

parameter ( $a = 4.26 \text{ \AA}$ ) and the density ( $\rho = 6.1 \text{ g cm}^{-3}$ ) show that there must be 4 Cu and 2 O atoms in the unit cell. Now get a copy of the *International Tables* and show, by elimination, that the only possible cubic symmetry is  $Pn\bar{3}m$  (in which case the structure must be that given in Exercise 8) or  $P\bar{4}3m$ .<sup>1</sup> (Why can  $P23$ ,  $P4_232$  and  $Pn\bar{3}$  be ruled out?). [Hint: begin by eliminating all space groups in which positions  $a$  (which have the lowest multiplicity) consist of more than 2 points].

10. The structure of zircon,  $\text{ZrSiO}_4$ , has been described as:

$I4_1/amd$ ,  $a = 6.607$ ,  $c = 5.982 \text{ \AA}$ . Origin at  $\bar{4}2m$

Zr in 4  $a$ :  $I + (0,0,0; 0,1/2,1/4)$ . Si in 4  $b$ :  $I + (0,0,1/2; 0,1/2,3/4)$

O in 16  $h$ :  $I + (0,\pm x,z; \pm x,0,\bar{z}; 0,1/2\pm x,1/4-z; \pm x,1/2,1/4+z)$ ,  $x = 0.1839$ ,  $z = 0.3203$

Transforming to an origin at a center (see § 3.7.4, p.91):

Zr in 4  $a$ :  $I \pm (0,3/4,1/8)$ . Si in 4  $b$ :  $I \pm (0,1/4,3/8)$

O in 16  $h$ :  $I \pm (0,x,z; 0,1/2-x,z; 1/4+x, 1/4,3/4+z; 3/4-x,1/4,3/4+z)$ ,  $x = 0.0661$ ,  $z = 0.1953$

11. An important structure type is that of  $\text{CeCu}_2$ ;  $\text{KHg}_2$  has been described as having the same symmetry:

$\text{CeCu}_2$   $Imma$ ,  $a = 4.43$ ,  $b = 7.06$ ,  $c = 7.48 \text{ \AA}$

Ce in 4  $c$ :  $I \pm (0,1/4,z)$ ,  $z = 0.538$

Cu in 8  $h$ :  $I \pm (0,y,z; 0,1/2-y,z)$ ,  $y = 0.051$ ,  $z = 0.165$

$\text{KHg}_2$   $Imma$ ,  $a = 8.10$ ,  $b = 5.16$ ,  $c = 8.77 \text{ \AA}$

K in 4  $c$ :  $I \pm (0,1/4,z)$ ,  $z = 0.703$

Hg in 8  $h$ :  $I \pm (\pm x,1/4,z)$ ,  $x = 0.190$ ,  $z = 0.087$

Plot both structures in projection down the *shortest* axis and thus show that they are essentially the same (except for a change of scale).<sup>2</sup> An exactly equivalent description of the structure of  $\text{KHg}_2$  is (compare with that given for  $\text{CeCu}_2$ ):  $a = 5.16$ ,  $b = 8.10$ ,  $c = 8.77 \text{ \AA}$ . K in 4  $a$ ,  $z = 0.457$ ; Hg in 8  $h$ ,  $y = 0.060$ ,  $z = 0.163$ . [Hints: for some help with drawing structures see Chapter 4. These structures are nicely illustrated if the four shortest Cu-Cu or Hg-Hg bonds are drawn in (two of these superimpose in projection)—see § 7.3.5]

12. Use the *International Tables A* to find the maximal *non-polar*  $t$  subgroups ( $H$ ) of  $G = Pm\bar{3}m$ . [Hint: they will be found as maximal subgroups of maximal subgroups; the two highest symmetries have index 6 and 8 in  $G$  respectively. For the polar crystal classes, see p. 50.] These are the possible symmetries of the polar structures formed when a cubic perovskite (such as  $\text{BaTiO}_3$  or  $\text{SrTiO}_3$ ) deforms to polar structures at low temperature.

<sup>1</sup>Systematic absences in the powder pattern immediately point to  $Pn\bar{3}m$ . Specifically, reflections with indices  $hkl$  are absent for  $h+k$  odd (100, 210 etc.).

<sup>2</sup>This example is taken from *Elements of Inorganic Structural Chemistry* by E. Parthé (available from K. Sutter Parthé, 49 Chemin du Gué, CH-1213 Petit-Lancy, Switzerland).

## CHAPTER 4

### LATTICE GEOMETRY

In this chapter we explain how the directions of lines and the orientations of planes in a crystal are specified. The description necessarily involves reference to the coordinate system and if alternative unit cell descriptions are used the description of directions and so on. will change, so we next discuss unit cell transformations. Next we give a compendium of formulas useful for crystallographic calculations. Finally we present some comments and hints on drawing crystal structures.

#### 4.1 Directions in a crystal

##### 4.1.1 General

A direction in a crystal is specified by three integers  $u, v, w$  and is written  $[uvw]$ . The direction is then that of the vector  $ua + vb + wc$  where  $a, b$  and  $c$  are the unit cell (lattice) vectors. Normally  $u, v$  and  $w$  are integers that have no common factors other than 1 (i.e. they are *coprime*). Thus the direction of the  $x$ -axis is  $[100]$ , that of the  $y$ -axis is  $[010]$  and that of the  $z$ -axis is  $[001]$ . Note that  $[\bar{1}00]$  refers to the  $-x$  direction. Fig. 4.1 illustrates these and some other principal directions. In the figure the shape of the unit cell is to be considered quite general (i.e. not necessarily a cube) and the heavy lines meet at the origin; the filled circle is a point at  $0,1/2,1$ . In crystallography the symbol  $[uvw]$  is often said to represent a *zone axis* and all planes parallel to  $[uvw]$  are said to fall in that zone.

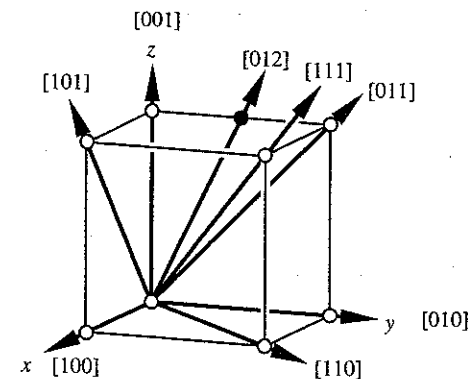


Fig. 4.1 Directions in a crystal.

The set of equivalent (symmetry-related) directions in a crystal is represented  $\langle uvw \rangle$ . Thus in a centrosymmetric cubic crystal  $\langle 111 \rangle$  represents the family of specific directions along the body diagonals:

$$[111], [\bar{1}\bar{1}\bar{1}], [1\bar{1}\bar{1}], [\bar{1}1\bar{1}], [\bar{1}\bar{1}1], [1\bar{1}1] \text{ and } [\bar{1}\bar{1}\bar{1}]$$

For the same symmetry,  $\langle 100 \rangle$  is similarly the set:

$$[100], [010], [001], [\bar{1}00], [0\bar{1}0] \text{ and } [00\bar{1}].$$

In the jargon  $\langle uvw \rangle$  is a *form* of zone axes.

Often  $[uvw]$  is used to represent not only a direction but is considered to have a magnitude associated with it. Usually the context makes this clear. Thus a vector of magnitude  $a/2$  along the  $x$  direction is written  $1/2[100]$ , and  $1/2[11\bar{1}]$  refers to  $(a+b-c)/2$ . Vector sums can be expressed as (e.g.)  $1/6[\bar{1}12] + 1/6[\bar{1}10] = 1/3[\bar{1}11]$  which is shorthand for  $(-a+b+2c)/6 + (-a+b)/6 = (-a+b+c)/3$ .

#### 4.1.2 Directions in hexagonal crystals

In the hexagonal system two systems are used for specifying directions. The first uses a four index symbol which we write  $[UVJW]$ . The corresponding direction is that of the vector  $Ua_1 + Va_2 + Ja_3 + Wc$  where  $a_1$  is the  $x$  direction,  $a_2$  is the  $y$  direction (at  $120^\circ$  to each other) and  $a_3 = -(a_1 + a_2)$  is the equivalent direction at  $120^\circ$  to both  $a_1$  and  $a_2$  (and at  $90^\circ$  to  $c$ ) as shown in Fig. 4.2. An important point is that as  $a_1$ ,  $a_2$  and  $a_3$  are not independent there are many choices of  $U$ ,  $V$  and  $J$  that correspond to the same direction. The choice made is such that  $J = -(U + V)$ . Although, as we will see, there are advantages to this system, it is not intuitive. Thus (see again Fig. 4.2) the  $y$  direction (parallel to  $a_2$ ) is  $[\bar{1}2\bar{1}0]$  and the vector  $a_2 = 1/3[\bar{1}2\bar{1}0]$ .

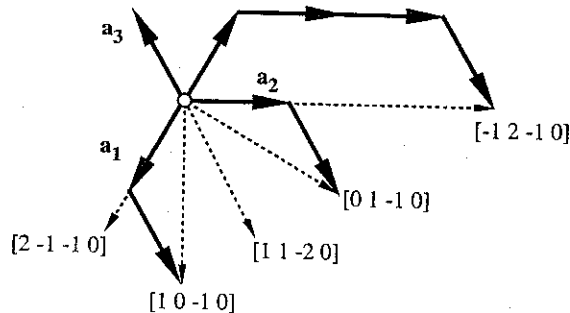


Fig. 4.2. Directions in hexagonal crystals.

Three-index symbols  $[uvw]$  can also be used for directions in hexagonal crystals. These are also sometimes written as  $[uv.w]$  or  $[uv0w]$  which can be confusing and definitely should be avoided. The four-index symbols are easily obtained from three-index symbols based on a cell with dimensions  $a_1$ ,  $a_2$ ,  $c$  as follows:

$$U = (2u - v)/3; V = (2v - u)/3; J = -(U + V); W = w \quad (4.1)$$

Note that  $U$ ,  $V$ ,  $J$  and  $W$  should be converted to the smallest possible integers by multiplying or dividing by a constant factor if necessary. Our recommendation is to use three-index symbols for all calculations (see e.g. sections 4.3 and 4.4) and to convert at the end to four-index symbols (to avoid ambiguity) for communication.

#### 4.2 Planes and Miller indices

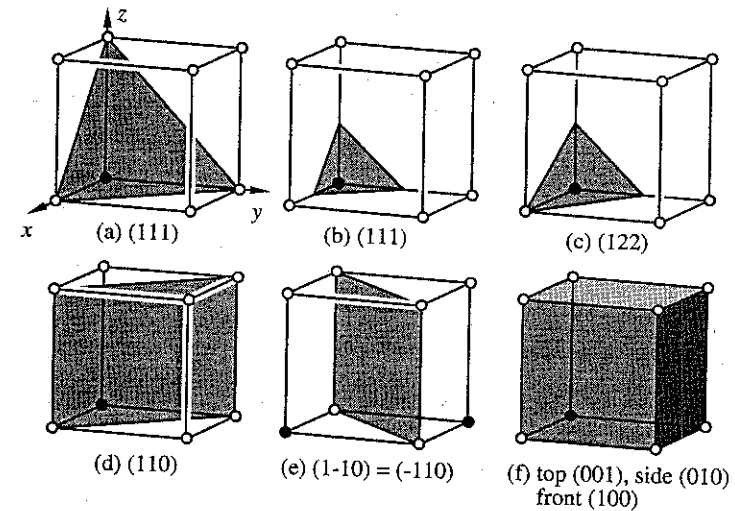


Fig. 4.3. Miller indices for planes.

The orientation of planes relative to a coordinate system defined by translation vectors  $a$ ,  $b$  and  $c$  is given by three integers  $h$ ,  $k$ ,  $l$  (known as Miller indices) and written  $(hkl)$ . The significance of these numbers is that the intercepts of the plane with the reference axes (in units of  $a$ ,  $b$  and  $c$  respectively) are in the ratio  $1/h : 1/k : 1/l$ . Again (as for the indices representing directions)  $h$ ,  $k$  and  $l$  are integers with no factor common to all three. Note that  $h$ ,  $k$  and  $l$  specify only the *orientation* of the plane, not its location. Thus all parallel planes

have the same Miller indices.<sup>1</sup> Planes which intersect lattice points are referred to as *lattice planes* or *net planes*. The equation of the plane in the lattice coordinate system is  $hx + ky + lz = \text{constant}$ . ( $hkl$ ) specifies the *orientation* of the plane and the constant specifies its *position* relative to the origin.

Figure 4.3 provides a number of examples of low-index planes with respect to a unit cell which may be triclinic. In (a) the plane intercepts the axes at  $1/1, 1/1, 1/1$  so its indices are (111). In (b) the intercepts are  $1/2, 1/2, 1/2$  so after factoring out a common 2, the indices are again (111). In (c) the intercepts are  $1/1, 1/2, 1/2$  so now the indices are (122). In (d) the plane is parallel to  $c$  so the intercept with that axis is at infinity ( $1/\infty = 0$ ). The plane shown is in fact (110). Part (e) of the figure shows a plane with intercepts either at  $1/1, 1/-1, 1/0$  or  $1/-1, 1/1, 1/0$  according to whether the origin is taken at one or other of the two filled circles shown. These planes are of course the same and thus should have the same indices which we could write either as  $(1\bar{1}0)$  or  $(\bar{1}10)$ . Part (f) shows planes (100), (010) and (001); they are parallel to the faces of the unit cell.

A form of planes (a set of planes related by symmetry) is represented by braces as in  $\{hkl\}$ ; thus the faces of a cubic unit cell are  $\{100\}$ .

### Hexagonal crystals

As for directions, four-index symbols are usually used for the orientation of planes in the hexagonal system. There is little chance for confusion now as a plane that intercepts  $a_1$  at  $1/h$  and  $a_2$  at  $1/k$  will inevitably intercept  $a_3$  at  $1/i$  where  $i = -(h+k)$ . Accordingly the three-index symbol ( $hkl$ ) becomes the four-index symbol ( $hkil$ ) with  $i = -(h+k)$ . The superfluous  $i$  is sometimes replaced by a point as in  $(hk.l)$ .

### 4.3 Relations between zones (directions) and planes

(a) The *zone law*: A plane ( $hkl$ ) lies in the zone  $[uvw]$  if:

$$hu + kv + lw = 0 \quad (4.2)$$

thus both  $(1\bar{1}0)$  and  $(10\bar{1})$  lie in the  $[111]$  zone.

(b) The zone  $[uvw]$  corresponding to the intersection of planes  $(h_1k_1l_1)$  and  $(h_2k_2l_2)$  is given by:

$$u = k_1l_2 - k_2l_1; v = l_1h_2 - l_2h_1; w = h_1k_2 - h_2k_1 \quad (4.3)$$

thus the intersection of  $(1\bar{1}0)$  and  $(10\bar{1})$  is  $[111]$  [compare (a) above].

<sup>1</sup> Authors of elementary texts often seem to us to get this point wrong, confusing Miller indices with Bragg indices which are discussed below (§ 4.7.2). Explicitly for example: no distinction should be made between a (222) and a (111) plane.

(c) Some perpendicularity conditions in different systems:

**orthorhombic**:  $[100]$ ,  $[010]$  and  $[001]$  are perpendicular to  $(100)$ ,  $(010)$  and  $(001)$  respectively.

**tetragonal**:  $[001]$  is perpendicular to  $(001)$  and  $[pq0]$  is perpendicular to  $(pq0)$ .

**hexagonal**:  $[0001]$  is perpendicular to  $(0001)$  and  $[pqi0]$  is perpendicular to  $(pqi0)$ .<sup>1</sup> In the three-index system one has  $[2p+q \ p+2q \ 0]$  perpendicular to  $(pq0)$  or equivalently,  $[pq0]$  perpendicular to  $(2p-q \ 2q-p \ 0)$ . More generally (four-index system)  $[p \ q \ i \ (3a^2/2c^2)l]$  is normal to  $(pqil)$ .

**rhombohedral**:  $[111]$  is perpendicular to  $(111)$  (but if a hexagonal cell is used, see above).

**cubic**:  $[pqr]$  is perpendicular to  $(pqr)$ .

### 4.4 Unit cell transformations

#### 4.4.1 General

There are many reasons why it would be desirable to describe a crystal structure with a unit cell other than the one provided. For example the original investigator may have chosen a "non-standard" setting of the axes, or a rhombohedral crystal might be more conveniently described using a hexagonal cell rather than a rhombohedral one. Sometimes structural relationships are made more evident using unconventional cells (such as a hexagonal cell for a cubic crystal).

Let a "new" unit cell defined by translation vectors  $a', b', c'$  be derived for a structure with an "old" cell defined by  $a, b, c$ . The relationship between the new and old cells is given by (using the notation of the 1965 *International Tables*, Vol I):

$$\begin{aligned} a' &= s_{11}a + s_{12}b + s_{13}c & a &= t_{11}a' + t_{12}b' + t_{13}c' \\ b' &= s_{21}a + s_{22}b + s_{23}c & b &= t_{21}a' + t_{22}b' + t_{23}c' \\ c' &= s_{31}a + s_{32}b + s_{33}c & c &= t_{31}a' + t_{32}b' + t_{33}c' \end{aligned} \quad (4.4)$$

Let  $S$  be the matrix of coefficients  $s_{ij}$  and  $T$  the matrix  $t_{ij}$ .<sup>2</sup> Then  $S$  and  $T$  are the

<sup>1</sup> This is one of the advantages of the 4-index system.

<sup>2</sup> Note that Boisen & Gibbs (*Mathematical Crystallography* in Book List) use  $S$  and  $T$  matrices that are the transposes of ours. The newer *International Tables* (volume A) uses  $P$  and  $Q$  that are also the transposes of our  $S$  and  $T$ . These authors consider (more logically) the set of lattice vectors to be a  $1 \times 3$  (row) vector rather than as a  $3 \times 1$  (column) vector. The system and notation we use appears to us to be simpler and is also to be found in most texts. This point is addressed in § 4.7.5 (p. 128).

inverses of each other (i.e.  $\mathbf{ST} = \mathbf{TS} = \mathbf{E}$ ). As the new and old cells are both unit cells the elements of the matrices will be rational numbers.

The ratio of the volumes of the new and old unit cells is  $\det(\mathbf{S})$  and likewise the ratio of the volumes of the old and new unit cells is  $\det(\mathbf{T})$ . Should the determinants be negative, the hand of the coordinate system has been changed in the transformation.

When the coordinate system is changed the indices representing the orientation of planes and directions will also transform, as will the coordinates of points in the unit cell. The rules for the transformations are as given below ( $\mathbf{T}^t$ ,  $\mathbf{S}^t$  are the transposes of  $\mathbf{T}$  and  $\mathbf{S}$  respectively):<sup>1</sup>

	new from old	old from new
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\mathbf{S}$	$\mathbf{T}$
$(hkl)$	$\mathbf{S}$	$\mathbf{T}$
$[uvw]$	$\mathbf{T}^t$	$\mathbf{S}^t$
$x, y, z$	$\mathbf{T}^t$	$\mathbf{S}^t$
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	$\mathbf{T}^t$	$\mathbf{S}^t$

The table shows that axes and indices of planes transform the same way as each other, and that coordinates of points and indices for lines also transform the same way as each other but using the transposed reciprocal matrix. The bottom row shows for completeness how reciprocal lattice vectors (discussed below) transform.

In calculating coordinates of points (e.g. atom positions), it must be taken into account that if the new and old unit cells have different volumes, the number of points in the cell will change accordingly. How this is handled should be clear from the examples below. To calculate the length of the new axes, note that e.g.  $\mathbf{a}' = s_{11}\mathbf{a} + s_{12}\mathbf{b} + s_{13}\mathbf{c}$  so that  $\mathbf{a}'$  is the distance from 0,0,0 to  $s_{11}, s_{12}, s_{13}$  in the *old* coordinate system. Likewise  $\alpha'$  is the angle between  $[s_{21} \ s_{22} \ s_{23}]$  and  $[s_{31} \ s_{32} \ s_{33}]$  (again in the *old* coordinate system). Calculating distances and angles is discussed in § 4.5.2 and § 4.5.3 and a general expression for unit cell parameters of transformed cells is given in § 4.5.4 (p. 112).

#### 4.4.2 Rhombohedral to hexagonal and vice versa

Rhombohedral crystals are often referred to hexagonal axes and the hexagonal cell is three times the volume of the rhombohedral one. Fig. 4.4 shows the relationship of the rhombohedral cell to the hexagonal one. The filled circles in the figure are at 0,0,0; 1,0,0; 1,1,0 and 0,0,1 in the rhombohedral cell and at cell corners (0,0,0; 1,0,0; etc.);  $2/3, 1/3, 1/3$ ;  $1/3, 2/3, 2/3$  in the hexagonal cell (see also Fig. 4.5). The open circles are the remaining corners of the rhombohedral cell that are in adjacent hexagonal cells. It may be seen that if the rhombohedral cell is rotated by  $60^\circ$  about  $c_h$  the hexagonal cell contains

<sup>1</sup>A simple derivation (using the same notation) of these rules is given by A. Kelly & G. Groves *Crystallography and Crystal Defects*, Addison-Wesley (1970).

points at  $1/3, 2/3, 1/3$  and  $2/3, 1/3, 2/3$ ; this is the so-called *reverse* setting which is not used. The setting used here (Fig. 4.4) is the "standard" one and is called the *obverse* setting.

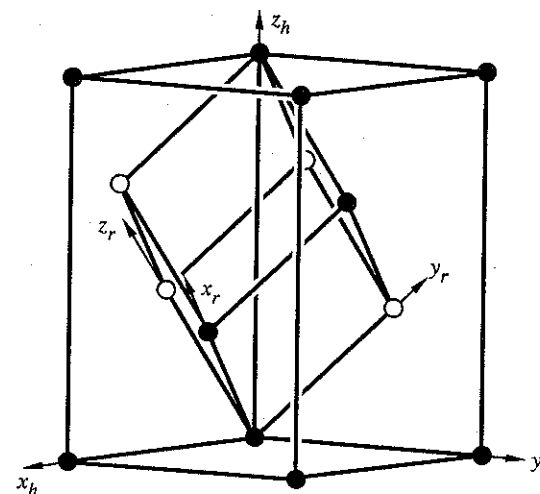


Fig. 4.4. The relationship between centered and primitive rhombohedral cells.

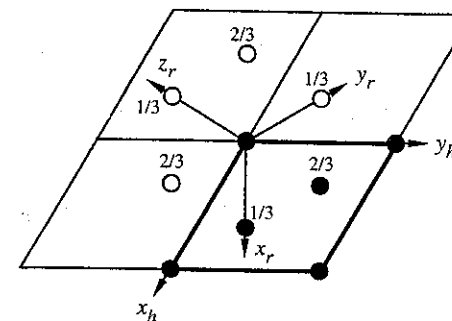


Fig. 4.5. The points of Fig. 4.4 projected down  $c_h$  (the  $z_h$  direction).

Figure 4.5 shows the same rhombohedral and hexagonal unit cells in projection along

the 3-fold axis. It should be observed that:

$$\begin{aligned} a_h &= a_r - b_r \\ b_h &= b_r - c_r \\ c_h &= a_r + b_r + c_r \end{aligned}$$

The transformation matrix is therefore  $S = (1 \ \bar{1} \ 0 / 0 \ 1 \ \bar{1} / 1 \ 1 \ 1)$  (rhombohedral  $\rightarrow$  hexagonal). Likewise:

$$\begin{aligned} a_r &= 2a_h/3 + b_h/3 + c_h/3 \\ b_r &= -a_h/3 + b_h/3 + c_h/3 \\ c_r &= -a_h/3 - 2b_h/3 + c_h/3 \end{aligned}$$

so  $T = (2/3 \ 1/3 \ 1/3 / -1/3 \ 1/3 \ 1/3 / -1/3 \ -2/3 \ 1/3)$  is the corresponding inverse matrix.

The relations between the unit cell parameters in the two cells are:

$$\begin{aligned} a_r &= \left(\frac{1}{3}\right)\sqrt{(3a_h^2 + c_h^2)} \\ \alpha &= 2\sin^{-1}\left(\frac{3}{2\sqrt{3 + (c_h^2/a_h^2)}}\right) \\ a_h &= 2a_r \sin(\alpha/2) \\ c_h &= a_r \sqrt{(3 + 6\cos\alpha)} \end{aligned}$$

As we use  $T^t$  to transform coordinates, a point with coordinates  $x, y, z$  in the rhombohedral cell will have coordinates  $(2x-y-z)/3, (x+y-2z)/3, (x+y+z)/3$  in the hexagonal cell. Note that  $1, 0, 0$  transforms to  $2/3, 1/3, 1/3$ ;  $0, 1, 0$  transforms to  $-1/3, 1/3, 1/3 \equiv 2/3, 1/3, 1/3$  and  $0, 0, 1$  transforms to  $-1/3, -2/3, 1/3 \equiv 2/3, 1/3, 1/3$ .  $1, 1, 0$  transforms to  $1/3, 2/3, 2/3$  and so on. Examination of all the possibilities shows that the rhombohedral lattice points correspond to  $0, 0, 0$  or  $2/3, 1/3, 1/3$  or  $1/3, 2/3, 2/3$  in the hexagonal cell. Accordingly, these quantities must be added to the new coordinates of each point calculated from the original  $x, y, z$  (recall that the hexagonal cell volume is three times that of the rhombohedral cell). The transformations may be summarized (note that we use three-index symbols for hexagonal):

#### rhombohedral $\rightarrow$ hexagonal

$$x, y, z \rightarrow (0, 0, 0; 2/3, 1/3, 1/3; 1/3, 2/3, 2/3) + (2x-y-z)/3, (x+y-2z)/3, (x+y+z)/3$$

$$\begin{aligned} [uvw] &\rightarrow (1/3)[2u-v-w \ u+v-2w \ u+v+w] \\ \text{(thus } [111]_r \text{ becomes } 1/3[003]_h &= [001]_h) \end{aligned}$$

$$\begin{aligned} (hkl) &\rightarrow (h-k \ k-l \ h+k+l) \\ \text{[thus } (111)_r \text{ becomes } (003)_h &= (001)_h \text{ etc.]} \end{aligned}$$

#### hexagonal $\rightarrow$ rhombohedral

$$x, y, z \rightarrow x+z, -x+y+z, -y+z.$$

$$\begin{aligned} [uvw] &\rightarrow [u+w \ v+w-u \ w-v] \\ \text{(thus } [001]_h \text{ becomes } [111]_r) \end{aligned}$$

$$\begin{aligned} (hkl) &\rightarrow (1/3)(2h+k+l \ -h+k+l \ -h-2k+l) \\ \text{[thus } (001)_h \text{ becomes } (1/3 \ 1/3 \ 1/3)_r &= (111)_r \text{ etc.]} \end{aligned}$$

When transforming from hexagonal cell to a rhombohedral one, and the new coordinates are expressed modulo 1, it will be found that sets of three points in the hexagonal cell reduce to one point in the rhombohedral cell.

#### 4.4.3 Cubic to hexagonal

Cubic crystals may be considered as special cases of rhombohedral symmetry, the  $P$ ,  $I$ , and  $F$  cells having primitive rhombohedral cells with  $\alpha = 90^\circ$ ,  $109.47^\circ$ , and  $60^\circ$  respectively. They can also be transformed to hexagonal cells (among other things this is very useful for drawing cubic structures projected down a 3-fold axis).

For the primitive cubic cell the transformation is exactly the same as outlined above. The centered cells should first be transformed to primitive cells before being converted to hexagonal ones. It should be clear that the final hexagonal cell will contain  $3/2$  times as many atoms as a body-centered cell, and  $3/4$  times as many atoms as the face-centered cell. For convenience the  $S$  and  $T$  matrices are:

$$\begin{aligned} \text{face-centered} &\rightarrow \text{primitive} & S &= (0 \ 1/2 \ 1/2 / 1/2 \ 0 \ 1/2 / 1/2 \ 1/2 \ 0) \\ & & T &= (\bar{1} \ 1 \ 1 / 1 \ \bar{1} \ 1 / 1 \ 1 \ \bar{1}) \end{aligned}$$

$$\begin{aligned} \text{face-centered} &\rightarrow \text{hexagonal} & S &= (-1/2 \ 1/2 \ 0 / 0 \ -1/2 \ 1/2 / 1 \ 1 \ 1) \\ & & T &= (-4/3 \ -2/3 \ 1/3 / 2/3 \ -2/3 \ 1/3 / 2/3 \ 4/3 \ 1/3) \end{aligned}$$

$$\begin{aligned} \text{body-centered} &\rightarrow \text{primitive} & S &= (-1/2 \ 1/2 \ 1/2 / 1/2 \ -1/2 \ 1/2 / 1/2 \ 1/2 \ -1/2) \\ & & T &= (0 \ 1 \ 1 / 1 \ 0 \ 1 / 1 \ 1 \ 0) \end{aligned}$$

$$\begin{aligned} \text{body-centered} &\rightarrow \text{hexagonal} & S &= (\bar{1} \ 1 \ 0 / 0 \ \bar{1} \ 1 / 1/2 \ 1/2 \ 1/2) \\ & & T &= (-2/3 \ -1/3 \ 2/3 / 1/3 \ -1/3 \ 2/3 / 1/3 \ 2/3 \ 2/3) \end{aligned}$$

In the hexagonal description of cubic cells the axes are (with subscript *c* for cubic and *h* for hexagonal):

primitive	$a_h = \sqrt{2}a_c$	$c_h/a_h = \sqrt{(3/2)} = 1.225$
body-centered	$a_h = \sqrt{2}a_c$	$c_h/a_h = \sqrt{(3/8)} = 0.614$
face-centered	$a_h = a_c/\sqrt{2}$	$c_h/a_h = \sqrt{6} = 2.449$

#### 4.4.4 Hexagonal to orthohexagonal

Hexagonal crystal structures are sometimes conveniently illustrated in projection normal to *c*. A good way to do this is to transform to an *orthohexagonal* cell as shown in Fig. 4.6 (old cell in light lines, new cell in heavier lines). As  $\mathbf{a}' = \mathbf{a} + \mathbf{b}$ ,  $\mathbf{b}' = -\mathbf{a} + \mathbf{b}$ ,  $\mathbf{c}' = \mathbf{c}$ , the transformation matrices are  $\mathbf{S} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ ,  $\mathbf{T} = \begin{pmatrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ . The unit cell parameters are  $a' = a$ ,  $b' = \sqrt{3}b$  and  $c' = c$ . Notice that the new cell is *C* centered (Fig. 4.6) so that 0,0,0 and 1/2,1/2,0 must be added to each  $x', y', z'$ .

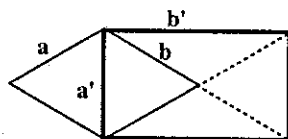


Fig. 4.6. Illustrating derivation of an orthohexagonal cell (heavy lines) from a hexagonal cell.

To plot normal to *c* usually project down  $\mathbf{a}'$  (the short axis) of the orthohexagonal cell [this is on (11 $\bar{2}$ 0) of the hexagonal cell]. Note that the same transformation is useful for plotting a cubic or tetragonal structure on (110) (i.e. along [110]).

If the original cell were rhombohedral, it should first be converted to a hexagonal cell and then to an orthohexagonal cell. The combined operation rhombohedral  $\rightarrow$  orthohexagonal is described by  $\mathbf{S} = \begin{pmatrix} 1 & 0 & 1 \\ 1 & 2 & 1 \\ 0 & 1 & 1 \end{pmatrix}$ ,  $\mathbf{T} = \begin{pmatrix} 1/2 & -1/6 & 1/3 \\ 0 & 1/3 & 1/3 \\ -1/2 & -1/6 & 1/3 \end{pmatrix}$ . Now the new unit cell is six times larger and (0,0,0 ; 1/2,1/2,0 ; 0,1/3,1/3 ; 1/2,5/6,1/3 ; 0,2/3,2/3 ; 1/2,1/6,2/3) must be added to the new coordinates.

See § 4.6.3 for some worked examples and for a transformation from face-centered cubic to orthohexagonal.

## 4.5 Crystallographic calculations

### 4.5.1 Unit cell volume and reciprocal lattice unit cell parameters

The volume of a unit cell is given by

$$V = abc\sqrt{1 + 2\cos\alpha\cos\beta\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma} \quad (4.5)$$

Special cases are:

Monoclinic	$V = abc\sin\beta$
Orthorhombic	$V = abc$
Hexagonal	$V = \sqrt{3}a^2c/2$

For many reasons it is convenient to define a lattice *reciprocal* to the lattice of a crystal. Let a lattice be defined by vectors *a*, *b* and *c*; then we define reciprocal lattice vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  such that  $\mathbf{a}^*$  is normal to the *bc* plane (i.e. the plane containing *b* and *c*),  $\mathbf{b}^*$  is perpendicular to the *ac* plane and  $\mathbf{c}^*$  is perpendicular to the *ab* plane.<sup>1</sup> The defining relationships are:

$$\begin{aligned} \mathbf{a} \cdot \mathbf{a}^* &= 1 & \mathbf{b} \cdot \mathbf{a}^* &= 0 & \mathbf{c} \cdot \mathbf{a}^* &= 0 \\ \mathbf{a} \cdot \mathbf{b}^* &= 0 & \mathbf{b} \cdot \mathbf{b}^* &= 1 & \mathbf{c} \cdot \mathbf{b}^* &= 0 \\ \mathbf{a} \cdot \mathbf{c}^* &= 0 & \mathbf{b} \cdot \mathbf{c}^* &= 0 & \mathbf{c} \cdot \mathbf{c}^* &= 1 \end{aligned} \quad (4.6)$$

From these equations it follows that the dimensions of the reciprocal lattice vectors are 1/distance (units e.g. Å<sup>-1</sup>).

The volume of the reciprocal lattice unit cell is  $V^* = 1/V$ .

The magnitudes of the reciprocal lattice vectors and the angles between them ( $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$ ) are

$$\begin{aligned} a^* &= bc\sin\alpha/V \\ b^* &= ac\sin\beta/V \\ c^* &= ab\sin\gamma/V \\ \cos\alpha^* &= (\cos\beta\cos\gamma - \cos\alpha)/\sin\beta\sin\gamma \\ \cos\beta^* &= (\cos\alpha\cos\gamma - \cos\beta)/\sin\alpha\sin\gamma \\ \cos\gamma^* &= (\cos\alpha\cos\beta - \cos\gamma)/\sin\alpha\sin\beta \end{aligned} \quad (4.7)$$

There is a set of equations analogous to Eq. 4.7 obtained by interchanging starred and unstarred quantities. Note the simplification if  $\alpha = \beta = \gamma = 90^\circ$ ; when  $a^* = 1/a$ ,  $b^* = 1/b$ ,  $c^* = 1/c$ ,  $\alpha^* = \beta^* = \gamma^* = 90^\circ$ . Other useful special cases are:

$$\text{Monoclinic: } a^* = 1/(a\sin\beta), b^* = 1/b, c^* = 1/(c\sin\beta), \beta^* = 180^\circ - \beta$$

$$\text{Hexagonal: } a^* = 2/(\sqrt{3}a), c^* = 1/c, \gamma^* = 60^\circ$$

The lattice reciprocal to *bcc* is *fcc* and *vice versa*. This may readily be confirmed by finding the reciprocal unit cell parameters of the primitive cells.<sup>2</sup>

<sup>1</sup>It is virtually impossible to do practical crystallography without reference to the reciprocal lattice. The direct lattice and reciprocal lattice are related as Fourier transforms.

<sup>2</sup>Thus find the reciprocal lattice parameters if  $a = b = c$ ,  $\alpha = \beta = \gamma = 60^\circ$ .

4.5.2 Interatomic distances and the  $\mathbf{G}$  matrix

We often need to calculate the distance between points  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$  (e.g. to determine bond lengths in a structure). Let  $\delta x = (x_2 - x_1)$ ,  $\delta y = (y_2 - y_1)$  and  $\delta z = (z_2 - z_1)$  then the distance  $d$  between the points is given by:

$$d^2 = (\delta x)^2 a^2 + (\delta y)^2 b^2 + (\delta z)^2 c^2 + 2(\delta x)(\delta y)ab\cos\gamma + 2(\delta y)(\delta z)bc\cos\alpha + 2(\delta z)(\delta x)ca\cos\beta \quad (4.8)$$

Remember in using Eq. 4.8 to keep the *signs* of  $\delta x$ ,  $\delta y$  and  $\delta z$ . For hand calculations it is worth taking into account the simplifications that arise for more symmetrical unit cells.

cubic  $d^2 = a^2[(\delta x)^2 + (\delta y)^2 + (\delta z)^2]$

tetragonal  $d^2 = a^2[(\delta x)^2 + (\delta y)^2] + c^2(\delta z)^2$

orthorhombic  $d^2 = a^2(\delta x)^2 + b^2(\delta y)^2 + c^2(\delta z)^2$

hexagonal  $d^2 = a^2[(\delta x)^2 + (\delta y)^2 - (\delta x)(\delta y)] + c^2(\delta z)^2$

rhombohedral  $d^2 = a^2[(\delta x)^2 + (\delta y)^2 + (\delta z)^2 + 2\{(\delta x)(\delta y) + (\delta y)(\delta z) + (\delta z)(\delta x)\}\cos\alpha]$

monoclinic  $d^2 = (\delta x)^2 a^2 + (\delta y)^2 b^2 + (\delta z)^2 c^2 + 2(\delta z)(\delta x)ca\cos\beta$

Equation 4.8 is conveniently expressed in matrix notation as follows. With

$$\mathbf{G} = \begin{pmatrix} a^2 & ab\cos\gamma & accos\beta \\ ab\cos\gamma & b^2 & bccos\alpha \\ accos\beta & bccos\alpha & c^2 \end{pmatrix} \quad (4.9)$$

If  $\delta$  is the column vector  $(\delta x / \delta y / \delta z)$  and  $\delta^t$  the corresponding row vector (i.e. the transpose of  $\delta$ ) then Eq. 4.8 may be written:

$$d^2 = \delta^t \mathbf{G} \delta \quad (4.8a)$$

The matrix  $\mathbf{G}^* = \mathbf{G}^{-1}$  (the inverse of  $\mathbf{G}$ ) is obtained by replacing the parameters in Eq. 4.9 by reciprocal unit cell parameters.  $\mathbf{G}$  and  $\mathbf{G}^*$  are known as the *metric tensor* and *reciprocal space metric tensor* respectively ( $\mathbf{G}$  is also called the Niggli matrix).

$$\mathbf{G}^* = \begin{pmatrix} a^{*2} & a^*b^*\cos\gamma^* & a^*c^*\cos\beta^* \\ a^*b^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ a^*c^*\cos\beta^* & b^*c^*\cos\alpha^* & c^{*2} \end{pmatrix}$$

Note that the unit cell volume is simply given as  $V^2 = \det(\mathbf{G})$  and that  $V^{*2} = \det(\mathbf{G}^*)$ .

## 4.5.3 Angles

The simplest way to calculate angles (especially if distances have already been calculated) is to use the cosine formula for the angle  $A$  between sides  $b$  and  $c$  of a triangle with opposite side  $a$ :

$$\cos A = (b^2 + c^2 - a^2)/2bc \quad (4.10)$$

A simple, if inelegant, way to calculate the dihedral angle  $ABCD$  (i.e. the angle between planes  $ABC$  and  $BCD$  intersecting in  $BC$ ) is to find the perpendicular equations of the planes  $ABC$  and  $BCD$  in Cartesian coordinates from which the angle between them is easily obtained (see below). Often the interest in dihedral angles lies in molecular chemistry when Cartesian coordinates are used. A familiar example is that of hydrogen peroxide where interest focuses on the H-O-O-H dihedral angle.

If the Miller indices of the planes are given and if  $\mathbf{g}$  is the column vector  $(h_1 / k_1 / l_1)$  and  $\mathbf{h}$  is the column vector  $(h_2 / k_2 / l_2)$ , the angle between the planes  $(h_1 k_1 l_1)$  and  $(h_2 k_2 l_2)$  is  $\phi$  given by

$$\cos\phi = \mathbf{g}^t \mathbf{G}^* \mathbf{h} / \sqrt{[(\mathbf{g}^t \mathbf{G}^* \mathbf{g})(\mathbf{h}^t \mathbf{G}^* \mathbf{h})]} \quad (4.11)$$

In the case of a cubic crystal the above formula simplifies to

$$\cos\phi = (h_1 h_2 + k_1 k_2 + l_1 l_2) / \sqrt{[(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)]} \quad (4.12)$$

Likewise if the indices of directions are given<sup>1</sup> and if  $\mathbf{u}$  is the column vector  $(u_1 / v_1 / w_1)$  and  $\mathbf{v}$  is the column vector  $(u_2 / v_2 / w_2)$ , the angle between the lines  $[u_1 v_1 w_1]$  and  $[u_2 v_2 w_2]$  is  $\phi$  given by:

$$\cos\phi = \mathbf{u}^t \mathbf{G} \mathbf{v} / \sqrt{[(\mathbf{u}^t \mathbf{G} \mathbf{u})(\mathbf{v}^t \mathbf{G} \mathbf{v})]} \quad (4.13)$$

In the case of a cubic crystal the above formula simplifies to

$$\cos\phi = (u_1 u_2 + v_1 v_2 + w_1 w_2) / \sqrt{[(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)]} \quad (4.14)$$

If the solid angle at a vertex  $D$  of a tetrahedron  $ABCD$  is wanted, it is simplest to calculate the angles  $\alpha = \angle CDB$ ,  $\beta = \angle ADC$  and  $\gamma = \angle ADB$ . The solid angle at  $D$  is then  $\omega$  given by:

$$\tan(\omega/4) = [\tan\sigma \tan(\sigma - \alpha/2) \tan(\sigma - \beta/2) \tan(\sigma - \gamma/2)]^{1/2} \quad (4.15)$$

where  $\sigma = (\alpha + \beta + \gamma)/4$

<sup>1</sup>Note that  $u_1, v_1, w_1, u_2, v_2, w_2$  do not have to be integers.

4.5.4 The  $\mathbf{G}$  matrix and unit cell parameters for transformed cells

Let a new unit cell (primed quantities) be obtained from an old one using the transformation matrix  $\mathbf{S}$  as described in § 4.4. The new  $\mathbf{G}'$  matrix is given in terms of the old by (see p. 128 for a derivation):

$$\mathbf{G}' = \mathbf{S}\mathbf{G}\mathbf{S}^t \quad (4.16)$$

As  $g_{11}' = a'^2$ ,  $g_{22}' = b'^2$ ,  $g_{33}' = c'^2$ , and  $g_{21}' = a'b'\cos\gamma'$ ,  $g_{31}' = a'c'\cos\beta'$ ,  $g_{23}' = b'c'\cos\alpha'$  the new unit cell parameters are readily obtained from the elements of the  $\mathbf{G}'$  matrix. The elements of  $\mathbf{G}'$  are:

$$g_{ij}' = \sum_{k=1}^3 \sum_{l=1}^3 s_{ik}s_{jl}g_{kl} \quad (4.16a)$$

## 4.5.5 Cartesian coordinates

Sometimes it is convenient to transform from crystal coordinates to Cartesian coordinates; for example, for drawing structures, for calculating volumes of polyhedra, etc. We take the Cartesian axis  $x_c$  to be along the crystal  $x$  direction (i.e. parallel to  $\mathbf{a}$ ). The  $y_c$  axis (perpendicular to  $x_c$ ) is in the  $ab$  plane and the  $z_c$  axis normal to  $x_c$  and  $y_c$ . Then:

$$\begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\cos\alpha\sin\beta \\ 0 & 0 & 1/c^* \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (4.17)$$

A useful special case is for a monoclinic crystal for which  $\alpha = \gamma = 90^\circ$ . The matrix then becomes  $(a \ 0 \ c\cos\beta / 0 \ b \ 0 / 0 \ 0 \ c\sin\beta)$ . Writing out Eq. 4.17 for this case:

$$x_c = ax + cz\cos\beta; y_c = by; z_c = cz\sin\beta \quad (4.18)$$

It may be convenient to change the relative orientations of the Cartesian and crystal axes according to the task at hand as described in § 4.6.1. The following table gives six choices that we find useful. To use the table, notice that each quantity on the right in Eq. 4.17 appears on the top row of the table. For the indicated orientation of Cartesian axes replace that quantity by the corresponding entry underneath in the appropriate row.

$x_c$ along $\mathbf{a}$ , $y_c$ in $\mathbf{ab}$ plane	$a$	$b$	$c, c^*$	$\alpha^*$	$\beta$	$\gamma$	$x$	$y$	$z$
$x_c$ along $\mathbf{a}$ , $y_c$ in $\mathbf{ac}$ plane	$a$	$c$	$b, b^*$	$\alpha^*$	$\gamma$	$\beta$	$x$	$z$	$-y$
$x_c$ along $\mathbf{b}$ , $y_c$ in $\mathbf{bc}$ plane	$b$	$c$	$a, a^*$	$\beta^*$	$\gamma$	$\alpha$	$y$	$z$	$x$
$x_c$ along $\mathbf{b}$ , $y_c$ in $\mathbf{ba}$ plane	$b$	$a$	$c, c^*$	$\beta^*$	$\alpha$	$\gamma$	$y$	$x$	$-z$
$x_c$ along $\mathbf{c}$ , $y_c$ in $\mathbf{ca}$ plane	$c$	$a$	$b, b^*$	$\gamma^*$	$\alpha$	$\beta$	$z$	$x$	$y$
$x_c$ along $\mathbf{c}$ , $y_c$ in $\mathbf{cb}$ plane	$c$	$b$	$a, a^*$	$\gamma^*$	$\beta$	$\alpha$	$z$	$y$	$-x$

Some expressions valid in Cartesian coordinates follow.

The plane through three points  $x_1, y_1, z_1$ ;  $x_2, y_2, z_2$ ;  $x_3, y_3, z_3$  is given by:

$$\begin{vmatrix} x & y & z & 1 \\ x_1 & y_1 & z_1 & 1 \\ x_2 & y_2 & z_2 & 1 \\ x_3 & y_3 & z_3 & 1 \end{vmatrix} = 0 \quad (4.19)$$

This can be written

$$Ax + By + Cz = D \quad (4.20)$$

with

$$A = \begin{vmatrix} y_1 & z_1 & 1 \\ y_2 & z_2 & 1 \\ y_3 & z_3 & 1 \end{vmatrix}, B = -\begin{vmatrix} x_1 & z_1 & 1 \\ x_2 & z_2 & 1 \\ x_3 & z_3 & 1 \end{vmatrix}, C = \begin{vmatrix} x_1 & y_1 & 1 \\ x_2 & y_2 & 1 \\ x_3 & y_3 & 1 \end{vmatrix}, D = \begin{vmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ x_3 & y_3 & z_3 \end{vmatrix} \quad (4.21)$$

Equation 4.20 can be written in the form (the perpendicular equation):

$$lx + my + nz = p \quad (4.22)$$

Here  $p$  is the length of the perpendicular from the plane to the origin and  $l, m$  and  $n$  are the cosines of the angles of this line with the  $x, y$  and  $z$  axes respectively. If  $s$  is the sign ( $\pm 1$ ) of  $D$  in Eq. 4.21 and  $Q$  is  $(A^2 + B^2 + C^2)^{-1/2}$  then:

$$l = sAQ; m = sBQ; n = sCQ; p = sDQ \quad (4.23)$$

The dihedral angle between two planes  $l_1x + m_1y + n_1z = 0$  and  $l_2x + m_2y + n_2z = 0$  is

$$\phi = \cos^{-1}(l_1l_2 + m_1m_2 + n_1n_2) \quad (4.24)$$

The volume of a tetrahedron with vertices  $x_i, y_i, z_i$  ( $i = 1, 2, 3, 4$ ) is:

$$V = \frac{1}{6} \begin{vmatrix} x_1 & y_1 & z_1 & 1 \\ x_2 & y_2 & z_2 & 1 \\ x_3 & y_3 & z_3 & 1 \\ x_4 & y_4 & z_4 & 1 \end{vmatrix} \quad (4.25)$$

In Eq. 4.25 the double lines indicate that the absolute value of the determinant is to be



taken. Note that Eq. 4.19 follows from Eq. 4.25.

#### 4.5.6 Distances between planes

Let  $\mathbf{h}$  be the column vector  $(h/k/l)$  where  $1/h$ ,  $1/k$  and  $1/l$  are the intercepts of a plane with the crystal axes in units of  $a$ ,  $b$  and  $c$  respectively. The equation of the plane in the lattice coordinate system is  $hx + ky + lz = 1$ . The perpendicular distance from the origin to the plane is then  $d_{hkl}$  which is given by

$$d_{hkl} = 1/\sqrt{\mathbf{h}^t \mathbf{G} \mathbf{h}} \quad (4.26)$$

This also gives the interplanar spacing between families of planes with Bragg indices  $hkl$  (see § 4.7.2). As such it is useful to have the simplified forms for the more symmetrical unit cells:

cubic	$d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$
tetragonal	$d_{hkl} = 1/\sqrt{(h^2 + k^2)/a^2 + l^2/c^2}$
orthorhombic	$d_{hkl} = 1/\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}$
hexagonal	$d_{hkl} = 1/\sqrt{4(h^2 + hk + k^2)/3a^2 + l^2/c^2}$

### 4.6 Drawing crystal structures and using cell transformations

#### 4.6.1 Orthographic and clinographic projections

By far the best way to "learn" a structure is by building a model; failing that it is good to draw it oneself. Many complex crystal structures can only be appreciated if a good model or drawing is available.

If a structure is to be communicated, at least one good drawing is essential, and this requires that a three-dimensional structure be projected onto the two dimensions of a page. Finding the best way to do this is a major problem. We have no patience at all with the crystallographer who determines a beautiful structure and then presents it as a projection of a unit cell with circles of different sizes representing the positions of different kinds of atoms. For some simple low-coordination structures "ball-and-stick" drawings may be satisfactory, but it is always almost always better to outline coordination polyhedra and to shade them in. It is a rare structure that does not profit from being drawn in more than one way; for example many "ionic" structures are usefully illustrated separately in terms of both anion coordination and cation coordination polyhedra. It is better to draw too many unit cells than too few.

Computer programs for drawing structures automatically are available. These will satisfy

many people, but we have yet to find one that does all that we want. Particularly if it is wanted to present a structure in a novel way it will be found useful to be able to draw structures oneself using a drawing program, and the rest of this section is devoted to providing some guidance in this respect. It will be found essential to use a program that allows translation of duplicated objects by precise amounts to simulate plotting.<sup>1</sup>

Many complex structures are most readily (and often best) shown as a projection down a principle axis (orthographic projection). Usually if there is more than one such axis (as e.g. for an orthorhombic crystal), the shortest axis is most appropriate. Sometimes all atoms are on a set of mirror planes so a projection normal to those planes is appropriate—the atoms will be at one of two heights separated by half the repeat distance along that axis. Some hexagonal structures with large  $c/a$  are best drawn in projection normal to  $c$ . In that case transform to an orthohexagonal cell using the transformation for axes described in § 4.4.4 (p. 108), and project along the new  $a$  axis (equal in length to the old  $a$ ). Other unit cell transformations that are useful in preparing drawings are described in § 4.6.3.

Sometimes, particularly when dealing with cubic structures, it may be found that projections along a principal axis are confusing, as atoms in a unit cell are superimposed. Then it is best to make a clinographic projection in which the view point is tilted away from a principal axis. The way to do this is first to obtain Cartesian coordinates as in Eq. 4.17. This involves just a simple scaling if the crystal is cubic, tetragonal or orthorhombic.

Now imagine the Cartesian coordinates so that  $x_c$  is horizontal on the paper (the  $H$  direction) and  $y_c$  is vertical on the paper (the  $V$  direction); the  $z_c$  axis is coming out of the paper (the  $O$  direction). The view is now along  $z_c$ ; we want to tilt away from this. First tilt the coordinate system by an angle  $\theta$  clockwise about the  $y_c$  axis and then by an amount  $\phi$  anticlockwise about an axis normal to  $y_c$  but in the plane of the paper (Fig. 4.7). Good choices of tilt angles are  $\theta = 20^\circ$  and  $\phi = 10^\circ$ .<sup>2</sup> The new coordinates for plotting the structure on paper are now  $H$  horizontal and  $V$  vertical on the paper. The points projected on the paper are really a distance  $O$  above that plane.  $H$ ,  $V$  and  $O$  are given by:

$$\begin{aligned} H &= x_c \cos \theta - z_c \sin \theta \\ V &= -x_c \sin \theta \sin \phi + y_c \cos \phi - z_c \cos \theta \sin \phi \\ O &= x_c \sin \theta \cos \phi + y_c \sin \phi + z_c \cos \theta \cos \phi \end{aligned} \quad (4.27)$$

<sup>1</sup>Most modern computer graphics programs have far too many "bells and whistles" to be useful in this context. All that is needed is the capability to draw (and duplicate) in black and white, simple objects such as lines, circles and polygons and to add shading and to control which objects are in front of which. All the drawings in this book were made using the original (1988) Cricket Draw<sup>®</sup> on a Macintosh<sup>®</sup> computer using coordinates generated by EUTAX. The drawing instructions that follow assume that the reader has such a program available.

<sup>2</sup>Imagine that we are looking at the coordinate axes in a three-dimensional world with the view along  $z_c$  and with  $y_c$  vertical. The rotations are equivalent to moving our point of view to the right and up. Long ago many authors chose  $\theta = \tan^{-1}(1/3) \approx 18.5^\circ$  and  $\phi = \tan^{-1}(1/6) \approx 9.5^\circ$  as a "standard." For a discussion of drawing macroscopic crystals (still an important aspect of mineralogy) see Smith (Book List). Another good discussion is given by de Jong (Book List). The brain soon gets used to clinographic projections at a certain angle. You have reached this stage when it is found that such illustrations look almost incomprehensible when viewed upside down.

Some authors prefer a perspective drawing with parallel lines not parallel on the page; except for very simple structures or stereo pairs this tends to make the illustration less clear (in contrast to e.g. architectural drawings) and, except in stereo pairs, we use drawings in which parallel lines in the structure are parallel on the page ("view from infinity"). Notice although parallel edges are parallel on the paper in the projection of a cube (Fig. 4.7) none of the angles between edges is  $90^\circ$ ; most drawings in the older literature incorrectly show the front face of a cube seen in clinographic projection as a rectangle, indeed commonly as a square.<sup>1</sup>

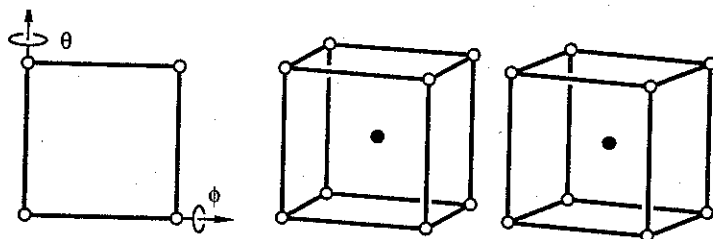


Fig 4.7. Obtaining a clinographic projection of a cube by rotation from a symmetry axis. Middle:  $\phi = 10^\circ$ ,  $\theta = 17^\circ$ ; Right:  $\phi = 10^\circ$ ,  $\theta = 23^\circ$ . The filled circle is at the cube body center.

Approximations to stereo pairs can be made by using two different values of  $\theta$  (the pair of cubes in Fig. 4.7 have  $\theta = 17^\circ$  on the left and  $\theta = 23^\circ$  on the right), but many people have difficulty merging the images.<sup>2</sup> In our experience, stereo pairs are most effective for stick models. Some stereo pairs of this sort are presented in § 7.11.8; if only one of each pair shown there is viewed it will be found to be rather uninformative.

For non-cubic crystals, it is necessary first to decide the point of view. Thus it must be decided which crystal plane will be parallel to the plane of the paper and which axis will be horizontal in that plane before tilting by  $\theta$  and  $\phi$ . In practice this means choosing one of the six orientations of Cartesian axes with respect to the crystal axes discussed in § 4.5.5.

#### 4.6.2 Examples of clinographic drawings (ZnS and $\text{CaF}_2$ )

We now go through the steps of drawing a simple structure, that of sphalerite ZnS. The procedure is more complicated to describe than to implement, as readers who work through the example will find. The structure is cubic with symmetry  $F\bar{4}3m$ ,  $a = 5.436 \text{ \AA}$ . Zn atoms are in 4 c:  $F + (1/4, 1/4, 1/4)$  and S atoms in 4 a:  $F + (0, 0, 0)$ . In this case (a cubic structure)

<sup>1</sup>We have erred several times in the past in this respect. But we are in very distinguished company.

<sup>2</sup>Making a true stereo pair is rather subtle. The reader is invited to merge the two images on the right of Fig. 4.7 (holding a piece of opaque paper perpendicular to the page so that each eye can only view one image helps). Most viewers will see the back face and circles of the cube as much larger than the front ones even though they are drawn exactly the same size—the brain is adding perspective that is absent in the drawings. For references to drawing true stereo images see C. K. Johnson in *Crystallographic Computing* (F. R. Ahmed, ed.), Munksgaard, Copenhagen (1970).

to get Cartesian coordinates we simply have to multiply all the atomic coordinates by  $a$ . To make a clinographic projection we will take a horizontal and  $b$  vertical and then rotate by  $\theta = 20^\circ$  and  $\phi = 10^\circ$ . Coordinates ( $H$ ,  $V$ , and  $O$ ) for plotting are then calculated as described in the previous section (Eq. 4.27).<sup>1</sup> For simplicity we take a scale of  $1 \text{ cm} = 1 \text{ \AA}$  for plotting (the drawings shown below have been subsequently shrunk to fit the page).

The first thing to do is to calculate the unit cell dimensions on the scale of the plot. The point at  $1, 0, 0$  has Cartesian coordinates (in  $\text{\AA}$ )  $5.409, 0, 0$ . We then calculate  $H = 5.409 \cos 20^\circ = 5.083 \text{ cm}$ ,  $V = -5.409 \sin 20^\circ \sin 10^\circ = -0.321 \text{ cm}$ . Although not needed for plotting it is useful to record the "out" coordinate  $O = 5.409 \sin 20^\circ \cos 10^\circ = 1.822$  to keep track of what is in front of what in the drawing. The coordinates of this point and the points  $0, 1, 0$  and  $0, 0, 1$  are listed below. It should be clear that adding the three sets of coordinates will give the plotting coordinates for  $1, 1, 1$  and so on. The calculation of S atom plotting coordinates from those  $(1/2, 1/2, 0)$  etc.) in the unit cell proceeds similarly and they are also listed.

$x$	$y$	$z$	$x_c$	$y_c$	$z_c$	$H$	$V$	$O$
1	0	0	5.409	0.0	0.0	5.083	-0.321	1.822
0	1	0	0.0	5.409	0.0	0.0	5.327	0.939
0	0	1	0.0	0.0	5.409	-1.850	-0.883	5.006
1	1	1	5.409	5.409	5.409	3.233	4.123	7.767
0	0	0	0.0	0.0	0.0	0.0	0.0	0.0
1/2	1/2	0	2.705	2.705	0.0	2.541	2.503	1.381
1/2	0	1/2	2.705	0.0	2.705	1.616	-0.602	3.414
0	1/2	1/2	0.0	2.705	2.705	-0.925	2.222	2.972

The top row in Fig. 4.8 shows some stages in the drawing of the structure. On the left, the S and Zn atoms are shown as open or filled circles plotted with the appropriate values of  $H$  and  $V$  relative to the origin of coordinates. Notice that S atoms are at the corners and face centers of the cell so we actually show 14 atoms. In the middle, Zn-S bonds are drawn in to make a ball and stick drawing. Notice the use of broken lines as depth cues.<sup>2</sup> On the right the same pattern is shown as  $\{\text{Zn}\}\text{S}_4$  tetrahedra sharing corners. The "tetrahedra" of the drawing are actually two triangles corresponding to the two visible (front) faces of each tetrahedron. It is generally best to consider coordination polyhedra to be opaque so the centering Zn atom and the back faces are omitted. We often (as here) shade the visible faces of polyhedra with a density that varies from one side to the other as this allows overlapping polyhedra to be more easily differentiated.

Notice that the structure is the same if the Zn and S positions are interchanged (this just corresponds to a shift of origin by  $1/4, 1/4, 1/4$ ) so the figure on the right could equally be illustrating  $\{\text{S}\}\text{Zn}_4$  tetrahedra.

<sup>1</sup>EUTAX will calculate  $H$ ,  $V$  and  $O$  for a specified orientation and scale. However this program recognizes that most computer drawing programs consider the positive direction of vertical coordinates as down the page, and reports  $V$  coordinates as the negative of those given here.

<sup>2</sup>In the drawings shown, we actually have slightly thicker opaque white lines immediately behind black lines, so the white lines occlude black lines that are in turn behind them. All computer drawing programs that we have examined keep track of which objects are behind which, and usually allow changing the order.

The structure of fluorite  $\text{CaF}_2$  can be illustrated similarly. The structure is cubic:  $Fm\bar{3}m$ ,  $a = 5.463 \text{ \AA}$ . Ca atoms are in 4  $a$ :  $F + (0,0,0)$  and F in 8  $c$ :  $F \pm (1/4, 1/4, 1/4)$ . Again we show metal atoms as filled circles. A ball and stick drawing on the bottom left of Fig. 4.8 shows that F atoms are in  $\{\text{F}\}\text{Ca}_4$  tetrahedra. These polyhedra are shown in the center where it may be seen that tetrahedra now share edges.

As there are twice as many F atoms as Ca atoms, the latter must be in eight coordination. This is not immediately apparent from the ball and stick drawing, so parts of adjacent unit cells need to be added as shown in the figure on the bottom right, which shows that the Ca atoms are in  $\{\text{Ca}\}\text{F}_8$  cubes (shown here as three differently shaded quadrilaterals). The question of how much to include is always tricky—too little does not show all aspects of the structure, and too much leads to too great an overlap of the component parts.

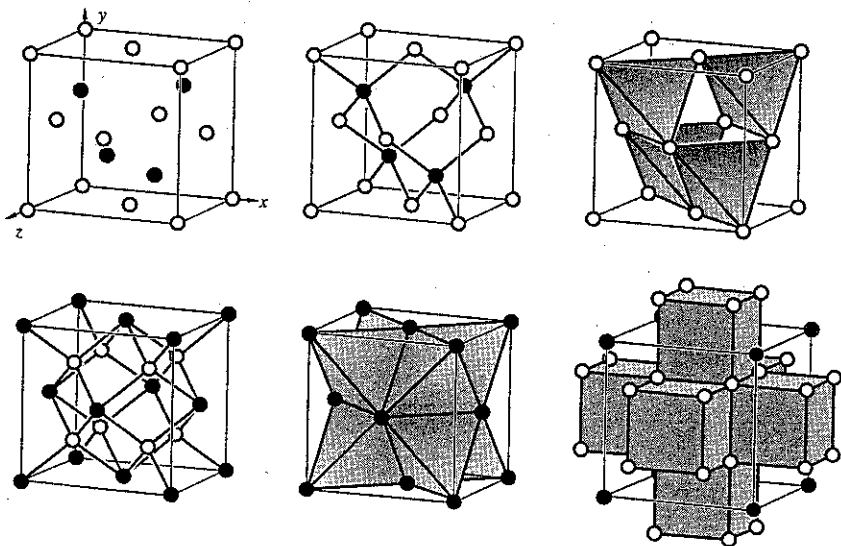


Fig. 4.8. Aspects of the structures of sphalerite,  $\text{ZnS}$  (top) and fluorite,  $\text{CaF}_2$  (bottom). See the text for discussion.

#### 4.6.3. Projections of some structures with octahedral coordination: $\text{NaCl}$ , $\text{NiAs}$ and $\text{TiP}$ . Using orthohexagonal cells for cubic and hexagonal structures

In this section we consider three structure types of composition  $\text{AX}$  in which metal atoms are  $\{\text{A}\}\text{X}_6$  octahedra. For the purpose of illustration we use idealized versions of  $\text{NaCl}$ ,  $\text{NiAs}$  and  $\text{TiP}$  (recall that bold face formulas refer to structures not compounds) with regular octahedra of unit edge. The structures then are:

$\text{NaCl}$   $Fm\bar{3}m$ ,  $a = 1.414$ ; Na in 4  $b$ :  $F + (0,0,1/2)$ ; Cl in 4  $a$ :  $F + (0,0,0)$

$\text{NiAs}$   $P6_3/mmc$ ,  $a = 1.0$ ,  $c = 1.633$ ; Ni in 2  $a$ :  $(0,0,0; 0,0,1/2)$ ; As in 2  $d$ :  $\pm(1/3, 2/3, 1/4)$

$\text{TiP}$   $P6_3/mmc$ ,  $a = 1.0$ ,  $c = 3.266$ ; Ti in 4  $f$ :  $\pm(1/3, 2/3, z; 1/3, 2/3, 1/2-z)$ ,  $z = 0.125$   
P(1) in 2  $a$ :  $(0,0,0; 0,0,1/2)$ ; P(2) in 2  $d$ :  $\pm(1/3, 2/3, 1/4)$

In these structures there are layers of octahedra sharing edges. In  $\text{NaCl}$  the layers are normal to  $[111]$ , in  $\text{NiAs}$  and  $\text{TiP}$  they are normal to  $c$ . To compare the three structures we will project them in a similar way in each case. For the hexagonal structures we project normal to  $c$ ; specifically along  $a$  of the orthohexagonal cell described in § 4.4.4.

For  $\text{NaCl}$  we convert from  $\text{fcc}$  to hexagonal by  $S_1 = (-1/2 \ 1/2 \ 0 / 0 \ -1/2 \ 1/2 / 1 \ 1 \ 1)$  (p. 107) and then from hexagonal to orthohexagonal by  $S_2 = (1 \ 1 \ 0 / \bar{1} \ 0 \ 0 / 0 \ 0 \ 1)$ . In fact we do not need to do each transformation individually, but instead transform by  $S = S_2 S_1 = (-1/2 \ 0 \ 1/2 / 1/2 \ \bar{1} \ 1/2 / 1 \ 1 \ 1)$ ; the inverse matrix,  $T = (\bar{1} \ 1/3 \ 1/3 / 0 \ -2/3 \ 1/3 / 1 \ 1/3 \ 1/3)$ . The final cell has  $3/2$  the volume of the original and contains 6 Na and 6 Cl.

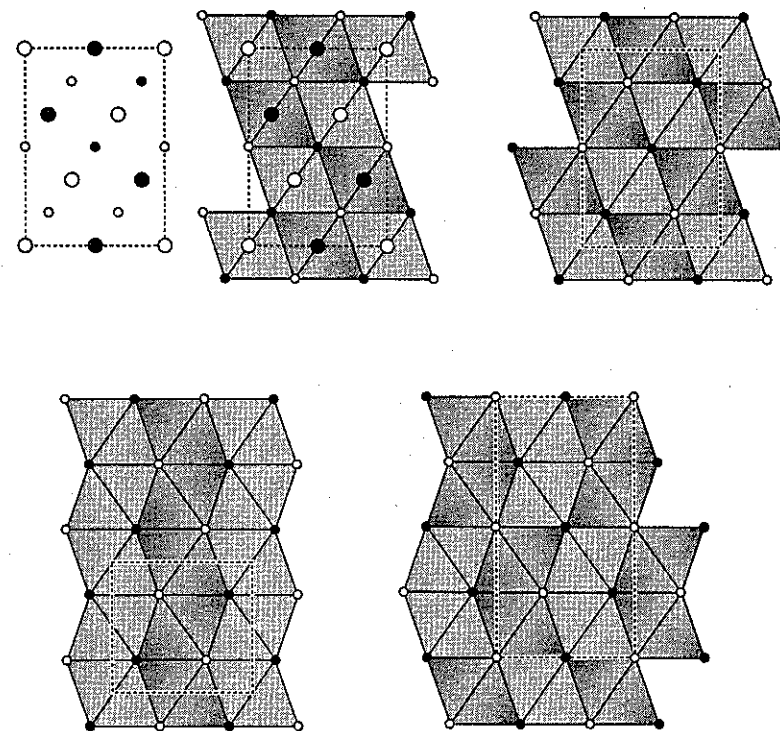


Fig. 4.9. Top; projection of  $\text{NaCl}$  normal to  $[111]$  (vertical on the page) showing  $\{\text{Na}\}\text{Cl}_6$  octahedra. Bottom:  $\text{NiAs}$  (left) and  $\text{TiP}$  (right) as  $\{\text{Ni}\}\text{As}_6$  or  $\{\text{Ti}\}\text{P}_6$  octahedra projected on  $(11\bar{2}0)$ . See text.

The hexagonal cell has  $a_h = a/\sqrt{2} = 1.000$ , and  $c_h = \sqrt{6}a_h = 2.450$ ; and the orthohexagonal cell has  $a_o = a_h = 1.000$ ,  $b_o = \sqrt{3}a_h = 1.732$  and  $c_o = c_h = 2.450$  (see pp 107-108). We get the CI coordinates using  $(x' / y' / z') = T^t(x / y / z)$ . (specifically, in this case,  $x' = -x+z$ ,  $y' = x/3-2y/3+z/3$ ,  $z' = x/3+y/3+z/3$ .) The set  $(1/2, 0, 0; 0, 1/2, 0; 0, 0, 1/2; 1/2, 1/2, 1/2)$  in the cubic cell transform to  $(1/2, 1/6, 1/6; 0, 2/3, 1/6; 1/2, 1/6, 1/6; 0, 0, 1/2)$  with due allowance for the equivalence of  $-1/2$  and  $1/2$ ,  $-1/3$  and  $2/3$  etc. Thus we have three distinct new coordinate triplets. Recalling that the orthohexagonal cell is  $C$  centered, we find the other three CI atoms in the cell by adding  $(1/2, 1/2, 0)$  to the coordinates of the first three. These, and the transformed Na coordinates, are listed below (notice that the new Na and CI coordinates differ by  $0, 0, 1/2$ ). Also listed are plotting coordinates using the scale  $b = 5$  cm; these are simply obtained as  $H = 5y$ ,  $V = 5zc/b = 7.071z$ .

Na					CI				
$x$	$y$	$z$	$H$	$V$	$x$	$y$	$z$	$H$	$V$
0	0	0	0	0	0	0	1/2	0	3.536
1/2	1/2	0	2.5	0	1/2	1/2	1/2	2.5	3.536
0	1/3	1/3	1.667	2.357	0	1/3	5/6	1.667	5.892
1/2	5/6	1/3	4.167	2.357	1/2	5/6	5/6	4.167	5.892
0	2/3	2/3	3.333	4.714	0	2/3	1/6	3.333	1.179
1/2	1/6	2/3	0.833	4.714	1/2	1/6	1/6	0.833	1.179

Transformed coordinates and  $H$  and  $V$  for the other two structures are obtained in a similar way using first a transformation from hexagonal to orthohexagonal.

In Fig. 4.9 we show, at top left, a transformed unit cell of NaCl with  $b$  horizontal and  $c$  vertical. Also shown are the positions of the Na atoms (large circles) and Cl atoms (small circles). The elevations of all atoms are either  $x = 0$  (open circles) or  $x = 1/2$  (filled circles). On the right of that we show a little more of the structure with the  $\{\text{Na}\}\text{Cl}_6$  octahedra outlined. Those with centers at  $x = 0$  are lighter shaded than those at  $x = 1/2$ . On the top right just the  $\{\text{Na}\}\text{Cl}_6$  octahedra are shown. In the bottom half of the figure NiAs and TiP are similarly depicted.

Notice that NaCl is the same if Na and Cl are interchanged, so Fig. 4.9 also depicts the arrangement of  $\{\text{Cl}\}\text{Na}_6$  octahedra. In contrast in NiAs there are  $\{\text{As}\}\text{Ni}_6$  trigonal prisms and in TiP there are both  $\{\text{P}\}\text{Ti}_6$  octahedra and triangular prisms. These aspects of these structures are met again in Chapter 6.

#### 4.6.4. Further example of projections of crystal structures. ZnS again

ZnS occurs in two forms known as sphalerite and wurtzite. Sphalerite was discussed and the structure given in § 4.6.2. Wurtzite is hexagonal, space group  $P6_3mc$ ,  $a = 3.823$ ,  $c = 6.261$  Å. Zn atoms are in  $2b$ :  $(1/3, 2/3, z; 2/3, 1/3, 1/2+z)$  with  $z = 0.0$ ; S atoms are in  $2b$  with  $z = 0.375$ .<sup>1</sup> In both structures there are  $\{\text{Zn}\}\text{S}_4$  tetrahedra linked by sharing corners, but the topology of linkage is different. We will illustrate the difference by

<sup>1</sup>Notice that this is an example of a polar structure. In particular  $z$  only enters as  $+z$  so the position of the origin on the  $z$  axis is arbitrary and it has been chosen so that the Zn atoms are at  $z = 0$  and  $z = 1/2$ .

projecting wurtzite down  $c$  and sphalerite down  $[111]$  of the cubic cell.

To calculate coordinates for plotting a hexagonal structure down  $c$  we take a scale for  $a$  (say  $a = s$  cm). Then plotting coordinates are horizontal  $H = s(y - x/2)$  and vertical  $V = \sqrt{3}sx/2$  (see Fig. 4.10). In wurtzite, Zn and S atoms with the same  $x$  and  $y$  coordinates differ in elevation by  $\delta z = 0.375c = 2.35$  Å (Zn below S) so we just plot the S atoms and make a mental note that the Zn atoms are underneath them. The plotting coordinates for the unit cell corners and S atoms are given below.

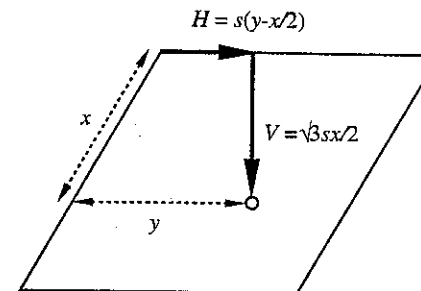


Fig. 4.10. Plotting coordinates  $H$  and  $V$  for a point  $(x, y, z)$  in a hexagonal cell with scale  $a = s$ .

Now the sphalerite structure is transformed to a hexagonal cell (§ 4.4.3, p. 107) for which it is found that  $a = 3.825$ ,  $c = 9.369$  Å. The atom coordinates in this new cell are for Zn:  $R + (0, 0, 1/4)$  and for S:  $R + (0, 0, 0)$ . Notice that Zn and S atoms with the same  $x$  and  $y$  coordinates differ in elevation by  $\delta z = c/4 = 2.34$  Å but now with S below Zn. In order to compare with wurtzite we would like to have Zn below S (cf. the previous paragraph) accordingly we reverse the direction of  $z$  and, to avoid changing hand of the axes, interchange  $x$  and  $y$ . The S coordinates are now  $(0, 0, 0; 2/3, 1/3, 2/3; 1/3, 2/3, 1/3)$  with Zn underneath by  $\delta z = 1/4$ . The S coordinates are also given in the table below.

The plotting coordinates ( $H$  and  $V$ ) in the two structures are (with  $s = 5$  cm) are:

wurtzite						sphalerite					
atom	$x$	$y$	$z$	$H$	$V$	atom	$x$	$y$	$z$	$H$	$V$
	0	1		-2.500	4.330		0	1		-2.500	4.330
	1	0		5.000	0.000		1	0		5.000	0.000
	1	1		2.500	4.330		1	1		2.500	4.330
S	1/3	2/3	0.375	2.500	1.433	S	0	0	0	0.000	0.000
S	2/3	1/3	0.875	0.000	2.887	S	1/3	2/3	1/3	2.500	1.433
						S	2/3	1/3	2/3	0.000	2.887

When the wurtzite structure is first plotted (Fig. 4.11, top left) the unit cell is outlined and the positions of two S atoms in the cell are plotted with a filled circle for the atom with  $z = 0.875$  and an open circle for the atom at  $z = 0.375$ . The Zn atoms below these two S atoms are in tetrahedra pointing up (see e.g. Fig. 2.19) and their other three neighbors form

a triangle at a lower elevation. The two tetrahedra are drawn in the figure. Notice that the darker tetrahedron around the Zn atom with  $z = 0$  has three S atoms at the base with elevation  $0.875 - 1 = -0.125$ . More of the structure is drawn on a smaller scale at the bottom left of the figure.

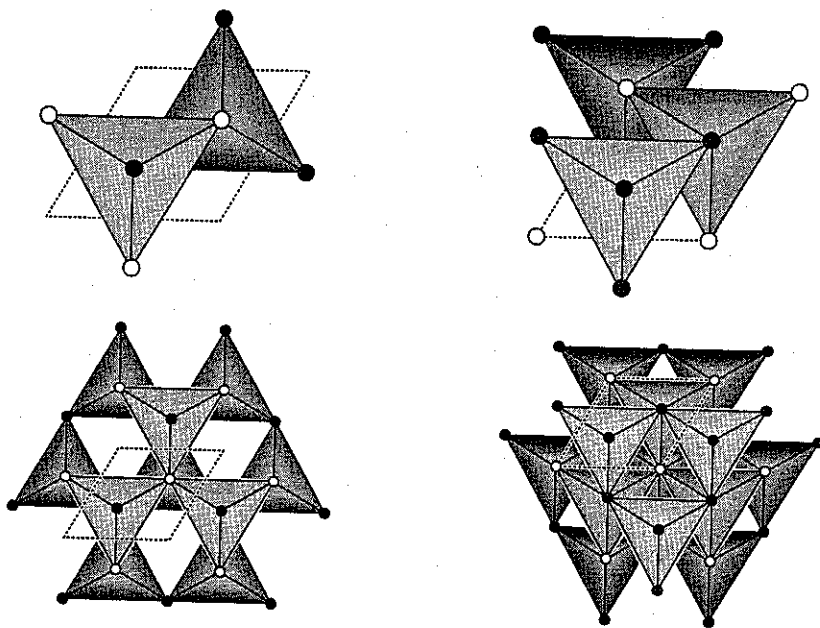


Fig. 4.11. The wurtzite (left) and sphalerite (right) forms of ZnS as  $\{Zn\}S_4$  tetrahedra.

The drawing of sphalerite proceeds similarly. Now there are three S atoms in the cell at  $z = 0, 1/3$  and  $2/3$  and these are shown as open, shaded and filled circles respectively in the top right of Fig 4.11. The tetrahedra about the three Zn atoms in the unit cell are also drawn. A larger portion of the structure is shown on a reduced scale underneath.

We will discuss these structures again in Chapters 6 and 7.

#### 4.6.5 Drawing monoclinic structures

Often monoclinic structures are drawn in projection down  $b$  (which is normal to  $a$  and  $c$ )—see Exercises 6 and 7 at the end of this chapter. Cartesian coordinates are given in equation 4.18 (p. 112). All that is necessary to do is to scale by a suitable amount: Thus if the scale chosen is  $a = s$ , the plotting coordinates for  $a$  horizontal are  $H = (s/a)x_c$  and  $V = (s/a)z_c$ . If it is wanted to have  $c$  horizontal on the page (Fig. 4.12) then the roles of  $a$  and  $c$  and of  $x$  and  $z$  must be interchanged in the formulas for  $H$  and  $V$ . Explicitly:

$$\begin{aligned} \text{a horizontal: } H &= sx + (szc/a)\cos\beta & V &= (szc/a)\sin\beta \\ \text{c horizontal: } H &= (szc/a) + sxc\cos\beta & V &= sxs\sin\beta \end{aligned}$$

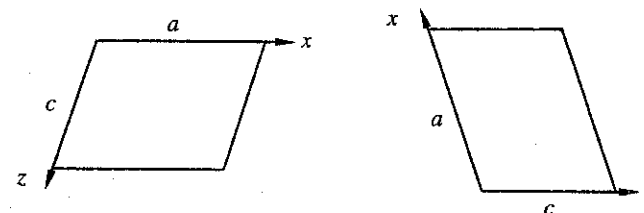


Fig. 4.12. Two orientations of a monoclinic cell projected down  $b$  (the positive sense of  $b$  is up out of the page in both cases). In the orientation on the left the coordinates  $H$  and  $V$  are to the right and down the page. In the orientation on the right the coordinates  $H$  and  $V$  are to the right and up the page.

For a projection of a monoclinic structure on (100) or (001), Cartesian coordinates should be calculated, but with the tilts  $\theta$  and  $\phi$  set equal to 0 in calculating  $H$  and  $V$ . An example of such a projection is to be found in Fig. 7.28 (p. 314).

Occasionally a projection down  $a$  or  $c$  [note: this is *not* the same as projection on (100) or (001)] is required. Such projections should be carried out just like clinographic projections. The cell in projection is rectangular: for a projection down  $a$  it has projected dimensions (i.e. on the page)  $b$  and  $c\sin\beta$  and for a projection down  $c$  it has projected dimensions  $b$  and  $a\sin\beta$ . The following table of tilts ( $\theta$  and  $\phi$ ) may be useful (as always we assume that  $a$ ,  $b$  and  $c$  form a right-handed coordinate system):

Projection down $a$	$b$ horizontal	$\theta = 0$	$\phi = 90^\circ - \beta$
	$b$ vertical	$\theta = 90^\circ - \beta$	$\phi = 0$
Projection down $c$	$b$ horizontal	$\theta = 0$	$\phi = \beta - 90^\circ$
	$b$ vertical	$\theta = 90^\circ - \beta$	$\phi = 0$

To illustrate some of these points we use the structure of  $MnB_4$  which was reported as:

$$\begin{aligned} MnB_4 & C2/m, a = 5.503, b = 5.367, c = 2.949 \text{ \AA}, \beta = 122.71^\circ \\ Mn \text{ in } 2a: & C + (0,0,0); B \text{ in } 8j: C \pm (x,\pm y,z), x = 0.200, y = 0.343, z = 0.197 \end{aligned}$$

First we project down  $b$ , i.e. on (010), with  $c$  horizontal and a scale  $a = 5$  cm. We calculate plotting coordinates  $H$  and  $V$  using the expressions given above. Thus for Mn at 0,0,0 we have  $H = 0.000$ ,  $V = 0.000$  and for Mn at  $1/2, 1/2, 0$   $H = -1.350$ ,  $V = 2.104$ . For B at 0.200, 0.343, 0.197 we find  $H = -0.013$ ,  $V = 0.841$  and so on (the reader may wish to verify these numbers and continue the calculation). In Fig 4.13 we have plotted the atoms in the unit cell and some in adjacent unit cells. For the atoms in the unit cell, elevations in multiples of  $b/100$  are indicated (notice that pairs of B atoms superimpose in projection). The B atoms form a network in which each is bonded to four neighbors; three of the bonds

are drawn in, the fourth joins pairs of atoms at  $y = 0.34$  and  $y = 0.66$  (open circles labeled  $\pm 34$ ) or pairs of atoms at  $y = \pm 0.16$  (filled circles). Thus we see that the B atoms are on puckered  $6^3$  2-dimensional nets that are linked by bonds "up" or "down" to similar nets to form the three-dimensional network. Mn atoms (shown as larger circles) are in the cavities of the B framework.

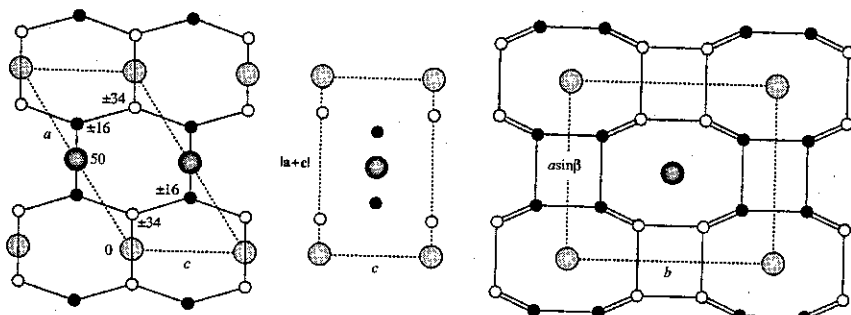


Fig. 4.13. The structure of  $\text{MnB}_4$  (large circles are Mn). Left projected down  $b$ . Middle: showing a body-centered ( $I2/m$ ) cell. Right: projected down  $c$ . See the text for further details.

Just a quick glance at Fig. 4.13 shows that the structure appears to be close to orthorhombic symmetry. In the middle of the figure a body-centered cell obtained by the transformation  $S = (1 \ 0 \ 1 / 0 \ 1 \ 0 / 0 \ 0 \ 1)$  is indicated.  $T = (1 \ 0 \ 1 / 0 \ 1 \ 0 / 0 \ 0 \ 1)$  is the inverse matrix. The description of the structure using this cell is:

$\text{MnB}_4$   $I2/m$ ,  $a' = 4.630$ ,  $b' = 5.367$ ,  $c' = 2.949 \text{ \AA}$ ,  $\beta = 90.31^\circ$   
 Mn in 2  $a$ :  $I \pm (0,0,0)$ ; B in 8  $j$ :  $I \pm (x', \pm y', z')$ ,  $x' = 0.200$ ,  $y' = 0.343$ ,  $z' = -0.003$

Actually the atoms are less than  $0.01 \text{ \AA}$  away from positions with symmetry  $Immm$ ; all that is needed is for  $\beta$  to be  $90^\circ$  and  $z'$  to be 0. The description would then be:

$\text{MnB}_4$   $Immm$ ,  $a' = 4.630$ ,  $b' = 5.367$ ,  $c' = 2.949 \text{ \AA}$   
 Mn in 2  $a$ :  $I \pm (0,0,0)$ ; B in 8  $n$ :  $I \pm (x', \pm y', 0)$ ,  $x' = 0.200$ ,  $y' = 0.343$

With this description of the structure, it is seen that the short axis ( $c'$ ) is a symmetry axis and a projection of the real structure down the corresponding  $c'$  axis should be rewarding. This is made on the same scale ( $a = 5 \text{ cm}$ ) as the original drawing. The unit cell edges in the drawing are  $b = 4.876 \text{ cm}$  and  $a \sin \beta = 4.207 \text{ cm}$ . The height of  $c$  out of the page is  $2.679 \text{ cm}$ . B atoms (in the original unit cell) have elevations  $-0.013$ ,  $-0.010$ ,  $1.341$  and  $-1.363 \text{ cm}$ . These correspond closely to elevations of  $z = 0$  and  $\pm 1/2$  ( $\pm 1.34 \text{ cm}$ ), and they are shown as open and filled circles in the drawing on the right side of the figure.

The B arrangement is a 4-connected net that we discuss in Chapter 7 (see § 7.3.3). In its most symmetrical form the net is tetragonal; it is named for  $\text{CrB}_4$  which is reported to be

orthorhombic, and it does seem likely that  $\text{MnB}_4$  is really orthorhombic also.<sup>1</sup>

## 4.7 Notes

### 4.7.1 Orientation of direct and reciprocal lattices

For crystals with orthogonal axes (cubic, tetragonal and orthorhombic) the reciprocal lattice vectors  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  are parallel to the direct lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ . For hexagonal crystals  $\mathbf{c}^*$  is parallel to  $\mathbf{c}$  and now  $\mathbf{a}^*$  and  $\mathbf{b}^*$  are not parallel to  $\mathbf{a}$  and  $\mathbf{b}$  (although these last four vectors are in the same plane) as shown in Fig. 4.14. Note that  $\mathbf{a}^*$  is perpendicular to  $\mathbf{b}$  and that  $\mathbf{b}^*$  is perpendicular to  $\mathbf{a}$ . In monoclinic crystals  $\mathbf{b}^*$  is parallel to  $\mathbf{b}$  and normal to  $\mathbf{a}$  and  $\mathbf{c}$ .

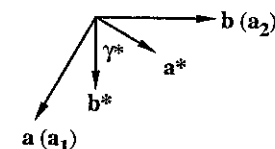


Fig. 4.14. The relative orientations of direct and reciprocal lattice vectors for a hexagonal lattice.  $\gamma^* = 60^\circ$ .

### 4.7.2 Bragg and Miller indices

Many text books do not distinguish between Miller indices of a plane and Bragg indices of a family of planes. In the Bragg condition for diffraction, which we write ( $\lambda$  is the wavelength and  $2\theta$  is the diffraction angle):

$$(2 \sin \theta) / \lambda = 1 / d_{hkl}$$

$d_{hkl}$  is the spacing between a family of parallel planes. It is the perpendicular distance from the origin to a plane that intercepts the axes at  $1/h$ ,  $1/k$ ,  $1/l$ , where now  $h$ ,  $k$  and  $l$  may have a common divisor and are written without parentheses as in 222.  $1/d_{hkl}$  is better thought of as the distance from the origin in reciprocal space to a reciprocal lattice point  $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$  (i.e. the length of a reciprocal lattice vector). Thus  $d_{111} = 2d_{222}$ . On the other hand Miller indices only give the orientation of a plane, and  $(222) \equiv (111)$ .

<sup>1</sup>It appears that many more structures than might be expected are reported with the wrong symmetry. For some typical corrections and a discussion of the importance of knowing correct space groups see R. E. Marsh & I. Bernal, *Acta Crystallogr.* B51, 300 (1995). This paper should be required reading for non-crystallographers who wish to interpret the details (bond lengths, angles, etc.) of crystal structures.

## 4.7.3 More equations for triangles and tetrahedra

Some occasionally useful results for triangles and tetrahedra include:

The *medians* of a triangle join the vertices to the midpoints of the opposite edges. They all intersect at a point, the *centroid*, which divides them in the ratio 2:1.

For a triangle with edges  $a$ ,  $b$  and  $c$ , and opposite angles  $A$ ,  $B$  and  $C$ , and with  $s = (a+b+c)/2$ :

The diameter of the circumscribed circle is:

$$a/\sin A = b/\sin B = c/\sin C$$

The perpendicular from  $C$  to  $AB$  is:

$$h = c/(\cot A + \cot B) = 2\sqrt{s(s-a)(s-b)(s-c)}/c$$

The area is given by:

$$\text{area} = hc/2 = \sqrt{s(s-a)(s-b)(s-c)}$$

The medians of a tetrahedron join the vertices and the centroids of opposite faces. They all intersect at a point, also called the centroid, which divides them in the ratio 3:1. The *bimedians* join the midpoints of opposite edges. They also pass through the centroid which bisects them.

For a tetrahedron of sides  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  and  $f$  with  $a$ ,  $b$ , and  $c$  meeting at a common vertex  $P$  the length  $l$  of the median from  $P$  is given by:

$$l^2 = (a^2 + b^2 + c^2)/3 + (d^2 + e^2 + f^2)/9$$

A *circumscribable* tetrahedron is one defined by the centers of four spheres, each in contact with the other three. If the radii of the spheres are  $1/p$ ,  $1/q$ ,  $1/r$  and  $1/s$ , the volume is:

$$V = [(p+q+r+s)^2 - 2(p^2+q^2+r^2+s^2)]^{1/2}/3pqrs$$

Consider a tetrahedral unit  $AX_1X_2X_3X_4$  (i.e.  $\{A\}X_4$ ). There are six angles  $\theta_{ij}$  between the vectors  $AX_i$  and  $AX_j$  ( $i \neq j = 1, 2, 3, 4$ ). These are related by:

$$\begin{vmatrix} 1 & \cos \theta_{12} & \cos \theta_{13} & \cos \theta_{14} \\ \cos \theta_{12} & 1 & \cos \theta_{23} & \cos \theta_{24} \\ \cos \theta_{13} & \cos \theta_{23} & 1 & \cos \theta_{34} \\ \cos \theta_{14} & \cos \theta_{24} & \cos \theta_{34} & 1 \end{vmatrix} = 0$$

Special cases that often arise (with symmetry) are:

$$(a) \bar{4}2m (D_{2d}) \quad \theta_{12} = \theta_{34} = \beta; \quad \theta_{13} = \theta_{14} = \theta_{23} = \theta_{24} = \alpha. \quad \cos \beta = -(1 + 2\cos \alpha)$$

$$(b) 3m (C_{3v}) \quad \theta_{12} = \theta_{13} = \theta_{14} = \alpha; \quad \theta_{23} = \theta_{24} = \theta_{34} = \beta \quad \sin \alpha = (2/\sqrt{3})\sin(\beta/2)$$

For a square-pyramidal group  $AX_1X_2X_3X_4X_5$  with  $X_1$  at the apex and with 4-fold symmetry  $4mm (C_{4v})$  so that  $\theta_{12} = \theta_{13} = \theta_{14} = \theta_{15} = \alpha$  and  $\theta_{23} = \theta_{34} = \theta_{45} = \theta_{25} = \beta$ ;  $\sin \alpha = \sqrt{2}\sin(\beta/2)$ .

## 4.7.4. Some matrix expressions written out explicitly

Our experience is that many people (such as ourselves) like to have matrix expressions written out explicitly in a handy place. Here are some involving the  $3 \times 3$  matrices used in this chapter.

1.  $Ax$  gives another vector [here  $x$  is the column  $(x_1 / x_2 / x_3)$ ]:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 \\ a_{21}x_1 + a_{22}x_2 + a_{23}x_3 \\ a_{31}x_1 + a_{32}x_2 + a_{33}x_3 \end{pmatrix}$$

2.  $\det A$  (the determinant of  $A$  which is scalar):

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}a_{22}a_{33} + a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} - a_{13}a_{22}a_{31}$$

3.  $A^{-1}$  (the inverse of  $A$ , another  $3 \times 3$  matrix):

$$A^{-1} = \frac{1}{\det A} \begin{pmatrix} a_{22}a_{33} - a_{23}a_{32} & a_{13}a_{32} - a_{12}a_{33} & a_{12}a_{23} - a_{13}a_{22} \\ a_{23}a_{31} - a_{21}a_{33} & a_{11}a_{33} - a_{13}a_{31} & a_{13}a_{21} - a_{11}a_{23} \\ a_{21}a_{32} - a_{22}a_{31} & a_{12}a_{31} - a_{11}a_{32} & a_{11}a_{22} - a_{12}a_{21} \end{pmatrix}$$

4.  $A^t$  (the transpose of  $A$ ): interchange rows and columns. In particular the column  $x = (x_1 / x_2 / x_3)$  becomes the row  $x^t = (x_1 \ x_2 \ x_3)$ .

5.  $x^t G y$  (a scalar; here  $G$  is a symmetric matrix with  $g_{ij} = g_{ji}$ ):

$$x^t G y = g_{11}x_1y_1 + g_{22}x_2y_2 + g_{33}x_3y_3 + g_{12}(x_1y_2 + x_2y_1) + g_{13}(x_1y_3 + x_3y_1) + g_{23}(x_2y_3 + x_3y_2)$$

6.  $AB = C$  (multiplication of two matrices gives a third). The elements  $c_{ij}$  of  $C$  are:

$$c_{ij} = a_{i1}b_{1j} + a_{i2}b_{2j} + a_{i3}b_{3j}.$$

$$7. (AB)^t = B^t A^t.$$

To derive Eq. 4.16 relating the  $G'$  matrix for a new cell to the  $G$  matrix for an old cell, we start with Eq. 4.8a for a distance between two points:

$$d^2 = \delta^t G \delta \quad (4.8a)$$

Now to express old coordinates in terms of new we use  $S^t$  so that  $\delta = S^t \delta'$  and, using 7 above,  $\delta^t = \delta'^t S$ . Substituting in Eq. 4.8a we get:

$$d^2 = \delta'^t S G S^t \delta' \quad (4.8b)$$

but as the distance between two points is independent of the coordinate system, we must have:

$$d^2 = \delta'^t G' \delta' \quad (4.8c)$$

Comparing Eqs. 4.8b and 4.8c, we see that  $G' = S G S^t$  which is Eq. 4.16. The elements of  $G'$  were given in Eq. 4.16a (p. 112).

#### 4.7.5 Unit cell transformations in *International Tables Vol. A*

For good reasons that we won't go into, in the *International Tables* volume A, the triplet of lattice vectors is written as a  $1 \times 3$  row matrix  $(a \ b \ c)$  and the transformation to a new cell expressed as  $(a' \ b' \ c') = (a \ b \ c)P$ . This means explicitly (with  $p_{ij}$  the elements of  $P$ ) that  $a' = p_{11}a + p_{21}b + p_{31}c$ ,  $b' = p_{12}a + p_{22}b + p_{32}c$ ,  $c' = p_{13}a + p_{23}b + p_{33}c$ . In Eq. 4.4 we write  $(a' / b' / c') = S(a / b / c)$  so that  $a' = s_{11}a + s_{12}b + s_{13}c$ ,  $b' = s_{21}a + s_{22}b + s_{23}c$ ,  $c' = s_{31}a + s_{32}b + s_{33}c$ . It should be clear that the matrix  $P$  is the transpose of  $S$ . With this convention  $G' = P^t G P$ . The inverse transformation is written as  $(a \ b \ c) = (a' \ b' \ c')Q$  and likewise  $Q$  is the transpose of our matrix  $T$ .

As there are two systems current, it is advisable, when specifying transformation matrices, always to specify also whether the transformation is effected by multiplying the column of lattice vectors by the matrix (i.e. using  $S$ ), or whether it is effected by multiplying the matrix by a row of lattice vectors (i.e. using  $P$ ). In this book, as in virtually all the literature up to the present time, we use the first system.

#### 4.8 Exercises

1. A good way to check computer programs for crystallographic calculations is to take a simple cubic structure and transform to a triclinic cell.

The transformation  $S = (2 \ \bar{1} \ 0 / 1 \ 3 \ 1 / \bar{1} \ \bar{1} \ 1)$  applied to a cubic cell with  $a = a_c$  will produce a ten-times larger unit cell with  $a = \sqrt{5}a_c$ ,  $b = \sqrt{11}a_c$ ,  $c = \sqrt{3}a_c$ ,  $\alpha = \cos^{-1}[-\sqrt{(3/11)}]$ ,  $\beta = \cos^{-1}(-1/\sqrt{15})$  and  $\gamma = \cos^{-1}(-1/\sqrt{55})$ . Interatomic distances, angles etc. in the new cell can be calculated and compared with the known values in the cubic cell.

[The inverse matrix is  $T = (0.4 \ 0.1 \ -0.1 / -0.2 \ 0.2 \ -0.2 / 0.2 \ 0.3 \ 0.7)$ .]

Show that the coordinates of *original* lattice points  $0,0,0$ ;  $0,0,1$ ; etc. (referred to the *old* cell) are in the *new* cell (there must be ten such points):

$$\begin{aligned} &0,0,0; 0,4,0.1,0.9; 0,2,0.3,0.7; 0,0.5,0.5; 0.8,0.2,0.8 \\ &0.6,0.4,0.6; 0.4,0.6,0.4; 0.2,0.8,0.2; 0.8,0.7,0.3; 0.6,0.9,0.1 \end{aligned}$$

Show that the *old*  $[111]$  and  $(111)$  become  $[232]$  and  $(15\bar{1})$  respectively in the *new* cell.

2. The general and special positions of space group  $Cmc2_1$  are

$$\begin{aligned} 8b \quad &C + (x,y,z; \bar{x},y,z; \bar{x},\bar{y},1/2+z; x,\bar{y},1/2+z) \\ 4a \quad &C + (0,y,z; 0,\bar{y},1/2+z) \end{aligned}$$

As the  $z$  coordinate appears only as  $+z$  or as  $1/2+z$  in each case the position of the origin on the  $z$  axis is arbitrary.

$Si_2N_2O$  has this space group:

$$\begin{aligned} Si_2N_2O \quad &Cmc2_1, a = 8.872, b = 5.491, c = 4.850 \text{ \AA} \\ &Si \ 8 \text{ in } b, x = 0.1767, y = 0.1511, z = 0.2815 \\ &N \ 8 \text{ in } b, x = 0.2191, y = 0.1228, z = 0.6267; O \ 4 \text{ in } a, y = 0.2127, z = 0.230 \end{aligned}$$

Plot the structure as a projection on  $(001)$ . It is made up of vertex-sharing  $\{Si\}N_3O$  tetrahedra which should be sketched in (cf. Fig. 4.11).

Calculate the Si-O and Si-N bond lengths. What are the coordinations of N and O by Si? The high-pressure phase of  $B_2O_3$  was reported to have space group  $Ccm2_1$ :

$$\begin{aligned} B_2O_3 \text{ (HP)} \quad &Ccm2_1, a = 4.613, b = 7.803 \text{ and } c = 4.129 \text{ \AA} \\ &B \text{ in } 8b, x = 0.161, y = 0.165, z = 0.436 \\ &O(1) \text{ in } 4a, x = 0.248, z = 0.5. O(2) \text{ in } 8b, x = 0.370, y = 0.291, z = 0.580 \end{aligned}$$

By appropriate transformation of axes (and coordinates) and shift of the origin show that these two structures are essentially the same. [Transform from  $Ccm2_1$  first.]

3. The structure of  $Ag_2O$  is given in § 3.4 (p. 77). Show that if the cell is transformed according to  $S = (1/2 \ 0 \ -1/2 / 1/2 \ -1 \ -1/2 / -1/2 \ -1 \ -1/2)$  the new cell is "almost" metrically cubic with  $a = 4.58 \text{ \AA}$ ,  $b = c = 4.84 \text{ \AA}$ ,  $\alpha = 87.9^\circ$ ,  $\beta = 92.6^\circ$  and  $\gamma = 87.4^\circ$ . The Ag atoms are arranged in a face-centered array if no distinction is made between the two kinds of Ag atom, but the new cell is not a true unit cell as it does not contain the same kind of Ag atom at every corner of the unit cell.

For comparison note that in  $Ag_2O$  (which has the  $Cu_2O$  structure Exercise 3.6) Ag is



exactly on the points of a face-centered cubic lattice with  $a = 4.74 \text{ \AA}$ . The change in volume in adding two O atoms to the unit cell in going from  $\text{Ag}_2\text{O} \rightarrow \text{AgO}$  is only  $0.6 \text{ \AA}^3$ .

Show that in  $\text{AgO}$ ,  $\text{Ag}(1)$  is bonded to two O atoms in a linear arrangement and that  $\text{Ag}(2)$  is bonded to four O atoms in an approximately square planar arrangement. (Calculate Ag-O bond lengths and O-Ag-O angles). [It is helpful to recognize that the Ag atoms are on inversion centers].

4. The zircon ( $\text{ZrSiO}_4$ ) structure was given in Chapter 3, Exercise 8, and that of rutile ( $\text{TiO}_2$ ) was given in § 3.4.

Zr is 8-coordinated in zircon. Draw the coordination polyhedron in clinographic projection.

Bragg, Claringbull & Taylor (Book List) state: "The structure of zircon...was first wrongly interpreted...as being similar to [that of] rutile" and "there is no relation between the two structures." Plot the cation positions in rutile in a projection on (110) and compare with a projection on (100) (on the same scale) of the cation positions in zircon. Be sure to draw several unit cells.

When you have finished read Hyde & Andersson (Book List) p. 285-288.

5. Data for  $\text{MgCl}_2$  are:

$\text{MgCl}_2$   $R\bar{3}m$ ,  $a_r = 6.252 \text{ \AA}$ ,  $\alpha = 33.81^\circ$   
Mg in 1 a: 0,0,0; Cl in 2 c:  $\pm(x,x,x)$ ,  $x = 0.2578$

Show that Mg has six Cl neighbors at the vertices of an octahedron. Calculate all the edge lengths of the octahedron.

Transform to a hexagonal cell and plot the structure projected on (11 $\bar{2}$ 0). The  $\text{MgCl}_6$  octahedra share edges to form layers normal to c. Outline these layers (cf.  $\text{NaCl}$ , p. 119).

6. Here are two monoclinic structures to draw in projection down b.

$\beta\text{-Ga}_2\text{O}_3$   $C2/m$ ,  $a = 12.23$ ,  $b = 3.04$ ,  $c = 5.80 \text{ \AA}$ ,  $\beta = 103.7^\circ$   
All atoms are in 4 i:  $C \pm(x,0,z)$  with:

	Ga(1)	Ga(2)	O(1)	O(2)	O(3)
$x =$	0.0904	0.3414	0.1674	0.4957	0.8279
$z =$	0.7948	0.6857	0.1011	0.2553	0.4365

$\text{NaCuO}_2$   $C2/m$ ,  $a = 6.351$ ,  $b = 2.747$ ,  $c = 6.103 \text{ \AA}$ ,  $\beta = 120.77^\circ$   
Na in 2 d:  $C + (0,1/2,1/2)$ ; Cu in 2 a:  $C + (0,0,0)$ ; O in 4 i: 0.333,0,0.777

Determine the coordination of *all* the atoms and illustrate as cation-centered polyhedra. [Hints: See § 4.6.5 for a discussion of how to draw monoclinic structures. In  $\text{Ga}_2\text{O}_3$  one Ga is in octahedral coordination and the other is in tetrahedral coordination by oxygen (i.e.  $\{\text{Ga}\}\text{O}_6$  and  $\{\text{Ga}\}\text{O}_4$ ). In  $\text{NaCuO}_2$ , Cu is in square planar  $\{\text{Cu}\}\text{O}_4$  groups and Na is in  $\{\text{Na}\}\text{O}_6$  octahedra.]

These structures are examples of an interesting phenomenon: surprisingly many monoclinic crystals can be described by an almost (metrically) orthorhombic cell. Transform the  $\beta$ -gallia cell by  $S = (2 \ 0 \ 1 / 0 \ 1 \ 0 / 0 \ 0 \ 1)$  and find the new unit cell parameters [you should find  $\alpha' = \gamma' = 90^\circ$  and  $\beta' = 89.98^\circ (= 90^\circ \text{ within the precision of the unit cell parameters given})$ ]. Your drawing should also convince you, however, that the structure is *not* orthorhombic. If it were orthorhombic there would be mirror/glide planes and/or 2-fold axes parallel to a and c. (Contrast the situation in  $\text{MnB}_4$ , § 4.6.5.)

Repeat with the appropriate S for  $\text{NaCuO}_2$ . Compare your structure drawing with that for  $\text{MgCl}_2$  (Exercise 5). You should have similar layers of  $\{\text{Mg}\}\text{Cl}_6$  and  $\{\text{Na}\}\text{O}_6$  octahedra sharing edges.

7. Another monoclinic structure that is nice to plot in projection down b is that of  $\text{Li}_4\text{Al}_9$ . All atoms lie at  $y = 0$  and  $y = 1/2$ . A good way to illustrate the structure is to use large and small circles for Li and Al and to use open and filled circles for  $y = 0$  and  $y = 1/2$ .

$\text{Li}_4\text{Al}_9$   $C2/m$ ,  $a = 19.155$ ,  $b = 4.499$ ,  $c = 5.429 \text{ \AA}$ ,  $\beta = 107.67^\circ$   
Li(1) in 2 a:  $C + (0,0,0)$   
Li(2) in 4 i:  $C \pm(x,0,z)$ ,  $x = 0.0863$ ,  $z = 0.531$   
Li(3) in 4 i:  $x = 0.2326$ ,  $z = 0.622$ ; Li(4) in 4 i:  $x = 0.3080$ ,  $z = 0.144$   
Li(5) in 4 i:  $x = 0.4564$ ,  $z = 0.239$   
Al(1) in 4 i:  $x = 0.1505$ ,  $z = 0.087$ ; Al(2) in 4 i:  $x = 0.3853$ ,  $z = 0.706$

The  $\beta$ -brass structure of alloys AB has symmetry  $Pm\bar{3}m$  with A at 0,0,0 and B at  $1/2, 1/2, 1/2$ . Transform this structure by  $S = (4 \ 4 \ 1 / \bar{1} \ 1 \ 0 / -0.5 \ -0.5 \ 3/2)$  using  $a = 3.25 \text{ \AA}$  for the cubic cell and plot down the new b axis using a similar convention to illustrate atoms. You should discover that the  $\text{Li}_4\text{Al}_9$  structure is closely related to that of  $\beta$ -brass.

8. A triclinic structure to test computer programs for transformations is that of kyanite,  $\text{Al}_2\text{SiO}_5$ , which has symmetry  $P\bar{1}$  with  $a = 7.126$ ,  $b = 7.852$ ,  $c = 5.572 \text{ \AA}$ ,  $\alpha = 89.99^\circ$ ,  $\beta = 101.11^\circ$ ,  $\gamma = 106.03^\circ$ . The unit cell volume is  $293.56 \text{ \AA}^3$ .

It is claimed that the structure is based on a cubic packing of O atoms.

Show that the transformation  $S = (0.4 \ 0.1 \ -0.4 / 0 \ 0.5 \ 0 / 0.4 \ 0.1 \ 0.6)$  indeed gives a subcell (not a unit cell!) of  $1/5$  the volume with  $a' = 3.8627$ ,  $b' = 3.9260$ ,  $c' = 3.8744 \text{ \AA}$ ,  $\alpha' = 90.02^\circ$ ,  $\beta' = 92.14^\circ$ ,  $\gamma' = 90.03^\circ$  that is "nearly cubic."

The inverse matrix  $S^{-1}$  is  $T = (1.5 \ -0.5 \ 1 / 0 \ 2 \ 0 / \bar{1} \ 0 \ 1)$ .

9. Cartesian coordinates for a regular tetrahedron are 1,1,1 (−1,−1,1)κ. Calculate:

- the edge length
- the volume
- the dihedral angle
- the solid angle at a vertex
- the distance from a vertex to the centroid (at 0,0,0)
- the angle subtended at the centroid by an edge.

Repeat for an octahedron. Cartesian coordinates for the vertices are:  $(\pm 1, 0, 0)\kappa$ .