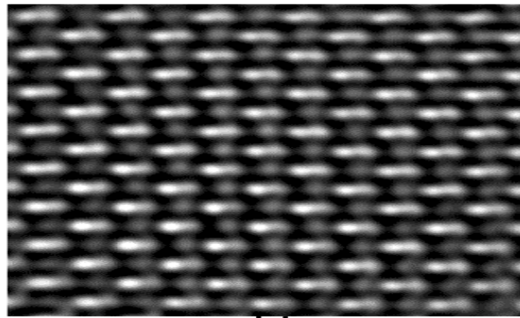


CHAPTER 3

Crystalline Structure–Perfection



113 pm

The transmission electron microscope (Section 4.7) can be used to image the regular arrangement of atoms in a crystalline structure. This atomic-resolution view is along individual columns of gallium and nitrogen atoms in gallium nitride. The distance marker is 113 picometers or 0.113 nm. (Courtesy of C. Kisielowski, C. Song, and E. C. Nelson, National Center for Electron Microscopy, Berkeley, California.)

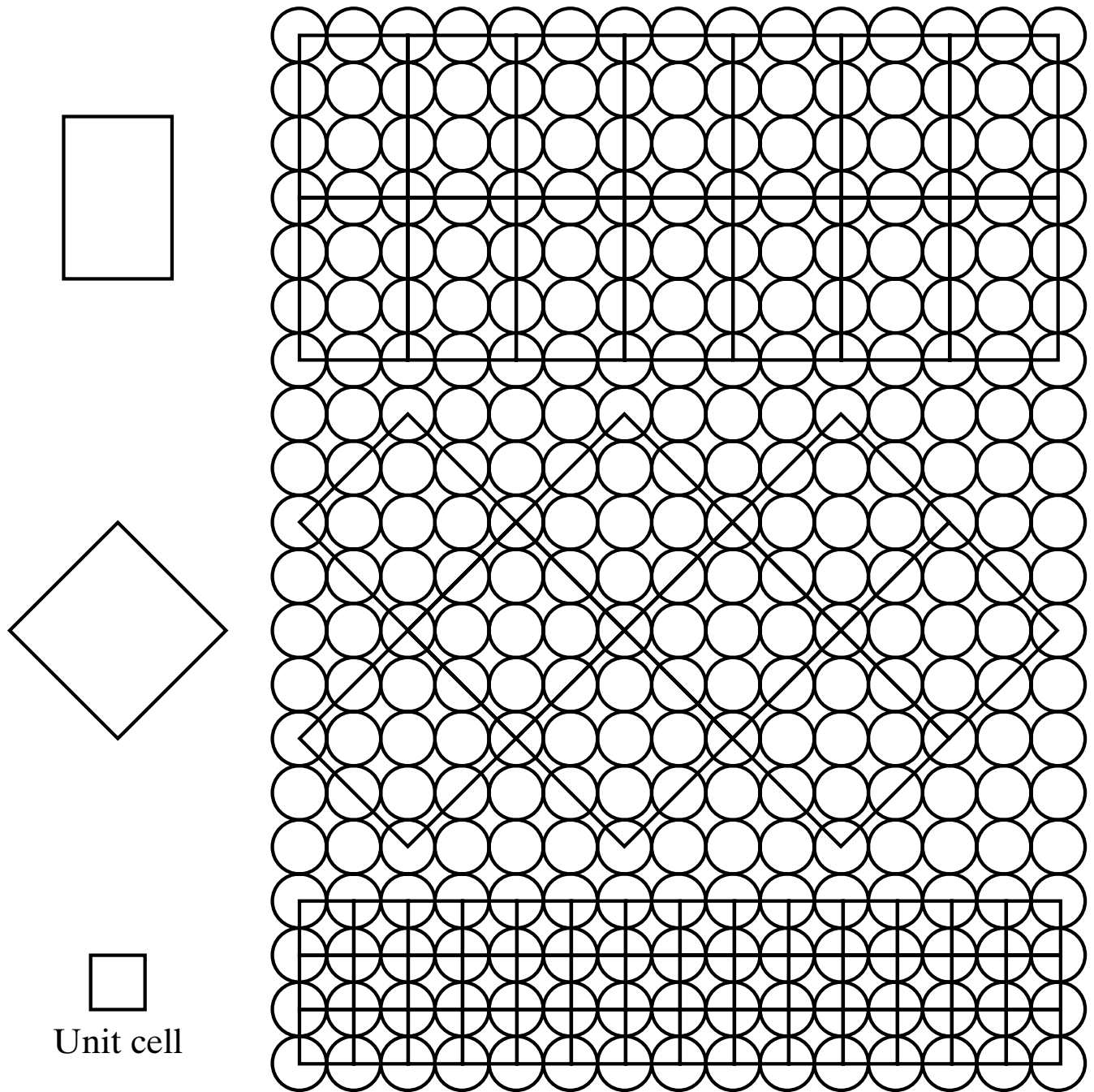


Figure 3-1 Various structural units that describe the schematic crystalline structure. The simplest structural unit is the unit cell.

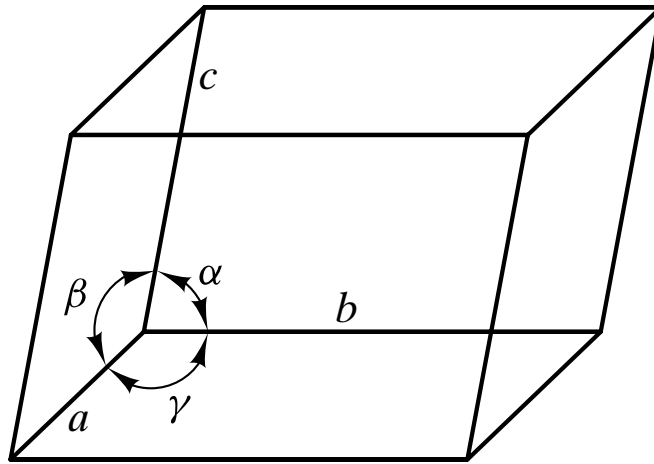


Figure 3-2 *Geometry of a general unit cell.*

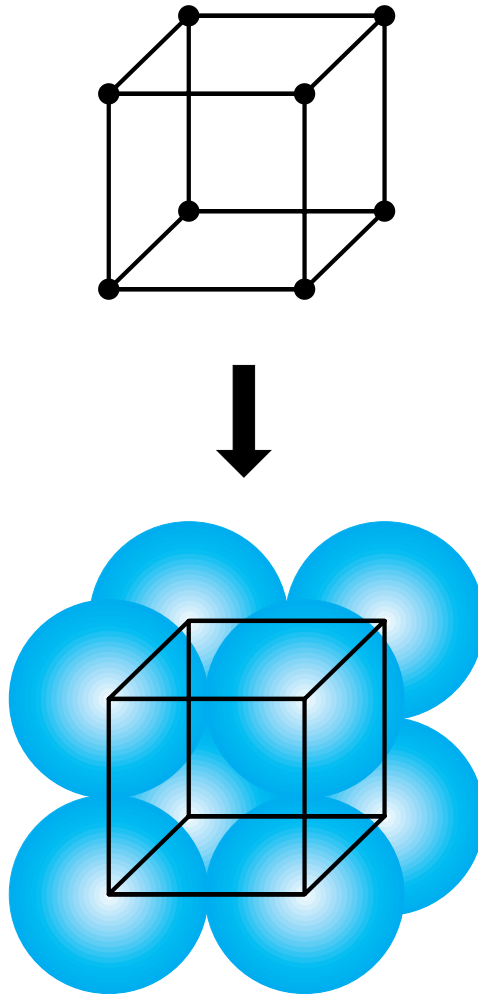
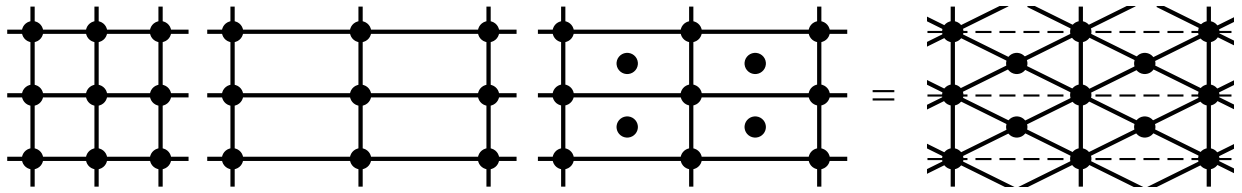


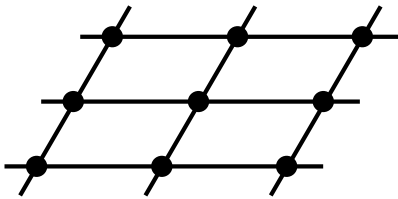
Figure 3-3 *The simple cubic lattice becomes the simple cubic crystal structure when an atom is placed on each lattice point.*



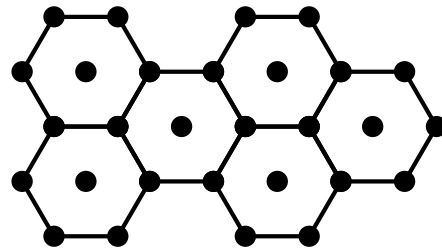
(i)

(ii)

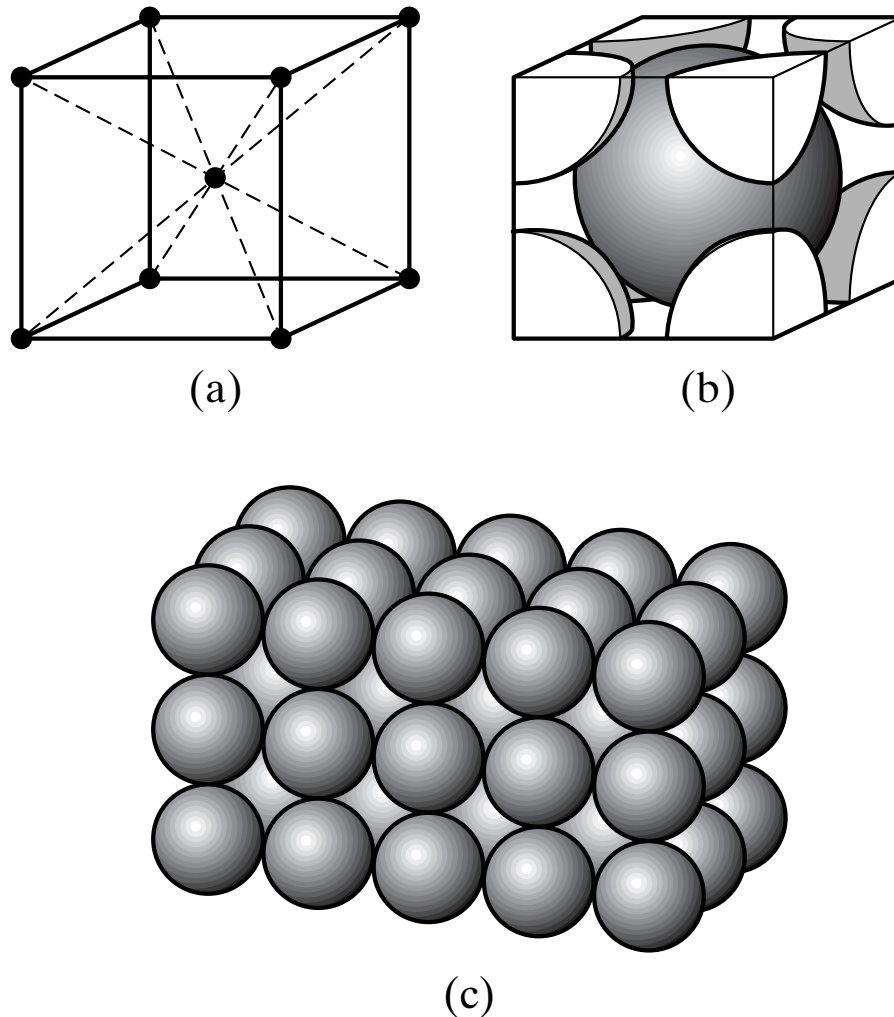
(iii)



(iv)



(v)



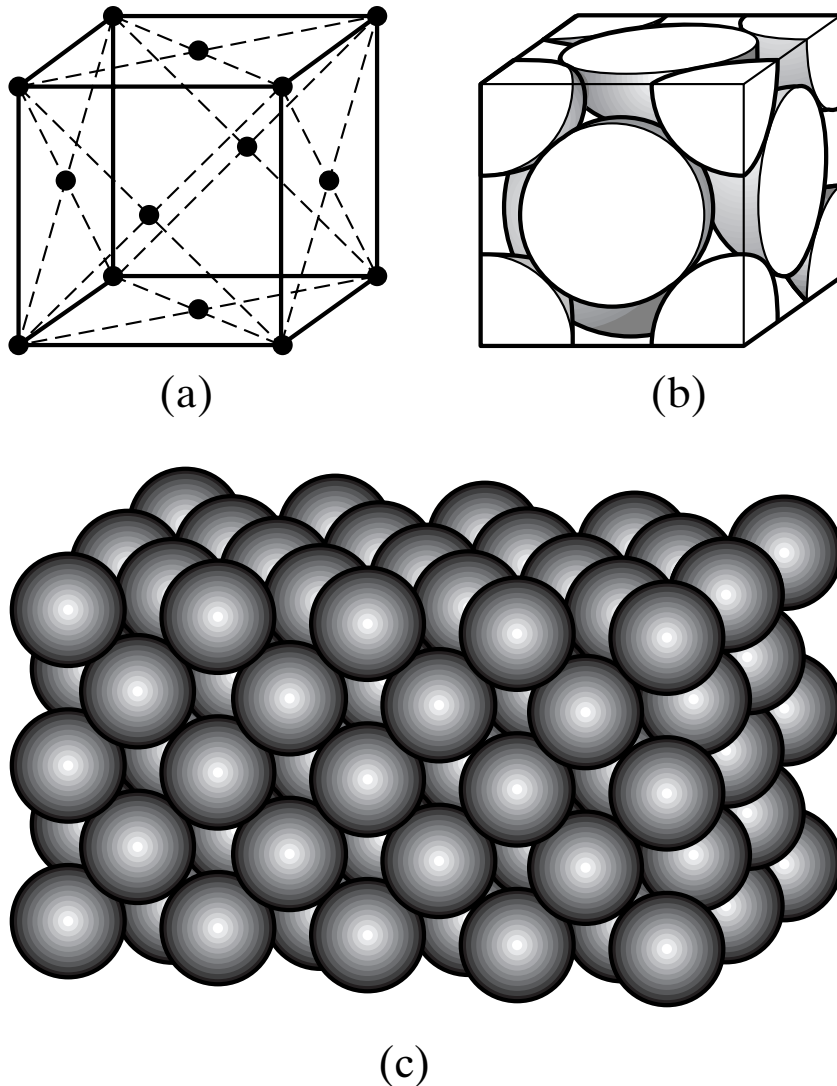
Structure: body-centered cubic (bcc)

Bravais lattice: bcc

Atoms/unit cell: $1 + 8 \times \frac{1}{8} = 2$

Typical metals: α -Fe, V, Cr, Mo, and W

Figure 3-4 *Body-centered cubic (bcc) structure for metals showing (a) the arrangement of lattice points for a unit cell; (b) the actual packing of atoms (represented as hard spheres) within the unit cell; and (c) the repeating bcc structure, equivalent to many adjacent unit cells (Part (c) courtesy of Molecular Simulations, Inc.).*



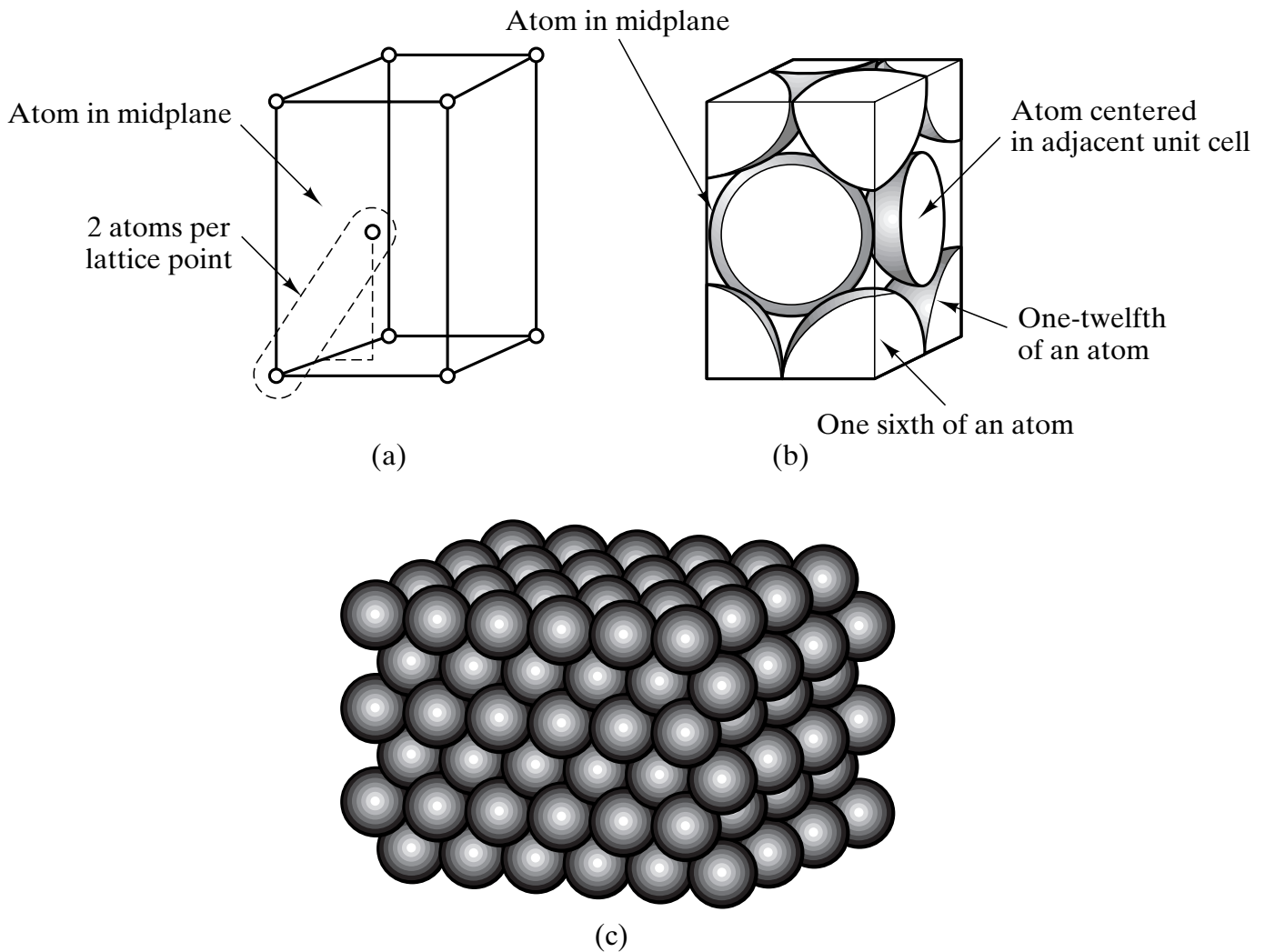
Structure: face-centered cubic (fcc)

Bravais lattice: fcc

Atoms/unit cell: $6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4$

Typical metals: γ -Fe, Al, Ni, Cu, Ag, Pt, and Au

Figure 3-5 *Face-centered cubic (fcc) structure for metals showing (a) the arrangement of lattice points for a unit cell; (b) the actual packing of atoms within the unit cell; and (c) the repeating fcc structure, equivalent to many adjacent unit cells (Part (c) courtesy of Molecular Simulations, Inc.).*



Structure: hexagonal close-packed (hcp)
 Bravais lattice: hexagonal
 Atoms/unit cell: $1 + 4 \times \frac{1}{6} + 4 \times \frac{1}{12} = 2$
 Typical metals: Be, Mg, α -Ti, Zn, and Zr

Figure 3-6 Hexagonal close packed (hcp) structure for metals showing (a) the arrangement of atom centers relative to lattice points for a unit cell. There are two atoms per lattice point (note the outlined example). (b) The actual packing of atoms within the unit cell. Note that the atom in the midplane extends beyond the unit cell boundaries. (c) The repeating hcp structure, equivalent to many adjacent unit cells (Part (c) courtesy of Molecular Simulations, Inc.).

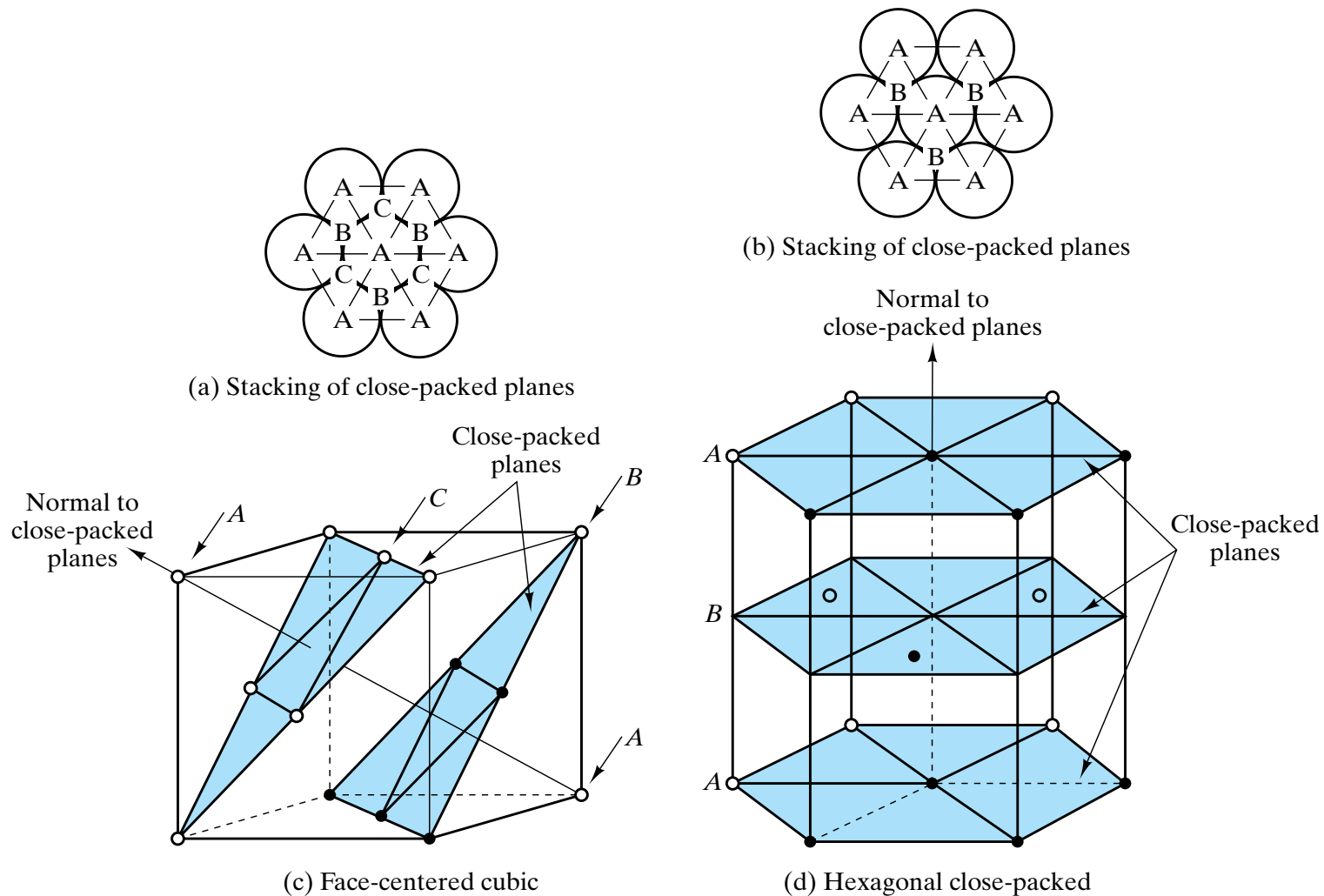
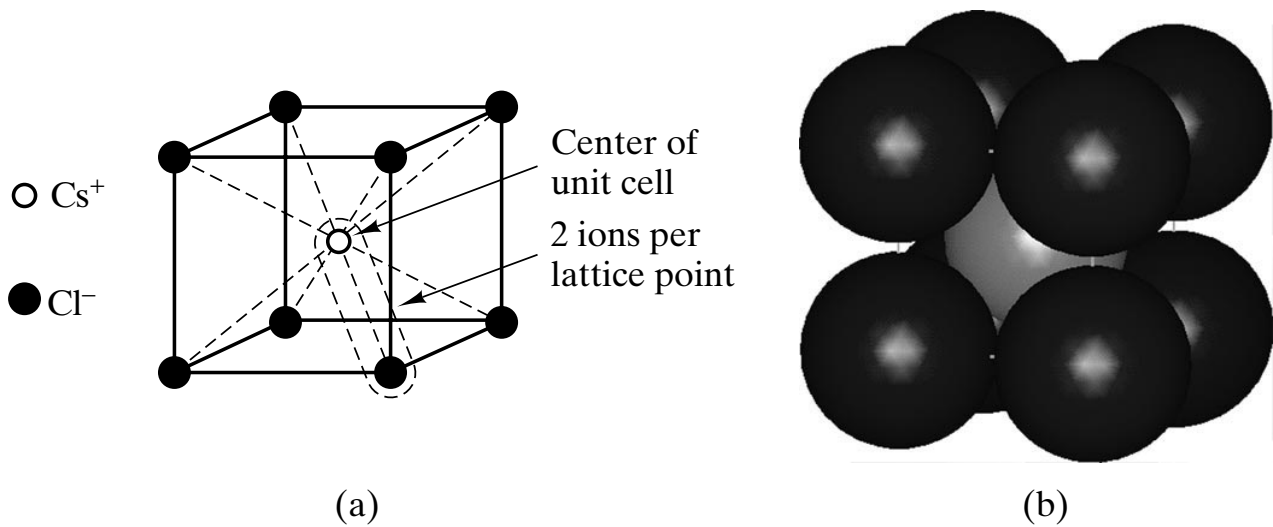
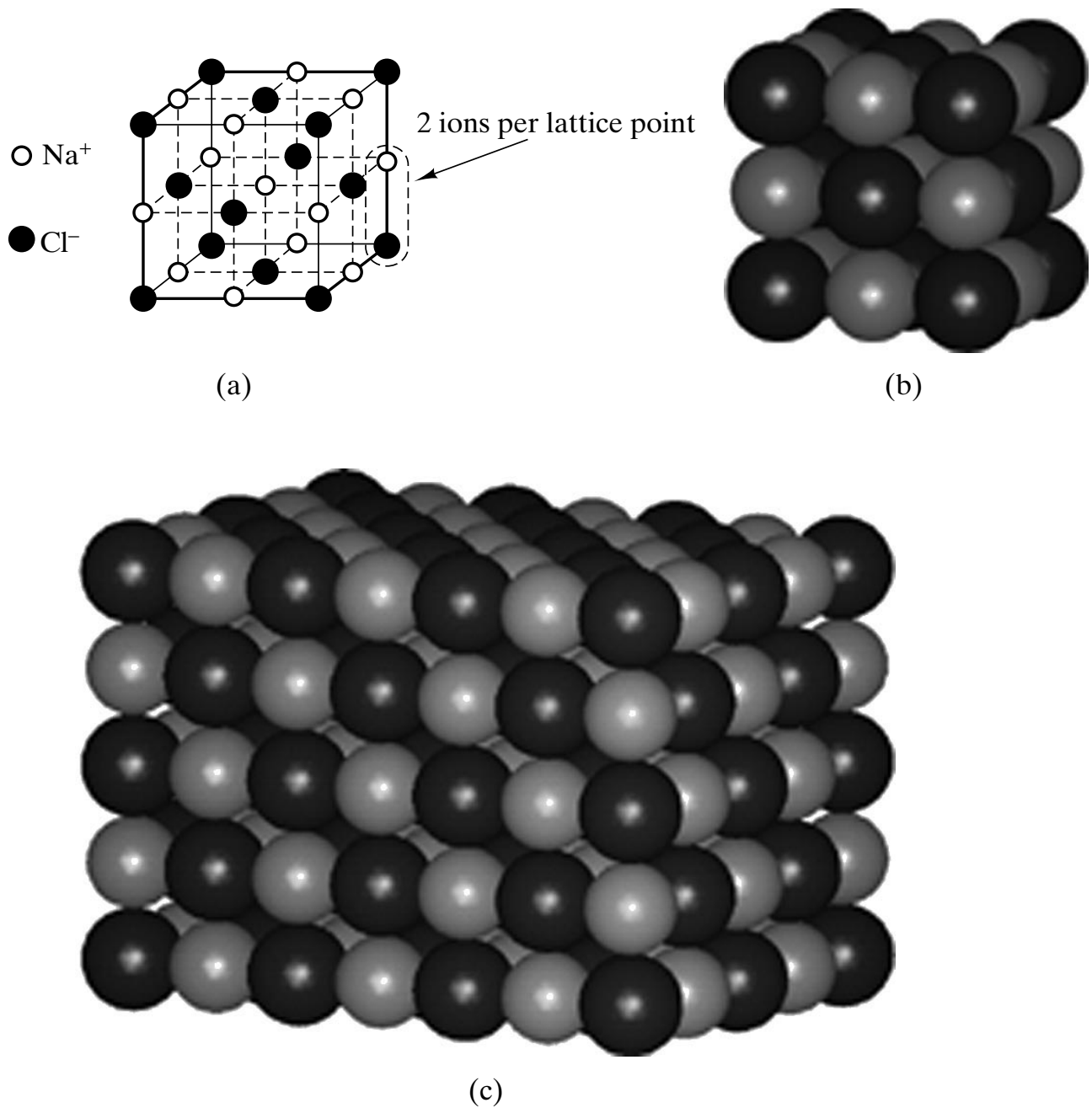


Figure 3-7 Comparison of the fcc and the hcp structures. They are each efficient stackings of close-packed planes. The difference between the two structures is the different stacking sequences. (After B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1978.)



Structure: CsCl-type
 Bravais lattice: simple cubic
 Ions/unit cell: $1\text{Cs}^+ + 1\text{Cl}^-$

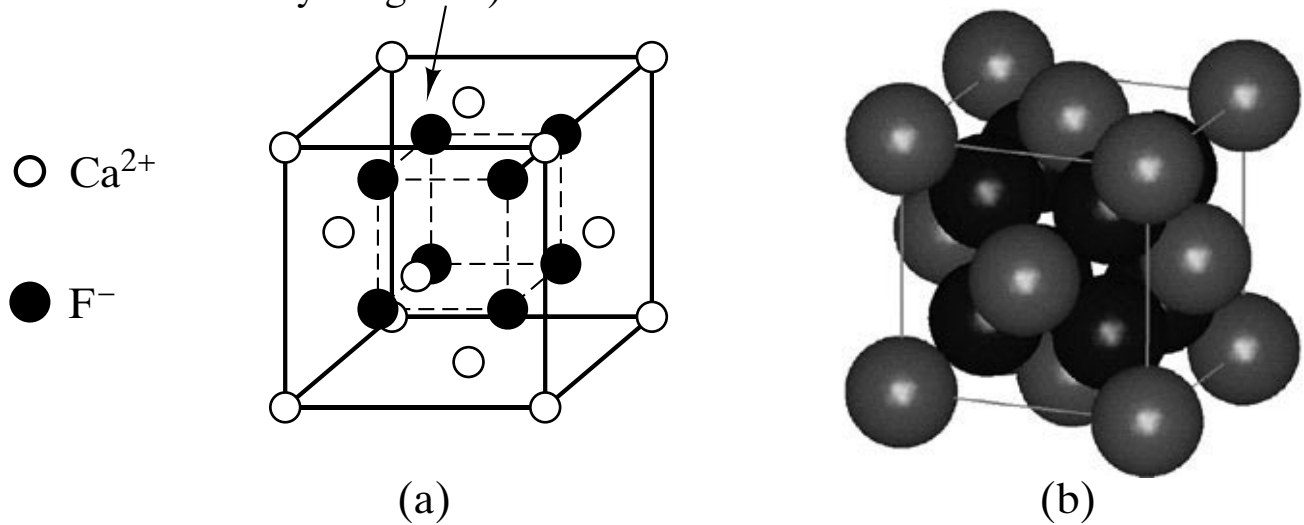
Figure 3-8 Cesium chloride (CsCl) unit cell showing (a) ion positions and the 2 ions per lattice point, and (b) full-size ions. Note that the $\text{Cs}^+ - \text{Cl}^-$ pair associated with a given lattice point is not a molecule because the ionic bonding is nondirectional and a given Cs^+ is equally bonded to eight adjacent Cl^- , and vice versa. (Part (b) courtesy of Molecular Simulations, Inc.)



Structure: NaCl-type
 Bravais lattice: fcc
 Ions/unit cell: 4Na⁺ + 4Cl⁻
 Typical ceramics: MgO, CaO, FeO, and NiO

Figure 3-9 Sodium chloride (NaCl) structure showing (a) ion positions in a unit cell, (b) full-size ions, and (c) many adjacent unit cells. (Parts (b) and (c) courtesy of Molecular Simulations, Inc.)

F⁻ ions located at corners of a cube (at one-quarter of the distance along the body diagonal)



Structure: fluorite (CaF₂)-type

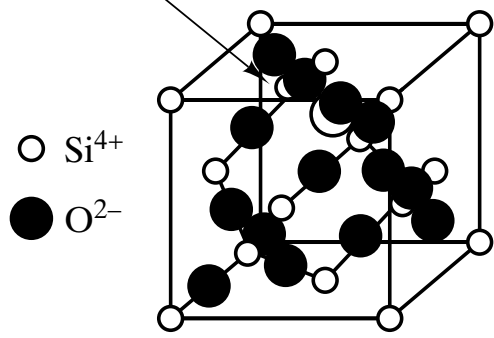
Bravais lattice: fcc

Ions/unit cell: 4Ca²⁺ + 8F⁻

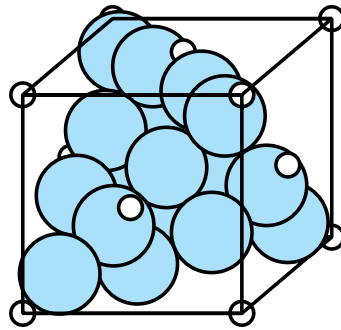
Typical ceramics: UO₂, ThO₂, and TeO₂

Figure 3-10 Fluorite (CaF₂) unit cell showing (a) ion positions and (b) full-size ions. (Part (b) courtesy of Molecular Simulations, Inc.)

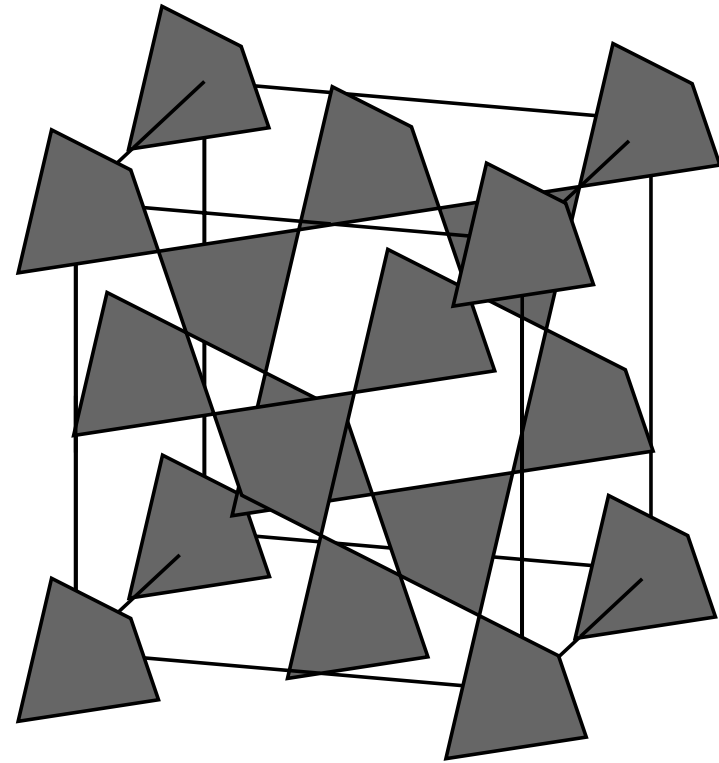
Interior Si^{4+} located at positions one-quarter of the distance along the body diagonal



(a)



(b)



(c)

Structure: cristobalite (SiO_2) -type

Bravais lattice: fcc

Ions/unit cell: $8\text{Si}^{4+} + 16\text{O}^{2-}$

Figure 3-11 The cristobalite (SiO_2) unit cell showing (a) ion positions, (b) full-size ions, and (c) the connectivity of SiO_4^{4-} tetrahedra. In the schematic, each tetrahedron has a Si^{4+} at its center. In addition, an O^{2-} would be at each corner of each tetrahedron and is shared with an adjacent tetrahedron. (Part (c) courtesy of Molecular Simulations, Inc.)

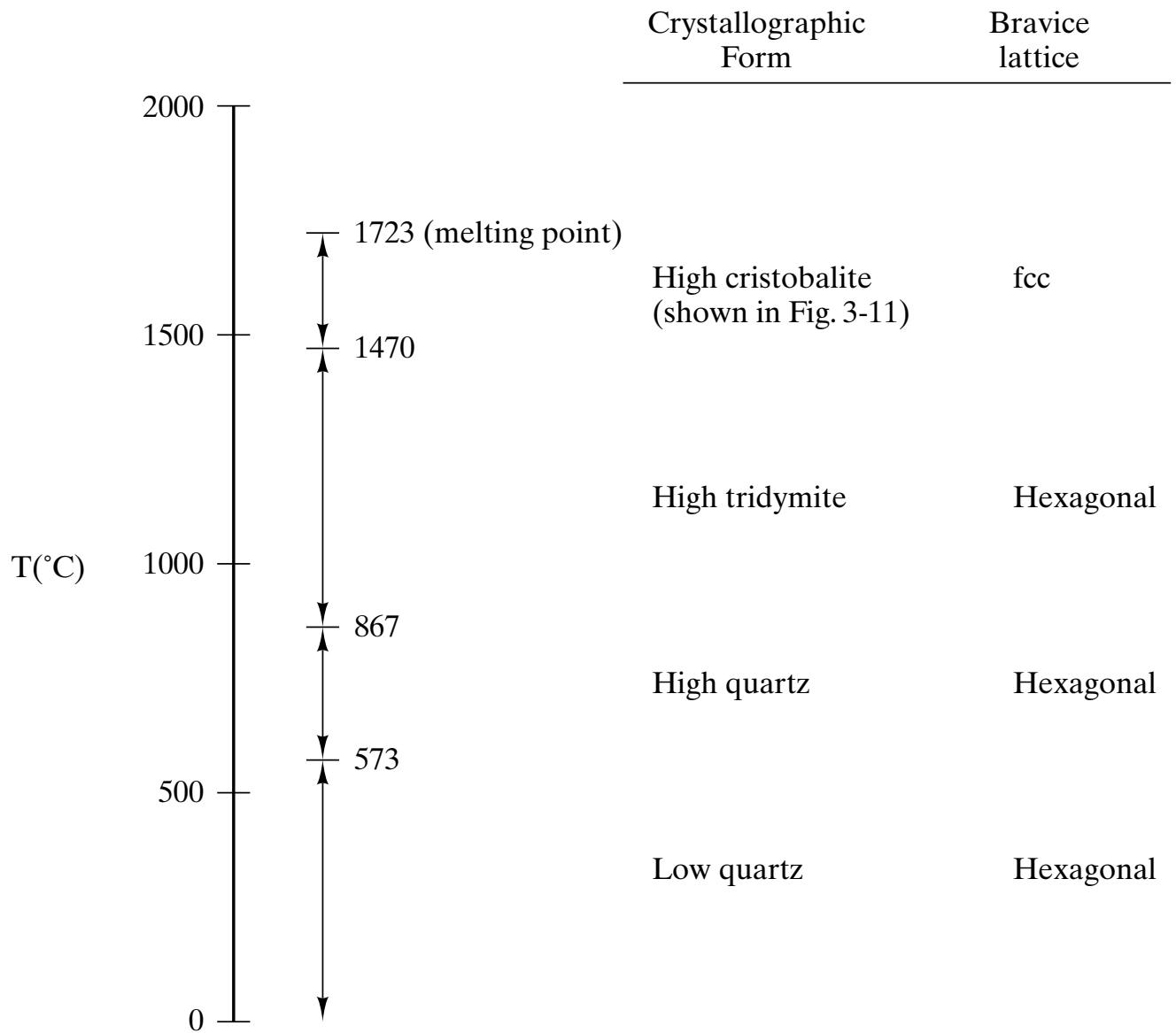


Figure 3-12 Many crystallographic forms of SiO_2 are stable as they are heated from room temperature to the melting temperature. Each form represents a different way to connect adjacent SiO_4^{4-} tetrahedra.

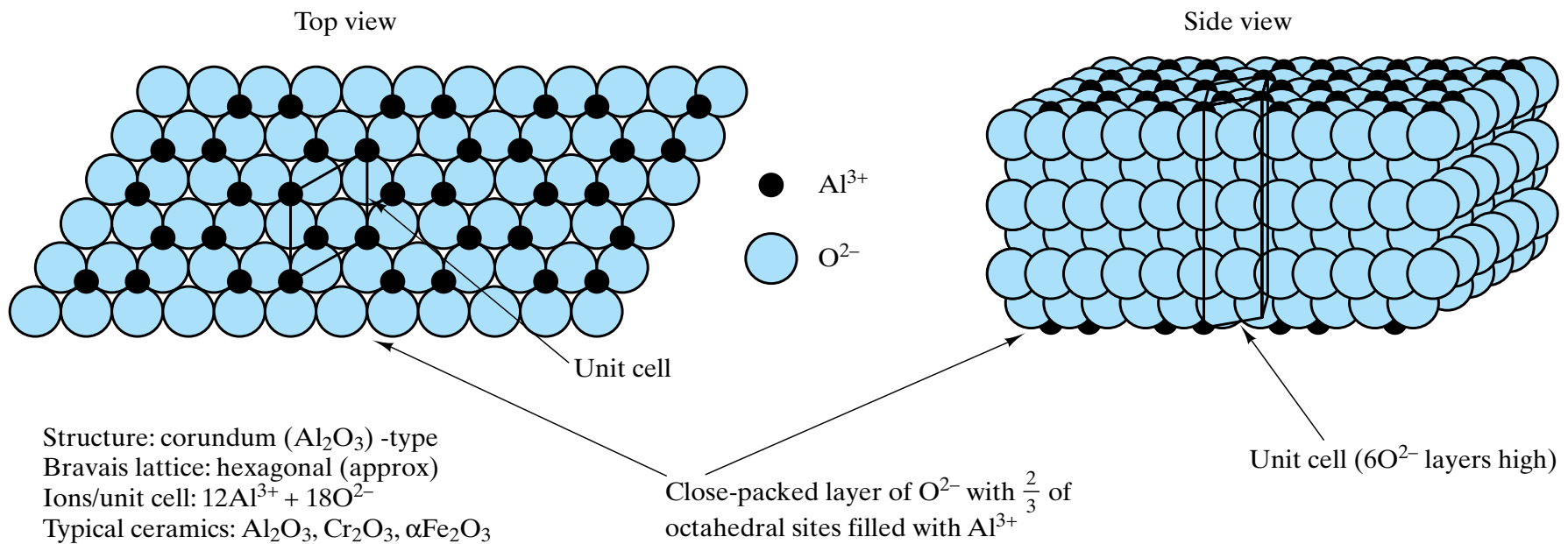
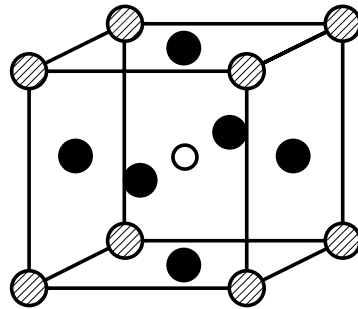


Figure 3-13 The corundum (Al_2O_3) unit cell is shown superimposed on the repeated stacking of layers of close-packed O^{2-} ions. The Al^{3+} ions fill two-thirds of the small (octahedral) interstices between adjacent layers.

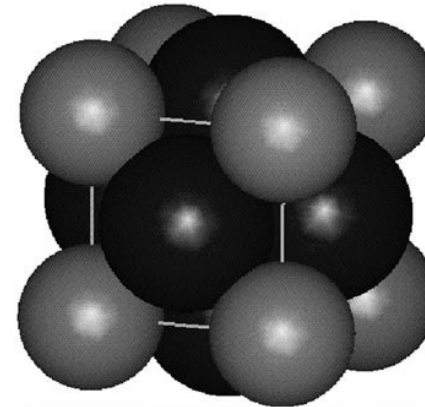
○ Ti^{4+} : at the body center

⊗ Ca^{2+} : at corners

● O^{2-} : at face centers



(a)



(b)

Structure: perovskite (CaTiO_3)-type

Bravais lattice: simple cubic

Ions/unit cell: $1\text{Ca}^{2+} + 1\text{Ti}^{4+} + 3\text{O}^{2-}$

Typical ceramics: CaTiO_3 , BaTiO_3

Figure 3-14 Perovskite (CaTiO_3) unit cell showing (a) ion positions and (b) full-size ions. (Part (b) courtesy of Molecular Simulations, Inc.)

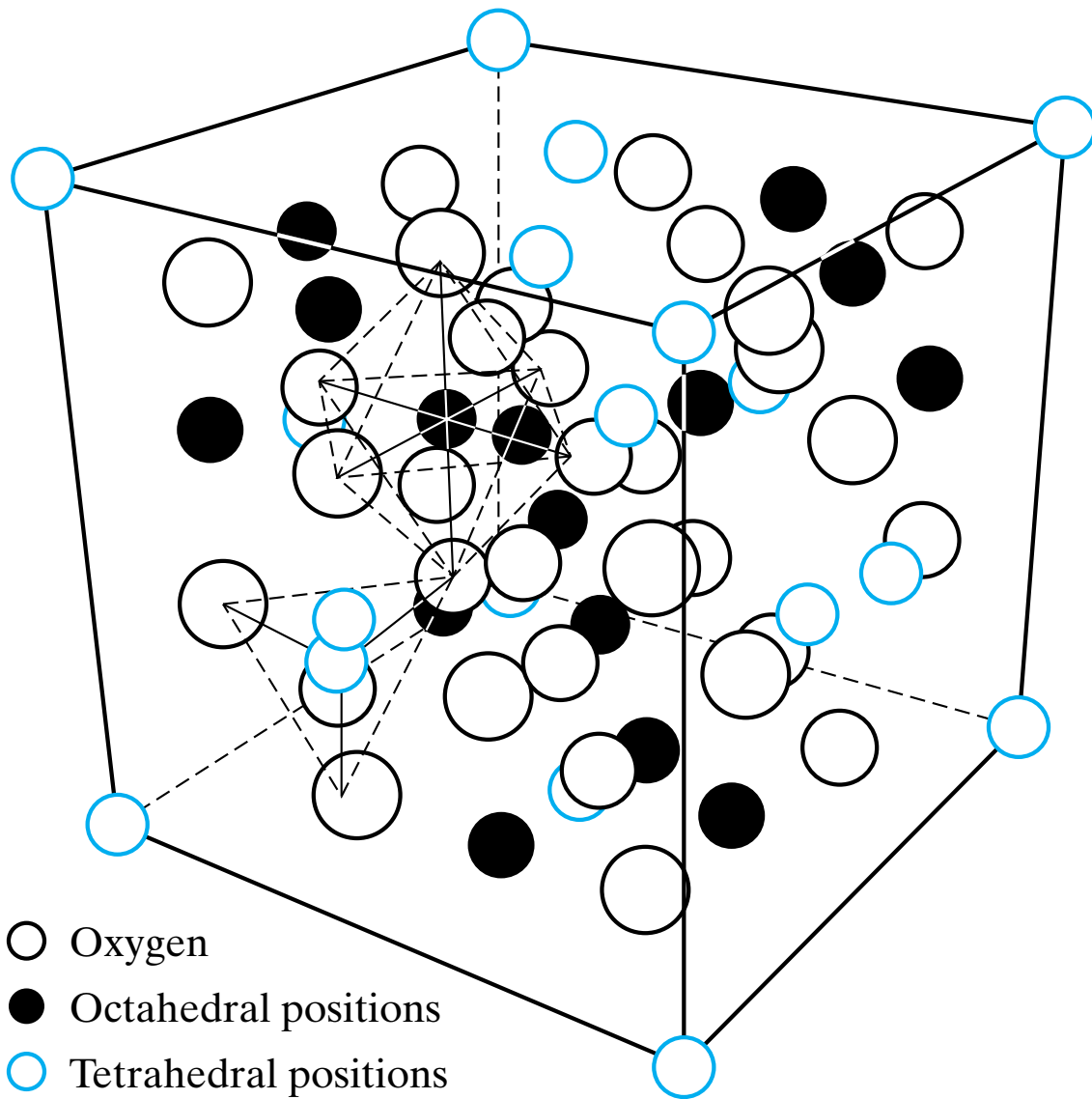


Figure 3-15 Ion positions in the spinel ($MgAl_2O_4$) unit cell. The circles in color represent Mg^{2+} ions (in tetrahedral or four-coordinated positions), and the black circles represent Al^{3+} ions (in octahedral or six-coordinated positions). (From F. G. Brockman, Bull. Am. Ceram. Soc. 47, 186 (1967).)

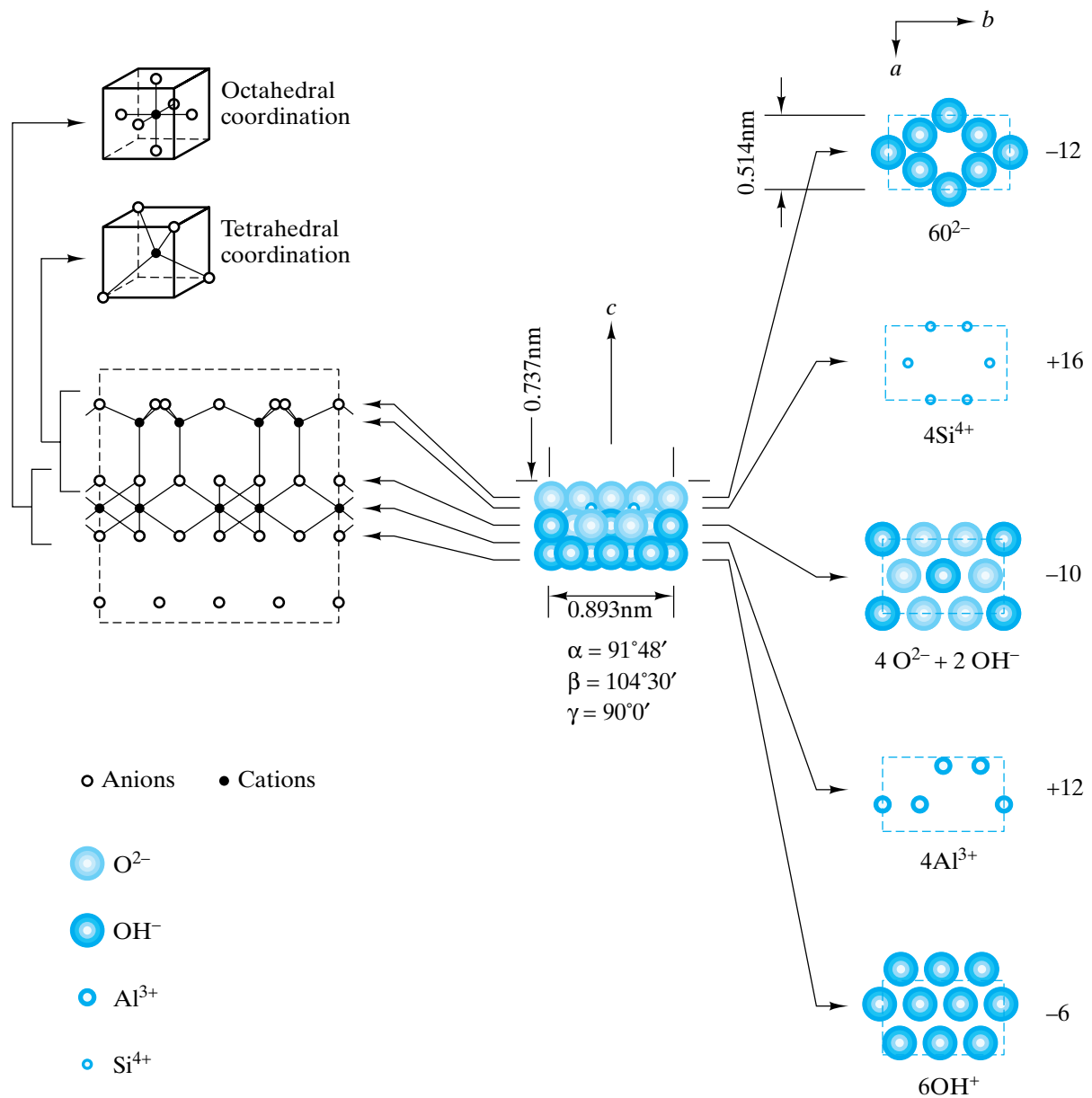


Figure 3-16 Exploded view of the kaolinite unit cell, $2(OH)_4Al_2Si_2O_5$. (After F. H. Norton, *Elements of Ceramics*, 2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1974.)

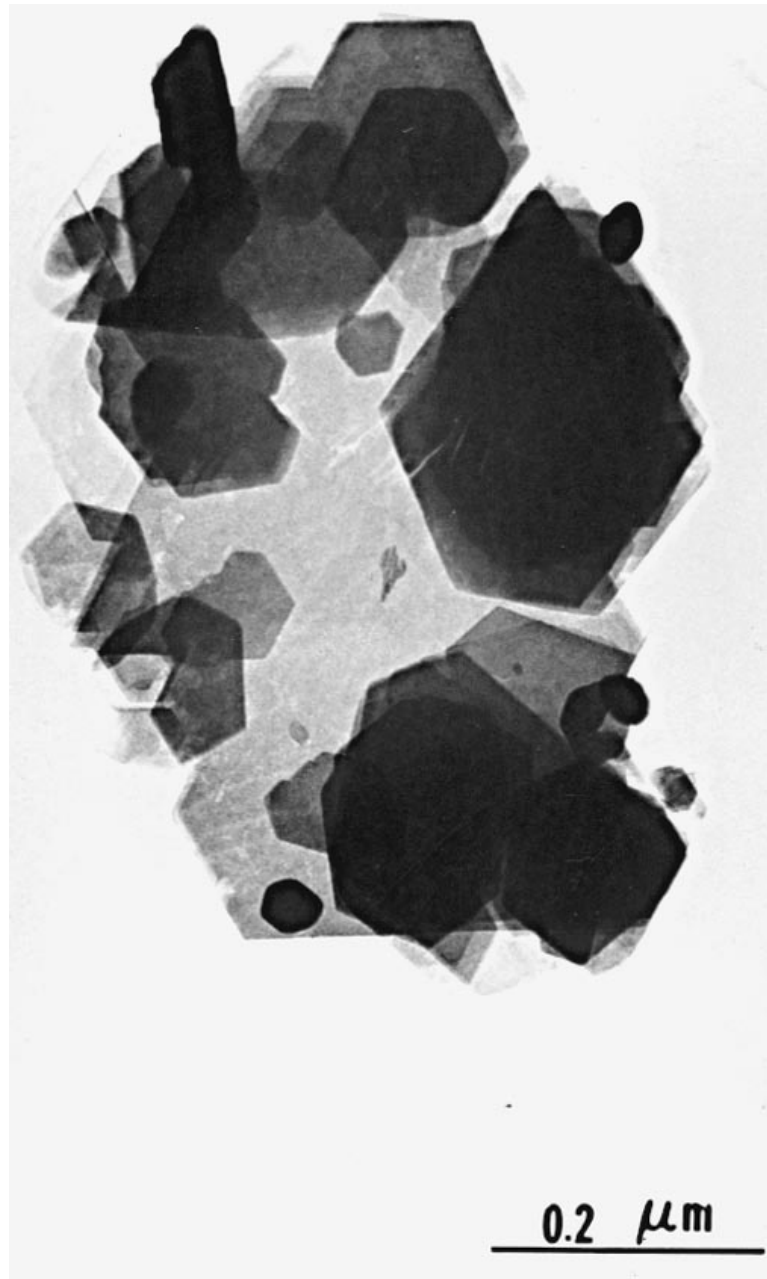


Figure 3-17 *Transmission electron micrograph (see Section 4.7) of the structure of clay platelets. This microscopic-scale structure is a manifestation of the layered crystal structure shown in Figure 3-16. (Courtesy of I. A. Aksay)*

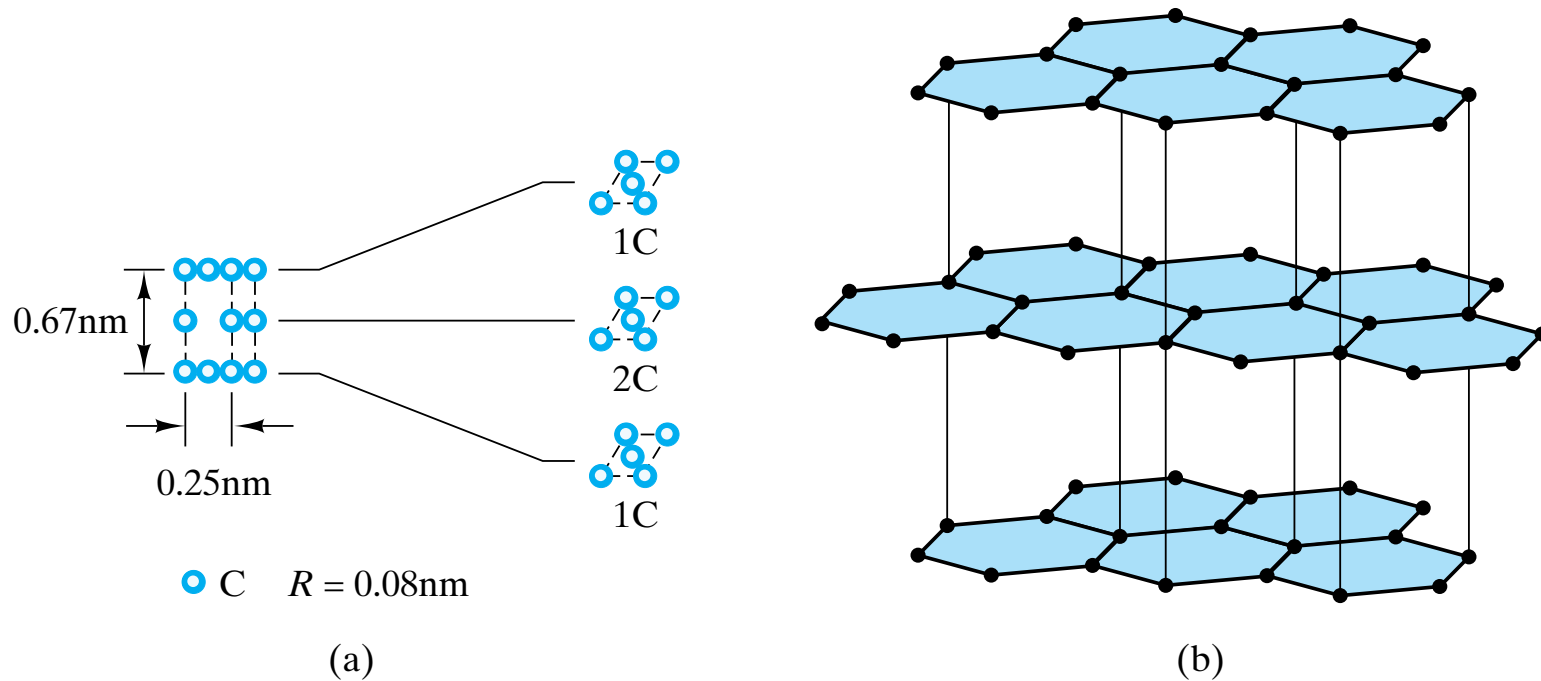
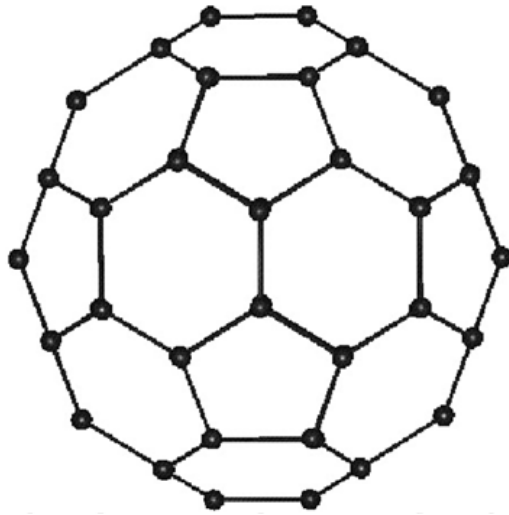
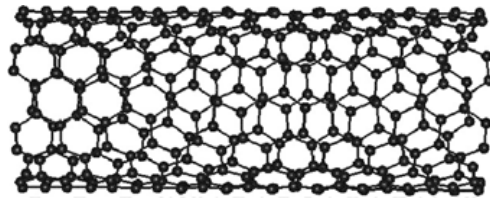


Figure 3-18 (a) An exploded view of the graphite (C) unit cell. (From F. H. Norton, *Elements of Ceramics, 2nd ed.*, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1974.) (b) A schematic of the nature of graphite's layered structure. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction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



(a)



(b)

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

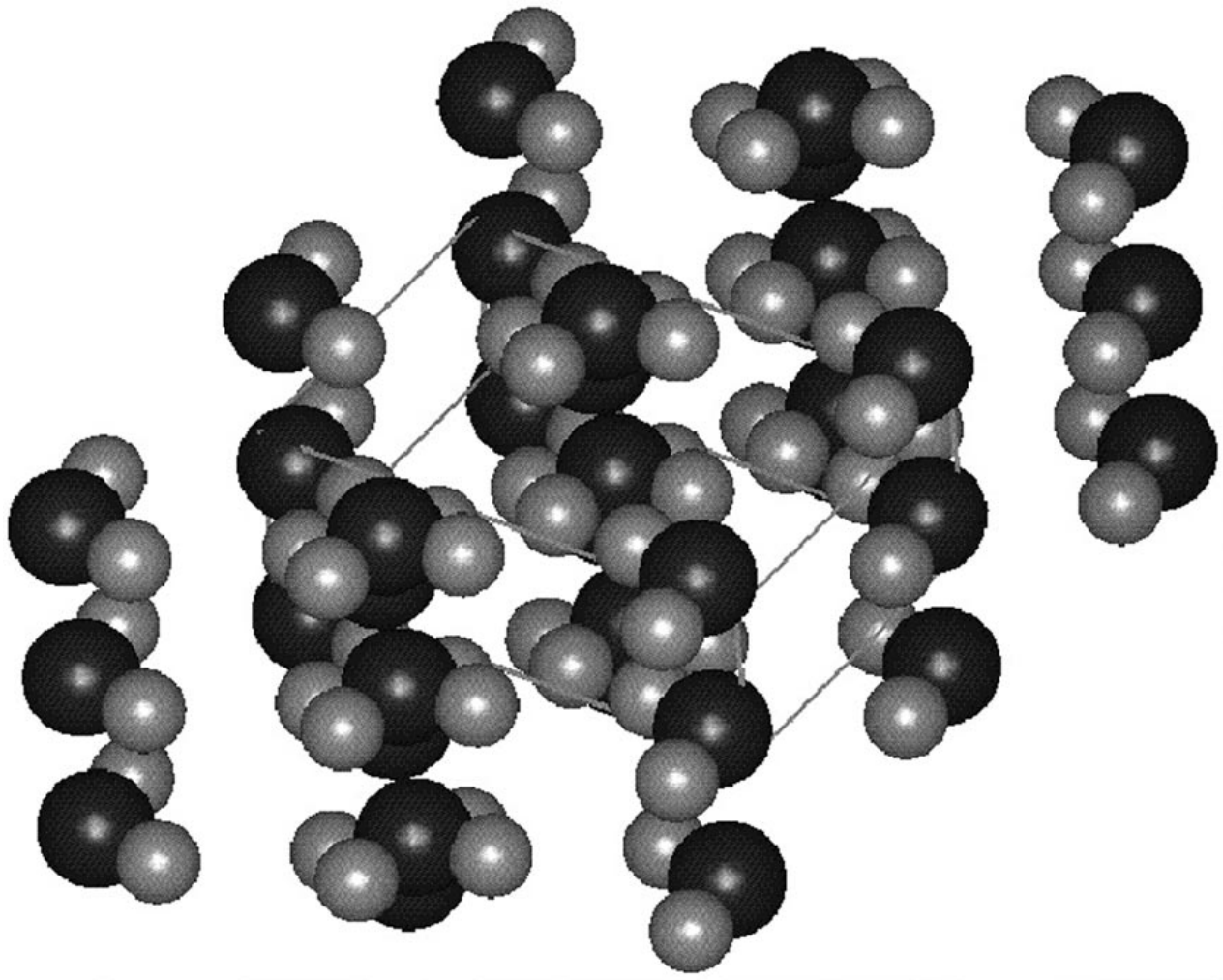


Figure 3-20 *Arrangement of polymeric chains in the unit cell of polyethylene. The dark spheres are carbon atoms, and the light spheres are hydrogen atoms. The unit cell dimensions are $0.255 \text{ nm} \times 0.494 \text{ nm} \times 0.741 \text{ nm}$. (Courtesy of Molecular Simulations, Inc.)*

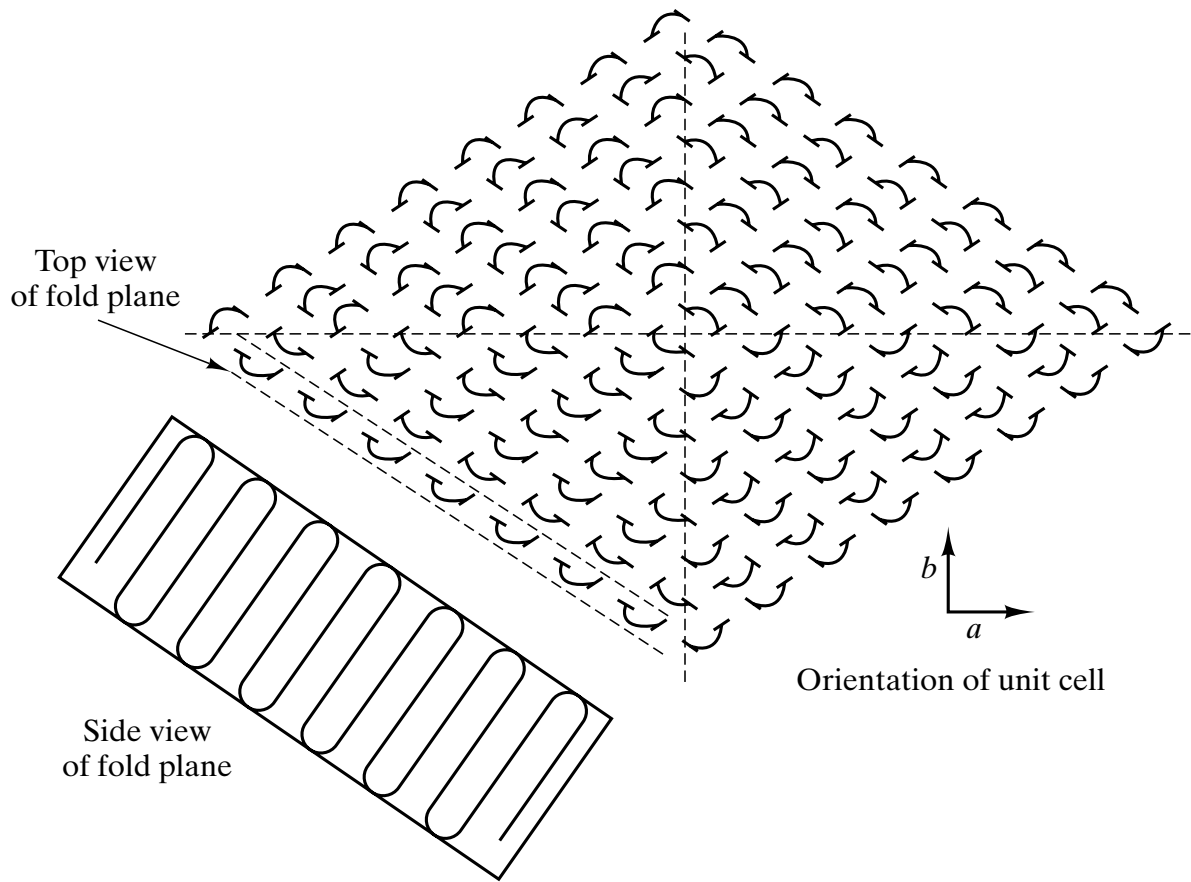


Figure 3-21 Weaving-like pattern of folded polymeric chains that occurs in thin crystal platelets of polyethylene. (From D. J. Williams, *Polymer Science and Engineering*, Prentice Hall, Inc., Englewood Cliffs, N.J., 1971.)

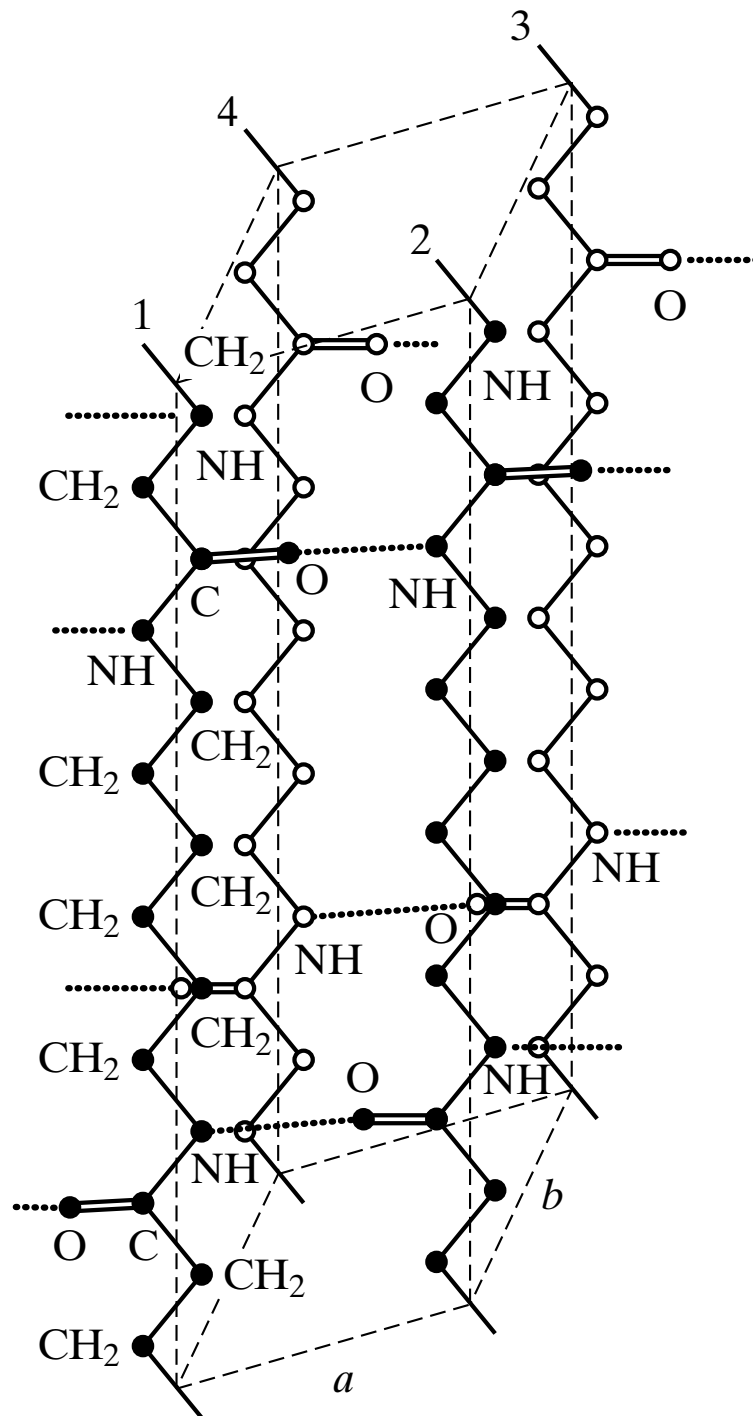
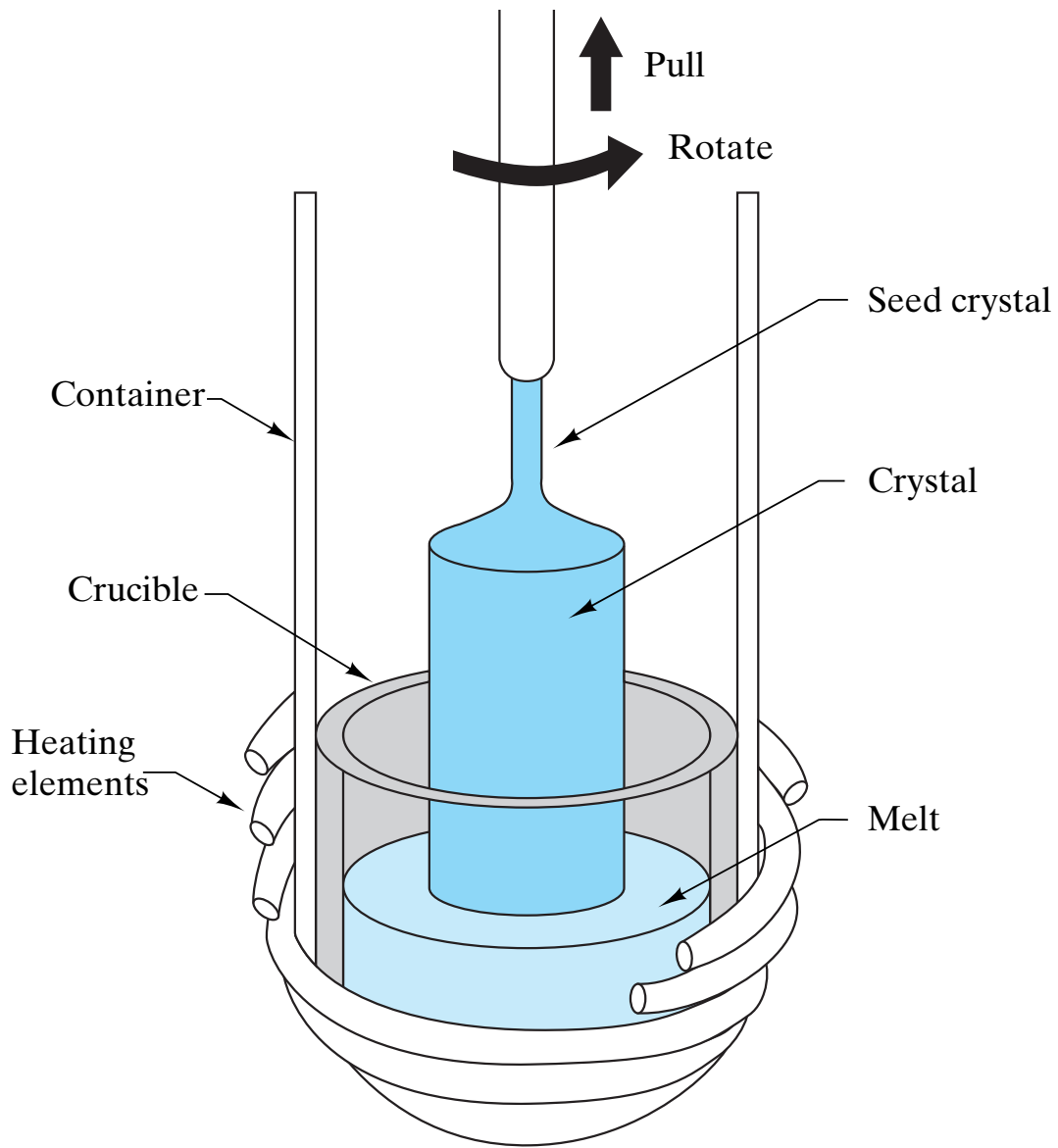


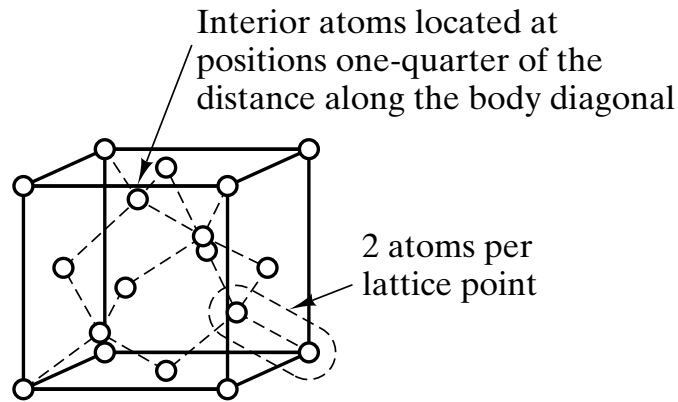
Figure 3-22 Unit cell of the α -form of polyhexamethylene adipamide or nylon 66. (From C. W. Bunn and E. V. Garner, "Packing of nylon 66 molecules in the triclinic unit cell: α form, *Proc. Roy. Soc. Lond.* 189A, 39 (1947).)



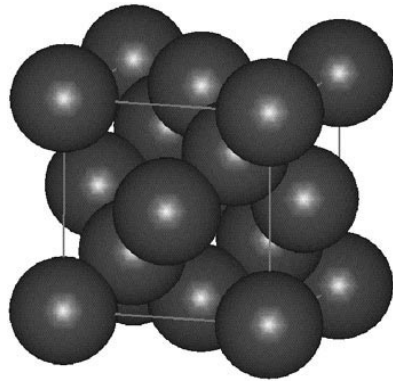
Courtesy of SEAMATECH.



*Schematic of growth of single crystals using the Czochralski technique. (After J. W. Mayer and S. S. Lau, *Electronic Materials Science: For Integrated Circuits in Si and GaAs*, Macmillan Publishing Company, New York, 1990.)*



(a)



(b)

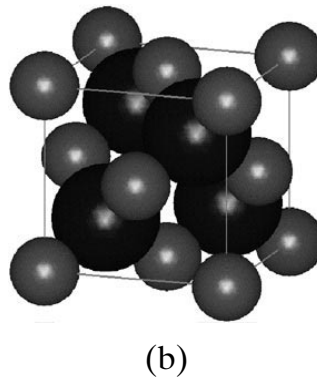
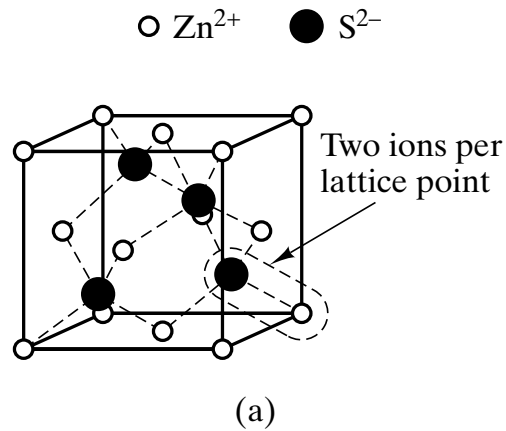
Structure: diamond cubic

Bravais lattice: fcc

Atoms/unit cell: $4 + 6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 8$

Typical semiconductors: Si, Ge, and gray Sn

Figure 3-23 *Diamond cubic unit cell showing (a) atom positions. There are two atoms per lattice point (note the outlined example). Each atom is tetrahedrally coordinated. (b) The actual packing of full-size atoms associated with the unit cell. (Part (b) courtesy of Molecular Simulations, Inc.)*



Structure: Zinc blende (ZnS)-type

Bravais lattice: fcc

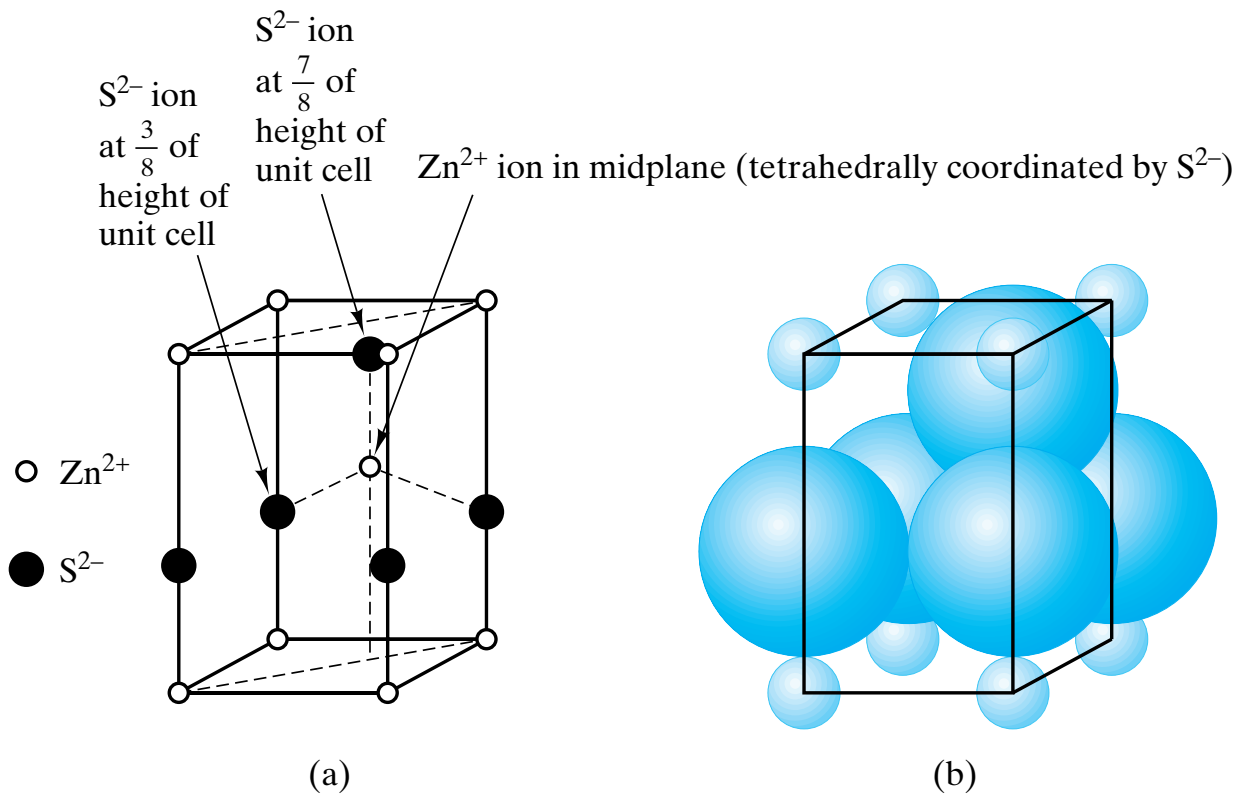
Ions/unit cell: $4\text{Zn}^{2+} + 4\text{S}^{2-}$

Typical semiconductors:

GaAs , AlP , InSb (III-V compounds),

ZnS , ZnSe , CdS , HgTe (II-VI compounds)

Figure 3-24 Zinc blende (ZnS) unit cell showing (a) ion positions. There are two ions per lattice point (note the outlined example). Compare this with the diamond cubic structure (Figure 3-23a). (b) The actual packing of full-size ions associated with the unit cell. (Part (b) courtesy of Molecular Simulations, Inc.)



Structure: wurtzite (ZnS)-type
 Bravais lattice: hexagonal
 Ions/unit cell: $2Zn^{2+} + 2S^{2-}$
 Typical semiconductors: ZnS, CdS, and ZnO.

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

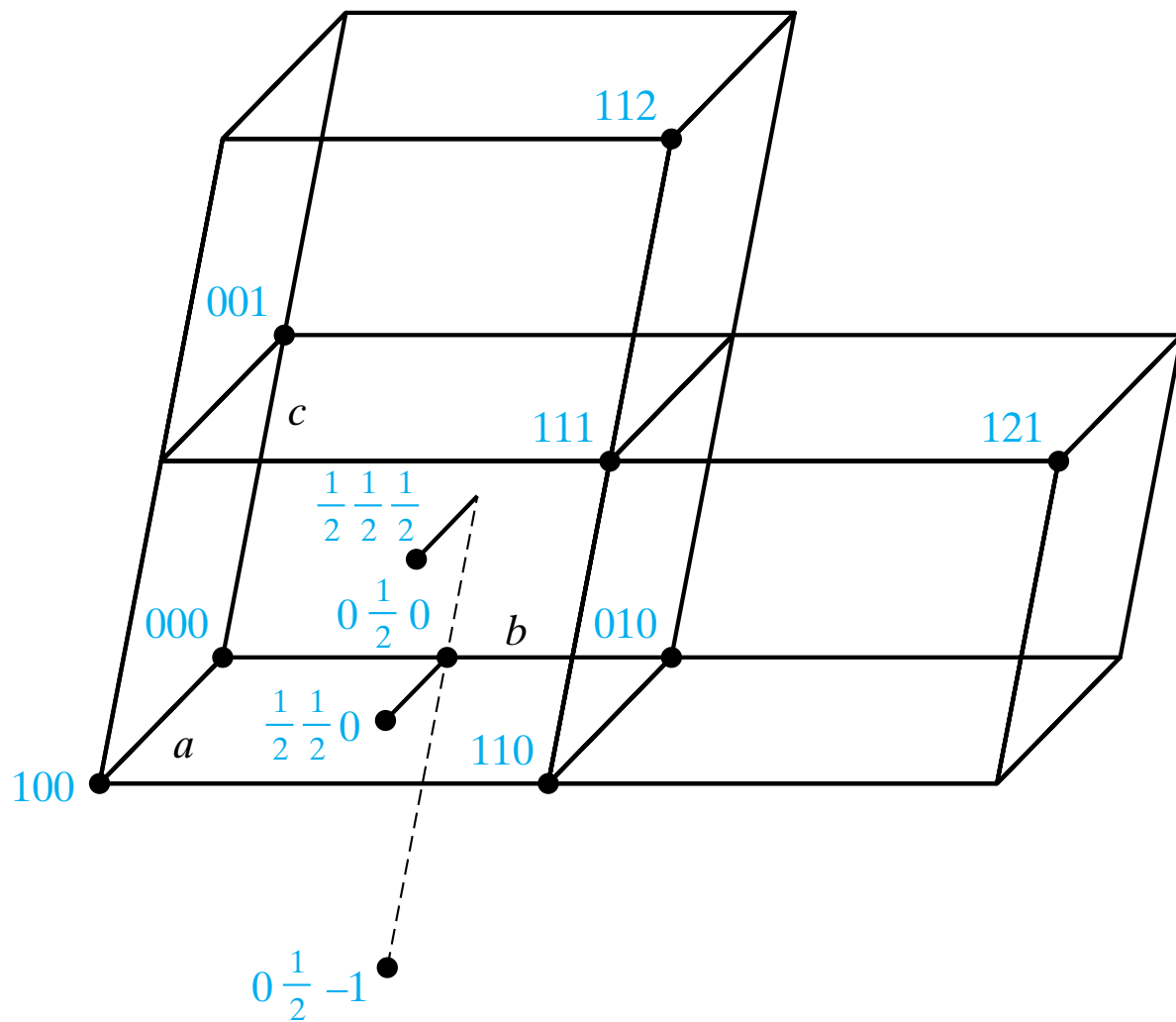


Figure 3-26 *Notation for lattice positions.*

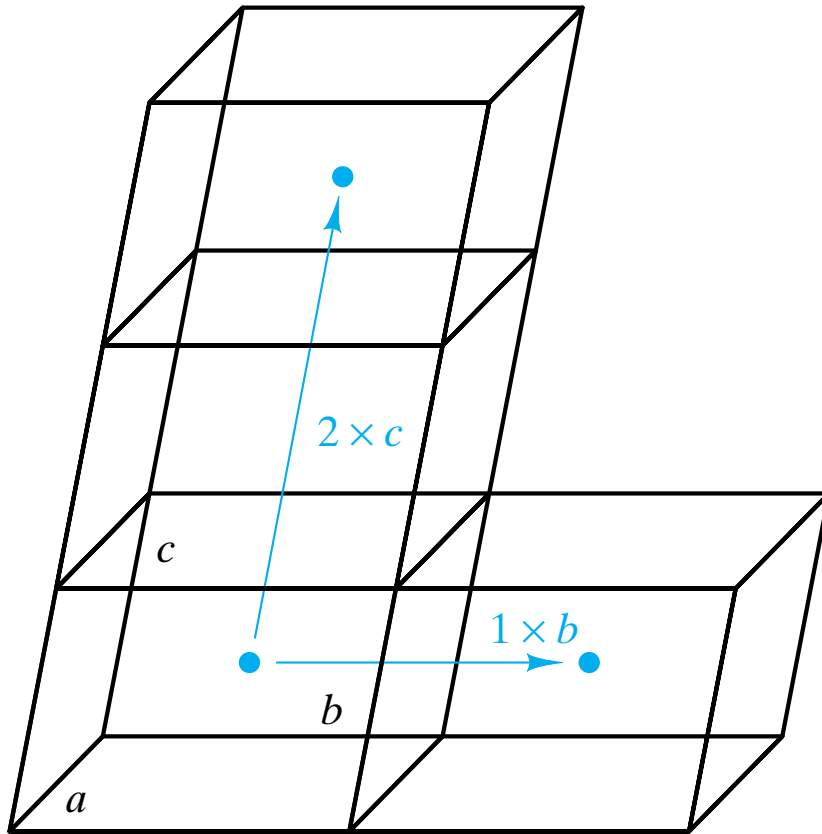


Figure 3-27 Lattice translations connect structurally equivalent positions (e.g., the body center) in various unit cells.

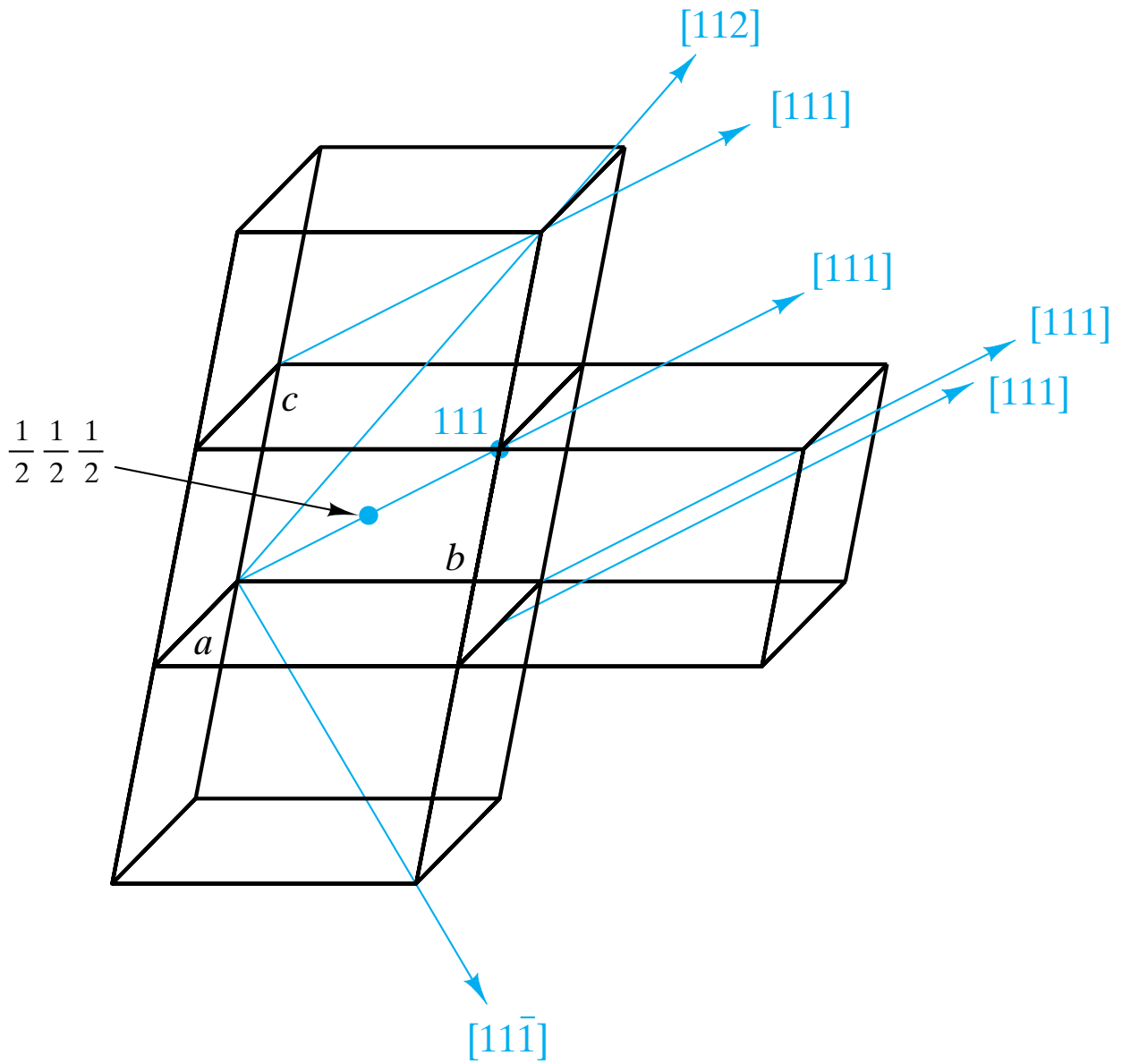


Figure 3-28 Notation for lattice directions. Note that parallel $[uvw]$ directions (e.g., $[111]$) share the same notation because only the origin is shifted.

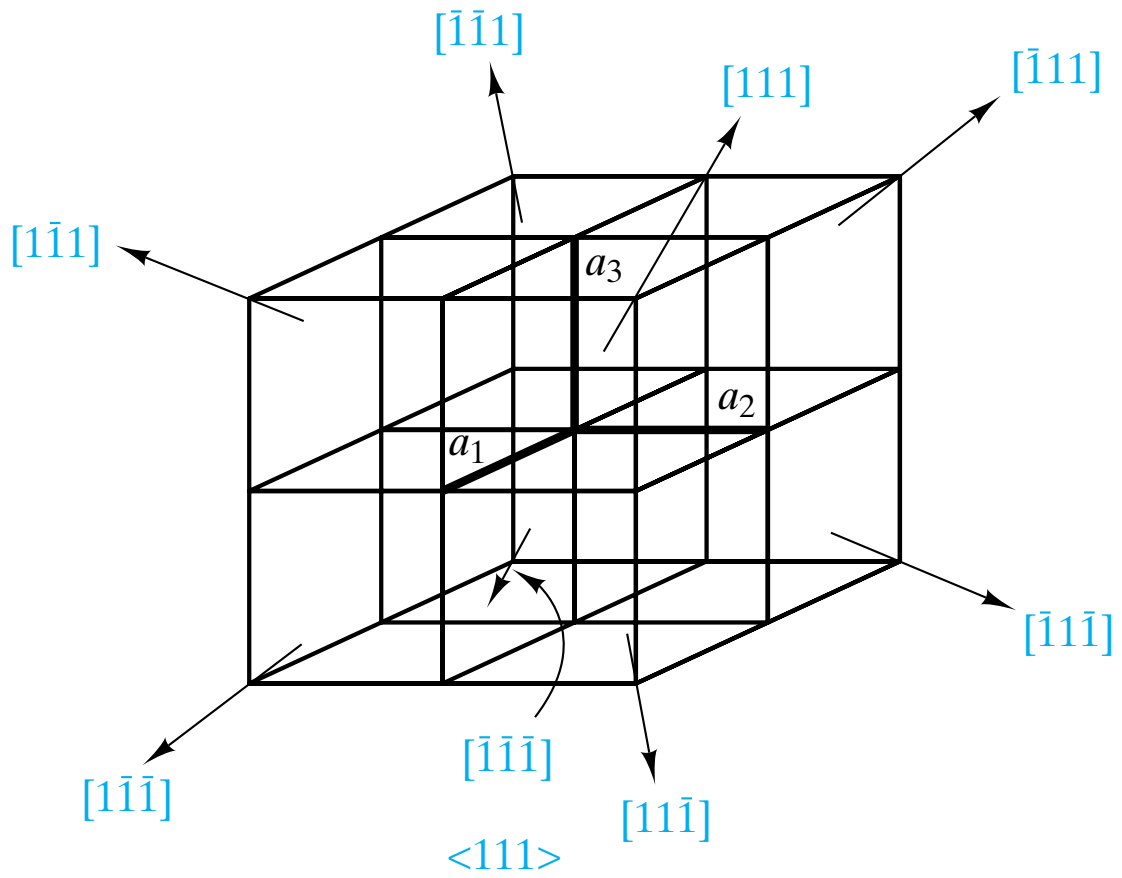


Figure 3-29 Family of directions, $\langle 111 \rangle$, representing all body diagonals for adjacent unit cells in the cubic system.

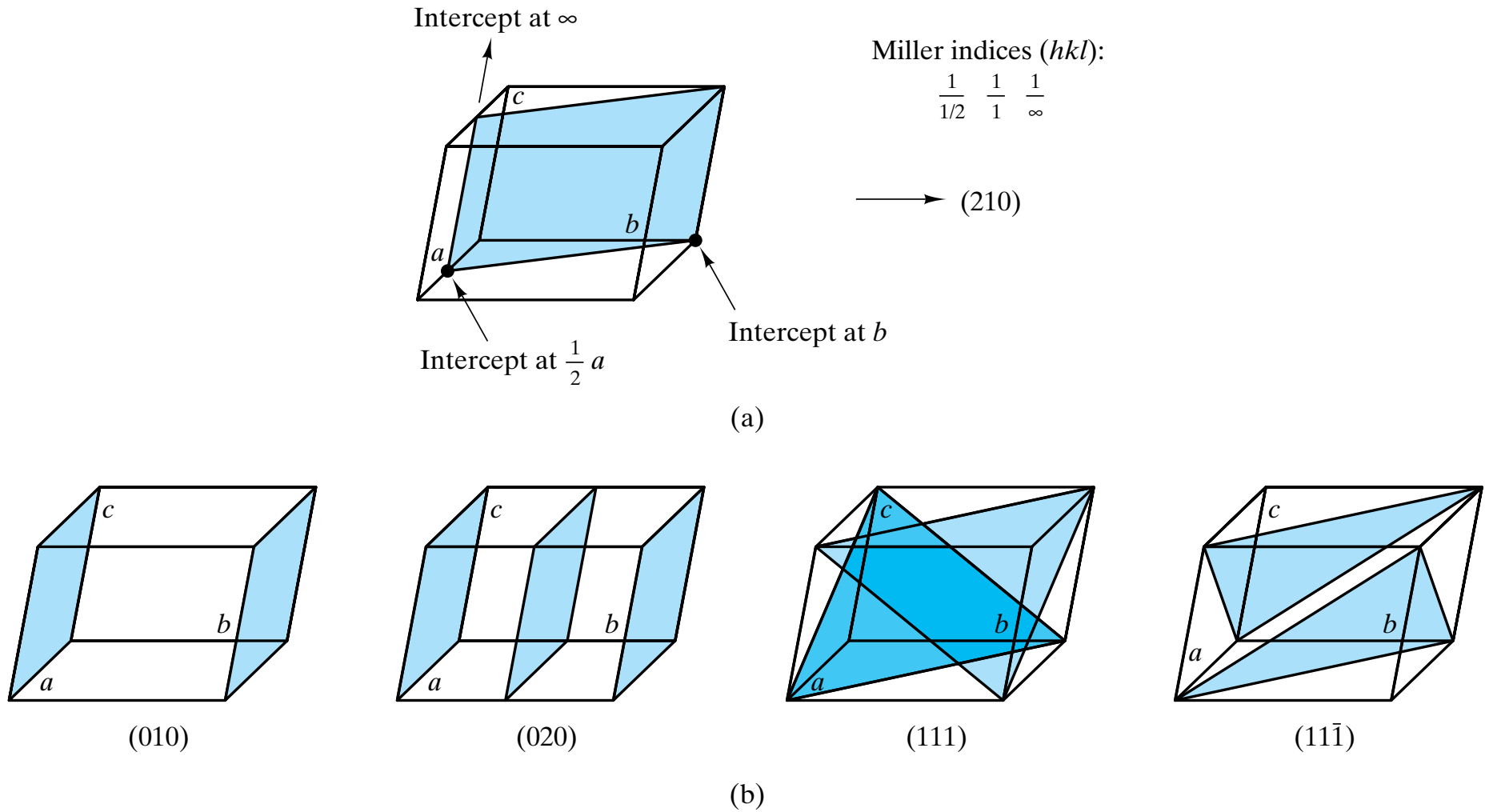
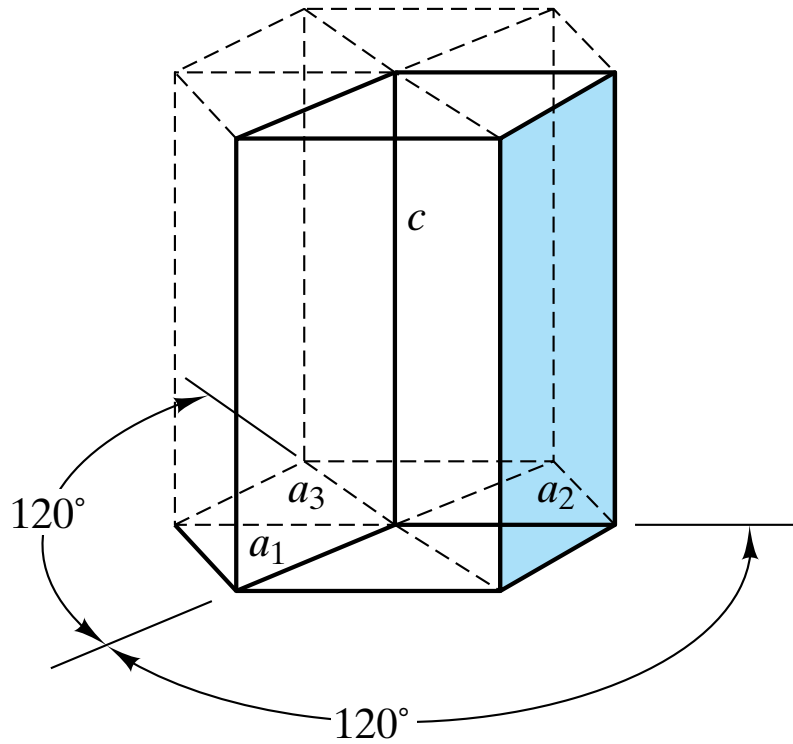


Figure 3-30 Notation for lattice planes. (a) The (210) plane illustrates Miller indices (hkl) . (b) Additional examples.



Miller-Bravais indices ($hkil$): $\frac{1}{\infty}, \frac{1}{1}, \frac{1}{-1}, \frac{1}{\infty} \rightarrow (01\bar{1}0)$
 Note: $h + k = -i$

Figure 3-31 Miller-Bravais indices, ($hkil$), for the hexagonal system.

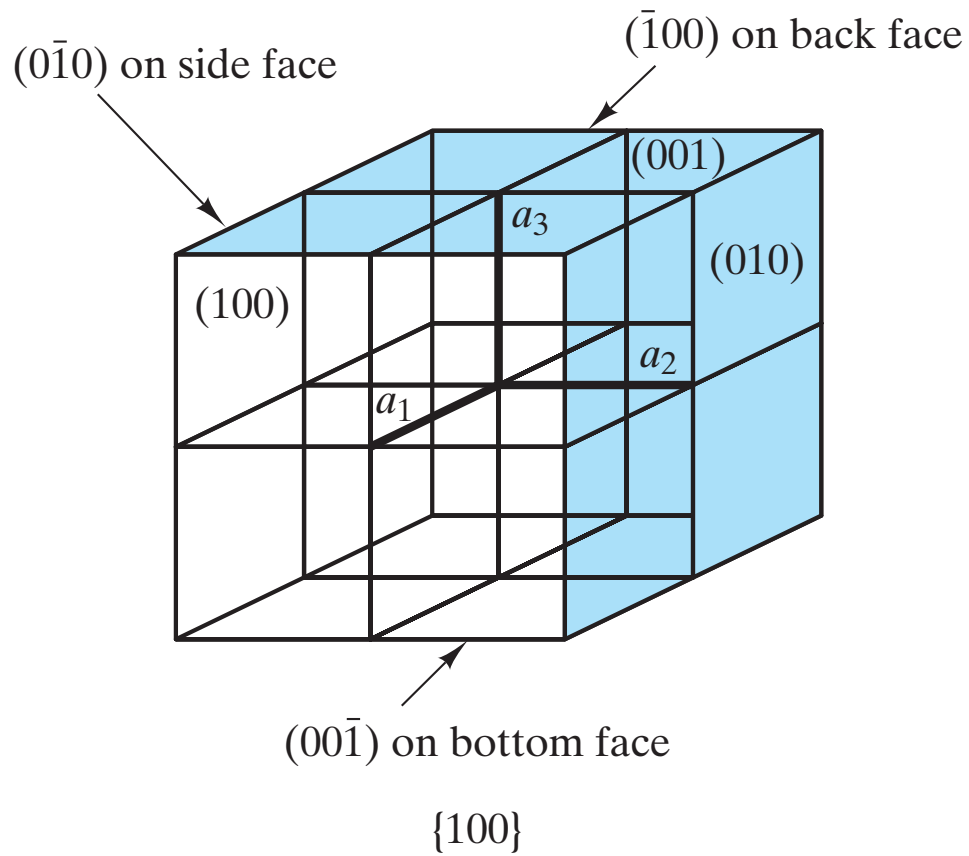
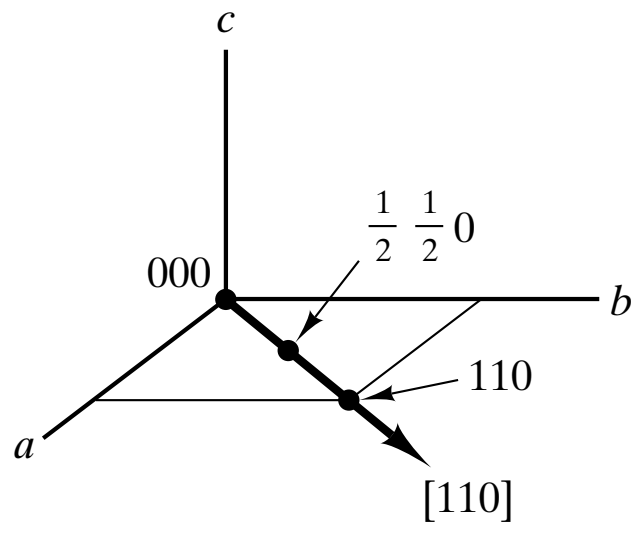
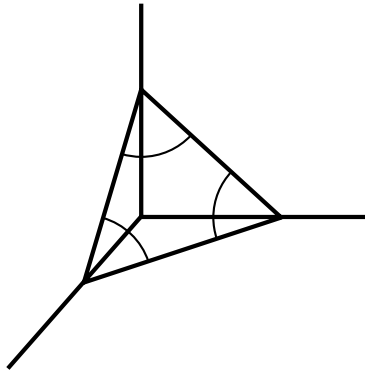
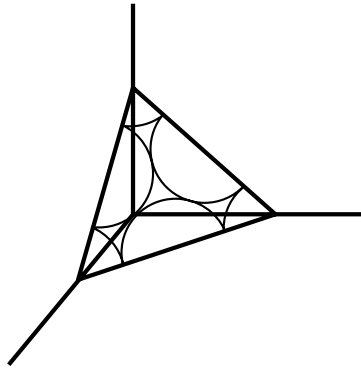
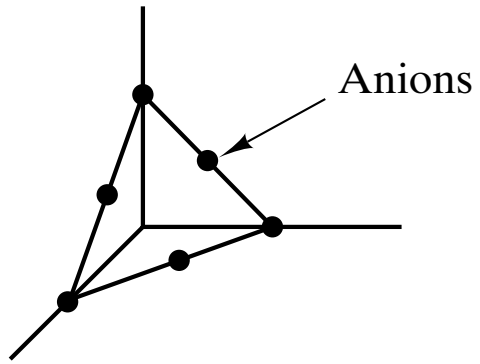


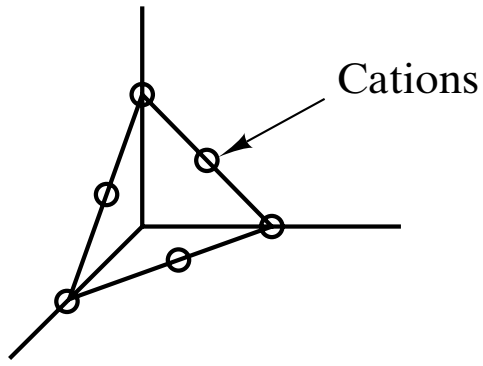
Figure 3-32 Family of planes, $\{100\}$, representing all faces of unit cells in the cubic system.











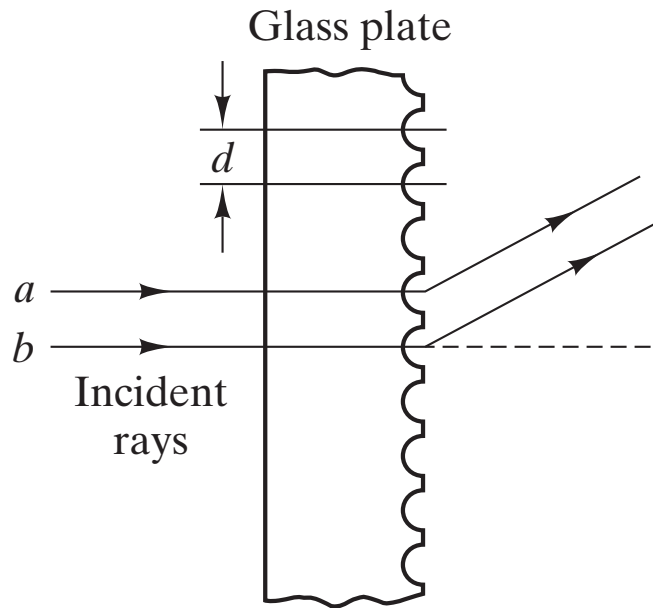


Figure 3-33 *Diffraction grating for visible light. Scratch lines in the glass plate serve as light-scattering centers. (After D. Halliday and R. Resnick, Physics, John Wiley & Sons, Inc., New York, 1962.)*

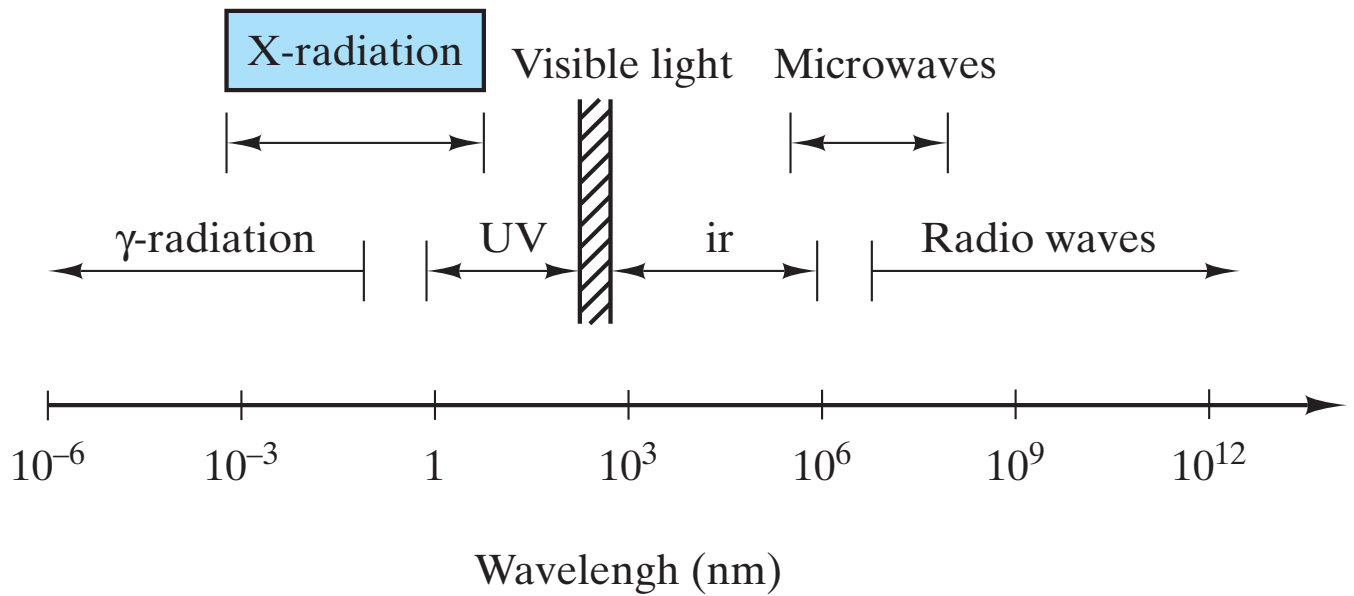
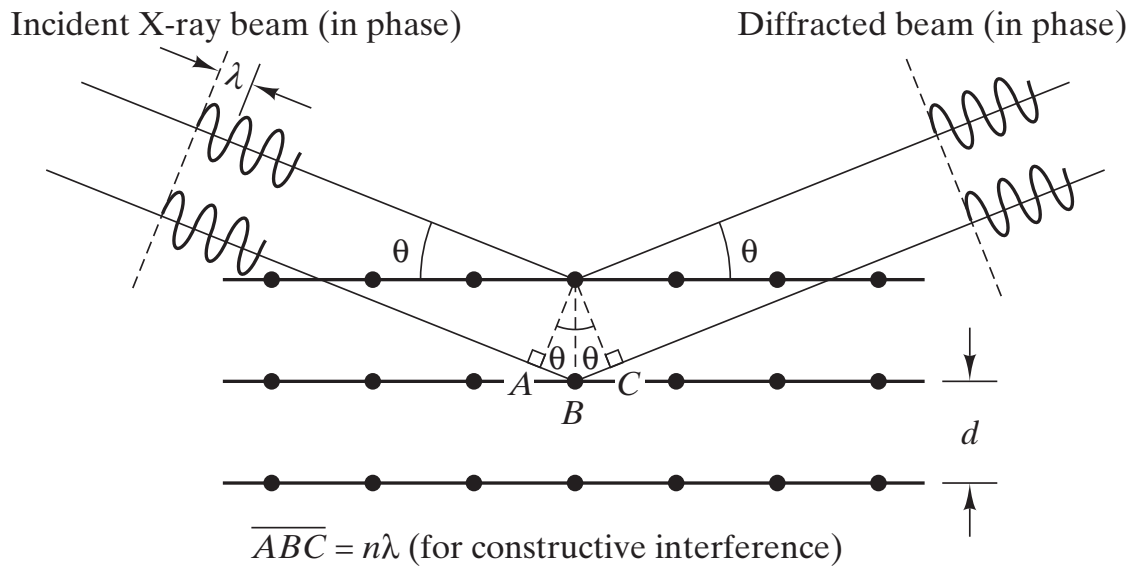


Figure 3-34 *Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.*



$$\overline{AB} = \overline{BC} = d \sin \theta$$

Therefore

$$n\lambda = 2d \sin \theta$$

Figure 3-35 Geometry for diffraction of x-radiation. The crystal structure is a three-dimensional diffraction grating. Bragg's law ($n\lambda = 2d \sin \theta$) describes the diffraction condition.

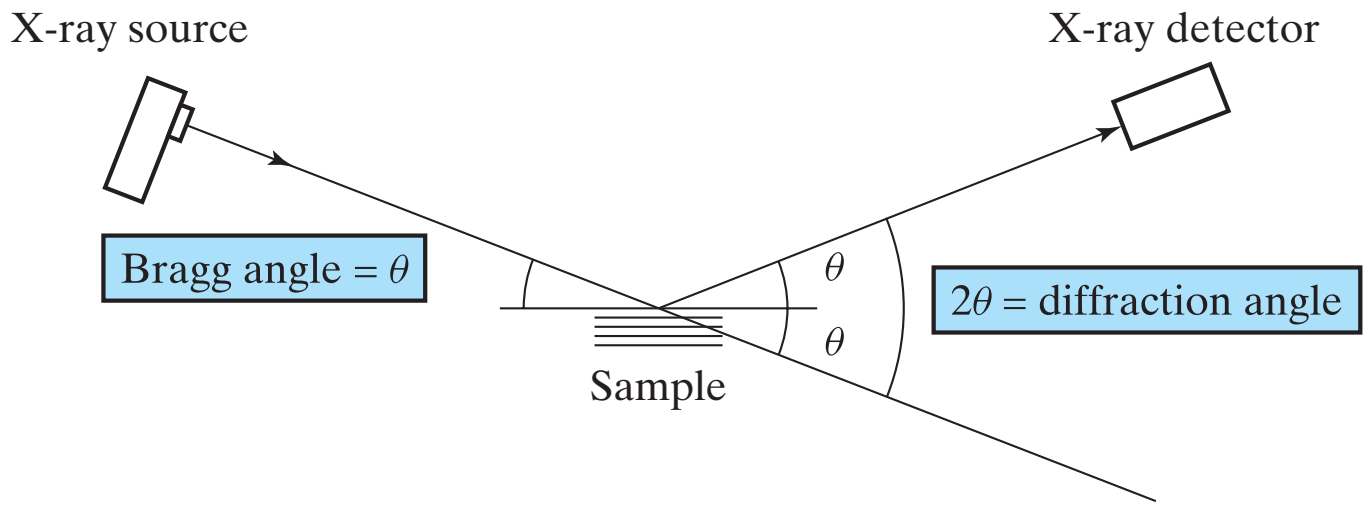


Figure 3-36 Relationship of the Bragg angle (θ) and the experimentally measured diffraction angle (2θ).

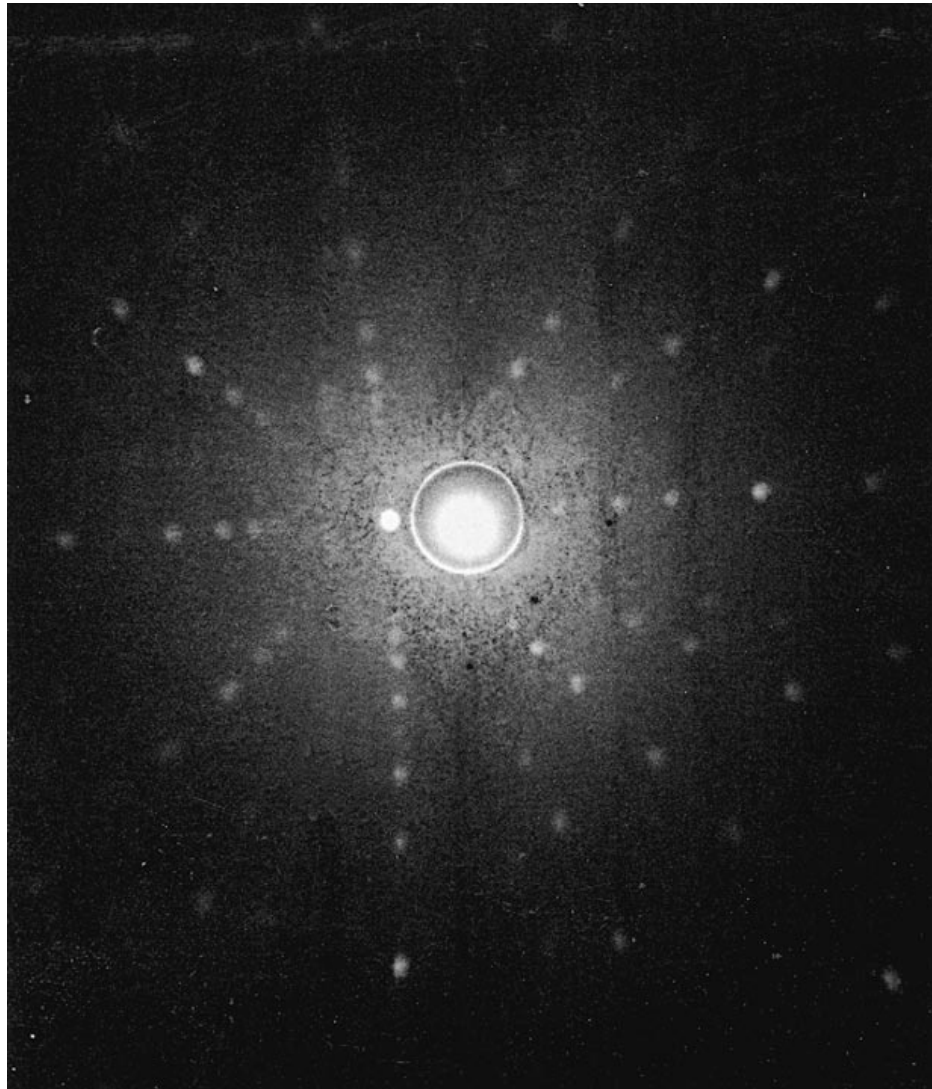
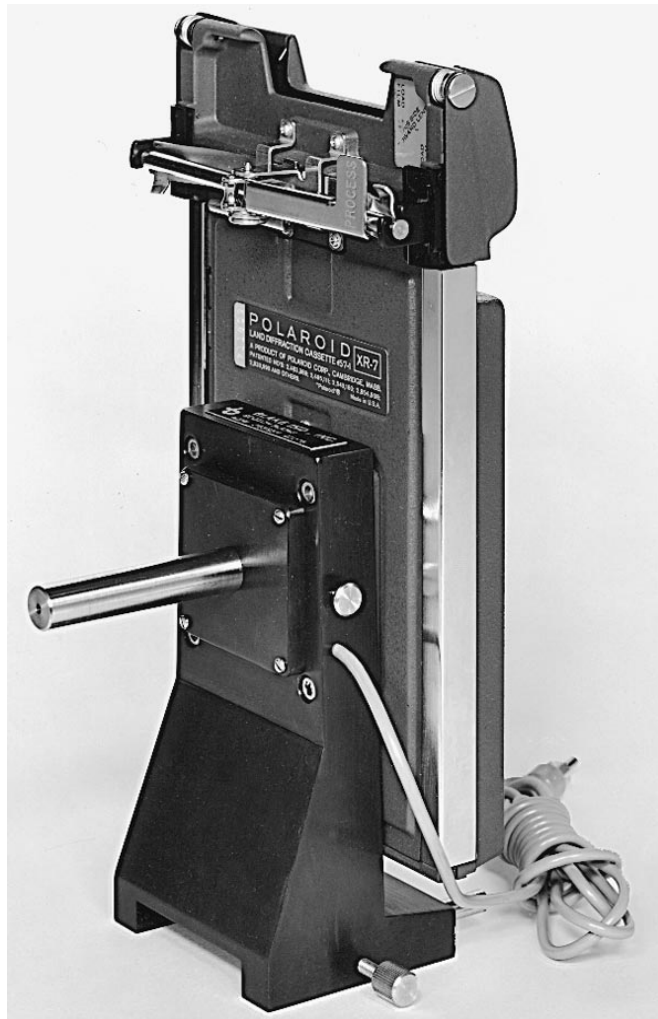
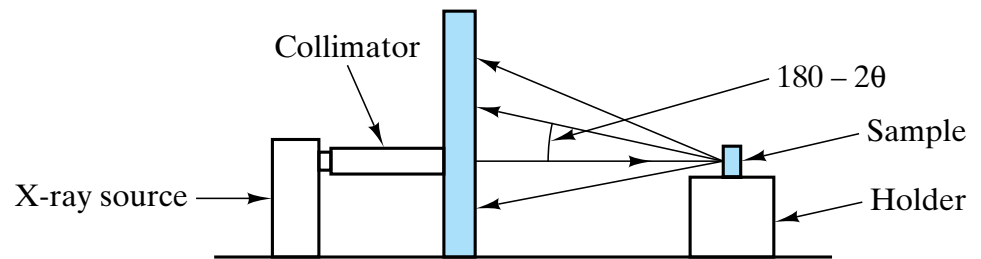


Figure 3-37 *Diffraction pattern of a single crystal of MgO (with the NaCl structure of Figure 3-9). Each spot on the film represents diffraction of the x-ray beam from a crystal plane (hkl).*



(a)



(b)

Figure 3-38 (a) Single-crystal diffraction camera (or Laue camera). (Courtesy of Blake Industries, Inc.)
(b) Schematic of the experiment.

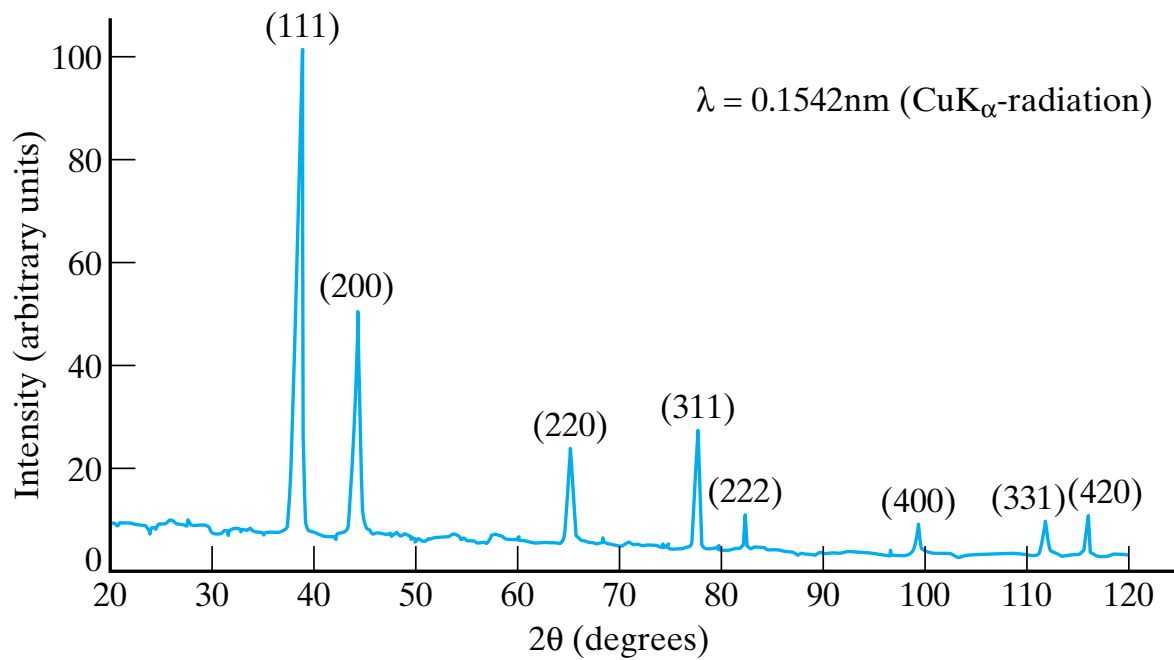
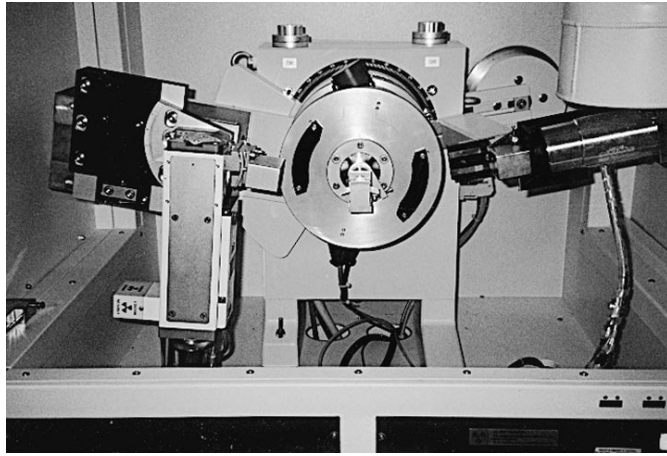
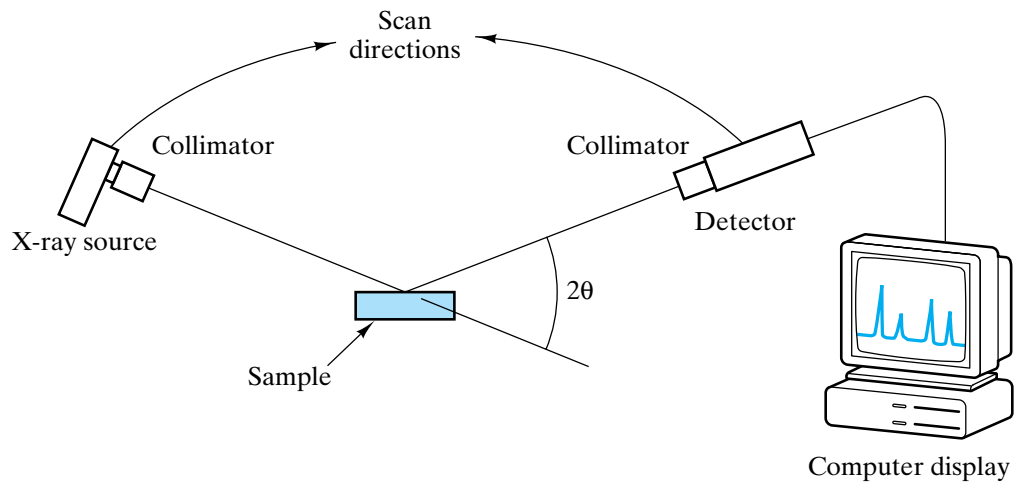


Figure 3-39 *Diffraction pattern of aluminum powder. Each peak (in the plot of x-ray intensity versus diffraction angle, 2θ) represents diffraction of the x-ray beam by a set of parallel crystal planes (hkl) in various powder particles.*



(a)



(b)

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

