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Fundamentals of Powder Diffraction and Structural Characterization of Materials

Second Edition

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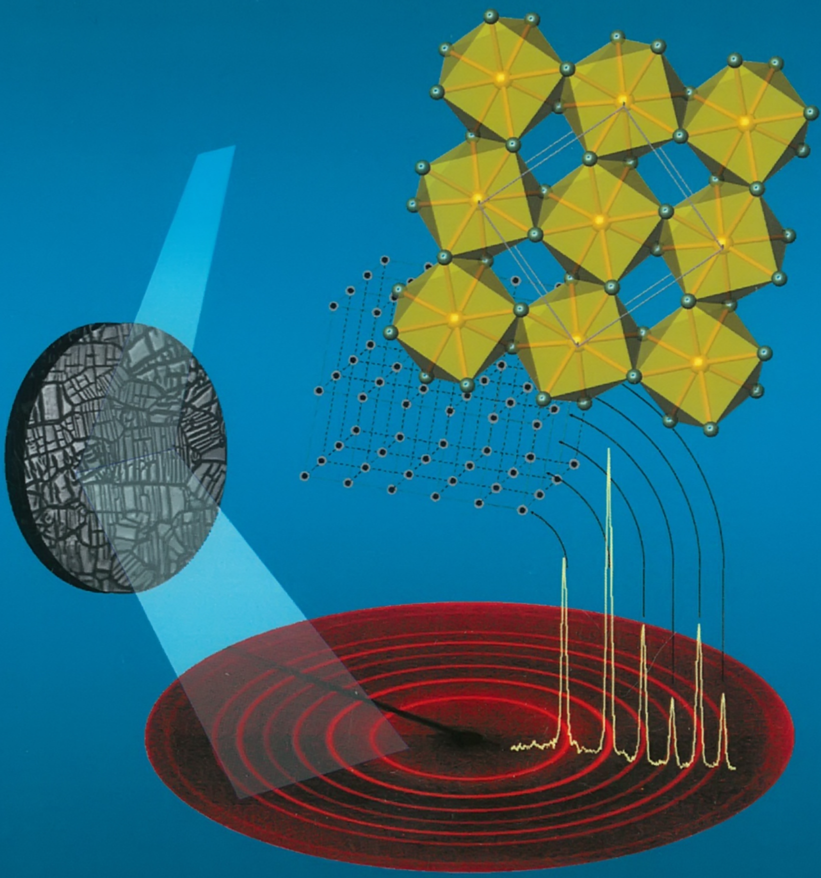

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Chapter 2
Finite Symmetry Elements and Crystallographic Point Groups

In addition to simple translations, which are important for understanding the concept of the lattice, other types of symmetry may be, and are present in the majority of real crystal structures. Here we begin with considering a single unit cell, because it is the unit cell that forms a fundamental building block of a three-dimensionally periodic, infinite lattice, and therefore, the vast array of crystalline materials.

2.1 Content of the Unit Cell

To completely describe the crystal structure, it is not enough to characterize only the geometry of the unit cell. One also needs to establish the distribution of atoms in the unit cell, and consequently, in the entire lattice. The latter is done by simply translating each point inside the unit cell using (1.1). Hence, the three noncoplanar vectors **a**, **b**, and **c** form a basis of the coordinate system with three noncoplanar axes X, Y, and Z, which is called the crystallographic coordinate system or the crystallographic basis. The coordinates of a point inside the unit cell, i.e., the coordinate triplets x, y, z, are expressed in fractions of the unit cell edge lengths, and therefore, they vary from 0 to 1 along the corresponding vectors (**a**, **b**, or **c**).[1] Thus, the coordinates of the origin of the unit cell are always $0, 0, 0$ ($x = 0$, $y = 0$ and $z = 0$), and for the ends of **a**-, **b**-, and **c**-vectors, they are $1, 0, 0$; $0, 1, 0$ and $0, 0, 1$, respectively. Again, using capital italic X, Y, and Z, we will always refer to crystallographic axes coinciding with **a**, **b**, and **c** directions, respectively, while small italic x, y, and z are used to specify the corresponding fractional coordinates along the X, Y, and Z axes.

An example of the unit cell in three dimensions and its content given in terms of coordinates of all atoms is shown in Fig. 2.1. Here, the centers of gravity of three atoms ("large," "medium," and "small" happy faces) have coordinates x_1, y_1, z_1; x_2, y_2, z_2 and x_3, y_3, z_3, respectively. Strictly speaking, the content of the unit cell

[1] In order to emphasize that the coordinate triplets list fractional coordinates of atoms, in crystallographic literature these are often denoted as x/a, y/b, and z/c.

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should be described by specifying other relevant atomic parameters in addition to the position of each atom in the unit cell. These include types of atoms (i.e., their chemical symbols or sequential numbers in a periodic table instead of "large," "medium" and "small"), site occupancy, and individual displacement parameters. All these quantities are defined and explained later in the book, see Chap. 9.

2.2 Asymmetric Part of the Unit Cell

It is important to realize that the case shown in Fig. 2.1 is rarely observed in reality. Usually, unit cell contains more than one molecule or a group of atoms that are converted into each other by simple geometrical transformations, which are called *symmetry operations*. Overall, there may be as many as 192 transformations in some highly symmetric unit cells. A simple example is shown in Fig. 2.2, where each unit cell contains two molecules that are converted into one another by 180° *rotation* around imaginary lines, which are perpendicular to the plane of the figure. The location of one of these lines (*rotation axes*) is indicated using small filled ellipse. The original molecule, chosen arbitrarily, is white, while the derived, symmetrically related molecule is black.

The independent part of the unit cell (e.g., the upper right half of the unit cell separated by a dash-dotted line and hatched in Fig. 2.2) is called the asymmetric unit. It is the only part of the unit cell for which the specification of atomic positions and other atomic parameters are required. The entire content of the unit cell can be established from its asymmetric unit using the combination of symmetry operations present in the unit cell. Here, this operation is a rotation by 180° around the line perpendicular to the plane of the projection at the center of the unit cell. It is worth noting that the rotation axis shown in the upper left corner of Fig. 2.2 is not the only axis present in this crystal lattice – identical axes are found at the beginning and in the middle of every unit cell edge as shown in one of the neighboring cells.[2]

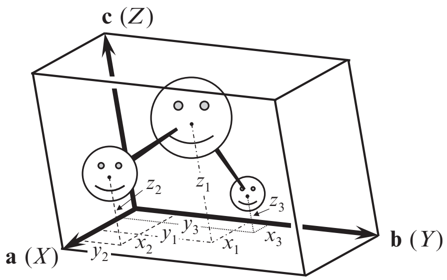

Fig. 2.1 Illustration of the content of the unit cell. The coordinates of the center of gravity of each atom are given as triplets, i.e., x_1, y_1, z_1; x_2, y_2, z_2 and x_3, y_3, z_3.

[2] The appearance of additional rotation axes in each unit cell is the result of the simultaneous presence of both rotational and translational symmetry, which interact with one another (see Sects. 2.5 and 3.3, below).

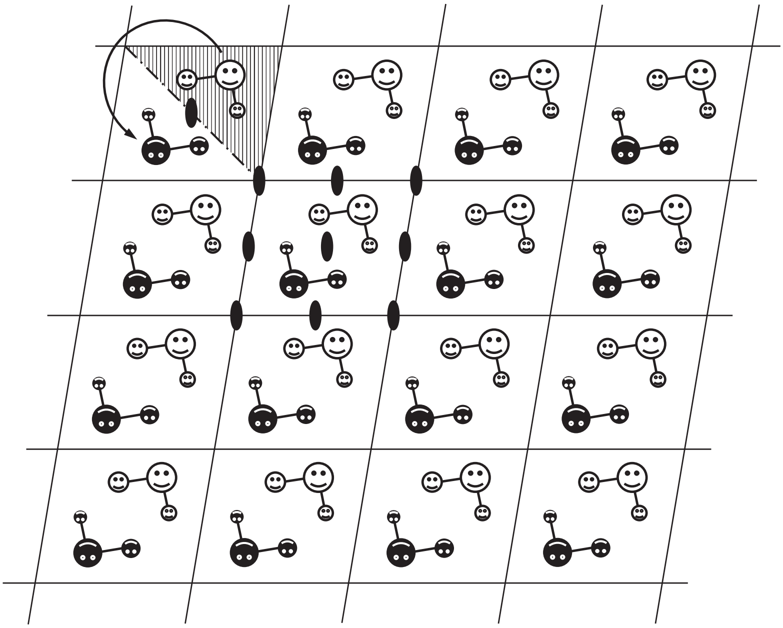

Fig. 2.2 Asymmetric unit (*hatched vertically*) contains an independent molecule, which is clear. Black molecules are related to clear molecules in each unit cell via rotation by 180° around the lines perpendicular to the plane of the projection at the center of each unit cell. The difference in color is used only to highlight symmetrical relationships, since the clear and the black molecules are indeed identical. All rotation axes intersecting every unit cell are shown in a neighboring cell.

Symmetry operations, therefore, can be visualized by means of certain symmetry elements represented by various graphical objects. There are four so-called simple symmetry elements: a point to visualize inversion, a line for rotation, a plane for reflection, and the already mentioned translation is also a simple symmetry element, which can be visualized as a vector. Simple symmetry elements may be combined with one another, producing complex symmetry elements that include roto-inversion axes, screw axes, and glide planes.

2.3 Symmetry Operations and Symmetry Elements

From the beginning, it is important to acknowledge that a symmetry operation is not the same as a symmetry element. The difference between the two can be defined as follows: a symmetry operation performs a certain symmetrical transformation and yields only one additional object, for example, an atom or a molecule, which is symmetrically equivalent to the original. On the other hand, a symmetry element is a graphical or a geometrical representation of one or more symmetry operations, such as a mirror reflection in a plane, a rotation about an axis, or an inversion through a point. A much more comprehensive description of the term "symmetry element" exceeds the scope of this book.[3]

Without the presence of translations, a single crystallographic symmetry element may yield a total from one to six objects symmetrically equivalent to one another. For example, a rotation by 60° around an axis is a symmetry operation, whereas the sixfold rotation axis is a symmetry element which contains six rotational symmetry operations: by 60°, 120°, 180°, 240°, 300°, and 360° about the same axis. The latter is the same as rotation by 0° or any multiple of 360°. As a result, the sixfold rotation axis produces a total of six symmetrically equivalent objects counting the original. Note that the 360° rotation yields an object identical to the original and literally converts the object into itself. Hence, symmetry elements are used in visual description of symmetry operations, while symmetry operations are invaluable in the algebraic or mathematical representation of crystallographic symmetry, for example, in computing.

Four simple symmetry operations – rotation, inversion, reflection, and translation – are illustrated in Fig. 2.3. Their association with the corresponding geometrical objects and symmetry elements is summarized in Table 2.1. Complex symmetry elements are shown in Table 2.2. There are three new complex symmetry elements, which are listed in italics in this table:

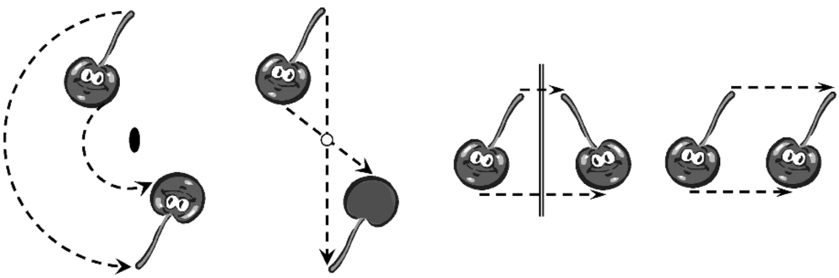

Fig. 2.3 Simple symmetry operations. From *left* to *right*: rotation, inversion, reflection, and translation.

[3] It may be found in: P.M. de Wolff, Y. Billiet, J.D.H. Donnay, W. Fischer, R.B. Galiulin, A.M. Glazer, Marjorie Senechal, D.P. Schoemaker, H. Wondratchek, Th. Hahn, A.J.C. Wilson, and S.C. Abrahams, Definition of symmetry elements in space groups and point groups. Report of the International Union of Crystallography ad hoc committee on the nomenclature in symmetry, Acta Cryst. **A45**, 494 (1989); P.M. de Wolff, Y. Billiet, J.D.H. Donnay, W. Fischer, R.B. Galiulin, A.M. Glazer, Th. Hahn, M. Senechal, D.P. Schoemaker, H. Wondratchek, A.J.C. Wilson, and S.C. Abrahams, Symbols for symmetry elements and symmetry operations. Final report of the International Union of Crystallography ad hoc committee on the nomenclature in symmetry, Acta Cryst. **A48**, 727 (1992); H.D. Flack, H. Wondratchek, Th. Hahn, and S.C. Abrahams, Symmetry elements in space groups and point groups. Addenda to two IUCr reports on the nomenclature in symmetry, Acta Cryst. **A56**, 96 (2000).

Table 2.1 Simple symmetry operations and conforming symmetry elements.

Symmetry operation	Geometrical representation	Symmetry element
Rotation	Line (axis)	Rotation axis
Inversion	Point (center)	Center of inversion
Reflection	Plane	Mirror plane
Translation	Vector	Translation vector

Table 2.2 Derivation of complex symmetry elements.

Symmetry operation	Rotation	Inversion	Reflection	Translation
Rotation	–	*Roto-inversion axis*[a]	No[b]	*Screw axis*
Inversion	–	–	No[b]	No[b]
Reflection	–	–	–	*Glide plane*
Translation	–	–	–	–

[a] The prefix "roto" is nearly always omitted and these axes are called "inversion axes."
[b] No new complex symmetry element is formed as a result of this combination.

- Roto-inversion axis (usually called inversion axis), which includes simultaneous rotation and inversion.[4]
- Screw axis, which includes simultaneous rotation and translation.
- Glide plane, which combines reflection and translation.

Symmetry operations and elements are sometimes classified by the way they transform an object as proper and improper. An improper symmetry operation inverts an object in a way that may be imaged by comparing the right and left hands: the right hand is an inverted image of the left hand, and if you have ever tried to put a right-handed leather glove on your left hand, you know that it is quite difficult, unless the glove has been turned inside out, or in other words, inverted. The inverted object is said to be enantiomorphous to the direct object and vice versa. Thus, symmetry operations and elements that involve inversion or reflection, including when they are present in complex symmetry elements, are improper. They are: center of inversion, inversion axes, mirror plane, and glide planes. On the contrary, proper symmetry elements include only operations that do not invert an object, such as rotation and translation. They are rotation axes, screw axes, and translation vectors. As is seen in Fig. 2.3 both the rotation and translation, which are proper symmetry operations, change the position of the object without inversion, whereas both the inversion and reflection, that is, improper symmetry operations, invert the object in addition to changing its location.

Another classification is based on the presence or absence of translation in a symmetry element or operation. Symmetry elements containing a translational component, such as a simple translation, screw axis, or glide plane, produce infinite numbers of symmetrically equivalent objects, and therefore, these may be called

[4] Alternatively, roto-reflection axes combining simultaneous rotation and reflection may be used, however, each of them is identical in its action to one of the roto-inversion axes.

infinite symmetry elements. For example, the lattice is infinite because of the presence of translations. All other symmetry elements that do not contain translations always produce a finite number of objects, and they may be called finite symmetry elements. Center of inversion, mirror plane, rotation, and roto-inversion axes are all finite symmetry elements. Finite symmetry elements and operations are used to describe the symmetry of finite objects, for example, molecules, clusters, polyhedra, crystal forms, unit cell shape, and any noncrystallographic finite objects, for example, the human body. Both finite and infinite symmetry elements are necessary to describe the symmetry of infinite or continuous structures, such as a crystal structure, two-dimensional wall patterns, and others. We begin the analysis of crystallographic symmetry from simpler finite symmetry elements, followed by the consideration of more complex infinite symmetry elements.

2.4 Finite Symmetry Elements

Symbols of finite crystallographic symmetry elements and their graphical representations are listed in Table 2.3. The full name of a symmetry element is formed by adding "N-fold" to the words "rotation axis" or "inversion axis." The numeral N generally corresponds to the total number of objects generated by the element,[5] and it is also known as the order or the multiplicity of the symmetry element. Orders of axes are found in columns 2 and 4 in Table 2.3, for example, a threefold rotation axis or a fourfold inversion axis.

Note that the onefold inversion axis and the twofold inversion axis are identical in their action to the center of inversion and the mirror plane, respectively. Both the center of inversion and mirror plane are commonly used in crystallography, mostly

Table 2.3 Symbols of finite crystallographic symmetry elements.

Rotation angle, φ	Rotation axes		Roto-inversion axes	
	International symbol	Graphical symbol[a]	International symbol	Graphical symbol[a]
360°	1	none	$\bar{1}$[b]	
180°	2		$\bar{2} = m$[c]	
120°	3		$\bar{3} = 3 + \bar{1}$	
90°	4		$\bar{4}$	
60°	6		$\bar{6} = 3 + m \perp 3$	

[a] When the symmetry element is perpendicular to the plane of the projection.
[b] Identical to the center of inversion.
[c] Identical to the mirror plane.

[5] Except for the center of inversion, which results in two objects, and the threefold inversion axis, which produces six symmetrically equivalent objects. See (4.27) and (4.28) in Sect. 4.2.4 for an algebraic definition of the order of a symmetry element.

because they are described by simple geometrical elements: point or plane, respectively. The center of inversion is also often called the "center of symmetry."

Further, as we see in Sects. 2.4.3 and 2.4.5, below, transformations performed by the threefold inversion and the sixfold inversion axes can be represented by two independent simple symmetry elements. In the case of the threefold inversion axis, $\bar{3}$, these are the threefold rotation axis and the center of inversion present independently, and in the case of the sixfold inversion axis, $\bar{6}$, the two independent symmetry elements are the mirror plane and the threefold rotation axis perpendicular to the plane, as denoted in Table 2.3. The remaining fourfold inversion axis, $\bar{4}$, is a unique symmetry element (Sect. 2.4.4), which cannot be represented by any pair of independently acting symmetry elements.

Numerals in the international symbols of the center of inversion and all inversion axes are conventionally marked with the bar on top[6] and not with the dash or the minus sign in front of the numeral (see Table 2.3). The dash preceding the numeral (or the letter "b" following the numeral – shorthand for "bar"), however, is more convenient to use in computing for the input of symmetry data, for example, -1 (or 1b), -3 (3b), -4 (4b), and -6 (6b) rather than $\bar{1}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$, respectively.

The columns labeled "Graphical symbol" in Table 2.3 correspond to graphical representations of symmetry elements when they are perpendicular to the plane of the projection. Other orientations of rotation and inversion axes are conventionally indicated using the same symbols to designate the order of the axis with properly oriented lines, as shown in Fig. 2.4. Horizontal and diagonal mirror planes are normally labeled using bold lines, as shown in Fig. 2.4, or using double lines in stereographic projections (see Table 2.3 and Sect. 2.8).

When we began our discussion of crystallographic symmetry, we used a happy face and a cherry to illustrate simple concepts of symmetry. These objects are inconvenient to use with complex symmetry elements. On the other hand, the commonly used empty circles with or without a comma inside to indicate enantiomorphous objects, for example, as in the International Tables for Crystallography,[7] are not intuitive. For example, both inversion and reflection look quite similar. Therefore, we will use a trigonal pyramid, shown in Fig. 2.5. This figure illustrates two pyra-

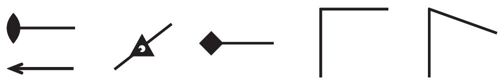

Fig. 2.4 From *left* to *right*: horizontal twofold rotation axis (*top*) and its alternative symbol (*bottom*), diagonal threefold inversion axis inclined to the plane of the projection, horizontal fourfold rotation axis, horizontal, and diagonal mirror planes. *Horizontal* or *vertical lines* are commonly used to indicate axes located in the plane of the projection, and *diagonal lines* are used to indicate axes, which form an angle other than the right angle or zero with the plane of the projection.

[6] As in the "Crystallography" true-type font for Windows developed by Len Barbour. The font file is available from http://x-seed.net/freestuff.html. This font has been used by the authors to typeset crystallographic symbols in the manuscript of this book.

[7] International Tables for Crystallography, vol. A, Fifth revised edition, Theo Hahn, Ed., Published jointly with the International Union of Crystallography (IUCr) by Springer, Berlin (2002).

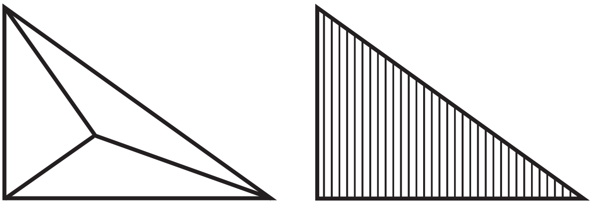

Fig. 2.5 Trigonal pyramid with its apex up (*left*) and down (*right*) relative to the plane of the paper. Hatching is used to emphasize enantiomorphous objects.

mids, one with its apex facing upward, where lines connect the visible apex with the base corners, and another with its apex facing downward, which has no visible lines. In addition, the pyramid with its apex down is hatched to accentuate the enantiomorphism of the two pyramids.

To review symmetry elements in detail we must find out more about rotational symmetry, since both the center of inversion and mirror plane can be represented as rotation plus inversion (see Table 2.3). The important properties of rotational symmetry are the direction of the axis and the rotation angle. It is almost intuitive that the rotation angle: (φ) can only be an integer fraction (1/N) of a full turn (360°), otherwise it can be substituted by a different rotation angle that is an integer fraction of the full turn, or it will result in the noncrystallographic rotational symmetry. Hence,

$$\varphi = \frac{360^\circ}{\mathrm{N}} \tag{2.1}$$

By comparing (2.1) with Table 2.3, it is easy to see that N, which is the order of the axis, is also the number of elementary rotations required to accomplish a full turn around the axis. In principle, N can be any integer number, for example, 1, 2, 3, 4, 5, 6, 7, 8… However, in periodic crystals only a few specific values are allowed for N due to the presence of translational symmetry. Only axes with N = 1, 2, 3, 4, or 6 are compatible with the periodic crystal lattice, that is, with translational symmetry in three dimensions. Other orders, such as 5, 7, 8, and higher will inevitably result in the loss of the conventional periodicity of the lattice, which is defined by (1.1). The not so distant discovery of fivefold and tenfold rotational symmetry continue to intrigue scientists even today, since it is quite clear that it is impossible to build a periodic crystalline lattice in two dimensions exclusively from pentagons, as depicted in Fig. 2.6, heptagons, octagons, etc. The situation shown in this figure may be rephrased as follows: "It is impossible to completely fill the area in two dimensions with pentagons without creating gaps."

It is worth noting that the structure in Fig. 2.6 not only looks ordered, but it is indeed perfectly ordered. Moreover, in recent decades, many crystals with fivefold symmetry have been found and their approximant structures have been determined with various degrees of accuracy. These crystals, however, do not have translational symmetry in three directions, which means that they do not have a finite unit cell

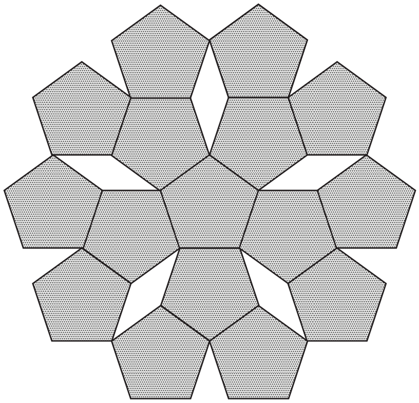

Fig. 2.6 Filling the area with *shaded pentagons*. *White parallelograms* represent voids in the two-dimensional pattern of *pentagons*.

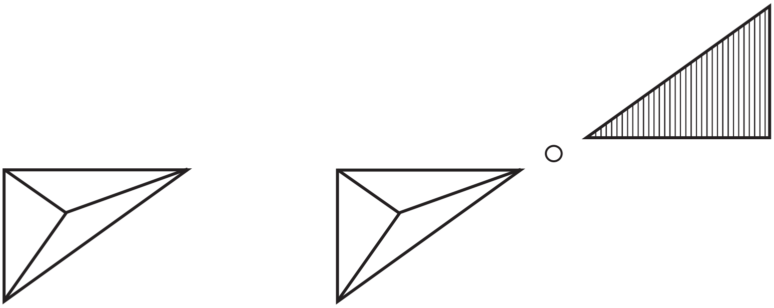

Fig. 2.7 Onefold rotation axis (*left*, unmarked since it can be located anywhere) and center of inversion (*right*).

and, therefore, they are called quasicrystals: quasi – because there is no translational symmetry, crystals – because they produce discrete, crystal-like diffraction patterns.

2.4.1 Onefold Rotation Axis and Center of Inversion

The onefold rotation axis, shown in Fig. 2.7 on the left, rotates an object by 360°, or in other words converts any object into itself, which is the same as if no symmetrical transformation had been performed. This is the only symmetry element which does not generate additional objects except the original.

The center of inversion (onefold inversion axis) inverts an object through a point as shown in Fig. 2.7, right. Thus, the clear pyramid with its apex up, which is the original object, is inverted through a point producing its symmetrical equivalent – the hatched (enantiomorphous) pyramid with its apex down. The latter is converted back into the original clear pyramid after the inversion through the same point. The center of inversion, therefore, generates one additional object, giving a total of two related objects.