# CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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## Lecture 32: Combination of Three Rotation Axes in 3D - II

In the previous lecture, certain equations were derived from which it is possible to deduce how three rotation axes, meeting at a single point in three-dimensional space, can be combined. The solution obtained was presented in the slide, where three rotation axes $A$, $B$, and $C$ were considered. Axis $A$ has a rotation of α, axis $B$ has a rotation of β, and axis $C$ has a rotation of $\gamma$.

From this configuration, a spherical triangle is constructed whose interior angles are $\alpha/2$, $\beta/2$, and $\gamma/2$. The angles between the rotation axes are defined such that the angle between axes $A$ and $B$ is $c$, the angle between $A$ and $C$ is $b$, and the angle between $B$ and $C$ is $a$. The equations derived relate the rotation angles α, β, and γ to the interaxial angles $a$, $b$, and $c$. One specific problem that was solved involved three twofold rotation axes meeting at a point. It was shown that the only way such axes can meet is when the angles $a$, $b$, and $c$ are all $90^{\circ}$, implying that the twofold rotation axes are mutually orthogonal.

In this lecture, a more general case is considered. Let us examine a combination of axes of the type $n22$. In this case, there is one $n$-fold rotation axis and two twofold rotation axes. The $n$-fold axis is placed along $A$, while the two twofold axes are placed along $B$ and $C$. Consequently, the rotation angles are $\alpha = 2\pi/n$, $\beta = \pi$, and $\gamma = \pi$.

The objective is to determine the angles $a$, $b$, and $c$. Substituting $\alpha = 2\pi/n$ and $\beta = \gamma = \pi$ into the three equations, one finds that

$$cos a = cos\left(\frac{\pi}{n}\right),$$

which implies that angle $a$ is simply $\pi/n$. Further, $cos b = cos c = 0$, which means that the angles $b$ and $c$ are each equal to $90^\circ$. This provides the solution to the more general case.

It is now instructive to examine different values of $n$. The angles $b$ and $c$ are always $90^\circ$. If $n = 2$, corresponding to a twofold rotation axis, angle $a$ is $\pi/2$ or $90^\circ$, which is the same result obtained earlier for the combination of three twofold rotation axes. For $n = 3$, angle $a = \pi/3$ or $60^\circ$. For $n = 4$, angle $a = \pi/4$ or $45^\circ$. Finally, for the last crystallographic axis, a sixfold axis, $n = 6$, angle $a = \pi/6$ or $30^\circ$.

Essentially, angle $a$ is the angle between the axes associated with $\beta$ and $\gamma$. In the present case, $\beta$ and $\gamma$ are both $\pi$, corresponding to twofold rotation axes. Thus, angle $a$ is the angle between the twofold rotation axes, while angles $b$ and $c$ represent the angles that the twofold rotation axes make with the $2\pi/n$ axis, each being $90^\circ$.

Consider now the case $n = 3$. The case $n = 2$ has already been discussed previously. For $n = 3$, angle $a$ is $60^\circ$. Pictorially, one can draw a threefold rotation axis vertically. There is one twofold rotation axis and a second twofold rotation axis, both at $90^\circ$ to the threefold axis. The threefold axis generates a third twofold axis as well. In this configuration, all the twofold rotation axes lie in a horizontal plane, each making an angle of $90^\circ$ with the threefold rotation axis, while the angles between the twofold rotation axes are $60^\circ$.

This arrangement corresponds to a three-dimensional point group. The notation for this point group is 32. Only two characters are used because all the twofold rotation axes are related through the action of the threefold rotation axis, that is, by a rotation of $120^\circ$ about the threefold axis.

Next, consider $n = 4$. In this case, there is a fourfold rotation axis, around which several twofold rotation axes are arranged. Again, the twofold rotation axes are at $90^{\circ}$ to the fourfold rotation axis. All the twofold rotation axes lie in the same plane, and the angle between adjacent twofold axes is $45^{\circ}$, while each twofold axis is perpendicular to the fourfold axis. This point group is denoted by 422.

Now consider $n = 6$. Here, there is a sixfold rotation axis around which several twofold rotation axes are arranged. The twofold axes are again at $90^{\circ}$ to the sixfold axis, while the angles between the twofold axes are $30^{\circ}$. The corresponding point group is denoted by 622. These are examples of axial point groups involving only rotational symmetries.

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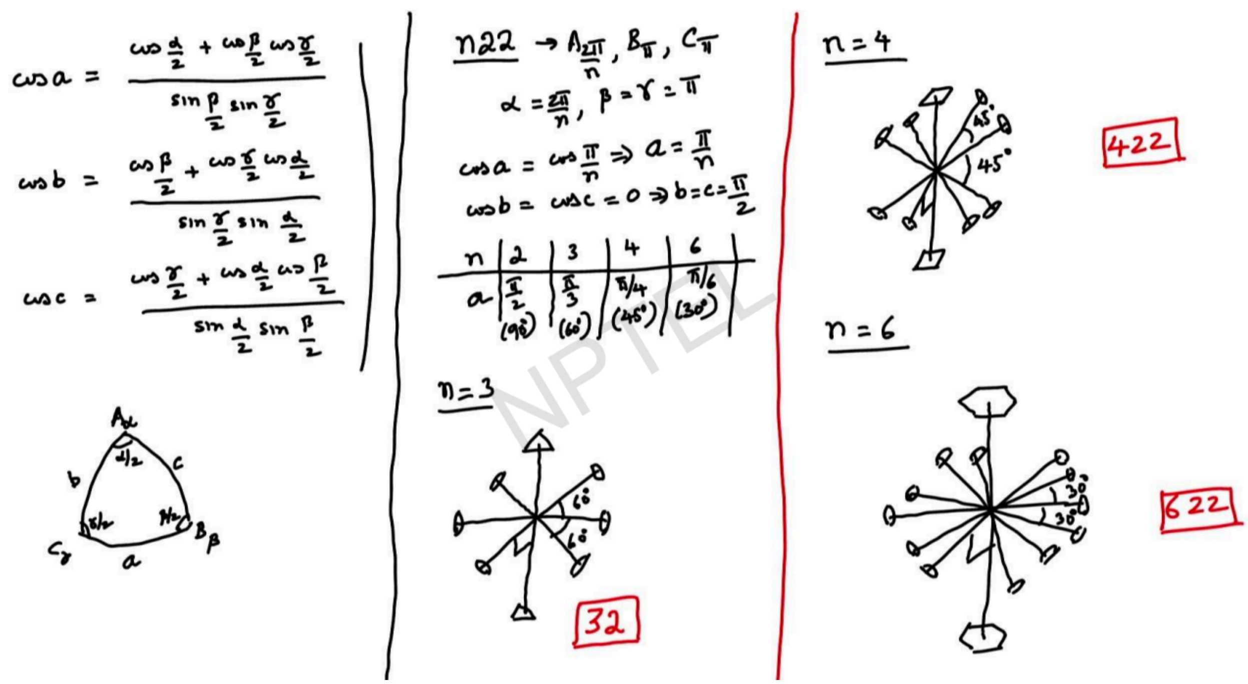


Let us now consider a different combination, namely 642. In this case, there is a sixfold rotation axis, a fourfold rotation axis, and a twofold rotation axis. The rotation angles are $\alpha = 2\pi/6$, $\beta = 2\pi/4$, and $\gamma = \pi$, corresponding to $60^{\circ}$, $90^{\circ}$, and $180^{\circ}$, respectively. Substituting these values into the equations, one obtains

$$cosa = \frac{\sqrt{3}}{2} . \frac{\sqrt{2}}{1} = \frac{\sqrt{3}}{\sqrt{2}}.$$

Similarly, one finds $cosb = \sqrt{2}$ and $cosc = \sqrt{3}$. All these values are greater than 1, which is not physically meaningful, since the cosine of an angle must lie between $-1$ and $+1$. Therefore, no angles $a$, $b$, and $c$ can be defined for this combination, and it is an invalid combination. Hence, no point group can be formed from the combination of sixfold, fourfold, and twofold rotation axes.

Consider next the combination 233. In this case, $\alpha = \pi$ and $\beta = \gamma = 2\pi/3$. Substituting these values into the equations yields $a = 70.5^{\circ}$ and $b = c = 54.7^{\circ}$. Another combination is 432, for which $\alpha = 90^{\circ}$, $\beta = 120^{\circ}$, and $\gamma = 180^{\circ}$. The resulting angles are $a = 35.3^{\circ}$, $b = 45^{\circ}$, and $c = 54.7^{\circ}$.

To better understand these combinations, it is useful to draw the corresponding spherical triangles. For the 233 case, there is a twofold rotation axis with rotation $\pi$, and two threefold rotation axes with rotations $2\pi/3$. The angles between the rotation axes are labeled $A$, $B$, and $C$. For the 432 case, the axes correspond to a fourfold rotation ($2\pi/4$), a threefold rotation ($2\pi/3$), and a twofold rotation ($\pi$), with interaxial angles labeled $a$, $b$, and $c$.

One may now ask what kind of object can exhibit these combinations of rotation axes. A canonical example is the cube. A cube can accommodate both the 233 and 432 combinations. In the 233 case, the threefold rotation axes lie along the body diagonals of the cube, while the twofold rotation axes are parallel to the cell edges. The angle $a = 70.5^{\circ}$ corresponds to the angle between two threefold rotation axes, while angles $b$ and $c$, equal to $54.7^{\circ}$, correspond to the angles between a twofold and a threefold rotation axis.

In the 432 case, the fourfold rotation axes are parallel to the cube edges, the threefold rotation axes remain along the body diagonals, and the twofold rotation axes join the midpoints of opposite edges. In this configuration, the angle between the twofold and threefold axes is $35.3^{\circ}$, the angle between the twofold and fourfold axes is $45^{\circ}$, and the angle between the threefold and fourfold axes is $54.7^{\circ}$.

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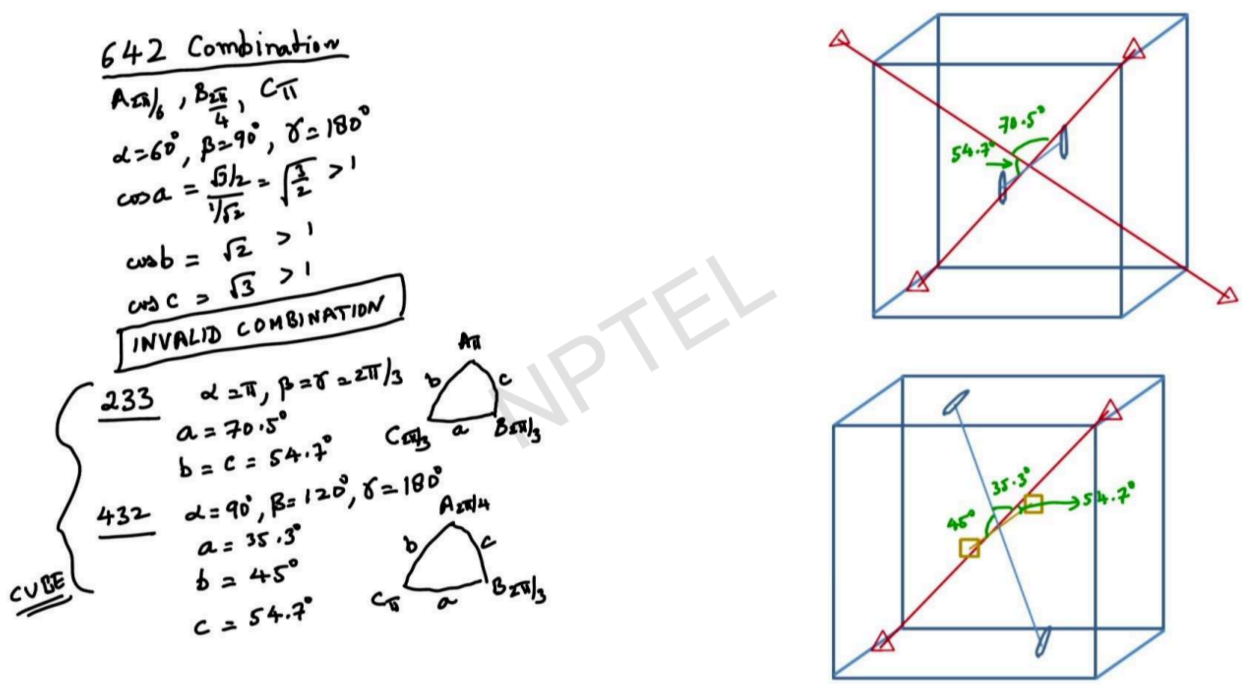


Allowing these axes to operate on one another generates the full symmetry of the object. In the 233 case, the threefold rotations generate twofold axes parallel to all cell edges, and threefold axes along all body diagonals. In the 432 case, fourfold axes appear along all cell edges, threefold axes along the body diagonals, and twofold axes joining the midpoints of all pairs of opposite edges. These features are evident in the corresponding diagrams.

The point group corresponding to the 233 combination is denoted by 23, and the point group corresponding to the 432 combination is denoted by 432. A point of caution is necessary here. For the $n22$ combination, the notation used was 32, whereas here the notation is 23. These represent two distinct point groups, differing only in the order of the symbols.

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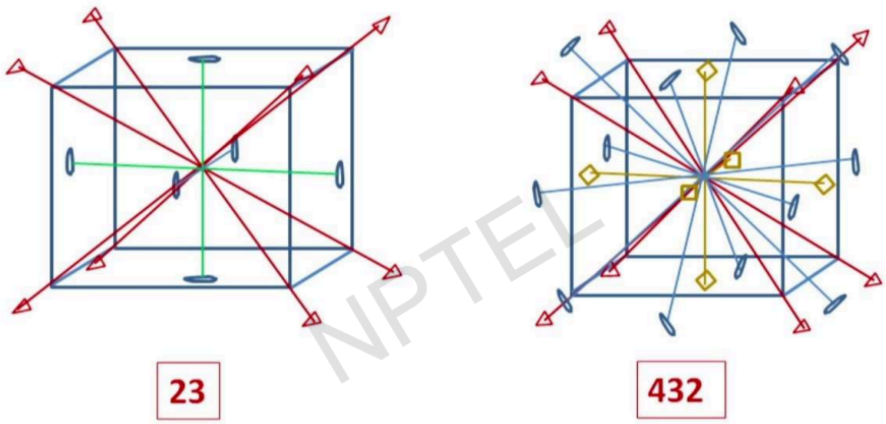




Finally, consider a combination involving a rotation axis and a mirror plane. Take a threefold rotation axis with a mirror plane perpendicular to it. Consider a motif labeled 1, which is right-handed. A right-handed threefold rotation of $120^{\circ}$ moves this motif to position 2, and a further $120^{\circ}$ rotation moves it to position 3. All three motifs lie in the same horizontal plane above the mirror. The mirror reflects these motifs to positions 4, 5, and 6, which are left-handed counterparts of motifs 1, 2, and 3, respectively.

Consider the transformation from motif 1 (right-handed) to motif 5 (left-handed). One way to achieve this is to rotate motif 1 by $120^{\circ}$ to motif 2 and then reflect it. This two-step operation is called *roto-reflection symmetry*. It is a point symmetry operation because there is an invariant point at the intersection of the mirror plane and the threefold rotation axis.

An alternative description is to rotate motif 1 by $-60^{\circ}$ and then performs an inversion. This operation is called *roto-inversion*. Both operations lead to the same result. For a $120^{\circ}$ rotation followed by reflection, the notation used is a threefold symbol with a tilde, indicating threefold roto-reflection. For the second case, involving a $60^{\circ}$ rotation followed by inversion, the notation is a sixfold symbol with a bar on top, indicating sixfold roto-inversion. Since both descriptions are equivalent, the preferred notation is that of roto-inversion. Thus, a $\bar{6}$ operation is equivalent to threefold roto-reflection.

Henceforth, only roto-inversion will be used. The crystallographic roto-inversion symmetries are $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$.

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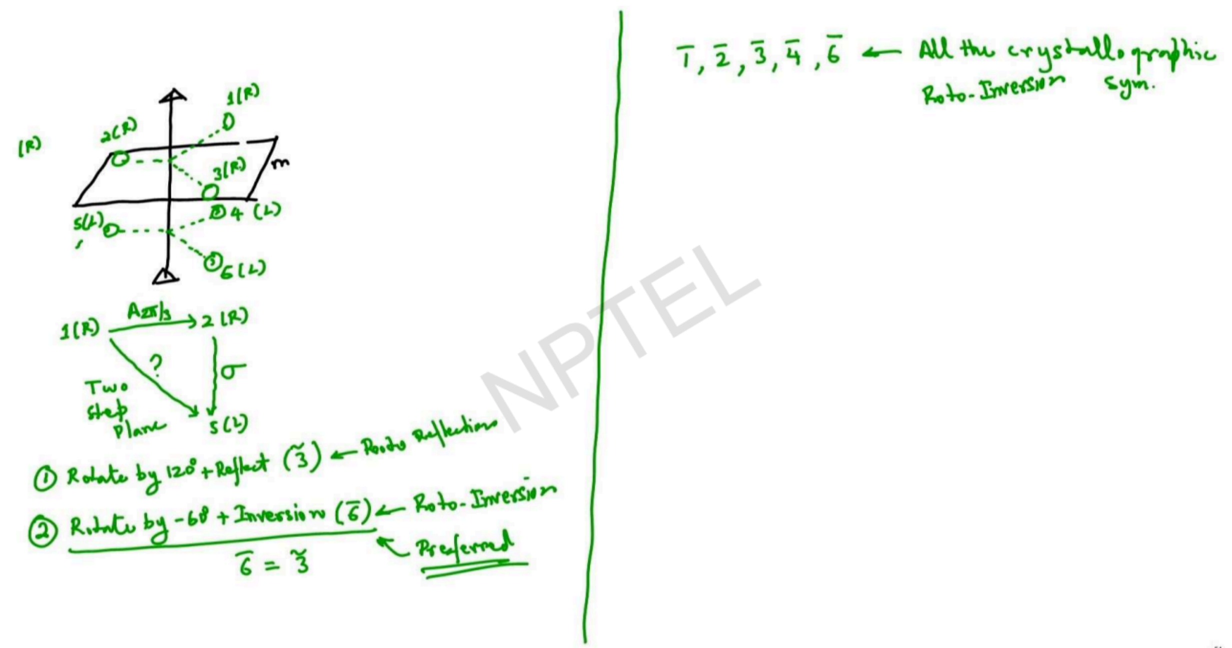


In the next lecture, a more effective method for representing three-dimensional symmetries will be introduced. Drawing three-dimensional diagrams can be confusing and tedious, so a systematic approach for representing these symmetries on a two-dimensional plane will be developed.