Chapter 2

Crystallographic Point Groups

Cyrstals are characterized by periodic structure, or symmetry. The notion of a *point group* has to do with the symmetry operations on a geometric object, with a fixed point, that is, those operations such as rotations and reflections which leave the object invariant. Those point symmetries which are also consistent with periodic crystal structure (translational symmetry) yield the *Crystallographic Point Groups.* Thus, for example, the symmetry of the cube is consistent with crystal structure, while that of the icosahedron is not. To be explicit, we have the definition:

Def: A three-dimensional lattice of points is said to have *translational symmetry* if there exists some set of "primitive" translations, $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ such that every point in the lattice may be reached from another point by a translation of the form:

$$\mathbf{T}(t_1, t_2, t_3) = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 + t_3\mathbf{a}_3, \tag{2.1}$$

where t_1, t_2, t_3 are integers.

There are a total of 32 Crystallographic Point Groups (we'll just say "point groups" here for brevity). These are listed in this chapter.

2.1 Notation

We use the notation $R_x(\theta)$ to indicate a rotation by angle θ about the x axis. We use the notation M_x to indicate a mirror plane in which the normal to the mirror is along the x-axis.

There exists more than one system of notation for the groups we discuss here. The simple **Schönflies** notation will suffice here. In this notation, a C_n

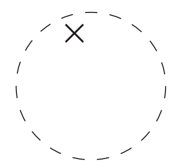

Figure 2.1: The uniaxial group C_1.

is used to designate an n-fold rotation axis. For example, C_4 implies a four-fold rotation axis (with associated rotations of $\pm\pi/2$, π, $e = 2\pi$). The notation may also be used to indicate a particular rotation, e.g., C_3 indicates a rotation by $2\pi/3$ about the designated axis, while C_3^{-1} indicates a rotation by $-2\pi/3$.

We may add the inversion operator (parity) $\mathcal{I}$ to obtain the improper rotations. In Schönflies notation, $S_2 = \mathcal{I}$. Closely associated with this is the mirror reflection, indicated by σ (for a reflection in a plane). If the reflection is through a plane perpendicular to a specified rotation axis, then an h subscript is added, giving σ_h. It is readily seen that a reflection followed by a rotation by π about the axis perpendicular to the mirror plane is the same as an inversion:

$$S_2 = \mathcal{I} = C_2\sigma_h. \tag{2.2}$$

We generalize the S_2 notation to include n-fold axes. Hence,

$$S_n = C_n\sigma_h = \sigma_h C_n. \tag{2.3}$$

It is helpful to have a pictorial representation. We will adopt something known as "stereograms". This will be developed in the course of listing the 32 point groups.

2.2 The 32 Crystallographic Point Groups

We start with a theorem, which limits the possible symmetry axes that need to be considered:

Theorem: The only possible proper rotations consistent with translational symmetry are $C_n, n = 1, 2, 3, 4, 6$.

Proof of this is left to the reader.

We are ready to make the list. We'll start with the groups with the least symmetry. We start with what are known as the "uniaxial" groups, those with a single n-fold axis. The first is C_1, see Fig. 2.1.

In this figure, we see a dashed circle and a $\times$. For now, the reader may wish to imagine that there is a disk, represented by the circle, with a peg sticking up above the plane of the disk at the $\times$. Thus, there is no symmetry, either under rotations or mirrors (we suppose that there is no symmetry under splitting the

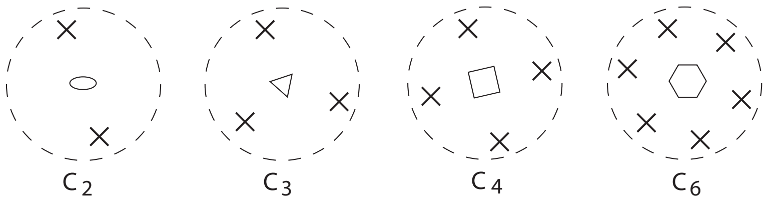

Figure 2.2: The uniaxial groups C_2, C_3, C_4, and C_6.

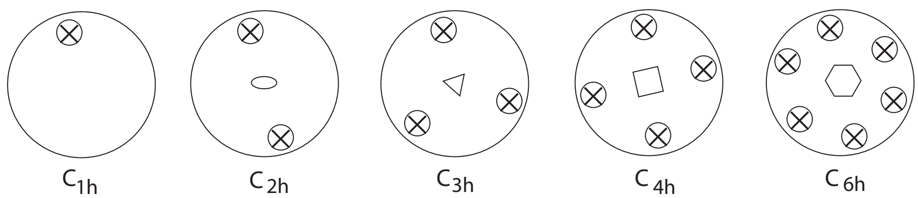

Figure 2.3: The uniaxial groups $C_{1h}, C_{2h}, C_{3h}, C_{4h}$, and C_{6h}.

peg lengthwise in half). An anisotropic array of lattice sites may have this symmetry (or lack of symmetry).

Next, Fig. 2.2 shows the remaining uniaxial groups containing no mirror planes. Again, you may imagine that the $\times$ marks are pegs sticking up from the plane of the disk. Alternatively, you may imagine that the disk has only one peg, and the additional $\times$ marks show what happens to the peg under the actions of the group. Thus, for example, C_3 has a three-fold symmetry: rotations by $\pm 2\pi/3$ leave it invariant.

Next, we add a mirror plane, first in the plane of the "disk", see Fig. 2.3. We have added two new features to our graphical notation: The outline of the disk has become solid, rather than dashed. This indicates that there is a mirror plane in the plane of the disk. Also, we have added small circle symbols (each here overlapping a $\times$, but this isn't always the case). You may think of the circle as indicating a peg sticking out below the plane of the disk. Thus, the illustration for C_{1h} indicates symmetry with respect to a mirror reflection through the plane of the disk. The "h" in the Schönflies notation indicates a horizontal mirror plane, where "horizontal" is the plane of the disk.

We get four more groups by taking away the horizontal mirror plane and adding a vertical mirror plane, see Fig. 2.4. Note that C_{1v} is the same as C_{1h}, since there is no uniquely defined principal axis. Also, note that adding one vertical mirror plane implies others in general. For example, in the case of C_{2v}, adding a mirror plane (M_y) in the $x - z$ plane gives one also in the $y - z$ plane (assuming the principal two-fold rotation axis is the z-axis), since:

$$R_z(\pi)M_y = M_x. \tag{2.4}$$

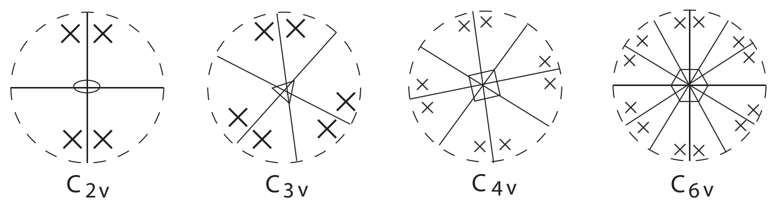

Figure 2.4: The uniaxial groups C_{2v}, C_{3v}, C_{4v}, and C_{6v}.

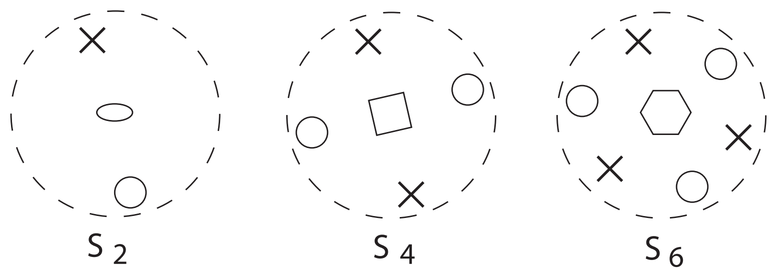

Figure 2.5: The uniaxial groups S_2, S_4, and S_6.

We may also consider the improper rotations, starting with the simple inversion, S_2. The inversion followed by a rotation by angle π is the same as a mirror, e.g., C_{1h}, hence does not generate a new group. The inversion followed by a rotation by $\pi/2$ generates S_4. Ultimately, we end up with three new groups by considering the improper rotations with a single principal axis, see Fig. 2.5. Note that S_2 and S_6 contain the inversion symmetry, while S_4 does not. Also, be aware that the notation for these groups has nothing to do with the overlapping notation for the permutation groups.

This completes the "uniaxial" groups. We next consider adding a two-fold rotation axis perpendicular to the principal axis of C_n, obtaining the "dihedral" groups, D_n. These are shown in Fig. 2.6. Note that adding such a two-fold axis to C_1 just gives C_2, as C_1 doesn't have any well-defined axis in the first place.

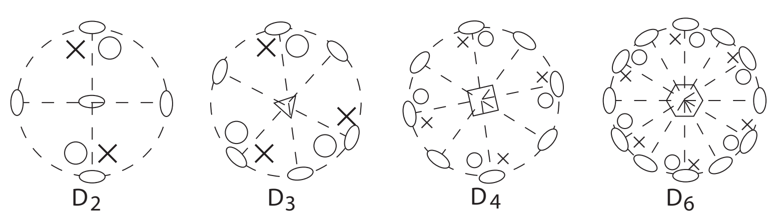

Figure 2.6: The dihedral groups D_2, D_3, D_4, and D_6.

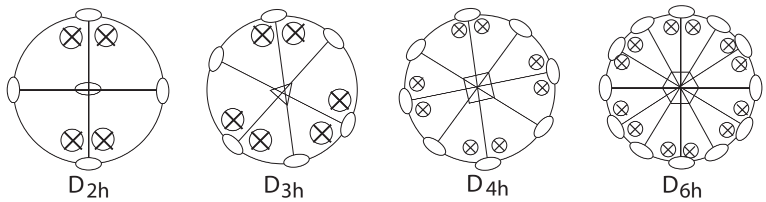

Figure 2.7: The dihedral groups D_{2h}, D_{3h}, D_{4h}, and D_{6h}.

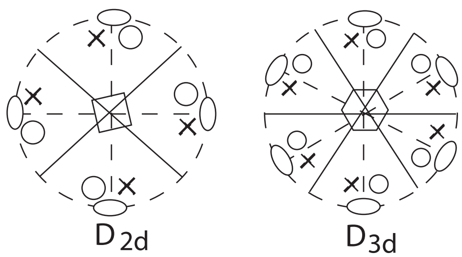

Figure 2.8: The dihedral groups D_{2d} and D_{3d}.

We may likewise add a two-fold rotation axis perpendicular to the principal axis of C_{nh}, obtaining the additional dihedral groups, D_{nh}, see Fig. 2.7. Adding such an axis to C_{1h} just gives C_{2v}, rather than a new group.

We may also add a two-fold axis perpendicular to the principal axis for the improper rotation groups S_n. In the case of S_2, we obtain C_{2h} rather than a new group. Thus, we have two new dihedral groups, called D_{2d} and D_{3d}. They are graphed in Fig. 2.8.

This brings the total to 27 groups so far. There are an additional five groups, known as the "cubic groups" that do not have a principal axis with all other axes perpendicular to it. All of these remaining five have a three-fold axis equidistant from three mutually perpendicular two- or four-fold axes. The first group is the group of proper rotations of the tetrahedron (that is, those rotations which take a tetrahedron with some orientation into a tetrahedron with the same orientation, with indistinguishable faces). This group is labeled T.

The second of these groups is the full tetrahedral symmetry group, T_d, including mirror planes. The third group, T_h, is obtained by adding the inversion operation to T. Note that the tetrahedron is not invariant under the operations of this group. The fourth group, O, is the group of proper rotations of the octahedron. Equivalently, it is the group of proper rotations of the cube, noting that the faces of the octahedron may be identified with the vertices of a cube, and vice versa. The final group is the full symmetry group O_h of the octahedron, obtained by adding the inversion to O or to T_d.

2.3 Exercises

1. Give the multiplication table for D_{3h}.

2. List the classes of C_{6v}.

3. Consider the symmetry group, C_{4v}, of the square, consisting of the rotations about the axis perpendicular to the square, and reflections about the vertical, horizontal, and diagonal axes in the plane of the square (but no mirror plane in the plane of the square). List all of the group elements, and classify them into classes of equivalent elements. Find all subgroups and identify the invariant subgroups.

4. List the elements of the tetrahedral symmetry group T_d, and categorize by class.

5. We have looked at the permutation group S_4 and the tetrahedral symmetry group T_d. Show that these two groups are isomorphic, giving an explicit mapping between the elements of the two groups.