Nature and Properties of Materials Professor Bishak Bhattacharya Department of Mechanical Engineering Indian Institute of Technology Kanpur Lecture 07 Bonding between Atoms

Till last lecture we have talked about the material properties, specifically the mechanical properties of materials. Now these mechanical properties actually evolve if you look at it starting from the atomic structure itself or let us say how the atoms are getting bonded because there are certain ways in which the metals get bonded, there are certain ways in which the nonmetallic systems on the ceramic systems get bonded.

So we will today go inside deep inside this atomic bonding and we will try to find out the answers for some of the reasons of the mechanical properties. Now it must be say that not all the mechanical properties can be answered in terms of atomic bonding because atomic bonding is just the very micro level phenomena and the smallest link scale, which affect undoubtedly the mechanical properties.

But then from that scale as we go towards suppose larger and larger scales, then many other mechanisms occur which also contributes to the mechanical properties of the system. So let us start our journey from the atomic bonding level.



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Now, the issue that we will try to address in while talking about the bonding between atoms because it is a very vast subject, but we will keep ourselves focused on what promotes bonding that is very important. And what types of bonds or how many types of bonds are there and which properties can be inferred from the bonding. Now let us try to look into these sorts of things.



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Now you should always have a clear idea of the periodic table while discussing about it because there are 2 very important things that happens if you look at the periodic table from the from our interest point of view. And that is that where the or how the electro positivity is changing, this is one thing okay. And which actually talks about that how readily the atoms can give up the electron.

And just the counterpart that how the electronegativity is changing, that means the capacity or the eagerness to acquire electrons, how that changes and periodic table can very clearly tell you about it. Say for example, if we look at the left most corner of the periodic table then we can see that this is the region where all this atoms can actually give one electron, giving my electron is very easy for them.

So that means they are in top in terms of the electro positivity okay, they can anytime very easy lose that electron and become electro positive. So for example, hydrogen is there, lithium is there; Sodium is often referred as one of the most active material in terms of making compounds like Sodium chlorides and all other things so they are very active.

And then you have potassium, Rubidium, calcium and all these materials are there okay. So that is the group or the column is that group which can become electro positive very fast. The next placed are the group which can actually leave 2 electrons instead of 1 electron. And the

most important metals that come into picture there are something like magnesium are very important okay.

And then even lesser degree of electro positivity like 3 electrons can be donated by things like there are materials like yttrium, et cetera. As we travel towards the right side; we are getting lesser and lesser electro positivity. So in that way we will come all the way up to you can say up to this region more or less the Zinc, cadmium, et cetera, where we can always get some amount of electro positivity.

Beyond that, it becomes more and more you will see the materials will become less and less active. And particularly, we will gradually go inside the domain of the transition materials for example, here we have a good group of transition materials and beyond that you see the reverse phenomena for example, this group okay Oxygen and then you have this the Sulphur okay the all the other rear earth materials, they can accept electrons like 2 electrons they can accept okay.

So they are electron negative of course, not very high. The higher degree of electronegativity you will find in terms of for example, this group where most of the halides are there like chlorine, bromine, iodine, et cetera, so they can you readily become electron negative. And then you have the last group which of course has they are inert gases that means their outer layer is full of that magic 8 number of electrons and hence they are neither electro positive nor electronegative.

The periodic table also tells you through the colour you can check that which are the metals okay, up to what distance you are going to get metals for example, somewhere up to this range you are going to get the metals with you okay. So and then which are transition materials, intermediates neither metals nor nonmetals okay.

Boron, silicon, arsenic, selenium, all these things okay and then you are getting perfectly nonmetals which are like you can say see these which the materials which are perfectly nonmetals. So thus periodic table gives us a fairly good idea about how to classify the materials in terms of their valance structure, metals and nonmetals and inter metallics.



Now let us try to look at 2 important issues. The 2 important issues in terms of atomic bonding are of course number 1 is Interatomic bonds okay. And this is something like how much of force is acting between the atoms so that they can hold together and acts like a spring okay. So something like a spring analogy you can bring in this case particularly, if you look at many of these bonds like ionic bonding or covalent bonding.

And then the other issue is the Atomic packing, this signifies the way in which the atoms are packed together, because okay fine there are these items which are bonded or holds together with the help of some kind of a spring, let us think of it. But the springs we need not think is just a unidirectional in nature, okay depending on the atomic packing okay, we will see more of this various types of possible atomic packing, so you will discuss about the crystal structure.

But depending on the atomic packing, so this directionality that will come in these springs and that also for example, affects the material properties of the system. So here we will talk about 2 types of bonds that the primary bond which are actually very powerful bonds okay they are if you can see in terms of the melting or breaking of the bonds something like 1000 to 4000 Kelvin, so that is why they are very strong bonds.

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And then there are secondary bonds which are like Vander waals bonds or hydrogen bonds, they are relative weak and they melt between 100 to 500 Kelvin. So these are 2 groups of bonds, the primary bond which has the ionic, covalent and metallic bonds. And the secondary bonds where we will mostly consider Vander waals bonds and hydrogen bonds. So let us look into these bonds now more carefully.

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Primary Interatomic Bonding 1. Ionic Bonds ✓ Found in compounds that are composed of both metallic and nonmetallic element. ✓ Large difference in electronegativity required, means bonding occurs between elements that are situated at the horizontal extremities of the periodic table. ✓ Requires electron transfer to achieve stabilized outermost electronic configuration. ✓ The bonding forces are **Coulombic**, i.e., attraction between opposite charges. ✓ Example : NaCl, AgCl, CsCl, ZnS, CaF₂, LiF, MgO, Al₂O₃ Laboratory IIT Kanpur R

Okay, so 1st we will talk about the ionic bonds. Ionic bonds are found in compounds that are composed of both metallic and nonmetallic elements because you need to have one highly electronegative or say electronegative and 1 electro positive in order to make an ionic bond.

So hence you will get compounds that will have a metallic part and a nonmetallic part okay. So for example, you consider Sodium chloride okay.

You have Sodium as the metallic part and chlorine from the nonmetallic part. Similarly, Argentum chloride, Caesium chloride, Zinc Sulphide, Calcium Chloride, Lithium chloride, okay or Magnesium oxide, Aluminium oxide, invariably you will see that one from the metallic part and one from the nonmetallic part. Yes, one important thing on the ionic bonds are the oxides for example okay.

Many oxides are there which actually formed because of the high degree of electronegativity or so to say because of the high degree of reactivity of the metals with oxygen and hence there are abundant forms of oxides and sometimes as single oxide or sometimes as we call that peroxide and many other forms.

So they actually form good part of the minerals from which we actually extract through the process of mechanical and chemical processes through a series of that, we expect the metals. So that is very abundant, the oxides okay and that is very typical of a ionic bond. Now, these ionic bonds they require definitely electron transfer to achieve stabilized outermost electronic configuration.

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Anion = negatively charged io Cation = positively charged io Ionic Bonding in NaCl Sodium atom transfers its valence electron (absorbing 5.14 eV of work) to a vacant position in a chlorine atom releasing 4.02 eV of energy. Net work done to make isolated ions, U_i = 5.14 - 4.02 = 1.12eV The force between opposite charges is $\mathbf{F} = \frac{(Z_1 e)(Z_2 e)}{1 + (Z_2 e)}$ $4\pi\epsilon_0 r^2$ Z_1, Z_2 : Valences of the two ion types : Electronic charge = $1.6 \times 10^{19} C$ NaCl - ionic bond formation ε_o: Permittivity of vacuum (8.85X 10-12 F/m) r : Separation between the ions $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ The work done as the ions are brought to a Na atom radius = 0.19 nm Na* radius = 0.10 nm separation r is $U = \int_{r}^{\infty} F dr = \frac{q^2}{4\pi \epsilon_0 r}$ Clatom radius = 0.08 nm Ct radius = 0.18 nm For r < 1 nm, ionic bond becomes more stable. POTENTIAL ENERGY For stable NaCl, r = 0.28 nm (1nm = 10⁻⁹m). + Below a certain 'r' repulsion starts. 0~8 Reference: Engineering Materials 1: Ashby &

And the bonding forces are actually columbic and the attraction between the opposite charges okay. So let's say one of the examples, let us go through it okay. So this we are talking about the ionic bonds in Sodium chloride okay. Now, Sodium atom as I have shown you in the periodic table earlier that they can very easily give up one electron okay and chlorine can accept that electron.

So Sodium atom transfers its valence electron, absorbing about 5.14 electro Volt of work to a vacant position in a chlorine atom and that will release about 4.02 electro Volt of energy, so the net work that will be done if you one to take one electron from Sodium okay, making it Sodium positive. And if you put one here okay, in one of the vacant is in chlorine, then the net work that will be done is the difference between these two 5.14 electron volt you are absorbing and 4.02 you are leasing, so the difference is 1.12 electron volt.

That means you have to do some amount of work okay even though there is an affinity. If you keep one Sodium atom very far away from the chlorine, it will not actually it will not be able to form the bond because you supplied this 1.12 electron volt in order to make this bond possible.

Now what will make this bond possible? Okay, so if you look at that the moment Sodium is ready to give up this electron and chlorine is ready to take it up, so let us say that choose some kind of a journey this chlorine and the Sodium are coming together closer and closer. So then as they are coming closer, the columbic force will come into action and this is something very much similar like other forces like electromagnetic forces and where the force actually varies inversely with the square of the distance of separation between the 2 elements of opposite charges.

So naturally, beyond a certain distance this force is very weak, so as they come closer and closer, depending on the valences of the ion types and the electron volt for each one of them, this is basically the q 1 q 2, replaces the q 1 and q 2, so this is q 1 and this is q 2 okay. So that is the Coulomb force by definition, so they actually become more and more significant okay.

Now you can also calculate that what is the work that is being done for bringing them from infinity to odd by integrating this force A with different d r with each unit advancement of d r, and if you integrate that, you will get this q square over 4 pie Epsilon 0 r, where this q square is nothing but q 1 times q 2 actually. So q square here is nothing but q 1 times q 2, okay.

Now you will be able to actually find out that what is the total energy that is there in the system. So initially you need U i that is this your 1.12 electron volt of work and then as it is

coming closer and closer, these attractive force is giving the energy of q square by 4 pie Epsilon 0 1 that comes into picture okay, so that is getting reduced from U i.

Also, there is a limit of it if you think of it that it is coming closer and closer together, it will never happen that one is going to collapse on the other, so there is and the moment these 2 are coming very close, then their nucleus which are positive they would start to actually so after penetration of the electron clouds, they will start to have a kind of a repulsion.

So that repulsion is actually modeled by a constant divided by r to the power n, where the n is approximately 8, so that is what gives us the total energy in the system. Now, one can show actually that from the minimisation of the energy point of view, about 0.28nanometre range you will see that the minimum energy comes to the system, which means it comes into an equilibrium okay.

So that is what is very important for Sodium chloride bond to become stable. Now you can see another very interesting thing here that Sodium atom radius is 0.19nanometre to begin with, and the chlorine atom radius is about 0.08nanometre to begin. But the moment Sodium actually gives up the electron of the valence from the valency, then it shrinks, it becomes actually 0.10nanometre.

And chlorine becomes, its electron cloud increases, it becomes about 0.18nanometre. So as far as the ion is concerned chlorine ion is actually bigger than the Sodium ion, okay. And as far as the atoms are concerned, Sodium atom is actually bigger than the chlorine atom, okay. So that is what happens because of the exchange of the electrons from one to the other okay.

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Now so this picture which I have shown for Sodium Chloride let us try to understand this picture from generalize energy point of view for ionic bond formation. So here we distance r as the x axis okay and for moving the atoms and U as the energy that is there in the system. And I already told you that the bond will be stable at a point where this energy is actually minimum okay.

So the minimisation of the energy point of view and here we will only consider interaction between 2 atoms just to keep the whole thing very simple. So in one hand we have the separate ions here, Sodium plus chlorine okay and they have an internal energy already like we said that the U i in this case was somewhere like 1.12 electron volt, so that is what is the U i, the initial energy in the system.

So that is where the whole system is starting its journey, okay. So where basically the Sodium and the chlorine are very far away, so that is where they are very far away okay. And then they are coming closer and closer, so as they are approaching the distance between the 2 okay, so r is the distance between the 2 that is actually coming down okay and as it is coming down, you can see that this is how the attraction energy is increasing exponentially.

But I also told you that these 2 atoms will never collapse with each other, why because beyond a certain point somewhere here you would see that there is a repulsion curve that will come into picture because the atoms will then start to repel each other and that also expands exponentially at a much faster rate, so hence if I superimpose this repulsion over this internal energy plus, the energy due to attraction okay. So we have U i, we have the attraction part and we have the repulsion part, then we get this kind of a net energy curve and that net energy curve has a minima, you can see it, right? So because there are these 2 counter active forces working and that minimum point is where the bond becomes stable. So for each and every combination of electric positive and the electronegative atoms in a ionic bond formation, you can find out what is this distance where the bond becomes very stable okay so that is one can actually calculate and generally it is in the nanometer level

(Experiment demonstration)

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When we talk about equilibrium in terms of the ionic bonding, I can give you an analogy that suppose you consider that you have 3 such atoms okay atomic positions. Now there exists a kind of a stable position if a 4th atom is going to come in between. As you can see, if I just keep it somewhere here, they are going to collapse, so these are all unstable locations.

But there is a stable location which is stable because all the forces exactly balance at that location and you will not be able to get any further collapsing so which actually says that this is the minimum in terms of the energy, the total energy if you consider in the system is the minimum point in terms of the energy and hence this reaches the stability point. So this is through a very simple students and the kids (())(21:31) students. They are very simple equilibrium of magnetic systems; you can actually explain this concept.

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Now the overall properties that we can talk about it from the ionic bond perspective are that they are non directional, why they are non directional? Because these are the 2 ions and they can get attracted from any direction okay. So if we consider one positive and one negative, they can get attracted either any of the ways right. So, any of the directions they can come. So that is one important property that ionic bonds are non directional okay.

So which actually can give some kind of an isotropic property some of the isotropic properties we can kind of guess that will come wherever there is ionic bond predominantly. They have high melting point okay why because the there the bonding energy in ionic bond is pretty high. Something likes 600 to 1500 kilojoules per mole or 3 to 8 electron volt per atom.

So it is very high and hence you need a lot of energy to break this bond, which means that they will be having a high melting point. And also, they are often very hard okay, so that hardness is also coming because the bond is very strong. And that hardness may also result in terms of brittle materials, which we will see later on. That many times the hardness and brittleness are come together particularly in the context of ceramic materials.

Now also we have to note that they are good insulators why because they do not have almost any free electron available with them, their all electrons from one to the other is already gone inside the bond. So hence they are good insulators in the solid state, but the reverse thing happens when they are in a dissolved situation or in a modern state because then the ions are actually getting separated and which means that they become good conductors of electricity okay in the molten state or at the dissolved state. So that is the property of an ionic bond.

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Now let us go to another important Inter atomic bonding that is called Covalent bond. Covalent bonds stable electronic configurations which are obtained not through this electric positive and electronegative attraction, but through the sharing of electrons between the adjacent atoms okay. So naturally, this sharing cannot happen from any direction, this is actually directional in nature; covalent bond is directional in nature.

So that means the material which will show this high covalent bonding, they can also show anisotropic in support. And the number of covalent bonds in a particular atom actually depends on that from that 8 in the valence shall minus N that is the number of valence electrons that many actually that is the capability to absorb that many number of electrons into the system.

Now, there are couples of materials which are very famous for covalent bonding okay. Of course, there are nonmetallic molecules, hydrogen, fluorine, chlorine, et cetera. Then we have these molecules containing dissimilar atoms CH4, H2O, HNO3, etc. We have the elemental solids for example, Carbon for covalent bond, then Silicon or germanium.

We have solid compounds like Gallium arsenide, Indium antimonide, and Silicon Carbide okay. And we have some polymers which have some primary bonding, but they also contain a secondary bond that is why polymers are not very strong because they also contain the secondary bonds. So what is the nature of this covalent bond? Let us look into one particular example like say Hydrogen.

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So Hydrogen it has one electron to donate from the periodic table we have seen. Suppose 2 Hydrogen atoms agreeable to share one electron each, then you gets a Hydrogen molecule okay, where the shared electrons are actually paired between both of them. If you think of another example, so this is between the same type of atoms, but 2 dissimilar atoms, then you see that carbon can actually absorb 4 electrons.

Okay, so Hydrogen can give one electron can share, so 1 pair, 2 pair, 3 pair and 4 pair. That is how CH4 or methane is formed okay, so between the sharing of 4 Hydrogen atoms with one Carbon, so that is between 2 dissimilar atoms.

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Another example is actually diamond where carbon is sharing electron with another carbon, but that his not in any arbitrary way only when this kind of a pet tetragonal packing comes into picture. This tetragonal packing okay then only this is happening and this is one of the strongest bonds available in any material, available in nature you know.

And this is because number of covalent bonds here is very high. Of course it is highly directional, which means it is strong in a particular direction. But the bond energy is very high and hence diamond has the highest melting temperature, it has the highest thermal conductivity okay. And also it has one of the highest hardness also as we have seen in the hardness scale, we have shown diamond to be one of the hardest material.

That is because this tetragonal structure which is having maximum number of covalent bonds possible per unit cell and that gives a very large Inter atomic strength and hence it becomes very hard. That is why diamond is used in applications such as cutting tools, polishing wheels, precision bearings, et cetera. So for quite some time, there was almost no material to challenge this unless particular point of time we obtained carbon nano tubes, then only diamond could be challenged because carbon nano tube has comparable or even better properties.

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Now for covalent bond, the story is not exactly same because you do not have any initial energy because you are actually sharing, so you have one energy due to attraction and one energy due to repulsion okay. The repulsion starts at a very smaller length scale, but here also

you get this net diagram and hands you get a region actually where you can expect the bond to be stable.

And the expression is somewhat similar except that you do not have any U I here and you have an m here and a n here and m and n value varies between 5 to 12. So when m is less than n, then is the attraction prevails and when n is greater than m then it is the repulsion that prevails, so that is how the combination of attraction and repulsion creates a stable bonding.

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Very few co	ompounds exhibit pure ionic or covalent bonding.	
Usually par	rtially ionic and partially covalent.	
More diffe	rence in electronegativity : lonic bond predominate tronegativity difference : Covalent bond predomina	tes
The percen (most elect	tage ionic character of a bond between elements A tronegative) and B is given by:	
% lo	pnic character = { $1 - \exp[-(0.25)(X_A - X_B)^2]$ x 100	
	where $X_{\rm A}$ and $X_{\rm B}$ are the electronegativity's for element λ	A&B.

The important points then about covalent bonds are that, very few compounds exhibit pure ionic or covalent bonding that is why you will always get a mix of it. And usually you will get partially ionic or partially covalent bonding. If there is more difference in electronegative within 2 atoms, ionic bond will predominate. And if there is a small electronegativity difference, covalent bond is going to predominate.

The percentage ionic character of bond between elements A and B you can actually if the X A and X B the electronegativity, you will be knowing that what is the ionic character percentage of the bond. So if it is smaller, then it is the covalent dominating, which means it will be directional. If it is not, then it will be ionic which means it will not be directional.

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Now, other than these bonds of course there is another primary inter atomic bond which is also known as the metallic bonds. For metals, this happens somewhat in the different manner. Every metallic atom is ready to give up some of the electrons and form a general pool of electrons which is also sometimes known as an electron cloud. So you can actually define a metal to be something like the core part which is positive each one of them okay.

So it is kind of a gets ionized inside and then that it is having a glue of electrons which are all around it, the free electrons which act as a glue across all the ion cores, so that is what that gives this kind of a metallic bonding. So this infers properties which has a high strength, malleability, ductility, lustre, conduction of heat and electricity because you have many free electrons available, so you get actually good conduction of electricity in the system.

And also you get a good bonding, why because you have this the positive cores, which are glued by the electron clouds, so you get a good bonding via this electron clouds okay, so that is what makes the metallic bonding. Then we have 2 other inter atomic bonding, which are actually secondary inter atomic bonding. These are one is one of them is called Van der waals bonding.

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Her also you have the charge positive and negative charge responsible for the bonding, but this not come from the atoms, it rather comes from the combination of atoms which creates a dipole, so there is a dipole-dipole interaction, positive and negative dipoles which creates this Vander Waals force.

And if this is if this specifically happens with respect to Hydrogen, then these are also known as the Hydrogen bonding, which has dipole-dipole interactions because of the Hydrogen positive attracting the H minuses a similar thing. And this happens in for example water and that is why it expands upon freezing because it is of that kind of a very weak bond is found when the water actually freezes okay.

So in fact that is why you would see that ice had actually lower density than liquid water because at that time the hydrogen bond is form and that gives the density that gives a very low density to the system okay. So that is one typical example of a hydrogen bond, but by and large both of these bonds are actually very weak. You can see for example, the energy here is something like 10 kg joule per mole, which is quite an order of magnitude of work, then the ionic or the covalent bonding.

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Ceramics	High bond energy
(Ionic & covalent bonding):	ing): Large elastic modulus E
	Small coefficient of expansion of
Metals	Variable bond energy
(Motallia banding):	moderate Tm
(metanic bonding).	moderate E
	moderate α
Polymers	Directional Properties
(Covalent & Secondary):	Secondary bonding dominates
(oovalent & becondary).	small T _m
	small E
	large a

So let us summarize the whole thing now that means we have talked about the ionic bonds and this is particularly for the ceramics which shows ionic and some amount of covalent bonding. And that characterizes the high bond energy, high melting temperature for the ceramics, large elastic modulus and very small coefficient of expansion.

From the metals which have a different kind of bonding, it is somewhat ionic in nature but it is not between dissimilar atoms, but the same atoms itself. So there you will see that the bond energy varies although, it is not as high as the ceramics, but it is still significantly high and that is why you get a moderate melting point temperature, slightly lower than the ceramics, moderate modulus of elasticity and moderate coefficient of expansion.

Now, so the coefficient of expansion here is of course higher with respect to the coefficient of expansion for the ceramics. Finally, we come to the polymers, they have directional properties because they have some amount of this carbon-carbon bonding which are actually directionally strong and they also have secondary bonding. It varies, but generally the secondary bonding dominates.

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And you get a small melting point, temperature, small modulus of elasticity and you get large coefficient of expansion. So that much we can actually predict from the atomic bonding of these various types of atoms, thank you. In the next class then we will talk about the crystal structure okay, and we will discuss about crystalline solids, amorphous solids, unit cells and cubic structures, thank you.