MATERIALS SCIENCE and ENGINEERING

An Introduction

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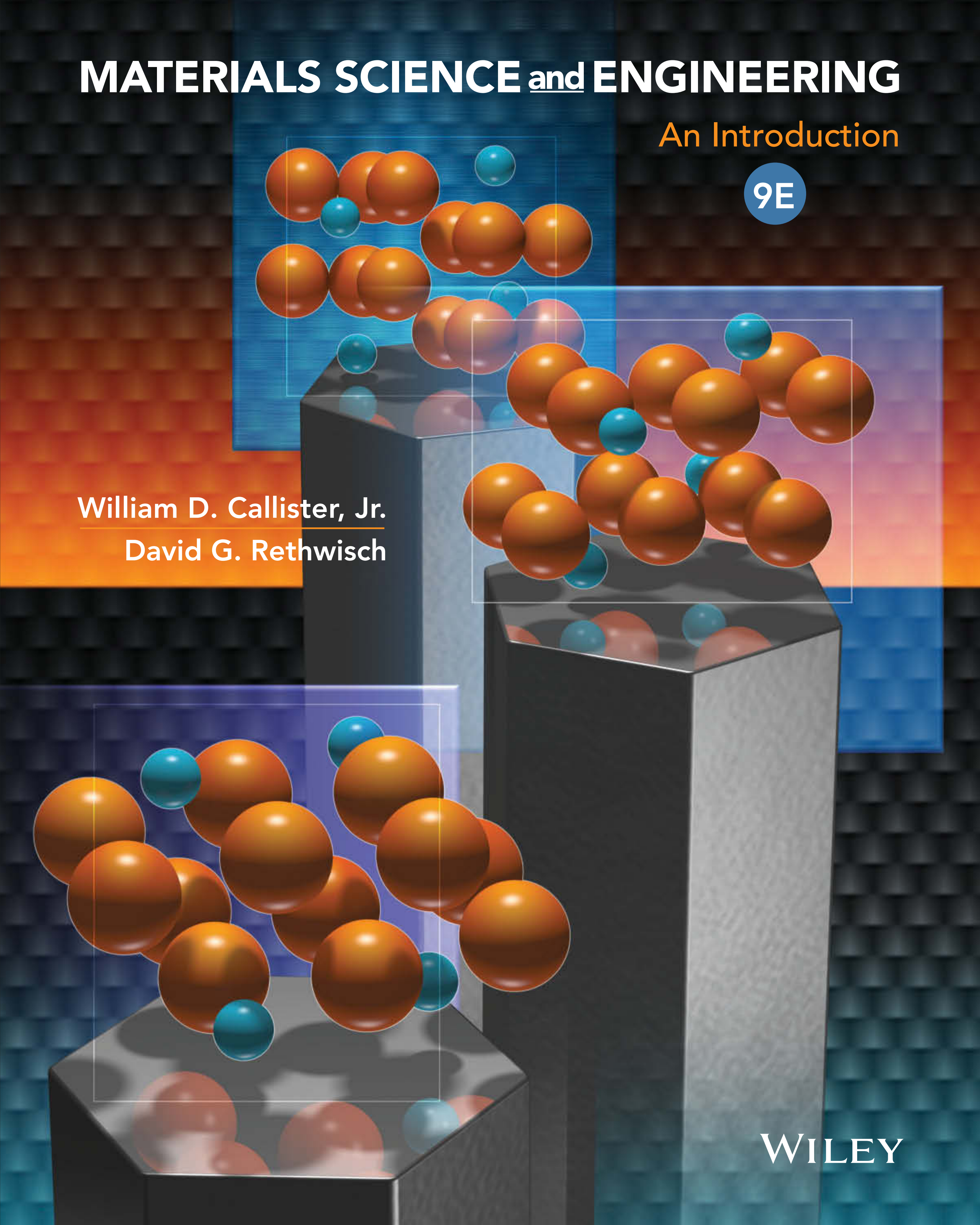

William D. Callister, Jr.

David G. Rethwisch

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Characteristics of Selected Elements

Element	*Symbol*	*Atomic Number*	*Atomic Weight (amu)*	*Density of Solid, 20°C (g/cm^3)*	*Crystal Structure, 20°C*	*Atomic Radius (nm)*	*Ionic Radius (nm)*	*Most Common Valence*	*Melting Point (°C)*
Aluminum	Al	13	26.98	2.71	FCC	0.143	0.053	3+	660.4
Argon	Ar	18	39.95	—	—	—	—	Inert	−189.2
Barium	Ba	56	137.33	3.5	BCC	0.217	0.136	2+	725
Beryllium	Be	4	9.012	1.85	HCP	0.114	0.035	2+	1278
Boron	B	5	10.81	2.34	Rhomb.	—	0.023	3+	2300
Bromine	Br	35	79.90	—	—	—	0.196	1−	−7.2
Cadmium	Cd	48	112.41	8.65	HCP	0.149	0.095	2+	321
Calcium	Ca	20	40.08	1.55	FCC	0.197	0.100	2+	839
Carbon	C	6	12.011	2.25	Hex.	0.071	~0.016	4+	(sublimes at 3367)
Cesium	Cs	55	132.91	1.87	BCC	0.265	0.170	1+	28.4
Chlorine	Cl	17	35.45	—	—	—	0.181	1−	−101
Chromium	Cr	24	52.00	7.19	BCC	0.125	0.063	3+	1875
Cobalt	Co	27	58.93	8.9	HCP	0.125	0.072	2+	1495
Copper	Cu	29	63.55	8.94	FCC	0.128	0.096	1+	1085
Fluorine	F	9	19.00	—	—	—	0.133	1−	−220
Gallium	Ga	31	69.72	5.90	Ortho.	0.122	0.062	3+	29.8
Germanium	Ge	32	72.64	5.32	Dia. cubic	0.122	0.053	4+	937
Gold	Au	79	196.97	19.32	FCC	0.144	0.137	1+	1064
Helium	He	2	4.003	—	—	—	—	Inert	−272 (at 26 atm)
Hydrogen	H	1	1.008	—	—	—	0.154	1+	−259
Iodine	I	53	126.91	4.93	Ortho.	0.136	0.220	1−	114
Iron	Fe	26	55.85	7.87	BCC	0.124	0.077	2+	1538
Lead	Pb	82	207.2	11.35	FCC	0.175	0.120	2+	327
Lithium	Li	3	6.94	0.534	BCC	0.152	0.068	1+	181
Magnesium	Mg	12	24.31	1.74	HCP	0.160	0.072	2+	649
Manganese	Mn	25	54.94	7.44	Cubic	0.112	0.067	2+	1244
Mercury	Hg	80	200.59	—	—	—	0.110	2+	−38.8
Molybdenum	Mo	42	95.94	10.22	BCC	0.136	0.070	4+	2617
Neon	Ne	10	20.18	—	—	—	—	Inert	−248.7
Nickel	Ni	28	58.69	8.90	FCC	0.125	0.069	2+	1455
Niobium	Nb	41	92.91	8.57	BCC	0.143	0.069	5+	2468
Nitrogen	N	7	14.007	—	—	—	0.01–0.02	5+	−209.9
Oxygen	O	8	16.00	—	—	—	0.140	2−	−218.4
Phosphorus	P	15	30.97	1.82	Ortho.	0.109	0.035	5+	44.1
Platinum	Pt	78	195.08	21.45	FCC	0.139	0.080	2+	1772
Potassium	K	19	39.10	0.862	BCC	0.231	0.138	1+	63
Silicon	Si	14	28.09	2.33	Dia. cubic	0.118	0.040	4+	1410
Silver	Ag	47	107.87	10.49	FCC	0.144	0.126	1+	962
Sodium	Na	11	22.99	0.971	BCC	0.186	0.102	1+	98
Sulfur	S	16	32.06	2.07	Ortho.	0.106	0.184	2−	113
Tin	Sn	50	118.71	7.27	Tetra.	0.151	0.071	4+	232
Titanium	Ti	22	47.87	4.51	HCP	0.145	0.068	4+	1668
Tungsten	W	74	183.84	19.3	BCC	0.137	0.070	4+	3410
Vanadium	V	23	50.94	6.1	BCC	0.132	0.059	5+	1890
Zinc	Zn	30	65.41	7.13	HCP	0.133	0.074	2+	420
Zirconium	Zr	40	91.22	6.51	HCP	0.159	0.079	4+	1852

Values of Selected Physical Constants

Quantity	*Symbol*	*SI Units*	*cgs Units*
Avogadro's number	N_A	6.022×10^{23} molecules/mol	6.022×10^{23} molecules/mol
Boltzmann's constant	k	1.38×10^{-23} J/atom · K	1.38×10^{-16} erg/atom · K 8.62×10^{-5} eV/atom · K
Bohr magneton	μ_B	9.27×10^{-24} A · m^2	9.27×10^{-21} erg/gauss[a]
Electron charge	e	1.602×10^{-19} C	4.8×10^{-10} statcoul[b]
Electron mass	—	9.11×10^{-31} kg	9.11×10^{-28} g
Gas constant	R	8.31 J/mol · K	1.987 cal/mol · K
Permeability of a vacuum	μ_0	1.257×10^{-6} henry/m	unity[a]
Permittivity of a vacuum	ϵ_0	8.85×10^{-12} farad/m	unity[b]
Planck's constant	h	6.63×10^{-34} J · s	6.63×10^{-27} erg · s 4.13×10^{-15} eV · s
Velocity of light in a vacuum	c	3×10^{8} m/s	3×10^{10} cm/s

[a] In cgs-emu units.
[b] In cgs-esu units.

Unit Abbreviations

A = ampere
Å = angstrom
Btu = British thermal unit
C = Coulomb
°C = degrees Celsius
cal = calorie (gram)
cm = centimeter
eV = electron volt
°F = degrees Fahrenheit
ft = foot
g = gram
in. = inch
J = joule
K = degrees Kelvin
kg = kilogram
lb_f = pound force
lb_m = pound mass
m = meter
Mg = megagram
mm = millimeter
mol = mole
MPa = megapascal
N = newton
nm = nanometer
P = poise
Pa = Pascal
s = second
T = temperature
μm = micrometer (micron)
W = watt
psi = pounds per square inch

SI Multiple and Submultiple Prefixes

Factor by Which Multiplied	*Prefix*	*Symbol*
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{-2}	centi[a]	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

[a] Avoided when possible.


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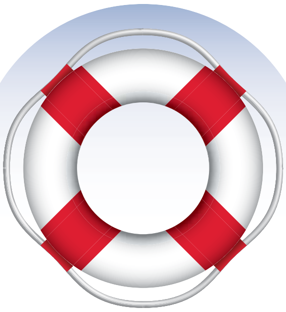

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9th Edition

Materials Science and Engineering

AN INTRODUCTION

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WILEY

Front Cover: Depiction of a unit cell for iron carbide (Fe_3C) from three different perspectives. Brown and blue spheres represent iron and carbon atoms, respectively.
Back Cover: Three representations of the unit cell for body-centered cubic iron (α-ferrite); each unit cell contains an interstitial carbon atom.

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Dedicated to
Bill Stenquist, editor and friend

Preface

In this ninth edition we have retained the objectives and approaches for teaching materials science and engineering that were presented in previous editions. **The first, and primary, objective** is to present the basic fundamentals on a level appropriate for university/college students who have completed their freshmen calculus, chemistry, and physics courses.

The **second objective** is to present the subject matter in a logical order, from the simple to the more complex. Each chapter builds on the content of previous ones.

The third objective, or philosophy, that we strive to maintain throughout the text is that if a topic or concept is worth treating, then it is worth treating in sufficient detail and to the extent that students have the opportunity to fully understand it without having to consult other sources; in addition, in most cases, some practical relevance is provided.

The fourth objective is to include features in the book that will expedite the learning process. These learning aids include the following:

- Numerous illustrations, now presented in full color, and photographs to help visualize what is being presented
- Learning objectives, to focus student attention on what they should be getting from each chapter
- "Why Study . . ." and "Materials of Importance" items as well as case studies that provide relevance to topic discussions
- "Concept Check" questions that test whether a student understands the subject matter on a conceptual level
- Key terms, and descriptions of key equations, highlighted in the margins for quick reference
- End-of-chapter questions and problems designed to progressively develop students' understanding of concepts and facility with skills
- Answers to selected problems, so students can check their work
- A glossary, a global list of symbols, and references to facilitate understanding of the subject matter
- End-of-chapter summary tables of important equations and symbols used in these equations
- Processing/Structure/Properties/Performance correlations and summary concept maps for four materials (steels, glass-ceramics, polymer fibers, and silicon semiconductors), which integrate important concepts from chapter to chapter
- Materials of Importance sections that lend relevance to topical coverage by discussing familiar and interesting materials and their applications

The fifth objective is to enhance the teaching and learning process by using the newer technologies that are available to most instructors and today's engineering students.

New/Revised Content

Several important changes have been made with this Ninth Edition. One of the most significant is the incorporation of several new sections, as well as revisions/amplifications of other sections. These include the following:

- Numerous new and revised example problems. In addition, all homework problems requiring computations have been refreshed.
- Revised, expanded, and updated tables
- Two new case studies: "Liberty Ship Failures" (Chapter 1) and "Use of Composites in the Boeing 787 Dreamliner" (Chapter 16)
- Bond hybridization in carbon (Chapter 2)
- Revision of discussions on crystallographic planes and directions to include the use of equations for the determination of planar and directional indices (Chapter 3)
- Revised discussion on determination of grain size (Chapter 4)
- New section on the structure of carbon fibers (Chapter 13)
- Revised/expanded discussions on structures, properties, and applications of the nanocarbons: fullerenes, carbon nanotubes, and graphene (Chapter 13)
- Revised/expanded discussion on structural composites: laminar composites and sandwich panels (Chapter 16)
- New section on structure, properties, and applications of nanocomposite materials (Chapter 16)
- Tutorial videos. In *WileyPLUS*, Tutorial Videos help students with their "muddiest points" in conceptual understanding and problem-solving.
- Exponents and logarithms. In *WileyPLUS*, the exponential functions and natural logarithms have been added to the Exponents and Logarithms section of the Math Skills Review.
- Fundamentals of Engineering homework problems and questions for most chapters. These appear at the end of Questions and Problems sections and provide students the opportunity to practice answering and solving questions and problems similar to those found on Fundamentals of Engineering examinations.

Online Learning Resources—Student Companion Site at www.wiley.com/college/callister.

Also found on the book's website is a Students' Companion page on which is posted several important instructional elements for the student that complement the text; these include the following:

- **Answers to Concept Check questions**, questions which are found in the print book.
- **Library of Case Studies.** One way to demonstrate principles of *design* in an engineering curriculum is via case studies: analyses of problem-solving strategies applied to real-world examples of applications/devices/failures encountered by engineers. Five case studies are provided as follows: (1) Materials Selection for a Torsionally Stressed Cylindrical Shaft; (2) Automobile Valve Spring; (3) Failure of an Automobile Rear Axle; (4) Artificial Total Hip Replacement; and (5) Chemical Protective Clothing.
- **Mechanical Engineering (ME) Module.** This module treats materials science/engineering topics not covered in the printed text that are relevant to mechanical engineering.
- **Extended Learning Objectives.** This is a more extensive list of learning objectives than is provided at the beginning of each chapter. These direct the student to study the subject material to a greater depth.

- **Student Lecture PowerPoint® Slides**. These slides (in both Adobe Acrobat® PDF and PowerPoint® formats) are virtually identical to the lecture slides provided to an instructor for use in the classroom. The student set has been designed to allow for note taking on printouts.
- **Index of Learning Styles.** Upon answering a 44-item questionnaire, a user's learning-style preference (i.e., the manner in which information is assimilated and processed) is assessed.

Online Resources for Instructors—Instructors Companion Site at www.wiley.com/college/callister.

The Instructor Companion Site is available for instructors who have adopted this text. Please visit the website to register for access. Resources that are available include the following:

- **All resources found on the Student Companion Site.** (Except for the Student Lecture PowerPoint® Slides.)
- **Instructor Solutions Manual.** Detailed solutions for all end-of-chapter questions and problems (in both Word® and Adobe Acrobat® PDF formats).
- **Homework Problem Correlation Guide—8th edition to 9th edition.** This guide notes, for each homework problem or question (by number), whether it appeared in the eighth edition and, if so, its number in this previous edition.
- ***Virtual Materials Science and Engineering* (*VMSE*).** This web-based software package consists of interactive simulations and animations that enhance the learning of key concepts in materials science and engineering. Included in VMSE are eight modules and a materials properties/cost database. Titles of these modules are as follows: (1) Metallic Crystal Structures and Crystallography; (2) Ceramic Crystal Structures; (3) Repeat Unit and Polymer Structures; (4) Dislocations; (5) Phase Diagrams; (6) Diffusion; (7) Tensile Tests; and (8) Solid-Solution Strengthening.
- **Image Gallery**. Illustrations from the book. Instructors can use them in assignments, tests, or other exercises they create for students.
- **Art PowerPoint Slides.** Book art loaded into PowerPoints, so instructors can more easily use them to create their own PowerPoint Slides.
- **Lecture Note PowerPoints.** These slides, developed by the authors and Peter M. Anderson (The Ohio State University), follow the flow of topics in the text, and include materials taken from the text as well as other sources. Slides are available in both Adobe Acrobat® PDF and PowerPoint® formats. [*Note:* If an instructor doesn't have available all fonts used by the developer, special characters may not be displayed correctly in the PowerPoint version (i.e., it is not possible to embed fonts in PowerPoints); however, in the PDF version, these characters will appear correctly.]
- **Solutions to Case Study Problems.**
- **Solutions to Problems in the Mechanical Engineering Web Module.**
- **Suggested Course Syllabi for the Various Engineering Disciplines.** Instructors may consult these syllabi for guidance in course/lecture organization and planning.
- **Experiments and Classroom Demonstrations.** Instructions and outlines for experiments and classroom demonstrations that portray phenomena and/or illustrate principles that are discussed in the book; references are also provided that give more detailed accounts of these demonstrations.

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Feedback

We have a sincere interest in meeting the needs of educators and students in the materials science and engineering community, and therefore we solicit feedback on this edition. Comments, suggestions, and criticisms may be submitted to the authors via email at the following address: billcallister@comcast.net.

Acknowledgments

Since we undertook the task of writing this and previous editions, instructors and students, too numerous to mention, have shared their input and contributions on how to make this work more effective as a teaching and learning tool. To all those who have helped, we express our sincere thanks.

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In addition, we thank the many instructors who participated in the fall 2011 marketing survey; their valuable contributions were driving forces for many of the changes and additions to this ninth edition.

We are also indebted to Dan Sayre, Executive Editor, Jennifer Welter, Senior Product Designer, and Jessica Knecht, Editorial Program Assistant, for their guidance and assistance on this revision.

Last, but certainly not least, we deeply and sincerely appreciate the continual encouragement and support of our families and friends.

William D. Callister, Jr.
David G. Rethwisch
October 2013

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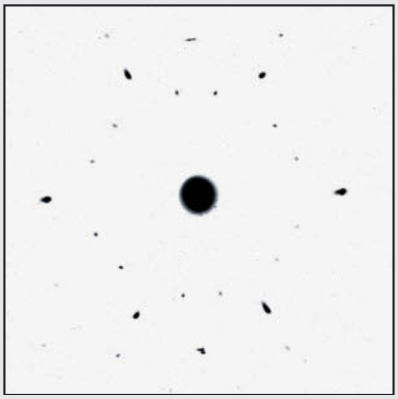
Chapter 3 The Structure of Crystalline Solids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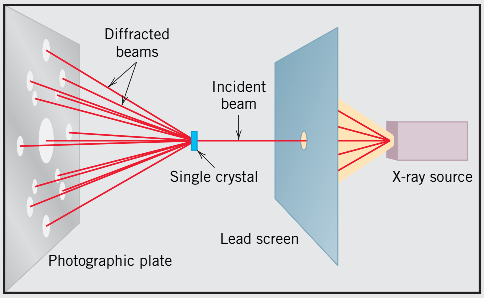
(a)



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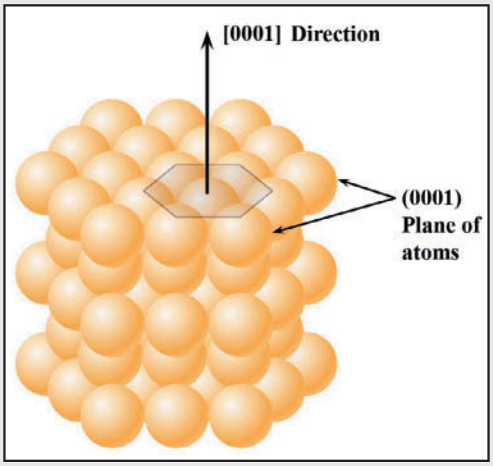

(c)

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(*a*) X-ray diffraction photograph [or Laue photograph (Section 3.16)] for a single crystal of magnesium. (*b*) Schematic diagram illustrating how the spots (i.e., the diffraction pattern) in (*a*) are produced. The lead screen blocks out all beams generated from the x-ray source, except for a narrow beam traveling in a single direction. This incident beam is diffracted by individual crystallographic planes in the single crystal (having different orientations), which gives rise to the various diffracted beams that impinge on the photographic plate. Intersections of these beams with the plate appear as spots when the film is developed. The large spot in the center of (*a*) is from the incident beam, which is parallel to a [0001] crystallographic direction. It should be noted that the hexagonal symmetry of magnesium's hexagonal close-packed crystal structure [shown in (*c*)] is indicated by the diffraction spot pattern that was generated.

(*d*) Photograph of a single crystal of magnesium that was cleaved (or split) along a (0001) plane—the flat surface is a (0001) plane. Also, the direction perpendicular to this plane is a [0001] direction.

(*e*) Photograph of a *mag wheel*—a lightweight automobile wheel made of magnesium.

[Figure (*b*) from J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Copyright © 2004 by John Wiley & Sons, Hoboken, NJ. Reprinted by permission of John Wiley & Sons, Inc.]

WHY STUDY *The Structure of Crystalline Solids?*

The properties of some materials are directly related to their crystal structures. For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than are pure and undeformed metals such as gold and silver that have yet another crystal structure (see Section 7.4).

Furthermore, significant property differences exist between crystalline and noncrystalline materials having the same composition. For example, noncrystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semicrystalline) form tend to be opaque or, at best, translucent.

Learning Objectives

After studying this chapter, you should be able to do the following:

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

3.1 INTRODUCTION

Chapter 2 was concerned primarily with the various types of atomic bonding, which are determined by the electron structures of the individual atoms. The present discussion is devoted to the next level of the structure of materials, specifically, to some of the arrangements that may be assumed by atoms in the solid state. Within this framework, concepts of crystallinity and noncrystallinity are introduced. For crystalline solids, the notion of crystal structure is presented, specified in terms of a unit cell. The three common crystal structures found in metals are then detailed, along with the scheme by which crystallographic points, directions, and planes are expressed. Single crystals, polycrystalline materials, and noncrystalline materials are considered. Another section of this chapter briefly describes how crystal structures are determined experimentally using x-ray diffraction techniques.

Crystal Structures

3.2 FUNDAMENTAL CONCEPTS

crystalline

Solid materials may be classified according to the regularity with which atoms or ions are arranged with respect to one another. A **crystalline** material is one in which the atoms are situated in a repeating or periodic array over large atomic distances—that is, long-range order exists, such that upon solidification, the atoms will position themselves

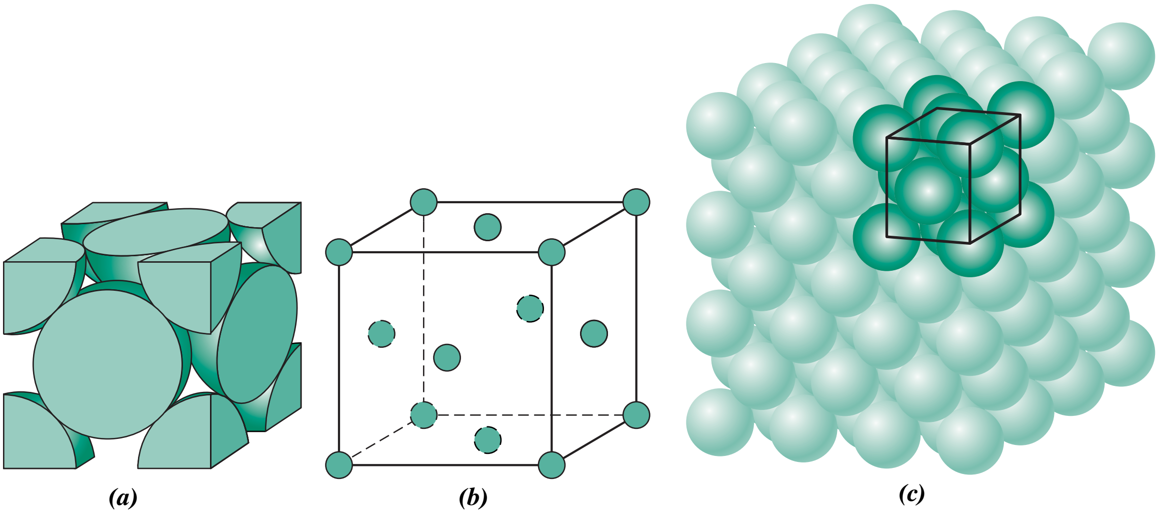

Figure 3.1 For the face-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms.
[Figure (*c*) adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.]

in a repetitive three-dimensional pattern, in which each atom is bonded to its nearest-neighbor atoms. All metals, many ceramic materials, and certain polymers form crystalline structures under normal solidification conditions. For those that do not crystallize, this long-range atomic order is absent; these *noncrystalline* or *amorphous* materials are discussed briefly at the end of this chapter.

crystal structure

Some of the properties of crystalline solids depend on the **crystal structure** of the material, the manner in which atoms, ions, or molecules are spatially arranged. There is an extremely large number of different crystal structures all having long-range atomic order; these vary from relatively simple structures for metals to exceedingly complex ones, as displayed by some of the ceramic and polymeric materials. The present discussion deals with several common metallic crystal structures. Chapters 12 and 14 are devoted to crystal structures for ceramics and polymers, respectively.

lattice

When crystalline structures are described, atoms (or ions) are thought of as being solid spheres having well-defined diameters. This is termed the *atomic hard-sphere model* in which spheres representing nearest-neighbor atoms touch one another. An example of the hard-sphere model for the atomic arrangement found in some of the common elemental metals is displayed in Figure 3.1*c*. In this particular case all the atoms are identical. Sometimes the term **lattice** is used in the context of crystal structures; in this sense *lattice* means a three-dimensional array of points coinciding with atom positions (or sphere centers).

3.3 UNIT CELLS

unit cell

The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystal structures, it is often convenient to subdivide the structure into small repeat entities called **unit cells.** Unit cells for most crystal structures are parallelepipeds or prisms having three sets of parallel faces; one is drawn within the aggregate of spheres (Figure 3.1*c*), which in this case happens to be a cube. A unit cell is chosen to represent the symmetry of the crystal structure, wherein all the atom positions in the crystal may be generated by translations of the unit cell integral distances along each of its edges. Thus, the unit cell is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within. Convenience usually dictates that parallelepiped corners coincide with centers of the hard-sphere atoms. Furthermore, more than a single unit cell may be chosen for a particular crystal structure; however, we generally use the unit cell having the highest level of geometrical symmetry.

3.4 METALLIC CRYSTAL STRUCTURES

The atomic bonding in this group of materials is metallic and thus nondirectional in nature. Consequently, there are minimal restrictions as to the number and position of nearest-neighbor atoms; this leads to relatively large numbers of nearest neighbors and dense atomic packings for most metallic crystal structures. Also, for metals, when we use the hard-sphere model for the crystal structure, each sphere represents an ion core. Table 3.1 presents the atomic radii for a number of metals. Three relatively simple crystal structures are found for most of the common metals: face-centered cubic, body-centered cubic, and hexagonal close-packed.

The Face-Centered Cubic Crystal Structure

face-centered cubic (FCC)

The crystal structure found for many metals has a unit cell of cubic geometry, with atoms located at each of the corners and the centers of all the cube faces. It is aptly called the **face-centered cubic (FCC)** crystal structure. Some of the familiar metals having this crystal structure are copper, aluminum, silver, and gold (see also Table 3.1). Figure 3.1*a* shows a hard-sphere model for the FCC unit cell, whereas in Figure 3.1*b* the atom centers are represented by small circles to provide a better perspective on atom positions. The aggregate of atoms in Figure 3.1*c* represents a section of crystal consisting of many FCC unit cells. These spheres or ion cores touch one another across a face diagonal; the cube edge length *a* and the atomic radius *R* are related through

Unit cell edge length for face-centered cubic

$$a = 2R\sqrt{2} \tag{3.1}$$

This result is obtained in Example Problem 3.1.

Table 3.1
Atomic Radii and Crystal Structures for 16 Metals

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

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.
[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

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Crystal Systems and
Unit Cells for Metals

On occasion, we need to determine the number of atoms associated with each unit cell. Depending on an atom's location, it may be considered to be shared with adjacent unit cells—that is, only some fraction of the atom is assigned to a specific cell. For example, for cubic unit cells, an atom completely within the interior "belongs" to that unit cell, one at a cell face is shared with one other cell, and an atom residing at a corner is shared among eight. The number of atoms per unit cell, N, can be computed using the following formula:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \tag{3.2}$$

where

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

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Tutorial Video: FCC Unit Cell Calculations

For the FCC crystal structure, there are eight corner atoms ($N_c = 8$), six face atoms ($N_f = 6$), and no interior atoms ($N_i = 0$). Thus, from Equation 3.2,

$$N = 0 + \frac{6}{2} + \frac{8}{8} = 4$$

or a total of four whole atoms may be assigned to a given unit cell. This is depicted in Figure 3.1*a*, where only sphere portions are represented within the confines of the cube. The cell is composed of the volume of the cube that is generated from the centers of the corner atoms, as shown in the figure.

Corner and face positions are really equivalent—that is, translation of the cube corner from an original corner atom to the center of a face atom will not alter the cell structure.

coordination number

atomic packing factor (APF)

Two other important characteristics of a crystal structure are the **coordination number** and the **atomic packing factor (APF).** For metals, each atom has the same number of nearest-neighbor or touching atoms, which is the coordination number. For face-centered cubics, the coordination number is 12. This may be confirmed by examination of Figure 3.1*a*; the front face atom has four corner nearest-neighbor atoms surrounding it, four face atoms that are in contact from behind, and four other equivalent face atoms residing in the next unit cell to the front (not shown).

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

Definition of atomic packing factor

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} \tag{3.3}$$

For the FCC structure, the atomic packing factor is 0.74, which is the maximum packing possible for spheres all having the same diameter. Computation of this APF is also included as an example problem. Metals typically have relatively large atomic packing factors to maximize the shielding provided by the free electron cloud.

The Body-Centered Cubic Crystal Structure

body-centered cubic (BCC)

Another common metallic crystal structure also has a cubic unit cell with atoms located at all eight corners and a single atom at the cube center. This is called a **body-centered cubic (BCC)** crystal structure. A collection of spheres depicting this crystal structure is shown in Figure 3.2*c*, whereas Figures 3.2*a* and 3.2*b* are diagrams of BCC unit cells with the atoms represented by hard-sphere and reduced-sphere models, respectively. Center

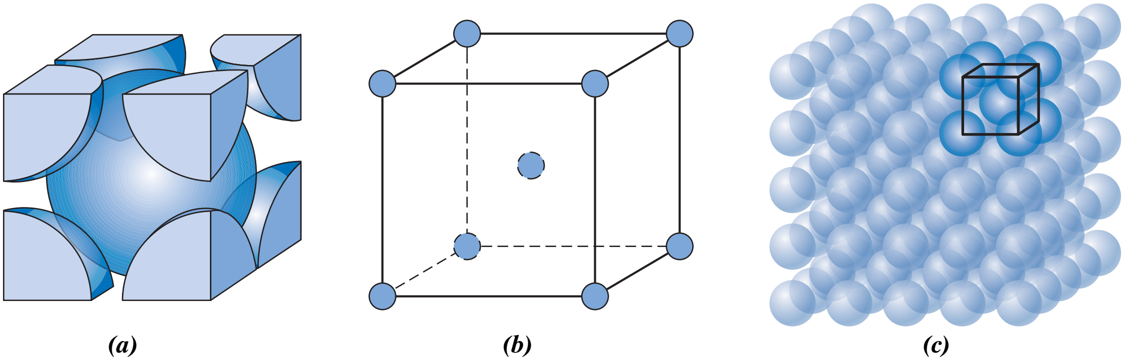

Figure 3.2 For the body-centered cubic crystal structure, (*a*) a hard-sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms.
[Figure (*c*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.]

and corner atoms touch one another along cube diagonals, and unit cell length a and atomic radius R are related through

Unit cell edge length for body-centered cubic

$$a = \frac{4R}{\sqrt{3}} \tag{3.4}$$

Chromium, iron, tungsten, and several other metals listed in Table 3.1 exhibit a BCC structure.

Each BCC unit cell has eight corner atoms and a single center atom, which is wholly contained within its cell; therefore, from Equation 3.2, the number of atoms per BCC unit cell is

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Crystal Systems and Unit Cells for Metals

$$\begin{aligned} N &= N_i + \frac{N_f}{2} + \frac{N_c}{8} \\ &= 1 + 0 + \frac{8}{8} = 2 \end{aligned}$$

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Tutorial Video: BCC Unit Cell Calculations

The coordination number for the BCC crystal structure is 8; each center atom has as nearest neighbors its eight corner atoms. Because the coordination number is less for BCC than for FCC, the atomic packing factor is also lower for BCC—0.68 versus 0.74.

It is also possible to have a unit cell that consists of atoms situated only at the corners of a cube. This is called the *simple cubic* (*SC*) *crystal structure*; hard-sphere and reduced-sphere models are shown, respectively, in Figures 3.3*a* and 3.3*b*. None of the metallic elements have this crystal structure because of its relatively low atomic packing factor (see Concept Check 3.1). The only simple-cubic element is polonium, which is considered to be a metalloid (or semi-metal).

The Hexagonal Close-Packed Crystal Structure

hexagonal close-packed (HCP)

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 3.4*a* shows a reduced-sphere unit cell for this structure, which is termed **hexagonal close-packed (HCP);** an assemblage of several HCP unit cells is presented in Figure 3.4*b*.[1] The top and bottom

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[1] Alternatively, the unit cell for HCP may be specified in terms of the parallelepiped defined by the atoms labeled A through H in Figure 3.4*a*. Thus, the atom denoted J lies within the unit cell interior.

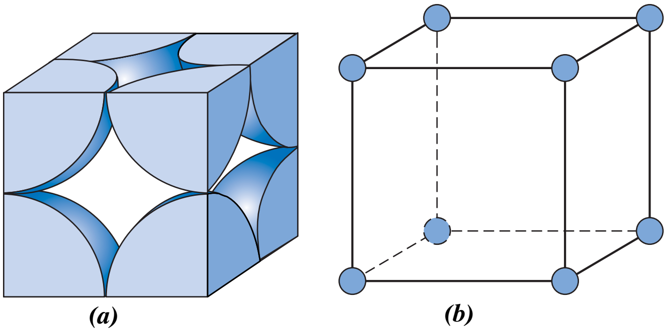

Figure 3.3 For the simple cubic crystal structure, (*a*) a hard-sphere unit cell, and (*b*) a reduced-sphere unit cell.

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Crystal Systems and Unit Cells for Metals

faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes.

In order to compute the number of atoms per unit cell for the HCP crystal structure, Equation 3.2 is modified to read as follows:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{6} \tag{3.5}$$

That is, one-sixth of each corner atom is assigned to a unit cell (instead of 8 as with the cubic structure). Because for HCP there are 6 corner atoms in each of the top and bottom faces (for a total of 12 corner atoms), 2 face center atoms (one from each of the top and bottom faces), and 3 midplane interior atoms, the value of N for HCP is found, using Equation 3.5, to be

$$N = 3 + \frac{2}{2} + \frac{12}{6} = 6$$

Thus, 6 atoms are assigned to each unit cell.

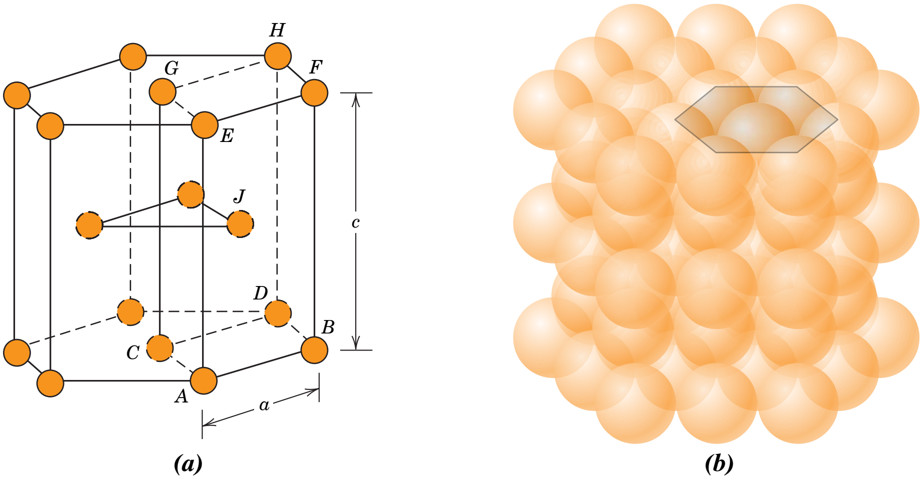

Figure 3.4 For the hexagonal close-packed crystal structure, (*a*) a reduced-sphere unit cell (*a* and *c* represent the short and long edge lengths, respectively), and (*b*) an aggregate of many atoms.
[Figure (*b*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.]

If a and c represent, respectively, the short and long unit cell dimensions of Figure 3.4*a*, the c/a ratio should be 1.633; however, for some HCP metals, this ratio deviates from the ideal value.

The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively. The HCP metals include cadmium, magnesium, titanium, and zinc; some of these are listed in Table 3.1.

EXAMPLE PROBLEM 3.1

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Determination of FCC Unit Cell Volume

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

Solution

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

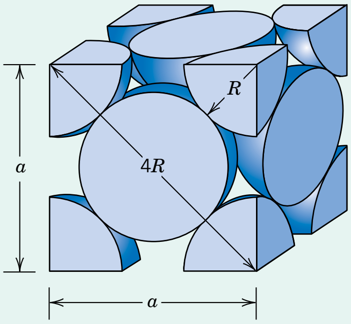
$$a^2 + a^2 = (4R)^2$$

or, solving for a,

$$a = 2R\sqrt{2} \tag{3.1}$$

The FCC unit cell volume V_C may be computed from

$$V_C = a^3 = (2R\sqrt{2})^3 = 16R^3\sqrt{2} \tag{3.6}$$



EXAMPLE PROBLEM 3.2

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Computation of the Atomic Packing Factor for FCC

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

Solution

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

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

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

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

From Example Problem 3.1, the total unit cell volume is

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

Therefore, the atomic packing factor is

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

Concept Check 3.1

(a) What is the coordination number for the simple-cubic crystal structure?

(b) Calculate the atomic packing factor for simple cubic.

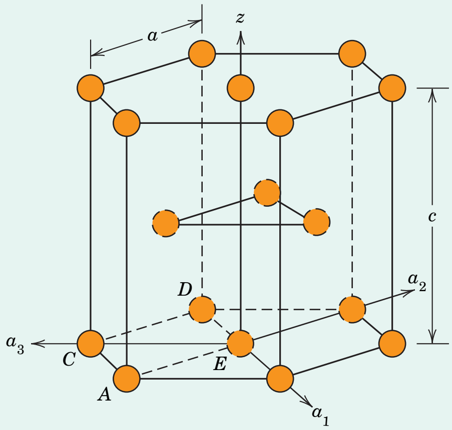
[*The answer may be found at www.wiley.com/college/callister* (*Student Companion Site*).]

EXAMPLE PROBLEM 3.3

Determination of HCP Unit Cell Volume

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

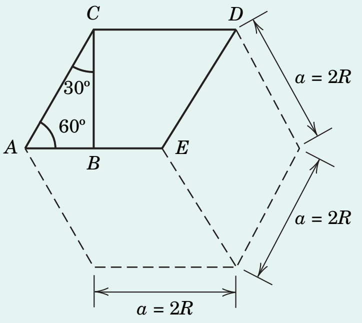
(b) Now provide an expression for this volume in terms of the atomic radius, R, and the c lattice parameter.



Solution

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

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



The area of $ACDE$ is just the length of $\overline{CD}$ times the height $\overline{BC}$. But $\overline{CD}$ is just a, and $\overline{BC}$ is equal to

$$\overline{BC} = a\cos(30^\circ) = \frac{a\sqrt{3}}{2}$$

Thus, the base area is just

$$\text{AREA} = (3)(\overline{CD})(\overline{BC}) = (3)(a)\left(\frac{a\sqrt{3}}{2}\right) = \frac{3a^2\sqrt{3}}{2}$$

Again, the unit cell volume V_C is just the product of the AREA and c; thus,

$$\begin{aligned} V_C &= \text{AREA}(c) \\ &= \left(\frac{3a^2\sqrt{3}}{2}\right)(c) \\ &= \frac{3a^2c\sqrt{3}}{2} \end{aligned} \tag{3.7a}$$

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

$$a = 2R$$

Now making this substitution for a in Equation 3.7a gives

$$\begin{aligned} V_C &= \frac{3(2R)^2c\sqrt{3}}{2} \\ &= 6R^2c\sqrt{3} \end{aligned} \tag{3.7b}$$

3.5 DENSITY COMPUTATIONS

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

Theoretical density for metals

$$\rho = \frac{nA}{V_C N_A} \tag{3.8}$$

where

n = number of atoms associated with each unit cell
A = atomic weight
V_C = volume of the unit cell
N_A = Avogadro's number (6.022×10^{23} atoms/mol)

EXAMPLE PROBLEM 3.4

Theoretical Density Computation for Copper

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

Solution

Equation 3.8 is employed in the solution of this problem. Because the crystal structure is FCC, n, the number of atoms per unit cell, is 4. Furthermore, the atomic weight A_{Cu} is given as 63.5 g/mol. The unit cell volume V_C for FCC was determined in Example Problem 3.1 as $16R^3\sqrt{2}$, where R, the atomic radius, is 0.128 nm.

Substitution for the various parameters into Equation 3.8 yields

$$\begin{aligned}\rho &= \frac{nA_{Cu}}{V_C N_A} = \frac{nA_{Cu}}{(16R^3\sqrt{2})N_A} \\ &= \frac{(4 \text{ atoms/unit cell})(63.5 \text{ g/mol})}{[16\sqrt{2}(1.28 \times 10^{-8}\text{ cm})^3/\text{unit cell}](6.022 \times 10^{23}\text{ atoms/mol})} \\ &= 8.89 \text{ g/cm}^3\end{aligned}$$

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

3.6 POLYMORPHISM AND ALLOTROPY

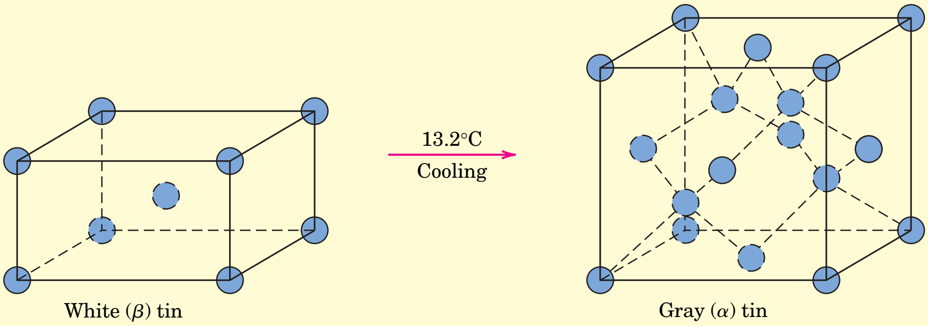
polymorphism
allotropy

Some metals, as well as nonmetals, may have more than one crystal structure, a phenomenon known as **polymorphism.** When found in elemental solids, the condition is often termed **allotropy.** The prevailing crystal structure depends on both the temperature and the external pressure. One familiar example is found in carbon: graphite is the stable polymorph at ambient conditions, whereas diamond is formed at extremely high pressures. Also, pure iron has a BCC crystal structure at room temperature, which changes to FCC iron at 912°C (1674°F). Most often a modification of the density and other physical properties accompanies a polymorphic transformation.

MATERIAL OF IMPORTANCE

Tin (Its Allotropic Transformation)

Another common metal that experiences an allotropic change is tin. White (or β) tin, having a body-centered tetragonal crystal structure at room temperature, transforms, at 13.2°C (55.8°F), to gray (or α) tin, which has a crystal structure similar to that of diamond (i.e., the diamond cubic crystal structure); this transformation is represented schematically as follows:



The rate at which this change takes place is extremely slow; however, the lower the temperature (below 13.2°C) the faster the rate. Accompanying this white-to-gray-tin transformation is an increase in volume (27%), and, accordingly, a decrease in density (from 7.30 g/cm^3 to 5.77 g/cm^3). Consequently, this volume expansion results in the disintegration of the white tin metal into a coarse powder of the gray allotrope. For normal subambient temperatures, there is no need to worry about this disintegration process for tin products because of the very slow rate at which the transformation occurs.

This white-to-gray tin transition produced some rather dramatic results in 1850 in Russia. The winter that year was particularly cold, and record low temperatures persisted for extended periods of time. The uniforms of some Russian soldiers had tin buttons, many of which crumbled because of these extreme cold conditions, as did also many of the tin church organ pipes. This problem came to be known as the *tin disease*.

Specimen of white tin (left). Another specimen disintegrated upon transforming to gray tin (right) after it was cooled to and held at a temperature below 13.2°C for an extended period of time.
(Photograph courtesy of Professor Bill Plumbridge, Department of Materials Engineering, The Open University, Milton Keynes, England.)

3.7 CRYSTAL SYSTEMS

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Because there are many different possible crystal structures, it is sometimes convenient to divide them into groups according to unit cell configurations and/or atomic arrangements. One such scheme is based on the unit cell geometry, that is, the shape of the appropriate unit cell parallelepiped without regard to the atomic positions in the cell. Within this framework, an xyz coordinate system is established with its origin at one of the unit cell corners; each of the x, y, and z axes coincides with one of the three parallelepiped edges that extend from this corner, as illustrated in Figure 3.5. The unit cell geometry is completely defined in terms of six parameters: the three edge lengths a, b, and c, and the three interaxial angles α, β, and γ. These are indicated in Figure 3.5, and are sometimes termed the **lattice parameters** of a crystal structure.

lattice parameters

On this basis there are seven different possible combinations of a, b, and c and α, β, and γ, each of which represents a distinct **crystal system.** These seven crystal systems are cubic, tetragonal, hexagonal, orthorhombic, rhombohedral,[2] monoclinic, and triclinic. The lattice parameter relationships and unit cell sketches for each are represented in Table 3.2. The cubic system, for which $a = b = c$ and $\alpha = \beta = \gamma = 90°$, has the greatest degree of symmetry. The least symmetry is displayed by the triclinic system, because $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$.

crystal system

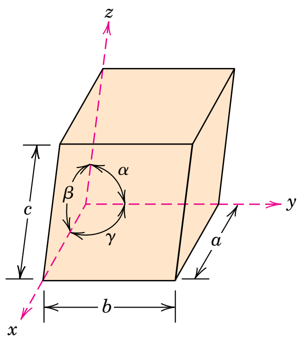
From the discussion of metallic crystal structures, it should be apparent that both FCC and BCC structures belong to the cubic crystal system, whereas HCP falls within the hexagonal system. The conventional hexagonal unit cell really consists of three parallelepipeds situated as shown in Table 3.2.

Concept Check 3.2 What is the difference between crystal structure and crystal system?

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site).*]

It is important to note that many of the principles and concepts addressed in previous discussions in this chapter also apply to crystalline ceramic and polymeric systems (Chapters 12 and 14). For example, crystal structures are most often described in terms of unit cells, which are normally more complex than those for FCC, BCC, and HCP. In addition, for these other systems, we are often interested in determining atomic packing factors and densities, using modified forms of Equations 3.3 and 3.8. Furthermore, according to unit cell geometry, crystal structures of these other material types are grouped within the seven crystal systems.

Figure 3.5 A unit cell with x, y, and z coordinate axes, showing axial lengths (a, b, and c) and interaxial angles (α, β, and γ).



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[2] Also called *trigonal*.

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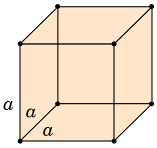
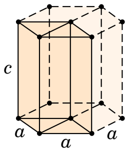
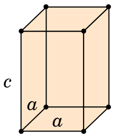
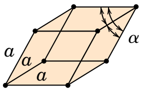
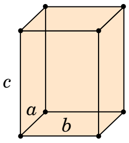
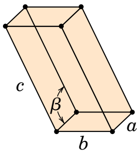
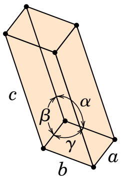
Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Crystallographic Points, Directions, and Planes

When dealing with crystalline materials, it often becomes necessary to specify a particular point within a unit cell, a crystallographic direction, or some crystallographic plane of atoms. Labeling conventions have been established in which three numbers or indices are used to designate point locations, directions, and planes. The basis for determining index values is the unit cell, with a right-handed coordinate system consisting of three (x, y, and z) axes situated at one of the corners and coinciding with the unit cell edges, as shown in Figure 3.5. For some crystal systems—namely, hexagonal, rhombohedral, monoclinic, and triclinic—the three axes are *not* mutually perpendicular, as in the familiar Cartesian coordinate scheme.

3.8 POINT COORDINATES

Sometimes it is necessary to specify a lattice position within a unit cell. This is possible using three *point coordinate indices:* q, r, and s. These indices are fractional multiples of a, b, and c unit cell edge lengths—that is, q is some fractional length of a along the x axis, r is some fractional length of b along the y axis, and similarly for s; or

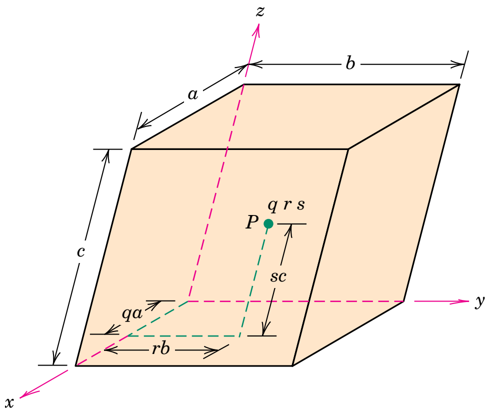
$$qa = \text{lattice position referenced to the } x \text{ axis} \tag{3.9a}$$

$$rb = \text{lattice position referenced to the } y \text{ axis} \tag{3.9b}$$

$$sc = \text{lattice position referenced to the } z \text{ axis} \tag{3.9c}$$

To illustrate, consider the unit cell in Figure 3.6, the x-y-z coordinate system with its origin located at a unit cell corner, and the lattice site located at point P. Note how the location of P is related to the products of its q, r, and s coordinate indices and the unit cell edge lengths.[3]

Figure 3.6 The manner in which the q, r, and s coordinates at point P within the unit cell are determined. The q coordinate (which is a fraction) corresponds to the distance qa along the x axis, where a is the unit cell edge length. The respective r and s coordinates for the y and z axes are determined similarly.



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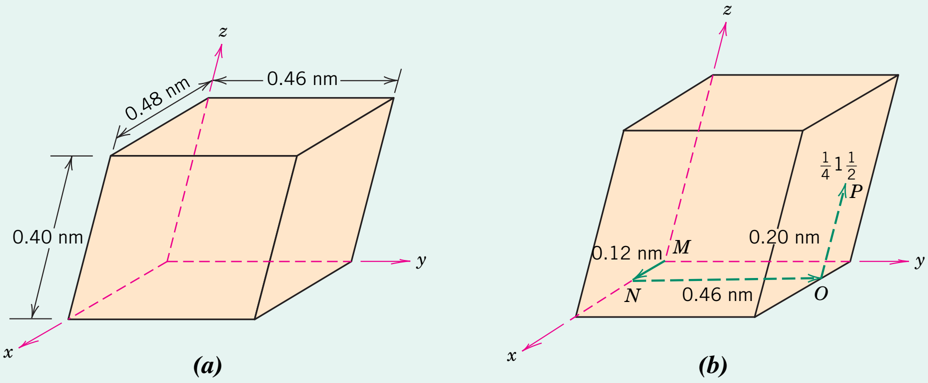
[3] We have chosen not to separate the q, r, and s indices by commas or any other punctuation marks (which is the normal convention).

EXAMPLE PROBLEM 3.5

Location of Point Having Specified Coordinates

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



Solution

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

$$\text{lattice position referenced to the } x \text{ axis} = qa$$
$$= \left(\tfrac{1}{4}\right)a = \tfrac{1}{4}(0.48\text{ nm}) = 0.12\text{ nm}$$

$$\text{lattice position referenced to the } y \text{ axis} = rb$$
$$= (1)b = (1)(0.46\text{ nm}) = 0.46\text{ nm}$$

$$\text{lattice position referenced to the } z \text{ axis} = sc$$
$$= \left(\tfrac{1}{2}\right)c = \left(\tfrac{1}{2}\right)(0.40\text{ nm}) = 0.20\text{ nm}$$

To locate the point having these coordinates within the unit cell, first use the *x* lattice position and move from the origin (point *M*) 0.12 nm units along the *x* axis (to point *N*), as shown in (*b*). Similarly, using the *y* lattice position, proceed 0.46 nm parallel to the *y* axis, from point *N* to point *O*. Finally, move from this position 0.20 nm units parallel to the *z* axis to point *P* (per the *z* lattice position), as noted again in (*b*). Thus, point *P* corresponds to the $\frac{1}{4}\,1\,\frac{1}{2}$ point coordinates.

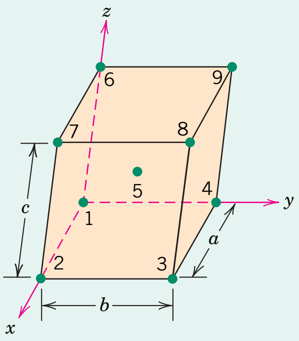
EXAMPLE PROBLEM 3.6

Specification of Point Coordinate Indices

Specify coordinate indices for all numbered points of the unit cell in the illustration on the next page.

Solution

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



Point 1 is located at the origin of the coordinate system, and, therefore, its lattice position indices referenced to the x, y, and z axes are $0a$, $0b$, and $0c$, respectively. And from Equations 3.9a through 3.9c,

$$\text{lattice position referenced to the } x \text{ axis} = 0a = qa$$
$$\text{lattice position referenced to the } y \text{ axis} = 0b = rb$$
$$\text{lattice position referenced to the } z \text{ axis} = 0c = sc$$

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

$$q = \frac{0a}{a} = 0$$
$$r = \frac{0b}{b} = 0$$
$$s = \frac{0c}{c} = 0$$

Therefore this is the 0 0 0 point

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

$$\text{lattice position index referenced to the } x \text{ axis} = a = qa$$
$$\text{lattice position index referenced to the } y \text{ axis} = 0b = rb$$
$$\text{lattice position index referenced to the } z \text{ axis} = 0c = sc$$

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

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

Hence, point 2 is 1 0 0.

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

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

3.9 CRYSTALLOGRAPHIC DIRECTIONS

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Crystallographic Directions

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Tutorial Video: Crystallographic Planes and Directions

A *crystallographic direction* is defined as a line directed between two points, or a *vector*. The following steps are used to determine the three directional indices:

1. A right-handed x-y-z coordinate system is first constructed. As a matter of convenience, its origin may be located at a unit cell corner.
2. The coordinates of two points that lie on the direction vector (referenced to the coordinate system) are determined—for example, for the vector tail, point 1: x_1, y_1, and z_1; whereas for the vector head, point 2: x_2, y_2, and z_2.
3. Tail point coordinates are subtracted from head point components—that is, $x_2 - x_1$, $y_2 - y_1$, and $z_2 - z_1$.
4. These coordinate differences are then normalized in terms of (i.e., divided by) their respective a, b, and c lattice parameters—that is,

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

which yields a set of three numbers.

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

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

$$u = n\left(\frac{x_2 - x_1}{a}\right) \tag{3.10a}$$

$$v = n\left(\frac{y_2 - y_1}{b}\right) \tag{3.10b}$$

$$w = n\left(\frac{z_2 - z_1}{c}\right) \tag{3.10c}$$

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

For each of the three axes, there are both positive and negative coordinates. Thus, negative indices are also possible, which are represented by a bar over the appropriate index. For example, the $[1\bar{1}1]$ direction has a component in the $-y$ direction. Also, changing the signs of all indices produces an antiparallel direction; that is, $[\bar{1}1\bar{1}]$ is directly opposite to $[1\bar{1}1]$. If more than one direction (or plane) is to be specified for a particular crystal structure, it is imperative for maintaining consistency that a positive–negative convention, once established, not be changed.

The [100], [110], and [111] directions are common ones; they are drawn in the unit cell shown in Figure 3.7.

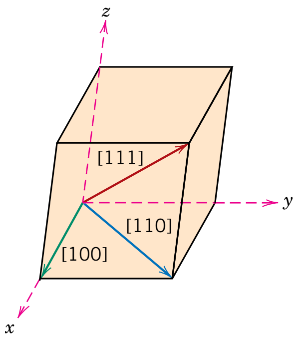
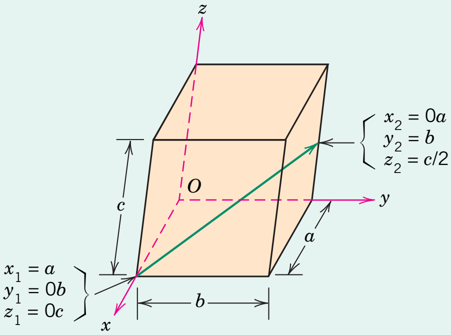


Figure 3.7 The [100], [110], and [111] directions within a unit cell.

EXAMPLE PROBLEM 3.7

Determination of Directional Indices

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



Solution

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

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

For the head coordinates,

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

Now taking point coordinate differences,

$$\begin{aligned} x_2 - x_1 &= 0a - a = -a \\ y_2 - y_1 &= b - 0b = b \\ z_2 - z_1 &= c/2 - 0c = c/2 \end{aligned}$$

It is now possible to use Equations 3.10a through 3.10c to compute values of u, v, and w. However, because the $z_2 - z_1$ difference is a fraction (i.e., $c/2$), we anticipate that in order to have integer values for the three indices, it is necessary to assign n a value of 2. Thus,

$$\begin{aligned} u &= n\left(\frac{x_2 - x_1}{a}\right) = 2\left(\frac{-a}{a}\right) = -2 \\ v &= n\left(\frac{y_2 - y_1}{b}\right) = 2\left(\frac{b}{b}\right) = 2 \\ w &= n\left(\frac{z_2 - z_1}{c}\right) = 2\left(\frac{c/2}{c}\right) = 1 \end{aligned}$$

And, finally enclosure of the −2, 2, and 1 indices in brackets leads to $[\bar{2}21]$ as the direction designation.[4]

This procedure is summarized as follows:

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

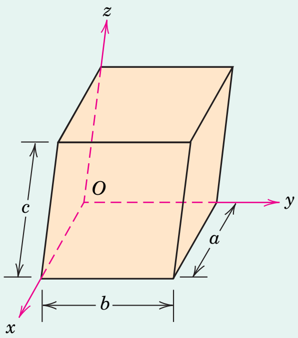
---

[4] If these u, v, and w values are not integers, it is necessary to choose another value for n.

EXAMPLE PROBLEM 3.8

Construction of a Specified Crystallographic Direction

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



Solution

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

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

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

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

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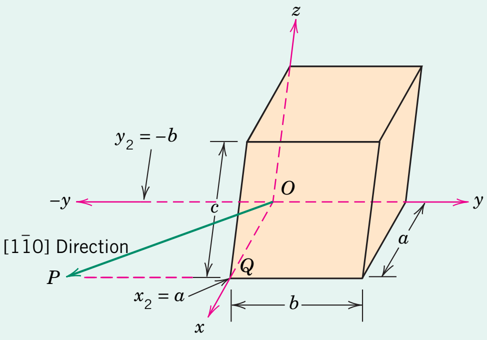
We now want to solve for the coordinates of the vector head—that is, x_2, y_2, and z_2. This is possible using rearranged forms of Equations 3.10a through 3.10c and incorporating the above values for the three direction indices (u, v, and w) and vector tail coordinates. Taking the value of n to be 1 because the three direction indices are all integers leads to

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

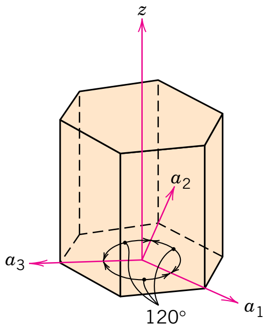
The construction process for this direction vector is shown in the following figure.

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



For some crystal structures, several nonparallel directions with different indices are *crystallographically equivalent*, meaning that the spacing of atoms along each direction is the same. For example, in cubic crystals, all the directions represented by the following indices are equivalent: [100], $[\bar{1}00]$, [010], $[0\bar{1}0]$, [001], and $[00\bar{1}]$. As a convenience, equivalent directions are grouped together into a *family,* which is enclosed in angle

Figure 3.8 Coordinate axis system for a hexagonal unit cell (Miller–Bravais scheme).



brackets, thus: ⟨100⟩. Furthermore, directions in cubic crystals having the same indices without regard to order or sign—for example, [123] and $[\bar{2}1\bar{3}]$—are equivalent. This is, in general, not true for other crystal systems. For example, for crystals of tetragonal symmetry, the [100] and [010] directions are equivalent, whereas the [100] and [001] are not.

Directions in Hexagonal Crystals

A problem arises for crystals having hexagonal symmetry in that some equivalent crystallographic directions do not have the same set of indices. For example, the [111] direction is equivalent to $[\bar{1}01]$ rather than to a direction with indices that are combinations of 1s and −1s. This situation is addressed using a four-axis, or *Miller–Bravais*, coordinate system, which is shown in Figure 3.8. The three a_1, a_2, and a_3 axes are all contained within a single plane (called the *basal plane*) and are at 120° angles to one another. The z axis is perpendicular to this basal plane. Directional indices, which are obtained as described earlier, are denoted by four indices, as $[uvtw]$; by convention, the u, v, and t indices relate to vector coordinate differences referenced to the respective a_1, a_2, and a_3 axes in the basal plane; the fourth index pertains to the z axis.

Conversion from the three-index system to the four-index system as

$$[UVW] \rightarrow [uvtw]$$

is accomplished using the following formulas[5]:

$$u = \frac{1}{3}(2U - V) \tag{3.11a}$$

$$v = \frac{1}{3}(2V - U) \tag{3.11b}$$

$$t = -(u + v) \tag{3.11c}$$

$$w = W \tag{3.11d}$$

Here, uppercase U, V, and W indices are associated with the three-index scheme (instead of u, v, and w as previously), whereas lowercase u, v, t, and w correlate with the Miller–Bravais four-index system. For example, using these equations, the [010] direction becomes $[\bar{1}2\bar{1}0]$. Several directions have been drawn in the hexagonal unit cell of Figure 3.9.

When plotting crystallographic directions for hexagonal crystals it is sometimes more convenient to modify the four-axis coordinate system shown in Figure 3.8 to that of Figure 3.10; here, a grid has been constructed on the basal plane that consists of sets of lines parallel to each of the a_1, a_2, and a_3 axes. The intersections of two sets of parallel

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[5] Reduction to the lowest set of integers may be necessary, as discussed earlier.

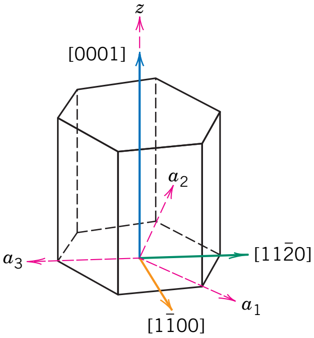


Figure 3.9 For the hexagonal crystal system, the [0001], [1$\bar{1}$00], and [11$\bar{2}$0] directions.

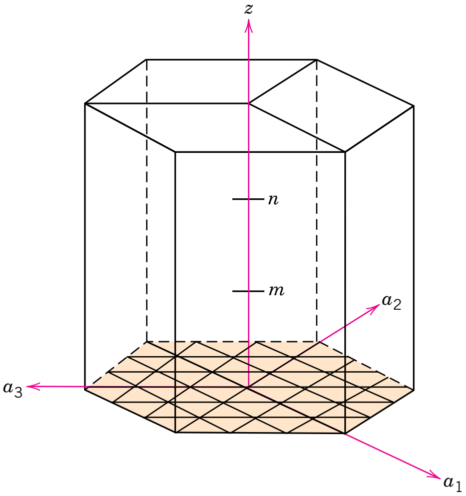


Figure 3.10 Ruled-net coordinate axis system for hexagonal unit cells that may be used to plot crystallographic directions.

lines (e.g., those for a_2, and a_3) lie on and trisect the other axis (i.e., divide a_1 into thirds) within the hexagonal unit cell. In addition, the z axis of Figure 3.10 is also apportioned into three equal lengths (at trisection points m and n). This scheme is sometimes referred to as a *ruled-net coordinate system*.

Construction of a direction specified by four indices is carried out using a procedure similar to the one used for other crystal systems—by the subtraction of vector tail point coordinates from head point coordinates. For the four coordinate axes of Figure 3.10, we use the following designations for head and tail coordinates:

Axis	***Head Coordinate***	***Tail Coordinate***
a_1	a_1'	a_1''
a_2	a_2'	a_2''
a_3	a_3'	a_3''
z	z'	z''

Using this scheme, the u, v, t, and w hexagonal index equivalents of Equations 3.10a through 3.10c are as follows:

$$u = 3n\left(\frac{a_1' - a_1''}{a}\right) \tag{3.12a}$$

$$v = 3n\left(\frac{a_2' - a_2''}{a}\right) \tag{3.12b}$$

$$t = 3n\left(\frac{a_3' - a_3''}{a}\right) \tag{3.12c}$$

$$w = 3n\left(\frac{z' - z''}{c}\right) \tag{3.12d}$$

In these expressions, the parameter n is included to facilitate, if necessary, reduction of the u, v, t, and w to integer values.

EXAMPLE PROBLEM 3.9

Conversion and Construction of Directional Indices for a Hexagonal Unit Cell

(a) Convert the [111] direction into the four-index system for hexagonal crystals.
(b) Draw this direction within a ruled-net coordinate system (per Figure 3.10).
(c) Now draw the [111] direction within a hexagonal unit cell that utilizes a three-axis (a_1, a_2, z) coordinate scheme.

Solution

(a) This conversion is carried out using Equations 3.11a–3.11d, in which

$$U = 1 \qquad V = 1 \qquad W = 1$$

Thus,

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

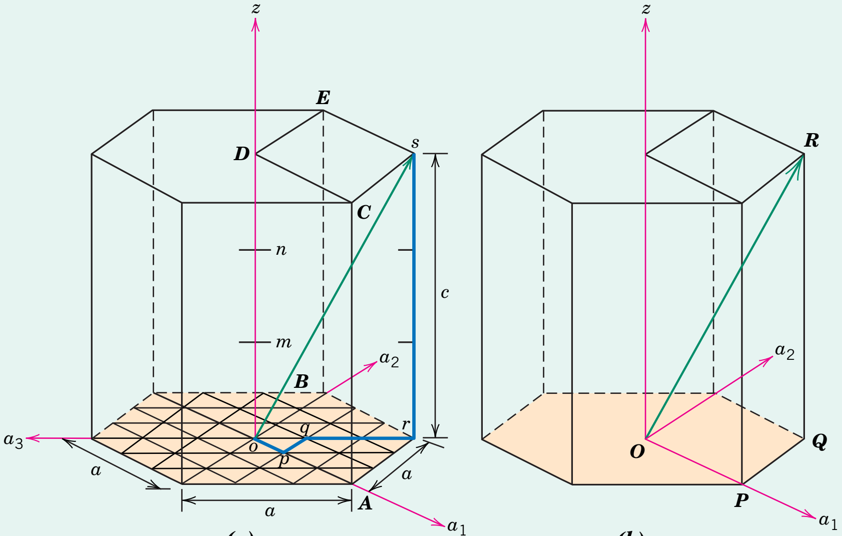
$$v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(1) - 1] = \frac{1}{3}$$

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

$$w = W = 1$$

Multiplication of the preceding indices by 3 reduces them to the lowest set, which yields values for u, v, t, and w of 1, 1, −2, and 3, respectively. Hence, the [111] direction becomes $[11\bar{2}3]$.

(b) The following sketch (*a*) shows a hexagonal unit cell in which the ruled-net coordinate system has been drawn.



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

Also, one of the three parallelepipeds that makes up the hexagonal cell is delineated—its corners are labeled with letters *o*-*A*-*r*-*B*-*C*-*D*-*E*-*s*, with the origin of the a_1-a_2-a_3-z axis coordinate system located at the corner labeled *o*. It is within this unit cell that we draw the $[11\bar{2}3]$ direction. For the sake of convenience, let us position the vector tail at the origin of the coordinate system, which means that $a_1'' = a_2'' = a_3'' = 0a$ and $z'' = 0c$. Coordinates for the vector head (a_1', a_2', a_3', and z') may be determined using rearranged forms of Equations 3.12a–3.12d, taking the value of n to be unity. Thus,

$$a_1' = \frac{ua}{3n} + a_1'' = \frac{(1)(a)}{(3)(1)} + 0a = \frac{a}{3}$$

$$a_2' = \frac{va}{3n} + a_2'' = \frac{(1)(a)}{(3)(1)} + 0a = \frac{a}{3}$$

$$a_3' = \frac{ta}{3n} + a_3'' = \frac{(-2)(a)}{(3)(1)} + 0a = \frac{-2a}{3}$$

$$z' = \frac{wc}{3n} + z'' = \frac{(3)(c)}{(3)(1)} + 0c = c$$

In constructing this direction vector, we begin at the origin (point o), and first proceed $\frac{a}{3}$ units along the a_1 axis to point p; next, from this point parallel to the a_2 axis $\frac{a}{3}$ units to point q; then parallel to the a_3 axis $-\frac{2a}{3}$ units to point r; and finally we continue parallel to the z axis c units to point s. Thus, the $[11\bar{2}3]$ direction is represented by the vector that is directed from point o to point s, as noted in the sketch.

(c) Of course, it is possible to draw the equivalent [111] direction using a three-coordinate-axis (a_1-a_2-z) technique, as shown in (b). In this case, we modify Equations 3.10a–3.10c to read as follows:

$$U = n\left(\frac{a_1' - a_1''}{a}\right) \tag{3.13a}$$

$$V = n\left(\frac{a_2' - a_2''}{a}\right) \tag{3.13b}$$

$$W = n\left(\frac{z' - z''}{c}\right) \tag{3.13c}$$

where again, single and double primes for a_1, a_2, and z denote head and tail coordinates, respectively. When we locate tail coordinates at the origin (i.e., take $a_1'' = a_2'' = 0a$ and $z'' = 0c$) and make the vector head (i.e., single-primed) coordinates of the above equations dependent parameters (while assuming $n = 1$), the following result:

$$a_1' = \frac{Ua}{n} + a_1'' = \frac{(1)(a)}{(1)} + 0a = a$$

$$a_2' = \frac{Va}{n} + a_2'' = \frac{(1)(a)}{(1)} + 0a = a$$

$$z' = \frac{Wc}{n} + z'' = \frac{(1)(c)}{(1)} + 0c = c$$

To locate the vector head, we begin at the origin (point O), then proceed a units along the a_1 axis (to point P), next parallel to the a_2 axis a units (to point Q), and finally parallel to the z axis c units (to point R). Hence, the [111] direction is represented by the vector that passes from O to R, as shown.

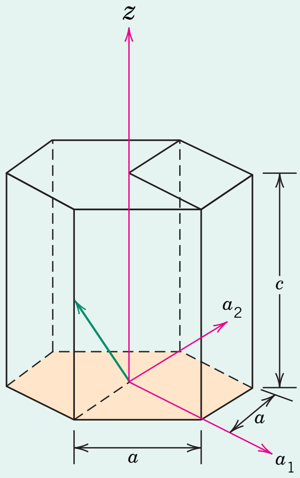
It may be noted that this [111] direction is identical to $[11\bar{2}3]$ from part (b).

The alternative situation is to determine the indices for a direction that has been drawn within a hexagonal unit cell. For this case, it is convenient to use the a_1-a_2-z three-coordinate-axis system and then convert these indices into the equivalent set for the four-axis scheme. The following example problem demonstrates this procedure.

EXAMPLE PROBLEM 3.10

Determination of Directional Indices for a Hexagonal Unit Cell

Determine the indices (four-index system) for the direction shown in the accompanying figure.



Solution

The first thing we need to do is determine U, V, and W indices for the vector referenced to the three-axis scheme represented in the sketch; this is possible using Equations 3.13a through 3.13c. Because the vector passes through the origin, $a_1'' = a_2'' = 0a$ and $z'' = 0c$. Furthermore, from the sketch, coordinates for the vector head are as follows:

$$a_1' = 0a$$

$$a_2' = -a$$

$$z' = \frac{c}{2}$$

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

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

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

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

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

Now it becomes necessary to convert these indices into an index set referenced to the four-axis scheme. This requires the use of Equations 3.11a–3.11d. For this $[0\bar{2}1]$ direction,

$$U = 0 \qquad V = -2 \qquad W = 1$$

and

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

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

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

$$w = W = 1$$

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

3.10 CRYSTALLOGRAPHIC PLANES

WileyPLUS: VMSE Crystallographic Planes

Miller indices

The orientations of planes for a crystal structure are represented in a similar manner. Again, the unit cell is the basis, with the three-axis coordinate system as represented in Figure 3.5. In all but the hexagonal crystal system, crystallographic planes are specified by three **Miller indices** as (hkl). Any two planes parallel to each other are equivalent and have identical indices. The procedure used to determine the h, k, and l index numbers is as follows:

1. If the plane passes through the selected origin, either another parallel plane must be constructed within the unit cell by an appropriate translation, or a new origin must be established at the corner of another unit cell.[6]
2. At this point, the crystallographic plane either intersects or parallels each of the three axes. The coordinate for the intersection of the crystallographic plane with each of the axes is determined (referenced to the origin of the coordinate system). These intercepts for the x, y, and z axes will be designed by A, B, and C, respectively.
3. The reciprocals of these numbers are taken. A plane that parallels an axis is considered to have an infinite intercept and therefore a zero index.
4. The reciprocals of the intercepts are then normalized in terms of (i.e., multiplied by) their respective a, b, and c lattice parameters. That is,

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

5. If necessary, these three numbers are changed to the set of smallest integers by multiplication or by division by a common factor.[7]
6. Finally, the integer indices, not separated by commas, are enclosed within parentheses, thus: (hkl). The h, k, and l integers correspond to the normalized intercept reciprocals referenced to the x, y, and z axes, respectively.

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

$$h = \frac{na}{A} \tag{3.14a}$$

$$k = \frac{nb}{B} \tag{3.14b}$$

$$l = \frac{nc}{C} \tag{3.14c}$$

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

An intercept on the negative side of the origin is indicated by a bar or minus sign positioned over the appropriate index. Furthermore, reversing the directions of all indices specifies another plane parallel to, on the opposite side of, and equidistant from the origin. Several low-index planes are represented in Figure 3.11.

---

[6] When selecting a new origin, the following procedure is suggested:

If the crystallographic plane that intersects the origin lies in one of the unit cell faces, move the origin one unit cell distance parallel to the axis that intersects this plane.

If the crystallographic plane that intersects the origin passes through one of the unit cell axes, move the origin one unit cell distance parallel to either of the two other axes.

For all other cases, move the origin one unit cell distance parallel to any of the three unit cell axes.

[7] On occasion, index reduction is not carried out (e.g., for x-ray diffraction studies described in Section 3.16); for example, (002) is not reduced to (001). In addition, for ceramic materials, the ionic arrangement for a reduced-index plane may be different from that for a nonreduced one.

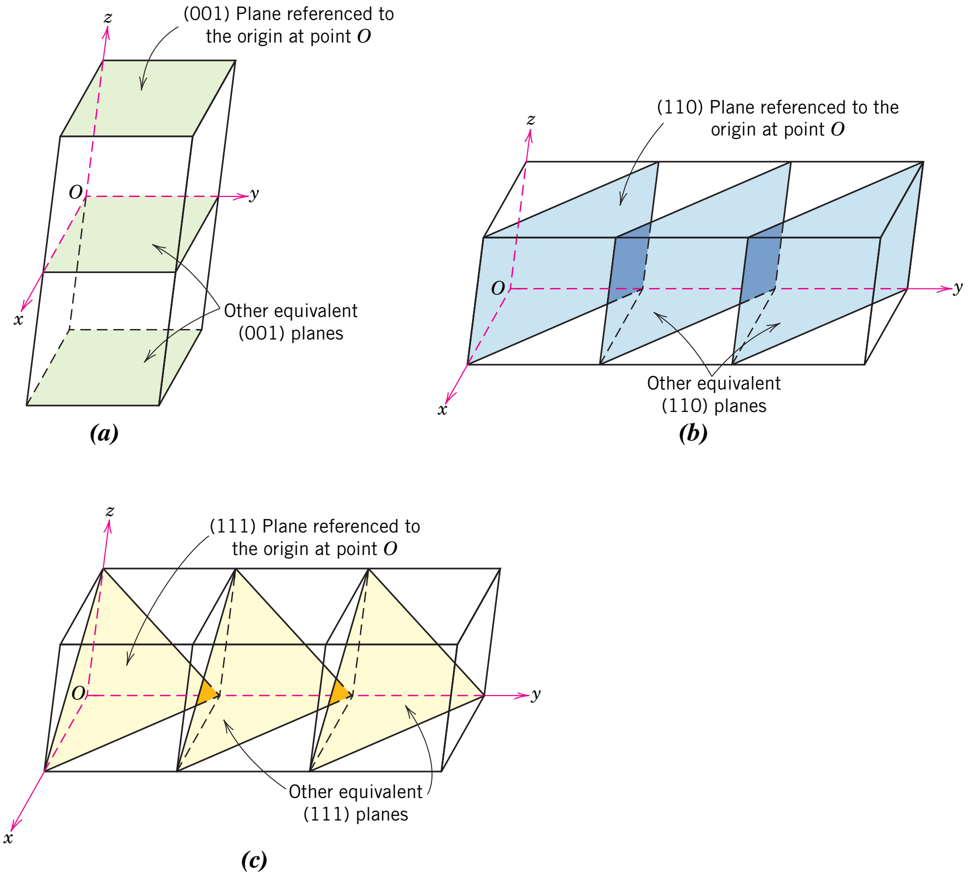


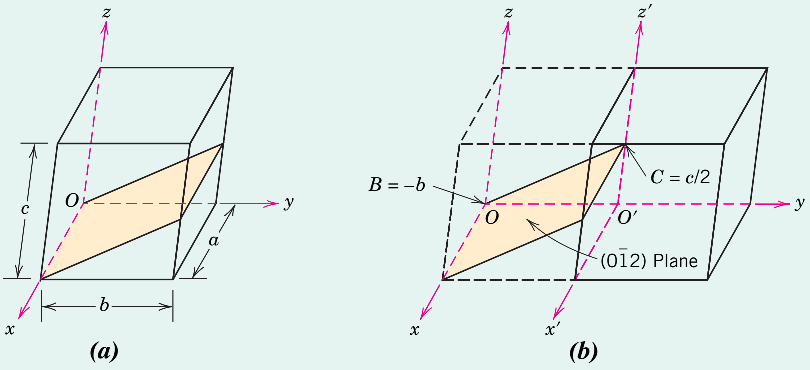
Figure 3.11 Representations of a series each of the (*a*) (001), (*b*) (110), and (*c*) (111) crystallographic planes.

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

EXAMPLE PROBLEM 3.11

Determination of Planar (Miller) Indices

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



Solution

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

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

It is now possible to use Equations 3.14a–3.14c to determine values of h, k, and l. At this point, let us choose a value of 1 for n. Thus,

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

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

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

And finally, enclosure of the 0, −1, and 2 indices in parentheses leads to $(0\bar{1}2)$ as the designation for this direction.[8]

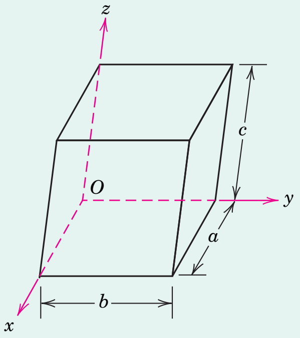
This procedure is summarized as follows:

	x	y	z
Intercepts (A, B, C)	∞a	$-b$	$c/2$
Calculated values of h, k, and l (Equations 3.14a–3.14c)	$h = 0$	$k = -1$	$l = 2$
Enclosure		$(0\bar{1}2)$	

EXAMPLE PROBLEM 3.12

Construction of a Specified Crystallographic Plane

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



(a)

Solution

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

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

---

[8] If h, k, and l are not integers, it is necessary to choose another value for n.

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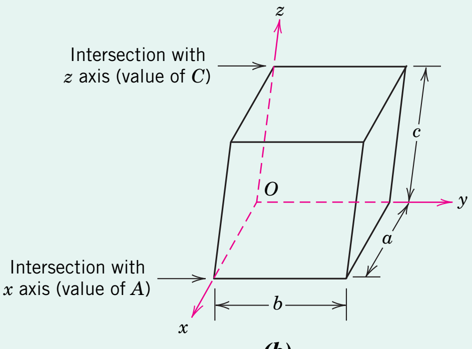
Using these h, k, and l indices, we want to solve for the values of A, B, and C using rearranged forms of Equations 3.14a–3.14c. Taking the value of n to be 1—because these three Miller indices are all integers—leads to the following:

$$A = \frac{na}{h} = \frac{(1)(a)}{1} = a$$

$$B = \frac{nb}{k} = \frac{(1)(b)}{0} = \infty b$$

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

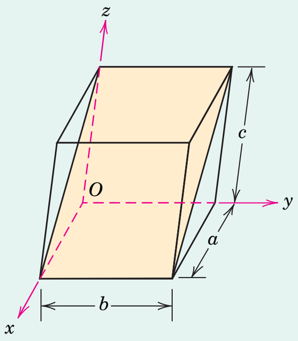


(b)

Thus, this (101) plane intersects the x axis at a (because $A = a$), it parallels the y axis (because $B = \infty b$), and intersects the z axis at c. On the unit cell shown next are noted the locations of the intersections for this plane.

The only plane that parallels the y axis and intersects the x and z axes at axial a and c coordinates, respectively, is shown next.

Note that the representation of a crystallographic plane referenced to a unit cell is by lines drawn to indicate intersections of this plane with unit cell faces (or extensions of these faces). The following guides are helpful with representing crystallographic planes:



(c)

- If two of the h, k, and l indices are zeros [as with (100)], the plane will parallel one of the unit cell faces (per Figure 3.11*a*).
- If one of the indices is a zero [as with (110)], the plane will be a parallelogram, having two sides that coincide with opposing unit cell edges (or edges of adjacent unit cells) (per Figure 3.11*b*).
- If none of the indices is zero [as with (111)], all intersections will pass through unit cell faces (per Figure 3.11*c*).

Atomic Arrangements

WileyPLUS: VMSE
Planar Atomic
Arrangements

The atomic arrangement for a crystallographic plane, which is often of interest, depends on the crystal structure. The (110) atomic planes for FCC and BCC crystal structures are represented in Figures 3.12 and 3.13, respectively. Reduced-sphere unit cells are also included. Note that the atomic packing is different for each case. The circles represent atoms lying in the crystallographic planes as would be obtained from a slice taken through the centers of the full-size hard spheres.

A “family” of planes contains all planes that are *crystallographically equivalent*—that is, having the same atomic packing; a family is designated by indices enclosed in braces—such as {100}. For example, in cubic crystals, the (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}11)$, $(1\bar{1}\bar{1})$, $(11\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, and $(1\bar{1}1)$ planes all belong to the {111} family. However, for tetragonal

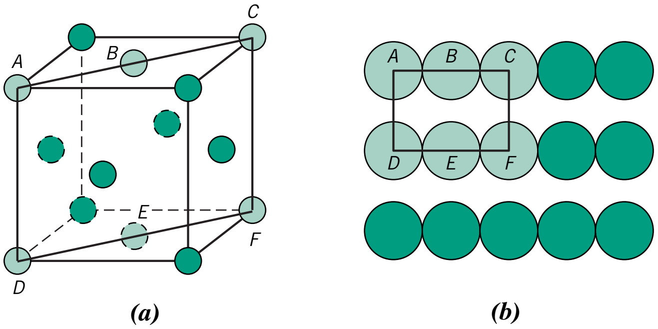


Figure 3.12 (*a*) Reduced-sphere FCC unit cell with the (110) plane. (*b*) Atomic packing of an FCC (110) plane. Corresponding atom positions from (*a*) are indicated.

crystal structures, the {100} family contains only the (100), $(\bar{1}00)$, (010), and $(0\bar{1}0)$ planes because the (001) and $(00\bar{1})$ planes are not crystallographically equivalent. Also, in the cubic system only, planes having the same indices, irrespective of order and sign, are equivalent. For example, both $(1\bar{2}3)$ and $(3\bar{1}2)$ belong to the {123} family.

Hexagonal Crystals

For crystals having hexagonal symmetry, it is desirable that equivalent planes have the same indices; as with directions, this is accomplished by the Miller–Bravais system shown in Figure 3.8. This convention leads to the four-index (*hkil*) scheme, which is favored in most instances because it more clearly identifies the orientation of a plane in a hexagonal crystal. There is some redundancy in that *i* is determined by the sum of *h* and *k* through

$$i = -(h + k) \tag{3.15}$$

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

We determine these indices in a manner analogous to that used for other crystal systems as described previously—that is, taking normalized reciprocals of axial intercepts, as described in the following example problem.

Figure 3.14 presents several of the common planes that are found for crystals having hexagonal symmetry.

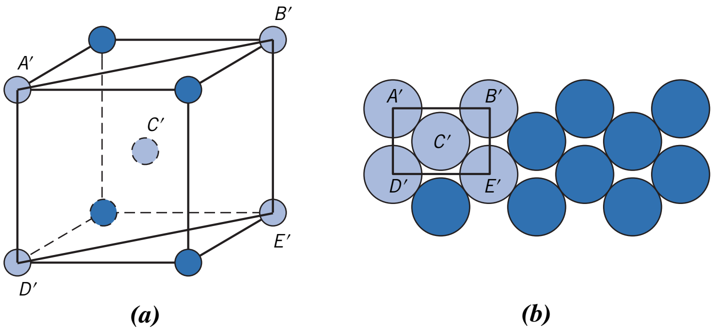


Figure 3.13 (*a*) Reduced-sphere BCC unit cell with the (110) plane. (*b*) Atomic packing of a BCC (110) plane. Corresponding atom positions from (*a*) are indicated.

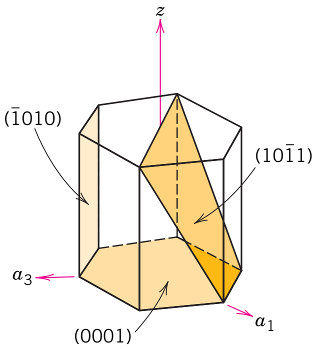
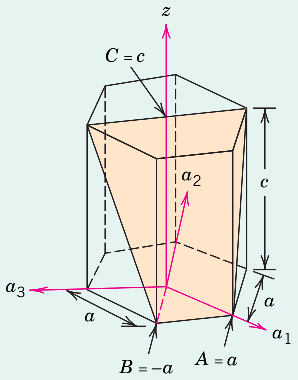


Figure 3.14 For the hexagonal crystal system, the (0001), $(10\bar{1}1)$, and $(\bar{1}010)$ planes.

EXAMPLE PROBLEM 3.13

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

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



Solution

These indices may be determined in the same manner that was used for the x-y-z coordinate situation and described in Example Problem 3.11. However, in this case the a_1, a_2, and z axes are used and correlate, respectively, with the x, y, and z axes of the previous discussion. If we again take A, B, and C to represent intercepts on the respective a_1, a_2, and z axes, normalized intercept reciprocals may be written as

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

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

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

values of h, k, and l, may be determined using Equations 3.14a–3.14c, as follows (assuming $n = 1$):

$$h = \frac{na}{A} = \frac{(1)(a)}{a} = 1$$

$$k = \frac{na}{B} = \frac{(1)(a)}{-a} = -1$$

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

And, finally, the value of i is found using Equation 3.15, as follows:

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

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

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

This concludes our discussion on crystallographic points, directions, and planes. A review and summary of these topics is found in Table 3.3.

Table 3.3 Summary of Equations Used to Determine Crystallographic Point, Direction, and Planar Indices

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

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

3.11 LINEAR AND PLANAR DENSITIES

The two previous sections discussed the equivalency of nonparallel crystallographic directions and planes. Directional equivalency is related to *linear density* in the sense that, for a particular material, equivalent directions have identical linear densities. The corresponding parameter for crystallographic planes is *planar density,* and planes having the same planar density values are also equivalent.

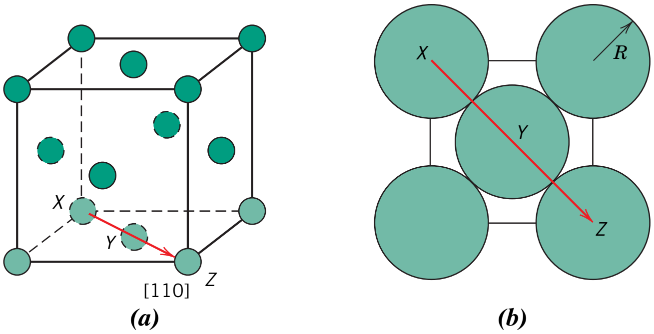
Linear density (*LD*) is defined as the number of atoms per unit length whose centers lie on the direction vector for a specific crystallographic direction; that is,

$$\mathrm{LD} = \frac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}} \tag{3.16}$$

The units of linear density are reciprocal length (e.g., nm^{-1}, m^{-1}).

For example, let us determine the linear density of the [110] direction for the FCC crystal structure. An FCC unit cell (reduced sphere) and the [110] direction therein are shown in Figure 3.15*a*. Represented in Figure 3.15*b* are the five atoms that lie on the bottom face of this unit cell; here, the [110] direction vector passes from the center of atom *X*, through atom *Y*, and finally to the center of atom *Z*. With regard to the numbers of atoms, it is necessary to take into account the sharing of atoms with adjacent unit cells (as discussed in Section 3.4 relative to atomic packing factor computations). Each of the *X* and *Z* corner atoms is also shared with one other adjacent unit cell along this [110] direction (i.e., one-half of each of these atoms belongs to the unit cell being considered), whereas atom *Y* lies entirely within the unit cell. Thus, there is an equivalence of two atoms along the [110] direction vector in the unit cell. Now, the direction vector length is equal to $4R$ (Figure 3.15*b*); thus, from Equation 3.16, the [110] linear density for FCC is

$$\mathrm{LD}_{110} = \frac{2\text{ atoms}}{4R} = \frac{1}{2R} \tag{3.17}$$



(a) (b)

Figure 3.15 (*a*) Reduced-sphere FCC unit cell with the [110] direction indicated. (*b*) The bottom face-plane of the FCC unit cell in (*a*) on which is shown the atomic spacing in the [110] direction, through atoms labeled *X*, *Y*, and *Z*.

In an analogous manner, *planar density* (*PD*) is taken as the number of atoms per unit area that are centered on a particular crystallographic plane, or

$$\mathrm{PD} = \frac{\text{number of atoms centered on a plane}}{\text{area of plane}} \tag{3.18}$$

The units for planar density are reciprocal area (e.g., nm^{-2}, m^{-2}).

For example, consider the section of a (110) plane within an FCC unit cell as represented in Figures 3.12*a* and 3.12*b*. Although six atoms have centers that lie on this plane (Figure 3.12*b*), only one-quarter of each of atoms *A*, *C*, *D*, and *F* and one-half of atoms *B* and *E*, for a total equivalence of just 2 atoms, are on that plane. Furthermore, the area of this rectangular section is equal to the product of its length and width. From Figure 3.12*b*, the length (horizontal dimension) is equal to $4R$, whereas the width (vertical dimension) is equal to $2R\sqrt{2}$ because it corresponds to the FCC unit cell edge length (Equation 3.1). Thus, the area of this planar region is $(4R)(2R\sqrt{2}) = 8R^2\sqrt{2}$, and the planar density is determined as follows:

$$\mathrm{PD}_{110} = \frac{2\text{ atoms}}{8R^2\sqrt{2}} = \frac{1}{4R^2\sqrt{2}} \tag{3.19}$$

Linear and planar densities are important considerations relative to the process of *slip*—that is, the mechanism by which metals plastically deform (Section 7.4). Slip occurs on the most densely packed crystallographic planes and, in those planes, along directions having the greatest atomic packing.

3.12 CLOSE-PACKED CRYSTAL STRUCTURES

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Close-Packed
Structures (Metals)

You may remember from the discussion on metallic crystal structures (Section 3.4) that both face-centered cubic and hexagonal close-packed crystal structures have atomic packing factors of 0.74, which is the most efficient packing of equal-size spheres or atoms. In addition to unit cell representations, these two crystal structures may be described in terms of close-packed planes of atoms (i.e., planes having a maximum atom or sphere-packing density); a portion of one such plane is illustrated in Figure 3.16*a*. Both crystal structures may be generated by the stacking of these close-packed planes on top of one another; the difference between the two structures lies in the stacking sequence.

Let the centers of all the atoms in one close-packed plane be labeled *A*. Associated with this plane are two sets of equivalent triangular depressions formed by three adjacent atoms, into which the next close-packed plane of atoms may rest. Those having the triangle vertex pointing up are arbitrarily designated as *B* positions, whereas the remaining depressions are those with the down vertices, which are marked *C* in Figure 3.16*a*.

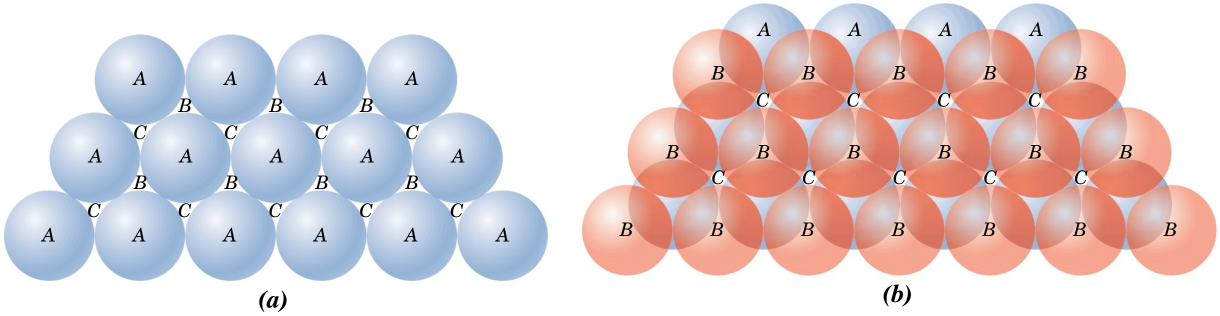


Figure 3.16 (*a*) A portion of a close-packed plane of atoms; *A*, *B*, and *C* positions are indicated. (*b*) The *AB* stacking sequence for close-packed atomic planes.
(Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure,* p. 50. Copyright © 1964 by John Wiley & Sons, New York.)

A second close-packed plane may be positioned with the centers of its atoms over either *B* or *C* sites; at this point, both are equivalent. Suppose that the *B* positions are arbitrarily chosen; the stacking sequence is termed *AB*, which is illustrated in Figure 3.16*b*. The real distinction between FCC and HCP lies in where the third close-packed layer is positioned. For HCP, the centers of this layer are aligned directly above the original *A* positions. This stacking sequence, *ABABAB* . . . , is repeated over and over. Of course, the *ACACAC* . . . arrangement would be equivalent. These close-packed planes for HCP are (0001)-type planes, and the correspondence between this and the unit cell representation is shown in Figure 3.17.

For the face-centered crystal structure, the centers of the third plane are situated over the *C* sites of the first plane (Figure 3.18*a*). This yields an *ABCABCABC* . . . stacking sequence; that is, the atomic alignment repeats every third plane. It is more difficult to correlate the stacking of close-packed planes to the FCC unit cell. However, this relationship is demonstrated in Figure 3.18*b*. These planes are of the (111) type; an FCC unit cell is outlined on the upper left-hand front face of Figure 3.18*b* to provide perspective. The significance of these FCC and HCP close-packed planes will become apparent in Chapter 7.

The concepts detailed in the previous four sections also relate to crystalline ceramic and polymeric materials, which are discussed in Chapters 12 and 14. We may

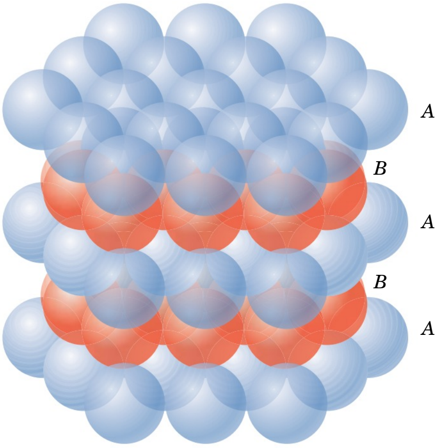


Figure 3.17 Close-packed plane stacking sequence for the hexagonal close-packed structure.
(Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure,* p. 51. Copyright © 1964 by John Wiley & Sons, New York.)

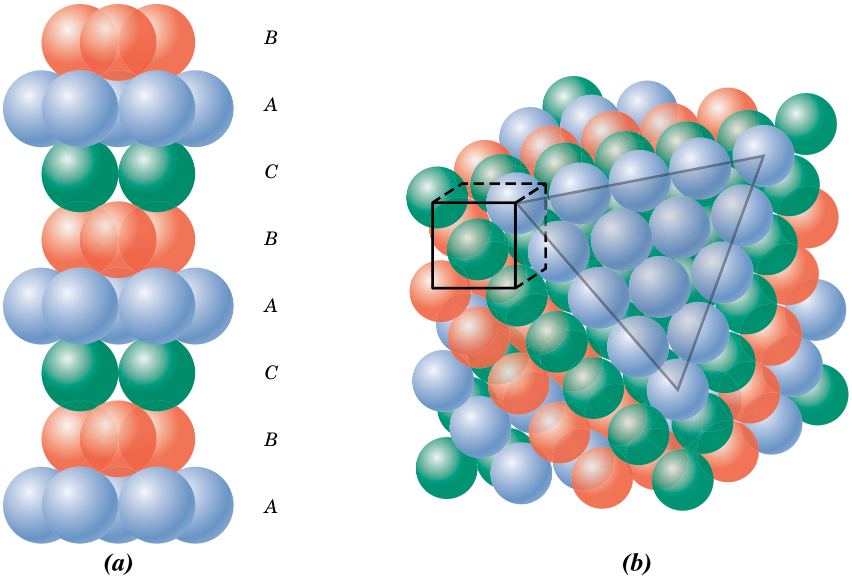


Figure 3.18 (*a*) Close-packed stacking sequence for the face-centered cubic structure. (*b*) A corner has been removed to show the relation between the stacking of close-packed planes of atoms and the FCC crystal structure; the heavy triangle outlines a (111) plane. [Figure (*b*) from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials,* Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York.]

specify crystallographic planes and directions in terms of directional and Miller indices; furthermore, on occasion it is important to ascertain the atomic and ionic arrangements of particular crystallographic planes. Also, the crystal structures of a number of ceramic materials may be generated by the stacking of close-packed planes of ions (Section 12.2).

Crystalline and Noncrystalline Materials

3.13 SINGLE CRYSTALS

single crystal

For a crystalline solid, when the periodic and repeated arrangement of atoms is perfect or extends throughout the entirety of the specimen without interruption, the result is a **single crystal.** All unit cells interlock in the same way and have the same orientation. Single crystals exist in nature, but they can also be produced artificially. They are ordinarily difficult to grow because the environment must be carefully controlled.

If the extremities of a single crystal are permitted to grow without any external constraint, the crystal assumes a regular geometric shape having flat faces, as with some of the gemstones; the shape is indicative of the crystal structure. A garnet single crystal is shown in Figure 3.19. Within the past few years, single crystals have become extremely important in many modern technologies, in particular electronic microcircuits, which employ single crystals of silicon and other semiconductors.

3.14 POLYCRYSTALLINE MATERIALS

grain

polycrystalline

Most crystalline solids are composed of a collection of many small crystals or **grains;** such materials are termed **polycrystalline.** Various stages in the solidification of a polycrystalline specimen are represented schematically in Figure 3.20. Initially, small

Figure 3.19 A garnet single crystal that was found in Tongbei, Fujian Province, China. (Photograph courtesy of Irocks.com, Megan Foreman photo.)

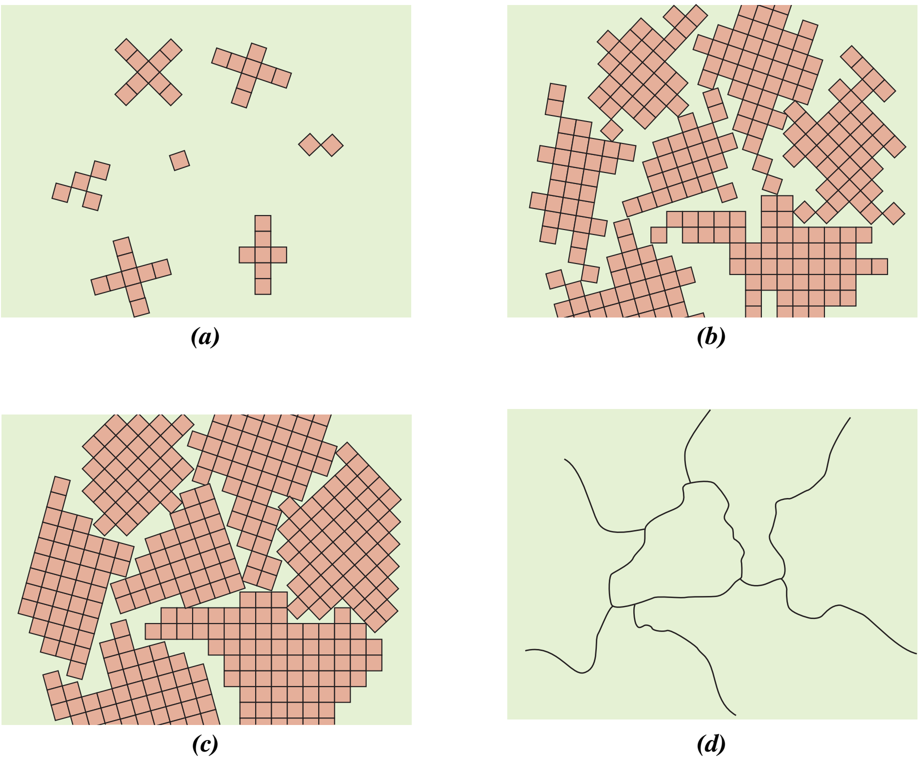


Figure 3.20 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy,* 2nd edition, Constable & Company Ltd., London, 1915.)

crystals or nuclei form at various positions. These have random crystallographic orientations, as indicated by the square grids. The small grains grow by the successive addition from the surrounding liquid of atoms to the structure of each. The extremities of adjacent grains impinge on one another as the solidification process approaches completion. As indicated in Figure 3.20, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a **grain boundary,** is discussed in more detail in Section 4.6.

grain boundary

3.15 ANISOTROPY

The physical properties of single crystals of some substances depend on the crystallographic direction in which measurements are taken. For example, the elastic modulus, the electrical conductivity, and the index of refraction may have different values in the [100] and [111] directions. This directionality of properties is termed **anisotropy,** and it is associated with the variance of atomic or ionic spacing with crystallographic direction. Substances in which measured properties are independent of the direction of measurement are **isotropic.** The extent and magnitude of anisotropic effects in crystalline materials are functions of the symmetry of the crystal structure; the degree of anisotropy increases with decreasing structural symmetry—triclinic structures normally are highly anisotropic. The modulus of elasticity values at [100], [110], and [111] orientations for several metals are presented in Table 3.4.

anisotropy

isotropic

For many polycrystalline materials, the crystallographic orientations of the individual grains are totally random. Under these circumstances, even though each grain may be anisotropic, a specimen composed of the grain aggregate behaves isotropically. Also, the magnitude of a measured property represents some average of the directional values. Sometimes the grains in polycrystalline materials have a preferential crystallographic orientation, in which case the material is said to have a "texture."

The magnetic properties of some iron alloys used in transformer cores are anisotropic—that is, grains (or single crystals) magnetize in a ⟨100⟩-type direction easier than any other crystallographic direction. Energy losses in transformer cores are minimized by utilizing polycrystalline sheets of these alloys into which have been introduced a *magnetic texture*: most of the grains in each sheet have a ⟨100⟩-type crystallographic direction that is aligned (or almost aligned) in the same direction, which is oriented parallel to the direction of the applied magnetic field. Magnetic textures for iron alloys are discussed in detail in the Material of Importance box in Chapter 20 following Section 20.9.

Table 3.4
Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

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

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials,* 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

3.16 X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Historically, much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials. We now give a brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced.

The Diffraction Phenomenon

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.

Consider waves 1 and 2 in Figure 3.21*a*, which have the same wavelength (λ) and are in phase at point O–O'. Now let us suppose that both waves are scattered

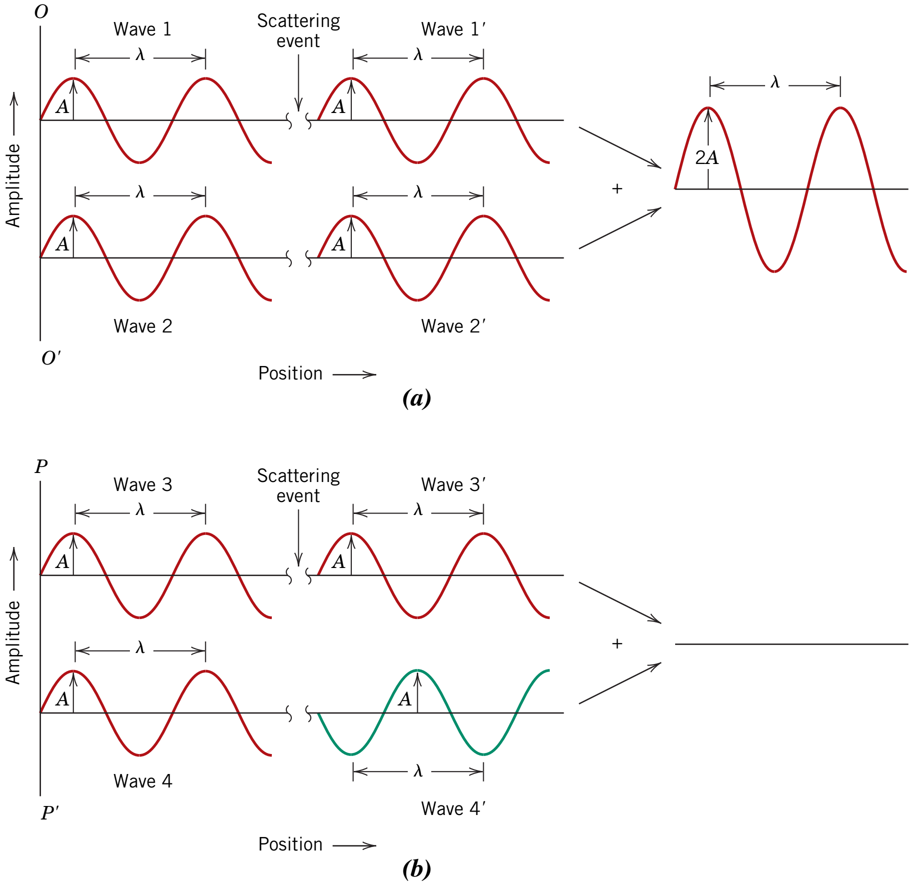


Figure 3.21 (*a*) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1′ and 2′) constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave. (*b*) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3′ and 4′) destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.

in such a way that they traverse different paths. The phase relationship between the scattered waves, which depends upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in Figure 3.21*a*, these scattered waves (now labeled 1′ and 2′) are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction,** and we refer to a *diffracted beam* as one composed of a large number of scattered waves that mutually reinforce one another.

diffraction

Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Figure 3.21*b*, in which the path length difference after scattering is some integral number of *half*-wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel or annul one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the right side of the figure. Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

X-Ray Diffraction and Bragg's Law

X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam is scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Consider the two parallel planes of atoms A–A' and B–B' in Figure 3.22, which have the same h, k, and l Miller indices and are separated by the interplanar spacing d_{hkl}. Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ. Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q. Constructive interference of the scattered rays 1′ and 2′ occurs also at an angle θ to the planes if the path length difference between 1–P–1′ and 2–Q–2′ (i.e., $\overline{SQ} + \overline{QT}$) is equal to a whole number, n, of wavelengths—that is, the condition for diffraction is

$$n\lambda = \overline{SQ} + \overline{QT} \tag{3.20}$$

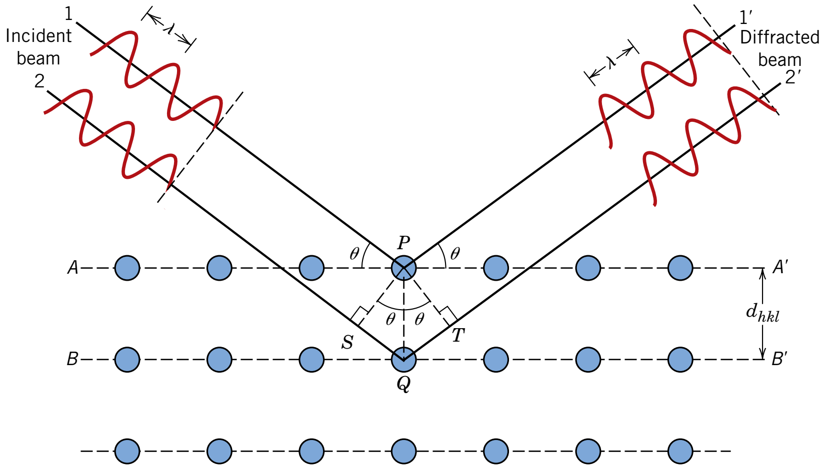


Figure 3.22 Diffraction of x-rays by planes of atoms (A–A' and B–B').

or

Bragg's law—relationship among x-ray wavelength, interatomic spacing, and angle of diffraction for constructive interference

$$n\lambda = d_{hkl} \sin\theta + d_{hkl} \sin\theta$$

$$= 2d_{hkl} \sin\theta \tag{3.21}$$

Bragg's law

Equation 3.21 is known as **Bragg's law;** n is the order of reflection, which may be any integer (1, 2, 3, . . .) consistent with sin θ not exceeding unity. Thus, we have a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg's law is not satisfied, then the interference will be nonconstructive so as to yield a very low-intensity diffracted beam.

The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices (h, k, and l) as well as the lattice parameter(s). For example, for crystal structures that have cubic symmetry,

Interplanar spacing for a plane having indices h, k, and l

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{3.22}$$

in which a is the lattice parameter (unit cell edge length). Relationships similar to Equation 3.22, but more complex, exist for the other six crystal systems noted in Table 3.2.

Bragg's law, Equation 3.21, is a necessary but not sufficient condition for diffraction by real crystals. It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that, according to Equation 3.21, should be present. Specific sets of crystallographic planes that do not give rise to diffracted beams depend on crystal structure. For the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur, whereas for FCC, h, k, and l must all be either odd or even; diffracted beams for all sets of crystallographic planes are present for the simple cubic crystal structure (Figure 3.3). These restrictions, called *reflection rules*, are summarized in Table 3.5.[9]

Concept Check 3.3 For cubic crystals, as values of the planar indices h, k, and l increase, does the distance between adjacent and parallel planes (i.e., the interplanar spacing) increase or decrease? Why?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

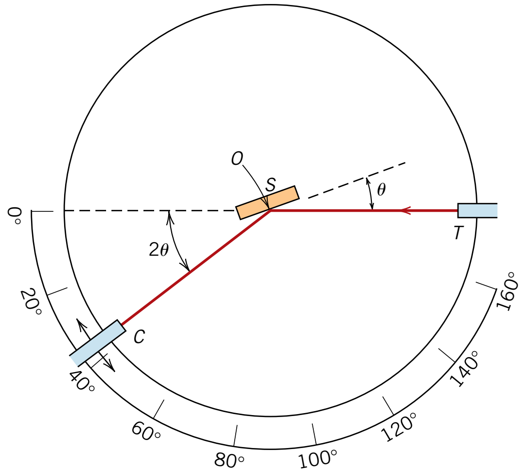
Table 3.5
X-Ray Diffraction Reflection Rules and Reflection Indices for Body-Centered Cubic, Face-Centered Cubic, and Simple Cubic Crystal Structures

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

---

[9] Zero is considered to be an even integer.

Figure 3.23 Schematic diagram of an x-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate.



Diffraction Techniques

One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation. Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

The *diffractometer* is an apparatus used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure 3.23. A specimen S in the form of a flat plate is supported so that rotations about the axis labeled O are possible; this axis is perpendicular to the plane of the page. The monochromatic x-ray beam is generated at point T, and the intensities of diffracted beams are detected with a counter labeled C in the figure. The specimen, x-ray source, and counter are coplanar.

The counter is mounted on a movable carriage that may also be rotated about the O axis; its angular position in terms of 2θ is marked on a graduated scale.[10] Carriage and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this ensures that the incident and reflection angles are maintained equal to one another (Figure 3.23). Collimators are incorporated within the beam path to produce a well-defined and focused beam. Utilization of a filter provides a near-monochromatic beam.

As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ; 2θ is termed the *diffraction angle*, which is measured experimentally. Figure 3.24 shows a diffraction pattern for a powdered specimen of lead. The high-intensity peaks result when the Bragg diffraction condition is satisfied by some set of crystallographic planes. These peaks are plane-indexed in the figure.

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

---

[10] Note that the symbol θ has been used in two different contexts for this discussion. Here, θ represents the angular locations of both x-ray source and counter relative to the specimen surface. Previously (e.g., Equation 3.21), it denoted the angle at which the Bragg criterion for diffraction is satisfied.

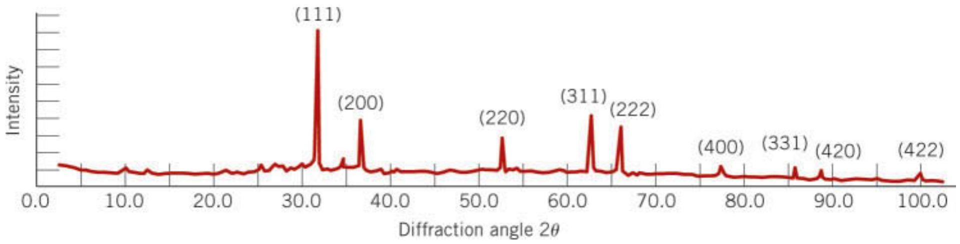


Figure 3.24 Diffraction pattern for powdered lead. (Courtesy of Wesley L. Holman.)

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

X-rays, as well as electron and neutron beams, are also used in other types of material investigations. For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs. The chapter-opening photograph (*a*) was generated using an incident x-ray beam that was directed on a magnesium crystal; each spot (with the exception of the darkest one near the center) resulted from an x-ray beam that was diffracted by a specific set of crystallographic planes. Other uses of x-rays include qualitative and quantitative chemical identifications and the determination of residual stresses and crystal size.

EXAMPLE PROBLEM 3.14

Interplanar Spacing and Diffraction Angle Computations

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

Solution

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.22, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$ because we are considering the (220) planes. Therefore,

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

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

(b) The value of θ may now be computed using Equation 3.21, with $n = 1$ because this is a first-order reflection:

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790\text{ nm})}{(2)(0.1013\text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = 124.26°$$

EXAMPLE PROBLEM 3.15

Interplanar Spacing and Lattice Parameter Computations for Lead

Figure 3.24 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also, determine the lattice parameter of Pb for each of the peaks. For all peaks, assume the order of diffraction is 1.

Solution

For each peak, in order to compute the interplanar spacing and the lattice parameter we must employ Equations 3.21 and 3.22, respectively. The first peak of Figure 3.24, which results from diffraction by the (111) set of planes, occurs at $2\theta = 31.3°$; the corresponding interplanar spacing for this set of planes, using Equation 3.21, is equal to

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

And, from Equation 3.22, the lattice parameter a is determined as

$$\begin{aligned} a &= d_{hkl}\sqrt{h^2 + k^2 + l^2} \\ &= d_{111}\sqrt{(1)^2 + (1)^2 + (1)^2} \\ &= (0.2858\text{ nm})\sqrt{3} = 0.4950\text{ nm} \end{aligned}$$

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

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

3.17 NONCRYSTALLINE SOLIDS

noncrystalline

amorphous

It has been mentioned that **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances. Sometimes such materials are also called **amorphous** (meaning literally "without form"), or supercooled liquids, inasmuch as their atomic structure resembles that of a liquid.

An amorphous condition may be illustrated by comparison of the crystalline and noncrystalline structures of the ceramic compound silicon dioxide (SiO_2), which may exist in both states. Figures 3.25*a* and 3.25*b* present two-dimensional schematic diagrams for both structures of SiO_2. Even though each silicon ion bonds to three oxygen ions for both states, beyond this, the structure is much more disordered and irregular for the noncrystalline structure.

Whether a crystalline or an amorphous solid forms depends on the ease with which a random atomic structure in the liquid can transform to an ordered state during solidification. Amorphous materials, therefore, are characterized by atomic or molecular structures that are relatively complex and become ordered only with some difficulty.

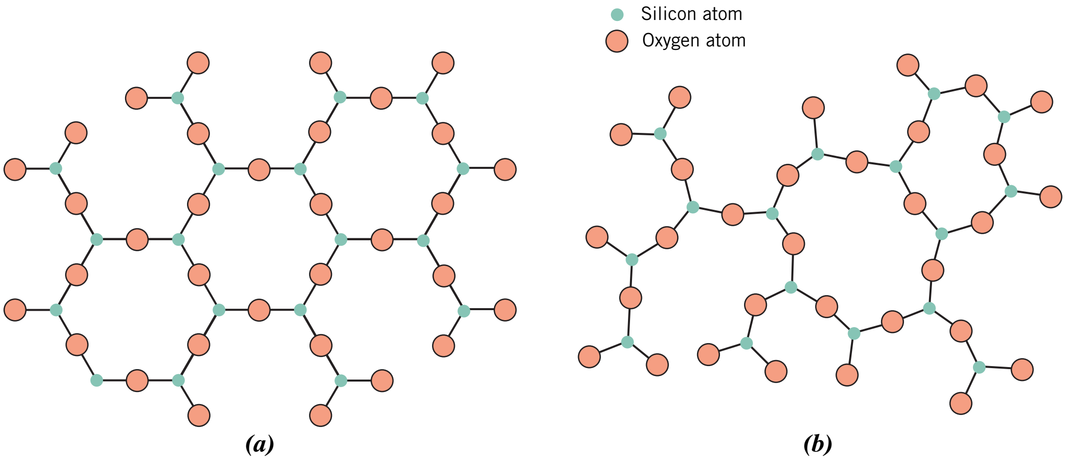


Figure 3.25 Two-dimensional schemes of the structure of (*a*) crystalline silicon dioxide and (*b*) noncrystalline silicon dioxide.

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

Metals normally form crystalline solids, but some ceramic materials are crystalline, whereas others—the inorganic glasses—are amorphous. Polymers may be completely noncrystalline or semicrystalline consisting of varying degrees of crystallinity. More about the structure and properties of amorphous ceramics and polymers is contained in Chapters 12 and 14.

Concept Check 3.4 Do noncrystalline materials display the phenomenon of allotropy (or polymorphism)? Why or why not?

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site)*.]

SUMMARY

Fundamental Concepts

- Atoms in crystalline solids are positioned in orderly and repeated patterns that are in contrast to the random and disordered atomic distribution found in noncrystalline or amorphous materials.

Unit Cells

- Crystal structures are specified in terms of parallelepiped unit cells, which are characterized by geometry and atom positions within.

Metallic Crystal Structures

- Most common metals exist in at least one of three relatively simple crystal structures:
  Face-centered cubic (FCC), which has a cubic unit cell (Figure 3.1).
  Body-centered cubic (BCC), which also has a cubic unit cell (Figure 3.2).
  Hexagonal close-packed, which has a unit cell of hexagonal symmetry, [Figure 3.4(*a*)].
- Unit cell edge length (a) and atomic radius (R) are related according to
  Equation 3.1 for face-centered cubic, and
  Equation 3.4 for body-centered cubic.

- Two features of a crystal structure are

    Coordination number—the number of nearest-neighbor atoms, and

    Atomic packing factor—the fraction of solid sphere volume in the unit cell.

Density Computations

- The theoretical density of a metal (ρ) is a function of the number of equivalent atoms per unit cell, the atomic weight, unit cell volume, and Avogadro's number (Equation 3.8).

Polymorphism and Allotropy

- *Polymorphism* is when a specific material can have more than one crystal structure. *Allotropy* is polymorphism for elemental solids.

Crystal Systems

- The concept of a crystal system is used to classify crystal structures on the basis of unit cell geometry—that is, unit cell edge lengths and interaxial angles. There are seven crystal systems: cubic, tetragonal, hexagonal, orthorhombic, rhombohedral (trigonal), monoclinic, and triclinic.

Point Coordinates

Crystallographic Directions

Crystallographic Planes

- Crystallographic points, directions, and planes are specified in terms of indexing schemes. The basis for the determination of each index is a coordinate axis system defined by the unit cell for the particular crystal structure.

    The location of a point within a unit cell is specified using coordinates that are fractional multiples of the cell edge lengths (Equations 3.9a–3.9c).

    Directional indices are computed in terms of differences between vector head and tail coordinates (Equations 3.10a–3.10c).

    Planar (or Miller) indices are determined from the reciprocals of axial intercepts (Equations 3.14a–3.14c).

- For hexagonal unit cells, a four-index scheme for both directions and planes is found to be more convenient. Directions may be determined using Equations 3.11a–3.11d and 3.12a–3.12d.

Linear and Planar Densities

- Crystallographic directional and planar equivalencies are related to atomic linear and planar densities, respectively.

    Linear density (for a specific crystallographic direction) is defined as the number of atoms per unit length whose centers lie on the vector for this direction (Equation 3.16).

    Planar density (for a specific crystallographic plane) is taken as the number of atoms per unit area that are centered on the particular plane (Equation 3.18).

- For a given crystal structure, planes having identical atomic packing yet different Miller indices belong to the same family.

Close-Packed Crystal Structures

- Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes of atoms on top of one another. With this scheme A, B, and C denote possible atom positions on a close-packed plane.

    The stacking sequence for HCP is *ABABAB*. . . .

    The stacking sequence for FCC is *ABCABCABC*. . . .

- Close-packed planes for FCC and HCP are {111} and {0001}, respectively.

Single Crystals

Polycrystalline Materials

- *Single crystals* are materials in which the atomic order extends uninterrupted over the entirety of the specimen; under some circumstances, single crystals may have flat faces and regular geometric shapes.
- The vast majority of crystalline solids, however, are *polycrystalline*, being composed of many small crystals or grains having different crystallographic orientations.
- A *grain boundary* is the boundary region separating two grains where there is some atomic mismatch.

Anisotropy

- *Anisotropy* is the directionality dependence of properties. For isotropic materials, properties are independent of the direction of measurement.

X-Ray Diffraction: Determination of Crystal Structures

- *X-ray diffractometry* is used for crystal structure and interplanar spacing determinations. A beam of x-rays directed on a crystalline material may experience diffraction (constructive interference) as a result of its interaction with a series of parallel atomic planes.
- Bragg's law specifies the condition for diffraction of x-rays—Equation 3.21.

Noncrystalline Solids

- Noncrystalline solid materials lack a systematic and regular arrangement of atoms or ions over relatively large distances (on an atomic scale). Sometimes the term *amorphous* is also used to describe these materials.

Equation Summary

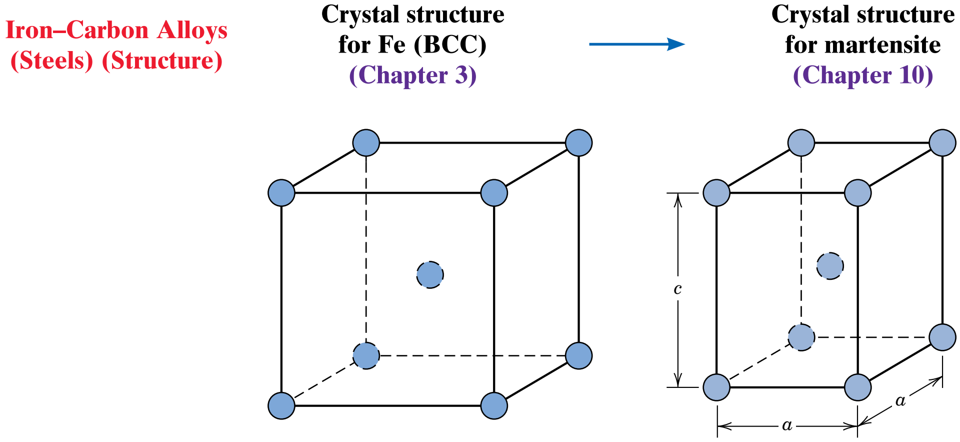
Equation Number	*Equation*	*Solving For*	*Page Number*
3.1	$a = 2R\sqrt{2}$	Unit cell edge length, FCC	54
3.3	$\text{APF} = \dfrac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \dfrac{V_S}{V_C}$	Atomic packing factor	55
3.4	$a = \dfrac{4R}{\sqrt{3}}$	Unit cell edge length, BCC	56
3.8	$\rho = \dfrac{nA}{V_C N_A}$	Theoretical density of a metal	60
3.9a	$q = \dfrac{\text{lattice position referenced to the } x \text{ axis}}{a}$	Point coordinate referenced to x axis	64
3.10a	$u = n\left(\dfrac{x_2 - x_1}{a}\right)$	Direction index referenced to x axis	67
3.11a	$u = \dfrac{1}{3}(2U - V)$	Direction index conversion to hexagonal	70
3.12a	$u = 3n\left(\dfrac{a_1' - a_1''}{a}\right)$	Hexagonal direction index referenced to a_1 axis	71
3.14a	$h = \dfrac{na}{A}$	Planar (Miller) index referenced to x axis	75
3.16	$\text{LD} = \dfrac{\text{number of atoms centered on direction vector}}{\text{length of direction vector}}$	Linear density	81
3.18	$\text{PD} = \dfrac{\text{number of atoms centered on a plane}}{\text{area of plane}}$	Planar density	82
3.21	$n\lambda = 2d_{hkl}\sin\theta$	Bragg's law; wavelength–interplanar spacing–angle of diffracted beam	89
3.22	$d_{hkl} = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$	Interplanar spacing for crystals having cubic symmetry	89

List of Symbols

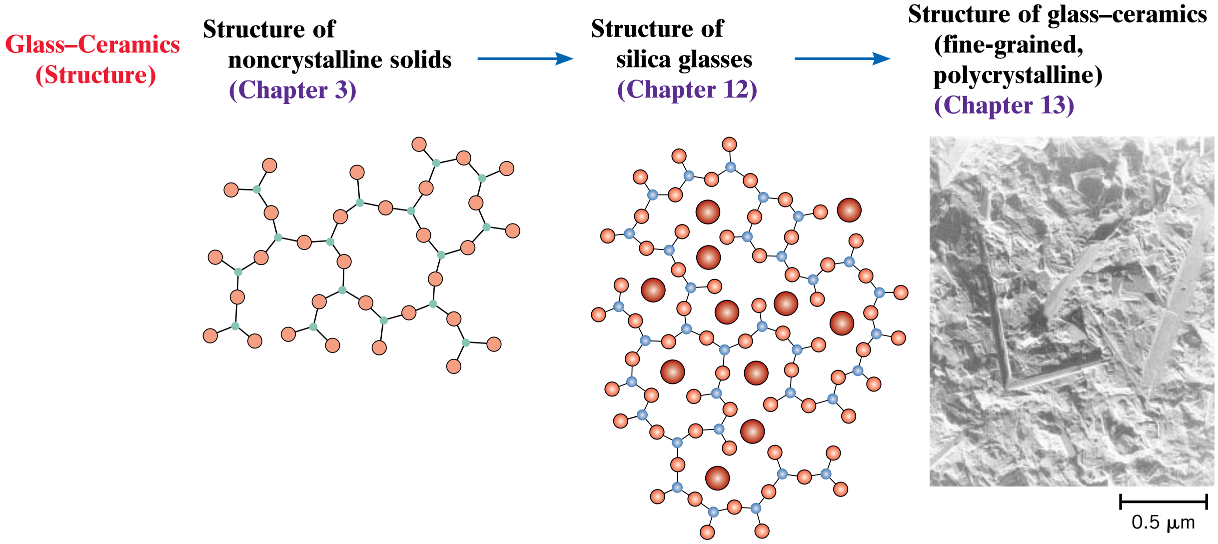
Symbol	*Meaning*
a	Unit cell edge length for cubic structures; unit cell x-axial length
a_1'	Vector head coordinate, hexagonal
a_1''	Vector tail coordinate, hexagonal
A	Atomic weight
A	Planar intercept on x axis
d_{hkl}	Interplanar spacing for crystallographic planes having indices h, k, and l
n	Order of reflection for x-ray diffraction
n	Number of atoms associated with a unit cell
n	Normalization factor—reduction of directional/planar indices to integers
N_A	Avogadro's number (6.022×10^{23} atoms/mol)
R	Atomic radius
V_C	Unit cell volume
x_1	Vector tail coordinate
x_2	Vector head coordinate
λ	X-ray wavelength
ρ	Density; theoretical density

Processing/Structure/Properties/Performance Summary

In this chapter, we discussed crystal structure, the body-centered cubic crystal structure, and the ability of a metal to experience a change in its crystal structure (polymorphism). A knowledge of these concepts helps us understand the transformation of BCC iron to martensite (which has another crystal structure) in Chapter 10. This relationship is represented by the following concept map:



Also discussed was the notion of a noncrystalline material. Glass–ceramics (Chapter 13) are formed as noncrystalline silica glasses (Chapter 12), which are then heat-treated so as to become crystalline in nature. The following concept map notes this relationship:


Glass–Ceramics (Structure)

Structure of noncrystalline solids (Chapter 3) → **Structure of silica glasses (Chapter 12)** → **Structure of glass–ceramics (fine-grained, polycrystalline) (Chapter 13)**

Important Terms and Concepts

allotropy
amorphous
anisotropy
atomic packing factor (APF)
body-centered cubic (BCC)
Bragg's law
coordination number
crystalline
crystal structure
crystal system
diffraction
face-centered cubic (FCC)
grain
grain boundary
hexagonal close-packed (HCP)
isotropic
lattice
lattice parameters
Miller indices
noncrystalline
polycrystalline
polymorphism
single crystal
unit cell

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QUESTIONS AND PROBLEMS

⊕ *Problem available (at instructor's discretion) in* WileyPLUS

Fundamental Concepts

3.1 ⊕ What is the difference between *atomic structure* and *crystal structure*?

Unit Cells

Metallic Crystal Structures

3.2 ⊕ If the atomic radius of lead is 0.175 nm, calculate the volume of its unit cell in cubic meters.

3.3 ⊕ Show for the body-centered cubic crystal structure that the unit cell edge length a and the atomic radius R are related through $a = 4R/\sqrt{3}$.

3.4 ⊕ For the HCP crystal structure, show that the ideal c/a ratio is 1.633.

3.5 ⊕ Show that the atomic packing factor for BCC is 0.68.

3.6 ⊕ Show that the atomic packing factor for HCP is 0.74.

Density Computations

3.7 Molybdenum (Mo) has a BCC crystal structure, an atomic radius of 0.1363 nm, and an atomic weight of 95.94 g/mol. Compute and compare its theoretical density with the experimental value found inside the front cover of the book.

3.8 Strontium (Sr) has an FCC crystal structure, an atomic radius of 0.215 nm, and an atomic weight of 87.62 g/mol. Calculate the theoretical density for Sr.

3.9 Calculate the radius of a palladium (Pd) atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm^3, and an atomic weight of 106.4 g/mol.

3.10 Calculate the radius of a tantalum (Ta) atom, given that Ta has a BCC crystal structure, a density of 16.6 g/cm^3, and an atomic weight of 180.9 g/mol.

3.11 A hypothetical metal has the simple cubic crystal structure shown in Figure 3.3. If its atomic weight is 74.5 g/mol and the atomic radius is 0.145 nm, compute its density.

3.12 Titanium (Ti) has an HCP crystal structure and a density of 4.51 g/cm^3.

(a) What is the volume of its unit cell in cubic meters?

(b) If the *c*/*a* ratio is 1.58, compute the values of *c* and *a*.

3.13 Magnesium (Mg) has an HCP crystal structure and a density of 1.74 g/cm^3.

(a) What is the volume of its unit cell in cubic centimeters?

(b) If the *c*/*a* ratio is 1.624, compute the values of *c* and *a*.

3.14 Using atomic weight, crystal structure, and atomic radius data tabulated inside the front cover of the book, compute the theoretical densities of aluminum (Al), nickel (Ni), magnesium (Mg), and tungsten (W), and then compare these values with the measured densities listed in this same table. The *c*/*a* ratio for Mg is 1.624.

3.15 Niobium (Nb) has an atomic radius of 0.1430 nm and a density of 8.57 g/cm^3. Determine whether it has an FCC or a BCC crystal structure.

3.16 The atomic weight, density, and atomic radius for three hypothetical alloys are listed in the following table. For each, determine whether its crystal structure is FCC, BCC, or simple cubic and then justify your determination.

Alloy	*Atomic Weight (g/mol)*	*Density (g/cm^3)*	*Atomic Radius (nm)*
A	43.1	6.40	0.122
B	184.4	12.30	0.146
C	91.6	9.60	0.137

3.17 The unit cell for uranium (U) has orthorhombic symmetry, with *a*, *b*, and *c* lattice parameters of 0.286, 0.587, and 0.495 nm, respectively. If its density, atomic weight, and atomic radius are 19.05 g/cm^3, 238.03 g/mol, and 0.1385 nm, respectively, compute the atomic packing factor.

3.18 Indium (In) has a tetragonal unit cell for which the *a* and *c* lattice parameters are 0.459 and 0.495 nm, respectively.

(a) If the atomic packing factor and atomic radius are 0.693 and 0.1625 nm, respectively, determine the number of atoms in each unit cell.

(b) The atomic weight of In is 114.82 g/mol; compute its theoretical density.

3.19 Beryllium (Be) has an HCP unit cell for which the ratio of the lattice parameters *c*/*a* is 1.568. If the radius of the Be atom is 0.1143 nm, **(a)** determine the unit cell volume, and **(b)** calculate the theoretical density of Be and compare it with the literature value.

3.20 Magnesium (Mg) has an HCP crystal structure, a *c*/*a* ratio of 1.624, and a density of 1.74 g/cm^3. Compute the atomic radius for Mg.

3.21 Cobalt (Co) has an HCP crystal structure, an atomic radius of 0.1253 nm, and a *c*/*a* ratio of 1.623. Compute the volume of the unit cell for Co.

Polymorphism and Allotropy

3.22 Iron (Fe) undergoes an allotropic transformation at 912°C: upon heating from a BCC (α phase) to an FCC (γ phase). Accompanying this transformation is a change in the atomic radius of Fe—from R_{BCC} = 0.12584 nm to R_{FCC} = 0.12894 nm—and, in addition, a change in density (and volume). Compute the percentage volume change associated with this reaction. Does the volume increase or decrease?

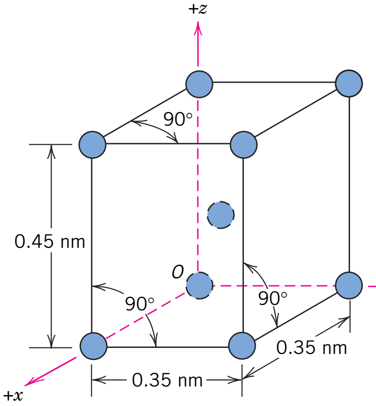
Crystal Systems

3.23 The accompanying figure shows a unit cell for a hypothetical metal.

(a) To which crystal system does this unit cell belong?

(b) What would this crystal structure be called?

(c) Calculate the density of the material, given that its atomic weight is 141 g/mol.



3.24 Sketch a unit cell for the face-centered orthorhombic crystal structure.

Point Coordinates

3.25 List the point coordinates for all atoms that are associated with the FCC unit cell (Figure 3.1).

3.26 List the point coordinates of both the sodium (Na) and chlorine (Cl) ions for a unit cell of the NaCl crystal structure (Figure 12.2).

3.27 List the point coordinates of both the zinc (Zn) and sulfur (S) atoms for a unit cell of the zinc blende (ZnS) crystal structure (Figure 12.4).

3.28 Sketch a tetragonal unit cell, and within that cell indicate locations of the $1\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{4}\frac{1}{2}$ point coordinates.

3.29 Sketch an orthorhombic unit cell, and within that cell indicate locations of the $0\frac{1}{2}1$ and $\frac{1}{3}\frac{1}{4}\frac{1}{4}$ point coordinates.

3.30 Using the Molecule Definition Utility found in the "Metallic Crystal Structures and Crystallography" and "Ceramic Crystal Structures" modules of *VMSE* located on the book's web site [*www.wiley.com/college/callister* (Student Companion Site)], generate (and print out) a three-dimensional unit cell for β tin (Sn), given the following: (1) the unit cell is tetragonal with a = 0.583 nm and c = 0.318 nm, and (2) Sn atoms are located at the following point coordinates:

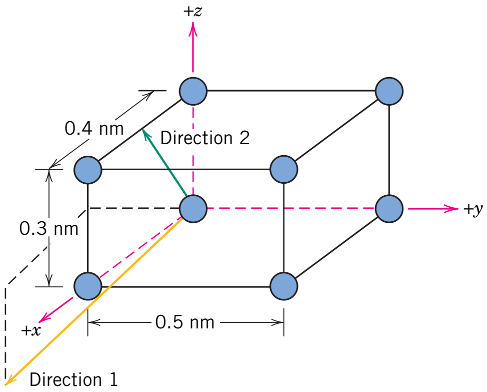
0 0 0	0 1 1
1 0 0	$\frac{1}{2}\,0\,\frac{3}{4}$
1 1 0	$\frac{1}{2}\,1\,\frac{3}{4}$
0 1 0	$1\,\frac{1}{2}\,\frac{1}{4}$
0 0 1	$0\,\frac{1}{2}\,\frac{1}{4}$
1 0 1	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$
1 1 1	

Crystallographic Directions

3.31 Draw an orthorhombic unit cell, and within that cell, a $[2\bar{1}1]$ direction.

3.32 Sketch a monoclinic unit cell, and within that cell, a $[\bar{1}01]$ direction.

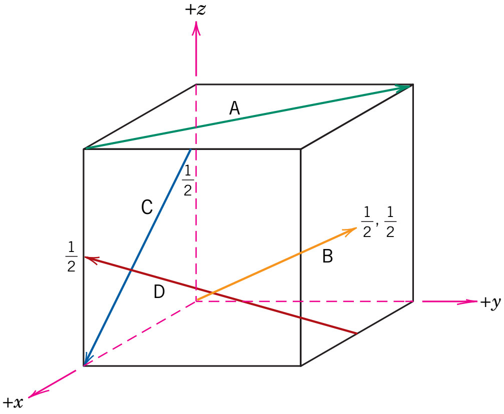
3.33 What are the indices for the directions indicated by the two vectors in the following sketch?



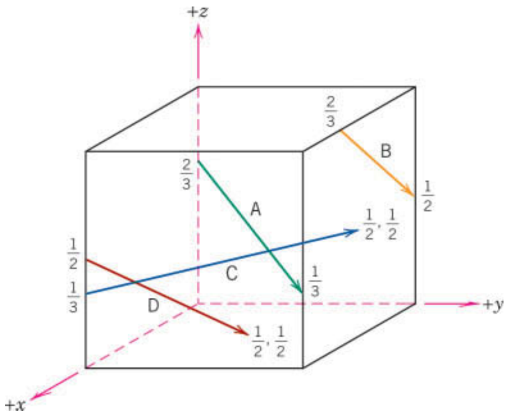
3.34 Within a cubic unit cell, sketch the following directions:

(a) [101]	**(e)** $[\bar{1}1\bar{1}]$
(b) [211]	**(f)** $[\bar{2}12]$
(c) $[10\bar{2}]$	**(g)** $[3\bar{1}2]$
(d) $[3\bar{1}3]$	**(h)** [301]

3.35 Determine the indices for the directions shown in the following cubic unit cell:



3.36 Determine the indices for the directions shown in the following cubic unit cell:



3.37 (a) What are the direction indices for a vector that passes from point $\frac{1}{4}\,0\,\frac{1}{2}$ to point $\frac{3}{4}\,\frac{1}{2}\,\frac{1}{2}$ in a cubic unit cell?

(b) Repeat part **(a)** for a monoclinic unit cell.

3.38 (a) What are the direction indices for a vector that passes from point $\frac{1}{3}\,\frac{1}{2}\,0$ to point $\frac{2}{3}\,\frac{3}{4}\,\frac{1}{2}$ in a tetragonal unit cell?

(b) Repeat part **(a)** for a rhombohedral unit cell.

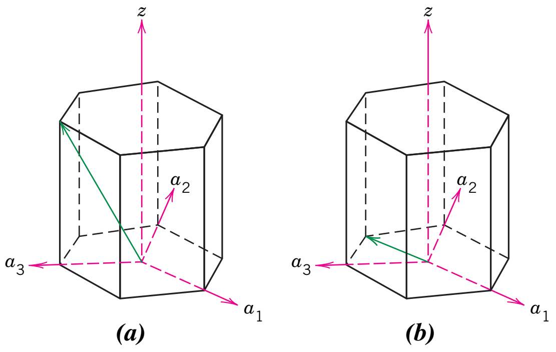
3.39 For tetragonal crystals, cite the indices of directions that are equivalent to each of the following directions:

(a) [011]

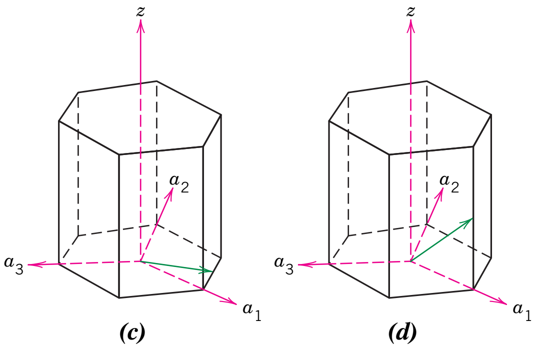
(b) [100]

3.40 Convert the [110] and $[00\bar{1}]$ directions into the four-index Miller–Bravais scheme for hexagonal unit cells.

3.41 Determine the indices for the directions shown in the following hexagonal unit cells:



(a) *(b)*



(c) *(d)*

3.42 Sketch the $[01\bar{1}0]$ and $[\bar{2}\bar{2}43]$ directions in a hexagonal unit cell.

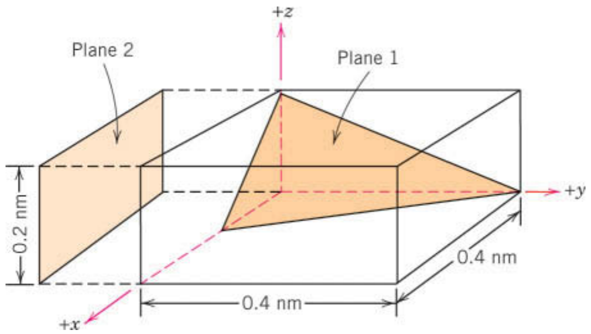
3.43 Using Equations 3.11a–3.11d, derive expressions for each of the three *U*, *V*, and *W* indices in terms of the four *u*, *v*, *t*, and *w* indices.

Crystallographic Planes

3.44 (a) Draw an orthorhombic unit cell, and within that cell, a $(02\bar{1})$ plane.

(b) Draw a monoclinic unit cell, and within that cell, a (200) plane.

3.45 What are the indices for the two planes drawn in the following sketch?



3.46 Sketch within a cubic unit cell the following planes:

(a) $(10\bar{1})$

(b) $(2\bar{1}1)$

(c) (012)

(d) $(3\bar{1}3)$

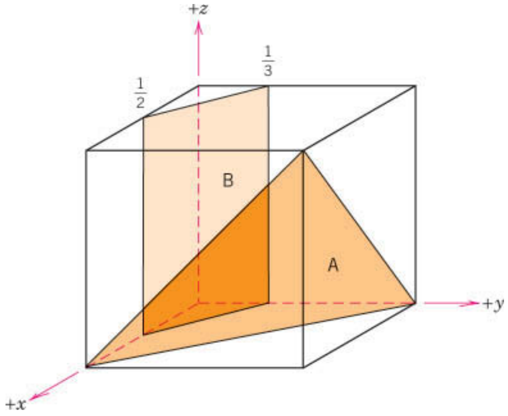
(e) $(\bar{1}1\bar{1})$

(f) $(\bar{2}12)$

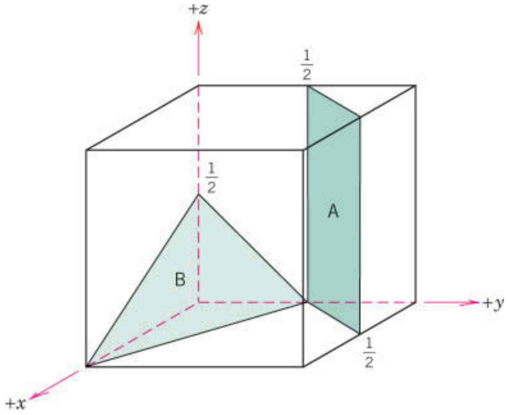
(g) $(3\bar{1}2)$

(h) (301)

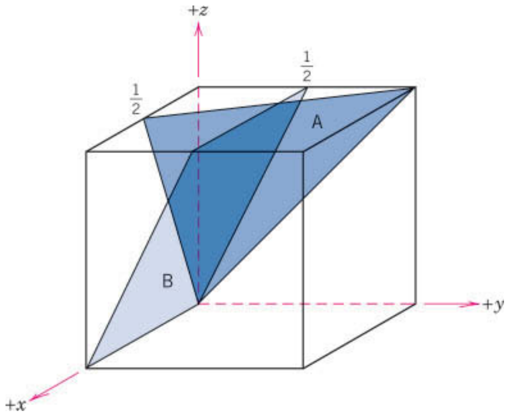
3.47 Determine the Miller indices for the planes shown in the following unit cell:



3.48 Determine the Miller indices for the planes shown in the following unit cell:



3.49 Determine the Miller indices for the planes shown in the following unit cell:



3.50 Cite the indices of the direction that results from the intersection of each of the following pairs of planes within a cubic crystal:

(a) The (110) and (111) planes

(b) The (110) and $(1\bar{1}0)$ planes

(c) The $(11\bar{1})$ and (001) planes

3.51 Sketch the atomic packing of the following:

(a) The (100) plane for the FCC crystal structure

(b) The (111) plane for the BCC crystal structure (similar to Figures 3.12*b* and 3.13*b*).

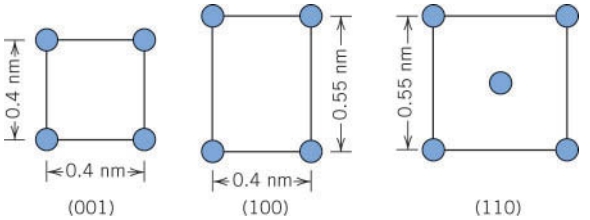
3.52 Consider the reduced-sphere unit cell shown in Problem 3.23, having an origin of the coordinate system positioned at the atom labeled *O*. For the following sets of planes, determine which are equivalent:

(a) (100), $(0\bar{1}0)$, and (001)

(b) (110), (101), (011), and $(\bar{1}01)$

(c) (111), $(1\bar{1}1)$, $(11\bar{1})$, and $(\bar{1}1\bar{1})$

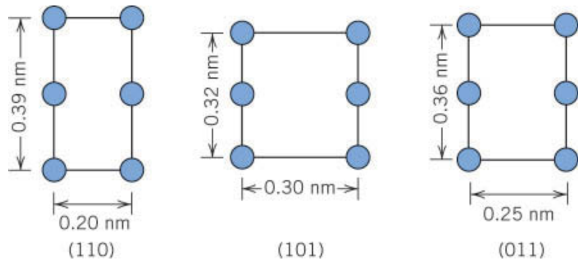
3.53 The accompanying figure shows three different crystallographic planes for a unit cell of a hypothetical metal. The circles represent atoms.



(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

3.54 The accompanying figure shows three different crystallographic planes for a unit cell of some hypothetical metal. The circles represent atoms.



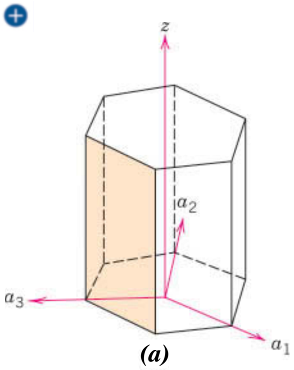
(a) To what crystal system does the unit cell belong?

(b) What would this crystal structure be called?

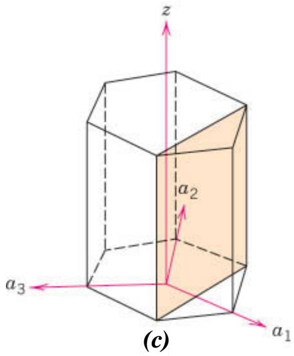
(c) If the density of this metal is 18.91 g/cm^3, determine its atomic weight.

3.55 Convert the (111) and $(0\bar{1}2)$ planes into the four-index Miller–Bravais scheme for hexagonal unit cells.

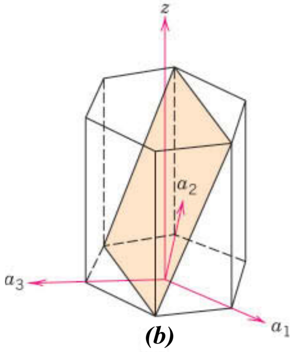
3.56 Determine the indices for the planes shown in the following hexagonal unit cells:



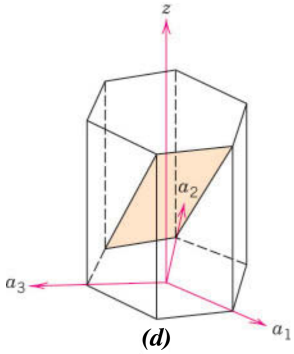
(a)



(c)



(b)



(d)

3.57 Sketch the $(01\bar{1}1)$ and $(2\bar{1}\bar{1}0)$ planes in a hexagonal unit cell.

Linear and Planar Densities

3.58 **(a)** Derive linear density expressions for FCC [100] and [111] directions in terms of the atomic radius *R*.

(b) Compute and compare linear density values for these same two directions for copper (Cu).

3.59 **(a)** Derive linear density expressions for BCC [110] and [111] directions in terms of the atomic radius *R*.

(b) Compute and compare linear density values for these same two directions for iron (Fe).

3.60 **(a)** Derive planar density expressions for FCC (100) and (111) planes in terms of the atomic radius *R*.

(b) Compute and compare planar density values for these same two planes for aluminum (Al).

3.61 **(a)** Derive planar density expressions for BCC (100) and (110) planes in terms of the atomic radius *R*.

(b) Compute and compare planar density values for these same two planes for molybdenum (Mo).

3.62 **(a)** Derive the planar density expression for the HCP (0001) plane in terms of the atomic radius *R*.

(b) Compute the planar density value for this same plane for titanium (Ti).

Polycrystalline Materials

3.63 Explain why the properties of polycrystalline materials are most often isotropic.

X-Ray Diffraction: Determination of Crystal Structures

3.64 The interplanar spacing d_{hkl} for planes in a unit cell having orthorhombic geometry is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where *a*, *b*, and *c* are the lattice parameters.

(a) To what equation does this expression reduce for crystals having cubic symmetry?

(b) For crystals having tetragonal symmetry?

3.65 Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.

3.66 Using the data for α-iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.

3.67 Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium (Cr) when monochromatic radiation of wavelength 0.0711 nm is used.

3.68 Determine the expected diffraction angle for the first-order reflection from the (111) set of planes for FCC nickel (Ni) when monochromatic radiation of wavelength 0.1937 nm is used.

3.69 The metal rhodium (Rh) has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute the following:

(a) The interplanar spacing for this set of planes

(b) The atomic radius for a Rh atom

3.70 The metal niobium (Nb) has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute the following:

(a) The interplanar spacing for this set of planes

(b) The atomic radius for the Nb atom

3.71 For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel (Ni) when monochromatic radiation having a wavelength of 0.1542 nm is used?

3.72 For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for BCC tantalum (Ta) when monochromatic radiation having a wavelength of 0.1937 nm is used?

3.73 Figure 3.26 shows the first five peaks of the x-ray diffraction pattern for tungsten (W), which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.

(a) Index (i.e., give *h*, *k*, and *l* indices) each of these peaks.

(b) Determine the interplanar spacing for each of the peaks.

(c) For each peak, determine the atomic radius for W, and compare these with the value presented in Table 3.1.

3.74 The following table lists diffraction angles for the first four peaks (first-order) of the x-ray diffraction pattern for platinum (Pt), which has an FCC crystal structure; monochromatic x-radiation having a wavelength of 0.0711 nm was used.

Plane Indices	*Diffraction Angle* (2θ)
(111)	18.06°
(200)	20.88°
(220)	26.66°
(311)	31.37°

(a) Determine the interplanar spacing for each of the peaks.

(b) For each peak, determine the atomic radius for Pt, and compare these with the value presented in Table 3.1.

3.75 The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.1397 nm was used.

(a) Determine whether this metal's crystal structure is FCC, BCC, or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	*Diffraction Angle* (2θ)
1	34.51°
2	40.06°
3	57.95°

3.76 The following table lists diffraction angles for the first three peaks (first-order) of the x-ray diffraction pattern for some metal. Monochromatic x-radiation having a wavelength of 0.0711 nm was used.

(a) Determine whether this metal's crystal structure is FCC, BCC, or neither FCC or BCC, and explain the reason for your choice.

(b) If the crystal structure is either BCC or FCC, identify which of the metals in Table 3.1 gives this diffraction pattern. Justify your decision.

Peak Number	*Diffraction Angle* (2θ)
1	18.27°
2	25.96°
3	31.92°

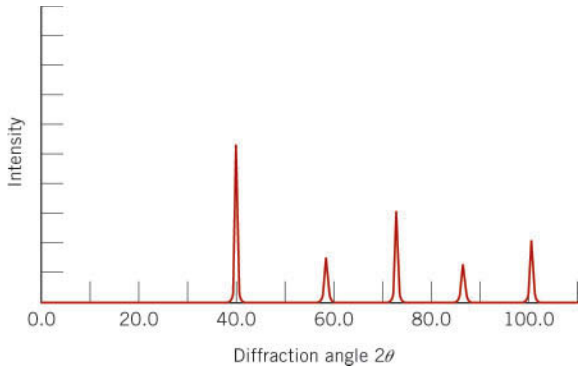


Figure 3.26 Diffraction pattern for powdered tungsten. (Courtesy of Wesley L. Holman.)

Noncrystalline Solids

3.77 Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more likely or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)

Spreadsheet Problem

3.1SS For an x-ray diffraction pattern (having all peaks plane-indexed) of a metal that has a unit cell of cubic symmetry, generate a spreadsheet that allows the user to input the x-ray wavelength, and then determine, for each plane, the following:

(a) d_{hkl}

(b) The lattice parameter, a

FUNDAMENTALS OF ENGINEERING QUESTIONS AND PROBLEMS

3.1FE A hypothetical metal has the BCC crystal structure, a density of 7.24 g/cm^3, and an atomic weight of 48.9 g/mol. The atomic radius of this metal is

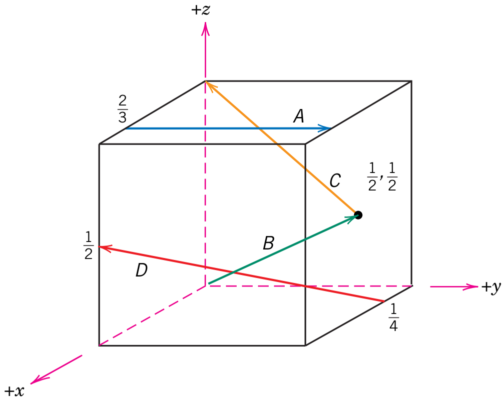
(A) 0.122 nm

(B) 1.22 nm

(C) 0.0997 nm

(D) 0.154 nm

3.2FE In the following unit cell, which vector represents the [121] direction?



3.3FE What are the Miller indices for the plane shown in the following cubic unit cell?

(A) (201)

(B) $(1\infty\frac{1}{2})$

(C) $(10\frac{1}{2})$

(D) (102)