

1 Structures of Crystalline Materials

This book is about functional materials—those that perform a task or a technological operation. By the end of the book, we'll see that all useful properties can ultimately be traced back to structure and dynamics at the atomic level of materials. Understanding structure is therefore of crucial importance.

In this chapter we'll investigate the structures of crystalline materials—those in which atomic arrangements are repeated periodically in three-dimensional (3D) space. Non-crystalline materials are covered in Chapter 15. In the first section, we will discuss the symmetry and crystallography concepts that are important for the description of crystalline substances. A brief introduction to structure databases will follow. In the third section, we'll cover the nomenclature and electron counting rules needed to understand the composition of solids; before learning in the fourth section how structures are built up by packing spheres, connecting coordination polyhedra, or via networks. In the fifth and last section, we'll discuss some structure types encountered later in the book. In addition to the figures and descriptions given in the chapter, readers might find it useful to draw models of important structures with the included structural coordinates.

1.1 Symmetry

In the first section of this chapter, we'll develop the language required to describe the structures of crystalline compounds. We know from everyday life that such materials frequently display an amazing regularity and symmetry on the macroscopic scale—salt crystals can grow as “perfect” cubes and many minerals and gemstones display wonderfully symmetric facets. The origin of this macroscopic symmetry can ultimately be traced back to the symmetry that's present at the atomic scale (\AA or 10^{-10} m). This local symmetry is replicated millions of times by translational symmetry to produce symmetric macroscopic objects. It's perhaps worth stating at the outset that there is nothing “magical” about the high-symmetry structures materials adopt. As we will see in Chapter 5, local bonding

2 Structures of Crystalline Materials

interactions have inherent symmetry, and dense packing of such units is favorable energetically.

1.1.1 Translational Symmetry

To describe a crystal structure, it is useful to introduce the concept of **lattice**; a spatial pattern of points of equal and equally oriented surroundings. We then define a **motif**, which might be a small group of atoms, a molecule, or a collection of several molecules. If we associate this motif with each of the lattice points, a crystal structure is built as shown in Figure 1.1. We can think of this “association” as re-drawing the motif at a constant displacement from each lattice point. The lattice is an operator of **translational symmetry** of crystal structures, of their periodicity. We can see in Figure 1.1 that the translational symmetry defined by the lattice produces a structure in which the individual atoms in the motif achieve a sensible bonding environment.

The small spatial segment that fully represents the entire structure upon periodic repetition is called the **unit cell**.¹ We can use the analogy of tiles (2D) or bricks (3D) being stacked side by side. In 3D, the unit cell is a parallelepiped, a box whose sides are parallelograms. The size and shape of the unit cell is described with three lattice vectors **a**, **b**, **c** of lengths *a*, *b*, *c*, and angles α , β , γ . The angle α is between **b** and **c**, β between **a** and **c**, and γ between **a** and **b**. Together, *a*, *b*, *c*, α , β , γ are called **lattice parameters** or **unit-cell parameters**.

Positions of atoms inside the unit cell are expressed with **relative or fractional coordinates** *x*, *y*, *z* in terms of fractions of the lattice vectors that define the unit cell. Fractional coordinates define the position (or radius) vector **r** from the unit-cell origin to the atomic position as $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. They can always be expressed on a 0 to 1 scale. Because of translational symmetry, a coordinate of 1.2 is equivalent to 0.2, or a coordinate -0.2 is equivalent to $-0.2 + 1 = 0.8$.

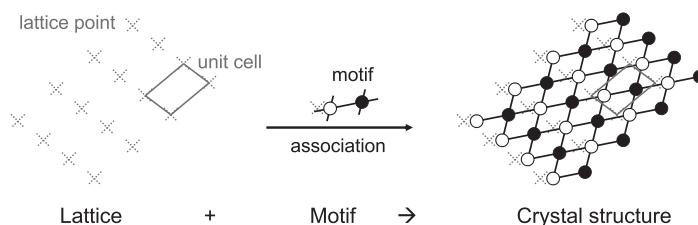


Figure 1.1 Association of an atomic motif with a lattice produces a crystal structure.

¹ The following rules apply for choosing the unit cell: (a) its rotational symmetry is the same as that of the lattice, (b) the edges and angles are made as similar to each other as possible, (c) the number of right angles is maximized, and (d) the volume is minimized. Where applicable, the origin coincides with the inversion center of symmetry (Section 1.1.2). In some cases (Section 1.1.4), the cell contains more than one lattice point.

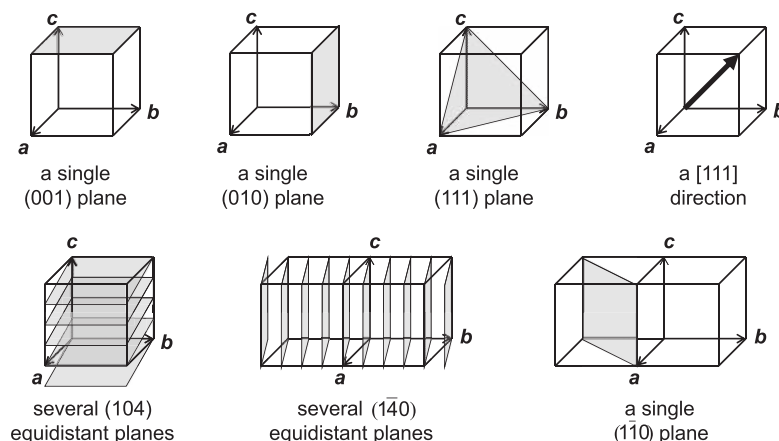


Figure 1.2 Description by indices of lattice planes and lattice directions with respect to the unit cell. An extra cell is drawn in order to show cases where planes facing the origin intercept the lattice vector at negative values.

Directions in the lattice are given with a $[uvw]$ notation. When a line is drawn from the origin, parallel to the desired direction, then u, v, w are simply the relative/fractional coordinates of any point that line goes through, multiplied to give integer values. If it goes through $\frac{1}{2}, 1, \frac{1}{2}$, the direction is $[121]$. Symbols $[242]$ and $[484]$ would represent the same direction. A set of symmetrically equivalent lattice directions, such as $[100]$, $[010]$, $[001]$, $[-100]$, $[0-10]$, $[00-1]$ in a cubic lattice, is collectively referred to using angle brackets, $\langle 100 \rangle$.

It's often useful to define a **set of parallel equidistant planes** in a lattice. These are represented by an hkl notation. Starting with the plane that contains the origin, an hkl set of equidistant planes divides the unit-cell vector a into h sections, b into k sections and c into l sections (Figure 1.2). Dividing into 0 sections is possible and means that the set of planes is parallel with that axis. If the plane that faces the origin crosses a , b , or c at negative values, the appropriate h , k , or l of that set has negative sign (often put above the index, like \bar{h}). An (hkl) symbol refers to a plane or to a crystal face (Miller indices). A set of their symmetry-equivalent orientations is denoted in curly brackets, $\{hkl\}$.

1.1.2 Rotational Symmetry

A **point group**² is a set of symmetry operations that fulfill the mathematical requirements of being a group³ and act on an isolated geometrical object. The number of

² At least one point of the object remains unshifted under point-group symmetry operations. Elementary knowledge of point-group symmetry may be an advantage for the reader; see Further Reading.

³ A group must have a closure (combination of two elements yields an element of the group), fulfill the mathematic associative law (the result of combination of the elements is independent of the order they are applied), have an identity (an element that converts other elements into themselves), and have an inversion (every element has an inverse element; when combined together, they yield the identity element).

4 Structures of Crystalline Materials

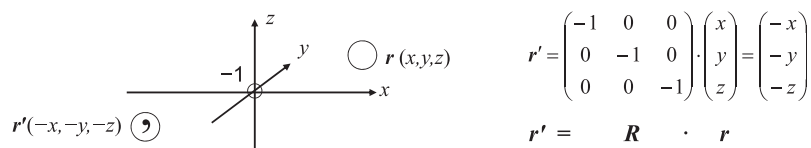


Figure 1.3 Inversion center (symbol -1 or $\bar{1}$) at the origin operates on an object at the endpoint of the object's radius vector r . The comma symbolizes a change in handedness (left- to right-hand relationship).

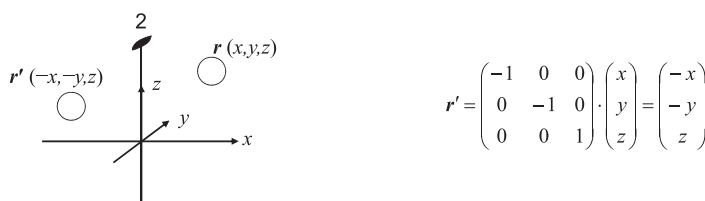


Figure 1.4 Operation of the twofold rotation axis (of symbols 2 in text and \blacklozenge in graphics) on an object at the point r .

symmetry operations defines the **order of the group**; the higher the order, the higher the symmetry. The symmetry operations are performed by the **elements of point symmetry**; the identity, inversion center, mirror plane, rotation axis, and rotoinversion axis. All objects possess the **identity**; other symmetry elements may or may not be present.

Let's start with the **inversion center**. Figure 1.3 shows a point x, y, z represented by its radius vector r and the effect on that point of an inversion center at the origin of the coordinate system (shown by a small circle). Inversion moves x, y, z to $-x, -y, -z$. Mathematically, we can describe this transformation of r to r' with the equation $r' = R \cdot r$, where R is the matrix of the point-symmetry element, describing its operation.⁴ Inversion is given the symbol -1 , often typeset as $\bar{1}$.

Symmetry elements that unify a point in lattice space with another one by rotating it in steps of $1/n$ ($n = 1, 2, 3, 4, 6$) of the full circle are called n -fold **rotation axes**. The full-circle rotation ($n = 1$) is the identity, a twofold axis ($n = 2$) rotates by $1/2$ of the full circle and has symbol 2 , etc. As can be seen in Figure 1.4, twofold rotation around the z axis moves a point of fractional coordinates x, y, z to $-x, -y, z$. A **rotoinversion axis** is a single element, the operation of which combines rotation and inversion. However, the twofold rotoinversion axis -2 , shown in Figure 1.5, operates like a mirror plane, m , as can be also demonstrated by

⁴ The three columns in this matrix are the products of the particular symmetry operation on the end-points of the respective unit-cell vectors $(1, 0, 0)$, $(0, 1, 0)$, and $(0, 0, 1)$. This is conveniently used to set up the matrix.

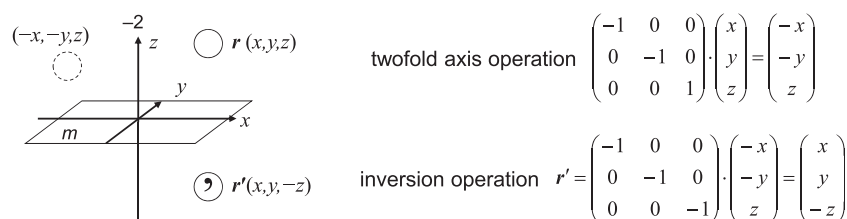


Figure 1.5 Rotoinversion axis $\bar{2}$ is identical with mirror m .

multiplying together the matrices representing 2 and -1 . Since $m \equiv \bar{2}$, all point-symmetry elements are in fact **elements of rotational symmetry**; the rotational axes $1, 2, 3, 4, 6$ and the rotoinversion axes $\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{6}$. Accordingly, the operation matrix of each of them has the symbol R .

1.1.3 Crystallographic Point Groups and Crystal Systems

Due to the infinite number of rotation axes, infinitely many point groups are possible for *isolated objects*. However, in crystal structures, the translational symmetry of space filling is only compatible with a small number of rotation axes. Consider that we can tile a plane perfectly with identical rectangular tiles (twofold axis present), isosceles triangles (threefold), squares (fourfold), or hexagons (sixfold), but we can't with pentagons (fivefold) or heptagons (sevenfold), etc. This argument extends to the 3D space filled by the "bricks" of unit cells (Figure 1.1). The point groups with symmetry elements $1, 2, 3, 4, 6, \bar{1}, m (\equiv \bar{2}), \bar{3}, \bar{4}, \bar{6}$, which are compatible with translational symmetry, are called **crystallographic point groups**, also known as **crystal classes**.

There are 32 crystallographic point groups and they are classified into seven **crystal systems**; cubic, tetragonal, hexagonal, trigonal, orthorhombic, monoclinic, and triclinic. Each crystal system is defined by its minimum point-group symmetry (Table 1.1, see also Appendix A). If we take the cubic system as an example, the minimum-symmetry point group has symbol 23 . It means that at each lattice point, the twofold axes along the x -, y -, and z -coordinate-system axes repeat the threefold axis of the symbol along all body diagonals of the adjacent cells. These threefold axes are easier to visualize and remember as the symmetry condition for the cubic crystal system. So if the actual crystal structure has four intersecting threefold axes, it is cubic. If you do not see intersecting threefold axes, the structure cannot be cubic even if the unit cell has right angles and equal edges.

1.1.4 Bravais Lattices

As noted earlier, a lattice is a collection of points with identical surroundings. Having the highest rotational symmetry of each crystal system, 14 types of **Bravais lattices** are possible

6 Structures of Crystalline Materials

Table 1.1 Sorting 32 crystallographic point groups into seven crystal systems.

Crystal system	Minimum symmetry	Higher-symmetry point groups
Triclinic	1	$\bar{1}$
Monoclinic	2, m	2/m
Orthorhombic	222	$mm2$, mmm
Tetragonal	4, $\bar{4}$	4/m, 422, 4mm, $\bar{4}2m$, 4/mmm
Hexagonal	6, $\bar{6}$	6/m, 622, 6mm, $\bar{6}m2$, 6/mmm
Trigonal	3, $\bar{3}$	32, 3m, $\bar{3}m$
Cubic	23	$m\bar{3}$, $\bar{4}3m$, 432, $m\bar{3}m$

(Figure 1.6), which represent 14 types of translational symmetry in 3D lattice space⁵ of relative coordinates (Section 1.1.1). Some unit cells have lattice points only at the corners, and their lattices are called **primitive Bravais lattices**, labeled with symbol P . Others have lattice points located also at the centers of some or all unit-cell faces or at the unit-cell center, and these are called **centered Bravais lattices**. The body-centered lattice has symbol I (the cell has an additional lattice point at $\frac{1}{2}a + \frac{1}{2}b + \frac{1}{2}c$ relative to a P lattice). The face-centered lattices have symbol F when all unit-cell faces are centered. Symbol A , B , or C is used when just two opposite unit-cell sides are centered, along one direction, a , b , or c . Thus, **C -centering**⁶ adds an additional lattice point at $\frac{1}{2}a + \frac{1}{2}b$ relative to a P lattice. A special type of centering, R , occurs in the hexagonal lattice, Figure 1.6. This R -centered lattice is equivalent to a P lattice with a *rhombohedral*⁷ unit cell, see Table 1.2. The rhombohedral lattice occurs only in those structures of the trigonal crystal system that carry the symbol R in their symmetry description. The remaining trigonal structures are described with a primitive hexagonal cell P . It is often convenient to express also the R structures on a hexagonal cell (not just the P). Having triple the volume of the rhombohedral cell, the hexagonal cell contains three rhombohedral lattice points: 0,0,0 and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ with $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$, shown in Figure 1.6 labelled as hR .

Figure 1.7 gives an idea why only certain types of centering are possible for certain crystal systems. For example, a C -centered tetragonal cell could always be described with a smaller primitive cell, an F -centered tetragonal with a smaller I -centered cell. Similarly, a monoclinic B cell becomes a smaller P cell, monoclinic F cell becomes a smaller C cell, and a monoclinic I cell is equivalent to a C cell via an A cell rotated around b . However, there are cases where it is useful to choose a non-standard Bravais cell; for example in order to illustrate similarity between two structures.

⁵ The lattice space defines the orientation and angles of the coordinate-system axes applied to each unit cell of this space.

⁶ While International Tables for Crystallography use the British-English forms “centre”, “centring”, and “centred”, the alternative spellings “center”, “centering”, and “centered” prevail in the USA.

⁷ Terms like *trigonal*, *tetragonal*, and *hexagonal* originate in the rotational symmetry; the term *rhombohedral* implies that the Bravais cell is a rhombohedron, hence it refers to the lattice.

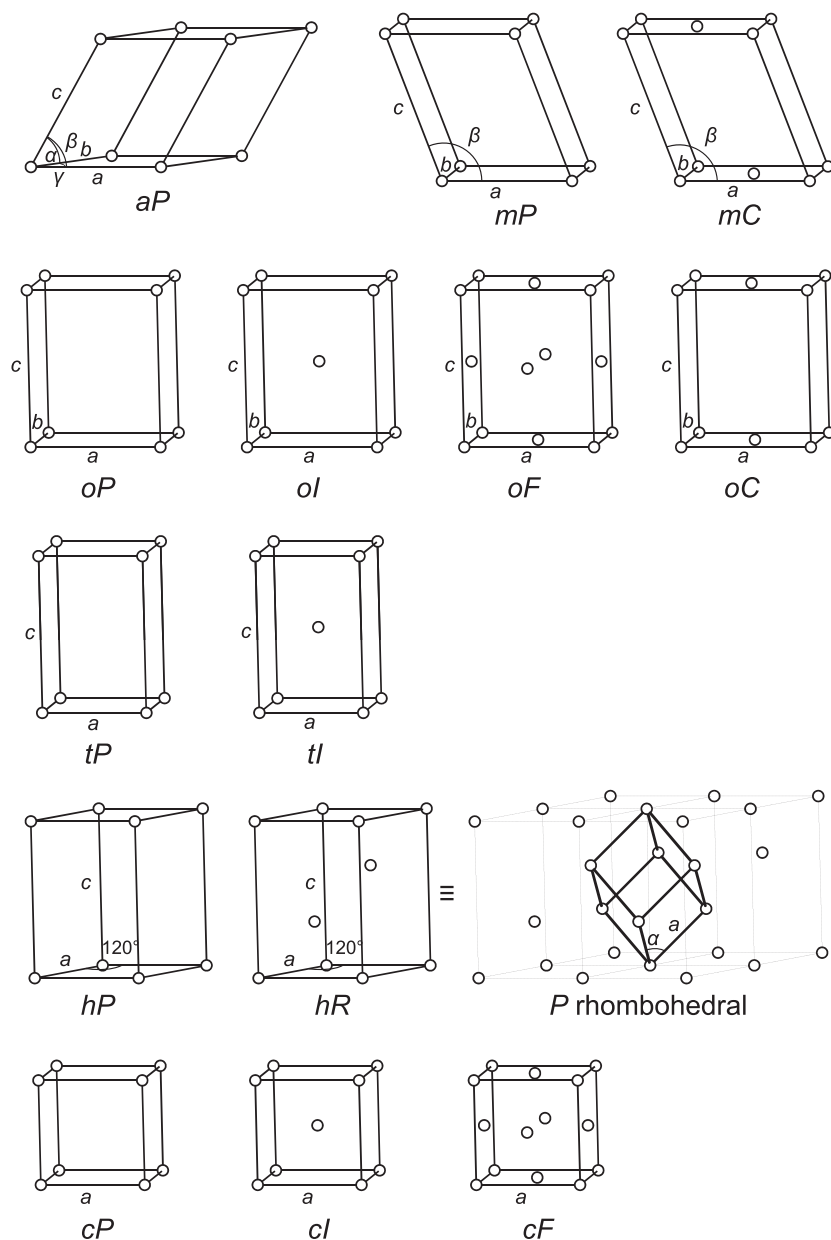


Figure 1.6 Standard settings of the 14 Bravais lattices. Lower-case letters: *a* = anorthic/triclinic, *m* = monoclinic, *o* = orthorhombic, *t* = tetragonal, *h* = hexagonal and *c* = cubic. Upper-case letters refer to centering. The primitive rhombohedral lattice is often described on its equivalent *hR* cell.

8 Structures of Crystalline Materials

Table 1.2 Metrics of lattices. Parameters not listed can take any values.

Lattice	Conditions for lattice parameters
Triclinic (anorthic)	None*
Monoclinic	$\alpha = \gamma = 90^\circ$
Orthorhombic	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b, \alpha = \beta = \gamma = 90^\circ$
Rhombohedral	$a = b = c, \alpha = \beta = \gamma$
Hexagonal	$a = b, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$

* For limits on triclinic angles, see ref. [1].

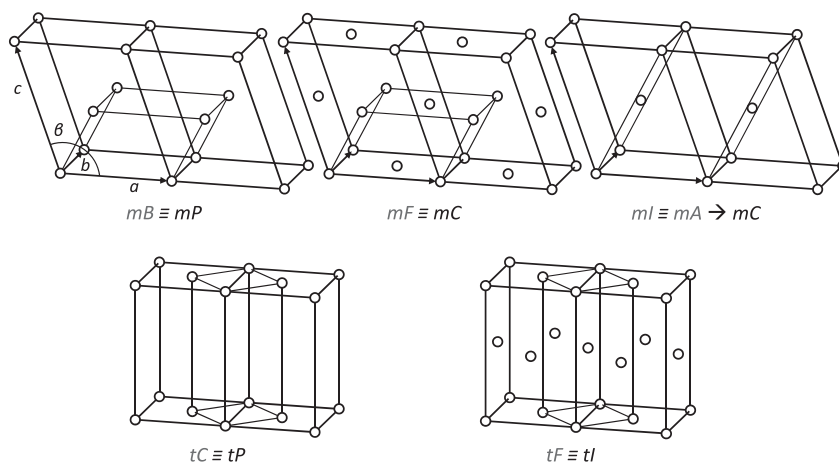


Figure 1.7 Non-standard centering of monoclinic (top) and tetragonal Bravais cells (bottom). Drawing two cells reveals the true cell of the same crystal system.

1.1.5 Introduction to Space Groups

We've seen that there are 32 crystallographic point groups and 14 Bravais lattices. Their combination gives a total of 230 space groups (we'll see where this number comes from in Section 1.1.7). A **space group** defines both the translational symmetry (type of the Bravais lattice) and the rotational symmetry (point group) of the structure. Of the 230 space groups, 73 do not involve any symmetry other than that already present in the Bravais lattice and point group alone; these are called **symmorphic space groups**. The remaining 157 space groups are **non-symmorphic** and possess translations by suitable fractions of lattice vectors, brought about by screw axes or glide planes. Before we explain these two terms, a note on symmetry operators.

When discussing point groups, it was convenient to introduce the matrix operator \mathbf{R} that acts on a point r of the relative-coordinate vector \mathbf{r} such that $\mathbf{r}' = \mathbf{R} \cdot \mathbf{r}$. Because space groups

may include the above-mentioned additional fractional translations, this symbolic language is extended into a **Seitz operator**, $(\mathbf{R} | \mathbf{t}) = \mathbf{R} \cdot \mathbf{r} + \mathbf{t}$, which combines rotations (matrix \mathbf{R}) and the possible translations (vector \mathbf{t}). If we consider a symmetry element that involves no translations, such as the inversion $\bar{1}$, the Seitz symbol is $(\mathbf{R} | 0)$ hence $(\bar{1} | 0)$. A rotational axis has a direction $[uvw]$ that must be included. The Seitz symbol $(2[001] | 0)$ then refers to a twofold rotation around the z axis. A plane has a direction as well—the direction of its normal vector that is oriented perpendicular to the plane. As an example, the mirror in the xy plane of Figure 1.5 has the Seitz symbol $(m[001] | 0)$. The Seitz operators that include the fractional translations are explained in the subsection below.

1.1.6 Symmetry Elements That Combine Rotation and Translation

The periodicity of crystal structures (their translational symmetry) means that the set of rotational symmetry elements repeats at each lattice point. This creates additional symmetry elements in between lattice points and may give rise to two types of symmetry elements that aren't present in isolated molecules,⁸ screw axes and glide planes. A **screw axis** combines rotation with translation along the axis of rotation. An N_M screw axis ($M < N$) rotates anticlockwise by $360/N$ degrees while shifting the image by a distance equal to an M/N fraction of the lattice periodicity along that axis. As an example, the twofold screw axis 2_1 in Figure 1.8 rotates by 180° and shifts by $1/2$ of the vector c (the axis is along z). A 6_3 axis rotates by increments of 60° and each time shifts by $3/6 = 1/2$ of c .

Figure 1.9 shows the symmetry operations of axes 6_2 and 6_4 , illustrating that screw axes N_M and $N_{(N-M)}$ produce mirror images of each other. The “tailed hexagon” is the graphic symbol of the sixfold screw axes.

A **glide plane** operates as a mirror plus a plane-parallel shift by half a vector length between two lattice points. When the shift is half of one lattice vector (either a , b , or c), the glide is called an **axial glide plane** a , or b , or c . The operation of the, say, c glide plane is a reflection

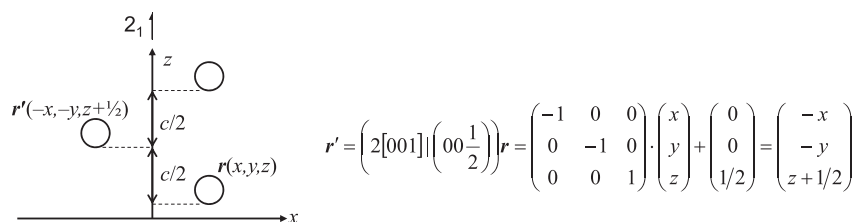


Figure 1.8 The screw axis $2_1[001]$ rotates 180° and shifts by $1/2$ of the vector c . The graphical symbol of 2_1 parallel to the drawing plane is a half-arrow.

⁸ In the point groups used for isolated molecules, all symmetry elements intersect at a point; in space groups this is no longer true.

10 Structures of Crystalline Materials

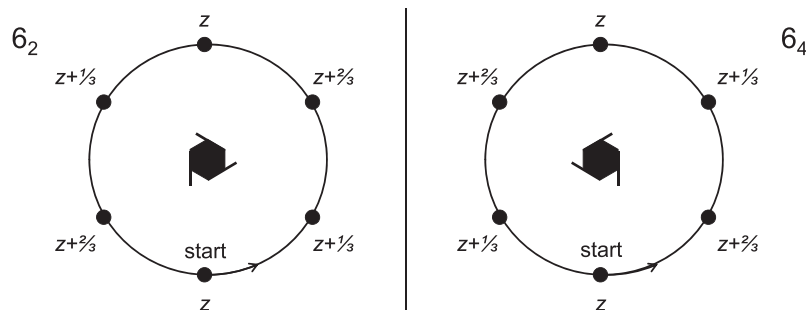


Figure 1.9 Screw axes rotate anticlockwise. Axes 6_2 and 6_4 produce mirror images of each other. The 6_2 axis rotates by 60° and translates by $\frac{2}{6}c$, the 6_4 axis rotates by 60° and translates by $\frac{4}{6}$ of the unit-cell length c . Due to translational symmetry, integers are subtracted from fractional coordinates ≥ 1 , such as $\frac{3}{3} \equiv 0$ or $\frac{10}{3} \equiv \frac{1}{3}$.

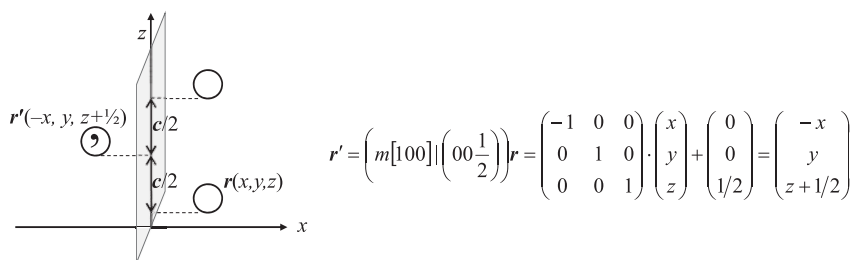


Figure 1.10 The glide plane $c[100]$ creates a mirror image shifted by $c/2$.

followed by shift along c by half the c -length. This is shown in Figure 1.10 with the c -glide plane oriented in the direction of x .⁹ Note that an equally oriented plane with a translation along y would be called a b glide. In rare cases (five of the 230 space groups), centering creates a situation when the two alternative shift directions along a glide plane result in the same point. The symbol a , b , or c of such a glide plane is then changed to e (for equivalent or either), a **double glide plane**.

When the shift length is half the sum of two lattice vectors (half the vector to the diagonal lattice point), we have a **diagonal glide plane**, denoted by the symbol n . An example for $a/2 + b/2$ is in Figure 1.11.

When the shift is half of the F - or I -centering vector, we have a **diamond glide plane**, symbol d . This shift can be decomposed into components along lattice vectors $(a/4) + (b/4)$ or $(a/4) + (c/4)$ or $(b/4) + (c/4)$ for the F -centered orthorhombic and cubic lattices, and into $(a/4) + (b/4) + (c/4)$ for the I -centered tetragonal and cubic lattices.

⁹ As noted above (Section 1.1.5), the direction of a plane is the direction of the plane's normal.