CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

Prof. Sandeep Sangal
IIT Kanpur

Lecture 02: Lattice, Motif, Crystals and Unit Cells

In the last lecture, we described what is called a lattice and what its defining feature is. The defining feature of a lattice is its translation symmetry. Now, we want to come to the concept of a crystal and understand how it is different from a lattice. So, let me write this in the form of an equation:

$$Crystal = Lattice + Motif$$

So, a crystal will have atoms, and where are these atoms going to come from? The atoms are going to come from the motif.

So, let us take some examples to understand this better. This addition of lattice plus motif is actually an addition of vectors, as we will see a little later. Let us first take a one-dimensional example. Consider a lattice which is simply a row of points in one dimension, stretching again from minus infinity to plus infinity.

Now, what do I do? I take a motif which consists of one atom. I place this atom such that the center of the atom coincides with the lattice point. That is one way I can place this atom at every lattice point. So now, I have a crystal structure, a one-dimensional crystal structure, where an atom is present at every lattice point.

But then, a motif can be more complex than this. It can consist of two atoms, and let us say this motif consists of two atoms like this. So now, I have a two-atom motif, and just the way the atoms are arranged in the motif, that is the same way the atoms will be present at every lattice point. As you can see here, one atom has its center coinciding with the lattice point, and the second atom is somewhat shifted.

Now, the motif need not consist of the same kind of atom. Let's consider a second motif that looks something like this. Now, I have a motif made up of two different atoms, one is a green-colored atom and the other is a red-colored atom. Let us take this example as well, and this time, I decided not to make any atom's center coincide with the lattice point. For example, I first place the green atom, and as you can see, its center does not coincide with the lattice point, and then the second, the red atom goes here.

So, neither of the atom centers coincides with the lattice point and that is absolutely fine. Whether the center of the atom coincides with the lattice point or not, it does not matter if the overall arrangement of atoms in the crystal remains identical. Therefore, we are actually free to choose the origin. However, we will see later that there are certain preferred choices for the origin in a crystal, but we will discuss that at a much later stage in the course.

Now, I can extend the same idea to two dimensions. Let's take a motif that consists of two atoms. Say, one type of atom and another type arranged in a certain orientation. As you can see, this motif has a specific orientation, and that same orientation must be maintained throughout the lattice. So, for example, I can first place the green atoms at their respective positions and then place the red atoms accordingly. By maintaining the same orientation everywhere, we obtain a two-dimensional crystal.

Now, let us look at these crystals a bit more closely. For instance, take the one-dimensional crystal whose lattice has a translation vector $\bar{a}$. You will notice that the individual atoms in the motif also follow exactly the same translation, that is, when the lattice is translated by $\bar{a}$, the entire motif repeats in the same manner.

For example, the atom whose center coincides with the lattice point will have the same translation as the lattice, which is $\bar{a}$, and similarly, the second atom will also follow the

same translation. So, what we observe is that the individual atoms in the motif follow exactly the same translation as dictated by the lattice.

The same is true for the second one-dimensional crystal pattern, if the lattice translation is $\overline{a}$, then both the green and red atoms will translate by $\overline{a}$. However, one important point to note here is that even though all atoms are identical in the first case, there exist pairs of atoms that are not translationally equivalent.

What does that mean? It means that this is not a translation vector, and this is important to note. In the second case, if the lattice has translations $\overline{a}$ and $\overline{b}$, the green atoms follow the translation $\overline{a}$, and similarly, they also follow the translation $\overline{b}$. The red atoms also follow the translations $\overline{a}$ and $\overline{b}$. Again, I emphasize that the individual atoms in the motif follow exactly the same translations as the lattice.

Now, whether it is one-dimensional or two-dimensional, these are all infinite arrangements of atoms. Therefore, to describe the structure efficiently, we need to reduce it to a smaller representative unit. This is done by defining a unit cell. Let us consider the two-dimensional case and define the unit cell with respect to a lattice. Here is a two-dimensional lattice.

In order to describe the lattice, I will define a small unit. One such unit can be a parallelogram. It may appear more like a square or a rectangle here, but it can be any arbitrary parallelogram. This is one such example. Now, what does it do? Let us say the translation vectors are $\overline{a}$ and $\overline{b}$. If I translate the entire unit cell by $\overline{a}$, the two-dimensional lattice will be replicated. Similarly, if I translate it by $\overline{b}$, the lattice is again replicated. In this way, by translations through $\overline{a}$ and $\overline{b}$, I can replicate the entire lattice.

Now, is this the only possible unit cell I can have? No, other unit cells are also possible. For example, I can have a unit cell like this, in which case the translation vectors could be different. Here, one vector is $\overline{a}$, and the other, let us call it $\overline{b'}$. In fact, I can draw even more skewed unit cells, which are all perfectly valid. For instance, I can have a unit cell like this. Again, one vector is $\overline{a}$, and the translation along this direction can be called $\overline{b''}$.

So, I have these different unit cells that can be defined, but when I translate them by the respective translation vectors: $\overline{a}$ and $\overline{b}$, or $\overline{a}$ and $\overline{b'}$, or $\overline{a}$ and $\overline{b''}$ in the three different cases. I will end up generating the same lattice. One can also consider a unit cell like this. In this case, it is a larger unit cell than any of the previous ones and contains a greater number of lattice points. Here, the translation vectors would be $2\overline{a}$ and $\overline{b}$. Even with this larger unit cell, translating it through $2\overline{a}$ and $\overline{b}$ will generate the identical lattice.

Let us first consider the smaller unit cells, the three unit cells that I have drawn: cell 1, cell 2, and cell 3. In all three unit cells, let us examine how many lattice points are present per unit cell. In each case, the lattice points are located at the corners of the unit cell.

For example, consider a lattice point here. If I draw another unit cell next to it, you can see very clearly that this particular lattice point is shared by four unit cells. This means that effectively, only one-fourth of a lattice point belongs to a single unit cell. Since there are four such lattice points, one at each corner, the effective number of lattice points per unit cell is:

$$4 \times \frac{1}{4} = 1$$

Thus, there is one lattice point per unit cell.

The same is true for cell 2 and cell 3. Now, consider cell 4. In this case, there are the usual corner lattice points, and additionally, there are two more lattice points at the

centers of two opposite edges. From the corner lattice points, we effectively get one lattice point. Thus, the number of lattice points per unit cell from the corners is 1.

Now look at the other two lattice points out here and out here again you will notice that I can draw one more unit cell next above this and therefore, this particular lattice point in the center of the edge will be shared by two unit cells. So, effectively half a lattice point is there in the unit cell and there are two such lattice points which means the contribution would be one from the edge center and one from the corners effectively giving me two lattice points per unit cell.

Another property that can be observed with simple geometry is that cells 1, 2, and 3 all have the same area, which is easy to verify. In the case of cell 4, the area is obviously larger. In fact, it is precisely twice the area of cells 1, 2, or 3. So, cell 4 has an area that is two times that of cells 1, 2, or 3. We give a special name to cells like 1, 2, and 3; all such cells that contain only one lattice point per unit cell are called primitive unit cells. A cell like cell 4 is called a non-primitive unit cell.

Now, if we consider how many primitive unit cells can be defined, the answer is that we can, in fact, have an infinite number of primitive unit cells. Similarly, for non-primitive unit cells, we can draw even larger cells including more lattice points, or we can have different shapes containing the same number of lattice points again, an infinite number of possibilities. Therefore, any lattice can be described by one of the infinitely many available unit cells.

One conclusion from this is that there is an infinite choice of unit cells. However, there exists a conventional choice of unit cells, and we will gradually develop an understanding of how these conventional choices are made.

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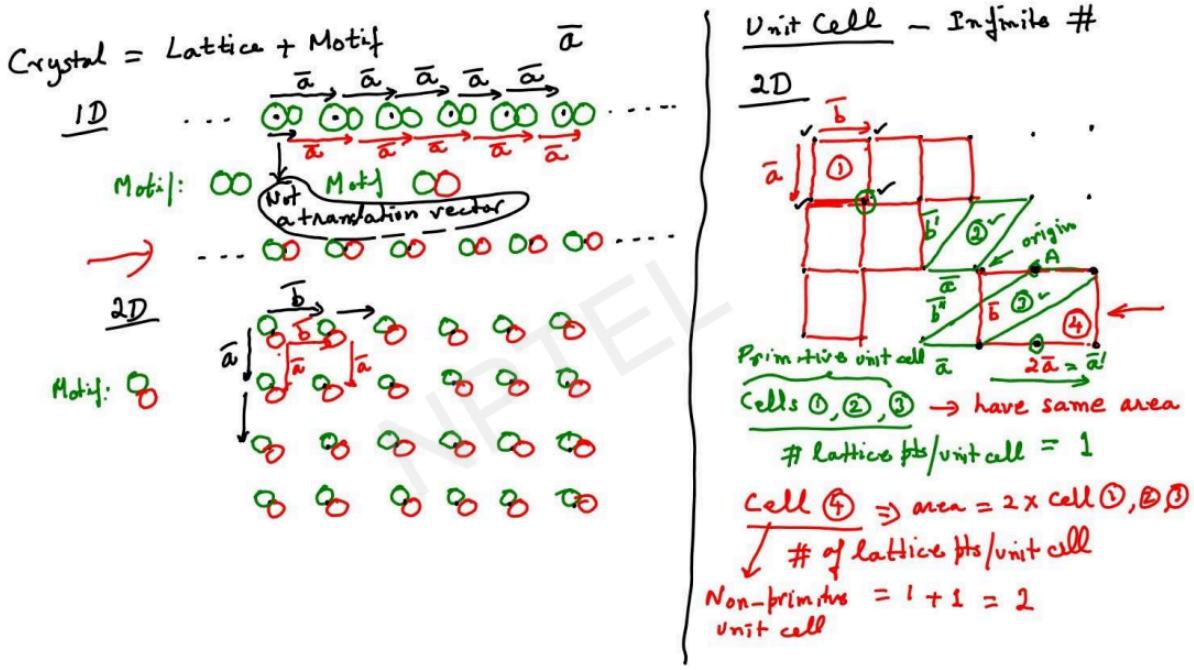

Now, we come to another concept called the primitive translation vector.

Consider the translation vectors $\bar{a}$ and $\bar{b}$, here we are looking at two dimensions, but the same concept applies to three dimensions as well. Vectors $\bar{a}$ and $\bar{b}$ are considered primitive translation vectors if the unit cell they define has the smallest area among all possible unit cells. As we have just seen, cells 1, 2, and 3 are primitive unit cells, and their areas are indeed the smallest. Thus, $\bar{a}$ and $\bar{b}$ are called primitive translation vectors if they define a unit cell with the minimum area.

In three dimensions, we will obviously have three vectors: $\bar{a}$, $\bar{b}$, and $\bar{c}$. If these vectors are primitive, they define a unit cell with the smallest volume. Similarly, if we have primitive translation vectors, we can also define non-primitive translation vectors.This means that a non-primitive translation vector will define a unit cell that has a larger area in two

dimensions, or a larger volume in three dimensions, compared to the primitive unit cell as is the case for cell number 4 here.

Now, does that make a difference? In the sense of defining a lattice translation vector, which describes all the lattice points, a lattice translation vector $\bar{r}$ is defined as:

$$\bar{r} = n_1\bar{a} + n_2\bar{b}$$

where n_1 and n_2 are integers.

In the case of a non-primitive unit cell, what happens is that if we write the lattice translation vector as

$$\bar{r} = n_1\bar{a} + n_2\bar{b}$$

where n_1 and n_2 can take fractional values.

This can be easily seen here.

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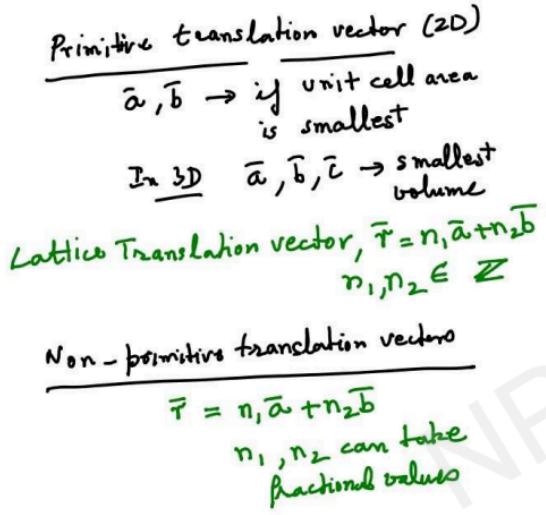

For example, consider this point as the origin. If I want to define a lattice translation that takes me from the original lattice point to another lattice point, say the one designated as $\overline{a}$, the total lattice parameter in this case is $2\overline{a}$, which I can call $\overline{a'}$. Then, the translation vector required to reach this point would be $\frac{\overline{a'}}{2}$, which means it takes a value equal to half the lattice parameter.

So, now I will close this lecture here and in the next lecture we are going to extend the same idea to 3 dimensions.