

# Crystal Symmetry Groups

Symmetry plays an important role in crystallography. The ways in which atoms and molecules are arranged within a unit cell and unit cells repeat within a crystal are governed by symmetry rules. In ordinary life our first perception of symmetry is what is known as *mirror symmetry*. Our bodies have, to a good approximation, mirror symmetry in which our right side is matched by our left as if a mirror passed along the central axis of our bodies. Our hands illustrate this most vividly; so much so that the image is carried over to crystallography when one speaks of a molecule as being either “right”- or “left”- handed. Those of us who live in an old-fashioned duplex will also recognize that such houses are built with mirror symmetry so that the arrangement of the rooms, hallways, and doors are disposed about an imaginary mirror passing through the common wall between the two halves of the house. There are many other examples of this kind of mirror symmetry in ordinary life. We can also see more complex symmetry in the patterns around us. It can be found in wallpaper patterns, floor-tile arrays, cloth designs, flowers, and mineral crystals. The basic mathematics of symmetry also applies to music, dance (particularly folk and square dance), and even the operations needed to solve Rubik’s cube.

The rules that govern symmetry are found in the mathematics of group theory. Group theory addresses the way in which a certain collection of mathematical “objects” are related to each other. For example, consider all the positive and negative integers and zero. They can constitute a group because under certain circumstances the relationships

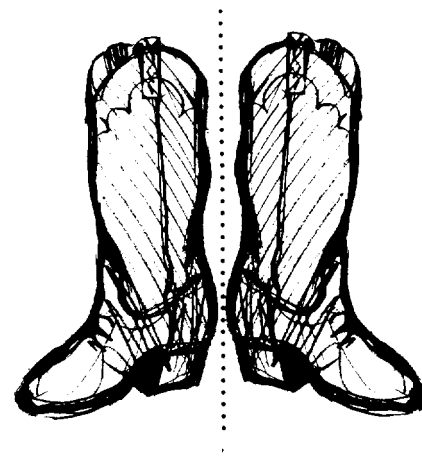
between the integers obey the rules of group theory:

- There must be defined a procedure for combining two elements of the group to form a third. For the integers one can choose the addition operation so that  $a + b = c$  is the operation to be performed and  $a$ ,  $b$ , and  $c$  are always elements of the group.
- There exists an element of the group, called the *identity element* and denoted  $e$ , that combines with any other element to give the second one unchanged. In the case of the integers, the identity element is zero because any integer plus zero gives that integer ( $a + 0 = a$ ).
- For every element of the group, there exists another element that combines with the first to give the identity element; these are known as *inverse elements*. The negative integers constitute the inverses of the positive integers because their pairwise sums all equal zero, the identity element ( $a + (-a) = 0$ ).
- Group operations in sequence obey the associative law. For addition of integers this means that  $(a + b) + c = a + (b + c)$ . Notice that the commutative law,  $a + b = b + a$ , is not required even though it is true for this particular group.

You might be tempted to say that the positive integers, when related by multiplication ( $a \times b = c$ ), also constitute a group with the identity element now being one ( $a \times 1 = a$ ). In fact, the positive integers do not constitute a group under these conditions because, to obey the group-theory rules, the noninteger inverses ( $1/a$ ) as well as all the rational fractions ( $b/a$ ) would have to be included. The expanded set of positive

rational numbers is a group under multiplication, and both it and the integer group already discussed are examples of infinite groups because they each contain an infinite number of elements.

In the case of a symmetry group, an element is the operation needed to produce one object from another. For example, a mirror operation takes an object in one location and produces another of the opposite hand located such that the mirror doing the operation is equidistant between them (Fig. 1). These manipulations are usually called *symmetry operations*. They are combined by applying them to an object se-



## THE MIRROR SYMMETRY OPERATION

**Fig. 1. A pair of left- and right-“footed” boots illustrates the mirror-plane symmetry operation. The right boot can be positioned identically on the left boot by reflection through a mirror between them and vice versa.**

quentially. For example, doing a mirror operation twice on a right-handed object will, with the first operation, move it to the left-handed position, and with the second operation, place it back on its original right-handed position. In fact, applying a mirror operation twice in succession is equivalent to the identity

operation, so that a mirror operation is its own inverse.

The two operations, mirror and identity, obey the four rules of group theory, and thus constitute one of the simplest symmetry groups. A mathematical representation of these operations is

$$m^{-1} = m \text{ and} \\ mm^{-1} = mm = I.$$

Further, a “multiplication table” between these two operations can be set up to show the products that any pair of symmetry operations gives in this finite group (Fig. 2).

There are three types of symmetry operations in crystallography. The simplest type is the set of *translation operations* needed to fill a two-dimensional infinite plane or a three-dimensional infinite space. These operations form a group by themselves and have essentially the same characteristics as the example group of integers discussed above. The difference is that the translation group has two or three sets of integers depending on whether a two-dimensional plane or a three-dimensional space is filled. These translation operations make the concept of a unit cell possible, because once the unit cell for a crystal is specified, it takes only the right combination of translation operations to construct the full crystal lattice.

There is also a type of translation operation that relates objects *within* a unit cell so that the same objects are found at coordinates that are half multiples of unit-cell distances along two or three of the axes. These last operations are, for example, responsible for the face- and body-centered lattices found in three dimensions (Fig. 3). The possible combinations of this full set of translations for plane- and space-filling arrays (along with the restrictions on the rotation-symmetry operations that will

be discussed next) gives only five possible plane lattices and fourteen possible space lattices (Fig. 3).

The second type of crystallographic symmetry is *rotation*. For it to be a valid symmetry operation, however, the rotation angle  $\theta$  must be an integer divisor of 360 degrees, that is,  $\theta = 360/n$ , where  $n$  is an integer. The rotation-symmetry operations will then all be multiples of this rotation angle. For example, if  $n = 6$  the rotation angle is 60 degrees and the operations can be represented by the unique set  ${}^1C_6$ ,  ${}^2C_6$ ,  ${}^3C_6 (= {}^1C_2)$ ,  ${}^4C_6$ ,  ${}^5C_6$ , and  ${}^6C_6 (= I)$  in which the subscript gives the fraction of

	$I$	$m$
$I$	$I$	$m$
$m$	$m$	$I$

### A FINITE SYMMETRY GROUP

**Fig. 2. This example of a simple, finite group obeying all the rules of group symmetry consists solely of the Identity element,  $I$ , and the mirror-plane symmetry operation  $m$ . The multiplication table shown above for the group gives the products for any pairwise application of the two symmetry operations.**

a full circle for each operation (here  $1/6$ ) and the superscript gives the multiple of 60 degrees used for the rotation (Fig. 4). Because  ${}^6C_6$  is the identity operation, these six rotation operations constitute a group, symbolized by  $C_6$

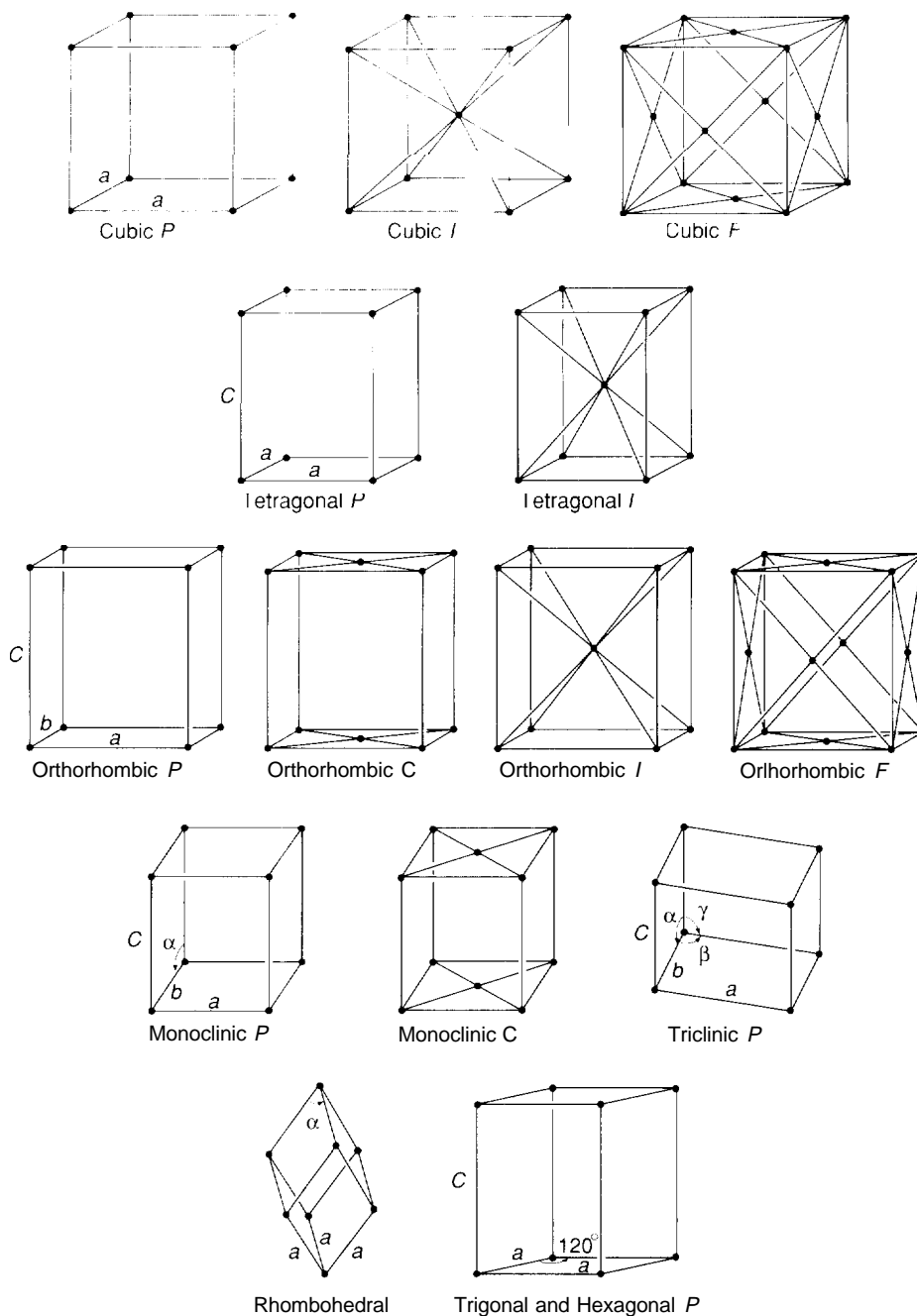
If the symmetry is local with no translation component, then the integer  $n$  can take on any value from one to infinity. An object that has the extreme case of  $C_\infty$  symmetry is a bowling pin, which an infinitesimally small rotation leaves looking the same (ignoring any painted design). However, when the rotation symmetry is part of a plane- or space-filling symmetry with translation operators, only five different rotation angles ( $n = 1, 2, 3, 4, \text{ or } 6$ ) can be used. Replication of a unit cell with a rotation symmetry other than these cannot fill a plane surface or three-dimensional space without leaving voids or having overlapping regions. The situation is more complicated in the three-dimensional case because a unit cell may also have different rotation symmetry in different directions. Many different groups result from the various combinations of these rotations.

An extension to the concept of rotation symmetry is to include in each rotation operator a translation component (Fig. 5). The resulting objects are helical or screwlike; hence, these operations are called *screw rotations*. These symmetry operations are most prevalent in crystal lattices in which the unit-cell repeat requirement means that the translation operations have the same integer fraction, or some simple multiple, as the rotation operations. For example, the screw rotation  $6_1$  describes an operation in which the rotation of 60 degrees is accompanied by a translation of  $1/6$  of the unit cell along the rotation axis. The  $6_4$  screw rotation has the same 60-degree rotation but this time is accompanied by a translation of  $4/6$  of the unit cell along the axis. A sufficient number of these is superimposed to give the required unit-cell translation (Fig. 5), and the resulting arrangement is different from that obtained with a  $6_1$  screw rotation.

The one facet common to the translation, rotation, and screw operations is

## THE BRAVAIS SPACE LATTICES

Fig. 3. The fourteen unit cells depicted above represent the only possible ways that space can be filled without gaps or overlaps between cells, that is, consonant with the restrictions of translation and rotation symmetry. The cubic cells at the top all have three orthogonal sides of equal length; the body-centered (*I*) and face-centered cubic cells (*F*) cannot be fully specified without also using translation operations in terms of half-cell distances. The tetragonal and orthorhombic cells also have sides that are mutually orthogonal, but either one side differs in length from the other two sides (tetragonal) or all three sides differ in length (orthorhombic). The monoclinic and triclinic cells have three unequal lengths but now either one angle (monoclinic) or all three angles (triclinic) between the sides do not equal 90 degrees. The rhombohedral cell can be thought of as a cubic cell that has been stretched or squeezed along a diagonal: the three sides are equal but the three angles, although equal, are not 90 degrees. The hexagonal cell has two angles of 90 degrees and one of 120 degrees; only two of its three sides are equal.

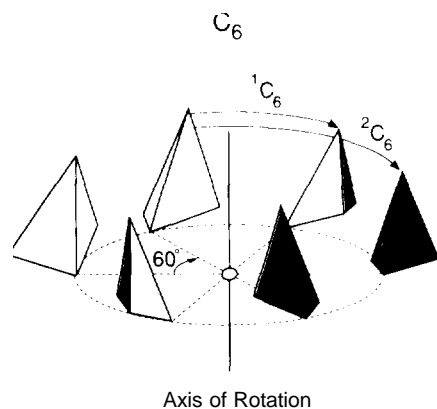


that none of these change the handedness of an object, and *changing handedness* is the major feature of the third type of crystallographic symmetry. We have already mentioned the mirror-symmetry operation that relates right- and left-handed objects across a plane. A similar operation is *inversion* (Fig. 6) in which right- and left-handed objects are arranged on opposite sides of a point, called an inversion center. The presence of an inversion center in a crystal is one of the primary classification features for crystal structures: such crystal structures are *centrosymmetric*. An example of the importance of inversion centers is that almost all biologically important molecules (proteins, amino acids, et cetera) do not have a self-contained inversion center and exist

in nature only in one-handed forms. Thus, they always crystallize in noncentrosymmetric crystal structures because the other-handed molecules do not exist.

In analogy to the operations combining rotations with translations to form

screw operations, mirror reflection can be combined with a fractional translation (always one-half of the unit cell) to form a new operation (Fig. 7). This is known as a *glide* operation, and the mirror part of the operation occurs at



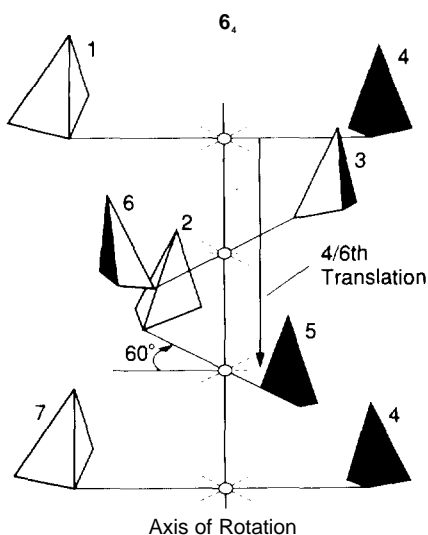
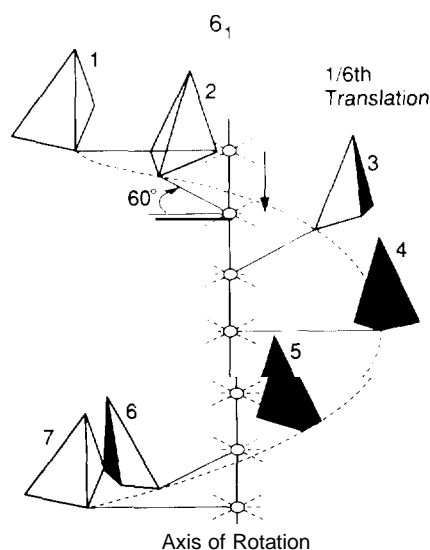
## ROTATION OPERATIONS

Fig. 4. The  $C_6$  rotation symmetry group consists of all the rotations about an axis that carry an object through angles that are multiples of 60 degrees. Two of the operations in the symmetry group,  ${}^1C_6$  and  ${}^2C_6$ , are labeled in the figure;  $C_6$  is the identity operation that carries the object a full 360 degrees back into itself.

a glide plane. Just as for the screw operation, glide operations are only found in crystal lattices where the repetition of translation and reflection can extend indefinitely. Similarly, an inversion operation can be combined with a rotation (Fig. 8). Because this operation occurs about a point, however, it is found in both isolated objects and in extended lattices,

When these operations are combined in ways that form two-dimensional planar arrays, only 17 unique plane groups are found. With three dimensions, the combination of operations gives just 92 centrosymmetric and 138 noncentrosymmetric space groups for a total of 230.

An additional type of operation worth considering is one that in a two-dimensional plane would, say, change the color of the object (see the opening figure of the main article). The simplest case is a "black-white" operator,



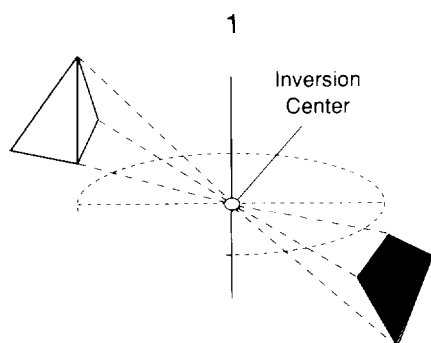
and such a color-reversal operator can also be combined with the other operators discussed earlier. An application of this type of operation is to describe the ordering of magnetic moments found in some materials by neutron scattering. Frequently, the moments arrange themselves in an alternating pattern so that every other one is "up" and all the others are "down." The symmetry of these arrangements can be described by including the color-reversal operation, which expands the total number

## SCREW ROTATIONS

Fig. 5. a) The  $6_1$  screw rotation is the application of a 60-degree rotation about a given axis of the unit cell followed by a translation along that axis of one-sixth of the unit-cell distance. This combination of symmetry operations is repeated successively along the full length of the unit cell (in the figure, the tetrahedrons generated by each successive combination of operations are numbered consecutively). Note that the placement of the tetrahedrons in this figure resembles the placement of the tetrahedrons for rotation alone (Fig. 4) except that the circle has been "stretched out" into an arc because of the vertical translation along the axis of rotation. After six rotation-translation operations, the tetrahedron has returned to its original orientation but is translated a full unit along one of the cell's axes. b) The  $6_2$  screw rotation is the same as the  $6_1$  screw rotation except the translation is now for four-sixths (two-thirds) of the unit distance. To fill in the whole pattern, the next rotation-translation operation (which ends up one-third of the way into the next unit distance) and successive operations are superimposed on the original unit distance. Note that in the figure the dashed line has been eliminated (because successive operations are superimposed), but the tetrahedrons generated by successive operations are still numbered consecutively. After three of these combined operations, the tetrahedron will have moved an integral number of unit distances (and thus can be pictured at either the bottom or top of the figure) but will have rotated only 180 degrees. In this manner, the tetrahedron ends up on both sides of the axis at each point along the way. Once again, after six combined operations the tetrahedron has assumed its original orientation.

of space groups to 1728 in 36 Bravais lattices.

Because there is an intimate relationship between the arrangement of atoms found in real space and the pattern of structure factors in reciprocal space,

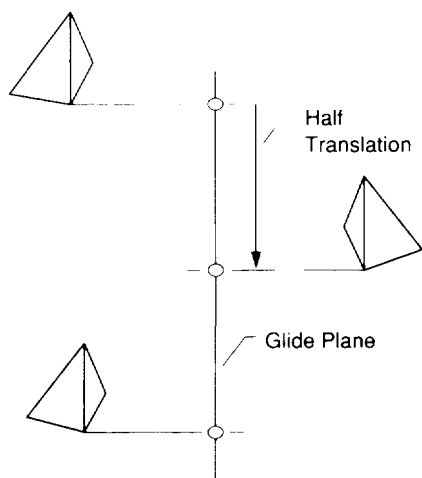


### INVERSION CENTER

**Fig. 6.** An inversion, denoted  $\bar{1}$ , is accomplished by “reflecting” everything through point or “inversion center” between the objects. The three dashed lines drawn between tips on the tetrahedrons and passing through the inversion center illustrate this operation.

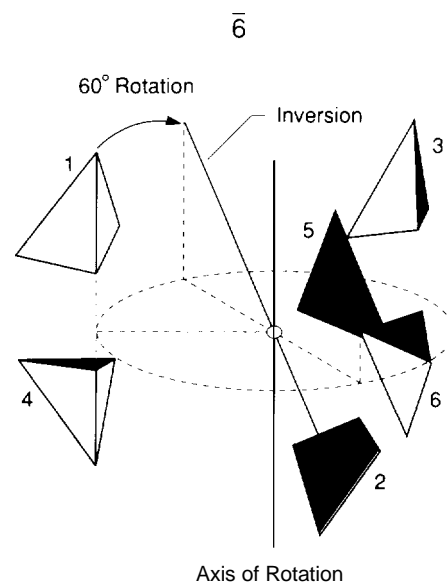
the symmetry of real space must have counterparts in reciprocal space. However, some of the symmetry aspects of reciprocal space may at first glance be surprising. Unlike crystallographic real space, which consists of a multitude of identical unit cells each with its own origin, reciprocal space has just a single origin and an infinite array of reciprocal-lattice points associated with differing and possibly complex numbers ( $F_h$ 's). Thus, none of the translational aspects of the crystallographic symmetry can show up in the reciprocal lattice other than in the dimensions of the reciprocal lattice itself. However, the rotation, mirror, and inversion symmetries present in the lattice are also present in the pattern of  $|F_h|^2$ 's on the reciprocal-lattice (that is, in the diffraction pattern). For example, the intensities and locations of the two-dimensional diffraction patterns shown in Figs. 4 and 5 in the main article have the same rotation and mirror symmetries as the two-dimensional patterns of scatterers that generated those patterns.

What of the other possible symmetry elements? A diffraction pattern almost always has a center of inversion—an inversion center is absent only for a noncentrosymmetric crystal containing an atom with a complex scattering factor. Half-cell translations and screw and glide-plane operations are revealed by *systematic extinctions*, that is, certain classes of reciprocal-lattice points with zero intensity. For example, in the diffraction pattern for a face-centered cubic lattice, the only points that have a nonzero intensity are those for which the  $hkl$  indices are all even (for example, 422) or all odd (for example, 311). Likewise, a glide operation whose glide plane is perpendicular to the  $c$  crystallographic axis and whose glide direction is parallel to the  $a$  axis causes the points with  $hk0$  indices and *odd*  $h$  to have zero intensity (for example, 120, whereas 210 has nonzero intensity). Systematic extinc-



### THE GLIDE OPERATION

**Fig. 7.** Here, mirror reflection and translation for one-half the unit distance are combined to form a glide operation. Note that the tetrahedron on the right side of the glide plane is the mirror image of the tetrahedrons on the left side; however, each tetrahedron is displaced a half unit from the last one.

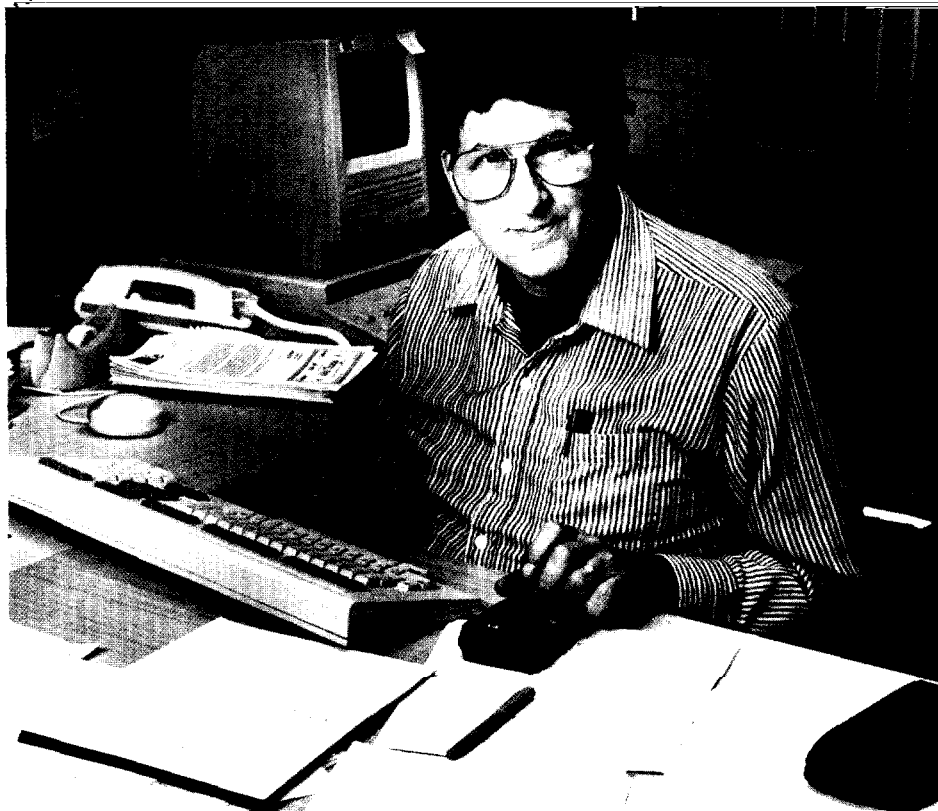


### AN INVERSION-ROTATION OPERATION

**Fig. 8.** The  $\bar{6}$  symmetry operation is a combination of a 60-degree rotation followed by an inversion. Note that the three tetrahedrons above the plane are the same as the tetrahedrons in Fig. 4 for rotations of 0, 120, and 240 degrees (that is,  $I$ ,  ${}^2C_6$ , and  ${}^4C_6$ ). This happens because performing two successive  $\bar{6}$  operations is equivalent to performing the  ${}^2C_6$  operation (or two  ${}^1C_6$  operations). Lines showing the first combination of a 60-degree rotation and inversion operation are given on the figure as well as consecutive numbers for the successively generated tetrahedrons.

tions arise because the symmetry operation causes all the atoms to scatter with destructive interference for particular reciprocal-lattice points.

Thus, by examining both the symmetry of a diffraction pattern and the systematic extinctions, a crystallographer can usually identify one or two possible space groups for any crystal. However, some ambiguity may remain because of cases in which pairs of space groups display the same diffraction symmetry and systematic extinctions. ■



**Robert B. Von Dreele** has been a staff member at Los Alamos since 1986. (He had, however, established a connection with the Laboratory earlier by doing neutron powder diffractometry at the Omega West Reactor and by consulting at what is now LANSCE during the summers of 198&85.) His current responsibilities include the High Intensity Powder Diffractometer at LANSCE. He received his B.S. in Chemical Engineering and Ph.D. in Chemistry from Cornell University in 1966 and 1971, respectively. Immediately after completing his Ph.D. he joined the faculty of the Department of Chemistry at Arizona State University, where he remained until he joined the Laboratory. In 1971 he was a National Science Foundation Postdoctoral Fellow at Oxford University, where he worked on one of the first applications of the Rietveld refinement technique to neutron powder-diffraction data. A subsequent sabbatical year was spent as the first visitor to the "Neutron Beam Research Unit" (now ISIS) at the Rutherford-Appleton Laboratory in England. There he developed the first computer code capable of Rietveld refinement with time-of-flight powder-diffraction data from a spallation source. He later visited ISIS for seven months as a Fulbright Scholar.

## Further Reading

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