Solid State Physics
Lecture 16
Ionic Crystals

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So, after understanding the inert gas crystals where van der Waals interaction and Pauli kind of repulsion plays the attractive and repulsive forces in the picture. Let us move on to understand the ionic crystals. (Refer Slide Time: 00:44)

Ionic crystals, for example, sodium chloride, NaCl, we have discussed the structure of sodium chloride. These are made up of positive and negative ions for sodium chloride plus 1 and minus 1 ion. Thus the electrostatic attraction binds them together, holds them together as a crystal as a solid. We conclude that the cohesion energy comes from the electrostatic interaction, and we can calculate this cohesive energy, the electrostatic interaction energy. So, the this energy was first calculated by a scientist called Madelung. Therefore, this energy is called Madelung energy. How did the calculation proceed? The long range interaction between ions with it has the ions will have charges $\pm q$ in general, and the long range interaction would be of electrostatic nature, the electrostatic interaction can be expressed as $\pm \frac{q^2}{r}$. We are considering sodium chloride like ions. So, it is $+1$, -1, or we this also goes for $+2$, -2 kind of ions; otherwise there would be some other factor to q, $\frac{q^2}{r}$ is the interact electrostatic interaction energy. It is attractive for ions with opposite charges and repulsive for ions with same charge charges which is obvious. Now, the ions arrange themselves in such a way that the attractive interaction is maximized and the repulsive one is minimized. So, the total energy must be minimum that is the way the ions will arrange themselves. The repulsive and attractive interactions that we have seen in case of inert gas that also is present here. However, that interaction is much weaker than the ionic interaction. So, the main contributor to the binding of the ionic crystal is electrostatic energy, and that electrostatic energy is called the Madelung energy. Now, let us consider U_{ij} as the interaction between the i^{th} and j^{th} atom interaction energy between the i^{th} and j^{th} atom ion rather. And we define U_i that is the potential felt by the i^{th} atom for every other atom in the crystal that can be given as $\Sigma'_j U_{ij}$, similar to our earlier prime excludes $i = j$ ok. Now, we suppose that U_{ij} may be written as the sum of a central field kind of a repulsive potential. So, we write and on top of that this electrostatic interaction. So, the central field kind of repulsive potential, we will call it a repulsive potential from now onwards. This is of Pauli exclusion kind of origin which we will write as $\lambda \exp -\frac{r}{\rho}$. λ and ρ, these are parameters yet to be determined. So, we are taking an exponential form instead of r^{-12} kind of a form that we have considered earlier. This difference is just mainly for historical reason, but here the reason that we consider this kind of a difference is that in case of ionic crystals we do not have their gas form. So, this one does not require any reference to the gas form while r^{-12} requires reference to the gas form to determine the coefficients that is the reason this one works better in this context. And on top of that, we must have the Coulomb potential $\pm \frac{q^2}{r}$. (Refer Slide Time: 06:43)

That means, this potential U_{ij}, U_{ij} this quantity can be given as $\lambda \exp\left(-\frac{r_{ij}}{\rho}\right) \pm \frac{q^2}{r_{ij}}$. Now, this is expressed in CGS unit, in fact, everything every electrostatics that we are doing here is expressed in CGS unit. And there is no difference in the physics that we obtained from CGS and SI units. So, we do not care about conversion of the units. Again the + sign is for like charges, and the - sign for unlike charges here. The, so we treat the strength of this repulsive potential λ, and range that is ρ as constants to be determined from observed values of lattice constants and compressible compressibility. We have used an exponential form here as we have discussed earlier that is used more useful for ionic solids. And the exponential repulsive term describes the fact that each ion resists overlap with electrons distributed in its neighbor. So, for the ions, we do not have gas phase data that is the reason this form is better suited. In sodium chloride structure, the value of U_i does not depend on whether the reference ion i is positive or negative. Just because you will see that this quantity if it if the i^{th} ion is positive, it will have interaction with other positive atoms the plus sign will come interaction with other negative atoms the minus sign will come. If i^{th} is negative for interaction with other, negative ions plus will come and therefore positive minus sign will come. So, it remains the same. There is no essential difference in it. Now, we can arrange the sum to make it converge rapidly, so that its value will not depend on the site of the reference ion in the crystal as long as it is not near the boundary. And in considering this bulk system, we will ignore the boundary. We will ignore the surface of the system. And now if we have N molecules in case of sodium chloride NaCl that is one formula in it, we are calling that a molecule, that means, we have 2N, in case of sodium chloride 2N ions. We can write the total energy as NU_i we are not writing $2NU_i$ because U_i considers the interaction energy coming from two atoms sorry two ions. So, we need to we should not double count in order to exclude counting each interaction twice, it is NU_i that is the total energy, U_{tot}. The total lattice energy is defined as the energy required to separate the crystal into individual ions. And those individual ions will move at infinite distances. There would be no interaction. So, the amount of energy that we put into the system that takes all the ions at infinite distance that is the amount of energy that the lattice stores, so that is the lattice energy. So, now, we again introduce the p_{ij} kind of terms. So, r_{ij} the distance between two ions is now written as $p_{ij}R$, where capital R is the nearest neighbor separation. If we include the repulsive interaction only among the nearest neighbors, so the repulsive interaction of this exponential form that we have considered, we will consider that this interaction acts only among the nearest neighbors not beyond. So, what was the origin of this interaction? There were electron clouds that were overlapping and Pauli Exclusion Principle caused this interaction, so that will not anyway be valid for ions staying far apart. This assumption that this interaction is only for nearest neighbors that is quite valid. And if we perform that kind of an approximation, we can write $U_{ij} = \lambda \exp\left(\frac{-R}{\rho}\right) - \frac{q^2}{R}$only because it is among the nearest neighbors - sign because the nearest neighbor would be opposite charged ion oppositely charged ions. So, this holds for the nearest neighbors and the interaction would be $U_{ij} = \pm\frac{1}{p_{ij}}\frac{q^2}{R}$ otherwise, if the ions are far apart or not nearest neighbor that is all. (Refer Slide Time: 13:35)

So, using this expression and summing over j first and then summing over i, we can write the total energy $U_{tot} = NU_i = N(z\lambda e^{(-\frac{R}{\rho})} - \frac{\alpha q^2}{R})$, α is a new parameter that we have introduced here. z is the coordination number that is the number of nearest neighbors. So, by summing over everything, we will have the nearest neighbor term coming like this. And this is the Coulomb interaction term. Now, what is α? α as you can see if you look at this expression and then sum over it, you will find that α can be given as $\Sigma'_j \frac{(\pm)}{p_{ij}}$. And this quantity is yet to be determined. This is called the Madelung constant. The sum should include the nearest neighbor contribution which is just z the value of the Madelung constant is crucial for the theory of ionic crystals because this one gives us the electrostatic interaction. Now, if we consider the equilibrium separation just like earlier U_{tot} if the total energy would be minimum. So, this derivative $\frac{dU_{tot}}{dR}|_{R=R_0} = 0$ which means we will have $N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho}\exp\left(-R/rho\right) + \frac{N\alpha q^2}{R^2} = 0$. And putting R_0 in place of R and solving for this we can find R_0 equals let us not write R_0 equals because this expression is not that simple. It is ${R_0}^2\exp\left(-R_0/\rho\right)$ this quantity becomes $\frac{\rho\alpha q^2}{z\lambda}$. Now, this determines the equilibrium separation. If we know the parameters lambda and rho, then this equation can easily be solved. There is no problem. What about the total lattice energy of the crystal? (Refer Slide Time: 17:48)

The total lattice energy for 2N ions at their equilibrium separation R_0 that can be written as in this expression we will just put the value of R_0 which will now become this. And here we have this pre factor that is $-\frac{N\alpha q^2}{R_0}$, this is the Madelung energy. Now, we shall find ρ is of the order of 0.1 R_0. So, rho is something like this; it has this kind of a value. So, the repulsive interaction as you can see has very short range.