Defects in Crystalline Solids (Part-I)
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Lecture - 05
Self-interstitial Defect + Frenkel Defects

So we were discussing that how to characterise or how to measure vacancy concentration. And in the last lecture, we saw the method of expansion. Today we will discuss the method for heat capacity.

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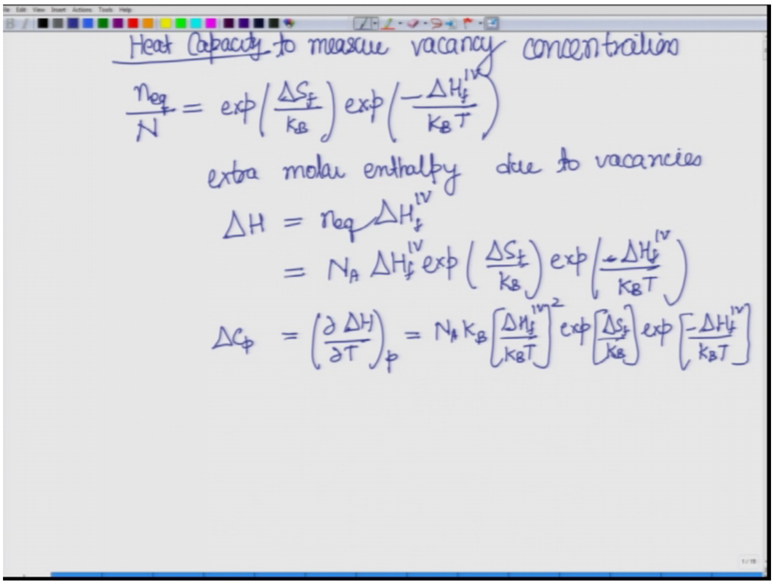

Heat Capacity to measure vacancy concentration

$$\frac{n_{eq}}{N} = \exp\left(\frac{\Delta S_f}{K_B}\right)\exp\left(-\frac{\Delta H_f^{1V}}{K_B T}\right)$$

extra molar enthalpy due to vacancies

$$\Delta H = n_{eq}\Delta H_f^{1V}$$
$$= N_A \Delta H_f^{1V} \exp\left(\frac{\Delta S_f}{K_B}\right)\exp\left(\frac{-\Delta H_f^{1V}}{K_B T}\right)$$

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p = N_A K_B \left[\frac{\Delta H_f^{1V}}{K_B T}\right]^2 \exp\left[\frac{\Delta S_f}{K_B}\right]\exp\left[\frac{-\Delta H_f^{1V}}{K_B T}\right]$$

So, we can also use heat capacity to measure vacancy concentration. So, how do we do that? Now we know that x which is the equilibrium concentration of vacancies which can also be written as n equilibrium by upper case N equal to expand then we have this entropy formation term and the entropy as and the exponential for delta enthalpy term.

So, now extra molar enthalpy can; because of this presence of vacancies can be written as due to. So, due to vacancies, this can be written as; this is the extra molar enthalpy which is now if this number is n eq for the vacancy, then it is n eq times delta H f 1 v, this is the extra molar enthalpy.

Now, we have a relation for n equilibrium, we can write it as n which is per molar, if we take then it is Avogadro number this is delta H f 1 v and then the rest of the exponential terms as it occurred in the previous equation right.

Now, delta C p is as we know the definition is nothing, but the derivative of this enthalpy with respect to temperature at constant pressure. So, this equation becomes let us hope that this we complete this in this line, it will become something like this. So, you see that this increase in this C p, it capacity can be related to this relation. And therefore, we can use this relation to find the concentration of the vacancies if we know delta C p which is the change in the enthalpy. So, this is one method.

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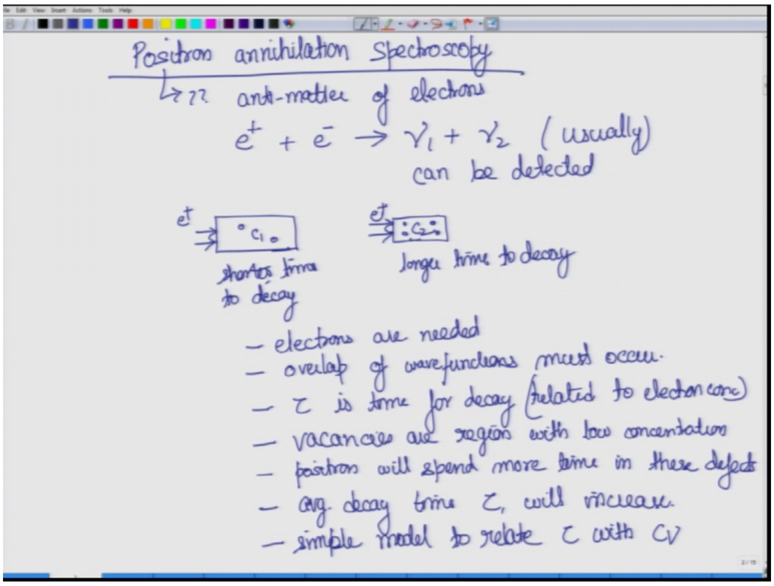

Positron annihilation Spectroscopy

↳ ?? anti-matter of electrons

$e^+ + e^- \rightarrow \gamma_1 + \gamma_2$ (usually)

can be detected

- electrons are needed
- overlap of wavefunctions must occur.
- τ is time for decay (related to electron conc)
- vacancies are region with low concentration
- positron will spend more time in these defects
- avg. decay time τ, will increase.
- simple model to relate τ with C_V

Now, let us look at still another method which is used which is kind of you can say exotic method which is called positron annihilation spectroscopy. So, the first question here is what is positron what is positron? Positron is nothing, but antimatter of electrons.

What does antimatter imply antimatter implies that if you have electron and this antimatter which is positron, then they are together they will annihilate each other and since they have some mass it will result in energy. So, you will get some you will get some energy in the form of light wave. So, it will the equation can be usually written in this form e plus which is your positron. This is e minus which is your electron when they combine together, you will get something like this gamma 1 plus gamma 2 which are the wavelengths of two different gamma radiations usually, it comes out in this form that is why I written. Otherwise you can also in a more general way you can just say gamma which will be the energy in terms of photons.

And now here these are the gamma that can be detected, but what else why are we able to detect how this detection of the gamma after this positron annihilation is going to help us. Let say you have mass with different concentration and over here you in pungent with positron. So, this has some concentration C 1, this has some concentration C 2.

Now, the basic principle is that if the if there are defects somewhere inside it. So, the let us say C 2 is higher. Now these defects act as a trap, because they have lower electron densities. And therefore, the electron the positron can spend more time meaning it will have less probability to any get annihilated. And therefore, the total time it takes for this positron to get annihilated by electron is lower over here and higher; sorry the other way round because it has more number of defects. So, it has lesser probability. So, it will take longer time to decay and here it will take shorter time to decay. So, that is the basic principle.

So, by measuring this difference by measuring the time that it takes to decay one can find out what will be the concentration defect we will see in a little bit more detail. So, what are the things that are needed for positron to get trapped or basically for the even before that trapping for the positron to get annihilated what you need is electrons are needed when there are electrons. Then overlap of wave function must occur meaning the electrons which are can also be represented by a waveform wave function, and positron which can also be represented by a wave function they must overlap and once they overlap properly, then you will they will get annihilated.

So, overlap of this wave functions must occur tau which is the time tau is time for decay. So, the for example, here we talked about the total time that it takes for positron then you inject it over here and the time that it gets annihilated. So, the lower number of defects it means it will quickly pass on it will keep on moving and it will not decay easily over here it will get trapped in defects. And therefore, it will have longer time to decay. So, that is the time we are calling that is the tau is the total time for decay and it is related to electron concentration and we know that vacancies are regions with low electron concentration.

So, now this is relation between the defect which is the vacancy over here and the tau because now vacancies have lower concentration. So, positron will spend more time they will innovate get trapped positron will spend more time in these defects and because of this the average decay time average decay time which is tau will increase. And you can model have a simple model to its relate tau with concentration of vacancies, we will look at this is simple model that we have that can be easily formulated.

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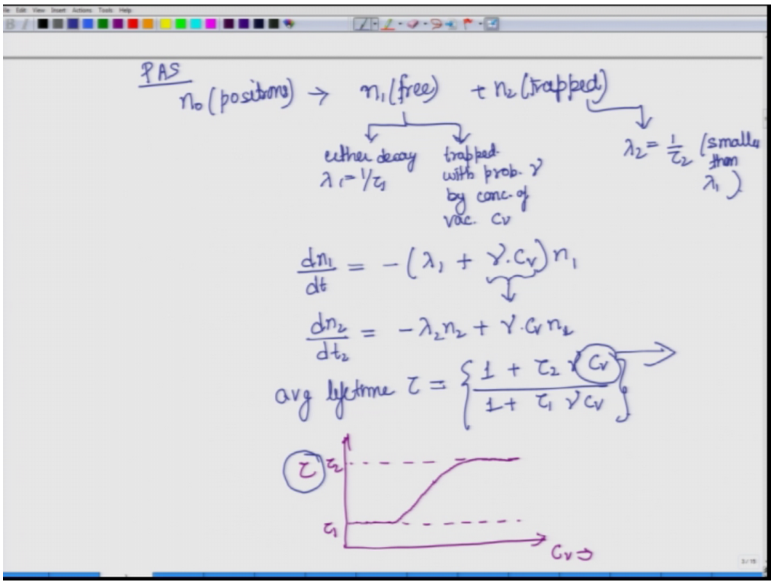

PAS

n_0 (positrons) → n_1 (free) + n_2 (trapped)

either decay $\lambda_1 = 1/\tau_1$

trapped with prob. γ by conc. of vac. C_v

$\lambda_2 = \frac{1}{\tau_2}$ (smaller than λ_1)

$$\frac{dn_1}{dt} = -(\lambda_1 + \underbrace{\gamma . C_v}_{\downarrow}) n_1$$

$$\frac{dn_2}{dt_2} = -\lambda_2 n_2 + \gamma . C_v n_2$$

$$\text{avg lifetime } \tau = \left\{ \frac{1 + \tau_2 \gamma \boxed{C_v}}{1 + \tau_1 \gamma C_v} \right\} \rightarrow$$

So, let us go to the simple model. So, we are talking about positron annihilation spectroscopy and a simple model. So, let us say that you inject it with n number of positrons. Now this positron will split into two different kinds one that is free. So, let us call it n one which is free and n 2 which gets trapped in defects where they will spend more time.

Now, one that is the number n one which is free it can either decay if it is decaying then you need to know the rate constant and let us say it is lambda one which is equal to 1 over tau 1 or it can get trapped. So, even the free one they may initially be free, but at some point, it may get trapped. And therefore, it can get trapped with probability let us say nu. So, probabilities then of getting trapped is nu by concentration of vacancies C v.

On the other hand n 2; it is trapped and it will have some other decay constant let us say lambda 2 which will be equal to 1 by tau 2 and this lambda two will be smaller than lambda 1 because it is trapped. So now, we have a relation and. So, we can formulate it into a equation and the question will look like this. So, dn 1 by dt is decaying only decreasing. So, there is a minus sign ahead of it with rate constant lambda one times n, but there is also it is getting converted with a probability mu times concentration of vacancy C C v. So, this term gets added and over here we have n one

On the other hand, d and the n 2 which is already trapped it is only decaying. And therefore, their this is a minus lambda two sign lambda sign and it is this is the rate constant and plus this quantity that you see over here is the trapped one is actually getting transferred or getting converted to this n 2 form. So, there is a increase in this number. So, we can say this is the increase which is equal to this.

Now, once you have a equation like this it is very easy to show that the average lifetime of this positron annihilation can now be related with tau 1 tau 2 and C v and one can show that this will be something like this. So, what you see here is that the average lifetime keeps increasing with increasing concentration of C v in. In fact, if you plot it will look something like this. So, on the x axis I have concentration vacancies and on y axis, I have average lifetime and over here let me plot tau 1 which is the rate which is the lifetime for the free vacancies sorry, the free positrons in tau 2 which is the lifetime for the ones that are trapped and as you can see, I have already shown tau 2 to be larger.

So, if you had only free electrons sorry the free positrons meaning it does not get trapped it is only free and it goes from one end to the other end then it will have something like this. So, for some concentration which is very very low let us say almost close to 0. The average lifetime will be equal to tau 1. Now as you keep increasing the concentration, this will increase and there will come a time where most of them get trapped most of the most of the positrons get trapped. And therefore, the max this will have lifetime equal to tau t tau 2. So, this is how this plot would look like in general.

Now, another interesting aspect is that when these positrons are generated they actually emit some gamma radiation. Now when they are annihilated then again they generate a gamma radiation like the when I showed over here like according to that relation. So, both the birth and death are corresponds to some gamma radiation and this helps in detecting or the time when this event took place.

So, you would you can easily characterise what was the time when this positron was generated and what was the time, when it was annihilated and that way you know the time total time or the total lifetime of this positrons. So, that makes the measurement of tau very easy. And once you have this tau then you can go back and find what should be the C v value. And this is another way to find the concentration of the vacancies. There are some more methods which are used for measuring vacancies.

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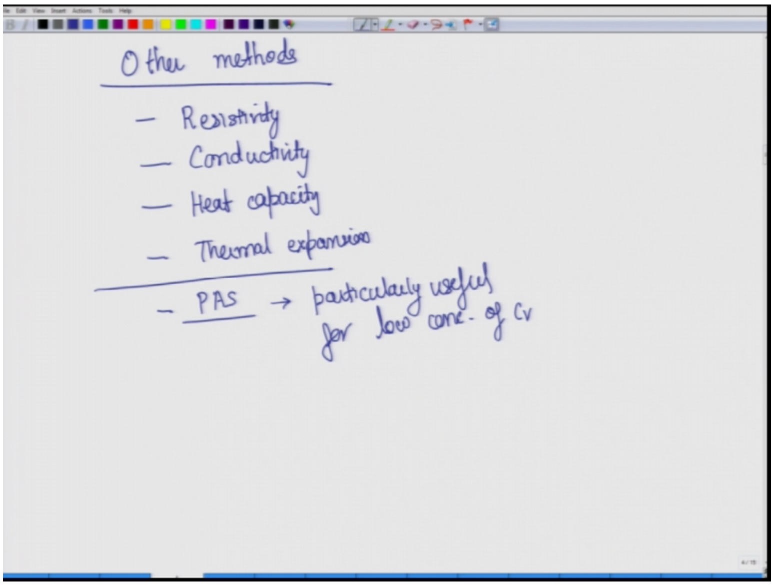

Other methods

- Resistivity
- Conductivity
- Heat capacity
- Thermal expansion
- PAS → particularly useful for low conc. of C_v

And the main the most important problem with most of this technique is that the concentration of vacancies are inside the bulk you cannot just measure on the surface, because on the surface there will be the surface is not the true representation of bulk. So, this has to be characterisation technique which measures bulk properties.

So, some other techniques which are used are measuring properties measuring bulk properties. For example, resistivity we will not go into details I am just listing out couple of these and related to resistivity is conductivity the other one that we have already looked at is heat capacity and thermal expansion. So, some properties are measured which relate to the vacancy concentration the bulk properties which depend on the consent vacancy concentration.

So, these are the only methods this there are not too many methods which are which can be used for vacancy characterisation. And the last one that we discussed which was the positron annihilation spectroscopy the most important aspect of this method is that it is particularly useful for low concentration

Now, most of the other methods will work only when you have certain minimum number of concentration they will be able to measure the change. However, positron annihilation spectroscopy as advantage that it is useful particularly for low concentration of C v. So, now, you have a wide gamut of techniques wall limited in number which can measured from very low concentration to good number of concentration.

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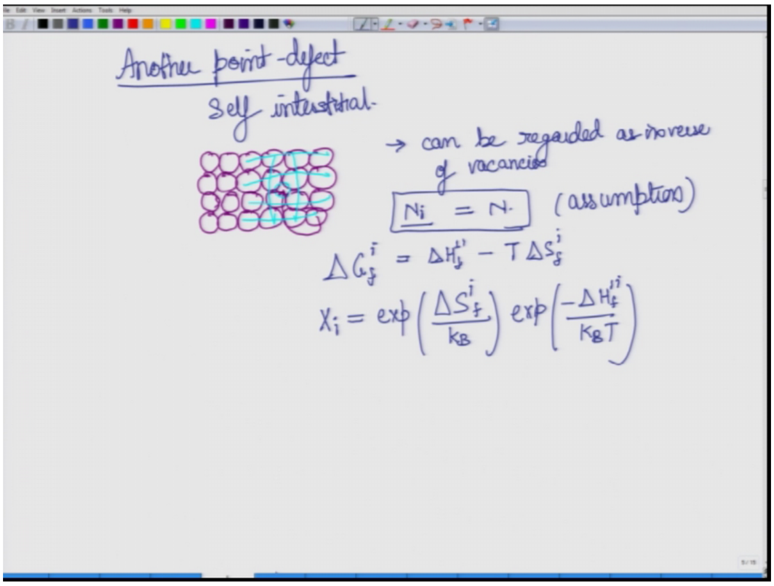

Another point-defect

Self interstitial

→ can be regarded as inverse of vacancies

$\boxed{N_i = N}$ (assumption)

$$\Delta G_f^i = \Delta H_f^i - T\Delta S_f^i$$

$$X_i = \exp\left(\frac{\Delta S_f^i}{k_B}\right)\exp\left(\frac{-\Delta H_f^i}{k_B T}\right)$$

So, with that we will move on to another defect. So, we have led only at one particular point effect which was the simplest of this which was vacancy. Now, let us move on to another point defect which is another simplest point defect that you know it is self interstitial. So, what is the self interstitial as the name suggests that you have some pure element; and this element one of the atom moves from its lattice site and goes in to one of the interstitials not meant for those atom positions. So, that is the interstitial.

So, that is the kind of defect which is called self interstitial and I will schematically draw it. So, let say we have. So, this will be just schematics. So, do not as you can see that I am drawing the atoms that I am drawing are not equal in shape which is not really the case. So, just take it as a schematic. So, now let us say one of these atoms moves to somewhere over here. So, there will be the stress field around this the atoms over here will have to move to adjust this extra atom. So, this is this kind of defect is called self interstitial.

Now, this particular kind of defect can be regarded as inverse of vacancies why what is vacancies is this absence of atom from its place and what is interstitial it is an extra atom in that same number of lattice site. So, that is why you can treat interstitials as inverse of vacancies

However, one must note that when we are saying that you have to assume that the number of interstitial sites which I am representing by N i is equal to number of lattice sites only in that case we can directly use the relation that we have obtained for vacancies. And therefore, over here if we write delta g formation for interstitial it will become delta H f 1, I just to represent that I am talking about one interstitial delta s formation i, then X i or the equilibrium concentration of interstitial would be given by exponential. Thus the same relation except that the entropy formation and the enthalpy formation would represent that for interstitial self interstitial; so this will become like this.

Now, you have to keep in mind that this is a assumption over here when we are doing it like this, what when this is not true we will see some other defects we have as we go on we will talk about some other kind of defects for example, the Frenkel and the Schottky defect and we will see what will happen when N i is not equal to N.

But for this particular case to begin with, to understand the concept of self interstitial. Since we are regarding it as inverse of vacancies.; in this particular case we are assuming N i is equal to N which is number of interstitial sites is equal to the total number of lattice sites.

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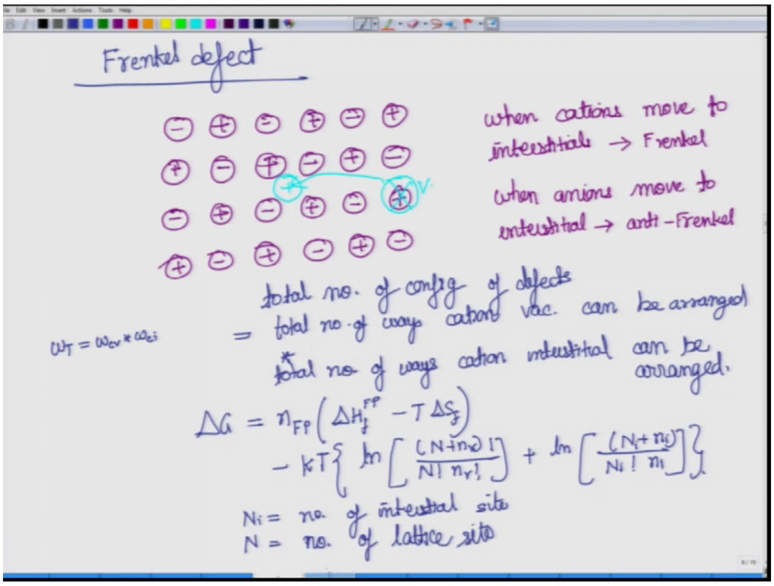

Frenkel defect

when cations move to interstitials → Frenkel

when anions move to interstitial → anti-Frenkel

$\omega_T = \omega_{cv} * \omega_{ci}$

total no. of config of defects
= total no. of ways cation vac. can be arranged
* total no of ways cation interstitial can be arranged.

$$\Delta G = n_{FP}\left(\Delta H_f^{FP} - T\Delta S_f\right) - kT\left\{\ln\left[\frac{(N+n_v)!}{N!\,n_v!}\right] + \ln\left[\frac{(N_i+n_i)}{N_i!\,n_i}\right]\right\}$$

N_i = no. of interstitial site
N = no. of lattice site

So, now let us move on to. So, this was self interstitial now let us move on to still another defect which is Frenkel defect ok. So, let us first draw schematically. Now

Frenkel defect is something that will mostly occur in ionic substance. So, we will have let us assume simple system where there is one cation and one anion the ratio is one is to one. So, it will have something like this, so their alternating and as you can see that charge neutrality has to be maintained. So, in order to show that I will draw equal number of cations and equal number of anions, you can count that I have equal number of cations and equal number of anions.

Now, what is the Frenkel defect? Frenkel defect is when cations which are the smaller of the two move to interstitial ok. So, here again we are talking about interstitials. So, how does that happen? Let us see something like this let us say this is a cation and it moves to interstitial. And here I have shown it a little separated away unlike the ones in the self interstitial just for clarity of the picture how the atoms are actually oriented will depend on which orientation you are looking at what is the crystal structure of that.

So, all on all those aspects and here just for simple illustration I am taking it as a square lattice in two d plane and over here the atoms are separated apart so that these cations can move over here. So, now these cation move from here. So, this becomes a vacancy and the cation comes over to this place. So, this will be called a Frenkel defect and why it is that can only cations move, it is because cations are usually the smaller in size, but there are of course, possibilities that anions can also move now when can when anions which are usually larger, but still is cases that can move when anions move to interstitial then they are actually called anti Frenkel defect. So, this becomes Frenkel when cations move and when the anions move they are called anti Frenkel defect.

Now, over here we will the formulation would be similar to the one that we have been using for vacancies and that the one that we used for self interstitial now; however, if you look at the total number of configuration of the defects total number of configuration of defects, this will be equal to total number of ways cation vacancy can be arranged times total number of ways cation interstitial can be arranged ok.

So, other things remaining same the only thing that will be different over here is how the entropy term is taken into account ok. So, the original equation would be something like this delta g equal to n fp which is the Frenkel pair we are talking about one pair. So, n number of pairs, it is not just one vacancy it is one pair there will be one vacancy in the cation and one interstitial in the one cation in the interstitial. So, this will be formation

Frenkel pair minus t delta s formation which is for Frenkel pair minus there will be the entropy term which is K T.

And since we have to we have said that the entropy the total number of ways that, these defects can be distributed is the multiplication of the ways cation vacancy can be distributed times the ways cation interstitial can be distributed. Therefore, there will be multiplication factor of that ww 2. So, it is as good as saying that wt is equal to w cation vacancies into w cation interstitials and since this is in log we can take a sum of the log instead of multiplying them instead in the in inside the log.

So, it will look something like this n plus nv factorial by n factorial by nv factorial plus this is for the vacancy term and the other one will be for the interstitial term N plus N i, and this n has to be actually number of interstitial sites. So, this will be what is N i here like I said earlier N i is the number of interstitial site n is number of lattice site.

Now, at this juncture, we will have to make some assumption; what is that assumption that we may have to take?

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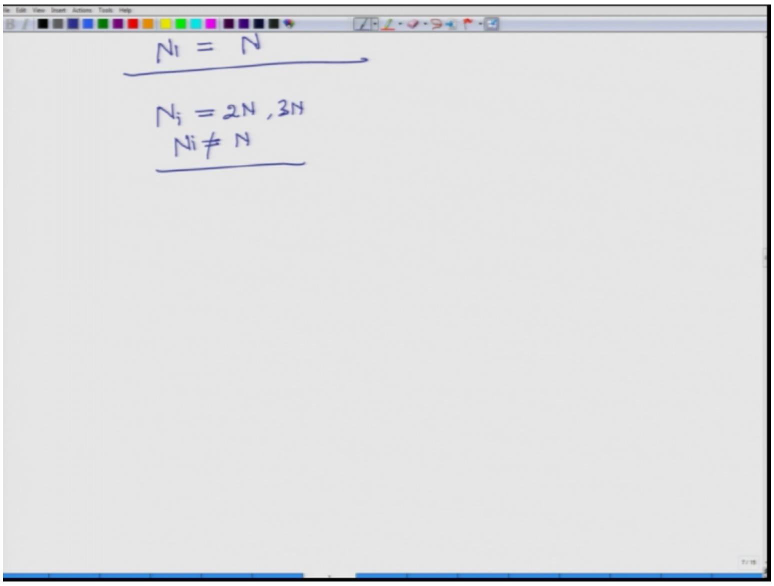

$N_1 = N$

$N_i = 2N, 3N$

$N_i \neq N$

What is the relation between N i and n for example, if we take simple system and I will be equal to n in other cases N i cannot be equal to one maybe it can be two and three and or we can just let it be two different entities N i and N.

So, in the next lecture what we will do is; we will see how it will be different when we have N i or the number of interstitial site equal to the lattice site and when number of interstitial site is not equal to. So, let me put it like this not equal to, it can be any other function of N. So, we will be derive for these two. And, in the meantime I will suggest you try it on your own, and then you would know how to derive this relation and we will do it in the next.

Thanks.