

# Supplementary XRD Theory

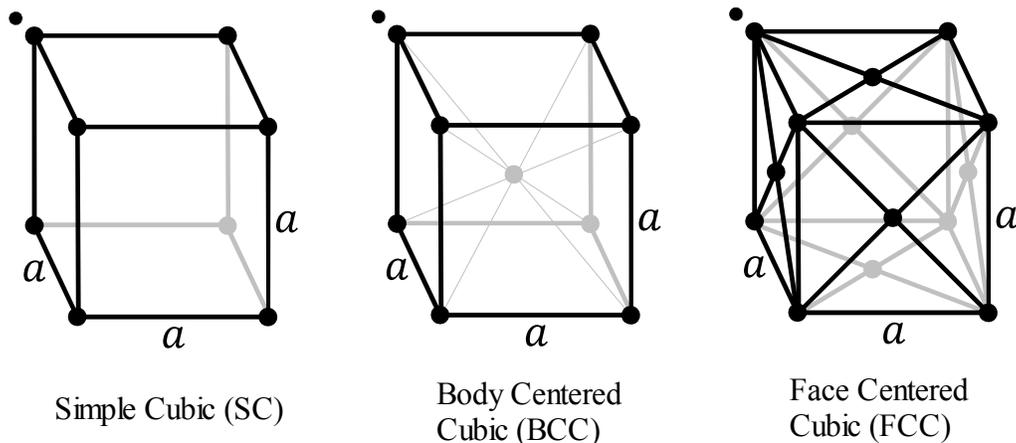
John Hunt - 04.01.08

The structure of a crystalline material may be described by a crystal lattice structure and the locations of atoms in this lattice. The *crystal lattice* is a 3-dimensional periodic array that defines the symmetries, i.e. shape, of the crystal. There are seven possible crystal lattices: cubic, hexagonal, tetragonal, rhombohedral, orthorhombic, monoclinic and triclinic. When we define the possible arrangements of atoms at a point in the crystal lattice, for each lattice, we arrive at the Bravais lattices, sometimes called *bases*, of which there are 14 possible configurations, divided among the seven crystal lattices.

Consider the cubic crystal lattice. It is like a stack of equally sized cubes where the corners of the cubes represent the lattice points. Inside each of these cubes we may arrange equally sized spheres, representing possible atomic sites. The set of possible arrangements that do not repeat within the cube, and cannot be represented by sums of other configurations, are the bases. The six other crystal lattices are represented by various distortions (reductions of the symmetry) of the cubes, or in the case of the hexagonal lattice, the use of hexagonal prisms.

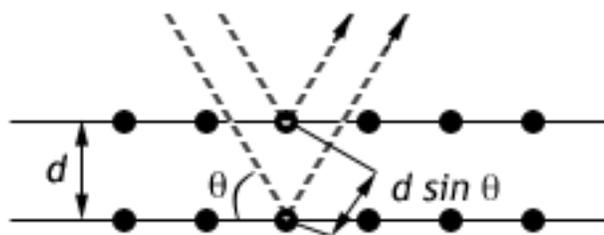
A particular crystal can then be defined by placing the appropriate atoms in the appropriate locations in a basis, thus defining the unit cell for the crystal. This unit cell may then be translated in three dimensions, according to the symmetries of the crystal lattice, to generate the entire crystal.

In this lab, all the crystals you will investigate have cubic symmetry. For the cubic lattice there are three distinct basis (**Fig. 1**). The length of the side of the unit cell,  $a$  or  $a_0$ , is known as the lattice constant.



**Fig. 1**

Note that while **Fig. 1** shows atoms at all positions in the basis, this is for only for conceptual clarity. To prevent duplication of atoms during translation of the unit cell, the true basis contains only those atoms which remain in the cell after an infinitesimal shift along the  $(1,1,1)a_0$  vector. Thus the SC unit cell contains only one atom located at  $(0,0,0)$ , the BCC unit cell contains only the atoms located at  $(0,0,0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})a_0$ , and the FCC unit cell contains only the atoms located at  $(0,0,0)$ ,  $(\frac{1}{2}, 0, \frac{1}{2})a_0$ ,  $(\frac{1}{2}, \frac{1}{2}, 0)a_0$  and  $(0, \frac{1}{2}, \frac{1}{2})a_0$ .



**Fig. 2**

In XRD, Bragg diffraction off of different sets of crystallographic planes occurs (Fig. 2) according to the Bragg condition,

$$n\lambda = 2d \sin(\theta) \quad (1)$$

Thus it is necessary to define different planes in the unit cell and the distances between them. To define a plane in the unit cell, we select the intercepts of the plane with the crystal lattice vectors (which for the cubic lattice are just the x, y and z Cartesian axes) and divide by  $a_0$ . These new coordinates are called *relative coordinates* and will be used from here on to denote plane intersections, atom positions and distances in the unit cell. The reciprocals of these normalized intercepts,  $h$ ,  $k$  and  $l$  are known as the *Miller indices* of the plane and the plane is called the  $hkl$  plane. When multiplied by  $a_0$ , the Miller indices define the vector  $(ha_0, ka_0, la_0)$  which is normal to the  $hkl$  plane.

For example, the plane in the FCC unit cell shown in Fig. 3 intersects the crystal lattice vectors at  $x = \frac{1}{2}$ ,  $y = 1$ ,  $z = \text{infinity}$  (never intersects). The inverse of these coordinates gives  $h=2$ ,  $k=1$ ,  $l=0$  and so this is called the 210 plane. The  $(2,1,0)$  vector normal to the plane is also shown. Fig. 4 shows other planes in an SC crystal.

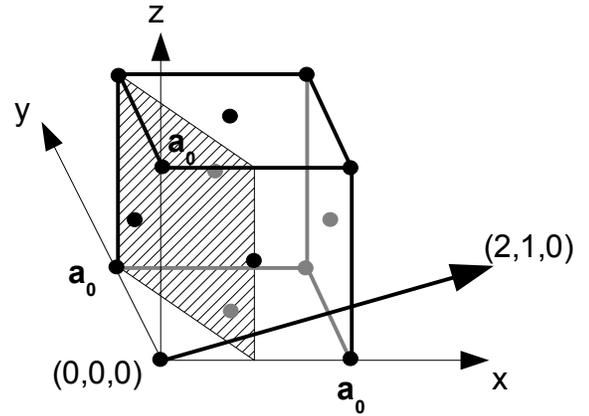


Fig. 3

Writing the  $hkl$  plane in parenthesis,  $(hkl)$ , defines the set of planes parallel to the  $hkl$  plane and with constant separation between planes. The separation between planes in set  $(hkl)$  is the distance from plane  $hkl$  to the origin. All possible spacings between planes in the SC lattice are then given by,

$$d(hkl) = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

For instance, the (100) planes and the (200) planes are parallel but the (100) planes have separation of one while the (200) planes have separation  $\frac{1}{2}$ . Substituting (2) into (1) gives the condition for Bragg diffraction between different sets of planes, as defined by their Miller indices,

$$\lambda = 2 \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \sin \theta \quad (3)$$

The n's in eqn. (1) and eqn. (2) cancel out because, for instance, the 2<sup>nd</sup> order reflection from the (100) plane,  $n = 2$  in (1), can be considered the first order reflection from the (200) plane with  $n = 1$  in (2).

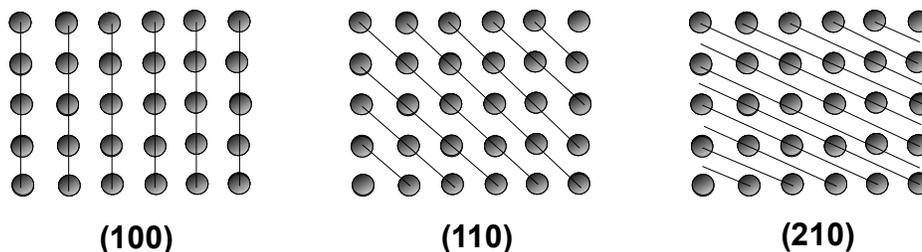


Fig. 4

Eqn. (3) assumes a constant intensity for all reflections. In reality, the density of atoms in each plane decreases as  $hkl$  get large (**Fig. 4**) and the intensity of the corresponding peak decreases. Even more significant is the effect of interactions between additional atoms in the basis, as in the case of an FCC or BCC structure. These additional atoms may produce reflections which interfere constructively or destructively with the peak predicted by eqn. (3), in some cases resulting in the complete absence of a peak. If we denote the position of atom  $j$  in the unit cell with relative coordinates  $u_j, v_j, w_j$ , then the intensity of the peak from the  $(hkl)$  planes will be proportional to the square of the crystal structure factor,  $F(hkl)$ ,

$$F(hkl) = \sum_j f_j e^{2\pi i(hu_j + kv_j + lw_j)} \quad (4)$$

where we are summing over all atoms  $j$  in the unit cell. The term  $f_j$  is a proportionality constant unique to the type of atom  $j$  and decreases with increasing diffraction angle.

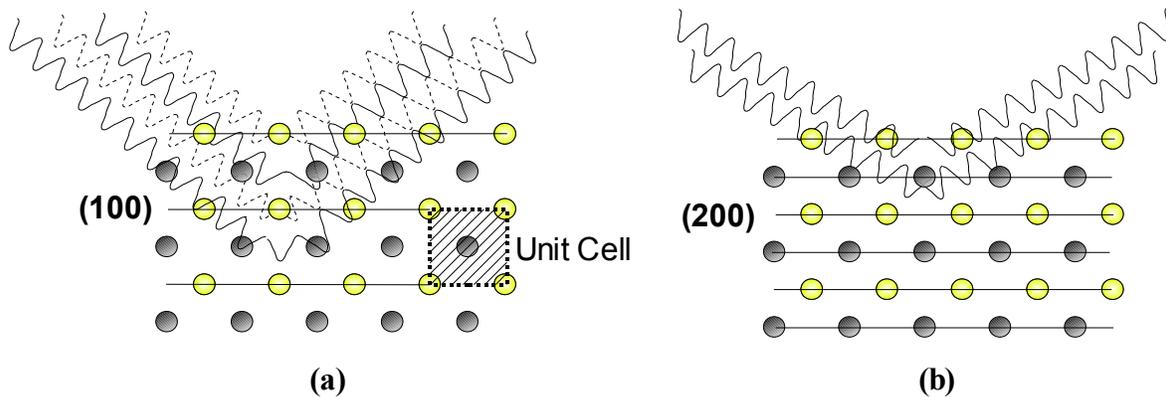
Consider a CsCl crystal having BCC structure. The unit cell consists of one atom, say Cs, located at relative coordinates  $(0,0,0)$  and the other, Cl, located at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Then for the  $(100)$  reflection, the crystal structure factor becomes,

$$F(100) = \sum_{j=Cs, Cl} f_j e^{2\pi i(hu_j + kv_j + lw_j)} = f_{Cs} e^{2\pi i(1*0+0*0+0*0)} + f_{Cl} e^{2\pi i(1*\frac{1}{2}+0*\frac{1}{2}+0*\frac{1}{2})} = f_{Cs} - f_{Cl} \quad (5)$$

in other words, the intensity of the peak is the intensity of the reflection from the Cs planes minus the intensity of the reflection from the Cl planes, and the intensity of this peak is nearly zero. For the reflection from the  $(200)$  planes, which occurs at a *different* angle satisfying eqn. (3), the crystal structure factor becomes,

$$F(200) = f_{Cs} e^{2\pi i(2*0+0*0+0*0)} + f_{Cl} e^{2\pi i(2*\frac{1}{2}+0*\frac{1}{2}+0*\frac{1}{2})} = f_{Cs} + f_{Cl} \quad (6)$$

and this peak has large intensity. **Fig. 4** shows this schematically.



**Fig. 4**

*Note that the Bragg condition is not strictly satisfied in these drawings. The yellow/lighter atoms represent the Cs and the grey/darker atoms represent Cl. In (a) the reflections from the  $(100)$  planes, i.e. the Cs atoms, have a path length difference of  $\lambda$  and interfere constructively as expected from eqn. 3. However, there are also reflections from the Cl atoms which have a path length difference of  $\lambda$  with each other and are in phase, but a difference of  $\lambda/2$  with the Cs reflections so these two sets of reflections destructively interfere and no peak is observed, as expected from eqn. (5). (b) shows the reflections from the  $(200)$  planes, i.e. alternating Cs – Cl planes. As expected from (6), these are in phase and a peak is seen for this reflection.*

The crystal structure factor for the BCC unit cell with only one type of atom in the basis may be generalized to,

$$F_{BCC}(hkl) = f(1 + e^{\pi i(h+k+l)}) \quad (7)$$

so a peak is seen when the sum  $h+k+l$  is even and no peak is seen when the sum is odd. The generalized crystal structure factor for the FCC unit cell is,

$$F_{FCC}(hkl) = f(1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}) \quad (8)$$

so a peak is seen when  $hkl$  are all even or all odd.

## Analysis

To analyze an XRD spectrum you must assign a wavelength value (from your source) and  $hkl$  set to each peak. When these values are correctly assigned, eqn. (3) will yield a consistent value for  $a_0$ . The set of  $hkl$  values that are found can be used with eqn. (7) and (8), or in general eqn.(4), to determine the crystal structure.

An XRD spectrum will have a series of peaks of decreasing magnitude, due to the decreasing density of atoms in each layer as the angle increases. For our setup, these peaks will come in sets of two for each  $hkl$ -theta combination; a larger peak corresponding to the more intense 0.154nm xrays will be located to the right of a smaller peak corresponding to the 0.138nm xrays. At larger values of theta these two peaks may separate enough to overlap other sets of peaks, and at this point you will have to try to group the peaks intelligently. For each set of peaks you must then assign an  $hkl$  combination.

If the crystal structure is unknown, this may be done blindly until a correct combination is hit upon. In our case it is assumed that the crystal structure for each sample is known and we want to find  $a_0$  for each sample, so we only pick  $hkl$  combinations that satisfy the conditions given by eqn. (7) or (8) depending on the known crystal structure. This still sounds like an impossible task but we know that the peak intensity decreases with decreasing plane spacing,  $d$ , (**Fig. 4**) and  $d$  decreases as the sum of squares of  $hkl$  increases (eqn.2). Then the lowest  $hkl$  sum of squares that satisfies the conditions set by eqn. (7) or (8) should be used for the most intense (i.e. left-most) peaks. So, for LiF, having an FCC crystal structure (actually a sum of two offset FCC bases, one with Li atoms and one with F atoms), the first  $h, k, l$  combination would be 1,1,1.

Make a table with columns labeled:

- (a) the scattering angle  $2\Theta$ ,
- (b) the true angle  $\Theta$ ,
- (c) xray wavelength (0.154 or 0.138nm),
- (d)  $h, k, l$ ,
- (e)  $h^2+k^2+l^2$ ,
- (f) calculated  $a_0$  from eqn.(3)

Record the  $2\Theta$  location for every peak, then assign the appropriate source wavelength. For each peak, fill in the associated  $hkl$  combination consistent with eqn. (7) or (8) where the sum of squares of  $h, k$  and  $l$  increases with increasing  $\Theta$ . Report the average of the calculated  $a_0$ .