# CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES


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## Lecture 45: Structure Factor Calculations

In the last lecture, I had derived the equation for the structure factor. This is a very important equation because it contains information regarding the positions of atoms in a unit cell. In this lecture, we are now going to perform some example calculations of the structure factor.

So, the structure factor that we derived in the last lecture is denoted by the capital $F$, which is defined as a sum over all the atoms present in the unit cell. In this equation, $F$ is the structure factor, $f_j$ is the atomic scattering factor for the $j^{th}$ atom, $h$, $k$, and $l$ are the Miller indices of the planes from which X-rays are being reflected, and $u_j$, $v_j$, $w_j$ represent the position vector of the $j^{th}$ atom.

Now, this relationship is analyzed when the Bragg condition is satisfied, or equivalently when the Laue conditions are satisfied. Therefore, we expect a finite intensity when a Bragg relationship is satisfied. However, if the structure factor goes to zero, then we would obtain extinction of that particular reflection. Thus, for $F \neq 0$ at the Bragg condition, one should observe a reflection, whereas if $F = 0$, we get extinction. It is precisely these extinctions that give us a clue regarding the type of crystal structure and the locations of atoms within the unit cell.

Therefore, as we have written earlier as well, the intensity produced is proportional to the product of the structure factor and its complex conjugate, that is, $FF^*$.

Before proceeding to an example, let us note that the structure factor is a complex quantity. Hence, it is instructive to recall some useful identities associated with complex quantities. If we consider a complex function $e^{ix}$, then in the context of the structure factor, $x$ is simply $2\pi(hu_j + kv_j + lw_j)$. We can expand $e^{ix}$ in terms of trigonometric functions as

$$e^{ix} = cosx + isinx.$$

The first identity we consider is when $x$ is an integral multiple of π. In that case, we can write $e^{in\pi}$, where $n$ is an integer. This quantity is equal to either $+ 1$ or $- 1$ depending on whether $n$ is even or odd. Very clearly, $e^{in\pi} =+ 1$ for even $n$ and $e^{in\pi} =- 1$ for odd $n$.

Another useful identity is $e^{in\pi} = e^{-in\pi}$.

A third identity involves the sum $e^{ix} + e^{-ix}$.

If we expand both terms, one contains $cosx + isinx$ and the other contains $cos(- x) + isin(- x)$. Since $cos(- x) = cosx$ and $sin(- x) =- sinx$, the imaginary terms cancel out, leaving

$$e^{ix} + e^{-ix} = 2cosx.$$

Keeping these identities in mind, let us now proceed to Example 1.

In Example 1, we take the simplest possible case of a crystal whose lattice is a primitive lattice. The unit cell is primitive, and the motif, or basis, added to this primitive unit cell is monoatomic. What does this mean? It means that there is only one atom per lattice point, and its position is at $(0, 0, 0)$. This implies that the same kind of atom is present at every lattice point in the primitive unit cell. Since the lattice is primitive, the atom is present only at the corners of the unit cell.

Therefore, how many atoms are present per unit cell? The number of atoms per unit cell is simply 1. From the structure factor equation, this implies that $m = 1$. The position vector $(u_j, v_j, w_j)$ then takes the value $(0, 0, 0)$. Hence, if we write down the structure factor, we obtain the atomic scattering factor multiplied by $e^{i2\pi(0)}$.

Since the exponential term is unity, the structure factor in this case is simply equal to the atomic scattering factor.

If we now look at the intensity, it is proportional to $FF^*$, and therefore, it is proportional to $f^2$. What does this expression tell us? It tells us that irrespective of the values of $h$, $k$, and $l$, there will never be any extinction of X-rays. In other words, the structure factor is never zero, and hence there is no extinction. This was a very simple case.

Let us now take another example, which we will call Example 2. In this example, consider a crystal whose lattice is end-centered, or base-centered, monoclinic. The motif is again monoatomic, so there is only one kind of atom present, and the atomic position is $(0, 0, 0)$. This implies that the same kind of atom is populated at each lattice point. However, in this case, the atom is present at the corners of the unit cell and also at the centers of two opposite faces of the unit cell.

Let us describe the structure. We have the same kind of atom present at all the corners, and let us say that the atoms are present on two opposite faces, which we call the A faces. The axes are labeled as the $a$, b, and $c$ axes. The atoms present on the A faces correspond to faces parallel to the $BC$ plane. This structure is therefore called an end-centered monoclinic lattice and is denoted by the symbol $A$. The twofold axis in this case is along $C$, meaning that the $C$ axis is the unique axis. Since the $C$ axis is unique, one cannot place the end-centered atoms on the $C$ face; they can only be placed on the rectangular faces of the monoclinic cell.

Now, let us determine the position vectors $(u_j, v_j, w_j)$. In this case, there are two atoms of the same kind per unit cell. Their position vectors are $(0, 0, 0)$ for the atom at the origin and $(0, \frac{1}{2}, \frac{1}{2})$ for the end-centered atom. You may wonder about the other atoms at the corners of the unit cell. Those atoms belong to adjacent unit cells and can be considered as origins of those unit cells. Therefore, we only need to consider the atoms that are present within this unit cell.

Thus, we label the atom at the origin as atom 1 and the atom at $(0, \frac{1}{2}, \frac{1}{2})$ as atom 2. Since there are two atoms, there will be two terms in the structure factor. The atomic scattering factor $f_j$ is the same for both atoms, so it can be taken outside the summation. The structure factor then becomes

$$F = f\left[1 + e^{i\pi(k+l)}\right].$$

Now, it is very clear that $F = 0$ if the term $e^{i\pi(k+l)} = -1$. When does this happen? Since $k + l$ is always an integer, we can write $k + l = n$. Then $e^{in\pi} = -1$ when $n$ is odd. Therefore, if $k + l$ is odd, $F = 0$, which also implies $F^* = 0$, and hence we get extinction.

If $k + l$ is even, then $e^{i\pi(k+l)} = +1$, and hence $F = 2f$. This implies that $FF^* = 4f^2$, and we obtain a finite intensity for this structure.

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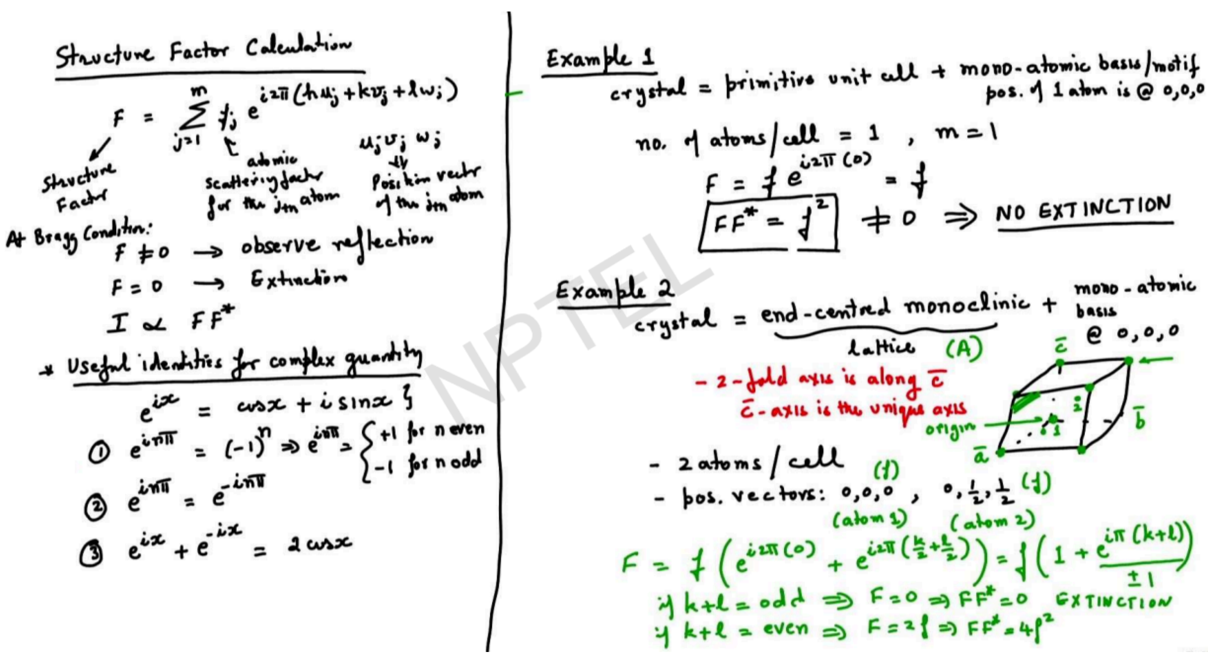

Let us now take a third example. In Example 3, we consider a crystal with more atoms in the structure. Let us take a face-centered cubic lattice. Face-centered cubic lattices can occur in cubic systems and also in orthorhombic systems. Once again, we consider a monoatomic basis, meaning that the same kind of atom is present at every lattice point, with one atom located at $(0, 0, 0)$.

In this case, there are four lattice points per unit cell, and hence four atoms per unit cell. A typical example of such a crystal is copper, which has a face-centered cubic structure, although similar arrangements can also occur in orthorhombic crystal systems. The position vectors $(u_j, v_j, w_j)$ for the four atoms are $(0, 0, 0)$ for the corner atoms and $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$ for the face-centered atoms.

Substituting these values into the structure factor equation and taking the common atomic scattering factor $f$ outside the summation, we obtain four terms. The first term corresponding to $(0, 0, 0)$ is 1. The second term is $e^{i\pi(h+k)}$, the third term is $e^{i\pi(h+l)}$, and the fourth term is $e^{i\pi(k+l)}$. Each of these exponential terms can take only the values $+ 1$ or $- 1$ because $h + k$, $h + l$, and $k + l$ are integers.

Now, let us analyze when all these exponential terms are equal to $+ 1$. For $h + k$ to be even, $h$ and $k$ must both be even or both be odd. The same argument applies to $h + l$ and $k + l$. This condition is satisfied when $h$, $k$, and $l$ are either all even or all odd. Such indices are referred to as unmixed indices. In this case, each exponential term is $+ 1$, and hence $F = 4f$, which implies

$$FF^* = 16f^2.$$

Therefore, there is no extinction, and diffraction takes place.

Now, consider the case when some of the indices $h$, $k$, and $l$ are even and some are odd. This is referred to as the mixed case. Let us consider an example where $h$ is even, $k$ is even, and $l$ is odd. Then $h + k$ is even, so $e^{i\pi(h+k)} =+ 1$. However, $h + l$ is odd, so

$e^{i\pi(h+l)} = -1$, and $k + l$ is also odd, so $e^{i\pi(k+l)} = -1$. Adding all the terms, we find that $F = 0$, and hence we get extinction.

Let us take another example where $h$ is odd, $k$ is even, and $l$ is odd. In this case, $h + k$ is odd, so the corresponding exponential term is $-1$. The sum $h + l$ is even, so the corresponding term is $+1$. The sum $k + l$ is odd, giving another $-1$. Once again, the total structure factor becomes zero, and we get extinction. Thus, whenever $h$, $k$, and $l$ are mixed, extinction occurs for a face-centered cubic lattice with a monoatomic basis.

Finally, let us consider Example 4. Here, we take a body-centered unit cell with a monoatomic basis. An example of such a structure is iron, which crystallizes in a body-centered cubic structure with one iron atom at $(0, 0, 0)$. In this case, there are iron atoms at the corners of the cubic cell and one iron atom at the body center. Therefore, the number of atoms per unit cell is $m = 2$.

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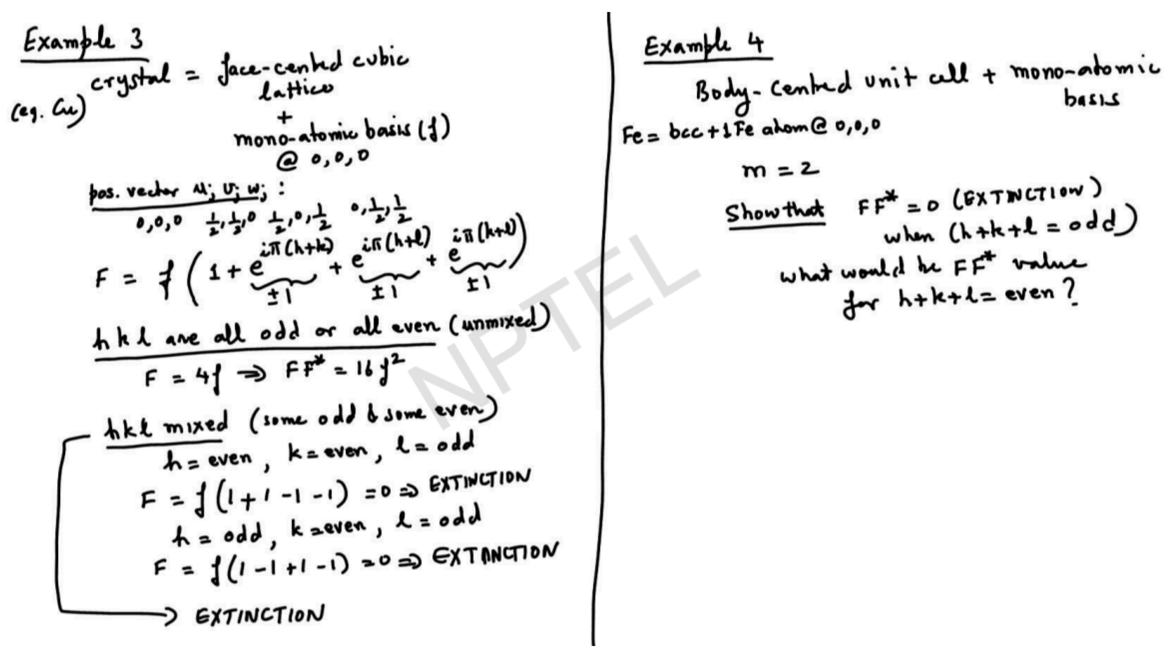

I will leave this as a problem for you to solve. Show that $FF^* = 0$, which corresponds to extinction, when $h + k + l$ is an odd number. Also determine the value of $FF^*$ when $h + k + l$ is even. This is a simple problem that you should try to solve on your own.

I will conclude this part of the lecture here. In the next lecture, we will examine more complicated structures that contain more than one atom in the basis, and in some cases, the atoms may be of different types. Thank you.