

Computational Materials Physics (2023-10-23)

Week 4 : crystallography

(automated transcription)

This is the feedback webinar on crystallography. A quite different topic compared to the last two weeks, where we have been going deep inside density functional theory with sometimes surprising theorems. Now, in the past week, things were much more visualizable and down to earth in how to build crystals and how to represent them. About the project, very shortly about the project, so there were six teams formed and before this webinar all six teams have submitted their work plan. I will give some feedback on these work plans soon, so today or tomorrow the teams will receive this. It will not happen during this webinar. That was the only housekeeping part of information, so we can immediately start with crystallography. Based on the comments, there are two types of attitudes that you can have with respect to the material you studied in the past week. Some people say, well, it's something that either I have seen already or something that compared to these nice mathematical theorems of density functional theory, compared to that, this was rather dull. That's one attitude. Or there are other people who say, well, this was something I could really play with on my computer and I like visual information. So, these two kinds of attitudes are possible and if you find yourself in one of these two areas, then know that this is just normal. Depends on your background, depends on your interest, but I hope that whatever is your attitude, that you will be convinced by the end of this module that this is something you need before you can do calculations with quantum physics for crystals. The first part was about CIF files. What are CIF files and where can you find CIF files? One of the important pieces of information here was a list of crystallographic databases of various kinds. So, it's good to, I repeat the list here, that is how it appeared in the core site, but it's good to keep that list at hand. If you need to look up crystals, well, these are the places where you can start. And in order to understand what CIF files are, I asked you to look at a specific crystal, Neptunite, with a quite gigantic chemical formula. Deliberately a difficult chemical formula, because this should be a crystal where you have no urge at all to try to do something manually about this. Such complicated crystals, if you don't have an information infrastructure behind this, you will never be able to work with these crystals. So, let's use that complicated example to see what is possible. And I asked you, first convert this CIF file that you can find for this crystal, convert it to a format that your density functional theory code, which for most of us will be quantum espresso, that your DFT code can process. And that is something you have done in the past weeks. So when you made the basic example for the silicon crystal, then you started from a CIF file. You didn't know back then what a CIF file was, but now you know that. You start from a CIF file from a database, and you convert that to the input format for quantum espresso. That was here, the line that you see here, was for that basic example. If you download that Neptunite CIF file from COD, then it will be a file with the number you see there. And in exactly the same way as for silicon, you can convert that to an input file for quantum espresso. Why is that CIF file useful, you could ask? Because I have to convert it to an input file for quantum espresso. Wouldn't it be just better to store in these databases the input files for quantum espresso? The reason why that is not done is that quantum espresso is not the only DFT code that is around. There are many DFT codes, and I just give as an example here four widespread codes. And if you work in DFT, it sometimes happens that you do a calculation in one code, and then you have to do something related for the same crystal in a different code. So you would need to transform input files from one code, crystal structures from one code, to another code. This is always the same crystallographic information, so it is not too difficult to write converters for that. But if you have four DFT codes, you see here how many converters you need. And if you have n DFT codes, the number of needed converters scales with n squared. So you need many converters to maintain, and therefore it is more efficient if you have one common format, and that will be the SIF format, and that you can convert that SIF format into the input format for each DFT code and back. This way, with two transformations, you can go from any DFT code to any other DFT code. That is one of the reasons why that SIF format is so useful. We apply this to our neptunite crystal, and I told you it is deliberately a complicated crystal. Here you see a picture of the unit cell. You don't want to write or type coordinates of these atoms by hand, I can assure you. So how will we work with crystallography in this module? We will not discuss the theory of crystallography, we will rather stick to practical crystallography.

How can we use the tools of crystallography to say something meaningful about such complicated crystals? How can we tell our DFT codes which crystal it has to calculate? I will use that example to say a few more things about the content of such a CIF file. Things you may have realized if you looked into that CIF file yourself while making these exercises, or maybe you didn't realize that, and by hearing the discussion here, you will see more in CIF files. So this is the header of a CIF file, and I am very much disturbed by some noise here. There is a farmer who was working in the nearby land and who passes with two big trucks in front of the window making a lot of noise that you hopefully do not hear on the camera too much. But once they are out of the street we will be rid of that problem. So here you see the header of the CIF file for this neptunite crystal, and one of the important pieces of information in the beginning is the space group number. Space groups, they are numbered from 1 to 230, and they have different naming schemes, and you see two of the names given here. 232 space groups, here is the list of all of them, and we are here dealing with space group number 9, so if I would look in that list I see there two entries, and you see that there are two ways to specify that space group, we will come to that a bit later, and with space group number 9. A very important piece of information is how the unit cell looks like, the box in which the atoms are, how does that box look like, and that box is specified here by three lengths, so the lengths of the three vectors that span the box, and I draw here a picture that you have seen in the video, the three vectors A, B and C, they define that unit cell, you can specify the length of each of these three vectors, these are the A, B and C that are given here, and the three angles, these are the other pieces of information needed to define the box, which are in this case twice 90 degrees, and for the beta angle 115 degrees. So with these three lengths and these three angles, you fully specify the box. Inside that box you have to put the atoms, and in order to specify where the atoms are in the box, you have these x, y, z coordinates, they are given here in fractional coordinates, which means they are between 0 and 1, or they can be negative, but you can always make them between 0 and 1 by adding 1 to them, if you see here, minus 0.08, that is the same as plus 0.92. Furthermore, apart from the coordinate lines, you also have symmetry operations, and these symmetry operations, you can apply them to the coordinates, and you can find new coordinates inside the box, where there is an atom that is symmetrically completely equivalent to the atom where you started from. So if you take an atom with coordinates x, y, z, and x, y, z that can be then any of these lines here, well then you know that an atom at a position x plus one-halfs, y plus one-halfs, and z, that that atom will be completely equivalent to the original one. This is the content of the CIF file, you have translated this to an input file for Quantum Espresso, and how does that look like? I have here the same two pieces of information, the box, how does the box look like, and where are the atoms in the box. The box in Quantum Espresso is not specified by a, b, c, alpha, beta, gamma, but by a matrix. A matrix where the first line of the matrix are the three components for that lattice vector a, and then there under you have the lattice vector b, and then the lattice vector c. So you get the three components of the three vectors, and with these three vectors you unambiguously make the unit cell. So that's the way how Quantum Espresso specifies the box. And then the positions of the atoms inside the box, that's in the same way with fractional coordinates. As some of you experienced, if you download such a CIF file from a database, and you try to make that conversion from CIF file to Quantum Espresso, then it may happen that you run into warning messages. And one series of warning messages is what you see here, and silicon 2a is not a chemical element. I can reproduce that error, so if I do this myself on my laptop, I get exactly the same error. Where does it come from? Some people have noticed, if you do this with this CIF file, you will have the error. If you take a different CIF file for the same neptunite crystal, because the database lists multiple CIF files, then it does work. And if you would remove all these labels for the elements, rather than silicon 1, you write silicon, rather than silicon a, you write silicon, then it will work as well. And this has been discussed on the forum, you see that some people have asked the question, and other people have provided the solution. So if you ran into that problem, you can have seen the solution there. So it simply means that the converter that goes from CIF files to quantum espresso input, it cannot read element names that contain extra characters. So if you have silicon 1, or oxygen 4, that works, but if you would call it silicon a, that does not work. That's allowed in CIF files, but that converter does not know that. So if that is the problem you run into, just remove the labels, that's the safest, just the chemical names, and then it will work. Another message I found on the forum, somebody said, well I removed these character labels, but I still get a warning message. Namely this one here, site occupancies not found, assuming all occupancies equal 1. What is that? Well, in a CIF file, you can have next to the line with the coordinates, also a number that indicates what is the chance that you will find an actual atom at that coordinate. If that number would be 0.6, a silicon atom, a coordinate, and 0.6, it would mean there is a 60%

chance that you have on that position a silicon atom. And maybe that coordinate appears a second time, maybe for iron, and then it is followed by 0.4, then it means you have 40% chance that that position is occupied by iron. So 60% silicon, 40% iron. Or that coordinate will never appear again, and then you have 60% silicon and 40% nothing, so a partially occupied atom site. This is all very relevant for experimental structures, where you can have site disorder, where you can have two elements that occupy with a given probability the same site, but in a DFT calculation that is not possible. There either is an atom at a given position, or there is no atom. You cannot solve a Schrodinger equation for a mixed atom, or for a fraction of an atom. So therefore, for input SIF files that serve as input for a DFT calculation, we always have full occupancy. So that occupancy factor is 1. And therefore, this warning message that you see here is harmless. It just tells you, well, I read your SIF file, I see you did not indicate any occupancies, and therefore I assume that they are all 1. And that is exactly what you want. So this is not a warning to worry about. Someone else noticed, if I do this for this complicated neptunite crystal, and if I count the atoms that I have in my final input file, I find two formula units. Is this normal? Is this correct? And that is a good observation, and that gives me an excuse to discuss the difference between a formula unit and a unit cell. If you look at the top of that SIF file, one of the first lines will have been this chemical formula sum, and if you count the indices that are there for every element, 2 for iron, 1 for potassium, and so on, you have 40 atoms. But if I look in the content of the input file, this NOT, the number of atoms that are in the unit cell, that is 80. So apparently I have here in my unit cell twice as many atoms, I have two formula units. And that can be perfectly normal. It is not the case that if you have a crystal that you can describe by some formula unit, that then necessarily your smallest possible unit cell will contain exactly one formula unit. You can have unit cells where two formula units are needed to describe the entire unit cell. And that is what happens with neptunite. So in chemistry, if you just look at the names of a crystal, names given by their stoichiometric formula, there the formula unit is the smallest possible building block. But if you look at a crystal as a 3-dimensional object and search for the unit cell, the smallest possible building block to generate that 3-dimensional crystal, well there you will find that sometimes you need more than one chemical formula unit in order to construct your 3-dimensional smallest building block. So good observation and with this the confirmation that nothing was wrong with your unit cell or with your input file. Let me have a look at the chat whether there are any questions. Nothing so far, so feel free to post your questions in the chat. I regularly look at it and I will try to answer on the spot. Good, second part of the module was meant to look more deeply into what is available in a CIF file and more particular can you make sense of the words space group, unit cell and Wyckoff position. And can you use the Bilbao crystallographic server to find all Wyckoff positions for a given space group. That will be something that you will regularly need so let's train that. And all of that was illustrated by the task that you see here. You get one piece of input one piece of information the name Lita Arch, the name of a crystal and I ask you a lot of questions that have to be derived just from knowing that name. And I didn't ask you to submit your answers to this task, but I will go with you through the different steps and you can compare whether that is similar to what you found. So we start from Lita Arch and the first thing I asked you was Google for the chemical formula. And your friend Google will come up with something. You have for instance the Wikipedia page of Lita Arch and if you start reading that Wikipedia page already in the second line you will see that Lita Arch has the chemical formula lead-oxygen with indices 1 so equal amounts of lead and oxygen. And if you read a little deeper I put it here as bonus information you see already information about the space group and I will change to the pointer because we may need that in the following slides. So we know the chemical formula then we have to search lead crystal in the COD database or in any other database. What do we find if we search for lead-oxygen in the COD database? Well this list of crystals here of which three have the chemical composition lead-oxygen and one another one so definitely it is not this oxygen-4-lead-3 it is one of these other three and we have seen in Wikipedia that the space group was P4NNN and that first line and last line they have these space groups. There is another symbol following 1 or 2 we will come to that but it is definitely not that third line PBCN. So by googling for the chemical formula and some space group information and then searching in the COD database I can immediately find a CIF file that has this crystal in the correct space group. Some people ask if I do this maybe not for litharge but for another crystal I often find multiple possibilities I find that the same chemical formula has several entries and that can have several entries and the question is which one do I then need to take? There can be different situations it could be that you have different crystals for the same stoichiometry if I go back to the previous page you have here the lead-oxygen crystal in space group P4NNN but I also have the lead-oxygen crystal in space group PBCN same chemical formula but the atoms are arranged differently in space which

one of these two do you need? It depends on the purpose if somebody told you calculate me the energy difference between some possible crystal structures for lead-oxygen then you need both if somebody asks you for that crystal structure you have to take the line that corresponds to that specified crystal structure depending on the context you may want to pick one particular line it could also be that you find the same chemical formula the same space group but just different experimental papers about that space group and then it's often a good choice to take the most recent entry because that will also often be the most precise one or third possibility and we will elaborate on that later it can be that you can have the same chemical formula for the same space group but a different setting for the space group we will define that a bit more precisely but you can consider this as different ways how you can describe the same space group and that's what happens here in the first line and the fourth line so depending on what is the reason you can have different reasons why there are multiple entries for the same chemical formula and depending on what is your goal and what is the reason for the different entries you can make a decision what to take good, the next question was what is the space group of that litharge crystal that was mentioned in Wikipedia and we can read it from the COD database if you go searching into the table with the 232 space groups then you will find it is number 129 P4NMM and it is listed here with an origin choice 1 or 2 again we will elaborate on this a bit further what are the Wyckoff positions for all the atoms in that crystal that's the next question and therefore you have to use the Wyckoff tool from the Bilbao crystallographic server and in the Bilbao crystallographic server if you select that tool you have to choose your space group you are confronted with this screen where people wondered which of these three buttons do I have to take the standard setting, the non-conventional setting or the ITA setting what does that mean, what are the differences and let me start from the right hand side ITA, these are the international tables for crystallography volume A this was originally a book series where the conventions that are currently used for space groups have been in a very detailed way elaborated defined actually everybody in crystallography uses these ITA settings a space group can have multiple settings that are mentioned in ITA and if you would click that button you would see a list of all possibilities one of these possibilities is taken as the standard setting so if nothing else is specified in all crystallographers now then we use that setting and that is the one you will find that you will use if you take the left hand the button at the left hand side so most often, not to say always you will use that standard setting in the very specialized situations where you will want a setting that is not listed in ITA then you can define it yourself and here take any setting you want and what do I mean by setting perhaps I should have mentioned that in the beginning these are things as where do I take the origin of my axis system and in which direction will my x, y and z vectors point like relative to the crystal if we take the standard setting for the space group 129 you will get this list of Wyckoff positions and some people who never heard about Wyckoff positions before will wonder at this stage what do they mean but we will illustrate further what this table means the important point so far is that you can get to that table for a given space group in the standard setting you can find a table with the Wyckoff positions next step was show a picture of the unit cell which you could do directly in the COD database for every CIF file there is a corresponding page with a viewer and if you right click on the viewer and select symmetry and then from that submenu the string with 444 and 555 and so on if you do that then you will see that's a picture where all the atoms in the unit cell are explicitly drawn so this is a correct visualization of the unit cell of litharge you can also visualize this in Vesta this is a picture from Vesta and depending on how you set up Vesta it shows you, here in this situation it shows you also the neighboring atoms just outside the unit cell that gives a bit better a 3 dimensional view for instance that you can recognize in this picture the one you had on the page before so the lead atom with 2 oxygen atoms the lead atom with 2 oxygen atoms and the other oxygen atoms that would be outside the unit cell they are drawn here explicitly good, in Vesta or in the COD viewer I can click on the atoms to read the coordinates and if I do this for this lead atom here I find 1 quarter 1 quarter, 0.23 so meaning I go 1 quarter in the x direction and I take 1 quarter of this I go 1 quarter in the y direction and I go somewhat less than 1 quarter in the z direction and that is how I find this atom while the other lead atom is at these coordinates 3 quarters in the x direction 3 quarters in the y direction and a bit more than 3 quarters in the z direction like here if I now compare that with the Wyckoff table then I see here one position 2c that has coordinates that are very similar 1 quarter, 1 quarter and some number z and 3 quarters, 3 quarters and a number minus z if you add in 1 if you add 1 to minus z then that is the same number let me compare with these coordinates 1 quarter, 1 quarter z and 1 quarter, 1 quarter sorry 3 quarters, 3 quarters minus z so minus 0.23 minus 0.23 plus 1 and that is plus 0.77 so this number here is indeed minus z so my 2 lead atoms they are at exactly the coordinates described by this line with z having

the value 0.23 therefore we say that the Wyckoff site for lead with the arch crystal is 2c and inversely if somebody would tell you well I have here a crystal in space group 129 with the lead atom at position 2c then you can look in this table and find aha, then it must have these coordinates and wait a minute there is an unspecified number in here that is able to tell me the value of z otherwise I cannot draw that crystal so you see how useful that information is a question many people will ask at that stage is but what then about that number z where do we get it from can we just choose it for instance and I have an example of this more at the end of the webinar that I can say already now no you cannot choose that number if you choose it let me start in a different way the reason why that number is not specified means whatever value you take between 0 and 1 it is still the same symmetry but in reality nature will pick a value if you take the lead oxygen crystal in this space group the lead atom will be at z equals 0.23 and not at z equals 0.25 or 0.37 no it will be 0.23 nature has chosen that and in experimental crystallography people will measure what this value of z is in the next two weeks when we will study geometry optimization with DFT you will learn how you can predict what that value of z is and then you can compare prediction and experiment so that number is not a free choice it just tells you that whatever that number is symmetry will not be affected but a crystal is more than just symmetry some things are not determined by symmetry and so the value of z is not determined by symmetry this was a copy of something that appeared on the discussion forum and yeah the question here was what I just explained for the litharge crystal with reading these coordinates not everybody finds the same and that has much to do with the fact that we have these two different settings here number 1 and number 2 I will illustrate that if you go to the box of ITA settings you will find there that you have indeed two possible settings for space group 129 two settings that are defined in the international tables of crystallography and the difference between them is a translation over minus one fourth plus one fourth and that leads to two sets of Wyckoff positions so the Wyckoff positions one quarter, one quarter z if you do plus one fourth minus one fourth then you have one half zero z so that is what you get here as coordinates for the second setting and that means the litharge crystal, the one we had before in origin choice 2 if I would draw it in origin choice 1 it would look like this and the coordinates would be one half zero z and zero one half minus z so wait a moment so we get zero one half minus z zero in the x direction one half in the y direction and some distance in the z direction and that distance, let's call this here minus z it would have been a bit, well that is equivalent it would have been a bit easier to talk about z here but minus z is as good a number as anything else and the other position is then one half zero z so I go one half in the x direction zero in the y direction and now the complement of this z in the z direction so I end up here so these two atoms are described in the other setting but now I see four lead atoms and not two no, you see only two lead atoms because this one here is in the left phase and therefore by periodic boundary conditions it also appears here and both of these, because they are in a phase are only for one half present in the unit cell so this is half of an atom but they are equivalent so together that is one atom and the same here, twice half of an atom so together that is one atom so we have here still two lead atoms in the unit cell in origin choice one these origin choices they have consequences and I can illustrate that in the following way let's take origin choice two and I will focus on the plane that is given here in green and I take the origin of my axis system here at the corner of the unit cell and the ABC directions are given here in that plane there will be two lead atoms the ones here I can redraw that plane here the green plane with the two lead atoms and now I can look at neighboring planes to the left, to the bottom and I have here four neighboring planes you will see if you go from that lead atom through the origin and then the same distance into the next cell so this way through the origin and the same distance in the next cell by periodic boundary conditions you arrive here so there is a lead atom here you can mirror through the origin a point mirroring through the origin and you find another lead atom if I would do this with origin choice one let's take this plane here that contains one lead atom I go through the origin and I end up here and there is no lead atom there so in other words in origin choice two I do have inversion symmetry about the origin the origin of the axis system is an inversion center I can mirror every atom through the origin and I will find an equivalent atom at the other side if I use exactly the same crystal structure but I take my origin choice one and I take here the origin inside an oxygen atom then this inversion symmetry is not there well, working with settings that do have inversion symmetry are there any applications mathematically more convenient than working without inversion symmetry so if you can if there is an origin available that has inversion symmetry we will prefer that and that is why origin choice two is the standard setting for space group 129 and that is summarized here if you know you have here the coordinates in the standard setting with inversion symmetry and this here are the coordinates in the setting that is also an ITA setting origin choice one but the one without

inversion symmetry the positions of these coordinates fulfill that list now, in a sieve file you will often see less coordinate lines than there are atoms I told you already you have two lead atoms in this unit cell but in my sieve file for Littard I will see only one coordinate line so how do we find the other ones I find here one quarter, one quarter point two three, so that is this atom but I have no coordinate for this ok, I could look into the table of Wyckoff positions and there I find the other coordinates but can I find that also from the sieve file and the answer is yes because that is given in this list with symmetry operations start from this coordinate and let me take the first highlighted symmetry operation here I have to take my x coordinate at the same value where originally the y coordinate is so x would be point twenty five I have to take my y coordinate as minus the original x coordinate plus one half so that would be zero sorry no, sorry minus 0.25 plus one half that is plus 0.25 so my new x coordinate was point 25, my new y coordinate will also be point 25 and z is unchanged so this first symmetry operation has transformed this position onto itself nothing has changed I have 16 symmetry operations and if you would apply all 16 then you would see that 8 of them transform the atom into itself but 8 other ones will bring the atom to this new position and you see this with the second one that is highlighted here the new x coordinate is the old x plus one half so point 25 plus one half is point 75 the new y coordinate is minus the old y coordinate so minus 0.25 but minus 0.25 that is the same as minus 0.25 plus one so plus 0.75 so we have point 75 and the new z coordinate is minus the old z coordinate so minus 0.237 which means we can add one and plus 0.763 so that is exactly this position here three quarters, three quarters, 0.763 so the other 8 symmetry operations will transform the coordinates into the new position so with that single coordinate line from your cif file and the symmetry operations you can find all the other positions of that same atom in the unit cell and if you would do that in the other origin choice I will not go through that but then you find exactly the same so if you were hesitating on the confidence statement I can tell something meaningful with space group, unit cell and Wyckoff positions then hopefully with this information you will be able to do that to tell something meaningful and if I want to summarize these concepts in one slide I would say that your space group that is a kind of symmetry identification an ID card for the global symmetry properties of your crystal and then the unit cell that is the size and the shape of the box in which you will put the atoms and that is partially constrained by the space group if you have a cubic space group you will not have a tetragonal shape of the unit cell so part of the degrees of freedom is determined by the symmetry information by the space group once you have the box with its size and shape you still have to answer the question where are the atoms in the box and also that is partially constrained by the symmetry of the crystal so that is why the Wyckoff positions appear the Wyckoff positions that are consistent with the given space group these are those positions where you can put atoms without altering the symmetry the unit cell together with the Wyckoff positions that completely determines the space group so once you know the unit cell with the Wyckoff positions there are unique algorithms not the other way around if you have the space group you know only partially how the unit cell looks like and how the Wyckoff positions are occupied that has practical implications so if we give crystal information to a DFT code we will give it a file that contains the size and the shape of the box, the unit cell with all the occupied Wyckoff positions so that has fully determined the crystal and we know that some of this information is determined by symmetry and some of it is not determined by symmetry so the unit cell can have degrees of freedom if you have a tetragonal unit cell then the C over A ratio is not determined by symmetry unlike for a cubic unit cell if you have Wyckoff positions like this 2C for LiDARCH there is a 3Z parameter and so some of the positions are not fully determined by symmetry so we have it in a ZIF file where we have made a choice for all the numbers everything is fixed and you can ask DFT to calculate the energy for that particular crystal and we will do interesting things with that in the next two weeks when it will be about geometry optimization To conclude that part let me elaborate on a question that people regularly ask why are these free parameters in the Wyckoff positions why are they really free and I have one explicit example for that again I go back to LiDARCH I focus on that same lead atom there at the bottom left one quarter, one quarter Z and I look at one symmetry element that is part of the point group of that atom and that is a 4-fold rotation axis so the green line that you see is a 4-fold rotation axis I can rotate the LiDARCH crystal about that line over 90 degrees and nothing will change and you see that better if we look from the top so here you look at the top of the previous unit cell you still see the projection of the unit cell here and this atom with the 4-fold rotation axis let's say that I have drawn it here well you see that there is 4-fold rotational symmetry about that axis this square of lead atoms this square of oxygen atoms if you rotate this crystal by 90 degrees nothing will change so that is a proper symmetry operation if however I would put my lead atoms not at here 3 quarters 3 quarters and that Z but at 0.6, 0.6 and that Z so this atom

would shift to here so this atom would shift in the same way this atom would shift in the same way this atom would shift in the same way so what would happen with my original symmetry axis this is not a 4-fold rotation axis anymore it is not anymore in the center of this square of lead atoms and even if you would move and even if you would move forget that last sentence so it is not anymore in the center of that square of lead atoms so by having my atom not in 1 quarter, 1 quarter not in 3 quarters, 3 quarters Z but in something else that is not that nice 3 quarters, you kill the symmetry element so you break the symmetry so that is a reason why that Wyckoff site must have 3 quarters, 3 quarters that still did not specify the Z that still did not specify the Z so now let us look from the side and I see here my 2 lead atoms now with a somewhat rotated unit cell that we look exactly in this way we see that there is inversion symmetry to a point that is here in the center from this lead atom to that lead atom this is drawn for a particular value of Z our Z of 0.23 so this distance here, this height is 0.23 this height is minus Z plus 1 0.77 roughly and that remains true if I would have taken a different choice of Z if rather than 0.23 I would take something like 0.4 then my atoms would look like this but we would have inversion symmetry or if I take 0.6 for Z we have this you keep having this inversion symmetry if however I would break this relationship and take Z and the other value here not in that same not as complements so I take here 0.23 and I take here 0.6 so then you move this atom down but that atom stays at the same place and that means that your inversion center has disappeared so it is really needed that you have this Z minus Z relationship here to keep all the symmetry elements if you break it you are in a different symmetry so you will be in a different space group but if you keep that relation whatever value of Z you take so that is the reason why some of these positions are free if you go here to this situation whatever you do to the 0.25, 0.25 if it is not exactly 0.25, 0.25 you will lose the 4-fold rotation symmetry and here you have more freedom you can take any value for Z as long as they have this Z minus Z complementarity good that was a detailed discussion of Littard let's go back to the chat I see there are some questions that appeared here regarding the number of degrees of freedom can we say that Littard has 2 degrees of freedom I have to think was it 2 because we discussed now the lead position let me go back to the one with the Wyckoff sites here but where were the oxygen atoms and I don't have coordinates here but they are here at 0 probably the oxygens will be at 2a and that is one without degrees of freedom and the box here will be the tetragonal box so that means that you have no freedom for the XY plane A equals B but C can have a different length so the C over A ratio is something you can choose so you have 1 degree of freedom due to C over A so for the tetragonal box no degrees of freedom for the lead positions no degrees of freedom for the oxygen positions so in total 2 degrees of freedom ok we are back here another question in the chat in the visualization the 2 atoms that are outside the box so the unit cell itself does not have these atoms but sometimes it is more insightful to draw also the atoms that are near to the edges of the unit cell and that is what was done there and the last question I see right now can you find the geometrical degrees of freedom from the CIF file yes, in a way what I just discussed for Littard this is a chain of reasoning that gives you the geometrical degrees of freedom so you count how many degrees of freedom do I have for my box for my unit cell if you know it is a cubic box you have only 1 degree of freedom the edge of the box once you know that the entire box is specified but the box is specified by 6 quantities ABC, alpha, beta, gamma so 5 of them are free to choose if you look at symmetry if you look at exact sizes you can go from 5 degrees of freedom to 1 degree of freedom for the box and then for the positions inside the box and there you have to count the degrees of freedom for the Wyckoff positions from the table and another question appears must the corner points and the center points be exact 1 quarter, 3 quarter I am not sure what you mean by corner points and center points so what I could tell is the choice of origin is in principle free wherever in space you can take the origin but the ITA settings they list the choices of origins that are for one reason or another interesting to work with and in the choices of origin that have been taken there the positions with these like with this 4 fold rotation axis these positions appear at 1 quarter, 1 quarter if you take a totally different origin they will have different coordinates but the symmetry elements will remain but I am not sure whether that answers your question so you can come back to that and in the next round when going through the chat I will see whether I can add something more and then then we come to more visualization so we still have that LiDARCHE crystal and I ask you now well you can always try to write a CIF file yourself and sometimes, especially for simple crystals this is helpful, this gives insight so I gave you in the course site a template for a CIF file with no symmetry at all and I asked you write the positions in there for a LiDARCHE crystal and when people do that then many people run into such situations so here with origin choice 1 and you say let's look at the oxygen atoms I have an oxygen here at the origin of my axis system coordinates 000 I also have an oxygen here at coordinates 100 and at 010 and at 111 I could write

oxygen coordinates for all of this and if you then try to visualize this depending on the software you can see strange things happening like all the position coordinates for oxygen have been brought back to 000 and if you then give such a file to that Stokes FineSim algorithm then it will break so what has happened there the answer is be careful with periodic boundary conditions this atom here at the origin of the axis system that is by periodic boundary conditions repeated 8 times at all 8 corners of the unit cell and how much of this atom is inside that unit cell if I look at that atom in the origin only 1/8th of that atom because there are 7 other unit cells touching here in that point and each take 1/8th of this oxygen atom but if every corner contributes 1/8th to this unit cell and you have 8 corners then you have 1 atom inside the unit cell so this atom here at the origin represents 1 oxygen position in that unit cell and you don't need to consider any of the others anymore so you don't have to specify 8 coordinate lines just 1 is sufficient because you have only 1 atom if you would specify a separate coordinate line for each of these positions all of them would be copied by periodic boundary conditions and you would have at every position 8 coinciding atoms which is obviously not physical and therefore that FineSim algorithm will break so be careful with periodic boundary conditions periodic boundary conditions you can see by the naked eye you don't need mathematics for that so if you see that something is at the corners or the edges or in the faces of a unit cell then look where the other copy is and depending on whether it is at a corner an edge or a face well you know the number of coordinate lines so if I would do this exercise for the P1 CIF file here now in origin choice 2 this would be the result the A and B lattice parameters same length the C lattice parameter different all angles 90 degrees this is a tetragonal case and that shows me here ok and I realize now I have to correct myself so this shows we have indeed a tetragonal shape so there is 1 degree of freedom due to the C over A ratio but there is of course another degree of freedom due to the choice of A or B so there is 1 degree of freedom for the tetragonal box and only 1 degree of freedom for the cubic box and an additional degree of freedom for the Wyckoff position of the lead atom so the Littard crystal has 3 degrees of freedom not 2 as I just said that was not right, 3 degrees of freedom 2 for the size and shape of the unit cell 1 for the lead positions but this P1 cell is manually constructed just by reading the coordinates from the picture that was the goal of that exercise and if you now run that one through the FindSim crystal then you will find this CIF file with all the symmetry information added it will have determined the correct space group 139 here with origin choice 2 it will have determined the Wyckoff positions so 2C for lead it gives you really the name of the Wyckoff site and 2A for oxygen as we just determined and it even indicates that the lead position that you can have a variation in the Z coordinate so wherever there is a zero it is fixed by symmetry and it is only here that you have a degree of freedom so what would be the easiest way to count the number of degrees of freedom prepare your CIF file run it through the FindSim program count the number of places here where you have this freedom and then look whether your cell is cubic or tetragonal or hexagonal or monoclinic or whatever and find your 1 to 6 degrees of freedom there and all together that is the total number of degrees of freedom we will elaborate, we will use that in the next two weeks when it is about symmetry optimization and if you want something to play with a kind of exercise I think it was suggested in the video but I really recommend to make that exercise it is a very simple crystal as far as chemical formula is concerned YFS is really the chemical formula of this crystal and you have enough information on this slide to construct the CIF file by hand and to run it through the FindSim program to determine the space group and to determine the number of degrees of freedom ok let me look back at the chat yeah recording of course the webinars are always recorded if you go back to the webinar link of last week so in the course site always the bottom part and perhaps in a few hours from now if you would go to the crystallography module and you look at webinar for week 4 then you will see there the video of this week that is always the case a few hours after the webinar has been broadcast for next week we will start the topic of geometry optimization that will keep us busy during two weeks and that goes together with some exercises in the let's play section a practical notice especially for people who watch these webinars outside the European time zone so in the next weekend we will go from summertime to daylight saving time in Europe and that means nothing will change the broadcast hour within Europe but if you are in different time zones then it's worth verifying with a good time zone converter website whether there is not an extra one hour difference depending on whether you and your time zone moves to a different hour yes or no or at a later moment the time when you can watch live good again I leave you five minutes to summarize for yourself the content of this module and to formulate an exam question write it down in this form here and in five minutes from now I will look back again at the chat and see if there are other questions left okay thanks for your input let's then go back to the chat to see whether there are any additional questions I don't see so that means we can close the books for

the crystallography topic and I will see you next week for the first part of the geometry optimization module
bye bye