Lecture 2 — Symmetry in the solid state -

Part II: Crystallographic coordinates and Space Groups.

1 Coordinate systems in crystallography and the mathematical form of the symmetry operators

1.1 Why don't we employ Cartesian coordinates?

In crystallography, we almost only employ coordinate systems with **basis vectors coinciding with either primitive or conventional translation operators**. **When primitive translations** are used as basis vectors **points of the pattern related by translation will differ by *integral values of x,y and z***. **When conventional translations** are used as basis vectors, **points of the pattern related by translation will differ by either *integral* or *simple fractional (either n/2 or n/3) values of x,y and z***. This advantage **far outweighs the convenience of using Cartesian coordinates**.

It is important to remark the distinction between **points** of the space and **vectors**. **Points** themselves are not vectors, but **"differences" between points are uniquely associated with vectors**. We may then write

$$p_2 - p_1 = \mathbf{v} \tag{1}$$

and its inverse, i.e., the *sum* of a point with a vector, yielding another point.

$$p_2 = p_1 + \mathbf{v} \tag{2}$$

Once an *origin point* "o" and a *basis for the vector space* are chosen, the *coordinates* of a point p are the *components* of the difference vector $p - o$, a.k.a., the *position vector*. A *coordinate transformation* therefore involves two things: (a) An *origin change* and (b) a *basis change* [1].

Naturally, once a choice of basis has been made, that basis can be used to express vectors *other* than position vectors in terms of their *components*.

In crystallography, *basis vectors* have the dimension of a *length*, and *coordinates* (position vector components) are *dimensionless*.

[1] For a full treatment of the coordinate transformations in crystallography, see [2]

1.2 Notation

We will denote the basis vectors as $\mathbf{a}_i$, where the correspondence with the usual crystallographic notation is

$$\mathbf{a}_1 = \mathbf{a};\ \mathbf{a}_2 = \mathbf{b};\ \mathbf{a}_3 = \mathbf{c} \tag{3}$$

We will sometimes employ explicit array and matrix multiplication for clarity. In this case, the array of basis vectors is written as a *row*, as in $[\mathbf{a}] = [\mathbf{a}_1\, \mathbf{a}_2\, \mathbf{a}_3]$. The corresponding *column* array will be denoted as $[\mathbf{a}]^T$.

Components of a generic vector **v** will be denoted as v^i, where

$$v^1 = v_x;\ v^2 = v_y;\ v^3 = v_z; \tag{4}$$

Components will be expressed using *column* arrays, as in $[v] = \begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix}$, whereas the *row* vector will be denoted by $[v]^T$. As a reminder of this, we use *subscripts* for row arrays and *superscripts* for column arrays.

A ‘vector is then written as

$$\mathbf{v} = \sum_i \mathbf{a}_i v^i \tag{5}$$

Note that a vector not involving an origin choice as written in eq. 5 is an *invariant quantity*, i.e., it does not depend on the choice of coordinates.

1.3 Determination of distances and angles: the metric tensor

In Cartesian coordinates, the scalar product between two vectors takes the familiar form

$$\mathbf{v} \cdot \mathbf{u} = [v]^T[u] = a^2 \sum_{i,j} \delta_{ij} v^i u^j \tag{6}$$

where $a^2 = |\mathbf{a}|$ is the length of the basis vector in whatever units (with dimensions) are employed (it is generally 1 for Cartesian coordinates with a dimensionless basis). We shall now see how

eq. 6 can be generalised to non-Cartesian coordinates. Remembering the generic expression of **v** and **u** we can write

$$\mathbf{v} \cdot \mathbf{u} = \sum_i \mathbf{a}_i v^i \cdot \sum_j \mathbf{a}_j v^j = \sum_{i,j} \left[\mathbf{a}_i \cdot \mathbf{a}_j\right] u^i v^j \tag{7}$$

The quantities in square bracket represent the elements of a **symmetric matrix**.

$$G_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j \tag{8}$$

This matrix is known as the **metric tensor**, and has the dimension of a *length square*. The metric tensor G_{ij} enables one to calculate the dot product in *any* coordinate system, as

$$\mathbf{v} \cdot \mathbf{u} = \sum_{i,j} G_{ij} v^i u^j \tag{9}$$

Once the dot product is known, one can easily determine distances and angles between points in any coordinate system. Here is how the metric tensor can be constructed given the lattice parameters, and how distances and angles are calculated:

A dummies' guide to calculating lengths and angles

- You are generally given the **lattice parameters** $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, α, β and γ. In terms of these, the metric tensor can be written as

$$\boldsymbol{G} = \begin{bmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{bmatrix} \tag{10}$$

- To measure the **length** v of a vector **v**:

$$v^2 = |\mathbf{v}|^2 = \begin{bmatrix} v^1 & v^2 & v^3 \end{bmatrix} \boldsymbol{G} \begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix} \tag{11}$$

- To measure the **angle** θ between two vectors **v** and **u**:

$$\cos\theta = \frac{1}{uv} \begin{bmatrix} u^1 & u^2 & u^3 \end{bmatrix} \boldsymbol{G} \begin{bmatrix} v^1 \\ v^2 \\ v^3 \end{bmatrix} \tag{12}$$

2 The mathematical form of the symmetry operators

One of the merits of introducing coordinates is that we can **express symmetry operators in a mathematical form**. As we here recall briefly, **a symmetry operator define a correspondence between points of the space**, to that to each point $p(1)$ is associated another point $p(2)$ that **receives its attributes**.

$$x^i(2) = t^i + D^i_j x^j(1) \text{ or, in matrix form } [x(2)] = [t] + D[x(1)] \tag{13}$$

In eq. 13, t^i are the **components of the translational part**, and D represents the **rotational part**.

In 3 dimensions, the matrix D has determinant 1 or -1. In the former case, it describes a **proper rotation**, in the latter an **improper rotation**, such as reflection or inversion.

Improper rotations are operations that change the **handedness** (left- to right- hand or vice versa). It can be shown that **all improper rotations can be obtained by composing a proper rotation with the inversion**. We shall see more improper rotations later on.

2.1 Dual basis and coordinates: the reciprocal space

Let us assume a basis vector set $\mathbf{a}_i$ for our vector space as before, and let us consider the following set of *new* vectors.

$$\mathbf{b}^i = 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki} \tag{14}$$

From Eq. 8 follows:

$$\mathbf{a}_i \cdot \mathbf{b}^j = \mathbf{a}_i \cdot 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki} = 2\pi \sum_k G_{ik} (G^{-1})^{kj} = 2\pi \delta^j_i \tag{15}$$

Note that the vectors $\mathbf{b}^i$ have dimensions $length^{-1}$. Since the $\mathbf{b}_i$ are linearly independent if the $\mathbf{a}^i$ are, one can use them as new basis vectors, forming the so-called ***dual basis***. This being a perfectly legitimate choice, can express any vector on this new basis, as

$$\mathbf{q} = \sum_i q_i \mathbf{b}^i \tag{16}$$

As we just said, we can write any vector on this new basis, but vectors expressed using **dimensionless coordinates** on the dual basis have dimensions $length^{-1}$, and cannot therefore be summed to the position vectors. We can consider these vectors as *representing the position vectors of a separate space*, the so-called ***reciprocal space***.

Position vectors in reciprocal space are linear combinations of the dual basis vectors with *dimensionless* components. Their dimension is *length*$^{-1}$. If a *primitive basis* is used for "direct" (normal) space, then *reciprocal lattice vectors* are reciprocal-space position vectors with *integral components*. See next lecture for a fuller discussion).

The dot product between position vectors in real and reciprocal space is a dimensionless quantity, and has an extremely simple form (eq. 17):

$$\mathbf{q} \cdot \mathbf{v} = 2\pi \sum_i q_i x^i \tag{17}$$

In particular, the dot product of integral multiples of the original basis vectors (i.e., ***direct* or *real* lattice vectors**), with integral multiples of the dual basis vectors (i.e., ***reciprocal* lattice vectors**) are integral multiples of 2π. This property will be used extensively to calculate Fourier transforms of lattice functions.

Recap of the key formulas for the dual basis

- From **direct** to **dual** bases (eq. 14)

$$\mathbf{b}^i = 2\pi \sum_k \mathbf{a}_k (G^{-1})^{ki}$$

- Dot product relation between the two bases (eq. 15)

$$\mathbf{a}_i \cdot \mathbf{b}^j = 2\pi \delta_i^j$$

- Dot product between vectors expressed on the two *different* bases (eq. 17)

$$\mathbf{q} \cdot \mathbf{v} = 2\pi \sum_i q_i x^i$$

2.1.1 Dual basis in 3D

In 3 dimensions, there is a very useful formula to calculate the dual basis vectors, which makes use of the properties of the vector product:

$$
\begin{aligned}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\
\mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\end{aligned}
\tag{18}
$$

Note that

$$
v = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = abc \left(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma\right)^{1/2} \tag{19}
$$

is the **unit cell volume**. In crystallographic textbooks, the dual basis vectors are often written as $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$.

3 Symmetry in three dimensions

3.1 Key differences with respect to 2D

- Whereas in **2 dimensions, inversion is indistinguishable from 2-fold rotation around** z, in 3D these become two distinct operators. Likewise, a **mirror line** in 2D can be interpreted either as a **mirror plane** or as an **in-plane 180° rotation**. As we have already mentioned, in 3D these operators have a different behaviour with respect to **handedness**. 180° rotations (and, in general, all the rotations around an axis) are **proper rotations**, and their matrices have $\det = 1$. Mirrors and the inversion are **improper rotations**, and their matrices have $\det = -1$.

- There are several new **improper rotations**, most notably the **inversion operator** ($(x, y, z), \rightarrow (-x, -y, -z)$) and all the possible composition between **inversion** and **axes of order higher than 2** (the composition between inversion and a 2-fold axis is a mirror plane). These are known as **roto-inversions**.

- There is a **new type of roto-translation operator: the *screw axis***, resulting from the composition of a **rotation** with a **non-primitive translation *parallel* to it**.

3.2 The new generalized (proper & improper) rotations in 3D

The inversion We indicate it with the symbol I, and represent it graphically by a small circle ($\circ$), which can be combined with other symbols, if required (see for instance the roto-inversion

$\bar{3}$ below).

The roto-inversions obtained by composition of an axis r of order higher than two with the inversion, as $I \circ r$. These operators are $\bar{3}$ ( ), $\bar{4}$ ( ) and $\bar{6}$ ( ), and their action is summarized in Fig. 1. The symbols are chosen to emphasize the existence of another operator inside the "belly" of each new operator. Note that $\bar{3} \circ \bar{3} \circ \bar{3} = \bar{3}^3 = I$, and $\bar{3}^4 = 3$, i.e., symmetries containing $\bar{3}$ also contain the inversion and the 3-fold rotation. Conversely, $\bar{4}$ and $\bar{6}$ do not automatically contain the inversion. In addition, symmetries containing both $\bar{4}$ (or $\bar{6}$) and I also contain 4 (or 6).

Clearly, more orientations of all the allowed axes are possible than in the 2D case, so some kind of convention has to be established to draw the stereographic projections. Generally, the axis of highest order is chosen to be perpendicular to the projection plane).

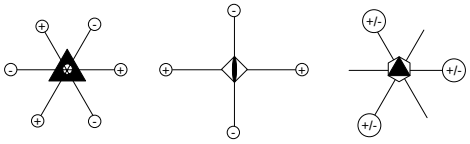

Figure 1: Action of the $\bar{3}$, $\bar{4}$ and $\bar{6}$ operators and their powers. The set of equivalent points forms a trigonal antiprism, a tetragonally-distorted tetrahedron and a trigonal prism, respectively. Points marked with "+" and "-" are above or below the projection plane, respectively. Positions marked with "+/-" correspond to pairs of equivalent points above and below the plane.

3.3 The 32 point groups in 3D

3.3.1 The 3D point groups with a 2D projection

We can derive 27 of the 32 3D point groups directly from the 10 2D point groups by a process of "extrusion". The procedure is outlined with an example in fig. 2. Basically, one looks for possible 3D groups that have a 2D point group as a "projection" onto a plane *perpendicular* to the highest-order axis.

3.3.2 The other 3D point groups: the 5 cubic groups

In the 3D point groups we have seen so far, in-plane operators are proper or improper 2-fold rotation, all forming angles of 90° with the highest-order axis. The missing groups will therefore involve at least two higher-order axes, either at 90° with each other or set at different angles. It can be shown that only two such rotations can exist, **both related to the symmetry of the cube**.

1. 3-fold axes set at 70.53° ($\cos\gamma = \frac{1}{3}$), as the diagonals of a cube. Composition of two such rotations in the *same* direction gives a 2-fold axis through one of the cube faces.

Composition in *opposite* direction yields another 3-fold axis. By subsequent composition and graph symmetry, one retrieves all the four 3-fold axes and three 2-fold axes through faces and diagonals of a cube.

3. 4-fold axes set at $90°$, as through the faces of a cube. Compositions in *any* direction gives a 3-fold axis through the cube diagonals. By subsequent composition and graph symmetry, one retrieves all the four 3-fold axes and three 4-fold axes, plus six 2-fold axes through the cube edges.

From these two groups, composed with proper rotation only, plus compositions with the inversion, one can obtain the 5 cubic point groups. Their Hermann-Mauguin symbols are similar to those of the other groups, with the **cube faces as primary symmetry direction** (first symbol), the **cube diagonal as secondary** and the **cube edges as tertiary**. The cubic symmetry directions are shown in fig. 3. The Schoenflies symbol (see extended notes) is T (for tetrahedral) or O (for octahedral) depending on the absence or presence of proper 4-fold rotations.

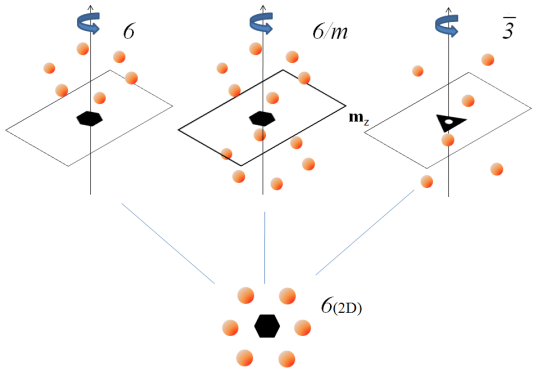

Figure 2: Schematic representation of the method employed to generate, from 2D point groups, 3D groups that have that 2D group as a projection.

23 (Schoenflies notation T). Corresponds to the group described in item 1 above, and is the symmetry of a "chiral" tetrahedron (e.g., with faces marked with a 3-fold propeller).

$2/m\bar{3}$ ($m\bar{3}$ in short, Schoenflies notation T_h). The same generators as 32 plus the inversion. It is the symmetry of a double tetrahedron yielding a centrosymmetric solid.

432 (Schoenflies notation O). Corresponds to the group described in item 2 above, and is the symmetry of a "chiral" cube, for example, with faces marked with a 4-fold propeller. Note that the 2-fold axis along the tertiary direction is obtained by composition of the 4-fold axis (say along the z direction) with a 4^2 2-fold axis (say, along the x direction).

$\bar{4}3m$ (Schoenflies notation T_d). This is the full symmetry of the tetrahedron. It is obtained from the previous group by replacing the 4-fold axis with $\bar{4}$. By the previous argument, the tertiary 2-fold axes are now replaced by mirrors.

$4/m\bar{3}2/m$ ($m\bar{3}m$ in short, Schoenflies notation O_h). It represents the full symmetry of a cube or octahedron.

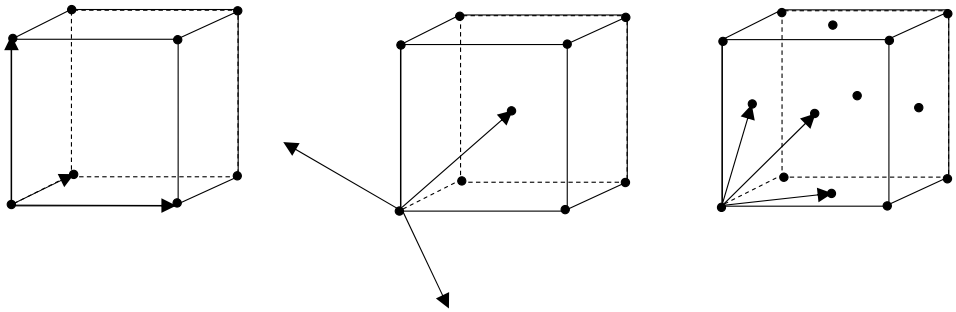

Figure 4: Primitive and conventional cells for the three cubic lattices - Primitive - P (**left**), Body-centered-I (**middle**) and Face-centered-F (**right**).

3.4 The 14 Bravais lattices in 3D

The procedure followed to derive the 14 Bravais lattices in 3D is closely related to the one used for the 2D case. However, there are many more possibilities to obtain "centered" lattices, i.e., lattices in which the primitive translations are *not* orthogonal. For example, fig. 4 shows **the three lattices with cubic symmetry: Primitive, Face Centred Cubic (BCC) and Body-Centred Cubic (BCC)** (you have probably encountered these lattices already). Here, we simply list the 14 Bravais lattices with their symmetry (holohedry) and the **crystal classes** they support.

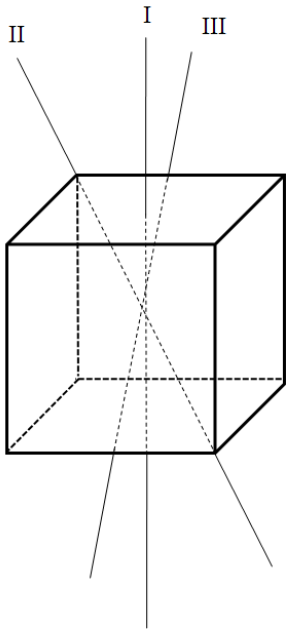

Figure 3: The symmetry directions of a cube: **primary** (I) - three 4-fold axes through the faces; **secondary** (II) four 3-fold axes through the corners and **tertiary** (III) six 2-fold axes through the edges.

Triclinic system (Classes 1 and $\bar{1}$, holohedry $\bar{1}$, lattice P). There is no symmetry restriction on the basis vectors, which are therefore allowed to be at any angle with each other. There is a *single* **primitive** lattice and its symbol is P

Monoclinic system (Classes 2, m and $2/m$, holohedry $2/m$, lattices P and C)

- No face is centred: the lattice is **monoclinic primitive** (symbol P).
- One of the faces *containing* the "unique" 2-fold axis is centred: the lattice is **monoclinic face-centred** (symbol C).

Orthorhombic system (Classes 222, $mm2$ and mmm, holohedry mmm, lattices P, C, F and I).

- *No* face is centred: the lattice is **orthorhombic primitive** (symbol P).
- *One* of the faces is centred: the lattice is **orthorhombic A-, B- or C-centred, depending on which face is centered (this is to some extent arbitrary — the ITC convention is normally C)**. The symbols are A, B or C.
- *All* of the faces are centred: the lattice is **orthorhombic face-centred**, symbol F.
- The *body* (middle) of the cell is centred: the lattice is **body-centered orthorhombic** (symbol I).

Tetragonal system (Classes 4, $\bar{4}$, 422, $4/m$, $4mm$, $\bar{4}m2$, $4/mmm$, holohedry $4/mmm$, lattices P and I).

- *No* face is centred: the lattice is **primitive tetragonal** (symbol P).
- The *body* (middle) of the cell is centred (face-centering can be reduced to body-centering by a cell transformation): the lattice is **body-centred tetragonal** (symbol "I").

Trigonal system (Classes 3, $3m1$, 321, $\bar{3}m1$, lattices P and R). This system is peculiar, in that each class can be supported by two lattices, P and R, with different holohedries.

- The **trigonal primitive** P lattice is simply the 3D extension of the 2D hexagonal lattice by a translation along the z axis, and has holohedry P6/mmm. Here, the unit cell is a hexagonal prism.
- In the **trigonal rhombohedral** R lattice, the primitive cell is a **rhombohedron**, i.e., a cube "stretched" along one of the body diagonals (it is easy to see that a rhombohedron has 3-fold symmetry). A conventional larger hexagonal cell (3 times the volume) can be constructed ("hexagonal" setting; both cells are shown in fig. 5). Both rhombohedral and hexagonal settings are used and are listed in the ITC.

Hexagonal system (Classes 6, $\bar{6}$, $6/m$, 622, $\bar{6}m2$, $6mm$, $6/mmm$, holohedry $6/mmm$, lattice P). This system supports a single lattice, the **primitive hexagonal lattice** (symbol P); the unit cell is a hexagonal prism.

Cubic system (Classes 23, $m\bar{3}$, 432, $\bar{4}3m$ and $4\bar{3}m$, holohedry $4\bar{3}m$, lattices P, I and F). See (Fig. 4).

- *No* face is centred: the lattice is **primitive cubic** (P), and the primitive unit cell is a cube.
- The *body* of the cubic cell is centred: the primitive cell is a rhombohedron with angles between edges $\alpha = 109.3°$ ($\cos\alpha = -\frac{1}{3}$). The lattice is **body-centered cubic (BCC)** — symbol I.
- *All* of the faces are centred: The primitive cell is a rhombohedron with angles between edges $\alpha = 60°$. The lattice is **face-centered cubic (FCC)** — symbol F.

3.5 3D space group symmetry

There are **230 space groups** in 3 dimensions, resulting from the combination of each of the 14 Bravais lattices with its supported classes and systematic replacement of the proper/improper rotations with roto-translations. With some practice, it is possible to construct the complete group diagram from its symbol for most space groups (for cubic groups, this is a rather tedious procedure). Here, we will simply introduce **the new roto-translations operators** that we have so far not seen.

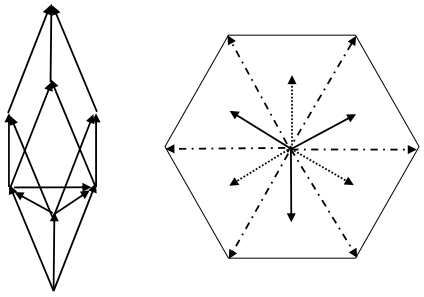

Figure 5: The rhombohedral primitive cell (**left**) and its projection in the larger, hexagonal conventional cell (**right**)

3.5.1 Roto-translations in 3D

These remaining operators will therefore be **compositions of proper rotations with translation *parallel* to them**, and are known as **screw axes**. Note that *improper* screw axes are not roto-translations, because they have invariant points, and correspond to displaced improper rotations.

The following properties can be easily proven:

- For an axis of order n, **the n^{th} power of a screw axis is a primitive translation** t . Therefore, the translation component must be $\frac{m}{n}t$, where m is an integer. We can limit ourselves to $m < n$, all the other operators being composition with lattice translations. Roto-translation axes are therefore indicated as n_m, as in 2_1, 6_3 etc.
- Screw axes can be **chiral** (e.g., right- or left-handed), whence the name **screw**. Space groups that contain chiral axes but do not contain reflections are themselves chiral, and they always

come in **enantiomorphic** (e.g., left- and right-handed) pairs (e.g., $P4_12_12$ and $P4_32_12$). If reflections are present, the space group will contain both types of chirality.

3.5.2 Glide planes in 3D

Glide planes in 3D are not essentially different from the 2D case, since they are compositions of a mirror plane with a translation in the same plane, and their square is a pure lattice translation. However, since mirror planes in 3D are truly 2-dimensional (unlike the 2D mirror "lines"), the translation can be oriented at different angles with respect to the symmetry directions lying in the plane.

3.6 Graphical notation for 3D symmetry operators

A table with all the graphical symbols for the 3D symmetry operators is given in the ITC-Volume A [1] on pages 7-10. A the most important symbols that we have not encountered so far are collected in Fig. 6. Another important "novelty" in the 3D case is the use of fractions to indicate the vertical fractional coordinate of features such as inversion centers and horizontal reflection planes and axes (see, for example, the diamond glides in Fig. 6.)

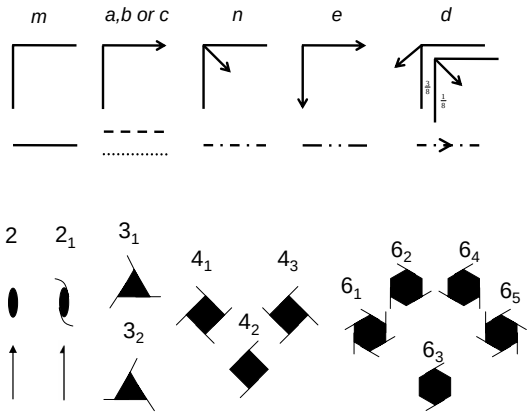

Figure 6: **Top** Graphical symbols for mirror and glide planes. From left to right, *mirror planes m* top and side view, *glide planes a, b, and c*, top view and side view with glide translation in the plane of the sheet (dashed line) and orthogonal to it (dotted line). *diagonal glide n* top and side view, *double glide plane e* top and side view, *pair of diamond glides d* top and side view. **Bottom** roto-translation screw axes of all orders. Twofold axes are also shown in projection.

References

[1] T. Hahn, ed., *International tables for crystallography*, vol. A (Kluver Academic Publisher, Do- drecht: Holland/Boston: USA/ London: UK, 2002), 5th ed.

[2] Paolo G. Radaelli, *Symmetry in Crystallography: Understanding the International Tables* , Oxford University Press (2011)