

# Crystallography and Phase Equilibria A Review: Part I—Basics

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## 1. Introduction

Phase equilibria, as shown by phase diagrams in combination with kinetic considerations, provide information relevant to the processing of materials to produce specific properties. The properties of a material are themselves dependent upon the composite material structure, which involves both microstructure and crystal structure. Each grain in a microstructure is a crystal. Some knowledge of crystallography is important for people interested in phase equilibria since each solid phase has its own characteristic crystal structure. A diffraction pattern is characteristic of the atomic arrangement within a crystal. Thus, such patterns provide “fingerprints” for phase identification and may be used to determine boundaries between phase fields. Simple powder diffraction patterns are adequate for these purposes and require no detailed knowledge of the atomic geometries within the crystals.

However, for people who are interested in phases that have ranges of homogeneity, more detailed knowledge of the atomic arrangement of atomic species in a crystal structure allows insight into where and how substitutional atomic replacements, atomic vacancies, and/or interstitial atoms may be introduced into a crystal structure to provide composition variation. Also importantly, detailed knowledge of atomic geometry within crystals can allow a determination as to whether a particular solid-state transition is required to be a first-order transition or is an allowable higher-order transition without a phase change. This article is the first in a series of three and covers the basics of crystallography: crystal systems, Bravais lattices, and point group symmetries. The second article will cover space group symmetry, symmetry constraints upon atomic loci, and the information necessary for crystal structure determination. The final article will cover the Landau conditions for allowable second-order transitions as well as other aspects of crystallography that relate to thermodynamics and phase relationships.

A crystal structure is the arrangement of atoms within a crystal. Structure determination allows specification of the atomic species at each location; this provides information concerning interatomic distances and relative geometric arrangement of all atoms within the crystal. Symmetry is used to determine constraints upon the locations of atoms to minimize the number of numerical quantities that need to be

evaluated for definition of the atomic locations within a crystal structure of given symmetry.

## 2. Primary Considerations

The nature of a crystal is the topic herein under consideration, but it should be borne in mind that grain sizes, relative grain orientations, and grain perfection are all factors that affect the macroproperties of a material. For instance, if the processing of a material produces a texture, the material will have directional physical properties that reflect the directionality of the preferentially oriented crystalline grains. A crystal is a multiple periodic repetition of an atomic array. The repetition is accomplished by translations in three independent directions. This represents long-range order and is in contrast to metastable glasses, which have only short-range order. In a perfect crystal at absolute zero, the locations of all atomic species in the crystal are defined with a unit probability for the configuration. Thus, Boltzmann's equation for entropy yields zero for the configurational entropy. This is not true of glasses in which the boundaries between regions of short-range order are not well defined.

The repeated atomic array in a crystal is the lattice point and may be as simple as a single atom (e.g., elemental Fe) or may consist of tens or even hundreds of atoms (e.g., NaCd<sub>2</sub>)\*. The symmetry of the lattice point is known as the point group symmetry. The repetitive translation of the basic atomic array forms the crystal lattice. The lengths of the translational repetitions and the angular relationships among the linear translations define the lattice parameters. Lattice parameters are vectorial quantities for which both magnitude and direction need to be defined. The volume of a prism outlined by the lattice parameters is the unit cell, and the crystal may be viewed as a stacking of unit cells side to side, end to end, and top to bottom (Fig. I-1).

## 3. Crystal Systems and Crystal Lattices

The concept of crystal systems arose from studies of well-developed crystals. The early studies were made on crystals of minerals that had grown naturally. Examples of such crystals are those that are formed in caves or geodes

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\*NaCd<sub>2</sub> exists over a range of composition of NaCd<sub>1.99</sub> to NaCd<sub>2.12</sub> with 1120-1190 atoms in a cubic unit cell. The crystal structure was determined by S. Samson,<sup>[1]</sup> who subsequently solved the structures of a number of substances with hundreds of atoms per unit cell (e.g., Al<sub>3</sub>Mg<sub>2</sub> and Na<sub>6</sub>Tl).

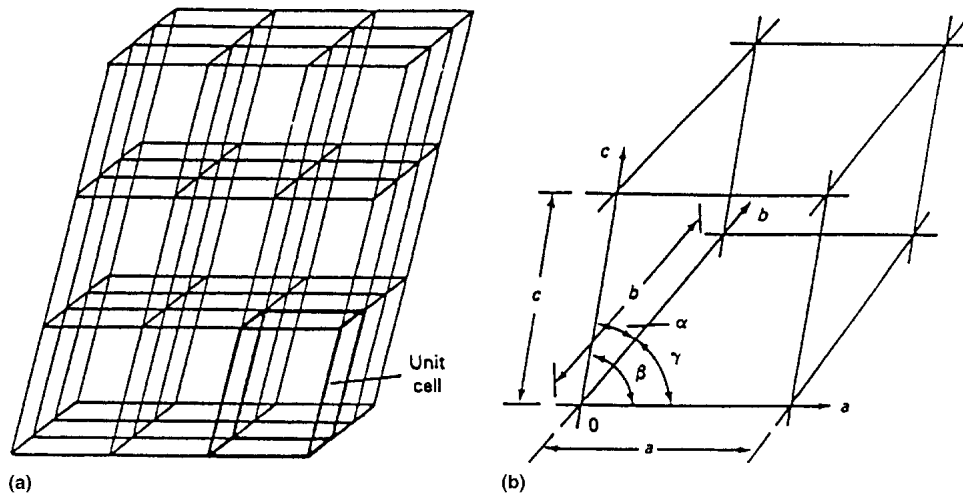


Fig. I-1 (a) A bare space lattice. (b) A general unit cell with its six parameters

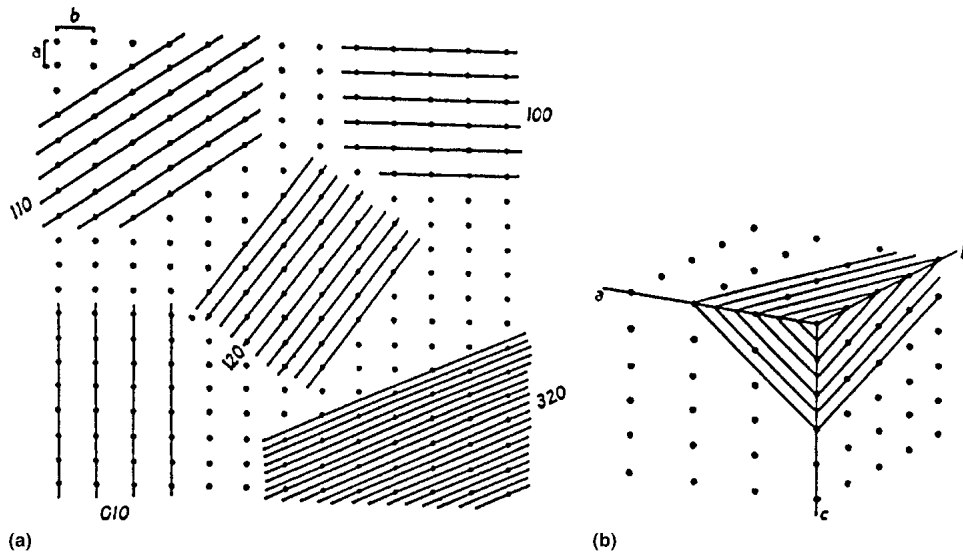


Fig. I-2 (a) Projections of various crystallographic planes onto a two-dimensional grid to illustrate Miller indices. (b) Three-dimensional illustration of a set of (312) planes

Table I-1 Crystal systems and associated lattice parameters

System	Minimum symmetry	Parametric constraints(a)	Parameters to be specified
Triclinic	Asymmetric	$ a  \neq  b  \neq  c ; \alpha \neq \beta \neq \gamma \neq 90^\circ$	6
Monoclinic	One unique axis of symmetry	$ a  \neq  b  \neq  c ; \alpha = \beta = 90^\circ; \gamma \neq 90^\circ$	4
Orthorhombic	Two axes of symmetry, twofold or mirror	$ a  \neq  b  \neq  c ; \alpha = \beta = \gamma = 90^\circ$	3
Tetragonal	Two axes of symmetry, one being fourfold	$ a  =  b  \neq  c ; \alpha = \beta = \gamma = 90^\circ$	2
Hexagonal	Two axes of symmetry, one being sixfold	$ a  =  b  \neq  c ; \alpha = \beta = 90^\circ; \gamma = 120^\circ$	2
Rhombohedral	Two axes of symmetry, one being threefold	$ a  =  b  \neq  c ; \alpha = \beta = 90^\circ; \gamma = 120^\circ$	2
	or	$ a  =  b  =  c ; \alpha = \beta = \gamma \neq 90^\circ$	2
Cubic	Two threefold axes of symmetry	$ a  =  b  =  c ; \alpha = \beta = \gamma = 90^\circ$	1

(a)  $\neq$  means "not necessarily equal." There is no restriction that says a fortuitous equality cannot occur.

where crystal surface geometry develops without inhibition by barriers. In such cases, the slow kinetics of growth allows the development of a geometry that results from the

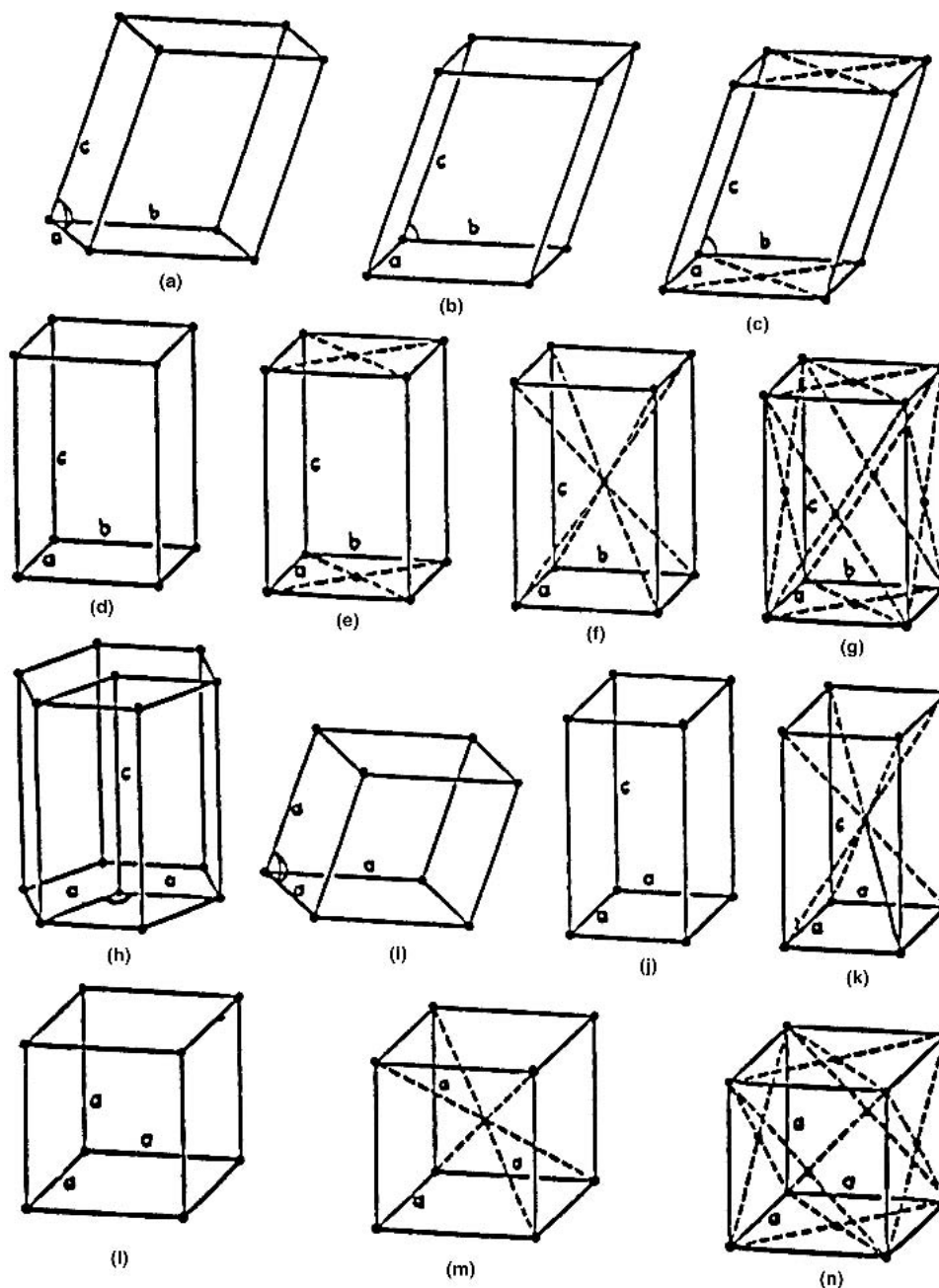
minimization of surface energies by the formation of faces with densely packed atoms. Studies of such natural crystals allowed the enunciation of Steno's law in the very early

1600s: “the angles between equivalent faces of different crystals of the same substance at the same temperature are the same.” It was also found that symmetries among the angular relationships of the faces of a given substance are characteristic of that substance; studies of these angular relationships for various substances led to the concept of crystal systems.

Seven crystal systems have been defined. These are triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, and cubic. In the crystallographic literature, it will be found that some authorities include rhombohedral as

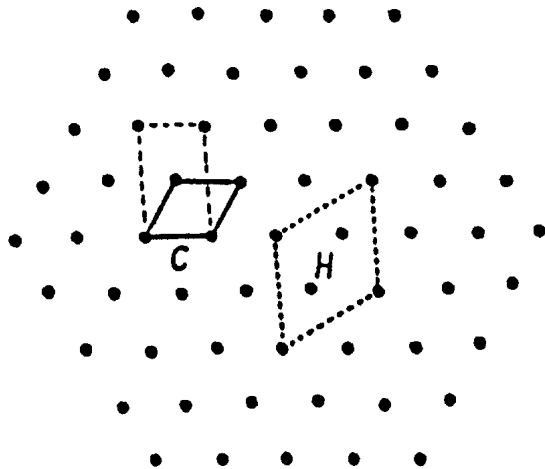
a subsystem of hexagonal to reduce the number of systems to six. Other names also have been used for some of the systems. Examples are anorthic for triclinic, rhombic for orthorhombic, and trigonal for rhombohedral. Table I-1 shows the utility of crystal systems in reducing the number of quantities that are needed to define the lattice parameters. Specifically, Table I-1 shows that an increase in symmetry from triclinic to cubic is attended by a decrease from six to one in the number of parameters needing specification.

Figure I-2(a) shows a two-dimensional section of lattice of points wherein  $\mathbf{a}$  and  $\mathbf{b}$  represent the lattice parameters in



**Fig. I-3** The 14 Bravais lattices: (a) triclinic (P); (b) monoclinic (P); (c) monoclinic C; (d) orthorhombic (P); (e) orthorhombic (C); (f) orthorhombic (I); (g) orthorhombic (F); (h) hexagonal (P); (i) rhombohedral (R); (j) tetragonal (P); (k) tetragonal (I); (l) cubic (P); (m) cubic (I); (n) cubic F

the plane of the paper, and *c* represents the lattice parameter out of the plane of the paper. Various sets of planes are sketched onto this two-dimensional section. Miller indices are used to define the crystallographic planes. By convention the Miller indices defining a specific set of planes are enclosed in parentheses as (*hkl*), while families of crystallographically equivalent planes are shown as {*hkl*}. Each Miller index is the reciprocal of the intercept of the plane at the first crossing of a lattice parameter. An equivalent way of stating this is that the Miller index is the number of

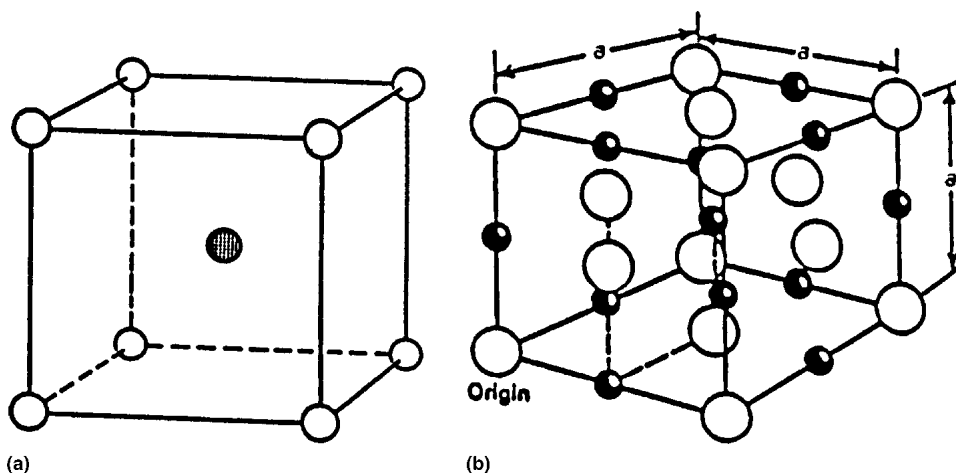


**Fig. I-4** Alternative unit cell bases for hexagonal crystals. The primitive (P) hexagonal base is shown by the solid lines, the end-centered (C) base is shown superimposed by dashed lines on the primitive base, and a third alternative (H) base is also shown. The C and H unit cells have volumes that are two and three times, respectively, the volume of the primitive unit cell.

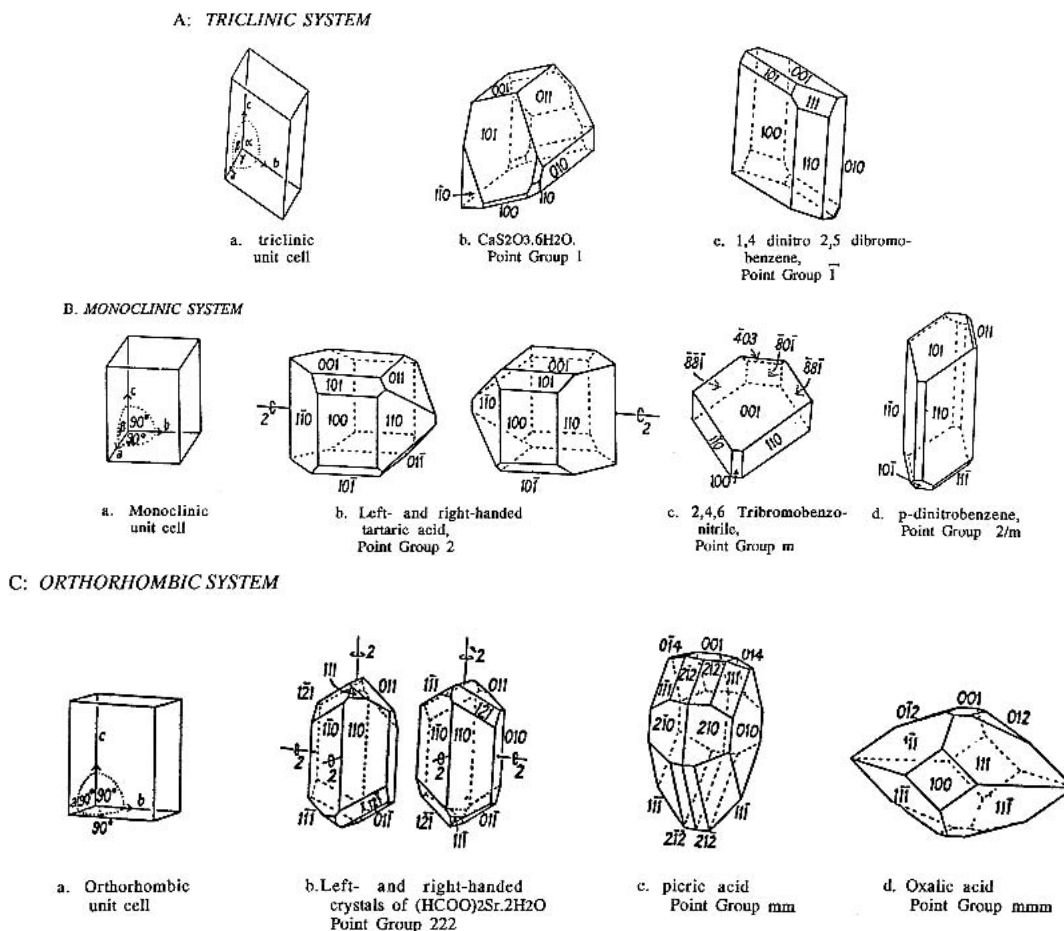
equivalent planes crossing a unit length of the lattice parameter. For instance, reference to the set of planes in the upper left section of Fig. I-2(a) shows that there is only one intersection per unit length of the lattice parameter in each of the *a* and *b* directions. Thus, the first two Miller indices are 11; the 0 for the third index indicates that the planes have no intercept on the *c*-axis because the *c*-axis lies in a (001) plane. How this can occur is illustrated in Fig. I-2(a), wherein the (100) planes have no intercept on the *b* parameter and the (010) planes have no intercept on the *a* parameter. Figure I-2(b) shows a three-dimensional lattice with a set of (312) planes sketched onto the lattice.

Bravais lattices are the 14 simplest ways that points may be repeated in three-dimensional space with repetitions in conformity with the seven crystal systems. These 14 lattices are illustrated in Fig. I-3. Some of these lattices include one or another type of centering of lattice points. However, each point still represents an identical array of atoms, so that, although the number of Bravais lattices is limited, the number of possible crystal structures is not restricted. Also note that any lattice could be described in a more complicated form. For instance, any lattice could be described with a triclinic representation, but the Bravais lattices represent the simplest reduction of any periodic point array. Any alternative choice simply complicates the problem of elaborating the crystal structure.

Among the space lattices of the Bravais group, those lattices in which only a single point is reproduced by unit translations are designated as primitive (the symbol P), whereas those with points generated by centering operations have designations indicating the nature of the centering. With a pattern of roses on wallpaper as a two-dimensional example, any part of a rose at one location must be reproduced by an equivalent part of another rose at each unit lattice translation, and, if centering is present, the rose pat-



**Fig. I-5** (a) A cubic unit cell with atoms at the origin and the cube center. If both atoms are the same species, this is the body-centered cubic structure of many metallic elements. If the two atoms are different species, the body centering is destroyed, and the lattice becomes primitive, with the translated group being the pair of unlike atoms. In this case, the structure is that typified by CsCl or  $\beta$ -brass. (b) A face-centered cubic unit cell with unlike atoms at the origin and at the midpoints of the cube edges. This puts an atom of type A at 0,0,0 plus face-centering translations of  $1/2, 1/2, 0$ ;  $0, 1/2, 1/2$ ; and  $1/2, 0, 1/2$  with atoms of type B at  $1/2, 0, 0$ ;  $0, 1/2, 0$ ;  $1/2, 1/2, 1/2$ ; and  $0, 0, 1/2$ . Such an array is typified by NaCl.



**Fig. I-6** (A)-(C) The crystal systems illustrating the geometry of the unit cells and representative crystal habits of materials crystallizing in the systems. Note that a single substance may have more than one crystal habit, with the habit that is observed depending upon growth conditions the kinetics bias of which yields the resultant shape. However, the habits must exhibit the same point group symmetry. (A) Triclinic system: (a) triclinic unit cell; (b)  $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , Point Group 1; (c) 1,4-dinitro-2,5-dibromobenzene, Point Group 1. (B) Monoclinic system: (a) monoclinic unit cell; (b) left- and right-handed tartaric acid, Point Group 2; (c) 2,4,6-tribromobenzonitrile, Point Group m; (d) p-dinitrobenzene, Point Group 2/m; (C) Orthorhombic system: (a) orthorhombic unit cell; (b) left- and right-handed crystals of  $(\text{HCOO})_2\text{Sr} \cdot 2\text{H}_2\text{O}$ , Point Group 222; (c) picric acid, Point Group mm; (d) oxalic acid, Point Group mmm

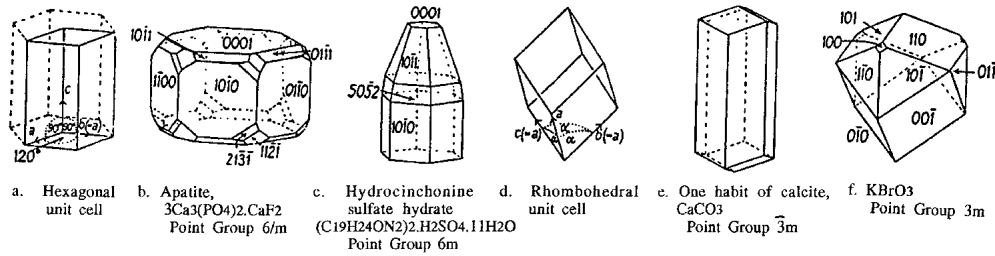
tern must also be repeated at all  $\mathbf{a}/2 + \mathbf{b}/2$  translations. In Fig. I-3(f), (k), and (m), the centering is body-centered and is designated by the symbol I. Such centering requires each detail of all points to be reproduced by  $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$  translations as well as by unit translations of the lattice parameters. In Fig. I-3(g) and (n), the centering is face-centered (the symbol F), with translations of  $(\mathbf{a} + \mathbf{b})/2$ ,  $(\mathbf{a} + \mathbf{c})/2$ , and  $(\mathbf{b} + \mathbf{c})/2$  as well as unit translations. In Fig. I-3(c) and (e), the centering is end-centered (or base-centered). Since the choice of lattice parameters is the prerogative of the crystallographer, end centering can be denoted by symbols A, B, or C, depending upon which lattice parameter lies out of the centered plane. The two examples of end centering in Fig. I-3 are both C-centered, and this is the conventional choice.

The rhombohedral lattice is denoted by the symbol R. The hexagonal lattice in current practice is denoted by the symbol P, but in older literature it was commonly denoted by C because the hexagonal lattice also can be described as end-centered orthorhombic (Fig. I-4). During the determi-

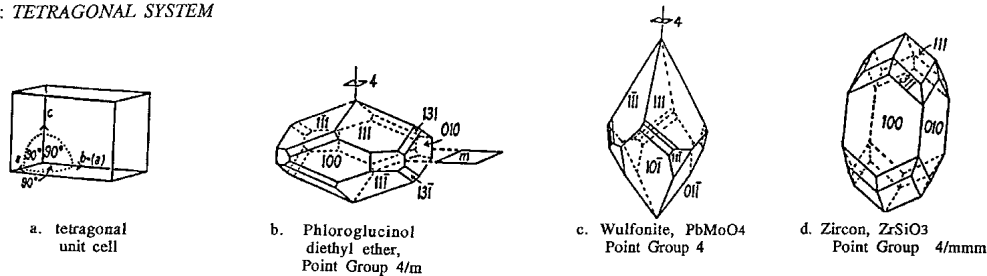
nation of a crystal structure, the crystallographer may infer hexagonal symmetry with  $\mathbf{a}$  and  $\mathbf{b}$  parameters larger than necessary. With adequate diffraction data, this is readily corrected, but it has occurred sufficiently often that such a cell has been given the designation H and is also illustrated in Fig. I-4.

The inclusion of centering allows the utilization of a higher symmetry for a structure than is possible with a primitive representation. To get a feel for the utility of centering, consider the structures in Fig. I-5. Figure I-5(a) shows a cubic unit cell with each open circle representing an atomic array (point group), wherein each atom in an array is duplicated in another array by a translation of  $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$ . Such duplication is requisite for a body-centered cubic lattice, I. If the point group is a single atom, the figure represents the simple bcc structure of many metallic elements with one-eighth of each atom at a corner plus the complete atom at the center yielding two atoms per unit cell for a density calculation. This simple bcc struc-

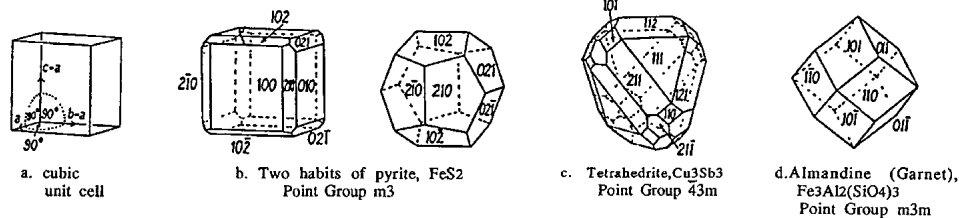
D: HEXAGONAL AND RHOMBOHEDRAL SYSTEMS



E: TETRAGONAL SYSTEM



F. CUBIC SYSTEM



**Fig. I-6** (D)-(F) The crystal systems illustrating the geometry of the unit cells and representative crystal habits of materials crystallizing in the systems. Note that a single substance may have more than one crystal habit, with the habit that is observed depending upon growth conditions the kinetics bias of which yields the resultant shape. However, the habits must exhibit the same point group symmetry. (D) Hexagonal and rhombohedral systems: (a) hexagonal unit cell; (b) apatite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ , Point Group  $6/m$ ; (c) hydrocinchonine sulfate hydrate,  $(\text{C}_{19}\text{H}_{24}\text{ON}_2)_2 \cdot \text{H}_2\text{SO}_4 \cdot 11\text{H}_2\text{O}$ , Point Group  $6m$ ; (d) rhombohedral unit cell; (e) one habit of calcite  $\text{CaCO}_3$ , Point Group  $3m$ ; and (f)  $\text{KBrO}_3$ , Point Group  $3m$ . (E) Tetragonal system: (a) tetragonal unit cell; (b) phloroglucinol diethyl ether, Point Group  $4/m$ ; (c) wulfonite,  $\text{PbMoO}_4$ , Point Group 4; (d) zircon,  $\text{ZrSiO}_4$ , Point Group  $4/mmm$ . (F) Cubic system: (a) cubic unit cell; (b) two habits of pyrites,  $\text{FeS}_2$ , Point Group  $m\bar{3}$ ; (c) tetrahedrite,  $\text{Cu}_3\text{Sb}_3$ , Point Group  $43m$ ; (d) almandine (Garnet),  $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ , Point Group  $m\bar{3}m$

ture also can occur in random solid solutions if the probability of occupancy of the origin site and the body-centered site by a given atomic species is the same. An example of such random occupancy is the high-temperature form of  $\beta$ -brass (Cu-Zn alloy). However, at lower temperatures the site occupancy probabilities tend to shift, with the origin position being preferentially occupied by one atomic species and the cell center by the other species. Body centering is thereby lost, and the unit cell becomes primitive, P. The point group then becomes a combined Cu-Zn pair with each pair being repeated only by unit translations. Similarly, Fig. I-5(b) shows an NaCl type structure with the large, open circles representing one species of atom and the small, filled circles representing the other species. In this structure, the pair of atoms is again the point array, but now it may be noted that the array itself is face-centered (F), because each and every atom can be reproduced by the face-centering translations of  $(\mathbf{a} + \mathbf{b})/2$ ,  $(\mathbf{a} + \mathbf{c})/2$ , and  $(\mathbf{b} + \mathbf{c})/2$ . The presence of centering is readily identified after a diffraction pattern has been indexed. This will be explained in Part II of this review.

#### 4. Symmetry Elements and Point Group Symmetry

The macrosymmetry of a crystal reflects the point group symmetry because the surfaces are formed with terminal points of the repeated lattice translations. Most often, the surface planes of well-developed crystals will be planes with low-number Miller indices because these planes have high densities of lattice points (Fig. I-2). However, the nature of the atomic array of each lattice point that terminates on a surface will determine which specific planes will have the higher atomic densities as required for minimization of the surface energies. Thus, macrosymmetry and point group symmetry are intertwined, and the macrosymmetry is a projection of the point group symmetry.

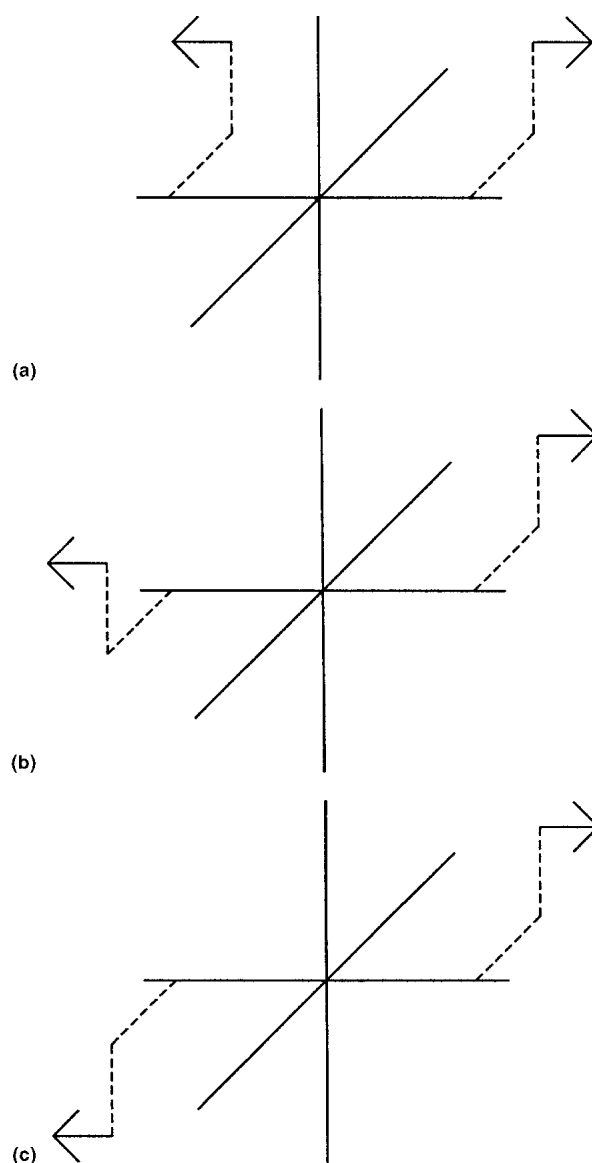
The ratios of the magnitudes and the angular relations among the lattice parameters can be determined from the macrosymmetry, but the actual numerical magnitudes of the lattice parameters require diffraction experiments for their evaluation. Examples of crystal geometries represented by a

variety of substances are shown in Fig. I-6. The crystals represent all seven crystal systems, with the first figure of each system representing the geometry of the unit cell for that specific crystal system. Several substances in each crystal system are represented. The specific geometry of the crystal for each substance is called its crystal habit. For substances in which the surface energies of competing planes are closely comparable, the resultant crystal geometry may exhibit more than one habit (e.g., Fig. I-6Fb shows two habits of pyrite,  $\text{FeS}_2$ ). The crystal habit that develops depends upon growth conditions, but all habits of the same crystalline substance must conform to the same point group symmetry.

The three primary types of symmetry that define point group symmetry are mirror symmetry, rotational symmetry, and inversion symmetry. Figure I-7 shows how these three symmetry operations differ. In Fig. I-7(a), the mirror plane is normal to the horizontal **a**-axis, so any point  $xyz$  is reproduced point by a point at  $\bar{x}yz$ . The twofold rotation in Fig. I-7(b) is referred to the vertical **c**-axis and reproduces a point  $xyz$  at  $\bar{x}\bar{y}z$ . The inversion symmetry of Fig. I-7(c) reproduces a point  $xyz$  at  $\bar{x}\bar{y}\bar{z}$  (by convention a bar above a coordinate indicates a minus value). Note that for rotational or mirror symmetry, the associated symmetry direction determines which coordinates change signs, but inversion symmetry is independent of the choice of coordinate system and direction. One macrosymmetry illustrating both a twofold rotor and a mirror plane is shown in Fig I-6(Bd), in which a mirror plane passes through the midpoint of the crystal from front to back and a twofold rotor passes through the center of the crystal from left to right. When all points of a geometric configuration are duplicated by inversion, the configuration is said to have a center of symmetry (commonly denoted by  $i$ ), and a macrosymmetry showing only a center of symmetry is shown in Fig. I-6(Ac).\*

Although the rotation in Fig. I-7(b) is twofold, other rotational symmetries are possible. By definition, an  $n$ -fold rotor reproduces points by rotation at every  $360^\circ/n$ . A molecule in the gas phase has no restriction on  $n$ ; however, in crystals the requirement of translational repetition within a crystal limits  $n$  to 1, 2, 3, 4, or 6, and rotors are commonly denoted by those numbers. Rotation-inversion symmetry is simply a sequential combination of rotation followed by inversion or vice versa. As an example, a vertical twofold rotation-inversion axis would first take a point  $xyz$  to  $\bar{x}\bar{y}z$ , and inversion would then duplicate the point at  $xy\bar{z}$ . It may be noted that the result is the same as a simple mirror normal to the vertical axis. Rotation-inversion axes are normally designated with a bar over the rotation number. While a  $\bar{1}$  rotor does not differ from a center of inversion  $i$  and a  $\bar{2}$  rotor does not differ from a mirror,  $\bar{3}$ ,  $\bar{4}$ , and  $\bar{6}$  rotors do produce different arrays, as shown in Fig. I-8. Again,  $\bar{6}$  is equivalent to a combination of a threefold rotor normal to a mirror plane,  $3/m$ , but no combination of the three simple symmetry operations can reproduce  $\bar{3}$  or  $\bar{4}$  rotors. An ex-

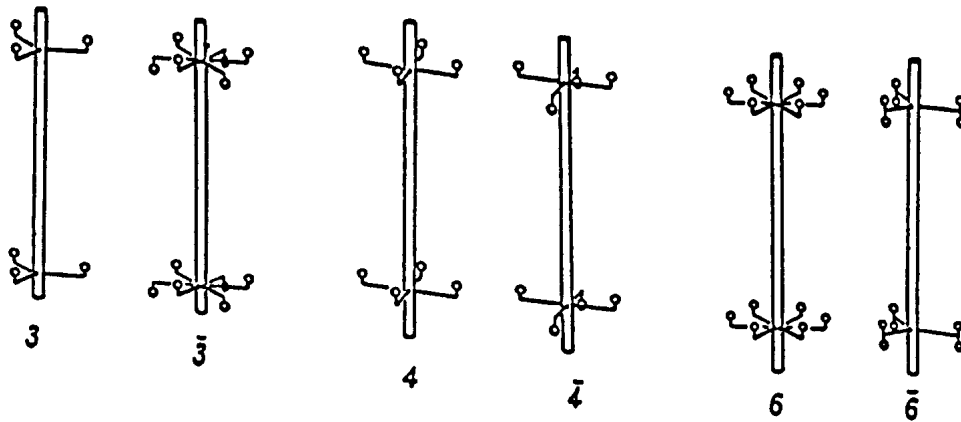
\*Planes of high atomic density also can be developed by deep etching. Thus, the surfaces of deep etch pits may be used to provide information as to the presence of symmetry elements of the point group symmetry.



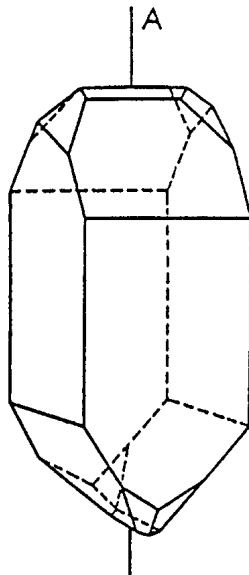
**Fig. I-7** Comparison of the basic symmetry elements (a) mirror symmetry, (b) rotational symmetry, and (c) inversion symmetry. In (a), the mirror plane is normal to the horizontal **a**-axis. In (b), the rotation axis is the vertical **c**-axis. In (c), the inversion is valid for any choice of axis.

ample of a macrosymmetry illustrating fourfold rotation-inversion symmetry is shown in Fig. I-9.

It should be emphasized that symmetry is reflected in physical properties such as optical, electrical, magnetic, and elastic response, as well as in crystal habit. Illustrations of one or more of the symmetry elements can be found in each of the variety of geometric illustrations in Fig. I-6. Of course, onefold rotational symmetry is present in any three-dimensional object, and any axis of rotation may be chosen for 1 or  $\bar{1}$  point group symmetry (Fig. I-6A). The repetition of a general point  $x,y,z$  is shown for each rotational symmetry element in Table I-2, in which the rotation axis is chosen as the **c**-axis and the mirror plane is chosen as the



**Fig. I-8** Comparison of normal rotation and rotation-inversion for threefold, fourfold, and sixfold axes. Note that the points are reproduced in the vertical direction by unit translations, and, although not shown in the figure, the points are also reproduced in the other two parametric directions by unit translations.



**Fig. I-9** Macrosymmetry of copper pyrite showing a fourfold rotation-inversion axis that is oriented along the vertical direction (labeled A)

plane containing both **a** and **b**. The following equivalencies may be noted:  $\bar{1}$  and  $i$ ;  $\bar{2}$  and  $m$ ;  $\bar{6}$  and  $3/m$ , where the  $m$  in the denominator represents a mirror normal to the threefold axis. Point group symmetries are representations of the total rotational, mirror, inversion, and rotation-inversion symmetries that may be present in a single crystal. Figure I-10 shows point representations of the positional relations in the 32-point groups of the seven crystal systems. In Fig. I-10, the solid points represent positions above the midplane and the open circles represent points below the midplane. Table I-3 lists the 32 point groups in the same order as they appear in Fig. I-10 and gives both the older Schoenflies notation and the more recent Hermann-Mauguin notation for the point groups. The table shows the full Hermann-Mauguin notation, which in literature reports is fre-

**Table I-2** Reproduction of a general point,  $xyz$ , by various symmetry operations where  $n$ -fold rotation is designated by  $n$  number and mirroring is designated by  $m$

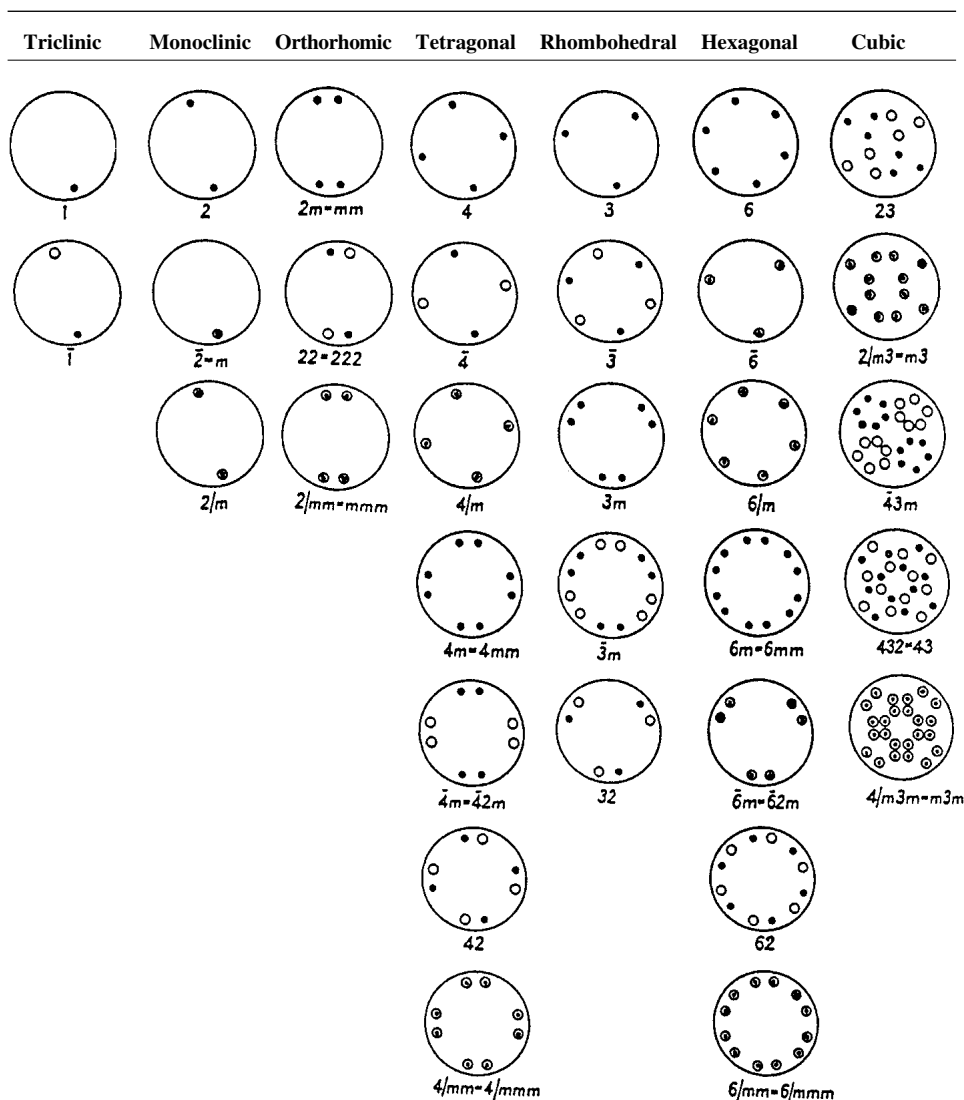
Symmetry operation(a)	Initial locus	Reproduced loci(a)
1	$x,y,z$	$x,y,z$
$\bar{1} = i$	$x,y,z$	$\bar{x},\bar{y},\bar{z}$
2	$x,y,z$	$\bar{x},\bar{y},z$
$m = \bar{2}$	$x,y,z$	$x,y,\bar{z}$
3	$x,y,z$	$\bar{y},(x-y),z; (y-x),\bar{x},z$
$\bar{3}$	$x,y,z$	$y,(y-x),\bar{z}; (y-x),\bar{x},z; \bar{x},\bar{y},\bar{z}; \bar{y},(x-y),z; (x-y),x,\bar{z}$
4	$x,y,z$	$y,\bar{x},z; \bar{x},\bar{y},z; \bar{y},x,z$
$\bar{4}$	$x,y,z$	$\bar{y},x,\bar{z}; \bar{x},\bar{y},z; y,\bar{x},\bar{z}$
6	$x,y,z$	$(x-y),x,z; \bar{y},(x-y),z; \bar{x},\bar{y},z; (y-x),\bar{x},z; y,(y-x),z$
$\bar{6} = 3/m$	$x,y,z$	$(y-x),\bar{x},\bar{z}; \bar{y},(x-y),z; x,y,\bar{z}; (y-x),\bar{x},z; \bar{y},(x-y),\bar{z}$

(a) A bar over a rotor indicates inversion-rotation while a bar over a coordinate indicates a negative value. In this table the rotation axis is considered to be the  $z$ -axis and the mirror plane is considered to be the  $xy$  plane.

quently given in abbreviated form. An abbreviated form is sufficient to generate all related points, and Fig. I-6 and I-10 include some of the abbreviated forms.

Several details need elaboration and/or explanation. For anyone interested in the details of the atomic array around a lattice point, the symmetry is useful in the following sense. In the simple triclinic point group  $\bar{1}$ , a center of symmetry must be present in the local atomic array of a lattice point as well as in the crystal en toto. The center of symmetry requires that an atom at  $xyz$  must be duplicated at  $\bar{x}\bar{y}\bar{z}$ . Thus, the stoichiometry of the atomic array must occur in multiples of two except for a unique atom that may sit exactly on the center of symmetry at  $000$  and invert into itself. Figure I-10 shows that increasing symmetry is accompanied by an increasing number of positional constraints, so the number of constraints on atomic loci increases with increasing symmetry. Thus, specification of the coordinates of one





**Fig. I-10** Point repetition due to symmetry constraints for the 32 point groups showing the distribution of point groups within the seven crystal systems. Points above the plane of the paper are indicated by the solid dots, points below the paper are indicated by the open circles, and points that reflect across the plane of the paper are shown as a solid dot within a circle. Note that in Point Group 1 the position of each point (atom) must be determined, while in Point Group  $m\bar{3}m$ , the symmetry position of 48 points (atoms) are linked together so that one set of coordinates defines the positions of all 48.

atom determines the coordinates of symmetry-related atoms. For instance, Fig. I-10 shows that in point group  $m\bar{3}m$  the symmetry operations generate 48 interrelated points. Thus, the determination of the coordinates  $xyz$  of a single atom can determine the coordinates of a total of 48 atoms.

As already noted, there is no direction of symmetry associated with the point groups 1 or  $\bar{1}$ . However, a rotor has a direction that is the axis of rotation or a mirror has a direction that is the normal to the mirror. Thus, the monoclinic point groups 2,  $m$ , and  $2/m$  all have a unique direction of symmetry, so that one crystal lattice parameter, normally the  $c$  parameter, may be chosen along that symmetry direction. Because lattice points as well as atoms within the atomic array of a lattice point conform to the point group symmetry, there must be layers of lattice points normal to

the  $c$  direction. This is so because a rotor duplicates adjacent lattice points in the same plane or a mirror reflects across a defined plane (e.g., if a lattice point and its  $a$  or  $b$  translation were tilted with respect to the mirror plane, the image points would be tilted with opposite angle and the  $c$  translational repetition would be violated). Therefore, the  $a$  and  $b$  parameters can be selected  $90^\circ$  to the  $c$ -axis. Thus, two of the three angles needing specification for definition of the lattice parameters are fixed at  $90^\circ$  by monoclinic symmetry.

If a second direction of symmetry is present, the point group symmetry is orthorhombic or higher. For instance, if a twofold axis is perpendicular to the normal of a mirror plane, the two symmetry elements will interact to form another mirror the normal of which is orthogonal to both the other two directions. Similar arguments apply to other com-

**Table 3 The 32 point groups of crystallography in both the older Schoenflies and more recent Hermann-Mauguin notations**

System	Schoenflies	Hermann-Mauguin	
		Abbreviated	Full
Triclinic	$C_1$	1	1
	$C_i$	$\bar{1}$	$\bar{1}$
Monoclinic	$C_2$	2	2
	$C_S$	$\bar{2}$ or $m$	$m$
	$C_{2h}$	$2/m$	$2/m$
Orthorhombic	$C_{2v}$	$2m$ or $mm$	$2mm$
	$V$	22	222
	$V_h$	$mmm$	$2/m2/m2/m$
Tetragonal	$C_4$	4	4
	$S_4$	$\bar{4}$	$\bar{4}$
	$C_{4h}$	$4/m$	$4/m$
	$C_{4v}$	$4m$	$4mm$
	$V_d$	$\bar{4}m$	$\bar{4}2m$
	$D_4$	42	422
	$D_{4h}$	$4/mmm$	$4/mmm$
Rhombohedral	$C_3$	3	3
	$C_{3i}$	$\bar{3}$	$\bar{3}$
	$C_{3v}$	$3m$	$3m$
	$D_{3d}$	$\bar{3}m$	$\bar{3}m$
	$D_3$	32	32
Hexagonal	$C_6$	6	6
	$C_{3h}$	$\bar{6}$	$\bar{6}$
	$C_{6h}$	$6/m$	$6/m$
	$C_{6v}$	$6m$	$6mm$
	$D_{3h}$	$\bar{6}m$	$\bar{6}2m$
	$D_6$	62	62
	$D_{6h}$	$6/mmm$	$6/mmm$
Cubic	$T$	23	23
	$T_h$	$m\bar{3}$	$2/m\bar{3}$
	$T_d$	$\bar{4}3m$	$\bar{4}3m$
	$O$	432	432
	$O_h$	$m\bar{3}m$	$4/m\bar{3}m$

binations of symmetry elements. Crystallographic directions are indicated as vectorial sums of integers times lattice parameters (e.g.,  $h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$ ). Such directions are indicated by  $[hkl]$  to distinguish them from the Miller indices of  $(hkl)$  planes. An  $[hkl]$  direction is normal to an  $(hkl)$  plane only in the cubic system. Crystallographically equivalent directions are specified by  $\langle hkl \rangle$ . As an example, in the cubic system the three parametric directions  $[100]$ ,  $[010]$ , and  $[001]$  are crystallographically equivalent because they can be arbitrarily interchanged, and the group would be designated  $\langle 100 \rangle$ .

If one considers the interaction of symmetry elements of higher symmetry, the interactions generate a higher multiplicity of equivalent points. Again if cubic symmetry is taken as an example, the equivalency of the lattice parameters requires that the cube diagonals, the  $\langle 111 \rangle$  directions, be axes with threefold rotational symmetry. Then, if there are fourfold rotors along the parametric  $\langle 100 \rangle$  directions, the

two symmetry operations interact to generate the 24 inter-related points of point group 432. The arrangement of the 24 related points is illustrated for point group 432 in Fig. I-10. Examination of the figure will show that the 432 combination generates twofold rotors along the  $\langle 110 \rangle$  face diagonals, but this additional symmetry element generates no additional points. Thus, the abbreviated point group in Hermann-Mauguin notation is 432, while the full point group notation is 432.

## 5. Summary

In this article, a crystal has been defined as a solid substance in which points are translated with regular repetition in three-dimensional space. The magnitudes and directions of the regular repetition are the lattice parameters, and the 14 simplest patterns for such repetitions are the Bravais lattices. The interrelations between magnitudes and angular directions of the lattice parameters lead to the concept of crystal systems. The symmetry elements make possible the definition of constraints, which allow the choosing of lattice parameters of the highest symmetry. Further, the interactions among the rotational, mirror, and inversion symmetry elements have been outlined, and these lead to the definition of point group symmetries, which are the symmetries associated with the translated lattice points. The following are salient conclusions:

- 1) There are seven crystal systems, 14 Bravais lattices, and 32 point group symmetries.
- 2) The macrosymmetry of a well-developed crystal can be used to determine the point group symmetry of the crystal. This symmetry is also the symmetry of the atomic arrays of the translated points within the crystal. The macrosymmetry also can be used to determine the relative magnitudes of the lattice parameters but not their absolute magnitudes.

The additional information that can be gleaned from diffraction data will be considered in Part II of this review. Diffraction data show directly all symmetry components except centers of inversion but add information about translational components including the magnitudes of the lattice parameters. This additional information allows the definition of space group symmetry. Space group symmetry in combination with intensity data of diffraction reflections allows determination of crystal structures.

## Suggestions for Further Reading

- **H. Baker**, Introduction to Alloy Phase Diagrams, *Alloy Phase Diagrams*, Vol 3, *ASM Handbook*, ASM International, 1992, p1-1 to 1-29
- **C.S. Barrett**, *Structure of Metals*, McGraw-Hill, 1942, Chap. I
- **C.W. Bunn**, *Chemical Crystallography*, Oxford University Press, 1945, Chap. I-IV

## References

1. S. Samson, *Nature*, Vol 195, 1962, p 259