CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES
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Lecture 29: Decoding the International Tables - I

This is the concluding lecture on two-dimensional crystallography, and here we introduce what is called the International Tables for Crystallography, Volume A. Although several volumes exist, our focus is on Volume A for now. We will also return to these tables again when we study three-dimensional crystallography. At first glance the tables may appear cryptic or even overwhelming, but with everything we have already learned, they can be decoded quite easily. The idea is to take a few plane groups and understand what the International Tables are communicating.

Let us begin with the plane group pm. In the table, the top-left entry shows this plane group. As we already know, any plane group beginning with the letter p indicates a primitive unit cell. This group belongs to the rectangular two-dimensional crystal system, and therefore it represents a primitive rectangular lattice on which other symmetry elements are placed. Below the symbol pm, you will notice the number 3. This number simply indicates its position in the standard sequence of plane groups. The first two groups in the sequence are $p1$ and $p2$, and the third is pm, which we are now examining.

Along with the short notation pm, the table also provides a long notation for the same plane group. This long notation becomes particularly useful when dealing with non-standard configurations of symmetry. As already explained earlier, the long notation consists of four symbols. The first symbol is p or c, indicating whether the lattice is primitive or centered. The second symbol contains the highest rotational symmetry present; for example, if both a three-fold and a six-fold are present, the symbol would be 6. The third symbol denotes the symmetry plane, either a mirror or a glide that is perpendicular to the a-axis. The fourth symbol similarly describes the symmetry plane at

an angle α relative to the *a*-axis. Thus, the long notation can be constructed systematically using these rules.

In the diagram shown in the table, the bold horizontal lines represent mirror planes. The vertical lines are not bold, and therefore they are not mirrors. Because the difference is subtle, this sometimes causes confusion, but in this case the mirror lines are clearly horizontal. This diagram fully represents the symmetry present in plane group *pm*. A second diagram, placed alongside it, removes the explicit symmetry symbols and instead shows motifs, right-handed, left-handed, and so on. This version illustrates how the motifs are moved around by translation symmetry and by operations such as mirror reflections, glides, and rotations.

From this motif diagram, we can see that there are two motifs per unit cell, one right-handed and one left-handed. However, these motifs could easily be replaced by a single atom, especially if the atom is achiral and therefore does not change under reflection. Alternatively, they could represent a molecule that repeats exactly as dictated by the symmetry operations.

The phrase "origin on *m*" indicates that the origin has been placed on the mirror plane. Typically, we place the point of highest symmetry at the corners of the unit cell. Here the highest symmetry element is the mirror, and therefore the lattice points at the corners naturally lie on the mirror plane itself. The origin corresponds to the same position we have used in earlier lectures: the lower-left corner of the cell, with the *a*-axis drawn horizontally and the *b*-axis vertically.

Next, consider the line labelled "asymmetric unit", which states

$$0 \leq x \leq \tfrac{1}{2}, \qquad 0 \leq y \leq 1.$$

Here the *x*-coordinate corresponds to the direction of the *a*-vector, and the *y*-coordinate corresponds to the *b*-translation. This rectangular region defines the asymmetric unit.

When the symmetry operations of pm act on this region, the entire motif pattern shown in the diagram is generated.

Here we remember that this direction is x or a and the vertical direction is y or b. The origin is at the lower-left corner, and the asymmetric unit occupies exactly half the area of the unit cell. If I place single atoms as motifs, then the total number of atoms per unit cell becomes 2. Therefore, the area of the asymmetric unit is simply 1 divided by the number of atoms per unit cell. In other words, it is half the total unit-cell area.

$$Area = \frac{1}{2}(Total\ area\ of\ unit\ cell)$$

The meaning of this asymmetric unit is straightforward. All objects placed inside this region, whether atoms or more complicated motifs, are acted upon by translation, reflection, glide, and other symmetry operations to generate the entire pattern. We only need to define a very small region, and the symmetry operations will automatically populate the rest of the infinite plane. Whatever atoms are placed in this asymmetric unit will be reproduced everywhere in the pattern once the full symmetry of the plane group is applied.

The next part of the table lists the symmetry operations. The first one is the identity operator, which is always present. The second is the mirror symmetry. Its location is written as $(0, y)$, which means $x = 0$ and y can be any value. This corresponds to the vertical line $x = 0$, which is one of the mirror planes of the group. Because the pattern continues infinitely in both directions, the line is written using the same coordinate notation everywhere.

Then we come to the section labelled "Generators selected". These are the minimum symmetry operations required to generate the entire plane group. The first two symbols are the translations. The operation $t(1, 0)$ is translation along the a-direction and $t(0, 1)$ is translation along the b-direction. The remaining operation corresponds to the mirror, and together these minimal operations can generate all symmetry operations of the group.
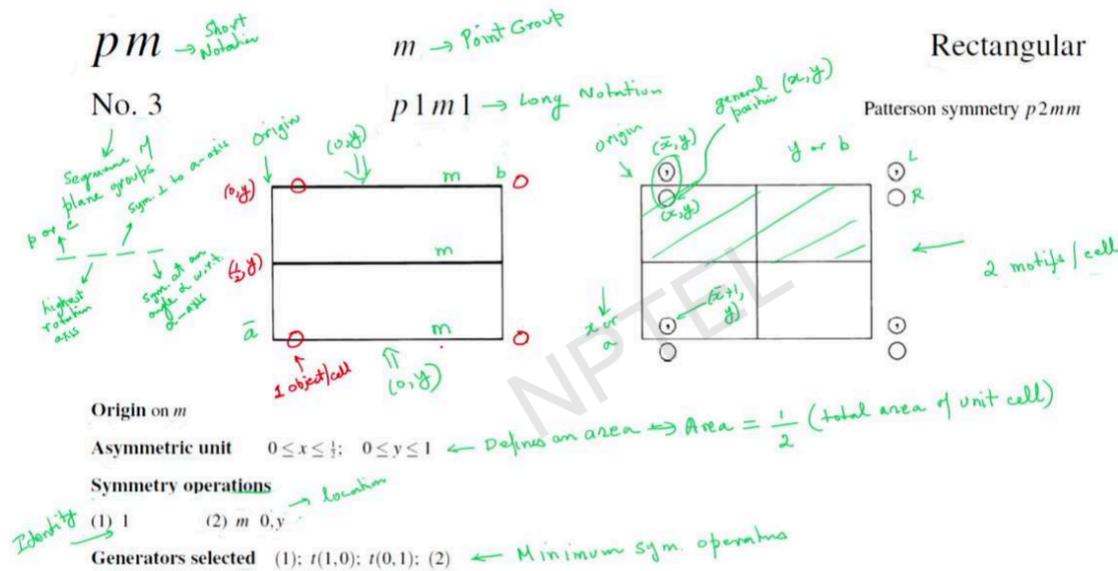
Excerpt from International Tables for Crystallography, Volume A

This was only one half of the table. The second half introduces multiplicity, the Wyckoff letter, site symmetry, and the coordinates of positions. The multiplicity column shows how many motifs appear per unit cell when a single motif is placed at that type of position. The middle column shows the Wyckoff letter, labelled a, b, c, and so on. The next column lists the site symmetry, which indicates whether the position lies on a symmetry element or not. The remaining columns list the coordinates generated by the symmetry operations.

To understand this better, consider again that a motif placed at a position not lying on any symmetry element is said to be in a general position. Its coordinates are written as (x, y). This point is not on the mirror plane and therefore has no point symmetry acting on it directly. If I place a single atom at this point and apply the mirror symmetry, the new coordinate becomes $(\bar{x}, y)$, where $\bar{x}$ means $-x$. Thus, from a single atom, the symmetry generates two atoms. If it were a molecule instead of an atom, it would have generated two molecules. This number of generated motifs per unit cell is exactly what multiplicity refers to.

In the table this is written as

$$(x, y), \quad (\bar{x}, y).$$

One could also shift the second point by a lattice translation and write it as $(\bar{x} + 1, y)$ using fractional coordinates. Since fractional coordinates treat a translation of a or b as "one unit", both notations are equivalent. For convenience the table keeps the coordinates within the chosen reference unit cell, so (x, y) and $(\bar{x}, y)$ are sufficient.

The site symmetry for this general position is 1, meaning no point symmetry acts at that site. It does not lie on any symmetry element. In contrast, a special position lies exactly on a symmetry element. If a point lies on the mirror plane, the site symmetry becomes m. This indicates that the motif sits on the mirror plane which is perpendicular to the x-axis.

To see why this matters, imagine the diagram. If I place a motif slightly away from the mirror, the reflection produces a pair. But if I place the motif directly on the mirror itself, the reflection simply maps the motif onto itself. The motif is not duplicated. This reduces the multiplicity and changes the site symmetry from 1 to m.

When the mirror operates on the atom lying exactly on the mirror plane, the atom coincides with itself. It does not produce a second copy. However, lattice translations still act on it. A translation along $\bar{a}$ creates one atom at the adjacent position, and translation along $\bar{b}$ creates atoms above and below. If the initial motif is a single atom, the contributions become half from one boundary, half from the other boundary, and zero from the remaining two sides. Together these add up to one atom per unit cell. If the motif is a molecule, it must possess the same reflection symmetry in order to lie on the mirror plane. In such a case, the molecule again appears only once per unit cell. Thus, the multiplicity becomes 1, meaning one object per cell.

This is precisely what the table indicates. The multiplicity for this special position is written as 1. There are two such mirror planes within the reference cell. One lies at the

coordinate $(0, y)$, meaning $x = 0$ and y arbitrary. The other lies at $(\frac{1}{2}, y)$, which is the central mirror plane. The equivalent mirror in the adjacent cell corresponds to $(0, y)$ again because of periodicity. Both special positions have the same multiplicity and belong to the same type of symmetrical environment.

The Wyckoff letters follow a simple ordering. The lowest row in the table is assigned the letter a, the next row b, and the next row c. These letters are merely labels, so a crystal structure can be concisely described by saying that an atom occupies Wyckoff position **a** in a particular plane group. This single line already defines the symmetry constraints, multiplicity, and coordinates of that site without additional explanation.

Some additional entries appear in the table such as reflection conditions or structure-factor rules. These require a basic understanding of structure factors, which is covered later in the x-ray diffraction section. For now, they can be ignored since they lie beyond the immediate scope.

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Excerpt from International Tables for Crystallography, Volume A

Consider now another plane group, namely cm. The letter c indicates a centered lattice. In two dimensions, a centered lattice automatically implies a rectangular system since that is the only 2D Bravais lattice that can contain a centering point. The point group is the same in form, and the origin once again lies on the mirror plane so that the highest symmetry is always chosen.

Examining the asymmetric unit in this plane group, we can count four motifs inside it: one, two, three, and four. Therefore, four atoms or four molecules belong to a single unit cell. Consequently, the area of the asymmetric unit must be one quarter of the total unit-cell area.

$$Area = \frac{1}{4}\ (Total\ area\ of\ unit\ cell)$$

Indeed, the diagram shows x ranging from 0 to $\frac{1}{2}$ and y ranging from 0 to $\frac{1}{2}$, which clearly encloses one quarter of the full cell. As always, symmetry operations acting on the motifs within this asymmetric unit generate the entire pattern.

The symmetry operations now become slightly more involved. The reference point $(0,0)$ is a lattice corner, while $(\frac{1}{2}, \frac{1}{2})$ is the centered lattice point. For $(0,0)$ the identity operation is present, and the mirror plane appears just as in the plane group pm. The centering translation also appears, written as $t(\frac{1}{2}, \frac{1}{2})$, which moves motifs from the corner to the center.

Another symmetry element listed is a glide. Its coordinate is written as $(\frac{1}{4}, y)$, which means $x = \frac{1}{4}$ and y arbitrary. Since the mirror in this group lies at $(0, y)$, this new line at $x = \frac{1}{4}$ represents a glide plane. The table writes it using the letter b rather than g, indicating that the glide translation is along the b-direction. Thus, the letter b identifies a b-glide, where the direction of glide is parallel to the b axis.

The minimum generators are then listed as identity, the translations along a and b, the centering translation $(\bar{a}/2 + \bar{b}/2)$, and the mirror at $(0, y)$. These are sufficient to generate all symmetry operations of the cm plane group.

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Excerpt from International Tables for Crystallography, Volume A

The second part of the table contains the Wyckoff positions again, including both special and general positions. The special positions lie on symmetry elements, while the general positions lie off all symmetry elements and therefore have multiplicities greater than one.

This special position has a multiplicity of 4, but the table initially shows only two coordinates. The reason is that these two coordinates must be combined with the lattice translations listed above them. The table instructs us to add $(0, 0)$ to the given coordinates, which simply reproduces the original two positions (x, y) and $(\bar{x}, y)$. For the second pair, we add $(\frac{1}{2}, \frac{1}{2})$ to each coordinate.

This produces the remaining two positions: $(x + \frac{1}{2}, y + \frac{1}{2})$ and $(\bar{x} + \frac{1}{2}, y + \frac{1}{2})$. In this way we obtain all four coordinates, and you can verify them directly from the

plane-group diagram. These form the general position of the group, while the ones on the mirror plane form the special position. For the special case where the motif lies on the mirror line at $(0, y)$, adding the translation $(\frac{1}{2}, \frac{1}{2})$ gives the second coordinate $(\frac{1}{2}, y + \frac{1}{2})$. There are exactly two such positions, so the multiplicity becomes 2.

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... "cm" continued

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates $(0,0)+ \quad (\frac{1}{2},\frac{1}{2})+$				Reflection conditions

4 b 1   (1) x,y (2) $\bar{x}, y$ (3) $x+\frac{1}{2}, y+\frac{1}{2}$ (4) $(\bar{x}+\frac{1}{2}, y+\frac{1}{2})$

General position (handwritten)

Special position (handwritten)

General:

$hk:\ h+k = 2n$
$h0:\ h = 2n$
$0k:\ k = 2n$

Special: no extra conditions

2 a .m.   0,y   *or $\frac{1}{2}, y+\frac{1}{2}$* (handwritten)

Maximal non-isomorphic subgroups
I   [2] c1 (p1, 1)   1+
IIa   [2] pg (4)   1; 2 + (½,½)
     [2] pm (3)   1; 2
IIb   none

Maximal isomorphic subgroups of lowest index
IIc   [3] cm (a' = 3a) (5); [3] cm (b' = 3b) (5)

Minimal non-isomorphic supergroups
I   [2] c2mm (9); [3] p3m1 (14); [3] p31m (15)
II   [2] pm (a' = ½a, b' = ½b) (3)

Excerpt from International Tables for Crystallography, Volume A

This completes that plane group. Moving to the next example, the group $p4mm$ is based on the point group $4mm$ and corresponds to a primitive square lattice. As always, the origin is chosen on the highest-symmetry site. The asymmetric unit is slightly more restrictive here. The coordinates satisfy $0 \le x \le \frac{1}{2}$, $0 \le y \le \frac{1}{2}$, and additionally $x \le y$.

These conditions carve out a single triangle out of the full cell. When a motif is placed inside this triangular region, the mirror reflects it into a left-handed partner, and the four-fold rotation takes this pair and rotates it by $90°$. All together these generate a total of eight motifs per unit cell.

$$Area = \frac{1}{8} (Total\ area\ of\ unit\ cell)$$

Therefore, the asymmetric unit must occupy one-eighth of the full area. Any one of the symmetric triangular regions works, but the table refers to a particular one; nevertheless, the choice is arbitrary because all such triangles are symmetry equivalent. A single motif in this triangular region generates the full pattern when the rotation and mirror symmetries are applied.

The list of symmetry operations becomes richer here. There are mirrors, two-fold axes, the four-fold axis, and the associated translations. The minimum generating set consists of the identity, the primitive translations along a, b, and c, and then the three symmetry elements required to produce the entire group. These are the mirror, the two-fold, and the four-fold operation.
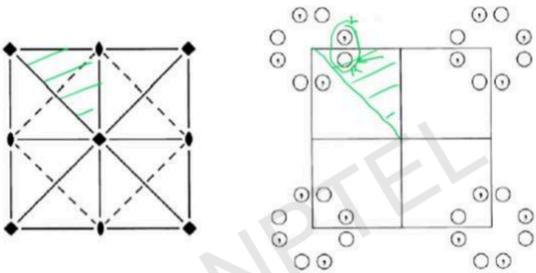
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p4mm   4mm   Square

No. 11   p4mm   Patterson symmetry p4mm

8 moh/i/cell

Origin at 4mm

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $x \le y$ $Area = \frac{1}{8}(Total\ Area)$

Symmetry operations

(1) 1   (2) 2 0,0   (3) 4 0,0   (4) 4 0,0
(5) m 0,y   (6) m x,0   (7) m x,x   (8) m x,x̄

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

Excerpt from International Tables for Crystallography, Volume A

The table that follows lists all Wyckoff positions. The position with site symmetry $4mm$ has multiplicity 1. The position with symmetry $2mm$ has multiplicity 2. Three special positions have multiplicity 4, and the general position has multiplicity 8. All remaining

positions are special. These can be worked out directly from the symmetry operations as an exercise.

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Positions

Multiplicity, Wyckoff letter, Site symmetry | Coordinates | Reflection conditions | … "p4mm" continued

General:

| 8 | g | 1 | (1) x,y (2) $\bar{x},\bar{y}$ (3) $\bar{y},x$ (4) $y,\bar{x}$ | no conditions |
| | | | (5) $\bar{x},y$ (6) $x,\bar{y}$ (7) y,x (8) $\bar{y},\bar{x}$ | |

Special:

4	f	..m	x,x	$\bar{x},\bar{x}$	$\bar{x},x$	$x,\bar{x}$	no extra conditions
4	e	.m.	$x,\frac{1}{2}$	$\bar{x},\frac{1}{2}$	$\frac{1}{2},x$	$\frac{1}{2},\bar{x}$	no extra conditions
4	d	.m.	$x,0$	$\bar{x},0$	$0,x$	$0,\bar{x}$	no extra conditions
2	c	2mm.	$\frac{1}{2},0$	$0,\frac{1}{2}$			$hk: h+k=2n$
1	b	4mm	$\frac{1}{2},\frac{1}{2}$				no extra conditions
1	a	4mm	$0,0$				no extra conditions

Maximal non-isomorphic subgroups

I   [2] $p411$ ($p4$, 10)   1; 2; 3; 4
     [2] $p21m$ ($c2mm$, 9)   1; 2; 7; 8
     [2] $p2m1$ ($p2mm$, 6)   1; 2; 5; 6

IIa   none
IIb   [2] $c4mg$ ($a'=2a, b'=2b$) ($p4gm$, 12)

Maximal isomorphic subgroups of lowest index

IIc   [2] $c4mm$ ($a'=2a, b'=2b$) ($p4mm$, 11)

Minimal non-isomorphic supergroups

I   none
II   none

Excerpt from International Tables for Crystallography, Volume A

The final example comes from the hexagonal lattice, specifically the plane group $p31m$. This group has mirror planes along the edges and one mirror plane along the short diagonal, along with glide planes. A motif placed in one of the asymmetric regions is first reflected to its partner, and this pair is then rotated by the three-fold axis, generating a total of six motifs in the unit cell. Again, the origin is placed at the highest-symmetry point. The A and B axes form the 120° hexagonal geometry. The asymmetric unit now must have an area equal to one-sixth of the full cell.

The table provides the vertices of this region. The vertices are $(0,0)$, $(\frac{1}{2},\frac{1}{2})$, $(\frac{2}{3},\frac{1}{3})$, and again $(\frac{1}{2},\frac{1}{2})$ which lies at the cell center. Connecting these gives the triangular region that forms the asymmetric unit. Any motifs placed here get repeated by the action of the three-fold rotation and the mirrors. To confirm that this region really has area one-sixth of the whole, we can break the hexagonal cell into equilateral triangles.

There are eight such triangles around the central region. Each equilateral triangle contributes an area of $\frac{1}{8}A_{total}$. The asymmetric region occupies one triangle plus an additional one-third of another, producing an area equal to

$$\frac{1}{3} \times \frac{1}{8}A_{total} + \frac{1}{8}A_{total} = \frac{1}{6}A_{total}.$$

$$Area = \frac{1}{6}(Total\ area\ of\ unit\ cell)$$

$$= \frac{1}{8}(Total\ Area) + \frac{1}{8} \times \frac{1}{3}(Total\ Area)$$

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The table again lists general and special positions. All special positions lie either on mirror planes or on rotation axes. For example, in the group cm, the special position lies on the mirror plane even though the group also contains glide planes. A glide plane does not define a special position because the glide translation simply shifts a motif from one position to another without reducing its multiplicity.

If an atom lies exactly on a glide plane, the glide translates it to the corresponding shifted coordinate but does not reduce the number of symmetry-generated positions. Therefore, glide planes do not create special Wyckoff positions; only pure mirror lines and rotation axes do.

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Excerpt from International Tables for Crystallography, Volume A

These ideas will reappear more clearly when we study three-dimensional crystallography and x-ray diffraction. The two-dimensional groups provide an accessible foundation, and now that these concepts are clear, understanding the 32 three-dimensional point groups and the 230 space groups become far easier. This concludes the discussion of two-dimensional point groups and plane groups.