Defects in Materials
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Lecture – 07
3-d Crystals

Welcome you all to this class on Defects in Material. So far we have learnt how to constrict from one dimensional lattice to two dimensional lattice, and two type two dimensions to three dimensions what all types of symmetries which are associated with it on the basis of the symmetry elements which are associated with a point as well as with the lattice, how they are grouped into distinct to (Refer Time: 00:46) base groups. This gives some examples they are considering and how to understand what is the type from the table which is provided in the international union of cryptographic for different types of crystal symmetry how to read and understand. And now we will talk about how to use this to construct a crystal in the material.

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Construction of perfect crystal

Information required

1. Crystal system
2. Primitive or non primitive (P, I, F, A, B or C)
3. Lattice parameters
4. Elements / stoichiometry
5. Molecular formula
6. Position of atoms / motif in the unit cell

So, when we say that we have to construct a perfect crystal or an ideal crystal what are the information which is required. The first thing which we required is; what is a crystal system to which it belongs is it triclinic monoclinic or cubic or tetragonal or hexagonal this is the information which we require. Then what is the second information which we require is that whether it is a primitive or an non primitive lattice, then if you have to construct the actual crystal we should know what the lattice parameters are. But as far as from the symmetry considerations when we wanted to recount it constructed crystal structure lattice parameters are just not necessary, but what is required is the symmetry information then the information which is required is that what all elements which are percent and what is the stochiometry. Then the third information the fifth information which we require is what is the molecular formula or essentially how many atoms are going to be in the unit cell.

Then the next which comes is that if that information is available; what are the positions which the atom should occupy in the crystal that is provided by the position of atom which is there in the Wyckoff table. These are all the information, if these information's are available we can construct a crystal structure, but we look into that table of international cryptography for the 230 space groups, these information almost all these information are provided there, but what is not provided is stoichiometry of the alive and the molecular formula.

The rest of the information like the crystal system if it is primitive or not what is the type of because each of the, each one are a specific type of a symmetry element which we consider that crystal having a particular space group if we consider that table that table gives all the information what is the crystal system, whether it is primitive or not then what is the position of atoms in the unit cell, what all positions it can add terms occupy. Looking at it we can get some information about what sort of molecular formulas that crystals can have, what sort of stoichiometry it can have that is what we discussed in the last class.

But another, information which is required is that then we talk of most of the materials especially when we talk with respect to metallic systems. Many a time two different elements can be present, but the material itself could be we called as a disordered material by disordered what I mean it is not a positional disordering it is chemical disordering that is, if two elements are there a and b, and a element can occupy has got some concentration say some 60 percentage and b element is 40 percentage are they occupying in each specific position in the lattice are not.

If that is not the case that we say chemically disordered a and b randomly occupy essentially the same position in the lattice. Suppose it occupies the best which can (Refer

Time: 04:42) one a position can be occupied because of that is essentially the corners whether an a atom or a b atom can occupy, the probability of occupation is divided by I given by what the concentration which we have chosen.

Suppose it is an order element, if it is an ordered alloy then a atom will occupy a specific position and b atom will occupy under this position specific position. So, in order compound each element will occupy a specific type of a position in the lattice.

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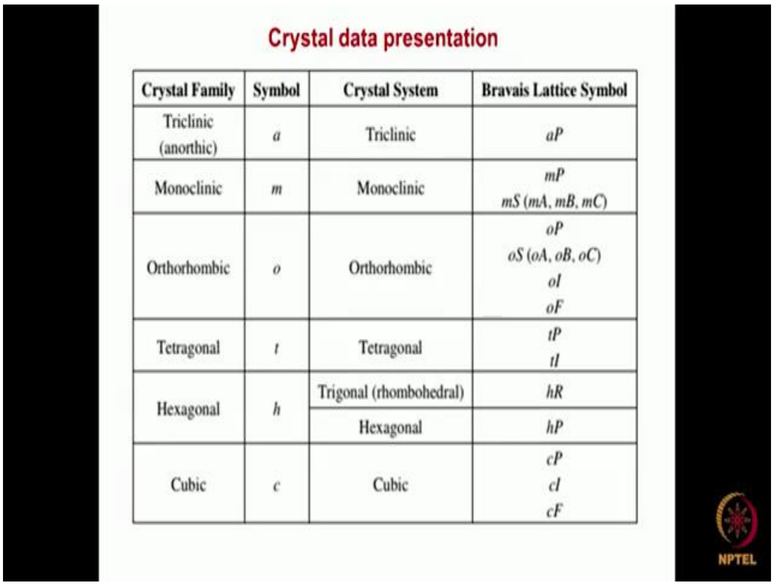

Crystal data presentation

Crystal Family	Symbol	Crystal System	Bravais Lattice Symbol
Triclinic (anorthic)	*a*	Triclinic	*aP*
Monoclinic	*m*	Monoclinic	*mP* *mS* (*mA*, *mB*, *mC*)
Orthorhombic	*o*	Orthorhombic	*oP* *oS* (*oA*, *oB*, *oC*) *oI* *oF*
Tetragonal	*t*	Tetragonal	*tP* *tI*
Hexagonal	*h*	Trigonal (rhombohedral)	*hR*
		Hexagonal	*hP*
Cubic	*c*	Cubic	*cP* *cI* *cF*

Another, information which we should have is that how are this crystal structure data because if you look at it, many of the crystal structure have been determined already data is available. If we have to construct a crystal we can go to that crystal structure information data book and try to understand how they are represented. We also follow some convention, so if you look at that how exactly is being done for a triclinic crystal the symbol which they use it is a, monoclinic m, orthorhombic o. It is not what the space group symbols which are used then tetragonal t, hexagonal h and cubic c, and then in addition to it if the crystal is primitive it will be written as sub triclinic aP and if you take for example, orthorhombic structure which is body centered it will be written as oI this sort of information could be used to represent essentially the Bravais lattice.

And with the same Bravais lattice we can have crystal with n number of atoms within the unit cell how is that represented that is essentially given. Now form that after this symbol the number n is given, the n represents how many number of what is the total number of atoms which is going to be present in the unit cell.

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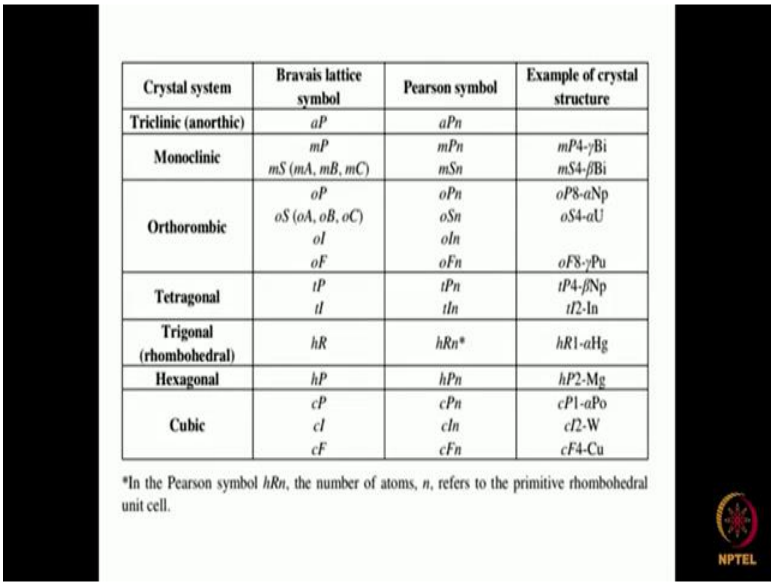

Crystal system	Bravais lattice symbol	Pearson symbol	Example of crystal structure
Triclinic (anorthic)	*aP*	*aPn*	
Monoclinic	*mP* *mS* (*mA*, *mB*, *mC*)	*mPn* *mSn*	*mP*4-γBi *mS*4-βBi
Orthorombic	*oP* *oS* (*oA*, *oB*, *oC*) *oI* *oF*	*oPn* *oSn* *oIn* *oFn*	*oP*8-αNp *oS*4-αU *oF*8-γPu
Tetragonal	*tP* *tI*	*tPn* *tIn*	*tP*4-βNp *tI*2-In
Trigonal (rhombohedral)	*hR*	*hRn**	*hR*1-αHg
Hexagonal	*hP*	*hPn*	*hP*2-Mg
Cubic	*cP* *cI* *cF*	*cPn* *cIn* *cFn*	*cP*1-αPo *cI*2-W *cF*4-Cu

*In the Pearson symbol *hRn*, the number of atoms, *n*, refers to the primitive rhombohedral unit cell.

This is what we call it as a, these symbols are called as a Pearson symbol because these Pearson's data handbook is available where all the crystals where experiments have been carried out and crystal structure information has been generated from x-ray or neutron diffraction they are tabulated and what are position is different type of atoms or molecules will occupy all the information available. The different take of crystal data are available, in all of them they follow this sort of a convention for example, suppose we take a cubic system - in a cubic system suppose for copper or for aluminum it has to be uniquely represented then the symbol which will be used for since it is FCC, c will be used to represent.

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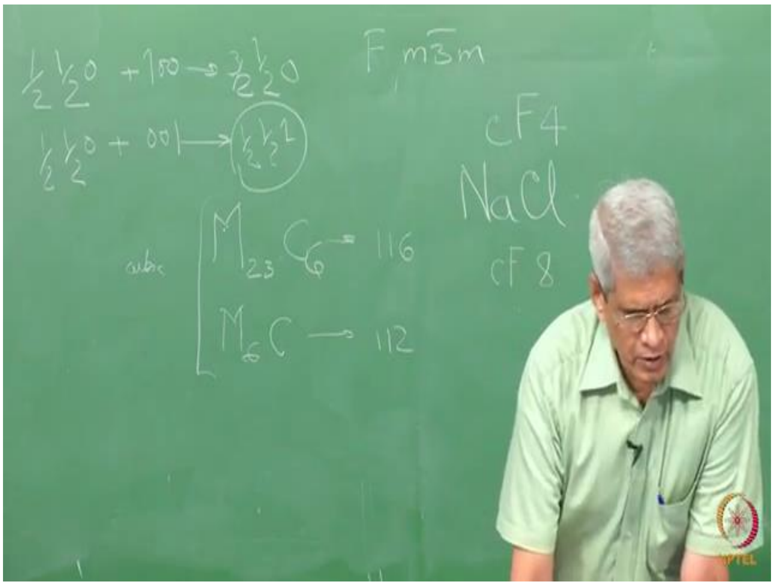

C F is for the phase center and 4 will be used; that means, that this is, it contains 4 atoms per unit cell. Another crystal with the same crystal structure a compound which forms is sodium chlorate, in sodium chlorate here essentially we have 8 atoms are going to be there - 4 atoms of sodium and 4 atoms of chorine. So, this will be c F 8 this is how it will be represented. So, looking at this symbol notation tells about how many. So, this helps us immediately to decide what all position Wyckoff positions the atoms can occupy in the unit cell to understand that.

Another important one which we should see it is that in the literature if we look there are so many ways in which this crystal structures are represented - one is called as a structure bearish, in the symbol notation which lot of metallurgist follow where if you see that FCC structure is generally represented that a 1 the symbol which is used. Then a 2 represents cubic, a 3 represents h c p, these sort of symbols are there this is one that is in the literature you will see all these.

Then if chemistry people use see they will use the Schoenflies symbol which will be used to represent the different crystal structure then another also if that just writing FCC, b c c, simple cubic that is one notation which is being followed and another is that space group from the international union of cryptography whatever is the symbol which has been that (Refer Time: 10:22), McGuinn crystal system that is used. These are all various ways in which it is being represented.

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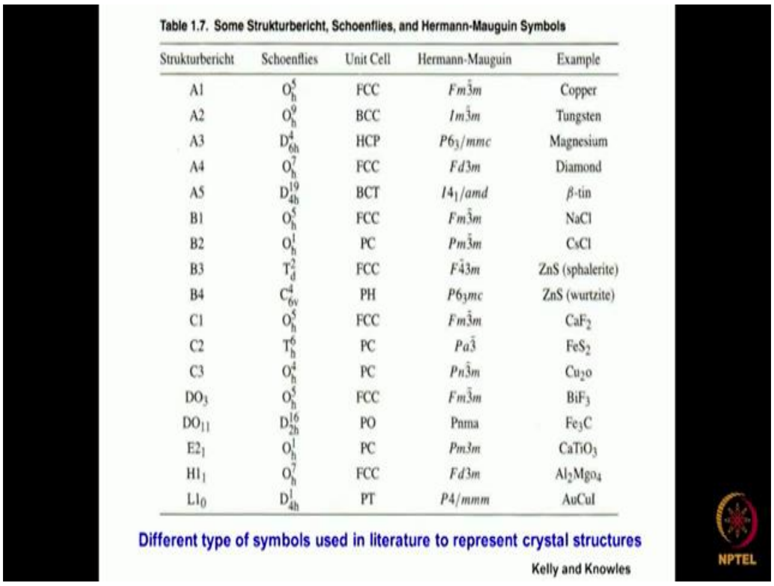

Table 1.7. Some Strukturbericht, Schoenflies, and Hermann-Mauguin Symbols

Strukturbericht	Schoenflies	Unit Cell	Hermann-Mauguin	Example
A1	O_h^5	FCC	$Fm\bar{3}m$	Copper
A2	O_h^9	BCC	$Im\bar{3}m$	Tungsten
A3	D_{6h}^4	HCP	$P6_3/mmc$	Magnesium
A4	O_h^7	FCC	$Fd3m$	Diamond
A5	D_{4h}^{19}	BCT	$I4_1/amd$	β-tin
B1	O_h^5	FCC	$Fm\bar{3}m$	NaCl
B2	O_h^1	PC	$Pm\bar{3}m$	CsCl
B3	T_d^2	FCC	$F\bar{4}3m$	ZnS (sphalerite)
B4	C_{6v}^4	PH	$P6_3mc$	ZnS (wurtzite)
C1	O_h^5	FCC	$Fm\bar{3}m$	CaF_2
C2	T_h^6	PC	$Pa\bar{3}$	FeS_2
C3	O_h^4	PC	$Pn\bar{3}m$	Cu_2o
DO_3	O_h^5	FCC	$Fm\bar{3}m$	BiF_3
DO_{11}	D_{2h}^{16}	PO	Pnma	Fe_3C
$E2_1$	O_h^1	PC	$Pm3m$	$CaTiO_3$
$H1_1$	O_h^7	FCC	$Fd3m$	Al_2Mgo_4
$L1_0$	D_{4h}^1	PT	$P4/mmm$	AuCuI

Different type of symbols used in literature to represent crystal structures

Kelly and Knowles

Nowadays as a convention is being said that it is better to follow the symbols which are used in space group, international union of space group table, but still in people who work on a solid state chemistry and molecular chemistry they prefer to use the Schoenflies symbols because they represent this crystal structure as far as they are concerned the type of symmetry which they look for it becomes quite obvious.

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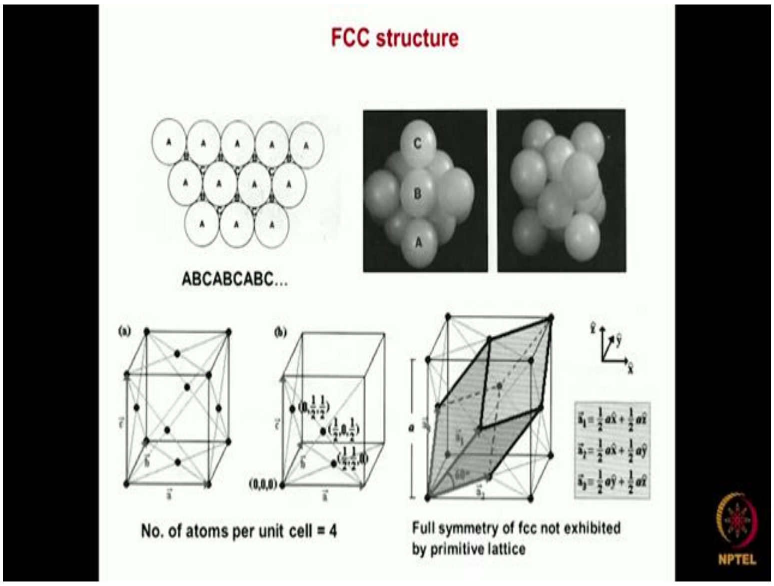

FCC structure

ABCABCABC...

$\vec{a}_1 = \frac{1}{2}a\hat{x} + \frac{1}{2}a\hat{z}$

$\vec{a}_2 = \frac{1}{2}a\hat{x} + \frac{1}{2}a\hat{y}$

$\vec{a}_3 = \frac{1}{2}a\hat{y} + \frac{1}{2}a\hat{z}$

No. of atoms per unit cell = 4

Full symmetry of fcc not exhibited by primitive lattice

Now let us look at some of the simple structures like FCC crystal if you consider it. In a pure element there could be copper, nickel or aluminum. We have seen that striking of different types of hexagonal layer one on top of the other we can generate the crystal structure that is what is being shown which is an A B C A B C type of a striking sequence. Then adjacent eta had shown on the hard sphere model if we take ball and try to keep them to generate different type of layers how this structure will look like. The same structure it is an keeping on the one one one there is a hexagonal layers one on top of each other that is what it is been shown one.

The other picture especially this one shows essentially the same structure, but the waving direction is different because the weaving direction is along either 1 0 0 direction we are you trying to do it, so that we can see that cubic symmetry associated with its structure. In this, this is the direction which we are trying to do it which is essentially nothing but 111 directions.

So, generally when we draw the crystal structure in three dimension this is the way we represent that crystal structure, this itself there are many types of projections are there which are being used this is one particular type of a projection in which we try to represent the cubic lattice and then these are all the three equivalent position, these equivalent positions how do we show them. For this equivalent position that is around each of the atom position we can mark what is the coordinates which are (Refer Time: 13:13) coordinates corresponding to them. Since it is a non primitive lattice we can consider primitive lattice also for this structure.

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If we construct the punitive lattice it is constructed by taking the all the atoms on the face interaction the nearest neighbors with respect to coordinate. Then we can and the unit cell which we can construct is going to be having a trigonal structure. In this particular one this a 1, a 2, a 3 that is in terms of the simple fcc lattice parameters if you take them as the unit vectors, how to represent the vectors a 1 and a 2 corresponding to the various coordinates of the primitive lattice what is being shown.

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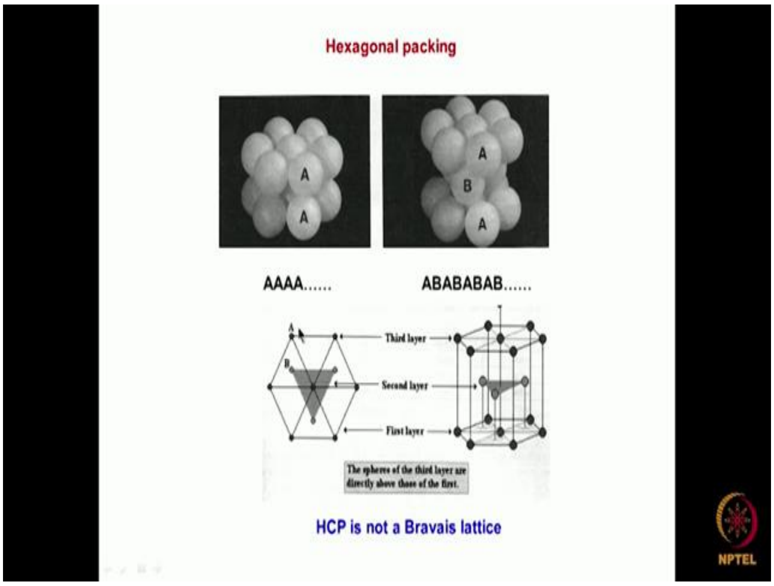
Hexagonal packing

AAAA……

ABABABAB……

The spheres of the third layer are directly above those of the first.

HCP is not a Bravais lattice

Similarly, we can have a hexagonal close packing also if they saying FCC structure. In this if we wanted to construct a Bravais lattice there is only one possibility that one plane is kept and other is the hexagonal lattice one hexagonal lattices if we are contracted with the (Refer Time: 14:30) model. The next one has to be kept only on top of them only a simple example and generally many crystals going to the crystal structure which we called hexagonal close packed structure.

A hexagonal close packed structure one should understand that it is not a Bravais lattice and as I mentioned in earlier classes there are many ways of projection, one way in which we can project it is the hexagonal lattice can be projected. Then we can project, the next layer can be projected on top of it and we can mention what positions these occupy then that. The third layer which will come will be coming on top of it which is an layer this way also the crystals can be represented. The other crystal structure to it most of the elements they form is body centered cubic structure.

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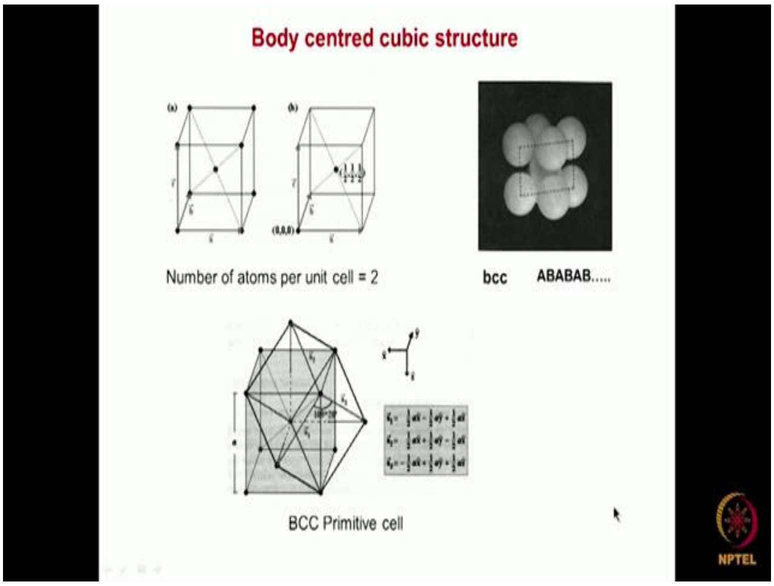
Body centred cubic structure

Number of atoms per unit cell = 2

bcc ABABAB.....

BCC Primitive cell

Similar way in which is being represented here if you look at this particular structure with a hard sphere model, it is essentially square lattice which we generated which is being kept on top of each other to generate a body centered (Refer Time: 15:53). So, if we keep one square lattice on top of the other hard sphere model create a simple cubic lattice, but if we keep one layer and the next layer on top of it which is at the middle third layer on top of the first layer if you try to keep there it will generously create a body centered tetragonal structure. But in that each of the square layer if atoms are shifted they are not touching each other the balls they are moved a little bit then for a particular distance we can have it as a body centered tetragonal cubic lattice.

Here again since it is a primitive lattice we can construct primitive, since it is a non primitive lattice we can construct a primitive lattice choosing the specific vector, these vectors which are chosen of from the center find out which are the nearest atom version because we have to choose to construct a primitive lattice we choose the shortest translation vectors. So, the shortest translation vector in the case of a b c c is essentially along the body diagonal, atom which is at the center correct then you find out with respect to a origin another three non coplanar position with which the primitive lattice could be constructed. This is also essentially a rhombohedra or a trigonal structure, but we do not use these structures to represent the simple cubic because the full symmetry cannot be seen for this particular structure.

Now, let us look at this FCC crystals where with for example, for a pure element like a (Refer Time: 17:51) to be (Refer Time: 17:52) we have already constructed the lattice. Once the lattice has been constructed what do we wanted to do is that we wanted to find out if the second element we are trying to put it what position which it can go into the lattice. One way to look at it is that you construct the unit cell, three dimensional unit cell find out what are the positions where this atom enter into it, the second element. So, there are only spaces which are vacant in the unit cell where it can go. So, those positions are shown by this open circle these are called as octahedral sites.

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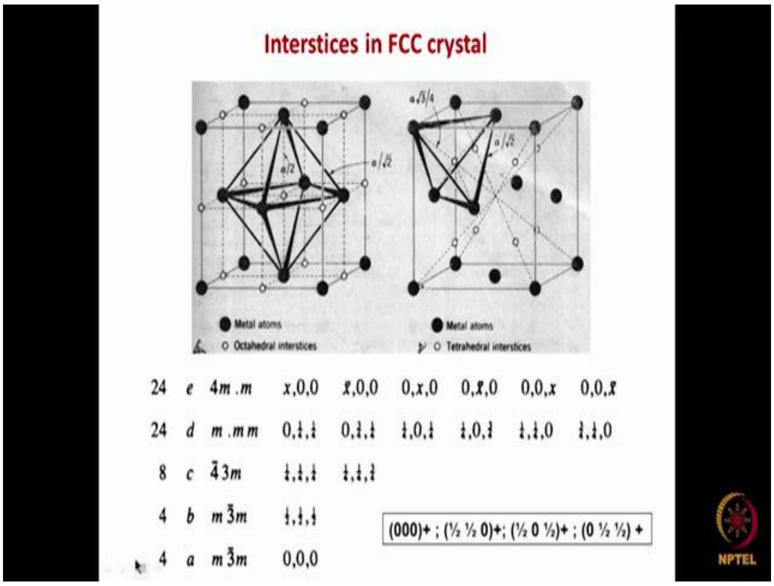

Interstices in FCC crystal

24	*e*	4*m*.*m*	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
24	*d*	*m*.*mm*	$0,\frac{1}{4},\frac{1}{4}$	$0,\frac{3}{4},\frac{1}{4}$	$\frac{1}{4},0,\frac{1}{4}$	$\frac{1}{4},0,\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{1}{4},0$
8	*c*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$				
4	*b*	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
4	*a*	$m\bar{3}m$	$0,0,0$					

(000)+ ; (½ ½ 0)+; (½ 0 ½)+ ; (0 ½ ½) +

The number of positions which are available if we inspect this figure we can find out that one at the center then at the corner or the edges we get it cannot on, not on the faces. So, then we can find out a position which is at the edge how many unit cells are going to share it under bases we can get this information correct this we can calculate it. But this is essentially a cumbersome process, but inserts the same information we can get it if you look at the Wyckoff position table which is given there, here only the relevant Wyckoff position table which I had given. Here if we look at it in this table the a corresponds to the one having the maximum symmetric m 3 bar m.

And the number 4 which is giving me the equivalent position how to find out the equivalent positions. What we have to do it that one more information which is been providers is that far the Bravais lattice, what all position equivalent position which are available that information is given. So, if we add with respect to this 0 0 coordinate of one atom position we can generate the other positions which the atoms will occupy correct.

That is what essentially has to be done to generate this, this will tell the positions which atom can occupy, but the unit cell if we consider like in this particular case essentially we are going to have edge at the corner then we request another 6 at the center correct, so 14 positions are necessary to construct the unit cell. But these tables' gives only a four positions correct to essentially. How that can be generated is that. Now we apply a translational symmetry to each of the point elements that will generate if we apply translational symmetry to this 0 0 position 8 positions will be generated that will take care of a corner.

Similarly if we applied then find out some of the positions will be outside of the unit cell for example, suppose we take half half 0, 100 if we apply, this will be 3 by 2 half 0, this position is going to be outside of the unit cell. If you take this translation vector of the unit cell if you apply it becomes half of 1 this position will be.

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Now, going to be on the unit cell; this way we generate the table for each of the position try to find out how many atom positions will be there that is applying translation symmetry because for to generate the, to construct the unit cell we require all the atom position. For that we have to the symmetry positions which are given the translational symmetry also as we added to it then we can find out which all positions are going to be there on the lattice or within the lattice only thus it has to be used to construct the crystal.

Like that if we try to do it we can find out the atom position. Now if you look here that this positions the c position if we consider it, it has got a 4 bar 3 m symmetry, the site symmetry and the position that the atoms it can occupy or given here and the other one if you consider this one particularly here is has got 4 positions are there the position which atoms can occupy or where the interstitials can be there because these are all the opposition which has been failed because it is a nickel, the element nickel we are trying to look at that crystal structure. Once these positions are failed the vacant position is going to be next one is going to be this particular one, this is what the octahedral intuition. Looking at this table itself we get the information this is going to be 4.

Now, tetrahedral sites if you try to look at it; the tetrahedral interstices will be mean by tetrahedral the types of symmetry which it will have a threefold and a mirror symmetry is what it will be associated with it correct. The tetrahedral sites are essentially going to be 8 correct, 8 are going to be there these sites. Essentially if you look at the next sites the c position Wyckoff position c, the atomic position which are possible are it is given only corresponding to one particular the tetrahedral sites are given by the Wyckoff position c that can give one tetrahedral position which is shown here in this unit cell which you can see it.

The number of tetrahedral positions which are there are 8 and the site symmetry each of the tetrahedral is 4 bar 3 m which is essentially a cubic symmetry and the positions of the tetrahedral are shown here. Two positions are shown with respect to 0 0 position if we multiply these to these terms then we will be able to obtain positions of all the 8 tetrahedral positions.

So, just looking at this table itself we get information that if an atom has occupied this position what are the other interstitial positions where the next atom would be kept or which are the positions which are vacant positions which are available for the next atom to be placed. This convention when we use octahedral or tetrahedral, these words essentially in our mind we talk with respect to symmetry which is associated with it also correct.

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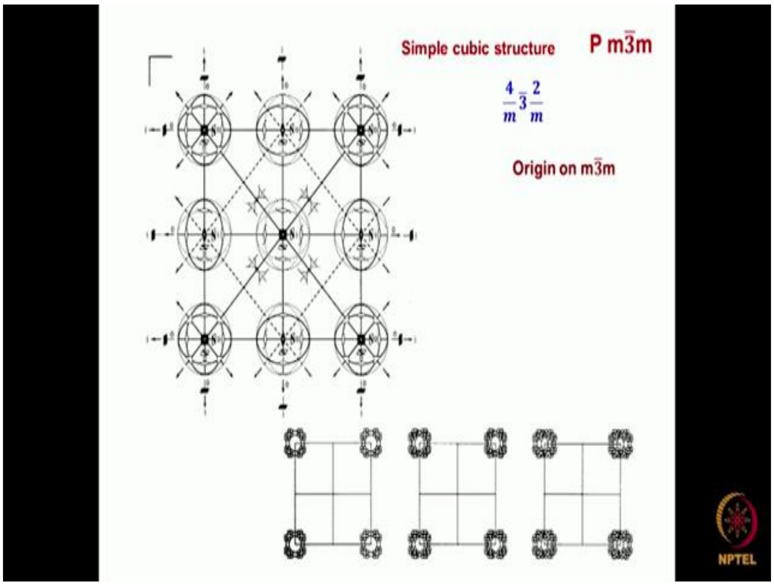

Simple cubic structure

$P\,m\bar{3}m$

$\frac{4}{m}\bar{3}\frac{2}{m}$

Origin on $m\bar{3}m$

What I have done it is that here I have just so far when I have taken an example I have taken with respect to the crystal which has got lower symmetry, when a crystal has which has got a higher symmetry if you try to look at the base group symmetry table or the graphical representation of the symmetry elements associated with it, it is very complicated structure and it is difficult to understand.

Just I had shown how complicated it is, it is just for a primitive lattice cubic with m 3 bar m symmetry the maximum symmetry element, you can make off that various symmetry elements which are being represented it will take a very long time to make one to understand that and there only each lattice point if we try to look at it there are going to be about something like 48 happens, 48 equivalent positions that is if we put an atom around the lattice point or a motif around the lattice point equivalent 48 positions where the motif of the atom has to be play, so that this symmetry of this simple cubic lattice can be satisfied.

But in pure elements that is where a generally only polonium I think from simple cubic structure where the atom will be occupying the maximum symmetry element. So, we will be referring only a number of atoms per unit cell is going to be only one. So, are if you have to construct a unit cell we require only 8 positions.

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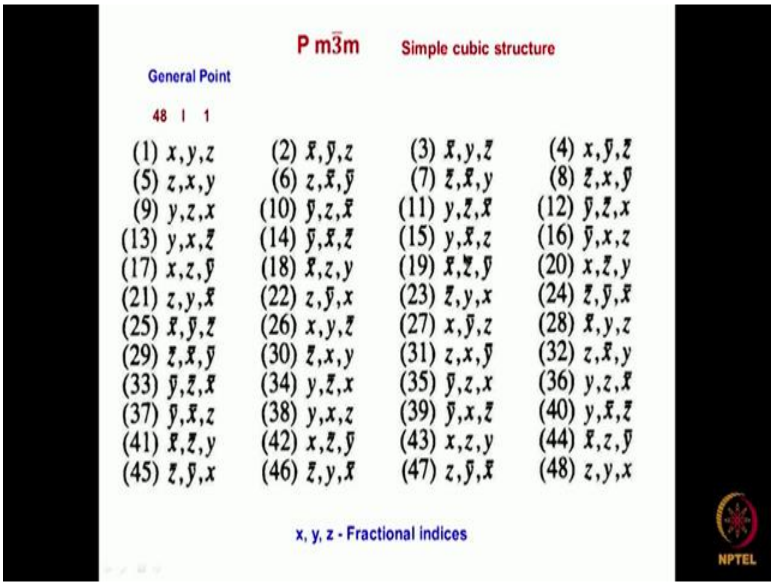

$P\,m\bar{3}m$ Simple cubic structure

General Point

48 l 1

(1) x,y,z (2) $\bar{x},\bar{y},z$ (3) $\bar{x},y,\bar{z}$ (4) $x,\bar{y},\bar{z}$
(5) z,x,y (6) $z,\bar{x},\bar{y}$ (7) $\bar{z},\bar{x},y$ (8) $\bar{z},x,\bar{y}$
(9) y,z,x (10) $\bar{y},z,\bar{x}$ (11) $y,\bar{z},\bar{x}$ (12) $\bar{y},\bar{z},x$
(13) $y,x,\bar{z}$ (14) $\bar{y},\bar{x},\bar{z}$ (15) $y,\bar{x},z$ (16) $\bar{y},x,z$
(17) $x,z,\bar{y}$ (18) $\bar{x},z,y$ (19) $\bar{x},\bar{z},\bar{y}$ (20) $x,\bar{z},y$
(21) $z,y,\bar{x}$ (22) $z,\bar{y},x$ (23) $\bar{z},y,x$ (24) $\bar{z},\bar{y},\bar{x}$
(25) $\bar{x},\bar{y},\bar{z}$ (26) $x,y,\bar{z}$ (27) $x,\bar{y},z$ (28) $\bar{x},y,z$
(29) $\bar{z},\bar{x},\bar{y}$ (30) $\bar{z},x,y$ (31) $z,x,\bar{y}$ (32) $z,\bar{x},y$
(33) $\bar{y},\bar{z},\bar{x}$ (34) $y,\bar{z},x$ (35) $\bar{y},z,x$ (36) $y,z,\bar{x}$
(37) $\bar{y},\bar{x},z$ (38) y,x,z (39) $\bar{y},x,\bar{z}$ (40) $y,\bar{x},\bar{z}$
(41) $\bar{x},\bar{z},y$ (42) $x,\bar{z},\bar{y}$ (43) x,z,y (44) $\bar{x},z,\bar{y}$
(45) $\bar{z},\bar{y},x$ (46) $\bar{z},y,\bar{x}$ (47) $z,\bar{y},\bar{x}$ (48) z,y,x

x, y, z - Fractional indices

That is what turns out to be much simpler, but if the same atom we are seeing that it is been placed at a position which is at a random position (Refer Time: 27:28) no symmetry then it is structure looks very complicated and if you look at the Wyckoff tables this give that information about all the equivalent position x y is that corresponds to a particular position where we put one motif then what all the equivalent position the motif when we kept.

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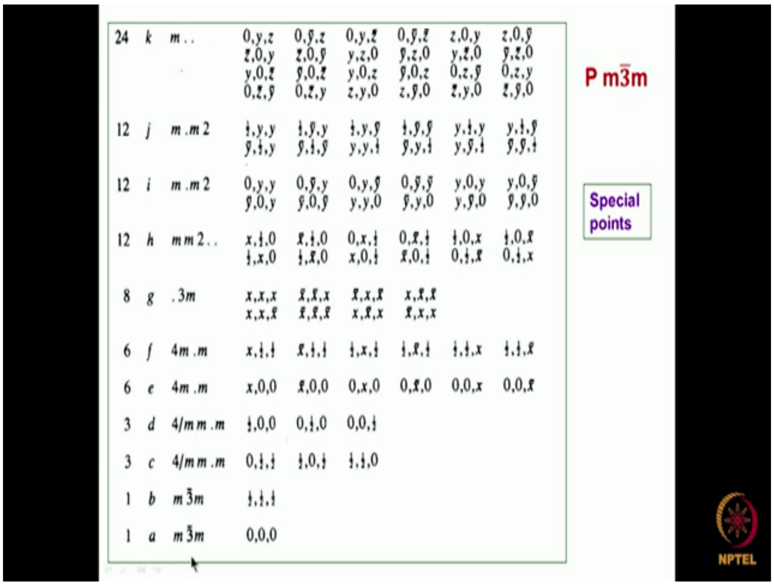

$Pm\bar{3}m$

Special points

24	k	$m..$	$0,y,z$ $\bar{z},0,y$ $y,0,\bar{z}$ $0,\bar{z},\bar{y}$	$0,\bar{y},z$ $\bar{z},0,\bar{y}$ $\bar{y},0,\bar{z}$ $0,\bar{z},y$	$0,y,\bar{z}$ $y,z,0$ $y,0,z$ $z,y,0$	$0,\bar{y},\bar{z}$ $\bar{y},z,0$ $\bar{y},0,z$ $z,\bar{y},0$	$z,0,y$ $y,\bar{z},0$ $0,z,\bar{y}$ $\bar{z},y,0$	$z,0,\bar{y}$ $\bar{y},\bar{z},0$ $0,z,y$ $\bar{z},\bar{y},0$
12	j	$m.m2$	$\tfrac{1}{2},y,y$ $\bar{y},\tfrac{1}{2},y$	$\tfrac{1}{2},\bar{y},y$ $\bar{y},\tfrac{1}{2},\bar{y}$	$\tfrac{1}{2},y,\bar{y}$ $y,y,\tfrac{1}{2}$	$\tfrac{1}{2},\bar{y},\bar{y}$ $\bar{y},y,\tfrac{1}{2}$	$y,\tfrac{1}{2},y$ $y,\bar{y},\tfrac{1}{2}$	$y,\tfrac{1}{2},\bar{y}$ $\bar{y},\bar{y},\tfrac{1}{2}$
12	i	$m.m2$	$0,y,y$ $\bar{y},0,y$	$0,\bar{y},y$ $\bar{y},0,\bar{y}$	$0,y,\bar{y}$ $y,y,0$	$0,\bar{y},\bar{y}$ $\bar{y},y,0$	$y,0,y$ $y,\bar{y},0$	$y,0,\bar{y}$ $\bar{y},\bar{y},0$
12	h	$mm2..$	$x,\tfrac{1}{2},0$ $\tfrac{1}{2},x,0$	$\bar{x},\tfrac{1}{2},0$ $\tfrac{1}{2},\bar{x},0$	$0,x,\tfrac{1}{2}$ $x,0,\tfrac{1}{2}$	$0,\bar{x},\tfrac{1}{2}$ $\bar{x},0,\tfrac{1}{2}$	$\tfrac{1}{2},0,x$ $0,\tfrac{1}{2},\bar{x}$	$\tfrac{1}{2},0,\bar{x}$ $0,\tfrac{1}{2},x$
8	g	$.3m$	x,x,x $x,x,\bar{x}$	$\bar{x},\bar{x},x$ $\bar{x},\bar{x},\bar{x}$	$\bar{x},x,\bar{x}$ $x,\bar{x},x$	$x,\bar{x},\bar{x}$ $\bar{x},x,x$		
6	f	$4m.m$	$x,\tfrac{1}{2},\tfrac{1}{2}$	$\bar{x},\tfrac{1}{2},\tfrac{1}{2}$	$\tfrac{1}{2},x,\tfrac{1}{2}$	$\tfrac{1}{2},\bar{x},\tfrac{1}{2}$	$\tfrac{1}{2},\tfrac{1}{2},x$	$\tfrac{1}{2},\tfrac{1}{2},\bar{x}$
6	e	$4m.m$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
3	d	$4/mm.m$	$\tfrac{1}{2},0,0$	$0,\tfrac{1}{2},0$	$0,0,\tfrac{1}{2}$			
3	c	$4/mm.m$	$0,\tfrac{1}{2},\tfrac{1}{2}$	$\tfrac{1}{2},0,\tfrac{1}{2}$	$\tfrac{1}{2},\tfrac{1}{2},0$			
1	b	$m\bar{3}m$	$\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}$					
1	a	$m\bar{3}m$	$0,0,0$					

This part of it gives the special points which have got some symmetry associated with it what are the special partitions, how many atoms are, how many positions are associated with it, equivalent position associated with it in the unit cell that is the information which is given.

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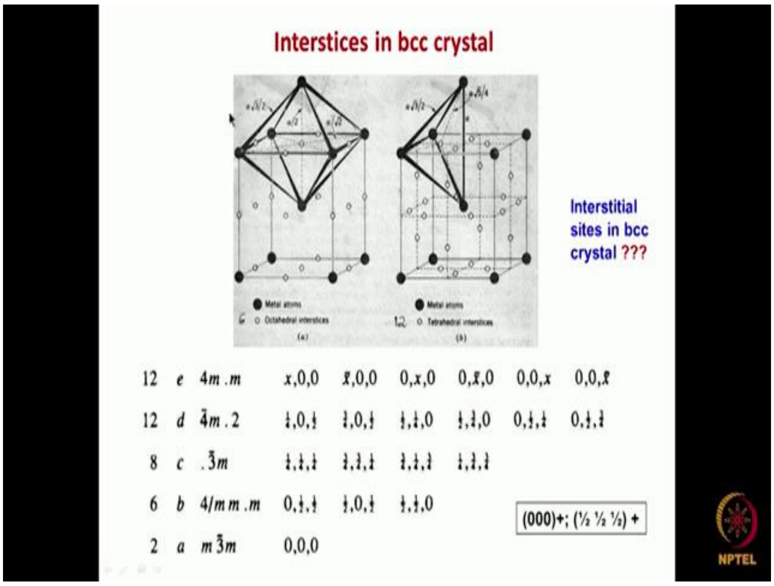


Interstices in bcc crystal

Interstitial sites in bcc crystal ???

12	*e*	4*m*.*m*	*x*,0,0	$\bar{x}$,0,0	0,*x*,0	0,$\bar{x}$,0	0,0,*x*	0,0,$\bar{x}$
12	*d*	$\bar{4}$*m*.2	$\frac{1}{4}$,0,$\frac{1}{2}$	$\frac{3}{4}$,0,$\frac{1}{2}$	$\frac{1}{2}$,$\frac{1}{4}$,0	$\frac{1}{2}$,$\frac{3}{4}$,0	0,$\frac{1}{2}$,$\frac{1}{4}$	0,$\frac{1}{2}$,$\frac{3}{4}$
8	*c*	.$\bar{3}$*m*	$\frac{1}{4}$,$\frac{1}{4}$,$\frac{1}{4}$	$\frac{3}{4}$,$\frac{3}{4}$,$\frac{1}{4}$	$\frac{3}{4}$,$\frac{1}{4}$,$\frac{3}{4}$	$\frac{1}{4}$,$\frac{3}{4}$,$\frac{3}{4}$		
6	*b*	4/*m m*.*m*	0,$\frac{1}{2}$,$\frac{1}{2}$	$\frac{1}{2}$,0,$\frac{1}{2}$	$\frac{1}{2}$,$\frac{1}{2}$,0			
2	*a*	*m*$\bar{3}$*m*	0,0,0					

(000)+; (½ ½ ½) +

Now, if you look at bcc crystal look at the same way we can look at it the what all positions which are available. That in either we draw the crystal structure and then try to find out what all positions which atoms are occupying and which is the position which is a vacant position we can identify, octahedral or tetrahedral positions which we can identify. Because for a pure metal if we consider it when the metal occupies all the lattice points the interstitial positions the next atom can occupy is the one which is as got the maximum wide size correct and then the energetic also will decide.

I had shown here again the relevant part of the table from the Wyckoff table which is given in the international union of cryptography. Here again if we look at it the number of equivalent points we just got m 3 bar m symmetry is only 2 that is one of the corner and one at the center of it correct that by when we add this origin to the equivalent position of lattice point then we get that information.

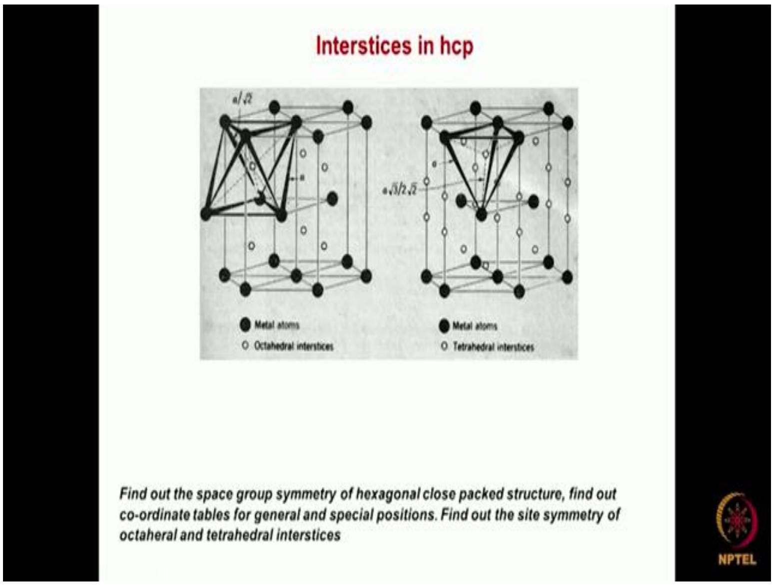
And then the next one if we consider it these are all the face centers at the face center's if you look at these are all the position where an atom can occupy the next atom or this is the position which we call it as an octahedral y. For a bcc structure if we look at this y the nearest neighbors where are they placed? 4 are placed on the face and these are at a by rho 2 distance when a is a lattice parameter, and 2 work place perpendicular to this plane what are the distance of a by 2. So, since they are not at equal distance is itself immediately you can make this has got a symmetry which is tetragonal type of structure.

That is why you look at the site symmetry which is being given here, the site symmetry is 4 by m m m, that 4 by m m m corresponds to essentially a octagonal structure.

And how many equivalent positions are going to be there? 6. So, essentially we will have 6 octahedral whites and then if you look at those tetrahedral whites also this corresponds to the Wyckoff position d. This Wyckoff position b also here you have 4 bar 2 this is again a tetrahedral one, that is why if you look at the with respect to the central position where the nearest neighbors are there going to be at the center because unequal distance that is from the center position 4 of them are going to be at an distance of a by root 2 and another two are going to be at a distance of a by 2 this you can make out, not a by 2 this one can calculate it right.

That is this atom from this, this position, this position, this one, this one is going to be at a different distance correct. So, this is not a regular tetrahedral contract. So, in a FCC if we consider in a regular tetrahedral from the center at a equal distance all other neighboring atoms are situated.

(Refer Slide Time: 32:11)



Interstices in hcp

Find out the space group symmetry of hexagonal close packed structure, find out co-ordinate tables for general and special positions. Find out the site symmetry of octaheral and tetrahedral interstices

Similar type of, in a similar way we can find out interstitial positions in hexagonal lattice as well this I will not going to the detail, but I am just giving the figure and what I would like you people to do is just looking to the international of cryptographic table, find out the space group symmetric correspond, identify the positions of tetrahedral and octahedral whites.

When this sort whites are there especially in many of the structures where different type of elements we added we said that by filling up these white we can generate different types of compounds correct, if a and b elements are there two elements are there, especially in ionic or covalent bonded compounds normally what happens is that in this interstitial whites are filled up because whenever they form for example, ionic compound sodium chloride responds when sodium takes one electron and it forms, no when sodium gives one electron and the chlorine accepts one electron the size of the chlorine ion becomes very large and that of the sodium (Refer Time: 33:39) and it becomes very smart. So, both have got that cation has got a smaller size and the anion has got a larger size. So, essentially the cations having smaller sizes can go into these voids they generate the crystal.

So, what we are considering it now is how the structures can be constructed based on filling up of these interstitials.

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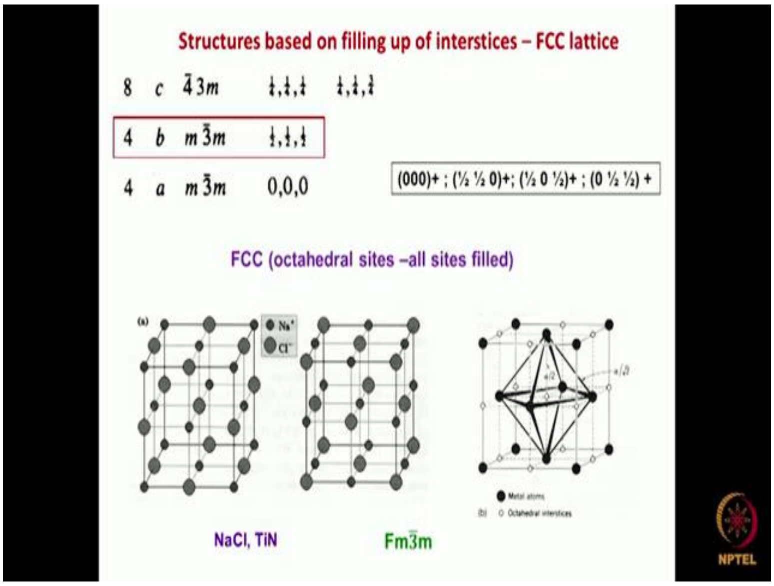

Structures based on filling up of interstices – FCC lattice

8	*c*	$\bar{4}3m$	¼,¼,¼	¼,¼,¾
4	*b*	$m\bar{3}m$	½,½,½	
4	*a*	$m\bar{3}m$	0,0,0	

(000)+ ; (½ ½ 0)+; (½ 0 ½)+ ; (0 ½ ½) +

FCC (octahedral sites –all sites filled)

NaCl, TiN

Fm$\bar{3}$m

Let us just take an example with respect to FCC. That as I mentioned earlier this position the 4 a position which corresponds to the corners and the phase centers are being occupied by 1 a type of an atom then the possibility for the b type of an atom which can come is the next one is this tetrahedral position. Suppose we assume that in this particular case like we take an example of sodium chloride, the sodium chloride has got the space group symmetry which is f m 3 bar m.

That means, that in this one the sodium atom the lattice which is constructed with both the sodium as well as the chlorine both of them have to have an FCC structure so; that means, that the then the sodium atom assume that the sodium atom is first used to construct the lattice then it is occupying all the carbon atom positions. Then the chlorine atoms if we do it, it has to go into one at the middle and at all the corners all the edges and that is how to be constructing this lattice which also has got and now the composition which it can have is a be stoichiometry right.

The composition is a 50-50 composition. The same structure could be constructed either taking chlorine at the origin both ways, but both are equivalent or we can construct another way this can be filled is that one type of an atom a atom occupies this, the b atom can occupy this particular position.

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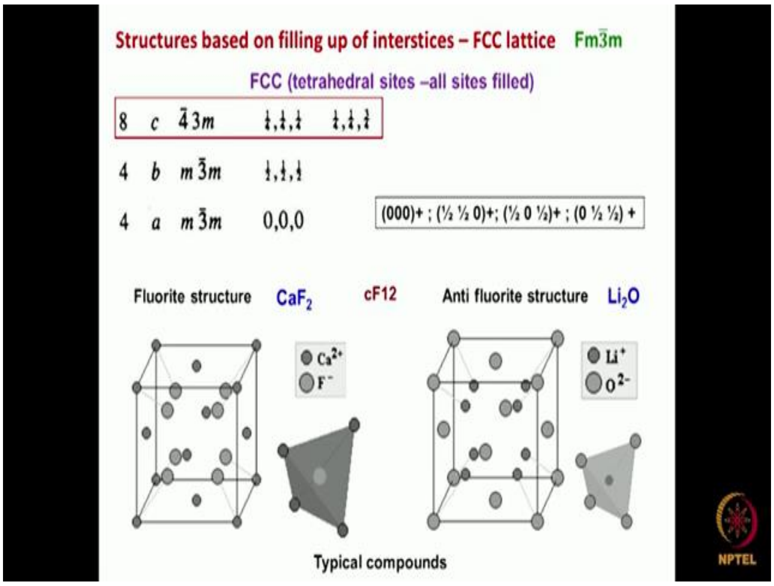

Structures based on filling up of interstices – FCC lattice $Fm\bar{3}m$

FCC (tetrahedral sites –all sites filled)

8 c $\bar{4}3m$ ¼,¼,¼ ¾,¾,¾

4 b $m\bar{3}m$ ½,½,½

4 a $m\bar{3}m$ 0,0,0

(000)+ ; (½ ½ 0)+; (½ 0 ½)+ ; (0 ½ ½) +

Fluorite structure CaF_2 cF12 Anti fluorite structure Li_2O

Typical compounds

Let us just look at this particular one case then what will be the stoichiometry which it will have a b 2, typical example is a fluorite structure calcium fluorite has got an a b two structure. Here all that calcium atom will occupy the corners of the cube which is essentially given by a Wyckoff position for a and the proof.

Student: It can also either (Refer Time: 37:02).

4 a or 4 b both the options are available, then the edges will be occupied by this one.

Student: (Refer Time: 37:22).

There is no sorry not the edges the corner atoms are occupying.

Students: (Refer Time: 37:29).

4 a position, 8 c positions are going to be occupied by the fluorine ions. So, this way; that means that this will be at the unit cell itself can be subdivided into 8 small cubes and the center, the body diagonal at the center of each of the unit cubes can be occupied by fluorine atoms correct.

And another way in which this sort of construction we can represent because if we look at the unit cells there are so many atom positions are going to be there it is going to be extremely difficult to visualize it, for which what it can be done is that one can have a cage like this where it is being shown that the center is chlorine because he is occupying at a tetrahedral site and that all the corners the corner of that tetrahedral the calcium iron is going to be there. Instead of showing these types for all the atom positions with these type of a tetrahedral also we can construct the crystal structure right. That I will come to later in some specific structures where when the number of atoms becomes very large.

Now, for example, or in metallurgy especially in steels and most of the nickel based super alloys the type of carbides which they form of two type of carbides which they form - one is called as m 23 c 6, that m represents metal and c the carbon. Another type of carbide which forms r m 6 c: in these both of them going to a crystal structure which is essentially a cubic one. Here if you look at the total number of the stoichiometry base there is 29 if you look at the space group table 29 cannot be there, the number of atoms which are going to be there in this unit cell is essentially going to be 116 in this particular case it is going to be 112 atoms will be there in the unit cell. If you have to draw a unit cell like that and then try to look at its going to be very complicated. So, for that purpose this octahedral and tetrahedral cages are shown where the nearest neighbor coordination will tell what sort of ion is going to be adjacent to it, with that sort of cages one can try to construct a unit cell.

Then similar to the CaF 2 another type of a structure which is that call as an anti fluorite structure. What is that anti fluorite structure are typical examples is Li 2 O, here the oxygen atoms are going to be 4 lithium atoms are going to be 8. So, in this particular case that oxygen atoms will occupy all the corners that is essentially the oxygen ions that cation is going to occupy the corners and the center of each of the small 8 cubes are going to be occupied by lithium ions because the structure if you look because the cation and anions in these two are here anion occupies the corner and here cation occupies a corner and this is a fluorite structure. So, this is called as an anti fluorite it is only a terminology which it used.

In this one if Pearson's symbol if you try to use it, it will be called as cF 12 this is how it will be seemed as the total number of atoms are going to be 8 plus 12, 12 atoms are going to be present in the unit cell. There are many typical compounds are there which we use see it on structure right table Pearson's data book or any other books on chemistry or a metallurgy you can get all this information.

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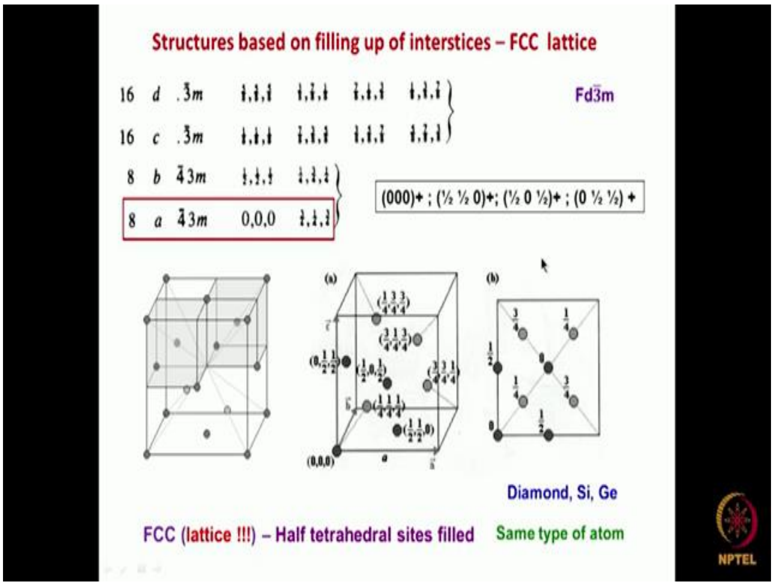

Structures based on filling up of interstices – FCC lattice

16	d	.$\bar{3}m$	[illegible]	[illegible]	[illegible]	[illegible]
16	c	.$\bar{3}m$	[illegible]	[illegible]	[illegible]	[illegible]
8	b	$\bar{4}3m$	[illegible]	[illegible]		
8	a	$\bar{4}3m$	0,0,0	[illegible]		

$Fd\bar{3}m$

(000)+ ; (½ ½ 0)+; (½ 0 ½)+ ; (0 ½ ½) +

Diamond, Si, Ge

FCC (lattice !!!) – Half tetrahedral sites filled

Same type of atom

Then in another structure which we because these are all on FCC lattice which we consider it, another one on an FCC lattice where we can have if that the structure which we know very well is diamond cubic. In diamond cubic we say that only there are 8 atoms per unit cell, generally we describe this crystal as telling that carbon atoms occupy all the face centers in addition to it some positions along the body diagonal are also being occupied, but when that atom occupies corner alone if we consider with respect to the a crystal structure if only those positions, if they have a Wyckoff position specific one then it cannot as that as I mentioned in the last class the same atom cannot occupy in another Wyckoff position because the same type of an atom has to occupy all the Wyckoff positions. That means, that the carbon should have carbon atom should have 8 Wyckoff position should be there in the unit cell.

If that is going to be there then this cannot have the same crystal structure as that of considering it as an FCC, though the Bravais lattices is FCC now if you look at the crystal structure that is why if you look at the Wyckoff positions which is being given for the carbon. Here you can immediately see that 8 atoms are going to be there with 4 bar 3 m symmetry and in fact, the symmetry of this one also if you look at this space group symmetry is not here it is f m 3 bar m for most of the structure that sodium chloride, calcium fluorite and all these structures and for diamond it is F d 3 bar m. What the d represents essentially is that there is a along the body diagonal there is a glide is also going to be there.

So, it is said (Refer Time: 44:17) a different crystal structure it is not the same as that of a sodium chloride or copper that one should keep it in mind. Other elements which form into these structures are silicon, germanium, tin, all of them; most of them exhibit the like silicon germanium and tin exhibits some semi kind of tin properties also correct and the type of bonding which all of them exhibit are covalent type of a bonding. In tin it is a beta tin and the unit cell is being shown here what are positions which can be occupied equivalent positions are represented.

As I mentioned there are two ways in which we can represent it either we show the full unit cell or the position which is very difficult to understand looking at it or it can be just shown the projection 001 projection and that 0 this corresponds to the position which the atoms occupy and then these positions half positions are where the atoms are going to be there on these two say. And then the other positions are 1 by 4 this shows that at what height they are being placed this way also we can represent the crystal structure.

There are many ways in which it been its a half tetrahedral sites are filled in FCC, but that is not the correct way to locate it that is FCC Bravais lattices he considered it, it is different, but essentially these have got a different type of a space group symmetry itself they are not the same as that of a copper structure that one should always keep it in mind.

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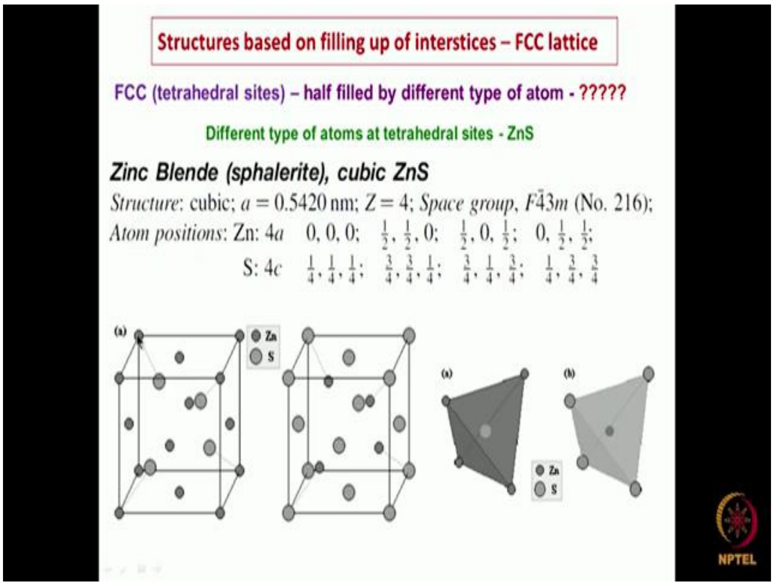

Structures based on filling up of interstices – FCC lattice

FCC (tetrahedral sites) – half filled by different type of atom - ?????

Different type of atoms at tetrahedral sites - ZnS

Zinc Blende (sphalerite), cubic ZnS

Structure: cubic; $a = 0.5420$ nm; $Z = 4$; *Space group*, $F\bar{4}3m$ (No. 216);

Atom positions: Zn: $4a$ $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$;

S: $4c$ $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$; $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$

Now, we consider one because so far what we consider the two structures are where in the FCC lattice it is essentially the octahedral sites are getting filled. Now let us look at our tetrahedral sites which are getting filled that are what we looked at it. This is another one where the lattice is FCC like zinc sulfate if we consider it what all positions which the atoms can occupy. Here also if you look at what is the space group it is a cubic structure, but it is 4 bar 3 m.

So, for all of them the lattice is FCC, but once atoms occupy specific position the symmetry has changed and the information about the crystal structure if you look at the Pearson’s data handbook they give all these information what are that structure is cubic, lattice parameters are given, e z equals 4, the how many molecular cells are going to be there in the structure, then the space group is given because there each type of atom is 4 are going then what are the atom positions they are also given here.

If this information is available we can consider the crystal structure. So, here again the way in which it is being represented is that with either sink or the sulfur at the corners we are trying to represent how the crystal structure is formed. In this particular case the sink atom occupies the corner in this particular case the sulfur atom occupies and as I mentioned earlier these tetrahedral sites we can just show them as a cage where they are the sink, the sulfur is at the center and sink are occupying carbon positions or sink at the center and sulfur occupying corner positions this is a tetrahedral and then we can draw the various types of tetrahedral around each of these that will also join together and form a unit cell.

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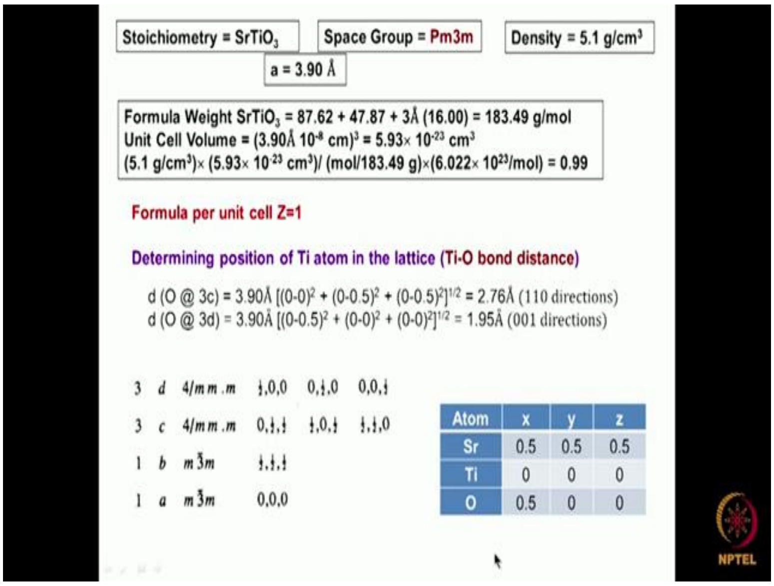

Stoichiometry = $SrTiO_3$

Space Group = Pm3m

Density = 5.1 g/cm^3

a = 3.90 Å

Formula Weight $SrTiO_3$ = 87.62 + 47.87 + 3Å (16.00) = 183.49 g/mol
Unit Cell Volume = (3.90Å 10^{-8} cm)^3 = 5.93× 10^{-23} cm^3
(5.1 g/cm^3)× (5.93× 10^{-23} cm^3)/ (mol/183.49 g)×(6.022× 10^{23}/mol) = 0.99

Formula per unit cell Z=1

Determining position of Ti atom in the lattice (Ti-O bond distance)

d (O @ 3c) = 3.90Å $[(0-0)^2 + (0-0.5)^2 + (0-0.5)^2]^{1/2}$ = 2.76Å (110 directions)
d (O @ 3d) = 3.90Å $[(0-0.5)^2 + (0-0)^2 + (0-0)^2]^{1/2}$ = 1.95Å (001 directions)

3	*d*	4/*mm*.*m*	½,0,0	0,½,0	0,0,½
3	*c*	4/*mm*.*m*	0,½,½	½,0,½	½,½,0
1	*b*	*m*$\bar{3}$*m*	½,½,½		
1	*a*	*m*$\bar{3}$*m*	0,0,0		

Atom	x	y	z
Sr	0.5	0.5	0.5
Ti	0	0	0
O	0.5	0	0

That is a way we can do it that can be structures which are based on not one two element, but there can be more than two elements can be there. Let us consider a case where it is a strontium titanate this is also if you look at it there it has three elements which are present and it has a symmetry which is p m 3 bar m or p m same. From this one can make out that is first primitive lattice and the information which are available in a density is given and then the lattice parameter is given.

If you know how to find out whether the stoichiometry that the molecular formula is the same as that of the stoichiometry or whether there is a difference is going to be there for which what we require is that if you know the lattice parameter and if you know the density we will be getting some information about that what is going to be the molecular weight we can find out at that volume. From the stoichiometry we can find out what is going to be the molecular weight, if both of them turn out to be the same then it is a the molecular formula and stoichiometry that is the ratio if we take it is going to be one.

If that is not the case then some integer value will come that will tell you how many molecules are there in that unit cell with that stoichiometry that is what essentially is being done in this calculation. In this specific case it is going to be only one, then essentially what is important is that if you look at the crystal structure this is a b 3 right this particular stoichiometry what is the type of structure which it can form. I had just shown further since it is a primitive cubic structure, shown the Wyckoff table positions which are relevant, and then looking at the Wyckoff table we can immediately make out that is the structure with this type of a symmetry is possible.

Now, strontium atom can occupy either 1 a or b if strontium occupies a position the b position will be I by titanium or vice versa. Then as far as oxygen is concerned there are two choices are going to be there which is it, which it is going which will occupy this depends upon suppose we have that information about the atomic radius not atomic radius if you have the information about the lattice parameter which is available.

If the lattice parameter information is available immediately we can find out which position because these ions have got specific radius size, if I occupy a particular position that lattice parameter itself could be calculated for knowing the ionic radiai using that data we can get some information about which positions there will be occupying. Here already it is this, this particular table it is given the strontium has to occupy these positions and titanium at a position, there is b position is occupied by strontium oxygen is going to occupy out of these it is 3 d.

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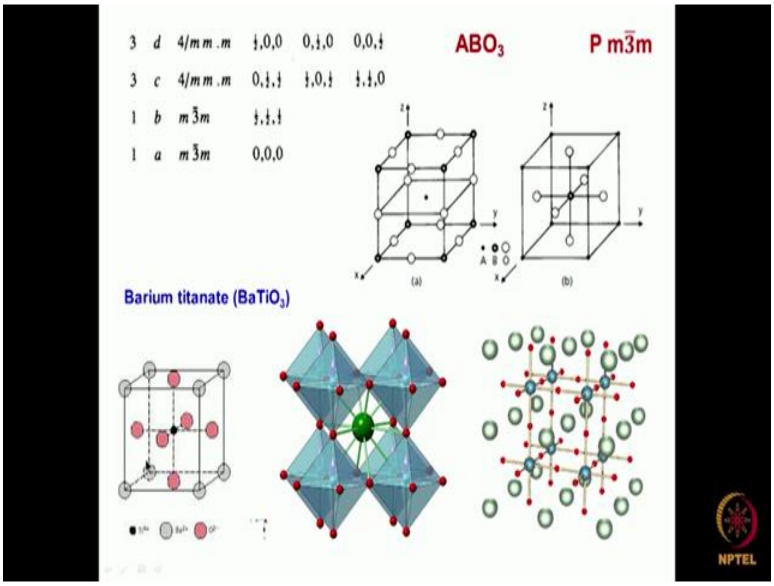

3	*d*	4/*mm*.*m*	½,0,0	0,½,0	0,0,½
3	*c*	4/*mm*.*m*	0,½,½	½,0,½	½,½,0
1	*b*	*m*$\bar{3}$*m*	½,½,½		
1	*a*	*m*$\bar{3}$*m*	0,0,0		

ABO_3

P m$\bar{3}$m

Barium titanate ($BaTiO_3$)

If you construct the unit cell with respect to this is how it will look like strontium occupying the position.

Student: (Refer Time: 52:53).

Titanium occupying the.

Student: A position.

A position and oxygen occupying the as e position; and you see this particular there are many ways in which the structure is being represented you look at this particular structure. This way what we have taken it is that around your very titanium position there is a octahedral cage is going to be there right, with an octagonal cage itself we can show these structures when the number of atoms are going to be there that is what essentially being. This is the same structure which is being shown with all the atom positions, you can make out that this is much more complicated to visualize it where this becomes much easier for virtualization correct, this is what is being done in many cases.

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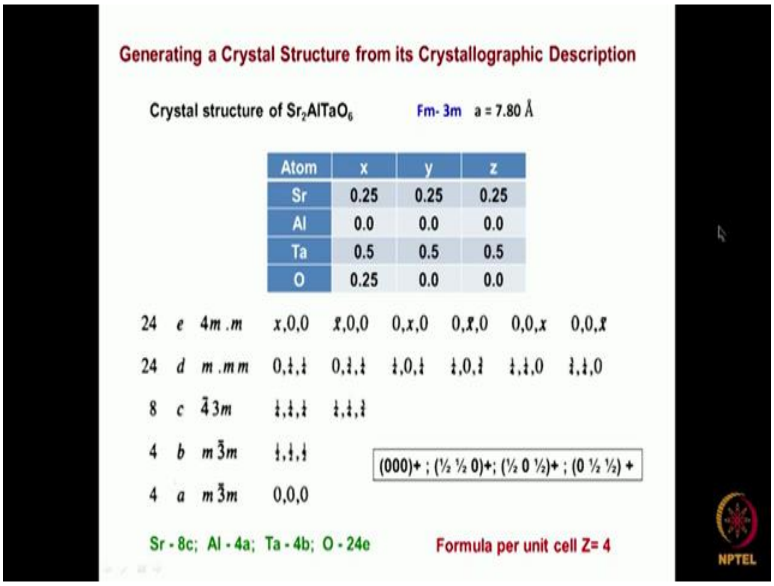


Generating a Crystal Structure from its Crystallographic Description

Crystal structure of Sr_2AlTaO_6 Fm- 3m a = 7.80 Å

Atom	x	y	z
Sr	0.25	0.25	0.25
Al	0.0	0.0	0.0
Ta	0.5	0.5	0.5
O	0.25	0.0	0.0

24	*e*	$4m.m$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
24	*d*	$m.mm$	$0,\frac{1}{4},\frac{1}{4}$	$0,\frac{3}{4},\frac{1}{4}$	$\frac{1}{4},0,\frac{1}{4}$	$\frac{1}{4},0,\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{1}{4},0$
8	*c*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$				
4	*b*	$m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
4	*a*	$m\bar{3}m$	$0,0,0$					

(000)+ ; (½ ½ 0)+; (½ 0 ½)+ ; (0 ½ ½) +

Sr - 8c; Al - 4a; Ta - 4b; O - 24e

Formula per unit cell Z= 4

There is an another one, this is also taken from the literature this is for a crystal which is Sr 2 AlTa that is tantalum and oxygen which contains this is the stoichiometry Sr 2 AlTa. So, these are all the positions which atoms can occupy and it has a lab, got a symmetry which it has got it in space group in f m 3 bar m and the lattice parameter is around 7.8. This is the positions have been determined using x ray diffraction these are all the values which are given. What all positions which the atoms can occupy? This only tells about the fractional coordinates of the different atom positions correct.

Now what we have to construct a crystal structure we should know all the coordinates which we have the generate. Here if we look at the relevant Wyckoff position table we can immediately make out that this position the aluminum will occupy this position, the tantalum only one is going to be there because in the sociology aluminum and tantalum if you consider. So, the aluminum our tantalum will occupy corner and the body centre and the strontium can occupy the face center correct you know strontium will occupy the position with respect to the structures these are all the positions which.

Students: (Refer Time: 55:47).

The strontium, then the position which oxygen can occupy this is one particular position which is there and this is another position which is there, these two possibilities which are there. What has been determined in the crystal structure is that it occupies this a opposition because here we are showing only one particular position, but finally, what we have to do it is that we have to multiply it by that add to this equivalent positions and generate what all positions which the atom will be occupying, when we do that.

Student: (Refer Time: 56:32).

No, it is not this one 24 d it is occupying 24 e position, 24 e that only the value of x that the other two are 0, this is the position which it is occupying that has been seen the value of x turns out to be one-forth. So, how many atoms are going to be there in the unit cell? This, since it is a FCC structure this is going to be aluminum has to be 4 because the stoichiometry if we say Al, but the number of atoms in the unit cell has be 4, tantalum has to be 4, then oxygen has to be 24, strontium has to be 8 correct these are all the.

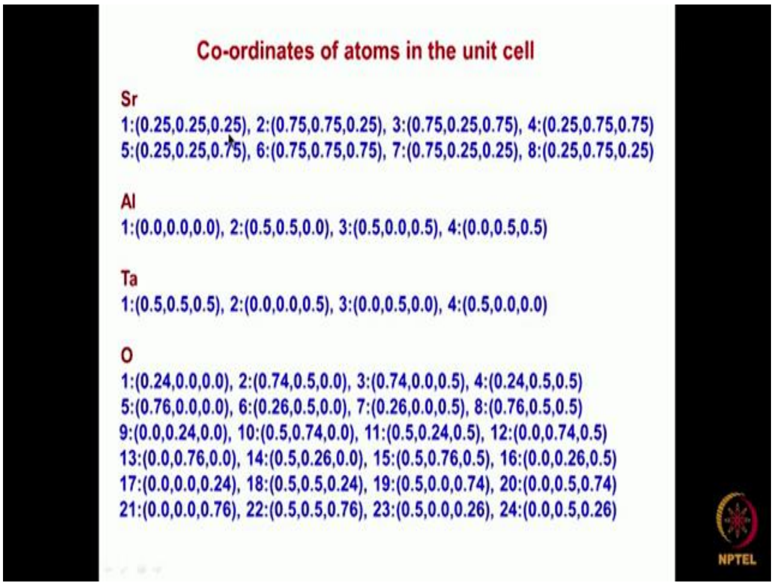
Student: (Refer Time: 57:20).

So, formula per unit cell will be 4 that is this is telling that this stoichiometry the 4 times it has to be multiplied to get it.

Student: (Refer Time: 57:32).

Correct.

(Refer Slide Time: 57:35)



Co-ordinates of atoms in the unit cell

Sr

1:(0.25,0.25,0.25), 2:(0.75,0.75,0.25), 3:(0.75,0.25,0.75), 4:(0.25,0.75,0.75)
5:(0.25,0.25,0.75), 6:(0.75,0.75,0.75), 7:(0.75,0.25,0.25), 8:(0.25,0.75,0.25)

Al

1:(0.0,0.0,0.0), 2:(0.5,0.5,0.0), 3:(0.5,0.0,0.5), 4:(0.0,0.5,0.5)

Ta

1:(0.5,0.5,0.5), 2:(0.0,0.0,0.5), 3:(0.0,0.5,0.0), 4:(0.5,0.0,0.0)

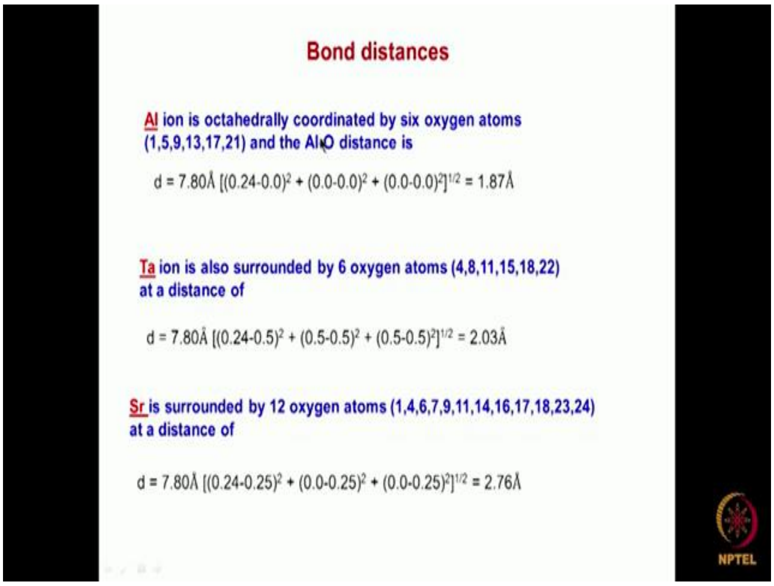
O

1:(0.24,0.0,0.0), 2:(0.74,0.5,0.0), 3:(0.74,0.0,0.5), 4:(0.24,0.5,0.5)
5:(0.76,0.0,0.0), 6:(0.26,0.5,0.0), 7:(0.26,0.0,0.5), 8:(0.76,0.5,0.5)
9:(0.0,0.24,0.0), 10:(0.5,0.74,0.0), 11:(0.5,0.24,0.5), 12:(0.0,0.74,0.5)
13:(0.0,0.76,0.0), 14:(0.5,0.26,0.0), 15:(0.5,0.76,0.5), 16:(0.0,0.26,0.5)
17:(0.0,0.0,0.24), 18:(0.5,0.5,0.24), 19:(0.5,0.0,0.74), 20:(0.0,0.5,0.74)
21:(0.0,0.0,0.76), 22:(0.5,0.5,0.76), 23:(0.5,0.0,0.26), 24:(0.0,0.5,0.26)

Now this coordinates can be calculated what are the positions the atom will be occupying the strontium, aluminum, tantalum, oxygen, all this and once these positions information is available one can construct that crystal structure. If you look at this table this position is being given us 0.24 not exactly even 0.25.

The reason essentially is that many of this position here that x what it corresponds to it is a fractional indices, but the value has to be determined, it can be in any position it can be. What will be the value of x will be determined by the type of bonding which is present there and in many of these compounds essentially their electrostatic force also comes into the picture that will decide the exact position which the atom is going to occupy because of it, it may not be occupying a position with a specific a fractional indices. It can have values, it can be slightly different from that value which is given that is why here you can see that it is 0.24 not 0.25.

(Refer Slide Time: 58:51)



Bond distances

Al ion is octahedrally coordinated by six oxygen atoms (1,5,9,13,17,21) and the Al-O distance is

$$d = 7.80\text{Å}\,[(0.24-0.0)^2 + (0.0-0.0)^2 + (0.0-0.0)^2]^{1/2} = 1.87\text{Å}$$

Ta ion is also surrounded by 6 oxygen atoms (4,8,11,15,18,22) at a distance of

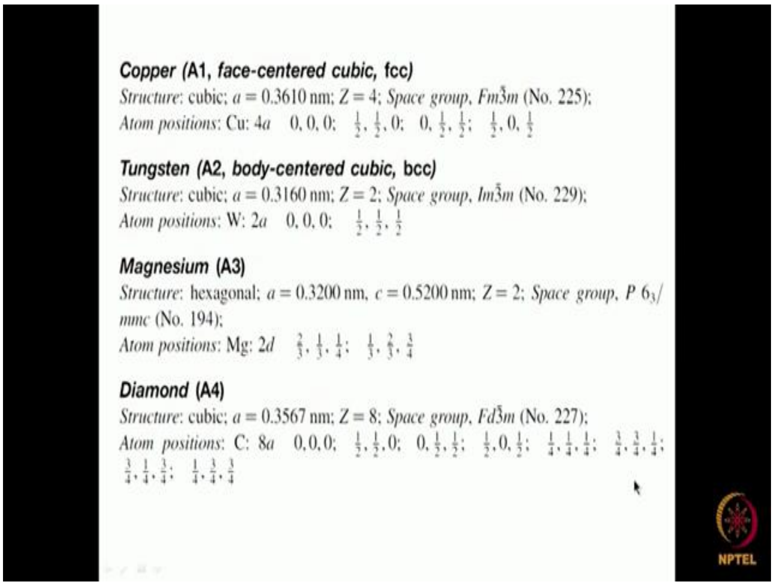
$$d = 7.80\text{Å}\,[(0.24-0.5)^2 + (0.5-0.5)^2 + (0.5-0.5)^2]^{1/2} = 2.03\text{Å}$$

Sr is surrounded by 12 oxygen atoms (1,4,6,7,9,11,14,16,17,18,23,24) at a distance of

$$d = 7.80\text{Å}\,[(0.24-0.25)^2 + (0.0-0.25)^2 + (0.0-0.25)^2]^{1/2} = 2.76\text{Å}$$

Now, if this information is available, now, one can find out the bond distances also how many oxygen atoms will be there around aluminum or tantalum and strontium and then one can construct the unit cell also.

(Refer Slide Time: 59:03)



Copper (A1, face-centered cubic, fcc)

Structure: cubic; $a = 0.3610$ nm; $Z = 4$; *Space group*, $Fm\bar{3}m$ (No. 225);

Atom positions: Cu: $4a$ $\;0, 0, 0;\; \frac{1}{2}, \frac{1}{2}, 0;\; 0, \frac{1}{2}, \frac{1}{2};\; \frac{1}{2}, 0, \frac{1}{2}$

Tungsten (A2, body-centered cubic, bcc)

Structure: cubic; $a = 0.3160$ nm; $Z = 2$; *Space group*, $Im\bar{3}m$ (No. 229);

Atom positions: W: $2a$ $\;0, 0, 0;\; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

Magnesium (A3)

Structure: hexagonal; $a = 0.3200$ nm, $c = 0.5200$ nm; $Z = 2$; *Space group*, $P\,6_3/mmc$ (No. 194);

Atom positions: Mg: $2d$ $\;\frac{2}{3}, \frac{1}{3}, \frac{1}{4};\; \frac{1}{3}, \frac{2}{3}, \frac{3}{4}$

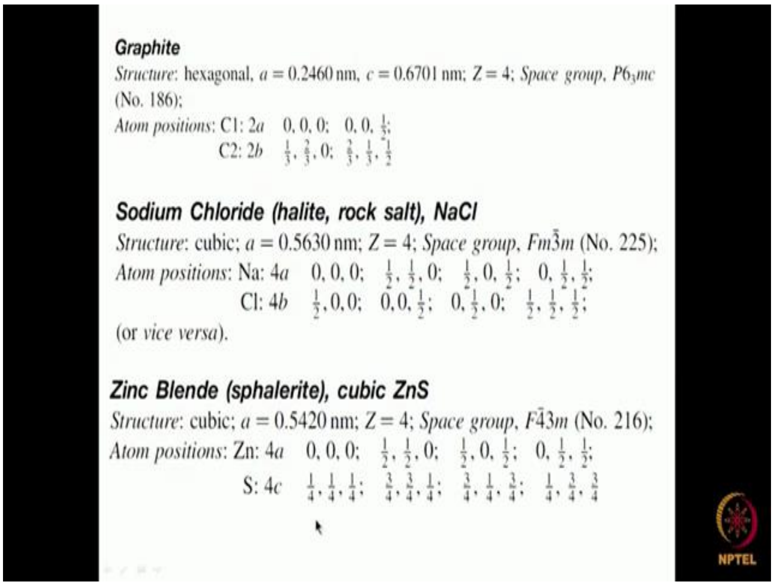
Diamond (A4)

Structure: cubic; $a = 0.3567$ nm; $Z = 8$; *Space group*, $Fd\bar{3}m$ (No. 227);

Atom positions: C: $8a$ $\;0,0,0;\; \frac{1}{2}, \frac{1}{2}, 0;\; 0, \frac{1}{2}, \frac{1}{2};\; \frac{1}{2}, 0, \frac{1}{2};\; \frac{1}{4}, \frac{1}{4}, \frac{1}{4};\; \frac{3}{4}, \frac{3}{4}, \frac{1}{4};\; \frac{3}{4}, \frac{1}{4}, \frac{3}{4};\; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}$

If you look into the literature there are like especially in Pearson's table for various elements this is the sort of information it is being provided like for copper if you look at it, it is one. You see this a one which is being the one is the structure bearish symbol which I mentioned face centered cubic fcc and then the space group is also given. The space group number is also given so that which number we look for and the lattice parameter which is determine and the positions of the atoms that is it is 4 a, that is 4 atoms here positions Wyckoff position that information is given.

(Refer Slide Time: 59:50)



Graphite

Structure: hexagonal, $a = 0.2460$ nm, $c = 0.6701$ nm; $Z = 4$; *Space group*, $P6_3mc$ (No. 186);

Atom positions: C1: 2*a* $0, 0, 0;\ 0, 0, \frac{1}{2};$

C2: 2*b* $\frac{1}{3}, \frac{2}{3}, 0;\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$

Sodium Chloride (halite, rock salt), NaCl

Structure: cubic; $a = 0.5630$ nm; $Z = 4$; *Space group*, $Fm\bar{3}m$ (No. 225);

Atom positions: Na: 4*a* $0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{1}{2};$

Cl: 4*b* $\frac{1}{2}, 0, 0;\ 0, 0, \frac{1}{2};\ 0, \frac{1}{2}, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2};$

(or *vice versa*).

Zinc Blende (sphalerite), cubic ZnS

Structure: cubic; $a = 0.5420$ nm; $Z = 4$; *Space group*, $F\bar{4}3m$ (No. 216);

Atom positions: Zn: 4*a* $0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{1}{2};$

S: 4*c* $\frac{1}{4}, \frac{1}{4}, \frac{1}{4};\ \frac{3}{4}, \frac{3}{4}, \frac{1}{4};\ \frac{3}{4}, \frac{1}{4}, \frac{3}{4};\ \frac{1}{4}, \frac{3}{4}, \frac{3}{4}$

Similarly, for these some few examples which I had given for graph 8 if it is hexagonal the space group symbol is being given how many atom positions are going to be there all these information's are provided correct.

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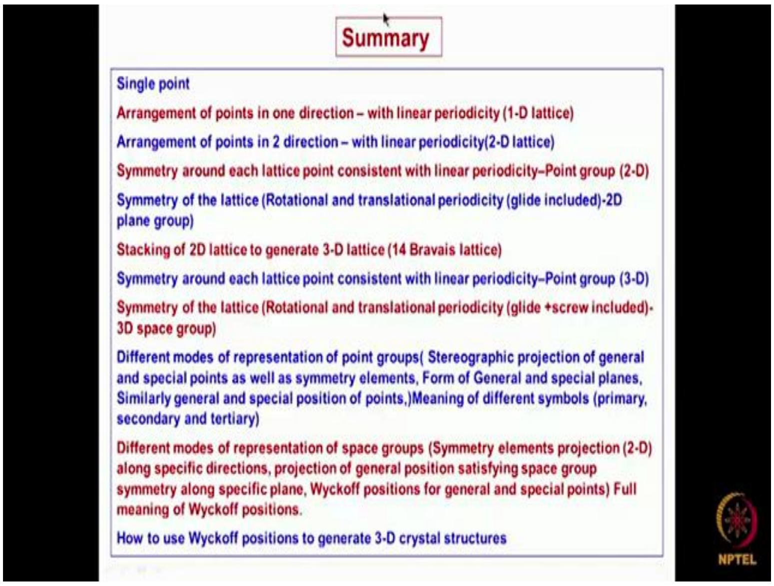

Summary

- Single point
- Arrangement of points in one direction – with linear periodicity (1-D lattice)
- Arrangement of points in 2 direction – with linear periodicity(2-D lattice)
- Symmetry around each lattice point consistent with linear periodicity–Point group (2-D)
- Symmetry of the lattice (Rotational and translational periodicity (glide included)-2D plane group)
- Stacking of 2D lattice to generate 3-D lattice (14 Bravais lattice)
- Symmetry around each lattice point consistent with linear periodicity–Point group (3-D)
- Symmetry of the lattice (Rotational and translational periodicity (glide +screw included)-3D space group)
- Different modes of representation of point groups(Stereographic projection of general and special points as well as symmetry elements, Form of General and special planes, Similarly general and special position of points,)Meaning of different symbols (primary, secondary and tertiary)
- Different modes of representation of space groups (Symmetry elements projection (2-D) along specific directions, projection of general position satisfying space group symmetry along specific plane, Wyckoff positions for general and special points) Full meaning of Wyckoff positions.
- How to use Wyckoff positions to generate 3-D crystal structures

Similarly, for zincblende, in summary if you look at it we started this entire section on perfect crystal starting from a taking a single point a lattice point then how they can be arranged in one dimension, then from that one dimensional arrangement what all symmetries associated with it, then this one dimensional lattice if we arrange them we can generate two dimensional lattice, what all types of symmetries aware which are they are point group symmetry and on this if you put a motifs around this two dimensional lattice what all types of symmetries which the crystals can have, the same we have done it for a three dimensional crystal.

That from two dimensional three dimensional crystal how to construct it, what all types of Bravais lattices, how many types of Bravais lattices we can have space group lattice, then in those lattices if you are putting motifs around them what are types of specific crystal structures which can be formed which are 200, in total 230 are possible.

Then looking into the space group table if you have to construct a crystal structure what all positions at which the atoms have to be placed, how to go about it when we know the stoichiometry and how to find out the molecular weight if you get the information about the crystal structure and also that information about the density of the material and if you know the lattice parameter we can find out whether the molecular formula and the stoichiometry case that same or is it that many more molecular formula crystals are there in the unit cell that information which we can calculate it. So, effectively how to construct a perfect crystal we have looked at it.

In the next class we will look at defects in the crystal materials. So, we will start with point defects in the material. A lot of assignments which I will give once you do this assignment one will be able to understand how exactly the space group table has to be used to generate different type of crystal structures.

We will stop here.