CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES
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Lecture 39: Decoding the International Tables - II

So, this is the final lecture on the crystal symmetry part of this course. Before getting into what we will do in this lecture, which is to take another look at the *International Tables for Crystallography, Volume A* that we had earlier discussed while studying plane groups, I want to examine these tables now from the perspective of three-dimensional space groups. Before doing so, it is useful to briefly summarize what we covered in the last couple of lectures.

We discussed glide planes in considerable detail and also examined screw axes. However, in the earlier lectures, the six-fold screw axis was not discussed explicitly. Therefore, let me first summarize all the possible screw axes that can occur in space groups. In general, a screw axis is written as n_m, where $m < n$, and m can take integer values from 1 up to $n - 1$. For example, if we consider a two-fold screw axis, m can only be 1. For a three-fold screw axis, m can be either 1 or 2, and so on.

The operation associated with a screw axis consists of a rotation by $\frac{2\pi}{n}$ followed by a screw translation vector τ, where $\tau = \frac{m}{n}$ times the lattice translation along the direction of the screw axis. This translation is a lattice translation along the screw axis itself. For instance, if we consider a 2_1 screw axis, the operation involves a rotation of π, followed by a translation of half a lattice parameter along the axis. Here, $m = 1$ and $n = 2$. If we consider a 3_2 screw axis, the operation consists of a rotation of $\frac{2\pi}{3}$ or 120 degrees, followed by a translation equal to $\frac{2}{3}$ of the lattice translation along the axis. These concepts have already been discussed earlier and are summarized here for completeness.

Now, let us list all the possible crystallographic screw axes and their graphical symbols. We begin with the pure two-fold rotation axis, whose graphical symbol is an ellipse. The two-fold screw axis 2_1 is represented by a similar ellipse, but with two fins extending from either end to indicate the screw component.

Next, we have the pure three-fold rotation axis, represented by a triangle. The 3_1 screw axis is depicted by a triangle with fins extending in one direction, whereas the 3_2 screw axis is drawn using the same triangular base, but with the fins extending in the opposite direction.

For the pure four-fold rotation axis, the graphical symbol is a square. The 4_1 screw axis is drawn by starting with a square and extending fins in a manner analogous to the three-fold case. We also have 4_2 and 4_3 screw axes. For 4_3, the fins are extended in the opposite direction compared to 4_1. In the case of 4_2, the square has only two fins, one at the top and one at the bottom, and this symbol also reflects the presence of a pure two-fold rotation as a subset of the 4_2 screw symmetry.

Now, consider the six-fold case. As discussed earlier, for a general screw axis n_m, m can take values from 1 to $n - 1$. Therefore, for a six-fold axis, there are five possible screw axes: 6_1, 6_2, 6_3, 6_4, and 6_5. The pure six-fold rotation axis is represented by a hexagon. The 6_1 screw axis is obtained by starting with the hexagon and extending fins in one direction. For 6_5, the fins are extended in the opposite direction compared to 6_1, which becomes evident when the two symbols are compared.

For 6_2, the hexagon is drawn with three fins, clearly indicating that a pure three-fold rotation is a subset of the 6_2 screw symmetry. The 6_4 screw axis also contains a pure three-fold rotation as a subset, but the fins are drawn in the opposite direction relative to

6_2. Finally, for the 6_3 screw axis, the symbol again starts with a hexagon, but only two fins are drawn, indicating that a pure two-fold rotation is a subset of the 6_3 screw symmetry. This completes the summary of all crystallographically allowed screw axes.

With this background, let us now return to the *International Tables for Crystallography, Volume A*. We have already examined these tables for plane groups, and now we will look at a few examples involving space groups. As a first example, consider the space group $C121$. Here, the letter C indicates an end-centered lattice, and the presence of a

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two-fold rotation implies that this space group belongs to the monoclinic crystal system. Specifically, it is an end-centered monoclinic lattice with the C face as the centering face, and the unique axis is $\bar{b}$, as discussed earlier.

Examining the corresponding diagram in the international tables, the base appears as a parallelogram corresponding to the AC face, with the b axis perpendicular to this face.

The two-fold rotational symmetry is shown, and these two-fold axes are populated at the corners as well as at the edge centers. If a motif is placed above the plane, a 180-degree rotation will map it to another position while remaining above the plane, with no change in handedness. All such motifs are related through lattice translations.

There is also a centering translation corresponding to the lattice point at the center of the C face, or equivalently the AB face, since the b axis is perpendicular to the diagram. This centering translation corresponds to a shift of $\frac{1}{2}\bar{a} + \frac{1}{2}\bar{b} + 0c$. Applying this translation moves motifs to half-plus positions, resulting in additional motifs appearing in the diagram. The arrangement obtained in this way is identical to the motif-only diagram shown in the international tables.

In this diagram, if we label motifs as 1, 2, and 3, then going from motif 1 to motif 3 involves a screw axis located at an intermediate position, and similar screw axes appear at other equivalent locations. The diagram shown corresponds to a projected view, with the projection taken along the unique b axis.

Another diagram in the tables shows a different projection, namely along the a axis. In this case, the projected face is the BC rectangle. The b axis and the projected c axis, denoted $\bar{c}_p$, are shown, along with the origin. In this projection, all the two-fold rotation axes and the two-fold screw axes that lie along the a direction line up and project onto the same line. This is indicated by a half-arrow symbol, showing that both pure two-fold and two-fold screw axes are being projected onto the same position.

In contrast, when the projection is taken along the c axis, the two-fold rotation axes and the two-fold screw axes become distinguishable in the plane of the diagram. In this view, one can clearly see separate symbols corresponding to 2 and 2_1 axes, all lying in the plane of the diagram. These diagrams therefore represent different perspectives of the same space group.

The space group $C2$ is the short symbol used in the list of the 230 space groups, and it corresponds to space group number 5. The associated point group is point group 2. The tables also specify that the origin lies on a two-fold axis. The asymmetric unit is defined by the ranges $0 \leq x \leq \frac{1}{2}$, $0 \leq y \leq \frac{1}{2}$, and $0 \leq z \leq 1$. Unlike plane groups, where the asymmetric unit is an area, here it is a volume element in three-dimensional space.

Interpreting this asymmetric unit, with C taken along the z direction, z varies from 0 to 1, a corresponds to x varying from 0 to $\frac{1}{2}$, and b corresponds to y varying from 0 to $\frac{1}{2}$. Thus, the asymmetric unit extends halfway along the $\overline{b}$ direction. The listed symmetry operations include the identity operation, which is always present, and a two-fold rotation located at $(0, y, 0)$, indicating that the two-fold axis passes through all points with arbitrary y values along that axis. Additional symmetry operations arise from the centering translation, combined with two-fold rotations at positions such as $(0, \frac{1}{2}, 0)$ and $(\frac{1}{4}, y, 0)$.

As in the case of plane groups, not all symmetry operations are listed as generators. The generators include the fundamental translation symmetries along $\overline{a}$, $\overline{b}$, and $\overline{c}$, the centering translation, and selected rotational symmetries. The notation "1" in brackets refers to the identity operation, while "2" refers to the two-fold rotation at $(0, y, 0)$. This completes the discussion for this example and illustrates how the international tables describe three-dimensional space groups.

So, these are all the minimal set of generators required to produce the entire space group. Now, once again, we come to the Wyckoff positions, analogous to what we had seen earlier in the case of plane groups. Starting here, this is the general position, and it has a multiplicity of 4. By general position, we mean that all of these motifs that you see are representing the general positions. So, this is actually a general position.

There should be four coordinates associated with this, but you only see two coordinates written. We start from (x, y, z). When there is a two-fold rotation and the two-fold axis is along y, which is the unique axis, the other two coordinates will change. Specifically, x will go to $-x$ and z will go to $-z$. So, this gives only two coordinates. However, since the multiplicity is 4, there should be two more coordinates.

To obtain these, we first add $(0, 0, 0)$ to these two coordinates, which gives the same coordinates. Then we add $(\frac{1}{2}, \frac{1}{2}, 0)$. This gives the third coordinate as $(x + \frac{1}{2}, y + \frac{1}{2}, z)$, and the fourth coordinate will be $(\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z})$. That is how we obtain four positions. You can also see that there are four general positions inside the unit cell, which we can label as 1, 2, 3, and 4.

For the general position, we could have given coordinates for each of these, but instead of doing that, we select a unique set of four coordinates for convenience. Now, these are the special positions. The site symmetry is 2 in both cases. One is at $(0, y, 0)$, which corresponds to a two-fold axis passing through the origin, and the other is at $(0, y, \frac{1}{2})$, which corresponds to a two-fold axis passing through the center.

Once again, the multiplicity is 2 in both cases, but you only see one coordinate listed. The second coordinate can be obtained by adding $(\frac{1}{2}, \frac{1}{2}, 0)$, just as we did earlier. So, for example, this gives $(\frac{1}{2}, y + \frac{1}{2}, 0)$ and $(\frac{1}{2}, y + \frac{1}{2}, \frac{1}{2})$. These are the various positions corresponding to the special positions. Thus, for this particular space group, there are only three Wyckoff positions.

Now, this is again a space group that we have already seen, and this is an excerpt from the International Tables. Essentially, what we have done is taken a primitive monoclinic lattice, added a two-fold screw axis, and included a glide plane where the glide direction is along c. If we look at this diagram again, the unique axis is b in this case, and the complete symbol is $P\,1\,2_1/c\,1$.

These symbols represent the screw axes, and these represent the centers of inversion. This diagram is a projection along $\bar{b}$. The next diagram is a projection along $\bar{a}$. As a result, if

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Excerpt from International Tables for Crystallography, Volume A
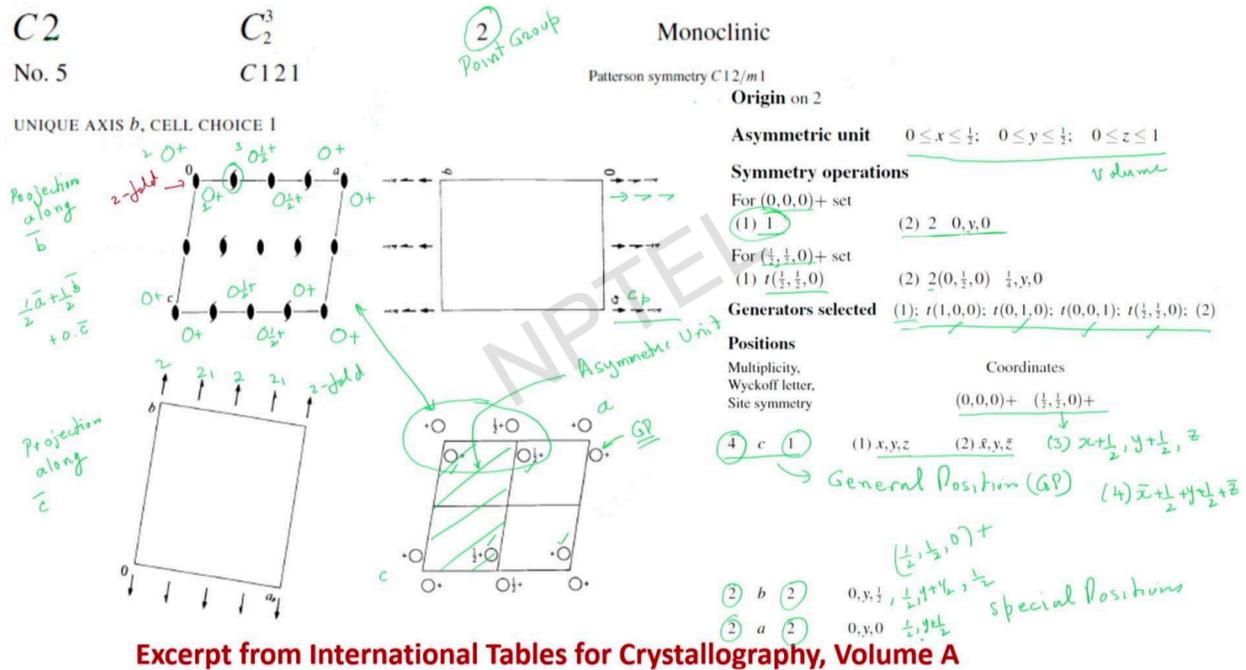
we look at the glide plane, the glide plane is the AC plane. Now, if we do a projection along $\bar{a}$, where this is the origin, this is the b axis, and this is the projected c axis, denoted as $\bar{c}_p$, the glide plane is essentially parallel to the AC plane. That is why, in this figure, the glide planes are perpendicular to the figure. The glide direction is along $\bar{c}$.

The next diagram is a projection along the c axis. In this case, you can see the screw axes indicated by half arrows, and there is a one-quarter written here, which means that the screw axis is one-quarter up in this diagram. These two diagrams essentially use the same axis system. Here this is c, this is a, and this illustrates how the general positions move when the symmetry operations are applied.

This shaded region represents the asymmetric unit, where x varies between 0 and $\frac{1}{2}$, y varies between 0 and $\frac{1}{4}$, and z varies between 0 and 1. I will leave it to you to work out how the asymmetric unit is obtained by shading the appropriate region. These are the symmetry operations present: the identity, the two-fold rotation, inversion symmetry, and the c glide.

A minimal set of generators required to generate the space group is given by the generators selected. The bracketed numbers 1, 2, and 3 refer to the corresponding symmetry operations listed earlier. These are the Wyckoff positions. The general position has a multiplicity of 4, and this shows how the general position coordinates transform under the symmetry operations. The remaining entries correspond to special positions.

You can see that the special positions occur only where there is an inversion center. There is no special position associated with the screw axis. In fact, even in the earlier case, there was no special position on the two-fold screw axis, because the screw translation prevents the formation of a special position. Even if an atom is placed on a screw axis, it will still generate the full multiplicity of the general position. The same is true for an atom placed on a glide plane. In this case, although there is a glide plane, none of the positions on it are special, and they always have the multiplicity of the general position.

Now, this is the $P222$ space group. Here, we do not have a unique axis. We simply label this as a, this as b, and the c axis is perpendicular. One can see how the general positions are distributed. We have the asymmetric unit shown here, the symmetry operations, and a relatively large Wyckoff table with many special positions. All of these are special positions, while this one corresponds to the general position.

One can study this in detail, and you should look at it carefully to understand how all positions are either general or special. If you look at the Wyckoff letters, they start from a then b, c, d, and so on, going all the way up to u. You can see that positions with multiplicity 1 occur when the special position lies at the intersection of three two-fold

Excerpt from International Tables for Crystallography, Volume A

axes. Positions with multiplicity 2 occur when the site lies on a two-fold axis. Finally, positions with site symmetry 1, meaning no symmetry, correspond to the general position with multiplicity 4.

Next, consider the $P4mm$ space group. Here, this is the a axis, this is the b axis, and this is the origin. This is space group number 99, and it belongs to the tetragonal crystal system. The asymmetric unit is defined by $0 \leq x \leq \frac{1}{2}, 0 \leq y \leq \frac{1}{2}, 0 \leq z \leq 1$, along with the additional condition $x \leq y$.

If we look at how many general positions exist within the unit cell, we can count 1, 2, 3, 4, 5, 6, 7, and 8. Therefore, the volume of the asymmetric unit must be one-eighth of the volume of the unit cell. This also explains the relationship between x and y. If this condition were not present, the entire region would be the asymmetric unit with z varying from 0 to 1. Instead, the asymmetric unit is only half of that region.
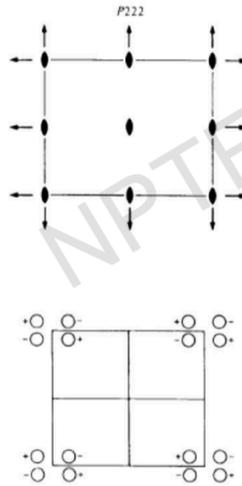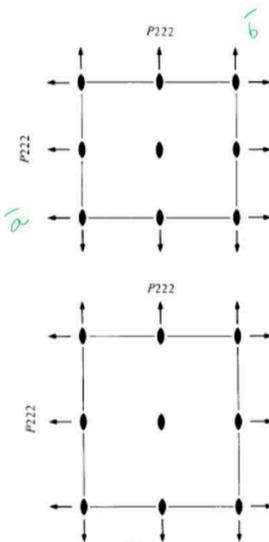
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P222 **D_2^1** 222 Orthorhombic

No. 16 P222 Patterson symmetry $Pmmm$

Origin at 222

Asymmetric unit $0 \leq x \leq \frac{1}{2}$; $0 \leq y \leq \frac{1}{2}$; $0 \leq z \leq 1$

Symmetry operations

(1) 1 (2) 2 0,0,z (3) 2 0,y,0 (4) 2 x,0,0

Excerpt from International Tables for Crystallography, Volume A

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Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions
Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

P222 *continued* **D_2^1** 222 Orthorhombic

4	u	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$

General Position

2	t	..2	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$
2	s	..2	$0,\frac{1}{2},z$	$0,\frac{1}{2},\bar{z}$
2	r	..2	$\frac{1}{2},0,z$	$\frac{1}{2},0,\bar{z}$
2	q	..2	$0,0,z$	$0,0,\bar{z}$
2	p	.2.	$\frac{1}{2},y,\frac{1}{2}$	$\frac{1}{2},\bar{y},\frac{1}{2}$
2	o	.2.	$\frac{1}{2},y,0$	$\frac{1}{2},\bar{y},0$
2	n	.2.	$0,y,\frac{1}{2}$	$0,\bar{y},\frac{1}{2}$
2	m	.2.	$0,y,0$	$0,\bar{y},0$
2	l	2..	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$
2	k	2..	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$
2	j	2..	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$
2	i	2..	$x,0,0$	$\bar{x},0,0$

1	h	222	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
1	g	222	$0,\frac{1}{2},\frac{1}{2}$
1	f	222	$\frac{1}{2},0,\frac{1}{2}$
1	e	222	$\frac{1}{2},\frac{1}{2},0$
1	d	222	$0,0,\frac{1}{2}$
1	c	222	$0,\frac{1}{2},0$
1	b	222	$\frac{1}{2},0,0$
1	a	222	$0,0,0$

Excerpt from International Tables for Crystallography, Volume A

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P4mm C_{4v}^1 4mm Tetragonal

No. 99 P4mm Patterson symmetry $P4/mmm$

Asymmetric Unit

origin b

a
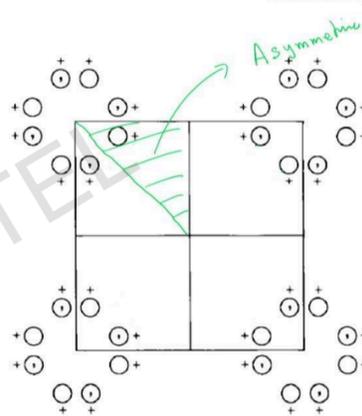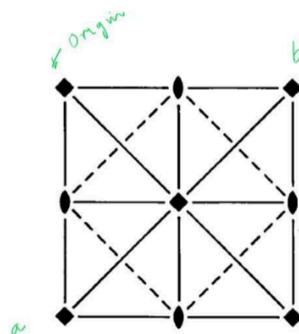
Origin on 4mm

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le 1$; $x \le y$

Symmetry operations

(1) 1 (2) 2 0,0,z (3) 4^+ 0,0,z (4) 4^- 0,0,z
(5) m x,0,z (6) m 0,y,z (7) m x,$\bar{x}$,z (8) m x,x,z

Excerpt from International Tables for Crystallography, Volume A

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P4mm
continued C_{4v}^1 4mm Tetragonal

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates		
8	g	1	(1) x,y,z (2) $\bar{x},\bar{y},z$ (3) $\bar{y},x,z$ (4) $y,\bar{x},z$	
			(5) $x,\bar{y},z$ (6) $\bar{x},y,z$ (7) $\bar{y},\bar{x},z$ (8) y,x,z	
4	f	.m.	$x,\frac{1}{2},z$ $\bar{x},\frac{1}{2},z$ $\frac{1}{2},x,z$ $\frac{1}{2},\bar{x},z$	
4	e	.m.	$x,0,z$ $\bar{x},0,z$ $0,x,z$ $0,\bar{x},z$	
4	d	..m	x,x,z $\bar{x},\bar{x},z$ $\bar{x},x,z$ $x,\bar{x},z$	
2	c	2mm.	$\frac{1}{2},0,z$ $0,\frac{1}{2},z$	
1	b	4mm	$\frac{1}{2},\frac{1}{2},z$	
1	a	4mm	$0,0,z$	

Excerpt from International Tables for Crystallography, Volume A

P3   **C₃¹**   3   Trigonal
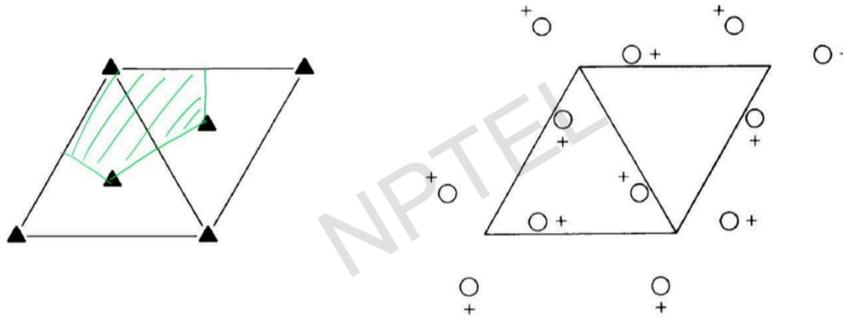
No. 143   *P*3   Patterson symmetry $P\bar{3}$

Asymmetric unit $0 \le x \le \frac{2}{3}$; $0 \le y \le \frac{2}{3}$; $0 \le z \le 1$; $x \le (1+y)/2$; $y \le \min(1-x,(1+x)/2)$

Vertices $0,0,0$ $\frac{1}{2},0,0$ $\frac{2}{3},\frac{1}{3},0$ $\frac{1}{3},\frac{2}{3},0$ $0,\frac{1}{2},0$

$0,0,1$ $\frac{1}{2},0,1$ $\frac{2}{3},\frac{1}{3},1$ $\frac{1}{3},\frac{2}{3},1$ $0,\frac{1}{2},1$

Symmetry operations

(1) 1   (2) 3^+ $0,0,z$ (3) 3^- $0,0,z$

Excerpt from International Tables for Crystallography, Volume A

P3 *continued*   **C₃¹**   3   Trigonal

Generators selected   (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)

Positions

Multiplicity,   Coordinates
Wyckoff letter,
Site symmetry

3   *d*   1   (1) x,y,z (2) $\bar{y},x-y,z$ (3) $\bar{x}+y,\bar{x},z$

1   *c*   3.. $\frac{2}{3},\frac{1}{3},z$

1   *b*   3.. $\frac{1}{3},\frac{2}{3},z$ } special Position

1   *a*   3.. $0,0,z$

There are several special positions in this space group, and the general position has a multiplicity of 8. Starting from one general position (x, y, z), applying the symmetry operations generates 8 equivalent positions. A special position located at the intersection of two mirrors and a four-fold axis has a multiplicity of only 1.

Finally, consider the $P3$ space group. This is a very simple space group, and I want to point out only one aspect here, namely the asymmetric unit. The asymmetric unit looks more complicated in this case. Here, x varies from 0 to $\frac{2}{3}$, y varies from 0 to $\frac{2}{3}$, and z varies from 0 to 1, but there is also a more complicated relationship between x and y. If we join the appropriate boundaries, this region defines the asymmetric unit.

The point to note here is that the asymmetric unit need not be a rectangle, square, or triangle; it can have a more complicated shape. There are relatively few special positions in this space group, and the general position has a multiplicity of 3. With this, I conclude this lecture. In the next lecture, we will begin the diffraction part of this course.