INORGANIC MATERIALS SYNTHESIS AND FABRICATION

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PREFACE

With our first textbook, *Principles of Inorganic Materials Design,* we set out to fulfill our stated goal of preparing a single-source presentation of inorganic materials design. Accordingly, the primary emphasis was on structure–property correlation. A comprehensive treatment of the broader general topic of inorganic materials science necessitates that we discuss chemical, synthetic, and fabrication processes, topics we now take up in detail.

Customarily, chemists have been interested in the submicroscopic length scale, studying the compositions and structures of solids, their relationships to properties, and processes that bring about changes in those entities. The physicists who deal with condensed matter have had similar goals working at the electronic length scale, where they have been concerned primarily with describing various physical properties quantitatively. The focus of materials scientists and engineers, on the other hand, has evolved from studying microstructural features and processes to a state in which they now also draw on the body of knowledge acquired by chemists and physicists in order to design improved materials for utilization in specific engineering applications. Today, the artificial demarcation between the various disciplines is beginning to vanish. Becoming consistently common objectives are synthesis and fabrication, which inherently require consideration of details spanning multiple length scales.

To serve the need to educate science and engineering students in this area, in this book we take an interdisciplinary approach, as we did in our first book, but with the focus shifted to describing how chemical reactions proceed between *single-phase* inorganic solids (molecular and nonmolecular) and other substances that result in the transformation of the solid, to a new single phase with composition differing from that of the original material. Such reactions are conveniently categorized here as being of the solid–vapor, solid–liquid, or solid–solid type. In general, synthetic schemes may be thought of as bottom-up processes where the chemical transformation occurs at the interface between the reacting phases.

This book is about the preparation of single-phase inorganic materials. The design concerns and associated process flows for multiphase/heterostructure devices (e.g., composite materials, semiconductor integrated circuits) are better covered in specialized engineering texts and so are omitted here. However, we cover top-down materials fabrication processes, such as plastic deformation and consolidation processing in some detail, topics that have traditionally been restricted to materials science and engineering courses. As with our first textbook, this book takes on a distinct historical tone and includes short biographical sketches of some of the people who have made seminal contributions to the field over the past century. We believe that students appreciate learning about their heritage, and the history of science is, after all, a worthy scholarly endeavor in and of itself.

To maximize the level of expertise applied to this endeavor, invitations were extended to two additional authors, Professor E. E. Carpenter and Dr. N. F. Dean, both of whom enthusiastically agreed to participate, and we are very grateful for their contributions. The four of us believe that this book would make an excellent companion to *Principles of Inorganic Materials Design,* together serving not only as strong introductory texts to materials science and engineering, chemistry, and physics students, but also as welcomed reference sources for working professionals. Some of the topics covered in our first book actually fit equally well here, being, in fact, essential components to discussions on the interplay between chemical structure, reaction energetics, and kinetics. We are very grateful to the publisher for allowing us to reproduce those portions in this work.

J. N. Lalena
D. A. Cleary
E. E. Carpenter
N. F. Dean

1 Crystallographic and Microstructural Considerations

The bulk properties of a solid, such as conductivity, magnetism, and second harmonic generation, hinge on the solid's structure, which, in turn, is normally that arrangement of a material's fundamental particles (molecules, atoms, or ions), with the lowest potential energy as a function of all the atomic positions. We have learned through computational approaches that interatomic potential energy is a function of short-range, long-range, and many-body interactions. For molecular-based substances, one must also consider van der Waals interactions, hydrogen bonds, and capillary and hydrophobic forces. At first glance, these noncovalent forces may seem of secondary importance, but their influence on governing the particular structure adopted by a substance, and hence its resulting properties, can be striking. Organic chemists have long been aware of this. For example, the double-helical structure of DNA is, to a large degree, a consequence of hydrogen bonding between the base pairs. In recent years, supramolecular chemists have focused attention on noncovalent structure-directing intramolecular and intermolecular interactions in the spontaneous formation of ordered aggregates, appropriately termed *chemical self-assembly processes*. It has been applied increasingly to the synthesis of hybrid organic–inorganic materials. However, due to certain limitations, self-assembly of purely inorganic substances, particularly materials in the micro- to millimeter size range (Section 1.5.2), is still in its infancy.

Externally, crystals typically possess morphologies showing the highest symmetry consistent with the chemical and spatial growth constraints imposed. The crystal faces tend to follow the *holohedral*, or *holosymmetric* symmetry, of the crystal class (i.e., they belong to the point group with the highest symmetry of its crystal system). However, as the relatively recently coined terms *crystal engineering* and *grain boundary engineering* (for polycrystalline materials) imply, to attain the optimal properties needed in any given engineering or functional application, it is often desirable—indeed, sometimes necessary—to control morphology (crystal shape, orientation) and/or microstructure (grain size, shape, and texture).

Perhaps the most common scenario is the need to produce crystals with specific crystallographic orientations. For example, large single-crystalline silicon wafers

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Inorganic Materials Synthesis and Fabrication, By John N. Lalena, David. A. Cleary,
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with particular crystallographic orientations are required for the fabrication of microelectronic devices. The atomic-scale surface topography of each orientation gives rise to a unique interfacial structure between the silicon substrate and films, either deposited or grown thermally. The interface is a significant portion of the total film volume in today's devices, where film thicknesses are in the nanometer range. With metal–oxide semiconductor field-effect transistor (MOSFET) devices, (100)-oriented silicon slices are currently used because they give more reliable gate oxides on thermal oxidation. However, for bipolar devices, the (111) orientation is used.

There are numerous other situations in which particular crystal orientations are required as starting material for the fabrication of devices. For example, high-quality quartz crystals are grown from seeds with specific orientations to maximize the obtainable number of parallelepiped units, called *cuts*, of that particular type for the production of crystal oscillators. The mode of vibration, and hence the corresponding frequency band for which it may be used, is dependent on the unit's crystallographic orientation and thickness, while the angle of the cut relative to the crystal face controls the frequency deviation over a specified temperature range. In a similar fashion, potassium titanyl phosphate, which is widely used for sum frequency generation (e.g., frequency doubling) requires cuts of specific crystallographic orientations that are determined solely by the nonlinear optical process for which it will be used.

Specific crystallographic orientations and symmetry-dependent properties may also be exploited in synthetic schemes in which solids are used as starting materials. Properties and phenomena are facilitated along, or may even be restricted to, specific crystallographic directions or orientations. Examples of anisotropy so utilized include:

- *Transport properties.* Ionic conduction and atomic diffusion are usually easier along certain crystallographic directions or planes.
- *Epitaxial and topotactic controlled reactions.* There are preferred crystallographic orientations for substrates on which single-crystalline films are grown via *homoepitaxy* (the film is the same substance and has the same orientation as the substrate) or heteroepitaxy (the film is a different substance and may have a different orientation than the substrate). Because of lattice matching between reactant and product phases, epitaxial reactions (surface structure controlled), as well as topotactic reactions (bulk crystal structure controlled), proceed under milder synthetic conditions. The kinetic control afforded by the surface step structure in these processes makes possible the obtainment of phases that are thermodynamically metastable but kinetically stable. For example, $YMnO_3$ crystallizes in the hexagonal system at atmospheric pressure, but cubic perovskite films have been grown on $NdGaO_3$ substrates.
- *Chemical activity (functionality).* Some crystal facets may be significantly more chemically reactive than others. For example, the (100) face of vanadyl

pyrophosphate is active for the oxidation of n-butane to maleic anhydride, whereas the other faces are not.

- *Magnetic anisotropy.* In conjunction with slip casting, magnetic alignment of anisotropic particles may be used to produce polycrystalline materials with a preferred orientation, or texture.
- *Plasticity.* Slip, the gliding motion of full planes of atoms or partial planes, called *dislocation*, allows for the deformation processing of polycrystalline metals (forging, extrusion, rolling, swaging, and drawing). Slip occurs much more readily across close-packed planes in close-packed directions.

Because the central topic of this book is synthesis and fabrication, the correlation of crystal *structure* with physical properties is not of primary importance. Nonetheless, as the preceding paragraphs imply, a discussion of the correlation between crystal *symmetry* and physical properties would be wise. The question is: At what point should we make that presentation? Crystal symmetry/physical property correlations were elucidated by physicists in the early to mid-nineteenth century, concurrent with mineralogists' work on the classification of crystals based on geometric form, decades before space group theory and its experimental confirmation by x-ray diffraction made possible crystal structure determination. It therefore seems fitting to place that treatment here, followed by morphological crystallography, the theory of space lattices, surface and interfacial structure, and finally, the crystallographic and morphological considerations pertinent to various preparative routes, which is in roughly the same chronological order as their development.

It must first be recognized that morphological (external) symmetry is not always identical with a specimen's true crystallographic symmetry. As a result, discrepancies between the observed and expected symmetry of a physical property may arise when the symmetry of the crystal is deduced solely from its external appearance. *Consequently, it is more appropriate to deduce the structure and symmetry of a crystal from its physical properties*. An auspiciously unambiguous relationship exists between crystallographic symmetry and physical properties. This principle, which is a basic postulate of crystal physics, was first recognized by Franz Ernst Neumann (1798–1895) in the 1830s (Neumann, 1833) and was later formalized by Neumann's students Woldemar Voigt (1850–1918) and Bernhard Minnigerode (1837–1896) in the 1880s. It may be stated as follows: *The symmetry of a physical phenomenon is* [*at least*] *as high as the crystallographic symmetry*. Similarly, the orientation of the principal axes of the matter tensor representing the physical property must also be consistent with the crystal symmetry (Section 1.1). In addition to physical properties such as electronic and thermal conductivity, mechanical properties such as elasticity, hardness, and yield strength also comply with the crystallographic symmetry.

There are two important points to remember regarding the applicability of Neumann's principle. First, forces *imposed* on a crystal, including mechanical stresses and electric fields, can have any arbitrary direction or orientation. These types of forces are represented mathematically with field tensors, not matter tensors, and so are not subject to Neumann's principle. Second, Neumann's principle applies strictly to physical properties only. Nevertheless, because of crystalline anisotropy, chemical activity (e.g., oxidation rate, corrosion rate, etch rate) is also found to be either direction- or orientation-dependent. The degree of surface chemical activity generally correlates with the density of bonds (particularly dangling bonds), which, in turn, is influenced by energy-lowering surface reconstructions, a topic we cover in Section 2.3.1.3. For example, the silicon (111) face etches more slowly than, but oxidizes nearly twice as rapidly as, the Si(001) face.

1.1. RELATIONSHIP BETWEEN PHYSICAL PROPERTIES AND CRYSTALLOGRAPHIC SYMMETRY

Neumann's principle asserts that the symmetry elements of any physical property of a crystal must include, at least, all the symmetry elements of the point group of the crystal. Single crystals are generally not isotropic. Hence, the physical properties of single crystals generally will be anisotropic, that is, dependent on the direction in which they are measured. For example, only with cubic crystals or polycrystals possessing a random crystallite orientation are the directions of heat flow (the flux) and the temperature gradient (the driving force) parallel. Accordingly, it is necessary to use mathematical expressions known as *tensors* to explain anisotropic properties in the most precise manner.

A tensor is an object with many components that look and act like components of ordinary vectors. The number of components necessary to describe a tensor is given by p^n, where p is the number of dimensions in space and n is called the *rank*. For example, a zero-rank tensor is a scalar, which has $3^0 = 1$ component regardless of the value of p. A first-rank tensor is a vector; it has three components in three-dimensional space (3^1), the projections of the vector along the axes of some reference frame (e.g., the mutually perpendicular axes of a Cartesian coordinate system). Although the magnitude and direction of a physical quantity, intuitively, do not depend on our arbitrary choice of a reference frame, a vector is defined by specifying its components from projections onto the individual axes of the reference system. Thus, a vector can be defined by the way these components change, or transform, as the reference system is changed by a rotation or reflection. This is called a *transformation law*. For example, a vector becomes the negative of itself if the reference frame is rotated 180°, whereas a scalar is invariant to coordinate system changes (Lalena and Cleary, 2005).

Second-rank tensors such as transport properties relate two first-rank tensors, or vectors. Thus, a second-rank tensor representing a physical property has nine components (3^2), usually written in 3×3 matrixlike notation. Each component is associated with two axes: one from the set of some reference frame and one from the material frame. Three equations, each containing three terms on the right-hand side, are needed to describe a second-rank tensor exactly. For a general second-rank tensor τ that relates two vectors, **p** and **q**, in a coordinate system with axes x_1, x_2, x_3, we have

$$\begin{aligned} p_1 &= \tau_{11}q_1 \quad \tau_{12}q_2 \quad \tau_{13}q_3 \\ p_2 &= \tau_{21}q_1 \quad \tau_{22}q_2 \quad \tau_{23}q_3 \\ p_3 &= \tau_{31}q_1 \quad \tau_{32}q_2 \quad \tau_{33}q_3 \end{aligned} \tag{1.1}$$

The tensor, with components τ_{ij}, is written in matrixlike notation as

$$\begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{bmatrix} \tag{1.2}$$

Note that each component of **p** is related to all three components of **q**. Thus, each component of the tensor is associated with a pair of axes. For example, τ_{32} gives the component of **p** parallel to x_3 when **q** is parallel to x_2. In general, the number of indices assigned to a tensor component is equal to the rank of the tensor. Tensors of all ranks, like vectors, are defined by their transformation laws. For our purposes, we need not consider these.

Fortunately, several simplifications can be made (Nye, 1957). Transport phenomena, for example, are processes whereby systems transition from a state of nonequilibrium to a state of equilibrium. Thus, they fall within the realm of irreversible or nonequilibrium thermodynamics. *Onsager's theorem*, which is central to nonequilibrium thermodynamics, dictates that as a consequence of time-reversible symmetry, the off-diagonal elements of a transport property tensor are symmetrical (i.e., $\tau_{ij} = \tau_{ji}$). This is known as a *reciprocal relation*. The Norwegian physical chemist Lars Onsager (1903–1976) was awarded the 1968 Nobel Prize in Chemistry for reciprocal relations. Thus, the tensor above can be rewritten as

$$\begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{12} & \tau_{22} & \tau_{23} \\ \tau_{13} & \tau_{23} & \tau_{33} \end{bmatrix} \tag{1.3}$$

Note the perhaps subtle, but very important, change in subscripts from Eq. 1.2, leaving us with merely six independent components.

Finally, symmetrical tensors can also be diagonalized. For second-rank tensors, three mutually perpendicular unit vectors can be found that define three *principal axes*, such that if these axes are used as coordinate axes, the matrices are diagonal. This leaves

$$\begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \tag{1.4}$$

Because of this further simplification, only three independent quantities in a symmetrical second-rank tensor are needed to define the magnitudes of the principal components. The other three components (from the initial six), however, are still needed to specify the directions of the axes with respect to the original coordinate system.

In the case of physical properties, crystal symmetry imposes even more restrictions on the number of independent components (Nye, 1957). A tensor representing a physical property must be invariant with regard to every symmetry operation of the given crystal class. Tensors that must conform to the crystal symmetry in this way are called *matter tensors*. The orientation of the principal axes of a matter tensor must also be consistent with the crystal symmetry. The principal axes of crystals with orthogonal crystallographic axes will be parallel to the crystallographic axes. In the monoclinic system, the x and z crystallographic axes are orthogonal to each other but nonorthogonal to y. For triclinc crystals, there are no fixed relations between either the principal axes or crystallographic axes, and no restrictions on the directions of the principal axes. The effects of crystal symmetry on symmetrical second-rank matter tensors are given below.

For cubic crystals and nontextured polycrystals, we have

$$\begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{11} & 0 \\ 0 & 0 & \tau_{11} \end{bmatrix} \tag{1.5}$$

For tetragonal, trigonal, and hexagonal crystals,

$$\begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{11} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \tag{1.6}$$

For orthorhombic crystals,

$$\begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \tag{1.7}$$

For monoclinic crystals,

$$\begin{bmatrix} \tau_{11} & 0 & \tau_{13} \\ 0 & \tau_{22} & 0 \\ \tau_{13} & 0 & \tau_{33} \end{bmatrix} \tag{1.8}$$

For triclinic crystals,

$$\begin{bmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{12} & \tau_{22} & \tau_{23} \\ \tau_{13} & \tau_{23} & \tau_{33} \end{bmatrix} \tag{1.9}$$

The diagonal elements in the tensors above follow from the indistinguishability of the axes in their respective crystal classes. For example, if we denote the normalized unit length of the three crystallographic axes in each crystal class with the letters a, b, c and denote the angles between these three axes with the Greek letters α, β, γ, we can see that there are three indistinguishable orthonormal dimensions (orthogonal axes normalized to the same unit length) in the cubic class ($a = b = c$; $\alpha = \beta = \gamma = 90^\circ$); two orthonormal dimensions in the tetragonal class ($a = b \neq c$; $\alpha = \beta = \gamma = 90^\circ$); two orthonormal dimensions in the trigonal class ($a = b = c$; $\alpha = \beta = \gamma \neq 90^\circ$); two orthonormal dimensions in the hexagonal class ($a = b \neq c$; $\alpha = \beta = 90^\circ, \gamma = 120^\circ$); no orthonormal dimensions in the orthorhombic class ($a \neq b \neq c$; $\alpha = \beta = \gamma = 90^\circ$); no orthonormal dimensions in the monoclinic class ($a \neq b \neq c$; $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$); and no orthonormal dimensions in the triclinic class ($a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90^\circ$). The off-diagonal elements in the monoclinic and triclinic crystals give the additional components necessary to specify the tensor. Notice that a cubic single crystal is isometric and so has isotropic properties. The same is also true for polycrystals with a random crystallite orientation (e.g., powders), regardless of the crystal class to which the substance belongs. Thus, a single scalar quantity is sufficient for describing the conductivity in crystals of the cubic class and nontextured polycrystalline materials (Lalena and Cleary, 2005).

It is sometimes possible to use the anisotropy in certain physical properties advantageously during fabrication processes. For example, the magnetic susceptibility, which describes the magnetic response of a substance to an applied magnetic field, is a second-rank matter tensor. It is the proportionality constant between the magnetization of the substance and the applied field strength. When placed in a magnetic field, a crystal with an anisotropic magnetic susceptibility will rotate to an angle in order to minimize the magnetic free-energy density. This magnetic alignment behavior can aid in texture control of ceramics and clays if the particles are sufficiently dispersed to minimize particle–particle interactions, which can be accomplished with slip casting or another powder suspension process (Section 7.3.2). The route has been used to prepare many bulk substances and thin films, including some with only a small anisotropic paramagnetic or diamagnetic susceptibility, such as gadolinium barium copper oxide, zinc oxide, and titanium dioxide (anatase), with textured (grain-aligned) microstructures and correspondingly improved physical properties (Lalena and Cleary, 2005).

1.1.1. Geometrical Representation of Tensors

The components of a symmetrical second-rank tensor, referred to its principal axes, transform like the three coefficients of the general equation of a second-degree surface (a quadric) referred to its principal axes (Nye, 1957). Hence, if all three of the quadric's coefficients are positive, an ellipsoid becomes the geometrical representation of a symmetrical second-rank tensor property (e.g., electrical and thermal conductivity, permittivity, permeability, dielectric and magnetic susceptibility). The ellipsoid has inherent symmetry *mmm*. The relevant features are that (1) it is centrosymmetric, (2) it has three mirror planes perpendicular to the

TABLE 1.1 Relationships Between the Quadric and Crystal Axes for Symmetrical Second-Rank Tensors

Crystal Class	Tensor Components to Be Measured	Restrictions on Principal Directions and Principal Values
Cubic	One value	Principal directions must be parallel to crystal axes; all three principal values equal in magnitude (isotropic)
Tetragonal	Two values	Principal directions must be parallel to crystal axes; two principal values equal in magnitude
Orthorhombic	Three values	Principal directions aligned with crystal axes; no restrictions on values
Hexagonal	Two values	One principal direction aligned with three-fold crystal axis; two principal values equal in magnitude
Trigonal	Two values	One principal direction aligned with three fold crystal axis; two principal values equal
Monoclinic	Three values plus one angle	One principal direction aligned with two-fold crystal axis; no restrictions on values
Triclinic	Three values plus three directions	No restrictions on directions or values; need to measure three directions and three values

principal directions, and (3) its twofold rotation axes are parallel to the principal directions. We have already stated that the orientation of the principal axes of the matter tensor representing a physical property must be consistent with the crystal symmetry. What this means is that the exact shape of the tensor property and its quadric, as well as the orientation of the quadric with respect to the crystal, are all restricted by the crystallographic symmetry. Table 1.1 lists the relationships between the quadric and the crystal axes for the various crystal classes.

1.1.2. Measurement of Physical Properties of Crystals

The most straightforward method for the measurement of a physical property on a single crystal along its principal axes often involves the initial removal of a uniform regularly shaped section (e.g., a parallelepiped or circular disk) from the crystal. This, in turn, usually requires that the single crystal first be oriented, for example, by using a Laue back-reflection technique. Consider the coefficient of thermal expansion (CTE) along the two independent crystallographic axes of a crystal belonging to the tetragonal crystal class, which may be measured using a thermomechanical analyzer (TMA). Measurement of this property is accomplished by first orienting the crystal, followed by cutting out a rectangular parallelepiped specimen (e.g., using a diamond saw blade), and finally, taking the length change along the crystal axes (a, c) directly from the TMA measurements along both the shorter and longer dimensions of the parallelepiped. Of course, the CTE, as with other intensive properties (which are independent of the mass of the sample) such as conductivity, cannot really be measured directly but rather, must be calculated from measuring the corresponding extensive property.

Often, it is not possible to obtain single crystals that are large enough to be worked with in a convenient manner. In those cases, physical properties must be measured on polycrystalline samples. There is always discrepancy, or disagreement, between measured physical properties of single crystals and polycrystals due to microstructural effects. Hence, physical properties measured from polycrystalline samples are sometimes considered less reliable from a reproducibility standpoint.

1.2. MORPHOLOGICAL CRYSTALLOGRAPHY

Before the advent of diffractometry, crystallographers could only visually examine crystals. However, an entire classification system was developed that is still in use today for describing a crystal's morphology, or external appearance, and for assigning a crystal's external symmetry to a point group. Mineralogists in the early nineteenth century focused on the theory of crystal forms from purely geometrical points of view. Although these systems do not make reference to primitive forms or any other theory of internal structure, they are perfectly valid approaches. The theory of crystal forms was developed independently by Christian Samuel Weiss (1780–1856), professor of geology and mineralogy at the University of Berlin, and by the mineralogist Friedrich Karl Mohs (1773–1839), in 1816 and 1822, respectively. Weiss was able to derive four definite crystal form classes: tessular (isometric, or cubic), pyramidal (tetragonal), prismatic (orthorhombic), and rhombohedral (hexagonal), by choosing as coordinate axes lines drawn joining opposite corners of certain forms. The monoclinic and triclinic systems were considered by Weiss to be hemihedral and tetragonal modifications of the prismatic system, but were considered distinct in Mohs' more advanced treatment (Lalena, 2006).

Weiss and Mohs also developed notation systems relating each face to the coordinate axes, but these were surpassed in use by a system first introduced by the British polymath William Whewell (1794–1866) during a crystallography fellowship period in 1825, and later incorporated in an 1839 book by his student William Hallowes Miller (1801–1880). The notation system, now named after Miller, is discussed further in Section 1.3.2.

Just as there is a correspondence between the symmetry of crystals and that of their physical properties, there is also a connection between the symmetry exhibited by a crystal at the macroscopic and microscopic length scales, in other words, between the "external" crystal morphology and true "internal" crystal structure. Under favorable circumstances, the point group (but not the space group) to which a crystal belongs can be determined solely by examination of the crystal morphology, without the need of confirmation by x-ray diffraction. It is not always possible because although many crystal forms (a collection of equivalent faces related by symmetry) are normally apparent in a typical crystal specimen, some forms may be absent or show unequal development.

If a crystal is grown in a symmetrical growth environment (e.g., freely suspended in a liquid), its morphological symmetry is exactly that of the isogonal point group (the point group with the same angular relations as that) of the space lattice. Morphological symmetry may depart from the true point group symmetry of the space lattice because of differing intrinsic growth rates of the various faces or because of nonsymmetrical growth conditions (Buerger, 1978). Even the presence of dislocations is believed to influence the growth rates and thus the development of various forms (Dowty, 1976). A comprehensive treatment of geometric crystallography, including morphological and internal symmetry, their interrelationship, and a systematic derivation of all the crystallographic point groups and space groups can be found in Buerger's classic textbook *Elementary Crystallography* (Buerger, 1978).

1.2.1. Single-Crystal Morphology

There are four commonly used terms for describing morphology which should be understood: zone, form, habit, and twin. A *zone* is a volume enclosed by a set of faces that intersect one another along parallel edges. The zone axis is the common edge direction. For example, the crystallographic axes and the edges of a crystal are all zone axes. A crystal *form* is a collection of equivalent faces related by symmetry (e.g., a polyhedron). One can choose the directions of three edges of a crystal as coordinate axes (x, y, z) and define unit lengths (a, b, c) along these axes by choosing a plane parallel to a crystal face that cuts all three axes. For any other crystal face, integers (h, k, l) can be found such that the intercepts the face makes on the three axes are in the ratios $a:h$, $b:k$, $c:l$. Together, these three integers describe the orientation of a crystal face. The integers are prime and simple (small) and they may be positive or negative in sign.

In a cube (a hexahedron), all the faces are equivalent. The six faces have indices (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001), and $(00\bar{1})$, but the set is denoted as {100}, signifying the entire cube, whereas (100) signifies just one face. In a similar fashion, an octahedron has the form symbol {111} and consists of the following eight faces: (111), $(\bar{1}\bar{1}\bar{1})$, $(1\bar{1}1)$, $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, $(\bar{1}11)$, and $(11\bar{1})$. One or more crystal forms are usually apparent in the crystal morphology, and these may be consistent with the point group symmetry of the lattice. A crystal of α-quartz (low quartz), for instance, may display five external forms showing trigonal point group symmetry. Symmetry considerations limit the number of possible types of crystal forms to 47. However, when we look at crystals from the lattice-based viewpoint, there are only seven crystal systems. This is because there are 15 different forms, for example, in the cubic (isometric) crystal system alone. The 47 forms are listed in Table 1.2, grouped by the crystal systems to which they belong. Included in the table are representative examples of minerals exhibiting these form developments.

TABLE 1.2 The 47 Possible Forms Distributed Among the Various Crystal Systems

Crystal Class	Symmetry Elements[a]	Forms Occurring in the Respective Crystal Class	Representative Inorganic/Mineral Substances
Triclinic			
1	E	Pedion	$Ca_8B_{18}Cl_4 \cdot 4H_2O$
$\bar{1}$	E, i	Pinacoid	$MnSiO_3$
Monoclinic			
2	E, C_2	Sphenoid, pedion, pinacoid	$FeAl_2(SO_4)_4 \cdot 22H_2O$
m	E, σ_h	Sphenoid, pedion, pinacoid	$CaMg(AsO_4)F$
$2/m$	E, C_2, I, σ_h	Prism, pinacoid	As_2S_3
Orthorhombic			
222	E, C_2, C_2', C_2'	Disphenoid, prism, pinacoid	$ZnSO_4 \cdot 7H_2O$
$mm2$	$E, C_2, \sigma_v, \sigma_v$	Pyramid, prism, dome, pinacoid, pedion	$BaAl_2Si_3O_{10} \cdot 2H_2O$
mmm	$E, C_2, C_2', C_2', \sigma_v, \sigma_v, \sigma_h$	Dipyramid, prism, pinacoid	Sulfur
Tetragonal			
4	$E, 2C_4, C_2$	Tetragonal pyramid, tetragonal prism, pedion	None known
$\bar{4}$	$E, 2S_4, C_2$	Tetragonal disphenoid, tetragonal prism, pinacoid	$Ca_2B(OH)_4AsO_4$
$4/m$	$E, 2C_4, C_2, i, 2S_4, \sigma_h$	Tetragonal dipyramid, tetragonal prism, pinacoid	$PbMoO_4$
422	$E, 2C_4, C_2, 2C_2', 2C_2''$	Tetragonal trapezohedron, tetragonal dipyramid, ditetragonal prism, tetragonal prism, pinacoid	$Pb_2CO_3Cl_2$
$4mm$	$E, 2C_4, C_2, 2\sigma_v, 2\sigma_d$	Ditetragonal pyramid, tetragonal pyramid, ditetragonal prism, tetragonal prism, pedion	$Pb_2Cu(OH)_4Cl_2$
$\bar{4}2m$	$E, C_2, 2C_2', 2\sigma_d, 2S_4$	Tetragonal scalenohedron, tetragonal disphenoid, tetragonal bipyramid, ditetragonal prism, tetragonal prism, pinacoid	Cu_2FeSnS_4

(*continued overleaf*)

TABLE 1.2 **(*continued*)**

Crystal Class	Symmetry Elements[a]	Forms Occurring in the Respective Crystal Class	Representative Inorganic/Mineral Substances
$4/mmm$	E, $2C_4$, C_2, $2C_2'$, $2C_2''$, i, $2S_4$, σ_h, $2\sigma_v$, $2\sigma_d$	Ditetragonal dipyramid, tetragonal dipyramid, ditetragonal prism, tetragonal prism, pinacoid	Rutile
Trigonal (rhombohedral)			
$\underline{3}$	E, $2C_3$	Trigonal pyramid	$NaIO_4 \cdot 3H_2O$
3	E, $2C_3$, i, $2S_6$	Rhombohedron, hexagonal prism, pinacoid	$FeTiO_3$
32	E, $2C_3$, $3C_2'$	Trigonal trapezohedron, rhombohedron, trigonal dipyramid, ditrigonal prism, hexagonal prism, trigonal prism, pinacoid	Low quartz
$3m$	E, $2C_3$, $3\sigma_v$	Ditrigonal pyramid, trigonal pyramid, hexagonal pyramid, ditrigonal prism, trigonal prism, hexagonal prism, pedion	$KBrO_3$
$\bar{3}$m	E, $2C_3$, $3C_2'$	Hexagonal scalenohedron, rhombohedron, hexagonal dipyramid, dihexagonal prism, hexagonal prism, pinacoid	Corundum
Hexagonal			
$\underline{6}$	E, $2C_6$, $2C_3$, C_2	Hexagonal prism, pedion	Nepheline
6	E, $2C_6$, σ_h, $2S_3$	Trigonal dipyramid, trigonal prism, pinacoid	None
$6/m$	E, $2C_6$, $2C_3$, C_2, i, $2S_3$, $2S_6$, σ_h	Hexagonal dipyramid, hexagonal prism, pinacoid	Apatite
622	E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$	Hexagonal trapezohedron, hexagonal dipyramid, dihexagonal prism, hexagonal prism, pedion	High quartz

6*mmm*	E, $2C_6$, $2C_3$, C_2, $3\sigma_v$, $3\sigma_d$	Dihexagonal pyramid, hexagonal pyramid, dihexagonal prism, hexagonal prism, pedion	Wurtzite
$\bar{6}$m2	E, $2C_3$, $3C_2'$, σ_h, $2S_3$, $3\sigma_v$	Ditrigonal dipyramid, trigonal dipyramid, hexagonal dipyramid, ditrigonal prism, hexagonal prism, trigonal prism, pinacoid	$BaTiSi_3O_9$
6/*mmm*	E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, i, $2S_3$, $2S_6$, σ_h, $3\sigma_v$, $3\sigma_d$	Dihexagonal dipyramid, hexagonal dipyramid, dihexagonal prism, hexagonal prism, pinacoid	Beryl
Cubic			
23	E, $8C_3$, $3C_2$	Tetartoid, deltohedron, tristetrahedron, pyritohedron, tetrahedron, dodecahedron, cube	$NaBrO_3$
*m*3	E, $8C_3$, $3C_2$, i, $8S_6$, $3\sigma_h$	Diploid, trisoctahedron, trapezohedron, pyritohedron, octahedron, dodecahedron, cube	Pyrite
432	E, $8C_3$, $3C_2$, $6C_2$, $6C_4$	Gyroid, trisoctahedron, trapezohedron, tetrahexahedron, octahedron, dodecahedron, cube	None
$\bar{4}$3m	E, $8C_3$, $3C_2$, $6\sigma_d$, $6S_4$	Hextetrahedron, deltohedron, tristetrahedron, tetrahexahedron, tetrahedron, dodecahedron, cube	Sphalerite
*m*3*m*	E, $8C_3$, $3C_2$, $6C_2$, $6C_4$, $6\sigma_d$, i, $8S_6$, $3\sigma_h$, $3\sigma_h$, $6S_4$	Hexoctahedron, trisoctahedron, trapezohedron, tetrahexahedron, octahedron, dodecahedron, cube	Diamond

Source: Buerger (1978), pp. 112–168.

[a] *E*, identity element; i, inversion center; C_n, n-fold proper rotation axis; S_n, n-fold improper rotation (rotoreflection) axis; σ_v, vertical mirror plane (reflection plane contains principal axis); σ_h, horizontal mirror plane (reflection plane perpendicular to principal axis); σ_d, diagonal mirror plane (reflection plane contains principal axis and bisects the angle between the twofold axes normal to the principal axis).

The cube and octahedron are both referred to as *closed forms* because they are comprised of a set of equivalent faces that enclose space completely. All 15 forms in the isometric system, which include the cube and octahedron, are closed. One of the isometric forms, the hexoctahedron, has 48 faces. Six forms have 24 faces (tetrahexahedron, trisoctahedron, trapezohedron, hextetrahedron, gyroid, and diploid). Five forms have 12 faces (dodecahedron, tristetrahedron, pyritohedron, deltahedron, and tetartoid). The final three isometric and closed forms are, perhaps, more familiar to the chemist. These are the tetrahedron (4 faces), cube (6 faces), and octahedron (8 faces). Nonisometric closed forms include the dipyramids (6, 8, 12, 16, or 24 faces), scalenohedrons (8 or 12 faces), the rhombic and tetragonal disphenoids (4 faces), the rhombohedron (6 faces), the ditrigonal prism (6 faces), the tetragonal trapezohedron (8 faces), and the hexagonal trapezohedron (12 faces). *Open forms* do not enclose space. These include the prisms with 3, 4, 6, 8, or 12 faces, parallel to the rotation axis. These parallel faces are equivalent but do not enclose space. Other open (and nonisometric) forms include the pyramid (3, 4, 6, 8, or 12 faces), domes (2 faces), sphenoids (2 faces), pinacoids (2 faces), and pedions (1 face). Open forms may only exist in combination with a closed form or with another open form.

As mentioned earlier, a crystal's external morphology may not be consistent with the true point group symmetry of the space lattice. This may be due to (1) one or more forms being absent or showing anisotropic development of equivalent faces, or (2) the true symmetry of the unit cell simply not being manifested macroscopically upon infinite translation in three dimensions. Let's first consider anisotropic development of faces. The growth rates of faces—even crystallographically equivalent faces and faces of crystals belonging to the isotropic (cubic) crystal class—need not be identical. This may be due to kinetic or thermodynamic factors.

One possible reason is a nonsymmetrical growth environment. For example, the nutrient supply may be blocked from reaching certain crystal faces by foreign objects or by the presence of habit-modifying impurities. Since visible crystal faces correspond to the slow-growing faces, the unblocked faces may grow so much faster that only the blocked faces are left visible where as the fast-growing faces transform into vertices. Consider pyrite, which belongs to the cubic system. Crystal growth relies on a layer-by-layer deposition on a nucleus via an *external* flux of adatom species, which may very well be anisotropic. Hence, unequal development of crystallographically equivalent {100} faces can lead to pyrite crystals exhibiting acicular and platelike morphologies instead of the anticipated cube shape. In fact, not all crystals exhibit distinct polyhedral shapes. Those that do not are termed *nonfaceted crystals*. The word *habit* is used to describe the overall external shape of a crystal specimen. Habits, which can be polyhedral or nonpolyhedral, may be described as cubic, octahedral, fibrous, acicular, prismatic, dendritic (treelike), platy, blocky, or bladelike, among many other terms.

As a second example of a mineral with several possible form developments, let's consider, in a little more detail, quartz (Figure 1.1). Quartz belongs to the symmetry class 32, which has two threefold rotation axes and three twofold axes.

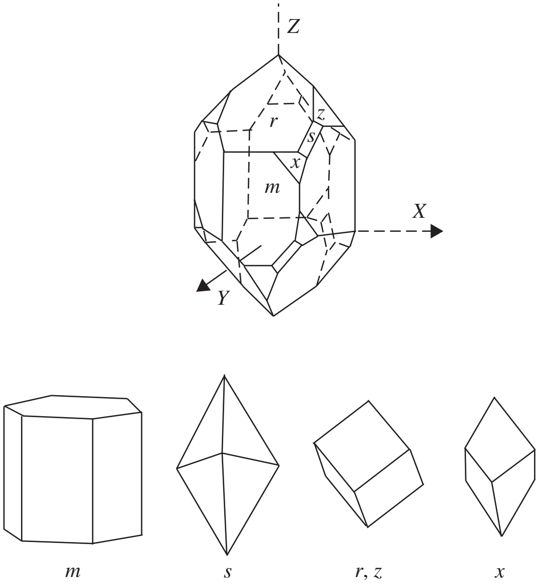

Figure 1.1 Top: Quartz crystal exhibiting the true symmetry of the crystal class to which quartz belongs. Bottom: The forms comprising such a quartz crystal. From left to right, the hexagonal prism, trigonal dipyramid, rhombohedron, and trigonal trapezohedron.

Five forms must necessarily be present to reveal this symmetry: the $\{10\bar{1}0\}$, the {1011}, the {0111}, the {1121}, and the {5161}. These correspond, respectively, to a hexagonal prism; a dominant, or “positive,” rhombohedron; a subordinate, or “negative,” rhombohedron; a trigonal (triangular) dipyramid; and a trigonal trapezohedron. In mineralogy, these are labeled, in the order given, with the lowercase letters *m, r, z, s*, and *x*. Three orthogonal crystallographic axes are defined as: *X*, bisecting the angle between adjacent hexagonal prism faces; *Y*, which runs through the prism face at right angles to *X*; and *Z*, an axis of threefold symmetry.

As illustrated in Figure 1.1, both rhombohedra (*r* and *z*) cap, or terminate, the quartz crystal on each end. Each rhombohedron has a set of three faces. By convention, the larger set of three faces is considered the positive rhombohedron. When present, the trigonal trapezohedron (*x*) is seen at the junction of two prism faces (*m*) and the positive rhombohedron and it displays a trapezohedral planar shape. The trigonal pyramid (*s*) is at the junction of the positive rhombohedron and the prism, which is in line vertically with the negative rhombohedron. It typically forms an elongated rhombus-shaped face. However, in some specimens, one or more of the aforementioned forms are missing or show development inconsistent with the true point group symmetry of quartz. In fact, most quartz crystals do not display the trigonal dipyramid or trapezohedron faces, the former being especially rare. With these two forms absent, the rhombohedra may exhibit either equal or unequal development. The latter case implies the highest apparent (but still false) crystal symmetry, as the hexagonal prism appears to be terminated at both ends with hexagonal pyramids. It is also possible for the hexagonal prism to be absent, in which case the combination of the two rhombohedra results in a hexagonal dipyramid (or bipyramid), termed a *quartzoid*.

We mentioned earlier that the true symmetry of the unit cell may not simply be manifested macroscopically upon infinite translation in three dimensions. Buerger has illustrated this with the mineral nepheline, $(Na,K)AlSiO_4$ (Buerger, 1978). The true symmetry of the nepheline crystal lattice, the symmetry of the unit cell, consists merely of a sixfold rotation axis (class 6) as would be exhibited by a hexagonal prism with nonequivalent halves. That is, there is no mirror plane perpendicular to the rotation axis. However, the absence of this mirror plane is obviously not macroscopically visible in the hexagonal prism form development of nepheline, implying a higher apparent symmetry ($6/mmm$).

The situation with crystallized iodoform, CHI_3, is similar. The molecules are strictly pyramidal, but the crystal contains complementary "positive" and "negative" pyramids capping a hexagonal prism, as do the minerals zinkenite ($Pb_9Sb_{22}S_{42}$) and finnemanite [$Pb_5(AsO_3)_3Cl$]. In fact, no crystals showing form development consistent with class 6 symmetry have been observed. It is observed, rather, that form developments tend to follow the holohedral or holosymmetric symmetry of the crystal class (i.e., the point group with the highest symmetry of its crystal system). This is most commonly manifested by equal development of complementary forms in the merosymmetric classes (i.e., those with less symmetry than the lattice).

Often, the habit assumed by a particular specimen is under kinetic control, being dependent primarily on the growth environment. If crystals grow into one another, as they do in solidification products and polycrystals, it is possible that no forms will be well developed. However, when multiple crystal forms are present, it is possible that some forms (sets of equivalent faces) might have intrinsically higher growth rates than others. Form developments tend to lower the surface energy of the crystal. Surface energy is a function of several parameters:

- The distance of the face from the center of the crystal
- The face orientation, or Miller (hkl) indices
- Surface roughness
- The radius of curvature

Under equilibrium growth conditions, the fastest crystal growth will occur in the direction perpendicular to the face with the highest surface energy. As a consequence of this tendency, the total area of high-energy faces is reduced while that of low-energy faces is increased, which effectively results in an overall lowering of the surface energy of the crystal. For nonfaceted crystals, a smaller radius of curvature possesses a higher energy than one with a larger radius of curvature. The effect of surface energy on crystal morphology is discussed in detail in Section 2.3.

Two methods have traditionally been used to rationalize morphology resulting from the differing growth rates of various faces in terms of the lattice symmetry of the crystal. The first is the *Donnay–Harker method* (Donnay and Harker, 1937), which extends the work of Auguste Bravais (1811–1863) and Georges Friedel (1865–1933). The Bravais–Friedel empirical rule (Bravais, 1866; Friedel, 1907) was that the relative morphological importance of crystal forms is in the same order as the concentration of lattice points on their crystal faces, the *reticular density*. The dominant faces represent those planes cutting through the greatest densities of lattice points. Ranking the crystal forms in order of decreasing importance is also equivalent to ranking them in order of increasing reticular area or to decreasing interplanar spacings, which is proportional to the Miller indices of the faces. Hence, those faces with low Miller indices tend to be the morphologically most important. Because the interplanar spacing is the same for all crystal classes in a system, the morphological importance of the various forms tends to follow the holosymmetric symmetry of the system (Buerger, 1978). Joseph D. H. Donnay (1902–1994) and David Harker (1906–1991) later refined the idea to account for all equivalence points, including not only lattice points but also nonlattice sites of identical internal coordinates (Donnay and Harker, 1937). Although it is often successful, the Donnay–Harker method takes no account of atomic arrangement or bonding and is not applicable to the prediction of surface structure (Dowty, 1976).

Bravais rule is an empirical observation, not a scientific law. Recently, it has been proposed that it may, arguably, be viewed as a manifestation of the Curie–Rosen principle of maximum symmetry from information theory, which states that *the degree of symmetry in an isolated system either remains constant or increases as the system evolves*. To understand the relevance of this principle here, it is necessary to define precisely what symmetry is, correlate it with *information entropy*, and establish the link between entropy in information theory and entropy in thermodynamics, which deals with physical nature. Shu-Kun Lin has attempted this (Lin, 1996). Symmetry is regarded as *invariance* of an object when it is subjected, as a whole, to certain transformations in the space of the variables describing it (e.g., rotation, reflection, translation). The degree of symmetry correlates with the degree of *information entropy*, or information loss (Lin, 1996, 2001; Rosen, 1996). For example, a high degree of information entropy is associated with a high degree of similarity. The maximum possible information entropy, indistinguishability (total loss of information), corresponds to perfect symmetry, or highest symmetry, and low orderliness. By contrast, low symmetry corresponds to distinguishability and high orderliness. The principle of maximum symmetry would then seem to imply that crystals should exhibit the highest possible symmetry consistent with the growth constraints imposed. Unfortunately, the link between informational entropy and thermodynamic entropy may only be philosophical; it is still a hotly debated topic. Nevertheless, the principle of maximum symmetry serves as a useful heuristic.

The second, more recent approach at explaining the different rates of growth along different crystallographic directions, addresses all of these aspects, and is known both as the *Hartman–Perdok theory* and the *periodic bond chain* (PBC) *method* (Hartman and Perdok, 1955a,b,c). It was developed originally by Piet Hartman and Wiepko Gerhardus Perdok (1914–2005), professor of applied crystallography at the University of Groningen, and was built on earlier work by Paul Niggli (1883–1953) and Robert Luling Parker (1893–1973). Hartmann and Perdok showed that crystal structure determines which directions will exhibit rapid growth rates due to a large energy gain which they called the *attachment energy*. As a result of this rapid growth, those faces grow themselves out of existence, becoming "consumed" by the slow-growing faces. In the PBC method, one first identifies infinite stoichiometric chains of atoms connected by strong bonds (the periodic bond chains). These chains do not have dipole moments perpendicular to their crystallographic direction. The strong bonds are the short bonds in the first coordination sphere formed during crystallization. Crystal faces either have two or more PBCs (flat, or F, faces), one PBC (stepped, or S, faces), or none (kinked, or K, faces). The F faces grow the slowest and are thus the morphologically important ones, while the K and S faces grow so quickly they should not be present in the crystal forms. We discuss the PBC method in more detail in Section 4.2.4. For crystal growth to proceed, it is necessary for the surface to capture and incorporate adatoms. Hence, another factor is the availability of surface sites that readily accommodate new growth units. The theory most successful at dealing with this issue is the terrace–ledge–kink (TLK) model, which is discussed further in Sections 1.4.1 and 2.3.1.2.

1.2.2. Twinned Crystals

A *twin* is a symmetrical intergrowth of two or more crystals, or "individuals," of the same substance (Figure 1.2). A *simple twin* contains two individuals; a *multiple twin* contains more than two individuals. The *twin element* is the geometric element about which a twin operation is performed, relating the different individuals in the twin. The twin element may be a reflection plane (*contact twins*) or a rotation axis (*penetration twins*). The twin operation is a symmetry operation for the twinned edifice only, not for the individuals. In *twinning by merohedry*, the twin and the individual lattice point group, as well as their translational symmetry, coincide. If both the point group and translational symmetries of the twin and individual differ, it is referred to as *twinning by reticular merohedry*. Most commonly, twinning is by *syngonic merohedry*, in which the twin operation is a symmetry element of the holohedral point group (one of the seven point groups exhibiting the complete symmetry of the seven crystal systems) while the point group of the individual crystals is a subgroup, exhibiting less then complete (holohedral) symmetry. With *metric merohedry*, the individual lattice has an accidentally specialized metric corresponding to a higher holohedry and a twin operation exists belonging only to the higher holohedry. For example, a twin operation belonging to an orthorhombic lattice may exist for a twinned edifice comprised of two monoclinic crystals. The empirical rule of merohedral twinning was developed originally by Auguste Bravais, François-Ernest Mallard (1833–1894), and, later, Georges Friedel.

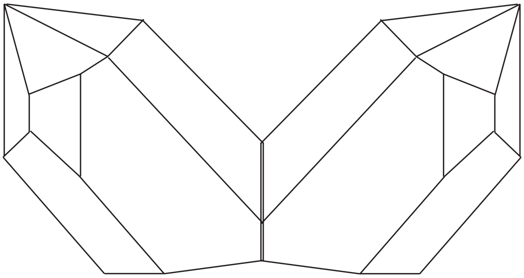

Figure 1.2 "Japan law" contact twin quartz crystal. This type of twinning was discovered in 1829 by C. S. Weiss in quartz crystal from the La Gardette mine in France. However, because of the abundance of these specimens in Japan, they are now known as *Japanese twins*.

Like a grain boundary, the twin boundary is a higher-energy state relative to the crystal. However, because a twin boundary is highly ordered, it is of much lower energy than a typical nontwin grain boundary. Recognizing this, Buerger later proposed that *if the crystal structure is of such a nature that, in detail, it permits a continuation of itself in alternative twin junction configuration, without involving violation of the immediate coordination requirements (the first coordination sphere) of its atoms, the junction has low energy and the twin is energetically possible* (Buerger, 1945).

Twins may also be divided into the following categories based on their origin: *transformation twins* and *growth twins, gliding twins. Growth twins* originate at the nucleation stage under conditions of supersaturation, where there is greater likelihood for the arrival of clusters of atoms, already coordinated, at the twin position. Such twins persist and grow if subsequent clusters of adatoms continue to arrive in that fashion. *Glide twinning* is caused by a specific type of structural shear in plastic deformation. The lower-energy nontwined crystals absorb part of the energy supplied in the plastic deformation process, and if the crystal structure permits it, a layer of atoms glide into a twin position. With continued stress, gliding takes place in the next layer. Because gliding in all the parallel layers does not take place simultaneously, twin lamella form. Calcite is an example of a crystal that forms glide twins readily at low differential stresses ($\sim$10 MPa). Twinning is possible along three glide planes. *Transformation twinning* occurs during the transformation from a high-temperature phase to a lower-symmetry low-temperature phase: for example, when sanidine (monoclinic $KAlSi_3O_8$) is cooled to form microcline (triclinic $KAlSi_3O_8$). In such a process, there is spontaneous formation of nuclei in different orientations, which subsequently grow into one another. Each member of the aggregate is either in parallel or twinned orientation with respect to other members. This follows from the fact that they could be brought into coincidence by one of the possible symmetry operations of the high-temperature phase that vanished in the formation of the low-temperature phase, which has a symmetry that is a subgroup of the high-temperature phase (Buerger, 1945).

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Martin Julian Buerger (1903–1986) received his Ph.D. in mineralogy in 1929 from the Massachusetts Institute of Technology MIT, where he remained as an assistant professor. As a graduate student, he attended lectures on x-ray diffraction delivered by W. L. Bragg in 1927, at which point he began his lifelong investigations into crystal structure–property correlation. In the 1930s, Buerger established an x-ray laboratory at MIT, out of which he revised or invented many different types of x-ray cameras and diffractometers as well as carrying out many crystal structure determinations. He also wrote 12 books on crystallography. In addition to being a pioneer in crystal structure analysis, Buerger contributed to a range of other topics within crystallography, crystal growth, polymorphism, twinning, and early (predislocation model) plastic deformation theories. He served as president of both the American Society for X-ray and Electron Diffraction and the Crystallographic Society of America, which later were combined into the American Crystallographic Association. Buerger helped to organize the International Union of Crystallography. He also served as editor-in-chief of *Zeitschrift für. Kristallographie*, and he contributed diagrams, notes, and corrections to the *International Tables of Crystallography*. In 1956, Buerger was the second person to be appointed institute professor at MIT, after John Clarke Slater. He received the Day Medal of the Geological Society of America (1951), the Roebling Medal of the Mineralogical Society of America (1958), and was the first recipient of the Fankuchen Award in 1971. Buerger became university professor emeritus at MIT in 1968 and then accepted an appointment at the University of Connecticut, becoming emeritus there in 1973. The ACA established the triannual *M. J. Buerger Award* in his memory in 1983. Buerger was elected to the U.S. National Academy of Sciences in 1953 and was a member of several foreign academies. He also has a mineral named after him: buergerite, $NaFe_3Al_6(BO_3)_3[Si_6O_{18}]O_3F$.

Source: Obituary by Leonid V. Azároff, *J. Appl. Crystallogr*, **1986**, *19*, 205.