Guide to Space groups

There are only 230 ways (space groups) to describe how identical objects can be arranged in orderly arrays in an infinite three-dimensional lattice network. That's it? Well yes but it gets better than that! If your structure contains a chrial center then any space group that has a mirror or an inversion operation can be rejected. Of the 230 space groups only 74 space groups are allowed for chiral structures. It gets better! It appears, from observing the frequencies for space groups reported in the literature that only 5 space groups (P-1, $P2_1$, $P2_1/c$, C2/c and $P2_12_12_1$) account for over 75% of all groups reported! It seems that there is a preference for packing objects into space. The reasons for this are beyond the scope of this work and the reader should consult the literature.

Let face facts. Nature packs molecules (atoms) the way it wants to and we ignorantly attempt to describe that packing in the form of a space group assignment. So to say there is only one true space group for any given arrangement of atoms in space is perhaps a tad presumptuous. The truth is that molecules (atoms) pack inefficiently at best and that there will always be slight imperfections in the crystal. It can be said that the only true space group is P1. Be that as it may we tend to choose space groups of highest symmetry. Why? Well for starters the mathematics works the best at higher symmetry.

To describe objects in lower and lower symmetry one must often group adjacent molecules together in some supra-molecular arrangement where the relationship between the molecules is best described by pseudo symmetry. When this happens the mathematical equations that best minimize the differences between the observed data and the modeled data begin to break down and correlation between the mathematical parameters is seen. This break down is reflected most significantly in the position of the atoms in the unit cell and thus their bond lengths. For this reason alone it is best to use the highest symmetry available.

The second reason to pursue higher symmetry is in the ascetics of the structure. Many people, including reviewers and this author, tend to see high symmetry as pleasing to the eye. Their view is that nature tends toward high symmetry (e.g. the obvious mirror symmetry in our own bodies) and thus it is good and fitting that a crystal will pack this way. This of course is a bias view but one that is very entrenched in the scientific community. To please the community one must therefore search out the highest symmetry available. After all they are the ones signing off on your hard earned work!

To understand space groups we must first grasp the notation that is used.

First space group notation.

The notation for space group enumeration follows the Hermann structure.

Notation

L ijk

L = lattice
capital letter for 3D lattice
ijk = symmetry elements of space group for the different symmetry directions

where **i** =primary, **j** = secondary and **k** = tertiary directions

The space group notation begins with a capitol letter. This letter represents the Bravias lattice. The letter can only be *A, B, C, I, F, P* standing for the five centered cells and the primitive cell. The primitive cell *P* is by far the most reported. All seven cell systems have primitive lattices. On the other hand not all of the centered lattices are allowed in all seven cell systems. For example the primitive cell has no centering operations (only inversion symmetry) and thus L will equal P for triclinic cells. Likewise for the monoclinic system only the C-centered lattice is seen. But wait you say, I have seen people report the space group B2? What's that all about? The non-standard space group B2 is just a different way of building a P2 cell. The B-centering introduces the pseudo transnational symmetry (again for mathematical reasons) and is not needed to describe the relationship of objects in the monoclinic cell. We shall return to this later.

The next letters and numbers that follow the capitol letter are the symmetry operators, again in Hermann format. The symmetry operator can be either a single character e.g. 2 or a number with a subscript e.g. 2_1 or a number followed by a slash and then a letter e.g. 2/m or 2_1/m. Their position relative to the capitol letter tells you in what symmetry direction they are either orthogonal to or coincident with. Operators that are orthogonal to the symmetry direction are always noted by small letters (i.e a, b, c, n or m). These operators all contain mirrors. Operators that are coincident with the symmetry direction are always letters or letters with subscripts (i.e. 2, 2_1, 3, 3_1, 3_2, 4, 4_1, 4_2 , 4_3, 6, 6_1, 6_2, 6_3, 6_4 or 6_5). This can be confusing because the symmetry direction does not necessarily have to be along the cell axis. Let us divide the space groups into those groups whose symmetry direction is coincident with the all of the cell axis and those that are not.

For the monoclinic and orthorhombic systems, the symmetry directions and the cell axis a coincident. The orthorhombic space group $P2_12_12_1$ is a good example to work with. To read the notation separate the symbol and add spaces $P2_12_12_1$ becomes P 2_1 2_1 2_1. Note that 2_1 is a lone symmetry operator (see above). The three symmetry directions are coincident with the three cell axis thus the directions, i, j, k are in the direction of cell axis a, b, c. We therefore read the notation as Primitive lattice with a two-fold screw axis (2_1) along a, a two-fold screw axis (2_1) along b and a two-fold screw axis (2_1) along c.

The notation does not necessarily need to note all symmetry operations in the unit cell. Some of them can be implied from the notation itself. Thus the orthogonal space group P nma notes that the group is Primitive lattice with a n-glide perpendicular to the a axis, a mirror plane perpendicular to the b axis and a a-glide perpendicular to the c axis. However from symmetry discussions we know that if two symmetry operations meet in space that a third operation is formed. Thus the intersection of a mirror perpendicular to the a axis and a mirror perpendicular to the b axis will give rise to a 2 fold axis along c. Add to this that one of the mirrors is part of an n-glide, one must now add translation to the 2-fold symmetry operation to render it into a screw axis. Take this into consideration the formal notation for the symmetry operator in the j direction is $2_1/a$. Employing similar arguments for the i and j symmetry directions the formal notation for Pnma can be deduced as P $2_1/n$ $2_1/m$ $2_1/a$. Pnma is the shorthand notation for this space group.

Another orthorhombic space group is Cmm2. Is there any hidden symmetry operations implied by this notation? No. Let us see why. In this case we see that the notation tells us that there is a mirror plane perpendicular to a and b. These symmetry actions give rise to a two-fold operation along c, which is stated in the notation Cmm2. Likewise a 2-fold operation along c will intersect with a mirror plane perpendicular to b to give rise to a mirror operator that is perpendicular to a. No other operations are generated from these three basic operations and thus the formal notation for Cmm2 is Cmm2.

Wait a minute, you say, I see monoclinic space groups noted as $P2_1$ what is that all about. The notation for monoclinic space groups is often shorthand for the formal notation. For example if the space group is $P2_1$ and the unique axis is chosen as *b* then the full formal notation is P 1 2_1 1. If you see a single symbol operator you must assume that the other operators are 1 (identity). Another example for a monoclinic space group is $P2_1/c$. The formal notation (with the b axis unique) is P 1 $2_1/c$ 1. What gives you say? Did we not drop the 2_1 notation in the examples for the orthorhombic space group Pnma ? Yes we did because the 2_1 can be implied by the intersection of the symmetry operations. In this case there is only the identity operator along a and c. Thus the space groups $P2_1/c$ and Pc are unique and the 2_1 cannot be dropped. There is intersecting symmetry operations in $2_1/c$ that is the 2_1 and the c-glide. This of course gives rise to an inversion center (implied by the notation). No such intersecting symmetry operations are seen for Pc and thus no inversion center is present. Thus the two space groups are unique.

Now we journey on to high symmetry space groups. In the high symmetry groups at least one axis is equal to another axis. If one notes an operation along one axis then a similar operations is noted down the equal axis. Also there is a relationship between the axis so that symmetry operations are also related. Thus one notes that symmetry operations are generally along one unique axis (c axis by definition), another is along both of the other axis and often a third is diagonal to the two equal axis. The exemption

is of course the cubic system where all three axis are equal. These directions are shown in table 1.

A good example of a higher symmetry space group is P 4_2/ncm. Again separate the symmetry operations with spaces so that P 4_2/ncm becomes P 4_2/n c m. The first operation is 4_2/n which is a 4_2 skrew axis along the c axis and a n-glide perpendicular to the c axis. The second symmetry operation is a c-glide perpendicular to the a axis and a c-glide perpendicular to the b axis. Finally the third notation tells us that there is a mirror plane perpendicular to the diagonal formed from the a and b axis (a+b). The full formal notation can be deduced from the shorthand notation. In the shorthand we see a n-glide that is perpendicular to c and a c-glide perpendicular to a (b). This gives rise to a 2 fold axis along the k symmetry direction (the diagonal of a and b). In this case the combinations of the glide translations cancel out and the operation is just a two-fold axis. The combination of the n-glide with the mirror (k symmetry operation) along a and b gives rise to a screw axis along the j direction (along a and b). Thus the formal notation is P 4_2/n 2_1/c 2/m.

System	Symmetry Directions
Triclinic	none
Monoclinic	i – along a axis j – along b axis k – along c axis
Orthorhombic	i – along a axis j – along b axis k – along c axis
Tetragonal	i – along c axis (4-fold) j – along a and b axis k – along diagonal of a and b
Trigonal/Hexagonal	i – along c axis (3-fold) j – along a and b axis k – along diagonal of a and b
Cubic	i – along a and b and c j – along diagonal of a and b ; b and c; and a and c k – along diagonal of a and b and c