An Introduction to Materials: Nature and Properties
(Part 1: Structure of Materials)
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Lecture - 20
Covalent Solids (contd.)
Ionic Solids

[noise]

So, we could not finish the covalent solids in the last lecture.

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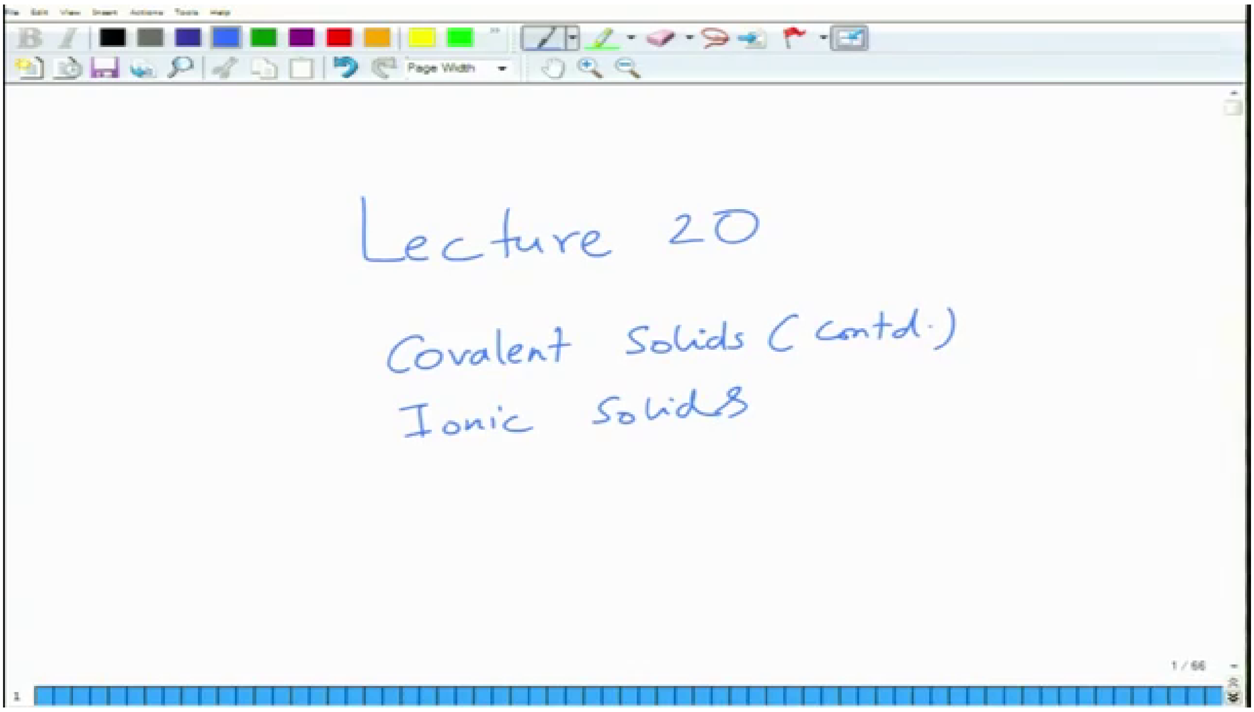

Lecture 20

Covalent Solids (contd.)

Ionic Solids

So, we will do the remaining part here and [vocalized-noise] then we will continue with the ionic solids the introduction to ionic solids. So, we were talking about the formation of covalent solids, we talked about why hybridization is important just more just beyond the orbital overlap because, orbital overlap it is not sufficient to explain why certain kind of bonding occur why covalent bonding occurs with 4 neighbors in solids like methane and silicon and carbon [vocalized-noise] and that is where the concept of hybridization came.

So, we are looking at the structure of graphite; graphite is the sp 2 bonded material in which carbon atoms are sp 2 hybridized and bonded in the plane. So, it makes a hexagonal sheet and, but the sheets are themselves ah bonded to each other with Vander Waals or secondary bonding and that is why [vocalized-noise] the interaction between the sheets is weaker and so when you apply force to graphite graphite the sheets get sheared very easily, as a result graphite is used as a lubricant. Second form of carbon that we going to talk about is ah diamond [noise] which is again a form of carbon ah.

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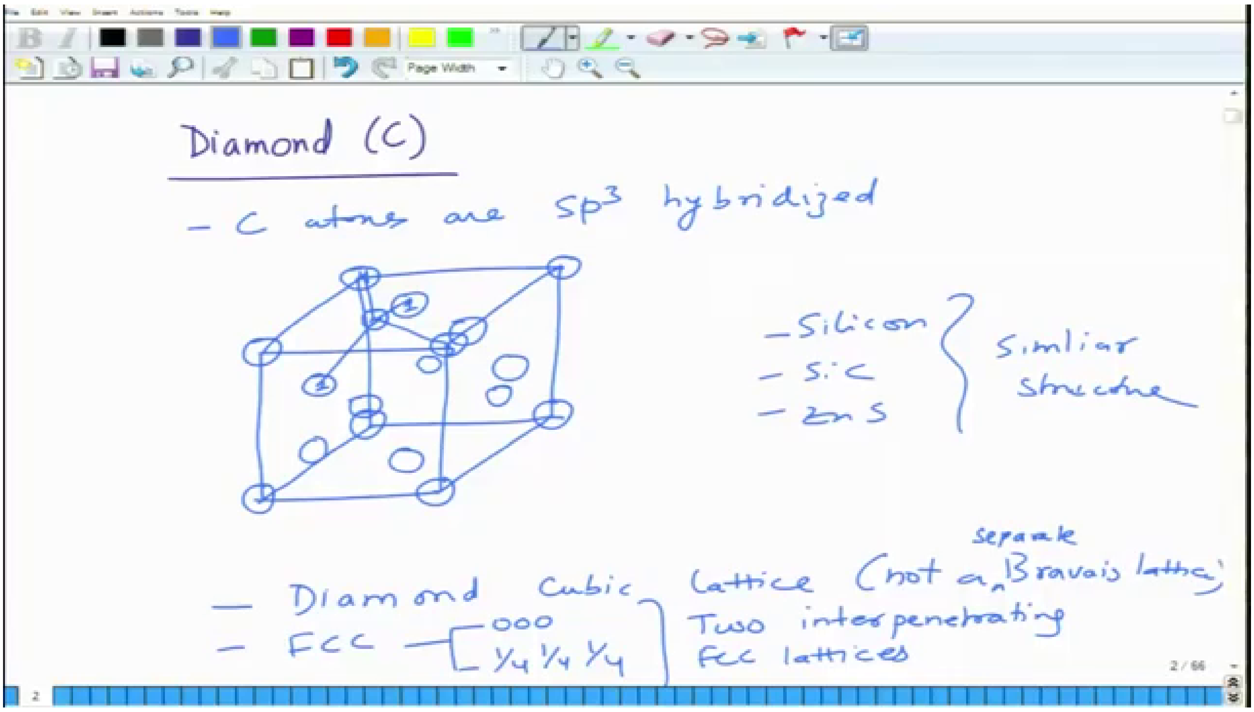

Diamond (C)

- C atoms are sp^3 hybridized

- Silicon
- SiC
- ZnS

} Simliar structure

- Diamond Cubic lattice (not a separate Bravais lattice)
- FCC — [000, $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$] } Two interpenetrating FCC lattices

So, in this case carbon atoms are [noise] sp3 hybridized and ah very strong directional because the angle has to be maintained, the covalent bond can only form at certain angle and certain direction that is why there is very strong directionality with the covalent bond. So, this I forgot to mention in my earlier lecture that covalent bonds, because of this necessity to for the orbital's to align and overlap at all along certain axis there is a very strong directionality with the covalent bond.

So, [vocalized-noise] for example in case of diamond what happens is that if you make a unit cell of diamond [vocalized-noise], so in this case carbon atoms are arranged [noise] on the face centers of a cube [noise] and then carbon atoms are arranged in such a fashion so they are also present at the tetrahedral sites, but not all [vocalized-noise] tetrahedral sites are present otherwise you will violate the co covalent bonding.

So, carbon atoms are present in such a fashion you have a carbon atom here which is covalently bonded with respect to this that ah uh and the one ah here and the one here ok, so they will make a tetrahedral. So, you will it will make a bond here ah sorry this is let me just draw it, again it will make 4 bonds. So, this is first neighbor, this is second neighbor, this is third neighbor and this is fourth neighbor.

Similarly, you will have 1 atom here just across the phase diagonal [vocalized-noise], other 2 carbon atoms do not ah go in the bottom side they go here. So, 1 carbon atom goes here and 1 carbon atom goes here, if you [noise] put carbon atom on all the tetrahedral sides then some carbon atoms will end up having 8 neighbors and that is not ah permitted by sp 3 hybridization and bonding. So, as a result you have to arrange the carbon fashion carbon atoms in such a fashion, so that you have a [vocalized-noise] tetrahedral coordinated structure [noise]. So, let me just show you ah 1 ah [vocalized-noise] view graph of this structure how it looks like.

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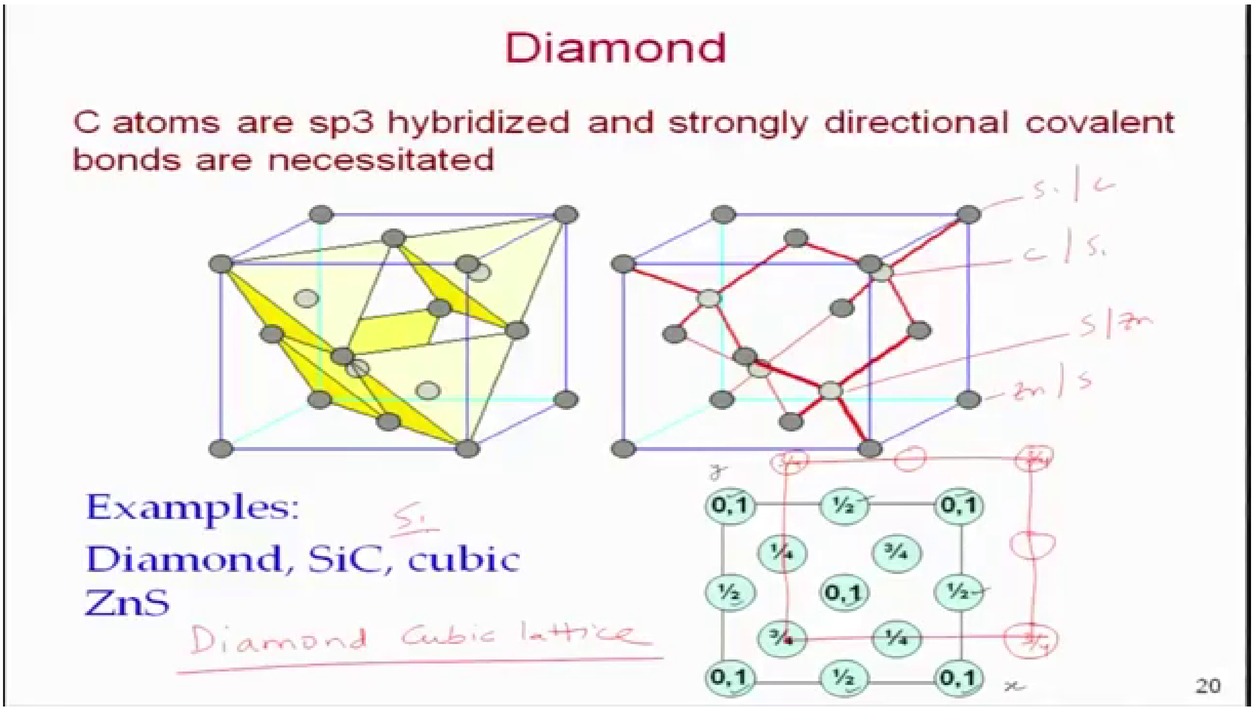

Diamond

C atoms are sp3 hybridized and strongly directional covalent bonds are necessitated

Examples:
Diamond, SiC, cubic ZnS

Si

Diamond Cubic lattice

So ah this is the ah view graph of diamond ah cubic structure, in which carbon atoms are of course, it is sp 3 hybridized. So, this is the unit cell the 1 ah you see a so this ah the 1 in the blue is the unit cell, so this there are 4 atoms. So, these gray ones are the 4 atoms the dark gray ones and the light gray ones are same atoms there are carbon atoms, but they just [vocalized-noise] colored slightly differently, you can see that this is first tetrahedra this is second tetrahedra and the other tetrahedra is this and that.

So, the other tetrahedra on the bottom side, is not directly below the tetrahedra which is on the top. So, there is a alternating kind of arrangement of carbon atoms you can see that [noise] in this the 1 on the right; this is the first carbon atom, this is a second carbon atom and this is the third carbon atom this is the fourth carbon atom, you can see that each of them is tetrahedrally coordinated.

And same is true about the carbon atom sitting at the corners and face centers they are also tetrahedrally coordinated because [vocalized-noise], if you if you if you keep the unit cell corner from dark gray to light gray, then what you will see is that the light gray will make a FCC unit cell and that dark gray will occupy the tetrahedral voids. So, basically diamond cubic structure is 2 interpenetrating FCC lattices shifted to each other with respect to ah by by a vector 1 by 4 1 by 4 1 by 4.

So, this is the structure you can see ah this is the top view so this one. So, this is the ah this this this this this these make the original lattice ok FCC lattice, these are the tetrahedral ones 1 by 4; 3 by 4; 3 by 4 1 by 4 xy you can see is obvious. So, this is if this is x this is y what you see is only the z. Now you can make the unit cell by placing the by shifting the unit cell a little bit I can make the unit cell here, if I can take if I make a unit cell like this; I can make a very well unit cell which is this if I do that I have an atom here which is equivalent to this atom at 3 by 4 3 by 4, I will have an atom here which is equivalent to ah this atom 3 by 4 again at 3 by 4 and again I will have this atom [vocalized-noise].

Now if you make 3 by 4 as 0 now 1 by 4 will become half alright; so, you will make FCC lattice off these and tetrahedral atoms will become this will become a tetrahedral atom, this will become a tetrahedral atom, this will become a tetrahedral atom and this will become a tetrahedral atom.

So, basically these are 2 interpenetrating FCC lattices into each other shifted by a vector quarter quarter quarter ok and this lattice is called as diamond cubic lattice [noise] and this is followed by diamond, it is followed by silicon, but it is also followed by silicon carbides cubic zinc sulfide ok.

So, what happens in silicon carbide is that ah in silicon carbide this atom will be silicon and this atom will be carbon or you can say this is sil carbon this is silicon both are possible right, you just have to shift the lattice corner. Similarly in case of zinc oxide this would be zinc, this would be or sulfide this would be sulfur, you can make this as zinc this has sulfur both are possible representations ok, but zinc sulfide a slightly ionic character. So, that is why we will discuss the structure of zinc sulfide in case of ionic solids, but [vocalized-noise] diamond silicon carbide or even silicon [noise] has this kind of structure which is called as diamond cubic lattice.

But diamond cubic lattice is not a brovise lattice ok remember it is not a Bravis lattice, it is still a face centered cubic lattice this is still a face centered cubic lattice, but the motif is different motif is face centered cubic lattice [vocalized-noise] 0 0 0 and 1 by 4 1 by 4 1, by 4 that will the motif because you have 2 atoms. So, [vocalized-noise] it is a it is a lattice which contains 8 atoms ok you can calculate the packing fraction, you can see that diamond atom is sitting carbon atom is sitting as a tetrahedral site tetrahedral site size is point 2 to 5 r and you have the same sized atom sitting there which means the lattice has to dilate.

So, lattice of silicon or carbon is bigger than what it would have been if there was no tetrahedral atom [vocalized-noise] ok, of course that is not possible bonding wise, but imagine if carbon only made FCC lattice then the packing fraction would be same as 0.74, but in this case packing fraction would be lower because you have to dilate the lattice. So, you can calculate the packing fraction by yourself all right [vocalized-noise].

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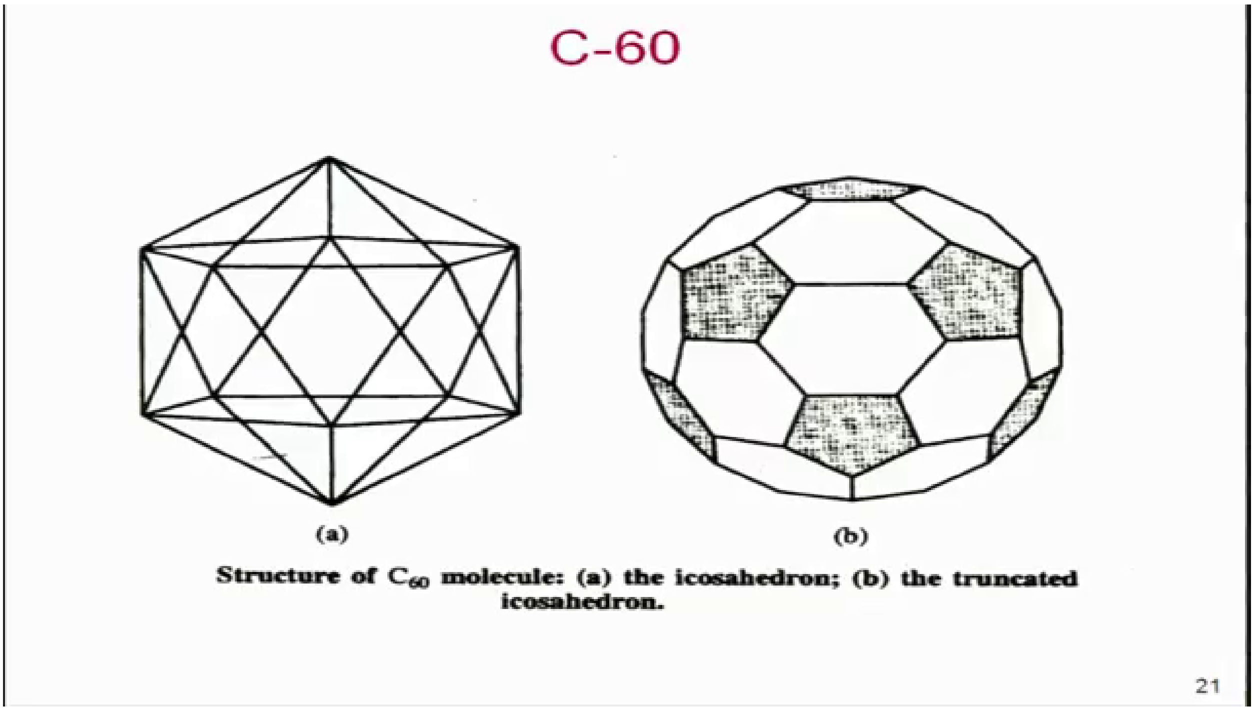

C-60

Structure of C_{60} molecule: (a) the icosahedron; (b) the truncated icosahedron.

This is the structure of ah diamond this is the structure of another ah covalent material called as C60, which is the fullerene ah buck ball kind of structure. So, it has a football shaped structure where carbon atoms are arranged in such a fashion. So, that ah you you see these truncated you see these hexagons and pentagons arranged. So, you can see that if you only had pentagons it will not make a structure, but if you put pentagons separated by hexagons then it can make a ball kind of structure [vocalized-noise]. So, this is a C60 molecule which is called as fullerene and that is the structure of this is again a covalently bonded materials you can see that each atom having 3 neighbors here sp 2 hybridized structure.

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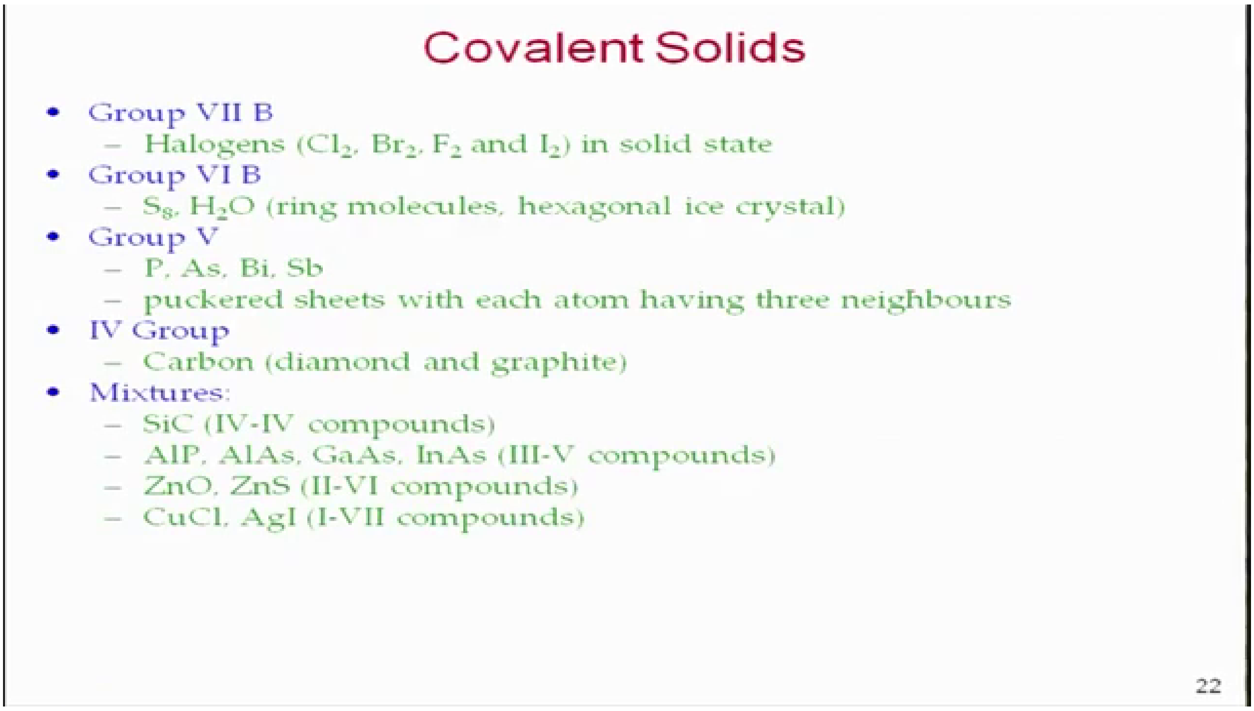

Covalent Solids

- Group VII B
  - Halogens (Cl_2, Br_2, F_2 and I_2) in solid state
- Group VI B
  - S_8, H_2O (ring molecules, hexagonal ice crystal)
- Group V
  - P, As, Bi, Sb
  - puckered sheets with each atom having three neighbours
- IV Group
  - Carbon (diamond and graphite)
- Mixtures:
  - SiC (IV-IV compounds)
  - AlP, AlAs, GaAs, InAs (III-V compounds)
  - ZnO, ZnS (II-VI compounds)
  - CuCl, AgI (I-VII compounds)

And then there are some other covalent solids these are the ones which I discussed in the beginning.

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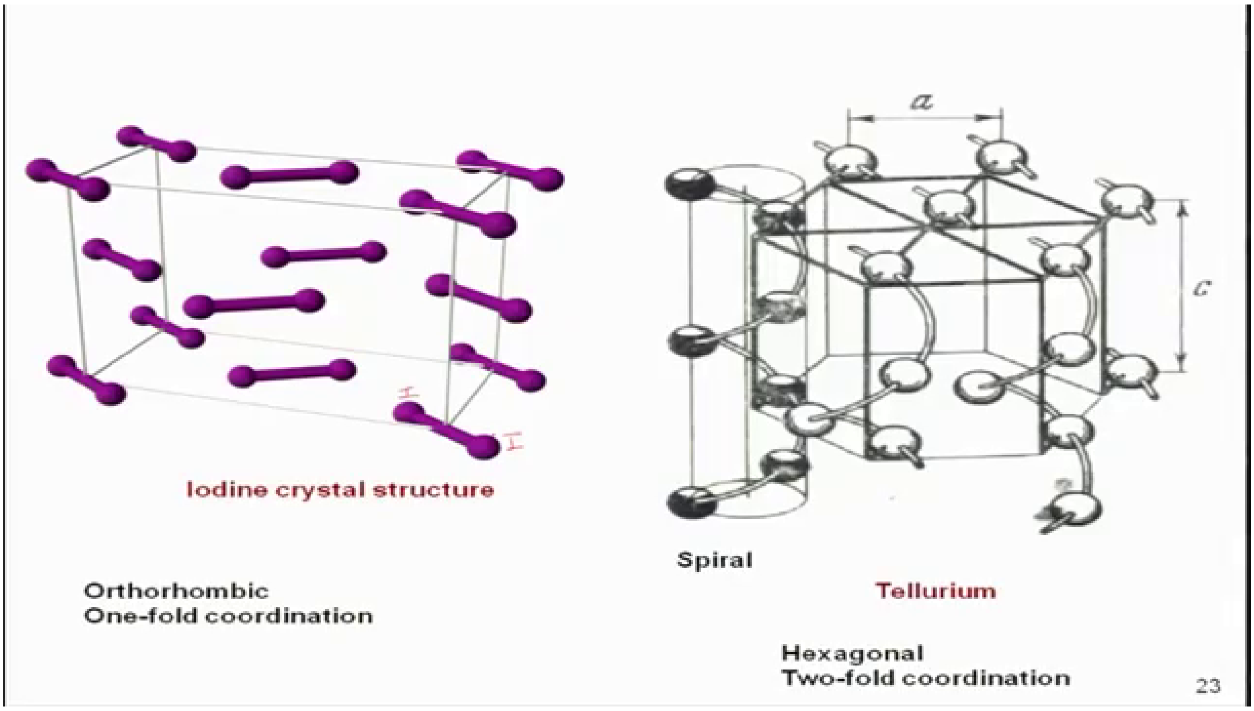

Iodine crystal structure

Orthorhombic
One-fold coordination

Spiral

Tellurium

Hexagonal
Two-fold coordination

So, for example, iodine makes a structure like this, so iodine is an orthorhombic structured material it has linear 1 fold coordination. So, the these are iodine atoms, this is

1 I this is second I, so it has only 1 neighbor. So, dumbbell shaped molecules ah arranged in an orthorhombic lattice [vocalized-noise], ah this is structure of tellurium which is a spiral structure, it is a hexagonal it again has to fold it has to fold coordination ah in a in a in a spiral network.

So, these are the basically covalently bonded structured materials which we wanted to ah discuss in this ah lecture. So, what we will do now is ah we will move on to, ah [vocalized-noise] we will continue what we were doing uh ok. So, [vocalized-noise] ah that I will just write here so we have other examples are silicon, silicon carbide zinc sulfide similar structures [noise]. So, you can say structure is diamond cubic lattice [noise] not a Bravis lattice very important to remember not a separate Bravis lattice.

So, basically Bravis lattice is FCC with motif at 0 0 0 and 1 by 4 1 by 4 1 by 4 1 by 4 ok. So, basically it is a it is a mixture of ah 2 inter penetrating FCC [noise] FCC lattices in case of silicon carbides zinc sulphide there will be 2 FCC lattices 1 of silicon and 1 of carbon, similarly in zinc oxide it will be 1 of zinc and 1 of sulfur.

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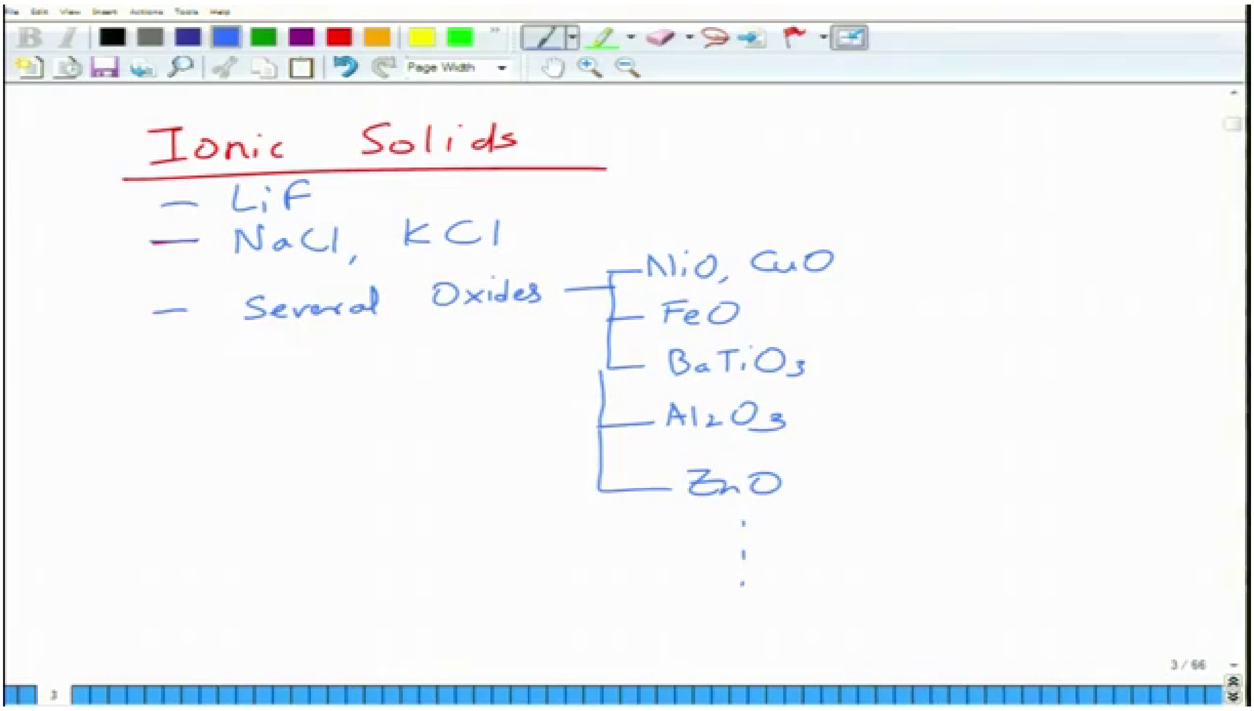

Ionic Solids

- LiF
- NaCl, KCl
- Several Oxides
  - NiO, CuO
  - FeO
  - $BaTiO_3$
  - Al_2O_3
  - ZnO
  - ⋮

So, now we will start ah the discussion on ionic solids [noise] and this discussion is important because, many compounds that we see ac ah a around us they are all ironically bonded materials and ah for example, ah if you see ah some pounds like sodium chloride, potassium chloride, several oxides [noise] [vocalized-noise] nickel oxide copper oxide iron oxide compounds such as barium titanate and [vocalized-noise] alumina, even zinc oxide several materials they are all ironically bonded [noise] materials and ion they not they may not be 100 percent ionic because, that is determined by because ionic bond forms when there is a large difference between the electro negativity of 2 atoms.

For example, in case of sodium ah you have lithium fluoride another example. So, [vocalized-noise] then the element diff when the elements have large difference in the electonegativity electro negativity bond is predominantly ionic [vocalized-noise] in some cases, when that the [vocalized-noise] difference is not large and the bond may be partly covalent, in most cases it is partly covalent and partly ionic, but they fall in the category of predominantly with ionic character.

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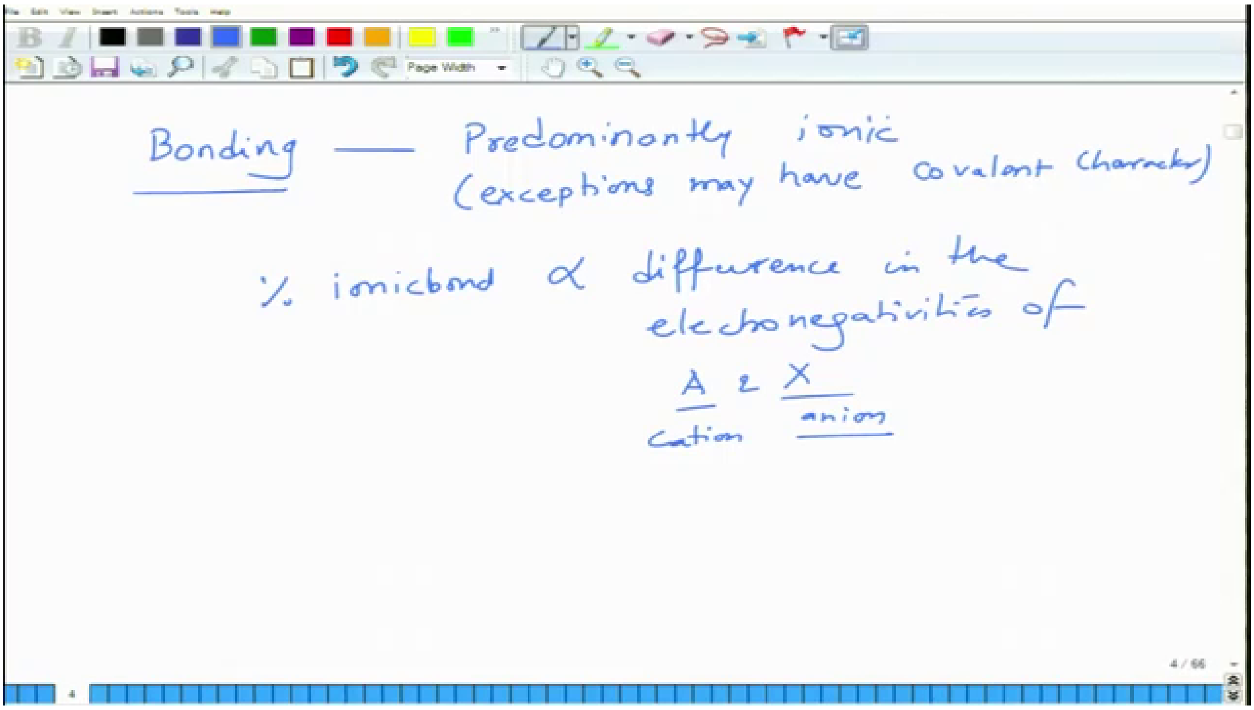

Bonding — Predominantly ionic
(exceptions may have covalent character)

% ionicbond $\propto$ difference in the electronegativities of A & X

A: cation

X: anion

So, bonding in this case is bonding is predominantly [noise] ionic ah exceptions ah may have covalent character. So, for example zinc oxide, zinc sulphide, silicon carbide and all that. So, percentage [noise] iconicity or ionic bond is proportional to difference in the [noise] in the electro negativity of [noise] of let us say A and X, where A is cation X is anion [noise].

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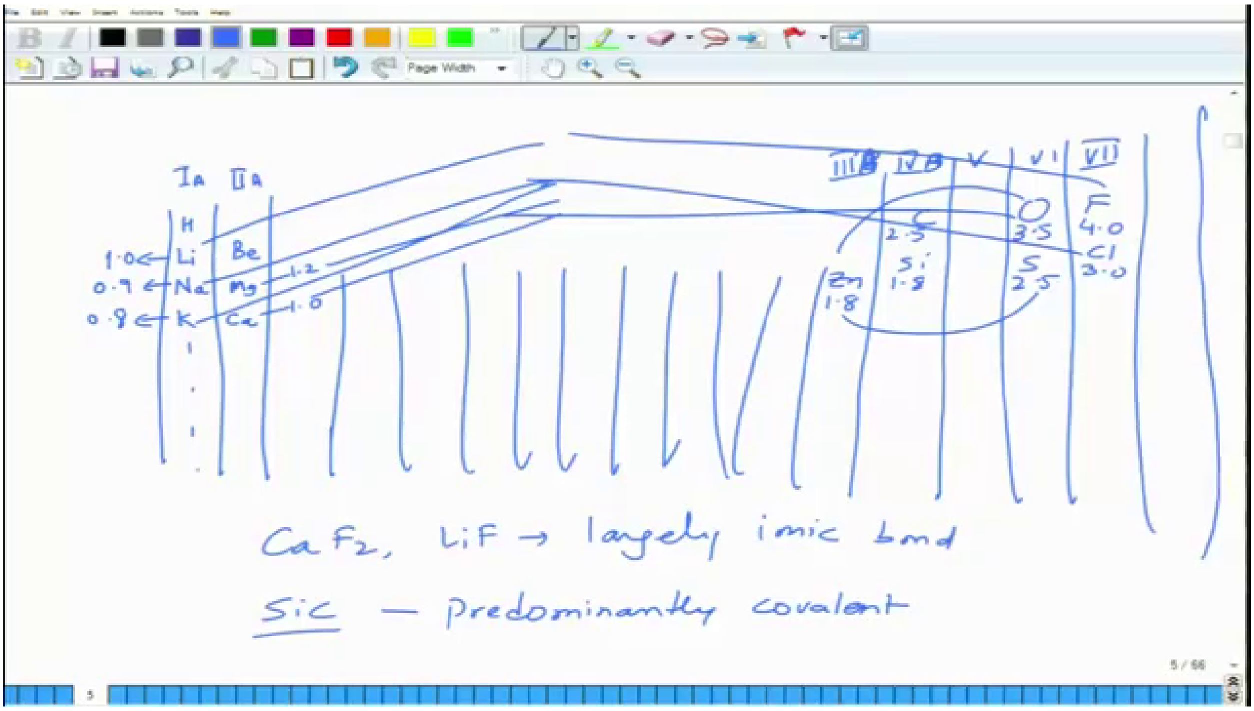

CaF_2, LiF → largely ionic bond

SiC — predominantly covalent

If I if you look at for example the periodic table, on the left we have let us say 1 a then we have 2A and in 1A, we start with hydrogen lithium and we have sodium then we have potassium and so on and so far.

Lithium has a electro negativity of ah 1.0sodium has a potta [vocalized-noise] electronegative 0.9, potassium has a negativity of ah 0.8. In the second one we start with beryllium then we have ah magnesium then we have calcium magnesium has electro negativity of 1.2, calcium has a negative electro negativity of nearly 1 and then of course, you go to group 3 ah these transition elements in between and then we how many of them ah 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 ah 1, 2, 3, 4, 5, 6, 7, 8 [vocalized-noise] and then we go to group ah 3B and then we have 4 sorry 3A I think this is 4A and then we have ah [noise] [vocalized-noise] and then we have 5 then we have 6 and then we have 7 and of course then we have inert gases.

So, on this side we have on in in group 4 we have atoms like carbon silicon ah and there are bismuth and all that to carbon has an electro negativity of 2.5 silicon has electro negativity of 1.8 and then a important 1 is again group 6 where you have oxygen [noise], which has a electro negativity of 3.5 and then you have sulfur which has a electro negativity of 2.5 and then we have fluorine which has a electro negativity of 4, chlorine has a negativity of 3 so on and so far, I am not writing for all of them.

But when you mix these compounds for example, lithium and fluorine it is a large difference in the electro negativity, if you mix chlorine and sodium it is a large difference between the electro negativity. If you mix for example, potassium with chlorine you can have large difference in the electro negativity, you can mix magnesium with oxygen calcium with oxygen these all have very large difference in the electro negativity and these all give you ah large ah iconicity in ah the bonding.

So, for example anything like calcium fluorite, lithium fluoride will give you a [noise] largely ionic bond [vocalized-noise], but on the other hand if you look at silicon carbide silicon carbon the difference is hardly any difference 1.8 2.5. So they this is predominantly [noise] covalent; similarly, if you look at zinc oxide, zinc sulfide zinc is ah is just before column three. So, this is zinc, zinc has a ah electronegative 1.8 if you look at the zinc oxide zinc oxide is more ionic, but zinc sulphide is less ionic zinc sulfide is more covalent in nature.

So, this is ah the the the the reason why you have this variety of [vocalized-noise], compounds showing predominantly ionic behavior compound showing predominantly covalent behavior and compound showing pred mixed behavior ok, but all of them they they have certain ionic character that is why they they fall in the category of ionic solids. So, first before we go into how ionic solids form let us first lack look into what makes [noise] ionic structures [noise] what makes them stable.

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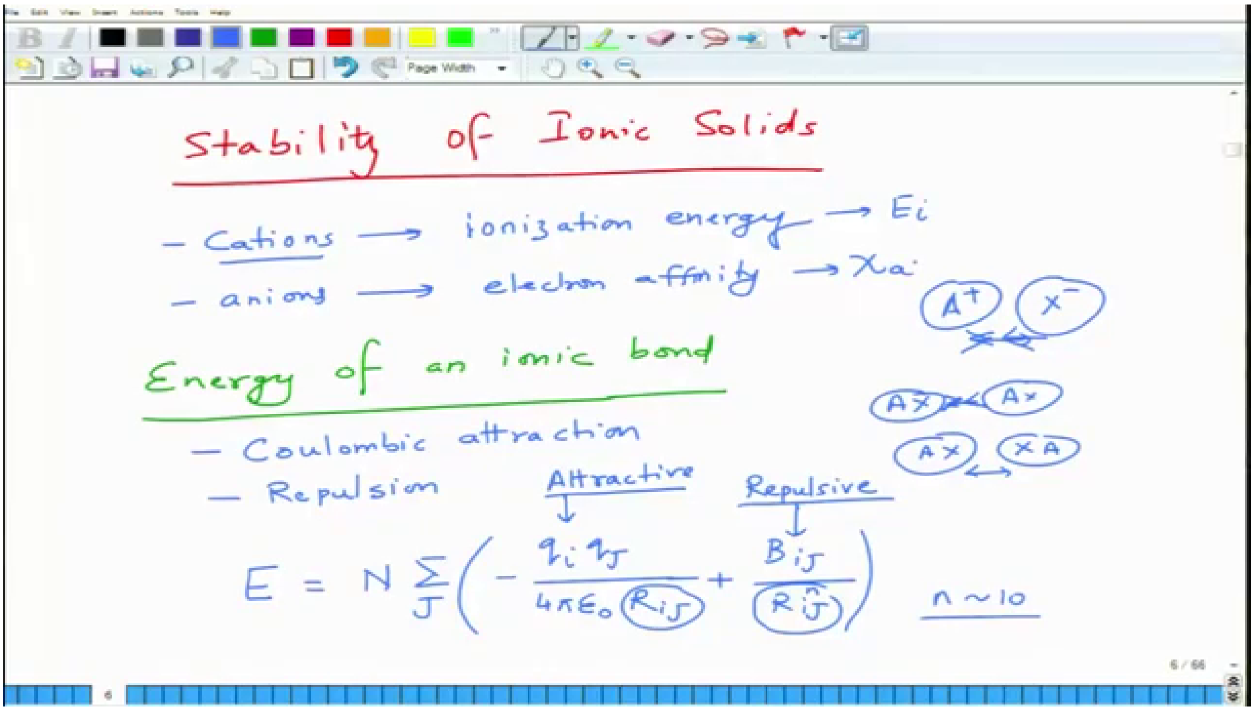

Stability of Ionic Solids

- Cations → ionization energy → E_i
- anions → electron affinity → X_a

Energy of an ionic bond

- Coulombic attraction
- Repulsion

Attractive

Repulsive

$$E = N \sum_J \left(- \frac{q_i q_J}{4\pi\varepsilon_0 \boxed{R_{iJ}}} + \frac{B_{iJ}}{\boxed{R_{iJ}^n}} \right)$$

$n \sim 10$

So, [vocalized-noise] why do [vocalized-noise] why is that the ah is when you put ah [vocalized-noise] several anions and cations together, they form these structures [vocalized-noise] which are periodic in nature ah they have certain crystal structures [vocalized-noise], the regular periodicity rather than making isolated molecules.

Why cannot you just have 1 silicon carbide or [vocalized-noise] maybe 1 zinc oxide molecule other zinc oxide molecule, then why do you [vocalized-noise] have why do they have to arrange themselves in a periodic fashion, why cannot just you have zinc oxide molecule that is it. So, you can have several zinc oxide molecules which are randomly located in their space [vocalized-noise]; now this is to do with the energetic.

So, here ah if you look at ah basically [vocalized-noise] a the cations are defined by their [noise] the energy that we consider, in case of cations is ionization energy right [noise], energy required to ionize them. In case of anions what we consider is electron [noise] affinity because, they they they are ready to accept the electron that is why we talk about electron affinity. The energy of an ionic bond [noise] is determined by [noise] ah when you put these atoms together you have columbic attraction and you have repulsion [noise] ok, repulsion is often called as poly repulsion ok.

So, when you put A and X this is a plus x minus there is [noise] a tendency to sorry attract, but suppose you has a you have AX molecule ok you have another ax molecule in the vicinity. Suppose if it was in this position it will have tendency to attract, suppose you have a x and the neighboring molecules is it was oriented in such a fashion. So, that there is XA coming closer this will have tendency to repel. So, the balance of these attractive and repulsive forces, eventually leads to a structure which is periodic in nature that is why the molecules are not randomly just arranged because, some what if molecules are randomly arranged you will have a close to each other in some cases you will you will have AX closing. So, [vocalized-noise] you have to have a balance of forces.

So, basically the energy expression of this structure is something like that you have n number of atoms and this is epsilon j minus of qi qj divided by 4 pie epsilon naught Rij. So, I is the reference atom or reference ion and then you have these 2 terms 1 is the attraction term second is the repulsion term Bij divided by Rij to the power n and b is a constant here and n takes a value of about 10 in this case. So, for every J th neighbor [vocalized-noise] a for every J th neighbor you got to sum this energy and multiply by n which is a number of molecules in the system [vocalized-noise].

So, this will eventually give you a energy landscape which will ah. So, basically ah you have 2 terms here first term goes as minus of 1 over r [vocalized-noise] and the second term goes as r to the power n ok it is the communist. So, this is this is the force which is [noise] attractive in nature and this is a force which is repulsive in nature, it is the balance of these 2 forces which will determine whether you will have a minima in energy for a structure when you arrange the atoms in a periodic fashion. So, there are pu multiple possibly there are multiple possibilities you try possibilities and see for which possibility the energy is minimum.

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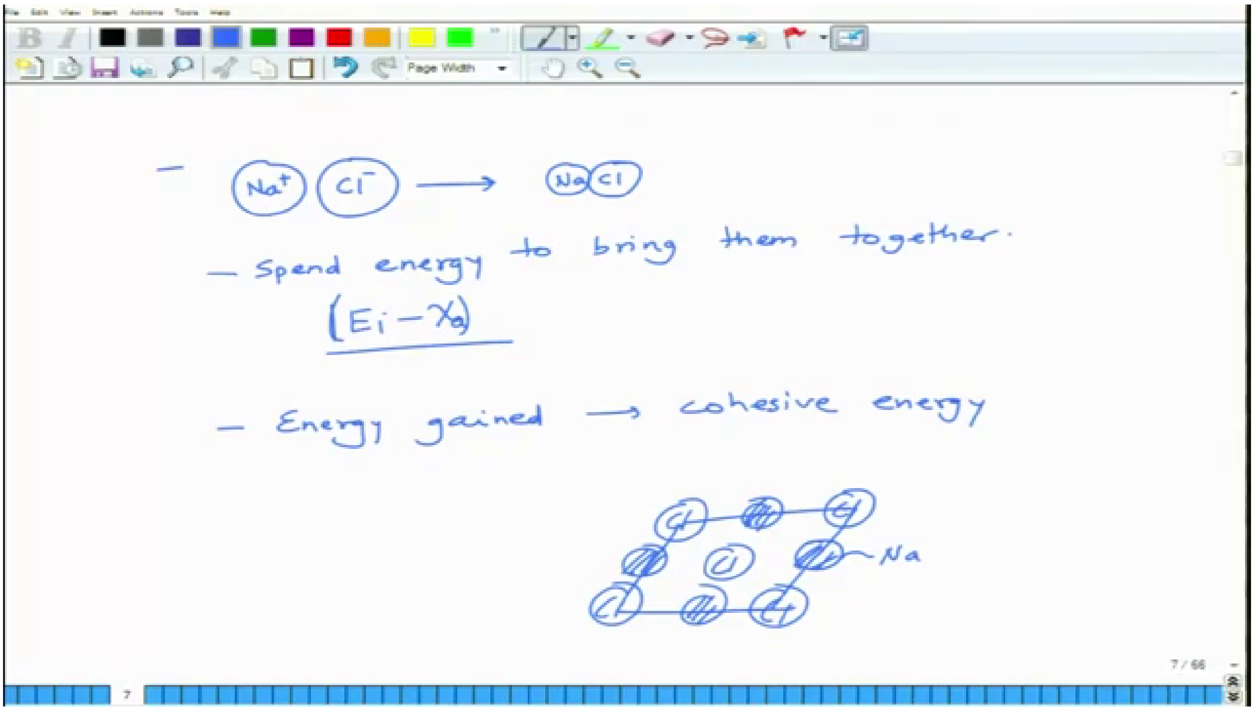

- Na^+ Cl^- $\longrightarrow$ NaCl

- Spend energy to bring them together.

$(E_i - \chi_a)$

- Energy gained → cohesive energy

So, ah basically ah basically [vocalized-noise] you bring for example sodium and chlorine together, let us say you have sodium plus [noise] and you have chlorine when you bring them together you form Na Cl bond it is not exact relation, but sort of NaCl bond.

So, this is basically when you bring them together you spend energy. So, you spend energy to [noise] to bring them together and what is that energy which is so I wrote earlier ionization energy let us say I write it as E1 Ei and electron affinity I can write it as chi a ok. So, it is the difference between a Ei and chi a this is the amount of energy I need to spend in creating a bond and then second is the energy gained [noise] energy gained is called as cohesive energy, which is achieved by bringing the atoms together. So, what you do is that you you make a periodic structure in that case. So, you will have ah for example, this is a sodium atom this is chlorine this is chlorine this is chlorine and so on and so far you will have this n symbol of ions ah in this fashion ah.

So, basically you arrange them in a periodic fashion it is not exact representation, but I understand I hope you ah [vocalized-noise] understand what I mean. So, this is ah not this is not a right way to do it let me just ah show you. So, the bottom [noise] 1 plane would be something like [vocalized-noise] that, this is chlorine atom these will be sodium atoms these are all sodium [noise] these are all chlorine [noise] this is sodium. So, you put them together when you bring them together you gain energy in the form of cohesive energy [vocalized-noise] and you need to then worry about whether there is a net attraction or not. If there is a net attraction then the structure is stable if there is no attraction it says more repulsion structure is not [noise] stable.

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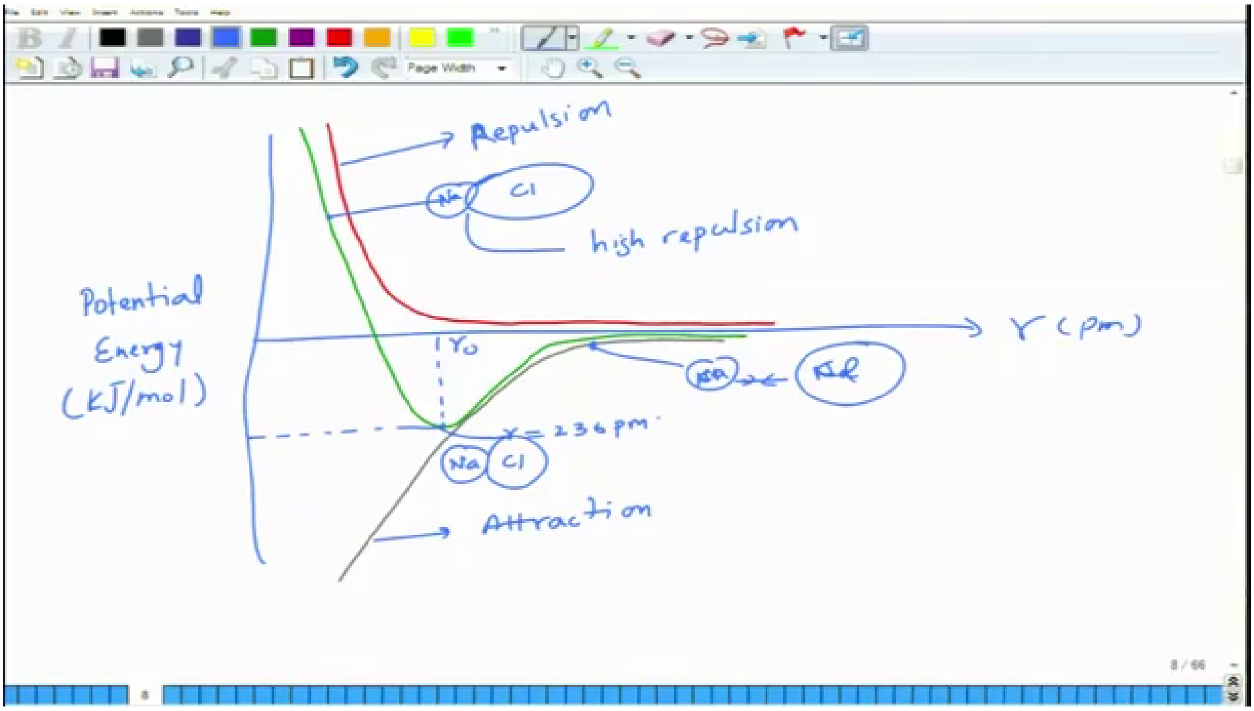

So, ah the overall curve the the energy landscape would look like that. So, if you draw ah this is potential energy [noise] and typically in kilojoules per mole and this is the distance r. So, your repulsion your repulsion term goes [noise] rather rapidly something like that very rapidly this is the repulsion [vocalized-noise] and then you have that total energy and your attraction term goes very much [noise] [vocalized-noise] close to what this is basically.

So, this would be the term which is this is attraction and this is what is keep going to give you the the minima. So, this is the potential energy minima this is the equilibrium separation are not, this is ah [vocalized-noise] nearly 236 picometer approximately; you can see that higher distances give you higher energy. So, at this distance you have ah lower energy, so this is in r in picometer and ah at very low ah values you have very high repulsion.

So, if you go lower than 236 your deposition increases and if you go higher 236, then again it although it is attractive the energy is not minimum the energy tends to increase.

So, this is the point at which you hang around to it mean silicon and so [vocalized-noise] if you if you talk about very uh large small distances it is like this silicon and chlorine sodium and chlorine is squashed together [noise] really very close; so that means, high repulsion this will mean high repulsion [noise] and if you come somewhere here then it would mean situation like this sorry NaCl.

So, they will tend to attract, but then they are too far off ok, so they become like isolated atoms. So, chlorine is somewhere there sodium is there is attraction, but that that is a weak attraction and then you are somewhere here that is where you are sodium and chlorine they are happily without squashing each other happy with each other.

So, this is ah the energetics of ionic solids and we look at the details of this energetics a little bit more in the next class for a [vocalized-noise] there is a term called as Madeleine constant, which is a useful term to know in the context of ionic solids and then we will see there are certain rules which 1 needs to know to form the ionic solid structures ok which are called as Pauling rules and we look at the structure of some of the common ionic solids ok.

Thank you [noise].