Crystal Structure: A Brief Primer

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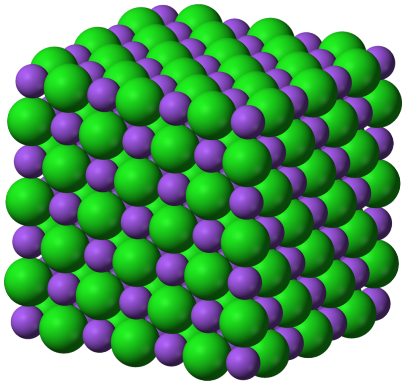


Figure 1: Crystal structure of table salt (NaCl)

From looking at images of crystal structures, you will almost always see some symmetry, or at the very least order. Symmetry is an intrinsic property of crystals, and so we can use this to our advantage to describe a large crystal using only a small section of it: a unit cell.

A unit cell is simply "the smallest repeating unit having the full symmetry of the crystal structure". So, we wish to take a small slice off of the larger structure, to end up with just one repeat of the crystal.

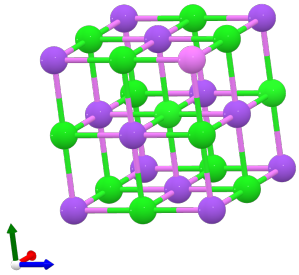


Figure 2: Unit cell of table salt (NaCl)

This allows us to look more finely at the whole crystal, given it is comprised solely of repetitions of this cell. We can also describe this cell, as there are only so many repeating cells we can do in 3D.

Now, at this point, I wish to split the cell into two parts: the 'box' (which contains all the atoms), and the atoms themselves (you'll see why in a second). To describe the box, we will use 3 vectors, which each have a length, and an angle relative to each other.

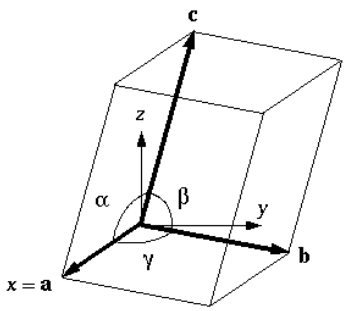


Figure 3: An example of unit cell vectors

As seen in the image above, the convention is to use the letters (a, b, c) to describe the lengths of the vectors (or the dimensions of the box), and the Greek letters (α, β, γ) to describe the angles (so α is the difference in angle between **a** and **c**, for example).

Now we have some values to describe the box, which we call the **lattice parameters**, we can fit this box into a category, of which there are only 7.

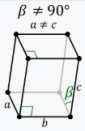
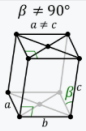
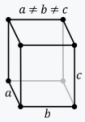
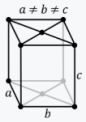
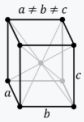
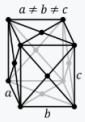
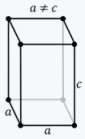
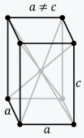
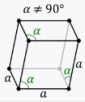
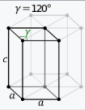
Crystal Family	Lattice System	Schönflies	14 Bravais Lattices			
			Primitive (P)	Base-centered (C)	Body-centered (I)	Face-centered (F)
Triclinic		C_i				
Monoclinic		C_{2h}				
Orthorhombic		D_{2h}				
Tetragonal		D_{4h}				
Hexagonal	Rhombohedral	D_{3d}				
	Hexagonal	D_{6h}				
Cubic		O_h				

Figure 4: A table showing the 7 lattice systems and constituent Bravais lattices (table from Wikipedia)

There are 7 categories (or more formally the **lattice systems** we can put these cells in, given these lattice parameters:

- Cubic - $a = b = c$ **and** $\alpha = \beta = \gamma = 90°$
- Hexagonal - $a = b \neq c$ **and** $\alpha = \beta = 90°$ **and** $\gamma = 120°$
- Rhombohedral - $a = b = c$ **and** $\alpha = \beta = \gamma \neq 90°$
- Tetragonal - $a = b \neq c$ **and** $\alpha = \beta = \gamma = 90°$
- Orthorhombic - $a \neq b \neq c$ **and** $\alpha = \beta = \gamma = 90°$
- Monoclinic - $a \neq b \neq c$ **and** $\alpha = \beta = 90°$ **and** $\gamma \neq 90°$
- Triclinic - $a \neq b \neq c$ **and** $\alpha \neq \beta \neq \gamma \neq 90°$

Now you might notice that some of the lattices have multiple kinds, and this is down to the second part: the atoms in the box. Depending on where the atoms are in a unit cell, we can describe that cell more specifically. There are 4 arraignments possible, although not all of the lattice systems feature all arraignments.

- Primitive - atoms are found **only** at the corners of the unit cell
- Base-centered - atoms are found at the corners and the centre of the top and bottom of the unit cell (i.e. in the **a**-**b** plane)
- Body-centered (abbreviated as BCC) - atoms are found at the corners and in the centre of the unit cell
- Face-centered (abbreviated as FCC) - atoms are found at the corners and in the centre of each face of the unit cell

Adding up each of the arraignments of the 7 lattice systems gives us 14 cells, which are collectively known as the **Bravais lattices** - which are *essentially* all of the possible lattice types[1] You will however notice that the specifications for the arraignments are far less specific than the ones for the lattice systems. This is because in the current form of the unit cell, there are a lot of atoms, and some of them are described unnecessarily (i.e. we don't need to know their position in the unit cell to know the structure of the crystal as a whole). The 'unnecessary' atoms are the ones which are added into the cell when we tessellate or repeat the cell in all directions. Take for example, our table salt from earlier:

[1] Any other lattice defined would be isomorphic relative to one of the Bravais lattices, and thus the transformation into one of the Bravais lattices would be invariant with respect to the cell configuration. For more details on this if you are interested in some reading material, please drop me an email.

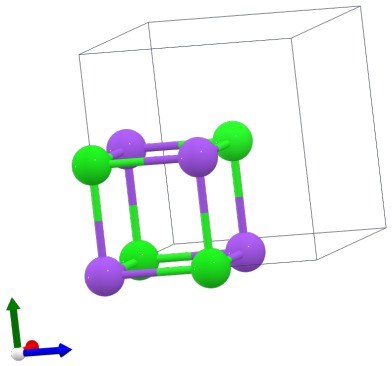


Figure 5: Primitive cell of table salt (NaCl)

As we can see, if we repeat the cell on the right or the top, the atoms that were originally on the boundary of the cell are filled in. This 'stripped down' cell is often referred to as the **primitive cell**, as opposed to the unit cell (which is sometimes called the 'conventional unit cell', to avoid confusion).

The primitive cell is useful, as it is 1) the most simple description of any given cell and 2) it tessellates. The latter is particularly important for molecular modelling, as if you tessellate conventional unit cells, you will end up with two atoms in the same place, which will give you an error[2]. Given this, we can describe only the atoms necessary, in a form such as this:

- Primitive (1 point) - $a_1 = \{0, 0, 0\}$
- BCC (2 points) - $a_1 = \{0, 0, 0\}$, $a_2 = \left\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right\}$
- FCC (4 points) - $a_1 = \{0, 0, 0\}$, $a_2 = \left\{\frac{1}{2}, \frac{1}{2}, 0\right\}$, $a_3 = \left\{\frac{1}{2}, 0, \frac{1}{2}\right\}$, $a_4 = \left\{0, \frac{1}{2}, \frac{1}{2}\right\}$
- Base-centered (2 points) - $a_1 = \{0, 0, 0\}$, $a_2 = \left\{\frac{1}{2}, \frac{1}{2}, 0\right\}$

Such that each coordinate represents a proportion of the corresponding unit cell vector $\{a, b, c\}$. Now you may think "hang on, the table salt unit cell you just showed has 8 atoms in it - what gives?", and this is a reasonable observation to make. For multi-element crystals, often they are comprised of two *interlocking* lattices, which you can see if we select Cl^- as the atom at $\{0, 0, 0\}$, instead of Na^+ - the lattice is fundamentally the same.

So, now from quickly looking at the example of table salt, we can see that it seems isometric, meaning it is a cubic lattice, and has atoms of the same kind at $\left\{\frac{1}{2}, \frac{1}{2}, 0\right\}$, $\left\{\frac{1}{2}, 0, \frac{1}{2}\right\}$ and $\left\{0, \frac{1}{2}, \frac{1}{2}\right\}$, meaning it is FCC. As such, we would describe table salt to have a FCC cubic lattice.

[2]This is a result of the Pauli exclusion principle - "two or more identical fermions cannot simultaneously occupy the same quantum state within a system described by quantum mechanics".