CHAPTER 2

THREE-DIMENSIONAL POINT GROUPS

2.1 Point symmetry operations in three dimensions

A major difference between point operations in two and three dimensions is that in three dimensions there are rotation *axes* which leave lines invariant (instead of rotation points that leave points invariant in two dimensions) and mirror *planes* which leave planes invariant (instead of mirror lines which leave lines invariant).[1] Accordingly we expect a new symmetry operation in three dimensions that leaves a point invariant.

This new symmetry operation is *inversion* in a point (discussed below). It is convenient to consider the point symmetry operations of three-dimensional space as (a) rotation and (b) rotation *combined* with inversion. The corresponding symmetry elements are often referred to as *proper* and *improper* axes respectively. A proper operation acting on an asymmetric object merely moves it through space whereas an improper operation also converts it into its mirror image. Two successive improper operations convert an asymmetric object first into its mirror image and then back again to the original form, so that a *combination* of two improper operations is equivalent to a proper operation. We shall see that a mirror reflection in a plane (an improper operation) can be considered as combination of a 2-fold rotation plus inversion.

As in the case of two dimensions, we are restricted to 1-, 2-, 3-, 4-, and 6-fold symmetry axes in crystal symmetries. There are therefore five proper and five improper axes for a total of ten different kinds of point symmetry element. We will see that there are 32 distinct crystallographic point symmetry groups that contain combinations of these symmetry elements. We will not actually demonstrate that the number of groups is exactly 32. We will describe 32 groups and ask the reader to accept that our enumeration is complete. The dissatisfied reader is directed to § 2.5.3.

Those trained in molecular chemistry will be familiar with point group symmetry, and their task will be mainly to learn new symbols for these groups, although some point group symmetries do not have simple molecular examples. It will prove a rewarding exercise to verify the symmetries of the polyhedra discussed in Appendix 4 (some of which occur as carbon molecules). Another useful exercise is to check off the point groups listed in Tables 2.1 (§ 2.2.6) and 2.2 (§ 2.2.8) as they are described. In our experience the only way to acquire a useful working knowledge of point group symmetries is to constantly practice identifying the symmetries of objects such as molecules and polyhedra.[2] Only when the groups are well known is it possible to appreciate a rigorous mathematical treatment (which we will not develop).

[1] In one dimension the only point symmetry element is a mirror *point*.

[2] We use several examples of polyhedra in this chapter. The reader unfamiliar with such objects will find them described in § 5.1.

The discussion of point symmetries in terms of pure rotation and roto-inversion axes is the approach that proves most useful in crystallography. An alternative approach, using rotation-reflection axes, is embodied in the Schoenflies system that is favored by molecular chemists; as it leads to a more elegant mathematical treatment the latter is also preferred by mathematicians. The crystallographic system with its associated symbolism (Hermann-Mauguin symbols) is distinctly better for space groups and is now in universal use by crystallographers and solid state chemists. A concordance between the Hermann-Mauguin symbols and the Schoenflies symbols for the crystallographic point groups is given in the tables at the end of the book, and for non-crystallographic groups (those involving rotations of order different from 1, 2, 3, 4 or 6) in § 2.5.6.

The five proper axes should provide little difficulty. If coordinate axes are chosen so that the z direction is along the rotation axis, the x and y coordinates will transform as in the two dimensional case of rotation about a point, and z will remain unchanged. The positive sense of rotation is anticlockwise when viewed along the $+z$ to $-z$ direction. We will discuss the improper operations individually.

2.1.1 Inversion in a center

Inversion in a center[1] at the origin 0,0,0 will convert a point at x,y,z to a point at $\bar{x},\bar{y},\bar{z}$ regardless of the coordinate system used. Fig 2.1 illustrates the inversion of an asymmetric object through a center at the origin of coordinates (we always take the origin at the center if it is present). Inversion is symbolized $\bar{1}$ (1-fold rotation plus inversion). This would also be the symbol for the point group if the inversion center were the only symmetry element (other than the identity) of the object. Objects that include an inversion center in their symmetry are said to be *centrosymmetric*. Those that do not are *acentric*.[2]

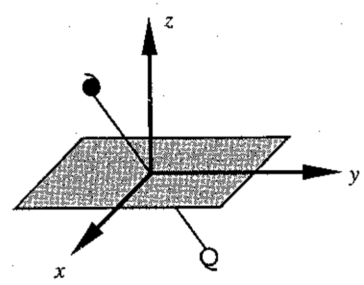


Fig. 2.1. Illustrating the inversion operation.

[1] The term *center* is synonymous with *inversion center* in this context.

[2] Objects (including molecules) other than crystals belonging to symmetry group $\bar{1}$ are rather rare (try to identify some). A pair of shoes (or gloves) can be arranged so that the assembly has $\bar{1}$ symmetry.

Figure 2.1 also illustrates the choice of a *right handed* set of coordinate axes (this is the "standard" choice). Interchanging any two axes will change the hand of the coordinate system unless the *direction* of one of the axes is also reversed. Cyclic permutations such as $x \rightarrow y \rightarrow z \rightarrow x$ or the reverse will not change the hand of the coordinate system.

2.1.2 Rotation plus inversion: axes $\bar{N}$

The combination of a 2-fold rotation with inversion is equivalent to reflection in the plane normal to the 2-fold axis and containing the inversion point. The combined operation is illustrated in Fig. 2.2. A 2-fold rotation axis through the origin and parallel to z converts a point at x,y,z to $\bar{x},\bar{y},z$. Inversion through a center at 0,0,0 will convert $\bar{x},\bar{y},z$ to $x,y,\bar{z}$. The net result is to transform x,y,z to $x,y,\bar{z}$—it should be clear that this is equivalent to reflection in the plane $z = 0$. This symmetry element which could be symbolized $\bar{2}$ is in fact symbolized m (for *mirror*). In the figure it may be seen that rotation by 180° around the axis shown, followed by inversion, is also the same as inversion followed by rotation about the axis, and in either case equivalent to reflection in the plane normal to the 2-fold axis. The orientation of a mirror plane is always specified by giving the direction of the normal to the plane.

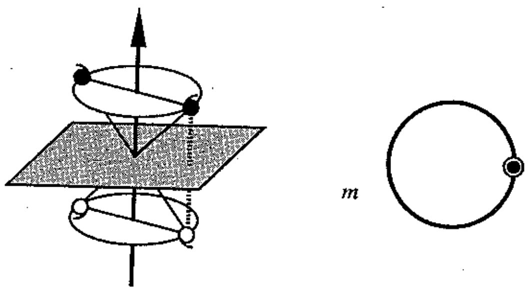


Fig 2.2. (Left) Illustrating that $\bar{2}$ is equivalent to reflection. An object (white) is rotated about the two-fold axis (arrow) to give a similar object which is the inverted through the center to give a mirror-image object (black). (Right) showing the two symmetry-related points in projection along z.

On the right in Fig 2.2 a stylized view down the z axis is shown where the original object above the plane $z = 0$ is shown as an open circle and its reflection below the plane is shown as a smaller filled circle. Such diagrams are very useful to show the effects of other symmetry elements and combinations of symmetry elements. It is important to recognize that the circles in such diagrams really represent a general asymmetric objects.

It should be clear that an object (such as a chair) that has only one mirror plane (and the identity) for symmetry elements, has neither a 2-fold axis nor a center of symmetry. In general an N-fold inversion axis only contains a separate N-fold rotation axis and a separate inversion center for N odd. Indeed, as explained in the next paragraphs, $\bar{3}$ is the only crystallographic symmetry operation (other than $\bar{1}$ itself) that contains a separate $\bar{1}$.

Fig 2.3 shows the effects of $\bar{3}$, $\bar{4}$ and $\bar{6}$ axes on a point. The $\bar{3}$ operation (rotation by one-third of a circle followed by inversion) has to be carried out six times before the original point is returned to. The reader should verify the *separate* existence of a $\bar{1}$ and a 3 axis.[1] In the diagrams in Fig. 2.3, the symbol in the center is the symbol for the symmetry element. The small circles represent a general asymmetric object and thus in these examples, filled and open circles should really be replaced by asymmetric objects related one to the other by inversion or reflection (i.e. of opposite hand).

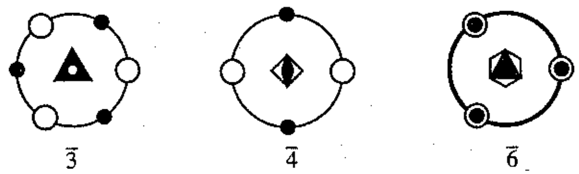


Fig. 2.3. Illustrating the effects of $\bar{3}$, $\bar{4}$ or $\bar{6}$ axes (see text). Filled and empty circles are points on opposite sides of the horizontal plane (the plane of the paper). In $\bar{6}$ such points are superimposed in projection and the heavier outline of the circle indicates the presence of a horizontal mirror plane.

A $\bar{4}$ axis (Fig. 2.3) generates four distinct points on repeated application; two above and two below the plane. It should be clear that an object with only $\bar{4}$ symmetry is not centrosymmetric (but does have a 2-fold rotation axis).

A $\bar{6}$ axis generates six points (Fig. 2.3 again). Note again the absence of an independent inversion center. This symmetry element includes a separate 3 axis and a mirror normal to that axis (indicated in the figure by a heavier outline for the circle).[2]

It should be obvious that in order to completely specify the position of a $\bar{3}$, $\bar{4}$ or $\bar{6}$ axis we have to specify the direction of the axis *and* the location of the inversion point even though $\bar{4}$ and $\bar{6}$ do not contain a *separate* inversion center.

A quick sketch should convince the reader that whether one rotates and then inverts, or first inverts and then rotates, is immaterial. The combined operation is the same; i.e. the component operations *commute*.

A word on terminology is in order. We refer to an N axis as N-fold as in "2-fold," "3-fold," etc. More commonly perhaps (as in the *International Tables*) the usage "twofold," "threefold," etc. is seen. We find our usage clearer in such phrases as "four 3-fold axes." Other authors refer to 1-, 2-, 3-, 4- and 6-fold rotation axes as "monads," "diads," "triads," "tetrads," and "hexads" respectively. A difficulty arises in the case of $\bar{3}$ and $\bar{6}$. As can be seen from Fig. 2.3 both these operations require *six* repetitions to produce the identity yet we refer to the former as a "3-fold inversion axis" and the latter as a

[1] The reader is urged to verify that (a) applying the rotation+inversion operation three times is equivalent to inversion alone and (b) applying the combined operation four times is equivalent to rotation alone. (Remember that rotations are by convention anticlockwise when viewed from the +z direction.)

[2] An N-fold rotation axis with a mirror normal to it is written N/m so $\bar{6}$ is sometimes written as $3/m$. However this obscures the 6-fold nature of the axis and this notation should be avoided.

"6-fold inversion axis."[1] Crystals with parallel 3-fold axes (including $\bar{3}$) but without 6-fold axes are classed as *trigonal*. Crystals with 6-fold axes (including $\bar{6}$) are classified as *hexagonal*. $\bar{3}$ is also referred to as an "inversion triad" and $\bar{6}$ as an "inversion hexad." The difficulty is compounded by the fact that in the Schoenflies system (see Exercise 17) $\bar{3}$ is labeled S_6 and $\bar{6}$ is labeled S_3.

2.2 Enumeration of the point groups

There are 10 point groups corresponding to the presence of just one of the symmetry elements we have described. These are 1, 2, 3, 4, 6, $\bar{1}$, *m*, $\bar{3}$, $\bar{4}$ and $\bar{6}$. There are 22 more (crystallographic) groups to be obtained by combining several symmetry elements. We will not derive these groups very systematically, but it is worth seeing why there is only a relatively small number of them. The serious student of solid state science will get to know them all intimately. The material in this section is rather condensed—the reader interested in fully appreciating it would be well advised to have a pencil and paper at hand to make sketches to verify some of the statements. We find sketches of the sort shown in Fig. 2.3 to be particularly helpful.

2.2.1 *Pure rotation groups: dihedral groups N2(2)*

We start by considering just those cases in which we have proper rotation axes only. The groups in this case are the *pure rotation* groups. We will have to consider two intersecting rotation axes inclined to each other. Combination of two such rotations always produces a rotation about a new axis through the point of intersection of the first two axes.[2] (Remember we are considering point group symmetry so there must be one point at which all symmetry elements intersect). It is important to recognize that we consider the rotation axes to be fixed with respect to the coordinate system and only the rotated object to move.

Fig. 2.4 shows two 2-fold axes (labeled 1 and 2) lying in a plane and inclined at an angle ϕ. Rotation of the point *a* above the plane about axis 1 will produce point *b* below the plane. Rotation of *b* about axis 2 will now produce point *c* above the plane. It should be clear that the transition $a \to c$ is equivalent to a rotation by 2ϕ about an axis normal to 1 and 2 and passing through their point of intersection (small shaded circle in the diagram).

In general we consider rotation about an axis X_1 by an amount ρ_1 followed by rotation by an amount ρ_2 about an axis X_2 inclined to X_1 by an angle ϕ_3. This is equivalent to

[1]Curiously, the *International Tables* (which usually is our arbiter in such matters) names other symmetry axes (p. 9) but avoids the issue for inversion axes as in "Inversion axis: '3 bar'" for $\bar{3}$. The fraction of the world population that cares, appears to be approximately equally divided into those who use "bar three" and those who use "three bar" in speech for $\bar{3}$. We prefer the former, as "bar" is to be considered as standing for "minus".

[2]As rotations are proper operations they will not change the hand of an asymmetric object. The operation corresponding to two rotations about axes intersecting in a point must be another proper operation leaving that point invariant and thus can only be a rotation. The result of combining rotations about axes without a common point will also include a component of translation (also a proper operation).

rotation by an amount ρ_3 about a third axis X_3 inclined to axes X_1 and X_2 by angles of ϕ_2 and ϕ_1 respectively. These angles are related by an equation due to Rodrigues:[1]

$$\cos(\rho_3/2) = \cos\phi_3 \sin(\rho_1/2)\sin(\rho_2/2) - \cos(\rho_1/2)\cos(\rho_2/2) \tag{2.1}$$

Two additional equations are obtained by cyclic permutation of indices $1 \to 2 \to 3 \to 1$. This gives us three equations for the unknowns ρ_3, ϕ_2 and ϕ_1.

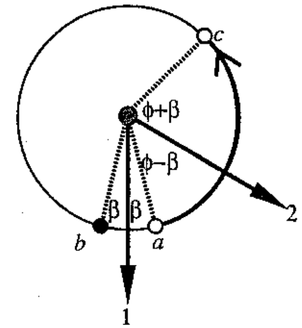


Fig. 2.4. Two 2-fold rotations about axes at an angle of ϕ to each other (about 1 to take *a* to *b*, then about 2 to take *b* to *c*) are equivalent to rotation (by 2ϕ) about an axis orthogonal to the 2-fold axes (*a* to *c*).

Equation 2.1 is general, but if the rotations are limited (as they will be from now on) to integral fractions of a circle so that $360°/\rho_i = p_i$ (an integer) then it is not difficult to show (see § 2.5.1) that all possible pure rotation groups are generated[2] by rotations such that:

$$\sum_{i=1}^{3} \frac{1}{p_i} > 1 \tag{2.2}$$

Further analysis shows that the possible solutions of Eq. 2.2 fall into two classes: (a) the dihedral groups in which there is an *N*-fold axis with 2-fold axes at right angles to that axis ($p_3 = N$, $p_1 = p_2 = 2$ which gives in turn from Eq. 2.1, $\phi_3 = 360°/2N$). (b) the *cubic* and *icosahedral* groups in which there are more than one rotation axis of order greater than two.

Consider category (a) first. When $\phi = 360°/N$ with N an integer, the two 2-fold axes generate a finite number of symmetry elements as shown in Fig. 2.5 for the case $\phi_3 = 45°$.

[1]This equation is often ascribed to Euler. For a nice account both of the historical importance of the equation and of Rodrigues see *Icons and Symmetries* by S. L. Altmann (Oxford, 1992). For a derivation of Eqs. 2.1 and 2.2 see the Note § 2.5.1 at the end of this chapter.

[2]Strictly speaking only two rotation axes are needed to generate all the rotations of the group: the third rotation entering into the sum in Eq. 2.2 being generated by the other two.

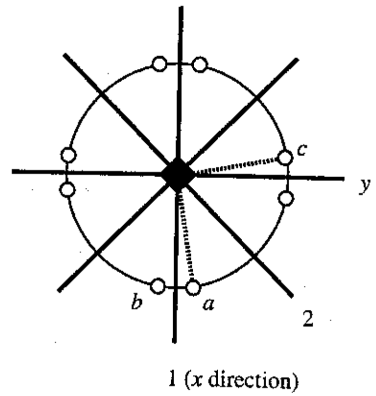


Fig. 2.8. Group 4*mm*. *b* is the image of *a* obtained by reflection in line 1 and *c* is the image of *b* obtained by reflection in line 2. $a \rightarrow c$ corresponds to rotation by a fourth of a circle about the center point.

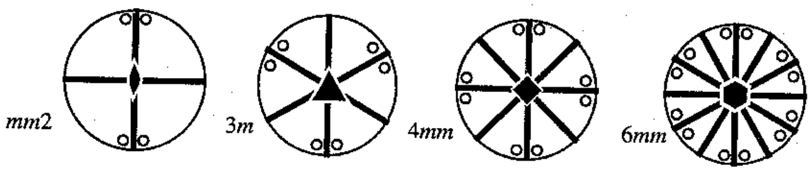


Fig. 2.9. Illustrating the symmetry elements of groups *mm*2, 3*m*, 4*mm* and 6*mm*. The heavy lines are the traces of mirror planes normal to the paper. Compare with Fig. 2.6.

2.2.3 Groups N/m

In the next set of point symmetry groups, mirrors are added normal to the rotation axes of groups *N* giving groups *N*/*m*. As we will see later, it is convenient to consider *N*/*m* to be one symbol (because the *N*-fold rotation axis and the normal to the mirror are in the same direction).

1/*m* is the same as *m* so that is not a new group. 3/*m* is the same as $\bar{6}$, so that is not a new group either. Thus the new groups are 2/*m*, 4/*m* and 6/*m*. Note that the combination of an even order rotation axis (which contains a 2 axis) with a mirror plane normal to it generates an inversion center at the point of intersection (refer back to Fig. 2.1) so that 2/*m*, 4/*m* and 6/*m* all contain such a center. In particular 2/*m* is of order 4; the symmetry operations being the mirror reflection, the 2-fold rotation, the inversion and the identity. Fig. 2.10 illustrates these groups in the same way as used in Figs. 2.6 and 2.9. It should be apparent from the figure (compare with Fig. 2.3) that 4/*m* includes a $\bar{4}$ axis, and that 6/*m* includes $\bar{3}$ and $\bar{6}$ axes.

A useful mental exercise is to imagine a two-dimensional object (such as a letter S) with symmetry 2. Now give it some thickness in the third dimension by translation normal to the plane—the three-dimensional symmetry is 2/*m*. Repeat for plane objects with symmetry 4 and 6. Although 2/*m* is an unusual symmetry for molecules, it is one of the most common point symmetries of crystals (the crystal class).

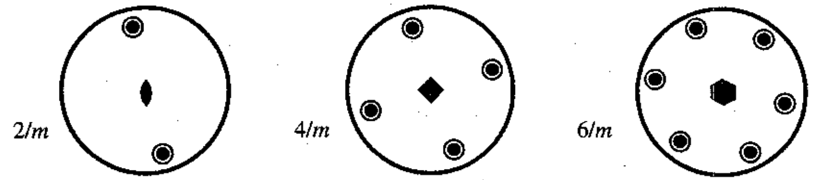


Fig. 2.10. Illustrating, from left to right, symmetry groups 2/*m*, 4/*m* and 6/*m*. Symbols have the same significance as in Figs. 2.6 and 2.9. Note that in each case there is a horizontal mirror plane whose presence is indicated by the heavy outline of the large circle (contrast e.g. Fig. 2.9).

2.2.4 Groups N/m 2/m 2/m

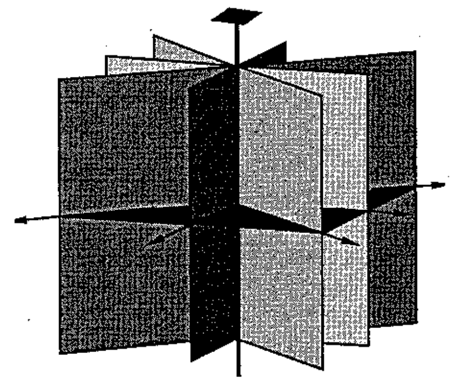


Fig. 2.11. Group 4/*mmm*. The 4-fold rotation axis is vertical, arrows show the location of 2-fold rotation axes and mirror planes are shaded.

The next set of groups is obtained by adding mirror planes normal to rotation axes in *N*22 giving *N*/*m* 2/*m* 2/*m*. Again it is helpful to consider *N*/*m* as one symbol corresponding to a single axis. The possibilities here are 2/*m* 2/*m* 2/*m*, 4/*m* 2/*m* 2/*m* and 6/*m* 2/*m* 2/*m*. The symbols for these groups are often abbreviated *mmm*, 4/*mmm* and 6/*mmm* respectively. *mmm* is the symmetry of a brick with three different edge lengths. 4/*mmm* is the symmetry of a right square prism (a brick with a square cross section). The arrangement of symmetry elements of this group is illustrated in Fig. 2.11 in which 2-fold axes are shown as arrows

The 2-fold axes 1 and 2 in that figure generate the 4-fold axis which in turn generates the other 2-fold axes shown (note that co-linear axes are really just one axis). The set of symmetry elements form a group symbolized 422. The first position is for the principle axis and the second and third positions in the point group symbol are for the two sets of 2-fold rotation axes.[1]

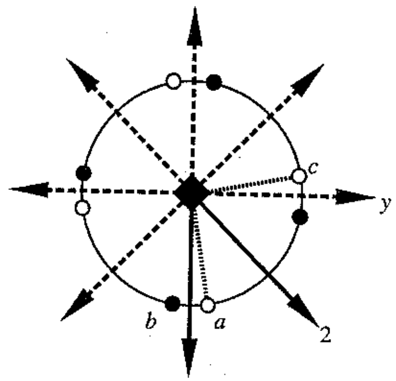


Fig. 2.5. Group 422. Arrows represent 2-fold rotation axes. See also Fig. 2.6.

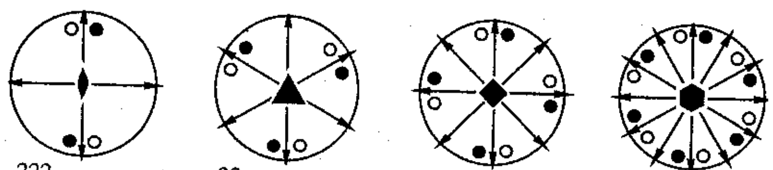


Fig. 2.6. Illustrating the symmetry elements of groups 222, 32, 422 and 622. Lines terminating in arrow heads represent 2-fold rotation axes in the plane of the paper. Small circles are sets of points generated by the group operations acting on an arbitrary point. Filled and open circles are on opposite sides of the plane of the two-fold axes. The symbol in the center of the large circle is that for the *N*-fold axis (also a 2-fold axis for 222) normal to the plane of the 2-fold axes.

Likewise there are groups 222, 32 and 622 generated by 2-fold axes at 90°, 60° and 30°. Note that there is only one distinct set of 2-fold axes in 32. This is because 2-fold axes inclined to each other by 60° are also inclined to each other at 120°. These groups (together with 422) are called the *dihedral* groups. It should be obvious that pure rotation groups contain only proper operations and so do not contain a center of symmetry. In Fig. 2.6 the

[1]Cf. the discussion in § 1.1 of the sets of mirror lines in two-dimensional point groups such as 4*mm*.

location of the symmetry elements of these groups is shown. A set of points generated by the symmetry operations acting on an arbitrary point is also shown. Notice that (in contrast to the case of Fig. 2.3) the filled and open circles now represent asymmetric objects of the *same* hand.

2.2.2 Groups Nm(m)

In Fig. 2.7, the two 2-fold axes of Fig. 2.4 are replaced with vertical mirror planes. It should be clear that two reflections in mirrors with normals in the same plane and at an angle ϕ also produce a rotation 2ϕ. (The point *b*, which was a filled circle in Fig. 2.4, is now an open circle in Fig. 2.7).

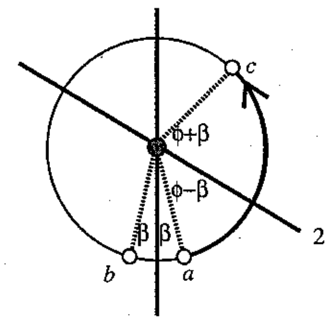


Fig. 2.7. Two reflections (in mirror 1 to take *a* to *b*, then in mirror 2 to take *b* to *c*) are equivalent to rotation about an axis along the line of intersection of the mirrors (*a* to *c*). Compare with Fig. 2.4 above.

The result of having two mirrors at 45° is to generate group 4*mm* shown in Fig. 2.8 (which should be compared with Fig 2.5).

Analogously we can generate the groups 2*mm* (usually written *mm*2) from two mirrors at 90°; 3*m* with mirrors at 60° (now just one *set* of mirrors related by 120° rotations); and 6*mm* from mirrors at 30° (giving two sets each of three mirrors analogous to the two sets of 2-fold rotation axes in 622).[1] Fig 2.9 illustrates these groups in a way similar to Fig. 2.6.

Symmetry *mm*2 is commonly encountered; it is for example, the symmetry of the water molecule. If the writing were to be erased, a book would have symmetry *mm*2 also. The (non-planar) NH_3 molecule has symmetry 3*m*. More generally *Nm*(*m*) is the symmetry of a pyramid with a regular *N*-gon as a base. The groups *Nm*(*m*) do not contain a center of symmetry (think of the pyramids).

[1]It can be rewarding to experiment with two small rectangular mirrors hinged together at one edge with sticky tape and inclined at different angles to generate these rotations.

and mirrors as planes. *6/mmm* is the symmetry of a right hexagonal prism; a diagram representing its symmetry elements would be similar to Fig. 2.11 but there would be six mirror planes intersecting in the 6-fold axis and six 2-fold rotation axes in those planes and normal to the 6-fold axis.

Fig. 2.12 illustrates the symmetry elements of these groups in a projection down the principle axis in a way that should now be familiar (compare Figs. 2.6, 2.9 and 2.10).

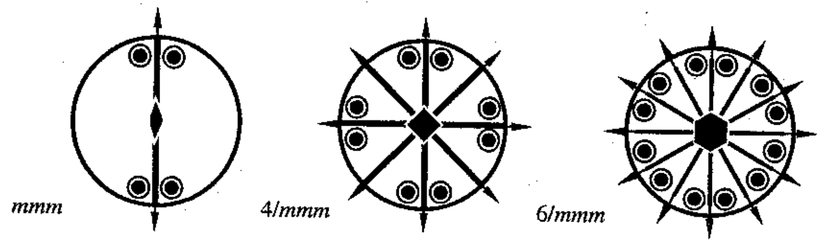


Fig. 2.12. Illustrating symmetry groups *mmm*, *4/mmm* and *6/mmm*. Note the presence of a mirror plane in the plane of the paper.

As a 2-fold axis normal to a mirror generates a center of inversion, these groups all include a center of symmetry among their symmetry elements. Indeed the groups may alternatively be generated by adding an inversion center to 222, 422 and 622. If a center is added to 32 the group $\bar{3}m$ is generated as discussed in the next section.

2.2.5 Groups $\bar{3}m$, $\bar{4}2m$ and $\bar{6}m2$

There are no new (in the sense of not being already encountered above) symmetry groups to be obtained by adding mirrors normal to inversion axes (do Exercise 11 to verify this statement). But we get new groups by adding mirrors with their normals perpendicular to the $\bar{N}$ axis so that the mirror planes contain the $\bar{N}$ axis. This procedure also generates 2-fold axes normal to the $\bar{N}$ axis.

The case of $N = 2$ corresponds to mirror planes at right angles (recall that $\bar{2} \equiv m$) and generates *mm*2, which is not new.

The other possibilities ($N = 3$, 4 or 6) generate $\bar{3}2/m$ (often abbreviated to $\bar{3}m$), $\bar{4}2m$ and $\bar{6}m2$ which are new.[1] The reader is urged to demonstrate this by starting with a $\bar{N}$ axis ($N = 3$, 4, or 6) and a mirror plane containing this axis and to allow the symmetry operations of these symmetry elements to operate on an arbitrary point (i.e. one not on the mirror plane) and identify the generated symmetry elements. If the roto-inversion axis and the mirror plane are vertical you should generate diagrams like those in Fig. 2.13, in which the

[1]The significance of the order of the symbols in the last two groups is explained below. For the moment note that in $\bar{4}2m$ and $\bar{6}m2$, the 2 and the *m* respectively refer to 2-fold axes and to mirrors with normals not parallel to the 2 axes as illustrated in Fig. 2.13.

symmetry elements of these groups are shown in projection. Note also the symbols used to represent $\bar{3}$, $\bar{4}$ and $\bar{6}$ axes (compare Fig. 2.3).

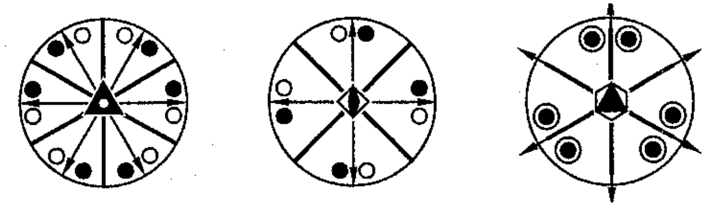


Fig 2.13. Illustrating groups $\bar{3}m$, $\bar{4}2m$ and $\bar{6}m2$. Mirror planes are shown as heavy lines and 2-fold axes as lighter lines terminating with arrow heads. See also the legends of Figs. 2.6 and 2.9.

An example of $\bar{3}m$ symmetry is the ethane (C_2H_6) molecule in its staggered conformation (Fig. 2.14, right). A right triangular prism and eclipsed ethane (Fig. 2.14, left) have symmetry $\bar{6}m2$. A tetrahedron with only one pair of opposite edges at right angles[1] (see Fig. 2.15) has symmetry $\bar{4}2m$. A baseball or tennis ball (taking into account the seams, but not any other markings that may be on it) also has symmetry $\bar{4}2m$.

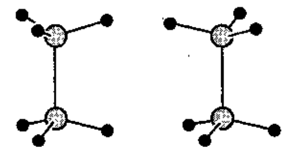


Fig. 2.14. Illustrating ethane in its eclipsed (left) and staggered (right) forms.

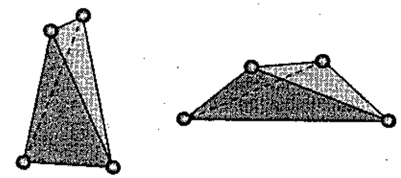


Fig. 2.15. Tetrahedra with symmetry $\bar{4}2m$. *The* $\bar{4}$ axis runs up the page.

$\bar{3}$ already contains a center of symmetry, therefore $\bar{3}m$ does also. It should be clear from the pattern of points in Fig. 2.13 as well as Figs. 2.14 and 2.15 that $\bar{4}2m$ and $\bar{6}m2$ do not include a center of symmetry.

[1]This is a necessary, but not a sufficient, condition for a tetrahedron to have $\bar{4}2m$ symmetry.

2.2.6 *Summary of the non-cubic crystallographic point groups*

Table 2.1 lists the 27 crystallographic point groups we have enumerated so far. The columns in the Table correspond to the order in which the groups have been described in the indicated sections. A feature of these groups is that they contain at most one N-fold axis for $N > 2$. For an extension of the table to non-crystallographic groups see § 2.5.6.

Table 2.1. The non-cubic crystallographic point groups. Symbols in parentheses are short symbols corresponding to the long symbols immediately above them.

N § 2.1	$\bar{N}$ § 2.1	$N2(2)$ § 2.2.1	$Nm(m)$ § 2.2.2	N/m § 2.2.3	$N/m2/m2/m$ § 2.2.4	$\bar{N}+m$ § 2.2.5
1	$\bar{1}$					
2	m	222	$mm2$	$2/m$	$2/m2/m2/m$ (mmm)	
3	$\bar{3}$	32	$3m$			$\bar{3}2/m$ ($\bar{3}m$)
4	$\bar{4}$	422	$4mm$	$4/m$	$4/m2/m2/m$ ($4/mmm$)	$\bar{4}2m$
6	$\bar{6}$	622	$6mm$	$6/m$	$6/m2/m2/m$ ($6/mmm$)	$\bar{6}m2$

2.2.7 *Cubic and icosahedral rotation groups*

The dihedral rotation groups result from the solutions of Eq. 2.2 (p. 33) with p_1, p_2 and p_3 equal to 2, 2 and N. Three other possible solutions for p_1, p_2, p_3 are 2, 3, 3 ; 2, 3, 4 and 2, 3, 5 and these will lead to three new pure rotation groups. The last possibility containing 5-fold rotations will not give rise to a crystallographic point group, but is of sufficient interest to detain us briefly.

Consider the case $p_1 = 2, p_2 = 3$ and $p_3 = 3$, i.e. $\rho_1 = 180°, \rho_2 = \rho_3 = 120°$. Equation 2.1 shows that $\phi_1 = \cos^{-1}(1/3) = 70.53°$ and that $\phi_2 = \phi_3 = \cos^{-1}(1/\sqrt{3}) = 54.74°$. It is remarkable that starting with two of these three rotation axes (at the angles indicated!) we generate a finite group with four 3-fold and three 2-fold axes. Their orientations can be visualized with reference to a cube (Fig. 2.16). The 3-fold axes are parallel to the body diagonals and the 2-fold axes parallel to the cube edges. Of course all the rotation axes have a point in common. This symmetry group, symbolized 23, is in fact one of the five *cubic* point groups.[1]

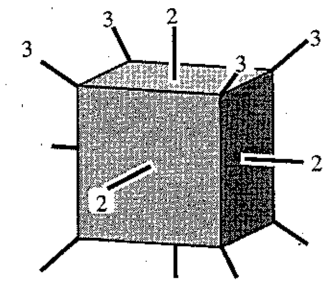


Fig 2.16. Group 23. 3-fold rotation axes are symbolized by "3" and 2-fold by "2."

Now consider the case $p_1 = 2, p_2 = 3$ and $p_3 = 4$, i.e. $\rho_1 = 180°$, $\rho_2 = 120°$ and $\rho_3 = 90°$. Equation 2.1 shows now that $\phi_1 = \cos^{-1}(1/\sqrt{3}) = 54.74°$, $\phi_2 = 45°$ and $\phi_3 = \cos^{-1}(\sqrt{2}/\sqrt{3}) = 35.26°$. Again we get a finite group, this time containing three 4-fold axes, four 3-fold axes and six 2-fold axes, and again the axes are oriented along principle directions of a cube. The 4-fold axes are parallel to the cube edges (i.e. as the 2-fold axes in group 23, Fig. 2.16), the 3-fold axes are parallel to the body diagonals (as in 23) and the 2-fold axes are parallel to the face diagonals as shown in Fig. 2.17. This second cubic group is symbolized 432. As discussed below, the order of the numbers (such as 23 or 432) in the group symbol indicates the orientation of the rotation axes.

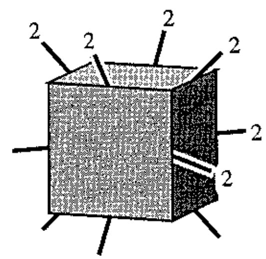


Fig 2.17. The 2-fold axes of group 432 (compare Fig. 2.16).

The last pure rotation group has $p_1 = 2, p_2 = 3$ and $p_3 = 5$. The generated group has six 5-fold, ten 3-fold and fifteen 2-fold axes. Their orientations can be related to a regular icosahedron (see Fig. 2.18). The 5-fold axes are along the directions joining the six pairs of opposite vertices, the 3-fold axes are along lines joining the centers of the ten pairs of

[1]A point group is *cubic* if it contains exactly four 3-fold axes among the symmetry elements.

opposite faces and the 2-fold axes are along lines joining the midpoints of the fifteen pairs of opposite edges. The smallest angle between 5-fold axes is 63.43°, the smallest angle between 3-fold axes is 41.81°, and the smallest angle between 2-fold axes is 36°. The smallest angle between a 2-fold and a 3-fold axis is 20.90° and between a 2-fold and a 5-fold axis it is 37.38°. The group is the *icosahedral* rotation group, often symbolized *I*; we will also use the symbol 235. Note that although, for simplicity, we use an icosahedron to illustrate the orientation of the axes of 235, the icosahedron has additional symmetry elements (mirror planes and a center). For more on this group (including the angles between axes) see Exercises 15 & 16, and see Appendix 4 for some examples of objects with symmetry 235.

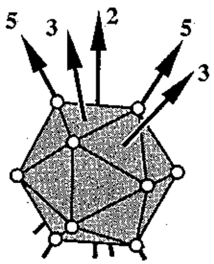


Fig. 2.18. The location of some of the symmetry axes of group 235 shown with respect to an icosahedron. For a regular icosahedron the axes marked "2" are $2/m$, those marked "3" are $\bar{3}$, and those marked "5" are $\bar{5}$.

2.2.8 Cubic and icosahedral groups $m\bar{3}$, $m\bar{3}m$, $\bar{4}3m$ and $m\bar{3}\bar{5}$

The remaining symmetry groups to be considered are obtained by adding mirrors to the icosahedral and the two cubic rotation groups in a way that is suggested in Table 2.2 below in which the last two groups are icosahedral. The results (with short symbols[1] in parentheses) are: $4/m\,\bar{3}\,2/m$ ($m\bar{3}m$), $2/m\bar{3}$ ($m\bar{3}$) $\bar{4}3m$, and $2/m\bar{3}\bar{5}$ ($m\bar{3}\bar{5}$). Underneath each Hermann-Mauguin symbol is the Schoenflies symbol.

We generate $2/m\bar{3}$ (short symbol $m\bar{3}$) by adding a center to 23. The combination of a center and a 2-fold axis generates mirror planes normal to the 2-fold axes and converts 3 to $\bar{3}$.

Similarly $4/m\,\bar{3}\,2/m$ (short symbol $m\bar{3}m$) is generated from 432. In this case we generate mirror planes normal to the 4-fold and 2-fold axes of 432 and again convert 3 to $\bar{3}$.

The final cubic group $\bar{4}3m$ is obtained as a subgroup of $m\bar{3}m$ and is not centrosymmetric.

The group $2/m\bar{3}\bar{5}$ is similarly obtained by adding a center to the icosahedral rotation

[1]The short symbols follow the usage in Volume A of the *International Tables* (1983). Previously, the bar was removed over the $\bar{3}$ in $m\bar{3}$ and $m\bar{3}m$ so in the older literature the short symbols were written as $m3$ and $m3m$ respectively.

group 235. The 2 axes become $2/m$ and the 3 and 5 axes become $\bar{3}$ and $\bar{5}$ respectively. This is the group of all the symmetries of a regular icosahedron (Figs. 2.18 and 2.25) and is also symbolized I_h.

Table 2.2. The cubic and icosahedral point groups.

rotation group	plus center	other group
23 T	$2/m\bar{3}$ ($m\bar{3}$) T_h	
432 O	$4/m\,\bar{3}\,2/m$ ($m\bar{3}m$) O_h	$\bar{4}3m$ T_d
532 I	$2/m\bar{3}\bar{5}$ ($m\bar{3}\bar{5}$) I_h	

We now adduce examples of familiar objects with these cubic symmetries.

$\bar{4}3m$ is the symmetry of a *regular* tetrahedron or of the molecule CH_4. The tetrahedron has three $\bar{4}$ axes along the lines joining the centers of opposite edges and four 3 axes along the lines joining the vertices to the centers of opposite faces. There are also six mirror planes, each of which contains an edge and the center of the opposite edge. These symmetry elements should be identifiable in Fig. 2.19 which shows (from left to right) a clinographic projection of a regular tetrahedron, a projection down a $\bar{4}$ axis, a projection along a 3 axis and a projection normal to a mirror plane.[1] Objects with $\bar{4}3m$ symmetry are often said to have *tetrahedral* symmetry. Note the absence of an inversion center and the fact that $\bar{4}$ includes a 2 axis.

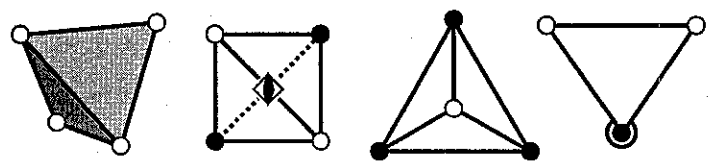


Fig. 2.19. Different views of a tetrahedron.

Fig 2.20 shows how the six mirror planes of $\bar{4}3m$ are arranged with respect to the framework of a cube. The $\bar{4}$ axes are parallel to the cube edges and the 3 axes are parallel to

[1]There is really no substitute for holding a model of a polyhedron and identifying its symmetry elements. The reader who finds cubic symmetry difficult is urged to make models of a tetrahedron, an octahedron and a cube by taping or gluing together equilateral triangles or squares of light cardboard.

the body diagonals. The same set of mirror planes also occurs (together with others parallel to the cube faces) in $m\bar{3}m$.

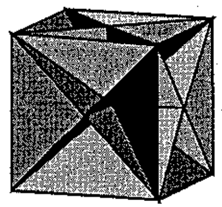


Fig. 2.20. The mirror planes of $\bar{4}3m$.

$4/m\,\bar{3}\,2/m$ (abbreviated to $m\bar{3}m$) is the symmetry of a cube itself. A regular octahedron and an octahedral molecule such as SF_6 also have symmetry $m\bar{3}m$. Objects with this symmetry are said to have *octahedral* symmetry. Fig 2.21 shows different views of an octahedron similar to those of the tetrahedron in Fig. 2.19. Second from the left is a view down a $4/m$ axis, third from the left is a view down a $\bar{3}$ axis and on the right is a view down a $2/m$ axis.

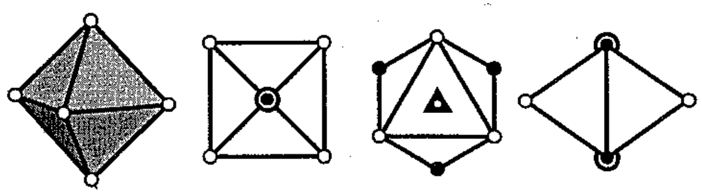
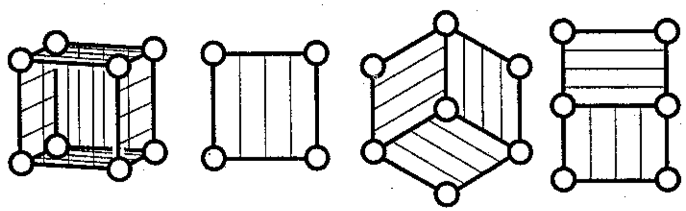


Fig 2.21. Different views of an octahedron.



(*a*) (*b*) (*c*) (*d*)

Fig. 2.22. (*a*) A cube with parallel markings (light lines) on each face (opposite faces are marked in the same direction) to produce an object with $m\bar{3}$ symmetry. (*b*) A projection on a cube face (down a $2/m$ axis of the marked cube). (*c*) A view down a body diagonal ($\bar{3}$ axis). (*d*) A projection down a face diagonal (note the absence of a 2-fold axis normal to the paper in this projection).

To summarize the symmetry elements of $m\bar{3}m$ (the most complex of the crystallographic point groups—the order is 48): there are three $4/m$ axes (by this is meant a 4 axis with a mirror plane normal to it) parallel to the edges of a reference cube, four $\bar{3}$ axes parallel to the body diagonals of the cube, and six $2/m$ axes parallel to the face diagonals of the cube.

$m\bar{3}$ is quite a common symmetry in crystals but rare for molecules. Crystals of pyrite ("fool's gold" = FeS_2) often crystallize as spectacular cubes but if examined closely, striations will be noticed on the faces. Fig 2.22 shows schematically how these markings remove the 4-fold axes of the cube and also eliminate the symmetry elements parallel to the face diagonals. The pyritohedron described on p. 195 (Fig. 5.68) has this symmetry.

2.3 Point groups by system

In the next chapter we will discuss three-dimensional lattices and unit cells. We will identify crystal systems just as in two dimensions, and find seven of them (see Chapter 3). For reference the point groups are listed by system in the tables at the end of the book (p. 440). Also given in the list is the Schoenflies symbol for each group.

A crystal symmetry is obtained by combining translations with point symmetries. The point group of the crystal is its *class*. If the crystal point group contains an inversion center, the crystal will be centrosymmetric. The table lists the space group numbers corresponding to each class and also indicates whether that class is centrosymmetric.

2.4 Coordinate systems and the order of symbols

The symbols for the point groups assume a reference coordinate system which may differ from one crystal system to another. In a crystal, the axes are always chosen parallel to lattice vectors and this determines the reference coordinate system used. This in turn determines the symbols of the derived space groups, so it is very well worth the little effort it requires to memorize the system. Remember that the orientation of a mirror plane is specified by the direction of its normal.

In the **triclinic** system there is at most an inversion center which is at the origin of coordinates. Triclinic point groups are 1 and $\bar{1}$.

In the **monoclinic** system there is a unique 2-fold axis. The point groups are 2, m and $2/m$. Coordinates are usually chosen so the y axis is parallel to the 2-fold axis (normal to the mirror in m). Occasionally other choices are made: then symbols for the symmetry elements parallel to the x, y, and z axes are used, as illustrated for $2/m$. (1 means no symmetry parallel to that axis and acts as a place marker).

$2/m$ parallel to x	$2/m11$
$2/m$ parallel to y	$12/m1$ (or just $2/m$)
$2/m$ parallel to z	$112/m$

In the **orthorhombic** system there are three mutually perpendicular 2-fold axes. The axes (parallel to the symmetry axes) are also mutually at right angles.The point groups are 222, *mm*2 and *mmm*. The first position in the symbol for the group refers to a symmetry element parallel to *x*, the second parallel to *y* and the third parallel to *z*. It should be clear that 2*mm*, *m*2*m* and *mm*2 refer to the same point group but with the direction of the 2-fold rotation axis labeled *x*, *y* and *z* respectively.

In the **tetragonal** system there is a unique 4-fold axis and the *z* axis is always chosen to coincide with it. The first position of the point group symbol is the symbol for this axis (4 or $\bar{4}$). The *x* and *y* axes (at right angles to each other and to *z*) are equivalent by symmetry and the second position of the point group symbol is the symbol for symmetry elements (if present) along *x and y*. The third position refers to symmetry elements at 45° to *x* and *y*. Note in particular that $\bar{4}2m$ can also (with a 45° rotation of the coordinate system about *z*) be written $\bar{4}m2$, so there are two *different* symbols for the *same* point group.
Tetragonal point groups are 4, $\bar{4}$, 4/*m*, 422, 4*mm*, $\bar{4}2m$, and 4/*mmm*.

In the **trigonal** and **hexagonal** systems there is a unique 3-fold or 6-fold axis and the *z* axis is always chosen to coincide with it. The first position of the point group symbol is occupied by the symbol (3, $\bar{3}$, 6 or $\bar{6}$) for this axis. The *x* and *y* axes are chosen at right angles to *z* and at 120° to each other, so that the *x* and *y* axes are equivalent by symmetry. The second position of the group symbol is then taken by the symbol for symmetry elements parallel to *x* and *y* [and to the third equivalent direction at 120° to both *x* and *y*, i.e. −(*x*+*y*)]. The third position is reserved for the symbol for symmetry elements at right angles to *x* or *y*. Fig. 2.23 should make clear the directions referred to in the second and third positions.

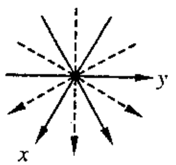


Fig. 2.23. The directions corresponding to the second (solid lines) and third (broken lines) positions in the symbols for the trigonal and hexagonal symmetry groups.

Note that 3*m* can also be written as 3*m*1 and (with a 30° rotation of the coordinate system about *z*) as 31*m* (see Fig. 1.6). Likewise 32 can be 321 or 312 and $\bar{6}m2$ can also be $\bar{6}2m$.
Some trigonal crystals can be referred to a **rhombohedral** unit cell with equi-inclined axes. We defer a discussion of that case until later (Chapter 3).
Trigonal point groups are 3, $\bar{3}$, 32, 3*m* and $\bar{3}m$.
Hexagonal point groups are 6, $\bar{6}$, 6/*m*, 622, 6*mm*, $\bar{6}m2$ and 6/*mmm*.

In the **cubic** system we always use axes at right angles to each other. Imagine these axes imbedded in a cube with the origin as the center and *x*, *y* and *z* parallel to the cube edges. The first position in the point group symbol refers to symmetry elements parallel to *x*, *y* and *z*. The second position refers to symmetry elements parallel to the four body diagonals (so the second symbol will always be 3 or $\bar{3}$—this is diagnostic of a cubic group). The third position refers to symmetry elements (either 2, *m* or 2/*m*) parallel to the six face diagonals if they are present.
Cubic point groups are 23, 432, $m\bar{3}$, $\bar{4}3m$ and $m\bar{3}m$.

2.5 Notes

2.5.1 Rotations

Eq. 2.1 is derived by Boisen & Gibbs (see Book List). A useful expression in this regard is that for the *Cartesian rotation matrix* which determines how a point *x*,*y*,*z* is transformed by rotation about an axis. Let **i**, **j** and **k** be unit vectors in the *x*, *y* and *z* directions respectively. A unit vector from the origin is given by $\mathbf{r} = l\mathbf{i} + m\mathbf{j} + n\mathbf{k}$ where $l^2 + m^2 + n^2 = 1$. (*l*, *m* and *n* are the direction cosines of **r**.) Consider a rotation by an angle ρ about this axis; the new coordinates *x'*, *y'* and *z'* are given by:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} ll(1-c)+c & lm(1-c)-ns & ln(1-c)+ms \\ ml(1-c)+ns & mm(1-c)+c & mn(1-c)-ls \\ nl(1-c)-ms & nm(1-c)+ls & nn(1-c)+c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad (2.3)$$

Here $c = \cos\rho$ and $s = \sin\rho$ and, as a mnemonic aid, l^2 is written as *ll* etc. For the special case of rotation about the *z* axis ($l = m = 0, n = 1$), the matrix greatly simplifies to (c $-s$ 0 / s c 0 / 0 0 1). Note that the inverse of a rotation matrix (corresponding to rotation in the opposite sense) is the transpose of the original matrix.
For a roto-inversion, change the sign of all the matrix elements. For reflection ($\bar{2}$), $c = -1$ and $s = 0$ and remember that *l*, *m*, and *n* are the direction cosines of the normal to the mirror. Thus for reflection in the plane $z = 0$, the matrix is (1 0 0 / 0 1 0 / 0 0 $\bar{1}$). [Compare with ($\bar{1}$ 0 0 / 0 $\bar{1}$ 0 / 0 0 1) for a 2-fold rotation about *z*.]
If we imagine the three rotation axes (X_1, X_2 and X_3; § 2.2.1) to intersect a unit sphere and the points to be connected by arcs of great circles, then the surface of the sphere is divided into congruent spherical triangles. This is illustrated in Fig. 2.24 which shows two 2-fold rotation axes separated by an angle of $\rho/2$ in a horizontal plane. The generated rotation axis is a 360°/ρ–fold axis. It should be clear that the angles of the spherical triangle (heavy outline) are 180°/2 (twice) and $\rho/2$. If 360°/ρ is an integer, the sphere can be exactly covered by triangles congruent to the one shown.
More generally, the spherical triangles on a unit sphere corresponding to any rotation group will have sides equal to ϕ_1, ϕ_2 and ϕ_3 (the angles between the axes) and angles

$\rho_1/2$, $\rho_2/2$ and $\rho_3/2$ (using the same symbols as in Eq. 2.1). As $\rho_1/2 = 180°/p_1$ and so on, Eq. 2.2 then follows from the fact that the sum of the angles of a spherical triangle must be greater than 180° (i.e. $\rho_1/2 + \rho_2/2 + \rho_3/2 > 180°$).

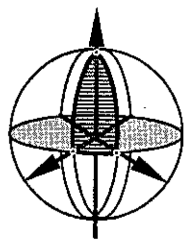


Fig. 2.24. See text.

Equation 2.1 refers to rotation axes fixed with respect to the coordinate system. Usually when tilting something, such as a crystal on a goniometer stage, by sequential rotations, the rotation axes move with the crystal. The net rotation is usually described in terms of rotations by Euler angles about such moving axes. A useful text is *Mathematical Methods for Physicists* [3rd ed. Academic Press, New York (1985)] by G. Arfken who warns that "There are almost as many definitions of Euler angles as there are authors."

2.5.2 Groups of symmetry operations and their orders

A group of symmetry operations consists of all the operations associated with the symmetry elements. Thus the group 4 consists of four members: a quarter-turn ($4^1 = 4^+$), two quarter-turns ($4^2 = 2^1$), three quarter-turns ($4^3 = 4^-$) and four quarter-turns ($4^4 = 1$). Any combination of these will produce another. As there are four symmetry operations the order of the group is four.

The order of $\bar{1}$ is two (the two symmetry operations are the identity and the inversion). Reference to Fig. 2.3 (p. 31) should make it apparent that the order of $\bar{3}$ is six, the order of $\bar{4}$ is four and of $\bar{6}$ is six.

The group $2/m$ consists of four elements: a half-turn (2^1), two half-turns (1), reflection (m) and also an inversion ($\bar{1}$) which is the result of combining the rotation with reflection (and of course a reflection is the result of a half-turn combined with inversion).

The group $4/m$ requires a little more thought. The 4-fold axis along z will generate four points with the same value of z. Reflection in the plane $z = 0$ will generate four more for a total of eight so the order of the group is eight. The symmetry operations are the four rotations 4^1, 4^2 ($= 2^1$), 4^3, 4^4 ($= 1$) and the result of combining these with the mirror reflection which are: (4^1 then m) $= \bar{4}^3$, (4^2 then m) $= \bar{1}$, (4^3 then m) $= \bar{4}^1$, (4^4 then m) $= m$.

Now consider the group 23. There are three 2-fold axes and four 3-fold axes. In enumerating the different symmetry operations, we agree not to count the identity for a moment. The symmetry operations are 2^1 in three different directions and 3^1 and 3^2 in four directions for a total of $3 + 4 \times 2 = 11$ different rotations. Counting also the identity we see that the order of the group is 12.

The largest crystallographic point group is $m\bar{3}m$ for which the order is 48. The full symbol is $4/m\bar{3}2/m$. There are three $4/m$ axes, four $\bar{3}$ axes and six $2/m$ axes. We agree now not to count the identity and the point of inversion until we have counted the other operations. Besides the identity and inversion each $4/m$ contains six operations (see above) so we get $3 \times 6 = 18$ distinct operations from the three of them. A $\bar{3}$ axis contains six operations which again include the identity and inversion ($\bar{3}^4 = \bar{1}$) which we agreed not to count for the moment, so from the four $\bar{3}$ axes we get $4 \times 4 = 16$ new operations. From the six $2/m$ we get (counting only the m and 2^1) $6 \times 2 = 12$ new operations. Adding in the identity and inversion we find $18 + 16 + 12 + 1 + 1 = 48$ for the order of the group.

The order of 432, $6/mmm$, $\bar{4}3m$ and $m\bar{3}$ is 24 in each case; all other crystallographic groups are smaller (their order is a divisor of 48). The order of 235 (I) is 60 and the order of $m\bar{3}\bar{5}$ (I_h) is 120.

It is worth noting that 432 and $\bar{4}3m$ are isomorphic to each other (as are several other sets of groups) so they do not represent different abstract groups.

2.5.3 Derivation of the point groups

The enumeration of the crystallographic point groups can be done starting from the eleven pure rotation groups. The eleven centrosymmetric groups are then obtained by adding an inversion center (in mathematical terms this corresponds to group multiplication of the rotation groups by the group $\bar{1}$). Ten subgroups of the centrosymmetric groups that do not contain a center, but that do contain elements other than pure rotations, can then be found. This scheme is outlined in Table 2.3.

Table 2.3. The crystallographic point groups as pure rotation groups, centrosymmetric groups and other groups.

rotation group	centrosymmetric group	other groups
1	$\bar{1}$	
2	$2/m$	m
3	$\bar{3}$	
4	$4/m$	$\bar{4}$
6	$6/m$	$\bar{6}$
222	mmm	$mm2$
32	$\bar{3}m$	$3m$
422	$4/mmm$	$4mm$ $\bar{4}2m$
622	$6/mmm$	$6mm$ $\bar{6}m2$
23	$m\bar{3}$	
432	$m\bar{3}m$	$\bar{4}3m$

A good account of the derivation of the groups in this way is given by M. B. Boisen & G. V. Gibbs, *Amer. Mineral.* **61**, 145-165 (1976). For the more mathematically inclined *Geometry and Symmetry* by P. B. Yale [Dover, New York 1988] is recommended.

2.5.4 Curie's law, Friedel's law, Laue classes, optical activity and polarity

Curie's law states that an effect cannot have lower symmetry than its cause so that any asymmetry of an effect must be found in its cause. Thus the result of an experiment can give information about symmetry, but symmetry arguments should not be used to predict *a priori* the result of an experiment.[1] In X-ray diffraction it is often found that the three-dimensional diffraction pattern is of higher symmetry than that of the crystal (but never of lower symmetry). In the absence of anomalous dispersion the diffraction pattern is in fact always centro-symmetric (*Friedel's law*). The point group of the diffraction pattern is therefore that obtained by adding a center of symmetry to the point group of the crystal and the apparent crystal class is that of one of the centrosymmetric groups. The *Laue Classes* are comprised of those groups that result in the same centrosymmetric group when a center is added. In Table 2.3 (p. 49), each Laue class consists of a centrosymmetric group and the non-centrosymmetric (*acentric*) groups on the same line (thus one of the eleven Laue classes consists of groups 422, $4mm$, $\bar{4}2m$ and $4/mmm$).

The *enantiomorphous* groups consist of those in the first column of Table 2.3. Crystals belonging to these classes will have left- and right-handed forms (that cannot be superimposed on their mirror images). They will also be optically active (rotate the plane of polarized light). Contrary to a belief popular among chemists, enantiomorphism is not a necessary condition for optical activity, which may also be found in crystals of classes m, $mm2$, $\bar{4}$, and $\bar{4}2m$. In these latter cases, both left- and right-handed rotations will occur.

The acentric crystal classes are often referred to as *polar* by crystallographers, but this term is correctly given a more restricted meaning: those classes in which a spontaneous electric polarization is possible.[2] In this more restricted sense (which we use subsequently) the *polar* classes are 1, 2, m, $mm2$, 4, $4mm$, 3, $3m$, 6 and $6mm$. In all but 1 and m, there is a definite polar axis: **b** in class 2, **c** in the rest.

In piezoelectric crystals (quartz is a notable example) a polarization can be induced by stress; piezoelectricity is possible in all acentric classes except 432.

Good references to symmetry constraints on crystal properties are *Physical Properties of Crystals* by J. F. Nye (Oxford, 1955) and *Tensors and Group Theory for the Physical Properties of Crystals* by W. A. Wooster (Oxford, 1973).

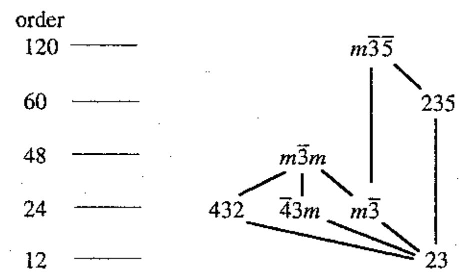
[1]Crystallographers, who are otherwise admirable people, sometimes put the cart before the horse, and say that a certain structural feature (such as an 180° bond angle) is *required* by symmetry. The structure, and its symmetry, is determined by the often inscrutable interplay of interatomic forces, and if these dictate a certain symmetry, so be it.

[2]See the discussion in the *International Tables A*, p. 782. The polarization is defined as dipole moment per unit volume.

2.5.5 Cubic and icosahedral groups; generators

Objects with symmetry $\bar{4}3m$ and $m\bar{3}m$ are commonly found. Four points at the vertices of a regular tetrahedron have symmetry $\bar{4}3m$ and six points at the vertices of an octahedron have symmetry $m\bar{3}m$. By contrast a minimum of twelve points is required make an arrangement with symmetry 23 or $m\bar{3}$ so it is not surprising that this group is not often encountered in molecular chemistry; as a minimum a molecule of the form A_{12} or AB_{12} is needed—a possible candidate is neopentane, $C(CH_3)_4$. A minimum of 24 points is needed to make an arrangement with symmetry 432—the vertices of a *snub cube* ($3^4.4$) provide the simplest example (see Fig. 2.26). Very few examples of crystals in this class are known (β-Mn is one). Twelve points at the vertices of a regular icosahedron have symmetry $m\bar{3}\bar{5}$ (I_h) but a minimum of 60 points is required to generate a pattern with symmetry 235 (I) so examples of molecules with this symmetry are also hard to find.[1] The snub dodecahedron, $3^4.5$ (§ 5.1.3, p. 136) with 60 vertices is the simplest object with this symmetry. Further information (and other useful information about subgroup relations) is to be found in a classic paper by H. A. Jahn & E. Teller, *Proc. Roy. Soc. (London)*, A**261**, 220 (1937).

The symmetry elements of 432, $\bar{4}3m$ and $m\bar{3}$ are all to be found in $m\bar{3}m$ so they are all *subgroups* of $m\bar{3}m$. The symmetry elements of 23 are contained in all the other cubic groups so they are all *supergroups* of 23. The cubic subgroups of $m\bar{3}\bar{5}$ are $m\bar{3}$ and 23 and 23 is also a subgroup of 235. The group hierarchy is therefore:



We mentioned in § 2.2.1 that rotations about two axes at an angle and through a common point would generate all the pure rotation groups. The two rotations are *generators* of the group. We can specify the orientation of an axis through the origin 0,0,0 of a Cartesian coordinate system by giving the coordinates of another point. Thus in group 23 we can take as generators a 2-fold rotation about an axis passing through 1,0,0 and a 3-fold rotation about an axis passing through 1,1,1. We can label positive rotations about the these axes as $2^+(100)$ and $3^+(111)$ respectively. The ten other operations of the group are

[1]In Appendix 4 we mention a possible "fullerene" molecule C_{140} with symmetry I. However, theoretical studies indicate that this molecule will undergo a Jahn-Teller distortion to lower symmetry.

then generated as combinations of these two. Thus a rotation first about the 3-fold axis and then about the 2-fold axis is equivalent to a positive rotation about a 3-fold axis passing through −1,1,−1. We can symbolize this as $2^+(100)*3^+(111) = 3^+(\bar{1}1\bar{1})$. Other examples are:

$$2^+(111)*2^+(111) = 1$$
$$3^+(111)*3^+(111) = 3^-(111)$$
$$3^-(111)*3^+(\bar{1}1\bar{1}) = 3^+(111)*3^+(111)*2^+(100)*3^+(111) = 2^+(001)$$

The other cubic and icosahedral groups are similarly generated starting from two generators. Particularly convenient sets involving a 3-fold and a 2-fold axis are given below. Note that the orientation of mirror planes through the origin are specified by a point on the normal to the plane from the origin and that $q = (3-\sqrt{5})/2$.

$m\bar{3}\bar{5}$	$\bar{3}^+(1q0)$	$m(100)$
235	$3^+(1q0)$	2(100)
$m\bar{3}m$	$\bar{3}^+(111)$	$m(100)$
432	$3^+(111)$	2(110)
$\bar{4}3m$	$3^+(111)$	$m(110)$
23	$3^+(111)$	2(100)

2.5.6 Non-crystallographic point groups

Molecules with a non-crystallographic symmetry are common and their symmetries are almost invariably described by the Schoenflies symbol. Right prisms with a regular *N*-gonal base have symmetries D_{Nh} in the Schoenflies notation. C_{70} (see Appendix 4) is an example of a molecule with D_{5h} symmetry. A special case of interest is a cylinder for which $N = \infty$ and for which the symmetry is $D_{\infty h}$. Linear molecules with a center of symmetry such as O_2 or CO_2 have this symmetry. So does a cricket ball (a ball with an equatorial seam).

Pyramids with a regular *N*-gon base have symmetry C_{Nv} in the Schoenflies notation. A cone is the special case with $N = \infty$ and has symmetry $C_{\infty v}$. A linear molecule without a center such as CO also has this symmetry.

Other group symbols worth knowing about include K_h for the symmetry of a sphere. C_{3i} ($\bar{3}$) is sometimes labeled S_6 and D_2 is sometimes labeled *V*.

The symmetry of an antiprism with a regular *N*-gon base is D_{Nd} in the Schoenflies notation. The symmetry of a regular square antiprism (§ 5.1.4, p. 139) contains a $\bar{8}$ axis and may be written $\bar{8}2m$ (D_{4d} in Schoenflies notation). Thus the only *regular* antiprism that can occur in crystal structures is the triangular antiprism (symmetry $\bar{3}2/m = D_{3d}$) although figures approximating square antiprisms are rather common. Ferrocene, $Fe(C_5H_5)_2$, should be familiar (to chemists at least) as an example of a molecule with the symmetry of a pentagonal antiprism (D_{5d}).

To generalize Table 2.1 to axes of arbitrary order *N* and to show the correspondence to

the Schoenflies notation we have to consider three cases (here *n* is an integer): (a) The order of the axis is 4*n*. (b) The order of the axis is 4*n*+2. (c) The order of the axis is 2*n*+1. The first two cases (*N* even) result in identical Hermann-Maugin symbols, but require different Schoenflies symbols when there is a $\bar{N}$ axis (see exercise 17). Table 2.4 below gives the Hermann-Maugin symbol with the corresponding Schoenflies symbol directly underneath under the same headings as in Table 2.1. Table 2.4 combined with Table 2.2 (p. 43) gives a complete listing of all the finite point symmetry groups in three dimensions.

What happens as *N* goes to infinity? See Appendix A.1 (§ A1.5) for the surprising answer.

Table 2.4. Point symmetry groups other than cubic or icosahedral.

$N =$	N	$\bar{N}$	$N2(2)$	$Nm(m)$	N/m	$N/m2/m2/m$	$\bar{N}+m$
4*n*	N C_n	$\bar{N}$ S_N	$N22$ D_N	Nmm C_{Nv}	N/m C_{Nh}	$N/m2/m2/m$ D_{Nh}	$\bar{N}2m$ $D_{N/2d}$
4*n*+2	N C_n	$\bar{N}$ $C_{N/2h}$	$N22$ D_N	Nmm C_{Nv}	N/m C_{Nh}	$N/m2/m2/m$ D_{Nh}	$\bar{N}2m$ $D_{N/2h}$
2*n*+1	N C_n	$\bar{N}$ C_{Ni}	$N2$ D_N	Nm C_{Nv}			$\bar{N}2m$ D_{Nd}

2.5.7 Symmetry, and relations between polyhedra

We take axes oriented as described in § 2.4 for cubic symmetry. The operations of $m\bar{3}$ on an arbitrary point *x,y,z* will produce a pattern of 24 points with symmetry $m\bar{3}$. If the point is on a mirror plane (e.g. 0,*y*,*z*) only 12 points are produced. For special values of *y* and *z* the symmetry may be higher. Thus if the point is 0,1,1 the vertices of a *cuboctahedron* (symbol 3.4.3.4) are produced with symmetry $m\bar{3}m$. If the point is $0,1/\tau,1$ [τ is the golden ratio $(1 + \sqrt{5})/2 = 1.6180$] the vertices of a regular icosahedron (3^5) are produced with symmetry $m\bar{3}\bar{5}$. This illustrates that $m\bar{3}$ is a subgroup of both $m\bar{3}m$ (the symmetry of the cuboctahedron) and $m\bar{3}\bar{5}$ (the symmetry of the icosahedron).

Fig. 2.25 shows on the left a cuboctahedron and in the center a regular icosahedron. The {Si}Cr_{12} icosahedron in the Cr_3Si structure (§ 6.6.4) is obtained from a point at 0,1/2,1 and is illustrated on the right in the figure. The darker-shaded triangles are normal to 3-fold axes in each case.

The operations of 432 applied to a point *x,y*,1 will produce a snub cube ($3^4.4$, see Fig. 2.26) if *x* is the solution of $x^3 + x^2 + 3x = 1$ and $y = (1 - x)/(1 + x)$. [The solution of the first equation is $x = q - 8/9q - 1/3$, where $q = (26/27 + \sqrt{44}/\sqrt{27})^{1/3}$ giving $x = 0.2956$, *y*

= 0.5437.] Interchanging x and y produces the mirror image polyhedron.

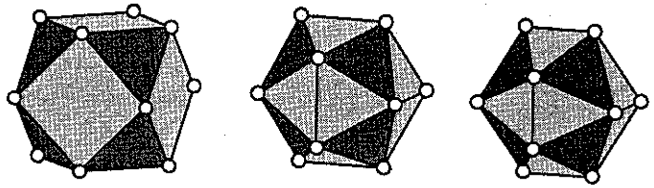


Fig. 2.25. Relationship between a cuboctahedron (left) and an icosahedron (see text).

Fig 2.26 shows on the left a snub cube and on the right its enantiomorph. In the center is an intermediate case with $x = y = \sqrt{2} - 1 = 0.414$. This polyhedron is a *rhombicuboctahedron* (symbol 3.4^3) and it is centrosymmetric (symmetry $m\bar{3}m$). This illustrates that 432 is a subgroup of $m\bar{3}m$. In the diagram the triangular faces normal to 3-fold axes are darker shaded.

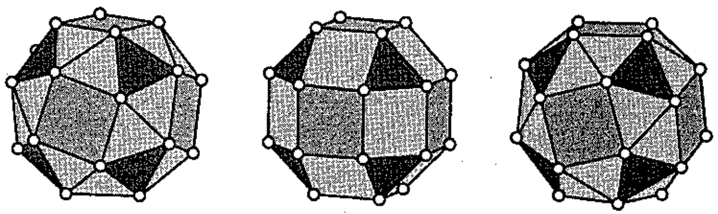


Fig. 2.26. Relationship between a rhombicuboctahedron (center) and a snub cube (see text).

2.5.8 *Antisymmetry: magnetic or black-and-white groups*

We have been discussing transformations of a point whose position is described by three coordinates (x, y and z). Students of quantum mechanics will know that in addition to positional coordinates an electron has a fourth (spin) coordinate that can take one of two values (commonly signified α and β or ↓ and ↑). We could consider the set of symmetry operations that change not only coordinates, but which also change α to β and *vice versa*. Such an operator is called an antisymmetry operator. The discussion is often in terms of *black-and-white* symmetry groups in which the antisymmetry operation changes black to white or *magnetic* symmetry groups in which the antisymmetry operation reverses the direction of magnetization.

Let us signify an antisymmetry operation by underlining; so that for example an antimirror is $\underline{m}$ and an anti-2-fold rotation is $\underline{2}$. An antimirror reflects in a plane and changes black to white and *vice versa*. The symmetry operation $\underline{3}$ cannot occur as it will repeatedly change a black point at a given place to a white point at the same place and then back to black and a given point must be either black or white (but not black *and* white). In fact there is an antisymmetry operation corresponding to all the crystallographic point operations except 1 and 3 (the only ones of odd period).

Some simple binary crystal structures AB have antisymmetry in the sense that interchanging A and B produces the same structure. Examples are the structures of CsCl, NaCl and the polytypes of SiC.

As well as the classical group $2/m$ there are the black and white groups $\underline{2}/m$, $2/\underline{m}$ and $\underline{2}/\underline{m}$. In all there are 58 crystallographic antisymmetry groups for a total of 90 (= 58 + 32) crystallographic black-and-white (or magnetic) point groups.

If the fourth coordinate can have a finite number (>2) of values the *polychromatic* symmetry groups are obtained. If the fourth coordinate can have *any* value we have of course reached four dimensions.

A good place to start reading about such groups is Shubnikov & Kopstik (Book List). Magnetic space groups are obviously of interest in the description of ordered magnetic structures in solids.

2.6 Exercises

1. A right triangular prism with equilateral faces has symmetry $\bar{6}m2$. Locate the symmetry elements.

2. The square antiprism (see § 5.1.4, p.139) has symmetry D_{4d}. It has a $\bar{8}$ axis. What are its other symmetry elements?

3. Another common 8-coordination figure is one with atoms at the vertices of a bisdisphenoid (see § 5.1.6, p. 141). The symmetry of this figure is $\bar{4}2m$ and there are two sets of bonds with bonds of one set unrelated by symmetry to those of the other set. Locate the 2-fold axes in this polyhedron.

4. Show that adding an inversion center to 622 will produce $6/mmm$.

5. For 2-fold rotations about the x, y and z directions respectively the matrix in Eq. 2.3 becomes:

$$(1\,0\,0 / 0\,\bar{1}\,0 / 0\,0\,\bar{1}),\ (\bar{1}\,0\,0 / 0\,1\,0 / 0\,0\,\bar{1}),\ (\bar{1}\,0\,0 / 0\,\bar{1}\,0 / 0\,0\,1)$$

Thus the transformed coordinates for 222 are x,y,z ; $x,\bar{y},\bar{z}$; $\bar{x},y,\bar{z}$; $\bar{x},\bar{y},z$

6. For a rotation by one-third of a circle about a body diagonal in the $+x$, $+y$, $+z$ direction the matrix in Eq. 2.3 reduces to (0 0 1 / 1 0 0 / 0 1 0). For a two-thirds rotation the matrix becomes (0 1 0 / 0 0 1 / 1 0 0). Operation of these matrices corresponds to cyclic permutation of the coordinates.

7. The transformed coordinates for the operations of group 23 are now easily derived from the matrices (given above) for the identity and rotations about the three 2-fold axes followed by rotations about a 3-fold axis. They are:

$$x,y,z\ ;\ z,x,y\ ;\ y,z,x\ ; \qquad x,\bar{y},\bar{z}\ ;\ \bar{z},x,\bar{y}\ ;\ \bar{y},\bar{z},x$$
$$\bar{x},y,\bar{z}\ ;\ \bar{z},\bar{x},y\ ;\ y,\bar{z},\bar{x}\ ; \qquad \bar{x},\bar{y},z\ ;\ z,\bar{x},\bar{y}\ ;\ \bar{y},z,\bar{x}$$

8. For each of the symbols given in Exercise 7 identify the symmetry operation that generates it from x,y,z. Incidentally, we have confirmed that the order of 23 is twelve.

9. Multiplying the matrices corresponding to the symbols in Exercise 7 by the identity: (1 0 0 / 0 1 0 / 0 0 1) and by the inversion: ($\bar{1}$ 0 0 / 0 $\bar{1}$ 0 / 0 0 $\bar{1}$) will now produce the symbols for $m\bar{3}$. They are simply the twelve given above plus the twelve obtained by changing the signs of all coordinates.

10. Still with Cartesian coordinates, a mirror in the plane $x = y$ will interchange x and y coordinates of a point and leave z unchanged (cf. Fig. 1.4) so the matrix representation of this symmetry operation is (0 1 0 / 1 0 0 / 0 0 1). Multiplying the coordinates of Exercise 9 by this matrix (interchanging the first two coordinates in each triplet) and by the identity will now produce the transformed coordinates for $m\bar{3}m$. They are all the 48 permutations of $\pm x,\pm y,\pm z$.

11. Verify the assertion that adding mirrors normal to inversion axes will not produce new groups. In particular "$\bar{3}/m$" ≡ $6/m$ and "$\bar{4}/m$" ≡ $4/m$. What is "$\bar{6}/m$"? A simple way to do this is to construct diagrams like those shown in Fig. 2.3 and 2.10. (Hence $4/m$ includes $\bar{4}$, and $6/m$ includes $\bar{3}$.)

12. Show that successive reflections in mirror planes normal to Cartesian x, y and z axes is equivalent to inversion through the point in common to the three mirror planes. (Three improper operations combine to produce another improper operation). In optics such a configuration of mirrors is known as a corner cube.

13. We have seen that combinations of rotation by a 1/2 circle ($\rho_1 = 180°$) and by 1/3 circle ($\rho_2 = 120°$) can result in rotation (ρ_3) equal to 360°/N, where N = 2, 3, 4 or 5. Find the angles between the three rotation axes in each case. Hint: from Eq. 2.1, $\cos\phi_3 = (2/\sqrt{3})\cos(\rho_3/2)$.

14. If you don't have one, make or borrow a model of a regular icosahedron (which has symmetry I_h). Convince yourself that the lines joining opposite vertices are $\bar{5}$ axes, the lines joining the centers of opposite faces are $\bar{3}$ axes and the lines joining the mid-points of opposite edges are $2/m$ axes. We therefore write I_h as $2/m\bar{3}\bar{5}$ (short symbol $m\bar{3}\bar{5}$).

15. The smallest angle between two 5-fold axes in $I = 235$ (or $I_h = m\bar{3}\bar{5}$ is 63.435° = $2\tan^{-1}(1/\tau)$ where $\tau = (1 + \sqrt{5})/2$. The combination of a fifth turn about each these two axes is a third turn.

16. With three of the 2-fold axes of 235 aligned along Cartesian x, y and z axes (as for 23), a 5-fold axis is in the yz plane at $\tan^{-1}(1/\tau) = 31.717°$ from z. The Cartesian rotation matrix (Eq. 2.3) for a fifth turn about this axis is **R** = (c_1 $-c_2$ 1/2 / c_2 1/2 c_1 / $-1/2$ c_1 c_2) where $c_1 = \cos(\pi/5) = (\tau-1)/2$ and $c_2 = \cos(\pi/10) = \tau/2$. Transforming the 12 points of 23 (Exercise 7) by multiplying by powers of **R** (**R**, $\mathbf{R}^2$, $\mathbf{R}^3$, $\mathbf{R}^4$, $\mathbf{R}^5$ = **E**) will produce the 60 transformed coordinates for 235 for this orientation of Cartesian axes. Adding an inversion (reversing the signs of all coordinates) will result in the 120 symbols for $m\bar{3}\bar{5}$. [Hint: see the drawing of an icosahedron in Fig. 2.18.]

17. Instead of using rotation + inversion axes $\bar{N}$, the point groups can be generated using rotation + reflection axes S_N which involve N-fold rotation followed by reflection in a plane normal to the rotation axis (this is the Schoenflies system). The correspondence between the S_N symmetry elements and the $\bar{N}$ symmetry elements is:

$$S_1 \leftrightarrow m\ (=\bar{2})\ ;\ S_2 \leftrightarrow \bar{1}\ ;\ S_3 \leftrightarrow \bar{6}\ ;\ S_4 \leftrightarrow \bar{4}\ ;\ S_6 \leftrightarrow \bar{3}$$

Generalize for S_N. (Hint: there are three cases to consider, $N = 4n$, $N = 4n+2$ and $N = 2n+1$, where n is an integer).

18. What is the result of combining 1/6 turns about intersecting axes at right angles?