(h, k, l) all odd or all even	(h, k, l) not all odd or all even

Table 3.7 Miller indices of the diffracting planes for BCC and FCC lattices

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

BCC and FCC crystal structures of a cubic metal. Let us assume that we have a metal with either a BCC or an FCC crystal structure and that we can identify the principal diffracting planes and their corresponding 2θ values, as indicated for the metal tungsten in Figure 3.28.

By squaring both sides of Eq. 3.12 and solving for $\sin^2\theta$, we obtain

$$\sin^2\theta = \frac{\lambda^2(h^2 + k^2 + l^2)}{4a^2} \tag{3.13}$$

From X-ray diffraction data, we can obtain experimental values of 2θ for a series of principal diffracting $\{hkl\}$ planes. Since the wavelength of the incoming radiation and the lattice constant a are both constants, we can eliminate these quantities by forming the ratio of two $\sin^2\theta$ values as

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2} \tag{3.14}$$

where θ_A and θ_B are two diffracting angles associated with the principal diffracting planes $\{h_A k_A l_A\}$ and $\{h_B k_B l_B\}$, respectively.

Using Eq. 3.14 and the Miller indices of the first two sets of principal diffracting planes listed in Table 3.7 for BCC and FCC crystal structures, we can determine values for the $\sin^2\theta$ ratios for both BCC and FCC structures.

For the BCC crystal structure, the first two sets of principal diffracting planes are the $\{110\}$ and $\{200\}$ planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. 3.14 gives

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{1^2 + 1^2 + 0^2}{2^2 + 0^2 + 0^2} = 0.5 \tag{3.15}$$

Thus, if the crystal structure of the unknown cubic metal is BCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.5.

For the FCC crystal structure, the first two sets of principal diffracting planes are the $\{111\}$ and $\{200\}$ planes (Table 3.7). Substitution of the Miller $\{hkl\}$ indices of these planes into Eq. 3.15 gives

$$\frac{\sin^2\theta_A}{\sin^2\theta_B} = \frac{1^2 + 1^2 + 1^2}{2^2 + 0^2 + 0^2} = 0.75 \tag{3.16}$$

Thus, if the crystal structure of the unknown cubic metal is FCC, the ratio of the $\sin^2\theta$ values that correspond to the first two principal diffracting planes will be 0.75.

Example Problem 3.16 uses Eq. 3.14 and experimental X-ray diffraction data for the 2θ values for the principal diffracting planes to determine whether an unknown cubic metal is BCC or FCC. X-ray diffraction analysis is usually much more complicated than Example Problem 3.16, but the principles used are the same. Both experimental and theoretical X-ray diffraction analysis has been and continues to be used for the determination of the crystal structure of materials.

EXAMPLE PROBLEM 3.16

An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure shows diffraction peaks at the following 2θ angles: 40, 58, 73, 86.8, 100.4, and 114.7. The wavelength of the incoming X-ray used was 0.154 nm.

a. Determine the cubic structure of the element.
b. Determine the lattice constant of the element.
c. Identify the element.

■ Solution

a. *Determination of the crystal structure of the element.* First, the $\sin^2\theta$ values are calculated from the 2θ diffraction angles.

2θ(deg)	**θ(deg)**	**$\sin\theta$**	**$\sin^2\theta$**
40	20	0.3420	0.1170
58	29	0.4848	0.2350
73	36.5	0.5948	0.3538
86.8	43.4	0.6871	0.4721
100.4	50.2	0.7683	0.5903
114.7	57.35	0.8420	0.7090

Next, the ratio of the $\sin^2\theta$ values of the first and second angles is calculated:

$$\frac{\sin^2\theta}{\sin^2\theta} = \frac{0.117}{0.235} = 0.498 \approx 0.5$$

The crystal structure is BCC since this ratio is ≈ 0.5. If the ratio had been ≈ 0.75, the structure would have been FCC.

b. *Determination of the lattice constant.* Rearranging Eq. 3.14 and solving for a^2 gives

$$a^2 = \frac{\lambda^2}{4}\frac{h^2+k^2+l^2}{\sin^2\theta} \tag{3.17}$$

or

$$a = \frac{\lambda}{2}\sqrt{\frac{h^2+k^2+l^2}{\sin^2\theta}} \tag{3.18}$$

Substituting into Eq. 3.18 $h = 1$, $k = 1$, and $l = 0$ for the h, k, l Miller indices of the first set of principal diffracting planes for the BCC crystal structure, which are the {110} planes, the corresponding value for $\sin^2\theta$, which is 0.117, and 0.154 nm for λ, the incoming radiation, gives

$$a = \frac{0.154 \text{ nm}}{2}\sqrt{\frac{1^2+1^2+0^2}{0.117}} = 0.318 \text{ nm} \blacktriangleleft$$

c. *Identification of the element.* The element is tungsten since this element has a lattice constant of 0.316 nm and is BCC.

3.12 AMORPHOUS MATERIALS

As discussed previously, some materials are called amorphous or noncrystalline because they lack long-range order in their atomic structure. It should be noted that, in general, materials have a tendency to achieve a crystalline state because that is the most stable state and it corresponds to the lowest energy level. However, atoms in amorphous materials are bonded in a disordered manner because of factors that inhibit the formation of a periodic arrangement. Atoms in amorphous materials, therefore, occupy random spatial positions as opposed to specific positions in crystalline solids. For clarity, various degrees of order (or disorder) are shown in Figure 3.29.

Most polymers, glasses, and some metals are members of the amorphous class of materials. In polymers, the secondary bonds among molecules do not allow for the formation of parallel and tightly packed chains during solidification. As a result, polymers such as polyvinylchloride consist of long, twisted molecular chains that are entangled to form a solid with amorphous structure, similar to Figure 3.29*c*. In some polymers such as polyethylene, the molecules are more efficiently and tightly packed in some regions of the material and produce a higher degree of regional long-range order. As a result, these polymers are often classified as *semicrystalline*. A more detailed discussion of semicrystalline polymers will be given in Chapter 10.

Inorganic glass based on glass-forming oxide, silica (SiO_2), is generally characterized as a ceramic material (ceramic glass) and is another example of a material with an amorphous structure. In this type of glass, the fundamental subunit in the molecules is the SiO_4^{4-} tetrahedron. The ideal crystalline structure of this glass is shown in Figure 3.29*a*. The schematic shows the Si–O tetrahedrons joined corner to corner to form long-range order. In its viscous liquid state, the molecules have limited mobility, and, in general, crystallization occurs slowly. Therefore, a modest cooling rate suppresses the formation of the crystal structure, and instead the tetrahedra join corner to corner to form a network lacking in long-range order (Fig. 3.29*b*).

In addition to polymers and glasses, some metals also have the ability to form amorphous structures (*metallic glass*) under strict and often difficult-to-achieve conditions. Unlike glasses, metals have very small and mobile building blocks under molten

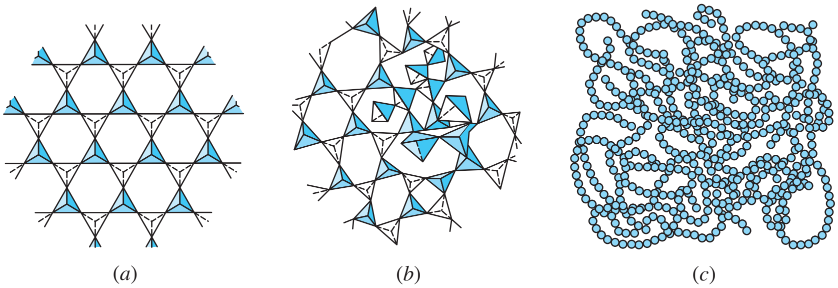

(*a*) (*b*) (*c*)

Figure 3.29
A schematic showing various degrees of order in materials: (*a*) long-range order in crystalline silica, (*b*) silica glass without long-range order, and (*c*) amorphous structure in polymers.

conditions. As a result, it is difficult to prevent metals from crystallizing. However, alloys such as 78%Fe–9%Si–13%B that contain a high percentage of semimetals, Si and B, may form metallic glasses through rapid solidification at cooling rates in excess of 10^8 °C/s. At such high cooling rates, the atoms simply do not have enough time to form a crystalline structure and instead form a metal with an amorphous structure, that is, they are highly disordered. In theory, any crystalline material can form a noncrystalline structure if solidified rapidly enough from a molten state.

Amorphous materials, because of their structure, possess properties that are superior. For instance, metallic glasses possess higher strength, better corrosion characteristics, and magnetic properties when compared to their crystalline counterparts. Finally, it is important to note that amorphous materials do not show sharp diffraction patterns when analyzed using X-ray diffraction techniques. This is due to a lack of order and periodicity in the atomic structure. In future chapters, the role of structure of the material on its properties will be explained in detail.

3.13 SUMMARY

Atomic arrangements in crystalline solids can be described by a network of lines called a *space lattice.* Each space lattice can be described by specifying the atom positions in a repeating *unit cell.* The crystal structure consists of space lattice and *motif* or *basis.* Crystalline materials, such as most metals, possess long-range atomic order. But some materials, such as many polymers and glasses, possess only short-range order. Such materials are called semicrystalline or amorphous. There are seven crystal systems based on the geometry of the axial lengths and interaxial angles of the unit cells. These seven systems have a total of 14 sublattices (unit cells) based on the internal arrangements of atomic sites within the unit cells.

In metals, the most common crystal structure unit cells are: *body-centered cubic* (BCC), *face-centered cubic* (FCC), and *hexagonal close-packed* (HCP) (which is a dense variation of the simple hexagonal structure).

Crystal directions in cubic crystals are the vector components of the directions resolved along each of the component axes and reduced to smallest integers. They are indicated as $[uvw]$. Families of directions are indexed by the direction indices enclosed by pointed brackets as $\langle uvw \rangle$. *Crystal planes* in cubic crystals are indexed by the reciprocals of the axial intercepts of the plane (followed by the elimination of fractions) as (hkl). Cubic crystal planes of a form (family) are indexed with braces as $\{hkl\}$. Crystal planes in hexagonal crystals are commonly indexed by four indices $h, k, i,$ and l enclosed in parentheses as $(hkil)$. These indices are the reciprocals of the intercepts of the plane on the a_1, a_2, a_3, and c axes of the hexagonal crystal structure unit cell. Crystal directions in hexagonal crystals are the vector components of the direction resolved along each of the four coordinate axes and reduced to smallest integers as $[uvtw]$.

Using the hard-sphere model for atoms, calculations can be made for the volume, planar, and linear density of atoms in unit cells. Planes in which atoms are packed as tightly as possible are called *close-packed planes,* and directions in which atoms are in closest contact are called *close-packed directions.* Atomic packing factors for different crystal structures can also be determined by assuming the hard-sphere atomic model. Some metals have different crystal structures at different ranges of temperature and pressure, a phenomenon called *polymorphism.*

Crystal structures of crystalline solids can be determined by using X-ray diffraction analysis techniques. X-rays are diffracted in crystals when the *Bragg's law* ($n\lambda = 2d \sin \theta$) conditions are satisfied. By using the X-ray diffractometer and the *powder method,* the crystal structure of many crystalline solids can be determined.

3.14 DEFINITIONS

Sec. 3.1

Amorphous: lacking in long-range atomic order.

Crystal: a solid composed of atoms, ions, or molecules arranged in a pattern that is repeated in three dimensions.

Crystal structure: a regular three-dimensional pattern of atoms or ions in space.

Space lattice: a three-dimensional array of points each of which has identical surroundings.

Lattice point: one point in an array in which all the points have identical surroundings.

Unit cell: a convenient repeating unit of a space lattice. The axial lengths and axial angles are the lattice constants of the unit cell.

Motif (or Basis): a group of atoms that are organized relative to each other and are associated with corresponding lattice points.

Sec. 3.3

Body-centered cubic (BCC) unit cell: a unit cell with an atomic packing arrangement in which one atom is in contact with eight identical atoms located at the corners of an imaginary cube.

Face-centered cubic (FCC) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central atom. The stacking sequence of layers of close-packed planes in the FCC crystal structure is *ABCABC*. . . .

Hexagonal close-packed (HCP) unit cell: a unit cell with an atomic packing arrangement in which 12 atoms surround a central identical atom. The stacking sequence of layers of close-packed planes in the HCP crystal structure is *ABABAB*....

Atomic packing factor (APF): the volume of atoms in a selected unit cell divided by the volume of the unit cell.

Sec. 3.5

Indices of direction in a cubic crystal: a direction in a cubic unit cell is indicated by a vector drawn from the origin at one point in a unit cell through the surface of the unit cell; the position coordinates (x, y, and z) of the vector where it leaves the surface of the unit cell (with fractions cleared) are the indices of direction. These indices, designated u, v, and w, are enclosed in brackets as $[uvw]$. Negative indices are indicated by a bar over the index.

Sec. 3.6

Indices for cubic crystal planes (Miller indices): the reciprocals of the intercepts (with fractions cleared) of a crystal plane with the x, y, and z axes of a unit cube are called the Miller indices of that plane. They are designated h, k, and l for the x, y, and z axes, respectively, and are enclosed in parentheses as (hkl). Note that the selected crystal plane must *not* pass through the origin of the x, y, and z axes.

Sec. 3.9

Volume density ρ_v: mass per unit volume; this quantity is usually expressed in Mg/m^3 or g/cm^3.

Planar density ρ_p: the equivalent number of atoms whose centers are intersected by a selected area divided by the selected area.

Linear density ρ_l: the number of atoms whose centers lie on a specific direction on a specific length of line in a unit cube.

Repeat Distance: The distance between two consecutive lattice points along a specific direction.

Sec. 3.10

Polymorphism (as pertains to metals): the ability of a metal to exist in two or more crystal structures. For example, iron can have a BCC or an FCC crystal structure, depending on the temperature.

Sec. 3.12

Semicrystalline: materials with regions of crystalline structure dispersed in the surrounding, amorphous region, for instance, some polymers.

Metallic glass: metals with an amorphous atomic structure.

3.15 PROBLEMS

Answers to problems marked with an asterisk are given at the end of the book.

Knowledge and Comprehension Problems

3.1 Define the following terms: (*a*) crystalline solid, (*b*) long-range order, (*c*) short-range order, and (*d*) amorphous.

3.2 Define the following terms: (*a*) crystal structure, (*b*) space lattice, (*c*) lattice point, (*d*) unit cell, (*e*) motif, and (*f*) lattice constants.

3.3 What are the 14 Bravais unit cells?

3.4 What are the three most common metal crystal structures? List five metals that have each of these crystal structures.

3.5 For a BCC unit cell, (*a*) how many atoms are there inside the unit cell, (*b*) what is the coordination number for the atoms, (*c*) what is the relationship between the length of the side *a* of the BCC unit cell and the radius of its atoms, and (*d*) what is the atomic packing factor?

3.6 For an FCC unit cell, (*a*) how many atoms are there inside the unit cell, (*b*) what is the coordination number for the atoms, (*c*) what is the relationship between the length of the side *a* of the FCC unit cell and the radius of its atoms, and (*d*) what is the atomic packing factor?

3.7 For an HCP unit cell (consider the primitive cell), (*a*) how many atoms are there inside the unit cell, (*b*) what is the coordination number for the atoms, (*c*) what is the atomic packing factor, (*d*) what is the ideal *c/a* ratio for HCP metals, and (*e*) repeat (*a*) through (*c*) considering the "larger" cell.

3.8 How are atomic positions located in cubic unit cells?

3.9 List the atom positions for the eight corner and six face-centered atoms of the FCC unit cell.

3.10 How are the indices for a crystallographic direction in a cubic unit cell determined?

3.11 What are the crystallographic directions of a family or form? What generalized notation is used to indicate them?

3.12 How are the Miller indices for a crystallographic plane in a cubic unit cell determined? What generalized notation is used to indicate them?

3.13 What is the notation used to indicate a family or form of cubic crystallographic planes?

3.14 How are crystallographic planes indicated in HCP unit cells?

3.15 What notation is used to describe HCP crystal planes?

3.16 What is the difference in the stacking arrangement of close-packed planes in (*a*) the HCP crystal structure and (*b*) the FCC crystal structure?

3.17 What are the closest-packed directions in (*a*) the BCC structure, (*b*) the FCC structure, and (*c*) the HCP structure?

3.18 Identify the close-packed planes in (*a*) the BCC structure, (*b*) the FCC structure, and (*c*) the HCP structure.

3.19 What is polymorphism with respect to metals?

3.20 What are X-rays, and how are they produced?

3.21 Draw a schematic diagram of an X-ray tube used for X-ray diffraction, and indicate on it the path of the electrons and X-rays.

3.22 What is the characteristic X-ray radiation? What is its origin?

Tutorial

3.23 Distinguish between destructive interference and constructive interference of reflected X-ray beams through crystals.

Application and Analysis Problems

3.24 Tungsten at 20°C is BCC and has an atomic radius of 0.137 nm. (*a*) Calculate a value for its lattice constant a in nanometers. (*b*) Calculate the volume of the unit cell.

3.25 Lead is FCC and has an atomic radius of 0.175 nm. (*a*) Calculate a value for its lattice constant a in nanometers. (*b*) Calculate the volume of the unit cell in nm^3.

3.26 Verify that the atomic packing factor for the FCC structure is 0.74.

3.27 Calculate the volume in cubic nanometers of the cobalt crystal structure unit cell (use the larger cell). Cobalt is HCP at 20°C with $a = 0.2507$ nm and $c = 0.4069$ nm.

3.28 Consider a 0.05-mm-thick, 500 mm^2 (about three times the area of a dime) piece of aluminum foil. How many unit cells exist in the foil? If the density of aluminum is 2.7 g/cm^3, what is the mass of each cell?

3.29 Draw the following directions in a BCC unit cell, and list the position coordinates of the atoms whose centers are intersected by the direction vector. Determine the repeat distance in terms of the lattice constant in each direction.

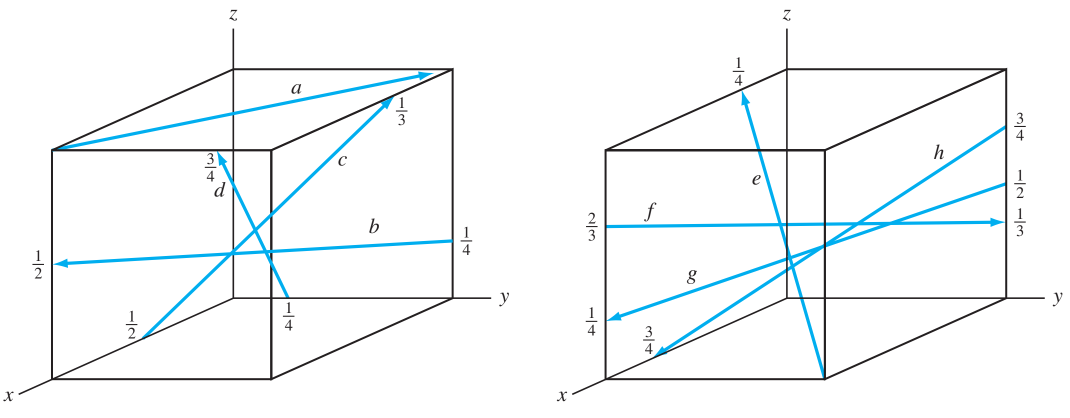
(*a*) [010] (*b*) [011] (*c*) [111]

(*d*) Find the angle between directions in (*b*) and (*c*).

3.30 Draw direction vectors in an FCC unit cell for the following cubic directions, and list the position coordinates of the atoms whose centers are intersected by the direction vector. Determine the repeat distance in terms of the lattice constant in each direction.

(*a*) $[\bar{1}\bar{1}1]$ (*b*) $[10\bar{1}]$ (*c*) $[2\bar{1}\bar{1}]$ (*d*) $[\bar{1}3\bar{1}]$

(*e*) Find the angle between directions in (*b*) and (*d*).



(*a*) (*b*)

Figure P3.32

3.31 Draw direction vectors in unit cells for the following cubic directions:
(*a*) $[1\bar{1}\bar{2}]$ (*b*) $[1\bar{2}3]$ (*c*) $[\bar{3}31]$ (*d*) $[0\bar{2}1]$ (*e*) $[2\bar{1}2]$ (*f*) $[2\bar{3}3]$
(*g*) $[\bar{1}01]$ (*h*) $[12\bar{1}]$ (*i*) $[321]$ (*j*) $[10\bar{3}]$ (*k*) $[1\bar{2}\bar{2}]$ (*l*) $[\bar{2}\bar{2}3]$

3.32 What are the indices of the directions shown in the unit cubes of Figure P3.32?

3.33 A direction vector passes through a unit cube from the $(\frac{3}{4}, 0, \frac{1}{4})$ to the $(\frac{1}{2}, 1, 0)$ positions. What are its direction indices?

3.34 A direction vector passes through a unit cube from the $(1, 0, \frac{3}{4})$ to the $(\frac{1}{4}, 1, \frac{1}{4})$ positions. What are its direction indices?

3.35 What are the directions of the $\langle 10\bar{3}\rangle$ family or form for a unit cube? Draw all directions in a unit cell.

3.36 What are the directions of the $\langle 111\rangle$ family or form for a unit cube? Draw all directions in a BCC unit cell. Can you identify a special quality of these directions?

3.37 What $\langle 110\rangle$ type directions lie on the (111) plane of a cubic unit cell? Draw those directions in an FCC unit cell. Can you identify a special quality of these directions?

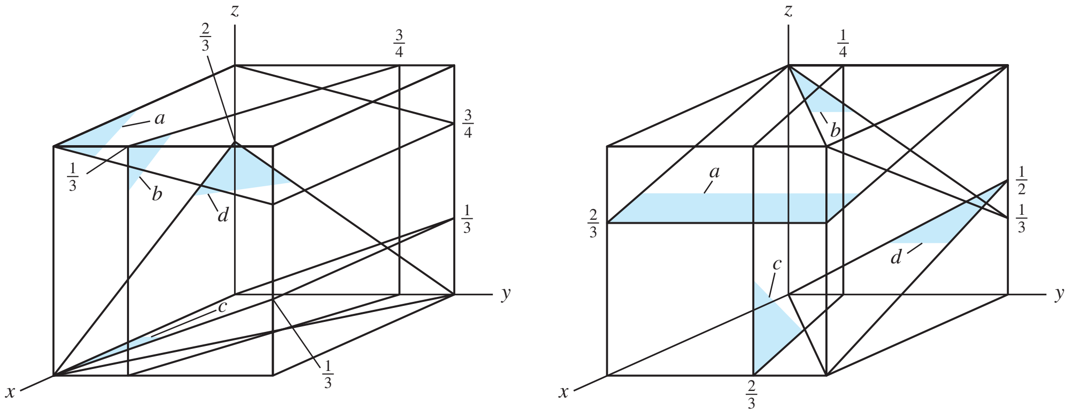
3.38 What $\langle 111\rangle$ type directions lie on the (110) plane of a BCC unit cell? Draw those directions in a unit cell. Can you identify a special quality of these directions?

3.39 Draw in unit cubes the crystal planes that have the following Miller indices:
(*a*) $(1\bar{1}\bar{1})$ (*b*) $(10\bar{2})$ (*c*) $(1\bar{2}\bar{1})$ (*d*) $(21\bar{3})$ (*e*) $(\bar{3}21)$ (*f*) $(30\bar{2})$
(*g*) $(20\bar{1})$ (*h*) $(\bar{2}1\bar{2})$ (*i*) $(\bar{2}32)$ (*j*) $(13\bar{3})$ (*k*) $(3\bar{1}2)$ (*l*) $(\bar{3}3\bar{1})$

3.40 What are the Miller indices of the cubic crystallographic planes shown in Figure P3.40?

3.41 What are the {100} family of planes of the cubic system? Draw those planes in a BCC unit cell and show all atoms whose centers are intersected by the planes. What is your conclusion?

3.42 Draw the following crystallographic planes in a BCC unit cell, and list the position of the atoms whose centers are intersected by each of the planes:
(*a*) (010) (*b*) (011) (*c*) (111)



(*a*) (*b*)

Figure P3.40

3.43 Draw the following crystallographic planes in an FCC unit cell, and list the position coordinates of the atoms whose centers are intersected by each of the planes:
(*a*) (010) (*b*) (011) (*c*) (111)

Tutorial

3.44 A cubic plane has the following axial intercepts: $a = \frac{1}{3}$, $b = -\frac{2}{3}$, $c = \frac{1}{2}$. What are the Miller indices of this plane?

3.45 A cubic plane has the following axial intercepts: $a = -\frac{1}{2}$, $b = -\frac{1}{2}$, $c = \frac{2}{3}$. What are the Miller indices of this plane?

3.46 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: $(1, \frac{1}{2}, 1)$; $(\frac{1}{2}, 0, \frac{3}{4})$; $(1, 0, \frac{1}{2})$.

3.47 Determine the Miller indices of the cubic crystal plane that intersects the following position coordinates: $(0, 0, \frac{1}{2})$; $(1, 0, 0)$; $(\frac{1}{2}, \frac{1}{4}, 0)$.

3.48 Rodium is FCC and has a lattice constant *a* of 0.38044 nm. Calculate the following interplanar spacings:
(*a*) d_{111} (*b*) d_{200} (*c*) d_{220}

3.49 Tungsten is BCC and has a lattice constant *a* of 0.31648 nm. Calculate the following interplanar spacings:
(*a*) d_{110} (*b*) d_{220} (*c*) d_{310}

3.50 The d_{310} interplanar spacing in a BCC element is 0.1587 nm. (*a*) What is its lattice constant *a*? (*b*) What is the atomic radius of the element? (*c*) What could this element be?

3.51 The d_{422} interplanar spacing in an FCC metal is 0.083397 nm. (*a*) What is its lattice constant *a*? (*b*) What is the atomic radius of the metal? (*c*) What could this metal be?

3.52 Draw the hexagonal crystal planes whose Miller-Bravais indices are:
(*a*) $(10\bar{1}1)$ (*b*) $(01\bar{1}1)$ (*c*) $(\bar{1}2\bar{1}0)$ (*d*) $(1\bar{2}12)$ (*e*) $(2\bar{1}\bar{1}1)$ (*f*) $(1\bar{1}01)$
(*g*) $(\bar{1}2\bar{1}2)$ (*h*) $(2\bar{2}00)$ (*i*) $(10\bar{1}2)$ (*j*) $(\bar{1}100)$ (*k*) $(\bar{2}111)$ (*l*) $(\bar{1}012)$

3.53 Determine the Miller-Bravais indices of the hexagonal crystal planes in Figure P3.53.

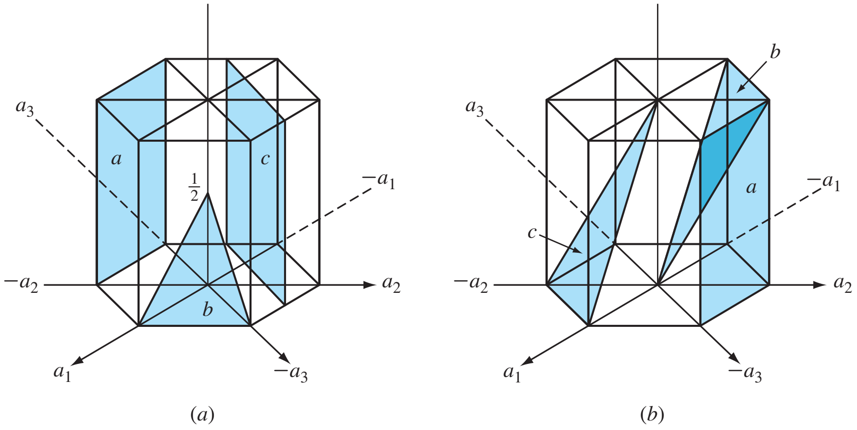


Figure P3.53

3.54 Determine the Miller-Bravais direction indices of the $-a_1$, $-a_2$, and $-a_3$ directions.

3.55 Determine the Miller-Bravais direction indices of the vectors originating at the center of the lower basal plane and ending at the endpoints of the upper basal plane as indicated in Figure 3.16*d*.

3.56 Determine the Miller-Bravais direction indices of the basal plane of the vectors originating at the center of the lower basal plane and exiting at the midpoints between the principal planar axes.

3.57 Determine the Miller-Bravais direction indices of the directions indicated in Figure P3.57.

3.58 The lattice constant for BCC tantalum at 20°C is 0.33026 nm and its density is 16.6 g/cm^3. Calculate a value for its relative atomic mass.

3.59 Calculate a value for the density of FCC platinum in grams per cubic centimeter from its lattice constant *a* of 0.39239 nm and its atomic mass of 195.09 g/mol.

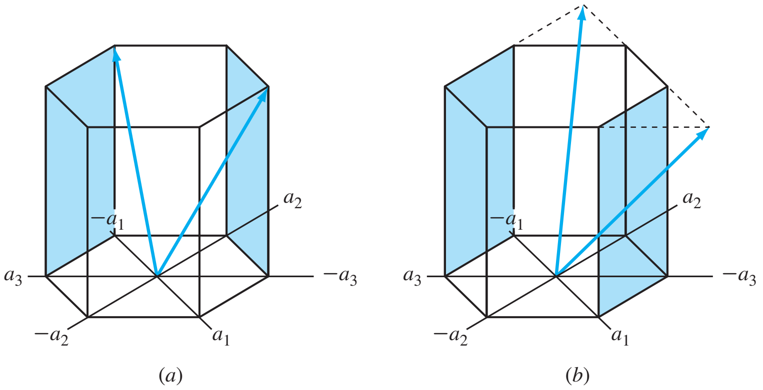


Figure P3.57

3.60 Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in BCC chromium, which has a lattice constant of 0.28846 nm. Compare the values and draw a conclusion. (*a*) (100), (*b*) (110), (*c*) (111).

3.61 Calculate the planar atomic density in atoms per square millimeter for the following crystal planes in FCC gold, which has a lattice constant of 0.40788 nm. Compare the values and draw a conclusion. (*a*) (100), (*b*) (110), (*c*) (111).

3.62 Calculate the planar atomic density in atoms per square millimeter for the (0001) plane in HCP beryllium, which has a lattice constant $a = 0.22856$ nm and a c constant of 0.35832 nm. Can you make any observations about this plane?

3.63 Calculate the linear atomic density in atoms per millimeter for the following directions in BCC vanadium, which has a lattice constant of 0.3039 nm: (*a*) [100], (*b*) [110], (*c*) [111]. Determine the repeat distance along each direction.

3.64 Calculate the linear atomic density in atoms per millimeter for the following directions in FCC iridium, which has a lattice constant of 0.38389 nm: (*a*) [100], (*b*) [110], (*c*) [111]. Determine the repeat distance along each direction.

3.65 Titanium goes through a polymorphic change from BCC to HCP crystal structure upon cooling through 332°C. Calculate the percentage change in volume when the crystal structure changes from BCC to HCP. The lattice constant a of the BCC unit cell at 882°C is 0.332 nm, and the HCP unit cell has $a = 0.2950$ nm and $c = 0.4683$ nm.

3.66 Pure iron goes through a polymorphic change from BCC to FCC upon heating through 912°C. Calculate the volume change associated with the change in crystal structure from BCC to FCC if at 912°C the BCC unit cell has a lattice constant $a = 0.293$ nm and the FCC unit cell $a = 0.363$ nm.

3.67 Derive Bragg's law by using the simple case of incident X-ray beams being diffracted by parallel planes in a crystal.

3.68 A sample of BCC metal was placed in an X-ray diffractometer using X-rays with a wavelength of $\lambda = 0.1541$ nm. Diffraction from the {221} planes was obtained at $2\theta = 88.838°$. Calculate a value for the lattice constant a for this BCC elemental metal. (Assume first-order diffraction, $n = 1$.)

3.69 X-rays of an unknown wavelength are diffracted by a gold sample. The 2θ angle was 64.582° for the {220} planes. What is the wavelength of the X-rays used? (The lattice constant of gold = 0.40788 nm; assume first-order diffraction, $n = 1$.)

3.70 An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 41.069°, 47.782°, 69.879°, and 84.396°. The wavelength of the incoming radiation was 0.15405 nm. (X-ray diffraction data courtesy of the International Centre for Diffraction Data.)

(*a*) Determine the crystal structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

3.71 An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 38.60°, 55.71°, 69.70°, 82.55°, 95.00°, and 107.67°. Wavelength λ of the incoming radiation was 0.15405 nm.

(*a*) Determine the crystal structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

3.72 An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 36.191°, 51.974°, 64.982°, and 76.663°. The wavelength of the incoming radiation was 0.15405 nm.

(*a*) Determine the crystal structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

3.73 An X-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 40.663°, 47.314°, 69.144°, and 83.448°. Wavelength l of the incoming radiation was 0.15405 nm.

(*a*) Determine the crystal structure of the element.
(*b*) Determine the lattice constant of the element.
(*c*) Identify the element.

Synthesis and Evaluation Problems

3.74 Do you expect iron and silver to have the same (*a*) atomic packing factor, (*b*) volume of unit cell, (*c*) number of atoms per unit cell, and (*d*) coordination number? How about gold and silver? How about titanium and silver?

3.75 In a cubic unit cell, draw the (111) and (011) planes. Highlight the intersection of the two planes. What are the direction indices of the intersection line?

3.76 In a cubic unit cell, draw the (011) and (110) planes. Highlight the intersection of the two planes. What are the direction indices of the intersection line?

3.77 Show using geometry that the ideal *c*/*a* ratio of the hexagonal close-packed unit cell (when atoms are perfect spheres) is 1.633. Hint: Draw the center atom in the top basal plane in contact with the three atoms in the center of the HCP cell; connect the centers of the three atoms inside the HCP cell to each other and to the atom at the center of one of the basal planes.

3.78 Assuming that the volume of an HCP metal cell (larger cell) is 0.09130 nm^3 and the *c*/*a* ratio is 1.856, determine (*a*) the values for *c* and *a,* and (*b*) the radius, *R,* of the atom. (*c*) If you were told that the metal is zinc, would you be surprised? How do you explain the discrepancy?

3.79 Assuming that the volume of an HCP metal cell (larger cell) is 0.01060 nm^3 and the *c*/*a* ratio is 1.587, determine (*a*) the values for *c* and *a,* and (*b*) the radius, *R,* of the atom. (*c*) If you were told that the metal is titanium, does the calculated R match that of Ti? How do you explain the discrepancy?

3.80 The structure of NaCl (an ionic material) is given in Figure 2.18*b*. Determine (*a*) its lattice constant *a,* and (*b*) its density. Hint: Since NaCl is ionic, use the ion radius data and note the atomic radii.

3.81 The unit cell structure of the ionic solid, CsI, is similar to that in Figure 2.18*a*. Determine (*a*) its packing factor, and (*b*) compare this packing factor with that of BCC metals. Explain the difference, if any.

3.82 Iron (below 912°C) and tungsten are both BCC with significantly different atomic radii. However, they have the same atomic packing factor of 0.68. How do you explain this?

3.83 Verify that there are eight atoms inside a diamond cubic structure (see Figure 2.23*b* and *c*). Draw a 3D schematic of the atoms inside the cell.

3.84 The lattice constant for the diamond cubic structure of diamond is 0.357 nm. Diamond is metastable, meaning that it will transform to graphite at elevated temperatures. If this transformation occurs, what percent volume change will occur? (Density of graphite is 2.25 gr/cm^3)

3.85 Calculate the center-to-center distance between adjacent atoms of gold along the following directions: (*a*) [100], (*b*) [101], (*c*) [111], and (*d*) [102]. Speculate as to why such information may be important in understanding the behavior of the material.

3.86 Calculate the center-to-center distance between adjacent atoms of tungsten along the following directions: (*a*) [100], (*b*) [101], (*c*) [111], and (*d*) [102]. Speculate as to why such information may be important in understanding the behavior of the material.

3.87 A plane in a cubic crystal intersects the x axis at 0.25, the y axis at 2, and is parallel to the z axis. What are the Miller indices for this plane? Draw this plane in a single cube and show all key dimensions.

3.88 A plane in a cubic crystal intersects the x axis at 3, the y axis at 1, and the z axis at 1. What are the Miller indices for this plane? Draw this plane in a single cube and show all key dimensions.

3.89 A plane in a hexagonal crystal intersects at the a_1 axis at -1, the a_2 axis at 1, and the c axis at infinity. What are the Miller indices for this plane? Draw this plane in a hexagonal unit cell and show all key dimensions.

3.90 A plane in a hexagonal crystal intersects at the a_1 axis at 1, the a_2 axis at 1, and the c axis at 0.5. What are the Miller indices for this plane? Draw this plane in a hexagonal unit cell and show all key dimensions.

3.91 Without drawing any of the hexagonal planes given below, determine which of the planes is, in fact, not a plane. (*a*) $(\bar{1}0\bar{1}0)$, (*b*) $(10\bar{1}0)$, and (*c*) $(\bar{1}1\bar{1}0)$.

3.92 Name as many carbon allotropes as you can, and discuss their crystal structure.

3.93 A thin layer of aluminum nitride is sometimes deposited on silicon wafers at high temperatures (1000°C). The coefficient of thermal expansion and the lattice constant of the silicon crystal is different than that of aluminum nitride. Will this cause a problem? Explain.

3.94 An unknown material is being analyzed using X-ray diffraction techniques. However, the diffraction patterns are extremely broad (no clear peaks are visible). (*a*) What does this tell you about the material? (*b*) What are some of the tests that you can perform to help identify the material or narrow the possibilities?

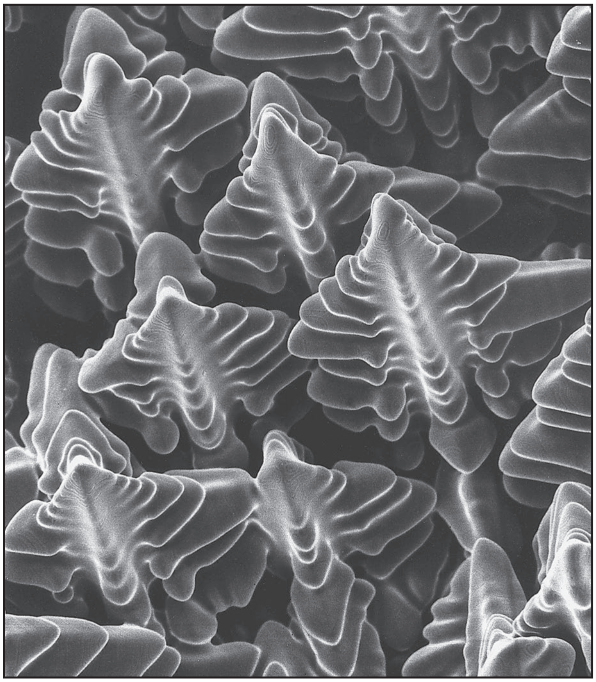
3.95 Explain, in general terms, why many polymers and some ceramic glasses have an amorphous or semicrystalline structure.

3.96 Explain how ultra-rapid cooling of some metal alloys produces metallic glass.

CHAPTER

4

Solidification and Crystalline Imperfections



(Courtesy of Stan David and Lynn Boatner, Oak Ridge National Library)

When molten alloys are cast, solidification starts at the walls of the mold as it is being cooled. The solidification of an alloy (as opposed to a pure metal) takes place not at a specific temperature but over a range of temperatures. While the alloy is in this range, it has a pasty form that consists of solid, treelike structures called *dendrites* (meaning *treelike),* and liquid metal. The size and shape of the dendrite depends on the cooling rate. The liquid metal existing among these three-dimensional dendritic structures eventually solidifies to form a completely solid structure that we refer to as the grain structure. The study of dendrites is important because they influence compositional variations, porosity, and segregation and therefore the properties of the cast metal. The figure shows the three-dimensional structure of dendrites. The figure shows a "forest" of dendrites formed during the solidification of a nickel-based superalloy.[1] ■

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[1] http://mgnews.msfc.nasa.gov/IDGE/IDGE.html