**Foundations of Computational Materials Modelling**
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**Lecture 15**
**Generation of Monoclinic Lattice**

So good afternoon, so today we are going to continue creating a couple of, couple of other crystal structures from different space groups.

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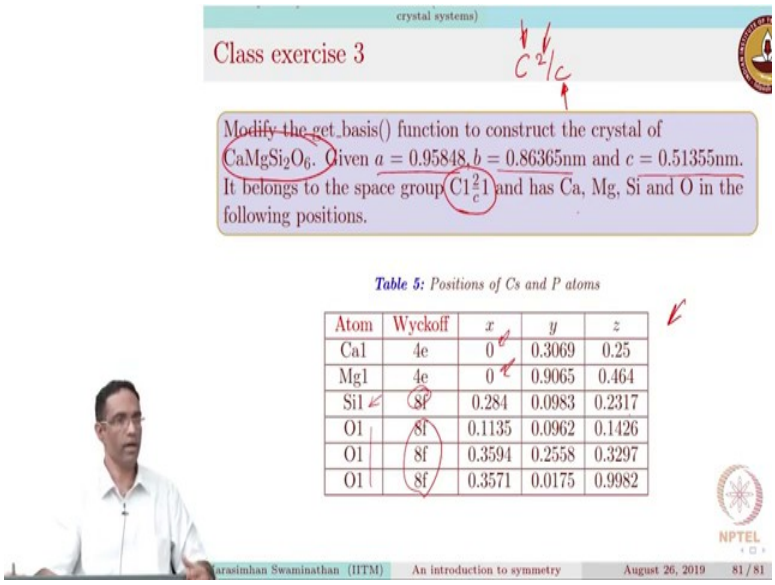


There are some nuances that one might have to keep track of when you are constructing these crystal structures. So, I am first going to demonstrate what will happen if you have a mono clinic space group. So, the crystal that we are going to construct is this one $CaMgSi_2O_6$ and it is told here that this particular crystal belongs to the C 1 to over 6 1 space group or it can also be written as C2 over C space group which means that there is a C glide, there is a two fold rotation and there is also some centering, that is actually associated with this crystal C centering is associated with this crystal.

And you have given you have been given the a, b, and c lattice constants for this crystal and the Wyckoff positions for all the atoms calcium, magnesium, silicon and oxygen are given in this table right here. So, there is calcium belongs to 4e mg belongs to 4e and then there is there is a silicon atom which belongs to 8f and there are also three Oxygen atoms which belongs to 8f.

So, some of them are special, special positions as you can see, there is a 0 here well, the others probably are general positions that are given to us, so we have to refer back to our

crystallographic table in order to generate the entire crystal, we have to know what are the other points that are existing within the unit itself.

Before we do that, it is important for you to for us to understand how the lattice vectors are actually specified for the mono clinic unit cell. So, this particular point came up last class also. So, why is it so important to actually keep track of this lattice vectors. So, whenever they, when we are talking about the mono clinic units cell, it is important for us to know how these lattice vectors are actually pointed with respect to our x y z axis.

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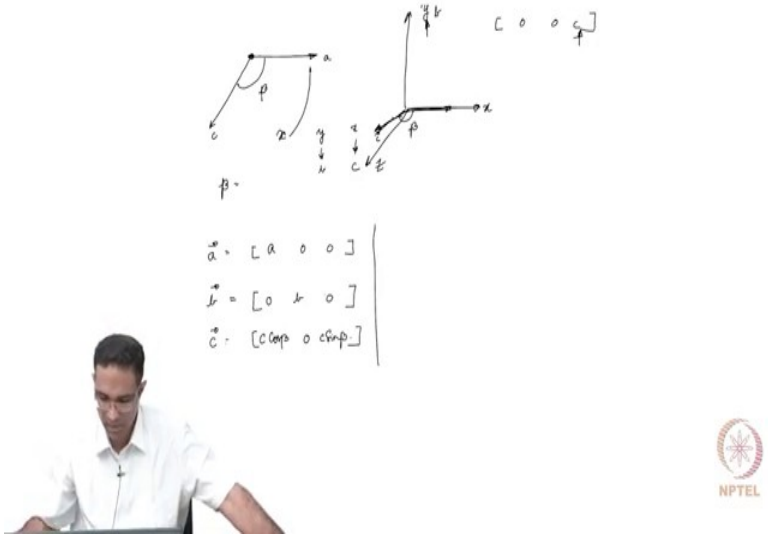


So, this is our x y z axis, right handed, forming right handed system and if you refer to the international tables of crystallography this particular space group would have been specified in the following manner you would see here a pointing to the right and you would see a c pointing that way and the beta that is given to you is basically the included angle that is existing between a and c.

Now, how do you give the lattice vectors for this particular system you should understand that the x fractional coordinate is associated with a the y fractional coordinate is associated with b and z fractional coordinate is associated with the c direction, the c direction c direction. So, we have to be careful in the manner we specify the lattice vectors for this, so it is obvious that the a lattice vector if you write try to write it in terms of our Cartesian coordinate system is nothing but a 0, 0.

The b lattice vector and the c lattice vector need to be specified. So, if our a is pointing in this direction and our c is pointing in this direction. Then our, so in what plane does the c vector

lie? lies in the x-z plane, it lies in the x-z plain. So, consequently your c vector will have what as the competence here it will have c, this is beta. So, what would it be? Can you please help me out here, what would the x component of the c vector be? This would be c vector. Because you are looking at it from the top. So, this is what we want our b to be.

Student: Sir, is the position of c vector in the x-z plane?

Professor: The position of c vector is in the x-z is a plane

Student: x-z plane

Professor: x-z plane. So, that is what, I am giving it that way you can actually associate any way you want. As long as you are careful about doing it, you will not have a problem. But being careful about is kind of important it is not too obvious, as you will see, because whenever until now, whenever we gave the c vector we just did this. It was the last or the z component, which had a nonzero value in the lattice vectors.

But in this case, the projection is given on the b from as viewed from the, from the b axis. So, if you call this as b and this as x, this as a then c has to lie in the x-z plane with an included angle of beta in between them. So, what would be the x component of the c cos beta maybe,

Student: c cos beta

Professor: Then this would have any y component, no y component

Student: 0

Professor: And what would be the z component?

Student: c sin beta

Professor: Now what about the b vector the b vector is?

Student: 0.

Professor: 0 b z.

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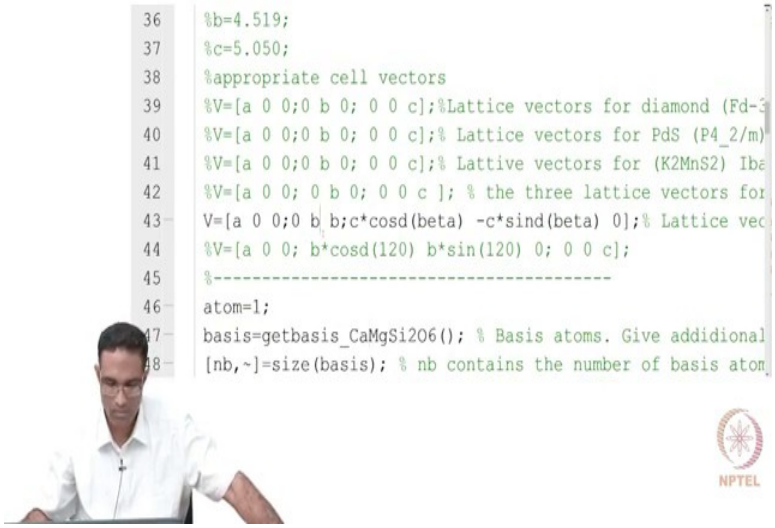


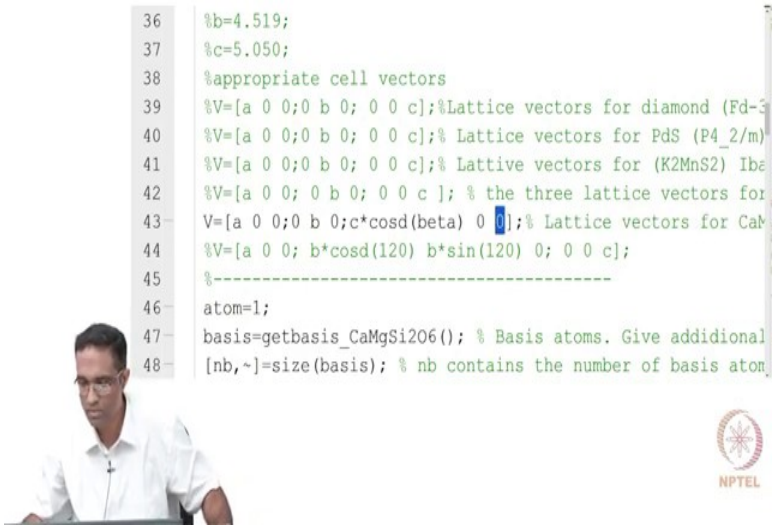


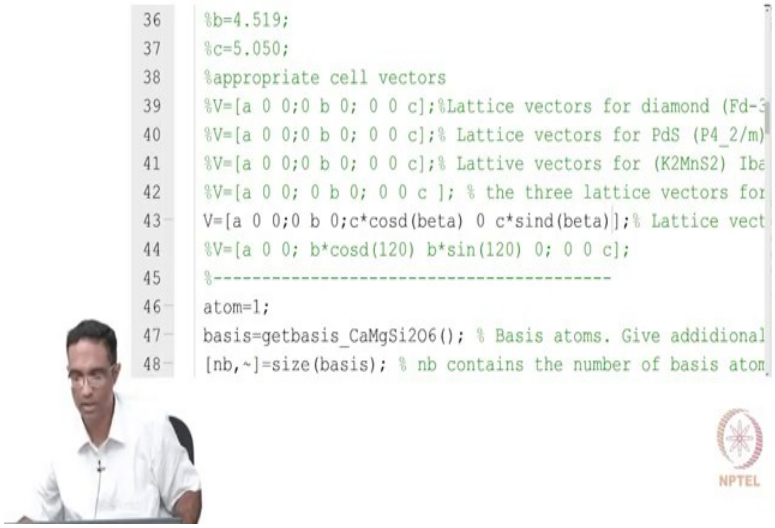

So, let us first go to our MATLAB script and do that so, we had 0, b 0 then I had c cos d beta, 0 c star sine d beta. So, now we have defined our lattice vectors that we want to use for constructing our crystal system. The next task is to basically look at the Wyckoff positions and then define the various other atoms that are present within the unit cell.

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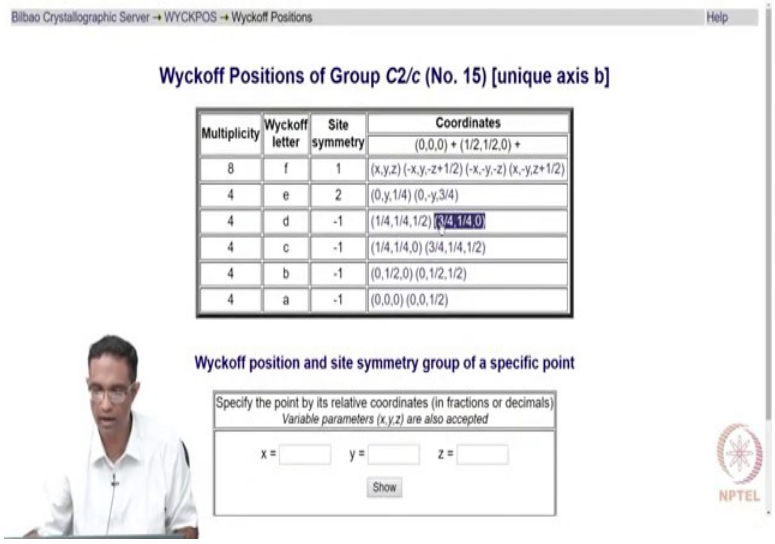


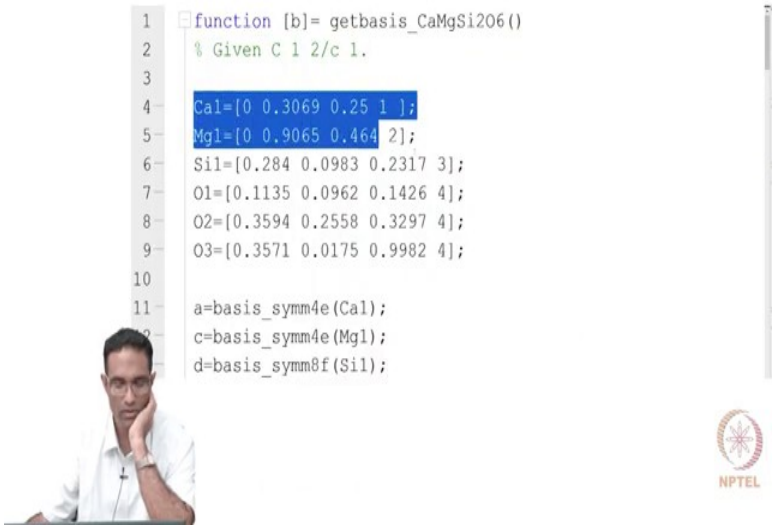

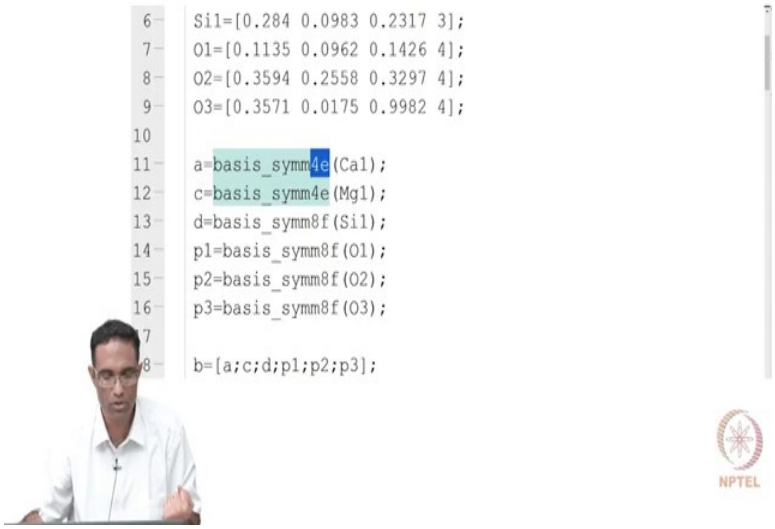


So, once again we have to refer back to our crystallographic space group, Wyckoff position will choose the Wyckoff position from this, we choose the space group first, the space group is proceed to over c. So, that belongs to the mono clinic structure I have C2 over c right here, so it is 15 and these are the Wyckoff positions that I have.

So, the first thing is that calcium is present in position 4e. So, it is 0 y, quarter and 0 minus y, 3 by 4. So, these are the various is there something wrong here, 0, y, quarter and 0, minus y, 3 by 4, zero some value of y, quarter and other values can actually be defined in the corresponding function which grabs the basis where you would have defined the basis for each and every Wyckoff position.

So, this function basis underscore symm4e is defined here, that all the other symmetry equivalent points have been defined just like how we did for the other cases. Similar or you can actually gives Ca2 since it only contains two points. You do not necessarily have to try a separate function, like for example 4e contains only how many points does 4a contain?

It contains 1, 2, 3 and 4 points. If you do not want to define the 4 points you can simply give all the 4 points as a concatenated array for Ca1. It is a same thing, but we will do here we will do it here slightly differently we will give the first value and then the subsequent values will be defined in the basis underscore symm4e function.

Now Mg1, where is Mg1, Mg1 is now also in a 4e position and therefore, we can therefore use the same basis function, we can use the same basis function because as far as 4e is concerned, the set of equivalent points will essentially be generated the same way the only

thing that is different is the value of the coordinates that you are giving it is different, but it is still a position it is still a 4e position Wyckoff position is still 4e.

Student:

Professor: Yeah this there is a probably a mistake here the Mg1 if it is going to be present in a 4e each position then I should have this also as 0.25.

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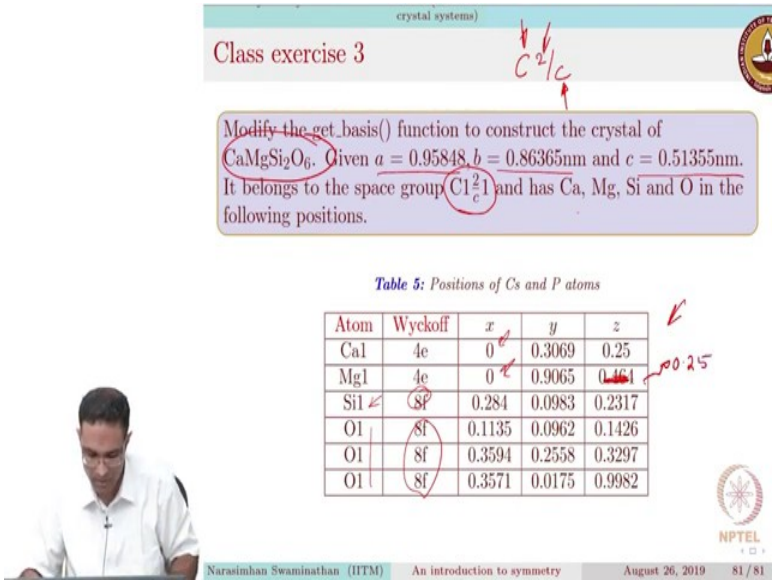


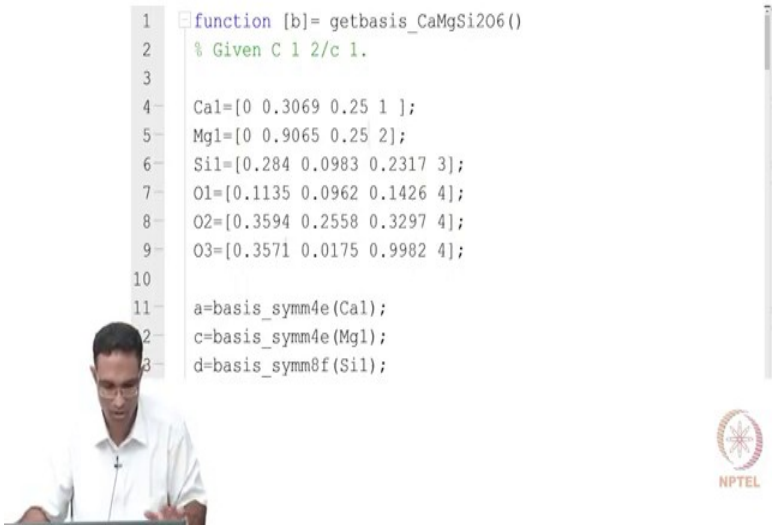

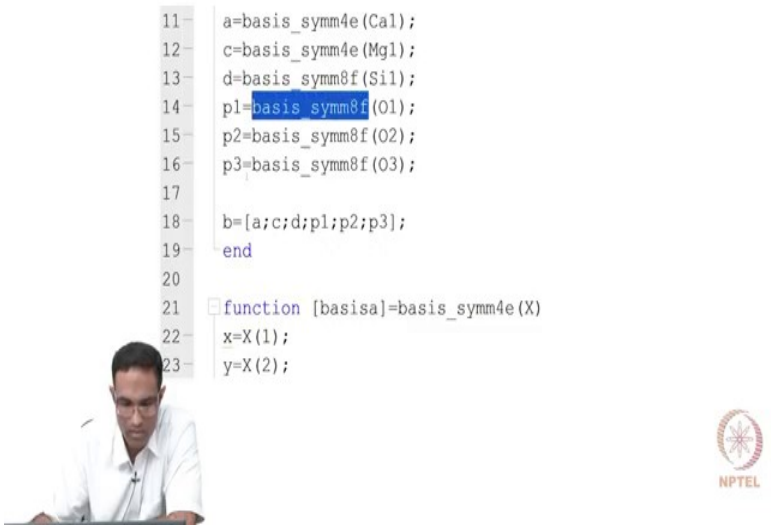


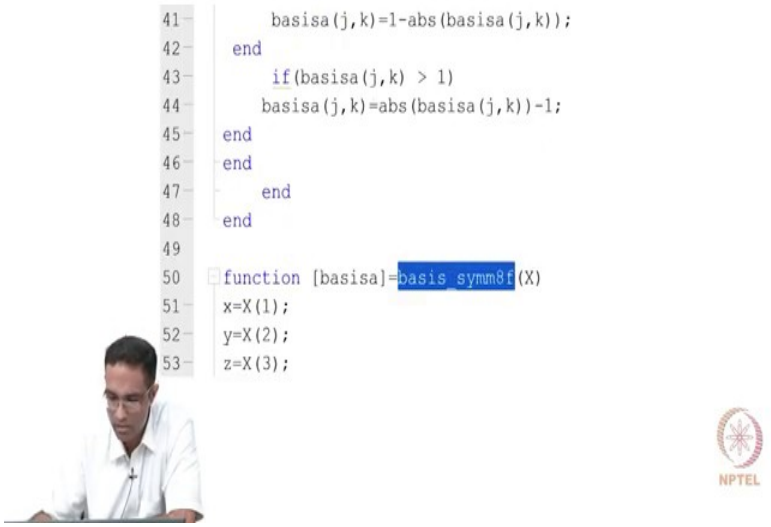


So this is probably 0.25 so let us change that if it is 4e position, I might have made a mistake, we can check that quickly. So, maybe not maybe not. So let us have this as a 4e position and continue to have it as 0.25.

The next to silicon atom is actually in 8f position. So these are the general coordinates and all the other Oxygen atoms are also in the 8f position, so, consequently I need to write only 8 one 8f function and that function is right here with all the things defined according to the as required by this, these things.

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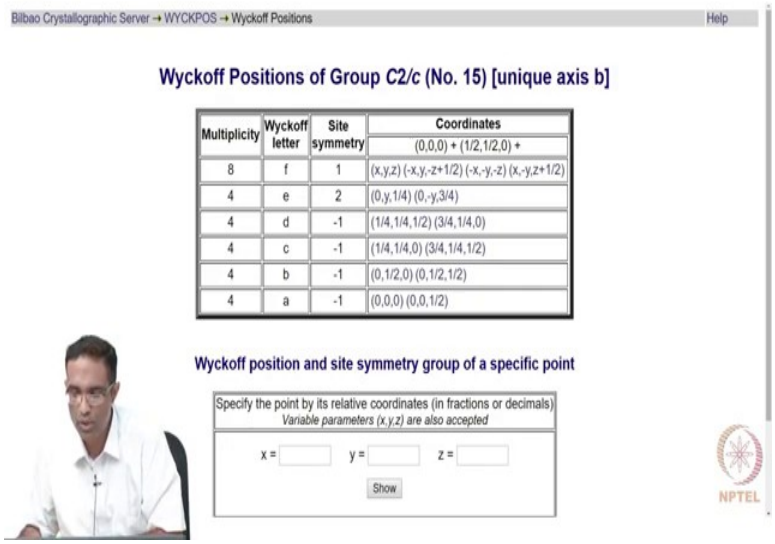


So, you see here in this table, Wyckoff positions of group C2 c number 15 the unique axis is b. So, they have made it important they told you that the unique axis is b or the corresponding y coordinates that are existing here are going to be associated with that. So, if you if you are not careful about this, then you will switch the definitions of the b and the c vectors and you will not be getting the right crystal structure and this can mean a lot of things because the distances are changed now, between the atoms and when you give this to a molecular dynamics simulation, it can, not converge to the right energy value, because you are giving it a different crystal structure.

So, keeping track of how the origin and how the lattice vectors are actually defined is extremely important. So, now Smarak is that is that aspect clear? You asked this question yesterday last class. Why this? You asked why this is important to how does it matter whether we do something like this.

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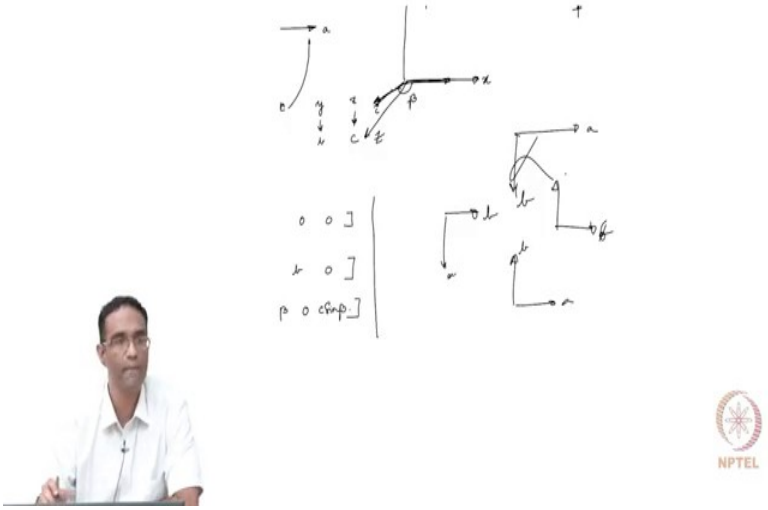

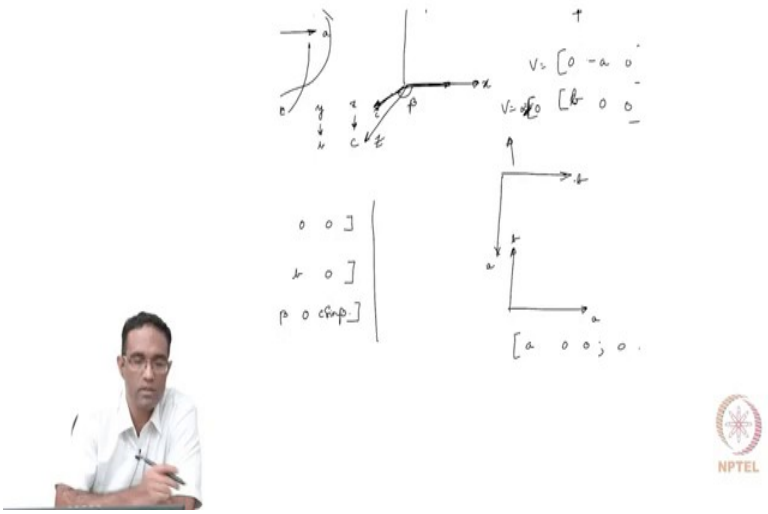

So, usually this would be a and this would be b. So, how does it matter whether this is a, this is b or this is b, it will be like this, b and a and how would it matter if we wrote it this way? So, in this case, it does not matter. Are you following? Yesterday we wrote something like this. I told you that in the international tables of crystallography, in international tables of crystallography, you would found find something like this, you will find this to be a, this to b maybe for the tetragonal space group or maybe for the orthogonal space group.

And I also pointed out this could also be written this way, it is the same thing you just performing rotation and all your Cartesian coordinates remain exactly the same and does nothing much changed. In fact, you could define a if you are using this sort of representation,

we could define our a vector or first lattice vector to b 0, the a vector could be 0 minus a, 0 this one could be b, 0, 0 and it would still our code would still work.

It is not necessarily that you do a, 0 0, 0 b 0, 0 0, c. In mono clinic systems the fact that they have mentioned that we are looking at a unique b axis, which essentially means the b axis is what is pointing outside the board and the oblique plane that is the a-c plane not the a-b plane and this is important that you could not treat the c as a b, because then it would get map to the wrong basis fractional coordinates.

So, for this reason, it is important for us to keep track of how these lattice vectors are actually defined in the international tables of crystallography. So, once we do this and define our all our basis atoms want save it and I can defined everything here and around this code.

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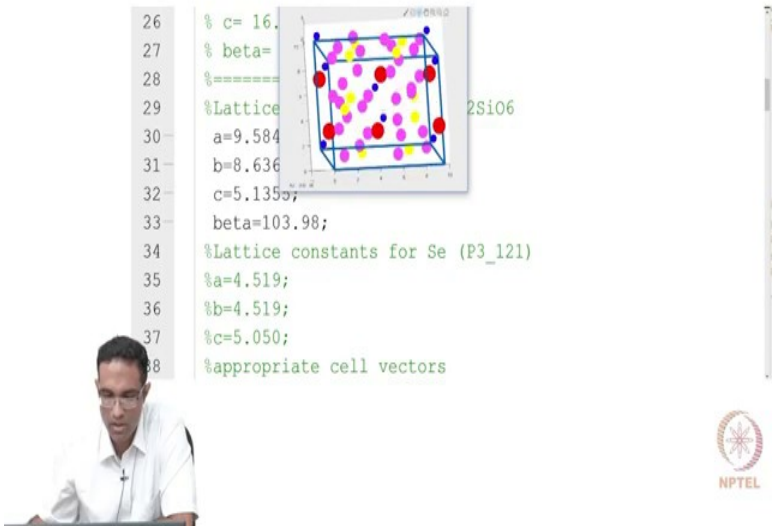

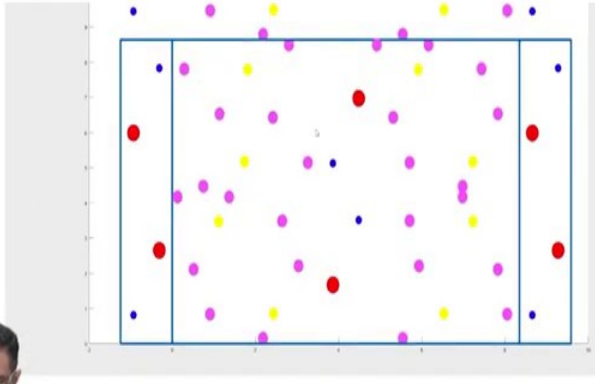


```
1  function [b]= getbasis_CaMgSi2O6()
2  % Given C 1 2/c 1.
3
4  Ca1=[0 0.3069 0.25 1 ];
5  Mg1=[0 0.9065 0.25 2];
6  Si1=[0.284 0.0983 0.2317 3];
7  O1=[0.1135 0.0962 0.1426 4];
8  O2=[0.3594 0.2558 0.3297 4];
9  O3=[0.3571 0.0175 0.9982 4];
10
11 a=basis_symm4e(Ca1);
12 c=basis_symm4e(Mg1);
13 d=basis_symm8f(Si1);
```


```
76                 X1(atom)=X;
77                 Y1(atom)=Y;
78                 Z1(atom)=Z;
79 %==========================================================
80  % Add as many of these statements (depending on the numbe
81  %or mark them with different sizes on the scatter3 commar
82  %line
83                 if(floor(basis(b,4))==1)
84                 T1(atom)=800; % Sizes of the atoms
85                 TPE(atom)=1;
86                 C1(atom,1:3)=[1 0 0]; % Colors of the atom
87                 end
88
```

```
86                  C1(atom,1:3)=[1 0 0]; % Colors of the atom
87                  end
88
89                  if(floor(basis(b,4))==2)
90                  T1(atom)=200;
91                  TPE(atom)=2;
92                  C1(atom,1:3)=[0 0 1];
93                  end
94
95
96                  if(floor(basis(b,4))==3)
97                  T1(atom)=400;
98                   TPE(atom)=3;
```


```
101
102                 if(floor(basis(b,4))==4)
103                     T1(atom)=500;
104                    TPE(atom)=4;
105                     C1(atom,1:3)=[1 0.5 2];
106                 end
107                 atom=atom+1;
108             end
109             end
110         end
111     end
112 end
113 %These section of the code, draws the unit cell.
```


```
91                  TPE(atom)=2;
92                  C1(atom,1:3)=[0 0 1];
93                  end
94
95
96                  if(floor(basis(b,4))==3)
97                  T1(atom)=400;
98                   TPE(atom)=3;
99                  C1(atom,1:3)=[1 1 0];
100                 end
101
102                 if(floor(basis(b,4))==4)
103                     T1(atom)=500;
```

This is what I end up with. This is the crystal structure of my $CaMg_2$ I would like to view it in a slightly different way but I need to try something here. So, this is your crystal structure for $CaMg_2SiO_6$.

Student: Sir which color corresponds to which so which atom

Professor: which?

Student: which color corresponds to which atom type?

Professor: So, which color corresponds to which, so the if it is one, then it Ca1, two is Mg1, three is a silicon and four is oxygen so we go back to our main website, the main program. So, 1 0 0 is the red, red is probably the first one Ca. One is Ca and red Ca then red, green, blue this one is the other one, which is magnesium, the third one is the silicon and then the remaining ones are oxygen, four is oxygen which is the not not, not the red, not the blue, and I do not know about these two colors. If you put one here I do not know what color it turns out to but it is you can find it out easily.

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This one is definitely the calcium.

Student: Sir.

Professor: What is that? Yes

Student: Can you go to definition of symmetry 4e?

Professor: Definition of symmetry 4e something wrong there

Student: the multiplicity is 2

Professor: Multiplicities is 2. Multiplicity is no, 4e you have to add see in that it is a center lattice. So, the multiplicity is you have to add half, half to the 0 and the y coordinates when you are trying to define this. So this 1 0 adding 0 does not change it then if you add half to the 0 and the x and the y coordinates will give you additional two points and therefore the multiplicities is 4

Student: Is side symmetry basically a two fold rotation?

Professor: Correct that is right. The site symmetry is two fold is lying on a point which has a two fold rotation, which has a two fold rotation is that clear? this is how you generate for the mono clinic structure

Student: if calcium and magnesium are both present in position 4e Wyckoff position so number in the unit cell is same?

Professor: Correct.

Student: I mean to say the number of atoms in units cell is the same?

Professor: Yes, if calcium and magnesium are both present in position 4e then the multiplicity is 4. So, there will be 4 calcium atoms and 4 magnesium atoms 8 silicon atoms and there will be 24 oxygen atoms. Are there any questions with this mono clinic lattice construction?

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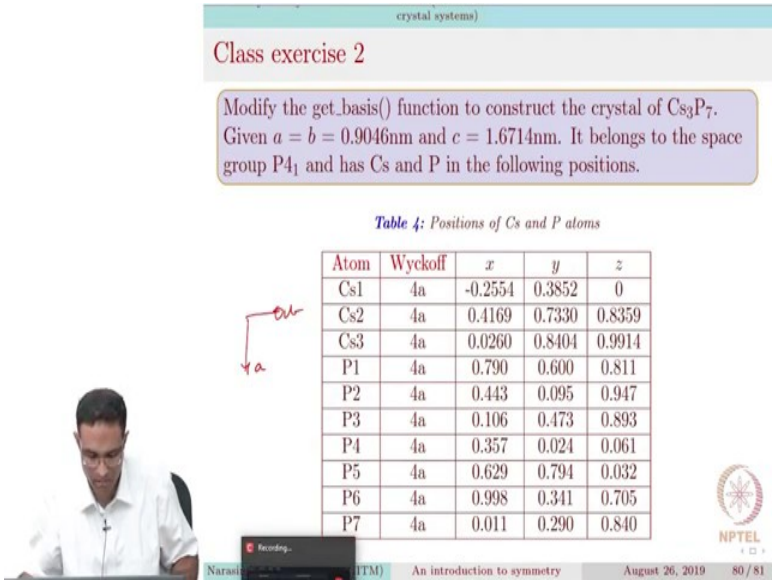


The next one is slightly more, has more number of things to keep track of which is basically the P4 space group, so tetragonal structure. In tetragonal structure, once again it is viewed through the c, it is viewed from the c axis. So, this is b and this is a. So, you will be viewing a square. So, the axis which has a maximum symmetry is basically taken as the c axis. So, you have a and b given to you which are both equal and c is 1.6714 nanometers given P4 1 space group and these are the various positions of Cs and P and all of them are in position 4a.

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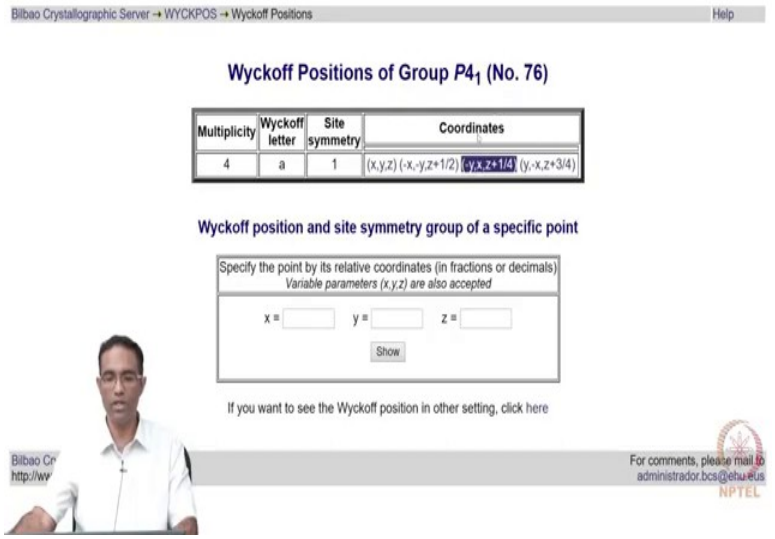


So, let us take a look at this particular space group. What did I say was this group was 4 P4 1 these are the various atoms there is one general position that's it. There is no other there are no special positions in this entire thing. So, x y z and all these things can be easily generated.

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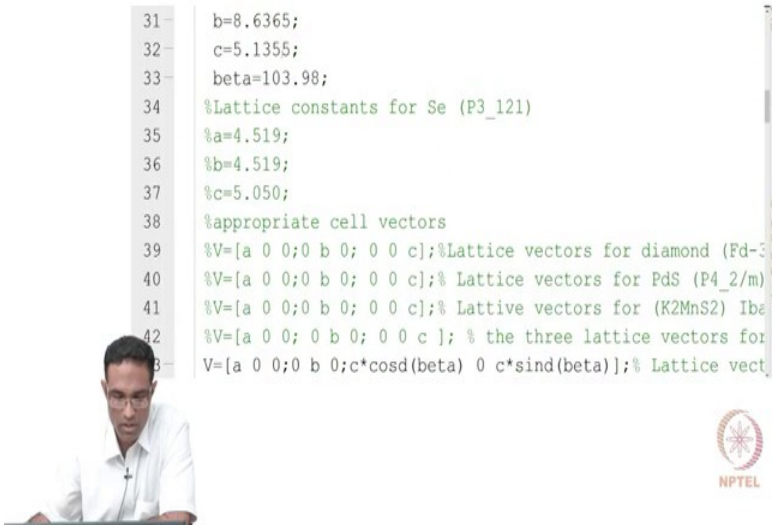


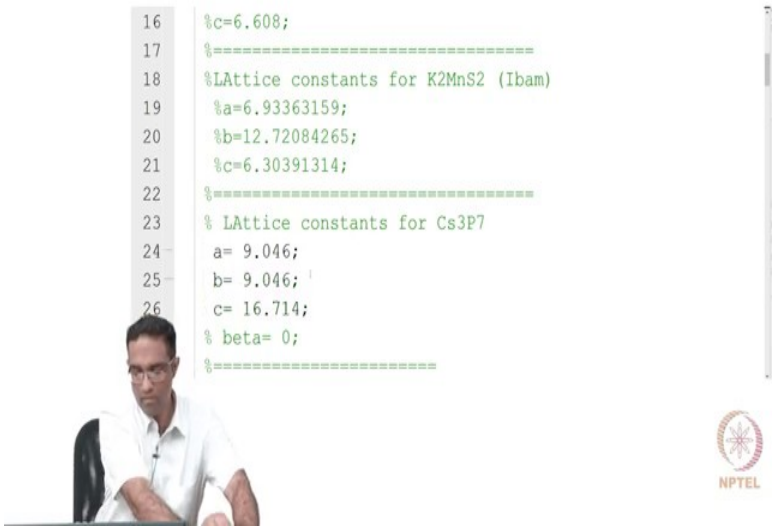


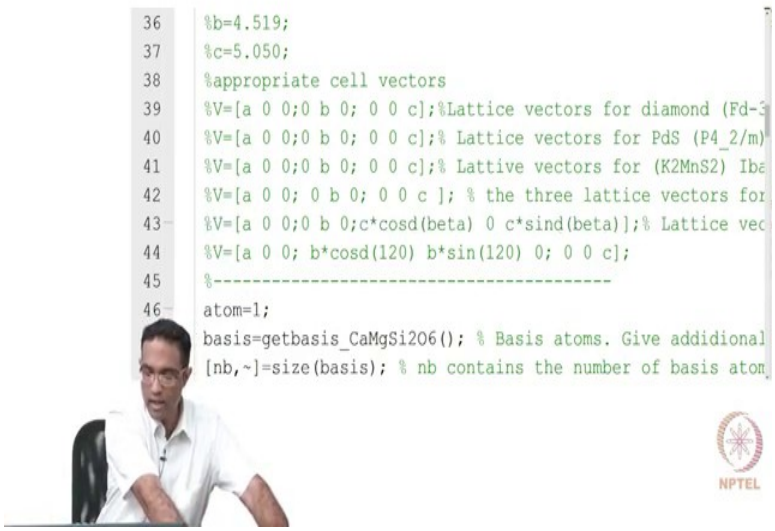

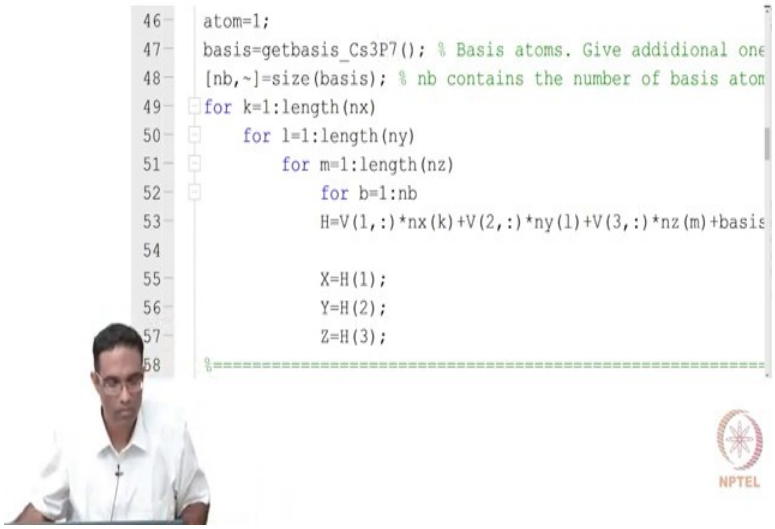


So, once again we go back to our original code, what do we have to change we have to change a very few things actually, we just have to change the corresponding lattice vectors. I will I will comment out the lines that we had for calcium magnesium silicate and uncomment these lines and of course, I have to define the appropriate lattice vectors. So, which I have already defined here and then finally I just have to change the corresponding function that I will call Cs3P7

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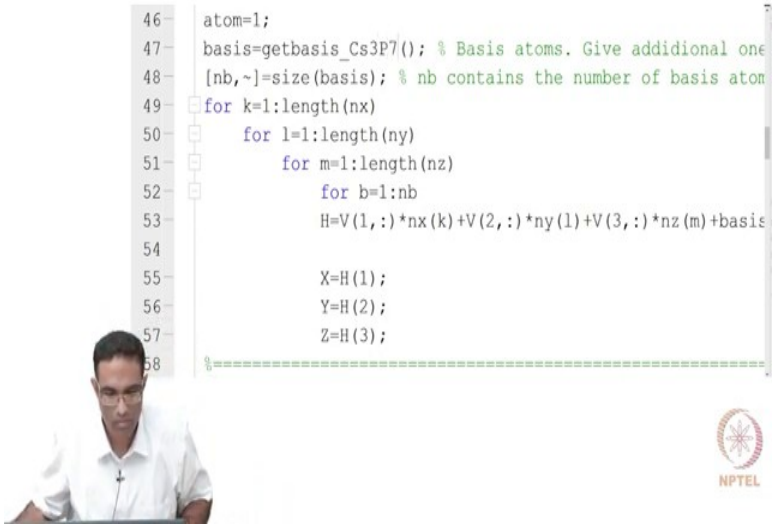


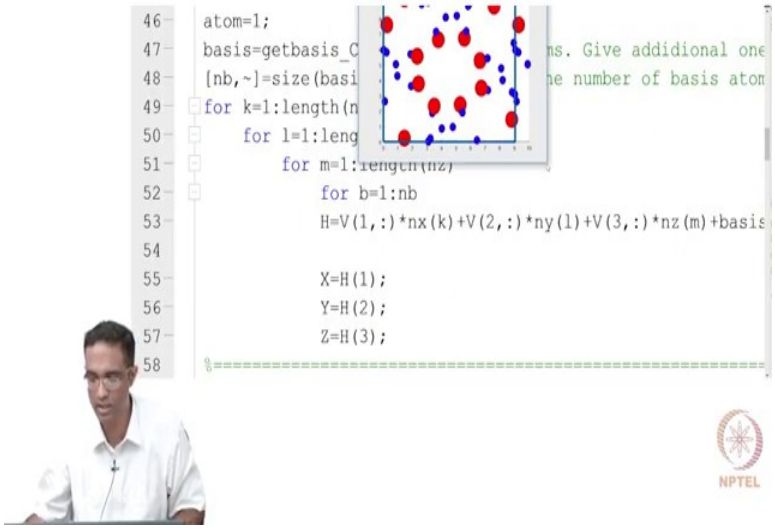


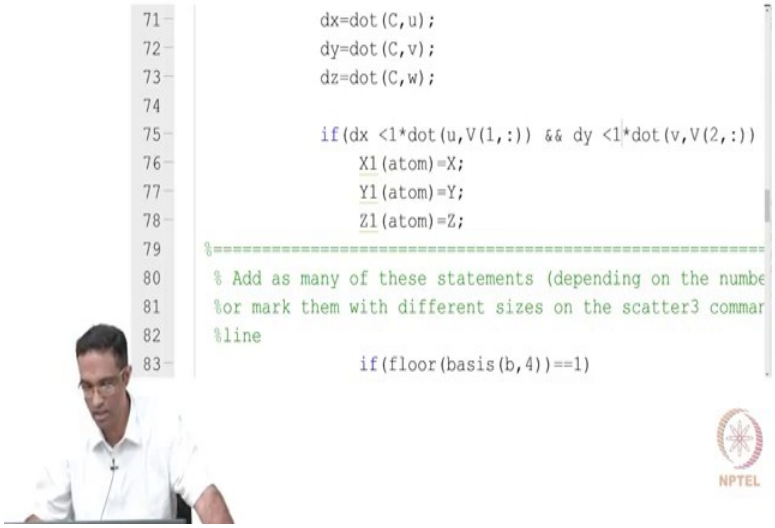

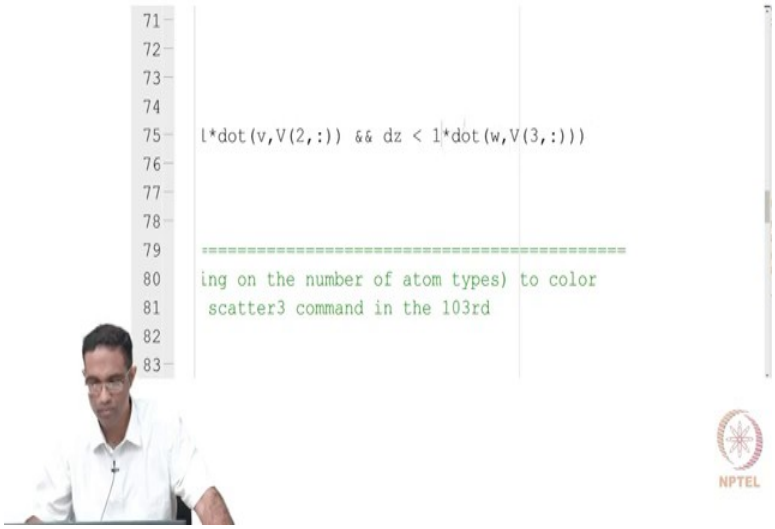


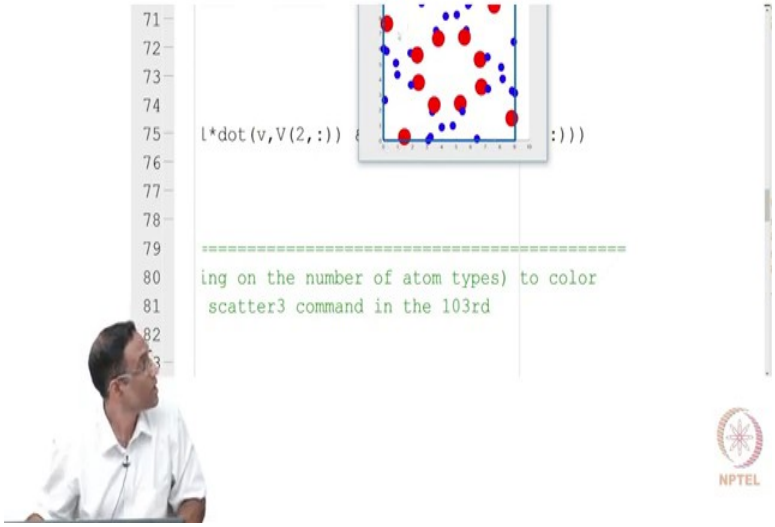


And that is the crystal structure for CS3 P7. The one unit cell just one unit cell which of which of course, the some of the boundary atoms are turning up here and the reason for that is that we have said you print 1.1 here if I change this to just 1 as I mentioned in last class, you will not see those atoms, right this this is how the axis view this is the x y axis.

So, this is going to be the a and this one is going to be b. The y axis is b here this is actually a square this is actually a square you are looking at it from the top, the c axis is pointing outside the board. The rest of it all pretty straightforward it's all quite similar.

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For this it is for this particular space group the advantages because there is only one function that you need to write there is only one Wyckoff position in which both the CCM as well as the phosphorous atoms are actually located.

Student: In that website, there is option x,y,z  so can we get all the optional atoms

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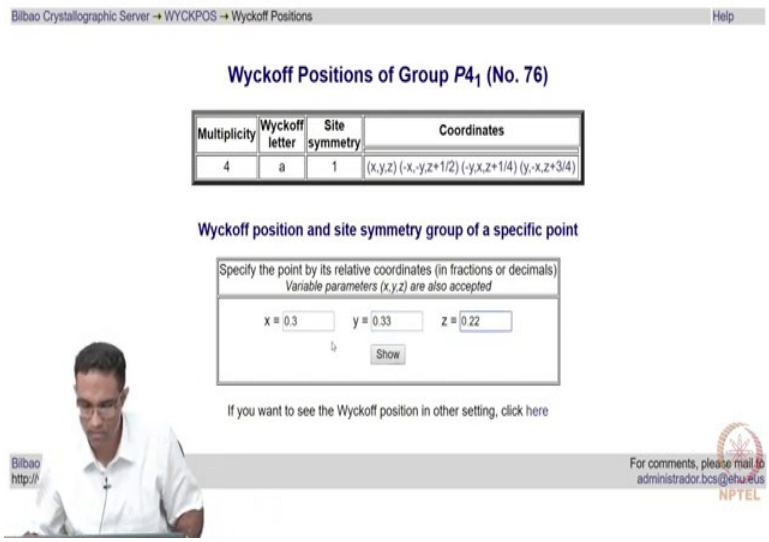


Professor: So, one of the questions in this website there is x y z, so it can be put some number here and get all the optional atoms.

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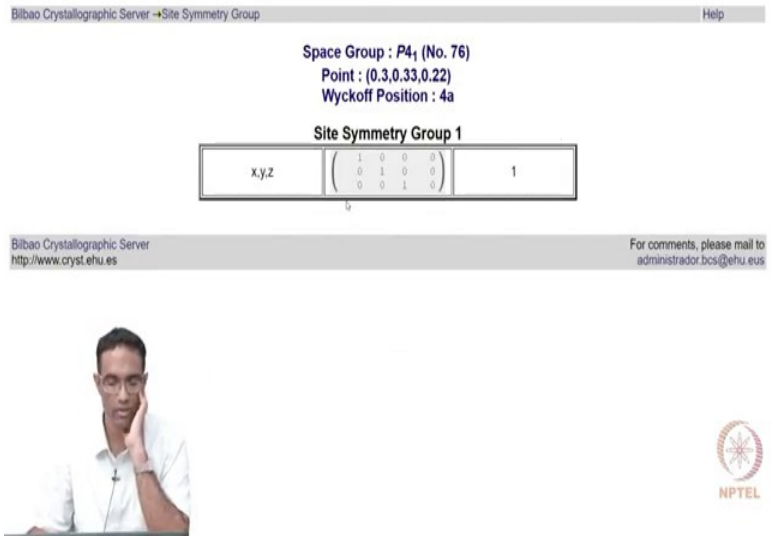


Let us try this is what it gives. So, it gives you the Wyckoff position is 4a and it does not give you the gives you the entire list, like what you are expecting. But let us see this one?

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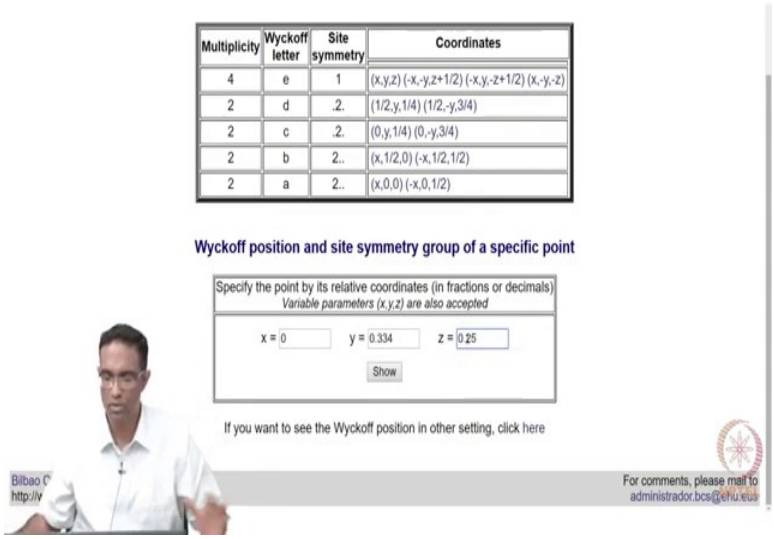


Basically, if you give the fractional coordinates, it is going to tell you what is the Wyckoff what does the Wyckoff position for example, I am going to say 0, that I am going to say 0.334 and then I am going to say here 0.25.

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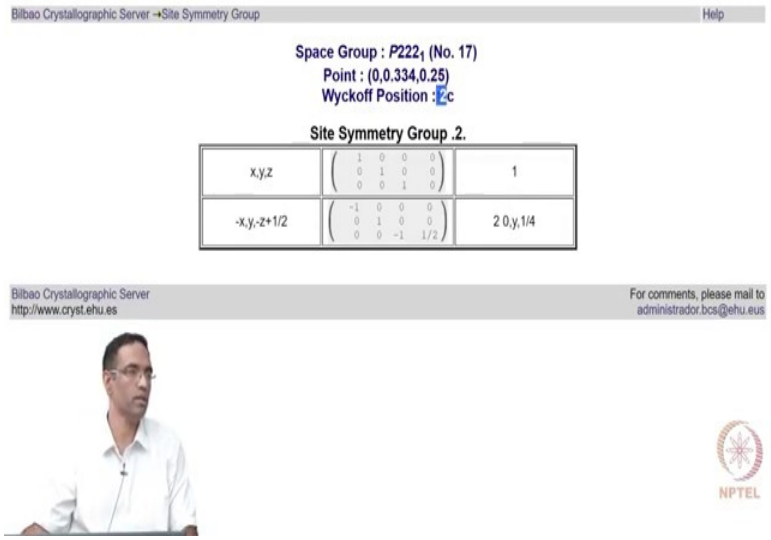


So, so it says that it is 2c it says that the position is 2c, so I am able to give the position and it is telling me what is the Wyckoff position in which that particular point is located usually we do not have that sort of problem, we only have the other problem we only are given the Wyckoff positions and we have to generate the crystal structure.

Now let me do one last example where we have, I want to show you the structure of selenium which is trigon. So, this one will take a look at it first from the website. Selenium has a trigonal structure and it space group is P3 suffix 1 to 1.

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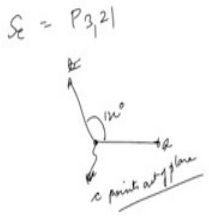

So, this is the space group. So we use what do we use for such trigonal systems? What is the unit cell that we use, we use the hexagonal unit cell with 120 degrees included angle between a and b and c is pointing upwards. So, this would be the lattice vector something like this would be the lattice vector and c is pointing outwards.

Student: c point outwards or b.

Professor: Oh sorry, this is b and c points outwards this is b. b, it is b not c.

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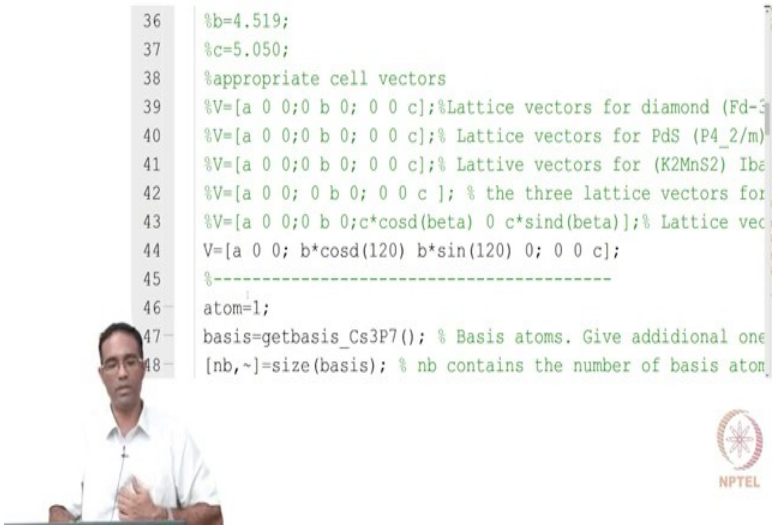


So, these are the lattice vectors a, 0, 0. b cos d 120 b sine d 120 0; 0 0 c is basically my c vector.

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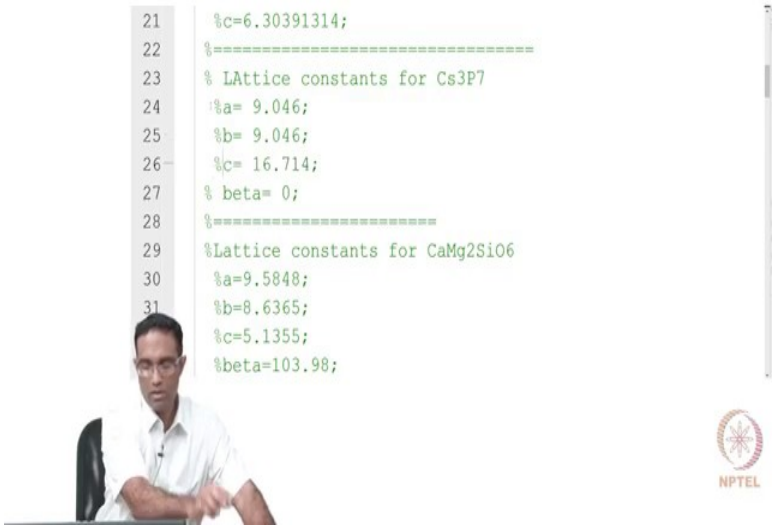

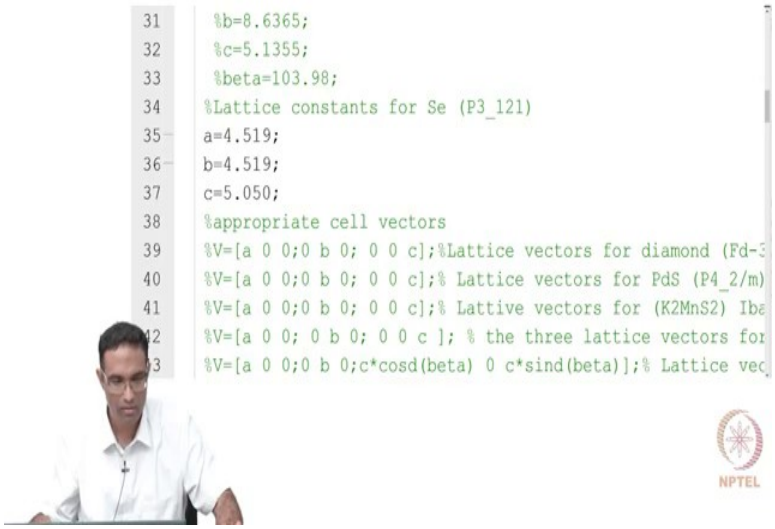


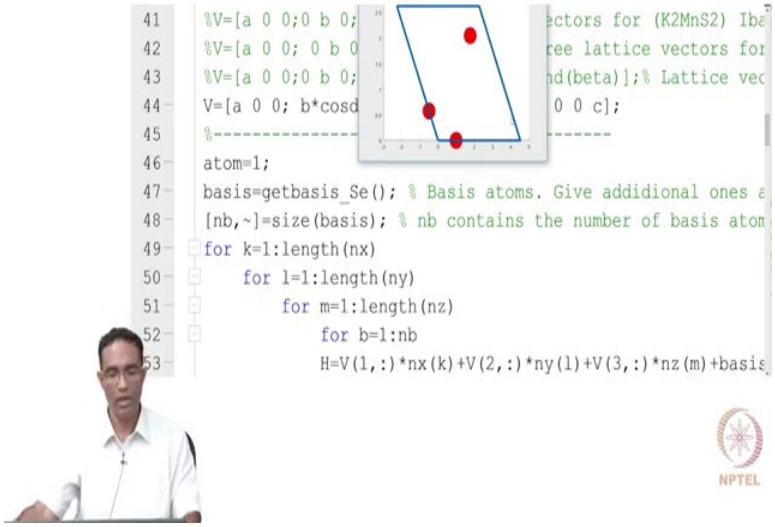


And I am going to comment them and look for my Selenium thing right here these are the lattice constant. By looking at the lattice constant, you can know this is a this is b and this has to be c this pointing outwards and I have to change my this one to Se that's it.

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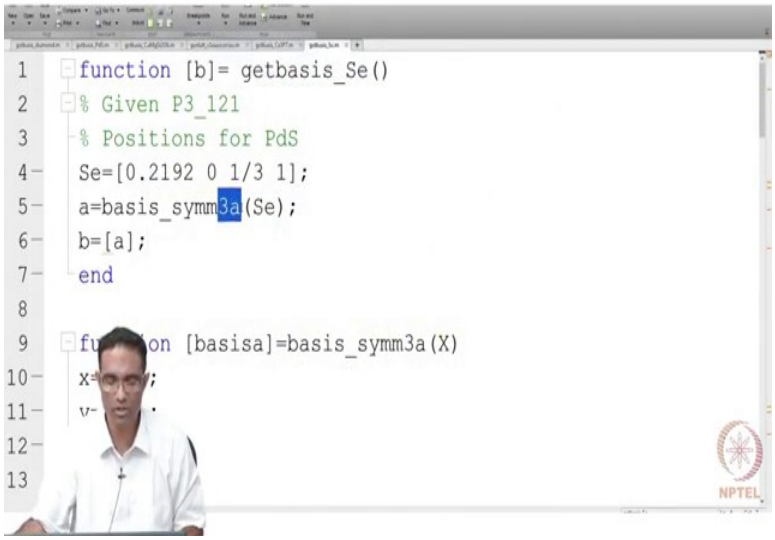


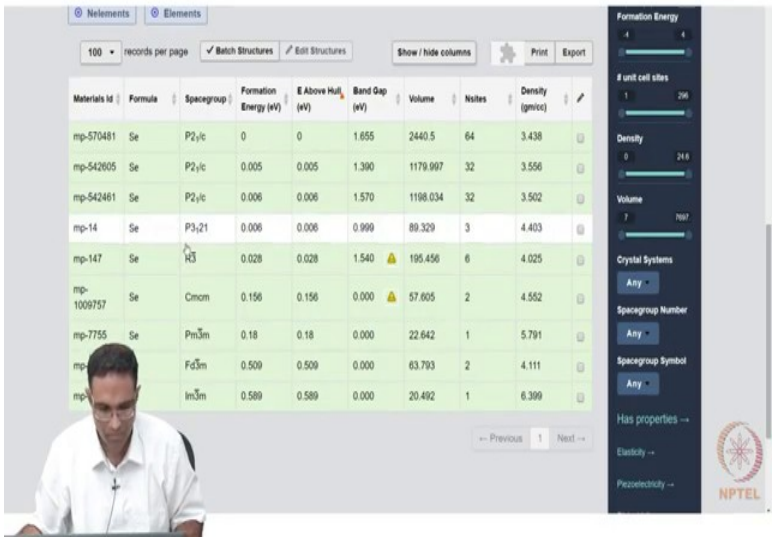


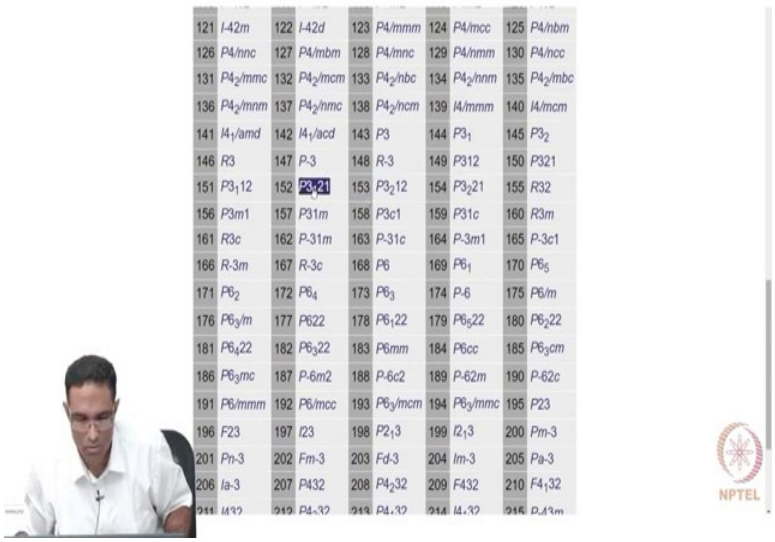

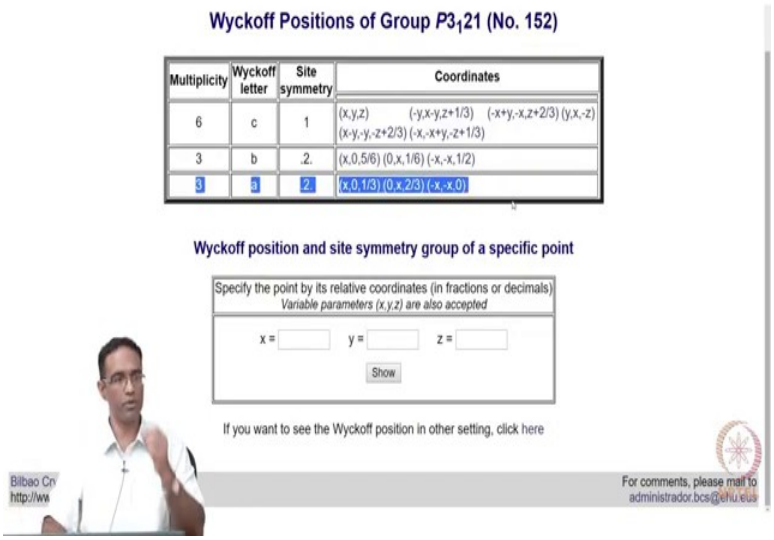


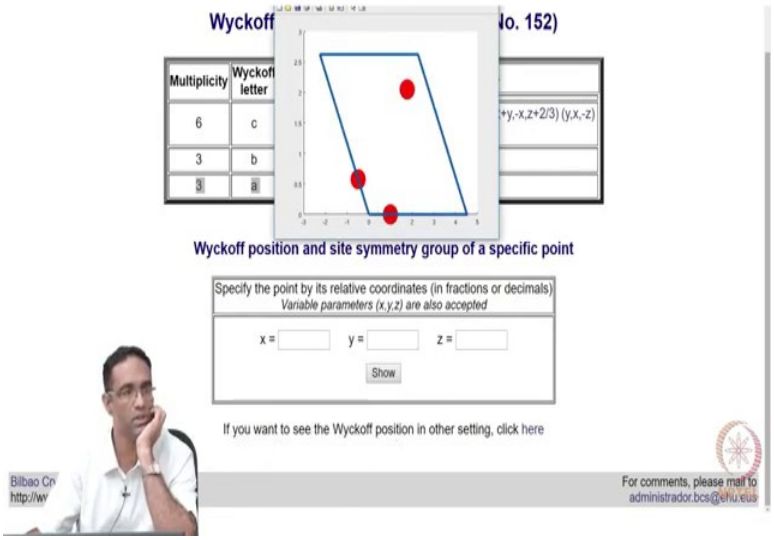


So, let us take a look at that these atoms are actually located symmetry position is 3a, P3 1 2 1 from the materials project website and we can also look at our P3 1 2 or 2 1

Student: 2 1 .

Professor: What? This one right, so this is the general, this is a position, so they are at positions 3a, so there will be only three atoms present inside the unit cell and as you can see when we generated it there are just exactly three atoms that is associated with the unit cell and you can also check if this is correct by going to your materials project and look at this.

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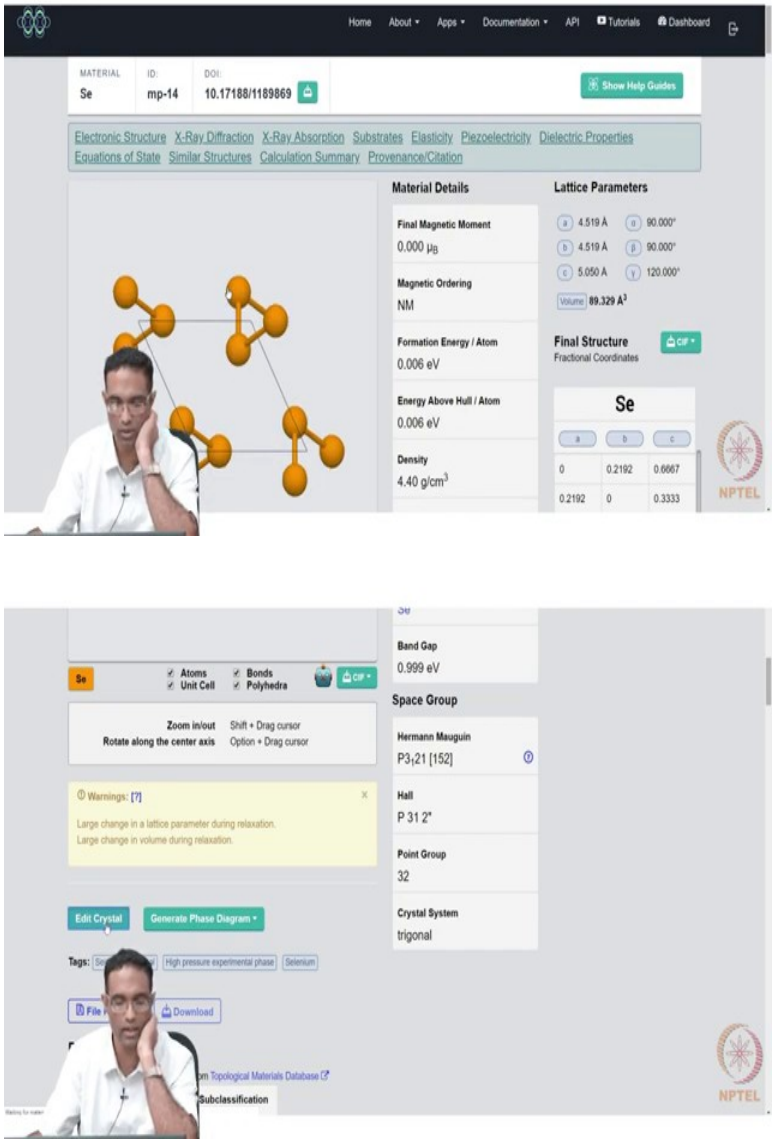


So, now if you see, there is one, two and three all the other atoms are located outside of this unit cell. So, so, you can make other you can you can like I had showed it the other day you can click edit crystal and then remove the other atoms that are present outside the unit cell and convince yourself that whatever you have created is in fact.

So, this is a very good way of checking your coats. So, one of the first things that you want you will be doing whenever you are running molecular dynamics simulations is to create the crystal structure. Not always our crystal structures you know bcc or fcc for which the you can get away with writing some simple quotes, when they are mono clinic and tetragonal you have to be careful and each when each unit cell contains a large number of atoms, then you

know it becomes extremely careful for you it becomes extremely important for you to generate the structures correctly.

And also check them right you can create a unit cell on your MATLAB check them and give and use that to generate your crystal structures for the molecular simulation package that you are going to you that you are going to be using.

So, with that actually I have completed the first module of this course, which involves create creation of crystal structures, interpreting space groups, point groups, understanding them and how you use them Hermann mauguin symbol and the corresponding Wyckoff positions for every space group to generate any crystal that is given to you.

So, from the next class onwards, we will start with the next module, which will involve some introduction to statistical mechanics. So, statistical mechanics is a vast subject in itself, is not something that we can actually cover in one third of the course. But it so happens that the molecular dynamics the reason why molecular dynamics framework works.

Why does giving you useful results is because of the framework that is established in statistical mechanics, so it is a good idea to actually look at statistical mechanics first to see what that framework basically tells us and then come back to molecular dynamics simulations and you will be able to better appreciate the kind of results that it is producing, and also interpret these results whenever you are doing your research work.