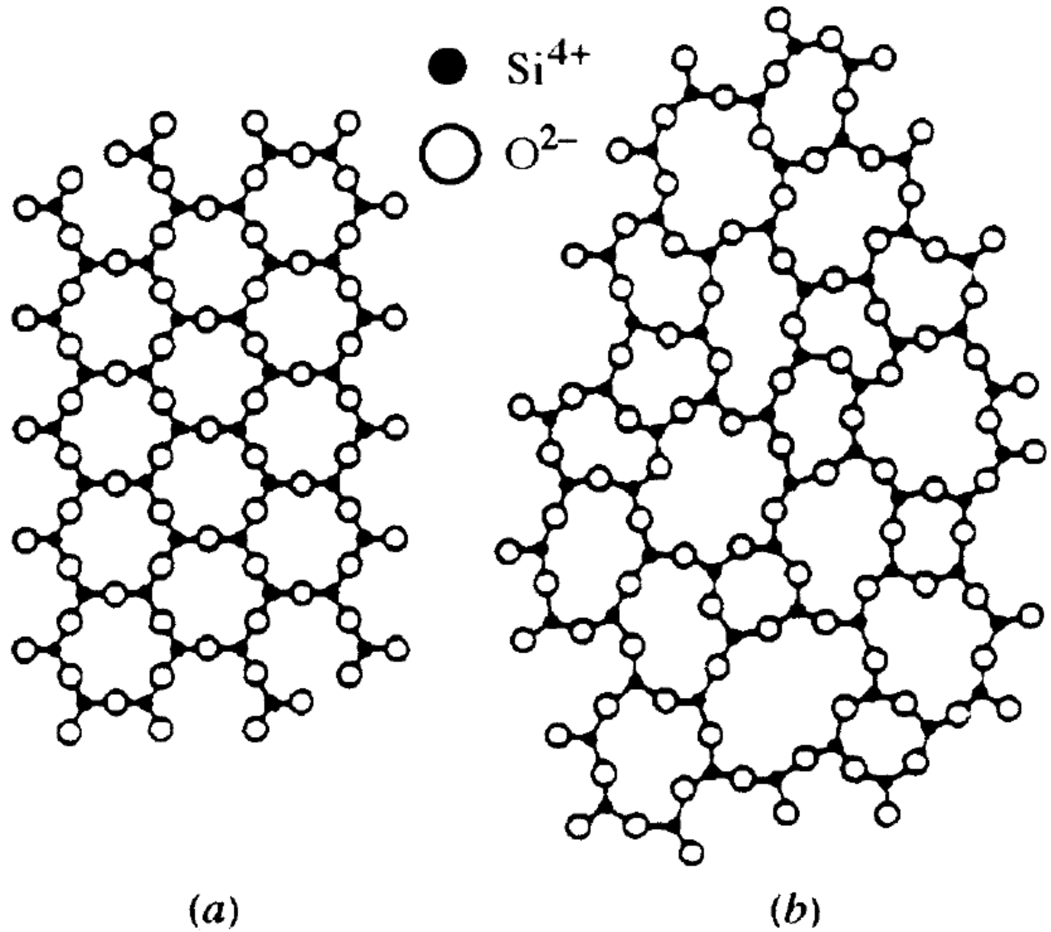


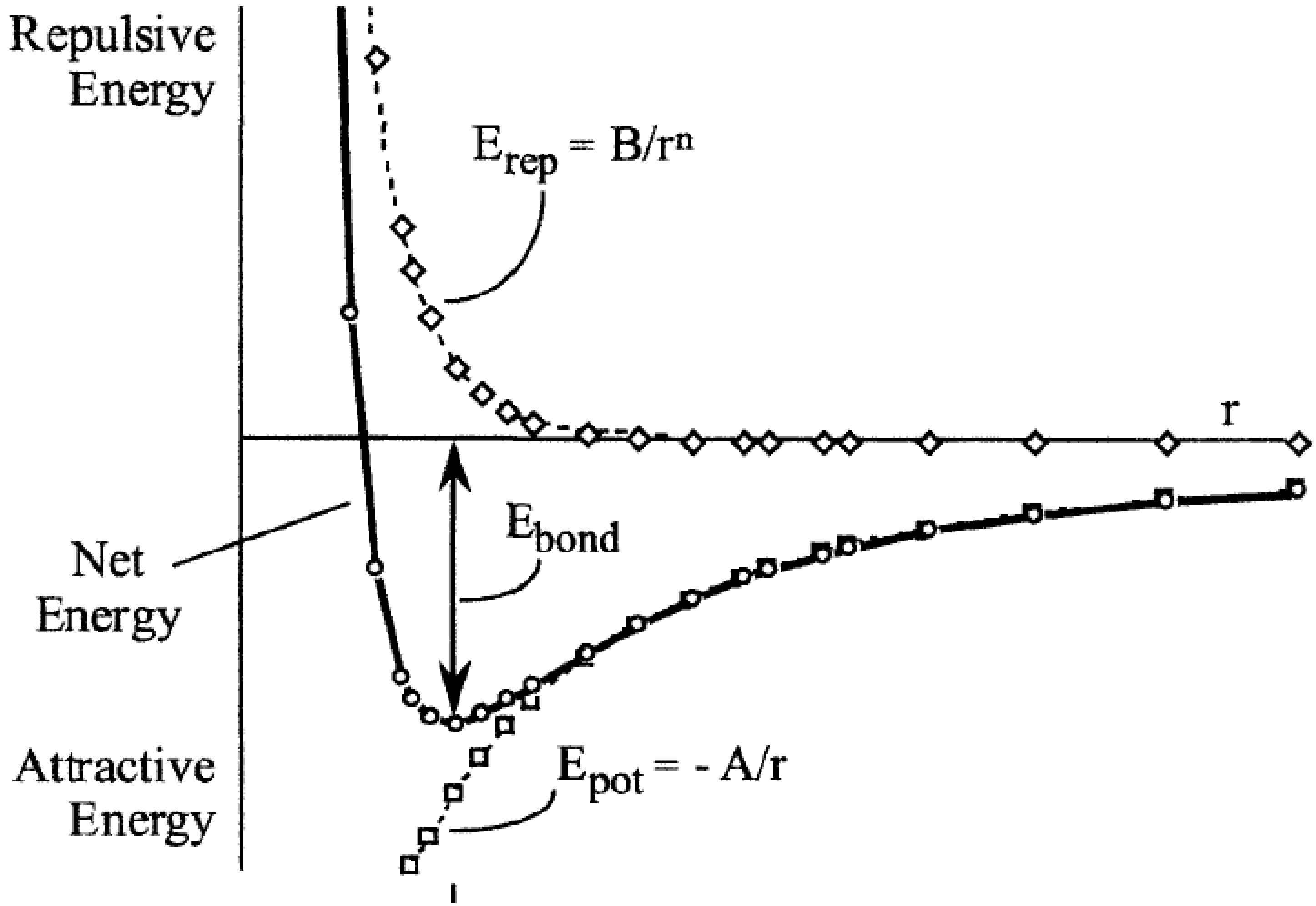
(*a*) Long-range order; (*b*) short-range order.

Table 1.1. Properties and applications of advanced ceramics.

Property	Applications (examples)
Thermal	
Insulation	High-temperature furnace linings for insulation (oxide fibers such as SiO_2, Al_2O_3, and ZrO_2)
Refractoriness	High-temperature furnace linings for insulation and containment of molten metals and slags
Thermal conductivity	Heat sinks for electronic packages (AlN)
Electrical and dielectric	
Conductivity	Heating elements for furnaces (SiC, ZrO_2, $MoSi_2$)
Ferroelectricity	Capacitors (Ba-titanate-based materials)
Low-voltage insulators	Ceramic insulation (porcelain, steatite, forsterite)
Insulators in electronic applications	Substrates for electronic packaging and electrical insulators in general (Al_2O_3, AlN)
Insulators in hostile environments	Spark plugs (Al_2O_3)
Ion-conducting	Sensor and fuel cells (ZrO_2, Al_2O_3, etc.)
Semiconducting	Thermistors and heating elements (oxides of Fe, Co, Mn)
Nonlinear *I-V* characteristics	Current surge protectors (Bi-doped ZnO, SiC)
Gas-sensitive conduct	Gas sensors (SnO_2, ZnO)
Magnetic and superconductive	
Hard magnets	Ferrite magnets [(Ba, Sr)O·6Fe_2O_3]
Soft magnets	Transformer cores [(Zn, M)Fe_2O_3, with M = Mn, Co, Mg]; magnetic tapes (rare-earth garnets)
Superconductivity	Wires and SQUID magnetometers ($YBa_2Cu_3O_7$)

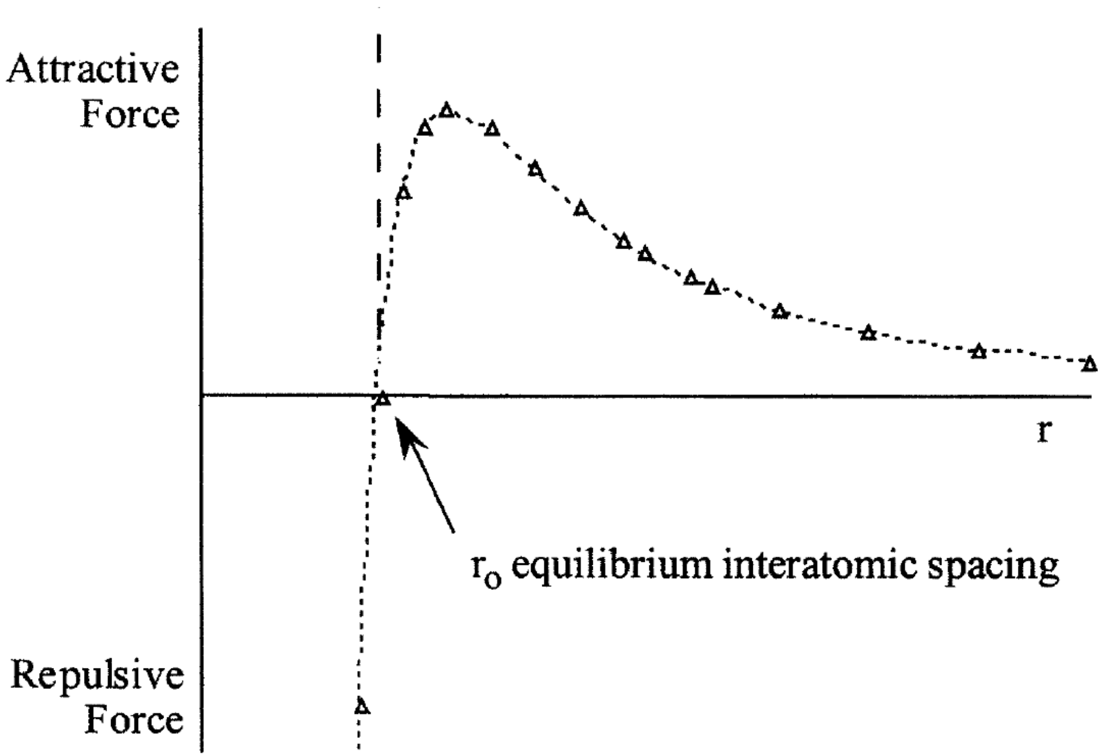
Optical	
Transparency	Windows (soda-lime glasses), cables for optical communication (ultra-pure silica)
Translucency and chemical inertness	Heat- and corrosion-resistant materials, usually for Na lamps Al_2O_3MgO)
Nonlinearity	Switching devices for optical computing ($LiNbO_3$)
IR transparency	Infrared laser windows (CaF_2, SrF_2, NaCl)
Nuclear applications	
Fission	Nuclear fuel (UO_2, UC), fuel cladding (C, SiC), neutron moderators (C, BeO)
Fusion	Tritium breeder materials (zirconates and silicates of Li, Li_2O); fusion reactor lining (C, SiC, Si_3N_4)
Chemical	
Catalysis	Filters (zeolites); purification of exhaust gases
Anticorrosion	Heat exchangers (SiC), chemical equipment in corrosive environments
Biocompatibility	Artificial joint prostheses (Al_2O_3)
Mechanical	
Hardness	Cutting tools (SiC whisker-reinforced Al_2O_3, Si_3N_4)
High-temperature strength retention	Stators and turbine blades, ceramic engines (Si_3N_4)
Wear resistance	Bearings (Si_3N_4)

(a)



Repulsive Energy
$E_{rep} = B/r^n$
r
Net Energy
E_{bond}
Attractive Energy
$E_{pot} = - A/r$

$$\left.\frac{dE_{\text{net}}}{dr}\right|_{r=r_0} = 0 = -\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$



$$\boxed{E_{\text{bond}} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)}$$

$$F_{\text{net}} = \frac{dE_{\text{net}}}{dr} = -\frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r^2} - \frac{nB}{r^{n+1}}$$

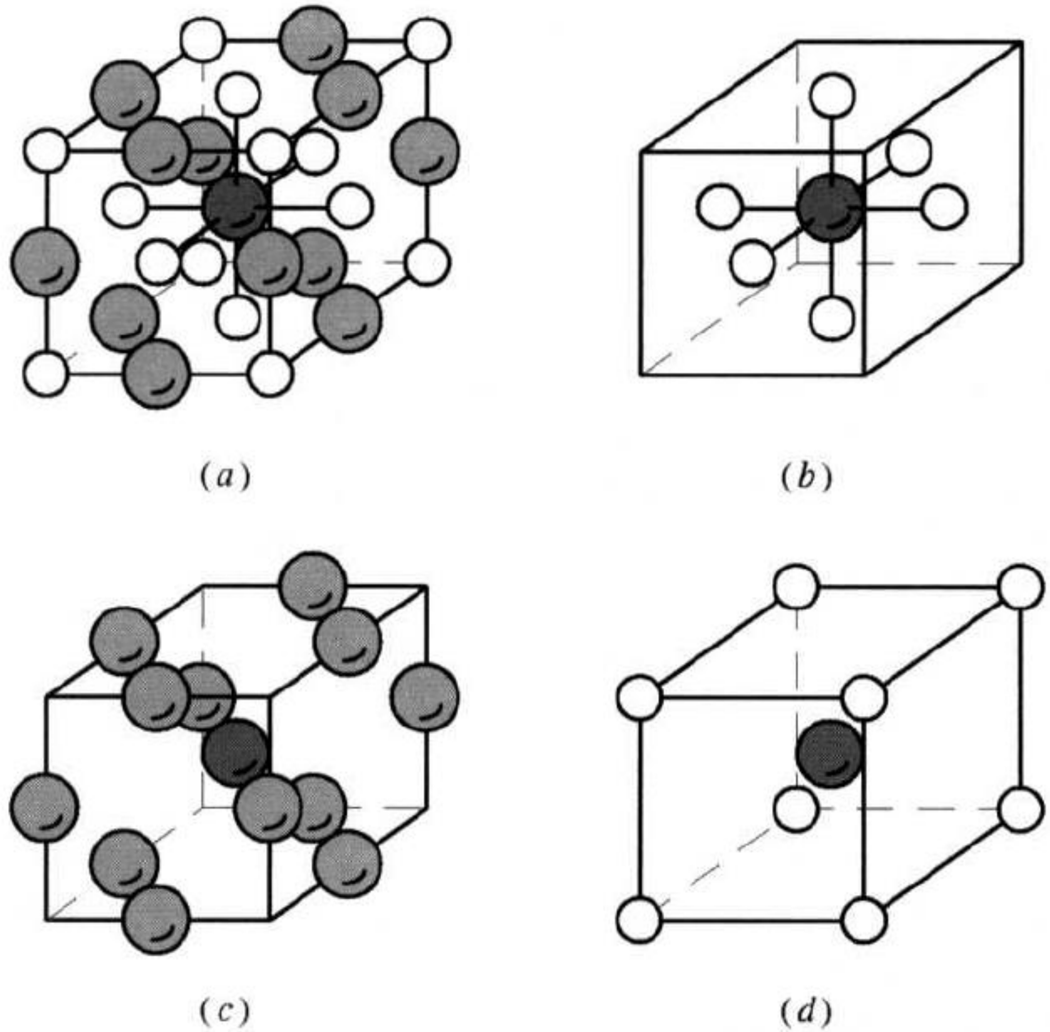


Figure 2.5 (*a*) Schematic of the NaCl structure. (*b*) The first 6 nearest neighbors are attracted to the central cation, (*c*) the second 12 nearest neighbors at a distance $\sqrt{2}r_0$ are repelled, (*d*) the third 8 nearest neighbors are attracted, etc.

$$E_{\text{sum}} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)\left(\frac{6}{1} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \cdots\right)$$

$$= \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)\alpha \tag{2.17}$$

The second term in parentheses is an alternating series that converges to some value α, known as the **Madelung constant.** Evaluation of this constant,

Structure	Coordination number	α †	α_{conv} ‡
NaCl	6 : 6	1.7475	1.7475
CsCl	8 : 8	1.7626	1.7626
Zinc blende	4 : 4	1.6381	1.6381
Wurtzite	4 : 4	1.6410	1.6410
Fluorite	8 : 4	2.5190	5.0387
Rutile	6 : 3	2.4080§	4.1860§
Corundum	6 : 4	4.1719§	25.0312§

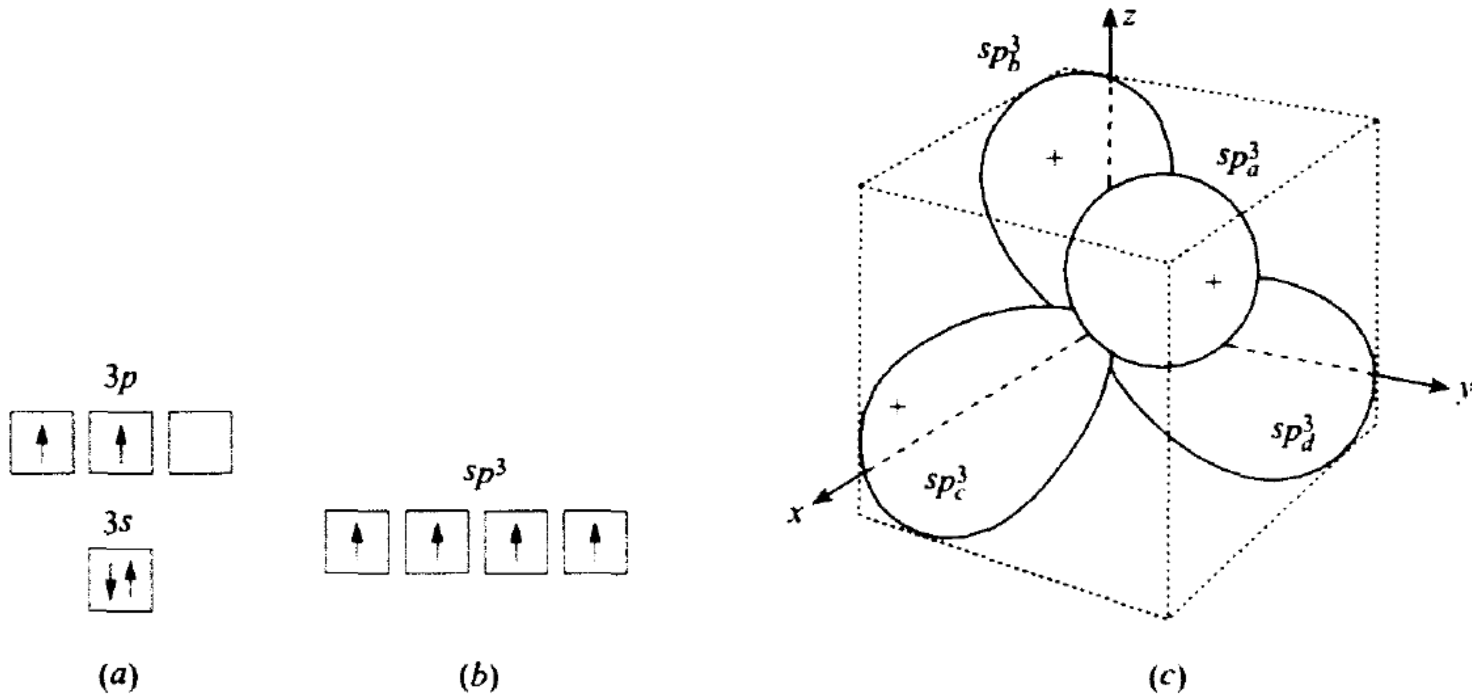
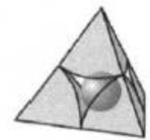
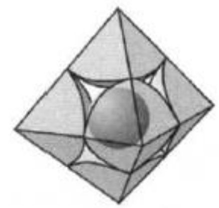
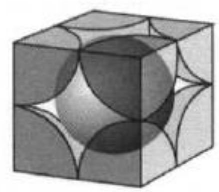
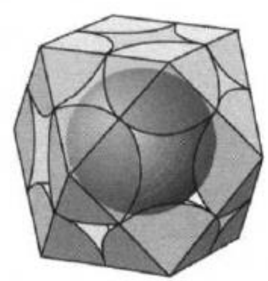


Figure 2.9 (*a*) Ground state of Si atom. (*b*) Electronic configuration after hybridization. (*c*) Directionality of sp^3 bonds. Note that each bond lobe contains one electron, and thus

Coordination number	Arrangement of ions around central ion	Range of cation/anion ratios	Structure
3	corners of a triangle	≥ 0.155	
4	corners of a tetrahedron	≥ 0.225	
6	corners of a octahedron	≥ 0.414	
8	corners of a cube	≥ 0.732	
12	corners of a cuboctahedron	≈ 1.000	

WORKED EXAMPLE 3.1

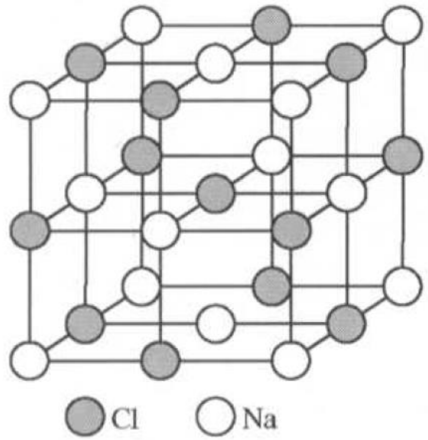
Derive the critical radius ratio for the tetrahedral arrangement (second from top in Fig. 3.3).

Answer

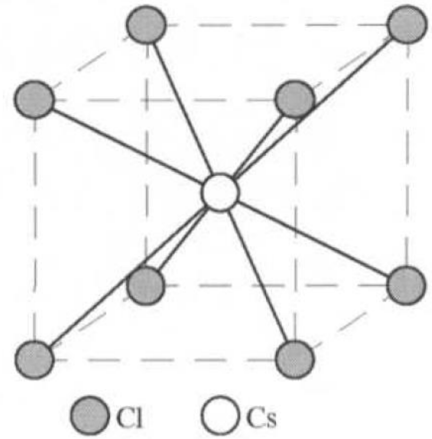
The easiest way to derive this ratio is to appreciate that when the radius ratio is critical, the cations just touch the anions, while the latter in turn are just touching one another (i.e., the anions are closely packed). Since the coordinates of the tetrahedral position in a close-packed arrangement (Fig. 3.4*b*) are 1/4, 1/4, 1/4, it follows that the distance between anion and cation centers is

$$r_{\text{cation}} + r_{\text{anion}} = \sqrt{\left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2} = \sqrt{3}\,\frac{a}{4}$$

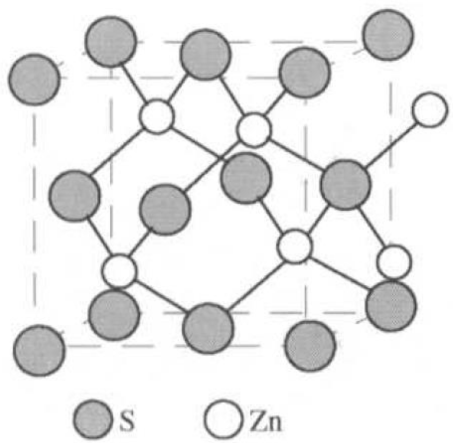
where a is the lattice parameter. Referring to Fig. 3.4*b*, the critical condition implies that the anions are just touching along the face diagonal, thus $4r_{\text{anion}} = \sqrt{2}a$. Combining these two equations yields $r_{\text{cation}}/r_{\text{anion}} = 0.225$.



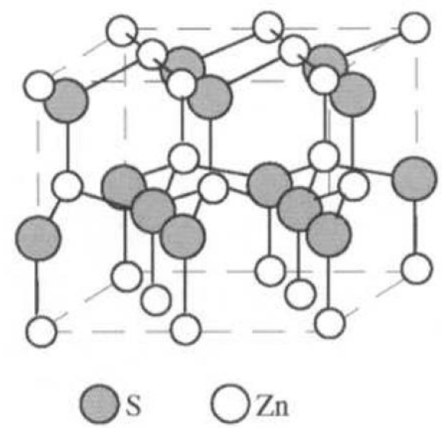
(a)



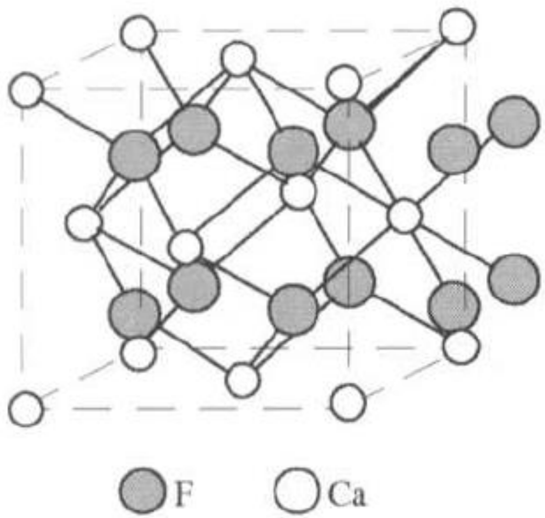
(b)



(c)



(d)



(*e*)

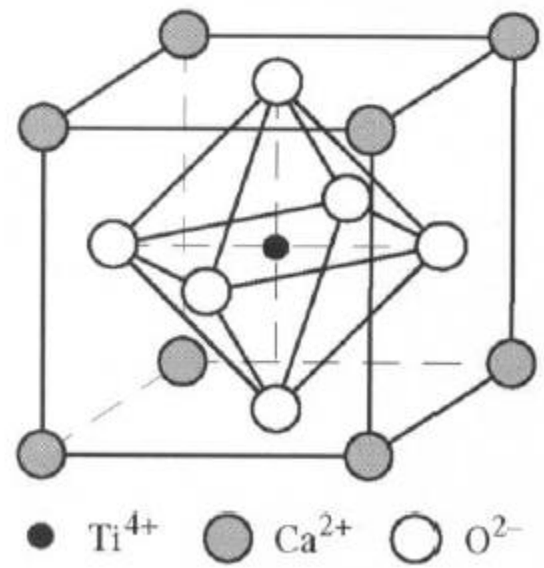


Figure 3.9. The perovskite structure centered on the Ti ion. See Fig. 3.8*b* for representation centered on a Ca ion.

3.4.2 Spinel Structure

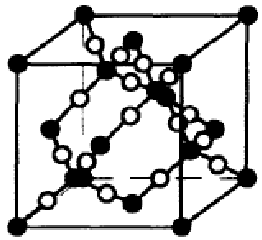
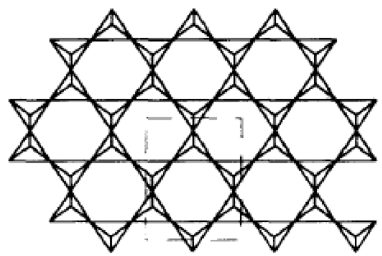
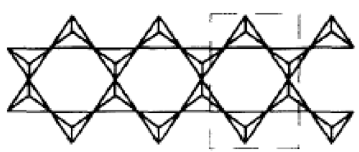
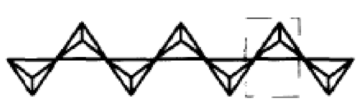
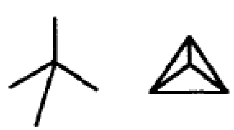
This structure is named after the naturally occurring mineral $MgAl_2O_4$, and its general formula is AB_2O_4, where the A and B cations are in the +2 and +3

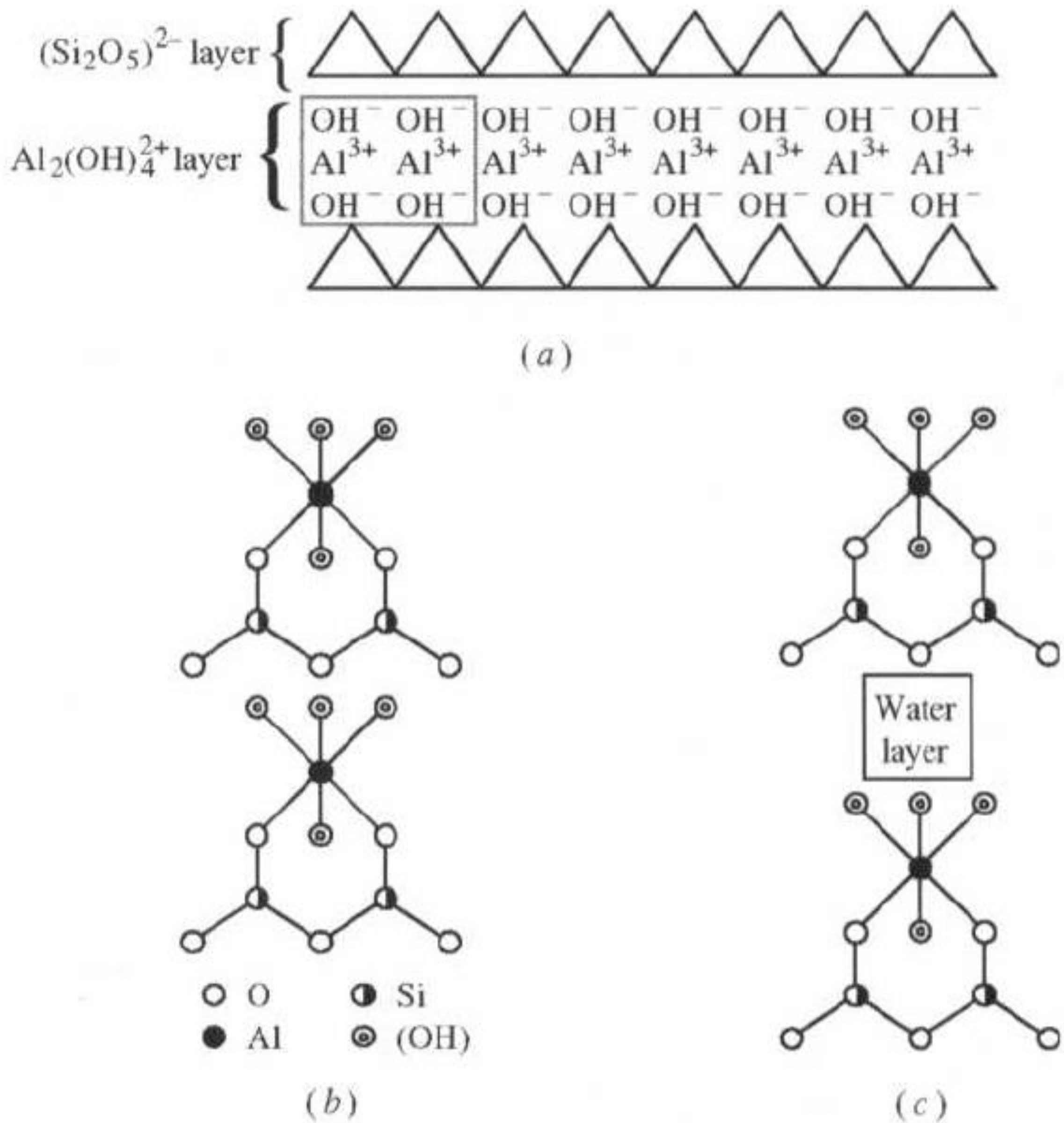
oxidation states, respectively. The structure is shown in Fig. 3.10*a*, where emphasis is on the FCC stacking[31] of the oxygen ions; the cations, on the other hand, occupy one-eighth of the tetrahedral sites and one-half of the octahedral sites (see Table 3.3). The same structure, when viewed from a unit cell perspective, is shown in Fig. 3.10*b*.

When the A^{2+} ions exclusively occupy the tetrahedral sites and the B^{3+} ions occupy the octahedral sites, the spinel is called a **normal spinel**. Usually the larger cations tend to populate the larger octahedral sites, and vice versa. In the **inverse spinel**, the A^{2+} ions and one-half the B^{3+} ions occupy the octahedral sites, while the other half of the B^{3+} ions occupy the tetrahedral sites.

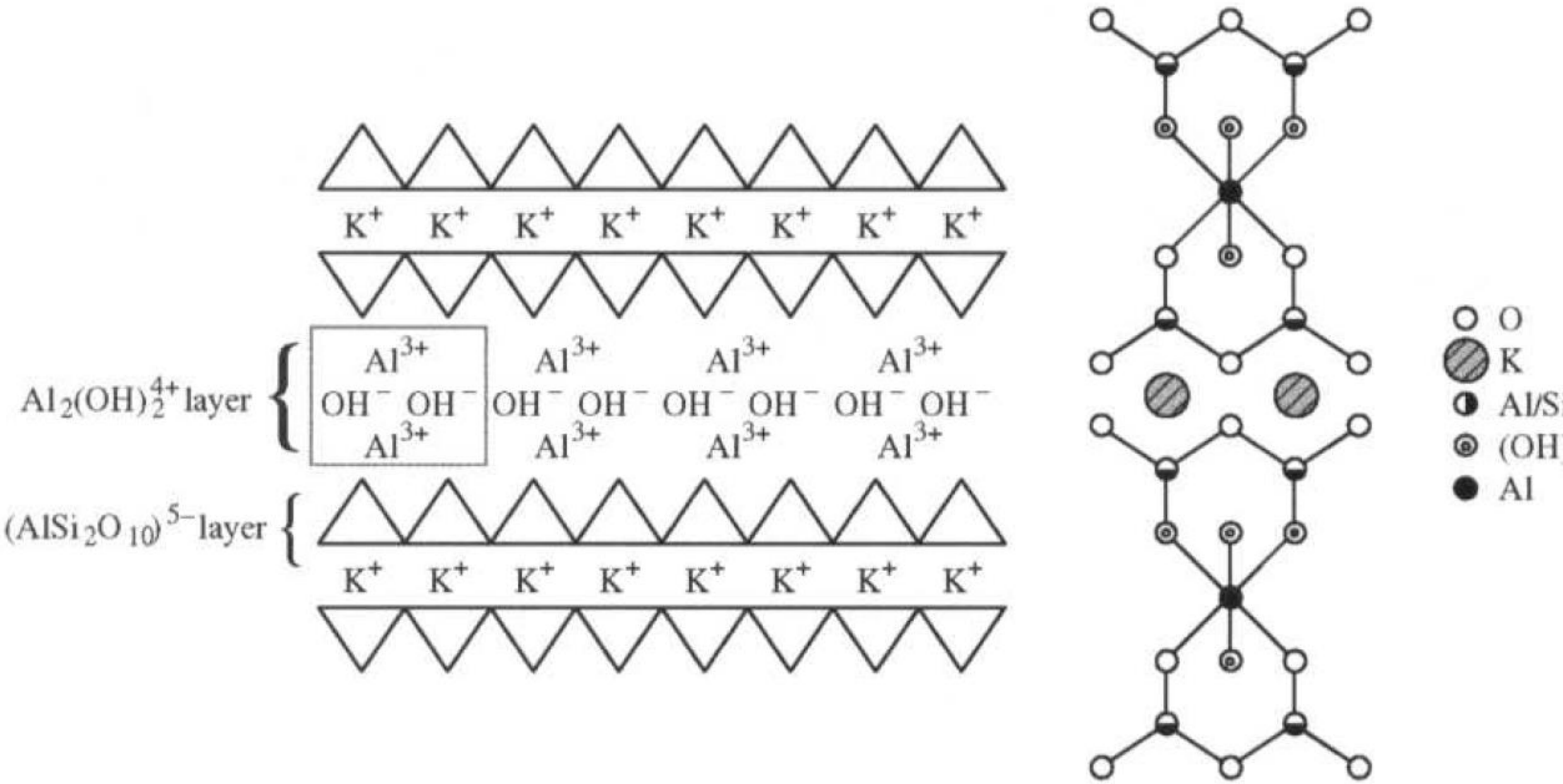
As discussed in greater detail in Chap. 6, the oxidation states of the cations in spinel need not be restricted to +2 and +3, but may be any combination as long as the crystal remains neutral. This important class of ceramics is revisited in Chap. 15, when magnetic ceramics are dealt with.

Table 3.4. Relationship between silicate structure and the O/Si ratio

Structure	O/Si ratio	No. of oxygens per Si: Bridg.	No. of oxygens per Si: Non-bridg.	Structure and examples
	2.00	4.0	0.0	Three-dimensional network quartz, tridymite, cristabolite are all polymorphs of silica
 Repeat unit $(Si_4O_{10})^{4-}$	2.50	3.0	1.0	Infinite sheets $Na_2Si_2O_5$ Clays (kaolinite)
 Repeat unit $(Si_4O_{11})^{6-}$	2.75	2.5	1.5	Double chains, e.g., asbestos
 Repeat unit $(SiO_3)^{2-}$	3.00	2.0	2.0	Chains $(SiO_3)_n^{2n-}$, Na_2SiO_3, $MgSiO_3$
 Repeat unit $(SiO_4)^{4-}$	4.00	0.0	4.0	Isolated SiO_4^{4-}, tetrahedra Mg_2SiO_4 olivine, Li_4SiO_4



$(Si_2O_5)^{2-}$ layer
$Al_2(OH)_4^{2+}$ layer
OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻
Al^{3+} Al^{3+} Al^{3+} Al^{3+} Al^{3+} Al^{3+} Al^{3+} Al^{3+}
OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻ OH⁻
(a)
O
Si
Al
(OH)
(b)
Water layer
(c)


K⁺ K⁺ K⁺ K⁺ K⁺ K⁺ K⁺ K⁺
$Al_2(OH)_2^{4+}$ layer
Al^{3+} Al^{3+} Al^{3+} Al^{3+}
OH^- OH^- OH^- OH^- OH^- OH^- OH^- OH^-
Al^{3+} Al^{3+} Al^{3+} Al^{3+}
$(AlSi_2O_{10})^{5-}$ layer
K⁺ K⁺ K⁺ K⁺ K⁺ K⁺ K⁺ K⁺
O
K
Al/Si
(OH)
Al

(*d*) (*e*)