Condensed Matter Physics
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Lecture – 8
Cohesion in solids – Worked Examples

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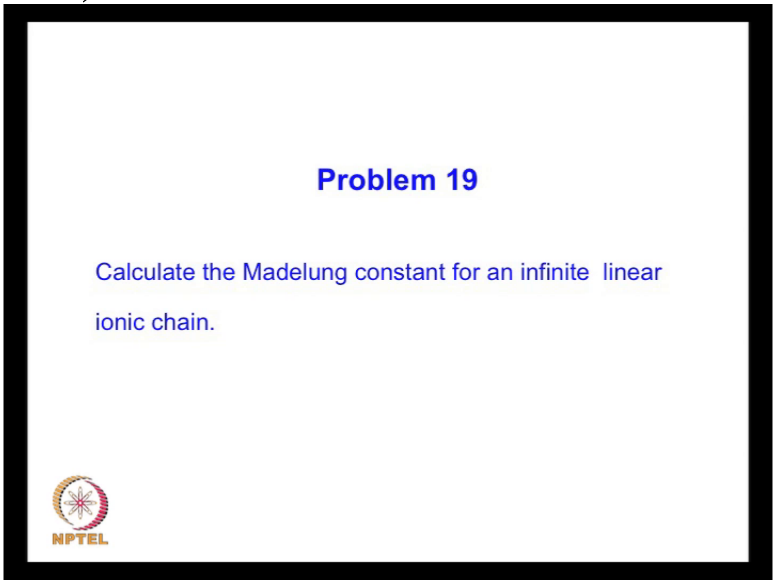

In the next problem, we are ask to find the Madelung constant for an infinite linear ionic chain.

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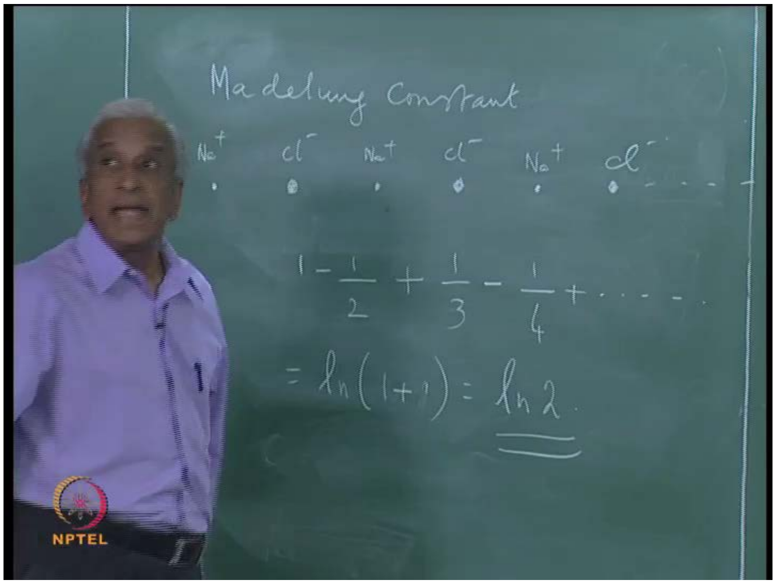

Madelung constant is nothing but the lattice sum of the geometrical factor in the lattice sum in the coulomb potential interactions. So you have positive and negative terms in a linear ionic lattice such as this, for example, sodium and chlorine – Na plus and Cl minus, Na plus Cl minus, Na plus Cl minus, that is the typical linear lattice, that's goes on, it is an infinity lattice. So if we want the Madelung constant which means that we take out factor out the terms involving the electronic charge, the distance and so on, express only the geometric ratio. For example, between near neighbor, it is one unit; and then between the next distance is twice this, so it is minus half, because of the inverse distance the dependent of this potential on the inverse separation.

So the next one is the positive term, repulsive term between light charges sodium plus and sodium plus minus one four plus etcetera. And that is as you can recognize this is nothing but the logarithmic series of one plus x, where x is also one; log one plus x is one minus x by two plus x square by three etcetera. So this is just log one plus one, which is log 2 that is the Madelung constant.

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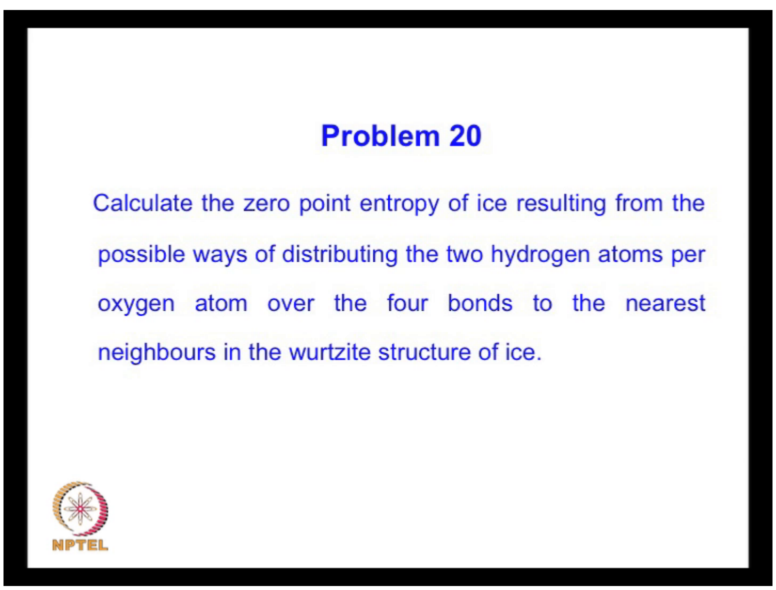

Next problem is the rather interesting situation, which is associated with the fact that the hydrogen bonds in the ice, have two position.

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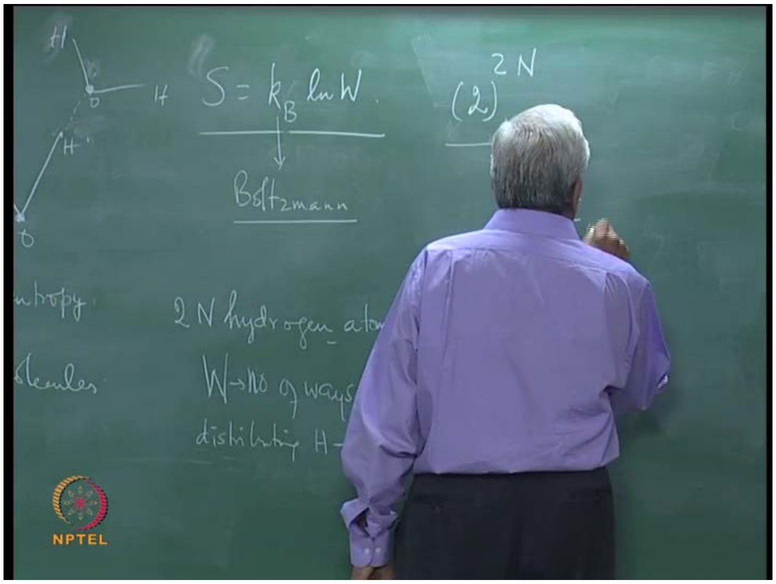

You consider water molecules in ice, you have two hydrogen atoms and one oxygen atoms. So I have an OH bond and another OH bond. Now in a hydrogen-bonded network up ice, this hydrogen atoms links to another water molecule here and so on. It is the network of hydrogen-bonded network. They are all different atoms here and so on. So this as two things like this, all the tetrahedral lines and so on. Structure is extended in three dimensions. Now there are two ways of distributing the two hydrogen atoms per oxygen atoms over the four bonds, there are in all four bonds to the near neighbors, because it is a tetrahedral structure, so there are four bonds different way are distributing two hydrogen atoms per which two hydrogen atoms for each oxygen atom. They have to be distributed over the four bonds. So this gives rights to a certain disorder, associated with this disorder is as entropy, so this is a zero point entropy because even at absolute zero this disorder persist, because it is essentially a structural disorder associated with the number of different ways of distributing to hydrogen atom over four bond.

So in a, if there are n water molecules, then there are two N hydrogen atom, because each oxygen in the water molecule has two hydrogen atoms, therefore two N hydrogen atoms in the total. Now we have to find disordered associated with distributing these two N hydrogen atoms. Now, associated with this disordered, if this number of ways of distributing W, then this number of ways of distributing these hydrogen atoms, now if this is the number of ways, then the famous Boltzmann's formula for the entropy is known as K B log W, S equal to K B log W. So, we find the number of ways and then multiply Boltzmann constant, this is Boltzmann constant. We take the logarithm of the number of ways – W and multiply it by the Boltzmann constant and that gives us the entropy associated with this.

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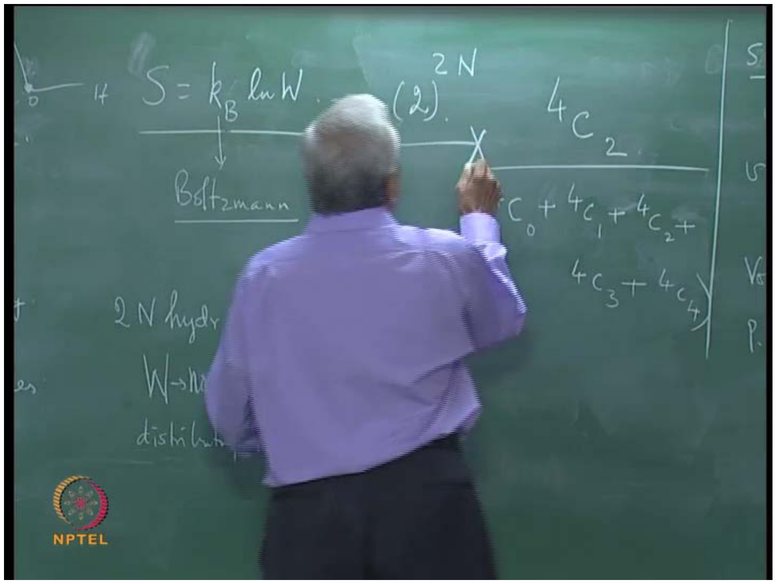

So let us calculate this now. So we have two hydrogen atoms, two position for each hydrogen atoms, so there are two N hydrogen atoms, so the total number of ways possibilities is two to the power two n, but we have only two hydrogen atoms to be distributed among four position. So the total, this is now all these are not available, so we have a combinatorial problem of distributing two hydrogen atoms among four bonds, so the total number of ways is four C naught plus four C one plus four C two plus four C three plus four C four, these are the total number.

There are four bonds, I need not put any hydrogen atoms that is four C naught. I can put one hydrogen atoms over these four bonds that the number of ways is four C one. This is four C two is the number of ways of putting two hydrogen atoms in among four molecules four bonds. Four C three and four C four, this is the total number of ways of which we only get the possibility of distributing two hydrogen atoms over these, so it is four C two. So it is the ratio of these together multiplied by the total two to the power two N which gives you W. And this ratio as you can readily verify.

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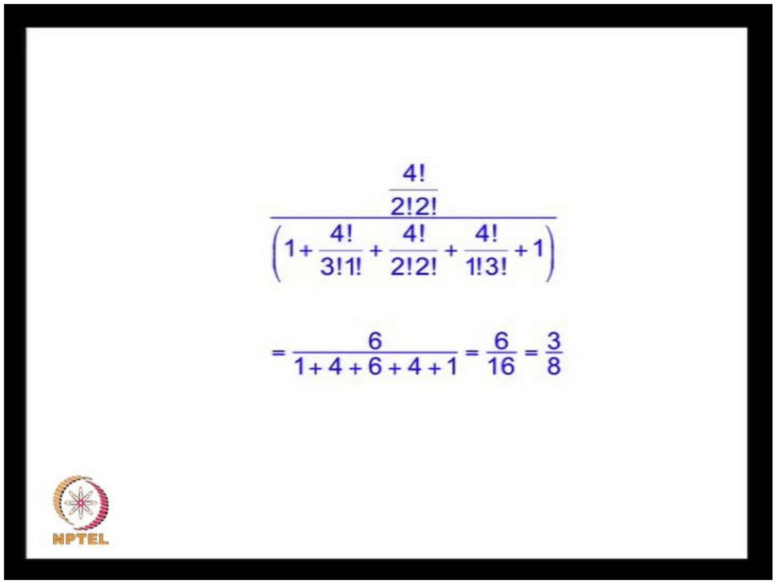

So it this will be two to the power two N times three by eight, to the power N. This will be two square, so four into three by eight to the power N that is three by two to the power N.

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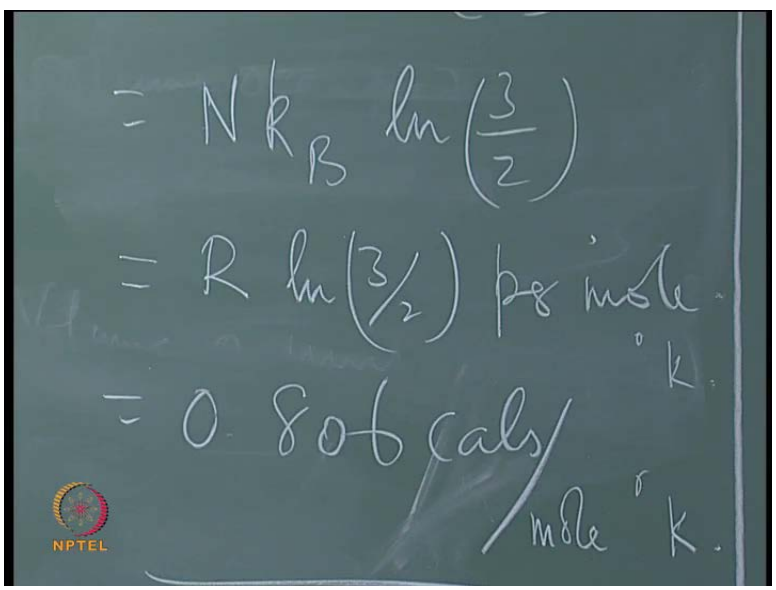

So the entropy, S is K B log three by two to the power N which is N K B log three by two. And the N K B is nothing but the universal gas constant R, so it is R log three by two per mole. So putting in the value of R, we get it as zero point eight zero six calories per mole degree K calories per mole degree K that would be the residual entropy of ice. Even at zero K, this entropy this amount of disorder and the associated entropy persist.

We will continue with our problem solving session today. The problem that we have to solve now is to determine the isothermal bulk modulus and the lattice energy per ion pair for sodium chloride given that the repulsive potential varies as the inverse ninth power of the nearest neighbor power separation and that the Madelung constant is 1.748.

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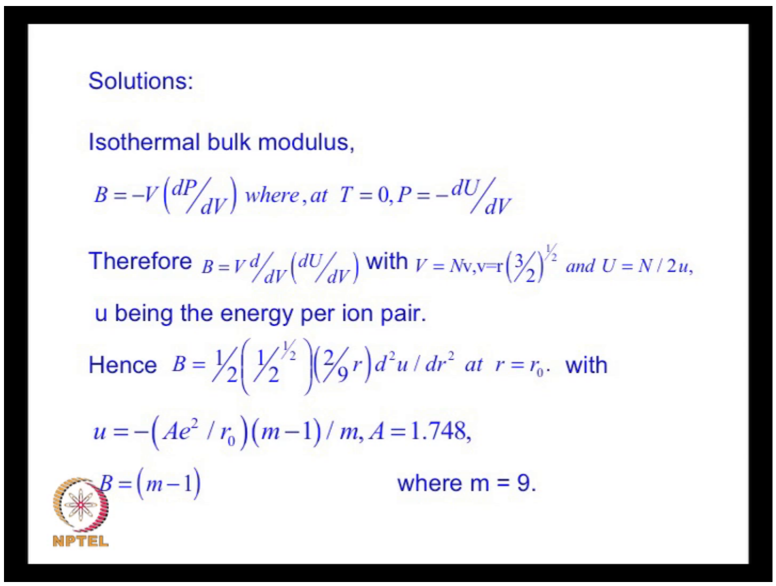

We already saw what is the Madelung constant, it gives you the lattice sum for the coulomb potential with terms of alternating signs. So for a face centered cubic lattice of the sodium chloride solid, we can calculate the Madelung constant that has been given as 1.748.

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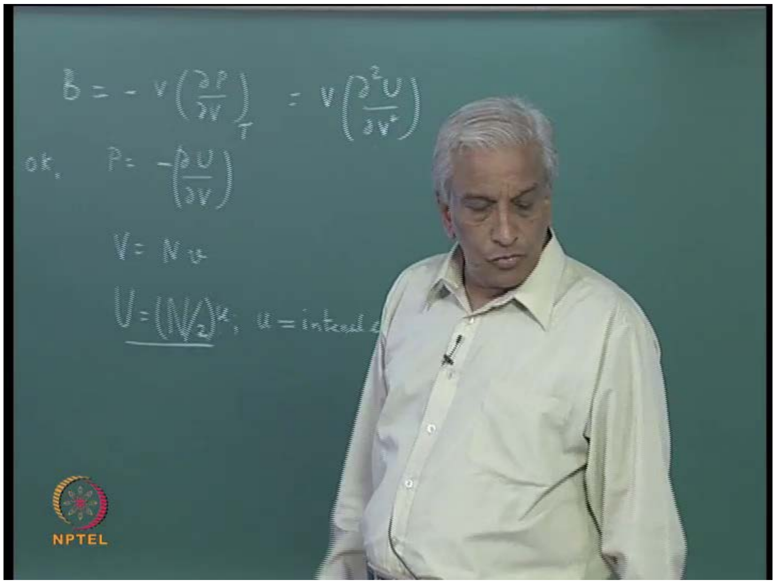

So the isothermal bulk modulus B is minus v dp by dv at constant temperature, where at T equal to zero, our calculation are all at absolute zero, so we have p the pressure is just minus dU by dV, where U is the internal energy. Therefore, we can write this as V d square U by d V square.

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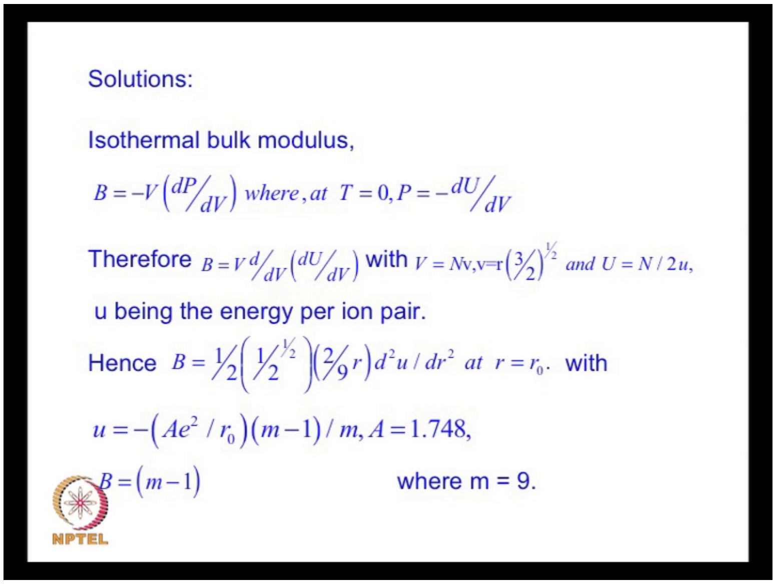

And here this V is N times v, where N is the number of atoms and we also have the equilibrium the internal energy U is N by two times U, because U is the energy – internal energy per ion pair for sodium plus and Cl minus.

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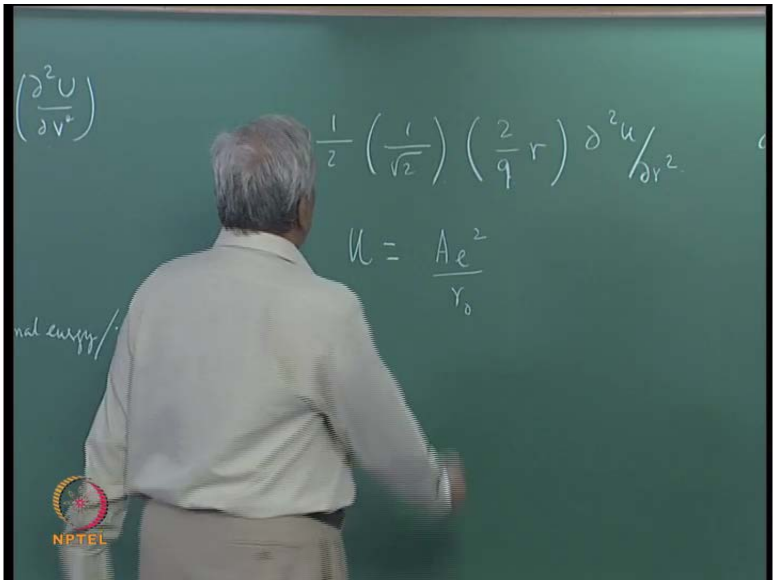

So this is what we have and therefore, the bulk modulus can be calculated as for the face centered cubic structure half into one by root two into two by n ion r into d square U by d r square. Taking the relation between the r – the atomic radius, the ionic radius and the volume of the unit cell, so this is at r equal to r zero, this is something that we get by setting the by minimizing the energy. Where U itself is A e square by r zero, this is coming from the form of the coulomb potential times minus one, where A is given in the problem as one point seven power eight, this is the Madelung constant. And in the problem, the index m is also given to be nine. So we will use that later. We will right now write it just as m and solve everything, so the bulk modulus becomes m minus one into eighteen A e square by r naught square when m is nine, so that is the bulk modulus.

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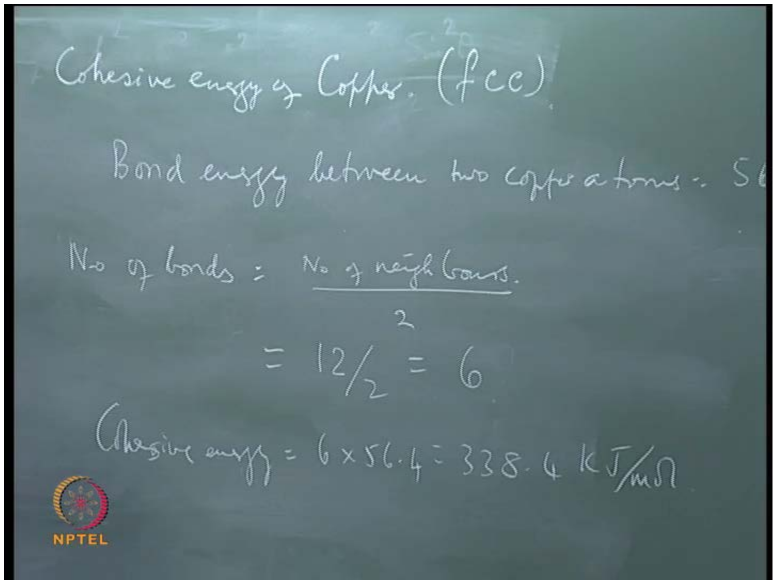

Concerns the cohesive energy of copper an f c c structure – face centered cubic structure gave, we are given that the bond energy between two copper atoms is given to be fifty-six point four kilo joule per mole.

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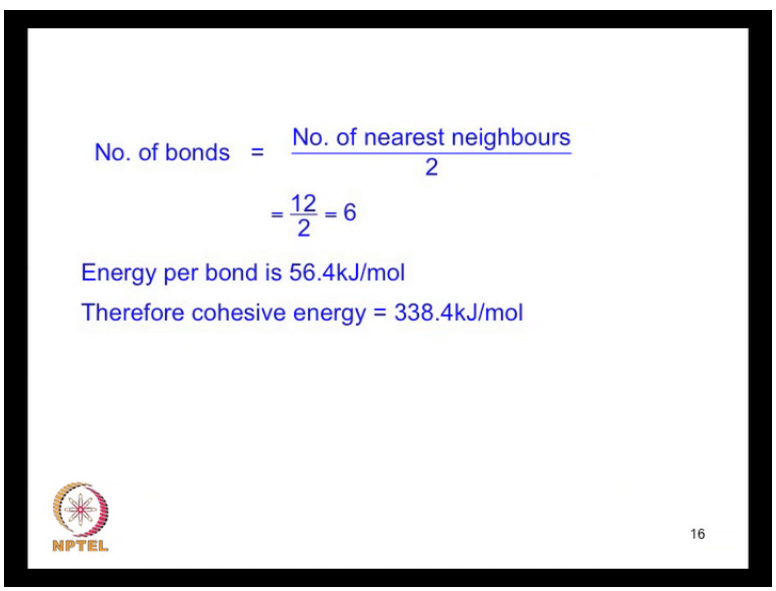

And how do we calculate this, we have to remember that it is a face centered cubic structure, so we have number of bonds is number of neighbors - near neighbors divided by two. So this is number of neighbors in f c c structure is twelve, so it is twelve by two which is six. And energy per bond is given as this, therefore cohesive energy is just six times this, which is three hundred and thirty eight point four kilo joule per mole.