

Space Groups & The International Tables for Crystallography

From examination of a space group in "The International Tables for Crystallography" Vol. A, you should be able to ascertain the following information:

- Herman-Mauguin (H-M) Symbol (Long, Short)
- Point Group (H-M, Schoenflies)
- Locate and identify symmetry elements
- Understand Wyckoff site multiplicity and symmetry
- Distinguish general and special positions
- Extinction conditions
- Identify possible subgroups and supergroups

Understanding the Herman-Mauguin Space Group Symbol

Space groups are typically identified by their short Herman-Mauguin symbol (i.e. Pnma, I4/mmm, etc.). The symmetry elements contained in the short symbol are the minimum number needed to generate all of the remaining symmetry elements. This symbolism is a very efficient, condensed form of noting all of the symmetry present in a given space group. We won't go into all of the details of the space group symbol, but I will expect you to be able to determine the crystal system, Bravais Lattice and point group from the short H-M symbol. You should also be able to determine the presence and orientation of certain symmetry elements from the short H-M symbol and vice versa.

The H-M space group symbol can be derived from the symmetry elements present using the following logic.

The first letter identifies the centering of the lattice; I will hereafter refer to this as the lattice descriptor:

- P → Primitive
- I → Body centered
- F → Face centered
- C → C-centered
- B → B-centered
- A → A-centered

The next three symbols denote symmetry elements present in certain directions, those directions are as follows:

Crystal System	Symmetry Direction		
	Primary	Secondary	Tertiary
Triclinic	None		
Monoclinic	[010]		
Orthorhombic	[100]	[010]	[001]
Tetragonal	[001]	[100]/[010]	[110]
Hexagonal/ Trigonal	[001]	[100]/[010]	[120]/[1 $\bar{1}$ 0]
Cubic	[100]/[010]/ [001]	[111]	[110]

[100] - Axis parallel or plane perpendicular to the x-axis.

[010] - Axis parallel or plane perpendicular to the y-axis.

[001] - Axis parallel or plane perpendicular to the z-axis.

[110] - Axis parallel or plane perpendicular to the line running at 45° to the x and y axes.

[1 $\bar{1}$ 0] - Axis parallel or plane perpendicular to the long face diagonal of the ab face of a hexagonal cell.

[111] - Axis parallel or plane perpendicular to the body diagonal.

For a better understanding see specific examples from class notes. However, with no knowledge of the symmetry diagram we can identify the crystal system from the space group symbol.

- Cubic - The secondary symmetry symbol will always be either 3 or -3 (i.e. Ia3, Pm3m, Fd3m)
- Tetragonal - The primary symmetry symbol will always be either 4, (-4), 4_1 , 4_2 or 4_3 (i.e. P4₁2₁2, I4/m, P4/mcc)
- Hexagonal - The primary symmetry symbol will always be a 6, (-6), 6_1 , 6_2 , 6_3 , 6_4 or 6_5 (i.e. P6mm, P6₃/mcm)

- Trigonal - The primary symmetry symbol will always be a 3, (-3) 3_1 or 3_2 (i.e. $P31m$, $R3$, $R3c$, $P312$)
- Orthorhombic - All three symbols following the lattice descriptor will be either mirror planes, glide planes, 2-fold rotation or screw axes (i.e. $Pnma$, $Cmc2_1$, $Pnc2$)
- Monoclinic - The lattice descriptor will be followed by either a single mirror plane, glide plane, 2-fold rotation or screw axis or an axis/plane symbol (i.e. Cc , $P2$, $P2_1/n$)
- Triclinic - The lattice descriptor will be followed by either a 1 or a (-1) .

The point group can be determined from the short H-M symbol by converting glide planes to mirror planes and screw axes to rotation axes. For example:

Space Group = $Pnma \rightarrow$ Point Group = mmm

Space Group = $I \bar{4}c2 \rightarrow$ Point Group = $\bar{4}m2$

Space Group = $P4_2/n \rightarrow$ Point Group = $4/m$

Wyckoff Sites

One of the most useful pieces of information contained in the International Tables are the Wyckoff positions. The Wyckoff positions tell us where the atoms in a crystal can be found. To understand how they work consider the monoclinic space group Pm . This space group has only two symmetry elements, both mirror planes perpendicular to the b -axis. One at $y = 0$ and one at $y = \frac{1}{2}$ (halfway up the unit cell in the b direction). Now let's place an atom in the unit cell at an arbitrary position, x, y, z . If we now carry out the symmetry operation associated with this space group a second atom will be generated by the mirror plane at $x, -y, z$. However, if we were to place the atom on one of the mirror planes (its y coordinate would have to be either 0 or $\frac{1}{2}$) then the reflection operation would not create a second atom.

All of the information in the preceding paragraph is contained in Wyckoff positions section of the International Tables. Pm has three Wyckoff sites as shown in the table below:

Multiplicity	Wyckoff Letter	Site Symmetry	Coordinates
2	c	1	(1) x,y,z (2) $x,-y,z$
1	b	m	$x,\frac{1}{2},z$
1	a	m	$x,0,z$

The multiplicity tells us how many atoms are generated by symmetry if we place a single atom at that position. In this case for every atom we insert at an arbitrary position (x,y,z) in the unit cell a second atom will be generated by the mirror plane at $x,-y,z$. This corresponds to the uppermost Wyckoff position 2c. The letter is simply a label and has no physical meaning. They are assigned alphabetically from the bottom up. The symmetry tells us what symmetry elements the atom resides upon. The uppermost Wyckoff position, corresponding to an atom at an arbitrary position never resides upon any symmetry elements. This Wyckoff position is called the general position. The coordinates column tells us the coordinates of all of the symmetry related atoms (two in this case).

All of the remaining Wyckoff positions are called special positions. They correspond to atoms which lie upon one of more symmetry elements, because of this they always have a smaller multiplicity than the general position. Furthermore, one or more of their fractional coordinates must be fixed. In this case the y value must be either 0 or $\frac{1}{2}$ or the atom would no longer lie on the mirror plane.

Generating a Crystal Structure from its Crystallographic Description

Using the space group information contained in the International Tables we can do many things. One powerful use is to generate an entire crystal structure from a brief description.

Consider the following description of the crystal structure of $\text{Sr}_2\text{AlTaO}_6$.

Space Group = $\text{Fm } \bar{3}m$

$a = 7.80 \text{ \AA}$

Atomic Positions

Atom	x	y	z
Sr	0.25	0.25	0.25
Al	0.0	0.0	0.0
Ta	0.5	0.5	0.5

Next we compare the number of atoms in the unit cell with the multiplicities of the Wyckoff sites.

- From the multiplicities of the special positions in space group $Pm\bar{3}m$ we see that Sr must occupy either the 1a or 1b positions (otherwise there would be more than one Sr in the unit cell).
- By the same reasoning Ti must also reside in either the 1a or 1b position, and, since there are no free positional parameters (x,y or z) in either 1a or 1b, the two ions cannot occupy the same site.
- To maintain 3 oxygen ions in the unit cell it must reside at either site 3c or 3d.

If we arbitrarily put Ti at the origin (1a), then by default Sr must go to 1b. To evaluate the prospects of putting O at either 3c or 3d we calculate the Ti-O bond distances:

$$D(O @ 3c) = 3.90 \times [(0-0)^2 + (0-0.5)^2 + (0-0.5)^2]^{1/2} = 2.76 \text{ \AA}$$

$$D(O @ 3d) = 3.90 \times [(0-0.5)^2 + (0-0)^2 + (0-0)^2]^{1/2} = 1.95 \text{ \AA}$$

Of these two the latter (3d) is obviously more appropriate for a Ti-O bond (consult tables of ionic radii to convince yourself of this statement).

Thus we obtain the structure of $SrTiO_3$ to be

Space Group = $Pm\bar{3}m$

$a = 3.90 \text{ \AA}$

Atomic Positions

Atom	x	y	z
Sr	0.5	0.5	0.5
Ti	0	0	0
O	0.5	0	0

O	0.25	0.0	0.0
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From the space group tables we see that the atoms are located on the following Wyckoff sites

- Sr →8c
- Al →4a
- Ta →4b
- O →24e

The number associated with the Wyckoff sites tells us how many atoms of that type there are in the unit cell. So there are 40 atoms in the unit cell, with stoichiometry $\text{Sr}_8\text{Al}_4\text{Ta}_4\text{O}_{24}$ which reduces to the empirical formula $\text{Sr}_2\text{AlTaO}_6$. Since the number of atoms in the unit cell is four times the number of atoms in the formula unit, we say that $Z = 4$.

Using the face centering generators $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$ together with the coordinates of each Wyckoff site we can generate the fractional coordinates of all atoms in the unit cell:

- Sr
- 1:(0.25,0.25,0.25), 2:(0.75,0.75,0.25), 3:(0.75,0.25,0.75), 4:(0.25,0.75,0.75)
5:(0.25,0.25,0.75), 6:(0.75,0.75,0.75), 7:(0.75,0.25,0.25), 8:(0.25,0.75,0.25)

- Al
- 1:(0.0,0.0,0.0), 2:(0.5,0.5,0.0), 3:(0.5,0.0,0.5), 4:(0.0,0.5,0.5)

- Ta
- 1:(0.5,0.5,0.5), 2:(0.0,0.0,0.5), 3:(0.0,0.5,0.0), 4:(0.5,0.0,0.0)

- O
- 1:(0.24,0.0,0.0), 2:(0.74,0.5,0.0), 3:(0.74,0.0,0.5), 4:(0.24,0.5,0.5)
5:(0.76,0.0,0.0), 6:(0.26,0.5,0.0), 7:(0.26,0.0,0.5), 8:(0.76,0.5,0.5)
9:(0.0,0.24,0.0), 10:(0.5,0.74,0.0), 11:(0.5,0.24,0.5), 12:(0.0,0.74,0.5)
13:(0.0,0.76,0.0), 14:(0.5,0.26,0.0), 15:(0.5,0.76,0.5), 16:(0.0,0.26,0.5)
17:(0.0,0.0,0.24), 18:(0.5,0.5,0.24), 19:(0.5,0.0,0.74), 20:(0.0,0.5,0.74)
21:(0.0,0.0,0.76), 22:(0.5,0.5,0.76), 23:(0.5,0.0,0.26), 24:(0.0,0.5,0.26)

From these fractional coordinates you can sketch out the structure of $\text{Sr}_2\text{AlTaO}_6$. With some luck I will provide a link to a picture of the structure here, at some point in the future.

We can also work out bond distances from this information. The first Al ion is octahedrally coordinated by six oxygens (1,5,9,13,17,21) and the Al-O distance is

$$d = 7.80 \times [(0.24-0.0)^2 + (0.0-0.0)^2 + (0.0-0.0)^2]^{1/2} = 1.87 \text{ \AA}$$

while the first Ta ion is also surrounded by 6 oxygens (4,8,11,15,18,22) at a distance of

$$d = 7.80 \times [(0.24-0.5)^2 + (0.5-0.5)^2 + (0.5-0.5)^2]^{1/2} = 2.03 \text{ \AA}$$

and Sr is surrounded by 12 oxygens (1,4,6,7,9,11,14,16,17,18,23,24) at a distance of

$$d = 7.80 \times [(0.24-0.25)^2 + (0.0-0.25)^2 + (0.0-0.25)^2]^{1/2} = 2.76 \text{ \AA}$$

Determining a Crystal Structure from Symmetry & Composition

Another use is that given the stoichiometry, space group and unit cell size (which can typically be determined from diffraction techniques) and the density of a compound we can often deduce the crystal structure of relatively simple compounds.

As an example consider the following information:

Stoichiometry = SrTiO_3

Space Group = $\text{Pm}\bar{3}\text{m}$

$a = 3.90 \text{ \AA}$

Density = 5.1 g/cm^3

To derive the crystal structure from this information the first step is to calculate the number of formula units per unit cell :

$$\text{Formula Weight } \text{SrTiO}_3 = 87.62 + 47.87 + 3 \times (16.00) = 183.49 \text{ g/mol}$$

$$\text{Unit Cell Volume} = (3.90 \times 10^{-8} \text{ cm})^3 = 5.93 \times 10^{-23} \text{ cm}^3$$

$$(5.1 \text{ g/cm}^3) \times (5.93 \times 10^{-23} \text{ cm}^3) \times (\text{mol}/183.49 \text{ g}) \times (6.022 \times 10^{23} / \text{mol}) = 0.99$$

Thus there is one formula unit per unit cell ($Z=1$), and the number of atoms per unit cell is : 1 Sr, 1 Ti and 3 O.

Next we compare the number of atoms in the unit cell with the multiplicities of the Wyckoff sites.

- From the multiplicities of the special positions in space group $Pm\bar{3}m$ we see that Sr must occupy either the 1a or 1b positions (otherwise there would be more than one Sr in the unit cell).
- By the same reasoning Ti must also reside in either the 1a or 1b position, and, since there are no free positional parameters (x,y or z) in either 1a or 1b, the two ions cannot occupy the same site.
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