CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 46: Structure Factor Calculations

In the previous lecture, simple crystal structures with a monoatomic basis were examined, and the structure factor was evaluated in order to determine which (hkl) planes produce diffraction reflections and for which (hkl) plane extinction occurs, even when Bragg's law is satisfied. In the present lecture, attention is turned to comparatively more complex crystal structures that possess a multi-atomic basis.

Accordingly, crystals containing more than one atom in the basis are considered. These atoms may be identical or different. As a first illustration, referred to here as Example 1, the structure of diamond is examined. As discussed in an earlier lecture, the diamond crystal consists of a face-centered cubic unit cell to which a two-atom basis is added, namely two carbon atoms located at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

Since a face-centered cubic lattice contains four lattice points per unit cell and the basis consists of two atoms, the total number of carbon atoms per unit cell is eight. Of these, four arise from the corner and face-center lattice points, while the remaining four correspond to atoms lying along the four body diagonals.

The next step is to determine the atomic positions. In this case, there are eight position vectors, and these can be written in a convenient manner. First, the face-centered cubic lattice translation vectors are written as $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$. These represent the four lattice points within the unit cell; the remaining lattice points, as explained earlier, belong to neighboring unit cells.

To these lattice translations, the two carbon atom basis vectors, $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, are added. Adding $(0, 0, 0)$ to all lattice translations yields the positions of four carbon atoms, while adding $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ to the same lattice translations yields the positions of the remaining four carbon atoms, which lie along the body diagonals.

Rather than explicitly writing all eight position vectors, the structure factor can be expressed in a simpler form. Although in this case the total number of atoms m is eight and the structure factor formally contains eight terms, it is more instructive to decompose the structure factor into two parts: a motif (or basis) contribution and a lattice contribution. Since all atoms are carbon atoms, they possess the same atomic scattering factor. This common atomic scattering factor can therefore be taken outside the summation and denoted by f.

The motif contribution is written first. Substituting the coordinates of the two carbon atoms yields $1 + e^{i2\pi\left(\frac{h}{4}+\frac{k}{4}+\frac{l}{4}\right)}$. The lattice contribution corresponds to the face-centered cubic translations and is given by

$$1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}.$$

If these two contributions are multiplied, one clearly obtains eight terms, corresponding to the eight atomic positions. However, the factorized form makes the analysis considerably simpler.

From the previous lecture, the behavior of the lattice contribution is already known. This term vanishes when (hkl) are mixed and equals 4 when (hkl) are unmixed. If (hkl) are mixed, extinction occurs and no further analysis is required. Therefore, only the case of unmixed (hkl) is considered.

When (hkl) are unmixed, the lattice contribution yields a factor of 4, and the structure factor becomes $4f$ multiplied by the motif term. In the motif term, the first contribution is unity, since it corresponds to $e^{i2\pi\cdot 0} = 1$, while the second contribution is $e^{i\pi\frac{h+k+l}{2}}$. At this point, one may ask whether the structure factor can still vanish. This is indeed possible if this exponential term equals -1.

This situation occurs when $(h + k + l)/2$ is an odd integer, or equivalently when $h + k + l$ is an odd multiple of 2. In that case, $e^{i\pi\frac{h+k+l}{2}} = -1$, and the two terms in the motif cancel each other. Consequently, the structure factor becomes zero, leading to extinction. This extinction is additional to the extinctions that already arise from the face-centered cubic lattice itself, and therefore represents an extra extinction condition.

Now, if $\frac{h+k+l}{2}$ is an even number, this implies that

$e^{i\pi(h+k+l)/2} = +1$, and hence the structure factor F becomes $8f$, because

$1 + e^{i\pi(h+k+l)/2} = 2$.

Thus, $2 \times 4 = 8$, and consequently $F = 8f$, or $F^{*} = 64f^{2}$.

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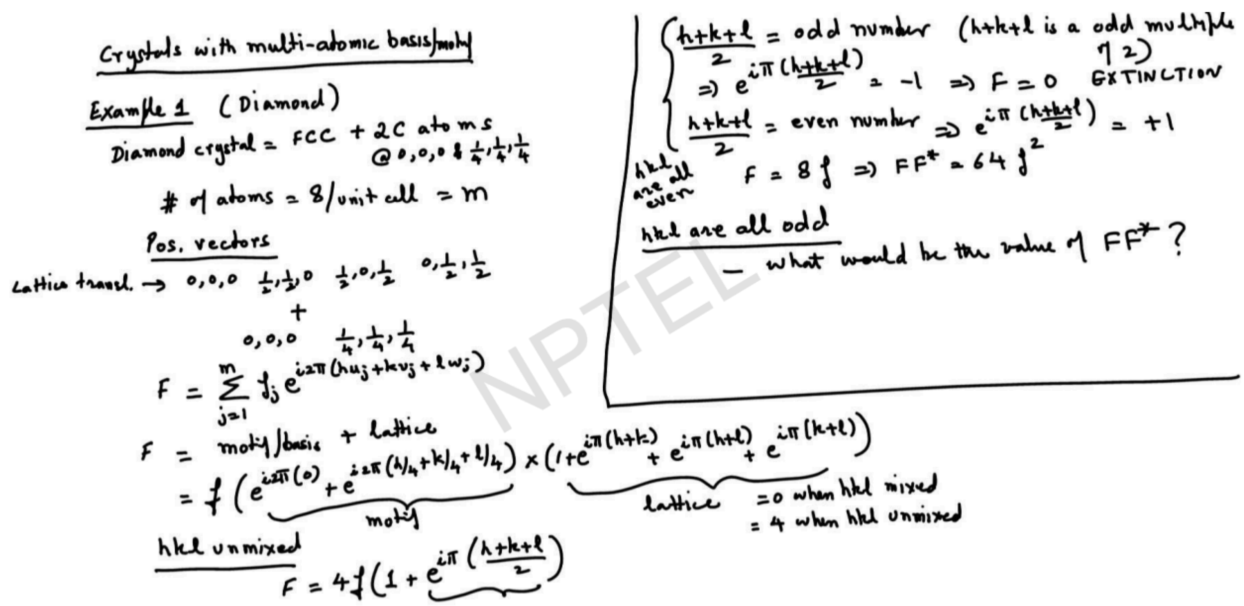

Therefore, in the unmixed case, one observes a specific situation in which necessarily h, k, and l are all even. However, there also exists a situation in which h, k, and l are all odd. In that case, $\frac{h+k+l}{2}$ becomes a fractional value, and I leave it to you to determine the value of FF^{*} when h, k, and l are all odd.

Now, let me consider another case, or rather, generalize the approach adopted so far. In general, the structure factor can be decomposed into two components, as previously stated: the motif and the lattice.

Let the lattice point coordinates within the unit cell be given by (u_j, v_j, w_j), where j ranges from 1 to m. If the unit cell is primitive, there will be only one lattice point; if it is body-centered or end-centered, there will be two lattice points; and if it is face-centered, there will be four lattice points. Thus, m can take values 1, 2, or 4.

The motif may consist of a large number of atoms in many cases. Let the fractional coordinates of the pth atom in the motif be (x_p, y_p, z_p), and let the corresponding atomic scattering factor be f_p. These coordinates are fractional coordinates within the crystal lattice.

If the motif contains n atoms, which may be identical or different in any combination, the structure factor can be written in a compact form as follows:

$$F = \sum_{p=1}^{n} f_p e^{i2\pi(hx_p + ky_p + lz_p)} \sum_{j=1}^{m} e^{i2\pi(hu_j + kv_j + lw_j)}.$$

This expression is particularly useful when the motif contains a large number of atoms and one wishes to analyze the resulting structure factor. If this equation is applied to earlier examples, such as the diamond structure, it yields the same result.

Now, let us consider an example. Let this be Example 2, corresponding to a sodium chloride (NaCl) crystal. This structure can be described as a face-centered cubic lattice with a motif consisting of a chlorine ion at $(0, 0, 0)$ and a sodium ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

In this structure, chlorine ions occupy the corners and face centers, while sodium ions occupy the body-centered positions and the centers of all edges. To calculate the structure factor, we begin with the motif contribution. Since there are two atoms in the motif, $n = 2$, and for the FCC lattice, $m = 4$.

The first motif term corresponds to the chlorine atom. Let its atomic scattering factor be f_{Cl}. Substituting $(0, 0, 0)$ into the exponential term gives unity, so the first contribution is simply f_{Cl}.

The second term corresponds to the sodium atom, with atomic scattering factor f_{Na}. Substituting $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ yields the exponential term $e^{i\pi(h+k+l)}$.

Next, we write the lattice contribution. For a face-centered cubic lattice, this is given by

$$1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}.$$

As already discussed, this term becomes zero for mixed values of h, k, and l, and equals 4 for unmixed values. Therefore, it is sufficient to analyze only the unmixed case, since the structure factor vanishes otherwise.

For unmixed hkl, the structure factor becomes

$$F = 4\left(f_{Cl} + f_{Na}e^{i\pi(h+k+l)}\right).$$

This expression is straightforward to analyze. When $h + k + l$ is even, the exponential term equals $+ 1$, and when $h + k + l$ is odd, it equals $- 1$. Hence,

$$F = 4(f_{Cl} + f_{Na}) \quad for\, h + k + l\, even,$$

$$F = 4(f_{Cl} - f_{Na}) \quad for\, h + k + l\, odd.$$

The intensity is then obtained from FF^*.

Finally, let me consider one last example before concluding. Let us examine a titanium crystal. Titanium can crystallize in a structure known as hexagonal close-packed. It should be noted that there is no distinct lattice called hexagonal close-packed; rather, the term refers to the densest packing of spheres within a hexagonal unit cell. Structurally, the crystal consists of a primitive or simple hexagonal unit cell containing two titanium atoms.

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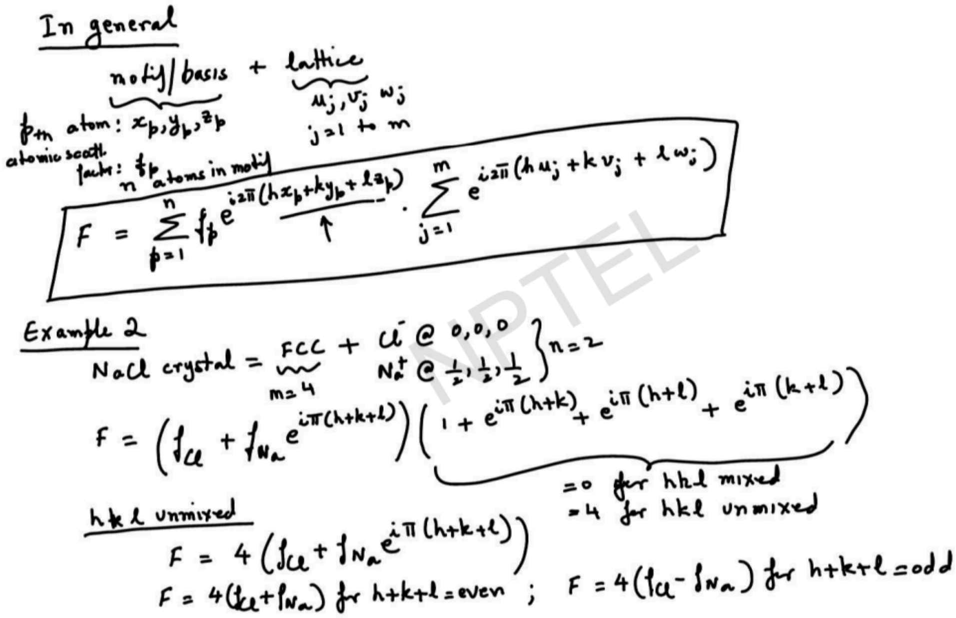

In this case, once again, there is more than one atom in the basis; however, the unit cell itself is primitive. The two titanium atoms are located at $(0, 0, 0)$ and $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$.

The structure factor F can now be written by first considering the motif contribution. Since both atoms are of the same type, the atomic scattering factor is identical for each atom, and we denote it by f_{Ti}. The motif contains two atoms, so there are two terms in the motif summation. Thus, $n = 2$. As the lattice is primitive, there is only one lattice point per unit cell, so $m = 1$.

Factoring out f_{Ti}, the structure factor becomes

$$F = f_{Ti}\left[1 + e^{i2\pi\left(\frac{h+2k}{3} + \frac{l}{2}\right)}\right].$$

The lattice contribution corresponds to a single lattice point at $(0, 0, 0)$ and therefore equals unity. As already discussed, a primitive lattice does not produce systematic extinctions.

To simplify the expression, let us define a parameter q such that

$$q = \frac{2(h+2k)}{3} + l.$$

Introducing this definition allows the structure factor to be written as

$$F = f_{Ti}\left(1 + e^{i\pi q}\right).$$

It is clear that F becomes zero when $e^{i\pi q} = -1$, which occurs when q is an odd integer. However, q can also take fractional values, in which case the structure factor remains complex. A more systematic approach is therefore to examine the intensity, which is proportional to FF^*, the product of the structure factor and its complex conjugate.

Thus, we write

$$FF^* = f_{Ti}\left(1 + e^{i\pi q}\right) f_{Ti}\left(1 + e^{-i\pi q}\right).$$

Expanding this expression yields

$$FF^* = f_{Ti}^2\left[2 + e^{i\pi q} + e^{-i\pi q}\right].$$

Recalling from earlier discussions that

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

we obtain

$$FF^* = 2f_{Ti}^2(1 + cos\pi q).$$

This form eliminates the complex terms and allows direct analysis. The intensity becomes zero when $cos\pi q = -1$, which occurs for odd integer values of q. For even values of q, $cos\pi q = +1$.

To determine when q is odd, recall that

$$q = \frac{2(h+2k)}{3} + l.$$

If $\frac{h+2k}{3}$ is an integer, say n, then the first term becomes $2n$, which is even. If l is odd, the sum of an even and an odd number yields an odd value of q. In this case, $FF^* = 0$, leading to extinction.

If l is even, then q is even, $cos\pi q =+ 1$, and the bracketed term equals 2. Consequently,

$$FF^* = 4f_{Ti}^2.$$

We now consider other possible cases. Since h and k are integers, $h + 2k$ can be written as $3n$, $3n + 1$, or $3n - 1$. The case $3n$ has already been discussed.

As an example, consider the (111) reflection. Here, $h + 2k = 3$, which is a multiple of 3, and l is odd. Hence, extinction occurs. For the (112) reflection, $h + 2k$ remains a multiple of 3, but l is even, resulting in nonzero intensity.

Now consider the case where $h + 2k = 3n \pm 1$. Substituting into the expression for q, we obtain

$$q = \frac{2(3n\pm1)}{3} + l = 2n + l \pm \frac{2}{3}.$$

Thus,

$$cos\pi q = cos\left[(2n + l)\pi \pm \frac{2\pi}{3}\right].$$

Since $\frac{2\pi}{3}$ corresponds to 120°, and $2n + l$ may be either even or odd, we analyze the two cases separately.

If $2n + l$ is odd, then

$$cos\pi q =- cos\frac{2\pi}{3}.$$

Since $cos\frac{2\pi}{3} =- \frac{1}{2}$, this gives $cos\pi q = \frac{1}{2}$. Substituting into the intensity expression yields

$$FF^* = 3f_{Ti}^2.$$

Because $2n$ is always even, $2n + l$ is odd only when l is odd. Therefore, when $h + 2k = 3n \pm 1$ and l is odd, the structure factor is nonzero and equal to $3f_{Ti}^2$. There is no extinction, but the intensity differs from the case where $h + 2k$ is a multiple of 3.

If l is even, then $2n + l$ is even, and

$$cos\pi q = cos\frac{2\pi}{3} = -\frac{1}{2}.$$

Substituting this value gives

$$FF^* = f_{Ti}^2.$$

In this manner, all possible cases have been considered for the titanium crystal, or for any crystal possessing a primitive hexagonal unit cell with two identical atoms arranged to form a hexagonal close-packed structure.

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