

CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 04: Crystal Systems in 3D

In the last lecture, I had introduced the concept of a unit cell in a 3D lattice, and as you can see here pictorially, a 3D lattice unit cell in general can be called a parallelepiped, and this is a general unit cell. It has six lattice parameters: a , b , c , α , β , and γ as can be seen from the figure. Now, we need to populate this parallelepiped with lattice points.

So, where can I put the lattice points so that I have translation symmetry in the lattice? One of the places I can put the lattice points is at the corners. This is an example of a unit cell with lattice points only at the corners of the cell; hence, this is called a primitive unit cell, since it will have effectively one lattice point per unit cell.

Now, in addition to the lattice points at the corners, I can also add a lattice point in the center of the cell, called the body-centered position, as shown here with a light-colored dot. One thing I must emphasize again is that the lattice points are shown as somewhat bigger circles just so they are visible, but they should not be confused with atoms. This distinction between lattice points and atoms must always be kept in mind.

So, here I have lattice points at the corners plus a lattice point at the body-centered position, and you will also note that for the first cell, the primitive cell, the symbol used for all primitive cells is “P.” Similarly, for the body-centered cell, where I have lattice points at the corners and one lattice point at the body-centered position, the symbol used is “I.”

Similarly, instead of adding a lattice point at the body-centered position, I can add two lattice points at two opposite faces of this parallelepiped. So now, I have lattice points at

the corners plus two additional lattice points, one at the top face and the other at the bottom face. Such a cell is called a base-centered or end-centered cell, and the symbol used could be either A, B, or C, depending on which pair of opposite faces the additional lattice points are placed on.

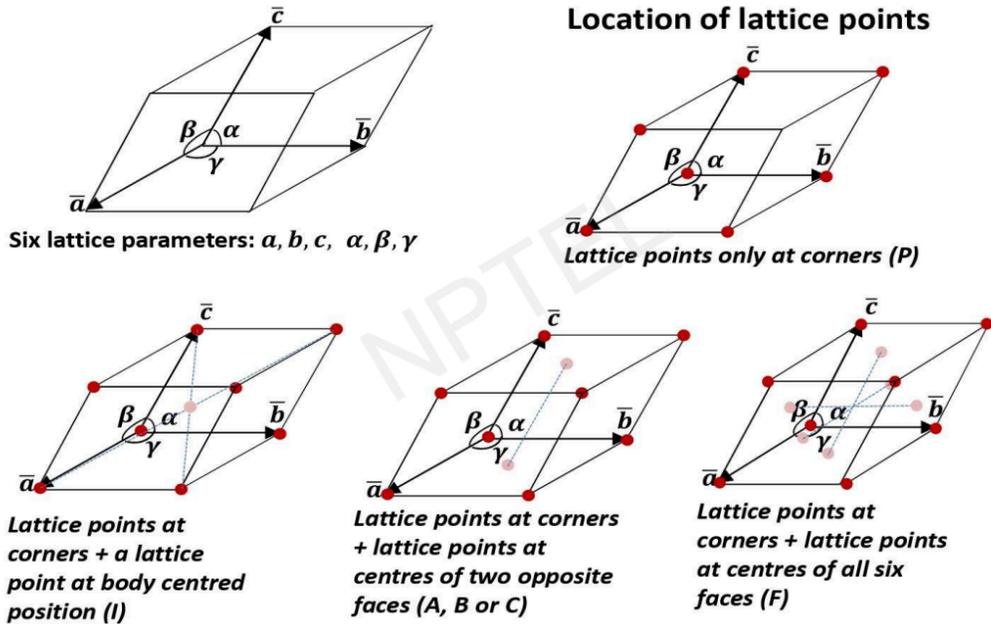
For example, in this particular figure, I have chosen the C face, because the C face is parallel to the A and B axes, and the C axis comes out of the top and bottom faces. So, that face is called the C face. Now, why am I using three possible symbols: A, B, or C? Well, I can put lattice points on the C face, but I can also put lattice points on the A face, where the A face would correspond to the front and rear faces of the unit cell.

Similarly, I can put two lattice points on the B face, which are the left and right faces. So, depending on where I put these two lattice points, the symbol I will use would be A, B, or C. A fourth possibility is having lattice points at the corners and lattice points at the centers of all the six faces. Such a cell is called a face-centered cell, and the symbol used for it is "F." So, in this way, I have four possible lattices that I can get out of a parallelepiped.

Now, the next question that we have to address is: what should this parallelepiped cell look like? There is a set of what are called conventional cells, which I am sure all of you would have come across in any basic course on material science. There are seven different parallelepipeds, which are conventional and are described by some specific relationships between a , b , c and α , β , γ .

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Unit Cell for a 3D Lattice (parallelepiped)



So, let us consider this, those seven cells are called crystal systems. Now, here are the seven crystal systems: Cubic, Tetragonal, Orthorhombic, Hexagonal, Rhombohedral, Monoclinic, and Triclinic.

Now, this is the commonly used definition you will find in most books, where the axial and angular relationships, that is, the relationship between the parameters a, b, c and α, β, γ . So, for the cubic system, you will generally find in most elementary material science books that it is defined by:

$$a = b = c \text{ and } \alpha = \beta = \gamma$$

Similarly, for the tetragonal system, $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$. For the orthorhombic system, again all three angles are 90° , but $a \neq b \neq c$. So, the first three conventional cells that we have are defined by such relationships, and similarly, we can go down the list for the remaining systems.

Now, there is a very big problem in this kind of definition. In fact, this is perhaps one of the biggest misconceptions that is present in a very large number of books as well as publications, and this is what I call a big misconception. And what is the misconception? That this is an incorrect definition that axial relationships determine the crystal system. As I said, this is given in innumerable sources, including textbooks on material science.

Now, how do I look at this and how do I define the seven crystal systems? The classification of the seven crystal systems is decided by symmetry, and the axial and angular relationships for the conventional unit cells are a consequence of that symmetry. In this course, we will therefore go into symmetry in considerable depth, and with that understanding we will determine the crystallographic basis for the crystal systems, and then extend this to examine the implications within each of these crystal systems.

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Common Definition of Seven Crystals Systems

Crystal System	Axial and Angular Relationships
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a \neq b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$

Misconception

INCORRECT definition that axial relationships determine the crystal system. Given in innumerable sources including textbooks on Materials Science

Crystal system classification is decided by symmetry and axial relationships for the conventional unit cells are the consequence.

Now, we put the lattice points according to what we had shown earlier that we have four possibilities of placing them: lattice points at the corners, lattice points at the corners and body-centered position, lattice points at the corners and end centers, and lattice points at the corners and centers of all the faces. If I combine these four possible arrangements with the seven crystal systems, I should, in principle, have 28 lattices.

But if you look closely at the actual list, you will notice something interesting: for the cubic system, we have only three lattices, not four; for tetragonal, we have only two primitive and body-centered; for orthorhombic, we have all four possibilities; for hexagonal, only one, primitive; for rhombohedral, one, primitive; for monoclinic, two; and for triclinic, only one.

If we add up all of these, this constitutes what are called the 14 Bravais lattices, which are introduced in an undergraduate material science course. Now, if you look at the cubic system, you will notice that it includes simple, body-centered, and face-centered lattices. Here, I have written oblique primitive, but note that the words simple and primitive mean the same thing. Conventionally, in the context of Bravais lattices, the term simple is typically used, though primitive cubic would also be correct.

I have body-centered cubic and face-centered cubic, but I do not have a base-centered or end-centered cubic. In the tetragonal system, I have only two, primitive and body-centered. So, the first that I have crossed out does not mean that if I take a cubic unit cell, that is, if I have a cube as the unit cell, then these relationships: $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ would have to be obeyed. Rather, these relationships are not the basis for defining a unit cell as cubic.

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Bravais Lattices – Conventional Choice of Unit Cell

Crystal System	Axial and Angular Relationships	Bravais Lattice*	No. of lattice points/cell
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple/Primitive Cubic (P)	1
		Body Centred Cubic (I)	2
		Face Centred Cubic (F)	4
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Tetragonal (P)	1
		Body Centred Tetragonal (I)	2
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple Orthorhombic (P)	1
		Body Centred Orthorhombic (I)	2
		Base/End Centred Orthorhombic (C)	2
		Face Centred Orthorhombic (F)	4
Hexagonal	$a \neq b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Simple Hexagonal (P)	1
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Simple Rhombohedral (P)	1
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	Simple Monoclinic (P)	1
		Base/End Centred Monoclinic (C)	2
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple Triclinic (P)	1

Now, let us take some examples and try to understand why an end-centered cubic lattice is not present. Explanations for this omission are given in many publications and books, and most of the time one finds that the explanation provided is actually wrong.

So, let us first look at what kind of an explanation that is given. So, let us take an end-centered cubic cell. So, I have lattice points at the corners, and let me put the lattice point at two opposite faces: the top face and the bottom face. So, this, and I have this as a . So, since it is cubic, $a = b = c$, and all the vectors are orthogonal to each other, that is, $\alpha = \beta = \gamma = 90$ degrees.

Now, let us construct another unit cell next to it, adjacent to it. So, again, I have lattice points at the corners of the same cell, and this is basically a translated unit cell by the

vector b . Now, in this, I do a construction where I join the lattice points like this. In fact, this becomes a new or an alternate unit cell for the same lattice, where now I have lattice points only at the corners. So, it becomes a primitive unit cell.

Now, as we had seen in an earlier lecture, any lattice can have any number of cells. In fact, there can be an infinite variety of primitive unit cells. So, let us look at the dimensions for this cell. Let us say this is a' , this is vector b' , and this is c' . Very clearly, $a' = b'$, however, $c' \neq a'$.

In fact, if I want to express these vectors in terms of the parameters of the larger cubic cell, then $a' = b'$, which is basically half the face diagonal, and the length of the face diagonal will be $\frac{a}{\sqrt{2}}$, while c' would be equal to c , the dimension of the cubic cell.

Now, what about the corresponding angles? α' , which is the angle between b' and c' , would be equal to β' , which is the angle between c' and a' , and finally, γ' , which is the angle between a' and b' . They will all be 90° .

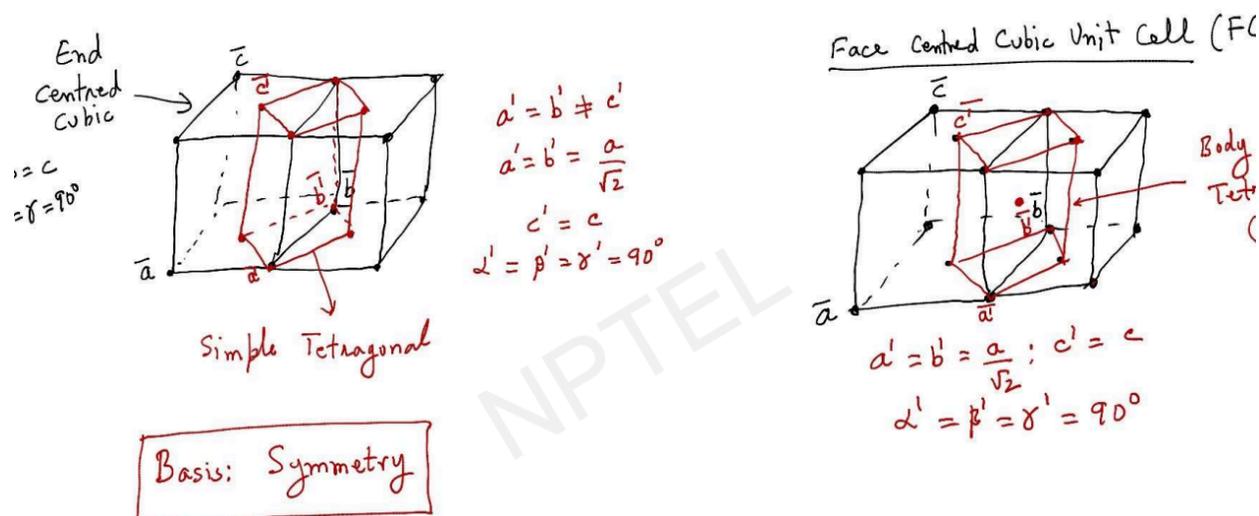
So, now I have a cell where two dimensions are equal and one dimension is not, while the angles are still 90 degrees. If I go back to my lattice, I would say, and this is what is stated in many books, that this is why we do not have an end-centered cubic cell, because we can represent it as a simple tetragonal unit cell. A simple tetragonal unit cell would have $a = b \neq c$, with all angles being 90° , and it is a primitive cell. So, we say that this is a simple tetragonal.

Now, while this statement is correct, an end-centered cubic cell will not exist. The reason for its absence is not that it can be represented as a simple tetragonal cell. So, let me take one more example to further explain this point. Let us now consider a face-centered cubic (FCC) unit cell.

So, we had started with the end-centered case. Now, let us take a face-centered cubic (FCC) unit cell. If I take this and draw an adjacent unit cell, as I had done in the previous case, I will have lattice points at the corners and lattice points at the centers of all the faces. I will not draw all the lattice points, but I will show the common face, the center of this face, as well as the top and bottom faces in both cells. I will keep only these to avoid cluttering the diagram.

And let us do a joining in a similar way as I had done earlier, that is, let me join this lattice point, this lattice point, this lattice point, this lattice point, and similarly, this one, this one, this one, this one, and this one. So now, at first, this is a , this is b , and this is c . The new vectors for the unit cell become a' , b' , and c' . As before, I will have $a' = b' = \frac{a}{\sqrt{2}}$ and $c' = c$, and I will have $\alpha' = \beta' = \gamma' = 90^\circ$.

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So, I have orthogonal angles again; this should suggest to me that this should belong to the tetragonal crystal system. This time, if I look at the lattice, I have lattice points at the corners and one lattice point at the body-centered position, which means that this should be a body-centered tetragonal lattice, symbol used is I.

Now, for this new cell, the dimensions are:

- $a' = b' = \frac{a}{\sqrt{2}}$
- $c' = c$
- And the angles are: $\alpha = \beta = \gamma = 90^\circ$

But I already have a cell which is face-centered cubic (FCC), so if it was just a question of using a smaller cell having fewer lattice points, then I should remove the face-centered cubic unit cell as well from this list and put it under the tetragonal system. Taking a third example just to take the point home. In fact, in all cases, whether it is cubic, monoclinic, or hexagonal, all the 14 Bravais lattices can be represented by some or the other primitive unit cell as well.

So, an example of that, let us take an example of that. Let us look at this face-centered cubic (FCC) lattice, where all lattice parameters are equal and all angles are 90 degrees. This unit cell is described by the vectors a , b , and c . Now, I have drawn some of the lattice points here. I have shown only two of the corner lattice points and left the others blank to avoid any confusion, but I have included all six lattice points at the centers of the six faces.

Now, suppose I take the lattice point at the origin from where I have drawn the vectors a , b , and c . From this point, I join three lattice points: one to the center of the top face, one to the center of the left face, and one to the center of the rear face. I label these joining

vectors as a' , b' , and c' . You can clearly see that the magnitudes of all three vectors are equal, and each of them is equal to $\frac{a}{\sqrt{2}}$.

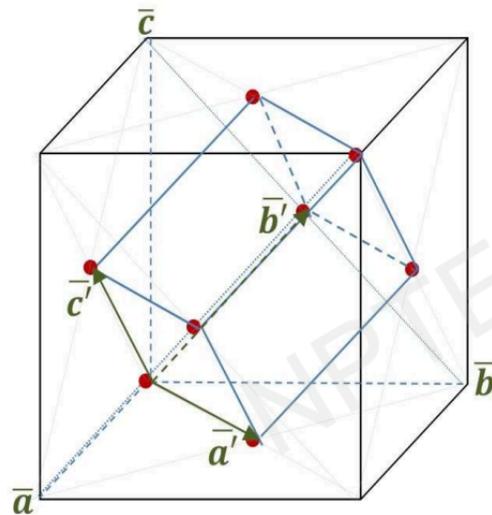
So, in fact, the lattice parameter of the alternate unit cell that I am going to get out of this would be that all three vectors a' , b' , c' will be equal, and their magnitudes will be $a' = b' = c' = \frac{a}{\sqrt{2}}$, where a is the lattice parameter for the original larger cell. If I look at the angles, here α is the angle between b and c , β between c and a , and γ between a and b . Analogously, here α' is the angle between b' and c' , β' between c' and a' , and γ' between a' and b' .

It is very easy to calculate because this is a Cartesian system. The end point of vector a' would be $(\frac{a}{2}, \frac{a}{2}, 0)$, the end point of the vector b' would be would have zero along a , but half along b and c , so $(0, \frac{a}{2}, \frac{a}{2})$; and the end point of vector c' would be $(\frac{a}{2}, 0, \frac{a}{2})$, since $a = b = c$.

So, I have coordinates $(0, \frac{a}{2}, \frac{a}{2})$. Now, just take the dot product of any two of these vectors and you will find the angle is 60° . In each case, for all combinations, all angles turn out to be 60° .

If I just go back to this, I find that I am in the rhombohedral crystal system, where $a = b = c$ and the three angles are equal, but they are not equal to 90° . Let me complete the cell. I got this rhombohedral unit cell. This means that I can also represent the face-centered cubic unit cell as a simple rhombohedral cell. But that is not the case, the face-centered cubic unit cell, or the lattice, does not belong to the simple rhombohedral lattice.

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Face-Centred Cubic

Lattice Parameters

$$a = b = c$$

$$\alpha = \bar{b} \text{ \& } \bar{c} = 90^\circ$$

$$\beta = \bar{c} \text{ \& } \bar{a} = 90^\circ$$

$$\gamma = \bar{a} \text{ \& } \bar{b} = 90^\circ$$

Lattice Parameters of
the alternate unit cell

$$\bar{a}' = \bar{b}' = \bar{c}' = \frac{a}{\sqrt{2}}$$

$$\alpha' = \beta' = \gamma' = 60^\circ$$

Simple Rhombohedral (P)

So, where do we stand? I would say that this is something we have not come across before, but through this course, we have to remove this misconception and also determine the correct basis for identifying whether a lattice belongs to the cubic system, the rhombohedral system, the tetragonal system, and so on. The basis for that is symmetry.

So, we will stop here and continue in the next lecture.