CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 34: The 32 Point Groups in 3D

In the earlier lectures, we began the development of three-dimensional point groups, and in this lecture, we completed the derivation of all the thirty-two crystallographic point groups in three dimensions. We begin by considering only the axial crystallographic point groups, in which no mirror symmetries are involved and only rotational axes or rotoinversion axes are present. In fact, all such groups have already been developed, and what is presented here is essentially a summary of these axial groups.

These axial point groups are divided into different categories. The leftmost column of the table directly lists the point groups that arise from two-dimensional axial groups, where only a single rotational axis is involved. The allowed rotational axes in this case are 1, 2, 3, 4, and 6. Next, we consider combinations of rotational axes and determine the valid combinations that are crystallographically permissible. In the second column of the table, these axial groups correspond to combinations of three rotational axes of the type $n22$, as discussed in the previous lecture.

Further, two additional combinations were identified in the last lecture, namely those of the type 233 and 432. These particular combinations are accommodated naturally within a cube, and therefore they correspond to the cubic point groups. Finally, one rotoinversion axis is also included, namely $\bar{4}$. As discussed earlier, the rotoinversion axes $\bar{1}$, $\bar{2}$, $\bar{3}$, and $\bar{6}$ do not appear independently in the axial crystallographic groups. The axis $\bar{1}$ corresponds simply to inversion symmetry, while $\bar{2}$, $\bar{3}$, and $\bar{6}$ can be decomposed into other point groups. Consequently, they are not included among the axial crystallographic groups, although they will reappear later in this lecture. The rotoinversion axis $\bar{4}$, however, is unique in that it cannot be decomposed into other symmetry operations. Thus, we arrive at a total of twelve axial crystallographic point groups.

To these axial groups, we now add reflection and inversion operations in a manner analogous to what was done earlier for the two-dimensional point groups. When adding a mirror, it must be done carefully so as not to introduce additional symmetry elements that would destroy the original symmetry of the group.

Before proceeding with the addition of mirrors, it is useful to clarify some of the terminology. Dihedral groups are denoted by the symbol D and are of the type $n22$, where n may be 2, 3, 4, or 6. In these groups, the twofold rotational axes are perpendicular to the primary rotational axis. These are referred to as dihedral groups.

The tetrahedral group derives its name from the fact that the symmetry elements can be accommodated within a cube by inscribing a tetrahedron inside it. A tetrahedron allows threefold rotational axes to be defined by drawing axes from each vertex to the center of the opposite face. Since a tetrahedron has four vertices, there are four threefold rotational axes in this cubic point group. The twofold rotational axes, on the other hand, join the midpoints of opposite edges of the tetrahedron. Groups of this type are called tetrahedral groups and are denoted by the symbol T.

Next, consider the octahedral group, corresponding to the 432 symmetry. In this case, the threefold rotational axes lie along the body diagonals of the cube, as in the tetrahedral group. The fourfold rotational axes are perpendicular to the faces of the cube, and the twofold rotational axes join the midpoints of opposite edges of the cube. An octahedron can be inscribed in the cube by joining the midpoints of all six faces. As in the tetrahedron, the faces of the octahedron are equilateral triangles, but in this case, there are eight such faces. The fourfold rotational axes are obtained by joining opposite vertices of the octahedron, giving three fourfold rotational axes. In a similar manner, the threefold and twofold rotational axes are accommodated within the octahedron. This group is therefore called the octahedral group and is denoted by the symbol O. Rotoinversion symmetry has already been discussed in the previous lecture.

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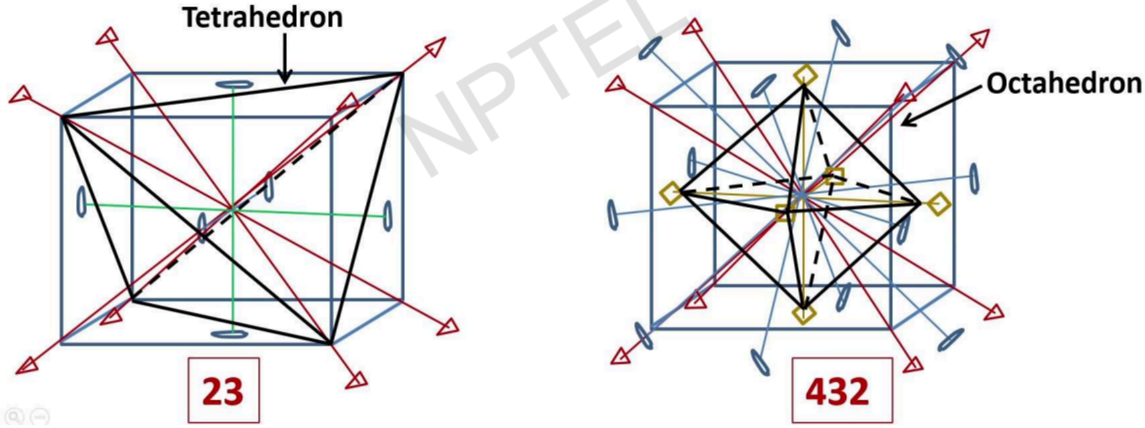
Axial Crystallographic Groups (3D)

2D	Dihedral Group (D)	Tetrahedral Group (T)	Octahedral Group (O)	Roto-Inversion
1	222	23 } 233	432	$\bar{4}$
2	32 } n22			
3	422			
4	622			
6				



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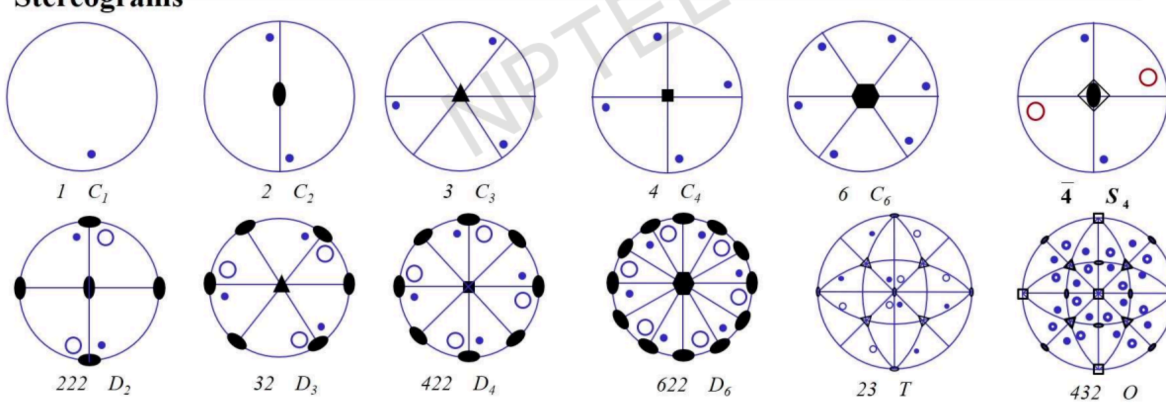
Axial Crystallographic Groups (3D)

2D	Dihedral Group (D)	Tetrahedral Group (T)	Octahedral Group (O)	Roto-Inversion
1	222	23	432	$\bar{4}$
2	32			
3	422			
4	622			
6				

Stereograms



We now proceed to add mirrors to these axial groups. Before doing so, the stereographic projections of all the axial groups are shown, with the exception of the 23 and 432 groups. The stereograms for these two groups will be discussed later in the lecture, since in those cases some of the symmetry axes are inclined with respect to the plane of the stereogram, making the representations more complex.

The symmetry elements that will be added to the axial groups are mirrors and inversion. A horizontal mirror, denoted by σ_h, is a mirror plane perpendicular to the primary rotational axis. For point groups 1, 2, 3, 4, and 6, such a mirror can be added in an obvious way. In the case of 222, the mirror is added perpendicular to one of the twofold axes. For 32, the mirror is added perpendicular to the threefold axis, and similar considerations apply to the other groups. A horizontal mirror is therefore defined as a mirror plane perpendicular to the principal rotational axis.

A vertical mirror, on the other hand, contains the primary rotational axis. This configuration is illustrated accordingly (denoted by σ_v). A third type of mirror is the diagonal mirror, which lies between two rotational axes. In this case, the mirror bisects the angle between two twofold axes while containing one of them. Diagonal mirrors cannot be defined for point groups 1, 2, 3, 4, and 6, since these groups contain only a single rotational axis. In some cases, the addition of a diagonal mirror would generate additional rotational axes, thereby destroying the original symmetry. Hence, mirrors must be added with care so as not to alter the rotational symmetry of the group. Finally, an inversion center may also be added, as illustrated, and this requires little additional explanation.

We now proceed to construct the thirty-two crystallographic point groups. Of these, twelve axial groups have already been identified, and we now generate the remaining groups. The top row of the table shows the first three axial groups, namely groups 1, 2, and 3, along with their Schoenflies notations C_1, C_2, and C_3.

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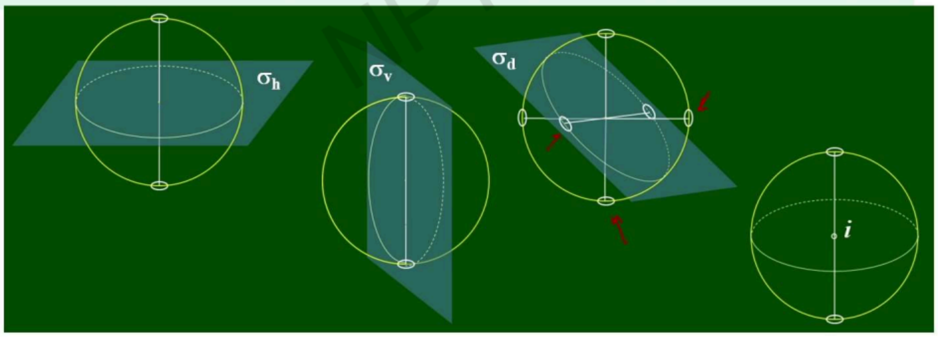
Development of the 32 Crystallographic Point Groups

	Axial Groups											
	1	2	3	4	6	222	32	422	622	23	432	$\bar{4}$

Add other symmetry elements to the axial groups: *σ_h : horizontal mirror* *σ_v : vertical mirror* *σ_d : diagonal mirror* *i: inversion centre*



In the second row, a horizontal mirror is added. Consider first the case of point group 1. Since there was no symmetry to begin with, the addition of a horizontal mirror introduces a new symmetry element. The stereogram then shows a blue filled circle and a red open circle. In this notation, the blue color indicates that the point lies in the upper hemisphere of the sphere used for stereographic projection, while the open circle indicates that the point lies below the projection plane or equatorial plane. The red color denotes a left-handed object, while blue denotes a right-handed object. With this convention, the effect of the horizontal mirror is clear: the blue dot in the upper hemisphere is reflected downward to a red open circle, with a change in handedness due to reflection.

Next, consider adding a horizontal mirror to point group 2. In this case, there are two points in the upper hemisphere, and both are reflected downward through the mirror, resulting in the corresponding arrangement of motifs. In the accompanying figure, one diagram shows the motifs, while the adjacent diagram shows the symmetry elements. The central twofold rotational axis is indicated, and the circumference of the stereogram is drawn as a bold black line to represent the mirror. Within the twofold rotational symmetry, a small white circle indicates the presence of inversion. The point group notation in this case is $2/m$, indicating that the mirror is perpendicular to the twofold axis. In Schoenflies notation, this corresponds to adding a horizontal mirror to the cyclic group C_2.

When a horizontal mirror is added to the threefold rotation axis, the mirror is again perpendicular to the threefold axis, and the projection plane itself serves as the mirror, represented by the bold black circle. The three points in the upper hemisphere are reflected downward, with a change in handedness. This group has already been encountered in the discussion of rotoinversion symmetry as $\overline{6}$, which can be decomposed into a threefold rotation and a mirror. The Schoenflies notation reflects this by appending h to C_3.

Now consider the addition of a vertical mirror. If a vertical mirror is added to point group 1, the mirror reflects the point laterally, with a change in handedness. This configuration corresponds simply to the point group m, differing only in perspective. Adding a vertical mirror to point group 2 places the twofold axis within the mirror plane. As discussed earlier in the context of two-dimensional point groups, the presence of a twofold axis within a mirror plane automatically generates a second mirror perpendicular to the first. Consequently, the point group becomes $2mm$, identical in form to the corresponding two-dimensional point group, and the Schoenflies notation is C_{2v}, indicating the presence of vertical mirrors.

Similarly, a vertical mirror can be added to the threefold rotation axis. The resulting symmetry is evident from the stereogram and follows directly from the same principles. Diagonal mirrors are undefined for all groups that contain only a single rotational axis, and therefore no further cases arise here.

Add an inversion center to point group 1. This is achieved simply by placing an inversion center, indicated by a small circle, and that becomes the only symmetry element present. In this case, an upward-pointing motif is inverted to a downward-pointing motif, accompanied by a change in handedness.

If an inversion center is added to point group 2, one essentially obtains the same group that was already discussed, namely the $2/m$ point group. This can be understood by noting that the addition of inversion generates symmetry elements that already exist in that group, and hence no fundamentally new point group is produced.

Now, consider adding an inversion center to the threefold rotational axis. This results in a threefold rotoinversion axis, which we have already encountered in the previous lecture. Similarly, adding a horizontal mirror to the fourfold rotational axis produces the corresponding stereograms, and adding a horizontal mirror to the sixfold rotational axis also yields stereograms that are straightforward to interpret.

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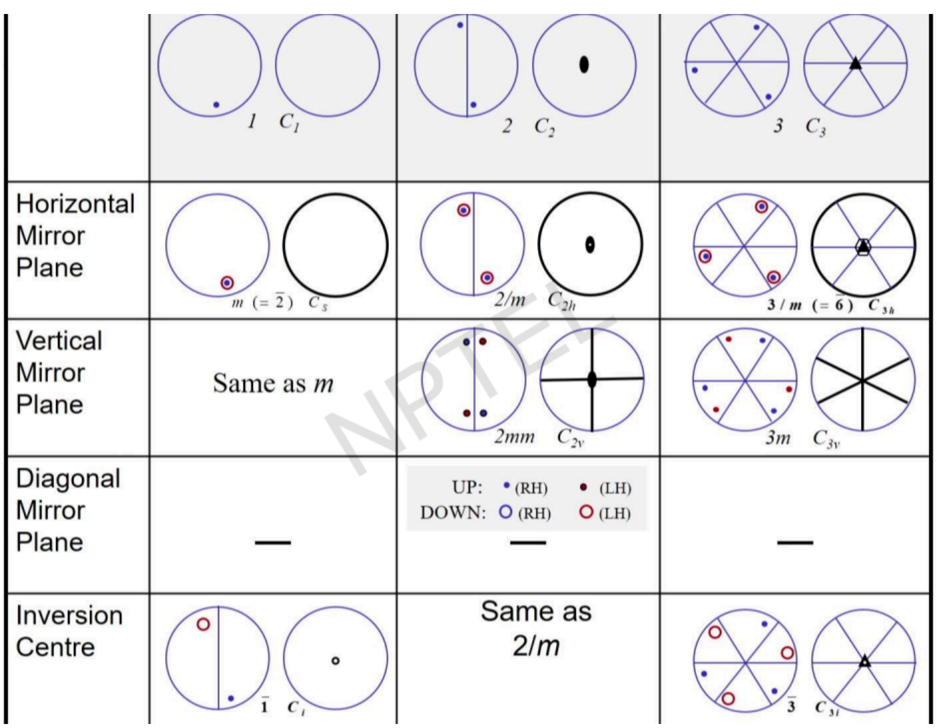

Next, consider the 222 point group. When a horizontal mirror is added, it is perpendicular to one of the twofold axes. The stereogram changes accordingly, as can be observed. This operation generates two additional mirrors: one mirror perpendicular to the horizontal mirror, and a third mirror lying in the equatorial plane. All these mirrors are mutually perpendicular, and each mirror contains a twofold rotational axis. Consequently, this point group is denoted as $2/m\,2/m\,2/m$, since there is a mirror perpendicular to each of the twofold axes. The Schoenflies notation for this group is D_{2h}. Essentially, this group now falls under the category of dihedral groups. The original 222 group corresponds to the D_2 group, and the addition of the horizontal mirror is indicated by the suffix h.

Next, consider adding vertical mirrors to the point group 4. The vertical mirror contains the fourfold axis. As recalled from earlier discussions, this operation generates a mirror perpendicular to it, as well as mirrors that bisect the angles between these two perpendicular mirrors. Thus, mirrors appear at 45° orientations. The Schoenflies notation for this group is C_{4v}, and the international notation is simply $4mm$. This point group can be viewed as a direct extension of the corresponding two-dimensional plane group.

Similarly, adding vertical mirrors to the sixfold rotational axis yields a group that is directly obtained by extending the $6mm$ point group from two dimensions. This should be clear from the earlier discussion.

If a vertical mirror is added to the 222 point group, the vertical mirror will also contain a twofold axis. As a result, two more mirrors are generated, and the resulting point group is identical to the one already discussed. Therefore, it is not listed separately.

Now consider the case of adding a diagonal mirror. A diagonal mirror is undefined for the point groups 4 and 6, but it can be introduced for the point group 222. When a diagonal mirror is added, a perpendicular mirror is generated due to the twofold rotational symmetry. Upon reflection in this diagonal mirror, motifs undergo a change in handedness, and the resulting stereogram reflects this operation. An additional mirror also appears as a consequence of symmetry. The resulting point group can be analyzed as follows. The principal axis is a $\bar{4}$ axis, that is, a fourfold rotoinversion axis. We have already seen that a subset of the fourfold rotoinversion axis includes a twofold axis, often indicated by a dark ellipse within a square in stereographic representations. In international notation, only the independent symmetry elements are listed, giving $\bar{4}2m$. The Schoenflies notation corresponds to a dihedral group. Importantly, adding an inversion center in this context does not generate any new point groups, so we move on.

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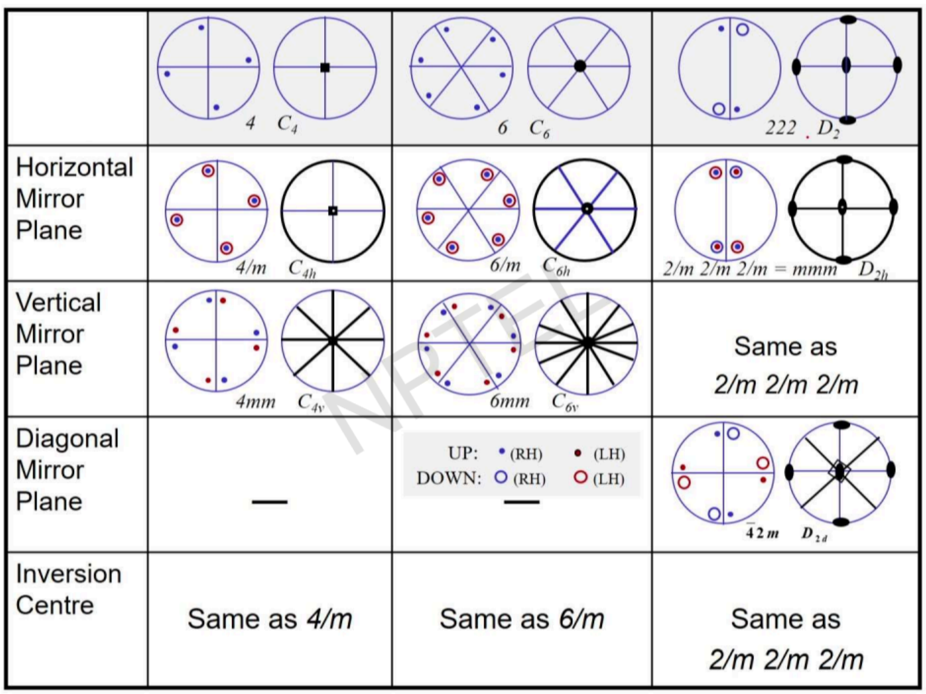

The next dihedral group to consider is the point group 32. When a horizontal mirror is added to this group, the mirror is perpendicular to one of the axes, and additional mirrors are generated by symmetry. The international notation for this group is $3/m\,m\,2$.

Moving on to the point groups 422 and 622, these are left as exercises for analysis. Similarly, the groups obtained by adding a horizontal mirror to D_4 and D_6 may be analyzed independently. Adding vertical mirrors to the top axial threefold point groups does not generate any new point groups, and we can proceed to the case of diagonal mirrors.

In this case, a diagonal mirror is added between two twofold axes. The threefold rotational axis then rotates this diagonal mirror by 120°, generating two additional mirrors. The stereogram can be constructed by starting from the 32 point group, adding the diagonal mirrors, and reflecting the motifs accordingly, which results in additional motifs with a change in handedness.

If a diagonal mirror is added to the point group 422, an interesting result emerges: a point group with an $\bar{8}$ axis, that is, an eightfold rotoinversion axis. Since the eightfold axis is non-crystallographic, such a group is not of interest. A similar situation arises when a diagonal mirror is added to 622, resulting in a twelvefold rotoinversion axis, which is also non-crystallographic. Again, adding an inversion center produces nothing new, and we move on.

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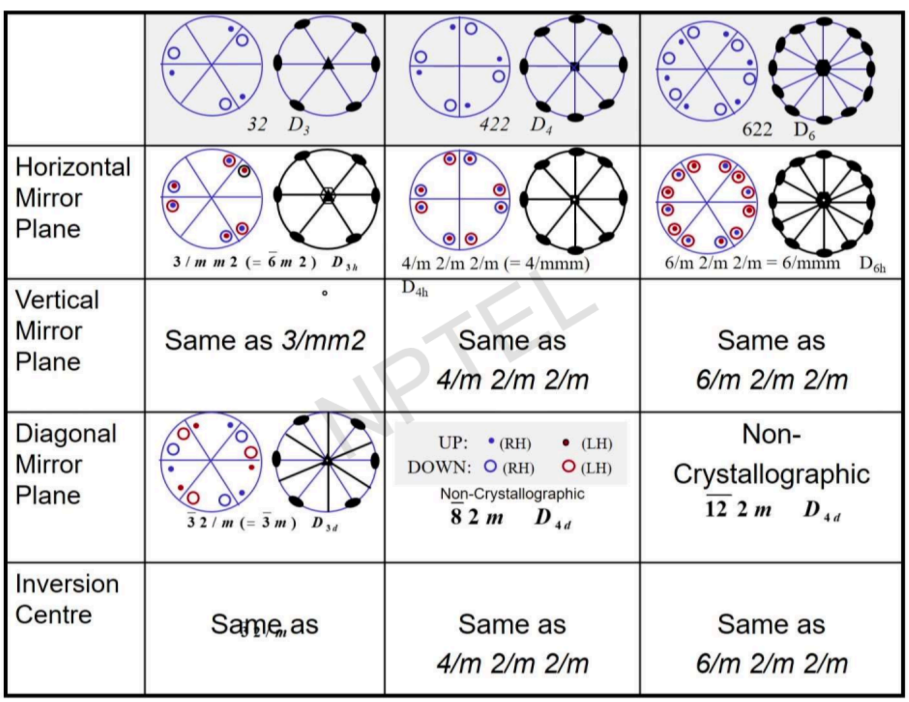

Next, we consider the cubic point groups. Before doing so, recall the $\bar{4}$ axis, or fourfold rotoinversion axis, which in Schoenflies notation is denoted as S_4. This was discussed in the previous lecture, so it does not require further elaboration here. Adding horizontal or vertical mirrors or an inversion center to this group merely reproduces point groups that have already been discussed. A diagonal mirror cannot be added in this case, since there is only a single $\bar{4}$ axis and the concept of a diagonal mirror is undefined.

We now turn to the tetrahedral point groups, beginning with 23. In an enlarged stereographic projection, the threefold axes are observed to run along the body diagonals of the cube. These axes are not oriented at 90° to each other, and they appear accordingly in the stereogram. When projecting from the sphere, each rotational axis drawn from the center intersects the sphere at points that are then projected onto the plane. There are four threefold axes in the 23 group. The twofold rotational axes are perpendicular to the cube faces and therefore appear at the center and the periphery of the stereogram. There are three mutually perpendicular twofold axes: one horizontal, one vertical, and one perpendicular to the plane of the figure. Since this is a purely axial group, there is no change in handedness of the motifs.

Now consider adding a horizontal mirror to the 23 point group. The horizontal mirror lies in the equatorial plane of the sphere. All motifs above the plane are reflected below, with a corresponding change in handedness. The twofold axes remain unchanged, as do the threefold axes. However, the threefold axes are now indicated with an open circle, signifying that they have become threefold rotoinversion axes. The group is denoted as $2/m$, indicating that the twofold axis is perpendicular to the mirror, and $\bar{3}$ denotes the rotoinversion axis. This case is relatively straightforward.

Next, consider the point group T_d, which is obtained by adding a diagonal mirror to the 23 point group. Here, T denotes the tetrahedral group in Schoenflies notation. The diagonal mirror introduces a fourfold rotoinversion axis, and the threefold axes remain at their original locations. There are three fourfold rotoinversion axes, mutually perpendicular to each other: one perpendicular to the plane of the figure, one horizontal, and one vertical. The international notation for this point group is $\bar{4}3m$, and the Schoenflies notation is T_d.

We are now left with the octahedral axial group and the group obtained by adding a horizontal mirror to it. In the octahedral axial group, fourfold, threefold, and twofold axes are combined. The stereographic projection reveals the angular relationships among these axes. As this is a purely axial group, there is no change in handedness of the motifs.

When a horizontal mirror is added to this group, the resulting group is denoted by the Schoenflies notation O_h, indicating the octahedral group with a horizontal mirror. The international notation reflects the presence of a mirror perpendicular to the fourfold axis.

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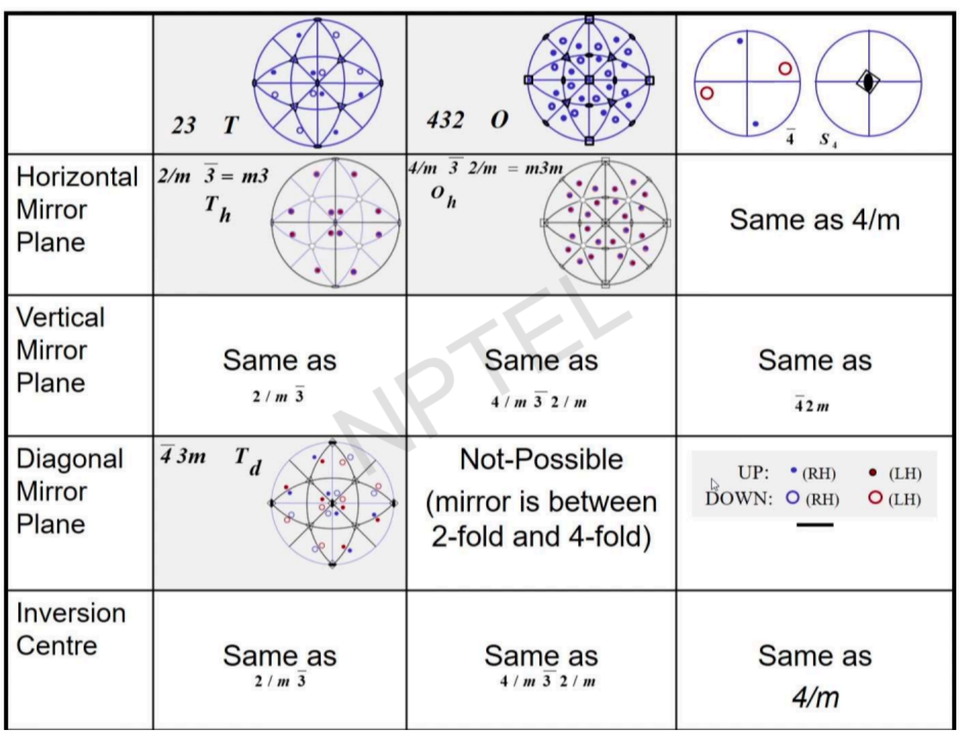

	23 T	432 O	$\bar{4}$ S_4
Horizontal Mirror Plane	$2/m\ \bar{3} = m3$ T_h	$4/m\ \bar{3}\ 2/m = m3m$ O_h	Same as 4/m
Vertical Mirror Plane	Same as $2/m\ \bar{3}$	Same as $4/m\ \bar{3}\ 2/m$	Same as $\bar{4}2m$
Diagonal Mirror Plane	$\bar{4}3m$ T_d	Not-Possible (mirror is between 2-fold and 4-fold)	UP: • (RH) • (LH) DOWN: ○ (RH) ○ (LH)
Inversion Centre	Same as $2/m\ \bar{3}$	Same as $4/m\ \bar{3}\ 2/m$	Same as 4/m

In an enlarged diagram, one can observe that adding a single horizontal mirror generates several additional mirrors due to the presence of other rotational axes. The curved lines seen in the stereographic projection represent great circles, which correspond to mirror planes projected onto the plane. These mirrors appear at various orientations as a result of the combined symmetry operations of the twofold and threefold axes.

If a vertical mirror is added to the 432 point group, the resulting point group is the same as that obtained by adding a horizontal mirror. This is because the addition of a horizontal mirror automatically generates vertical mirrors through symmetry operations. Adding a diagonal mirror to 432 is not possible. If one attempts to add a diagonal mirror, the twofold axes would be reflected onto the fourfold axes and vice versa, thereby destroying the symmetry. Consequently, such an operation is not allowed.

Adding an inversion center once again produces the same group as the octahedral group with a horizontal mirror. At this point, we have completed the discussion of all 32 possible point groups in three dimensions.

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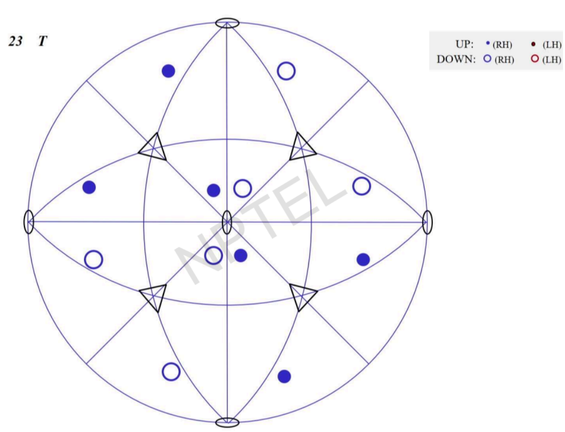

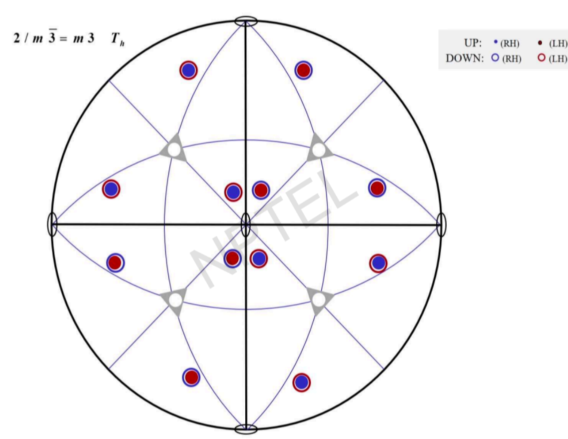

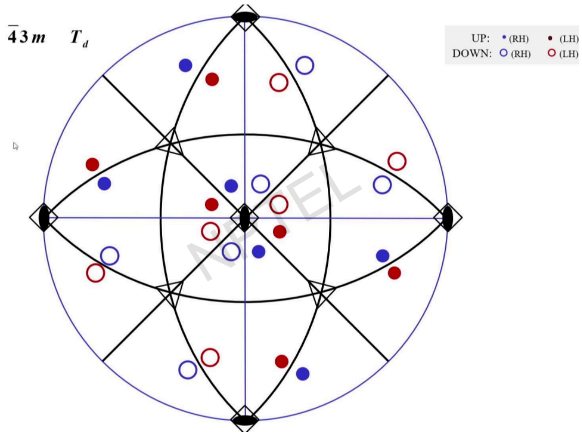

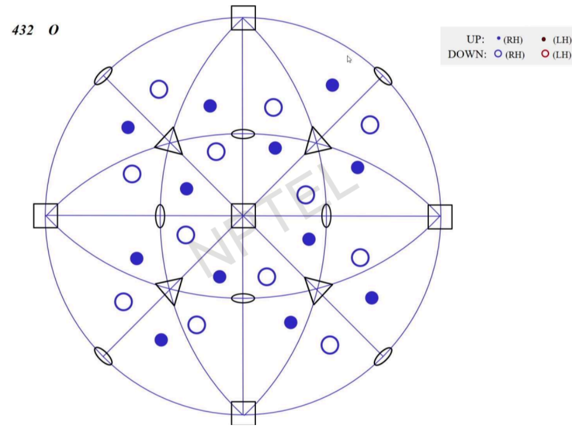

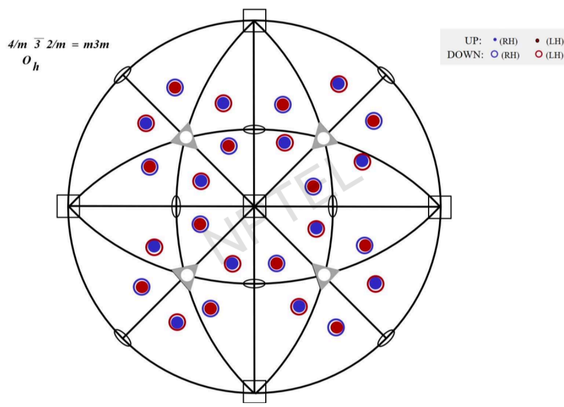

In the subsequent lectures, we will examine the three-dimensional Bravais lattices and how they emerge from symmetry considerations. We will then add symmetry elements to these lattices to obtain the space groups in three dimensions.