CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 05: Crystals Based on 3D

So, in the last class we had a brief discussion on crystal systems and Bravais lattices, and one important point that emerged from that class was that the crystal systems, which are usually defined in terms of their lattice parameters a, b, c and their angles α, β, γ is not a correct way of defining the crystal systems. So, for instance, if we say it is a cubic crystal, we take a cubic unit cell and we say that the parameters should be $a = b = c$ and $\alpha = \beta = \gamma = 90°$.

So, as we progress in this course, I would like to remove this misconception and bring in symmetry. Symmetry is the basis for these crystal systems, and not the relationship or the constraints on the parameters. In fact, you know, one can also say that you can choose any kind of unit cell.

We have already seen that you can have any type of unit cells for any of those lattices. Whether it is, you know, even for face-centered cubic, we saw that we can choose a primitive unit cell. But even if you choose a primitive unit cell, it will still belong to the cubic system.

Now, in this lecture, I would like to look at some very common crystal structures and the way to define them in terms of the rules of crystallography. So, let us take a very simple structure first.

Let us take the crystal structure of iron. At room temperature, iron is a body-centered cubic structure. So, what this means is that its lattice is body-centered cubic. So, if I take a conventional unit cell from the Bravais lattice for the BCC lattice, then I will have lattice points at the corners, and I will have a lattice point in the body-centered position. Now, in this lattice, I put iron atoms. So, I put an iron atom at every lattice point, and I form this body-centered cubic structure for iron.

Let me consider another example: a face-centered cubic structure, let us say for copper. So, if this is going to be an FCC lattice, then I will have lattice points this time at the corners, and I will have lattice points at the centers of all the six faces. And I can put a copper atom whose center coincides with the lattice points. So, I put copper atoms at all the corners, then I put them at the face centers, forming a face-centered cubic structure for copper.

So, here what have we done? We should realize that, go back to a couple of lectures. We had defined a crystal, a relationship for a crystal, in terms of *crystal = lattice + motif*. So, let us look at this relationship and how it applies to this structure.

So, in the first case, the body-centered cubic structure for iron, what have we done? What is the lattice? Well, the lattice is a BCC lattice. Plus, what is the motif? The motif is one iron atom at coordinates (0, 0, 0).

So now, remember, going back maybe two lectures, we said that *crystal = lattice + motif* is a vector addition. So essentially, what we are going to do is we add up this vector, or another way you can look at it is that we add the motif vector or motif location from every lattice point. So, I go to every lattice point in the unit cell, and I put an iron atom at the location (0, 0, 0). Now obviously, that simply is a vector at the lattice point itself, and that is how the iron atom comes out in this way.

In the same way, if I come now to the copper structure: here I have an FCC lattice plus one copper atom at (0, 0, 0). Same thing that from every lattice point, I draw a vector, taking that lattice point as the origin, I draw a vector to (0, 0, 0), which means that the atom will fall on the lattice point, or the atom center will coincide with the lattice point.

Now, let us take another structure. Let us take the structure of, let us say, cesium chloride. Let us see how that structure looks first, and then we will try to figure out what is the lattice for this structure. It is again a cubic structure, so it belongs to the cubic crystal system. And let me put cesium ions and chlorine ions in their appropriate locations. So, the chlorine ions go at the corners, and the smaller cesium ion I put at the body-centered position.

Now, let us look at the structure and try to figure out what its lattice is. Very often, just because we see atoms at the corners and at the body-centered position in a cube, we assume it is a body-centered cubic structure, which is incorrect. So, let me first say that is it a BCC lattice? It is incorrect. So, how is it incorrect? Let us also look at that.

Remember, all crystal structures have to be based on one of the Bravais lattices. Now, this means that if a lattice has a certain translation symmetry, the same translation symmetry should exist in the crystal with atoms in it. Now, a body-centered cubic lattice. So, if I were to draw a body-centered cubic lattice separately and let us look at what translation symmetry is permitted.

So, let us say this is a, b, and c, and the translation symmetry that I can have is taken from any lattice point. So, let me put these body-centered cubic lattice points. So, what are the translations permissible? Well, there is a translation obviously along **a**, along **b,** and along **c**, of the magnitude a, b, and c, in fact. So, in fact, $a = b = c$ would be the case for this cubic crystal. But this is also a permissible translation, and this vector in this case would be $(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$.

It joins from one lattice point to another lattice point, and this is a perfectly correct lattice as far as translation symmetry is concerned. So, here we have some translation symmetry which would be some factors multiplied into the vectors **a**, vector **b**, and vector **c**. Some of them are going to be integers, and some of them are going to be factors which bring the lattice point to the body-centered position in this case.

Now, coming back to this, if I apply this translation symmetry $(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$, this will take me a chlorine ion will be taken to the position of the cesium ion, which means symmetry is violated. So, therefore, this cannot be a body-centered cubic structure. So then, what is this structure? How about if we consider a different lattice? How about if I consider the lattice points to be only at the corners?

So, I now have lattice points only at the corners. If I put a lattice point where the Cs^+ ion is, I will have to put if we assume this is a body-centered cubic structure but then we have seen this violates the translation symmetry because a Cl^- ion is displaced to the position of a Cs^+ ion. So, the translation symmetry is not maintained. However, if I take this with the lattice points only at the corners, it works perfectly fine. So, this actually becomes a simple cubic structure.

So, my lattice is going to be a simple cubic lattice, but then what will be the motif, because I have to have both the Cs^+ ions and the Cl^- ions? Therefore, this motif is going to consist of two atoms and not one atom. In the previous case for iron and copper, we had a motif with only one atom. So, where is my Cl^- ion? Therefore, let us figure out what the motif is.

So, one chlorine ion, since the chlorine ions are all located at the lattice points. Its position is going to be (0, 0, 0). Then I have a cesium ion; its location would be $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. So, I am using this system of fractional coordinates, not $(\frac{a}{2}, \frac{b}{2}, \frac{c}{2})$, but just $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. So, in crystal space what we do is we take the **a, b, c** vectors as basically unit vectors along the x-, y-, and z-directions and therefore we just need to specify positions by the fractional coordinates within the unit cell.

So, a simple cubic lattice and this becomes my motif of two atoms. This is another point where many sources mistakenly call such a structure body-centered cubic. In fact, it should be called only a simple cubic structure. It has cubic symmetry and its lattice is that of the simple cubic.

Now, consider one more structure, which is sodium chloride. Let me first draw the structure and then we will try to figure out what its lattice is, what its Bravais lattice is, and what its motif is. Again, the sodium chloride structure also belongs to the cubic crystal system; let me put the sodium ions and the chlorine ions at their specific locations in this.

So, the chlorine ions go at the corners and at all the face centers. So, these are chlorine ions. The sodium ions go to the center of all the edges, and one sodium ion will go to the body-centered position, which I will just shade to separate this out. The shaded sodium ion is at the body-centered position. So, there are a lot of atoms in this. So now, how do I describe this structure? What is its Bravais lattice and what is its motif?

So, very often such a structure is described as two interpenetrating. So let me just write this down that often the structure is defined as interpenetrating FCC. In fact, I should say two interpenetrating FCC lattices, one containing the chlorine ions and the other one supposedly containing the sodium ions. So, this is somewhat of a problematic description, and I would like to avoid this way of describing the structure of sodium chloride.

First of all, there can only be one lattice for any crystal structure, however complicated the structure may be, or how many atoms that structure may have. So, by saying two interpenetrating FCC lattices, we are saying there are a lot of lattice points all around. But lattice points cannot be there for the same reason that the lattice point could not have been there for the cesium ion in the cesium chloride crystal.

In the same way I can say that I can put the lattice points at all the chlorine ions, but not on the sodium ions here. So, if I put the lattice points in this structure at the corners, in fact, there should have been a sodium ion here as well, then I will put the lattice points at all the face centers. Essentially what I am saying is that this is an FCC lattice, but then in order to describe the structure I now need a motif, the same way as we did for cesium chloride. Let us look at it.

How many chlorine ions are there in this unit cell? Well, if you consider the corners, remember each corner gives us a $\frac{1}{8}$ contribution to the unit cell. So, there is $8 \times \frac{1}{8} = 1$ chlorine ion coming from the corners, plus contributions from each of the six face centers: $6 \times \frac{1}{2} = 3$ chlorine ions from the faces. Thus $1 + 3 = 4$ chlorine ions per unit cell.

In the same way, you will notice that the centre-edge sodium ion is shared between four unit cells, so it contributes $\frac{1}{4}$. There are 12 edges, so $12 \times \frac{1}{4} = 3$ sodium ions from the edges, plus 1 sodium ion from the body-centred position that lies completely inside the unit cell. Therefore the total sodium count is $3 + 1 = 4$.

I have effectively 4 sodium ions and 4 chlorine ions in this unit cell, and I know that this is an FCC lattice; I have 4 lattice points per unit cell as well. So, what I can do now is say: if one chlorine ion goes at location (0, 0, 0), that means that all the sodium ions will go to the remaining lattice points of the unit cell. Therefore they will occupy the corners and the face-centres.

What about the lattice points? Their centres will correspond to the lattice points. Now, how about the sodium ions? Sodium ions are also equal in number; the stoichiometry is sodium chloride, NaCl. So, one sodium ion, how do I put it? Let us take one specific sodium ion and find its coordinates.

If my coordinate system is **a, b, c** in this way, the sodium ion lies at $(\frac{a}{2}, 0, 0)$ in absolute coordinates. If I remove the lattice-vector scale and use fractional coordinates, this sodium ion is at $(\frac{1}{2}, 0, 0)$. Therefore this sodium ion is part of the motif. So, the motif is again a 2-atom motif: Cl at $(0, 0, 0)$ and Na at $(\frac{1}{2}, 0, 0)$. This motif, when placed at every lattice point of the FCC lattice, reproduces the full NaCl structure.

So, for example, if I come to a specific lattice point, let us say I come to the lattice point where this is my origin, then from this lattice point I draw a vector $(\frac{1}{2}, 0, 0)$. If I draw the vector $(\frac{1}{2}, 0, 0)$, I come to the sodium ion, and it will populate the unit cell with the correct locations for the sodium ions and the chlorine ions. So, I will again reiterate that this is what we will always consider: that a crystal can be related to a lattice plus a motif. So, sodium chloride has a face-centered cubic lattice with a motif of one chlorine ion and one sodium ion at the specific locations.

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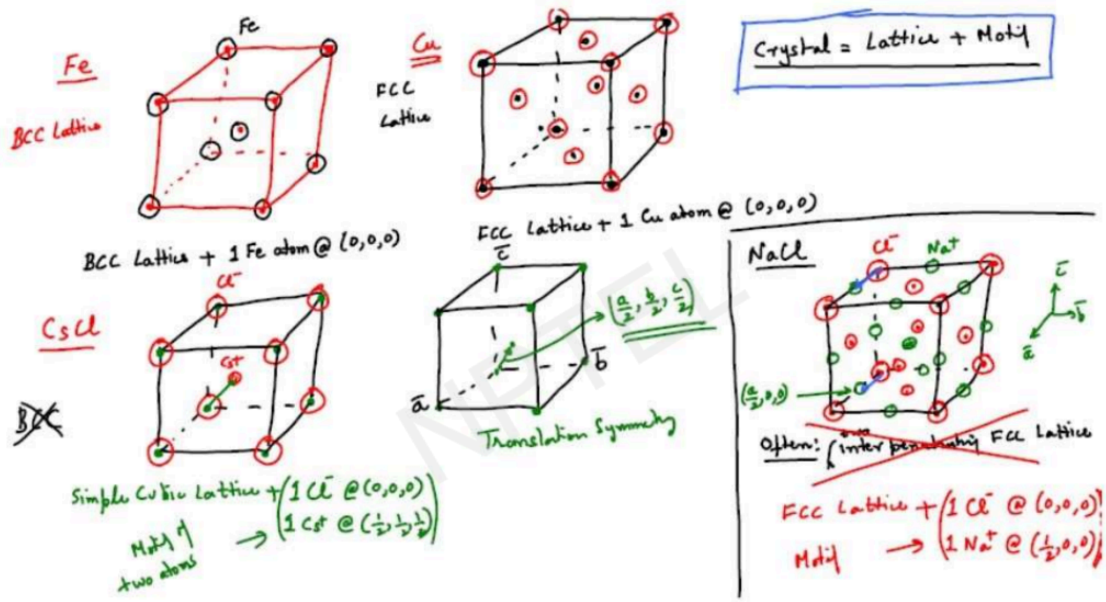

There is one more structure I could consider. Let us take the structure of diamond. Now, in this structure basically we have only carbon atoms. So, let me put the carbon atoms. Carbon atoms will go at the corners. This is also a cubic cell. And the carbon atoms will go at the face-centered locations. There are another four carbon atoms that will also go inside the unit cell, which would be located on the body diagonals.

So, for example, let me draw the body diagonals first. Body diagonals mean you are joining the opposite corners of the cube. So, there is a carbon atom which will go here, one-quarter along this particular body diagonal. Another carbon atom would come here, one-quarter from this particular vertex. Similarly, there will be a carbon atom that will come here, and there will be a carbon atom somewhere here.

So, this again, if you look at it. First of all, the red atoms, I mean the red and the green, they are all carbon atoms. But the red ones are located at the corners and the face-centered positions, whereas the green ones are lying along the body diagonals. If you look at the number of carbon atoms, one will find that there are 8 carbon atoms per unit cell. Now, what is its lattice?

The lattice is face-centered cubic (FCC), which means the lattice points can only be at the corners and at the face-centered locations. Therefore, this crystal, or the diamond structure, can be described by an FCC lattice plus a motif of two carbon atoms.

One carbon atom is at the position (0,0,0), which means it occupies the lattice point. The second carbon atom; if I take this particular atom here which is located one quarter along the body diagonal joining this vertex to the opposite vertex. In mathematical terms, that carbon atom is at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$

What will be its fractional coordinates in terms of *a, b,* and *c*? The fractional coordinates are going to be $(\frac{a}{4}, \frac{b}{4}, \frac{c}{4})$. So, we can just remove the *a, b,* and *c* and just write the fractional coordinates. Then the fractional coordinates are simply: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. So, this becomes the motif for this structure.

Now, very often this structure is loosely; in fact, not the structure. It is loosely called a Diamond cubic lattice. It is so often used, but there is no such lattice in the list of Bravais lattices. So again, we should avoid using this terminology. This is incorrect terminology. If at all you have to use such a terminology, you can say a *"Diamond structure"*, which basically refers to how the atoms are arranged.

But there is no such thing as a diamond cubic lattice. However, there is the face-centered cubic lattice. So, the diamond structure is based on the face-centered cubic lattice, and we should not use the nomenclature "Diamond cubic lattice."

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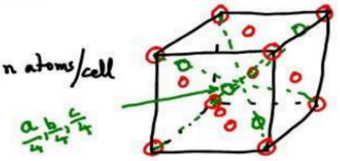
Diamond

8 Carbon atoms/cell



$$\text{Diamond} = \underline{\text{FCC Lattice}} + \begin{pmatrix} \text{1 C atom @ } (0,0,0) \\ \text{1 C atom @ } \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \end{pmatrix} \leftarrow \text{Motif}$$

~~Diamond Cubic Lattice~~