5

Models, Crystals, and Chemistry

CHAPTER PREVIEW

Most ceramics are crystalline. The exception is glass, which we usually discuss separately. Not only do the properties of ceramic crystals depend on how the atoms or ions are arranged, but the type and nature of defects also depend on crystal structure. You probably first encountered crystallography when discussing metals. In all, 65 (almost 90%) of the metallic elements are either cubic or hexagonal. In ceramics, many of the most important materials are neither cubic nor hexagonal, so we need to be more familiar with the rest of the subject. It is recommended that you learn by heart the main structures described in Chapters 6 and 7. In this chapter, we provide the means to make this study more systematic.

To understand why ceramics have particular structures and why certain defects form in these structures, it is really important to understand Pauling's rules. These rules require that you can visualize a tetrahedron and an octahedron and see how they fit together. To understand properties such as piezoelectricity or the mechanisms of phase transformations, you must be able to visualize the crystal structure of the material. This requirement is especially true when we want to predict the properties of single crystals. We summarize the features of crystallography that we use throughout the text and give references to more specialized resources for rigorous proof of theorems and more detailed discussion.

An important point to keep in mind is that the term "ceramic" generally refers to materials that have been processed in the laboratory or the factory plant, but these materials often exist in nature. Sometimes the natural minerals are rare, such as moissanite, which is now being manufactured as a gemstone. There are far more materials and structures in nature than are used in technology. Understanding the basic principles and knowing where to learn more about minerals may help you find the next monazite or at least to know why it might be useful. A great source for further reading is the mineralogical literature.

5.1 TERMS AND DEFINITIONS

We begin by defining the vocabulary of the subject. Most of this section should be familiar to you from other courses.

Crystal lattice: A three-dimensional array of points related by translational symmetry. The translation can occur in three independent directions, giving three independent base vectors. We can fully describe such a lattice by three vectors **a**, **b**, **c**, and three angles, α, β, γ. The special property of a crystal lattice is that the lattice points are identical: if we have an atom at or near one point, there must be an identical atom at the same position relative to every other lattice point.

Unit cell: The vectors **a**, **b**, **c** define a cell. There is, in principle, an infinite number of ways to define a unit cell in any crystal lattice. However, as in many areas of crystallography, there is a convention:

1. The unit cell should have the same symmetry as the crystal—the base vectors are parallel to symmetry axes or perpendicular to symmetry planes.
2. The origin of the unit cell is usually a center of symmetry.
3. The base vectors should be as short as possible—the cell volume should be as small as possible. The exceptions arise when choosing a longer vector, and a larger cell makes the symmetry more obvious.
4. The angles between the axes should be as close as possible to 90° or, if not, then >90°.
5. A unit cell having the smallest possible volume is called a primitive cell.

Lattice parameters: The vectors **a**, **b**, **c** and the angles, α, β, γ are called the lattice parameters of the unit cell. Tabulated lattice parameters are, unless otherwise stated, values at room temperature and pressure. They vary with changes in temperature or pressure.

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
DOI 10.1007/978-1-4614-3523-5_5, © Springer Science+Business Media New York 2013

TABLE 5.1 The Seven Crystal Systems

System	*Relationship between lattice parameters*	*Example*
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Turquoise Kyanite Albite feldspar
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monazite Titanite Orthoclase
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Olivine Brookite Stibnite
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Zircon Rutile Hausmannite
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 20^\circ$	High quartz Wurtzite Beryl
Rhombohedral (or trigonal)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Ilmenite Calcite Corundum
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Halite Magnetite Garnet

Crystal system: There are seven unique shapes that can each be used to fill three-dimensional space. These are the seven crystal systems into which all crystals are classified. They are listed in order of increasing symmetry in Table 5.1.

CRYSTAL SYSTEMS
All crystals belong to one of the seven crystal systems

Bravais lattices: There are 14 different ways to arrange lattice points. These are constructed as three separate types.

- Primitive (P) lattices—one lattice point per unit cell
- Body-centered (I) lattices—a lattice point at the corners and one in the center of the cell
- A-, B-, C- or F-centered lattices—a lattice point at the corners and others at one (A, B, C) or all three (F) of the faces

The 14 Bravais lattices are shown in Figure 5.1. For reasons of symmetry (Rule 1, above) we don't always choose a primitive cell. The face-centered cubic cell may be referred to the rhombohedral cell (which is primitive), but the cubic cell reflects the higher symmetry of the lattice.

Lattice points per cell: Primitive cells have only one lattice point per cell, whereas nonprimitive cells have more than one. A lattice point in the interior of a cell (N_i) can be thought of as belonging entirely to that cell; one in a cell face (N_f) is shared by two cells; and a corner one (N_c) is shared by eight. The number of lattice points (N) per cell is given by

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \qquad (5.1)$$

Basis: Group of atoms associated with each and every lattice point. We can describe crystal structures in terms of a Bravais lattice and a Basis

$$\text{Bravais Lattice} + \text{Basis} \;=\; \text{Crystal Structure} \qquad (5.2)$$

This approach is often used by solid-state physicists and is particularly useful when we want to determine the structure factor of a crystal. Crystal structures are formed by placing a basis of atoms either on the points of a Bravais lattice or in some fixed relation to those points. There may be no atoms actually located on the lattice points.

Coordination number (CN): Number of nearest neighbors.

Symmetry elements: These symmetry elements are easy to understand because you can see them by handling real crystals or crystal shapes. For example, crystals of MgO are cubic, and calcite ($CaCO_3$) is trigonal, as shown in Figure 5.2. They apply to macroscopic shapes but we limit our choice by ignoring those where the shape could not correspond to the unit cell of a crystal.

- *Rotation axis*. Clockwise rotation of 360°/*n* about axis. Crystals may have twofold (diad), threefold (triad), fourfold (tetrad), or sixfold (hexad) rotation axes; the onefold axis is always present. Any other rotation, such as a fivefold axis, is not consistent with the definition that a crystal lattice must have translational symmetry.
- *Mirror plane*. When a plane can be chosen such that all features on one side of the plane appear, as if in a mirror, on the other side of the plane, the crystal has a mirror plane (also known as a plane of symmetry). We call this an m plane.
- *Center of symmetry*. If every feature in or on the object can be joined to an identical feature by an imaginary line through the center of the object, we say the object has a center of symmetry.
- *Inversion axis*. If when any point is rotated about an axis and then moved through the center of symmetry it arrives at an identical point, the object has an inversion axis. We refer to such axes as $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, or $\bar{6}$ axes. Notice that the $\bar{1}$ axis is, in fact, describing a center of symmetry. The $\bar{2}$ axis is an alternative description of an m plane.

There are other symmetry elements, such as screw axes, that are meaningful for crystals but not to our macroscopic crystal shapes. Figure 5.3 illustrates some of the symmetry elements for a cube. The most important are the four threefold axes along the <111> diagonals.

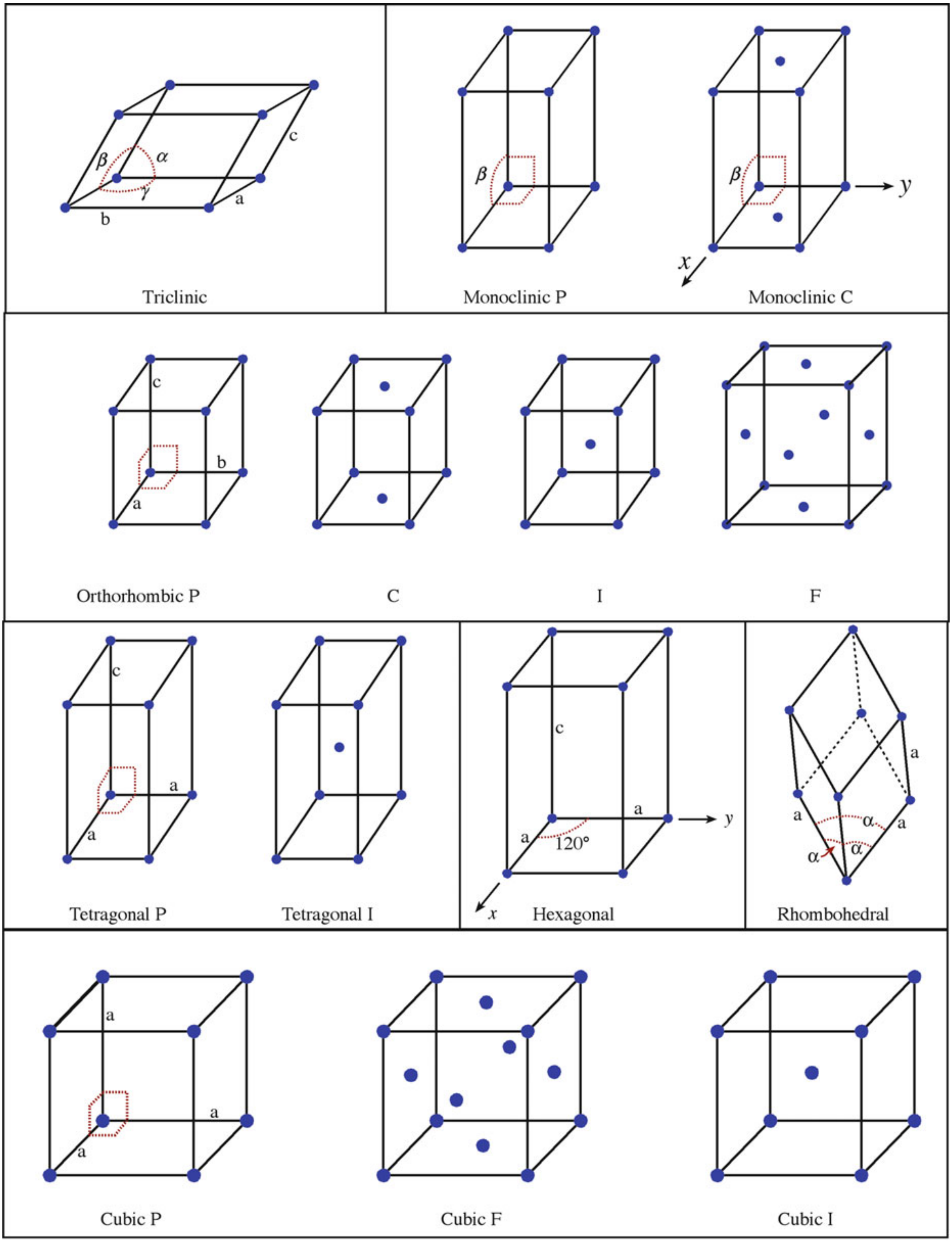

FIGURE 5.1. The 14 Bravais lattices.

5.2 SYMMETRY AND CRYSTALLOGRAPHY

Describing the symmetry of crystals is often more complicated than that of solid shapes such as the cube in Figure 5.3. For example, the crystal may have a cubic shape and belong to the cubic crystal system but not have the maximum internal symmetry.

Table 5.2 lists the Hermann-Mauguin notation for expressing the symmetry operators. Some combinations of symmetry elements produce the same answer. For

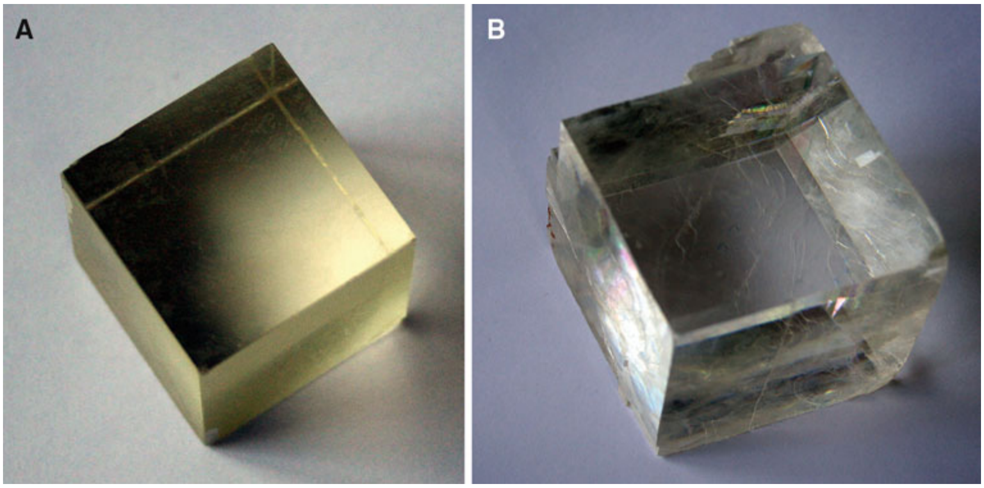

FIGURE 5.2. Crystals with faceted surfaces, illustrating macroscopic symmetry elements. (A) MgO. (B) Calcite.

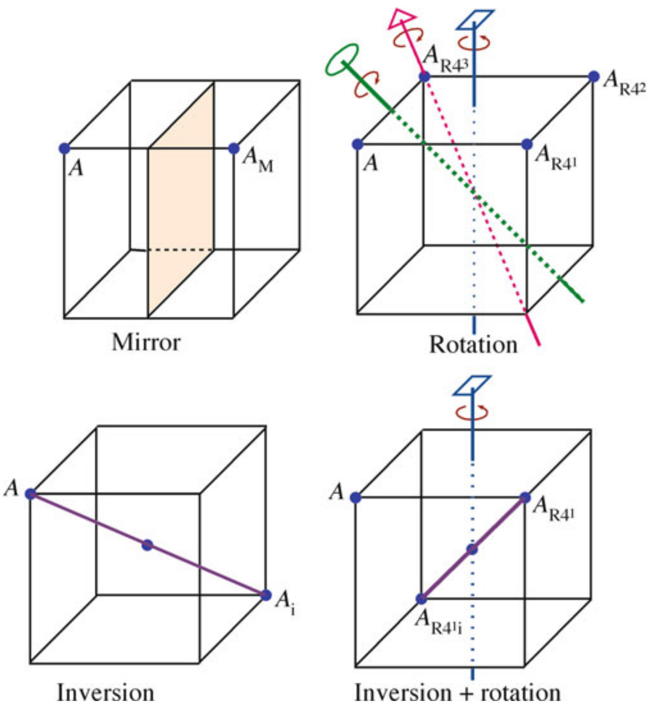

FIGURE 5.3. Symmetry elements for a simple cube.

TABLE 5.2 Symmetry Operators (Hermann-Mauguin Notation)

X	Rotation axis alone
$\bar{X}$	Inversion axis alone
X/m	Rotation axis with a symmetry plane *normal* to it
Xm	Rotation axis with a symmetry plane that is not normal to it (usually a vertical symmetry plane)
$\bar{X}$m	Inversion axis with a symmetry plane not normal to it
X2	Rotation axis with a diad normal to it
X/mm	Rotation axis with a symmetry plane normal to it and another not so

In writing the symbol, the principal symmetry axis is placed first. For cubic, 3 is always second

example, m is the same as $\bar{2}$ and $\bar{2}3$ and 2m3 are both the same as 2/m3, which is written as m3. Therefore, as with any convention, the only way to get it right is to memorize it. Table 5.3 lists the symmetry operations associated with each of the seven crystal systems. The final column in Table 5.3 has the maximum possible symmetry and is called the holosymmetric point group. For example, NaCl is m3m, and FeS_2 is m3. Both crystals are cubic, but they have different symmetries; we show the reasons in Chapter 6. The notation is not always the same as indicated at the top of the column. The symbols given here are known as the international convention. Actually, we could write them out fully, but the reduced description contains the essentials; for example, m3m is actually $\bar{4}$/m3m, and 43 is actually 432.

You can find the full details of the international convention in the *International Tables for Crystallography* (1983). These symmetry operations or elements can be combined to provide 32 crystal classes. The crystal classes are often called the crystal point groups. They are the point groups that are consistent with the translational symmetry of a crystal.

5.3 LATTICE POINTS, DIRECTIONS, AND PLANES

The notation used for identifying planes and faces of crystals is that of W.H. Miller and is referred to as the Miller Indices of a plane. The lengths of the unit cell are *a*, *b*, and *c*. A family of planes cuts these axes at the origin and at $\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$. The plane is then defined by the indices *h, k,* and *l*. If these indices are not all integers we multiply by the quotient to make them integers. Thus, the intercepts $\frac{3}{2}a$, $4b$, $1c$ give h,k,l values of $^2/_3$, $^1/_4$, and 1; and this *hkl* is 8.3.12. We only use periods to separate the numbers if one of them is >9. If the intercept is negative, we write $\bar{h}$ (bar *h*, sometimes read as *h* bar).

TABLE 5.3 The 7 Crystal Systems and the 32 Crystal Point Groups

Crystal system	*Essential symmetry*	*X*	$\bar{X}$	*X/m*	*Xm*	$\bar{X}m$	*X2*	*X/mm*
Triclinic	1-fold axis	1	$\bar{1}$	—	—	—	—	—
Monoclinic	2-fold axis (parallel to y)	2	m	2/m	—	—	—	—
Orthorhombic		—	—	—	mm	—	222	mmm
Trigonal	3-fold axis (parallel to z)	3	$\bar{3}$	—	3 m	$\bar{3}$m	32	—
Cubic	Four 3-fold axes	23	—	m3	—	$\bar{4}$3m	43	m3m
Tetragonal	4-fold axis (parallel to z)	4	$\bar{4}$	4/m	4 mm	$\bar{4}$32	42	4/mmm
Hexagonal	6-fold axis (parallel to z)	6	$\bar{6}$	6/m	6 mm	$\bar{6}$m2	62	6/mmm

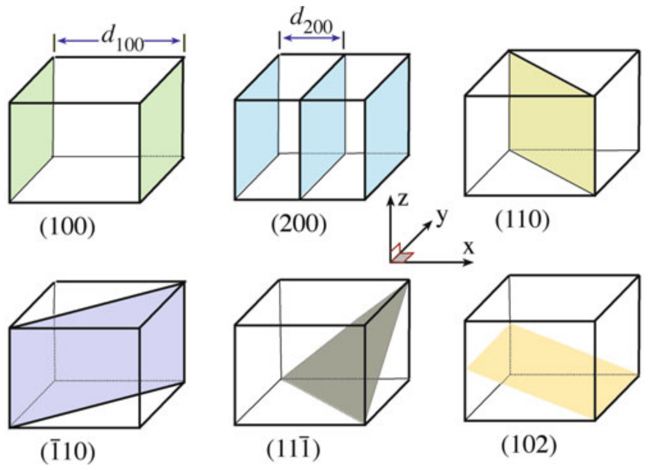

FIGURE 5.4. Miller indices of some lattice planes. The lattice-plane spacing is given by d_{hkl}.

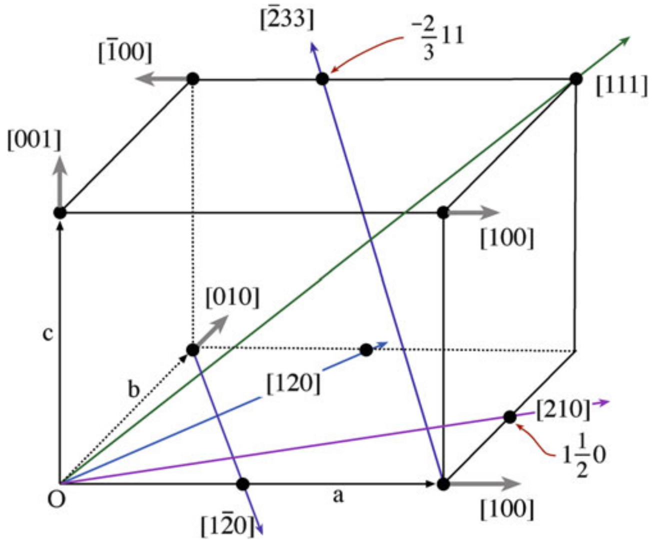

FIGURE 5.5. Indices of directions in an orthorhombic unit cell with examples of vectors included.

MILLER INDICES

Low-index planes have small values h, k and l (and i). All are integers.

FINDING THE ZONE AXIS

$$[UVW] = [h_1k_1l_1] \times [h_2k_2l_2]$$

$$U = k_1\,l_2 - l_1\,k_2$$

$$V = l_1\,h_2 - h_1\,l_2$$

$$W = h_1\,k_2 - k_1\,h_2$$

Figure 5.4 illustrates some of low-index planes in the orthorhombic crystal system. Because there may be different combinations of *hkl* that give symmetry-equivalent planes, we use (*hkl*) to denote a particular plane and {*hkl*} to denote an equivalent set of planes. The faces of the cube form the set of {100} planes.

Directions are easier to define. The vector $U\mathbf{a} + V\mathbf{b} + W\mathbf{c}$ is simply written as [*UVW*]. We can then write <*UVW*> to denote all the equivalent directions formed by permuting U, V, and W. The vector $U\mathbf{a}-V\mathbf{b} + W\mathbf{c}$ is denoted by $[U\bar{V}W]$. Some low-index directions in the orthorhombic system are illustrated in Figure 5.5.

A special direction, known as the zone axis, is the one that is common to two planes $h_1k_1l_1$ and $h_2k_2l_2$. The directions $[h_1k_1l_1]$ and $[h_2k_2l_2]$ are the normals to the two planes, and the zone axis [*UVW*] is then given by the vector cross product. The zone axis has particular significance in electron microscopy because it represents the direction of the incident electron beam with respect to the sample.

When discussing crystals with hexagonal symmetry, it is helpful to use Miller-Bravais indices because they clarify the symmetrically equivalent planes. In this scheme, a fourth index, i, is introduced such that $i = -(h + k)$. Figure 5.6 shows some planes and directions in the hexagonal system. The advantage of the four index Miller-Bravais system, and the main reason for its use, is that similar planes have similar indices (as we saw in the case of the Miller system). For example, the planes $(10\bar{1}0)$, $(01\bar{1}0)$, $(\bar{1}100)$, $(\bar{1}010)$, $(0\bar{1}10)$, $(1\bar{1}00)$ are the six side planes (called prism planes) of the hexagonal lattice; they clearly are of similar type. In the Miller system, however, they are (100), (010), $(\bar{1}10)$, $(\bar{1}00)$, $(0\bar{1}0)$, and $(1\bar{1}0)$; and they are definitely not of a similar type.

CONVERTING NOTATION: MILLER AND MILLER-BRAVAIS

$$\begin{aligned} U &= u - t & u &= (2U - V)/3 \\ V &= v - t & v &= (2V - U)/3 \\ W &= w & t &= -(u + v) \\ & & &= -(U + V)/3 \\ & & w &= W \end{aligned}$$

To transform directions, it is helpful to remember from Figure 5.6 that the vector [1 1 1 0] is a null vector: it has no length! Thus, we can change the three-index direction [1 1 0] in Figure 5.6 to its four-index form as follows [1 1 0] → [1 1 0 0] → $[1{+}f\ 1{+}f\ f\ 0]$, so our four-index notation for directions is the same as for planes (i.e., $U + V + W = 0$), we want $2 + 3f$ to be zero. Thus, $f = -\frac{2}{3}$, and the direction is $[\frac{1}{3}\,\frac{1}{3} - \frac{2}{3} 0]$ or $[11\bar{2}0]$.

The two notations are related, and it is straightforward to convert between them. The Miller-Bravais system is widely used in ceramics because alumina (sapphire) often behaves as if it were hexagonal although it's actually trigonal.

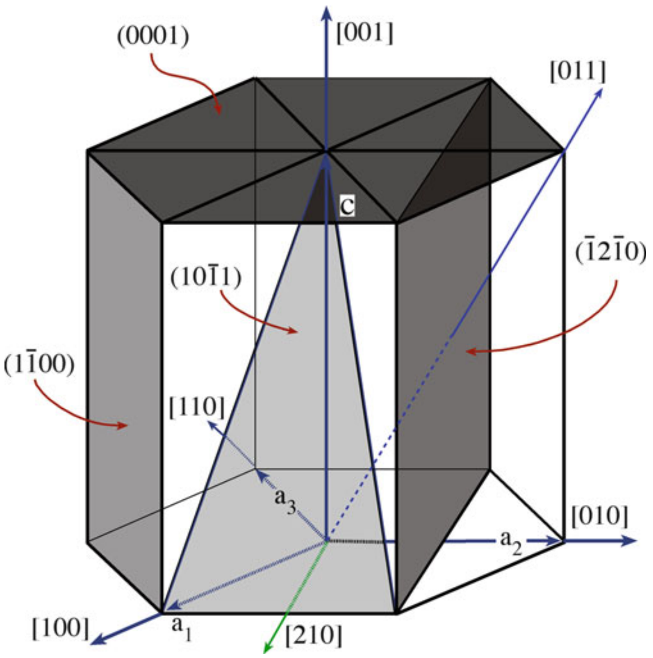

FIGURE 5.6. Indices of planes (using Miller-Bravais notation) and directions (using three-index Miller notation) in the hexagonal unit cell.

5.4 IMPORTANCE OF CRYSTALLOGRAPHY

Understanding the crystalline structure of ceramics is critical to understanding many of their properties.

- *Diffusion*. Often depends on size and number of interstitial sites; both functions of the crystal structure.
- *Deformation by slip or twinning*. In ceramics there are both crystallographic and electrostatic considerations. The slip direction is usually along a close-packed direction. The slip plane is usually a closely packed plane or one that does not put like charges in juxtaposition. Twin planes are usually special low-index planes.
- *Piezoelectricity*. Crystals must be noncentrosymmetric.
- *Thermal conductivity*. Phonon conductivity is most efficient in simple crystal structures formed by small atoms.
- *Fracture*. Often crystallographic but not always (e.g., glass and cubic zirconia).
- *Cleavage*. Always crystallographic. Cleavage planes have high atomic density, but we also need to consider charge.
- *Ferrimagnetism*. In ferrimagnets the coordination number of the magnetic cation (usually a Fe ion) determines its behavior in an applied magnetic field.

To really appreciate the importance, and complexities, of the relationships between crystallography and properties, see Nye (1985).

5.5 PAULING'S RULES

Ceramic materials are often thought of as being ionically bonded, and ions are thought of as being charged spheres. Many important ceramics are oxides, where the oxygen anion is much larger than the cation. The crystal structure adopted by the material is based on a balance between the attractive and repulsive forces in the crystal. The electrostatic attractive force between ions of unlike charge implies that an ion with a high CN would be more stable than an ion with a low CN (i.e., the electrostatic attraction is maximized). However, if too many ions of the same charge are clustered around an individual ion of the opposite charge, they begin to interfere with one another (i.e., the electrostatic repulsion is maximized). There exists a CN where the attraction is maximized and the repulsion is minimized. This number is determined by the ratio of the radii of the two ions. Questions then arise as to why certain oxides have the structure they do and how does this affect mixing or doping of oxides.

A MNEMONIC

Ca^{2+} is a cation.

MX

M is the cation and is often a metal.
X is the anion and is never a metal.
You'll sometimes see CA or + − instead of MX.

Pauling proposed a set of rules to use when discussing such topics. These rules work so well that they are sometimes regarded as laws, which they are not. We discuss the origin of the rules and then the rules themselves.

The idea is simply that ions of opposite sign pack together in such a way as to keep ions of like sign apart.

- *Rule 1*: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii, and the CN is determined by the radius ratio.
- *Rule 2*: In a stable structure, the total strength of the bonds that reach an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.
- *Rule 3*: The polyhedra in a structure tend not to share edges or faces. If the edges are shared, the shared edges are shortened. Shared faces are the least favorable.
- *Rule 4*: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other.
- *Rule 5*: The number of essentially different kinds of constituents in a crystal tends to be small.

When reading the discussion of these rules, keep in mind the following questions and remember that all rules have exceptions.

- Why do CsCl and NaCl have different structures?
- Why do Mg^{2+} ions tend to occupy tetrahedral sites whereas Al^{3+} ions occupy octahedral sites in spinel, when both ions occupy octahedral sites in MgO and Al_2O_3?
- Why do zinc blende and wurzite have different structures when both are ZnS? Why does GaAs have one structure and AlN have the other?
- What determines the structure of silicates? Are any other structures like this?
- Is the structure of $BaTiO_3$ important regarding its properties?

On Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii. CN is determined by the radius ratio:

$$\text{Radius ratio} = \frac{r_M}{r_X} \tag{5.3}$$

A given CN is stable only when the ratio of cation to anion radius is greater than some critical value. These limits are given in Table 5.4. The derivation of these limits is strictly geometrical, as shown in Figure 5.7.

Why are the radius ratio and CN related? Coulomb interactions mean that like signs should be as far apart as possible and opposite signs as close together as possible. Crystal structures are thus at their most stable when the cations have the maximum CN allowed by r_X. In many well-known ceramics, the cation coordination polyhedron is the basic building block.

On Rule 2: In a stable structure, the total electrostatic strength of the bonds, S, reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion

$$S = \frac{Z_M}{CN} \tag{5.4}$$

where CN is the coordination number, and Z_M = the charge on the cation. The fundamental idea is that the crystal must be electrically neutral.

We can illustrate this idea for the oxygen anion. Each O^{2-} might bond to a combination of cations.

- Si^{4+} ions, $S = 4/4 = 1$. Two bonds of strength 1 reach the shared oxygen ion from the surrounding silicon ions. This is the case in, for example, cristobalite (a polymorph of SiO_2). The Si^{4+} are surrounded by four O^{2-} ions in a tetrahedral arrangement.
- Al^{3+} ions, $S = 3/6 = 1/2$. Each O^{2-} ion is surrounded by four Al^{3+}, each with a bond strength of 1/2. The Al^{3+} is surrounded by six O^{2-} ions in an octahedral arrangement. This is the case in, for example, corundum.
- In the mineral kyanite, Al_2SiO_5, we have one Si^{4+} plus two Al^{3+} ions surrounding each O^{2-}ion. There are six O^{2-} around each octahedral Al^{3+} ion.

TABLE 5.4 Pauling's Critical Radius Ratios

Polyhedron	*CN*	*Minimum (=r_M/r_X)*
Cube	8	0.732
Octahedron	6	0.414
Tetrahedron	4	0.225
Triangle	3	0.155

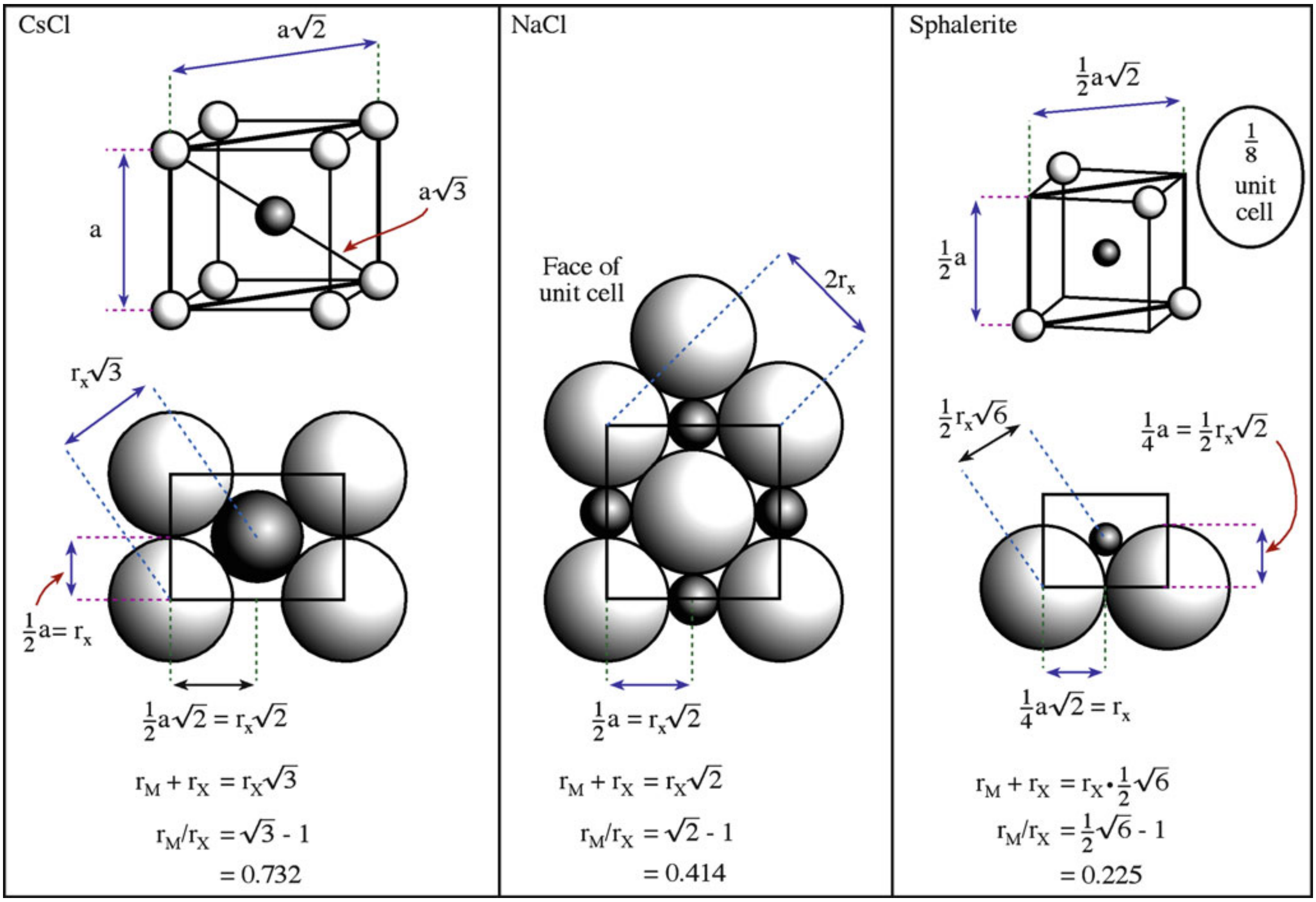

FIGURE 5.7. Geometric method for calculating limiting radius ratios.

- In forsterite, Mg_2SiO_4, we have one Si^{4+} ion plus three octahedral Mg^{2+} ions ($S = 2/6$). We need three Mg^{2+} ions to balance the charge.

In silicates, the Si atoms are each surrounded by four O^{2-} anions, so each O ion has an additional charge of -1 that must be used to bond to another ion. Thus, for an aluminosilicate, we need a large cation with a charge of +1 or +2 so it can be surrounded by eight or more oxygen ions. Calcium (with CN = 8) fits this requirement to give calcium aluminosilicate. Table 5.5 shows predicted CN and S values for various cations.

On Rule 3: Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, at least three edges are also shared.

TABLE 5.5 Predicted Coordination and Strength of the Bond

Ion	*r_M/r_X*	*Predicted coordination*	*Strength of bond*
Si^{+4}	0.37	4	1
Al^{+3}	0.41	4 or 6	$^{3}/_{4}$ or $^{1}/_{2}$ ($^{3}/_{4}$ or $^{3}/_{6}$)
Mg^{+2}	0.47	6	$^{1}/_{3}$ ($^{2}/_{6}$)
Ti^{+4}	0.55	6	$^{2}/_{3}$ ($^{4}/_{6}$)
K^{+1}	0.75	8	$^{1}/_{8}$

This effect is large for cations with high valence and a small CN. In the first case, the charge on the cation is large, increasing the Coulomb repulsion. It is especially large when the radius approaches the lower limit of stability of the polyhedron. Thus, if two anion polyhedra have an edge or face in common, the cations are being brought too close together. We can give an alternative statement of the rule. The existence of edges, and particularly faces, common to two anion polyhedra in a coordinated structure decreases its stability.

Examples

CsCl: The anions sit at the corners of cube and share faces.

NaCl: The anions sit at the corners of octahedra and share edges.

ZnS: The anions sit at corners of tetrahedra and share vertices.

If polyhedra share edges, these edges tend to be shortened. We can think of this shortening as concentrating more "anion" between cations, which are too close together! The converse of the rule is that if you find an apparent violation it is likely that the bonding is not ionic. However, many materials with the ZnS structure, which does the best job of separating like ions, have predominantly covalent bonding. Determination of the fraction of ionic character in a bond can be made using Equation 4.24.

GARNET

$Ca_3Al_2Si_3O_{12}$, is not only a gemstone but also a ceramic. Other garnets such as yttrium aluminum garnet (YAG) and gallium gadolinium garnet (GGG) are technologically much more important materials.

Ion:	Ca^{2+}	Al^{3+}	Si^{4+}
O^{2-} coordination	8	6	4
O bond strength, S	$^2/_8 = {}^1/_4$	$^3/_6 = {}^1/_2$	$^4/_4 = 1$

Some Examples In FeS_2 (iron pyrites, fool's gold, and a ceramic), the $[FeS_6]$ octahedra are linked by shared edges that are longer than expected.

Silicates contain $[SiO_4]^{4-}$ tetrahedra; in all cases, they only share corners due to strong mutual repulsion between Si^{4+}. Again, there is actually a large covalent component to the bonding. It is thus a geometric rule again but is nonetheless important. For example, the edges of the occupied octahedra in Al_2O_3 are 0.25 nm long, not 0.28 nm long.

On Rule 4: Crystals containing different cations of high valence and a small CN tend not to share polyhedron elements with each other. Sharing parts of polyhedra decreases the stability of the structure, so this rule is really a corollary to rule 3.

As an example, in $CaTiO_3$, $[CaO_{12}]$ polyhedra share edges, and $[TiO_6]$ polyhedra share corners. The Ti^{4+} cation is more highly charged than the Ca^{2+} cation, so the CN is smaller; the Coulombic repulsion between cations is proportional to the product of the charges.

On Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small. As far as possible, the environments of chemically similar atoms are similar (and Pauling's analysis assumes that the bonding is all ionic.)

If all types of bonding are possible, it is a bit difficult to predict what will happen; but if every oxygen has the same environment, there is only one possibility. The result is actually found in garnet. This rule only requires the ions to be *similarly coordinated.* Their actual geometric positions need *not* be equivalent. They are *not* structurally indistinguishable. The rule actually has limited value because in a majority of silicates the oxygen ions do not have like environments.

5.6 CLOSE-PACKED ARRANGEMENTS: INTERSTITIAL SITES

A close-packed structure is one that has the maximum volume of the unit cell occupied by atoms. The occupied fraction of the unit cell can be determined by calculating the atomic packing factor (APF)

$$\mathrm{APF} = \frac{\text{number of atoms per cell} \times \text{volume of one atom}}{\text{volume of unit cell}} \tag{5.5}$$

The *maximum* possible APF for packing of spheres all having the same size is 0.74. This arrangement is the one seen in grocery stores in which oranges in adjacent layers sit off-center, resting within the pocket created by the oranges sitting side-by-side below. Materials scientists and crystallographers (as well as greengrocers) have known that this is the most efficient way to stack a bunch of round objects but mathematicians took a long time to be convinced (see the interesting book on this topic and other mathematical riddles by Singh 1997). A mathematical proof for what is known as the Kepler Conjecture was announced in 1998 and the manuscript published 7 years later (Hales 2005).

Crystal structures having an APF of 0.74 are called close-packed structures. There are only two close-packed structures

- Face-centered cubic (fcc)
- Hexagonal close-packed (hcp)

We consider the fcc and hcp structures in some detail because they are so common. For the fcc structure, all the points are actually lattice points. In the hcp structure, this is not the case. Thus, we should never say the "hcp lattice," but we do. The hcp structure describes a particular arrangement of similar atoms, but it is not a lattice of identical points.

The relationship between the fcc and hcp structures is illustrated in Figure 5.8A. The atoms on the (111) planes of the fcc structure are arranged in a hexagonal pattern just like the atoms on the (0002) planes of the hcp structure. The only difference between the two structures is the way in which these hexagonal sheets of atoms are arranged above one another. In the hcp structure, the atoms in the second layer are above the hollows in the first layer, and the atoms in the third layer are above the atoms in the first layer, so the stacking sequence can be summarized as A B A B A B . . .. The stacking in the hcp structure is illustrated in Figure 5.8B. The first two atom layers in the fcc structure are put down in the same way, but the atoms of the third layer are placed in the hollows of the second layer; not until the fourth layer does a position repeat. The stacking sequence for fcc is therefore A B C A B C A . . .. This sequence is illustrated in Figure 5.8C.

In predominantly ionically bonded oxide ceramics, the O^{2-} ion approximates to a sphere. Therefore, we can view these structures as based on a close-packed arrangement of spheres and then filling the remaining space. We must remember that the anions are not necessarily touching but are merely arranged in a way that is the same as that in close-packed structures.

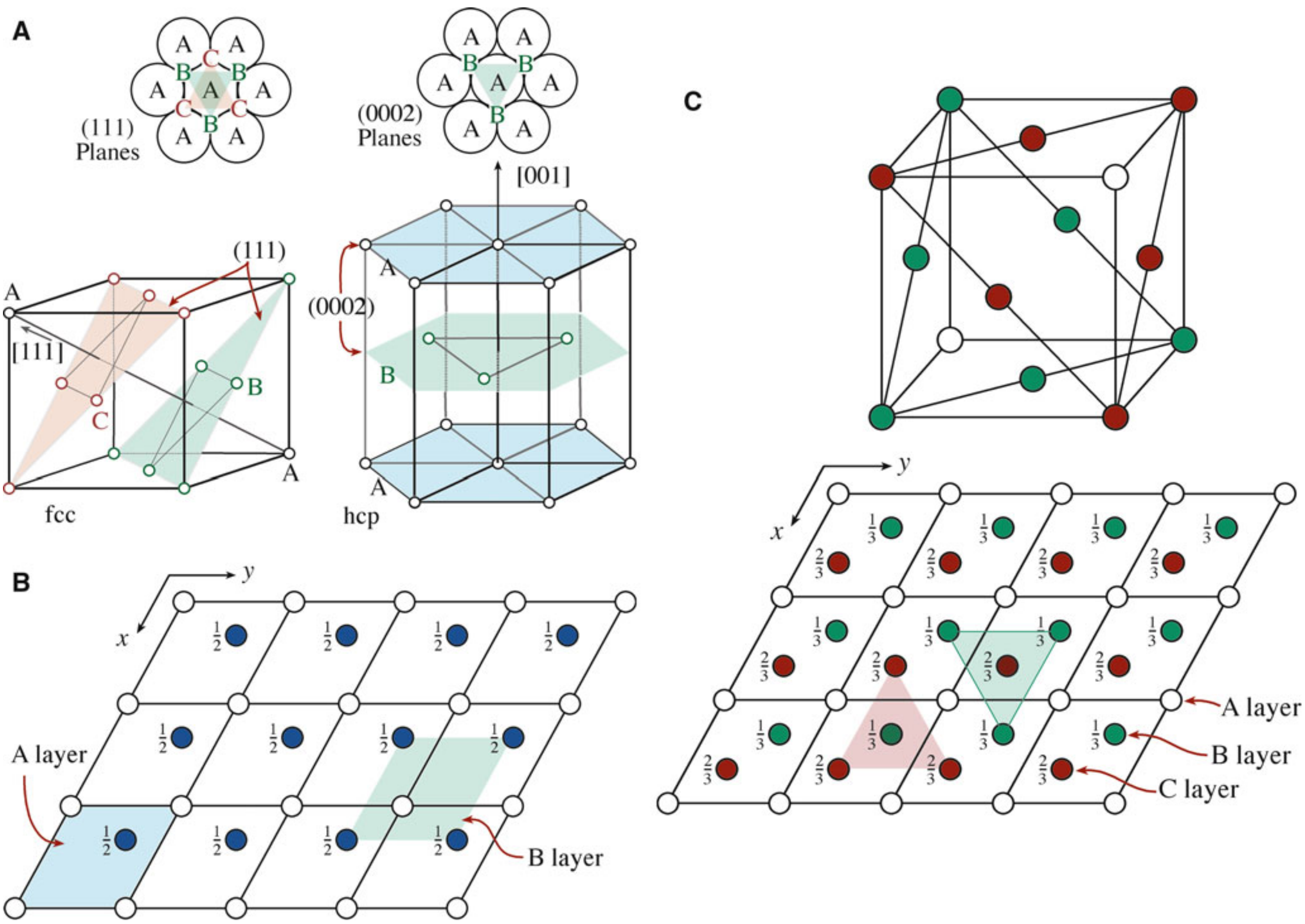

FIGURE 5.8. (A) Comparison of fcc and hcp structures using the stacking of close-packed rafts of atoms (spheres). (B) Stacking sequence in hcp. (C) Stacking sequence in fcc.

The questions we need to answer now are:

- Where are the interstitial sites?
- What is their CN?
- How many sites are there?

The fcc and hcp arrangements offer both octahedral and tetrahedral interstices, making them good hosts for cations because two size ranges can be incorporated. Both fcc and hcp arrangements can be stabilized by filling just the tetrahedral sites or just the octahedral sites. The fcc lattice can be stabilized by filling a combination of tetrahedral and octahedral sites. In the fcc arrangement, there are eight tetrahedral sites and four octahedral sites per cell. The locations of these sites are shown in Figure 5.9A. There are four tetrahedral sites and two octahedral sites per cell in the hcp arrangement. The locations of these sites are shown in Figure 5.9B.

In ceramics, the APF is always <0.74, even though we have increased the number of atoms per cell. As an example, if we fill all the octahedral sites in an fcc arrangement of O^{2-} with cations (e.g., Mg^{2+}) as we'll see in Chapter 6, the APF is 0.69. In other words, 69% of the cell volume is occupied by ions.

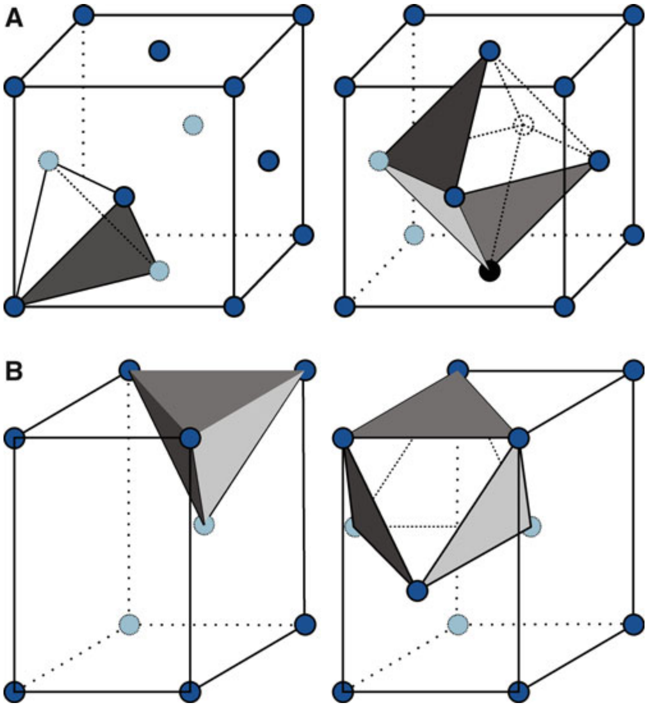

FIGURE 5.9. (A) Interstitial sites in the fcc structure, (B) Interstitial sites in the hcp structure.

5.7 NOTATION FOR CRYSTAL STRUCTURES

One of the things you'll notice is that many crystal structures are named after particular materials (often a naturally occurring mineral) that exhibits the structure. There are no systematic names for crystal structures, as there are, for example, for organic compounds, which are named using a system recommended by the International Union of Pure and Applied Chemistry (IUPAC). This system provides us with a systematic way of naming many organic compounds on sight, and the name indicates the structure of the compound. A similar system is not used for naming crystal structures. However, there are several notations for specifying crystal structures that can be very useful.

- *Strukturbericht*. The symbol consists of a letter that characterizes the type of structure and a number designating a specific type within a letter category. The rules are given in Table 5.6.
- *Pearson*. The symbols give, successively, the crystal system, the Bravais lattice symbol, and the number of atoms per unit cell. The notation is summarized in Table 5.7. Even though you can find out the crystal system, the Bravais lattice, and the number of atoms from this notation, you can't differentiate among different structures with similar notations. For example, cF8 refers to sodium chloride, diamond cubic, and zinc blende structures, which are different from one another.

TABLE 5.6 The Strukturbericht Notation

Symbol	*Definition*	*Symbol*	*Definition*
A	Element	E-K	Complex
B	AB compounds	L	Alloys
C	AB_2	O	Organic
D	A_mB_n	S	Silicates

TABLE 5.7 Symbols Used in the Pearson Notation

Symbol	*System*	*Lattice*
aP	Triclinic (anorthic)	P
mP	Simple monoclinic	P
mC	Base-centered monoclinic	C
oP	Simple orthorhombic	P
oC	Base-centered orthorhombic	C
oF	Face-centered orthorhombic	F
oI	Body-centered orthorhombic	I
tP	Simple tetragonal	P
tI	Body-centered tetragonal	I
hP	Hexagonal	P
hR	Rhombohedral	R
cP	Simple cubic	P
cF	Face-centered cubic	F
cI	Body-centered cubic	I

TABLE 5.8 Notation for Different Crystal Structures

Strukturbericht	*Prototype*	*Pearson*	*Space group*
A1	Cu	cF4	Fm3m
A2	W	cI2	Im3m
A3	Mg	hP2	P6_3/mmc
A9	graphite	hP4	P6_3/mmc
B_h	WC	hP2	P6m2
B_k	BN	hP4	P6_3/mmc
B1	NaCl	cF8	Fm3m
B2	CsCl	cP2	Pm3m
B3	sphalerite	cF8	F43m
B4	wurtzite	hP4	P6_3mc
B10	PbO	tP4	P4/nmm
B26	CuO	mC8	C2/c
C2	FeS_2 (pyrite)	cP12	Pa3
C3	Ag_2O	cP6	Pn3m
C4	TiO_2 (rutile)	tP6	P4_2/mnm
C6	CdI_2	hP3	P3m1
C7	MoS_2	hP6	P6_3/mmc
C8	High quartz	hP9	P$6_2$22
C9	β Cristobalite	cF24	Fd3m
C10	β Tridymite	hP12	P6_3/mmc
C18	FeS_2 (marcasite)	oP6	Pnnm
C21	TiO_2 (brookite)	oP24	Pbca
C43	ZrO_2	mP12	P2_1/c
$D0_9$	ReO_3	cP4	Pm3m
$D0_{11}$	Fe_3C	oP16	Pnma
$D5_1$	α-Al_2O_3	hR10	R3c
$D5_2$	La_2O_3	hP5	P3c1
$D5_3$	Mn_2O_3	cI80	Ia3
$E2_1$	$CaTiO_3$	cP5	Pm3m
$H1_1$	$MgAl_2O_4$	cF56	Fd3m
$L1_0$	AuCu	tP2	P4/mmm
$L1_1$	CuPt	hR32	R3m
$L1_2$	$AuCu_3$	cP4	Pm3m

Examples of Strukturbericht and Pearson symbols are given in Table 5.8.

5.8 STRUCTURE, COMPOSITION, AND TEMPERATURE

Many ceramics exist in different structures at different temperatures. These structures are known as polymorphs, and we give some examples in Chapter 6. The most stable structure at any particular temperature is governed by its free energy, G. The polymorph with the lowest free energy is the most stable. Expressions for the free energy and internal energy were given in Chapter 3. Both the internal energy, E, and the entropy, S, depend on crystal structure.

The following rules can be given for the temperature and pressure dependence of thermodynamically stable structures.

- At $T = 0$, $G = E$ (i.e., the free energy is fixed by the internal energy).

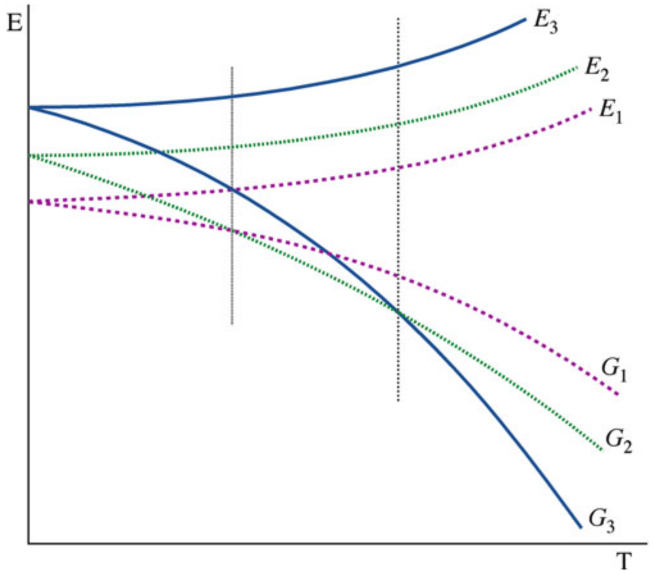

FIGURE 5.10. Relationship between internal energy E and free energy G of three polymorphic forms: $E_3 > E_2 > E_1$ and $S_3 > S_2 > S_1$. The form with the lowest G is the one usually found at a specific temperature.

- At $T > 0$, the TS term becomes increasingly important, and structures with a low degree of order are favored.
- At a sufficiently high temperature, a polymorph with a larger S may achieve a lower G despite its larger E, as illustrated in Figure 5.10. The increased values of E and S of the high-temperature forms correspond to more open structures (larger specific volumes) with higher symmetry.
- There are two components to entropy (both increase as T increases): thermal entropy and configurational entropy.
- In the liquid state, the order is even lower; and it is the lowest in the gaseous state. Raising the temperature leads to melting and finally to evaporation.
- Higher pressures favor structures that occupy a lower volume (i.e., that have a higher density).

The crystal structure of a ceramic also depends on composition. As an example, consider three oxides of iron.

1. Wüstite (FeO): Cubic rock salt structure. Iron is in the 2+ oxidation state.
2. Hematite (Fe_2O_3): Rhombohedral corundum structure. Iron is in the 3+ oxidation state.
3. Magnetite (Fe_3O_4): Cubic spinel structure. Iron is in the 3+ and 2+ oxidation states.

The reasons for these differences are explained by Pauling's rules.

There is another factor that can influence the equilibrium structure of a material, and that is surface energy. The effect of surface energy has become of increasing importance with the interest in nano-sized particles of ceramics. When particle size is very small, the fraction of atoms on the surface is very large. Surface energy effects can then dominate, as illustrated in Figure 5.11, which shows that γ-Al_2O_3, rather than α-Al_2O_3, can become the thermodynamically stable phase of aluminum oxide when the surface area exceeds ~175 m^2/g. The key thing to remember is that nanomaterials don't always behave the same as the bulk material.

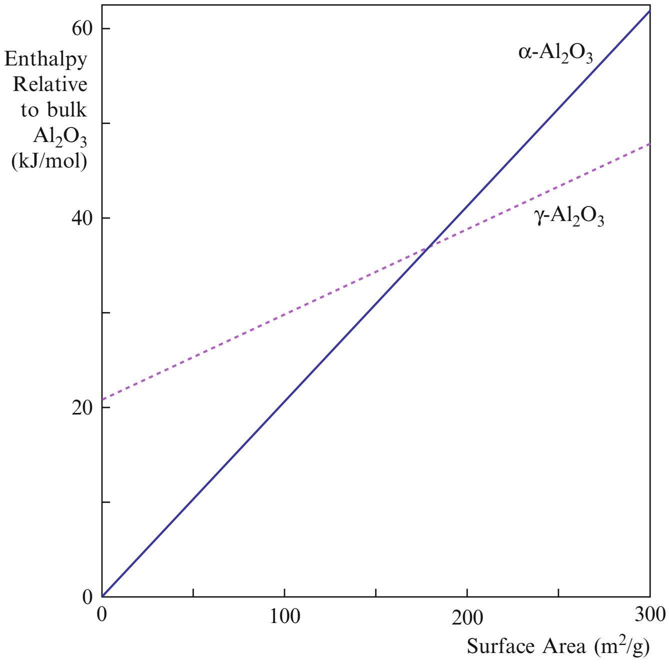

FIGURE 5.11. Calculated enthalpy of alumina (γ- and α-) polymorphs as it varies with the surface area. The calculation is a molecular dynamic (MD) simulation using data for small surface areas. Large surface area per gram implies small particles.

5.9 CRYSTALS, GLASS, SOLIDS, AND LIQUID

Classically, there are three distinct states of matter: gas, liquid, and solid. (The newer two, plasma and Bose-Einstein condensates, are not applicable to our discussion so we omit them here.) In the previous section we noted how as temperature increases it is thermodynamically favorable for transitions to occur, from a more ordered form to a less ordered one. The atoms or molecules that make up a gas are randomly arranged (E and S are high) and widely separated. A gas fills all the available space inside a container. The atoms or molecules that make up a liquid are also randomly arranged, but they are closer together than those in a gas; and they move relative to one another. The characteristic of a liquid is that it fill a container to the extent of its own volume. The third state of matter is solid, which can be defined as having a fixed shape. Solids can be classified as either *crystalline* or *noncrystalline*.

When we discuss crystals, we are concerned with interatomic bonding, interatomic distances, the environment of the ions, and long-range ordering. All of these concepts, except for long-range ordering, are relevant to noncrystalline materials such as glass. In fact, when we discuss silica-based glasses, the main point is how we do or do not link SiO_4 tetrahedra together. The concept of order that is important is separating the different classes of condensed matter. The basic differences are summarized below:

Crystal	Ordering on lattice: long-range order
Glass	Short-range order
Liquid	No order to short-range order

There are many amorphous ceramics (glasses). There are fewer amorphous semiconductors and some amorphous metal alloys. The main consideration, as you'll see in Chapter 21, is the rate of cooling necessary to avoid crystallization. In many oxides, the critical rate of cooling is very easy to achieve because the number of components is large and we have directional (covalent) bonding. The latter consideration also holds for semiconductors, but for metal alloys we usually can rely only on frustrating crystallization using complex compositions and rapid quenching.

5.10 DEFECTS

One reason we need to understand the structure of perfect crystals is so we can begin to understand imperfect crystals. The topic is not specific just to ceramics. The interaction of defects is often most important to us. For ceramics, a special example of such interactions occurs in grain growth. Grain-boundary movement in ceramics usually involves the movement of point defects.

Understanding atomic bonding helps us understand the structures of crystals and glass. When we think of crystals, we think of atoms arranged in a perfect way. We traditionally think in terms of crystal defects, but we also consider how these ideas apply to defects in glass.

One question we must keep in mind is: "How is this feature different from metals?" The answer is not always as obvious as it might seem because we often compare ceramic materials to particularly simple (usually fcc) metals. Apart from carbon and the elemental semiconductors Si and Ge, all ceramics contain two or more different atoms so we should at least compare them with metal alloys, not pure metals. The next question is: "How do defects influence the properties of the ceramic?" For that we first need to understand defects.

We classify defects as having zero, one, two, or three dimensions, as shown in Table 5.9. Actually, all of the defects we discuss are three-dimensional. Ceramics usually have mixed bonding (i.e., a combination of ionic and covalent bonding). Hence, when we introduce defects, we usually change the local distribution of charge or break bonds, depending on which type of bond predominates. Any change in charge distribution can produce long-range effects. A broken covalent bond is known as a dangling (unpaired electron) bond that also behaves like a localized charge.

TABLE 5.9 Hierarchy of Crystal Lattice Defects

"Dimension"	*Defect*	*Some topics*
0	Point defects	Geometry, strain energy, charge
1	Line defects	Geometry, energy
2	Surfaces	Thermodynamics
	Grain boundaries	Structure, chemistry, wetting
	Phase boundaries	Phase distribution
3	Volume defects	Precipitates, particles, and voids

We've discussed the packing of ions in terms of coordination polyhedra. When we create defects in a crystal, we can create new polyhedra that are not found in the perfect crystal. Pauling's rules were developed for perfect crystals, but the principles still apply when we examine defects. One complication is that as we introduce grain boundaries, for example, new sites are produced that depend on the detailed nature of the grain boundary. Amorphous materials present a new challenge when describing point defects. Two amorphous materials can have different structures that depend on the processing history even if the chemistry is the same.

5.11 COMPUTER MODELING

Computer modeling of oxide structures and of defects in oxides is becoming more important, in part because the code is improving but mainly because faster computers can make more realistic calculations. The problems for ceramic materials are those discussed in Chapters 3 and 4. If the bonding is ionic, the ion–ion interactions are both strong and long range. If there is a covalent component to the bonding, the bonds have a directional character. (Glasses exist in a metastable state, so their structure is by definition not the equilibrium one.) The problem is twofold. We need computer code that can handle the long-range interactions. Even simple ceramics can have large unit cells, which means that the computer must also be able to handle a large number of atoms.

We summarize the approaches being used by different researchers to calculate properties of ceramics. This discussion is very brief and incomplete, but it should give an idea of how the subject is developing. One encouraging feature is that software packages suitable for the knowledgeable researcher who is not an expert programmer are becoming available commercially. These packages fall into two categories that can be linked. In one, the atomic structure of a ceramic crystal can be displayed after inputting the appropriate crystal parameters. Such programs are simply using the rules of crystallography to generate the structures. The other, and far more complex, programs also use the interatomic potentials to deduce features of the structure and are performed using molecular dynamic (MD) approaches.

5.11.1 Terms Used in Modeling

We begin by listing some of the terms you will encounter.

Pseudo-potential: This is an expression that is used to represent a real crystal potential. An equation such as Equation 4.1 is chosen, and the parameters are changed until a calculated value is obtained that agrees well with the known value of a physical parameter. This process is carried out simultaneously for several parameters that are chosen to have some relevance to what you would like to calculate.

Electronic structure calculation: Although ceramics are thought of as insulators, the electrons are important in understanding optical properties, for example.

5.11.2 Computer Modeling of Structures: The Need for Potentials

Most ceramics cannot be modeled from first principles simply because we don't know the potentials well enough. Therefore, the challenge with modeling crystals is that we have to use a model for the potential. These are available for Si and are quite good for Al_2O_3 and MgO. We can summarize the problems for modeling ceramics as follows.

- Ceramics usually contain charged species. This means that the interionic forces extend over very large distances (remember the Madelung constant). To model such materials we need large unit cells. This problem becomes more difficult when we model defects.
- When the ceramic is covalent or has a large covalent component to the bonding, directions are important. Si is the classic example of a covalent material. It can be modeled but only because enormous effort can be justified by its commercial importance. Modeling silicates, which also have a large covalent component, is less developed.

Ceramics lag behind metals for two reasons. Firstly, most ceramics contain more than one component, so we need to have potentials for each ion. (FeO contains three ions for this purpose.) Secondly, the potentials have to be used to predict known quantities, and these are not usually as well known as they are for metals.

A number of software packages are now available as shareware or commercially. One such program is GULP: the acronym stands for Generalized Utility Lattice Program. GULP can be used to perform different types of simulation on 3D periodic solids and on isolated defects in such materials. GULP simulates structures of ionically bonded materials using a shell model and uses the crystal symmetry to accelerate the calculations and to simplify the input. These two factors can make it faster and more efficient than other programs. If you use GULP, for example, you have access to at least 23 different potentials or models, including Buckingham, Morse, Coulomb, and Stilinger-Weber. Examples of the uses of GULP are modeling Al_2O_3, defects in garnets, zeolites, and molecular sieves, and the structure of Al_2SiO_5 polymorphs. Cerius™, another software package for simulating structures, also includes diffraction modules. The state-of-the-art approach is to use first principles computations. Three widely used packages are Siesta, VASP, and FHI-aims. All are being used for ceramic materials. Exploring takes time—or a career.

CHAPTER SUMMARY

This is the chapter where we introduced crystallography. Some students object to having to learn this material. Our view is that you cannot understand point defects, piezoelectricity, grain boundaries, elasticity of noncubic crystalline materials, and so on unless you understand the differences between crystal structures; and for this you must understand the principles of crystallography. Pauling's rules for ionic ceramics give us a set of tools that allow us to predict the coordination of ions and even to guess the structure of a crystal that may be new to us. The exceptions to these rules often result from the presence of a covalent component to the bonding, which itself gives clues to the coordination. Once we know the crystal structure, we can predict what point defects might occur and even guess at the energies involved—just from counting broken bonds, for example. The best-known examples of such point defect sites are the octohedra and tetrahedra in close-packed (fcc or hcp) lattices, but we find these polyhedra in many different crystal structures although they may be more difficult to recognize elsewhere. Therefore, just by considering Pauling's rules, we are introduced to one of the most useful concepts of solid-state chemistry—the concept of crystals being constructed by arranging polyhedra. The polyhedra are clusters of atoms that behave in quite systematic ways. As we'll see in the following chapters, the most important of these polyhedra is the tetrahedron, formed by four oxygen ions with a Si ion at the center. However, it is certainly not the only polyhedron of interest to us.

PEOPLE AND HISTORY

Bravais, Auguste (1811–1863) presented his ideas on crystallography to the French Academy of Sciences in 1849. He was interested in a number of fields including botany, astronomy, and physics. It is for his work in crystallography that he is best remembered.

Goldschmidt, Victor Moritz was born in Zurich but spent his scientific career in Norway (1888–1947). Like Pauling, he derived rules for ionic radii.

Haüy, René-Just (1743–1822) published his essay in 1784 on a theory of the structure of crystals. The story is that his interest in crystals began when he examined a specimen of calcite that he had accidentally just dropped.

Hooke, Robert (1635–1703) published *Micrographica* in 1665 showing images taken with his microscope. A genius.

Miller, William Hallowes (1801–1880) was born in South Wales and was Professor of Mineralogy at Cambridge University from 1832 until he died. He wrote the book that explained the notation developed by William Whewell. Although he gave full credit to the pioneering work of his mentor, Whewell, we still refer to Miller indices.

Whewell, William (1794–1866) (see Miller above). One-time President of the Geological Society (hence the indices), he is now remembered as a philosopher. He also invented the word scientist for Coleridge; and anode, cathode, and ion for Faraday! He was sometimes called a polymath—read about him and be impressed.

Wulff, Georgii (Yurii) Viktorovich was a Russian crystallographer born in 1863. The initial "G" was used in translations of his papers rather than "Y". He died in 1925 in Moscow.

Wyckoff, Ralph Walter Graystone was born in 1897 and died in 1994. He authored the classic book, *The Structure of Crystals* (1931).

EXERCISES

5.1 Calculate the percentage of free space in an fcc stacking of spheres and a simple cubic stacking of spheres. Relate the result to two important ceramic structures.

5.2 How do you expect the lattice parameters of Si and SiO_2 (high cristobalite) to compare? How does this fit with the experiment? Discuss.

5.3 When the {111} planes of SiC stack with the sequence ABABAB, the SiC has hexagonal symmetry. When they stack with the sequence ABCABC, it has cubic symmetry. What symmetry does it have when it stacks ABCBABCBABCBA? Explain your reasoning.

5.4 The face-centered cubic cell may be referred to the rhombohedral cell. Using a sketch, show the relationship between the two cells.

5.5 Are there any intersticies in hcp that are not present in fcc?

5.6 Why is there no Bravais lattice called orthorhombic A, monoclinic B, or tetragonal C?

5.7 If a sapphire crystal showed only one type of rhombohedral plane and the two basal planes, what would the shape of the crystal be?

5.8 FeS is a more complicated structure than FeO. Why would you not be surprised at this result?

5.9 In calcite ($CaCO_3$) the Ca^{2+} ion has a CN 6. Using the appropriate Pauling rule determine the ion environment around each O^{2-} ion.

5.10 From the ionic radii given, estimate the coordination numbers for the following oxides: (a) MgO. (b) Al_2O_3. (c) Li_2O, Li^+ 76 pm; O^{2-} 140 pm; Mg^{2+} 72 pm; Al^{3+} 54 pm.

5.11 From the literature (reference your sources): What are the lattice parameters of calcite and aragonite? Why and when do each occur? How are they related?

5.12 Without looking at the chapter, write down three examples for each of the seven crystal systems. Then, write down two more examples by looking through the literature (reference your sources).

5.13 Look at Table 5.3 and replace all the dashed symmetry elements with one that is already in the table.

5.14 What is the zone axis for the following pairs of planes: (a) (111) and (112), (b) (001) and (123), (c) (135) and (853)? How do these answers change if the crystal is orthorhombic instead of cubic?

5.15 What are the [1234], [2345], and [8642] directions better known as?

5.16 Why do ceramists use the Pauling rules and not the Goldschmidt rules? Why do many now use the Shannon-Prewitt values for ionic radii? Give any references that you use when probing the literature to answer the question.

5.17 Use the literature to make a list of as many different garnets as you can find. Which of these are already commercially important? Do you expect Pauling's rules to apply to all of them?

5.18 "Crystals are more difficult to understand than glasses because they can have many different structures." Justify your criticism of this claim.

5.19 Assuming all the particles are the same size and almost equiaxed. What are the dimensions of the particles at the crossover point in Figure 5.11?

5.20 We normally draw the unit cell of fluorite one way, but Pauling says we should draw it differently. Explain this sentence and draw the two different unit cells.

REFERENCES

There are many books on crystals and crystallography—which is best for you depends on your background and interests. A great source for further reading is the mineralogical literature. The books by Putnis (1992) and Deer, Howie, and Zussman (1992), among others, provide great insight, as does the literature from solid-state chemistry, such as the books of Wells (1970), Hyde and Anderson (1989), and others. These references are given in Chapters 6 and 7.

GENERAL REFERENCES

Barrett CS, Massalski TB (1980) Structure of metals, 3rd edn. Pergamon, New York, Together with Pearson (below) gives more on the Strukturbericht notation

Buerger M (1978) Elementary crystallography. MIT Press, Cambridge, MA, One of the best introductions to the subject. At the level of this text

Burdett JK (1995) Chemical bonding in solids. Oxford University Press, Oxford

De Graef M, McHenry ME (2007) Structure of materials: an introduction to crystallography, diffraction and symmetry. Cambridge University Press, New York

Gale JD (1996) Empirical potential derivation for ionic materials. Philos Mag B 73:3–19

Giacovazzo C et al (2002) Fundamentals of crystallography, 2nd edn. IUCr/Oxford University Press, New York, Comprehensive

Hammond C (1997) The basics of crystallography and diffraction, 3rd edn, International union of crystallography texts on crystallography. Oxford University Press, Oxford, A clear introduction

Hahn T (ed) (2002) International tables for crystallography, vol A, 5th edn. D. Reidel, Boston

Materials Studio (Accelys) is found at http://accelrys.com/products/materials-studio

Nyberg M, Nygren MA, Pettersson LGM, Gay DH, Rohl AL (1996) Hydrogen dissociation on reconstructed ZnO surfaces. J Phys Chem 100:9054–9063

Phillips FC (1972) An introduction to crystallography, 4th edn. Wiley, New York, Includes a clear description of the Herman-Mauguin notation and the 32 classes of crystal symmetry. First published in 1946. A favorite with many old Professors!

SPECIFIC REFERENCES

Gale JD (1997) GULP—a computer program for the symmetry adapted simulation of solids. JCS Faraday Trans 93:629

Hales TC (2005) A proof of the Kepler conjecture. Ann Math 162:1065, The paper is 121 pages long! Twelve reviewers spent more than 4 years reviewing it

Nye JF (1985) Physical properties of crystals: their representation by tensors and matrices. Clarendon, Oxford, Solid—may challenge your math

Pearson WB (1972) The crystal chemistry and physics of metals and alloys. Wiley, New York, Gives many more details on crystal notation (see also Villars below)

Singh S (1997) Fermat's last theorem. Fourth Estate, London

Villars P (1998) Pearson's handbook: desk edition: crystallographic data for intermetallic phases. ASM International, Metals Park, ~$1,000

WWW

Crystal modeling using CrystalMaker. http://www.crystalmaker.co.uk on a Mac or PCis easy

http://projects.ivec.org/gulp/ still a source for GULP in version 3.4

www.crystalmaker.com/ building models, not modeling in version 8.5

http://cms.mpi.univie.ac.at/vasp/ for access to VASP of course (V is for Vienna; 4.6 and 5.2)

www.icmab.es/siesta/ for SIESTA in version 3.1

http://aimsclub.fhi-berlin.mpg.de/ for the FHI-aims package from Fritz-Haber (release 071711)